Supporting Information

A novel photochromic calcium–based metal–organic framework derived from naphthalene diimide chromophore

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1. Synthesis of compound 1a:

The mixture of $Ca(NO_3)_2 \cdot 4H_2O$ (47.5 mg, 0.2 mmol), H_4BIPA–TC (59.3 mg, 0.1 mmol) were dissolved in N,N-dimethylformamide (3 mL). The resulting solution were stirred for half an hour and then sealed in a stainless-steel tube with a Teflon liner and heated at 100 °C for 3 days. The resulting yellowish single crystals of **1a** were collected and washed with N,N-dimethylformamide. The yield of is ca. 77 %. Anal. Calcd. for $C_{24}H_{26}CaN_4O_9$ (%): C 51.98, H 4.73, N 10.10; found (%): C 51.73, H 4.47, N 10.22. IR(KBr, cm^{-1}): 3423(m), 1716(w), 1666(vs), 1615(s), 1559(vs), 1441(m), 1354(s), 1255(s), 1202(w), 1112(w), 985(w), 777(w), 736(m), 653(m), 548(w).

2. Experimental characterization

Elemental analyses were carried out on an Elementar Vario EL III analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. Photoluminescence spectra were measured at room temperature with an Edinburgh FL-FS90 TCSPC system. Thermogravimetric measurements were performed from room temperature to 800 ℃ on crystalline samples using a Seiko Exstar6000 TG/DTA6300 apparatus at a heating rate of 10 ℃/min. UV−visible (UV−vis) spectra were recorded at room temperature on a PerkinElmer Lambda 900 UV/vis/NIR spectrophotometer equipped with an integrating sphere in the wavelength range of 200−1200 nm. $BaSO_4$ plates were used as a reference (100% reflection), on which the finely ground power of the sample was coated. Powder X-ray diffraction (PXRD) patterns were collected with a Rigaku MiniFlex II diffractometer powered at 30 kV and 15 mA for Cu Kα (λ = 1.54056 Å). Simulated patterns were produced using the Mercury Version 1.4 software and single-crystal reflection diffraction data. ESR spectra were recorded on a Bruker ER-420 spectrometer with a 100 kHz magnetic field in X band at room temperature.

3. Single-crystal X-ray diffraction

The diffraction data of **1a** were collected on a Bruker Apex II CCD area-detector diffractometer (Mo Kα, λ = 0.71073 Å). Absorption correction was applied by using multiscan program SADABS. The structure was solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package. Anisotropic thermal parameters were applied to all non-hydrogen atoms of

1a. The positions of H atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement.

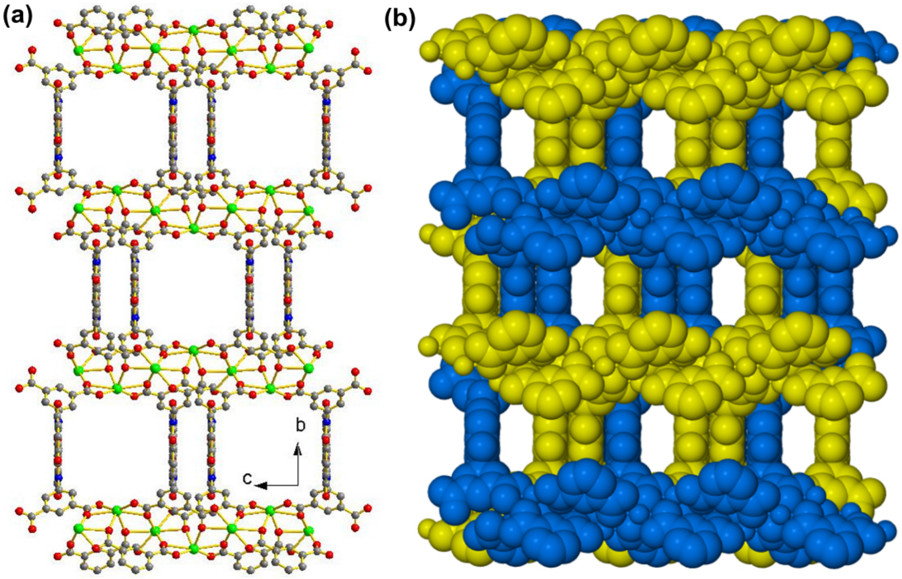

Fig. S1. View of the single 3D network of **1a** with channels (a) and space–filling representation of the doubly interpenetrated network showing strong π···π interactions (b), along crystallographic *a* axis.

