Size-Selective Formation of C_{78} Fullerene from a Three-Dimensional Polyyne Precursor

Yoshito Tobe,*[a] Rui Umeda,[a] Motohiro Sonoda,[a] and Tomonari Wakabayashi[b]

Abstract: Multicyclic cagelike cyclophanes **2a** and **2b** containing cyclobutene rings have been prepared as precursors of three-dimensional polyynes $C_{78}H_{18}$ (**1a**) and $C_{78}H_{12}Cl_6$ (**1b**), respectively. Laser irradiation of **2a** and **2b** induced expulsion of the aromatic fragment, indane, to give the three-dimensional polyyne anions $C_{78}H_{18}^-$ and $C_{78}H_{12}Cl_6^-$, respectively. Whereas the former anion lost only four hydrogen atoms to form $C_{78}H_{14}^-$, complete loss of all hydrogen and chlorine atoms was observed from the latter anion, to yield a C_{78}^- ion that has a fullerene structure which was proven by its characteristic fragmentation pattern.

Keywords: alkynes · cyclophanes · fullerenes · macrocycles · polycycles

Introduction

Since the discovery of fullerene[1] and its preparative-scale production,[2] the chemistry of fullerenes has been extensively developed mainly for the most abundant C_{60} and C_{70}. However, little has been done for fullerenes larger than C_{70}, even though the larger fullerenes are expected to display interesting properties that are not conceivable with C_{60} and C_{70}.[3] This is mainly because the larger fullerenes are formed in low yields as hard-to-isolate mixtures of by-products of the production of C_{60} and C_{70} and because there exists an increasing number of possible isomers with an increasing number of the carbon atoms.[4] The only exception to this trend is the endohedral fullerenes,[5] most of which have a carbon cage larger than C_{82}, but there are still a very limited number of them available. Thus, the size-selective and geometry-selective formations of large fullerenes are two important problems hitherto unsolved in fullerene science. The chemical synthesis of fullerenes from structurally well-defined precursors is promising in these respects compared to the nonselective methods such as vaporization of graphite and combustion of hydrocarbons. Indeed, Scott et al. have shown that the appropriately designed polycyclic aromatic hydrocarbon $C_{60}H_{30}$ converts into the C_{60}^+ ion selectively upon laser irradiation in the gas phase by C–C bond formation accompanying the dehydrogenation.[6] Moreover, they reported the first size-selective preparation of C_{60} by the high-temperature pyrolysis of the related chlorohydrocarbon $C_{60}H_{27}Cl_3$.[7] Cyclic polyynes can be regarded as viable precursors of C_{60} fullerene, since Roskamp and Jarrold proposed a mechanism for C_{60} fullerene formation to explain ring formation between spiraling polyyne chains.[8] It should be pointed out that they also predicted that similar polyyne cyclization of appropriate precursors would form larger fullerenes as well through similar pathways. Experimentally, Diederich and co-workers first observed the size-selective formation of the fullerene C_{60}^+ by the gas-phase coalescence of the cyclic polyyne C_{30}^+, which was produced size-selectively from a well-defined precursor.[9] Although a relatively strong peak for the C_{70}^+ ion was detected by similar coalescence of C_{18}^+ and C_{24}^+, many other carbon clusters ions were also formed; size-selective formation of larger fullerenes has not so far been achieved.[10] In connection with the polyyne route to fullerenes, Rubin and co-workers and our group have developed independently an approach to C_{60} from well-defined, three-dimensional (3D) polyyne precursors $C_{60}H_6$ and $C_{60}Cl_6$, which were generated from the corresponding precursors by expulsion of stable fragments such as carbon monoxide[11] or indane[12] by laser irradiation. Indeed, the 3D polyynes collapsed into C_{60} ions (both negative and positive) accompanied by the loss of hydrogen and/or chlorine atoms. Even though the preparative-scale synthesis of C_{60} has not yet been achieved by this route, we planned to extend it to the size-selective formation of larger

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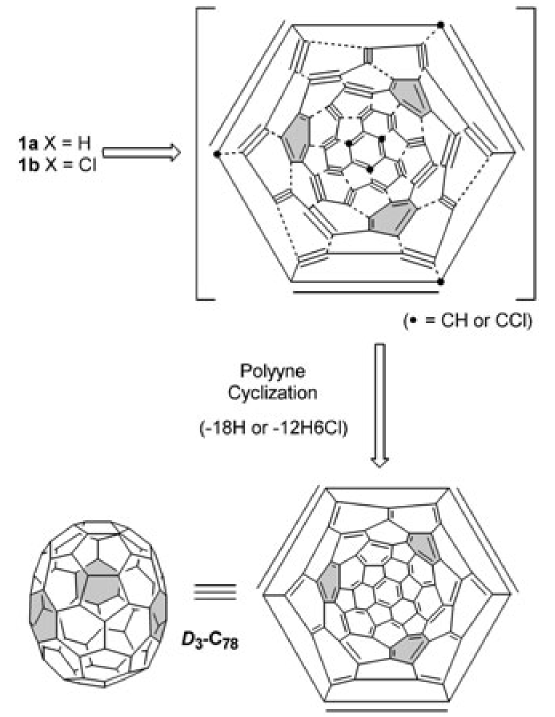
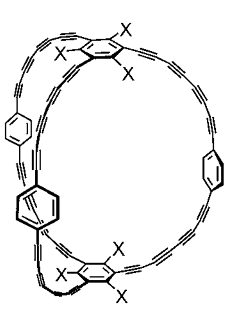
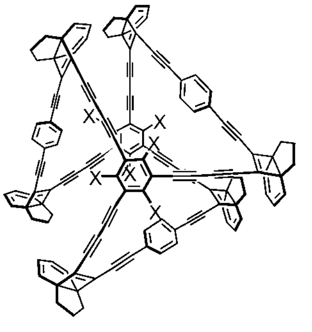


Scheme 1. A speculation for the spiraling polyyne cyclization for $C_{78}H_{18}$ and $C_{78}H_{12}Cl_6$ to form C_{78}.

fullerenes. Namely, on the basis of a speculative mechanism for polyyne cyclization,[12b,13] we envisioned that insertion of benzene (shaded in Scheme 1) or phenylene units into the polyyne chain of the C_{60} precursor would lead to the formation of higher fullerenes of C_{60+18n} ($n=1$, 2 …), as shown in Scheme 1 for D_3-C_{78} as an example. Accordingly, we designed 3D polyynes **1a** and **1b** as precursors of C_{78} and cage-like cyclophanes **2a** and **2b** having [4.3.2]propellane units as precursors of the polyynes **1a** and **1b**, respectively.[14] We disclose here the synthesis of cyclophanes **2a** and **2b**, the generation of polyynes **1a** and **1b** from them, and the size-selective formation of C_{78} fullerene from the chlorine-containing polyyne **1b**.



