

Supplementary material

Three Pillared-Layered Inorganic-Organic Hybrid Polymers with Efficient Luminescence

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Additional plots of the structures

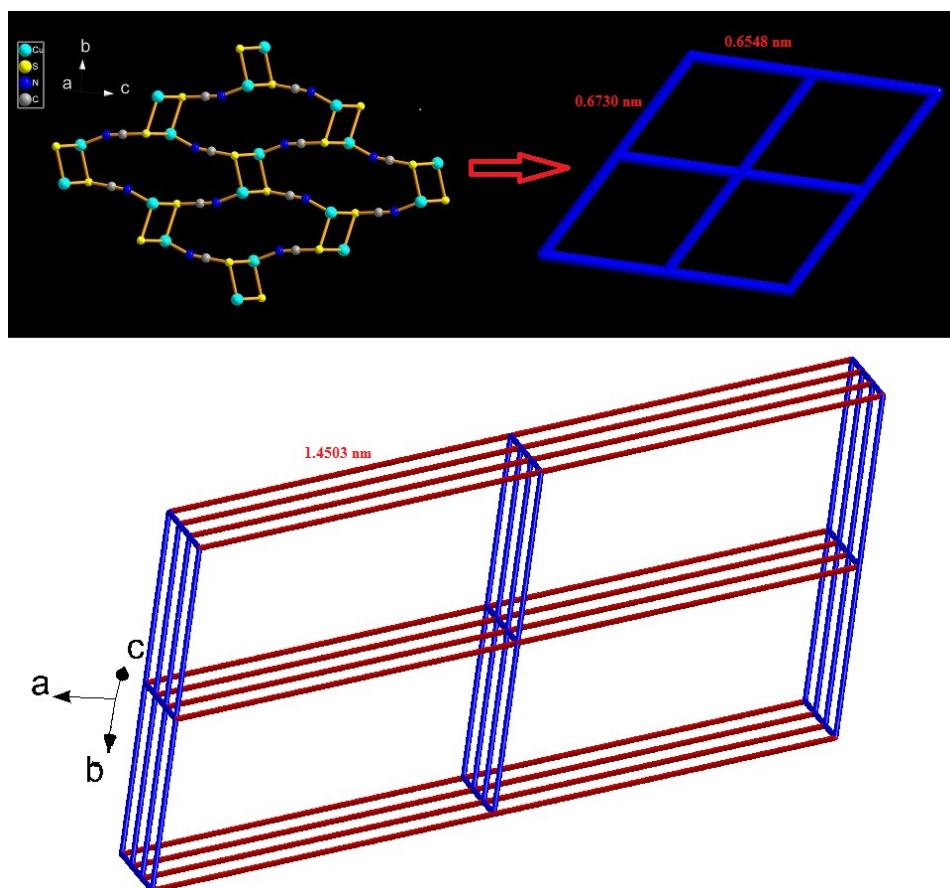


Fig. S1 The wave-like [Cu₂(SCN)₂]_n layers (simplified as blue grid) are linked by 4,4'-Hbpt ligands (represented as red lines) to form a 3-D structure of **1** with pcu topology. The [Cu₂] subunits are regarded as 6-connected nodes, while SCN⁻ groups and 4,4'-Hbpt ligands are considered as bridging linkers.

