

## Supporting Information

### Non-linear Optical and Ferroelectric Properties of a 3-D Cd(II) Triazolate Complex with a Novel $(6^3)_2(6^{10}.8^5)$ Topology†

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#### Materials and Methods:

Crystals of  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  were obtained from freezing the concentrated resulting solution of  $\text{HClO}_4$  reacting with  $\text{CdCO}_3$ . Htrtr was prepared according to the literature method.<sup>1</sup> Other reagents of A.R. grade were used as purchased without further purification. The FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer in the region of 4000–400  $\text{cm}^{-1}$  using KBr pellets as bases. The solid-state photoluminescent determinations were performed on JY Fluorolog-322 at room temperature (excitation and emission slits, 2.0 nm; increment, 1.0 nm and integration time, 0.2 s). The TG/DTA curve of **1** was measured on NETZSCH STA 449C under a  $\text{N}_2$  atmosphere with a ramp rate of 10 K/min.

The measurement of electric hysteresis loop: The ferroelectric property of a solid state sample was measured using a powdery sample in the form of a pellet using an aixACCT TF Analyzer 2000 ferroelectric tester at room temperature while the sample was immersed in insulating oil.

The UV-vis spectrum was recorded at room temperature on computer-controlled PE Lambda 900 UV-vis spectrometer equipped with an integrating sphere in the wavelength

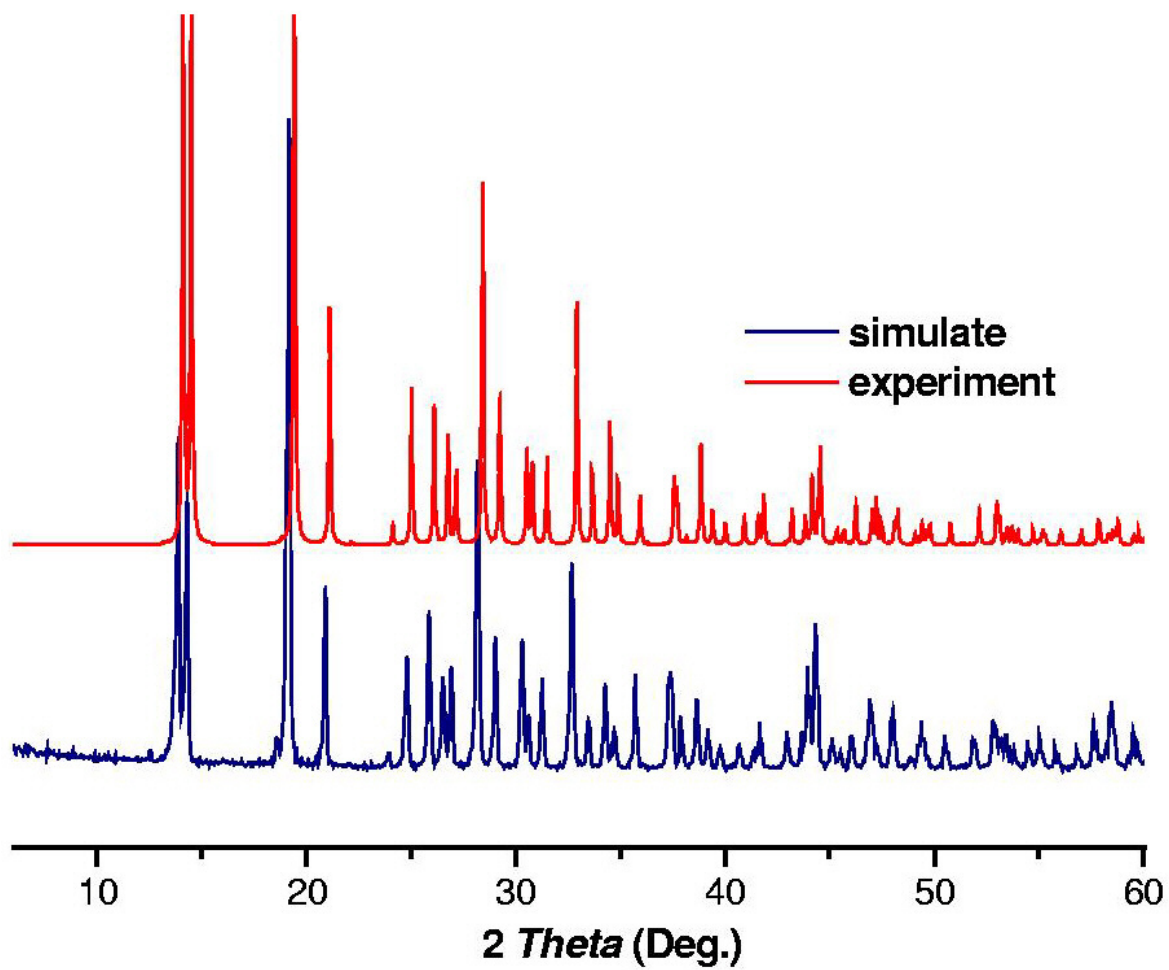
range 200–2000 nm. A BaSO<sub>4</sub> plate was used as a reference, on which finely ground powder of the sample was coated. The absorption spectrum was calculated from reflection spectra by the Kubelka-Munk function:<sup>[2]</sup>  $\alpha/S = (1-R)^2/2R$ , where  $\alpha$  is the absorption coefficient,  $S$  is the scattering coefficient that is practically wavelength independent when the particle size is larger than 5  $\mu\text{m}$ , and  $R$  is the reflectance. The band gap value was determined as the intersection point between the energy axis at the absorption offset and the line extrapolated from the linear portion of the absorption edge in the  $\alpha/S$  versus  $E$  (eV) plot.

