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Synthesis and properties of novel fullerene derivatives having dendrimer units and the fullerenyl anions generated therefrom

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Benzyl-ether type dendrimers from the first to fourth generations having a fullerene cage as an electroactive core, **$GnC_{60}H$** (n = 1–4), were synthesized using convergent methods. All dendrimers were highly soluble in common organic solvents. Their structures in solution were investigated by ^1H and ^{13}C NMR and UV-vis spectroscopy and molecular dynamics calculations. The presence of an attractive interaction between the dendrimer moieties and the fullerene cage was proved by an upfield shift of the NMR signals and the appearance of a new absorption in the UV-vis spectra. The electrochemical study indicated that **GnC_{60}^-** (n = 1–4) anions can be electrochemically generated and are further reduced to the trianion stage. Anions **GnC_{60}^-** (n = 1–4) were subjected to chemical one-electron oxidation with iodine and gave new fullerene dimers carrying a dendrimer unit on each fullerene cage.

Introduction

The synthesis and characterisation of dendrimers, cascade molecules, and related hyper-branched systems is currently attracting great interest in the field of materials science.[1] Dendrimers are nanosized hyperbranched macromolecules with well-defined three-dimensional structures and are potential building blocks for the construction of organised functional materials with nanosize precision. Incorporation of functional cores such as photoactive[2] and/or redox-active[3] moieties at the center of dendrimers is one of the important issues in dendrimer chemistry particularly from the viewpoint of utilization of these dendrimers as molecular devices.[4]

Fullerene C_{60} is a spherically π-conjugated all-carbon molecule[5] which can accept six electrons successively in solution.[6] Thus, it is considered as one of the most attractive units for incorporation as a functional core in dendrimers. Actually, a C_{60} cage has been used as a core[7] as well as branches[8] of the dendrimers. In all the dendrimers having a fullerene cage as a core reported so far,[7,8] the dendrons are connected to the C_{60} cages by a formal [2 + 1] cycloaddition like pattern **A** shown in Chart 1, including carbon, nitrogen, and iridium elements directly attached to the C_{60} cage. On the other hand, C_{60}-based dendrimers with the addition pattern **B** are quite intriguing because the electronic and chemical properties of the central C_{60} cage should be dramatically changed by abstraction of the proton directly attached to the C_{60} cage.[9,10] In this paper, we report synthesis, characterisation, structure, and electrochemical properties of the first C_{60}-based dendrimers having various generations of dendrons with the addition pattern **B**.

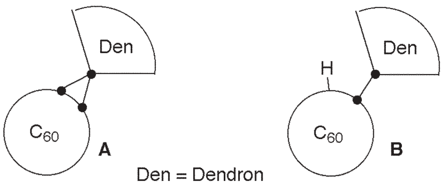


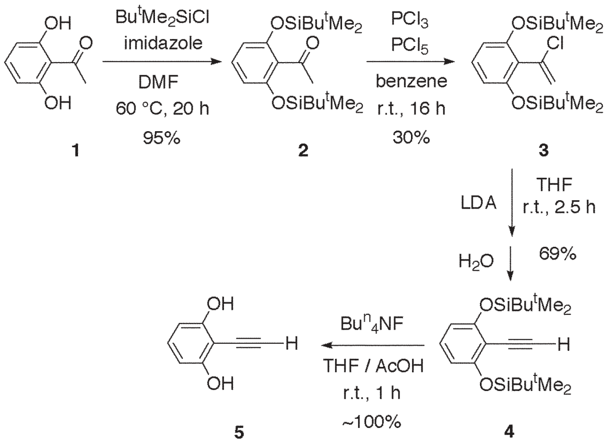
Chart 1 Addition patterns of organic addends to fullerene C_{60}.

Results and discussion

Synthesis

We chose benzyl-ether type dendrons **[Gn]-Br** (n = 0–3) as building blocks, expecting the occurrence of some attractive interactions between the dendrons and the fullerene core.[7e,11] An acetylene unit was selected as a bridge between the dendrons and the fullerene core because ethynylated fullerenes having various substituents at the other end of the triple bond are known to be synthesized in relatively high yield.[9c,10,12] Thus, 2,6-dihydroxyethynylbenzene (**5**) as the junction moiety was synthesized from 2,6-dihydroxyacetophenone (**1**) by protection of hydroxy groups, chlorovinylation, and dehydrochlorination, followed by desilylation, using the reported procedure for the synthesis of 2-ethynyl-1,3-dimethoxybenzene,[13] as shown in Scheme 1.

Fréchet's method of convergent approach[14] was applied for the synthesis of dendritic phenylacetylenes **GnA** (n = 1–4). Coupling of 2 equiv. of dendritic benzyl bromide **[Gn]-Br** (n = 0–3)[14] with **5** was performed in refluxing acetone in the



Scheme 1 Synthesis of 2,6-dihydroxyethynylbenzene **5**.

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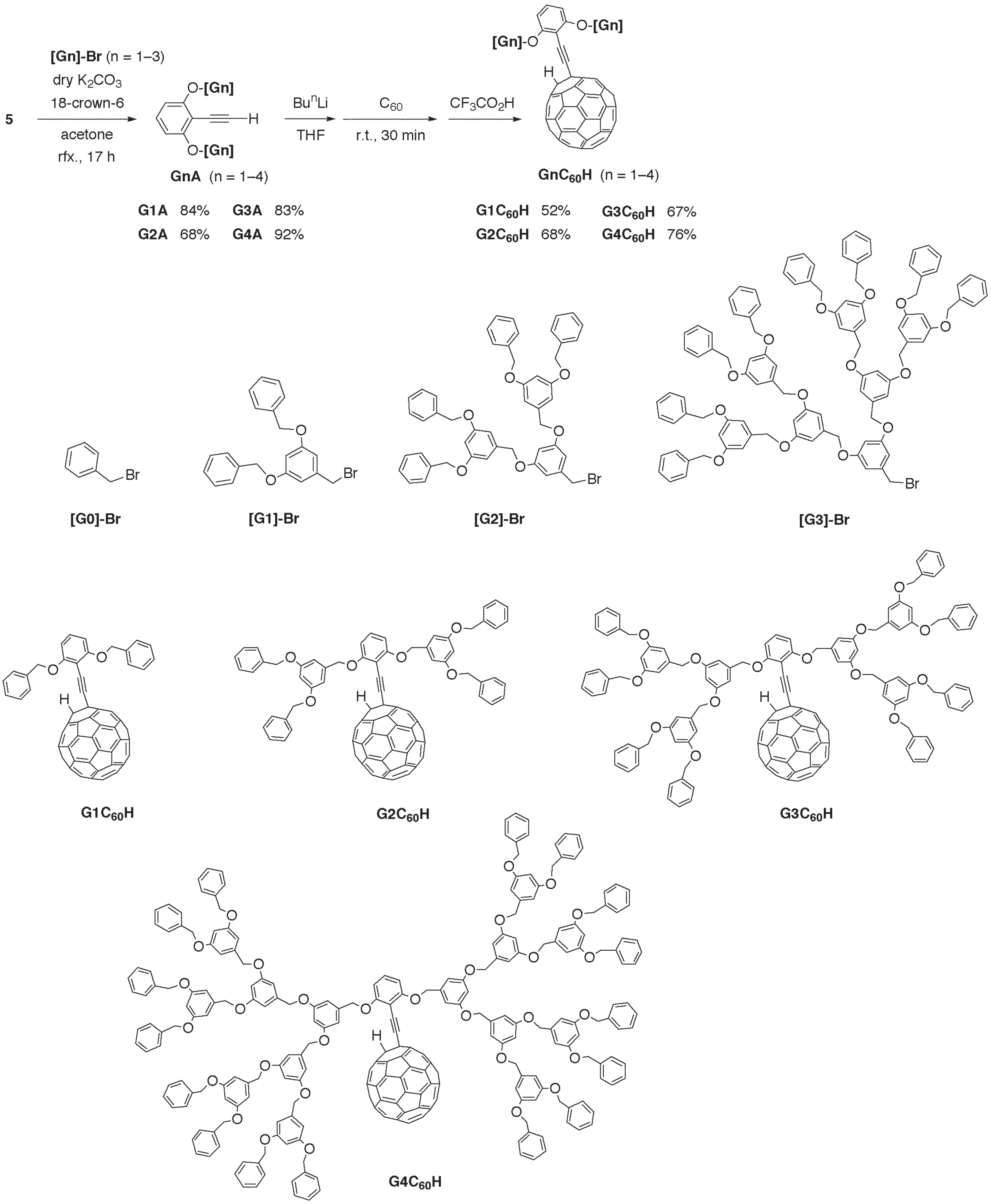
presence of K_2CO_3 and 18-crown-6 to afford dendritic phenylacetylene **GnA** (n = 1–4) in good yields as shown in Scheme 2. Previously we noticed that the reaction of fullerene C_{60} with lithium acetylides in THF can afford the ethynylated C_{60} in high yields after protonation although the solubility of starting C_{60} in THF is negligibly low.[10] Similarly, the reaction of C_{60} with lithium acetylides generated from **GnA** (n = 1–4) in THF gave the desired fullerene derivatives having dendrimer units **GnC$_{60}$H** (n = 1–4) in good yields as brown powders. No isolable amount of bisadduct was produced in any of these reactions. The reaction of the acetylides and C_{60} could be monitored by the change in appearance of the mixture from a brown suspension to a dark green solution. It was observed that the acetylide with a smaller dendron reacted faster reflecting the smaller steric effects of the dendrons, the approximate times required for completion of the reaction ranging from a few minutes to 30 minutes at room temperature. The dendritic fullerenes **GnC$_{60}$H** (n = 1–4) are highly soluble in common organic solvents. Their structures were characterised as 1,2-addition products with the ethynyl group and a proton added at a 6,6-bond on the fullerene cage, as previously reported for the various nucleophilic additions,[9c,10,12] by ^1H



Scheme 2 Synthesis of fullerene derivatives **GnC$_{60}$H** (n = 1–4) having dendrimer units.

and ^{13}C NMR, UV-vis, and MALDI-TOF MS spectroscopies and elemental analysis.

