

## Reversely Swellable Porphyrin-linked Microporous Polyimide Networks with Super-adsorption for Volatile Organic Compounds<sup>\*</sup>

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**Abstract** A series of microporous polyimide networks with porphyrin units (Pr-MPIs) were facilely synthesized through a one-step solution polymerization process. Of particular interest is that Pr-MPI-1 containing distorted spirobisindane unit revealed the highest BET surface area (953 m<sup>2</sup>/g), total pore volume (0.75 cm<sup>3</sup>/g), and extreme hysteresis between the N<sub>2</sub> adsorption and desorption isotherm. Further study revealed the prepared Pr-MPI-1 exhibited a synergistic structural effect on exceptional uptake of volatile organic compounds (VOCs) due to the high porosity and highly distorted spirobisindane structure enabled large interface and the swellability. This new approach would open up a facile approach toward the preparation of highly swellable high performance polymeric microporous materials, which are deeply wanted for environment-related applications such as VOCs adsorption and oil/water separation.

**Keywords:** Microporous polyimides; Spirobisindane; Swellability; Adsorption.

### INTRODUCTION

In recent years, the design and synthesis of microporous organic polymers (MOPs) with pore size < 2 nm have attracted tremendous attention in both academia and industry owing to their potential applications in gas storage, separation and catalysis<sup>[1–4]</sup>. The presence of light elements (C, H, N, and O) makes MOPs have extremely lower density than other known porous materials like molecular sieves, and the vast choice of organic building blocks and synthetic strategies allow fine-tuning of the pore capacities and pore microenvironments. Besides, the strong covalent bonding in the polymeric networks would lead to high thermal and chemical stability than their counterparts like metal-organic frameworks, thus, the MOPs are considered as superior porous materials with a great degree of recyclability.

Polyimides are a class of representative high performance polymers with high thermal stability and good mechanical properties, thus are widely used in electronic and engineering areas<sup>[5–7]</sup>. Polyimides can be facilely prepared through polycondensation of bifunctional carboxylic acid dianhydrides and diamines. Because of their excellent thermal stability and chemical resistance, several microporous polyimide networks have been synthesized and used in gas storage, adsorbents and catalysis areas<sup>[8, 9]</sup>.

Porphyrins are an important class of compounds that have unique electronic, optical, photochemical and catalytic properties. Recently, porphyrinic porous organic frameworks have emerged as a new generation of multi-porphyrin architectures; their three-dimensional networks constructed from inter-connected porphyrin unit exhibit not only outstanding thermal and physicochemical stability, but also comparable high surface area and

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pore volumes, which are benefit for potential applications such as gas adsorption, sensing and catalysis. For example, Jiang and Ma synthesized various kind of conjugated porphyrin microporous polymers and metal organic frameworks, and reported their efficiency in the uptake of both amines, CO<sub>2</sub> and catalysis<sup>[10–15]</sup>, Wang *et al.* prepared metalloporphyrin-based CMP nanoparticles that enabling colorimetric detection and quantitation of gaseous SO<sub>2</sub><sup>[16]</sup>, while Mu *et al.* constructed a new metallo-porphyrin CMP with excellent uptake for iodine in gas and liquid<sup>[17, 18]</sup>.

Here we report a facile one-pot approach to the synthesis of a series of porphyrin-linked microporous polyimide networks (Pr-MPIs); of particular interest is the Pr-MPI-1 containing distorted spirobisindane units revealed the highest BET surface area and total pore volume of 953 m<sup>2</sup>/g and 0.75 cm<sup>3</sup>/g, respectively. Besides, Pr-MPI-1 also showed large hysteresis between the N<sub>2</sub> adsorption and desorption isotherm. Further study revealed the prepared Pr-MPI-1 exhibit a synergistic structural effect on exceptional uptake of volatile organic compounds (VOCs) in gas and liquid state due to the high porosity and highly distorted spirobisindane structure enabled a large interface and the swellability.

## EXPERIMENTAL

### Materials

5,10,15,20-Tetra(4-aminophenyl)porphyrin (TAPP) and spirobisindane dianhydride were prepared and purified according to our previous reports<sup>[19]</sup>. Pyromellitic dianhydride, 3,3',4,4'-bipthalic dianhydride, and 4,4'-oxydiphthalic dianhydride were purchased from Shanghai Institute of Synthetic Resins. *m*-Cresol was purified by distillation under reduced pressure and dried with 4 Å molecular sieves.

