

Derivatized Fullerenes Bearing Multiple Electron Donors: Synthesis and Charge Transfer Properties

Huaping Li, Weijie Huang, Zhixin Guo, Radhakishan Guduru, and Ya-Ping Sun*

Department of Chemistry and Laboratory for Emerging Materials and Technology, Clemson University, Clemson, South Carolina 29634-0973

Received: December 16, 2004; In Final Form: March 16, 2005

A series of methano-C₆₀ adducts bearing up to six electron donating *N,N*-dimethylaniline units (denoted as **D** compounds), along with their analogues without the dimethylamino groups as references (**R** compounds), were synthesized. The redox properties of the **D** compounds in solutions were evaluated spectroscopically in reference to the **R** compounds. According to UV/vis absorption results, there are obviously ground-state intramolecular charge-transfer complexes in the **D** series, and the charge-transfer effects apparently become saturated with only two donor units in the molecule. The photoinduced intramolecular electron-transfer properties of the **D** compounds were investigated via fluorescence measurements. The emission from intramolecular exciplexes can be found only in the **D** molecule with two electron donor units. Throughout the **D** series, the fluorescence properties are highly sensitive to the solvent polarity, with the emission completely quenched for all of the molecules in a polar solvent like methylene chloride. Mechanistic implications of the results are discussed.

Introduction

Fullerenes are well-known as excellent electron acceptors.^{1–4} For intramolecular electron transfers and the generation of charge separated species, fullerene C₆₀ has been coupled with a variety of electron donors in the construction of redox dyads and triads.^{1–15} Among simple electron donor molecules that have often been paired with fullerenes are aromatic amines such as *N,N*-dimethylaniline (DMA) and *N,N*-diethylaniline (DEA).^{2,16–19} In fact, these electron donors were already popular in the early days of fullerene research for their formation of ground-state charge-transfer complexes with C₆₀ and C₇₀.^{16–18} More recently, DMA species have been incorporated into C₆₀-derived redox-active molecules for the investigation of strong intramolecular charge-transfer interactions.^{11–14} For example, Williams et al. synthesized redox dyads in which the electron donating DMA moiety is separated from the C₆₀ cage by rigid bridges of mostly σ -bonds.¹¹ Their spectroscopic results suggest that the electron transfer in these molecules is dependent on the bridge length (number of bonds in the bridge), which is due to changes in both through-bond and through-space electronic couplings.¹¹ Other examples involving DMA or analogue as electron donor included the redox dyads reported by Liu et al. and Ohno et al.^{12,13} In the former thiophene units were used as the bridge,¹² and in the latter there were ground-state intramolecular charge transfers according to the UV/vis absorption spectral results.¹³

An interesting and unique property of C₆₀ is its ability to accept up to 6 electrons.²⁰ C₆₀ is also a highly symmetric molecule, with the cage capable of accommodating mono and multiple additions in different patterns.²¹ Although the reduction of C₆₀ through electrochemically injecting multiple electrons has been demonstrated,^{20,22} the decoration of C₆₀ cage with multiple electron donors for the purpose of exploiting the unique redox property has been scarce.²³ On the other hand, the derivatization of C₆₀ cage through multiple additions has been well-established.²¹ In a preliminary account,²⁴ we reported the

synthesis of several methano-C₆₀ derivatives containing up to 6 DMA units as electron donors and some molecular spectroscopic results on their electron-transfer properties. We have since expanded the list of the C₆₀-derived redox molecules, and we have also synthesized structurally comparable methano-C₆₀ derivatives without the amino moieties to serve as references (Chart 1). Reported here are results from a more systematic evaluation of these C₆₀ derivatives containing a variable number of electron donating DMA units, along with their corresponding reference compounds, for an improved understanding of the intramolecular charge-transfer properties.

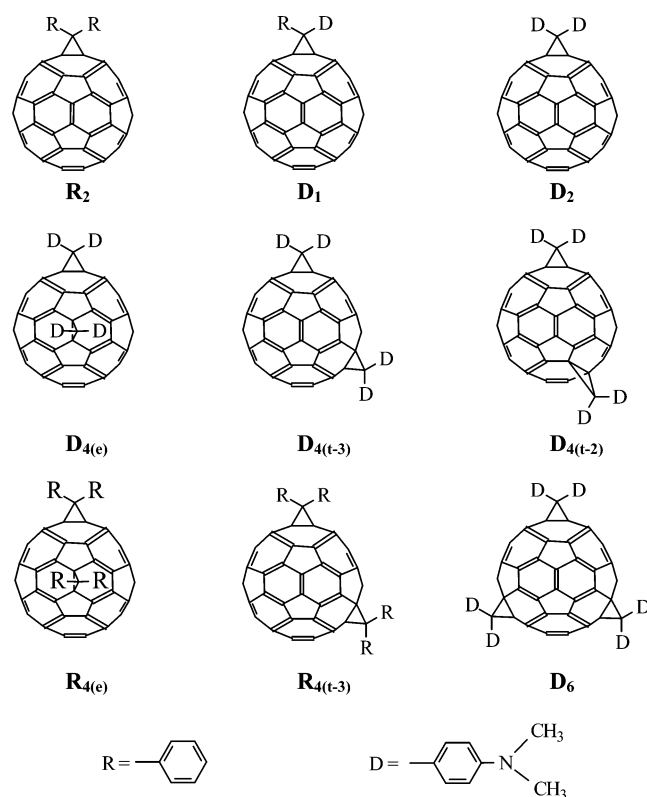
Experimental Section

Materials. Fullerene C₆₀ was purchased from the Southern Chemical Group (purity > 99.5%) and BuckyUSA (purity > 99%). 4,4'-(Dimethylamino)benzophenone (98%) was obtained from Avocado Research Chemicals, and benzophenone hydrozone (98+%) from Acros. Reagent grade solvents for column chromatography were distilled before use. Spectrophotometry grade solvents were used as received in absorption and emission measurements because no interference from impurity was observed in the applicable wavelength region according to spectroscopic measurements of the solvents. All other chemicals and solvents were used either as received or after simple purification. Deuterated NMR solvents and tetramethylsilane (TMS) were supplied by the Cambridge Isotope Laboratories.

