Ultra-high uptake and selective adsorption of organic dyes with a novel polyoxomolybdate-based organic-inorganic hybrid compound^{\dagger}

Yan-Qiu Zhang ^a, Chong-Chen Wang^{*a,b}, Tian Zhu ^a, Peng Wang ^a, Shi-Jie Gao ^a

1. Experimental

1.1 Materials and Methods

All starting materials and solvents were purchased commercially and used without further purification. X-ray diffraction (XRD) patterns of the samples were determined by a Dandonghaoyuan DX-2700B diffractometer in the range of $2\theta = 5^{\circ} - 40^{\circ}$, with Cu K α radiation. The Fourier transform infrared (FTIR) spectra, in the range of 4000-400 cm⁻¹, were recorded from KBr pellets on Nicolet 6700 spectrometer. UV-vis diffuse reflectance data was collected by PerkinElmer lambda 650s in the range of 200-800 nm, in which barium sulfate (BaSO₄) was used as the standard with 100% reference. The surface area of the sample was obtained from N₂ adsorption-desorption isotherms at 77 K using Brunauer-Emmett-Teller nitrogen-helium absorption method (BET, V-Sorb 2800P, Gold APP Instruments Co., Ltd). Thermo gravimetric analysis (TGA) in the temperature range of 0 - 700 °C under air atmosphere was also analyzed by TA SDT Q600. The microstructures were examined using a FEI Quanta 250 FEG scanning electron microscope (SEM). Transmission electron microscopy (TEM) images were obtained on an FEI Talos F200X transmission electron microscope, using an accelerating voltage of 200KV. X-ray photoelectron spectra (XPS) measurement was performed with Thermo ESCALAB 250XI. The surface charge of the particles was assessed by zeta potential measurements using the Malvern zeta sizer Nano ZS and by applying the field strength of 20 V/cm.



Fig. S1 SEM of 1 before and after absorbing MB

1.2 Synthesis of organic-inorganic hybrid compound [(4-Hap)₄(Mo₈O₂₆)] (1)

A mixture of $CdCl_2 \cdot 2.5H_2O$ (0.3 mmol, 0.0685 g), ammonium molybdate tetrahydrate (H₂₄Mo₇N₆O₂₄·4H₂O, 0.6 mmol, 0.7415 g) and 4-aminopyridine (4-ap, 0.3 mmol, 0.028 g) with molar ratio of 1:2:1 was sealed in a 25 mL Teflon-lined stainless steel Parr bomb containing deionized H₂O (20 mL), heated at 160 °C for 72 h, and then cooled down to room temperature. White block-like crystals, [(4-Hap)₄(Mo₈O₂₆)] (1) were isolated and washed with deionized water and ethanol. In this reaction, $CdCl_2 \cdot 2.5H_2O$ acts probably as catalyst, as the synthesis did not succeed without it. Anal. Calcd. for 1, $C_{20}H_{28}Mo_8N_8O_{26}$: C, 15.3; N, 7.2; H, 1.8. Found: C, 15.2; N, 7.2; H, 2.0. IR (KBr, cm⁻¹) : 3455.04, 3264.02, 3226.32, 3153.92, 3115.20, 2969.00, 1694.79, 1625.39, 1581.82, 1531.72, 1398.85, 1200.88, 1002.04, 941.01, 915.41, 844.76, 765.53, 696.78, 660.72, 645.23, 552.27, 517.29, 497.29, 402.12.

1.3 X-ray Single Crystal Analysis:

X-ray single-crystal data collection for **1** was performed with Bruker CCD area detector diffractometer with a graphite-monochromatized Mo K_{α} radiation ($\lambda = 0.71073$ Å) using φ - ω mode at 298(2) K. The SMART software ¹ was used for data collection and the SAINT software ² for data extraction. Empirical absorption corrections were performed with the SADABS program. ³ 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 package.⁴ Crystallographic data and structural refinements for **1** are summarized in Table S1. Selected bond lengths and angles for **1** are listed in Table S2. The hydrogen bonds for **1** are listed in Table **S3**.

