Supporting Information

Amino-Functionalized Porphyrin-based Porous Organic Polymers for CO$_2$ Capture and Hg^{2+} Removal

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1. EXPERIMENTAL SECTION

1.1. Chemicals and reagents.

Benzaldehyde was purchased from Sinopharm Chemical Reagent Co. Ltd. Pyrrole was provided from Aladdin Chemical Reagent Co. Ltd. Trimesoyl chloride (TMC), Melamine (MA), $Cd(NO_3)_2 \cdot 3H_2O$, $MnCl_2 \cdot 3H_2O$, $Pb(NO_3)_3$, anhydrous $CaCl_2$, $Cu(NO_3)_2 \cdot 3H_2O$, $ZnCl_2$, anhydrous $MgCl_2$ and anhydrous $FeCl_3$ were supplied by Aladdin Reagent Co. Ltd. (Shanghai). 1,2-dichloroethane (DCE), chloroform, methanol, ethanol, and Dimethyl sulfoxide (DMSO) was purchased from Xilong Chemicals. $HgCl_2$ was received from Sinopharm Chemical Reagent Co. Ltd. The standard aqueous solution of the nine metal ions with the concentration of 1000 $mg \cdot L^{-1}$ was purchased from National Analysis Center for Iron & Steel (Beijing, China). All these reagents were analytical agents and used without further purification.

1.2. Synthesis of 5,10,15,20-tetraphenylporphyrin.

Propionic acid (100 ml) was joined in a flask-3-neck, slowly heated up to 140 °C and kept the temperature about 10 min. Benzaldehyde benzaldehyde (0.03 mol) and steamed pyrrole (0.03 mol) had slowly added to the reaction flask, maintain 146 °C keeping 1.5 h. After cooling to room temperature, adding suitable amount of methanol let stand up for the night. The crystal products was filtered by recrystallization of chloroform and methanol, purified with methanol and water sufficiently and dried for 24 h under a vacuum for 24 hours.

1.3. Preparation of HTM.

The precursor HTM is obtained by the Friedel-Craft acylation reaction. Typically, TPP (1.5 mmol), TMC (4 mmol), and anhydrous $AlCl_3$ (24 mmol) were joined to dissolve in 50 mL DCE under the N_2 atmosphere. The mixture was stirred and reacted

at 90 ℃ for 24 h. The products were obtained by filtration and washed with DCE, ethanol, HCl/H_2O as well as hot water. The product was further purified in the Soxhlet extractor with ethanol for 24 h and dried under vacuum at 60℃ for 24 h.

1.4 Preparation of HTM -MA.

HTM-MA was synthesized by Schiff base reaction. Typically, 0.25 g HTM was dispersed in 50 mL DMSO and 0.75 g MA was dissolved in above DMSO. The reaction mixture was stirred and heated to 160 ℃ for 72 h under N_2 atmosphere. The product was washed with DMSO, methanol as well as hot water and further purified in a Soxhlet extractor with methanol for 24 h. Finally, the product was collected after dried under vacuum at 60℃ for 24 h.

1.5 Characterization

The Fourier transform infrared (FT-IR) spectra of the polymers were detected by a Nicolet 6700 Fourier transform infrared spectrophotometer (Thermo Scientific Co., United States). Micromeritics ASAP 2020 surface area (Micromeritics, USA) was used to conduct the pore structure and BET surface area of the polymers. CHNOS elementar (Vario Micro Cube, Germany) was used to examine the elemental analysis (EA). The X-ray photoelectron spectroscopy (XPS) characterization was investigated via Thermo ESCALAB spectrometer with an Al K-α source. Field emission scanning electron microscope (FESEM, Nova Nano SEM 230) operating was used to detect the morphology of the polymers. High-resolution transmission electron microscopy (HRTEM) was characterized on an FEI Titan G2 60-300 microscope. The thermogravimetric analysis (TGA) of the polymers was exhibited by thermobalance (STA-499C, NETZSCH). The metal ions concentration was displayed applying TAS-990 atomic absorption spectrum (AAS).

