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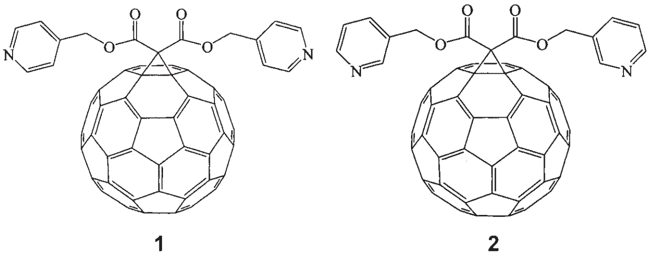
Controlled Assembly of Silver(I)-Pyridylfullerene Networks**

Jian Fan, Yu Wang, Alexander J. Blake, Claire Wilson, E. Stephen Davies, Andrei N. Khlobystov, and Martin Schröder**

Fullerene-containing supramolecular architectures[1] are attracting attention because of their unusual physicochemical properties and potential applications as superconductors[2] and ferromagnetic materials,[3] in optical and quantum devices,[4] and for inhibition of HIV protease.[5] Controlling the positions and orientations of fullerenes in the solid-state and on surfaces has been addressed by various methods, such as encapsulation of fullerenes within carbon nanotubes,[6] adsorption on nanopatterned surfaces,[7] and cocrystallization with a variety of organic,[8] metal–porphyrin,[9] organometallic,[10] and inorganic molecules.[11] Although fullerene chemistry has been of major interest for the past 20 years, supramolecular structures based upon metal coordination to functionalized fullerenes are still quite rare, and very few such systems have been unambiguously structurally characterized.[12,13] The majority of examples are based on porphyrin architectures, which assemble by apical coordination of an nitrogen donor of the functionalized fullerene to a metal ion bound equatorially to the porphyrin.[12] To date no examples of polymeric aggregates of functionalized fullerenes with transition-metal ions and coordinate bonding have been structurally characterized, and the nature of complexation within such a system remains unknown. The assembly of fullerenes within coordination-polymer frameworks will afford flexible control of interfullerene distances and interactions in the solid-state, and will allow utilization of the structural and stereochemical diversity of coordinate bonding to construct optically and electronically active fullerene structures. We describe herein the control of fullerene–fullerene separations and orientations by coordination to metal ions, and report the first example of a chain coordination polymer containing a fullerene-functionalized ligand.

Diederich and co-workers have reported[13] the first example of a binuclear cyclophane-fullerene using a metal-directed self-assembly procedure in which only one type of structure can be formed, which is partly due to the rigidity of the ligand employed. We have adopted an alternative approach in which greater ligand flexibility and ligand-donor angularity have been incorporated within two exobidentate ligands, bis(pyridin-4-ylmethyl)-3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]fullerene-3′,3′-dicarboxylate (**1**), and bis(pyridin-3-ylmethyl)-3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]fullerene-3′,3′-dicarboxylate (**2**; Scheme 1). The ligands **1** and **2** are isomers and may be expected to exhibit diverse structural behavior when binding to metal ions as a consequence of the conformational flexibility of the $-CH_2-O-$ group linking the fullerene cage with the pyridyl donor. We chose Ag^I salts to react with **1** and **2** since these metal centers are sufficiently labile and have relatively controllable coordination chemistry in supramolecular assembly.[14]



1 **2**

Scheme 1. Ligands **1** and **2**.

Ligands **1** and **2** were synthesized by the Bingel cyclopropanation method.[15] Complexes **3**–**5** were obtained by

$[(\text{Ag-}\mathbf{1})_2](PF_6)_2 \cdot 5\,C_6H_6 \cdot 6\,CH_3CN$ **3**

$\{[\text{Ag-}\mathbf{1}]PF_6 \cdot C_6H_6 \cdot C_6H_5CN\}_\infty$ **4**

$[(\text{Ag-}\mathbf{2})_2](PF_6)_2 \cdot 5\,C_6H_6$ **5**

reaction of $AgPF_6$ and the ligands **1** and **2** by solution-layering methods at ambient temperature. The dark red crystals of the products are stable in air, insoluble in common organic solvents and have been characterized by single crystal X-ray diffraction.[16]

