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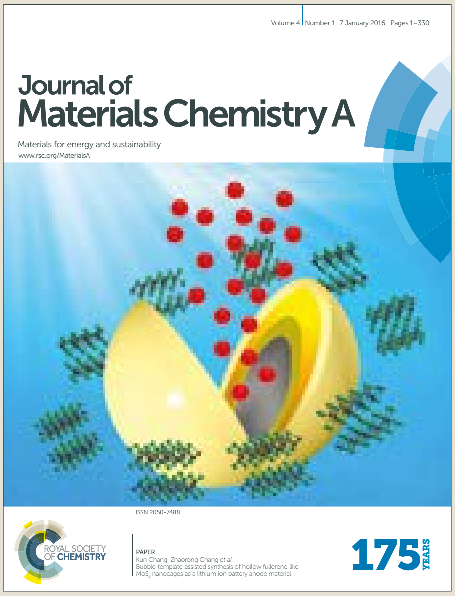

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ARTICLE

# Pillar[5]arene-based 3D network polymer for rapid removal of organic micropollutants from water

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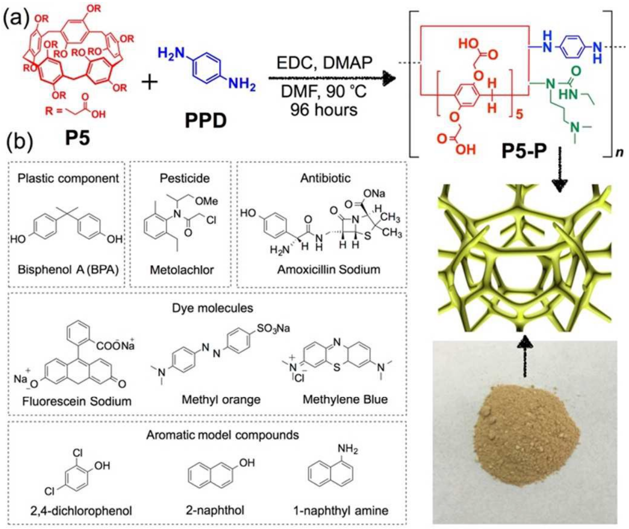
Organic micropollutants are posing great challenges to the global water resources, especially for those non-biodegradable synthetic chemicals. In this study, carboxyl-derivatived pillar[5]arene (**P5**) and *p*-phenylenediamine (**PPD**) were crosslinked to produce a 3D network polymer **P5-P** for the adsorption and removal of organic micropollutants from water. This 3D network polymer sequesters a variety of organic micropollutants in water with rapid adsorption rates and large uptake amounts much greater than those of conventional activated carbon. Especially, this polymer demonstrates superior adsorption performance for fluorescein sodium and methyl orange and it can be fully regenerated multiple times by a mild washing procedure. The structure of this 3D network polymer and its adsorption mechanisms have been clarified by solid-state nuclear magnetic resonance (NMR). The excellent pollutant removal ability demonstrates the promise of the pillar[5]arene-based 3D network polymer for rapid waste-water treatment.

## Introduction

Organic micropollutants such as pharmaceuticals, hormones, pesticides and industrial chemicals circulating in water systems may have detrimental effect on human health and aquatic ecosystems even at very low concentrations.[1] Many of these organic micropollutants, in particular aromatic compounds, are biologically non-degradable because of their synthetic origins.[2] The development of rapid, efficient and economical chemical and physical water-treatment processes is an urgent task for the global scientific community including materials chemists. Among various treatment methods such as chemical oxidation, filtration, adsorption, coagulation, and flocculation, the adsorption technique is usually preferred considering efficiency, simplicity, and versatility.[3] However, for many hydrophilic micropollutants in water, the performance of activated carbon (AC), the most commonly used adsorbent, is suboptimal.[4] Furthermore, the regeneration process of activated carbon, e.g. heating up to 500–900 ºC, is energy intensive and often unable to fully restore the original performance.[5] Therefore, it is still a great challenge to design and synthesize renewable adsorbent materials with rapid adsorption and large uptake for the removal of organic micropollutants from water.

