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Synthesis and characterization of a *trans*-1 hexakis-fullerene linker that forms crystalline polymers with silver salts†

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A new flexible hexakis-fullerene adduct with two bis(pyridin-4-ylmethyl)malonate groups located at *trans*-1 positions was synthesized. *Via* reaction with $Ag(PF_6)$ under two different conditions, two new 1D coordination polymers were obtained; under a nitrogen atmosphere, the silver ions are connected by argentophilic interactions but under an ambient atmosphere, the silver ions exhibit no interaction between them but coordination to the $(H_2PO_4)^-$ ions.

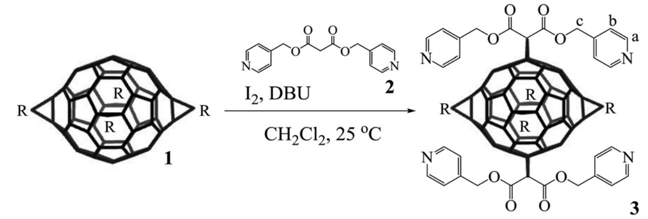
Introduction

Fullerene derivatives possess unique physicochemical properties and have potential applications as electronic, magnetic, catalytic, biological and optical materials.[1–10] The three-dimensional structure of the carbon sphere and the multiple reactive bonds on C_{60} make it an ideal candidate as a building block for the construction of interesting and functional supramolecular architectures.[11,12] So far, the synthesis of fullerene-based coordination polymers has been reported in only a few cases. For example, the piperazine adduct of C_{60}, $C_{60}(N(CH_2CH_2)_2N)$ was shown to react with $Ag(O_2CCF_3)$ to form a crystalline linear polymer,[13] and it also reacted with $Rh_2(O_2CCH_3)_4$ to afford a fullerene-containing network that can encapsulate free C_{60} and C_{70}.[14] Echegoyen *et al.* used the Kräutler's synthetic strategy[15] together with a Bingel–Hirsch reaction to prepare a *trans*-1 hexakisfullerene adduct with two *N*-containing 4,5-diazafluorene groups. This fullerene linker reacted with Ag(I) to form a one dimensional (1D) linear coordination polymer.[16] Similarly, a hexakisfullerene adduct with two pairs of phenylpyridine groups arranged in a *trans*-1 geometry was treated with cadmium nitrate to build a two-dimensional (2D) fullerene-based MOF.[12] Khlobystov, Schröder *et al.* synthesized bis(pyridin-4-ylmethyl)malonate fullerenes as flexible coordination linkers to react with $Ag(PF_6)$ resulting in the formation of dimeric and polymeric metallacyclic products.[17] Most fullerene linkers are rigid structures that react with metal ions to form the desired coordination polymers. Herein, we report a new flexible fullerene linker, compound **3**, which reacts with $Ag(PF_6)$ under different conditions to afford different coordination polymers.

Results and discussion

The synthetic procedure used to prepare the *trans*-1 hexakisfullerene linker **3** is shown in Scheme 1. Tetrakis[di(ethoxycarbonyl)methano]-C_{60} (**1**)[15] reacts with bis(pyridin-4-ylmethyl)malonate (**2**)[17] to afford the yellow *trans*-1 hexakisfullerene linker **3**.

The ^1H NMR spectrum of **3** (Fig. 1) displays two quartets centered at δ = 4.37 and 4.33 ppm and two triplets centered at δ = 1.35 and 1.33 ppm, that can be assigned to the methylene and methyl protons of the equatorial ethyl malonate groups. The ^{13}C resonances for the methylene and methyl carbons of the ethyl malonate groups appear at δ = 63.21, 63.13 and δ = 14.22, 14.20 ppm (Fig. S2†). The three signals (δ = 8.56, 7.18 and 5.26 ppm) in the downfield region of the ^1H NMR spec-



Scheme 1 Synthesis of compound **3**, R = $[C\text{-}(OOC_2H_5)_2]$.

