

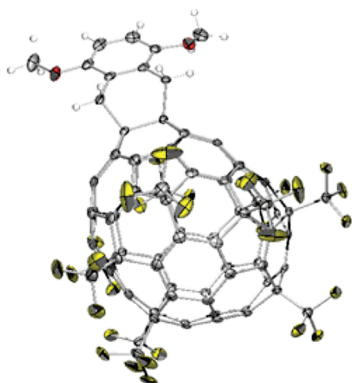
Efficient Regioselective [4 + 2] Cycloaddition of  
*o*-Quinodimethane to C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub>

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Received July 6, 2009



The Diels–Alder reaction of C<sub>1</sub>–C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub> and 3,6-dimethoxy-1,2-quinodimethane leads regioselectively to the formation of a new cycloadduct that has been fully characterized by spectroscopic and electrochemical methods as well as by X-ray diffraction.

Among fullerene derivatives with strong electron-withdrawing groups, perfluoroalkylfullerenes (PFAFs)<sup>1</sup> and perfluoromethanofullerenes<sup>2</sup> are notable for their remarkable

physicochemical properties and the stability of their radical anions in solution.<sup>1d,2,3</sup> These derivatives offer improved alternatives to bare fullerenes or more typical organofullerenes for the construction of high-performance donor–acceptor devices.<sup>4</sup> High-yield high-temperature syntheses of PFAFs with R<sub>f</sub>I reagents have been developed for C<sub>60</sub>, C<sub>70</sub>, and C<sub>74–90</sub>.<sup>1</sup> In many cases only a few relatively abundant and stable fullerene (R<sub>f</sub>)<sub>n</sub> isomers are formed for n ≤ 12. The most selective synthesis of a PFAF is the reaction of C<sub>70</sub> with CF<sub>3</sub>I, for which the C<sub>1</sub> isomer 1,4,10,19,25,41,49,60,66,69-C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub> (hereinafter denoted C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub>), was obtained in 89% yield.<sup>1b,5</sup>

Among the most useful reactions for the chemical modification of fullerenes are [4 + 2] cycloadditions.<sup>6</sup> A single Diels–Alder cycloaddition to C<sub>60</sub> produces a single isomer: the diene adds across a C<sub>60</sub> double bond (i.e., a 6:6 junction). However, there are several types of 6:6 junctions in C<sub>70</sub> (and in higher fullerenes) with similar reactivities,<sup>7</sup> and therefore such reactions with C<sub>70</sub> usually result in two or more regioisomers.<sup>8</sup>

Ten of the twelve pentagons in C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub> include a C(sp<sup>3</sup>) atom bearing a CF<sub>3</sub> group. The remaining two pentagons are connected by a unique, sterically unencumbered 6:6 junction, which should be the most reactive site for [4 + 2] cycloadditions. Therefore, C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub> could give rise to a family of regiospecific C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub>(cycloadduct) derivatives for a variety of optoelectronic applications. To test this possibility, dimethoxy *o*-quinodimethane **2** (3,6-DMQDM) was generated in the presence of C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub> by thermolysis of sultine **1**<sup>9</sup> at 80 °C in toluene (Scheme 1). As expected, reactive intermediate **2** was efficiently trapped by the dienophilic C33–C34 bond of C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub> (see the original numbering of C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub> in Figure 1).

Compound **3**, C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub>(3,6-DMQDM), was isolated from unreacted starting material and byproduct by single-step HPLC in 73% yield based on consumed C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub>. The purity of **3** was established based on <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR

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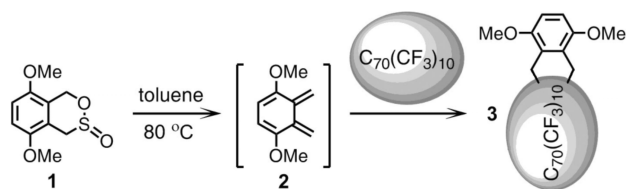
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SCHEME 1. Synthesis of **3** from Sultine **1** and  $C_{70}(CF_3)_{10}$ 

spectroscopy and MALDI-TOF-MS. The structure of cycloadduct **3** (Figure 1) was determined by X-ray diffraction (see the Experimental Section). The new six-membered ring is in a boat conformation and is not disordered despite the similar arrangement of  $CF_3$  groups on both sides of the molecule. The C33–C34 single-bond distance is 1.586(4) Å.

