

Vijayaraj Anantharaj, Jayant Bhonsle, Taizoon Canteenwala and Long Y. Chiang*

Center for Condensed Matter Sciences, Taiwan University, Taipei 106, Taiwan

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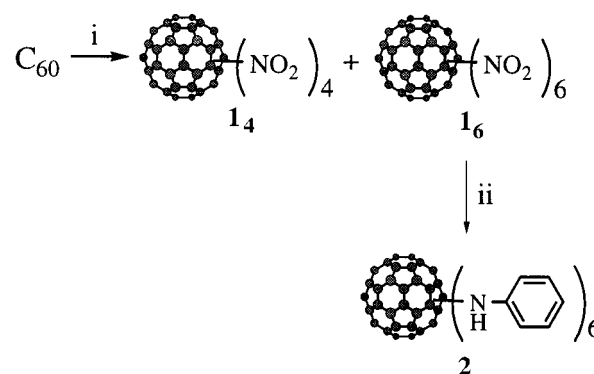
A synthetic method for the preparation of monodisperse hexanitro[60]fullerenes **1₆** was developed. The use of **1₆** as a reactive precursor in the synthesis of organo-amino derivatives of C₆₀ was also demonstrated. The allylic *tert*-nitro moieties in hexanitro[60]fullerenes were found to be excellent leaving groups for nucleophilic substitutions by amino nucleophiles, such as anilines, leading to the formation of hexaanilino[60]fullerenes. Negative ion desorption chemical ionization mass spectra (DCI⁻-MS) of both hexaanilino[60]fullerene and hexanitroso[60]fullerene, a hydride-reduced product of **1₆**, were utilized for substantiation of the number of nitro groups per C₆₀ in **1₆**. Detection of the molecular ion of C₆₀(NO)₆ at *m/z* 901 was correlated to the composition of its parent compound **1₆**, as hexanitro[60]fullerenes containing 6 nitro addends per C₆₀ cage.

Nitration of fullerene molecules has been carried out under different conditions and nitration reagents, including a mixture of conc. HNO₃ and sodium nitrite,¹ dinitrogen tetroxide,² fuming nitric acid,³ and a mixture of aqueous sodium nitrite, FeSO₄, and H₂SO₄ in the presence of air.⁴ Hydrolysis of the resulting polynitrofullerene intermediates occurred readily *in situ* when water molecules were present in the reaction medium. Even upon prolonged contact with moisture, polynitrofullerenes react slowly with H₂O to yield partially hydroxylated products of poly(hydroxynitro)fullerenes. In the presence of an aqueous alkaline solution, rapid and complete hydrolysis of polynitrofullerenes was observed to produce fullereneol molecules containing at least 16 hydroxy groups per C₆₀ cage.¹ In these reactions, allylic or doubly allylic nitro functional groups of polynitrofullerenes and water molecules acted as potent leaving groups and weak nucleophiles, respectively. Nucleophilic replacement of nitro leaving groups by multifunctional nucleophiles may represent a facile synthetic approach for the preparation of new polyfunctionalized fullerene derivatives. Nevertheless, the reagent applied required higher nucleophilicity than that of water to overcome frequently occurring partial hydrolysis during the reaction.

Previously reported reaction methods and conditions for the C₆₀ nitration have led to poorly characterized tetra-nitro-adducts, polynitro-adducts, or partially hydrolyzed polynitrofullerene mixtures.¹⁻⁴ Here we report the synthesis and characterization of nearly pure hexanitro[60]fullerenes **1₆**. Subsequent multiple substitutions of fullerene nitro groups of **1₆** by primary or secondary organo-amino compounds resulted in efficient preparation of the corresponding hexa-organoamine derivatives of C₆₀.

Results and discussion

The nitronium ion (NO₂⁺) was first reported as a nitration agent in the reaction with fullerene molecules forming reactive polynitrofullerene carbocation intermediates, which were utilized directly in the preparation of polyhydroxylated C₆₀.⁵ For the synthesis of separable nitrofullerene derivatives, nitrogen dioxide ([•]NO₂) was the commonly used nitration reagent. It was generated by a number of preparative methods, including the thermal decomposition of heavy metal nitrate, the oxidation of nitric acid, the reaction of dinitrogen trioxide with dinitrogen pentoxide, the reaction of nitric acid with sulfur dioxide, phosphorus pentoxide or copper, the reaction of nitrosyl chloride with silver nitrate, and the reaction of nitro-



Scheme 1 Reagents and conditions: i, gaseous [•]NO₂/N₂O₄ (from conc. HNO₃ and Cu powder), toluene, 60 °C for 5 h or 30 °C for 16 h; ii, aniline (excess), Et₃N, THF, 50 °C, 6 h.

