

Supramolecular Chemistry

Design, Synthesis, and X-Ray Crystal Structure of a Fullerene-Linked Metal–Organic Framework**

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Abstract: Given the unique structural and electronic properties of C_{60} , metal–organic frameworks (MOFs) containing C_{60} linkers are expected to exhibit interesting characteristics. A new hexakisfullerene derivative possessing two pairs of phenyl pyridine groups attached to two methano-carbon atoms located at the *trans*-1 positions was designed and synthesized. The four pyridyl nitrogen atoms define a perfectly planar rectangle. This new C_{60} derivative was used to assemble the first fullerene-linked two-dimensional MOF by coordination with Cd^{2+} .

Metal–organic frameworks (MOFs) are a relatively new class of hybrid organic-inorganic polymers derived from ordered networks formed from organic ligands and secondary building units or metal ions. Since MOFs were originally reported by Yaghi et al. and Kitagawa et al. to exhibit permanent porosity, they have attracted considerable interest and have been extensively studied because of their structural diversity, intrinsic variety of topologies, and unusual properties.^[1] These new hybrid materials are promising for applications in nonlinear optics,^[2] gas storage,^[3] catalysis,^[4] and for chemical separations.^[5] The synthesis of new MOFs is very challenging, with many choices of metals and organic ligands. Different combinations of metal centers and organic ligands have resulted in elaborate designs with interesting structures and properties.^[6]

C_{60} is a well-known electron acceptor which also possesses good thermal stability, and these properties have resulted in its applications in organic solar cells,^[7] superconductors,^[8] and ferromagnetic materials.^[9] The spherical shape, high degree of symmetry, and coordinating geometries of C_{60} make it an ideal candidate for the construction of supramolecular architectures. MOFs containing C_{60} linkers in well-defined geometries would be expected to exhibit unique structures and properties.

The first supramolecular architecture based on a C_{60} linker was reported by Diederich et al. in 1998.^[10] A fullerene ligand with two pyridyls connected to a methano-carbon atom was synthesized using the Bingel–Hirsch reaction and was

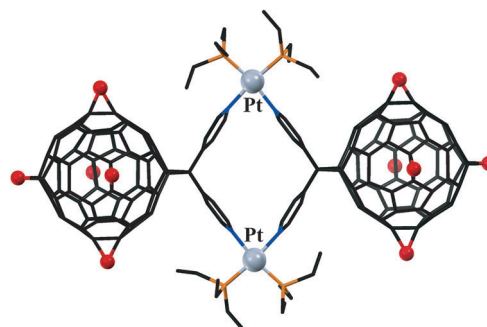


Figure 1. Fullerene-based supramolecular structure reported by Diederich.^[10] The malonate groups $[C(OOC_2H_5)_2]$ denoted by red balls and H omitted for clarity. P orange, N blue.

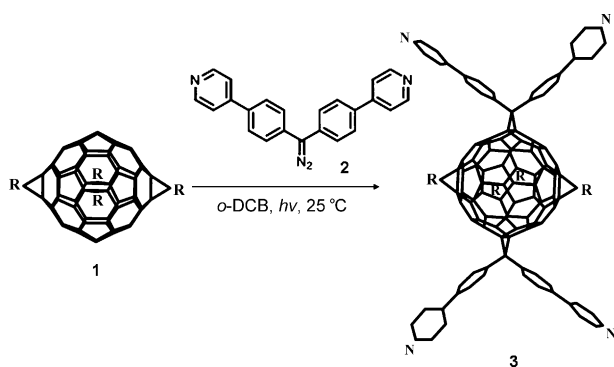
used to build a discrete fullerene-containing dimer assembled by the coordination of two Pt^{II} centers (Figure 1). In 2007, Khlobystov, Schröder et al. synthesized two dipyrindyl-functionalized fullerenes which were used as efficient coordination linkers with Ag^I cations, and two dimeric and one polymeric metallacyclic products were formed instead of a fullerene-based metal–organic framework.^[11] Muller, Bräse et al. designed and synthesized fullerene bis(malonate)s possessing pyridine or cyano groups at the terminal position for building metal–organic frameworks, however, only a copper complex was synthesized, and no metal–organic frameworks were reported.^[12] We recently reported the design and synthesis of a hexakisfullerene adduct with two N-containing 4,5-diazafluorene groups attached at the *trans*-1 positions of C_{60} . This molecule was expected to bind to Ag^I cations to build fullerene-based MOFs, however, only a one-dimensional (1D) linear coordination polymer was obtained.^[13] Although there have been a few MOFs reported to incorporate C_{60} molecules as pillars between the layers^[14] or trapped in the pores or cavities,^[15,16] there have been no reports of C_{60} derivatives incorporated as structure-directing linkers in MOFs. Herein we report the design and synthesis of a hexakisfullerene adduct with four pyridyl groups whose nitrogen atoms reside in a rectangle, which was employed as a linker to build the first two-dimensional (2D) fullerene-based MOF. The 2D layers packed in the crystal with interlayers composed of isolated hexakisfullerene molecules form an intricate three-dimensional (3D) structure.

