

Supporting Information:

Table S1. The H-bonds in the structure of **FJ-17**

D-H \cdots A	<i>d</i> (D-H)	<i>d</i> (H \cdots A)	<i>d</i> (D \cdots A)	\angle (DHA)
N1-H1D \cdots O11	0.89	1.88	2.762(5)	173.3
N1- H1E \cdots O12	0.89	2.11	2.974(5)	162.6
N3- H3A \cdots O1	0.89	2.13	2.964(5)	155.1
N3- H3A \cdots O10	0.89	2.16	2.847(5)	134.1
N3- H3B \cdots O3	0.89	2.01	2.837(5)	153.4
N3- H3C \cdots O2	0.89	2.19	2.909(5)	137.7

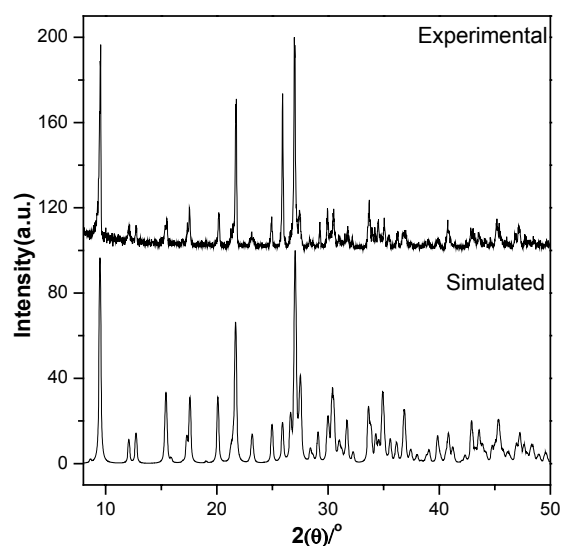


Figure S1. Experimental and simulated X-ray powder diffraction pattern of **FJ-17**.

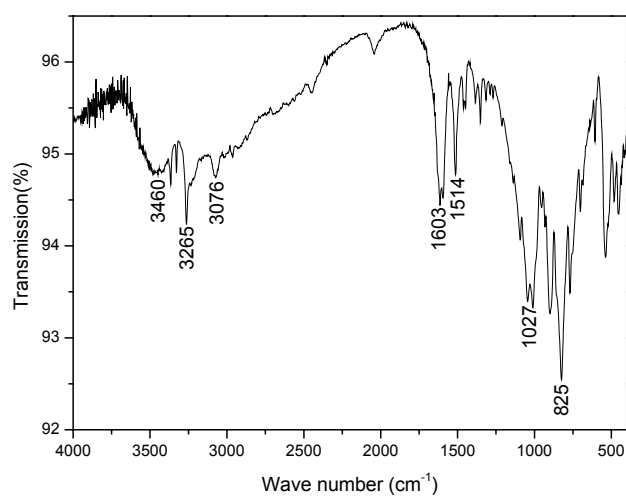


Figure S2. IR curve of **FJ-17**.

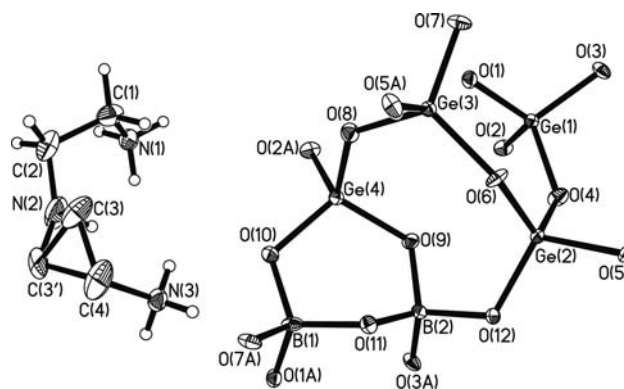


Figure S3. The ORTEP view of the coordination environments for Ge and B atoms in **FJ-17**, with 50% thermal ellipsoids and the atom-labeling scheme.

