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Unusual flexibility of 2,5-bis(4-pyridylethynyl)thiophene self-assembled with $Co(NCS)_2$ in a novel coordination polymer

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A novel coordination polymer containing $Co(NCS)_2$ and a rigid ligand, 2,5-bis(4-pyridylethynyl)-thiophene showing unusual flexibility was synthesized.

The self-assembly process is one of the most convenient and popular methodologies for the synthesis of intricate complexes favoured by humans and nature. One of the rare and interesting phenomena occurring during self-assembly is a conformational change of a building block, which may result in the increase of enthalpy of the building block. For example, compared to a rigid building block, a flexible building block with conformational freedom often shows a supramolecular isomerism by altering the geometry of the building block.[1] In other words, rigid building blocks are anticipated to retain their geometry and numerous target supramolecules based on fixed geometry have been designed and synthesized by crystal engineers. If conformational changes were to be found in a rigid building block in a self-assembly process, it would be a rare event.

Compared to linear ligands, bent ligands are relatively less frequently used as building blocks for coordination polymers due to the difficulty in predicting structure. However, there is a higher possibility of obtaining the unexpected, unpredictable, and interesting structure depending on the biting angle of chelation ligands. With this in mind, our research has been focused on the synthesis of novel coordination polymers using bent ligands.[2] During our continuous investigations on self-assembly with bent ligands, we surprisingly discovered the flexibility of a bent ligand, 2,5-bis(4-pyridylethynyl)thiophene, **L1**, which usually has a rigid geometry. Namely, it can act like a linear ligand by a conformational change resulting in the generation of a strain energy in the building block. We wish here to communicate our preliminary observation.

We synthesized **L1** by a method from the literature.[3] Recently it has been used as a building block for the synthesis of discrete metallocycles. The reaction between **L1** and $Re(CO)_5Br$ yielded a novel bimetallic or trimetallic complex.[4] We used **L1** as a building block in self-assembly with $Co(NCS)_2$ for the synthesis of novel coordination polymers. Slow diffusion of a methanolic solution of **L1** to aqueous $Co(NCS)_2$ over one week produced red crystals at the interface of the two layers.

The crystals showed high stability in air at room temperature and even after exposure to vacuum dryness. A single crystal X-ray analysis of the crystal revealed the formation of a supramolecular structure $[Co(NCS)_2(\mathbf{L1})_2]_\infty$ with the monoclinic space group $P2_1/c$.[5] Each cobalt atom is in an octahedral environment.

Surprisingly, the ligand **L1** shows two conformations, bent (red color) and linear forms (blue color) (Fig. 1). The bent conformation of **L1** was similar to a free bent ligand, but the other acts like a pseudo-linear ligand. This was an unexpected observation because **L1** is usually considered to be a bent rigid ligand. The biting angle of the bent form is 147° and that of the linear form is 173°. As expected, the linear form is longer than the bent form by 0.5 Å.

Recently, compounds having a deformed alkyne and aromaticity under highly deformed circumstance have attracted considerable research interest, both experimental and theoretical.[6] The triple bond in **L1** having a pseudo-linear geometry was deformed and the angles C1–C2–C3 and C2–C3–C4 are 172.6. and 172.5°, respectively (Fig. 1). It is noteworthy that, compared to other reported compounds synthesized by delicate strategies, the deformation of the triple bond in **L1** occurred spontaneously by coordination of cobalt ions during the self-assembly process.

We were curious as to what extent the pseudo-linear ligand possesses a strain energy. In order to quantify this, we performed a calculation of the strain-energy varying the **a** angle of the ligand from 120 to 136° (Fig. 2).

