

# High yield synthesis of a new fullerene linker and its use in the formation of a linear coordination polymer by silver complexation†‡

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**A new hexakis-fullerene adduct with two 4,5-diazafluorene groups strategically located at *trans*-1 positions to allow linear polymerization was selectively synthesized in very high yield. By reaction with Ag(triflate), a one dimensional metal-organic coordination polymer was obtained.**

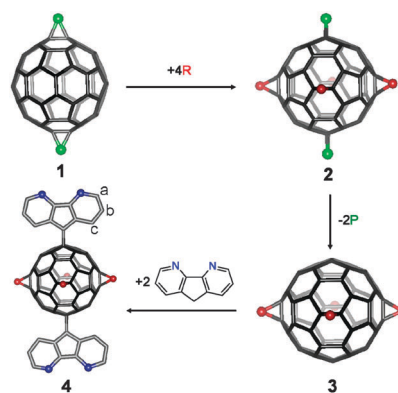
The spherical shape, high degree of symmetry and multiplicity of reactive bonds of C<sub>60</sub> make it an ideal candidate for the assembly of supramolecular structures.<sup>1</sup> However, the use of C<sub>60</sub> linkers to make new materials has been limited by the relatively low yields of regioselectively functionalized C<sub>60</sub>. Controlling the regioselectivity of *trans*-1 additions to C<sub>60</sub> in high yield is a challenging task.<sup>2</sup> A method called orthogonal transposition was introduced by Kräutler and co-workers in 1997, where the C<sub>60</sub> sphere was protected-functionalized-deprotected and the *trans*-1 positions remained for further functionalizations.<sup>3</sup> Based on this protection-deprotection synthetic strategy, a series of *trans*-1 hexakis-fullerene adducts using a 1,3-dipolar cycloaddition reaction were prepared, however, the yields were very low due to the presence of multiple isomers.<sup>4-6</sup>

Herein we report the use of Kräutler's synthetic method together with a Bingel-Hirsch reaction at room temperature to prepare *trans*-1 hexakis-fullerene adduct **4** in very high yield. Compound **4** exhibits two ligands in a linear *trans*-1 arrangement, offering the opportunity to form a 1D coordination polymer by assembly with metal ions.

The synthesis of **4** was accomplished following Scheme 1, starting with bisadduct of C<sub>60</sub> **1** with anthracene protecting groups, followed by the symmetric addition of four diethyl malonate groups to the equatorial positions to yield **2** as previously reported

by Kräutler *et al.*<sup>3</sup> The anthracene groups were removed by a retro-Diels-Alder reaction to yield **3**.<sup>7,8</sup> Subsequently, reaction of **3** with 4,5-diazafluorene in dichloromethane at room temperature produced the hexakis *trans*-1 adduct **4** in a remarkable 91% yield. A similar compound was previously synthesized by Rubin and Qian using a multi-step sequence which resulted in extremely low product yields.<sup>9</sup> The reasons for selecting 4,5-diazafluorene are that, not only does this compound have good Bingel-Hirsch regioselectivity and high polarity for relatively easy purification,<sup>10</sup> but it has also been widely studied as a dinitrogen chelating ligand which exhibits exceptional affinity for metal ion coordination.<sup>11,12</sup> It is worth mentioning that the 4,5-diazafluorenes are planar and ideally lie essentially perpendicular to the fullerene surface, thus the bipyridine groups are situated at 180° relative to each other, which makes this compound an ideal linear linking component.

