INTRAMOLECULAR ELECTRON-TRANSFER OF C60-OLIGOANILINE LEUCOEMERALDINE CONJUGATES UPON PHOTOACTIVATION

Taizoon Canteenwala[a]; Vijayaraj Anantharaj[a]; Sambhaji V. Patil[a]; Manas Halder[a]; Long Y. Chiang[ab]

[a] Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan [b] Department of Chemistry, Institute of Nanoscience and Engineering, University of Massachusetts—Lowell, Lowell, MA, U.S.A.

PLEASE SCROLL DOWN FOR ARTICLE

INTRAMOLECULAR ELECTRON-TRANSFER OF C$_{60}$-OLIGOANILINE LEUCOEMERALDINE CONJUGATES UPON PHOTOACTIVATION

Taizoon Canteenwala,[1] Vijayaraj Anantharaj,[1] Sambhaji V. Patil,[1] Manas Halder,[1] and Long Y. Chiang[1,2,]*

[1]Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan
[2]Department of Chemistry, Institute of Nanoscience and Engineering, University of Massachusetts—Lowell, Lowell, MA 01854

ABSTRACT

Conductive starburst C$_{60}$-derived macromolecules were synthesized using C$_{60}$(NO$_2$)$_6$ as a precursor intermediate for linking π-conjugate oligomers, such as tetraaniline and hexadecaaniline, directly onto the fullerene cage. Subsequent phenylhydrazine reduction of the resulting hexa(tetra-anilino)[60]fullerene and hexa(hexadecaanilino)[60]fullerene emeraldines produced the corresponding leucoemeraldine donors. Photoexcitation of these hexa(oligoanilino)[60]fullerene leucoemeraldines under N$_2$ induced intramolecular electron-transfer from benzenoid moieties of oligoaniline arms to the C$_{60}$ cage, that regenerated the emeraldine structure in oligoaniline arms. Proceeding on the number of electrons transferred was followed and estimated by in situ chemical trapping method on the reaction of electrophiles with fullerenic anions generated. That substantiated the capability of the fullerene cage to accept multiple electrons during the irradiation process.

Key Words: Fullerene; Tetraaniline; Hexadecaaniline; Hexa(tetra-anilino)[60]fullerene; Hexa(hexadecaanilino)[60]fullerene; Intramolecular electron-transfer

*Corresponding author. E-mail: Long_Chiang@uml.edu

INTRODUCTION

Fullerene cage molecule exhibits high electron affinity that allows its acceptance of multiple electrons consecutively.[1] One of the most extensively studied physical properties of C_{60}-containing dyads, triads, and polymers may be photoinduced charge-transfer or energy-transfer[2] from the chemically attached donor arm to the C_{60} cage. In the presence of potent electron donors, such as tetrakis(dimethylamino)ethylene (TDAE),[3] the electron transfer process is spontaneous, forming the corresponding D−A charge-transfer complex containing anionic C_{60} species. Whereas the electron transfer from weak to moderate organic donors, such as electron-rich conjugates and polymers, to the fullerene molecule and its derivatives can be made by providing external photoactivation energy. Several donor-fullerene dyads and triads containing carotene−porphyrin,[4] porphyrin,[5−10] terpyridine or bipyridine ruthenium complex,[11−12] ferrocene,[13] tetrathiafulvalene,[14] and pyrazine[15] were synthesized for the study of their intramolecular photo-induced electron or energy transfer properties. In most of these fullerene monoadducts, only one electron was involved in the intramolecular transfer process onto each C_{60} molecule. It is mainly due to an elevated oxidation potential of the monocationically charged donor moiety, as compared with its ground state energy, that makes the formation of a dicationic donor moiety difficult.

Conjugated polymers are excellent electron donors. Linking their oligomer analog macromolecules with C_{60} forming the corresponding fullerene conjugates[16,17] was recently reported. Direct attaching conjugated oligomer arms onto the fullerene cage may allow us to determine the intramolecular electron tunneling efficiency in relationship to the distance effective for the electron-transfer upon photoexcitation and the maximum electron-accepting capacity of the fullerene cage with or without the trapping reaction of anionic fullerene intermediates. By utilizing oligoaniline leucoemeraldine arms as donors synthesized from the parent starburst structure of hexa(tetra-anilino)[60]fullerene **1** and hexa(hexadecaanilino)[60]fullerene **2**, we demonstrate that the number of electrons transferred onto the C_{60} cage can be multiple and trapped by electrophilic reagents.

EXPERIMENTAL

Materials and Methods

Pure C_{60}(99.5%) was purchased from Southern Chemical Group, Georgia and checked by chromatography prior to the use. Infrared spectra were recorded as KBr pellets on a Nicolet 750 series FT-IR spectrometer. ^{1}H-NMR spectra were recorded on a Bruker AC-300 spectrometer. UV−Vis

spectra were recorded on a Hitachi U-3410 UV spectrometer. HPLC analyses and separations were performed on a Waters Delta Prep. 4000 HPLC system equipped with a Waters 486 UV detector operated at 340 nm controlled and processed by Millinum software. Benzene and toluene were dried and distilled over Na.

Mass spectroscopic studies were performed by the use of either the positive ion fast atom bombardment (FAB) technique with a direct probe on a JEOL JMS-HX110 high performance mass spectrometer or the negative ion desorption chemical ionization (DCI) technique with a direct probe on a JEOL JMS-SX102A mass spectrometer at the NSC instrumentation center of National Tsing-Hwa University, Taiwan.

