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Assembling Isomeric heterocyclic disulfide ligands with copper(I) iodide: effect of ligand structure on their assembly structures and S–S reactivity

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Self-assembly of two isomeric heterocyclic disulfide ligands, **n-ppds** (**n-ppds** = di[n-(pyridin-2-yl) pyrimidinyl]disulfide, $n = 3, 4$), with copper(I) iodide in acetonitrile/toluene produced different assembled structures and S–S reactivity, exhibiting profound influence of disulfide structure. For **3-ppds**, a 2D layered structure **1** based on [CuI(**3-ppds**)]$_2$ was obtained. Homolytic cleavage of the S–S bond occurred in **4-ppds**, resulting in a 1D staircase double-chain structure **2**. **1** and **2** have been characterized by single-crystal X-ray diffraction; solid-state diffuse-reflectance UV–vis spectra show that **1** and **2** are semiconductors with band gaps of 2.88 and 2.16 eV, respectively.

Keywords: Heterocyclic disulfide; S–S bond cleavage; Copper iodide; Crystal structure; Band gap

1. Introduction

Heterocyclic disulfide ligands, e.g. 4-dpds and 2-dpds (4-dpds=di(4-pyridyl)disulfide, 2-dpds=di(2-pyridyl)disulfide), have received interest stemming from structural characteristics (e.g. axial chirality and semi-rigid conformation) [1–3] and also *in situ* transformations of disulfide (S–S) bond [4,5]. In the latter regard, thio(thione)-disulfide interconversion, for instance, have found applications in generation of dynamic combinatorial libraries and self-replicating systems [6–9]. Heterocyclic disulfides can exhibit various *in situ* changes pertinent to labile S–S bond, such as *in situ* S–S reductive cleavage [10,11], oxidative scission of S–S [12] and insertion reactions of S–S bonds [13–15]. There is growing interest in exploring *in situ* metal/heterocyclic disulfide reactions that take advantage of the reactivity of disulfide function, in the hope of establishing new reactions [16] or constructing functional materials (e.g. electrically conductive materials), etc. [5,17,18]. Though mechanisms involved in *in situ* disulfide transformations remain an enigma [19,20], *in situ* S–S reactions of heterocyclic disulfides have close dependence on the metal salts used [4]. We have demonstrated variable *in situ* transformations of **2-ppds** (**2-ppds**=di[2-(pyridin-2-yl)pyrimidinyl]disulfide) promoted by different metal salts, further proving the critical role of metal salt [16,21,22].

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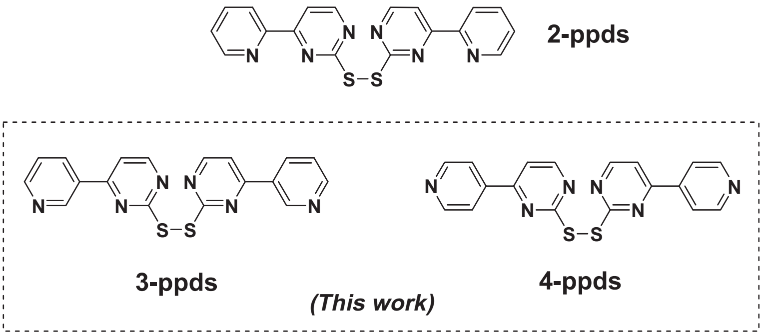

Chart 1. Schematic illustration of **n-ppds** ($n = 2, 3, 4$).

Despite interest in disulfide chemistry, the influence of disulfide structure seems rarely covered in assembly chemistry or *in situ* S–S reactions. Disulfide structure has a remarkable impact on assembly chemistry as exemplified by heterocyclic disulfide isomers, **n-ppds** ($n = 2, 3, 4$), that merely differ in the nitrogen position in the pyridine (chart 1). **2-ppds** readily undergoes metal-mediated *in situ* S–S bond reactions [16,21,22] while both **3-ppds** and **4-ppds** generally are semi-rigid bridging linkers like 4-dpds [23–25]. Here, we report solution assembly of two isomeric disulfides, viz. **3-ppds** and **4-ppds**, with copper(I) iodide, underlining the influence of disulfide structure on assembly structures and S–S reactivity.