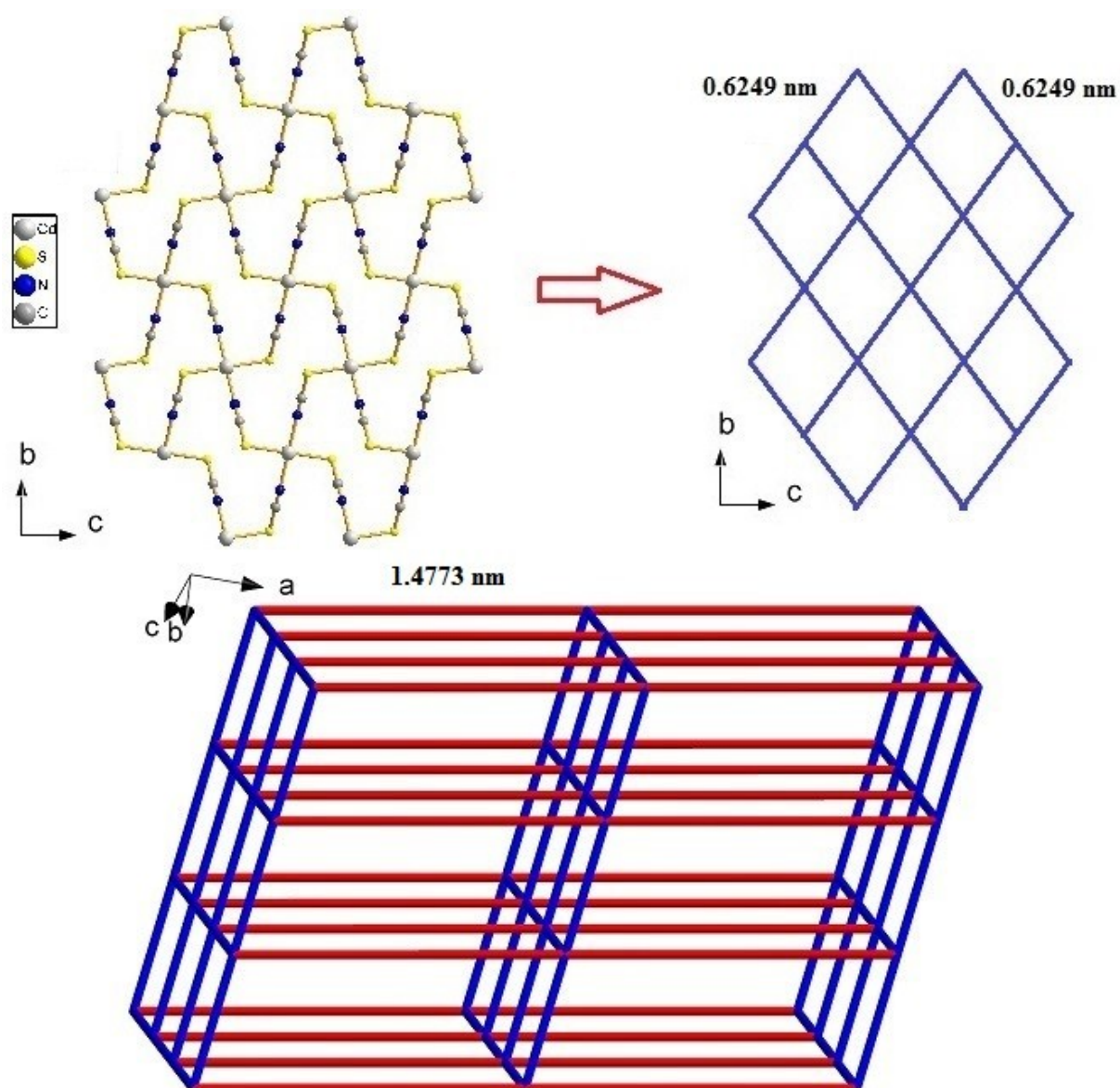


Fig. S2 The fluctuant $[\text{Cd}(\text{SCN})_2]_n$ layers (simplified as blue grid) are linked by 4,4'-Hbpt ligands (represented as red lines) to form a 3-D structure of **2** with pcu topology. The Cd(II) cations are regarded as 6-connected nodes, while SCN^- groups and 4,4'-Hbpt ligands are considered as bridging linkers.

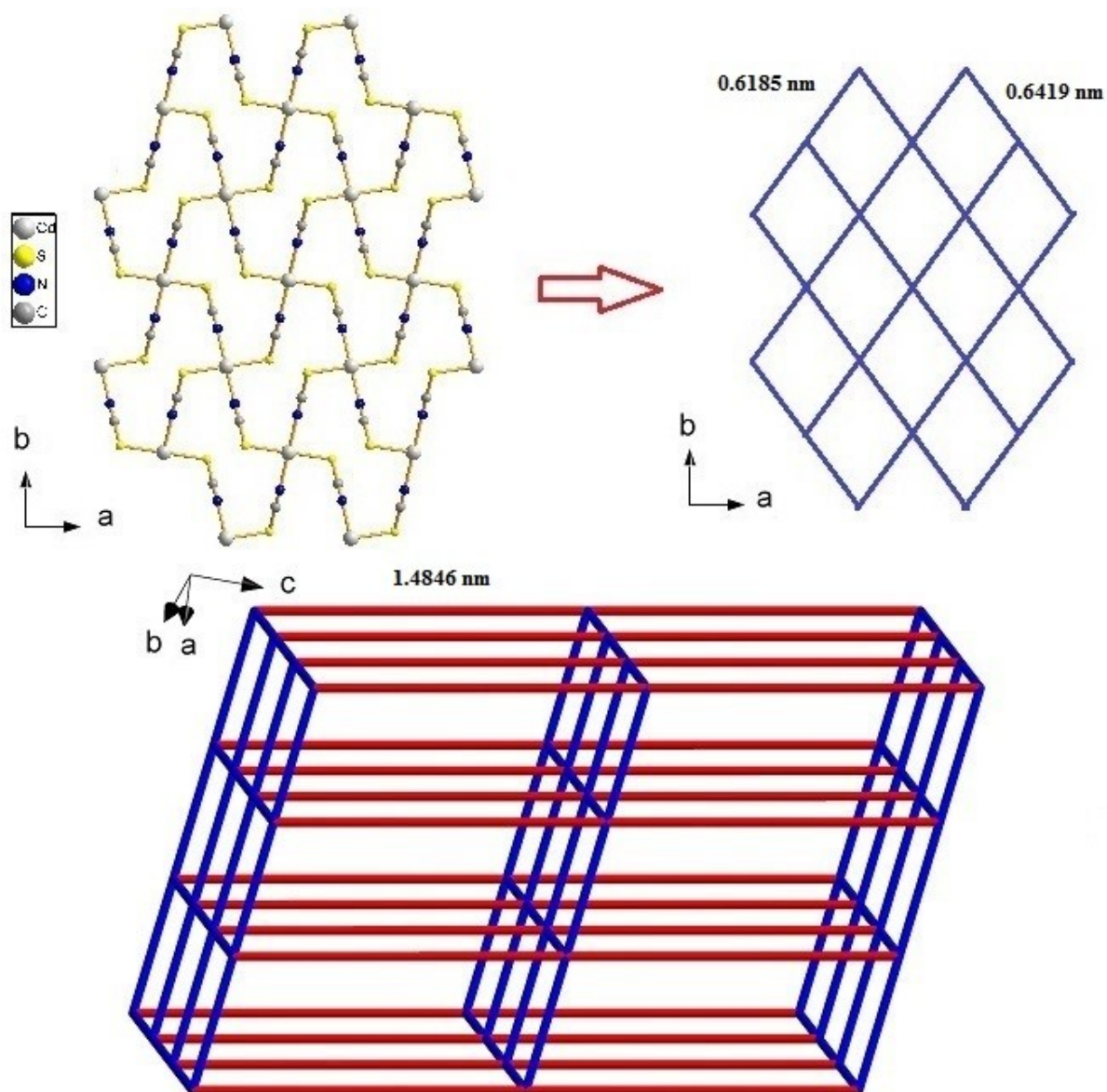


Fig. S3 The fluctuant $[Cd(SCN)_2]_n$ layers (simplified as blue grid) are linked by 4,4'-Hbpt ligands (represented as red lines) to form a 3-D structure of **3** with *pcu* topology. The Cd(II) cations are regarded as 6-connected nodes, while SCN^- groups and 4,4'-Hbpt ligands are considered as bridging linkers.

DFT Calculation Approach Methodology

The crystallographic data of the present complexes determined by X-ray were used to calculate the electronic band structures. Calculations of the electronic band structures along with density of states (DOS) was carried out with density functional theory (DFT) using one of the three nonlocal gradientcorrected exchange-correlation functionals (GGA-PBE) and performed with the CASTEP code,¹ which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential² for the core electrons. The number of plane waves included in the basis was determined by a cutoff energy E_c of 800 eV for **1** and 700 eV for **2** and **3**. Pseudoatomic calculations were performed for H-1s¹, C-2s²2p², N-2s²2p³, S-3s²3p⁴, Cu-3d¹⁰4s¹, and Cd-4d¹⁰5s². The parameters used in the calculations and convergence criteria were set by the default values of the CASTEP code, e.g., reciprocal space pseudopotentials representations, total energy convergence tolerance of 1×10^{-5} eV, eigenenergy convergence tolerance of approximate 5×10^{-7} eV. All of calculations were performed by CASTEP program in Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China.

