Supporting Information

Pillar[5]arene-based 3D polymer network for efficient iodine capture in aqueous solution

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Supporting Information (12 pages)

1. Materials and methods

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 spectroscopy

Solid-state nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER 400WB AVANCE III spectrometer. 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 recycle delay (40 s recycle delay for PPD) with 5000 to 10000 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 pillar[5]arene units.

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Thermo Nicolet iS10 spectrometer.

Transmission electron microscopy

Transmission electron microscopy investigations were carried out on a HITACHI HT-7700 instrument.

Scanning electron microscopy

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

Thermogravimetric analysis

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

Surface area measurements

Surface area measurements were conducted on a BELSORP-Max Accelerated Surface Area and Porosimetry Analyzer. The sample (101 mg) was degassed at 100 ℃ 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 spectroscopy

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

Surface area measurements

Surface area measurements were conducted on a BELSORP-Max Accelerated Surface Area and Porosimetry Analyzer. The sample (101 mg) was degassed at 100 ℃ 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 1.00 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).

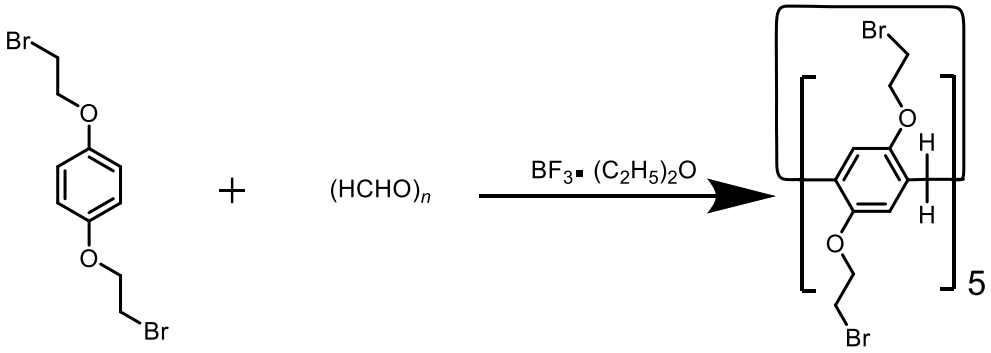
Scanning electron microscopy

Scanning electron microscopy (SEM) samples were prepared by dispersing 2.00 mg of polymer **DTTP5** in 10.0 mL of water and adding the suspension to the wafer *via* the vacuum freeze-drying methodology.

Transmission electron microscopy

Transmission electron microscopy (TEM) samples were prepared by dispersing 2.00 mg of polymer **DTTP5** in 10.0 mL of water and adding the suspension to the copper mesh *via* the vacuum freeze-drying methodology.

*2. Synthesis of **DBEP5**[S1]*



Scheme S1. Synthetic route to **DBEP5**.

1,4-Bis(2-bromoethoxy)benzene (6.74 g, 23.0 mmol) and paraformaldehyde (0.698 g, 23.0 mmol) were added into a round-bottom flask with 200 mL of 1,2-dichloroethane, and then BF_3•OEt_2 (2.91 mL, 20.6 mmol) was added to the mixture as a catalyst. The reaction was monitored by TLC. 80.0 mL of water was added to quench the reaction. The organic layer was concentrated. The mixture was purified through column chromatography using hexane:dichloromethane = 1:1 as the eluent to obtain pure **DBEP5** as a white solid (2.42g, 34%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 6.93 (s, 10H), 4.23 (t, J = 5.6 Hz, 20H), 3.86 (s, 10H), 3.62 (t, J = 5.6 Hz, 20H).

