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Selective Syntheses of Novel Polyether Fullerene Multiple Adducts

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We have applied a modified macrocyclic tether approach to control multiple additions to C_{60}. The technique of ^{3}He NMR was used to confirm the selective formation of specific C_{60} multiple adducts by the macrocyclic tether approach. An oligoglycol was used as a flexible linker to produce macrocyclic polyether-linked malonates **5**, **6**, **8**, and **9** under solid−liquid PTC (phase-transfer-catalysis) conditions. The formation of a single C_{60} tris-adduct, **3**, from macrocyclic malonate **1** and ^{3}He@C_{60} was proven by ^{3}He NMR. Similarly, multiple additions to C_{60} of macrocyclic polyether malonate **5** gave C_{60} bis-adduct **10** selectively, while the reaction of C_{60} with macrocyclic malonate **8** gave bis-adducts **11** and **12**. A similar process with macrocyclic malonate **6** gave tris-adduct **13** with high selectivity as well. Saponification of these C_{60} multiple adducts gives the corresponding polyacids that are potentially useful in biological applications. Macrocyclic polyether fullerenes are a new class of ionophores, which could be interesting for molecular recognition and for the development of biosensors.

Introduction

Since the discovery of C_{60}, syntheses and properties of its derivatives have become the focus of intensive study.[1] C_{60} multiple adducts have been widely used in a variety of fields of science. In particular, multiple adducts with a defined three-dimensional structure are of increasing interest with respect to their electrochemical,[2] chiroptical,[3] spectroscopic,[4] biological,[5−8] and material properties.[9−11] The usual method for syntheses of C_{60} multiple adducts is stepwise addition. For the widely used Bingel−Hirsch reaction,[12] the second addition of diethyl malonate leads to a mixture of eight bis-isomers. Although the equatorial and *trans*-3 bis-adducts are favored, the selectivity is quite poor. Further addition to certain bis-adducts shows higher selectivity, but chromatographic separation of isomers becomes increasingly more difficult. To overcome these difficulties, several research groups have independently developed synthetic methods to produce isomeric bis- and tris-adducts with higher selectivity.[13−15] Recently, Hirsch and co-workers have come up with a tether-directed approach, in which macrocyclic malonates incorporating alkyldiols as linkers between the malonate groups were used to control multiple additions to C_{60}.[16]

We are interested in designing and developing C_{60} multiple adducts with defined three-dimensional structures, which have poly-oxygen binding sites for complexation with biologically relevant substances, such as metal cations and alkylammonium ions. We modified Hirsch's approach for the selective preparation of polyether fullerene bis- and tris-adducts, using macrocyclic polyether malonates to control the remote multifunctionalization of C_{60}. The technique of ^{3}He NMR has been found to be a powerful and reliable tool for characterization of C_{60} multiple adducts,[17,18] and it was used to confirm the

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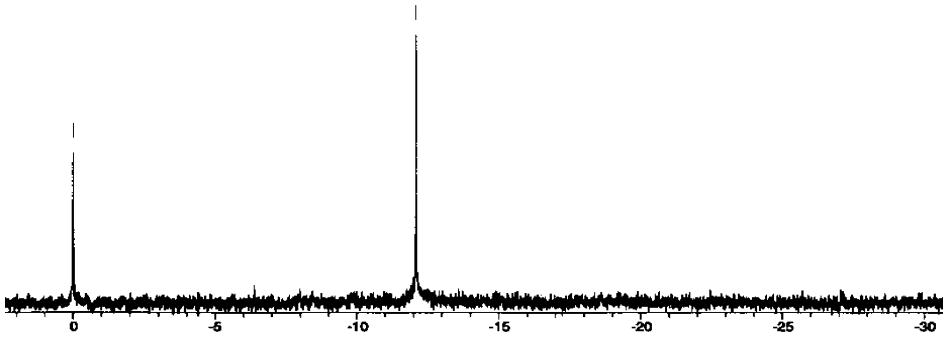


