Supplementary Information (SI) for ChemComm.

Pillar[5]arene-Based Crosslinked Covalent Network for Efficient Heavy Metal Ion Adsorption

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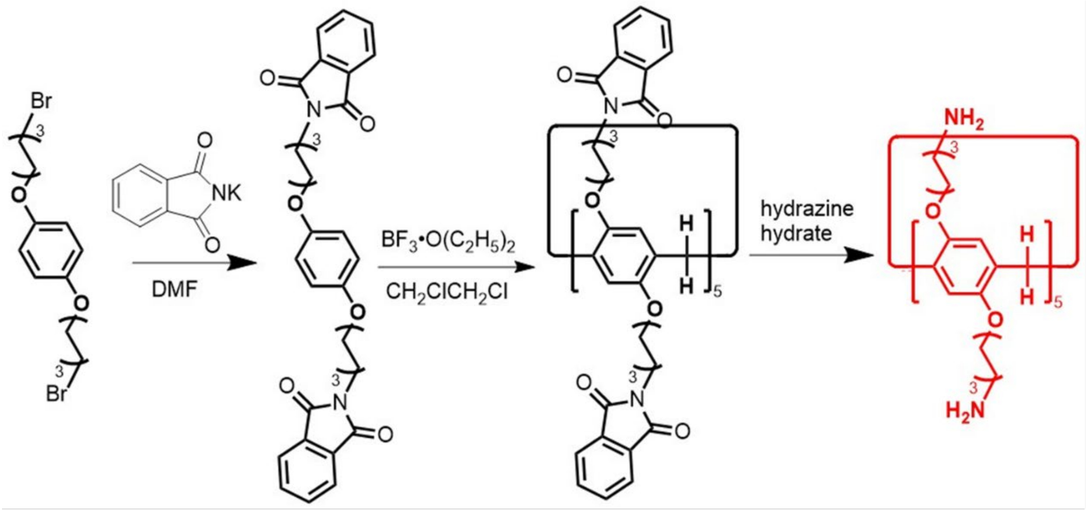
Supplementary Information (16 pages)

1. Materials and methods

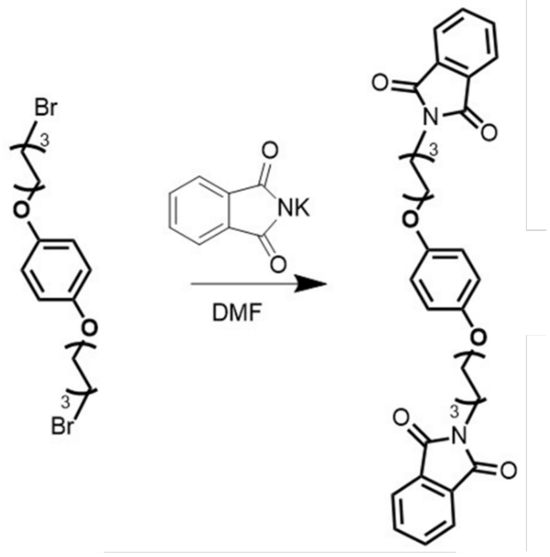
All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature.[1] NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer or a Bruker Avance DMX 500 spectrophotometer with the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Fourier-transform infrared (FT-IR) spectra were obtained on a Thermo Scientific Nicolet iS50 FT-IR spectrometer instrument (Thermo Fisher Scientific Co., Waltham, MA, USA) with KBr disk samples (400−4000 cm^{-1}). Scanning electron microscope and energy-dispersive spectroscopy were carried out on a HITACHI SU-8010 instrument.

2. Synthesis of ***P5-10NH₂***



1 **2** **3** **P5-10NH$_2$**

Scheme S1. Synthetic route to **P5-10NH$_2$**



1 **2**

Scheme S2. Synthetic route to compound **2**

Synthesis of compound **2**

Compound **1** (24 g, 0.076 mol) and potassium phthalimide (12.74 g, 0.069 mol) were dissolved in anhydrous DMF (150 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 6 h, after which deionized water (300 mL) was added to precipitate the product. The resulting suspension was centrifuged, and the supernatant was decanted. The solid residue was dried under vacuum to yield compound **2** as an off-white powder (7.32 g, 56.14%). The ^{1}H NMR spectrum of compound **2** is shown in Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.85–7.83 (q, *J* = 4 Hz, 4H), 7.72–7.69 (q, *J* = 4 Hz, 4H), 6.78 (s, 4H), 3.90–3.86 (q, *J* = 8 Hz, 4H), 3.71–3.67 (q, *J* = 8 Hz, 4H), 1.76–1.69 (m, 8H), 1.54–1.38 (m, 8H). The ^{13}C NMR spectrum of **2** is shown in Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 168.43, 153.16, 133.83, 132.20, 123.15, 115.42, 68.44, 37.94, 29.23, 28.53, 26.63, 25.69.

