Electronic Supplementary Information for Dalton Transactions

Supporting Information

Two unprecedented porous anionic frameworks: organoammonium templating effects and structural diversification

Xiang-Rong Hao, Xin-Long Wang, Zhong-Min Su,* Kui-Zhan Shao, Ya-Hui Zhao, Ya-Qian Lan and Yao-Mei Fu

Institute of Functional Materials, College of Chemistry, Northeast Normal University, Changchun 130024, China. Email: zmsu@nenu.edu.cn

X-ray structure analysis: Crystal data of 1: $C_{62}H_{76}Cd_2N_6O_{16}$, *M*r = 1386.12 orthorhombic, space group $I2_12_12_1$, a = 8.207(5) Å, b = 27.618(5) Å, c = 28.692(5) Å, $\alpha = \beta = \gamma = 90°$, V = 6503(4) Å^3, Z = 4, ρ_{calc} = 1.416 g cm^3, T = 293(2) K, *R*int = 0.0325, GOF = 1.083, Flack parameter = 0.49(3), R1 = 0.0397 and wR2 = 0.1134 for 6906 independent reflections [$I > 2\sigma(I)$]. CCDC 652570.
Crystal data of 2: $C_{44}H_{64}Cd_2N_9O_{16}$, *M*r = 1199.84, orthorhombic, *C*mmm, a = 16.835(4) Å, b = 14.862(4) Å, c = 14.532(4) Å, $\alpha = \beta = \gamma = 90°$, V = 3635.9(2) Å^3, Z = 2 ρ_{calc} = 1.096 g cm^3, T = 153(2) K, Rint = 0.0771 GOF = 1.049, R1 = 0.0409 and wR2 = 0.0942 for 2264 independent reflections [I >2σ(I)]. CCDC 682374.

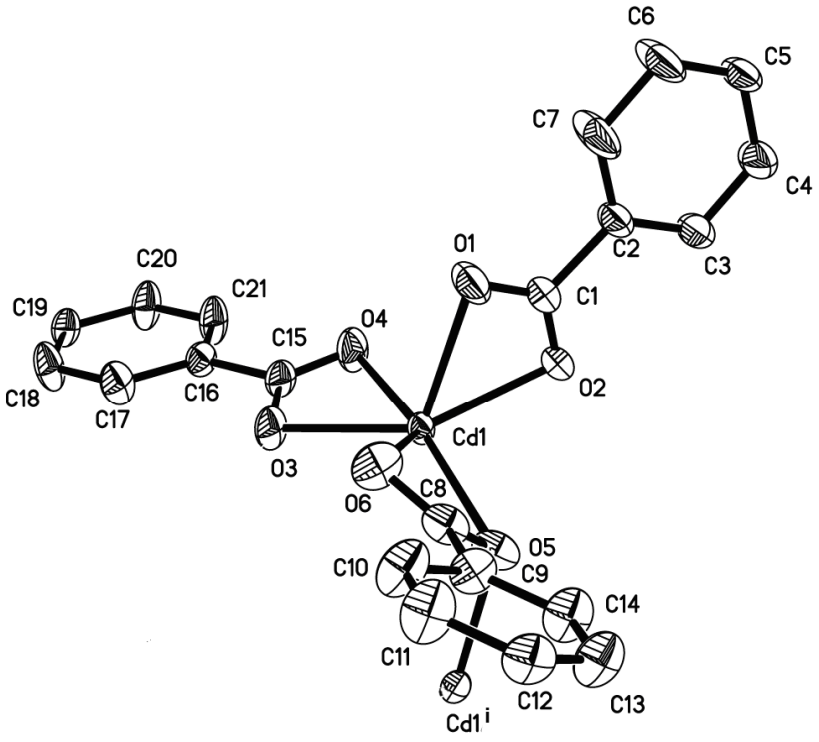
The crystal data of **1** was collected on a Bruker Apex CCD diffractometer at 293(2) K with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073Å). The structure was solved by direct method and refined by full-matrix least-squares methods with SHELXL.[1] The anion and DMA molecules were highly disordered and could not be modeled properly, thus the SQUEEZE routine, a part of the PLATON package of crystallographic software, was applied to calculate the solvent disorder area and remove its contribution to the overall intensity data. Despite the disorder, identification of the guest molecules is readily accomplished by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **1** recorded in D_2O exhibits a set of well-resolved proton signals. The signals at 2.88, 2.73 and 1.91 ppm attributed to three CH_3 groups of DMA,[2] while the signal at 2.54 ppm ascribes to the CH_3 group of dimethylamine. Furthermore, HNMR analysis reveals that the relative molar ratio of dimethylamine and DMA is approximately 1:2. The IR spectrum of **1**, as expected, exhibits a sharp band at 1648 cm^{-1} corresponding to $\tilde{\upsilon}$C=O stretching frequency, which is indicative of DMA molecule. According to the previous literature, the peaks of 1535 and 1397 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of the carboxylate group of bpdc ligand.[3] The peak at ca. 3419 cm^{-1} is attributed to the N-H absorption vibration of dimethylamine. Further information supporting the formula of **1** is obtained by thermogravimetric analysis, elemental analysis and the consideration of charge balance.

