

Supporting Information

Highly selective removal of thiophene from benzene by cucurbit[6]uril in both mixed vapors and solutions

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Table of Contents

| | |
|---|----|
| 1. <i>Materials</i> | 1 |
| 2. <i>Methods</i> | 1 |
| 3. <i>Crystallographic Data</i> | 3 |
| 4. <i>Characterization of Cucurbit[6]uril (Q[6])</i> | 5 |
| 5. <i>Uptake of a p Benzene/Thiophene Mixture by Q[6]</i> | 8 |
| 6. <i>Recyclability of Q[6] Crystals</i> | 15 |
| 7. <i>References</i> | 18 |

1. Materials

All chemicals and solvents were commercially available: Benzene (Ben) (>99 %), and thiophene (TPE) (>99 %) were purchased from Adamas-beta Co., Ltd. Q[6] were synthesized by a reported method in our laboratory.¹ Then desolvated Q[6] were prepared as adsorbent materials, Q[6] used in this experiment needs to be recrystallized with 3 M hydrochloric acid in advance and vacuum dried for 12 hours at 80 °C.

2. Methods

2.1. Solution NMR

Solution ¹H NMR spectra were recorded at 400 MHz using a JEOL JNM-ECZ 400s spectrometer. Before measurements, the adsorbents underwent a preheating process at a temperature of 20 °C for a duration of 10 minutes to eliminate any surface physically adsorbed vapors.

2.2. Powder X-Ray Diffraction

Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultimate-IV X-ray diffractometer operating at 40 kV/30 Ma using the Cu K α line ($\lambda = 1.5418 \text{ \AA}$). Data were measured over the range of 5–50° in 10°/min steps over 8 min.

2.3. Single crystal X-ray diffraction

Single crystal X-ray data were obtained on a Bruker D8 Venture diffractometer with a graphite-monochromated Mo K α radiation source ($\lambda = 0.71073 \text{ \AA}$).

2.4. Gas Chromatography

Gas chromatographic (GC) analysis: GC measurements were carried out using an SHIMADZU GC2014C instrument configured with an FID detector and a OV-1301 column (30 m \times 0.53 mm \times 1.0 μ m). Samples were analyzed using headspace injections and were performed by incubating the sample at 70 °C for 15 min followed by sampling 1 mL of the headspace. The following GC method was used: the oven was programmed from 50 °C, and ramped in 10 °C min⁻¹ increments to 100 °C with 5 min hold; the total run time was 15 min; injection temperature was 250 °C; detector temperature was 280 °C with air, and H₂ of 300, and 40 mL min⁻¹, respectively; nitrogen (carrier gas) flow-rate was 1 mL min⁻¹. The samples were injected in the split mode (50:1).

2.5. Adsorption experiments

2.5.1 The evaluation of performance for separating Ben and TPE

A 20 mL sealed vial was utilized to enclose an open 5 mL vial, which contained 0.0200 g of Q[6] adsorbent devoid of any guest molecules. The 20 mL vial contained 1 mL of an

equimolar mixture of Ben and TPE. The uptake of Ben or TPE by Q[6] was monitored hourly by fully dissolving the crystals and quantifying the ratio of Ben or TPE to Q[6] using ^1H NMR spectroscopy. The relative adsorption capacities of Ben and TPE by Q[6] were also quantified through thermal desorption of the adsorbed vapors from the crystals, followed by gas chromatographic (GC) analysis to determine the relative amounts of Ben and TPE in the desorbed vapor.

2.5.2 Chemical Industry Separation Simulation

In the solid-vapor experiment, about 5 mg of Q[6] was added to a 5 ml vial, which was then placed into a 20 ml vial containing 5 ml of Ben/TPE ($V_{\text{Ben}}:V_{\text{TPE}} = 50:1$) mixture, sealed and left to adsorb for 9 hours. Then Q[6] was taken out and heated under vacuum at 20 °C for 10 min to remove the molecules adsorbed on the surface and the selectivity of Q[6] was investigated by GC.

In the solid-liquid experiments, 20 mg of Q[6] was directly added to 5 mL of Ben/TPE ($V_{\text{Ben}}:V_{\text{TPE}} = 50:1$) mixed liquid with continuous stirring for 24 h. The content of TPE in the liquid before and after the adsorption was measured by GC, which was used to investigate the removal ability of Q[6] on TPE.

2.5.3 Recycle experiments

Adsorption experiments were performed using 10 mg of adsorbent in 2 ml of a mixed solution comprising equal volumes of Ben/TPE with continuous stirring for 9 hours. Subsequently, the adsorbed TPE was desorbed from Q[6] by heating under vacuum at 100 °C, and then the Q[6] adsorbent was used for multiple cycles of selective adsorption of TPE within the Ben/TPE system, and its reusability was evaluated by ^1H NMR and GC.

2.6. Single Crystal Growth

Q[6] (10 mg, 0.008 mmol) was added to 3 M HCl and slightly heated to dissolve it. A mixture of thiophene and DMSO dissolved in 4 times the molar amount of Q[6] was then added to the solution. The resulting clear solution was slowly evaporated and colorless transparent crystals were obtained after one month.

2.7. Solvent Desorption

Q[6] was heated at 20 °C for 10 min to remove unbound benzene or thiophene molecules adsorbed on the surface. Organic solvents were then added to it and ultrasonicated for more than 30 minutes, and the liquid was centrifuged and the supernatant was tested.

3. Crystallographic Data

Table S1. Experimental single crystal X-ray data for TPE@Q[6] structures.

| Identification code | TPE@Q[6] |
|---|--|
| Empirical formula | C ₁₆₀ H ₁₆₀ N ₉₆ O ₄₈ S ₄ |
| Formula weight | 4324.07 |
| Temperature/K | 273.15 |
| Crystal system | orthorhombic |
| Space group | <i>P</i> 2 ₁ 2 ₁ 2 ₁ |
| a/Å | 16.7329(10) |
| b/Å | 29.2039(19) |
| c/Å | 11.5629(8) |
| α /° | 90 |
| β /° | 90 |
| γ /° | 90 |
| Volume/Å ³ | 5650.4(6) |
| Z | 1 |
| ρ_{calc} /cm ³ | 1.271 |
| μ /mm ⁻¹ | 0.133 |
| F(000) | 2240.0 |
| Crystal size/mm ³ | 0.17 × 0.13 × 0.13 |
| Radiation | MoK α (λ = 0.71073) |
| 2 Θ range for data collection/° | 4.504 to 56.968 |
| Index ranges | -22 ≤ h ≤ 22, -39 ≤ k ≤ 38, -15 ≤ l ≤ 15 |
| Reflections collected | 181363 |
| Independent reflections | 14193 [R _{int} = 0.0905, R _{sigma} = 0.0439] |
| Data/restraints/parameters | 14193/836/695 |
| Goodness-of-fit on F ² | 2.014 |
| Final R indexes [I >= 2 σ (I)] | R ₁ = 0.1361, wR ₂ = 0.2166 |
| Final R indexes [all data] | R ₁ = 0.1494, wR ₂ = 0.2354 |
| Largest diff. peak/hole / e Å ⁻³ | 2.47/-1.32 |
| Flack parameter | 0.41(18) |
| CCDC | 2312878 |