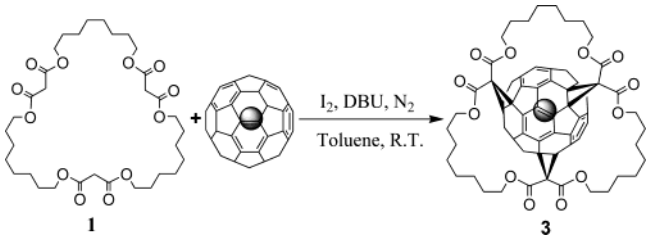
FIGURE 1. ^{3}He NMR spectrum of reaction mixture of **1** with ^{3}He@C_{60} (the peak at −0.001 ppm is gaseous ^{3}He).

selectivity of the new tether-directed approach and to identify the formation of specific C_{60} bis- and tris-adducts. Instead of alkyldiols, triethylene glycol and tetraethylene glycol were used as flexible linkers to produce macrocyclic malonates with two or three Bingel reacting species. These macrocyclic malonates gave specific bis- or tris-addition to C_{60} depending on the length and flexibility of the linkers incorporated between the malonate groups. One advantage of this approach is that the saponification of the C_{60} multiple adducts gives the corresponding *tetra*-acids or *hexa*-acids with defined three-dimensional structures. These fullerene polyacids are very important from the point of biological applications, which are landmarked by the discovery of the neuroprotective properties of water-soluble C_3- and D_3−C_{60} *hexa*-acids by Dugan.[6] In addition, macrocyclic polyether fullerenes represent a new class of ionophores, which are potentially size-selective synthetic receptors in molecular recognition for alkali metal cations and biologically relevant alkylammonium ions, including protonated amines, guanidinium ions, amino acids, and dendritic oligoamines. Therefore, macrocyclic polyether fullerenes could be of interest for the development of biosensors.[19]

Results and Discussion

Synthesis and ^{3}He NMR Characterization of *e,e,e* C_{60} Tris-adduct. The technique of ^{3}He NMR has been found to be a reliable and convenient tool for characterization of C_{60} bis- and tris-adducts.[17,18] We employed this technique to confirm the selective formation of specific C_{60} multiple adducts by the tether-directed approach. First, we used ^{3}He NMR to determine the selectivity of Hirsch's tether approach. Macrocyclic malonate **1** was prepared following the reported procedure, by condensation of octanediol with malonyl dichloride.[16] Reaction of macrocyclic malonate **1** with C_{60} under Bingel conditions gave only one isomer of tris-adduct **2**, identified as the *e,e,e* tris-adduct with C_3 symmetry based on ^{13}C NMR, MS, and UV−vis data.[16] Similarly, the reaction of macrocyclic malonate **1** with ^{3}He@C_{60} in place of pristine C_{60} under Bingel conditions produced one single isomer of tris-adduct **3** (Scheme 1). Without any purification, the

SCHEME 1



reaction mixture from **1** and ^{3}He@C_{60} was directly subjected to ^{3}He NMR analysis. The ^{3}He NMR spectrum afforded only one sharp peak at −12.085 ppm, which is the precise ^{3}He chemical shift for a C_{60} tris-adduct with the *e,e,e* addition pattern (Figure 1).[18] Therefore, ^{3}He NMR was used to monitor the selectivity of our modified tether-directed approach.

Preparation and Characterization of Macrocyclic Polyether Malonates. Macrocycles **5** and **6** with two and three identical linkers, respectively, were prepared from the condensation of malonyl dichloride with triethylene glycol under solid−liquid phase-transfer-catalysis (PTC) conditions using KF as base and template, triethyl(benzyl)ammonium chloride (TEBA) as catalyst, and dichloromethane as solvent (Scheme 2).[20] Macrocycles with different ring size were separated by flash chromatography. Macrocycles with more than three malonate units were also obtained. The yields of **5** and **6** were improved, compared with those in the absence of PTC conditions. Macrocycles **5** and **6** were fully characterized by ^{1}H NMR, ^{13}C NMR, and mass spectrometry.

Similarly, the condensation of tetraethylene glycol with malonyl dichloride under PTC conditions afforded a series of macrocycles with identical linkers in different ring sizes. Macrocycle **7** with one malonate unit, **8** with two malonate units, and **9** with three malonate units were separated in pure form and fully characterized, but the yields of **8** and **9** were lower than those of **5** and **6**, respectively (Scheme 3).