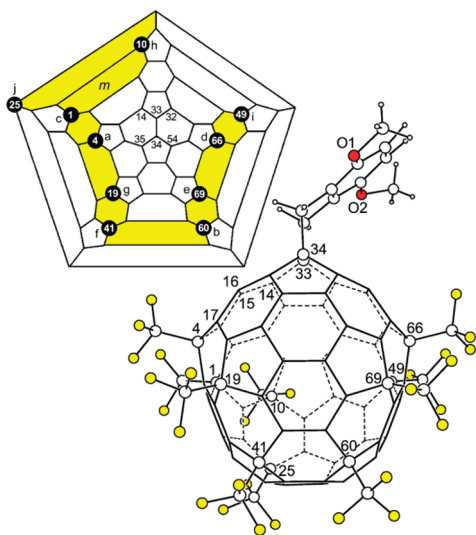


FIGURE 1. Schlegel diagram of  $C_{70}(CF_3)_{10}$  and the structure of **3**.

The C33–C34 double bond in  $C_{70}(CF_3)_{10}$ , at 1.386(3) Å,<sup>5</sup> is the shortest bond in that compound that has no connections to  $C(sp^3)$  vertexes. Thus, there are both steric and electronic reasons that such a high yield of regioisomer **3** is formed in the [4+2] reaction. This conclusion was also reached by Goryunkov et al. regarding the regioselective Bingel ([2+1] cyclopropanation) reaction of  $C_{70}(CF_3)_{10}$ .<sup>1c</sup> In their cycloadduct, the C33–C34 bond is also elongated (1.61(1) Å),<sup>1c</sup> but the lower precision of that structure precludes a more in-depth comparison of it and **3**. In the structure of  $C_{70}(4,5\text{-DMQDM})$ , the corresponding C33–C34 single-bond distance is 1.603(3) Å.<sup>8b</sup>

The  $^1H$  NMR spectrum of **3** is shown in Figure 2 and the  $^{19}F$  NMR  $\delta$  and through-space  $^{10}J_{FF}$  values of **3** and  $C_{70}(CF_3)_{10}$  are listed in Table 1. The methylene  $^1H$  resonances appear as distinct AB systems at 228 K:  $\delta_A$  3.58,  $\delta_B$  4.27,  $J_{AB}$  = 14.1 Hz;  $\delta_C$  3.65,  $\delta_D$  4.54,  $J_{CD}$  = 14.1 Hz. The signals coalesce at 298 K and become broad singlets at  $\delta$  ca. 4.1 and 4.0 at 323 K, indicating a dynamic process that we attribute to a boat-to-boat inversion of the six-membered ring containing C33 and C34, although only one boat conformation is observed in the solid state. The  $\Delta G^\ddagger$  value for this process,

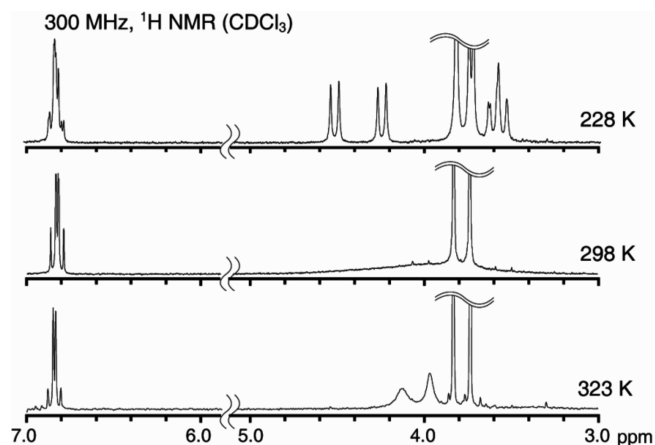


FIGURE 2. Variable-temperature  $^1H$  NMR spectra of **3**.

