Electronic Supplementary Information

Exceptional Organic Solvents Uptake by Disulfide–linked Polymeric Networks

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Experimental

Materials

Trimethylolpropane tris(3–mercaptopropionate), 98% and pentaerythritol tetrakis(3–mercaptopropionate), 98% are obtained from Sigma–Aldrich. Dimethyl sulfoxide (99.5%), tetrahydrofuran (98%) and methanol (98%) are purchased from SAMCHUN, Republic of Korea. All chemicals were used as received.

Synthesis of covalent organic polymers (COPs)

COP-65:

5 mL of trimethylolpropane tris(3–mercaptopropionate) is added into 25 mL of dimethyl sulfoxide. The solution is heated at 80 °C for 24h with vigorous stirring. The reaction mixture is cooled down to room temperature and excess of methanol (50 mL) was added which resulted into precipitates. The precipitates were centrifuge and soaked in tetrahydrofuran (THF) for 12 h. The liquid was decanted and again soaked in THF for 12 h. This procedure was repeated four times. Finally, gel-like material was dried at 50 °C for 2 h and 100 °C for 5 h under vacuum. CHNSO: % C: 44.26 (45.55), % H: 6.12 (5.86), % S: 24.15 (24.32), % O: 24.95 (24.27).

COP-66:

5 mL of pentaerythritol tetrakis(3–mercaptopropionate) is added into 25 mL of dimethyl sulfoxide. The solution is heated at 80 °C for 24 h with vigorous stirring. Transparent gel-like material formed which was soaked in tetrahydrofuran (THF) for 12 h. The liquid was decanted and again soaked in THF for 12 h. This procedure was repeated four times. Finally, gel-like material was dried at 50 °C for 2 h and 100 °C for 5 h under vacuum. CHNSO: % C: 42.31 (42.13), % H: 5.38 (4.99), % S: 25.12 (26.47), % O: 26.71 (26.41).

Swelling study:

The COPs were dried at 80°C in vacuum overnight. 0.5 g of COPs were soaked in 5 mL of various organic solvents and continuously stirred for 12 h at room temperature. The swelled COPs were retrieved from the solvents and excess solvent on the surface of the COPs was drained. The final weight of swelled COPs measured and difference between initial-final weights gave net uptake of solvents. The swelled COPs were easily regenerated for several cycles by heating at appropriate temperature with respect to boiling point of the solvent in vacuum.

Sorption study from the mixture of water:dioxane and water:THF:

For this study, synthetic mixture of water:dioxane or water:THF in the ratio of 0 to 100 (v/v) were used. The COPs were dried at 80°C in vacuum overnight. 0.5 g of COPs were soaked in 5 mL of water:solvents mixtures and continuously stirred for 12 h at room temperature. The swelled COPs were retrieved from the solvents and excess solvent on the surface of the COPs was drained. The final weights of solvent adsorbed in COPs were measured and difference between initial-final weights gave net uptake of solvents. The used COPs were easily regenerated for several cycles by heating at appropriate temperature with respect to boiling point of the solvent in vacuum (Fig. S4).

Characterization:

CP/MAS ^{13}C–NMR spectra were recorded on a Bruker DMX400 NMR spectrometer. Solid-state cross polarization magic angle spinning (CP/MAS) NMR spectra were recorded on a Bruker Anence III 400 WB NMR spectrometer. FT–IR spectra were recorded as KBr pellet using a Perkin-Elmer FT–IR spectrometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH-TG 209 F3 instrument by heating the samples to 800 °C at 10 °C min^{-1} in N_2 or air atmosphere. CHNSO analyses were performed on elemental analyzer ThermoQuest Italia S.P.A (CE instrument). In order to evaluate the porosity of COPs, Ar adsorption isotherms were obtained with a Micromeritics ASAP 2020 accelerated surface area and porosimetry analyzer at 87 K, after the samples had been degassed at 150 °C for 5 h under vacuum. The adsorption–desorption isotherms were obtained to give the BET (P/P_o = 0.01–0.25) and Langmuir (P/P_o =

0.1–0.35) surface area. Powder X-ray diffraction patterns of the COPs were acquired from 0.5 to 80° by a Rigaku D/MAX-2500 (18kW) Micro area X-ray diffractometer.

