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Quasi-Planar Organic Synthon and $S \cdots X$ (X = S or H–C) Contacts in Flat Copper Coordination Chains: Syntheses, Structures and Conductive Behaviour

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A new organic building block, TEPB, has been synthesized that comprises three 2-ethylthio-substituted pyrimidine groups coupled to one central phenyl ring at the 1-, 3- and 5-positions. TEPB exhibits a quasi-planar conformation due to its intramolecular C-H···N hydrogen bonds. The assembly of TEPB with Cul and CuCl₂ produced two flat coordination chains **1** and **2**, both exhibiting similar assembly hierarchies from chain through 2D layer to 3D architecture. It was found that extensive S···S and C-H···S contacts exist in the 2D layers of **1** and **2**, respectively. Between the 2D layers of **2**, there are O-H···Cl hydrogen-bonding interactions between water molecules and coordinated Cl atoms that provide a proton-

Introduction

In recent years there has been an upsurge of interest in the design of conductive coordination polymers $(CPs)^{[1-4]}$ due to their great potential in solid-state electronic devices.^[5] Although conductive CPs can be categorized into two general families according to their conduction mechanism (electron or ion), the key to their success is in establishing an either electrical or ionic conduction pathway. For electrically conductive CPs, there are several strategies that have been systematically explored over the past decade. For example, the incorporation of metal coordination bonds has been attempted to promote electronic communication across organic molecules by enhancing intermolecular interactions beyond the van der Waals limit, which has been well demonstrated by Xu and co-workers' work on multiple thioether-substituted polycyclic aromatic hydrocarbons (PAHs) with BiX_3 (X = Cl, Br).^[6,7] In addition, elaboration of a p_{π} -d_{π} conjugated spine through coordinative interactions between metal centres (including mixed valence) and organic bridging molecules or halogen atoms is another

transfer network. Complex 2 exhibits a smaller optical band gap (1.11 eV) than 1 (1.93 eV), which has been attributed to d-electron transition in the copper(II) ion. The d.c. conductivities of 1 and 2 at room temperature were measured to be 2.84×10^{-12} and $2.42 \times 10^{-10} \, \mathrm{S \, cm^{-1}}$, respectively. The a.c. conductivity of 2 obtained at room temperature by the complex impedance technique is about $5.90 \times 10^{-9} \, \mathrm{S \, cm^{-1}}$, which can be attributed largely to proton conduction. Moreover, the a.c. conductivity of 2 decreases almost linearly with increasing temperature, presumably as a result of its temperaturesensitive O–H···Cl hydrogen-bonding network that allows for proton conduction.

productive approach towards conductive CPs, as exemplified by the well-known $MX^{[8-10]}$ or MMX chains (M = metal)^[11-15] and "Shish-Kebab" molecular systems.^[16] Moreover, CPs based on metal thiolate bonds have received long-standing interest because the π -donating character of the sulfur p orbital would improve metal-to-ligand electron exchange.^[17-23] One practical strategy for gaining greater electrical conduction or even superconduction is to fabricate columnar organic molecular stacking with closely overlapping π orbitals in CPs, which constitute the principal electron transport pathway. In this regard, outstanding examples are provided by CPs based on organic radical molecules such as DCNQI,^[24,25] TCNQ,^[26-28] TANC,^[29] and tetrathiafulvalene (TTF) derivatives.[30] For ion-conductive CPs, ion transport is primarily governed by two important factors, namely the ion carrier and their transport networks, for which there is an excellent review recently published by Kitagawa and co-workers.[31]

In sharp contrast with their numerous applications in, for example, gas storage, separation and catalysis,^[32–34] the development of conductive properties in CPs is yet in its infancy, and there still is great scope for imaginative design in this interdisciplinary field. To the best of our knowledge, small-molecule organic semi-conductors have led to great improvements in organic field effect transistors (OFETs) and organic semi-conductors (OSCs), largely due to the good understanding of the relationship between device performance and molecular structure.^[35,36] For example, it is