Formula	$C_{20}H_{28}Mo_8N_8O_{26}$	M (Mo,K α) (mm ⁻¹)	2.591
М	1564.02	Total Reflections	4863
Crystal	Triclinic	Unique	3351
space group	Pī	F (000)	748
<i>a</i> , (Å)	9.906(4)	Goodness-of-fit on F^2	1.078
<i>b</i> , (Å)	10.108(4)	$R_{ m int}$	0.0255

Table S1 Details of X-ray data collection and refinement for 1

<i>c</i> , (Å)	10.995(4)	<i>R</i> 1	0.0419
α, (°)	66.978(4)	ω <i>R</i> 2	0.1172
β, (°)	84.193(5)	R1 (all data)	0.0640
γ, (°)	74.144(4)	$\omega R2$ (all data)	0.1392
V, (Å ³)	974.7(6)	Largest diff. peak and hole (e/Å ³)	1.493, -1.199
Ζ	1		

Table S2 Selected bond lengths (Å) and angles (°) for 1						
Bond lengths (Å)						
Mo(1)-O(5)	1.695(6)	Mo(1)-O(4)	1.703(6)	Mo(1)-O(6)	1.899(5)	
Mo(1)-O(1)	1.998(5)	Mo(1)-O(3)	2.273(5)	Mo(1)-O(2)	2.368(5)	
Mo(1)-Mo(3)	3.1970(12)	Mo(2)-O(9)	1.691(6)	Mo(2)-O(8)	1.703(5)	
Mo(2)-O(7)	1.891(5)	Mo(2)-O(2)	2.010(5)	Mo(2)-O(1)	2.332(5)	
Mo(2)-O(3)#1	2.345(5)	Mo(3)-O(11)	1.702(5)	Mo(3)-O(10)	1.747(5)	
Mo(3)-O(1)	1.946(5)	Mo(3)-O(2)#1	1.951(5)	Mo(3)-O(3)	2.168(5)	
Mo(3)-O(3)#1	2.350(5)	Mo(4)-O(12)	1.704(6)	Mo(4)-O(13)	1.708(6)	
Mo(4)-O(7)	1.915(6)	Mo(4)-O(6)#1	1.932(6)	Mo(4)-O(10)	2.309(6)	
Mo(4)-O(3)#1	2.488(5)					
Bond angles (°)						
O(5)-Mo(1)-O(4)		105.5(3)	O(5)-Mo(1)-O	(6)	98.4(3)	
O(4)-Mo(1)-O(6)		101.5(3)	O(5)-Mo(1)-O	(1)	101.2(3)	
O(4)-Mo(1)-O(1)		97.7(3)	O(6)-Mo(1)-O	(1)	147.7(2)	
O(5)-Mo(1)-O(3)		158.8(3)	O(4)-Mo(1)-O	(3)	95.7(2)	
O(6)-Mo(1)-O(3)		78.2(2)	O(1)-Mo(1)-O	(3)	74.2(2)	
O(5)-Mo(1)-O(2)		86.8(2)	O(4)-Mo(1)-O	(2)	165.2(2)	
O(6)-Mo(1)-O(2)		84.4(2)	O(1)-Mo(1)-O	(2)	71.35(19)	
O(3)-Mo(1)-O(2)		72.00(18)	O(5)-Mo(1)-M	0(3)	136.5(2)	
O(4)-Mo(1)-Mo(3	3)	85.66(19)	O(6)-Mo(1)-M	lo(3)	120.87(16)	
O(1)-Mo(1)-Mo(3	3)	35.31(15)	O(3)-Mo(1)-M	lo(3)	42.67(12)	
O(2)-Mo(1)-Mo(3	3)	79.67(12)	O(9)-Mo(2)-O	(8)	105.3(3)	
O(9)-Mo(2)-O(7)		103.1(3)	O(8)-Mo(2)-O	(7)	100.9(2)	
O(9)-Mo(2)-O(2)		98.5(3)	O(8)-Mo(2)-O	(2)	97.8(2)	
O(7)-Mo(2)-O(2)		146.5(2)	O(9)-Mo(2)-O	(1)	89.6(2)	
O(8)-Mo(2)-O(1)		163.3(2)	O(7)-Mo(2)-O	(1)	82.8(2)	
O(2)-Mo(2)-O(1)		71.9(2)	O(9)-Mo(2)-O	(3)#1	160.2(2)	
O(8)-Mo(2)-O(3)	#1	93.9(2)	O(7)-Mo(2)-O	(3)#1	77.7(2)	
O(2)-Mo(2)-O(3)	#1	73.45(19)	O(1)-Mo(2)-O	(3)#1	70.80(18)	
O(11)-Mo(3)-O(1	0)	104.0(3)	O(11)-Mo(3)-O	D(1)	101.3(2)	
O(10)-Mo(3)-O(1	.)	97.4(2)	O(11)-Mo(3)-O	D(2)#1	100.8(3)	
O(10)-Mo(3)-O(2	2)#1	97.1(2)	O(1)-Mo(3)-O	(2)#1	149.6(2)	
O(11)-Mo(3)-O(3	5)	98.6(2)	O(10)-Mo(3)-O	D(3)	157.4(2)	
O(1)-Mo(3)-O(3)		77.7(2)	O(2)#1-Mo(3)	-O(3)	78.73(19)	
O(11)-Mo(3)-O(3	5)#1	173.7(2)	O(10)-Mo(3)-0	D(3)#1	82.3(2)	

