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High thermal stability, pH responsive organogels of 2*H*-benzo[*d*]1,2,3-triazole derivatives as pharmaceutical crystallization media.

Iván Torres-Moya[a,b], Basanta Saikia[c], Pilar Prieto[b*], José R. Carrillo[b], Jonathan W. Steed[a*]

[a] Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK.

[b] Department of Organic Chemistry. University of Castilla La Mancha, 13071 Ciudad Real, Spain.

[c] Department of Chemical Sciences, Tezpur University, Napaam-784028, Assam, India.

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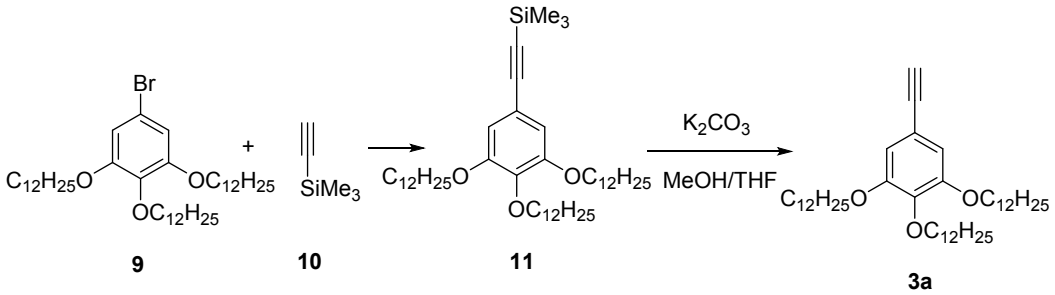
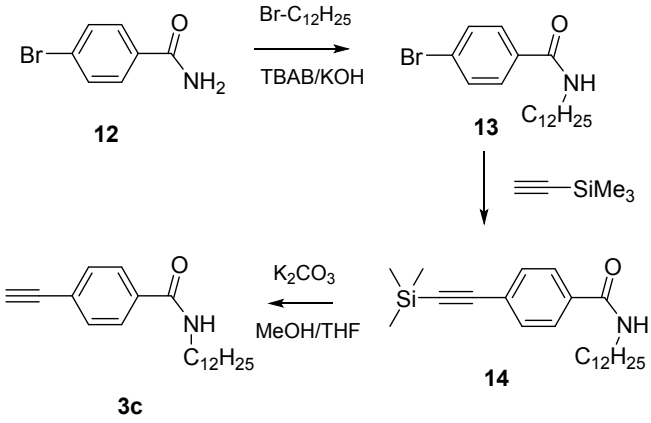
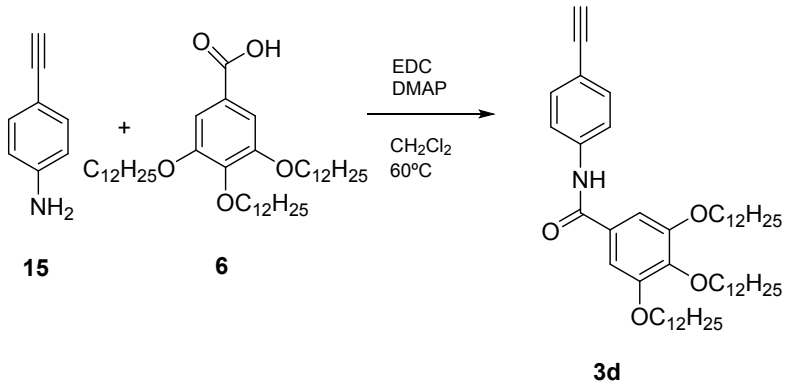


Scheme S1. Synthesis of the alkynyl derivative **3a**.



Scheme S2. Synthesis of the alkynyl derivative **3c**.



Scheme S3. Synthesis of the alkynyl derivative **3d**.

