Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Self-assembly and thermotropic liquid crystal property of a hexavacant germanomolybdate: $[Ge_2Mo_{16}O_{58}]^{12-}$

Yan-Qing Gao, Zhi-Ming Zhang,* Jian-Qiang Shen, Yue Jia, Zhu-Jun Liu, En-Bo Wang*

Key laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Renmin Street No.5268, Changchun, Jilin, 130024, P. R. China.

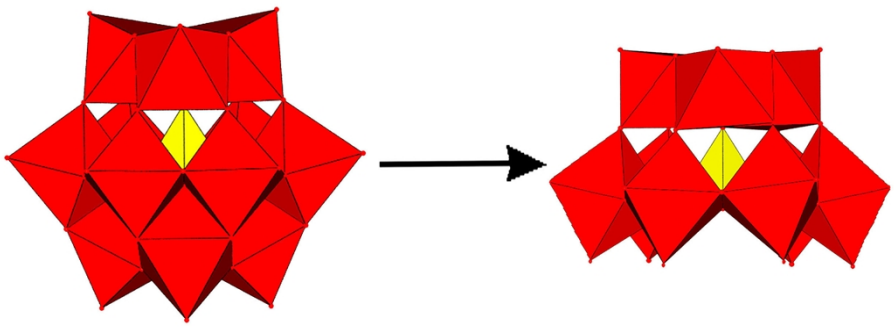

Fig. S1. The formation of {β-*A*-$GeMo_9O_{34}$}.

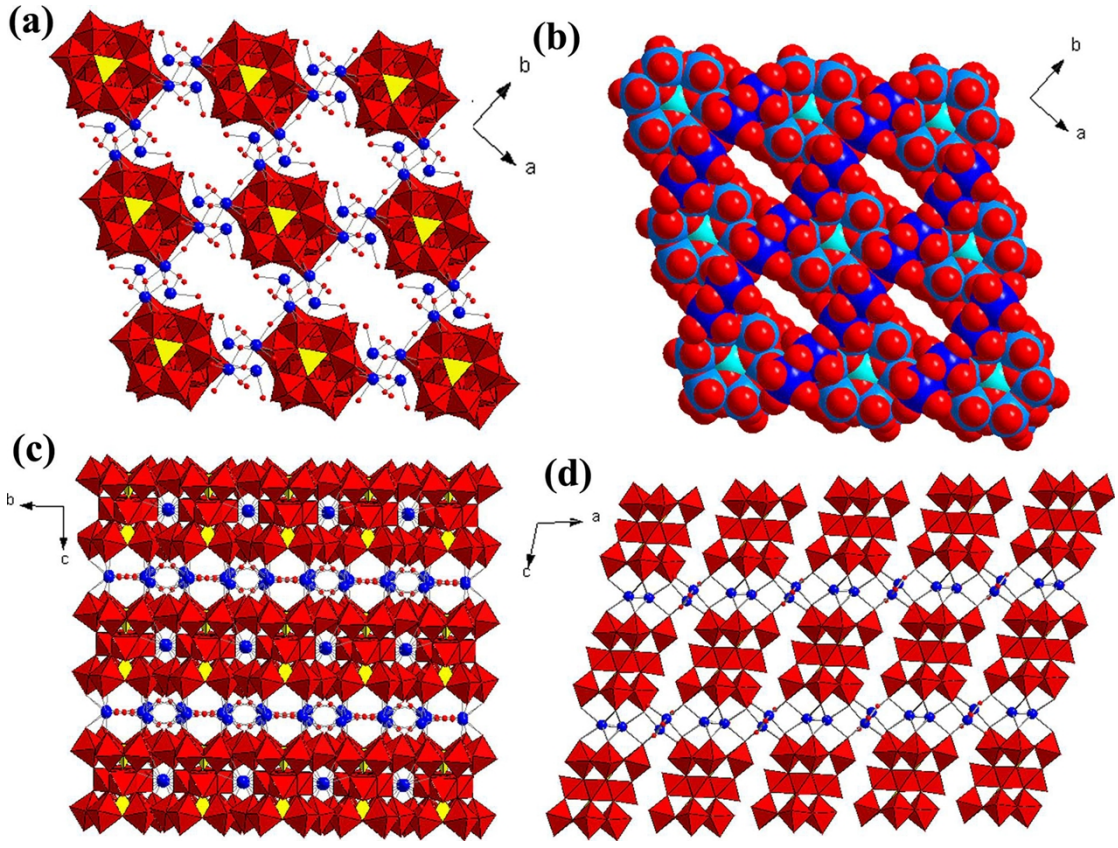

Fig. S2. The 3D framework of compound **2** along different directions.

