Supporting Information

Ionothermal Synthesis of Discrete Supertetrahedral T*n* (*n* = 4, 5) Clusters with Tunable Components, Band Gaps, and Fluorescence Properties.

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Table S1. Selected bond lengths (Å) for compounds **1**-**3**

$[Bmmim]_5[(CH_3)_2NH_2]_4[NH_4][Mn_4In_{16}S_{31}(SH)_4]\cdot 6H_2O$ (**1**)			
Mn(1)-S(6)	2.402(5)	In(3)-S(5)	2.500(3)
Mn(1)-S(10)#1	2.435(3)	In(4)-S(9)	2.441(3)
Mn(1)-S(10)#2	2.435(3)	In(4)-S(11)	2.444(3)
Mn(1)-S(10)	2.435(3)	In(4)-S(10)	2.494(3)
Mn(2)-S(6)	2.411(2)	In(4)-S(5)	2.492(3)
Mn(2)-S(5)	2.428(3)	In(5)-S(12)	2.434(3)
Mn(2)-S(8)#2	2.426(3)	In(5)-S(9)#1	2.446(3)
Mn(2)-S(4)	2.442(3)	In(5)-S(8)	2.483(3)
In(1)-S(2)#2	2.459(3)	In(5)-S(10)	2.497(3)
In(1)-S(2)	2.459(3)	In(6)-S(7)	2.441(4)
In(1)-S(2)#1	2.459(3)	In(6)-S(12)	2.463(4)
In(1)-S(1)	2.495(6)	In(6)-S(11)	2.475(4)
In(2)-S(3)	2.442(3)	In(6)-S(13)	2.488(5)
In(2)-S(2)	2.449(3)	In(3)-S(8)	2.483(3)
In(2)-S(4)#2	2.490(3)	In(3)-S(3)#1	2.442(3)
In(2)-S(4)	2.491(3)	In(3)-S(7)	2.438(3)
$[Bmmim]_5[(CH_3)_2NH_2]_4[NH_4][Zn_4In_{16}S_{31}(SH)_4]\cdot 6H_2O$ (**2**)			
Zn(1)-S(6)	2.325(3)	In(3)-S(5)	2.4983(18)
Zn(1)-S(10)#1	2.3551(17)	In(4)-S(9)	2.433(2)
Zn(1)-S(10)#2	2.3551(17)	In(4)-S(11)	2.4386(18)
Zn(1)-S(10)	2.3551(17)	In(4)-S(10)	2.4858(18)
Zn(2)-S(6)	2.3391(11)	In(4)-S(5)	2.4897(18)
Zn(2)-S(8)#2	2.3518(18)	In(5)-S(12)	2.4307(19)
Zn(2)-S(5)	2.3533(17)	In(5)-S(9)#1	2.4356(19)
Zn(2)-S(4)	2.3556(18)	In(5)-S(8)	2.4780(18)
In(1)-S(2)#2	2.458(2)	In(5)-S(10)	2.4940(18)
In(1)-S(2)	2.458(2)	In(6)-S(7)	2.437(2)
In(1)-S(2)#1	2.458(2)	In(6)-S(12)	2.454(2)
In(1)-S(1)	2.468(4)	In(6)-S(11)	2.464(2)
In(2)-S(3)	2.4307(18)	In(6)-S(13)	2.478(2)
In(2)-S(2)	2.4427(19)	In(3)-S(8)	2.4816(17)
In(2)-S(4)	2.4900(16)	In(3)-S(7)	2.4344(18)

In(2)-S(4)#2	2.4906(17)	In(3)-S(3)#1	2.4295(18)

$[Bmmim]_5[(CH_3)_2NH_2]_4[NH_4][Cd_4In_{16}S_{31}(SH)_4]\cdot 6H_2O$ (**3**)

Cd(1)-S(6)	2.479(3)	In(3)-S(5)	2.497(2)
Cd(1)-S(10)#1	2.524(2)	In(4)-S(9)	2.438(2)
Cd(1)-S(10)#2	2.524(2)	In(4)-S(11)	2.440(2)
Cd(1)-S(10)	2.524(2)	In(4)-S(10)	2.485(2)
Cd(2)-S(6)	2.4966(12)	In(4)-S(5)	2.486(2)
Cd(2)-S(8)#2	2.513(2)	In(5)-S(12)	2.433(2)
Cd(2)-S(5)	2.520(2)	In(5)-S(9)#1	2.443(2)
Cd(2)-S(4)	2.522(2)	In(5)-S(8)	2.471(2)
In(1)-S(2)#2	2.457(2)	In(5)-S(10)	2.498(2)
In(1)-S(2)	2.457(2)	In(6)-S(7)	2.437(3)
In(1)-S(2)#1	2.457(2)	In(6)-S(12)	2.458(3)
In(1)-S(1)	2.485(5)	In(6)-S(11)	2.473(3)
In(2)-S(3)	2.432(2)	In(6)-S(13)	2.483(3)
In(2)-S(2)	2.445(2)	In(3)-S(8)	2.480(2)
In(2)-S(4)#2	2.484(2)	In(3)-S(3)#1	2.435(2)
In(2)-S(4)	2.489(2)	In(3)-S(7)	2.434(2)

Symmetry transformations used to generate equivalent atoms: #1 -*x*+*y*, -*x*+1, *z*; #2 -*y*+1, *x*-*y*+1, *z*.

