Synthesis of the singly bonded fullerene dimer $C_{120}H_2$ and the difullerenylacetylene $C_{122}H_2$, and generation of the all-carbon dianion $C_{122}{}^{2-}$

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1,1′,2,2′-Tetrahydrobi[60]fulleren-1-yl $C_{120}H_2$ (**9**) and bis(1,2-dihydro[60]fulleren-1-yl)acetylene $C_{122}H_2$ (**11**) were prepared, and their structures were determined based on ^{1}H and ^{13}C NMR, MS, and UV–VIS spectroscopies. While the deprotonation of $C_{120}H_2$ with *t*-BuOK caused dissociation and resulted in the formation of the radical anion $C_{60}{}^{\bullet-}$, the generation of dianion $C_{122}{}^{2-}$ (**12**$^{2-}$) from $C_{122}H_2$ (**11**) was confirmed by visible–near-IR and ^{13}C NMR spectroscopies. The electrochemical studies indicated that dianion $C_{122}{}^{2-}$ (**12**$^{2-}$) was formed also during the reduction process of $C_{122}H_2$ (**11**). The oxidation process of the dianion **12**$^{2-}$ was found to be irreversible suggesting that the radical species produced undergoes rapid coupling.

Introduction

The synthesis and characterization of molecules having two directly connected [60]fullerene cages are important because such molecules are considered building blocks of pearl-necklace type [60]fullerene polymers. The recombination of $RC_{60}{}^{\bullet}$ radicals was reported to give such directly connected dimers RC_{60}–$C_{60}R$ (**1**),[1,2] but few of these dimers have been fully characterized [3,4] due to the difficulty in isolation of the dimer in pure form from various positional, stereo, and rotational isomers.[5] In contrast, directly linked dimers connected by a cyclobutane ring, *i.e.* C_{120} (**2**),[6] or by a tetrahydrofuran and/or cyclopentane ring(s) such as $C_{120}O$ (**3**),[7,8] $C_{120}O_2$ (**4**),[9] and $C_{121}H_2$ (**5**)[7] were isolated in pure form owing to their rigid structures. Molecules having two [60]fullerene frameworks across a double bond or a triple bond are also regarded as model structural units of carbon-rich C_{60} networks, and compounds **6**,[10] **7**,[11] or **8** [11,12] have been synthesized as such examples.

Here we describe the preparation of 1,1′,2,2′-tetrahydro-

R = *n*-C$_{12}$H$_{25}$

7

R = *n*-C$_{12}$H$_{25}$, CH$_2$Ph, CH$_2$OThp

8

bi[60]fulleren-1-yl $C_{120}H_2$ (**9**), the simplest form of the directly bonded [60]fullerene, and its deprotonation to the dianion **10**$^{2-}$, which resulted in rapid dissociation into the radical anion $C_{60}{}^{\bullet-}$. Also we report the preparation of the simplest form of the fullerene–acetylene–fullerene triad, bis(1,2-dihydro[60]-fulleren-1-yl)acetylene $C_{122}H_2$ (**11**), and its conversion to the all-carbon gigantic dianion $C_{122}{}^{2-}$ (**12**$^{2-}$).

9

10^{2-}

11

12^{2-}
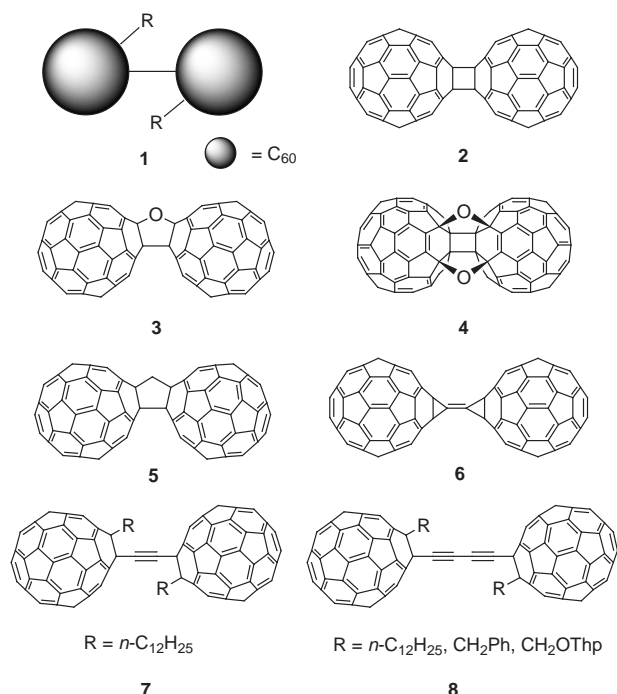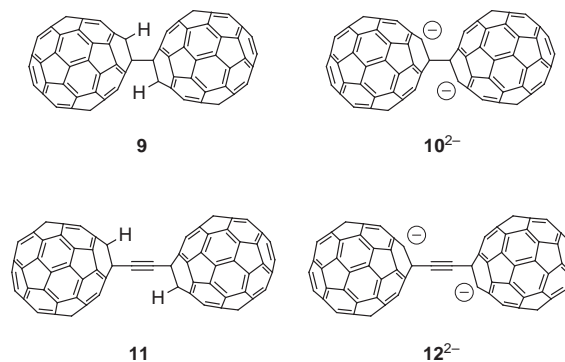
Results and discussion