Synthesis of Hexa(Tetraanilino)[60]Fullerene (HTAF) 1

In a dry flask with a magnetic stirring bar, hexanitro[60]fullerene (0.39 g, 0.39 mmol) dissolved in THF (10 mL) was charged under N$_2$. To this solution, tetraaniline (1.03 g, 2.82 mmol, 7.2 equiv.) in dry THF (15 ml) was added, followed by triethylamine (3.0 g). The deep blue-colored reaction mixture was stirred at 50°C for 6.0 h and quenched by the addition of water and THF. The organic layer was then washed three times with brine and dried over anhydrous Na$_2$SO$_4$. After removal of most of the solvents, the dark blue products were precipitated upon the addition of ether (50 mL). The precipitates were filtered and washed with ether until no blue coloration in the washings was observed. The solids were then dried in vacuum at 40°C and purified by preparative TLC [SiO$_2$, R_f = 0.1 using THF−CHCl$_3$ (1:1) as eluent] to yield hexa(tetraanilino)[60]fullerene 1 (0.82 g, 72%). IR v_{max} (KBr) 3381 (br, N−H), 3031 (C−H), 1596, 1509 (s), 1303, 1245, 1171, 1071, 828, 748, 694, and 501 cm^{-1}; UV-vis (THF, 2.5 × 10^{-6} M): λ_{max} 303 and 548 nm.

Synthesis of Hexa(Hexadecaanilino)[60]Fullerene (HHDAF) 2

In a dry flask purged with nitrogen, hexanitro[60]fullerenes (0.11 g, 0.11 mmol) dissolved in THF (5.0 mL) was charged under N$_2$. To this solution hexadecaaniline (0.96 g, 0.66 mmol, 6.0 equiv.) in dry THF (20 mL) was added followed by triethylamine (3.0 g). To enhance the solubility of the products in solution, N-methyl pyrolidinone (7.0 mL) was also added. The deep violet-colored reaction mixture was stirred at 50°C for 24 h. At the end of reaction, THF was removed by rotary evaporation. The remaining black-colored solution was poured into water (40 mL) causing precipitation of the products. The dark violet-colored precipitates were washed several times with water (10 mL each) and filtered. The solids were further washed several times with acetonitrile (10 mL each) for removal of unreacted hexadecaaniline until

no violet color shown in the washings and dried under vacuum at 40°C to afford hexa(hexadecaanilino)[60]fullerene **2** (0.98 g) in 94% yield. Chromatographic purification of **2** was performed on TLC [SiO$_2$, R_f = 0.8 for hexadecaaniline and R_f = 0.1 for **2** using THF−CHCl$_3$ (1:1) as eluent]. IR v_{max} (KBr) 3407 (br, N−H), 2934 (C−H), 2855, 1658, 1594, 1507 (s), 1303, 1262, 1183, 1143, 1051, 824, 755, 696, and 508 cm^{-1}; UV-vis (THF, 2.5 × 10^{-6} M): λ_{max} 229, 317, and 584 nm.

Reduction of Oligoaniline Arms and Photoactivation Reaction

A dry flask equipped with a stirring bar and a condenser was charged with hexa(hexadecaanilino)[60]fullerene **2** (100 mg) and EtOH (5.0 mL) under N$_2$. The solution was degassed by bubbling with N$_2$ for 10 min and covered with an aluminum foil to prevent light exposure. It was added phenylhydrazine (0.5 mL). The reaction mixture was stirred at 0°C for a period of 15.0 h. At the end of the reaction, the solvent was evaporated under vacuum. The residue was then washed 4 times with acetonitrile (20 mL each, degassed by bubbling with N$_2$) in the dark and dried in vacuum. The fully reduced light brown solids of the product were dissolved in DMSO (freshly distilled, 20 mL, degassed by bubbling with N$_2$) and mixed with ethyl iodide (3.0 mL). The reaction mixture was subjected to photo-exposure, using a W-lamp (100 watt) as a light source, for a period of 2.0 h. A progressive change of the color of solution to green was observed. The solution was then quenched with water to effect precipitation of pasty solids. The solids were washed with acetonitrile and dissolved in DMSO (8.0 mL). The DMSO solution was added slowly by water (20 mL) to result in a colloidal mixture, which were treated with aqueous NH$_4$OH, causing precipitation of blue solids. The solids were dissolved again in DMSO (8.0 mL), following by the addition of water (20 mL) and treatment of aqueous NH$_4$OH for complete neutralization of the products. The solid products were isolated by centrifuge and washed with 1,4-dioxane (10 mL) and acetonitrile (10 mL) sequentially. The resulting blue solids were dried under vacuum at 40°C to yield ethylated hexa(hexadecaanilino)[60]fullerene **6** (80 mg).

RESULTS AND DISCUSSION

Nitration reaction of C$_{60}$ was carried out in benzene using nitrogen dioxide radical as a reagent, which was generated as a brown gas upon the treatment of copper powder with conc. HNO$_3$.[18,19] The gas was dried over a CaCl$_2$ tube and carried over into the C$_{60}$-benzene solution by N$_2$. Generation of nitrated fullerenes was evident upon disappearance of the purple color in accompany with the formation of orange solid suspension in the reaction

medium. Dinitration and tetranitration of C$_{60}$ followed a fast kinetic rate at 60°C.

Addition of two more nitro groups to the product of hexanitro[60]fullerene (HNF), C$_{60}$(NO$_2$)$_6$, was apparently a slow process at ambient temperature. Purity of HNF was determined by chromatography with a retention time of roughly 3.3 min using a HPLC setup with a reverse-phase MCH−5 column and a solvent mixture of CH$_3$CN-CHCl$_3$ in a ratio of 4:1, as eluent, at a flow rate of 0.8 cm^3/min.

