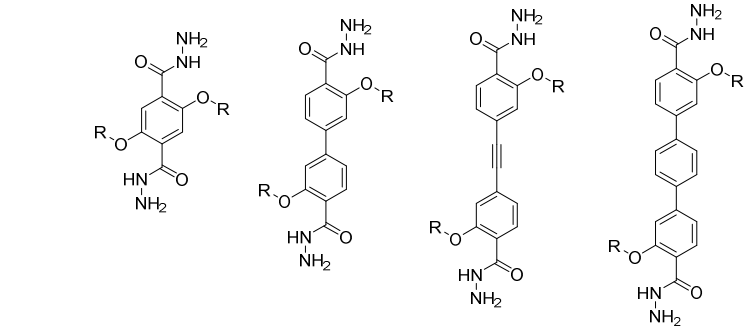
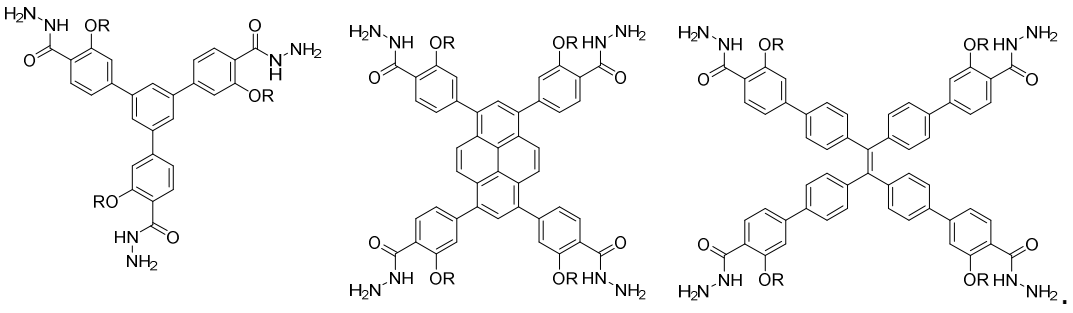
Claims

1. A method of fabricating a covalent organic framework (COF), comprising: stirring a first monomer comprising an optionally substituted 2-alkoxybenzohydrazidyl moiety or optionally substituted 2-benzyloxybenzohydrazidyl moiety with second monomer comprising a benzaldehydyl moiety under heat and in open air for at least 15 min in order to form an acylhydrazone bond;
wherein the COF is formable after about 15 min; and
wherein the optionally substituted 2-alkoxybenzohydrazidyl moiety is selected from optionally substituted 2-(C_1–C_6)alkoxybenzohydrazidyl.

2. The method according to claim 1, wherein the optionally substituted 2-alkoxybenzohydrazidyl moiety is optionally substituted 2-(C_3)alkoxybenzohydrazidyl.

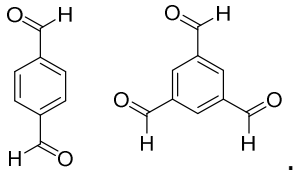
3. The method according to claim 1 or 2, wherein the first monomer is selected from one of the following:





4. The method according to any one of claims 1 to 3, wherein the optionally substituted 2-alkoxybenzohydrazidyl moiety is 2-propoxybenzohydrazidyl, 2-allyloxybenzohydrazidyl, 2-propargyloxybenzohydrazidyl.

