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Supporting Information

Ionic Covalent Organic Polymer toward Highly Selective Removal of Anionic Organic Dyes in Aqueous Solution

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1. Materials

Chemicals and solvents were obtained from Energy Chemical（Tianjing Chemical Works）and used without further purification unless specified. All the organic reactions were performed under an inert atmosphere of Argon, and the prepared chemicals were dried under vacuum. IR spectra were collected on a Nicolet impact 410 FTIR spectrometer as KBr pellets in the 400–4000 cm^{-1} region. The morphology and microstructure of the samples were investigated by Field-Emission Scanning Electron Microscopy (FESEM, ULTRA Plus, Zeiss). Transmission electron microscopy (TEM, TECNAI G2 F20 STWIN D2278, FEI) and high-resolution TEM (HRTEM) were carried out on microscope operated at an accelerating voltage of 200 kV. The absorbance data of spectrophotometer were measured on ultraviolet-visible (UV-Vis, Unicosh UV-2800) spectrophotometer. ^{1}H NMR spectra were obtained (Bruker DRX-600 NMR). ^{13}C CP/MAS NMR spectra were obtained (Bruker AVANCE III 600). TGA data were recorded on a Perkin–Elmer TGA-7 thermogravimetric analyzer under an air atmosphere from room temperature to 1000℃ (heating rate of 10℃min^{-1}). XPS tests were performed with the Physical Electronics PHI-5702 spectrometer. N_2 gas sorption isotherms were determined using the gas sorption instrument (AUTOSORB-Iq2, USA). The specific surface area data were determined by BET method. Pore size distributions of samples were obtained according to BJH theory. Dyes adsorption performance of COPs was monitored by UV-Vis spectra measurement on UV-2401PC spectrophotometer (Shimadzu, Japan).

1-(3,5-dibromopheny)-1*H*-1,2,4-triazole

After evacuating and circulating three times with a standard of nitrogen,0.21g of Cu_2O (0.0015 mol), 0.52 g of 1,10-phenanthroline (0.0029 mol) was added to an overdried Schlenk tube equipped with a magnetic stir bar.1.0g of 1H-1, 2, 4-triazole (0.0145 mol), 6.9256 g of 1,3,5-tribromobenzene (0.022 mol) and 6.01g of K_2CO_3 (0.044 mol). The tube was evacuated, filled with nitrogen and sealed to the nozzle. DMF (10 mL) was added via syringe. The reaction mixture was stirred at 120 ℃ under a positive pressure of nitrogen for 48 hours. After cooling to room temperature, it was diluted with 20mL of dichloromethane, filtered with a Buchner funnel, and the filter cake was further washed with dichloromethane. The resulting organic layer was washed three times with water and brine then dried over Na_2SO_4. The crude product was purified by flash column chromatography on silica gel. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.12 (s, 1H), 7.84 (d, J = 1.7 Hz, 2H), 7.70 (t, J = 1.6 Hz, 1H).

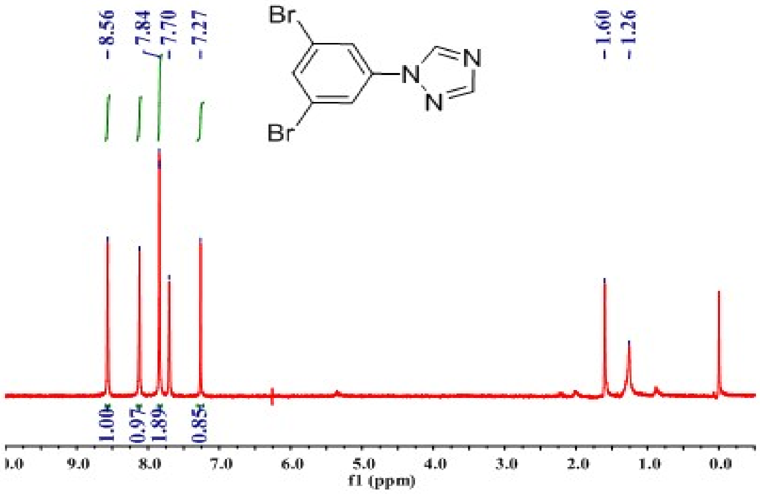

Fig. S1. ^{1}H NMR spectra of 1-(3, 5-dibromopheny)-1H-1, 2, 4-triazol.