Fig. 1 shows the <sup>1</sup>H NMR spectrum of **4**. The most notable features are the signals from the malonate groups. Two quartets centered at δ = 4.46 and 4.23 ppm and two triplets centered at δ = 1.42 and 1.25 ppm can be assigned to the methylene and methyl groups of the malonates located on the equatorial belt of the C<sub>60</sub>. The three signals (δ = 8.82, 8.70 and 7.42 ppm) in the downfield



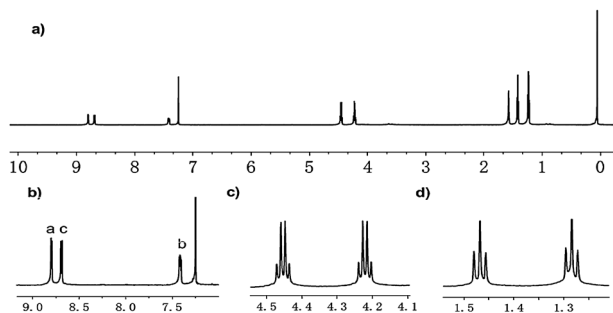
**Scheme 1** Synthesis of the *trans*-1 4,5-diazafluorene adduct of C<sub>60</sub>-tetramalonate, **4**, where P (green balls) are the protecting groups, anthracenes, and R (red balls) are the malonate groups, C(OOC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, blue balls are nitrogen atoms.

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† Dedicated to Prof. Maurizio Prato on the occasion of his C60th birthday.

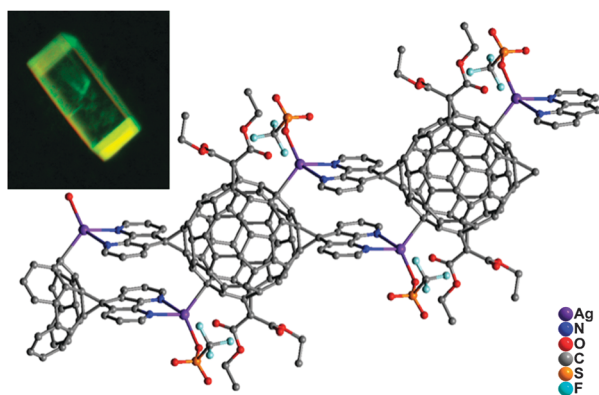
‡ Electronic supplementary information (ESI) available. CCDC 785701 and 785702. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc40697k



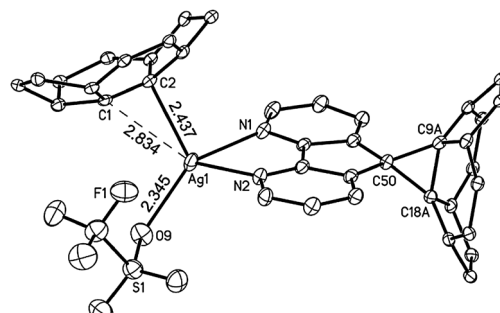
**Fig. 1** (a)  $^1\text{H}$  NMR spectrum of **4** (600 MHz,  $\text{CDCl}_3$ ) and expanded parts: (b) 9.10–7.25 ppm, (c) 4.60–4.20 ppm, and (d) 1.60–1.20 ppm.

region of the spectrum are assigned to the hydrogen atoms in the a, c and b positions of the 4,5-diazafluorene ring, respectively (see Scheme 1). The equivalency of the protons in both of the 4,5-diazafluorene groups and the two well-defined quartets and triplets from the two magnetically inequivalent ethyl groups of the equatorial malonates unequivocally verify that compound **4** contains *trans*-1 diazafluorene groups.

Yellow-green crystals of polymeric 4-2Ag(triflate)-5toluene, **4a**, were obtained by slow diffusion of Ag(triflate) in methanol into a solution of **4** in dichloromethane followed by the addition of toluene. The asymmetric unit of compound **4a** contains  $\frac{1}{2}$  of a molecule of **4**, one Ag(triflate), and  $2\frac{1}{2}$  toluene molecules. The rest of the structure is generated by inversion through a center of symmetry, which lies at the middle of the fullerene cage. No intermolecular interactions between fullerene units were observed due to the presence of four bulky equatorial ethyl malonate groups on the  $\text{C}_{60}$  cage. Fig. 2 shows a drawing of a portion of the polymeric chain. Each fullerene unit coordinates to two silver ions through the two *trans*-diazafluorene appendages. Additionally, these silver ions bind to carbon atoms of neighboring molecules of **4** in  $\eta^1$ -fashion. Face-to-face  $\pi$ - $\pi$  stacking interactions are clearly observed between diazafluorene rings on adjacent fullerenes, with a distance of 3.65 Å. Fig. 3 focuses on the local coordination environment of the silver ion in **4a**. Each silver ion is tetra-coordinated with bonds to one oxygen atom of a triflate group with a Ag–O distance of 2.345(2) Å, two nitrogen atoms from one diazafluorene unit with Ag–N distances of 2.360(2) and 2.433(2) Å, and one carbon atom from a neighboring