2. Gelation tests

(S= Soluble, I= Insoluble, P= Precipitate, PG= Partial Gel, G= Gel)

Table S1. Gelation test for **4a** at a concentration of 2% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	S	S	S	S	S
Dichloromethane	S	S	S	S	S
Diethyl ether	S	S	S	S	S
Diethylene glycol	S	P	P	P	P
DMSO	S	P	P	P	P
Ethanol	I	I	I	I	I
Hexane	S	S	S	S	S
THF	S	S	S	S	S
1,4-dioxane	S	S	S	S	S
1-butanol	S	S	P	P	P
1-pentanol	S	S	PG	G	G
1-propanol	S	P	P	P	P
1-butanol	S	P	P	P	P
2-propanol	S	G	G	G	G
Acetone	S	S	P	P	P
Acetonitrile	I	I	I	I	I
Benzyl alcohol	I	I	I	I	I
Methanol	S	S	S	G	G
Cyclopentanone	S	S	S	S	S
Cyclohexane	S	S	S	S	S
Water	S	S	S	S	S
Diisopropylether	S	S	S	S	S
DMF	I	I	I	I	I
1,4-butanediol	G	G	G	G	G
Ethyl acetate	I	I	I	I	I
1,2-dibromoethane	S	S	S	S	S
Toluene	S	S	S	S	S
Nitromethane	S	S	S	S	S
o-Xylene	S	S	S	S	S
1,2,4-trichlorobenzene	S	S	S	S	S

Table S2. Gelation test for **4a** at a concentration of 1% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	S	S	S	S	S
Dichloromethane	S	S	S	S	S
Diethyl ether	S	S	S	S	S
Diethylene glycol	S	P	P	P	P
DMSO	S	P	P	P	P
Ethanol	I	I	I	I	I
Hexane	S	S	S	S	S
THF	S	S	S	S	S
1,4-dioxane	S	S	S	S	S
1-butanol	S	S	P	P	P
1-pentanol	S	S	PG	G	G
1-propanol	S	P	P	P	P
1-butanol	S	P	P	P	P
2-propanol	S	S	S	S	S
Acetone	S	S	P	P	P
Acetonitrile	I	I	I	I	I
Benzyl alcohol	I	I	I	I	I
Methanol	S	S	S	S	S
Cyclopentanone	S	S	S	S	S
Cyclohexane	S	S	S	S	S
Water	S	S	S	S	S
Diisopropylether	S	S	S	S	S
DMF	S	S	S	S	S
1,4-butanediol	S	G	G	G	G
Ethyl acetate	I	I	I	I	I
1,2-dibromoethane	S	S	S	S	S
Toluene	S	S	S	S	S
Nitromethane	S	S	S	S	S
o-Xylene	S	S	S	S	S
1,2,4-trichlorobenzene	S	S	S	S	S

Table S3. Gelation test for **4a** at a concentration of 0.5% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	S	S	S	S	S
Dichloromethane	S	S	S	S	S
Diethyl ether	S	S	S	S	S
Diethylene glycol	S	P	P	P	P
DMSO	S	P	P	P	P
Ethanol	I	I	I	I	I
Hexane	S	S	S	S	S
THF	S	S	S	S	S
1,4-dioxane	S	S	S	S	S
1-butanol	S	S	P	P	P
1-pentanol	S	S	P	P	P
1-propanol	S	P	P	P	P
1-butanol	S	P	P	P	P
2-propanol	S	S	S	S	S
Acetone	S	S	P	P	P
Acetonitrile	I	I	I	I	I
Benzyl alcohol	I	I	I	I	I
Methanol	S	S	S	S	S
Cyclopentanone	S	S	S	S	S
Cyclohexane	S	S	S	S	S
Water	S	S	S	S	S
Diisopropylether	S	S	S	S	S
DMF	S	S	S	S	S
1,4-butanediol	S	P	P	P	P
Ethyl acetate	I	I	I	I	I
1,2-dibromoethane	S	S	S	S	S
Toluene	S	S	S	S	S
Nitromethane	S	S	S	S	S
o-Xylene	S	S	S	S	S
1,2,4-trichlorobenzene	S	S	S	S	S

Table S4. Gelation test for **4b** at a concentration of 2% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	S	S	S	S	S
Dichloromethane	S	S	S	S	S
Diethyl ether	S	S	S	S	S
Diethylene glycol	I	I	I	I	I
DMSO	S	S	S	S	S
Ethanol	S	P	P	P	P
Hexane	S	S	S	S	S
THF	S	S	S	S	S
1,4-dioxane	S	S	S	S	S
1-butanol	S	P	P	P	P
1-pentanol	S	P	P	P	P
1-propanol	S	P	P	P	P
1-butanol	S	P	P	P	P
2-propanol	S	P	P	P	P
Acetone	S	S	S	S	S
Acetonitrile	S	S	S	P	P
Benzyl alcohol	I	I	I	I	I
Methanol	S	S	S	S	S
Cyclopentanone	S	S	S	S	S
Cyclohexane	S	S	S	S	S
Water	S	S	P	P	P
Diisopropylether	S	S	S	S	S
DMF	S	S	S	S	S
1,4-butanediol	S	S	S	S	S
Ethyl acetate	S	S	S	S	S
1,2-dibromoethane	S	S	S	S	S
Toluene	S	S	S	S	S
Nitromethane	S	S	S	S	S
o-Xylene	S	S	P	P	P
1,2,4-trichlorobenzene	S	S	S	S	S