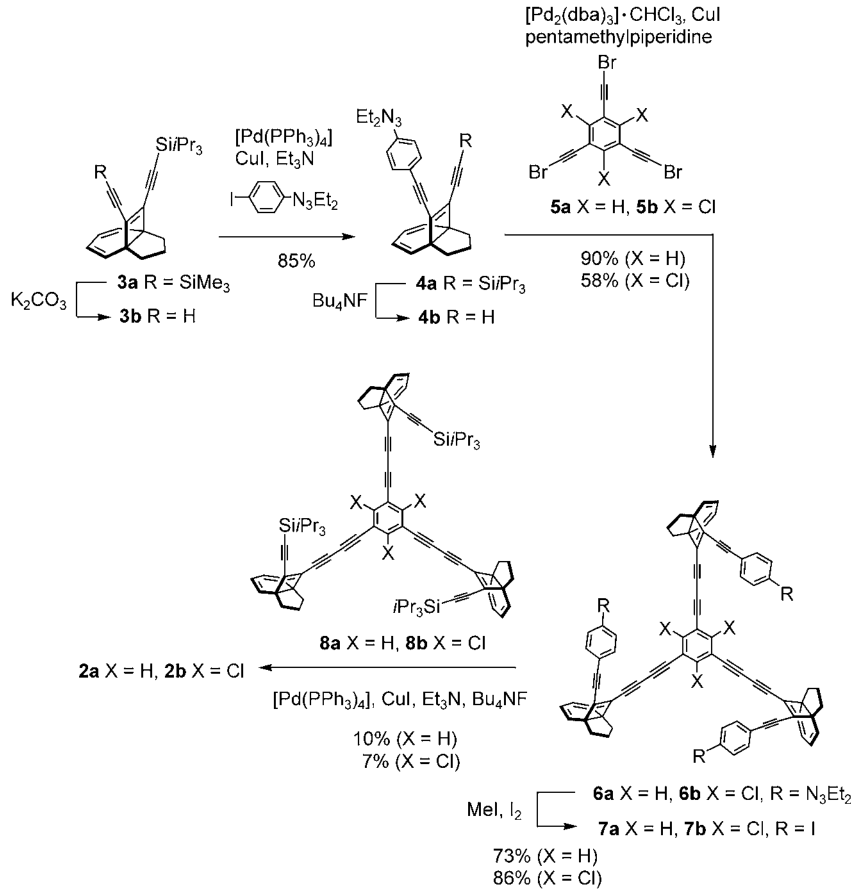
1a X=H ($C_{78}H_{18}$)
1b X=Cl ($C_{78}H_{12}Cl_6$)



2a X = H
2b X = Cl

Results and Discussion

The synthesis of precursors **2a** and **2b** is shown in Scheme 2.[15] Selective removal of the trimethylsilyl group from the diethynylpropellane derivative **3a**[14] gave **3b**. Subsequent Pd-catalyzed cross-coupling of **3b** with diethyl-(4-iodophenyl)triazene[16] gave compound **4a**, and deprotection of the triisopropylsilyl group gave **4b**. Pd-catalyzed cross-coupling of three equivalents of **4b** with the tris(bromoethynyl)benzene derivative **5a** afforded the triad **6a**, and the



Scheme 2. Synthesis of precursors **2a** and **2b** of three-dimensional polyynes **1a** and **1b**.

subsequent transformation of the triazene to iodo group gave **7a**. The final cross-coupling reaction of **7a** with an in situ generated terminal alkyne derived from **8a**[12] by removal of the triisopropylsilyl group yielded the multicyclic cage-like compound **2a**. Similarly, coupling of **4b** with the trichloro derivative **5b** to form **6b** followed by iodination gave **7b**, which was subjected to cross-coupling with an in situ prepared terminal alkyne derived from **8b**[12b] to furnish the hexachloro derivative **2b**.

Laser-desorption (LD) time-of-flight (TOF) mass spectra of **2a** and **2b** were recorded by irradiation of the solid samples with a nitrogen laser (337 nm) followed by detection of the negative ions in the reflectron mode (Figure 1). Laser ionization/desorption of **2a** leads principally to the formation of the negative ion of **1a** ($C_{78}H_{18}^-$) by extrusion of six indane fragments from the molecular ion, which is not detected (Figure 1a). The peaks due to the anions $[C_{78}H_{18}(\text{indane})]^-$ and $[C_{78}H_{18}(\text{indane})_2]^-$, in which one or two cyclobutene rings are still intact, are also observed. As shown in the inset of Figure 1a, the loss of four hydrogen atoms down to $C_{78}H_{14}^-$ (*m/z* 960) was observed. The isotope distribution of the peaks at *m/z* 960–962 strongly suggests the absence of intermediate anions such as $C_{78}H_{15}^-$ and $C_{78}H_{16}^-$, indicating that the loss of four hydrogen atoms takes place simultaneously. However, in contrast to the anion $C_{60}H_6^-$ which loses six hydrogen atoms to form C_{60}^-,[11,12] the anions $C_{78}H_{18}^-$ and $C_{78}H_{14}^-$ are resistant to further elimination of hydrogen, just as observed for $C_{60}H_{18}^-$,[17] indicating that the hydrogen losses accompanied by the polyyne cyclization are not kinetically favorable. In addition, further fragmentation due to the loss of C_2, the collapse process characteristic to fullerene cations[18] and anions,[19] from $C_{78}H_{14}^-$ was not observed. These results strongly suggest that the $C_{78}H_{14}$ anion does not possess a fullerene-like structure. On the other hand, the halogenated derivatives are known to serve better than the corresponding hydrocarbon as precursors of fullerenes,[7,12b,20] presumably because the facile cleavage of C–Cl bonds would provide favorable funnels for the intramolecular ring closure. Indeed, expulsion of most of the hydrogen and chlorine atoms takes place simultaneously from the chlorinated anion $C_{78}H_{12}Cl_6^-$ generated by laser ionization/desorption of precursor **2b** (Figure 1b and c). As shown in the inset of Figure 1b, the distribution of the peaks at *m/z* 936–944 indicates the presence of C_{78}^- together with $C_{78}H_2^-$ and $C_{78}H_4^-$ in which two or four hydrogen atoms are still intact. Figure 2a shows the observed peak distribution which is nicely reproduced by simulation assuming the distribution of C_{78}^-, $C_{78}H_2^-$, $C_{78}H_4^-$, and $C_{78}H_6^-$ in a ratio of 10:10:4:1 (Figure 2b). The relative ratio of these ions did not change upon increasing the laser fluence. It is rather surprising that the hydrogen-containing anions such as $C_{78}H_2^-$ and $C_{78}H_4^-$ are resistant to dehydrogenation in spite of their high degree of unsaturation. It is not clear, however, whether these species possess fullerene structures. On the other hand, the C_{78}^- ion is more likely to have a fullerene structure; as shown in Figure 1b, small peaks due to the fragmentation by loss of C_2 from C_{78}^- down apparently to C_{70}^- were observed at relatively high laser fluence, which are characteristic to the fullerene ions.[18,19] Carbon and hydrocarbon ions larger than C_{78}^- up to C_{86}^- formed by C_2 addition are also observed, similar to the situation for the C_{60} anion formed from its polyyne precursors.[11,12] These fragmentation peaks were not observed in the mass spectrum at low laser fluence (Figure 1c). For the lower mass region, the calculated isotope