Powder X-ray diffraction (PXRD) pattern was measured on a Rigaku DMAX2500 powder diffractometer at 40 kV and 100 mA using Cu- $K_{\alpha}$  ( $\lambda = 1.54056 \text{ \AA}$ ), with a scan speed of 0.375 s/step and a step size of 0.05 °. The simulated powder pattern was calculated using single-crystal X-ray diffraction data and processed by the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Centre.

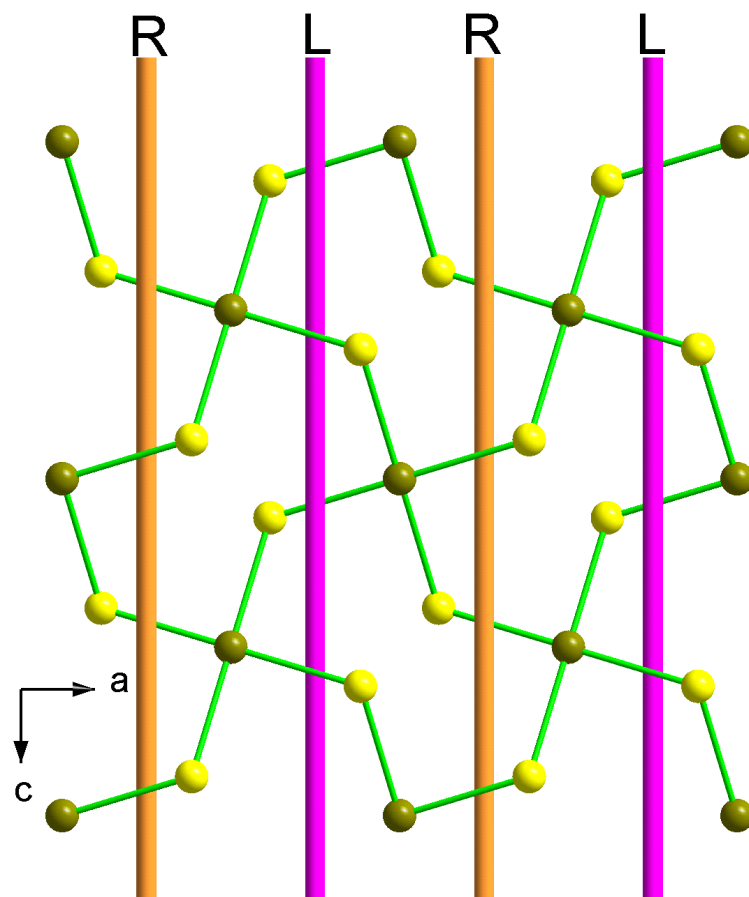
Elements analyses of C, H and N were carried out with an Elementar Vario MICRO.

The single-crystal X-ray diffraction measurement of **1** was performed on Rigaku Mercury CCD ( $T = 293(2) \text{ K}$ ) diffractometer, respectively, using graphite monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Intensity data set was collected using the  $\omega$  scan technique and corrected for  $Lp$  effects. The structure was solved by the direct method using the Siemens SHELXTL<sup>TM</sup> Version 5 package of crystallographic software.<sup>[3]</sup> The difference Fourier maps based on these atomic positions yield the other non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on  $F^2$ . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to the theoretical models.

