Photochemical and Thermal Reactions of C_{60} with *N*-Succinimidyl 4-Azido-2,3,5,6-tetrafluorobenzoate: A New Method for Functionalization of C_{60}†

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The first example of a photochemical reaction between C_{60} and an *N*-hydroxysuccinimide (NHS) functionalized perfluorophenyl azide (PFPA) is reported. Photolysis of a chlorobenzene solution of C_{60} and *N*-succinimidyl 4-azido-2,3,5,6-tetrafluorobenzoate (**1**) at 300 nm gave exclusively the monoadduct azamethanofullerene **2** in 10% yield (39% based on recovered C_{60}). The reaction is believed to take place via the addition of the photogenerated, highly reactive nitrene intermediate to a 6,6 double bond of C_{60}. The NHS active ester group present in **2** served as a site for attachment of other molecules by way of an acylation reaction. For example, **2** was allowed to react with L-glutamic acid diethyl ester or benzylamine to give the corresponding amides **3** or **4**. Thermal reaction of C_{60} and **1** in chlorobenzene at 105–108 °C gave the same adduct **2** in 25% yield (45% based on recovered C_{60}).

Introduction

The chemical reactivity of buckminsterfullerene (C_{60}) is an area of vigorous investigation.[1] It has been suggested that C_{60} acts like a closed-cage alkene rather than an aromatic molecule due to its poor electron delocalization.[1a] For example, C_{60} undergoes reactions associated with the electron-deficient alkenes. Such reactions include various addition reactions such as cycloaddition,[2,3] nucleophilic addition,[1d,4] radical addition,[5] and dipole addition.[6,7]

Recently, thermal reactions between C_{60} and azides were reported.[8–10] In one example using alkyl azides, the 5,6-azamethanoannulene was formed.[8] In another example using an azidoformate derivative, the 6,6-azamethanofullerene was produced.[9]

Perfluorophenyl azides (PFPAs) have recently emerged as a new class of photoaffinity labeling reagents owing to their significantly higher CH and NH insertion efficiencies as compared to their non-fluorinated analogs.[11] We have developed a series of functionalized PFPAs for protein cross-linking,[12] surface modification and subsequent enzyme immobilization,[13] and polymer cross-linking.[14] In the course of the surface functionalization studies using PFPAs, we observed that PFPAs could be used to modify the surface of graphite.[15] Encouraged by this result, we expected that it may be possible to photochemically derivatize C_{60} with a PFPA since both C_{60} and graphite are made up of carbon in the sp^2-hybridized state and C_{60} can be considered as a curved graphite sheet.

Herein we report on the first photochemical reaction of a PFPA with C_{60}. The reactions constitute a novel method for the functionalization of C_{60}. We also report on the thermal reaction between C_{60} and the PFPA. The use of a PFPA possessing a reactive functional group

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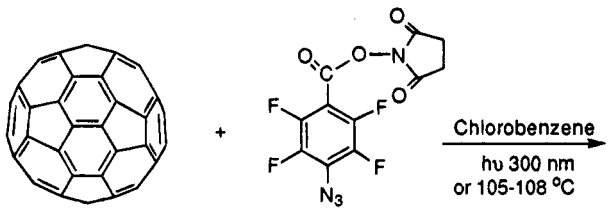
allows for the attachment of other organic or bioactive molecules to C_{60}. Thus, a variety of C_{60} derivatives may be generated using this method.

Results and Discussion

Photochemical Reaction of C_{60} with 1. The NHS PFPA ester **1** was chosen for the photoreaction because the NHS active ester is capable of reaction with a variety of NHS-reactive molecules including biomolecules such as amino acids and enzymes subsequent to the photolysis step.[13] The reaction was performed as follows. A solution of C_{60} and *N*-succinimidyl 4-azido-2,3,5,6-tetrafluorobenzoate (**1**)[11a] in dry chlorobenzene was purged with Ar and irradiated at 300 nm for 5 h (eq 1). The resulting mixture



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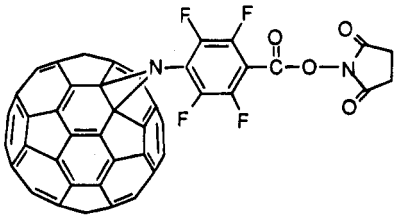


