Supporting Information

Synthesis of novel bis(Triol)-functionalized Anderson clusters serving as potential synthons for forming organic-inorganic hybrid chains on purpose

Experimental

General methods and materials

All the chemicals and solvents were purchased from commercial sources as reagent grade and used as received without further purification. Except acetonitrile (CH₃CN) was dried using calcium hydride (CaH₂). [NH₄]₃[MMo₆O₁₈(OH)₆] (M=Mn or Cr) was synthesized according to literature methods¹. Single-crystal X-ray diffraction (single-crystal XRD) data were collected on an Oxford Diffraction Gemini E four-circle X-ray diffractometer from Agilent Technologies. IR spectra were measured using KBr pellets and recorded on a Nicolet 8700/Continuum XL FT-IR spectrometer. Electrospray ionization mass spectrometry: ESI-MS data were collected using a Q-trap, time-of-flight MS instrument equipped with an electrospray (ESI) source supplied by Waters. All analyses were carried out in acetonitrile, collected in negative ion mode and the spectrometer was calibrated with the standard tune-mix to give a precision of ca. 1.5 ppm in the region of 300-2500 *m/z*. ¹H NMR spectra were recorded on Bruker AV-400 MHz spectrometer in DMSO-d₆. TGA measurements were performed on METTLER TOLEDO Series instrument. The heating rate employed was 10 °C/min under N₂ atmosphere over a temperature range of 25-1000°C

Synthesis of compound 1

 $[NH_4]_3[Cr(OH)_6Mo_6O_{18}](2.15g, 2 mmol)$ and dipentaerythritol (0.25 g, 1 mmol) were dissolved in 30 ml deionized water to form a clear pink solution. Then the resulting solution was sealed in 50-ml stainless steel reactor with a teflon liner and heated at 135 °C for 24 hours. After the reaction mixture was cooled down to room temperature, tetrabutylammonium bromide (abbreviated as TBA-Br, 6.5 mmol) was added into the solution and stirred, a small amount of precipitation was filtered off, and the filtrate was sealed to give crystals of compound **1** within 15 days to get pink block crystal. Yield: 73 % (based on Mo). FT-IR: v max/cm⁻¹. 2960-2873 (v C-H), 1131, 1127, 1028 (v C-O), 940, 917, 892 (v Mo=O), 660 (Mo-O-Mo) cm⁻¹. ESI mass spectrometry (MeCN): [H₄]{[CrMo₆O₁₈(OH)₃]₂[(CH₂O)₃CCH₂]₂O}²⁻=1092.78, {[CH₃(CH₂)₃]₃N}[TBA]₂[H]{[CrMo₆O₁₈(OH)₃]₂[(CH₂O)₃CCH₂]₂O}²⁻ calcd m/z = 1426.8, {[CH₃(CH₂)₃]₃N}₂[H]₂{[CrMo₆O₁₈(OH)₃]₂[(CH₂O)₃CCH₂]₂O]²⁻ calcd m/z = 1278.16, {[CH₃(CH₂)₃]₃N}[TBA]₃[H]{[CrMo₆O₁₈(OH)₃]₂[(CH₀O₀₁₈(OH)₃]₂[(CH₂O)₁₈(OH)₃]₂[(CH₂O)₁₈(OH)₃]₂[(CH₂O)₁₃CH₂]₂O]²⁻ calcd m/z = 3096.14, found 1091.76, 1278.78, 1427.13 and 3097.08 respectively.

