Supporting Information

for

Porous Pillar[6]arene-Based Polymers for Reversible Iodine Capture

Shujie Lin, Ziliang Zhang, Di Gao, Longming Chen, Chengyang Tian, Junyi Chen,* Qingbin Meng*

State Key Laboratory of National Security Specially Needed Medicines, Beijing Institute of Pharmacology and Toxicology, Beijing 100850, P. R. China.

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1 General materials and methods

1.1 Materials

All the reagents and solvents were commercially available and used as received unless other specified purification. Perhydroxylated pillar[6]arene (P6A-OH) was synthesized according to a literature method.[1] Hydroquinone (M-OH), decafluorobiphenyl (DFB) and iodine (I_2) were purchased from Innochem (Beijing, China). Potassium iodide (KI), n-hexane, potassium carbonate (K_2CO_3), N,N-dimethylformamide (DMF) and methanol (MeOH) were purchased from Sinopharm Chemical Reagent Beijing. Activated carbon (AC) was purchased from Henan Xingnuo Environmental Protection Material Co.,Ltd.

1.2 Instruments

Ultraviolet-visible (UV/vis) spectroscopy was performed on a Cary 300 Agilent UV/vis spectrometer. The morphology was imaged by scanning electron microscopy (SEM, Hitachi Regulus SU8010, operated at 5 kV). Fourier transform infrared spectroscopy (FT-IR) spectra was recorded on a JOSVOK FTIR-1500 spectrometer. The surface area and pore size distribution analysis of polymers were performed on a Quantachrome Autosorb-iQ gas adsorption and pore size analyzer, using N_2 adsorption and desorption at 77.3 K. Samples were degassed at 80 ^oC under high vacuum for 24 h prior to the N_2 adsorption and desorption analysis. Powder X-ray diffraction (PXRD) analysis was performed in X-ray powder diffractometer (Rigaku Ultima IV).

1.3 Iodine capture experiments in aqueous solution

In order to monitor the iodine capture of P-P6APs in aqueous solution, a time-dependent UV/vis measurement was carried out. AC and MPs were set up as positive and negative controls, separately. Firstly, prepare 100,000 ppm I_2/KI aqueous (1g KI and 1 g I_2 in 10 mL H_2O) and dilute it to 250 ppm $I_2/KI_{(aq)}$. Then, P-P6APs (6.0 mg), AC (6.0 mg) and MPs (6.0 mg) were added respectively to an 250 ppm $I_2/KI_{(aq)}$ (6 mL) with shaking. The UV/vis spectrum of the solution was recorded over time.

The $I_2/KI_{(aq)}$ concentration was determined with UV/vis spectroscopy according

to a standard curve.

The I_2 uptake efficiency was calculated with the following equation:

$$I_2 \text{ uptake efficiency} = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

C_0 (ppm) is the concentration of $I_2/KI_{(aq)}$ before uptake and C_t (ppm) is the concentration of $I_2/KI_{(aq)}$ at various time after adding adsorbent materials.

1.4 Iodine capture experiments in n-hexane

To further explore whether P-P6APs is also possible to capture iodine from organic solution, a UV/vis measurement based on iodine/n-hexane solution was carried out. In the same way, AC and MPs were set up as positive and negative controls, separately. P-P6APs (24.0 mg), AC (24.0 mg) and MPs (24.0 mg) were added respectively to an iodine/n-hexane solution (1.0 mM, 6 mL) with shaking. The UV/vis spectrum of the solution was recorded over time.

The concentration of iodine/n-hexane solution was determined with UV/vis spectroscopy according to a standard curve.

The I_2 uptake efficiency was calculated with the following equation:

$$I_2 \text{ uptake efficiency} = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

C_0 (mM) is the concentration of iodine/n-hexane solution before uptake and C_t (mM) is the concentration of iodine/n-hexane solution at various time after adding adsorbent materials.