(1)

2

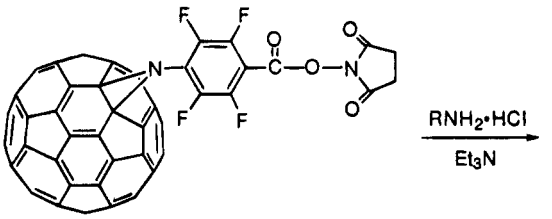
was concentrated and purified by flash chromatography with 10:1 toluene–ethyl acetate to give first C_{60} and then **2** as a brown solid in 10% yield (39% based on recovered C_{60}). Since azides are also capable of undergoing thermal addition reactions with C_{60},[8-10] control reactions between C_{60} and **1** in the dark were carried out. Only starting materials were observed after a solution of C_{60} and **1** in chlorobenzene was heated at 85 °C for 16 h as shown by analytical TLC.

NHS ester **2** is stable in air as well as in a solution of chloroform, benzene, or toluene. A small downfield shift of the succinimidyl protons was observed in the ^{1}H NMR spectrum of **2** (δ 2.954, s) as compared to that of **1** (δ 2.919, s), owing to the shifting effect of C_{60} as reported in many other C_{60} derivatives.[1c,6b,16] The ^{19}F NMR spectrum of **2** showed the typical AA′XX′ pattern, indicating that ring expansion of the (tetrafluorophenyl)-nitrene had not occurred. The FAB-MS of **2** contains the requisite M^+ isotope pattern at 1024–1027 and C_{60}^+ at 720–723. The FTIR spectrum of **2** shows strong carbonyl absorptions at 1745 cm^{-1} (ester) and 1649 cm^{-1} (imide). The UV–vis spectrum of **2** in hexanes is similar to that of C_{60}. Structure assignment of the C_{60} portion of **2** is based on the ^{13}C NMR spectrum of amides **3** and **4** (see below).

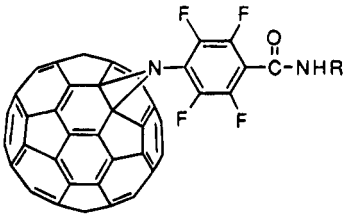
The photochemical reaction likely proceeds by an addition of the highly reactive nitrene intermediate generated by photolysis of **1** to a 6,6 double bond of C_{60} to give the aziridine **2**. Interestingly, only the monoadduct was observed. A photoreaction performed with a 5:1 molar ratio of **1**:C_{60} gave a similar result. Neither a bisadduct of **1** to C_{60} nor an improved yield of **2** was observed.

Perfluorophenyl azides have been reported to react with aromatic molecules such as benzene and toluene upon photolysis.[17] Thus, a control experiment was carried out in which **1** was photolyzed in chlorobenzene in the absence of C_{60}. TLC of the resulting solution showed several spots, all of which were more polar (R_f < 0.15) than **2** (R_f = 0.56). Evaporation of the solvent afforded a light brown solid which was only partially soluble in $CDCl_3$. The ^{1}H NMR spectrum of the soluble portion in $CDCl_3$ showed a broad peak at around δ 2.91 and several broad peaks in the aromatic region but no sharp singlet at δ 2.954. This control experiment indicates that reaction of the nitrene derived from **1** with the solvent chlorobenzene may contribute to the low yield of **2**.

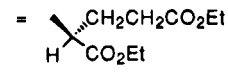
Generation of C_{60} Derivatives via 2. The reactivity of **2** was studied with NHS ester-reactive molecules such as an amino acid derivative, L-glutamic acid diethyl ester, and a simple amine, benzylamine (eq 2). Treatment of a



2



(2)

