# **Supporting Information**

An indole-derived porous organic polymer for efficiently visual colorimetric capture of iodine in aqueous media via the synergistic effects of cation- $\pi$  and electrostatic forces

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#### 1. General remarks

1,3,5-benzenetricarbonyl trichloride, fluorobenzene, indole and formaldehyde dimethylacetal were purchased from J & K Technology Co., Ltd., and used without further purification. The rest of the materials and reagents were obtained from different commercial sources and used without further purification. FT-IR spectra were recorded on a Nicolet 6700 FTIR spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were performed on a Bruker 400MHz NMR spectrometer with DMSO-d<sub>6</sub> or CDCl<sub>3</sub> as the internal standard. Solid-state cross-polarization magic-angle-spinning (CP/MAS) NMR spectrum was carried out on a Bruker Avance III 400 NMR spectrometer. The elemental analyses were performed using a Vario EL III apparatus. Thermogravimetric analysis (TGA) was performed on a Setarma TG-92 at a heating rate of 10 °C/min under nitrogen atmosphere. Scanning electron microscopy (SEM) was made on an S-4800 (Hitachi Ltd.) field emission scanning electron microscope system. Digital photos were taken using a Cannon 600D camera. Transmission electron microscope (TEM) was recorded on a Tecnai G2 F20 S-TWIN (FEI Company). Gas adsorption isotherms were measured by a volumetric method using a Micromeritics AR-JW-BK112 instrument. The samples were degassed 6 hours at 120 °C, and the obtained adsorption-desorption isotherms were evaluated to obtain the pore parameters, including Brunauer-Emmett-Teller (BET) specific surface area, pore size, and pore volume. The pore size distribution (PSD) was calculated from the adsorption branch using the nonlocal density functional theory (NLDFT) approach.

#### 2. The adsorption of iodine

The iodine solution (1000 mg  $L^{-1}$ ) was firstly prepared by dissolving 1 g nonradioactive iodine and 1.77 g sodium iodide in 1 L deionized water, the ratio of

iodide: iodine is 3:2. The solution was stored in darkness, due to decomposition in the light. The adsorption experiments were conducted by adding 5 mg adsorbents and 20 ml iodine solution with certain concentrations (8-210 mg mL<sup>-1</sup>) into a 20 ml glass vial.

#### Adsorption kinetic studies

Pseudo-first-order model:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$
(1)

Pseudo-second-order model:

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

where  $q_e$  and  $q_t$  are the amount of adsorbed iodine (mg g<sup>-1</sup>) at equilibrium and at time t (min), and  $k_1$  is the adsorption rate constant (min).  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the pseudo-second-order rate constant.

#### **Adsorption isotherm**

Langmuir isotherm models:

$$\frac{c_{e}}{q_{e}} = \frac{1}{bq_{m}} + \frac{c_{e}}{q_{m}}$$
(3)

where  $c_e$  is the equilibrium liquid-phase solid-phase of concentration respectively;  $q_e$  (mg g<sup>-1</sup>) is the equilibrium amount of dye adsorption;  $q_m$  (mg g<sup>-1</sup>) is the monolayer capacity of the adsorbent; and b (L mg<sup>-1</sup>) is a Langmuir constant related to the energy of adsorption, representing the affinity between adsorbent and adsorbate.

The Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter R<sub>L</sub>:

$$R_{\rm L} = \frac{1}{1 + bc_0} \tag{4}$$

where  $c_o \text{ (mg L}^{-1})$  is the initial concentration of iodine, and the  $R_L$  value indicates that the type of the isotherm is either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ).

Freundlich model:

$$\ln q_{e} = \ln k_{F} + \left(\frac{1}{n}\right) \ln c_{e}$$
(5)

where  $k_F$  (L mg<sup>-1</sup>) and n are Freundlich constants, representing the adsorption capacity and adsorption intensity, which are calculated from the plots of  $lnq_e$  versus  $lnc_e$ .

#### 3. Visual colorimetric detection of iodine

A series of iodine solutions (10 mL) were prepared with different concentrations (8-210 mg mL<sup>-1</sup>). Next, the optical image of water as recorded with the camera of a smart phone. The R, G and B values of the images were subtracted by Color Helper software. The adjusted intensity (I) was calculated by the following equation:

 $I = 1 - ((I_R + I_G + I_B)/(I'_R + I'_G + I'_B))$ 

where  $I_R$ ,  $I_G$ ,  $I_B$  and  $I'_R$ ,  $I'_G$ ,  $I'_B$  are the RGB component intensities of NaI aqueous solution in the presence and absence of  $I_2$ , respectively.