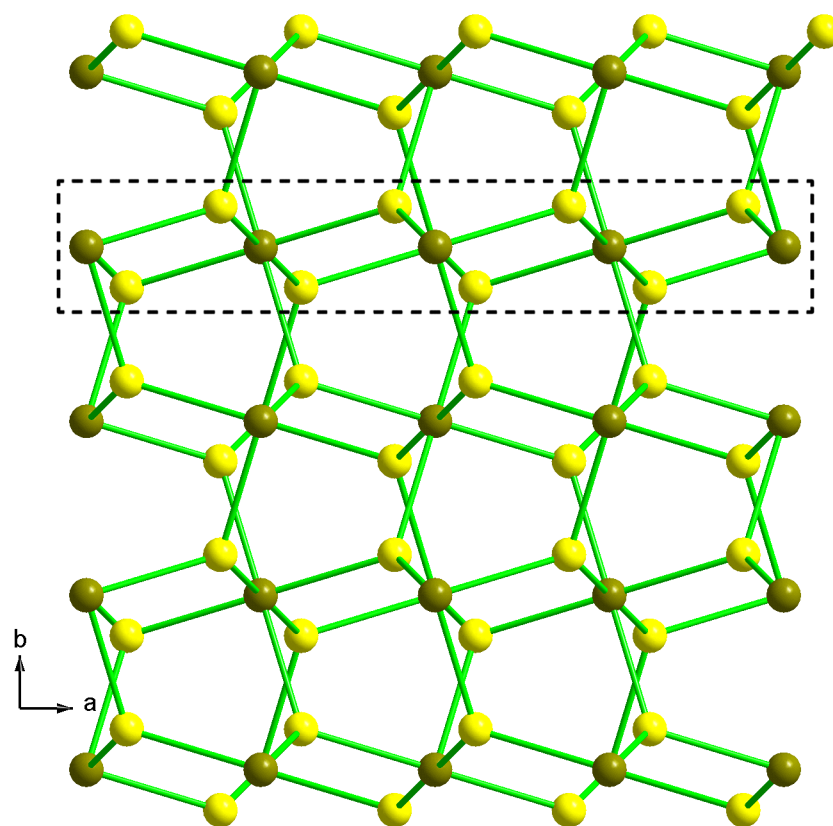
The crystallographic data of **1** determined by X-ray was used to calculate its electronic structure. The calculation of electronic structure was performed with the CASTEP code based on the density functional theory (DFT) using a plane-wave expansion of the wave functions and norm-conserving pseudopotential, in which the orbital electrons of N-2s<sup>2</sup>2p<sup>3</sup>, H-1s<sup>1</sup>, C-2s<sup>2</sup>2p<sup>2</sup>, and Cd-4d<sup>10</sup>5s<sup>2</sup> were treated as valence electrons. We used the generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Eruzerhof (PBE) to describe the exchange and correlation potential.



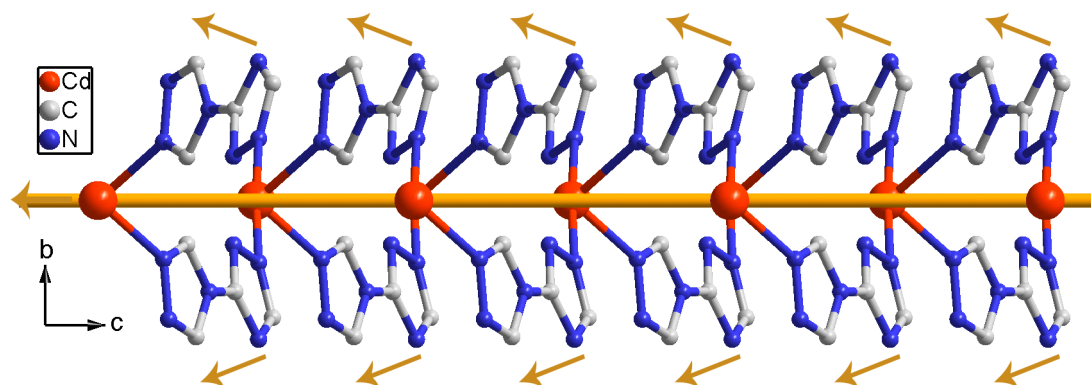
*Figure S1.* Powder X-ray diffraction profiles of 1.