Syntheses of 1,1′,2,2′-tetrahydrobi[60]fulleren-1-yl (9) and bis(1,2-dihydro[60]fulleren-1-yl)acetylene (11)

Although the radical $HC_{60}{}^{\bullet}$ was produced from a photochemically generated hydrogen atom and [60]fullerene (C_{60}) and the recombination of $HC_{60}{}^{\bullet}$ was supposed to give the dimer HC_{60}–$C_{60}H$ (**9**), the isolation of the dimer was not reported.[1] Now an attempt on the synthesis of dimer **9** was made by dimerization of $HC_{60}{}^{\bullet}$ generated by the protonation of the radical anion $C_{60}{}^{\bullet-}$.[13] A deep red suspension was prepared by treating C_{60} with sodium naphthalenide in THF [14] under thoroughly deaerated vacuum conditions. Addition of an excess amount of trifluoroacetic acid (TFA) gave a brown suspension. After evaporation of the solvent and TFA, the residue was redissolved in carbon disulfide. The analysis of the soluble product by HPLC indicated a new peak attributed to dimer **9** at a longer retention time than the monomeric compounds.[15] The separation by preparative HPLC gave recovered C_{60} (20.3%), 1,2-dihydro[60]fullerene $C_{60}H_2$ (**13**, 8.5%),[16] and dimer **9** (4.9%), with a rather poor yield due to the formation of a considerable amount of insoluble material, which could not be identified.
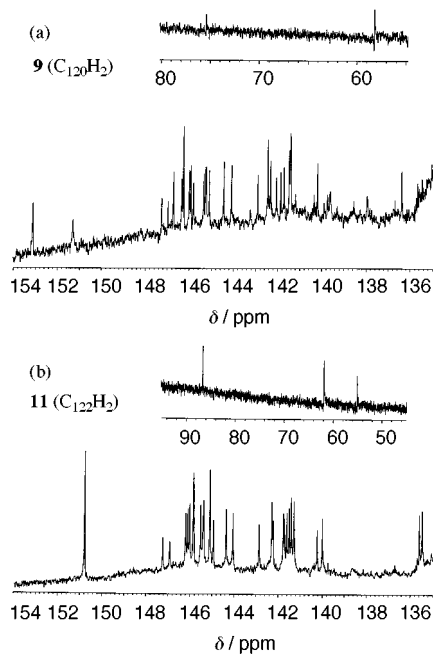
Fig. 1 ^{13}C NMR spectra of (a) dimer **9** and (b) difullerenylacetylene **11** (75 MHz, 1-chloronaphthalene–benzene-d_6 5:1).

Fig. 2 UV–VIS spectra of (a) dimer **9** (1.24×10^{-5} M) and (b) difullerenylacetylene **11** (1.38×10^{-5} M) in ODCB.

