Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information (14 pages)

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

Bingbing Shi,† Hanxi Guan,† Liqing Shangguan, Hu Wang, Danyu Xia, Xueqian Kong* and Feihe Huang*

State Key Laboratory of Chemical Engineering, Center for Chemistry of High-Performance & Novel Materials, Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

Email: fhuang@zju.edu.cn and kxq@zju.edu.cn

1. Materials and instrumentation

All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature.

Solid-state nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER 400WB AVANCE III spectrometer (B0 = 9.4T, lamor frequency 400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C, 40.54 MHz for ^{15}N) with an ^{1}H–^{13}C–^{15}N triple resonance 3.2 mm probe at room temperature. The magic-angle-spin (MAS) frequency was set to 12–17 kHz. ^{13}C cross-polarization at magic-angle-spin (CPMAS) NMR spectra were performed by using a 90º pulse length of 2.29 μs, 2 ms contact time, 2–10s recyle delay (40s recyle delay for **PPD**) with 5000 to 10000 scans. ^{15}N cross-polarization at magic-angle-spin (CPMAS) NMR spectras were recorded at the same condition but more scans. All the 2D ^{13}C–^{1}H correlation experiments were acquired using 10 ms mixing time in order to obtain intermolecular interaction. ^{13}C chemical shifts were referenced directly to adamantane (δ (CH_2) = 38.5 ppm) and ^{15}N chemical shifts were measured relative to Glycine (δ (NH_2) = 34.35 ppm).

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Thermo Nicolet iS10 spectrometer. Transmission electron microscopic investigations were carried out on a HITACHI HT-7700 instrument.

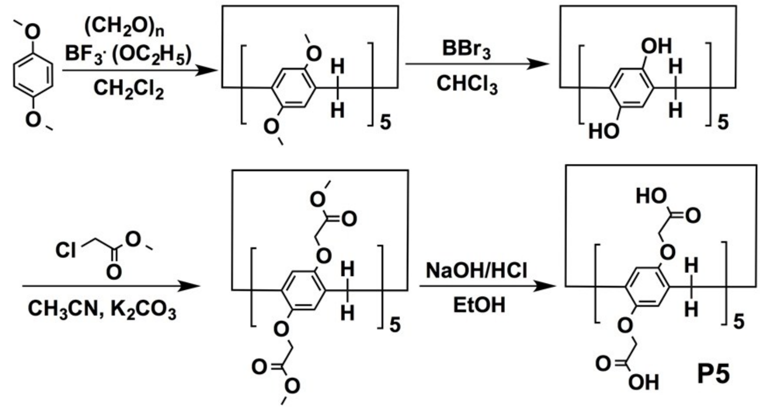
Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument. Elemental analyses were carried out on an EA1112 instrument.

Thermogravimetric Analysis (TGA) was carried out on a DSCQ1000 Thermal Gravimetric Analyzer.

Surface area measurements were conducted on a BELSORP-Max Accelerated Surface Area and Porosimetry Analyzer. The sample (91.3 mg) was degassed at 100 ºC for 12.0 h and then backfilled with N_2. N_2 isotherms were generated by incremental exposure to ultra high purity nitrogen up to 1.0 atm in a liquid nitrogen bath (77.0 K), and surface parameters were determined using BET adsorption models included in the instrument software (BELSORP-Max).

UV–vis spectra were taken on a PerkinElmer Lambda 35 UV–vis spectrophotometer.

2. Synthesis of P5 and quantitative ^{13}C CPMAS NMR spectrum of the P5-P



Scheme S1 The synthetic route of compound **P5**.

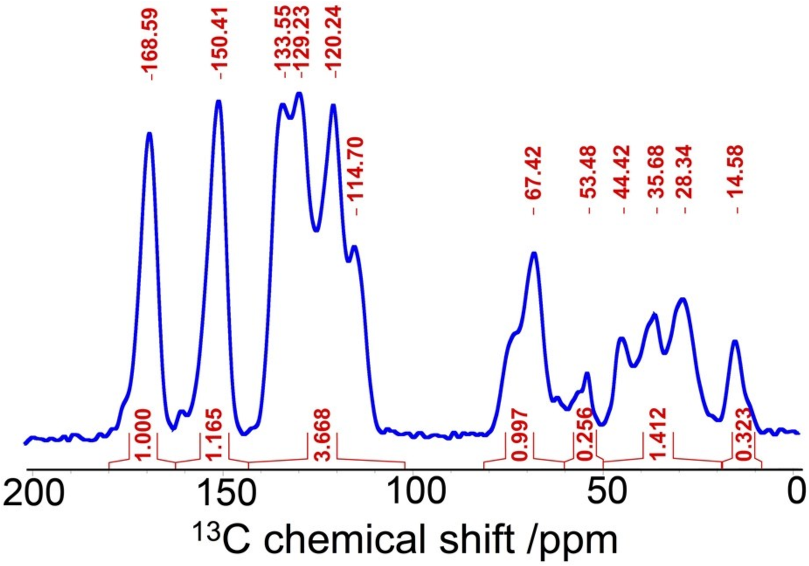


Fig. S1 Quantitative ^{13}C CPMAS NMR spectrum of the **P5-P** polymer. The peaks of the spectrum are assigned and the integrals of the peaks are labeled.