Measurements. NMR spectra were obtained on Bruker AC-300 and JEOL Eclipse +500 NMR spectrometers. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS analyses were performed on a Bruker Proflex III instrument. The matrix materials included 3,5-dimethoxy-4-hydroxycinnamic acid, α -cyano-hydroxycinnamic acid, 2,5-dihydroxybenzoic acid, and pyrene.

Photochemical reactions were carried out in an Ace Glass ACE-7861-type immersion-well photochemical reactor. The

CHART 1



light source was a 450-W Hanovia medium-pressure mercury lamp. The cooling water circulation jacket served as a near-IR filter, and an additional inner jacket was added to allow a solution filter. The sample was bubbled with an inert gas during photoirradiation, which was coupled to a condenser to minimize any solvent loss.

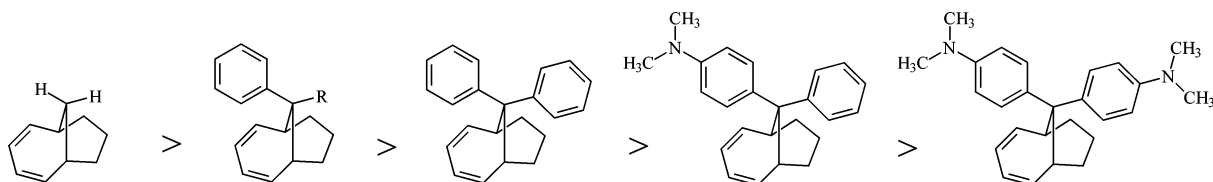
UV/vis absorption spectra were recorded on a Shimadzu UV-2101PC spectrophotometer. Fluorescence spectra were measured on a Spex Fluorolog-2 photon-counting emission spectrometer. The instrument is equipped with a 450-W xenon source, a Spex 340S dual-grating and dual-exit emission monochromator, and two detectors. The two gratings are blazed at 500 nm (1200 grooves/mm) and 1000 nm (600 grooves/mm). The room-temperature detector consists of a Hamamatsu R928P PMT operated at -950 V, and the thermoelectrically cooled detector consists of a near-infrared-sensitive Hamamatsu R5108 PMT operated at -1500 V. Unless specified otherwise, all emission spectra were corrected for nonlinear instrumental response by use of predetermined correction factors. Fluorescence decays were measured using the time-correlated single photon counting (TCSPC) method. The TCSPC setup consists of a Hamamatsu Stabilized Picosecond Light Pulser (PLP-02) as the excitation source, which produces ~ 33 ps (fwhm) light pulses at 632 nm with a repetition rate of 1 MHz. The 337 nm light was isolated using a band-pass filter (10 nm fwhm). Fluorescence decays were monitored through band-pass filters. The detector consists of a Phillips XP2254/B (red-sensitive version of XP2020) PMT in a thermoelectrically cooled housing. The PMT was operated at -2 kV using an EG&G Ortec 556 power supply. The detector electronics from EG&G Ortec include two 9307 discriminators, a 457 biased time-to-amplitude converter, and a 916A multi-channel analyzer. The instrument response function of the setup was ~ 1 ns (fwhm). All solutions used in emission measurements were deoxygenated in repeated freeze–pump–thaw cycles.

D₁, D₂, D₄'s, and D₆. The derivatized C₆₀ molecules were prepared in diazo addition reactions.^{21a} For the synthesis of **D₁**,

C₆₀ (120 mg, 0.17 mmol) was dissolved in toluene (130 mL). To the solution was added (*N,N*-dimethylamino-phenyl)phenyldiazomethane (83 mg, 0.34 mmol). After reaction for 4 h, the reaction mixture was separated on a silica gel column with toluene/hexane (1/1, v/v) as eluent to obtain **D₁** (45% yield). ¹H NMR (500 MHz, CS₂/CDCl₃): δ 7.97 (d, J = 7.33 Hz, 2H), 7.80 (d, J = 8.71 Hz, 2H), 7.40 (t, J = 7.30, 7.73 Hz, 2H), 7.29 (t, J = 7.20 Hz, 1H), 6.68 (d, J = 8.71 Hz, 2H), and 2.99 (s, 6H) ppm. ¹³C NMR (125 MHz, CS₂/CDCl₃): δ 149.87 (1C, Ph-C), 148.71 (2C), 148.68 (2C), 145.59 (2C), 145.56 (2C), 145.31 (2C), 145.29 (2C), 145.23 (2C), 145.22 (2C), 144.89 (1C), 144.84 (2C), 144.81 (2C), 144.79 (1C), 144.71 (2C), 144.41 (2C), 143.99 (4C), 143.12 (2C), 143.08 (2C), 143.07 (4C), 143.05 (4C), 142.42 (2C), 142.39 (2C), 142.29 (2C), 142.24 (2C), 140.98 (4C), 139.79 (1C, Ph-C), 138.53 (2C), 138.30 (2C), 131.83 (2C, Ph-C), 130.83 (2C, Ph-C), 128.83 (2C, Ph-C), 127.96 (1C, Ph-C), 126.28 (1C, Ph-C), 112.50 (2C, Ph-C), 79.60 (2C), 58.32 (1C, methano-bridge carbon), and 40.53 (2C, NCH₃) ppm. MALDI-TOF MS (M^+): 929.1. The synthesis and characterization of **D₂** were similar, with details already available in the literature.²⁴

