Supporting Information

Functionalized polyoxometalate–based metal–organic cuboctahedra for selective adsorption toward cationic dyes in aqueous solution

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Contents

Materials and Physical Measurements

All chemical reagents were purchased from commercial sources and used without further purification. PXRD patterns were recorded ranging from 5° to 50° at room temperature on a Siemens D5005 diffractometer with Cu Kα (λ = 1.5418 Å). Thermogravimetric analysis (TGA) of the samples was performed using a PerkinElmer TG-7 analyzer heated from 25 °C to 800 °C at the heating rate of 10 °C·min^{-1} under a dry nitrogen flow. Elemental analyses (CHN) were conducted on a PerkinElmer 2400 CHN Elemental analyzer. The FT-IR spectra were measured on an Alpha Centaurt FT/IR spectrophotometer in the range 4000−400 cm^{-1} using KBr pellets. The UV-Vis spectra of the dye solutions were measured at room temperature using a VU-2550 UV-Vis spectrophotometer.

Table S1. Crystallographic data for **VMOP-18**.

Empirical formula	$C_{164}H_{284}N_{16}O_{124}V_{28}$
Formula weight	5890.37

Crystal system	Cubic
Space group	*I-43m*
Temperature	173 K
Wavelength	1.54178 Å
Unit-cell dimensions	a = b = c =27.2524(3) Å α = β =γ = 90°
Volume	20240.2(7) $Å^3$
Z	2
Density (calculated)	0.967 g/cm^3
Absorption coefficient	5.666 mm^{-1}
F(000)	6032
Limiting indices	-17<=h<=30, -23<=k<=22, -11<=l<=30
Theta range for data collection	5.132-63.676°
Reflections collected	13432
Independent reflections	2894 [R(int) = 0.1630]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3467 / 263 / 132
Goodness-of-fit on F^2	0.992
Final R indices [I > 2sigma(I)]	R1 = 0.1478, wR2 = 0.4155
R indices (all data)	R1 = 0.2000, wR2 = 0.4837
Largest diff. peak and hole	0.48 and -0.65 eA^{-3}

Table S2. Crystallographic data for **VMOP-19**.

Empirical formula	$C_{156}H_{252}N_{20}O_{108}S_4V_{24}$
Formula weight	5486.56
Crystal system	Cubic
Space group	*I-43m*
Temperature	173.02 K
Wavelength	0.71073 Å
Unit-cell dimensions	a = b = c =27.216(2) Å α = β =γ = 90°
Volume	20160(4) $Å^3$
Z	2
Density (calculated)	0.904 g/cm^3
Absorption coefficient	0.603 mm^{-1}
F(000)	5616
Limiting indices	-32<=h<=25, -23<=k<=32, -21<=l<=29
Theta range for data collection	2.59-25.03°
Reflections collected	20589
Independent reflections	3265 [R(int) = 0.1932]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3270 / 360 / 128
Goodness-of-fit on F^2	0.943

Final R indices [I > 2sigma(I)]	R1 = 0.1039, wR2 = 0.2400
R indices (all data)	R1 = 0.2107, wR2 = 0.2917
Largest diff. peak and hole	0.48 and -0.53 eA^{-3}

Table S3. Bond Lengths for**VMOP-18.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
V1	V1[1]	3.066(10)	O4	V1[1]	1.969(14)
V1	O1	1.964(11)	O4	C9	1.30(4)
V1	O2	1.929(14)	O5	C1	1.255(11)
V1	O3	1.549(17)	O6	V1[4]	2.302(15)
V1	O4	1.969(14)	N1	C6	1.305(13)
V1	O5	2.047(12)	N1	C6[5]	1.305(13)
V1	O6	2.302(15)	C1	O5[4]	1.255(11)
V2	O6	1.46(2)	C1	C2	1.488(13)
V2	O6[2]	1.46(2)	C2	C3	1.248(18)
V2	O6[3]	1.46(2)	C2	C3[4]	1.248(18)
V2	O7	1.46(3)	C3	C4	1.41(2)
O1	V1[4]	1.2987(5)	C4	C5	1.335(19)
O1	C7	1.55(5)	C5	C4[4]	1.335(19)
O2	V1[1]	1.929(14)	C5	C6	1.43(3)
O2	C8	1.39(4)	C6	N1[6]	1.305(13)