1.5 Iodine vapor uptake experiments

To examine the uptake ability of P-P6APs for iodine vapor, time-dependent iodine vapor uptake experiments based on gravimetric measurements were performed in the following procedure: Similarly, AC and MPs were set up as positive and negative controls, separately. 15 mg of adsorbent materials, namely, P-P6APs, AC and MPs were taken in a preweighed glass vessel (2 mL). And then the glass vessel containing samples was transferred in bigger sealed glass vial (20 mL). 500 mg molecular iodine was placed in bigger glass vial maintaining no physical contact between iodine and adsorbent materials. Next, the closed container was heated at 80 ^oC in bake oven. After iodine vapor adsorption over time, the iodine-loaded adsorbent

materials were cooled down to room temperature and weighted. The iodine uptake capacities for adsorbent materials were calculated by weight gains:

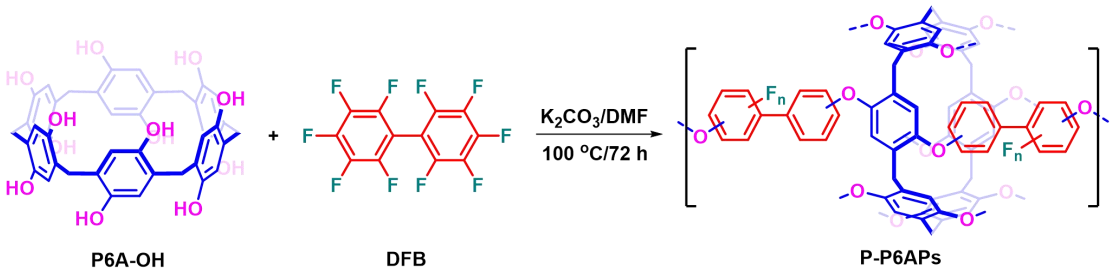
$$I_2 \text{ uptake efficiency} = \frac{(W_a - W_b)}{W_b} \times 100\text{wt}\%$$

W_a is the mass weight of adsorbent materials before iodine vapor adsorption and W_b is the mass weight of adsorbent materials after iodine vapor adsorption at various time.

1.6 Regeneration and recycling experiments

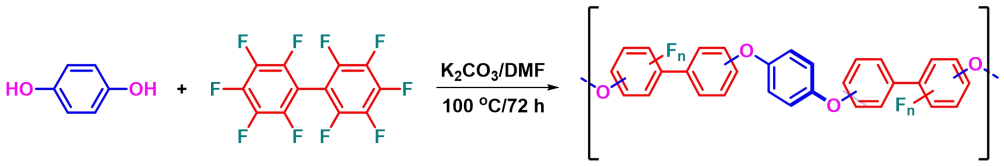
I_2@P-P6APs were immersed in MeOH (2mL) for desorption of the iodine/iodide, during which the solvent was decanted and washing repeatedly several times. After complete release (no color change happened when the samples were immersed in MeOH), the resultant samples were desolvated under vacuum at 100 ^oC over 4 h to achieve regeneration and the regenerated samples were used for the next cycle under the same adsorption conditions. Repeat 5 regenerative cycles and calculate I_2 adsorption efficiency to appraise the recyclability of P-P6APs.

2 Synthetic procedures



P6A-OH DFB P-P6APs

Syntheses of P-P6APs: A suspension of P6A-OH (0.50 g, 0.68 mmol), decafluorobiphenyl (0.27 g, 0.82 mmol) and K_2CO_3 (1.69 g, 12.24 mmol) in DMF (25 mL) was heated at 100 °C for 72 h under N_2. The precipitate was filtered and washed with 1N HCl (25 mL × 3), H_2O (25 mL × 3), MeOH (25 mL × 3), THF (25 mL × 3) and DCM (25 mL × 3). The solid was dried under high vacuum to yield P-P6APs as a black solid.



M-OH DFB MPs

Syntheses of MPs: A suspension of M-OH (4.01 g, 36.33 mmol), decafluorobiphenyl (2.20 g, 6.58 mmol) and K_2CO_3 (13.00 g, 94.06 mmol) in DMF (150 mL) was heated at 100 °C for 72 h under N_2. The precipitate was filtered and washed with 1N HCl (100 mL × 3), H_2O (100 mL × 3), MeOH (100 mL × 3), THF (100 mL × 3) and DCM (100 mL × 3). The solid was dried under high vacuum to yield MPs as a white solid.