The reaction of $AgPF_6$ with **1** in a mixture of benzene and acetonitrile affords the binuclear metallacycle **3**. In the single crystal X-ray structure (Figure 1), each Ag^I ion is bound to two nitrogen donors, each coming from two different ligands **1** (Ag–N 2.151(9) and 2.150(9) Å, $<$N–Ag–N 166.1(4)°). The

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[*] Dr. J. Fan, Y. Wang, Prof. Dr. A. J. Blake, Dr. C. Wilson, Dr. E. S. Davies, Dr. A. N. Khlobystov, Prof. Dr. M. Schröder
School of Chemistry
The University of Nottingham
University Park, Nottingham, NG7 2RD (UK)
Fax: (+44) 115-9513563
E-mail: Andrei.Khlobystov@nottingham.ac.uk
Martin.Schroder@nottingham.ac.uk

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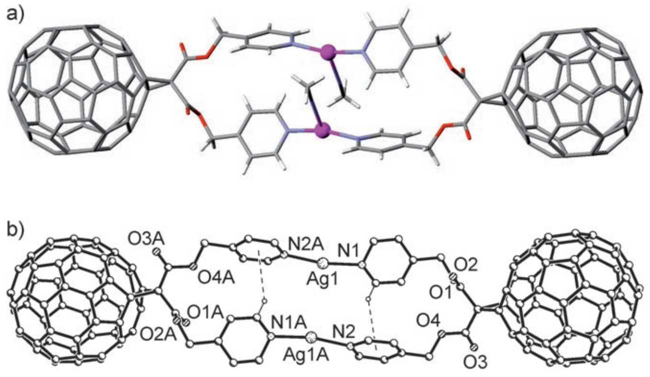

Figure 1. a) The binuclear cation in **3**; b) View of **3** with the C−H⋯π interactions indicated by dashed lines. Atoms labeled with the suffix A are related to the corresponding unsuffixed atoms by inversion (symmetry operation A: $1\frac{1}{2}-x$, $\frac{1}{2}-y$, $1-z$). O red, N blue, Ag pink.

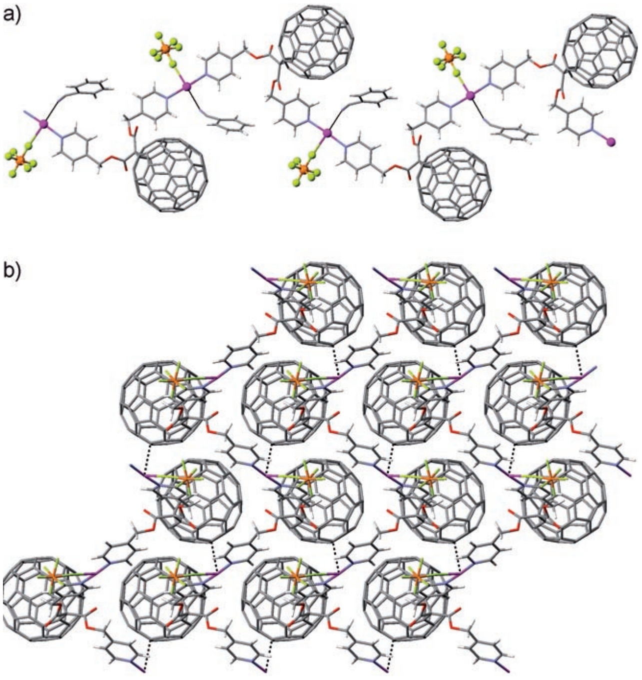

Figure 2. a) A one-dimensional zigzag chain in compound **4**; b) View of the chains in **4** propagating along the [101] direction. Ag⋯C24 ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$) interactions are shown as dashed lines linking the zigzag chains into two-dimensional sheets. Coordinated benzonitrile ligands have been removed for clarity. O red, N blue, Ag pink, P orange, F green.