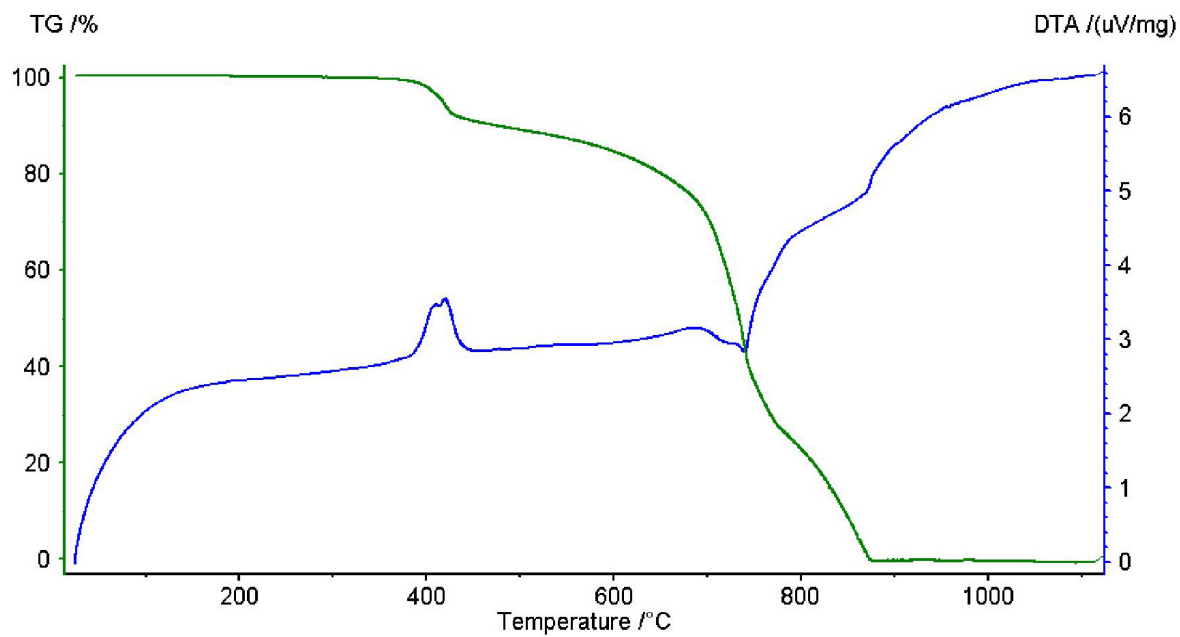
**Figure S2.** A (4,4) sheet made up of alternate right- and left-helical chains in the structure of FeS<sub>2</sub>. Key: Fe, green; S, yellow.



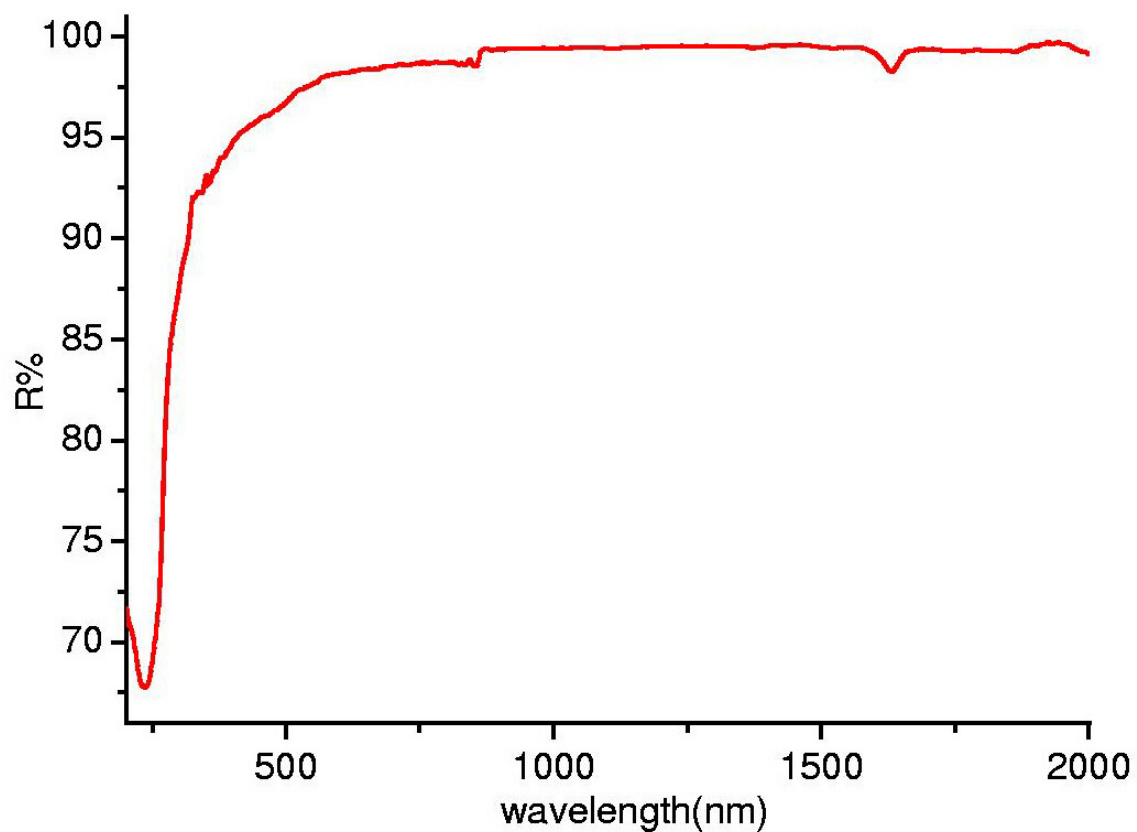
**Figure S3.** The  $(6^3)_2(6^{12}.8^3)$  topology of 3-D network of FeS<sub>2</sub> based on (4,4) sheets interlinked by Fe-S bonds. Key: Fe, green; S, yellow.