(1) (a) Segall, M.; Linda, P.; Probert, M.; Pickard, C.; Hasnip, P.; Clark, S.; Payne, M. *Materials Studio CASTEP*, version 5.5; Accelrys: San Diego, CA, **2010**. (b) Segall, M.; Linda, P.; Probert, M.; Pickard, C.; Hasnip, P.; Clark, S.; Payne, M. *J. Phys.: Condens. Matter* **2002**, *14*, 2717–2744.

(2) Hamann, D. R.; Schluter, M.; Chiang, C. *Phys. Rev. Lett.* **1979**, *43*, 1494–1497.

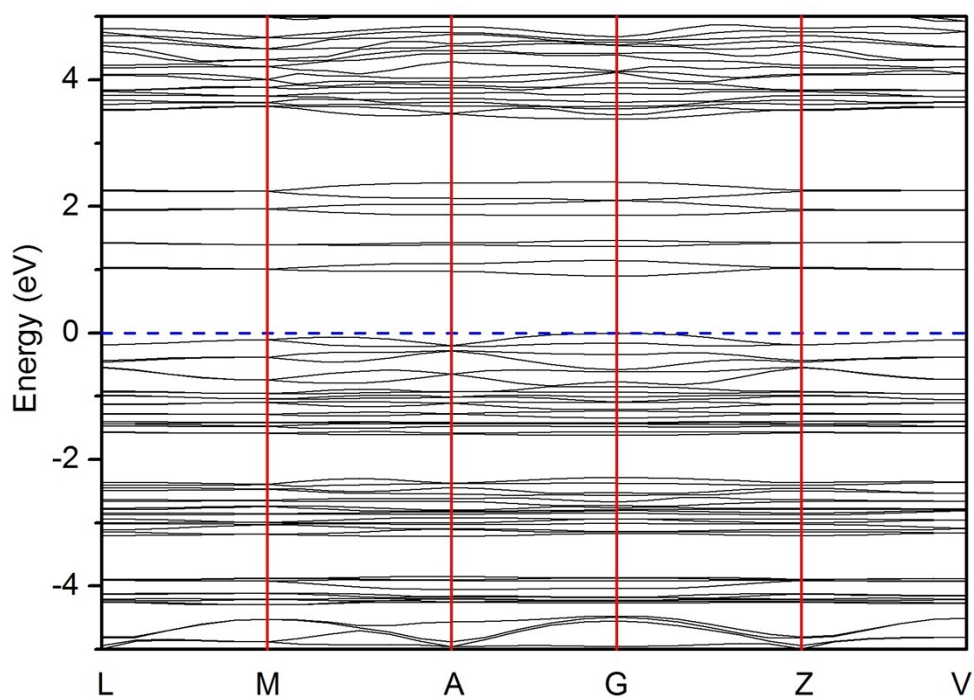


Fig. S4 Energy band structures of **1**. Energy bands are shown only between -5 and 5 eV for clarity, and the Fermi level is set at 0 eV.

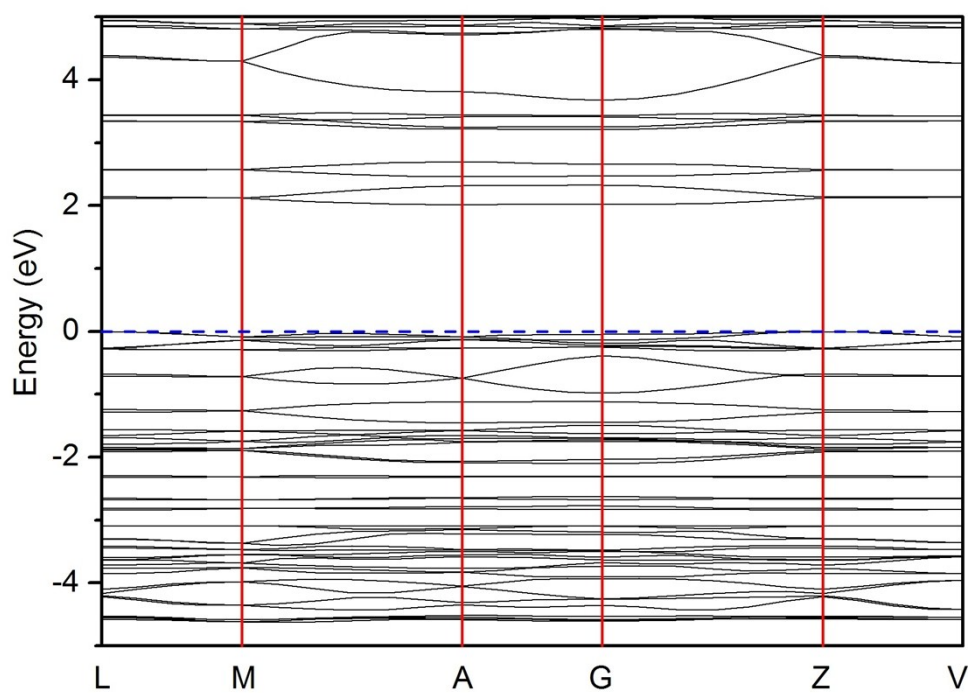


Fig. S5 Energy band structures of **2**. Energy bands are shown only between -5 and 5 eV for clarity, and the Fermi level is set at 0 eV.

