4-(4-Pyridyl)benzoic Acid (PybenH) Dimer: An Efficient and Reasonable Design for a Long Linear Bidentate Building Block Employed in Metal–Organic Coordination Framework

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Self-assembly of 4-(4-pyridyl)benzoic acid (pybenH), Ni^{2+}, SCN^- and an aromatic guest (naphthalene or dibenz[*a*,*h*]anthracene) gave two isostructural inclusion compounds, in which pybenH ligands form the corresponding dimers acting as bidentate building blocks with a length of ca. 20.86 Å.

Organic building blocks employed in metal–organic coordination frameworks are generally covalently bonded single molecules.[1,2] Those consisting of two components held together by hydrogen bonding still remain rare, in spite of their advantages in solubility and in easy preparation of building blocks.[3] In this communication, we will describe the usefulness of this design strategy for the preparation of *a long linear bidentate building block* through introduction of two new inclusion compounds formulated by $[Ni(SCN)_2(pybenH)_2]\cdot x(G)$, where pybenH is 4-(4-pyridyl)benzoic acid and G is naphthalene ($x = 1$) (**1**) or dibenz[*a*,*h*]anthracene ($x = 1/2$) (**2**).

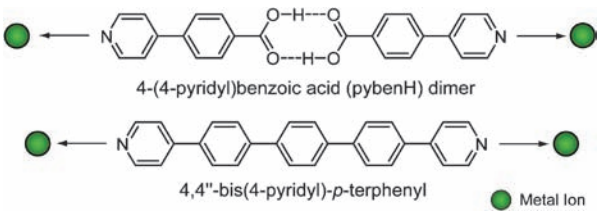
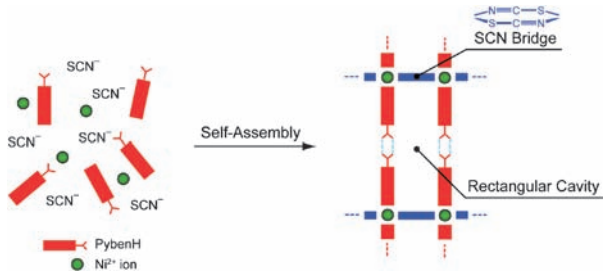


Chart 1.

PybenH was employed as a component of a building block, because its corresponding carboxylic acid dimer (CAD) is a potential linear bidentate building block (Chart 1). The resultant CAD is a supramolecular analogue of a single molecular bidentate building block of 4,4″-bis(4-pyridyl)-*p*-terphenyl. CAD synthon was selected for a connecting unit of two components because of its high probability of formation and strong directionality.[4] We anticipated that the combination of pybenH with Ni^{2+} and SCN^-, which self-assemble to give 1D chain under appropriate conditions,[5] gives a coordination layer with rectangular cavities defined by two pybenH dimers and two SCN bridges (Scheme 1).

Inclusion compounds **1** and **2** were obtained from methanol solutions containing Ni^{2+}, SCN^-, pybenH,[6] and the corresponding aromatic molecules after slow evaporation of the solvents at ambient temperature.[7] **1** and **2** crystallized in the triclinic crystal system with space group $P\bar{1}$ (#2).[8,9] Their crystals are isostructural and are characterized by layered structures. Each layer is composed of Ni^{2+}, SCN^-, and pybenH, and has an almost identical architecture to that designed. As representative, the framework of a layer formed in **1** is shown in Figure 1.[10] The asymmetric unit contains two Ni^{2+} ions with octahedral coordination geometries, two $\mu_{1,3}$-SCN^- ions, two pybenH ligands, and a naphthalene guest. The Ni^{2+} ions lie on crystallographic inversion centers. Four equatorial coordination sites of each Ni^{2+} ion are ligated by two nitrogen atoms from SCN^- ions and two sulfur atoms from SCN^- ions in trans configurations. Adjacent Ni^{2+} ions are doubly connected by two SCN^- ions in antiparallel fashion with a Ni/Ni separation of 5.537(2) Å to form an 1D chain propagating along the *b* axis. Two pybenH ligands are bonded to the two axial sites of each Ni^{2+} ion via pyridyl nitrogen atoms. Each pybenH ligand forms CAD with a pybenH ligand of an adjacent 1D chain and the resultant one acts as bidentate building block with a dimer length (a N/N distance) of 20.846(5) Å (The corresponding dimer length found in **2** is 20.869(7) Å.).