1-(3, 5-dibromo-phenyl)-4-methyl-1H-[1, 2, 4] triazole-4-iodo

1-(3, 5-dibromopheny)-1H-1, 2, 4-triazole(1.9571g, 4.4mmol, 1equiv) was dissolved in 10mL of THF in the high pressure reaction bomb was and methyl iodide (2.4981g, 17.6mmol,4equiv) was added. The reaction bomb was capped and heated up to 110℃ for 12 hour, during what the white precipitate has formed. After the mixture was cooled down to room temperature, the precipaitate was filtered and washed with DCM. The second portion of product was obtained after reducing the volume of filtrate. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.94 (s, 1H), 9.41 (s, 1H), 8.19 (s, 3H), 4.00 (s, 3H).

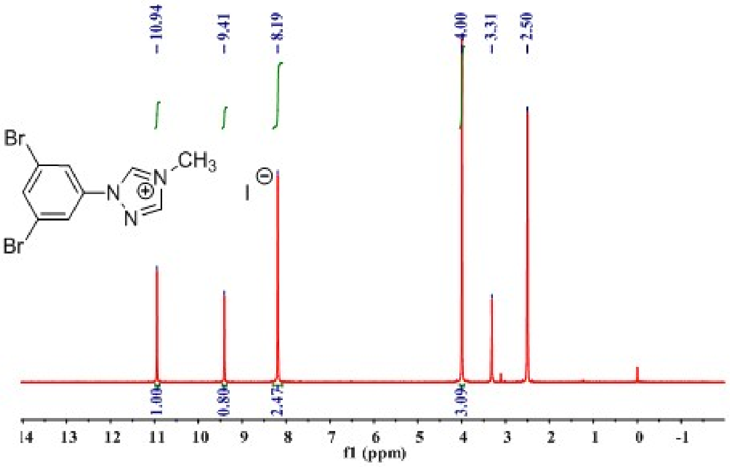

Fig. S2. ^{1}H NMR spectra of 1-(3, 5-dibromo-phenyl)-4-methyl-1H-[1, 2, 4] triazole-4-iodo.

Pyrene-2, 7-bis(4, 4, 5, 5-tetramethyl-[1, 3, 2]dioxaborolane)

[(Ir(μ-OMe)cod)$_2$] (0.060g, 0.09mmol) , 4, 4'-di-tert-butyl-2, 2'-bipyridine (dtbpy, 0.048 g) in a nitrogen-filled Schlenk 0.18 mmol) and B$_2$pin$_2$ (0.10 g, 0.39 mmol) were dissolved in THF (5 mL). The above mixture was added to a Schlenk tube containing hydrazine (1.80 g, 8.90 mmol) and B$_2$ pin$_2$ (4.86 g, 19.1 mmol). Then, THF (10 mL) was added, the tube was sealed, and the mixture was stirred at 80 °C. Then, the mixture was passed through a 5 cm silica plug (eluent: CH_2Cl_2) and the solvent was removed under reduced pressure. It was then washed with refluxing hexane (100 mL) to give 2 (3.80 g, 94%). ^{1}H NMR. (400MHz, $CDCl_3$): $\delta = 8.63$ (S, 4H), 8.09 (S, 4H), 1.46 ppm (S, 24H);

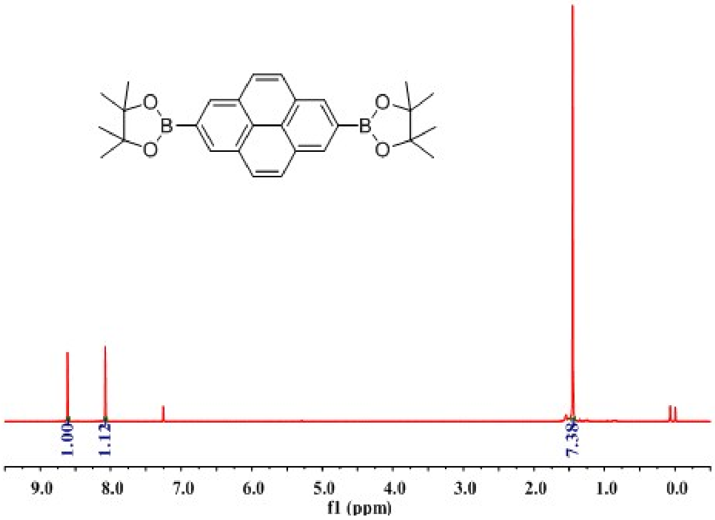

Fig. S3. ^{1}H NMR spectra of Pyrene-2, 7-bis(4,4,5,5-tetramethyl-[1, 3, 2]dioxaborolane).