two pyridyl groups of one ligand extend on the same side of the fullerene cage with a dihedral angle between these two rings of 51.0°. Thus, the bis(pyridine)fullerene ligand in **3** adopts a cisoid-conformation, which is essential for the formation of the discrete 2+2 metallacycle (Figure 1). Furthermore, each Ag^I ion is bound by one acetonitrile molecule located on either side of the macrocycle (Ag−N 2.653(9) Å), to give a distorted T-shaped coordination environment at Ag^I ions. The binuclear metallacyclic structure is further stabilized by intramolecular end-on C−H⋯π interactions[17] ($\measuredangle$C−H⋯X 136°, H⋯X 3.08, Ag⋯Ag 4.190 Å, where X is centroid of the pyridyl group).

In contrast to **3**, reaction of $AgPF_6$ with **1** in a mixture of benzene, methanol, and benzonitrile results in the formation of the one-dimensional chain polymer **4** (Figure 2) with the chain propagating through the operation of the *n*-glide along the [101] direction (Ag⋯Ag 14.101 Å). The asymmetric unit of **4** contains one Ag^I ion, a PF_6^- ion and one molecule each of coordinated ligand, benzene, and benzonitrile with each Ag^I ion bound in a linear fashion to two nitrogen donors from two different fullerene ligands (Ag−N 2.157(5), 2.163(4) Å, $\measuredangle$N−Ag−N 176.6(2)°). Planar coordination at Ag^I is completed by interaction with a fluorine atom from the PF_6^- ion (Ag⋯F 2.637(9) Å) and from a nitrogen donor from a benzonitrile molecule (Ag−N 2.776(5) Å) with *cis* angles at Ag^I ranging from 88.3(2) to 93.3(2)°. In contrast to **3**, the two pyridyl groups in **4** are directed to opposite sides of the fullerene cage. More interestingly, an interaction between Ag^I and the fullerene cage is seen in **4**, with a shortest intermolecular Ag⋯C(fullerene) distance of 2.801 Å at C24 ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$). This situation is comparable to complexes of Ag^I with aromatic systems (2.47–2.92 Å),[18] and is reminiscent of the interactions in adducts of $AgNO_3$ with C_{60} reported by Balch and co-workers.[11] It is, therefore, tempting to rationalize the formation of **4** as being driven in part by the Ag^I⋯fullerene interactions which template inter-chain contacts leading to the formation of a 2D sheet structure (Figure 2b) from 1D chains.

To determine what effect the disposition of donor groups attached to the fullerene cage have on the geometry of resultant complexes, binding of ligand **2** to Ag^I was explored. The complex **5** was obtained by the reaction of $AgPF_6$ and **2** in a mixed solution of benzene, methanol, and acetonitrile. The asymmetric unit of compound **5** contains one Ag^I ion coordinated by one ligand molecule, one PF_6^- ion, and two-and-a-half benzene molecules. In **5**, the cisoid conformation of the ligand, the coordination environment at Ag^I, and the binuclear structure are similar to those found in compound **3** (Ag−N 2.131(7), 2.108(8) Å, $\measuredangle$N−Ag−N 178.7(3)°). The two Ag^I centers are clipped together by two F−P−F units from two PF_6^- ions (Figure 3a; Ag⋯F 2.820, 2.951 Å, Ag⋯Ag separation 3.769 Å). The main difference between complexes **3** and **5** is that pyridyl donor groups in the ligand **2** are more angular with respect of the $-O-CH_2-$ linker-group to the fullerene cage, compared to the pyridyl donors in ligand **1** which are more linear. As a result, the binuclear metallacycle in **5** is more puckered than in **3** and there is a significant shortening of the distance between the fullerene cages within complex **5**, which has a center-to-center interfullerene distance of 22.027 Å compared to 26.839 Å in the structural isomer **3**. Also, in **5**, the dihedral angle between the adjacent pyridine rings in the ligand is reduced to 22.0° compared to 51.0° in **3**, and the centroid–centroid distance of the pyridine rings is 3.827 Å, suggesting possible long-range π⋯π interaction (Figure 3b).[19]

