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Effects of ethylenediamine in the formation of macro-, micro, and nanostructures based on $[W^{VI}(Cat)_2O_2]^{2-}$

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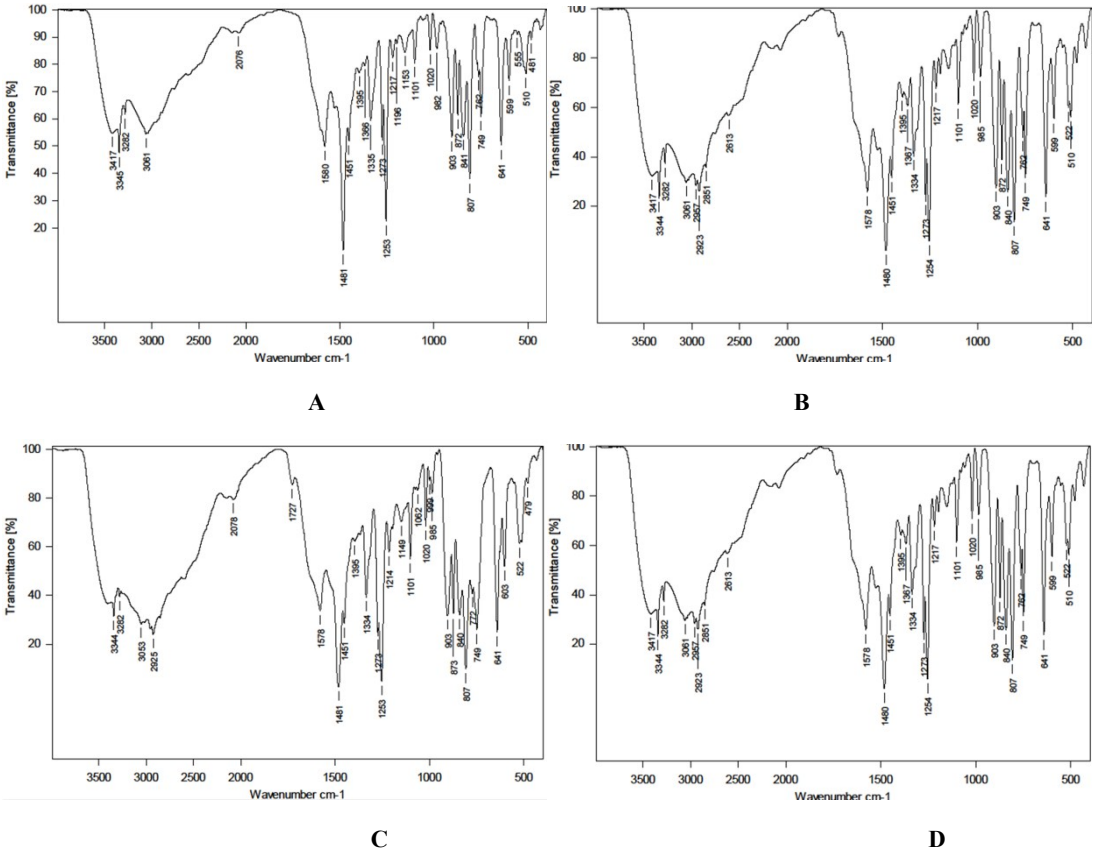

Figure S1. IR spectra of crystal 1 (A) and its nanostructure (C), and crystal 2 (B) and its nanostructure (D).

Using a Bruker EQUINOX55 spectrometer, KBr disks of compounds 1 and 2 were scanned to obtain the infrared spectra, from which the bonding patterns of compounds 1 and 2 can be implied. IR spectra of compounds 1 and 2 are summarized in Table S1. We can see that the data are all in the reasonable range, which is consistent with the results of X-ray diffraction. The IR spectra of the nanostructures are almost the same as the IR spectra of the bulk crystals.