1.6 Hg^{2+} adsorption

The equilibrium adsorption of Hg^{2+} on the polymers was performed by mixing 0.02 g of the polymers with 50 mL of Hg^{2+} aqueous solution, the initial concentration ranges of Hg^{2+} varied from 100 to 500 mg/L. The adsorption was performed at 298 K with 2 h to make the adsorption reach equilibrium. The residual concentrations of Hg^{2+} were diluted to an appropriate concentration and determined by AAS. The equilibrium capacity was calculated as follows,

$$q_e=(C_0-C_e)V/W$$

where q_e (mg/g) is the equilibrium capacity after the Hg^{2+} adsorption, C_0 (mg/L) and C_e (mg/L) represent the initial and equilibrium concentration of Hg^{2+}, respectively. V is the volume of the total adsorption aqueous solution (L) and W is the mass of the polymers (mg).

Table S1 Elemental analysis of the polymers from XPS

Sample	C1s (%)	N1s (%)	O1s (%)
HTM	88.16	1.39	12.45
HTM-MA	54.57	42.08	3.35

Table S2 Textual properties and the CO_2 uptake of various adsorbents

Samples	BET ($m^2 \cdot g^{-1}$)	CO$_2$ Uptake (mg·g^{-1})		Q$_{st}$	Selectivity (S$_{CO2/N2}$) IAST	Ref.
		273 K	298 K			
NOP-52@COOH	738	159	81	34.5	57	25
CBAP-2	726	141.9	97.9	33.6	15.4	26
CBAP-2 (EDA)	228	124.0	86.3	46.4	87.8	26
CAP-DAP	517	153.2	99.5	46.6	86.22	27
MTPA	481	126	94	30.7	91.8	37
SNW-1	821	/	96	35	50	40
DMP-II	106	/	88	28	35	41
TH-COF-1	684	128	97	31	19	42
NAN-2	56	65.6	39.6	31.5	72.7	43
COP-98A	88	115	99.2	/	/	44
HTM-MA	587	172	120	31.3	58.4	This work

Table S3 Comparison of The Hg2+ adsorption with various adsorbents.

Samples	q_{max}/(mg/g)	Ref
ZIF-90-SH	22.4	47
NOM	230	35
thiol-functionalized mesoporous silica	401	48
ACOF	175	49
SMP	595	3
PAF-1-SH	1000	50
sulfur-functionalized mesoporous carbon	435	51
CBAP-1 (AET)	232	28
TAPB-BMTTPA-COF	734	52
COF-LZU8	236	29
HTM-MA	328	This work

Table S4 Correlative parameters of the kinetic data, Langmuir model and Freundlich models for Hg^{2+} adsorption on HTM-MA

	parameters	HTM	HTM-MA
	q_m /(mg/g)	271.6	328.1
Langmuir model	K_L /(L/mg)	0.003	0.024
	R^2	0.971	0.993
	K_F /((mg/g)(L/mg)$^{1/n}$)	5.0	60.1
Freundlich model	n	1.7	3.6
	R^2	0.988	0.996
Pseudo-first-order	k_1 /(min^{-1})	/	0.5239
	R^2	/	0.958
Pseudo-second-order	k_2 /(g/(mg·min))	/	0.0031
	R^2	/	0.990

