Electronic Supplementary Material

A novel carboxylic-functional indole-based aerogel for high effective removal of heavy metals from aqueous solution via synergistic effects of face-point and point-point interactions

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Main materials and measurements

4-Hydroxyindole was purchased from J & K Technology Co., Ltd., and was purified by column chromatography on 100-200 mesh silica gel with petroleum ether (PE) : ethyl acetate (EA)=3.5 : 1. Resorcinol, formaldehyde and 5-Benzyloxyindole were purchased from J & K Technology Co., Ltd., and used without further purification. Nickel (II) chloride hexahydrate (NiCl₂·6H₂O), copper(II) sulfate pentahydrate (CuSO₄·5H₂O), chromium(III) chloride hexahydrate (CrCl₃·6H₂O) and zinc(II) sulfate hexahydrate (ZnSO₄·6H₂O) were supplied by Aladdin. The rest of the materials and reagents were obtained from different commercial sources and used without further purification.

FT-IR spectrum was recorded on a Nicolet 6700 FTIR spectrometer. Solid-state cross-polarization magic-angle-spinning (CP/MAS) NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer. ¹H NMR was performed on AVANCE 300 MHz NMR spectrometers in dimethylsulfoxide (DMSO)- d_6 . UV-Visable spectroscopies were analysized on the UV-3150 instrument. Scanning electron microscopy (SEM) was recorded on an S-4800 (Hitachi Ltd) field emission scanning electron microscope. Digital photos were taken using a Cannon 600D camera. N₂ sorption isotherms were measured at –196 °C by using a Autosorb IQ instrument, where the specific surface area (S_{BET}) and pore size distribution was evaluated using the Brunauer–Emmett–Teller (BET) method (P/P₀)

= 0.05 - 0.30)^[1] and Barrett–Joyner–Halenda (BJH) method^[2] (desorption branches of nitrogen isotherms), respectively. The metal ion concentrations in solutions before and after adsorption were measured using ICP-AES (Jarrel-ASH, ICAP-9000) and ICP-MS (NexION 300X) for much low concentrations. For determining the compositions of the solid samples, ICP-AES (~0.1 M HNO₃ solution was used to dissolve the solids).

Supercritical drying

The acetone-filled gel was exchanged for the liquefied CO_2 in the autoclave. After partial exchange of the acetone with CO_2 , part of the acetone was drained, then the autoclave was refilled with CO_2 . The CO_2 -filled gel was dried at 45°C and 7.5 Mpa for 7 days.

Heavy Metal Uptake Experiments

The heavy metal uptakes from aqueous solutions with various concentrations were studied using the batch method. 0.02 g CHIFA solid was mixed with 25 mL (V/m = 1250 mL g⁻¹) of each solution, under stirring for 24 h. After the adsorption experiments completed, centrifugation was performed, and the solid samples were dried in air for further characterization. Meanwhile, the metal concentrations in the supernatant solutions and their mother solutions were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and ICP-MS for much low concentrations. The experiments were repeated three times and the result was presented as average at room temperature. The pH value of Ni(II), Cu(II), Cr(III) and Zn(II) solutions were adjusted using 0.1 mol L⁻¹ HNO₃ or 0.1 mol L⁻¹ NaOH solution. Fresh prepared solutions were utilized for all experiments.

Equilibrium adsorption isotherm studies for Ni(II), Cu(II), Cr(III) and Zn(II): The concentrations of Ni(II), Cu(II), Cr(III) and Zn(II) ions were in the range of 10–1000 ppm to ensure adsorption equilibration was achieved. An amount of 0.02 g CHIFA added in 25 mL solution was used to have a V/m value of 1250 mL g⁻¹. The contact time was about 24 h.

Adsorption kinetics of Ni(II), Cu(II), Cr(III) and Zn(II): An amount of 0.04 g CHIFA was added into the 50 mL (V/m = 1250 mL g⁻¹) solution with a concentration of \approx 10 ppm, undergoing vigorous stirring continuously for 2 min, 5 min, 30 min, 1 h, 2 h, 3 h and 4 h. The contact time was varied to check the adsorption kinetics.