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well recognized that intermolecular π - π stacking together with S…S or C-H…S contacts are responsible for the charge transport in sulfur-containing organic conductors (e.g., TTF and its derivatives) in which the delocalized π orbital generally shows a planar or quasi-planar conformation.^[37-39] Moreover, it has also been discovered that S···S interactions can direct molecular stacking from a herringbone motif to a face-to-face π - π overlapping motif, which is believed to facilitate charge transport.^[40-42] Learning from the design rules of organic conductors, we have devised a new organic building block, namely 1,3,5-tris[2-(ethylthio)pyrimidin-4-yl]benzene (TEPB; Scheme 1) in order to construct CPs showing conductive properties. The design of TEPB has taken into account the following issues. First, the intramolecular C-H···N hydrogen bonds between the central phenyl ring and the outer pyrimidinyl ring are believed to lock the molecule into a quasi-planar conformation, maximizing π -orbital delocalization. Secondly, the presence of the thioether S atom is expected to form S···S or C-H. S contacts. Thirdly, it was hoped that the choice of the modest-sized ethyl substituent would influence the molecular packing but without blocking the metal coordination to the pyrimidine N atom due to steric hindrance because introduction of a substituent at the periphery of the organic conductor backbone has been reported to promote



Scheme 1. Schematic representation of the TEPB molecule.

intermolecular columnar stacking.^[43–46] Finally, the two unequal pyrimidine N atoms may allow different modes of coordination for structural diversity. In this paper we report on our initial results of the assembly of TEPB with CuI and CuCl₂, the Cu^I and Cu^{II} atoms being selected as metal centres because of their redox-active nature which might enhance metal–ligand electronic communication (e.g., MLCT or LMCT).

Results and Discussion

Synthesis and Characterization of TEPB

The synthetic procedure for TEPB was developed on the basis of our previous work on heterothione ligands.[47-49] As outlined in Scheme 2, the title organic molecule, TEPB, was prepared in three steps starting from 1,3,5-triacetylbenzene (P1). Aldol condensation of P1 with N,N-dimethylformamide dimethyl acetal almost quantitatively produced the intermediate P2. Under basic conditions, the reaction of P2 with thiourea furnished P3 bearing three pyrimidinylthiol groups, which was ethylated with EtI as the alkylating agent in the presence of sodium methoxide to give TEPB. The molecular structure of TEPB was characterized by spectroscopic methods and confirmed by microanalysis techniques. The ¹H NMR spectrum of TEPB in CDCl₃ shows a singlet of the central phenyl proton at $\delta = 8.93$ ppm (3 H), the pyrimidine units of TEPB give rise to two resonances at δ = 8.65 (d, J = 5.1 Hz, 3 H) and 7.52 ppm (d, J = 5.2 Hz, 3 H), and the ethyl groups of TEPB appear at δ = 3.30 (-CH₂-) and 1.51 ppm (CH₃). The observation of only one set of ¹H NMR signals for TEPB suggests that the rotation of pyrimidine units with respect to the central phenyl ring occurs faster in solution than the NMR timescale.



Reaction conditions: (i) DMF, reflux; (ii) Na/EtOH, reflux ; (iii) Na/MeOH, r.t

Scheme 2. Synthesis of TEPB.

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Note that the TEPB molecule is intrinsically chiral according to the definition of chirality, and should exhibit planar chirality with the central phenyl ring as its chiral plane. Nevertheless, it should remain racemic in solution as isomerization occurs easily by the so-called Kurland flip mechanism.^[50] Indeed, a solution of TEPB in ethyl acetate shows no optical rotation. Interestingly, single-crystal X-ray diffraction analysis showed that the crystallized TEPB forms in the chiral space group P65 with a flack parameter of 0.0(2), which indicates that crystallization of TEPB leads to spontaneous resolution of its racemate. As shown in Figure 1, the TEPB molecule has three identical 2-ethylthiopyrimidin-4-yl functional groups coupled through C-C bonds to the central phenyl ring at its 1-, 3- and 5-positions, and are arranged clockwise in terms of space orientation of three S-C(ethyl) bonds around the central phenyl ring. As we expected, there exist intramolecular C-H···N hydrogen bonds (C22-H22A···N2, C20-H20A···N4 and C24-H24A...N6) between the central phenyl ring and the three pyrimidinyl rings leading to small dihedral angles (9.87, 14.51 and 1.68°). As a consequence, the TEPB molecule exhibits a quasi-planar conformation with four rings almost in the same plane.