The crystal data of **2** were collected on a Bruker Apex CCD diffractometer at 153(2) K. The anion and DMA molecules were highly disordered and could not be modeled properly, thus the SQUEEZE routine, a part of the PLATON package of crystallographic software, was applied to calculate the solvent disorder area and remove its contribution to the overall intensity data. For the crystal 2 was very unstable, The formula was obtained by elemental analysis, ^{1}H NMR and the consideration of charge balance.

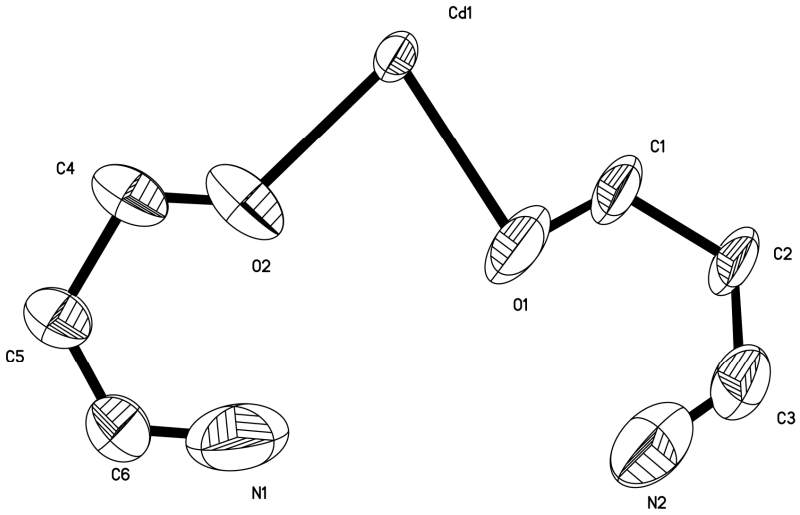
[1] G. M. Sheldrick, SHELXL, Version 5.1. Siemens Industrial Automation, Inc., Madison, WI, 1997.

[2] L. Carlucci, G. Ciani, D. M. Proserpio, F. Porta, *Angew. Chem. Int. Ed.* 2003, **42**, 317.

