Supporting Information

Cyclodextrin-Threaded Covalent Organic Polyrotaxanes with Tunable Solid-State Emissive Activity for Efficient Iodine Capture

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Contents

Section 1. Experimental Section

1.1. Materials

All regents were purchased from commercial suppliers and used directly without further purification.

1.2 Synthesis

Synthesis of CD-inclusion

The preparation was conducted according to our previous reports.[1]

Section 2. Methods

2.1 Physical Characterization

Fourier transform infrared spectroscopy (FT-IR, PerkinElmer, 2000 FTIR spectrometer, Cambridge, UK) was recorded at wavelengths ranging from 400 to 4000 cm^{-1}. Solid-state ^{13}C CP/MAS NMR were collected on Bruker SB Avance III 500 MHz spectrometer. Thermal gravimetric analysis (TGA) was recorded using NETZSCH STA 449C analyzer from 30 to 800 °C at a heating rate of 10 °C/min under the protection of N_2. Transmission electron microscope (TEM) were conducted on a FEI model Tecani 20 microscope and a JEOL model JSM-2100F. Powder X-ray diffraction (PXRD) parameters were obtained using a Rigaku-DMAX 2500 diffractometer at a rate of 5^o min^{-1} from 5^o to 80^o.

2.2 Iodine vapor adsorption

Small open glass vials containing 20 mg of adsorbent and sufficient amount of iodine monomers were placed in large glass vials with tightly closed milled mouths, and the whole closed vials were placed in an oven at 348.15 K and 1.0 bar, and the change in mass of the adsorbent with respect to time was recorded at regular intervals. And the amount of adsorption was calculated according to the following equation:

$$q = \frac{m_t - m_0}{m_0} \quad \text{(S1)}\ [3]$$

Where 'q' is the amount adsorbed at time t, 'm_t' is the mass of the adsorbent at time t, and 'm_0' is the mass of initial adsorbents.

2.3 Adsorption of iodine in water:

The adsorption to iodine in iodine-saturated aqueous pipette solutions was recorded using a UV-Vis spectrophotometer. The iodine-saturated aqueous solution was prepared by adding 0.1 g of I_2 to 50 ml of aqueous solution and sonicated for 30 min. Five milligrams of adsorbent was placed in a vial containing 5 ml of iodine saturated aqueous solution (1.14 mmol). Periodically, 2 ml of the solution was withdrawn from the mother liquor, UV-visible adsorption was recorded and then transferred back to the reaction vial.

2.4 Iodine release

Time-dependent UV-Vis measurements were performed in MeOH.

2.5 Fitting of Langmuir and Freundlich adsorption isotherm

The adsorption behavior of TPE-COP and TPE-CD-COPR towards iodine in iodine-saturated aqueous pipette solutions was recorded using a UV-Vis spectrophotometer. The iodine-saturated aqueous solution was prepared by adding 0.1 g of I_2 to 50 ml of aqueous solution and sonicated for 30 min. Five milligrams of adsorbent was placed in a vial containing 5 ml of iodine saturated aqueous solution (1.14 mmol). Periodically, 2 ml of the solution was withdrawn from the mother liquor, UV-visible adsorption was recorded and then transferred back to the reaction vial.

