J|A|C|S
A R T I C L E S

Preparation and Photophysical Studies of a Fluorous Phase-Soluble Fullerene Derivative

Stephen R. Wilson,*,[†] Michael E. Yurchenko,[†] David I. Schuster,[†]
Eduard N. Yurchenko,[‡] Olga Sokolova,[†] Silvia E. Braslavsky,[§] and Gudrun Klihm[§]

*Contribution from the Department of Chemistry, New York University,
New York, New York 10003, Perlucid Corporation, Nesconset, New York 11767, and
Max-Planck-Institut für Strahlenchemie, Mülheim, Germany*

Abstract: We report the first synthesis of a well-characterized "Teflon ponytail" fullerene adduct (**3**) via the Hirsch–Bingel reaction with a malonate bearing two perfluorinated alkyl chains. This C_3 tris-adduct shows excellent solubility in perfluorinated solvents, such as FC-72 and FC-75. Compound **3** was found to be an efficient sensitizer for singlet oxygen formation in fluorous media, which has potential in biphasic systems and in photobiology.

Introduction

In recent years, there has been increasing interest concerning perfluorinated materials and the so-called "Fluorous Phase."[1] Because of their unique physical and chemical properties, perfluorinated materials are constantly finding new areas of application. The high solubilities of oxygen, carbon dioxide, and nitric oxide in perfluorocarbons and the excellent toxicological properties have prompted medical applications of such perfluorinated materials in the areas of blood substitutes, wound healing, eye surgery, liquid lung ventilation, and cosmetics (skin rehabilitation).[2–6]

The fact that fluorous solvents are not only immiscible with water, but also with most standard organic solvents at ambient temperatures, brings about yet another useful application—a second organic phase for synthetic and catalytic chemistry.[7,8] In these types of applications, liquid–liquid biphase systems are used with the fluorous phase, for the purpose of facile separation of fluorous soluble reactants from purely organic-soluble products by simple extraction.[1,7,8]

Fullerenes are known to be excellent photosensitizers for singlet molecular oxygen generation[9] and have been a target of extensive research for possible applications in photodynamic

therapy (PDT).[10a–c] Given that perfluorinated solvents show the highest oxygen solubility[11] and longest lifetime of singlet molecular oxygen[12,13] among known solvents, the sensitizing properties of fluorous fullerenes in perfluorinated solvents in principle should be better for PDT and related applications.[14] While there has been some work on perfluorocarbon-soluble porphyrin sensitizers,[15] one attempt to prepare a perfluorocarbon-soluble fullerene sensitizer was not successful.[16]

Results and Discussion

We report herein the synthesis and characterization of the first "Teflon ponytail"[17] C_{60} derivative **3** that is soluble in perfluorocarbon solvents (eq 1).
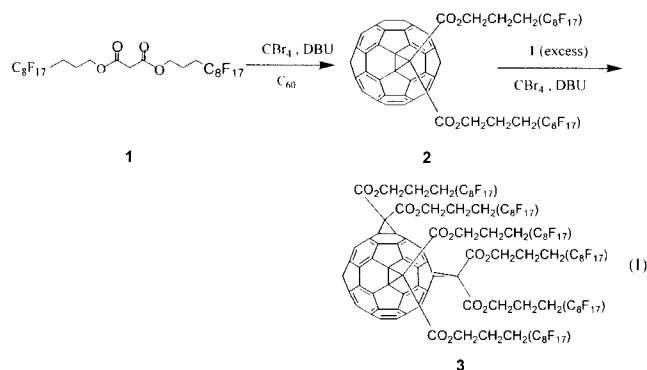
Our synthetic strategy employed common fullerene chemistry, namely, the Hirsch-Bingel reaction, which has been well-studied

[†] New York University.

[‡] Perlucid Corporation.

[§] Max-Planck-Institut für Strahlenchemie.

(1) Horvath, I. T. *Acc. Chem. Res.* **1998**, *31*, 641–650.

(2) Nucci, M. L.; Abuchowski, A. *Sci. Am.* **1998**, 61–65.

(3) Whitney, J. D. *Heart Lung* **1989**, *18*, 466–471.

(4) Paris, C. L. *Retina* **1991**, *11*, 301–4.

(5) (a) Shaffer, T. H. *Artif. Cells, Blood Substitutes, Immobilization Biotechnol.* **1994**, *22*, 315–26. (b) Cox C. A. *Neonatal Network* **1996**, *15*, 31–43.