For the **D₄** and **D₆** compounds, C₆₀ (120 mg, 0.16 mmol) was reacted with 10 equivalent of di(*N,N*-dimethylamino-phenyl)diazomethane (470 mg, 1.6 mmol) in toluene at room temperature for 48 h. The reaction mixture was separated into two major fractions containing **D₄** isomers and **D₆** isomers via silica gel flash column chromatography with toluene/ethyl acetate (10/1, v/v) as eluent. Both fractions in toluene were refluxed for 12 h (conversion of [5,6]-open to [6,6]-closed). The **D₄** fraction was further separated via silica gel flash column chromatography with toluene/ethyl acetate (30/1, v/v) as eluent to isolate the isomers **D_{4(t-2)}** ($\sim 8\%$ yield), **D_{4(t-3)}** ($\sim 4\%$ yield), and **D_{4(e)}** ($\sim 7\%$ yield) from the mixture. Similar silica gel flash column chromatography with toluene/chloroform/acetonitrile (40/3/1, v/v/v) allowed the isolation of **D₆** ($\sim 2\%$ yield) from the other fraction. **D_{4(t-2)}**: ¹H NMR (500 MHz, CDCl₃) δ 8.11 (d, J = 8.70 Hz, 4H), 7.89 (d, J = 8.70 Hz, 4H), 6.91 (d, J = 8.25 Hz, 4H), 6.75 (d, J = 8.70 Hz, 4H), 3.07 (s, 12H), and 2.93 (s, 12H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 149.82 (2C, Ph-C), 149.61 (2C, Ph-C), 147.45 (2C), 147.41 (2C), 146.30 (2C), 146.26 (2C), 146.05 (2C), 145.94 (2C), 145.91 (2C), 145.45 (2C), 145.26 (2C), 145.24 (2C), 144.68 (2C), 144.46 (2C), 144.26 (2C), 144.17 (2C), 143.65 (2C), 143.52 (2C), 143.48 (2C), 142.84 (2C), 142.40 (2C), 142.14 (2C), 142.03 (2C), 141.95 (2C), 141.27 (2C), 140.84 (2C), 139.91 (2C), 139.74 (2C), 136.82 (2C), 136.70 (2C), 131.69 (4C, Ph-C), 131.34 (4C, Ph-C), 128.06 (2C, Ph-C), 128.02 (2C, Ph-C), 112.53 (4C, Ph-C), 112.30 (4C, Ph-C), 79.23 (2C), 79.05 (2C), 55.12 (2C, methano-bridge carbon), 40.65 (4C, NCH₃), and 40.53 (4C, NCH₃); MALDI-TOF MS (M^+) 1223.8. **D_{4(t-3)}**: ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, J = 9.15 Hz, 4H), 7.77 (d, J = 8.75 Hz, 4H), 6.80 (d, J = 8.70 Hz, 4H), 6.70 (d, J = 9.20 Hz, 4H), 2.98 (s, 12H), and 2.93 (s, 12H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 150.45 (2C, Ph-C), 149.93 (2C, Ph-C), 149.73 (2C), 149.63 (2C), 149.60 (2C), 149.26 (2C), 147.72 (2C), 146.71 (2C), 146.42 (2C), 146.25 (4C), 146.11 (2C), 145.46 (2C), 145.29 (2C), 144.56 (2C), 144.51 (2C), 144.12 (2C), 144.05 (2C), 143.99 (2C), 143.76 (2C), 143.35 (2C), 143.08 (2C), 142.39 (2C), 142.01 (2C), 141.64 (2C), 141.59 (2C), 141.29 (2C), 140.75 (2C), 138.16 (2C), 137.72 (2C), 131.42 (4C, Ph-C), 131.30 (4C, Ph-C), 128.07 (2C, Ph-C), 127.84 (2C, Ph-C), 112.35 (4C, Ph-C), 112.23 (4C, Ph-C), 80.14 (2C), 79.65 (2C), 56.99 (2C, methano-bridge carbon), 40.56 (4C, NCH₃), and 40.50 (4C, NCH₃); MALDI-TOF MS (M^+) 1223.7. **D_{4(e)}**:

SCHEME 1



^1H NMR (500 MHz, CDCl_3) δ 7.75 (d, J = 8.25 Hz, 2H), 7.72 (d, J = 8.25 Hz, 4H), 7.70 (d, J = 8.25 Hz, 2H), 6.78 (d, J = 9.15 Hz, 2H), 6.72 (d, J = 8.70 Hz, 2H), 6.67 (d, J = 9.15 Hz, 4H), 3.04 (s, 6H), 2.96 (s, 6H), and 2.92 (s, 12H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 151.19 (2C, Ph-C), 149.81 (1C, Ph-C), 149.71 (1C, Ph-C), 149.62 (2C), 149.56 (2C), 148.08 (2C), 147.63 (2C), 147.01 (2C), 146.44 (2C), 146.11 (2C), 145.45 (1C), 145.37 (2C), 145.29 (2C), 144.78 (2C), 144.57 (1C), 144.47 (4C), 144.32 (2C), 144.27 (2C), 144.20 (2C), 144.04 (1C), 143.94 (2C), 143.62 (2C), 143.14 (2C), 142.79 (2C), 142.52 (1C), 142.16 (2C), 141.78 (2C), 141.34 (2C), 141.20 (2C), 141.08 (2C), 138.84 (2C), 137.99 (2C), 131.41 (2C, Ph-C), 131.20 (1C, Ph-C), 130.96 (1C, Ph-C), 128.72 (1C, Ph-C), 127.90 (1C, Ph-C), 127.59 (2C, Ph-C), 112.78 (2C, Ph-C), 112.22 (2C, Ph-C), 112.11 (4C, Ph-C), 80.93 (2C), 80.47 (1C), 74.55 (1C), 59.93 (1C, methano-bridge carbon), 56.69 (1C, methano-bridge carbon), 40.75 (2C, NCH_3), 40.56 (2C, NCH_3), and 40.53 (4C, NCH_3) ppm; MALDI-TOF MS (M^+) 1223.8. The results of characterization for **D**₆ are already available in the literature.²⁴