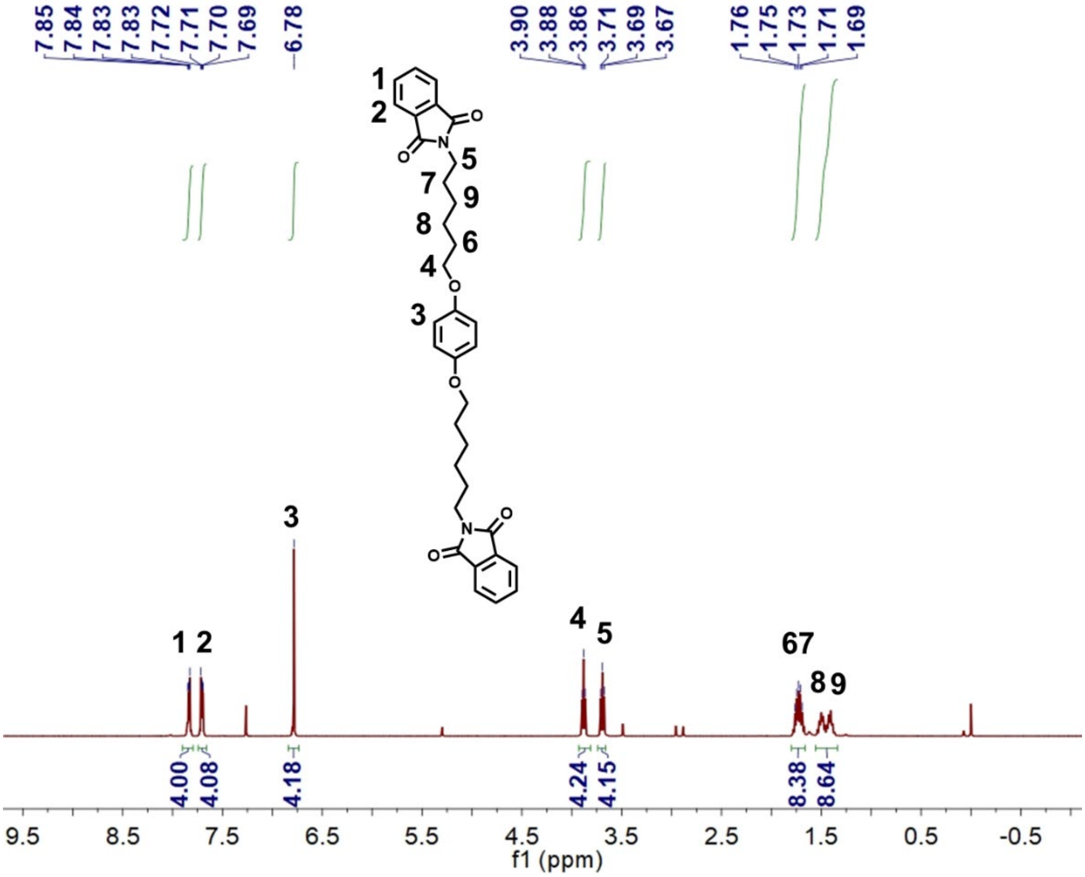


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **2**.

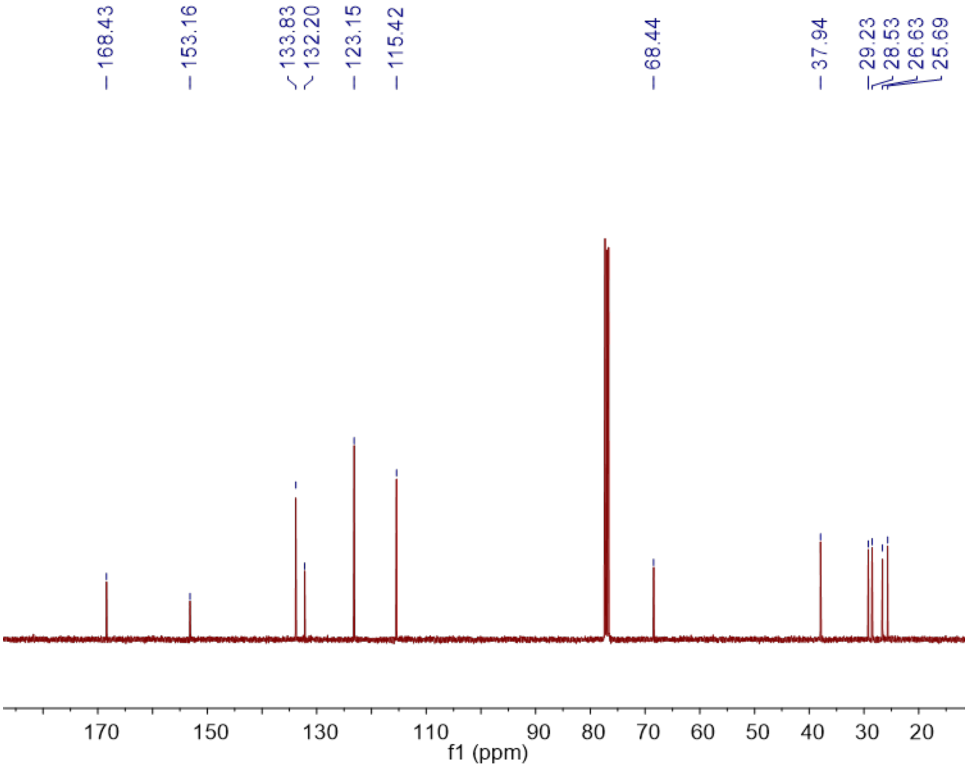


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **2**.

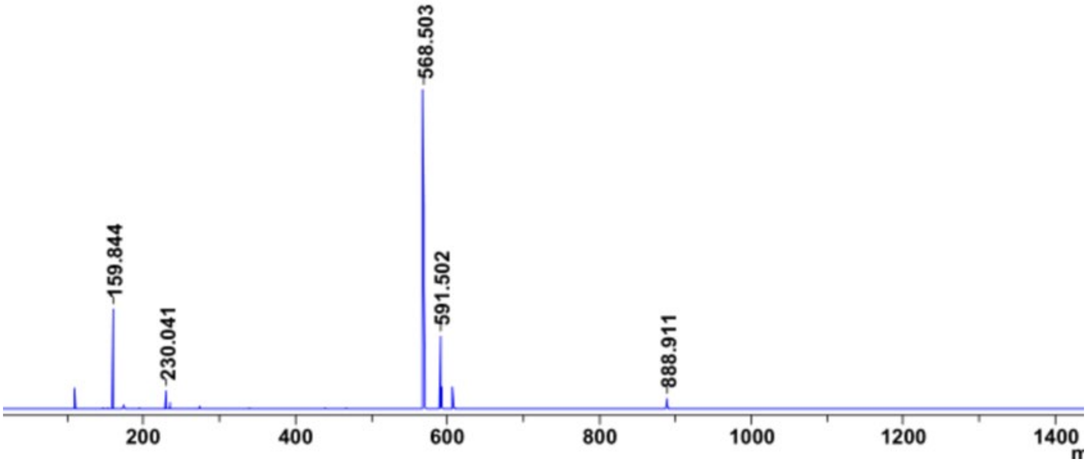
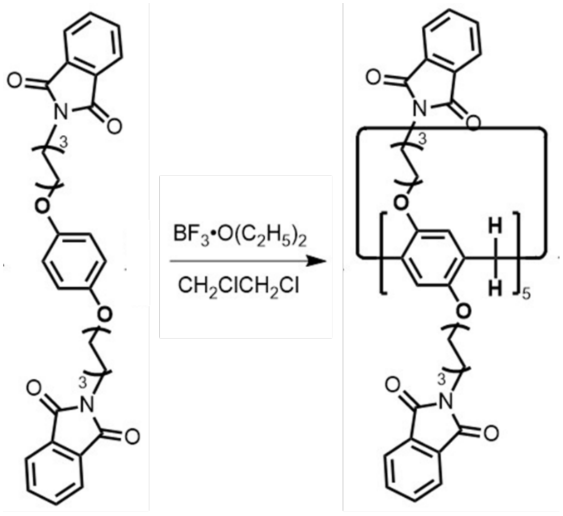


Figure S3. MALDI-TOF MS mass spectrum of **2**.