Figure 1. Molecular structure of TEPB with the numbering of the selected atoms (the central phenyl plane is highlighted in pink and the C–H···N hydrogen bonds are denoted with a green dotted line).

In its solid-state packing, the TEPB molecules are linked through C–H···S interactions into a 2D sheet-like network parallel to the *ab* plane (see Figure S1 in the Supporting Information). All the 2D sheets are packed one above another with equivalent interplanar spacings of 3.830 Å (see Figure S2 in the Supporting Information). Each TEPB molecule in one sheet is stacked over another TEPB molecule from the adjacent sheet in an offset manner such that aromatic π – π interactions can be observed between the central phenyl ring and pyrimidinyl rings.

Synthesis and Characterization of 1 and 2

The assembly of TEPB with CuI in the ternary solvent system $CH_3CN/H_2O/CH_2Cl_2$ by a layering method produced orange block crystals of **1**. The presence of the water buffer layer is important for the growth of single crystals because the binary solvent system CH_3CN/CH_2Cl_2 gives

only a microcrystalline powder. It is assumed that the water slows the rate of reaction between TEPB and CuI, which assists single-crystal growth. Dark-green plate-like crystals of **2** were readily obtained from the binary diffusion system EtOH/CH₂Cl₂ in which an EtOH solution of CuCl₂ was layered over a CH₂Cl₂ solution of TEPB. Compounds **1** and **2** are insoluble in common solvents, which precludes further solution characterization. The phase purity of **1** and **2** was confirmed by comparing their simulated and experimental PXRD patterns (see Figure S3 in the Supporting Information).

Crystal Structure of 1

Assembly 1 crystallizes in the monoclinic crystal system and C2/c space group. As shown in Figure 2, assembly 1 has a one-dimensional (1D) chain structure with alternate linking of the Cu₄I₄ cluster and TEPB molecule pairs. Each Cu_4I_4 cluster comprises four copper atoms, two μ -4 I atoms and two µ-2 I atoms, all being related by a local symmetric centre. Specifically, four copper atoms are organized into a planar square with the two Cu-Cu lengths being 2.438 Å and 3.204 Å. The two μ -4 I atoms are located above and below the plane defined by Cu₄ with Cu–I distances ranging from 2.773 to 2.838 Å. In contrast, the two μ -2 I atoms are coplanar with the Cu₄ plane and situated near the short sides of the Cu₄ square with Cu-I bond lengths of 2.590 and 2.643 Å. In the coordination chain of 1, each Cu_4I_4 cluster serves as a four-connecting inorganic node because each tetrahedral Cu atom has only one coordination site available. However, the coordination directions of the four Cu atoms are almost parallel due to their square-planar arrangement, which limits the structural dimension of 1. Alongside the coordination chain of 1, adjoining Cu_4I_4 clusters are spaced by a pair of TEPB molecules through four Cu-N coordination bonds, with a mean Cu-N distance of 1.983 Å, and the N-Cu-Cu linkage is approximately linear. Also, the Cu₄I₄ clusters are orientated in such a way that the Cu₄ planes from two neighbouring Cu₄I₄ clusters are tilted towards each other with a dihedral angle of 76.64°. A single TEPB molecule behaves as a bis(mono-



Figure 2. One-dimensional chain structure of **1** (I atom: purple ball; Cu atom: yellow ball).



dentate) bridging ligand with one 2-ethylthiopyrimidinyl (EP) unit free of coordination, which also accounts for the low dimension of **1**. The ethylthiol S atoms of TEPB are not involved in metal coordination, the mean Cu–S distance of about 3.122 Å being far beyond the sum of the covalent radii of copper(I) and S (2.39 Å). The two TEPB molecules between two Cu₄I₄ clusters are stacked in a slipped face-to-face fashion and close aromatic π - π interactions are observed, as manifested by short centroid-to-centroid distances ranging from 3.439 to 3.581 Å (Figure S4 in the Supporting Information). In particular, the two chiral TEPB molecules in one pair display the same absolute configuration, but the neighbouring pairs are totally opposite in configuration. Therefore the whole coordination chain is essentially achiral.

