Supporting Information for

Anion-Selectivity of Cationic Cluster-Organic Nanosphere Based on Nest-shaped $[MS_4Cu_3X_3]$ Clustermonomer with Ditopic Ligand

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Experimental Details

Syntheses of $\{[(WS_4Cu_3)_2(L)_6](CuCl_3)(H_2O)_8\}$ (1) and $\{[(MoS_4Cu_3)_2(L)_6](CuCl_3)(H_2O)_8\}$ (2): A well-ground mixture of $[NH_4]_2[WS_4]$/$[NH_4]_2[MoS_4]$ (174/130mg, 0.5 mmol), CuCl (198mg, 2.0mmol) and Et_4NCl (83mg, 0.5mmol) was added to a mixture of DMF/CH_3CN (15 mL; v/v 1:2). After stirring for 10 h, the filtrate was layered onto 10 mL DMF solution of L (420mg, 2.0 mmol) with the DMF/CH_3CN (5mL; v/v 1:1). Red prism-shaped single crystals suitable for X-ray diffraction were obtained several days later. Yields of the reactions were ca. 60 % and 33 % based on L ligand. Elemental analysis calcd (%) for **1** ($C_{72}H_{76}Cl_3Cu_7N_{24}O_8S_8W_2$): C, 33.48; H, 2.94; N, 13.02. Found: C, 33.26; H: 3.08; N, 13.10. IR (KBr, cm^{-1}): 3441(s), 3097(s), 1661(s), 1613(s), 1510(s), 1385(w), 1316(w), 1288(m),1264(m), 1109(m), 1067(m), 1001(m), 931(w), 786(w), 748(m), 650(m), 621(w), 434(w). Elemental analysis calcd (%) for **2** ($C_{72}H_{76}Cl_3Cu_7N_{24}O_8S_8Mo_2$); C, 35.96; H, 3.18; N, 13.98. Found: C, 32.82; H, 2.96; N, 14.17. IR (KBr, cm^{-1}): 3427(s), 3098(s), 1664(s), 1612(s), 1510(s), 1384(m), 1317(m), 1288(m), 1263(m), 1109(m), 1067(s), 1001(m), 931(w), 783(w), 748(m), 650(m), 621(w), 447(w).

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Synthesis of {[$(WS_4Cu_3)_2(L)_6$]($CuBr_3$)(H_2O)$_7$} (3): A well-ground mixture of $[NH_4]_2[WS_4]$ (174 mg, 0.5 mmol), CuBr (287 mg, 2.0 mmol) and Et_4NBr (105 mg, 0.5 mmol) was added to a mixture of DMF/CH_3CN (15 mL; v/v 1:2). After stirring for 10 h, the filtrate was layered onto 10 mL DMF solution of L (420 mg, 2.0 mmol) with the DMF/CH_3CN (5 mL; v/v 1:1). Red prism-shaped single crystals suitable for X-ray diffraction were obtained several days later. Yield of the reaction was ca. 27 % based on L ligand. Elemental analysis calcd (%) for **3** ($C_{72}H_{74}Br_3Cu_7N_{24}O_7S_8W_2$): C, 32.07; H, 2.77; N, 12.47. Found: C, 32.12; H: 2.81; N, 12.53. IR (KBr, cm^{-1}): 3442(s), 3105(w), 2922(w), 1665(s), 1615(s), 1509(s), 1380(w), 1316(w), 1285(w),1266(m), 1108(m), 1069(m), 1001(w), 956(w), 777(w), 748(m), 683(m), 651(w), 449(w).

Physical Measurements.

Crystallographic measurements were carried out using a Bruker SMART APEX-CCD diffractometer, φ-ω scans, graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å), SMART for data collection, SAINT for data integration, and SADABS for absorption correction. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL (version 6.10) package of crystallographic software. The IR spectra were obtained as KBr pellets on a VECTOR 22 spectrometer. Elemental analyses were performed on a Perkin-Elmer model 240C analyzer. UV-Vis measurements were conducted on a RF-5301PC SHIMADZU. Luminescent spectra were recorded with a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature. The morphology and crystal lattice of the samples were characterized by field-emission scanning electron microscopy (FESEM; JEOL, JSM-6700F with an accelerating voltage of 5 kV).