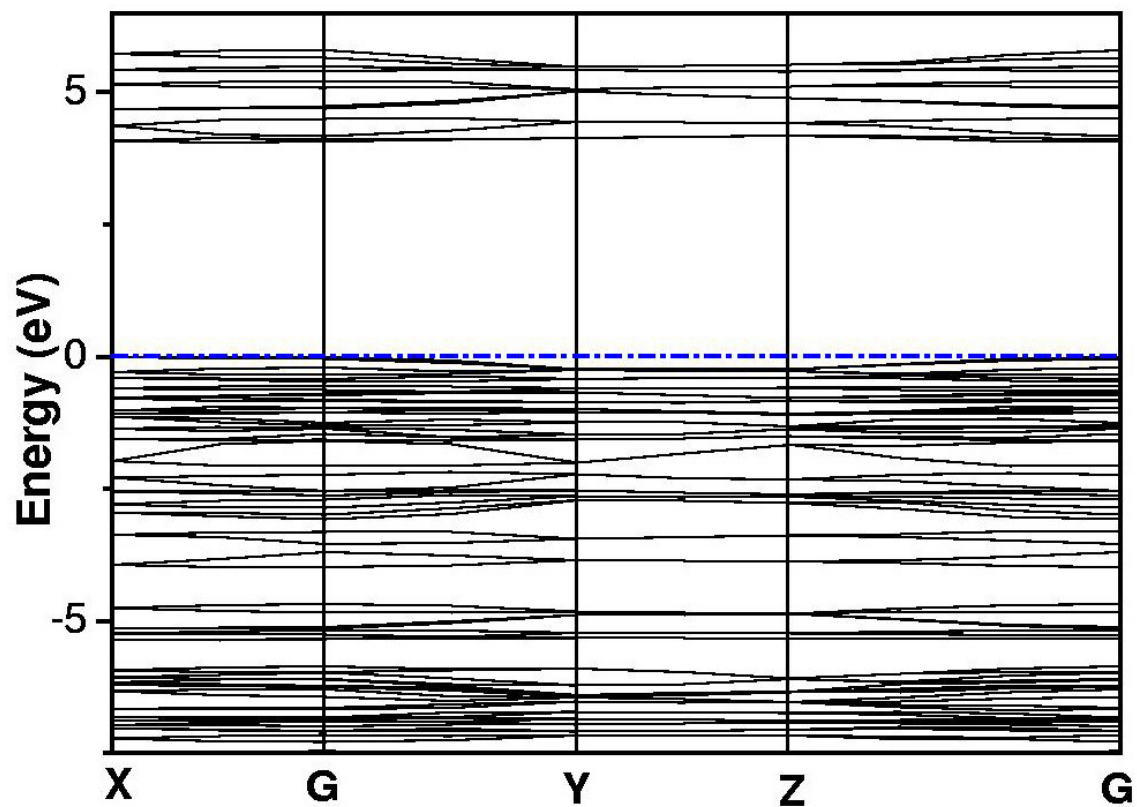
**Figure S4.** Side view of a (4,4) sheet of **1** (yellow arrows represents dipoles of trtr ligands).