Table S5. Gelation test for **4b** at a concentration of 1% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	S	S	S	S	S
Dichloromethane	S	S	S	S	S
Diethyl ether	S	S	S	S	S
Diethylene glycol	I	I	I	I	I
DMSO	S	S	S	S	S
Ethanol	S	S	P	P	P
Hexane	S	S	S	S	S
THF	S	S	S	S	S
1,4-dioxane	S	S	S	S	S
1-butanol	S	S	P	P	P
1-pentanol	S	P	P	P	P
1-propanol	S	P	P	P	P
1-butanol	S	S	P	P	P
2-propanol	S	P	P	P	P
Acetone	S	S	S	S	S
Acetonitrile	S	S	S	P	P
Benzyl alcohol	I	I	I	I	I
Methanol	S	S	S	S	S
Cyclopentanone	S	S	S	S	S
Cyclohexane	S	S	S	S	S
Water	S	S	P	P	P
Diisopropylether	S	S	S	S	S
DMF	S	S	S	S	S
1,4-butanediol	S	S	S	S	S
Ethyl acetate	S	S	S	S	S
1,2-dibromoethane	S	S	S	S	S
Toluene	S	S	S	S	S
Nitromethane	S	S	S	S	S
o-Xylene	S	S	P	P	P
1,2,4-trichlorobenzene	S	S	S	S	S

Table S6. Gelation test for **4b** at a concentration of 0.5% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	S	S	S	S	S
Dichloromethane	S	S	S	S	S
Diethyl ether	S	S	S	S	S
Diethylene glycol	I	I	I	I	I
DMSO	S	S	S	S	S
Ethanol	S	P	P	P	P
Hexane	S	S	S	S	S
THF	S	S	S	S	S
1,4-dioxane	S	S	S	S	S
1-butanol	S	P	P	P	P
1-pentanol	S	P	P	P	P
1-propanol	S	P	P	P	P
1-butanol	S	P	P	P	P
2-propanol	S	P	P	P	P
Acetone	S	S	S	S	S
Acetonitrile	S	S	S	S	S
Benzyl alcohol	I	I	I	I	I
Methanol	S	S	S	S	S
Cyclopentanone	S	S	S	S	S
Cyclohexane	S	S	S	S	S
Water	S	S	P	P	P
Diisopropylether	S	S	S	S	S
DMF	S	S	S	S	S
1,4-butanediol	S	S	S	S	S
Ethyl acetate	S	S	S	S	S
1,2-dibromoethane	S	S	S	S	S
Toluene	S	S	S	S	S
Nitromethane	S	S	S	S	S
o-Xylene	S	S	S	S	S
1,2,4-trichlorobenzene	S	S	S	S	S

Table S7. Gelation test for **4c** at a concentration of 2% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	S	P	P	P	P
Dichloromethane	S	S	S	S	S
Diethyl ether	I	I	I	I	I
Diethylene glycol	S	S	S	S	S
DMSO	S	S	S	S	S
Ethanol	S	S	S	S	S
Hexane	S	P	P	P	P
THF	S	S	S	S	S
1,4-dioxane	I	I	I	I	I
1-butanol	S	S	S	S	S
1-pentanol	S	S	S	S	S
1-propanol	S	S	S	S	S
2-butanol	S	S	S	S	S
2-propanol	S	S	S	S	S
Acetone	S	S	S	S	S
Acetonitrile	P	P	P	P	P
Benzyl alcohol	S	S	S	S	S
Methanol	S	S	S	S	S
Cyclopentanone	P	P	P	P	P
Cyclohexane	S	S	S	P	P
Water	S	S	S	S	S
Diisopropylether	I	I	I	I	I
DMF	S	S	S	S	S
1,4-butanediol	S	PG	PG	PG	PG
Ethyl acetate	I	I	I	I	I
1,2-dibromoethane	I	I	I	I	I
Toluene	I	I	I	I	S
Nitromethane	P	P	P	P	P
o-Xylene	I	I	I	I	I
1,2,4-trichlorobenzene	I	I	I	I	I