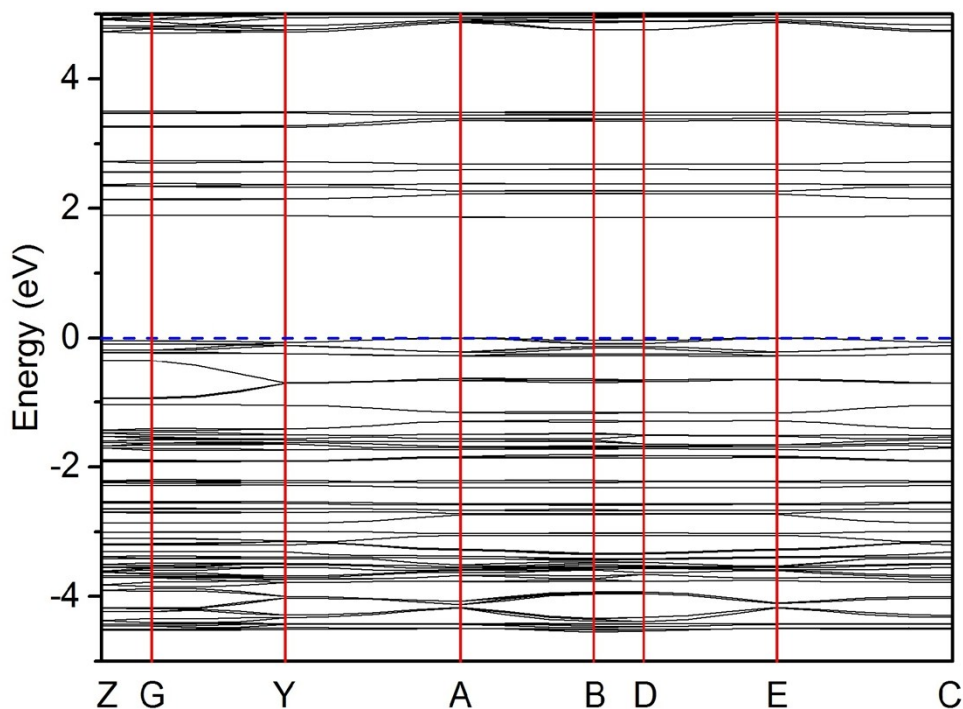


Fig. S6 Energy band structures of **3**. Energy bands are shown only between -5 and 5 eV for clarity, and the Fermi level is set at 0 eV.

Computational Descriptions/Explanation

The calculated band structure of **1** along high symmetry points of the first Brillouin zone is plotted in Figure S4, where the labeled k-points are present as L (-0.5, 0, 0.5), M (-0.5, -0.5, 0.5), A (-0.5, 0, 0), G (0, 0, 0), Z (0, -0.5, 0.5), and V(0, 0, 0.5). It is observed that both the top of valence bands (VBs) and the bottom of conduction bands (CBs) have very small dispersion. The lowest energy (0.90 eV) of conduction bands (CBs) is localized at the G point, and the highest energy (0.00 eV) of VBs is also localized at the G point, indicating compound **1** shows a narrow gap semiconductor character with a direct band gap of 0.90 eV. The bands can be assigned according to total and partial densities of states (DOS).

The SCN^- -2s and 4,4'-Hbpt-2s states, mixing with small SCN^- -2p and 4,4'-Hbpt-2p states, create the VBs localized at about -24.0 and -14.0 eV, While the SCN^- -2p and 4,4'-Hbpt-2p states, mixing with small SCN^- -2s, and 4,4'-Hbpt-2s states, create the VBs localized at about -14.0 and -3.5 eV. The VBs between energy -3.5 eV and the Fermi level (0.0 eV) are mostly formed by the hybridizations of Cu-3d state (29.2 electrons/eV), SCN^- -2p states (12.1

electrons/eV) and 4,4'-Hbpt-2p states (17.3 electrons/eV). The CBs between 0.5 and 3.0 eV are almost contribution from the 4,4'-Hbpt-2p states (10.7 electrons/eV), while the CBs between 3.0 and 9.0 eV are almost formed by SCN⁻-2p (11.0 electrons/eV), 4,4'-Hbpt-2p states (11.1 electrons/eV) mixing with small Cu-4s (1.7 electrons/eV), SCN⁻-2s (2.2 electrons/eV) and 4,4'-Hbpt-2s states (3.2 electrons/eV). Accordingly, the origin of the emission band of **1** may be mainly ascribe to the coupling of metal-to-ligand charge transfer (MLCT) and ligand-to-ligand charge transfer (LLCT). For MLCT, the electrons are transferred from the copper (Cu-3d state, VBs) to the unoccupied π^* orbitals of 4,4'-Hbpt ligands (4,4'-Hbpt-2p states, CBs), while for LLCT, the electrons are transferred from the occupied π orbitals of SCN⁻ groups and 4,4'-Hbpt ligands (SCN⁻-2p and 4,4'-Hbpt-2p states, VBs) to the unoccupied π^* orbitals of 4,4'-Hbpt ligands (4,4'-Hbpt-2p states, CBs).

The calculated band structure of **2** along high symmetry points of the first Brillouin zone is plotted in Figure S5, where the labeled k-points are present as L (-0.5, 0, 0.5), M (-0.5, -0.5, 0.5), A (-0.5, 0, 0), G (0, 0, 0), Z (0, -0.5, 0.5), and V(0, 0, 0.5). Both the top of VBs and the bottom of CBs have very small dispersion. The lowest energy (2.01 eV) of conduction bands (CBs) is localized at the A point, and the highest energy (0.00 eV) of VBs is also localized at the Z point, indicating compound **2** shows a semiconductor character with an indirect band gap of 2.01 eV. The bands can be assigned according to total and partial densities of states (DOS).

The SCN⁻-2s and 4,4'-Hbpt-2s states, mixing with small SCN⁻-2p and 4,4'-Hbpt-2p states, create the VBs localized at about -24.0 and -12.7 eV, While the SCN⁻-2p, 4,4'-Hbpt-2p and Cd-4d states, mixing with small SCN⁻-2s, and 4,4'-Hbpt-2s states, create the VBs localized at about -12.7 and -2.3 eV. The VBs between energy -2.3 eV and the Fermi level (0.0 eV) are mostly formed by the hybridizations of SCN⁻-2p states (20.3 electrons/eV) and 4,4'-Hbpt-2p states (20.2 electrons/eV). The CBs between 1.5 and 4.1 eV are almost contribution from the 4,4'-Hbpt-2p states (13.8 electrons/eV), while the CBs between 4.1 and 9.6 eV are almost formed by SCN⁻-2p (11.7 electrons/eV), 4,4'-Hbpt-2p states (11.6 electrons/eV) mixing with small Cd-5s (2.9 electrons/eV), SCN⁻-2s (2.2 electrons/eV) and 4,4'-Hbpt-2s states (1.8 electrons/eV). Accordingly, the origin of the emission band of **2** may be mainly ascribe to ligand-to-ligand charge transfer (LLCT) where the electrons are transferred from the occupied

π orbitals of SCN^- groups and 4,4'-Hbpt ligands (SCN^- -2p and 4,4'-Hbpt-2p states, VBs) to the unoccupied π^* orbitals of 4,4'-Hbpt ligands (4,4'-Hbpt-2p states, CBs).