5. The method according to any one of claims 1 to 4, wherein the second monomer is selected from:



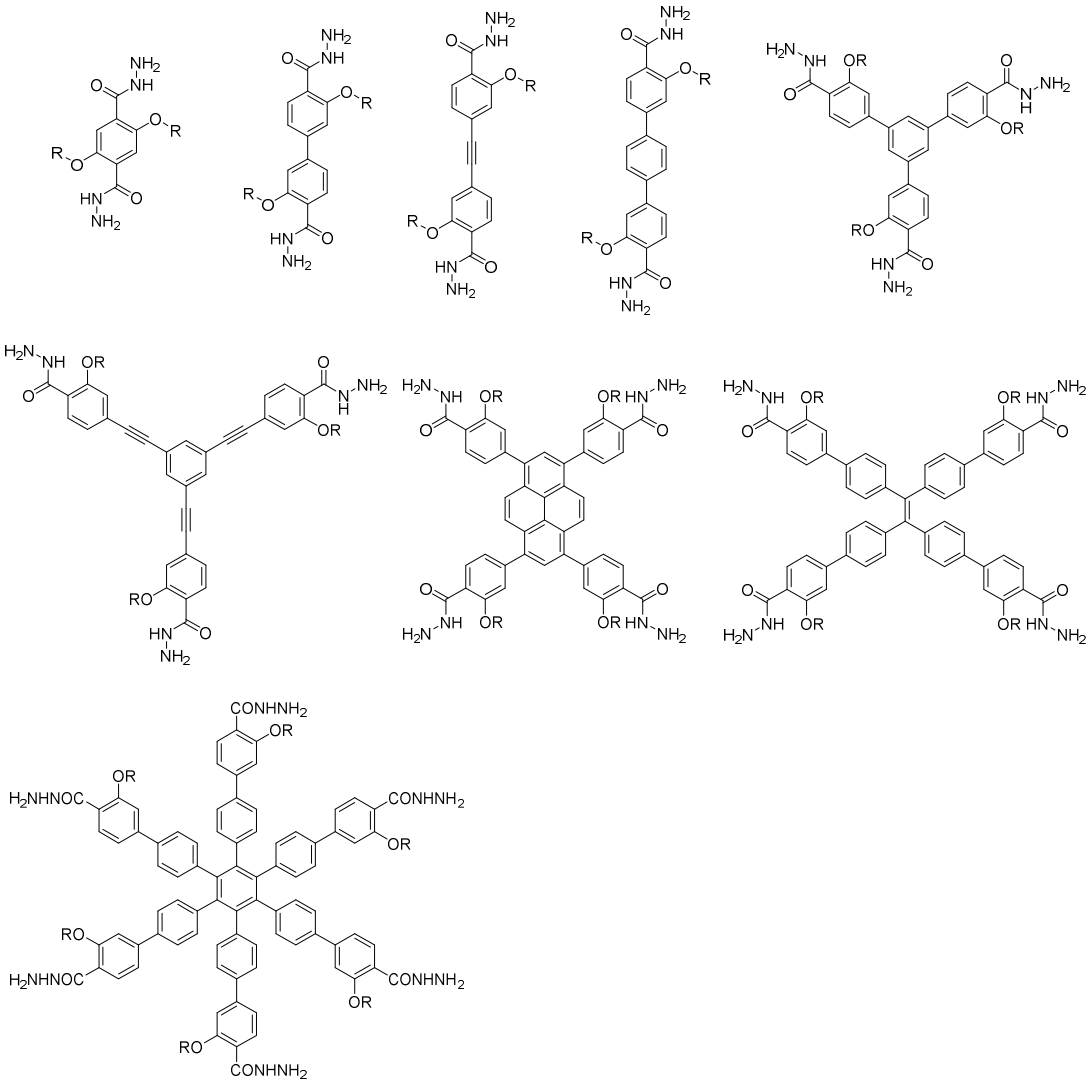
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6. The method according to any one of claims 1 to 5, wherein the stirring is performed under heat at not less than 100 °C.

7. The method according to any one of claims 1 to 6, wherein stirring is performed in the presence of 17M acetic acid at about 1:50 ($V/V_{solvent}$).

8. A method of fabricating a covalent organic framework (COF), comprising:
stirring a first monomer comprising an optionally substituted 2-alkoxybenzohydrazidyl moiety, optionally substituted 2-benzyloxybenzohydrazidyl moiety or 2-(ethylthio)propoxybenzohydrazidyl moiety with second monomer comprising a benzaldehydyl moiety under heat and in open air for at least 15 min in order to form an acylhydrazone bond;
wherein the COF is formable after about 15 min;
wherein the first monomer and the second monomer has a total topicity of at least 5;
wherein the first monomer and the second monomer both independently have a conjugated pi bond system; and
wherein the optionally substituted 2-alkoxybenzohydrazidyl moiety is selected from optionally substituted 2-(C_1–C_6)alkoxybenzohydrazidyl.

