High-performance adsorption and separation of anionic dyes in water using a chemically stable graphene-like metal-organic framework

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Fig. S1 Structural formulae of tib and H₂adc.

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Fig. S2 Structural formulae of the dye molecules used in the dye adsorption and separation experiment.

Materials and Instruments

All chemicals were commercially available reagent grade and used without further purification. CHN Elemental analyses were performed using an Elementar Vario EL-III instrument. FTIR spectra were recorded on Nicolet-6700 Fourier transform infrared spectrophotometer in the region ranging from 4000 to 400 cm⁻¹. Powder X-ray diffraction (PXRD) patterns were recorded on a Dandonghaoyuan DX-2700B diffractometer with Cu-K α radiation. Thermogravimetric analyses were performed from 70 to 800 °C in an air stream at a heating rate of 10 °C min⁻¹ on a DTU-3c thermal analyzer using *a*-Al₂O₃ as a reference. X-ray photoelectron spectra (XPS) measurement was operated with Thermo ESCALAB 250XI.

Synthesis of BUC-17

A mixture of H₂adc (0.3 mmol, 0.0673 g), CoSO₄·7H₂O (0.3 mmol, 0.0843 g) and tib (0.3 mmol, 0.0828 g) was sealed in a 25 mL Teflon-lined stainless steel Parr bomb containing deionized H₂O (10 mL), heated at 140 °C for 72 h, and then cooled down to room temperature. Red block-like crystals of **BUC-17** (yield: 79% based on CoSO₄·7H₂O) were isolated and washed with deionized water and ethanol. Anal. Calcd. for **BUC-17**, $C_{30}H_{48}N_{12}O_{24}Co_3S_3$: C, 29.2%; N, 13.6%; H, 3.9%. Found: C,

29.3%; N, 13.6%; H, 4.1%. IR (KBr)/cm⁻¹: 3360, 3131, 1672, 1623, 1546, 1515, 1317, 1257, 1273, 1182, 1125, 1078, 1012, 974, 848, 817, 758, 663, 612, 449. It is worth that H₂adc did not participate in the formation of **BUC-17** in the final product. But we failed to synthesize **BUC-17** without the addition of H₂adc, implying H₂adc might play a role of a catalyst and pH regular.

X-ray crystallography

X-ray single-crystal data collection for **BUC-17** was performed with Bruker CCD area detector diffractometer with a graphite-monochromatized MoKa radiation ($\lambda = 0.71073$ Å) using $\varphi - \omega$ mode at 298(2) K. The SMART software¹ was used for data collection and the SAINT software² for data extraction. Empirical absorption corrections were performed with the SADABS program³. The structure has been solved by direct methods(SHELXS-97)⁴ and refined by full-matrix-least squares techniques on F^2 with anisotropic thermal parameters for all of the non-hydrogen atoms (SHELXL-97)⁴. All hydrogen atoms were located by Fourier difference synthesis and geometrical analysis. These hydrogen atoms were allowed to ride on their respective parent atoms. All structural calculations were carried out using the SHELX-97 program package⁴. Crystallographic data and structural refinement for **BUC-17** are summarized in Table S1. Selected bond lengths and angles are listed in Table S2.

Complex no.	BUC-17					
Formula	$C_{30}H_{48}N_{12}O_{24}Co_3S_3\\$					
M	1233.77					
Crystal system	Rhombohedral					
Space group	R3c					
$a(\text{\AA})$	23.635(2)					
$b(\text{\AA})$	23.635(2)					
$c(\text{\AA})$	13.7616(14)					
α(°)	90					

Table S1 Details of X-ray data collection and refinement for BUC-17

$\beta(^{\circ})$	90
$\gamma(^{\circ})$	120
$V(Å^3)$	6657.4(11)
Ζ	6
μ (Mo, K α)(mm ⁻¹)	1.353
Total reflections	10773
Unique	2432
F(000)	3798
Goodness-of-fit on F ²	1.044
$R_{ m int}$	0.0326
R_0	0.0308
ωR_2	0.0685
$R_1(\text{all data})$	0.0369
$\omega R_2(\text{all data})$	0.0724
Largest diff. peak and hole($e/Å^3$)	0.392, -0.266

Table S2. Selected bonds and angles for BUC-17 [Å and °].

