

Supporting Information for

**Controllable incorporation of 1,2,4-triazolate into
cluster-based metal-chalcogenide frameworks**

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Experimental Section:

Chemicals and Materials. Indium nitrate hydrate ($\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$, $\geq 99.5\%$), thiourea ($\text{CH}_4\text{N}_2\text{S}$, 99%), sulfide powder (S , $\geq 99.5\%$), acetonitrile ($\text{C}_2\text{H}_3\text{N}$, $\geq 98\%$), 1,2,4-triazole ($\text{C}_2\text{H}_3\text{N}_3$, 98%), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 98%), 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), 1-(2-aminoethyl)piperazine (AEP, $>99.0\%$), 2-amino-1-butanol (AB, 98%), N,N-dimethylformamide (DMF, $\geq 98\%$) were all used without any further purification.

Synthesis of SCTF-1. A mixture of $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ (124 mg, 1 mmol), sulfide powder (96 mg, 3 mmol), 1,2,4-triazole (105 mg, 1.5 mmol), DMF (2 mL), AB (2 mL), DBN (2 mL) were stirred in a 23-mL Teflon-lined stainless steel autoclave for half an hour. The vessel was sealed and heated at 180 °C for 7 days, then the autoclave was cooled to room temperature. After the raw products were washed by absolute ethyl alcohol several times, a large number of colorless crystals were obtained. The phase purity was identified by powder X-ray diffraction measurements.

Synthesis of SCTF-2. A mixture of $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ (124 mg, 1 mmol), thiourea (76 mg, 1 mmol), 1,2,4-triazole (75 mg, 1 mmol), acetonitrile (1 mL), AEP (1 mL), DBU (3 mL) were stirred in a 23-mL Teflon-lined stainless steel autoclave for half an hour. The vessel was sealed and heated at 150 °C for 7 days, then the autoclave was cooled to room temperature. After the raw products were washed by absolute ethyl alcohol several times, a large number of yellowish crystals were obtained. The phase purity was identified by powder X-ray diffraction measurements.

Single Crystal X-ray Diffraction (SCXRD). Single-crystal X-ray diffraction measurements were performed on Photon II CPAD diffractometer controlled using graphite mono-chromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation at 120 K. The structure was solved by direct method using SHELXS-2014 and the refinements against all reflections of the compound were performed using SHELXL-2014.

Powder X-ray Diffraction (PXRD). PXRD data were collected on a desktop

diffractometer (D2 PHASER, Bruker, Germany) using Cu-K α ($\lambda = 1.54184 \text{ \AA}$) radiation operated at 30 kV and 10 mA. The samples were ground into fine powders for several minutes before the test.

Elemental Analysis. Energy dispersive spectroscopy (EDS) analysis was performed on scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) detector. An accelerating voltage of 25 kV and 40 s accumulation time were applied. Elemental analysis of C, H, and N was performed on VARIDEL III elemental analyzer. (**SCTF-1**, *Calcd.*: C, 19.66; N, 7.26; H, 2.55 wt%; *Found*: C, 19.27; N, 7.31; H, 3.42 wt%; and **SCTF-2** *Calcd.*: C, 18.76; N, 7.69; H, 2.41 wt%; *Found*: C, 22.10; N, 7.57; H, 3.78 wt%).

Thermogravimetric (TG) Measurement. A Shimadzu TGA-50 thermal analyzer was used to measure the TG curve by heating the sample from room temperature to 800 °C with heating rate of 10 °C /min under N₂ flow.

Fourier-Transform Infrared Absorption. Fourier transform-Infrared spectral analysis was performed on a Thermo Nicolet Avatar 6700 FT-IR spectrometer with cesium iodide optics allowing the instrument to observe from 600-4000 cm⁻¹.

