

**Two Sulfur and Nitrogen-rich Cobalt-Thiacalix[4]arene Compounds for
Selective Mercury Removal from Aqueous Solution**

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I. Experimental Section

Materials and General Methods.

p-*tert*-Butylthiacalix[4]arene (H₄TC4A) was synthesized by literature method[1] and other reagents were purchased from commercial sources without further purification. Single crystal diffraction measurements were performed using a Bruker D8 QUEST system with Cu-K α radiation ($\lambda = 1.54178\text{\AA}$). FT-IR spectra using KBr pellets were taken on a Bruker Vertex 70S spectrometer. TGA was performed on a NETZSCH STA449F3. Elemental analysis for C, H, N was recorded on a VarioEL instrument. Magnetic susceptibility measurement was performed on a Quantum Design MPMS XL-5 SQUID system in the temperature range of 2-300 K and diamagnetic corrections for the sample and sample holder were applied. N₂ adsorption and H₂ adsorption measurement were performed on a Micromeritics ASAP 2020 machine. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Thermo ESCALAB 250 spectrometer (VG Scientific) operated at 120 W. The composition of the products was obtained by using an inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer Optimal 8000). The pH value of the aqueous phase is measured by PHS-3C acidometer.

Synthesis of compounds CIAC-131 and CIAC-251.

Synthesis of compound $\{[Co_4(TC4A)(SO_4)]_6(L)_6(HCOO)_6\}^{12-}$ (CIAC-131). Pink bulk crystals were obtained from solvothermal reaction of the mixture of *p*-*tert*-butylthiacalix[4]arene (H₄TC4A, 0.037 g, 0.05mmol), CoSO₄·7H₂O (0.05 g, 0.18mmol), 1*H*-1,2,3-triazole-4,5-dicarboxylic acid (L, 0.025 g, 0.16mmol), CH₃OH (5.5 ml), DMF (0.5 ml), triethylamine (several drops) in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 20 °C at 4 °C·h⁻¹. The pink bulk crystals were isolated by filtration, which were washed by CH₃OH and then dried in air. Yield: ca. 80% based on H₄TC4A. Elemental analysis (%) for C₃₄₂H₄₅₀Co₂₄N₃₀O₈₄S₃₀ (including 12(C₂H₅)₃NH⁺ counter cations, excluding the disordered solvents): calculated C 47.21, H 5.21, N 4.83; found (after drying in vacuum) C 47.93, H 5.30, N 4.95.

Synthesis of compound $\{[Co_4(TC4A)_2]_2L\}^{3-}$ (CIAC-251). Green bulk crystals were synthesized by a similar procedure as **CIAC-131** except $CoSO_4 \cdot 7H_2O$ was replaced with $CoCl_2 \cdot 6H_2O$ (0.05 g, 0.21mmol). The green bulk crystals were isolated by filtration, which were washed by CH_3OH and then dried in air. Yield: ca. 50% based on H_4TC4A . Elemental analysis (%) for $C_{182}H_{221}Co_8N_6O_{20}S_{16}$ (including $3(C_2H_5)_3NH^+$ counter cations, excluding the disordered solvents): calculated C 57.57, H 5.87, N 2.21; found (after drying in vacuum) C 57.65, H 5.96, N 2.33.

Adsorption experiments of Hg(II)

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

$$q_t = \frac{(C_i - C_t)V}{m} \quad (2)$$

$$R = \frac{(C_i - C_e)}{C_i} \times 100\% \quad (3)$$

Where C_e (mg/L), C_t (mg/L) and C_i (mg/L) represent the metal concentrations at equilibrium, t time and the beginning (or before mixing), respectively. And q_e (mg/g) and q_t (mg/g) represent the amount of adsorbed metal ions at equilibrium and t time, respectively. R is removal rate/efficiency of metal ions. V (L) is the volume of test solutions and m (mg) is the amount of adsorbent.

Langmuir isotherm models

The Langmuir adsorption model was further employed to study the equilibrium adsorption isotherm, the adsorption capacity of **CIAC-131** and **CIAC-251** were calculated by the equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m} \quad (4)$$

Where C_e (mg/L) and q_e (mg/g) represent the concentration and adsorption amount of Hg(II) at equilibrium, respectively. q_m (mg/g) is the adsorption capacity (mg/g), while

k_L is the Langmuir constant (L/mg).