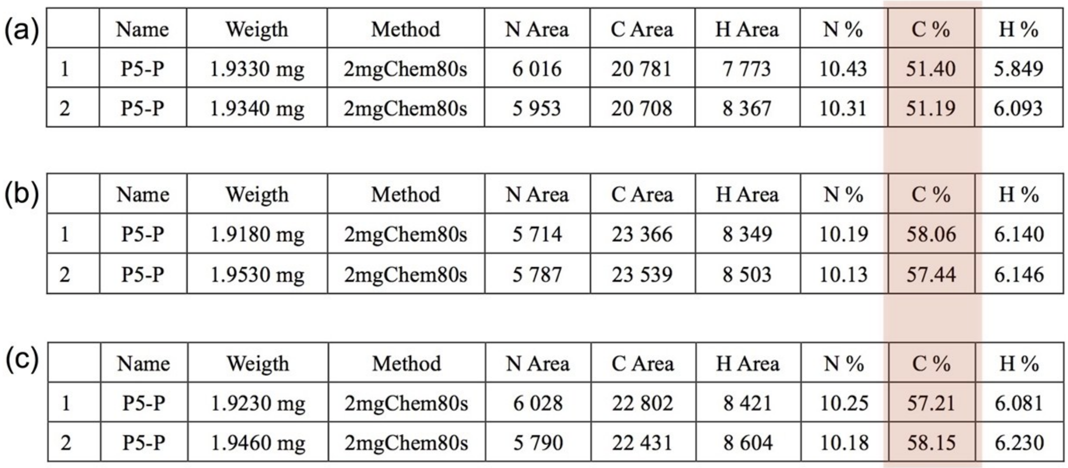
3. SEM sample preparation

SEM samples were prepared by dispersing 2.00 mg of polymer **P5-P** in 10.0 mL of DMF and adding the suspension to the wafer *via* the vacuum freeze-drying methodology.

4. TEM sample preparation

TEM samples were prepared by dispersing 2.00 mg of polymer **P5-P** in 10.0 mL of DMF and adding the suspension to the copper mesh *via* the vacuum freeze-drying methodology.

5. Elemental analysis



(a)

	Name	Weigth	Method	N Area	C Area	H Area	N %	C %	H %
1	P5-P	1.9330 mg	2mgChem80s	6 016	20 781	7 773	10.43	51.40	5.849
2	P5-P	1.9340 mg	2mgChem80s	5 953	20 708	8 367	10.31	51.19	6.093

(b)

	Name	Weigth	Method	N Area	C Area	H Area	N %	C %	H %
1	P5-P	1.9180 mg	2mgChem80s	5 714	23 366	8 349	10.19	58.06	6.140
2	P5-P	1.9530 mg	2mgChem80s	5 787	23 539	8 503	10.13	57.44	6.146

(c)

	Name	Weigth	Method	N Area	C Area	H Area	N %	C %	H %
1	P5-P	1.9230 mg	2mgChem80s	6 028	22 802	8 421	10.25	57.21	6.081
2	P5-P	1.9460 mg	2mgChem80s	5 790	22 431	8 604	10.18	58.15	6.230

Table S1 Elemental analysis data of polymer **P5-P** at different reaction times: (a) 72.0 hours; (b) 96.0 hours; (c) 120 hours.

Elemental analysis was used to track the polymerization reaction progress to determine the optimal reaction time for the preparation of the 3D network polymer. As shown in Table S1, the content of carbon element in the polymer **P5-P** remained constant after the reaction was carried out for 96.0 hours. Therefore, 96.0 hours was considered as the optimum reaction time for the preparation of the 3D network polymer with an optimum yield of 76.0%.

6. Solid-state ^{15}N-NMR spectra of EDC and P5-P

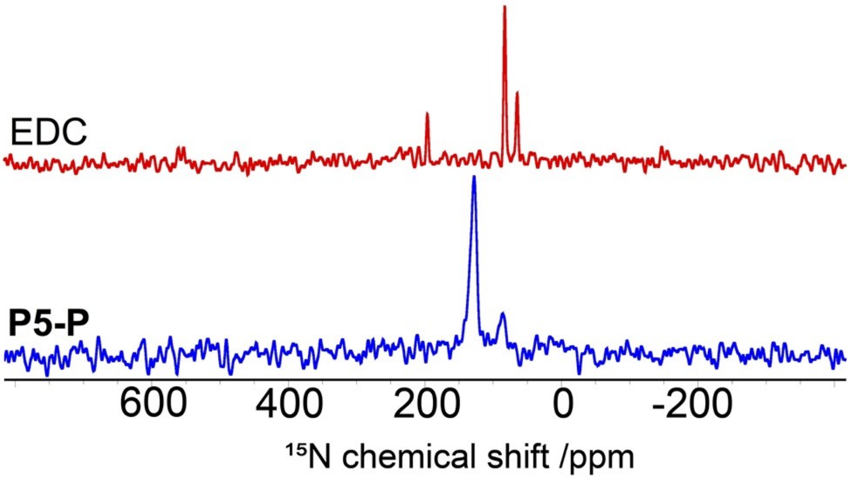


Fig. S2 ^{15}N CPMAS-NMR spectra of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (198.34, 85.07, 66.89 ppm) and **P5-P** (129.93, 88.26 ppm). The vanishing of the peak at 129.93 ppm of **P5-P** confirmed the rearrangement of EDC moiety in the polymer.