### One-pot Synthesis of Porphyrin-based Microporous Polyimide Networks (Pr-MPIs)

The Pr-MPIs were synthesized by a one-step solution polymerization method, a typical procedure for Pr-MPI-1 is as follows: In a dry three-necked flask fitted with a mechanical stirrer, gas inlet and condenser, a mixture of TAPP (300 mg, 0.44 mmol) and spirobisindane dianhydride (558.2 mg, 0.89 mmol) in 60 mL *m*-cresol was added, the mixture was stirred for 8 h in an ice bath, then several drops of isoquinoline were added into the solution as base catalyst. The solution was then slowly heated to room temperature and stirred for another 8 h, followed by 80 °C for 4 h, 120 °C for 4 h, 160 °C for 4 h and finally at 200 °C for 10 h to finish the polycondensation process. After cooling, the precipitated solid was isolated and washed successively with ethanol and tetrahydrofuran. The resultant Pr-MPI-1 powder was finally purified in a Soxhlet apparatus with tetrahydrofuran for 24 h and dried at 120 °C under vacuum for 12 h.

Pr-MPI-2, Pr-MPI-3, Pr-MPI-4 were prepared in similar procedures except that the dianhydride was 3,3',4,4'-bipthalic dianhydride, 4,4'-oxydiphthalic dianhydride and pyromellitic dianhydride respectively.

### Characterizations

FTIR spectra were measured with a Nicolet 560 spectrometer. <sup>1</sup>H-NMR spectra were recorded in DMSO-d<sub>6</sub> solution on a 400 MHz Bruker Avance 400 NMR spectrometer. Solid-state nuclear magnetic resonance (<sup>13</sup>C-NMR) spectra were recorded on a Bruker Avance III 500 MHz with a standard 4 mm Bruker MAS Probe at a sample spinning rate of 8.0 kHz. Element analysis was carried out on a Euro EA 3000 elemental analyzer. Powder X-ray diffraction (PXRD) data were collected with an X'Pert Pro MPD diffractometer operated at 30 kV and 15 mA with Cu Kα radiation, from 2θ = 1.5° to 40° with a scanning rate of 1 (°)/min. Scanning electron microscopy (SEM) was conducted with an Inspect F SEM at an accelerating voltage of 20 kV. Transmission electron microscopy observations were performed with a JEM 100CX II transmission electron microscope at an accelerating voltage 80 kV. The nitrogen absorption and desorption isotherms were measured at 77 K using a Tristar system. The samples were degassed at 150 °C for 10 h before the measurement. Surface area was calculated from the adsorption data using Brunauer-Emmett-Teller (BET) method. The pore width distribution curves were obtained from the adsorption branch using non-local density functional theory (NLDFT) method. The thermal properties were measured using a thermo gravimetric analysis (TGA) instruments (SDT Q600) over the temperature range of 33 °C to 800 °C with a heating rate of 10 K/min.

### Vapor Adsorption Measurement of Pr-MPIs

All vapor absorption capacities were evaluated at 30 °C and 0.1 MPa for 24 h. The increment in weight was utilized to evaluate the absorption capacity according to the followed formula:

$$\text{Adsorption capacity (wt)} = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  were the weight of wet and dry samples, respectively.