2 **3**

Scheme S3. Synthetic route to compound **3**

Synthesis of compound **3**

A mixture of compound **2** (4.00 g, 7.04 mmol), paraformaldehyde (634.2 mg, 21.12 mmol), and CH_2ClCH_2Cl (100 mL) was cooled in an ice bath for 5 min. Subsequently, BF_3•$O(C_2H_5)_2$ (868 μg) was introduced through a needle tube, and the reaction mixture was stirred at 0 ° C for 30 min. The temperature of the water bath was then increased to 45 °C, and the mixture was condensed and refluxed for 1 h. After cooling, saturated $NaHCO_3$ solution was added, and the mixture was stirred for 30 min, followed by quenching, extraction, and evaporation. The residue was purified by flash column chromatography on silica gel using a petroleum ether/ethyl acetate eluent (4/1, v/v), yielding compound **3** as a white solid (2.84 g, 55.63%). The ^1H NMR spectrum of compound **3** is shown in Figure S4. ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.78−7.77 (q, J = 4 Hz, 20H), 7.65−7.63 (q, J = 4 Hz, 20H), 6.75 (s, 10H), 3.91 (s, 10H), 3.69−3.66 (m, 40H), 1.76−1.68 (m, 40H), 1.57 (s, 20H), 1.46−1.41 (q, J = 8 Hz, 20H). The ^{13}C NMR spectrum of **3** is shown in Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 168.30, 149.74, 133.73, 132.18, 128.22, 123.09, 114.78, 68.23, 38.01, 29.84, 28.63, 26.95, 26.13.

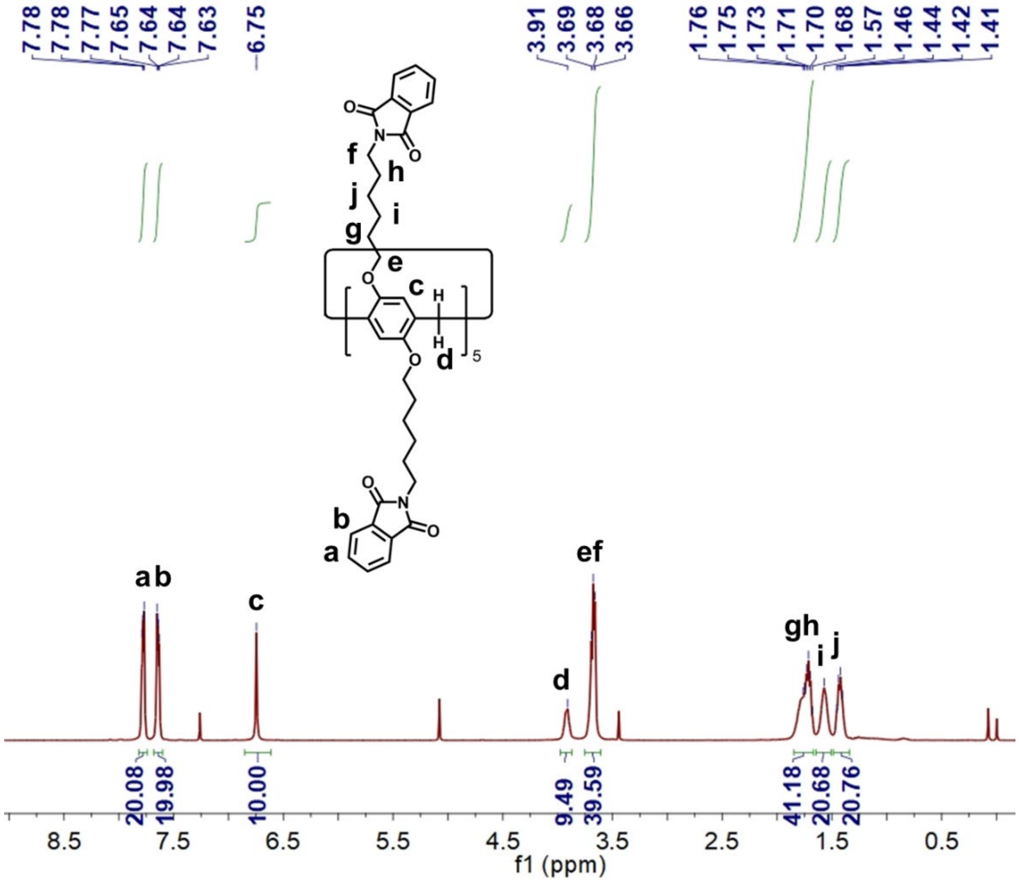


Figure S4. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of **3**.

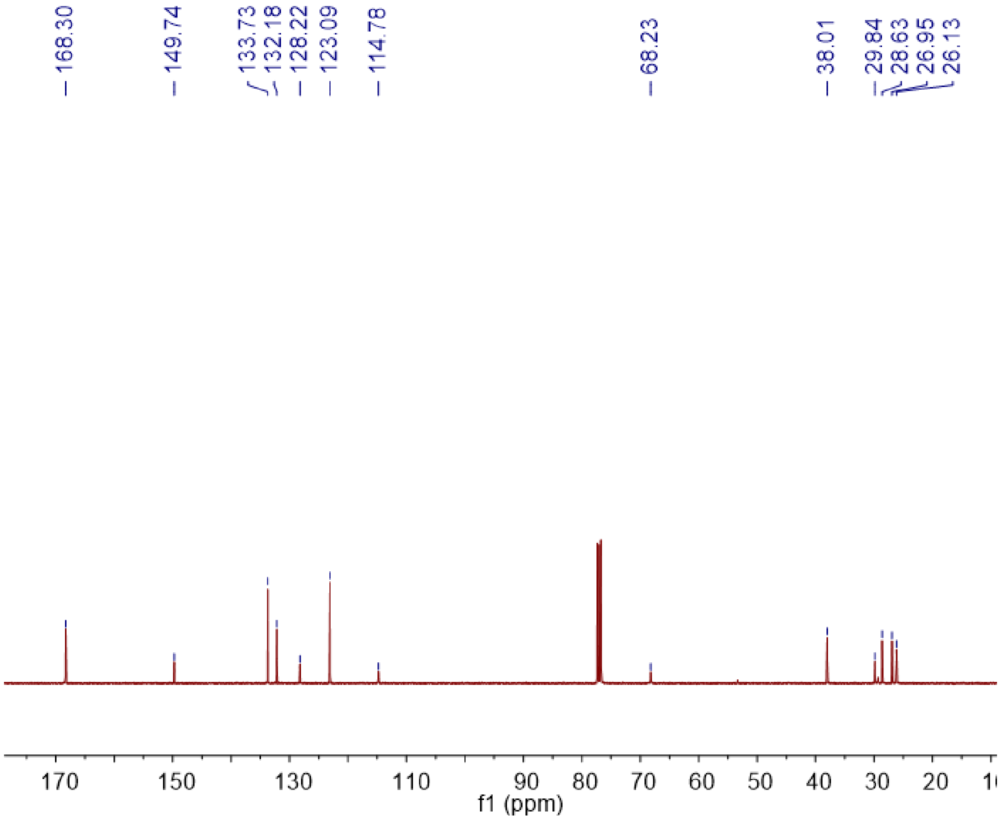


Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **3**.