On the other hand, reaction of C_{60} with an excess of dilithio-acetylene prepared by the reaction of trichloroethene with 3 equivalents of n-BuLi[17] gave a black suspension, which was quenched with an excess of TFA to give a brown suspension. The products were taken up in o-dichlorobenzene (ODCB) and the soluble components were separated by preparative HPLC to give recovered C_{60} (35.6%) and di[60]fullerenylacetylene **11** (6.6%).[15]

Structures of dimer 9 and di[60]fullerenylacetylene 11

The structures of dimer **9** and di[60]fullerenylacetylene **11** were determined by ^1H and ^{13}C NMR, MS, and UV–VIS spectroscopies. The ^1H NMR spectrum of dimer **9** showed a singlet signal at δ 7.59 corresponding to the proton directly attached to the C_{60} framework. Compared with the corresponding signal of 1,2-dihydro[60]fullerene (δ 6.30),[18] the signal of dimer **9** was shifted more than 1 ppm downfield, clearly demonstrating the effect of the ring current of the opposite [60]fullerene cage. The directly bonded fullerene dimers are known to be hardly soluble in common organic solvents. However, dimer **9** was found to be soluble in 1-chloronaphthalene[19] at a concentration of about 10 mg cm^{-3}, thus making it possible to acquire the ^{13}C NMR spectrum shown in Fig. 1(a). The ^{13}C NMR spectrum exhibited 27 signals in the region between δ 154 and 136, which were assigned to the sp^2-carbons of the [60]fullerene cage. Thus the molecule is considered to have a symmetry plane in the [60]-fullerene cage assuming that three signals are hidden by incidental overlapping. Signals for fullerenyl sp^3-carbons (δ 75.55 and 58.25) were also confirmed, and this compound was identified as 1,1′,2,2′-tetrahydrobi[60]fulleren-1-yl $C_{120}H_2$ (**9**). This structure was supported by the relatively sharp absorption at 433 nm in the UV–VIS spectrum which is typical for 1,2-dihydro[60]fullerene derivatives[20] [Fig. 2(a)]. The FAB mass spectrum (negative-ion mode) showed a peak at m/z 721 for $C_{60}H^-$, but the molecular-ion peak was not clear because of a facile dissociation of the intercage bond. However in the MALDI TOF mass spectrum, a weak peak was observed at m/z 1446 (M^+ + 4) together with a series of peaks corresponding to the loss of C_{2n} ($n = 1–5$) and a base peak at m/z 723.[21]

The fact that only the 1,2-1′,2′-isomer of $C_{120}H_2$ [1,1′,2,2′-tetrahydrobi[60]fulleren-1-yl] was obtained upon recombination of the radical $HC_{60}^{\bullet}$ is in sharp contrast to the results of
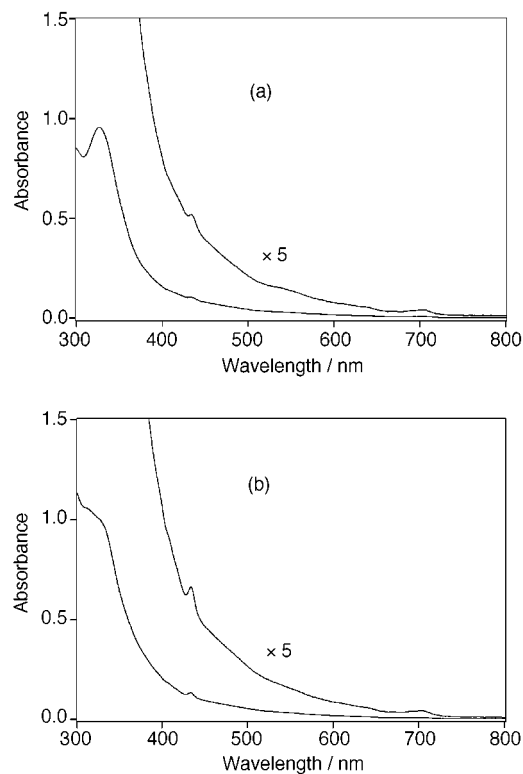
MM3 calculations by Osawa $et\ al.$,[5] in which the steric energy of the 1,2-1′,2′-isomer was shown to be higher than that of the 1,4-1′,4′-isomer.

As to the structure of di[60]fullerenylacetylene **11**, the APCI mass spectrum clearly exhibited the molecular-ion peak at m/z 1466. The ^1H NMR spectrum showed a singlet signal at δ 6.76 assigned to the fullerenyl proton. The ^{13}C NMR spectrum [Fig. 1(b)] exhibited 27 signals in the region between δ 151 and 135, which were assigned to the sp^2-carbons of the [60]fullerene cage, together with signals for the acetylenic carbon (δ 86.75) and fullerenyl sp^3-carbons (δ 61.95 and 55.16). The structure is most likely the 1,2-isomer **11**, assuming that three ^{13}C NMR signals are hidden by the incidental overlapping. The UV–VIS spectrum showed a relatively sharp peak at 433 nm, which is typical for 1,2-addition,[20] as shown in Fig. 2(b).

