Supplementary material

Doping Potassium Ions in Silver Cyanide Complexes for Green Luminescence

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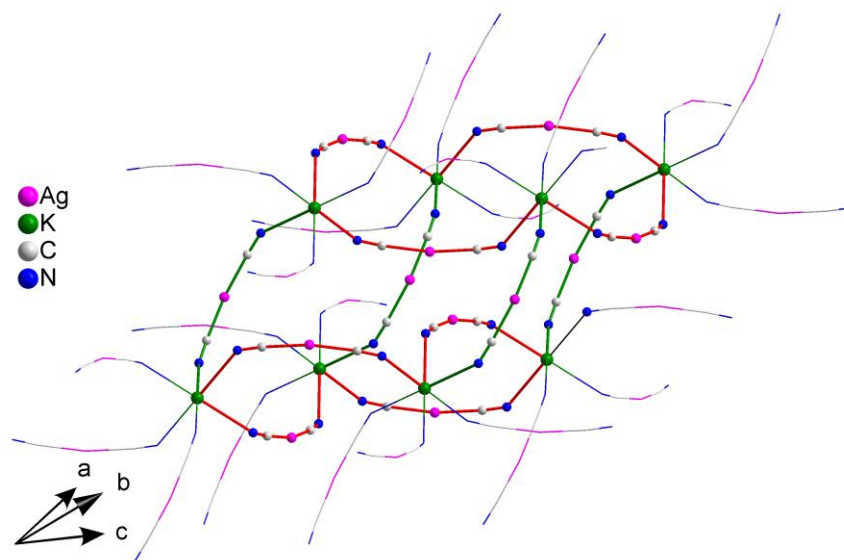
Additional plots of the structures

Fig. S1 A view of 3-D structure of **1** with a highly distorted simple cubic geometry. The [Me$_4$N]$^+$ cations are omitted for clarity.

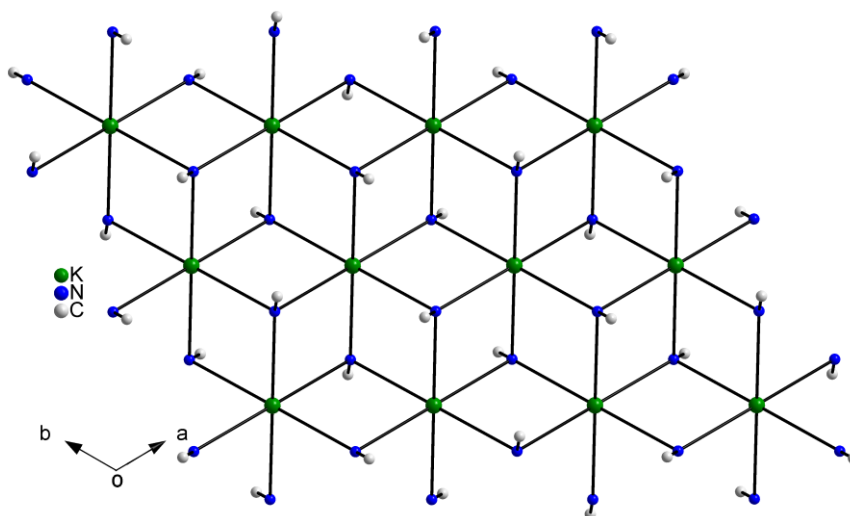**Fig. S2** A view of 2-D concave-convex $^\infty_2$[K(CN)$_2$] layer in **2**.

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 pseudopotential[2] for the core electrons. The number of plane waves included in the basis was determined by a cutoff energy Ec of 550 eV. Pseudoatomic calculations were performed for H-$1s^1$, C-$2s^22p^2$, N-$2s^22p^3$, and Ag-$4d^{10}5s^1$. 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^{-6} eV, band energy tolerance of 1×10^{-5} eV. All of calculations were performed by CASTEP program in the Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599, USA.

(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.