Structure of dendrimers GnC$_{60}$H (n = 1–4) in solution

Fullerene derivatives **GnC$_{60}$H** (n = 1–4) synthesized as described above have flexible benzyl-ether type dendrons surrounding the fullerene core. Benzyl-ether type dendrimers are reported to be able to act as a host for fullerene C$_{60}$.[11] Although the intermolecular association constants reported for the formation of the complex of C$_{60}$ with these dendrimers are not so high,[11] the intramolecular association would be preferable in **GnC$_{60}$H** (n = 1–4) since the dendrimer units are located in such close proximity to the C$_{60}$ cage. Thus, the structures of **GnC$_{60}$H** (n = 1–4) in solution were studied by the use of NMR and UV-vis spectra and molecular dynamics simulations.[15]

The dendritic fullerenes **GnC$_{60}$H** (n = 1–4) ^{1}H NMR spectra in CDCl$_3$ showed that the signal for the proton directly attached to the C$_{60}$ cage was upfield shifted as the generation number of the dendrimer increased: *i.e.*, δ 7.12 ppm for **G1C$_{60}$H**, 7.01 for **G2C$_{60}$H**, 6.99 for **G3C$_{60}$H**, and 6.95 for **G4C$_{60}$H**. The chemical shift of δ 7.12 for **G1C$_{60}$H** is comparable to the one for the corresponding proton of the phenylethynyl-C$_{60}$ derivative, Ph-C≡C-C$_{60}$-H (δ 7.13).[12a] Thus, the observed upfield shifts are attributed to the ring current effect of the increasing number of benzene rings of benzyl-ether type dendrons located near the RC$_{60}$H proton.

In the ^{13}C NMR spectra, 30 signals were observed for the sp^2 carbons of the C$_{60}$ cage, proving the presence of C_s symmetry as depicted in Scheme 2. Fig. 1 (a) shows the sp^2-carbon regions of the ^{13}C NMR spectra of **GnC$_{60}$H** (n = 1–4) in CDCl$_3$. The averaged values of the chemical shifts of the 58 sp^2 carbons in the fullerene cage are 144.10 ($\Delta\delta$ 0.00), 143.91 ($\Delta\delta$ −0.19), 143.86 ($\Delta\delta$ −0.25), and 143.80 ($\Delta\delta$ −0.30), for **G1C$_{60}$H**, **G2C$_{60}$H**, **G3C$_{60}$H**, and **G4C$_{60}$H**, respectively; the values in parentheses are the differences in chemical shifts with reference to that of **G1C$_{60}$H**. Thus, an upfield shift increasing in the order of the increasing generation number of the dendrimers is clearly observed. The observed $\Delta\delta$ values of −0.19, −0.25, and −0.30 are much larger than that reported for the intermolecular complex of C$_{60}$ with a benzyl-ether type dendrimer ($\Delta\delta$ −0.003 at 25 °C).[11b] These results are taken as evidence that the dendrimer units in **GnC$_{60}$H** (n = 1–4) efficiently surround the C$_{60}$ cage located at the centre of the molecule by an attractive interaction between the dendrimer units and the C$_{60}$ cage in solution.

In order to investigate which carbon in the C$_{60}$ cage is strongly influenced by the dendrimer units, the assignment of each fullerene signal in the ^{13}C NMR spectra was attempted by comparison with the chemical shifts calculated by the use of the GIAO method[16,17] for the model compound, ethynylfullerene **6**. The structure of **6** was fully optimized with C_s symmetry at the B3LYP/6-31G(d) level of theory and the GIAO calculations were conducted at the HF/6-31+G(d,p) level using the optimized geometry. The chemical shifts obtained by calculations are shown in Fig. 1 (b). The calculated ^{13}C NMR chemical shifts are about 2 to 6 ppm more downfield shifted than the experimental values, but the general tendency of the experimental spectra are modestly well reproduced for **GnC$_{60}$H** (n = 1–4). By comparison of the calculated ^{13}C NMR spectrum for **6** with observed ones for **GnC$_{60}$H** (n = 1–4), selected signals for C1, C2, C3, C4, C27, C28, C29, and C30 (Fig. 1 (c)) were assigned as shown in Fig. 1 (a). These assignments are in good agreement with the reported ones for the osmylated C$_{60}$ derivative with C_{2v} symmetry experimentally determined by 2D NMR.[18]

Based on the assignment described above, the chemical shifts of selected carbons and the differences in chemical shifts with reference to those of **G1C$_{60}$H** are summarized in Table 1. The upfield shifts of signals for all these carbons are observed according to the increase in the generation number of the dendrimer, suggesting the presence of an attractive interaction between the dendrimer units and the fullerene cage. The selected carbon atoms are those closest to the saturated 6,6 bond (C1 and C2), those near the middle part of the cage (C27 and C28), and the furthest carbons from the saturated carbons (C3 and C4). Among these carbons, C28 suffers the greatest influence from the dendrimer units as shown by the greatest change in $\Delta\delta$ values, indicating that the probability of the presence of the flexible dendrimer units is quite high near this

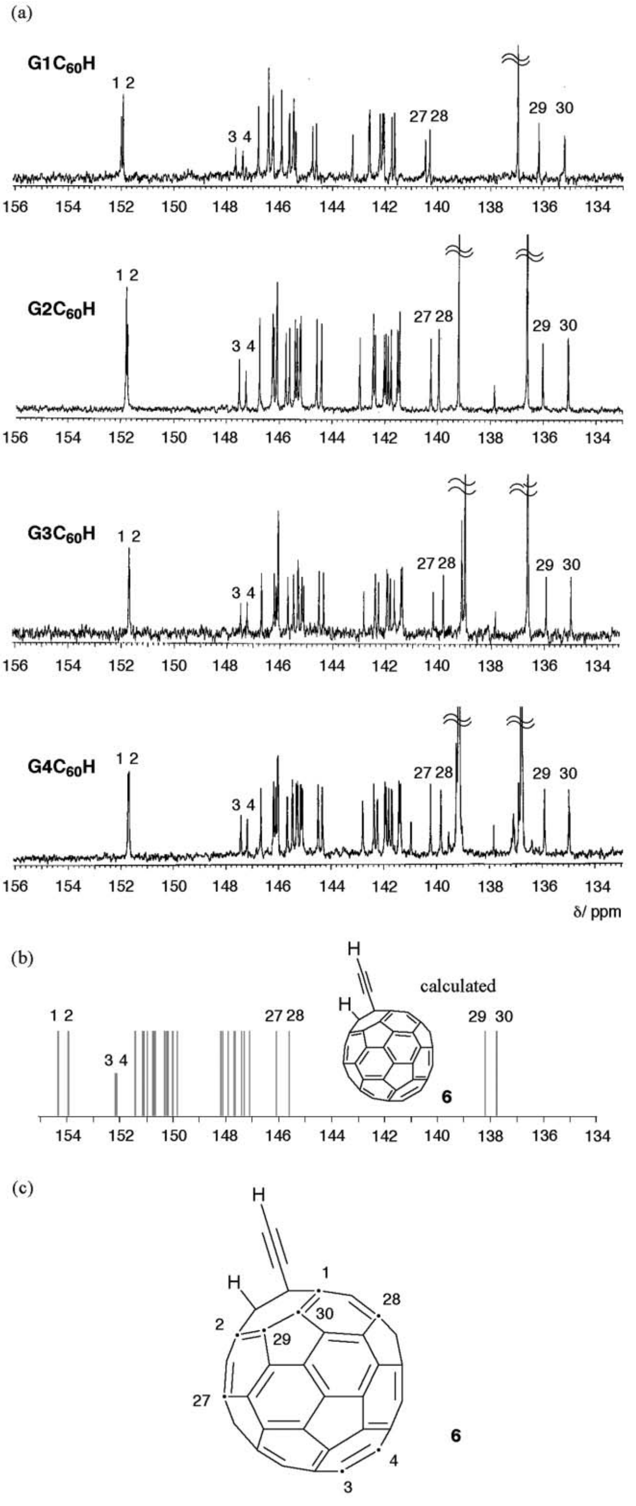


Fig. 1 ^{13}C NMR spectra of (a) dendrimers **GnC$_{60}$H** (n = 1–4) observed (75 MHz, CDCl$_3$) and (b) model compound **6** calculated by GIAO (SCF/6-31+G(d,p)//B3LYP/6-31G(d)). The signals are numbered based on the order of downfield shift and the corresponding carbons are shown in (c).

Table 1 Observed chemical shifts (ppm) of sp^2 carbons of the C_{60} cage for $\mathbf{GnC_{60}H}$ (n = 1–4)

Compd	C1 ($\Delta\delta$)[a]	C2 ($\Delta\delta$)[a]	C3 ($\Delta\delta$)[a]	C4 ($\Delta\delta$)[a]	C27 ($\Delta\delta$)[a]	C28 ($\Delta\delta$)[a]	C29 ($\Delta\delta$)[a]	C30 ($\Delta\delta$)[a]
$\mathbf{G1C_{60}H}$	151.99 (0.00)	151.93 (0.00)	147.65 (0.00)	147.39 (0.00)	140.46 (0.00)	140.29 (0.00)	136.18 (0.00)	135.20 (0.00)
$\mathbf{G2C_{60}H}$	151.80 (−0.19)	151.76 (−0.17)	147.51 (−0.15)	147.26 (−0.14)	140.25 (−0.21)	139.94 (−0.35)	136.01 (−0.17)	135.05 (−0.15)
$\mathbf{G3C_{60}H}$	151.72 (−0.27)	151.69 (−0.24)	147.49 (−0.17)	147.24 (−0.15)	140.23 (−0.23)	139.85 (−0.44)	135.92 (−0.26)	135.00 (−0.20)
$\mathbf{G4C_{60}H}$	151.71 (−0.29)	151.67 (−0.25)	147.40 (−0.25)	147.17 (−0.23)	140.19 (−0.27)	139.80 (−0.49)	135.87 (−0.31)	134.95 (−0.25)

[a] The difference in chemical shifts (ppm) from that of $\mathbf{G1C_{60}H}$.

carbon. With respect to C3 and C4 which are furthest from the saturated carbons, the upfield shifts are relatively small until the third generation of the dendrimer and a considerable upfield shift is observed for the fourth generation of the dendrimer. This is attributed to the supposition that only the fourth generation of the dendrimer can reach the bottom part of the C_{60} cage.

