Electronic Supporting Information (ESI) for

[Ba₁₃Sb₃₆Cl₃₄O₅₄]⁸⁻: High-nuclearity cluster for the assembly of nanocluster-based compounds

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1. Materials and methods

All reagents and chemicals were purchased from commercial sources and used without further purification. Elemental analyses for C, H and N were performed on a German Elementary Vario EL III instrument. Energy dispersive spectroscopy (EDS) and SEM mapping were obtained with a JEOL JSM-6700F scanning electron microscope. Powder X-ray diffraction (PXRD) patterns were collected in the angular range of $2\theta = 3.65$ ° on a Miniflex II diffractometer using Cu*Ka* radiation. Fluorescence spectra of the compounds in the solid state were recorded on a PerkinElmer LS55 fluorescence spectrometer. UV/Vis diffuse reflectance spectra were measured using a Shimadzu UV-2600 spectrometer equipped with a BaSO₄ plate as a standard (100% reflectance). A NETZSCH STA 449C thermogravimetric analyzer was used to obtain thermogravimetric (TG) curves in air atmosphere with a heating rate of 5 °C /min in the temperature range of 30-800 °C.

2. Synthetic procedures

Synthesis of compound 1: A mixture of SbCl₃ (0.684 g, 3 mmol), Ba(OH)₂ (0.171 g, 1 mmol), 5.0 mL 3-methylpyridine, and 1.5 mL H₂O was sealed in a stainless steel reactor with 20 mL Teflon liner, heated at 180 °C for 6 days, and then cooled to room temperature. The colourless block-like crystals of **1** were selected by hand, washed with ethanol, and then dried in the air. The yield of the crystals of **1** is 0.098 g, 12.4% based on SbCl₃. Anal. Calc. for $C_{60}H_{110}N_{10}Sb_{36}Ba_{13}O_{70}Cl_{34}$ (**1**): C 7.61; N 1.48; H 1.17; O 11.83; found: C, 7.52%; H, 1.12%; N, 1.46%; O, 12.02%.

Synthesis of compound 2: A mixture of SbCl₃ (0.684 g, 3 mmol), Ba(OH)₂ (0.171 g, 1 mmol), 5.0 mL pyridine, and 1.5 mL H₂O was sealed in a stainless steel reactor with 20 mL Teflon liner, heated at 180 °C for 6 days, and then cooled to room temperature. The colourless block-like crystals of **2** were selected by hand, washed with ethanol, and then dried in the air. The yield of the crystals of **2** is 0.125 g, 15.8% based on SbCl₃. Anal. Calc. for $C_{50}H_{106}N_{10}Sb_{36}Ba_{13}O_{78}Cl_{34}$ (**2**): C, 6.34%; H, 1.13%; N, 1.48%; O, 13.18%; found: C, 6.94%; H, 1.08%; N, 1.47%; O, 13.25%.

Through tuning the synthetic conditions, e.g., temperature and solvent, we aimed to increase the synthetic yields of the cluster compounds presented in this work (Table S1). Under different solvents, e.g., pyridine (py), and methyl pyridines, compounds with different structures were generated. Using 3-methylpyridine (3-Mepy) and pyridine as the solvents, block crystals of **1** and **2** presented in this work and unknown white powders were obtained, respectively; while using 4-methylpyridine (4-Mepy) or 3,5-lutidine (3,5-Mepy) as the solvent, a small amount of crystals along with a large amount of unknown white powder were generated; for the latter two types of crystals, we also measured their cell parameters through single crystal X-ray diffraction analyses (Table S1) and tried to collect the crystal data but failed due to the low quality of the crystals. In all the above syntheses, water was used as the co-solvent. Without water, only unknown powders could be generated. Reaction temperatures were also adjusted for compounds **1** and **2**, however, the yields have not been increased. Future study will try to further optimize the synthetic conditions to increase the yield of title reactions.

