

**A DYNAMIC CROSSLINKER, COVALENT ADAPTABLE NETWORK
COMPRISING POLYMER NETWORK CROSSLINKED BY
SAID DYNAMIC CROSSLINKER AND RELATED METHODS THEREOF**

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TECHNICAL FIELD

The present disclosure relates broadly to a dynamic crosslinker and a method of preparing said dynamic crosslinker. The present application also
10 relates to a covalent adaptable network (CAN) comprising polymer network crosslinked by said dynamic crosslinker, a method of preparing said covalent adaptable network (CAN), and a method of recycling said covalent adaptable network (CAN).

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BACKGROUND

Covalent adaptable networks (CANs) are a new class of cross-linked polymers which exhibit the best properties of both thermosets and thermoplastics. The covalent cross-links furnish these networks with high
20 mechanical strength. Moreover, their dynamicity endow the vitrimers with stimuli-activated reprocessability. With their high durability and potentially infinite recyclability, CANs are promising sustainable polymers.

However, currently available synthesis and preparation methods of CANs
25 have several disadvantages and drawbacks, and are far from desirable. Particularly, most CANs are prepared from functional monomers, or by crosslinking functionalised polymers, which typically requires tedious multi-step syntheses of functional monomers or functionalised polymers, thereby limiting the scalability of current methods.

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Recently, methods to transform existing thermoplastics into CANs has garnered significant interest due to potential for broad utilisation and high

scalability. For example, radical-mediated grafting methods using dynamic crosslinkers bearing precursors such as maleic anhydride, nitroxide and diarylsemipinacol to form radicals have been explored. Unfortunately, only low grafting rates (< 12%) have been achieved with these methods. Moreover, these free radical grafting methods inevitably cause chain scission and partial permanent cross-linking of polyolefins, leading to the non-uniform network and unpredictable behaviors, making such methods challenging to work with and undesirable. Another strategy which has been explored is the use of dynamic crosslinkers bearing precursors such as aziridines and azidoformates to form reactive singlet species. These crosslinkers decompose to form carbenes and nitrenes respectively, which can undergo C-H, O-H and N-H bond insertions. Unlike free radical grafting methods, no polymer-derived high-energy species is generated, thus suppressing unwanted side reactions which generate defects. However, the synthesis of these precursors require tedious multiple steps with low overall yield. Additionally, the low thermal stability of these precursors may be a problem for prolonged storage.

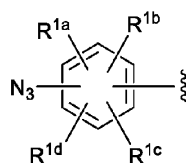
Thus, to date, it remains a challenge to find a suitable method for synthesizing CAN.

In view of the above, there is a need to address or at least ameliorate the above-mentioned problems. In particular, there is a need to provide a dynamic crosslinker such as one that is able to form non-radical-based reactive intermediate with high scalability and a method of preparing CANs that address or at least ameliorate the above-mentioned problems.

SUMMARY

In one aspect, there is provided a dynamic crosslinker comprising at least two aryl azide groups coupled together *via* one or more dynamic covalent moiety, wherein the dynamic covalent moiety comprises one or more dynamic covalent bonds that reversibly exchange, break and/or form under suitable conditions.

In one embodiment, each aryl azide group independently comprises a structure represented by general formula (1):

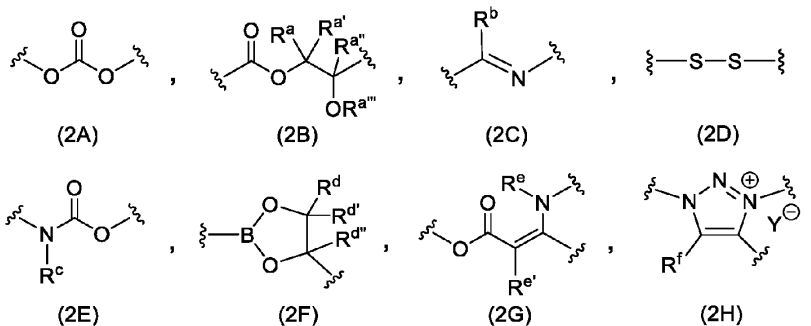


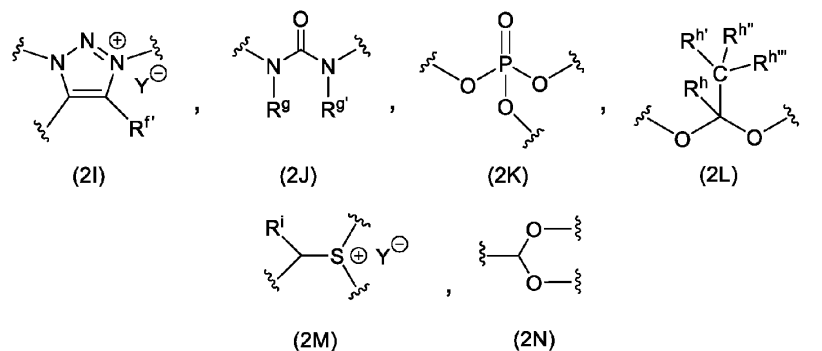
(1)

wherein

- 5 R^{1a}, R^{1b}, R^{1c} and R^{1d} are each independently halogen, hydrogen, hydroxyl, carboxyl, amine, amide, ester, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted oxycarbonylalkyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carboxylalkyl, 10 optionally substituted alkylcarboxylalkyl, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkynyl, or combinations thereof.

- In one embodiment, the dynamic covalent moiety comprises a structure 15 selected from the group consisting of general formula (2A), (2B), (2C), (2D), (2E), (2F), (2G), (2H), (2I), (2J), (2K), (2L), (2M), (2N), and combinations thereof:





wherein

R^a, R^{a'}, R^{a''}, R^{a'''}, R^b, R^c, R^d, R^{d'}, R^{d''}, R^e, R^{e'}, R^f, R^{f'}, R^g, R^{g'}, R^h, R^{h'}, R^{h''}, R^{h'''}, Rⁱ,
 5 R^j, R^{j'} and R^{j''} are each independently hydrogen, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof.

10

In one embodiment, each aryl azide group is coupled to a dynamic covalent moiety *via* a linker.

15 In one embodiment, each dynamic covalent moiety is coupled to another dynamic covalent moiety *via* a linker.

In one embodiment, the linker comprises an organic group selected from carbonyl-containing group, carbonyloxy-containing group, ester-containing group, amide-containing group, carbamate-containing group, amine-containing group, thiol-containing group, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted alkylcarbonyloxy, optionally substituted oxycarbonylalkyl, optionally substituted alkyloxycarbonyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carbonylaryl,
 20 optionally substituted arylcarbonylalkyl, optionally substituted alkylcarbonylaryl,
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optionally substituted arylcarbonylaryl, optionally substituted carbonyloxyaryl, optionally substituted arylcarbonyloxy, optionally substituted oxycarbonylaryl, optionally substituted aryloxy carbonyl, optionally substituted arylcarbonyloxyalkyl, optionally substituted alkylcarbonyloxyaryl, optionally substituted arylcarbonyloxyaryl, optionally substituted aryloxy carbonylalkyl, optionally substituted alkylcarbonyloxyaryl, optionally substituted aryloxy carbonylaryl, optionally substituted arylester, optionally substituted alkylester, optionally substituted arylamide, optionally substituted alkylamide, optionally substituted arylcarbamate, optionally substituted alkylcarbamate, optionally substituted arylamine, optionally substituted alkylamine, optionally substituted thioaryl, optionally substituted thioalkyl, optionally substituted alkoxy, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof.

In one embodiment, the one or more dynamic covalent bonds are configured to reversibly break and/or form under application of one or more of the following stimuli:

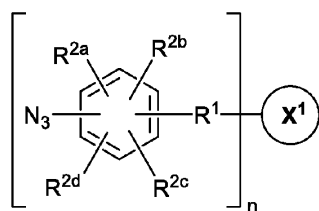
- (i) temperature that is from 20 °C to 300 °C;
- (ii) pressure that is from 0.1 MPa to 100 MPa;
- (iii) in the presence of a reactive chemical; and
- (iv) UV radiation.

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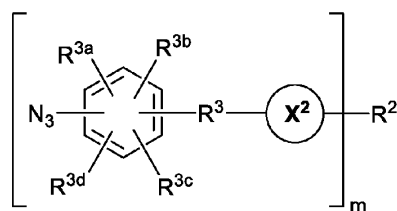
In one embodiment, the reactive chemical comprises alcohol, acid, base, reducing agent, oxidizing agent, dimethyl disulfide, dithiothreitol, or combinations thereof.

In one embodiment, the crosslinker comprises a structure selected from general formula (3), general formula (4), or combinations thereof:

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(3)



(4)

wherein

each of X^1 and X^2 is independently a dynamic covalent moiety;

each of R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} and R^{3d} is independently halogen,

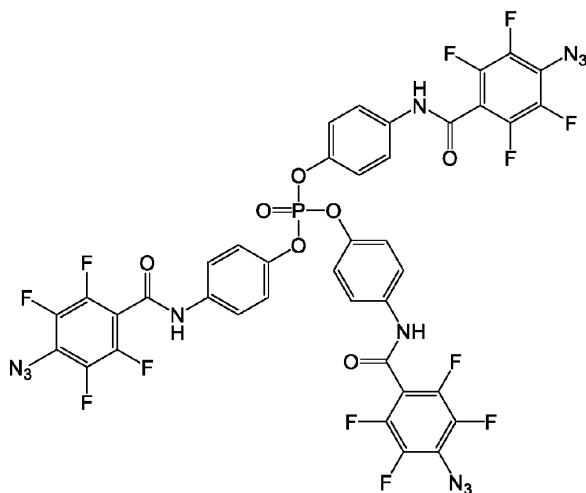
5 hydrogen, hydroxyl, carboxyl, amine, amide, ester, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted oxycarbonylalkyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted substituted carboxylalkyl, optionally substituted alkylcarboxylalkyl, optionally substituted alkyl,
 10 optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkynyl, or combinations thereof;

each of R^1 , R^2 and R^3 is optionally present as a linker selected from carbonyl-containing group, carbonyloxy-containing group, ester-containing group, amide-containing group, carbamate-containing group, amine-containing group, thiol-

15 containing group, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted alkylcarbonyloxy, optionally substituted oxycarbonylalkyl, optionally substituted alkyloxycarbonyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted substituted alkyloxycarbonylalkyl, optionally substituted carbonylaryl, optionally substituted arylcarbonylalkyl, optionally substituted alkylcarbonylaryl, optionally substituted arylcarbonylalkyl, optionally substituted carbonyloxyaryl, optionally substituted arylcarbonyloxy, optionally substituted oxycarbonylaryl, optionally substituted substituted aryloxycarbonyl, optionally substituted arylcarbonyloxyalkyl, optionally substituted alkylcarbonyloxyaryl, optionally substituted arylcarbonyloxyaryl,
 20 arylcarbonyloxyaryl, optionally substituted aryloxycarbonylalkyl, optionally substituted substituted alkyloxycarbonylaryl, optionally substituted aryloxycarbonylaryl,

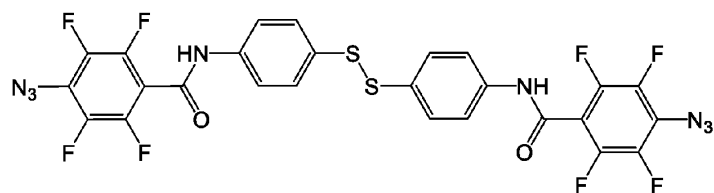
- optionally substituted arylester, optionally substituted alkylester, optionally substituted arylamide, optionally substituted alkylamide, optionally substituted arylcarbamate, optionally substituted alkylcarbamate, optionally substituted arylamine, optionally substituted alkylamine, optionally substituted thioaryl,
- 5 optionally substituted thioalkyl, optionally substituted alkoxy, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof;
- 10 $n \geq 2$; and
- $m \geq 2$.

In one embodiment, the crosslinker is selected from one of the following:

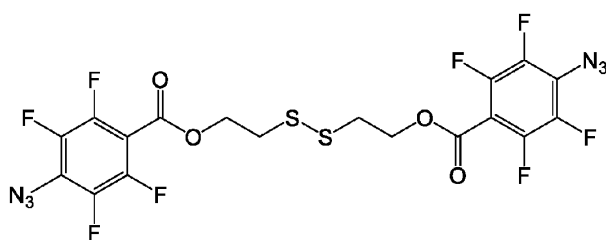


- 15 tris(4-(4-azido-2,3,5,6-tetrafluorobenzamido)phenyl) phosphate,

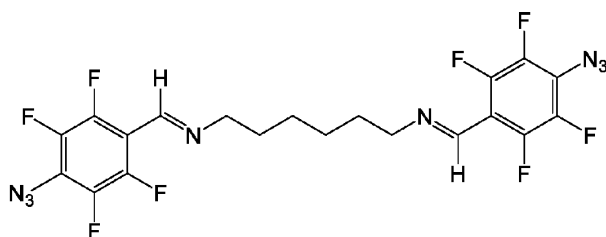
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N,N'-(disulfanediy)bis(4,1-phenylene)bis(4-azido-2,3,5,6-tetrafluorobenzamide),

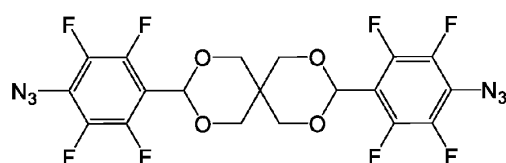


disulfanediybis(ethane-2,1-diyl) bis(4-azido-2,3,5,6-tetrafluorobenzoate),



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N,N'-(hexane-1,6-diyl)bis(1-(4-azido-2,3,5,6-tetrafluorophenyl)methanimine),
and



3,9-bis(4-azido-2,3,5,6-tetrafluorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane.

In one aspect, there is provided a method of preparing a dynamic crosslinker as disclosed herein, the method comprising:

- (a) coupling at least two aryl azide groups *via* one or more dynamic covalent moieties.

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In another aspect, there is provided a method of preparing a covalent adaptable network (CAN), the method comprising:

- (b-i) crosslinking a polymer with a dynamic crosslinker as disclosed herein to obtain a crosslinked polymer.

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In one embodiment, the method further comprises:

- (b-ii) adding a catalyst before, during and/or after step (b-i).

In one embodiment, the catalyst comprises 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), trioctylphosphine, 1,1,3,3-tetramethylguanidine, 1,8-diazabicyclo[5.4.0]undec-7-ene, 2-methylimidazole, 1-methylimidazole, 4-dimethylaminopyridine, zinc acetate, dibutyltin dilaurate, scandium(III) triflate, trifluoroacetic acid, or combinations thereof.

In one embodiment, the method comprises adding from 0.001 wt% to 25 wt% of the catalyst.

In one embodiment, the method comprises adding from 0.01 wt% to 30 wt% of the dynamic crosslinker.

25

In one embodiment, the polymer is selected from polycaprolactone (PCL), poly(ethylene-co-vinyl acetate) (PEVA), polystyrene-block-polybutadiene-block-polystyrene (PSBS), poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), polyethylene, low density polyethylene (LDPE), high density polyethylene (HDPE), propylene (PP), PP-LDPE blend, poly(styrene-co-acrylonitrile) (PSAN), ethylene propylene diene monomer (EPDM), polydimethylsiloxane (PDMS), natural rubber, or combinations thereof.

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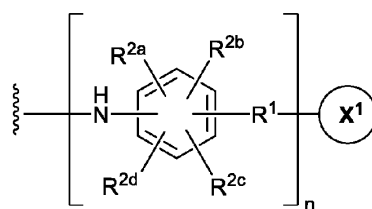
In one embodiment, the step of crosslinking is carried out under one or more of the following conditions:

- (i) temperature that is from 120 °C to 230 °C; and
- (ii) UV radiation.

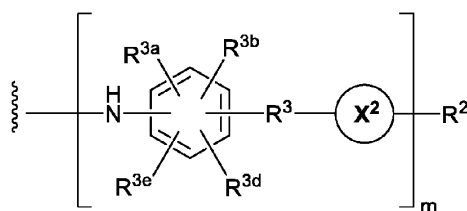
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In one aspect, there is provided a covalent adaptable network (CAN) comprising polymer chains coupled to the dynamic crosslinker disclosed herein *via* dynamic crosslinks.

10 In one embodiment, the dynamic crosslink comprises a structure selected from general formula (5), general formula (6) or combinations thereof:



(5)



(6)

wherein

- 15 each of X^1 and X^2 is independently a dynamic covalent moiety;
- each of R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} and R^{3d} is independently halogen, hydrogen, hydroxyl, carboxyl, amine, amide, ester, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted oxycarbonylalkyl, optionally substituted
- 20 alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carboxylalkyl, optionally substituted alkylcarboxylalkyl, optionally

substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkynyl, or combinations thereof;

each of R^1 , R^2 and R^3 is optionally present as a linker selected from carbonyl-containing group, carbonyloxy-containing group, ester-containing group, amide-containing group, carbamate-containing group, amine-containing group, thiol-containing group, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted alkylcarbonyloxy, optionally substituted oxycarbonylalkyl, optionally substituted alkylloxycarbonyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkylloxycarbonylalkyl, optionally substituted carbonylaryl, optionally substituted arylcarbonylalkyl, optionally substituted alkylcarbonylaryl, optionally substituted arylcarbonylaryl, optionally substituted carbonyloxyaryl, optionally substituted arylcarbonyloxy, optionally substituted oxycarbonylaryl, optionally substituted arylloxycarbonyl, optionally substituted arylcarbonyloxyalkyl, optionally substituted alkylcarbonyloxyaryl, optionally substituted arylcarbonyloxyaryl, optionally substituted arylloxycarbonylalkyl, optionally substituted alkylloxycarbonylaryl, optionally substituted arylloxycarbonylaryl, optionally substituted aryloxy, optionally substituted alkylester, optionally substituted arylester, optionally substituted arylamide, optionally substituted alkylamide, optionally substituted arylcarbamate, optionally substituted alkylcarbamate, optionally substituted arylamine, optionally substituted alkylamine, optionally substituted thioaryl, optionally substituted thioalkyl, optionally substituted alkoxy, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof;

$n \geq 2$; and

$m \geq 2$.

30 In one embodiment, the dynamic crosslinks are exchangeable/cleavable and/or the one or more dynamic covalent bonds are configured to reversibly break and/or form upon application of a stimulus.

In one embodiment, the dynamic crosslinks are exchangeable/cleavable and/or the one or more dynamic covalent bonds are configured to reversibly break and/or form upon application of one or more of the following stimuli:

- (i) temperature that is from 20 °C to 300 °C;
- 5 (ii) pressure that is from 0.1 MPa to 50 MPa;
- (iii) in the presence of a reactive chemical; and
- (iv) UV radiation.

In one embodiment, the reactive chemical comprises alcohol, acid, base,
10 reducing agent, oxidizing agent, dimethyl disulfide, dithiothreitol, or combinations thereof.

In one embodiment, the covalent adaptable network has a gel fraction from
15 30% to 100%.

In one aspect, there is provided a method of recycling a covalent adaptable network (CAN) as disclosed herein, the method comprising:

- (c-i) providing a covalent adaptable network (CAN) as disclosed herein; and
- (c-ii) applying a stimulus to the CAN to reversibly exchange/cleave the dynamic
20 crosslinks and/or reversibly break and/or form one or more dynamic covalent bonds in the CAN.

DEFINITIONS

25 The terms "crosslinked", "crosslink" and "crosslinking" or grammatical variations thereof as used herein broadly refer to the process of forming covalent bonds with and/or between chains of a polymer. In various embodiments, the "crosslinks" are reversible crosslinks such that the crosslinks between the polymer chains are readily exchangeable/breakable/cleavable upon exposure to
30 a stimulus (e.g., heat, radiation, reactive chemical etc).

The term "ultraviolet light" as used herein refers to irradiation by electromagnetic waves in the ultraviolet spectrum/wavelengths. The ultraviolet light may have a wavelength of from about 10 nm to about 400 nm, from about 100 nm to about 400 nm, from about 150 nm to about 350 nm, from about 200 nm to about 300 nm, or about 254 nm. The ultraviolet light may be obtained from a light source (e.g., a mercury lamp) having a power of from about 1 W to about 100 W.

The term "polymer" as used herein broadly refers to a chemical compound comprising repeating units and is created through a process of polymerization. The units composing the polymer are typically derived from monomers and/or macromonomers. The term also encompasses homopolymers which are made up of one type of monomer and copolymers which are made up of two or more different monomers. A polymer typically comprises repetition of a number of constitutional units or repeating structural units (typically more than about 10, more than about 20, more than about 30, more than about 40, or more than about 50).

The term "particle" as used herein broadly refers to a discrete entity or a discrete body. The particle described herein can include an organic, an inorganic, a composite particle or a biological particle. The particle used described herein may also be a macro-particle that is formed by an aggregate of a plurality of sub-particles or a fragment of a small object. The particle of the present disclosure may be spherical, substantially spherical, or non-spherical, such as irregularly shaped particles or ellipsoidally shaped particles. The term "size" when used to refer to the particle broadly refers to the largest dimension of the particle. For example, the term "size" when used in the context of nanoparticle can refer to the diameter of the nanoparticle although it is not limited as such. In various embodiments, when the particle is substantially spherical, the term "size" can refer to the diameter of the particle; or when the particle is substantially non-spherical, the term "size" can refer to the largest length of the particle.

The term "nano" as used herein is to be interpreted broadly to include dimensions in a nanoscale, *i.e.*, less than about 1000 nm, about 1 nm to less than about 1000 nm, about 1 nm to about 900 nm, about 1 nm to about 800 nm, about 1 nm to about 700 nm, about 1 nm to about 600 nm, about 1 nm to about 500 nm, about 1 nm to about 400 nm, about 1 nm to about 300 nm, about 1 nm to about 200 nm, or from about 1 nm to about 100 nm. Accordingly, the term "nanostructures", "nanoparticles", "nanomaterials" and the like as used herein may include structures that have at least one dimension in the range of no more than said range. The term "nanostructures", "nanoparticles", "nanomaterials" and the like as used herein may include structures that have at least one dimension that is no more than about 1,000 nm, no more than about 950 nm, no more than about 900 nm, no more than about 850 nm, no more than about 800 nm, no more than about 750 nm, no more than about 700 nm, no more than about 650 nm, no more than about 600 nm, no more than about 550 nm, no more than about 500 nm, no more than about 450 nm, no more than about 400 nm, no more than about 350 nm, no more than about 300 nm, no more than about 250 nm, no more than about 200 nm, no more than about 150 nm, no more about 100 nm, no more than about 90 nm, no more than about 80 nm, no more than about 70 nm, no more than about 60 nm, no more than about 50 nm, no more than about 40 nm, no more than about 30 nm, no more than about 20 nm, or no more than about 10 nm.

The term "micro" as used herein is to be interpreted broadly to include dimensions from about 1 micron to about 1000 microns, from about 1 micron to less than about 1000 microns, from about 1 micron to about 900 microns, from about 1 micron to about 800 microns, from about 1 micron to about 700 microns, from about 1 micron to about 600 microns, from about 1 micron to about 500 microns, from about 1 micron to about 400 microns, from about 1 micron to about 300 microns, from about 1 micron to about 200 microns, from about 1 micron to about 100 microns, or from about 1 micron to about 5 microns.

The term "bond" refers to a linkage between atoms in a compound or molecule. The bond may be a single bond, a double bond, or a triple bond.

In the definitions of a number of substituents below, it is stated that "the group may be a terminal group or a bridging group". This is intended to signify that the use of the term is intended to encompass the situation where the group is a terminal group/moiety as well as the situation where the group is a linker between two other portions of the molecule. Using the term "alkyl" having 1 carbon atom as an example, it will be appreciated that when existing as a terminal group, the term "alkyl" having 1 carbon atom may mean -CH_3 and when existing as a bridging group, the term "alkyl" having 1 carbon atom may mean $\text{-CH}_2\text{-}$ or the like.

The term "alkyl" as a group or part of a group refers to a straight or branched aliphatic hydrocarbon group having 1 to 20 carbon atoms, 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms. Examples of suitable straight and branched alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, hexyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl, nonyl, decyl and the like. The group may be a terminal group or a bridging group.

The term "alkenyl" as a group or part of a group denotes an aliphatic hydrocarbon group containing at least one carbon-carbon double bond and which may be straight or branched having 2 to 20 carbon atoms, 2 to 10 carbon atoms, 2 to 6 carbon atoms, or 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19

or 20 carbon atoms in the chain. The group may contain a plurality of double bonds and the orientation about each double bond is independently E or Z. Exemplary alkenyl groups include, but are not limited to, ethenyl, vinyl, allyl, 1-methylvinyl, 1-propenyl, 2-propenyl, 2-methyl-1-propenyl, 2-methyl-1-propenyl, 5 1-butenyl, 2-butenyl, 3-butenyl, 1,3-butadienyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1,3-pentadienyl, 2,4-pentadienyl, 1,4-pentadienyl, 3-methyl-2-butenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 1,3-hexadienyl, 1,4-hexadienyl, 2-methylpentenyl, 1-heptenyl, 2-heptenyl, 3-heptenyl, 1-octenyl, 2-octenyl, 3-octenyl, 1-nonenyl, 2-nonenyl, 3-nonenyl, 1-decenyl, 2-decenyl, 3-10 decenyl and the like. The group may be a terminal group or a bridging group.

The term "alkynyl" as a group or part of a group denotes an aliphatic hydrocarbon group containing at least one carbon-carbon triple bond and which may be straight or branched having 2 to 20 carbon atoms, 2 to 10 carbon atoms, 15 2 to 6 carbon atoms, or 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms in the chain. The group may contain a plurality of triple bonds. Exemplary alkynyl groups include, but are not limited to, acetylenyl, propynyl, 1-butynyl, 2-butynyl, 3-butynyl, 1-pentynyl, 2-pentynyl, 3-methyl-1-butynyl, 4-pentynyl, 1-hexynyl, 2-hexynyl, 5-hexynyl, 1-heptynyl, 2-heptynyl, 6-heptynyl, 1-20 octynyl, 2-octynyl, 7-octynyl, 1-nonynyl, 2-nonynyl, 8-nonynyl, 1-decynyl, 2-decynyl, 9-decynyl and the like. The group may be a terminal group or a bridging group.

The term "cyclic" as used herein broadly refers to a structure where one 25 or more series of atoms are connected to form at least one ring. The term includes, but is not limited to, both saturated and unsaturated 5-membered and saturated and unsaturated 6-membered rings. Examples of groups having a cyclic structure include, but are not limited to, cyclopentane, cyclopentene, cyclohexane, cyclohexene, benzene and the like. The term "cyclic" as used 30 herein includes "heterocyclic".

The term "heterocyclic" as used herein broadly refers to a structure where two or more different kinds of atoms are connected to form at least one ring. For example, a heterocyclic ring may be formed by carbon atoms and at least another atom (i.e. heteroatom) selected from oxygen (O), nitrogen (N) or (NR) and sulfur (S), where R is independently a hydrogen or an organic group. The term also includes, but is not limited to, saturated and unsaturated 5-membered, and saturated and unsaturated 6-membered rings. Examples of groups having a heterocyclic structure include, but are not limited to furan, thiophene, 1H-pyrrole, 2H-pyrrole, 1-pyrroline, 2-pyrroline, 3-pyrroline, 1-pyrazoline, 2-pyrazoline, 3-pyrazoline, 2-imidazoline, 3-imidazoline, 4-imidazoline, pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, 1,2,3-triazole, 1,2,4-triazole, 1,2,3-oxadiazole, disubstituted 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, tetrahydrofuran, tetrahydrothiophene, pyrrolidine, 1,3-dioxolane, 1,2-oxathiolane, 1,3-oxathiolane, pyrazolidine, imidazolidine, pyridine, pyridazine, pyrimidine, pyrazine, 1,2-oxazine, 1,3-oxazine, 1,4-oxazine, thiazine, 1,2,3-triazine, 1,2,4-triazine, 1,3,5-triazine, 2H-pyran, 4H-pyran, 2-pyrone, 4-pyrone, 1,4-dioxin, 2H-thiopyran, 4H-thiopyran, tetrahydropyran, thiane, piperidine, 1,4-dioxane, 1,2-dithiane, 1,3-dithiane, 1,4-dithiane, 1,3,5-trithiane, piperazine, morpholine, thiomorpholine and the like.

The term "aryl" as a group or part of a group denotes (i) an optionally substituted monocyclic, or fused polycyclic, aromatic carbocycle (ring structure having ring atoms that are all carbon) preferably having from 5 to 20, or 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms per ring. Examples of aryl groups include but are not limited to phenyl, tolyl, xylyl, naphthyl, anthracenyl, phenanthrenyl, fluorenyl, indenyl, indanyl, phenylene, tolylene, xylylene, naphthylene, anthracenylene, phenanthrenylene, fluorenylene, indenylene or indanylene and the like.

The term "heteroaryl" as a group or part of a group refers to groups containing an aromatic ring (preferably a 5- or 6- membered aromatic ring) having

one or more carbon atoms (for example 1 to 6 carbon atoms) in the ring replaced by a heteroatom. Suitable heteroatoms may include nitrogen (N) or (NH), oxygen (O) and sulfur (S). Examples of heteroaryl include but are not limited to thiophene, benzothiophene, benzofuran, benzimidazole, benzoxazole, benzothiazole, 5 benzisothiazole, naphtha[2,3-b]thiophene, furan, isoindolizine, xantholene, phenoxatine, pyrrole, imidazole, pyrazole, pyridine, pyrazine, pyrimidine, pyridazine, tetrazole, indole, isoindole, 1H-indazole, purine, quinoline, isoquinoline, phthalazine, naphthyridine, quinoxaline, cinnoline, carbazole, phenanthridine, acridine, phenazine, thiazole, isothiazole, phenothiazine, oxazole, 10 isooxazole, furazane, phenoxazine, 2-, 3- or 4-pyridyl, 2-, 3-, 4-, 5-, or 8-quinolyl, 1-, 3-, 4-, or 5-isoquinolyl, 1-, 2-, or 3-indolyl, and 2-, or 3-thienyl and the like. The group may be a terminal group or a bridging group.

The term "halogen" represents chlorine, fluorine, bromine or iodine. The 15 term "halide" represents chloride, fluoride, bromide or iodide.

The term "oxy" as used herein is intended to broadly refer to a group containing —O—.

20 The term "alkoxy" as used herein refers to straight chain or branched alkyloxy groups. The term "alkoxy" as used herein is intended to broadly refer to a group containing —O—R—, where R is alkyl as defined herein. The group may be a terminal group or a bridging group. Examples include methoxy, ethoxy, n-propoxy, isopropoxy, tert-butoxy, and the like.

25 The term "alkoxyalkyl" as used herein is intended to broadly refer to a group containing —R—O—R'—, where R and R' are alkyl as defined herein. The group may be a terminal group or a bridging group.

30 The term "carbonyl" as used herein is intended to broadly refer to a group containing —C(=O)—.

The term "alkylcarbonylalkyl" as used herein is intended to broadly refer to a group containing $-R-C(=O)-R'$, where R and R' are alkyl as defined herein. The group may be a terminal group or a bridging group.

5 The term "carbonyloxy" as used herein is intended to broadly refer to a group containing $-C(=O)-O-$.

The term "oxycarbonyl" as used herein is intended to broadly refer to a group containing $-O-C(=O)-$.

10

The term "ester" as used herein is intended to encompass the terms "carbonyloxy" and/or "oxycarbonyl". For example, the term "ester" as used herein is intended to broadly refer to a group containing $-C(=O)-O-R-$, where R is an organic group such as alkyl or aryl. The group may be a terminal group or a

15

The term "oxycarbonylalkyl" as used herein is intended to broadly refer to a group containing $-O-C(=O)-R-$, where R is alkyl as defined herein. The group may be a terminal group or a bridging group.

20

The term "carbonyloxyalkyl" as used herein is intended to broadly refer to a group containing $-C(=O)-O-R-$, where R is alkyl as defined herein. The group may be a terminal group or a bridging group.

25

The term "carbonylalkyl" as used herein is intended to broadly refer to a group containing $-C(=O)-R-$, where R is alkyl as defined herein. The group may be a terminal group or a bridging group.

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The term "alkylcarbonyl" as used herein is intended to broadly refer to a group containing $-R-C(=O)-$, where R is alkyl as defined herein. The group may be a terminal group or a bridging group.

The term "carboxyl" as used herein is intended to broadly refer to a group containing $-C(=O)-O-R$, where R is hydrogen or an organic group.

5 The term "carboxylalkyl" or "alkylcarboxyl" as used herein is intended to broadly refer to a group containing $-R-C(=O)-O-R'$, where R is alkyl and where R' is hydrogen or an organic group.