UV-Vis Absorption. Room-temperature solid-state UV-Vis diffusion reflectance spectra of **SCTF-1** and **SCTF-2** samples were measured on a SHIMADZU UV-3600 UV-Vis-NIR spectrophotometer coupled with an integrating sphere by using BaSO₄ powder as the reflectance reference. The absorption spectra were calculated from reflectance spectra by using the Kubelka-Munk function: $F(R) = \alpha/S = (1-R)^2/2R$, where R , α , and S are the reflection, the absorption and the scattering coefficient, respectively. In order to determine the band edge of the direct-gap semiconductor, the relation between the absorption coefficients (α) and the incident photon energy ($h\nu$) is exhibited as $\alpha h\nu = A(h\nu - E_g)^{1/2}$, where A is a constant that relates to the effective masses associated with the valence and conduction bands, and E_g is the optical transition gap of the solid material. The band gap of the obtained samples can be

determined from the Tauc plot with $[F(R) \cdot h\nu]^2$ vs. $h\nu$ by extrapolating the linear region to the abscissa.

Table S1. Crystallographic data and structure refinement parameters for **SCTF-1** and **SCTF-2**.

| Compound | SCTF-1 | SCTF-2 |
|---|-------------------------|----------------|
| Crystal system | monoclinic | orthorhombic |
| Space group | <i>P2₁/c</i> | <i>Pbca</i> |
| <i>Z</i> | 4 | 8 |
| <i>a</i> (Å) | 32.120(4) | 20.887(4) |
| <i>b</i> (Å) | 20.820(2) | 22.592(5) |
| <i>c</i> (Å) | 22.273(2) | 33.244(7) |
| α (deg.) | 90 | 90.00(3) |
| β (deg.) | 94.085(3) | 90.00(3) |
| γ (deg.) | 90 | 90.00(3) |
| <i>V</i> (Å ³) | 14857(3) | 15687(6) |
| GOF on <i>F</i> ² | 1.070 | 1.150 |
| <i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>)) | 0.0952, 0.2503 | 0.0274, 0.0504 |
| <i>R</i> ₁ , <i>wR</i> ₂ (all data) | 0.1159, 0.2646 | 0.0323, 0.0517 |

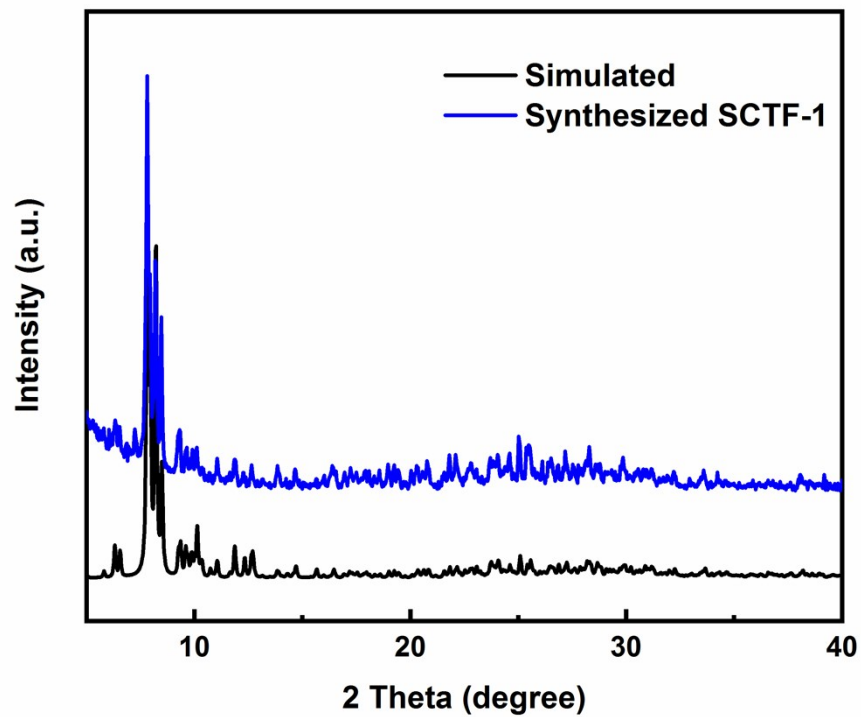


Figure S1. Powder X-ray diffraction (PXRD) pattern of as-synthesized SCTF-1 and its simulated one.