Deprotonation of dimer 9

An X-ray powder diffraction study for the solid dimeric phase of RbC_{60} and KC_{60}, indicated that the structure of C_{120}^{2-} is a singly bonded dimer.[22] It was of interest to examine whether the doubly negatively-charged dimer C_{120}^{2-} (**10**$^{2-}$) could be generated in the liquid phase. Thus, the generation of C_{120}^{2-} (**10**$^{2-}$) was attempted by deprotonation of dimer **9** with a base. To a suspension of **9** in benzonitrile (PhCN) was added 20 molar equivalents of t-BuOK. The suspension immediately changed to a reddish purple solution. The visible–near-IR spectrum of this solution (Fig. 3) showed only the absorption characteristic of the radical anion $C_{60}^{\bullet -}$ at 1080 nm.[23] It was concluded that the dianion **10**$^{2-}$ generated by the deprotonation was unstable in solution, in contrast to the solid state, and the dissociation of the intrinsically weak central bond took place to give the radical anion $C_{60}^{\bullet -}$. This instability of **10**$^{2-}$ can be ascribed to the coulombic repulsion between the two negatively charged C_{60} cages which are directly bonded.

Generation of dianion 12²⁻

Next, an attempt was made to generate an acetylene-connected di[60]fullerenyl dianion **12**$^{2-}$. This dianion is a precursor to the
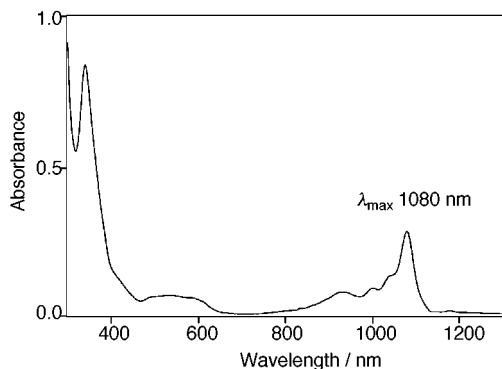
Fig. 3 Visible–near-IR absorption spectrum of the radical anion $C_{60}^{\bullet-}$ produced from dimer **9** and *t*-BuOK in benzonitrile.
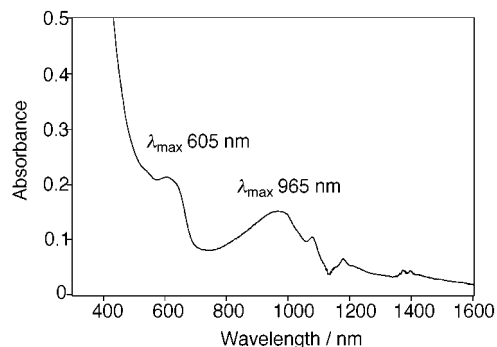

Fig. 4 Visible–near-IR absorption spectrum of the dianion 12^{2-} in benzonitrile (3.6×10^{-5} M).

acetylene-connected difullerenyl compound **7**, which was previously synthesized,[11] and should be stable compared with the directly bonded dianion C_{120}^{2-} (**10**$^{2-}$). In fact, the addition of a large excess of *t*-BuOK to a suspension of **11** in PhCN gave a green solution. The visible–near-IR spectrum (Fig. 4) exhibited absorptions at 605 and 965 nm, which are typical for the 2-substituted-1,2-dihydro[60]fulleren-1-yl anion RC_{60}^{-}.[24–26] The structure of dianion 12^{2-} was also confirmed by the ^{13}C NMR spectrum (Fig. 5), which exhibited signals for an acetylenic carbon (δ 89.56) and an sp^3-carbon of the C_{60} framework (δ 55.91) together with 28 signals for sp^2-carbons in the C_{60} framework in the region between δ 157 and 135 ppm: the chemical shifts of these sp^2-carbons are quite similar to those reported for the 2-*tert*-butyl-[2] and 2-(oct-1-ynyl)-1,2-dihydro-[60]fulleren-1-yl anions.[26] This dianion is composed of only carbon, and to the best of our knowledge is the largest all-carbon dianion.