10 The term "carbamate" or the like is intended to broadly refer to a group containing $-O-C(=O)NR_2$, where R is independently a hydrogen or an organic group. The group may be a terminal group or a bridging group.

15 The term "amine" or the like is intended to broadly refer to a group containing $-NR_2$, where R is independently a hydrogen or an organic group. The group may be a terminal group or a bridging group.

The term "amide" or the like is intended to broadly refer to a group containing $-C(=O)NR_2$, where R is independently a hydrogen or an organic group. The group may be a terminal group or a bridging group.

20 The term "arylamide" or the like is intended to broadly refer to a group containing $-C(=O)NR'R''$, where R' is a hydrogen or an organic group, and where R'' is an aryl group (e.g., phenylene). The group may be a terminal group or a bridging group.

25 The term "alkylamide" or the like is intended to broadly refer to a group containing $-C(=O)NR'R''$, where R' is a hydrogen or an organic group, and where R'' is an alkyl group (e.g., methylene, ethylene or propylene). The group may be a terminal group or a bridging group.

30 The term "optionally substituted," when used to describe a chemical structure or moiety, refers to the chemical structure or moiety wherein one or more of its hydrogen atoms is optionally substituted with a chemical moiety or

functional group such as alcohol, alkoxy, alkanoyloxy, alkoxycarbonyl, alkenyl, alkyl (e.g., methyl, ethyl, propyl, t-butyl), alkynyl, alkylcarbonyloxy ($-\text{OC}(\text{O})\text{alkyl}$), amide ($-\text{C}(\text{O})\text{NH-alkyl-}$ or $-\text{alkylNHC}(\text{O})\text{alkyl}$), amine (such as alkylamino, arylamino, arylalkylamino), aryl, aryloxy, azo, carbamoyl
5 ($-\text{NHC}(\text{O})\text{O-alkyl-}$ or $-\text{OC}(\text{O})\text{NH-alkyl}$), carbamyl (e.g., CONH_2 , as well as CONH-alkyl , CONH-aryl , and CONH-arylalkyl), carboxyl, carboxylic acid, cyano, ester, ether (e.g., methoxy, ethoxy), halo, haloalkyl (e.g., $-\text{CCl}_3$, $-\text{CF}_3$, $-\text{C}(\text{CF}_3)_3$), heteroalkyl, isocyanate, isothiocyanate, nitrile, nitro, phosphodiester, sulfide, sulfonamido (e.g., SO_2NH_2), sulfone, sulfonyl (including alkylsulfonyl, arylsulfonyl
10 and arylalkylsulfonyl), sulfoxide, thiol (e.g., sulfhydryl, thioether) or urea ($-\text{NHCONH-alkyl-}$).

The terms "coupled" or "connected" as used in this description are intended to cover both directly connected or connected through one or more
15 intermediate means, unless otherwise stated.

The term "associated with", used herein when referring to two elements refers to a broad relationship between the two elements. The relationship includes, but is not limited to a physical, a chemical or a biological relationship.
20 For example, when element A is associated with element B, elements A and B may be directly or indirectly attached to each other or element A may contain element B or vice versa.

The term "adjacent" used herein when referring to two elements refers to
25 one element being in close proximity to another element and may be but is not limited to the elements contacting each other or may further include the elements being separated by one or more further elements disposed therebetween.

The term "and/or", e.g., "X and/or Y" is understood to mean either "X and
30 Y" or "X or Y" and should be taken to provide explicit support for both meanings or for either meaning.

Further, in the description herein, the word "substantially" whenever used is understood to include, but not restricted to, "entirely" or "completely" and the like. In addition, terms such as "comprising", "comprise", and the like whenever used, are intended to be non-restricting descriptive language in that they broadly include elements/components recited after such terms, in addition to other components not explicitly recited. For example, when "comprising" is used, reference to a "one" feature is also intended to be a reference to "at least one" of that feature. Terms such as "consisting", "consist", and the like, may in the appropriate context, be considered as a subset of terms such as "comprising", "comprise", and the like. Therefore, in embodiments disclosed herein using the terms such as "comprising", "comprise", and the like, it will be appreciated that these embodiments provide teaching for corresponding embodiments using terms such as "consisting", "consist", and the like. Further, terms such as "about", "approximately" and the like whenever used, typically means a reasonable variation, for example a variation of +/- 5% of the disclosed value, or a variance of 4% of the disclosed value, or a variance of 3% of the disclosed value, a variance of 2% of the disclosed value or a variance of 1% of the disclosed value.

Furthermore, in the description herein, certain values may be disclosed in a range. The values showing the end points of a range are intended to illustrate a preferred range. Whenever a range has been described, it is intended that the range covers and teaches all possible sub-ranges as well as individual numerical values within that range. That is, the end points of a range should not be interpreted as inflexible limitations. For example, a description of a range of 1% to 5% is intended to have specifically disclosed sub-ranges 1% to 2%, 1% to 3%, 1% to 4%, 2% to 3% etc., as well as individually, values within that range such as 1%, 2%, 3%, 4% and 5%. The intention of the above specific disclosure is applicable to any depth/breadth of a range.

Additionally, when describing some embodiments, the disclosure may have disclosed a method and/or process as a particular sequence of steps. However, unless otherwise required, it will be appreciated that the method or

process should not be limited to the particular sequence of steps disclosed. Other sequences of steps may be possible. The particular order of the steps disclosed herein should not be construed as undue limitations. Unless otherwise required, a method and/or process disclosed herein should not be limited to the steps being
5 carried out in the order written. The sequence of steps may be varied and still remain within the scope of the disclosure.

Furthermore, it will be appreciated that while the present disclosure provides embodiments having one or more of the features/characteristics
10 discussed herein, one or more of these features/characteristics may also be disclaimed in other alternative embodiments and the present disclosure provides support for such disclaimers and these associated alternative embodiments.

It will also be appreciated that where priority is claimed to an earlier
15 application, the full contents of the earlier application is also taken to form part of the present disclosure and may serve as support for embodiments disclosed herein.

DESCRIPTION OF EMBODIMENTS

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Exemplary, non-limiting embodiments of a dynamic crosslinker, a method of preparing said dynamic crosslinker, a covalent adaptable network (CAN) comprising polymer network crosslinked by said dynamic crosslinker, a method of preparing said covalent adaptable network (CAN), a method of recycling said
25 covalent adaptable network (CAN) to reversibly exchange/rearrange dynamic crosslinks and/or reversibly break/cleave and/or form/reform/recombine one or more dynamic covalent bonds in the CAN are disclosed hereinafter.

DYNAMIC CROSSLINKER

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There is provided a compound comprising aryl azide groups. In various embodiments, the aryl azide groups are convertible/transformable/

decomposable/degradable or are capable of being converted/transformed/decomposed/degraded into reactive and/or active species or intermediates. In various embodiments, the azide ($-N_3$) moiety is converted into reactive species such as nitrene species or intermediates upon activation by or exposure to stimuli. For example, upon activation by or exposure to stimuli (e.g., thermally or by light irradiation/photolysis), the azide ($-N_3$) moiety converts into nitrene species with the release of a nitrogen (N_2) molecule. Advantageously, the presence of the aryl azide group/functionality equips the compound with or imparts the ability to produce reactive and/or active species, which readily form bonds or crosslinks (e.g., covalent bonds or covalent crosslinks) with polymers (e.g., hydrocarbon chains of polymers), thereby facilitating/enabling *in situ* or direct crosslinking of polymers. Advantageously, in various embodiments therefore, the design of the compound (due to presence of the azide group/functionality) allows for embodiments of the compound to be used as a crosslinker or a crosslinking agent.

In various embodiments, the aryl azide groups are designed to be coupled/bonded/attached together *via* one or more dynamic covalent moiety. In various embodiments, the dynamic covalent moiety comprises one or more dynamic covalent bond(s) or linkage(s) that is/are adaptable and/or flexible, allowing the one or more dynamic covalent bond(s) or linkage(s) to be exchangeable under suitable conditions. For example, the dynamic covalent moiety may undergo exchange or rearrangement of bond(s) or linkage(s) reversibly within/among itself under suitable conditions. In various embodiments, the reversible exchange or rearrangement of dynamic covalent bonds is carried out autonomously under ambient conditions or driven by external stimuli (such as heat, light etc). In various embodiments, the dynamic covalent moiety comprises one or more dynamic covalent bond(s) or linkage(s) that is/are capable of reversibly breaking/cleaving and/or forming/reforming/join/rejoining under suitable conditions. For example, the dynamic covalent bond(s) or linkage(s) may reversibly break and/or form/reform autonomously or in response to stimuli. Advantageously, the presence of the dynamic covalent moiety and/or dynamic

covalent bond(s) or linkage(s) equips the compound/crosslinker with or imparts the ability to reversibly break and reform bond(s), thereby allowing the compound/crosslinker to undergo reversible bond exchange or bond rearrangement within said compound/crosslinker. In various embodiments, dynamic covalent bonds are designed into the compound/crosslinker to enable reversible bond exchange. Advantageously, the reversible bond exchange/rearrangement may occur or take place between different compound/crosslinker molecules. The reversible bond exchange/rearrangement may also occur or take place between a compound/crosslinker molecule and another molecule or polymer having similar dynamic covalent bonds.

In various embodiments, the compound is designed/configured to allow the one or more dynamic covalent bonds to break/cleave upon exposure to or application of a stimulus. In various embodiments, the compound is also designed/configured to allow the one or more broken/cleaved dynamic covalent bonds to be reversibly formed/reformed/joined/rejoined upon exposure to or application of another stimulus. Advantageously, in various embodiments therefore, the design of the compound (due to presence of the dynamic covalent moiety and/or dynamic covalent bond(s)/linkage(s)) allows for embodiments of the compound to be used as a dynamic crosslinker or a dynamic crosslinking agent.

In various embodiments, the reactive intermediate formed from activation of the dynamic crosslinker (e.g., nitrene) is non-radical-based. Advantageously, by using a non-radical-based dynamic crosslinker, embodiments of the method reduce the possibility/risk of generating defects which would otherwise arise due to occurrence of unwanted side reactions from the presence of radicals.

In various embodiments, the number of aryl azide groups, dynamic covalent moieties and/or dynamic covalent bonds present in the dynamic crosslinker is/are customizable and/or adjustable as desired.

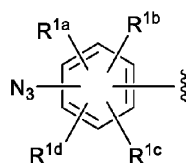
In various embodiments, the dynamic crosslinker is designed to comprise at least two, at least three, at least four, at least five, at least six, at least seven, at least eight, at least nine, or at least ten aryl azide groups. In various embodiments, the dynamic crosslinker comprises two aryl azide groups, three
5 aryl azide groups or four aryl azide groups.

In various embodiments, the aryl azide groups in the dynamic crosslinker are designed to couple/bond/attach together *via* one or more dynamic covalent moiety. In various embodiments, the aryl azide groups are
10 coupled/bonded/attached together *via* one or more, two or more, three or more, four or more, five or more, six or more, seven or more, eight or more, nine or more, or ten or more dynamic covalent moieties. In various embodiments, the dynamic crosslinker comprises one dynamic covalent moiety, two dynamic covalent moieties, three dynamic covalent moieties or four dynamic covalent
15 moieties.

In various embodiments, the dynamic covalent moiety is designed to comprise one or more, two or more, three or more, four or more, five or more, or six or more dynamic covalent bonds or linkages. In various embodiments, the
20 dynamic covalent moiety comprises one dynamic covalent bond/linkage, two dynamic covalent bonds/linkages, three dynamic covalent bonds/linkages or four dynamic covalent bonds/linkages.

In various embodiments, the aryl azide group is optionally substituted. In
25 various embodiments, the aryl azide group comprises phenyl azide or azidobenzene.

In various embodiments, each aryl azide group independently comprises a structure represented by general formula (1):

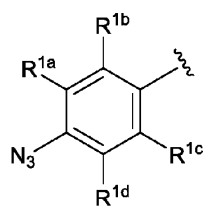


(1)

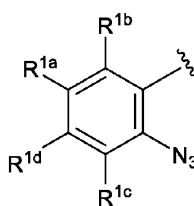
wherein

- 5 R^{1a} , R^{1b} , R^{1c} and R^{1d} are each independently halogen, hydrogen, hydroxyl, carboxyl, amine, amide, ester, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted oxycarbonylalkyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carboxylalkyl,
- 10 optionally substituted alkylcarboxylalkyl, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkynyl, or combinations thereof.

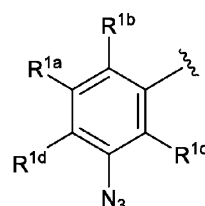
- In various embodiments, the aryl azide group comprises an azide (N_3) moiety in the 4-position (or para), 3-position (or meta), or 2-position (or ortho). For example, each aryl azide group may independently comprise a structure represented by general formula (1A), (1B) or (1C):
- 15



(1A)



(1B)



(1C)

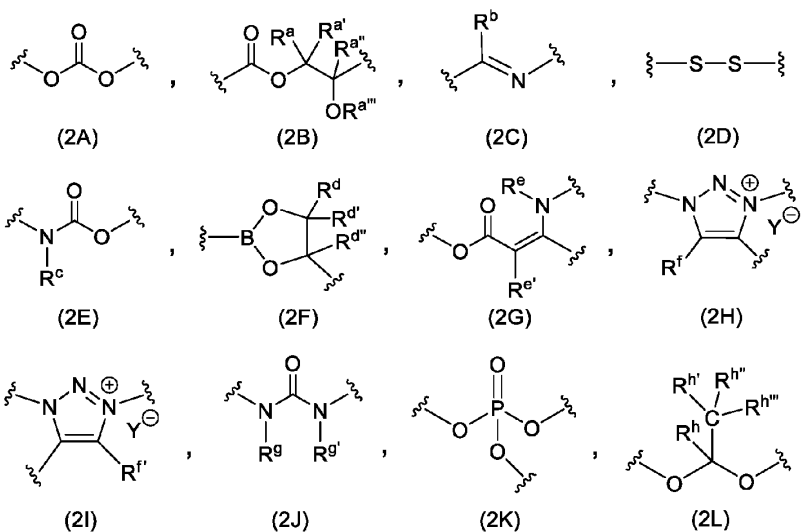
- wherein R^{1a} to R^{1d} contain one or more features and/or share one or more properties that are similar to those described above (e.g., as defined in general formula (1)).
- 20

In various embodiments, R^{1a} , R^{1b} , R^{1c} and R^{1d} are each independently halogen selected from the group consisting of fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and combinations thereof.

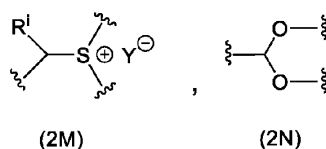
- 5 In various embodiments, R^{1a} , R^{1b} , R^{1c} and R^{1d} are each independently a straight, branched or cyclic alkyl, alkenyl or alkynyl group, having from 1 to 20 carbon atoms.

- 10 In various embodiments, R^{1a} , R^{1b} , R^{1c} and R^{1d} are each independently carbonylalkyl, alkylcarbonylalkyl, carbonyloxyalkyl, oxycarbonylalkyl, alkylcarbonyloxyalkyl, alkyloxycarbonylalkyl, carboxylalkyl or alkylcarboxylalkyl, having from 1 to 20 carbon atoms.

- 15 In various embodiments, the dynamic covalent moiety comprises a structure selected from the group consisting of general formula (2A), (2B), (2C), (2D), (2E), (2F), (2G), (2H), (2I), (2J), (2K), (2L), (2M), (2N) and combinations thereof:



29



wherein

$R^a, R^a', R^{a''}, R^{a'''}, R^b, R^c, R^d, R^{d'}, R^{d''}, R^e, R^{e'}, R^f, R^{f'}, R^g, R^{g'}, R^h, R^{h'}, R^{h''}, R^{h'''}, R^i,$
 R^j, R^j and $R^{j'}$ are each independently hydrogen, optionally substituted alkyl,
 5 optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof.

10 In various embodiments, $R^a, R^a', R^{a''}, R^{a'''}, R^b, R^c, R^d, R^{d'}, R^{d''}, R^e, R^{e'}, R^f, R^{f'}, R^g, R^{g'}, R^h, R^{h'}, R^{h''}, R^{h'''}, R^i, R^j$ and $R^{j'}$ are H.

In various embodiments, $R^a, R^a', R^{a''}, R^{a'''}, R^b, R^c, R^d, R^{d'}, R^{d''}, R^e, R^{e'}, R^f, R^{f'}, R^g, R^{g'}, R^h, R^{h'}, R^{h''}, R^{h'''}, R^i, R^j, R^{j'}$ and $R^{j''}$ are each independently an optionally substituted straight, branched or cyclic alkyl, alkenyl and/or alkynyl group having
 15 from 1 to 20 carbon atoms. In various embodiments, $R^a, R^a', R^{a''}, R^{a'''}, R^b, R^c, R^d, R^{d'}, R^{d''}, R^e, R^{e'}, R^f, R^{f'}, R^g, R^{g'}, R^h, R^{h'}, R^{h''}, R^{h'''}, R^i, R^j, R^{j'}$ and $R^{j''}$ are each independently an optionally substituted aryl group having from 6 to 20 carbon atoms.

20

In various embodiments, $R^a, R^a', R^{a''}, R^{a'''}, R^b, R^c, R^d, R^{d'}, R^{d''}, R^e, R^{e'}, R^f, R^{f'}, R^g, R^{g'}, R^h, R^{h'}, R^{h''}, R^{h'''}, R^i, R^j, R^{j'}$ and $R^{j''}$ are selected from optionally substituted alkyl, optionally substituted alkenyl or optionally substituted alkynyl. For example, $R^a, R^a', R^{a''}, R^{a'''}, R^b, R^c, R^d, R^{d'}, R^{d''}, R^e, R^{e'}, R^f, R^{f'}, R^g, R^{g'}, R^h, R^{h'}, R^{h''}, R^{h'''}, R^i, R^j$ and $R^{j'}$ may be selected from methyl, ethyl, n-propyl, 2-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, hexyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-

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ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl, nonyl, decyl, or the like or combinations thereof. For example, Rⁱ may be selected from methylene, ethylene, n-propylene, 2-propylene, isopropylene, *n*-butylene, isobutylene, *sec*-butylene, *t*-butylene, hexylene, amylene, 1,2-dimethylpropylene, 1,1-dimethylpropylene, pentylene, isopentylene, 4-methylpentylene, 1-methylpentylene, 2-methylpentylene, 3-methylpentylene, 2,2-dimethylbutylene, 3,3-dimethylbutylene, 1,2-dimethylbutylene, 1,3-dimethylbutylene, 1,2,2-trimethylpropylene, 1,1,2-trimethylpropylene, 2-ethylpentylene, 3-ethylpentylene, heptylene, 1-methylhexylene, 2,2-dimethylpentylene, 3,3-dimethylpentylene, 4,4-dimethylpentylene, 1,2-dimethylpentylene, 1,3-dimethylpentylene, 1,4-dimethylpentylene, 1,2,3-trimethylbutylene, 1,1,2-trimethylbutylene, 1,1,3-trimethylbutylene, 5-methylheptylene, 1-methylheptylene, octylene, nonylene, decylene, or the like or combinations thereof.

In various embodiments, each aryl azide group is directly coupled/bonded/attached to a dynamic covalent moiety and/or dynamic covalent bond/linkage. In various embodiments therefore, the dynamic crosslinker is substantially devoid of a linker or a linking moiety/group. In various embodiments, the dynamic crosslinker comprises a dynamic covalent moiety coupled/bonded/attached to another dynamic covalent moiety *via* a linker.

In various embodiments, each aryl azide group is optionally coupled/bonded/attached to a dynamic covalent moiety and/or dynamic covalent bond/linkage *via* a linker or a linking moiety/group. It will be appreciated that any suitable linking moiety or group that effectively couples/bonds/attaches/links an aryl azide group to a dynamic covalent moiety and/or dynamic covalent bond/linkage may be used as the linker.

In various embodiments, the linker comprises an organic group selected from carbonyl-containing group, carbonyloxy-containing group, ester-containing group, amide-containing group, carbamate-containing group, amine-containing group, thiol-containing group, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted alkylcarbonyloxy, optionally substituted oxycarbonylalkyl, optionally substituted alkyloxycarbonyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carbonylaryl, optionally substituted arylcarbonylalkyl, optionally substituted alkylcarbonylaryl, optionally substituted arylcarbonylaryl, optionally substituted carbonyloxyaryl, optionally substituted arylcarbonyloxy, optionally substituted oxycarbonylaryl, optionally substituted aryloxycarbonyl, optionally substituted arylcarbonyloxyalkyl, optionally substituted alkylcarbonyloxyaryl, optionally substituted arylcarbonyloxyaryl, optionally substituted aryloxycarbonylalkyl, optionally substituted alkyloxycarbonylaryl, optionally substituted aryloxycarbonylaryl, optionally substituted aryylester, optionally substituted alkylester, optionally substituted arylamide, optionally substituted alkylamide, optionally substituted arylcarbamate, optionally substituted alkylcarbamate, optionally substituted arylamine, optionally substituted alkylamine, optionally substituted thioaryl, optionally substituted thioalkyl, optionally substituted alkoxy, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof.

In various embodiments, the one or more dynamic covalent bonds (present in the dynamic covalent moiety) are designed/configured to undergo reversible bond exchange or bond rearrangement upon exposure to or under application of a stimulus. In various embodiments, the one or more dynamic covalent bonds (present in the dynamic covalent moiety) are designed/configured to reversibly break/cleave and/or form/reform/join/rejoin upon exposure to or

under application of a stimulus. In various embodiments, the dynamic covalent bonds are designed in such a way that an application of a stimulus facilitates (or results in) the bond breaking, cleaving and/or rearranging among themselves. In various embodiments, the dynamic covalent bonds are also designed in such a way that an application of a stimulus facilitates (or results in) the broken/cleaved bonds forming/reforming, joining/rejoining and/or rearranging among themselves. Such stimulus may include thermal energy (e.g., heat), pressure (e.g., mechanical pressure), chemical(s) (e.g., reactive chemical, acid or base, reducing or oxidising agents), ultraviolet light (e.g. irradiation by electromagnetic waves in the ultraviolet spectrum/wavelengths), visible light (e.g. irradiation by electromagnetic waves in the visible light spectrum/wavelengths), natural light, artificial light, ion addition, electric current, vibration, ultrasound and the like and combinations thereof.

In various embodiments, the one or more dynamic covalent bonds (present in the dynamic covalent moiety) are designed/configured to reversibly break/cleave and/or form/reform upon exposure to or under application of one or more of the following stimuli:

- (i) temperature;
- (ii) pressure;
- (iii) presence/exposure to chemical; and
- (iv) light irradiation.

In various embodiments, the one or more dynamic covalent bonds are configured to reversibly break/cleave and/or undergoes bond exchange/rearrangement at a temperature that is from about 20 °C to about 300 °C, from about 25 °C to about 290 °C, from about 30 °C to about 280 °C, from about 35 °C to about 270 °C, from about 40 °C to about 260 °C, from about 45 °C to about 255 °C, from about 50 °C to about 250 °C, from about 55 °C to about 245 °C, from about 60 °C to about 240 °C, from about 65 °C to about 235 °C, from about 70 °C to about 230 °C, from about 75 °C to about 225 °C, from about 80 °C to about 220 °C, from about 85 °C to about 215 °C, from about 90

°C to about 210 °C, from about 95 °C to about 205 °C, from about 100 °C to about 200 °C, from about 105 °C to about 195 °C, from about 110 °C to about 190 °C, from about 115 °C to about 185 °C, from about 120 °C to about 180 °C, from about 125 °C to about 175 °C, from about 130 °C to about 170 °C, from about 135 °C to about 165 °C, from about 140 °C to about 160 °C, from about 145 °C to about 155 °C, or about 150 °C. For example, un-crosslinking/de-crosslinking may occur at a temperature that is from about 20 °C to about 300 °C. In various embodiments, the temperature at which bond exchange of the dynamic crosslinks occurs is dependent on the glass transition temperature (T_g) of the covalent adaptable network (CAN) and/or activation energy (E_a) of the dynamic bonds.

In various embodiments, the one or more dynamic covalent bonds are configured to reversibly undergoes bond exchange/rearrangement at a pressure that is from about 0.1 MPa to about 100 MPa, from about 0.2 MPa to about 95.0 MPa, from about 0.5 MPa to about 90.0 MPa, from about 1.0 MPa to about 85.0 MPa, from about 1.5 MPa to about 80.0 MPa, from about 2.0 MPa to about 75.0 MPa, from about 2.5 MPa to about 70.0 MPa, from about 3.0 MPa to about 65.0 MPa, from about 3.5 MPa to about 60.0 MPa, from about 4.0 MPa to about 55.0 MPa, from about 4.5 MPa to about 50.0 MPa, from about 5.0 MPa to about 45.0 MPa, from about 5.5 MPa to about 40.0 MPa, from about 6.0 MPa to about 35.0 MPa, from about 6.5 MPa to about 30.0 MPa, from about 7.0 MPa to about 25.0 MPa, from about 7.5 MPa to about 20.0 MPa, from about 8.0 MPa to about 15.0 MPa, from about 8.5 MPa to about 10.0 MPa, or from about 9.0 MPa to about 9.5 MPa. In various embodiments, the one or more dynamic covalent bonds are configured to reversibly undergoes bond exchange/rearrangement at nominal pressure, e.g., nominal atmospheric pressure at about 1 atm or about 0.10 MPa. For example, exchange of dynamic covalent bonds may occur at a pressure that is from about 0.1 MPa to about 10.0 MPa, or about 0.5 MPa.

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In various embodiments, the one or more dynamic covalent bonds are configured to reversibly break/cleave and/or undergoes bond

exchange/rearrangement upon exposure or in the presence of one or more reactive chemicals. In various embodiments, the reactive chemical is selected from alcohol/alcoholic solvent, acid, base, reducing agent, oxidizing agent, dimethyl disulfide, dithiothreitol, the like, or combinations thereof. In various
5 embodiments, the alcohol comprises higher alcohol or alcohol with higher molecular weight. For example, the reactive chemical may be an alcohol selected from octanol (e.g., 1-octanol), nonanol, decanol, or combinations thereof. In various embodiments, reactive chemicals such as dimethyl disulfide and/or dithiothreitol is/are used for breaking/cleaving S–S bonds present in the covalent
10 adaptable network (CAN).

 In various embodiments, the reactive chemical comprises dual functionality, that is, the reactive chemical is not only capable of breaking/cleaving the dynamic covalent bonds in the CANs, but may also serve/act as a solvent to
15 substantially dissolve/contain the CANs in the composition. For example, an alcoholic solvent may be used as a reactive chemical (to break/cleave the dynamic bonds) and as a solvent to swell the CANs.

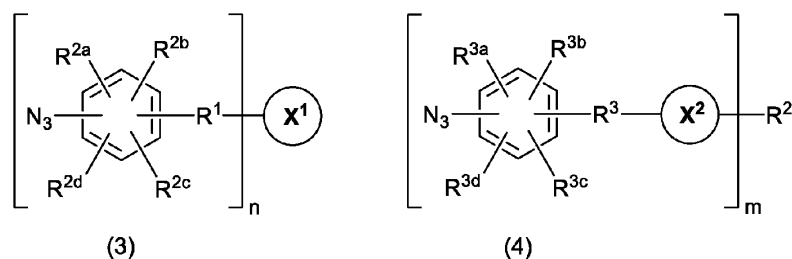
 In various embodiments, the reactive chemical comprises mono
20 functionality, that is, the reactive chemical is capable of breaking/cleaving the dynamic covalent bonds in the CANs, but may not be suitable for use as a solvent. In such embodiments, the reactive chemical is provided together with an additional solvent (e.g., organic solvent) to substantially dissolve/contain and/or compatibilise the reactive chemical and the CANs. The organic solvent may
25 comprise toluene or the like. For example, un-crosslinking/de-crosslinking may occur upon exposure or in the presence of one or more reactive chemicals and/or solvents. In various embodiments, the organic solvent used is not a reactive chemical which can break the dynamic bond e.g. toluene.

30 In various embodiments, the one or more aryl azide groups are configured to irreversibly lose N₂ gas to generate reactive nitrene species upon thermal activation or exposure to heat. For example, polymer crosslinking may occur at a

temperature that is from about 120°C to about 230°C, from about 125°C to about 225°C, from about 130°C to about 220°C, from about 135°C to about 215°C, from about 140°C to about 210°C, from about 145°C to about 205°C, from about 150°C to about 200°C, from about 155°C to about 195°C, from about 160°C to about 190°C, from about 165°C to about 185°C, from about 170°C to about 180°C, or about 175°C. These pertain to the activation of the aryl azide groups to perform the initial crosslinking, rather than the dynamic bond exchange step.

In various embodiments, the one or more aryl azide groups are configured to irreversibly lose N₂ gas to generate reactive nitrene species upon activation by or exposure to light irradiation. For example, polymer crosslinking may occur upon activation by or exposure to irradiation by electromagnetic waves in the ultraviolet spectrum/wavelengths (e.g., light/UV activation). The ultraviolet light may have a wavelength of from about 100 nm to about 400 nm, from about 150 nm to about 350 nm, from about 200 nm to about 300 nm, or about 254 nm.

In various embodiments, the dynamic crosslinker comprises a structure selected from general formula (3), general formula (4), or combinations thereof:



20

wherein

each of **X¹** and **X²** is independently a dynamic covalent moiety;

each of R^{2a}, R^{2b}, R^{2c}, R^{2d}, R^{3a}, R^{3b}, R^{3c} and R^{3d} is independently halogen, hydrogen, hydroxyl, carboxyl, amine, amide, ester, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted oxycarbonylalkyl, optionally substituted

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alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carboxylalkyl, optionally substituted alkylcarboxylalkyl, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkynyl, or combinations thereof;

- 5 each of R¹, R² and R³ is optionally present as a linker selected from carbonyl-containing group, carbonyloxy-containing group, ester-containing group, amide-containing group, carbamate-containing group, amine-containing group, thiol-containing group, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted alkylcarbonyloxy, optionally substituted oxycarbonylalkyl, optionally substituted alkyloxycarbonyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carbonylaryl, optionally substituted arylcarbonylalkyl, optionally substituted alkylcarbonylaryl, optionally substituted arylcarbonylaryl, optionally substituted carbonyloxyaryl, optionally substituted arylcarbonyloxy, optionally substituted oxycarbonylaryl, optionally substituted aryloxycarbonyl, optionally substituted arylcarbonyloxyalkyl, optionally substituted alkylcarbonyloxyaryl, optionally substituted arylcarbonyloxyaryl, optionally substituted aryloxycarbonylalkyl, optionally substituted aryloxycarbonylaryl, optionally substituted arylester, optionally substituted alkylester, optionally substituted arylamide, optionally substituted alkylamide, optionally substituted arylcarbamate, optionally substituted alkylcarbamate, optionally substituted arylamine, optionally substituted alkylamine, optionally substituted thioaryl, optionally substituted thioalkyl, optionally substituted alkoxy, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof;

n ≥ 2; and

- 30 m ≥ 2.

In various embodiments, n is an integer ≥ 2 . In various embodiments, $n \geq 2$, $n \geq 3$, $n \geq 4$, or $n \geq 5$.

In various embodiments, m is an integer ≥ 2 . In various embodiments, $m \geq 2$, $m \geq 3$, $m \geq 4$, $m \geq 5$, or $m \geq 6$. In various embodiments, when R^2 is branched, m may be more than 4.

In various embodiments where $n \geq 2$ or $m \geq 2$, the substituents X^1 , X^2 , R^1 , R^2 , R^3 , R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} and R^{3d} may be same or different. For example, when $n = 4$ and there are a total of four X^1 , each of the four X^1 may be same or different from each other.

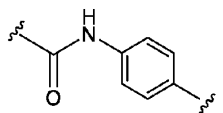
In various embodiments, R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} and R^{3d} contain one or more features and/or share one or more properties that are similar to those described above for R^{1a} to R^{1d} (as defined in general formula (1)).

In various embodiments, the dynamic crosslinker comprises a structure represented by general formula (3). In such embodiments, the dynamic crosslinker comprises one dynamic covalent moiety X^1 . In various embodiments, the dynamic crosslinker comprises two or more aryl azide groups which are each coupled to the dynamic covalent moiety X^1 via a linker. For example, the dynamic crosslinker may comprise two aryl azide groups coupled to the dynamic covalent moiety X^1 via two respective linkers R^1 . For example, the dynamic crosslinker may comprise three aryl azide groups coupled to the dynamic covalent moiety X^1 via three respective linkers R^1 .

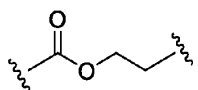
In various embodiments, the dynamic crosslinker comprises a structure represented by general formula (4). In such embodiments, the dynamic crosslinker comprises two or more dynamic covalent moiety X^2 . In various embodiments, the dynamic crosslinker comprises a dynamic covalent moiety linked to another dynamic covalent moiety via a linker. For example, the dynamic

crosslinker may comprise a dynamic covalent moiety X^2 linked to another dynamic covalent moiety X^2 via a linker R^2 .