Regeneration study: After the equilibrium study, metal-loaded CHIFA was collected and washed with deionized water and dried to the constant weight. Then the adsorbents (0.1 g) were shaken with 50 ml of HCl (1 mol L⁻¹) in 250 mL Erlenmeyer flasks at 150 rpm on an orbital shaker at 25°C for 2 h, filtered and soaked again until the concentration of heavy metal ions in the filtrate measured using ICP-MS (NexION 300X) decreased to below 0.01 ppm. After washing with deionized water, the treated CHIFA was ready for the next use.

Data treatment: The distribution coefficient (K_d) is defined by the equation of $K_d = (V[(C_0 - C_f)/C_f])/m$, where C_0 and C_f are, respectively, the initial and equilibrium concentrations of M^{n+} (ppm, µg mL⁻¹) after the contact, V is the solution volume (mL), and m is the solid amount (g). The % removal is calculated with the equation of $100 \times (C_0 - C_f)/C_0$. The removal capacity (q_m) is given by the equation: $q_m = 10^{-3} \times (C_0 - C_f) \cdot V/m$.

Synthesis and characterization of 5-Hydroxyindole-3-acetic acid

A solution of the 5-Benzyloxyindole (10.0 mmol) in anhydrous ether (50-75 ml) was added dropwise at 5 °C, during 5-20 min, to the Grignard reagent, prepared from magnesium turnings (20.0 mmol) and ethyl iodide (20.0 mmol) in anhydrous ether (10 ml). The solution was boiled under reflux for 45 ~min to complete the formation of the indole Grignard reagent. The solution was cooled to 10 °C, and ethyl chloroacetate) (11 mmol) added dropwise, with stirring, during 10 min. The resulting reaction mixture was cooled to 0 °C. and the stirring continued for a further 15 min. The reaction mixture was poured into ice-water and extracted with ether (3 \times 50 ml). The combined ether extracts were washed with saturated aqueous sodium bicarbonate, dried (Na₂SO₄), and concentrated to dryness in vacuum. The crude products was recrystallized from benzene - light petroleunm to afford 5-Benzyloxy-3-carbethoxyindole (yield 96%).

A solution of the 5-Benzyloxy-3-carbethoxyindole (0.2 g) in a mixture of 1propanol (30 ml), ethanol (3 ml), and 2 mol/L aqueous potassium hydroxide (14ml)) was heated at 75 °C for 5 h and at room temperature for 1 d. The solution was then evaporated to small bulk in vacuum, diluted with water, extracted with ether (3 \times 20 ml), and the ether extracts discarded. The pH of the aqueous solution was adjusted to 3 with hydrochloric acid and extracted with ether (3 \times 30 ml). The combined, dried (Na₂SO₄,) ether extracts were evaporated to dryness in vacuum to give the 5-Benzyloxyindoleacetic acid (yield 91%).

A solution of the 5-Benzyloxyindole-3-acetic acid (0.25 g) in methanol (50 ml) containing a palladium-on-charcoal catalyst (5 %; 0.125 g) was shaken in a hydrogen atmosphere at room temperature and under atmospheric pressure for 1 h. The reaction mixture was filtered through Celite 545 (Fisher) and concentrated to dryness in vacuum. The crude products were purified by recrystallization from benzene/ethanol to afford 5-Hydroxyindole-3-acetic acid (yield 81%) (Scheme S1).



Scheme S1. Synthesis of 5-Hydroxyindole-3-acetic acid



Fig. S1. FT-IR of 5-Hydroxyindole-3-acetic acid.



Fig. S2 ¹H NMR spectrum of 5-Hydroxyindole-3-acetic acid.



Fig. S3 ¹³C NMR spectrum of 5-Hydroxyindole-3-acetic acid.