The UV-vis spectra of $\mathbf{GnC_{60}H}$ (n = 1–4) were measured in *o*-dichlorobenzene (ODCB) in order to investigate the intramolecular electronic interaction between the dendrimer units and the C_{60} cage, and are shown in Fig. 2. All the dendritic fullerenes showed sharp absorptions at 435–436 nm and broad absorptions at 704–708 nm, which are characteristic for C_{60} derivatives having a saturated 6,6-bond.[19] To cancel out the experimental errors in concentrations, absorbance corrections using absorptions at 705 nm were applied to the spectra of all dendrimers. Then the spectra of $\mathbf{G1C_{60}H}$ and $\mathbf{G2C_{60}H}$ were found to be almost identical to each other. However, the absorption around 436 nm is stronger for $\mathbf{G3C_{60}H}$ and $\mathbf{G4C_{60}H}$ in the order of increasing generation number of the dendrimer. This is supposed to be due to the intramolecular electronic interaction between the benzyl ether moiety and the fullerene cage.[11b] Thus, it is considered that fullerene derivatives $\mathbf{GnC_{60}H}$ (n = 1–4) have such structures that the flexible dendrimer units surround the central fullerene cage in solution, most efficiently in the case of $\mathbf{G4C_{60}H}$.

The effect of the solvent polarity upon the ^1H NMR spectra of $\mathbf{G4C_{60}H}$ is expected to provide further evidence for the intramolecular complexation. Fig. 3 shows the ^1H NMR spectra of $\mathbf{G4C_{60}H}$ taken in $CDCl_3$–CD_3CN mixed solvents of ratios varying from 1 : 0 to 1 : 2 by volume. In accord with the increase in the solvent polarity, it was observed that the peaks become broader and shift to the upfield region. This suggests that the dendrimer units wrap the fullerene cage more tightly in the more polar solvent system. A similar phenomenon has been reported for the intramolecular folding of oligo(phenylene-ethynylene) in a polar solvent.[20]

For the computational determination of minimum-energy structures of dendrimers $\mathbf{GnC_{60}H}$ (n = 1–4) at 0 K in the gas phase, molecular dynamics (MD) simulations were carried out with the MM^+ forcefield implemented in the HYPERCHEM program package[15] to give the results shown in Fig. 4. The dense packing of the dendron branches around the fullerene cage is clearly observed in all dendrimers. The presence of favourable π–π stacking interactions is indicated by the face-to-face arrangements of the fullerene cage with several aromatic rings of the dendrons. Such interaction should have led to the

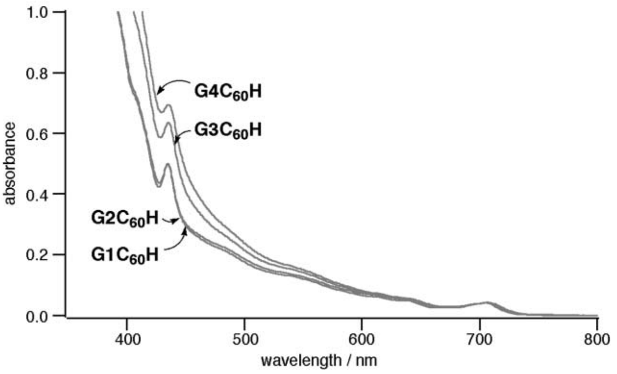


Fig. 2 UV-vis spectra (ODCB, 1×10^{-4} M) of $\mathbf{GnC_{60}H}$ (n = 1–4) after absorbance correction at 705 nm.

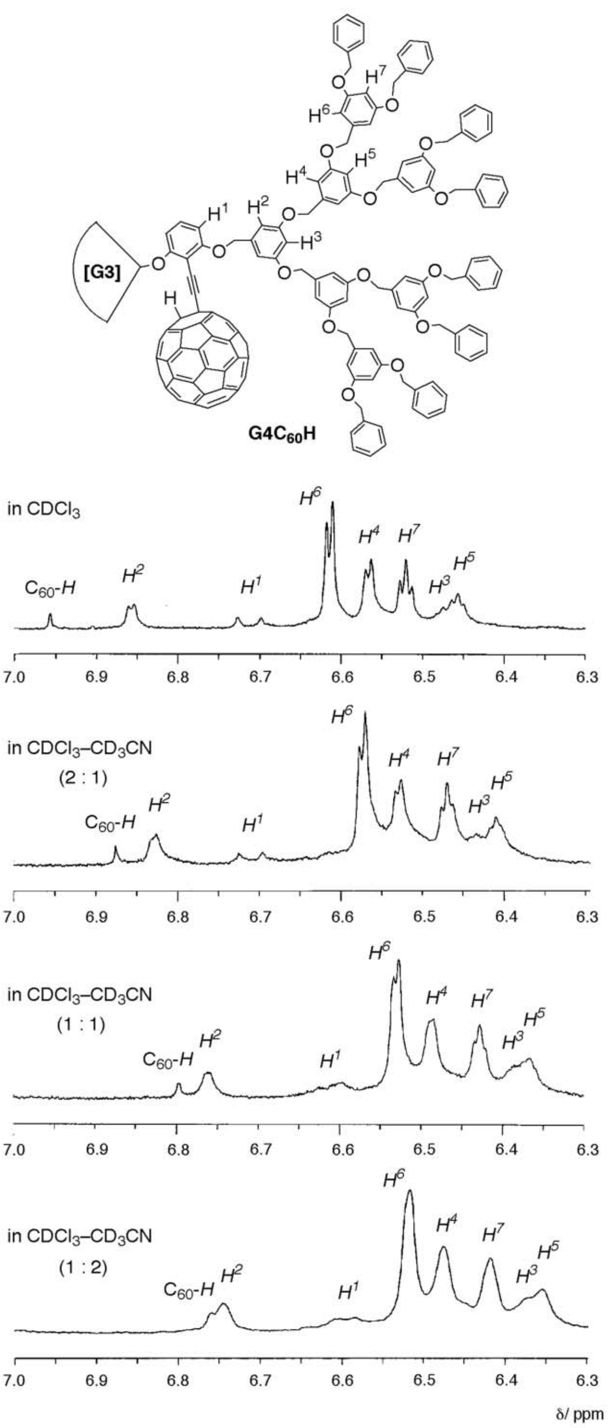


Fig. 3 ^1H NMR (300 MHz) spectra of dendrimer $\mathbf{G4C_{60}H}$ in different solvent systems.

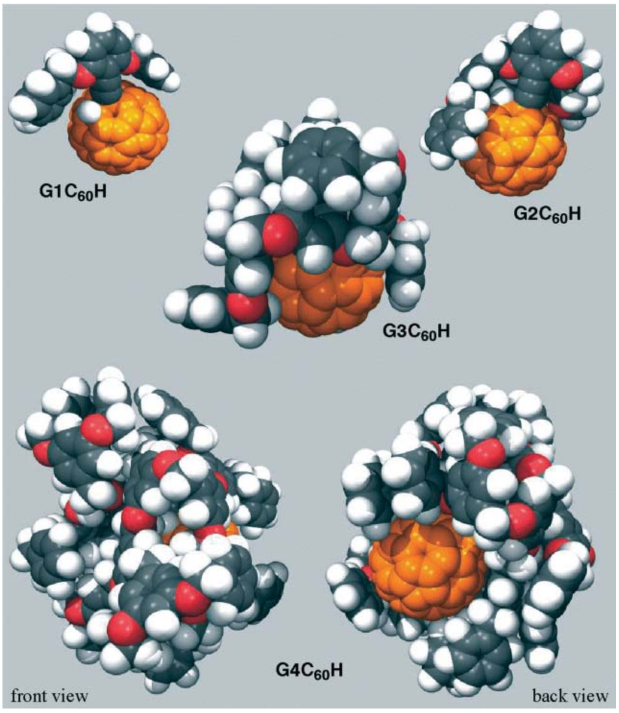


Fig. 4 Minimum energy structures at 0 K of **GnC$_{60}$H** (n = 1–4) after molecular dynamics (MD) simulation. All structures were preminimized with the MM$^+$ forcefield implemented in HYPERCHEM[15] prior to the MD simulation. During the MD simulations the structures were heated to 1000 K and kept at this temperature for equilibration before they were allowed to cool to 0 K to establish the minimum energy structure. Conditions[7d] for the simulated annealing: heat time: 5 ps, run time: 50 ps, cool time: 50 ps, step size: 0.001 ps, starting temperature: 0 K, simulation temperature: 1000 K, final temperature: 0 K, *in vacuo*, data collection period: 1 time step.

pronounced wrapping of the fullerene core with the dendron units.[7d]

Generation of the dendritic fullerenyl anions

In these dendrimers, the redox active central cores are fullerene moieties having a highly acidic proton[9] directly attached to the fullerene cage. The electronic properties of the central core should be greatly changed when it is transformed to the anion by abstraction of the acidic proton. When THF solutions of the dendrimers **GnC$_{60}$H** (n = 1–4) were treated with one equivalent of Bu^{t}OK, the initial brown solutions immediately turned into dark green, indicating the formation of fullerenyl anions[10] **GnC$_{60}$**$^-$ (n = 1–4) (Scheme 3). Accordingly, new absorptions at λ_{max} 634–638 and 959–964 nm appeared in the vis-NIR spectra, supporting the generation of **GnC$_{60}$**$^-$ (n = 1–4) anions. No significant difference in the maximum absorptions was observed among these dendrimers.

The formation of **GnC$_{60}$**$^-$ (n = 1–4) anions were further confirmed by the ^{1}H NMR spectra in THF-d_8, in which the signal for the proton attached to the C$_{60}$ cage disappeared while signals for all other protons corresponding to the dendrimer moieties remained.

On the other hand, the ^{13}C NMR spectra of all **GnC$_{60}$**$^-$ (n = 1–4) anions indicated that they have C_s symmetry as shown by the number of signals (30 signals) for the fullerenyl sp^2 carbons (Fig. 5 (a)). As has been reported previously,[10] these signals of the fullerenyl anions exhibit a general downfield shift as compared with those of the neutral molecules **GnC$_{60}$H** (n = 1–4). The averages of the chemical shifts of the 58 sp^2 carbons (30 signals) are 147.01 ($\Delta\delta$ 0.00), 146.89 ($\Delta\delta$ −0.12), 146.89 ($\Delta\delta$ −0.12), and 146.55 ($\Delta\delta$ −0.46), corresponding to **G1C$_{60}$**$^-$, **G2C$_{60}$**$^-$, **G3C$_{60}$**$^-$, and **G4C$_{60}$**$^-$, respectively: in the parentheses are shown the differences in chemical shifts with reference to that of **G1C$_{60}$**$^-$. The signal for the anion centre carbon appears at 120.71 ($\Delta\delta$ 0.00), 120.33 ($\Delta\delta$ −0.38), 120.29 ($\Delta\delta$ −0.42), and 119.79 ($\Delta\delta$ −0.92) ppm, corresponding to **G1C$_{60}$**$^-$, **G2C$_{60}$**$^-$, **G3C$_{60}$**$^-$, and **G4C$_{60}$**$^-$, respectively. Thus, also in the series of dendritic fullerenyl anions **GnC$_{60}$**$^-$ (n = 1–4), the upfield shift of the signals was observed according to the increase in the generation number of the attached dendrons as has been observed for the neutral dendrimers **GnC$_{60}$H** (n = 1–4). It appears that the benzyl-ether dendrimer units in anions **GnC$_{60}$**$^-$ (n = 1–4) also surround the negatively charged C$_{60}$ cage by the attractive interaction between the dendrimer units and the C$_{60}$ cage in the solution.

