Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Metal Ions-Assisted Carboxyl-Containing Covalent Organic Frameworks for the Efficient Removal of Congo Red

Jie-Yu Yue*‡, Ling Wang‡, Yu Ma*, Peng Yang, Ying-Qiu Zhang，Yu Jiang & Bo Tang*

College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Institutes of Biomedical Sciences, Shandong Normal University, Jinan 250014.

Corresponding Author: Dr. Bo Tang；Dr. Yu Ma；Dr. Jie-Yu Yue

*E-mail: tangb@sdnu.edu.cn; may@sdnu.edu.cn; yuejieyu@sdnu.edu.cn

Materials and Measurements

Tp was purchased from Yuhao Chemical Technology Co., Ltd. (China) and DBA was bought from Ariel chemical technology Co., Ltd. (China) and CR was purchased from J&K. All the chemicals used in this study were utilized without further purification. The powder X-ray diffraction (PXRD) pattern was collected on D8 ADVANCE with Cu Kα radiation (λ = 1.5405 Å) with a 2θ range from 2 to 40° at room temperature. Fourier transform infrared (FT-IR) spectroscopy was recorded (400-4000 cm^{-1} range) on a Bruker ALPHA FT-IR Spectrometer. ^{13}C Solid state NMR spectra were recorded on a Bruker Avance III 400 MHz instrument. Inductively coupled plasma (ICP) measurement was performed on an IRIS Intrepid (II) XSP and NU AttoM spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were obtained from PHI Versaprobe II. Thermogravimetric analysis (TGA) was conducted on TGA/SDTA851e under N_2 atmosphere at 10 °C·min^{-1} from 25 °C to 800 °C. Scanning electron microscopy (SEM) images were collected on a SUB010 scanning electron microscope with acceleration voltage of 20 kV. High resolution transmission electron microscopy (HRTEM) analysis was taken on a JEOL 2100 Electron Microscope at an operating voltage of 200 kV. The Brunauer–Emmett–Teller (BET) surface areas were taken on an ASAP 2020/TriStar 3000 (Micromeritics) at 77 K. Ultraviolet-visible (UV-Vis) spectra was performed on a U-4100 UV-visible spectrophotometer (HITACHI, Japan).

Supplementary Figures

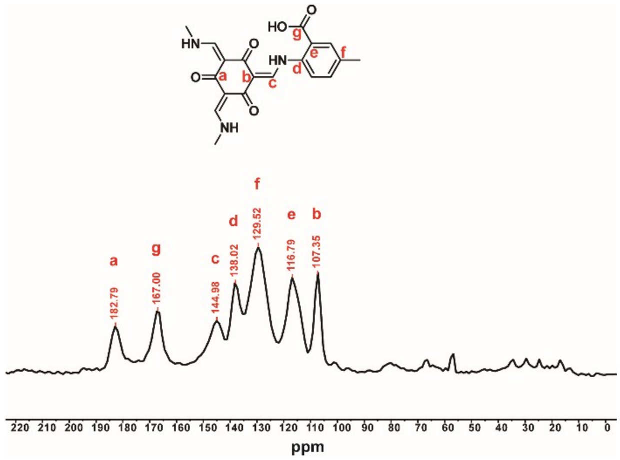

Fig. S1 The ^{13}C NMR spectra of COF-COOH.