Replacement of all fullerenic nitro groups by tetraaniline and hexadecaaniline was performed by the reaction of HNF with 6.0 equiv. the corresponding tetraaniline or hexadecaaniline (E.B.) in the presence of triethylamine at 50°C, as shown in Scheme 1. It gave the products of tetraanilino- and hexadecaanilino[60]fullerene heptaads **1**, C$_{60}$[(NHC$_6$H$_4$)$_2$(NC$_6$H$_4$)$_2$H]$_6$, and **2**, C$_{60}$[(NHC$_6$H$_4$)$_8$(NC$_6$H$_4$)$_8$H]$_6$, respectively, in >90% yield for the latter case. Accordingly, hexadecaaniline used in this study was prepared by the reaction of tetraaniline in its leucoemeraldine reduced form with (NH$_4$)$_2$S$_2$O$_8$ in aqueous HCl solution at ambient temperature for 2.0 h.[20] Tetraaniline leucoemeraldine can be generated by the
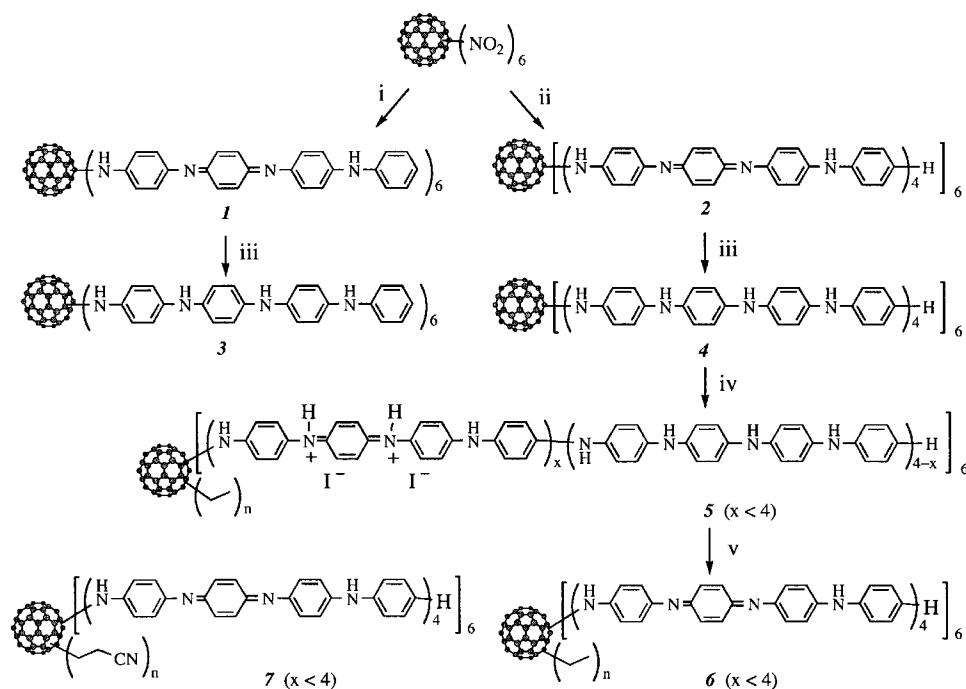
Scheme 1. Reagents and conditions: i, tetraaniline (EB, 6.6 equiv.), Et$_3$N, THF, 50°C, 6.0 h; ii, hexadecaaniline (EB, 6.6 equiv.), Et$_3$N, THF, 50°C, 6.0 h; iii, phenyl hydrazine, EtOH−DMF, r.t., 15 h, N$_2$ (degassed); iv, Et-I, DMSO, r.t., $h\upsilon$ (W-lamp, 100 watt), N$_2$, 2.0 h; v, O$_2$ (air), DMSO; H$_2$O, NH$_4$OH.

reduction of tetraaniline emeraldine using hydrazine (NH_2NH_2) as a redu-cing agent. Purification of the starting compound, tetraaniline emeraldine, was made by column chromatography (SiO_2, $R_f = 0.85$) with a mixture of pet ether−$CHCl_3$ (2:3) containing triethylamine (3%) as eluent. In the workup procedure of the hexadecaaniline preparation, the product mixture was neutralized with NH_4OH for removal of the acidic protons that led to the isolated hexadecaaniline in its blue emeraldine base form. Soluble impurities remaining in the product was subsequently removed by soxhlet extraction with diethyl ether. A small-scale chromatographic purification of hex-adecaaniline on TLC (SiO_2) was possible at $R_f = 0.6-0.75$ using THF−$CHCl_3$ (1:1) or THF−EtOAc (1:2) as eluent. The molecular ion mass group at m/z 1450−1458 depending on the number of quinonoid units in the structure of hexadecaaniline was detected in the negative ion desorption chemical ionization mass spectrum (DCI^-−MS).[16,21]

Nucleophilic substitution reactivity of the terminal amino group of each hexadecaaniline is apparently higher than that of the in-chain amino groups in replacing nitro groups of HNF. That makes the preparation of starbust C_{60}-derived oligoaniline possible. Reduction of **1** and **2** with phenylhydrazine in a solvent mixture of EtOH and DMF at ambient temperature for over-night, followed by decolorization with activated carbon at 75°C, gave the corresponding fully reduced leucoemeraldine products **3** and **4**, respectively, containing electron-rich oligoaniline donor arms.

Optical spectrum of the fully reduced form of hexadecaanilino[60]-fullerene **4** (leucoemeraldine) exhibited a clear band centered at 320 nm corresponding to the absorption of −(NH-C_6H_4)$_n$− moieties. As the number of oxidative quinonoid unit increased to emeraldine base form of **2**, a cor-responding absorption band appeared at 581 nm as shown in Fig. 1. Further oxidation of **2** by PbO_2 gave the fully oxidized permigraniline base form of hexadecaanilino[60]fullerene displaying a absorption band at 514 nm, a blue-shift of 67 nm from that of **2**. These reversible redox structures of oligoaniline agree well with those of high molecular weight polyaniline.