Table S8. Gelation test for **4c** at a concentration of 1% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	S	S	S	P	P
Dichloromethane	S	S	S	S	S
Diethyl ether	I	I	I	I	I
Diethylene glycol	S	S	S	S	S
DMSO	S	S	S	S	S
Ethanol	S	S	S	S	S
Hexane	S	P	P	P	P
THF	S	S	S	S	S
1,4-dioxane	I	I	I	I	I
1-butanol	S	S	S	S	S
1-pentanol	S	S	S	S	S
1-propanol	S	S	S	S	S
2-butanol	S	S	S	S	S
2-propanol	S	S	S	S	S
Acetone	S	S	S	S	S
Acetonitrile	S	P	P	P	P
Benzyl alcohol	S	S	S	S	S
Methanol	S	S	S	S	S
Cyclopentanone	P	P	P	P	P
Cyclohexane	S	S	S	P	P
Water	S	S	S	S	S
Diisopropylether	I	I	I	I	I
DMF	S	S	S	S	S
1,4-butanediol	S	S	PG	PG	PG
Ethyl acetate	I	I	I	I	I
1,2-dibromoethane	I	I	I	I	I
Toluene	I	I	I	I	S
Nitromethane	P	P	P	P	P
o-Xylene	I	I	I	I	I
1,2,4-trichlorobenzene	I	I	I	I	I

Table S9. Gelation test for **4c** at a concentration of 0.5% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	S	S	S	S	S
Dichloromethane	S	S	S	S	S
Diethyl ether	I	I	I	I	I
Diethylene glycol	S	S	S	S	S
DMSO	S	S	S	S	S
Ethanol	S	S	S	S	S
Hexane	S	P	P	P	P
THF	S	S	S	S	S
1,4-dioxane	I	I	I	I	I
1-butanol	S	S	S	S	S
1-pentanol	S	S	S	S	S
1-propanol	S	S	S	S	S
2-butanol	S	S	S	S	S
2-propanol	S	S	S	S	S
Acetone	S	S	S	S	S
Acetonitrile	S	S	P	P	P
Benzyl alcohol	S	S	S	S	S
Methanol	S	S	S	S	S
Cyclopentanone	P	P	P	P	P
Cyclohexane	S	S	S	P	P
Water	S	S	S	S	S
Diisopropylether	I	I	I	I	I
DMF	S	S	S	S	S
1,4-butanediol	S	S	S	S	S
Ethyl acetate	S	S	P	P	P
1,2-dibromoethane	I	I	I	I	I
Toluene	I	I	I	I	S
Nitromethane	P	P	P	P	P
o-Xylene	I	I	I	I	I
1,2,4-trichlorobenzene	I	I	I	I	I

Table S10. Gelation test for **4d** at a concentration of 2% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	S	S	S	S	S
Dichloromethane	S	S	S	S	S
Diethyl ether	S	S	S	S	S
Diethylene glycol	S	S	G	G	G
DMSO	S	S	S	P	P
Ethanol	S	P	P	P	P
Hexane	S	S	S	S	S
THF	S	S	S	S	S
1,4-dioxane	S	S	S	S	S
1-butanol	S	S	S	S	S
1-pentanol	S	S	S	S	S
1-propanol	S	S	S	S	S
2-butanol	S	S	S	S	S
2-propanol	S	S	S	S	S
Acetone	S	S	S	S	S
Acetonitrile	S	P	P	P	P
Benzyl alcohol	S	S	S	S	S
Methanol	S	S	S	S	P
Cyclopentanone	S	S	S	S	S
Cyclohexane	S	S	S	S	S
Water	S	P	P	P	P
Diisopropylether	S	S	S	S	S
DMF	S	S	G	G	G
1,4-butanediol	S	S	S	S	S
Ethyl acetate	S	S	S	S	S
1,2-dibromoethane	S	S	S	S	S
Toluene	S	S	S	S	S
Nitromethane	S	S	S	S	S
o-Xylene	S	S	S	S	S
1,2,4-trichlorobenzene	S	S	S	S	S