9. The method according to claim 8, wherein first monomer is selected from one of the following:

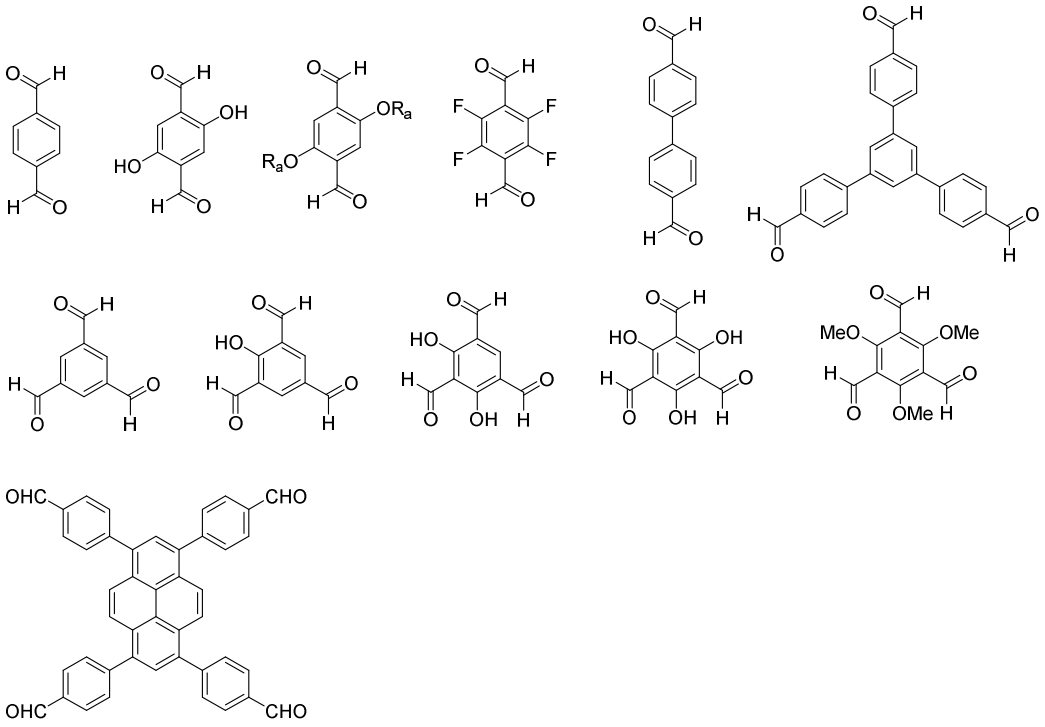


;

wherein R is optionally substituted (C_3–C_6)alkyl or optionally substituted benzyl.

10. The method according to claim 8 or 9, wherein the optionally substituted 2-alkoxybenzohydrazidyl moiety is selected from 2-propoxybenzohydrazidyl, 2-allyloxybenzohydrazidyl, and 2-propargyloxybenzohydrazidyl.

11. The method according to any one of claims 8 to 10, wherein the second monomer is selected from:



;

wherein R_a is optionally substituted C_1-C_6 alkyl.

12. The method according to any one of claims 8 to 11, wherein the stirring is performed in the presence of acetic acid from about 1:20 ($V/V_{solvent}$) to about 1:100 ($V/V_{solvent}$).

13. The method according to any one of claims 8 to 12, wherein the stirring is performed in the presence of acetic acid, the acetic acid having a concentration of about 1 M to about 17 M.

14. The method according to any one of claims 8 to 13, wherein the first monomer and the second monomer have a combined concentration of about 15 g L^{-1} to about 60 g L^{-1}.

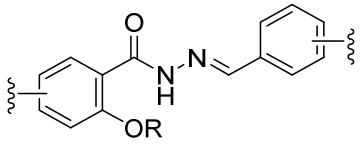
15. The method according to any one of claims 8 to 14, wherein the stirring is performed under heat of about 60 °C to about 200 °C.

16. The method according to any one of claims 8 to 15, wherein the stirring is performed in an aprotic non-polar solvent selected from 1,2-dichlorobenzene or mesitylene.

17. The method according to any one of claims 8 to 16, wherein solvent is added at a hydrazide:solvent mole ratio of about 1:200 to about 1:400.