In various embodiments, linker R^1 , R^2 and/or R^3 are optionally substituted
 5 arylamide. For example, R^1 , R^2 and/or R^3 may be phenylamide, i.e.



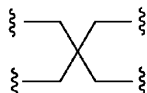
In various embodiments, linker R^1 , R^2 and/or R^3 are optionally substituted
 carbonyloxyalkyl. In various embodiments, R^1 , R^2 and/or R^3 are optionally
 10 substituted carbonyloxymethyl, optionally substituted carbonyloxyethyl or
 optionally substituted carbonyloxypropyl. For example, R^1 , R^2 and/or R^3 may be
 carbonyloxyethyl, i.e.



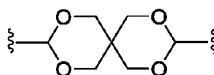
15 In various embodiments, linker R^1 , R^2 and/or R^3 are selected from straight,
 branched or cyclic optionally substituted alkyl, optionally substituted alkenyl or
 optionally substituted alkynyl. For example, R^1 , R^2 and/or R^3 may be selected
 from methylene, ethylene, n-propylene, 2-propylene, isopropylene, n-butylene,
 isobutylene, sec-butylene, t-butylene, hexylene, amylene, 1,2-
 20 dimethylpropylene, 1,1-dimethylpropylene, pentylene, isopentylene, 4-
 methylpentylene, 1-methylpentylene, 2-methylpentylene, 3-methylpentylene,
 2,2-dimethylbutylene, 3,3-dimethylbutylene, 1,2-dimethylbutylene, 1,3-
 dimethylbutylene, 1,2,2-trimethylpropylene, 1,1,2-trimethylpropylene, 2-
 ethylpentylene, 3-ethylpentylene, heptylene, 1-methylhexylene, 2,2-
 25 dimethylpentylene, 3,3-dimethylpentylene, 4,4-dimethylpentylene, 1,2-
 dimethylpentylene, 1,3-dimethylpentylene, 1,4-dimethylpentylene, 1,2,3-
 trimethylbutylene, 1,1,2-trimethylbutylene, 1,1,3-trimethylbutylene, 5-

methylheptylene, 1-methylheptylene, octylene, nonylene, decylene, or the like or combinations thereof.

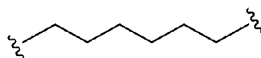
In various embodiments, linker R^1 , R^2 and/or R^3 are branched alkyl. For example, R^1 , R^2 and/or R^3 may be 3,3-dimethylpentylene, i.e.



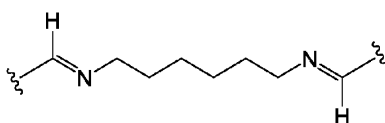
For example, in embodiments where the dynamic covalent moiety X^2 comprises a structure represented by general formula (2N), the dynamic crosslinker may comprise a dynamic covalent moiety X^2 linked to another dynamic covalent moiety X^2 via a linker R^2 as shown in the following structure:



In various embodiments, R^1 , R^2 and/or R^3 are linear alkyl. For example, R^1 , R^2 and/or R^3 may be hexylene, i.e.

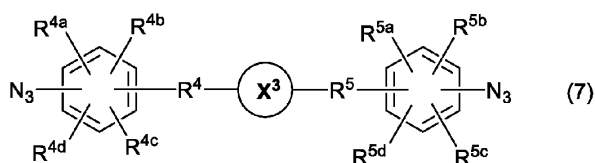


For example, in embodiments where the dynamic covalent moiety X^2 comprises a structure represented by general formula (2C), the dynamic crosslinker may comprise a dynamic covalent moiety X^2 linked to another dynamic covalent moiety X^2 via a linker R^2 as shown in the following structure:



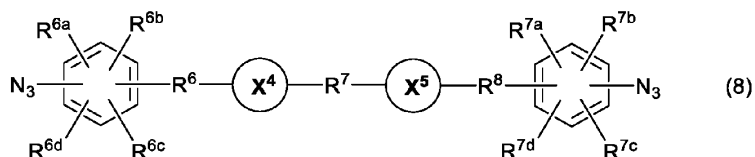
In various embodiments, the dynamic crosslinker comprises a structure selected from general formulae (7), (8), (9), (10) and/or (11).

In various embodiments, $n = 2$. In various embodiments, two aryl azide groups are coupled/bonded/attached together *via* one dynamic covalent moiety. In such embodiments, the dynamic crosslinker comprises a structure that is represented by general formula (7):



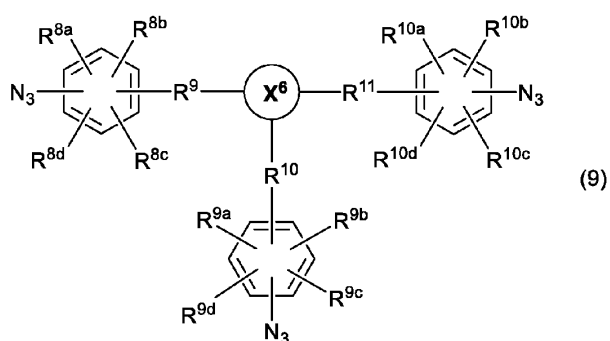
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In various embodiments, $m = 2$. In various embodiments, two aryl azide groups are coupled/bonded/attached together *via* two dynamic covalent moieties. In such embodiments, the dynamic crosslinker comprises a structure that is represented by general formula (8):



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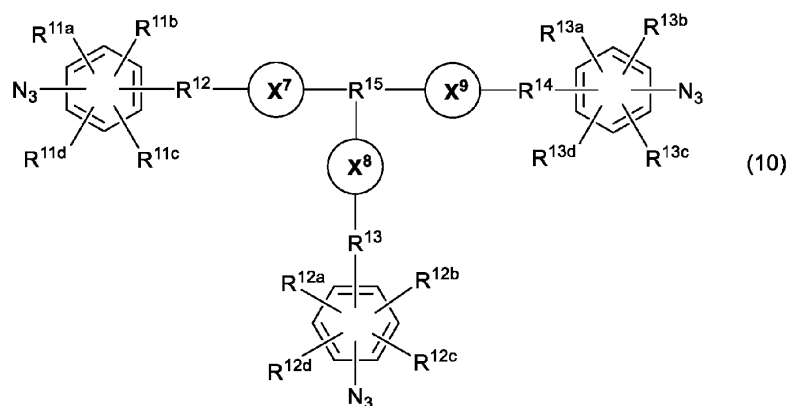
In various embodiments, $n = 3$. In various embodiments, three aryl azide groups are coupled/bonded/attached together *via* one dynamic covalent moiety. In such embodiments, the dynamic crosslinker comprises a structure that is represented by general formula (9):



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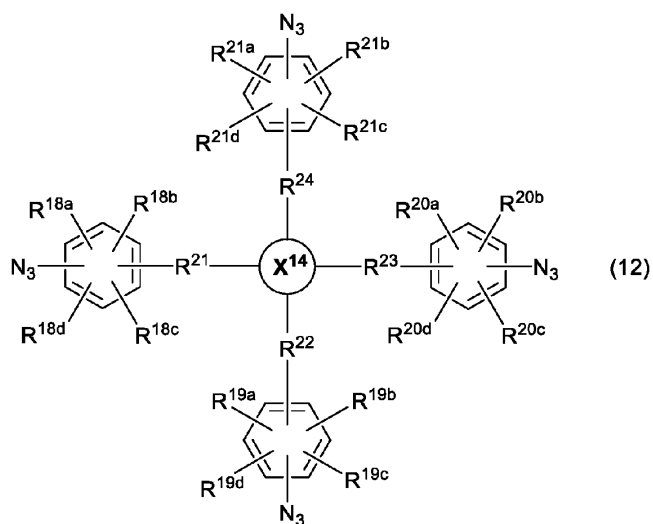
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In various embodiments, $m = 3$. In various embodiments, three aryl azide groups are coupled/bonded/attached together *via* three dynamic covalent moieties. In such embodiments, the dynamic crosslinker comprises a structure that is represented by general formula (10):



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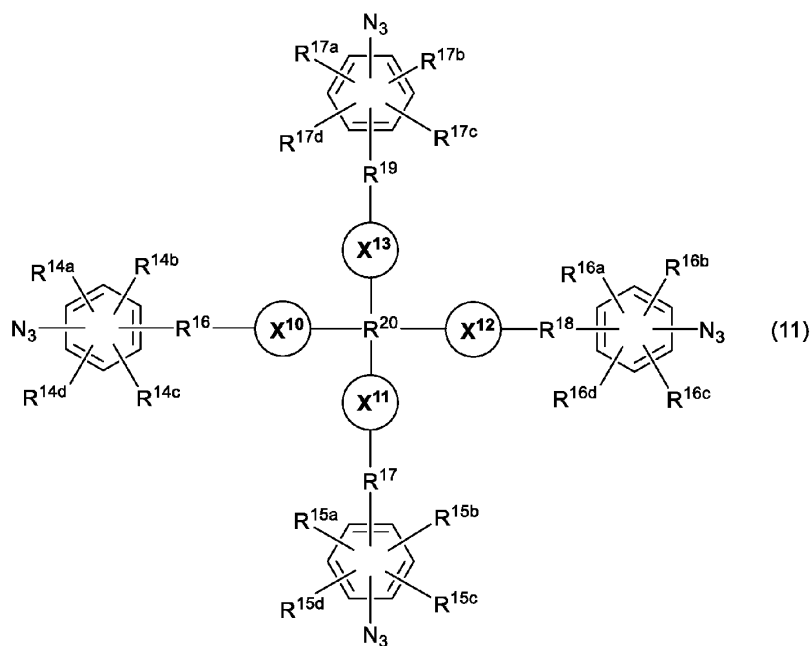
In various embodiments, $n = 4$. In various embodiments, four aryl azide groups are coupled/bonded/attached together *via* one dynamic covalent moiety. In such embodiments, the dynamic crosslinker comprises a structure that is represented by general formula (12):



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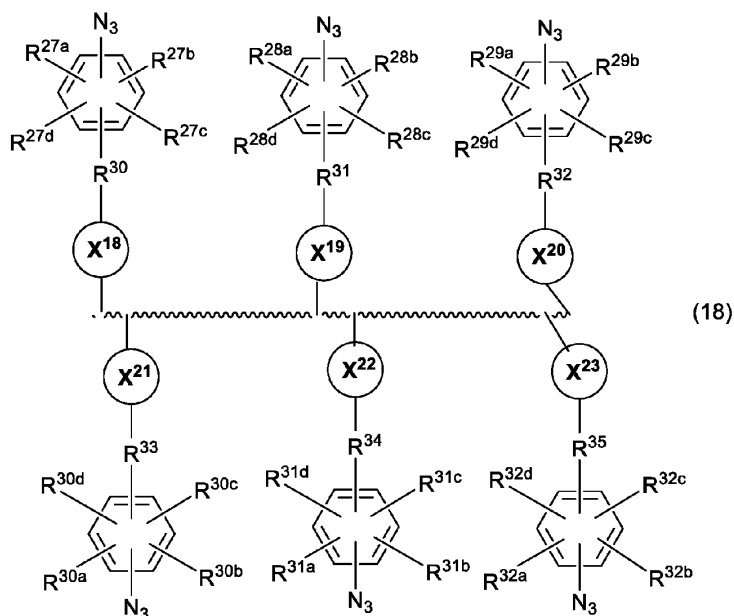
In various embodiments, $m = 4$. In various embodiments, four aryl azide groups are coupled/bonded/attached together *via* four dynamic covalent moieties. In such embodiments, the dynamic crosslinker comprises a structure that is represented by general formula (11):

5



In various embodiments, $m = 6$. In various embodiments, six aryl azide groups are coupled/bonded/attached together *via* six dynamic covalent moieties. In various embodiments, the six dynamic covalent moieties (e.g., as represented by X¹⁸, X¹⁹, X²⁰, X²¹, X²² and X²³) are coupled/bonded/attached/linked together *via* a branching agent. In such embodiments, the dynamic crosslinker comprises a structure that is represented by general formula (18):

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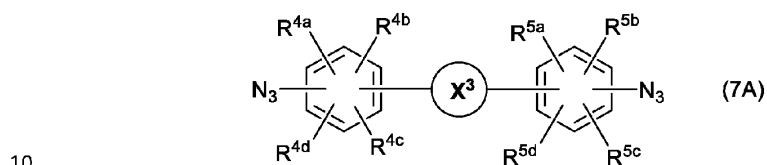
It will be appreciated that any suitable moiety, group or substituent that effectively couples/bonds/attaches/links the dynamic covalent moieties (e.g., 6
 5 dynamic covalent moieties represented by X^{18} , X^{19} , X^{20} , X^{21} , X^{22} and X^{23}) may be used as the branching agent.

In various embodiments, R^{4a} to R^{4d} , R^{5a} to R^{5d} , R^{6a} to R^{6d} , R^{7a} to R^{7d} , R^{8a} to R^{8d} , R^{9a} to R^{9d} , R^{10a} to R^{10d} , R^{11a} to R^{11d} , R^{12a} to R^{12d} , R^{13a} to R^{13d} , R^{14a} to R^{14d} ,
 10 R^{15a} to R^{15d} , R^{16a} to R^{16d} , R^{17a} to R^{17d} , R^{18a} to R^{18d} , R^{19a} to R^{19d} , R^{20a} to R^{20d} , R^{21a} to R^{21d} , R^{27a} to R^{27d} , R^{28a} to R^{28d} , R^{29a} to R^{29d} , R^{30a} to R^{30d} , and R^{31a} to R^{31d} contain one or more features and/or share one or more properties that are similar to those described above for R^{1a} to R^{1d} (as defined in general formula (1)).

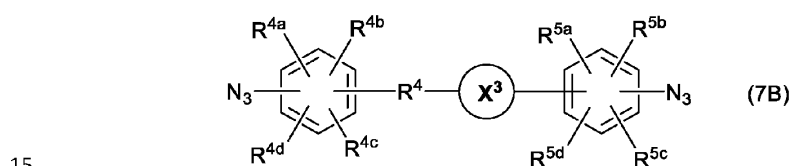
15 In various embodiments, X^3 , X^4 , X^5 , X^6 , X^7 , X^8 , X^9 , X^{10} , X^{11} , X^{12} , X^{13} , X^{14} , X^{18} , X^{19} , X^{20} , X^{21} , X^{22} and X^{23} contain one or more features and/or share one or more properties that are similar to those described above for X^1 to X^2 (as defined in general formula (2) and (3)).

In various embodiments, R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} , R^{24} , R^{30} , R^{31} , R^{32} , R^{33} , R^{34} and R^{35} are optionally present and contain one or more features and/or share one or more properties that are similar to those described above for R^1 to R^3 (as defined in
 5 general formula (2) and (3)).

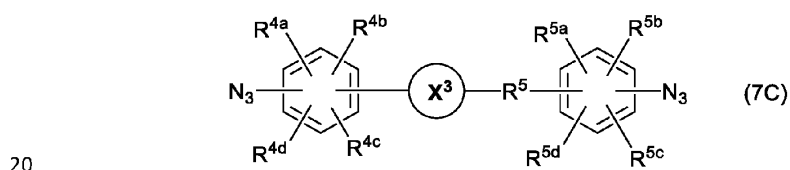
In various embodiments, R^4 and R^5 are absent from general formula (7). In such embodiments, the dynamic crosslinker comprises a structure represented by general formula (7A):



In various embodiments, R^5 is absent from general formula (7). In such embodiments, the dynamic crosslinker comprises a structure represented by general formula (7B):

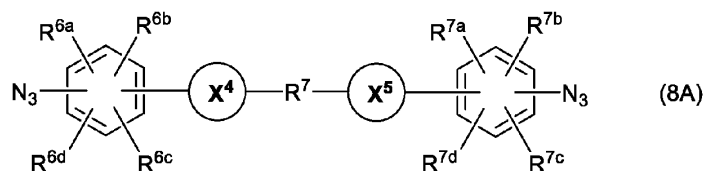


In various embodiments, R^4 is absent from general formula (7). In such embodiments, the dynamic crosslinker comprises a structure represented by general formula (7C):



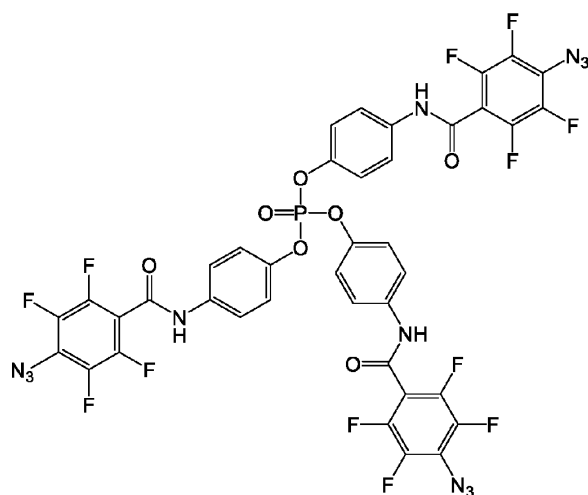
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In various embodiments, R^6 and R^8 are absent from general formula (8).
In such embodiments, the dynamic crosslinker comprises a structure represented by general formula (8A):



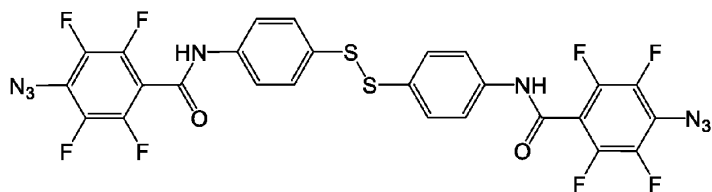
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In various embodiments, the dynamic crosslinker is selected from one of the following:



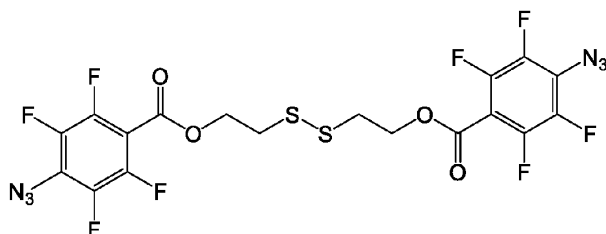
tris(4-(4-azido-2,3,5,6-tetrafluorobenzamido)phenyl) phosphate,

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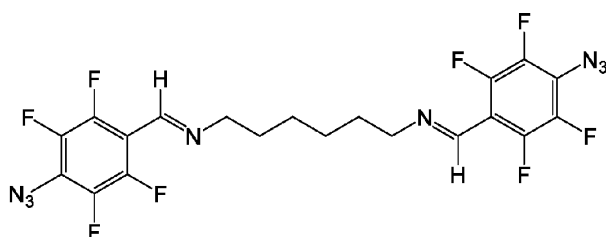


N,N'-(disulfanediylbis(4,1-phenylene))bis(4-azido-2,3,5,6-tetrafluorobenzamide),

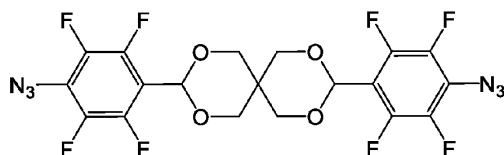
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disulfanediylbis(ethane-2,1-diyl) bis(4-azido-2,3,5,6-tetrafluorobenzoate),



N,N'-(hexane-1,6-diyl)bis(1-(4-azido-2,3,5,6-tetrafluorophenyl)methanimine),
and



3,9-bis(4-azido-2,3,5,6-tetrafluorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane.

REPRESENTATIVE METHODS OF PREPARING DYNAMIC CROSSLINKER

There is provided non-limiting representative methods of a method of preparing a dynamic crosslinker as disclosed herein. In various embodiments, the method comprising:

- (a) coupling/bonding/attaching at least two aryl azide groups together *via* one or more dynamic covalent moieties.

In various embodiments, step (a) comprises coupling/bonding/attaching at least two aryl azide groups directly to one or more dynamic covalent moieties. In

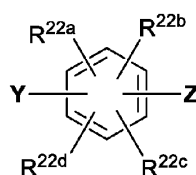
various embodiments, step (a) is substantially devoid of the use of a linker or a linking moiety/group. In various embodiments, step (a) comprises coupling/bonding/attaching at least two aryl azide groups to one or more dynamic covalent moieties *via* a linker or linking moiety/group.

5

In various embodiments, step (a) comprises:

- (a-i) reacting an aryl compound (e.g., two or more aryl compounds) represented by general formula (13) with a dynamic bond source to obtain the dynamic crosslinker, e.g., represented by general formula (3) and/or (4):

10



(13)

wherein

R^{22a} to R^{22d} contain one or more features and/or share one or more properties that are similar to those described above for R^{1a} to R^{1d} , as defined in general formula (1);

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Y is selected from azide, halide, or combinations thereof; and

Z comprises a carbonyl-containing group or a linker/linking moiety/group.

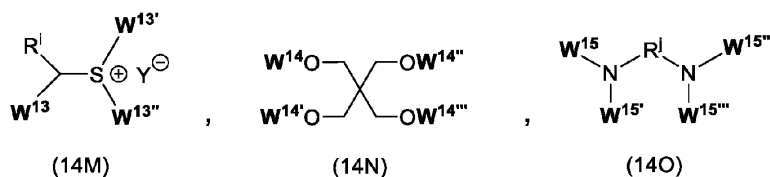
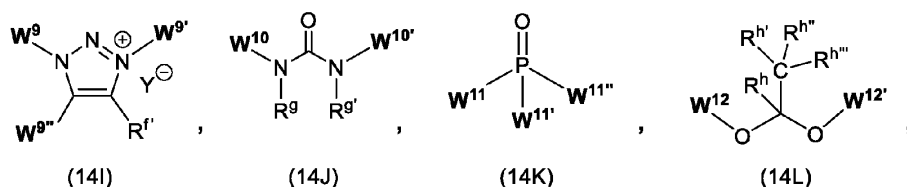
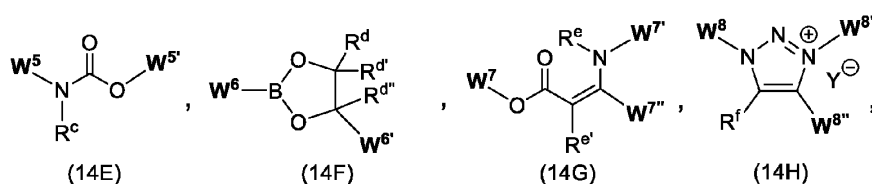
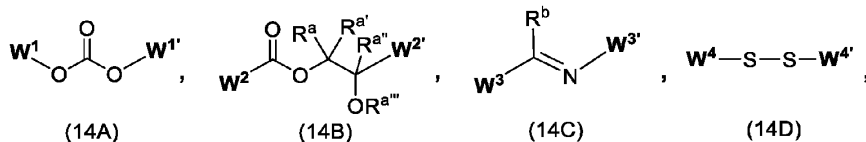
In various embodiments, the linker or linking moiety/group contain one or more features and/or share one or more properties that are similar to those described above. It will be appreciated that any suitable linking moiety or group that effectively couples/bonds/attaches/links an aryl azide group to a dynamic covalent moiety and/or dynamic covalent bond/linkage may be used as the linker.

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In various embodiments, the dynamic bond source comprises a structure selected from the group consisting of general formula (14A), (14B), (14C), (14D),

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(14E), (14F), (14G), (14H), (14I), (14J), (14K), (14L), (14M), (14N), (14O) and combinations thereof:



wherein

R^a, R^{a'}, R^{a''}, R^{a'''}, R^b, R^c, R^d, R^{d'}, R^{d''}, R^e, R^{e'}, R^f, R^{f'}, R^g, R^{g'}, R^h, R^{h'}, R^{h''}, R^{h'''}, Rⁱ and R^j are each independently hydrogen, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof;

W¹, W^{1'}, W², W^{2'}, W³, W^{3'}, W⁴, W^{4'}, W⁵, W^{5'}, W⁶, W^{6'}, W⁷, W^{7'}, W^{7''}, W⁸, W^{8'}, W^{8''}, W⁹, W^{9'}, W^{9''}, W¹⁰, W^{10'}, W¹¹, W^{11'}, W^{11''}, W¹², W^{12'}, W¹³, W^{13'}, W^{13''}, W¹⁴, W^{14'}, W^{14''}, W^{14'''}, W¹⁵, W^{15'}, W^{15''} and W^{15'''} are each independently hydrogen, halide, carbonyl-containing group, carbonyloxy-containing group, ester-containing

group, amide-containing group, carbamate-containing group, amine-containing group, thiol-containing group, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted alkylcarbonyloxy, optionally substituted oxycarbonylalkyl, optionally substituted alkyloxycarbonyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carbonylaryl, optionally substituted arylcarbonylalkyl, optionally substituted alkylcarbonylaryl, optionally substituted arylcarbonylaryl, optionally substituted carbonyloxyaryl, optionally substituted arylcarbonyloxy, optionally substituted oxycarbonylaryl, optionally substituted aryloxycarbonyl, optionally substituted arylcarbonyloxyalkyl, optionally substituted alkylcarbonyloxyaryl, optionally substituted arylcarbonyloxyaryl, optionally substituted aryloxycarbonylalkyl, optionally substituted alkyloxycarbonylaryl, optionally substituted aryloxycarbonylaryl, optionally substituted ary-lester, optionally substituted alkylester, optionally substituted arylamide, optionally substituted alkylamide, optionally substituted arylcarbamate, optionally substituted alkylcarbamate, optionally substituted arylamine, optionally substituted alkylamine, optionally substituted thioaryl, optionally substituted thioalkyl, optionally substituted alkoxy, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof.

25 In various embodiments, step (a-i) comprises preparing/synthesizing a dynamic crosslinker from a reagent that already contains a dynamic covalent moiety/bond. For example, step (a-i) may comprise synthesizing a dynamic crosslinker comprising disulfide bond(s) from a reagent already containing said disulfide bond(s). In various embodiments, disulfide crosslinkers are obtained
30 from step (a-i).

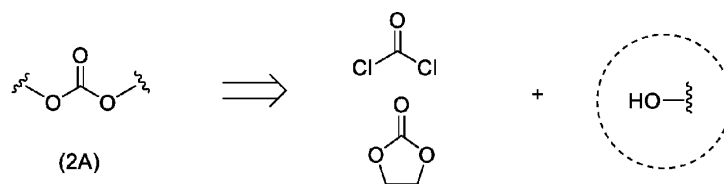
It will be appreciated that other methods (not described above) may also be used to obtain/prepare the dynamic crosslinker (e.g., represented by general formula (3) and/or (4)). For example, dynamic crosslinkers may also be formed from two reagents (e.g., two dynamic bond precursors), which each contributes/forms part of the dynamic covalent moiety/bond, as shown in the following schemes. In some embodiments where the method comprises preparing/synthesizing a dynamic crosslinker from a dynamic bond precursor (e.g., comprising components that are circled below), then said dynamic bond precursor contains an aryl azide or its precursor. For example, said dynamic bond precursor may be an aryl azide-bearing dynamic bond precursor. In some embodiments where the method comprises preparing/synthesizing a dynamic crosslinker from dynamic bond precursors (e.g., comprising components that are not circled below), then either of said dynamic bond precursors may contain the aryl azide.

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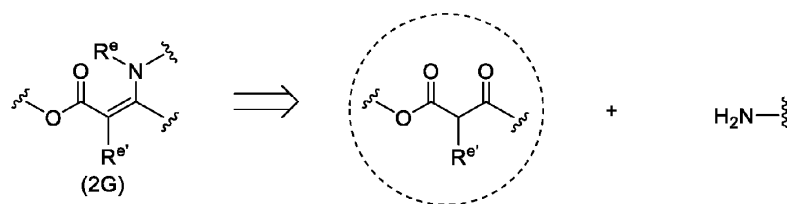
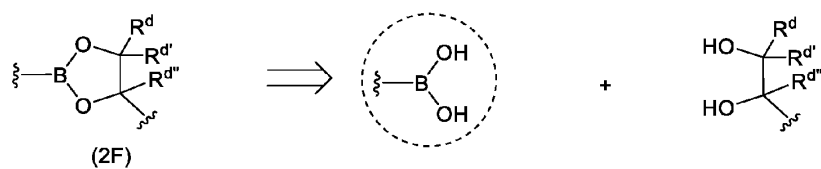
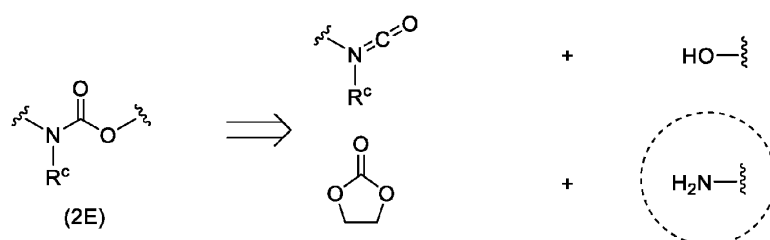
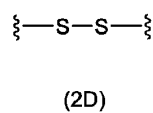
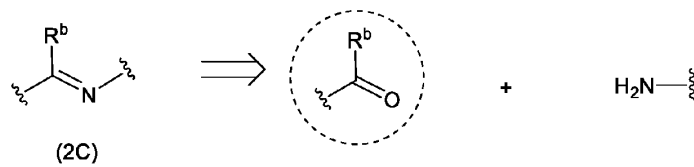
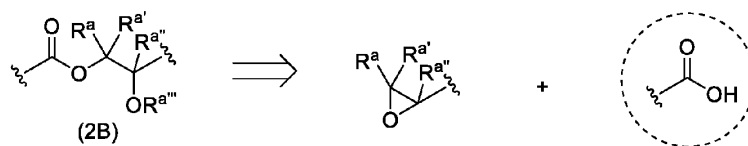
In various embodiments, step (a) comprises:

(d-i) reacting an aryl compound (e.g., two or more aryl compounds) represented by general formula (13) comprising a dynamic bond precursor (e.g. containing aldehyde, acid, acid chloride or the like) with another dynamic bond precursor to obtain the dynamic crosslinker (e.g., represented by general formula (3) and/or (4)). In various embodiments, step (d-i) comprises preparing/synthesizing a dynamic crosslinker from two or more reagents that do not contain a dynamic covalent moiety/bond. For example, step (d-i) may comprise synthesizing a dynamic bond(s) during the reaction.

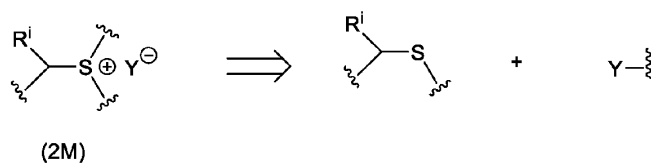
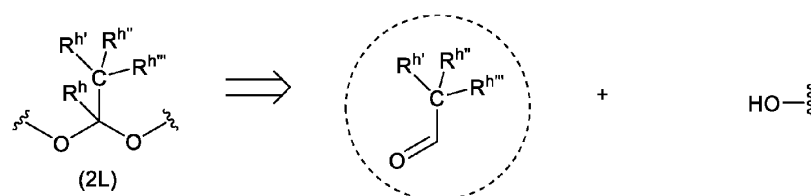
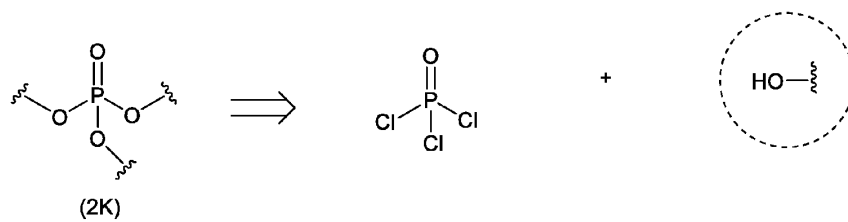
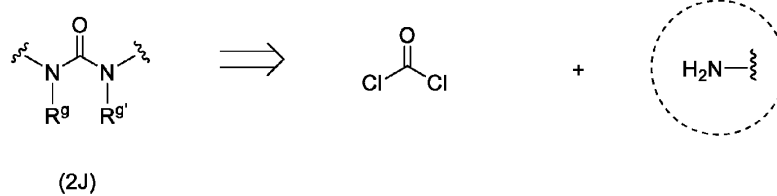
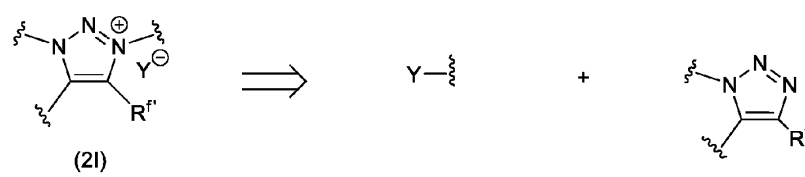
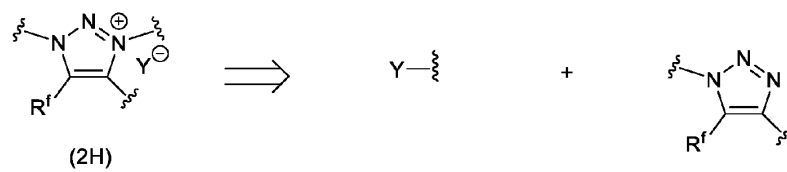
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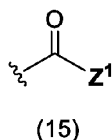


In various embodiments, both steps (a-i) and (d-i) may be either preceded by step (a-ii) or followed by step (a-iii).

