Electronic Supplementary Material (ESI) for Chemical Science

Largest Discrete Supertetrahedral Clusters Synthesized in Ionic Liquids

Wei-Wei Xiong, Jian-Rong Li, Bing Hu, Bin Tan, Ren-Fu Li, and Xiao-Ying Huang*

Supporting information

1. More structure figures and tables

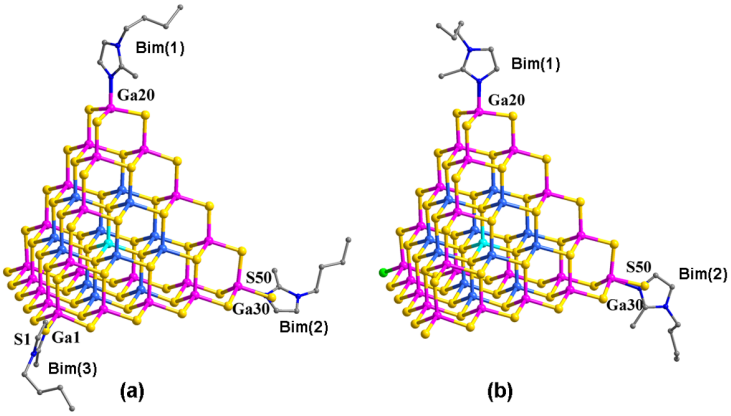

Figure S1. The T5 $[Cu_5Ga_{30}S_{52}(SH)_2(Bim)_2]^{11-}$ and $[Cu_5Ga_{30}S_{52}(SH)_{1.5}Cl(Bim)_{1.5}]^{11.5-}$ clusters in compounds **3** (a) and **4** (b) with numbering scheme of the terminal ligands. Hydrogen atoms are omitted for clarity.

Table S1. The terminal M-SH and M-Cl (M = Ga, In) bond lengths (Å) for compounds **1-4**.

Compound **1**		Compound **2**		Compound **3**		Compound **4**	
In(1)-X(1) (X(1) =S(54)/Cl(1))	2.447(2)	Ga(1)-S(1)	2.313(5)	Ga(1)-S(1)	2.304(10)	Ga(1)-Cl(1)	2.256(4)
In(20)-X(2) (X(2) = S(55)/Cl(2))	2.449(3)	Ga(9)-S(16)	2.311(2)	Ga(30)-S(50)	2.288(5)	Ga(30)-S(50)	2.288(7)
In(30)-X(3) (X(3) =S(49)/Cl(3))	2.462(2)			Ga(34)-S(55)	2.293(3)	Ga(34)-S(55)	2.274(3)
In(34)-X(4) (X(4) = S(56)/Cl(4))	2.447(4)						

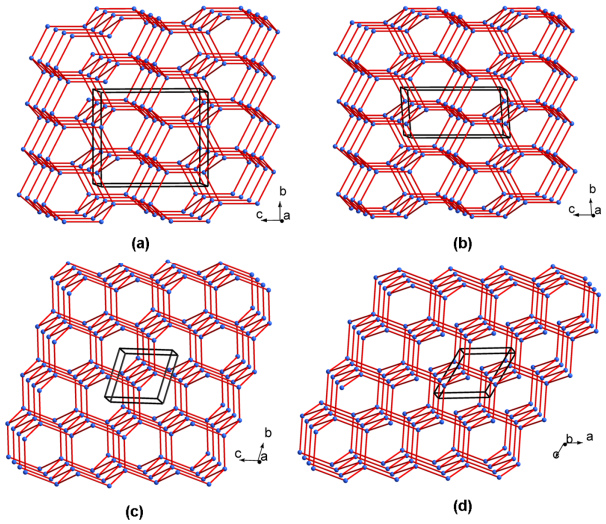

Figure S2. By connecting the barycenters of the discrete T5 clusters in compounds **1-4**, the topological type of the arrangements of **1** (a) and **2** (b) is distorted hexagonal diamond superlattice, while that of **3** (c) and **4** (d) is distorted cubic diamond lattice.