3 R = 

4 R = CH_2Ph

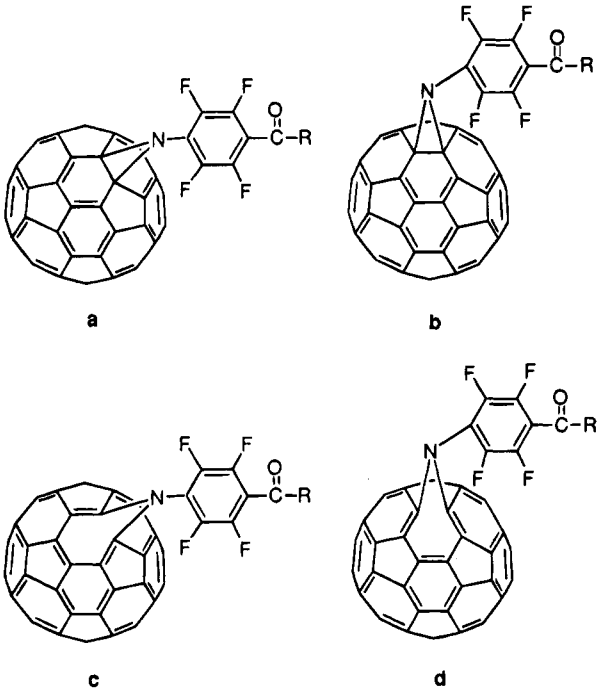
toluene solution of **2** with an ethanol solution of L-glutamic acid diethyl ester hydrochloride containing Et_3N gave amide **3** as a brown solid in 63% yield after purification by column chromatography.

Amide **3** is stable in air and in a solution of either chloroform or toluene. The ^{1}H NMR spectrum of **3** was consistent with its structure. The ^{19}F NMR spectrum of **3** showed the typical AA′XX′ patterns. The FTIR spectrum of **3** contained a strong amide carbonyl absorption at 1656 cm^{-1}. The FAB-MS of **3** displayed M^+ at *m/e* 1112–1114 and C_{60}^+ at *m/e* 720–723. The ^{13}C NMR spectrum of **3** exhibited seven aliphatic carbons at δ 62.10, 60.87, 52.60, 30.16, 27.22, 14.16, and 14.14 and three carbonyl peaks at δ 172.72, 171.06, and 157.89 (Figure 1b). The peaks at δ 127.09 and 110.62 were assigned to the carbons on the tetrafluorobenzene ring adjacent to the aziridine N and amide C, respectively.

(16) Smith, A. B., III; Strongin, R. M.; Brard, L.; Frust, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 5829.

(17) Poe, R.; Schnapp, K.; Young, M. J. T.; Grayzar, J.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 5054.

The carbons attached to a fluorine atom were not observed due to the strong coupling of ^{13}C with ^{19}F. There were 16 peaks in the region of δ 140–146, indicating that the C_{60} skeleton of the product has C_{2v} symmetry.[18] Thus, azamethanofullerene **3b** and azamethanoannulene **3d** with 5,6 junctions can be ruled out. The ^{13}C NMR spectrum also showed a peak at δ 80.37 (Figure 1a) which corresponded to the bridgehead carbon.[9,17] These data indicate that **3** is an aziridine at a 6,6 junction of C_{60} with fast pyramidal inversion at nitrogen.[9] Therefore, amide **3** and NHS ester **2** as well are assigned the 6,6-azamethanofullerene structures **3a** and **2a**, respectively.



2 R = O–N(succinimidyl)

3 R = HN, $CH_2CH_2CO_2Et$, H, CO_2Et

4 R = $NHCH_2Ph$

The NHS ester **2** was also allowed to react with benzylamine,[19] producing the amide **4** as a brown solid in 84% yield. Amide **4** is also stable in air and in a solution of either chloroform or toluene. The ^1H NMR spectrum of **4** contained a broad peak at δ 6.37 (amide proton) and a singlet at δ 4.72 (methylene protons) in a ratio of 1:2. The ^{19}F NMR spectrum of **4** showed the AA'XX' patterns similar to those of **2** and **3**. The FTIR spectrum of **4** contained a strong amide carbonyl absorption at 1651 cm^{-1}. The FAB-MS of **4** displayed M^+ at *m/e* 1017–1020 and C_{60}^+ at *m/e* 721–723. The ^{13}C NMR spectrum of **4** showed three peaks at δ 128.97, 128.00, and 127.90 which were assigned to five of the six carbon atoms on the benzyl aromatic ring and a peak at δ 44.50 which corresponded to the benzyl CH_2 (Figure 2b). There