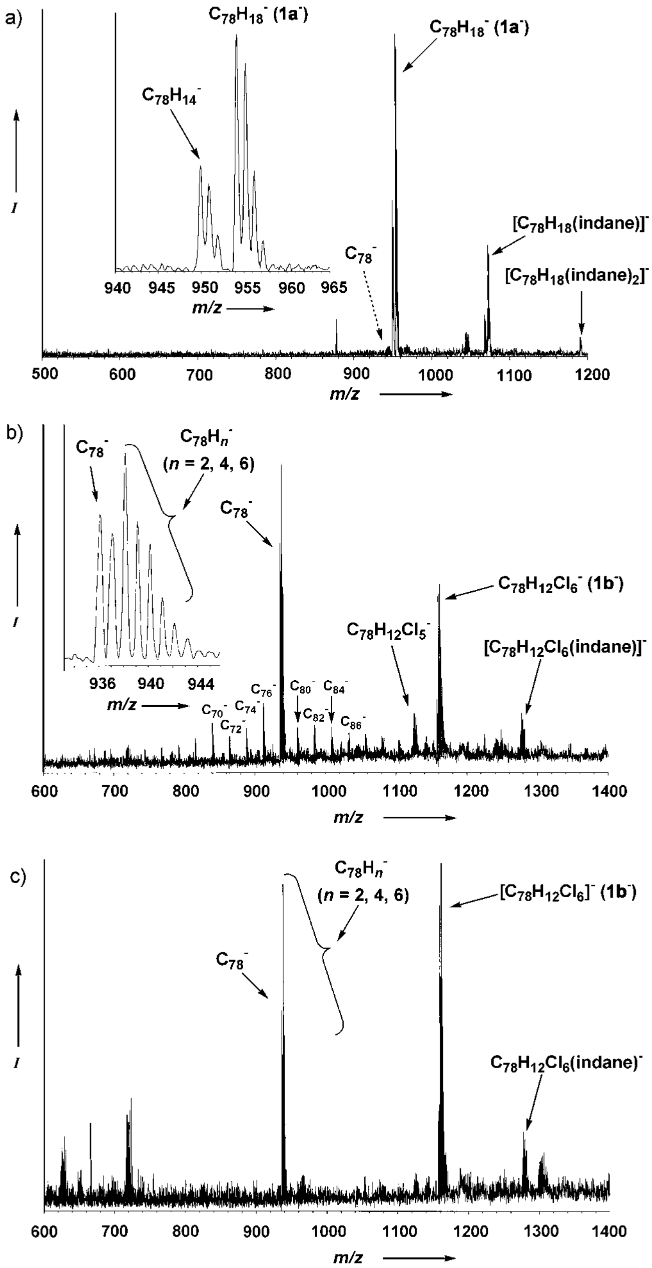


Figure 1. a) Negative-ion mode laser desorption TOF mass spectrum of **2a** $[C_{78}H_{18}(\text{indane})_6]^-$. Inset: Expansion of the spectrum for $C_{78}H_{18}^-$ and $C_{78}H_{14}^-$. b) Negative-ion mode laser desorption TOF mass spectrum of **2b** $[C_{78}H_{12}Cl_6(\text{indane})_6]^-$ at relatively high laser fluence. Inset: Expansion of the spectrum for C_{78}^- and $C_{78}H_n^-$ ($n=2$, 4, 6). c) Negative-ion mode laser desorption TOF mass spectrum of **2b** $[C_{78}H_{12}Cl_6(\text{indane})_6]^-$ at relatively low laser fluence.

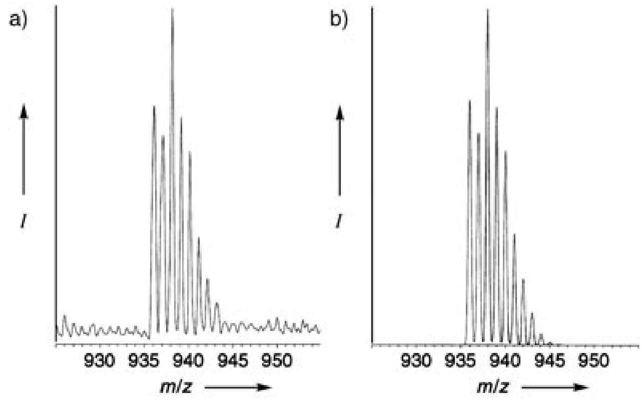


Figure 2. a) Observed peak distribution for C_{78}^- and $C_{78}H_n^-$ ($n=2$, 4, 6). b) Calculated peak distribution for C_{78}^-, $C_{78}H_2^-$, $C_{78}H_4^-$, and $C_{78}H_6^-$ in a ratio of 10:10:4:1.