Here we show that the challenge of removing hydrophilic micropollutants can be tackled via the emerging supramolecular chemistry[6] using a 3D network polymer of a pillar[5]arene with fine-tuned functionalities. Pillar[*n*]arenes are a new class of macrocyclic compounds composed of *n* hydroquinone units held together by methylene bridges (–$CH_2$–) and they possess unique pillar-shaped architectures with well-defined hollow space.[7] Pillar[*n*]arenes can be conveniently synthesized from inexpensive starting materials and can



**Scheme 1** (a) 3D network polymer derived from amidation reactions between compounds **P5** and **PPD**, a photograph of the polymer product, and cartoon representation of the 3D network structure of **P5-P**; (b) chemical structures of organic micropollutants studied in this work. EDC: 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride; DMAP: 4-dimethylaminopyridine.

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be easily functionalized to achieve a wide range of applications.[8] In this work, a carboxyl-derived pillar[5]arene (**P5**) is crosslinked with *p*-phenylenediamine (**PPD**) to generate a 3D network polymer **P5-P** by taking advantage of the unique pillar-shaped and rigid pillar[5]arene structure (Scheme 1). In addition, this **P5-P** polymer is functionalized with hydrophilic 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) groups to increase its hydrophilicity along with its residual carboxylate groups on **P5**. This polymer can rapidly sequester a variety of organic micropollutants in water with much greater uptake weight ratios and adsorption rates than those of conventional activated carbon. Moreover, the polymer can be conveniently regenerated using a mild washing procedure with no loss in performance. The chemical structure and morphology of **P5-P** were elucidated using solid-state nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy and electron microscopy. We attribute the outstanding adsorption performance to its high density of adsorption centers as well as its favorable swelling capability in water.

## Experimental section

### Synthesis of polymer P5-P

Compound **P5** was prepared according to a published procedure.[9]

In a 500 mL round bottom flask, compound **P5** (1.13 g, 1.00 mmol), *p*-phenylenediamine (**PPD**) (0.320 g, 3.00 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (2 g, 10.0 mmol), 4-dimethylaminopyridine (DMAP) (0.06 g, 0.500 mmol), and DMF (100 mL) were added. The reaction mixture was stirred at 95 ºC for 96 hours under argon. After the reaction, the solvent was removed. The solid was washed with $H_2O$ (100 mL), acetonitrile (100 mL), alcohol (100 mL), and actone (100 mL). Then, the solid was dried under high vacuum to afford the product **P5-P** as a light-yellow powder (1.26 g, 76% yield). The solid FT-IR spectrum of **P5-P** is shown in Fig. 1b. Solid FT-IR (KBr, $cm^{-1}$): 3048 (Ar–H), 2970 (–$CH_2$), 2932 (–$CH_2$), 1680 (–C=O). The solid-state $^{13}$C-NMR spectrum of **P5-P** is shown in Fig. S1. Solid-state $^{13}$C-NMR (298K) δ (ppm): 168.59, 150.41, 133.55, 129.23, 120.24, 114.70, 67.42, 53.48, 44.42, 35.68, 28.34, 14.58. Element Analysis (Table S1): N, 10.16; C, 57.75; H, 6.14.

### Water regain analysis method

Water regain is an important property of the materials for water treatment. **P5-P** were dispersed in deionized water for 1.00 hour and then the wet polymer was filtered by using Whatman filter paper. The polymer was collected and blotted by using additional Whatman filter paper, and then weighed. These experiments were carried out with three replicates to find the average as the water regain of the polymer **P5-P**. The water regain of **P5-P** polymer, which is expressed as the weight percent, was determined from the average of three measurements by using the following equation:

$$Water\ regain = \frac{W_w - W_d}{W_d} \times 100\%$$

in the equation, $W_w$ (mg) and $W_d$ (mg) are the masses of the wet and dry polymers, respectively.

### The efficiency of pollutant removal

The efficiency of pollutant removal (in %) by the adsorbent **P5-P** was determined by the following equation:[10]

$$\%\text{Pollutant removal efficiency} = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

where $C_0$ (mM) and $C_t$ (mM) are the initial and residual concentrations of the pollutants in the stock solutions and filtrates, respectively. Meanwhile, the amount of pollutant bound to the adsorbent was determined by the following equation:[11]

$$q_t = \frac{(C_0 - C_t)M_w}{m}$$

where $q_t$ (mg/g) is the amount of micropollutant adsorbed per gram of adsorbent **P5-P** at time *t* (min). $C_0$ (mmol/L) and *C* (mmol/L) are the initial and residual concentrations of micropollutants in the stock solutions and filtrates, respectively. m (mg) is the mass of adsorbent **P5-P** used in the experiment. $M_w$ (g/mol) is the molar mass of the micropollutant.