In a free ligand, the calculated **a** angle is 121.9°.[7] Full geometry optimizations were performed with the GAMESS program. Lee, Yang, and Parr's (LYP)[2] correlation functional, and Becke's three-parameter hybrid (B3)[3] exchange functionals were used for the gradient-corrected exchange-correlation functionals. All calculations were conducted with the 6-31G(d) basis sets. The strain energy in the linear ligand is 11 kcal mol^{-1}, which is 1.8 times the total strain energy of cyclopentane. This means that the coordination of the cobalt to a nitrogen in the pyridine ring which plays a role in sustaining the crystal lattice can result in withstanding the strain energy.

The two geometries of ligand **L1**, bent and linear, play a characteristic role in the construction of the supramolecular

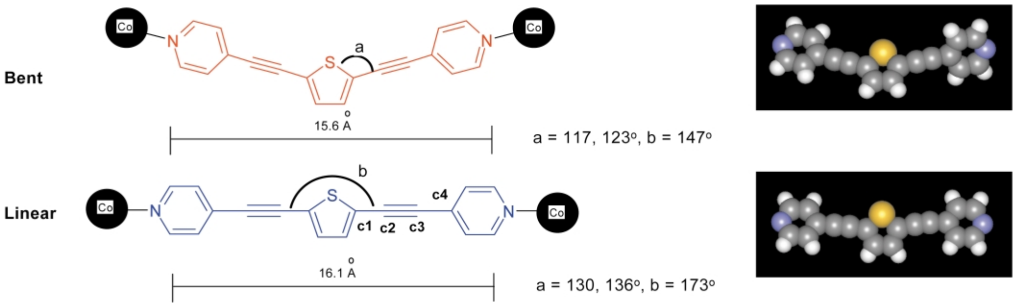

Fig. 1 Two forms of 2,5-bis(4-pyridylethynyl)thiophene, **L1**.

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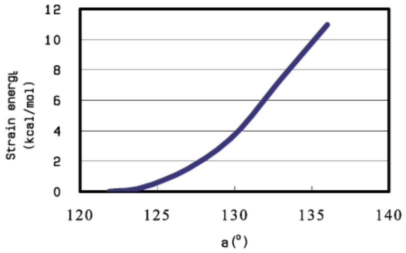

Fig. 2 Calculated strain energies depending on the angle **a**.

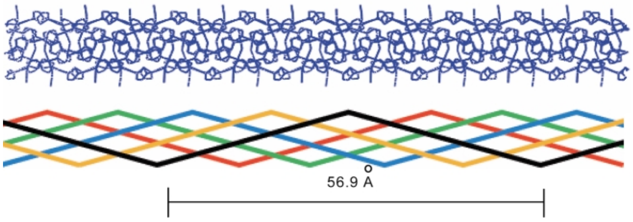

Fig. 4 A 5-fold 2D interwoven structure.

structure. The ligands of the two types are arrayed linearly in a 2-D square-grid (25.0 × 26.4 Å based on van der Waals radii) coordination polymer which introduces a nanoscale-wave in a 2-D coordination polymer plane (Fig.3). Interestingly, the bent ligands (red color) were located in the ridges and troughs of the wave and the pseudo-linear ligands (blue color) were located in between the ridges and troughs of the wave. The wavelength is 56.9 Å and the height of the wave is 11.7 Å. Recently, a novel wavy coordination polymer using a bent ligand was reported.[8] In this case, there are no pseudo-linear ligands and only bent ligands were located in the ridges and troughs of the wave. In contrast, some of the **L1** ligands act like a linear ligand in our case and are located between the ridges and troughs of the wave. Thus, the wavelength of our complex was relatively long.