Table S1. Elemental analysis (CHSO) of COPs

COPs	**%C**		**%H**		**%O**		**%S**	
	Theo.	**Exp.**	**Theo.**	**Exp.**	**Theo.**	**Exp.**	**Theo.**	**Exp.**
COP–65	45.55	44.26	5.86	6.12	24.27	24.95	24.32	24.15
COP–66	42.13	42.31	4.99	5.38	26.41	26.71	26.47	25.12

Table S2. Solvent uptakes by COP-65 and COP-66.

Solvents	**Uptake, g g^{-1}**	
	COP-65	**COP-66**
Hexane	0.0053	0.0058
Benzene	0.6348	0.2523
Toluene	0.4203	0.0706
DEE	0.0904	0.0268
Dioxane	3.1963	1.0344
Ethyl acetate (EA)	1.7930	0.2983
Tetrahydrofuran (THF)	0.5630	1.0449
Chloroform	1.1055	1.0818
Dichloromethane (DCM)	2.3875	1.6552
1,1,2,2-tetrachloroethane (TeCE)	5.2546	2.4718
Tetrachloroethylene (TeCEy)	0.2808	0.0469
Trichloroethylene (TrCEy)	0.9549	0.404
1,1,2-trichloroethane (TrCE)	4.6751	2.5437
1,2-dichloroethane (DCE)	2.0252	1.3885
1,2-dichlorobenzene (DCB)	1.1972	0.1913
Acetone	0.5433	0.3090
Acetonitrile (AcCN)	0.3200	0.2915
N,N-dimethylformamide (DMF)	0.5287	0.6733
Dimethyl sulfoxide (DMSO)	1.4208	0.9765
Acetic acid, glacial (AA)	0.4313	0.2598
n-Butanol	0.0458	0.0302
Isopropyl alcohol (IPA)	0.03	0.0270
Ethanol	0.0229	0.0257
Methanol	0.0432	0.0597
Water	0.0108	0.0228