The symmetry codes:[1]+X,+Z,+Y; [2]+Y,+Z,+X; [3]+Z,+X,+Y; [4]+Z,+Y,+X; [5]+Z,1-X,1-Y; [6]1-Y,1-Z,+X

Table S4. Bond Lengths for**VMOP-19.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
V1	O1	2.002(11)	O2	C10	1.535(19)
V1	O2	1.978(7)	O4	C9	1.53(2)
V1	O3	1.517(13)	O6	C8	1.48(2)
V1	O4	1.917(9)	N1	C2[3]	1.359(9)
V1	O5	2.320(12)	N1	C2	1.360(9)
V1	O6	1.961(10)	C2	C3	1.365(13)
S1	O5	1.480(15)	C3	C4[4]	1.352(10)
S1	O5[1]	1.480(15)	C3	C4	1.352(10)
S1	O5[2]	1.480(15)	C4	C5	1.352(11)
S1	O7	1.352(18)	C5	C6	1.355(10)
O1	C7	1.288(13)	C6	C7	1.46(3)

The symmetry codes: [1]1-Y,+Z,1-X; [2]1-Z,1-X,+Y; [3]1+Z,1-X,-Y; [4]1-Y,1-X,+Z

Table S5. BVS results for the vanadium ions in **VMOP-18**.

Atom	BVS calc. for V(Ⅳ)	BVS calc. for V(Ⅴ)
V1	**4.24**	4.46
V2	**4.09**	4.41
V3	**4.31**	4.51
V4	**4.18**	4.30
V5	**4.14**	4.36
V6	**4.15**	4.38

V7	4.82	**5.07**

Table S6. BVS results for the vanadium ions in **VMOP-19**.

Atom	**BVS calc. for V(Ⅳ)**	**BVS calc. for V(Ⅴ)**
V1	**4.006**	4.264
V2	**4.482**	4.769
V3	**4.006**	4.264
V4	**4.482**	4.769
V5	**4.006**	4.264
V6	**4.482**	4.769

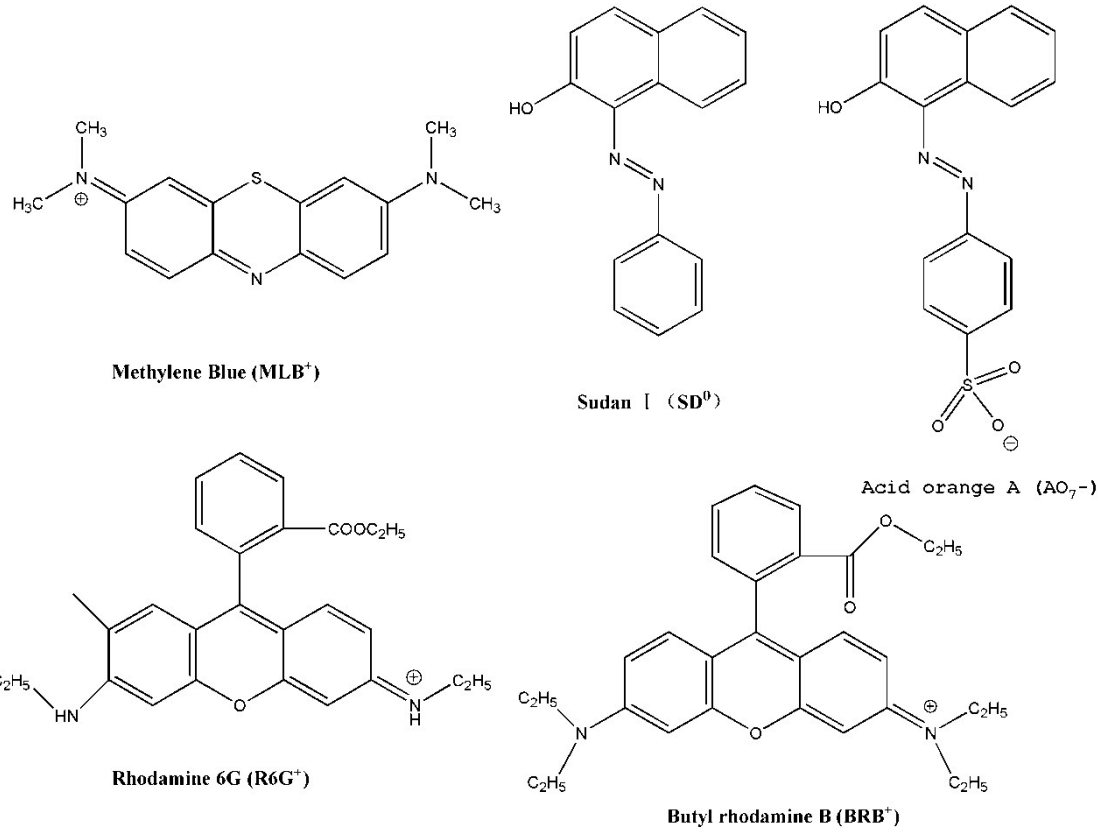

Figure S1. Chemical structures of dyes used in this study.