O(1)-Mo(3)-O(3)#1	77.56(19)	O(2)#1-Mo(3)-O(3)#1	78.15(19)					
O(3)-Mo(3)-O(3)#1	75.1(2)	O(11)-Mo(3)-Mo(1)	89.32(18)					
O(10)-Mo(3)-Mo(1)	133.76(19)	O(1)-Mo(3)-Mo(1)	36.38(15)					
O(2)#1-Mo(3)-Mo(1)	124.01(15)	O(3)-Mo(3)-Mo(1)	45.28(13)					
O(3)#1-Mo(3)-Mo(1)	86.21(12)	O(12)-Mo(4)-O(13)	106.3(3)					
O(12)-Mo(4)-O(7)	99.2(3)	O(13)-Mo(4)-O(7)	104.7(3)					
O(12)-Mo(4)-O(6)#1	97.6(3)	O(13)-Mo(4)-O(6)#1	101.4(3)					
O(7)-Mo(4)-O(6)#1	143.4(2)	O(12)-Mo(4)-O(10)	165.2(2)					
O(13)-Mo(4)-O(10)	88.4(2)	O(7)-Mo(4)-O(10)	77.7(2)					
O(6)#1-Mo(4)-O(10)	77.9(2)	O(12)-Mo(4)-O(3)#1	95.8(2)					
O(13)-Mo(4)-O(3)#1	157.7(2)	O(7)-Mo(4)-O(3)#1	73.8(2)					
O(6)#1-Mo(4)-O(3)#1	72.38(19)	O(10)-Mo(4)-O(3)#1	69.42(17)					
Symmetry transformations use	Symmetry transformations used to generate equivalent atoms: $#1 - x + 1, -y + 1, -z + 1$							

Table S3 Hydrogen bonds for 1 (Å and °).

D-H	d(D-H)	d(HA)	<dha< th=""><th>d(DA)</th><th>А</th></dha<>	d(DA)	А
N1-H1	0.860	2.177	149.25	2.949	O8 [-x, -y+1, -z+1]
N2-H2A	0.860	2.562	141.66	3.281	O10 [-x+1, -y, -z+1]
N2-H2A	0.860	2.584	146.27	3.333	O13 [-x+1, -y, -z+1]
N2-H2B	0.860	2.451	154.86	3.250	O6 [-x+1, -y+1, -z]
N3-H3	0.860	2.181	138.00	2.878	O4 [-x+1, -y+1, -z+1]
N3-H3	0.860	2.240	133.42	2.900	O11 [-x+1, -y+1, -z+1]
N4-H4A	0.860	2.449	162.46	3.279	O2 [-x, -y+2, -z+1]
N4-H4A	0.860	2.562	120.84	3.092	O5 [-x, -y+2, -z+1]
N4-H4B	0.860	2.179	161.89	3.008	O13 [-x, -y+1, -z+2]