The complexes **3**–**5** appear to be virtually insoluble in most organic solvents, which precluded characterization of their solution properties by conventional spectroscopic methods. For complex **3** the limited solubility in benzonitrile did allow cyclic voltammetry (CV) studies to be carried out, which indicated that in solution, the Ag^I complexes either dissociate into free ligand and Ag^I ions, or undergo dissoci-

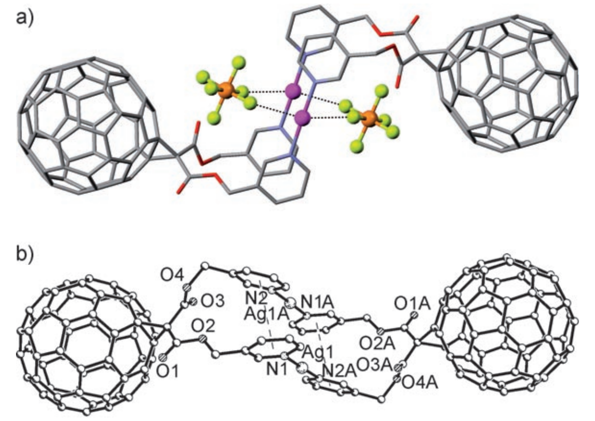

Figure 3. a) The binuclear cation in **5** with the Ag⋅⋅⋅F interactions indicated by dotted lines; O red, N blue, Ag pink, P orange, F green. b) View of **5** showing aromatic π⋅⋅⋅π interactions as dashed lines. Atoms labeled with the suffix A are related to the corresponding unsuffixed atoms by inversion (symmetry operation A: 2−*x*, −*y*, 1−*z*).

ation upon reduction (Supporting Information). Elemental and XPS (X-ray photoelectron spectroscopy) analysis of Ag^I–fullerene complexes confirmed that the composition and the metal/ligand ratio in bulk products of complexes are the same as in single crystals used for X-ray diffraction.

We have shown that pyridyl-functionalized fullerenes can act as efficient tectons with Ag^I cations to form polymeric and metallacyclic products. The arrangement of fullerenes in these supramolecular coordination systems can be controlled by conditions of synthesis and by the structure of the functional group on the fullerene with either $Ag^I\cdots C_{60}$ interactions as in **4**, or possible end-on C−H⋅⋅⋅aromatic interactions as in **3**, and face-to-face aromatic–aromatic interactions as in **5** stabilizing the structures. The structural difference between compounds **3** and **4** also reveals the importance of solvent mediation in the formation of discrete molecular or polymeric structures, with the latter templated by $Ag^I\cdots C_{60}$ interactions. Also, complexes **3**–**5** incorporate a significant amount of solvent in the cavities created by the loose-packing of fullerene cages, suggesting that, by replacing Ag^I with 5- or 6-coordinate metal ions, such as Zn^{II} or Cu^{II}, highly porous two- and three-dimensional fullerene frameworks should be formed for potential gas storage[20] as well as for the generation of unusual optoelectronic properties. Work in these areas is now in progress.

Experimental Section

Bis(pyridin-4-ylmethyl)malonate. A solution of malonyl dichloride (5.00 g, 35.5 mmol) in dichloromethane (50 cm^3) was added dropwise into a solution of 4-pyridylcarbinol (7.73 g, 71.0 mmol) and triethylamine (5 cm^3) in dichloromethane (100 cm^3) at room temperature. The mixture was stirred overnight, and then washed with water (3 × 50 cm^3). The organic phase was dried over anhydrous Na_2SO_4, separated by filtration, and the filtrate evaporated to dryness. The residue was purified by column chromatography (SiO_2; acetone as eluent) to afford the product as a brown oil. Yield 3.65 g, 36%. ^1H NMR (270 MHz, $CDCl_3$): $\delta = 8.57$ (m, 4H), 7.20 (m, 4H), 5.17 (s, 4H), 3.58 (s, 2H) ppm; ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 165.8$, 150.1, 144.1, 121.9, 65.3, 41.2 ppm. ESI-MS: *m*/*z* 287 (M^++H). Bis(pyridin-3-ylmethyl)malonate was synthesized by the similar procedure as bis(pyridin-4-ylmethyl)malonate, with a yield of 32% (3.25 g). ^1H NMR (270 MHz, $CDCl_3$): $\delta = 8.56$ (m, 4H), 7.63 (m, 2H), 7.27 (m, 2H), 5.16 (s, 4H), 3.47 (s, 2H) ppm; ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 166.0$, 150.0, 149.8, 136.2, 130.8, 123.6, 64.8, 41.3 ppm. ESI-MS: *m*/*z* 287 (M^++H).