The alignment of Cu_4I_4 clusters is almost linear in the chains of 1, whereas the TEPB molecule pairs are in a zigzag arrangement. Similarly to the free TEPB molecule, the coordinated TEPB molecules in 1 retain a nearly planar conformation due to intramolecular C–H···N hydrogen bonds, the corresponding dihedral angles varying from 7.06 to 14.85°. In summary, 1 might be viewed as a one-dimensional zig-zag double-decked chain constructed from quasiplanar TEPB molecules and Cu_4I_4 clusters. In the crystal packing of 1 (Figure 3), chains interact side-by-side through



Figure 3. Chains of 1 interacting through S····S contacts (red dotted line).

S···S contacts ($d_{\text{S···S}} = 3.680$ Å) to form a 2D sheet. The 2D sheets are overlain with an equal interplanar spacing of around 6.964 Å, with the chains in each layer displaced with respect to those in adjacent layers (see Figure S5 in the Supporting Information).

Crystal Structure of 2

Assembly 2 crystallizes in the same crystal system and space group as 1. As depicted in Figure 4, 2 also exhibits a 1D chain structure constructed from alternately linking single molecules of TEPB and the CuCl₂ inorganic component. The copper(II) atom in 2 is four-coordinate rather than a typical five- or six-coordinate structure and adopts a distorted square-planar geometry that is completed by two N atoms from two TEPB molecules and two chlorine atoms. The Cu-N bond lengths are identical [Cu1-N1: 2.012(3) Å, Cu1-N3: 2.011(3) Å], and the Cu-Cl bond lengths are almost equal [Cu1–Cl1: 2.220(1) Å, Cu1–Cl2: 2.230(1) Å]. The bond angles for N1-Cu1-N3 and Cl1-Cu1–Cl2 are 161.5(1) and 160.08(6)°, respectively. Similarly to 1, the TEPB molecule in 2 also acts as a bridging ligand in a bis(monodentate) coordination mode leaving one EP unit unbound. The distance between the sulfur atom in each coordinating EP unit and the copper(II) atom (Cu1-S1: 3.104 Å, Cu1–S2: 3.214 Å) is much longer than the sum of the covalent radii of the Cu^{II} and S atoms (2.34 Å), which suggests the absence of Cu-S interactions. Distinctive from 1, one EP unit in the TEPB molecule in 2 flips from one side to the other, thereby changing its molecular shape from a three-bladed propeller to an "m" shape. Despite its variation in shape, the TEPB molecule retains its chiral nature. Alongside the chain of 2, molecules of TEPB with opposite configurations are positioned sequentially in a broad Z shape just like the alignment of the copper(II) atoms. Notably, with the assistance of intramolecular C-H…N hydrogen bonds, the TEPB molecules in 2 exhibit a more rigid planar conformation with smaller dihedral angles (2.78, 5.48 and 4.55°) than 1. Moreover, all Cu^{II} atoms and TEPB molecules lie approximately in the same plane, showing a one-dimensional flat zig-zag coordination chain structure motif.



Figure 4. One-dimensional chain structure of 2.

In the crystal packing of **2**, the chains associate through C–H···S ($d_{\text{H···S}} = 2.748$ Å) interactions to form a 2D sheetlike network (Figure 5). However, the shortest S···S separation is 4.627 Å between two neighbouring chains in the same layer. The layers are parallel to each other and further stacked with an interplanar spacing of 6.940 Å, with every chain in one layer also displaced with respect to that in the neighbouring layer. Note that water molecules in one layer form O–H···Cl hydrogen bonds with the Cl atoms from adjacent layers, and thus parallel layers assemble to form a 3D hydrogen-bonded supramolecular architecture (see Figure S6 in the Supporting Information).



Figure 5. Interchain interactions of **2** through C–H···S contacts (shown by red dotted lines).