sonium hydrogen sulfate with potassium nitrate.⁶ The brown colored nitrogen dioxide exists in equilibrium with its dimer, dinitrogen tetroxide N₂O₄, which is colorless, at ambient temperature in a N₂O₄:[•]NO₂ ratio of roughly 84:16.⁷ The equilibrium content of [•]NO₂ increases as the temperature rises and reaches 99% of an NO_x mixture at 135 °C.⁶ Nitrogen dioxide is a reactive intermediate for nitration reactions of many organic olefins. The reaction is normally initiated by the attack of a nitronium ion, which is generated by the release of an odd electron from [•]NO₂, on an olefinic double bond. However, in the case of the fullerene analogue cage molecule, its high electron affinity allows a direct chemical attack by electron-deficient radicals. In fact, the C₆₀ molecule was proven to be highly reactive towards radical species.⁸ Its reactivity can be much greater than that of a typical olefin towards the same radical. That makes direct multiple radical additions of [•]NO₂ onto the fullerene cage possible.

In our fullerene nitration experiments, generation of nitrogen dioxide was by either the reaction of sodium nitrite with conc. HNO₃ or the reduction of conc. HNO₃ by copper powder, as shown in Scheme 1. Under these conditions, instantaneous production of red-brown [•]NO₂ gas was observed. Owing to a fast reaction of Cu with N₂O₄ during the [•]NO₂/N₂O₄ generation, [•]NO₂ is the only gaseous product available among several other possible nitrogen oxide species present in the nitric acid medium, including NO⁺, NO₂⁺, and NO₃⁻.⁹ Gaseous [•]NO₂ in excess quantity was carried over into a solution of C₆₀ in either benzene or toluene by a stream of dried nitrogen for a period of

30 min to 1.5 h. At the end of $\cdot\text{NO}_2$ injection, the mixture was stirred at 30 °C for an additional 16 h. The progress of the C_{60} nitration was monitored by disappearance of the purple color of the solution of C_{60} and the formation of red polynitrated fullerene products **1**. The nitration rate was both temperature and $[\cdot\text{NO}_2]$ dependent. Completion of the reaction was achieved within 1.0 h at 60 °C or 8 days at 15–20 °C.

The degree of nitration was followed by systematic evaluation of the intermediate products using the liquid chromatographic (HPLC) technique. Resolution of the chromatographic peak separation was found to be higher using an HPLC setup with a reversed-phase MCH-5 column and a solvent mixture of $\text{CH}_3\text{CN}-\text{CHCl}_3$ in a ratio of 4:1 as eluent at a flow rate of $0.8 \text{ cm}^3 \text{ min}^{-1}$. Relatively fast reaction kinetics at the early stage of nitration were observed at 15–20 °C. Nitrated fullerene intermediates containing a low number of nitro groups, perhaps 1–3, were detected in products obtained at a reaction time of 0.5 h, their HPLC peaks being recorded at retention times of 3.5, 4.7, and 5.8 min. The intensity of the latter two peaks decreased rapidly with formation of new peaks that shifted constantly to longer retention times during the first 2.0 h of reaction. At a reaction period of 2.5–5.5 h, the quantity of the intermediate nitro products reached a relatively steady ratio showing chromatographic peaks of dinitro[60]fullerenes (**I**₂), tetranitro[60]fullerenes (**I**₄), and hexanitro[60]fullerenes (**I**₆) at retention times of roughly 4.5, 5.0, and 3.3 min, respectively. This HPLC profile indicated that the fraction of **I**₄ isomers, each containing 4 nitro groups per C_{60} cage, was the major product of reaction. The yield of tetranitro[60]fullerenes was 2.7- and 4-fold higher than that of **I**₂ and **I**₆, respectively. After a reaction period of roughly 8.5 h, a slow decrease in intensity of the dinitro[60]fullerene peak accompanied by an increase in intensity of the hexanitro[60]fullerene peak was evident. At this stage, tetranitro[60]fullerenes still remained as the main reaction products. In a prolonged nitration reaction of C_{60} for 24 h, as shown in Fig. 1a, a comparable overall yield of **I**₄ and **I**₆ was detected as indicated by peaks at retention times of 4.5–5.5 and 3.0–3.5 min, respectively. The increase in complexity of each peak fraction revealed the formation of different regioisomers. A progressive decrease of tetranitro[60]fullerenes and increase of hexanitro[60]fullerenes in the yield were observed as the reaction period was increased from 48, 72, to 96 h as depicted in Figs. 1b, 1c, and 1d, respectively. Further nitration of the C_{60} molecules for a total of 5 (Fig. 1e) and 6 (Fig. 1f) days gave products showing a chromatographic profile consisting of a major peak of hexanitro[60]fullerenes. Apparently, the tetranitration of C_{60} was a relatively rapid process while further nitration steps to hexanitro adducts of C_{60} were kinetically slow processes at 15–20 °C. Nevertheless, selective synthesis of hexanitro[60]fullerenes becomes possible following an extended nitration period of C_{60} at ambient temperatures.