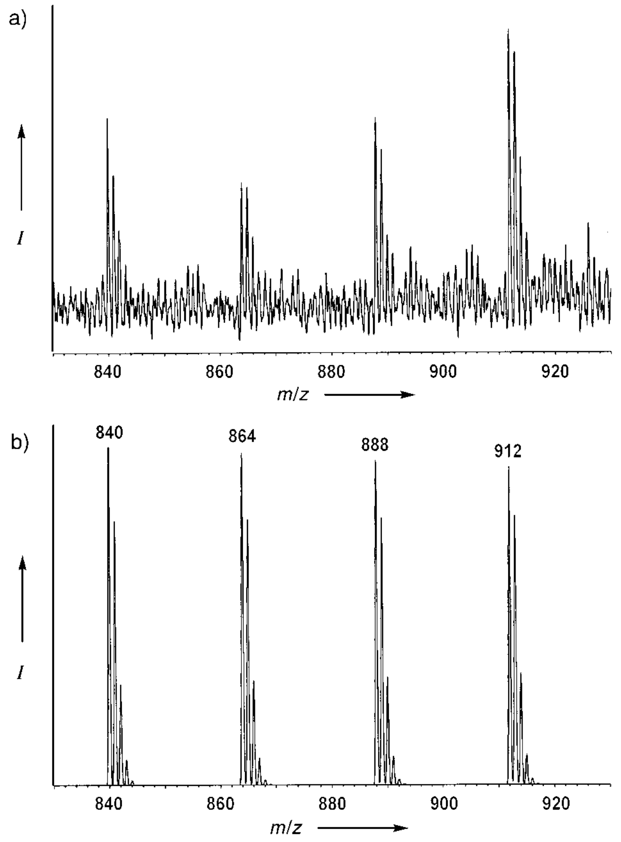


Figure 3. a) Observed spectrum for the lower mass region (C_{70}^-, C_{72}^-, C_{74}^-, and C_{76}^-). b) Calculated isotope distribution for C_{70} to C_{76}.

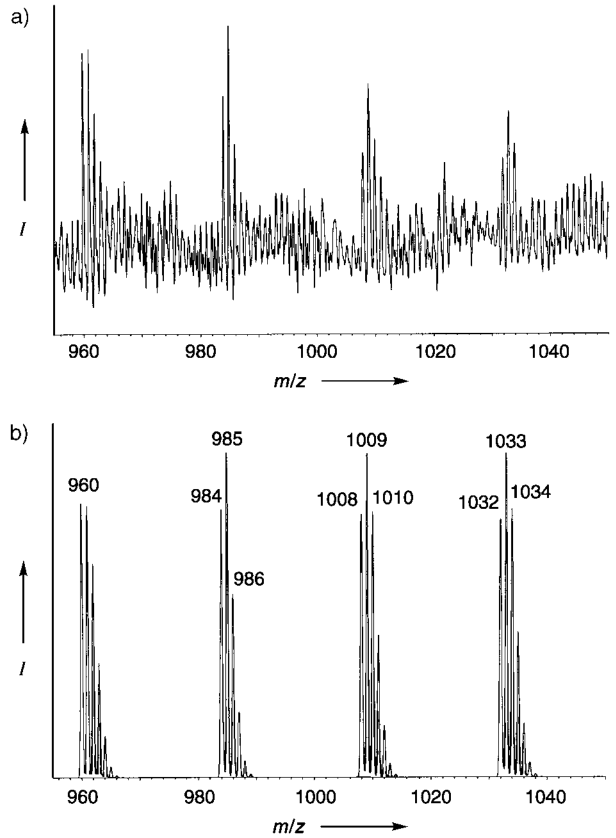
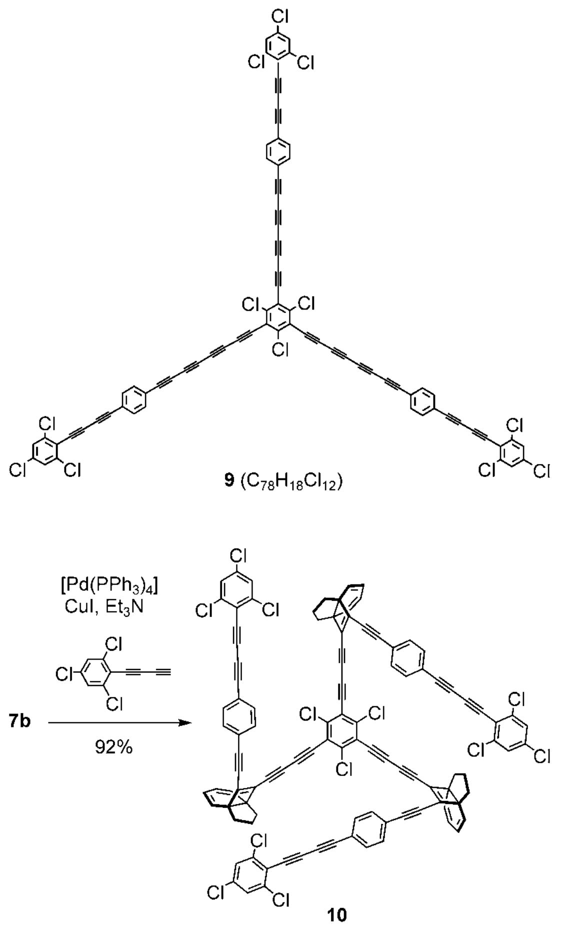


Figure 4. a) Observed spectrum for the higher mass region (C_{80}^-, C_{82}^-, C_{84}^-, and C_{86}^-). b) Calculated peak distributions assuming C_{80} + $C_{80}H$ + $C_{80}H_2$ (10:1:3), C_{82} + $C_{82}H$ (10:3), C_{84} + $C_{84}H$ + $C_{84}H_2$ (10:3:3), and C_{86} + $C_{86}H$ + $C_{86}H_2$ (10:3:3).

distributions for C_{76} to C_{70} (Figure 3b) fit the observed spectrum (Figure 3a), indicating that the C_2 loss occurs *exclusively* from the C_{78}^- ion. On the other hand, the peak distributions for the higher mass region (Figure 4b) calculated by assuming C_{80} + $C_{80}H$ + $C_{80}H_2$ (10:1:3), C_{82} + $C_{82}H$ (10:3), C_{84} + $C_{84}H$ + $C_{84}H_2$ (10:3:3), and C_{86} + $C_{86}H$ + $C_{86}H_2$ (10:3:3) fit the observed spectrum (Figure 4a), indicating that the C_2 uptake occurs to *both* C_{78}^- and $C_{78}H_2^-$. These results strongly suggest that the C_{78}^- ion generated from **1b** possesses a fullerene structure.

