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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, laor frequency 400.13 MHz for 1H, 100.61 MHz for 13C, 40.54 MHz for 15N) with an 1H–13C–15N triple resonance 3.2 mm probe at room temperature. The magic-angle-spin (MAS) frequency was set to 12–17 kHz. 13C 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 recycle delay (40s recycle delay for PPD) with 5000 to 10000 scans. 15N cross-polarization at magic-angle-spin (CPMAS) NMR spectra were recorded at the same condition but more scans. All the 2D 13C–1H correlation experiments were acquired using 10 ms mixing time in order to obtain intermolecular interaction. 13C chemical shifts were referenced directly to adamantane (δ (CH2) = 38.5 ppm) and 15N chemical shifts were measured relative to Glycine (δ (NH2) = 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 N₂. N₂ 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](image)

*Scheme S1* The synthetic route of compound P5.

![Fig. S1](image)

*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 \textbf{P5-P} in 10.0 mL of DMF and adding the suspension to the wafer \textit{via} the vacuum freeze-drying methodology.

4. TEM sample preparation

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

5. Elemental analysis

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
\textbf{Name} & \textbf{Weigth} & \textbf{Method} & \textbf{N Area} & \textbf{C Area} & \textbf{H Area} & \textbf{N %} & \textbf{C %} & \textbf{H %} \\
\hline
\textbf{P5-P} & 1.9330 mg & 2mgChem80s & 6 016 & 20 781 & 7 773 & 10.43 & 51.40 & 5.849 \\
\textbf{P5-P} & 1.9340 mg & 2mgChem80s & 5 953 & 20 708 & 8 367 & 10.31 & 51.19 & 6.093 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
\textbf{Name} & \textbf{Weigth} & \textbf{Method} & \textbf{N Area} & \textbf{C Area} & \textbf{H Area} & \textbf{N %} & \textbf{C %} & \textbf{H %} \\
\hline
\textbf{P5-P} & 1.9180 mg & 2mgChem80s & 5 714 & 23 366 & 8 349 & 10.19 & 58.06 & 6.140 \\
\textbf{P5-P} & 1.9530 mg & 2mgChem80s & 5 787 & 23 539 & 8 503 & 10.13 & 57.44 & 6.146 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
\textbf{Name} & \textbf{Weigth} & \textbf{Method} & \textbf{N Area} & \textbf{C Area} & \textbf{H Area} & \textbf{N %} & \textbf{C %} & \textbf{H %} \\
\hline
\textbf{P5-P} & 1.9230 mg & 2mgChem80s & 6 028 & 22 802 & 8 421 & 10.25 & 57.21 & 6.081 \\
\textbf{P5-P} & 1.9460 mg & 2mgChem80s & 5 790 & 22 431 & 8 604 & 10.18 & 58.15 & 6.230 \\
\hline
\end{tabular}
\end{table}

\textit{Table S1} Elemental analysis data of polymer \textbf{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 \textbf{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

![NMR spectra](image)

**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

![Molecular structures](image)

**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

![Image of N2 sorption isotherm and surface area data analysis of polymer P5-P]

*Fig. S4* N2 sorption isotherm (77.0 K) and surface area data analysis of polymer P5-P.

9. Water regain analysis

<table>
<thead>
<tr>
<th>$W_d$</th>
<th>$W_w$</th>
<th>Water regain</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.95 mg</td>
<td>6.85 mg</td>
<td>73.4%</td>
</tr>
<tr>
<td>3.96 mg</td>
<td>6.83 mg</td>
<td>72.3%</td>
</tr>
<tr>
<td>3.90 mg</td>
<td>6.88 mg</td>
<td>76.4%</td>
</tr>
</tbody>
</table>

*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).
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).

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

Table S4 The required contact time to reach equilibrium on the organic micropollutants adsorptions. aThe 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

![Graphs of pseudosecond-order plots for P5-P with various pollutants]

**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.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>$K_{obs}$ (mg/min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bisphenol A</td>
<td>0.160</td>
<td>0.999</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>4.26</td>
<td>1.00</td>
</tr>
<tr>
<td>Amoxicillin Sodium</td>
<td>9.32</td>
<td>1.00</td>
</tr>
<tr>
<td>Fluorescein Sodium</td>
<td>0.078</td>
<td>0.999</td>
</tr>
<tr>
<td>Methyl Orange</td>
<td>0.102</td>
<td>1.00</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>0.076</td>
<td>0.996</td>
</tr>
<tr>
<td>2,4-Dichlorophenol</td>
<td>3.04</td>
<td>1.00</td>
</tr>
<tr>
<td>2-Naphthol</td>
<td>26.6</td>
<td>1.00</td>
</tr>
<tr>
<td>1-Naphthyl Amine</td>
<td>87.3</td>
<td>1.00</td>
</tr>
</tbody>
</table>

**Table S5** Rates of each pollutant uptake by P5-P. *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

<table>
<thead>
<tr>
<th>References</th>
<th>Adsorbents</th>
<th>Fluorescein Sodium Uptake</th>
<th>References</th>
<th>Adsorbents</th>
<th>Methyl Orange Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir; 2000, 16, 10351–10358.</td>
<td>Zn-Al-Hydrotalcite</td>
<td>0.270 mg/g</td>
<td>ACS Appl. Mater. Interfaces, 2012, 4, 5749–5760.</td>
<td>Carbon nanotube</td>
<td>149 mg/g</td>
</tr>
<tr>
<td>This work</td>
<td>3D network polymer P5-P</td>
<td>2500 mg/g</td>
<td>This work</td>
<td>3D network polymer P5-P</td>
<td>909 mg/g</td>
</tr>
</tbody>
</table>

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](image) The regeneration cycles of P5-P after the adsorption of (a) fluorescein sodium and (b) methyl orange by washing with water at 65 °C.
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.