2. Experimental

2.1. *Materials and measurements*

All solvents and reagents of analytical grade were used as received. **3-ppds** and **4-ppds** were synthesized according to our reported method [23–25]. Infrared spectra were performed on a Bruker Vector 22 spectrophotometer with KBr pellets at 400–4000 cm^{-1}. Solid-state diffuse-reflectance UV–vis spectra were obtained on a Shimadzu UV/VIS MPC-3100 spectrometer.

2.2. *Synthesis*

2.2.1. General procedure. An acetonitrile solution (5 mL) of CuI (0.2 mmol) was layered above a toluene solution (5 mL) of **n-ppds** ($n = 3$ or 4) (0.1 mmol). In general, bulk crystals were generated in 2–3 weeks. Diffraction quality crystals were selected from the resulting crystals.

Compound **1**: Yield, 58.5% (based on **3-ppds**). IR (KBr, cm^{-1}) 3066 w, 1594 w, 1566 s (aromatic ring stretch), 1539 s (aromatic ring stretch), 1459 s (aromatic ring stretch), 1445 w, 1398 m, 1331 s, 1205 m (aromatic C–H stretch), 1183 m (aromatic C–H stretch), 1102 w (aromatic C–H stretch), 850 w, 826 w, 793 m, 762 m, 710 w, 653 w (C–S stretch). Anal. Calcd for $C_{18}H_{12}CuIN_6S_2$: C, 38.14; H, 2.13; N, 14.82%. Found: C, 38.22; H, 2.14; N, 14.80%.

Compound **2**: Yield, 62.4% (based on **4-ppds**). IR (KBr, cm^{-1}) 3448 s, 1637 m (aromatic ring stretch), 1565 m (aromatic ring stretch), 1529 m (aromatic ring stretch), 1498 w, 1424 m (aromatic ring stretch), 1408 m (aromatic ring stretch), 1185 m (aromatic C–H stretch), 1083 m (aromatic C–H stretch), 826 m, 766 w, 716 w (C–S stretch), 632 w. Anal. Calcd for $C_9H_7CuIN_3S$: C, 28.47; H, 1.86; N, 11.07%. Found: C, 28.42; H, 1.90; N, 11.12%.

2.3. *X-ray crystallography*

Diffraction intensities for **1** and **2** were collected at 298(2) K on a Bruker SMART CCD-4 K diffractometer employing graphite-monochromated Mo-*Kα* radiation (λ = 0.71073 Å). The data were collected using SMART and reduced by SAINT [26]. All structures were solved by direct methods and refined by full-matrix least squares on F^2_{obs} by using SHELXTL-PC software package [27]. All nonhydrogen atoms were refined anisotropically, whereas hydrogen atoms were calculated by geometrical methods and refined as a riding model. Crystallographic data for **1** and **2** are listed in table 1.

3. Results and discussion

Solution reactions of **3-ppds** and **4-ppds** with CuI in 1 : 2 molar ratio are schematically outlined in scheme 1. Single crystals suitable for X-ray diffraction analysis were obtained by a layering method, wherein an acetonitrile (upper layer)/toluene (lower layer) solvent system was used. For **3-ppds**, orange yellow block crystals of **1** were obtained and orange needle crystals of **2** for **4-ppds**. Both compounds are insoluble in common solvents and were structurally examined by X-ray crystallography.

Table 1. Crystallographic data for **1** and **2**.