<mark>Entry</mark>	Reaction	Final products
1	3SbCl ₃ + Ba(OH) ₂ + 3-Mepy (5.0 mL) + H ₂ O (1.5 mL), 180 °C/6d	Compound 1 and unidentified white powder.
2	3SbCl ₃ + Ba(OH) ₂ + py (5.0 mL) + H ₂ O (1.5 mL), 180 °C/6d	Compound 2 and unidentified white powder.
3	3SbCl ₃ + Ba(OH) ₂ + 4-Mepy (5.0 mL) + H ₂ O (1.5 mL), 180 °C/6d	Ultra-low-yield tiny block-like crystals with the <i>R</i> lattice and cell parameters of $a = 23.4767(3)$, $c = 30.7126(6)$ Å, $\gamma = 120^\circ$, and high yield unidentified white powder.
<mark>4</mark>	3SbCl ₃ + Ba(OH) ₂ + 3,5- Mepy (5.0 mL) + H ₂ O (1.5 mL), 180 °C/6d	Ultra-low-yield tiny block-like crystals the <i>P</i> lattice and cell parameters of $a = 25.4072(6)$, $c = 18.0163(4)$ Å, and high-yield unidentified white powder.
<mark>5</mark>	$3SbCl_3 + Ba(OH)_2 + 3-Mepy$ (5.0 mL), 180 °C/6d	Unidentified white powder.

Table S1 Comparison of the various synthetic conditions for Ba-Sb-O-Cl clusters.

6 3SbCl₃ + Ba(OH)₂ + py (5.0 mL), 180 °C/6d

Unidentified white powder.

Same conditions for 1 and 2 Low-yield tiny block-like crystals of the title compounds but under different and high-yield unidentified white powders.
 synthesized temperatures of 140 or 160 °C/6d

Py = pyridine, 3-Mepy = 3-methylpyridine, 4-Mepy = 4-methylpyridine, 3,5-Mepy = 3,5-lutidine

3. Proton conductivity measurements

The measurement was performed in a quasi-four-electrode alternating current (AC) impedance technique using a Solartron 1260 impedance/gain-phase analyzer. The powdered crystalline samples were compressed to 0.46 mm (1) and 0.76 mm (2) in thickness and 2.5 mm in diameter under a pressure of 101 MPa. Two sides of the pellet were connected to gold wires by gold paste. The sample pellet was measured at frequency ranging from 10⁷ to 1 Hz by varying temperature from 30 to 70 °C and relative humidity (RH) from 50 to 95%. The conductivity of the sample was deduced from the Debye semicircle in Nyquist plot.

4. X-ray crystallography

Single-crystal X-ray diffraction data of **1** and **2** were collected on an SuperNova Oxford diffractometer with graphite monochromated Mo*K* α radiation ($\lambda = 0.71073$ Å) at 293(2) K and Cu*K* α radiation ($\lambda = 1.54178$ Å) at 100(2) K, respectively. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-2016 program.¹⁰ Non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms bonded to C and N atoms were positioned with idealized geometry. For structure of **1**, the SQUEEZE procedure in PLATON (PWT 1.17) was applied to calculate the contribution of the highly disordered solvent/cation molecules to the calculated structure factors. The empirical formulae were confirmed by elemental analysis. Detailed crystallographic data and structure-refinement parameters are summarized in Table S1. CCDC Nos. 1576925 and 1516472 contain the supplementary crystallographic data for this paper.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

Compound	1	2					
Empirical formula	$C_{60}H_{110}N_{10}Sb_{36}Ba_{13}O_{70}Cl_{34}$	$C_{50}H_{106}N_{10}Sb_{36}Ba_{13}O_{78}Cl_{34}$					
Formula weight	9465.29	9469.16					
Crystal system	trigonal	orthorhombic					
Space group	<i>R</i> -3	Fmmm					
T/K	293(2)	100(2)					
λ / Å	0.71073	1.54178					
<i>a</i> / Å	23.1283(10)	22.1076(8)					
<i>b</i> / Å	23.1283(10)	23.5213(8)					
<i>c</i> / Å	30.459(2)	35.8807(14)					
$\alpha/^{o}$	90	90					
β/°	90	90					
γ/°	120	90					
V/ Å ³	14110.3(16)	18657.9(12)					
Ζ	3	4					
$D_c/\mathrm{Mg}\cdot\mathrm{m}^{-3}$	3.342	3.371					
μ/mm^{-1}	8.293	66.613					
<i>F</i> (000)	12726	16968					
Measured refls.	11417	10613					
Independent refls.	6959	4937					
R _{int}	0.0706	0.0434					
No. of parameters	207	267					
GOF	1.075	1.077					
${}^{a}R_{1}, wR_{2} [I > 2(I)]$	0.0639, 0.1301	0.0722, 0.1687					
R_1 , wR_2 (all data)	0.1195, 0.1570	0.0788, 0.1732					
${}^{a}R_{1} = \ F_{o} - F_{c} / \sum F_{o} . {}^{b}wR_{2} = [\sum w(F_{o}^{2}F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}$							

 Table S2 Crystallographic data and structural refinement details for 1 and 2.