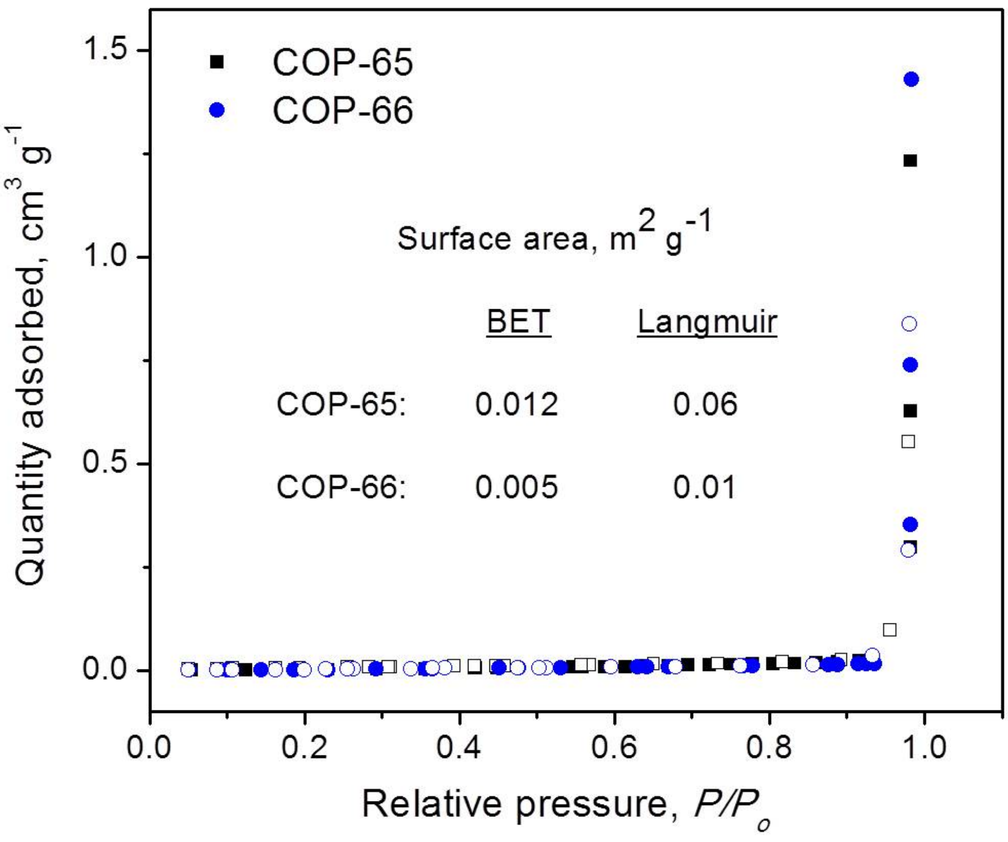


Fig. S1. Ar adsorption–desorption plots at 87 K of COPs.