Further spectroscopic characterization by, for example, ultraviolet photoelectron spectroscopy (UPS) should confirm this conjecture. For C_{78} fullerene, there are five possible geometrical isomers, three of which have been isolated and identified by the three different research groups.[21] The difference between the distributions of the isomers reported from the different groups was interpreted in terms of the temperature and pressure of a buffer gas, suggesting the presence of kinetically controlled pathways for the formation of the isomers rather than their equilibration.[22] Identification of the geometry of the C_{78}^- ion thus formed to clarify the geometrical selectivity is the subject of our current investigation.

The importance of the well-defined 3D structure for the efficient cyclization of the polyyne chains is exemplified by the failure to form C_{78} from the highly unsaturated acyclic polyyne **9** ($C_{78}H_{18}Cl_{12}$) having 78 carbon atoms under similar conditions. Compound **10**,[15] a precursor of polyyne **9**, was prepared by cross-coupling of **7b** with (2,4,6-trichlorophenyl)butadiyne (Scheme 3). As shown in Figure 5, the negative-mode laser desorption TOF mass spectrum of **10** exhibits strong peaks centered at *m/z* 1380 corresponding to poly-



Scheme 3. Synthesis of precursors **10** of acyclic polyyne **9**.

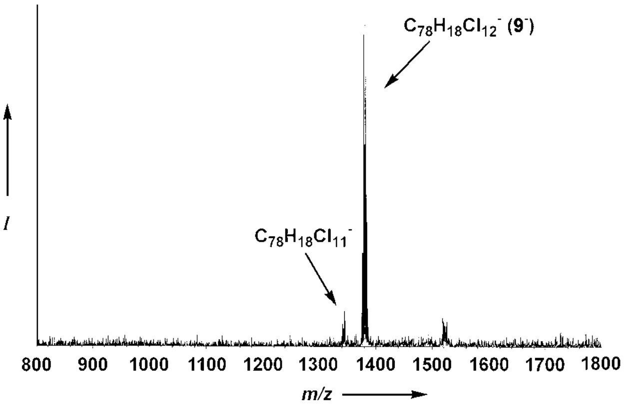


Figure 5. Negative-ion mode laser desorption TOF mass spectra of **10** [$C_{78}H_{18}Cl_{12}$(indane)$_3$], exhibiting peaks due to **9** ($C_{78}H_{18}Cl_{12}^-$) at *m/z* centered at 1380.

yne **9** formed by extrusion of three indane units from **10**. However, the loss of only one chlorine atom, forming $C_{78}H_{18}Cl_{11}^-$ (*m/z* centered at 1344), was observed from **9**. Further losses of hydrogen and chlorine atoms are not observed at all even under high laser fluence, apparently indicating the absence of kinetically favored pathways for the polyyne cyclization from ill-defined polyynes such as **9**.

In summary, we have synthesized the multicyclic compounds **2a** and **2b** containing cyclobutene rings as precursors of three-dimensional polyynes, $C_{78}H_{18}$ and $C_{78}H_{12}Cl_6$. Laser irradiation of **2a** and **2b** induced expulsion of the aromatic fragment, indane, giving the polyyne anions $C_{78}H_{18}^-$ and $C_{78}H_{12}Cl_6^-$, respectively, and subsequent cyclization of the polyyne chain of the latter anion gave rise to the size-selective formation of C_{78}^-. Since it should be possible to construct well-defined polyyne precursors larger than **2a** and **2b**, this method would be applicable to the size-selective formation of even larger, tubular fullerenes.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300, a JEOL JNM AL-400, or a Varian Unity Inova 500 spectrometer in $CDCl_3$ and with Me_4Si or residual solvent as an internal standard at 30 °C. The multiplicity in the ^{13}C NMR spectra was determined by DEPT spectra and was indicated by (s), (d), (t), and (q) for quaternary, tertially, secondary, and primary carbon atoms, respectively. IR spectra were recorded as KBr disks with a JASCO FTIR-410 spectrometer. Mass spectral analyses were performed on a JEOL JMS-700 spectrometer for EI and FAB ionization. The LD-TOF mass measurements were recorded on a Shimadzu/Kratos AXIMA-CFR spectrometer. Melting points were measured with a hot-stage apparatus and are uncorrected. Column chromatography and TLC were performed with Merck silica gel 60 (70–230 mesh ASTM) and Merck silica gel 60 F_{254}, respectively. Preparative HPLC was undertaken with a JAI LC-908 chromatograph using 600 mm × 20 mm JAIGEL-1H and 2H GPC columns with $CHCl_3$ as the eluent. All reagents were obtained from commercial suppliers and used as received. Solvents were dried (drying agent in parentheses) and distilled prior to use: THF ($LiAlH_4$ followed by sodium benzophenone ketyl), benzene (CaH_2), Et_3N (KOH), Et_2O (CaH_2).

