

Supplementary Information

Novel Cationic Covalent Organic Framework as Adsorbent for Simultaneous Removal of Methyl Orange and Hexavalent Chromium

Chang Du, Xiaodi Chen, Hongping Wu, Zilu Pan, Chunyan Chen,* Guanqun Zhong*
and Changqun Cai

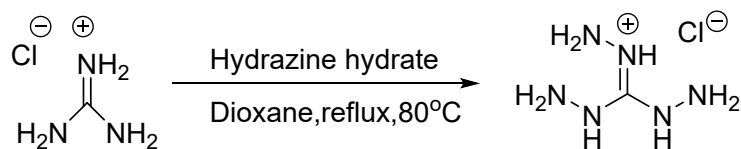
Key Laboratory for Green Organic Synthesis and Application of Hunan Province,
Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry
of Education, College of Chemistry, Xiangtan University, Xiangtan, 411105, China.

Supporting methods

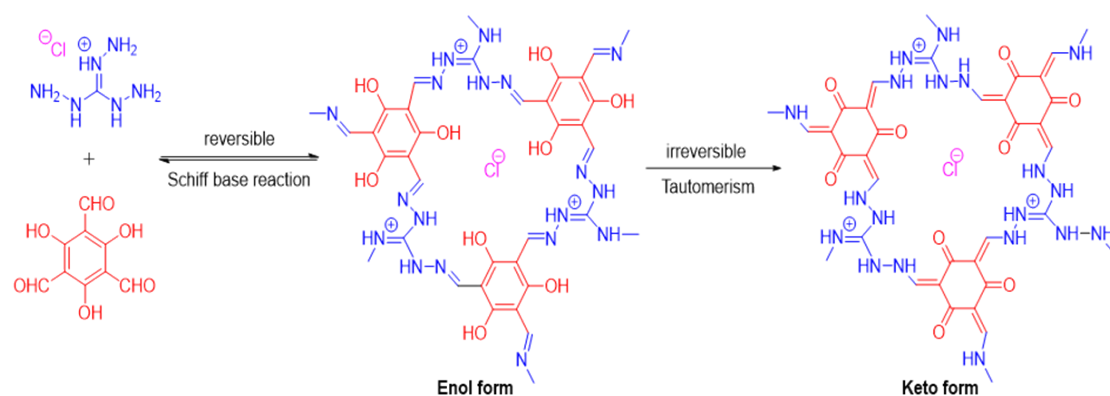
Chemicals and Materials. All materials were purchased from commercial sources and used without additional purification. 5,5'-(1,4-phenylene)dipicolinaldehyde(95%), 5,5'-Diformyl-2,2'-bipyridine(BPy, 97%), 1,3,5-Triformylphloroglucinol(Tp, 95%) and p-phenylenediamine(Pa, 98%) were purchased from Shanghai kaishu Chemical Technology Co., Ltd. Guanidine hydrochloride, Methyl orange (MO), $K_2Cr_2O_7$ were obtained in Saen Chemical Technology (Shanghai) Co., Ltd. Hydrazine hydrate (80 wt.%) and Ethanol absolute were obtained in Hunan Huihong Reagent Co., Ltd. Tetrahydrofuran (THF), N,N-dimethylformamide (DMF), O-dichlorobenzene were supplied from Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd. Concentrated hydrochloric acid, 1,4-dioxane, acetone were offered by Tianjin Kemiou Chemical Reagent Co., Ltd. Glacial acetic acid was provided by Fuyu Fine Chemical Co., Ltd.

Instruments and Characterization. The UV–vis absorption was obtained on an Agilent Cary 60 UV–vis spectrometer (Agilent, USA). Fourier transform infrared (FT-IR) spectrum was recorded using a Nicolet 6700 FT-IR spectrometer (Thermo Fisher, USA). The crystallographic structures of material were characterized by X-ray powder diffraction (XRD) (D8 ADVANCE, Germany). Scanning electron microscopic (SEM) imaging was measured on a Quanta FEG 250 (FEI, USA). Thermal stability of materials is characterized by thermogravimetric analysis (TGA, TG 209 F1, Germany). The specific surface area and pore distribution of adsorbents were analyzed by N_2 adsorption at 77 K with TriStar 3020 (Micromeritics, USA). The isoelectric point (pH_{iep}) of ICOF was measured by a Zeta potential instrument (Malvin, UK). pH was adjusted with 0.1 M HCl or 0.1 M NaOH, respectively.

