Supporting Information

Synthesis of anionic Ionic Liquids@Covalent Organic Materials for selective adsorption of cationic dye with superior capacity

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S1. General information

1.Materials and reagents

All chemicals and reagents used were at least of analytical grade. Ultrapure water was prepared in doubly deionized water (DDW, 18.2 MU cm^{-1}) from a Millipore water purication system (Millipore, Billerica, MA, USA). 1,3,5-Triformylphloroglucinol (Tp) was purchased from Yuhao Chemical Technology Co. Ltd. (Hangzhou, China). 2,5-Diaminobenzenesulfonic acid (Pa), and 2,2'-benzidinedisulfonic acid (Bd) were purchased from Macklin Biochemical Co. Ltd. (Shanghai, China). Imidazole, ethanol, methanol, N,N-dimethylformamide (DMF), 1,4-dioxane, mesitylene, phosphorous acid (H_3PO_4), disodium phosphate dodecahydrate ($NaH_2PO_4 \cdot 12H_2O$), sodium dihydrogen phosphate, ($Na_2HPO_4 \cdot 2H_2O$), hydrochloric acid (HCl), sodium hydroxide (NaOH) and acetonitrile (ACN) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 1-Phenylimidazole was obtained from TCI (Shanghai, China) and 1-butylimidazole was obtained from Alfa Aesar (Shanghai, China), respectively. Methylene Blue (MB), methyl orange (MO), reactive brilliant red K-2BP (RBR), basic red 5 (BR), crystal violet (CV), and basic orange 2 (BO) were purchased from Sanjiang Chemical Technology Co. Ltd. (Tianjin, China). Nile red (NR) and calcein (CA) were purchased from Yuanye Biotechnology Co. Ltd. (Shanghai, China). Auramine O (AO) was obtained from Adamas Reagent Co. Ltd. (Shanghai, China). Azure A (AZA), Azure B (AZB) and Azure C (AZC) were purchased from Amresco Co. Ltd. (USA). Congo red (CR) and bismarck brown R (BRR) were obtained from J&K Scientific Ltd. (Beijing, China). Arginine was obtained from Sigma-Aldrich (St., Louis, MO).

S2. Figures and Tables

Table S1. Cationic dye molecules and their properties used in HPLC-MS analyze

Analyte	Molecular mass	Parention (m/z)	Fragment ion (m/z) *	Cone voltage (V)	Collision energy (eV)	Charge
Methylene Blue	373.9	284.2	268.1	120	40	Positive
			252.2	120	50	
Azure A	291.8	255.8	213.7	130	30	
		255.8	198.8	130	40	
Azure B	305.8	269.8	253.7	130	28	
			227.8	130	30	
Azure C	277.8	241.9	226.8	130	33	
		241.9	199.8	130	26	
Auramine O	303.8	268	147	130	29	
		268	131	130	55	
		268	107	130	33	
Crystal Violet	373.5	372	356.1	130	40	
		372	340	130	51	
Basic Red 5	288.8	253.1	237.1	135	40	
			222	135	50	
			210.1	135	33	
Basic Orange 2	248.7	213.4	120.2	120	15	
			77.2	120	15	

* Quantitative ion.

Table S2. Fractional atomic coordinates for the unit cell of TpPa-SO_3

	TpPa-SO_3		
	Space group P 1		
	a = 22.8 Å, b =22.77 Å, c =4.52 Å, α = 90°, β = 90°, γ = 120°		
atom	x	y	z
C	0.01939	0.50187	0.5
C	0.13839	0.5297	0.5
C	0.20854	0.57990	0.5
C	0.23264	0.65104	0.5
C	0.25782	0.55190	0.5
N	0.08742	0.54403	0.5
O	0.19149	0.67203	0.5
O	0.23768	0.49668	0.5
C	0.30249	0.70059	0.5
C	0.32845	0.60643	0.5
C	0.34923	0.6768	0.5
O	0.411162	0.7191	0.5
C	0.32227	0.7707	0.5
N	0.38593	0..82389	0.5
C	0.40856	0.89167	0.5
C	0.37479	0.92767	0.5
C	0.47483	0.92911	0.5
S	0.296207	0.89281	0.5
O	0.29235	0.0.94741	0.5
O	0.28291	0.83109	0.5
O	0.23157	0.86508	0.5
H	0.006561	0.58192	0.5
H	0.10745	0.409597	0.5
H	0.10139	0.59135	0.5
H	0.12483	0.47965	0.5
H	0.28553	0.78279	0.5
H	0.42066	0.81197	0.5
H	0.500075	0.90501	0.5