Preparation of the RFA, HIFA and CHIFA aerogels

RFA: The RFA was prepared by mixing resorcinol with formaldehyde in deionized water in a molar ratio of 1 : 2. The total solid content in the pre-gelsolution was kept at 20%. Sodium carbonate was used as catalyst with the molar ratio of resorcinol : $Na_2CO_3 = 50$: 1. And the above solution was stirred for 20 min, then poured into ampoule bottles, followed by heat treatment at 80 °C for 24 h and was capable of gelling. Before supercritical drying, water in wet gel was replaced by solvent exchange with acetone for three times. After that, the gel was supercritical dried at 45 °C for 7 days and RFA was obtained, finally. **HIFA:** The HIFA was prepared by mixing 5-hydroxyindole with formaldehyde in CH_3CN in a molar ratio of 1 : 2. The total solid content in the pre-gelsolution was kept at 20%. Sodium carbonate was used as catalyst with the molar ratio of 5-Hydroxyindole : $Na_2CO_3 = 10$: 1. And the above solution was stirred for 20 min, then poured into ampoule bottles, followed by heat treatment at 60 °C for 60 min and was capable of gelling. Before supercritical drying, CH_3CN in wet gel was replaced by solvent exchange with acetone for three times. After that, the gel was supercritical dried at 45 °C for 7 days and HIFA was obtained, finally.

CHIFA: The CHIFA was prepared by mixing 5-Hydroxyindole-3-acetic acid with formaldehyde in deionized water in a molar ratio of 1 : 2. The total solid content in the pre-gelsolution was kept at 20%. Sodium carbonate was used as catalyst with the molar ratio of 5-Hydroxyindole-3-acetic acid : $Na_2CO_3 = 1 : 1.2$. And the above solution was stirred for 20 min, then poured into ampoule bottles, followed by heat treatment at 80 °C for 24 h and was capable of gelling. Before supercritical drying, water in wet gel was replaced by solvent exchange with acetone for three times. After that, the gel was supercritical dried at 45 °C for 7 days and CHIFA was obtained, finally.



Scheme S2 Synthesis of RFA



Scheme S3 Synthesis of HIFA



Scheme S4 Synthesis of CHIFA

In order to confirm the successful formation of the resulting CHIFA aerogel, it was characterized at molecular levels by a FTIR spectrometer and ¹³C CP/MAS NMR spectrometer. The FTIR spectrum for the porous material is shown in Fig. S4a, in which the broad absorption peak at about 3414 cm⁻¹ correspond to O–H and N–H stretching vibrations. The band at 1356 cm⁻¹ comes from O-H bending vibrations. The band at 1715 cm⁻¹ corresponds to C=O stretching vibration. whereas medium to weak absorption bands at 1213 and 1042 cm⁻¹ indicate that methylene ether linkages between indole rings are present but not dominant. The structural information of the prepared CHIFA was also obtained by ¹³C CP/MAS NMR spectroscopy (Fig. S4b). The peak at about 175 ppm is ascribed to the carbonyl group carbons, and the peak at about 147 ppm is ascribed to the phenolic carbons of substituted 5-Hydroxyindole-3-acetic acid. (Fig. S4b 3 and 12), the broad peaks at 132–109 ppm are ascribed to the indole group carbons (Fig. S4b 5– 11). Consistent with the IR spectrum, the smaller peak at 68 ppm is assigned to the small amount of CH₂-O-CH₂ bridges and the broad peak at about 31 ppm is assigned to the different types of CH₂ bridges, which is perfectly consistent with a previous study about acid-catalyzed resorcinol-formaldehyde aerogels.^[3] In conclusion, the characterization data can confirm that the desired aerogel has been synthesized successfully. Additionally, the RFA and HIFA aerogels were also characterized by a FTIR spectrometer and ¹³C CP/MAS NMR spectrometer. and the satisfactory results were in good agreement with the proposed structures.



Fig. S4 The characterizations of CHIFA aerogel, (a): FT-IR spectrum, (b): ¹³C CP/MAS NMR spectrum.



Fig. S5 The characterizations of HIFA aerogel, (a): FT-IR spectrum, (b): ¹³C CP/MAS NMR spectrum.



Fig. S6 FT-IR spectrum of RFA aerogel.

SEM image, nitrogen adsorption – desorption isotherms and the pore size distribution of RFA and HIFA



Fig. S7 (a) SEM image of RFA, (b) Nitrogen adsorption – desorption isotherms and the pore size distribution (inset) of RFA, (c) SEM image of HIFA, (d) Nitrogen adsorption – desorption isotherms and the pore size distribution (inset) of HIFA.