Table S11. Gelation test for **4d** at a concentration of 1% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	S	S	S	S	S
Dichloromethane	S	S	S	S	S
Diethyl ether	S	S	S	S	S
Diethylene glycol	S	S	S	S	S
DMSO	S	S	S	S	S
Ethanol	S	S	P	P	P
Hexane	S	S	S	S	S
THF	S	S	S	S	S
1,4-dioxane	S	S	S	S	S
1-butanol	S	S	S	S	S
1-pentanol	S	S	S	S	S
1-propanol	S	S	S	S	S
2-butanol	S	S	S	S	S
2-propanol	S	S	S	S	S
Acetone	S	S	S	S	S
Acetonitrile	S	S	P	P	P
Benzyl alcohol	S	S	S	S	S
Methanol	S	S	S	S	P
Cyclopentanone	S	S	S	S	S
Cyclohexane	S	S	S	S	S
Water	S	S	P	P	P
Diisopropylether	S	S	S	S	S
DMF	S	S	S	S	S
1,4-butanediol	S	S	S	S	S
Ethyl acetate	S	S	S	S	S
1,2-dibromoethane	S	S	S	S	S
Toluene	S	S	S	S	S
Nitromethane	S	S	S	S	S
o-Xylene	S	S	S	S	S
1,2,4-trichlorobenzene	S	S	S	S	S

Table S12. Gelation test for **4d** at a concentration of 0.5% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	S	S	S	S	S
Dichloromethane	S	S	S	S	S
Diethyl ether	S	S	S	S	S
Diethylene glycol	S	S	S	S	S
DMSO	S	S	S	S	S
Ethanol	S	S	P	P	P
Hexane	S	S	S	S	S
THF	S	S	S	S	S
1,4-dioxane	S	S	S	S	S
1-butanol	S	S	S	S	S
1-pentanol	S	S	S	S	S
1-propanol	S	S	S	S	S
2-butanol	S	S	S	S	S
2-propanol	S	S	S	S	S
Acetone	S	S	S	S	S
Acetonitrile	S	S	P	P	P
Benzyl alcohol	S	S	S	S	S
Methanol	S	S	S	S	P
Cyclopentanone	S	S	S	S	S
Cyclohexane	S	S	S	S	S
Water	S	S	P	P	P
Diisopropylether	S	S	S	S	S
DMF	S	S	S	S	S
1,4-butanediol	S	S	S	S	S
Ethyl acetate	S	S	S	S	S
1,2-dibromoethane	S	S	S	S	S
Toluene	S	S	S	S	S
Nitromethane	S	S	S	S	S
o-Xylene	S	S	S	S	S
1,2,4-trichlorobenzene	S	S	S	S	S

Table S13. Gelation test for **4e** at a concentration of 2% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	P	P	P	P	P
Dichloromethane	P	P	P	P	P
Diethyl ether	P	P	P	P	P
Diethylene glycol	I	I	I	I	I
DMSO	S	S	S	S	S
Ethanol	PG	G	G	G	G
Hexane	P	P	P	P	P
THF	P	P	P	P	P
1,4-dioxane	I	I	I	I	I
1-butanol	G	G	G	G	G
1-pentanol	P	P	P	P	P
1-propanol	G	G	G	G	G
2-butanol	PG	PG	PG	PG	PG
2-propanol	PG	PG	PG	PG	PG
Acetone	P	P	P	P	P
Acetonitrile	S	P	P	P	P
Benzyl alcohol	S	PG	PG	PG	PG
Methanol	G	G	G	G	G
Cyclopentanone	P	P	P	P	P
Cyclohexane	P	P	P	P	P
Water	S	S	S	S	S
Diisopropylether	I	I	I	I	I
DMF	PG	G	G	G	G
1,4-butanediol	PG	PG	PG	PG	PG
Ethyl acetate	S	S	S	S	P
1,2-dibromoethane	P	P	P	P	P
Toluene	P	P	P	P	P
Nitromethane	P	P	P	P	P
o-Xylene	P	P	P	P	P
1,2,4-trichlorobenzene	S	P	P	P	P

Table S14. Gelation test for **4e** at a concentration of 1% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	P	P	P	P	P
Dichloromethane	P	P	P	P	P
Diethyl ether	P	P	P	P	P
Diethylene glycol	I	I	I	I	I
DMSO	S	S	S	S	S
Ethanol	G	G	G	G	G
Hexane	S	S	S	G	G
THF	P	P	P	P	P
1,4-dioxane	P	P	P	P	P
1-butanol	G	G	G	G	G
1-pentanol	P	P	P	P	P
1-propanol	G	G	G	G	G
2-butanol	PG	G	G	G	G
2-propanol	G	G	G	G	G
Acetone	P	P	P	P	P
Acetonitrile	S	P	P	P	P
Benzyl alcohol	S	S	PG	PG	PG
Methanol	G	G	G	G	G
Cyclopentanone	P	P	P	P	P
Cyclohexane	P	P	P	P	P
Water	S	S	S	P	P
Diisopropylether	I	I	I	I	I
DMF	S	S	S	PG	PG
1,4-butanediol	PG	PG	G	G	G
Ethyl acetate	S	P	P	P	P
1,2-dibromoethane	P	P	P	P	P
Toluene	P	P	P	P	P
Nitromethane	P	P	P	P	P
o-Xylene	P	P	P	P	P
1,2,4-trichlorobenzene	S	P	P	P	P

Table S15. Gelation test for **4e** at a concentration of 0.5% wt.