1.4 UV-vis DRS

In order to explore the conductivity of 1, the measurement of diffuse reflectivity for a powder sample was used to obtain its band gap E_g . The band gap E_g was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in a plot of Kubelka - Munk function *F* against energy *E*. Kubelka - Munk function, $F = (1-R)^2/2R$, was converted from the recorded diffuse reflectance data, where *R* is the reflectance of an infinitely thick layer at a given wavelength. The *F* versus *E* plots for 1 was shown in Fig. S2, where steep absorption edges are displayed and the E_g of 1 can be assessed at 3.4 eV, which indicate that 1 is potential wide gap semiconductive material.



Fig. S2 Kubelka - Munk - transformed plot fitted by UV-vis diffuse reflectance spectra of 1

1.5 Adsorption experiments

Adsorption experiments on **1** were performed in batches. Before use, the crystals of **1** were ground to fine powder through a 200 mesh sieve. A desired amount (0.05 g) of **1** was added into 200 mL of the methylene blue (MB), methylene orange (MO) and rhodamine B (RhB) solution with the initial concentration (10 mg/L). All the mixtures were vibrated in constant temperature water bath oscillator with speed of 170 r/min at 303 K. Samples were drawn at a certain time interval with a 0.45 µm syringe filter (Tianjin Jinteng), and the residual concentration of dyes were calculated with an absorbance tested by Lasper Alpha-1860 spectrometer.

To study the adsorption performance of dyes on **1**, MB was selected as the removal target to carry out a batch adsorption experiment. A series of accurate amount of **1** as adsorbent (0.1 g, 0.15 g, 0.2 g) were put in the MB aqueous solutions (200 mL) in 250 mL conical flask respectively with initial concentration of 30, 50, 100 mg/L. The amount of MB uptake and the removal percentage by **1** was calculated using Eqs. (1) and (2).

$$q = \frac{(C_0 - C_e)V}{W}$$
(1)
$$\eta = \frac{(C_0 - C_e)}{C_0} \times 100\%$$
(2)

Where q is the amount of MB absorbed by 1 (mg/g), C_0 and C_e are the initial and final MB concentrations (mg/L), respectively. V is the volume of the solution (L), W is the absorbent weight (g), and η is the removal percentage of dye from the solution.



Fig. S3 Effect of different initial concentration of MB and different amount of 1 as absorbent on the

adsorption amount

1.5.1 Adsorption kinetics

The pseudo-first-order model can be expressed as Equation (3):

$$\ln(q_{e} - q_{t}) = \ln(q_{e}) - k_{1}t$$
(3)

Where q_t (mg/g) and q_e (mg/g) represent the amount of adsorbed at t and equilibrium time, respectively. k_t (min⁻¹) represents the adsorption rate constant which is calculated from the plot of ln(q_e - q_t) against t.

The pseudo-second-order model can be expressed as Equation (4):

$$\frac{t}{q_{t}} = \frac{1}{k_{2}q_{e}^{2}} + \frac{1}{q_{e}}t$$
(4)

Where k_2 (g/(mg min)) is the pseudo-second-order rate constant of sorption. The plot of t/q_t vs. t should exhibit a liner relationship, and the q_e and k_2 can be obtained from the slop and the intercept of the plot, respectively.