As the nitration temperature increased to 60 °C, the production rate of hexanitro[60]fullerene isomers was raised sharply within a reaction period of 5 h. However, the increase in rate was accompanied by products showing a more complicated HPLC profile at higher retention times, presumably owing to the formation of several polynitrated C_{60} isomers containing a number of nitro groups higher than 6. In addition, constant evaporation of $\cdot\text{NO}_2$ at a higher temperature than 50 °C tended to result in additional product fractions with a low nitration level. This broadened the number distribution of nitro groups per C_{60} in final products.

The solubility of **I**₄ and **I**₆ is comparable in THF and toluene. Hexanitro[60]fullerenes exhibit much higher solubility than tetranitro[60]fullerenes in acetone and acetonitrile. Therefore, acetonitrile can be used for preliminary separation and purification of either fraction from the other in a repetitive manner. The infrared spectrum of **1** showed two strong, sharp peaks at 1572 and 1328 cm^{-1} , corresponding to optical absorptions of the asymmetric (ν_{as}) and symmetric (ν_{s}) N–O stretching of NO_2

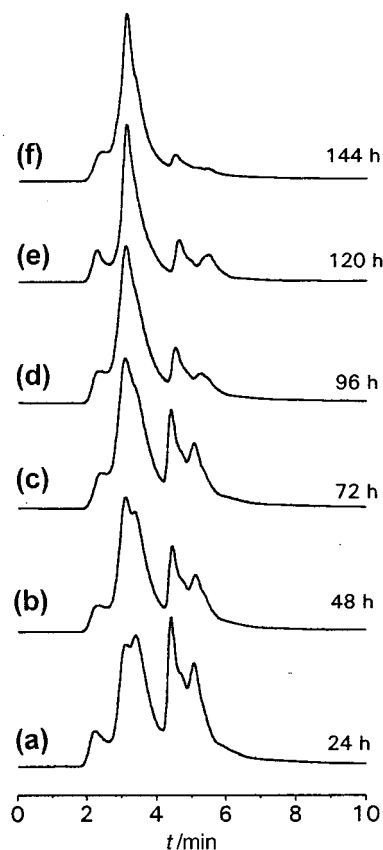


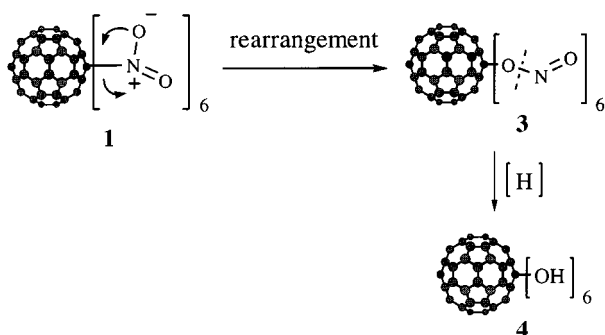
Fig. 1 The HPLC profile of polynitrated fullerene fractions synthesized by the reaction of C_{60} with NO_2 radicals at 15–20 °C for a reaction period indicated, showing evolution of the **I**₄ and **I**₆ fractions at a retention time of 4.5–5.5 and 3.0–3.5 min, respectively.

moieties, respectively. It also showed a broad band centered at 1085 cm^{-1} and a sharp absorption in medium intensity at 807 cm^{-1} corresponding to the N–O bending (δ) of NO_2 moieties, indicating the predominant presence of nitro groups on a C_{60} cage. The lack of IR absorptions at 1600–1630 cm^{-1} excludes the possibility of the presence of nitrite functional groups ($-\text{ONO}$) in **1**.

Even though rapid formation of N_2O_4 could occur *via* thermal equilibration between $\cdot\text{NO}_2$ and N_2O_4 as soon as $\cdot\text{NO}_2$ was injected into the reaction medium containing C_{60} molecules, its self-ionization into NO_2^+ and NO_2^- is known to be a slow process.¹⁰ That allows one to count on nitrogen dioxide radicals being the main species in reactions with C_{60} . An odd-numbered addition of NO_2 radicals onto a fullerene cage may give a net residual radical on each C_{60} . Therefore, an extremely low integrated intensity of EPR susceptibility ($S = 1/2$) measured for the polynitrated fullerene products allowed us to confirm that these products contain even-numbered nitro groups per C_{60} . This was consistent with the data obtained from elemental microanalyses of the **I**₆ fraction (containing >92% of hexanitro[60]fullerenes as shown by its HPLC profile in Fig. 1f) and the **I**_{4,6} fraction (containing roughly 65% of tetranitro[60]fullerenes based on its HPLC profile), showing a C:N ratio which fitted reasonably well with a formula of hydrated $\text{C}_{60}(\text{NO}_2)_{5,7}$ and $\text{C}_{60}(\text{NO}_2)_{4,3}$, respectively. The composition of polynitrated C_{60} may be expected to consist of a number of hexanitro regioisomers. However, the number of these regioisomers seems to be limited. This was deduced from observation of a series of sharp carbon peaks in the regions of both aromatic carbons and nitrated carbons with chemical shifts of 130–155 ppm and 75–90 ppm, respectively, in the ^{13}C NMR spectrum (600 MHz, $\text{THF}-d_8$) of microcrystalline **I**₄. This compound **I**₄ was synthesized by a 12 h reaction of C_{60} with $\cdot\text{NO}_2$ at 20 °C using a saturated solution of C_{60} containing some

