Supporting Information for

Synthesis and Structural Characterization of Three 3-D Aluminogermanates with Different Topologies

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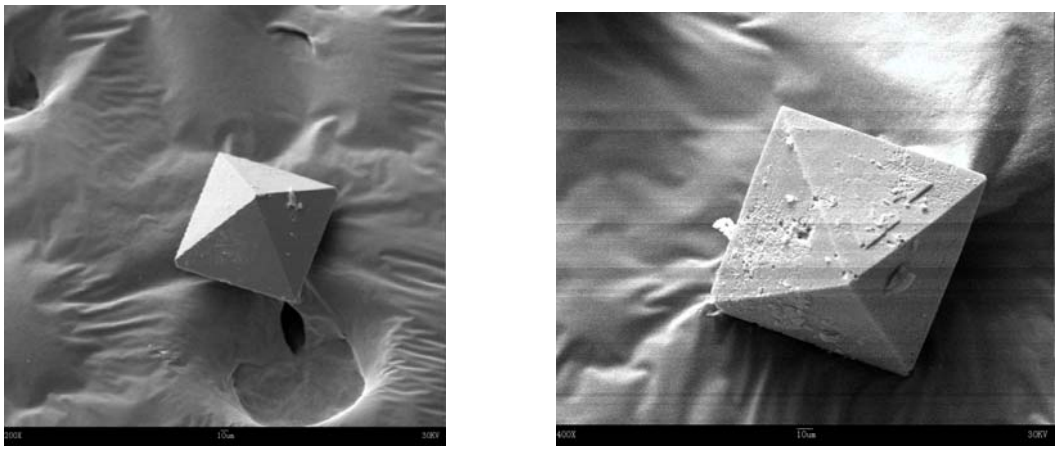


(a) **(b)**

Fig.S1 (a) The SEM of compound **1** or **2** (The shapes between compounds **1** and **2** are similar, so, we do not separate them when we do the SEM test); (b) The SEM of compound **3**.

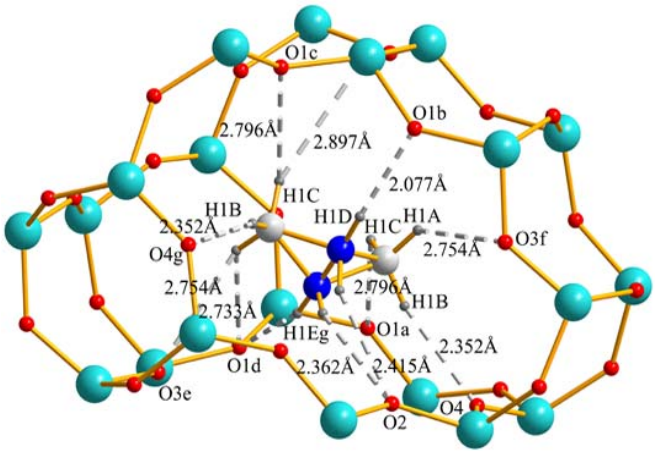


Fig.S2 The hydrogen bonding interactions between structure directing agents and framework. Symmetry codes: (a) 0.5-y, -0.5+x, -0.25+z; (b) 1+y, x, -z; (c) 1.5-x, 0.5+y, -0.25-z; (d) 1-x, -y, -0.5+z; (e) 0.5+y, 0.5-x, -0.75+z; (g) 1-y, 1-x, -0.5-z.