Compound 1						
Bond	Dist. (Å)	Bond	Dist. (Å)			
Ba(1)-Cl(2)	3.098(6)	Ba(3)-Cl(1)	3.119(4)			
Ba(1)-Cl(2)#1	3.098(6)	Ba(3)-O(3)#5	3.149(12)			
Ba(1)-Cl(1)	3.115(4)	Ba(3)-Cl(4)	3.186(6)			
Ba(1)-Cl(1)#2	3.115(4)	Ba(3)-O(7)	3.209(11)			
Ba(1)-Cl(1)#1	3.115(4)	Ba(3)-Cl(5)#6	3.610(5)			
Ba(1)-Cl(1)#3	3.115(4)	Sb(1)-O(1)	1.936(11)			
Ba(1)-Cl(1)#4	3.115(4)	Sb(1)-O(2)	1.967(12)			
Ba(1)-Cl(1)#5	3.115(4)	Sb(1)-O(3)	1.974(11)			
Ba(2)-O(4)#5	2.805(11)	Sb(2)-O(1)	1.947(11)			
Ba(2)-O(1)	2.839(11)	Sb(2)-O(4)	1.969(12)			
Ba(2)-O(5)#5	2.971(12)	Sb(2)-O(5)	1.975(10)			
Ba(2)-O(3)	2.975(11)	Sb(3)-O(4)	1.972(11)			
Ba(2)-O(6)	3.048(12)	Sb(3)-O(2)	1.980(10)			
Ba(2)-Cl(1)#2	3.101(4)	Sb(3)-O(6)#2	1.995(11)			
Ba(2)-Cl(1)	3.104(4)	Sb(4)-O(6)	1.972(12)			
Ba(2)-O(5)	3.145(12)	Sb(4)-O(5)	1.973(10)			
Ba(2)-O(7)#5	3.173(11)	Sb(4)-O(7)	1.978(11)			
Ba(2)-Cl(3)	3.211(6)	Sb(5)-O(7)	1.952(10)			
Ba(3)-O(9)	2.765(12)	Sb(5)-O(8)	1.964(11)			
Ba(3)-O(2)#5	2.779(11)	Sb(5)-O(7)	1.957(10)			
Ba(3)-O(6)	3.001(11)	Sb(5)-O(3)#2	1.976(10)			
Ba(3)-O(8)	3.044(12)	Sb(6)-O(9)#4	1.935(11)			
Ba(3)-O(8)#3	3.051(12)	Sb(6)-O(9)	1.992(11)			
Ba(3)-Cl(2)	3.104(2)	Sb(6)-O(8)	2.007(10)			

 Table S3 The selected bond lengths for compounds 1 and 2.

Symmetry transformations used to generate equivalent atoms of 1: #1 -x+2/3, -y+4/3, -z+1/3; #2 x-y+2/3, x+1/3, -z+1/3; #3 -x+y, -x+1, z; #4 -y+1, x-y+1, z; #5 y-1/3, -x+y+1/3, -z+1/3; #6 -y+1/3, x-y+2/3, z-1/3.