3. Supporting results and experimental raw data

3.1 FT-IR spectra of M-OH and MPs

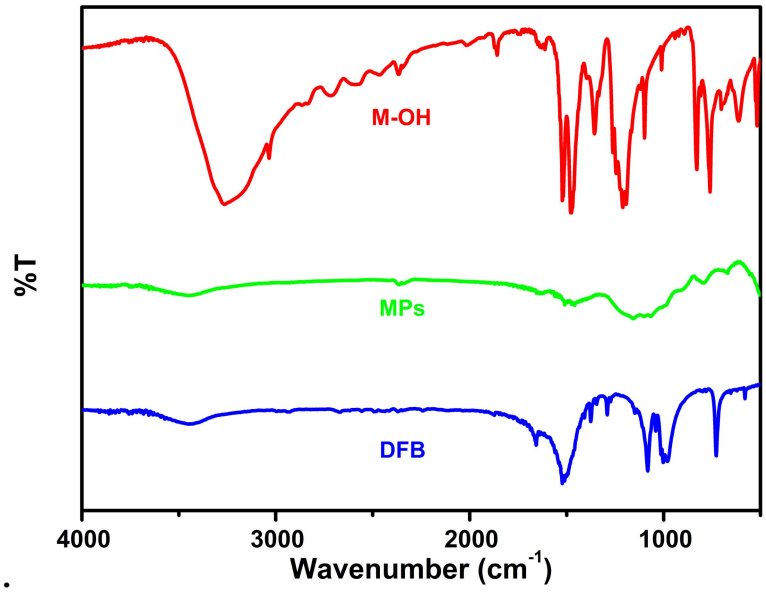


Fig. S1 FT-IR spectra of M-OH, DFB and MPs.

3.2 Gas adsorption and porosity measurements

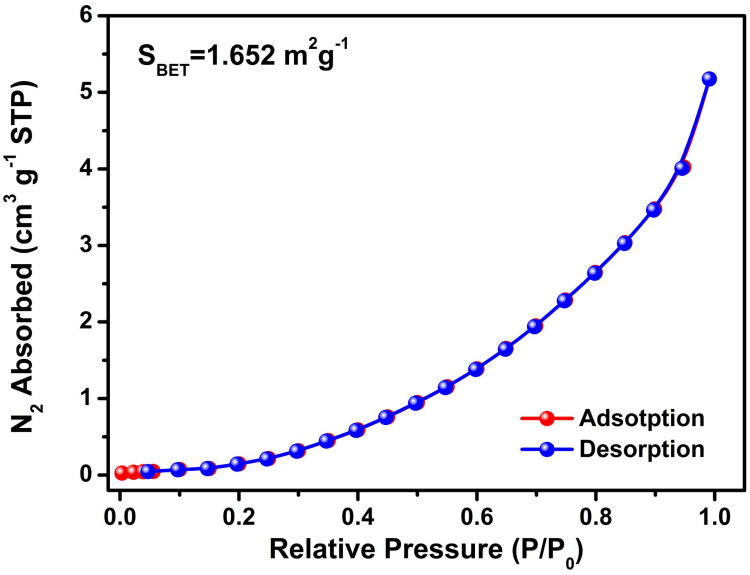


Fig. S2 N_2 adsorption/desorption isotherm of MPs.

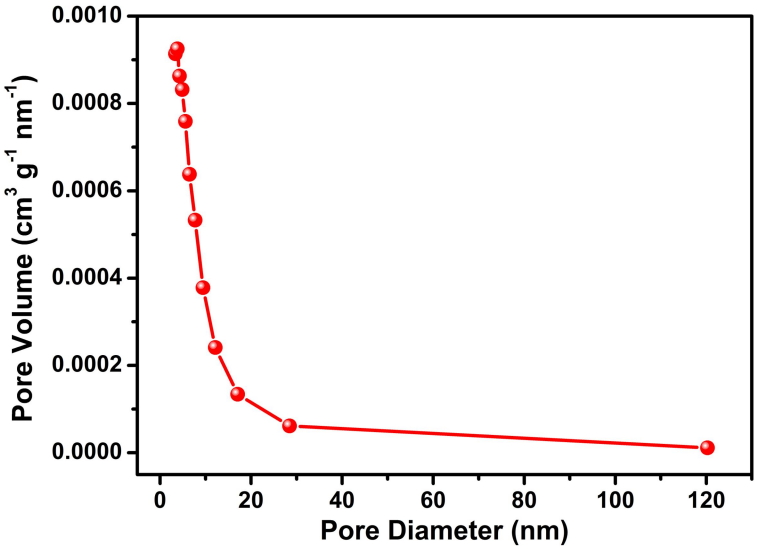


Fig. S3 The cumulative pore volume (pore diameter) measurement of MPs. The result suggests that MPs is nonporous.