(6) Lowe, K. C. *Artif. Cells, Blood Substitutes, Immobilization Biotechnol.* **2000**, *28*, 25–38.

(7) Studer, A.; Hadida, S.; Ferrito, R.; Kim, S.-Y.; Jeger, P.; Wipf, P.; Curran, D. P. *Science* **1997**, *275*, 823–826.

(8) Horvath, I. T.; Rabai, J. *Science* **1994**, *266*, 72–75.

(9) (a) Arbogast, J. W.; Darmanyan, A. P.; Foote C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11–12. (b) Anderson, J. L.; An, Y.-Z.; Rubin, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1994**, *116*, 9763–9764.
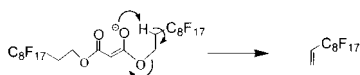
(10) (a) Tabata, Y.; Murakami, Y.; Ikada, Y. *Jpn. J. Cancer Res.* **1997**, *88*, 1108–1116. (b) Biological Applications of Fullerenes: A Review. Jensen, A. W.; Wilson, S. R.; Schuster, D. I. *Bioorg. Med. Chem.* **1996**, *4*, 767–779. (c) Wilson, S. R. Biological Aspects of Fullerenes. In *Fullerenes: Chemistry, Physics, and Technology*; Kadish, K., Ruoff, R., Eds.; John Wiley & Sons: New York, 2000.

and broadly utilized for fullerene derivatization.[18] Our fluorous malonate reagent for introducing fluoroalkyl chains onto C_{60} contains a three-carbon spacer[19] to insulate the electron-withdrawing effect of the fluoroalkyl chain. The compound can be prepared from commercially available 3-perfluorooctylpropyl alcohol, which was reacted with malonyl dichloride to yield malonate **1** in 68% yield. Spectral and analytical data for **1** are in good accordance with results for similar $CF_3(CF_2)_n$-derivatives.

The Hirsch−Bingel reaction was carried out on the mixture of malonate **1**, CBr_4, DBU, and C_{60} in toluene to yield monoadduct **2** in 35% yield. Compound **2** was fully characterized as a C_{60} monoadduct by ^{1}H NMR, ^{19}F NMR, MALDI, IR, UV−vis, and elemental analysis. The compound showed good solubility in Freon 113, but virtually no solubility in fully fluorinated solvents such as FC-72 (a mixture of perfluorohexanes) and FC-75 (a mixture of perfluorooctanes).[20] Because the insolubility of solid materials (crystals) sometimes has to do with poor wetting by the organic solvent under study, we decided to investigate the partitioning coefficient of **2** between toluene and FC-75. A partitioning experiment showed a fluorous/organic partition coefficient $\rho = 0.1$, indicating that compound **2** prefers the organic (toluene) rather than fluorous (FC-75) layer by about 10 to 1. This experiment indicates that for a fullerene derivative to be completely soluble in a fluorous phase, it is necessary to introduce multiple fluoroalkyl groups, consistent with our previously reported study.[21]

Hirsch reported that multiple malonate additions to C_{60} leads to the formation of two major tris-adducts with C_3 (orange-red color) and D_3 (dark-red color) symmetry. In the former, all malonate addends on the fullerene ball are positioned in an equatorial manner relative to each other.[22,23] Thus, the reaction of excess malonate **1**, CBr_4, DBU, and C_{60} was carried out. Monitoring the reaction by TLC revealed the optimal conditions for the formation of the orange-red C_3 tris-adduct **3**. This adduct

Figure 1. Absorption spectra of C_3 tris-adduct **3** (A) and perinaphthenone[23] (reference, B), both in *n*-perfluorohexane.

could be isolated in 14% yield from the reaction mixture using silica gel preparative TLC with a mixed-elution solvent [Freon 113 (1,1,2-trichlorotrifluoroethane) (160 mL): ethyl acetate (1 mL): perfluorohexane (2 mL)]. Unlike our earlier report on fluorous phase-soluble multiple Diels−Alder adducts of C_{60},[21] we did not observe any oxidized side products (fullerene oxides), according to mass spectra. As in the case of **1** and **2**, elemental analysis and MALDI mass spectra characterized the orange-red product **3** as a fullerene tris-adduct of **1**. The appearance in the ^{1}H NMR of two signals at $\delta = 4.43$ (distorted triplet, 6H; CH_2) and 4.35 (triplet, 6H; CH_2) are consistent with the C_3 symmetry of **3**.[22] Insulation of the electron density of the fluorous ponytails from C_{60} is important, for it allows the characteristic properties of the fullerene ball, such as sensitization of singlet oxygen, to remain intact. This insulation is evident from the ^{19}F NMR of compound **3**, which has J_{FH} and J_{FF} coupling values similar to compounds **1** and **2**.