Preparation and Characterization of Macrocyclic Polyether Fullerenes. Macrocycle **5** reacted cleanly with C_{60} to produce only one bis-adduct **10**, with the *cis*-3 addition pattern, in the presence of I_2 and DBU in toluene (Scheme 4). Compound **10** was obtained in pure form in

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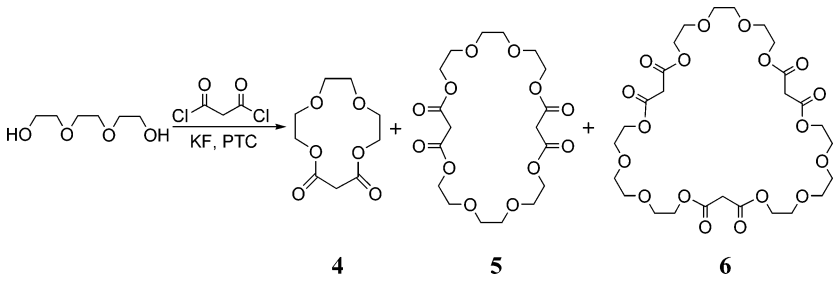
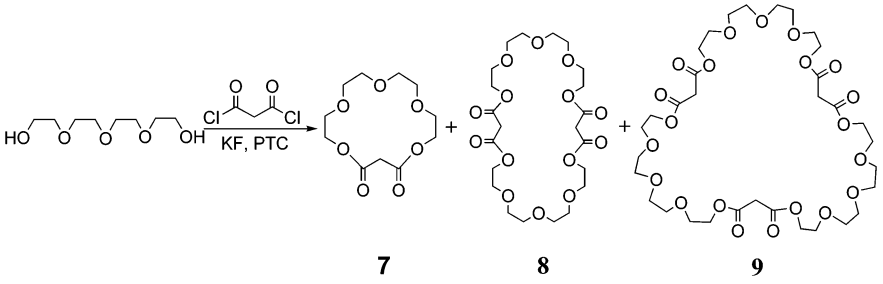
SCHEME 2



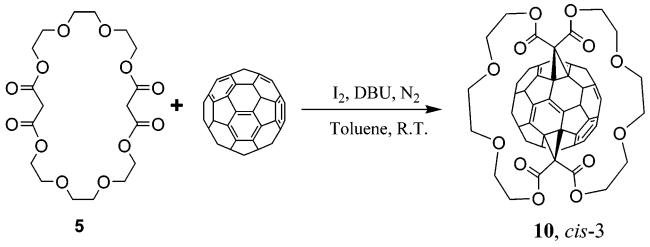
4 **5** **6**

SCHEME 3



7 **8** **9**

SCHEME 4



5 **10**, *cis*-3

up to 60% yield after unreacted C_{60} and oligomeric products were removed by flash chromatography. Polyether fullerene **10** was characterized by ^{1}H NMR, ^{13}C NMR, ^{3}He NMR, MS, and UV−vis spectral data. The UV−vis spectrum of **10**, shown in Figure 4, is identical to that of the *cis*-3 bis-adduct of diethyl malonate to C_{60}.[12] ^{3}He NMR analysis confirmed the formation of a single bis-adduct with the *cis*-3 addition pattern. The ^{3}He NMR spectrum of the crude reaction mixture from **5** and ^{3}He@C_{60} showed only one sharp peak for bis-adducts at −10.236 ppm (Figure 2), which is the precise chemical shift for the *cis*-3 C_{60} bis-adduct of diethyl malonate.[18]

Similarly, macrocyclic polyether malonate **8** reacted with C_{60} under Bingel conditions selectively to produce two isomeric C_{60} bis-adducts. Bis-adduct **11** with the *cis*-3 addition pattern and bis-adduct **12** with the equatorial addition pattern were separated by flash chromatography over silica gel and were obtained in pure form in a ratio of 3.5:1 (Scheme 5). Both isomers were characterized by NMR and mass data. The UV−vis spectrum of **11**, shown