### Pseudo-second-order model

The adsorption kinetics can be quantified by using the Ho and McKay's pseudo-second-order model where the apparent rate constant $k_{obs}$ can be obtained.[12]

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_{obs}q_e^2}$$

Here, $q_t$ and $q_e$ are the pollutant uptakes (mg of pollutant per gram of polymer **P5-P**) at time *t* (min) and at equilibrium, respectively; $k_{obs}$ is an apparent second-order rate constant (g $mg^{-1}$ $min^{-1}$). The rate constant $k_{obs}$ can be calculated from the intercept and slope of the plot of $t/q_t$ against *t*. The kinetics study was carried out at the initial adsorbent concentration of 0.100 mM and 298 K.

### The Langmuir adsorption isotherm

The Langmuir adsorption isotherm is shown in the following equation:[13]

$$\frac{1}{q_e} = \frac{1}{q_{max,e}} + \frac{1}{q_{max,e}\,KC}$$

where $q_e$ (mg/g) is the mass amount of the pollutant adsorbed at equilibrium, $q_{max,e}$ (mg/g) is the maximum adsorption amount of the adsorbent at equilibrium, *C* (mmol/L) is the residual pollutant concentration at equilibrium, and *K* (L/mol) is the equilibrium constant.

### Pollutant adsorption and removal experiments

We performed the experiments of pollutant removal at room temperature (25.0 ºC) in water. In the studies involving **P5-P**, the polymer (5.00 mg) was firstly washed with deionized water for 5.00 min and then filtered by a Whatman filter paper. Then, the polymer **P5-P** was transferred to a 10.0 mL round bottomed flask. A pollutant stock solution (0.100 mM, 5.00 mL) was added to the round bottomed flask. The mixture was immediately stirred and the suspension in the flask (1.00 mL) was taken by a syringe at certain intervals and then filtered immediately by using a LABMAX 0.2 µm inorganic membrane filter. UV–vis spectroscopy was used to

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determine the residual concentration of the pollutant in each sample. In the studies about **P5-P** and activated carbon (AC), the adsorbent (0.500 mg) was added to a 10.0 mL round bottomed flask for every test. Then, the stock solution of each pollutant (0.100 mM, 5.00 mL) was added to the flask. The mixture was stirred immediately and 1.00 mL aliquots of the suspension were taken by a syringe at certain intervals and then filtered immediately by using a LABMAX 0.2 μm inorganic membrane filter. UV–vis spectroscopy was also used to determine the residual concentration of the pollutant in each sample. The detection wavelengths were determined by the characteristic absorption peak of each sample: bisphenol A (BPA) (276 nm), metolachlor (213 nm), amoxicillin sodium (224 nm), fluorescein sodium (480 nm), methyl orange (462 nm), methylene blue (683 nm), 2,4-dichlorophenol (2,4-DCP) (284 nm), 2-naphthol (2-NO) (273 nm), and 1-naphthyl amine (1-NA) (305 nm).

### P5-P regeneration experiments

5.00 mg of **P5-P** was firstly soaked in 10.0 mL of deionized water for 5.00 min, and the wet polymer was filtered by a Whatman filter paper. The polymer was then transferred into a 10.0 mL round bottomed flask equipped with a magnetic stir bar, to which a fluorescein sodium/methyl orange stock solution (0.100 mM, 5.00 mL) was added. The mixture was stirred at room temperature for 10.0 min, and then filtered by using a LABMAX 0.2 μm inorganic membrane filter. The residual fluorescein sodium/methyl orange concentration in the filtrate was determined by UV–vis spectroscopy. **P5-P** was regenerated by soaking in DMF (5.00 mL) for 5.00 min and then acetone (5.00 mL) for 5.00 min or soaking in water (10.0 mL) and heated to 65 ºC for 5.00 min and then recovering by filtration and drying under vacuum at 80 ºC.

## Results and discussion

In the synthetic procedure, we crosslinked **PPD** and **P5** with a 3.00:1.00 crosslinking molar ratio and simultaneously introduced the EDC groups with a EDC:**P5** reaction molar ratio of 10.0:1.00. We obtained an optimum yield of 76% in *N,N*-dimethylformamide (DMF) solution at 90 ºC in 96 hours (Scheme 1) according to the elemental analysis result (Table S1). The polymer shows good stability up to 190 ºC as measured by thermogravimetric analysis (TGA) (Fig. 1a).