Table S1. Crystallographic Data and Structure Refinement Details for compounds **1-3**.

Compound	**1**	**2**	**3**
Formula	$C_{72}H_{76}Cl_3Cu_7N_{24}O_8S_8W_2$	$C_{72}H_{76}Cl_3Cu_7N_{24}O_8S_8Mo_2$	$C_{72}H_{74}Br_3Cu_7N_{24}O_7S_8W_2$
Formula Weight	2580.88	2405.06	2696.24
Crystal System	Hexagonal	Hexagonal	Hexagonal
Space group	$P6_3/m$	$P6_3/m$	$P6_3/m$
a = b (Å)	16.9317(8)	16.817(2)	17.0636(14)
c (Å)	22.0782(19)	22.226(6)	22.372(3)
V (Å^3)	5481.4(6)	5444.0(18)	5641.3(10)
Z	2	2	2
D_c (g cm^{-3})	1.564	1.467	1.587
μ(MoKa)(mm^{-1})	3.698	1.843	4.584
Theta Min-Max (Deg)	2.31, 26.00	1.67, 26.00	1.65, 25.99
Tot, Uniq. Data	29504, 3692	28792, 3675	30597, 3801
R(int)	0.0864	0.0488	0.0683
Observed data [I>2sigma(I)]	2798	3184	3059
Nref, Npar	3692, 204	3675, 204	3801, 232
R, wR2(all data)	0.0730, 0.0960	0.0653, 0.1320	0.0837, 0.1186
S	1.044	1.094	1.077
Max. and Av. Shift/Error	0.000, 0.000	0.000, 0.000	0.000, 0.000
Min, Max Resd Dens (e·Å^{-3})	-1.883, 1.557	-0.690, 0.667	-1.138, 0.548

Table S2 Selected Bond Distances (Å) and Angles (deg) for compounds **1**–**3**.

Compound 1			
Cl1 – Cu2	2.2388(19)	Cu1 - N1	1.952(5)
Cu1 – N3	2.076(5)	Cu1 - S2^{a}	2.2683(14)
Cu1 –S1	2.2705(10)	Cu2 – N3	1.990(5)
Cu2 – S1	2.2801(16)	Cu1 – W1	2.6753(7)
S1 – W1	2.263(2)	Cu2 – Cl1^{b}	2.239(2)
S2 – W1	2.1622(13)		
N1– Cu1– S2^{a}	113.81(17)	N3 – Cu1 – S2^{a}	111.74(17)
N1 – Cu1 – S1	116.59(18)	N3 – Cu1– S1	111.31(15)
S2^{a} – Cu1 – S1	104.77(7)	N1 – Cu1 – W1	134.96(16)
N3 – Cu1 – W1	126.14(18)	S2^{a} – Cu1 – W1	51.06(4)
S1 – Cu1 – W1	53.71(6)	Cl1^{a} – Cu2 – Cl1	120.000(1)
W1 – S1 – Cu1	72.33(6)	Cu1^{b} – S1 – Cu1	111.21(6)
W1 – S2 – Cu1^{b}	74.25(4)	S2 – W1 – S2^{a}	110.29(3)
S2 – W1 – S1	108.64(4)	S2 – W1 – Cu1^{b}	54.69(4)
S2 – W1 – Cu1	123.97(4)	S1– W1– Cu1	53.964(16)
Cu1^{b} – W1 – Cu1	88.90(2)	S2 – W1 – Cu1^{a}	125.70(4)
Compound 2			
Cl1 – Cu2	2.2233(14)	Cu1 – N1	1.963(3)
Cu1 – N3	2.083(4)	Cu1 – S2^{a}	2.2616(13)
Cu1 –S1	2.2310(8)	Cu1 – Mo1	2.6403(7)
Mo1 – S1	2.2455(19)	Mo1 – S2	2.1304(10)
N1 – Cu1 – N3	97.45(15)	N1 – Cu1 – S1	116.73(11)
N3 – Cu1 – S1	111.27(10)	N1 – Cu1 – S2^{a}	114.27(11)
N3 – Cu1 – S2^{a}	112.39(11)	S1 – Cu1 – S2^{a}	104.91(5)
N1 – Cu1 – Mo1	135.68(9)	N3 – Cu1 – Mo1	126.79(11)
S1 – Cu1 – Mo1	54.11(5)	S2^{a} – Cu1 – Mo1	50.80(3)

