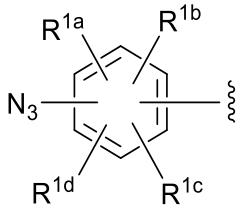
CLAIMS

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,

optionally wherein each aryl azide group independently comprises a structure represented by general formula (1):

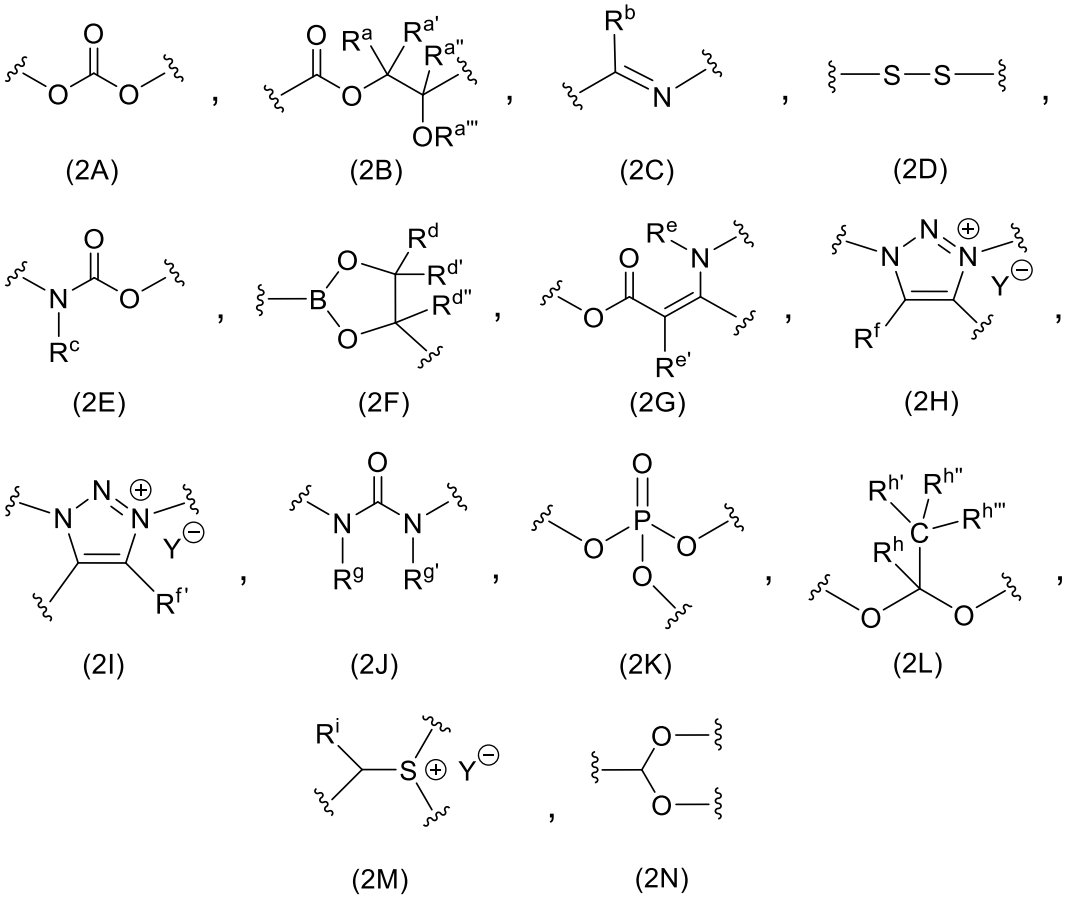


(1)

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.

2. The dynamic crosslinker of claim 1, 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:



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.

3. 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,

optionally 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.

4. 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,

optionally 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.

5. 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;

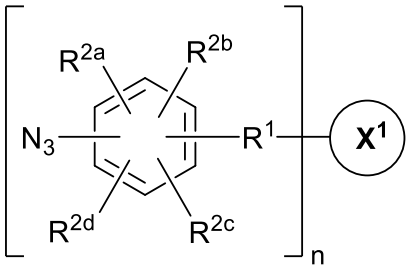
(ii) pressure that is from 0.1 MPa to 100 MPa;

(iii) in the presence of a reactive chemical, optionally wherein the reactive chemical comprises alcohol, acid, base, reducing agent,

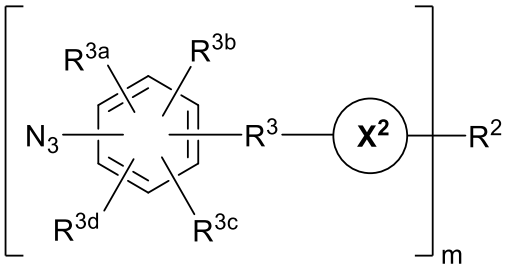
oxidizing agent, dimethyl disulfide, dithiothreitol, or combinations thereof; and

(iv) UV radiation.

