Supporting Information

Broad-Band Near-Infrared Doublet Emission in a Tetrathiafulvalene-Based Metal-Organic Framework

Feifan Wang¹, Jue Wang¹, Sebastian F. Maehrlein¹, Yingzi Ma¹, Fang Liu¹, X.-Y. Zhu^{1,*}

¹Department of Chemistry, Columbia University, New York, NY 10027, USA

Materials and Methods

Single crystal growth. The H₄TTFTB precursor was synthesized via the palladium-catalyzed tetraarylation reactions.¹ Pd(OAc)₂ (10.1 mg, 0.046 mmol, Aldrich), Cs₂CO₃ (293.2 mg, 0.90 mmol, Aldrich), PtBu₃·HBF₄ (32.6 mg, 0.11 mmol, Aldrich), and THF (1.0 mL) were placed in a 20-mL reaction flask in glovebox and stirred at 50 °C for 10 hours. A solution of TTF (92.1 mg, 0.45 mmol) and 4-bromotoluene (370 uL) in THF (3.0 mL) was added and refluxed for 24 hours. The Et₄TTFTB product were extracted with chloroform, washed with brine, dried over anhydrous MgSO₄, concentrated from chloroform via rotary evaporator, and purified via column chromatographic purification on silica gel by using hexane/ethyl acetate as an eluent. The H₄TTFTB was formed by first refluxing Et₄TTFTB and NaOH in degassed THF/methanol/H₂O for 12 hours and then protonating in degassed HCl solutions followed by vacuum dry. The Cd₂TTFTB single crystal was synthesized according to the reported work.² Cd(NO₃)₂·4H₂O (172 mg, 0.558 mmol) in H₂O/ethanol (12 mL, v/v = 1:1) and H₄TTFTB (103 mg, 0.154 mmol) in DMF/ethanol (8.4 mL, v/v = 3:1) was slowly mixed in a 20 mL scintillation vial. The reaction was conducted at 75 °C for 72 hours to form dark red needle-like single crystals.

UV oxidation experiments. The single crystal MOF samples were drop-deposited on glass slides. After dried in vacuum, the MOF samples were exposed under a UV lamp with wavelength of 254 nm and power density of 2.35 ± 0.14 mW cm⁻². The UV irradiation was performed under atmosphere at room temperature (295 K). The exposure was stopped by moving the sample out of UV light at different times (7 h, 16 h, and 40 h). The UV-treated samples were stored in dark in glovebox before photoluminescence characterization.

Iodine oxidation experiment: Cd₂TTFTB single crystals are placed in small uncapped vials, which is further placed in a big jar containing 2 g crystallized iodine. The jar is sealed and placed in an oven with constant temperature of 40 °C, which allowed the evaporated I₂ to oxidize the MOF crystals. The vials were taken out after post-synthetic oxidation 4.5 h. The uncapped vials were then put under vacuum for 6 h to remove the possible I₂ residuals on the surface of MOF crystals. The PL spectrum was conducted on these post-synthetic single crystals with 532 nm laser excitation at 77 K.

Scanning electron microscopy and single-crystal X-ray diffraction. The SEM images were collected on Zeiss Sigma VP SEM with imaging resolution of 5 nm. SCXRD was performed on an Agilent SuperNova instrument using an MiTeGen Micromount. Data collection was conducted using CrysAlis Pro while solution and subsequent refinement was done using ShelXT³ and ShelXL⁴, respectively. The temperature

^{*} To whom correspondence should be addressed. E-mail: xyzhu@columbia.edu

was controlled via an Oxford-Diffraction Cryojet system. In the temperature-dependent SCXRD experiments, the sample was stabilized for 15 min after reaching each target temperature.

Steady-state absorption. For solid-state measurements, a flake of Cd_2TTFTB crystal was cut with thickness of 70 um measured by the microscope. The reflectance and transmission spectra were collected and converted to the absorption spectrum. In the two cases, different white light sources were used with 40× objectives (S Plan Fluor, Nikon). Transmitted and reflected lights were spectrally resolved through a 4-f spectrometer (150 grooves/mm diffraction grating) and a visible, liquid nitrogen cooled CCD camera (Princeton Instruments). For the absorption of H₄TTFTB molecule, an ethanol solution was measured on a commercial UV-vis-NIR spectrometer (Agilent 8453).

Photoluminescence. Temperature-dependent photoluminescence experiments were performed on a homebuilt confocal microscope system. The sample was mounted in a liquid-helium recirculating optical cryostat (Montana Instruments Fusion/X-Plane) with a tunable temperature from 4 K to 350 K and a vacuum ($<10^{-4}$ torr) environment.

In steady-state photoluminescence measurements, a continuous wave (532 nm) laser beam was focused by a 100×, NA 0.75 objective (Zeiss LD EC Epiplan-Neofluar 100×/0.75 HD DIC M27) to a diffractionlimited spot on the sample. The PL emission was collected by the same objective in reflection geometry, spatially and spectrally filtered, dispersed by a grating and detected by an InGaAs photodiode array (PyLoN-IR, Princeton Instruments). The wavelength was calibrated by neon-argon and mercury atomic emission sources (IntelliCal, Princeton Instruments). The intensity was calibrated by an NIST traceable 400 to 1050 nm tungsten halogen lamp (StellarNet SL1-CAL).