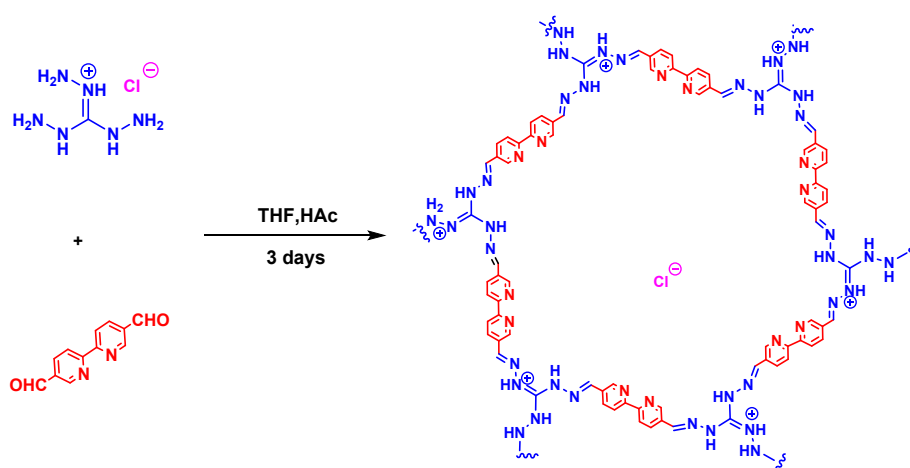
Synthesis of triaminoguanidinium chloride (TGCl). Triaminoguanidinium chloride was synthesized according to reported procedure¹. Briefly, 19.1 g of guanidine hydrochloride was added to 100 mL of 1,4-dioxane under stirring condition, 34.1 g of hydrazine hydrate was slowly added, the mixture was refluxed for 2 h. Then cooled to room temperature, filtered and washed with 1,4-dioxane to remove excess hydrazine hydrate and finally drying the crude in vacuum at 60 °C results to yield TGCl (Yield:97%. FT-IR: 3316, 3210, 1681, 1613, 1333, 1127, 950, 748, 617cm⁻¹. ¹³C NMR (D₂O, 60 MHz) (ppm): 160.85 ppm).



Synthesis of TpTGCl COF. TpTGCl COF was synthesized following a previous report¹. 1,3,5-triformylphloroglucinol (Tp) (0.2 mmol, 42 mg) and TGCl (0.2 mmol, 28 mg) in a sealed Pyrex tube using dioxane/water in the ratio 2:0.6 mL. The reaction mixtures were charged into Pyrex tube and sonicated for 20 min. The mixtures were degassed under liquid N₂ (77K) by freeze-pump-thaw cycles for three times, and the Pyrex tube was then vacuum sealed. The reaction mixtures were allowed to attend room temperature and then kept at 120 °C for 3 days. TpTGCl were obtained as a brown colored precipitate. The product was washed thoroughly with DMAc, water, and acetone, respectively, and dried at 90°C for overnight to obtain ~70% isolated yield.

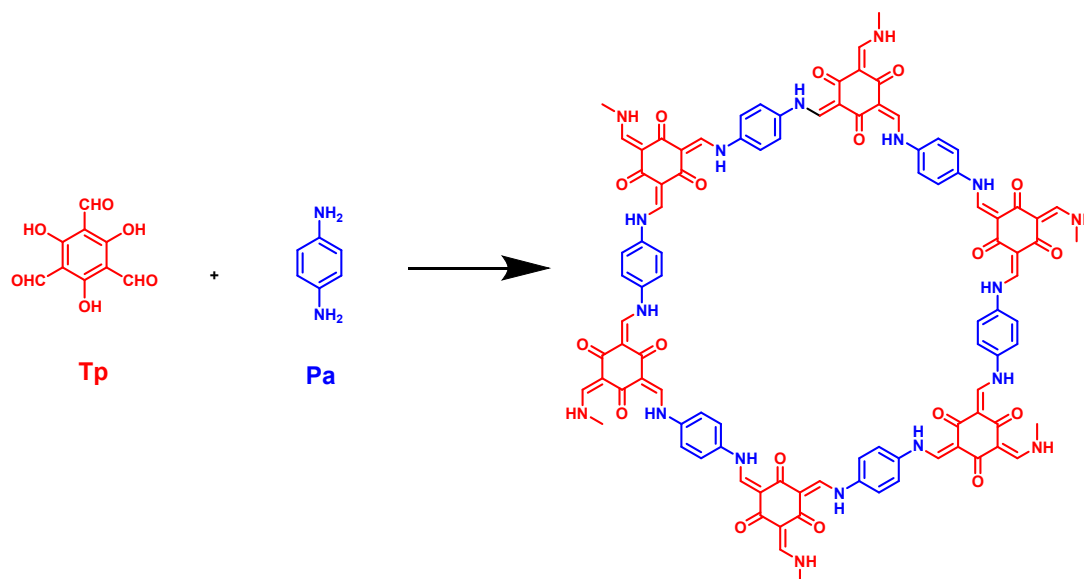


Synthesis of BpyTG_{Cl} COF. 5,5'-Diformyl-2,2'-bipyridine (0.06mol, 12.73 mg) and TG_{Cl} (0.04mmol, 5.62 mg) in 1.1 mL of tetrahydrofuran (THF)/3M HAc (1:0.1, v/v). The mixture was placed into in a Pyrex tube (10×8 mm² and length 20 cm) and sonicated for 15 min. After the mixture was degassed under liquid N₂ by freeze–pump–thaw cycles for three times, the tube was sealed and heated at 120 °C for 3 days. ICOF was obtained as red precipitates. The product was collected by centrifugation and washed with DMF, water and THF and dried at 60 °C under vacuum overnight in ca. 84% isolated yield.



Synthesis of TpPa COF. TpPa-1 was synthesized by previously reported method². In detail, 1,3,5-Triformylphoroglucinol (Tp, 126 mg) and p-phenylenediamine (Pa-1, 116.8 mg) were added to 60 mL of absolute ethanol, respectively. A uniformly

dispersed liquid mixture was obtained and subsequently transferred to an autoclave at 180 °C for 48 hours to form a reddish-brown suspension. The suspension was then centrifuged and the product was washed with DMF to further remove the unreacted reactants. Lastly, wash the product three times with ethanol. Reddish brown products were obtained after dried in a vacuum overnight.