Compound 2						
Bond	Dist. (Å)	Bond	Dist. (Å)			
Ba(1)-Cl(1)#1	3.108(4)	Ba(4)-O(4)#3	2.822(12)			
Ba(1)-Cl(1)#2	3.108(4)	Ba(4)-O(4)	2.822(12)			
Ba(1)-Cl(1)#3	3.108(4)	Ba(4)-O(6)#3	3.002(11)2.992(12)			
Ba(1)-Cl(1)#4	3.108(4)	Ba(4)-O(6)	2.992(12)			
Ba(1)-Cl(1)#5	3.108(4)	Ba(4)-O(5)	3.060(13)			
Ba(1)-Cl(1)#6	3.108(4)	Ba(4)-O(5)#3	3.060(13)			
Ba(1)-Cl(1)#7	3.108(4)	Ba(4)-Cl(1)#5	3.109(4)			
Ba(1)-Cl(1)	3.108(4)	Ba(4)-Cl(1)#2	3.109(4)			
Ba(2)-O(2)	2.813(12)	Ba(4)-O(9)	3.158(10)			
Ba(2)-O(2)#1	2.813(12)	Ba(4)-Cl(6)	3.173(8)			
Ba(2)-O(1)	3.006(12)	Sb(1)-O(3)	1.945(11)			
Ba(2)-O(1)#1	3.006(12)	Sb(1)-O(1)	1.977(12)			
Ba(2)-O(6)	3.055(12)	Sb(1)-O(2)	1.991(11)			
Ba(2)-O(6)#1	3.055(12)	Sb(2)-O(4)	1.949(11)			
Ba(2)-Cl(1)#5	3.081(4)	Sb(2)-O(3)	1.972(11)			
Ba(2)-Cl(1)#7	3.081(4)	Sb(2)-O(5)	1.973(11)			
Ba(2)-O(7)	3.155(9)	Sb(3)-O(2)	1.942(11)			
Ba(2)-Cl(2)	3.175(7)	Sb(3)-O(6)	1.967(11)			
Ba(3)-O(3)	2.828(12)	Sb(3)-O(4)	1.980(11)			
Ba(3)-O(3)#5	2.829(12)	Sb(4)-O(1)	1.964(11)			
Ba(3)-O(5)#5	2.996(13)	Sb(4)-O(1)#5	1.964(11)			
Ba(3)-O(5)	2.996(13)	Sb(4)-O(7)	1.973(12)			
Ba(3)-O(1)#5	3.059(12)	Sb(5)-O(5)#3	1.989(11)			
Ba(3)-O(1)	3.059(12)	Sb(5)-O(5)	1.989(11)			
Ba(3)-Cl(1)	3.142(4)	Sb(5)-O(8)	1.989(11)			
Ba(3)-Cl(1)#5	3.142(4)	Sb(6)-O(9)	1.984(15)			
Ba(3)-O(8)	3.163(8)	Sb(6)-O(6)#1	1.984(11)			
Ba(3)-Cl(4)	3.181(8)	Sb(6)-O(6)	1.984(11)			
Ba(3)-Cl(3)	3.2578(13)					

Symmetry transformations used to generate equivalent atoms of **2**: #1 -*x*+1, *y*, *z*; #2 *x*, -*y*+1, -*z*+1; #3 *x*, -*y*+1, *z*; #4 -*x*+1, -*y*+1, *z*; #5 *x*, *y*, -*z*+1; #6 -*x*+1, -*y*+1, -*z*+1; #7 -*x*+1, *y*, -*z*+1.

Compound 1								
Bond	Bond Dist. (Å) Bond							
Sb(1)-Cl(5)	3.0821(1)	Sb(4)-Cl(6)	3.1700(1)					
Sb(2)-Cl(6)	3.2547(1)	Sb(6)-Cl(7)	3.0727(1)					
Sb(3)-Cl(5)	3.0490(1)	Sb(6)-Cl(5)	3.1873(1)					
Sb(3)-Cl(6)#2	3.2749(1)							
	Compour	nd 2						
Bond	Dist. (Å)	Bond	Dist. (Å)					
Sb(1)-Cl(7)	3.159(5)	Sb(5)-Cl(4)#2	3.247(7)					
Sb(2)-Cl(5)	3.173(4)	Sb(5)-Cl(4)	3.247(7)					
Sb(3)-Cl(8)	3.174(4)	Sb(6)-Cl(8)	3.125(7)					
Sb(4)-Cl(2)	3.301(6)	Sb(6)-Cl(6)	3.260(6)					
Sb(4)-Cl(2)#5	3.301(6)	Sb(6)-Cl(6)#4	3.260(6)					
Sb(5)-Cl(5)	3.241(8)							

Table S4 The selected distances for the secondary bonding interactions between the Sb^{3+} and Cl^{-} ions in compounds 1 and 2.

Symmetry transformations used to generate equivalent atoms for 1: #2 x-y+2/3, x+1/3, -z+1/3; for 2: #2

x, -*y*+1, -*z*+1; #4 -*x*+1, -*y*+1, *z*; #5 *x*, *y*, -*z*+1.



Fig. S1 The coordination environment of Ba atoms in the $[Ba_{13}Sb_{36}Cl_8O_{54}]^{8-}$ cluster in compounds 1 (a) and 2 (b).



Fig. S2 The typical coordination environments of Ba (a) and Sb (b), and connection patterns of μ_3 -O and μ_4 -O (c) in the [Ba₁₃Sb₃₆Cl₈O₅₄]⁸⁻ cluster in compounds **1** and **2**.