The redox behavior of di[60]fullerenylacetylene 11 and dianion 12^{2-}

The singly bonded dimer **1** or the [2 + 2] type dimer **2** are known to easily dissociate into the monomer during the first reduction process,[6,26,27] whereas the electrochemical studies on $C_{120}O$ (**3**)[28] and biazafullerene $(C_{59}N)_2$[29] showed three pairs of reversible and stepwise reductions without dissociation indicating the electrochemical interaction between the two [60]fullerene cages. On the other hand, di[60]fullerenylacetylene **11** is formally considered as an acetylene–fullerene homoconjugated π-system with detachable protons, and its redox behavior attracted interest.

The cyclic voltammogram of di[60]fullerenylacetylene **11** in ODCB demonstrated three reversible reduction waves at $E_{1/2}$ −1.17, −1.52, −2.10 V *vs.* Fc/Fc$^+$. In addition, a reversible wave at $E_{1/2}$ −1.94 V and an irreversible oxidative peak at E_{pa} −0.58 V also appeared, which are most probably attributed to the reduction and oxidation of 12^{2-} produced by the deproton-
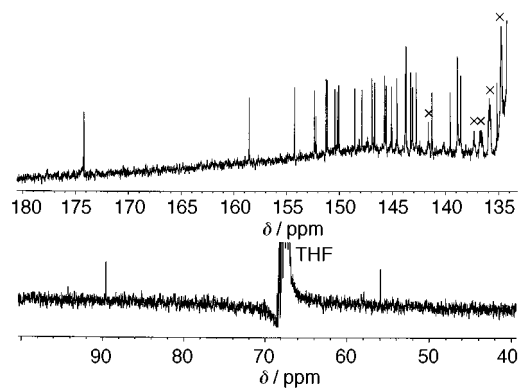

Fig. 5 ^{13}C NMR spectrum of dianion 12^{2-} (C_{122}^{2-}) (75 MHz, PhCN–THF-d_8 6:1): signals marked with × are side bands of the solvent signals.

ation which occurred during the reductive process.[25,30] The cyclic voltammetry of dianion 12^{2-} generated from **11** with *t*-BuOK in ODCB–DMSO (1:1) exhibited two reversible reductive waves at $E_{1/2}$ −1.34 and −1.82 V *vs.* Fc/Fc$^+$ and an irreversible oxidative peak at E_{pa} −0.45 V. It is assumed that two electrons are transferred to the two [60]fullerene cages at each of the reduction steps. Since no separation of the wave was observed for each of the stepwise reductions of **11**, the interaction between the two [60]fullerene cages is supposed to be negligible if any. The irreversibility of the oxidation process for 12^{2-} at −0.45 V suggests that the produced diradical $12^{\bullet\bullet}$ should be reactive and undergo rapid radical coupling to give a dimer or oligomers although no product study was conducted for this process.

Experimental

General

NMR spectra were recorded on a Varian Mercury-300 spectrometer (300 MHz for ^{1}H and 75.4 MHz for ^{13}C NMR). In ^{1}H NMR spectra, chemical shifts are recorded in ppm by using the residual proton's peak (2.04 ppm) of acetone-d_6 contained in a capillary tube as an external standard. In ^{13}C NMR spectra, chemical shifts are read by using the signal of benzene-d_6 (128.0 ppm) or THF-d_8 (25.5 ppm) as an internal standard. UV–VIS spectra were recorded with a Shimadzu UV-2100PC spectrometer. VIS–near-IR spectra were recorded with a Shimadzu UV-3101(PC)S spectrometer. FAB mass spectra were measured on a JEOL JMS700 mass spectrometer. MALDI TOF mass spectra were taken on a Finnigan-Mat VISION 2000 spectrometer. APCI mass spectra were taken on a Finigan-Mat TSQ700 mass spectrometer. HPLC analyses were conducted on a Shimadzu LC-10AD chromatograph, with detection at 326 nm, equipped with a Cosmosil Buckyprep column (4.6 × 250 mm) using toluene as an eluent. The preparative HPLC was performed using a Cosmosil 5PBB column (10 × 250 mm) with *o*-dichlorobenzene (ODCB) or carbon disulfide (CS$_2$) as an eluent. Cyclic voltammetry was conducted on a BAS CV-50W electro-analyzer using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/0.01 M AgNO$_3$ reference electrode. After each measurement ferrocene was added as an internal standard to correct the peak potential.