suspended fine, amorphous C_{60} solids in a limited amount of benzene. As the reaction proceeded, the less soluble tetranitrated C_{60} derivatives formed reached solubility saturation easily and precipitated from the solution without reacting further to give hexanitrated products. Precipitation of the tetranitrated C_{60} derivatives was also accompanied by slow dissolution of suspended C_{60} solids until completion of the reaction. Conversely, use of a dilute, fully dissolved C_{60} solution in the reaction, such as the one used for Fig. 1, gave a mixture of **1**₄ and **1**₆ at a reaction period of 12 h. Each tetranitro[60]-fullerene isomer comprising of 56 conjugated olefinic carbons should display at least 28 or 56 aromatic carbon peaks if the compound exhibits either a 2-fold, or no, structural symmetry, respectively. Therefore, as the number of regioisomers increases the total number of aromatic carbon peaks increases rapidly. This often results in a broad band of carbons centered at roughly δ 145. The fact that a finite number of distinguishable sharp carbon peaks, containing 7 major peaks and no more than 15 minor peaks at δ 75–95 for nitrated carbons, were detected for the compound **1**₄ can be accounted for by the formation of only few stable regioisomers during the early nitration of C_{60} .

Fullerene nitro functional groups were found to be somewhat unstable thermally in solution or on SiO_2 , which prohibits the direct purification and separation of polynitrated isomers **1** under prolonged chromatographic conditions. Therefore, secondary derivatives from **1** were prepared for the purpose of supporting the composition determination of **1**. The instability of **1** arises from the facile occurrence of the intramolecular rearrangement of allylic nitro groups on C_{60} since a partial overlap between *p*-electron orbitals of the oxygen atom in a nitro group and π -electron orbitals of the surrounding fullerene olefins makes them accessible for intramolecular electron coupling. The rearrangement results in formation of the corresponding nitrito groups attached to the fullerene cage, as shown in a partial structure of polynitritofullerenes **3** from polynitrofullerenes **1** in Scheme 2.



Scheme 2 Proposed reaction mechanism for formation of the polyhydroxylated C_{60} intermediate ions from the parent hexanitro[60]fullerenes. A partial structure of the corresponding fullerene derivatives is shown.

Similar transformation of nitro groups into nitrito groups occurred while the compound **1**₆ was injected under conditions of the mass spectroscopic measurements. Accordingly, the positive ion FAB mass spectrum (Fig. 2) of **1**₆ displayed a group of fragmented ions with a mass peak of the C_{60} ion in a maximum intensity at m/z 720. It was followed by a series of fragmented ion groups having a maximum intensity of each mass group recorded at m/z 736, 753, 769, 787, 805, 822, etc. These mass ion peaks were separated from the adjacent ion fragmentation peak by 16, 17, or 18 mass units corresponding to a gain or loss of one oxygen atom, a hydroxy group, or a water molecule, respectively. The lack of direct detection of C_{60} derivatives containing nitro groups in this FAB-MS data was indicative of the occurrence of either the nitro rearrangements or the substitution of nitro groups by water molecules during the procedure of MS data collection. Both reactions resulted in formation of

polyhydroxylated C_{60} **4**. In addition, the ion peaks with a higher mass than m/z 840, which were capable of producing more than 6 hydroxy-fragmented ion groups, were also detected. One plausible explanation was made by the high susceptibility of hydroxylated C_{60} intermediates toward secondary reactions with the fragmented NO_2 or NO ions *in situ* on the sample probe. Subsequent hydrolysis processes of the resulting products, similar to the one described above, may produce polyhydroxylated C_{60} ions with a mass reaching m/z 924 as a formula of dodecahydroxy[60]fullerenes, $C_{60}(OH)_{12}$ or higher.

Reduction of fullerene nitro groups was carried out with **1**₆ in a THF solution at 60 °C for 3 h using superhydride ($LiEt_3BH$) as a reducing reagent. An excess of superhydride (20.0 equiv. per C_{60}) was applied. At the end of the reaction, the reaction mixture was treated with H_2O for a period of 20 min and the organic layer was washed with brine. After evaporation of organic solvents, the solids obtained were re-dissolved in THF and then reprecipitated into diethyl ether to yield yellow solids **5**. Interestingly, the negative ion desorption chemical ionization mass spectrum (DCI⁻-MS, direct probe) of **5** gave a well-defined pattern of spectrum profile showing a fragmentation group of C_{60} ions with a maximum intensity at m/z 721. The group was immediately followed by a series of mass groups with a progressive increase of a nearly constant 30 mass units at m/z (the mass of a fragmented ion with a maximum peak intensity in each group) 753 ($n=1$), 783 ($n=2$), 813 ($n=3$), 841 ($n=4$), 871 ($n=5$), and 901 ($n=6$), as shown in Fig. 3. These ion fragmentations containing more nitroso (NO) functional group than the preceding ion fragment agree well with the formula $C_{60}(NO)_n^-$, as polynitroso[60]fullerene ions. Detection of the molecular ion of $C_{60}(NO)_6$ at m/z 901 can be correlated clearly back to the composition of its parent compound **1**₆, as hexanitro[60]fullerenes containing 6 nitro addends per C_{60} cage.

