

*Electronic Supplementary Information*

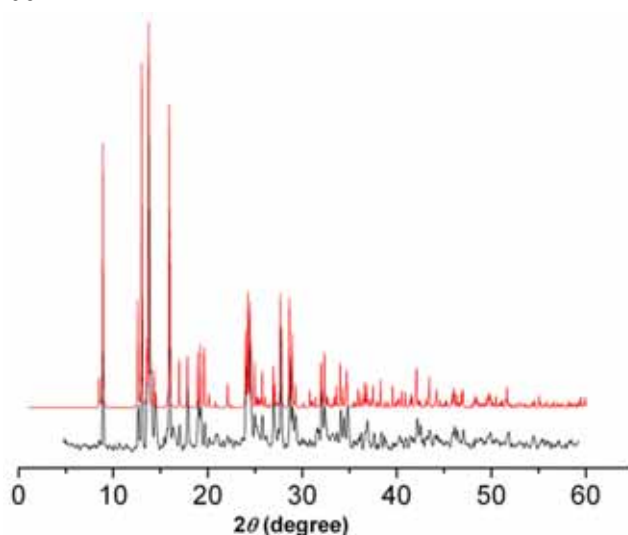
## Unprecedented self-penetrating 4-connected networks derived from a (3,4)-connected net of tfa-c topology

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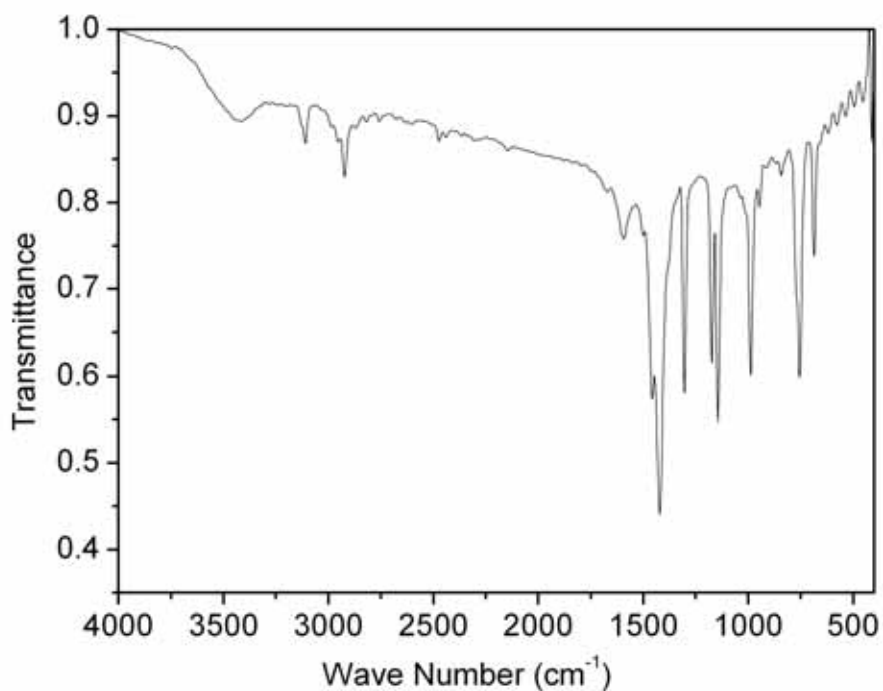
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### S1. X-ray structural analyses:

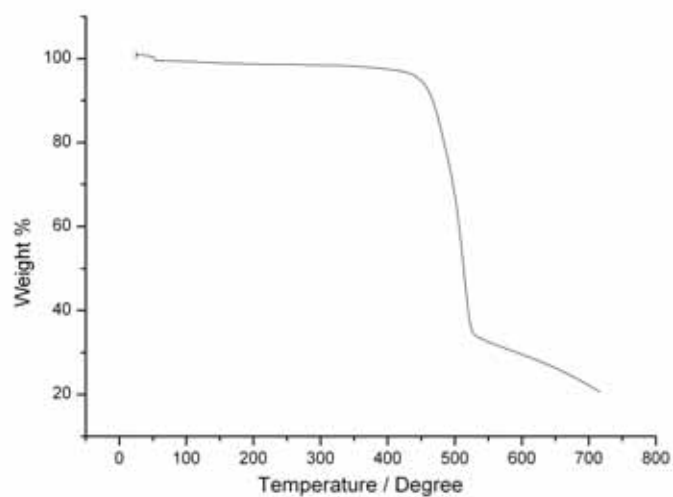
- X-ray single-crystal analysis: The data for **1** was collected on a Bruker SMART-APEX-II CCD diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods and refined by full-matrix least-square techniques on  $F^2$  using the SHELX program package. All non-hydrogen atoms except those disordered ones were refined anisotropically and the hydrogen atoms were generated and included in the structure calculations with assigned isotropic thermal parameters but not refined.
- X-ray powder diffraction (XRD) analysis was carried out on a Bruker D8 Advance



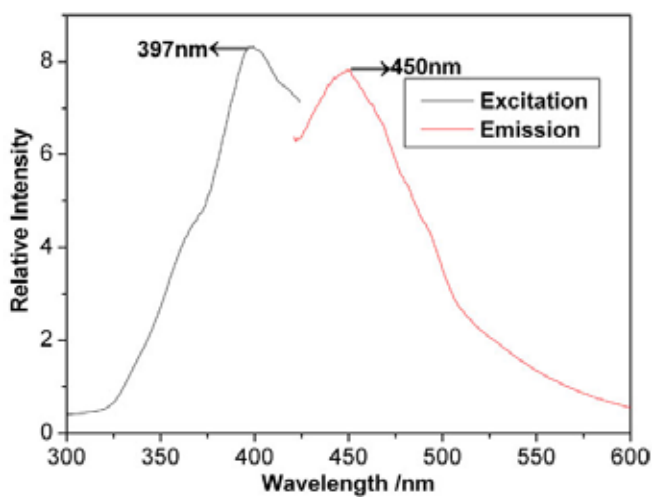
**Fig. S1** XRD pattern of **1**: the spectra from experimental measurement (black) and simulated from the single-crystal data (red).



**Fig. S2** IR spectrum of **1** (recorded (400-4000 cm<sup>-1</sup>) on a FT-IR spectrometer):



**Fig. S3** TGA of compound **1** (performed under nitrogen stream with a heating rate of 5 /min by using a Perkin-Elmer Diamond Thermogravimetric Analyzer).



**Fig. S4** The luminescent spectrum of compound **1** (performed on an AMINCO Bowman Series 2 Luminescence Spectrometer).

