Electronic Supplementary Information

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

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S1. X-ray structural analyses:

a) X-ray single-crystal analysis: The data for 1 was collected on a Bruker SMART-APEX-II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-square techniques on F² 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.

b) 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).](image-url)
Fig. S2 IR spectrum of 1 (recorded (400-4000 cm⁻¹) on a FT-IR spectrometer):

Fig. S3 TGA of compound 1 (performed under nitrogen stream with a heating rate of 5 °C/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 $(4^2)(4^2,6,8^2,12)$ topology.

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

**Fig. S9** $(6^4,8^3)(6^3,8^3)$-icf topology of ice IV derived from 2-fold interpenetrating (3,4)-connected net with $(6^3)(6^310^3)$ topology.
Fig. S10  the (6\(^3\))(6\(^3\)10\(^3\)) [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.