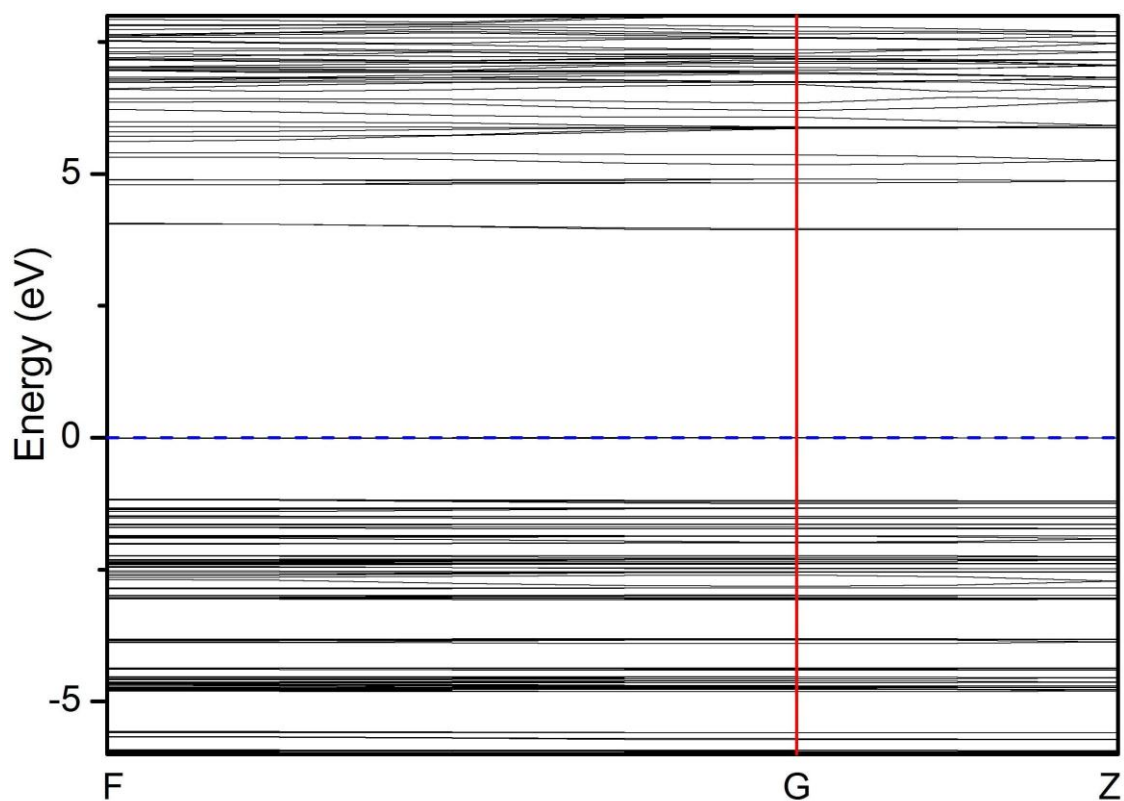(2) Hamann, D. R.; Schluter, M.; Chiang, C. *Phys. Rev. Lett.* **1979**, *43*, 1494–1497.