Scheme 1.

Each layer has rectangular cavities with a spindle-like shape defined by two pybenH dimers and two SCN bridges. The width of the cavity is varied from ca. 5.54 Å (the Ni/Ni separation subjected by the SCN bridge) to ca. 7.61 Å (a O/O distance between pybenH dimers). Its height is ca 24.91 Å, which is in consistent with a Ni/Ni separation subjected by the pybenH dimer.

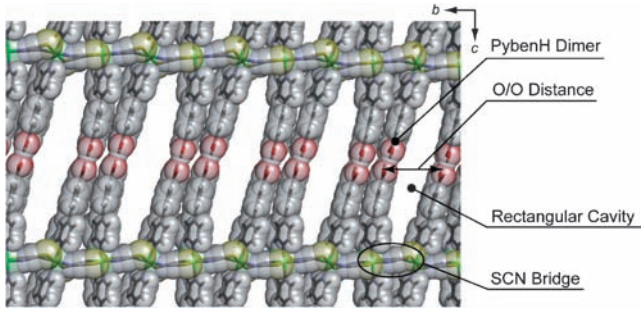


Figure 1. The framework with van der Waals surface of a coordination layer formed in **1**. Naphthalene guests are omitted for clarity. Color scheme: gray (carbon), white (hydrogen), blue (nitrogen), red (oxygen), yellow (sulfur), green (nickel).

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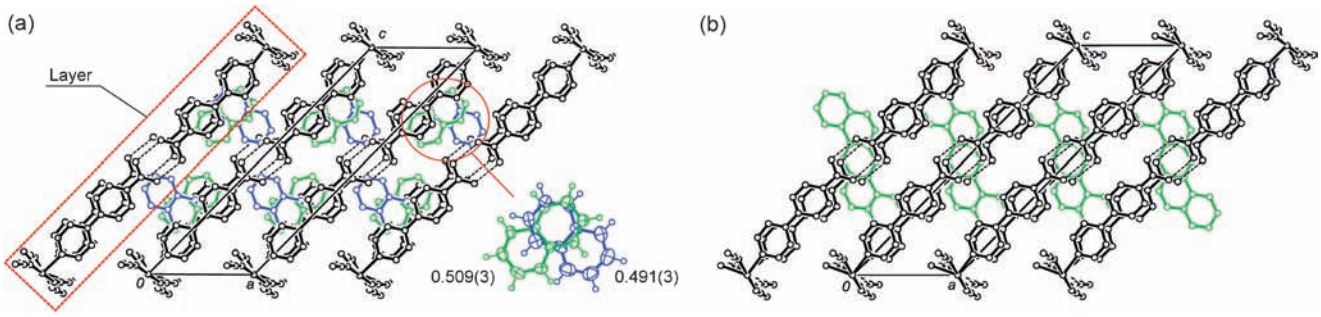

Figure 2. The crystal structures of (a) **1** and (b) **2** viewed down along the *b* axis. Naphthalene guests and dibenz[*a*,*h*]anthracene guests form two rows and a row in the respective 1D channels. Dotted lines show hydrogen bond. Hydrogen atoms are omitted for clarity.

Thus, the cavity dimension is 24.91 × 5.54–7.61 Å^2 (24.94 × 5.58–7.66 Å^2 of **2**).

The layers are stacked parallel to the *bc* plane to give the layered structures (Figure 2). Each rectangular cavity of a layer adjoins those of neighboring layers to form 1D channels propagating along the *a* axis,[11] where naphthalene guests (**1**) or dibenz[*a*,*h*]anthracene guests (**2**) form two rows or a row, respectively, with parallel orientation of their aromatic planes to those of pybenH dimers. The naphthalene guests are disordered over two positions with almost identical site occupancy factors (0.509(3) (green):0.491(3) (blue)).