The calculated band structure of **3** along high symmetry points of the first Brillouin zone is plotted in Figure S6, where the labeled k-points are present as Z(0, 0, 0.5), G(0, 0, 0), Y(0, 0.5, 0), A(-0.5, 0.5, 0), B(-0.5, 0, 0), D(-0.5, 0, 0.5), E(-0.5, 0.5, 0.5), and C(0, 0.5, 0.5). Both the top of VBs and the bottom of CBs have very small dispersion. The lowest energy (1.86 eV) of conduction bands (CBs) is localized at the D point, and the highest energy (0.00 eV) of VBs is also localized at the A point, indicating compound **3** shows a semiconductor character with an indirect band gap of 1.86 eV. The bands can be assigned according to total and partial densities of states (DOS).

The SCN^- -2s, CH_3CN -2s and 4,4'-Hbpt-2s states, mixing with small SCN^- -2p, CH_3CN -2p and 4,4'-Hbpt-2p states, create the VBs localized at about -24.0 and -12.4 eV, While the SCN^- -2p, CH_3CN -2p, 4,4'-Hbpt-2p and Cd-4d states, mixing with small SCN^- -2s, CH_3CN -2p, and 4,4'-Hbpt-2s states, create the VBs localized at about -12.4 and -2.2 eV. The VBs between energy -2.2 eV and the Fermi level (0.0 eV) are mostly formed by the hybridizations of SCN^- -2p states (41.7 electrons/eV) and 4,4'-Hbpt-2p states (44.2 electrons/eV). The CBs between 1.3 and 4.0 eV are almost contribution from the 4,4'-Hbpt-2p states (18.9 electrons/eV), mixing with small CH_3CN -2p states (6.2 electrons/eV), while the CBs between 4.0 and 9.6 eV are almost formed by SCN^- -2p (11.3 electrons/eV), 4,4'-Hbpt-2p states (23.6 electrons/eV) mixing with small Cd-5s (6.0 electrons/eV) and SCN^- -2s (2.2 electrons/eV). Accordingly, the origin of the emission band of **2** may be mainly ascribe to ligand-to-ligand charge transfer (LLCT) where the electrons are transferred from the occupied π orbitals of SCN^- groups and 4,4'-Hbpt ligands (SCN^- -2p and 4,4'-Hbpt-2p states, VBs) to the unoccupied π^* orbitals of 4,4'-Hbpt ligands and CH_3CN guest molecules(4,4'-Hbpt-2p and CH_3CN -2p states, CBs).

PXRD diagrams

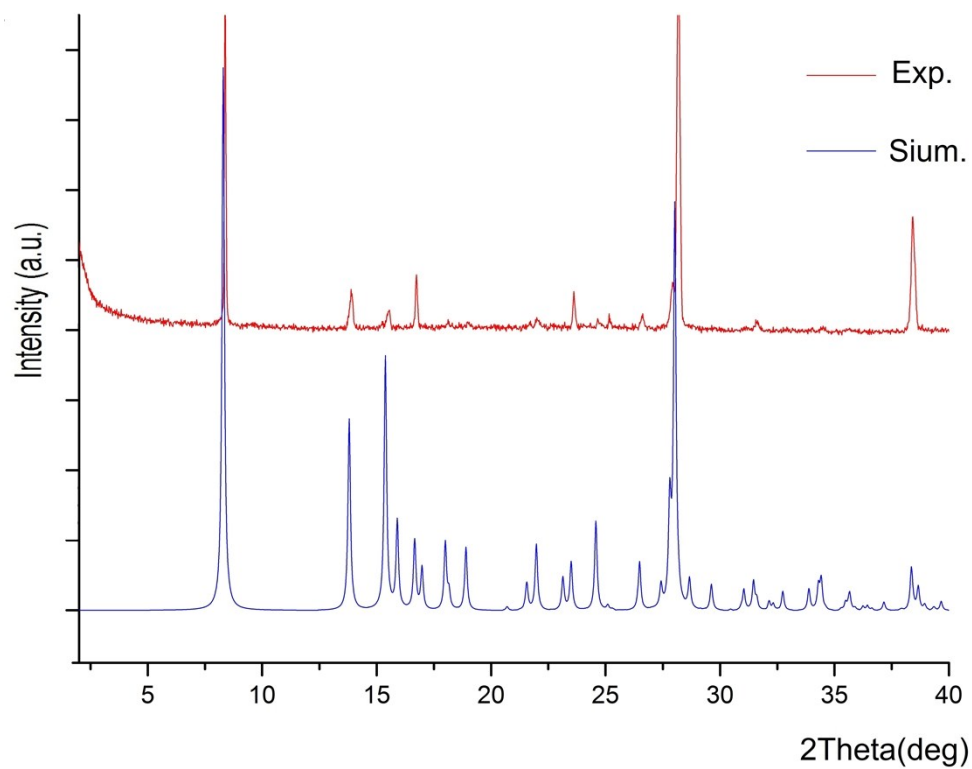


Fig. S7 Experimental and simulated PXRD patterns for bulk sample of **1**.