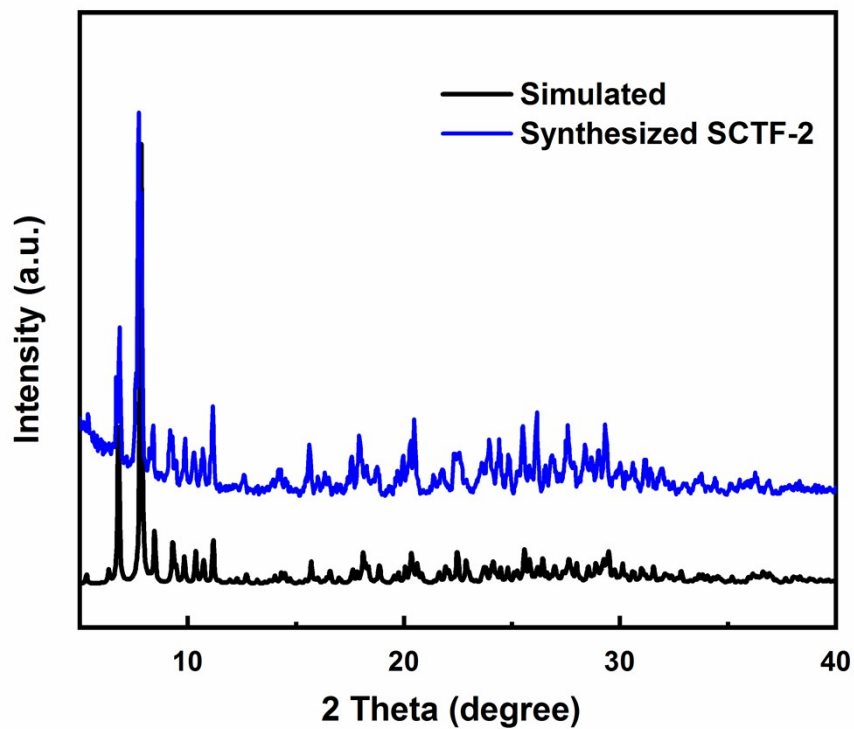


Figure S2. Powder X-ray diffraction (PXRD) pattern of as-synthesized SCTF-2 and its simulated one.

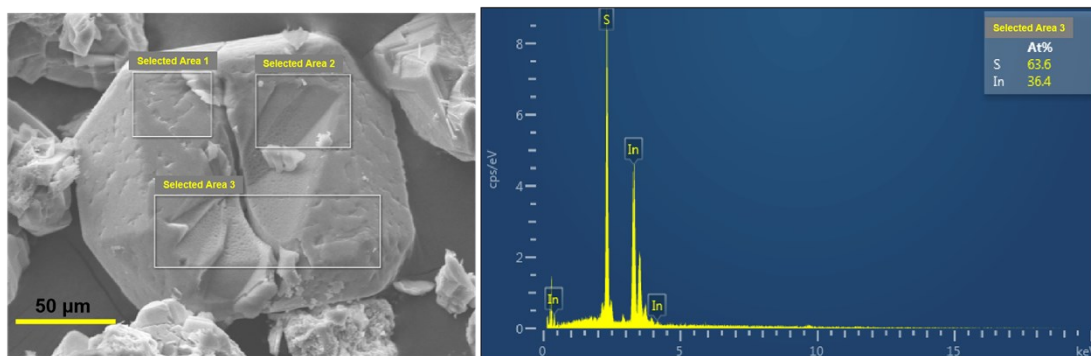


Figure S3. Left: SEM image of as-synthesized **SCTF-1** crystals. Right: energy dispersive spectroscopy (EDS) of **SCTF-1**. The results clearly confirmed the presence of In and S elements, and the measured molar ratio of S/In is 1.747, which is consistent with the theoretical value of 1.75.