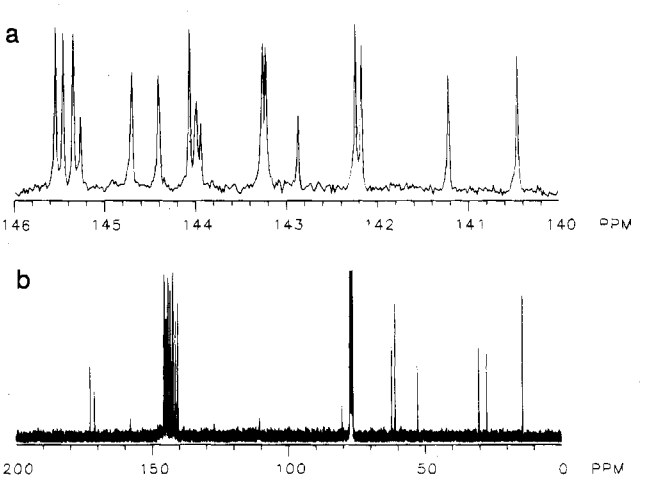


Figure 1. (a) Expanded and (b) full ^{13}C NMR spectra of **3** in $CDCl_3$.

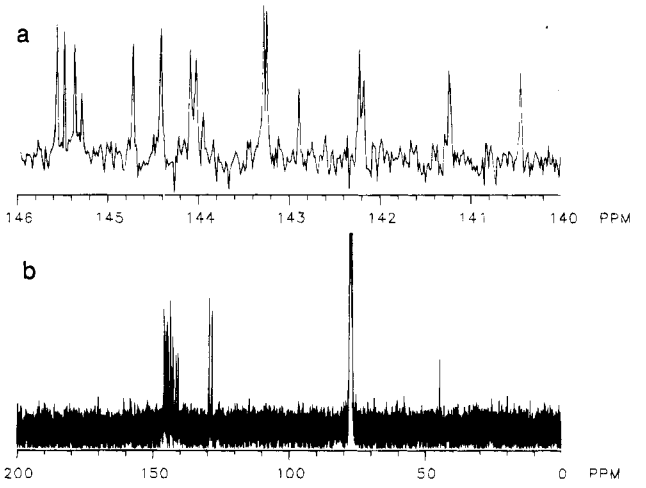


Figure 2. (a) Expanded and (b) full ^{13}C NMR spectra of **4** in $CDCl_3$.

were 16 peaks in the region of δ 140–146 (Figure 2a). The bridgehead carbon was not detected in the spectrum due to the low sample concentration. Amide **4** was assigned the 6,6-azamethanofullerene structure **4a** by analogy to **3**.

Thermal Reaction of C_{60} and 1. As azides are capable of undergoing thermal reactions with alkenes,[20] we next studied the thermal reaction of **1** with C_{60}. A solution of C_{60} and **1** in chlorobenzene was heated at 105–108 °C for 5 days (eq 1).[21] Flash chromatography of the concentrated mixture with 10:1 toluene–ethyl acetate gave first C_{60} and then a brown solid in 23% yield (45% based on recovered C_{60}). The brown solid has the same R_f value (0.56) as that of **2**. Its ^1H NMR, ^{19}F NMR, ^{13}C NMR, and FTIR spectra were also identical to those

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(19) A diamine, *p*-xylylenediamine, was also allowed to react with **2** in order to make a dumbbell-like molecule. A solution of **2** and *p*-xylylenediamine in toluene was stirred at 25 °C for 24 h. The resulting mixture was centrifuged and the solid washed with toluene followed by hexanes to give a brown solid in 28% yield. However, the solid was not soluble in any organic solvent.

(20) Smith, P. A. S. In *Azides and Nitrenes Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press Inc.: New York, 1984; pp 95–204.

