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Highly efficient chlorinated solvent uptake by novel covalent organic networks via thiol-ene chemistry

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Abstract

In this study, we synthesized an aliphatic–aromatic regular network as a novel covalent organic networks called TEPN-1 (Thiol-ene Polymer Network) and TEPN-2 via thiol-ene chemistry. TEPN-1 and TEPN-2 were analyzed by FTIR, ^{13}C-NMR, Brunauer–Emmett–Teller, thermogravimetric analysis and elemental analysis. Solvent uptake capacity of TEPN-1 and TEPN-2 was employed against 26 solvents which are frequently used in chemical industry. It is found that TEPN-1 has the highest swelling adsorption ratio with chloroform and DCM (13.7 and 11.5 g.g^{-1}, respectively), while TEPN-2 has 9.2 and 7.5 g.g^{-1}, respectively. Both TEPN-1 and TEPN-2 have very minimal water uptake (0.165 and 0.189 g.g^{-1}, respectively). TEPN-1 and TEPN-2 are efficient adsorbents for most of organic solvents including water-miscible organic solvents such as THF, dioxane and pyridine.

Keywords Solvent uptake · Covalent organic networks · Porous polymers · Thiol-ene chemistry · Adsorbent · Swelling · Trivalent · Tetravalent

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Introduction

Covalent organic networks are extended organic polymers obtained by linking building blocks to form porous and controllable network structures. There has been a great interest to covalent organic frameworks (COFs) in the recent years due to wide spectrum of application such as gas storage (hydrogen and methane) [1, 2], gas separation [3, 4] and removal of hazardous materials [5, 6] as well as in luminescent [7], photovoltaic field [8, 9], antibacterial materials [10] and catalyst [11]. Organic solvents are widely used in petroleum industry, cosmetics, pharmaceuticals and production of fine chemicals. In particular, water-miscible organic solvents such as THF and dioxane can easily mix with water cycle in the nature due to well solubility in water when they discharged to waste water. It is environmentally crucial to remove these harmful organic solvents before discharging the waste water to the nature by using efficient and cost effective systems [12]. Besides several chemical and biological methods to remove organic hazardous compounds from waste water [13, 14], several materials were developed such as porous polymers [15], zeolites [16], activated carbons [17], organoclays [18] and metal–organic frameworks [19]. COFs with controllable pore geometry and tunable functionality have been getting significant importance in recent years to remove of organic solvents from waste water [12, 15]. Poly (acrylic acid) [20], poly (lactic acid) [21], poly (orthocarbonate) [22], porous polymers [23] and cellulosic materials [24], were studied as superabsorbents in order to remove organic solvents and oil from water. However, synthesis of these materials required expensive monomers and catalyst. Additionally, these studies did not report separation of high concentration organic solvents from water.

Thiol-ene chemistry is successfully applied to obtain a polymer between thiol functional group and vinyl type monomers in the presence of photo-initiator [25–27] in order to create a polymeric COFs. In thiol-ene reaction mechanism, there are two pathways: ionic or free radical mechanism. Ionic mechanism is an example of Michael-type addition reaction where a base (mostly an amine) is required to create basic medium and this mechanism is efficient to compounds which are carrying electron-deficient unsaturation such as alpha, beta-unsaturated carbonyl compounds [28]. Free radical mechanism proceeds with an initiator which generates free radicals under thermal or UV irradiation. Free radicals generated by initiator attack to thiol groups to produce thiyl radicals which is necessary for the reaction to proceed [29].

In this study, we report the synthesis of two novel Thiol-ene polymer networks, TEPN-1 and TEPN-2, by reacting aliphatic monomers trivalent trimethylolpropane tris(3-mercaptopropionate) and tetravalent pentaerythritol tetrakis tris(3-mercaptopropionate), respectively, with divinyl benzene in the presence of photo-initiator through thiol-ene chemistry. TEPN-1 and TEPN-2 were analyzed by FTIR, ^{13}C-NMR, Brunauer–Emmett–Teller (BET), thermogravimetric analysis (TGA) and elemental analysis. Solvent uptake capacity of TEPN-1 and TEPN-2 was employed against 26 solvents which are frequently used in chemical industry. It is shown that TEPN-1 has the highest swelling adsorption ratio with chloroform and DCM