R₂ and **R**₄'s.²⁵ In a typical experiment for **R**₂, **C**₆₀ (93 mg, 0.129 mmol) was dissolved in toluene (80 mL) via sonication. Freshly prepared diphenyl diazomethane (24 mg, 0.123 mol) was added dropwise over 30 min in the dark, followed by the reaction for 45 min. The solvent was evaporated, and the reaction mixture was washed with hexane and ethanol to remove byproducts of the diazo reaction. The remaining sample was redissolved, and the solution was photoirradiated for ~6 h.²⁶ The compound **R**₂ was isolated (~20% yield) via silica gel flash chromatography with toluene/hexane (1/5, v/v) as eluent. The NMR results of the compound agree well with those in the literature.²⁷ MALDI-TOF MS: [M^+] 886.1.

For **R**_{4(t-3)} and **R**_{4(e)}, **C**₆₀ (166 mg, 0.23 mmol) was dissolved in toluene (150 mL). To the solution was added diphenyldiazomethane (123 mg, 0.63 mmol) in three fractions under nitrogen protection. After the reaction for 16 h and then solvent evaporation, the reaction mixture was washed with hexane and ethanol until no color in the washing solution. A solution of the mixture was prepared for photoirradiation for 6 h, followed by separation on a silica gel MPLC with toluene/hexane (1/5, v/v) as eluent to isolate **R**_{4(t-3)} and **R**_{4(e)} (both ~2% yield). **R**_{4(t-3)}: ^1H NMR (500 MHz, $\text{CS}_2/\text{CDCl}_3$) δ 8.09 (d, J = 8.25 Hz, 4H), 7.96 (d, J = 8.25 Hz, 4H), 7.47 (t, J = 7.75 Hz, 4H), 7.37 (t, J = 7.75 Hz, 4H), 7.36 (t, J = 7.75 Hz, 2H), and 7.28 (t, J = 7.75 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $\text{CS}_2/\text{CDCl}_3$) δ 149.43 (2C), 149.04 (2C), 148.80 (2C), 147.54 (2C), 146.73 (2C), 146.57 (2C), 146.49 (2C), 146.41 (2C), 146.39 (2C), 146.35 (2C), 145.51 (2C), 145.46 (2C), 144.70 (2C), 144.36 (2C), 144.30 (2C), 144.17 (2C), 143.98 (2C), 143.49 (2C), 143.41 (2C), 142.69 (2C), 141.90 (2C), 141.80 (2C), 141.68 (2C), 141.52 (2C), 140.73 (2C), 139.35 (2C), 139.20 (2C), 138.40 (2C), 137.81 (2C, Ph-C), 137.79 (2C, Ph-C), 131.05 (4C, Ph-C), 130.95 (4C, Ph-C), 128.89 (4C, Ph-C), 128.77 (4C, Ph-C), 128.23 (2C, Ph-C), 128.12 (2C, Ph-C), 78.93 (2C, bridgehead carbon), 78.44 (2C, bridgehead carbon), and 57.39 (2C, methano-bridge carbon) ppm; MALDI-TOF MS (M^+) 1053.0.

R_{4(e)}: ^1H NMR (500 MHz, $\text{CS}_2/\text{CDCl}_3$) δ 7.82 (d, J = 7.35 Hz, 2H), 7.80 (d, J = 7.35 Hz, 2H), 7.75 (d, J = 7.35 Hz, 4H), and 7.34–7.10 (m, 12H) ppm; ^{13}C NMR (125 MHz, $\text{CS}_2/\text{CDCl}_3$) δ 150.20 (2C), 147.26 (2C), 147.14 (2C), 146.96 (2C), 146.33 (1C), 146.32 (2C), 146.27 (2C), 146.17 (2C), 146.10 (2C), 145.41 (2C), 145.09 (2C), 144.86 (2C), 144.607 (1C), 144.60 (2C), 144.57 (2C), 144.44 (2C), 144.35 (2C), 144.10 (2C), 144.01 (2C), 143.64 (2C), 143.43 (2C), 142.91 (2C), 141.88 (2C), 141.68 (4C), 141.41 (2C), 141.00 (2C), 139.75 (1C, Ph-C), 139.51 (1C, Ph-C), 138.92 (2C), 138.75 (2C, Ph-C), 138.04 (2C), 130.86 (4C, Ph-C), 130.73 (2C–Ph-C), 130.50 (2C, Ph-C), 128.94 (2C, Ph-C), 128.67 (2C, Ph-C), 128.57 (4C, Ph-C), 128.60 (1C, Ph-C), 128.49 (1C, Ph-C), 128.29 (2C, Ph-C), 79.50 (2C, bridgehead carbon), 79.05 (1C, bridgehead carbon), 78.10 (1C, bridgehead carbon), 59.95 (1C, methano-bridge carbon), and 56.92 (1C, methano-bridge carbon) ppm; MALDI-TOF MS (M^+) 1053.0.