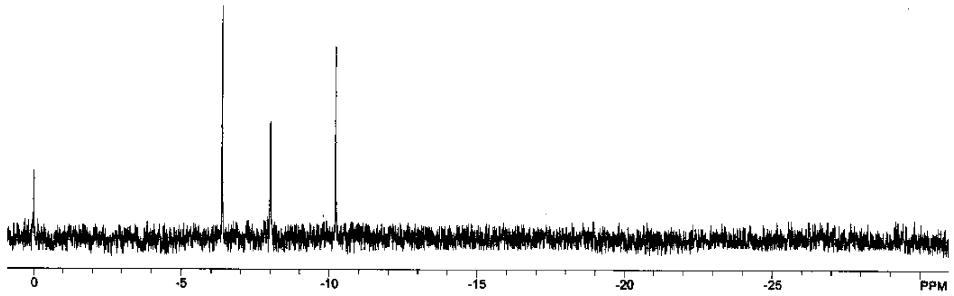
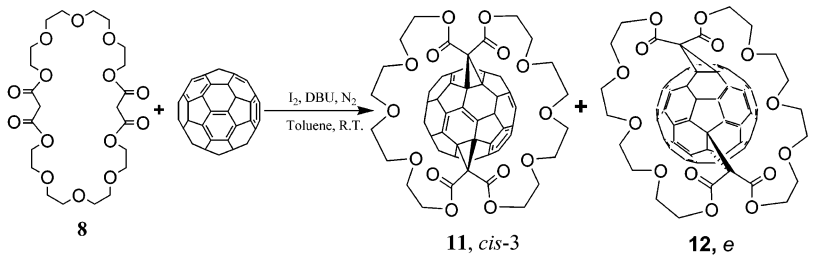


FIGURE 2. ^{3}He NMR spectrum of reaction mixture of **5** with ^{3}He@C_{60} showing a peak at −10.236 ppm for the *cis*-3 bis-adduct.[18] (Note: the peak at −0.009 is gaseous ^{3}He, the peak at −6.371 is ^{3}He@C_{60}, and the peak at −8.018 ppm is a mono-adduct).

SCHEME 5



8 **11**, *cis*-3 **12**, *e*

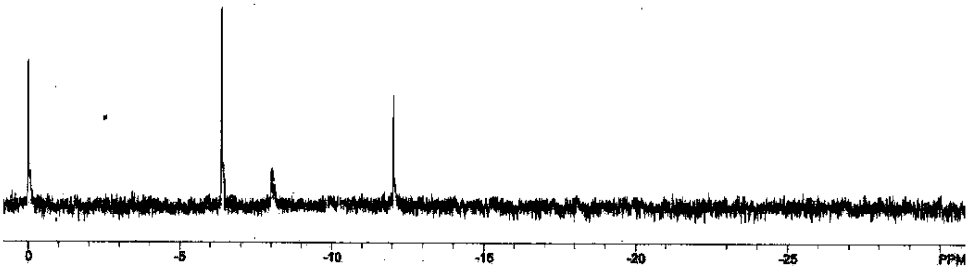


FIGURE 3. ^{3}He NMR spectrum of reaction mixture of **6** with ^{3}He@C_{60}. The peak at −12.040 corresponds to the expected C3 tris-adduct.[18] (Note: peak at −0.009 is gaseous ^{3}He, the peak at −6.373 is unreacted ^{3}He@C_{60}, and the peak at −8.016 ppm corresponds to an unknown mono-adduct).

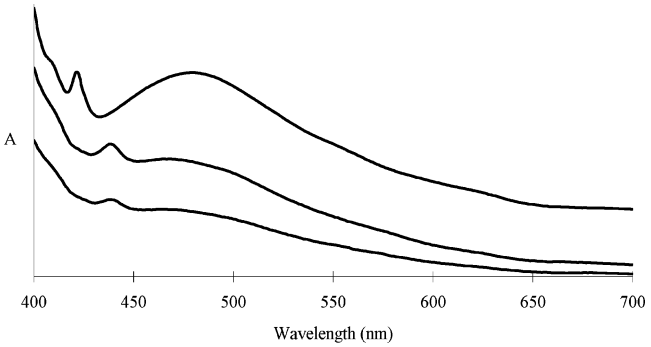
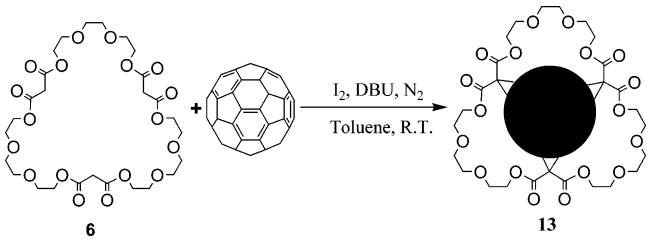