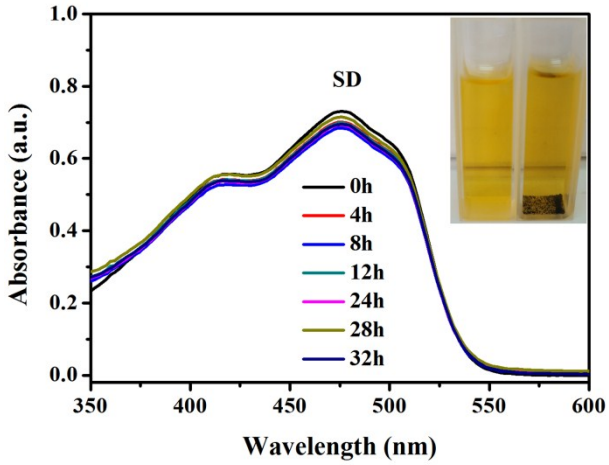

Figure S2. Temporal evolution of UV-vis absorption spectra for **SD^0**.

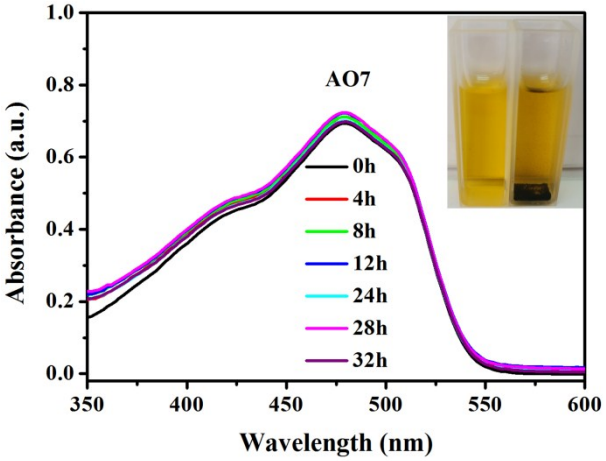

Figure S3. Temporal evolution of UV-vis absorption spectra for **AO^-.**

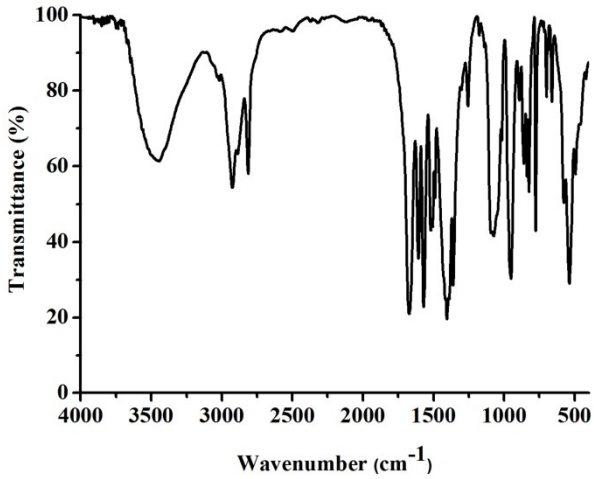

Figure S4. IR spectra of **VMOP-18.**

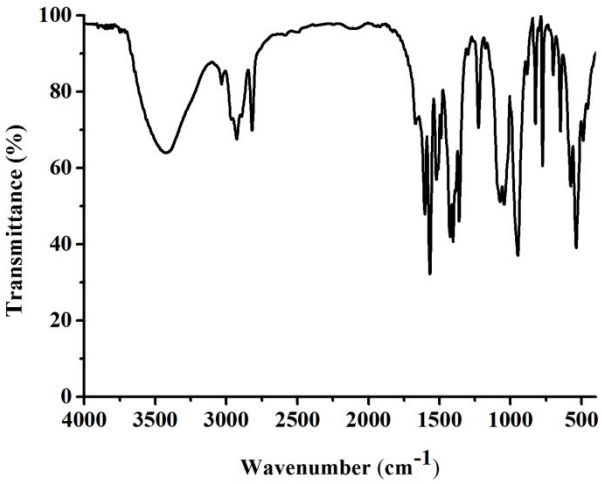

Figure S5. IR spectra of **VMOP-19.**