Fig. S3 Energy band structures of **1**. Energy bands are shown only between -6 and 8 eV for clarity, and the Fermi level is set at 0 eV.
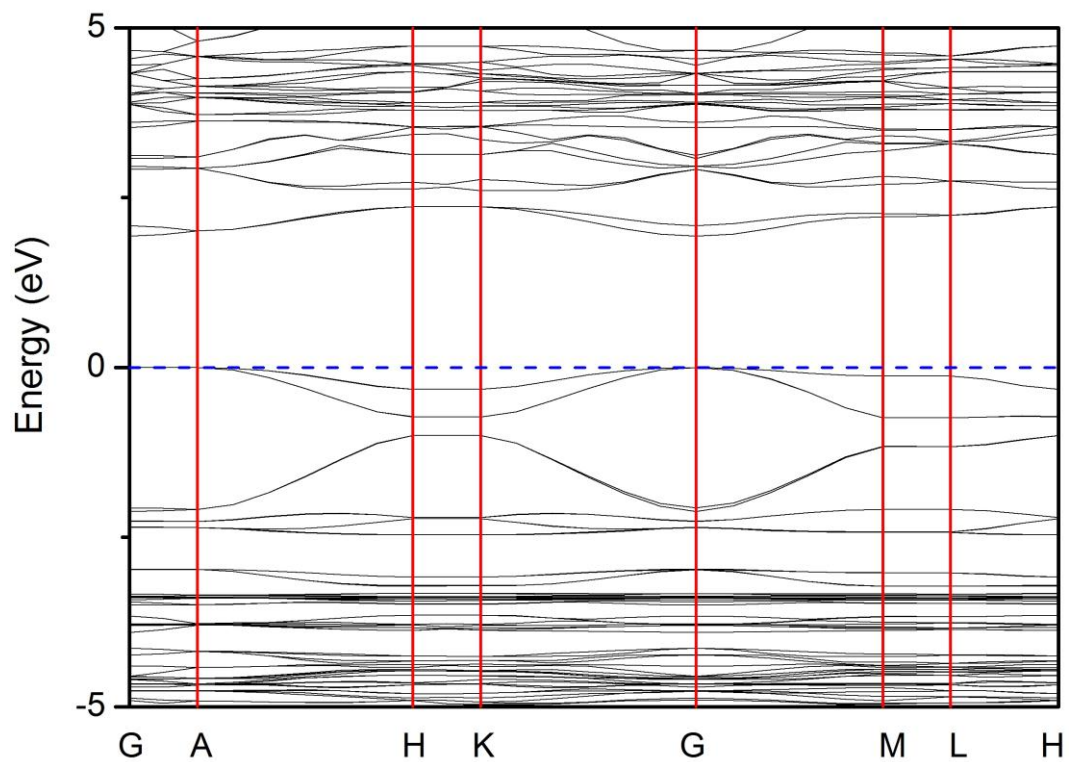

Fig. S4 Energy band structures of **2**. Energy bands are shown only between -5 and 5 eV for clarity, and the Fermi level is set at 0 eV.

Computational Descriptions/Explanation

The calculated band structure of **1** along high symmetry points of the first Brillouin zone is plotted in Figure S2, where the labeled k-points are present as F (0.5, 0.5, 0.0), G (0.0, 0.0, 0.0), and Z (0.5, 0.5, 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 (3.94 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 wide gap semiconductor character with a direct band gap of 3.94 eV. The bands can be assigned according to total and partial densities of states (DOS). The K-4p, Cyanide-2s, and $[Me_4N]^+$-2s,2p states, mixing with small Ag-4d, K-4s, and Cyanide-2p states, create the VBs localized at about -29.0 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 Ag-4d state (35.1 electrons/eV) and Cyanide-2p states (50.4 electrons/eV). The CBs between 3.4 and 9.1 eV are almost contributed from the Cyanide-2p states (23.2 electrons/eV) mixing with a small amount of Ag-5s state (2.9 electrons/eV), K-4p state (3.7 electrons/eV), and $[Me_4N]^+$-2s,2p states (5.6 electrons/eV). Accordingly, the origin of the emission band of **1** may be mainly ascribed 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 silver (Ag-4d state, VBs) to the unoccupied π^* orbitals of cyanide groups (Cyanide-2p states, CBs), while for LLCT, the electrons are transferred from the occupied π orbitals of cyanide groups (cyanide-2p states, VBs) to the unoccupied π^* orbitals of cyanide groups (Cyanide-2p states, CBs).

The calculated band structure of **2** along high symmetry points of the first Brillouin zone is plotted in Figure S3, where the labeled k-points are present as G (0.0, 0.0, 0.0), A (0.0, 0.0, 0.5), H (-1/3, 2/3, 0.5), K (-1/3, 2/3, 0), M (0.0, 0.5, 0.25), and L (-1/9, 5/9, 0.5). Both the top of VBs and the bottom of CBs have large dispersion. The lowest energy (1.93 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 **2** shows a semiconductor character with a direct band gap of 1.93 eV. The K-4s, Cyanide-2s, and O_{water}-2s state, mixing with a small amount of Cyande-2p state, create the VBs localized at about -31.0 and -15.0 eV. While the K-4p, and O_{water}-2p state, mixing with a small amount of Ag-4d state and Cyanide-2s,2p states,