18. The method according to any one of claims 8 to 17, wherein the stirring is performed in an aromatic solvent selected from toluene, xylenes, mesitylene, mono, di and trichlorobenzene, or a combination thereof, or in a polar protic solvent selected from water, C_1-C_4 alcohols, or a combination thereof, or in a solvent mixture, the solvent mixture selected from mesitylene/1,4-dioxane, ortho-dichlorobenzene (o-DCB)/n-butanol and mesitylene/acetonitrile.

19. A covalent organic framework (COF) comprising an optionally substituted 2-alkoxybenzohydrazonylene moiety of Formula (Ia):



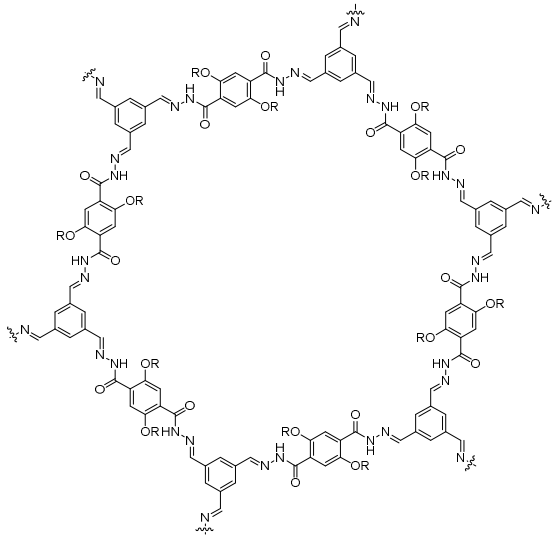
(Ia)

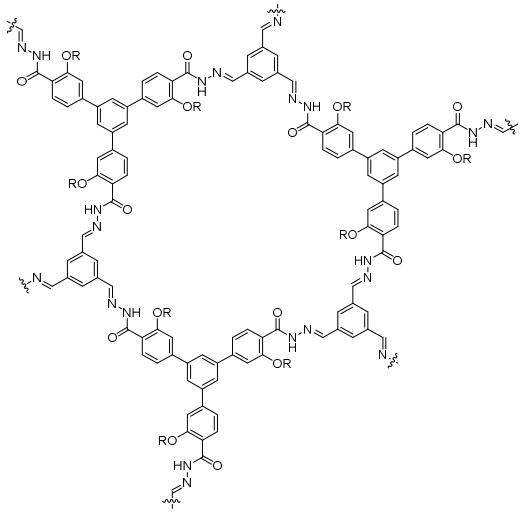
wherein R is optionally substituted (C_1–C_6)alkyl or benzyl; and

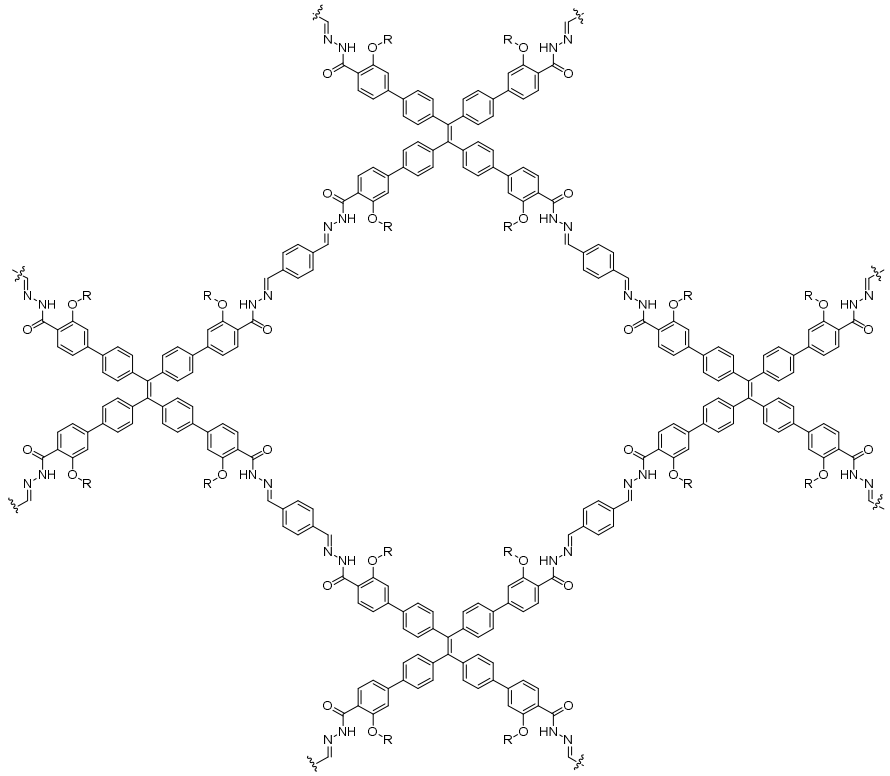
wherein ~ represents a linkage to the rest of the COF; and