Cl1^{a} – Cu2 – Cl1	120.000(1)	S2 – Mo1 – S2^{a}	109.99(3)
S2 – Mo1 – S1	108.95(3)	S2 – Mo1 – Cu1	124.10(3)
S2^{a} – Mo1 – Cu1	55.36(3)	S1 – Mo1 – Cu1	53.604(17)
S2 – Mo1 – Cu1	125.87(3)	S2^{a} – Mo1 – Cu1^{a}	124.10(3)
Cu1 – Mo1 – Cu1^{a}	88.39(2)	Cu1 – S1 – Cu1^{a}	111.17(4)
Cu1 – S1 – Mo1	72.29(5)	Mo1 – S2 – Cu1^{b}	73.84(4)
Compound 3			
Cu2 – Br1	2.3308(16)	Br1 – Br1^{b}	2.677(2)
N1 – Cu1	2.053(5)	N3 – Cu1	1.998(5)
S1 – W1	2.1953(15)	S1 – Cu1	2.3087(17)
S2 – W1	2.172(3)	S2 – Cu1	2.2594(10)
Cu1 – W1	2.6883(8)	W1 – S1^{a}	2.1953(15)
W1 – Cu1^{a}	2 .6883(8)		
Br1 – Cu2 – Br1^{c}	180.00(7)	Br1^{d} – Cu2 – Br1	109.89(4)
Br1^{b} – Cu2 – Br1	70.11(4)	Cu2 – Br1 – Br1^{b}	54.946(17)
W1 – S1 – Cu1	73.24(5)	W1– S2 – Cu1	74.67(7)
Cu1^{e} – S2 – Cu1	113.28(6)	S2 – Cu1 – W1	51.18(7)
N3 – Cu1 – N1	100.97(19)	N3 – Cu1 – S2	110.89(14)
N1 – Cu1 – S2	114.65(14)	N3 – Cu1 – S1	114.92(15)
N1 – Cu1 – S1	113.29(14)	S2 – Cu1 – S1	102.62(8)
N3 – Cu1 – W1	127.99(14)	N1 – Cu1 – W1	131.01(13)
S1 – Cu1 – W1	51.44(4)	S1 – W1 – Cu1^{f}	124.71(4)
S2 – W1 – S1	109.46(4)	S1 – W1 – Cu1	55.32(4)
S2 – W1 – Cu1	54.150(18)	Cu1^{a} – W1 – Cu1	89.17(3)
S1^{a} – W1 – Cu1	125.80(4)		

Symmetry transformations used to generate equivalent atoms:

a = -*y* + 1, *x* - *y* + 1, *z*; b = -*x* + *y*, -a*x* + 1, *z*. (compound **1**)

a = -*y* + 1, *x* - *y* + 1, *z*; b = -*x* + *y*, -*x* + 1, *z*. (compound **2**)

a = -*y* + 1, *x* - *y* + 1, *z*; b = *y* + 1, -*x* + *y* + 1, -z + 1; c = -*x* + 2, -*y*, -*z* + 1; d = –*y* + 1, *x* –y - 1, z; e = -*x* + *y*, -*x* + 1, *z*; f = –*y* + 1, *x* – *y* + 1, *z*. (compound **3**)

Table S3. Hydrogen-Bonding Geometry (Å, °) for compounds **1** and **2**.

D-H···A	d(H···A)	∠D-H···A
Complex **1**		
C3-H3···Cl1^{a}	2.54	147
C7-H7···Cl1^{a}	2.66	161
C10-H10···Cl1^{a}	2.65	146
C14-H14···Cl1^{a}	2.70	177
C9-H9···S2^{b}	2.62	173
Complex **2**		
C3-H3···Cl1^{a}	2.55	148
C7-H7···Cl1^{a}	2.64	161
C10-H10···Cl1^{a}	2.65	146
C14-H14···Cl1^{a}	2.69	178
C9-H9···S2^{b}	2.62	174

Symmetry codes: (a) - *x* + *y*, 1- *x*, *z*. (b) - *x*, 1 - *y*,1 - *z*.