7. Proposed molecular structures of P5-P

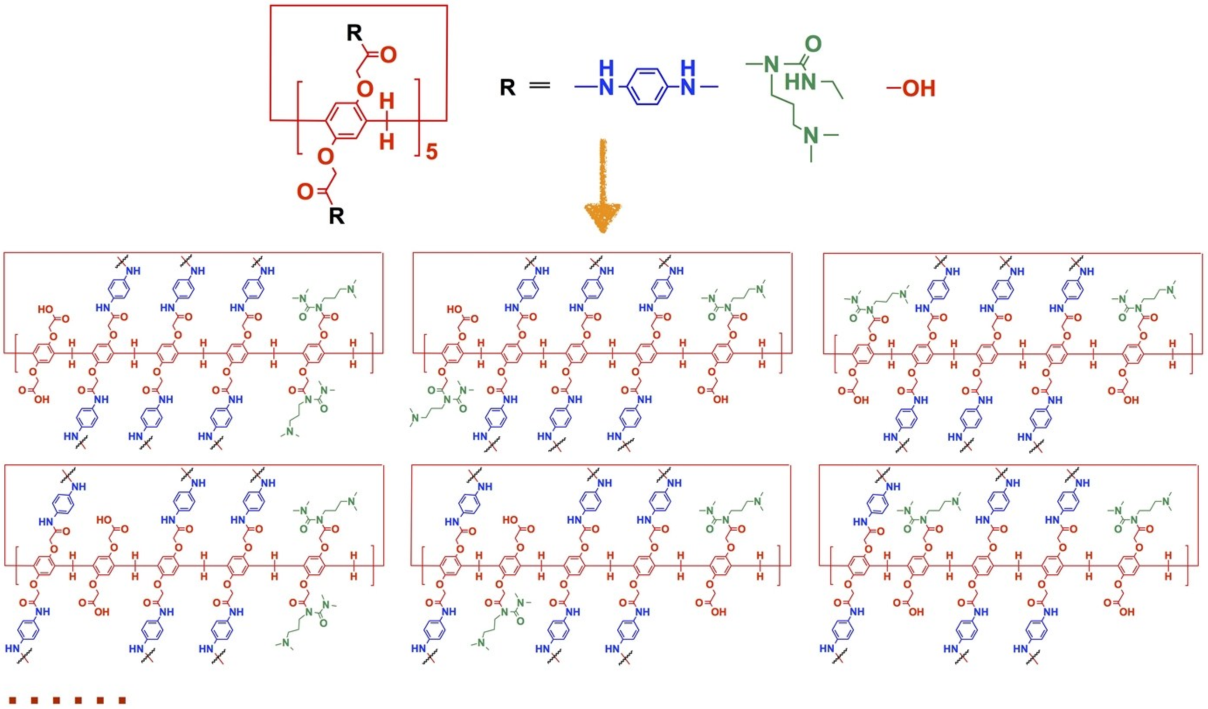


Fig. S3 Proposed molecular structures of 3D network polymer **P5-P** crosslinked by the amidation reaction between **PPD** and **P5**. The **PPD**:**P5** molar ratio is 3.00:1.00 and EDC:**P5** molar ratio is 2.00:1.00.

8. Porosity and surface area measurements for P5-P

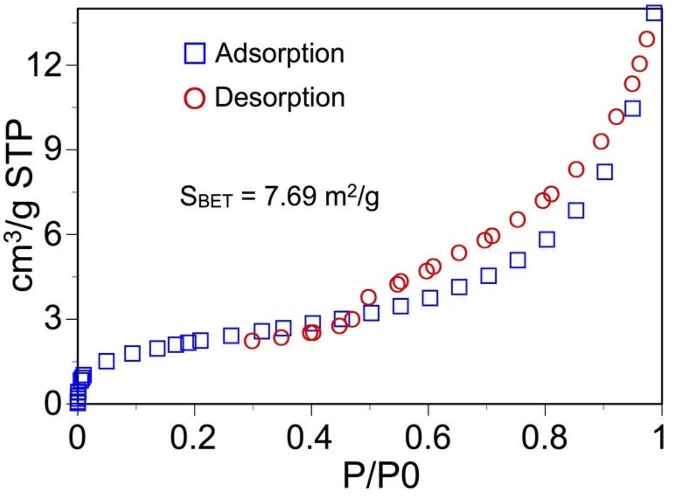


Fig. S4 N_2 sorption isotherm (77.0 K) and surface area data analysis of polymer **P5-P**.

9. Water regain analysis

W_d	W_w	Water regain
3.95 mg	6.85 mg	73.4%
3.96 mg	6.83 mg	72.3%
3.90 mg	6.88 mg	76.4%

Table S2 Water regain analysis of polymer **P5-P**. The water regain (expressed as weight percent) of the polymer **P5-P** was determined from the average (74.0%) of three measurements.