Section 3. Physical characterization on the TPE-COP

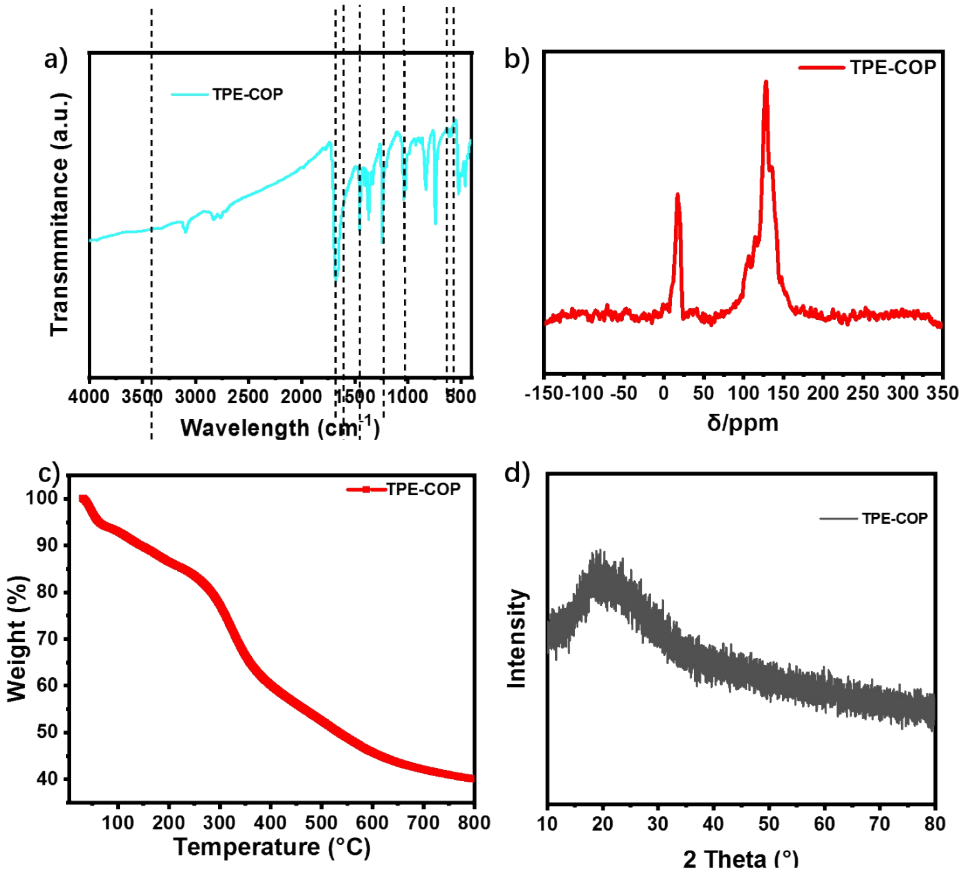


Figure S1. Physical characterization of TPE-COP. a) FT-IR of TPE-COP; b) solid state ^{13}C NMR of TPE-COP; c) TGA of TPE-COP; d) XRD of TPE-COP.

Figure S1. TGA of TPE-COP.

Section 4. TEM and EDS

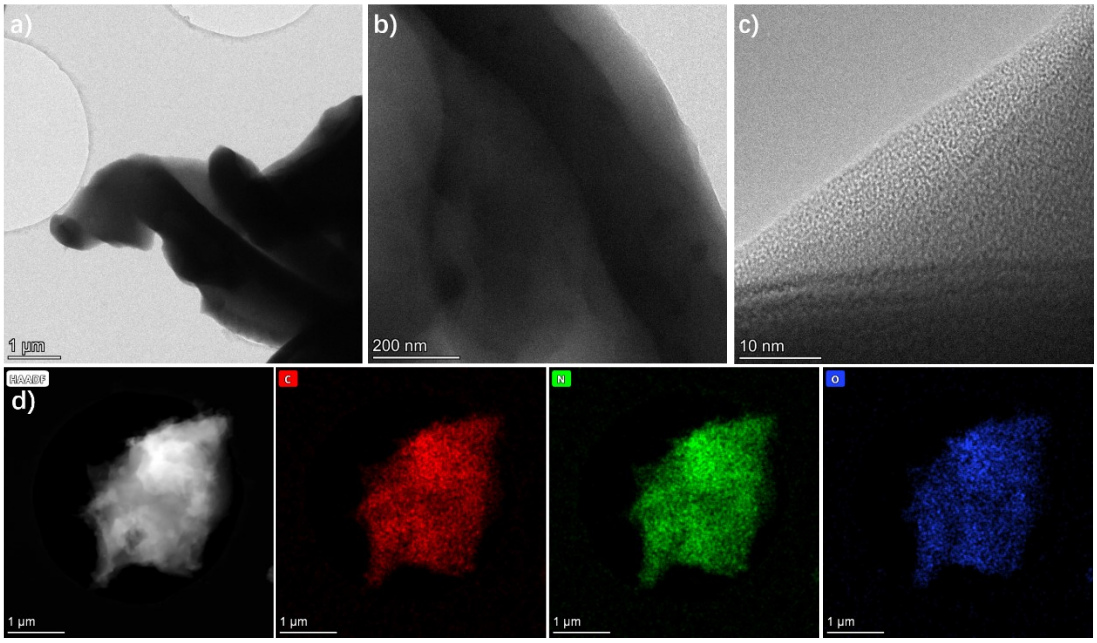
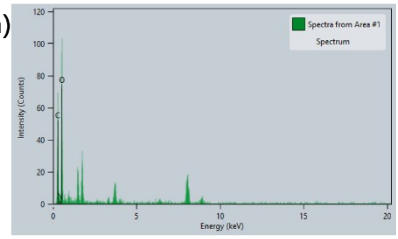


Figure S2. a-d) TEM of TPE-COP at the scale bar of 1000, 200 and 10 nm, respectively; d) Elemental Mapping of TPE-COPs.