In various embodiments, the dynamic bond source(s)/precursor(s) comprises amine, diol or combinations thereof (e.g., diamine, triamine, tetramine, diol, triol and tetraol). In various embodiments, the dynamic bond source/precursor is selected from phosphorus oxychloride (POCl_3), 4,4'-dithiodianiline, 2-hydroxyethyl disulfide, 1,6-diaminohexane, pentaerythritol, the like or combinations thereof. It will be appreciated that any suitable compound that can be used for effectively incorporating/introducing dynamic covalent moiety/bond into the resultant dynamic crosslinker may be used as the dynamic bond source/precursor.

In various embodiments, **Y** is azide ($-\text{N}_3$), fluoride ($-\text{F}$), chloride ($-\text{Cl}$), bromide ($-\text{Br}$), iodide ($-\text{I}$), sulfide ($-\text{S}^-$), diazonium ($-\text{N}_2^+$), the like or combinations thereof.

In various embodiments, **Z** is a group comprising carbonyl. In various embodiments, **Z** comprises a structure represented by general formula (15):

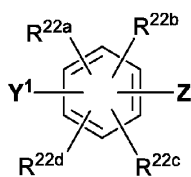


wherein

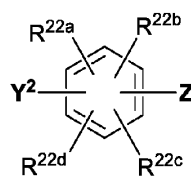
Z¹ is $-\text{H}$, $-\text{OH}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{OR}^k$, $-\text{NHR}^m\text{OH}$, the like or combinations thereof, where R^k is optionally substituted alkyl (e.g., methyl, ethyl or propyl), optionally substituted alkenyl or optionally substituted alkynyl and where R^m is optionally substituted alkyl or aryl. For example, R^m may be C_6H_4 and **Z¹** may be $-\text{NHC}_6\text{H}_4\text{OH}$.

In various embodiments, the step (a) optionally further comprises, prior to step (a-i):

- (a-ii) reacting an aryl compound represented by general formula (13A) with an azide source to obtain an aryl azide compound represented by general formula (13B):



(13A)



(13B)

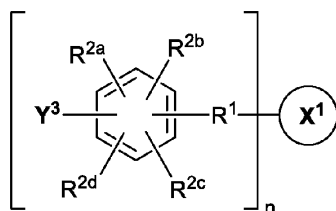
wherein

Y^1 is halide, sulfide or diazonium; and Y^2 is azide.

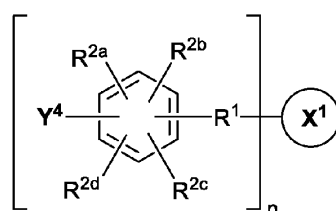
- 10 In various embodiments, the azide source comprises metal azides selected from sodium azide, potassium azide, or combinations thereof.

In various embodiments, the step (a) optionally further comprises,

- (a-iii) reacting an aryl compound represented by general formula (3A) and/or general formula (4A) with an azide source to obtain an aryl azide compound represented by general formula (3B) and/or (4B) respectively:

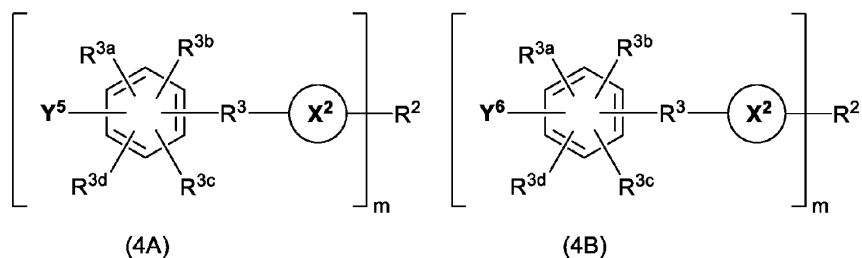


(3A)



(3B)

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wherein

Y^3 and Y^5 are each halide, sulfide or diazonium; and Y^4 and Y^6 are each azide.

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In various embodiments, the step (a) comprises carrying out/performing step (a-i) and (step (a-ii). In various embodiments, the step (a) comprises carrying out/performing step (a-i) and step (a-iii). In various embodiments, step (a-ii) is carried out before step (a-i). In various embodiments, step (a-i) is carried out before step (a-iii). It should be appreciated that the order of the steps is not limited to the steps being carried out in the order written herein, and they may be carried out in other order or sequence.

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METHOD OF PREPARING COVALENT ADAPTABLE NETWORK (CAN)

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In various embodiments, there is provided a method of preparing a covalent adaptable network (CAN), the method comprising:

(b-i) crosslinking a polymer with a dynamic crosslinker as disclosed herein to obtain a crosslinked polymer.

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Advantageously, in various embodiments, the dynamic crosslinker is designed/configured to allow the crosslinking or formation of crosslinks with 2 or more polymer chains, thereby forming/formulating/obtaining a crosslinked polymer. In various embodiments of the dynamic crosslinker, the aryl azide groups are convertible/transformable/decomposable/degradable or are capable of being converted/transformed/decomposed/degraded into reactive and/or

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active species or intermediates. For example, upon activation by or exposure to stimuli, the azide ($-N_3$) moiety converts into reactive species such as nitrene species or intermediates with the release of a nitrogen (N_2) molecule. In various embodiments, such reactive and/or active species readily/efficiently/promptly/easily form or are capable of readily/efficiently/promptly/easily forming bonds or linkages with a polymer (e.g., hydrocarbon chains of the polymer). Advantageously, in various embodiments, the presence of the aryl azide group/functionality equips said dynamic crosslinker with or imparts the ability to produce reactive and/or active species, which readily/efficiently/promptly/easily form bonds or crosslinks (e.g., covalent bonds or covalent crosslinks) with polymers, thereby facilitating/enabling *in situ* or direct crosslinking of polymers.

Advantageously, due to the presence of azide moiety/functionality, crosslinking of a polymer with embodiments of the dynamic crosslinker is performed readily/efficiently/promptly/easily upon activation by or exposure to stimuli (e.g., temperature, light irradiation etc). In various embodiments, the step (b-i) of crosslinking is carried out under one or more of the following stimuli:

- (i) temperature; and
- (ii) light irradiation.

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In various embodiments, the step (b-i) of crosslinking occurs upon activation by or exposure to heat (e.g., thermal activation). In various embodiments, the step of crosslinking occurs/is carried out at a temperature that is from about 120°C to about 230°C, from about 125°C to about 225°C, from about 130°C to about 220°C, from about 135°C to about 215°C, from about 140°C to about 210°C, from about 145°C to about 205°C, from about 150°C to about 200°C, from about 155°C to about 195°C, from about 160°C to about 190°C, from about 165°C to about 185°C, from about 170°C to about 180°C, or about 175°C.

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In various embodiments, the step (b-i) of crosslinking occurs upon activation by or exposure to light irradiation. In various embodiments, the step of

crosslinking occurs upon activation by or exposure to irradiation by electromagnetic waves in the ultraviolet spectrum/wavelengths (e.g, light/UV activation). The ultraviolet light may have a wavelength of from about 100 nm to about 400 nm, from about 150 nm to about 350 nm, from about 200 nm to about 300 nm, or about 254 nm.

In various embodiments, the step (b-i) of crosslinking comprises adding/mixing from about 0.01 wt% to about 30 wt%, or from about 1 wt% to about 20 wt% of the dynamic crosslinker. In various embodiments, the step (b-i) of crosslinking comprises adding/mixing from about 0.01 wt% to about 30 wt%, from about 0.02 wt% to about 29 wt%, from about 0.03 wt% to about 28 wt%, from about 0.04 wt% to about 27 wt%, from about 0.05 wt% to about 26 wt%, from about 0.06 wt% to about 25 wt%, from about 0.07 wt% to about 24 wt%, from about 0.08 wt% to about 23 wt%, from about 0.09 wt% to about 22 wt%, from about 0.1 wt% to about 21 wt%, from about 0.2 wt% to about 20 wt%, from about 0.3 wt% to about 19 wt%, from about 0.4 wt% to about 18 wt%, from about 0.5 wt% to about 17 wt%, from about 0.6 wt% to about 16 wt%, from about 0.7 wt% to about 15 wt%, from about 0.8 wt% to about 14 wt%, from about 0.9 wt% to about 13 wt%, from about 1 wt% to about 12 wt%, from about 1.5 wt% to about 11 wt%, from about 2 wt% to about 10 wt%, from about 2.5 wt% to about 9.5 wt%, from about 3 wt% to about 9 wt%, from about 3.5 wt% to about 8.5 wt%, from about 4 wt% to about 8 wt%, from about 4.5 wt% to about 7.5 wt%, from about 5 wt% to about 7 wt%, from about 5.5 wt% to about 6.5 wt%, or about 6 wt% of the dynamic crosslinker. In various embodiments, no more than about 30 wt% of the dynamic crosslinker is added to or mixed in step (b-i), to avoid the crosslinkers reacting with each other. In various embodiments, a low amount/concentration of about 0.01 wt% of dynamic crosslinker is added/used when crosslinking with high molecular weight polymers.

In various embodiments, the dynamic crosslinker links a chain/repeating unit to another chain/repeating unit of the polymer to form a crosslinked polymer. In various embodiments, the dynamic crosslinker is designed/configured to allow

the crosslinking or formation of crosslinks with/between two or more, three or more, four or more, five or more, six or more, seven or more, eight or more, nine or more, or ten or more polymer chains. For example, the dynamic crosslinker may link a total of two, three, four, five, six, seven, eight, nine, or ten polymer chains together. The polymer that may be crosslinked by embodiments of the dynamic crosslinker disclosed herein comprises a linear, substantially linear or slightly branched/non-linear polymer. In various embodiments, the polymer comprises thermoplastics, e.g., bulk thermoplastics. The polymer may comprise a polymer having an isotactic, syndiotactic and/or atactic structure. For example, the polymer may include but is not limited to polycaprolactone (PCL), poly(ethylene-*co*-vinyl acetate) (PEVA), polystyrene-*block*-polybutadiene-*block*-polystyrene (PSBS), poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), polyethylene, low density polyethylene (LDPE), high density polyethylene (HDPE), propylene (PP), PP-LDPE blend, poly(styrene-*co*-acrylonitrile) (PSAN), ethylene propylene diene monomer (EPDM), polydimethylsiloxane (PDMS), natural rubber, the like, or combinations thereof. Advantageously, in various embodiments, the method allows crosslinking of thermoplastic (or thermoplastic polymers) to form recyclable thermoset (or recyclable thermosetting polymers).

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In various embodiments of the dynamic crosslinker, the aryl azide groups are designed to be coupled/bonded/attached together *via* one or more dynamic covalent moiety. In various embodiments, the dynamic covalent moiety comprises one or more dynamic covalent bond(s) or linkage(s) that is/are adaptable and/or flexible, allowing the one or more dynamic covalent bond(s) or linkage(s) to undergo exchange or rearrangement reversibly within/among itself under suitable conditions. In various embodiments, the dynamic covalent moiety comprises one or more dynamic covalent bond(s) or linkage(s) that is/are capable of reversibly breaking/cleaving and/or forming/reforming/join/rejoining under suitable conditions. Advantageously, the presence of the dynamic covalent moiety and/or dynamic covalent bond(s) or linkage(s) equips the crosslinked polymer with or imparts the ability to reversibly break and reform bond(s), thereby

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allowing the crosslinked polymer to undergo reversible bond exchange or bond rearrangement within said crosslinked polymer. Advantageously, in various embodiments therefore, the crosslinked polymer disclosed herein is a covalent adaptable network (CAN) having one or more of the following properties:

5 reprocessable, recyclable, reconfigurable, self-healing, malleable, mechanically strong and/or tough.

In various embodiments, the method further comprises:

(b-ii) adding a catalyst.

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In various embodiments, step (b-ii) comprises infusing/embedding the crosslinked polymer with catalyst in order to facilitate bond exchange/arrangement (or dynamic bond exchange/rearrangement), and consequently facilitate the recycling/reconfiguration of the CAN.

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In various embodiments, the catalyst comprises 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,1,3,3-Tetramethylguanidine, 1,8-Diazabicyclo[5.4.0]undec-7-ene, phosphine (e.g., trioctylphosphine), Bronsted base (e.g., 2-methylimidazole, 1-methylimidazole or 4-

20 dimethylaminopyridine), Lewis acid (e.g., zinc acetate ($\text{Zn}(\text{OAc})_2$), dibutyltin dilaurate or scandium(III) triflate), organic acid such as trifluoroacetic acid.

Advantageously, the use/addition/infusion of catalyst increases the rate of dynamic bond exchange.

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In various embodiments where the dynamic covalent moiety/bond comprises phosphate group/linkage, the catalyst is selected from TBD, 1,1,3,3-Tetramethylguanidine, 1,8-Diazabicyclo[5.4.0]undec-7-ene, the like, or combinations thereof. Advantageously, in phosphate bond exchange, the TBD

30 catalyst acts as a nucleophile to cleave P–O bond.

In various embodiments where the dynamic covalent moiety/bond comprises disulfide group/linkage, the catalyst comprises phosphine (e.g. trioctylphosphine). Advantageously, in disulfide bond exchange, the phosphine catalyst acts as a nucleophile to cleave S–S bond.

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In various embodiments where the dynamic covalent moiety/bond comprises ester group/linkage, the catalyst is selected from Bronsted base (e.g., 2-methylimidazole, 1-methylimidazole or 4-dimethylaminopyridine), Lewis acid ($\text{Zn}(\text{OAc})_2$ or dibutyltin dilaurate), the like or combinations thereof.

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In various embodiments where the dynamic covalent moiety/bond comprises imine group/linkage, the catalyst is selected from organic acid (e.g., trifluoroacetic acid), Lewis acid (e.g., scandium(III) triflate), the like or combinations thereof.

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In various embodiments, the step (b-ii) comprises adding from about 0.001 wt% to about 25 wt%, from about 0.025 wt% to about 10 wt%, or from about 0.5 wt% to about 7.5 wt% of the catalyst. In various embodiments, the step (b-ii) comprises adding from about 0.001 wt% to about 25 wt%, from about 0.0025 wt% to about 24 wt%, from about 0.005 wt% to about 23 wt%, from about 0.0075 wt% to about 22 wt%, from about 0.01 wt% to about 21 wt%, from about 0.025 wt% to about 20 wt%, from about 0.05 wt% to about 19 wt%, from about 0.075 wt% to about 18 wt%, from about 0.1 wt% to about 17 wt%, from about 0.2 wt% to about 16 wt%, from about 0.3 wt% to about 15 wt%, from about 0.4 wt% to about 14 wt%, from about 0.5 wt% to about 13 wt%, from about 0.6 wt% to about 12 wt%, from about 0.7 wt% to about 11 wt%, from about 0.8 wt% to about 10 wt%, from about 0.9 wt% to about 9.5 wt%, from about 1 wt% to about 9 wt%, from about 1.5 wt% to about 8.5 wt%, from about 2 wt% to about 8 wt%, from about 2.5 wt% to about 7.5 wt%, from about 3 wt% to about 7 wt%, from about 3.5 wt% to about 6.5 wt%, from about 4 wt% to about 6 wt%, from about 4.5 wt% to about 5.5 wt%, or about 5 wt% of the catalyst. In various embodiments where crosslinking loading is low, a lower amount of catalyst is used/added.

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In various embodiments, the method further comprises adding a catalyst before the crosslinking step, during the crosslinking step, and/or after the crosslinking step. In various embodiments, the catalyst is added to the reaction mixture before the crosslinking step (b-i). In various embodiments, the catalyst is added after the crosslinking step. In such embodiments, the catalyst is only added after the crosslinked polymer has been prepared/formed/obtained in step (b-i). In various embodiments, the catalyst is added during the crosslinking step. In such embodiments, the catalyst is added to the reaction mixture containing a dynamic crosslinker and polymer to be crosslinked during the crosslinking step (b-i).

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In various embodiments, the step (a), (a-i), (a-ii), (a-iii), (b-i) and/or (b-ii) is/are performed in the absence/presence of an organic solvent. In various embodiments, any organic solvent that effectively serves as a medium to contain the components of the reaction mixture (e.g., reactants/substrates) may be used in embodiments of the reaction mixture disclosed herein. In various embodiments, the organic solvent is capable of substantially dissolving or swelling the components present in the reaction mixture. The organic solvent may be an organic solvent such as dichloromethane (DCM), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), acetonitrile, ethyl acetate, dimethylformamide (DMF), toluene, or the like or combinations thereof. In various embodiments, the organic solvent may not dissolve the crosslinked polymer, i.e. after step (b-i), but it may swell the polymer). In various embodiments, the organic solvent may be provided in a dry or anhydrous form. For example, prior to step (b-i), a step may comprise suspending, dispersing, mixing, stirring, dissolving, sonicating and/or ultrasonication the aryl compound represented by general formula (13) and a dynamic bond source in the presence of dry/anhydrous organic solvent. In various embodiments, the step (b-i) is performed/undertaken in the absence of a solvent. It will be appreciated that prior to step (b-i), a solvent may be used to first solubilize and mix all components, but the solvent is to be removed before the thermal/UV crosslinking step, to prevent/avoid the solvent from reacting/interacting with the crosslinker.

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COVALENT ADAPTABLE NETWORK (CAN)

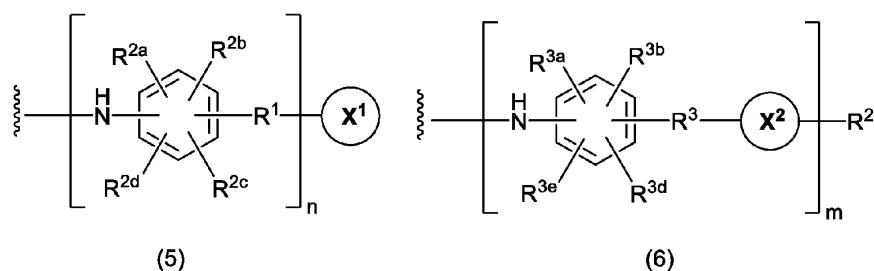
In various embodiments, there is provided a covalent adaptable network (CAN) obtained from the method disclosed herein. In various embodiments, the covalent adaptable network comprises a polymer network crosslinked by
 5 embodiments of the dynamic crosslinker as disclosed herein. In various embodiments, the covalent adaptable network (CAN) comprises polymer chains coupled to embodiments of the dynamic crosslinker as disclosed herein *via* dynamic crosslinks.

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In various embodiments, the covalent adaptable network (CAN) comprises two or more, three or more, four or more, five or more, six or more, seven or more, eight or more, nine or more, or ten or more polymer chains coupled to each dynamic crosslinker as disclosed herein *via* dynamic crosslinks.

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In various embodiments, the dynamic crosslink comprises a structure selected from general formula (5), general formula (6) or combinations thereof:



wherein

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each of **X¹** and **X²** is independently a dynamic covalent moiety;

each of R^{2a}, R^{2b}, R^{2c}, R^{2d}, R^{3a}, R^{3b}, R^{3c} and R^{3d} is independently halogen, hydrogen, hydroxyl, carboxyl, amine, amide, ester, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted oxycarbonylalkyl, optionally substituted
 25 alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carboxylalkyl, optionally substituted alkylcarboxylalkyl, optionally

substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkynyl, or combinations thereof;

each of R¹, R² and R³ is optionally present as a linker selected from carbonyl-containing group, carbonyloxy-containing group, ester-containing group, amide-containing group, carbamate-containing group, amine-containing group, thiol-containing group, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted alkylcarbonyloxy, optionally substituted oxycarbonylalkyl, optionally substituted alkyloxycarbonyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carbonylaryl, optionally substituted arylcarbonylalkyl, optionally substituted alkylcarbonylaryl, optionally substituted arylcarbonylaryl, optionally substituted carbonyloxyaryl, optionally substituted arylcarbonyloxy, optionally substituted oxycarbonylaryl, optionally substituted aryloxycarbonyl, optionally substituted arylcarbonyloxyalkyl, optionally substituted alkylcarbonyloxyaryl, optionally substituted arylcarbonyloxyaryl, optionally substituted aryloxycarbonylalkyl, optionally substituted alkyloxycarbonylaryl, optionally substituted aryloxycarbonylaryl, optionally substituted ary-lester, optionally substituted alkylester, optionally substituted arylamide, optionally substituted alkylamide, optionally substituted arylcarbamate, optionally substituted alkylcarbamate, optionally substituted arylamine, optionally substituted alkylamine, optionally substituted thioaryl, optionally substituted thioalkyl, optionally substituted alkoxy, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof;

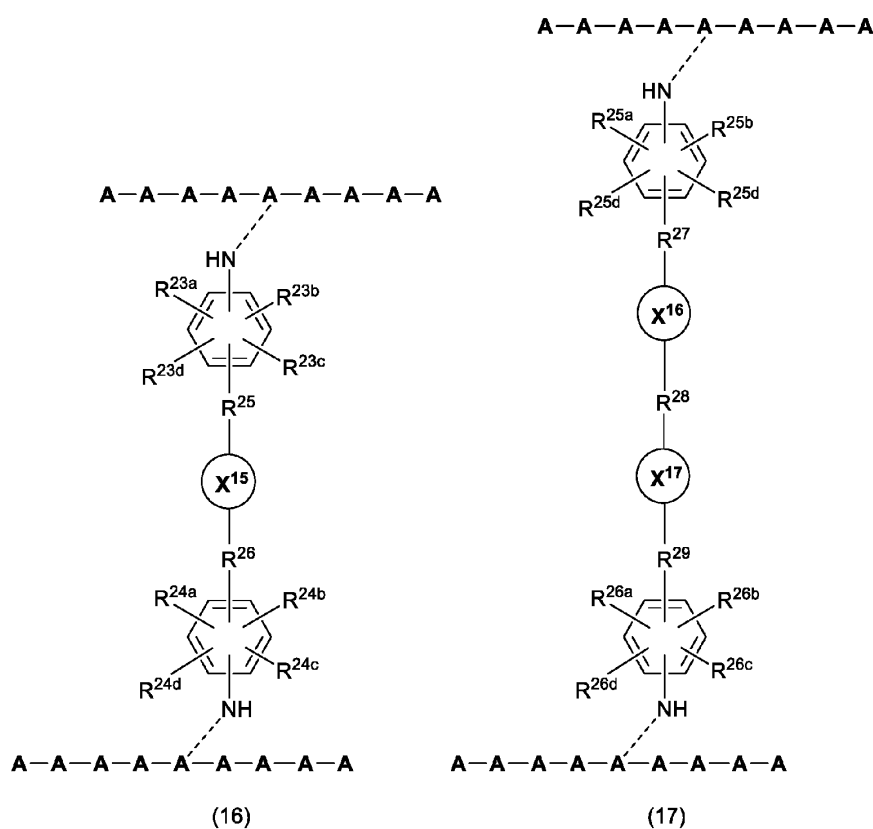
$n \geq 2$; and

$m \geq 2$.

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In various embodiments, the crosslinking of a polymer with embodiments of the dynamic crosslinker occurs between the azide moiety of the dynamic

crosslinker and a polymer chain. In various embodiments, the polymer chain is linked/connected to the dynamic crosslinker *via* –NH– linkage. For example, a dynamic crosslinker may link a polymer chain (–**A**–**A**–**A**–**A**–**A**–) to another polymer chain (–**A**–**A**–**A**–**A**–**A**–) *via* –NH– linkage, thereby forming a crosslinked polymer as shown in the following structure represented by general formula (16) when n = 2, or a crosslinked polymer as shown in the following structure represented by general formula (17) when m = 2:



wherein

10 R^{23a} to R^{23d}, R^{24a} to R^{24d}, R^{25a} to R^{25d} and R^{26a} to R^{26d} contain one or more features and/or share one or more properties that are similar to those described above for R^{1a} to R^{1d} (as defined in general formula (1));

X^{15} , X^{16} and X^{17} contain one or more features and/or share one or more properties that are similar to those described above for X^1 to X^2 (as defined in general formula (2) and (3)); and

- R^{25} , R^{26} , R^{27} , R^{28} and R^{29} are optionally present and contain one or more
- 5 features and/or share one or more properties that are similar to those described above for R^1 to R^3 (as defined in general formula (2) and (3)).

In various embodiments, the covalent adaptable network (CAN) comprises dynamic crosslinks at various sites of the polymer. As may be appreciated, there

10 may be one or more, two or more, three or more, four or more, five or more, six or more, seven or more, eight or more, nine or more, or ten or more dynamic crosslinks linking a chain/repeating unit of the polymer to another chain/repeating unit of the polymer, depending on the number of available $-NH-$ linkages (or corresponding $-N_3$ moiety present in the dynamic crosslinker). In various

15 embodiments, the $-NH-$ linkage(s) formed is/are permanent. It will be appreciated that in various embodiments, recycling (e.g., chemical and/or mechanical recycling) does not regenerate/reform $-N_3$ from $-NH-$ linkages as N_2 gas is irreversibly lost during the crosslinking process.

20 In various embodiments, the covalent adaptable network (CAN) has a gel fraction in the range of from about 30% to about 100%, or from about 55% to about 98%. In various embodiments, the covalent adaptable network (CAN) has a gel fraction in the range of from about 30% to about 100%, from about 35% to about 99%, from about 40% to about 98%, from about 45% to about 97%, from

25 about 50% to about 96%, from about 55% to about 95%, from about 60% to about 94%, from about 65% to about 93%, from about 70% to about 92%, from about 75% to about 91%, from about 80% to about 90%, from about 85% to about 89%, from about 86% to about 88%, or about 87%. In various embodiments, the gel fraction is representative of the degree of crosslinking in the covalent adaptable

30 network.

In various embodiments, the covalent adaptable network (CAN) comprises from about 0.01 wt% to about 30 wt%, or from about 1 wt% to about 20 wt% of the dynamic crosslinker. In various embodiments, the covalent adaptable network (CAN) comprises from about 0.01 wt% to about 30 wt%, from about 0.02 wt% to about 29 wt%, from about 0.03 wt% to about 28 wt%, from about 0.04 wt% to about 27 wt%, from about 0.05 wt% to about 26 wt%, from about 0.06 wt% to about 25 wt%, from about 0.07 wt% to about 24 wt%, from about 0.08 wt% to about 23 wt%, from about 0.09 wt% to about 22 wt%, from about 0.1 wt% to about 21 wt%, from about 0.2 wt% to about 20 wt%, from about 0.3 wt% to about 19 wt%, from about 0.4 wt% to about 18 wt%, from about 0.5 wt% to about 17 wt%, from about 0.6 wt% to about 16 wt%, from about 0.7 wt% to about 15 wt%, from about 0.8 wt% to about 14 wt%, from about 0.9 wt% to about 13 wt%, from about 1 wt% to about 12 wt%, from about 1.5 wt% to about 11 wt%, from about 2 wt% to about 10 wt%, from about 2.5 wt% to about 9.5 wt%, from about 3 wt% to about 9 wt%, from about 3.5 wt% to about 8.5 wt%, from about 4 wt% to about 8 wt%, from about 4.5 wt% to about 7.5 wt%, from about 5 wt% to about 7 wt%, from about 5.5 wt% to about 6.5 wt%, or about 6 wt% of the dynamic crosslinker. In various embodiments, no more than about 30 wt% of the dynamic crosslinker is used, to avoid the crosslinkers reacting with each other.

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In various embodiments, the covalent adaptable network (CAN) comprises a catalyst infused/embedded within said network. Advantageously, in various embodiments, presence of infused/embedded catalyst facilitates bond exchange/arrangement (or dynamic bond exchange/rearrangement), and consequently facilitate the recycling/reconfiguration of the CAN. In various embodiments, the catalyst comprises 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,1,3,3-Tetramethylguanidine, 1,8-Diazabicyclo[5.4.0]undec-7-ene, phosphine (e.g., trioctylphosphine), Bronsted base (e.g., 2-methylimidazole, 1-methylimidazole or 4-dimethylaminopyridine), Lewis acid (e.g., Zn(OAc)₂, dibutyltin dilaurate or scandium(III) triflate), organic acid such as trifluoroacetic acid.

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In various embodiments, the covalent adaptable network (CAN) comprises from about 0.001 wt% to about 25 wt%, from about 0.025 wt% to about 10 wt%, or from about 0.5 wt% to about 7.5 wt% of the catalyst. In various embodiments, the covalent adaptable network (CAN) comprises from about 0.001 wt% to about 25 wt%, from about 0.0025 wt% to about 24 wt%, from about 0.005 wt% to about 23 wt%, from about 0.0075 wt% to about 22 wt%, from about 0.01 wt% to about 21 wt%, from about 0.025 wt% to about 20 wt%, from about 0.05 wt% to about 19 wt%, from about 0.075 wt% to about 18 wt%, from about 0.1 wt% to about 17 wt%, from about 0.2 wt% to about 16 wt%, from about 0.3 wt% to about 15 wt%, from about 0.4 wt% to about 14 wt%, from about 0.5 wt% to about 13 wt%, from about 0.6 wt% to about 12 wt%, from about 0.7 wt% to about 11 wt%, from about 0.8 wt% to about 10 wt%, from about 0.9 wt% to about 9.5 wt%, from about 1 wt% to about 9 wt%, from about 1.5 wt% to about 8.5 wt%, from about 2 wt% to about 8 wt%, from about 2.5 wt% to about 7.5 wt%, from about 3 wt% to about 7 wt%, from about 3.5 wt% to about 6.5 wt%, from about 4 wt% to about 6 wt%, from about 4.5 wt% to about 5.5 wt%, or about 5 wt% of the catalyst. In various embodiments where crosslinking loading is low, a lower amount of catalyst is used/added.

In various embodiments, the covalent adaptable networks (CANs) are equipped with the ability to resist solvent and/or ability to withstand a certain amount of pressure or stress. Advantageously, in various embodiments, the covalent adaptable networks (CANs) are mechanically strong, firm and/or stable and yet recyclable, making them attractive for use in applications such as recyclable plastics for structural applications, fibre-reinforced polymers, biomedical applications, packaging/ encapsulation, electronics, energy storage, adhesives and/or membranes.

In various embodiments, the covalent adaptable networks (CANs) (or crosslinked polymer) are designed/configured to allow the one or more dynamic crosslinks/covalent moiety/bond(s)/linkage(s) to be reversibly exchanged/rearranged or broken/cleaved upon exposure to or application of a

stimulus. In various embodiments, the covalent adaptable networks (CANs) (or un-crosslinked/de-crosslinked polymer) are also designed/configured to allow the one or more broken/cleaved dynamic crosslinks/covalent moiety/bond(s)/linkage(s) to be reversibly reformed/ recombined upon exposure to or application of another stimulus, thereby regenerating the covalent adaptable networks (CANs) (or re-crosslinked polymer). In various embodiments, the covalent adaptable networks (CANs) (or crosslinked polymer) are designed/configured to be mechanically recycled, e.g., upon exposure to or application of a mechanical stimulus. For example, during mechanical recycling, the one or more dynamic covalent moiety/bond(s)/ linkage(s) may undergo bond exchange and/or rearrangement with/among themselves, thereby causing a shift/relocation of dynamic crosslinks to a new location/site. In various embodiments, the covalent adaptable networks (CANs) (or crosslinked polymer) are designed/configured to be chemically recycled, e.g., upon exposure to or application of a chemical stimulus. For example, during chemical recycling, the one or more dynamic covalent moiety/bond(s) /linkage(s) may be broken/cleaved and then consequently reformed/recombined at a new location/site. Advantageously, the reversible bond exchange/ rearrangement may occur or take place between different compound/crosslinker molecules. The reversible bond exchange/rearrangement may also occur or take place between a compound/crosslinker molecule and another molecule or polymer having similar dynamic covalent bonds.

Advantageously, in various embodiments therefore, the design and/or structure of the covalent adaptable networks (CANs) (due to presence of the dynamic covalent moiety and/or dynamic covalent bond(s)/linkage(s)) equips the covalent adaptable networks (CANs) with or imparts the ability to be recyclable, reconfigurable and/or reprocessable. In various embodiments, the covalent adaptable networks (CANs) disclosed herein are recyclable thermosets or recyclable thermosetting polymers. The covalent adaptable networks (CANs) may be capable of reverting into thermoplastic polymers upon exposure to or application of a stimulus. Advantageously, embodiments of the CANs allow for

the reversible conversion from a thermoset (or thermosetting polymer network) to a thermoplastic (or thermoplastic polymer).