Results and Discussion

Synthesis and Separation. It is known that the diazo reaction with **C**₆₀ produces [5,6]-open adducts.^{21a,26–28} However, because of the unavoidable partial conversion to [6,6]-closed adducts, which was an added complexity to the already complicated adduct mixtures in the synthesis of **D** and **R** compounds, the separation was particularly challenging. Thus, in the reported work the reaction mixtures were first converted completely to [6,6]-closed before the silica gel column chromatography.

The [5,6]-open to [6,6]-closed conversion was found to be considerably easier in the **D** adducts than in the **R** adducts. In the **D** series, the **D**₄ and **D**₆ compounds were easier than the **D**₁ and **D**₂ compounds. For example, the complete [5,6]-open to [6,6]-closed conversion in the **D**₄ and **D**₆ compounds could be accomplished readily via refluxing in a relatively low boiling point solvent. In **R**₂, on the other hand, the same conversion required prolonged photoirradiation. In fact, because of the ready conversion in the **D**₄ and **D**₆ compounds, the as-produced reaction mixture in their preparation via diazo bis- and tris-additions contained a substantial amount of partially converted molecules, which made the separation of the as-produced mixture very challenging, as discussed above. The complete conversion before separation described in the Experimental Section was required. In the literature, it was reported that the dihydro-fulleroid ([5,6]-open) could not be converted into dihydro-methanofullerene ([6,6]-closed) even in photolysis.²⁸ For the hydro-phenyl-fulleroid, Wudl and co-workers were able to prevent it from being converted to methanofullerene by controlling the low temperature during reaction and work up.²⁹ In light of all of these experimental results, it seems that the stability of [5,6]-open fullerene adducts against the conversion to [6,6]-closed structures is in the order shown in Scheme 1. Mechanistically, the electron donating groups may have a significant role here in the observed ready [5,6]-open to [6,6]-closed conversion in the **D** compounds. The presence of DMA–cage intramolecular charge-transfer effects in these molecules (see below) may result in a lower activation barrier for the

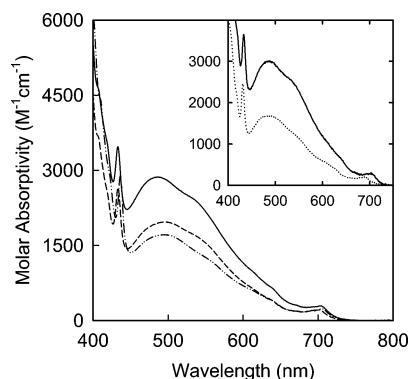


Figure 1. UV/vis absorption spectra of **R**₂ (---) in CS₂ and **D**₁ (---) and **D**₂ (—) in toluene solutions. Shown in the inset is a comparison between the spectra of **D**₂ in toluene without (—) and with (···) 2% (v/v) TFAA.

TABLE 1: Absorption Parameters of the D and R Compounds in Room-Temperature Solutions

compound	solvent	abs peak (nm)	ϵ_{MAX} ($\text{M}^{-1} \text{cm}^{-1}$)
R ₂	CS ₂	495	1850
D ₁	toluene	495	1970
D ₂	toluene	487	2860
D ₂	toluene + 2% TFAA	487	1760
R _{4(e)}	toluene	485	2450
D _{4(e)}	toluene	480	3930
D _{4(e)}	toluene + 2% TFAA	482	2670
R _{4(t-3)}	toluene	488	2730
D _{4(t-3)}	toluene	470	3990
D _{4(t-3)}	toluene + 2% TFAA	486	2450
D _{4(t-2)}	toluene	472	4000
D _{4(t-2)}	toluene + 1% TFAA	478	2800
D ₆	toluene	472	6200
D ₆	toluene + 2% TFAA	476	4100

conversion, though details remain to be explored in future investigations.

Ground-State Intramolecular Charge-Transfer Complexes. UV/vis absorption spectra of **R**₂, **D**₁, and **D**₂ in room-temperature solutions are compared in Figure 1. The absorption spectral profiles are typical of those of methano-C₆₀ monoadducts, with the weak 0–0 absorption band around 700 nm.^{2,30} In addition, they all consist of a broad absorption band in the visible, centered around 500 nm, for which the spectral parameters (the band maximum and the corresponding molar absorptivity) are summarized in Table 1. According to the extensive experimental results in the literature, methano-C₆₀ monoadducts should have similar absorption spectral properties.² However, these structurally (cage substitution wise) rather similar monoadducts show obviously different apparent molar absorptivities (Figure 1, Table 1). The observed significant difference is unique to these molecules with intramolecular electron donors, thus attributable to their different electronic properties. In both **D**₁ and **D**₂, there are ground-state intramolecular charge-transfer complexes, and these complexes are likely responsible for the extra contributions to the observed molar absorptivities. In fact, it is well-documented in the literature that *N,N*-dimethylaniline (DMA) serves as an electron donor to form intermolecular charge-transfer complexes with ground-state C₆₀ under various experimental conditions and that the equilibrium constant for the complex formation is on the order of 0.07 M⁻¹.¹⁸ The DMA-C₆₀ intermolecular charge transfer complexes are significantly more absorptive in the visible than free C₆₀.^{16–18} As a result, the apparent molar absorptivity obtained for C₆₀ in DMA is noticeably higher than that in toluene, 11 800 M⁻¹ cm⁻¹ vs 940 M⁻¹ cm⁻¹ at their