Supporting Figures

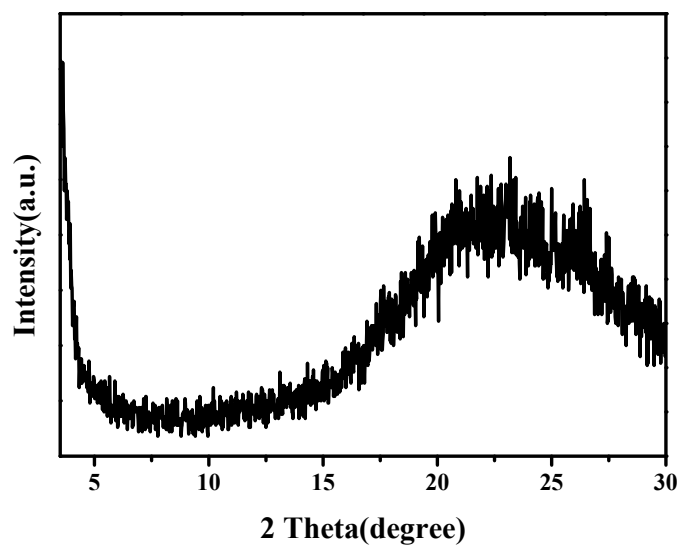


Fig. S1 PXRD of ICOF.

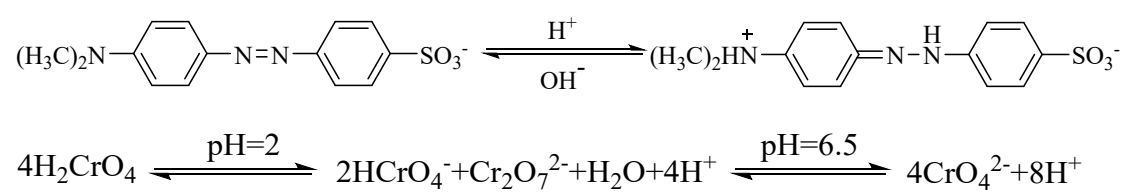


Fig. S2 The structure of MO molecule and Cr (VI).

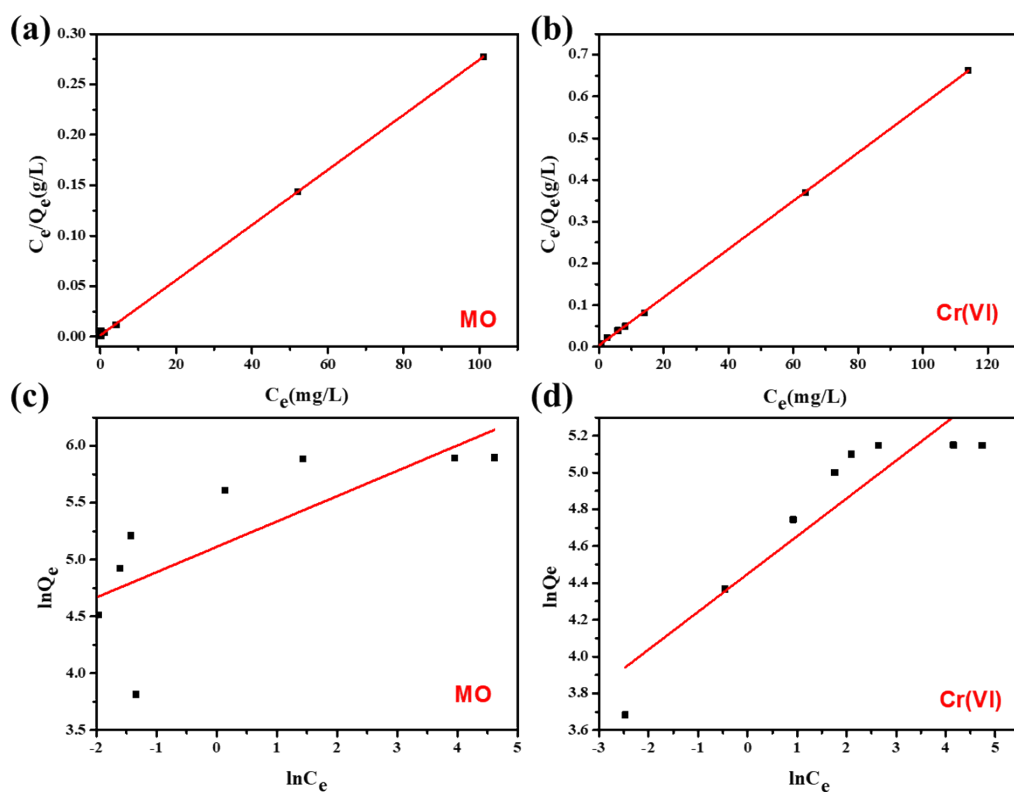


Fig. S3 Fitting curves of MO and Cr (VI) onto ICOF using Langmuir model (a, b) and Freundlich model (c, d)