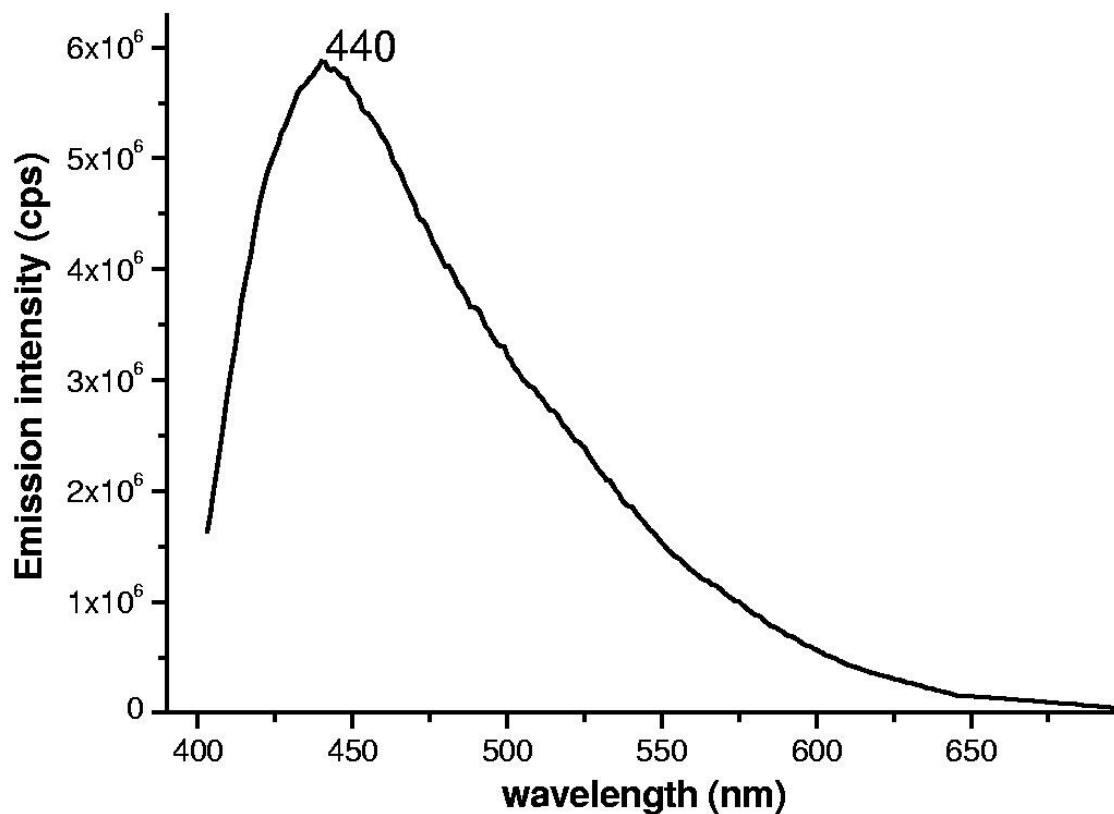
*Figure S5.* TG-DTA curve of **1**.



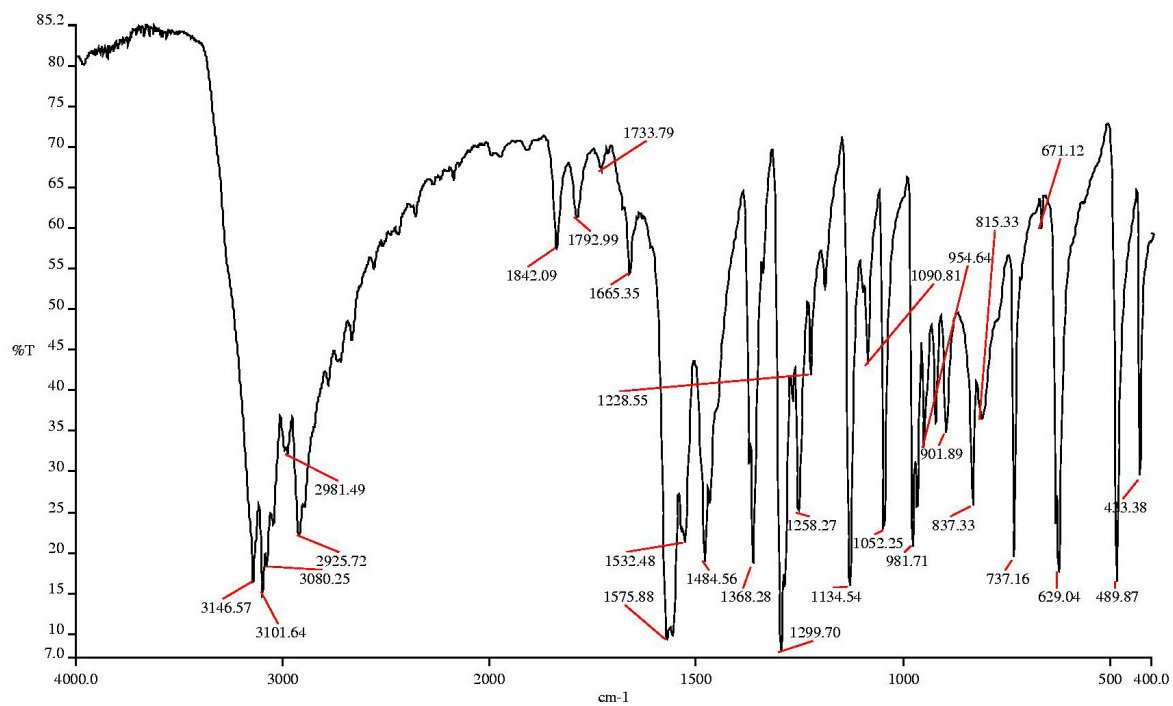
*Figure S6.* Diffuse reflection spectrum of **1**.



