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 purification 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',benzidinesulfonic 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\(_3\)PO\(_4\)), disodium phosphate dodecahydrate (NaH\(_2\)PO\(_4\)·12H\(_2\)O), sodium dihydrogen phosphate, (Na\(_2\)HPO\(_4\)·2H\(_2\)O), 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                    |        |
|              |                |                 | 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             | 268                | 130              | 29                    | Positive |
|              |                | 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           | 222                | 135              | 50                    |        |
|              |                |                 | 210.1              | 135              | 33                    |        |
| Basic Orange 2 | 248.7         | 213.4           | 120.2              | 120              | 15                    |        |

* Quantitative ion.
**Table S2.** Fractional atomic coordinates for the unit cell of TpPa-SO$_3$

| 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| 0.94741| 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|
| 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 (m²g⁻¹) | Pore volume (cm³g⁻¹) | Pore size (nm) |
|-------------------------|-----------------------|-----------------------|----------------|
| TpPa-SO₃                | 70.8                  | 0.1709                | 1.7, 2.9       |
| TpBd-(SO₃)₂             | 60.5                  | 0.1711                | 9.3            |
| TpCR-(SO₃)₂             | 9.6                   | 0.0190                | 2.9            |
| ImI@TpBd-(SO₃)₂         | 61.8                  | 0.1722                | 14.5, 23.8     |
| BulImI@TpBd-(SO₃)₂      | 33.7                  | 0.1245                | 2.3, 14, 21    |
| PhelImI@TpBd-(SO₃)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\textsubscript{3})\textsubscript{2} and ImI@TpBd-(SO\textsubscript{3})\textsubscript{2}
| 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$_3$O$_4$@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-(SO₃)₂ and ImI@TpBd-(SO₃)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$_3$)$_2$
| 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                 |
|                               | $q_{e,exp}$ (mg g$^{-1}$) | 2645.0        | 2873.2                 |
|                               | $q_e$ (mg g$^{-1}$) | 2627.0            | 2866.2                 |
|                               | $k_2$ (g mg$^{-1}$min$^{-1}$) | $1.6227\times10^{-5}$ | $3.493\times10^{-5}$ |
| Pseudo-second-order kinetics  | $R^2$              | 0.9971            | 0.9988                 |
Fig. S6 Recycle studies of MB adsorption in Iml@TpBd-(SO$_3$)$_2$
S3. References

[1] K. C. Bedin, A. C. Martins, A. L. Cazetta, O. Pezoti, V. C. Almeida, KOH-activated carbon prepared from sucrose spherical carbon: adsorption equilibrium, kinetic and thermodynamic studies for methylene blue removal, Chem. Eng. J. 286 (2016) 476-484.

[2] K. Mohanty, J.T. Naidu, B.C. Meikap, M. N. Biswas, Removal of crystal violet from wastewater by activated carbons prepared from rice husk, Ind. Eng. Chem. Res. 45 (2006) 5165-5171.

[3] S. Saber-Samandari, S Saber-Samandari, H. Joneidi-Yekta, M. Mohseni, Adsorption of anionic and cationic dyes from aqueous solution using gelatin-based magnetic nanocomposite beads comprising carboxylic acid functionalized carbon nanotube, Chem. Eng. J. 308 (2017) 1133-1144.

[4] K. Cui, B. Yan, Y. Xie, H. Qian, X. Wang, Q. Huang, Y. He, S. Jin, H. Zeng, Regenerable urchin-like Fe$_3$O$_4$@PDA-Ag hollow microspheres as catalyst and adsorbent for enhanced removal of organic dyes, J. Hazard. Mater. 350 (2018) 66-75.

[5] F. Zhao, E. Repo, D. Yin, Y. Meng, S. Jafari, M. Sillanpää, EDTA-Cross-Linked β-Cyclodextrin: An Environmentally Friendly Bifunctional Adsorbent for Simultaneous Adsorption of Metals and Cationic Dyes, Environ. Sci. Technol. 49 (2015) 10570-10580.

[6] S.A. Ali, I.Y. Yaagoob, M.A.J. Mazumder, H. A. Al-Muallem, Fast removal of methylene blue and Hg(II) from aqueous solution using a novel super-adsorbent containing residues of glycine and maleic acid, J. Hazard. Mater. 369 (2019) 642-654.

[7] B Wang, Q Zhang, G Xiong, F Ding, Y He, B Ren, L. You, X. Fan, C. Hardacre, Y. Sun, Bakelite-type anionic microporous organic polymers with high capacity
for selective adsorption of cationic dyes from water, Chem. Eng. J. 366 (2019) 404-414.

[8] T. Huang, M. Yan, K. He, Z. Huang, G. Zeng, A. Chen, M. Peng, H. Li, L. Yuan, G. Chen, Efficient removal of methylene blue from aqueous solutions using magnetic graphene oxide modified zeolite, J. Colloid Interface Sci. 543 (2019) 43-51.

[9] Viran P. Mahida, Manish P. Patel, Removal of some most hazardous cationic dyes using novel poly (NIPAAm/AA/N-allylisatin) nanohydrogel, Arab. J. Chem. (2016) 9 430-442.

[10] T. Yao, S. Guo, C. Zeng, C. Wang, L. Zhang, Investigation on efficient adsorption of cationic dyes on porous magnetic polyacrylamide microspheres, J. Hazard. Mater. 292 (2015) 90-97.