create the VBs localized at about -15.0 and -5.7 eV. The VBs between energy -5.7 eV and the Fermi level (0.0 eV) are mostly formed by the mixture of Ag-4d state (19.5 electrons/eV) and Cyanide-2p states (24.9 electrons/eV), in which the VBs energy around -4.6 eV are mainly formed by Cyanide-2p states, while the VBs energy around -3.4 eV are mainly formed by Ag-4d state. The CBs between 1.7 and 5.0 eV are almost contributed from the Cyanide-2p states (13.2 electrons/eV) mixing with a small amount of K-4s,4p states (1.5 and 1.9 electrons/eV respectively). Accordingly, the origin of the high-energy emission band at 375 nm of **2** may be mainly ascribe to ligand-to-ligand charge transfer (LLCT) where the electrons are transferred from the occupied π orbitals of cyanide groups (Cyanide-2p states, VBs) to the unoccupied π^* orbitals of cyanide groups (Cyanide-2p states, CBs), while the origin of the low-energy emission band at 530 nm of **2** may be mainly ascribe to metal-to-ligand charge transfer (MLCT) where the electrons are transferred from the silver (Ag-4d state, VBs) to the unoccupied π^* orbitals of cyanide groups (Cyanide-2p states, CBs).

TGA curves

The TGA curve shows that compounds **1**, **2** decompose at the decomposition point T_{onset} of about 230, 425°C. The detailed decomposition mechanisms of the two compounds are too complex to explain at present.
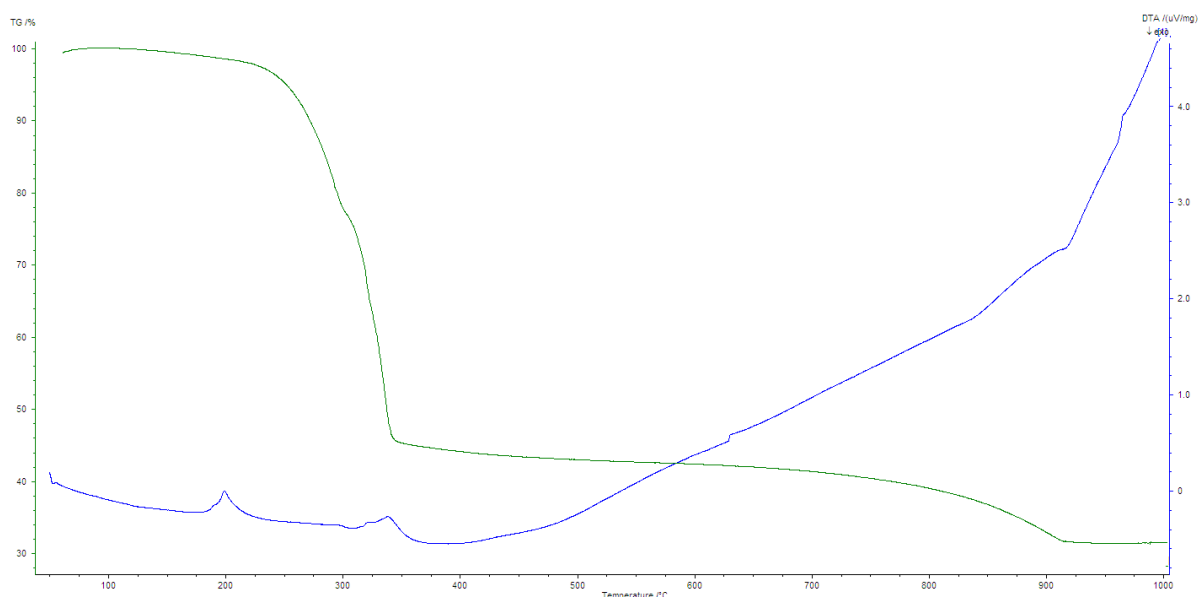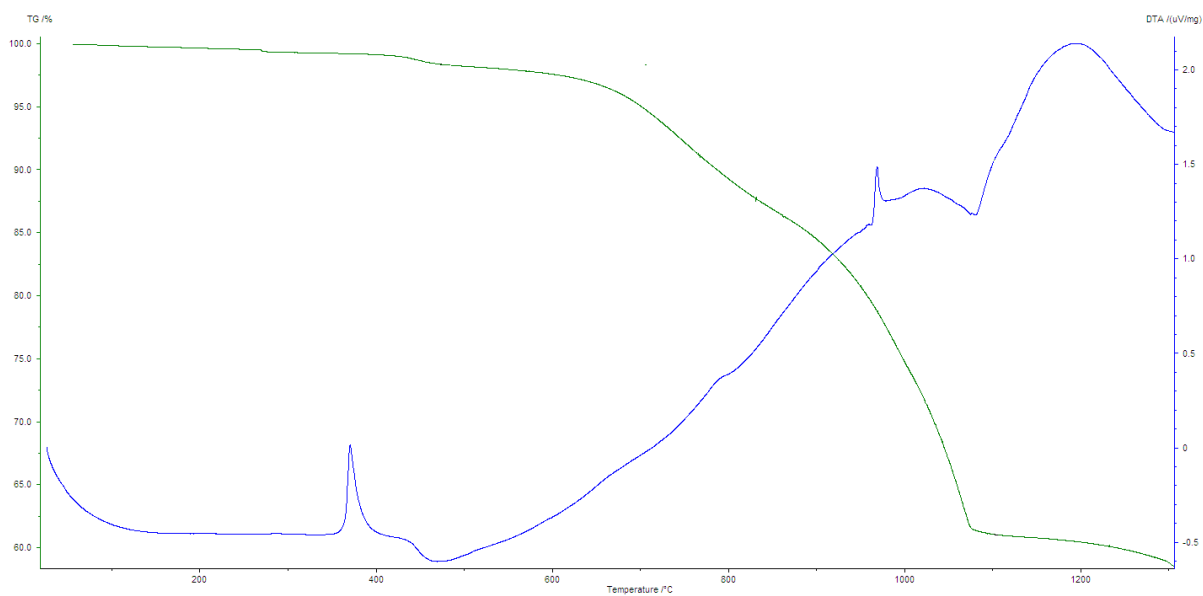