The term "covalent adaptable network" may comprise and/or may be used interchangeably with the terms "covalent adaptable networks", "CAN", "CANs", "crosslinked polymer", "recyclable polymer", "reprocessable polymer", "reconfigurable polymer", "vitimer", "recyclable thermosetting polymer", "recyclable thermoset" or the like. In various embodiments, the term "covalent adaptable network" encompasses the term "vitimer" where the exchange of the bonds are associative, i.e. the network can be reprocessed mechanically without bond cleavage.

In various embodiments, the dynamic crosslinks are exchangeable/cleavable and/or the one or more dynamic covalent bonds (present in the dynamic covalent moiety) are designed/configured to reversibly break/cleave and/or form/reform upon exposure to or under application of one or more of the following stimuli:

- (i) temperature;
- (ii) pressure;
- (iii) presence/exposure to chemical; and
- (iv) light irradiation.

In various embodiments, the covalent adaptable networks (CANs) are mechanically recyclable and/or chemically recyclable. The recycling of CANs may be carried out *via* mechanical and/or chemical means. In various embodiments, mechanical recycling comprises applying mechanical means/methods/treatments e.g., subjecting the covalent adaptable network to heat, pressure, stress, the like, or combinations thereof. In various embodiments, chemical recycling comprises applying chemical means/methods/treatments e.g., subjecting the covalent adaptable network to heat, pressure, stress, the like, or combinations thereof.

In various embodiments, the one or more dynamic covalent bonds are configured to reversibly break/cleave and/or undergoes bond exchange/rearrangement at a temperature that is from about 20 °C to about 300 °C, from about 25 °C to about 290 °C, from about 30 °C to about 280 °C, from about 35 °C to about 270 °C, from about 40 °C to about 260 °C, from about 45 °C to about 255 °C, from about 50 °C to about 250 °C, from about 55 °C to about 245 °C, from about 60 °C to about 240 °C, from about 65 °C to about 235 °C, from about 70 °C to about 230 °C, from about 75 °C to about 225 °C, from about 80 °C to about 220 °C, from about 85 °C to about 215 °C, from about 90 °C to about 210 °C, from about 95 °C to about 205 °C, from about 100 °C to about 200 °C, from about 105 °C to about 195 °C, from about 110 °C to about 190 °C, from about 115 °C to about 185 °C, from about 120 °C to about 180 °C, from about 125 °C to about 175 °C, from about 130 °C to about 170 °C, from about 135 °C to about 165 °C, from about 140 °C to about 160 °C, from about 145 °C to about 155 °C, or about 150 °C. For example, un-crosslinking/de-crosslinking to cause the dynamic crosslinks to exchange/rearrange/break/cleave may occur at a temperature that is from about 20 °C to about 300 °C. In various embodiments, the temperature at which bond exchange of the dynamic crosslinks occurs is dependent on the glass transition temperature (T_g) of the CANs and/or activation energy (E_a) of the dynamic bonds.

In various embodiments, the one or more dynamic covalent bonds are configured to reversibly undergo bond exchange/rearrangement at a pressure that is from about 0.1 MPa to about 100.0 MPa, from about 0.2 MPa to about 95.0 MPa, from about 0.5 MPa to about 90.0 MPa, from about 1.0 MPa to about 85.0 MPa, from about 1.5 MPa to about 80.0 MPa, from about 2.0 MPa to about 75.0 MPa, from about 2.5 MPa to about 70.0 MPa, from about 3.0 MPa to about 65.0 MPa, from about 3.5 MPa to about 60.0 MPa, from about 4.0 MPa to about 55.0 MPa, from about 4.5 MPa to about 50.0 MPa, from about 5.0 MPa to about 45.0 MPa, from about 5.5 MPa to about 40.0 MPa, from about 6.0 MPa to about 35.0 MPa, from about 6.5 MPa to about 30.0 MPa, from about 7.0 MPa to about 25.0 MPa, from about 7.5 MPa to about 20.0 MPa, from about 8.0 MPa to about 15.0

MPa, from about 8.5 MPa to about 10.0 MPa, or from about 9.0 MPa to about 9.5 MPa. In various embodiments, the one or more dynamic covalent bonds are configured to reversibly undergoes bond exchange/rearrangement at nominal pressure, e.g., nominal atmospheric pressure at about 1 atm or about 0.10 MPa.

- 5 For example, exchange of the dynamic crosslinks may occur at a pressure that is from about 0.1 MPa to about 10.0 MPa, or about 0.5 MPa.

In various embodiments, the one or more dynamic covalent bonds are configured to reversibly break/cleave and/or undergoes bond
10 exchange/rearrangement upon exposure or in the presence of one or more reactive chemicals. In various embodiments, the reactive chemical is selected from alcohol/alcoholic solvent, acid, base, reducing agent, oxidizing agent, dimethyl disulfide, dithiothreitol, the like, or combinations thereof. In various
15 embodiments, the alcohol comprises higher alcohol or alcohol with higher molecular weight. For example, the reactive chemical may be an alcohol selected from octanol (e.g., 1-octanol), nonanol, decanol, or combinations thereof. In various embodiments, reactive chemicals such as dimethyl disulfide and/or dithiothreitol is/are used for breaking/cleaving S–S bonds present in the CANs.

20 In various embodiments, the reactive chemical comprises dual functionality, that is, the reactive chemical is not only capable of breaking/cleaving the dynamic covalent bonds in the CANs, but may also serve/act as a solvent to substantially dissolve/contain the CANs in the composition. For example, an alcoholic solvent may be used as a reactive chemical (to break/cleave the
25 dynamic bonds) and as a solvent to swell the CANs.

In various embodiments, the reactive chemical comprises mono functionality, that is, the reactive chemical is capable of breaking/cleaving the dynamic covalent bonds in the CANs, but may not be suitable for use as a solvent.
30 In such embodiments, the reactive chemical is provided together with an additional solvent (e.g., organic solvent) to substantially dissolve/contain and/or compatibilise the reactive chemical and the CANs. The organic solvent may

comprise toluene or the like. For example, un-crosslinking/de-crosslinking may occur upon exposure or in the presence of one or more reactive chemicals and/or solvents. In various embodiments, the organic solvent used is not a reactive chemical which can break the dynamic bond e.g. toluene.

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In various embodiments, the one or more broken/cleaved dynamic covalent bonds are configured to reversibly form/reform/recombine and/or undergoes bond exchange/rearrangement upon thermal activation or exposure to heat in order to drive off the reactive chemicals used to cleave the bonds. For example, re-crosslinking to reversibly reform/recombine the dynamic crosslinks may occur at a temperature that is from about 50°C to about 300°C, from about 55 °C to about 245 °C, from about 60 °C to about 240 °C, from about 65 °C to about 235 °C, from about 70 °C to about 230 °C, from about 75 °C to about 225 °C, from about 80 °C to about 220 °C, from about 85 °C to about 215 °C, from about 90 °C to about 210 °C, from about 95 °C to about 205 °C, from about 100 °C to about 200 °C, from about 105 °C to about 195 °C, from about 110 °C to about 190 °C, from about 115 °C to about 185 °C, from about 120 °C to about 180 °C, from about 125 °C to about 175 °C, from about 130 °C to about 170 °C, from about 135 °C to about 165 °C, from about 140 °C to about 160 °C, from about 145 °C to about 155 °C, or about 150 °C. The re-crosslinking step may be undertaken at a pressure in the range of from about 100 Pa to about 5,000 Pa, from about 133 Pa to about 5,000 Pa, from about 2,000 Pa to about 5,000 Pa, from about 4,000 Pa to about 5,000 Pa, from about 100 Pa to about 4,000 Pa, from about 100 Pa to about 2,000 Pa, from about 100 Pa to about 133 Pa, or from about 133 Pa to about 4,000 Pa. The re-crosslinking step may be undertaken in vacuum. In various embodiments, the temperature at which the one or more broken/cleaved dynamic covalent bonds are reversibly reform/recombine is dependent on the activation energy (E_a) of the dynamic bonds, boiling point of the reactive chemicals used to break/cleave the dynamic bonds and/or the glass transition temperature (T_g)/melting temperature (T_m) of the CANs.

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In various embodiments, there is also provided a method of recycling a covalent adaptable network (CAN) as disclosed herein. In various embodiments, the method of recycling comprises undoing/reversing/removing the dynamic crosslinks and/or breaking/cleaving one or more dynamic covalent bonds (present in the dynamic crosslinks). In various embodiments, the method of recycling comprises performing un-crosslinking/de-crosslinking of the covalent adaptable network to obtain the un-crosslinked/de-crosslinked polymer.

In various embodiments, the method of recycling a covalent adaptable network (CAN) comprises:

- (c-i) providing a covalent adaptable network (CAN) as disclosed herein; and
- (c-ii) applying a stimulus to the CAN to reversibly remove the dynamic crosslinks and/or reversibly break/cleave one or more dynamic covalent bonds in the CAN.

BRIEF DESCRIPTION OF FIGURES

FIG. 1 shows ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{CO}$) spectrum of **4-azido-2,3,5,6-tetrafluoro-N-(4-hydroxyphenyl)benzamide (5)** in accordance with various embodiments disclosed herein.

FIG. 2 shows ^{13}C NMR (101 MHz, $(\text{CD}_3)_2\text{CO}$) spectrum of **4-azido-2,3,5,6-tetrafluoro-N-(4-hydroxyphenyl)benzamide (5)** in accordance with various embodiments disclosed herein.

FIG. 3 shows a magnified version of FIG. 2, i.e. ^{13}C NMR (101 MHz, $(\text{CD}_3)_2\text{CO}$) spectrum of **4-azido-2,3,5,6-tetrafluoro-N-(4-hydroxyphenyl)benzamide (5)** from 112 ppm to 158 ppm in accordance with various embodiments disclosed herein.

FIG. 4 shows ^{19}F NMR (471 MHz, $(\text{CD}_3)_2\text{CO}$) spectrum of **4-azido-2,3,5,6-tetrafluoro-N-(4-hydroxyphenyl)benzamide (5)** in accordance with various embodiments disclosed herein.

5 FIG. 5 shows ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{CO}$) spectrum of **tris(4-(4-azido-2,3,5,6-tetrafluorobenzamido)phenyl) phosphate (1)** in accordance with various embodiments disclosed herein.

FIG. 6 shows ^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{CO}$) spectrum of **tris(4-(4-azido-2,3,5,6-tetrafluorobenzamido)phenyl) phosphate (1)** in accordance with
10 various embodiments disclosed herein.

FIG. 7 shows a magnified version of FIG. 6, i.e. ^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{CO}$) spectrum of **tris(4-(4-azido-2,3,5,6-tetrafluorobenzamido)phenyl) phosphate (1)** from 112 ppm to 158 ppm in accordance with various
15 embodiments disclosed herein.

FIG. 8 shows ^{19}F NMR spectrum (471 MHz, $(\text{CD}_3)_2\text{CO}$) of **tris(4-(4-azido-2,3,5,6-tetrafluorobenzamido)phenyl) phosphate (1)** in accordance with
20 various embodiments disclosed herein.

FIG. 9 shows ^{31}P NMR (202 MHz, $(\text{CD}_3)_2\text{CO}$) spectrum of **tris(4-(4-azido-2,3,5,6-tetrafluorobenzamido)phenyl) phosphate (1)** in accordance with
25 various embodiments disclosed herein.

FIG. 10 is a graph showing thermogravimetric analysis of dynamic phosphate crosslinker **1** in accordance with various embodiments disclosed herein.

30 FIG. 11 shows fourier transform infrared spectroscopy (FTIR) spectra of PCL after crosslinking with dynamic phosphate crosslinker **1** and after TBD

infusion in accordance with various embodiments disclosed herein. As shown, the figure demonstrates successful crosslinking and catalyst infusion.

FIG. 12 shows mechanical recycling of (i) PEVA and (ii) PSBS samples crosslinked with 10% dynamic phosphate crosslinker **1** pre-mixed with 0.2 equiv. TBD in accordance with various embodiments disclosed herein.

FIG. 13 shows chemical recycling of PSBS crosslinked with 5% dynamic phosphate crosslinker **1** and 0.2 equiv. TBD, using 1-octanol as reactive solvent in accordance with various embodiments disclosed herein.

FIG. 14 shows ^1H NMR (500 MHz, DMSO) spectrum of **N,N'-(disulfanediylbis(4,1-phenylene))bis(2,3,4,5,6-pentafluorobenzamide)** (**7**) in accordance with various embodiments disclosed herein.

FIG. 15 shows ^{13}C NMR (126 MHz, CDCl_3) spectrum of **N,N'-(disulfanediylbis(4,1-phenylene))bis(2,3,4,5,6-pentafluorobenzamide)** (**7**) in accordance with various embodiments disclosed herein.

FIG. 16 shows ^{19}F NMR (376 MHz, DMSO) spectrum of **N,N'-(disulfanediylbis(4,1-phenylene))bis(2,3,4,5,6-pentafluorobenzamide)** (**7**) in accordance with various embodiments disclosed herein.

FIG. 17 shows ^1H NMR (400 MHz, DMSO) spectrum of **N,N'-(disulfanediylbis(4,1-phenylene))bis(4-azido-2,3,5,6-tetrafluorobenzamide)** (**6**) in accordance with various embodiments disclosed herein.

FIG. 18 shows ^{13}C NMR (101 MHz, CDCl_3) spectrum of **N,N'-(disulfanediylbis(4,1-phenylene))bis(4-azido-2,3,5,6-tetrafluorobenzamide)** (**6**) in accordance with various embodiments disclosed herein.

FIG. 19 shows ^{19}F NMR (376 MHz, DMSO) spectrum of **N,N'-(disulfanediyldis(4,1-phenylene))bis(4-azido-2,3,5,6-tetrafluorobenzamide)** (**6**) in accordance with various embodiments disclosed herein.

5 FIG. 20 is an infrared spectrum showing FTIR analysis of dynamic aryl disulfide crosslinker **6** in accordance with various embodiments disclosed herein.

FIG. 21 is a graph showing thermogravimetric analysis upon heating of dynamic aryl disulfide crosslinker **6** in accordance with various embodiments disclosed herein.

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FIG. 22 shows ^1H NMR (400 MHz, CDCl_3) spectrum of **disulfanediyldis(ethane-2,1-diyl) bis(2,3,4,5,6-pentafluorobenzoate)** (**9**) in accordance with various embodiments disclosed herein.

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FIG. 23 shows ^{13}C NMR (101 MHz, CDCl_3) spectrum of **disulfanediyldis(ethane-2,1-diyl) bis(2,3,4,5,6-pentafluorobenzoate)** (**9**) in accordance with various embodiments disclosed herein.

20 FIG. 24 shows ^{19}F NMR (376 MHz, CDCl_3) spectrum of **disulfanediyldis(ethane-2,1-diyl) bis(2,3,4,5,6-pentafluorobenzoate)** (**9**) in accordance with various embodiments disclosed herein.

FIG. 25 shows ^1H NMR (400 MHz, CDCl_3 , 50°C) spectrum of **disulfanediyldis(ethane-2,1-diyl) bis(4-azido-2,3,5,6-tetrafluorobenzoate)** (**8**) in accordance with various embodiments disclosed herein.

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FIG. 26 shows ^{19}F NMR (376 MHz, CDCl_3 , 50°C) spectrum of **disulfanediyldis(ethane-2,1-diyl) bis(4-azido-2,3,5,6-tetrafluorobenzoate)** (**8**) in accordance with various embodiments disclosed herein. As shown, NMR spectra of crystallized crosslinker **8** contains two sets of peaks at ambient temperature in CDCl_3 . One set of peaks diminishes upon heating to 50°C ,

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indicating interconversion. Data reported is for the major species at 50°C (1:0.17 ratio).

FIG. 27 shows ¹H NMR (400 MHz, CDCl₃) spectrum of **4-azido-2,3,5,6-tetrafluorobenzaldehyde (11)** in accordance with various embodiments disclosed herein.

FIG. 28 shows ¹⁹F NMR (376 MHz, CDCl₃) spectrum of **4-azido-2,3,5,6-tetrafluorobenzaldehyde (11)** in accordance with various embodiments disclosed herein.

FIG. 29 shows ¹H NMR (400 MHz, CDCl₃) spectrum of ***N,N'*-(hexane-1,6-diyl)bis(1-(4-azido-2,3,5,6-tetrafluorophenyl)methanimine) (10)** in accordance with various embodiments disclosed herein.

FIG. 30 shows ¹³C NMR (101 MHz, CDCl₃) spectrum of ***N,N'*-(hexane-1,6-diyl)bis(1-(4-azido-2,3,5,6-tetrafluorophenyl)methanimine) (10)** in accordance with various embodiments disclosed herein.

FIG. 31 shows ¹⁹F NMR (376 MHz, CDCl₃) spectrum of ***N,N'*-(hexane-1,6-diyl)bis(1-(4-azido-2,3,5,6-tetrafluorophenyl)methanimine) (10)** in accordance with various embodiments disclosed herein.

FIG. 32 shows ¹H NMR (500 MHz, CDCl₃) spectrum of **3,9-bis(4-azido-2,3,5,6-tetrafluorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (12)** in accordance with various embodiments disclosed herein.

FIG. 33 shows ¹³C NMR (126 MHz, CDCl₃) spectrum of **3,9-bis(4-azido-2,3,5,6-tetrafluorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (12)** in accordance with various embodiments disclosed herein.

FIG. 34 shows ^{19}F NMR (471 MHz, CDCl_3) spectrum of **3,9-bis(4-azido-2,3,5,6-tetrafluorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (12)** in accordance with various embodiments disclosed herein.

5 FIG. 35 shows ^1H NMR (500 MHz, toluene- d_8) spectrum obtained from an acetal exchange study described in Example 10. The symbols (★), (▲), (■) and (●) represent structures as shown in the acetal exchange model provided in Scheme 18.

10 FIG. 36 shows ^{19}F NMR (376 MHz, toluene- d_8) spectrum obtained from an acetal exchange study described in Example 10. The symbols (★), (▲), (■) and (●) represent structures as shown in the acetal exchange model provided in Scheme 18.

15 FIG. 37 is a graph showing thermogravimetric analysis of dynamic disulfide crosslinker **8** in accordance with various embodiments disclosed herein.

FIG. 38 is a graph showing thermogravimetric analysis of dynamic imine crosslinker **10** in accordance with various embodiments disclosed herein.

20 FIG. 39 is a graph showing thermogravimetric analysis of dynamic acetal crosslinker **12** in accordance with various embodiments disclosed herein.

FIG. 40 shows ^1H NMR (500 MHz, CDCl_3) spectrum of
25 **disulfanediylbis(ethane-2,1-diyl) bis(4-(cyclohexylamino)-2,3,5,6-tetrafluorobenzoate** in accordance with various embodiments disclosed herein.

FIG. 41 shows ^{13}C NMR (126 MHz, CDCl_3) spectrum of
30 **disulfanediylbis(ethane-2,1-diyl) bis(4-(cyclohexylamino)-2,3,5,6-tetrafluorobenzoate** in accordance with various embodiments disclosed herein.

FIG. 42 shows ^{19}F NMR (471 MHz, CDCl_3) spectrum of **disulfanediylbis(ethane-2,1-diyl) bis(4-(cyclohexylamino)-2,3,5,6-tetrafluorobenzoate** in accordance with various embodiments disclosed herein.

5 FIG. 43 shows ^1H NMR (500 MHz, CDCl_3) spectrum of **4,4'-(2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(N-cyclohexyl-2,3,5,6-tetrafluoroaniline)** diastereomer 1 in accordance with various embodiments disclosed herein.

10 FIG. 44 shows ^{13}C NMR (126 MHz, CDCl_3) spectrum of **4,4'-(2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(N-cyclohexyl-2,3,5,6-tetrafluoroaniline)** diastereomer 1 in accordance with various embodiments disclosed herein.

15 FIG. 45 shows ^{19}F NMR (471 MHz, CDCl_3) spectrum of **4,4'-(2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(N-cyclohexyl-2,3,5,6-tetrafluoroaniline)** diastereomer 1 in accordance with various embodiments disclosed herein.

20 FIG. 46 shows ultraviolet-visible (UV-vis) spectra of the dynamic disulfide crosslinker **8**, dynamic imine crosslinker **10** and dynamic acetal crosslinker **12**, in accordance with various embodiments disclosed herein.

FIG. 47 shows gel fraction of vitrimers formed by crosslinking different ratios (in wt%) of dynamic disulfide crosslinker **8** with various thermoplastics, in accordance with various embodiments disclosed herein.

25

FIG. 48 shows gel fraction of vitrimers formed by crosslinking different ratios (in wt%) of dynamic imine crosslinker **10** with various thermoplastics, in accordance with various embodiments disclosed herein.

30

FIG. 49 shows gel fraction of vitrimers formed by crosslinking different ratios (in wt%) of dynamic spiroacetal crosslinker **12** with various thermoplastics, in accordance with various embodiments disclosed herein.

5 FIG. 50 is an infrared spectrum showing FTIR analysis of LDPE crosslinked with different ratios (in wt%) of dynamic disulfide crosslinker **8** in accordance with various embodiments disclosed herein.

10 FIG. 51 is an infrared spectrum showing FTIR analysis of PP crosslinked with different ratios (in wt%) of dynamic disulfide crosslinker **8** in accordance with various embodiments disclosed herein.

15 FIG. 52 is an infrared spectrum showing FTIR analysis of PCL crosslinked with different ratios (in wt%) of dynamic disulfide crosslinker **8** in accordance with various embodiments disclosed herein.

20 FIG. 53 is an infrared spectrum showing FTIR analysis of PEO crosslinked with different ratios (in wt%) of dynamic disulfide crosslinker **8** in accordance with various embodiments disclosed herein.

25 FIG. 54 is an infrared spectrum showing FTIR analysis of LDPE crosslinked with 5 wt% of dynamic disulfide crosslinker **8** in accordance with various embodiments disclosed herein. "5 wt%" indicates before mechanical recycling; "5 wt% R1" indicates after mechanical recycling for 1 time; and "5 wt% R5" indicates after mechanical recycling for 5 times.

30 FIG. 55 is an infrared spectrum showing FTIR analysis of LDPE crosslinked with 5 wt% of dynamic disulfide crosslinker **8** in accordance with various embodiments disclosed herein. "5 wt%" indicates before chemical recycling; "Uncrosslinked" indicates after uncrosslinking step; and "Recrosslinked" indicates after recrosslinking step.

FIG. 56 is a Raman spectrum showing Raman analysis of LDPE crosslinked with different ratios (in wt%) of dynamic disulfide crosslinker **8** in accordance with various embodiments disclosed herein.

5 FIG. 57 is an infrared spectrum showing FTIR analysis of LDPE crosslinked with different ratios (in wt%) of dynamic imine crosslinker **10** in accordance with various embodiments disclosed herein.

10 FIG. 58 is an infrared spectrum showing FTIR analysis of PCL crosslinked with different ratios (in wt%) of dynamic imine crosslinker **10** in accordance with various embodiments disclosed herein.

15 FIG. 59 is an infrared spectrum showing FTIR analysis of LDPE crosslinked with different ratios (in wt%) of dynamic spiroacetal crosslinker **12** in accordance with various embodiments disclosed herein.

20 FIG. 60 is an infrared spectrum showing FTIR analysis of PCL crosslinked with different ratios (in wt%) of dynamic spiroacetal crosslinker **12** in accordance with various embodiments disclosed herein.

25 FIG. 61 is an infrared spectrum showing FTIR analysis of LDPE crosslinked with 5 wt% of dynamic spiroacetal crosslinker **12** in accordance with various embodiments disclosed herein. "5 wt%" indicates before chemical recycling; "Uncrosslinked" indicates after uncrosslinking step; "Hot-pressed" indicates after hot-pressing step; and "Recrosslinked" indicates after recrosslinking step.

30 FIG. 62 shows gel fraction of LDPE crosslinked with 5 wt% dynamic disulfide crosslinker **8** in accordance with various embodiments disclosed herein before mechanical recycling, after mechanical recycling for 1 cycle, and 5 cycles.

“5 wt%” indicates before mechanical recycling; “R1” indicates after mechanical recycling for 1 cycle; and “R5” indicates after mechanical recycling for 5 cycles.

FIG. 63 shows photographs of **LDPE-SS-5** (left) and pure LDPE samples
5 (right) heated on a hot plate at 130 °C at different time intervals (i.e. 0 minute, 45 minutes and 50 minutes), in accordance with various embodiments disclosed herein.

FIG. 64 shows photographs of **LDPE-SS-5** (left) and pure LDPE samples
10 (right) heated on a hot plate at 130 °C at different time intervals (i.e. 55 minutes, 60 minutes and 75 minutes), in accordance with various embodiments disclosed herein.

FIG. 65 shows rheological studies of **LDPE-SS-5** with 5% disulfide
15 crosslinker, in accordance with various embodiments disclosed herein. The graph shows temperature ramp at 1% strain, 1 Hz.

FIG. 66 shows rheological studies of **LDPE-SS-5** with 5% disulfide
crosslinker, in accordance with various embodiments disclosed herein. The graph
20 shows variable temperature stress relaxation experiments for temperatures between 170 and 200 °C at 1% strain.

FIG. 67 shows rheological studies of **LDPE-SS-5** and **LDPE-SS-5** with 10
mol% POct₃ (**LDPE-SS-5-POct₃**), in accordance with various embodiments
25 disclosed herein. The graph shows Arrhenius plot of horizontal shift factor at determined from TTS analysis.

FIG. 68 shows rheological studies of **LDPE-SS-5** with 5% disulfide
crosslinker, in accordance with various embodiments disclosed herein. The graph
30 shows master curve based on TTS of frequency sweep at varying temperatures for reference temperature $T_0 = 155$ °C.

FIG. 69 shows rheological studies of LDPE-SS-5 with 10 mol% POct₃ (**LDPE-SS-5-POct₃**), in accordance with various embodiments disclosed herein. The graph shows temperature ramp at 1% strain, 1 Hz.

5 FIG. 70 shows rheological studies of LDPE-SS-5 with 10 mol% POct₃ (**LDPE-SS-5-POct₃**), in accordance with various embodiments disclosed herein. The graph shows variable temperature stress relaxation experiments for temperatures between 120 and 150 °C at 1% strain.

10 FIG. 71 shows rheological studies of **LDPE-SS-5** and LDPE-SS-5 with 10 mol% POct₃ and (**LDPE-SS-5-POct₃**), in accordance with various embodiments disclosed herein. The graph shows Arrhenius plot of vertical shift factor 1/b_T determined from TTS analysis.

15 FIG. 72 shows rheological studies of LDPE-SS-5 with 10 mol% POct₃ (**LDPE-SS-5-POct₃**), in accordance with various embodiments disclosed herein. The graph shows master curve based on TTS of frequency sweep at varying temperatures for reference temperature T₀ = 155 °C.

20 FIG. 73 shows gel fraction of LDPE crosslinked with 5 wt% dynamic disulfide crosslinker **8** in accordance with various embodiments disclosed herein before chemical recycling, after uncrosslinking step, and after recrosslinking step. "5 wt%" indicates before chemical recycling; "Recrosslinked" indicates after recrosslinking step.

25 FIG. 74 shows ultimate tensile strength and toughness (left axis) and elongation at break and Young's modulus (right axis) of pure LDPE, virgin **LDPE-SS-5**, and **LDPE-SS-5** after mechanical recycling (MR 1, 3, and 5 cycles) and after chemical recycling (CR), in accordance with various embodiments disclosed
30 herein.

FIG. 75 shows gel fraction of PP-LDPE-SS-5, in accordance with various embodiments disclosed herein. "PP-LDPE" indicates before mechanical recycling; and "PP-LDPE MR1" indicates after mechanical recycling for 1 cycle.

5 FIG. 76 shows ultimate tensile strength, elongation at break and toughness (left axis) and Young's modulus (right axis) of PP-LDPE (3:7) blend and **PP-LDPE-SS-5**, in accordance with various embodiments disclosed herein.

10 FIG. 77 shows gel fraction of LDPE crosslinked with 5 wt% dynamic spiroacetal crosslinker **12**, in accordance with various embodiments disclosed herein. "5 wt% original" indicates before chemical recycling; "Uncrosslinked" indicates after uncrosslinking step; "Hot-pressed" indicates after hot-pressing step; and "Recrosslinked" indicates after recrosslinking step.

15 FIG. 78 shows ultimate tensile strength and toughness (left axis) and elongation at break and Young's modulus (right axis) of pure LDPE and **LDPE-Acetal-5** after chemical recycling (CR 1 and 2 cycles), in accordance with various embodiments disclosed herein.

20 **EXAMPLES**

Example embodiments of the disclosure will be better understood and readily apparent to one of ordinary skill in the art from the following examples, tables and if applicable, in conjunction with the figures. It should be appreciated
25 that other modifications related to structural, and/or chemical changes may be made without deviating from the scope of the invention. Example embodiments are not necessarily mutually exclusive as some may be combined with one or more embodiments to form new example embodiments. The example embodiments should not be construed as limiting the scope of the disclosure.

30

In the following examples, an aryl azide-functionalised dynamic crosslinker and a method of synthesising thereof has been developed. The dynamic

crosslinkers contain at least one dynamic covalent bond and at least two aryl azide groups. The following examples also describe methods of crosslinking linear polymers (thermoplastics) with aryl azide-functionalised dynamic crosslinker to form covalent adaptable networks (CANs). Crosslinking may be accomplished through UV or thermal curing. Advantageously, the CANs designed in accordance with various embodiments disclosed herein are mechanically and chemically recyclable. The following examples also describe methods of introducing catalyst into the CANs to improve mechanical recyclability. Catalyst may be introduced after CAN formation by solvent infusion or during CAN formation by pre-mixing with the crosslinker.

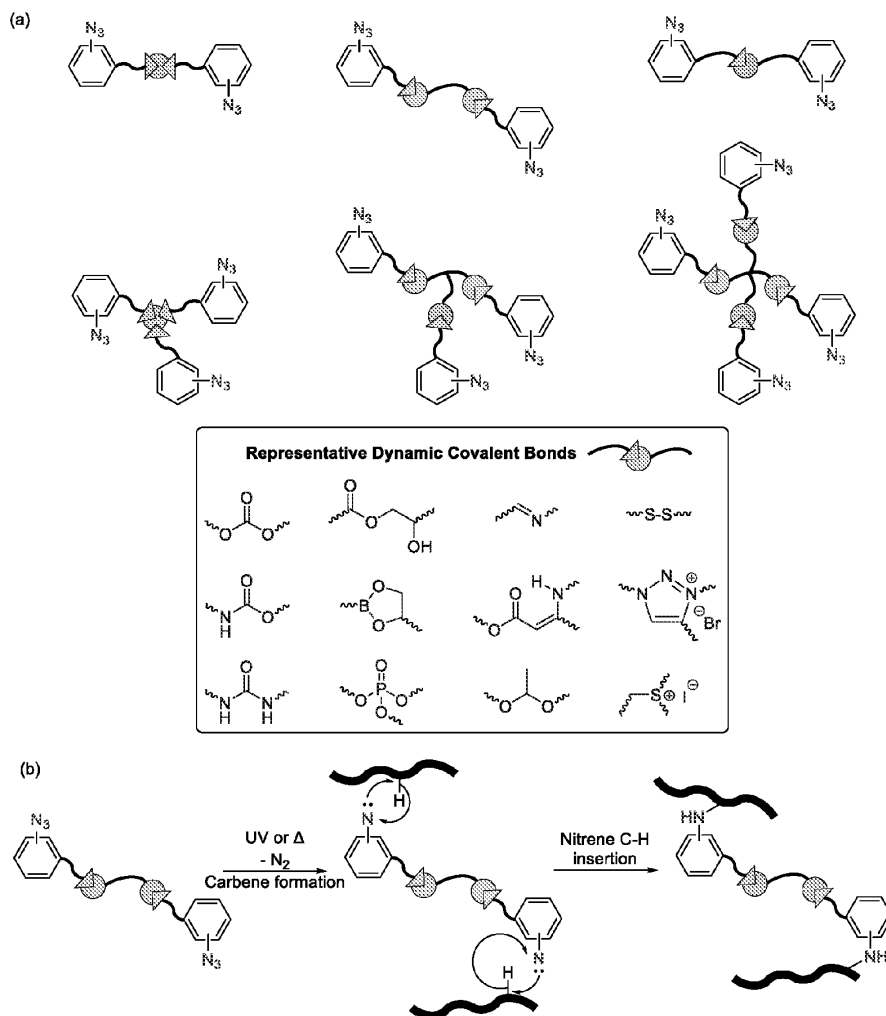
Dynamic covalent bonds are designed into the crosslinker to enable reversible bond exchange. The aryl azide-functionalised dynamic crosslinker can react with both thin-film (*via* UV activation) and bulk (*via* thermal activation) linear plastics to form covalent adaptable networks (CANs) which are (a) crosslinked and mechanically strong, yet (b) mechanically recyclable and/or (c) chemically recyclable.