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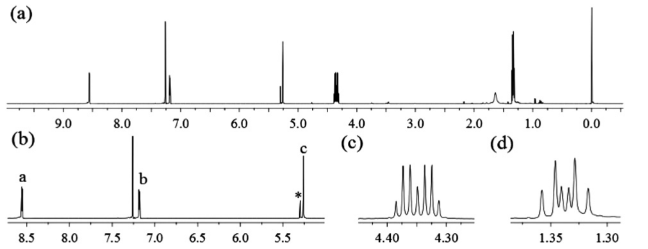

Fig. 1 (a) ^{1}H NMR spectrum of compound **3** (600 MHz, $CDCl_3$) and expanded parts: (b) 8.55–5.00 ppm, (c) 4.45–4.25 ppm, (d) 1.40–1.20 ppm. * represent solvent peak.

trum are assigned to the protons in the a, b and c positions of the bis(pyridin-4-ylmethyl)malonate, respectively (see Scheme 1). These features (the equivalency of the protons and carbons of the malonates and for the aromatic groups) clearly confirm the D_{2h} symmetry of **3**.

The UV-visible spectra of C_{60} derivatives are mainly determined by the properties of the cage, not by those of the addends.[18] The UV-visible absorption peaks of **3** in CH_2Cl_2 occur at λ_{max}: 271, 281, 317, 334 and 388 nm. This pattern is nearly identical to that for the *trans*-1 hexakis-[di(ethoxycarbonyl)methano]-C_{60} reported by Hirsch *et al.*[19] and to that of the *trans*-1 hexakis-fullerene adduct reported by Echegoyen *et al.*,[12] confirming the *trans*-1 hexakis-adduct structure determined by NMR.

Compound **3** contains a redox-active fullerene core, so its electrochemical properties were measured by cyclic voltammetry in dry, oxygen-free CH_2Cl_2 solution at 25 °C (Fig. S3†). Compound **3** exhibits an irreversible reduction at −1.79 V, which is attributed to the irreversible reductive removal of the cyclopropane rings, a process referred to as the "retro-Bingel reaction".[20–22]

Yellow-orange crystals of **3**·0.66(CH_2Cl_2) were grown by slow diffusion of hexane into a solution of **3** in dichloromethane. The X-ray diffraction structure of **3** is shown in Fig. 2, which again confirms that the two bis(pyridin-4-ylmethyl)malonate groups are in the *trans*-1 arrangement. The six cyclopropane rings that are fused to the C_{60} at 6 : 6-ring junctions have bond lengths in the range of 1.592(2)–1.604(2), which are typical of these C–C single bonds. The remaining C–C bond lengths are ~1.38 Å (6 : 6-junctions) and 1.45 Å (6 : 5-junctions). The C1, C2, C10, C17, C21 and C22 atoms are sp^3 hybridized and show distorted tetrahedral bonding patterns.

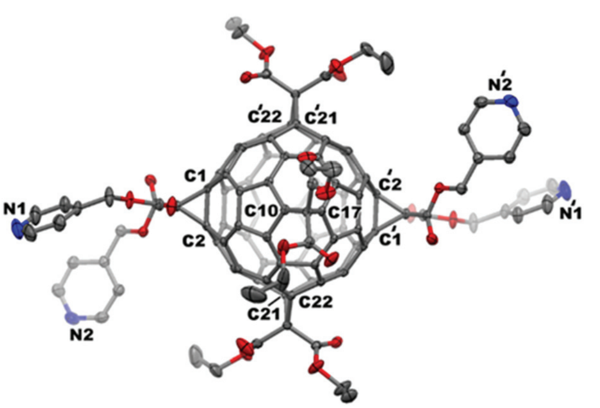

Fig. 2 A drawing of **3** with 30% thermal ellipsoids. Color code: carbon atoms, gray ellipsoids; oxygen atoms, red ellipsoids; nitrogen atoms, blue ellipsoids. Hydrogen atoms were omitted for clarity.