FT-IR spectra (Fig. 1b) confirmed the crosslinking between **P5** and **PPD** as indicated by the shift of stretching vibration adsorption of –C=O on **P5** from 1736 to 1680 cm$^{-1}$ and also the disappearance of the peaks of –NH$_2$ on **PPD** (3207–3417 cm$^{-1}$). As a further step, we used $^{13}$C and $^{15}$N solid-state NMR[14] to comprehensively elucidate the chemical structure of **P5-P**. In $^{13}$C cross-polarization at magic-angle-spin (CPMAS) spectra in Fig. 1c, 1d, and Fig. S1, the peak at 177.55 ppm of the carboxyl carbon of **P5** shifted upfield to 168.59 ppm, while in $^{15}$N CPMAS spectra shown in Fig. S2, the peak at 129.93 ppm corresponding to amide nitrogen appeared, which confirmed the formation of amide bonds between **P5** and **PPD** after the crosslinking. The peaks related to EDC were also observed in both $^{13}$C CPMAS and $^{15}$N CPMAS spectra of **P5-P**. Comparing to the $^{15}$N CPMAS spectra of EDC, the peak at 198.34 ppm assigned to the imide nitrogen atoms of EDC groups on **P5-P** vanished, providing the direct evidence for the rearrangement of EDC groups on **P5-P**. Furthermore, we determined the molecular composition of the **P5-P** polymer using quantitative $^{13}$C CPMAS spectra.[15] In the final product, the **PPD**:**P5** molar ratio is 3.00:1.00 while the EDC:**P5** molar ratio is 2.00:1.00 (Fig. S1). Based on these results, we clarified the proposed molecular structures of **P5-P** as drawn in Fig. S3.

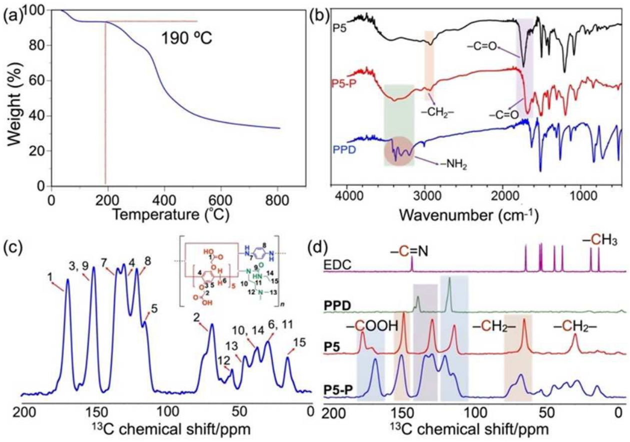

**Fig. 1** (a) Thermogravimetric analysis of polymer **P5-P**; (b) FT-IR spectra of **P5**, **PPD**, and polymer **P5-P**; (c) $^{13}$C CPMAS NMR spectra and the inferred structure of the polymer **P5-P**; (d) $^{13}$C CPMAS NMR spectra of EDC, **PPD**, **P5**, and **P5-P**.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were subsequently carried out to obtain the morphology of the polymer **P5-P**. As shown in Fig. 2, the product prepared in this work has a three-dimensional network structure with the voids ranging from several hundred nanometers to several micrometers. This 3D morphology facilitates the water flow through the polymer **P5-P** and maximizes its contact with micropollutants. In contrast to the common porous materials which possess permanent porosity and high surface area,[16] the **P5-P** polymer described here is nonporous with the surface area ($S_{BET}$) of 7.69 m$^2$/g (Fig. S4). However, **P5-P** is able to retain a decent amount of water, about 74.0% of its weight, which is an indication of favorable hydrophilicity (Table S2).

