



# Subtle side chain effect of methyl substituent on the self-assembly of polypseudorotaxane complexes: Syntheses, structural diversity and photocatalytic properties



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## ABSTRACT

Cation-templated self-assembly of 1,*n*-bis(4-methylpyridine)alkane cations ( $n = 3-7$ ) with CuSCN was studied and a series of new polymeric thiocyanate frameworks were obtained:  $\{(\text{bmpp})[\text{Cu}_2\text{Br}_2(\text{SCN})_2]\}_n$  (**1**),  $\{(\text{bmpt})[\text{Cu}_2(\text{SCN})_4]\}_n$  (**2**),  $\{(\text{bmppt})[\text{Cu}_2(\text{SCN})_4]\}_n$  (**3**),  $\{(\text{bmph})[\text{Cu}_4(\text{SCN})_6]\}_n$  (**4**),  $\{(\text{bmphp})[\text{Cu}_2(\text{SCN})_4]\}_n$  (**5**), ( $n = 3$ , bmpp;  $n = 4$ , bmpt;  $n = 5$ , bmppt;  $n = 6$ , bmph;  $n = 7$ , bmphp). The structures consist of 1-2D frameworks with the dications trapped within host network cavities. Compounds **1**, **2**, **3** and **5** possess the infinite two-dimensional polypseudorotaxane anion networks. Compound **4** has a novel 1D chain structure which looks like lotus root. The results demonstrate that the side chain of methyl substituent plays an important role in the fabrication of polypseudorotaxane structures. Furthermore, solid UV–Vis spectra, photoluminescence and photocatalytic properties at ambient temperature were also investigated.

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## 1. Introduction

In recent years, cation-templated self-assembly of supramolecular hybrid materials have been attracting extensive attention not only due to their intriguing architectures and topologies [1–3], but also to potential applications in optoelectronic, catalytic, magnetic and optical limiting materials [4–7]. Among the various families of supramolecular compounds, copper (I) pseudohalides (SCN, CN) are particularly interesting for their structural diversities and luminescent properties [8]. As far as we know, they have been reported to exhibit rich structures, including discrete 0-D clusters, 1-D chains, 2-D layers and 3-D frameworks [9,10]. However, to design and construct tunable template and then synthesize more functional materials are still great challenges because subtle changes of the organic cationic properties, such as size, shape, side chain, and distribution of the positive charges, may lead to diverse aggregates of metal halides [11]. In our previous work, we found that side chain of methyl substituent in 1,1'-dialkyl-4,4'-bipyridine and methylimidazole dications templates gave more interactions to enhance the inorganic–organic distribution homogeneously and facilitated the formation of polypseudorotaxane frameworks

[9]. In order to further confirm the regularity, we choose a series of novel bolaamphiphilic 1,*n*-bis(4-methylpyridine)alkanes as cationic templates ( $n = 3-7$ ) (Scheme 1) and SCN<sup>−</sup> group as host linker for its various bonding modes (Scheme 2,  $t$ -,  $\mu_2$ -,  $\mu_3$ -) and possible coligand effects. The combination of these two components might also lead to hybrid materials with potentially distinctive properties. As expected, we successfully synthesized five novel 1-2D complexes,  $\{(\text{bmpp})[\text{Cu}_2\text{Br}_2(\text{SCN})_2]\}_n$  (**1**),  $\{(\text{bmpt})[\text{Cu}_2(\text{SCN})_4]\}_n$  (**2**),  $\{(\text{bmppt})[\text{Cu}_2(\text{SCN})_4]\}_n$  (**3**),  $\{(\text{bmph})[\text{Cu}_4(\text{SCN})_6]\}_n$  (**4**),  $\{(\text{bmphp})[\text{Cu}_2(\text{SCN})_4]\}_n$  (**5**). Furthermore, we investigated their photophysical properties and photocatalytic performances.