(21) Another thermal reaction was performed in which a solution of C_{60} and **1** in chlorobenzene was refluxed at 132 °C for 16 h. TLC of the solution with 10:1 toluene–ethyl acetate showed two spots with R_f values of 0.56 and 0.61 in addition to that of C_{60}. The spot with R_f 0.56 corresponded to **2**. Column chromatography of the concentrated mixture gave first C_{60} and then a difficultly separable mixture of **2** and a new C_{60} derivative (**5**) in 25% yield (48% based on recovered C_{60}). The ^1H NMR spectrum of the mixture showed a slightly downfield singlet for **5** at δ 3.034 as compared to that of **2** (δ 2.954). The FAB-MS spectrum of the mixture contained peaks at *m/e* 1329–1331 which resulted from the addition of 2 equiv of **1** with C_{60}, indicating that **5** is a bisadduct of **1** to C_{60}.

of **2** even though all the expected peaks were not observed in the ^{13}C NMR spectrum due to its low solubility in $CDCl_3$ (see supplementary material). The thermal reaction between C_{60} and **1** likely proceeds via the addition of the azide to a 6,6-double bond in C_{60} to give the corresponding triazoline.[20] The triazoline may then spontaneously lose N_2 to give the aziridine **2**. The intermediate triazoline was not observed. Only starting materials and the product were present throughout the reaction as indicated by analytical TLC.

The photochemical and thermal functionalization of C_{60} herein described allows ready access to a variety of well-defined C_{60} derivatives which may find application in such a diverse area as biological studies[22] and as building blocks leading to well-defined fullerene-based materials for the construction of microelectronic devices.[23]

Experimental Section

General Considerations. ^1H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were recorded at 75 MHz. ^{19}F NMR spectra were recorded at 338.733 MHz with the chemical shifts reported in δ units externally referenced to trifluoromethylbenzene as δ 0. Photolysis was carried out in a Rayonet photoreactor with 300 nm lamps (400 W) under ventilation. C_{60} was used as received from MER Corporation, Tucson, AZ. L-Glutamic acid diethyl ester hydrochloride and benzylamine hydrochloride were used as received from Aldrich. Hexanes was distilled over Na. Ethyl acetate was distilled over CaH_2. Chlorobenzene was distilled over P_2O_5. Toluene was distilled over Na.

Photolysis of C_{60} and 1 To Give 2. To a quartz vessel containing a purple solution of C_{60} (156 mg, 0.22 mmol) in chlorobenzene (70 mL) was added *N*-succinimidyl 4-azido-2,3,5,6-tetrafluorobenzoate (**1**)[11a] (83 mg, 0.25 mmol). The solution was purged with Ar for 10 min and irradiated at 300 nm under stirring for 5 h. The NHS PFPA ester **1** was completely consumed over this time period as monitored by analytical TLC with 10:1 toluene–ethyl acetate as the developing solvent. The temperature in the reactor did not exceed 35 °C during the reaction. The brown solution obtained was concentrated and was purified by flash chromatography with 10:1 toluene–ethyl acetate as the eluting solvent to give first C_{60} (115 mg) and then **2** as a brown solid (23 mg, 10%, 39% yield based on recovered C_{60}). Further purification was carried out by dissolving **2** in toluene and adding the solution dropwise to hexanes. The mixture was centrifuged and the solid was washed with hexanes and dried under reduced pressure. The product showed a single spot on analytical TLC: ^1H NMR ($CDCl_3$) δ 2.953 (s); ^{19}F NMR ($CDCl_3$) δ −70.28 (m, 2 F), −85.78 (m, 2 F); FTIR (KBr) 2924, 2856, 1745, 1649, 1491, 1400 cm^{-1}; FAB-MS 1024–1027 (calcd for $C_{71}H_4N_2F_4O_4$ 1024.83), 720–723; UV–vis (hexanes) 214, 251, 314 nm.

Photolysis of 1 in Chlorobenzene. A solution of **1** (2.1 mg, 0.0064 mmol) in chlorobenzene (2.0 mL) was purged with Ar for 5 min and photolyzed at 300 nm for 70 min until **1** was completely consumed as indicated by analytical TLC using 10:1 toluene–ethyl acetate as the developing solvent. TLC of the resulting solution showed several spots with R_f < 0.15. Evaporation of the solvent afforded a light brown solid which was only partially soluble in $CDCl_3$: ^1H NMR ($CDCl_3$) δ 2.91 (br).