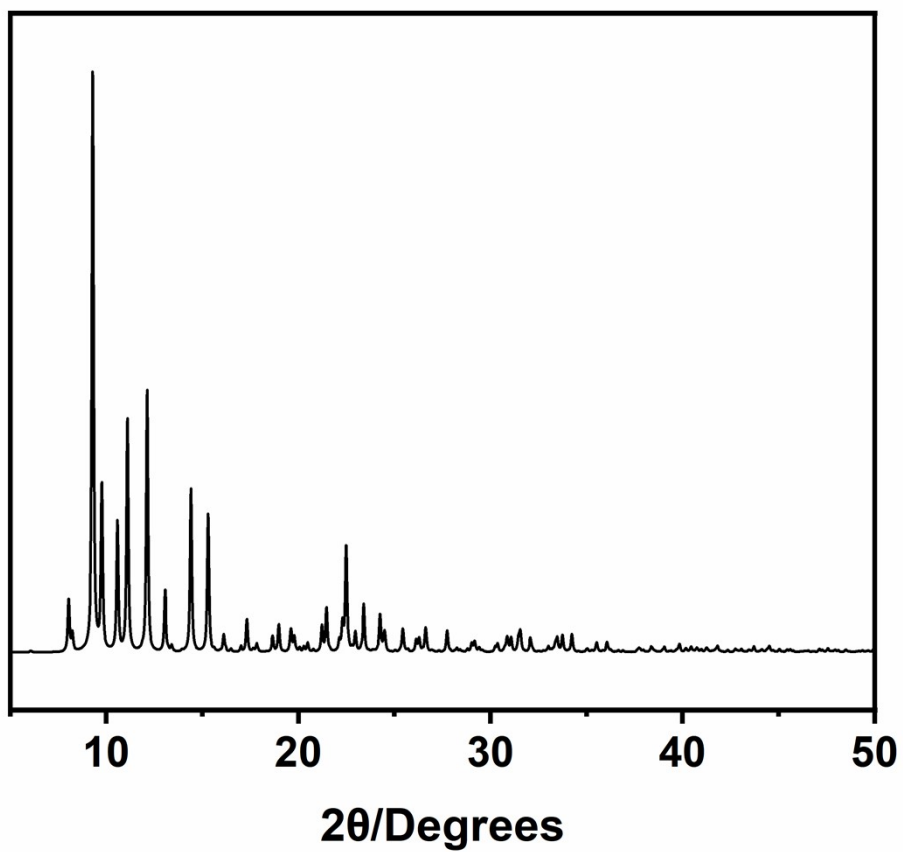


Fig. S1. Powder X-ray diffraction patterns of simulated from the single crystal structure of TPE@Q[6]

4. Characterization of Sorbent Crystalline Q[6]

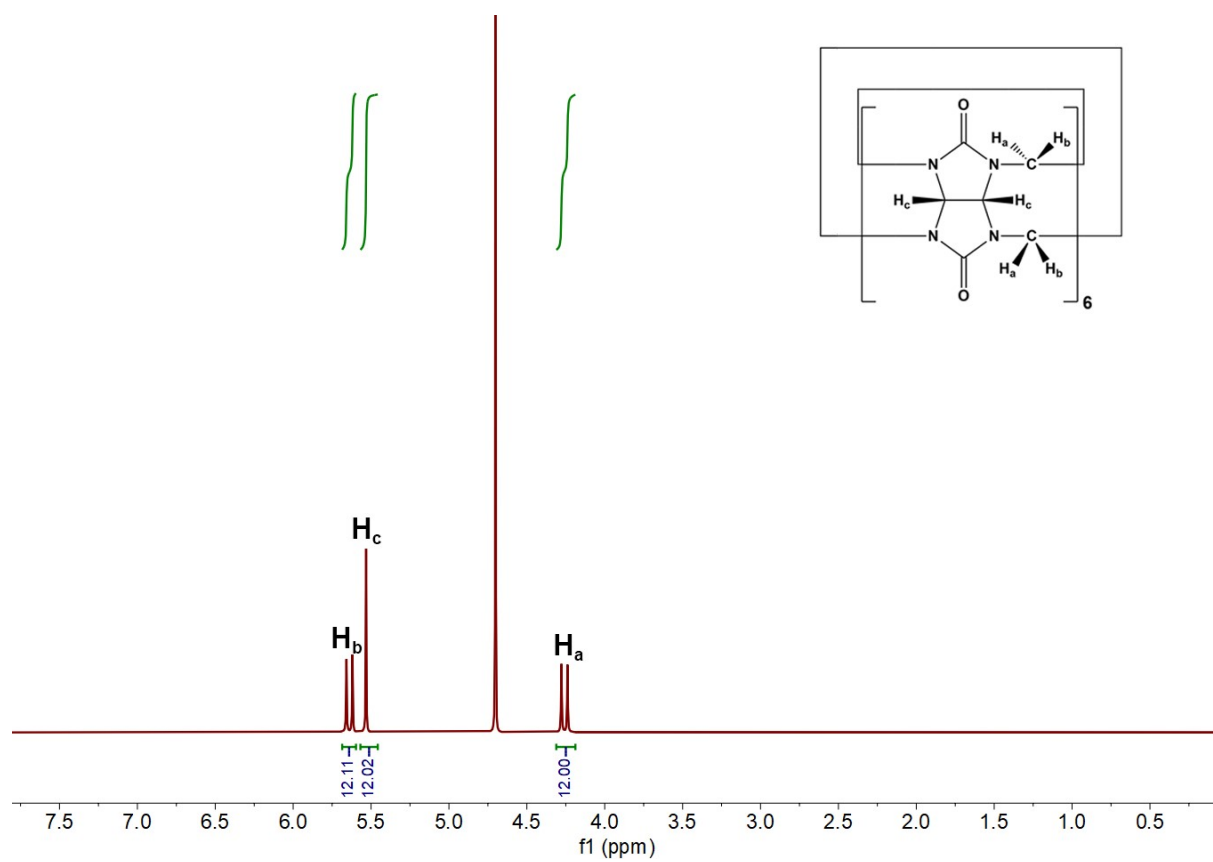


Fig. S2. ¹H NMR spectrum (400 MHz, D₂O, 298 K) of Q[6] in a 0.05 M Na₂SO₄ solution (Na₂SO₄ was added due to the poor solubility of Q[6] in water).