Table S2. The unit cell parameters of compounds **4** and **8**.

Compound reference	**8**	**4**
Empirical formula	$C_{90}H_{186}N_{23}Cu_5In_{30}S_{56}$	$C_{90}H_{186}N_{23}Cu_5Ga_{30}S_{56}$
Space group	$P6_3/m$	$P6_3/m$
a/ Å	23.9450(6)	23.018(3)
b/ Å	23.9450(6)	23.018(3)
c/ Å	43.3826(13)	42.321(7)
α/°	90.00	90.00
β/°	90.00	90.00
γ/°	120.00	120.00
V/ Å^3	21541.5(10)	19418(5)

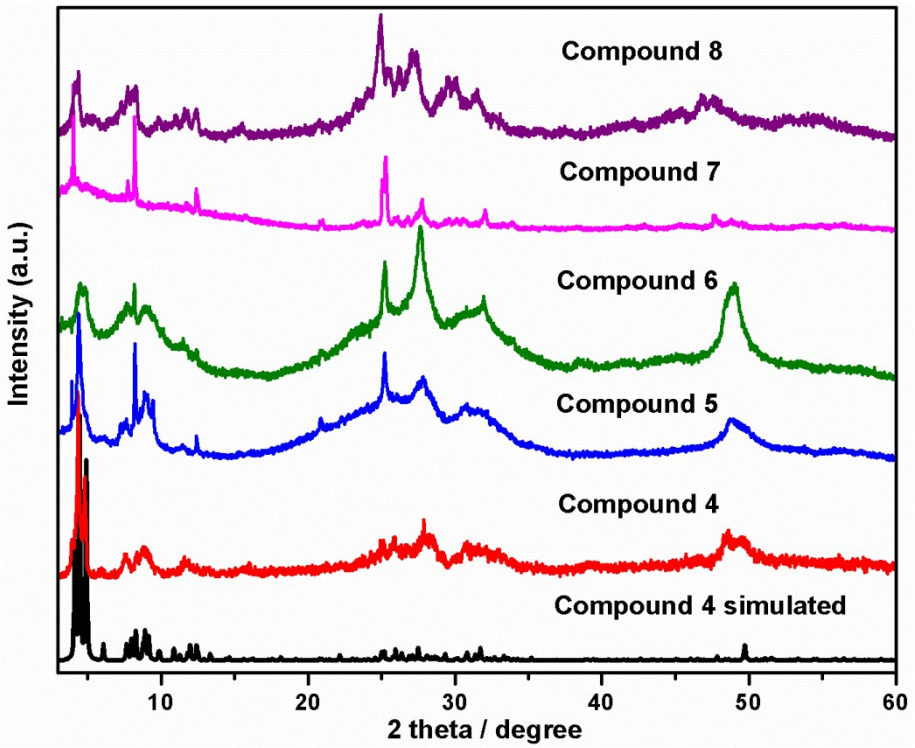

Fig. S1 The powder X-ray diffraction patterns of **4**-**8** and the simulated (black) PXRD pattern of **4**.

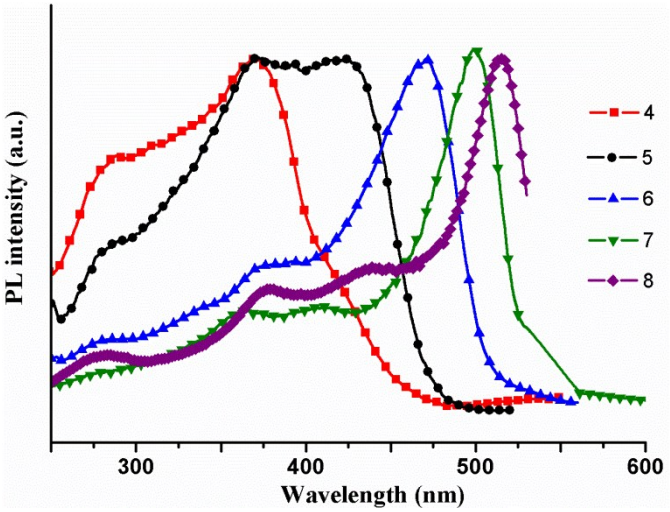

Fig. S2 Solid-state excitation spectra of compounds **4**-**8** at room temperature.