Synthesis of compound 2

The synthesis process and recrystallization is similar to synthesis of compound 1 while controlled the ligand and POM in a molar ratio of 1:1.4 (63% yields based on Mo) FT-IR: v max/cm⁻¹ 2961-2874 (v C-H), 1132 and 1033(v C-O). 917. 893 Mo=0), 659 (Mo-O-Mo) cm⁻¹. ESI (MeCN): 939, (v $[TBA]{[CrMo_6O_{18}(OH)_3][(CH_2O)_3CCH_2OCH_2C(CH_2OH)_3]]^{2-}(calcd)^{2-}$ m/z:730.16), $[TBA]_{2}\{[CrMo_{6}O_{18}(OH)_{3}][(CH_{2}O)_{3}CCH_{2}OCH_{2}C(CH_{2}OH)_{3}]\}^{*}(1702.86), which can find in 730.65, 1702.97 respectively.$

Synthesis of compound 3

 $[NH_4]_3[MnMo_6O_{18}(OH)_6]$ (1.07 g, 1 mmol) was dissolved in deionized H₂O (30 mL) with heating and stirring. The solution was then heated to reflux, and $(HOCH_2)_3CCH_2OCH_2C(CH_2OH)_3$ (0.711 g, 2.8 mmol) was added to the solution. The solution was heated at reflux for 3 h. Tetrabutylammonium (1.45 g, 4.5 mmol) was added into the solution to exchange the cation and formed a large quantity of precipitation, which were redissolved in DMF. After recrystallization, the title compounds could be obtained as orange crystalline products (84% yields based on Mo). FT-IR: v max/cm⁻¹ 2960-2873 (v C-H), 1152, 1127 and 1018 (v C-O), 940, 919, 891 (v Mo=O), 663 (Mo-O-Mo) cm⁻¹.

ESI mass spectrometry (MeCN): [H]{[MnMo₆O₁₈{(CH₂O)₃CCH₂OCH₂C(CH₂OH)₃}₂]²⁻(calcd m/z: 711.13),

 $[TBA]{[MnMo_6O_{18}{(CH_2O)_3CCH_2OCH_2C(CH_2OH)_3}_2]^{2-}(calcd m/z: 831.86), and$

 $[TBA]_{2}[MnMo_{6}O_{18}(CH_{2}O)_{3}CCH_{2}OCH_{2}C(CH_{2}OH)_{3}]_{2}]$ (calcd m/z: 1906.2), which can find in 711.86 , 831.93 and 1905.89 respectively.

A summary of crystal parameters and refinement details are shown in Table S1.

Spectra Characterization.

IR Spectra Characterization. IR spectra of these compounds are very similar, and in accordance with the typical Anderson-type structures. (see Figure S 1 in ESI⁺). The characteristic peaks at 941, 917and 892 cm⁻¹ in compound **1a** while 940, 919 and 891 cm⁻¹ in compound **2** and 939, 917 cm⁻¹ in compound **3** correspond to the vibrations of Mo=O groups and this at 660 cm⁻¹ in compound **1**, while 659 cm⁻¹ in compound **2**, 663 cm⁻¹ in compound **3** belong to the vibrations of the Mo–O–Mo groups. The characteristic peaks at 1131, 1028 cm⁻¹ in compound **1**

while1132, 1033 cm⁻¹ in compound 2, 1152, 1127, 1018 cm⁻¹ in compound **3** are assigned to the vibration peak of the C–O bonds bridging the Anderson-type POM and the L, demonstrating the grafting of triol onto the surface of the POMs successfully. The medium intensity bands at 3441 cm⁻¹ in compound **1a**, while 3438 cm⁻¹ in compound **2** and 3426 cm⁻¹ in compound **3** can be assigned to the O–H vibrations which can also explain the existence of the O–H···O hydrogen bonds in the structure.

ESI-MS

The molecular structures and compositions of compound **1a**, **2** and **3** were also confirmed by ESI-MS. (Figure S2-S4 and Table S1-S3). All the major peaks in the ESI-MS spectrum of compound **1a**, compound **2** and compound **3** can be assigned to the cluster anions and various combinations of counterions TBA, ${[CH_3(CH_2)_3]_3 N}^+$ and H^+ , which accord with the results of crystallography. In the case of compound **2** the main isotopic clusters are located at m/z 730. 65, 1702.97, which correspond to [TBA]{[CrMo₆O₁₈(OH)₃][(CH₂O)₃CCH₂OCH₂C(CH₂OH)₃] $}^{-}$ (calcd m/z: 730.16), [TBA]₂{[CrMo₆O₁₈(OH)₃][(CH₂O)₃CCH₂OCH₂C(CH₂OH)₃] $}^{-}$ (calcd m/z: 730.16), TBA]₂{[CrMo₆O₁₈(OH)₃][(CH₂O)₃CCH₂OCH₂C(CH₂OH)₃] $}^{-}$ (the main stability.