## 2. Experimental

### 2.1. General materials and methods

The dications 1,*n*-bis(4-methylpyridine)alkanes were prepared as bromides according to the literature [12]. Other chemicals and solvents were of reagent grade and used as purchased without further purification. The IR spectra were recorded on a Shimadzu IR435 spectrometer as KBr disk (4000–400 cm<sup>−1</sup>). Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 240 elemental analyzer. The UV–Vis diffuse reflectance spectra were measured at UV–Vis–NIR Cary 5000. UV–Vis absorption spectra were

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obtained using UV-5500 PC spectrophotometer. Photoluminescent measurements of **1–5** were conducted on the F-7000 FL spectrophotometer and the data was collected in solid state at room temperature. A model NETZSCHTG209 thermal analyzer was used to record simultaneous TG curves in flowing air atmosphere of 20 mL·min<sup>-1</sup> at a heating rate of 5 °C·min<sup>-1</sup> in the temperature range 45–800 °C using platinum crucibles. All powder patterns were collected on a Philips X-pert X-ray diffractometer at a scanning rate of 4 °min<sup>-1</sup> in the 2θ range from 5° to 50° with graphite monochromatized Cu Kα radiation (λ = 0.15418 nm).

**2.2. Synthesis of complexes**  $\{(bmpp)[Cu_2Br_2(SCN)_2]\}_n$  (**1**),  $\{(bmpt)[Cu_2(SCN)_4]\}_n$  (**2**),  $\{(bmppt)[Cu_2(SCN)_4]\}_n$  (**3**),  $\{(bmph)[Cu_4(SCN)_6]\}_n$  (**4**) and  $\{(bmphp)[Cu_2(SCN)_4]\}_n$  (**5**)

Compounds **1–5** are synthesized similarly. A methanol solution (2 ml) of 1,*n*-bis(4-methylpyridine)alkanes cations (0.1 mmol) was added into a stirring colorless solution of CuSCN (0.1 mmol) dissolved in 3 mL DMF/H<sub>2</sub>O (volume ratio of 4:1) with excess KSCN (0.2 mmol). The solution was then filtered and slowly evaporated in a vial at room temperature.

For compound **1**, yellow prismatic crystals were obtained after 2 days in about 75% yield based on copper ion. IR (cm<sup>-1</sup>, KBr): 3439(w), 2126(s), 2111(s), 1638(m), 1469(w), 1174(m), 852(w), 768(m), 700(w), 520(m); *Anal. Calc.*: C, 32.34; H, 3.19; N, 8.87. *Found*: C, 32.22; H, 3.25; N, 8.76%.

For **2**, light-yellow crystals were obtained after 1 day in about 61% yield. IR (cm<sup>-1</sup>, KBr): 3454(w), 2095(s), 2079(s), 1639(m), 1449(w), 1164(m), 832(m), 753(m), 704(w), 538(m); *Anal. Calc.*: C, 39.92; H, 3.68; N, 13.97. *Found*: C, 39.78; H, 3.92; N, 13.83%.

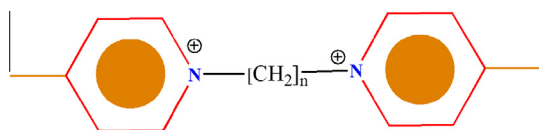
For **3**, after 4 days pale yellow crystals were obtained. Yield: 73%. IR (cm<sup>-1</sup>, KBr): 3440(w), 2087(s), 1634(m), 1460(m), 1278(w), 1168(m), 821(m), 755(m), 707(w), 547(m). *Anal. Calc.*: C, 40.96; H, 3.93; N, 13.65. *Found*: C, 41.01; H, 3.75; N, 13.56%.

For **4**, a week later, yellow crystals were obtained. Yield: 55%. IR (cm<sup>-1</sup>, KBr): 3432(m), 2932(w), 2106(s), 1637(m), 1468(m), 1203(w), 818(m), 771(m), 703(w), 568(w). *Anal. Calc.*: C, 33.02; H, 3.00; N, 12.83. *Found*: C, 33.14; H, 2.96; N, 12.74%.

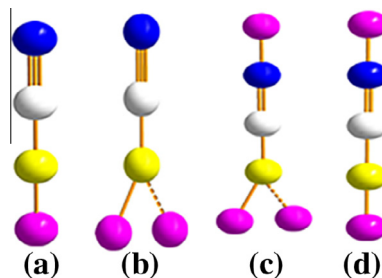
For **5**, yellow crystals were obtained after 2 days. Yield: 57%. IR (cm<sup>-1</sup>, KBr): 3431(m), 2934(w), 2085(s), 1635(s), 1468(m), 1172(m), 830(m), 760(m), 701(w), 557(w). *Anal. Calc.*: C, 42.91; H, 4.38; N, 13.05. *Found*: C, 42.71; H, 4.25; N, 13.23%.