estimated from the coalescence temperature,<sup>11</sup> is 17.4(1) kcal mol<sup>-1</sup>. This value is higher than the 14.7(1) kcal mol<sup>-1</sup> boat-to-boat  $\Delta G^\ddagger$  value for  $C_{70}(4,5\text{-DMQDM})$ <sup>8c</sup> or the 14.6–16.6 kcal mol<sup>-1</sup>  $\Delta G^\ddagger$  values for comparable  $C_{60}$  cycloadducts.<sup>9</sup> Note that each boat conformation of **3** should give rise to a pair of AB quartets at 228 K, but the similarity of the two boat conformations renders them pairwise nearly isochronous (the only evidence of this is the two resonances assigned to  $\delta_C$ ).

The  $^{19}F$  NMR spectrum of **3** at 298 K (Figure 3) also exhibits evidence of the boat-to-boat interconversion. The C4 and C66  $CF_3$  groups are each positioned “underneath” the aromatic ring of the DMQDM moiety ca. 50% of the time, and when so positioned should have  $\delta$  values considerably deshielded relative to their chemical shifts when the aromatic ring is on the other side of the molecule. Their time averaged values are therefore expected to deviate the most from the  $\delta$  value for the corresponding  $CF_3$  group in  $C_{70}(CF_3)_{10}$ , and multiplets **a** and **d** do indeed show the largest chemical-shift deviation and are the most broadened multiplets (the 298 K spectrum is presumably in the near-fast-exchange region). Multiplets **g** and **i** in the spectrum of **3** are also obviously broadened relative to their counterparts in the spectrum of  $C_{70}(CF_3)_{10}$ ; they are due to the  $CF_3$  groups on C19 and C49, which are nearest neighbors to the C4 and C66  $CF_3$  groups and therefore are closer to the DMQDM aromatic ring than four other  $CF_3$  groups (however, it is not clear why multiplets **c** and **e** are not broadened similarly to **g** and **i**, since these are due to  $CF_3$  groups that are also nearest neighbors of the C4 and C66  $CF_3$  groups).

The  $^{13}C$  NMR spectrum of **3** (Figures S3–S6, Supporting Information) exhibits 125 signals, in harmony with its  $C_1$  symmetry. The DMQDM methylene peaks are at  $\delta$  34.3 and 34.2. The peaks at  $\delta$  61.8 and 61.1 are assigned to C33 and C34. The quartets between  $\delta$  62.7 and 57.8 are due to the ten cage  $C(sp^3)$  atoms bearing  $CF_3$  groups ( $^2J_{FC}$  = 31.6–34.5 Hz), and the quartets between  $\delta$  123.0 and 122.4 ( $^1J_{FC}$  = 285.4–279.8 Hz) are due to the ten  $CF_3$  C atoms.

The UV–vis spectrum of **3** shows specific absorption bands of the Diels–Alder adduct at 450, 481, and 513 nm

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TABLE 1.  $^{19}\text{F}$  NMR Data<sup>a</sup>

compd	$-\delta$ value for multiplets a–j/cage C atom to which the $\text{CF}_3$ group is attached/ $J_{\text{FF}}$ , Hz									
$\text{C}_{70}(\text{CF}_3)_{10}$ : <sup>b</sup> $-\delta$	59.2 as (a)	61.5 as (b)	62.1 as (c)	62.2 as (d)	62.4 as (e)	62.8 as (f)	63.4 as (g)	64.3 as (h)	67.6 q (i)	70.7 q (j)
cage C w/ $\text{CF}_3$	C4	C60	C1	C66	C69	C41	C19	C10	C49	C25
$J_{\text{FF}}$ , Hz	11, 16	13–14	14–15	15–16	13–14	13–14	11, 16	10, 14	15.9	10.3
<b>3</b> : $-\delta$	61.3 br s (a)	62.5 as (b)	63.1 as (c)	63.7 um (e)	63.9 as (f)	64.5 br s (d)	64.7 br s (g)	65.6 as (h)	–69.2 q (i)	71.8 q (j)
cage C w/ $\text{CF}_3$	C4	C60	C1	C69	C41	C66	C19	C10	C49	C25
$J_{\text{FF}}$ , Hz		13–14	14–15		13–14			10.0, 13.9	15.5	10.1