PH effect on the removal of Ni²⁺, Cu²⁺, Cr³⁺ and Zn²⁺ by CHIFA



Fig. S8 pH effect on the removal of Ni²⁺, Cu²⁺, Cr³⁺ and Zn²⁺ by CHIFA ($C_0 = 100$ mg/L; m = 0.02 g, V = 25 mL, V/m = 1250 mL g⁻¹; Contact time: 24 h).

The pH of solution is one of the most important parameters affecting sorption process. Fig. S8 shows the dependences of the adsorption capacity for Ni²⁺, Cu²⁺, Cr^{3+} and Zn^{2+} on the pH value (2.0 – 6.0) over CHIFA in order to eliminate the effect of precipitation at higher pH values. Notably, that the ions adsorption of Ni²⁺, Cu^{2+} , Cr^{3+} and Zn^{2+} was increased with the increase of pH value from 2.0 to 6.0. The phenomenon could be explained that at lower pH, the relatively high H+ concentration would strongly compete with metal ions for the adsorption sites, resulting in low adsorption capacity. Meanwhile, the hydroxyl and carboxyl groups of the CHIFA would be protonated to form -OH²⁺ groups, which lead to electrostatic repulsion between the metal cations and the protonated groups, and prevent the uptake of the metal ions. With the increase of pH, the competition between H+ and other cations could be neglected, and the hydroxyl and carboxyl groups groups would be deprotonated to form -O- and -COO- groups and thereby enhancing the electrostatic attraction between the adsorbent sites and metal

cations. In view of the fact that the precipitation of Ni²⁺, Cu²⁺, Cr³⁺ and Zn²⁺ takes place at pH \geq 7, pH 6.0 was selected as the optimum pH for the following batch experiments to eliminate the effect of precipitation.

Kinetics data of Ni²⁺, Cu²⁺, Cr³⁺ and Zn²⁺ using CHIFA

C ₀ [ppm] ^{a)}	Time (min)	C _f [ppm]	Removal [%]	$K_{\rm d} \ [{ m mL} \ { m g}^{-1}]$
9.83	2	0.25	97.46	$4.8 imes 10^4$
	5	0.132	98.66	$9.2 imes 10^4$
	30	0.062	99.37	$2.0 imes 10^5$
	60	0.039	99.60	3.1×10^5
	120	0.018	99.82	$6.8 imes 10^5$
	180	0.014	99.86	$8.8 imes 10^5$
	240	0.01	99.90	1.2×10^{6}

 Table S1. Kinetics data of Ni²⁺ using CHIFA.

^{a)}m = 0.04 g, V = 50 mL, V/m = 1250 mL g⁻¹, pH value: 6.0.

C ₀ [ppm] ^{a)}	Time (min)	C _f [ppm]	Removal [%]	$K_{\rm d} \ [{ m mL} \ { m g}^{-1}]$
10.67	2	0.11	98.97	$3.5 imes 10^4$
	5	0.059	99.45	2.2×10^5
	30	0.024	99.78	$5.5 imes 10^5$
	60	0.016	99.85	$8.3 imes 10^5$
	120	0.009	99.92	1.5× 10 ⁶
	180	0.006	99.94	$2.2 imes 10^6$
	240	0.005	99.95	$2.7 imes 10^6$

Table S2. Kinetics data of Cu²⁺ using CHIFA.

^{a)}m = 0.04 g, V = 50 mL, V/m = 1250 mL g⁻¹, pH value: 6.0.

C ₀ [ppm] ^{a)}	Time (min)	C _f [ppm]	Removal [%]	$K_{\rm d} \ [{ m mL} \ { m g}^{-1}]$
9.81	2	0.223	97.73	$5.4 imes 10^4$
	5	0.19	98.06	6.3×10^{4}
	30	0.162	98.35	7.4×10^4
	60	0.143	98.54	$8.5 imes 10^4$
	120	0.132	98.65	9.2×10^4
	180	0.125	98.73	$9.7 imes 10^4$
	240	0.123	98.75	$9.8 imes 10^4$

Table S3. Kinetics data of Cr³⁺ using CHIFA.