The C_3 symmetric methanofullerene compound **3** contains six Teflon ponytails directed toward one side of the fullerene ball and thus might be expected to self-organize strongly at a fluorous-phase interface. For example, the compound readily stains a Teflon-coated stir-bar! Fluorous compound **3** is very soluble in perfluorinated solvents, FC-72 or FC-75,[20] and is much less soluble in more common organic solvents. A partitioning experiment between fluorous phase (FC-75) and organic phase (toluene) yielded a partition coefficient for **3** of $\rho = 0.94$ in favor of the fluorous layer (in complete contrast to the monoadduct above).

[1]O_2 Quantum Yields and Lifetimes. Having in hand a series of related fullerene derivatives, both soluble and insoluble in fluorous phases, we were able to compare the ability of these materials to sensitize singlet molecular oxygen generation in both fluorous and organic solvents. The quantum yield for singlet molecular oxygen $[O_2(^1\Delta_g)]$ production by each compound studied was measured in each experiment against a standard (perinaphthenone) in three solvents. Solutions of the compound to be examined and perinaphthenone at concentrations corresponding to a common absorbance ($A = 0.2$) at the excitation wavelength (355 nm) were prepared (Figure 1). The results are listed in Table 1.

The very long $O_2(^1\Delta_g)$ lifetime (τ_Δ) of 7 ms, measured in perfluorohexane, is still somewhat shorter than the previously

(11) (a) Linke W. F. *Solubilities*; American Chemical Society: Washington, DC, 1965; pp 1236. (b) Yamanouchi, K.; Heldebrant, C. *CHEMTECH* **1992**, *6*, 354−359.
(12) Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 663−1021.
(13) Schmidt, R.; Afshari, E. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *88*, 1971−1976.
(14) Fuchs, J.; Thiele, J. *Free Radical Biol. Med.* **1998** *24*, 835−847.
(15) DiMagno, S. G.; Dussault, P. H.; Schultz, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 5312−5313.
(16) Nagashima, H.; Hosoda, K.; Abe, T.; Iwamatsu, S.; Sonoda, T. *Chem. Lett.* **1999**, 469−470.
(17) Gladysz, J. A. *Science* **1994**, *266*, 55−56.
(18) Wilson, S. R.; Schuster, D. I.; Nuber, B.; Meier, M. S.; Maggnini, M.; Prato, M.; Taylor, R. Organic Chemistry of Fullerenes. In *Fullerenes: Chemistry, Physics, and Technology;* Kadish, K., Ruoff, R., Eds.; John Wiley & Sons: New York, 2000; pp 91−176.
(19) Curran[7] used an ethylene (two-carbon) spacer to insulate the reactive site of fluorous reagents from the electron-withdrawing effect of the fluoroalkyl chain. This strategy failed in our experiment. When subjected to the conditions of the Hirsch−Bingel reaction, the fluorous malonate with a two-carbon-insulating group underwent a fragmentaton reaction as shown. For this reason, we used a three-carbon insulator.