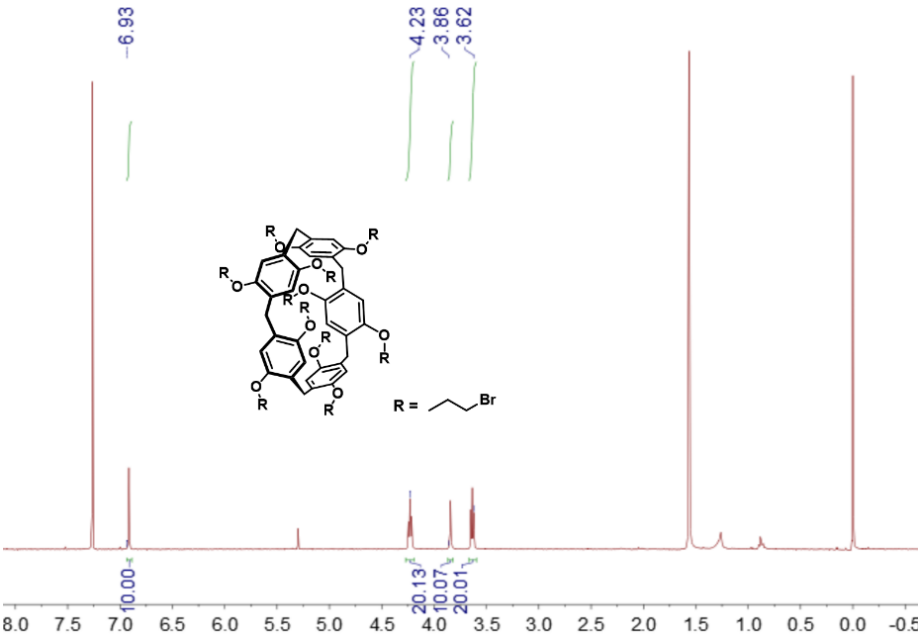
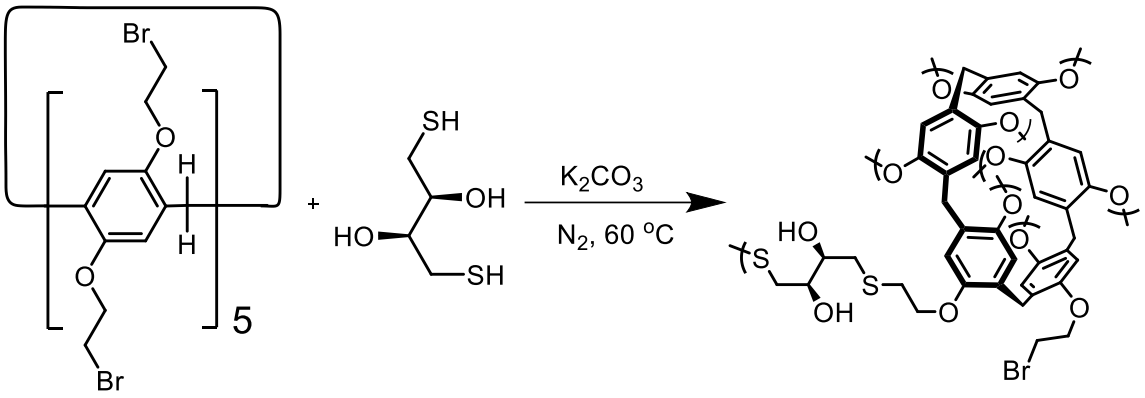


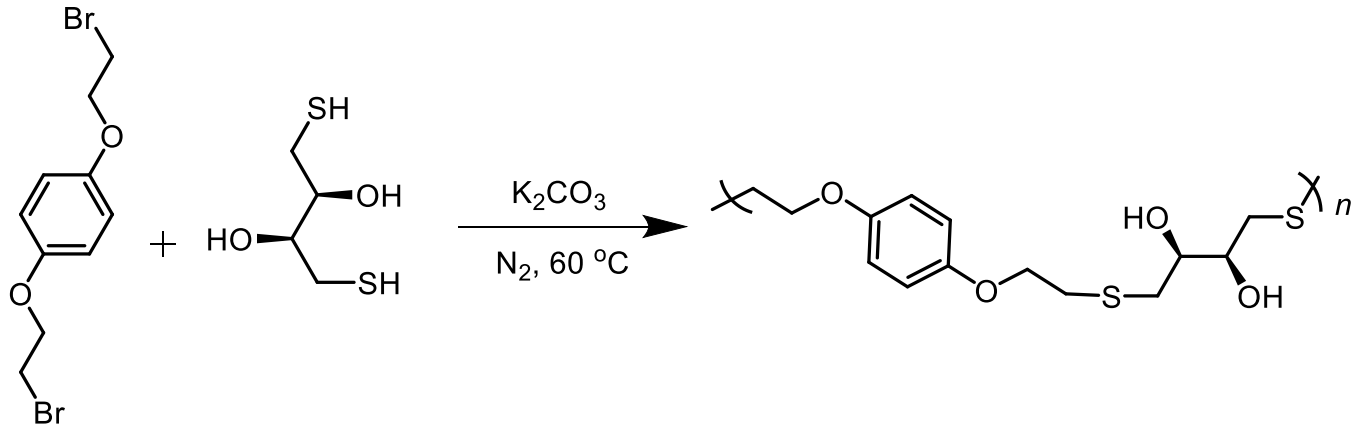
Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **DBEP5**.