(13.7 g.g^{-1} and 11.5 g.g^{-1}, respectively), while TEPN-2 has 9.2 g.g^{-1} and 7.5 g.g^{-1}, respectively. Both TEPN-1 and TEPN-2 have very minimal water uptake (0.165 and 0.189 g.g^{-1}, respectively). In terms of water-miscible solvents, THF and dioxane have been swollen by TEPN-1 and TEPN-2 with high ratio (5.560 g.g^{-1} and 5.464 g.g^{-1} for TEPN-1; 3.103 g.g^{-1} and 4.929 g.g^{-1} for TEPN-2, respectively) as well. Ultimately, we describe facile synthesis of novel COFs called TEPN-1 and TEPN-2 where the building blocks are composed of aliphatic–aromatic units via thiol-ene chemistry. TEPN-1 and TEPN-2 are efficient adsorbents for most of organic solvents and for water-miscible organic solvents such as THF and dioxane from their aqueous mixtures.

Experimental

Materials

Trimethylolpropane tris(3-mercaptopropionate) (MW = 398.56), pentaerythritol tetrakis(3-mercaptopropionate) (MW = 488.66), xylene, pyridine, dichloromethane (DCM), acetonitrile, benzene, aniline, benzonitrile were obtained from Sigma-Aldrich. 2,2-Dimethoxy-2-phenylacetophenone (MW = 256.30), propylene glycol and ethylene glycol were obtained from TCI. Tetrahydrofuran (THF), methanol, ethanol, 1-propanol, toluene, acetone and chloroform were obtained from VWR Prolabo Chemicals. Divinyl benzene, diphenyl ether, chlorobenzene, 1-octadecene and 1,2-dichlorobenzene were obtained from Alfa Aesar. 1,4-Dioxane, dimethylformamide (DMF), n-hexane, ethyl acetate, pyrrole and methyl sulfoxide (DMSO) were from Merck. All chemicals were used as they received. UV (Blak-Ray B-100AP /R High intensity UV Lamp 100 WATT-230 V, 50 Hz, 365 nm) was used as UV light source. The water used in the experiments was taken from Millipore deionized water system with resistivity of 18.2 mΩ.

Synthesis of trivalent and tetravalent COFs (TEPN-1 and TEPN-2)

0.797 g (2 mmol) trimethylolpropane tris(3-mercaptopropionate) and 0.390 g (3 mmol) p-divinylbenzene were dissolved in 5 ml THF in a 20 ml vial. Then, 0.030 g 2,2-Dimethoxy-2-phenylacetophenone as photo-initiator was added to mixture. The vial was placed under UV source with 10 cm distance. The reaction mixture under UV radiation was stirred at 500 rpm with magnetic stirrer at ambient conditions for 6 h. Light dirty gel-like elastic solid was obtained as product. The gel was removed from the vial and soaked in 50 ml THF for 24 h. This procedure was repeated three times. Finally, the product (TEPN-1) was dried at 80 °C under vacuum and stored at room conditions. For the synthesis of TEPN-2, 0.488 g pentaerythritol tetrakis(3-mercaptopropionate) and 0.260 g p-divinylbenzene were dissolved in 5 ml THF in a 20 ml vial. Then, 0.030 g 2,2-Dimethoxy-2-phenylacetophenone as photo-initiator was added to mixture. The following procedure is the same as in synthesis of TEPN-1.

Organic solvent uptake studies

Several organic solvents which are often used in chemical industry were treated with TEPN-1. Shortly, 250 mg of TEPN-1 was soaked in 3 ml of organic solvent for 12 h at room temperature. Then, the swollen TEPN-1 was removed from organic solvent. Excess organic solvent on the surface of TEPN-1 was drained away. Initial and final weight of TEPN-1 was measured. Dividing the difference of initial and final weights to dry-weight of used TEPN-1 gives the swelling percentage (or capacities) of the TEPN-1. The same procedure was repeated for TEPN-2. The organic solvent uptake capacities of TEPN-1 and TEPN-2 is reported in Table 2. The formula used in the calculations is;

$$\text{Solvent Uptake Capability} = \frac{W_{\text{final}} - W_{\text{initial}}}{W_{\text{initial}}}$$

whereas W_{final} and W_{initial} are the weights of the final weight of swelled TEPN and initial weight of dry TEPN, respectively.