A linear 1D polymer, **4** with composition $\{[Ag_2(\mathbf{3})]\cdot(PF_6)_2\cdot 2(CH_3CN)\}_n$, was obtained by diffusion of an acetonitrile solution of $Ag(PF_6)$ into a dichloromethane solution of **3** followed by diffusion of toluene under a nitrogen atmosphere. The structure of polymeric **4** consists of a linear strand of molecules of **3** connected by coordination of the nitrogen atom in each pyridine ring to a bridging silver ion as shown in Fig. 3. Each silver ion in the chain is coordinated by two pyridine ligands from different molecules of **3**. There is some disorder in the positions of the silver ions. Ag1A has 0.40 fractional occupancy. In addition, there is a second silver site, Ag1B, which also has 0.40 occupancy, and a third site, Ag1C with 0.20 occupancy (Fig. S5†). The chain constructed using Ag1B is virtually identical to that shown in Fig. 2. In both of these cases the silver ions make argentophilic interactions with one another.[23] The Ag1A···Ag1A′ distance is 2.986(5) and the corresponding Ag1B···Ag1B′ distance is 3.178(10) Å. The Ag–N distances (Ag1A–N1, 2.166(7); Ag1A–N2, 2.066(5) Å) are comparable to those in $[(py)_2Ag](PF_6)$ where the Ag–N distances are 2.127(3) and 2.123(3) Å.[24] In polymeric **4**, the N1–Ag1A–N2 angle (161.3(3)°) is bent in an inward direction that facilitates the argentophilic interaction between the silver ions. The simple salt $[(py)_2Ag](PF_6)$ also displays argentophilic interactions with the shortest Ag···Ag distance equal to 3.0001(5) Å.[24] In the crystal, strands of the linear polymer run diagonally parallel to the ac plane as seen in the packing diagram in Fig. S6.† These polymeric strands are closely packed so that there are no significant voids in the crystal, but there are π–π interactions between pyridyl groups in neighboring strands. The $(PF_6)^-$ ions are not coordinated to the silver ions.

A second linear 1D polymer, compound **5** with composition $\{[Ag_2(\mathbf{3})(H_2PO_4)_{1.5}]\cdot(PF_6)_{0.5}\cdot(CH_3CN)\}_n$, was obtained by diffusion of a moist acetonitrile solution of $Ag(PF_6)$ into a dichloromethane solution of **3** followed by diffusion of toluene under air. Under these conditions partial hydrolysis of the $(PF_6)^-$ ion occurred, as has been observed previously.[25] The structure of polymeric **5** is shown in Fig. 4. The structure of this polymer and its packing (Fig. S7†) are similar to that of compound **4**. Individual molecules of precursor **3** are connected together through silver ions, which coordinate to the pyridine arms of neighboring molecules of **3**. In this case there are no argentophilic interactions between the silver ions. However, each silver ion is three coordinate with T-shaped bonding to an $(H_2PO_4)^-$ ion and the two pyridine nitrogen atoms. The Ag–N distances (Ag1–N1, 2.173(8); Ag1–N2, 2.196(8) Å) are similar to those in polymeric **4**. The Ag–O16 distance is 2.544(9) Å. The N1–Ag1–N2 bond angle is 162.0(3)°; while the N1–Ag1–O16 and N2–Ag1–O16 bond angles are 98.08(45) and 102.85(44), respectively. A similar structural