*3. Synthesis of **DTTP5** and linear polymer*



Scheme S2. Synthetic route to **DTTP5**.

Synthesis of DTTP5: To a solution of DTT (0.250 g, 1.60 mmol) in 5.00 mL of CH_3CN was added K_2CO_3 (0.500 g, 3.60 mmol) and **DBEP5** (0.200 g, 0.120 mmol). The mixture was stirred under reflux for 3 days. After that, the insoluble solid was filtered. The white solid was washed thoroughly with dichloromethane, acetone, diluted HCl and water, and then dried in vacuum. The final product (0.180 g) is a white, insoluble powder.



Scheme S3. Synthetic route to linear polymer.

Synthesis of linear polymer: To a solution of DTT (0.250 g, 1.60 mmol) in 5 mL of CH_3CN was added K_2CO_3 (0.500 g, 3.60 mmol) and 1,4-bis(2-bromoethoxy)benzene (0.520 g, 1.60 mmol). The mixture was stirred under reflux for 2 days. After that, the insoluble solid was filtered. The white solid was washed thoroughly with dichloromethane, acetone, diluted HCl and water, and then dried in vacuum. The final product (0.420 g) is a white, insoluble powder.

4. Energy dispersive X-ray spectroscopy (EDX) analysis

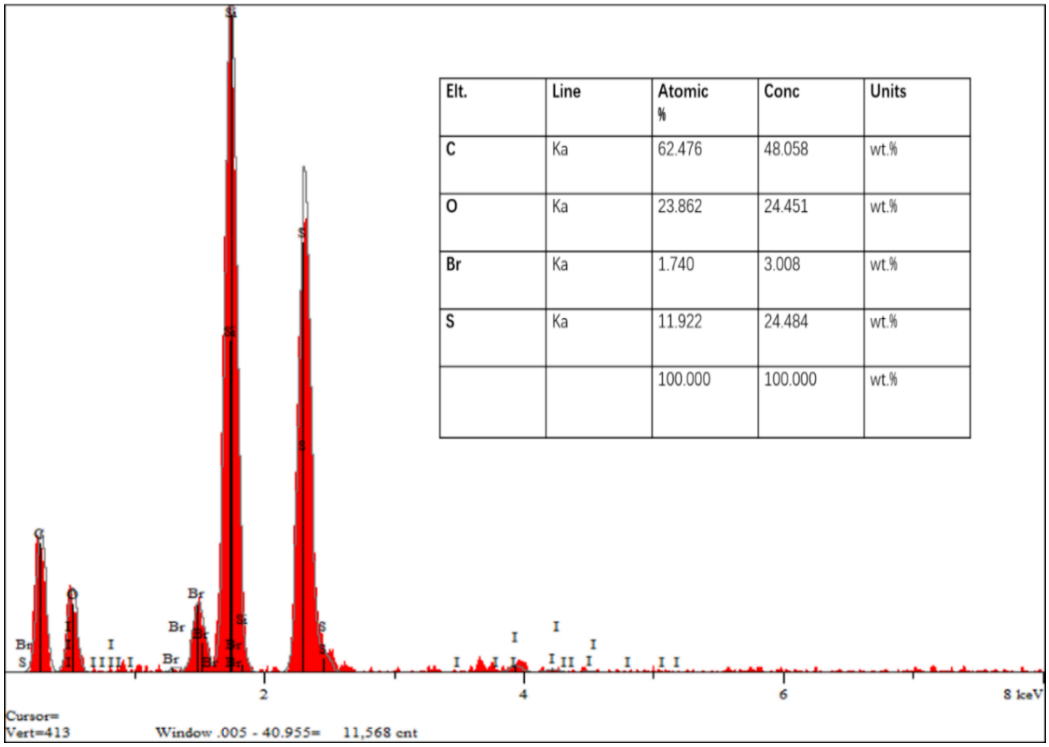


Fig. S2. EDX analysis of **DTTP5**. The spectra show the analyzed elements, and the table shows the approximate content of each element. The peaks of sulfur indicate DTT molecules were successfully loaded within the materials. The peaks of bromine are ascribed to the 2-bromoethyl groups in **DBEP5**. The peaks of silicon come from the silicon wafer used in SEM.