Hexanitro[60]fullerenes are highly electrophilic molecules toward reactions with various nucleophiles, such as organo-amine compounds. By transforming hexanitro[60]fullerenes into soluble organo-amino derivatives of C_{60} , characterization of the resulting products may allow us to further correlate and substantiate the number of nitro addends per fullerene cage in **1**. Therefore, synthesis of hexaanilino[60]fullerenes **2** was carried out accordingly. Upon treatment of $C_{60}(NO_2)_6$ in THF with freshly distilled aniline in the presence of triethylamine at 50 °C for 6 h under atmospheric pressure of nitrogen, dark brown solids of **2** were obtained in a yield of 94%. These products were isolated by repeated precipitation into hexane from a THF-ethyl acetate solution until no starting aniline was detected by thin-layer chromatography (TLC). Further purification of **2** by TLC (SiO_2 , $R_f=0.76$) was performed using a mixture of THF- $CHCl_3$ (1 : 1) as eluent.

It is interesting to notice that the polydispersity distribution of $C_{60}(\text{aniline})_n$ product fractions with a different number of substituents n correlated well with that of $C_{60}(NO_2)_n$ used as a starting material. As an example, the use of polydisperse polynitrated fullerene derivatives, containing a mixture of $C_{60}(NO_2)_{2-6}$ isomers, led to formation of 3 major chromatographic fractions of $C_{60}(\text{aniline})_{2-6}$ isomers, as depicted in Fig. 4a. The major product of $C_{60}(\text{aniline})_6$ isomers was isolated from these poly(anilinated) C_{60} mixtures on TLC to yield a nearly single chromatographic fraction as shown in its HPLC profile (Fig. 4b). Similarly, application of relatively pure **1**₆ isomers, giving an HPLC profile as shown in Fig. 1f, afforded a product of $C_{60}(\text{aniline})_6$ isomers showing a sharp single chromatographic peak (Fig. 4c).

The negative ion desorption chemical ionization mass spectrum (DCI⁻-MS, direct probe) of hexaanilino[60]fullerenes **2** displayed a sequence of fragmented ion groups with a highly distinguishable C_{60} ion at m/z 721, as shown in Fig. 5. It was immediately followed by mass groups with a progressive increase of nearly constant 91 mass units at m/z (the mass of an ion fragmentation with a maximum peak intensity in each

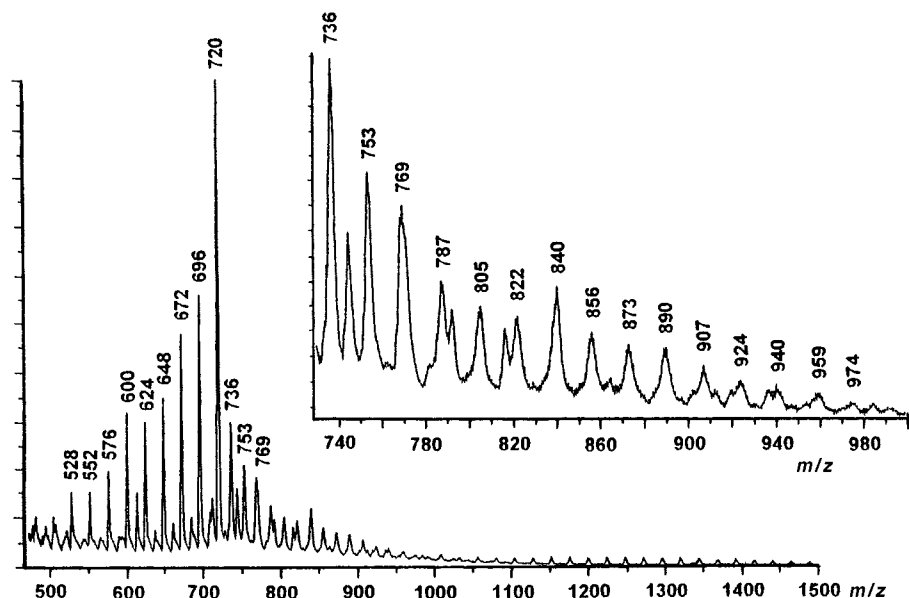


Fig. 2 Positive ion FAB mass spectrum (direct probe) of hexanitrofullerenes **1₆**, showing characteristics of polyhydroxylated C₆₀ ions instead. The lack of direct detection of polynitrofullerene ions in the data was indicative of either the nitro rearrangements or the substitution of nitro groups by water molecules during the procedure of MS data collection.