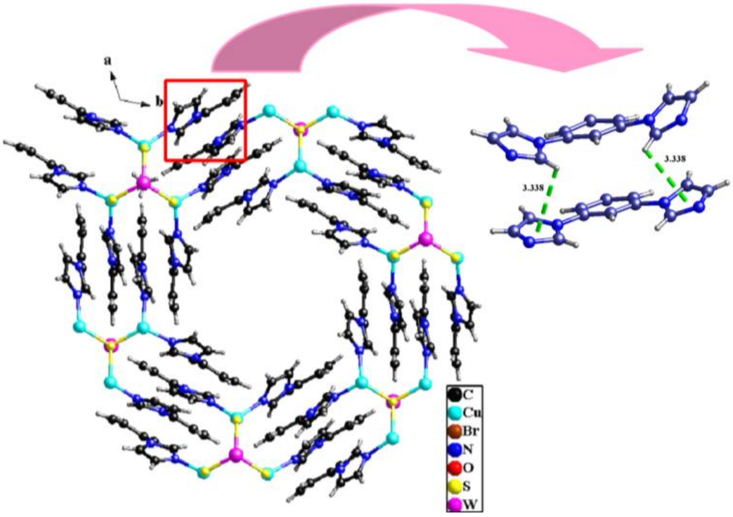

Fig. S1. Three dimensional supramolecular structure of **3** via the C-H…π interactions.

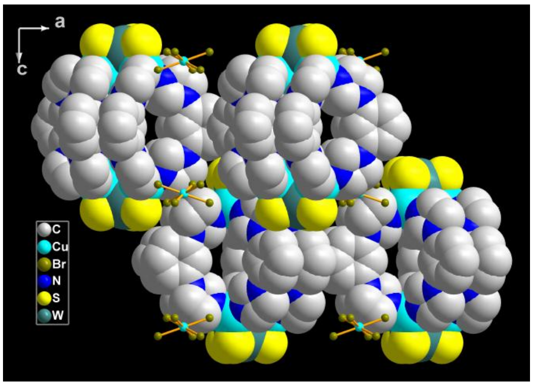

Fig. S2. The crystal packing of compound **3** along 010 plane is shown (The anion $[CuBr_3]^{2-}$ guests are shown in ball-stick mode, hydrogen atoms and solvent water molecules are omitted for calarity).

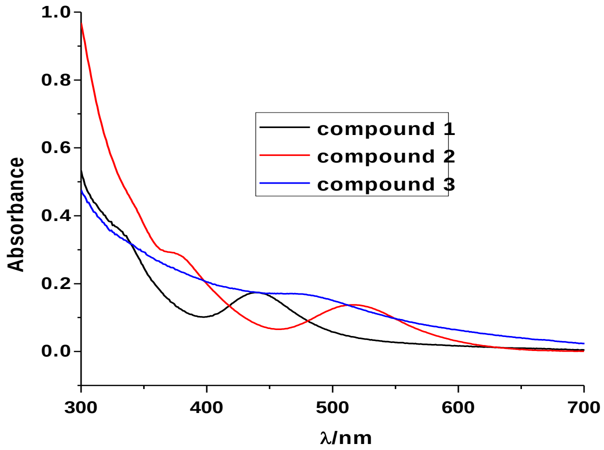

Fig. S3. UV-vis absorption spectrum of clusters dissolved in DMSO ($c = 2.0 \times 10^{-5}$ M).

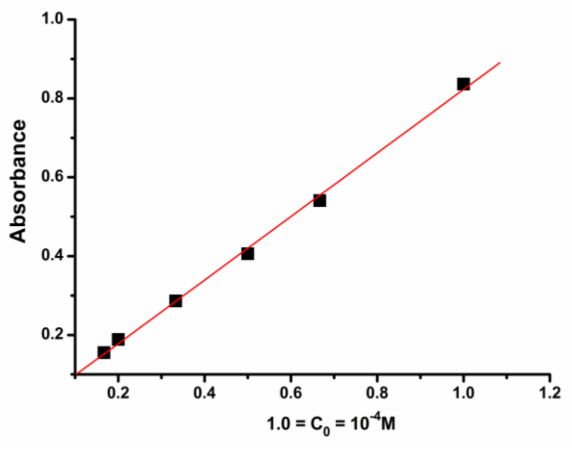

Fig. S4. The UV-vis absorption spectrum of clusters **1** follows the Lambert-Beer law.