Reaction of 2 with L-Glutamic Acid Diethyl Ester To Give 3. A solution of L-glutamic acid diethyl ester hydrochloride (5.8 mg, 0.024 mmol) and Et_3N (8.0 μL, 0.057 mmol) in absolute EtOH (0.5 mL) was stirred at 25 °C for 1 h. A solution of **2** (23 mg, 0.022 mmol) in toluene (3.0 mL) was added to the solution above. After stirring at 25 °C for 40 h, the solution was concentrated and then purified by flash chromatography with 10:1 toluene–ethyl acetate as the eluting solvent to give **3** as a brown solid (16 mg, 63%). Further purification was carried out by precipitating **3** from a toluene solution with hexanes. The product showed a single spot on analytical TLC: ^1H NMR ($CDCl_3$) δ 6.97 (d, J = 7.2 Hz, 1 H), 4.87 (m, 1 H), 4.28 (q, J = 7.2 Hz, 2 H), 4.16 (q, J = 7.2 Hz, 2 H), 2.49 (m, 2 H), 2.38 (m, 1 H), 2.17 (m, 1 H), 1.34 (t, J = 7.2 Hz, 3 H), 1.28 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.72, 171.06, 157.89, 145.54, 145.46, 145.34, 145.26, 144.70, 144.40, 144.06, 143.99, 143.94, 143.26, 143.22, 142.87, 142.24, 142.17, 141.22, 140.46, 127.09, 110.62, 80.37, 62.10, 60.87, 52.60, 30.16, 27.22, 14.16, 14.14; ^{19}F NMR ($CDCl_3$) δ −75.51 (m, 2 F), −83.97 (m, 2 F); FTIR (KBr) 2927, 2854, 1734, 1656, 1491, 1402, 1107 cm^{-1}; FAB-MS 1112–1114 (calcd for $C_{76}H_{16}N_2F_4O_5$ 1112.98), 720–723; UV–vis (hexanes) 341, 312, 272, 266, 246, 229 nm.

Reaction of 2 with Benzylamine To Give 4. A solution of benzylamine hydrochloride (0.84 mg, 0.0058 mmol) and Et_3N (2.0 mL, 0.014 mmol) in absolute EtOH (1.0 mL) was stirred at 25 °C for 1 h. A solution of **2** (5.5 mg, 0.0053 mmol) in toluene (6.0 mL) was added to the above solution, and the resulting solution was stirred at 25 °C for 4.5 h. The brown solution obtained was concentrated and was purified by flash chromatography with 10:1 toluene–ethyl acetate as the eluting solvent to give **4** as a brown solid (4.5 mg, 84%), R_f = 0.69. Further purification of **4** was carried out by precipitating a toluene solution of **4** with hexanes. The product showed a single spot on analytical TLC: ^1H NMR ($CDCl_3$) δ 7.3–7.4 (br, 5 H), 6.37 (m, 1 H), 4.72 (d, J = 5.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 145.56, 145.47, 145.36, 145.28, 144.72, 144.41, 144.08, 144.02, 143.94, 143.27, 143.24, 142.89, 142.22, 142.18, 141.23, 140.44, 128.97, 128.00, 127.90, 77.20, 44.50; ^{19}F NMR ($CDCl_3$) δ −75.19 (m, 2 F), −83.55 (m, 2 F); FTIR (KBr) 2927, 2855, 1651, 1485, 1403 cm^{-1}; FAB-MS 1017–1020 (calcd for $C_{74}H_8N_2F_4O$ 1016.90), 721–723; UV–vis (hexanes) 253, 312, 346 nm.

Thermal Reaction between C_{60} and 1. A solution of C_{60} (50 mg, 0.069 mmol) and **1** (25 mg, 0.075 mmol) in chlorobenzene (20 mL) was heated at 105–108 °C under N_2 for 5 days. The resulting dark brown mixture was concentrated and column chromatographed with 10:1 toluene–ethyl acetate to give first C_{60} (24 mg) and then **2** as a brown solid (17 mg, 23%, 45% yield based on recovered C_{60}). The product showed a single spot on analytical TLC: ^1H NMR ($CDCl_3$) δ 2.954 (s); FTIR (KBr) 2921, 2853, 1743, 1649, 1490, 1402 cm^{-1}; FAB-MS 1025–1027 (calcd for $C_{71}H_4N_2F_4O_4$ 1024.83), 720–723.

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Supplementary Material Available: ^{19}F NMR and FAB-MS spectra of **2**, UV–vis spectra of C_{60}, **2**, **3** and **4**, and ^{13}C NMR spectra of **2** and the product derived from the thermal reaction between C_{60} and **1** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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