Pseudo-Second-Order Kinetic models

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (5)$$

Where q_t (mg/g) and q_e (mg/g) represent the adsorption amounts at t time and equilibrium, respectively, while k_2 (g mg⁻¹ min⁻¹) is the rate constant.

Pretreatment sample. Obtained sample from mother liquor was dry at 70 °C for 5min.

Effect of pH. The effect of pH values from 1 to 6.5 (the pH value of water measured by PHS-3C acidometer) for the removal of mercury ions was studied. The samples of **CIAC-131** (5 mg) or **CIAC-251** (5 mg) were respectively put into the aqueous solution of Hg(II) with an initial concentration of 100 mg/L (5 mL) and stirred at 400 rpm at room temperature for 4 h. And then the solid samples were separated via the centrifuge and the residual concentration of Hg(II) was determined by ICP-OES.

Selective Adsorption. The samples of **CIAC-131** (5 mg) or **CIAC-251** (5 mg) were dispersed in a pH = 6 aqueous solution containing Hg(II) (50 mg/L) and other coexisting metal ions Mg(II), Ca(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) (50 mg/L), stirred at 400 rpm at room temperature for 4 h. And then the solid samples were separated via the centrifuge and the residual concentrations of the metal ions were determined by ICP-OES.

Adsorption isotherms. The samples of **CIAC-131** (5 mg) and **CIAC-251** (5 mg) were immersed into HgCl₂ aqueous solution (pH= 6) with the concentration range of 50-950 mg/L (5 mL) and stirred at 400 rpm at room temperature for 4 h. After saturated adsorption, the solid samples of **CIAC-131-Hg** or **CIAC-251-Hg** were separated via the centrifuge and the residual concentration of Hg(II) was determined by ICP-OES.

Adsorption kinetics measurements. The samples of **CIAC-131** (5 mg) were immersed into HgCl₂ aqueous solution (pH= 6) with an initial concentration of 50 mg/L (5 mL), stirred at 400 rpm at room temperature at a certain time interval, and

then separated via the centrifuge. The residual concentration of Hg(II) was determined by ICP-OES.

Control experiment. The mass of H₄TC4A and **L** were equivalent to the amount of H₄TC4A and **L** in 5 mg samples of **CIAC-131**. The same adsorption experiment was performed. That is, the samples of H₄TC4A and **L** were immersed into the aqueous solution with 550 mg/L HgCl₂ (5 mL) and stirred at 400 rpm at room temperature for 4 h. After adsorption, the solid samples were separated via the centrifuge and the residual concentration of Hg(II) was determined by ICP-OES.

II. Crystallographic Analysis

The single crystal diffraction data of **CIAC-131** and **CIAC-251** were collected on a Bruker D8 QUEST system with a Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). The direct method was chosen to solve the crystal structures, and the refinement was performed with full-matrix least-squares on F^2 using the reported SHELXL-2017 program[2]. The “SQUEEZE” method from the PLATON package was applied to subtract the electronic density of the solvent molecules from the crystal structure. The hydrogen atoms were generated theoretically and refined isotropically with fixed thermal factors. All non-hydrogen atoms except the disordered butyl groups were refined anisotropically. The molecular formula shown in this paper did not include the unidentified counter ions and solvent molecules. After the final refinement, the R factors were still relatively large, which should be due to the weak diffraction even at 190 K. The crystal data and refinement details are given in Table S1. The number CCDC2024025-2024026 have been assigned for **CIAC-131** and **CIAC-251**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk>.

Table S1. Crystal data and structure refinement for compounds **CIAC-131** and **CIAC-251**.