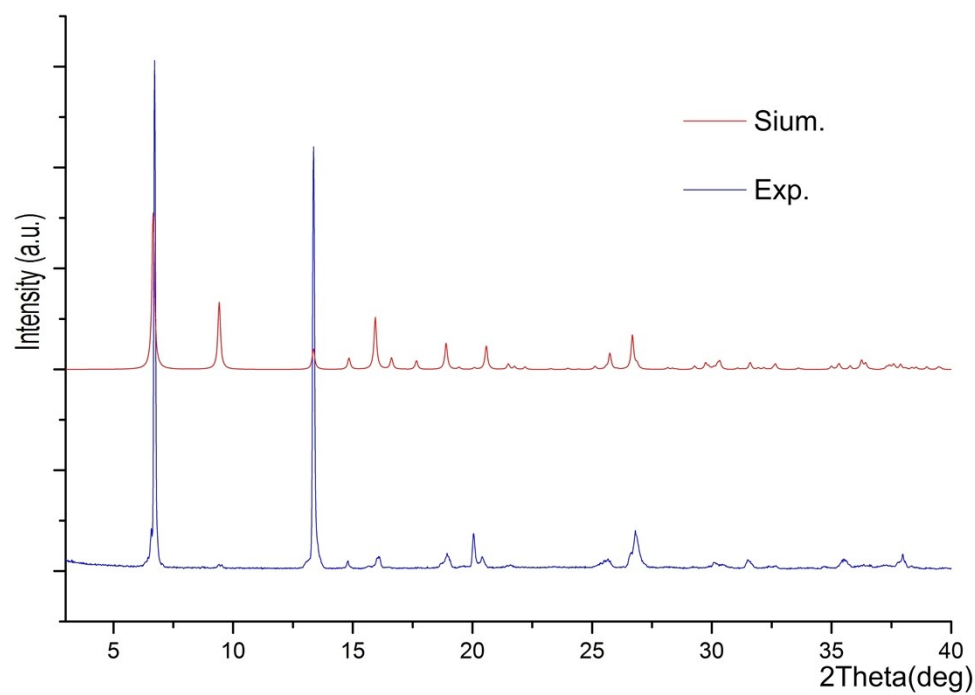


Fig. S8 Experimental and simulated PXRD patterns for bulk sample of **2**.

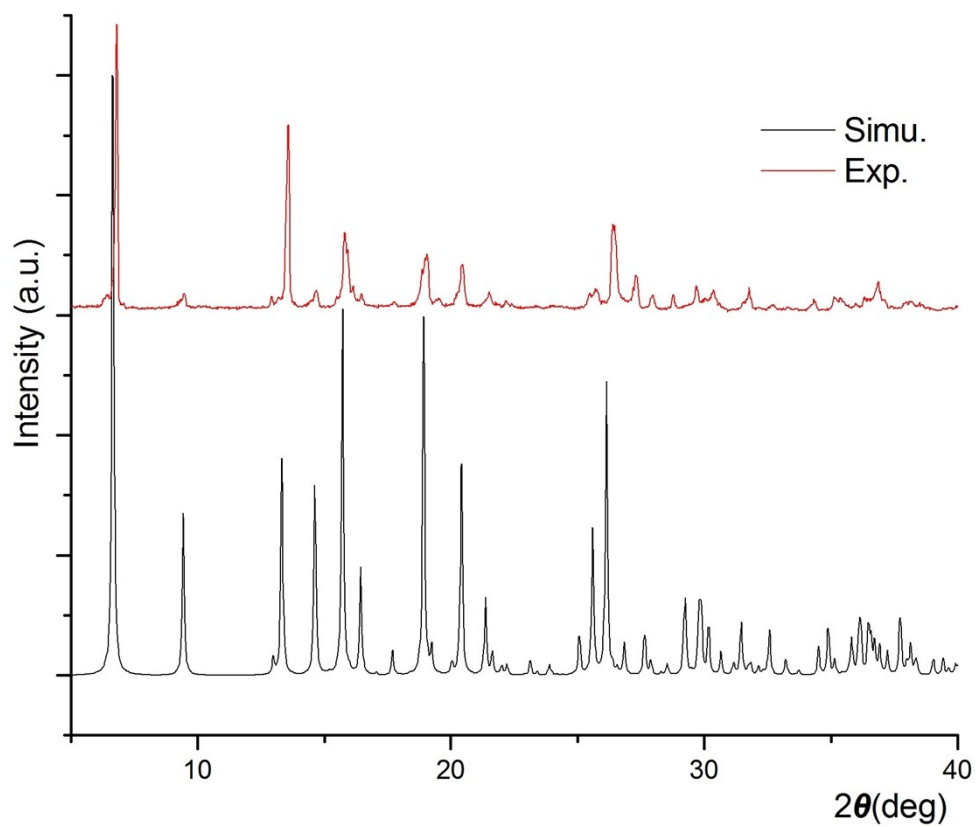


Fig. S9 Experimental and simulated PXR D patterns for bulk sample of **3**.

TGA curves

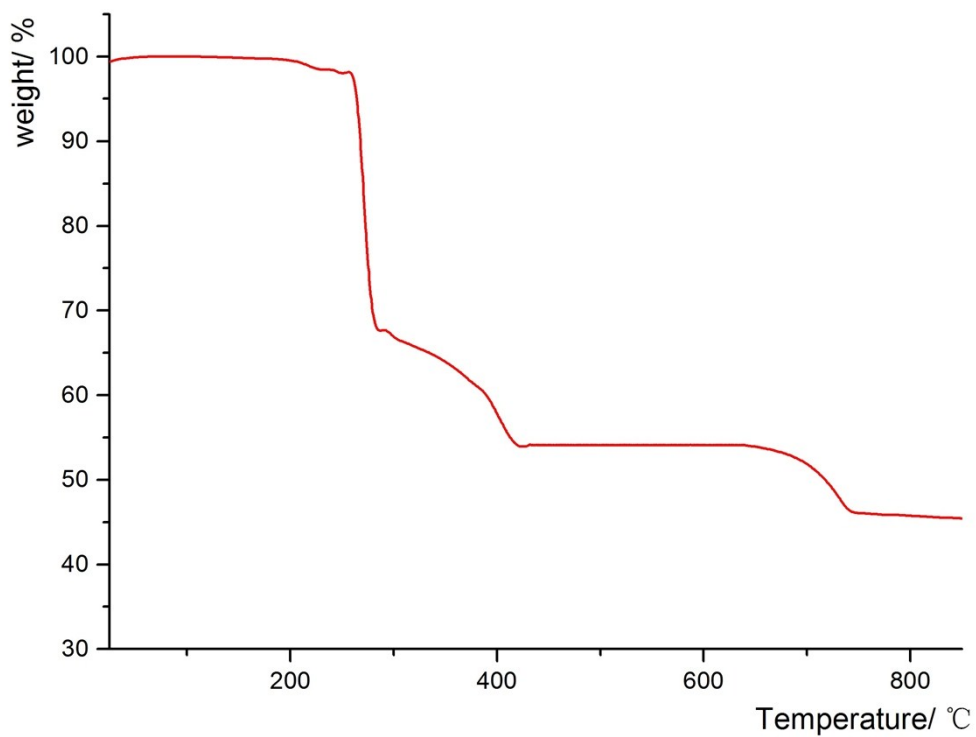


Fig. S10 TGA curve of **1** under air atmosphere.