BUC-17			
Bond lengths (Å)			
Co(1)-O(6)	2.068(3)	Co(1)-O(5)	2.090(3)
Co(1)-O(7)	2.108(3)	Co(1)-O(8)	2.137(3)
Co(1)-N(4)	2.151(4)	Co(1)-N(2)	2.163(4)
Bond angles (°)			
O(6)-Co(1)-O(5)	96.40(15)	O(6)-Co(1)-O(7)	87.93(13)
O(5)-Co(1)-O(7)	174.70(14)	O(6)-Co(1)-O(8)	171.67(14)
O(5)-Co(1)-O(8)	91.89(13)	O(7)-Co(1)-O(8)	83.83(12)
O(6)-Co(1)-N(4)	93.76(14)	O(5)-Co(1)-N(4)	87.43(14)
O(7)-Co(1)-N(4)	95.34(14)	O(8)-Co(1)-N(4)	85.80(13)
O(6)-Co(1)-N(2)	91.17(14)	O(5)-Co(1)-N(2)	83.74(14)
O(7)-Co(1)-N(2)	93.15(14)	O(8)-Co(1)-N(2)	90.51(13)
N(4)-Co(1)-N(2)	170.32(14)		

Table S3 Hydrogen bonds for $BUC\mbox{-}17$ (Å and $^{\rm o})$

Table S3 Hydrogen bonds for BUC-17 (A and °)									
D-H	d(D-H)	d(HA)	<dha< th=""><th>d(DA)</th><th>А</th></dha<>	d(DA)	А				
O5-H5C	0.850	1.951	153.59	2.739	O4 [-y+1/3, -x+2/3, z+7/6]				
O5-H5D	0.850	2.044	154.26	2.834	O8 [-x+y-1/3, -x+1/3, z+1/3]				
O6-H6C	0.850	1.926	171.75	2.770	O1 [<i>x</i> , <i>y</i> , <i>z</i> +1]				
O6-H6D	0.850	1.900	171.51	2.744	O3 [- <i>x</i> + <i>y</i> +1/3, - <i>x</i> +2/3, <i>z</i> +2/3]				
O6-H6D	0.850	2.996	160.49	3.808	S1 [- <i>x</i> + <i>y</i> +1/3, - <i>x</i> +2/3, <i>z</i> +2/3]				
O7-H7C	0.850	2.159	175.33	3.006	O1 [- <i>x</i> + <i>y</i> , <i>y</i> , <i>z</i> +1/2]				
O7-H7C	0.850	2.994	148.63	3.746	S1 [- <i>x</i> + <i>y</i> , <i>y</i> , <i>z</i> +1/2]				
07-H7D	0.850	1.892	175.18	2.740	O4 [-x+y+1/3, -x+2/3, z+2/3]				

O8-H8C	0.850	1.935	172.26	2.780	O1 [<i>x</i> -1/3, <i>x</i> - <i>y</i> +1/3, <i>z</i> +5/6]
O8-H8C	0.850	2.811	155.69	3.602	S8 [<i>x</i> -1/3, <i>x</i> - <i>y</i> +1/3, <i>z</i> +5/6]
O8-H8D	0.850	1.852	172.16	2.697	O3 [- <i>x</i> + <i>y</i> , <i>y</i> , <i>z</i> +1/2]
O8-H8D	0.850	2.828	156.83	3.624	S1 [- <i>x</i> + <i>y</i> , <i>y</i> , <i>z</i> +1/2]

Adsorption experiments

To study the organic dye adsorption ability of **BUC 17**, four representative organic dyes with different charges, anionic Congo Red (**CR**) and Mordant Blue 13 (**MB13**), cationic Methylene Blue (**MB**), and neutral Sudan I (**SI**), were chosen in this work. A solid sample (50 mg) of the CPs with 0.08 mm particle size were added to 200 mL of **CR** (100 mg L⁻¹), **MB13** (20 mg L⁻¹), **MB** (10 mg L⁻¹) aqueous or **SI** (20 mg L⁻¹) in ethanol solution in a 300 ml breaker, which were vibrated for a desired contact time in water bath shaker with speed of 150 r min⁻¹ at 293 K. Sample of 5 mL aliquots were extracted and separated from the adsorbent by centrifugation (ZONKIA SC-3610) at 5000 rpm for 10 min. A Laspec Alpha-1860 spectrometer was used to monitor the **CR**, **MB13**, **MB**, **SI** concentration changes by the maximum absorbance at 493 nm, 551 nm, 672 nm and 480 nm, respectively.

Separation experiments

Dye adsorption in the mixture of different changes of dyes

BUC-17 (10 mg) was added to 200 ml of dye-containing water solution with the initial concentration of **CR** (100 mg L^{-1})/**MB** (20 mg L^{-1}) and MB13 (20 mg L^{-1})/MB (20 mg L^{-1}). Then the mixtures were vibrated in constant temperature water of 25 °C bath shaker with speed of 150 r min⁻¹. At a certain time interval, UV-Vis absorption spectra were recorded to determine the concentration of the dye solutions.