Table S4 Parameters of kinetic model of MB with different concentration onto 1

		Pseudo-firs	t-order	Pseudo	-second-order		Experimental value
C_{θ} (mg/L)	k_1 (min ⁻¹)	$q_{\rm e}({\rm mg/g})$	R^2	k_2 (g/mg min ⁻¹)	$q_{\rm e}({\rm mg/g})$	R^2	of $q_{\rm e}$ (mg/g)
30 mg/L	0.0335	27.7	0.8583	5.27×10 ⁻³	54.3	0.9777	51.03

50 mg/L	0.0382	33.6	0.6312	2.37×10-3	107.5	0.9507	99.76
100 mg/L	0.0129	85.1	0.9128	1.99×10-3	158.7	0.9908	156.90

1.5.2 Adsorption isotherms

The effect of temperatures was studied with different MB solution initial concentration (300, 350, 400, 450, 500 mg/L) at different temperatures (298 K, 303 K, 308 K, 313 K and 318 K) using 0.1 g **1** and the adsorption isotherm was studied using Langmuir, Freundlich, and Dubinin - Radushevch (D-R) isotherm.

The adsorption isotherm models of Langmuir expressed as Equation (5):

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{q_0 b} \qquad (5)$$

Where C_e is equilibrium concentration of adsorbate (mg/L); q_e is the amount of adsorbate adsorbed (mg/g); q_0 is maximum adsorption capacity (mg/g); b is Langmuir constant (L/mg or L/mol).

Therefore, the q_0 and b can be calculated from slop and intercept of the plot, and the parameter values are listed in Table S5. The maximum capacity for MB of **1** in this study is satisfactorily fitted to the Langmuir maximum capacities as in Table S5. A dimensionless constant separation factor R_L can express the essential characteristics of the Langmuir isotherm, and R_L was calculated as Equation (6):

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

Where C_0 is the initial dye concentration (mg/L). R_L can be used to determine the feasibility of adsorption in a given concentration range over adsorbent.¹⁵ The R_L values of MB adsorbed onto **1** range from 0.0011 to 0.0051, which lie between 0 and 1, indicating that the adsorption of MB onto **1** is favorable.¹⁶

Freundlich isotherm can be used in adsorption of organic dye molecules from dilute solutions, and also be used to estimate the adsorption capacity of the adsorbent towards the adsorbate.¹⁷ It can be represented as Equation (7):

$$\log q_{e} = \log K_{f} + (1/n) \log C_{e}$$
 (7)

 K_{f} : the amount of adsorbed in per unit adsorbate; *n*: the Freundlich constant and 1/n indicates the surface heterogeneity of the adsorbent.

D-R isotherm can be represented as Equation (8):

$$\log q_e = \log q_m - K_{DR} \varepsilon^2 \quad (8)$$

 K_{DR} : the D-R constant related to the mean free energy of adsorption (mol²/J²); q_m : the theoretical saturation capacity (mol/g); ε : the polanyi potential (J/mol), which is related to the equilibrium concentration C_e (mg/L) as Equation (9):

$$\varepsilon^2 = RT(1+1/C_{\rho}) \qquad (9)$$

Where, R is the ideal gas constant (8.314 KJ/ (mol K)). And the mean free energy of adsorption (E, KJ/mol) means when 1 mol ion is transferred to surface of the solid from infinity in the solution, how much free energy change. Based on the determination coefficient shown in Table S5, Langmuir isotherm model showed a better fit with adsorption data than Freundlich and D-R isotherm models.

Table S5 Constants of Langmuir, Freundlich, and D-R isotherms for MB at the adsorption by 1 at different

	temperatures									
			Langmuir]	Freundlich			D-R	
Т	$q_{ m exp}$	$q_{ m max}$	b	R^2	K_F	1/ <i>n</i>	R^2	K_{DR}	Ε	R^2
(K)	(mg/g)	(mg/g)	(L/mg)		(L/g)				(KJ/mol)	
298	496.1	500.0	0.645	0.999	493.8	0.0002	0.0007	0.0005	0.031	0.018
303	501.0	526.3	0.904	0.999	461.3	0.0211	0.696	0.0004	0.035	0.695
308	558.6	555.6	0.947	0.997	552.3	0.0031	0.009	0.00002	0.158	0.004
313	626.6	625.0	1.454	0.999	597.1	0.0116	0.924	0.00002	0.158	0.876
318	680.3	666.7	1.666	0.991	605.1	0.0237	0.864	0.00003	0.129	0.976