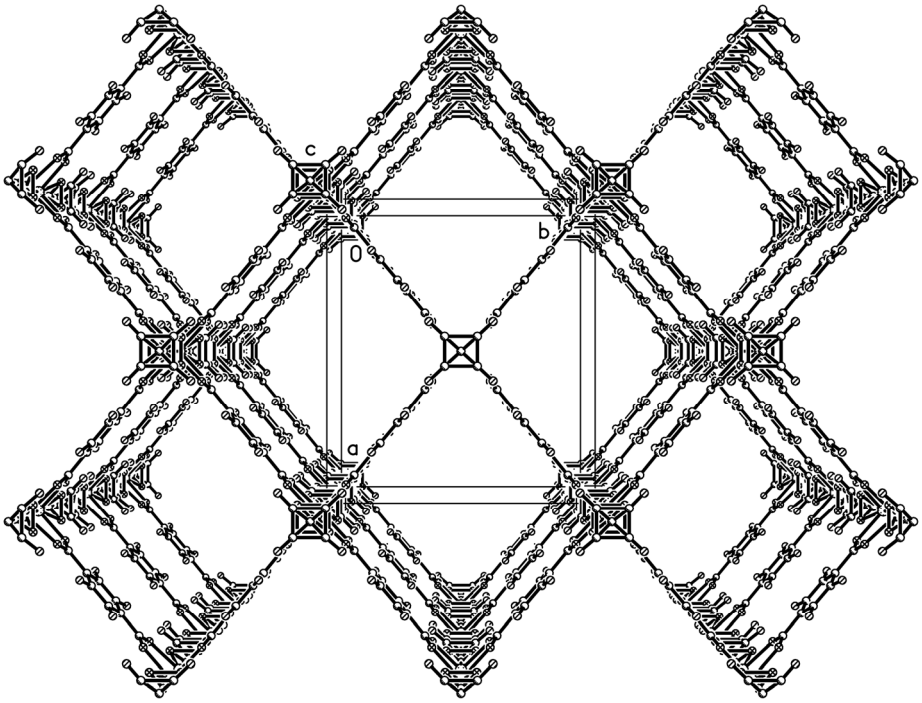
[3] a) F. A. Almeida Paz, Y. Z. Khimyak, A. D. Bond, J. Rocha, J. Klinowsk, *Eur. J. Inorg. Chem.* 2002, 2823; b) Q. R Fang, X. Shi, G. Wu, G. Tian, G. S. Zhu, R. W. Wang, S. L. Qiu, *J. Solid. State.* 2003, **176**, 1; c) Y. H. Wang, B. BredenkÖtter, B. Riegera, D. Volkmer, *Dalton Trans.* 2007, 689.



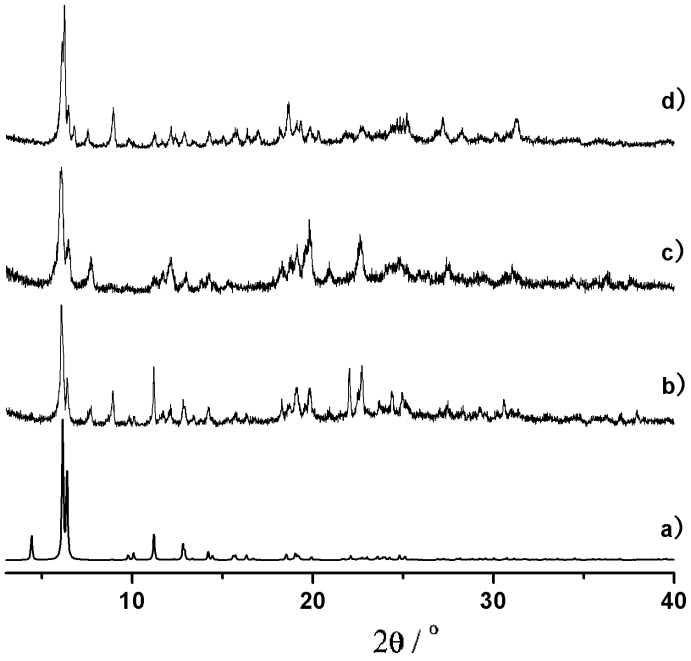
SI-1. Ortep view of the asymmetric unit of **1** with the atomic labeling scheme. Displacement ellipsoids are shown at the 30% probability level.



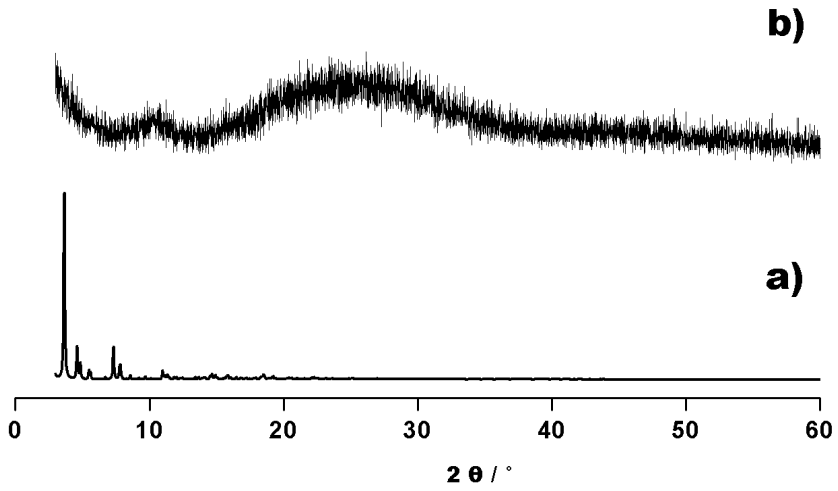
SI-2. Ortep view of the asymmetric unit of **2** with the atomic labeling scheme. Displacement ellipsoids are shown at the 30% probability level.