### 4. Preparation and characterization of TFBB and TIBB compounds

**TFBB:** To a one-necked flask equipped with magnetic stirrer, 1,3,5benzenetricarbonyl trichloride (0.05 mol), fluorobenzene (0.95 mol), anhydrous AlCl<sub>3</sub> (0.12 mol) were added. The reaction mixture was stirred 12 h at room temperature, and then heated to 90 °C under stirring for 2 h. The resulting solution was allowed to slowly cool down to room temperature, and subsequently poured into cold water, filtered, washed with water 3 times. The crude material was recrystallized from *N*,*N*-dimethylacetamide (DMAc) to afford 1,3,5-tris-(4-fluorobenzoyl)benzene as colorless crystals. Yield: 98%; M.p. 207 °C; FT-IR spectrum (KBr pellet, cm<sup>-1</sup>): 1664, 1597, 1500, 1406, 1253, 1157, 1008, 849, 751, 599; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 8.22$  (s, 3H), 7.94 (s, 6H), 7.43 (t, J = 8.0 Hz, 8.0 Hz, 6H) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 116.0$ , 132.9, 133.7, 1137.4, 163.8, 166.3, 192.9 ppm; HRMS (ESI-TOF) m/z: calcd for [M+H]<sup>+</sup>: 445.0973, found: 445.0947; Anal. Calcd for C<sub>27</sub>H<sub>15</sub>F<sub>3</sub>O<sub>3</sub>: C, 72.97; H, 3.38; Found: C, 72.81; H, 3.24.



Scheme S1 Synthesis of TFBB.

**TIBB:** 1,3,5-tris-(4-fluorobenzoyl)benzene (2.6585 g, 6 mmol), indole (2.1438 g, 18.3 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.4878 g, 18 mmol) were added into 20 mL of dry N-methylpyrrolidone and reacted in a nitrogen atmosphere at 180 °C for 12 h. The resulting solution was allowed to slowly cool down to room temperature, and subsequently poured into cold water, filtered, washed with water. The crude compound was purified by column chromatography on silica gel eluting with petroleum ether-CH<sub>2</sub>Cl<sub>2</sub> (2:1) to afford TFBB as light green powder (yield: 64%). M.p. 204 °C; FT-IR spectrum (KBr pellet, cm<sup>-1</sup>): 1660, 1593, 1563, 1454, 1336, 1255, 1179, 856, 743, 714; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.52 (s, 3H), 8.08 (d, *J* = 8.4 Hz, 6H), 7.70 (t, *J* = 7.9 Hz, 12H), 7.41 (d, *J* = 3.3 Hz, 3H), 7.28 – 7.18 (m, 6H), 6.76 (d, *J* = 3.3 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 193.62, 144.22, 138.41, 135.29,

133.89, 133.51, 132.02, 129.90, 127.25, 123.34, 123.08, 121.49, 121.21, 110.57, 105.47 ppm; HRMS (ESI-TOF) m/z: calcd for [M+H]<sup>+</sup>: 735.25, found: 735.19; Anal. Calcd for C<sub>51</sub>H<sub>33</sub>N<sub>3</sub>O<sub>3</sub>: C, 83.25; H, 4.52; N, 5.71; Found: C, 83.06; H, 4.49; N, 5.63.



Scheme S2 Synthesis of TIBB.



**Figure S1** Characterizations of the TIBB. (a) <sup>1</sup>H NMR spectrum; (b) <sup>13</sup>C NMR spectrum; (c) FT-IR spectrum.

## 5. Preparation of indole-based POP PTIBBL

**PTIBBL**: To a solution of TIBB (0.1838 g, 0.25 mmol) and FDA (0.2 mL, 2.2 mmol) in anhydrous 1, 2-dichloroethane (20 mL), anhydrous ferric chloride (0.325 g, 2 mmol) was added under nitrogen atmosphere. The mixture was heated at 80  $^{\circ}$ C for 12h. After polymerization, the desired polymer PTIBBL was fully washed with methanol and concentrated HCl solution. The brown solid was extracted with methanol and

dichloromethane for 12 hours to remove unreacted monomer. The solid was then dried in vacuum at 40  $\,^{\circ}$ C (yield 99%). Anal. Calcd for C<sub>57</sub>H<sub>45</sub>N<sub>3</sub>O<sub>3</sub>: C, 83.49; H, 5.53; N, 5.12; Found: C, 81.23; H, 5.41; N, 4.88.