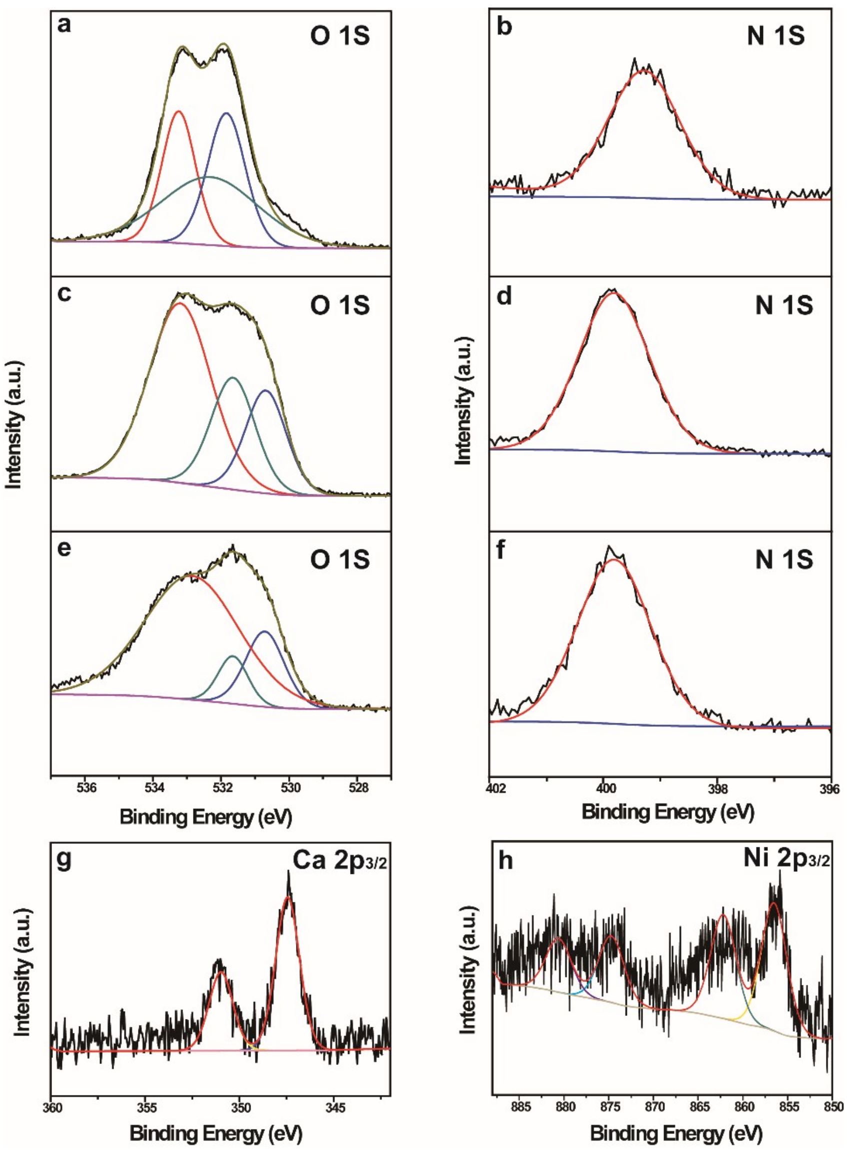

Fig. S2 The XPS spectrum of (a, b) COF-COOH; (c, d, g) COF-COOCa; (e, f, h) COF-COONi.

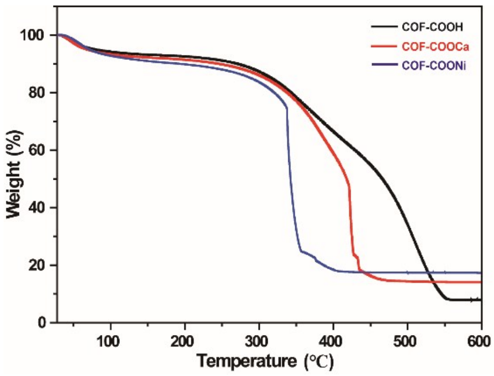

Fig. S3 The TGA curves of COF-COOH (black line), COF-COOCa (red line) and COF-COONi (blue line).

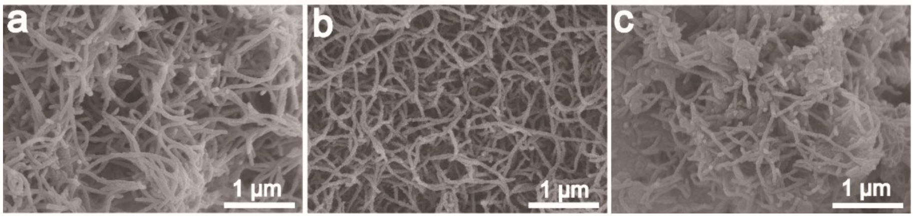

Fig. S4 SEM image of (a) COF-COOH; (b) COF-COOCa; (c) COF-COONi.

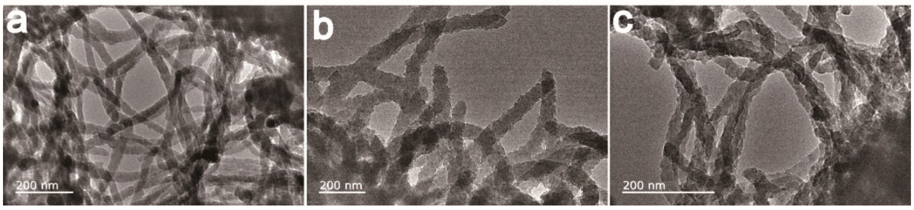

Fig. S5 TEM image of (a) COF-COOH; (b) COF-COOCa; (c) COF-COONi.