Conversion of insulating polyaniline to its conductive form was achieved by protonation with arylsulfonic acid or HCl, showing an extended optical absorption to a much longer wavelength. Similar phenomena were observed as the blue fullerene heptaad **2** being treated with HCl. Instant change of the color of the material to green was observed with enhancement of continuous optical absorption at longer wavelengths from 800−1400 nm (the bottom spectrum of Fig. 2). The relative intensity of these absorption bands is clearly higher than that of protonated hexadecaaniline (the top spectrum of Fig. 2), indicating a collective effect of the starburst structure of oligoaniline arms when attached onto the C_{60} cage. It also confirmed the generation of an extended conducting polaron state along the hexadecaani-line chain closely resembling that of polyanilines. Therefore, the use of
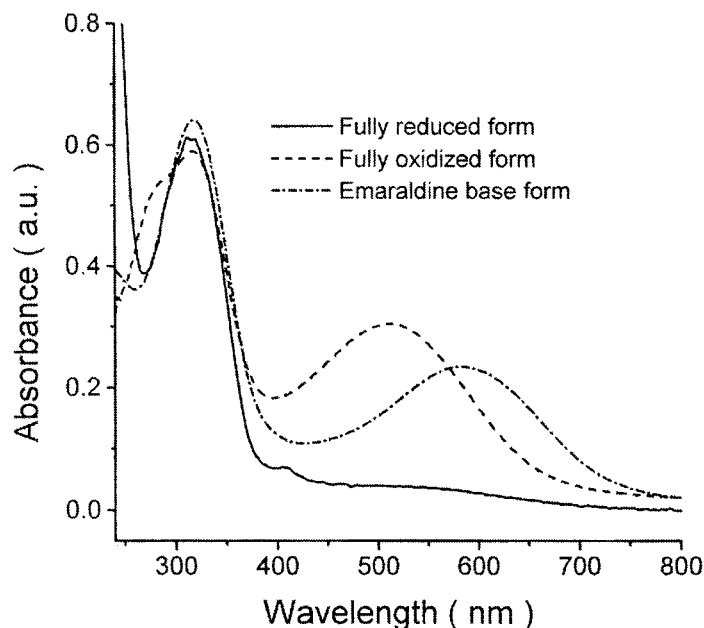
Figure 1. Comparison of UV-vis spectra of hexadecaanilino[60]fullerene heptaad **2**, C$_{60}$[(NHC$_6$H$_4$)$_8$(NC$_6$H$_4$)$_8$H]$_6$, in emeraldine base (EB) form, fully reduced (LE) form (leuco-emeraldine), and fully oxidized (PB) form (permigraniline base).

starburst **2** as a conductive precursor material for the design of electronic devices becomes feasible.

^{1}H-NMR spectrum of hexa(tetraanilino)[60]fullerene leucoemeraldine **3** (Fig. 3b) showed a proton peak pattern in close resemblance with that of tetraaniline leucoemeraldine (Fig. 3a). After treating both compounds with D$_2$O, the disappearance of N−H proton peaks at δ7.12, 7.34, and 7.65 was observed. In the case of hexa(hexadecaanilino)[60]fullerene leucoemeraldine **4**, the spectrum showed only three major broad bands at chemical shifts of aromatic protons (Fig. 3c) in a similar shape to that of **3**.

Upon light exposure of fullerene−leucoemeraldine conjugates **3** and **4** using a Hg lamp as the light source, regeneration of the emeraldine base structure along the oligoaniline chain was detected.[22] As shown in Figs. 4a and 4b, a progressive increase in intensity of a strong and broad absorption maximum centered at 575 nm, slightly (25 nm) less than that of polyaniline, occurred at different time intervals. The band corresponds to the optical absorption of quinonoid moieties of the arms. Changes of the IR optical absorption indicated efficient oxidative conversion of **3** and **4** into their emeraldine analogous **1** and **2**, respectively. Interestingly, exposure of hexa-(hexadecaanilino)[60]fullerene leucoemeraldine **4** in THF to the sunlight also gave a similar result with a progress increase of the quinonoid absorption band centered at 575 nm (Fig. 4c) in a slower rate than that of Fig. 4b.
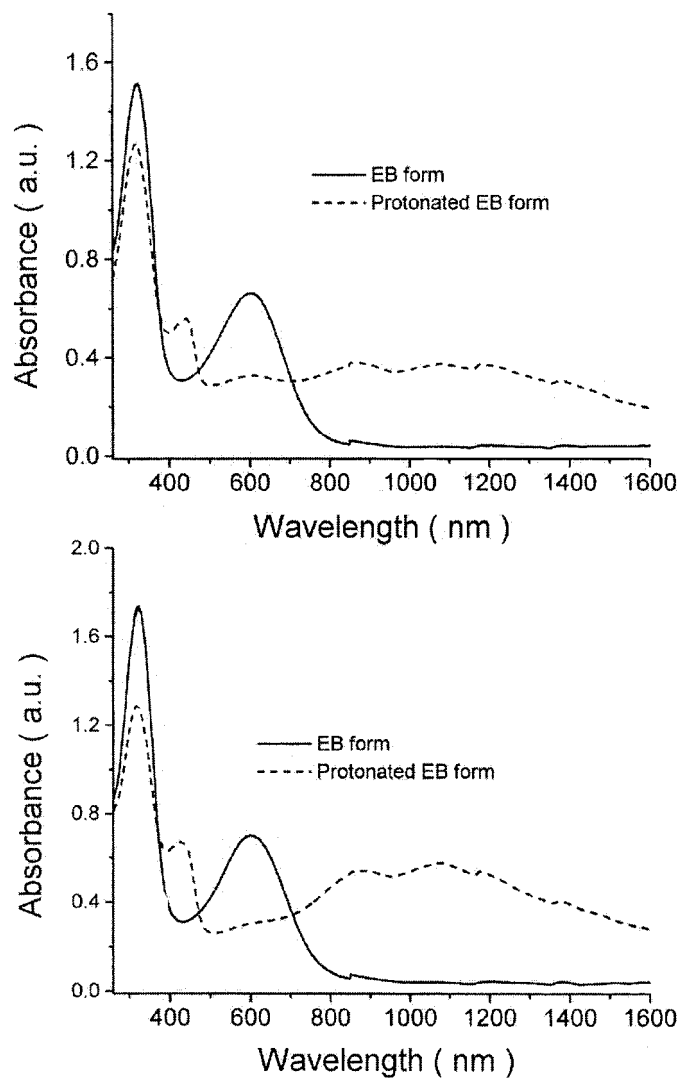
Figure 2. Comparison of UV-vis spectra of protonated hexadecaaniline (top spectrum) and protonated hexadecaanilino[60]fullerene heptaad **2** (bottom spectrum) with their corresponding parentemeraldine base (EB) compounds.