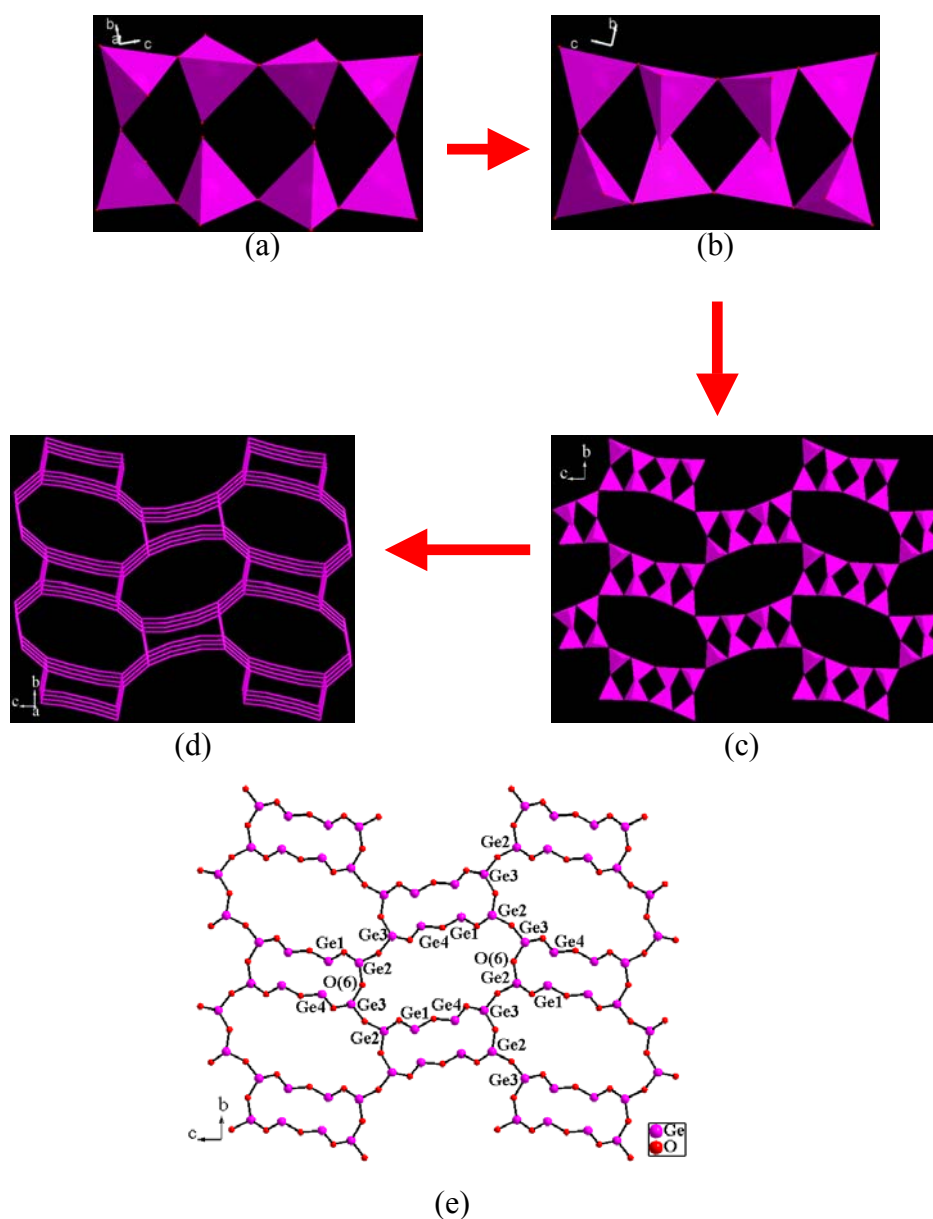


Figure S4. (a) and (b) View of the 8-ring of Ge_8O_{24} cluster along different directions; (c) View of the $\{\text{Ge}_8\text{O}_{24}\}_n$ layer with 8,12-net along the [100] direction; (d) The topology of the $\{\text{Ge}_8\text{O}_{24}\}_n$ layer along the [100] direction. (e) View of the $\{\text{Ge}_8\text{O}_{24}\}_n$ layer with 8,12-net (some O atoms in GeO_4 group are omitted for clarity)

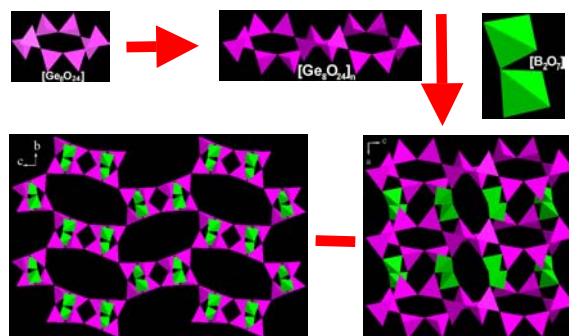


Figure 5. Schematic representation of the structure of **FJ-17**, showing the formation Ge_8O_{24} cluster to $\{\text{Ge}_8\text{O}_{24}\}_n$ layer and $\{(\text{BO}_2)_4(\text{GeO}_2)_8\}_n$ framework along the a (left) and b (right) axis, respectively.