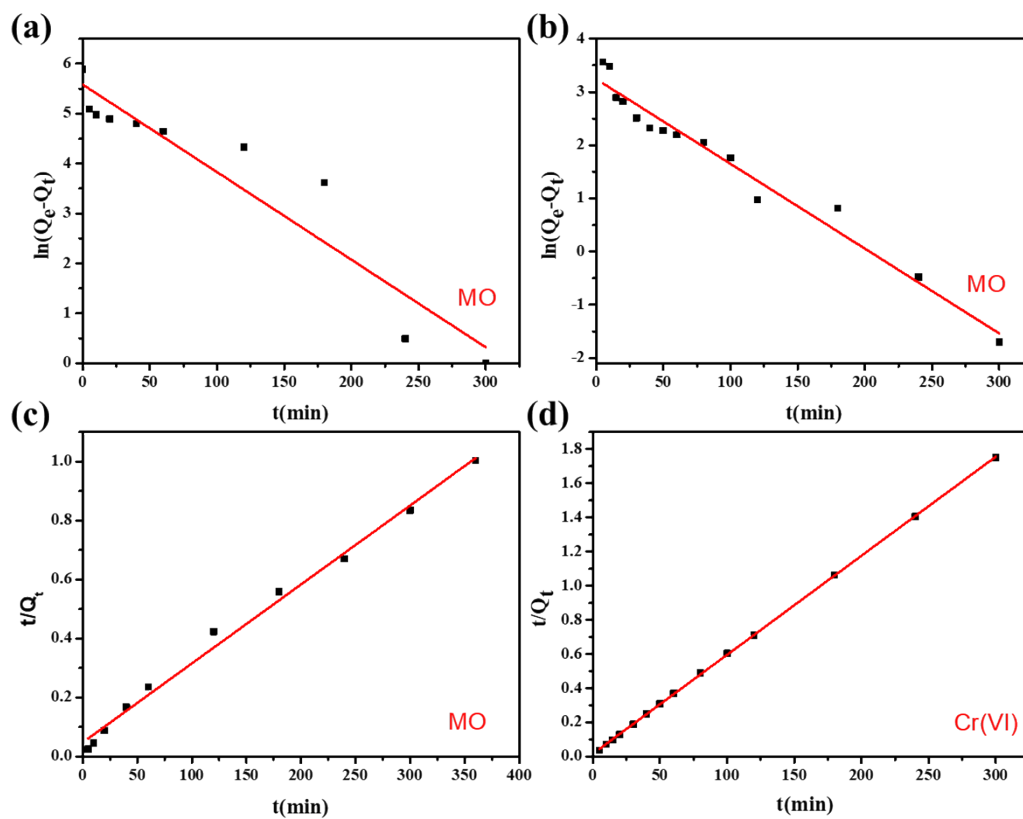


Fig. S4 The pseudo-first-order model (a, b) and the pseudo-second-order model (c, d) of MO and Cr (VI)

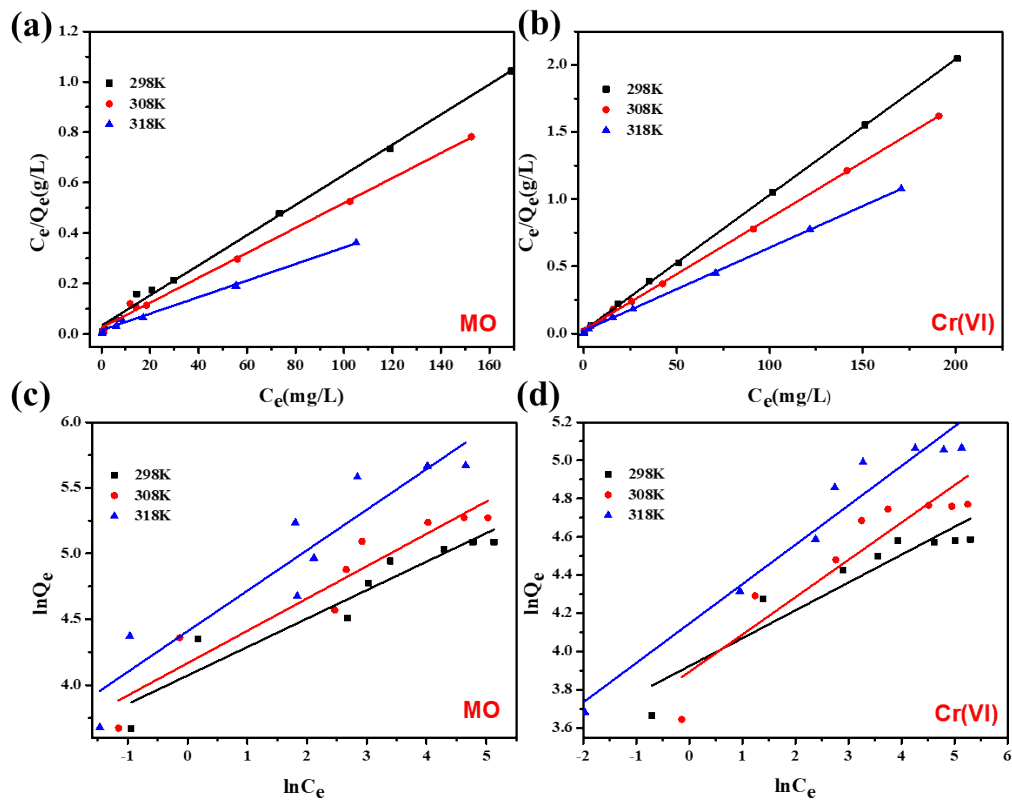


Fig. S5 Fitting curves of MO and Cr (VI) onto ICOF using Langmuir model (a, b) and Freundlich model (c, d)

