# **Supporting Information**

A novel indole-based conjugated microporous polymer for high effective removal of heavy metals from aqueous solution via double cation- $\pi$  interactions

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### Main materials and measurements

2-indolinone was purchased from J & K Technology Co., Ltd., and used without further purification. Iron(III) chloride, Nickel (II) chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O), copper(II) sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O), chromium(III) chloride hexahydrate (CrCl<sub>3</sub>·6H<sub>2</sub>O) and zinc(II) sulfate hexahydrate (ZnSO<sub>4</sub>·6H<sub>2</sub>O) 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. Solidstate cross-polarization magic-angle-spinning (CP/MAS) NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using Bruker AMX600 MHz NMR spectrometers in DMSO-*d*<sub>6</sub>. The elemental analysis characterization technique was performed using a Vario EL III apparatus. UV-Visible spectroscopies were analyzed on the UV-3150 instrument. Scanning electron microscopy (SEM) was recorded on an S-4800 (Hitachi Ltd) field emission scanning electron microscope. Morphological observation was performed with a Tecnai G2 F20 S-TWIN (FEI Company) transmission electron microscope. Digital photos were taken using a Cannon 600D camera. The nitrogen adsorption and desorption isotherms were measured at 77 K using a Autosorb IQ instrument. The sample was treated at 120 °C for 24 h before the measurement. The surface area was calculated by Brunauer-Emmett-Teller (BET) equation (0.01 < P/P0 < 0.1). The pore-size-distribution (PSD) curve was obtained from the adsorption branch using non-local density functional theory (NL-DFT) method. The total pore volume ( $V_{total}$ ) and micropore volume ( $V_{micro}$ ) were estimated from the adsorbed amount at a relative pressure P/P<sub>0</sub> of 0.995 and 0.1, 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 HNO<sub>3</sub> solution was used to dissolve the solids).

## Heavy metal uptake experiments

The heavy metal uptakes from aqueous solutions with various concentrations were studied using the batch method. 0.02 g PTIA solid was mixed with 25 mL (V/m = 1250 mL g<sup>-1</sup>) 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<sup>-1</sup> HNO<sub>3</sub> or 0.1 mol L<sup>-1</sup> 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 10–500 ppm to ensure adsorption equilibration was achieved. An amount of 0.02 g PTIA added in 25 mL solution was used to have a V/m value of 1250 mL g<sup>-1</sup>. 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 PTIA was added into the 50 mL (V/m = 1250 mL g<sup>-1</sup>) solution with a concentration of  $\approx$  10 ppm, undergoing vigorous stirring continuously for 1 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 PTIA 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<sup>-1</sup>) in 250 mL Erlenmeyer flasks at 150 rpm on an orbital shaker at 25°C for 2 h. After washing with deionized water, the treated PTIA 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<sup>-1</sup>) 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 TAT

TAT molecule was prepared with a slight modification to what was published in previous literature. <sup>[1]</sup> A mixture of 2-indolinone (2.0 g, 15 mmol) and 10 ml of POCl<sub>3</sub> was heated at 100°C for 8 h. Then, the reaction mixture was poured into ice and neutralized carefully with NaOH until pH 7-8. After neutralization, the precipitate was filtered to give the crude product as a brown solid. The crude solution in methanol (MeOH) was absorbed on silica-gel, dried, loaded and eluated through a thick silica-gel pad with a dichloromethane (DCM) as a mobile phase. After evaporation of eluate at reduced pressure and recrystallization from dimethylacetamide (DMAc), pure pale yellow solid was obtained. (0.81 g, 47 %). <sup>1</sup>H NMR (400 MHz, DMSO-*d*6)  $\delta$  = 11.86 (1s, 3H, N-H), 8.65 (1d, 3H, *J*=7 Hz, aromatic H), 7.76 (1d, 3H, J = 7.4 Hz, aromatic H), 7.34 (1m, 6H, aromatic H) ppm; <sup>13</sup>C NMR(100 MHz, (CD<sub>3</sub>)<sub>2</sub>S=O):  $\delta = 138.98$ , 134.09, 122.83, 122.66, 120.29, 119.51, 111.43, 100.88 ppm; FT-IR spectrum(KBr pellet, cm<sup>-1</sup>): 3436, 1608, 728. Anal. Calcd. For C<sub>24</sub>H<sub>15</sub>N<sub>3</sub>: C, 83.46; H, 4.38; N, 12.17; Found: C, 82.58; H, 4.19; N, 12.39.



Scheme S1. Scheme for the synthesis of 10,15-dihydro- 5H-diindolo[3,2-a:3',2'-c]carbazole (TAT).



Fig. S1. FT-IR of TAT.