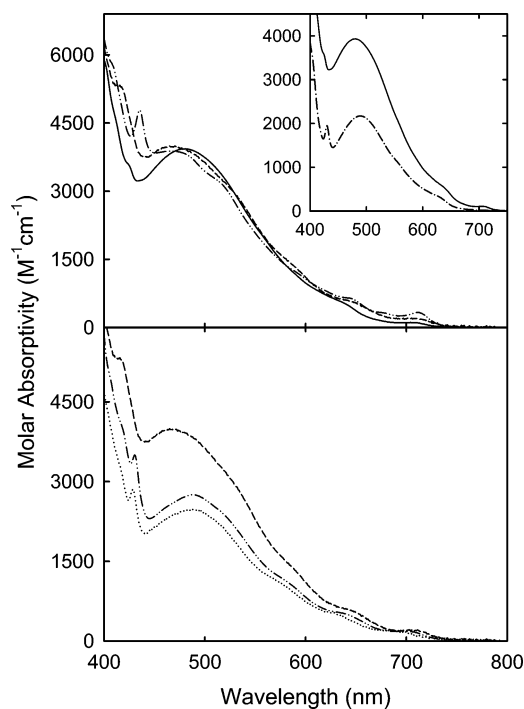


Figure 2. Top: UV/vis absorption spectra of **D**_{4(e)} (—), **D**_{4(t-3)} (---), and **D**_{4(t-2)} (···) in toluene, with the inset showing a comparison between the spectra of **D**_{4(e)} (—) and **R**_{4(e)} (···) in toluene. Bottom: A similar comparison between the spectra of **D**_{4(t-3)} in toluene (—) and **D**_{4(t-3)} in toluene without (---) and with (···) 1% (v/v) TFAA.

respective absorption maxima.¹⁸ It is thus reasonable to conclude that the molar absorptivities of the intramolecular charge transferred species in **D**₁ and **D**₂ are similarly higher than those of regular methano-C₆₀ monoadducts such as **R**₂.

The presence of intramolecular charge-transfer complexes in **D**₁ and **D**₂ was confirmed by the solvent acidity effect on absorption spectral properties. The apparent molar absorptivities of these compounds decreased when their solutions were acidified with the addition of trifluoroacetic acid (TFAA). For the **D**₂ solution in toluene as an example, the addition of TFAA to an equivalent of 2% (v/v) in the solution resulted in a decrease of the absorptivity to the level of **R**₂ absorption (Figure 1). The decrease in apparent absorptivity and the slight blue shift in the absorption spectrum are attributed to the protonation of the dimethyl amino group under the acidic solvent condition, which effectively shuts down the charge-transfer process. Similar solvent acidification effect was observed for **D**₁. The acidic solvent condition did not cause any damages to the **D**₁ and **D**₂ compounds. In sample recovery experiments, the solvent along with TFAA was evaporated, and the solid residue was carefully washed with water until neutral. The **D**₁ and **D**₂ samples thus recovered were found to be essentially identical to those never being in the acidified solutions.

Similarly, the absorption spectral properties of the methano-C₆₀ adducts containing 4 electron donating units (**D**_{4(t-2)}, **D**_{4(t-3)}, and **D**_{4(e)}) were compared with those of their corresponding adducts without the dimethyl amino moieties (**R**_{4(t-3)} and **R**_{4(e)}) (Figure 2). The apparent absorptivities of the **D**₄ compounds are again significantly higher than those of the **R**₄ compounds. The higher apparent absorptivities can also be attributed to contributions from the more absorptive intramolecular charge-transferred species. It is no surprise that the absorption spectral properties of the **D**₄ compounds were also subject to the solvent acidification effect. The intramolecular charge-transfer process in these molecules could largely be eliminated in the presence

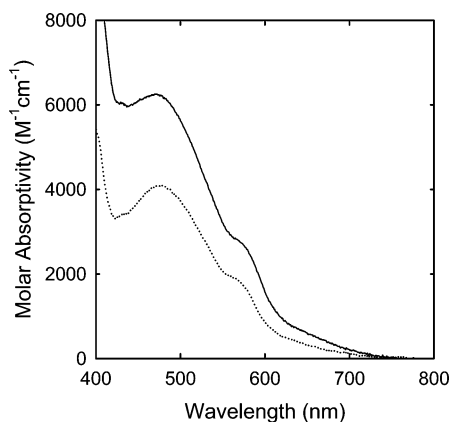


Figure 3. UV/vis absorption spectra of **D**₆ in toluene without (—) and with (···) 2% (v/v) TFAA.

of 1–2% (v/v) TFAA in the solutions, resulting in absorption spectra similar to those of their corresponding **R**₄ compounds (except for the slight blue shift due to the protonation of the dimethyl amino units).

The ground-state intramolecular charge transfers in the **D**₆ compound were evaluated by comparing absorption spectral properties in solutions without and with TFAA.²⁵ In Figure 3, the difference in apparent absorptivities can also be attributed to absorption contributions of the intramolecular charge-transferred species.

The contributions of intramolecular charge-transferred species to the apparent absorptivities are different in the series of **D** compounds, generally increasing with the number of electron donating units (Table 1). In a more quantitative but still simplified treatment, the intramolecular charge-transfer equilibrium may be expressed as $M \rightleftharpoons CT$, with an equilibrium constant K .

$$K = [CT]/[M] = (A_{CT}/\epsilon_{CT})/(A_M/\epsilon_M) = (A_{CT}/A_M)/(\epsilon_{CT}/\epsilon_M) \quad (1)$$

where A and ϵ represent absorbance and absorptivity, respectively. The absorption of M (A_M) in a **D** compound may be approximated by that of the corresponding **R** compound or the **D** compound in an acidified solution (both denoted as A_R). Under such an assumption,