3.3 Calibration curve of iodine in aqueous solution for adsorption study

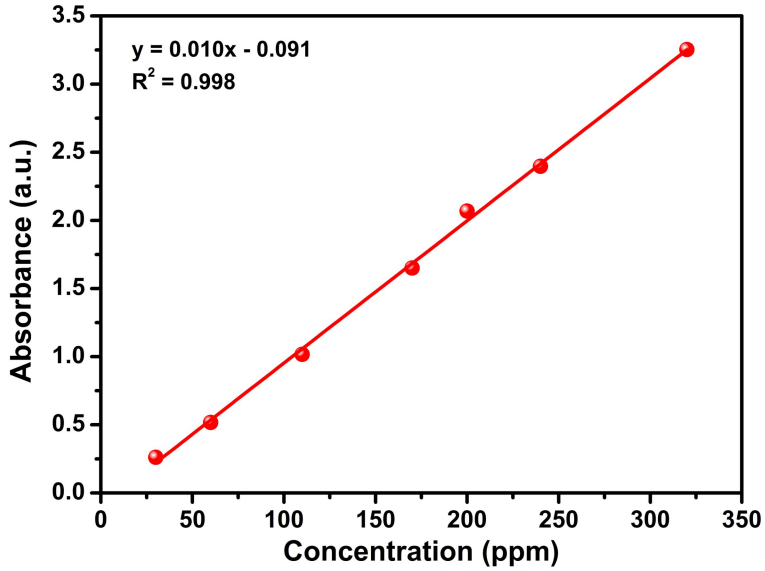


Fig. S4 Calibration curve obtained by the UV/vis absorption peak at 286 nm and used for calculating the $I_2/KI_{(aq)}$ concentration in the iodine capture study described in the main text.

3.4 Iodine capture speed monitoring in aqueous solution

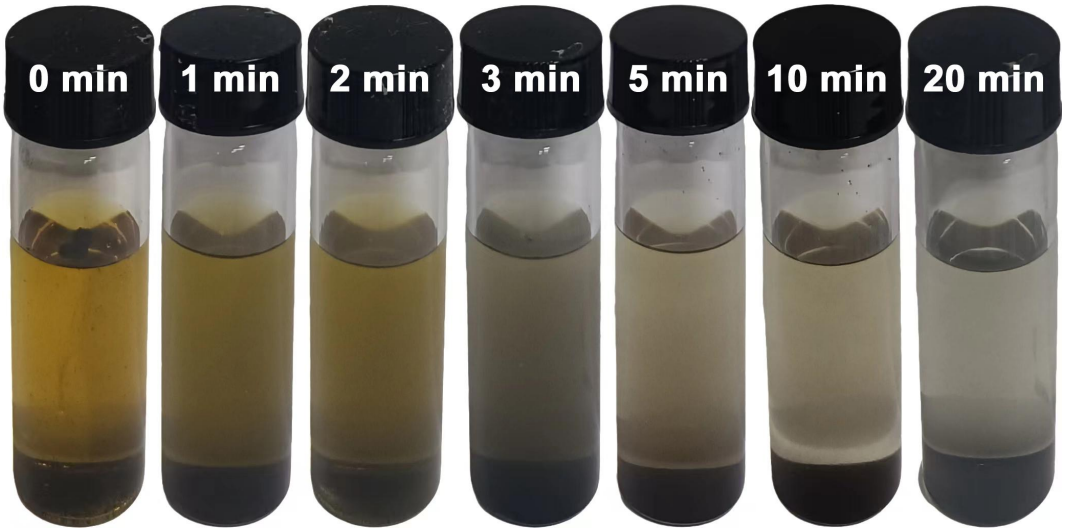


Fig. S5 Color changes of $I_2/KI_{(aq)}$ (250 ppm) upon addition of AC (6 mg).

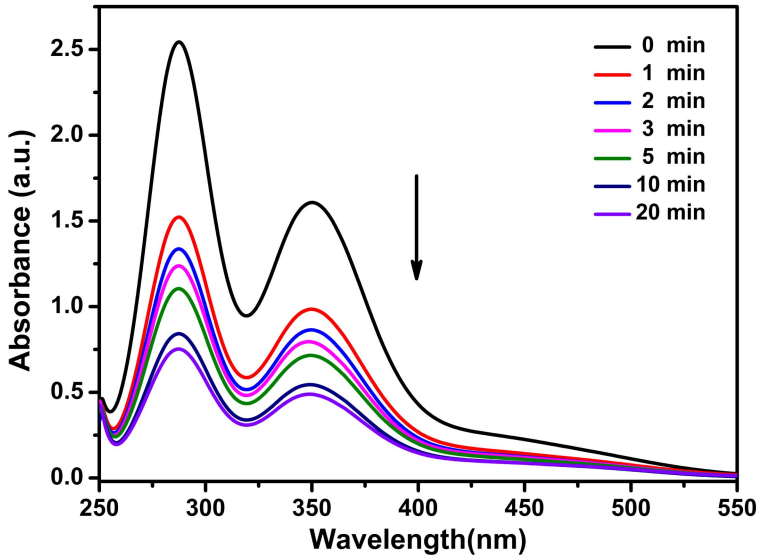


Fig. S6 Time-dependent UV/vis absorption spectra of $I_2/KI_{(aq)}$ (250 ppm) upon addition of AC (6.0 mg).