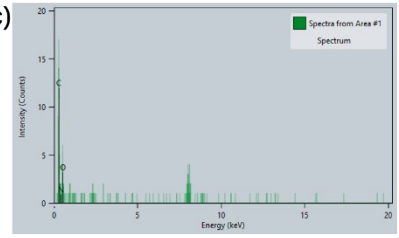
a)



b)

Element	Mass fraction (%)
C	47.8
N	1.50
O	50.7

c)



d)

Element	Mass fraction (%)
C	83.3
N	4.34
O	12.3

Figure S3. EDS and corresponding elemental contents of as-synthesized samples. a) EDS of TPE-CD-COPR; b) Element content of TPE-CD-COPR; c) EDS of TPE-COP; d) Element content of TPE-COP.

Section 5. Removal of iodine from water by β-CD

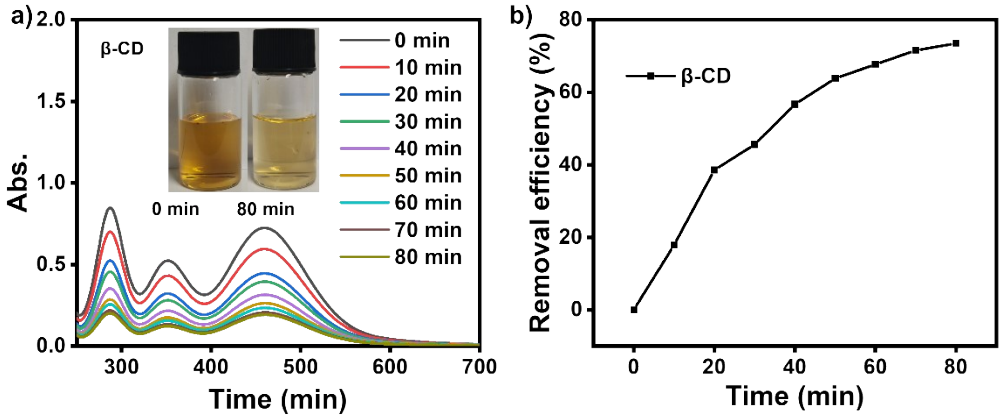


Figure S4. Removal of iodine from water by β-CD.