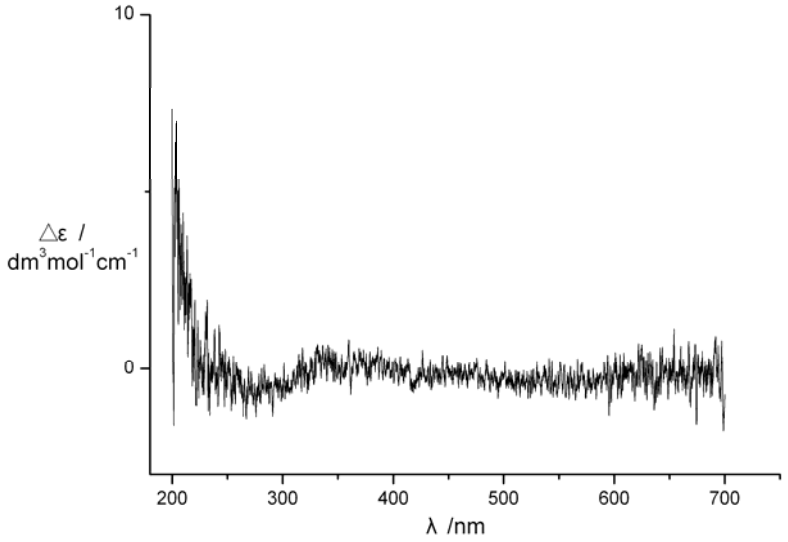
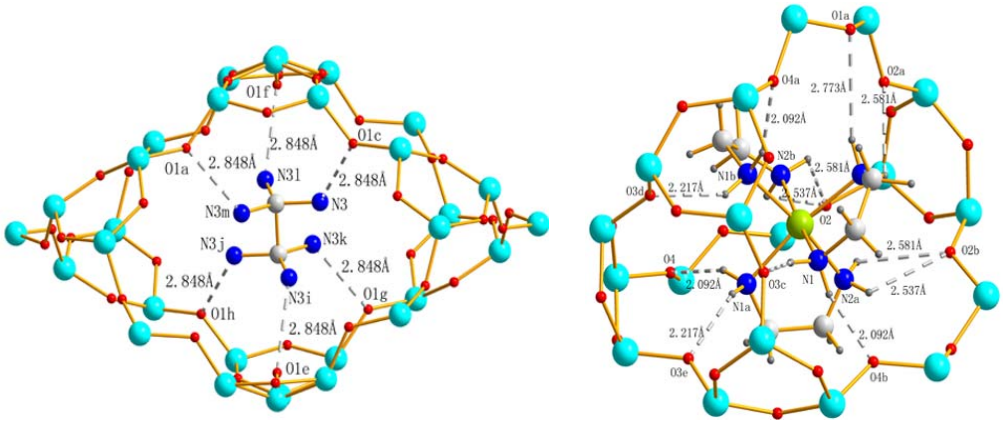


Fig.S3 CD spectrum for the mixture of **1** and **2**.



(a) (b)

Fig.S4 (a) The hydrogen bonding interactions between en and [$3^8.10^6$] cage; (b) The hydrogen

bonding interactions between $[Ni(en)_3]^{2+}$ and $[3^4.6.10^3]$ cage. Symmetry codes: (a) 1-y, 0.5+z, 0.5-x; (b) 0.5-z, 1-x, -0.5+y; (c) 0.5+z, 0.5-x, 1-y; (d) -0.5+y, 0.5-z, -x; (e) 0.5+x, 1.5-y, -z; (f) 0.5-x, 1-y, 0.5+z; (g) y, 0.5-z, 0.5+x; (h) 0.5-z, 0.5+x, y; (i) 1-y, 1-z, 1-x; (j) 1-x, 1-y, 1-z; (k) 1-z, 1-x, 1-y; (l) y, z, x; (m) z, x, y.

TG Analysis

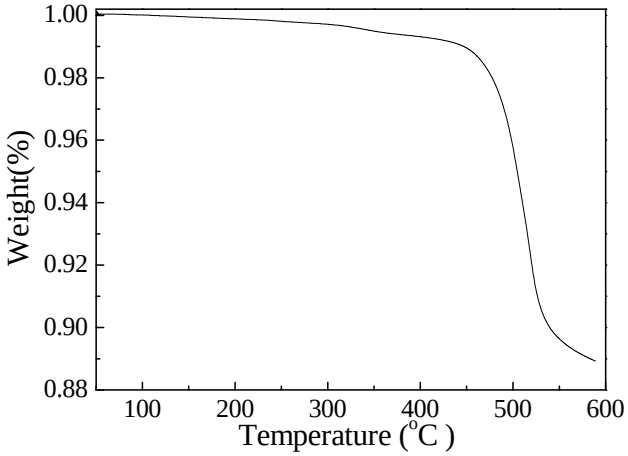


Fig.S5 TGA curve of mixed L- and D-$[C_2NH_8][AlGe_3O_8]$ (**1** and **2**).