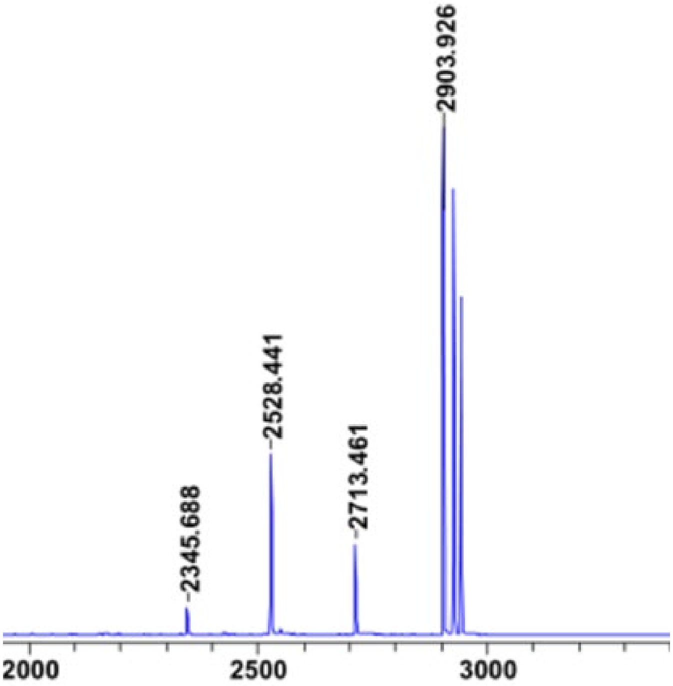
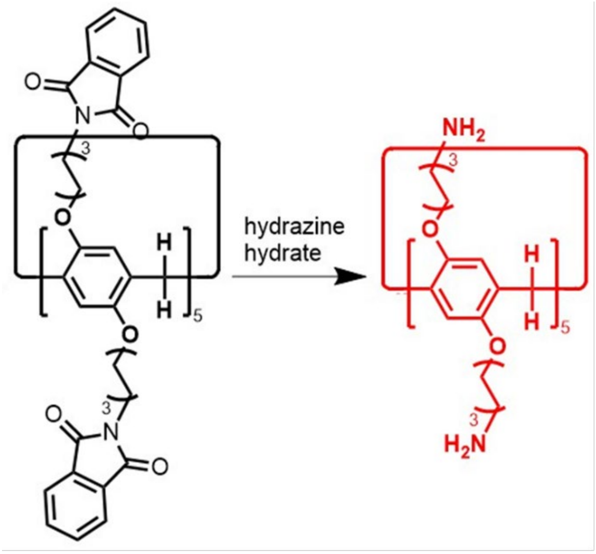


Figure S6. MALDI-TOF MS spectrum of **3**.



3

P5-10NH$_2$

Scheme S4. Synthetic route to compound **P5-10NH2**

Synthesis of compound **P5-10NH$_2$**

A mixture of compound **3** (15 g, 0.026 mol), methanol (10 mL), and hydrazine hydrate (10 mL) was subjected to condensing reflux at 75 °C for 48 h. After cooling to room temperature, the resulting precipitate was filtered, and the solid was washed with methanol. The filtrate was then concentrated to dryness by spinning. Subsequently, the residue was treated with an aqueous NaOH solution and stirred for 1 h. The solid was filtered, washed with deionized water, and dried at 60 °C to obtain compound **P5-10NH$_2$**. The ^{1}H NMR spectrum of compound **P5-10NH$_2$** is shown in Figure S7. ^{1}H NMR (400 MHz, CD$_3$OD, 298 K) δ (ppm): 6.80 (s, 10H), 3.82 (s, 20H), 3.63 (s, 10H), 2.50 (s, 20H), 1.77 (s, 20H), 1.48 (s, 20H), 1.34 (m, 40H). The ^{13}C NMR spectrum of **P5-10NH$_2$** is shown in Figure S8. ^{13}C NMR (100 MHz, CD$_3$OD, 298 K) δ (ppm): 149 .55, 128.16, 114.58, 68.35, 42.19, 33.91, 30.13, 29.26, 26.90, 26.22. HRESIMS is shown in Figure S9: *m*/*z* calcd for [M + H]$^+$ $C_{95}H_{161}N_{10}O_{10}^+$, 1603.2431; found 1603.2430.

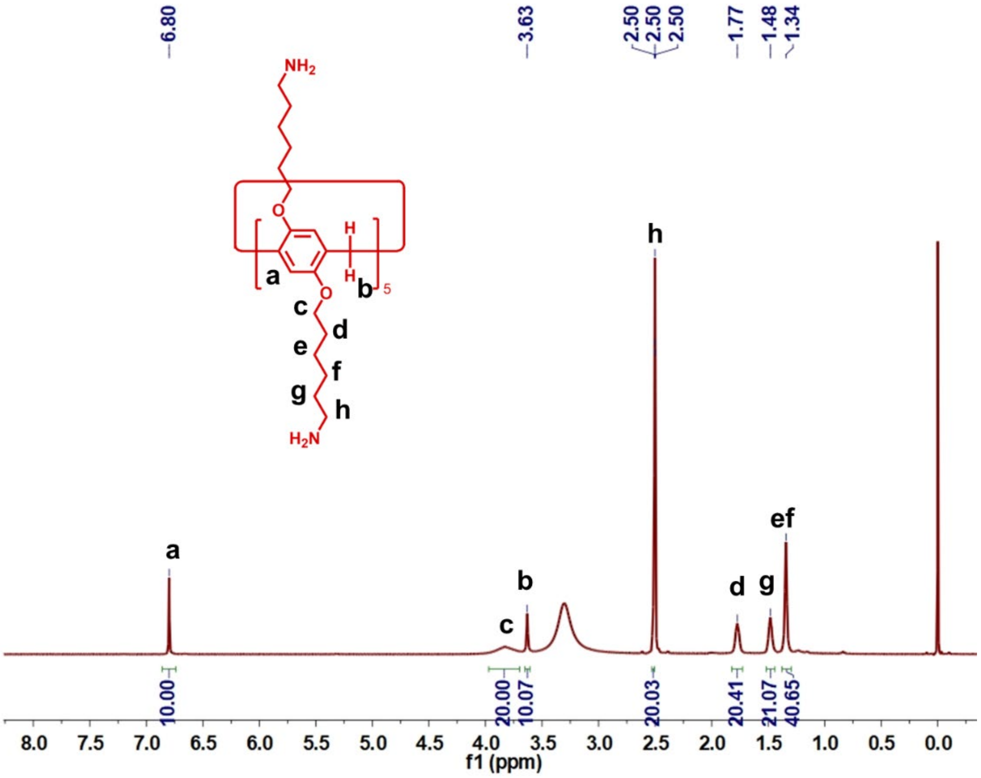


Figure S7. ^{1}H NMR spectrum (400 MHz, CD$_3$OD, 298 K) of **P5-10NH$_2$**.