The synthetic procedure used to prepare the *trans*-1 hexakis-fullerene adduct **3** is shown in Scheme 1. The previously reported tetrakis[di(ethoxycarbonyl)methano]- C_{60} (**1**)^[17] was used as a starting material and reacted with 4,4'-(4,4'-(diazomethylene)bis(4,1-phenylene))dipyridine (**2**) (see

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Scheme 1. Synthesis of the *trans*-1 hexakisfullerene adduct **3**. R = [C-(OOC₂H₅)₂].

the Supporting Information) to prepare the compound **3** under photoirradiation ($\lambda = 365$ nm) for 30 minutes. The pale-yellow compound **3** is very stable under atmospheric conditions and highly soluble in common organic solvents, such as CH₂Cl₂, DMF, and THF. The ¹H NMR spectrum of **3** is shown in Figure 2. Two quartets centered at $\delta = 4.45$ and 4.22 ppm

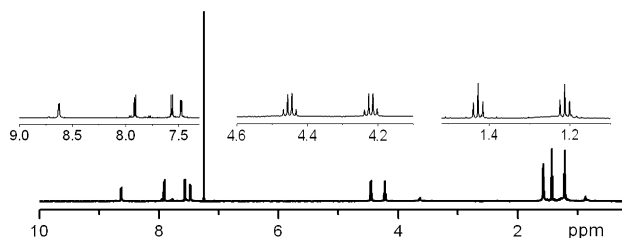


Figure 2. ¹H NMR spectrum of **3** (600 MHz, CDCl₃). The insets show the expanded regions.

and two triplets centered at $\delta = 1.43$ and 1.22 ppm can be respectively assigned to the methylene and methyl groups of the four malonate groups located on the equatorial belt of the C₆₀. Signals in the aromatic region were assigned to four different types of protons from the phenyl and pyridyl groups. These features (the equivalency of the protons of the malonates and for the aromatic groups) clearly indicate a *D*_{2h} symmetry for **3**, and establishes that all the addends are located at octahedral positions on the fullerene with the newly added groups in a *trans*-1 relationship to each other. The UV-visible spectrum of C₆₀ derivatives is diagnostic of the addition patterns because the absorption features are mainly determined by the structure of the cage instead of the structure of the addends.^[18] Figure 3 shows the UV-visible absorption of **3** in CH₂Cl₂. The absorption peaks located at $\lambda = 280$ nm, 320 nm and 339 nm are almost identical to those of the *trans*-1 hexakis-adduct reported by Hirsch and co-workers,^[19] and corroborates the *trans*-1 hexakis-adduct structure assigned based on the ¹H NMR spectrum.

The adduct **3** was designed to have four phenyl pyridine groups radiating from the photochemically added methanocarbon atoms, which are in the *trans*-1 arrangement. The four pyridyl nitrogen atoms should define a perfectly planar

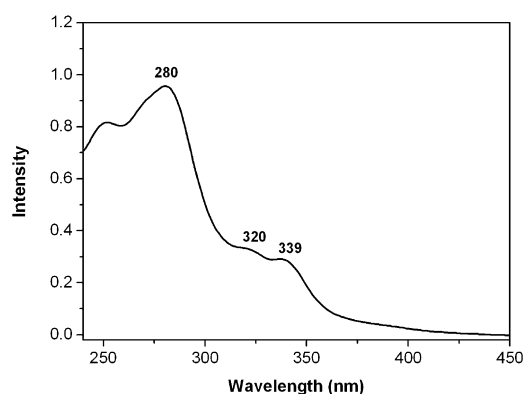


Figure 3. UV-visible absorption of **3** in CH₂Cl₂.

rectangle. Pyridine is one of the most versatile ligands for metal ion coordination to build supramolecules and MOFs. The phenyl group linkers help to increase the length of the ligand and reduce the steric hindrance upon metal coordination. A rectangular orientation of the four peripheral pyridine groups makes adduct **3** an ideal ligand to form an infinite number of layers upon coordination to metal ions.