Spectroscopic Properties

Figure 6 depicts the absorption spectra of 1 and 2. Assembly 1 shows a broad absorption in the visible region, the peaks at around 230 and 382 nm arising from a transition in the ligand itself, and the shoulder peak at around 466 nm has been attributed to metal-to-ligand charge transfer (MLCT). In contrast, assembly 2 displays a strong absorption at around 611 nm as well as two ligand-based absorption peaks at 222 and 346 nm. The absorption maximum at 611 nm has been ascribed to the d-electron transition in the copper(II) ion in 2, which might be enhanced by mixing of the d orbitals of the copper(II) ion and the HOMOs of the TEPB ligands. By using the equation $E_g = 1240/\lambda$ (absorp-



Figure 6. UV/Vis absorption spectra of 1 and 2 in the solid state [the absorption edge corresponds to the intersection point between the baseline along the wavelength axis and a line (dotted line) extrapolated from the linear portion of the threshold.].

tion edge),^[51] the HOMO–LUMO gaps (E_g = band gaps) of **1** and **2** were estimated from their absorption edges to be 1.93 and 1.11 eV, respectively. The HOMO–LUMO gap of **2** is comparable to the band gap of the Si semi-conductor (1.11 eV at 300 K). In comparison with **1**, a narrow HOMO–LUMO gap is observed in **2**, which may be attributed to 1) a low-energy d-electron transition in the copper(II) ion and 2) the more planar geometry of TEPB in **2** maximizing π -electron delocalization.

Conductive Properties

The conducting properties were studied by complex impedance spectroscopy $[Z^* = Z' - jZ'']$, in which $j = (-1)^{1/2}$, which gives the conductive properties of bulk materials as a function of temperature and frequency. The impedance measurements were conducted on pressed powder pellet samples sandwiched by a square brass electrode $(10.2 \times 10.2 \text{ mm}^2)$; the thicknesses of the pellet samples of 1 and 2 were 0.32 and 0.30 mm, respectively. ZView software was used to fit the experimental impedance data in the frequency range of 100 Hz-10 MHz to obtain bulk conductivity, which applies the least-squares fitting method to the equivalent model.^[52] In this case, the equivalent circuit comprises three resistances (R1, R2 and R3), two capacitances (C1 and C2) and one constant phase element (CPE3), with the R1-C1, R2-C2 and R3-CPE3 parallel circuits representing the resistances and capacitances corresponding to the bulk sample, grain boundary and electrode interfaces, respectively.^[53-55] The conductivities were calculated by using the equation $\sigma = 1/R 1 \times d/S$, in which d is the thickness of the pellet sample and S is the electrode area.

First, we examined the direct-current (d.c.) conductivities of 1 and 2 at room temperature (see Figure S7 in the Supporting Information). It was found that 1 behaves as an insulator with a conductivity of $2.84 \times 10^{-12} \, \mathrm{S \, cm^{-1}}$ whereas 2 exhibits a conductivity of $2.42 \times 10^{-10} \, \mathrm{S \, cm^{-1}}$ at room temperature. The higher d.c. conductivity of 2 compared with 1 agrees with its smaller band gap. According to the initial d.c. conductivity data, we also scrutinized the temperature dependence of the conductivity of 2 through the complex impedance technique. Figure 7 (a) shows the plots of Z'versus Z'' (Nyquist diagram) over a wide range of frequencies at different temperatures; the Nyquist plots present semi-circular arcs, the diameters of which increase with increasing temperature. Processed by using the ZView software, the conductivity-temperature (σ -1/T) profile was obtained, as shown in Figure 7 (b). Assembly 2 exhibits a.c. (a.c. = alternating current) conductivity of $5.90 \times 10^{-9} \,\mathrm{S \, cm^{-1}}$ at room temperature, which is one order of magnitude higher than its d.c. conductivity. Moreover, it was also observed that its a.c. conductivity decreases almost linearly with increasing temperature.

