Supporting Information

A novel indole-based conjugated microporous polymer for high effective removal of heavy metals from aqueous solution via double cation-π 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 (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 and ¹³C NMR spectra were recorded using Bruker AMX600 MHz NMR spectrometers in DMSO-<em>d</em>₆. 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 \((0.01 < P/P_0 < 0.1)\). 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 \(V_{\text{total}}\) and micropore volume \(V_{\text{micro}}\) were estimated from the adsorbed amount at a relative pressure \(P/P_0\) 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 (\(\sim 0.1\) M HNO\(_3\) 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\(^{-1}\)) 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 10–500 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⁻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 PTIA was added into the 50 mL (V/m = 1250 mL g⁻¹) solution with a concentration of ≈ 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⁻¹) 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 (Kₐ) is defined by the equation of 

\[ K_d = \frac{(V[(C_0 - C_f)/C_f])}{m}, \]

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 \(100 \times (C_0 - C_t)/C_0\). 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. \(^{[1]}\) A mixture of 2-indolinone (2.0 g, 15 mmol) and 10 ml of POCl\(_3\) 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 %).

\(^1\)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; \(^{13}\)C NMR(100 MHz, (\(CD_3\))\(_2\)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\(^{-1}\)): 3436, 1608, 728. Anal. Calcd. For C\(_{24}\)H\(_{15}\)N\(_3\): 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 $^1$H NMR spectrum of TAT.
Fig. S3 $^{13}$C NMR spectrum of TAT.

**Preparation of the PTIA**

TAT (690 mg, 2 mmol) was dispersed in 60 mL of dry CHCl$_3$ 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** $^{13}$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$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$ by PTIA**

![Graph showing pH effect on the removal of metal ions by PTIA](image)

Fig. S8 pH effect on the removal of Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$ by PTIA (C$_0$ = 100 mg/L; m = 0.02 g, V = 25 mL, V/m = 1250 mL g$^{-1}$; Contact time: 24 h).

**Kinetics data of Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$ using PTIA**

**Table S1.** Kinetics data of Ni$^{2+}$ using PTIA.

| C$_0$ [ppm]$^{\text{a)}$ | Time (min) | C$_f$ [ppm] | Removal [%] | K$_d$ [mL g$^{-1}$] |
|-------------------------|------------|-------------|-------------|------------------|
| 9.83                    | 1          | 0.272       | 97.23       | 4.4 × 10$^4$     |
|                         | 5          | 0.151       | 98.46       | 8.0 × 10$^4$     |
|                         | 30         | 0.074       | 99.25       | 1.6 × 10$^5$     |
Table S2. Kinetics data of Cu\(^{2+}\) using PTIA.

| C\(_0\) [ppm]\(^{a)}\) | Time (min) | C\(_f\) [ppm] | Removal [%] | K\(_d\) [mL g\(^{-1}\)] |
|-------------------------|------------|----------------|-------------|-----------------|
| 10.67                   | 1          | 0.17           | 98.41       | 4.2 \times 10^4 |
|                         | 5          | 0.087          | 99.18       | 1.5 \times 10^5 |
|                         | 30         | 0.031          | 99.71       | 4.3 \times 10^5 |
|                         | 60         | 0.016          | 99.85       | 8.3 \times 10^5 |
|                         | 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 \times 10^6 |

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

Table S3. Kinetics data of Cr\(^{3+}\) using PTIA.

| C\(_0\) [ppm]\(^{a)}\) | Time (min) | C\(_f\) [ppm] | Removal [%] | K\(_d\) [mL g\(^{-1}\)] |
|-------------------------|------------|----------------|-------------|-----------------|
| 9.81                    | 1          | 0.335          | 96.59       | 3.5 \times 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 \times 10^4 |

\(^{a)}\) m = 0.04 g, V = 50 mL, V/m = 1250 mL g\(^{-1}\), pH value: 6.0.
| Time (min) | $C_f$ [ppm] | Removal [%] | $K_d$ [mL g$^{-1}$] |
|-----------|-------------|-------------|---------------------|
| 10.10     | 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       | $8.5 \times 10^4$   |
| 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.

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

| Ions  | $q_{e,exp}$ (mg/g) | $k_2$ | $q_{e,cal}$ (mg/g) | $R^2$ |
|-------|--------------------|-------|--------------------|-------|
| Ni$^{2+}$ | 12.271            | 0.617 | 12.274             | 1     |
| Cu$^{2+}$ | 13.329            | 1.546 | 13.330             | 1     |
### Sorption data of PTIA toward Ni\textsuperscript{2+}, Cu\textsuperscript{2+}, Cr\textsuperscript{3+} and Zn\textsuperscript{2+}