Fig. S2 <sup>1</sup>H NMR spectrum of TAT.



Fig. S3 <sup>13</sup>C NMR spectrum of TAT.

# **Preparation of the PTIA**

TAT (690 mg, 2 mmol) was dispersed in 60 mL of dry CHCl<sub>3</sub> under the nitrogen environment. To this solution, we added iron(III) chloride (0.970 mg, 6 mmol), and the mixture was stirred at room temperature for 24 h. The resulting mixture was transferred to 100 mL of methanol. The precipitates were collected by filtration and washed with methanol, dilute HCl, distilled water, and methanol, sequentially. After washing, the precipitates were collected and dried under vacuum at 80 °C for 24 h and PTIA was obtained, finally.



Scheme S2 Synthesis of indole-based conjugated microporous polymer (PTIA).



Fig. S4 FT-IR spectrum of PTIA.



Fig. S5 <sup>13</sup>C CP/MAS NMR spectrum of PTIA.



Fig. S6  $N_2$  adsorption-desorption isotherm curves and the pore size distribution (inset) of PTIA.



Fig. S7 TEM of PTIA network (supplement for Fig. 1b).

pH effect on the removal of Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup> and Zn<sup>2+</sup> by PTIA



**Fig. S8** pH effect on the removal of Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup> and Zn<sup>2+</sup> by PTIA ( $C_0 = 100 \text{ mg/L}$ ; m = 0.02 g, V = 25 mL, V/m = 1250 mL g<sup>-1</sup>; Contact time: 24 h).

# Kinetics data of Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup> and Zn<sup>2+</sup> using PTIA

 <b>C</b> <sub>0</sub> [ppm] <sup>a)</sup>	Time (min)	C <sub>f</sub> [ppm]	Removal [%]	$K_{\rm d} \ [{ m mL} \ { m g}^{-1}]$			
9.83	1	0.272	97.23	$4.4 \times 10^4$			
	5	0.151	98.46	$8.0  imes 10^4$			
	30	0.074	99.25	$1.6 \times 10^{5}$			

Table S	1 Kinetics	data of Ni <sup>2+</sup>	using PTIA
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60	0.043	99.56	$2.8  imes 10^5$
120	0.031	99.68	$4.0 \times 10^{5}$
180	0.016	99.84	$7.7 \times 10^{5}$
240	0.013	99.87	9.4 × 10 <sup>5</sup>

 Table S2. Kinetics data of Cu<sup>2+</sup> using PTIA.

<sup>a)</sup>m = 0.04 g, V = 50 mL, V/m = 1250 mL g<sup>-1</sup>, pH value: 6.0.

<b>C</b> <sub>0</sub> [ppm] <sup>a)</sup>	Time (min)	C <sub>f</sub> [ppm]	Removal [%]	$K_{\rm d} \ [{ m mL} \ { m g}^{-1}]$
10.67	1	0.17	98.41	$4.2 \times 10^4$
	5	0.087	99.18	1.5× 10 <sup>5</sup>
	30	0.031	99.71	4.3 × 10 <sup>5</sup>
	60	0.016	99.85	8.3 × 10 <sup>5</sup>
	120	0.013	99.88	$1.0 \times 10^{6}$
	180	0.009	99.92	$1.5 \times 10^{6}$
	240	0.007	99.93	1.9 × 10 <sup>6</sup>

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

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	<b>C</b> <sub>0</sub> [ppm] <sup>a)</sup>	Time (min)	C <sub>f</sub> [ppm]	Removal [%]	$K_{\rm d} \ [{ m mL} \ { m g}^{-1}]$			
	9.81	1	0.335	96.59	$3.5  imes 10^4$			
		5	0.28	97.15	$4.3 \times 10^4$			
		30	0.231	97.65	$5.2 \times 10^4$			
		60	0.204	97.92	$5.9  imes 10^4$			

**Table S3.** Kinetics data of  $Cr^{3+}$  using PTIA.

120	0.185	98.11	$6.5  imes 10^4$
180	0.167	98.30	$7.2  imes 10^4$
240	0.163	98.34	$7.4  imes 10^4$

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

<b>C</b> <sub>0</sub> [ppm] <sup>a)</sup>	Time (min)	C <sub>f</sub> [ppm]	Removal [%]	$K_{\rm d} \ [{ m mL} \ { m g}^{-1}]$
10.10	1	0.289	97.14	$4.2 \times 10^4$
	5	0.227	97.75	$5.4 \times 10^4$
	30	0.173	98.29	$7.2 \times 10^4$
	60	0.147	98.54	$8.5  imes 10^4$
	120	0.125	98.76	$1.0 \times 10^{5}$
	180	0.113	98.88	$1.1 \times 10^{5}$
	240	0.101	99.00	$1.2 \times 10^{5}$

**Table S4.** Kinetics data of  $Zn^{2+}$  using PTIA.

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

Table S5. Kinetics parameters (	pseudo-second	l-order-model) f	for adsorbing	metal ions
onto PTIA.				