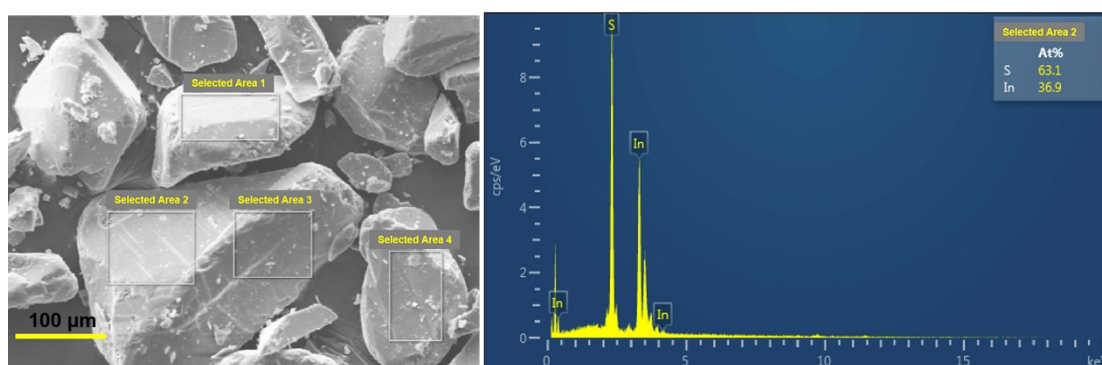


Figure S4. Left: SEM image of as-synthesized **SCTF-2** crystals. Right: energy dispersive spectroscopy (EDS) of **SCTF-2**. The results clearly confirmed the presence of In and S elements, and the measured molar ratio of S/In is 1.71, which is consistent with the theoretical value of 1.70.

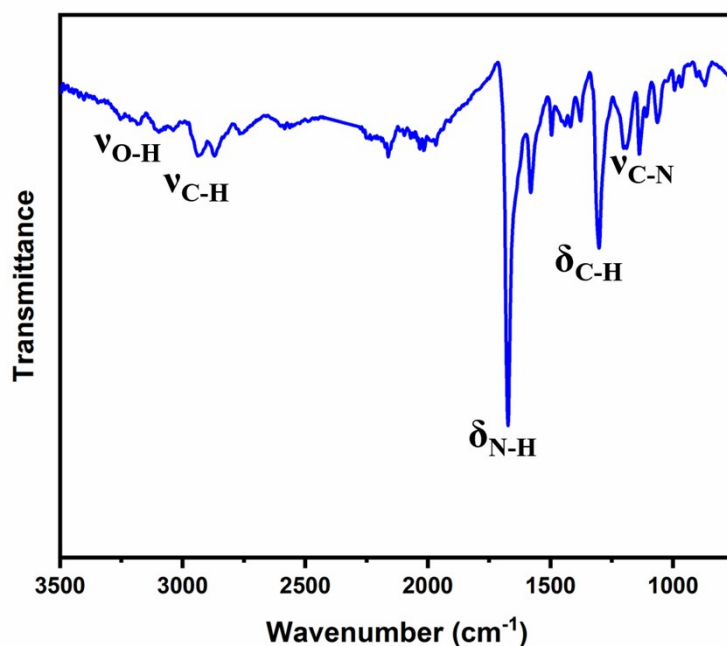


Figure S5. FT-IR spectrum of SCTF-1. The bands of IR at about 3235 cm^{-1} belong to the stretching vibration of the O-H. The IR bands at 2930 cm^{-1} , 2848 cm^{-1} and 1310 cm^{-1} belong to the stretching vibration and bending vibration of the C-H of organic amines. The IR bands at 1650 cm^{-1} indicate the presence of N-H group. The broad vibration bands of IR at 1310 cm^{-1} , 1208 cm^{-1} and 1102 cm^{-1} belong to the stretching vibration of C-N.