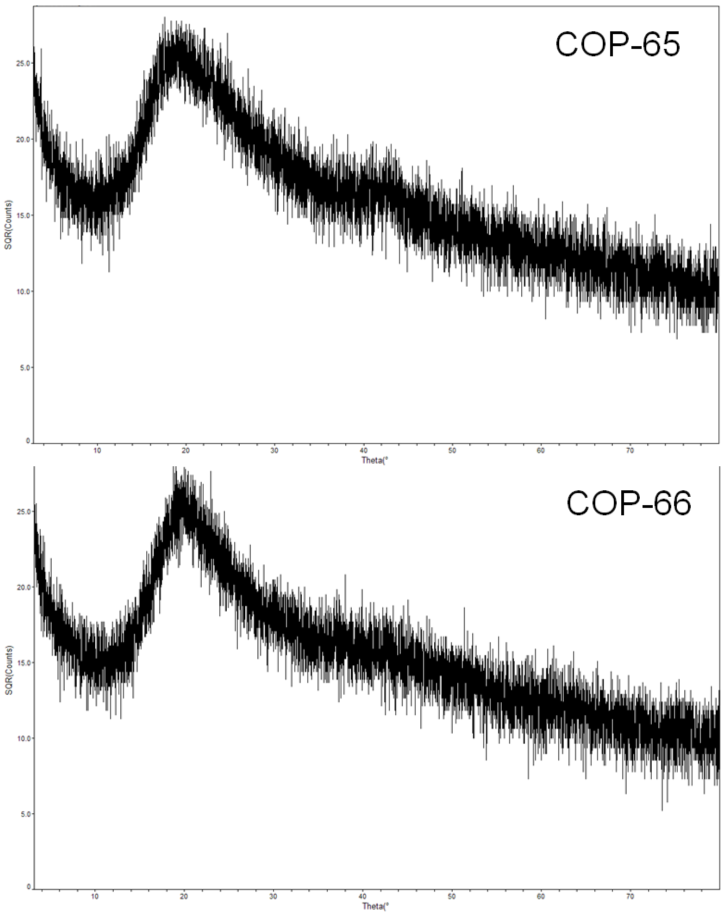
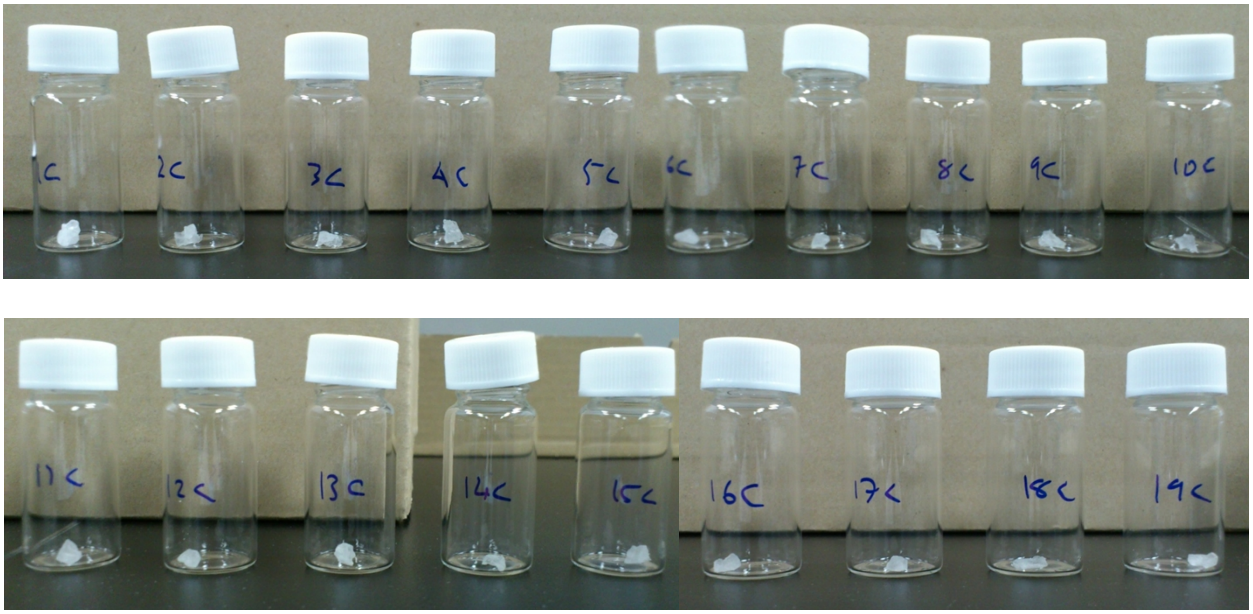
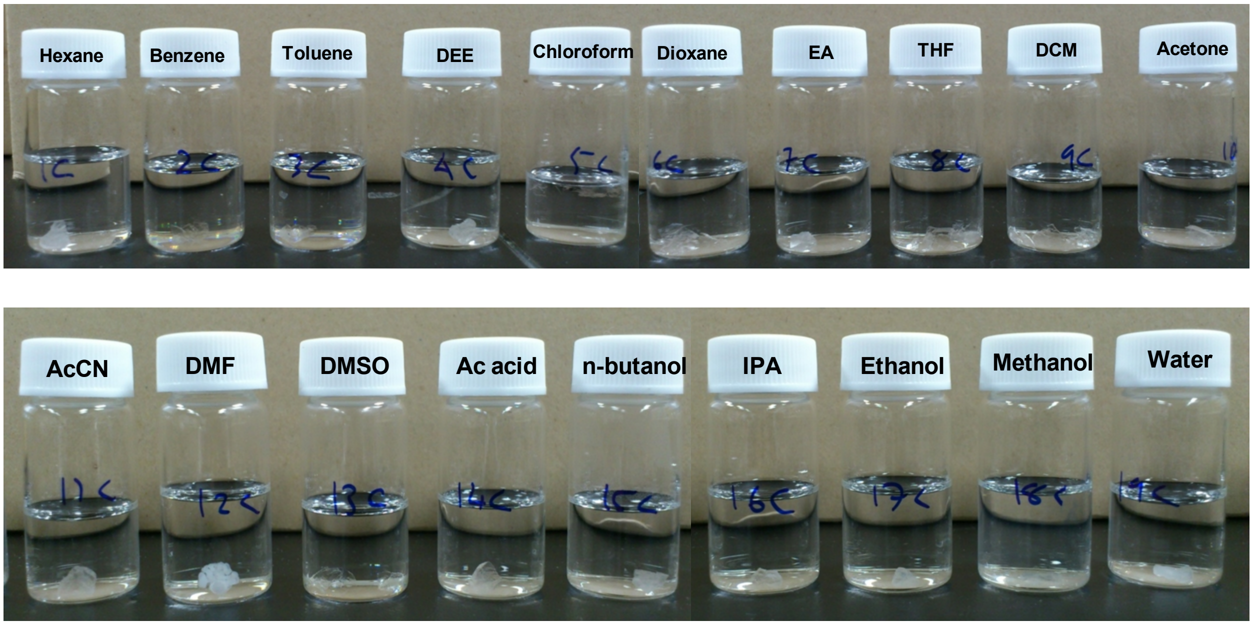