The preliminary thermal studies on compound **1-3** were conducted by using thermal gravimetric analyses (TGA). All compounds exhibit in general two weight-loss regions. The first step at 200–350 °C was the reduction in TBA counterions. The second step at 350–700°C was the decomposition of the organic triol moiety and the decomposition of the cluster. The detail results are shown in the Figure S5.

¹H-NMR spectra

The signals exhibited by these compounds in the chemical shift range of 1-5 ppm correspond to the protons of the TBA. A broad peak appearing at highly down fielded chemical shift region (60–66 ppm) is characteristic of the bis(Triol) moiety attached to the Anderson type cluster.

	Compound 1a	Compound 1b	Compound 2*	Compound 3
Empirical formula	Cr ₂ Mo ₁₂ O ₄₉ H ₂₂ C ₁₀ ·NC ₂ H ₈	Cr ₂ Mo ₁₂ O ₄₉ H ₂₂ C ₁₀	CrMo ₆ O ₂₈ H ₂₂ C ₁₀	MnMo ₆ O ₃₂ H ₃₈ C ₂₀
	5TBA·3.92DMF·2H ₂ O	14H ₂ O·K ₆	·3TBA·2H ₂ O·solvent*	3TBA·DMF
Formula weight	3762.53	2668.38	1981.32	2221.55
Crystal system	orthorhombic	triclinic	orthorhombic	monoclinic
Space group	Pnma	P-1	Pnma	P2 ₁ /c
<i>a</i> (Å)	24.6313(5)	13.6143(5)	27.1536(16),	27.6934(6)
<i>b</i> (Å)	43.4932(13)	15.9636(6)	24.9590(9),	13.7969(3)
<i>c</i> (Å)	14.5597(3)	17.0731(12)	13.8885(8)	24.7992(5)
α (deg)	90.00	110.894(5)	90.00	90.00
β (deg)	90.00	105.094(4)	90.00	92.869(2)
Y (deg)	90.00	98.427(3)	90.00	90.00
cell volume(Å3)/Z	15597.7(6)/4	3226.9(3)/2	9412.6(8)/4	9463.5(4)/4
ρ _{calc} g/cm ³	1.603	2.746	>1.398	1.559
μ (mm ⁻³)	9.378	3.076	0.950	0.976
F(000)	7683.0	2502	4076	4592
cryst size (mm ³)	$0.4 \times 0.35 \times 0.18$	0.15 × 0.14 × 0.01	0.25 × 0.20 × 0.13	0.25 × 0.21 × 0.08
θ (min, max) (deg)	(4.07, 71.04)	(3.01, 26)	(3.11, 25)	(3.16, 26)
h, k, l (min, max)	(-30, 19)(-52, 44),	(-16, 16)(-19, 19)	(-32, 22)(-27, 29)	(-34,34)(-13,17)
	(-17 , 16)	(-21, 21)	(-16, 15)	(-30,30)
reflns collected	39033	25992	27952	53886
independent reflns	14958	12661	8473	18547
Rint (inf-0.9Å)	0.0470	0.0555	0.0667	0.0469
data/restraints/param	14958/446/858	12661/18/854	8473/348/588	18547/114/1055
S				
GOF on F^2	1.091	1.023	1.062	1.148
final R indices	R1 = 0.1065,	R1=0.0652,	R1 = 0.1229,	R1=0.0777,
	wR2 = 0.2686	wR2=0.1343	wR2=0.2985	wR2=0.1772
R indices (all data)	R1 = 0.1268,	R1=0.1103,	R1 = 0.1644,	R1 = 0.0988,
	wR2 = 0.2835	wR2=0.1587	wR2=0.3233	wR2=0.1900
¢F(max, min) (eâÅ-3)	2.30/-1.82	2.746/-1.195	1.852/-1.623	1.743/-1.453
Completeness	0.979	0.998	0.997	0.998

Table S1 Crystal Data of compound 1-3

*It's difficult to get an ideal single-crystal data of compound **2**, this crystal data presented in Table S1 is the best one with some solvent was squeezed after a lot of recrystallization which the counter ions were changed by TBA, K^+ and Benzyl Triphenyl Phosphonium Bromide.