2. FTIR analysis

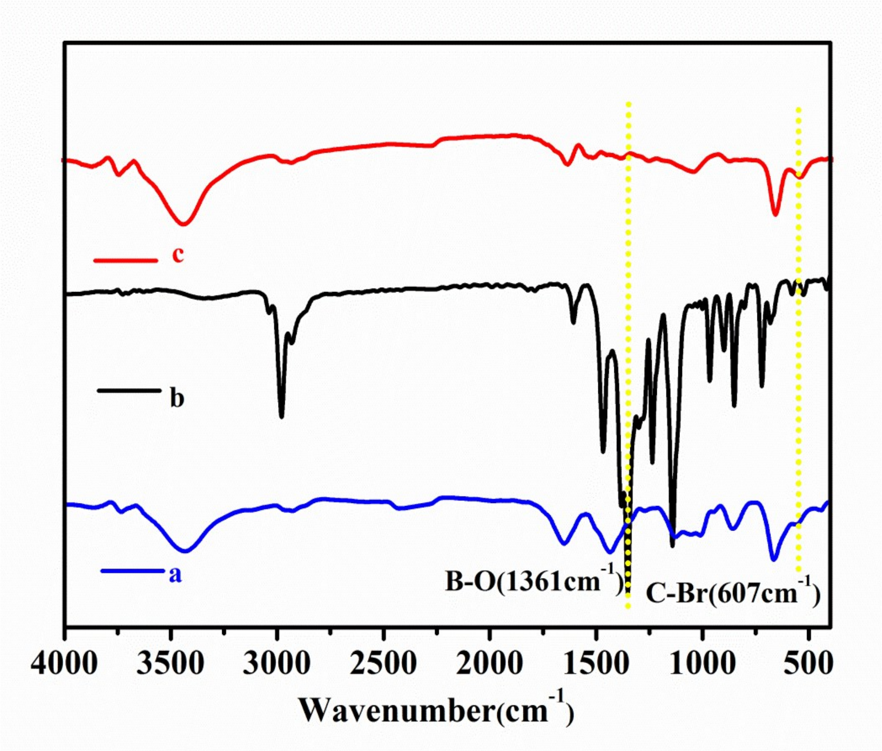

Fig. S4. FTIR spectra of 2, 7-bis(decene)oxime (a), 1-(3, 5-dibromo-phenyl)-4-methyl-1H-[1, 2, 4] triazole-4-iodo (b), ICOP (c).

Peak(cm^{-1})	Assignment and Notes for ICOP
3038.44(vw)	Aromatic N-H stretching
2922.73(vw)	Aromatic N-H stretching
2854.76(w)	Asymmetrical stretching of CH_3 from b
1689.64(s)	Aromatic C-C ring stretching
1597.06(s)	Aromatic C-C ring stretching
1505.97(m)	Aromatic C-C ring stretching
1433.76(m)	Aromatic C-C ring stretching
1261.74(s)	Aromatic C--N stretching
867.53(s)	Aromatic C-H out-of-plane bending from phenyl group
802.37(m)	Aromatic C-H out-of-plane bending from phenyl group
709.80(m)	Aromatic ring stretching