Fig. S2. Powder X–ray diffraction patterns of COPs

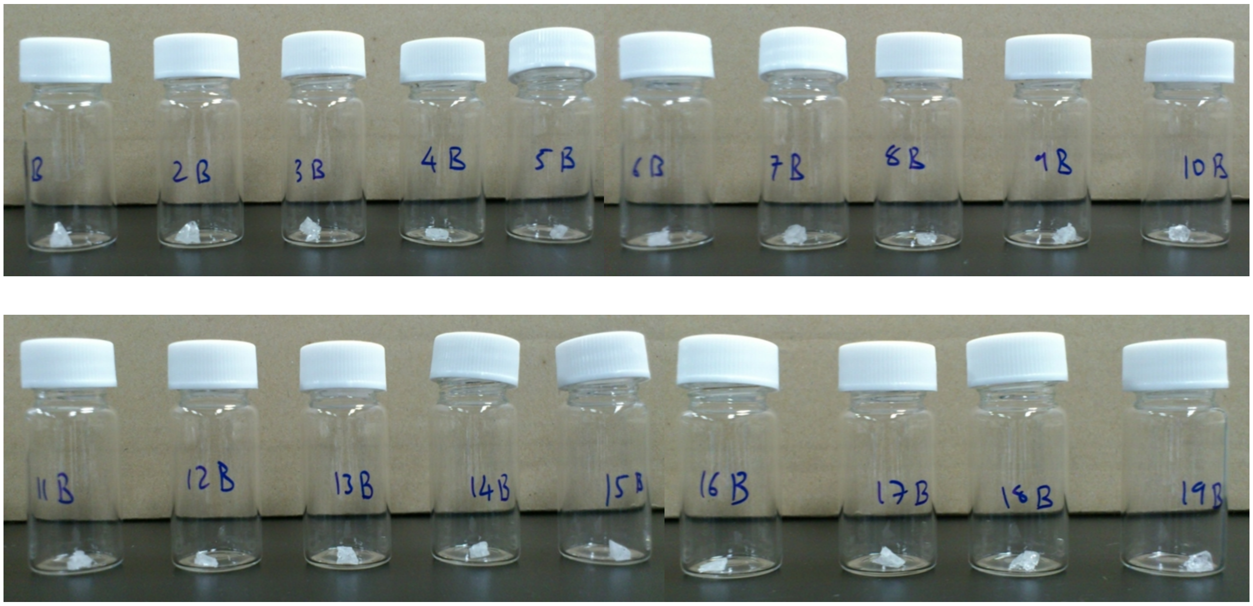


COP-65 (before)