	D-H-A	<dha< th=""><th>d(DA)</th><th>FUNCTION</th></dha<>	d(DA)	FUNCTION
Compound 1a	N103	166.18	2.755	Molecular
				recognition function
Compound 1b	033…043	158.45	2.716	
	031…034	152.96	2.989	dimeric structure
Compound 2	01… 019	174.52	2.896	hydrogen bond
	04…020	177.94	2.553	
Compound 3	014…01	169.02	2.857	2D network
	030025	175.49	2.850	
	031…016	168.55	2.732	

Table S2 The data of hydrogen bonds with H···A < r(A) + 2.000 Angstroms and <DHA > 110 deg.



Figure S1 FT-IR spectra of compound 1-3



Figure S2 ESI-MS spectra of compound 1 [(TBA)₆(cluster 1)]

Formula assigned	Calculated m/z	Observe m/z
[TBA] ₃ { [CrMo ₆ O ₁₈ (OH) ₃] ₂ [(CH ₂ O) ₃ CCH ₂] ₂ O } ³⁻	969.65	969.17
[H ₄]{[CrMo ₆ O ₁₈ (OH) ₃] ₂ [(CH ₂ O) ₃ CCH ₂] ₂ O} ²⁻	1092.78	1092.76
${[CH_3(CH_2)_3]_3N}_2[H]_2{[CrMo_6O_{18}(OH)_3]_2[(CH_2O)_3CCH_2]_2O}^{2-}$	1278.16	1278.29
${[CH_3(CH_2)_3]_3N}{TBA}_2[H]{[CrMo_6O_{18}(OH)_3]_2[(CH_2O)_3CCH_2]_2O}^{2-}$	1426.87	1427.14





Figure S3 ESI-MS spectra of compound 2

Formula assigned	Calculated m/z	Observe m/z
[TBA]{[CrMo ₆ O ₁₈ (OH) ₃][(CH ₂ O) ₃ CCH ₂ OCH ₂ C(CH ₂ OH) ₃] } ²⁻	730.16	730.65
[TBA] ₂ {[CrMo ₆ O ₁₈ (OH) ₃][(CH ₂ O) ₃ CCH ₂ OCH ₂ C(CH ₂ OH) ₃]} ⁻	1702.86	1702.97

Table S4 Assignment of the peak envelopes in the ESI-MS spectrum of compound ${\bf 2}$



Formula assigned	Calculated m/z	Observe m/z
[H]{[MnMo ₆ O ₁₈ {(CH ₂ O) ₃ CCH ₂ OCH ₂ C(CH ₂ OH) ₃ } ₂ } ²⁻	711.13	711.01
[TBA]{ [MnMo ₆ O ₁₈ {(CH ₂ O) ₃ CCH ₂ OCH ₂ C(CH ₂ OH) ₃ } ₂ } ²⁻	831.86	831.89
$[TBA]_{2}\{[MnMo_{6}O_{18}\{(CH_{2}O)_{3}CCH_{2}OCH_{2}C(CH_{2}OH)_{3}\}_{2}\}^{-1}$	1906.20	1905.89

Table S5 Assignment of the peak envelopes in the ESI-MS spectrum of compound 3



Figure S4 Thermal stability of asymmetrically triol-functionalized hybrids compounds 1-3.

1. T. T. K. Nomiya, T. Shirai and M. Miwa, Polyhedron Polyhedron, 1987, 6, 5.