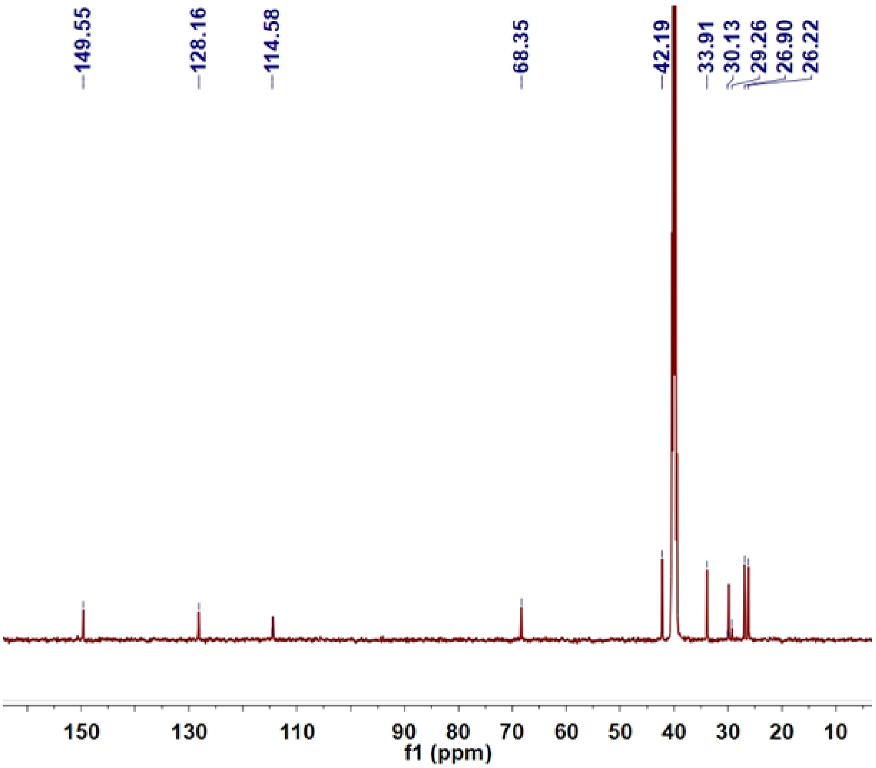


Figure S8. ^{13}C NMR spectrum (100 MHz, CD_3OD, 298 K) of **P5-10NH$_2$**.

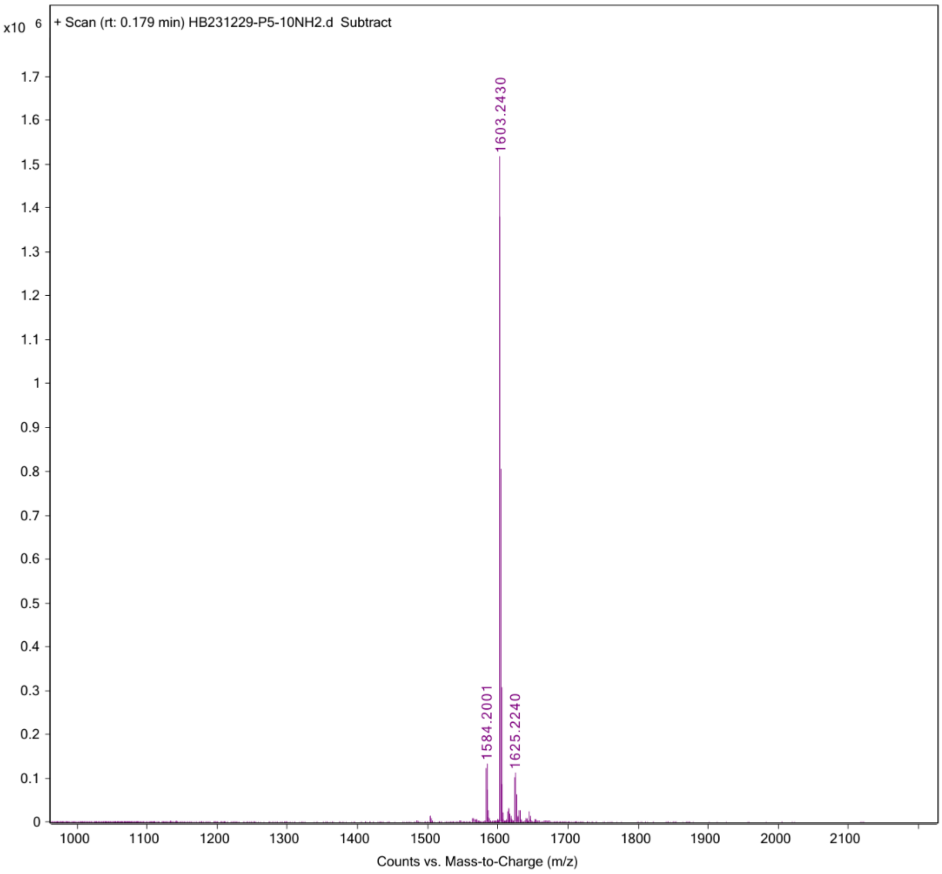
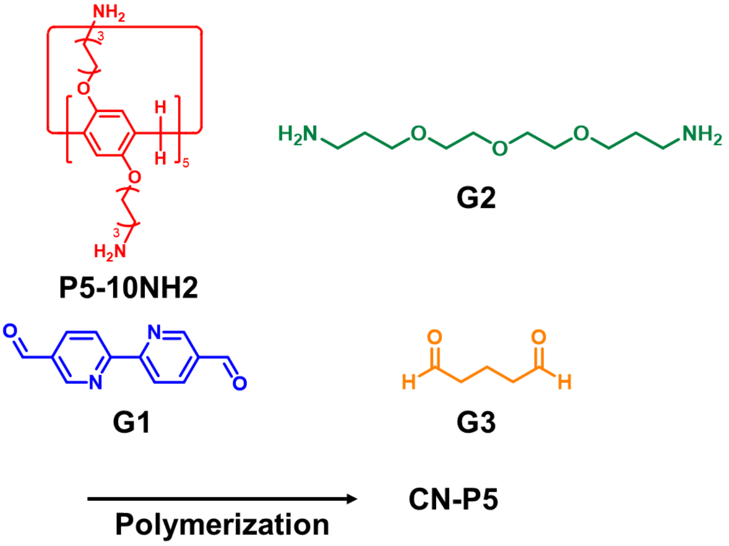


Figure S9. HRESIMS mass spectrum of **P5-10NH$_2$**.

*3. Synthesis of **CN-P5***



Scheme S5. The synthetic route of **CN-P5**.