^{a)}m = 0.04 g, V = 50 mL, V/m = 1250 mL g⁻¹, pH value: 6.0.

C ₀ [ppm] ^{a)}	Time (min)	C _f [ppm]	Removal [%]	$K_{\rm d} \ [{ m mL} \ { m g}^{-1}]$
10.10	2	0.244	97.58	$5.0 imes 10^4$
	5	0.179	98.23	$6.9 imes 10^4$
	30	0.135	98.66	9.2×10^4
	60	0.117	98.84	1.1×10^{5}
	120	0.092	99.09	1.4×10^{5}
	180	0.083	99.18	1.5×10^{5}
	240	0.071	99.30	1.8×10^5

Table S4. Kinetics data of Zn²⁺ using CHIFA.

^{a)}m = 0.04 g, V = 50 mL, V/m = 1250 mL g⁻¹, pH value: 6.0.

Ions	q _{e,exp} (mg/g)	<i>k</i> ₂	q _{e,cal} (mg/g)	<i>R</i> ²
Ni ²⁺	12.28	0.696	12.28	1
Cu^{2+}	13.33	1.736	13.33	1
Cr ³⁺	12.11	1.015	12.12	1
Zn^{2+}	12.54	0.533	12.53	1

Table S5. Kinetics parameters (pseudo-second-order-model) for adsorbing metal ions onto 4-HIFA.

Sorption data of CHIFA toward Ni²⁺, Cu²⁺, Cr³⁺ and Zn²⁺

C ₀ [ppm] ^{a)}	C _f [ppm]	Removal [%]	<i>q</i> _m [mg g⁻ ¹]	$K_{\rm d}$ [mL g ⁻¹]
9.88	0.0014	99.99	12.3	$8.8 imes 10^6$
51.1	0.158	99.69	63.7	4.0×10^5
99	1.97	98.01	121.3	6.2×10^{4}
196	25	87.24	213.8	8.6×10^{3}
509	279	45.19	287.5	1.0×10^{3}
996	758	23.90	297.5	3.9×10^2

Table S6. Sorption data of CHIFA toward Ni²⁺.

^{a)} m = 0.02 g, V = 25 mL, V/m = 1250 mL g⁻¹; contact time: 24 h; pH value: 6.0.

C ₀ [ppm] ^{a)}	C _f [ppm]	Removal [%]	<i>q</i> _m [mg g⁻ ¹]	$K_{\rm d} \ [{ m mL} \ { m g}^{-1}]$
10.52	0.0008	99.99	13.1	$1.6 imes 10^7$
49.6	0.046	99.91	61.9	$1.3 imes 10^6$
101	0.76	99.25	125.3	1.6×10^{5}
196	16	91.84	225.0	1.4×10^4
505	216	57.23	361.3	1.7×10^{3}
1005	699	30.45	382.5	5.5×10^{2}

Table S7. Sorption data of CHIFA toward Cu^{2+} .

a) m = 0.02 g, V = 25 mL, V/m = 1250 mL g⁻¹; contact time: 24 h; pH value: 6.0.

C ₀ [ppm] ^{a)}	C _f [ppm]	Removal [%]	<i>q</i> _m [mg g⁻ ¹]	$K_{\rm d} [m mL \ g^{-1}]$
9.62	0.067	99.30	11.9	1.8×10^5
46.8	0.76	98.38	57.6	7.6×10^4
98	13	86.73	106.3	8.2×10^{3}
203	88	56.65	143.8	1.6× 10 ³
489	338	30.88	188.8	5.6×10^{2}
981	825	15.90	195.0	2.4× 10 ²

Table S8. Sorption data of CHIFA toward Cr³⁺.

^{a)} m = 0.02 g, V = 25 mL, V/m = 1250 mL g⁻¹; contact time: 24 h; pH value: 6.0.

