A novel 3-D chiral bismuth-organic framework with mixed carboxylate, pyridine and thiolate donors exhibiting a semiconductive property

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Electronic Supplementary Information:

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X-ray Crystallography. Suitable single crystals were selected and mounted on a glass fiber. All data for compound **1** was collected with a Rigaku Saturn 724 CCD area-detector diffractometer at 293(2) K with a graphite-monochromated Mo–Kα radiation (λ=0.71073 Å) by multi-scan technique. The diffraction points of $I > 2\sigma(I)$ were selected to determine the structure of **1**, and solved by direct methods and refined by full-matrix least-squares methods using the SHELXS and SHELXL programs of SHELX 97 crystallographic software package. All metal atoms, oxygen, nitrogen, sulfur and partial of carbon were refined with anisotropic thermal parameters on F^2. Hydrogen atoms were generated theoretically onto the specific atoms with bond distance restraints of 0.90 Å for N–H and 0.86 Å for C–H, and refined with isotropic thermal parameters riding on the parent atoms. Powder X-ray diffraction (PXRD) patterns were recorded on an X'pert Pro diffractometer (Cu-Kα).

Materials and General Details. Commercially available solvents and chemicals were used without further purification. IR spectra were measured as KBr pellets on a Perkin-Elmer Spectrum 2000 FT-IR in the range 400-4000 cm^{-1}. Thermogravimetric data were collected on a Mettler Toledo TGA/SDTA 851 e analyzer in flowing nitrogen at a heating rate of 10 ºC/min.

In order to obtain the 2D IR correlation spectra, a series of dynamic IR spectra were recorded in the range 4000–400 cm^{-1} on a Perkin-Elmer FT–IR spectrum 2000 spectrometers using KBr pellets. The temperature variation was controlled by a Portable programmable temperature controller (Model 50–886, Love Control Corporation) from 50 to 120 °C at intervals of 10 °C. 2D-IR COS were obtained by treating a series of dynamic spectra with 2D-IR COS correlation analysis software provided by Tsinghua University.

The optical diffuse reflectance was obtained on Perkin-Elmer Lambda 900 spectrometer at the room

temperature, the scan range was from 200 to 800 nm. The absorption data R/S (R, absorption coefficient; S, scattering factor) was calculated from the reflectance data using the Kubelka-Munk function. The optical band gap was measured as the intersection point between the energy axis at the absorption offset and the line extrapolated from the sharp absorption edge in the K-M versus E (eV) plot.

The band structure and the density of states of **1** was calculated based on density functional theory (DFT) as implemented in CASTEP code. The exchange correlation energy was estimated using the generalized gradient approximation with the Perdew-Wang formula (PW-91). Ultrasoft pseudopotentials from the CASTEP pseudopotential library were used throughout minimize computation time. The number of k-points of 5×5×5 and the energy cutoff for plane-wave expansion of wave-functions of 430.0 eV were applied for the band structure and the density of states with the orbitals of H 1s, C $2s^2 2p^2$, O $2s^2 2p^4$, N $2s^2 2p^3$, S $3s^2 3p^4$, Bi $6s^2 6p^3$.

Syntheses of 1: A mixture of $Bi(NO_3)_3 \cdot 5H_2O$ (0.1500 g, 0.3 mmol), 2-Mercaptonanicotinic acid (0.2315 g, 1.5 mmol), KOH (0.03 g, 0.053 mmol) and 6 mL DMF was sealed in a 25 mL stainless steel reactor with teflon liner and heated at 100 ℃ for 3 days and then cooled to the room temperature naturally. Brown prism crystals of 1 were obtained by filtration, washed with distilled water and dried in air. Yield: 43% (**1**) (based on Bi). Anal. calc. for $C_{14}N_3O_4H_{14}S_2Bi$ **1**: C, 29.84; H, 2.47; N, 7.52. Found: C, 29.93; H, 2.50; N, 7.48%.

Table S1 Parameters of Hydrogen Bonds for **1** [Å] and [deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3B)...O(1)#5	0.90	2.03	2.819(15)	146.4
N(3)-H(3A)...O(3)	0.90	1.80	1.80	153.8

Symmetry codes: #5 x+1, y, z.

$$CH_3-\underset{\underset{O=CH}{|}}{N}-CH_3 \ + \ H_2O \xrightarrow{OH^-} \overset{O}{\overset{\|}{HCOH}} + HN(CH_3)_2 \rightleftharpoons HCO_2^- \ + \ H_2N(CH_3)_2^+$$