	CIAC-131	CIAC-251
Formula	C ₂₇₀ H ₂₇₀ Co ₂₄ N ₁₈ O ₈₄ S ₃₀	C ₁₆₄ H ₁₇₆ Co ₈ N ₃ O ₂₀ S ₁₆
Formula wt.	7487.14	3493.47
T/K	190(2)	200(2) K
Cryst. syst.	Trigonal	Trigonal
Space group	R-3	R-3c
a (Å)	36.5063(13)	49.4477(9)
b (Å)	36.5063(13)	49.4477(9)
c (Å)	28.7488(11)	39.5019(10)
α (°)	90	90
β (°)	90	90
γ (°)	120	120
V (Å ³)	33181(3)	83645(4)
Z	3	18
D _c /g cm ⁻³	1.124	1.248
μ /mm ⁻¹	8.642	7.579
F(000)	11448	32634
Tot. data	31629	117644
Uniq. Data	3491	6451
R _{int}	0.1522	0.1337
GOF	1.292	1.086
R ₁ ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.1198	0.0658
wR ₂ ^b (all data)	0.3424	0.1884

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)_2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

VOIDOO Calculations[3].

In order to determine the size of the inner cavity of $\{\text{Co}_{24}\}$, VOIDOO calculations based on the crystal structure were performed. When the virtual probe with a radius of 1.4 Å (set by default, water-sized) was employed, there was no effective cavity in the structure. When the probe size was reduced to 1.0 Å, the volume of the cavity is about 165 Å³ (Fig. S1a). If the internal sulfates were excluded, the volume of the cavity increases to 473 Å³(Fig. S1b).

The following parameters were changed from their default settings:

Maximum number of volume-refinement cycles: 30

Minimum size of secondary grid: 3

Grid for plot files: 0.1

Primary grid spacing: 0.1

Plot grid spacing: 0.1

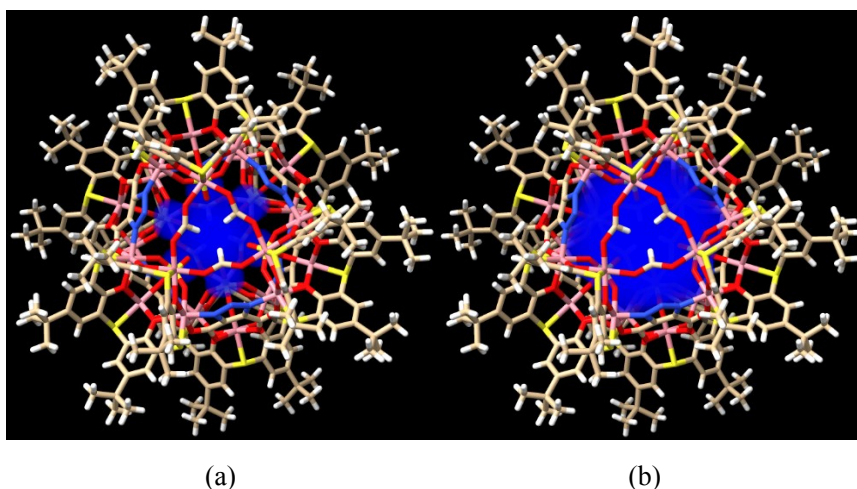


Fig. S1. VOIDOO-calculated void space as shown within the crystal structure of **CIAC-131**. (a) including SO_4^{2-} ; (b) excluding SO_4^{2-} .

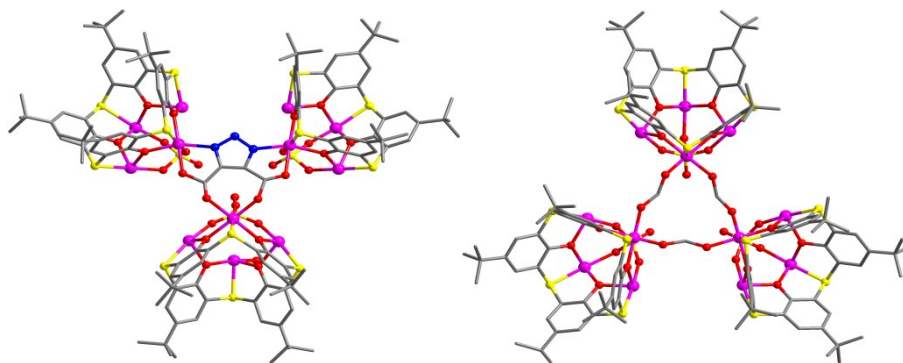


Fig. S2.The connection of Lligand and formate anion with SBUs in **CIAC-131**.