Figure S1 ^{1}H NMR spectrum of 5,10,15,20-tetraphenylporphyrin
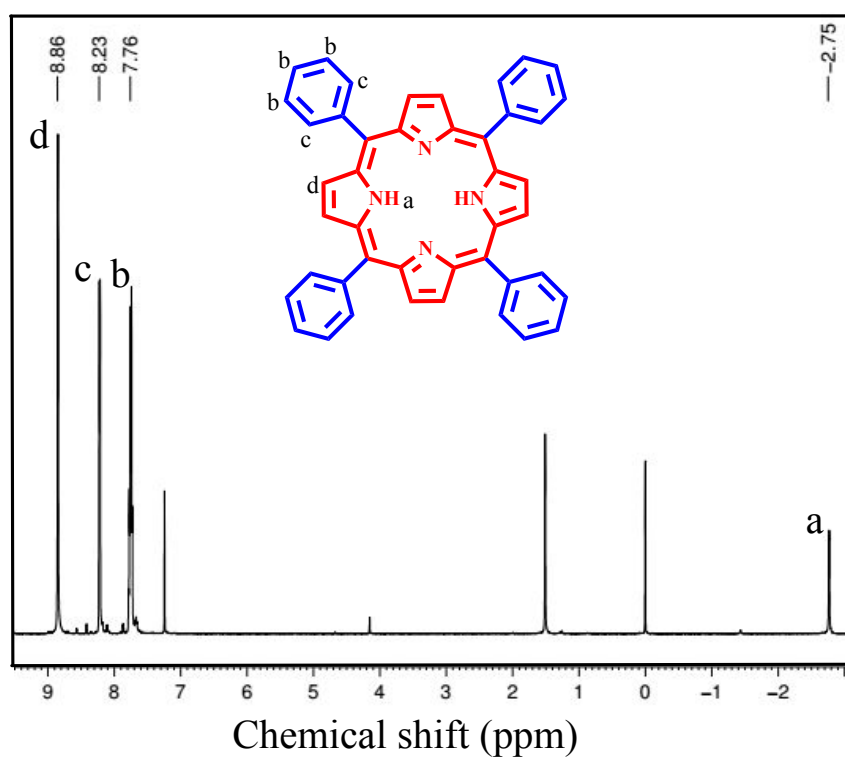
Figure S2 (a) survey and (b) O1s of the polymers
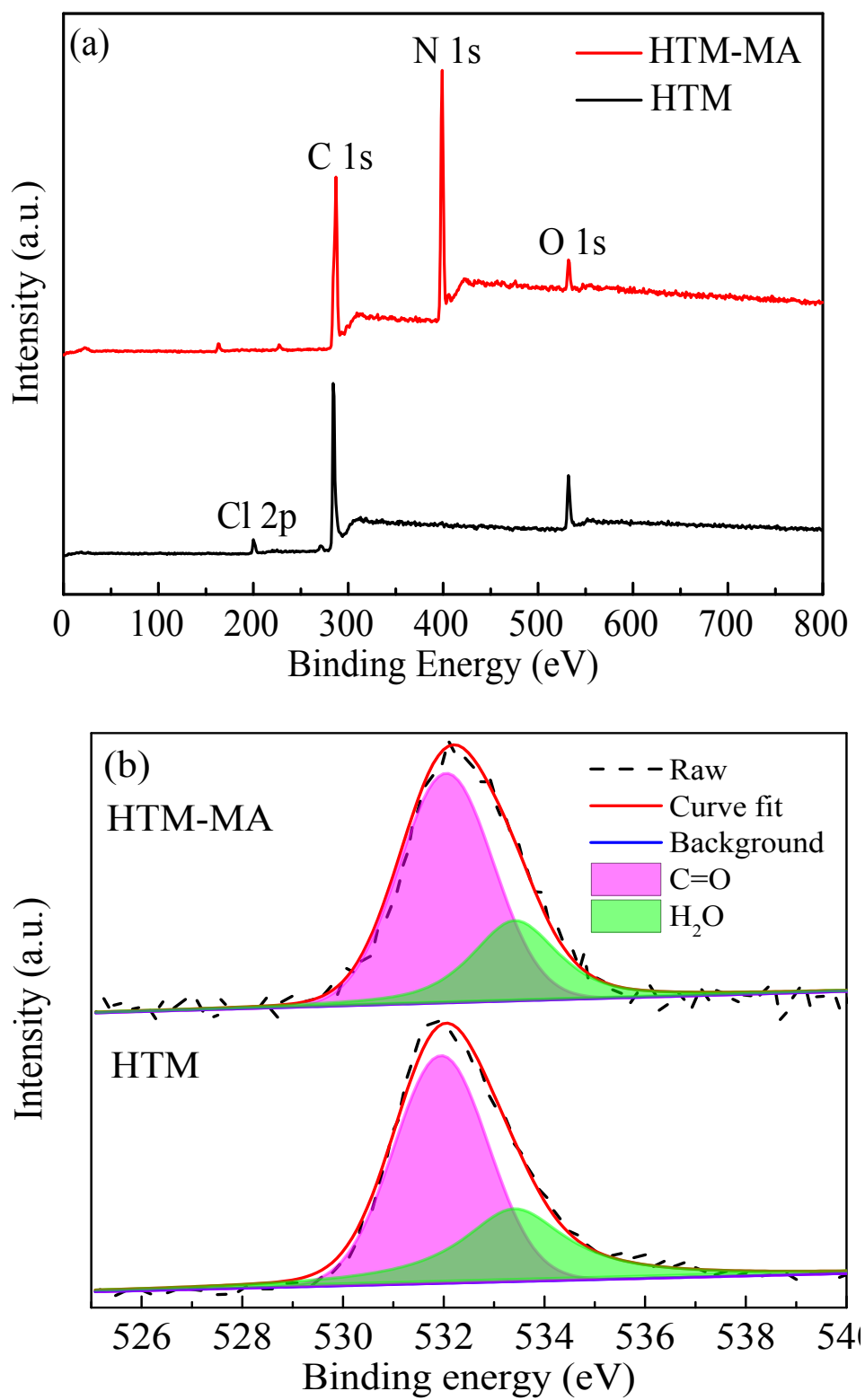