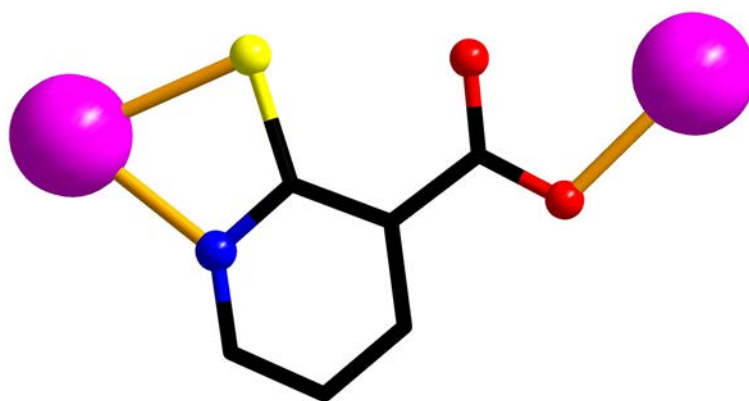**Scheme S1** DMA$^+$, formed via decomposition of DMF.

Fig. S1 The coordination modes of mna^{2+} in **1**.

As shown in Fig S1, Each mna^{2-} ligand forms a planar 4-membered N,S donor chelate rings to Bi (bite angle = 58.2(2)°and 61.3(2)°). The carboxylate group of the mna^{2-} ligand provides a monodentate mode, coordinating to one Bi atom.

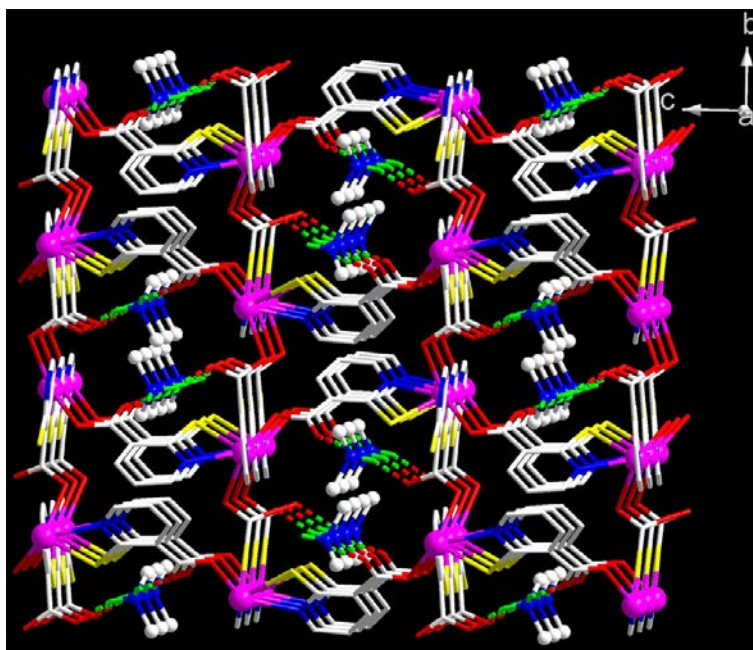**Fig. S2** The 3D framework of **1** along *a* axis.
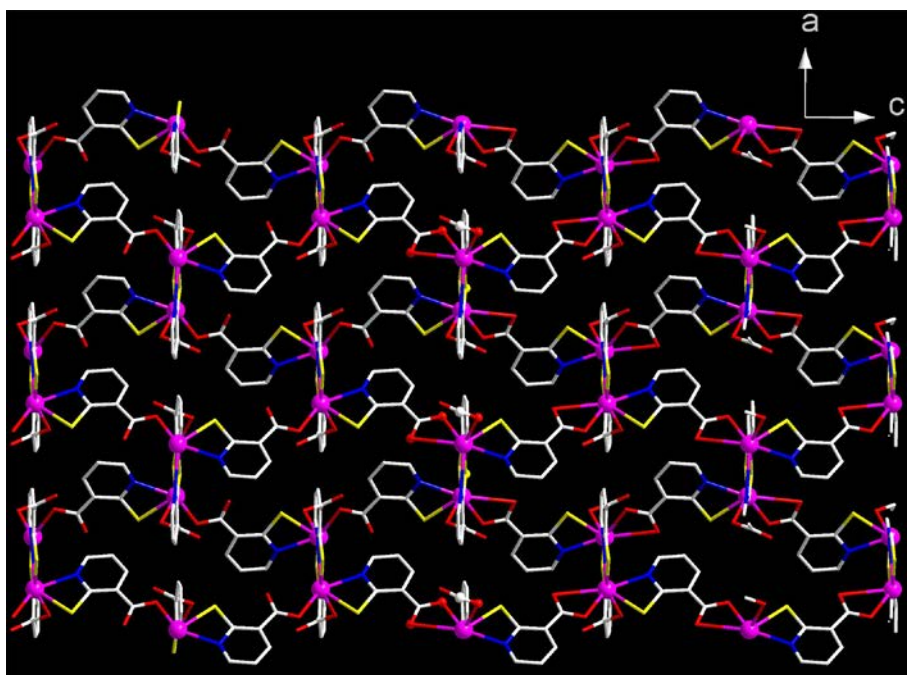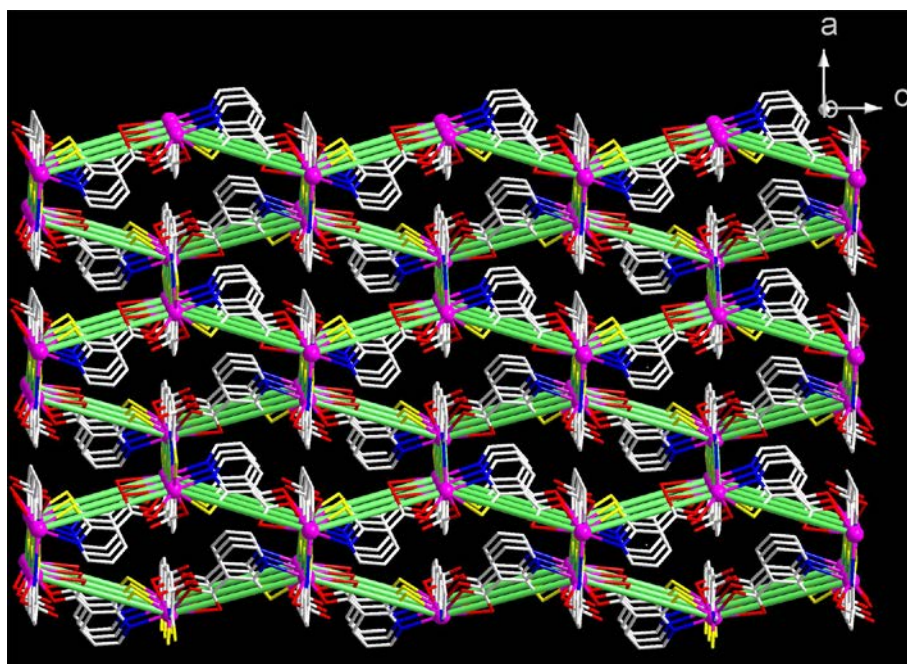
Fig. S3 The 3D framework of **1** along *b* axis.