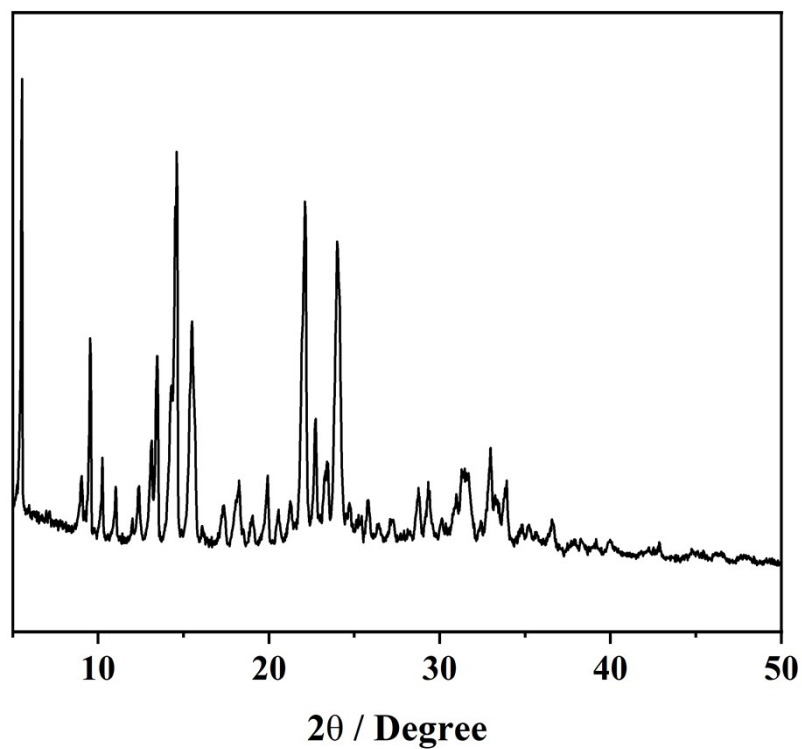


Fig. S3. Powder X-ray diffraction patterns of Q[6] crystals.

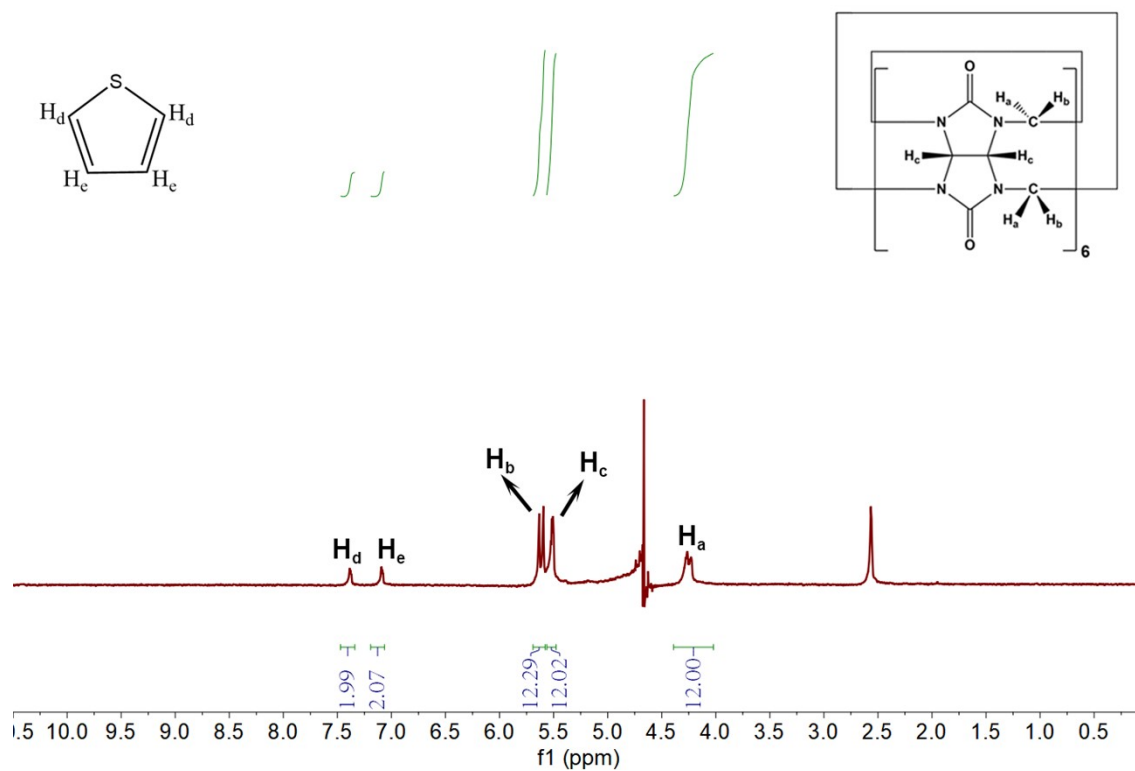


Fig. S4. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$: $\text{D}_2\text{O} = 1:10$, 298 K) of Q[6] after sorption of thiophene vapor (dissolved in a 0.05 M Na_2SO_4 aqueous solution).