<sup>a</sup>All data are from this work, unless otherwise noted. See the Schlegel diagram in Figure 1 for the correspondence between multiplet letters a–j and the cage C atoms to which each  $\text{CF}_3$  group is attached. Benzene-*d*<sub>6</sub> solutions at 20 °C;  $\text{C}_6\text{F}_6$  int. std. ( $\delta$  –164.9). Abbreviations: q, quartet; as, apparent septet (i.e., quartet of quartets); br s, broad singlet; um, unresolved multiplet. Coupling constants are known to  $\pm 0.2$  Hz for terminal  $\text{CF}_3$  quartets and  $\pm 1$  Hz for apparent septets. <sup>b</sup>Data from ref 10, which also reported the 2D spectrum with which assignments a–j were made.

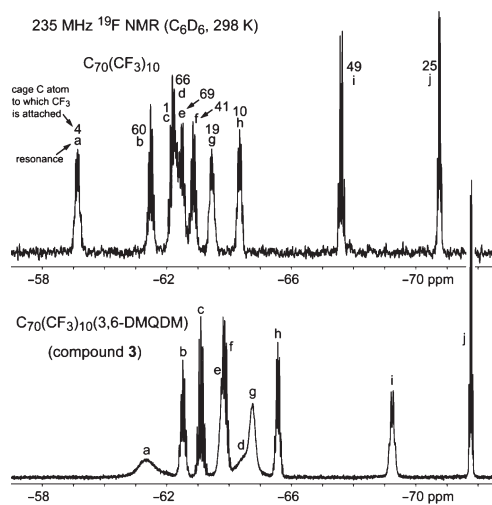


FIGURE 3. Room temperature  $^{19}\text{F}$  NMR spectra of  $\text{C}_{70}(\text{CF}_3)_{10}$  (top) and **3**.

(Figure S7, Supporting Information). The redox properties of **3** were examined by CV and differential pulse voltammetry (DPV) at 298 K (Table 2; Figure S8 in the Supporting Information). Compound **3** exhibited a total of 4 one-electron processes. Three of them are reductions of the PFAF moiety in **3** and are cathodically shifted by  $>250$  mV relative to the corresponding potentials for  $\text{C}_{70}(\text{CF}_3)_{10}$ , presumably because of the additional loss of a cage double bond in **3**. In addition, an oxidation wave was observed that has no counterpart in the electrochemistry of  $\text{C}_{70}(\text{CF}_3)_{10}$ .<sup>1b</sup> On this basis, it is assigned to the oxidation of the DMQDM moiety.

Much work has recently been done in improving organic solar cells.<sup>13</sup> One of the latest approaches is to use fullerene

TABLE 2. Redox Potentials of Compound **3** and  $\text{C}_{70}(\text{CF}_3)_{10}$ <sup>a</sup>

compd	$E_{\text{ox}}^1$	$E_{\text{red}}^1$	$E_{\text{red}}^2$	$E_{\text{red}}^3$
<b>3</b>	0.935	–1.214	–1.803	–2.291 <sup>b</sup>
$\text{C}_{70}(\text{CF}_3)_{10}$		–0.948	–1.532	–1.628

<sup>a</sup>Potentials are V vs.  $\text{Fe}(\text{Cp})^{+/0}$  and were obtained by DPV. Conditions: glassy carbon working electrode; platinum wire counter electrode;  $\text{Ag}/\text{AgNO}_3$  reference electrode; 0.1 M TBAP supporting electrolyte in THF; 50  $\text{mV s}^{-1}$  CV scan rate; 50 mV, DPV modulation amplitude; 25 mV, step potential; 5 mV, pulse width; 500 ms. <sup>b</sup>Irreversible.