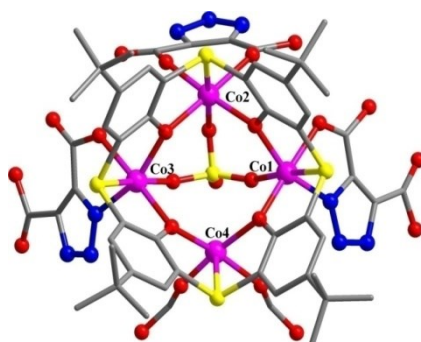


Fig. S3.The coordination of the Co sites in shuttlecock-like Co₄-TC4A SBU in **CIAC-131**.

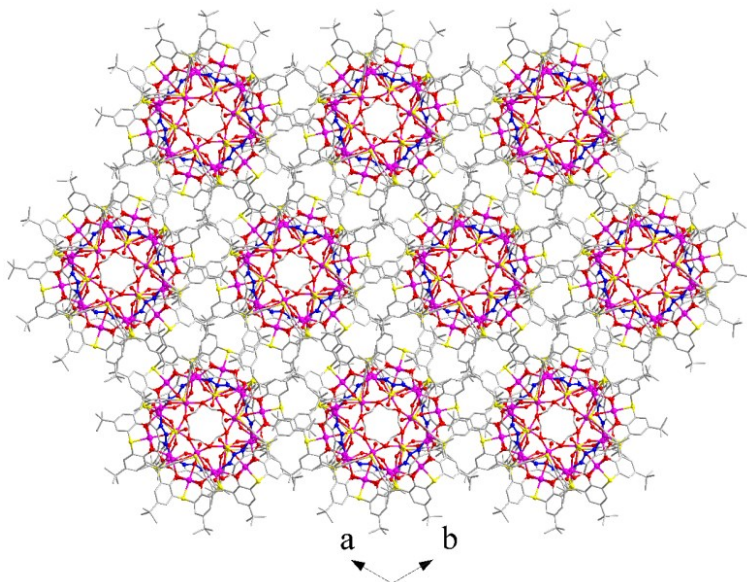


Fig.S4. Packing diagram viewed along the *c* axis of compound **CIAC-131**.

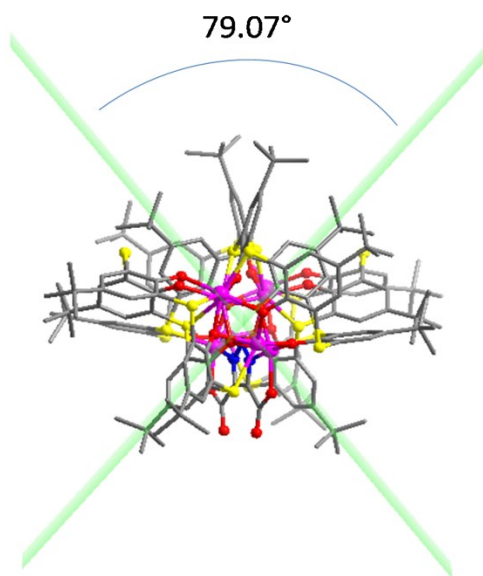


Fig. S5. The dihedral angle between the plates through two Co₄ cores of **CIAC-251**.

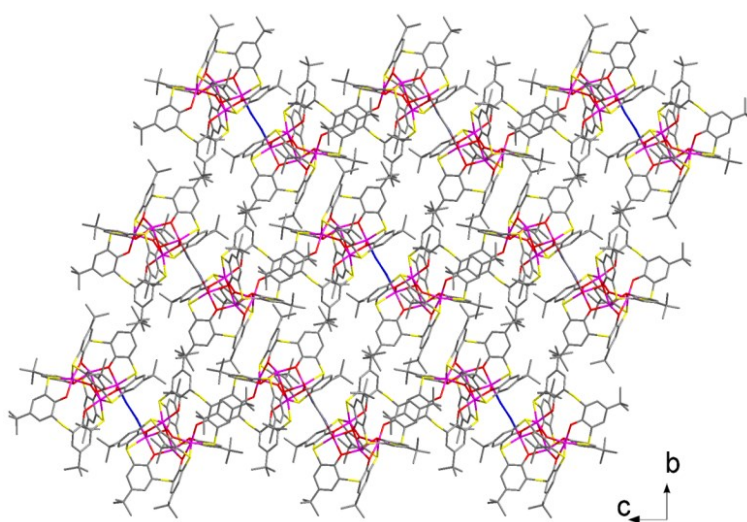


Fig.S6. Packing diagram viewed along the *c* axis of compound **CIAC-251**.