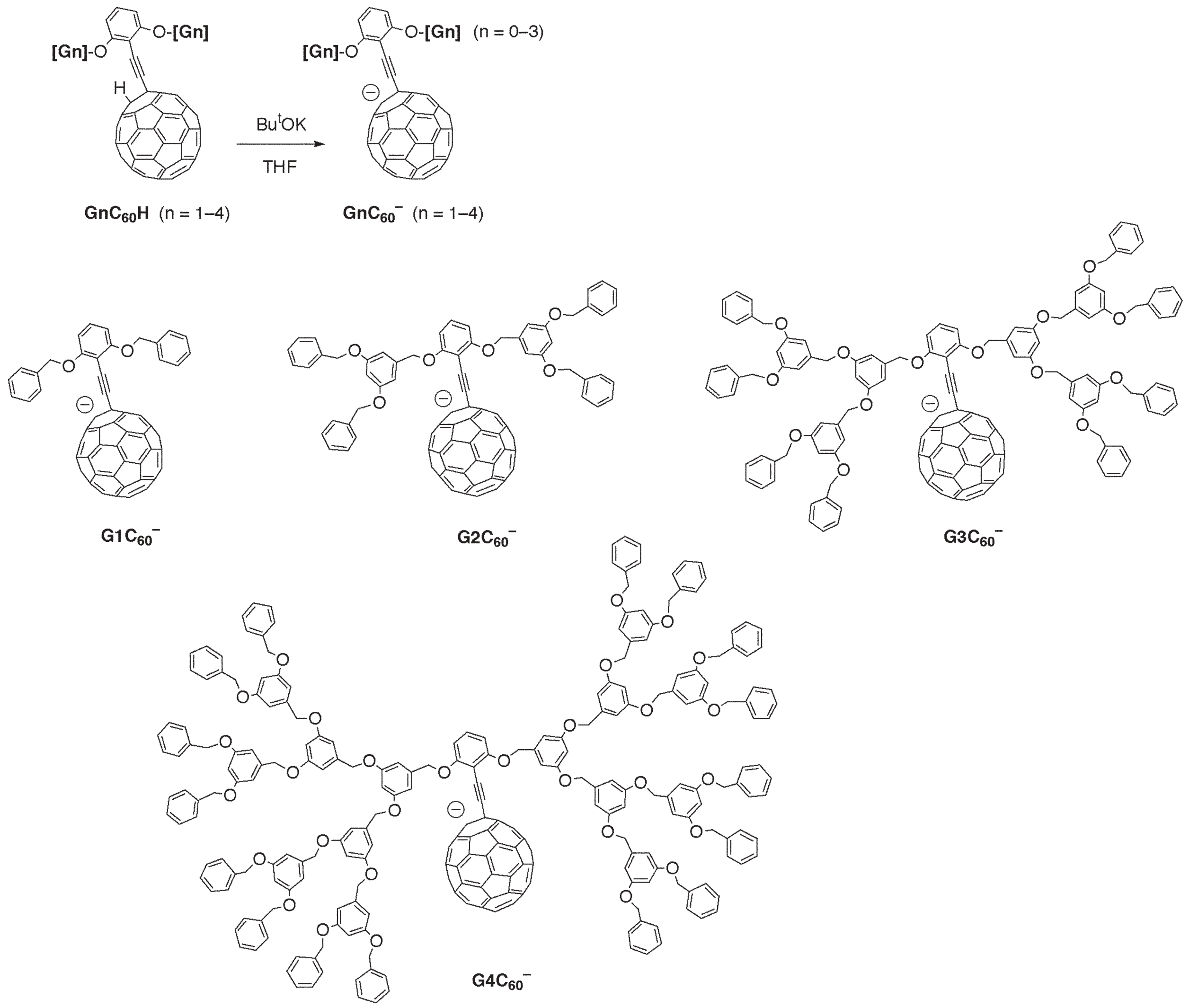
In order to assign the signals of the ^{13}C NMR spectra to appropriate carbons, the GIAO (SCF/6-31+G(d,p)//B3LYP/6-31G(d)) calculations were conducted for ethynylfullerenyl anion **7**$^-$ with Na$^+$ as a counter cation and for free anion **7**$^-$ as model compounds for the core of the dendrimer anions **GnC$_{60}$**$^-$. As shown in Fig. 5 (b), the calculated ^{13}C NMR chemical shifts for the ion pair Na$^+$**7**$^-$ exhibited slightly better agreement with those obtained experimentally than those calculated for free **7**$^-$. From this result, these fullerenyl anions are supposed to be present as ion pairs with the counter cation rather than free ions in solution. Although the agreement of the calculated ^{13}C NMR chemical shifts with experimental values is not sufficient to assign all the carbons, the selected signals for C1, C2, C30, and C$^-$ were assigned as shown in Fig. 5 (a) and Table 2. Again, upfield shifts of these selected signals are seen according to the increase of the generation number of the dendrimer.

Electrochemical properties of the dendritic fullerenyl anions

The redox behaviour of dendritic fullerenes **GnC$_{60}$H** (n = 1–4) was examined by the use of cyclic voltammetry in ODCB. It has been reported that deprotonation is induced by electrochemical reduction of hydrofullerenes such as C$_{60}$(CN)H.[9e] Similarly, it was observed that fullerenyl anions **GnC$_{60}$**$^-$ (n = 1–4) were generated on the electrode when a cathodic scan was conducted over the potential range beyond −1.5 V *vs.* Fc/Fc$^+$. Thus, the electrochemical properties of anions **GnC$_{60}$**$^-$ (n = 1–4) generated in the CV cell by the treatment of Bu^{t}OK were studied instead of **GnC$_{60}$H** (n = 1–4). The voltammograms observed for all the dendritic fullerenes are shown in Fig. 6, and the data are summarized in Table 3.

From the voltammograms shown in Fig. 6, a general tendency was observed that the redox current gradually decreased according to the increase of the generation number of the dendrimer. This is considered to be due to the decrease of the diffusion coefficients as has been reported for the dendrimers containing ferrocene as a core unit.[3h]

Apparently the most unusual features are concerned with the redox cycle at the lowest potential. For example, anion **G1C$_{60}$**$^-$ is oxidised to radical **G1C$_{60}$**$^\cdot$ at −0.48 V, but the corresponding reduction peak is cathodically shifted to −1.15 V, the difference of peak potentials being 0.67 V. This large negative shift of the cathodic peak is ascribed to some chemical process associated with the electron transfer, and this would most probably correspond to a rapid dimerization of **G1C$_{60}$**$^\cdot$ to **G1C$_{60}$–G1C$_{60}$** (Scheme 4). The reduction of dimer **G1C$_{60}$–G1C$_{60}$** to the original monomeric anion **G1C$_{60}$**$^-$ requires extra energy for the bond dissociation and also for a subtle structural change in the C$_{60}$ framework, which could have caused the cathodic shift as has been reported.[10] The next two reductions ($E_{red}{}^1$ and $E_{red}{}^2$) were nearly reversible as observed by individual redox waves at $E_{1/2}$ −1.49 and −1.91 V, respectively. Other dendritic fullerenyl anions **GnC$_{60}$**$^-$ (n = 2–4) exhibited the same redox behaviour as described above in spite of the larger size of the dendron moiety. This fact indicates that the presence of such a sterically



Scheme 3 Generation of fullerenyl anions having dendrimer units, **GnC$_{60}$**$^-$ (n = 1–4).

demanding group as the fourth-generation dendrimer unit cannot prevent the dimerization of the fullerenyl radical.

As to the values of the redox potentials, no systematic change was observed depending on the generation number of the attached dendron moieties.

Synthesis of fullerene dimers

Since the formation of dimers **GnC$_{60}$–GnC$_{60}$** (n = 1–4) on the electrode was suggested by cyclic voltammetry, macroscopic synthesis of the dimers was expected to be possible. Thus, the chemical one-electron oxidation was attempted for the fullerenyl anion bearing the largest dendron as an addend. When the anion **G4C$_{60}$**$^-$ was generated by deprotonation of **G4C$_{60}$H** with Bu^{t}OK in THF and was then oxidized with iodine, the separation by gel permeation chromatography (GPC) gave dimer **G4C$_{60}$–G4C$_{60}$** as a brown powder in 40% yield (Scheme 5) together with some small amounts of **G4C$_{60}$H** and a higher-molecular-weight compound of unknown structure. The structure of dimer **G4C$_{60}$–G4C$_{60}$** was confirmed by the MALDI-TOF MS spectrum shown in Fig. 7, which clearly displays the molecular ion peak at 8010 (M$^-$) in addition to fragment peaks at 4004 and 720 corresponding to **G4C$_{60}$**$^-$ and C$_{60}$, respectively.

When a benzene solution of dimer **G4C$_{60}$–G4C$_{60}$** was subjected to ESR measurement, a single-line signal (g = 2.0023, peak-to-peak width = 1.073 G) was observed, which most probably corresponds to the fullerenyl radical **G4C$_{60}$**$^\cdot$, as has been reported for singly bonded dimers.[21] Thus, the presence of the equilibrium between monomeric **G4C$_{60}$**$^\cdot$ and dimeric **G4C$_{60}$–G4C$_{60}$** was confirmed.

In exactly the same way, dimer **G3C$_{60}$–G3C$_{60}$** was synthesized in 41% yield, for which the MALDI-TOF MS spectrum showed a molecular ion peak at 4615 (M$^-$) and the ESR spectrum displayed a broad ESR signal (g = 2.0023, peak-to-peak width = 1.074 G). The ^{1}H NMR of these dimers displayed very complicated spectra suggesting that they are mixtures of meso and racemic structures.[21b]

In order to confirm that the formation of such a sterically congested molecule as dimer **G4C$_{60}$–G4C$_{60}$** is possible, the molecular dynamics calculations of **G4C$_{60}$–G4C$_{60}$** in both the 1,4- and 1,6-addition patterns were carried out. The results are shown in Fig. 8. Thus, in spite of the presence of a seemingly large addend the two C$_{60}$ cages can be connected by a single bond in the fashion of 1,4- or 1,6-addition patterns, owing to the great flexibility of the benzyl-ether type dendrimer structure.