Synthesis of **CN-P5**

In a 4 mL glass vial (vial A) of **P5-10NH$_2$** (10 mg, 0.006 mmol) was dissolved in methanol (5 μL), followed by addition of 4,7,10-trioxa-1,13-tridecanediamine (**G2**) (39 μL, 0.06 mmol). In a separate 4 mL vial (vial B), 2,2'-bipyridine-5,5'-dicarboxaldehyde (**G1**) (13.2 mg, 0.06 mmol) was dissolved in methanol (80 μL), to which glutaraldehyde (**G3**) (26 μL, 0.031 mmol) was added. The solution from vial A was then transferred to vial B and vigorously shaken to ensure complete mixing. The mixture in vial B formed a gel within approximately 5 seconds upon standing, yielding **CN-P5**. Subsequent solvent exchange and vacuum drying converted this network into an aerogel.

*4. SEM images of **CN-P5***

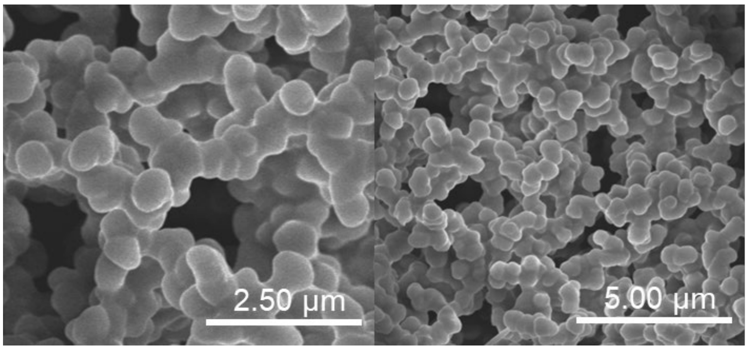


Figure S10 SEM image of the aerogel before adsorption of CF_3COOAg.

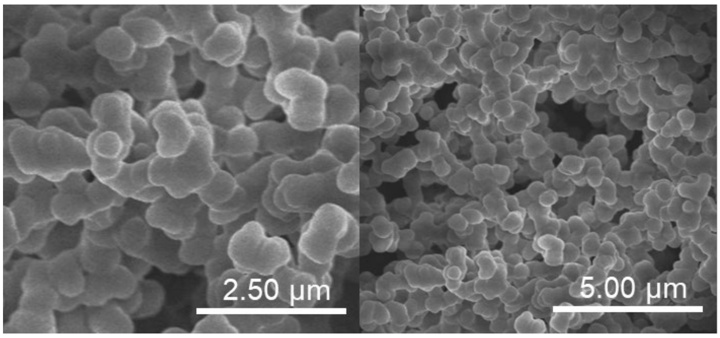


Figure S11 SEM image of the aerogel after adsorption of CF_3COOAg.

5. Adsorption experiments of $FeCl_3$ and $AgNO_3$

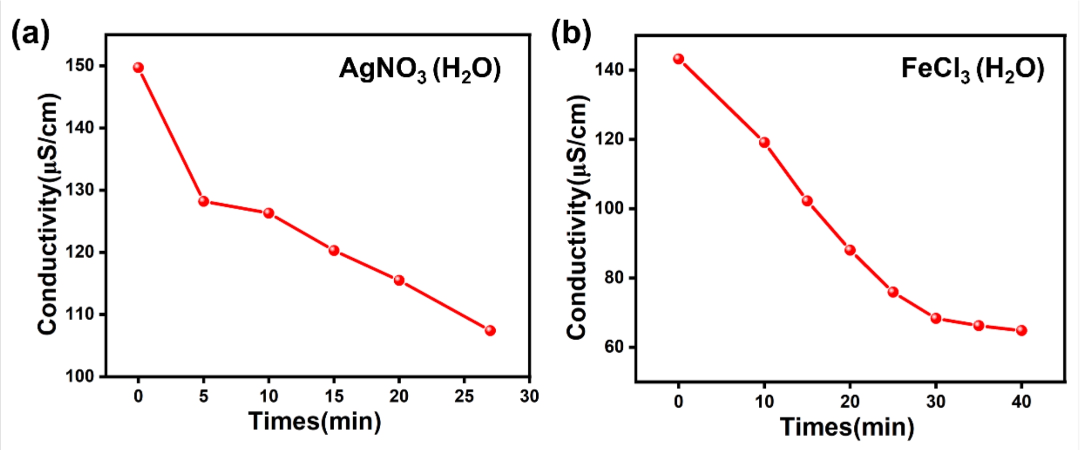


Figure S12 (a) The changes in conductivity of the $AgNO_3$ (4 mg) aqueous solution after the addition of 30 mg **Aero-P5** at different time intervals. (b) The changes in conductivity of the $FeCl_3$ (0.7 mg) aqueous solution after the addition of 30 mg **Aero-P5** at different time intervals.