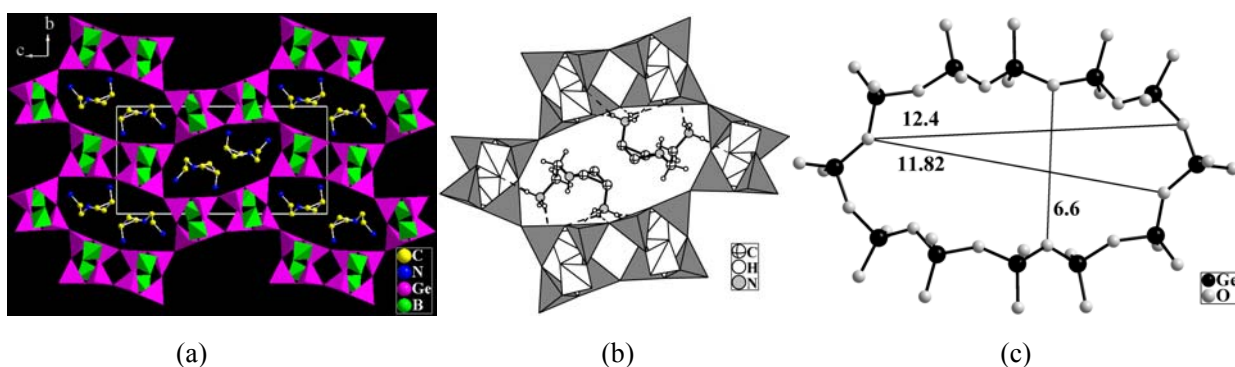


Figure S6. (a) View of the framework of $\{[\text{BO}_2]_4[\text{GeO}_2]_8\}_n$ along the $[100]$ direction in **FJ-17**, showing 12-rings large channels located by organic templates. (b) View the H-bonds interactions between the organic templates and the oxygen atoms from the inorganic frameworks. The important H-bonds are list in [Table S1](#). (c) The 12-rings structure in **FJ-17** viewed down $[100]$ with selected $\text{O}\cdots\text{O}$ distances noted.

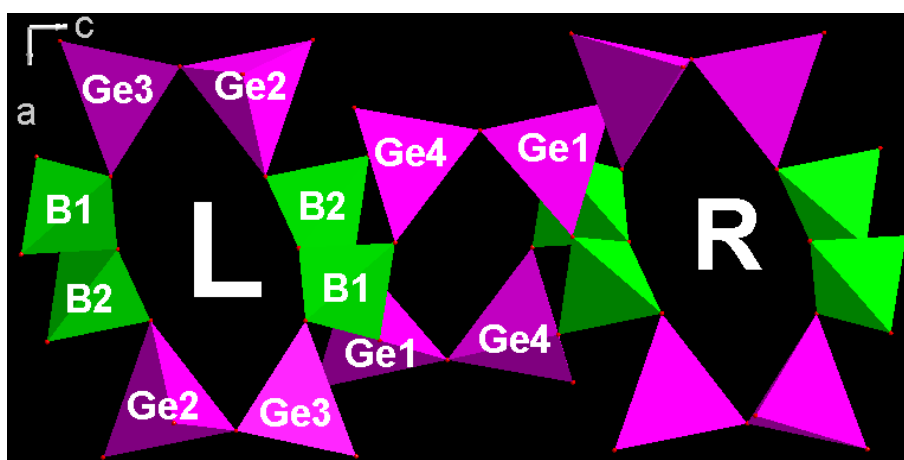


Figure S7. View of the left- and right-handed helical channels linked each other through the Ge_2O_7 dimeric cluster units containing Ge1 and Ge4 atoms.

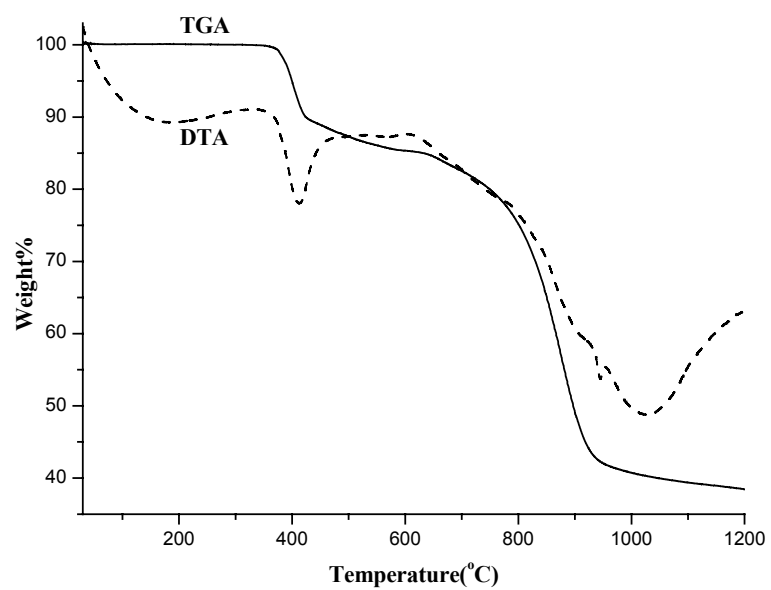


Figure S8. TG-DTA curve of **FJ-17** under N₂ atmosphere.