III. Bond valence sum calculations

Table S2-1. BVS for the Co1 atom in CIAC-131.

		Dist	R	B	BVal
Co1	O1	2.136	1.692	0.37	0.301
Co1	O2	2.076	1.692	0.37	0.354
Co1	O5	2.063	1.692	0.37	0.367
Co1	O12	2.106	1.692	0.37	0.327
Co1	S1	2.428	2.06	0.37	0.370
Co1	N3	2.042	1.84	0.37	0.579
					Sum2.298

Table S2-2. BVS for the Co2 atom in CIAC-131.

		Dist	R	B	BVal
Co2	O2	2.124	1.692	0.37	0.311
Co2	O3	2.111	1.692	0.37	0.322
Co2	O6	2.072	1.692	0.37	0.358
Co2	O9	2.062	1.692	0.37	0.368
Co2	O11	2.090	1.692	0.37	0.341
Co2	S2	2.420	2.06	0.37	0.378
					Sum2.078

Table S2-3. BVS for the Co3 atom in CIAC-131.

		Dist	R	B	BVal
Co3	O3	2.046	1.692	0.37	0.384
Co3	O4	2.011	1.692	0.37	0.422
Co3	O7	2.023	1.692	0.37	0.409
Co3	O10	2.171	1.692	0.37	0.274
Co3	S3	2.461	2.06	0.37	0.338
Co3	N1	2.072	1.84	0.37	0.534
					Sum2.361

Table S2-4. BVS for the Co4 atom in CIAC-131.

		Dist	R	B	BVal
Co4	O1	1.974	1.692	0.37	0.467
Co4	O4	2.075	1.692	0.37	0.355
Co4	O13	1.933	1.692	0.37	0.521
Co4	O14	1.992	1.692	0.37	0.444
Co4	S4	2.468	2.06	0.37	0.332
					Sum2.11
					9

Table S3-1. BVS for the Co1 atom in **CIAC-251**.

		Dist	R	B	BVal
Co1	O1	2.155	1.692	0.37	0.286
Co1	O4	2.064	1.692	0.37	0.366
Co1	O5	1.999	1.692	0.37	0.436
Co1	O8	2.005	1.692	0.37	0.375
Co1	S4	2.432	2.06	0.37	0.366
Co1	S8	2.533	2.06	0.37	0.278
					Sum 2.107

Table S3-2. BVS for the Co2 atom in **CIAC-251**.

		Dist	R	B	BVal
Co2	O1	2.036	1.692	0.37	0.394
Co2	O2	1.967	1.692	0.37	0.476
Co2	O6	2.099	1.692	0.37	0.333
Co2	O7	2.188	1.692	0.37	0.262
Co2	S1	2.490	2.06	0.37	0.313
Co2	S6	2.511	2.06	0.37	0.296
					Sum 2.074

Table S3-3. BVS for the Co3 atom in **CIAC-251**.

		Dist	R	B	BVal
Co3	O3	2.024	1.692	0.37	0.408
Co3	O4	2.014	1.692	0.37	0.419
Co3	O7	2.067	1.692	0.37	0.363
Co3	O8	2.134	1.692	0.37	0.303
Co3	S7	2.519	2.06	0.37	0.289
					Sum 1.782

Table S3-4. BVS for the Co4 atom in **CIAC-251**.

		Dist	R	B	BVal
Co4	O2	1.989	1.692	0.37	0.448
Co4	O3	1.999	1.692	0.37	0.436
Co4	O7	2.252	1.692	0.37	0.220
Co4	O9	2.049	1.692	0.37	0.381
Co4	S2	2.464	2.06	0.37	0.336
Co4	N1	2.031	1.84	0.37	0.597