The structure of PTIBBL was then characterized by Fourier-transform infrared. As shown in Fig. S2a, the peaks at 1658 cm<sup>-1</sup> and 1599 cm<sup>-1</sup> were due to the stretching vibrations of C=O and C-N, respectively. In addition, the peak at 2823 cm<sup>-1</sup> was ascribed to the stretching vibration of  $-CH_2$ - in the polymer framework. The <sup>13</sup>C CP/MAS NMR spectrum exhibited the peak at 200-180 ppm was assigned to the carbonyl carbons, and the broad peaks locating at 150-110 ppm corresponded to the aromatic carbons (Fig. S2b). The peaks at *ca*. 34 ppm were attributed to the methylene carbons attached to the indole rings. In addition, the elemental analysis of PTIBBL was further confirmed the successful preparation of the POP (Table S1). This was in good agreement with the FTIR and NMR results.



Scheme S3 Synthesis of PTIBBL.



Figure S2 Characterizations of the PTIBBL. (a) FTIR; (b) <sup>13</sup>C NMR; (c)XPS.



Figure S3 Characterizations of the PTIBBL. (a) TG; (b) XRD.

81.23

83.49

PTIBBL

Table S1 Elemental analysis for PTIBBL						
Sample	Expected	Found	Expected	Found	Expected	Found
	%C	%C	%H	%H	%N	%N

5.53

5.41

5.12

4.88

# 6. Adsorption performance



**Figure S4** (a) Adsorption kinetic of  $I_3^-$  on PTIBBL. Fitting results of  $I_3^-$  on PTIBBL for kinetic models: (b) Pseudo-first-order kinetic model; (c) Pseudo-second-order kinetic model.

 Table S2 Kinetic parameters of the adsorption of iodine onto PTIBBL at different temperatures

		Pseudo-First-Order Model			Pseudo-Second-Order Model			
Temperature	q <sub>e</sub> , <sub>exp</sub>	q <sub>e</sub>	k <sub>1</sub>	$\mathbf{R}^2$	q <sub>e</sub>	k <sub>1</sub>	$\mathbf{R}^2$	
(°C)	$(mg^{-1})$	$(mg g^{-1})$	$(\min^{-1})$	R	$(mg g^{-1})$	$(g mg^{-1} min^{-1})$	K	
10	373.75	15.49	0.00253	0.1628	370.74	$8.07 \times 10^{-4}$	0.9996	
20	380.29	23.54	0.00484	0.7500	381.68	6.19×10 <sup>-4</sup>	0.9999	
30	401.68	98.49	0.00852	0.8579	408.16	$2.07 \times 10^{-4}$	0.9992	



**Figure S5** (a) Adsorption isotherm of  $I_3^-$  on PTIBBL. Fitting results of  $I_3^-$  on PTIBBL for isotherm models: (b) Langmuir model; (c) Freundlich model.

Table S3 Characteristic parameters for the adsorption of iodine							
Experimental $q_{max}$ (mg g <sup>-1</sup> )	Freundlich			Langmuir			
	k <sub>F</sub>	1/n	$R^2$	$q_m$ (mg g <sup>-1</sup> )	b (L mg <sup>-1</sup> )	$R_{\rm L}$	$\mathbb{R}^2$
663.16 mg g <sup>-1</sup>	299.5	0.138	0.9734	$666.7 \text{ mg g}^{-1}$	0.098	0.02~0.09	0.9994



Figure S6 Comparison of adsorption effects for three different adsorbents.

Table S4 Comparison of adsorption capacities of various adsorbents for iodine

Adsorbents	Indine adsorption $q_m (mg g^{-1})$	References
PTIBBL	663.16	This work
Porous organic polytriphenylamine	525.10	13
CSU-CPOPs-2	374.12	15
NiP-CMP	326	21
porous carbons AK-2	336	28
n-CF@OCDs	190.1	31



Figure S7 The adsorptions of TIBB and PTIBBL for iodine solution with different concentration from 100 to 300 mg  $L^{-1}$ .



Figure S8 Reversibility tests showing that the absorption was reversible.



Figure S9 FT-IR spectra of PTIBBL, iodine-loaded PTIBBL and the recycled PTIBBL.



Figure S10 PXRD curves of PTIBBL, iodine-loaded PTIBBL and the recycled PTIBBL.



Figure S11 UV absorption changes of TIBB upon addition of  $I_2$  (10 equiv.) in the NaI solution.