Conclusion

A series of fullerene derivatives having benzyl-ether type dendrons, **GnC$_{60}$H** (n = 1–4), were newly synthesized. All dendrimers are highly soluble in common organic solvents. ^{1}H and ^{13}C NMR and UV-vis spectroscopy and molecular dynamics calculations indicated the presence of certain attractive interactions between the dendrimer moieties and the

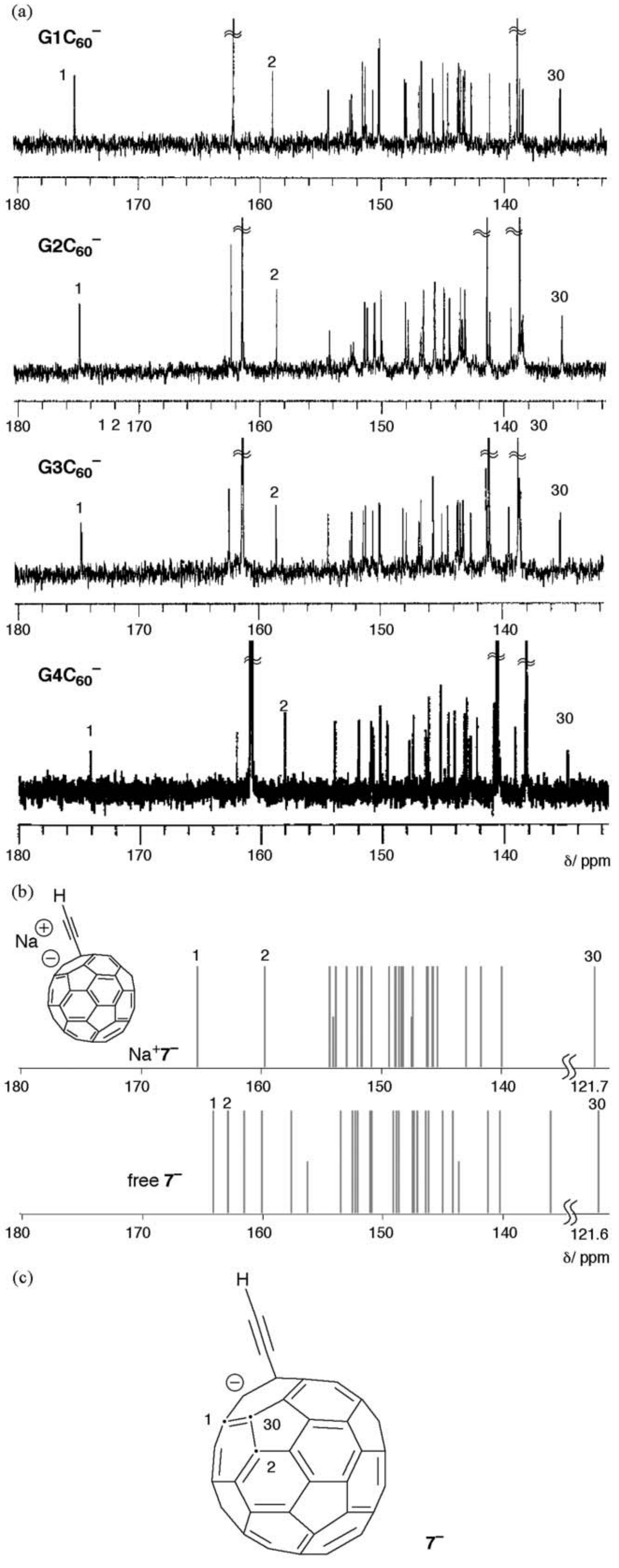


Fig. 5 ^{13}C NMR spectra of (a) dendritic $\mathbf{GnC_{60}}^-$ (n = 1–4) observed (75 MHz, THF-d_8) and (b) model compounds $Na^+\mathbf{7}^-$ and free $\mathbf{7}^-$ calculated by GIAO (SCF/6-31+G(d,p)//B3LYP/6-31G(d)). The signals are numbered based on the order of downfield shift and the corresponding carbons are shown in (c).

fullerene cage. The electrochemical study indicated that $\mathbf{GnC_{60}}^-$ (n = 1–4) anions can be electrochemically generated and are further reduced to the trianion stage. The formed anions were found to undergo facile dimerization upon reoxidation even when the fullerene core carried a large (**G3** to **G4**) dendritic addend. The dimer $\mathbf{G4C_{60}}$–$\mathbf{G4C_{60}}$ was chemically prepared and was found to be in equilibrium with the radical $\mathbf{G4C_{60}}^{\cdot}$ as confirmed by ESR measurements. The MD calculations indicated that the dendron moieties do not prohibit dimerization of the radical although they tend to wrap the fullerene core efficiently. This is ascribed to the flexibility of the benzyl-ether type dendrons.

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Experimental

General

All reagents and solvents were of commercial quality and were dried where necessary using standard procedures. All reactions were performed in standard glassware under an argon atmosphere. Dendrimer units **[Gn]-OH** and **[Gn]-Br** (n = 0–3) were synthesized according to the reported procedure.[14] Thin layer chromatography was performed on plastic plates coated with 0.2 mm thickness of silica gel 60 F_{254} (Merck). Medium pressure column chromatography (MPLC) was conducted by using silica gel 60 (230–400 mesh, Merck) columns and a Yamazen YFLC-540 pump. Recycling preparative gel permeation chromatography (GPC) was performed on a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H GPC columns using $CHCl_3$ as an eluent. Elemental analyses were performed at the Microanalysis Division of Institute for Chemical Research, Kyoto University. UV-vis spectra (λ_{max} in nm (log ε)) were measured on a Shimadzu UV-2100PC spectrometer. ^1H NMR spectra were recorded on Varian Mercury 300 and JEOL JNM-AL300 spectrometers; chemical shifts (δ) are quoted in ppm, relative to tetramethylsilane as an internal reference (0 ppm), and coupling constants (J) are quoted in Hz. MALDI-TOF mass spectra were obtained on an Applied Biosystems Voyager-DE STR spectrometer using dithranol as a matrix. FAB mass and EI mass spectra were obtained on a JEOL MStation JMS-700 spectrometer using 3-nitrobenzyl alcohol as a matrix in the case of FAB. Cyclic voltammetry (CV) was performed on a BAS CV-50W Voltammetric Analyser. The counter, working, and reference electrodes were Pt wire, glassy carbon, and Ag/$AgNO_3$, respectively. All solutions were purged with argon and retained under an argon atmosphere whilst the measurements were carried out. The potentials were corrected against ferrocene used as an internal standard added after each measurement.

Molecular Dynamics (MD) simulations were conducted using HYPERCHEM 6, Hypercube Inc.[15] All structure were preminimized with the MM^+ forcefield implemented in HYPERCHEM prior to the MD simulation. During the MD simulations the structures were heated to 1000 K and kept at this temperature for equilibration before they were allowed to cool to 0 K to establish the minimum energy structure. Conditions[7d] for the annealing: heat time, 5 ps; run time, 15 ps; cool time, 50 ps; step size, 0.001 ps; starting temperature, 0 K; simulation temperature, 1000 K; final temperature, 0 K; *in vacuo*; data collection period, 1 time step.

For the *ab initio* calculations, all the geometry optimizations and single-point NMR chemical shift calculations were carried out using the Gaussian 98 program.[22] The C_s symmetry was imposed throughout the calculations of **6**, $\mathbf{7}^-$ and $Na^+\mathbf{7}^-$. All ^{13}C chemical shifts are referenced to those of TMS calculated at the same level.

2,6-Bis(*tert*-butyldimethylsilyloxy)acetophenone (2)

To a solution of 2,6-dihydroxyacetophenone (**1**) (1.00 g, 6.60 mmol) in dry N,N-dimethylformamide (10 cm^3) was added *tert*-butyldimethylchlorosilane (2.01 g, 13.31 mmol) and

Table 2 Observed chemical shifts (ppm) of sp^2 carbons of the C_{60} cage for $\mathbf{GnC_{60}}^-$ (n = 1–4)

Compd	C1 ($\Delta\delta$)^a	C2 ($\Delta\delta$)^a	C30 ($\Delta\delta$)^a	C^- ($\Delta\delta$)^a
$\mathbf{G1C_{60}}^-$	175.27 (0.00)	158.95 (0.00)	135.46 (0.00)	120.71 (0.00)
$\mathbf{G2C_{60}}^-$	174.91 (−0.36)	158.60 (−0.35)	135.27 (−0.19)	120.33 (−0.38)
$\mathbf{G3C_{60}}^-$	174.72 (−0.55)	158.53 (−0.42)	135.23 (−0.23)	120.29 (−0.42)
$\mathbf{G4C_{60}}^-$	174.11 (−1.16)	158.09 (−0.86)	134.87 (−0.59)	119.79 (−0.92)

^{a}The difference in chemical shifts (ppm) from that of $\mathbf{G1C_{60}}^-$.