5. Thermogravimetric analysis

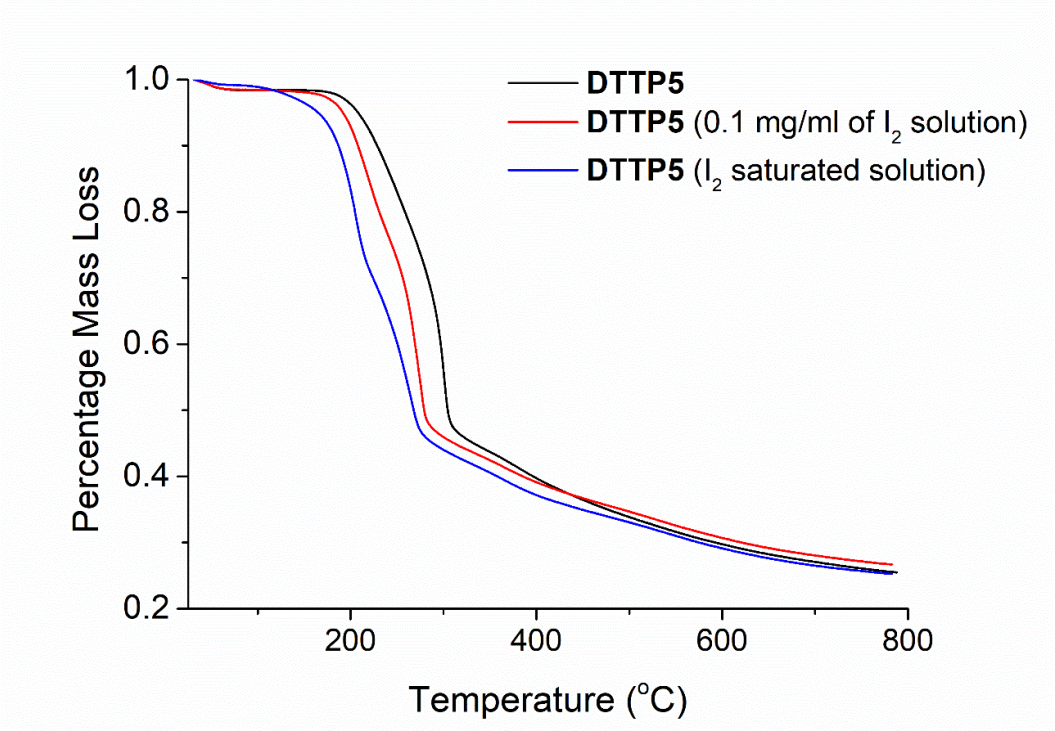


Fig. S3. Thermogravimetric curves of **DTTP5** (black line), **DTTP5-I₂** absorbed in a 0.100 mg/mL I_2 solution (red line), and **DTTP5-I₂** absorbed in an I_2 saturated solution (blue line).