6. 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:



(3)



(4)

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 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;

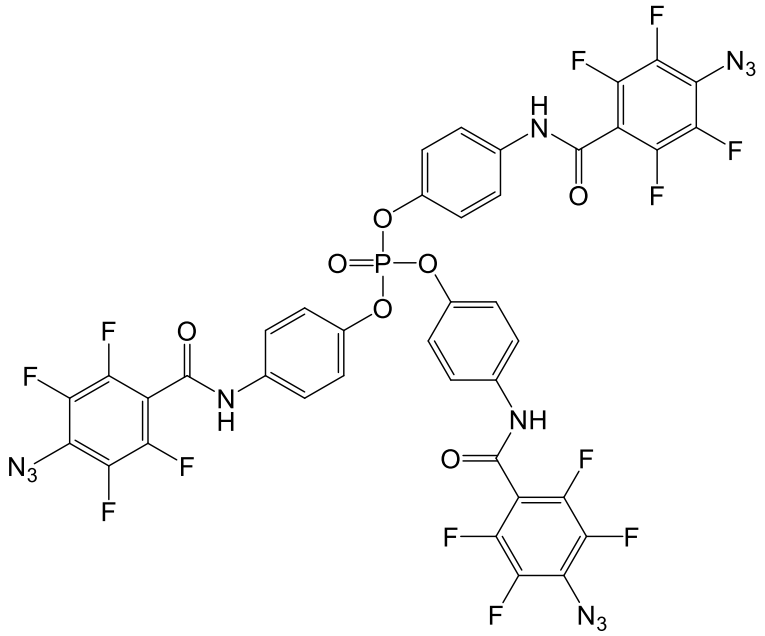
each of R^1, R^2 and R^3 is optionally present as a linker selected from carbonyl-containing group, carbonyloxy-containing group, ester-containing group, amide-containing group, carbamate-containing group, amine-containing group, thiol-containing group, optionally substituted carbonylalkyl, optionally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

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;

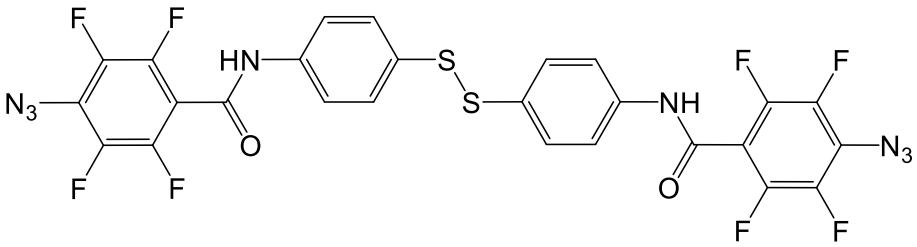
$n \geq 2$; and

$m \geq 2$.

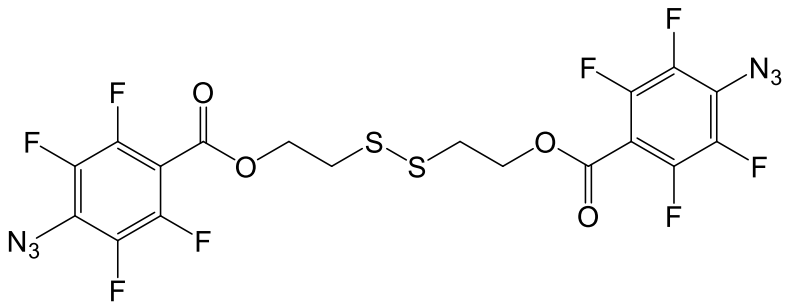
7. The dynamic crosslinker of any one of the preceding claims, wherein the crosslinker is selected from one of the following:



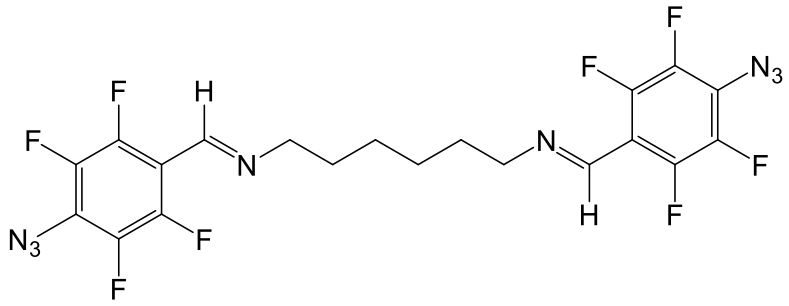
tris(4-(4-azido-2,3,5,6-tetrafluorobenzamido)phenyl) phosphate,



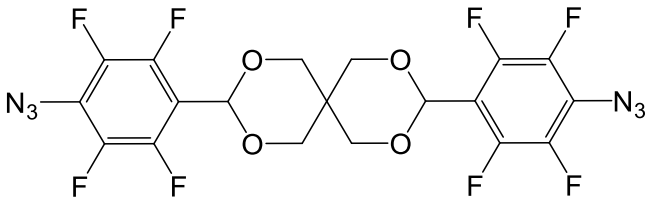
N,N'-(disulfanediylbis(4,1-phenylene))bis(4-azido-2,3,5,6-tetrafluorobenzamide),



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.

8. 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.

9. 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 7 to obtain a crosslinked polymer,

optionally 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), propylene (PP), PP-LDPE blend, poly(styrene-co-acrylonitrile) (PSAN), ethylene propylene diene monomer (EPDM), polydimethylsiloxane (PDMS), natural rubber, or combinations thereof.

10. The method of claim 9, wherein the method further comprises:

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

optionally 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.

11. The method of any one of claims 9 to 10, wherein the method comprises adding from 0.001 wt% to 25 wt% of the catalyst;

and/or the method comprises adding from 0.01 wt% to 30 wt% of the dynamic crosslinker;

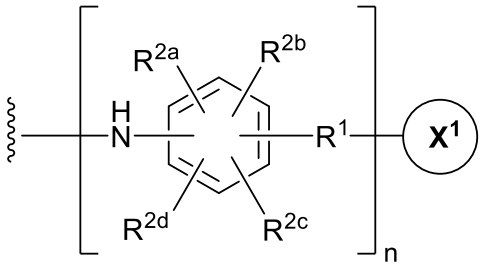
and/or the crosslinking is carried out under one or more of the following conditions:

(i) temperature that is from 120 °C to 230 °C; and

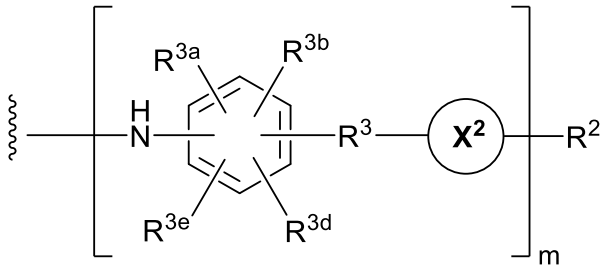
(ii) UV radiation.

12. A covalent adaptable network (CAN) comprising polymer chains coupled to the dynamic crosslinker as claimed in any one of claims 1 to 7 *via* dynamic crosslinks,

optionally wherein the dynamic crosslink comprises a structure selected from general formula (5), general formula (6) or combinations thereof:



(5)



(6)

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 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 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 ≥ 2; and

m ≥ 2.

13. The CAN of claim 12, 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,

optionally wherein the stimulus is selected from one or more of the following:

(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, optionally wherein the reactive chemical comprises alcohol, acid, base, reducing agent, oxidizing agent, dimethyl disulfide. dithiothreitol, or combinations thereof; and

(iv) UV radiation.

14. The CAN of any one of claims 12 to 13, wherein the covalent adaptable network has a gel fraction from 30% to 100%.

15. A method of recycling a covalent adaptable network (CAN) of any one of claims 12 to 14, the method comprising:

(c-i) providing a covalent adaptable network (CAN) of any one of claims 12 to 14; 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.