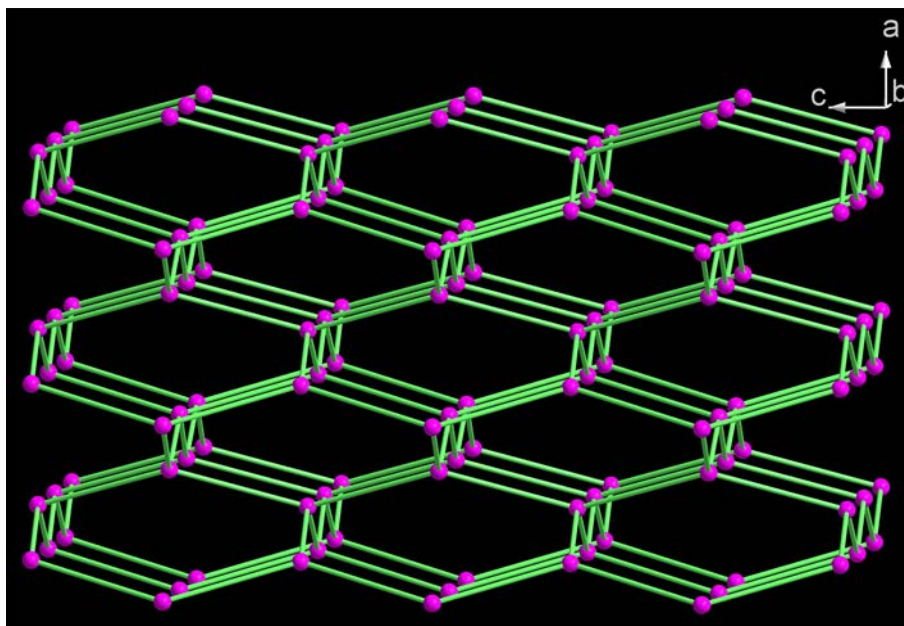**Fig. S4** The 3D 3D framework with *dia*-topology.

Fig. S5 The 3D net with *dia*-topology after simplification; Key: purple, Bi; the green lines represent mna^{2+} ligands.