Figure S3 TG curves of polymers HTM (red) and HTM-MA (black) in a nitrogen
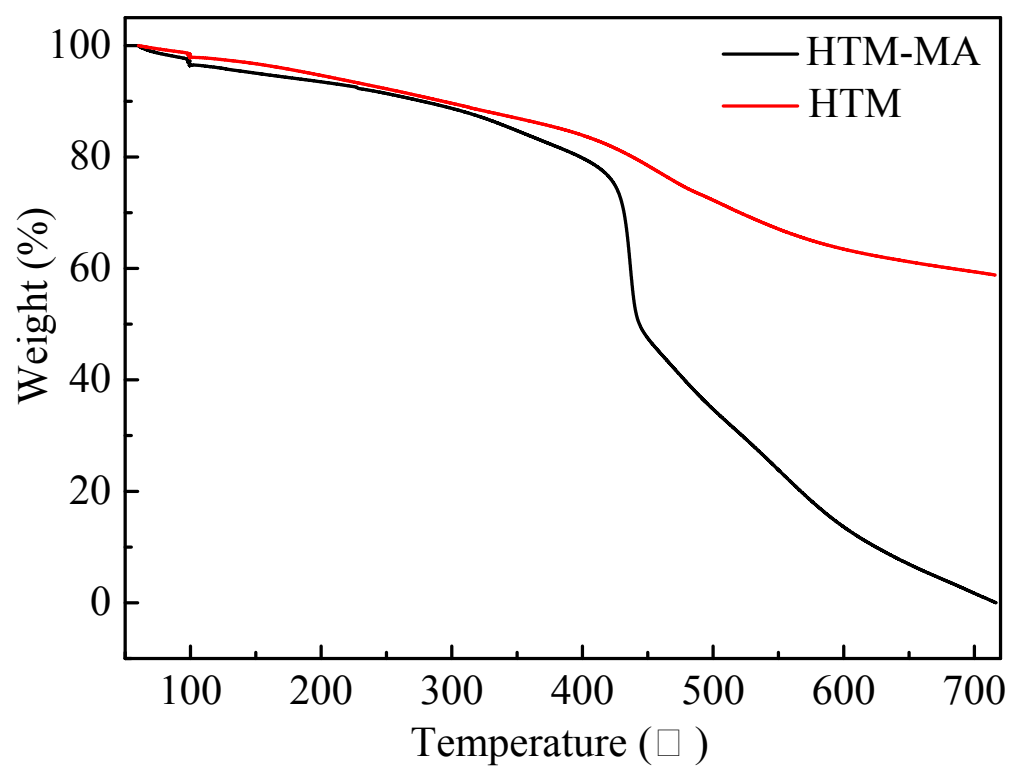
atmosphere
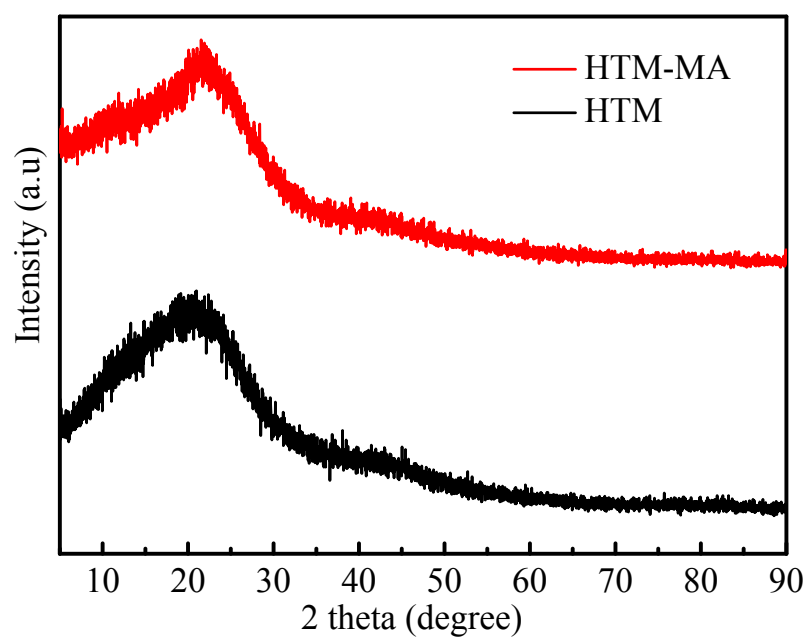
Figure S4 XRD patterns of the polymers.