THF was freshly distilled over sodium benzophenone ketyl. PhCN, ODCB, and DMSO were distilled over calcium hydride before use. [60]Fullerene (99.5%) was purchased from Term Co.

1,1′,2,2′-Tetrahydrobi[60]fulleren-1-yl (C$_{120}$H$_2$, 9)

A solution of sodium naphthalenide in THF (20 cm^3) was prepared by mixing sodium metal (0.341 g, 14.8 mmol) and

naphthalene (1.96 g, 15.3 mol) in THF at room temperature under argon. To a stirred suspension of C_{60} (202.1 mg, 0.280 mmol) in degassed THF (40 cm^3) under vacuum was added a 0.743 M THF solution of sodium naphthalenide (1.20 cm^3, 0.892 mmol) which was degassed by three freeze–pump–thaw cycles, to give a dark red suspension. After the mixture was stirred for 8 h at room temperature, trifluoroacetic acid (TFA) (0.7 cm^3, 9 mmol) was added to the mixture under vacuum. The resulting dark brown mixture was evaporated under reduced pressure to give a dark brown solid. The solid was dissolved in 90 cm^3 of CS_2 and was subjected to preparative HPLC using a Cosmosil 5PBB column and eluted with CS_2 to give compound **9** (9.9 mg, 4.9%), 1,2-dihydro[60]fullerene (17.3 mg, 8.5%), and C_{60} (41.1 mg, 20.3%).

9: δ_H (CS_2 locked with acetone-d_6 contained in a capillary tube) 7.59 (s, 1H); δ_C (1-chloronaphthalene–benzene-d_6 5:1) 153.16, 151.33, 147.28, 147.00, 146.76, 146.37, 146.31, 146.03, 145.96, 145.84, 145.38, 145.30, 145.26, 145.13, 144.47, 144.12, 142.93, 142.48, 142.35, 142.09, 141.90, 141.74, 141.51, 141.45, 141.44, 140.22, 136.40, 75.55, 58.25; λ_{max}(ODCB)/nm 325 (log ε 4.89), 433 (3.92) and 703 (2.83); m/z (FAB) 721; m/z (MALDI TOF)[21] 723 (100%), 1326 (0.5%), 1350 (1%), 1374 (2%), 1398 (4%), 1422 (6%) and 1446 (1%).

1,2-Dihydro[60]fullerene:[16,18] δ_H (CS_2 locked with acetone-d_6 contained in a capillary tube) 6.30 (s, 1H); δ_H (benzene-d_6) 5.90 (s, 1H); δ_C (1-chloronaphthalene–benzene-d_6 5:1) 151.85, 147.22, 146.97, 145.99, 145.92, 145.66, 145.07, 145.02, 144.31, 142.93, 142.17, 141.54, 141.49, 141.19, 139.90, 135.77, 52.52.

Reaction of $C_{120}H_2$ (9) with *t*-BuOK: visible–near-IR spectral measurement

A cell having two side arms was employed for the visible–near-IR measurements. Compound **9** (0.469 mg, 3.25×10^{-4} mmol) was weighed by the use of a microbalance in a tared glass tube, and then placed in one side arm. Then 2.5 cm^3 of PhCN and 0.35 cm^3 of 0.0184 M solution of *t*-BuOK (6.44×10^{-3} mmol) in THF were placed in another side arm. The solution was degassed by three freeze–pump–thaw cycles, and the whole apparatus was sealed off under vacuum. Compound **9** was dissolved in the solution containing *t*-BuOK, and the resulting colored solution was subjected to the visible–near-IR measurement: λ_{max}(PhCN)/nm 1080.