Ions	q <sub>e,exp</sub> (mg/g)	<i>k</i> <sub>2</sub>	$q_{ m e,cal}$ (mg/g)	<b>R</b> <sup>2</sup>
Ni <sup>2+</sup>	12.271	0.617	12.274	1
Cu <sup>2+</sup>	13.329	1.546	13.330	1

Cr <sup>3+</sup>	12.059	0.547	12.061	1
$Zn^{2+}$	12.499	0.510	12.498	1

# Sorption data of PTIA toward Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup> and Zn<sup>2+</sup>

C <sub>0</sub> [ppm] <sup>a)</sup>	C <sub>f</sub> [ppm]	Removal [%]	q <sub>m</sub> [mg g⁻ ¹]	$K_{\rm d} \ [{ m mL} \ { m g}^{-1}]$
9.83	0.0009	99.99	12.3	$1.4 \times 10^7$
51.1	0.036	99.93	63.8	$1.8  imes 10^6$
99	0.56	99.43	123.1	$2.2 \times 10^5$
196	2.9	98.52	241.4	$8.3  imes 10^4$
356	130	63.48	282.5	$2.2 \times 10^{3}$
518	286	44.79	290.0	$1.0  imes 10^3$

**Table S6.** Sorption data of PTIA toward  $Ni^{2+}$ .

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

C <sub>0</sub> [ppm] <sup>a)</sup>	C <sub>f</sub> [ppm]	Removal [%]	<i>q</i> <sub>m</sub> [mg g <sup>-</sup> <sup>1</sup> ]	$K_{\rm d} [{ m mL}~{ m g}^{-1}]$
10.67	0.0005	100.00	13.3	$2.7  imes 10^7$
52.7	0.026	99.95	65.8	$2.5  imes 10^6$
104	0.93	99.11	128.8	$1.4 \times 10^{5}$

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

209	11	94.74	247.5	$2.3  imes 10^4$
345	101	70.72	305.0	$3.0 \times 10^{3}$
508	249	50.98	323.8	$1.3  imes 10^3$

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

C <sub>0</sub> [ppm] <sup>a)</sup>	C <sub>f</sub> [ppm]	Removal [%]	<i>q</i> <sub>m</sub> [mg g⁻ <sup>1</sup> ]	$K_{\rm d}  [{ m mL}  { m g}^{-1}]$
9.81	0.047	99.52	12.2	$2.6 \times 10^{5}$
47.8	0.86	98.20	58.7	$6.8  imes 10^4$
96	16	83.33	100.0	$6.3 \times 10^{3}$
214	88	58.88	157.5	1.8× 10 <sup>3</sup>
359	223	37.88	170.0	$7.6 \times 10^{2}$
499	356	28.66	178.8	5.0× 10 <sup>2</sup>

**Table S8.** Sorption data of PTIA toward Cr<sup>3+</sup>.

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

C <sub>0</sub> [ppm] <sup>a)</sup>	C <sub>f</sub> [ppm]	Removal [%]	$q_{ m m}  [ m mg  g^{-}$	$K_{\rm d} \ [{ m mL} \ { m g}^{-1}]$
10.1	0.037	99.63	12.6	$3.4 \times 10^{5}$

**Table S9.** Sorption data of PTIA toward  $Zn^{2+}$ .

53	1.5	97.17	64.4	$4.3 \times 10^4$
103	12	88.35	113.8	$9.5  imes 10^3$
211	68	67.77	178.8	$2.6 \times 10^3$
349	193	44.70	195.0	$1.0 \times 10^3$
509	346	32.02	203.8	$5.9  imes 10^2$

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

**Table S10.** Adsorption constants of Langmuir models for the adsorption of  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Cr^{3+}$  and  $Zn^{2+}$  ions onto PTIA.