1: A solution of C_{60} (0.100 g, 0.14 mmol), bis(pyridin-4-ylmethyl)malonate (0.040 g, 0.14 mmol), and iodine (0.035 g, 0.14 mmol) in toluene (200 cm^3) was stirred at room temperature for 30 min. DBU (1,8-diazabicyclo[5.4.0]undec-7-ene; 0.021 g, 0.14 mmol) was then added and the mixture stirred for a further 2 days. Column chromatography (SiO_2; toluene, then chloroform/acetone 7:3, v/v) gave **1** as a dark brown powder. Yield 0.032 g, 23%. ^1H NMR (270 MHz, $CDCl_3$): $\delta = 8.65$ (m, 4H), 7.35 (m, 4H), 5.51 (s, 4H) ppm; ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 163.14$, 150.44, 145.43, 145.34, 145.08, 145.01, 144.83, 144.59, 144.57, 143.98, 143.22, 143.17, 143.13, 143.11, 142.28, 141.86, 141.15, 139.16, 122.57, 77.29, 71.09, 66.99 ppm. MALDI-MS: *m*/*z* 1004 (M^+). Elemental analysis (%) calcd for $C_{75}H_{12}N_2O_4$: C 89.64, H 1.19, N 2.79; found: C 89.53, H 1.14, N 2.74.

2 was synthesized by a procedure similar to that for **1**. Yield 0.029 g, 21%. ^1H NMR (270 MHz, $CDCl_3$): $\delta = 8.72$ (d, $J = 1.81$ Hz, 2H), 8.64 (dd, $J_1 = 4.82$, $J_2 = 1.67$ Hz, 2H), 7.76 (m, 2H), 7.34 (m, 2H), 5.49 (s, 4H) ppm; ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 163.25$, 150.45, 150.34, 145.38, 145.29, 145.04, 144.78, 144.76, 144.70, 144.58, 143.95, 143.18, 143.12, 143.08, 142.27, 141.85, 141.08, 139.08, 136.73, 130.24, 123.68, 77.29, 71.19, 66.43 ppm. MALDI-MS: *m*/*z* 1004 (M^+). Elemental analysis (%) calcd for $C_{75}H_{12}N_2O_4$: C 89.64, H 1.19, N 2.79; found: C 89.56, H 1.14, N 2.74.

3: A solution of $AgPF_6$ (0.003 g, 0.01 mmol) in acetonitrile (3 cm^3) was carefully layered over a solution of **1** (0.010 g, 0.01 mmol) in benzene (10 cm^3). Dark red crystals suitable for X-ray crystallographic studies were isolated by filtration after several weeks. Yield 0.013 g, 83%; elemental analysis (%) calcd for $C_{96}H_{36}AgF_6N_5O_4P$: C 73.15, H 2.28, N 4.44; found: C 73.07, H 2.20, N 4.36.

4: A solution of $AgPF_6$ (0.003 g, 0.01 mmol) in methanol/benzonitrile (4 cm^3, 1:3, v/v) was carefully layered over a solution of **1** (0.010 g, 0.01 mmol) in benzene (10 cm^3). Dark red crystals suitable for X-ray crystallographic studies were isolated by filtration after several weeks. Yield 0.011 g, 78%; elemental analysis (%) calcd for $C_{88}H_{23}AgF_6N_3O_4P$: C 73.39, H 1.60, N 2.92; found: C 73.45, H 1.47, N 2.84.