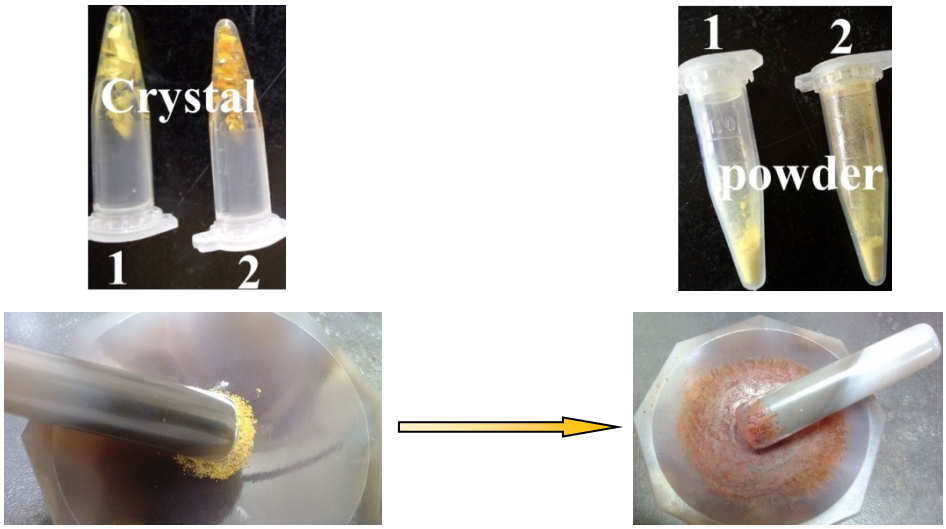

Figure S2. Through continuous grinding, the golden yellow powder of crystals change into dark yellow, which means the powder has been disassembled into nano-scale.

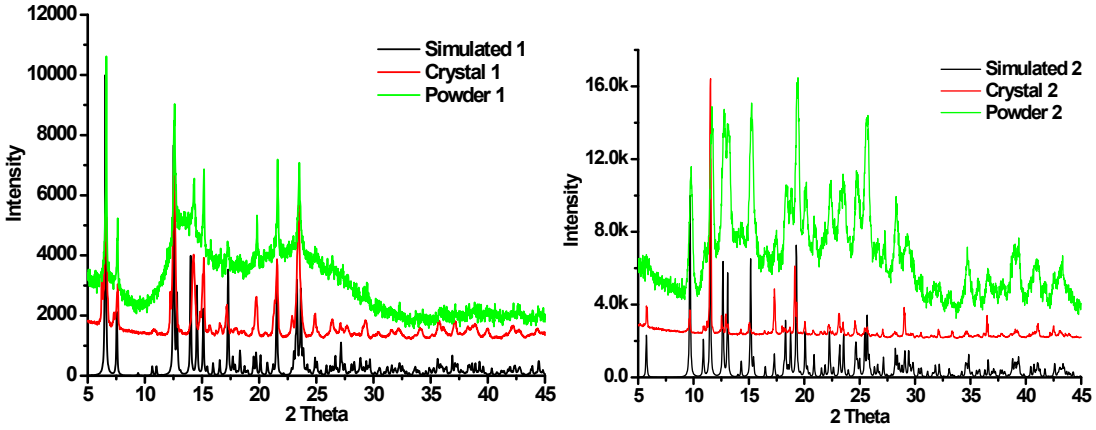

Figure S3. (A) Experimental and simulated powder X-ray diffraction patterns for the complex 1. The black line represents the simulated curves by Mercury from the CIF file (Supporting Information) of the single crystal structure, the red line represents the curve of the crystal, and the green line represents the curve of the nanostructure. (B) Experimental and simulated powder X-ray diffraction patterns for the complex 2. The black line represents the simulated curves by Mercury from the CIF (Supporting Information) file of the single crystal structure, the red line represents the curve of the crystal, and the green line represents the curve of the nanostructure.

UV-vis spectra of the complexes

Figure S4 (A) is the UV-vis spectra of the complex **1** and complex **2**, quite similar electronic feature from which can be seen. Complex**1** exhibited peak at 280 nm can be assigned to the transfer of the electrons of the coordinated catechol ligand from n-π to n-π^*, and the signal at 328

nm associated with the transition of the electrons between the d orbital to the catechol ligand. The spectra of the complex2 presented peaks at 286 nm, and 322 nm.