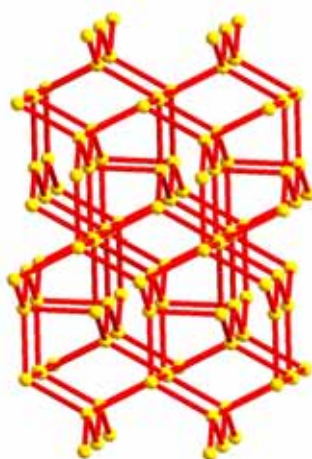


Fig S5. The topological structures of yqt1

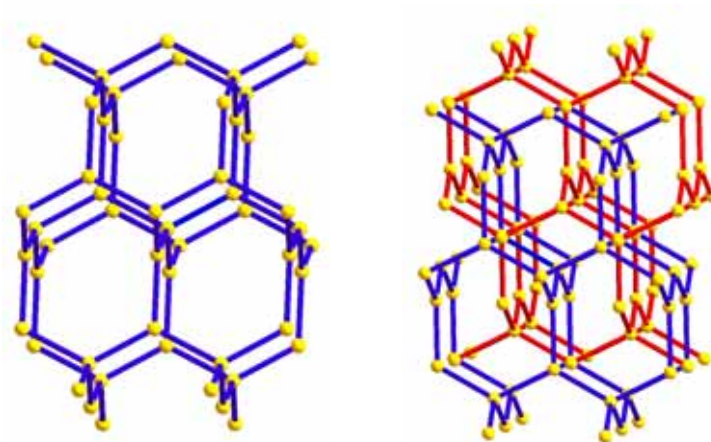
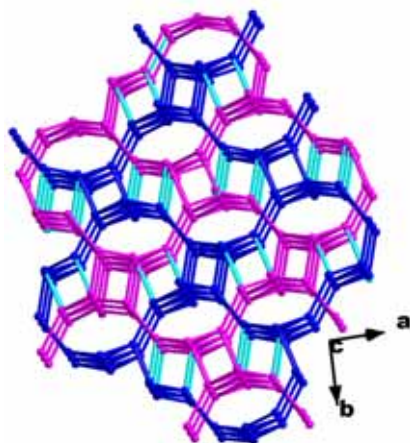
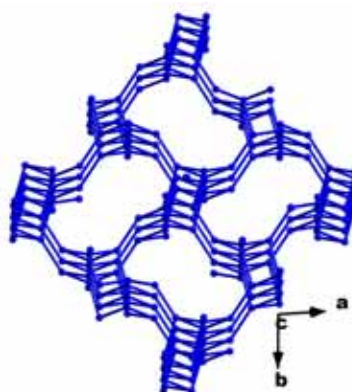


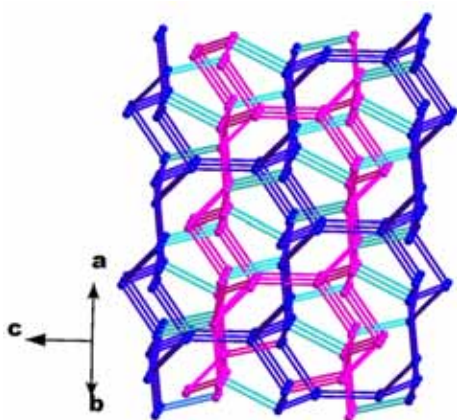
Fig S6. The topological structures of **tfa** (left) and **tfa-c** (right)



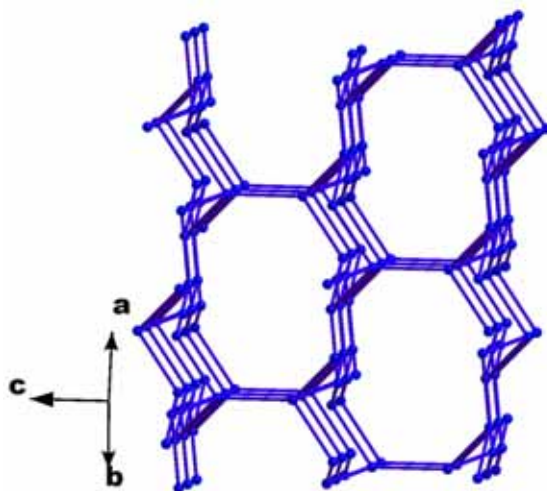
**Fig. S7**  $(4^2,6^2,8,9)(4^2,6,8^2,9)$ -coe topology of coesite derived from 2-fold interpenetrating (3,4)-connected net with  $(4,8^2)(4^2,6,8^2,12)$  topology.



**Fig. S8** the  $(4,8^2)(4^2,6,8^2,12)$  [long symbol  $(4,8,8)(4,8,4,12_4,6_2,8)$ ] topology of (3,4)-connected net embedding in the coesite network.



**Fig. S9**  $(6^4,8^2)(6^3,8^3)$ -icf topology of ice IV derived from 2-fold interpenetrating (3,4)-connected net with  $(6^3)(6^3 10^3)$  topology.



**Fig. S10** the  $(6^3)(6^310^3)$  [long symbol  $(6,6,6)(6,10_2,6,10_2,6,10_2)$ ] topology of  $(3,4)$ -connected net embedding in the ice IV network.