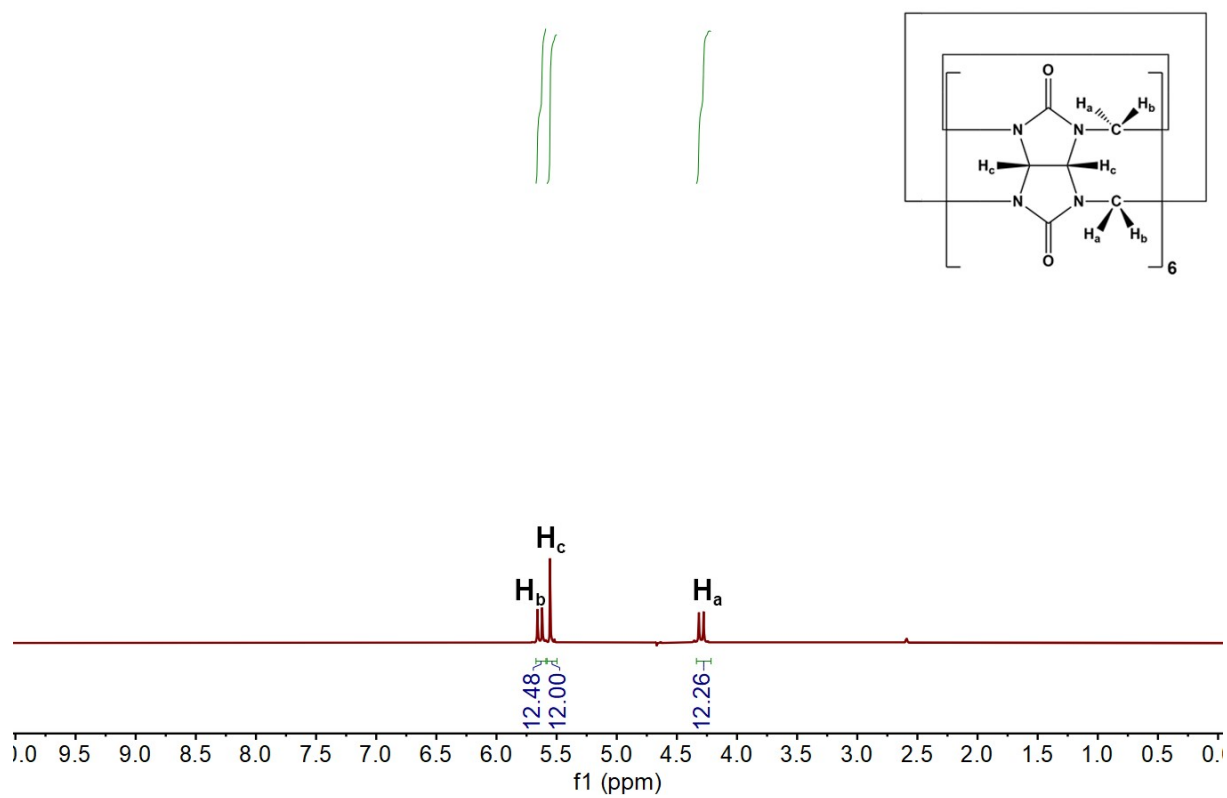


Fig. S5. ¹H NMR spectrum (400 MHz, DMSO-*d*₆:D₂O = 1:10, 298 K) of Q[6] after sorption of Benzene vapor (dissolved in a 0.05 M Na₂SO₄ aqueous solution).

5. Uptake from a Benzene/Thiophene Mixture by Q[6]

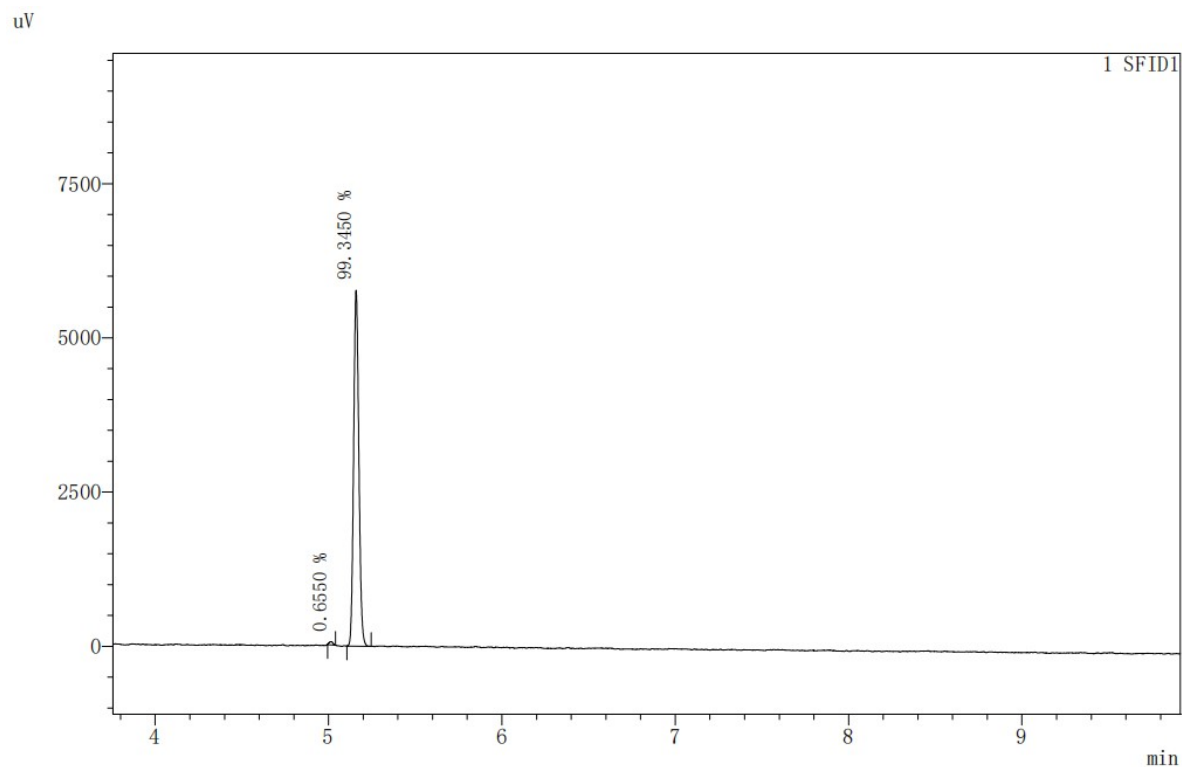


Fig. S6. Relative uptake of the benzene/thiophene mixture ($v:v = 50:50$) adsorbed by Q[6] (after adsorption of this mixture vapor for 9 hours) using gas chromatography.

Table S2. Relative uptake of the benzene/thiophene mixture ($v:v = 50:50$) adsorbed by Q[6] (after adsorption of this mixture vapor for 9 hours) using gas chromatography.

| Substance | RetTime [min] | Peak area | Separation purity |
|-----------|---------------|-----------|-------------------|
| Ben | 5.014 | 79 | 0.6550% |
| TPE | 5.159 | 12027 | 99.3450% |