Triazene 4a: A solution of **3a**[14] (3.00 g, 7.13 mmol) in THF (50 mL) was added to a solution of K_2CO_3 (2.02 g, 14.6 mmol) in MeOH (80 mL) with stirring at room temperature. After being stirred for 1 h, the reaction mixture was filtered and diluted with Et_2O. The solution was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to give the deprotected product which was used without purification. The crude sample was dissolved in Et_3N (ca. 20 mL), which had been degassed thoroughly by bubbling argon for 1 h, and the solution was added dropwise under an argon atmosphere to a solution of [$PdCl_2(PPh_3)_2$] (443 mg, 383 moμl), CuI (128 mg, 674 moμl), and *N*,*N*-diethyl-*N*′-(4-iodophenyl)triazene[16] (2.18 g, 7.19 mmol) in degassed Et_3N (25 mL) over 1 h. After being stirred for 2 h, the reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was passed through a short plug of silica gel (*n*-hexane/EtOAc 9:1). Purification by preparative HPLC afforded triazene **4a** (3.19 g, yield 85 % for two steps) as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.41$–7.33 (m, 4H), 5.89–5.85 (m, 4H), 3.77 (q, $J = 7.0$ Hz, 4H), 2.60–1.94 (m, 2H), 1.64–1.43 (m, 2H), 1.31–1.17 (m, 2H), 1.27 (t, $J = 7.0$ Hz, 6H), 1.10 ppm (br s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 151.24$ (s), 132.70 (s), 132.62 (d), 132.49 (s), 128.96 (d), 128.90 (d), 121.73 (d), 121.55 (d), 120.33 (d), 119.02 (s), 99.11 (s), 97.81 (s), 95.47 (s), 82.09 (s), 56.02 (s), 55.74 (s), 33.03 (t), 32.87 (t), 18.82 (t), 18.66 (q), 11.25 ppm (d) (the signals of diethyltriazenyl carbon atoms were not observed because of extensive broadening.); IR (KBr): $\tilde{\nu} = 3026$, 2941, 2864, 2189, 2126, 1573, 1463, 1432, 1396, 1329, 1238, 1108, 840, 761 cm^{-1}; MS (EI): *m/z* 523 [M^+]; HRMS (EI) calcd for $C_{34}H_{45}N_3Si$ 523.3383, found 523.3403.

Trispropellane 6a: A solution of tetra-*n*-butylammonium fluoride (TBAF) (1 M in THF, 3.9 mL, 3.9 mmol) was added dropwise to a solution of propellane **4a** (1.01 g, 1.98 mmol) in THF (50 mL). After being stirred for 1 h, the mixture was diluted with water, and then THF was removed by evaporation. The mixture was extracted with Et_2O, and the extract was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation to give **4b** which was used in the next step without purification. The crude samples of **4b** and **5a**[14] (194 mg, 502 µmol) were dissolved in benzene (21 mL), and the solution was added dropwise to a solution of $[Pd_2(dba)_3]\cdot CHCl_3$ (52.1 mg, 50.3 µ mol), CuI (11.3 mg, 59.3 µmol), and 1,2,2,6,6-pentamethylpiperidine (PMP) (360 µL, 309 mg, 1.99 mmol) in benzene (8.0 mL) over 15 min at room temperature. After being stirred for 2 h, the reaction mixture was concentrated and passed through a short plug of silica gel (Et_2O). The eluate was washed with 0.5 N HCl. The organic layer was washed with saturated $NaHCO_3$ solution and brine, and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, purification by preparative HPLC afforded **6a** (562 mg, yield 90 % for two steps) as a yellow solid: m.p. 141–143 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.55$ (s, 3H), 7.45 and 7.37 (AA′BB′, $J_{A,B} = 8.4$ Hz, 12H), 5.92–5.88 (m, 12H), 3.76 (q, $J = 7.2$ Hz, 12H), 2.04–2.00 (m, 6H), 1.76–1.50 (m, 6H), 1.35–1.23 (m, 6H), 1.26 ppm (t, $J = 7.2$ Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 151.59$ (s), 137.37 (s), 136.16 (d), 132.86 (d), 129.16 (s), 128.48 (d), 123.08 (s), 122.03 (d), 121.89 (d), 120.38 (d), 118.35 (s), 97.80 (s), 82.03 (s), 81.17 (s), 78.33 (s), 76.02 (s), 75.48 (s), 56.57 (s), 56.42 (s), 33.09 (t), 33.06 (t), 18.80 ppm (t) (the signals of diethyltriazenyl carbons were not observed because of extensive broadening.); IR (KBr): $\tilde{\nu} = 3027$, 2925, 2850, 2172, 2126, 1578, 1395, 1330, 1237, 1201, 1159, 1079, 842, 737, 734, 680 cm^{-1}; MS (FAB): *m/z* 1246 $[M^+]$.

Iodopropellane 7a: A solution of triazene **6a** (491 mg, 394 µmol) and I_2 (72.1 mg, 284 µmol) in MeI (55 mL) was charged to a pressure bottle. The reaction mixture was degassed thoroughly by bubbling argon for 15 min, and then the vessel was sealed with a screw cap and heated at 100 °C for 34 h. After the reaction mixture had cooled to room temperature, the solvent was removed under reduced pressure. The residue was diluted with Et_2O, and the solution was washed with aqueous sodium thiosulfate (10 %) and brine, and dried over anhydrous $MgSO_4$. After the solvent was removed in vacuo, the product was purified by chromatography on silica gel (*n*-hexane/$CHCl_3$ 9:1) to give **7a** (379 mg, 73 %) as a yellow solid: m.p. 124–126 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.67$ and 7.21 (AA′BB′, $J_{A,B} = 8.3$ Hz, 12H), 7.55 (s, 3H), 5.95–5.85 (m, 12H), 2.10–1.98 (m, 6H), 1.70–1.43 (m, 6H), 1.36–1.22 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 137.55$ (s), 137.37 (d), 136.48 (s), 136.23 (d), 133.41 (d), 130.64 (s), 128.24 (d), 128.20 (d), 123.03 (s), 122.21 (d), 122.01 (d), 121.88 (d), 95.55 (s), 95.14 (s), 83.22 (s), 81.36 (s), 78.73 (s), 75.92 (s), 75.15 (s), 56.73 (s), 56.56 (s), 33.02 (t), 18.81 ppm (t); IR (KBr): $\tilde{\nu} = 3024$, 2943, 2847, 2184, 2123, 1575, 1481, 1389, 1056, 1006, 905, 877, 861, 818, 742, 680 cm^{-1}; MS (FAB): *m/z* 1327 $[M^+ + H]$.