*Figure S7.* The band structure of **1** (the band is shown only between -7.5 and 6.5 eV for clarity, and dashed line indicates the position of the Fermi level).

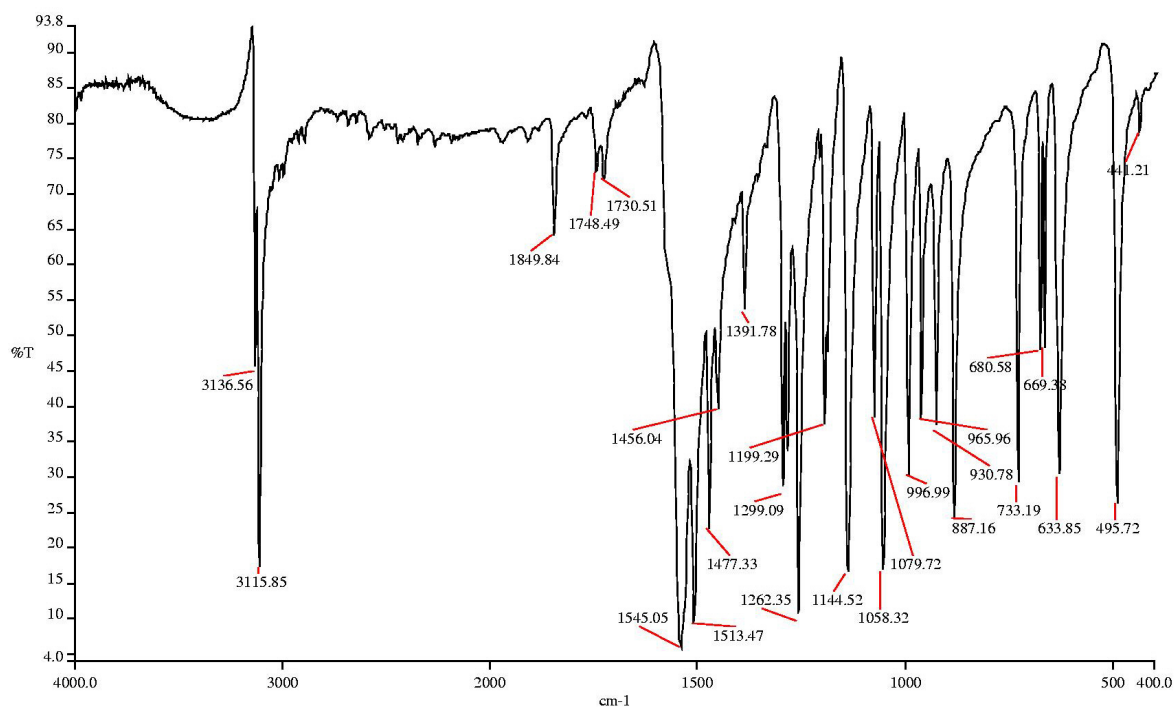


**Figure S8.** PL emission spectrum of pure Htrtr in the solid state with  $\lambda_{\text{ex}} = 383$  nm at room temperature.