C_8F_{17} ⟶ C_8F_{17}

(20) See 3M website for perfluorocarbon solvents: http://www.3m.com.
(21) Wilson, S. R.; Yurchenko, M. E.; Schuster, D. I, Khong, A.; Saunders: M. *J. Org. Chem.* **2000**, *65*, 2619−2623.
(22) (a) Hirsch, A.; Lamparth, I.; Karfunkel, H. R. *Angew. Chem.* **1994**, *106*, 453−455. (b) Hirsch, A.; Lamparth, I.; Grosser, T. *J. Am. Chem. Soc.* **1994**, *116*, 9385−9386.
(23) (a) Oliveros, E.; Murasecco, P. S.; Saghafi, T. A.; Braun, A. M.; Hansen, H. J. *Helv. Chim. Acta* **1991**, *74*, 79−90. (b) Oliveros, E.; Bossmann, S. H.; Nonell, S.; Marti, C.; Heit, G.; Tröscher, G.; Neuner, A.; Martinez, C.; Braun, A. M. *New J. Chem.* **1999**, *23*, 85−94.
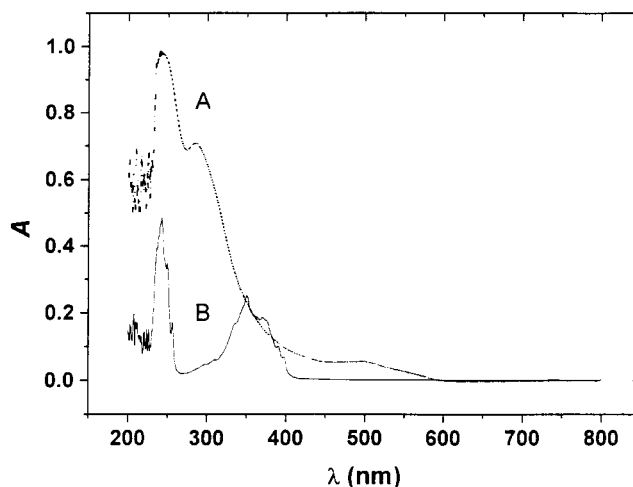
Table 1. Photophysical Data for Fullerene Derivatives, Including Quantum Yield of $O_2(^1\Delta_g)$ Production, Φ_Δ

substrate	solvent	$^1O_2$ lifetime μs	quantum yield (Φ_Δ)
2 (mono-R_F)[a]	benzene	24[b]	0.83
	toluene	24[b]	0.85
	perfluorohexane	−	not soluble[c]
3 (C_3 tris-R_F)[a]	benzene	24[b]	0.39
	toluene	24[b]	0.40
	perfluorohexane	7000 (this work)[d]	0.45[d]
4 (mono-alkyl)	benzene	24[b]	0.91
	toluene	24[b]	0.90
	perfluorohexane	−	not soluble
5 (C_3 tris-alkyl)	benzene	24[b]	0.42
	toluene	24[b]	0.43
	perfluorohexane	−	not soluble

[a] R_F = Teflon ponytail. [b] $O_2(^1\Delta_g)$ lifetime data taken from Wilkinson, et al.[12] [c] While the toluene/FC-75 partition coefficient of compound **2** is 0.1, suggesting some fluorous solubility, the fluorous phase in the partitioning experiment contains ~10% toluene. Compound **2** is not soluble in pure FC-75. [d] The singlet oxygen lifetime in perfluorohexane was reported as between 68 and 96 ms.[12,13]
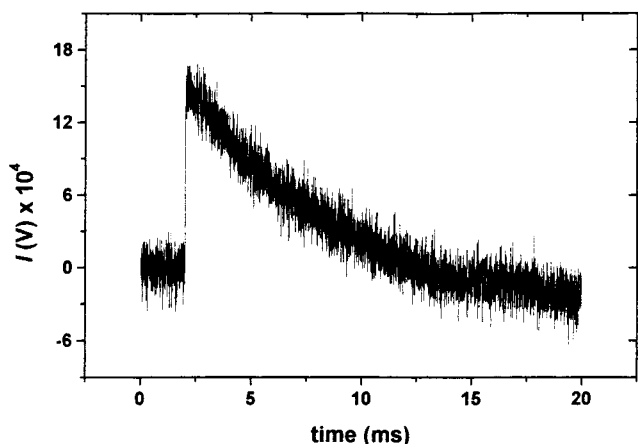

Figure 2. $O_2(^1\Delta_g)$ decay upon excitation of a *n*-perfluorohexane solution of C_3 tris-fluorous adduct **3** (A_{355} = 0.2) with laser pulses (ca. 8 ns) at 355 nm. Average of 20 shots. Detector: liquid-N$_2$-cooled Ge-diode. $O_2(^1\Delta_g)$ lifetime = τ_Δ = 7 ms, identical for the reference and for the sample solutions at all laser energies employed (see Figures 3 and 4).