Compound Formula	**1** $C_{18}H_{12}CuIN_6S_2$	**2** $C_9H_7CuIN_3S$
M_r	566.93	379.70
Crystal system	Monoclinic	Monoclinic
Space group	*P*21/*n* (No. 14)	*P*21/*c* (No. 14)
a (Å)	15.34(2)	4.1288(9)
b (Å)	8.152(8)	26.758(6)
c (Å)	16.71(2)	9.862(2)
α (°)	90	90
β	111.77(1)	95.177(4)
γ	90	90
V (Å^3)	1940(3)	1085.1(4)
Z	4	4
D_{calc} (g cm^{-3})	1.941	2.324
F(000)	1104	720
Reflns. collected	13,437	6720
Unique reflns.	3555	2537
$R_1[I > 2\sigma(I)]$	0.0279	0.0371
$wR_2[I > 2\sigma(I)]$	0.0558	0.1000
R_1 (all data)	0.0388	0.0517
wR_2 (all data)	0.0587	0.1059
GOF	1.03	1.07

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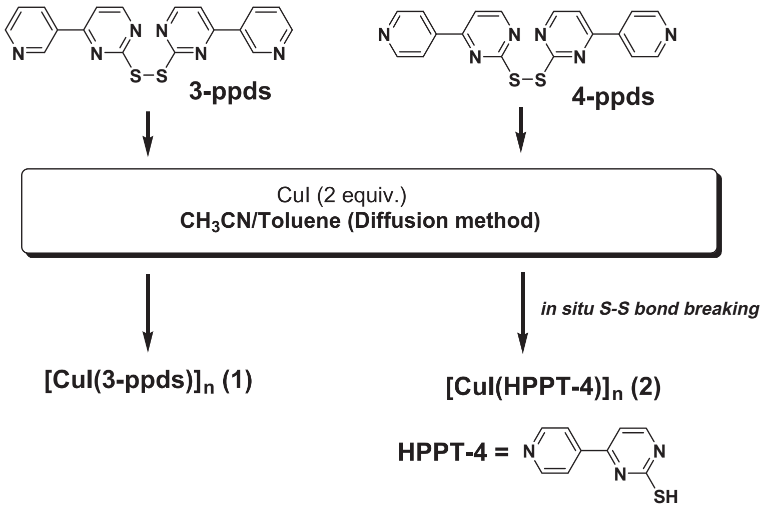

Scheme 1. Solution self-assembly of **n-ppds** ($n = 3, 4$) with CuI.

3.1. *Structure descriptions for 1 and 2*

Compound **1** crystallizes in the monoclinic crystal system and *P*21/*n* space group. As shown in figure 1, two **3-ppds** with opposite configurations (*P*- and *M*-configuration) join two individual CuI components in a bis(N-monodentate) fashion to form an achiral macrocyclic unit [CuI(**3-ppds**)]$_2$ (Cu1-I1, 2.640(2) Å; Cu1-N1, 2.053(3) Å; Cu1-N6, 2.079(3) Å) situated at the center of symmetry. Each macrocyclic unit is further linked to four neighboring ones via Cu–I bonding interactions (Cu1-I1A, 2.661(2) Å) to generate a two-dimensional (2D) network. As a result, each Cu in **1** is tetrahedral and each iodide is a μ-2 bridge. Cu–I bonding interactions also yield purely inorganic [CuI]$_n$ helical chains supported by racemic **3-ppds** ligands. The entire structure of **1** could be simplified as a 2D layered structure with binuclear macrocyclic [Cu$_2$(**3-ppds**)$_2$] as a four-connected node and I^- as a two-connected node (figure 2).

Single crystal X-ray diffraction analysis of **2** shows that **4-ppds** is converted into **HPPT-4** (**HPPT-4**=4-(pyridin-4-yl)pyrimidine-2-thiol) with S–S bond cleavage. Compound **2** crystallizes in the monoclinic system and *P*21/*c* space group with each asymmetric unit comprising one **HPPT-4**, one Cu, and one I^-. As depicted in figure 3, copper(I) iodide in **2** aggregates into a one-dimensional (1D) staircase double-chain [28,29], wherein each I^- is a μ-3 bridge linking three Cu ions with Cu–I bond distances varying from 2.6282(9) to 2.6922(9) Å. Such 1D staircase double-chain may also be viewed as linkage of two single zigzag (CuI)$_n$ chains via middle Cu–I rungs with adjoining Cu–Cu separations of 2.857(1) and 3.004(2) Å, respectively. The *in situ* generated **HPPT-4** coordinates to Cu through its terminal pyridine-N ($d_{\text{Cu-N}} = 2.047(4)$ Å) to fulfill the tetrahedral geometry of each Cu. Although all **HPPT-4** are parallel to each other and appended alternately above and below the staircase chain, there only exist very weak aromatic π–π interactions between adjacent **HPPT-4** ligands (centroid-to-centroid distance = 4.129(1) Å). Moreover, no aromatic stacking interactions are present amongst chains. The released thiol group is not involved in metal coordination despite the high affinity of soft metal ions (e.g. Cu^+ and Ag^+) for