The following examples describe the development of aryl azide-functionalised dynamic crosslinkers. The structures of the dynamic crosslinkers are shown in Scheme 1. Advantageously, the present application has demonstrated that these crosslinkers can be synthesised in as few as 2-4 steps with high overall yield. The aryl azide groups decompose to form reactive nitrene species under thermal activation or UV (254 nm) activation, thus enabling in situ crosslinking of thermoplastics with dynamic covalent bonds. The summarised steps for the synthesis of the crosslinkers, crosslinking of CANs and infusion of catalyst to facilitate dynamic bond exchange are indicated in Table 1.

As will be shown in the examples, the method developed in accordance with various embodiments disclosed herein enables the direct crosslinking of bulk thermoplastics to form mechanically strong and yet recyclable CANs. Advantageously, the method disclosed herein allows the CANs to be suitable for

use in applications such as recyclable plastics for structural applications, fibre-reinforced polymers, biomedical applications, packaging/ encapsulation, electronics, energy storage, adhesives and/or membranes.

5 Preparation of Covalent Adaptable Networks



Scheme 1. (a) Representative structures of aryl azide-functionalised dynamic crosslinkers; (b) Mechanism of nitrene C-H insertion of crosslinkers into polymers

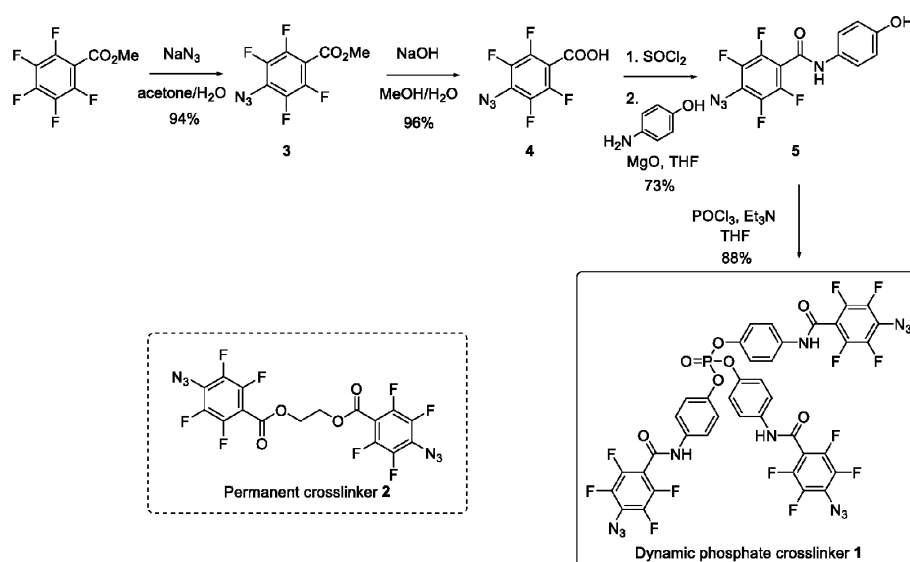
Preparation of covalent adaptable networks by crosslinking linear polymers with aryl azide-functionalised dynamic crosslinker

Table 1. Process steps for preparation of covalent adaptable networks (CANs)
5 by crosslinking linear polymers with aryl azide-functionalised dynamic crosslinkers

Step	Process	Comments
1	Synthesis of aryl azide-functionalised dynamic crosslinker	Structure contains at least one dynamic covalent bond and at least two aryl azide groups (Scheme 1). The aryl azide groups may contain fluorine atoms. In the following examples, a tris(fluorophenyl azide) dynamic phosphate crosslinker 1 is synthesised.
2	Crosslinking linear polymer with dynamic crosslinker 1	Thermal or UV crosslinking In the following examples, polymers demonstrated are polycaprolactone (70k-90k) (PCL), poly(ethylene-co-vinyl acetate) (CAS: 24937-78-8) (PEVA), polystyrene-block-polybutadiene-block- polystyrene (140k) (PSBS), poly(ethylene oxide) (200k) (PEO) or poly(methyl methacrylate) (Paraloid A14, PMMA).
3	Infusion of catalyst for dynamic bond exchange	Catalyst may be infused during or after crosslinking In the following examples, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) is used as catalyst.

Example 1:**STEP 1 – Synthesis of Aryl Azide-Bearing Phosphate Dynamic Crosslinker****1**

- 5 The steps for the synthesis of tris(fluorophenyl azide) dynamic phosphate crosslinker **1** are illustrated in Scheme 2. The steps may be adapted to synthesis other aryl azide dynamic crosslinkers, either by modifying the initial steps to install other functionalised aryl azides, or by modifying the final steps to install other dynamic covalent bonds.



10

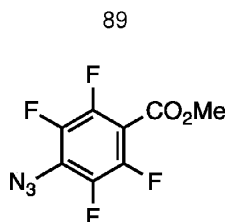
Scheme 2. Synthesis of tris(fluorophenyl azide) dynamic phosphate crosslinker **1** and structure of permanent crosslinker **2**

1.1. General procedure for synthesis of fluorophenyl azide precursor

15

Methyl 4-azidotetrafluorobenzoate (3)

Synthesis of methyl 4-azidotetrafluorobenzoate (Scheme 3) is described as follows.

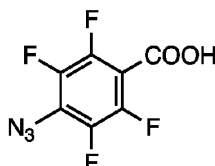


Scheme 3. Chemical structure of methyl 4-azidotetrafluorobenzoate (**3**)

To a RBF with stirrer bar was added methyl pentafluorobenzoate (15.3 g, 67.8 mmol, 1.0 equiv.), acetone (75 mL) and water (25 mL), followed by sodium azide (4.66 g, 71.7 mmol, 1.05 equiv.). The reaction mixture was heated to reflux at 80°C under Ar. After 6 hours, the mixture was concentrated *in vacuo*. The resulting mixture was diluted with DCM, and then washed with water and brine. The resulting organic phase was dried over anhydrous Na₂SO₄. The mixture was filtered, and the filtrate was concentrated *in vacuo*. The product was obtained as a yellow solid (15.8 g, 94%). ¹H NMR (400 MHz, CDCl₃) δ_H 3.97 (s, 3H). ¹⁹F NMR (470 MHz, (CD₃)₂CO) δ_F -138.5 (2F, m), -150.8 (2F, m).

4-azidotetrafluorobenzoic acid (**4**)

Synthesis of 4-azidotetrafluorobenzoic acid (Scheme 4) is described as follows.



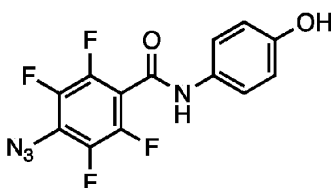
Scheme 4. Chemical structure of 4-azidotetrafluorobenzoic acid (**4**)

To a RBF with stirrer bar was added methyl 4-azidotetrafluorobenzoate (15.8 g, 63.4 mmol), methanol (252 mL), water (28 mL), followed by 20% NaOH (w/v) aqueous solution (21 mL). After 1 day, the mixture was cooled in an ice bath and acidified with 2M HCl (65 mL) to pH < 3, and then concentrated *in vacuo*. The resulting mixture was diluted with DCM, and then washed with water. The resulting organic phase was dried over anhydrous Na₂SO₄. The mixture was

filtered, and the filtrate was concentrated *in vacuo*. The product was obtained as a pale yellow solid (14.3 g, 96%). ^{19}F NMR (470 MHz, $(\text{CD}_3)_2\text{CO}$) δ_{F} -136.7 (2F, m), -150.6 (2F, m).

5 **4-azido-2,3,5,6-tetrafluoro-N-(4-hydroxyphenyl)benzamide (5)**

Synthesis of 4-azido-2,3,5,6-tetrafluoro-N-(4-hydroxyphenyl)benzamide (Scheme 5) is described as follows.



10 **Scheme 5.** Chemical structure of 4-azido-2,3,5,6-tetrafluoro-N-(4-hydroxyphenyl)benzamide (5)

To a RBF with stirrer bar was added 4-azidotetrafluorobenzoic acid (4.00 g, 17.0 mmol, 1.0 equiv.) and SOCl_2 (1M solution in DCM) (170 mL, 170 mmol, 10 equiv.). The reaction mixture was heated to reflux at 60°C under Ar. After 1 day, the mixture was concentrated *in vacuo*. The acid chloride was redissolved in tetrahydrofuran (15 mL) and added dropwise to a mixture of 4-aminophenol (1.845 g, 16.9 mmol, 1.0 equiv.) and MgO (0.77 g, 19.1 mmol, 1.1 equiv.) in tetrahydrofuran (15 mL). After 4 hours, the mixture was concentrated *in vacuo*. The resulting mixture was filtered with celite to remove solids, diluted with EtOAc, then washed with 0.1M HCl (2 x 100 mL), water (100 mL) and brine (50 mL). The resulting organic phase was dried over anhydrous Na_2SO_4 . The mixture was filtered, and the filtrate was concentrated *in vacuo*. The product was obtained as a brown solid (4.06 g, 73%).

25

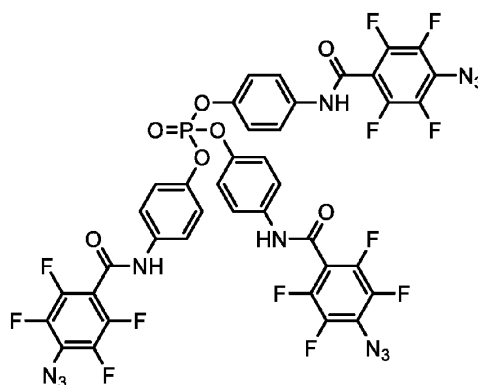
IR: ν_{max} = 3158 (O-H), 2927 (C-H), 2122 (N=N=N), 1724 (C=O), 1649 (C=C), 1625 (C=C), 1607 (C=C), 1564 (C=C), 1484 (C-F), 1250 (C-O). ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{CO}$) δ_{H} 9.77 (1H, s), 8.42 (1H, s), 7.52 (2H, m), 6.82 (2H, m);

^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{CO}$) δ_{C} 155.0, 154.7, 144.8 (m), 142.84 (m), 141.62 (m), 139.7 (m), 130.4, 121.8, 121.6 (m), 121.4, 115.6, 115.4, 113.1 (q); ^{19}F NMR (470 MHz, $(\text{CD}_3)_2\text{CO}$) δ_{F} -143.84 (2F, m), -152.86 (2F, m). HRMS (ESI⁺/Q-TOF) calc. for $\text{C}_{13}\text{H}_7\text{F}_4\text{N}_4\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 326.0427; found: 326.0429. The spectroscopic data obtained for 4-azido-2,3,5,6-tetrafluoro-*N*-(4-hydroxy-phenyl)benzamide (**5**) are shown in FIG. 1, FIG. 2, FIG. 3 and FIG. 4.

4-azido-2,3,5,6-tetrafluoro-*N*-(4-hydroxyphenyl)benzamide may be used to synthesise a variety of fluorophenyl azide-functionalised dynamic crosslinkers. In this example, tris(fluorophenyl azide) dynamic phosphate crosslinker **1** was prepared.

Tris(4-(4-azido-2,3,5,6-tetrafluorobenzamido)phenyl) phosphate (**1**)

Synthesis of tris(fluorophenyl azide) dynamic phosphate crosslinker (e.g., tris(4-(4-azido-2,3,5,6-tetrafluorobenzamido)phenyl) phosphate (Scheme 6) is described as follows.



Scheme 6. Chemical structure of tris(4-(4-azido-2,3,5,6-tetrafluorobenzamido)phenyl) phosphate (**1**)

20

To a RBF with stirrer bar was added 4-azido-2,3,5,6-tetrafluoro-*N*-(4-hydroxyphenyl)benzamide (489 mg, 1.50 mmol, 3.0 equiv.) and anhydrous THF (2 mL) under Ar, followed by POCl_3 (46.7 μL , 0.50 mmol, 1.0 equiv.). The reaction

mixture was cooled in an ice bath, and triethylamine (230 μ L, 3.13 mmol, 3.3 equiv.) was added to the reaction mixture. After 1 day, the mixture was concentrated *in vacuo*. The resulting mixture was filtered to remove solids, diluted by EtOAc, and then washed by water (2 x 100 mL) and brine (50 mL). The
5 resulting organic phase was dried over anhydrous Na_2SO_4 . The mixture was filtered, and the filtrate was concentrated *in vacuo*. Purification using silica gel column chromatography (1:99 – 5:95 MeOH/DCM) afforded the product as a pale brown solid (450 mg, 88%).

10 IR: ν_{max} = 3299 (N-H), 3079 (C-H), 2128 (N=N=N), 1667 (C=O), 1649 (C=C), 1613 (C=C), 1481 (C-F), 1294 (C-N), 1242 (C-O), 1186 (P=O), 969 (P-O). ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{CO}$) δ_{H} 10.12 (1H, s), 7.81 (2H, m), 7.37 (2H, m); ^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{CO}$) δ_{C} 156.4, 147.9, 145.7 (m), 143.7 (m), 142.5 (m), 140.5 (m), 136.8, 123.0 (t), 122.1, 122.0, 121.6, 121.5, 113.4 (t); ^{19}F NMR (470 MHz,
15 $(\text{CD}_3)_2\text{CO}$) δ_{F} -39.67 (6F, m), -48.76 (6F, m); ^{31}P NMR (470 MHz, $(\text{CD}_3)_2\text{CO}$) δ_{P} -13.23. HRMS (ESI⁺/Q-TOF) calc. for $\text{C}_{39}\text{H}_{16}\text{F}_{12}\text{N}_{12}\text{O}_7\text{P}^+$ $[\text{M}+\text{H}]^+$: 1022.0733; found: 1022.0709. The spectroscopic data obtained for tris(4-(4-azido-2,3,5,6-tetrafluorobenzamido)phenyl) phosphate (**1**) are shown in FIG. 5, FIG. 6, FIG. 7, FIG. 8 and FIG. 9.

20

1.2. Thermogravimetric analysis of dynamic phosphate crosslinker 1

Thermogravimetric analysis of crosslinker **1** was performed to determine the temperature required for thermal crosslinking (FIG. 10). Significant weight loss was observed from 152 $^{\circ}\text{C}$ to 214 $^{\circ}\text{C}$, with weight loss of 9 wt%
25 corresponding to the loss of 3 nitrogen molecules from crosslinker, indicating formation of the nitrene.

30

Example 2:**STEP 2 – Crosslinking Linear Polymer with Universal Dynamic Crosslinker****2.1. General procedure for thermal crosslinking of bulk samples**

5 Dynamic phosphate crosslinker **1** was dissolved in ethyl acetate (20 mg/mL) was added to a solution of linear polymer (Table 2), swirled for 10 seconds then transferred to a Teflon dish, followed by drying at under a stream of air at 60 °C for 1 hour and in a vacuum oven at 100 °C for 1 hour. The temperature of the vacuum oven was then raised to 150 °C for 1 day to enable
10 thermally activated crosslinking.

Examples of the solutions of linear polymer may be:

Polycaprolactone (70k-90k) (PCL), poly(ethylene-co-vinyl acetate) (CAS: 24937-78-8) (PEVA), polystyrene-block-polybutadiene-block- polystyrene (140k)
15 (PSBS), poly(ethylene oxide) (200k) (PEO) or poly(methyl methacrylate) (Paraloid A14, PMMA) dissolved in ethyl acetate at 60 °C (30 mg/mL).

2.2. General procedure for UV crosslinking of thin-film samples

Aryl azide-functionalised crosslinker **2** was dissolved in ethyl acetate (20
20 mg/mL), then appropriate amounts were added to PCL dissolved in ethyl acetate (50 mg/mL). The solution was spin-coated (200 rpm for 30 seconds) or drop casted on a glass slide, followed by curing under UV (254 nm) with the XL-1500 UV Crosslinker Spectrolinker, for 1 hour.

25 Example 3:**STEP 3 – Infusion of catalyst for dynamic bond exchange****3.1. General procedure for catalyst infusion after crosslinking**

100 mg of crosslinked polymer was soaked in 10 mL of DCM containing
30 catalyst for 2 days to enable TBD infusion. Subsequently, the catalyst-infused polymer sample was removed from the solution and the sample was then dried in a vacuum oven at 60 °C for 1 day.

In this example, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) is used as catalyst for dynamic bond exchange of universal phosphate crosslinker **1**. The amount of TBD is denoted by TBD wt% (Table 5), which is the mass of TBD in the DCM solution with respect to the mass of polymer sample. The concentration
5 of TBD may be calculated by the mass of TBD divided by the volume of DCM (mg/mL).

3.2. General procedure for catalyst infusion during crosslinking

Appropriate amounts of solutions of dynamic phosphate crosslinker **1** (80
10 mg/mL) and TBD (1 mg/mL) in THF were mixed and heated to 60°C to pre-form the crosslinker-catalyst adduct in different ratios (TBD:**1** = 0.1 to 3 equiv, Table 3).

Appropriate amounts of the solution of **1**-TBD adduct (1 to 10 wt%) was
15 then added to a solution of the linear polymer. The resultant solution was swirled for 10 seconds then transferred to a Teflon dish, followed by drying at under a stream of air at 60 °C for 1 hour and in a vacuum oven at 100 °C for 1 hour. The temperature of the vacuum oven was then raised to 150 °C for 16 h to enable thermally activated crosslinking.

20

Examples of the solutions of linear polymer may be:

Polycaprolactone (70k-90k) (PCL), poly(ethylene-co-vinyl acetate) (CAS: 24937-
78-8) (PEVA), polystyrene-block-polybutadiene-block- polystyrene (140k)
(PSBS) poly(ethylene oxide) (200k) (PEO) or poly(methyl methacrylate) (Paraloid
25 A14, PMMA) dissolved in THF at 70 °C (30 mg/mL).

Example 4: Characterisation of Crosslinked Polymers

4.1. Solvent resistance

30 A key feature of crosslinked polymers is their solvent resistance. Hence, the degree of crosslinking in the polymer network can be determined by the gel

fraction of the bulk polymer sample, or the film retention of the thin-film samples after exposure to solvent.

4.2. General procedure to determine gel fraction for bulk samples

5 The crosslinked polymer sample (~30 mg) was weighed (W_a), then soaked in a solvent which can solubilise its linear analog (20 mL) for 1 day. The sample was subsequently removed from the solvent and dried in a vacuum oven at 60 °C for 1 day, then the sample was weighed again (W_b). The gel fraction, which is the measure of the degree of crosslinking in the polymer network, can be calculated
10 by W_b/W_a .

4.3. General procedure to determine film retention measurements for thin-film samples

A cut was made on the polymer coated on the glass slide using a blade.
15 The depth of the cut was then measured with a Surface Profiler Alpha-Step-IQ. 500 μ L of a solvent which can solubilise its linear analog was dropped on the polymer and then spin-coated at 1000 rpm for 30 seconds. The solvent spin-coating was then repeated once. Thereafter, the depth of the cut is then measured to find out the film retention.

20

4.4. Gel fraction of bulk crosslinked polymers

Many polymers tested demonstrated increase in gel fraction (from zero) upon thermal crosslinking, even with as little as 1 wt% dynamic phosphate crosslinker **1** (Table 2).

25

Table 2. Gel fraction of bulk samples thermally crosslinked with dynamic phosphate crosslinker **1** without catalyst

Polymer backbone	Crosslinker wt%	Gel fraction ^a / %
PCL (70-90k)	1	85
PCL	2.5	95
PCL	5	95
PCL	10	95

PCL	20	95
SBS (140k)	10	62%
PEO (200k)	10	86%
PEVA (CAS 24937-78-8)	10	67%

^a Conditions for gel fraction: chloroform at room temperature.

Even when the catalyst was incorporated during crosslinking, significant gel fraction was achieved (Table 3).

5 **Table 3.** Gel fraction of bulk samples thermally crosslinked with dynamic phosphate crosslinker **1** with catalyst added during crosslinking

Polymer backbone	Crosslinker wt%	TBD equiv.	Gel fraction / %
PCL (70-90k)	2.5	0.2	87 ^a
PCL	2.5	0.25	98 ^b
PCL	2.5	0.5	93 ^b
PCL	2.5	1	94 ^b
PCL	2.5	2	56 ^b
PCL	2.5	3	68 ^b
SBS (140k)	10	0.2	76 ^a
SBS	10	0.1	76 ^a
SBS	10	0.05	76 ^a
SBS	5	0.2	68 ^a
PEO (200k)	5	0.2	68 ^a
PEVA (CAS 24937-78-8)	10	0.2	55 ^a
PMMA (Paraloid A14)	10	0.2	56 ^a

Conditions for gel fraction: ^aTHF at 75 °C; ^bCHCl₃ at RT.

4.5. Film retention of thin-film crosslinked PCL

10 Addition of 2.5 wt% of aryl azide-functionalised crosslinker **2** was sufficient to crosslinker the thin-film PCL samples, increasing the film retention from 0 to ~30% (Table 4).

Table 4. Film retention of thin-film PCL samples UV-crosslinked with crosslinker 2

Crosslinker wt%	Film retention / %
0	0
0.5	0
1.0	2.8
2.5	34.1
5.0	26.3

4.6. Infrared Spectroscopy

Fourier-transform infrared (FTIR) was performed to identify the functional groups present in the linear polymer, after crosslinking and after catalyst infusion (FIG. 11). The azide functional group from crosslinker 1 was fully consumed in the crosslinked polymer, but new peaks corresponding to C-F and P=O bonds were observed, indicating successful incorporation of the crosslinker and dynamic covalent bond. Similarly, upon TBD infusion, new peaks corresponding to C=N bond were observed, indicating successful uptake of the catalyst.

Example 5: Recyclability of CANs

The dynamic covalent bonds introduced *via* the crosslinker enable the CAN to undergo both mechanical and chemical recycling.

5.1. General procedure for mechanical reprocessing

The polymer samples were cut into pieces then were hot pressed between PTFE sheets under various conditions (temperature, time, pressure).

5.2. General procedure for chemical recycling

~40 mg of crosslinked polymer was added into a 20 mL vial containing 2 mL of 1-octanol. The vial was sealed and refluxed overnight. For SBS crosslinked polymer, vial was cooled to room temperature, and ethanol was added. The suspension was centrifuged (6000 rpm, 10 min). The pellet was washed with ethanol and dried in a vacuum oven at 90 °C.

5.3. Mechanical recycling

While the permanent crosslinker **2** and the phosphate dynamic crosslinker **1** without catalyst could not be mechanically reprocessed even at 200 °C, catalyst-infused samples with the phosphate dynamic crosslinker **1** could undergo reprocessing at elevated temperatures (Table 5). NMR studies estimate that the uptake of TBD resulted in a **1**:TBD ratio of 1:3.5.

When the TBD was added during crosslinking, mechanical reprocessing (FIG. 12) was possible even with lower amounts of catalyst (Table 6).

5.4. Chemical recycling

Although the crosslinked polymers could not be dissolved in common solvents, they can be chemically recycled in reactive solvents.

In this example, PSBS crosslinked with 5% dynamic phosphate crosslinker **1** and 0.2 equiv. TBD was dissolved in 1-octanol under reflux overnight (FIG. 13).

In summary, a dynamic phosphate crosslinker **1** which was synthesised in 4 steps with 58% overall yield (Scheme 2) has been demonstrated as an example. A permanent crosslinker **2** was also prepared as a comparison. Both crosslinkers could react with a variety of thermoplastics (e.g., PCL, PEVA, PSBS, PEO and PMMA) under thermal activation at 150 °C or UV (254 nm) activation to form CANs. The resultant crosslinked polymers which are solvent resistant and mechanically firm at ambient temperatures. The polymer network crosslinked with the permanent crosslinker **2** could not be reprocessed upon heating. In contrast, upon infusion with TBD catalyst, CANs crosslinked with dynamic phosphate crosslinker **1** are reprocessable under thermal activation (FIG. 12). Chemical recycling of the CANs can be performed by refluxing with higher alcohols such as octanol (FIG. 13).

Table 5. Reprocessing conditions of bulk samples crosslinked with dynamic phosphate crosslinker **1** with post-crosslinking infusion of catalyst

Polymer backbone	Crosslinker	Crosslinker wt%	TBD wt%	[TBD] (mg/mL)	Reprocessing Conditions		
					Temp. / °C	Pressure / MPa	Time / s
PCL (70-90k)	2	2.5	0	0	200	0.5	N.R. ^a
PCL	1	1	0.0625	0.00625	170	0.5	360
PCL	1	2.5	0.125	0.0125	200	0.5	600
PCL	1	2.5	0.075	0.0075	200	0.5	3600
PCL	1	2.5	0.025	0.0025	200	0.5	N.R. ^a
PCL	1	2.5	0	0	200	0.5	N.R. ^a
PCL	1	5	2.5	0.25	170	0.5	360
PCL	1	10	5	0.5	170	0.5	360
PCL	1	20	10	1	180	0.5	500
PEO (200k)	1	10	5	0.5	100	0.5	300

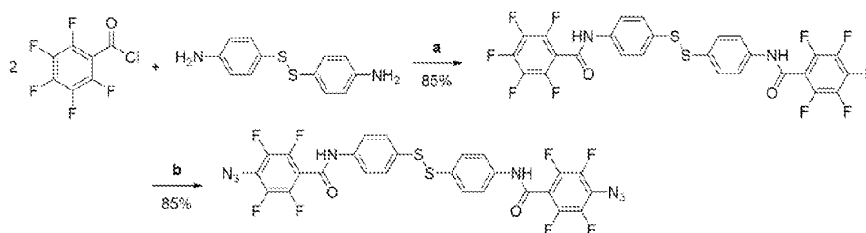
^a N.R. = not reprocessible

Table 6. Reprocessing conditions of bulk samples crosslinked with dynamic phosphate crosslinker **1** with catalyst added during crosslinking

Polymer backbone	Crosslinker wt%	TBD equiv. ^a	Reprocessing Conditions		
			Temp. / °C	Pressure / MPa	Time / s
PCL (70-90k)	2.5	0.2	200	0.5	3600
PCL	2.5	0.25	200	0.5	3600
PCL	2.5	0.5	200	0.5	7200
PCL	2.5	1	200	0.5	7200
PCL	2.5	2	140	0.5	600
PCL	2.5	3	140	0.5	600
SBS (140k)	10	0.2	160	0.5	600
SBS	10	0.1	180	0.5	600
SBS	10	0.05	160	0.5	600
SBS	5	0.2	140	0.5	600
PEO (200k)	5	0.2	160	0.5	600
PEVA (CAS 24937-78-8)	10	0.2	140	0.5	600
PMMA (Paraloid A14)	10	0.2	160	0.5	600

Example 6: Dynamic Aryl Disulfide Crosslinker**6.1. Synthesis of dynamic aryl disulfide crosslinker**

The steps for the synthesis of dynamic aryl disulfide crosslinker **6** are illustrated in Scheme 7.

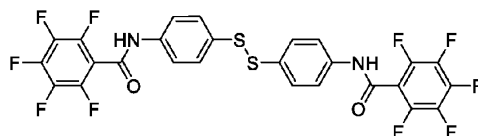
**Scheme 7.** Synthesis of dynamic aryl disulfide crosslinker **6**

a: Et₃N, DCM, 0°C to RT, 16 h, 85%

b: NaN₃ (2.1 equiv.), DMSO, RT, 16 h, 85%

N,N'-(disulfanediylbis(4,1-phenylene))bis(2,3,4,5,6-pentafluorobenzamide)

Synthesis of N,N'-(disulfanediylbis(4,1-phenylene))bis(2,3,4,5,6-pentafluorobenzamide) (Scheme 8) is described as follows.

**Scheme 8.** Chemical structure of N,N'-(disulfanediylbis(4,1-phenylene))bis(2,3,4,5,6-pentafluorobenzamide) (**7**)

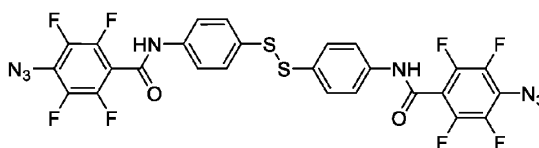
To a RBF under Ar with stirrer bar was added 4,4'-dithiodianiline (2.0 g, 8.05 mmol, 1.0 equiv.), anhydrous dichloromethane (DCM, 100 ml) and triethylamine (2.34 ml, 16.9 mmol, 2.1 equiv.). In a separate vial under Ar with stirrer bar, 2,3,4,5,6-pentafluorobenzoyl chloride (1.71 g, 16.9 mmol, 2.1 equiv.) was dissolved in 10 ml anhydrous DCM. The acid chloride was added drop-wise

into the aforementioned RBF cooled in an ice-bath. The ice-bath was removed when all the acid chloride was added. The reaction mixture was then left to stir at room temperature for 16 h. The mixture was concentrated *in vacuo*, followed by the addition of 50 mL deionized water. The mixture was vacuum filtered using a
 5 Buchner funnel and the residue was dried by heating at 100°C. The product was obtained as a white solid (4.36 g, 85.1% yield).

¹H NMR (500 MHz, DMSO) δ_H 11.19 (s, 2H, NH), 7.68 (d, *J* = 8.8 Hz, 4H, Ar-H), 7.56 (d, *J* = 8.8 Hz, 4H, Ar-H); ¹³C NMR (126 MHz, DMSO) δ_C 155.1 (C=O),
 10 144.3 – 142.3 (m), 142.7 – 140.7 (m), 138.1 – 136.1 (m), 137.9, 131.5, 129.7, 120.6, 112.3 (m); ¹⁹F NMR (376 MHz, DMSO) δ_F –141.6 to –141.7 (m, 4F), –151.8 (t, *J* = 22.0 Hz, 2F), –160.7 to –160.8 (m, 4F). HRMS (ESI⁺/Q-TOF) calc. for C₂₆H₁₀F₁₀N₂O₂S₂ [M]⁺: 636.0024; found: 636.0025. The spectroscopic data obtained for N,N'-(disulfanediyldis(4,1-phenylene))bis(2,3,4,5,6-
 15 pentafluorobenzamide) (**7**) are shown in FIG. 14, FIG. 15 and FIG. 16.

N,N'-(disulfanediyldis(4,1-phenylene))bis(4-azido-2,3,5,6-tetrafluorobenzamide)

Synthesis of N,N'-(disulfanediyldis(4,1-phenylene))bis(4-azido-2,3,5,6-tetrafluorobenzamide) (Scheme 9) is described as follows.
 20



Scheme 9. Chemical structure of N,N'-(disulfanediyldis(4,1-phenylene))bis(4-azido-2,3,5,6-tetrafluorobenzamide) (**6**)

25

To a RBF under Ar with stirrer bar was added bis(pentafluorobenzamide) (0.92 g, 1.45 mmol, 1.0 equiv.) and anhydrous DMSO (40 ml). NaN₃ (0.197 g, 3.04 mmol, 2.1 equiv.) was added portion-wise. The reaction mixture was stirred at RT for 16 h. The resulting mixture was quenched with water (50 ml), then

extracted with DCM (30 ml x 3). The mixture was concentrated *in vacuo*, followed by the addition of 30 mL deionized water. The mixture was vacuum filtered using a Buchner funnel and the residue was dried by heating at 100°C. The product was obtained as a light-brown solid (0.99 g, 85% yield).

5

IR: ν_{max} = 3312 (N-H), 2130 (N=N=N), 1665 (C=O), 1257 (C-N), 991 (C-F); ^1H NMR (400 MHz, DMSO) δ_{H} 7.69 (d, J = 8.8 Hz, 4H, Ar-H), 7.55 (d, J = 8.8 Hz, 4H, Ar-H); ^{13}C NMR (101 MHz, DMSO) δ_{C} 155.5 (C=O), 144.3 – 141.9 (m), 141.4 – 138.9 (m), 138.0, 131.4 (m), 129.8, 121.9 – 121.6 (m), 120.6, 111.9 (t, J = 20.8 Hz); ^{19}F NMR (376 MHz, DMSO) δ_{F} –142.5 to –142.6 (m, 4F), –151.1 to –151.0 (m, 4F). HRMS (ESI⁺/Q-TOF) calc. for $\text{C}_{26}\text{H}_{10}\text{N}_8\text{O}_2\text{F}_8\text{S}_2$ $[\text{M}]^+$: 682.0240; found 682.0240. The spectroscopic data obtained for N,N'-(disulfanediylbis(4,1-phenylene))bis(4-azido-2,3,5,6-tetrafluorobenzamide) (**6**) are shown in FIG. 17, FIG. 18, FIG. 19 and FIG. 20.