6. Powder X-ray diffraction (XRD) analysis

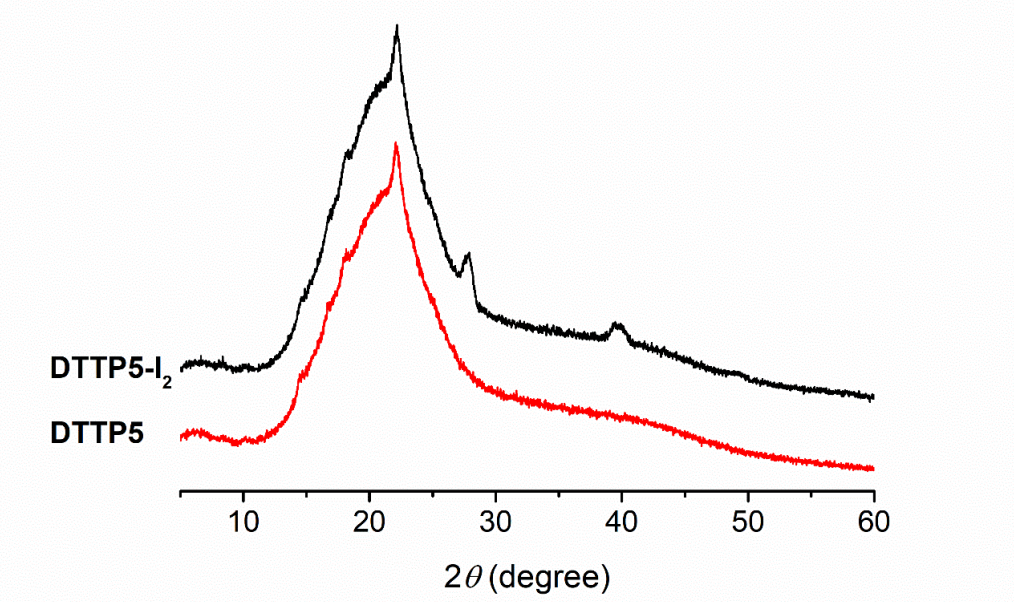


Fig. S4. Powder XRD analysis of **DTTP5** (red line) and **DTTP5-I₂** (black line).

7. Porosity and surface area measurements for ***DTTP5***

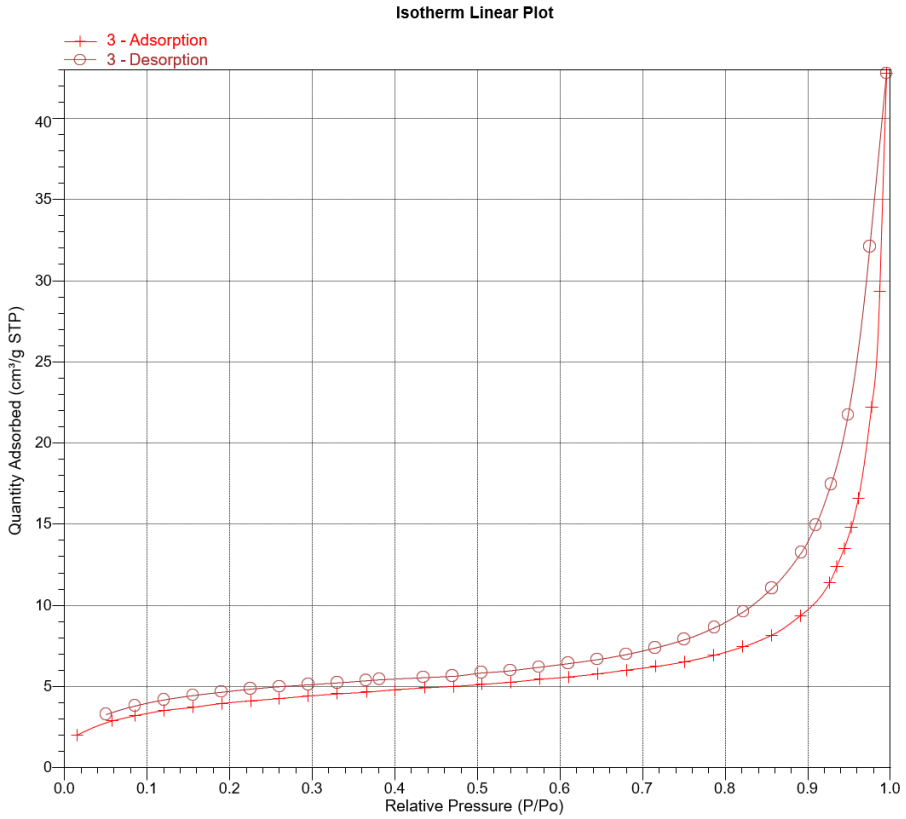


Fig. S5. N_2 sorption isotherm (77.0 K) and surface area data analysis of polymer **DTTP5**. BET surface area = 14.9 m^2/g.