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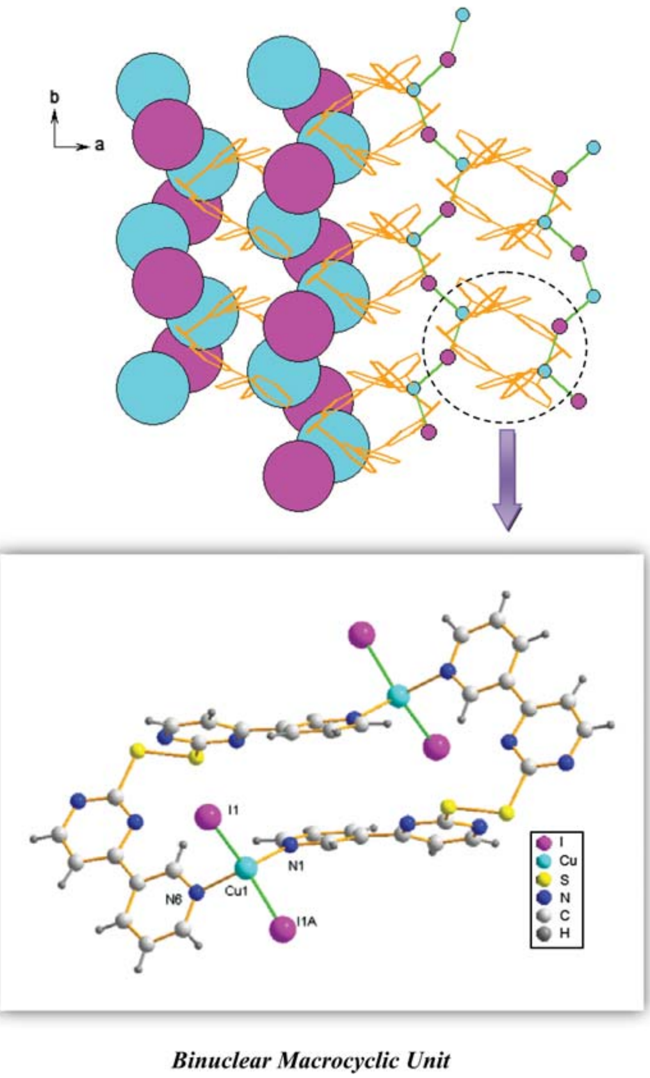

Figure 1. Purely inorganic $[CuI]_n$ helical chains (left, space-filling model) and binuclear macrocyclic unit (right, ball, and stick model) in **1**.

chalcogenide [30–32], but hydrogen bonded to aromatic hydrogen (C8–H8…S1: $d_{C8\ldots S1} = 3.755(7)$ Å). Conversion of **4-ppds** to **HPPT-4** occurred through reductive S–S cleavage. However, there is no evidence showing that Cu^{+} is a reducing agent in this process since solution color change characteristic of Cu^{2+} formation is not observed. I^{-} involved in this reductive process can also be ruled out because no iodine can be detected by potassium iodide-starch solution. Investigation on this reaction mechanism is currently ongoing in our laboratory. Such *in situ* S–S bond cleavage effected under mild conditions remains scarce since most examples of such transition have been reported from the hydro (solvo)thermal reactions.