Subsequent treatment of leucoemeraldine **4** in DMSO (degassed) with ethyl iodide under photoexcitation for a period of 2.0 h at ambient temperature, using a W-lamp (100 watts) as a light source, induced regeneration of the quinonoid structure along each oligoaniline arm. The structural change accompanied with recovery of its characteristic bright blue in
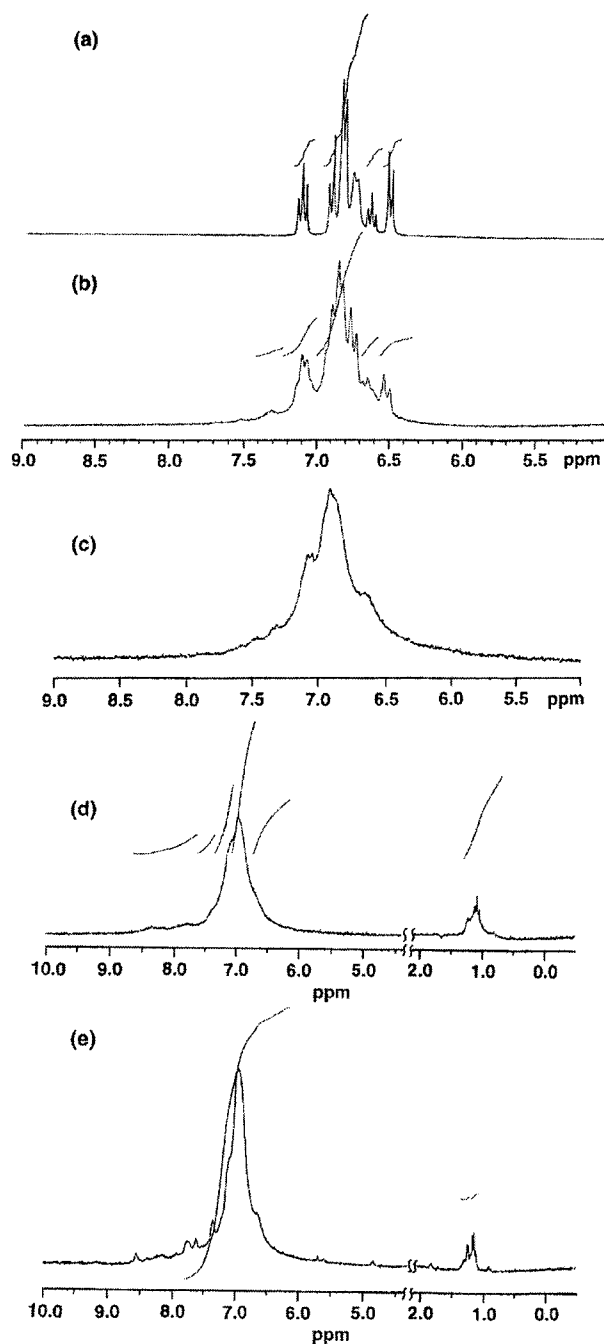
Figure 3. ^{1}H-NMR spectra (DMSO-d_6-D$_2$O) of (a) tetraaniline leucoemeraldine, (b) hexa-(tetraanilino)[60]fullerene leucoemeraldine **3**, (c) hexa(hexadecaanilino)[60]fullerene leucoemer-aldine **4**, (d) ethylated hexa(hexadecaanilino)[60]fullerene emeraldine **6**, and (e) cyanoethylated derivative **7**.
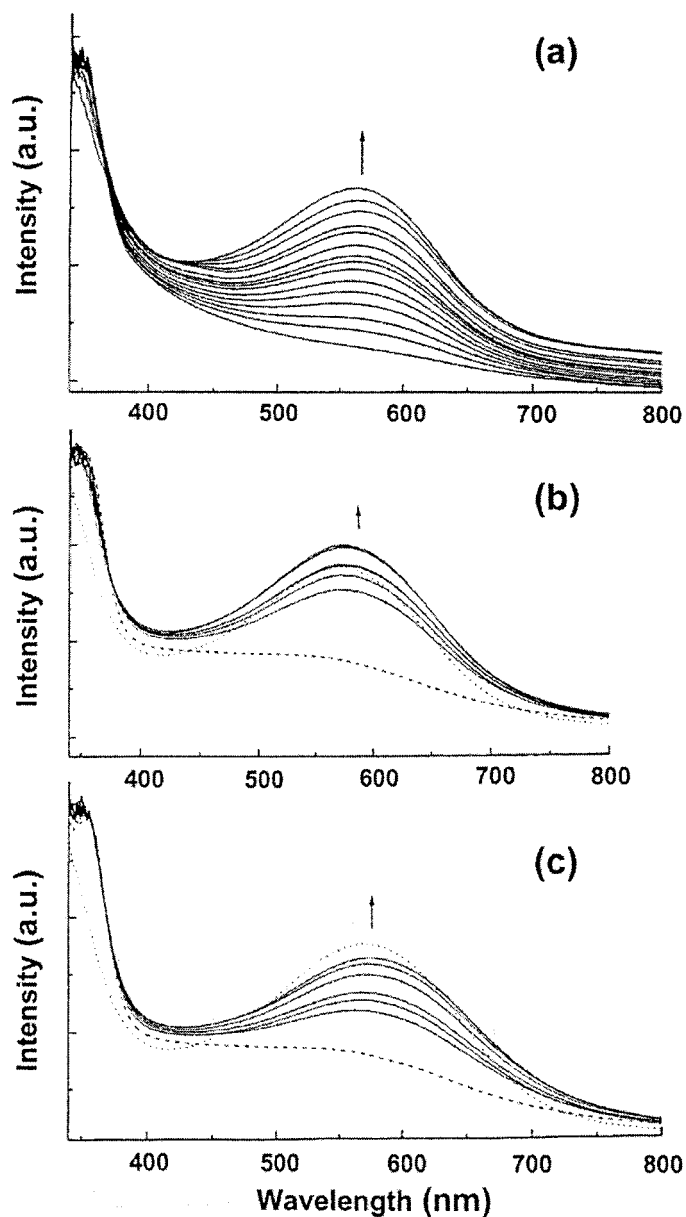
Figure 4. UV-vis spectra of photoexcitation intermediates of (a) hexa(tetraanilino)[60]-fullerene leucoemeraldine **3** and (b) hexa(hexadeca-anilino)[60]fullerene leucoemeraldine **4** in the presence of $(n-Bu)_4N-ClO_4$ electrolyte in THF in a quartz tube with a Hg lamp at ambient temperature for 30 min, and (c) **4**/$(n-Bu)_4N-ClO_4$/THF under sunlight exposure.