IV. Magnetic Studies.

The magnetic properties of compounds **CIAC-131** and **CIAC-251**, measured in an applied field of 1000 Oe at 2-300 K, is shown in Fig.S7. The $\chi_M T$ values at room temperature are $66.8 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and $21.8 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **CIAC-131** and **CIAC-251**, respectively. Both decrease gradually first and then fall rapidly in the lower temperature region to $2.03 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and $4.05 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. For each Co(II) center of **CIAC-131** and **CIAC-251**, the experimental $\chi_M T$ value at room temperature are $2.78 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and $2.73 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which are accord with the typical value of the Co(II) (the $\chi_M T$ value normally ranges from 2.7 to 3.4 $\text{cm}^3 \text{ mol}^{-1} \text{ K}$ for Co(II)). For these two compounds **CIAC-131** and **CIAC-251**, fitting the experimental data in the range of 50-300 K to the Curie-Weiss law of $1/\chi_M = (T - \theta)/C$ with Curie constant (C) of $78.62 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and $24.65 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, and Weiss constant (θ) of -52.99 K and -37.85 K , respectively. The negative Weiss constant (θ) value suggest antiferromagnetic interaction between the Co(II) centers[4].

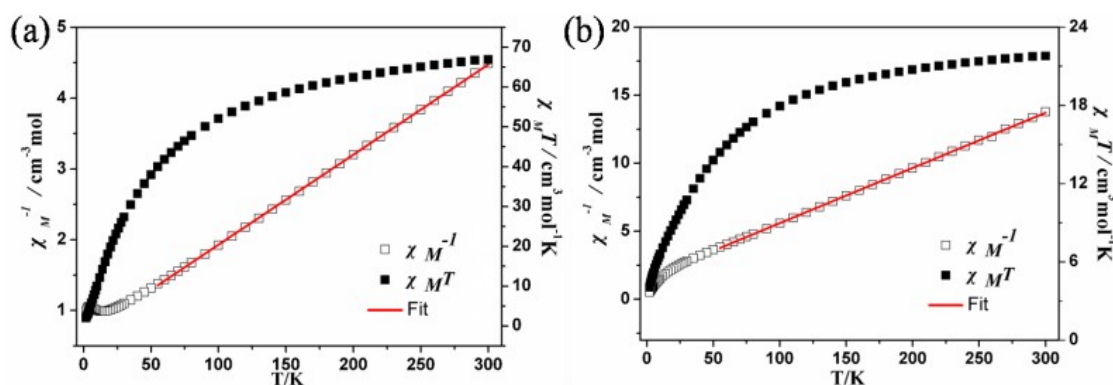


Fig.S7. Plots of $\chi_M T$ vs. T and $1/\chi_M$ vs. T for **CIAC-131**(a) and **CIAC-251**(b) in a 1000 Oe field at 2-300 K.

V. pH Effect on Hg(II) adsorption

The effect of pH on Hg(II) adsorption by **CIAC-131** and **CIAC-251** were investigated. As shown in Fig. S8, the removal efficiency of Hg(II) by **CIAC-131** and **CIAC-251** are 97.5% and 77.5%, respectively. That is, {Co₂₄} cage has better adsorption performance towards Hg(II) than {Co₈} cluster. When pH is less than 2, the removal efficiency are not high for both adsorbents because there are a lot of hydrogen ions in the aqueous solution which would compete with Hg(II) to bond the binding sites on the adsorbent surface [5] and the high acidity of the aqueous solution would lead to the partial collapse of **CIAC-131** and **CIAC-251** skeleton. The removal efficiency increase continuously when pH = 3 ~ 6, which is due to the less and less hydrogen ions in the solution to compete with Hg(II) to be adsorbed. The removal efficiency reach the maximum at pH = 6. And then the removal efficiency of Hg(II) by **CIAC-131** decreased obviously with the increasing pH value while the decrease is not obvious for **CIAC-251**. And when pH > 6.47, mercury ions mainly exist as Hg(OH)₂ which cannot enter the cage cavity of **CIAC-131**.