**Figure S9.** The IR spectrum of Htrtr.





**Figure S10.** The IR spectrum of **1**.

**Table 1.** Crystal Data and Structure Refinement for **1**.

Empirical formula	C <sub>8</sub> H <sub>6</sub> CdN <sub>12</sub>
Formula weight	382.65
Temperature(K)	293(2)
Crystal system, Space group	Orthorhombic, Fdd2
Unit cell dimensions	$a = 16.024(5) \text{ \AA}$ , $\alpha = 90^\circ$ $b = 18.856(6) \text{ \AA}$ , $\beta = 90^\circ$ $c = 7.319(2) \text{ \AA}$ , $\gamma = 90^\circ$ $2211.4(11) \text{ \AA}^3$
Z, Density(cal.)	8, 2.299 g/cm <sup>3</sup>
Absorption coefficient	1.994 mm <sup>-1</sup>
F(000)	1488
Crystal Size (mm)	0.40 × 0.20 × 0.20 mm <sup>3</sup>
Theta range for data collection	3.25 to 25.35°
Limiting indices	-19 ≤ h ≤ 18, -22 ≤ k ≤ 20, -8 ≤ l ≤ 8

Reflections collected / unique	3594 / 1011 ( $R_{\text{int}} = 0.0166$ )
Observed Reflection	973 ( $I > 2\sigma(I)$ )
Data Completeness measured	1.000
Relative Transmission Factor	0.8742, -1.0000
Refinement Method	Full-matrix least-squares on $F^2$
Parameter/Restraints/Data(obs.)	96 / 1 / 973
Goodness-of-fit	1.015
Final R indices ( $I > 2\sigma(I)$ )	$R1 = 0.0138$ , $wR2 = 0.0352$
R indices (all)	$R1 = 0.0147$ , $wR2 = 0.0356$
Largest difference peak	0.465, -0.243 $e/\text{\AA}^3$

Table 2. Atomic coordination and thermal parameters.

atom	x	y	z	U(eq)
Cd(1)	0.0000	0.5000	0.32993(9)	0.01428(8)
C(1)	-0.10754(17)	0.41703(15)	-0.1099(4)	0.0217(6)
C(2)	-0.09678(15)	0.30371(13)	-0.1388(4)	0.0225(6)
C(3)	0.13403(15)	0.39345(14)	0.1319(3)	0.0187(5)
C(4)	0.02278(16)	0.36160(14)	0.0130(3)	0.0167(5)
N(1)	-0.17460(14)	0.39547(12)	-0.1968(4)	0.0265(5)
N(2)	-0.16781(13)	0.32202(11)	-0.2125(3)	0.0205(5)
N(3)	-0.05745(13)	0.36189(11)	-0.0685(3)	0.0171(5)
N(4)	0.06829(13)	0.30434(11)	0.0089(3)	0.0209(5)
N(5)	0.14247(12)	0.32596(10)	0.0884(3)	0.0167(4)
N(6)	0.05785(11)	0.42011(10)	0.0882(4)	0.0183(4)

Table 3. Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ).

Cd(1)-N(5)#1	2.241(2)	N(5)#2-Cd(1)-N(2)#3	85.58(8)
Cd(1)-N(2)#3	2.426(2)	N(2)#3-Cd(1)-N(2)#4	102.47(11)
Cd(1)-N(6)	2.502(2)	N(5)#1-Cd(1)-N(6)#5	85.39(8)
N(5)#1-Cd(1)-N(5)#2	176.82(14)	N(5)#2-Cd(1)-N(6)#5	96.87(7)

N(2)#4-Cd(1)-N(6)#5	168.80(7)	N(6)#5-Cd(1)-N(6)	89.98(11)
N(5)#1-Cd(1)-N(2)#3	92.42(8)	N(2)#3-Cd(1)-N(6)#5	84.53(8)

Symmetry codes #1:  $-x+1/4, y+1/4, z+1/4$  #2:  $x-1/4, -y+3/4, z+1/4$  #3:  $-x-1/4, y+1/4, z+3/4$  #4  
 $x+1/4, -y+3/4, z+3/4$  #5:  $-x, -y+1, z$

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- [<sup>1</sup>] P. M. Aouial, P. Viallefont and L. E. Ammari, *Acta. Cryst.*, 1991, **C47**, 1866.
- [<sup>2</sup>] a) W. W. Wendlandt and H. G. Hecht, *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966; b) G. Kortüm, *Reflectance Spectroscopy*; Springer-Verlag: New York, **1969**.
- [<sup>3</sup>] Siemens, *SHELXTL<sup>TM</sup> Version 5 Reference Manual*, Siemens Energy & Automation Inc., Madison, Wisconsin, USA, **1994**.