C ₀ [ppm] ^{a)}	C _f [ppm]	Removal [%]	<i>q</i> _m [mg g⁻ ¹]	$K_{\rm d} \ [{ m mL} \ { m g}^{-1}]$
10.06	0.032	99.68	12.5	$3.9 imes 10^5$
53	1.4	97.36	64.5	$4.6 imes 10^4$
105	11	89.52	117.5	1.1×10^4
204	68	66.67	170.0	2.5×10^{3}
507	343	32.35	205.0	6.0×10^{2}
1009	836	17.15	216.3	$2.6 imes 10^2$

Table S9. Sorption data of CHIFA toward Zn^{2+} .

a) m = 0.02 g, V = 25 mL, V/m = 1250 mL g⁻¹; contact time: 24 h; pH value: 6.0.

Ions	$q_{ m m}$ (mg/g)	<i>b</i> (L/mg)	<i>R</i> ²
Ni ²⁺	298.5	0.2343	0.9997
Cu^{2+}	383.1	0.2119	0.9994
Cr ³⁺	196.9	0.0868	0.9985
Zn ²⁺	217.4	0.1054	0.9992

Table S10. Adsorption constants of Langmuir models for the adsorption of Ni²⁺, Cu²⁺, Cr^{3+} and Zn^{2+} ions onto CHIFA.

Table S11. Comparison of adsorption capacities of various adsorbents for heavy metal ions.

target ions	adsorbents	$q_{ m m}~[{ m mg~g^{-1}}]$	References
Ni ²⁺	CHIFA	297.5	This work
	PMCNa hybrid	224	5
	hydrogels	224	5
	Polyvinyl		
	alcohol/corn starch	7.3	6
	hydrogel		
	Fireweed carbon	10.12	7
	Graphene – chitosan	49.3	8
	$-Mn_3 O_4$	ту.5	0
	high-pressure		
	steaming hide waste	61.92	9
	(HWSAC)		
Cu ²⁺	CHIFA	382.5	This work
	polypyrrole/MoS ₄	111	10
	$^{2-}$ (MoS ₄ -Ppy)	111	10
	SPI/PEI composite	136.2	11

	hydrogels		
	EDTA-silica	79	12
	CCS-g-PGMA-c-	220	13
	PEI microspheres	229	15
	PEI-cellulose	90.1	1/
	nanofiber	90.1	14
Cr ³⁺	CHIFA	195.0	This work
	Biomass based		
	hydrogel (SESD-	41.7	4
	PAA)		
	nano chelating resin		
	2-amino		
	pyridine-functionali	22	15
	zed polyacrylonitrile		
	(CPN-AP)		
	PMHS-g-	16.8	16
	PyPz(OEt)2Allyl	40.0	10
Zn^{2+}	CHIFA	216.3	This work
	Biomass based		
	hydrogel (SESD-	121.2	4
	PAA)		
	Iron Oxide (Fe ₃ O ₄)	11.1	17
	Nanomaterial	11.1	1 /
	Coffee husk (CH)	12.53	18

Adsorption cycle test



Fig. S9 Adsorption ($C_0 = 100 \text{ mg/L}$; m = 0.02 g, V = 25 mL, $V/m = 1250 \text{ mL g}^{-1}$; Contact time: 24 h, pH = 6) of metal ions on CHIFA after repeated adsorption cycle (treated by 1 mol L⁻¹ HCl).

Fig. S9 shows Ni²⁺, Cu^{2+,} Cr³⁺ and Zn²⁺ adsorption recycled for 4 times, after 1 cycles reused, metal ions adsorption decreased most, which may due to that part metal ions, that not be desorbed by HCl, occupied part of the adsorption sites. The metal ions adsorption for regeneration 2, 3 and 4 times were relatively close to each other. After 4 cycles reused, the amount of metal ions adsorption for Ni²⁺, Cu²⁺, Cr³⁺ and Zn²⁺ ions was 100, 113, 85 and 102 mg g⁻¹, which was 80%, 84.3%, 80.2% and 87.2% of adsorption for the fresh sample, respectively. The excellent recyclability of the metal ions on CHIFA is very helpful for practical applications, suggesting the long-term use in water purification.

Adsorption contrast



Fig. S10 (a) Sorption isotherms: (a) Sorption capacity change following initial concentration, (b) Concentration change following contact time of Cu^{2+} adsorption for all three types of aerogels.