**Fig. 2** A portion of the structure of **4a**, a 1D polymer, showing the face-to-face  $\pi$ - $\pi$  interaction of the 4,5-diazafluorene ligand. Front and back malonate addends have been omitted for clarity. The inset shows a photograph of a crystal of the polymer.



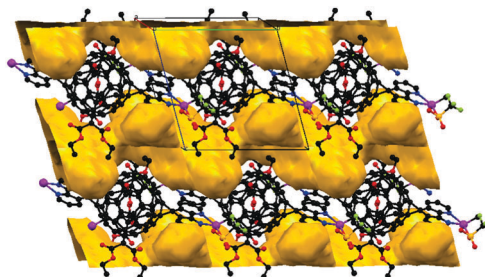
**Fig. 3** The coordination environment in **4a** of Ag(triflate) and the  $\text{C}_{60}$  fullerene with the 4,5-diazafluorene from the adjacent fullerene with 50% thermal contours.

$\text{C}_{60}$  cage with a Ag–C distance of 2.437(2) Å, which is in agreement with reported values for Ag–C bonds.<sup>13,14</sup> The second closest contact between silver and the  $\text{C}_{60}$  cage is at a distance of 2.834(3) Å, so the silver fullerene coordination is described as  $\eta^1$ , not  $\eta^2$ . The angles about the silver ion are N1–Ag1–N2, 75.49(6)°; N1–Ag1–C2, 90.02(7)°; N2–Ag1–C2, 124.34(7)°; O9–Ag1–N1, 140.26(6)°; O9–Ag1–N2, 104.42(7)°; O9–Ag1–C2, 118.90(7)°. Therefore, the coordination geometry of the silver center can be considered as distorted tetrahedral. The silver atom deviates from the plane of the 4,5-diazafluorene ligand by 0.312(3) Å towards the triflate group and away from the closest fullerene. The interaction between a  $\text{Ag}^+$  and a fullerene cage was observed early in 1996 using spectroscopic techniques,<sup>15,16</sup> but the first example of direct coordination between  $\text{C}_{60}$  and  $\text{Ag}^+$  was observed crystallographically by Balch *et al.* in  $\text{C}_{60}\{\text{Ag}(\text{NO}_3)\}_5$ .<sup>17</sup>

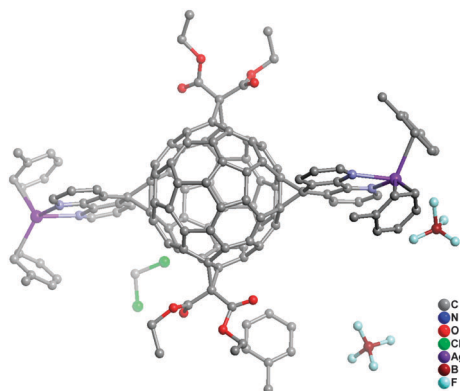
Given that each silver ion was expected to be coordinated by two pairs of 4,5-diazafluorene nitrogen atoms from two different fullerene units, an infinite polymeric chain structure with alternate silver ions and fullerene units was anticipated. Although the bidentate 4,5-diazafluorene ligand promotes the polymerization process, and an unexpected Ag–C( $\text{C}_{60}$ ) and Ag–O(– $\text{SO}_3$ ) coordination occurs, producing a different result from the expected straight polymeric chain structure.