Figure S5 CO_2 adsorption-desorption isotherms (a) and PSD (b) of the polymers(HTM-MA: red lines and symbols; HTM: black lines and symbols).
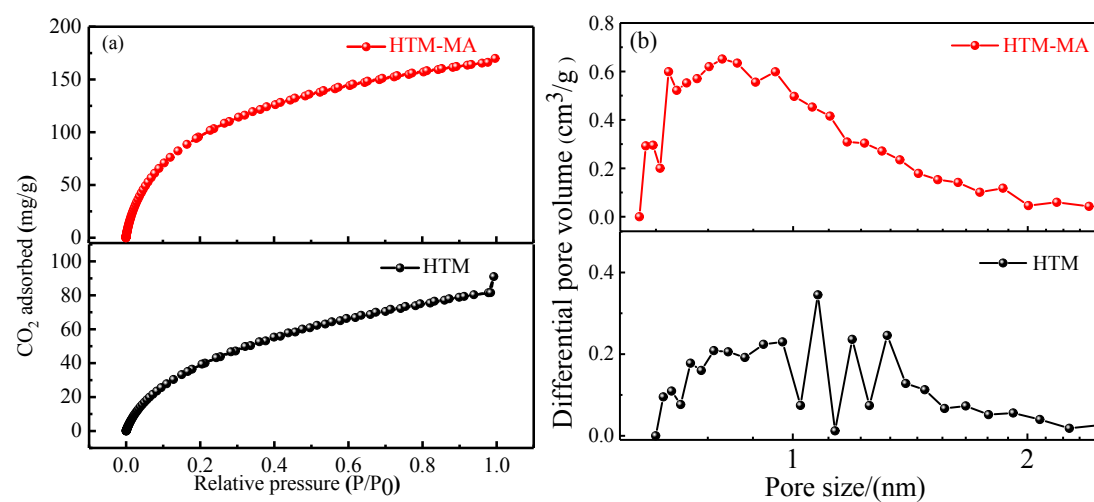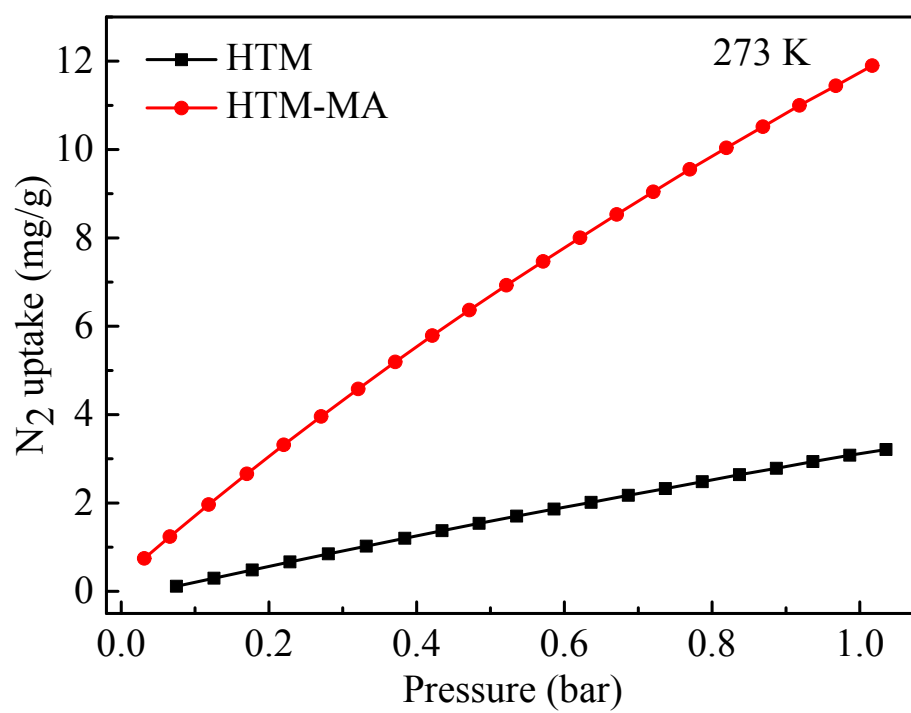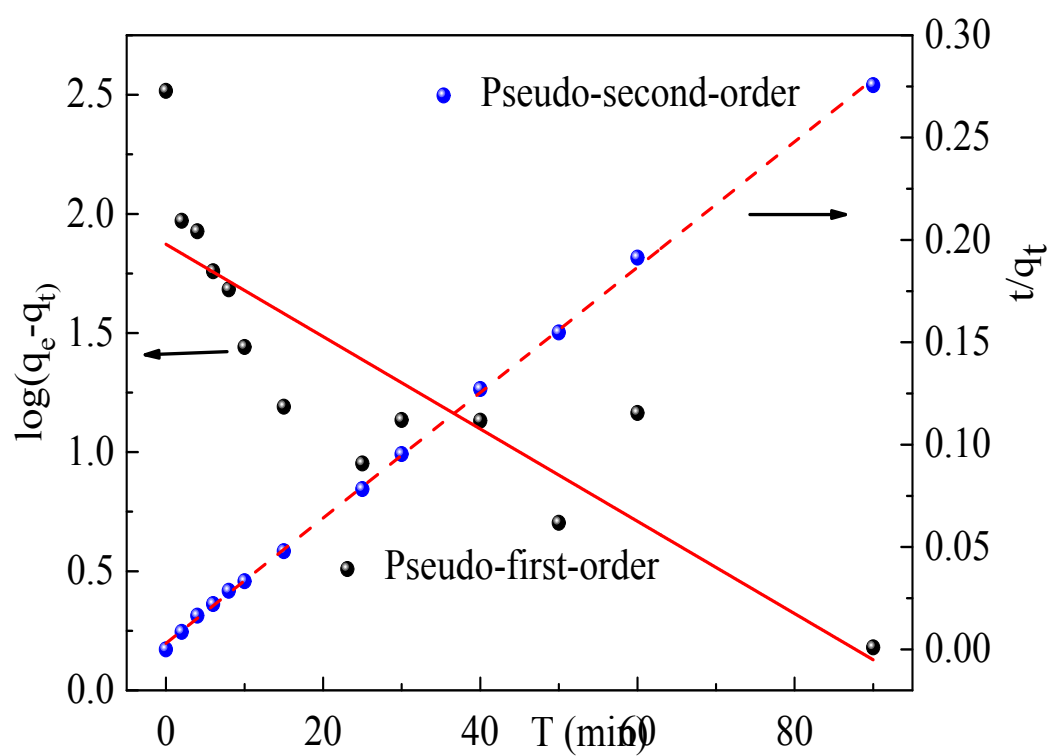
Figure S6 N_2 isotherms of the polymers

Figure S7 Fitting results of the kinetic adsorption of Hg^{2+} on HTM-MA

Scheme S1 Illustration of the possible chelating interaction between Hg^{2+} and HTM-MA