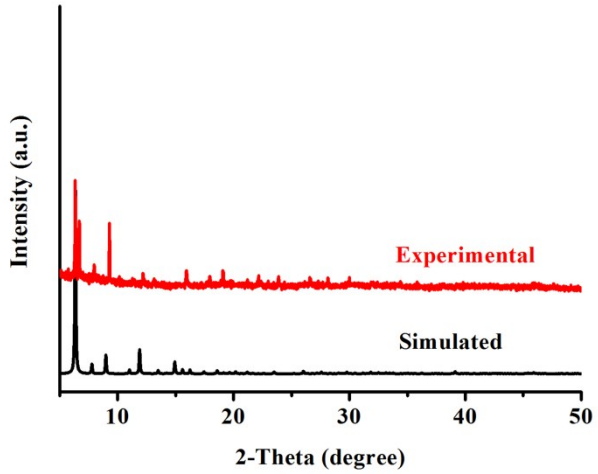

Figure S6. The experimental and simulated powder X-Ray diffraction patterns for**VMOP-18.**

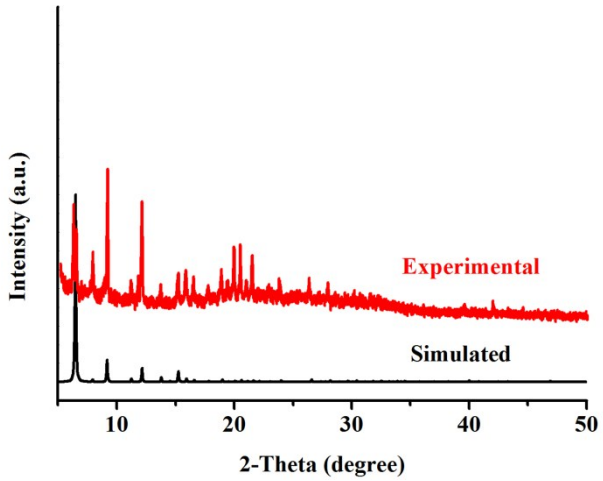

Figure S7. The experimental and simulated powder X-Ray diffraction patterns for**VMOP-19**.

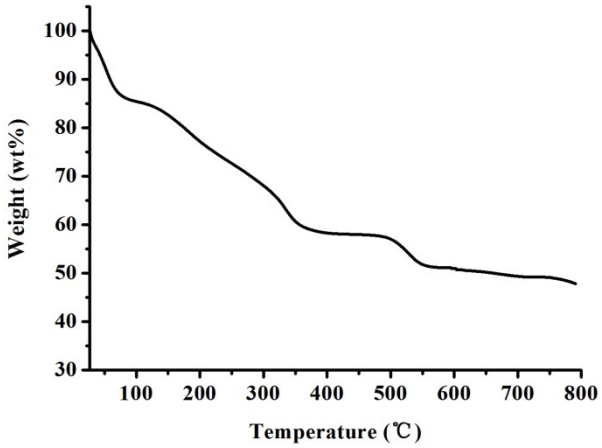

Figure S8. TGA curves of **MOP-18.**

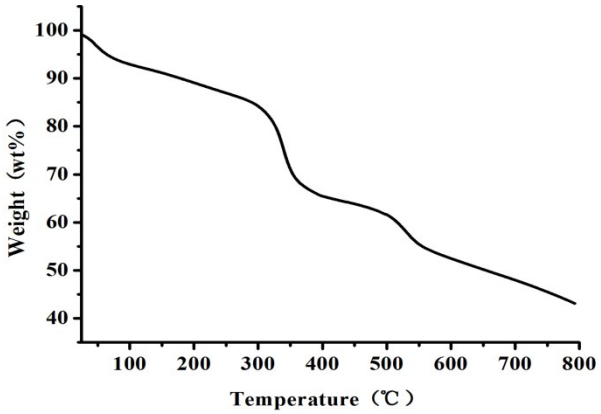

Figure S9. TGA curves of **MOP-19.**