Removal of water-miscible organic solvents from aqueous mixtures

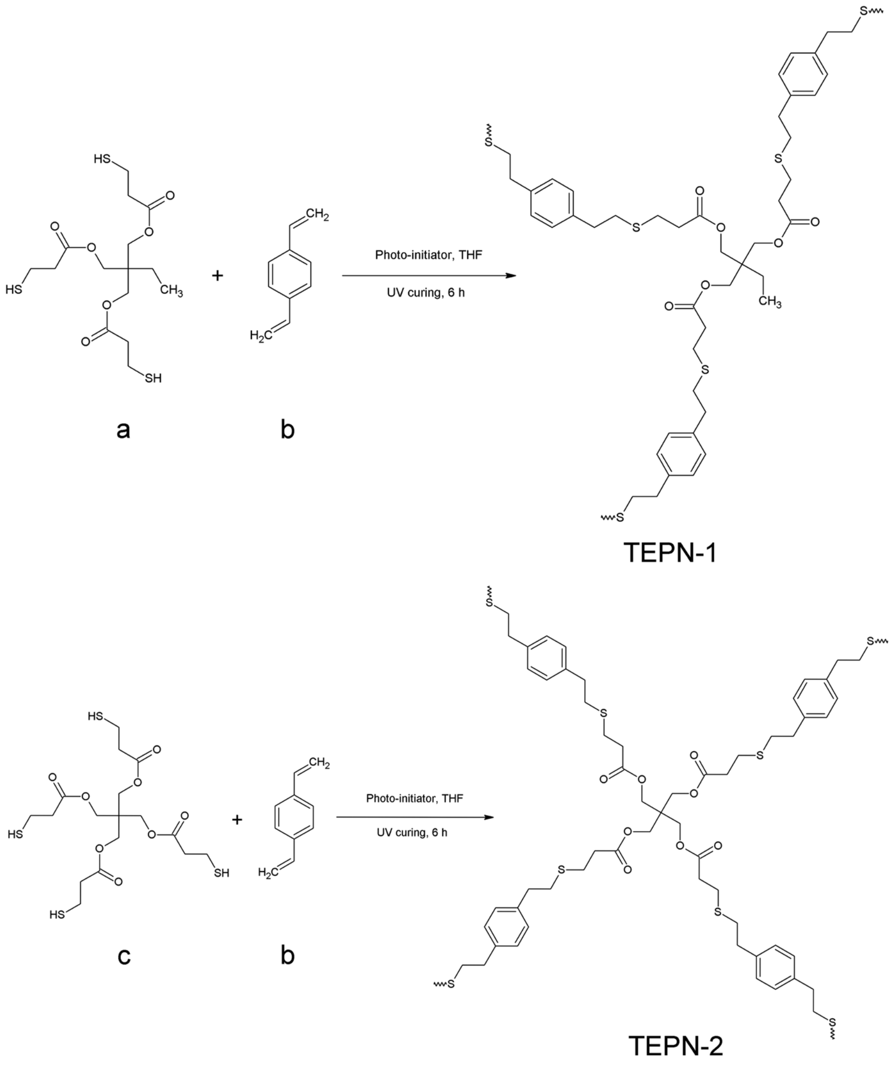
In this study, mixtures of water/dioxane, water/THF or water/pyridine in the ratio of 0 to 100 (v/v) were used. 0.4 g of dried TEPN-1 or TEPN-2 polymer networks were soaked into 5 mL of the mixtures and stirred for 12 h at room temperature. The swelled polymer networks were retrieved from the solvents, and excess solvent on the surface of the TEPN-1 or TEPN-2 was drained. Initial and final weight of TEPN-1 or TEPN-2 was measured to give the uptake efficiency of solvents.

Characterization of TEPN-1 and TEPN-2

TEPN-1 and TEPN-2 were characterized by FTIR spectroscopy Hitachi-7000 model. CP/MAS ^{13}C-NMR spectra were recorded by Bruker Avance 399 MHz (7 T) spectrometer. Elemental analyses were measured by LECO CHNS-932 elemental analyzer. Thermal stability of TEPN-1 and TEPN-2 under oxidative and inert (N_2) medium was measured by thermogravimetric analysis TGA/DSC 2 Star System Metler Toledo by heating the samples to 800 °C at 10 °C min^{-1} in N_2 and air. Ar adsorption isotherms obtained with Micromeritics Tri Star II 3020 analyzer at 87 K, after samples had been degassed at 150 °C for 6 h under vacuum in order to evaluate porosity of samples.