1.5.3 Thermodynamic parameters

Adsorption enthalpy (ΔH^{0} , KJ/mol), adsorption free energy (ΔG^{0} , KJ/mol), and adsorption entropy (ΔS^{0} , [J/ (mol K)]) were determined using Eqs. (10) - (11):

$$\Delta G^{0} = -RT \ln K_{L} \qquad (10)$$
$$\ln K_{L} = \frac{\Delta S^{0}}{R} - \frac{\Delta H^{0}}{RT} \qquad (11)$$

Where *R* is the ideal gas constant [8.314 KJ/ (mol K)], *T* is the absolute temperature (K), K_L is the distribution coefficient at different temperatures. From Equation (10), ΔG^0 can be figured out, and the values of ΔS^0 and ΔH^0 can be obtained from the slope and the intercept of the linear plot of $\log K_L$ vs.1/*T*, respectively, as illustrated in Table S6.

Table S6 Thermodynamic parameters for sorption process of MB on 1 at different temperatures

T/K	$K_{\rm L}({\rm L}\cdot{\rm mg}^{-1})$	$\Delta G^0(\mathrm{kJ}\cdot\mathrm{mol}^{-1})$	$\Delta S^0 (J \cdot \text{mol}^{-1} \cdot K^{-1})$	$\Delta H^0 (\text{kJ} \cdot \text{mol}^{-1})$
298	110492.2	-31.33		
303	435444.0	-32.71	230.77	37.40

308	455959.0	-33.37	
313	700163.7	-35.02	
318	802299.6	-35.94	



Fig. S4 The picture of SPE setup, in which the original packing material C18 was replaced by 1

References

- 1 Bruker AXS, SMART, Version 5.611, Bruker AXS, Madison, WI, USA, 2000.
- 2 Bruker AXS, SAINT, Version 6.28, Bruker AXS, Madison, WI, USA, 2003.
- 3 SADABS, V2.03, Bruker AXS, Madison, WI, 2000.
- 4 G. M. Sheldrick, SHELX-97, Göttingen University, Germany, 1997.
- 5 (a) J. Ma, F. Yu, L. Zhou, L. Jin, M. Yang, J. Luan, Y. Tang, H. Fan, Z. Yuan and J. Chen, ACS Appl. Mat. Interfaces, 2012, 4, 5749; (b) L. Ai, C. Zhang, F. Liao, Y. Wang, M. Li, L. Meng and J. Jiang, J. Hazard. Mater., 2011, 198, 282.
- 6 E. Haque, J. W. Jun and S. H. Jhung, J. Hazard. Mater., 2011, 185, 507.
- 7 V. Basava Rao and S. Ram Mohan Rao, Chem. Eng. J., 2006, 116, 77.
- 8 V. Vadivelan and K. V. Kumar, J. Colloid Interface Sci, 2005, 286, 90.
- 9 C. Namasivayam and S. Sumithra, J. Environ. Manage., 2005, 74, 207.
- 10 A. Gürses, Ç. Doğar, M. Yalçın, M. Açıkyıldız, R. Bayrak and S. Karaca, J. Hazard. Mater., 2006, 131, 217.
- 11 S. Dutta, A. Bhattacharyya, A. Ganguly, S. Gupta and S. Basu, Desalination, 2011, 275, 26.
- 12 H. Chen, J. Zhao and G. Dai, J. Hazard. Mater., 2011, 186, 1320.
- 13 M. Al-Ghouti, M. Khraisheh, S. Allen and M. Ahmad, J. Environ. Manage., 2003, 69, 229.
- 14 M. T. Uddin, M. A. Islam, S. Mahmud and M. Rukanuzzaman, J. Hazard. Mater., 2009, 164, 53.
- 15 T. W. Weber and R. K. Chakravorti, AIChE J., 1974, 20, 228.
- 16 G. McKay, J. Chem. Technol. Biotechnol., 1982, 32, 759.
- 17 C. Wang, J. Zhang, P. Wang, H. Wang and H. Yan, Desalin. Water Treat., 2015, 53, 3681.