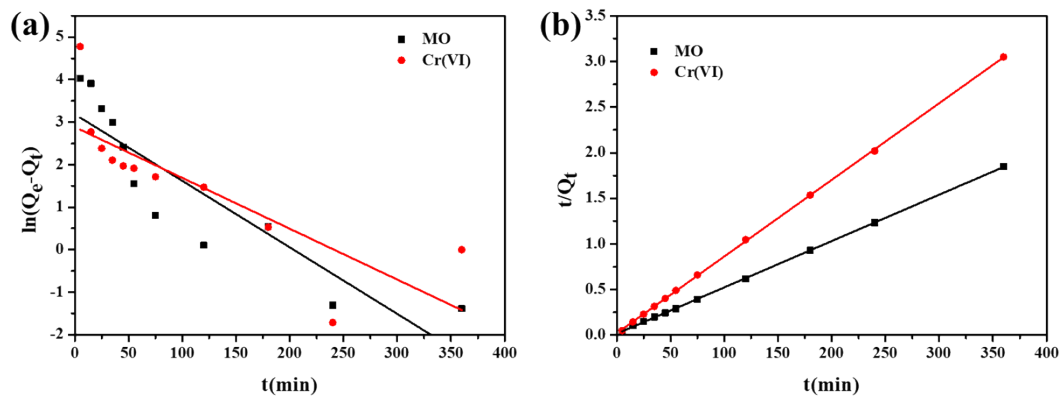


Fig. S6 The pseudo-first-order model (a) and the pseudo-second-order model (b) of MO and Cr (VI)

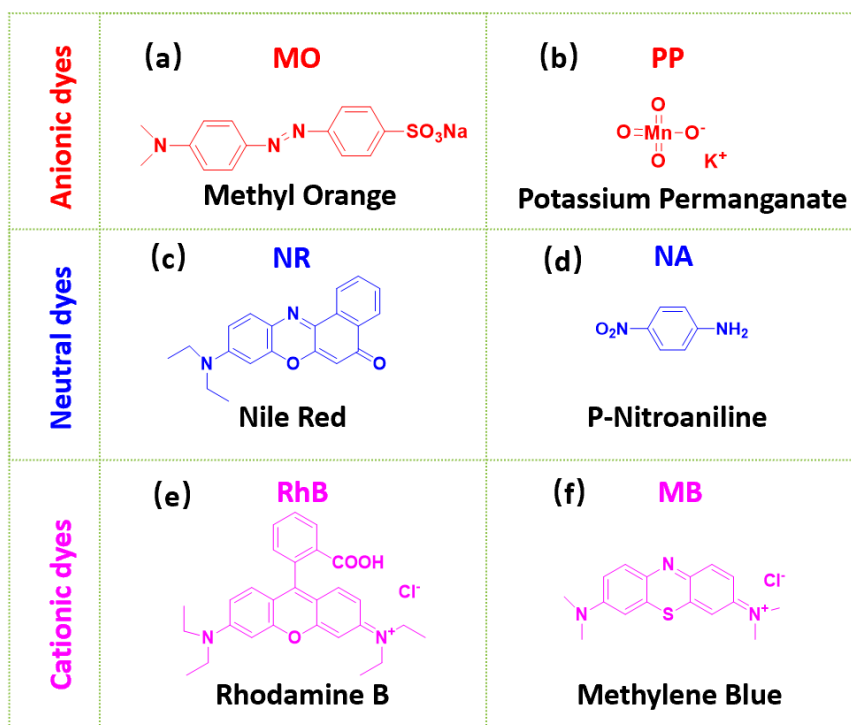


Fig. S7 Chemical structures of dye molecules/ions. (a) MO (methyl orange); (b) PP (potassium permanganate); (c) NR (nile red); (d) NA (p-nitroaniline); (e) RhB (rhodamine B); (f) MB (methylene blue)

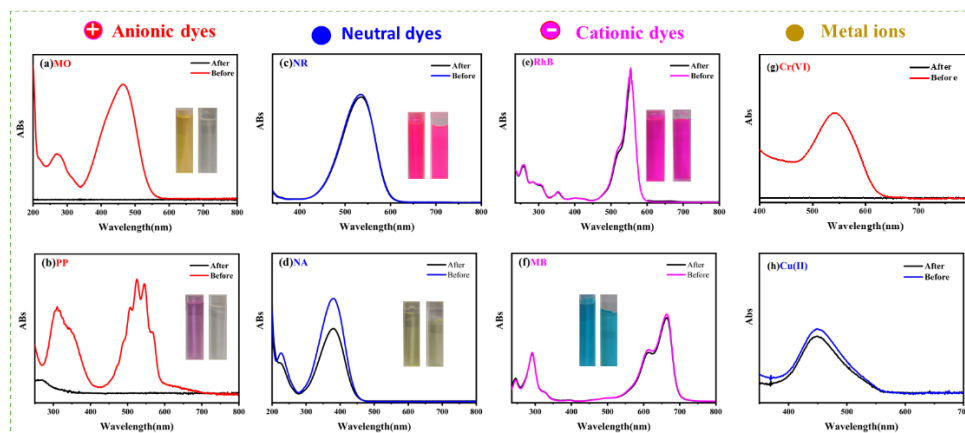


Fig. S8 UV-vis absorption spectra of different dyes solutions of (a) MO, (b) PP, (c) NR, (d) NA, (e) RhB and (f) MB before absorption and after absorption by ICOF, respectively. (Color change of different dye solutions before and after absorption are shown in inset photographs); UV-vis absorption spectra of metal ions solutions of (g)Cr(VI) and (h)Cu²⁺ before absorption and after absorption by ICOF (Initial concentration:20 mg/L; adsorbent mass: 2 mg; Volume: 2 mL).