### Liquid Adsorption Measurement of Pr-MPIs

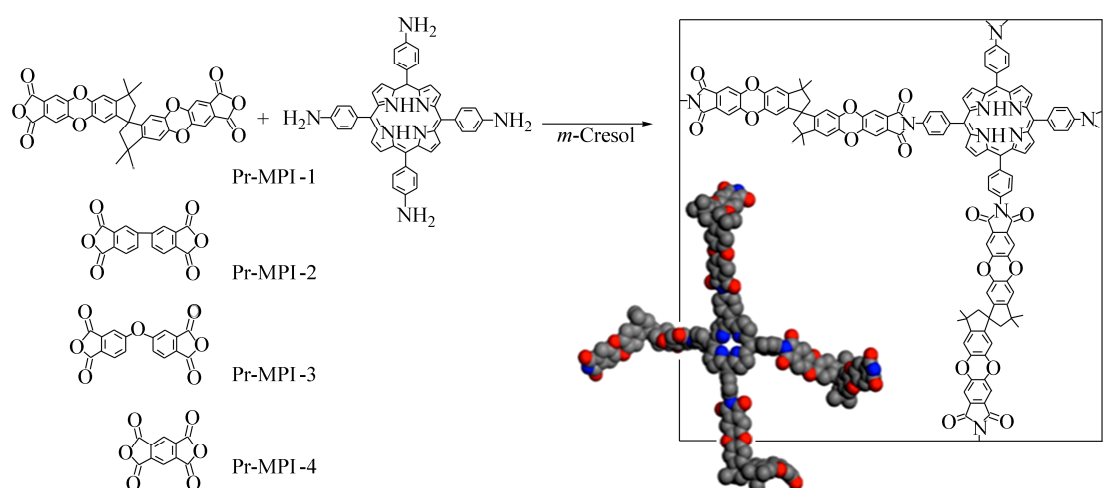
Liquid adsorption experiments were carried out at ambient condition, Pr-MPIs were immersed in the liquid for 10 min, after that, the wet samples were centrifuged out and weighted at once ( $W_{\text{wet}}$ ). The increment in weight was utilized to evaluate the adsorption capacity according to the followed formula:

$$\text{Adsorption capacity (wt)} = (W_{\text{wet}} - W_{\text{dry}}) / (W_{\text{dry}} - W_{\text{tube}})$$

where  $W_{\text{tube}}$  was the weight of a tube as a container of samples and liquid.

## RESULTS AND DISCUSSION

The synthesis route of the Pr-MPIs is displayed in Scheme 1. When the reaction temperature was heated to 80 °C, a color-changing of the mixture from dark purple to green could be observed, it is mainly due to the formation of polyamic acid intermediate, meanwhile, an increase in the solution viscosity was also observed. After further imidization at higher temperatures, the mixture finally changed to purple red color.



**Scheme 1** Synthesis route of porphyrin-linked microporous polyimide networks (Pr-MPIs)

The successful preparation of Pr-MPIs was confirmed by FTIR and solid-state  $^{13}\text{C}$ -NMR. The FTIR spectra of the polyimide networks were shown in Fig. 1(a), all of the four Pr-MPIs exhibit apparent absorption peaks at  $1778\text{ cm}^{-1}$  and  $1726\text{ cm}^{-1}$  which resulted from the characteristic symmetric and asymmetric vibration of  $\text{C}=\text{O}$  groups in five-membered imide rings, the stretching vibration of  $\text{N}-\text{C}-\text{N}$  can also be observed at  $1369\text{ cm}^{-1}$ . Meanwhile, the characteristic band at around  $1846\text{ cm}^{-1}$  corresponding to the  $\text{C}=\text{O}$  group in anhydride monomer totally disappeared. Additionally, for Pr-MPI-1, there are several weak absorption peaks from  $2854\text{ cm}^{-1}$  to  $2962\text{ cm}^{-1}$ , which are belonged to the characteristic bands of methyl and methylene groups of spirobisindane dianhydride monomers. The absorption at  $1278\text{ cm}^{-1}$  is attributed to the ether band in 4,4'-oxydipthalic dianhydride.

In solid-state  $^{13}\text{C}$ -NMR spectra, the polymeric structure of the networks caused significant broadening of the occurring peaks (Fig. 1b), it is difficult to assign every individual signals. The characteristic peak of the carbonyl carbon in five-membered imide ring appeared at around  $\delta = 170$ , the signal around  $\delta = 145$  is attributed

to the carbon adjacent to the nitrogen atom. The overlapping peaks at  $\delta = 124$  to  $\delta = 136$  belong to the aromatic carbons in phenyl rings and porphyrin rings. While, in the case of Pr-MPI-1, the alkyl carbons in the spirobisindane structure are clearly identified at  $\delta = 62, 47$  and  $34$ .