The one-dimensional polymer, **4a**, propagates in the crystallographic *b* direction and therefore has a repeat of 14.330(3) Å. In the unit cell, five toluene molecules occupy a large space of 854 Å<sup>3</sup> per unit cell between the 1-dimensional polymer chains. This space, shown in yellow in Fig. 4, comprises approximately 31% of the unit cell volume.<sup>18</sup>

Unlike many adducts of  $\text{C}_{60}$ , which form nearly black solids, the addition pattern in **4** produces more optically transparent compounds with only a light yellow color (**4**,  $\lambda_{\text{max}}$ : 245, 285, 316,



**Fig. 4** Toluene solvent voids in **4a** shown in yellow occupying approximately 31% of 4-2Ag(triflate)-5toluene.

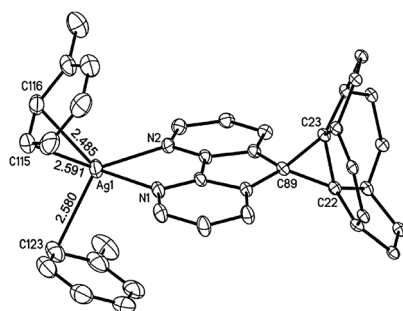


**Fig. 5** A drawing of the structure of **4b**. Hydrogen atoms and front and back malonate groups have been omitted for clarity.

340 and 392 nm).<sup>19,20</sup> As seen in the inset of Fig. 2, crystals of polymeric **4a** also have a transparent, yellow color with virtually no absorption in the visible region (**4a**,  $\lambda_{\text{max}}$ : 365, and 421 nm). Thus, **4** is a building block for new materials in which chromophoric components absorbing in the visible range can be introduced and detected without interference from the fullerene absorption.

Yellow crystals of the salt  $[4\cdot\{\text{Ag}(\text{toluene})_2\}_2](\text{BF}_4)_2\cdot\text{CH}_2\text{Cl}_2$ , **4b**, were obtained by slow diffusion of  $\text{AgBF}_4$  in methanol into a solution of **4** in dichloromethane followed by addition of a layer of toluene. A drawing of the molecular structure of **4b** is shown in Fig. 5. Two malonate groups are omitted in the drawing. There is no crystallographic symmetry in the structure. However, in other respects, the hexakis fullerene adduct is the same as that in **4a**. Surprisingly and in contrast to **4a**, **4b** is not polymeric, since each silver ion is bound to two toluene molecules, a situation that disrupts any sort of chain propagation. Additionally, **4b** is a salt with  $\text{BF}_4^-$  anions that do not coordinate to the silver ions.

Fig. 6 shows the local coordination environment of  $\text{Ag1}$  in **4b**. The distances between  $\text{Ag1}$  and the nitrogen atoms are



**Fig. 6** A view of the local environment of  $\text{Ag1}$  in **4b** showing how polymerization cannot occur due to capping of the silver ion by two molecules of toluene. Drawn with 50% thermal contours.

2.382(2) Å and 2.363(2) Å, respectively. As expected, these distances are similar to the analogous Ag–N distances in **4a**. The tetrahedrally coordinated silver ion exhibits an  $\eta^1$  coordination to one toluene with an Ag1–C123 distance of 2.580(3) Å and an  $\eta^2$  coordination to the second toluene with Ag1–C115 and Ag1–C116 distances of 2.591(4) and 2.485(3) Å, respectively. The local coordination environment of  $\text{Ag2}$  in **4b** is similar to that of  $\text{Ag1}$ , but one of the toluene ligands is disordered.

In summary, a new hexakis fullerene adduct with two 4,5-diazafluorene groups located at *trans*-1 positions was prepared in remarkable high yield and converted into a linear chain through coordination of  $\text{Ag}(\text{triflate})$ .

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