Solvent	30 min	4h	24h	48h	72h
Chloroform	S	P	P	P	P
Dichloromethane	S	P	P	P	P
Diethyl ether	P	P	P	P	P
Diethylene glycol	I	I	I	I	I
DMSO	S	S	S	S	S
Ethanol	G	G	G	G	G
Hexane	S	P	P	P	P
THF	S	P	P	P	P
1,4-dioxane	I	I	I	I	I
1-butanol	G	G	G	G	G
1-pentanol	S	S	S	S	S
1-propanol	G	G	G	G	G
2-butanol	G	G	G	G	G
2-propanol	G	G	G	G	G
Acetone	S	P	P	P	P
Acetonitrile	S	P	P	P	P
Benzyl alcohol	S	S	S	P	P
Methanol	PG	PG	PG	PG	PG
Cyclopentanone	P	P	P	P	P
Cyclohexane	P	P	P	P	P
Water	S	S	P	P	P
Diisopropylether	I	I	I	I	I
DMF	S	S	S	S	S
1,4-butanediol	G	G	G	G	G
Ethyl acetate	S	S	S	S	P
1,2-dibromoethane	P	P	P	P	P
Toluene	S	P	P	P	P
Nitromethane	P	P	P	P	P
o-Xylene	P	P	P	P	P
1,2,4-trichlorobenzene	S	P	P	P	P

Figure S1. Gels for **4a** at 1% wt in (from left to right) 1-pentanol and 1,4-butanediol.

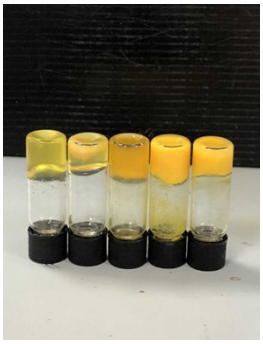


Figure S2. Gels for **4e** at 2% wt in (from left to right) in DMF, Ethanol, Methanol, 1-butanol and 1-propanol.

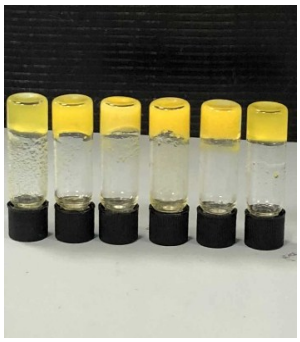


Figure S3. Gels for **4e** at 0.5% wt in (from left to right) in Ethanol, 1-butanol, 1-propanol, 2-butanol, 2-propanol and 1,4-butanediol.