The pybenH dimer has an almost linear structure (Figure 3).[10] Comparison of the dimer length of 20.846(5) Å with lengths of single molecular bidentate building blocks, the pybenH dimer amounts to three times as long as 4,4′-bipyridine (7.129(6) Å)[12a] and is much longer than 1,4-bis(4-pyridyl)-benzene (11.398(3) Å)[12b] and 4,4′-bis(4-pyridyl)biphenyl (15.756(3) Å).[12b] No example in which 4,4″-bis(4-pyridyl)-*p*-terphenyl is employed as a bidentate building block of a coordination framework has been reported to date. Probably, this is closely related to its solubility toward solvents. These results clearly exemplify that the method, that is, the construction of a bidentate building block through self-assembly of two components with assistance of CAD formation is both efficient and reasonable one for the preparation of a long linear bidentate building block. This design strategy would be applied to other systems where a long and/or large building block is required to construct a target coordination framework.

The fact that the differently sized guests form the isostructural packing is of interest. In general, only guests with similar structures (ex. benzene and toluene) form an isostructural packing. Subtle change in a molecular structure of a guest often induces significant perturbation on overall crystal structure, because it inherently depends largely on subtle balance between host components and guests included. The result exemplifies the architectural robustness of our system. This enables the present system to include the differently sized guests to give the isostructural inclusion compounds.

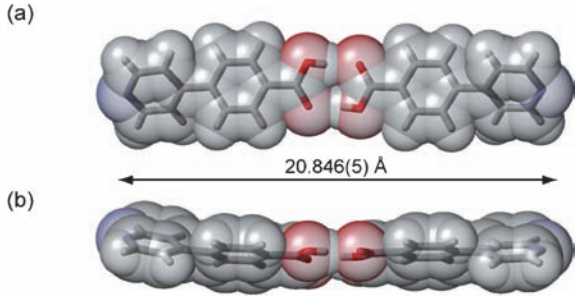

Figure 3. (a) The front and (b) the side views of the pybenH dimer. Color scheme: gray (carbon), white (hydrogen), blue (nitrogen), red (oxygen).

In addition to this feature, the fact that the 1D array of the rectangular cavities gives a 1D channel suggests a potential rich inclusion property of the present system. The survey of this possibility is currently in progress.

In summary, we have employed pybenH as a component of a long linear bidentate building block. Self-assembly of Ni^{2+}, SCN^-, pybenH, and an aromatic guest of either naphthalene or dibenz[*a*,*h*]anthracene gave two isostructural inclusion compounds **1** and **2**. In both crystals, pybenH ligands form the corresponding dimers acting as bidentate building block with a length of ca. 20.86 Å.

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7 A typical synthetic procedure of the inclusion compounds is described in Electronic Supporting Information.
8 Crystal data for **1**: $C_{36}H_{26}N_4O_4S_2Ni$, $M_r = 701.5$, triclinic, space group $P\bar{1}$ (#2), $a = 8.314(2)$ Å, $b = 11.075(3)$ Å, $c = 24.363(5)$ Å, $\alpha = 90.78(1)^\circ$, $\beta = 48.65(1)^\circ$, $\gamma = 74.420(9)^\circ$, $V = 1564(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.49$ g cm^{-3}, μ(Mo Kα) = 0.802 mm^{-1}. A total of 9038 reflections (3.230.0) were processed of which 5577 were unique and significant with $I_{net} > 2\sigma(I_{net})$. Final residuals for $I_{net} > 2\sigma(I_{net})$ were $R_1 = 0.050$ and $wR2 = 0.085$ (GOF = 0.938) for 518 parameters. CCDC-605498.
9 Crystal data for **2**: $C_{37}H_{25}N_4O_4S_2Ni$, $M_r = 712.5$, triclinic, space group $P\bar{1}$ (#2), $a = 8.230(2)$ Å, $b = 11.155(3)$ Å, $c = 24.355(5)$ Å, $\alpha = 90.47(1)^\circ$, $\beta = 48.22(1)^\circ$, $\gamma = 74.568(7)^\circ$, $V = 1552(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.52$ g cm^{-3}, μ(Mo Kα) = 0.809 mm^{-1}. A total of 8791 reflections (3.230.0) were processed of which 6809 were unique and significant with $I_{net} > 2\sigma(I_{net})$. Final residuals for $I_{net} > 2\sigma(I_{net})$ were $R_1 = 0.039$ and $wR2 = 0.096$ (GOF = 1.032) for 438 parameters. CCDC-266545.
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