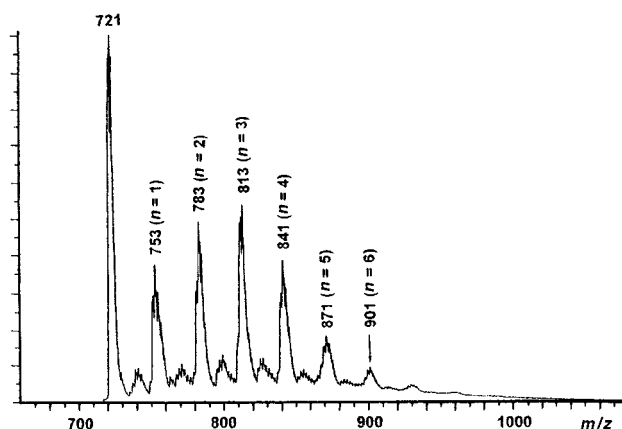


Fig. 3 Negative ion desorption chemical ionization mass spectrum (DCI-MS, direct probe) of **5**, showing a consecutive fragmentation of C₆₀(NO)_n ions derived from hexanitroso[60]fullerenes.

group) 813 (*n* = 1), 904 (*n* = 2), 995 (*n* = 3), 1086 (*n* = 4), and 1177 (*n* = 5). The peak intensity of the next ion group with a higher mass at *m/z* 1268 (*n* = 6) falls, unfortunately, within the background noise level of the spectrum. These ion fragmentations containing one more dehydrogenated aniline (C₆H₅N) functional group than the preceding ion fragment agree well with the formula C₆₀(NC₆H₅)_n⁻. These results are consistent with the previous conclusion on the composition of the parent compound **1₆**.

In conclusion, we developed a synthetic method for the preparation of hexanitrofullerenes and demonstrated their use as reactive precursors for the synthesis of organo-amino derivatives of C₆₀. The allylic *tert*-nitro moieties in structures **1₆** and **1₄** were found to be excellent leaving groups for nucleophilic substitutions by nucleophiles, such as anilines. Detection of the molecular ion of C₆₀(NO)₆ at *m/z* 901 can be correlated to the composition of its parent compound as hexanitro[60]fullerenes (**1₆**) containing 6 nitro addends per C₆₀ cage. As far as the regiostructures of **1₆** are concerned, the quantum-chemical semi-empirical computations of **1₂** and **1₄** indicated that the low energy structure of dinitro[60]fullerene isomer consists of two nitro groups located at the *para* position to each other on one hexagon,¹¹ whereas the structure of tetranitro[60]fullerene isomer **6** with the lowest energy, Δ*H*_{f, 298}^o = 757.1 kcal mol⁻¹,

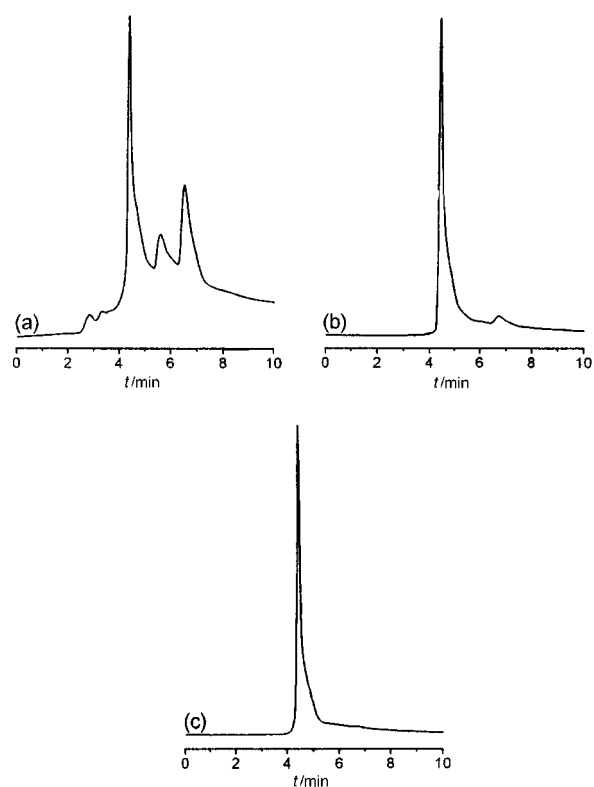


Fig. 4 HPLC profile of poly(anilino)fullerene fractions synthesized by the reaction of polynitro[60]fullerenes (**1₂₋₆**), as shown in (a) and (b), and hexanitro[60]fullerenes (**1₆**), as shown in (c), with aniline and Et₃N, displaying a sharp peak of hexanilino[60]fullerene isomers in (b) and (c) after TLC purification. A reversed-phase MCH-5 column was used with acetonitrile as an eluent at a flow rate of 0.6 cm³ min⁻¹.