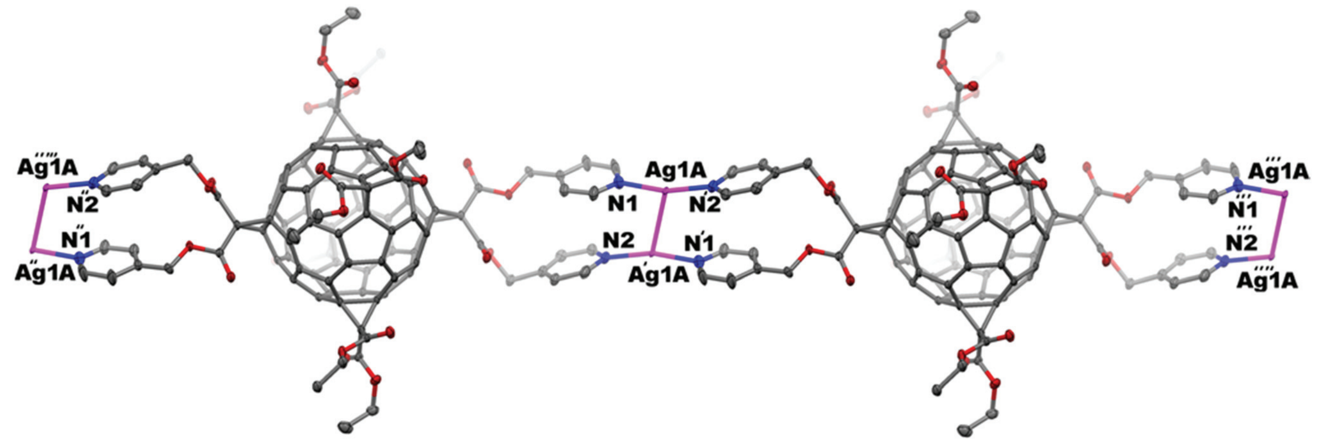

Fig. 3 A drawing of **4** with 30% thermal ellipsoids. Color code: carbon atoms, gray ellipsoids; oxygen atoms, red ellipsoids; nitrogen atoms, blue ellipsoids; silver ions, violet ellipsoids. For clarity, the anions and solvate molecules are not shown. Ag1A has 0.40 partial occupancy; the structure with Ag1B with 0.40 occupancy is virtually identical.

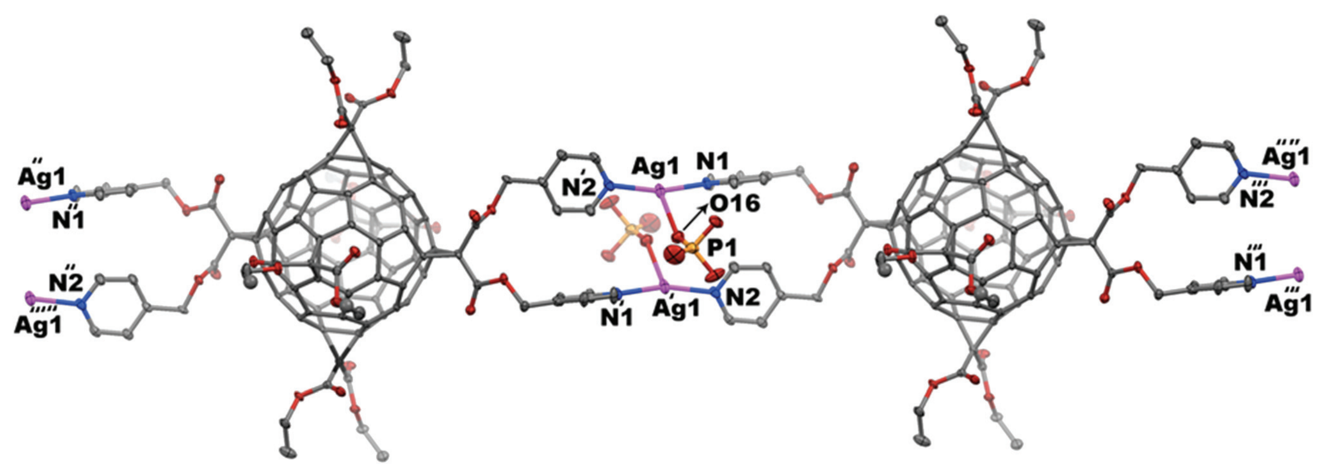

Fig. 4 A drawing of **5** with 30% thermal ellipsoids. Color code: carbon atoms, gray ellipsoids; oxygen atoms, red ellipsoids; nitrogen atoms, blue ellipsoids; silver ions, violet ellipsoids; phosphorous, yellow ellipsoids. For clarity, the disordered anions and solvate molecules are not shown.

arrangement is seen in the ladder polymer, [(Ag(4,4′-bipy)*n*-(H_2PO_4)]$_n$·(H_3PO_4)$_n$ which has Ag–N distances of 2.133(3) and 2.126(3) Å and an Ag–O distance (2.822(2) Å) that is significantly longer than the corresponding distance in polymeric **5**.[26] The hydrolysis reaction is incomplete since the $(H_2PO_4)^-$ site is shared by *ca.* 25% $(PF_6)^-$ in compound **5**.