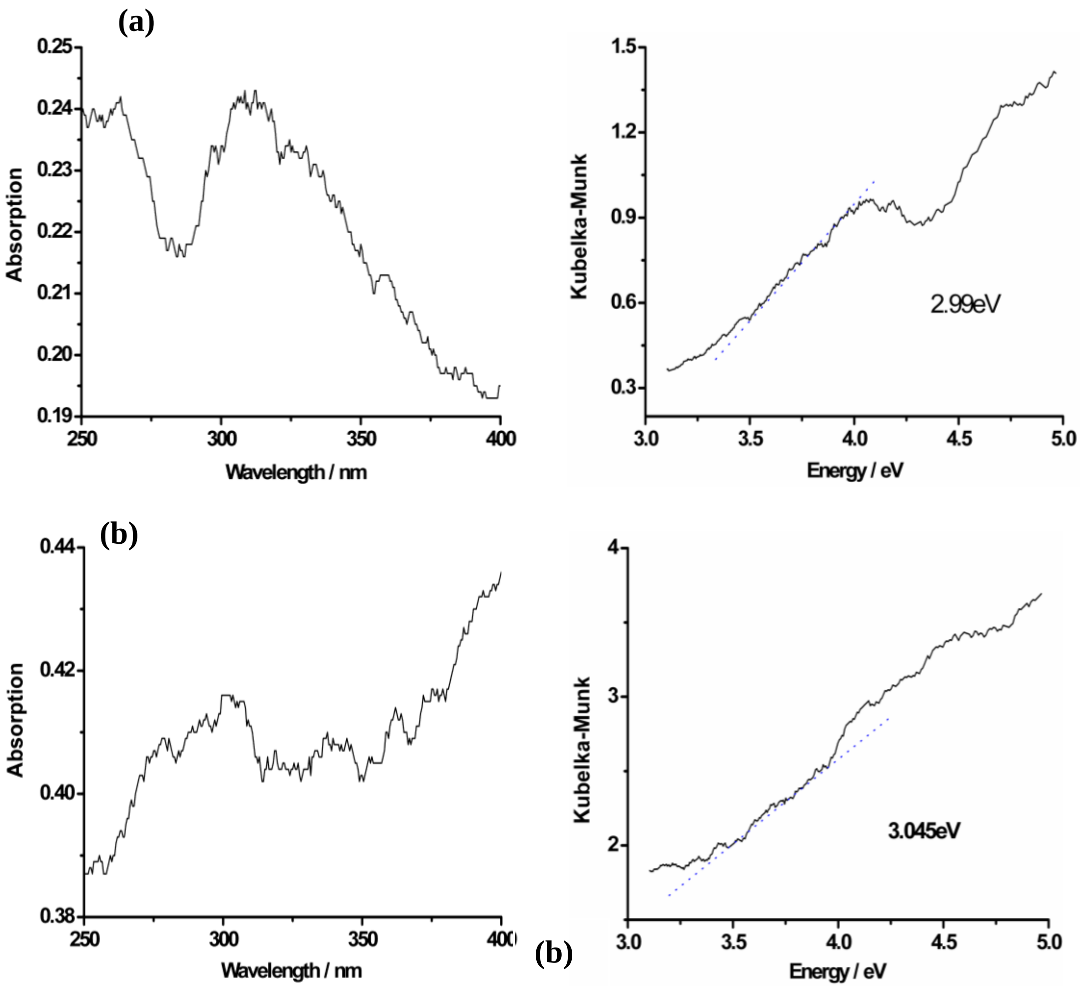

Fig. S5. The Kubelka-Munk equation transformed UV-Vis absorption of **1**(a) and **2**(b).