10. Adsorption of different pollutants

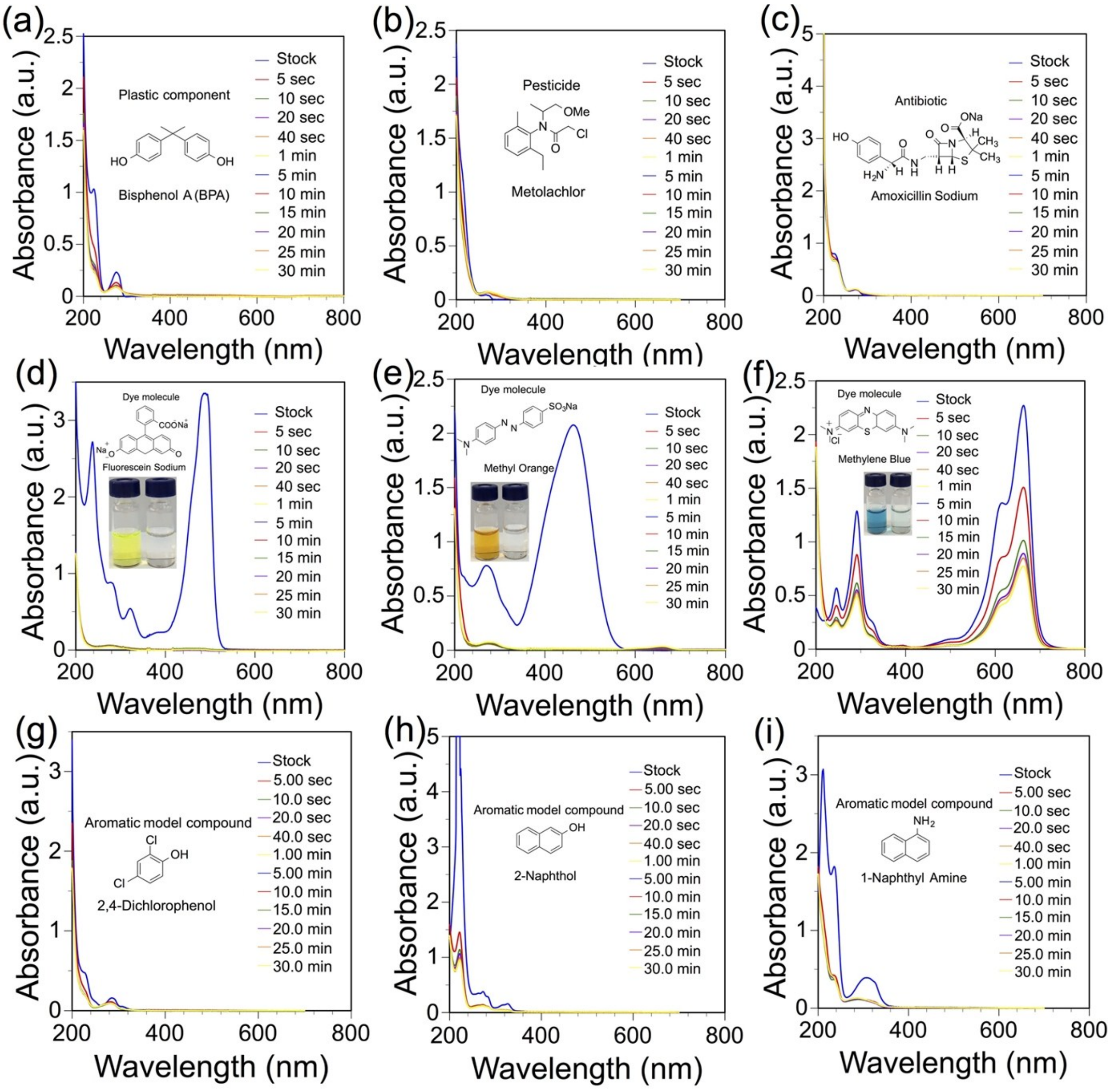


Fig. S5 UV–vis spectra recorded as a function of contact times with **P5-P** (1.00 mg/mL): (a) bisphenol A (0.100 mM), (b) metolachlor (0.100 mM), (c) amoxicillin sodium (0.100 mM), (d) fluorescein sodium (0.100 mM), insert: photographs of the 0.100 mM aqueous solutions of fluorescein sodium before and after the adsorption by **P5-P**, (e) methyl orange (0.100 mM), insert: photographs of the 0.100 mM aqueous solutions of methyl orange before and after the adsorption by **P5-P**, (f) methylene blue (0.100 mM), insert: photographs of the 0.100 mM aqueous solutions of methylene blue before and after the adsorption by **P5-P**, (g) 2,4-dichlorophenol (0.100 mM), (h) 2-naphthol (0.100 mM), and (i) 1-naphthyl amine (0.100 mM).

Pollutant	%Uptake in 10.0 sec	%Uptake at equilibrium
Bisphenol A	53.9	62.1
Metolachlor	36.8	45.6
Amoxicillin Sodium	14.8	17.0
Fluorescein Sodium	99.8	—
Methyl Orange	99.7	—
Methylene Blue	46.8	65.0
2,4-Dichlorophenol	41.8	41.8
2-Naphthol	65.1	67.2
1-Naphthyl Amine	72.4	75.0

Table S3 Percentage removal efficiency after 10.0 sec and equilibrium removal efficiency of each pollutant adsorbed by **P5-P**. The adsorption is almost reaching equilibrium uptake in the early stages of the adsorption process (within 10.0 sec).

Pollutant	Equilibrium time
Bisphenol A	1.00 min
Metolachlor	40.0 sec
Amoxicillin Sodium	20.0 sec
Fluorescein Sodium[a]	1.00 min
Methyl Orange[a]	1.00 min
Methylene Blue	1.00 min
2,4-Dichlorophenol	10.0 sec
2-Naphthol	1.00 min
1-Naphthyl Amine	1.00 min

Table S4 The required contact time to reach equilibrium on the organic micropollutants adsorptions. [a]The amount of the adsorbent used in this study is 0.100 mg/mL.