FIGURE 4. UV−vis spectra of C_{60} bis-adducts (**10**, **11**, and **12** from bottom to top) in the region of 400−700 nm.

SCHEME 6



in Figure 4, matches the UV−vis spectrum of C_{60} bis-adducts with the same addition pattern, such as compound **10**. Compound **12** shows the characteristic UV−vis absorption spectrum of a C_{60} bis-adduct with the equatorial addition pattern in the region of 400−700 nm (Figure 4).[12]

The specific addition patterns of C_{60} bis-adducts prepared by our tether-directed method depend on the distance between the two malonate groups that is determined by the length and flexibility of the linkers incorporated between the two malonate groups. Macrocyclic bis-malonates bearing two identical linkers prefer to give C_2-symmetric bis-addition patterns, while those bearing two proper different-length linkers prefer to give C_s-symmetric bis-addition patterns to avoid introducing ring strains.[16] In our study, only identical linkers were used, so the macrocyclic bis-malonates preferably generated bis-adducts with C_2 symmetry, which explained the lower yield of C_s-symmetric bis-adduct **12** in the ratio of 1:3.5 to C_2-symmetric bis-adduct **11**.

Tris-malonate macrocycle **6** reacted with C_{60} to afford only one tris-adduct isomer, **13**, in the presence of I_2 and DBU in toluene at room temperature (Scheme 6). The isolated yield was about 51%, slightly lower than that of bis-adduct **10**. Tentatively, the structure of tris-adduct **13** can be assigned as *trans*-4, *cis*-3, *cis*-3. Compound **13** was characterized by NMR, MS, and UV−vis. Its UV−vis spectrum did not match that of any previously reported tris-adduct of C_{60}. The ^{3}He NMR spectrum of the crude reaction mixture of **6** and ^{3}He@C_{60} confirmed the formation of only one tris-adduct, which showed a sharp peak at −12.040 ppm (Figure 3). But polyether tris-malonate **9** did not react with C_{60} under similar conditions, which could be explained by the highly polar nature of tris-malonate **9**.

Conclusions

An approach for directed selective syntheses of multiple adducts of C_{60} employing macrocyclic bis- and tris-malonates incorporating flexible polyether linkers was explored, and ^{3}He NMR spectrometry was used to confirm the selective formation of specific C_{60} multiple adducts. Macrocyclic malonate **1** gave only one isomeric tris-adduct with the *e,e,e* addition pattern, identified using ^{3}He NMR. A polyether macrocycle with two malonate units, **5**, afforded exclusively the C_2-symmetric *cis*-3 bis-adduct **10** in high yield. However, its analogue **8** gave two isomeric bis-adducts, **11** with a C_2-symmetric *cis*-3 addition pattern and **12** with a C_s-symmetric equatorial addition pattern. The specific bis-addition patterns depend on the distance between the two malonate groups, which is governed by the length and flexibility of the linkers, and the symmetry of the respective bis-addition patterns. Similarly, an analogous polyether macrocycle **6** with three malonate units led to the specific formation of a single tris-adduct, **13** in high yield, but polyether tris-malonates **9** did not react with C_{60} under similar conditions. All the polyether fullerene multiple adducts and the corresponding precursors were characterized using ^{1}H NMR, ^{13}C NMR, ^{3}He NMR, UV−vis spectroscopy, and mass spectrometry. Saponification of our C_{60} multiple adducts results in the corresponding fullerene polyacids that are potentially biological active.[6] Macrocyclic polyether fullerenes also represent a new class of ionophores, which can noncovalently bind with biologically relevant species including metal cations and alkylammonium ions.[20] Therefore, they could be interesting for the development of biosensors and for molecular recognition.[21] The approach provides a facile access to functionalized polyether fullerenes with specific three-

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dimensional structures, which could be interesting for the construction of self-assembled nanoscale architectures. Their applications in biological aspect and molecular recognition are currently under investigation.