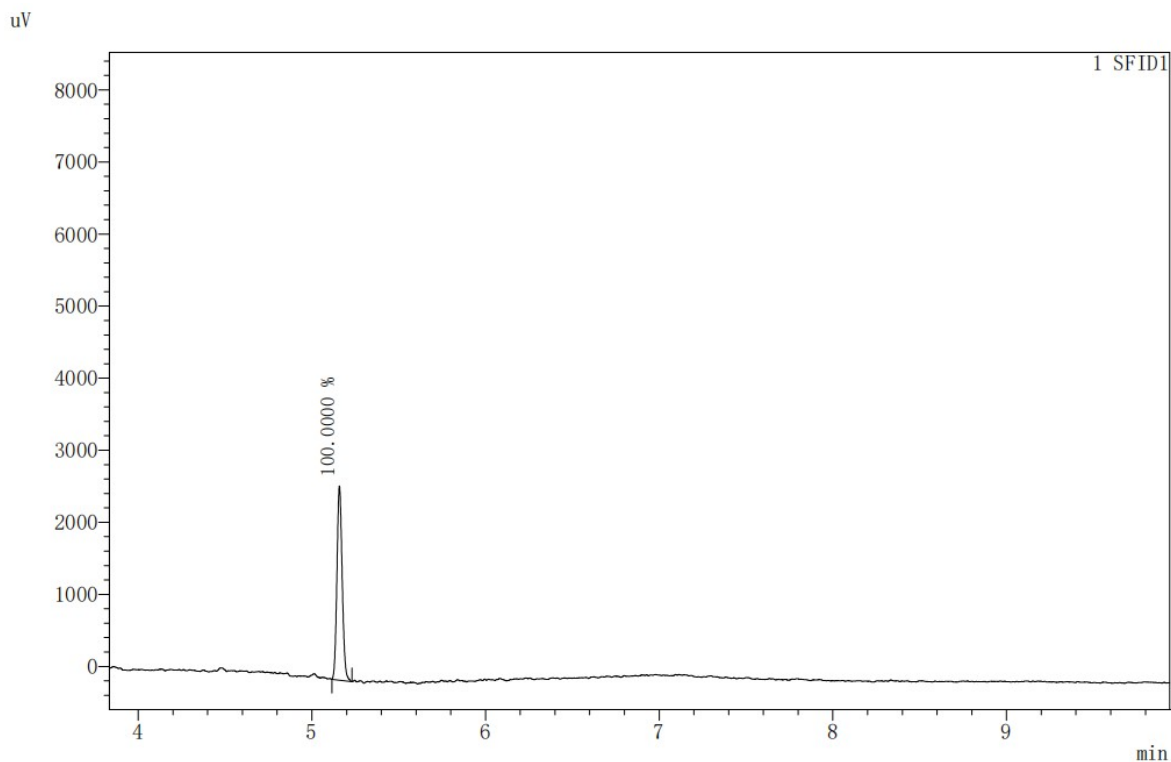


Fig. S7. Relative uptake of the benzene/thiophene mixture ($v:v = 1:1$) adsorbed by Q[6] (after immersion in this mixture for 9 hours) using gas chromatography.

Table S3. Relative uptake of the benzene/thiophene mixture ($v:v = 1:1$) adsorbed by Q[6] (after immersion in this mixture for 9 hours) using gas chromatography.

| Substance | RetTime [min] | Peak area | Separation purity |
|-----------|---------------|-----------|-------------------|
| TPE | 5.159 | 5684 | 100% |

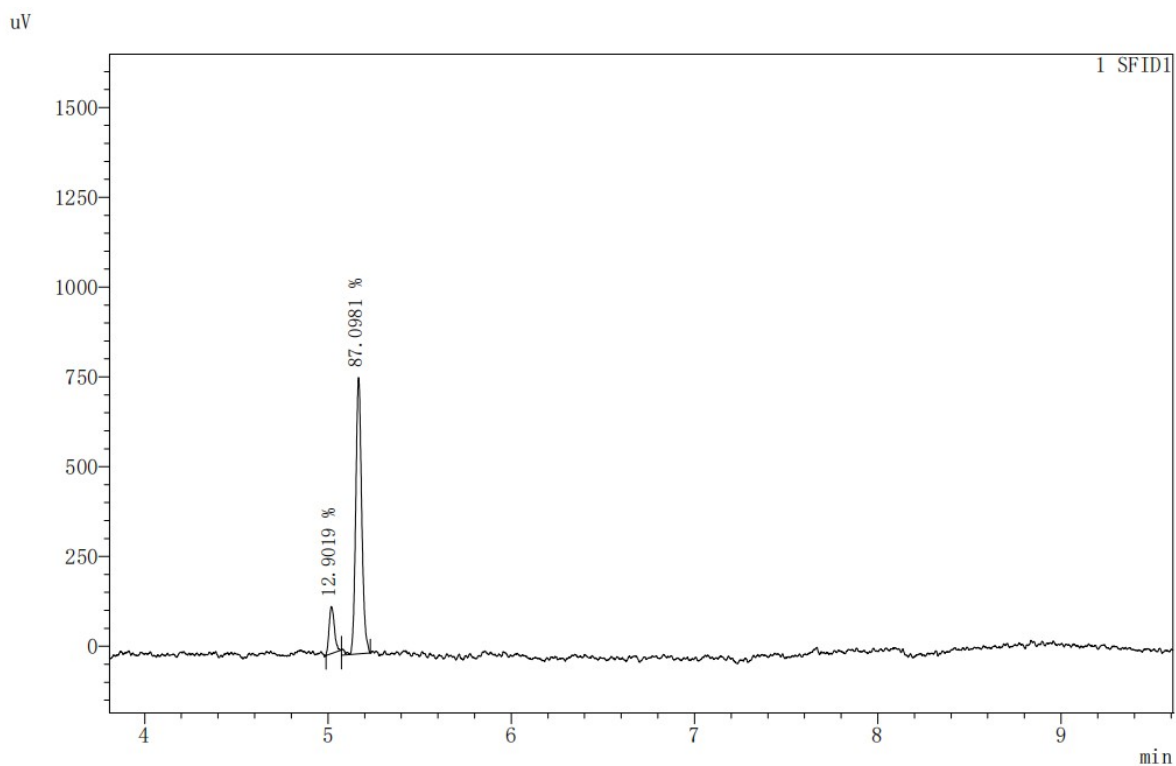


Fig. S8. Relative uptake of the benzene/thiophene mixture ($v:v = 50:1$ 5mL) adsorbed by Q[6] (after adsorption of this mixture vapor for 9 hours) using gas chromatography.

Table S4. Relative uptake of the benzene/thiophene mixture ($v:v = 50:1$ 5mL) adsorbed by Q[6] (after adsorption of this mixture vapor for 9 hours) using gas chromatography.

| Substance | RetTime [min] | Peak area | Separation purity |
|-----------|---------------|-----------|-------------------|
| Ben | 5.019 | 260 | 12.9019% |
| TPE | 5.167 | 1754 | 87.0981% |