Fig. S5 TGA curves of **1** under N_2 atmosphere.

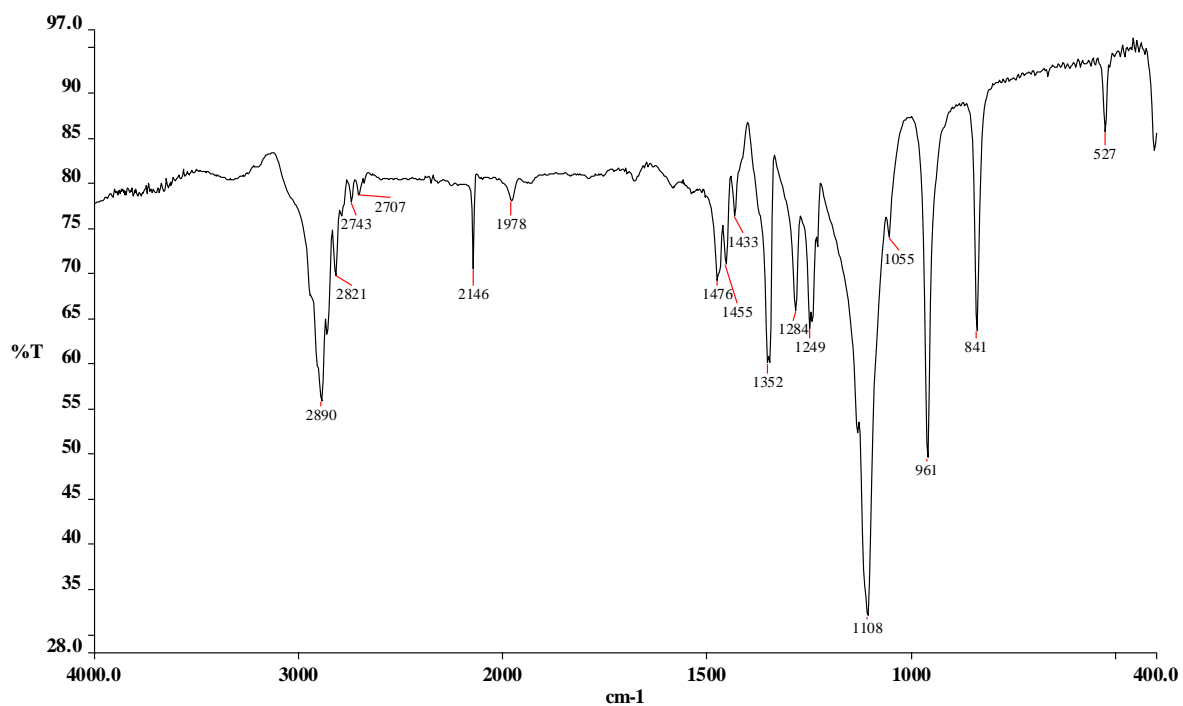**Fig. S6** TGA curves of **2** under N$_2$ atmosphere.