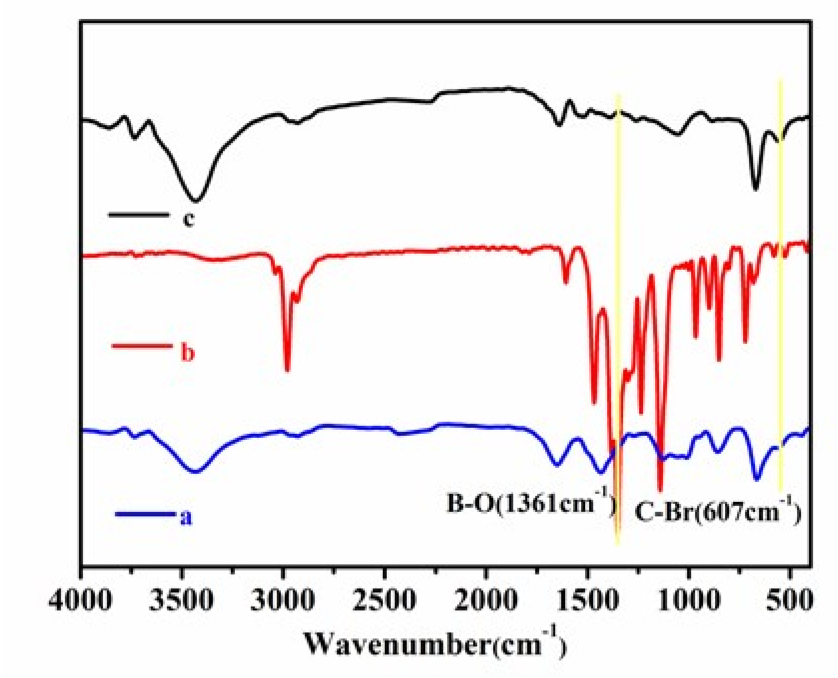

Fig. S5. FTIR spectra of 1-(3, 5-dibromopheny)-1H-1, 2, 4-triazole (a), 2, 7-bis(decene)oxime (b), COP (c).

Peak(cm^{-1})	Assignment and Notes for COP
3038.44(vw)	Aromatic C-H stretching
2922.73(vw)	Aromatic C-H stretching
2854.76(w)	Asymmetrical stretching of CH_3 from b
1689.64(s)	Aromatic C-C ring stretching
1597.06(s)	Aromatic C-C ring stretching
1505.97(m)	Aromatic C-C ring stretching
1433.76(m)	Aromatic C-C ring stretching
1261.74(s)	Aromatic C--N stretching
867.53(s)	Aromatic C-H out-of-plane bending from phenyl group
802.37(m)	Aromatic C-H out-of-plane bending from phenyl group
709.80(m)	Aromatic ring stretching

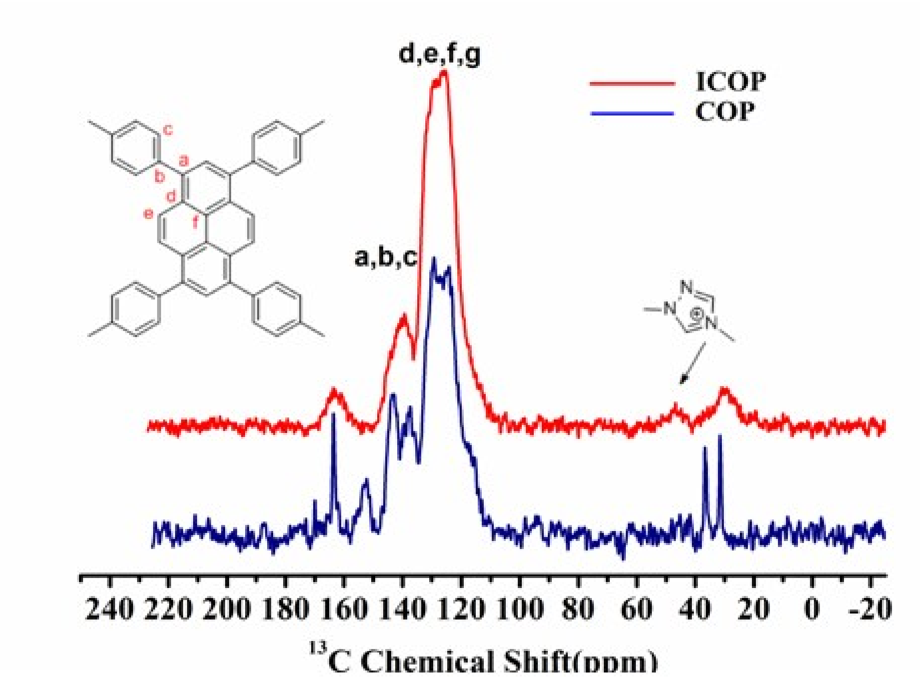

Fig. S6. Solid-state ^{13}C CP/MAS NMR spectra of COP and ICOP.