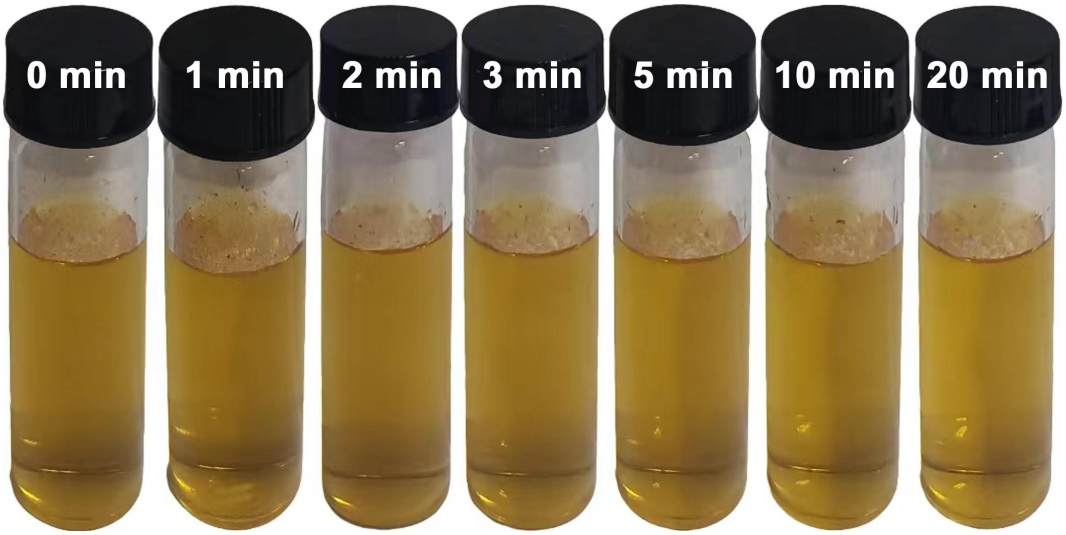


Fig. S7 Color changes of $I_2/KI_{(aq)}$ (250 ppm) upon addition of MPs (6 mg).

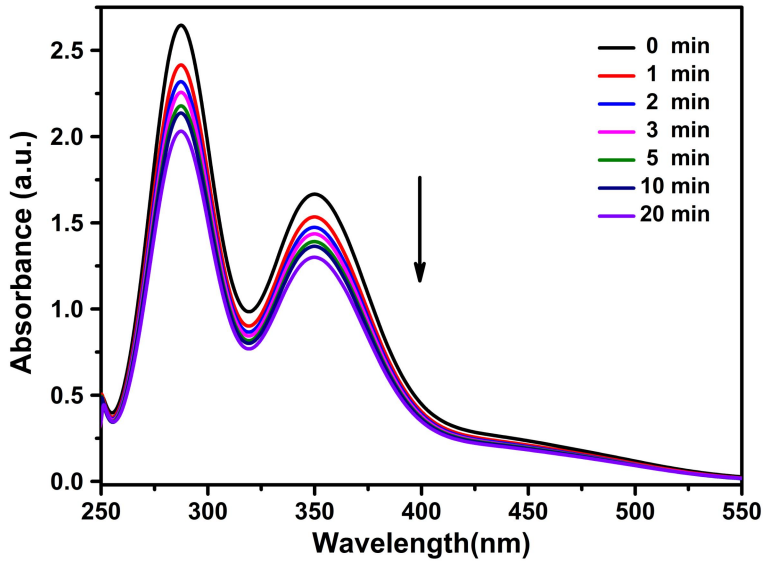


Fig. S8 Time-dependent UV/vis absorption spectra of $I_2/KI_{(aq)}$ (250 ppm) upon addition of MPs (6.0 mg).