Results and discussion

The reaction of trivalent molecule, trimethylolpropane tris(3-mercaptopropionate) and tetravalent molecule pentaerythritol tetrakis(3-mercaptopropionate) with divinylbenzene in the presence of photo-initiator is shown in Scheme 1. Divinylbenzene



Scheme 1 Synthesis scheme of TEPN-1 and TEPN-2. **a** Trimethylolpropane tris(3-mercaptopropionate), **b** Divinylbenzene, **c** Pentaerythritol tetrakis(3-mercaptopropionate), photo-initiator: 2,2-dimethoxy-phenylacetone, UV curing at $\lambda = 365$ nm

is the linking agent between thiol groups of these tri/tetravalent molecules to build the network structure called as TEPN-1 and TEPN-2.

The reaction between thiol and vinyl type functional groups is a convenient tool for establishment of carbon–sulfur linkage. This type of reaction is often called as “thiol-ene click chemistry” due to lack of byproducts, high yield and air tolerance [30]. In this study, we used 2, 2-dimethoxy-phenylacetone as photo-initiator which dissociates to free radicals under UV radiation at ambient conditions. No other

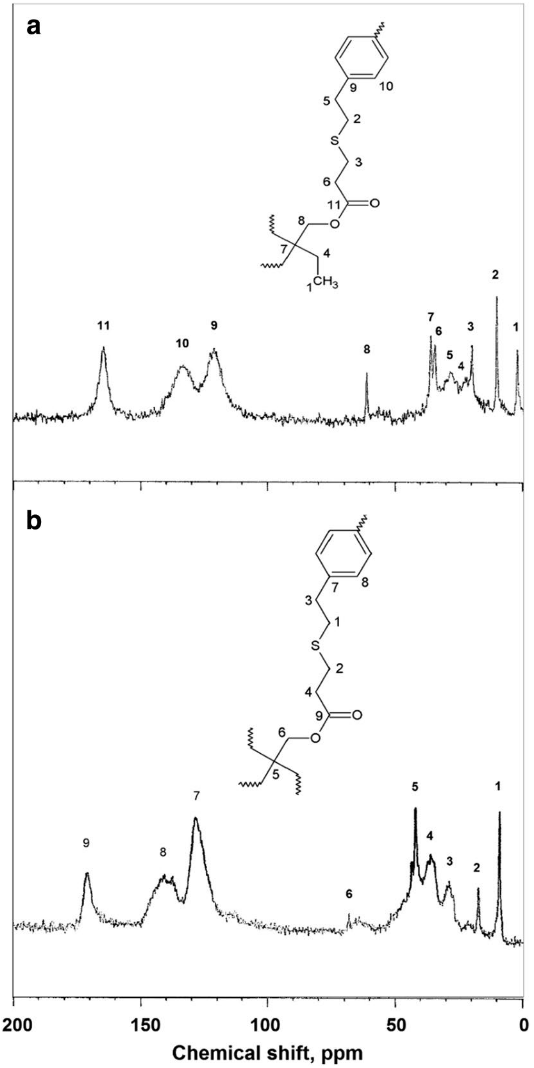


Fig. 1 CP/MAS ^{13}C-NMR spectrum of **a** TEPN-1 **b** TEPN-2

catalyst is needed for the reaction. Within 3 h, a gelation started to form and the reaction was completed in 6 h.

In Fig. 1, CP/MAS ^{13}C-NMR spectra confirm the polymeric structures of TEPN networks by characteristic chemical shifts. In both spectra, two types of carbons, aliphatic and aromatic carbons, are shown. Divinylbenzene (DVB) is the same reactant in both TEPN synthesis and the chemical shifts of vinyl groups in DVB should disappear after completion of thiol-ene reaction. In the literature, the chemical shifts of vinyl carbons in DVB are at around 137 (methine, =CH) and 113 (methylene, CH2=) ppm [31, 32]. Due to benzene structure in the networks and broad peaks in CP/MAS ^{13}C-NMR spectra, we could not identify the disappearance of methine carbon in the spectra, but on the other hands, the chemical shift of terminal methylene carbon in vinyl group at around 113 ppm is clearly disappeared in both spectra which is a proof of thiol-ene final products, TEPN networks. As shown in Fig. 1a, the chemical shifts of carbons at 2.5, 10.4, 19.8, 25.1, 27.0, 44.1, 47.8, 61.2 ppm correspond to the aliphatic carbons. Each numbered carbon is assigned on the chemical structure of TEPN-1 in Fig. 1a. The other carbons at 134.1 and 121.5 belong to the aromatic benzene carbons, substituted and unsubstituted aromatic carbons, respectively. The peak at 164.0 ppm is for carbonyl group (C=O) of TEPN-1. In case of TEPN-2 (shown in Fig. 1b), the chemical shifts at 10.8, 20.1, 28.9, 37.8, 42.5, 68.2 ppm are for aliphatic carbons, and 141.1 and 129.5 ppm for aromatic benzene carbons, and at 171.0 ppm for carbonyl carbon.