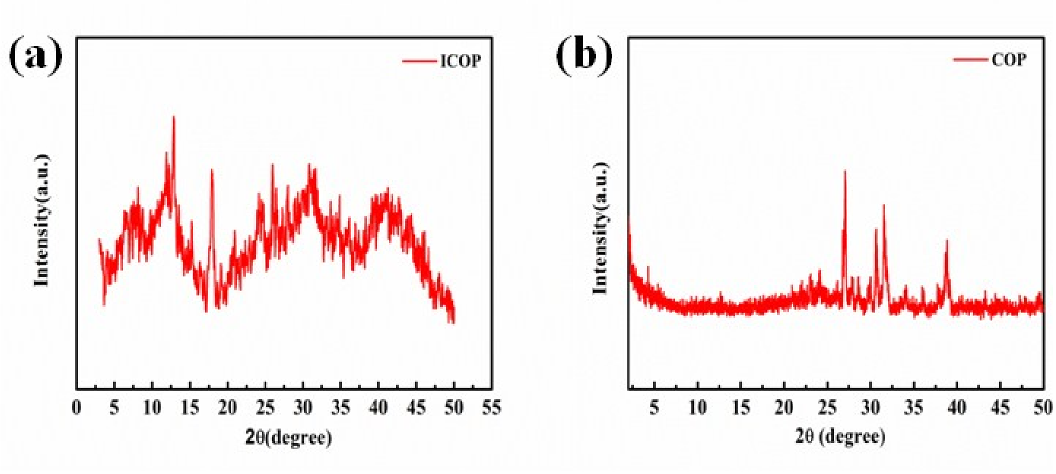

Fig. S7. PXRD patterns of (a) COP and (b) ICOP.

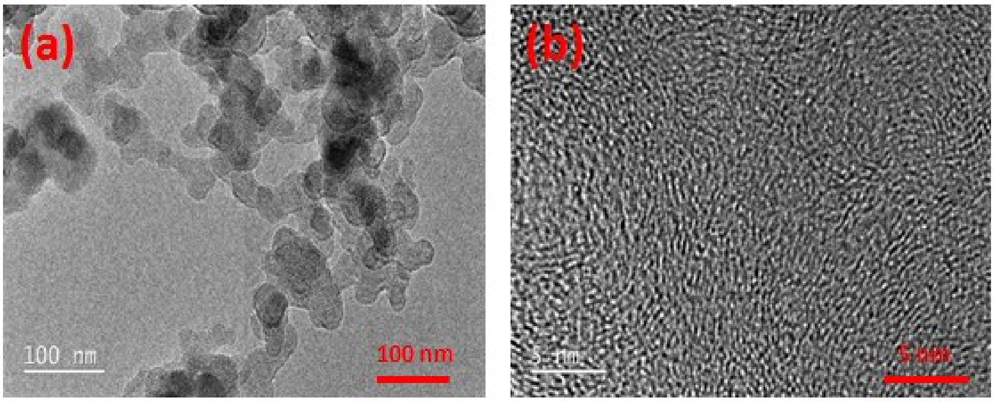

Fig. S8. TEM images of COP Scale bar =100nm and 5nm.

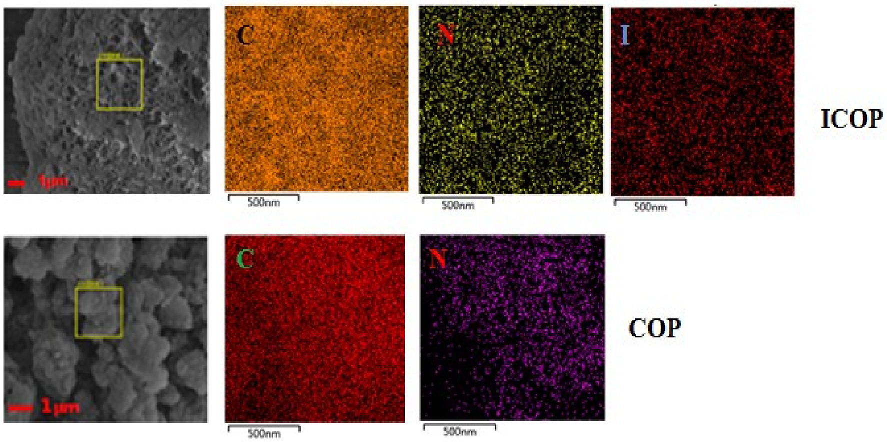

Fig. S9. EDS mapping of ICOP and COP, Scale bar=1μm.