Experimental Section

Preparation of Macrocycle 1. To a stirred solution of octanediol (6.7 mmol, 1.0 g) in 500 mL of dry dichloromethane was added pyridine (1.1 mL, 13.5 mmol). Then a solution of malonyl dichloride (6.9 mmol, 1.0 g) in 250 mL of dry dichloromethane was slowly added to the above mixture over 8 h, under N_2 at room temperature. Upon completion of addition, the solution was stirred for an additional 3 h. Saturated $NaHCO_3$ solution was added to the reaction mixture, and the organic layer was separated and dried over anhydrous $MgSO_4$. After removal of solvents, the crude reaction mixture was separated by flash chromatography over silica gel by using ethyl acetate/hexanes (1/5) to give initial fractions, followed by elution using ethyl acetate/hexanes (1/3) to give compound **1** (0.119 g, 8.1%): ^{1}H NMR of **1** ($CDCl_3$) δ 1.32 (24 H, m), 1.64 (12 H, m), 3.37 (6 H, s), 4.15 (12 H, t); ^{13}C NMR of **1** ($CDCl_3$) δ 26.1, 28.8, 29.4, 42.2, 65.9, 167.1; *m*/*z* 643.2 (M + 1).

Preparation of C_{60} Tris-adduct 2. To a stirred solution of C_{60} (72.0 mg, 0.1 mmol), **1** (64.2 mg, 0.1 mmol), and iodine (76.2 mg, 0.3 mmol) in 100 mL of dry toluene was dropwise added a solution of DBU (114.0 mg, 0.75 mmol) in 25 mL of dry toluene under argon at room temperature. Upon completion of addition, the resulting reaction mixture was stirred for 0.5 h. The reaction mixture was washed twice with water and then dried over anhydrous $MgSO_4$. The raw mixture was subjected to flash chromatography on silica gel. Unreacted C_{60} was removed by using toluene, and then the eluant was changed to toluene/ethyl acetate (98/2) to give **2** (80.5 mg, 59%): ^{13}C NMR of **2** ($CDCl_3$) δ 25.6, 26.3, 28.9, 29.0, 29.1, 29.3, 54.4, 66.3, 67.1, 70.5, 71.3, 140.9, 141.1, 141.7, 142.5, 142.7, 143.6, 143.8, 144.4, 144.5, 145.5, 145.5, 146.3, 146.4, 146.4, 146.5, 146.6, 146.7, 147.9, 162.5, 162.8; *m*/*z* 1357 (M + 1); ^{3}He NMR of **3**, ^{3}He@**2** δ −0.001 (gaseous ^{3}He), −6.363 (^{3}He@C_{60}), −12.085 (^{3}He@**2**) ppm.

Preparation of Macrocycles 5 and 6. To a stirred solution of triethylene glycol (7.5 mmol, 1.13 g), KF (30.0 mmol, 1.74 g), and TEBA (0.3 mmol, 60.0 mg) in 50 mL of dry dichloromethane was added dropwise a solution of malonyl dichloride (15.0 mmol, 2.12 g) in dry dichloromethane under N_2 at room temperature. Upon completion of addition, the solution was stirred for 4 h. Water was added to the reaction mixture, and the organic layer was separated. The aqueous phase was extracted three times with chloroform, and the organic layers were combined, washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude reaction mixture was separated by flash chromatography over silica gel by using ethyl acetate/hexanes (4/1) to give initial fractions containing compound **4**, followed by elution using ethyl acetate to give compound **5** (0.266 g, 16.2%) and finally elution with ethyl acetate /methanol (98/2) to give compound **6** (0.151 g, 9.2%): ^{1}H NMR of **5** ($CDCl_3$) δ 3.41 (4 H, s), 3.62 (8 H, s), 3.72 (8 H, t), 4.32 (8 H, t); ^{13}C NMR of **5** ($CDCl_3$) δ 41.9, 65.2, 69.3, 71.1, 167.5; *m*/*z* 459 (M + Na^+); ^{1}H NMR of **6** ($CDCl_3$) δ 3.48 (6 H, s), 3.66 (12 H, s), 3.73 (12 H, t), 4.33 (12 H, t); ^{13}C NMR of **6** ($CDCl_3$) δ 42.8, 64.7, 68.9, 69.8, 166.6; *m*/*z* 677 (M + Na^+).