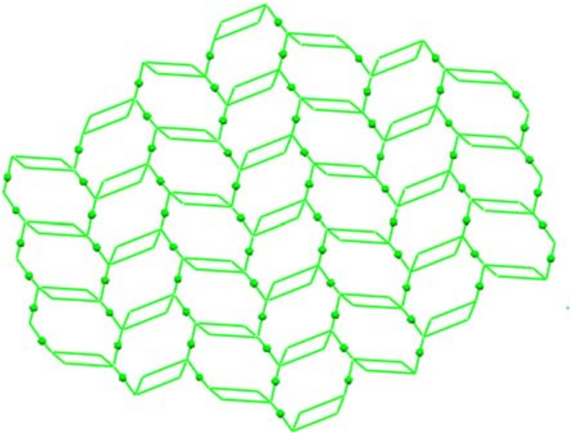

Figure 2. 2D layered structure of **1** (ball: I^-; rhomboid: $[Cu_2(\mathbf{3\text{-}ppds})_2]$).

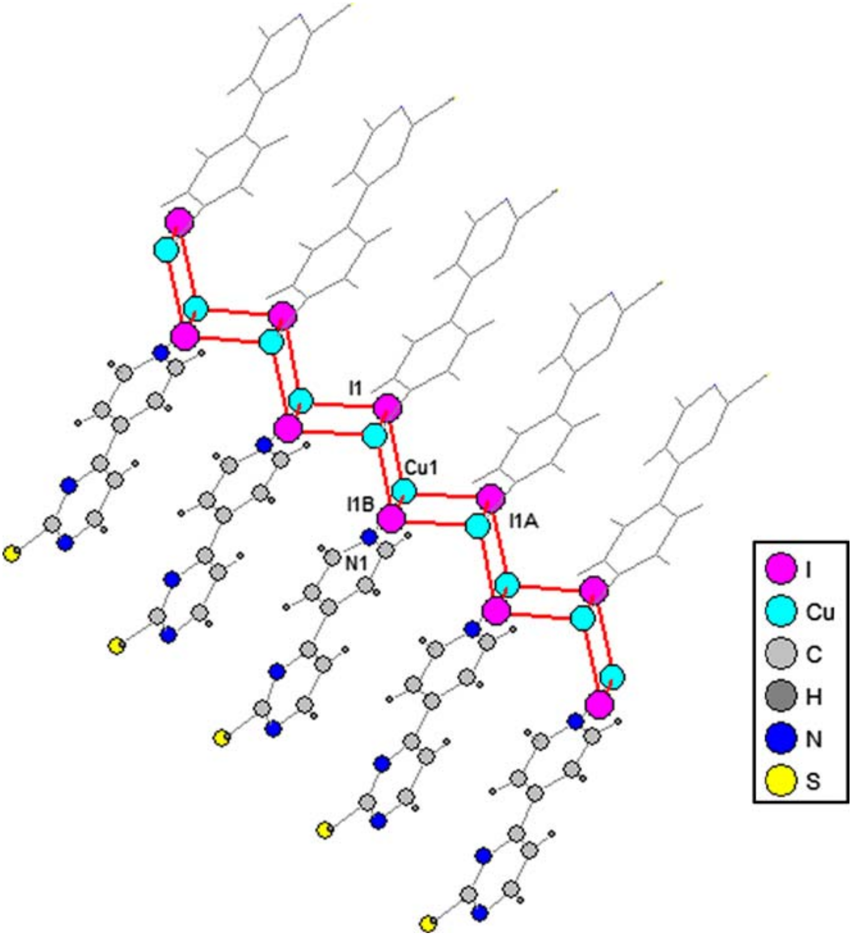

Figure 3. 1D staircase double-chain structure of **2**.