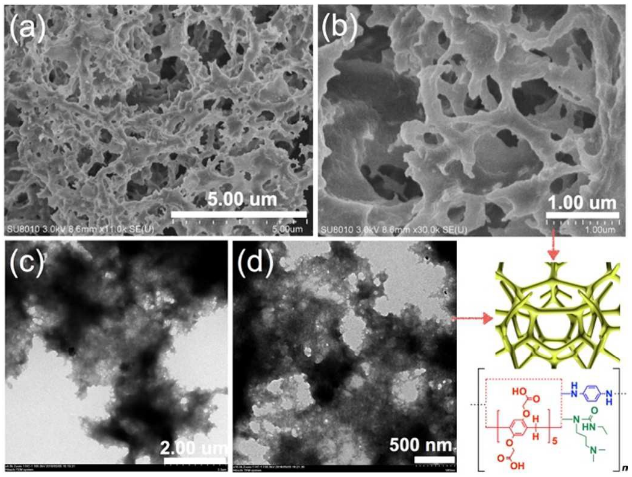

**Fig. 2** (a), (b) SEM images of the 3D network polymer **P5-P**; (c), (d) TEM images of the 3D network polymer **P5-P**.

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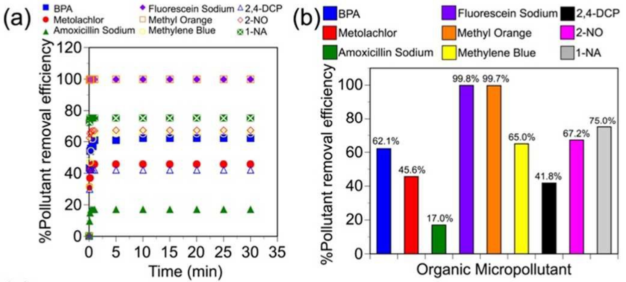
To test the performance of **P5-P** in organic micropollutant removal, we evaluated a series of natural and anthropogenic contaminants with negative consequences on human health and environment (Scheme 1): bisphenol A (BPA), metolachlor, amoxicillin sodium, fluorescein sodium, methyl orange, methyl blue, 2,4-dichlorophenol (2,4-DCP), 2-naphthol (2-NO), and 1-naphthyl amine (1-NA). We submersed 5.00 mg of polymer **P5-P** into an aqueous solution of the selected micropollutant (0.100 mM, 5.00 mL) for 30.0 minutes and used UV–vis absorbance data to calculate pollutant removal efficiency and the pollutant uptake (Fig. S5).



(c)

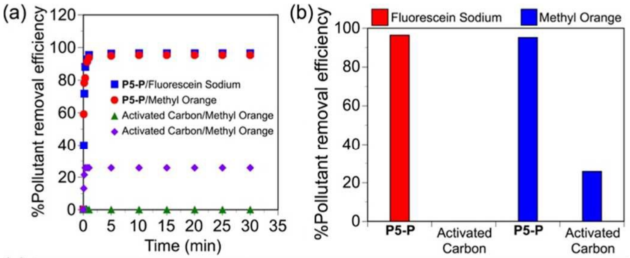
| Pollutant | %Uptake | Uptake $q_e$ (mg/g) |
|---|---|---|
| Bisphenol A | 62.1 | 14.2 |
| Metolachlor | 45.6 | 12.9 |
| Amoxicillin Sodium | 17.0 | 6.80 |
| Fluorescein Sodium$^a$ | 96.4 | 360.8 |
| Methyl Orange$^a$ | 95.2 | 311.6 |
| Methylene Blue | 65.0 | 20.9 |
| 2,4-Dichlorophenol | 41.8 | 6.00 |
| 2-Naphthol | 67.2 | 9.70 |
| 1-Naphthyl Amine | 75.0 | 10.7 |

**Fig. 3** (a) The time-dependent adsorption process of each organic micropollutant (0.100 mM) by **P5-P** (1.00 mg/mL); (b) percentage removal efficiency of each organic micropollutant by **P5-P** determined after the contact time of 30.0 min; (c) the equilibrium uptake percentage and amount of bound micropollutant of **P5-P**. $^a$The amount of the adsorbent used in this study is 0.100 mg/mL.

As shown in Fig. 3, the **P5-P** polymer can effectively remove the organic micropollutants from water with large uptakes. Especially, our results show that **P5-P** can almost completely remove fluorescein sodium (96.4%) and methyl orange (95.2%) from water; the equilibrium uptakes reach 360.8 mg/g and 311.6 mg/g, respectively. Overall, **P5-P** demonstrated a remarkable enhancement on the pollutant removal efficiency than activated carbon, as shown in Fig. 4 and Fig. S6.