The complex **4** [(**3**)₂·Cd(NO₃)₂]_∞ was obtained by the reaction of **3** with Cd(NO₃)₂·4H₂O in DMF at 100 °C overnight. When the solution cooled to room temperature, methanol was carefully layered over the solution, and yellow crystals were obtained after several weeks. Single-crystal X-ray diffraction analysis shows that it is a fullerene-linked MOF.^[20] Figure 4 shows the single layer formed by the

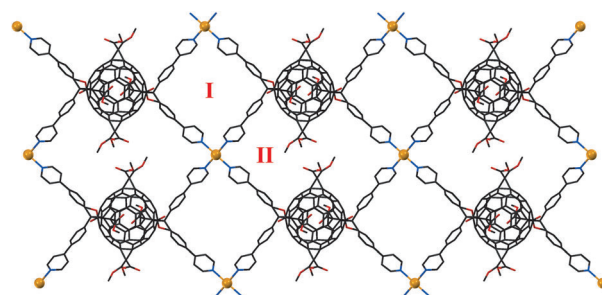


Figure 4. 2D layer of **4** viewed along the *b*-axis (H omitted for clarity). Cd gold, N blue, O red, C black.

coordination of **3** with cadmium ions. The NO₃⁻ counteranions were not observed in the structure, probably because they are in the disordered volume. Each fullerene unit coordinates to four cadmium ions through the four pyridyl appendages and each cadmium ion is tetracoordinated to four nitrogen atoms of pyridyl groups from four different molecules of **3**, and the Cd-N distances are 2.336(5) and 2.346(5) Å, respectively. The Cd ions are bridged by four phenyl pyridine groups and the four angles around the cadmium ion are close to 90° [N(1)#2-Cd(1)-N(2)#3, 91.9(2)°; N(1)-Cd(1)-N(2)#3, 88.1(2)°; N(1)#2-Cd(1)-N(2)#4, 88.1(2)°; N(1)-Cd(1)-N(2)#4, 91.9(2)°]. Therefore, the connections between Cd ions and adduct **3** molecules lead to the square pore I and rectangular pore II in the 2D network (see

Figure 4). In the square pore, the distances between the two Cd ions and the two C atoms located at the corners are 15.62 Å and 15.07 Å, respectively. The distance between the two Cd ions is 24.86 Å in pore II structures. Typically, 2D sheets with open porous networks contain solvent molecules in the pore of the supramolecular cavities.^[21] In the network of **4**, solvent molecules are not observed in pore II because of the presence of two bulky ethyl malonate groups in those spaces. Noncoordinated molecules of **3** fill the space between the 2D MOF layers and these point to the centers of two pore-I structures (see Figures 5a and b). Incorporation of isolated

MOF layers, and are located over the centers of two type I pores from adjacent layers. On the basis of these results, we are in the process of building a 3D MOF by connecting metal centers of the 2D fullerene layers with dipyrindine-based pillars to provide large open pores.

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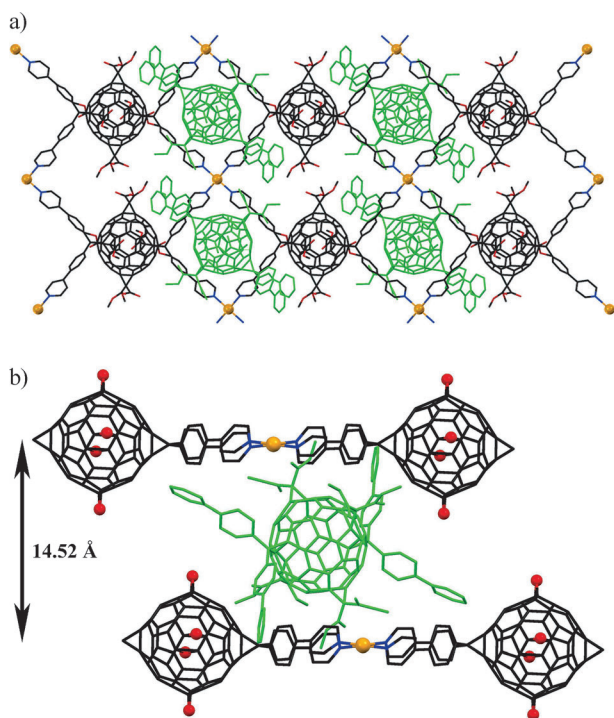


Figure 5. a) Crystal packing of **4** viewed along *b*-axis (H omitted for clarity). b) Orientation of 2D layers viewed along *a*-axis (malonate addends denoted by red balls and H omitted for clarity).

molecules of **3** in the interlayer results in a distance of 14.52 Å between Cd-linked 2D MOF layers (Figure 5b). The shortest distance between the interlayer fullerenes and those in the 2D network is about 4.39 Å, which is much shorter than the shortest distance (15.07 Å) between the fullerenes in the 2D network. The fullerene pillars exhibit interactions with the layers surrounding it. There are η^2 -type C-H $\cdots\pi$ and C-O \cdots H interactions between the phenyl pyridine moieties and the malonate groups. These interactions are important for the packing observed and expand the 2D network into a 3D system.

In summary, we designed and synthesized a new hexakisfullerene derivative possessing two pairs of phenyl pyridine groups attached to two methano-carbon atoms located at *trans*-1 positions, and it was used to assemble the first fullerene-linked 2D metal-organic framework. The 2D sheets contain two types of pores (I, II), and noncoordinated hexakisfullerene molecules serve as pillars between the 2D

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