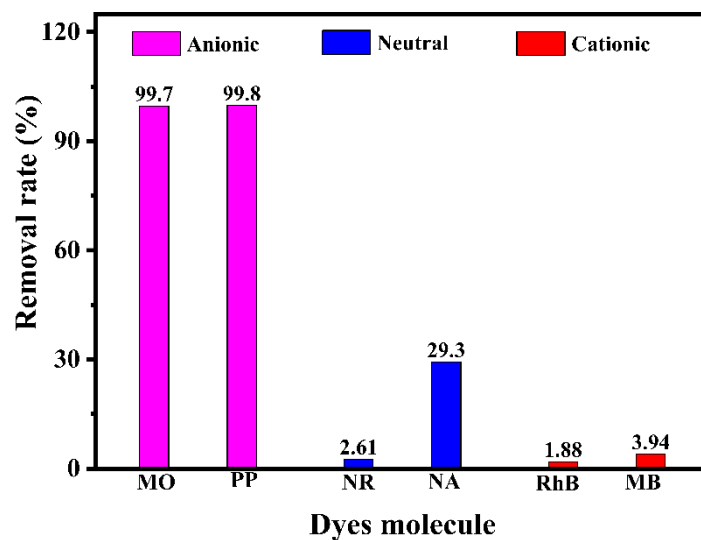


Fig. S9 The removal rate of ICOF for different dyes.

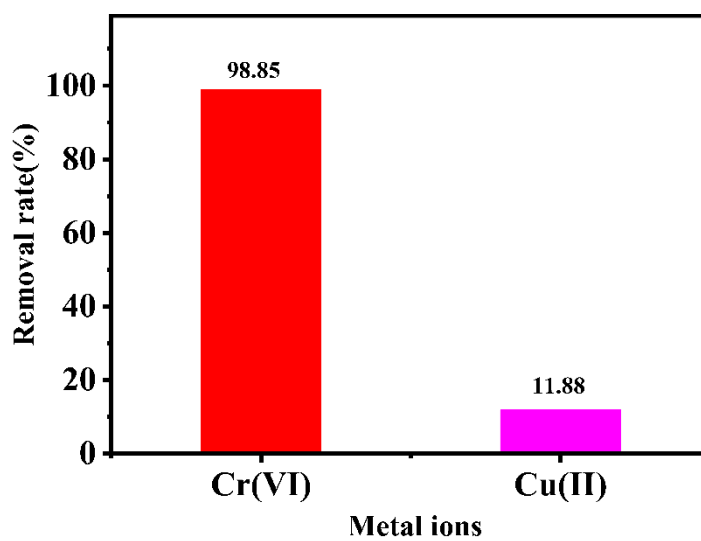


Fig. S10 The removal rate of ICOF for different metal ions.

