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Supplementary Information

A nickel-substituted Andserson-type arsenomolybdate used as adsorbents with high efficiency and selectivity toward methylene blue

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Table S1 Crystallographic data and structural refinements for Z1

Empirical formula	$C_6H_{24}As_6Cl_2Mo_6N_6NiO_{30}$
Formula weight	1923.18
Crystal system	Triclinic
Space group	*P-1*
a / Å	9.4190(6)
b / Å	10.8612(8)
c / Å	11.0976(8)
α /deg	95.6890(10)
β / deg	92.6460(10)
β / deg	90.8800(10)
V / Å	1128.28(14)
Z	1
D_c / g cm^{-3}	2.830
μ/ mm^{-1}	6.614
Limiting indices	–11 ≤ h ≤ 11
	-9 ≤ k ≤ 12
	–12≤ l ≤ 13
Measured reflections	5788
Independent reflections	3970
R_{int}	0.0817
Data/restrains/parameters	3970 / 0 / 287
GOF on F2	0.998
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.1189
R indices (all data)	R_1 = 0.0492, wR_2 = 0.1218

Table S2 Selected bond length (Å) for Z1

Mo(1)-O(4)	1.701(5)	Mo(1)-O(1)	1.712(4)	Mo(1)-O(7)	1.922(4)
Mo(1)-O(9)	1.930(4)	Mo(1)-O(10)	2.299(4)	Mo(1)-O(12)	2.337(4)
Mo(2)-O(2)	1.710(5)	Mo(2)-O(5)	1.711(4)	Mo(2)-O(7)#1	1.924(4)
Mo(2)-O(8)	1.926(4)	Mo(2)-O(11)	2.313(4)	Mo(2)-O(12)#1	2.322(4)
Mo(3)-O(3)	1.702(4)	Mo(3)-O(6)	1.706(4)	Mo(3)-O(9)	1.922(4)
Mo(3)-O(8)	1.933(4)	Mo(3)-O(11)	2.314(4)	Mo(3)-O(10)	2.334(4)
Ni(1)-O(12)	2.051(4)	Ni(1)-O(12)#1	2.051(4)	Ni(1)-O(10)	2.062(4)
Ni(1)-O(10)#1	2.062 (4)	Ni(1)-O(11)	2.066 (4)	Ni(1)-O(11)#1	2.066 (4)
As(1)-O(13)	1.790(4)	As(1)-O(14)	1.797(4)	As(1)-O(12)	1.806(4)
As(2)-O(15)	1.784(4)	As(2)-O(14)	1.789(4)	As(2)-O(11)	1.810(4)

As(3)-O(15)#1	1.789(3)	As(3)-O(13)	1.790(4)	As(3)-O(10)	1.809(4)

Table S3 Bond valence and Σs of Mo, Ni, and As in Z1

Bond	Valence	Bond	Valence	Bond	Valence	Atom	Σs
Mo(1)-O(4)	1.7123	Mo(1)-O(1)	1.6938	Mo(1)-O(7)	0.9602		
Mo(1)-O(9)	0.9397	Mo(1)-O(10)	0.3466	Mo(1)-O(12)	0.3128	Mo(1)	5.9654
Mo(2)-O(2)	1.6711	Mo(2)-O(5)	1.6984	Mo(2)-O(7)	0.9551		
Mo(2)-O(8)	0.9499	Mo(2)-O(11)	0.3337	Mo(2)-O(12)	0.3257	Mo(1)	5.9339
Mo(3)-O(3)	1.7402	Mo(3)-O(6)	1.7216	Mo(3)-O(9)	0.9602		
Mo(3)-O(8)	0.9321	Mo(3)-O(11)	0.3329	Mo(3)-O(10)	0.3153	Mo(1)	6.0023
Ni(1)-O(12)	0.3571	Ni(1)-O(12#1)	0.3571	Ni(1)-O(10)	0.3466		
Ni(1)-O(10#1)	0.3466	Ni(1)-O(11)	0.3429	Ni(1)-O(11#)	0.3429	Ni(1)	2.0932
As(1)-O(13)	0.9973	As (1)-O(14)	0.9786	As (1)-O(12)	0.9551	As(1)	2.9310
As(2)-O(15)	1.0136	As (2)-O(14)	1	As (2)-O(11)	0.9448	As(1)	2.9448
As(3)-O(15#1)	0.9973	As (3)-O(13#1)	0.9786	As (3)-O(10)	0.9551	As(1)	2.9310

Experimental Section

2.1 Materials

All reagents used in the present investigation were of analytical grade and utilized without further purification. $Na_2MoO_4{\cdot}2H_2O$, Na_3AsO_3, $NiCl_2{\cdot}6H_2O$, ethylenediamine, methyl orange (MO), rhodamine B (RhB) and methylene blue (MB) were purchased from Macklin reagent Inc. (P. R. China). Milli–Q water (Merck) was used to prepare all of the solutions, and a Millipore filter (0.22 μm) was used for all filtrations.