Another crucial advantage of **P5-P** is its fast adsorption kinetics. For a flow-through types of water treatment, a fast adsorption of the micropollutants is often the priority. It can be seen in Tables S3 and S4 that the adsorptions of the micropollutants rapidly reach maximum in less than 1.00 min. In the demonstration videos S1–S4, the adsorption processes on fluorescein sodium and methyl orange were recorded. By simple shaking operation, the contaminants were removed from water in the matter of seconds.

The adsorption kinetics can be quantified by using the Ho and McKay's pseudo-second-order model where the apparent rate constant $k_{obs}$ can be obtained (Fig. S7).[17] Values of $k_{obs}$ and correlation coefficient ($R^2$) for each pollutant are then listed in Table S5. The apparent fast rate constants ($k_{obs}$) of **P5-P** for the pollutants enable **P5-P** to be a promising adsorbent for rapid waste-water treatment.

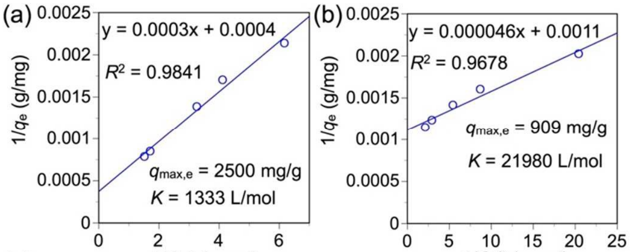


(c)

| Adsorbent | Fluorescein Sodium %Uptake in 30.0 min | Methyl Orange %Uptake in 30.0 min | Fluorescein Sodium Uptake in 30.0 min (mg/g) | Methyl Orange Uptake in 30.0 min (mg/g) |
|---|---|---|---|---|
| P5-P | 96.4 | 95.2 | 360.8 | 311.6 |
| Activated Carbon | 0 | 25.8 | 0 | 84.4 |

**Fig. 4** (a) Time-dependent adsorption of fluorescein sodium and methyl orange (0.100 mM) by **P5-P** and activated carbon (0.100 mg/mL); (b) percentage removal efficiency of fluorescein sodium and methyl orange by **P5-P** and activated carbon obtained after the contact time of 30.0 min; (c) uptake of fluorescein sodium and methyl orange by **P5-P** and activated carbon after the contact time of 30.0 min. The amount of the adsorbent used in this study is 0.100 mg/mL.

Using Langmuir adsorption equation, we obtained the maximum adsorption amounts of the adsorbent at equilibrium for fluorescein sodium and methyl orange.[18] As shown in Fig. 5, the maximum adsorption capacity ($q_{max,e}$) of **P5-P** is 2500 mg/g for fluorescein sodium ($R^2$ = 0.9841) and 909 mg/g for methyl orange ($R^2$ = 0.9678). These results indicated that the adsorption capacities of **P5-P** for fluorescein sodium and methyl orange are superior to those of many previously reported adsorbents as shown in Table S6.[19,20,21]



(c)

| Pollutant | $K$ (L/mol) | $q_{max,e}$ (mg/g) |
|---|---|---|
| Fluorescein Sodium$^a$ | 1333 | 2500 |
| Methyl Orange$^a$ | 21980 | 909 |

**Fig. 5** (a) Langmuir isotherm of fluorescein sodium adsorption by **P5-P**; (b) Langmuir isotherm of methyl orange adsorption by **P5-P**; (c) adsorption equilibrium constants and maximum equilibrium adsorption capacity for fluorescein sodium and methyl orange onto **P5-P**. $^a$The amount of of the adsorbent used in this study is 0.100 mg/mL.

The reusability is an essential property of the adsorbent materials. In contrast to the energy intensive and degradative regeneration processes of activated carbons, the **P5-P** polymer shows exceptional recyclability with a rather simple and energy-conservative regeneration procedure. By simply washing with DMF and acetone

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at room temperature (25.0 ºC), fluorescein sodium and methyl orange could be easily removed from **P5-P**. We performed ten consecutive recycling tests yet **P5-P** exhibited almost no loss in performance (Fig. 6). Furthermore, we can perform five consecutive recycling tests yet **P5-P** exhibited about 30% loss in performance by washing with water at 65 ºC. (Fig. S8) With low synthetic cost and good reusability, **P5-P** is economical and practical for waste-water treatment.