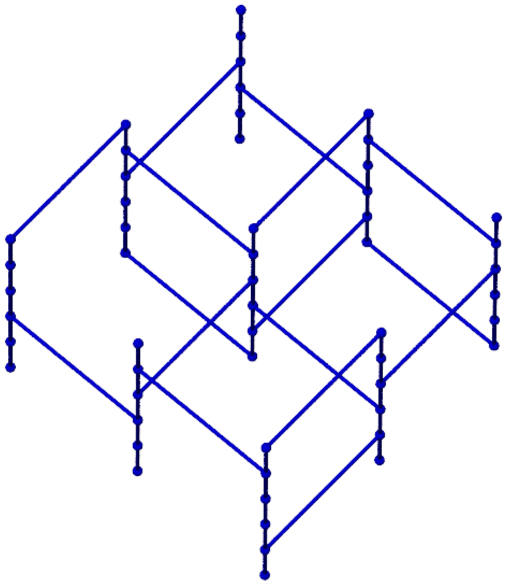

Fig. S2. The T–type 3–connected net.

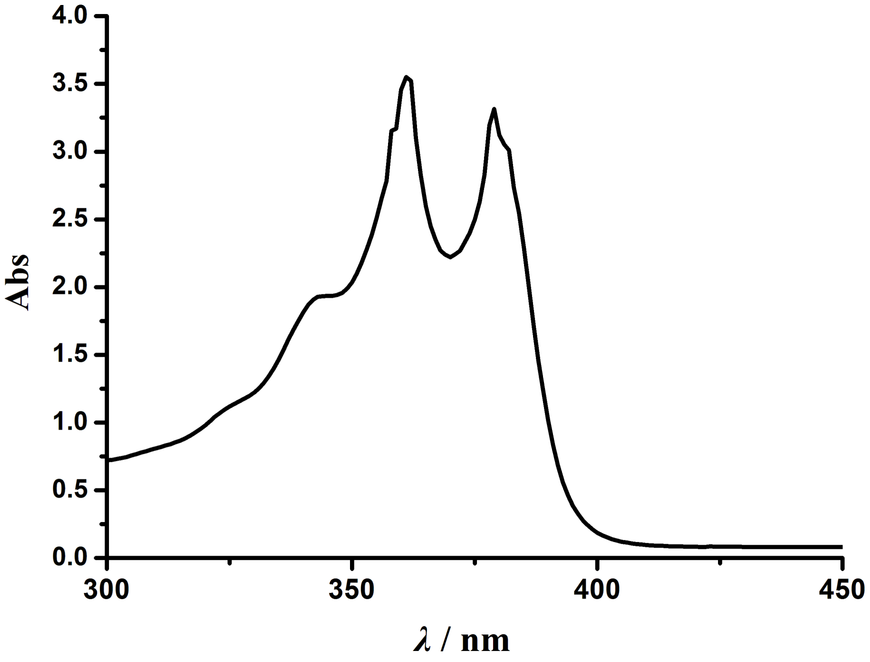

Fig. S3. The UV/Vis spectra of ligand H_4BIPA–TC.

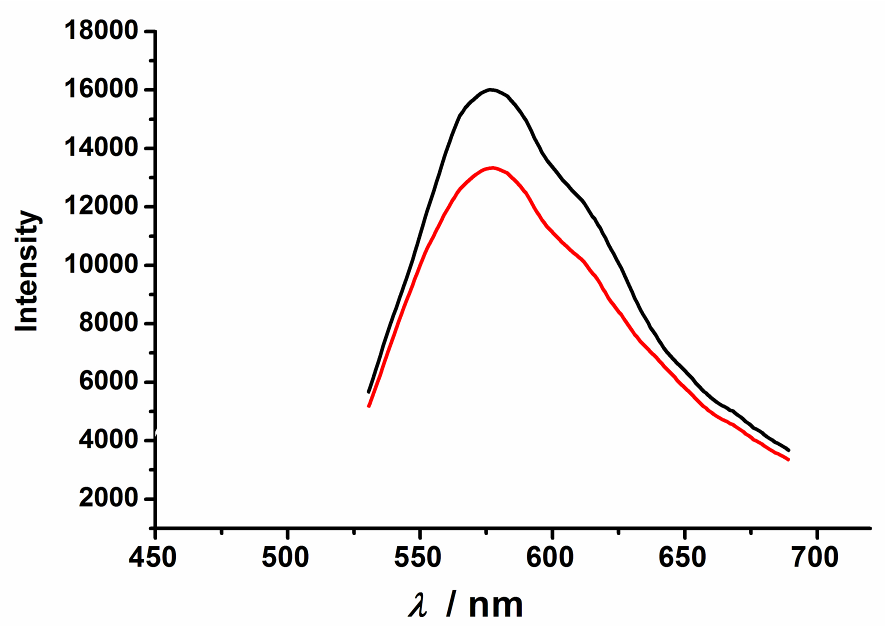

Fig. S4. The emission spectra of **1a** and **1b** in the solid state at room temperature.