derivatives with a higher energy LUMO relative to the LUMO energy of [6,6]-phenyl- $\text{C}_{61}$ -butyric acid methyl ester (PCBM) in order to minimize the donor  $\rightarrow$  acceptor electron-transfer energy loss in bulk heterojunction solar cells.<sup>14</sup> In this sense, the reduction potentials of  $\text{C}_{70}(\text{CF}_3)_{10}$  and its Diels–Alder derivative **3**—both of which are highly soluble in typical organic solvents such as toluene, carbon disulfide, chloroform, or dichloromethane—make them good candidates to test in photovoltaic assemblies and devices.

In summary, a Diels–Alder cycloadduct of  $\text{C}_{70}(\text{CF}_3)_{10}$  has been efficiently synthesized. Its structure was unambiguously elucidated by spectroscopy, electrochemistry, and X-ray crystallography. Fluorine-19 and variable-temperature  $^1\text{H}$  NMR spectra revealed the conformational mobility of the six-membered exohedral carbocycle. The use of sultines to further functionalize fullerene( $\text{CF}_3$ )<sub>n</sub> derivatives by [4 + 2] cycloadditions should be general in scope, and will be particularly useful for the preparation of thermally stable regioselective  $\text{C}_{70}(\text{CF}_3)_{10}$ (cycloadduct) derivatives for device applications.

## Experimental Section

Compound **1**<sup>9</sup> and  $\text{C}_{70}(\text{CF}_3)_{10}$ <sup>1b</sup> were prepared according to the previously reported synthetic procedure and showed identical spectroscopic properties to those reported therein.

**Synthesis of the Diels–Alder Adducts  $\text{C}_1$ – $\text{C}_{70}(\text{CF}_3)_{10}\text{C}_2\text{H}_4$ – $[\text{C}_6\text{H}_2(\text{MeO})_2]$  (**3**).** A solution of  $\text{C}_1$ – $\text{C}_{70}(\text{CF}_3)_{10}$  (20.0 mg,  $1.21 \times 10^{-5}$  mol) and sultine **1** (3.29 mg,  $1.44 \times 10^{-5}$  mol) in 25 mL of toluene was degassed by ultrasonicator under reduced pressure, followed by stirring and heating at 80 °C under argon atmosphere. After 1 h, 8.8 mg of the starting fullerene was consumed, and then the reaction mixture was separated by one-step HPLC

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separation (a Buckyprep column,  $\phi$  10 mm  $\times$  250 mm). Toluene/MeOH 3/1 (v/v) was used as the eluent.

**C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub>[C<sub>2</sub>H<sub>4</sub>C<sub>6</sub>H<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>] (3):** 73% yield (based on consumed starting material from HPLC analysis); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 323 K)  $\delta$  6.94 (d, 1H,  $J$  = 9.0 Hz), 6.90 (d, 1H,  $J$  = 9.0 Hz), 4.19 (br, 2H), 4.04 (br, 2H), 3.90 (s, 3H), 3.81 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  156.6, 156.5, 156.0, 155.2, 155.0, 153.9, 153.8, 153.1, 153.0, 152.3, 152.0, 152.0, 151.3, 150.8 (2C), 150.6, 150.5, 150.4, 150.0, 149.9, 149.8, 148.8, 148.6, 148.4, 148.0, 148.0, 147.6, 147.2, 146.6, 146.2, 146.0, 145.9, 145.6, 145.2, 144.7, 144.6, 144.5, 144.4, 144.2, 143.0 (2C), 142.7, 142.4, 141.8, 141.4, 141.3, 140.9, 138.6, 138.4, 138.3, 134.8, 132.4, 131.5, 130.7, 129.6, 129.4, 128.8, 128.2, 127.9, 127.7, 125.8, 125.6, 123.0 (q, 2C,  $J_{C-F}$  = 280.7 Hz), 122.9 (q, 2C,  $J_{C-F}$  = 285.4 Hz), 122.7 (q,  $J_{C-F}$  = 281.9 Hz), 122.7 (q,  $J_{C-F}$  = 281.3 Hz), 122.6 (q,  $J_{C-F}$  = 282.1 Hz), 122.4 (q,  $J_{C-F}$  = 279.8 Hz), 110.1 (2C), 62.7 (q,  $^2J_{C-F}$  = 34.5 Hz), 62.1 (q,  $^2J_{C-F}$  = 33.6 Hz), 61.8, 61.3 (q, 2C,  $^2J_{C-F}$  = 33.1 Hz), 61.1 (q, 2C,  $^2J_{C-F}$  = 32.4 Hz), 61.1, 60.4 (q, 2C,  $^2J_{C-F}$  = 34.0 Hz), 60.0 (q,  $^2J_{C-F}$  = 31.6 Hz), 57.8 (q,  $^2J_{C-F}$  = 33.7 Hz), 56.2, 56.2, 34.3, 34.2 ppm; UV-vis (CHCl<sub>3</sub>)  $\lambda_{max}$  450, 481, 513 nm; MALDI-TOF MS calcd for C<sub>90</sub>H<sub>12</sub>F<sub>30</sub>O<sub>2</sub> ([M]<sup>+</sup>) 1694.04, found 1694.09 *m/z*.