Conclusions

In summary, the transparent, yellow, linear polymers **4** and **5** were prepared from a flexible fullerene linker compound, **3**, and Ag(PF_6) by crystallization under a nitrogen atmosphere or under ambient conditions, respectively. The silver ions in compound **4** are connected by argentophilic interactions while for compound **5** these interactions are replaced by $(H_2PO_4)^-$ and silver ion interactions. In both **4** and **5** the flexible, pyridine-containing arms adopt a parallel alignment that facilitates linear polymer formation. However, we expect that other molecules made from **3** may use these flexible arms to form two-dimensional networks as well, and may find applications in gas adsorption/storage and adsorption of organic molecules.

Experimental

General procedure

All reactions were conducted under an atmosphere of purified dinitrogen using standard Schlenk techniques. All chemicals were obtained from commercial sources and used without further purification. Infrared spectra were recorded on a Bruker Tensor27 IR spectrometer. The NMR spectra were recorded using a JEOL 600 NMR spectrometer. The UV-vis spectrum was recorded using a Cary 5000 UV-vis-NIR spectrophotometer. Matrix-assisted laser desorption ionization (MALDI) mass spectra were recorded on a Bruker Microflex LRF mass spectrometer. Cyclic voltammetry was carried out in a one compartment cell using a BAS 100B workstation in a solution of dichloromethane containing 0.1 M n-Bu_4NPF_6. A 2 mm diameter glassy carbon disk was used as the working electrode, silver wire as a pseudo reference and a platinum wire as a counter electrode. Ferrocene was added to the solution at the end of each experiment as an internal potential standard. Tetrakis-[di(ethoxycarbonyl)methao]-C_{60} and bis-(pyrindin-4-ylmethyl)malonate were prepared as described in the literature.[15,17]

Synthesis of *trans*-1 hexakis-adduct 3

To a solution of 100.0 mg (0.074 mmol) of **1**, 41.5 mg (0.163 mmol) of I_2, and 46.5 mg (0.162 mmol) of bis-(pyrindin-4-ylmethyl)malonate **2** in 50 mL of CH_2Cl_2 was added 44 μL (0.294 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The reaction mixture was allowed to stir at room temperature overnight. The solvent was then removed under reduced pressure and the mixture was purified by silica gel column to get a light yellow solid (48.6 mg, 34% yield). ^1H NMR ($CDCl_3$, 20 °C): δ = 8.56 (s, 8H), 7.18 (d, 8H, J = 6 Hz), 5.26 (s, 8H), 4.37 (q, 8H, J = 7.2 Hz), 4.33 (q, 8H, J = 7.2 Hz), 1.35 (t, 12H, J = 7.2 Hz), 1.33 ppm (t, 12H, J = 7.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 163.81, 163.47, 150.24, 146.07, 145.95, 145.84, 143.31, 141.36, 141.31, 140.71, 122.54, 69.31, 69.16, 68.94, 66.68, 63.21, 63.13, 45.67, 45.54, 44.54, 14.22, 14.20 ppm. MALDI-TOF-MS: (positive ionization 1,1,4,4-tetraphenyl-1,3-butadiene as matrix): [M^+] 1920.40. UV-vis (CH_2Cl_2): λ_{max}/nm (ε, 10^3 M^{-1} cm^{-1}) = 271 (127), 281 (132), 317 (84), 334 (68) and 388 (9).