the color of the solution. Thus, progress of this photoinduced phenomenon can be followed visually. Since the solution was fully deoxygenated, oxidation of leucoemeraldine **4** by molecular oxygen may not occur. Change of the solution color can be considered mainly due to the photoinduced effect. Chemically, conversion of a benzenoid moiety into the corresponding quinonoid moiety was accomplished by the loss of two unpaired electrons from two benzenoid nitrogen atoms. These electrons were transferred onto the fullerene acceptor upon photoactivation. For each electron accepted by C$_{60}$, a fullerenic anion is formed. The carbanion can be trapped by the reaction in situ with ethyl iodide at ambient temperature, resulted in the formation of ethylated fullerene derivatives **5** from **4**, as shown in Scheme 1. Theoretically, the number of ethyl groups chemically bound on each fullerene cage may represent the total number of electrons accepted by the C$_{60}$ cage intramolecularly from several hexadecaaniline arms if the trapping reaction gave a quantitative yield.

Experimently, the photoinduced reaction products were collected as the solids from a solvent mixture of DMSO$-$H$_2$O. Further oxidation of
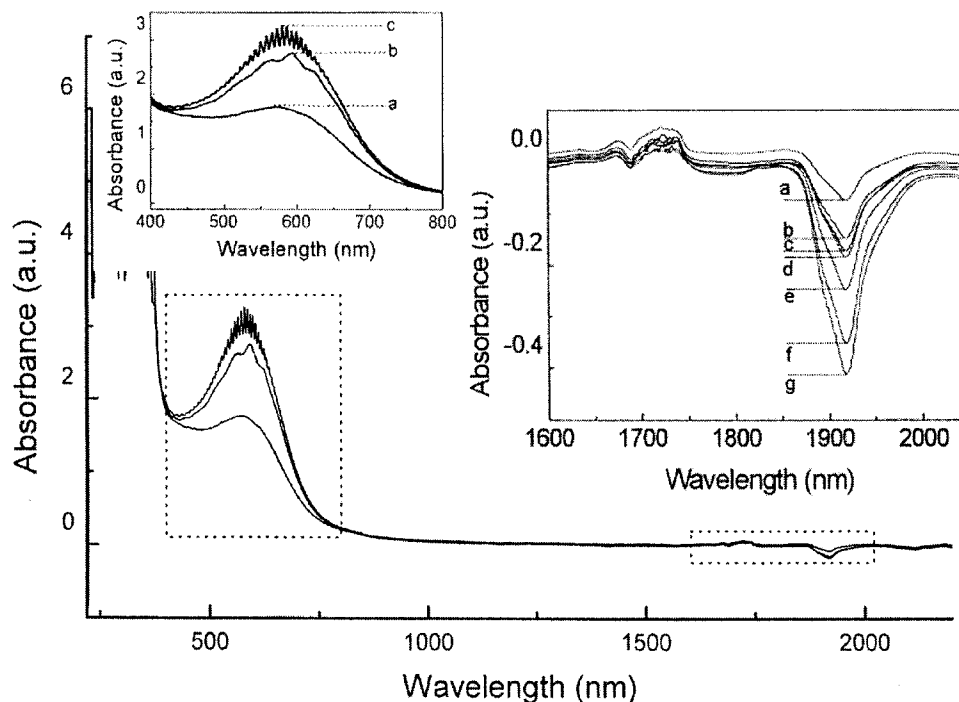

Figure 5. UV-vis-near IR spectra of hexa(hexadecaanilino)[60]fullerene leucoemeraldine **4** (conc. 2.64×10^{-4} M) in the presence of (n-Bu)$_4$N-ClO$_4$ electrolyte in THF in a quartz tube at a time interval of (a) 0.0 min; (b) 10 min; (c) 20 min; (d) 30 min; (e) 2.0 h; (f) 4.0 h; and (g) 5.3 h after irradiation with a Hg lamp at ambient temperature for 30 min.

oligoaniline arms of the reaction intermediate **5** by oxygen (air) led to a stable, protonated hexadecaaniline emeraldine derivatives of fullerene. Removal of the charged protons on quinonoid units of these derivatives by the treatment with NH_4OH in DMSO, followed by precipitation of the products upon the addition of H_2O and drying in vacuum, gave the corresponding compound **6**, ethylated hexa(hexadecaanilino)[60]fullerene, as blue solids. ^1H NMR spectrum of **6**, after the purification, in DMSO-d_6-D_2O (Fig. 3d) displayed clear peaks at $\delta 1.05-1.2$ corresponding to the chemical shift of aliphatic protons. Since the product solids were rinsed with CH_3CN and precipitated from DMSO-H_2O, we assumed that all unreacted Et-I were fully removed. The trapping reaction was performed under mild conditions to minimize the possibility of alkylation on aniline subunits with ethyl iodide. Lack of the detection of proton peaks at $\delta 2.5-4.0$ allows one to rule out the contribution of aminoethyl or iodoethyl proton peaks at $\delta 1.05-1.2$. Reaction of the fullerenic anions with Et-I should afford ethyl carbon bonds on the