Adsorption mechanism

Fig. S11 (a) FT-IR spectra of CHIFA samples before and after Ni²⁺, Cu²⁺, Cr³⁺ or Zn²⁺ adsorption, (b) UV absorption spectra of 5-Hydroxyindole-3-acetic acid (4-HI-COOH) (100 μ M) and its 1:1 complex with Cu²⁺ at pH 7 (1 mM HEPES buffer).

To identify the interaction between CHIFA samples and heavy metal ions during the adsorption process, FT-IR spectra of the CHIFA before and after Ni²⁺, Cu²⁺, Cr³⁺ and Zn²⁺ adsorption are compared. As illustrated in Fig. S11a, the intensity of O-H stretching vibrations at 3414 cm⁻¹ slightly shifted to upper wave numbers after the adsorption of Ni²⁺, Cu²⁺, Cr³⁺ or Zn²⁺, which can be attributed to the complexation of metal ions with the ionized O-H group of "free" hydroxyl groups and bonded O-H bands of carboxylic acids.^[19] Meanwhile, the band at 1356 cm⁻¹, originated from O-H bending vibrations, almost vanished after the Ni²⁺, Cu²⁺, Cr³⁺ or Zn²⁺ adsorption, due to the complexation of hydroxyl group with Ni²⁺, Cu²⁺,

 Cr^{3+} or Zn^{2+} on the adsorption sites. Furthermore, the band at 1715 cm⁻¹, originated from C=O stretching vibration significantly decreased and shifted to upper wave numbers at 1558 cm⁻¹ after the adsorption of Ni²⁺, Cu²⁺, Cr³⁺ or Zn²⁺, which indicated involvement of binding metal ions. Besides, the wavenumber difference between asymmetric and symmetric vibrations of COO group at 1400-1600 cm⁻¹ could be used to confirm the point-point interaction type.^[20] To gain insight into the mechanism and the interaction of indole with Cu^{2+} , UV absorption was performed. Fig. S11b shows the absorption spectra of 5-Hydroxyindole-3-acetic acid (5-HI-COOH) in the absence and presence of equimolar Cu^{2+} , together with the difference spectrum 5-HI-COOH-Cu²⁺ minus 5-HI-COOH. The difference spectrum 5-HI-COOH-Cu²⁺ (red line) reveals a negative band at 218 nm and a positive band at 230 nm attributable to a Cu2+-5-HI-COOH interaction. An analogous UV difference spectrum with a negative/positive band pair around 220/230 nm has been observed for an indolyl model compound of the cation- π interaction,^[21] a cation- π interaction between a positively charged His imidazole ring and a nearby Trp indole ring has also been reported to produce an analogous band pair.^[22] The similarity of the UV difference spectrum of 5-HI-COOH-Cu²⁺ with those reported previously for other types of cation- π interactions indicates that the Cu²⁺-5-HI-COOH interaction in 5-HI-COOH-Cu²⁺ is also categorized as a cation- π interaction.



Fig. S12 Fully optimized geometries of model interactions calculated using DFT method. (a) The point-to-point interactions carboxyl of CHIFA and Cu²⁺, (b) the face-to-point cation- π conformation of CHIFA with Cu²⁺, (c) the point-to-point interactions hydroxyl of CHIFA with Cu²⁺.

Simulation method

The Density functional theory (DFT) calculation was utilized to investigate the adsorption mechanism. All the calculations reported here were fulfilled with Materials Studio DMol3 program (Accerlrys. USA). ^[23-25] For the exchange correlation term of the energy functional, the generalized gradient corrected functional GGA and PW91 functional as implemented, were applied for all the geometry optimizations.^[20] The double numerical plus polarization (DNP) basis sets was employed. All the energy values were determined for 298 K. No restrictions on symmetries were imposed on the initial structures. The frequency analysis was performed on all DFT structures to ensure the absence of imaginary frequency and verify the existence of a true minimum. The computed interaction enthalpies at 298 K for the complexes were defined as,

$$-\triangle \mathbf{E} = - \begin{bmatrix} E_{complex} & - \begin{pmatrix} E_{Cu^{2+}} + E_{A} \end{pmatrix} \end{bmatrix}$$
(1),

where A represents CHIFA.

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