Dye release

BUC-17 powder was immersed in **CR** dye solution and the dye loaded powders were collected and dried, thus obtaining **CR@BUC-17**. Then 5.0 mg **CR@BUC-17** was placed in two cuvettes with 3.0 mL deionized water and 3.0 mL saturated Na₃PO₄ solution, respectively. During the releasing process, the absorbance values of the CR in solution were recorded by UV-Vis spectrophotometry at different time interval until 12 h.



Fig. S3 (a) Packing view of the framework assembled with the aid of H bonding interactions seen from *a*-axis for **BUC-17**. (b) Packing view of the framework of **BUC-17** from *c*-axis.



Fig. S4 UV-vis absorption spectra of CR (a) and MB13 (b) with BUC-17.

Table S4 Comparison of the adsorption capacities of CR onto some typical adsorbents

	Adsorption capacity	
Adsorbents	(mg g ⁻¹)	Ref.
BUC-17	4923.7	This work
Hypercrosslinked poly(styrene-co-divinylbenzene) resin	2326	5
$[Ag_4(dpe)_4] \cdot (butca) \cdot 13H_2O$	739	6
MIL-100(Fe)	714	7
$\{[Cu_3(btb)_3(nbta)_2] \cdot (H_2O)\}_n$ complex	656	8
CoFe ₂ O ₄	245	9
HTMAB-modified attapulgite	189	10
Coal-based mesoporous activated carbon	52-189	11
Chitosan hydrobeads	92.59	12
Magnetic (Fe ₃ O ₄) cellulose activated carbon	66.09	13
Acid-activated bentonite	61.5	14



Fig. S5 (a) Comparison of XRD patterns of the simulated one from single crystal data, **BUC-17** before and after adsorption. (b) XPS wide scans spectra of **BUC-17** before and after **CR** adsorption.

Adsorption kinetic

BUC-17 adsorbing **CR** was selected as the removal target to study the kinetic adsorption process. 10 mg **BUC-17** was added into 200 mL of CR (150, 200, 250 mg L⁻¹) solution at 293 K. All the mixtures were vibrated in constant temperature water bath shaker with speed of 150 r min⁻¹. 5 mL sample was drawn at a certain time interval, immediately centrifuged to remove the particles as above. And the adsorption of dye was determined by Laspec Alpha-1860 spectrometer.

Pseudo-first-model¹⁵ and Pseudo-second-model¹⁵ are widely used for the adsorption of an adsorbate from an aqueous solution. They can be expressed as linear form by Equations (1) and (2):

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(2)

where q_t (mg g⁻¹) and q_e (mg g⁻¹) is the amount of adsorbates adsorbed onto absorbents at t and at equilibrium time, respectively. k_l (min⁻¹) represents the adsorption rate constant which is calculated from the plot of ln ($q_e - q_t$) against t. k_2 (g mg⁻¹ min⁻¹) represents the pseudo-second-order rate constant of sorption. The plot of t/q_t vs. t should exhibit a linear relationship, and the q_e and k_2 can be obtained by the slope and intercept of the plot, respectively.

Table S5. Parameters of kinetic model of CR with different concentration onto BUC-17

	Pseudo-first-order			Pseudo-	Experimental		
$C_0(\text{mg L}^{-1})$	$k_1(\min^{-1})$	$q_{\rm e}({\rm mg~g}^{-1})$	R^2	$k_2(g mg^{-1} min^{-1})$	$q_{\rm e}({\rm mg \ g^{-1}})$	R^2	value(mg g ⁻¹)
150	0.0794	1380.2	0.686	2.17×10-4	2720.3	0.990	2685.5
200	0.0409	2662.2	0.835	8.64×10 ⁻⁵	3402.6	0.997	3254.6
250	0.0374	3656.5	0.936	2.81×10-5	5082.6	0.996	4923.7

Adsorption isotherms

In addition, the bath adsorption was adopted to study the effect of temperature. 10 mg of **BUC-17** was added to 200 mL **CR** aqueous solution with initial concentration of 150, 200, 250, 300, 350 mg L⁻¹. The mixtures were agitated in constant temperature water bath shaker with speed of 150 r min⁻¹ at different temperature (288, 293, 298, 303 and 308 K), respectively. When adsorption equilibrium was reached, the suspensions were centrifuged, and the concentrations of residual dye were also determined by Laspec Alpha-1860 spectrometer.

The Langmuir, Freundlich, and Dubinin–Radushevich (D-R) adsorption isotherm models were selected to describe equilibrium adsorption data of the **CR** and **BUC-17**.