11. Adsorption data of fluorescein sodium and methyl orange

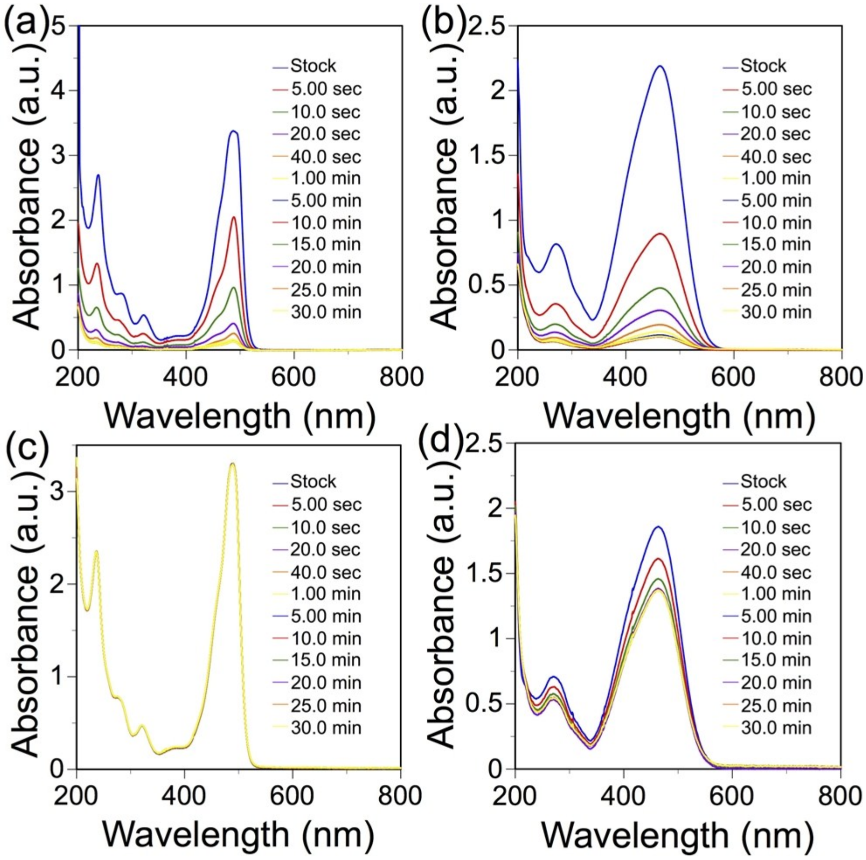


Fig. S6 UV–vis spectra recorded as a function of contact times of (a) fluorescein sodium and (b) methyl orange with **P5-P** (0.100 mg/mL); UV–vis spectra recorded as a function of contact times of (c) fluorescein sodium and (d) methyl orange with activated carbon (0.100 mg/mL).

12. Pseudo-second-order model

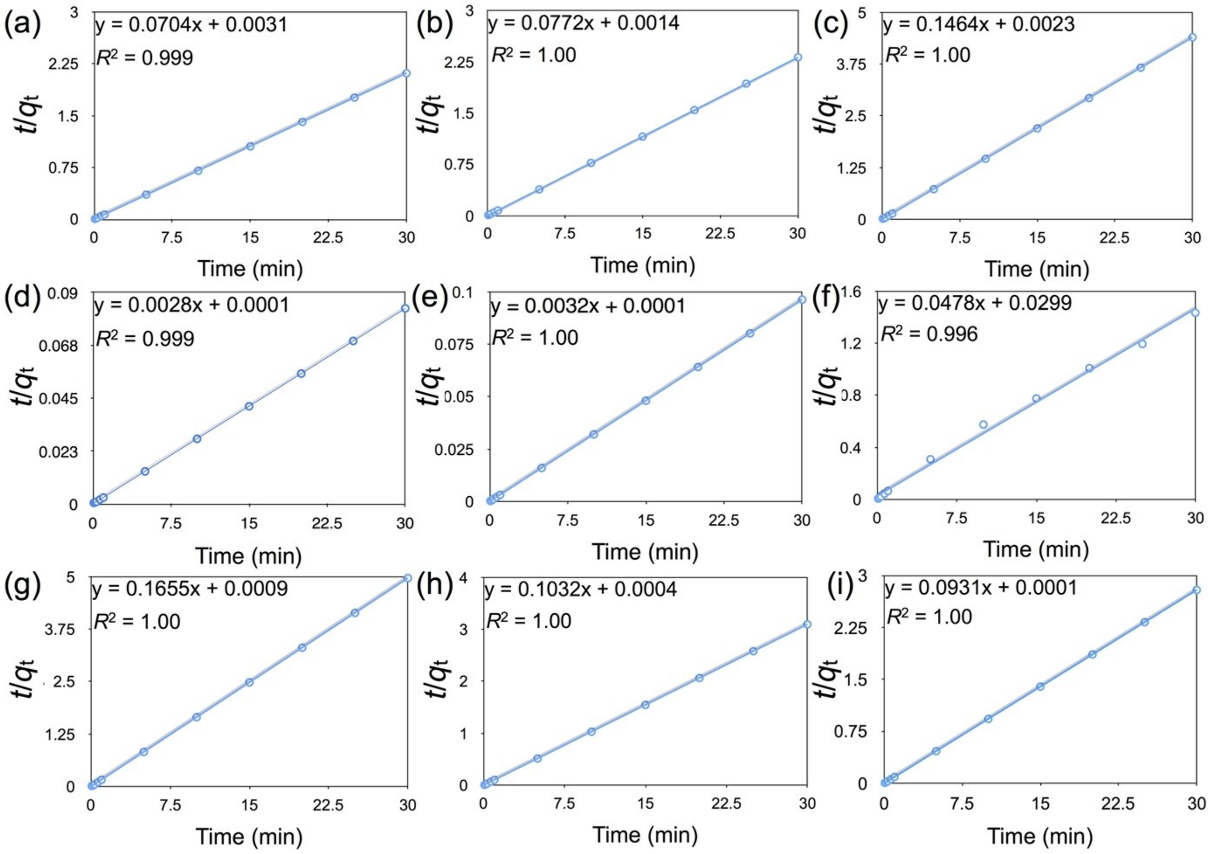


Fig. S7 Pseudo-second-order plots for **P5-P**: (a) bisphenol A, (b) metolachlor, (c) amoxicillin sodium, (d) fluorescein sodium, (e) methyl orange, (f) methylene blue, (g) 2,4-dichlorophenol, (h) 2-naphthol, and (i) 1-naphthyl amine. Here t (in min) is the contact time of each pollutant solution with **P5-P** and q_t (in mg/g) is the amount of each pollutant adsorbed per gram of **P5-P**.

Pollutant	K_{obs} (mg/g min)	R^2
Bisphenol A	0.160	0.999
Metolachlor	4.26	1.00
Amoxicillin Sodium	9.32	1.00
Fluorescein Sodium^a	0.078	0.999
Methyl Orange^a	0.102	1.00
Methylene Blue	0.076	0.996
2,4-Dichlorophenol	3.04	1.00
2-Naphthol	26.6	1.00
1-Naphthyl Amine	87.3	1.00

Table S5 Rates of each pollutant uptake by **P5-P**. ^{a}The amount of the adsorbent used in this study is 0.100 mg/mL.