FTIR analysis in Fig. 2 is conducted to understand the formation of thiol-ene product, TEPN networks. Figure 2a and b shows FTIR spectra of TEPN-1 and TEPN-2,

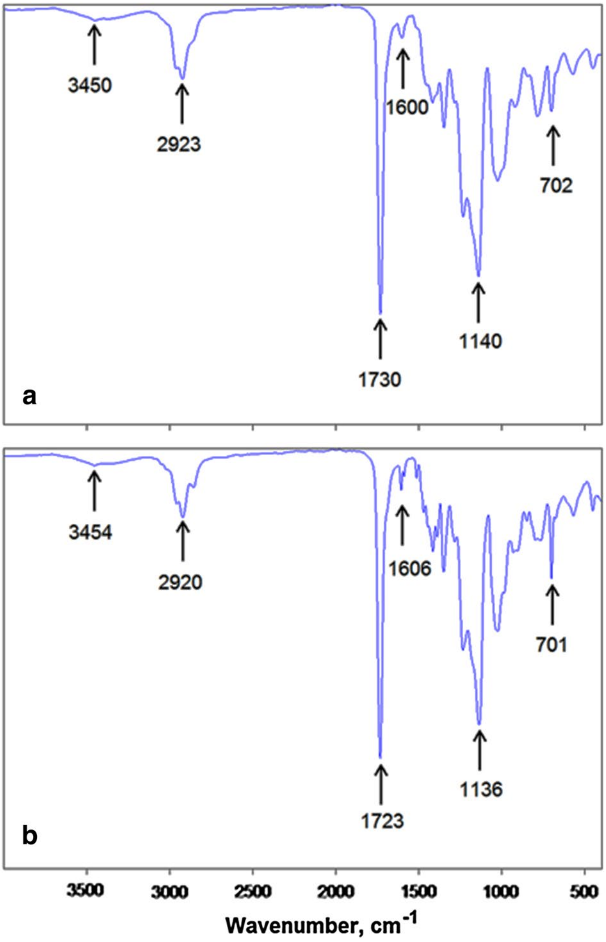


Fig. 2 FTIR spectrum of **a** TEPN-1 **b** TEPN-2

Table 1 Elemental (CHSO) analysis of TEPN-1 and TEPN-2

	C%		H%		S%		O%	
	Theo	Exp	Theo	Exp	Theo	Exp	Theo	Exp
TEPN-1	60.67	60.70	6.97	7.52	16.20	15.41	16.16	16.37
TEPN-2	59.32	60.07	6.47	7.17	17.12	15.78	17.09	19.98

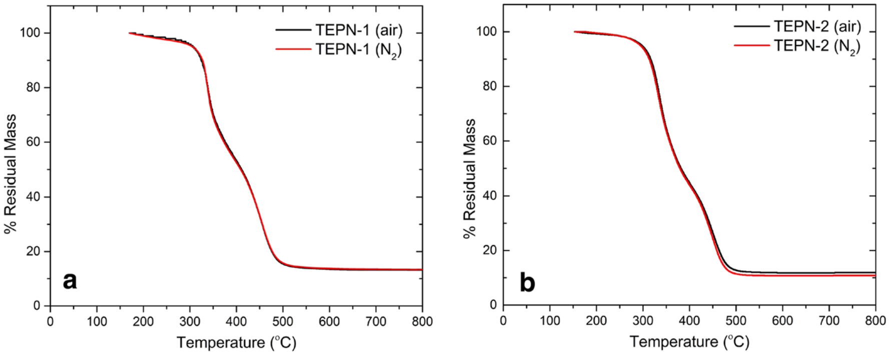


Fig. 3 Thermogravimetric curves of **a** TEPN-1 **b** TEPN-2 under N_2 and air atmosphere