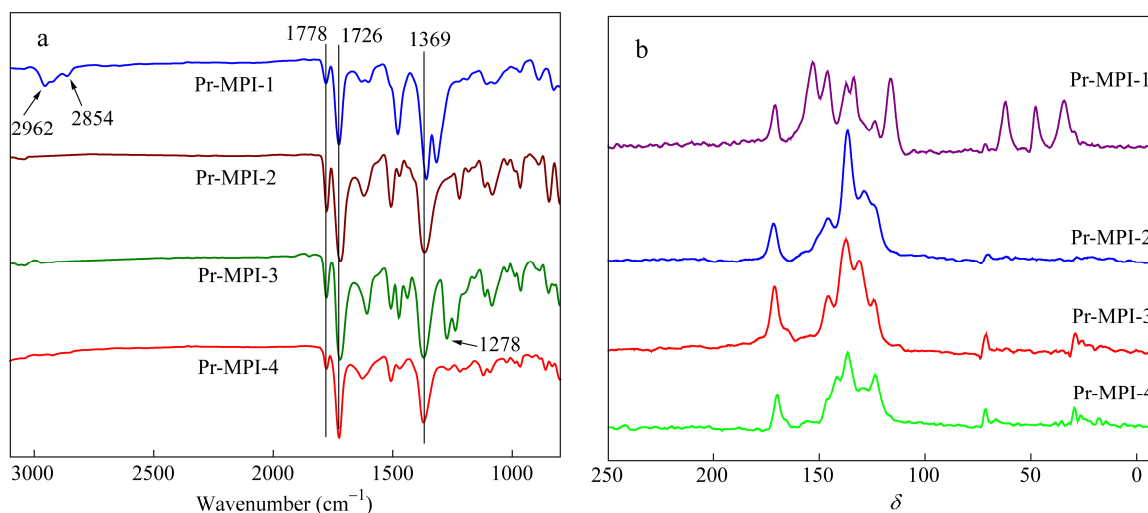


**Fig. 1** (a) FTIR spectra and (b) solid state <sup>13</sup>C-NMR spectra of porphyrin-linked microporous polyimide networks Pr-MPI-1, 2, 3 and 4 respectively

The morphologies of the prepared Pr-MPIs were observed by field-emission scanning electron microscopy. All of the four kinds of polyimide network samples were composed of loosely agglomerated nanoparticles with rough surface and irregular shape (Fig. 2).

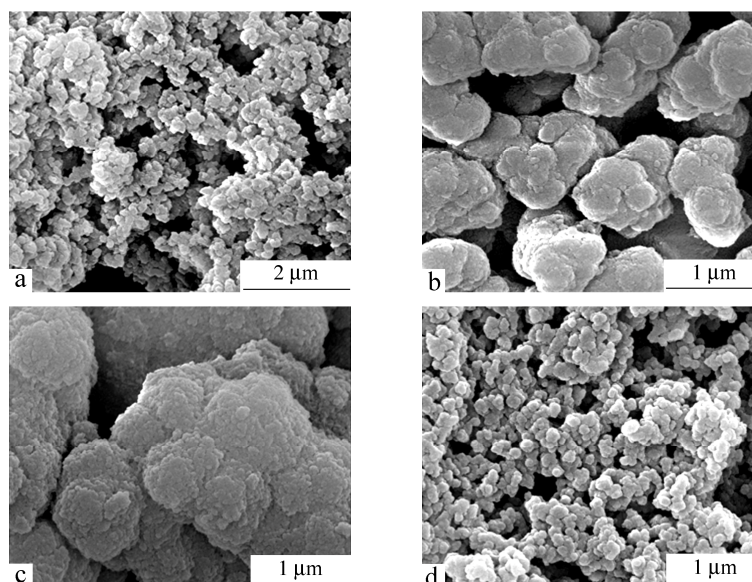


**Fig. 2** The SEM images of the as prepared porphyrin-linked microporous polyimide networks: (a) Pr-MPI-1, (b) Pr-MPI-2, (c) Pr-MPI-3 and (d) Pr-MPI-4

It is quite important to consider the chemical and thermal stability of the prepared Pr-MPIs for their potential applications in tough environments. Polyimides are a class of representative high-performance polymers with extremely high thermal stability; all of the prepared Pr-MPIs can't be dissolved in any organic

solvents, suggesting their hypercrosslinked network structures. The thermal stabilities of the Pr-MPIs were evaluated by thermogravimetric analysis (TGA) under a nitrogen atmosphere from room temperature to 800 °C, the results are presented in Fig. 3. All of the four Pr-MPIs exhibit high decomposition temperature above 500 °C, indicating their excellent thermal resistance. The char yields at 800 °C are 56 wt%, 65 wt%, 60 wt% and 61 wt% for Pr-MPI-1, Pr-MPI-2, Pr-MPI-3 and Pr-MPI-4, respectively.