has four nitro groups chemically bound on carbons in a *para-para* arrangement on two hexagons separated by a pentagon.¹² The second low-energy tetranitro[60]fullerene isomer **7** (Δ*H*_{f, 298}^o = 764.9 kcal mol⁻¹) has four nitro groups chemically bound on carbons in a *para* position on two hexagons located at the opposite site of the cage. Based on the structure of **6** and **7**, addition of two more nitro groups is proposed to occur at carbons indicated in the compounds **8** and **9**, the low energy

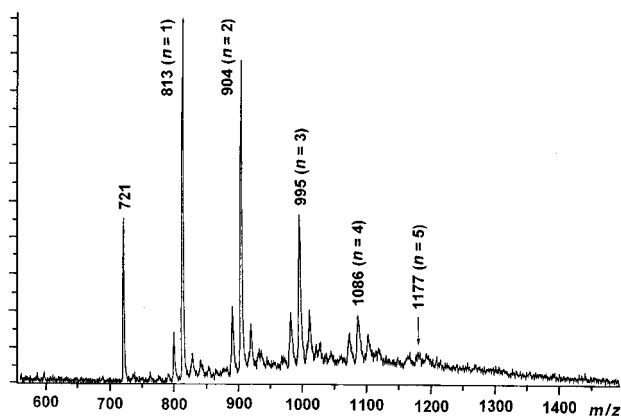
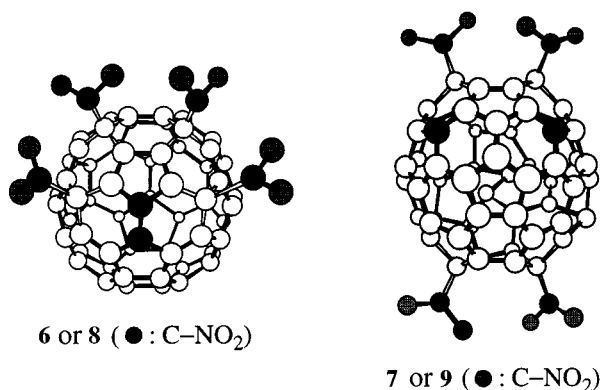


Fig. 5 Negative ion desorption chemical ionization (DCI⁻) mass spectrum of hexanilino[60]fullerenes showing a consecutive fragmentation of C₆₀(aniline)_n ions.

forms, following the attack of [•]NO₂ radicals on the reactive double bonds across two pentagons. The structure of **8** thus resembles that of C₆₀Br₆ reported.¹³ Further investigation on this issue will be carried out.



Experimental

General

Pure C₆₀ was purchased from either Bucky USA or Southern Chemical Co. and used as received. Infrared spectra were recorded as KBr pellets on a Nicolet 750 series FT-IR spectrometer or a JASCO FT-IR-300E spectrometer. ¹³C NMR spectra were recorded on a Varian Gemini-200 spectrometer or Bruker DMX-600 spectrometer. Mass spectroscopic studies were performed by use of either the negative ion fast atom bombardment (FAB⁻) technique on a JEOL JMS-HX110 high performance mass spectrometer with a direct probe or the negative ion desorption chemical ionization (DCI⁻) technique on a JEOL JMS-SX102A mass spectrometer. Benzene and toluene were dried and distilled over Na. Both sodium nitrite and nitric acid were purchased from Merck Inc. Elemental analyses of fullerene derivatives were carried out at either National Cheng Kung University, Taiwan or the E + R Microanalytical Laboratory, Inc., Corona, New York.

Hexanitro[60]fullerenes **1**₆

A two-necked reaction flask A (50 cm³) was equipped with a vertical dropping funnel with a stopcock on one neck and a connecting gas-bubbling tube on the other. The gas-bubbling tube was attached with a drying tube (CaCl₂) and inserted into the second two-necked reaction flask B. The other neck of flask B was attached with a bubbling tube, which was extended into a trapping flask containing aqueous sodium hydroxide solution (2 M). To minimize the back-flow of moisture from the alkaline

solution, a drying tube (CaCl₂) was installed in between flask B and the trapping flask. A steady inert gas (N₂) flow was allowed starting from the top of the dropping funnel, through the reaction flasks A and B in sequence, into the alkaline solution in the trapping flask.