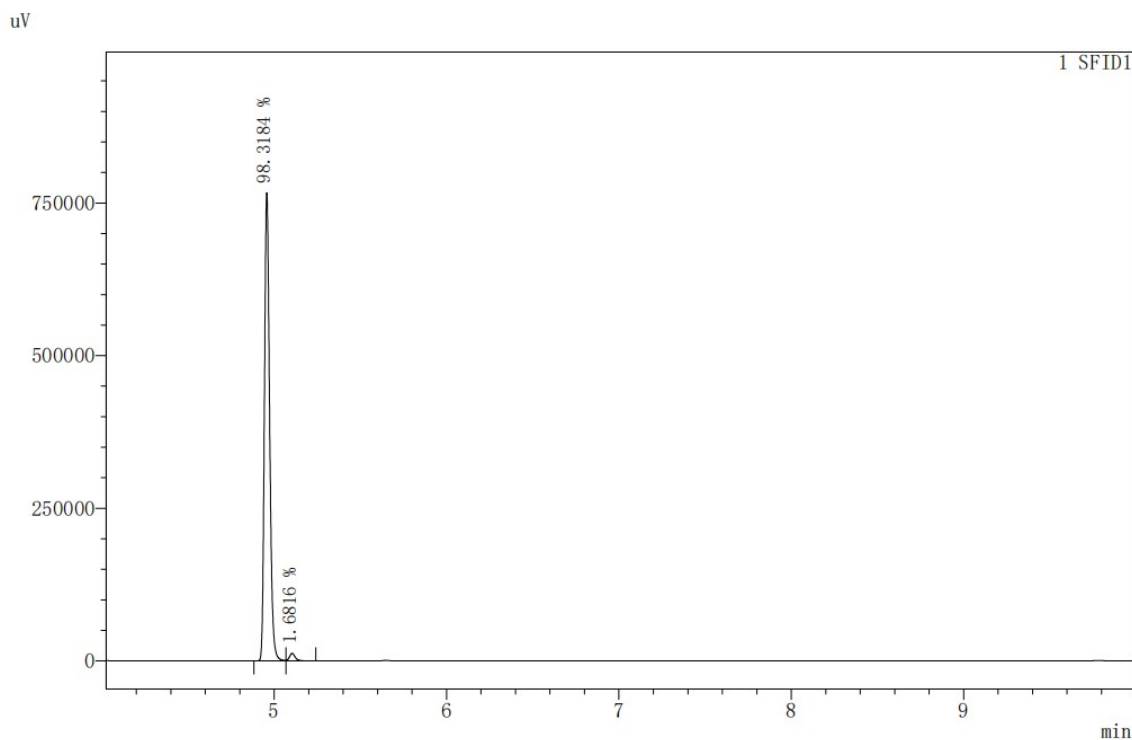


Fig. S9. Gas chromatography of the benzene/thiophene mixture ($v:v = 50:1$, 5 mL) before adsorption by Q[6].

Table S5. Gas chromatography of the benzene/thiophene mixture ($v:v = 50:1$, 5 mL) before adsorption by Q[6].

| Substance | RetTime [min] | Peak area | Separation purity |
|-----------|---------------|-----------|-------------------|
| Ben | 4.957 | 1604974 | 98.3184% |
| TPE | 5.104 | 27451 | 1.6816% |

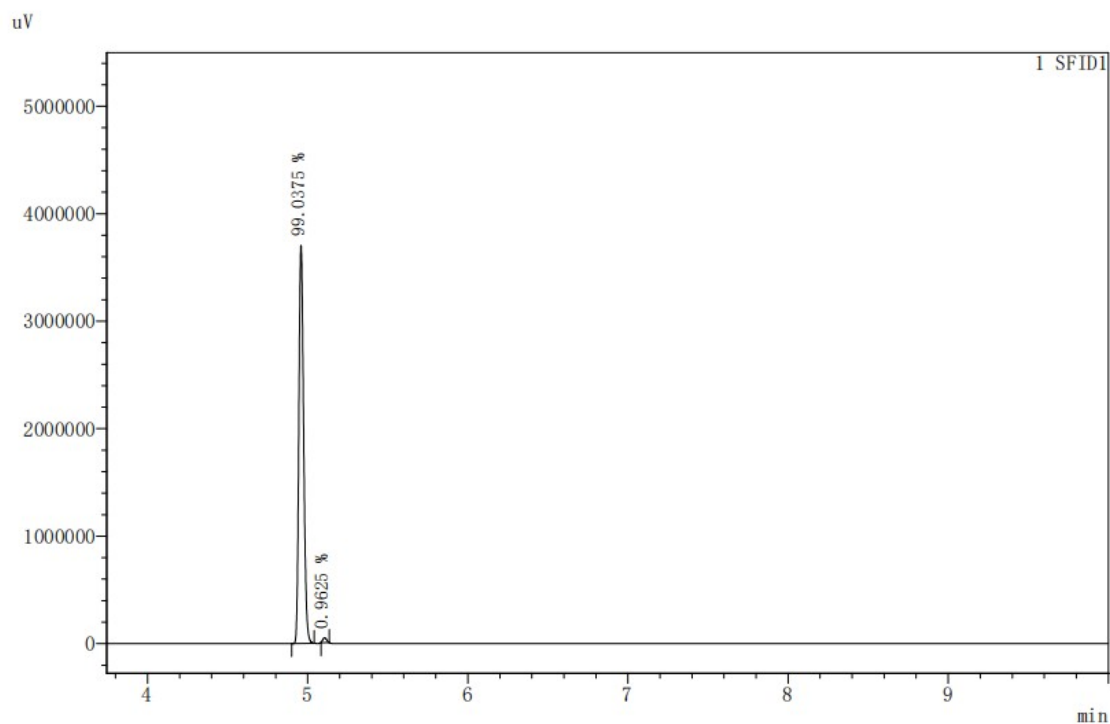


Fig. S10. Gas chromatography of the benzene/thiophene mixture ($v:v = 50:1$, 5 mL) after 5 mg of Q[6] was immersed in this mixture for 24 hours.

Table S6. Gas chromatography of the benzene/thiophene mixture ($v:v = 50:1$, 5 mL) after 5 mg of Q[6] was immersed in this mixture for 24 hours.

| Substance | RetTime [min] | Peak area | Separation purity |
|-----------|---------------|-----------|-------------------|
| Ben | 4.958 | 7644021 | 99.0375% |
| TPE | 5.105 | 74290 | 0.9625% |