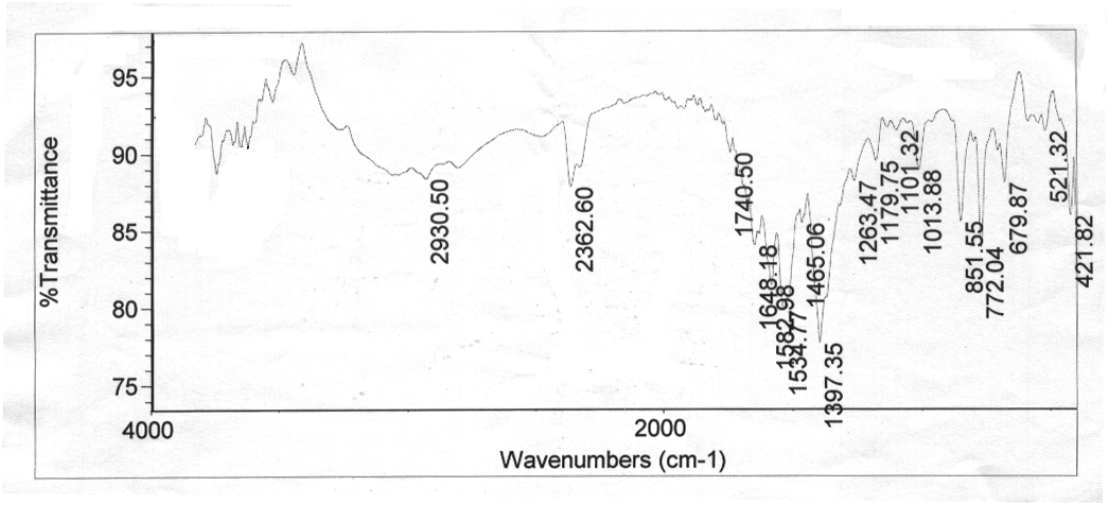
SI-3. Packing view of **2** along the *c* axis.



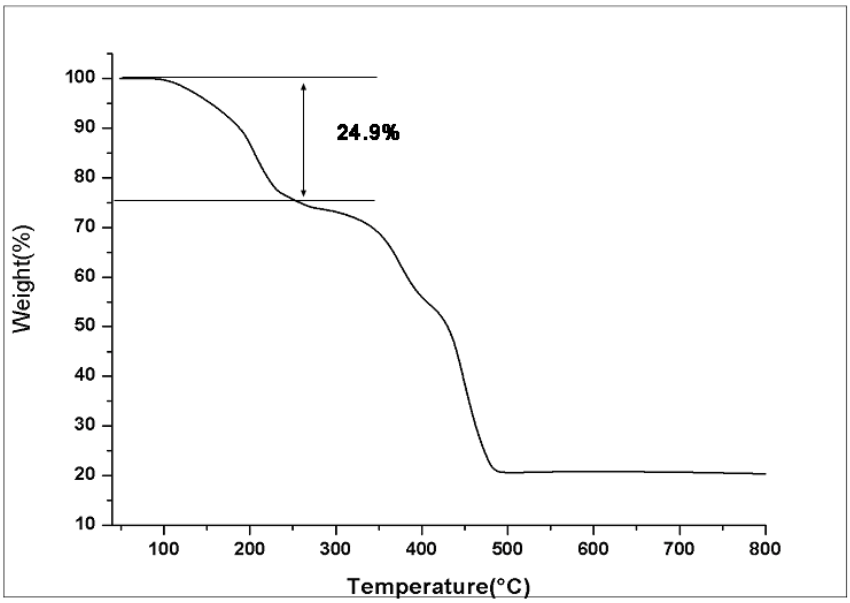
SI-4. PXRD patterns for **1**: (a) simulated from single-crystal X-ray diffraction data, (b) as-synthesized solids, (c) after removal of guest solvent molecules, (d) after re-adsorption of dma solvent molecules. and (e) after the ammonium acetate added in dmso-D6.