Table S3 Comparison of element analyses of C, N, H, and S

Materials	C (%)	N (%)	H (%)	S (%)
TpPa-SO_3	42.21	11.58	5.35	13.35
TpBd-$(SO_3)_2$	41.93	8.60	5.15	10.04
TpCR-$(SO_3)_2$	34.67	6.23	3.06	8.05
ImI@TpBd-$(SO_3)_2$	46.59	8.66	6.08	8.85
BuImI@TpBd-$(SO_3)_2$	42.94	8.62	5.69	9.97
PheImI@TpBd-$(SO_3)_2$	43.1	8.28	5.77	10.89

Table S4 Comparison of surface area and pore volume of the as-prepared materials

Materials	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore size (nm)
TpPa-SO_3	70.8	0.1709	1.7, 2.9
TpBd-$(SO_3)_2$	60.5	0.1711	9.3
TpCR-$(SO_3)_2$	9.6	0.0190	2.9
ImI@TpBd-$(SO_3)_2$	61.8	0.1722	14.5, 23.8
BuImI@TpBd-$(SO_3)_2$	33.7	0.1245	2.3, 14, 21
PheImI@TpBd-$(SO_3)_2$	40.2	0.1125	6.8

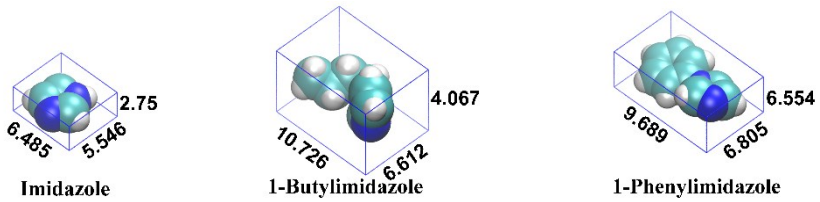

Fig. S1 The molecular models of imidazole derivatives were displayed in the Bondi van der waals (VDW) style (blue, carbon; white, hydrogen; blue, nitrogen) calculated by Multiwfn; Imidazole with a size of 6.485×5.546×2.75 Å, 1-buthylimidazole with a size of 10.726×6.612×4.067 Å, and 1-phenylimidazole with a size of 9.689×6.805×6.554 Å

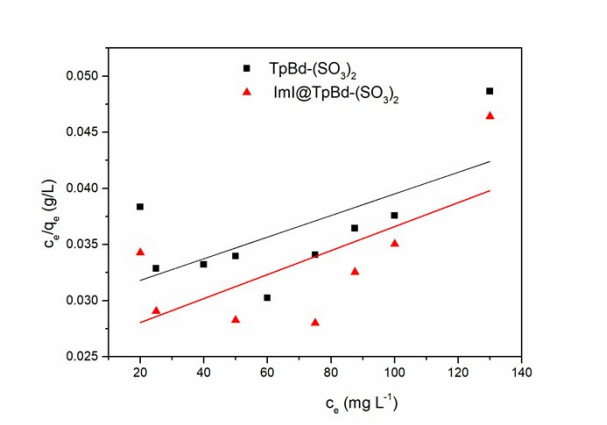

Fig. S2 Langmuir model of MB in TpBd-$(SO_3)_2$ and ImI@TpBd-$(SO_3)_2$

Table S5 Comparison of cationic dyes adsorption

Materials	q_e (mg g^{-1})	Ref
KOH-activated carbon from sucrose	MB 704.2	S1
Sulfuric acid activated (RHS) activated rice husk carbon	CV 64.9	S2
Magnetic nanocomposite beads comprising carboxylic acid functionalized carbon nanotube	MB 465.5; Direct red 380.7	S3
Fe_3O_4@polydopamine-Ag hollow microspheres	MB 102.0	S4
EDTA-Cross-Linked β-Cyclodextrin	MB 88.5; CV 114	S5
Aminocarboxylate/maleic acid resin	MB 2101; Hg(II) 263	S6
Bakelite-type anionic microporous organic polymers	MB 712.2; MG 593.6	S7
Magnetic graphene oxide modified zeolite	MB 97.3	S8
Poly (NIPAAm/AA/N-allylisatin) nanohydrogel	MB 392.2; AO 337.8; BO 961.5	S9
Magnetic polyacrylamide microspheres	MB 1990; GV 1850; BR 1937	S10
ImI@TpBd-$(SO_3)_2$	MB 2865.3; AZB 1015; BBR 974.1; AZC 936.3; AZA, AO, CV, BR, BO 597.9-763.1	This work