Bis(1,2-dihydro[60]fulleren-1-yl)acetylene ($C_{122}H_2$, 11)

Following a literature procedure,[17] a solution of dilithioacetylene in THF was prepared as follows. To a mixture of 5.0 cm^3 of THF and 2.2 cm^3 of 1.6 M solution of *n*-BuLi (3.52 mmol) in hexane cooled at −78 °C, was added dropwise a 1.11 M solution of trichloroethylene in THF (1.00 cm^3, 1.11 mmol) over 3 min. The mixture was stirred at −78 °C for 20 min, at 0 °C for 20 min, and then at room temperature for 30 min. To a stirred solution of C_{60} (102.0 mg, 0.142 mmol) in ODCB (20 cm^3) was added the dilithioacetylene solution (7.0 cm^3, 0.948 mmol) over 3 min at room temperature. After the mixture was stirred for 1 h at room temperature, TFA (0.4 cm^3, 5 mmol) was added. The mixture was evaporated under reduced pressure to give a dark brown solid. The solid was dissolved in 27 cm^3 of ODCB and was subjected to preparative HPLC using a Cosmosil 5PBB column and was eluted with ODCB to give compound **11** (6.8 mg, 6.6%) and C_{60} (36.3 mg, 35.6%).

11: δ_H (CS_2 locked with acetone-d_6 contained in a capillary tube) 6.76 (s, 1H); δ_C (1-chloronaphthalene–benzene-d_6 5:1) δ 150.81, 147.27, 146.95, 146.23, 146.13, 146.05, 145.88, 145.55, 145.45, 145.41, 145.12, 144.97, 144.39, 144.09, 142.89, 142.30, 142.25, 141.77, 141.73, 141.62, 141.52, 141.41, 141.29, 140.24, 140.01, 135.59, 135.46, 86.75, 61.95, 55.16; λ_{max}(ODCB)/nm 313 (log ε 4.88), 433 (3.98) and 703 (2.79); m/z (−APCI) 720 (100%) and 1466 (100%).

Ethyne-1,2-diylbis[60]fulleride dianion (12^{2-})

(a) ^{13}C NMR spectrum. For the ^{13}C NMR measurement, a glass tube connected to a vacuum line through a stopcock and with an NMR tube as a side arm was employed. To a stirred suspension of **11** (14.9 mg, 0.0102 mmol) in PhCN (0.6 cm^3) in the glass tube was added 1.03 cm^3 of a 0.0208 M solution of *t*-BuOK (0.0214 mmol) in THF under argon by the use of a syringe. The mixture was stirred for 20 min under argon to give a dark green solution. To remove THF and *t*-BuOH, the mixture was evaporated under reduced pressure. The dark green solution was degassed by three freeze–pump–thaw cycles. Through a vacuum line, 0.1 cm^3 of pre-dried THF-d_8 (over Na) was transferred by vacuum distillation onto the solution. The apparatus was disconnected under vacuum and the solution was poured into the NMR tube, which was then sealed off and subjected to the NMR measurement.

12^{2-}: δ_C (PhCN–THF-d_8 6:1) 174.24, 158.55, 154.23, 152.33, 152.20, 151.24, 151.11, 150.40, 150.16, 150.03, 148.54, 147.86, 146.92, 146.67, 145.72, 145.58, 145.06, 144.56, 143.77, 143.71, 143.29, 143.10, 142.74, 141.26, 139.54, 138.85, 138.54, 135.11, 89.56, 55.91.

(b) Visible–near-IR spectrum. For the visible–near-IR measurement was employed a cell with two side arms. Compound **11** (0.318 mg, 2.17×10^{-4} mmol) was weighed by the use of a microbalance in a tared glass tube, which was then placed in one side arm. Then 6.00 cm^3 of PhCN and 0.200 cm^3 of a 0.0250 M solution of *t*-BuOK (5.00×10^{-3} mmol) in THF were placed in another side arm. The solution was degassed by three freeze–pump–thaw cycles, and the whole apparatus was sealed off under vacuum. Compound **11** was dissolved in the solution containing *t*-BuOK, and the resulting colored solution was subjected to the visible–near-IR measurement. 12^{2-}: λ_{max}(PhCN)/nm 605 (log ε 3.75) and 965 (3.58).

(c) Cyclic voltammetry. Cyclic voltammetry was conducted for 12^{2-} after the treatment of **11** (0.898 mg, 6.12×10^{-4} mmol) with a 0.0216 M solution of *t*-BuOK in THF (0.063 cm^3, 1.36×10^{-3} mmol) in 1.20 cm^3 of ODCB–DMSO (1:1) under an argon atmosphere.

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