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3.2. *Photophysical properties of 1 and 2*

Copper(I) iodide has been employed in construction of electrically conductive coordination polymers with copper(I) iodide generally existing in a polymeric form [5,17,33,34]. In **1** and **2**, copper(I) iodide is present in the motif of 1D $[\mathrm{CuI}]_n$ helical chain and 1D $[\mathrm{Cu_2I_2}]_n$ staircase chain, respectively, which promotes us to investigate their potential conductive properties. Optical properties of **1** and **2** were examined by solid-state diffuse-reflectance UV–vis spectroscopy. Diffuse reflectance spectra of both compounds from 200 to 800 nm are depicted in figure 4 (inset, upper-left) as % reflectance vs. wavelength. For **1**, spectra exhibit a steadily decreasing reflectance corresponding to increasing absorption with decreasing incident wavelength from 800 nm down to 614 nm; at 614 nm, there is a sharper decrease in reflectance. For **2**, similar trend is also observed, wherein there is a steady reflectance decrease from 800 to 616 nm and a sharper decrease at 616 nm. There is almost total absorption of the incident light at 400 nm for both compounds. Diffuse-reflectance spectra of samples were further treated by Kubelka–Munk equation, $F(R) = (1-R)^2/2R$ [35] (figure 4). The optical band gaps obtained by intersection between the linear fit and the photon energy axis are estimated as 2.66 eV for **1** and 2.18 eV for **2**, both of which are lower than the value of the low temperature semiconductor γ-CuI (3.1 eV) [36]. Thereby, **1** and **2** may have application as semiconductor materials. As seen from the Kubelka–Munk treated spectra, absorption for **1** occurs at 466 nm (2.66 eV), whereas the starting absorption for **2** is red-shifted to 569 nm (2.18 eV). Furthermore, strong absorptions at 4.8 eV (259 nm) for **1** and at 4.15 eV (300 nm) for **2** may be related to $\pi-\pi^*$ transition and $n-\pi^*$ transition of the lone pairs of thiol.

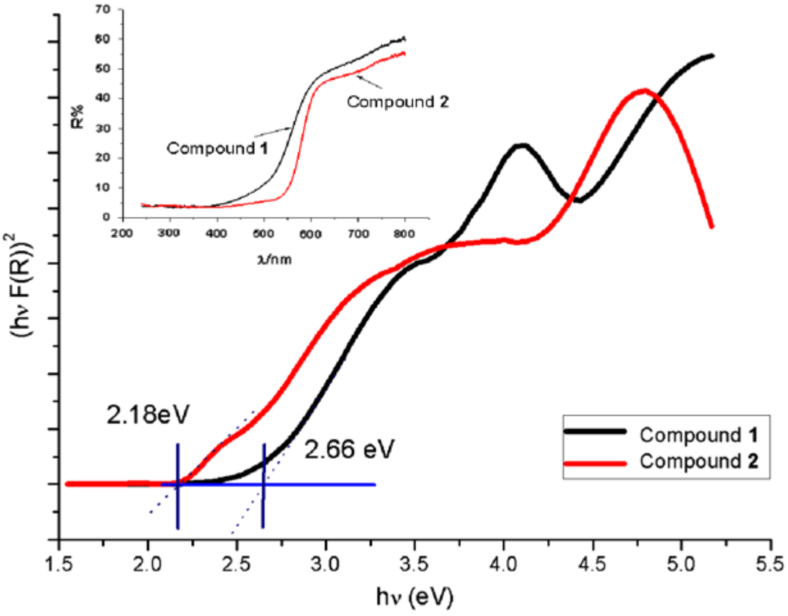

Figure 4. Kubelka–Munk transformed reflectance spectra of **1** and **2** (the original diffuse-reflectance spectra shown in the inset).

4. Conclusion

For heterocyclic disulfide, the examples described herein demonstrate the pronounced influence of disulfide structure on assembly structures and S–S reactivity. Under the same condition, a 2D layered structure with **3-ppds** was obtained with binuclear macrocycle unit [Cu_2(**3-ppds**)$_2$] as four-connected node and I^- as two-connected one. In sharp contrast, a 1D staircase double-chain structure resulted for **4-ppds**, wherein *in situ* homolytic S–S cleavage occurs.

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Supplementary material

CCDC 881172 and 832571 contain the supplementary crystallographic data for the structures of 1 and 2. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk).

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