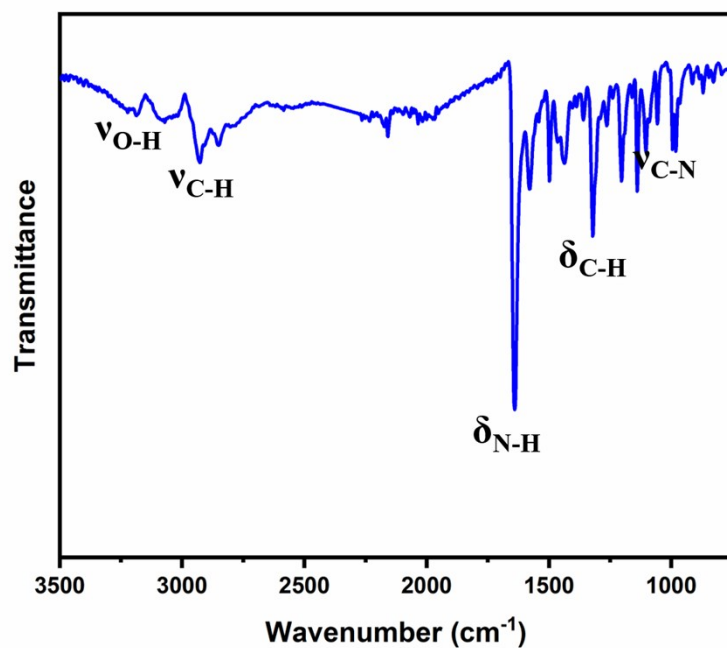


Figure S6. FT-IR spectrum of SCTF-2. Important data (cm^{-1}): 3228(w), 2935(w), 2827(w), 1643(s), 1442(m), 1228(m), 1105(m).

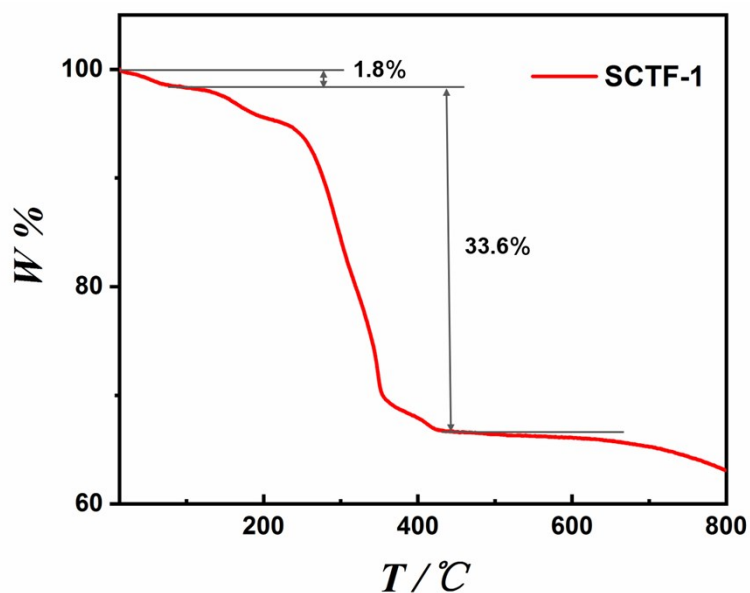


Figure S7. Thermal gravimetric (TG) measurement of **SCTF-1**. The initial gradual weight loss of 1.8% between 30-100 °C could be attributed to loss of moisture and solvent adsorbed on the surface of **SCTF-1**. An abrupt weight loss of 33.6% between 100-400 °C is attributed to the carbonization of template and TZ ligands.