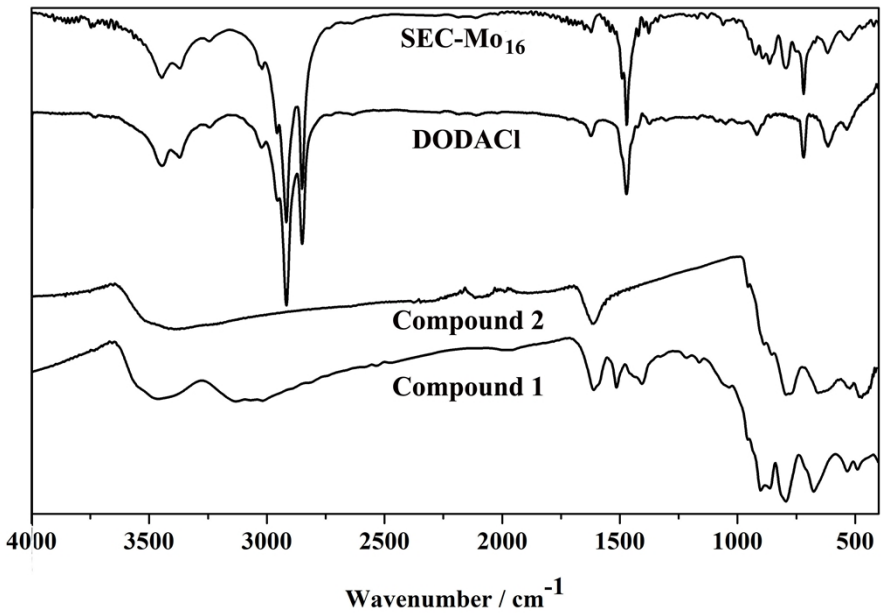

Fig. S3. The IR spectra of compound **1**, compound **2**, DODACl and **SEC-Mo$_{16}$**.

The IR spectra of compound **1** shows the characteristic bands at 900-676 cm^{-1}, corresponding to terminal Mo-Ot vibrations, Ge-O vibrations and Mo-O bridges vibrations, respectively. In addition, the vibration bands at 1611-1405 cm^{-1} can be assigned to the bending vibration bands of $-NH_2$, $-CH_3$ and $-CH_2$. Moreover, the stretching bands of -OH and $-NH_2$ groups are observed at 3462 and 3131 cm^{-1}, respectively. The IR spectra of compound **2** shows the characteristic bands at 883-654 cm^{-1}, corresponding to terminal Mo-Ot vibrations, Ge-O vibrations and Mo-O bridges vibrations, respectively. In addition, the vibration bands at 1610 and 3397 cm^{-1} can be assigned to the bending vibration band and stretching band of -OH, respectively. By comparison the IR spectra of compound **1**, compound **2**, DODACl and **SEC-Mo$_{16}$**, we can clearly observe that the difference between **SEC-Mo$_{16}$** and DODACl is the peaks in the low-wave number region, corresponding to the characteristic peaks of compound **1** and compound **2,** indicating the existence of $DODA^+$ and polyoxoanion

$[Ge_2Mo_{16}O_{58}]^{12-}$ in **SEC-Mo$_{16}$**.