Fig. S3 The typical secondary bonding interactions between the Sb^{3+} and Cl^{-} ions in the clusters (highlighted in dotted line) in compounds 1 and 2.

In compound **1**, there are 26 outer Cl⁻ ions which can be divided into three types due to their different coordination modes, i.e. 12 terminal Cl⁻ ions coordinated to outer 12 Ba²⁺ ions, 8 capping Cl⁻ ions having secondary bonding interactions to three Sb³⁺ ions from the same cluster core with the Sb...Cl distances of 3.095(3)~3.251(3) Å

(Fig.s S1a and S4a), and 6 Cl⁻ ions forming secondary bonding interactions with three Sb³⁺ ions from two neighbouring clusters (Sb...Cl distances of 3.099(2)~3.259(2) Å, Fig. S4c). While in compound **2**, there are 28 outer Cl⁻ ions, Fig. S1b. In addition to the 12 terminally coordinated Cl⁻ ions, there exist extra four terminal Cl⁻ ions coordinated to Ba(4), and four bridging Cl⁻ ions which link two Ba3 from two neighbouring clusters. For the remaining 8 non-coordinated Cl⁻ ions in the peripheral of the cluster core of **2**, four of them are in capping mode via secondary bonding interactions with three Sb³⁺ atoms from the same cluster (Sb...Cl distances of 3.125(7)~ 3.174(4) Å, Fig. S4b), and other four Cl⁻ are in bridging mode via secondary bonding interactions with Sb³⁺ atoms from neighbouring clusters (Sb...Cl distances of 3.159(5) Å, Fig. S4d). Overall the outer 12 Ba²⁺ ions exhibit different coordinated, while there are four 10-coordinated and eight 11-coordinated ones in compound **2**.



Fig. S4 The packing diagram for compound **2**. The [pyH]⁺ cations act as counterions located at the intervening spaces.



Fig. S5 Nyquist plots for **1** at 30 °C under 50 to 95 RH (a, b) and different temperature conditions at 95% RH (c).



Fig. S6 Nyquist plots for **2** at 30 °C under 50 to 95 RH (a, b) and different temperature conditions at 95% RH (c).

Compound 1								
RH %	50	60	70	80	95			
σ (S cm ⁻¹)	0.16×10-6	0.44×10-6	0.36×10-4	0.67×10 ⁻⁴	0.13×10-2			
Compound 2								
RH %	50	60	70	80	95			
σ (S cm ⁻¹)	0.71×10-7	0.15×10-6	3.15×10-4	4.94×10-4	0.58×10-2			

Table S5. Proton conductivity (σ) values of 1 and 2 at 30 °C and varied RH conditions.

Table S6. Proton conductivity (σ) values of **1** and **2** under 95% RH and at different temperatures.

Compound 1								
T/°C	30	40	50	60	70	80		
$\sigma (10^{-2} \text{ S cm}^{-1})$	0.13	0.26	0.32	0.39	0.41	0.31		
Compound 2								
T/°C	30	40	50	60	70	80		
$\sigma (10^{-2} \text{ S cm}^{-1})$	0.58	0.90	1.95	2.05	2.38	1.55		



Fig. S7 PXRD patterns of the title compounds along with the simulated patterns based on single crystal X-ray diffraction data.



Fig. S8 The profiles of energy dispersive spectroscopy (EDS) of 1 (a) and 2 (b), respectively.

Table S7	Selected	EDS	analysis	results	for compound	is 1 and 2.

	Compour	nd 1	Compound 2		
Element	Subtotal Mass %		Subtotal Mass %		
	Experimental	Calculated	Experimental	Calculated	
Cl	<mark>6.19</mark>	<u>12.73</u>	<mark>15.40</mark>	12.73	
Sb	<mark>20.75</mark>	<mark>46.31</mark>	<mark>50.48</mark>	<mark>46.29</mark>	
Ba	<mark>8.16</mark>	<mark>18.86</mark>	<mark>19.51</mark>	<mark>18.85</mark>	



Fig. S9 SEM mapping for compounds 1 (a) and 2 (b).



Fig. S10 Solid state absorption spectra of compounds 1 and 2.



Fig. S11 Emission spectra of compounds 1 and 2 at the solid state ($\lambda_{em} = 455$ and 520 nm when excited with 395 and 450 nm wavelengths).



Fig. S12 TG curves for compounds 1 and 2.