**Crystallographic Data.** Dark brown crystals of **3** were obtained by slow evaporation of a toluene solution at 253 K. X-ray diffraction data were collected on a Rigaku R-Axis RAPID equipped with an imaging plate area detector, using Mo K $\alpha$  radiation ( $6.10^\circ < \theta < 64.56^\circ$ ). For **3**·2(C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>): C<sub>104</sub>H<sub>28</sub>F<sub>30</sub>O<sub>2</sub>,  $M_w$  = 1879.26, orthorhombic, *Pbcn*,  $a$  = 17.8857(12) Å,  $b$  = 25.3005(12) Å,  $c$  = 31.4601(16) Å,  $V$  = 14236.2(14) Å<sup>3</sup>,  $Z$  = 8,  $D_{calc}$  = 1.754 Mg/m<sup>3</sup>,  $\mu$  = 0.159 mm<sup>-1</sup>,  $T$  = 90(2) K, crystal

size 0.40  $\times$  0.30  $\times$  0.14 mm<sup>3</sup>; 107 956 reflections (13 977 unique), 9 446 with  $I > 2\sigma(I)$ ;  $R(int)$  = 0.0929,  $R_1$  = 0.0553 [ $I > 2\sigma(I)$ ];  $wR_2$  = 0.1266 (all data); GOF (on  $F^2$ ) = 1.013; maximum residual electron density = 1.013 e Å<sup>-3</sup>; CCDC 724753.

**Acknowledgment.** This work has been supported by the MEC of Spain (CTQ2008-00795, Consolider-Ingenio 2010 CSD2007-0010, Nanociencia Molecular), Comunidad de Madrid (P-PPQ-000225-0505), the Russian Foundation for Basic Research (06-03033147-a), the U.S. NSF (Grant CHE-0707223), a Grant-in-Aid for Scientific Research on Innovation Areas (No. 20108001, "pi-Space"), a Grant-in-Aid for Scientific Research (A) (No. 20245006), The Next Generation Super Computing Project (Nanoscience Project), Nanotechnology Support Project, and a Grant-in-Aid for Scientific Research on Priority Area (Nos. 20036008 and 20038007) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. We also thank Dr. Beatriz Illescas for providing us with sultine **1** for initial investigations.

**Supporting Information Available:** General experimental methods, profiles of the reaction mixture and isolated **3**, MALDI-TOF mass, <sup>13</sup>C NMR and DEPT135 NMR spectrum of **3**, <sup>13</sup>C NMR Gauss fitting, UV-vis absorption spectra of **3** and C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub>, and cyclic voltammograms of **3** and C<sub>70</sub>(CF<sub>3</sub>)<sub>10</sub>. This material is available free of charge via the Internet at <http://pubs.acs.org>.