Cage compound 2a: A solution of TBAF (1 M, 64 µL, 64 µmol) in THF (17 mL), which had been degassed thoroughly by bubbling argon for 1 h, was dropwise by using a syringe pump (0.17 $mL\,min^{-1}$) to a solution of $[Pd(PPh_3)_4]$ (38.4 mg, 33.2 µmol), CuI (4.7 mg, 25 µmol), **8a**[14] (34.7 mg, 29.2 µmol), and **7a** (38.2 mg, 28.8 µmol) in degassed Et_3N (20 mL) under an argon atmosphere at room temperature. After being stirred for 1 h, HCl (ca. 200 mL, 0.5 N) was slowly poured at 0 °C, and the reaction mixture was extracted with Et_2O. The extract was washed with saturated $NaHCO_3$ solution and brine, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subjected to chromatography on silica gel (*n*-hexane/AcOEt 7:3). The product was further purified by preparative HPLC to afford **2a** (2.7 mg, 11 %) as a yellow solid: decomposed gradually from about 140 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.54$ (s, 6H), 7.42 (s, 12H), 5.94–5.85 (m, 24H), 2.10–1.96 (m, 12H), 1.72–1.44 (m, 12H), 1.38–1.20 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta =$ 136.66 (s), 136.15 (s), 131.76 (d), 130.74 (s), 128.05 (d), 128.02 (d), 122.86 (s), 122.65 (s), 122.03 (d), 121.90 (d), 96.05 (s), 84.17 (s), 81.22 (s), 78.67 (s), 75.77 (s), 75.02 (s), 56.77 (s), 56.56 (s), 33.20 (t), 19.02 ppm (t); IR (KBr): $\tilde{\nu} = 3026$, 2932, 2850, 2187, 1577, 1438, 1375, 1076, 876, 836, 756, 734, 691 cm^{-1}; LD TOF-MS (Figure 1 a).

Trispropellane 6b: A solution of TBAF (1 M in THF, 1.5 mL, 1.5 mmol) was added dropwise to a solution of propellane **4a** (320 mg, 0.611 mmol) in THF (15 mL). After being stirred for 1 h, the mixture was diluted with water and extracted with Et_2O. The extract was washed with brine, and dried over anhydrous $MgSO_4$, and the solvent was removed by evaporation to give a crude sample of **4b**. This product **4b** and **5b**[14] (93.8 mg, 191 µmol) were dissolved in benzene (10 mL), which had been degassed thoroughly by bubbling argon for 1 h, and the solution was added dropwise to a solution of $[Pd_2(dba)_3]\cdot CHCl_3$ (20.5 mg, 19.8 µmol), CuI (3.7 mg, 19 µmol), PMP (150 µL, 129 mg, 839 µmol) in degassed benzene (10 mL) over 15 min at room temperature. After being stirred for 2 h, the reaction mixture was concentrated and passed through a short plug of silica gel (Et_2O). The eluate was washed with 0.5 N HCl (100 mL). The organic layer was washed with saturated $NaHCO_3$ solution and brine, and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, purification by preparative HPLC afforded **6b** (151 mg, yield 58 % for two steps) as a yellow solid: m.p. 142–144 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.47$ and 7.38 (AA′BB′, $J_{A,B} = 8.5$ Hz, 12H), 5.92 (s, 12H), 3.77 (q, $J = 7.2$ Hz, 12H), 2.12–2.02 (m, 6H), 1.71–1.47 (m, 6H), 1.36–1.20 (m, 6H), 1.27 ppm (t, $J = 7.2$ Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 151.66$ (s), 141.00 (s), 138.28 (s), 132.90 (d), 128.64 (s), 128.45 (d), 128.35 (d), 128.30 (d), 122.33 (s), 122.11 (d), 121.93 (d), 120.40 (d), 118.23 (s), 98.38 (s), 85.40 (s), 82.10 (s), 78.69 (s), 77.89 (s), 75.67 (s), 56.77 (s), 56.51 (s), 33.16 (t), 33.08 (t), 18.82 ppm (t) (the signals of diethyltriazenyl carbons were not observed because of extensive broadening.); IR (KBr): $\tilde{\nu} = 3026$, 2933, 2872, 2850, 2178, 1577, 1423, 1395, 1328, 1237, 1201, 1158, 1096, 841, 774, 723, 674 cm^{-1}; MS (FAB): *m/z* 1346–1352 (the most abundant peak at 1349, $[M^+]$).

Iodopropellane 7b: A solution of triazene **6b** (447 mg, 331 µmol) and I_2 (59 mg, 0.23 µmol) in MeI (50 mL) was charged to a pressure bottle. The reaction mixture was degassed thoroughly by bubbling argon for 15 min, and then the vessel was sealed with a screw cap and heated at 100 °C for 63 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure. The residue was diluted with Et_2O, and the solution was washed with aqueous sodium thiosulfate (10 %) and brine, and dried over anhydrous $MgSO_4$. After the solvent was concentrated in vacuo, the residue was dissolved in $CHCl_3$ and *n*-hexane was added to this solution to give a yellow precipitate, which was collected by filtration and washed with *n*-hexane to give **7b** (369 mg) as a yellow solid. The filtrate was concentrated in vacuo, the residue was purified by chromatography on silica gel (*n*-hexane/$CHCl_3$ 8:2) to afford an additional sample of **7b** (40 mg, combined yield 86 %): decomposed gradually from about 170 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.68$ and 7.21 (AA′BB′, $J_{A,B} = 8.2$ Hz, 12H), 5.98–5.84 (m, 12H), 2.10–1.98 (m, 6H), 1.72–1.44 (m, 6H), 1.36–1.24 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 141.15$ (s), 137.58 (d), 137.37 (s), 133.44 (d), 130.12 (s), 128.22 (d), 128.09 (d), 122.30 (d), 122.12 (d), 121.78 (s), 96.06 (s), 95.28 (s), 85.26 (s), 83.22 (s), 78.32 (s), 78.25 (s), 77.20 (s), 75.81 (s), 56.83 (s), 56.79 (s), 33.10 (t), 33.04 (t), 18.82 ppm (t); IR (KBr): $\tilde{\nu} = 3026$, 2945, 2847, 2850, 2186, 1569, 1481, 1389, 1317, 1057, 1006, 846, 819, 774, 740, 674 cm^{-1}; MS (FAB): *m/z* 1428–1433 (the most abundant peak at 1430, $[M^+]$).