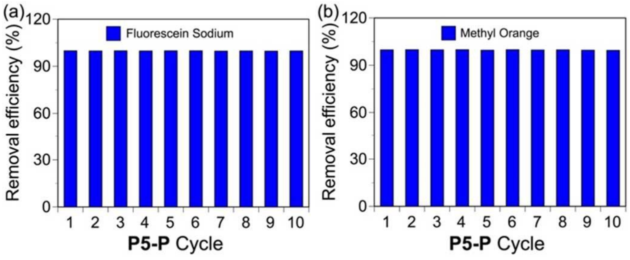

**Fig. 6** The regeneration cycles of **P5-P** after the adsorption of (a) fluorescein sodium and (b) methyl orange by washing with DMF and acetone at room temperature.

The mechanisms accounting for **P5-P**'s high and fast adsorption of fluorescein sodium and methyl orange arise from two aspects. First, the reversible hydrogen bonding interactions between the EDC groups and carboxylate groups on **P5-P** and the negatively charged groups of adsorbates allows the fast, large adsorption and facile recycling. It is verified by $^{15}$N solid-state NMR (Fig. S9) that the signal of the nitrogen atoms related to the **PPD** group showed upfield shift and the signal of the nitrogen atoms of EDC group on **P5-P** became broad after the adsorption of fluorescein sodium. We also investigated the solid-state $^{13}$C-NMR spectra of fluorescein sodium, methyl orange, the as-prepared polymer **P5-P**, and fluorescein sodium or methyl orange adsorbed **P5-P**. As shown in Fig. S10 and S11, the chemical shifts of the dye molecules and the polymer **P5-P** didn't show any significant changes after the adsorption. In order to further confirm the hydrogen bonding interactions between the pollutant molecules and **P5-P**, we performed the pollutant removal experiments at different pH values in water. As shown in Fig. S12 and S13, with the decrease of the pH values, the adsorption efficiencies of **P5-P** towards fluorescein sodium and methyl orange were obviously decreased, which can be attributed to the protonation of the negatively charged groups on the pollutant molecules at low pH values and the decrease of the hydrogen bonding interactions between the pollutant molecules and **P5-P**. Second, the flexible and expandable polymer matrix built on crosslinked pillar[5]arenes allows the full accessibility of all adsorption sites. In the 2D $^{13}$C–$^{1}$H heteronuclear correlation (HETCOR) spectra of **P5-P** treated with fluorescein sodium or methyl orange, the cross peaks (emphasized by red circles in Fig. S14 and S15) between the **P5-P** and adsorbates are clearly observable. This suggests that the adsorbates are well-dispersed into the polymer matrix within the length scale of nanometers. This favorable feature is also inferred by its swelling in water which facilitates the adsorbate diffusion and the exposure of functionalities (Fig. S16). These results indicated that the adsorption of fluorescein sodium and methyl orange were physical adsorption processes and mainly relied on the hydrogen bonding interactions between the pollutant molecules and **P5-P**.

## Conclusions

In summary, a 3D network polymer **P5-P** for the removal of organic micropollutants from water with high adsorption efficiency has been successfully prepared by crosslinking a carboxyl-derived pillar[5]arene and *p*-phenylenediamine. Specifically, the **P5-P** polymer is a superior adsorbent for fluorescein sodium and methyl orange with low synthetic costs, fast uptake kinetics and high removal capacity. In addition, the polymer can be regenerated at least ten times by using a mild washing procedure with no loss in performance. These excellent findings demonstrate that this pillar[5]arene-based 3D network polymer can contribute to the removal of a wide range of micropollutants during water and waste-water treatment. Its potential application can also enrich the field of chemical separation and environmental pollution treatment.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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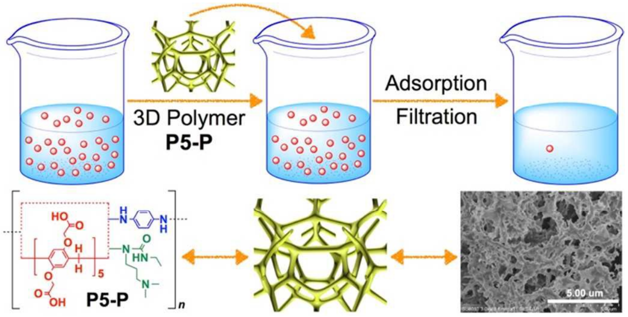
## Toc Graphic:



## Text:

3D network polymer **P5-P** for the removal of organic micropollutants from water with high adsorption efficiency has been successfully prepared by crosslinking a carboxyl-derived pillar[5]arene and *p*-phenylenediamine.