2.2 Synthesis of Z1

Dissolve 0.41 g (1.69 mmol) $Na_2MoO_4{\cdot}2H_2O$ in 14 mL distilled water, then add 0.32 g (1.69 mmol) Na_3AsO_3 and stir to dissolve as solution A.In a separate beaker, slowly add 2.8 mL (44.88 mmol) ethylenediamine dropwise to 0.33 g (1.39 mmol) $NiCl_2{\cdot}6H_2O$, and stir until clear to obtain solution B. Mix solutions A and B and stir for 15 min. Adjust the pH of the mixture to 6.10 using 4 mol/L HCl, transfer to a flask, and react in a 90°C water bath for 1 h.After cooling and filtering the mixed solution, allow the filtrate to evaporate at room temperature.Pale green rod-shaped crystals are obtained after 2 weeks, with a yield of 24%.

Intensity data of Z1 was collected on a Bruker Apex-2 diffractometer with a CCD detector using graphite monochromatized Mo Kαradiation (λ = 0.71073 Å) at 296 K. Data integration was performed using *SAINT*.[1] Routine Lorentz and polarization corrections were applied. Multiscan absorption corrections were performed using *SADABS*.[2] The structure was solved by direct methods and refined using full-matrix least squares on F2. The remaining atoms were found from successive full-matrix least-squares refinements on F2 and Fourier syntheses. All calculations were performed using the SHELXL–2018 program package.[3] No hydrogen atoms associated with the water molecules were located from the difference Fourier map. Positions of the hydrogen atoms attached to the carbon and nitrogen atoms were geometrically placed. All hydrogen atoms were refined isotropically as a riding mode using the default SHELXTL parameters. A summary of crystal data and structure refinements for Z1 is listed in Table S1.

2.3 UV-Vis spectra and stability

Z1 is dissolved in distilled water, and its pH is adjusted with HCl (6 mol L^{-1}) or NaOH (2 mol L^{-1}) solution. The UV-Vis spectra were recorded on a UV-3600 spectrometer from 190 to 600 nm.

2.4 Adsorption of methylene blue (MB)

The Z1 (5,10,15,30,55 mg) was mixed with 5 mL methylene blue solution (80μM) and stirred in the darkroom for 30 min. The UV–vis spectra of supernatant were recorded on a UV–3600 spectrometer from 200 to 900 nm. The IR spectra of Z1 before and after incubated by MB were recorded on a NICOLET iS10 spectrometer in the range of 400–4000 cm^{-1}.

2.5 Adsorption of Methylene Blue in Binary Mixed Dyes

Z1 (20 mg) was mixed with equal volumes of MB (80 μM)-MO (80 μM) mixture (2.5 ml MB + 2.5 ml MO), MB (80 μM)-RhB (80 μM) mixture (2.5 ml MB + 2.5 ml MO), MO (40 μM) solution (5 ml) and RhB (40 μM) solution (5 ml), respectively, and stirred for 30 min. After centrifugation, the supernatant was taken, and the UV spectrum of the supernatant was measured by UV–3600 in the wavelength range of 200–900 nm.

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[1] S. Bruker, AXS Inc., Madison WI. 2007.
[2] N. E. Brese and M. O'Keeffe, Acta Crystallogr B Struct Sci, 1991, 47, 192–197.
[3] G.M. Sheldrick, SHEXTL–2018, Programs for Crystal Structure Refinements, University of Göttingen, Germany, 2018.

A 30 mg sample of Z1 crystals was ground and subjected to ultrasonic fragmentation, followed by the addition of 80 μM MB (5 mL) solution with thorough mixing. After the suspension clarified, centrifugation was performed, and the resulting pellet was transferred to a second tube containing fresh 80 μM MB solution (5 mL). This process was repeated iteratively until no significant fading of the solution color was observed, indicating saturation of dye adsorption. Samples were collected for elemental analysis by using Shimadzu ICP-MS 2030 inductively coupled plasma-mass spectrometer. The above experiments were performed in triplicate under the same conditions.