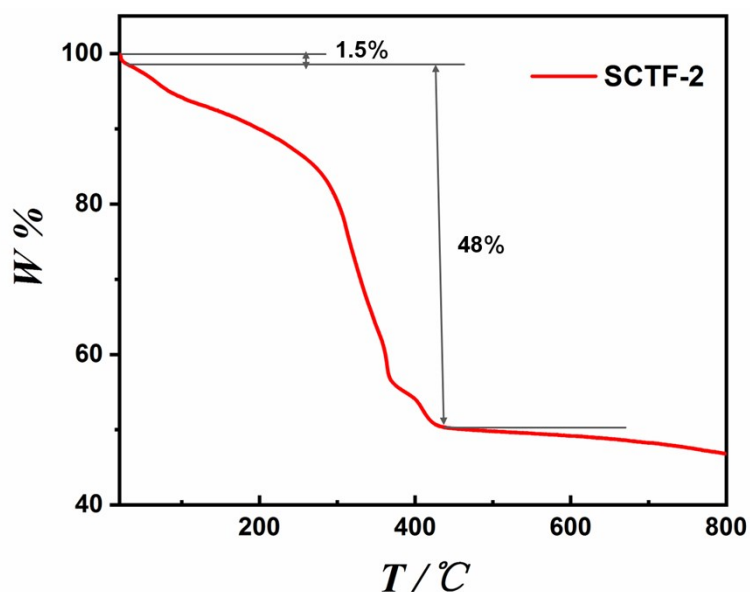


Figure S8. Thermal gravimetric (TG) measurement of **SCTF-2**. The initial gradual weight loss of 1.5% between 30-100 °C could be attributed to loss of moisture and solvent adsorbed on the surface of **SCTF-2**. An abrupt weight loss of 48% between 100-400 °C is attributed to the carbonization of template and TZ ligands.

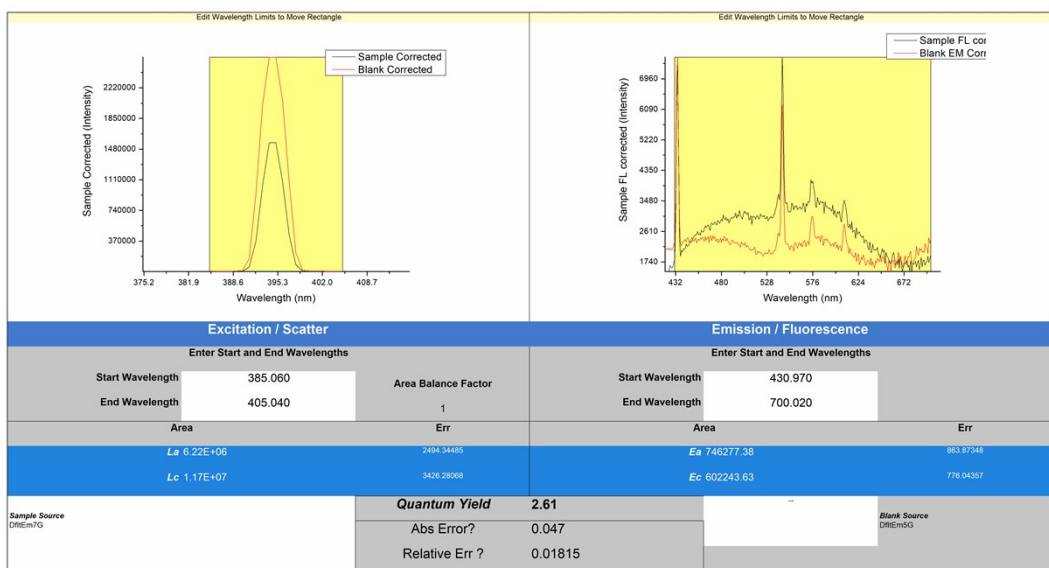


Figure S9. PL quantum yield of SCTF-1.