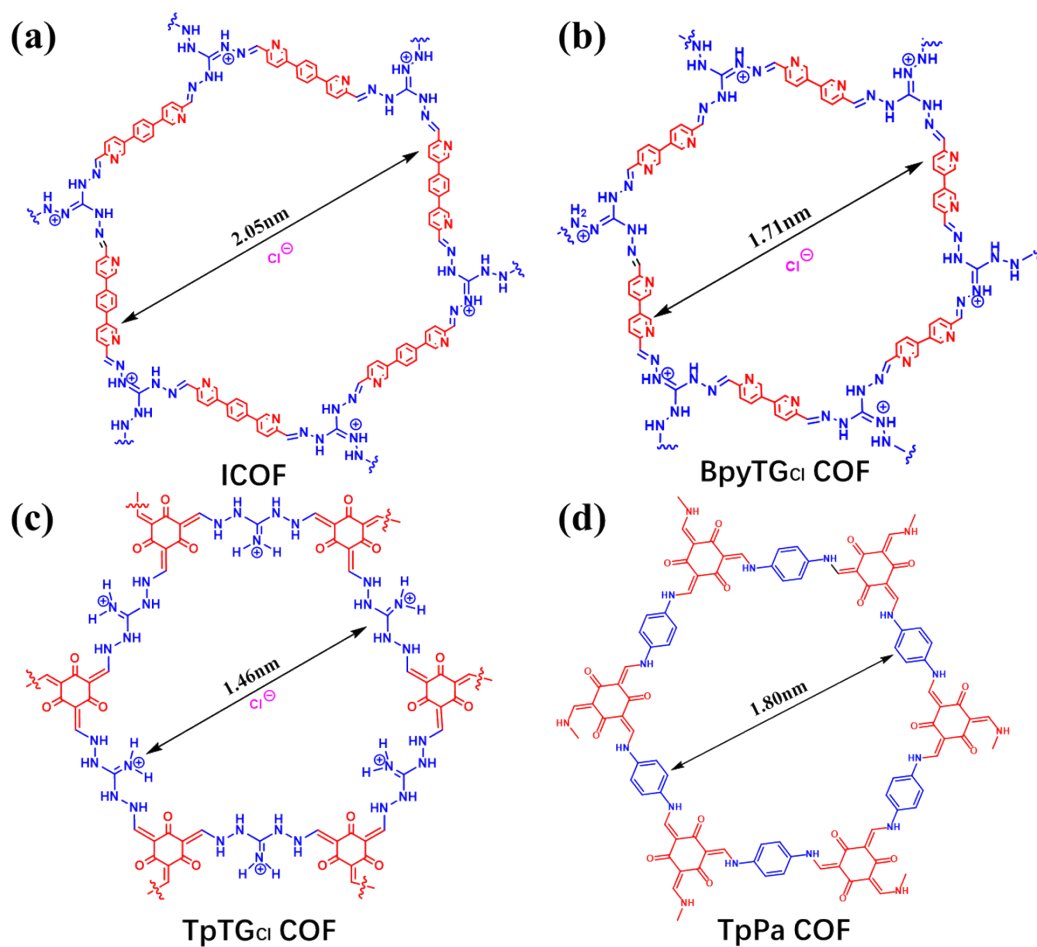


Fig. S11 The structure of different adsorbents

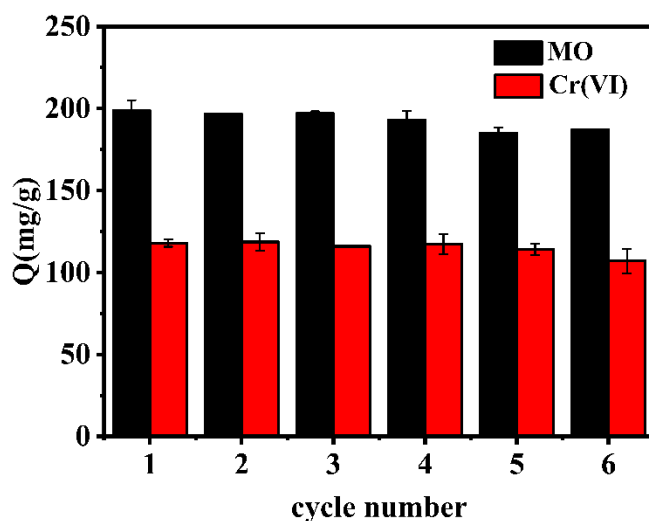


Fig. S12 Adsorption capacity of MO and Cr(VI) in six successive adsorption and desorption cycles (Initial concentration: 200 mg/L; adsorbent mass: 3mg; Volume: 6 mL; pH: 3; Temperature: 310 K).

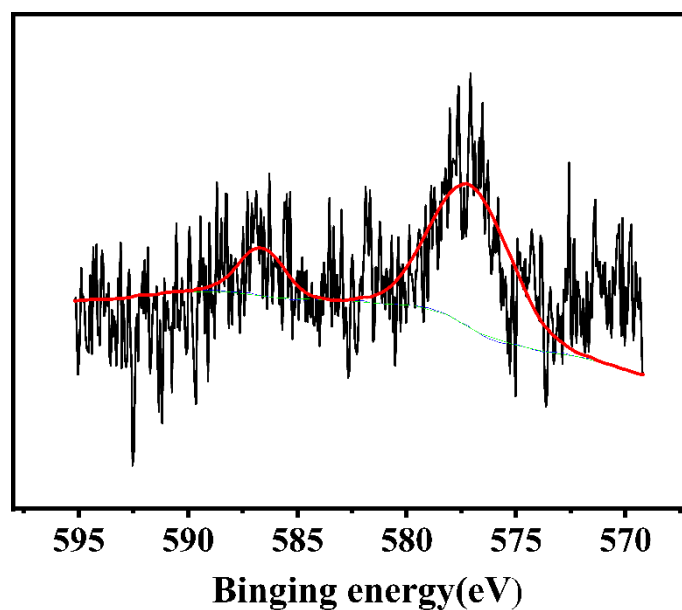


Fig. S13 Cr2p spectra of ICOF

Supporting Tables

Table S1 Equilibrium parameters for the adsorption of MO and Cr (VI) onto ICOF.

| | Langmuir model | | | Freundlich model | | |
|---------|-------------------|-------------------|--------|-------------------|-------|--------|
| | $K_s (mg L^{-1})$ | $Q_m (mg g^{-1})$ | R^2 | $K_f (mg L^{-1})$ | n | R^2 |
| MO | 1.820 | 366.3 | 0.9998 | 166.1 | 4.492 | 0.5090 |
| Cr (VI) | 1.667 | 200.0 | 0.9999 | 85.56 | 4.870 | 0.8274 |

Table S2 Kinetic model parameters for the adsorption of MO and Cr (VI).

| | Pseudo-first order model | | | Pseudo-second order model | | |
|---------|--------------------------|-------------------|--------|----------------------------|-------------------|--------|
| | $K_1 (min^{-1})$ | $Q_e (mg g^{-1})$ | R^2 | $K_2 (g mg^{-1} min^{-1})$ | $Q_e (mg g^{-1})$ | R^2 |
| MO | 0.01754 | 266.11 | 0.8873 | 0.000150 | 373.13 | 0.9922 |
| Cr (VI) | 0.01594 | 25.641 | 0.9658 | 0.002116 | 172.414 | 0.9999 |

Table S3. Comparison of ICOF with other adsorbents in previous reports for simultaneous binding MO and Cr (VI).

| Adsorbent | Operating Conditions | Adsorption capacity (mg/g) | | Ref. |
|----------------------------|------------------------------------------------------------------------------------------------------------------------------|----------------------------|---------|------------|
| | | MO | Cr (VI) | |
| Ppy @magnetic chitosan | dosage:100 mg C _{Cr(VI), MO initial} :100 mg/L Volume: 50 mL contact time: 40 min 298 K; pH 4.5 | 95 | 105 | 3 |
| Chitosan–sericin composite | dosage:5 mg C _{Cr(VI), MO initial} :50 mg/L Volume: 10 mL contact time: 60 min 295 K; pH 3.0 | 94 | 87 | 4 |
| Ni/Al @PAB | dosage:10 mg C _{Cr(VI) initial} =30 mg/L, C _{MO initial} =280 mg/L Volume: 50 mL 303 K; pH:4.5 | 455 | 64.5 | 5 |
| ICOF | dosage:3 mg C _{Cr(VI), MO initial} :200 mg/L Volume: 6 mL contact time: 60 min 318 K; pH 3.0 | 290 | 158 | This study |