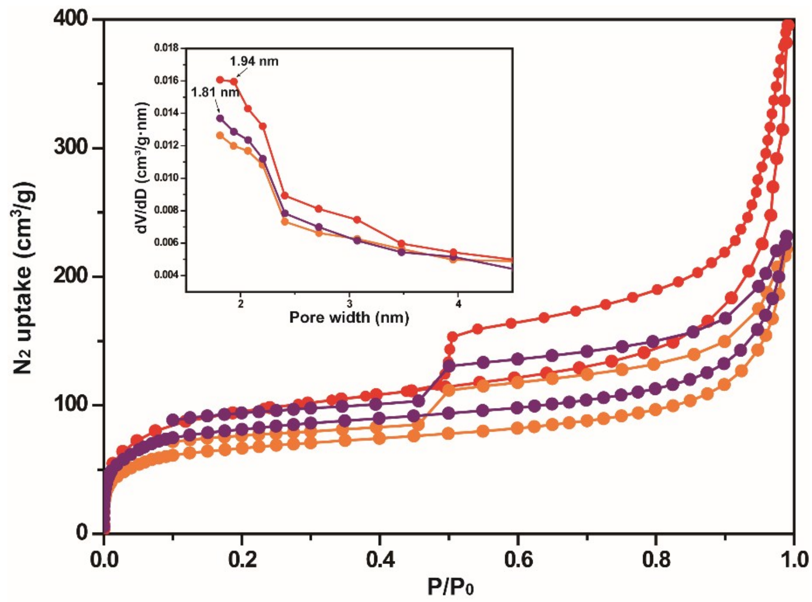

Fig. S6 The BET surface areas and pore size distribution of COF-COOH (red line), COF-COOCa (orange line) and COF-COONi (purple line).

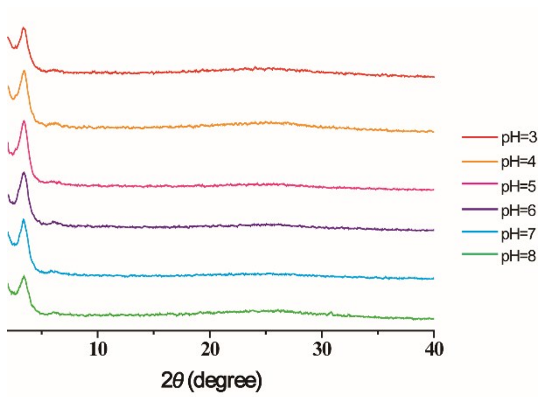

Fig. S7 The PXRD patterns of COF-COOH at different pH after 24 h.

Adsorbents	Langmuir parameters			Freundlich parameters		
	q_{max} (mg/g)	b (L/mg)	R^2	K_f ($mg^{1-1/n}L^{1/n}/g$)	n	R^2
COF-COOCa	704.23	0.0368	0.923	23.667	0.814	0.876
COF-COONi	781.25	0.128	0.931	101.328	1.528	0.847

Table S1 The calculated parameters of Langmuir models and Freundlich models of CR adsorption on COF-COOCa. Langmuir models: $\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}b}$; Freundlich models: $q_e = C_e^{1/n} K_f$.

Adsorbents	q_{max} (mg/g)	References
NiO microspheres	397	1
Hierarchical porous ZnO	334	2
Fe_3O_4@ZTB-1	458	3
IL-PVE	503	4
pyrimidine-based POPs	400	5
ZrO_2 fibers	103	6
3D copper(II) MOF	656	7
TS-COF-1	319	8
COF-COOCa	704.23	this work
COF-COONi	781.25	this work

Table S2 Comparison of maximum adsorption capacities of CR in this study with the previous reported materials.

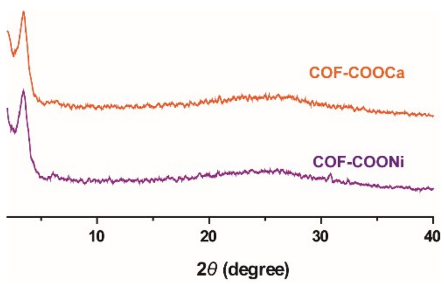

Fig. S8 The PXRD patterns of COF-COOCa and COF-COONi after four adsorption-desorption cycles.

References

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