3.5 Selective adsorption experiments

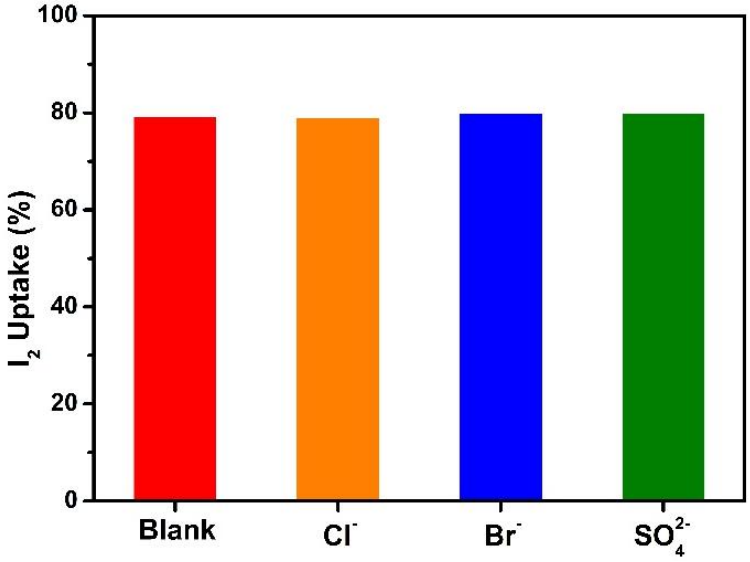


Fig. S9 Uptake efficiencies of P-P6APs for saturated iodine aqueous solution (250 ppm) in the presence of competing anions (as their potassium salts).

3.6 Comparison of adsorption capacity

Table S1 Iodine uptake capacities of different macrocycle-based crosslinked polymers from aqueous phase.

Adsorbents	S_{BET} ($m^2 \cdot g^{-1}$)	Conditions (P: I_2, S: adsorbent)	Adsorption amount (g/g)	Ref.
P-P6APs	366.09	P=250 ppm, S=1 mg mL^{-1}	0.2	Here
C[4]P-TEPM	138.4	P=1.2 mM, S=1 mg mL^{-1}	0.29	[2]
C[4]P-HEPM	277.6	P=1.2 mM, S=1 mg mL^{-1}	0.30	[2]
CMP-4	9.5	P=1 mM	/	[3]
C[4]P-BTP	20.5	P=1.2 mM, S=1 mg mL^{-1}	0.30	[4]
C[4]P-DPP	110.0	P=1.2 mM, S=1 mg mL^{-1}	0.14	[4]
CaCOP1	10.86	P=100,000 ppm, S=17 mg mL^{-1}	2.40	[5]
CaCOP2	20.16	P=100,000 ppm, S=17 mg mL^{-1}	2.81	[5]
CaCOP3	81.09	P=100,000 ppm, S=17 mg mL^{-1}	3.1	[5]
DTTP5	14.9	P=0.1 mg mL^{-1}, S=1 mg mL^{-1}	0.09	[6]
Δ@PPG3	0.0006	P=0.3 mM, S=2 mg mL^{-1}	0.035	[7]
Δ@PPG6	0.0097	P=0.3 mM, S=2 mg mL^{-1}	0.035	[7]

3.7 Calibration curve of iodine in n-hexane for adsorption study

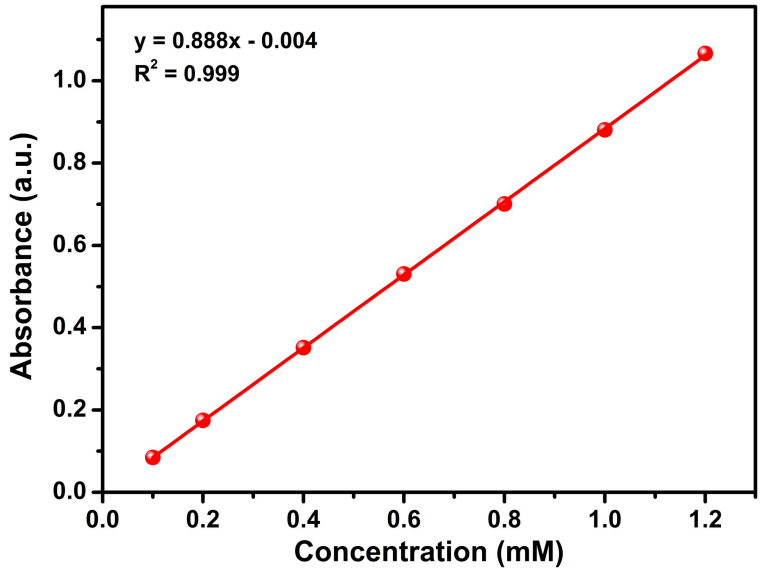


Fig. S10 Calibration curve obtained by the UV/vis absorption peak at 520 nm and used for calculating the iodine/n-hexane solution concentration in the iodine capture study described in the main text.