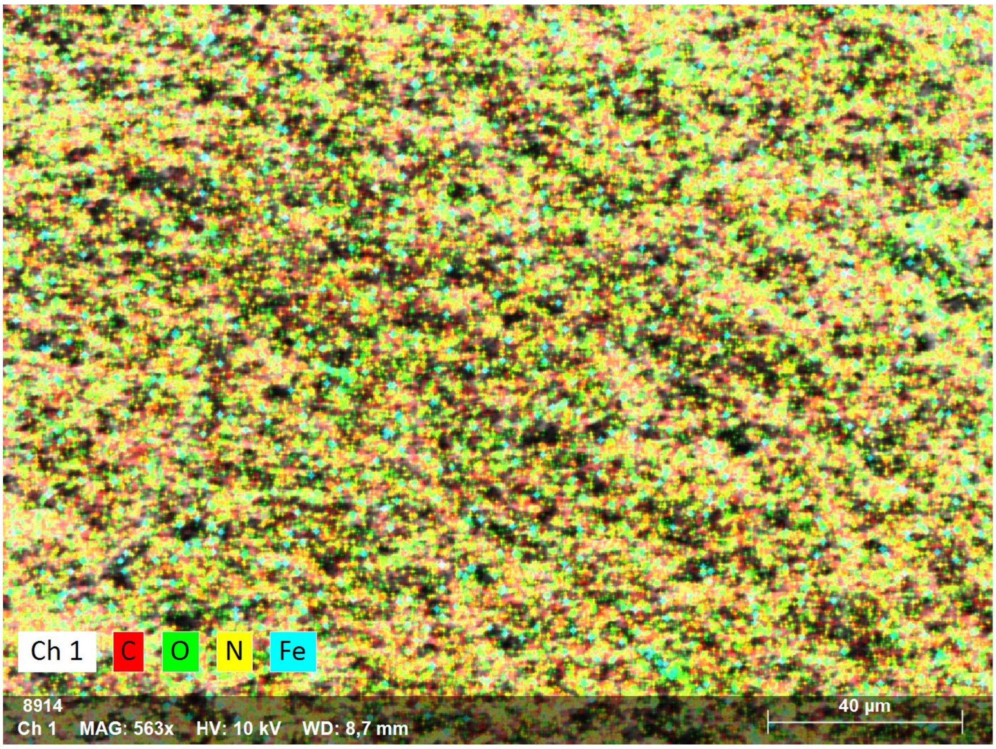
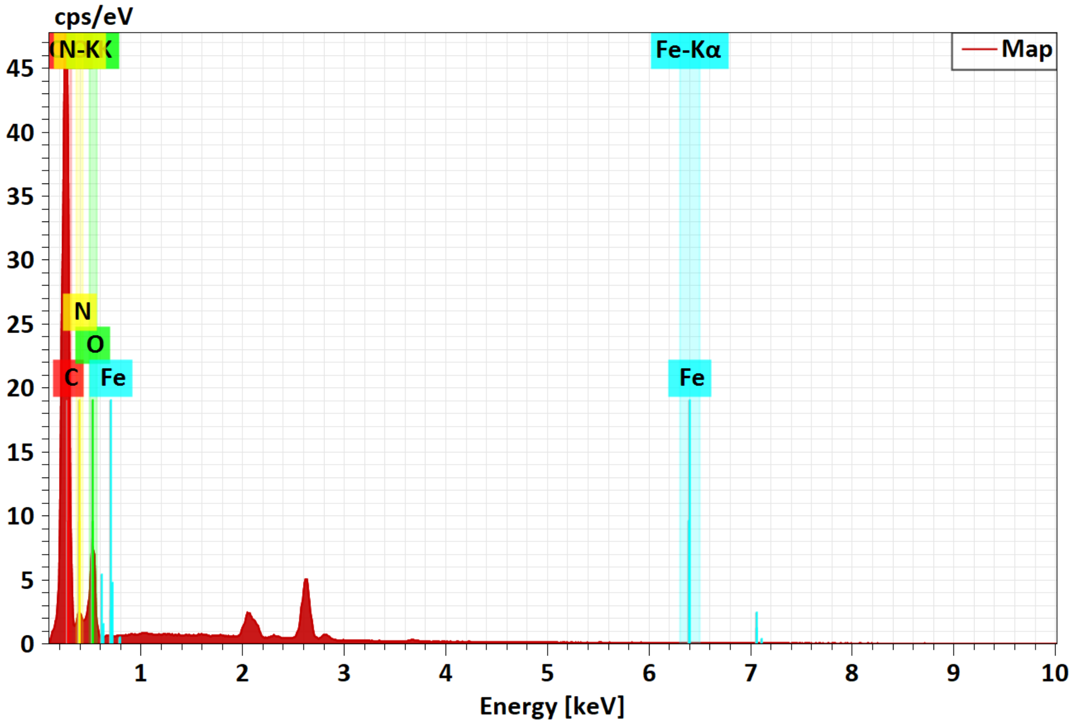
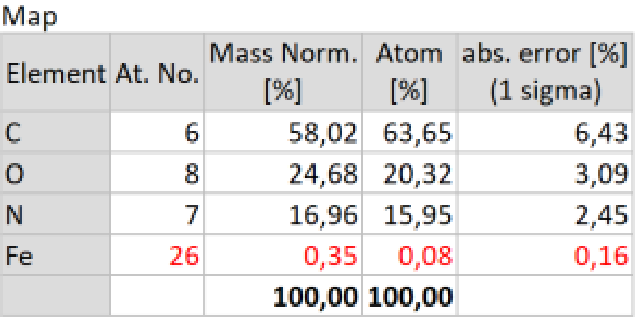


Figure S13 EDS image of **Aero-P5** after adsorption of $FeCl_3$.





Map

Element	At. No.	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
C	6	58,02	63,65	6,43
O	8	24,68	20,32	3,09
N	7	16,96	15,95	2,45
Fe	26	0,35	0,08	0,16
		100,00	**100,00**	

Figure S14 EDS map of **Aero-P5** after adsorption of $FeCl_3$.