13. Fluorescein sodium and methyl orange maximum uptakes of P5-P and other adsorbents

References	Adsorbents	Fluorescein Sodium Uptake	References	Adsorbents	Methyl Orange Uptake
Langmuir, 2000, **16**, 10351–10358.	Zn-Al-Hydrotalcite	0.270 mg/g	*ACS Appl. Mater. Interfaces,* 2012, **4**, 5749–5760.	Carbon nanotube	149 mg/g
			J. Mater. Chem. A 2015, **3**, 10031–10037.	Graphene	70.0 mg/g
This work	3D network polymer **P5-P**	2500 mg/g	This work	3D network polymer **P5-P**	909 mg/g

Table S6 Maximum adsorption capacities of **P5-P** and previously reported adsorbents for fluorescein sodium and methyl orange. It should be noted that the adsorption materials for fluorescein sodium have rarely been reported.

14. P5-P regeneration tests by washing with water

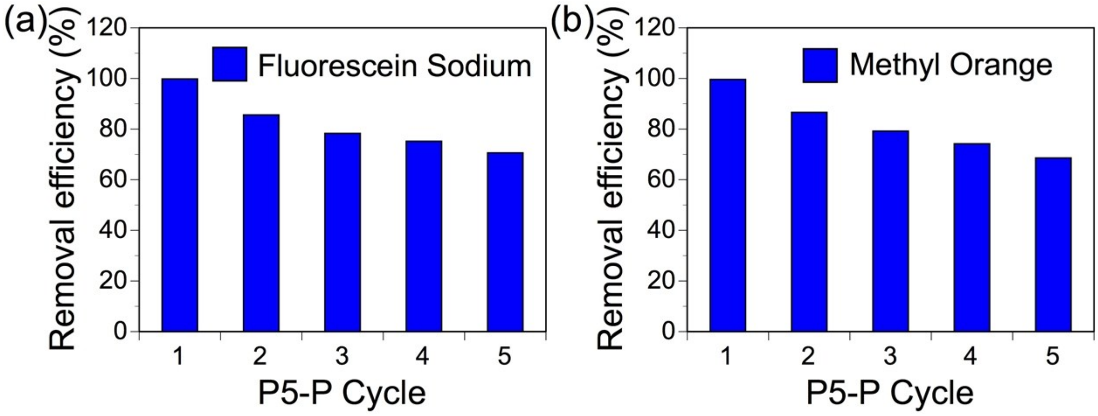


Fig. S8 The regeneration cycles of **P5-P** after the adsorption of (a) fluorescein sodium and (b) methyl orange by washing with water at 65 ºC.

15. Solid-state NMR results

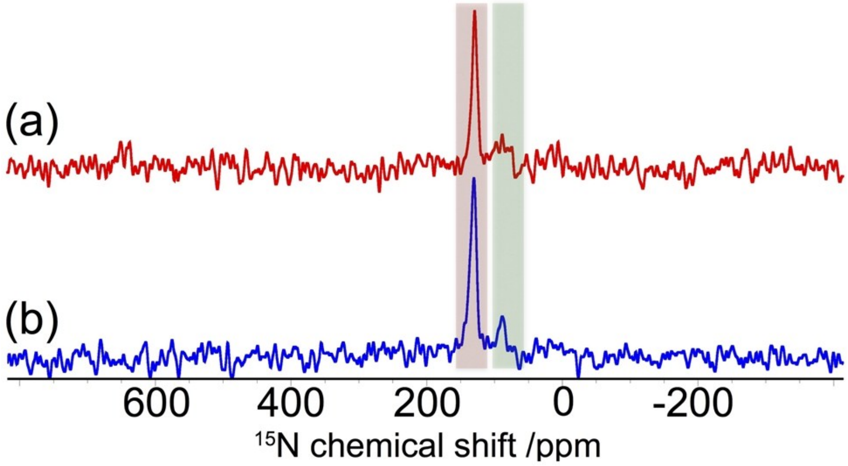


Fig. S9 Solid-state ^{15}N-NMR spectra of (a) fluorescein sodium adsorbed polymer **P5-P** and (b) **P5-P**.

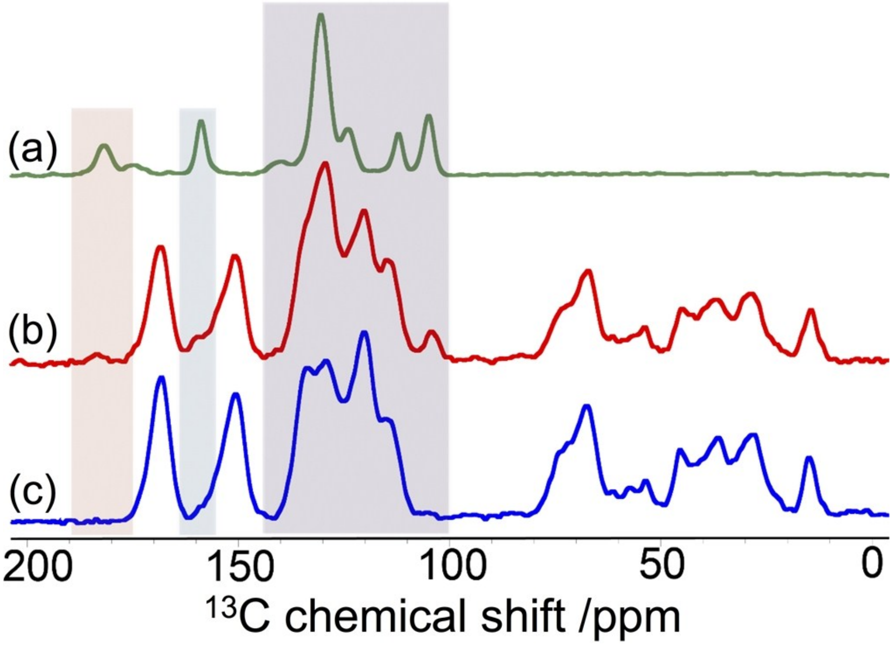


Fig. S10 Solid-state ^{13}C-NMR spectra of (a) fluorescein sodium, (b) fluorescein sodium adsorbed polymer **P5-P**, and (c) **P5-P**. The peak at 104.22 ppm in (b) can be easily distinguished to the carbon of fluorescein sodium.