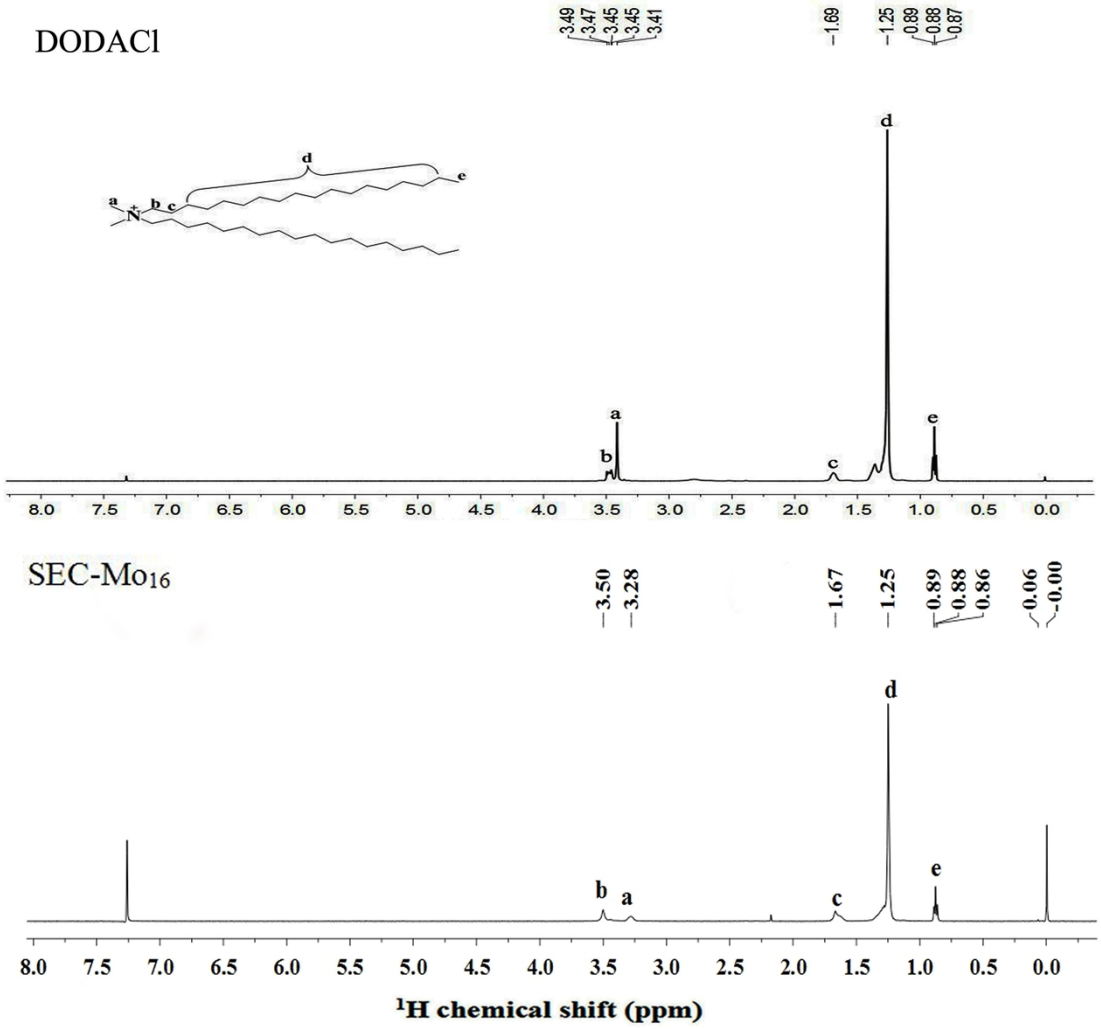

Fig. S4. The ^{1}H NMR spectra of DODACl and **SEC-Mo$_{16}$**.

The ^{1}H NMR spectra of DODACl exhibts five types of hydrogens of different chemical environments, which can also been observed in the ^{1}H NMR spectra of **SEC-Mo$_{16}$**, indicating the existence of $DODA^+$ in **SEC-Mo$_{16}$**.