The dropping funnel and reaction flask A were charged with conc. HNO₃ (50 cm³) and copper powder (40 g), respectively. In reaction flask B was placed a solution of C₆₀ (1.0 g) in dry benzene (100 cm³). The inert gas bubbling through the C₆₀ solution in flask B was adjusted to a flow rate of 5 cm³ per min. The fullerene solution was deoxygenated for at least 5 min prior to the reaction. Concentrated HNO₃ solution was then added dropwise into flask A. Brown fumes were produced immediately upon the contact of conc. HNO₃ with Cu. It was carried by the steady flow of N₂ gas and bubbled through the C₆₀ solution in the flask B. Within 1.0 h of reaction, the purple solution of C₆₀ was changed to orange-red progressively. The mixture was stirred at 30 °C for an additional 16 h to give an orange solution with suspended solids. At the end of the reaction, excessive nitrogen dioxide (NO₂) was removed by bubbling N₂ gas and destroyed in the trapping solution. Benzene was then evaporated from the product solution at reduced pressure to give a bright orange solid. The solid was suspended in anhydrous *n*-hexane, separated from *n*-hexane solution by the centrifuge technique, washed with hexane, and dried under vacuum at 40 °C to afford solids of hexanitro[60]fullerenes **1**₆ (1.3 g). IR ν_{\max} (KBr)/cm⁻¹ 1572 [s, ν_{as} (N–O)], 1328 [s, ν_{s} (N–O)], 1085, 807 [δ (N–O)], 733 (w), 696 (w), and 545. Compounds **1**₆ exhibited appreciable solubility in common organic solvents, including THF, DMF, CH₂Cl₂, CHCl₃, CH₃OH, and DMSO. UV-VIS (THF, *ca.* 3.0 × 10⁻⁴ M): λ_{\max} 302 nm. For compounds **1**₆: ¹³C NMR (600 MHz, THF-*d*₈, peaks with a higher intensity, Fig. 2) δ 77.3, 79.1, 80.0, 83.4, 83.8, 83.84, 85.6, 88.2, 89.78, 89.8, 91.1, 129.8, 133.5, 136.4, 138.5, 139.1, 141.2, 141.4, 143.1, 143.16, 143.22, 144.3, 144.4, 144.5, 145.1, 145.3, 145.97, 145.98, 146.07, 146.08, 146.1, 146.3, 146.32, 146.8, 147.1, 148.65, 148.72, 148.8, 148.9, 149.0, 149.1, 149.3, 149.55, 149.56, 150.1, 150.23, 150.24, 150.31, 150.32, 150.38, 150.4, 150.9, 151.2, 151.4, 151.8, 153.1, 154.5. Anal. calc. for C₆₀H₁₈N_{5.7}O_{20.4} as C₆₀(NO₂)_{5.7}·9H₂O: C, 62.94; H, 1.57; N, 6.98; O, 28.50. Found: C, 62.09; H, 1.38; N, 6.41; O, 29.62%.

For compounds **1**₄₋₆: Anal. calc. for C₆₀H₁₆N_{4.3}O_{16.6} as C₆₀(NO₂)_{4.3}·8H₂O: C, 67.80; H, 1.51; N, 5.67; O, 25.01. Found: C, 67.61; H, 1.29; N, 5.68; O, 25.58%.

Hexaanilino[60]fullerenes **2**

A round bottomed flask (dried, 50 cm³) equipped with a condenser and a magnetic stirring bar was charged with hexanitro[60]fullerenes, C₆₀(NO₂)₆, (**1**₆, 400 mg, 0.4 mmol) and THF (10 cm³) under N₂. Freshly distilled aniline (1.13 g, 12.0 mM, 30 equiv.) in THF (5 cm³) was added to the flask, followed by triethylamine (1.0 g). The reaction mixture was stirred at 50 °C for 6 h. It was then cooled and quenched with a mixture of water, THF and ethyl acetate. The organic layer (THF and ethyl acetate) was washed three times with brine and once with H₂O. The solution was dried over anhydrous Na₂SO₄ and filtered. Most of the solvents were then removed until a viscous dark brown liquid was obtained. Products were precipitated from the liquid by addition of an excess of hexane. The precipitated solids were centrifuged, washed with hexane until no detection of aniline on TLC, and dried under vacuum to yield hexaanilino[60]fullerenes **2** (475 mg, 94%). IR ν_{\max} (KBr)/cm⁻¹ 3392 (br, N–H), 3052 (C–H), 2978 (C–H), 1600 (s), 1495 (s), 1314, 1252, 1067, 751 (s), 693 (s), and 536; UV-VIS (THF, *ca.* 5.0 × 10⁻⁴ M): ν_{\max} 248 nm. ¹H NMR (CDCl₃) δ 1.58 and 6.7–7.3. MS (DCI⁻-MS, direct probe, negative ion, mass of the highest ion peak in the fragmentation group, Fig. 5), *m/z* 721, 813 (*n* = 1, rel intensity 100), 904 (*n* = 2), 995 (*n* = 3), 1086 (*n* = 4), 1177 (*n* = 5), and 1268 (*n* = 6), consistent with anionic

polynitrated C₆₀ formula of C₆₀(NC₆H₅)_n⁻. Anal. calc. for C₉₆H₆₆N₆O₁₅ as C₆₀(NHC₆H₅)₆·15H₂O: C, 74.71; H, 4.28; N, 5.45; O, 15.56. Found: C, 74.34; H, 4.54; N, 5.44; O, 15.68%.

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