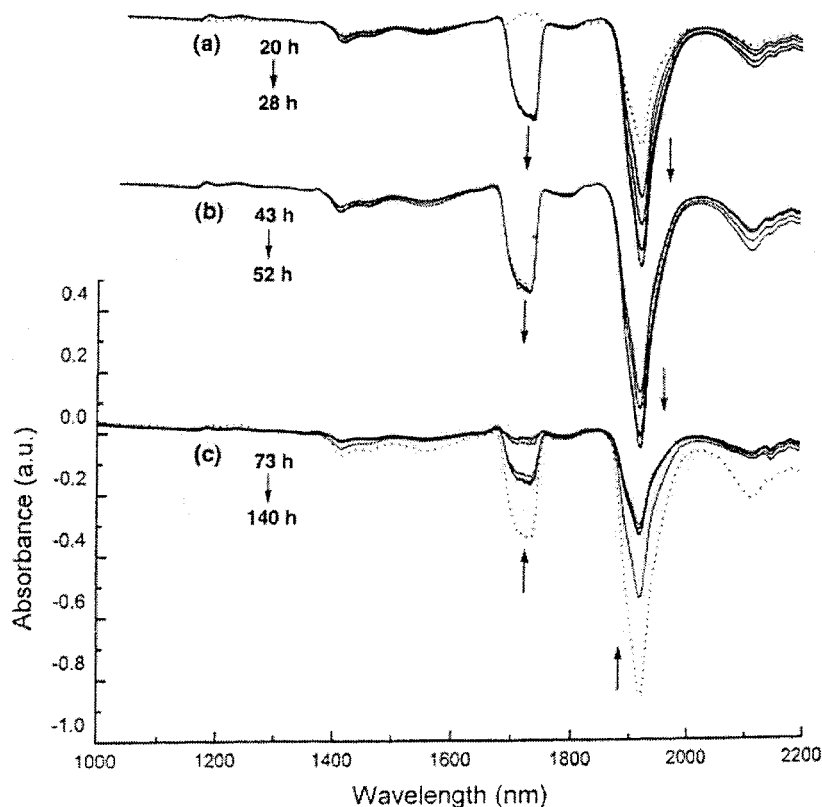***Figure 6.*** UV-vis-near IR spectra of hexa(hexadecaanilino)[60]fullerene leucoemeraldine **4** in the presence of (n-Bu)$_4$N-ClO$_4$ electrolyte in THF in a quartz tube at a time interval of (a) 20−28 h, (b) 43−52 h, and (c) 73−140 h after irradiation with a Hg lamp at ambient temperature for 30 min.

C$_{60}$ cage, as the only source for aliphatic protons bound on fullerene. Measurement of the integration ratio between the aliphatic and aromatic protons gave an estimation of more than 16 ethyl groups bound on one C$_{60}$ cage on average.

Similar results were obtained when 2-bromoethyl nitrile was used as the trapping agent in replacement of ethyliodide, as shown in Fig. 3e. In this case, aliphatic proton peak in a less relative intensity ratio (I_{arom}/I_{aliph}) was observed, indicating no more than 12 cyanoethyl groups bound on C$_{60}$ on average. These results substantiated the photoinduced intramolecular electron transfer from the hexadecaaniline arms to the C$_{60}$ core forming the corresponding anion. If the anions are continuously trapped by electrophiles in situ during the photoexcitation process, more electrons can be transferred onto the fullerene acceptor.

Interestingly, a slow relaxation of the functionalized fullerene cage in its excited state was also detected with two emission bands at 1720 and 1915 nm in the UV-vis-near IR spectrum, as shown in Figs. 5 and 6. Emission intensity of the peak at 1915 nm was actually observed to increase during the time interval of 20−52 h (Figs. 6a and 6b) after irradiation. It began to decrease in intensity afterwards in the time interval of 73−140 h (Fig. 6c) after irradiation. This long duration of energy release was contributed from the hexadecaaniline bound fullerene moieties since irradiation on the hexadecaaniline sample did not give the similar emission phenomena. We suggested involvement of a forbidden transition from the triplet excited state of hexa(hexadecaanilino)[60]fullerene to its singlet ground state.

CONCLUSION

Radical nitration of C$_{60}$ proceeded by a fast kinetic rate for the formation of tetranitro[60]fullerene with a slow rate for further nitroaddition steps. By using C$_{60}$(NO$_2$)$_6$ as a precursor intermediate for linking π-conjugate oligomers, such as tetraaniline and hexadecaaniline, directly onto the fullerene cage, conductive starburst C$_{60}$-derived macromolecules were synthesized. Subsequent phenylhydrazine reduction of the resulting hexa-(tetraanilino)[60]fullerene and hexa(hexadecaanilino)[60]fullerene emeraldines produced the corresponding leucoemeraldine donors. Direct bonding of conjugate donors on the C$_{60}$ acceptor forming the corresponding derivatives facilitates the electronic tunneling efficiency between donor and acceptor moieties. Irradiation of these hexa(oligoanilino)[60]fullerene leucoemeraldines under N$_2$ induced intramolecular electron-transfer from benzenoid moieties of oligoaniline arms to the C$_{60}$ cage, that regenerated the emeraldine structure in oligoaniline arms. Proceeding on the number of electrons transferred was followed and estimated by in situ chemical trapping method on the reaction of fullerenic anions generated with electrophiles. The results

substantiated the capability of the fullerene cage to accept multiple electrons during the irradiation process. Slow energy relaxation processes associated with emissions at 1720 and 1915 nm were detected upon photoexcitation of hexa(hexadecaanilino)[60]fullerene. A forbidden transition from the triplet excite state of **2** to its singlet ground state was proposed.

ACKNOWLEDGMENTS

REFERENCES

1. Xie, Q.; Perez-Cordero, E.; Echegoyen, L. Electrochemical Detection of C_{60}^6 and C_{70}^{6-}: Enhanced Stability of Fullerides in Solution. J. Am. Chem. Soc. **1992**, *114*, 3978−3980.

2. Armaroli, N.; Barigelletti, F.; Ceroni, P.; Eckert, J.F.; Nicoud, J.F.; Nierengarten, J.F. Photoinduced Energy Transfer in a Fullerene-oligophenylenevinylene Conjugate. Chem. Comm. **2000**, 599−600.