respectively. As reported in the literature, the absorption peak of S–H stretching band in the thiol-containing reactants is located at 2570 cm^{-1} [12, 33]. After the thiol-ene reaction, as shown in Scheme 1, this mercapto group (–S–H) is converted to sulfide bonds (–C–S–) which results a disappearance of S–H stretch in FTIR spectrum. In both Fig. 2a and b, there is no peak around 2570 cm^{-1} which indicates mercapto groups are transformed into sulfide groups and suggests the completion of the thiol conversion [34, 35]. The FTIR spectrum in Fig. 2a shows the characteristic C=O, C–O–C (symmetric and asymmetric stretching vibrations), and C-S bands of TEPN-1 at 1730, 1230 (symmetric), 1140 (asymmetric) and 702 cm^{-1}, respectively. The intense peak between 2800 and 3000 cm^{-1} corresponds to aliphatic C–H stretching, and the broad signal above 3000 cm^{-1} is for aromatic C–H stretching. A similar spectrum in Fig. 2b was recorded for TEPN-2, and the typical vibration peaks for aromatic and aliphatic C–H, C=O, C–O–C and C–S are at above/below 3000, 1723, 1140 and 702 cm^{-1}.

Table 1 shows the elemental content of TEPN-1 and TEPN-2. The results obtained from instrumental elemental analysis of TEPN-1 and TEPN-2 are in convenience with theoretical calculations which further supports desired polymeric network.

Thermal stability of TEPN-1F and TEPN-2 was measured by thermogravimetric analysis (TGA) under nitrogen and air. TGA curves in terms of percent residual weight of sample with increasing temperature are shown in Fig. 3. Polymeric networks of TEPN-1 and TEPN-2 are thermally stable up to 313 °C and show basically single-step decomposition in both air and inert atmosphere. The Brunauer–Emmett–Teller (BET) measurements showed polymeric networks of TEPN-1 and TEPN-2 are nonporous materials with negligible porosity. BET surface area of TEPN-1 and TEPN-2 was recorded as 0.3483 m^2/g and 0.6369 m^2/g where single point adsorption pore volumes are 0.030991 cm^3/g and 0.034289 cm^3/g.

Organic solvent uptake

The uptake capacities of TEPN-1 and TEPN-2 against several organic solvents which are frequently used in chemical industry were examined. The uptake capacities are listed in Table 2. Figure 4 shows graphical representation of solvent uptake capabilities of TEPN-1 and TEPN-2.

According to these results, TEPN-1/TEPN-2 has the highest uptake capacity of chloroform and DCM (aliphatic chlorinated solvents) with 13.717/11.646 $g.g^{-1}$ and 9.216/7.522 $g.g^{-1}$, respectively. In our previous work, we reported the uptake capacity of chloroform and DCM as 1.1055 and 2.3875 $g.g^{-1}$, respectively, by using

Table 2 Solvent uptake capacities of TEPN-1 and TEPN-2

Solvents	Removal capacities, $g.g^{-1}$	
	TEPN-1	TEPN-2
Chloroform	13.7167	9.2159
Dichloromethane (DCM)	11.6460	7.5220
Tetrahydrofuran (THF)	5.5603	3.1027
Dioxane	5.4636	4.9288
Aniline	5.4289	5.0838
Benzonitrile (BN)	5.2942	5.2942
1,2-Dichlorobenzene (DCB)	5.1907	5.2384
Pyridine	4.9212	4.6858
Chlorobenzene (CB)	4.3374	2.6790
Benzene	2.6091	0.8809
Dimethylsulfoxide (DMSO)	2.2920	0.0026
Diphenyl ether (DPE)	2.1608	0.5678
Toluene	1.9984	0.8292
Dimethylformamide (DMF)	1.8230	2.1081
Ethyl acetate (EA)	1.2433	0.5505
Xylene	1.2122	1.2122
Propylene glycol (PG)	0.9938	0.9938
Ethylene glycol (EG)	0.9400	0.6994
Acetone	0.7585	0.4215
Methanol	0.4556	0.2197
Acetonitrile (AcCN)	0.4023	0.3912
Octadecene (OD)	0.3799	0.2805
Hexane	0.3436	0.2114
Ethanol	0.2851	0.1953
Propanol	0.2261	0.1593
Water	0.1646	0.1888