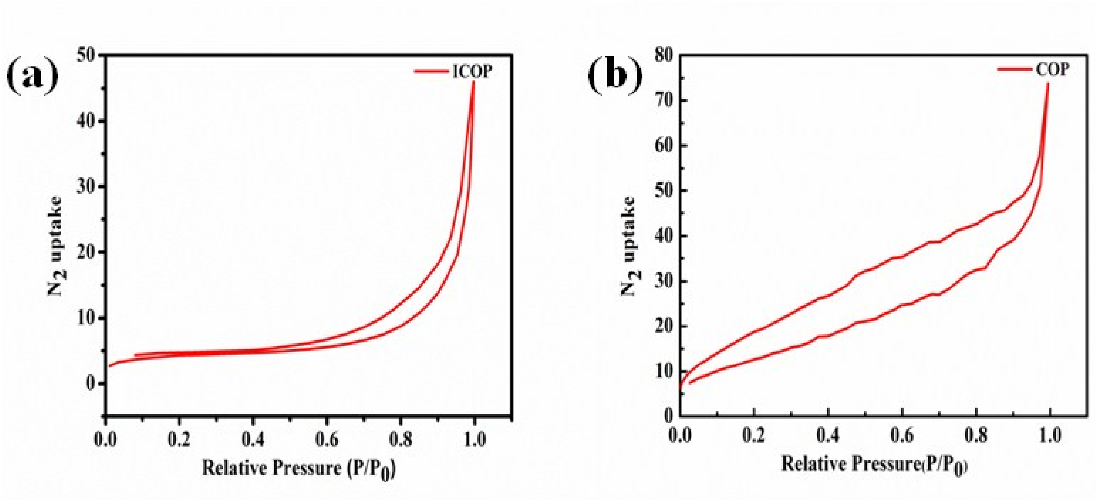

Fig. S10. N_2 adsorption-desorption isotherms of (a) ICOP and (b) COP.

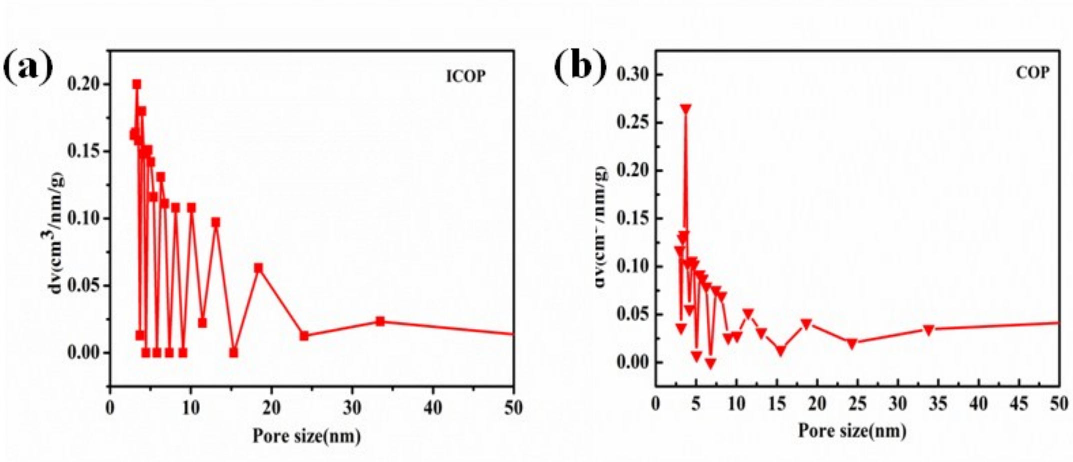

Fig. S11. Pore size distribution histogram of (a) COP and (b) ICOP.