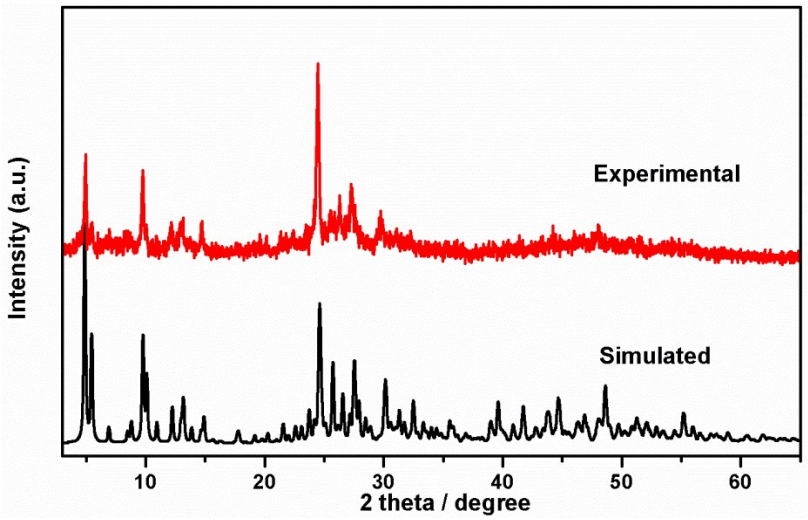

Fig. S3 The experimental (red) and simulated (black) PXRD patterns (red) of compound **1**.

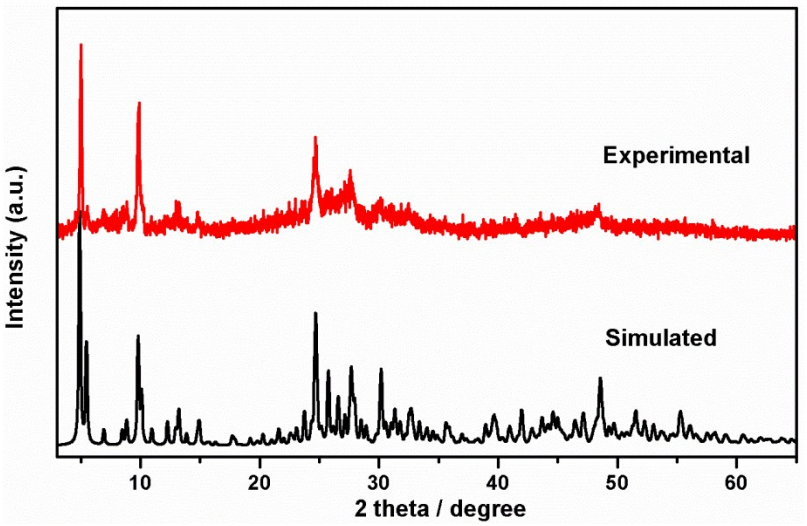

Fig. S4 The experimental (red) and simulated (black) PXRD patterns (red) of compound **2**.

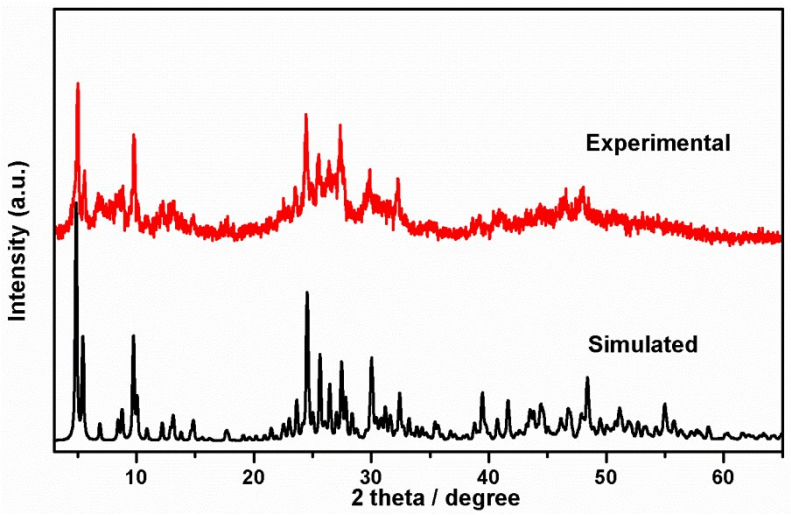

Fig. S5 The experimental (red) and simulated (black) PXRD patterns (red) of compound **3**.