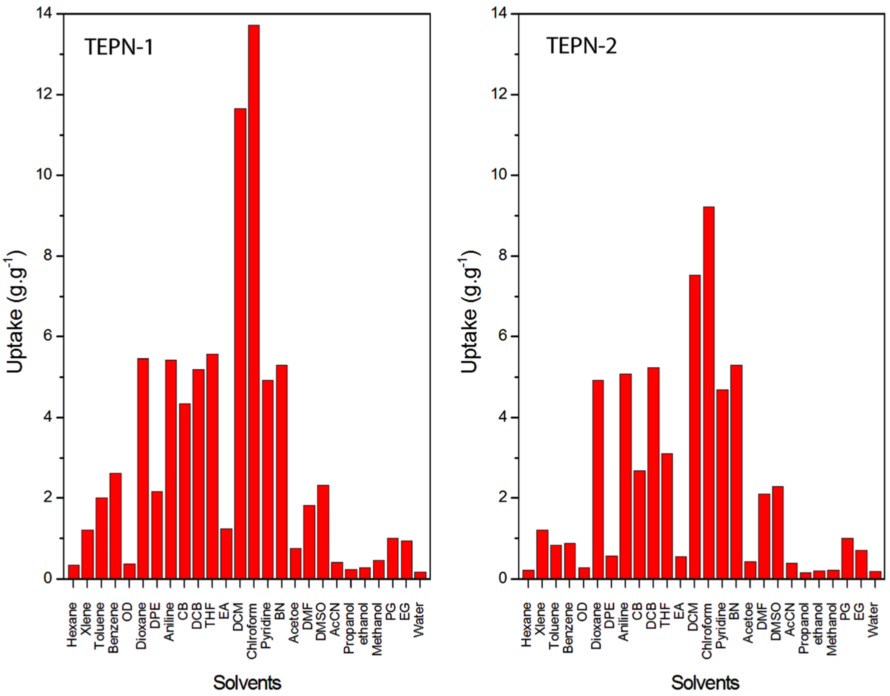


Fig. 4 Solvent uptake capacities of TEPN-1 and TEPN-2

disulfide-linked trimethylolpropane tris(3-mercaptopropionate) (COP65) and pentaerythritol tetrakis(3-mercaptopropionate) (COP66)-based polymer networks [12]. Also, in the literature, porous networks were reported to have much lower uptake capacities such as 2.46 g.g^{-1} for DCM uptake, 3.38 g.g^{-1} for chloroform uptake, 0.14 g.g^{-1} for DCM [36–38]. In this new system, we introduced a benzene ring in TEPN-1 and TEPN-2 network structures. This benzene unit creates an extra π-system in the network. We assume that the lone pair electrons (n-type) of chlorine atom in the chlorinated solvents could make lone pair-π interaction with benzene units in the TEPN networks as reported in the literature [39, 40]. Therefore, TEPN-1

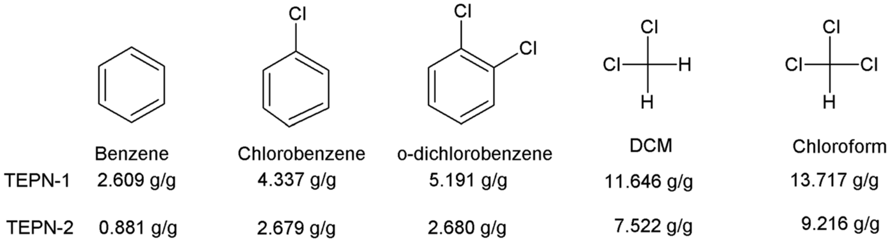


Fig. 5 Comparative representation of uptake capacities of TEPN-1/TEPN-2 against benzene and chlorosolvents

and TEPN-2 show great uptake values of chlorinated solvents (Fig. 5) than COP network reported in our previous work. The uptakes of aromatic chlorinated solvents such as chlorobenzene and dichlorobenzene by TEPN-1/TEPN-2 are 4.337/2.679 and 5.191/5.238 g.g^{-1}, respectively, which much better than unchlorinated or pure benzene (2.609/0.881 g.g^{-1}). However, the uptakes of aromatic chlorinated solvents are much below than aliphatic chlorinated ones which could be due to the delocalization of lone pair electrons through benzene ring in the aromatic chlorinated solvents.