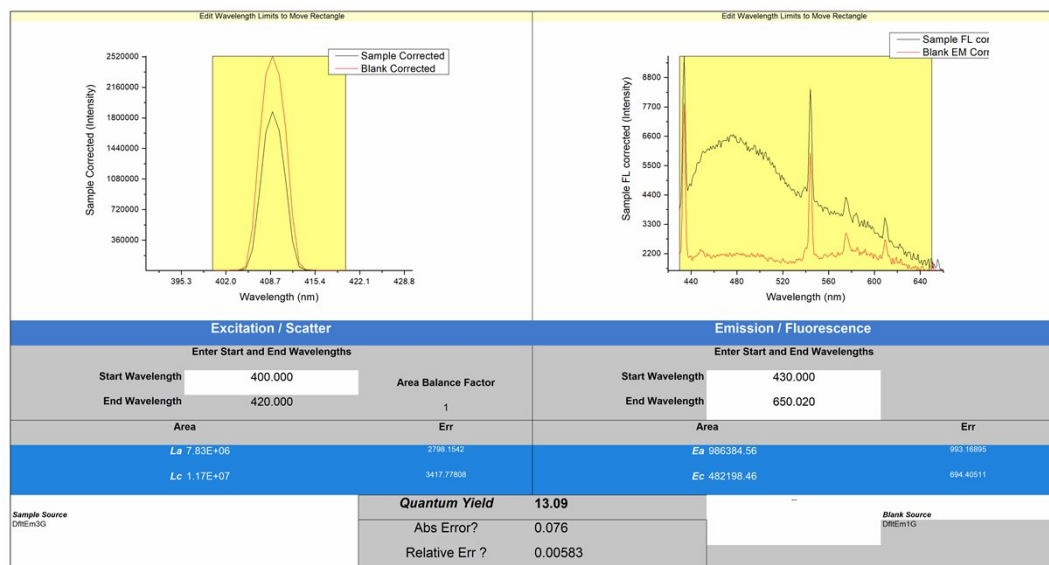


Figure S10. PL quantum yield of SCTF-2.

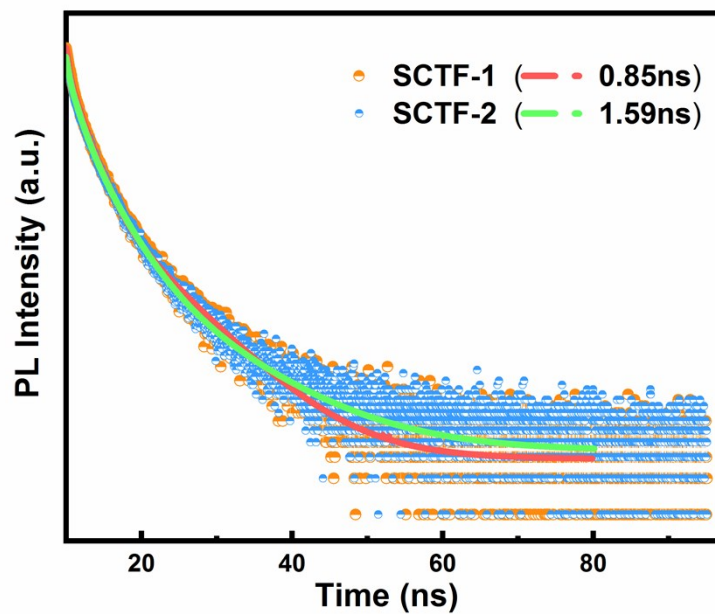


Figure S11. The room-temperature PL decay curves of SCTF-1 and SCTF-2.

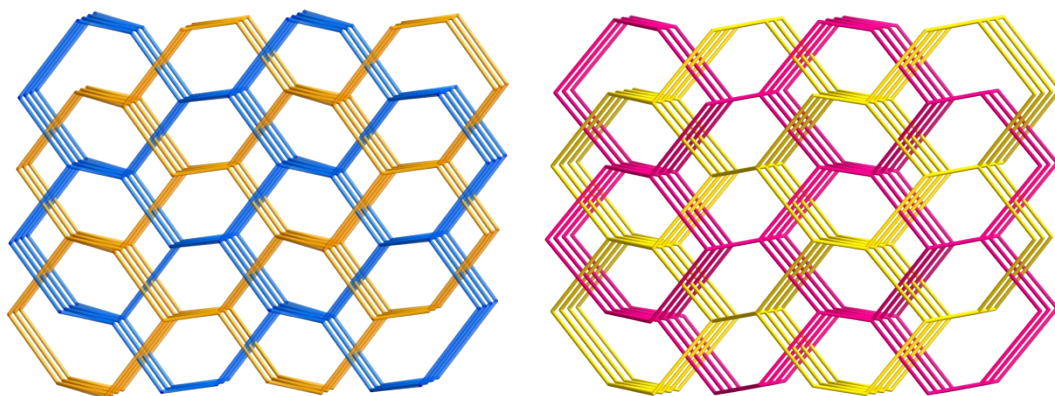


Figure S12. Double-interpenetrated *dia* topology of SCTF-1 and SCTF-2 viewed along b axis. (left: SCTF-1, right: SCTF-2).