**2.3. X-ray crystallography**

The crystallographic data for compound **1** were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo Kα radiation while compounds **2–5** were collected Mo Kα radiation (λ = 0.71073 Å) at 293 K. Absorption corrections were applied by using SADABS. The crystal structures of **1–5** were solved by the direct method and refined on F<sup>2</sup> by full-matrix least-squares techniques with the SHELXTL-97 program [13]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restraints. The key crystallographic information for **1–5** are summarized in Table S1. Selected bond lengths and angles are put in Table S2. In order to confirm the phase purity of the bulk materials, Powder X-ray



**Scheme 1.** Conformations of the title cations (*n* = 3, bmpp; *n* = 4, bmpt; *n* = 5, bmppt; *n* = 6, bmph; *n* = 7, bmphp).



**Scheme 2.** Schematic representation of the bonding modes. (a) Terminal (t-) mode; (b) end-on μ<sub>2</sub>-bridging mode; (c) 1,1,3-μ<sub>3</sub>-bridging mode; (d) end-to-end μ<sub>2</sub>-bridging mode. (C, white; N, blue; S, yellow; metal, purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

diffraction (PXRD) experiments were carried out for compounds **1–5**, in which the experimental spectra were consistent with their simulated spectra (Fig. S1).

**3. Results and discussion**

**3.1. Synthesis**

The preparation of the compounds is straightforward, and the yields were more than 55%. Based on the addition of a methanol solution of quaternary ammonium salt of bis(4-methylpyridine)alkane cations to a DMF solution of CuSCN with excess KSCN crystal precipitation was observed within a week. Compared with other complexes, compound **4** was obtained in a long time, which shows a weak directing ability for bmph. Compounds **1–5** cannot dissolve in water and common organic solvents, such as THF, MeCN, DMF, and DMSO. The elemental analysis was consistent with the chemical formulas. In this series of researches of 1,*n*-bis(4-methylpyridine)alkanes cations as templates, when *n* = 1–2, attempt to get the crystal products failed.

**3.2. Crystal structure of (1)**

Single-crystal X-ray diffraction analysis revealed that this compound crystallized in the orthorhombic system with space group *Pbcn*. The asymmetric unit contains a [Cu<sub>2</sub>Br<sub>2</sub>(SCN)<sub>2</sub>]<sup>2-</sup> anion and a bmpp<sup>2+</sup> cation as shown in Fig. 1(a), each Cu(1) in [Cu<sub>2</sub>Br<sub>2</sub>(SCN)<sub>2</sub>]<sup>2-</sup> unit coordinates to two μ<sub>2</sub>-Br(1) and two S of SCN<sup>-</sup> group (end-to-end μ<sub>2</sub>-bridging mode) in distorted tetrahedral geometries. Each [Cu<sub>2</sub>Br<sub>2</sub>(SCN)<sub>2</sub>]<sup>2-</sup> net comprises a large ring which contains two small Cu<sub>2</sub>Br<sub>2</sub> four-membered rings, four SCN<sup>-</sup> groups and two Cu atoms, as shown in Fig. 1(b). The bmpp cation is located in a large cavity. The large ring extends into a 2D polypseudorotaxane structure. To our knowledge, this penetrating structure which contains four-membered rings is first reported. The crystal packing diagram of **1** is shown in Fig. 1(c).

**3.3. Crystal structures of (2), (3) and (5)**

Compounds **2**, **3** and **5** have similar anionic structures, therefore, only the structure of **2** is taken as an example to be described in detail. The structure of compound **2** is shown in Fig. 2 and the structural diagrams for compounds **3** and **5** are available in Figs. S2 and S3. They all feature a faveolate architectures and are made up of infinite 2D inorganic [Cu<sub>2</sub>(SCN)<sub>4</sub>]<sub>n</sub><sup>2n-</sup> networks with the corresponding dications trapped inside. Cuprous and thiocyanate ions form a dually bridged two dimensional infinite network. In compound **2**, Cu1–S1 = 2.3593(8) Å, Cu1–S2 = 2.4532(8) Å, Cu1–N1 = 1.993(3) Å, Cu1–N2 = 2.002(3) Å. The difference in bond

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