Interpenetration phenomena are found to frequently occur during the self-assembly process. Recently, an 8-fold interpenetrated 3D-diamondoid frame was reported by the Ciani group.[9] In the case of the interpenetration of 2D wavy layers, which was denoted as specifically interwoven, two types supramolecular structures were generally formed. Firstly, a 3D supramolecular structure can be formed by an infinite interpenetration in the vertical direction between 2D layers. In this case, a 2D wavy plane interpenetrated by four different 2D wavy planes (5-fold) was reported.[10] Secondly, a thick 2D layer can be formed by interpenetration in the parallel direction. In this case, 2- or 3-fold interwoven structures were reported.[11] In our case, the inner space of the square-grid in the 2D-coordination polymer is huge and the basic 2D-coordination polymers have an undulating shape. To our surprise, a 5-fold interwoven structure formed (Fig. 4). The four different 2D-coordination planes penetrate the inner space of the square grid. The shift distance of the wave is 11.4 Å. To the best of our knowledge, this interwoven structure is the first example of 5-fold 2D wavy layers formed by parallel interpenetration. We envisage that the driving force for the linear structure of **L1** is an enhancement of the stability of the structure by the increased interpenetration.

Next we investigated the thermal behavior of the supramolecular structure. The crystal was stable up to 150 °C, but above 150 °C the crystal started to lose mass slowly. We believed that the mass loss could be attributed to release of the linear ligand from the lattice. In DSC, as the temperature was increased, the crystal slowly showed exothermic behavior implying that the crystal possesses strain energy in the lattice. Through X-ray analysis, the supramolecular structure was found to have a conjugated layer structure and the crystal a thin plane shape. Consequently, the conductivity was tested. However, the material turned out to be an insulator. SQUID measurements show primarily paramagnetic behavior at 300 K.

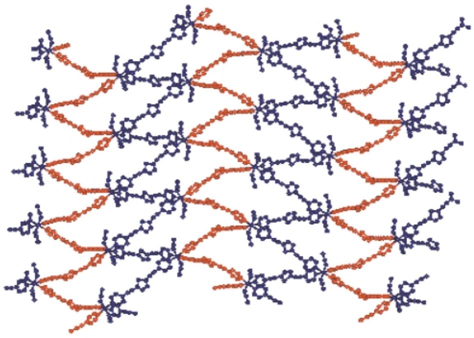

Fig. 3 Undulated behavior of 2D-plane constructed by **L1** and $Co(NCS)_2$, showing bent forms (red color) and linear forms (blue color).

In conclusion, we synthesized a novel coordination polymer by self-assembly between **L1** and $Co(NCS)_2$ in which the rigid igand **L1** showed an unusual flexibility and pseudo-linear geometry. It is a rare example showing conformational change of a rigid ligand during the self-assembly process. By computational calculation, the strain energy of each ligand is determined to be 11 kcal mol^{-1}. The supramolecular structure produced by **L1** and $Co(NCS)_2$ showed a 5-fold 2D coordination polymer.

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5 Slow diffusion of methanolic solution (7 mL) of **L1** (50 mg) to aqueous (7 mL) $Co(NCS)_2$ (15 mg) solution for a week yielded red crystals. Crystal data for $[Co(NCS)_2(\mathbf{L1})_2]_\infty$, (60 mg, 94%) ($C_{38}H_{20}CoN_6S_4$): CCDC 212562 (see http://www.rsc.org/suppdata/cc/b3/b307392k/ for crystallographic data in .cif format), monoclinic, $P2_1/c$, $a = 27.065(1)$, $b = 11.383(1)$, $c = 27.046(1)$ Å, $\beta = 118.993(1)°$, $V = 7288.1(7)$ Å ^{3}, $Z = 4$, density = 1.363 mg m^{-3}, Theta range for data collection 2.89 to 27.49°. Limiting indices $- 35 \leqslant h \leqslant 35$, $-14 \leqslant k \leqslant = 13$, $-33 \leqslant l \leqslant 35$, Reflections collected/unique = 16183/884, [R(int) = 0.0725], Goodness-of-fit on $F^2 = 0.962$, Final R indices $[I > 2\sigma(I)]$ $R^1 = 0.0698$, $wR^2 = 0.1796$. Anal. calc. H, 2.70; C, 61.04; N, 11.24; S, 17.15: observed H, 2.89; C, 61.08; N, 11.13; S, 17.04%.

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