3. SEM Images

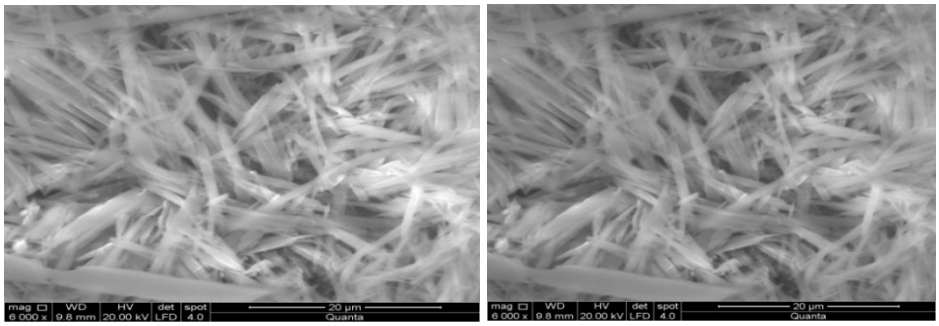


Figure S4. SEM images for compound **4a.**

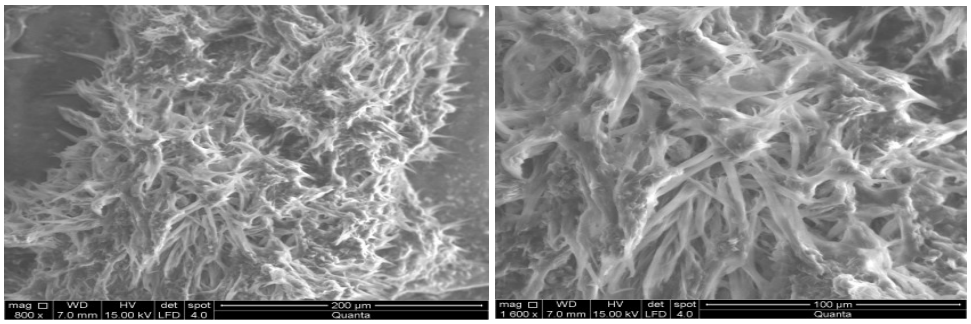


Figure S5. SEM images for compound **4c.**

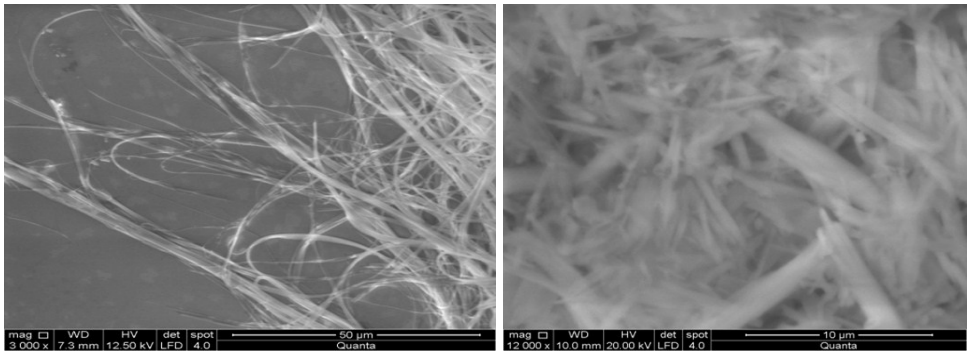


Figure S6. SEM images for compound **4d.**

4. Rheology experiments

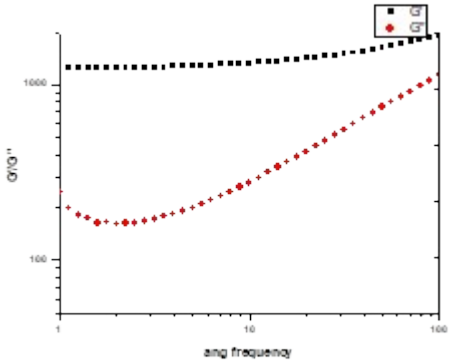
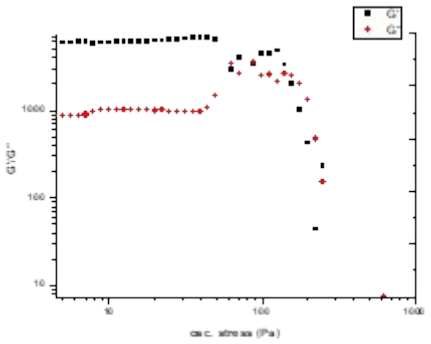
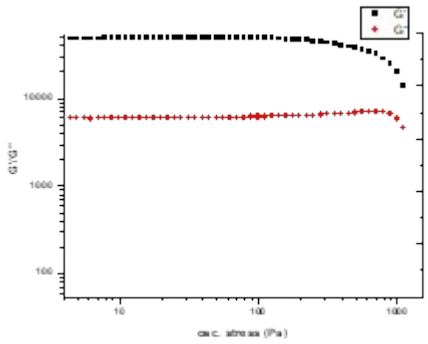


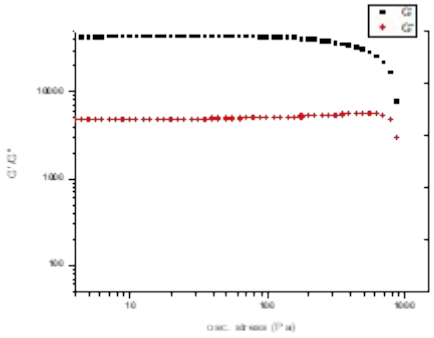
Figure S7. Frequency sweep for **4a** at 2% wt in 1,4-butanediol.