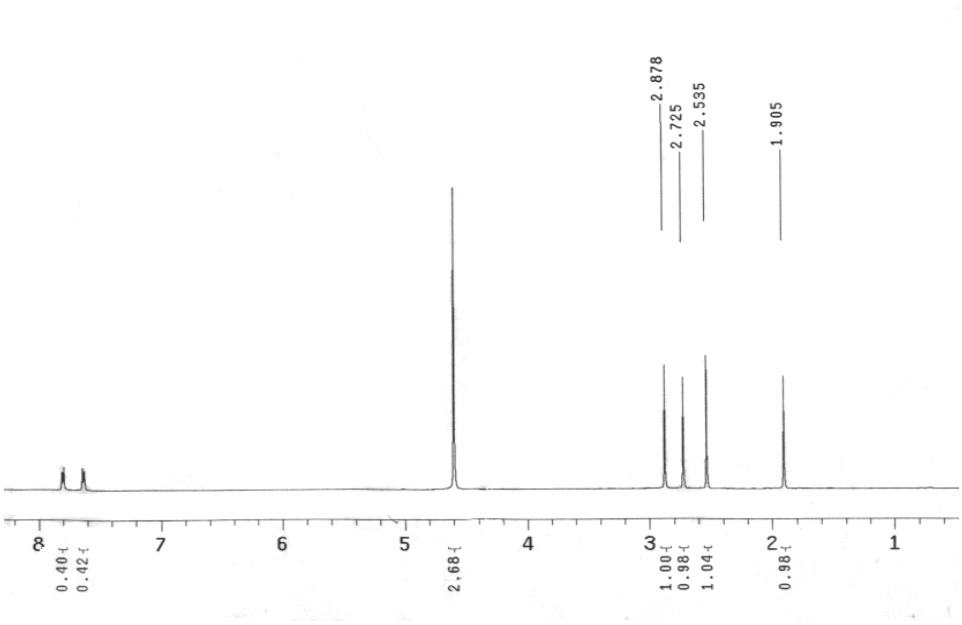
SI-5. PXRD patterns for **2**: (a) simulated from single-crystal X-ray diffraction data, (b) as-synthesized solids under air atmosphere for 15 min, showing the compound became amorphous.



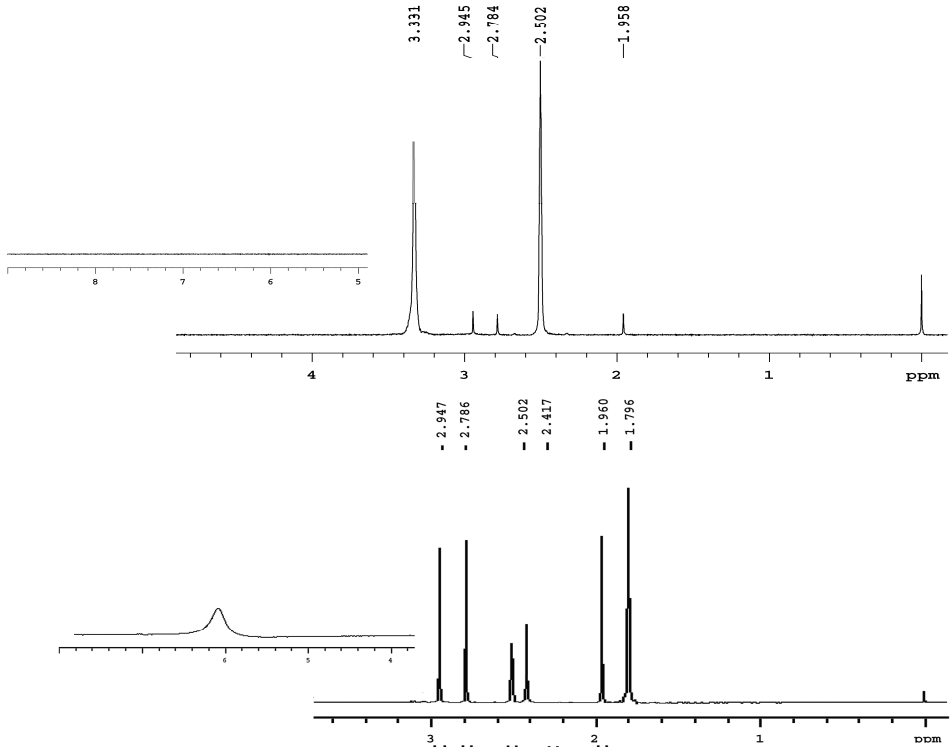
SI-6. FT-IR spectrum of as-synthesized **1**.