5: A solution of $AgPF_6$ (0.003 g, 0.01 mmol) in methanol/acetonitrile (3 cm^3, 1:2, v/v) was carefully layered over a solution of **2** (0.010 g, 0.01 mmol) in benzene (10 cm^3). After several weeks the reaction mixture contained single crystals of **5** and an unknown solid which were collected by filtration. The bulk sample did not give satisfactory results by elemental analysis.

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[16] Crystal data for **3**. $M_r = 3152.3$, monoclinic, $a = 17.189(2)$, $b = 9.9375(14)$, $c = 75.236(11)$ Å, $\beta = 96.089(2)°$, $U = 12779(5)$ Å^3, $T = 150(2)$ K, space group $C2/c$ (No. 15), $Z = 4$, $\rho_{\mathrm{calcd}} = 1.638$ g cm^{-3}, $\mu(\mathrm{Mo}_{K\alpha}) = 0.428$ mm^{-1}, 11698 unique reflections measured and used in all calculations. Final R_1 (6303 $F \geq 4\sigma(F)$) = 0.113 and wR(all F^2) was 0.261. Crystal data for **4**. $M_r = 1438.93$, monoclinic, $a = 23.927(2)$, $b = 9.9394(7)$, $c = 25.538(2)$ Å, $\beta = 113.721(1)°$, $U = 5560.3(11)$ Å^3, $T = 150(2)$ K, space group $P2_1/n$ (*Alt.* $P2_1/c$ No. 14), $Z = 4$, $\rho_{\mathrm{calcd}} = 1.719$ g cm^{-3}, $\mu(\mathrm{Mo}_{K\alpha}) = 0.482$ mm^{-1}, 10380 unique reflections measured and used in all calculations. Final R_1 (5125 $F \geq 4\sigma(F)$) = 0.0571 and wR(all F^2) was 0.149. Crystal data for **5**. $M_r = 2905.9$, triclinic, $a = 10.012(3)$, $b = 10.188(3)$, $c = 27.931(8)$ Å, $\alpha = 99.213(3)$, $\beta = 97.550(3)$, $\gamma = 94.202(3)°$, $U = 2774.9(14)$ Å^3, $T = 153(2)$ K, space group $P\bar{1}$ (No. 2), $Z = 1$, $\rho_{\mathrm{calcd}} = 1.739$ g cm^{-3}, $\mu(\mathrm{Mo}_{K\alpha}) = 0.483$ mm^{-1}, 11150 unique reflections measured and used in all calculations. Final R_1 (7449 $F \geq 4\sigma(F)$) = 0.0909 and wR(all F^2) was 0.286. The datasets for **3** and **4** were collected on a Bruker APEX CCD diffractometer; the dataset for **5** was acquired using a Bruker APEXII CCD diffractometer on Station 9.8 of the Daresbury Synchrotron Radiation Source. The structures were solved by direct methods using SIR92[21a] and refined by full-matrix least-squares on F^2 using SHELXL97.[21b] Hydrogen atoms were calculated in ideal positions and thereafter constrained to ride on their respective carbon atoms. In **3**, disorder was identified in two of the benzene solvent molecules; these molecules were refined as idealized planar hexagons with occupancies of 0.5 for each atom. A correction for nonmerohedral twinning by 180°-rotation about [−201] led to a refined twin fraction of 0.0506(11). In **4**, disorder in the $\mathrm{PF_6}^-$ ion was modeled by allowing two alternative positions for each fluorine atom. Similarity restraints were applied to the P−F bonds and F−P−F angles. The fluorine atom occupancies refined to approximately 0.5. Disorder was found in the phenyl ring of one of the solvent molecules: the ring was refined split over two orientations, each with half-occupancy atoms and with distance and planarity restraints applied to each component. CCDC 637360 (**3**), CCDC 637361 (**4**), and CCDC 637362 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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