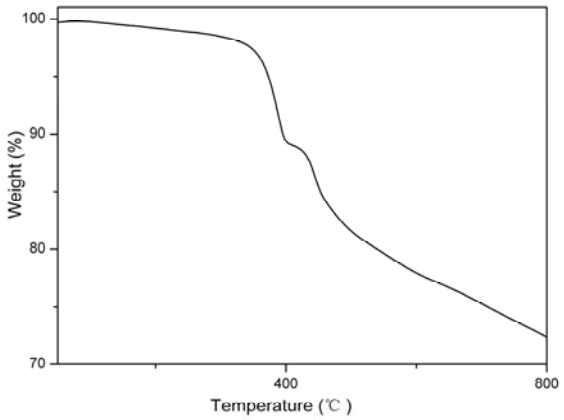


Fig.S6 TGA curve of spectra of compound **3**.

IR Spectra

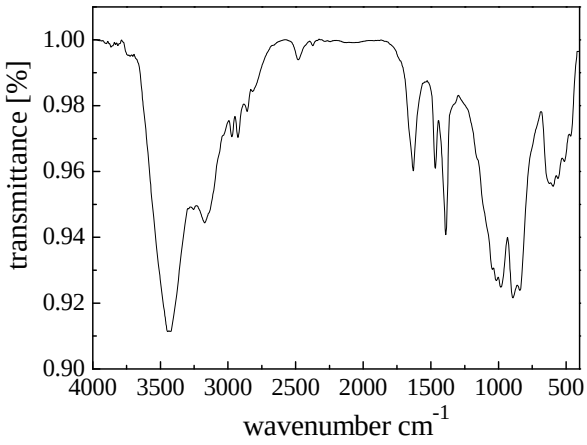


Fig.S7 The IR spectra of mixed L- and D-$[C_2NH_8][AlGe_3O_8]$ (**1** and **2**).

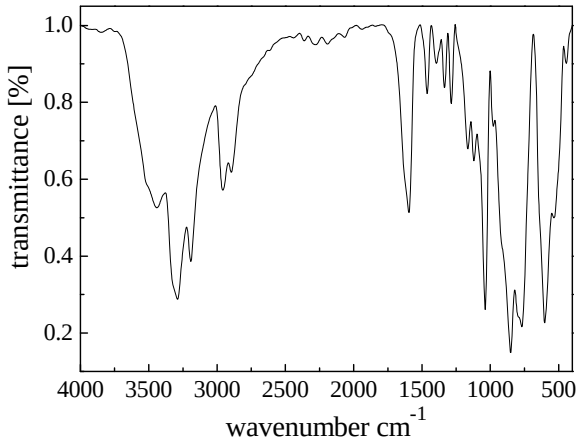


Fig.S8 The IR spectra of compound **3**.

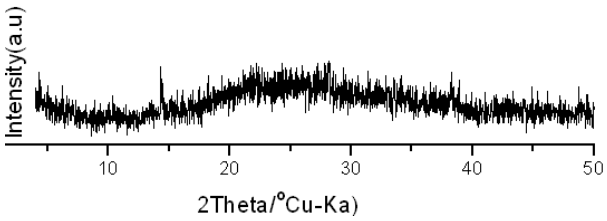


Fig.S9 Powder XRD patterns of compound **3** heated under 400 °C for about 5 hours, which shows the diffraction peaks could not match with the simulated, indicates that the skeleton of compound **3** has been broken.

Table 1. Selected bond distances (Å) and angles (°) in (**1**)

Ge(1)–O(4)	1.727(9)	$O(1)^{\#1}$–T(1)–O(3)	105.8(4)
Ge(1)–O(1)	1.738(9)	O(1)–T(1)–$O(1)^{\#1}$	107.2(5)
Ge(1)–$O(1)^{\#1}$	1.760(9)	O(4)–T(1)–$O(1)^{\#1}$	111.8(5)
Ge(1)–O(3)	1.782(9)	O(4)–T(1)–O(3)	110.5(5)
Ge(2)–O(2)	1.707(10)	O(2)–T(3)–$O(2)^{\#5}$	110.6(6)
Ge(2)–$O(2)^{\#2}$	1.707(10)	O(2)–T(2)–$O(3)^{\#3}$	107.1(4)
Ge(2)–$O(3)^{\#3}$	1.728(10)	O(2)–T(2)–$O(3)^{\#4}$	111.9(5)
Ge(2)–$O(3)^{\#4}$	1.728(10)	O(2)–T(2)–$O(2)^{\#2}$	101.5(7)
Ge(3)–O(4)	1.755(10)	$O(3)^{\#3}$–T(2)–$O(3)^{\#4}$	116.4(6)
Ge(3)–$O(4)^{\#5}$	1.755(10)	O(4)–T(3)–$O(4)^{\#5}$	117.1(6)
Ge(3)–O(2)	1.758(9)	O(4)–T(3)–O(2)	103.1(5)
Ge(3)–$O(2)^{\#5}$	1.758(9)	$O(4)^{\#5}$–T(3)–O(2)	111.5(5)
O(1)–T(1)–O(3)	111.4(4)	O(4)–T(3)–$O(2)^{\#5}$	111.5(5)
O(1)–T(1)–O(4)	110.1(4)	$O(4)^{\#5}$–T(3)–$O(2)^{\#5}$	103.1(5)