8. Glass transition temperature (T_g) measurement for ***DTTP5***

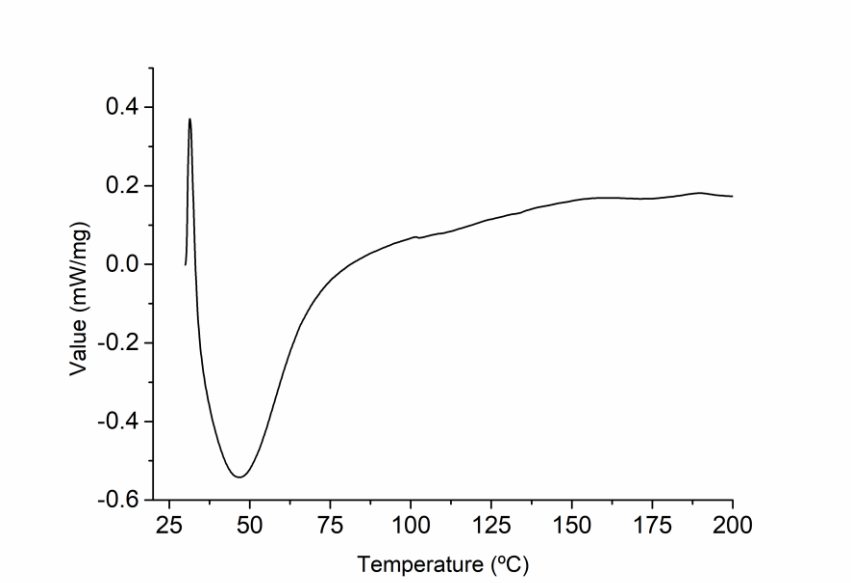


Fig. S6. Differential scanning calorimetry (DSC) analysis of **DTTP5**. The T_g of the polymer is 68.0 °C.

*9. The influence of the molar ratio between **DBEP5** and DTT*

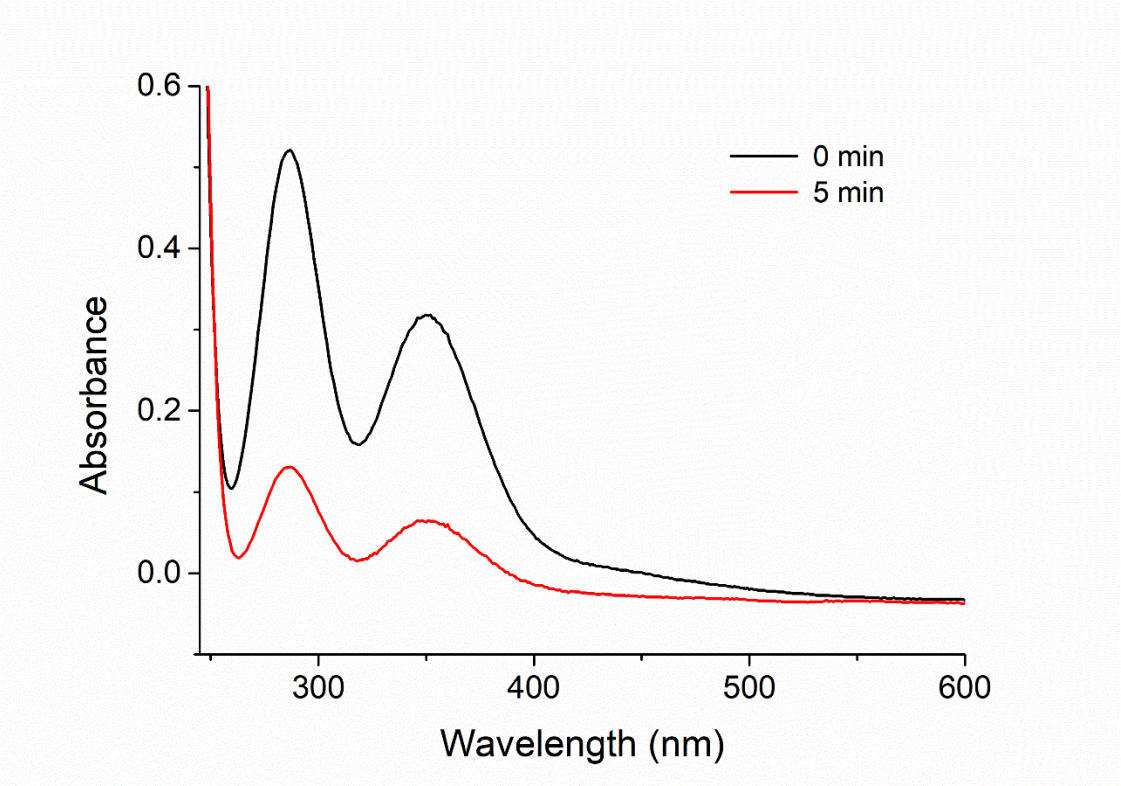


Fig. S7. UV-vis spectra of an I_2 aqueous solution (0.100 mg/mL) after adding the material prepared by **DBEP5** and DTT with a ratio of 1:6 and shaking for 5 min.