Uptake values of TEPN-1/TEPN-2 for aromatic solvents such as benzene, toluene, aniline, benzonitrile and pyridine are 2.609/0.881 g.g^{-1}, 1.998/0.829 g.g^{-1}, 5.294/5.294 g.g^{-1} and 4.921/4.686 g.g^{-1}, respectively. As expected, TEPN-1 and TEPN-2 are good adsorbent for these aromatic solvents which is due to π–π interaction of aromatic solvents [41] with the benzene unit in these networks. TEPN-1 and TEPN-2 are also effective adsorbents for THF and dioxane which are cycloethers with higher uptake values (5.560/3.103 g.g^{-1} and 5.464/4.929 g.g^{-1} for TEPN-1/TEPN-2, respectively). However, TEPN-1 and TEPN-2 are poor adsorbents for polar solvents (methanol, ethanol, propanol, water less than 0.500 g.g^{-1}). As a result, inserting benzene rings in the network structure greatly increased solvent uptake capacities of polymer networks. TEPN-1 performed better swelling characteristics than TEPN-2, and this could be due to more flexible framework which features from trivalent aliphatic building blocks instead of a tetravalent geometry.

We have shown that TEPN-1/TEPN-2 polymer networks are water-phobic with minimal water uptake. This is a unique property for removal of water-miscible organic solvents such as dioxane, THF and pyridine from their aqueous mixtures. Among these water-miscible solvents, boiling point of dioxane (101.2 °C) is very close to water. Therefore, it is really hard to purify dioxane-water mixture by distillation. In this aspect, the polymer networks we synthesized in this study promise an efficient adsorbent material for dioxane. 1,4-Dioxane which is a cyclic ether is a broad environmental contaminant in industrial fields such as textile, paper processing, cosmetics and electronics because it is a well solvent stabilizer [42]. US Environmental Protection Agency considers dioxane as a human carcinogen (EPA/635/R-09–005-F, 2010) [43, 44]. In this aspect, dioxane removal from industrial waste water streams has particular importance. We carried out further studies to determine solvent uptake efficiency of dioxane, THF and pyridine from

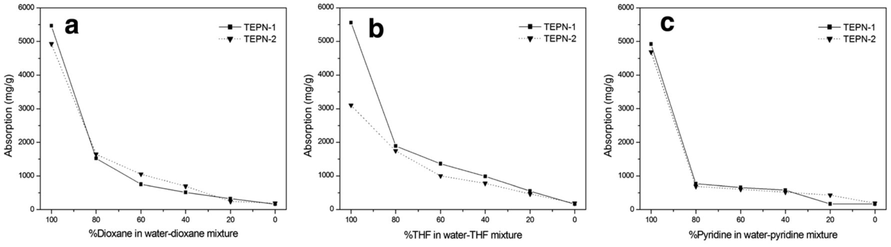


Fig. 6 **a** Dioxane, **b** THF and **c** pyridine uptake from their aqueous mixtures (v/v)

the aqueous mixture of these solvents. Figure 6 shows the solvent uptake efficiency of TEPN-1 and TEPN-2 from their aqueous mixture.

As clearly seen from Fig. 6, uptake of dioxane, THF and pyridine decreases with increasing water content in the mixture for both TEPN-1 and TEPN-2 due to water-phobic nature of organic networks.

Conclusion

We have presented facile single-step synthesis of trivalent and tetravalent organic networks including aliphatic and aromatic parts via thiol-ene chemistry shortly called TEPN-1 and TEPN-2. TEPN-1 and TEPN-2 have remarkable uptake ability to most of organic solvents used in industry especially to chloroform, dichloromethane, dioxane, THF, aniline, chlorobenzene, dichlorobenzene and pyridine within the range of 5.000–14.000 $g.g^{-1}$. These organic networks are water-phobic with minimal water uptake. Therefore, water-miscible organic solvents such as dioxane, THF and pyridine can be removed from industrial waste water stream by TEPN-1 and TEPN-2. Swelling capacities of TEPN-1/TEPN-2 in pure dioxane, THF and pyridine are 546/493%, 560/310% and 492/469%, respectively, while the respective swelling capacities of TEPN-1/TEPN-2 are in 60% aqueous mixture of dioxane/THF/pyridine are 75/105%, 136/100% and 66/60%. Furthermore, the highest swelling capacities are measured against chloroform and DCM for TEPN-1 (1372% and 1165%, respectively). With these features, TEPN-1 and TEPN-2 are excellent materials for removal of most solvents and have potential to treat a mixture which contains chloro-substituent compound(s). These polymeric networks, TEPN-1 and TEPN-2, are thermally stable in oxidative atmosphere.

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