Cage compound 2b: A solution of TBAF (1 M, 136 µL, 136 moµl) in THF (17 mL), which had been degassed thoroughly by bubbling argon 1 h, was dropwise by a syringe pump (0.17 $mL\,min^{-1}$) to a solution of $[Pd(PPh_3)_4]$ (36.0 mg, 31.2 µmol), CuI (6.1 mg, 32 µmol), **8b**[14] (42.4 mg, 32.8 moµl), and **7b** (46.8 mg, 32.7 moµl) in degassed Et_3N (27 mL) under an argon atmosphere at room temperature. After the mixture had been stirred for 1 h, HCl (ca. 200 mL, 0.5 N) was slowly added, and the reaction mixture was extracted with $CHCl_3$. The extract was washed with saturated $NaHCO_3$ solution and brine, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subjected to chromatography on silica gel (*n*-hexane/$CHCl_3$ 1:1). The product was further purified by preparative HPLC to afford **2b** (4.0 mg, 7 %) as a yellow solid: decomposed gradually from 150 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.43$ (s, 12H), 5.95–5.85 (m, 24H), 2.10–1.98 (m, 12H), 1.72–1.44 (m, 12H), 1.38–1.24 ppm (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 141.40$ (s), 137.53 (s), 132.03 (d), 130.34 (s), 128.19 (d), 128.09 (d), 122.78 (s), 122.26 (s), 122.13 (d), 96.54 (s), 85.13 (s), 84.22 (s), 78.25 (s), 78.15 (s), 75.58 (s), 56.79 (s), 56.66 (s), 33.12 (t), 33.03 (t), 18.81 ppm (t); IR (KBr): $\tilde{\nu} = 3028$, 2948, 2850, 2191, 1391, 1075, 836, 774, 695 cm^{-1}; LD TOF-MS (Figure 1b and c).

1-(2,4,6-Trichlorophenyl)-4-(trimethysilyl)butadiyne:[23] A solution of MeLi–LiBr in Et_2O (1.5 M, 0.75 mL, 1.13 mol) was added to a solution of

1,4-bis(trimethylsilyl)butadiyne (203 mg, 1.04 mmol) in Et_2O (6.0 mL) with stirring at 0 °C, and then mixture was slowly warmed up room temperature. After being stirred for 24 h, the reaction mixture was slowly poured into a saturated aqueous NH_4Cl solution cooled to 0 °C (ca. 50 mL). The aqueous phase was extracted with Et_2O, and the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure below room temperature, and the residue was dissolved in Et_3N (ca. 6 mL), which had been degassed thoroughly by bubbling argon for 1 h. The above solution was added under an argon atmosphere into a solution of $[Pd_2(dba)_3]\cdot CHCl_3$ (63.3 mg, 61.2 μmol), CuI (20.2 mg, 106 μmol), PPh_3 (84.2 mg, 321 μmol), and 1,3,5-trichroro-2-iodobenzene (115 mg, 374 μmol) in degassed Et_3N (1.0 mL) at 50 °C. After being stirred for 4 h, the reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was passed through a short plug of silica gel (*n*-hexane). Purification by preparative HPLC afforded the butadiyne derivative (63.4 mg, yield 56 % for two steps) as a colorless solid; m.p. 64–65 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.33$ (s, 2 H), 0.26 ppm (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 138.86$ (s), 134.92 (s), 127.67 (d), 120.61 (s), 94.90 (s), 86.93 (s), 84.63 (s), 69.06 (s), –0.23 ppm (q); IR (KBr): $\tilde{\nu} =$ 3113, 3076, 2957, 2925, 2853, 2101, 1561, 1536, 1449, 1385, 1371, 1251, 1090, 1019, 974, 849, 761, 655 cm^{-1}; MS (EI): *m/z* 304, 302, 300 (rel. intensity ca. 1:2:2, $[M^+]$); HRMS (EI) calcd for $C_{13}H_{11}{}^{35}Cl^{37}Cl_2Si$, $C_{13}H_{11}{}^{35}Cl_2{}^{37}Cl_1Si$, and $C_{13}H_{11}{}^{35}Cl_3Si$ 303.9640, 301.9667, and 299.9696, found 303.9643, 301.9658, and 299.9679, respectively.

Acyclic polyyne precursor 10: A solution of the above butadiyne (55.3 mg, 183 μmol) in THF (3.0 mL) was added to a solution of K_2CO_3 (46.7 mg, 338 μmol) in MeOH (3.0 mL) with stirring at room temperature. After being stirred for 1 h, the reaction mixture was filtered and diluted with Et_2O. The solution was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to give a crude sample of the deprotection product. The crude product was dissolved in Et_3N (ca. 8 mL), which had been degassed thoroughly by bubbling argon for 1 h, and the solution was added under an argon atmosphere to a solution of $[Pd(PPh_3)_4]$ (14.5 mg, 12.5 μmol), CuI (3.2 mg, 17 μmol), and **7b** (53.5 mg, 37.4 μmol) in degassed Et_3N (3.0 mL) at room temperature. After being stirred for 2 h, the reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was passed through a short plug of silica gel (*n*-hexane/$CHCl_3$ 1:1). Purification by preparative HPLC afforded **10** (59.9 mg, yield 92 % for two steps) as a brown solid: decomposed gradually from about 140 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$ and 7.46 (AA′BB′, $J_{AB} = 7.3$ Hz, 12 H), 7.34 (s, 6 H), 5.95–5.84 (m, 12 H), 2.10–1.99 (m, 6 H), 1.72–1.43 (m, 6 H), 1.37–1.22 ppm (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 140.96$ (s), 138.66 (s), 136.95 (s), 134.96 (s), 132.30 (d), 131.87 (d), 130.31 (s), 127.99 (d), 127.87 (d), 127.70 (d), 123.41 (s), 122.13 (d), 122.16 (d), 122.00 (d), 121.55 (s), 96.20 (s), 85.20 (s), 84.62 (s), 84.55 (s), 84.26 (s), 78.47 (s), 78.27 (s), 77.20 (s), 75.93 (s), 75.58 (s), 75.24 (s), 56.98 (s), 56.91 (s), 33.29 (t), 33.22 (t), 19.04 ppm (t); IR (KBr): $\tilde{\nu} = 3026$, 2943, 2848, 2207, 1601, 1572, 1533, 1448, 1387, 1371, 1318, 1185, 1139, 1081, 1016, 857, 836, 818, 774, 759, 702, 674 cm^{-1}; LD TOF-MS (Figure 5).

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