3.8 Iodine capture speed monitoring in n-hexane

Fig. S11 Color changes of I_2 (1 mM) in n-hexane upon addition of AC (24 mg).

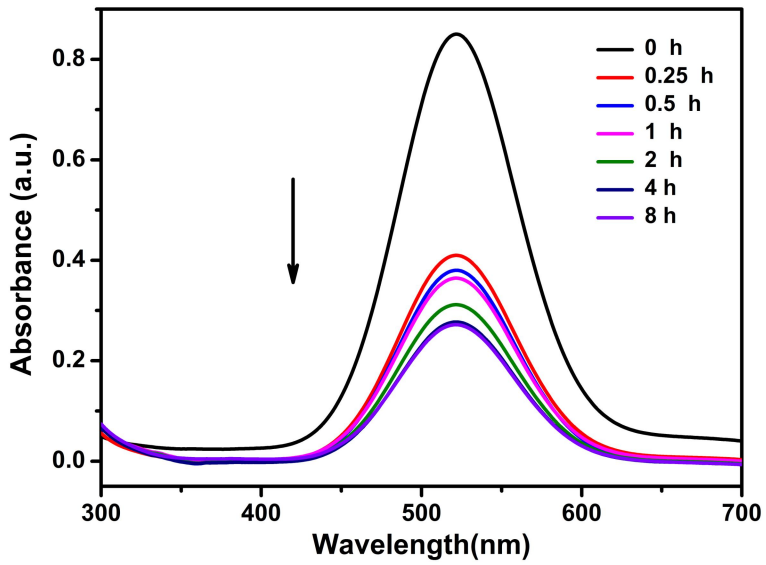


Fig. S12 Time-dependent UV/vis absorption spectra of iodine/n-hexane solution (1 mM) upon addition of AC (24.0 mg).

Fig. S13 Color changes of I_2 (1 mM) in n-hexane upon addition of MPs (24 mg).

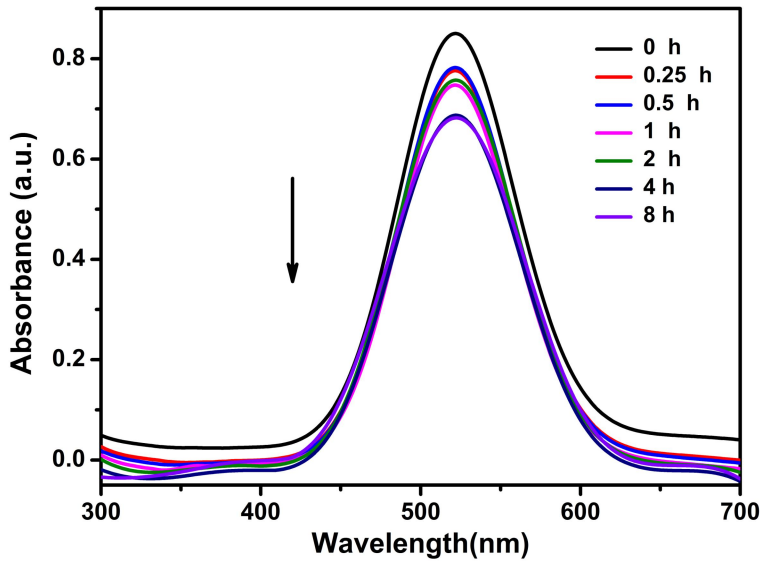


Fig. S14 Time-dependent UV/vis absorption spectra of iodine/n-hexane solution (1 mM) upon addition of MPs (24.0 mg).