10. Inductively coupled plasma mass spectrometry (ICP-MS) analysis of iodine

Table S1. ICP-MS analysis of an iodine solution after absorbed by **DTTP5** with shaking for evaluating the content of iodine. The solution was diluted for ICP-MS analysis.

Sample Id	^{127}I (ppm)	^{127}I （mg/mL）
0.100 mg/mL Iodine aqueous solution	98.7	0.0987
Solution after absorption for 5 min	7.42	0.00730
Solution after absorption for 30 min	5.35	0.00530

Table S2. ICP-MS analysis of an iodine solution after absorbed by the linear polymer with shaking for evaluating the content of iodine. The solution was diluted for ICP-MS analysis.

Sample Id	^{127}I (ppm)	^{127}I （mg/mL）
0.100 mg/ml iodine aqueous solution	102	0.103
Solution absorbed after 5 min	57.1	0.0571
Solution absorbed after 30 min	48.1	0.0481

11. UV-vis spectra of iodine absorption with the linear polymer

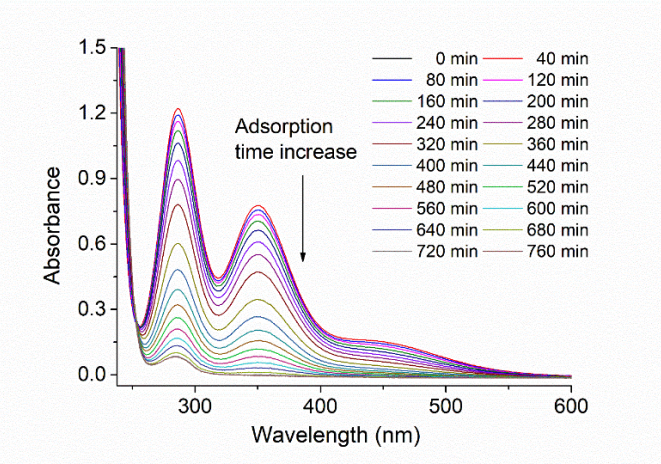


Fig. S8. UV-vis spectra of an I_2 aqueous solution (0.100 mg/mL) recorded every 40 min after adding the linear polymer without shaking.

12. Removal of dyes from water

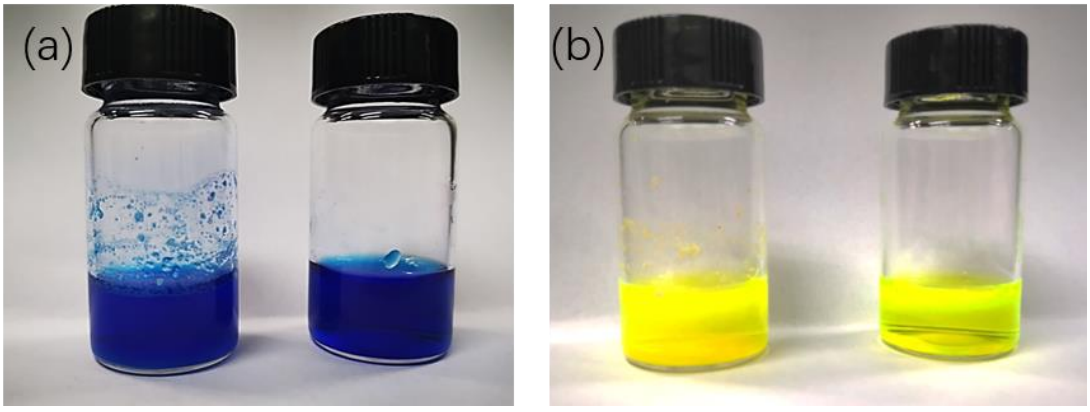


Fig. S9. Photographs of solutions of (a) methylene blue and (b) sodium fluorescein before (right) and after (left) adding **DTTP5**.

13. Reference

[S1] H. Zhu, B. Shi, L. Gao and F. Huang, *Polym. Chem.* 2017, **8**, 7108.