Figure S4 (B) is the CV curve of the complex **1** and complex **2**, quite similar electrochemical properties of the complexes can be seen from it. Complex**1** exhibited oxidize electronic potential peak at +0.414V and deoxidation electronic potential peak at +0.086V and the peak of the complex2 presented at +0.382V, and +0.100 nm.

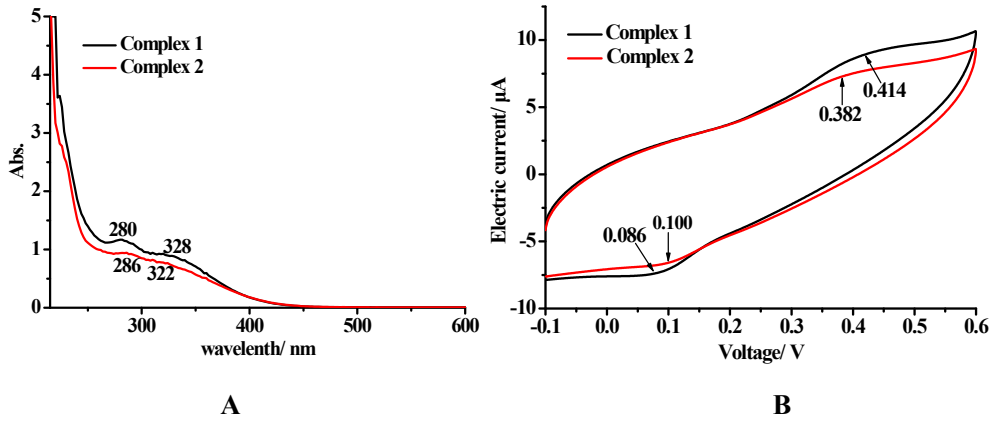

Figure S4. (A) The UV-vis spectra (A) and the CV-curve (B) of the complex1 and complex2

The UV-vis spectra test of complex1 and complex2 was carried in water with 10^{-4}mM, PH=7, scanning range from 600 to 200nm. (B) The electrochemical properties of complexes **1**and **2** were studied by cyclic voltammetry (CV) at a glassy carbon electrode (GCE) under an envelope of purified nitrogen in PBS buffer solution containing 80mmM complex at 25 °C in the potential range of –0.1 to +0.6 V.

Table S1. Characteristic IR data (cm^{-1}) of complex 1 and 2

Assignment	Complex 1	Complex 2
ν Mo-O	841,807,	836,807
ν Mo=O	903,872	906,873
ν =CH	3061	3056
ν C=C	1580, 1451	1592,1452
ν C-O	1273, 1253	1273,1253
ν N-H	3345	3338
γ =C-H	749, 641	749,640

Table S2.Crystal data and structure refinement of crystals 1 and2

crystal	1	2
Empirical formula	C17H30N5O6W	C16H26N4O6W
Formula mass	584.31	554.26
Calcd density, Mg/m3	1.858	1.857
Crystal system	Monoclinic	Monoclinic
a/Å	7.1077(6)	16.5081(7)
b/Å	30.934(3)	23.4259(8)
c /Å	9.8061(8)	10.2617(3)
α /°	90	90
β /°	102.769(2)	92.433(3)
γ /°	90	90
Vol,Å 3	2089.1(3)	3964.8(2)
Temperature (K)	293(2)	293(2)
space group	P2(1)/c	P2(1)/c
Z	4	8
Radiation type	MoK\a	CuK\a
Absorption coefficient, μ/mm-1	11.152	11.152
No. of reflections measured	2606	5775
No. of independent reflections	2844	4900
Rint	0.0962	0.085
F(000)	1156	2176
Final R1 values (I > 2σ(I))	0.0577	0.0840
Final wR(F2) values (I > 2σ(I))	0.1067	0.1897
Final R1 values (all data)	0.0820	0.1131
Final wR(F2) values (all data)	0.1171	0.2009
Goodness of fit on F2	1.087	1.178
completeness	100%	99.9%
CCDC NO.	1028585	1028584