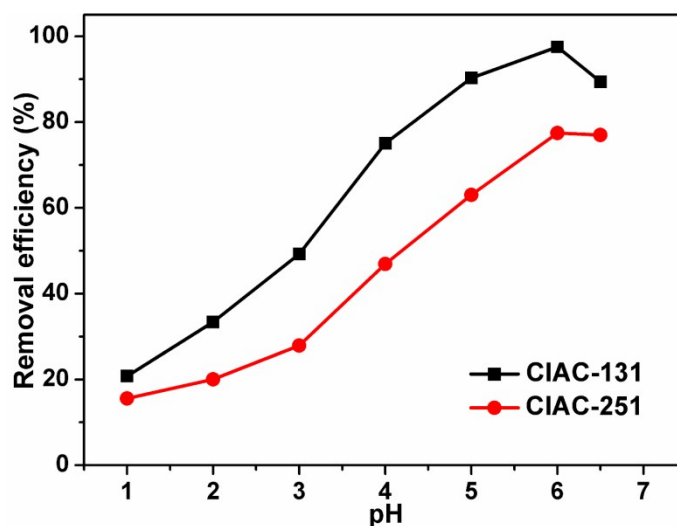


Fig.S8. Effect of pH on Hg(II) adsorption by **CIAC-131** and **CIAC-251**. ($C_i = 100$ mg/L)

VI. Selective Adsorption

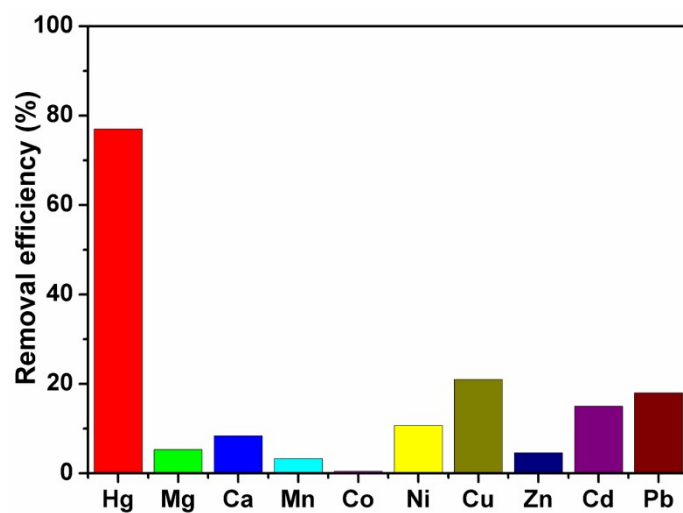


Fig. S9. Adsorption of different metal ions from a mixture solution by CIAC-251.

VII. Adsorption isotherm

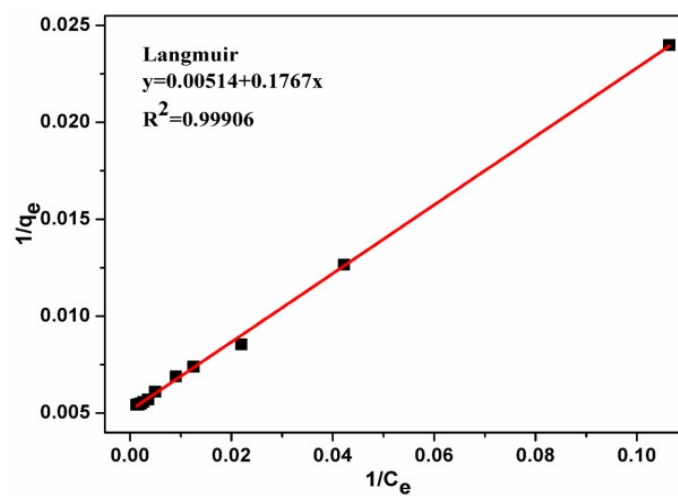


Fig. S10. The Langmuir plot for the Hg(II) adsorption of CIAC-251.

VIII. FT-IR Spectra

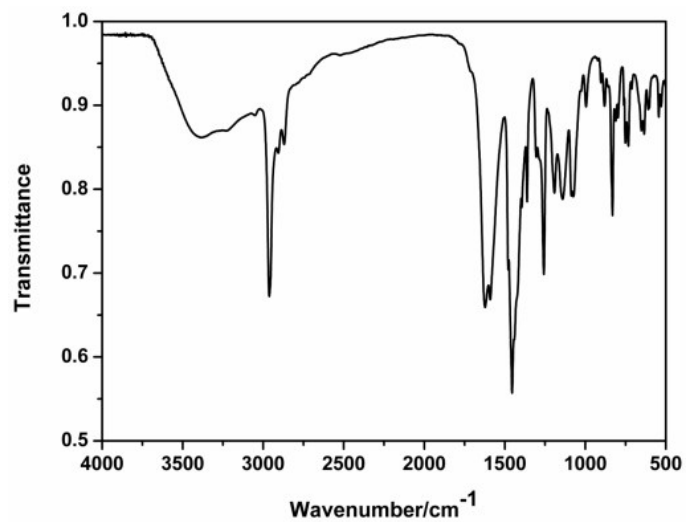


Fig. S11. FT-IR spectra of CIAC-131.