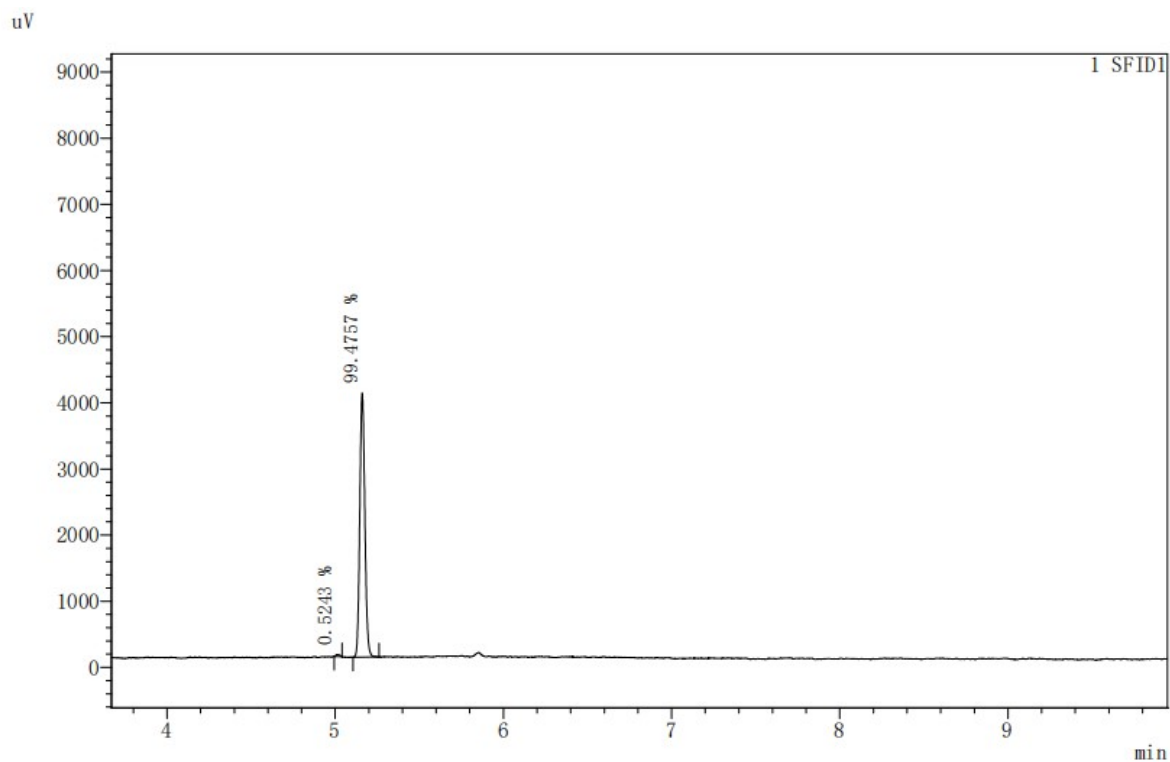


Fig. S11. Relative uptake of the desorption solution adsorbed by Q[6] (after immersion in this mixture for 9 hours) using gas chromatography.

Table S7. Relative uptake of the desorption solution adsorbed by Q[6] (after immersion in this mixture for 9 hours) using gas chromatography.

| Substance | RetTime [min] | Peak area | Separation purity |
|-----------|---------------|-----------|-------------------|
| Ben | 5.012 | 44 | 0.5243% |
| TPE | 5.161 | 8357 | 99.4757% |

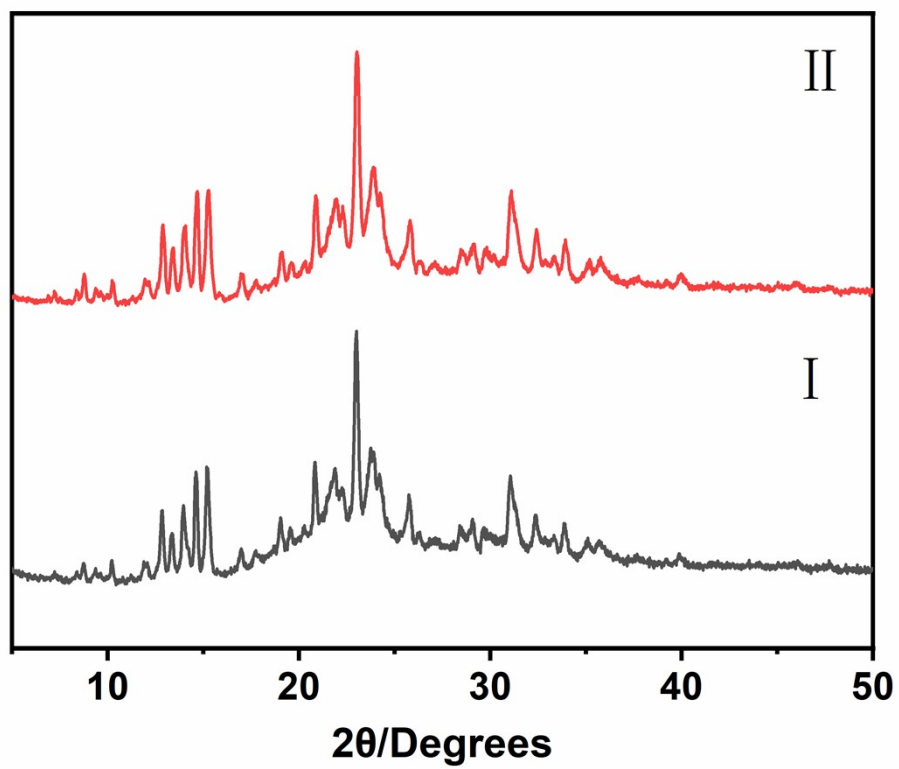


Fig. S12. Powder X-ray diffraction patterns: (I) after adsorption of Ben/TPE mixture vapor; (II) after adsorption of Ben/TPE mixture solution.

6. Recyclability of Q[6]

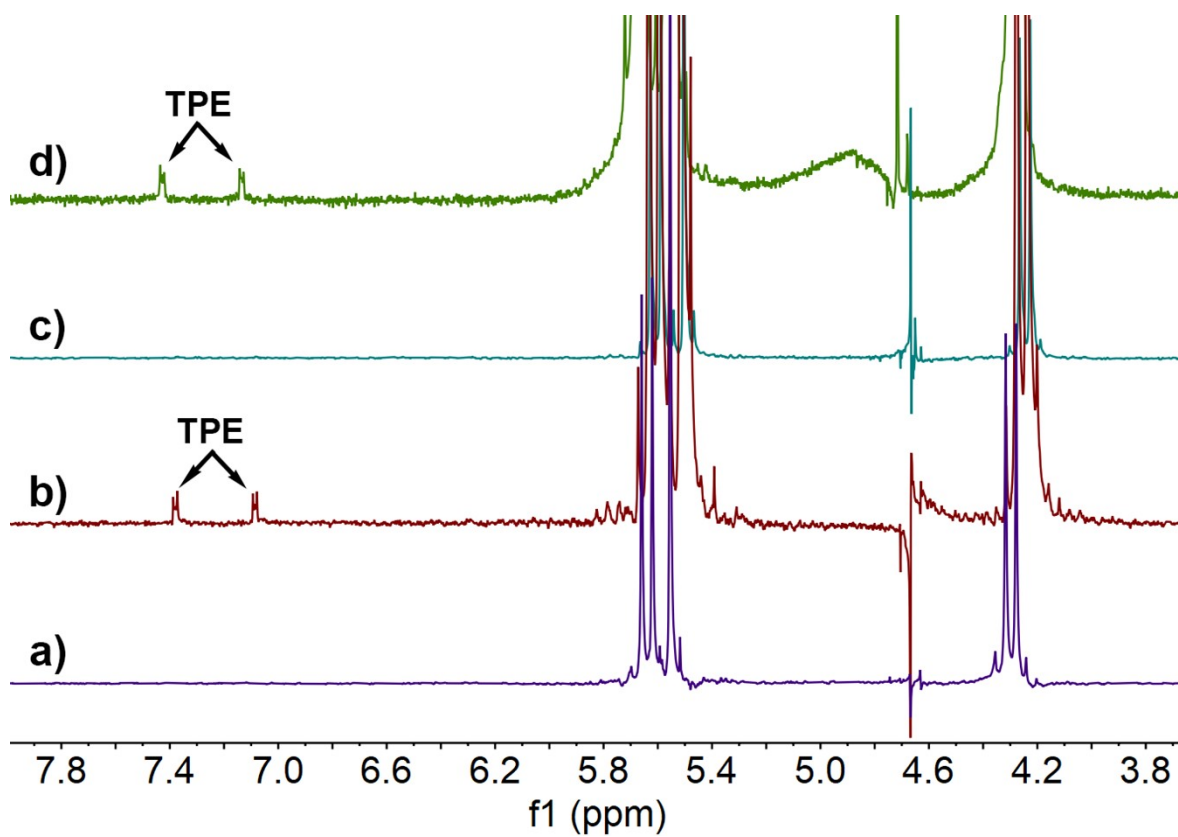


Fig. S13. ¹H NMR spectra (400 MHz, DMSO-*d*₆:D₂O = 1:10, 298 K): (a) original Q[6]; (b) Q[6] after adsorption of TPE; (c) TPE@Q[6] after removal of TPE; (d) desolvated TPE@Q[6] after adsorption of TPE vapor.