$$A_{OBS} = A_R + A_{CT} \quad (2)$$

where A_{OBS} is the observed absorption of a **D** compound. Thus,

$$(\epsilon_{CT}/\epsilon_M)K = (A_{OBS}/A_R) - 1 \quad (3)$$

A plot of $[(A_{OBS}/A_R) - 1]$ vs the number of DMA units for the series of **D** compounds is shown in Figure 4, where the A values correspond to the visible band maxima in the absorption spectra (Table 1). Apparently, the term $(\epsilon_{CT}/\epsilon_M)K$, which is equal to $[(A_{OBS}/A_R) - 1]$ (eq 3), increases quickly from **D**₁ to **D**₂ and then reaches a plateau in the compounds containing more DMA units. In methano-C₆₀ derivatives the intrinsic molar absorptivity ϵ_M increases from mono- to tris-adducts.^{2,30} Therefore, two possible scenarios may be considered to explain the nearly constant $(\epsilon_{CT}/\epsilon_M)K$. One is that the molar absorptivities ϵ_{CT} are similar for intramolecular charge-transferred species in **D**₂ to **D**₆, so that the equilibrium constant K increases in the same series. The other is that K remains constant in the series whereas ϵ_{CT} increases from **D**₂ to **D**₆. The first scenario seems less likely because the intramolecular charge-transferred species are still

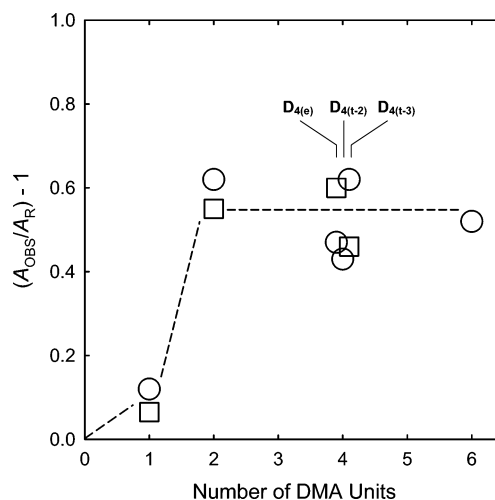


Figure 4. The plot of $[(A_{OBS}/A_R) - 1]$ vs the number of DMA units in the **D** series: (□) A_R from the corresponding **R**; (○) A_R from solutions with TFAA.

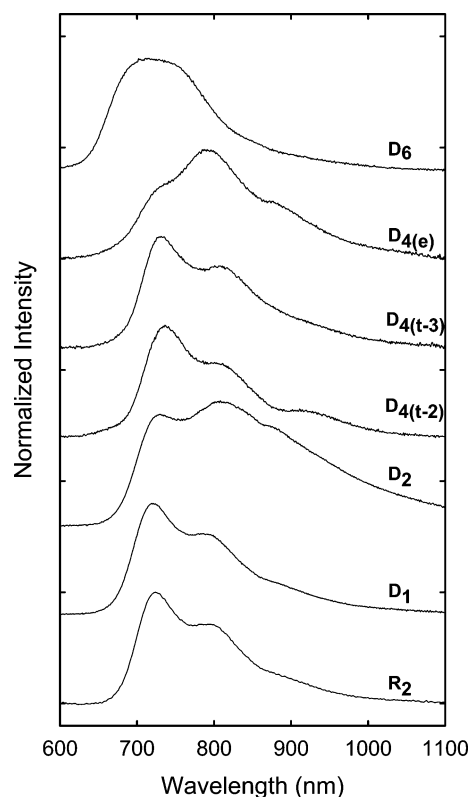


Figure 5. Fluorescence spectra of **R**₂ in CS₂ and **D** compounds in toluene.

based on the derivatized fullerene cage, thus dependent on the number and pattern of the cage addition. More probably might be that the equilibrium constant only varies slightly from **D**₂ to **D**₆, and ϵ_{CT} changes similarly to ϵ_M from compound to compound in the series, thus to keep $(\epsilon_{CT}/\epsilon_M)K$ approximately constant. Interestingly, because **D**₁ is clearly an exception, an inevitable conclusion from these results and analyses is that the ground-state intramolecular charge transfer “saturates” with only two electron donating DMA units in the methano-C₆₀ adducts.³¹

Fluorescence Properties. Fluorescence spectra of **D** compounds in the series are dependent on the number of DMA units (Figure 5). This is not surprising, considering the fact that C₆₀ cages with various addition numbers and patterns generally exhibit different fluorescence spectra.^{2,30} The compound **D**₂ is obviously a special case, with the fluorescence spectrum

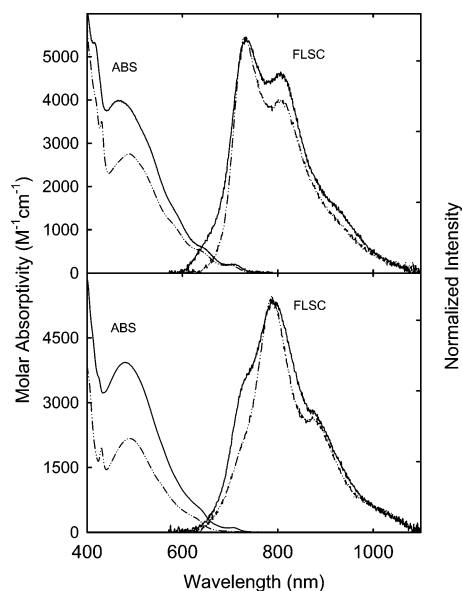


Figure 6. Absorption and fluorescence spectra in toluene solutions. Top: $D_{4(t-3)}$ (—) and $R_{4(t-3)}$ (---). Bottom: $D_{4(e)}$ (—) and $R_{4(e)}$ (---).