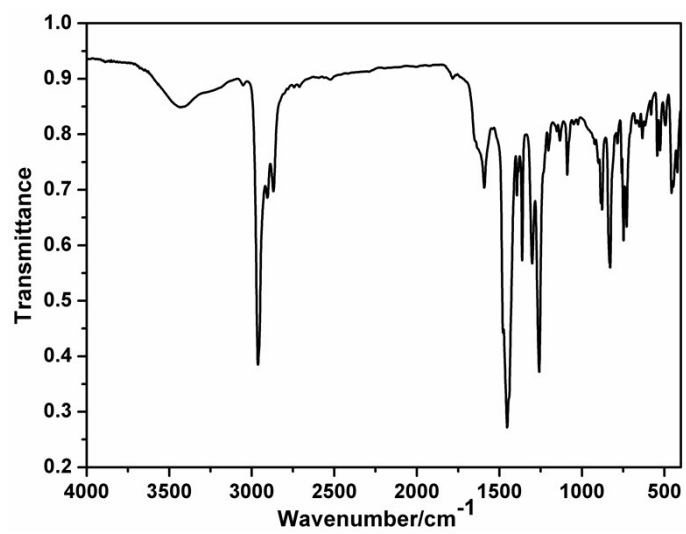


Fig. S12. FT-IR spectra of CIAC-251.

IX. TG Analysis

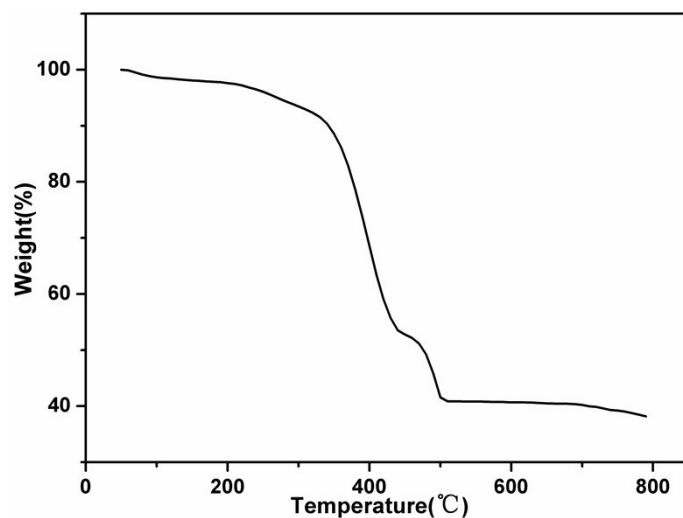


Fig. S13. TG curve of CIAC-131.

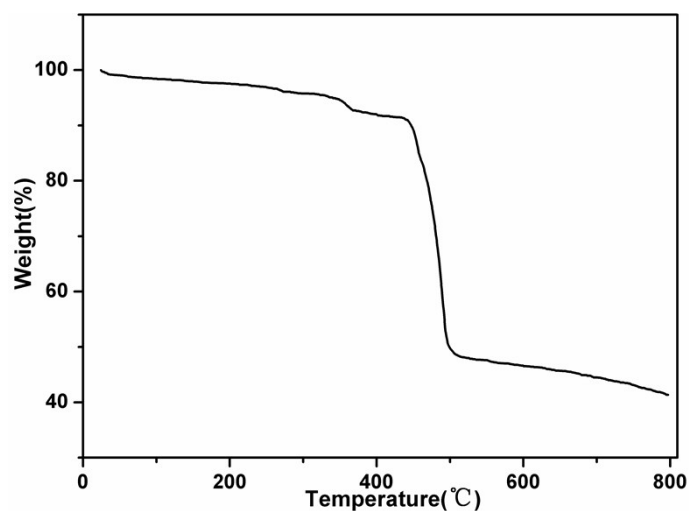


Fig. S14. TG curve of CIAC-251.

X. References

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