15

6.2. Thermogravimetric analysis of dynamic aryl disulfide crosslinker 6

For dynamic aryl disulfide crosslinker 6, as shown in FIG. 21, significant weight loss was observed from 142°C to 192°C, with weight loss of 9.2 wt% corresponding to the loss of 2 nitrogen molecules (expected weight loss = 8.2%), indicating formation of the bis-nitrene.

20

6.3. Crosslinking of dynamic aryl disulfide crosslinker 6

Table 7 shows gel fraction of examples of thermoplastics (i.e. LDPE, PP, PEO and PCL) crosslinked with dynamic aryl disulfide crosslinker 6.

25

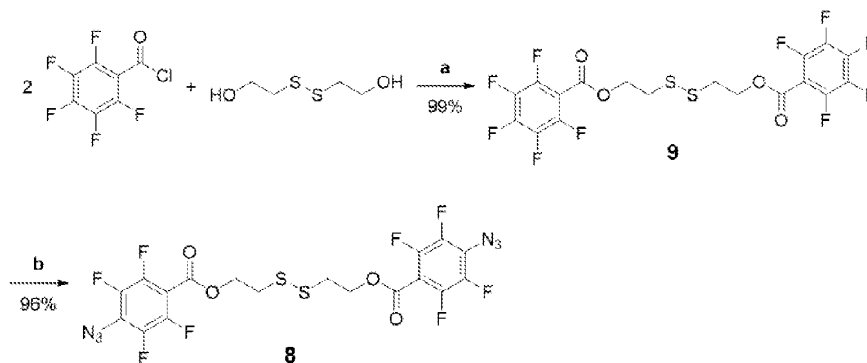
30

Table 7. Crosslinking of thermoplastics with dynamic aryl disulfide crosslinker 6

Polymer	Dynamic aryl disulfide crosslinker 6 (wt%)	Gel fraction (%)
LDPE	5	8.9 ± 1.1
LDPE	10	16.3 ± 6.8
PP	5	94 ± 1
PP	10	95.6 ± 1.3
PEO	5	66.1 ± 0.5
PCL	5	96.2 ± 0.5
HDPE	5	96.9 ± 0.1
HDPE	5 + 10 mol% POct ₃ catalyst	88.7 ± 1.7

Example 7: Dynamic Disulfide Crosslinker5 **7.1. Synthesis of dynamic disulfide crosslinker**

The steps for the synthesis of dynamic disulfide crosslinker **8** are illustrated in Scheme 10.

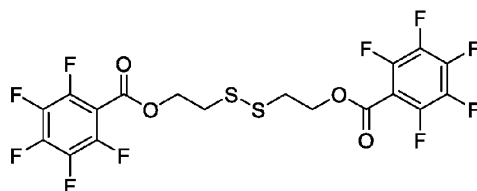
10 **Scheme 10.** Synthesis of dynamic disulfide crosslinker **8**

a: Et₃N, DCM, 0°C to RT, 4 h, 99%

b: NaN₃ (2.0 equiv.), DMSO, RT, 16 h, 98%

Disulfanediylbis(ethane-2,1-diyl)bis(2,3,4,5,6-pentafluorobenzoate) (9)

15 Synthesis of disulfanediylbis(ethane-2,1-diyl) bis(2,3,4,5,6-pentafluorobenzoate) (Scheme 11) is described as follows.



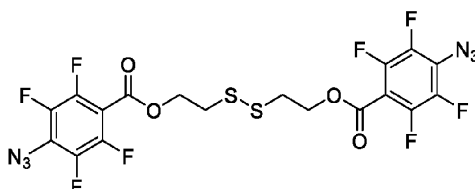
Scheme 11. Chemical structure of disulfanediyldis(ethane-2,1-diyl) bis(2,3,4,5,6-pentafluorobenzoate) (**9**)

5 To a RBF under Ar with stirrer bar was added 2-hydroxyethyl disulfide (1.51 g, 9.76 mmol, 1.0 equiv.), anhydrous dichloromethane (DCM, 45 ml) and triethylamine (1.98 ml, 19.5 mmol, 2.0 equiv.). In a separate vial under Ar with stirrer bar, 2,3,4,5,6-pentafluorobenzoyl chloride (4.50 g, 19.5 mmol, 2.0 equiv.) was dissolved in 45 ml anhydrous DCM. The acid chloride was added drop-wise
10 into the aforementioned RBF cooled in an ice-bath. The ice-bath was removed when all the acid chloride was added. The reaction mixture was then left to stir at room temperature for 4 h. To the resulting mixture, 2 M aq. Na₂CO₃ (2 ml) was added and the layers were separated. The aqueous layer was extracted with DCM (10 ml x 3). The combined organic layers were then washed with brine (50
15 ml) and dried over anhydrous MgSO₄. The mixture was filtered, and the filtrate was concentrated *in vacuo*. The ester was obtained as an off-white solid (5.22g, 99% yield).

R_f 0.38 (EtOAc:hexane, 1:4). IR: ν_{max} = 2957 (C-H), 1732 (C=O), 1651
20 (C=C), 1491 (C=C), 1222 (C-O), 987 (C-F). ¹H NMR (400 MHz, CDCl₃) δ _H 4.65 (t, *J* = 6.6 Hz, 4H, OCH₂), 3.05 (t, *J* = 6.6 Hz, 4H, SCH₂); ¹³C NMR (101 MHz, CDCl₃) δ _C 159.0 (C=O), 147.2 – 143.9 (m), 145.0 – 141.6 (m), 139.4 – 135.5 (m), 108.4 – 107.3 (m), 64.3 (OCH₂), 36.8 (SCH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ _F – 137.6 to –137.8 (m, 4F), –147.8 (tt, *J* = 20.9, 4.8 Hz, 2F), –160.0 to –160.2 (m,
25 4F). HRMS (ESI⁺/Q-TOF) calc. for C₁₈H₈F₁₀O₄S₂ [M]⁺: 541.9704; found: 541.9699. The spectroscopic data obtained for disulfanediyldis(ethane-2,1-diyl) bis(2,3,4,5,6-pentafluorobenzoate) (**9**) are shown in FIG. 22, FIG. 23 and FIG. 24.

Disulfanediylbis(ethane-2,1-diyl)bis(4-azido-2,3,5,6-tetrafluorobenzoate) (8)

Synthesis of disulfanediylbis(ethane-2,1-diyl) bis(4-azido-2,3,5,6-tetrafluorobenzoate) (Scheme 12) is described as follows.



5

Scheme 12. Chemical structure of disulfanediylbis(ethane-2,1-diyl) bis(4-azido-2,3,5,6-tetrafluorobenzoate) (**8**)

To a RBF under Ar with stirrer bar was added bis(pentafluorobenzoate) **9** (5.73 g, 10.6 mmol, 1.0 equiv.) and anhydrous DMSO (75 ml). NaN₃ (1.38 g, 21.2 mmol, 2.0 equiv.) was added portion-wise. The reaction mixture was stirred at RT for 16 h. The resulting mixture was quenched with water (25 ml), then extracted with Et₂O (50 ml x 5). The combined organic layers were then washed with brine (50 ml) and dried over anhydrous MgSO₄. The mixture was filtered, and the filtrate was concentrated *in vacuo*. The product was obtained as an off-white solid (5.98 g, 96% yield). The product is then dissolved in minimal amount of cold Et₂O/hexane (1:4), vacuum filtered and washed with cold Et₂O to obtain the disulfide crosslinker **8** as white crystals.

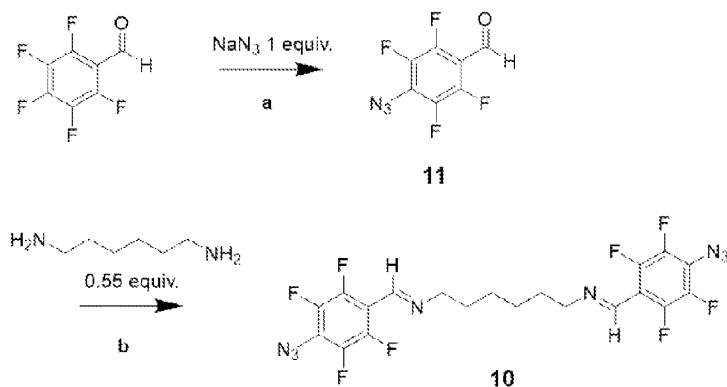
IR: ν_{max} = 2962 (C-H), 2128 (N₃), 1725 (C=O), 1640 (C=C), 1483 (C=C), 1252 (C-O), 1001 (C-F). ¹H NMR (400 MHz, CDCl₃) δ_H 4.62 (t, *J* = 6.6 Hz, 2H, OCH₂), 3.04 (t, *J* = 6.6 Hz, 2H, SCH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ_F -138.1 to -138.2 (m, 4F), -150.5 to -150.7 (m, 4F). Note: NMR spectra of crystallized crosslinker **8** contains two sets of peaks at ambient temperature, but one set of peaks diminishes as CDCl₃ is heated to 50 °C, suggesting the presence of rotamers. Data reported is for the major species at 50 °C. The spectroscopic data obtained for disulfanediylbis(ethane-2,1-diyl) bis(4-azido-2,3,5,6-tetrafluorobenzoate) (**8**) are shown in FIG. 25 and FIG. 26.

25

Example 8: Dynamic Imine Crosslinker**8.1. Synthesis of dynamic imine crosslinker**

The steps for the synthesis of dynamic imine crosslinker **10** are illustrated

5 in Scheme 13.



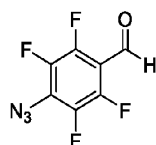
Scheme 13. Synthesis of dynamic imine crosslinker **10**

a: NaN_3 (1.0 equiv.), DMSO, RT, 6 h

10 **b:** 1,6-diaminohexane (0.55 equiv.), ethanol, RT, 16 hr.

4-azido-2,3,5,6-tetrafluorobenzaldehyde (11)

Synthesis of 4-azido-2,3,5,6-tetrafluorobenzaldehyde (Scheme 14) is described as follows.



15

Scheme 14. Chemical structure of 4-azido-2,3,5,6-tetrafluorobenzaldehyde (**11**)

To a RBF under Ar with stirrer bar was added 2,3,4,5,6-pentafluorobenzaldehyde (5.00 mL, 40.5 mmol, 1.0 equiv.), and anhydrous
 20 DMSO (80 ml). NaN_3 (2.77 g, 40.5 mmol, 1.0 equiv.) was added portion-wise.
 The reaction mixture was stirred at RT for 6 h under Ar. The resulting mixture was

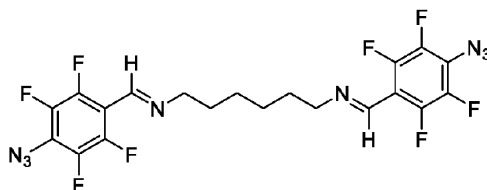
quenched with water (200 ml), then extracted with Et₂O (50 ml x 5). The combined organic layers were then washed with brine (200 ml) and dried over anhydrous MgSO₄. The mixture was filtered, and the filtrate was concentrated in vacuo. The aldehyde was obtained as an off-white solid (8.67 g, 39.6 mmol, 98% yield).

- 5 Recrystallisation from Et₂O/hexane (1:5), vacuum filtration and washing with cold Et₂O afforded white crystals (7.06 g, 32.2 mmol, 80% yield).

¹H NMR (400 MHz, CDCl₃) δ_H 10.2 (s, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ_F -144.8 to -144.9 (m, 2F), -150.8 to -150.9 (m, 2F). The spectroscopic data
10 obtained for 4-azido-2,3,5,6-tetrafluorobenzaldehyde (11) are shown in FIG. 27 and FIG. 28.

**N,N'-(hexane-1,6-diyl)bis(1-(4-azido-2,3,5,6-tetrafluorophenyl)
methanimine) (10)**

- 15 Synthesis of N,N'-(hexane-1,6-diyl)bis(1-(4-azido-2,3,5,6-tetrafluorophenyl)methanimine) (Scheme 15) is described as follows.



Scheme 15. Chemical structure of N,N'-(hexane-1,6-diyl)bis(1-(4-azido-2,3,5,6-tetrafluorophenyl)methanimine) (**10**)

20

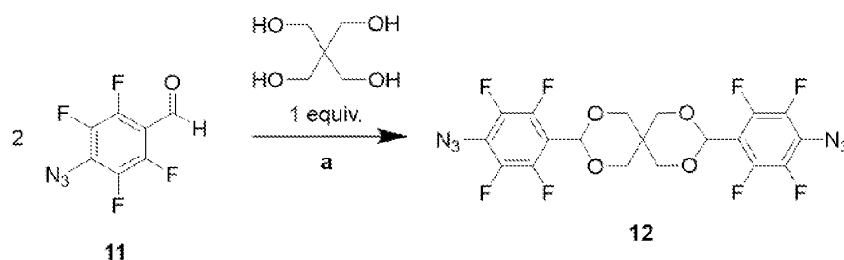
- To a RBF with stirrer bar was added 4-azido-2,3,5,6-tetrafluorobenzaldehyde (0.4g, 1.83 mmol, 1.0 equiv.), 5ml ethanol, and 1,6-diaminohexane (0.117 g, 1.00 mmol, 0.55 equiv.). After stirring the reaction mixture at room temperature for 5 minutes, glacial acetic acid (2 μL, 0.0365 mmol, 0.02 equiv.) was added. The reaction mixture was stirred in RT for 16 hours and
25 then blow dried with N₂ gas at 90°C. The product was concentrated *in vacuo* to obtain the imine crosslinker 2 as yellow crystals (0.397 g, 83.9%).

IR: $\nu_{\max}$ = 2921 (C-H), 2121 (N_3), 1639 (C=N), 1477 (C=C), 1240 (C-N), 989 (C-F). ^1H NMR (400 MHz, CDCl_3) δ_{H} 8.37 (s, 2H, NCH), 3.68 (t, J = 6.9 Hz, 4H, NCH₂), 1.81 – 1.67 (m, 4H, NCH₂CH₂), 1.43 (d, J = 6.4 Hz, 4H, NCH₂CH₂CH₂); ^{13}C NMR (101 MHz, CDCl_3) δ_{C} 149.46 (NCH), 147.0 – 144.4 (m), 141.9 – 139.5 (m), 121.3 (m), 111.4 (m), 63.4 (NCH₂), 30.6 (NCH₂CH₂), 27.0 (NCH₂CH₂CH₂); ^{19}F NMR (376 MHz, CDCl_3) δ_{F} –143.04 to –144.11 (m, 4F), –151.66 to –152.95 (m, 4F). HRMS (ESI⁺/Q-TOF) calc. for $\text{C}_{20}\text{H}_{14}\text{F}_8\text{N}_8$ [M]⁺: 518.1214; found: 518.1208. The spectroscopic data obtained for N,N'-(hexane-1,6-diyl)bis(1-(4-azido-2,3,5,6-tetrafluorophenyl)methanimine) (**10**) are shown in FIG. 29, FIG. 30 and FIG. 31.

Example 9: Dynamic Spiroacetal Crosslinker

9.1. Synthesis of dynamic spiroacetal crosslinker 12

The step for the synthesis of dynamic spiroacetal crosslinker **12** is illustrated in Scheme 16.



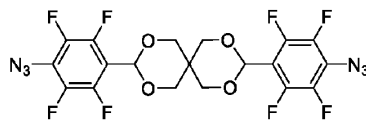
Scheme 16. Synthesis of dynamic spiroacetal crosslinker **12**

a: pentaerythritol, acetonitrile, reflux, 2 hr.

3,9-bis(4-azido-2,3,5,6-tetrafluorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (**12**)

Synthesis of 3,9-bis(4-azido-2,3,5,6-tetrafluorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (Scheme 17) is described as follows.

110



Scheme 17. Chemical structure of 3,9-bis(4-azido-2,3,5,6-tetrafluorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (**12**)

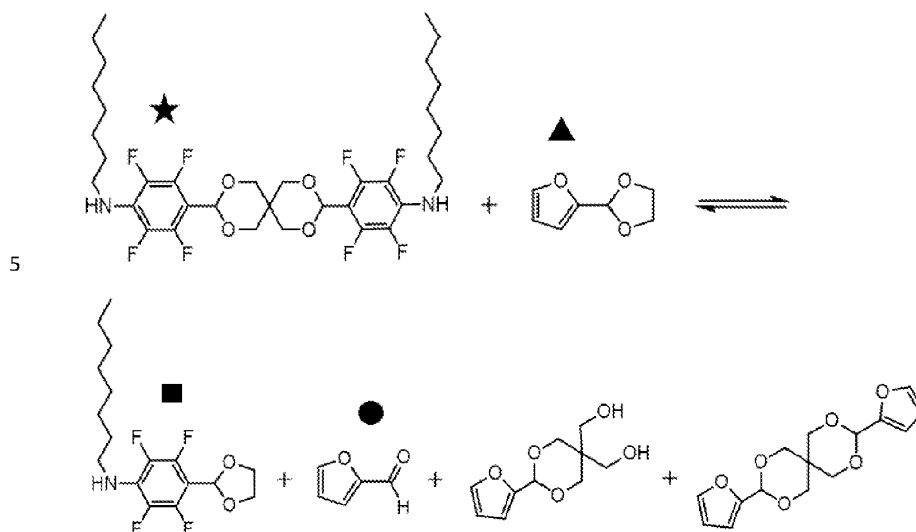
5 To a mixture of 4-azido-2,3,5,6-tetrafluorobenzaldehyde **11** (877 mg, 4.00 mmol, 2.0 equiv.) and pentaerythritol (272 mg, 2.00 mmol, 1.0 equiv.) with a stirrer bar in acetonitrile (10 mL) was added p-toluenesulfonic acid monohydrate (3.8 mg, 0.04 mmol, 2 mol%). The reaction mixture was refluxed for 2 h until TLC showed completion, then blown down under a stream of N₂ at 90 °C to afford a
10 pale yellow powder. The powder was redissolved in dichloromethane, filtered and dried to obtain spiroacetal **12** as an off-white powder (1.03 g, 1.91 mmol, 96%).

R_f 0.28 (EtOAc:hexane, 1:4). IR: ν_{max} = 2856 (C-H), 2136 (N₃), 1652 (C=C), 1490 (C=C), 1232 (C-O), 1007 (C-F). ¹H NMR (500 MHz, CDCl₃) δ _H 5.80 (s, 2H, CHAr), 4.93 (dd, *J* = 11.7, 2.9 Hz, 2H, CH₂O), 3.82 (d, *J* = 11.7 Hz, 2H, CH₂O), 3.79 (dd, *J* = 11.5, 2.6 Hz, 2H, CH₂O), 3.60 (d, *J* = 11.7 Hz, 2H, CH₂O); ¹³C NMR (126 MHz, CDCl₃) δ _C 148.2 – 142.9 (m), 142.4 – 137.1 (m), 121.8 – 120.5 (m), 112.0 (t, *J* = 14.4 Hz), 95.5 (CHAr), 71.3 (CH₂O), 70.7 (CH₂O), 33.0 (C(CH₂O)₄); ¹⁹F NMR (471 MHz, CDCl₃) δ _F -142.29 to -142.41 (m, 2F), -151.53
15 to -151.65 (m, 2F). HRMS (ESI⁺/Q-TOF) calc. for C₁₉H₁₀F₈N₆O₄ [M+H]⁺: 539.0709; found: 539.0720. The spectroscopic data obtained for 3,9-bis(4-azido-2,3,5,6-tetrafluorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (**12**) are shown in FIG. 32, FIG. 33 and FIG. 34.
20

25 Example 10: Acetal Exchange Model Studies

A NMR tube was added 4,4'-(2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(2,3,5,6-tetrafluoro-N-octylaniline) (4.5 mg, 6.33 μmol), 2-(furan-2-yl)-1,3-dioxolane (3.7 μL, 31.7 μmol), dodecanoic acid (1.52 mg, 7.60 μmol). p-toluenesulfonic acid (0.24mg, 1.27 μmol) and toluene-d₈ as solvent (1 mL). The
30

tube was sealed and heated to 120°C for 48 hours. The ratio of 4,4'-(2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(2,3,5,6-tetrafluoro-N-octylaniline) to 4-(1,3-dioxolan-2-yl)-2,3,5,6-tetrafluoro-N-octylaniline was obtained as 46:54. ¹H NMR and ¹⁹F NMR spectra are shown in FIG. 35 and 36.



Scheme 18. Acetal exchange model

Example 11: Thermogravimetric Analysis of Dynamic Crosslinkers

Thermogravimetric analysis of crosslinkers **8**, **10** and **12** were performed to determine the temperature required for thermal crosslinking. *ca.* 5 mg was placed into an alumina pan and heated from 30 to 600 °C with a ramp rate of 5 °C/min in nitrogen at a flow rate of 60 mL/min.

For disulfide crosslinker **8** (FIG. 37), significant weight loss was observed from 139 °C to 185 °C, with weight loss of 9.7 wt% corresponding to the loss of 2 nitrogen molecules (expected weight loss = 9.5%), indicating formation of the bis-nitrene.

For imine crosslinker **10** (FIG. 38), significant weight loss was observed from 140 °C to 190 °C, with weight loss of 12.1 wt% corresponding to the loss of 2 nitrogen molecules (expected weight loss = 10.8%), indicating formation of the bis-nitrene.

5

For acetal crosslinker **12** (FIG. 39), significant weight loss was observed from 145 °C to 192 °C, with weight loss of 9.7 wt% corresponding to the loss of 2 nitrogen molecules (expected weight loss = 10.4%), indicating formation of the bis-nitrene.

10

Example 12: Thermal Crosslinking Model Studies

Model studies were performed with cyclohexane as a model for polyolefins to demonstrate the reactivity of the crosslinkers.

15

General procedure for thermal crosslinking with cyclohexane: A pressure tube was charged with crosslinker and cyclohexane as solvent (~0.005 M) under Ar. The tube was sealed and heated to 160 °C (careful: gas evolution, overpressure!) for 16 h. The reaction vessel was allowed to cool to room temperature and the crude mixture was concentrated. The crude mixture was purified by preparative thin layer chromatography. All fractions were analyzed by ¹H-, ¹⁹F-NMR, and HRMS.

20

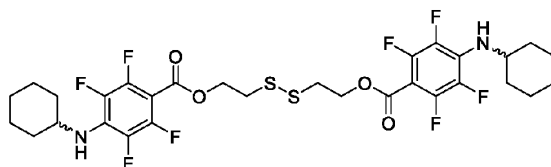
12.1. Crosslinker 8 with Cyclohexane

25

A pressure tube was charged with (43.9 mg, 74.5 μmol) of crosslinker **8** and cyclohexane as solvent (0.005 M, 14.9 mL) under Ar. The tube was sealed and heated to 160 °C (careful: gas evolution, overpressure!) for 16 h. The reaction vessel was allowed to cool to room temperature and the crude mixture was concentrated. The crude mixture was purified by preparative thin layer chromatography (DCM/hexane 2:1) to obtain a colourless oil (19.6 mg, 38%) as a 85:15 mixture of diastereomers.

30

Disulfanediylbis(ethane-2,1-diyl) bis(4-(cyclohexylamino)-2,3,5,6-tetrafluorobenzoate)



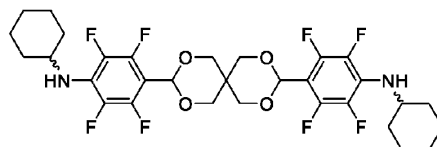
Scheme 19. Chemical structure of disulfanediylbis(ethane-2,1-diyl) bis(4-(cyclohexylamino)-2,3,5,6-tetrafluorobenzoate)

R_f 0.56 (DCM:hexane 2:1). IR: $\nu_{\max}$ = 3368 (N-H), 2929 (C-H), 2854 (C-H), 1722 (C=O), 1646 (C=C), 1499 (C=C), 1217 (C-O), 988 (C-F). ¹H NMR (500 MHz, CDCl₃) δ_{H} 4.57 (t, J = 6.6 Hz, 4H, OCH₂), 3.71 – 3.63 (m, 2H, CHNH), 3.04 (t, J = 6.6 Hz, 4H, SCH₂), 2.06 – 2.02 (m, 4H, Cy), 1.77 (dt, J = 13.1, 3.2 Hz, 4H, Cy), 1.65 (dt, J = 12.9, 3.9 Hz, 2H, Cy), 1.44 – 1.31 (m, 5H, Cy), 1.22 – 1.14 (m, 7H, Cy); ¹³C NMR (126 MHz, CDCl₃) δ_{C} 160.7 (C=O), 148.7 – 144.7 (m), 137.7 – 135.2 (m), 131.6 – 130.37 (m), 97.7 (t, J = 14.0 Hz), 63.3 (OCH₂), 53.78 (NCH), 37.2 (SCH₂), 34.7 (Cy), 25.6 (Cy), 24.8 (Cy). ¹⁹F NMR (471 MHz, CDCl₃) δ_{F} –35.2 (2F, m), –56.2 (2F, m, major diastereomer), –57.1 (m, minor diastereomer). HRMS (ESI⁺/Q-TOF) calc. for C₃₀H₃₂F₈N₂O₄S₂ [M+H]⁺: 701.1749; found: 701.1745. The spectroscopic data obtained for disulfanediylbis(ethane-2,1-diyl) bis(4-(cyclohexylamino)-2,3,5,6-tetrafluorobenzoate) are shown in FIG. 40, FIG. 41 and FIG. 42.

12.2. Crosslinker 12 with Cyclohexane

A pressure tube was charged with (60.8 mg, 113 μ mol) of crosslinker 12 and cyclohexane as solvent (0.004 M, 28 mL) under Ar. The tube was sealed and heated to 160 °C (careful: gas evolution, overpressure!) for 16 h. The reaction vessel was allowed to cool to room temperature and the crude mixture was concentrated. The crude mixture was purified by preparative thin layer chromatography (EtOAc/hexane 3:7) to obtain a diastereomer 1 (6.4 mg, 9%) and diastereomer 2 (6.6 mg, 9%) as colourless oils.

4,4'-(2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(N-cyclohexyl-2,3,5,6-tetrafluoroaniline)



Diastereomer 1

- 5 R_f 0.70 (EtOAc:hexane 3:7). ¹H NMR (500 MHz, CDCl₃) δ_H 5.73 (s, 2H, CHO₂), 4.95 (dd, *J* = 11.6, 2.5 Hz, 2H, CCH₂O), 3.80 (d, *J* = 11.7 Hz, 2H, CCH₂O), 3.77 (dd, *J* = 11.7, 2.7 Hz, 2H, CCH₂O), 3.71 (br s, 2H, NH), 3.59 (d, *J* = 11.7 Hz, 2H, CCH₂O), 3.57 – 3.52 (m, 2H, CHNH), 2.00 (dq, *J* = 12.2, 3.8 Hz, 4H, Cy), 1.74 (dt, *J* = 13.7, 3.8 Hz, 4H, Cy), 1.63 (dt, *J* = 12.9, 3.9 Hz, 2H, Cy), 1.34 (qp, *J* = 12.6, 3.6 Hz, 4H, Cy), 1.20 (tt, *J* = 12.4, 3.6 Hz, 2H, Cy), 1.13 (qd, *J* = 11.0, 3.6 Hz, 4H, Cy); ¹³C NMR (126 MHz, CDCl₃) δ_C 148.6– 142.2 (m), 137.3 (dd, *J* = 239.2, 16.2 Hz), 129.0 – 127.5 (m), 106.4 – 100.8 (m), 96.0, 71.4, 70.8, 53.8, 34.5, 32.8, 25.7, 24.8; ¹⁹F NMR (471 MHz, CDCl₃) δ_F –145.6 (m), –160.2 (m). HRMS (ESI⁺/Q-TOF) calc. for C₃₁H₃₄F₈N₂O₄ [M+H]⁺: 651.2464; found: 651.2460.
- 15 The spectroscopic data obtained for 4,4'-(2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(N-cyclohexyl-2,3,5,6-tetrafluoroaniline) diastereomer 1 are shown in FIG. 43, FIG. 44 and FIG. 45.

Diastereomer 2

- 20 R_f 0.41 (EtOAc:hexane 3:7). ¹H NMR (500 MHz, CDCl₃) δ_H 5.73 (d, *J* = 4.3 Hz, 2H, CHO₂), 4.94 (dt, *J* = 11.5, 2.3 Hz, 2H, CCH₂O), 4.05 (br s, 2H, NH), 3.79 (d, *J* = 11.9 Hz, 2H, CH₂O), 3.76 (dd, *J* = 11.8, 2.8 Hz, 2H, CCH₂O), 3.77– 3.69 (m, 1H, CHNH), 3.58 (d, *J* = 11.7 Hz, 2H, CCH₂O), 3.57 – 3.51 (m, 1H, CHNH), 1.99 (dd, *J* = 12.2, 3.3 Hz, 2H, Cy), 1.73 (dp, *J* = 13.7, 4.1 Hz, 2H, Cy), 1.62 (dp, *J* = 13.1, 3.6 Hz, 1H, Cy), 1.59 – 1.37 (br s, 1H, Cy), 1.34 (qt, *J* = 12.2, 3.6 Hz, 4H, Cy), 1.29 – 1.24 (m, 4H), 1.25 – 1.16 (m, 3H), 1.16 – 1.07 (m, 3H); ¹³C NMR (126 MHz, CDCl₃) δ_C 147.1 – 143.3 (m), 138.8 – 135.1 (m), 128.8 – 126.9 (m), 104.6 – 102.7 (m), 96.0, 71.4, 70.8, 53.8, 34.5, 32.8, 29.8, 25.7, 24.8; ¹⁹F NMR (471 MHz, CDCl₃) δ_F –145.3 (m, 2F), –145.5 (m, 2F), –160.2 (m, 2F), –162.2 (m,
- 25

2F). HRMS (ESI⁺/Q-TOF) calc. for C₃₁H₃₄F₈N₂O₄ [M+H]⁺: 651.2464; found: 651.2459.

Example 13: UV-Vis Analysis of Dynamic Crosslinkers

5

Ultraviolet-visible (UV-vis) spectra were recorded for each of the dynamic disulfide crosslinker **8**, dynamic imine crosslinker **10** and dynamic acetal crosslinker **12**, as shown in FIG. 46.

10 Example 14: Thermal Crosslinking of Thermoplastics with Dynamic Crosslinkers **8**, **10** and **12**

14.1. Thermal crosslinking & Gel fraction

15 **General procedure for thermal crosslinking of thermoplastics:** Linear thermoplastic (210 mg) was dissolved in an appropriate solvent (7 mL); LDPE (melt index 25g/10min) and PP (isotactic, M_w ~340,000) were dissolved in toluene at 90 °C and 110 °C respectively, while PCL (M_w 70,000-90,000) and PEO (M_w 200,000) were dissolved in ethyl acetate at 60 °C. An appropriate amount of
20 crosslinker was then added to the thermoplastic solution and the resulting solution was stirred for 2 min. Thereafter, the solution was transferred to a Teflon dish, followed by drying at under a stream of air at 60 °C for 1 h and in a vacuum oven at 110 °C for 1 h. The temperature of the vacuum oven was then raised to 160 °C for 10 h to enable thermally activated crosslinking.

25

General procedure for gel fraction experiment: The crosslinked network (~30 mg) was weighed (W_a), then soaked in a solvent which can solubilise its linear precursor (20 mL). The mixture was heated to reflux for 2 h. Upon cooling, the sample was removed from the solvent and rinsed with solvent thrice, then dried
30 in a vacuum oven at 80 °C for 2 h. Thereafter, the sample was weighed again (W_b). The gel fraction, which is the measure of the degree of crosslinking in the polymer network can be calculated by the following equation:

$$\text{Gel fraction} = \frac{w_b}{w_a} \times 100\%$$

Three replicates of the gel fraction experiment were performed for each crosslinked polymer.

5 Gel fraction of CANs formed by crosslinking different ratios (in wt%) of dynamic disulfide crosslinker **8** with various thermoplastics, crosslinking different ratios (in wt%) of dynamic imine crosslinker **10** with various thermoplastics, and crosslinking different ratios (in wt%) of dynamic spiroacetal crosslinker **12** with various thermoplastics are shown respectively in FIG. 47, FIG. 48 and FIG. 49.

10 FTIR analysis of a variety of thermoplastics (i.e. LDPE, PP, PCL and PEO) crosslinked with different ratios (in wt%) of dynamic disulfide crosslinker **8** are shown in FIG. 50, FIG. 51, FIG. 52, FIG. 53, FIG. 54 and FIG. 55. Raman analysis of LDPE crosslinked with different ratios (in wt%) of dynamic disulfide crosslinker
15 **8** is shown in FIG. 56.

FTIR analysis of a variety of thermoplastics (i.e. LDPE and PCL) crosslinked with different ratios (in wt%) of dynamic disulfide crosslinker **10** are shown in FIG. 57 and FIG. 58.