reported value in the same solvent, possibly due to the presence of water.[12,13] The lifetime τ_Δ was the same for the reference compound and for the sample solutions. This, and the fact that O_2-($^1\Delta_g$) decay is monoexponential (Figure 2), indicates that there are no reactions occurring between the photosensitizers investigated (data not shown for compounds **2**, **4**, and **5**) and O_2-($^1\Delta_g$). The values of the quantum yield Φ_Δ were the same for **2**, **4**, and **5** in both benzene and toluene, while Φ_Δ for C_3 fluoroadduct **3** was slightly higher in the perfluorinated solvent than in benzene or toluene (Figures 3 and 4A ,B). The origin of the lower Φ_Δ values for compounds **3** and **5** remains to be explained, but it is tempting to speculate that the ca. 50% decrease with respect to compounds **1** and **4** is due to a decreased accessibility of O_2 to the crowded fullerenes **3** and **5**. Independent measurements of the triplet yields by flash photolysis should help to clarify this point.

Conclusions

The perfluoroalkylated fullerene **3** is a good sensitizer for generation of $O_2(^1\Delta_g)$ in both fluorous and nonfluorous solvent media. Compound **3** was found to be stable toward oxidation, as there was no evidence of reaction of **3** with $O_2(^1\Delta_g)$. The

4   **5**   **Perinaphthenone**
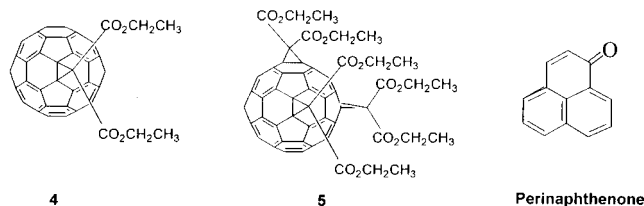
value of τ_Δ in perfluorohexane on sensitization by **3** was extremely long (7 ms), about 300 times greater than in benzene and toluene. This value is also ~2000 times larger than τ_Δ measured in water, ca. 4 μs.[12]

Because of the high solubility of oxygen in perfluorocarbon media, investigations of fluorous materials are of intense current interest as blood substitutes[5,14,24] and perfluorocarbon-based materials are currently in clinical development. For example, a perfluorocarbon emulsion called Oxycyte is being investigated for several therapeutic applications.[25] Inasmuch as the lifetime of $O_2(^1\Delta_g)$, one of the major "killing species" in photodynamic therapy (PDT), is so much longer in fluorous media than in water, fullerene sensitizers such as **3** could potentially provide significant PDT activity when used in conjunction with fluorous artificial blood as a delivery medium.

A potential synthetic application of our fluorous-soluble fullerene **3** could be as a photosensitizer for biphasic singlet oxygenation reactions, where the photosensitizer could localize in a separate fluorous phase from that containing the substrate being oxidized.[15] In a similar manner, solid-phase bound photosensitizers such as polystyrene-Rose Bengal[26] are widely used, wherein the sensitizer is immobilized in a separate solid phase to facilitate product separation.

Experimental Section

General Procedures. All reagents and solvents were purchased from commercial sources and used as received. ^1H NMR spectra were obtained on a Varian Gemini 200 MHz spectrometer, ^{19}F NMR (operating at 376.5 MHz) and ^{13}C NMR (operating at 110.61 MHz) were recorded at Brookhaven National Laboratory on a Bruker DRX-400 spectrometer. All MALDI data were obtained at the NIH Mass Spectrometry Facility at Michigan State University in East Lansing, MI, on a PerSeptive Biosystems (Framingham, MA) Voyager Elite delayed-extraction time-of-flight mass spectrometer equipped with a nitrogen laser (337 nm, 3 s pulse). IR spectra were recorded as KBr pellets on a Matteson Instruments FTIR Galaxy System.

Preparation of Malonate 1. A methylene chloride solution of 10.0 g (21 mmol) of 3-(perfluorooctyl)-propanol (Aldrich) was reacted with freshly distilled malonyl dichloride (1.0 mL, 10 mmol) and excess of 4-(dimethylamino)pyridine under nitrogen. The mixture was stirred overnight at room temperature, then washed with water, extracted with ether, and the ether fraction dried over anhydrous sodium sulfate. Evaporation of the ether, vacuum-drying, and crystallization of the residual material from 95% ethanol, produced 6.8 g (6.9 mmol) of crystals (mp = 36°) in 68% yield. The crystals were often slightly colored (violet, yellow, green) but could be decolorized by treatment with activated charcoal. ^1H NMR (200 MHz, CDCl$_3$) (δ): 4.26 (4H, t, J_{HH} = 6.4 Hz), 3.44 (2H,s), 2.06 (4H,m), 1.98 (4H,m, J = 4.9 Hz); ^{13}C NMR (CDCl$_3$) (δ): 166.0, 120−115 (indistinguishable cluster of peaks due to CF$_2$), 64.4, 41.8, 28.3, 20.3; ^{19}F NMR (CDCl$_3$) (δ):