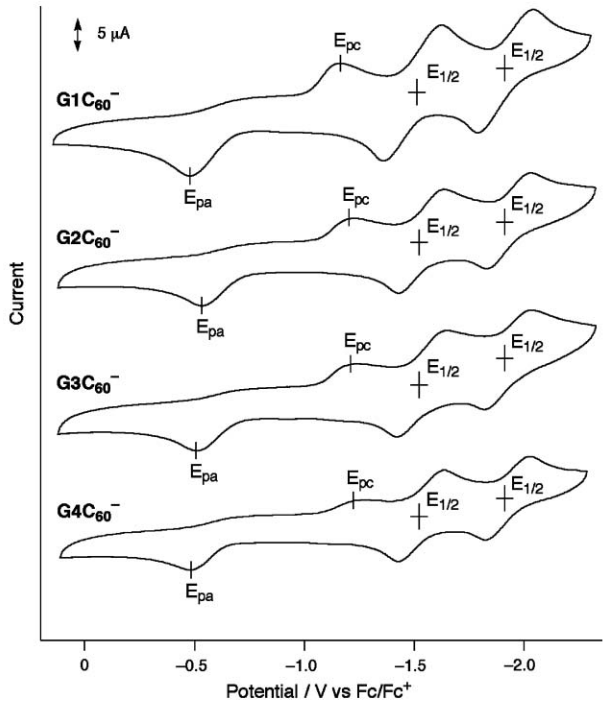
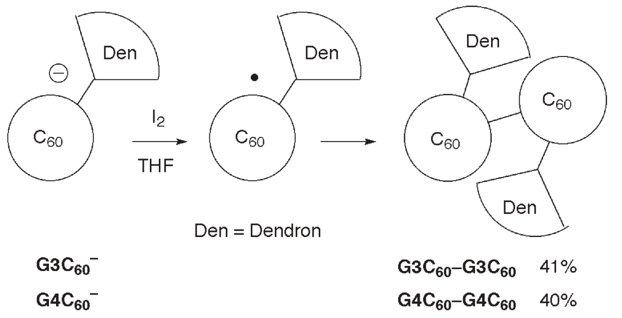


Fig. 6 Cyclic voltammograms of fullerenyl anions $\mathbf{GnC_{60}}^-$ (n = 1–4) in ODCB (c = 1 mM): scan rate, 0.1 V s^{-1}; supporting electrolyte, Bu_4NBF_4 (0.1 M).

Table 3 Results of cyclic voltammetry^a

Compd	E_{pa}	E_{pc}	$E_{red}{}^1$	$E_{red}{}^2$
$\mathbf{G1C_{60}}^-$	−0.48	−1.15	−1.49	−1.91
$\mathbf{G2C_{60}}^-$	−0.54	−1.20	−1.54	−1.93
$\mathbf{G3C_{60}}^-$	−0.51	−1.21	−1.53	−1.93
$\mathbf{G4C_{60}}^-$	−0.49	−1.23	−1.53	−1.92

^{a}Potential in volts *vs.* ferrocene/ferrocenium in ODCB with Bu_4NBF_4 as a supporting electrolyte (0.1 M); scan rate, 0.1 V s^{-1}.



Scheme 5 Synthesis of fullerene dimers, $\mathbf{G3C_{60}}$–$\mathbf{G3C_{60}}$ and $\mathbf{G4C_{60}}$–$\mathbf{G4C_{60}}$.

imidazole (1.79 g, 26.30 mmol), and the solution stirred at 60 °C for 20 h. The resulting mixture was then poured into water and extracted with diethyl ether. The extract was washed with brine, dried over $MgSO_4$, and evaporated to afford 2.4 g (96%) of **2** as a white solid (Analysis found: C, 63.23; H, 9.63; $C_{20}H_{36}O_3Si_2$ requires: C, 63.10; H, 9.53%); m/z (+FAB) 381 (M^+ + 1); δ_H ($CDCl_3$) 7.04 (1 H, t, J 8.4), 6.44 (2 H, d, J 8.4),

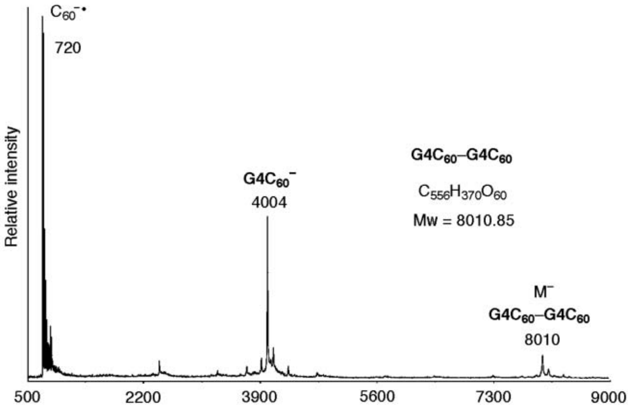
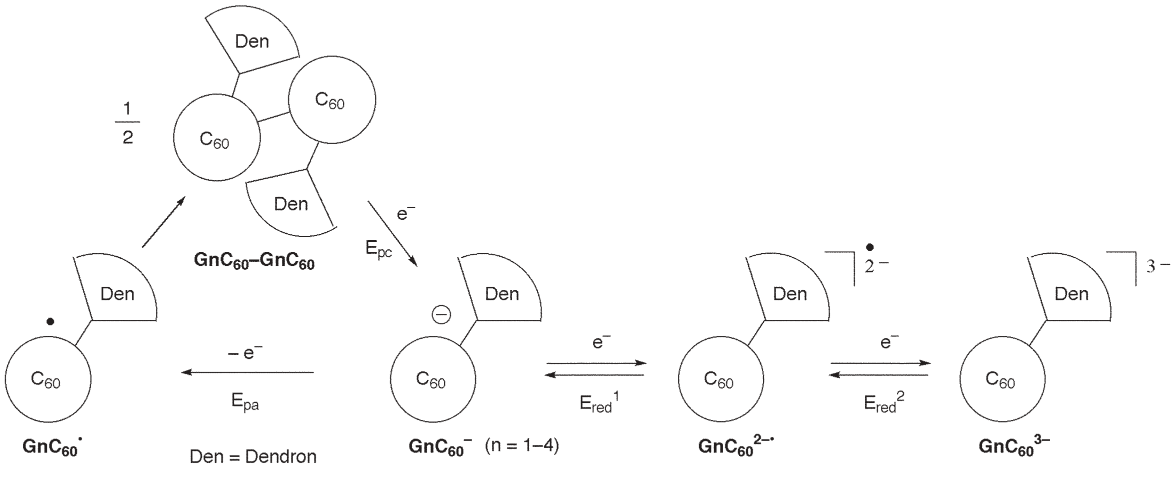


Fig. 7 MALDI-TOF MS (negative-ion, dithranol) of $\mathbf{G4C_{60}}$–$\mathbf{G4C_{60}}$.



Scheme 4 Electrochemical reactions of $\mathbf{GnC_{60}}^-$ (n = 1–4) on the electrode.

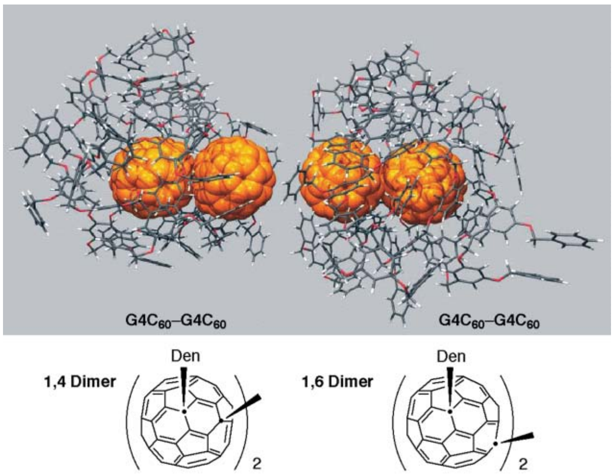


Fig. 8 Minimum energy structures at 0 K of 1,4- and 1, 6 derivatives of **$G4C_{60}$–$G4C_{60}$** after molecular dynamics (MD) simulation. All structures were preminimized with the MM^+ forcefield implemented in HYPERCHEM[15] prior to the MD simulation. During the MD simulations the structures were heated to 1000 K and kept at this temperature for equilibration before they were allowed to cool to 0 K to establish the minimum energy structure. Conditions[7d] for the simulated annealing: heat time, 5 ps; run time, 50 ps; cool time, 50 ps; step size, 0.001 ps; starting temperature, 0 K; simulation temperature, 1000 K; final temperature, 0 K; *in vacuo*; data collection period, 1 time step.

2.46 (3 H, s), 0.95 (18 H, s), 0.20 (12 H, s); δ_C ($CDCl_3$) 202.65, 152.61, 129.47, 126.66, 112.02, 32.38, 25.54, 18.02, −4.39.

2,6-Bis(*tert*-butyldimethylsilyloxy)-1-(1-chloroethenyl)benzene (3)

To a solution of **2** (508 mg, 1.33 mmol) in dry benzene (3 cm^3) was added phosphorus trichloride (0.63 cm^3, 7.22 mmol) and phosphorus pentachloride (340 mg, 1.63 mmol), and the solution stirred at room temperature for 20 h. The resulting mixture was then poured into ice-water and extracted with diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was chromatographed (SiO_2, hexane) to give 206 mg (39%) of **3** as a white solid (Analysis found: C, 59.92; H, 8.92; $C_{20}H_{35}ClO_2Si_2$ requires: C, 60.19; H, 8.84%); *m*/*z* (+FAB) 397 (M^+); δ_H ($CDCl_3$) 7.07 (1 H, t, *J* 8.2), 6.50 (2 H, d, *J* 8.2), 5.68 (1 H, d, *J* 0.9), 5.34 (1 H, d, *J* 0.9), 1.05 (18 H, s), 0.27 (12 H, s); δ_C ($CDCl_3$) 154.22, 133.36, 129.36, 123.16, 118.29, 111.93, 25.65, 18.17, −4.21.

2,6-Bis(*tert*-butyldimethylsilyloxy)-1-ethynylbenzene (4)

To a stirred solution of **3** (2.34 g, 5.86 mmol) in dry THF (10 cm^3) was added a 2.0 M solution of lithium diisopropylamide in THF (14.7 cm^3, 29.4 mmol) at −78 °C and the solution stirred at 0 °C for 3 h. The resulting mixture was then poured into water and extracted with diethyl ether. The extract was washed with saturated NH_4Cl solution and dried over Na_2SO_4. The solvent was removed *in vacuo* and the residue was chromatographed [SiO_2, hexane–toluene (97 : 3 v/v)] to give 1.47 g (69%) of **4** as a white solid (Analysis found: C, 66.11; H, 9.60; $C_{20}H_{34}O_2Si_2$ requires: C, 66.24; H, 9.45%); *m*/*z* (+EI) 362 (M^+); δ_H ($CDCl_3$) 7.02 (1 H, t, *J* 8.2), 6.45 (2 H, d, *J* 8.2), 3.30 (1 H, s), 1.02 (18 H, s), 0.22 (12 H, s); δ_C ($CDCl_3$) 158.55, 129.17, 112.69, 108.20, 84.89, 78.17, 25.77, 18.30, −4.24.