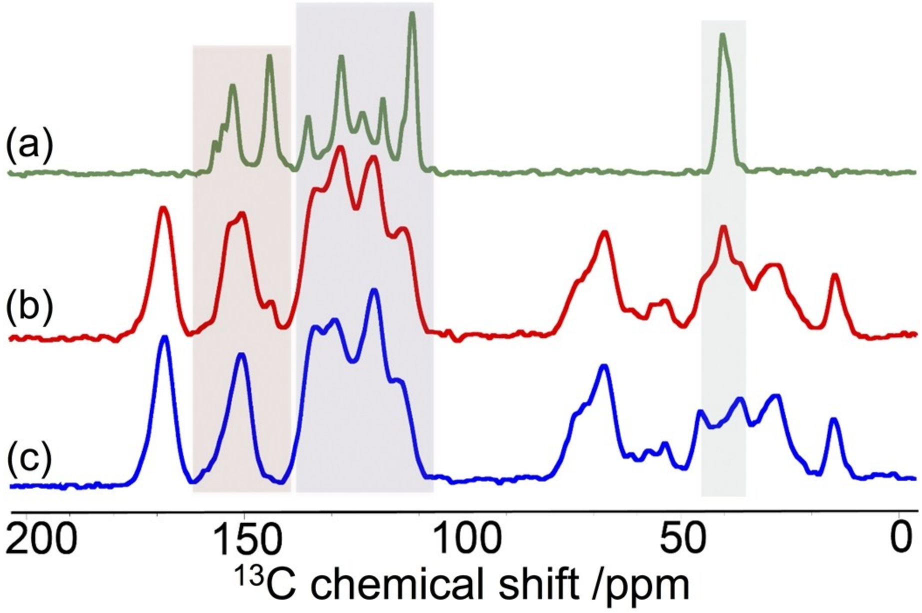


Fig. S11 Solid-state ^{13}C-NMR spectra of (a) methyl orange, (b) methyl orange adsorbed polymer **P5-P**, and (c) **P5-P**. The peak at 40.07 ppm was enhanced after methyl orange was absorbed into **P5-P**.

16. Adsorption of fluorescein sodium and methyl orange at different pH values

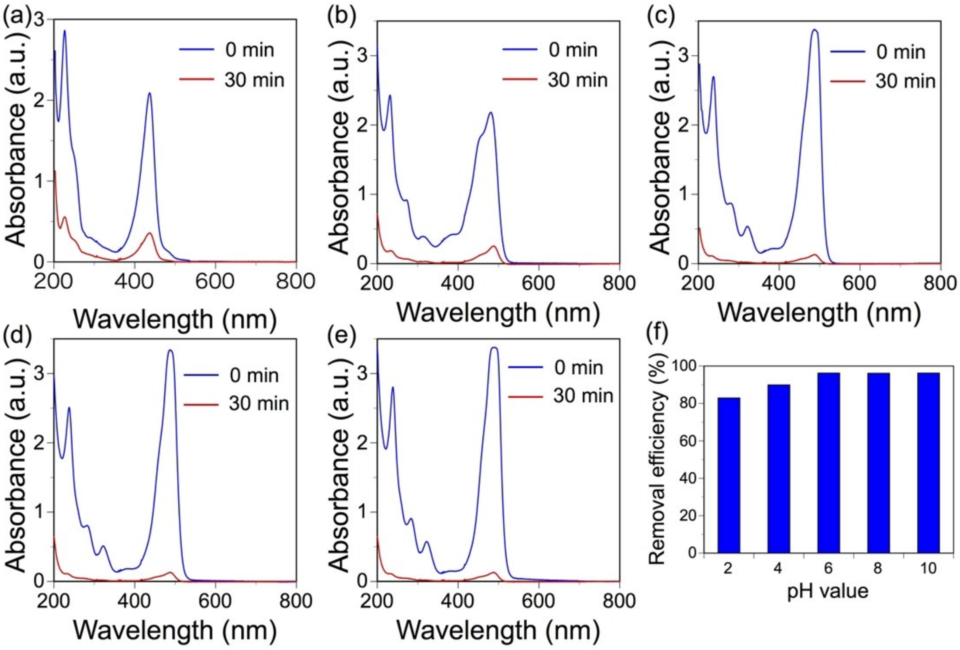


Fig. S12 UV–vis spectra of fluorescein sodium recorded as a function of contact times with **P5-P** at different pH values (0.100 mg/mL): (a) pH = 2.00, (b) pH = 4.00, (c) pH = 6.00, (d) pH = 8.00, (e) pH = 10.0. (f) Percentage removal efficiency of fluorescein sodium by **P5-P** determined after the contact time of 30.0 min at different pH values.