In time and energy resolved photoluminescence measurements, the pulsed excitation light (400 nm, 3 eV) from second harmonic generation of the output of a Ti:sapphire regenerative amplifier (Coherent RegA 9050, 250 kHz, 800 nm, 100 fs) by a β -barium borate crystal was focused onto the sample. The collected PL was sent to a monochromator (CS130, Oriel) where PL at a certain wavelength was selected by the angle of grating. The PL was focused onto a single-photon avalanche photodiode (ID100-50, IDQ) coupled with a time-correlated single-photon counting module (SPC-130, Becher & Hickl GmbH) where the time solved PL was recorded. The different collection efficiency at different wavelengths was calibrated by an NIST traceable 400 to 1050 nm tungsten halogen lamp (StellarNet SL1-CAL). The instrument response function has an FWHM of 100 ps corresponding to a time resolution of ~20 ps.

Transient absorption. The fundamental ultrafast pulse (energy of 0.8 mJ, center wavelength of 800 nm, duration of ~30 fs, and repetition rate of 10 kHz) was delivered by a Ti:sapphire regenerative amplifier (modified KMLabs Wyvern). The pump pulse centered at 520 nm was generated from a homebuilt, noncolinear one-stage SHG-pumped OPA with duration compressed to ~30 fs. The probe pulse was formed via continuum white light generation by focusing the fundamental laser on a sapphire crystal. The absorption spectrum was acquired using a line scan camera (E2V, Ikona imaging). The TA measurement was performed on a thin flake of Cd₂TTFTB crystal with thickness of ~50 um and in-plane size of ~150 um. A 100 um size pinhole was used to cover the sample in order to eliminate the pump scattering from the crystal edges. The sample was sealed in nitrogen atmosphere, showing no sample degradation over measurement period.

Non-resonance Raman spectroscopy. Data were collected on a home-built microscopic low-frequency Raman setup with a 1064 nm YAG laser. A volume Brag grating beamsplitter filter (BPF, OptiGrate, Inc.) was used to purify the incident laser wavelength and guided the laser towards the sample in a cryostat (Oxford Instruments Microstat HiRes2) with vacuum of 10-6 to 10-5 Torr. A 40× objective with a numerical aperture of 0.6 (S Plan Fluor, Nikon) was applied to focus the beam and collect the scattered light. Three

ultra-narrow band BVG notch filters was used to attenuate the Rayleigh line each with O. D. > 3.0, then the light containing large enough portion of Raman signal was sent through a spatial filter into a 4-f spectrometer with 600 grooves/mm diffraction grating. The signal was read out by an InGaAs CCD camera (Pylon IR 1024, Princeton Instruments) with liquid nitrogen cooling (resolution of 0.8 cm⁻¹). Each spectrum was acquired after the sample was stabilized at the target temperature for 10 min.



Figure S1. Scanning electron microscopy image (a) and single-crystal X-ray diffraction pattern (b) of Cd₂TTFTB single crystals.



Figure S2. Normalized absorbance and PL spectra of Rh101 in ethanol and MOF single crystal at room temperature excited at 532 nm. Numbers in legend are the scaling factors.

The calculation of PL quantum yield is according to the following equation⁵

$$\Phi_{\rm f}^{i} = \Phi_{\rm f}^{s} \frac{f_{s}\left(\lambda_{\rm ex}\right)}{f_{i}\left(\lambda_{\rm ex}\right)} \frac{\int_{\lambda_{\rm em}} F^{i}\left(\lambda_{\rm em}\right)}{\int_{\lambda_{\rm em}} F^{s}\left(\lambda_{\rm em}\right)} \frac{n_{i}^{2}}{n_{s}^{2}}$$

where $\Phi_{\rm f}^{i}$ and $\Phi_{\rm f}^{s}$ is the unknown sample and the fluorophore with known quantum yield, $f_{x}(\lambda_{\rm ex}) = 1 - 10^{-A_{x}(\lambda_{\rm ex})}$ is the absorption factor of both sample (x = i) and standard (x = s) at the respective excitation wavelength, A is the absorbance, $F^{x}(\lambda_{\rm em})$ is the measured fluorescence at each emission wavelength, and n_{x} is the refractive index of environment. Plug $\Phi_{\rm f}^{s} = 0.913$ of Rh101, $A_{i}(532\text{nm}) = 3.26$, $A_{s}(532\text{nm}) = 0.2772$, $n_{i} = 1$, $n_{s} = 1.36$ of ethanol and $F^{x}(\lambda_{\rm em})$ from the following figure into the above equation, we get the PLQY = 0.30% of MOF at room temperature.



Figure S3. PL spectra of H₄TTFTB solid film, H₄TTFTB in ethanol, and Cd₂TTFTB crystal measured at room temperature with excitation at 532 nm. PL spectra were normalized to the laser power.