20 FTIR analysis of a variety of thermoplastics (i.e. LDPE and PCL) crosslinked with different ratios (in wt%) of dynamic spiroacetal crosslinker **12** are shown in FIG. 59, FIG. 60 and FIG. 61.

25 **Example 15: Thermomechanical and Recyclability Studies of LDPE Crosslinked with 5 wt% Dynamic Disulfide Crosslinker 8 (LDPE-SS-5)**

15.1. Sample Preparation of LDPE Crosslinked with 5 wt% Dynamic Disulfide Crosslinker 8 (LDPE-SS-5)

30 Samples were prepared by using Collin hot press (190 °C, 30 bar, 15 mins) to 1 mm thickness and cut into an ASTM D638 Type V dog-bone shape using a

mold. Mechanical re-processability was conducted by cutting up processed strips, followed by hot pressing the sample under the same conditions, and cutting into dog-bone shape for tensile strength analysis.

- 5 FIG. 62 shows gel fraction of LDPE crosslinked with 5 wt% dynamic disulfide crosslinker **8** before mechanical recycling, after mechanical recycling for 1 cycle, and 5 cycles.

15.2. Dimensional Stability of LDPE-SS-5

- 10 **LDPE-SS-5** and pure LDPE were shaped into ~ 1cm x 1 cm x 1 cm cubes by hot press, then heated to 130 °C on a hot plate. Photographs taken are shown in FIG. 63 and FIG. 64.

15.3. Rheological Analysis of LDPE Crosslinked with 5 wt% Dynamic Disulfide Crosslinker 8 (LDPE-SS-5)

15

LDPE-SS-5 (no catalyst)

- In rheological temperature ramp studies, LDPE-SS-5 exhibited a drop in both Storage (G') and Loss Modulus (G'') at ~110 °C, which is consistent with the
20 T_m of the LDPE backbone observed in DSC. The network was observed reach a rubbery plateau at temperatures above 120°C, due to the crosslinked nature of the material (FIG. 65).

- Stress relaxation studies were performed to determine the relaxation time,
25 i.e. time when material relaxes to 1/e of it's initial modulus. The parameters of the stress relaxation experiments are as follows; (i) axial force maintained at 0.2 N $\pm$ 0.1 N to ensure contact; (ii) 1% strain in 1 s strain rise, (iii) at temperatures between 170 °C and 200 °C. A Maxwell 3-element model is used to fit the curve (FIG. 66).

30

Time-temperature-superposition (TTS) was performed on frequency sweeps at varying temperatures, and the horizontal shift factor ($\ln a_T$) and vertical

shift factor $\ln(1/b_T)$ was plotted against $1000/T$. An Arrhenius fit was obtained for reference temperature, $T_0 = 155\text{ }^\circ\text{C}$, from which we determined the E_a from a_T of the dynamic disulfide bond to be at 186.1 kJ/mol (FIG. 67). E_a from $1/b_T$ related to network dissociation is negligible at 4.4 kJ/mol . The master curve was also
5 obtained based on the TTS analysis (FIG. 68).

LDPE-SS-5-POct₃ (with 10 mol% POct₃ catalyst)

In temperature ramp studies, the vitrimer exhibited a drop in modulus at $\sim 110\text{ }^\circ\text{C}$ and reached a rubbery plateau at temperatures above $120\text{ }^\circ\text{C}$, which is
10 similar to the behaviour of the uncatalyzed sample. However, the plateau is sloping down, indicative of dissociative CAN behaviour (FIG. 69).

Stress relaxation studies were performed to determine the relaxation time, The parameters of the stress relaxation experiments are as follows; (i) axial force
15 maintained at $0.2\text{ N} \pm 0.1\text{ N}$ to ensure contact; (ii) 1% strain in 1 s strain rise, (iii) at temperatures between $120\text{ }^\circ\text{C}$ and $150\text{ }^\circ\text{C}$. A Maxwell 2-element model is used to fit the curve (FIG. 70). The time required for stress relaxation of this sample with catalyst is significantly faster than that of the uncatalyzed sample.

20 Time-temperature-superposition (TTS) was performed on frequency sweeps and the horizontal shift factor (a_T) and vertical shift factor $\ln(1/b_T)$ was plotted against Temperature. Arrhenius fit was obtained for reference temperature, $T_0 = 155\text{ }^\circ\text{C}$. From the Arrhenius fit, we can determine the E_a from a_T of the catalysed disulfide bond to be at 122.4 kJ/mol (FIG. 67). As expected,
25 the E_a of the catalysed disulfide bond was lower than the uncatalysed bond. E_a from $1/b_T$ related to network dissociation is 35.6 kJ/mol (FIG. 71). The master curve was also obtained based on the TTS analysis (FIG. 72).

15.4. Chemical Recycling of LDPE Crosslinked with 5 wt% Dynamic Disulfide Crosslinker 8 (LDPE-SS-5)

Experimental procedure

5 To a RBF with stirrer bar was added **LDPE-SS-5** polymer sample (500 mg), trioctylphosphine (0.09 mL), toluene (100 mL). The mixture was then stirred and heated at 80 °C for 10 minutes. Dimethyl disulfide (2.5 mL) was added to the RBF and the mixture was stirred at 80 °C for 96 hours. The mixture was reprecipitated in a 50 mL centrifuge tube containing ethanol (30 mL). The
10 uncrosslinked product was obtained as the filtrate after centrifugation three times at 12000 rpm for 10 minutes, replacing the ethanol after each centrifugation. Thereafter, the uncrosslinked product was transferred to a Teflon dish, followed by drying under a stream of air at 90 °C for 1 h and in a vacuum oven at 110 °C for 1 h. The temperature of the vacuum oven was then raised to 160 °C for 16 h
15 to enable thermally activated crosslinking, obtaining the recrosslinked product.

Gel fraction

FIG. 73 shows gel fraction of LDPE crosslinked with 5 wt% dynamic disulfide crosslinker **8** before chemical recycling, after uncrosslinking step and
20 after recrosslinking step.

15.5. Tensile Testing of LDPE Crosslinked with 5 wt% Dynamic Disulfide Crosslinker 8 (LDPE-SS-5): Virgin, mechanical recycling and chemical recycling

25 FIG. 74 shows ultimate tensile strength and toughness (left axis) and elongation at break and Young's modulus (right axis) of pure LDPE, virgin **LDPE-SS-5**, and **LDPE-SS-5** after mechanical recycling (MR 1, 3, and 5 cycles) and after chemical recycling (CR).

Example 16: Thermomechanical and Recyclability Studies of Upcycled PP-LDPE Blend Crosslinked with 5 wt% Dynamic Disulfide Crosslinker 8 (PP-LDPE-SS-5)

5 **16.1. Sample Preparation of PP-LDPE Crosslinked with 5 wt% Dynamic Disulfide Crosslinker 8 (PP-LDPE-SS-5)**

Crosslinking method using post-consumer plastics

LDPE foam and PP container were dissolved separately in toluene at 90
10 °C and 110 °C respectively, followed by combining the solutions giving a LDPE:PP blend (70:30 wt%). An appropriate amount of crosslinker was then added to the thermoplastic solution and the resulting solution was stirred for 2 min. Thereafter, the solution was transferred to a Teflon dish, followed by drying at under a stream of air at 60 °C for 1 h and in a vacuum oven at 110 °C for 1 h.
15 The temperature of the vacuum oven was then raised to 160 °C for 10 h to enable thermally activated crosslinking.

Tensile sample preparation

Samples were prepared by using Collin hot press (190 °C, 30 bar, 30 mins)
20 to 1 mm thickness and cut into an ASTM D638 Type V dog-bone shape using a mold. Mechanical re-processability was conducted by cutting up processed strips, followed by hot pressing the sample under the same conditions, and cutting into dog-bone shape for tensile strength analysis.

25 **PP-LDPE blend only**

LDPE foam and PP container were dissolved separately in toluene at 90
°C and 110 °C respectively, followed by combining the solutions giving a LDPE:PP blend (70:30 wt%). Thereafter, the solution was transferred to a Teflon dish, followed by drying under a stream of air at 60 °C for 1 h and in a vacuum
30 oven at 110 °C for 1 h, obtaining the PP-LDPE blend.

Tensile samples were prepared by using Collin hot press (190 °C, 15 bar, 20 mins) to 1 mm thickness and cut into an ASTM D638 Type V dog-bone shape using a mold.

5 **Gel fraction**

FIG. 75 shows gel fraction of **PP-LDPE-SS-5** before mechanical recycling, and after mechanical recycling for 1 cycle.

Tensile Testing of PP-LDPE blend and PP-LDPE-SS-5

10 FIG. 76 shows ultimate tensile strength, elongation at break and toughness (left axis) and Young's modulus (right axis) of PP-LDPE (3:7) blend and **PP-LDPE-SS-5**.

Example 17: Chemical Recycling of LDPE Crosslinked with 5 wt% Dynamic Spiroacetal Crosslinker 12 (LDPE-Acetal-5)

15

17.1. Experimental procedure

To a RBF with stirrer bar was added **LDPE-Acetal-5** polymer sample (200 mg), p-TsOH (2 mg), ethanol (0.7 mL), toluene (10 mL). The mixture was then
20 stirred and heated at 95 °C for 24 hours. The uncrosslinked product was transferred to a Teflon dish, followed by drying under a stream of air at 110 °C for 1 h and in a vacuum oven at 110 °C for 1 h. The uncrosslinked product was pressed using Collin hot press (120 °C, 10 bar, 20 mins) to 1 mm thickness to obtain the hot-pressed sample. The hot-pressed sample was then heated in a
25 vacuum oven at 160 °C for 16 h to enable thermally activated crosslinking, obtaining the recrosslinked product.

17.2. Gel fraction

FIG. 77 shows gel fraction of LDPE crosslinked with 5 wt% dynamic spiroacetal crosslinker **12** before chemical recycling, after uncrosslinking step,
30 after hot-pressing step, and after recrosslinking step.

17.3. Tensile testing

Samples were prepared by cutting into an ASTM D638 Type V dog-bone shape using a mold. FIG. 78 shows ultimate tensile strength and toughness (left axis) and elongation at break and Young's modulus (right axis) of pure LDPE and

5 **LDPE-Acetal-5** after chemical recycling (CR 1 and 2 cycles).

Example 18: General Experimental Details

Materials: Unless otherwise stated, all commercially available reagents and
10 solvents were used as received. 2,3,4,5,6-pentafluorobenzoyl chloride and sodium azide were purchased from TCI Chemicals. 2-Hydroxyethyl disulfide (380474-50ml) was purchased from Sigma-Aldrich. Triethylamine was purchased from TCI, distilled and stored over KOH under an argon (Ar) atmosphere. Anhydrous methanol, tetrahydrofuran (THF) and dichloromethane (DCM) were
15 purchased from Acros Organics. Anhydrous dimethyl sulfoxide (DMSO) was purchased from Kanto Chemical Co. Inc. Diethyl ether ($\geq 99.5\%$) was purchased from Fisher Scientific, ethyl acetate was purchased from J.T. Baker Chemical Company, and toluene was purchased from Aik Moh Paints & Chemicals.

20 Unless otherwise stated, all reactions were carried out in oven-dried glassware under Ar atmosphere with anhydrous reaction solvents using standard Schlenk techniques.

Low density polyethylene (LDPE, Melt Index 25g/10min (190°C/2.16kg), 428043-
25 1kg), polypropylene (PP, isotactic, $M_w \sim 340,000$, average $M_n \sim 97,000$, 427861-1kg), polycaprolactone (PCL, M_w 70,000-90,000, 440744-500G) and poly(ethylene oxide) (PEO, average M_w 200,000, 191944-250G) were purchased from Sigma-Aldrich.

30 *Nuclear Magnetic Resonance Spectroscopy:* ^1H NMR spectra were recorded on a JEOL ECA-II 500 (500 MHz) or a JEOL ECZL 400 (400 MHz) and were referenced to residual non-deuterated solvent peaks in CDCl_3 ($d_H = 7.26$), CD_3CN

($d_H = 7.16$) or $(CD_3)_2CO$ ($d_H = 2.05$). Data are reported as follows: chemical shifts (d_H , reported in ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (J , reported to the nearest 0.1 Hz). $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL ECA-II 500 (126
5 MHz) or a JEOL ECZL 400 (100 MHz) and were referenced to residual non-deuterated solvent peaks in $CDCl_3$ ($d_C = 77.16$) or $(CD_3)_2CO$ ($d_C = 206.26$ or 29.84). Chemical shifts (d_C) are reported in ppm. ^{19}F NMR spectra were recorded on a JEOL ECA-II 500 (470 MHz) or a JEOL ECZL 400 (376 MHz) and were referenced with the residual non-deuterated solvent peaks 1H resonance.
10 Chemical shifts (d_F) are reported in ppm.

Chromatography: Flash column chromatography (FCC) refers to normal phase column chromatography[1] on Merck silica gel type 9385 230-400 mesh or Macherey-Nagel Silica 60 M (40-63 μm). Thin layer chromatography (TLC) was
15 performed on Merck silica gel 60, 0.25 mm with visualization by UV and/or phosphomolybdic acid, potassium permanganate or ninhydrin staining.

Fourier-transform infrared spectroscopy: FTIR spectra were recorded on a Bruker Vertex 80v FTIR spectrometer. Absorption maxima (λ_{max}) are quoted in
20 wavenumbers (cm^{-1}).

Thermogravimetric analysis: TGA was performed on a TA Instruments Q500. For the polymeric samples, ~10 mg was placed into an alumina pan and heated from 40 to 600 $^{\circ}C$ with a ramp rate of 20 $^{\circ}C/min$ in nitrogen at a flow rate of 60 mL/min.
25

Differential scanning calorimetry: DSC was performed on a TA Instruments Q100 calorimeter. About 10 mg of sample was placed into an aluminum hermetic pan. The first heating scan was performed to erase any thermal history, followed by isothermal for 2 min, cooling to $-80^{\circ}C$, and subsequent heating (second heating
30 scan). The heating and cooling rate for the scans was 10 $^{\circ}C/min$ under a nitrogen flow of 50 mL/min.

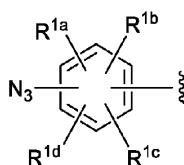
Rheology: Rheological analysis was performed on TA Instruments Rotational Rheometer DHR-3 equipped with an 8 mm parallel plate on samples of 8 mm diameter with thickness ranging between 900-2000 μm . Temperature ramp was performed from room temperature to 200 °C with the following parameters: (i) 1% strain, (ii) 1 Hz, (iii) at ramp rate of 10.0°C/min.

Tensile measurements: Tensile testing was conducted on ASTM D638 Type V dog bone-shaped specimens (~ 1 mm thickness) using an Instron 5569 Double Column Universal Tester apparatus in film tension geometry, applying a grip pressure of 4 bar, utilizing a 100N Instron static load cell. The experiments performed at room temperature included an average measurement derived from three out of the five samples tested for each trial. For the disulfide crosslinked samples, a strain rate of 10 mm/min.

It will be appreciated by a person skilled in the art that other variations and/or modifications may be made to the embodiments disclosed herein without departing from the spirit or scope of the disclosure as broadly described. For example, in the description herein, features of different exemplary embodiments may be mixed, combined, interchanged, incorporated, adopted, modified, included etc. or the like across different exemplary embodiments. The present embodiments are, therefore, to be considered in all respects to be illustrative and not restrictive.

CLAIMS

1. A dynamic crosslinker comprising at least two aryl azide groups coupled together *via* one or more dynamic covalent moiety, wherein the dynamic covalent moiety comprises one or more dynamic covalent bonds that reversibly exchange, break and/or form under suitable conditions.
2. The dynamic crosslinker of claim 1, wherein each aryl azide group independently comprises a structure represented by general formula (1):



(1)

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wherein

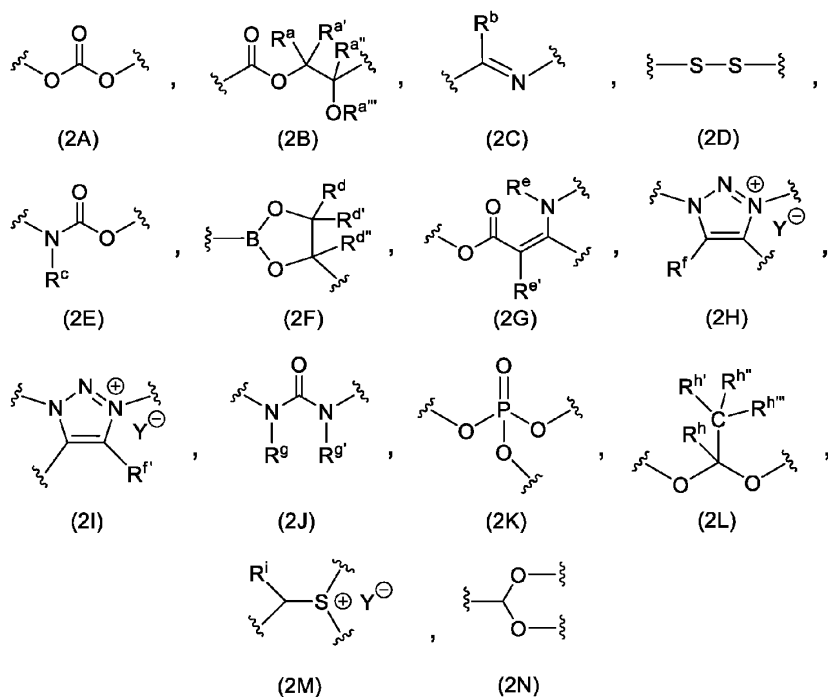
R^{1a} , R^{1b} , R^{1c} and R^{1d} are each independently halogen, hydrogen, hydroxyl, carboxyl, amine, amide, ester, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted oxycarbonylalkyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carboxylalkyl, optionally substituted alkylcarboxylalkyl, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkynyl, or combinations thereof.

20

3. The dynamic crosslinker of any one of the preceding claims, wherein the dynamic covalent moiety comprises a structure selected from the group consisting of general formula (2A), (2B), (2C), (2D), (2E), (2F), (2G), (2H), (2I), (2J), (2K), (2L), (2M), (2N), and combinations thereof:

25

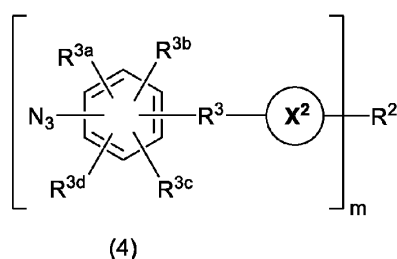
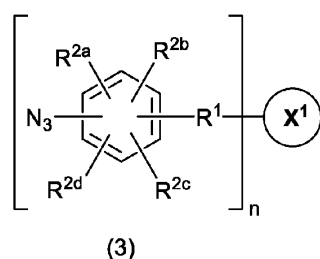
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- 5 wherein
- R^a , $R^{a'}$, $R^{a''}$, $R^{a'''}$, R^b , R^c , R^d , $R^{d'}$, $R^{d''}$, R^e , $R^{e'}$, R^f , $R^{f'}$, R^g , $R^{g'}$, R^h , $R^{h'}$, $R^{h''}$, $R^{h'''}$, R^i , R^j , $R^{j'}$ and $R^{j''}$ are each independently hydrogen, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof.
- 10
4. The dynamic crosslinker of any one of the preceding claims, wherein each aryl azide group is coupled to a dynamic covalent moiety *via* a linker.
- 15
5. The dynamic crosslinker of any one of the preceding claims, wherein each dynamic covalent moiety is coupled to another dynamic covalent moiety *via* a linker.

6. The dynamic crosslinker of claim 4 or claim 5, wherein the linker comprises an organic group selected from carbonyl-containing group, carbonyloxy-containing group, ester-containing group, amide-containing group, carbamate-containing group, amine-containing group, thiol-containing group, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted alkylcarbonyloxy, optionally substituted oxycarbonylalkyl, optionally substituted alkyloxycarbonyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carbonylaryl, optionally substituted arylcarbonylalkyl, optionally substituted alkylcarbonylaryl, optionally substituted arylcarbonylaryl, optionally substituted carbonyloxyaryl, optionally substituted arylcarbonyloxy, optionally substituted oxycarbonylaryl, optionally substituted aryloxycarbonyl, optionally substituted arylcarbonyloxyalkyl, optionally substituted alkylcarbonyloxyaryl, optionally substituted arylcarbonyloxyaryl, optionally substituted aryloxycarbonylalkyl, optionally substituted alkyloxycarbonylaryl, optionally substituted aryloxycarbonylaryl, optionally substituted arylester, optionally substituted alkylester, optionally substituted arylamide, optionally substituted alkylamide, optionally substituted arylcarbamate, optionally substituted alkylcarbamate, optionally substituted arylamine, optionally substituted alkylamine, optionally substituted thioaryl, optionally substituted thioalkyl, optionally substituted alkoxy, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof.

7. The dynamic crosslinker of any one of the preceding claims, wherein the one or more dynamic covalent bonds are configured to reversibly break and/or form under application of one or more of the following stimuli:
- (i) temperature that is from 20 °C to 300 °C;
 - (ii) pressure that is from 0.1 MPa to 100 MPa;
 - (iii) in the presence of a reactive chemical; and
 - (iv) UV radiation.
8. The dynamic crosslinker of claim 7, wherein the reactive chemical comprises alcohol, acid, base, reducing agent, oxidizing agent, dimethyl disulfide, dithiothreitol, or combinations thereof.
9. The dynamic crosslinker of any one of the preceding claims, wherein the crosslinker comprises a structure selected from general formula (3), general formula (4), or combinations thereof:



wherein

each of X^1 and X^2 is independently a dynamic covalent moiety;

- each of R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} and R^{3d} is independently halogen, hydrogen, hydroxyl, carboxyl, amine, amide, ester, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted oxycarbonylalkyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carboxylalkyl, optionally substituted alkylcarboxylalkyl, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkynyl, or combinations thereof;

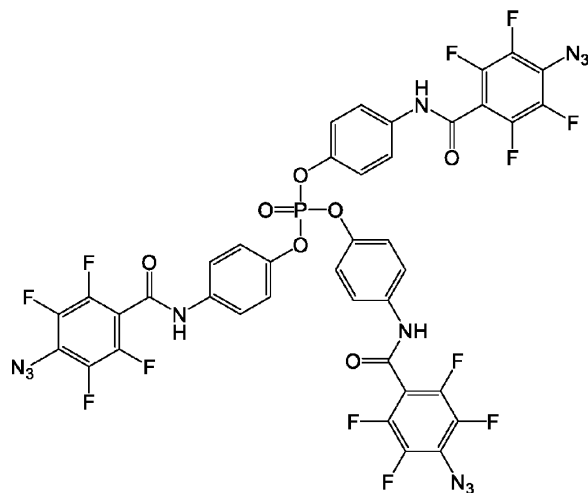
each of R¹, R² and R³ is optionally present as a linker selected from carbonyl-containing group, carbonyloxy-containing group, ester-containing group, amide-containing group, carbamate-containing group, amine-containing group, thiol-containing group, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted alkylcarbonyloxy, optionally substituted oxycarbonylalkyl, optionally substituted alkyloxycarbonyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carbonylaryl, optionally substituted arylcarbonylalkyl, optionally substituted alkylcarbonylaryl, optionally substituted arylcarbonylaryl, optionally substituted carbonyloxyaryl, optionally substituted arylcarbonyloxy, optionally substituted oxycarbonylaryl, optionally substituted aryloxycarbonyl, optionally substituted arylcarbonyloxyalkyl, optionally substituted alkylcarbonyloxyaryl, optionally substituted arylcarbonyloxyaryl, optionally substituted aryloxycarbonylalkyl, optionally substituted alkyloxycarbonylaryl, optionally substituted aryloxycarbonylaryl, optionally substituted arylester, optionally substituted alkylester, optionally substituted arylamide, optionally substituted alkylamide, optionally substituted arylcarbamate, optionally substituted alkylcarbamate, optionally substituted arylamine, optionally substituted alkylamine, optionally substituted thioaryl, optionally substituted thioalkyl, optionally substituted alkoxy, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof;

$n \geq 2$; and

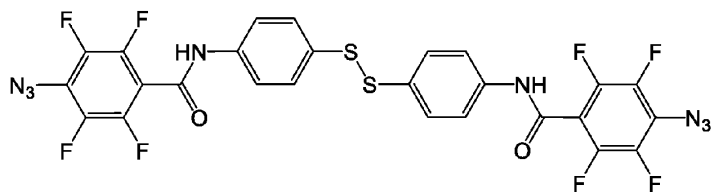
$m \geq 2$.

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10. The dynamic crosslinker of any one of the preceding claims, wherein the crosslinker is selected from one of the following:

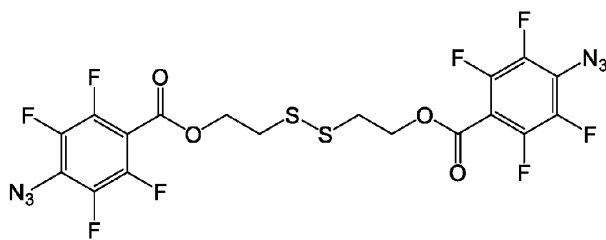


tris(4-(4-azido-2,3,5,6-tetrafluorobenzamido)phenyl) phosphate,



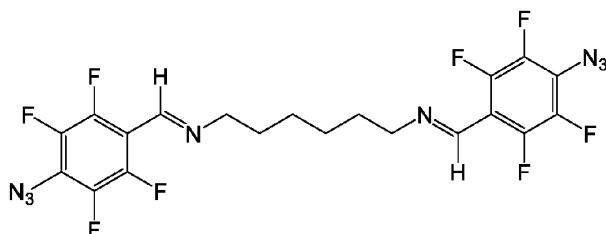
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N,N'-(disulfaneyldi(bis(4,1-phenylene)))bis(4-azido-2,3,5,6-tetrafluorobenzamide),

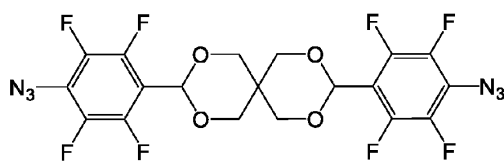


disulfaneyldi(bis(ethane-2,1-diyl) bis(4-azido-2,3,5,6-tetrafluorobenzoate)),

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N,N'-(hexane-1,6-diyl)bis(1-(4-azido-2,3,5,6-tetrafluorophenyl)methanimine),
and



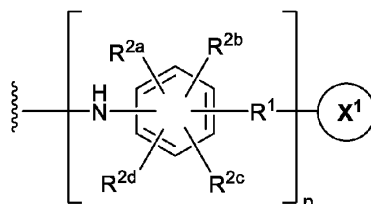
5 3,9-bis(4-azido-2,3,5,6-tetrafluorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane.

11. A method of preparing a dynamic crosslinker as claimed in any one of the preceding claims, the method comprising:
 - (a) coupling at least two aryl azide groups *via* one or more dynamic covalent moieties.
12. A method of preparing a covalent adaptable network (CAN), the method comprising:
 - (b-i) crosslinking a polymer with a dynamic crosslinker as claimed in any one of claims 1 to 10 to obtain a crosslinked polymer.
13. The method of claim 12, wherein the method further comprises:
 - (b-ii) adding a catalyst before, during and/or after step (b-i).
14. The method of claim 13, wherein the catalyst comprises 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), trioctylphosphine, 1,1,3,3-tetramethylguanidine, 1,8-diazabicyclo[5.4.0]undec-7-ene, 2-methylimidazole, 1-methylimidazole, 4-dimethylaminopyridine, zinc

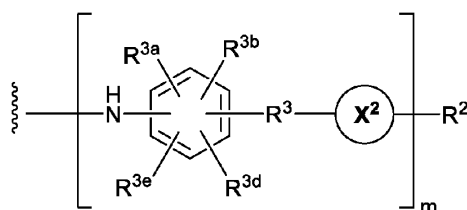
acetate, dibutyltin dilaurate, scandium(III) triflate, trifluoroacetic acid, or combinations thereof.

15. The method of any one of claims 13 to 14, wherein the method comprises
5 adding from 0.001 wt% to 25 wt% of the catalyst.
16. The method of any one of claims 12 to 15, wherein the method comprises adding from 0.01 wt% to 30 wt% of the dynamic crosslinker.
- 10 17. The method of any one of claims 12 to 16, wherein the polymer is selected from polycaprolactone (PCL), poly(ethylene-co-vinyl acetate) (PEVA), polystyrene-block-polybutadiene-block-polystyrene (PSBS), poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), polyethylene, low density polyethylene (LDPE), high density polyethylene (HDPE),
15 propylene (PP), PP-LDPE blend, poly(styrene-co-acrylonitrile) (PSAN), ethylene propylene diene monomer (EPDM), polydimethylsiloxane (PDMS), natural rubber, or combinations thereof.
18. The method of any one of claims 12 to 17, wherein the step of crosslinking
20 is carried out under one or more of the following conditions:
(i) temperature that is from 120 °C to 230 °C; and
(ii) UV radiation.
19. A covalent adaptable network (CAN) comprising polymer chains coupled
25 to the dynamic crosslinker as claimed in any one of claims 1 to 10 via dynamic crosslinks.

20. The CAN of claim 19, wherein the dynamic crosslink comprises a structure selected from general formula (5), general formula (6) or combinations thereof:



(5)



(6)

5

wherein

each of $\mathbf{X}^1$ and $\mathbf{X}^2$ is independently a dynamic covalent moiety;

each of R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} and R^{3d} is independently halogen, hydrogen, hydroxyl, carboxyl, amine, amide, ester, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally substituted carbonyloxyalkyl, optionally substituted oxycarbonylalkyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carboxylalkyl, optionally substituted alkylcarboxylalkyl, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkynyl, or combinations thereof;

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each of R^1 , R^2 and R^3 is optionally present as a linker selected from carbonyl-containing group, carbonyloxy-containing group, ester-containing group, amide-containing group, carbamate-containing group, amine-containing group, thiol-containing group, optionally substituted carbonylalkyl, optionally substituted alkylcarbonylalkyl, optionally

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substituted carbonyloxyalkyl, optionally substituted alkylcarbonyloxy, optionally substituted oxycarbonylalkyl, optionally substituted alkyloxycarbonyl, optionally substituted alkylcarbonyloxyalkyl, optionally substituted alkyloxycarbonylalkyl, optionally substituted carbonylaryl, optionally substituted arylcarbonylalkyl, optionally substituted alkylcarbonylaryl, optionally substituted arylcarbonylaryl, optionally substituted carbonyloxyaryl, optionally substituted arylcarbonyloxy, optionally substituted oxycarbonylaryl, optionally substituted aryloxycarbonyl, optionally substituted arylcarbonyloxyalkyl, optionally substituted alkylcarbonyloxyaryl, optionally substituted arylcarbonyloxyaryl, optionally substituted aryloxycarbonylalkyl, optionally substituted alkyloxycarbonylaryl, optionally substituted aryloxycarbonylaryl, optionally substituted aryloxyester, optionally substituted alkylester, optionally substituted arylamide, optionally substituted alkylamide, optionally substituted arylcarbamate, optionally substituted alkylcarbamate, optionally substituted arylamine, optionally substituted alkylamine, optionally substituted thioaryl, optionally substituted thioalkyl, optionally substituted alkoxy, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heterocycloalkyl, optionally substituted heterocycloalkenyl, optionally substituted heteroaryl, or combinations thereof;

$n \geq 2$; and

$m \geq 2$.

21. The CAN of any one of claims 19 to 20, wherein the dynamic crosslinks are exchangeable/cleavable and/or the one or more dynamic covalent bonds are configured to reversibly break and/or form upon application of a stimulus.

22. The CAN of claim 21, wherein the dynamic crosslinks are exchangeable/cleavable and/or the one or more dynamic covalent bonds are configured to reversibly break and/or form upon application of one or more of the following stimuli:
- 5 (i) temperature that is from 20 °C to 300 °C;
(ii) pressure that is from 0.1 MPa to 50 MPa;
(iii) in the presence of a reactive chemical; and
(iv) UV radiation.
- 10 23. The CAN of claim 22, wherein the reactive chemical comprises alcohol, acid, base, reducing agent, oxidizing agent, dimethyl disulfide, dithiothreitol, or combinations thereof.
24. The CAN of any one of claims 19 to 23, wherein the covalent adaptable
15 network has a gel fraction from 30% to 100%.
25. A method of recycling a covalent adaptable network (CAN) of any one of claims 19 to 24, the method comprising:
- 20 (c-i) providing a covalent adaptable network (CAN) of any one of claims 19 to 24; and
(c-ii) applying a stimulus to the CAN to reversibly exchange /cleave the dynamic crosslinks and/or reversibly break and/or form one or more dynamic covalent bonds in the CAN.