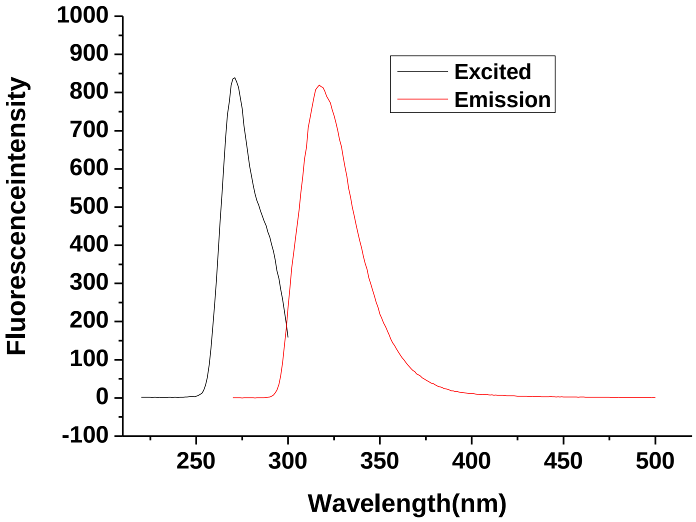

Fig. S6. Excited and Emission spectra of compound **1** dissolved in DMSO ($c = 2.0 \times 10^{-5}$ M).

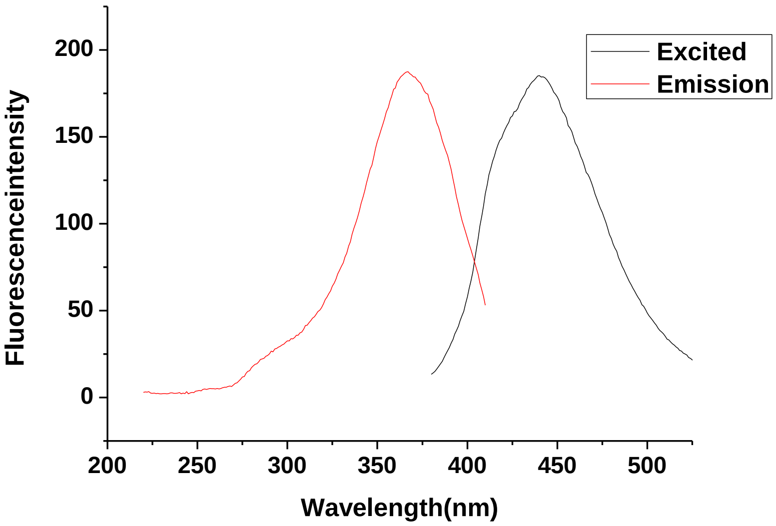

Fig. S7. Excited and Emission spectra of compound **2** dissolved in DMSO (c = 2.0 × 10^{-5} M).

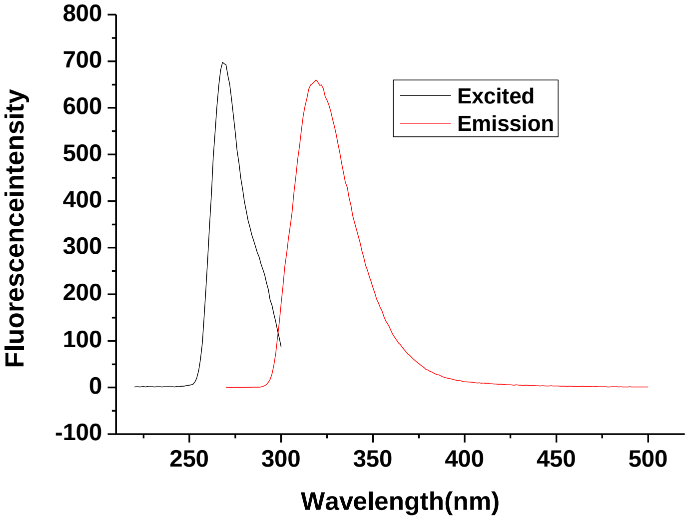

Fig. S8. Excited and Emission spectra of compound **3** dissolved in DMSO (c = 2.0 × 10^{-5} M).