wherein the COF has a x-ray diffraction 2-theta peak at about 3° with a full width half maximum (FWHM) of about 0.2° to about 0.4°.

20. The COF according to claim 19, selected from one of the following:

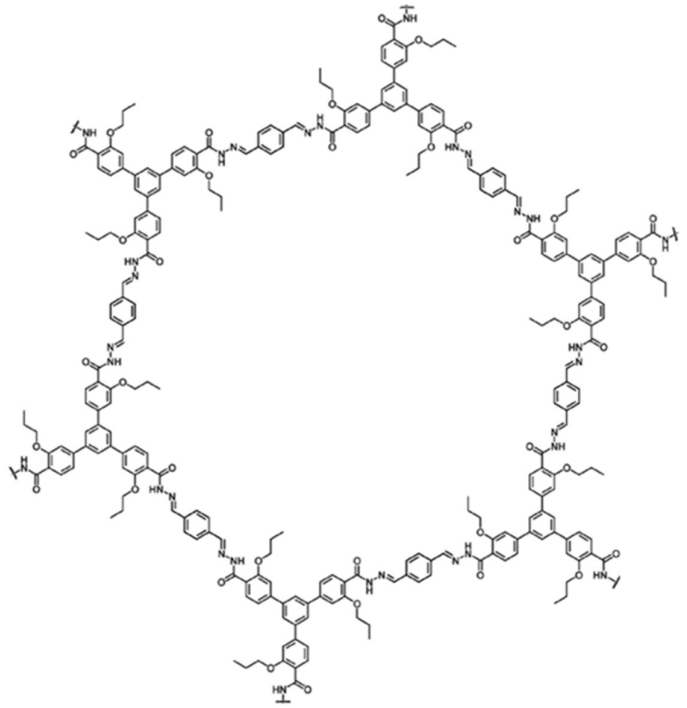






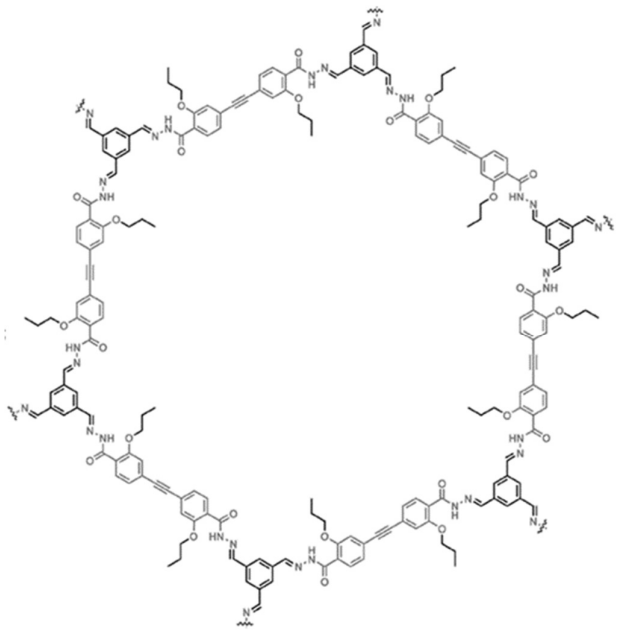
;

wherein R is selected from propyl, allyl, propargyl or benzyl, or



Df-THzOPr

or



Tf-DHzOPrY

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