(24) Sandford, G. *Philos. Trans. R. Soc. London, Ser. A* **2000** *358,* 455−471.
(25) (a) *Synthetic Blood Incorporated* (http://www.sybd.com). (b) Wang. L. *Science News* **2001**, *159* 206−207.
(26) (a) Neckers, D. C. *CHEMTECH* **1978**, 17, 269. (b) Blossey. E. C.; Neckers, D. C. *Benchmarks in Photochemistry*; Bowden, Hutchinson, and Ross: Stroudsburg, PA.
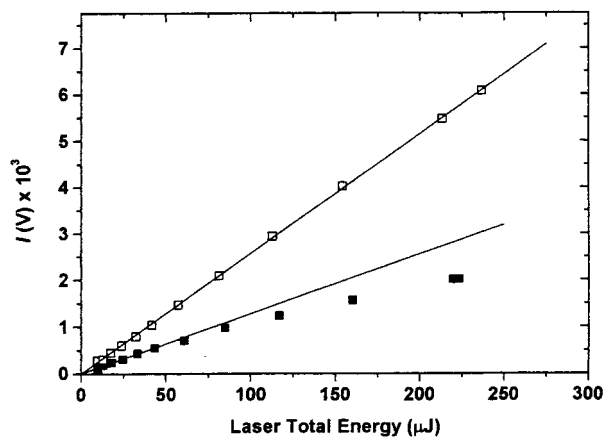
Figure 3. Zero-time amplitude of the $O_2(^1\Delta_g)$ decay vs the laser total energy per pulse, for perinaphthenone (□) and C_3 tris-adduct **3** (■) in *n*-perfluorohexane.

−127.10 (CF$_2$CF$_3$, 2F, J_{FF} = 12.4 Hz), −124.41, −123.71, −122.91, − 122.71 (CF$_2$)$_5$, −115.38 (CH$_2$CF$_2$, 2F, J_{FH} = 15.8 Hz), −81.79 (CF$_3$, J_{FF} = 9.8 Hz); MALDI (*m/z*): 1022.34 (M − 1); FT-IR (cm^{-1}): 2960−2890 (m),1757 (m), 1727 (m), 1245−1204 (vs), 1146 (vs), 1033 (w), 705 (w), 660 (w), 559−530 (w) Calcd for C$_{35}$F$_{34}$O$_4$H$_{14}$: C, 29.31; H, 1.37; F, 63.06. Found: C, 29.34; H, 1.61; F, 61.94.

Preparation of Monoadduct 2. A solution of 100.0 mg (0.14 mmol) of C$_{60}$ in 60 mL of toluene was prepared, to which 212.6 mg (0.21 mmol) of malonate **1**, 68.9 mg (0.21 mmol) of CBr$_4$, and excess DBU were added. The mixture was stirred at room temperature for 2 h and monitored by TLC. Upon completion, the reaction was quenched with water and monoadduct **2** was separated from reaction mixture by flash chromatography using 1:1 toluene:hexane as eluent. Compound **2** was isolated in 35% yield as a brown solid (85.4 mg, 0.05 mmol). ^{1}H NMR (200 MHz, CDCl$_3$/Freon 113) (δ): 4.6 (4H, t, J_{HH} = 6.0 Hz), 2.28−1.36 (8H, m); ^{19}F NMR (CDCl$_3$) (δ): −127.13(J_{FF} = 12.5 Hz), −124.37, −123.74, −122.93, − 122.71, −115.38 (J_{FH} = 15.9 Hz), −81.83 (J_{FF} = 9.6 Hz); MALDI (*m/z*): 1741.8 (M − 1); FT-IR (cm^{-1}): 2953−2920 (m), 1751 (m), 1730 (m), 1457 (w), 1262−1203 (s), 1150 (s), 1109−1027 (m), 799 (m), 705 (w), 657 (m), 559 (w), 529 (m). The UV−vis spectrum in toluene showed the following absorption maxima 376 nm, 428 nm (characteristic of fullerene monoadducts), 480 nm. Calcd for C$_{85}$F$_{34}$O$_4$H$_{12}$: C, 58.57; H, 0.70; F, 37.05. Found: C, 57.24; H, 1.24; F, 32.53.