6. ^{1}H NMR spectrum of model compound ***P5-10IM***

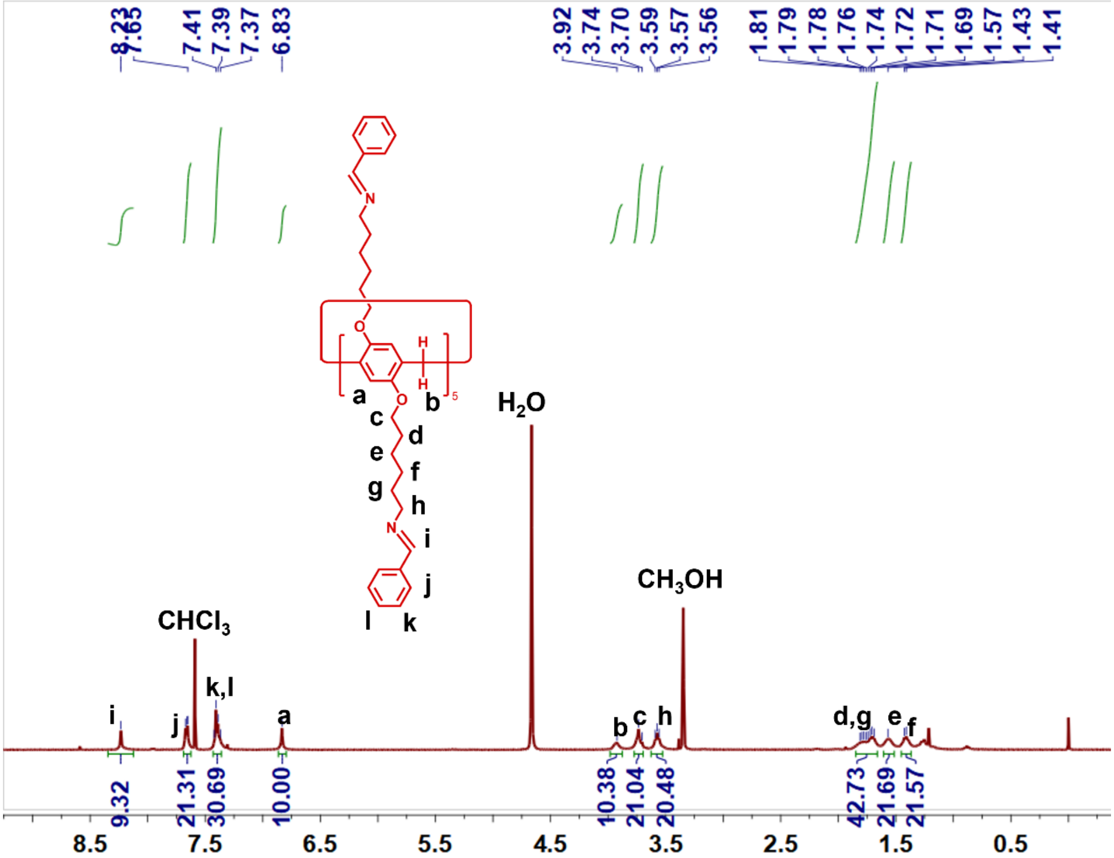


Figure S15 ^{1}H NMR spectrum of model compound **P5-10IM**

7. The recyclability of Ag^+ by competitive complexation

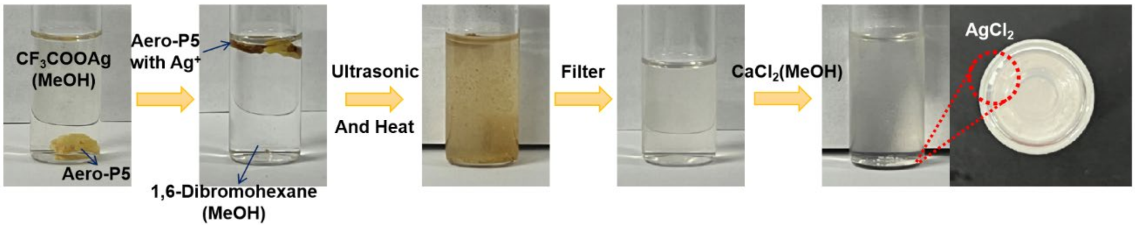
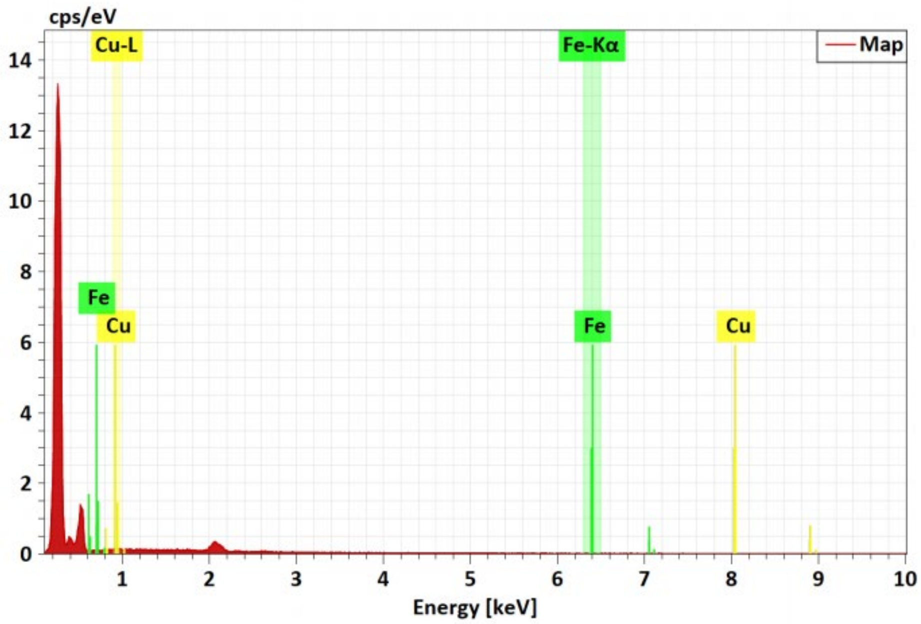


Figure S16 The recyclability of Ag^+ by adding 1,6-dibromohexane

8. Selective adsorption of mixed metal ions



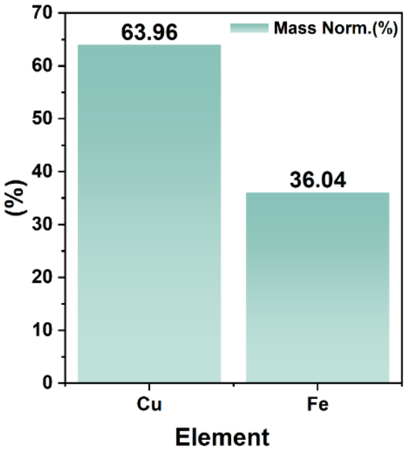


Figure S17 EDS map of **Aero-P5** after adsorption of $FeCl_3$ and $(CH_3COO)_2Cu$ and the adsorption ratio of metal ions.

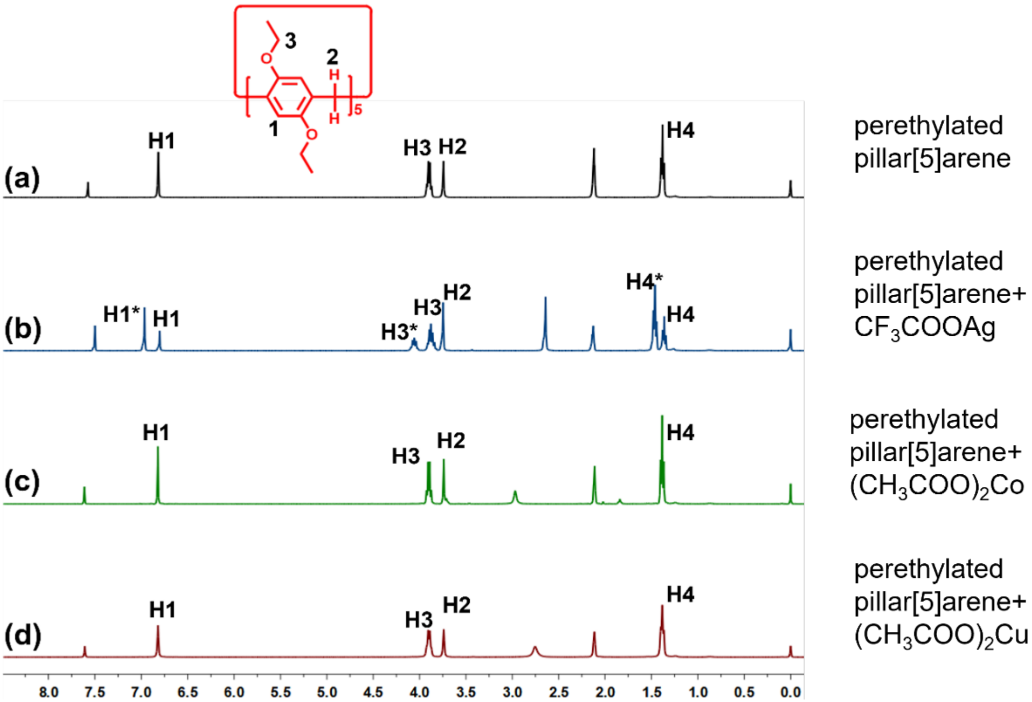


Figure S18 Partial ^{1}H NMR spectra (400 MHz, CD_3OCCD_3 : $CDCl_3$= 1 : 2, room temperature) of (a) perethylated pillar[5]arene, and perethylated pillar[5]arene with (b) CF_3COOAg, (c) $(CH_3COO)_2Co$, and (d) $(CH_3COO)_2Cu$. Peaks labeled with * are related to complexed pillar[5]arene.

9. Reference

1. D. N. Shurpik, L. I. Makhmutova, K. S. Usachev, D. R. Islamov, O. A. Mostovaya, A. A. Nazarova, V. N. Kizhnyaev and I. I. Stoikov, *Nanomaterials*, 2021, **11**, 947.