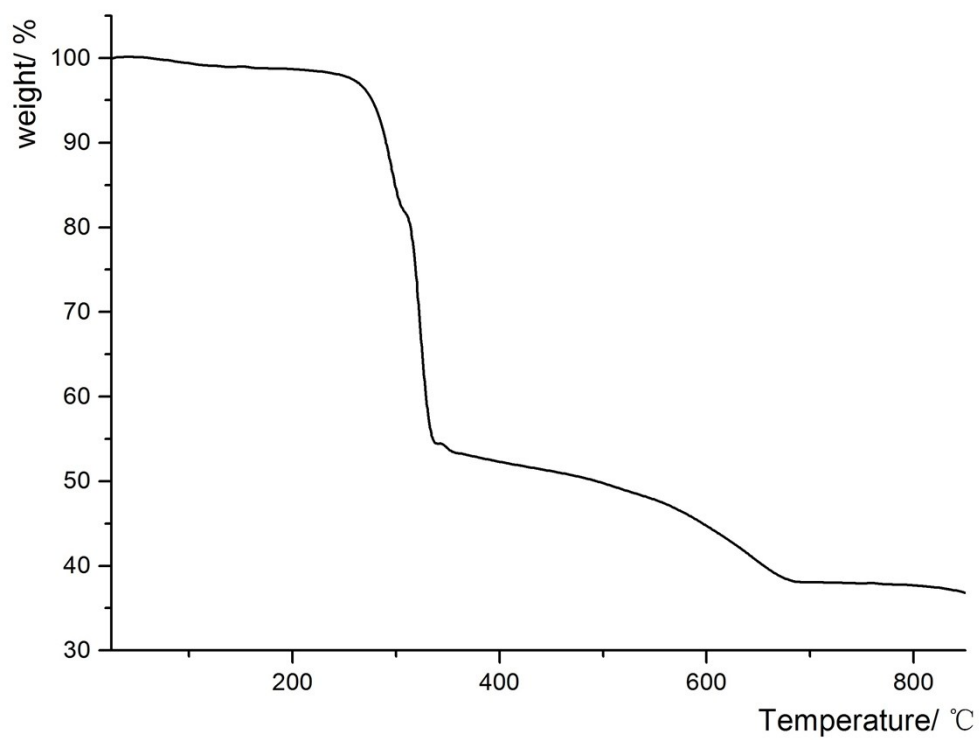


Fig. S11 TGA curve of **2** under air atmosphere.

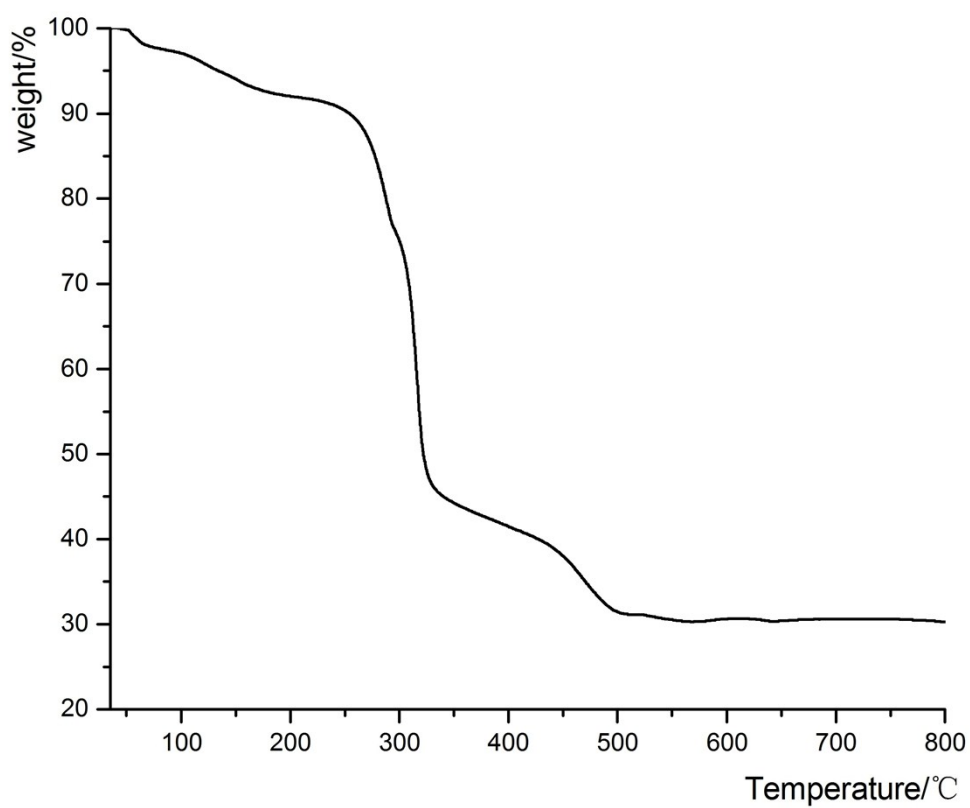


Fig. S12 TGA curve of **3** under air atmosphere.