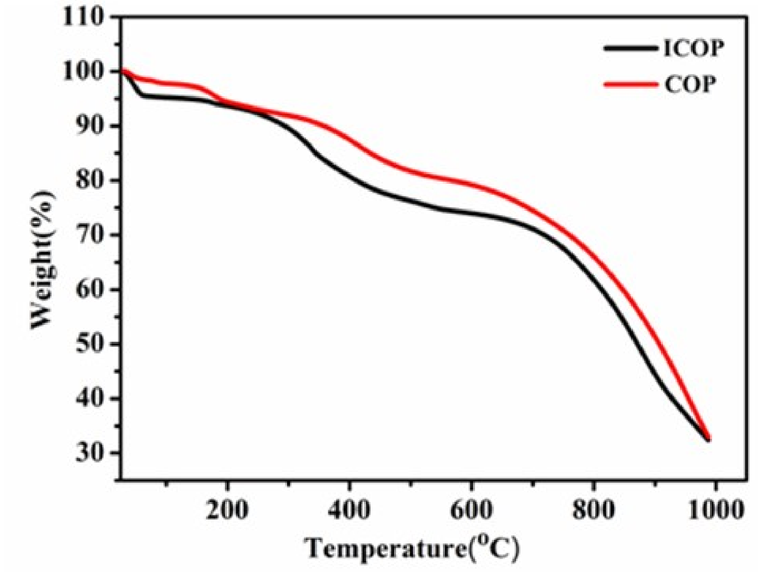

Fig. S12. TGA of ICOP and COP.

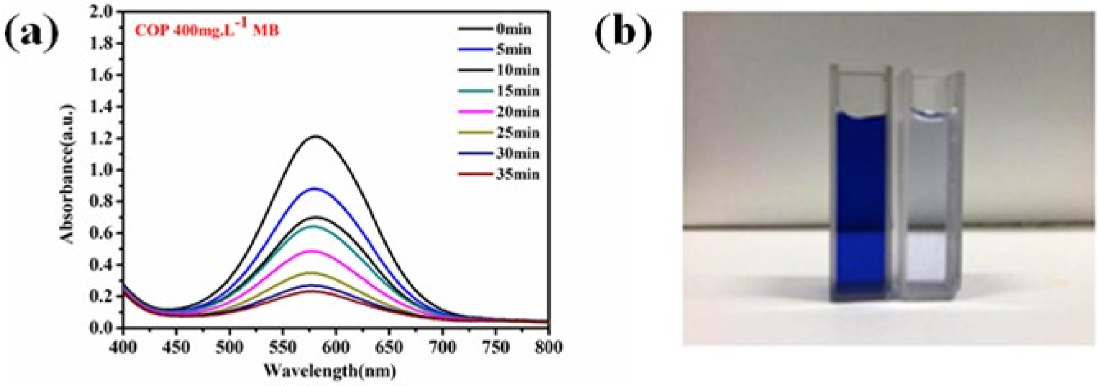

Fig. S13. (a) Time-dependent adsorption study of a mixture of 400mg L^{-1} Methyl blue solution with UV-Vis spectroscopy by COP. (b) Time dependent adsorption decolorisation of MB solution by COP.

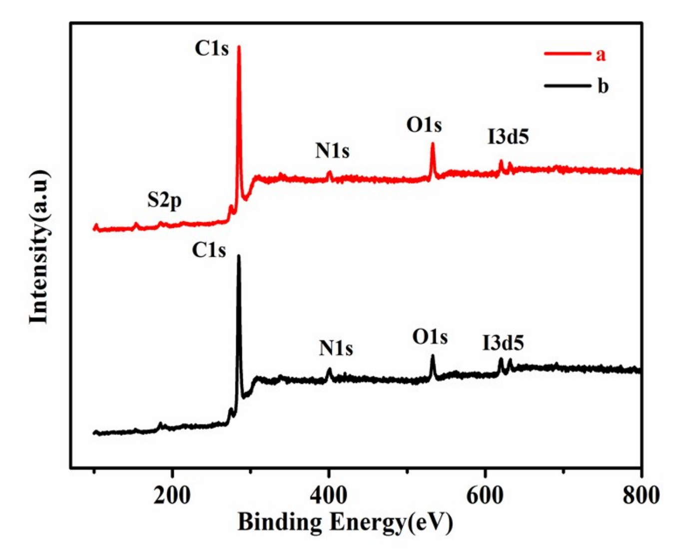

Fig. S14. XPS images of ICOP treated with water washing three times (a, red line) and ICOP (b, black line).