Section 6. Fitting of Langmuir and Freundlich adsorption isotherm data

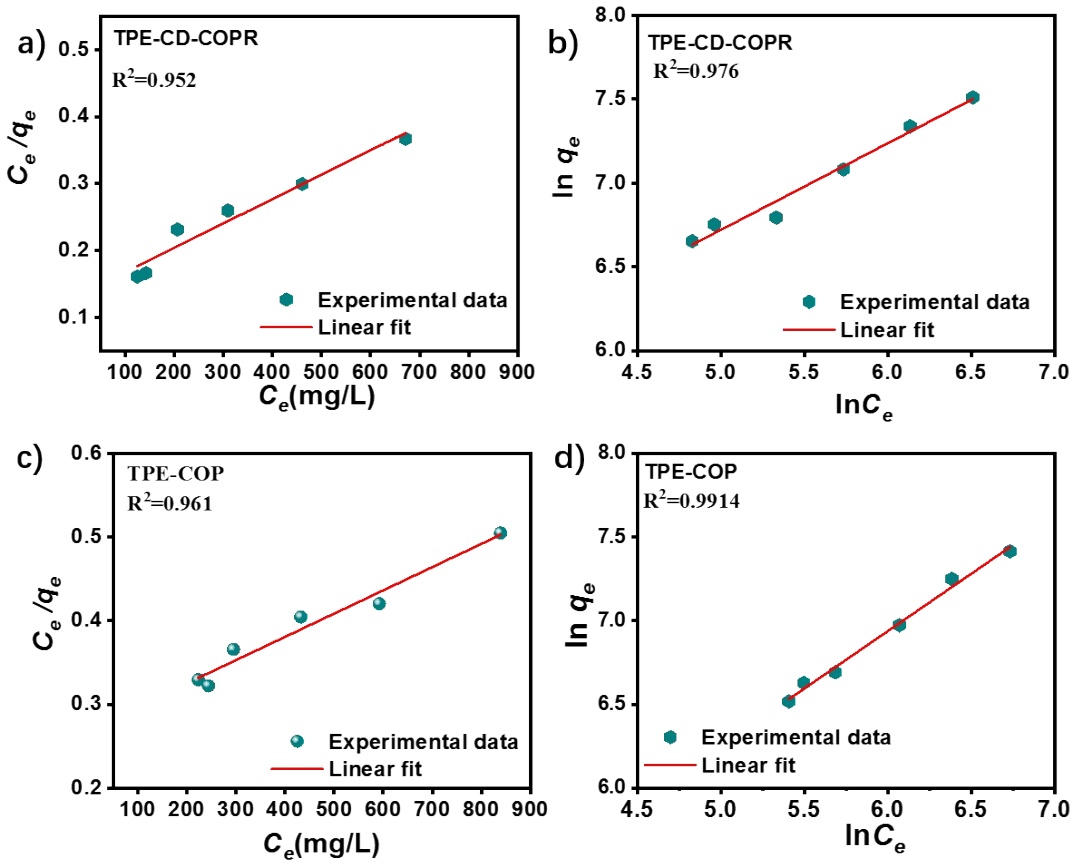


Figure S5. Fitting of Langmuir and Freundlich adsorption isotherm data for TPE-COP and TPE-CD-COPR in water. a) Langmuir models for TPE-COP; b) Langmuir models for TPE-CD-COP; c) Freundlich models for TPE-COP; d) Freundlich models for TPE-CD-COPR

Section 7. Iodine vapor capture

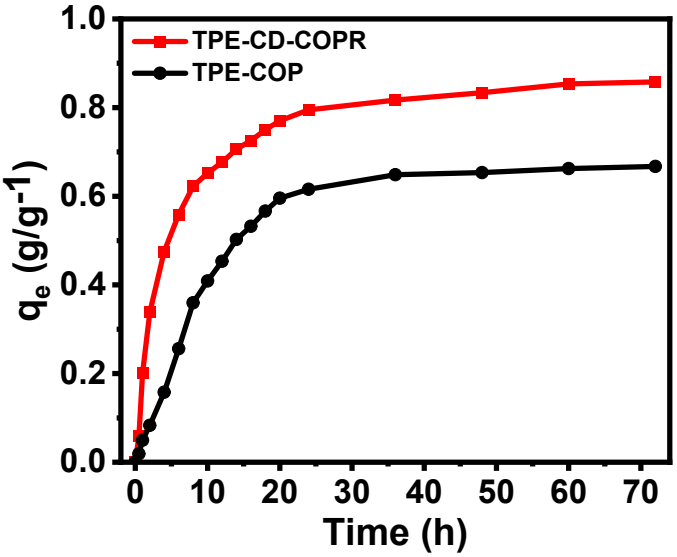


Figure S6. Iodine vapor capture of TPE-CD-COPR and TPE-COP.

Section 8. Supporting Tables

Table S1. Comparison of the TPE-CD-COPR with other porous polymers and cyclodextrin-based adsorbents for iodine capture from water.

Samples	Remove rate	Uptake equilibrium time	Reusability after 5 times	Reference
COPR-2	91%	80 min	-	[S1]
COPR-1	85%	80 min	-	[S1]
P-CDMs	81%	80 min	97.0%	[S2]
WFMC-1	100%	300 min	91.7%	[S3]
COPR-1	96.68±0.75 %	90 min	98.7±1.33 %,	[S4]
iFP-POP	100%	120 min	84.01%	[S5]
FO-POP	91.28%	140 min	73.80%	[S5]
Fc-PP-POP	99.31%	600 min	100%	[S6]
TAPB-BPDA COF	92%	60 mim	88%	[S7]
TPE-CD-COPR	100%	60 mim	99%	This work

Section 9. Supporting References

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[2] J. X. Wang, H. R. Shu, K. Guo, X. Wang and S. Zhang, Porous β-cyclodextrin polymer microspheres for iodine adsorption from aqueous solution, J. Mater. Sci., 2024, 59, 3327-3338.
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[5] C. Miao, N. Tang, L. Shi, S. Wang, P. Ji, J. Zhang, Z. Wang and B. Zhou, Ionic functionalized magnetic porous polymers as advanced materials for high-efficiency water decontamination: bactericidal and iodine adsorption, ACS Appl. Polym. Mater., 2023, 5, 8679-8692.
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[7] R. Chen, T. Hu and Y. Li, Stable nitrogen-containing covalent organic framework as porous adsorbent for effective iodine capture from water, React. Funct. Polym., 2021, 159, 104806.