Table S4. Isotherms parameters for the adsorption of MO and Cr (VI) onto ICOF.

| Temperature (K) | Langmuir model | | | Freundlich model | | |
|--------------------|-----------------------------|-----------------------------|--------|-----------------------------|-------|--------|
| | K_L (mg L ⁻¹) | Q_m (mg g ⁻¹) | R^2 | K_F (mg L ⁻¹) | n | R^2 |
| MO 298 | 0.1774 | 167.2 | 0.9960 | 58.71 | 4.619 | 0.8969 |

| | | | | | | | |
|---------|-----|--------|-------|--------|-------|-------|--------|
| | 308 | 0.1929 | 202.4 | 0.9948 | 64.50 | 4.067 | 0.8924 |
| | 318 | 0.2093 | 304.9 | 0.9880 | 82.19 | 3.242 | 0.8561 |
| | 298 | 0.4973 | 98.91 | 0.9997 | 50.60 | 6.869 | 0.8629 |
| Cr (VI) | 308 | 0.3620 | 119.6 | 0.9996 | 49.08 | 5.123 | 0.8417 |
| | 318 | 0.3130 | 161.5 | 0.9989 | 63.20 | 4.854 | 0.9422 |

Table S5. Thermodynamic parameters for the adsorption of MO and Cr (VI) on ICOF.

| | T (K) | K_c | ΔG (KJ/mol) | ΔH (KJ/mol) | ΔS (J/(mol K)) |
|---------|-------|-------|---------------------|---------------------|------------------------|
| | 298 | 1.350 | -0.743 | | |
| MO | 308 | 1.903 | -1.648 | 52.299 | 177.09 |
| | 318 | 5.221 | -4.369 | | |
| | 298 | 1.905 | -1.597 | | |
| Cr (VI) | 308 | 2.706 | -2.549 | 41.261 | 143.33 |
| | 318 | 5.544 | -4.528 | | |

Table S6. Kinetic model parameters for the adsorption of MO and Cr (VI).

| | Pseudo-first order model | | | Pseudo-second order model | | |
|---------|--------------------------|------------------------|---------|----------------------------------|------------------------|---------|
| | k_1 (min^{-1}) | Q_e ($mg\ g^{-1}$) | R^2 | k^2 ($g\ mg^{-1}\ min^{-1}$) | Q_e ($mg\ g^{-1}$) | R^2 |
| MO | 0.01565 | 24.17 | 0.78514 | 0.001595 | 196.85 | 0.99986 |
| Cr (VI) | 0.01196 | 17.90 | 0.61908 | 0.003161 | 119.05 | 0.99988 |

Table S7. dye molecules and their properties.

| Dye molecule | Charge | λ_{\max} (nm) | M_w (g/mol) | Molecule size(Å) |
|-----------------------------|---------|-----------------------|---------------|----------------------|
| Methyl Orange (MO) | - | 462 | 327.3 | 5.19×14.62 |
| Potassium Permanganate (PP) | - | 524 | 158.0 | 4.00×4.00 |
| Nile Red (NR) | neutral | 553 | 318.4 | 6.51×14.12 |
| p-Nitroaniline (NA) | neutral | 369 | 138.1 | 4.32×6.89 |
| Rhodamine B (RB) | + | 553 | 479.0 | 11.81×15.31 |
| Methylene Blue (MB) | + | 664 | 319.9 | 5.63×14.21 |

Table S8 binding energy (BE) values of existing elements

| | ICOF | ICOF (Adsorbed MO) | ICOF (Adsorbed Cr) | ICOF (Adsorbed MO and Cr) |
|------|--------|-----------------------|-----------------------|------------------------------|
| C1s | 284.77 | 284.78 | 284.81 | 284.81 |
| N1s | 399.32 | 399.5 | 399.62 | 399.76 |
| O1s | 532.07 | 532 | 532.28 | 532.37 |
| S2p | - | 167.65 | - | 167.62 |
| Cr2p | - | - | 577.27 | 577.06 |
| | | | 586.72 | 585.72 |

1. S. Mitra, S. Kandambeth, B. P. Biswal, M. A. Khayum, C. K. Choudhury, M. Mehta, G. Kaur, S. Banerjee, A. Prabhune, S. Verma, S. Roy, U. K. Kharul and R. Banerjee, *J Am Chem Soc*, 2016, **138**, 2823-2828.
2. C. Liu, J. You, R. Hu, W. Jiang, Y. Duan, J. Li, Z. Li, R. Zhu, Y. Li, Z. Liu, K. Wang and C. Chen, *Anal Lett*, 2020, **54**, 347-363.
3. N. S. Alsaiani, A. Amari, K. M. Katubi, F. M. Alzahrani, F. B. Rebah and M. A. Tahoon, *Processes*, 2021, **9**, 576-591.
4. Y. Lu, B. Jiang, L. Fang, F. Ling, J. Gao, F. Wu and X. Zhang, *Chemosphere*, 2016, **152**, 415-422.
5. S. Chen, Y. Huang, X. Han, Z. Wu, C. Lai, J. Wang, Q. Deng, Z. Zeng and S. Deng, *Chem Eng J*, 2018, **352**, 306-315.