Preparation of C_3 Tris-adduct 3. A solution of 130.0 mg of C$_{60}$ was prepared in 100 mL of toluene. To this solution, 3.3 equiv of malonate **1** (552 mg), 3.3 equiv of CBr$_4$ (180 mg), and excess DBU (6.6 equiv) in a Freon 113−toluene mixture was added in one portion. The mixture was stirred for 45 min at room temperature, after which an additional portion of 1.1 equiv of malonate **1**, 1.1 equiv of CBr$_4$, and 2.2 equiv of DBU was added in 10 mL of Freon 113. The reaction mixture was stirred for another 45 min and then an additional portion of reagents was added so that the total number of equivalents of malonate **1** reached 5.5. The reaction was carefully monitored by TLC during the process to maximize formation of C_3 tris adducts. The reaction mixture was allowed to stir for an additional 1 h and was then quenched with water. The mixture of the tris-adducts (principally the major C_3 isomer and a second compound, presumed to be the D_3 isomer) was separated on preparative silica gel plates employing a Freon 113 (160 mL):ethyl acetate (1 mL):perfluorohexane (2 mL) eluent mixture. Several separations on high-resolution silica gel plates using the same eluting mixture were required to isolate the C_3 compound **3** in pure form as a bright orange-red solid (30 mg, 14% overall yield.) ^{1}H NMR spectra were used as criteria of purity. The resulting material was found to be very soluble in perfluorinated solvents. ^{1}H NMR (400 MHz, CDCl$_3$) (δ): 4.43 (dist. t, 6H), 4.35 (t, 6H, J = 6.0 Hz), 2.16 (m, 12H), 2.06 (m, 12H). The ^{1}H NMR spectrum (residual Hs on the spacer
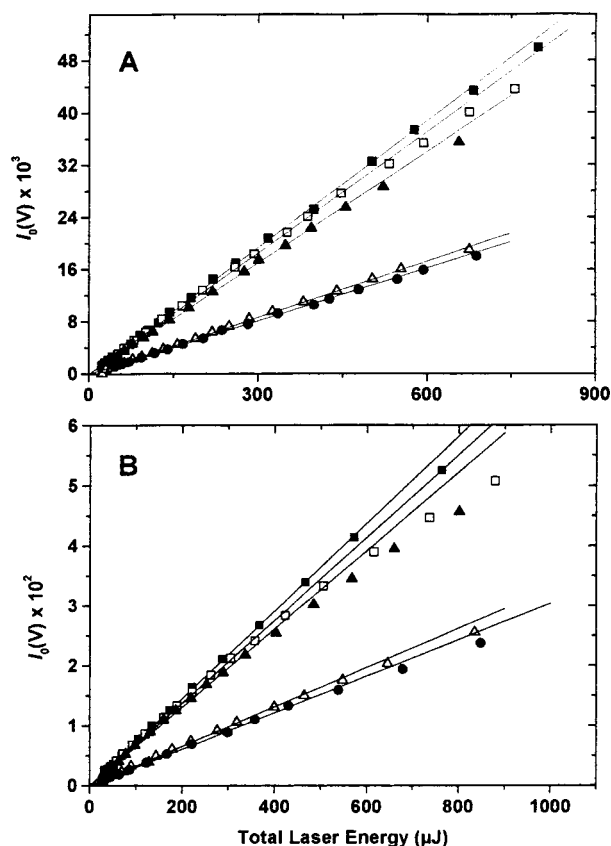

Figure 4. (A) Zero-time amplitude of the $O_2(^1\Delta_g)$ decay vs the laser total energy per pulse, for perinaphthenone (reference, full squares), and four fullerene compounds, *mono*- and tris- fluorous adducts **2** (▲) and **3** (●), and mono- and tris-ethyl ester adducts **4** (□) and **5** (△) in benzene. (B) Zero-time amplitude of the $O_2(^1\Delta_g)$ decay vs the laser total energy per pulse, for perinaphthenone (reference, ■), and four fullerene compounds, mono- and tris-fluorous adducts **2** (▲) and **3** (●), and mono- and tris-ethyl ester adducts **4** (□) and **5** (△) in toluene.