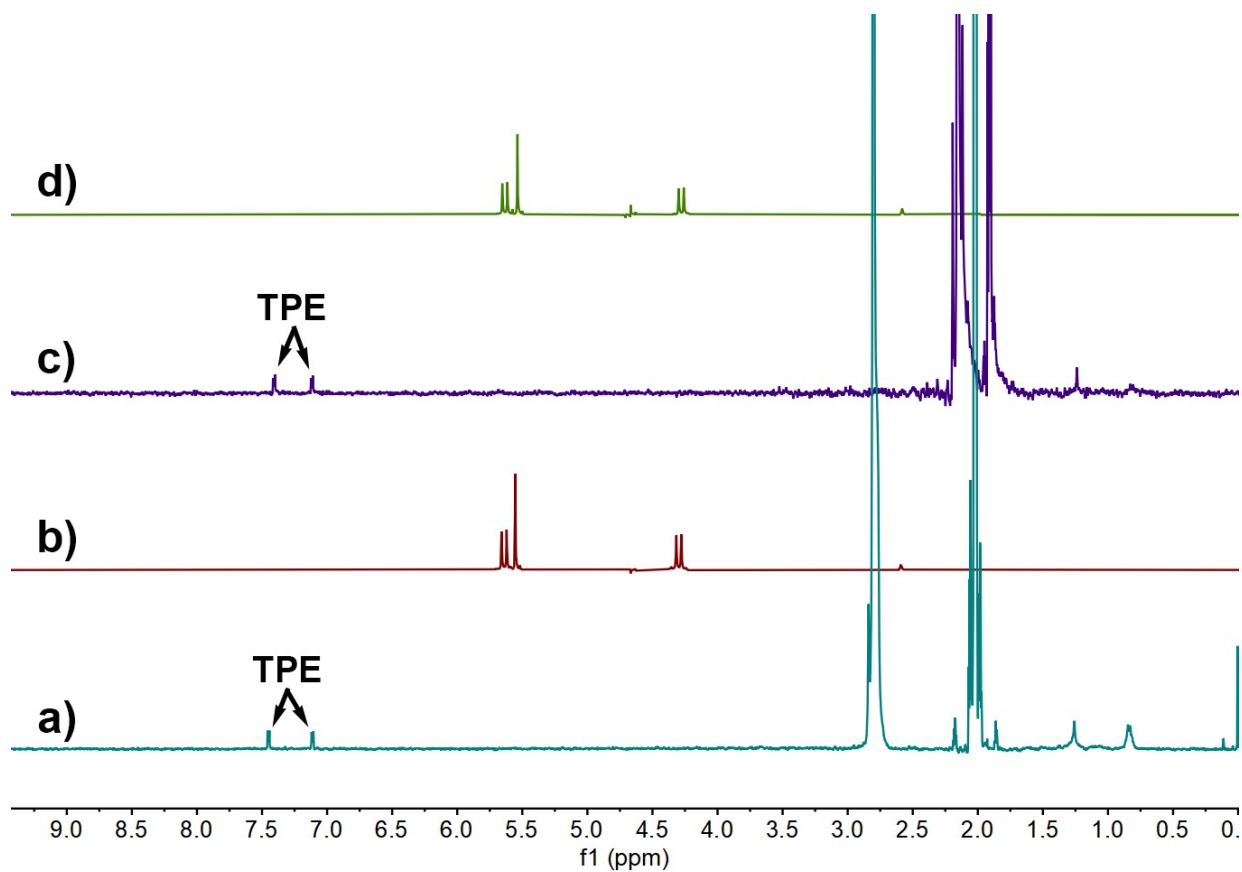


Fig. S14. (a) Acetone after completion of desorption, (b) TPE@Q[6] after desorption of TPE using acetone, (c) Acetonitrile after completion of desorption, and (d) TPE@Q[6] after desorption of TPE using acetonitrile.

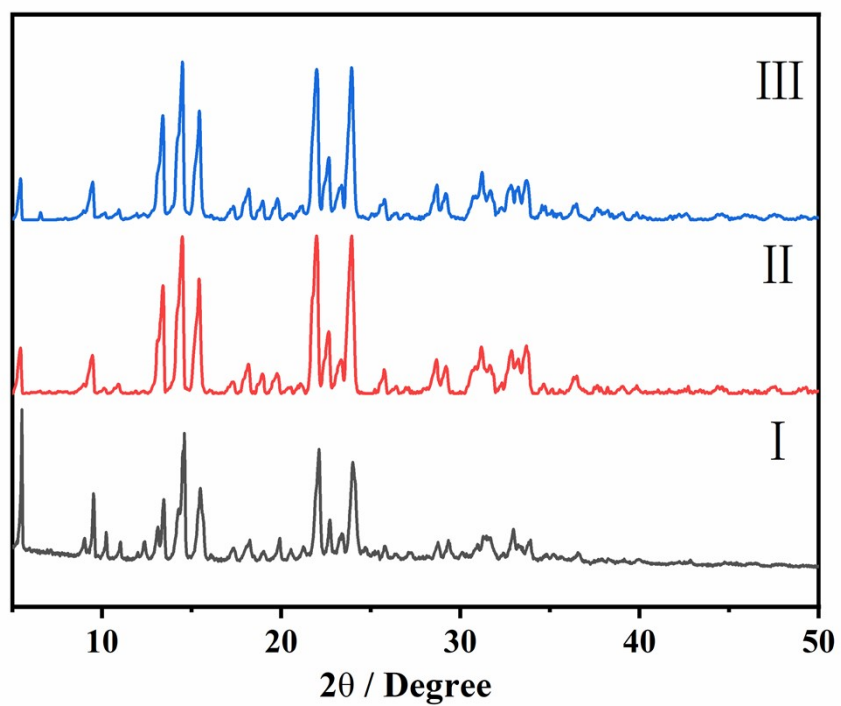


Fig. S15. The PXR D patterns of (I) original Q[6]; (II) After removal of TPE by thermal desorption TPE@Q[6]; (III) TPE@Q[6] after desorption of TPE using acetone or acetonitrile.

7. References

1. H. Cong, X. Ni, X. Xiao, Y. Huang, Q.-J. Zhu, S.-F. Xue, Z. Tao, L. F. Lindoy, G. Wei, *Org. Biomol. Chem.* 2016, **14**, 4335-4364.