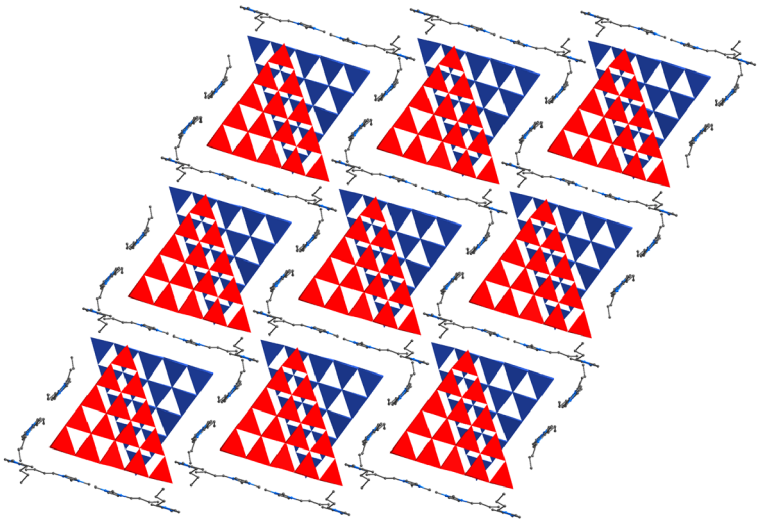

Figure S3. Taking the structure of compound **1** as an example, most of the $[Bmmim]^+$ cations are located between the tetrahedral faces of two T5 clusters, and the imidazolium rings of $[Bmmim]^+$ cations are parallel to the tetrahedral faces of T5 clusters.

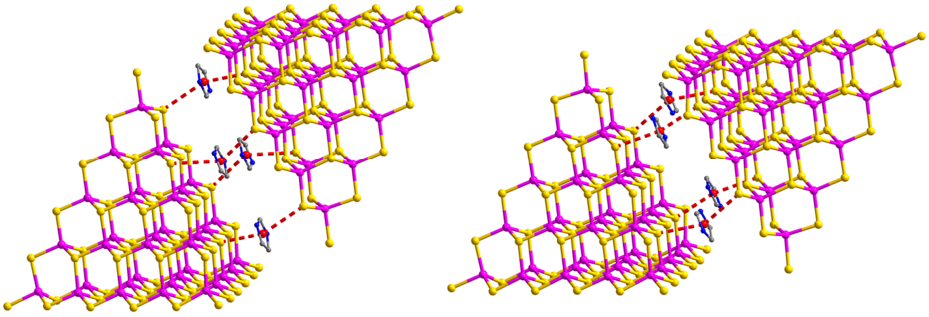

Figure S4. Taking the structure of compound **1** as an example, the anion–π interactions between the anions on the surfaces of T5 clusters and the imidazolium rings are showed as dotted lines.

2. More characterizations

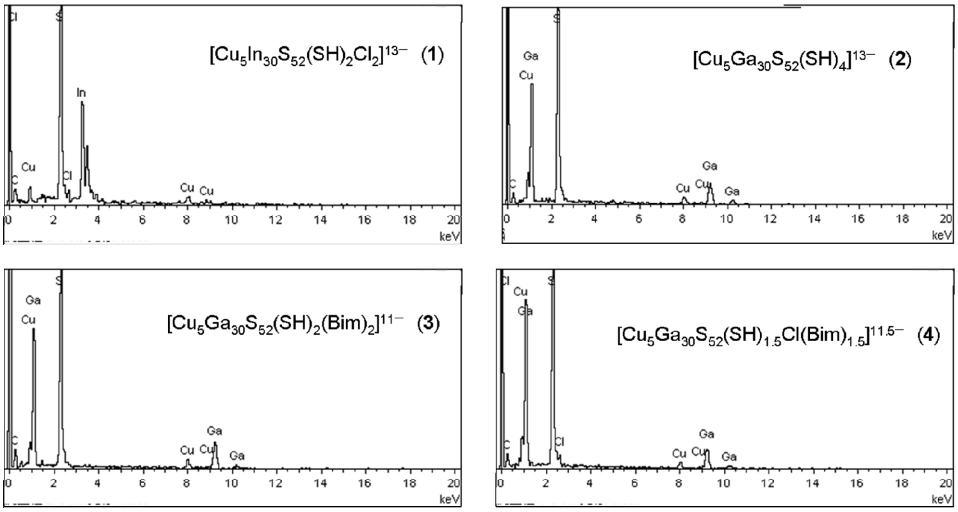

Figure S5. The energy dispersive X-ray (EDX) spectroscopy of compounds **1-4**. The energy dispersive X-ray (EDX) spectroscopy was performed on an Oxford INCA instrument.