Although 1 and 2 exhibit similar assembly hierarchies, both being from 1D chain through 2D layer to 3D architecture, the distinctive difference between them is that the 2D layer stacking in 2 is largely a result of O–H···Cl hydrogen



Figure 7. a) Complex impedance Z'-Z'' plot for 2; b) temperaturedependence of the a.c. conductivity of 2 (inset: equivalent circuit model for 2; red line represents the linear fit).

bonding between free water molecules and coordinating chlorine atoms. It is known that the a.c. conductivity obtained by the complex impedance technique includes both electrical and ionic contributions.^[56,57] On the basis of their structures, the free water molecules in 2 may contribute to the whole conductivity of 2 through a proton-conduction mechanism. By comparing its d.c. and a.c. conductivities, it is apparent that the a.c. conductivity of 2 is dominated by proton conduction, which should rely on the free water molecules and the O-H···Cl hydrogen-bonding network. The exact explanation for the decrease in the a.c. conductivity of 2 with increasing temperature remains to be explored, but one possible reason is that increasing temperature may destroy the temperature-sensitive O-H···Cl hydrogen-bonding network resulting in a drop in conductivity because thermal gravimetric analysis (TGA) has shown that 2 loses its water molecules in the temperature range of 40-100 °C (see Figure S8 in the Supporting Information).

Conclusions

In this work we have synthesized a new organic building block, TEPB, which contains three 2-ethylthio-substituted pyrimidine groups and shows a quasi-planar conformation even when coordinated to metal ions due to intramolecular C-H···N hydrogen bonds. The assembly of TEPB with CuI and CuCl₂ led to two flat coordination chains, **1** and **2**, respectively, both of which exhibit analogous assembly hierarchies from 1D chain through 2D layer to 3D architecture. It has been found that strong S···S and C-H···S contacts in 1 and 2, respectively link the chains to form 2D layers. Moreover, the stacking of 2D layers in 2 is reinforced through O-H···Cl hydrogen-bonding interactions involving free water molecules and coordinated chlorine atoms. The d.c. conductivity of 2 is almost 100 times greater than that of 1, which might be ascribed to its smaller band gap. Moreover, it was found that the a.c. conductivity of 2 arises mainly from proton conductivity as a result of free water molecules and the O-H···Cl hydrogen-bonding network. Furthermore, the results of this study also indicate that the electrical conductivities of 1 and 2 are still fairly low despite the presence of a quasi-planar organic synthon and extensive S…S (for 1) or C-H…S contacts (for 2), and are more likely limited by the lack of effective π -orbital stacking between 2D layers in 1 and 2. This issue is currently being investigated by our group.

Experimental Section

Materials and Measurements: All solvents and reagents of analytical grade were used as received without prior purification. 1,3,5-Triacetylbenzene (P1) was synthesized according to a literature method.^[58] IR spectra were recorded with a Thermo Scientific Nicolet 5700 FT-IR spectrophotometer with KBr pellets in the 400–4000 cm⁻¹ region. ¹H NMR spectra were recorded with a Bruker AVANCE-500 spectrometer. Electrospray ionization (ESI) mass spectra were recorded with a Finnigan MAT SSQ 710 mass spectrometer in the scan range 100–1200 amu. The solid-state UV/ Vis absorption spectra were recorded with a Shimadzu UV-2450 UV/Vis spectrophotometer. Electrochemical impedance spectra (EIS) were recorded with a CHI660D (Chenghua, Shanghai) electrochemistry workstation with an applied frequency range of 100 kHz to 1 Hz and an oscillation voltage of 100 mV.

Synthesis of P2: A mixture of P1 (1.22 g, 6.0 mmol) and *N*,*N*-dimethylformamide dimethyl acetal (2.86 g, 24.0 mmol) was stirred whilst heating under a gentle reflux for 10 h. After cooling to room temperature, the reaction solution was evaporated under vacuum to dryness. The resulting solid was triturated with diethyl ether, filtered and dried under vacuum to afford P2 as a yellow powder, yield 1.8 g, 81.1%. IR (KBr): $\tilde{v} = 2915$ (w), 2804 (w), 1634 (vs), 1593 (vs), 1543 (vs), 1414 (s), 1358 (m), 1277 (s), 1227 (m), 1196 (m), 1118 (s), 1085 (m), 977 (w), 946 (w), 850 (w), 777 (w), 693 (m) cm⁻¹. ¹H NMR (CDCl₃, 25 °C): $\delta = 8.53$ (s, 3 H), 7.82 (d, J = 12.3 Hz, 3 H), 5.86 (d, J = 12.3 Hz, 3 H), 3.16 (s, 9 H), 2.95 (s, 9 H) ppm. C₂₁H₂₇N₃O₃ (369.46): calcd. C 68.27, H 7.37, N 11.37; found C, 68.39, H 7.56, N 11.56.