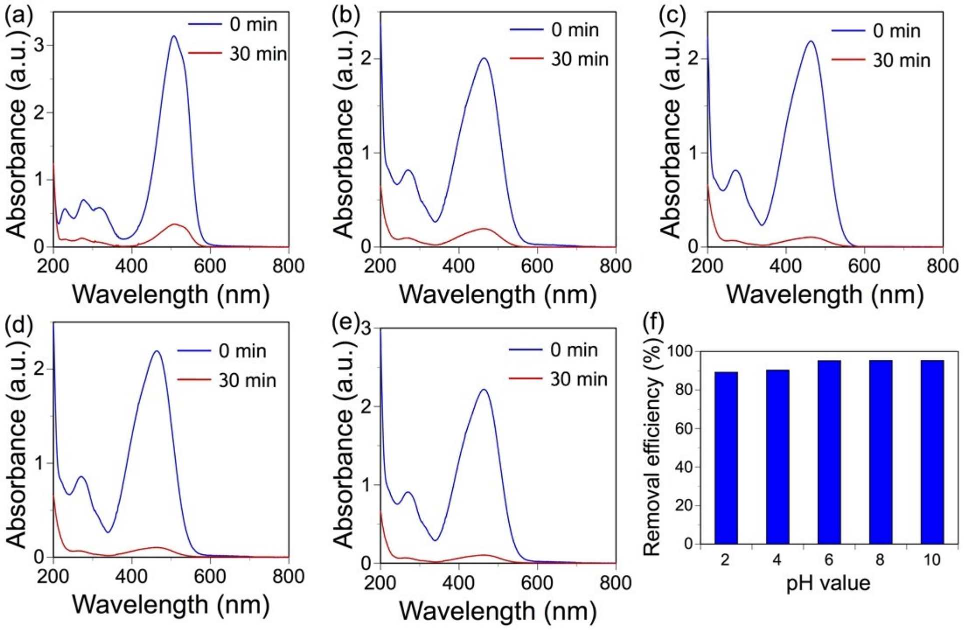


Fig. S13 UV–vis spectra of methyl orange recorded as a function of contact times with **P5-P** at different pH values (0.100 mg/mL): (a) pH = 2.00, (b) pH = 4.00, (c) pH = 6.00, (d) pH = 8.00, (e) pH = 10.0. (f) Percentage removal efficiency of methyl orange by **P5-P** determined after the contact time of 30.0 min at different pH values.

17. Solid-state 2D ^{13}C–^{1}H HETCOR MAS results

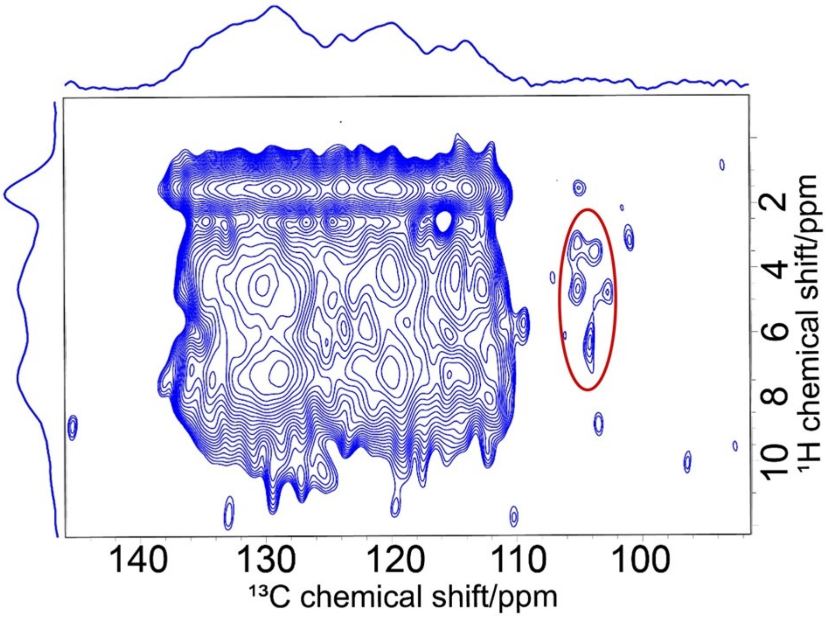


Fig. S14 Solid-state 2D ^{13}C–^{1}H HETCOR MAS spectrum of fluorescein sodium adsorbed polymer **P5-P** with a mixing time of 10 ms. The spectra exhibit the characteristic carbon signal of fluorescein sodium at 104.22 ppm are slightly correlated to the proton signal at 3.18–4.35 ppm which are assigned to the –CH_2 groups in the polymer **P5-P** (the signals are labeled).

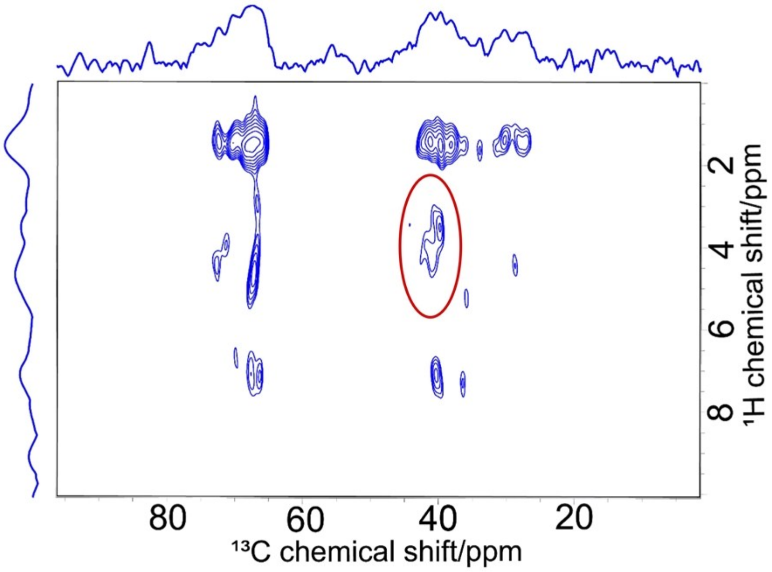


Fig. S15 Solid-state 2D ^{13}C–^{1}H correlation spectra of methyl orange adsorbed polymer **P5-P** with a mixing time of 10 ms. The labeled signal shows that the carbon signal at 40.07 ppm assigned to the methyl group of methyl orange also correlated to the identified proton signal at 3.18–4.35 ppm of **P5-P**.

18. Photos of the polymer P5-P after dispersion in water

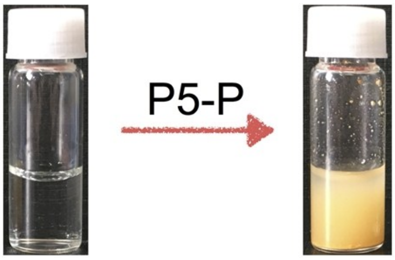


Fig. S16 **P5-P** swelled after dispersion in water.