From the topological point of view, the 3D framework of **1** was a 4-connected net. Each Bi^{3+} cations acted as four-connected node and every mna^{2-} ligand only functions as a bridge, the overall framework could be represented as a *dia*-topology with the point symbol of (6^6).
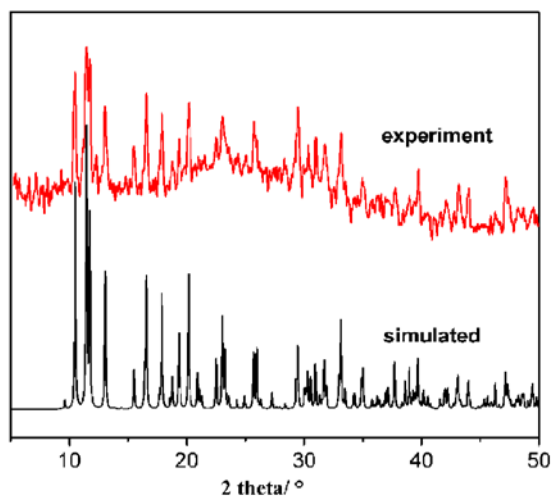
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Fig. S6 The XRD patterns of simulated and experiment for **1**.

The good accordance of the experimental XRD patterns with the simulated patterns indicates phase purity of **1**.
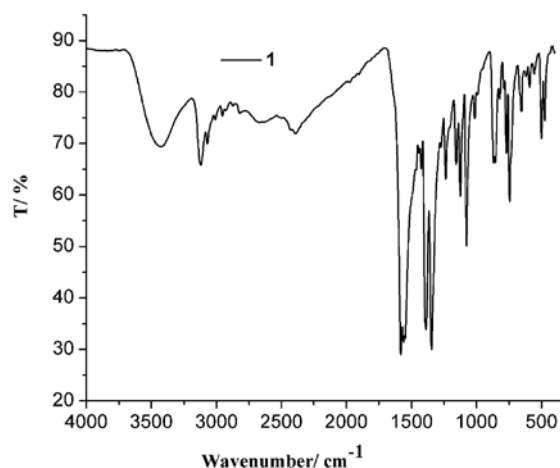
Fig. S7 The FT IR spectrum of compound **1**.

IR spectra of **1** exhibit a series of strong bands at 3430 and 3120 cm^{-1} for **1**, associated with v(N-H) of the DMA^{+} cation (Fig. S7). The stretching vibration of C-H from the –CH$_3$ is at the 2960 cm^{-1}. There is a Strong and sharp pick observed over 1581 cm^{-1} (v(C=O)) indicating that the carboxyl group is deprotonated, which are good agreement with the crystallographic data. The compounds also possess bands at 747 cm^{-1} for **1**, which are attributed to v(C–S).
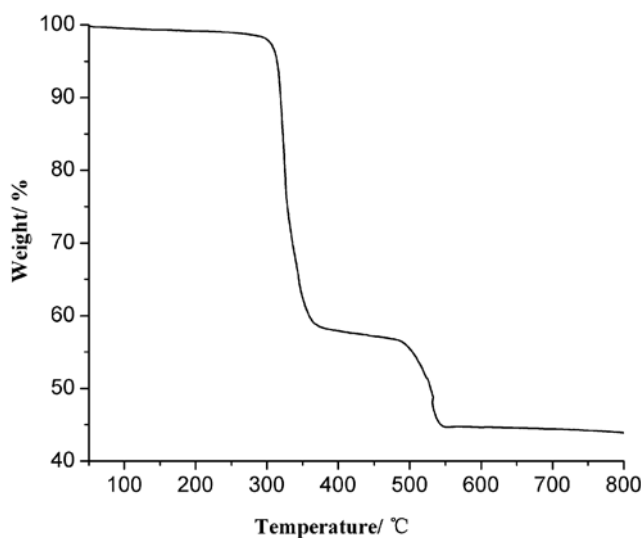

Fig. S8 The TG curve of compound **1**.

The thermal stability of **1** was studied by TGA in a dry nitrogen atmosphere from 50 to 800 °C (Fig. S8) The TGA curve of **1** exhibits two-step primary weight loss processes for the crystalline sample. The initial weight loss of 38.81% in the temperature range of 305 - 367 °C corresponds to the release of the DMA and pyridine molecules come from the decomposition of mna^{2-} at the high temperature (cacl. 36.18%). The second weight loss is observed from 489 to 550 °C and is attributed to the decomposition of remaining organic groups. The black residue might be a mixture of Bi$_2$O$_3$:Bi$_2$S$_3$ = 1:3 ((observed 44.69%, calc. 44.70%).