Preparation of Macrocycles 8 and 9. To a stirred solution of tetraethylene glycol (11.6 mmol, 2.3 g), KF (25.0 mmol, 1.5 g), and TEBA (0.3 mmol, 65.0 mg) in 50 mL of dry dichloromethane was added dropwise a solution of malonyl dichloride (17.4 mmol, 2.5 g) in dry dichloromethane under N_2 at room temperature. Upon completion of addition, the solution was stirred for 5 h. Water was added to the reaction mixture, and the organic layer was separated. The aqueous phase was extracted three times with chloroform, and the organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude reaction mixture was separated by flash chromatography over silica gel by using ethyl acetate to give initial fractions containing compound **7**, followed by elution using ethyl acetate/methanol (96/4) to give compound **8** (0.345 g, 11.4%) and finally elution with ethyl acetate/methanol (90/10) to give compound **9** (0.202 g, 6.6%): ^{1}H NMR of **8** ($CDCl_3$) δ 3.41 (4 H, s), 3.59 (16 H, m), 3.66 (8 H, t), 4.24 (8 H, t); ^{13}C NMR of **8** ($CDCl_3$) δ 42.3, 65.6, 69.8, 71.6, 71.7, 167.5; *m*/*z* 547.4 (M + Na^+); ^{1}H NMR of **9** ($CDCl_3$) δ 3.42 (6 H, s), 3.66 (24 H, m), 3.72 (12 H, t), 4.31 (12 H, t); ^{13}C NMR of **9** ($CDCl_3$) δ 41.9, 65.2, 69.3, 71.1, 71.2, 166.8; *m*/*z* 809.5 (M + Na^+).

Preparation of C_{60} Bis-adduct 10. To a stirred solution of C_{60} (72.0 mg, 0.1 mmol), **5** (43.6 mg, 0.1 mmol), and iodine (50.8 mg, 0.2 mmol) in 100 mL of dry toluene was dropwise added a solution of DBU (76.0 mg, 0.5 mmol) in 25 mL of dry toluene under argon at room temperature. Upon completion of addition, the resulting reaction mixture was stirred for 30 min. The reaction mixture was washed twice with water and then dried over anhydrous $MgSO_4$. The raw mixture was subjected to flash chromatography on silica gel. Unreacted C_{60} was removed by using toluene, and then the eluant was changed to toluene/ethyl acetate/methanol (60/30/10) to give **10** (69.1 mg, 60%): ^{1}H NMR of **10** ($CDCl_3$) δ 3.53 (2 H, m), 3.64 (4 H, m), 3.80 (6 H, m), 3.92 (4 H, m), 4.41 (4 H, m), 4.68 (2 H, m), 4.84 (2 H, m); ^{13}C NMR of **10** ($CDCl_3$) δ 50.2, 66.2, 66.6, 68.6, 69.5, 69.7, 70.4, 70.8, 71.4, 140.9, 141.2, 141.3, 142.4, 143.2, 143.5, 143.6, 143.6, 144.2, 144.3, 144.4, 144.5, 144.7, 145.0, 145.1, 145.3, 145.4, 145.6, 145.8, 146.1, 146.2, 147.3, 147.4, 147.5, 147.8, 148.3, 163.3, 163.5; *m*/*z* 1175 (M + Na^+); UV−vis spectrum, see Figure 4; ^{3}He NMR of ^{3}He@**10** δ −0.009 (gaseous ^{3}He), −6.371 (^{3}He@C_{60}), −8.016 (^{3}He@C_{60} monoadduct), −10.236 (^{3}He@**10**) ppm.