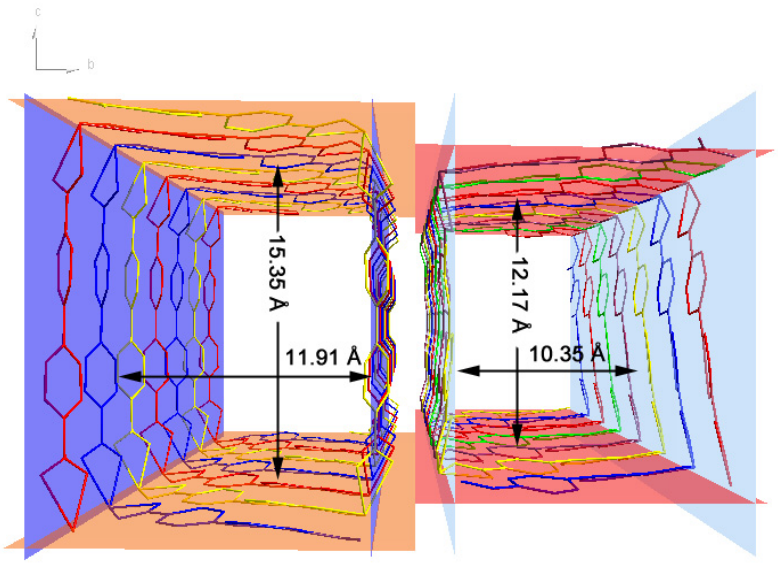
SI-7. TG curve of **1**.



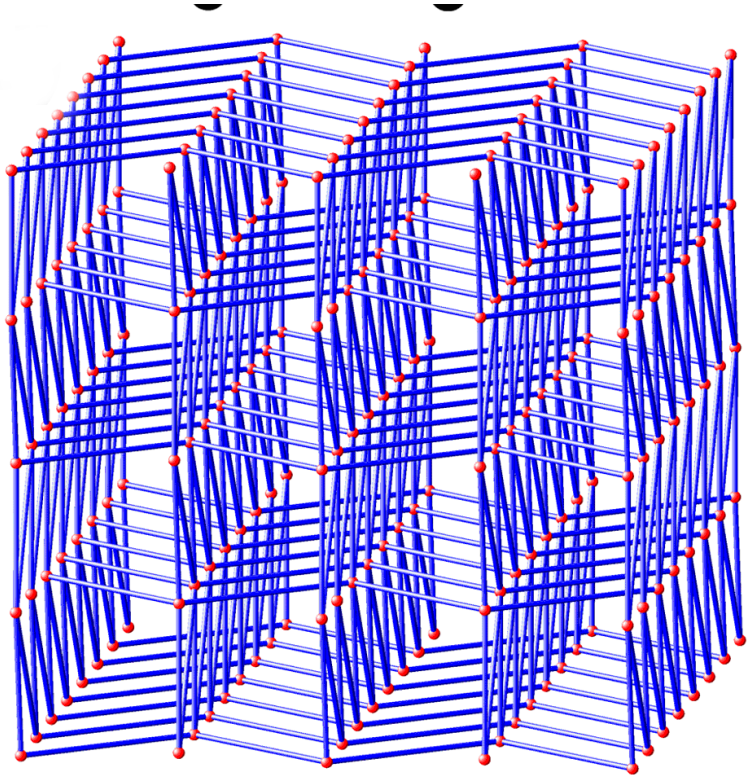
SI-8. The ^{1}H NMR spectrum of **1** recorded in D_2O.



SI-9. The ^{1}H NMR spectrum of **1** recorded in dmso-D6. top: before the ammonium acetate added. Bottom: after the ammonium acetate added and heating for 20 min.



SI-10. Type I and Type II channels are estimated to be about 15.4×11.9 and 12.2×10.4 Å, respectively, by calculating the distance between the least-square planes through the nearest parallel walls.



SI-11. The 6-connected net topology of **1**.