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

Table 2. Selected bond distances (Å) and angles (°) in (**3**)

T(1)–O(3)	1.739(3)	T(2)–O(4)$^{\#2}$	1.743(3)
T(1)–O(3)$^{\#1}$	1.745(3)	T(2)–O(1)	1.746(3)
T(1)–O(1)	1.750(3)	T(2)–O(4)	1.752(3)
T(1)–O(2)	1.755(3)	T(2)–O(2)$^{\#1}$	1.757(3)
Ni(1)–N(1)	2.100(4)	Ni(1)–N(2)	2.148(5)
Ni(1)–N(1)$^{\#3}$	2.100(4)	Ni(1)–N(2)$^{\#4}$	2.148(5)
Ni(1)–N(1)$^{\#4}$	2.100(4)	Ni(1)–N(2)$^{\#3}$	2.148(5)
O(3)–T(1)–O(3)$^{\#1}$	110.6(2)	N(1)$^{\#4}$–Ni(1)–N(2)$^{\#4}$	80.84(18)
O(3)–T(1)–O(1)	110.03(15)	N(2)–Ni(1)–N(2)$^{\#4}$	93.8(2)
O(3)$^{\#1}$–T(1)–O(1)	108.56(14)	N(1)–Ni(1)–N(2)$^{\#3}$	170.37(19)
O(3)–T1)–O(2)	107.61(14)	N(1)$^{\#3}$–Ni(1)–N(2)$^{\#3}$	80.84(18)
O(3)$^{\#1}$–T(1)–O(2)	108.96(16)	N(1)$^{\#4}$–Ni(1)–N(2)$^{\#3}$	94.5(2)
O(1)–T(1)–O(2)	111.09(15)	N(2)–Ni(1)–N(2)$^{\#3}$	93.8(2)
O(4)$^{\#2}$–T(2)–O(1)	112.01(15)	N(2)$^{\#4}$–Ni(1)–N(2)$^{\#3}$	93.8(2)
O(4)$^{\#2}$–T(2)–O(4)	107.62(19)	Ge(2)–O(1)–Ge(1)	131.24(18)
O(1)–T(2)–O(4)	108.89(15)	Ge(1)–O(2)–Al(2)$^{\#5}$	128.19(18)
O(1)–T(2)–O(2)$^{\#1}$	108.02(14)	Ge(1)–O(2)–Ge(2)$^{\#5}$	128.19(18)
O(4)–T(2)–O(2)$^{\#1}$	112.77(16)	Ge(1)–O(3)–Al(1)$^{\#5}$	127.05(18)
N(1)–Ni(1)–N(1)$^{\#3}$	91.59(17)	Ge(1)–O(3)–Ge(1)$^{\#5}$	127.05(18)
N(1)–Ni(1)–N(1)$^{\#4}$	91.59(17)	Al(2)$^{\#6}$–O(4)–Ge(2)	130.80(19)
N(1)$^{\#3}$–Ni(1)–N(1)$^{\#4}$	91.59(17)	Ge(2)$^{\#6}$–O(4)–Ge(2)	130.80(19)
N(1)–Ni(1)–N(2)	80.84(18)	C(2A)–N(2)–C(2)	32.7(10)
N(1)$^{\#3}$–Ni(1)–N(2)	94.5(2)	C(2A)–N(2)–Ni(1)	111.4(7)
N(1)$^{\#4}$–Ni(1)–N(2)	170.37(19)	C(2)–N(2)–Ni(1)	104.2(6)
N(1)–Ni(1)–N(2)$^{\#4}$	94.5(2)	C(1)–N(1)–Ni(1)	111.2(3)
N(1)$^{\#3}$–Ni(1)–N(2)$^{\#4}$	170.37(19)	O(4)$^{\#2}$–Ge(2)–O(2)$^{\#1}$	107.59(16)

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