portion of the Teflon ponytail) is in agreement with the splitting pattern for the C_3 tris-isomer (ethyl esters) reported by Hirsch et al.[22,23] ^{19}F NMR (CDCl$_3$) (δ): −127.18 (J_{FF} = 12.5 Hz), − 124.33, −123.79, −122.97, − 122.73, − 115.37 (J_{FH} = 15.9 Hz), − 81.89 (J_{FF} = 9.5 Hz); MALDI (*m/z*): 3782.1 (M$^+$ − 3). All attempts to obtain ^{13}C spectra failed due to the very low solubility of **3** in deuterated organic solvents. FT-IR (cm^{-1}): 2960−2851 (w), 1751 (m), 1457 (w), 1262 (s), 1206 (s), 1147 (m), 1114 (m), 1017 (w), 800 (m), 705 (w), 657 (m), 559 (w), 529 (w). FT-IR data reveals even less difference between symmetric and asymmetric vibrations of C=O groups (only one band at 1751 cm^{-1} is observed). UV−vis in CHCl$_3$ indicated the following absorption maxima: 252, 282, 300, 480, 524, 562 nm, which are all in agreement with UV−vis data reported by Hirsch et al. for the C_3 tris-adduct of diethyl malonate.[22,23] Calcd for C$_{135}$F$_{102}$O$_{12}$H$_{36}$: C, 42.78; H, 0.95; F, 51.19. Found: C, 42.38; H, 1.46; F, 49.19.

Solvent Partitioning Experiment. The experiment was conducted between two phases: toluene (organic) and FC-75 [FC-75 (perfluoro-octanes), were chosen for this particular experiment, because FC-75 is less miscible with organic solvents than FC-72]. Perfluorooctanes and toluene are not completely immiscible, and a small amount (<10%) of toluene still dissolves in FC-75 (according to UV−vis spectra). To obtain quantitative data on partitioning, all experiments were carried out in two solvent systems: FC-75 saturated with toluene and toluene saturated with FC-75. The absorbances at 428 nm for monoadduct **2** and 496 nm for C_3 tris-adduct **3**, were used for calculation of partition coefficients.

A solution of monoadduct **2** in toluene saturated with FC-75 was prepared (2.17 mg/mL) and the absorbance (*A*) was obtained. A 1 mL

portion of that solution was extracted with 1 mL of FC-75 saturated with toluene, and the layers were separated. The ratio of A for compound **2** in the organic layer before and after extraction provides the partition coefficient ($\rho = 0.1$).

A solution of C_3 tris-adduct **3** in FC-75 saturated with toluene was prepared (1.15 mg/mL). A 1 mL portion of that solution was extracted with 1 mL of toluene saturated with FC-75, and the layers were separated. The ratio of A of compound **3** in the fluorous layer before and after extraction provides the partition coefficient ($\rho = 0.94$).

Photophysical Experiments. $O_2(^1\Delta_g)$ decay in perfluorohexane solution at 1270 nm was measured upon excitation of a solution of C_{60} derivative 5 with laser pulses (average of 20 8-ns shots) at excitation wavelength 355 nm ($A_{355} = 0.2$) (Figure 2). The detector used was a liquid N_2-cooled Ge-diode (Northcoast EO817FP) with a time resolution of 200 ns. Similar data was collected for the perfluorohexane, benzene, and toluene solution of the reference (perinaphthenone). The ratio of the slopes of the zero-time extrapolated amplitude of the $O_2(^1\Delta_g)$ decay vs the total laser energy per pulse (Figures 3 and 4) (at low-energy density where linearity is observed) affords the ratio of quantum yields of $O_2(^1\Delta_g)$ production for the compounds studied and the standard. For example in the case of **3** ratio of slopes = 0.50 so that the ratio of quantum yields of $O_2(^1\Delta_g)$ production, $\Phi_\Delta(\mathbf{3})/\Phi_\Delta$perin = 0.50. With $\Phi_\Delta$perin = 0.95, $\Phi_\Delta(\mathbf{3})$ = 0.45 ± 0.05 (average of four series of measurements). Quantum yields for $O_2(^1\Delta_g)$ production by compounds **2**, **4**, and **5** in benzene and toluene were calculated in a similar fashion (see Figure 4, A and B, and Table 1).