2% wt 2-propanol
σ= 63 Pa

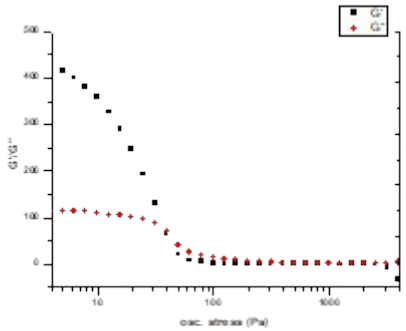


2% wt Methanol
σ= 1259 Pa



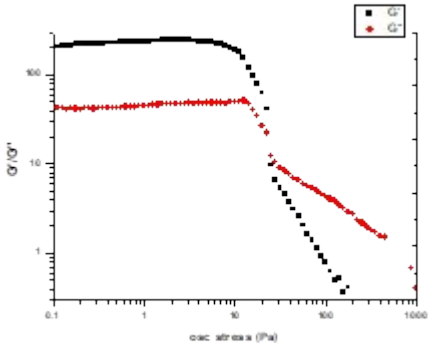
2% wt 1,4-butanediol
σ= 914 Pa

Figure S8. Stress sweep for **4a** at 2% wt in different solvents.

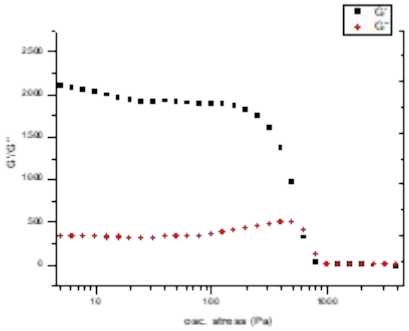


2% wt Diethylene glycol
σ= 40 Pa

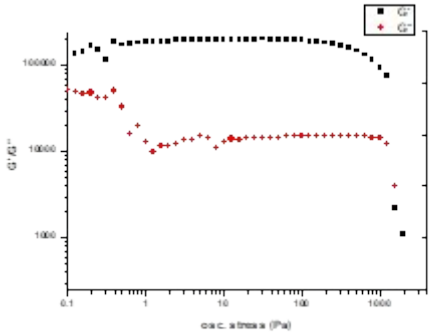
Figure S9. Stress sweep for **4d** at 2% wt in different solvents.



2% wt Methanol
σ= 25 Pa

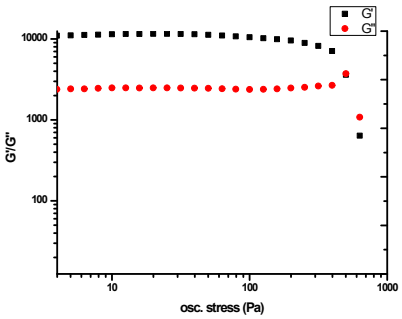


2% wt DMF
σ = 631 Pa

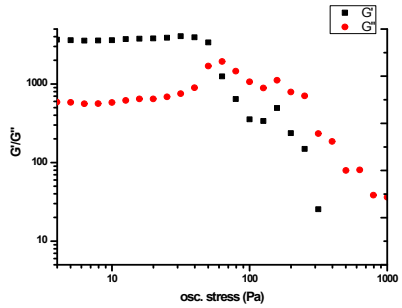


2% wt 1-butanol
σ= 1585 Pa

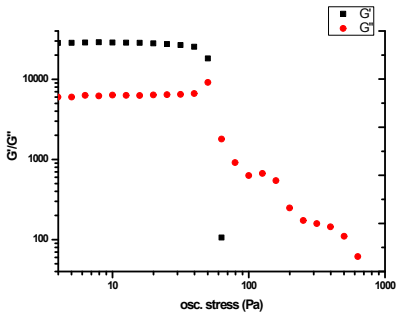
Figure S10. Stress sweep for **4e** at 2% wt in different solvents.



2% wt Ethanol
σ= 501 Pa



1% wt Ethanol
σ= 100 Pa



0.5% wt Ethanol
σ= 63 Pa

Figure S11. Comparison of the Stress sweep rheology in ethanol for **4e** at different concentrations.

5. Unit cell determination

a= 8.156(2)	**a= 8.8478 (4)**
b= 8.480(2)	**b= 13.352 (6)**
c= 15.406 (4)	**c= 14.1584 (6)**
V=1062.7(7)	**V= 1480.77**
Monoclinic P	**Orthorombic C**
Polymorph II	**Polymorph I**

Figure S12. Unit cell determination for crystallization of sulfathiazole in absence of the gel (left) or in presence of the gel (right).