3. Fujitsuka, M.; Luo, C.; Ito, O. Electron-Transfer Reactions Between Fullerenes (C_{60} and C_{70}) and Tetrakis(dimethylamino)ethylene in the Ground and Excited States. J. Phys. Chem. **1999**, *103*, 445−449.

4. Carbonera, D.; Di Valentin, M.; Corvaja, C.; Agostini, G.; Giacometti, G.; Liddell, P.A.; Kuciauskas, D.; Moore, A.L.; Moore, T.A.; Gust, D. EPR Investigation of Photoinduced Radical Pair Formation and Decay to a Triplet State in a Carotene-Porphyrin-Fullerene Triad. J. Am. Chem. Soc. **1998**, *120*, 4398−4405.

5. Imahori, H.; Hagiwara, K.; Aoki, M.; Akiyama, T.; Taniguchi, S.; Okada, T.; Shirakata, M.; Sakata, Y. Linkage and Solvent Dependence of Photoinduced Electron Transfer in Zincporphyrin-C_{60} Dyads. J. Am. Chem. Soc. **1996**, *118*, 11771−11782.

6. Imahori, H.; Yamada, K.; Hasegawa, M.; Tanguchi, S.; Okada, T.; Sakata, Y. A Seqential Photoinduced Electron Relay Accelerated by Fullerene in a Porphyrin-pyromellitimide-C_{60} Triad. Angew. Chem. Int. Ed. Engl. **1997**, *36*, 2626−2629.

7. Kuciauskas, D.; Lin, S.; Seely, G.R.; Moore, A.L.; Moore, T.A.; Gust, D.; Drovestskaya, T.; Reed, C.A.; Boyed, P.D.W. Energy and Photoinduced Electron Transfer in Porphyrin-Fullerene Dyads. J. Phys. Chem. **1996**, *100*, 15926−15932.

8. Bourgeois, J.P.; Diederich, F.; Echegoyen, L.; Nierengarten, J.F. Synthesis, and Optical and Electrochemical Properties of Cyclophane-Type Molecular Dyads Containing a Porphyrin in Close, Tangential Orientation Relative to the Surface of Trans-1 Functionalized C_{60}. Helv. Chim. Acta. **1998**, *81*, 1835−1844.

9. Dietel, E.; Hirsch, A.; Eichhorn, E.; Rieker, A.; Hackbarth, S.; Roder, B. A Macrocyclic [C$_{60}$] Fullerene-porphyrin Dyad Involving π-π Stacking Interactions. Chem. Comm. **1998**, 1981−1982.

10. Cheng, P.; Wilson, S.R.; Schuster, D.I. A Novel Parachute-shaped C$_{60}$-porphyrin Dyad. Chem. Comm. **1999**, 89−90.

11. Armspach, D.; Constable, E.C.; Diederich, H.; Housecroft, C.E.; Nierengarten, J.F. Bucky-ligands:fullerene-substituted Oligopyridines for Metallosupramolecular Chemistry. Chem. Comm. **1996**, 2009−2010.

12. Maggini, M.; Dono, A.; Scorrano, G.; Prato, M. Synthesis of a [60] Fullerene Derivative Covalently Linked to a Ruthenium(II) Tris(bipyridine) Complex. Chem. Comm. **1995**, 845−846.

13. Guldi, D.M.; Maggini, M.; Scorrano, G.; Prato, M. Intramolecular Electron Transfer in Fullerene/Ferrocene Based Donor-Bridge-Acceptor Dyads. J. Am. Chem. Soc. **1997**, *119*, 974−980.

14. Simonsen, K.B.; Konovalov, V.V.; Konovalova, T.A.; Kawai, T.; Cava, M.P.; Kispert, D.L.; Metzger, R.M.; Becher, J. Long-lived Photoproduced Radical Ions in Tetrathiafulvalenes Covalently Tethered to C$_{60}$. J. Chem. Soc., Perkin Trans. 2 **1999**, 657−665.

15. Guldi, D.M.; Torres-Garcia, G.; Mattay, J. Intramolecular Energy Transfer in Fullerene Pyrazine Dyads. J. Phys. Chem. A **1998**, *102*, 9679−9685.

16. Wang, L.Y.; Anantharaj, V.; Ashok, K.; Chiang, L.Y. Fullerene-derived Starburst Conjugated Polymers. Synth. Met. **1999**, *103*, 2350−2353.

17. Knorr, S.; Grupp, A.; Mehring, M.; Grube, G.; Effenberger, F. Photoinduced Electron-transfer Processes in Anthracene−quinquethiophene−fullerene Diads and Triads. J. Chem. Phys. **1999**, *110*, 3502−3508.

18. Anantharaj, V.; Bhonsle, J.; Canteenwala, T.; Chiang, L.Y. Synthesis and Characterization of Nitrated [60]fullerene Derivatives. J. Chem. Soc., Perkin Trans. 1 **1999**, 31−36.

19. Chiang, L.Y.; Bhonsle, J.B.; Wang, L.Y.; Shu, S.F.; Chang, T.M.; Hwu, J.R. Efficient One-flask Synthesis of Water-soluble [60]Fullerenols. Tetrahedron **1996**, *52*, 4963−4972.

20. Zhang, W.J.; Feng, J.; MacDiarmid, A.G.; Epstein, A.J. Synthesis of Oligomeric Anilines. Synth. Met. **1997**, *84*, 119−120.

21. Anantharaj, V.; Wang, L.Y.; Canteenwala, T.; Chiang, L.Y. Synthesis of Starburst Hexa(oligoanilinated)C$_{60}$ Using Hexanitro[60]fullerene as a Precursor. J. Chem. Soc., Perkin Trans. 1, **1999**, 3357−3366.

22. Anantharaj, V.; Patil, S.V.; Canteenwala, T.; Wang, L.Y.; Chiang, L.Y. Oxidation of C$_{60}$-bound Oligoaniline Leucoemeraldine upon Photoactivation. Synth. Met. **2001**, *121*, 1123−1124.