X-ray crystallography and data collection of 3

Crystals were grown by a slow diffusion of hexane into a solution of **3** in dichloromethane followed by diffusion of toluene into the resulting solution under an ambient atmosphere. Crystal data for **3**·0.66(CH_2Cl_2), $C_{118.66}H_{65.32}Cl_{1.32}N_4O_{24}$, M = 1977.78, orange prism, λ = 0.71073 Å, monoclinic, space group $P2_1/n$, a = 14.9602(5), b = 15.7483(5), c = 20.3226(6) Å, α = 90°, β = 103.750(2)°, γ = 90°, T = 100(2) K, V = 4650.7(3) Å^3, Z = 2, 58983 reflections measured, 13 168 unique (R_{int} = 0.0285), Bruker SMART APEX CCD; $2\theta_{max}$ = 59.36°; the ratio of minimum to maximum apparent transmission was 0.950 (multi-scan absorption correction applied); direct and Patterson methods solution; full-matrix least squares based on F^2 (SHELXT and SHELXL-2014); final w$R(F_2)$ = 0.2180 (all data), conventional R_1 = 0.0655 for 9605 reflections with $I > 2\sigma(I)$ with 742 parameters and 44 restraints.

X-ray crystallography and data collection of 4

Crystals were grown by a slow diffusion of an acetonitrile solution of $AgPF_6$ into a solution of **3** in dichloromethane followed by diffusion of toluene into the resulting solution under a nitrogen atmosphere. Crystal data for $\{3Ag_2(PF_6)_2\cdot 2(CH_3CN)\}_n$ (**4**). $C_{122}H_{70}Ag_2N_6O_{24}P_2F_{12}$ M = 2509.52, yellow needle, 0.200 × 0.075 × 0.025 mm, λ = 1.5417 Å, triclinic, space group $P\bar{1}$(no. 2), a = 10.1664(4), b = 14.1537(6), c = 20.4581(8) Å, α = 72.474(2)°, β = 81.9800(18)°, γ = 78.445(2)°, T = 90(2) K, V = 2740.3(2) Å^3, Z = 1, 39 479 reflections measured, 8706 unique (R_{int} = 0.0471) which were used in all calculations, Bruker Apex Duo; $2\theta_{max}$ = 136.5°; min/max transmission = 0.6088/0.7531 (multi-scan absorption correction applied); direct and Patterson methods solution; full-matrix least squares based on F^2 (SHELXT and SHELXL-2014); The final w$R(F_2)$ was 0.2323 (all data), conventional R_1 = 0.0884 computed for 866 reflections with $I > 2\sigma(I)$ using 875 parameters with 113 restraints. PLATON/SQUEEZE was employed to account for the missing electron density of disordered solvent molecules with low occupancies in the structure.

X-ray crystallography and data collection of 5

Crystals were grown by a slow diffusion of an acetonitrile solution of $AgPF_6$ into a solution of **3** in dichloromethane followed by diffusion of toluene into the resulting solution under an ambient atmosphere.

Crystal data for $\{3Ag_2(H_2PO_4)_{1.5}(PF_6)_{0.5}\cdot(CH_3CN)\}_n$ (5). $C_{120}H_{67}Ag_2F_3N_5O_{30}P_2$ M = 2393.46, yellow needle, 0.094 × 0.047 × 0.019 mm, λ = 1.0333 Å (synchrotron radiation at Beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley Laboratory), triclinic, space group $P\bar{1}$(no. 2), a = 10.0910(6), b = 14.7707(9), c = 16.9006(11) Å, α = 105.067(3)°, β = 94.215(4)°, γ = 93.227(3)°, T = 100(2) K, V = 2418.4(3) Å^3, Z = 1, 32870 reflections measured, 8653 unique (R_{int} = 0.0658) which were used in all calculations, Bruker ApexII; $2\theta_{max}$ = 76.99°; min/max transmission = 0.5944/0.7476 (multi-scan absorption correction applied); direct and Patterson methods solution; full-matrix least squares based on F^2 (SHELXT and SHELXL-2014); The final w$R(F_2)$ was 0.2214 (all data), conventional R_1 = 0.1057 computed for 6518 reflections with $I > 2\sigma(I)$ using 760 parameters with 8 restraints.

Acknowledgements

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