Table S3. Selected bond lengths (Å) and angles (deg) for crystal1 and 2

Selected Bond Lengths (Å)			Selected Angles (deg)		
crystal	1	2	crystal	1	2
W1-O1	2.11(1)	1.970(6)	O1-W1-O2	76.4(5)	75.6(3)
W1-O2	1.99(1)	2.133(6)	O1-W1-O3	86.1(5)	89.6(3)
W1-O3	2.01(1)	2.130(7)	O1-W1-O4	85.5(5)	158.9(3)
W1-O4	2.13(1)	1.982(6)	O1-W1-O5	91.7(5)	102.2(3)
W1-O5	1.77(1)	1.740(8)	O1-W1-O6	163.8(6)	90.8(3)
W1-O6	1.74(1)	1.737(6)	O2-W1-O3	158.6(5)	80.3(3)
O1-C1	1.35(2)	1.37(1)	O2-W1-O4	90.2(5)	86.8(3)
O2-C2	1.36(2)	1.31(1)	O2-W1-O5	104.9(5)	91.3(3)
N4(1)-C28(13)	1.35(3)	1.50(1)	O2-W1-O6	89.1(6)	162.2(3)
N8(5)-C32(17)	1.52(3)	1.43(1)	O3-W1-O5	87.6(5)	163.4(3)
C1-C2	1.41(3)	1.42(2)	O3-W1-O6	106.3(6)	88.3(3)
C1-C6	1.38(3)	1.37(2)	O4-W1-O5	163.7(5)	89.4(3)
C3-C4	1.38(3)	1.41(2)	O4-W1-O6	87.4(6)	103.8(3)
C25(13)-C26(14)	1.54(3)	1.47(1)	O5-W1-O6	98.9(6)	103.0(3)
C27(15)-C28(16)	1.49(4)	1.51(1)	W1-O1-C1	115(1)	120.0(6)
N1-H1A	0.89	0.889	W1-O2-C2	119(1)	115.3(6)
C3-H3	0.93	0.93	W1-O3-C7	118(1)	114.3(6)
C26(13)-H26(13)A	0.97	0.97	W1-O4-C8	115(1)	119.4(6)

Table S4 Selected hydrogen bond lengths (Å) and angles (deg) for crystal1 and 2

Complex	N-H…O	Å	N…O	Å	<N-H…O	deg
1	N1-H1A…O5	1.86	N1…O5	2.741(11)	<N1-H1A…O5	169.2
	N1-H1B…O2	2.41	N1…O2	3.291(12)	<N1-H1B…O2	169.1
	N3-H3B…O6	2.06	N3…O6	2.915(12)	<N3-H3B…O6	159.6
	N4-H4A…O5	2.48	N4…O5	3.312(13)	<N4-H4A…O5	155.9
	N4-H4B…O1	2.39	N4…O1	3.089(12)	<N4-H4B…O1	135.7
2	N8-H8B…O4	2.02	N8…O4	2.85(4)	<N8-H8B…O4	154.6
	N8-H8A…O10	2.17	N8…O10	3.01(3)	<N8-H8A…O10	156.1
	N7-H7B…O1	2.30	N7…O1	2.97(4)	<N7-H7B…O1	131.8
	N6-H6B…O3	2.13	N6…O3	3.00(3)	<N6-H6B…O3	167.0
	N6-H6A…O9	2.00	N6…O9	2.87(3)	<N6-H6A…O9	164.8
	N5-H5B…O7	2.20	N5…O7	2.96(4)	<N5-H5B…O7	143.6
	N4-H4B…O2	2.25	N4…O2	3.05(4)	<N4-H4B…O2	149.5
	N3-H3B…O5	2.05	N3…O5	2.83(3)	<N3-H3B…O5	145.3
	N3-H3A…O11	1.85	N3…O11	2.72(4)	<N3-H3A…O11	165.4
	N2-H2B….O8	2.12	N2….O8	2.98(4)	<N2-H2B….O8	161.6
	N1-H1B….O6	2.21	N1….O6	2.80(4)	<N1-H1B….O6	123.3
	N1-H1A…O12	1.94	N1…O12	2.81(4)	<N1-H1A…O12	164.3