IR spectra

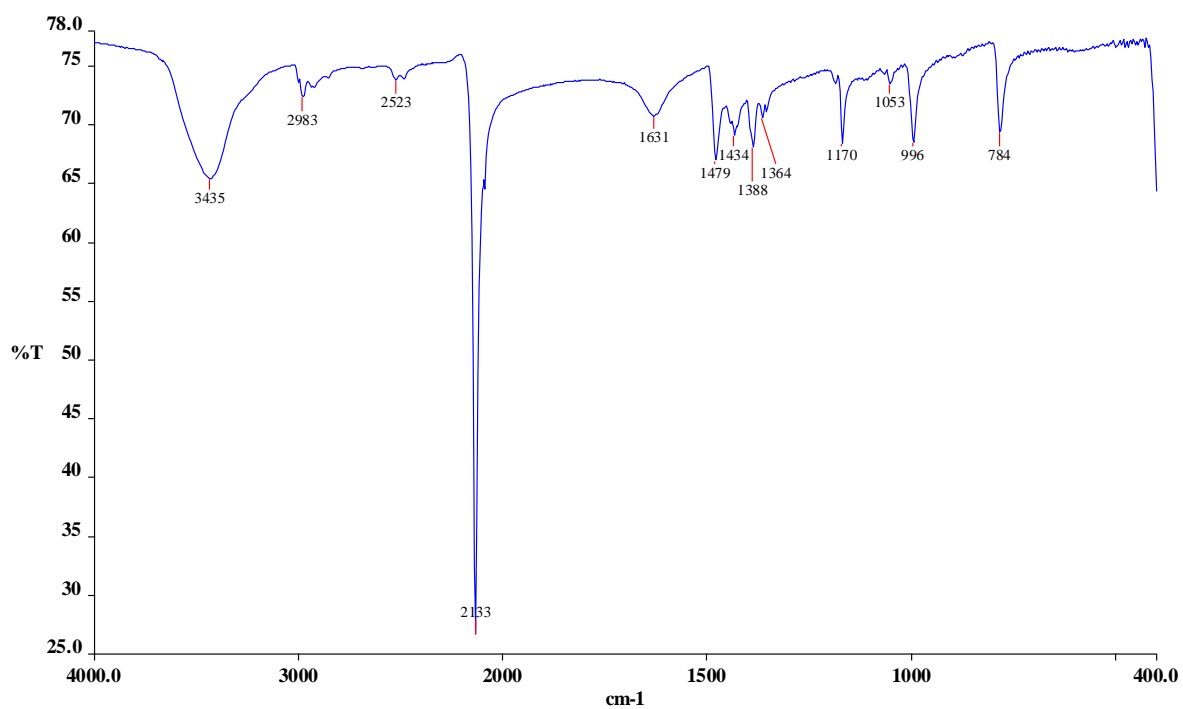**Fig. S7** The FT-IR spectrum of **1** at room temperature.

Fig. S8 The FT-IR spectrum of **2** at room temperature.