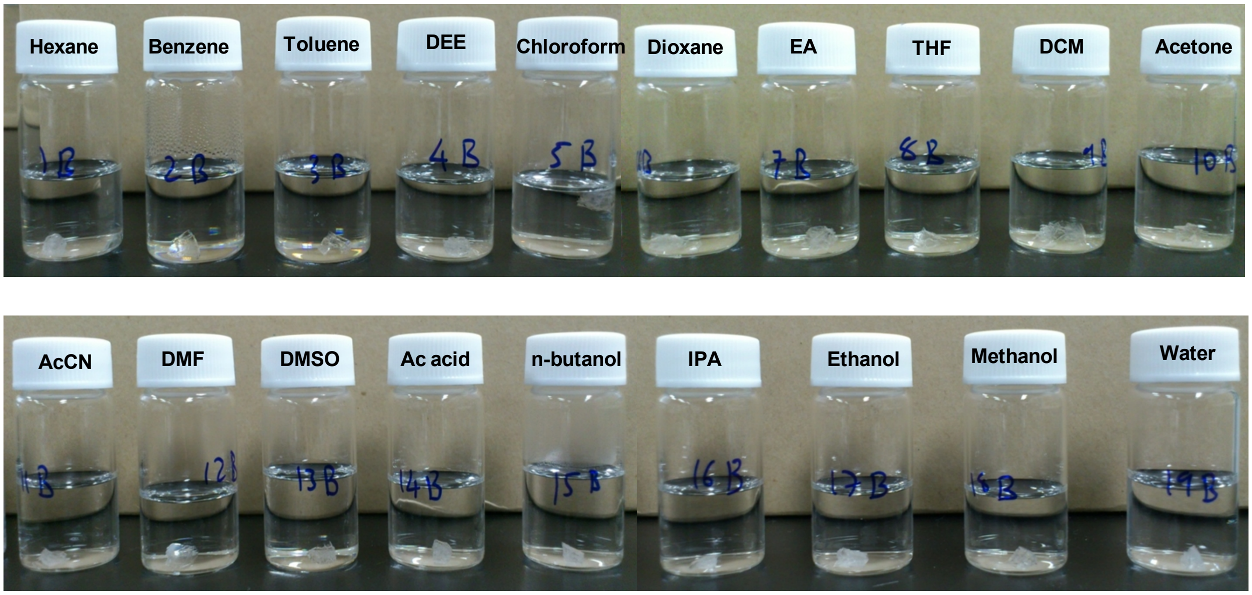


COP-65 (after soaking for 12 h)

Fig. S3a. Swelling of various solvents in COP–65.



COP-66 (before)



COP-66 (after soaking for 12 h)

Fig. S3b. Swelling of various solvents in COP–66.

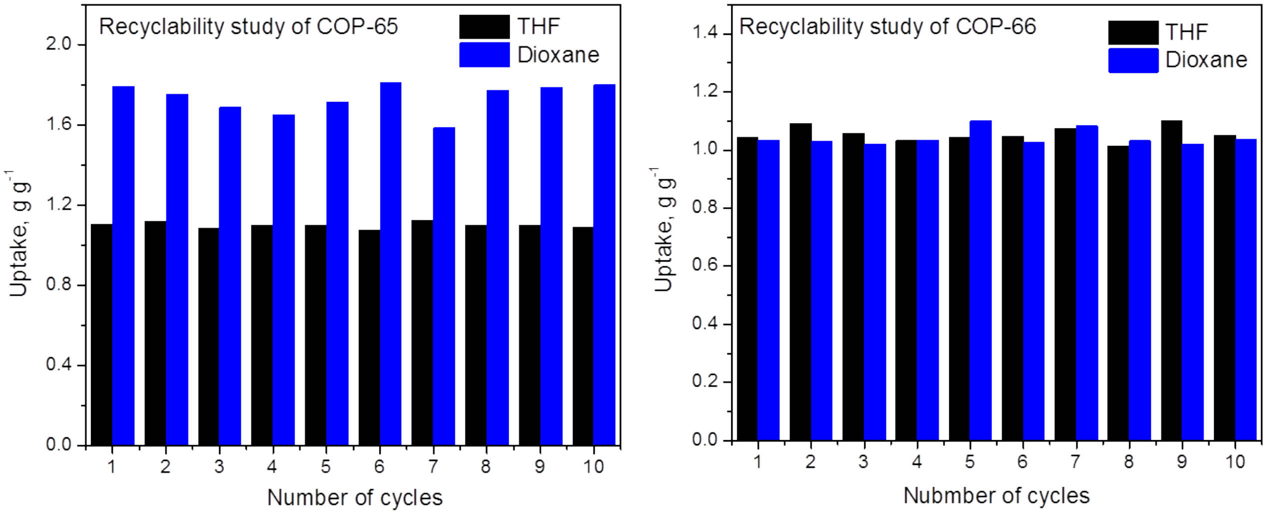


Fig. S4. Recyclability of COP-65 and COP-66 for THF and dioxane uptakes up to 10 cycles. COPs were dried (70 °C for THF and 100 °C for dioxane, the boiling point of THF and dioxane is 66 and 101.1 °C, respectively) under vacuum for 1 hour after each swelling experiments and swelled again.