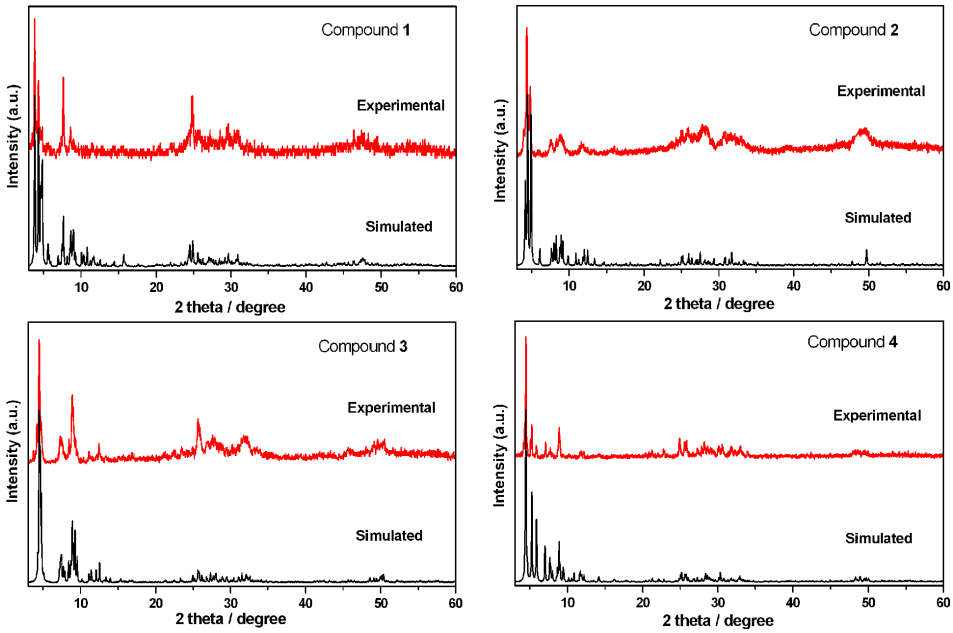

Figure S6. The experimental (red) and simulated (black) PXRD patterns (red) of compounds **1-4**. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku MiniFlex Ⅱ using Cu*Kα* radiation.

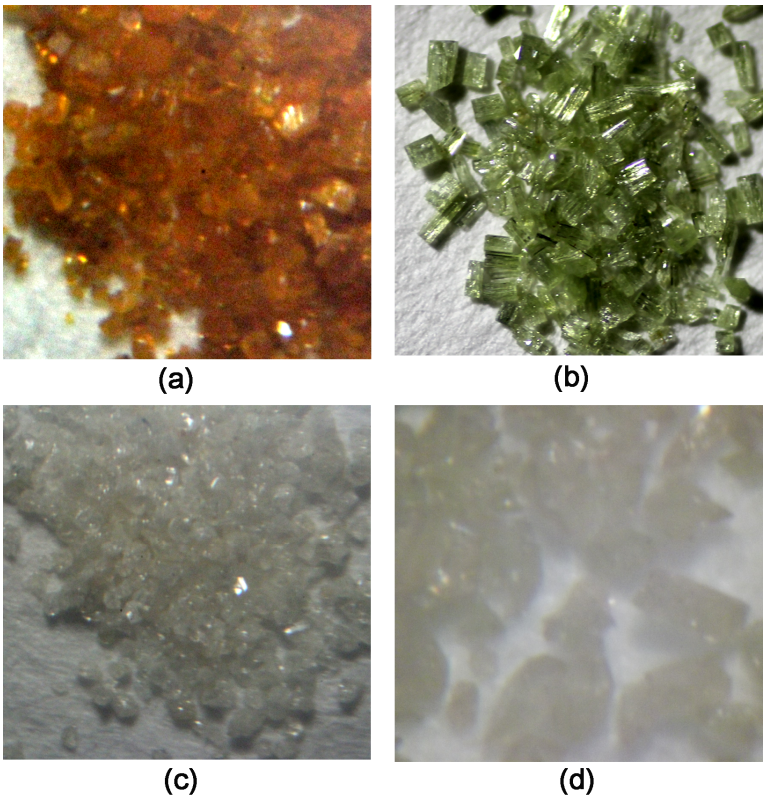

Figure S7. Photographs of the crystals of compounds **1** (a), **2** (b), **3** (c), **4** (d).