2,6-Dihydroxy-1-ethynylbenzene (5)

To a stirred solution of **4** (406 mg, 1.12 mmol) in THF (3 cm^3) was added acetic acid (0.15 cm^3) and a 1.0 M solution of tetrabutylammonium fluoride in THF (2.43 cm^3, 2.43 mmol), and the solution stirred at room temperature for 1 h. The resulting mixture was then poured into water and extracted with diethyl ether. The extract was washed with brine and dried over Na_2SO_4. The solvent was removed *in vacuo* to afford 150 mg of **5** in quantitative yield as a pale yellow solid, which was found to be unstable and was used for further reactions without purification; δ_H ($CDCl_3$) 7.15 (1 H, t, *J* 8.2), 6.52 (2 H, d, *J* 8.2), 5.56 (1 H, br), 3.80 (1 H, s); δ_C ($CDCl_3$) 157.66, 131.37, 106.94, 96.84, 90.49, 73.84.

General procedure for the synthesis of phenylacetylene derivatives having dendrimer units

A mixture of the appropriate dendritic benzyl bromide **[Gn]-Br** (*n* = 0–3) (2.2 equiv.), 2,6-dihydroxy-1-ethynylbenzene (**5**) (1.0 equiv.), potassium carbonate (2.5 equiv.), and 18-crown-6 (0.2 equiv.) in dry acetone was heated at reflux and stirred vigorously for 20–48 h. The mixture was allowed to cool, added to water and extracted with dichloromethane. The extracts were dried over Na_2SO_4 and evaporated to dryness. The crude product was purified as outlined below.

G1A

This compound was prepared from **[G0]-Br** and purified by MPLC [SiO_2, hexane–ethyl acetate (7 : 1 v/v)] to give **G1A** (84%) as a colourless oil (Analysis found: C, 84.05; H, 5.78; $C_{22}H_{18}O_2$ requires: C, 84.05; H, 5.77%); *m*/*z* (+EI) 314 (M^+); δ_H ($CDCl_3$) 7.46–7.27 (10 H, m), 7.09 (1 H, t, *J* 8.5), 6.50 (2 H, d, *J* 8.5), 5.14 (4 H, s), 3.54 (1 H, s); δ_C ($CDCl_3$) 161.17, 136.81, 129.85, 128.41, 127.64, 126.73, 105.57, 101.99, 85.80, 76.18, 70.41.

G2A

This compound was prepared from **[G1]-Br** and purified by GPC ($CHCl_3$) to give **G2A** (68%) as a colourless oil (Analysis found: C, 81.25; H, 5.72; $C_{50}H_{42}O_6$ requires: C, 81.23; H, 5.73%); *m*/*z* (+FAB) 739 (M^+ + 1); δ_H ($CDCl_3$) 7.43–7.31 (10 H, m), 7.12 (1 H, t, *J* 8.7), 6.74 (4 H, d, *J* 2.4), 6.55 (2 H, t, *J* 2.4), 6.51 (2 H, d, *J* 8.7), 5.13 (4 H, s), 5.03 (8 H, s), 3.49 (1 H, s); δ_C ($CDCl_3$) 161.04, 160.04, 139.35, 136.70, 130.00, 128.53, 127.94, 127.52, 105.56, 105.44, 101.79, 101.41, 85.67, 76.38, 70.26, 69.98.

G3A

This compound was prepared from **[G2]-Br** and purified by MPLC [SiO_2, toluene–ethyl acetate (20 : 1 v/v)] to give **G3A** (71%) as a colourless oil (Analysis found: C, 80.07; H, 5.69; $C_{106}H_{90}O_{14}$ requires: C, 80.18; H, 5.71%); *m*/*z* (+MALDI-TOF) 1609 (M^+ + Na); δ_H ($CDCl_3$) 7.38–7.13 (40 H, m), 7.05 (1 H, t, *J* 8.4), 6.69 (4 H, d, *J* 2.1), 6.43 (8 H, d, *J* 2.1), 6.53 (4 H, t, *J* 2.1), 6.50 (2 H, t, *J* 2.1), 6.44 (2 H, d, *J* 8.4), 5.03 (16 H, s), 4.95 (8 H, s), 4.91 (4 H, s), 3.50 (1 H, s); δ_C ($CDCl_3$) 161.03, 160.01, 159.89, 139.32, 139.15, 136.65, 128.94, 128.46, 128.13, 127.88, 127.70, 127.46, 106.21, 105.52, 101.74, 101.44, 85.84, 76.44, 70.22, 69.93, 69.80.

G4A

This compound was prepared from **[G3]-Br** and purified by MPLC [SiO_2, toluene–ethyl acetate (25 : 1 v/v)] to give **G4A** (92%) as a colourless oil (Analysis found: C, 80.19; H, 5.71; $C_{218}H_{186}O_{30}$ requires: C, 79.69; H, 5.71%); *m*/*z* (+MALDI-TOF) 3308 (M^+ + Na); δ_H ($CDCl_3$) 7.43–7.16 (80 H, m), 7.03 (1 H, t, *J* 8.1), 6.68 (4 H, d, *J* 2.1), 6.64 (16 H, d, *J* 2.1), 6.62 (8 H, d, *J* 2.1), 6.53 (8 H, t, *J* 2.1), 6.51 (2 H, t, *J* 2.1), 6.50 (4 H, d, *J* 2.1), 6.42 (2 H, d, *J* 8.1), 5.02 (4 H, s), 4.97 (32 H, s), 4.90 (24 H, s), 3.51 (1 H, s); δ_C ($CDCl_3$) 161.08, 160.09, 159.99, 139.24, 139.17, 136.79, 128.53, 127.95, 127.53, 106.34, 101.55, 85.11, 77.22, 70.04, 69.93.

General procedure for the synthesis of GnC$_{60}$H (n = 1–4)

To a vigorously stirred suspension of fullerene C_{60} (50–100 mg) in THF (7–15 cm^3), obtained by irradiation in a ultrasonic bath for 60 min, was added at room temperature the appropriate lithium acetylide (2 equiv.), prepared from **GnA** (n = 1–4) and Bu^{n}Li in THF. The mixture was stirred for 30 min, during which time the color changed into dark green. To the mixture was added two drops of trifluoroacetic acid to give a dark brown suspension. The solvent was removed *in vacuo* and the crude product was purified as outlined below.

G1C$_{60}$H

This compound was prepared from **G1A** and purified by MPLC [SiO$_2$, CS$_2$–toluene (5 : 1 v/v)] to give **G1C$_{60}$H** (52%) as a brown powder (Analysis found: C, 95.12; H, 1.69; $C_{82}H_{18}O_2$ requires: C, 95.16; H, 1.75%); *m/z* (–MALDI-TOF) 1034 (M$^-$); vis (ODCB) 435 (3.70), 705 (2.6); δ_H (CDCl$_3$) 7.67 (4 H, d, *J* 6.9), 7.38–7.23 (7 H, m), 7.11 (1 H, s), 6.77 (2 H, d, *J* 8.4), 5.32 (4 H, s); δ_C (CDCl$_3$) 161.25, 151.99, 151.93, 147.65, 147.39, 146.79, 146.42, 146.25, 145.93, 145.64, 145.48, 145.40, 144.75, 144.61, 143.23, 142.60, 142.58, 142.18, 142.08, 142.05, 141.73, 141.63, 140.46, 140.29, 136.97, 136.18, 135.20, 130.41, 128.51, 127.85, 126.81, 105.85, 102.77, 100.61, 77.18, 70.65, 62.13, 55.78.

G2C$_{60}$H

This compound was prepared from **G2A** and purified by MPLC [SiO$_2$, CS$_2$–toluene (1 : 1 v/v)] to give **G2C$_{60}$H** (68%) as a brown powder (Analysis found: C, 90.30; H, 2.88; $C_{110}H_{42}O_6$ requires: C, 90.52; H, 2.90%); *m/z* (–MALDI-TOF) 1458 (M$^-$); vis (ODCB) 435 (3.67), 705 (2.6); δ_H (CDCl$_3$) 7.36–7.15 (21 H, m), 7.01 (1 H, s), 6.87 (4 H, d, *J* 2.4), 6.73 (2 H, d, *J* 8.4), 6.49 (2 H, t, *J* 2.4), 5.22 (4 H, s), 4.97 (8 H, s); δ_C (CDCl$_3$) 161.15, 160.08, 151.80, 151.76, 147.51, 146.75, 146.26, 146.21, 146.10, 145.75, 145.62, 145.40, 145.33, 145.23, 145.19, 144.58, 144.40, 142.95, 142.44, 142.37, 142.03, 141.96, 141.87, 141.76, 141.52, 141.44, 140.25, 139.94, 139.19, 136.61, 136.00, 135.05, 130.37, 128.53, 127.94, 127.53, 106.49, 105.90, 102.70, 101.46, 101.25, 77.19, 70.96, 70.03, 62.09, 55.71.

G3C$_{60}$H

This compound was prepared from **G3A** and purified by MPLC (SiO$_2$, toluene) to give **G3C$_{60}$H** (67%) as a brown powder (Analysis found: C, 86.66; H, 3.85; $C_{166}H_{90}O_{14}$ requires: C, 86.37; H, 3.93%); *m/z* (–MALDI-TOF) 2307 (M$^-$); vis (ODCB) 436 (3.64), 707 (2.5); δ_H (CDCl$_3$) 7.39–7.16 (41 H, m), 6.99 (1 H, s), 6.87 (4 H, d, *J* 2.4), 6.76 (2 H, d, *J* 8.7), 6.60 (8 H, d, *J* 2.1), 6.50 (4 H, t, *J* 2.1), 6.47 (2 H, t, *J* 2.1), 5.20 (4 H, s), 4.96 (16 H, s), 4.90 (8 H, s); δ_C (CDCl$_3$) 161.14, 160.04, 159.98, 151.72, 151.69, 147.49, 147.24, 146.69, 146.22, 146.15, 146.08, 145.71, 145.49, 145.33, 145.31, 145.19, 145.12, 144.53, 144.36, 142.85, 142.42, 142.29, 141.97, 141.94, 141.84, 141.69, 141.44, 141.40, 140.23, 139.85, 139.12, 138.99, 136.61, 135.92, 135.00, 130.41, 128.55, 127.98, 127.57, 125.26, 106.40, 105.83, 102.45, 101.44, 101.26, 77.20, 70.92, 70.03, 69.92, 62.07, 55.66.