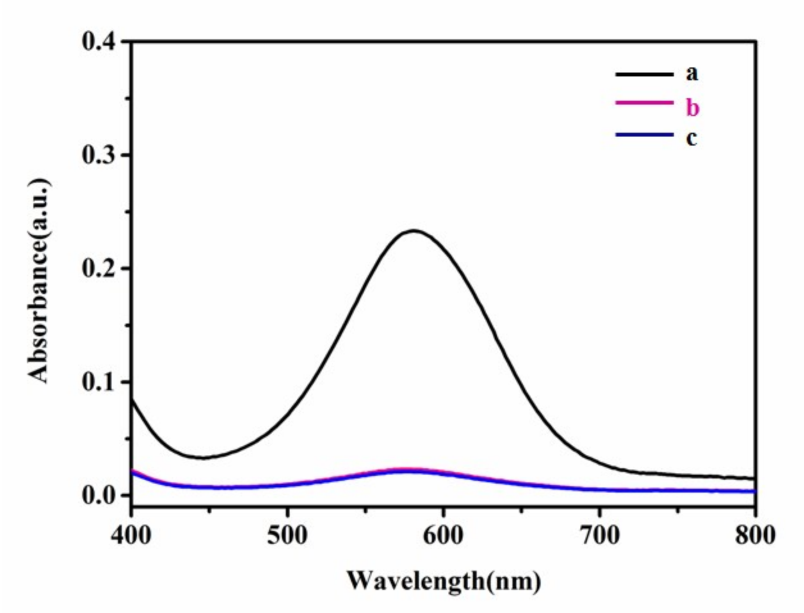

Fig. S15. UV-Vis absorption spectra of ICOP aqueous solution, ICOP with water washing three times（a, black line), ICOP with sodium iodide washing (b, red line), COP with water washing (c, blue line).

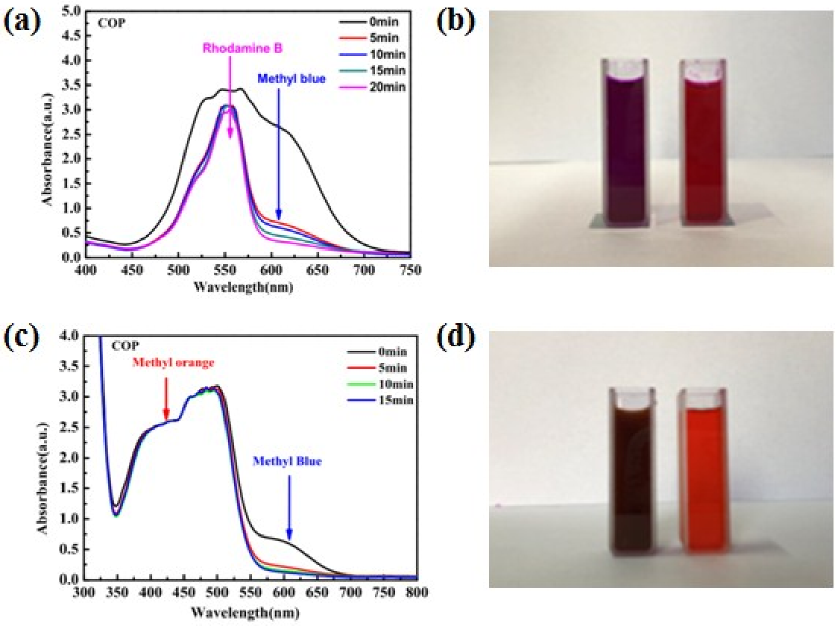

Fig. S16. (a) Time-dependent adsorption study of a mixture of 100mg.L^{-1} MB/RB solution with UV-Vis spectroscopy by COP. (b) Digital photograph of 100 mg L^{-1} MB/RB solution before and after the adsorption test. (c) Time-dependent adsorption study of a mixture of 100mg.L^{-1} MB/MO solution with UV-Vis spectroscopy by COP. (d) Digital photograph of 100 mg L^{-1} MB/MO solution before and after the adsorption test.

Table S1 Comparison of anionic dye maximum adsorption capacity (q_m) of various adsorbents.

Absorbents	Target dye	q_m(mg g^{-1})	Time	Reference
CMP-PM-Me	CR	400	120 min	S1
Polydopamine/GO	MO	89	250 min	S2
PVI-TFSI	MB	476	100 min	S3
Activate Carbon	MB	45	200 min	S4
ICOP	MB	393	25 min	This work
COP	MB	383	35 min	This work

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