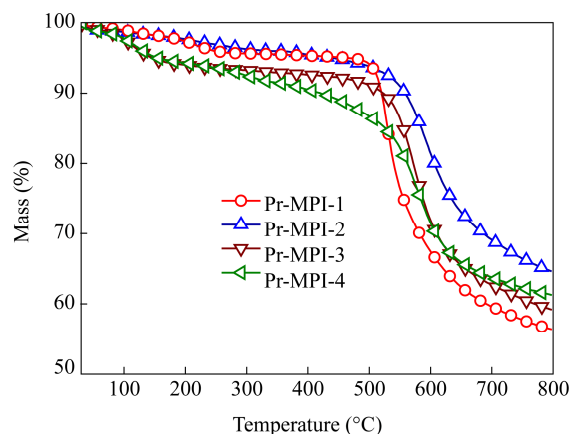


**Fig. 3** TGA curves of the as prepared porphyrin-linked microporous polyimide networks

The permanent porosities of the four Pr-MPIs were determined by nitrogen sorption measurements at 77 K. The sorption isotherms and pore distribution curves are shown in Fig. 4. The isotherms of Pr-MPI-1, Pr-MPI-2, Pr-MPI-3 and Pr-MPI-4 all exhibited a steep rise at low relative pressure ( $P/P_0 < 0.01$ ,  $P$  is partial vapour pressure of adsorbate gas in equilibrium and  $P_0$  is saturated pressure of adsorbate gas.) indicating their microporous characteristics. Additionally, at medium relative pressure ( $0.2 < P/P_0 < 0.8$ ), there is a slight rise in the four sorption isotherms, meaning that these materials also contain mesoporous structures. The existence of macropores in Pr-MPI-1 and Pr-MPI-4 were certified by the rise of their sorption isotherms at high relative pressure ( $P/P_0 > 0.8$ ). The calculation using density function theory (DFT) method based on the sorption isotherm data shows that the majority of the BET surface areas of these microporous polyimides were contributed by the micropores with pore size in the vicinity of 1.5 nm.

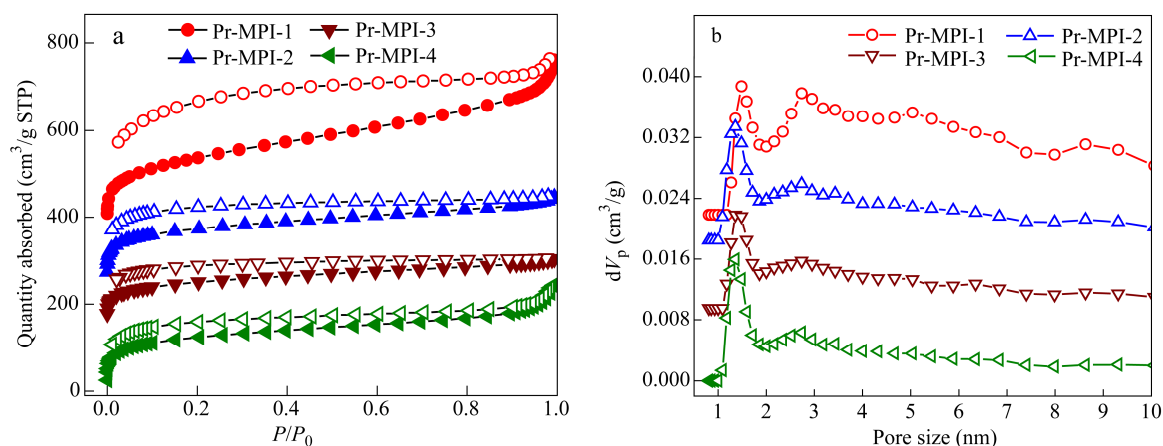


**Fig. 4** (a) Nitrogen adsorption and desorption isotherms measured at 77 K; (b) Pore size distribution curves by DFT model on the nitrogen adsorption isotherms of Pr-MPIs