Figure S4. PL spectra (upper) and peak intensity normalized PL spectra (lower) of Cd₂TTFTB crystals with or without ultraviolet irradiation in atmosphere at 295 K with wavelength 254 nm, power density of 2.35 ± 0.14 mW cm⁻². The total UV irradiation times are 0, 7, 16, and 40 hours. The shade area indicates the standard error of each spectrum from three different measurements at 4 K. Note that the PL intensity increases in the UV irradiation time window of 0-16 hours, but decreases at longer times (40 hours). The latter may be attributed to partial destruction of the MOF crystal with excessive UV irradiation.



Figure S5. Raman spectra of MOF single crystals from the UV irradiation experiments. 0 h, 7 h, 16 h, and 40 h represent the MOF samples without and with different lengths of UV irradiation time. The Raman spectrum show little change for UV irradiation times of 7 and 16 hours, indicating the crystal structure remains unchanged. There is a degradation of the Raman spectrum for a total UV irradiation time of 40 hours.



Figure S6. PL spectra of as-synthesized MOF single crystal (red) and one upon I₂ vapor oxidation for 4.5 h (blue). The top panel compares the PL spectra obtained under identical excitation conditions. The bottom panel shows rescaled spectrum for the as-synthesized crystal (x5). The gray area marks our estimated range of absorption in the presence of I₂, likely due to a charge transfer species association with incorporated I₂. Reabsorption of PL emission is likely responsible for the attenuation of PL intensity in this region.



Figure S7. PL spectra (a) and integrated intensity over all wavelength (b) of MOF crystal as a function of collection time at room temperature. The excitation wavelength is 532 nm and the power is $17 \pm 1 \mu$ W. MOF samples are maintained under vacuum (10^{-7} Torr). The spectrum is collected at every 5 s.



Figure S8. Spectral electrochemical measurement of Cd2TTFTB at 0.66 V (black) and 2.00 V (red), with reference to Fc/Fc^+ , adapted with permission from reference.5 Differential spectrum (blue) is obtained from subtracting the red spectrum by the black line. Orange line shows the absorption of the H4TTFTB precursor in THF solution.



Figure S9. Transient absorption spectrum (a) and integrated intensity kinetics (b) of H₄TTFTB precursor in THF solution. Single exponential decay fitting (red) is used in (b) with time constant of 54 ± 2 ps.



Figure S10. Spectrum-resolved TR-PL spectra and integrated kinetics of Cd₂TTFTB single crystals at 10 K, 30 K, and 140 K. Color scale indicates the collected photon number.



Figure S11. Normalized PL spectrum of TR-PL with 10 ns total time window.



Figure S12. Structure view of Cd_2TTFTB single crystals from temperature-dependent Raman spectra. Offresonance excitation at 1064 nm is used in order to eliminate the PL background. The peaks at 1400-1420 cm⁻¹ and 1542 cm⁻¹ are in line with the vibrations of TTF⁺⁺ radical cations and the modes at 1497, 1572, 1591, 1608 cm⁻¹ are assigned to those of neutral TTFTB moieties.⁶ The latter is also evidenced by the crystallography of the central C=C bonds in Cd₂TTFTB frameworks.^{6,7} Both suits of peaks are ascribed to the intramolecular motions, while the peaks at 1130-1300 cm⁻¹ are not.



Figure S13. Lattice parameter changes with temperature of Cd₂TTFTB single crystals by using singlecrystal X-ray diffraction. It maintains the space group P6₅ through the temperature window.

References

- (1) Mitamura, Y.; Yorimitsu, H.; Oshima, K.; Osuka, A. Straightforward Access to Aryl-Substituted Tetrathiafulvalenes by Palladium-Catalysed Direct C–H Arylation and Their Photophysical and Electrochemical Properties. *Chem. Sci.* **2011**, *2*, 2017–2021.
- (2) Park, S. S.; Hontz, E. R.; Sun, L.; Hendon, C. H.; Walsh, A.; Van Voorhis, T.; Dincă, M. Cation-Dependent Intrinsic Electrical Conductivity in Isostructural Tetrathiafulvalene-Based Microporous Metal–Organic Frameworks. J. Am. Chem. Soc. 2015, 137, 1774–1777.
- (3) Sheldrick, G. M. Crystal Structure Refinement with {\it SHELXL}. Acta Crystallogr. Sect. C 2015, 71, 3–8.
- (4) Sheldrick, G. M. A Short History of {\it SHELX}. Acta Crystallogr. Sect. A 2008, 64, 112–122.
- (5) Rurack, K.; Spieles, M. Fluorescence Quantum Yields of a Series of Red and Near-Infrared Dyes Emitting at 600–1000 nm. *Anal. Chem.* **2011**, *83*, 1232–1242.
- (6) Matsuzaki, S.; Moriyama, T.; Toyoda, K. Raman Spectra of Mixed Valent TTF Salts; Relation between Raman Frequency and Formal Charge. *Solid State Commun.* **1980**, *34*, 857–859.
- (7) Leong, C. F.; Wang, C.-H.; Ling, C. D.; D'Alessandro, D. M. A Spectroscopic and Electrochemical Investigation of a Tetrathiafulvalene Series of Metal–Organic Frameworks. *Polyhedron* 2018, 154, 334–342.