IR spectra

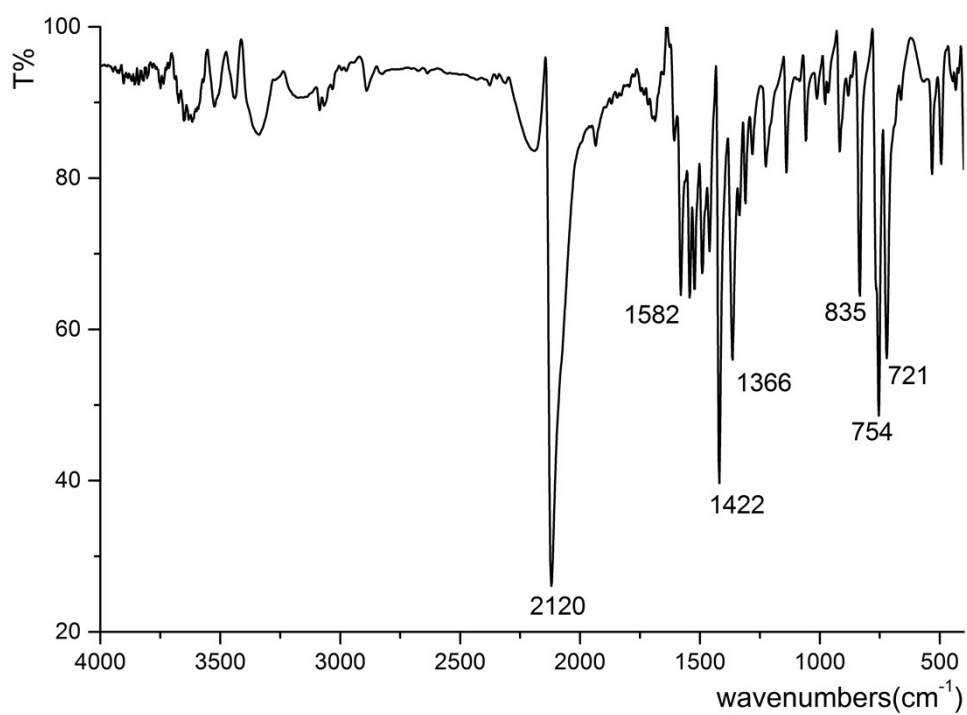


Fig. S13 The FT-IR spectrum of **1** at room temperature.

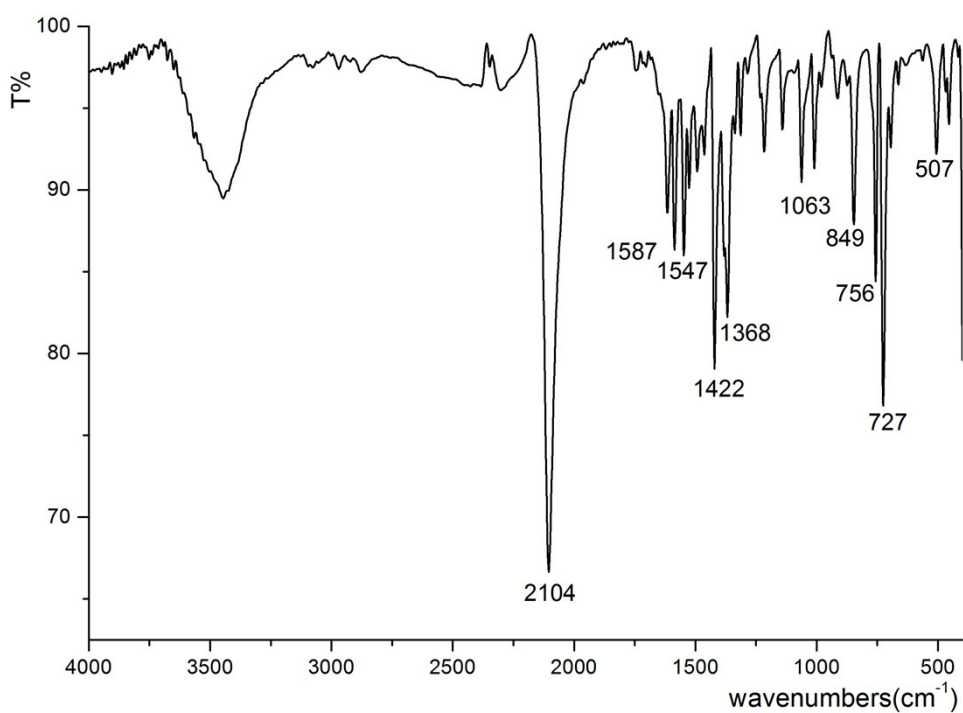


Fig. S14 The FT-IR spectrum of **2** at room temperature.

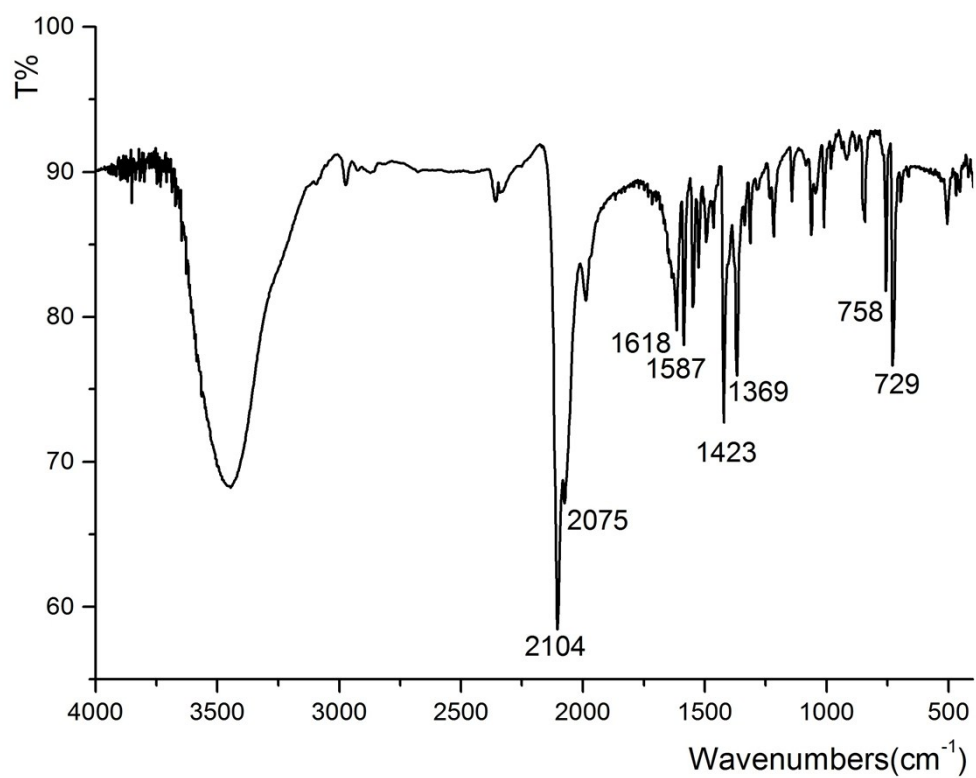


Fig. S15 The FT-IR spectrum of **3** at room temperature.