In our study, four dianhydride monomers with different geometry configurations were selected as building blocks. The surface properties of their corresponding microporous polyimides are summarized in Table 1. In Pr-MPI-1, a spirobisindane strut was introduced into the polymer networks to ensure that the adjacent porphyrin units are orthogonal to each other and can't effectively stack together, therefore, it is liable to generate large amount of pores in the networks. Indeed, the Pr-MPI-1 has the highest BET surface area and total pore volume of 953 m<sup>2</sup>/g and 0.75 cm<sup>3</sup>/g respectively. On the contrary, Pr-MPI-2, Pr-MPI-3 and Pr-MPI-4 have apparently lower BET surface areas and total pore volumes of 653 m<sup>2</sup>/g and 0.39 cm<sup>3</sup>/g, 522 m<sup>2</sup>/g and 0.30 cm<sup>3</sup>/g, and 673 m<sup>2</sup>/g and 0.47 cm<sup>3</sup>/g respectively, mainly because of the  $\pi$ - $\pi$  stacking between porphyrin rings. Thus it is reasonable to conclude that the dramatically enhanced BET surface area in Pr-MPI-1 is mainly due to the existence of spirobisindane strut in the polymer networks.

In addition, all the sorption isotherms show hysteresis loop. Among them, Pr-MPI-1 shows the most particular loop, this is attributed to the swelling effect of the polymer networks in liquid nitrogen, similar phenomena have been reported for other porous polymer network materials. The large hysteresis loops revealed the flexible characteristic and strong interaction between nitrogen and pore surface.

**Table 1.** Porosity parameters of the four Pr-MPIs gained from nitrogen adsorption isotherms

| Samples  | $S_{\text{BET}}$ (m <sup>2</sup> /g) | $S_{\text{micro}}$ (m <sup>2</sup> /g) | $V_{\text{total}}$ (cm <sup>3</sup> /g) |
|----------|--------------------------------------|----------------------------------------|-----------------------------------------|
| Pr-MPI-1 | 953                                  | 516                                    | 0.75                                    |
| Pr-MPI-2 | 653                                  | 495                                    | 0.39                                    |
| Pr-MPI-3 | 522                                  | 340                                    | 0.30                                    |
| Pr-MPI-4 | 673                                  | 522                                    | 0.47                                    |

The use of microporous polymers with high surface areas for the adsorption and separation of toxic gases and liquids provides many merits over the traditional methods. Among the four polyimide networks prepared, the Pr-MPI-1 has the highest BET surface area, besides, Pr-MPI-1 is unique in that it exhibits interesting large hysteresis loop in the sorption isotherm curve, which indicates that the polyimide skeletons are highly swellable. The swellability of Pr-MPI-1 should dramatically enhance its capacity to a super absorption regime. All of these characteristics prompted us to evaluate its adsorption capabilities for gases and liquids of toxic volatile organic compounds. The vapor adsorption of Pr-MPI-1 for various VOCs at 30 °C is displayed in Fig. 5(a). The adsorbed amounts by Pr-MPI-1 for benzene, toluene, xylene, *n*-pentane, and cyclohexane are 1.13, 1.20, 0.84, 0.85 and 1.01 g/g Pr-MPI-1, respectively (Fig. 5a), and thus showed high uptake capacities for VOC vapors.