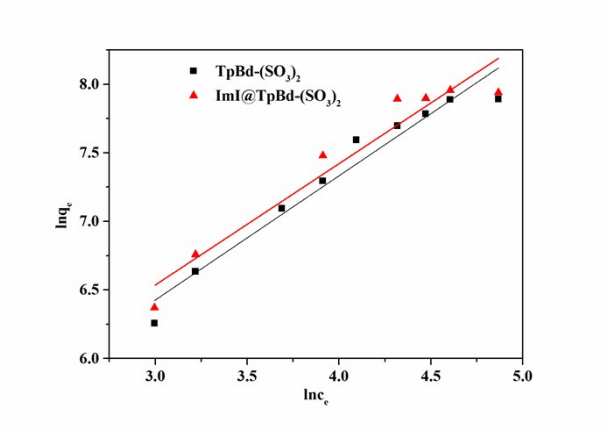

Fig. S3 Freundlich model of MB in TpBd-$(SO_3)_2$ and ImI@TpBd-$(SO_3)_2$

Table S6 Freundlich model constants and correlation coefficient

Materials	Freundlich model			
	K_F (mg g^{-1})	b_F	q_e(cal) (mg g^{-1})	R^2
TpBd-$(SO_3)_2$	40.703	0.906	2641.2	0.9496
ImI@TpBd-$(SO_3)_2$	48.444	0.885	2854.9	0.9297

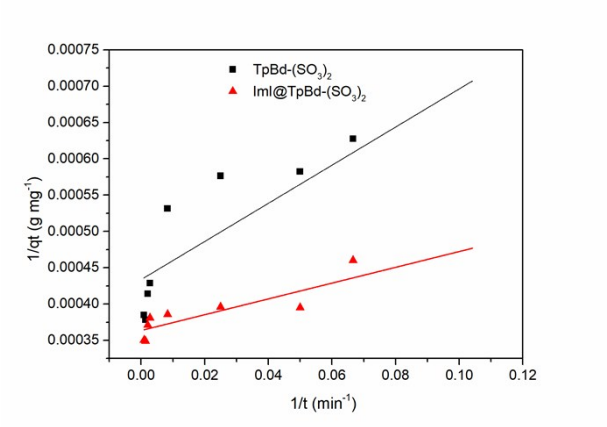

Fig. S4 Pseudo-first-order model of MB in TpBd-$(SO_3)_2$ and ImI@TpBd-$(SO_3)_2$

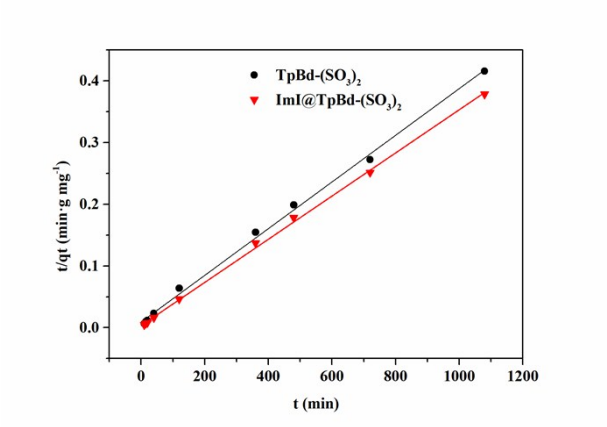

Fig. S5 Pseudo-second-order model of MB in TpBd-$(SO_3)_2$ and ImI@TpBd-$(SO_3)_2$

Table S7 Comparison of kinetic model parameters of TpBd-$(SO_3)_2$ and ImI@TpBd-$(SO_3)_2$

Type	Parameter	TpBd-$(SO_3)_2$	ImI@TpBd-$(SO_3)_2$
Pseudo-first-order kinetics	q_e (mg g^{-1})	2307.4	2748.7
	k_1 (min^{-1})	6.068	2.996
	R^2	0.7492	0.8449
Pseudo-second-order kinetics	$q_{e,exp}$ (mg g^{-1})	2645.0	2873.2
	q_e (mg g^{-1})	2627.0	2866.2
	k_2 (g $mg^{-1}min^{-1}$)	1.6227×10^{-5}	3.493×10^{-5}
	R^2	0.9971	0.9988

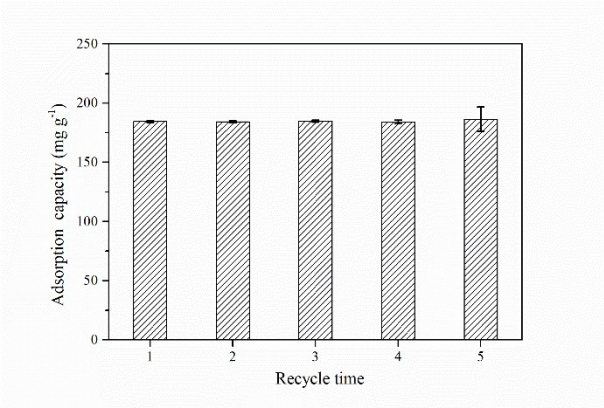

Fig. S6 Recycle studies of MB adsorption in ImI@TpBd-$(SO_3)_2$

S3. References

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