Preparation of C_{60} Bis-adducts 11 and 12. To a stirred solution of C_{60} (72.0 mg, 0.1 mmol), **8** (52.4 mg, 0.1 mmol), and iodine (50.8 mg, 0.2 mmol) in 100 mL of dry toluene was dropwise added a solution of DBU (76.0 mg, 0.5 mmol) in 25 mL of dry toluene under argon at room temperature. Upon completion of the addition, the resulting reaction mixture was stirred for 30 min. The reaction mixture was washed twice with water and then dried over anhydrous $MgSO_4$. The raw mixture was subjected to flash chromatography on silica gel. Unreacted C_{60} was removed by using toluene, and then the eluant was changed to toluene/ethyl acetate/methanol (60/38/2) to give **12** (10.0 mg, 8.1%), followed by the elution using toluene/ethyl acetate/methanol (60/35/5) to give **11** (34.8 mg, 28.1%): ^{1}H NMR of **11** ($CDCl_3$) δ 3.60−3.80 (20 H, m), 3.94 (4 H, t), 4.30 (2 H, m), 4.56 (2 H, m), 4.70 (2 H, m), 4.84 (2 H, m); ^{13}C NMR of **11** ($CDCl_3$) δ 49.5, 66.2, 66.3, 66.8, 67.6, 69.2, 70.2, 70.5, 70.9, 71.2, 71.5, 136.8, 137.2, 137.6, 137.8, 140.0, 141.0, 141.2, 142.4, 142.5, 143.4, 143.6, 143.7, 144.2, 144.3, 144.4, 144.5, 144.7, 145.0, 145.1, 145.3, 145.4, 145.7, 146.0, 146.2, 147.2, 147.3, 148.4, 162.9, 163.6; *m*/*z* 1262.2 (M + Na^+); UV−vis spectrum, see Figure 4; ^{1}H NMR of **12** ($CDCl_3$) δ 3.02 (1 H, m), 3.35−4.00 (22 H, m), 4.19 (3 H, m), 4.45 (1 H, m), 4.68 (1 H, m), 4.70 (2 H, m), 5.02 (2 H, m); *m*/*z* 1262.3 (M + Na^+); UV−vis spectrum, see Figure 4.

Preparation of C_{60} Tris-adduct 13. To a stirred solution of C_{60} (72.0 mg, 0.1 mmol), **6** (65.4 mg, 0.1 mmol), and iodine (76.2 mg, 0.3 mmol) in 100 mL of dry toluene was dropwise added a solution of DBU (114.0 mg, 0.75 mmol) in 25 mL of dry toluene under argon at room temperature. Upon completion of addition, the resulting reaction mixture was stirred for 30 min. The reaction mixture was washed twice with water and then dried over anhydrous $MgSO_4$. The raw mixture was subjected to flash chromatography on silica gel. Unreacted C_{60} was removed by using toluene, and then the eluant was changed to toluene/ethyl acetate/methanol (50/40/10) to give **13** (70.1 mg, 51%): ^{1}H NMR of **13** ($CDCl_3$) δ 3.12 (2 H, m), 3.42 (7 H, m), 3.70 (13 H, m), 3.92 (2 H, m), 4.28 (3 H, m),

4.52 (6 H, m), 4.68 (2 H, m), 5.00 (1 H, m); ^{13}C NMR of **13** ($CDCl_3$) δ 53.5, 54.0, 65.7, 65.8, 68.2, 68.6, 69.2, 69.8, 70.8, 70.2, 140.6, 141.0, 141.8, 141.9, 142.2, 143.0, 143.3, 143.6, 143.9, 144.4, 144.6, 144.7, 144.9, 145.1, 145.2, 145.3, 145.5, 145.8, 146.3, 146.4, 146.5, 146.6, 146.7, 146.8, 148.5, 162.9, 164.0; *m*/*z* 1391 ($M + Na^+$); ^{3}He NMR of ^{3}He@**13** δ −0.009 ppm (gaseous ^{3}He), −6.373 ppm (^{3}He@C_{60}), −8.018 (^{3}He@C_{60} monoadduct), −12.040 ppm (^{3}He@**13**).

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Supporting Information Available: Spectral data for compounds **1**, **2**, **5**, and **6**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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