G4C$_{60}$H

This compound was prepared from **G4A** and purified by MPLC [SiO$_2$, CS$_2$–diethyl ether (40 : 1 v/v)] to give **G4C$_{60}$H** (76%) as a brown powder (Analysis found: C, 83.38; H, 4.80; $C_{278}H_{186}O_{30}$ requires: C, 83.34; H, 4.68%); *m/z* (–MALDI-TOF) 4005 (M$^-$); vis (ODCB) 436 (3.71), 708 (2.5); δ_H (CDCl$_3$) 7.38–7.12 (81 H, m), 6.95 (1 H, s), 6.84 (4 H, d, *J* 2.1), 6.68 (2 H, d, *J* 8.7), 6.61 (16 H, d, *J* 2.1), 6.56 (8 H, d, *J* 2.1), 6.52 (8 H, t, *J* 2.1), 6.47 (2 H, t, *J* 2.1), 6.45 (4 H, t, *J* 2.1), 5.12 (4 H, s), 4.95 (32 H, s), 4.85 (24 H, s); δ_C (CDCl$_3$) 161.19, 160.08, 160.00, 151.71, 151.67, 147.40, 147.17, 146.65, 146.15, 146.07, 146.01, 145.98, 145.65, 145.44, 145.29, 145.24, 145.12, 145.07, 144.46, 144.30, 142.78, 142.34, 142.21, 141.93, 141.88, 141.79, 141.66, 141.39, 141.34, 140.19, 139.80, 139.22, 139.12, 139.09, 136.74, 135.87, 134.95, 130.40, 128.51, 127.92, 127.49, 106.44, 106.01, 102.68, 101.60, 101.27, 77.21, 70.97, 70.04, 69.98, 62.08, 55.69.

General procedure for the generation and measurement of ^{1}H and ^{13}C NMR spectra of GnC$_{60}$$^-$ (n = 1–4) anions

A solution of Bu^{t}OK in THF (1.1 equiv.) was added to **GnC$_{60}$H** (n = 1–4) (17–23 mg, 0.005–0.02 mmol) in a glass tube (outer diameter, 8 mm) equipped with an NMR tube as a side arm under an argon atmosphere to give a dark green solution. The whole system was connected to a vacuum line, and the solvent was evaporated. To the residue was added THF-d_8 (0.8 cm^3, distilled over Na mirror) by vacuum distillation and the whole system was subjected to a freeze–pump–thaw cycle three times. The whole system was sealed under vacuum ($< 10^{-4}$ mmHg). The solution was transferred into the NMR tube, which was sealed off and subjected to NMR measurements.

G1C$_{60}$$^-$

This anion was prepared from **G1C$_{60}$H**; δ_H (THF-d_8) 7.89 (4 H, d, *J* 8.1), 7.33–7.24 (5 H, m), 7.13 (2 H, t, *J* 7.2), 6.86 (2 H, d, *J* 8.4), 5.38 (4 H, s); δ_C (THF-d_8) 175.25, 162.16, 158.95, 154.39, 152.62, 152.41, 151.53, 151.33, 150.69, 150.18, 148.09, 147.96, 146.91, 146.72, 145.80, 145.75, 144.98, 144.58, 143.71, 143.68, 143.52, 143.31, 143.20, 142.65, 141.19, 139.54, 138.94, 138.75, 138.49, 135.46, 130.10, 129.33, 128.08, 127.47, 120.71, 107.11, 106.26, 101.20, 80.16, 71.22, 54.79.

G2C$_{60}$$^-$

This anion was prepared from **G2C$_{60}$H**; δ_H (THF-d_8) 7.35 (8 H, d, *J* 6.9), 7.25–7.15 (13 H, m), 6.92 (4 H, d, *J* 2.1), 6.74 (2 H, d, *J* 8.7), 6.49 (2 H, t, *J* 2.1), 5.41 (4 H, s), 5.02 (8 H, s); δ_C (THF-d_8) 174.91, 162.32, 161.39, 158.60, 154.26, 152.52, 152.32, 151.42, 151.19, 150.61, 150.05, 148.05, 147.84, 146.82, 146.61, 145.67, 144.90, 144.44, 143.65, 143.56, 143.40, 143.18, 141.38, 141.15, 139.44, 138.73, 138.58, 138.48, 135.27, 129.79, 129.15, 128.50, 128.36, 120.33, 108.37, 106.77, 102.46, 101.93, 80.25, 72.26, 70.73, 56.18.

G3C$_{60}$$^-$

This anion was prepared from **G3C$_{60}$H**; δ_H (THF-d_8) 7.35–7.12 (41 H, m), 6.91 (4 H, d, *J* 2.1), 6.76 (2 H, d, *J* 8.4), 6.66 (8 H, d, *J* 2.1), 6.48 (2 H, t, *J* 2.1), 6.47 (4 H, t, *J* 2.1), 5.37 (4 H, s), 4.96 (24 H, s); δ_C (THF-d_8) 174.72, 162.42, 161.33, 161.25, 158.53, 154.28, 152.50, 152.32, 151.38, 151.17, 150.60, 150.06, 149.98, 148.15, 147.85, 146.82, 146.62, 145.66, 144.93, 144.45, 143.69, 143.61, 143.44, 143.20, 143.15, 142.57, 141.28, 141.18, 141.03, 139.46, 138.67, 138.58, 138.48, 135.23, 129.92, 129.21, 128.96, 128.47, 128.41, 120.19, 108.43, 107.10, 106.72, 106.60, 106.25, 102.54, 102.28, 102.11, 80.36, 72.39, 70.70, 56.06.

G4C$_{60}$$^-$

This anion was prepared from **G4C$_{60}$H**; δ_H (THF-d_8) 7.35–7.09 (81 H, m), 6.91 (4 H, d, *J* 2.1), 6.70 (2 H, d, *J* 8.4), 6.65 (8 H, d, *J* 2.4), 6.64 (16 H, d, *J* 2.4), 6.50 (8 H, t, *J* 2.1), 6.48 (2 H, t, *J* 2.1), 6.46 (4 H, t, *J* 2.1), 5.32 (4 H, s), 4.95 (24 H, s), 4.89 (24 H, s); δ_C (THF-d_8) 174.11, 162.03, 160.97, 160.91, 160.83, 158.09, 153.93, 152.04, 151.95, 150.99, 150.80, 150.22, 146.71, 149.61, 147.83, 147.51, 146.51, 146.28, 145.32, 145.28, 144.63, 144.14, 143.35, 143.30, 143.15, 142.88, 142.80, 142.27, 140.94, 140.87, 140.70, 140.59, 140.41, 139.14, 138.31, 138.27, 138.19, 134.87, 129.50, 128.97, 128.91, 128.74, 128.70, 128.67, 128.30, 128.24, 128.19, 128.06, 127.94, 127.84, 119.79, 106.95, 106.85, 106.53, 102.47, 102.26, 102.07, 80.30, 72.28, 70.71, 70.57, 55.98.

General procedure for the generation and the measurement of vis-NIR spectra of GnC$_{60}^{-}$ (*n* = 1–4) anions

One drop of diazabicyclo[5.4.0]undec-7-ene (*ca.* 7 mg, *ca.* 50 mmol) was added to a solution of **GnC$_{60}$H** (*n* = 1–4) in ODCB under an argon atmosphere to give a dark green solution. The solution was transferred to a 10 mm cell under a nitrogen atmosphere and subjected to measurement.

G1C$_{60}^{-}$

This anion was generated from **G1C$_{60}$H** (1.038 mg, 1.003 × 10^{-3} mmol) in ODCB (10 cm^3); vis-NIR (ODCB) 542 (3.47), 638 (3.63), 963 (3.44).

G2C$_{60}^{-}$

This anion was generated from **G2C$_{60}$H** (1.562 mg, 1.070 × 10^{-3} mmol) in ODCB (10 cm^3); vis-NIR (ODCB) 540 (3.47), 637 (3.61), 964 (3.40).

G3C$_{60}^{-}$

This anion was generated from **G3C$_{60}$H** (1.154 mg, 4.999 × 10^{-4} mmol) in ODCB (5 cm^3); vis-NIR (ODCB) 543 (3.47), 636 (3.61), 959 (3.39).

G4C$_{60}^{-}$

This anion was generated from **G4C$_{60}$H** (1.603 mg, 4.001 × 10^{-4} mmol) in ODCB (4 cm^3); vis-NIR (ODCB) 543 (3.47), 636 (3.61), 959 (3.39).

General procedure for the generation and CV measurement of GnC$_{60}^{-}$ (*n* = 1–4) anions

A solution of Bu^{t}OK in THF (0.0945 M, 0.03 cm^3, 1 equiv.) was added to a 1 mM solution of **GnC$_{60}$H** (*n* = 1–4) in 0.1 M solution of Bu$_4$NBF$_4$ in ODCB (2.0 cm^3) under an argon atmosphere to give a dark green solution. The solution was subjected to the measurement of cyclic voltammetry.

Dimer G3C$_{60}$–C$_{60}$G3

To a solution of **G3C$_{60}$H** (10.2 mg, 4.42 × 10^{-3} mmol) in THF (5 cm^3) was added a 0.0945 M solution of Bu^{t}OK in THF (0.051 cm^3, 4.7 × 10^{-3} mmol) at room temperature under an argon atmosphere to give a dark green solution and the solution stirred at room temperature for 10 min. To the reaction mixture was added a 0.0039 M solution of iodine in THF (0.56 cm^3, 2.2 × 10^{-3} mmol) at room temperature. The solvent was removed *in vacuo* and the residue was purified by GPC to afford 4.1 mg (41%) of **G3C$_{60}$–C$_{60}$G3** as a brown solid; *m*/*z* (–MALDI-TOF) 4615 (M$^-$); δ_H (CDCl$_3$) 7.45–7.10 (m), 6.63–6.30 (m), 5.10–4.65 (m).

Dimer G4C$_{60}$–C$_{60}$G4

To a solution of **G4C$_{60}$H** (15.6 mg, 3.89 × 10^{-3} mmol) in THF (5 cm^3) was added a 0.0945 M solution of Bu^{t}OK in THF (0.045 cm^3, 4.3 × 10^{-3} mmol) at room temperature under an argon atmosphere to give a dark green solution and the solution stirred at room temperature for 10 min. To the reaction mixture was added a 0.0039 M solution of iodine in THF (0.52 cm^3, 2.0 × 10^{-3} mmol) at room temperature. The solvent was removed *in vacuo* and the residue was purified by GPC to give 5.6 mg (40%) of **G4C$_{60}$–C$_{60}$G4** as a brown solid; *m*/*z* (–MALDI-TOF) 8010 (M$^-$); δ_H (CDCl$_3$) 7.36–7.21 (m), 6.67–6.26 (m), 5.09–4.58 (m).

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