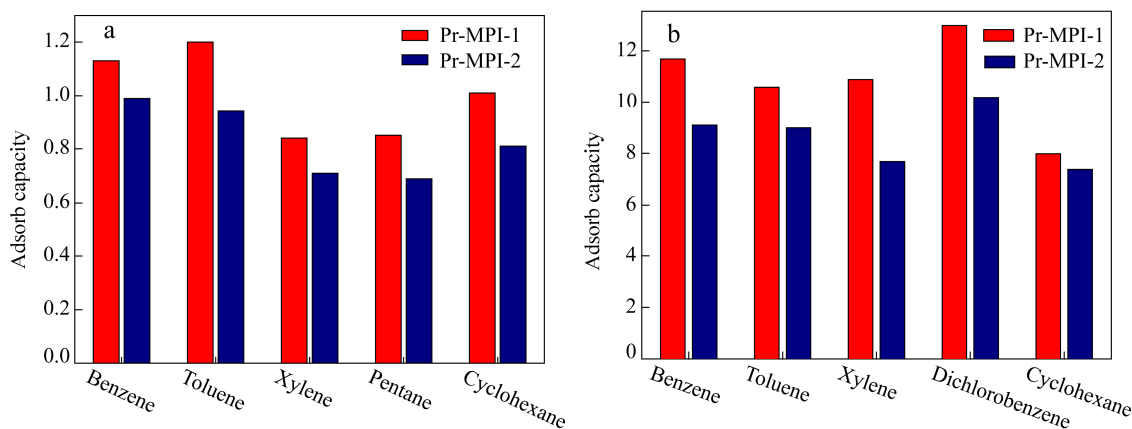


**Fig. 5** (a) Gases and (b) liquids adsorption of various volatile organic compounds by microporous polyimide networks Pr-MPI-1 and Pr-MPI-2

Besides, we can see the Pr-MPI-1 with a spirobisindane based distorted structures showed higher adsorption capacity than that of Pr-MPI-2. We also assessed the adsorptive capacities of Pr-MPI-1 for the VOCs in the liquid state (Fig. 5b), 1 g of the Pr-MPI-1 sample can adsorb around 11.7 g benzene, 10.6 g toluene, 10.9 g xylene, 13.0 g dichlorobenzene and 8.0 g cyclohexane. Thus the Pr-MPI-1 with high porosity and high swellability shows high adsorption capacities for both vapor and liquid VOCs.

The Pr-MPI-1 exhibits surface hydrophobicity due to their aromatic frameworks, besides, it exhibits large hysteresis loops in the sorption isotherm curves, which indicate that the porous skeletons are highly swellable. Indeed, when 100 mg Pr-MPI-1 powder samples were added to a plastic tube containing 0.5 mL toluene liquid, the powder swelled with the volume increased significantly (Fig. 6a). The swollen sample remained on the top of the tube even when the tube was turned upside down. The highest BET surface area and hydrophobicity together with its exceptional swell ability affords Pr-MPI-1 great potential for use in the cleanup of oil spill in water. As a proof-of-concept experiment, we revealed Pr-MPI-1 can be used to separate the mixed toluene/water solution (Fig. 6b), thus it has potential application in oil-spill treatment.

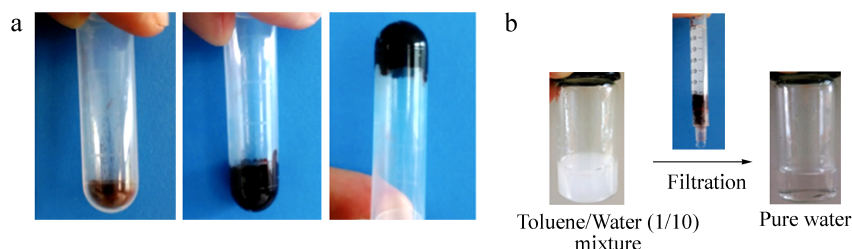


**Fig. 6** Digital photos of (a) Pr-MPI-1 before and after the uptake of toluene liquid and (b) Pr-MPI-1 used in toluene/water separation

## CONCLUSIONS

In conclusion, four kinds of microporous polyimide networks with porphyrin units were easily prepared from tetra(4-aminophenyl)porphyrin and various aromatic anhydrides, and were characterized in detail. Of particular interest is the Pr-MPI-1 containing distorted spirobisindane units revealed the highest BET surface area and total pore volume of 953 m<sup>2</sup>/g and 0.75 cm<sup>3</sup>/g respectively. The prepared Pr-MPI-1 exhibits a synergistic structural effect on exceptional uptake of VOCs in gas and liquid states. This new result would open up a facile approach toward the preparation of highly swellable high performance microporous polymeric materials, which are deeply wanted for environment-related applications.

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