**Table S6.** Sorption data of PTIA toward Ni\textsuperscript{2+}.

| \(C_0\) [ppm]\textsuperscript{a)} | \(C_f\) [ppm] | Removal [%] | \(q_m\) [mg g\textsuperscript{-1}] | \(K_d\) [mL g\textsuperscript{-1}] |
|---|---|---|---|---|
| 9.83 | 0.0009 | 99.99 | 12.3 | \(1.4 \times 10^7\) |
| 51.1 | 0.036 | 99.93 | 63.8 | \(1.8 \times 10^6\) |
| 99 | 0.56 | 99.43 | 123.1 | \(2.2 \times 10^5\) |
| 196 | 2.9 | 98.52 | 241.4 | \(8.3 \times 10^4\) |
| 356 | 130 | 63.48 | 282.5 | \(2.2 \times 10^3\) |
| 518 | 286 | 44.79 | 290.0 | \(1.0 \times 10^3\) |

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

**Table S7.** Sorption data of PTIA toward Cu\textsuperscript{2+}.

| \(C_0\) [ppm]\textsuperscript{a)} | \(C_f\) [ppm] | Removal [%] | \(q_m\) [mg g\textsuperscript{-1}] | \(K_d\) [mL g\textsuperscript{-1}] |
|---|---|---|---|---|
| 10.67 | 0.0005 | 100.00 | 13.3 | \(2.7 \times 10^7\) |
| 52.7 | 0.026 | 99.95 | 65.8 | \(2.5 \times 10^6\) |
| 104 | 0.93 | 99.11 | 128.8 | \(1.4 \times 10^5\) |
Table S8. Sorption data of PTIA toward Cr$^{3+}$.

| $C_0$ [ppm]$^a$ | $C_f$ [ppm] | Removal [%] | $q_m$ [mg g$^{-1}$] | $K_d$ [mL g$^{-1}$] |
|-----------------|-------------|-------------|---------------------|---------------------|
| 9.81            | 0.047       | 99.52       | 12.2                | $2.6 \times 10^5$   |
| 47.8            | 0.86        | 98.20       | 58.7                | $6.8 \times 10^4$   |
| 96              | 16          | 83.33       | 100.0               | $6.3 \times 10^3$   |
| 214             | 88          | 58.88       | 157.5               | $1.8 \times 10^3$   |
| 359             | 223         | 37.88       | 170.0               | $7.6 \times 10^2$   |
| 499             | 356         | 28.66       | 178.8               | $5.0 \times 10^2$   |

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

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

| $C_0$ [ppm]$^a$ | $C_f$ [ppm] | Removal [%] | $q_m$ [mg g$^{-1}$] | $K_d$ [mL g$^{-1}$] |
|-----------------|-------------|-------------|---------------------|---------------------|
| 10.1            | 0.037       | 99.63       | 12.6                | $3.4 \times 10^5$   |

$^a$ m = 0.02 g, V = 25 mL, V/m = 1250 mL g$^{-1}$; 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  | $q_m$ (mg/g) | $b$ (L/mg) | $R^2$ |
|-------|--------------|------------|-------|
| Ni$^{2+}$ | 289.9        | 1.3911     | 0.9992 |
| Cu$^{2+}$ | 323.6        | 0.5383     | 0.9978 |
| Cr$^{3+}$ | 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 | $q_m$ [mg g$^{-1}$] | References |
|-------------|------------|---------------------|------------|
| Ni$^{2+}$   | PTIA       | 289.9               | This work  |
|             | PMCNa hybrid hydrogels | 224     | 2          |
|             | Polyvinyl alcohol/corn | 7.3     | 3          |

a) $m = 0.02$ g, $V = 25$ mL, $V/m = 1250$ mL g$^{-1}$; contact time: 24 h; pH value: 6.0.
| Material/Composition                          | PTIA   | Notes       |
|-----------------------------------------------|--------|-------------|
| starch hydrogel                               | 10.12  | 4           |
| Fireweed carbon                               | 49.3   | 5           |
| Graphene – chitosan – Mn_3 O_4                |        |             |
| high-pressure steaming hide waste (HWSAC)     | 61.92  | 6           |
| Cu^{2+}                                       |        |             |
| polypyrrole/MoS_4                            | 111    | 7           |
| \( \text{MoS}_4 \text{-Ppy} \)               |        |             |
| 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+}                                       |        |             |
| Biomass based hydrogel (SESD–PAA)             | 41.7   | 16          |
| nano chelating resin 2-amino pyridine–        | 22     | 12          |
| functionalized polyacrylonitrile (CPN-AP)    |        |             |
| PMHS-g-\( \text{PyPz(OEt)}\text{2Allyl} \)  | 46.8   | 13          |
| Zn^{2+}                                       |        |             |
| PTIA                                          | 205.3  | This work   |
| Biomass based hydrogel (SESD–PAA)             | 121.2  | 16          |
| Iron Oxide (Fe_3O_4)                          | 11.1   | 14          |
| Nanomaterial                                  |        |             |
| Coffee husk (CH)                              | 12.53  | 15          |

**Adsorption cycle test**
**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 (Accelrys. USA). 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. 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,

$$-	riangle E = - [E_{\text{complex}} - (E_{Cu^2+} + E_A)]$$  \hspace{1cm} (1),
where A represents PTIA.

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