Synthesis of P3: Sodium metal (0.78 g, 34.0 mmol) was added portionwise to stirred anhydrous EtOH (50 mL) at room temperature. Upon disappearance of the sodium metal, P2 (1.11 g, 3.0 mmol) and thiourea (0.72 g, 9.5 mmol) were added in sequence to the solution, which was then heated at reflux for 12 h. After complete reaction, the reaction solution was poured into water (100 mL) and neutralized with 5% diluted HCl solution to pH 6–7. The precipitated orange yellow solid (P3) was collected by suction filtration and dried under vacuum at 40 °C overnight, yield 1.1 g, 89.4%. IR (KBr): $\tilde{v} = 3074$ (w), 2988 (w), 2921 (w), 1595 (s), 1562 (m), 1483 (w), 1439 (w), 1377 (w), 1247 (m), 1205 (w), 1163 (m), 976 (w), 794 (w), 724 (w) cm⁻¹. ¹H NMR ([D₆]DMSO, 25 °C): $\delta = 13.05$ (br., 3 H, SH), 8.99 (s, 3 H), 8.20 (d, J = 6.5 Hz, 3 H), 7.69 (d, J = 6.6 Hz,



3 H) ppm. C₁₈H₁₂N₆S₃ (408.51): calcd. C 52.92, H 2.96, N 20.57;

found C 52.89, H 2.76, N 20.86.

Synthesis of TEPB: Sodium metal (1.04 g, 45.0 mmol) was dissolved in anhydrous EtOH (30 mL) at room temperature to give a clear colourless solution. P3 (1.02 g, 2.5 mmol) was then added and the mixture stirred for 30 min to form a cloudy solution. Upon addition of EtI (14.0 g, 90.0 mmol), the resulting solution was stirred at room temperature for a further 24 h. The reaction was quenched by the addition of water (100 mL). The resultant precipitate was filtered and washed thoroughly with water. Upon decolourization with active carbon in CHCl₃, the final product TEPB was afforded as a pale-yellow solid. Single crystals of TEPB suitable for X-ray diffraction were obtained by slow diffusion of MeOH into its solution of CH_2Cl_2 , yield 0.6 g, 49.2%. IR (KBr): $\tilde{v} = 3079$ (w), 2971 (w), 2928 (w), 2868 (w), 1544 (s), 1448 (m), 1400 (m), 1343 (m), 1264 (w), 1200 (m), 1183 (m), 899 (w), 824 (m), 772 (w), 733 (m), 681 (w), 630 (m) cm⁻¹. ¹H NMR (CDCl₃, 25 °C): δ = 8.93 (s, 3 H), 8.66 (d, J = 5.1 Hz, 3 H), 7.52 (d, J = 5.2 Hz, 3 H), 3.30 (t, 6 H), 1.51 (t, 9 H) ppm. MS (ESI): m/z (%) = 493 (100) $[M + H]^+$. $C_{24}H_{24}N_6S_3$ (492.67): calcd. C 58.51, H 4.91, N 17.06; found C 58.62, H 4.96, N 17.26.

Preparation of 1: A CH₃CN solution (3.0 mL) containing CuI (0.06 mmol) was carefully layered above a CH2Cl2 solution (3.0 mL) of TEPB (0.02 mmol), with H₂O (5.0 mL) as a buffer layer being placed between them. Crystals of $\{[(C_{24}H_{24}N_6S_3)Cu_2I_2]\cdot$ CH_3CN_{n} (1) were formed over a period of 1 month. A single crystal suitable for X-ray diffraction analysis was selected from the bulk crystals.