The Langmuir isotherm model expressed as Equation $(3)^{16}$:

$$C_e / q_e = 1 / (K_L q_{\max}) + C_e / q_{\max}$$
 (3)

Where, q_{max} is the maximum amount of adsorption with complete monolayer coverage on the adsorbent surface (mg g⁻¹). K_{L} is the Langmuir constant related to the energy of adsorption which indicates the intensity of adsorption (L mg⁻¹); high K_{L} values mean strong bonding between the adsorbate and adsorbent. The K_{L} and q_{max} can be obtained from the linear plot of $C_e vs. C_e/q_e$.

The Freundlich isotherm model is listed in Equation $(4)^{17}$:

$$\log q_e = \log K_f + (1/n) \log C_e \tag{4}$$

Where $K_{\rm f}$ (mg g⁻¹) and n are the Freundlich adsorption isotherm constants, being indicate of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. 1/n and $\log K_{\rm f}$ can be calculated from the slope and intercept of the linear plot between $\log C_{\rm e}$ and $\log q_{\rm e}$, respectively.

The D-R isotherm can be represented as Equation $(5)^{18}$:

$$\ln q_e = \ln q_m - K_{DR} \varepsilon^2 \tag{5}$$

Where, K_{DR} the activity coefficient related to mean sorption energy (mol² J⁻²), q_m is the theoretical saturation capacity (mol g⁻¹), ε represents the potential (J mol⁻¹), which can be calculated using the equilibrium concentration C_e (mg L⁻¹) as Equation (6):

$$\varepsilon = RT \ln(1 + 1/C_e) \tag{6}$$

 K_{DR} and $q_{\rm m}$ can be obtained by the slope and intercept of the plot of $\ln q_{\rm e}$ vs ε^2 , respectively. The mean free energy of adsorption (*E*, kJ mol⁻¹) can by expressed by Equation (7)

$$E = \frac{1}{\sqrt{2K_{DR}}} \tag{7}$$

Table S6. Constants of Langmuir, Freundlich, and D-R for CR adsorption by BUC-17 at different

T/K	Langmuir			Freundlich			D-R		
	$q_{\rm max}({\rm mg~g}^{-1})$	$K_{\rm L}({\rm L~mg^{-1}})$	R^2	$K_{\rm f} ({\rm L}~{\rm g}^{-1})$	1/ <i>n</i>	R^2	$K_{\rm DR}$	E(KJ mol ⁻¹)	R^2
288	4153	20780	0.970	1041.69	0.251	0.541	1.13×10-4	0.664	0.760
293	4745	71985	0.970	2582.91	0.114	0.653	5.13×10 ⁻⁷	0.987	0.402
298	4957	135812	0.999	2666.93	0.132	0.919	6.60×10 ⁻⁷	0.871	0.736
303	5240	156447	0.999	2725.40	0.145	0.778	1.43×10-6	0.591	0.911
308	5407	321533	0.991	3325.06	0.115	0.474	5.97×10 ⁻⁷	0.915	0.903

temperatures

Thermodynamic parameters

Standard free energy (ΔG^0 , kJ mol⁻¹), change in enthalpy (ΔH^0 , kJ mol⁻¹) and change in entropy (ΔS^0 , J mol⁻¹ K⁻¹), were determined with the help of data obtained from Langmuir adsorption isotherm via Equations (8) and (9).

$$\Delta G^{0} = -RT \ln K_{L}$$

$$\ln K_{L} = \frac{\Delta S^{0}}{R} - \frac{\Delta H^{0}}{RT}$$
(8)
(9)

Where *R* is the universal gas constant (8.314 kJ mol⁻¹ K⁻¹) and *T* is the absolute temperature (K), K_L is equilibrium constant, which depends on the temperature. ΔG^0 could be figured out by Equation 8. According to Equation 9, ΔS^0 and ΔH^0 parameters can be obtained from the slope and the intercept of the linear plot of $\ln K_L vs. 1/T$, respectively.

<i>T</i> /K	$K_{\rm L}({\rm L~mg^{-1}})$	$\Delta G^{\circ}(\text{kJ mol}^{-1})$	$\Delta S^{o}(J \text{ mol}^{-1} \text{ K}^{-1})$	$\Delta H^{o}(kJ mol^{-1})$
288	4153	-23.80		
293	4745	-27.24		
298	4957	-29.28	407	92.62
303	5240	-30.13		
308	5407	-32.47		

Table S7. Thermodynamic parameters for sorption process of CR on BUC-17 at different temperatures



Fig. S6 Color changes of solutions containing (a) MB and (b) SI before (left) and after (right)



addition of BUC-17 (2 h).

Fig. S7 (a) UV-Vis spectral changes of the dye mixtures of **MB13** and **MB**. (b)The picture of SPE setup, in which the original packing material C18 of SPE column was replaced by **BUC-17**.

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