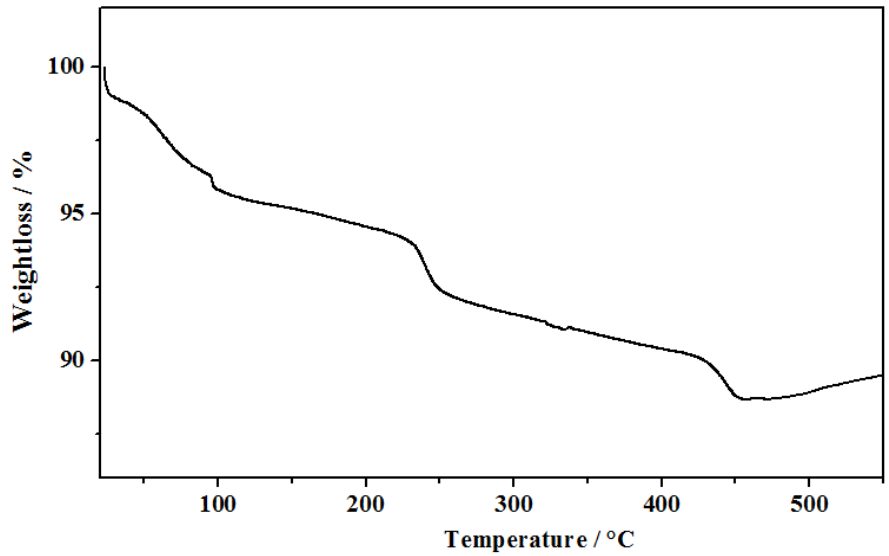

Fig. S5. The TG curve of compound **1.** The TG curve of compound **1** shows two steps of weight loss, the total loss is 11.4 % (calc. 14.7 %).

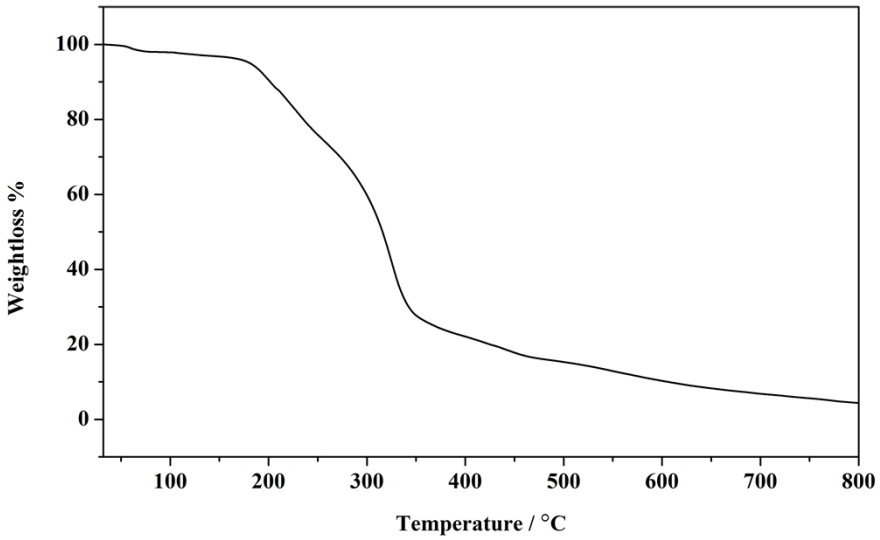

Fig. S6. The TG curve of **SEC-Mo$_{16}$**.

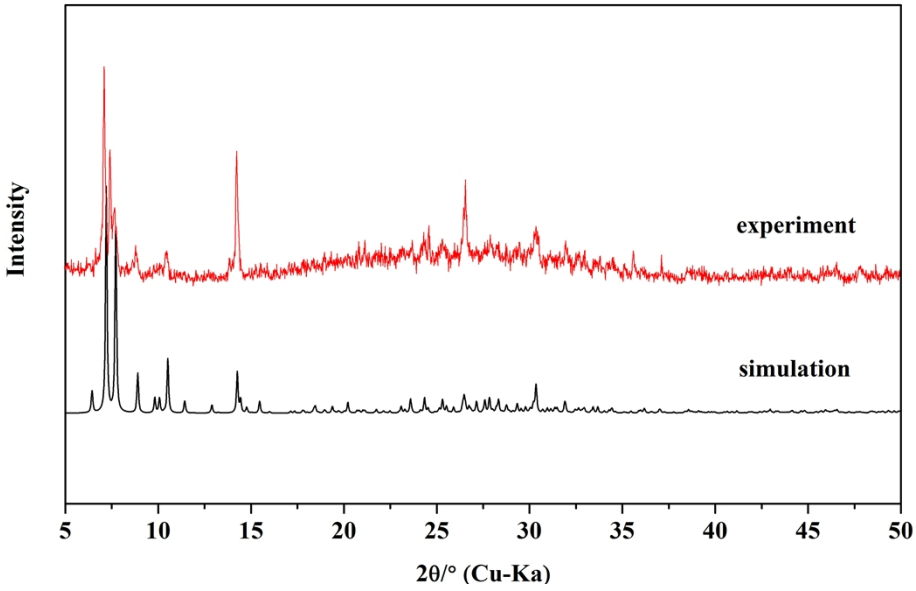

Fig. S7. The PXRD patterns of compound **1.**