Ions	$q_{ m m}$ (mg/g)	<i>b</i> (L/mg)	<i>R</i> <sup>2</sup>
Ni <sup>2+</sup>	289.9	1.3911	0.9992
$Cu^{2+}$	323.6	0.5383	0.9978
Cr <sup>3+</sup>	179.9	0.1421	0.9988
$Zn^{2+}$	205.3	0.1623	0.9999

**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 <sup>2+</sup>	PTIA	289.9	This work
	PMCNa hybrid hydrogels	224	2
	Polyvinyl alcohol/corn	7.3	3

	starch hydrogel		
	Fireweed carbon	10.12	4
	Graphene – chitosan – Mn <sub>3</sub> O <sub>4</sub>	49.3	5
	high-pressure steaming hide waste (HWSAC)	61.92	6
Cu <sup>2+</sup>	PTIA	323.6	This work
	polypyrrole/MoS <sub>4</sub> <sup>2-</sup> (MoS <sub>4</sub> -Ppy)	111	7
	SPI/PEI composite hydrogels	136.2	8
	EDTA-silica	79	9
	CCS-g-PGMA-c-PEI microspheres	229	10
	PEI-cellulose nanofiber	90.1	11
$Cr^{3+}$	PTIA	179.9	This work
	Biomass based hydrogel (SESD–PAA)	41.7	16
	amino pyridine-functionalize d polyacrylonitrile (CPN-AP)	22	12
	PMHS-g- PyPz(OEt)2Allyl	46.8	13
$Zn^{2+}$	PTIA	205.3	This work
	Biomass based hydrogel (SESD–PAA)	121.2	16
	Iron Oxide (Fe <sub>3</sub> O <sub>4</sub> ) Nanomaterial	11.1	14
	Coffee husk (CH)	12.53	15

# 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 PTIA after repeated adsorption cycle (treated by 1 mol L<sup>-1</sup> HCl).

### 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). <sup>[17-19]</sup> 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.<sup>[18]</sup> 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 PTIA.

# References

- L. G. Satriani, V. Casagrande, A. Bianco, G. Ortaggia, M. Franceschin, Org. & biomol. chem., 2009, 7, 2513.
- [2]. P. M. Spasojevic, V. V. Panic, M. D. Jovic, J. Markovic, C. V. Roost, I. G. Popovic,
  S. J. Velickovic, *J. Mater. Chem. A*, 2016, 4, 1680.
- [3]. M. N. K. Chowdhury, A. F. Ismail, M. D. H. Beg, G. Hegde, R. J. Gohari, New J. Chem., 2015, 39, 5823.
- [4]. A. D. Dwivedi, S. P. Dubey, M. Sillanpää, Y. N. Kwon, C. Lee, *Chem. Eng. J.*, 2015, 281, 713.
- [5]. X. Gu, Y. Yang, Y. Hu, M. Hu, C. Wang, Acs Sustain. Chem. Eng., 2015, 3, 1056.
- [6]. J. Kong, R. Gu, J. Yuan, W. Liu, J. Wu, Z. Fei, Q. Yue, *Ecotox. Environ. Saf.*, 2018, 156, 294.
- [7]. L. Xie, Z. Yu, S. M. Islam, K. Shi, Y. Cheng, M. Yuan, J. Zhao, G. Sun, H. Li, S. Ma, *Adv. Funct. Mater.*, 2018, 1800502.
- [8]. J. Liu, D. Su, J. Yao, Y. Huang, Z. Shao, X. Chen, J. Mater. Chem. A, 2017, 5, 4163.
- [9]. R. Kumar, M. A. Barakat, Y. A. Daza, H. L. Woodcock, J. N. Kuhn, J. Colloid Interf. Sci., 2013, 408, 200.

- [10]. L. Lv, J. Zhang, S. Yuan, L. Huang, S. Tang, B. Liang, S. O. Pehkonen, *Rsc Adv.*, 2016, 6, 78136.
- [11]. J. Wang, X. Lu, P. F. Ng, K. I. Lee, B. Fei, J. H. Xin, J. Y. Wu, J. Colloid Interf. Sci., 2015, 440, 32.
- [12]. S. M. El-Bahy, Z. M. El-Bahy, J. Environ. Chem. Eng., 2016, 4, 276.
- [13]. M. Cegłowski, G. Schroeder, Chem. Eng. J., 2015, 259, 885.
- [14]. S. E. Ebrahim, A. H. Sulaymon, H. S. Alhares, Desalin. Water Treat., 2015, 62, 1.
- [15]. B. G. Alhogbi, Z. F. Al-Enazi, J. Enc. Adsorpt. Sci., 2018, 08, 1.
- [16]. M. Zhang, L. H. Song, H. Jiang, S. Li, Y. Shao, J. Yang, J. Li, J. Mater. Chem. A, 2017, 5, 3434.
- [17]. W. Wang, C. Zhu and Y. Cao, Int. J. Hydrogen Energ., 2010, 35, 1951.
- [18]. K. J. Lee, W. L. Mattice, R. G. Snyder, J. Chem. Phys., 1992, 96, 9138.
- [19]. R. Lü, J. Lin and Z. Qu, Comput. Theor. Chem., 2012, 1002, 49.