3.9 PXRD patterns of iodine and I_2@P-P6APs

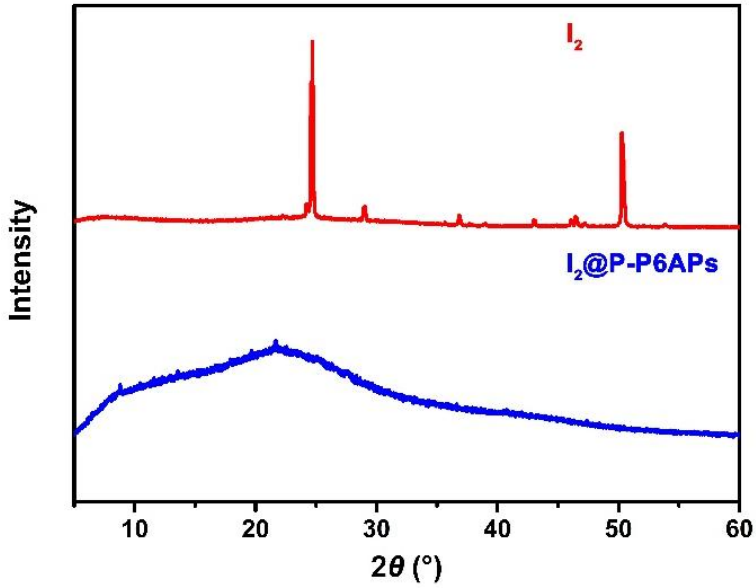


Fig. S15 PXRD patterns of iodine and I_2@P-P6APs.

3.10 FT-IR spectra of P-P6APs and I_2@P-P6APs

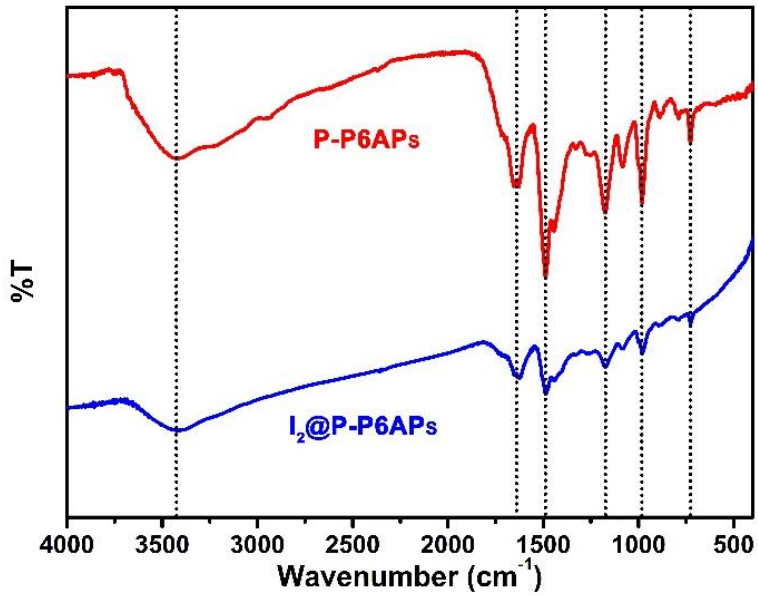


Fig. S16 FT-IR spectra of P-P6APs and I_2@P-P6APs.

3.11 The sixth recycling experiments

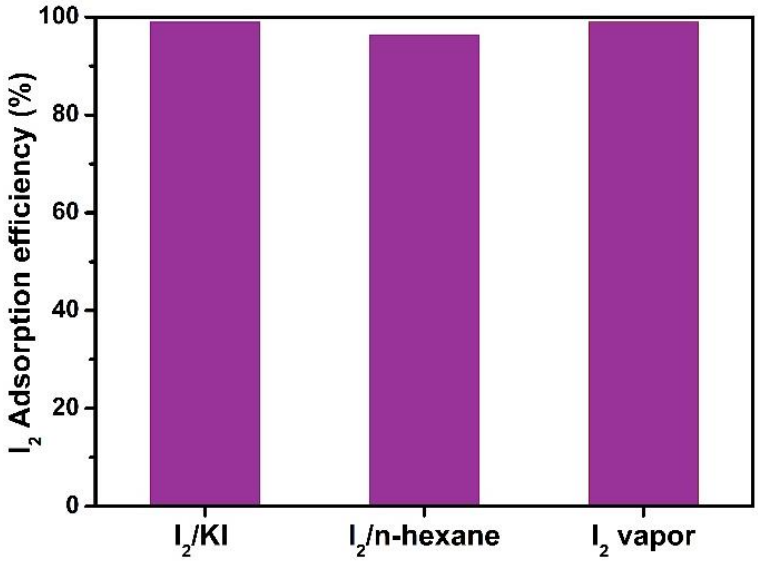


Fig. S17 Iodine adsorption efficiency of P-P6APs after 5 cycles of reuse.

References

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