1: Yield: 43.6% (based on TEPB). IR (KBr): $\tilde{v} = 3510$ (w), 3074 (w), 2962 (w), 2924 (w), 2363 (w), 1561 (s), 1449 (w), 1392 (m), 1338 (m), 1269 (w), 1203 (m), 1178 (m), 1119 (w), 821 (m), 732 (w), 635 (w) cm⁻¹. C₂₆H₂₇Cu₂I₂N₇S₃ (914.63): calcd. C 34.14, H 2.98, N 10.72; found C 34.25, H 2.80, N 10.78.

Preparation of 2: An EtOH solution (5.0 mL) containing CuCl₂·2H₂O (0.08 mmol) was carefully layered above a CH₂Cl₂ solution (5.0 mL) of TEPB (0.02 mmol). Crystals of $\{[(C_{24}H_{24}N_6S_3)CuCl_2] \cdot H_2O\}_n$ (2) were formed over a period of 1 week. A single crystal suitable for X-ray diffraction analysis was selected from the bulk crystals.

2: Yield: 53.5% (based on TEPB). IR (KBr): $\tilde{v} = 3593$ (w), 3507 (w), 3074 (w), 2930 (w), 2359 (w), 1567 (s), 1454 (m), 1420 (m), 1343 (m), 1365 (m), 1330 (m), 1260 (w), 1206 (m), 1181 (w), 828 (m), 799 (w), 771 (w), 732 (w), 691 (w), 649 (w), 638 (w) cm⁻¹. C₂₄H₂₆Cl₂CuN₆OS₃ (645.14): calcd. C 44.68, H 4.06, N 13.03; found C 44.72, H 4.12, N 13.38.

X-ray Crystallography: Diffraction intensity data for TEPB, 1 and 2 were collected at 298(2) K with a Bruker SMART CCD-4K diffractometer by employing graphite-monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å). The data were collected by using SMART and reduced by using the SAINT program.^[59] All the structures were solved by direct methods and refined by full-matrix leastsquares methods on F_{obs}^2 using the SHELXTL software package.^[60] Graphics for TEPB, 1 and 2 were generated by using MER-CURY 3.0.[61] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated by geometrical methods and refined as a riding model. The crystallographic data for TEPB, 1 and 2 are presented in Table 1.

CCDC-959773 (for TEPB), -959774 (for 1) and -959775 (for 2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for TEPB, 1 and 2.

	TEPB	1	2
Formula	$C_{24}H_{24}N_6S_3$	C ₂₆ H ₂₇ Cu ₂ I ₂ N ₇ S ₃	C24H26Cl2CuN6OS3
$M_{ m r}$	492.00	914.66	645.17
Crystal system	hexagonal	monoclinic	monoclinic
Space group	P65 (No.170)	C2/c (No. 15)	C2/c (No. 15)
a [Å]	13.6450(8)	31.272(1)	27.172(4)
b [Å]	13.6450(8)	14.5238(4)	14.924(2)
c [Å]	22.236(3)	14.0363(4)	14.398(2)
a [°]	90	90	90
β [°]	90	106.613(4)	105.306(2)
γ [°]	120	90	90
V [Å ³]	3585.4(3)	6109.0(3)	5632(1)
Z	6	8	8
$D_{\rm calc} [{ m gcm^{-3}}]$	1.369	1.989	1.522
F(000)	1548	3552	2648
Reflections collected	25515	17812	22912
Unique	4065	5380	2793
reflections			
R(int)	0.041	0.025	0.041
<i>R</i> 1, <i>wR</i> 2	0.0645,	0.0312,	0.0440,
$[I > 2\sigma(I)]$	0.1455	0.0737	0.1322
R1, wR2	0.0813,	0.0377,	0.0662,
(all data)	0.1577	0.0766	0.1454
GOF	1.03	1.00	1.01

Supporting Information (see footnote on the first page of this article): Packing structure graphics for TEPB and two coordination compounds, PXRD characterization of 1 and 2, I-V plots of 1 and 2, TGA data of 2.

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