TABLE 2: Fluorescence Parameters of the D and R Compounds in Room-Temperature Solutions

compound	solvent ^a	$\Phi_F (\times 10^{-3})$	τ_F (ns)
R_2	CS ₂	1.2	1.3
D_1	toluene	1.6	1.4
D_1	toluene + 2% TFAA	1.5	
D_1	CH ₂ Cl ₂ + 2% TFAA	1.4	1.3
D_2	toluene	1.4	1.3
D_2	toluene + 2% TFAA	1.6	
D_2	CH ₂ Cl ₂ + 2% TFAA	1.5	1.3
$R_{4(e)}$	toluene	4	
$D_{4(e)}$	toluene	1.7	$\sim 2.1^b$
$D_{4(e)}$	CH ₂ Cl ₂ + 2% TFAA	3	
$R_{4(t-3)}$	toluene	2.8	
$D_{4(t-3)}$	toluene	1.3	$\sim 2^b$
$D_{4(t-3)}$	CH ₂ Cl ₂ + 1% TFAA		$\sim 1.6^b$
$D_{4(t-2)}$	toluene	1.7	$\sim 1.8^b$
D_6	toluene	1.9	ne ^c
D_6	CH ₂ Cl ₂ + 1% TFAA	1.5	ne ^c

^a In CH₂Cl₂ no emissions were observed for all **D** compounds.

^b Close to monoexponential, with the presence of a shorter component.

^c Obviously nonexponential, with the longest component on the order of 9 ns.

containing substantial contributions from the intramolecular exciplex. Surprisingly, however, this is the only member in the series that shows significant intramolecular exciplex emission. As compared in Figure 6, the fluorescence spectra of the **D**₄ compounds are largely similar to those of their corresponding **R**₄ molecules, which are typical of the methano-C₆₀ bis-adducts.³⁰ It is interesting that **D**₂ is the only one in the series that exhibits intramolecular exciplex emission and it is also where the charge-transfer effects reach saturation.³¹ Whether this is simply coincidental or something more fundamental remains to be evaluated in further investigations.

The fluorescence quantum yields of the **D** compounds in toluene solutions are also comparable with those of the **R** compounds in general (Table 2), both of which are similar to those of other methano-C₆₀ mono-, bis-, and tris-adducts.^{2,30} On the other hand, in methylene chloride, a more polar solvent, the comparison between **D** and **R** compounds becomes very different. Although the **R** compounds remain similar to other C₆₀ derivatives in fluorescence quantum yields, without any substantial dependence on solvent polarity, all **D** compounds

in the series are nonfluorescent (yields less than 10⁻⁵) in methylene chloride solutions (Table 2). This is attributed to the quenching of electron transfer as a competing decay pathway to fluorescence for the **D** compounds in a polar solvent environment, where the formation of partially stabilized radical ion pairs is a strong possibility. The electron-transfer contribution to the fluorescence quenching is best illustrated by the results of acidification effect. When a small quantity (1–2 vol %) of a strong organic acid was added to the methylene chloride solutions, the fluorescence emissions of the **D** compounds reemerged, with fluorescence yields comparable with those of the same compounds in toluene solutions (Table 2). Here the acid can protonate the dimethylamino groups in the DMA units, thus limiting their electron donating ability and the associated fluorescence quenching effect.^{11,24}

The photophysical processes in the **D** molecules are likely complicated, especially because the excitation involves more than one ground-state species (M and CT in eq 1). Qualitatively, the excited-state intramolecular electron transfer seems relatively inefficient for the **D** molecules in a nonpolar solvent such as toluene. Except for **D**₂, no other **D** compounds in the series exhibit significant emission contributions from intramolecular exciplexes or charge-transferred excited states. Therefore, for these molecules in toluene solutions, the excited-state processes are dominated by the normal C₆₀ adduct (M in eq 1), which are similar to those in the corresponding **R** compounds. The ground-state intramolecular charge-transferred species (CT in eq 1) are probably excited into nonemissive states, which do not interfere with the fluorescence probing of excited-state processes in the **D** compounds (except for **D**₂, as discussed above).

The complete quenching of fluorescence for the **D** series in a polar solvent like methylene chloride represents the other extreme, with the intramolecular electron transfers dominating the excited-state processes. The photoexcitation of all ground-state species (both M and CT) results in the population of nonemissive intramolecular charge-transferred excited states. Therefore, these **D** molecules are excellent in uses that require the rapid generation of anionic fullerene species or fullerene-derived intramolecular charge separated species. The properties of the nonemissive intramolecular charge-transferred excited states in these molecules may be investigated by ultrafast pump–probe spectroscopy methods, which is beyond the scope of this work. Nevertheless, we do not expect dramatically different properties from those of other fullerene dyads and triads with DMA-derived electron donors.¹¹

In summary, a series of methano-C₆₀ derivatives bearing multiple electron donating DMA units (**D** compounds), along with their analogues without the amino moieties as references (**R** compounds), were synthesized and evaluated spectroscopically for redox properties. In the **D** series, there are obviously ground-state intramolecular charge-transfer complexes according to UV/vis absorption results, and the charge-transfer effects apparently become saturated with only two DMA units in the molecule. The fluorescence results suggest that the photoinduced electron transfers in the **D** series are strongly dependent on the medium polarity. The **D** molecules in a polar solvent like methylene chloride are essentially dark (nonemissive). Because the aromatic amines are the electron donors in these molecules, their protonation in the presence of an organic acid in the solutions may result in a complete elimination of the intramolecular electron-transfer processes in both ground and excited states. The acid effect is reversible without any damage to the **D** compounds, which might be exploited for potential applications in further investigations.

Acknowledgment. We thank Dr. Y. Lin for assistance. Financial support from the National Science Foundation is gratefully acknowledged.

References and Notes

- (1) Foote, C. S. In *Topics in Current Chemistry: Electron-Transfer I*; Mattay, J., Ed.; Springer-Verlag: Berlin, 1994; p 347.
- (2) (a) Sun, Y.-P. In *Molecular and Supramolecular Photochemistry*; Ramamurthy, V., Shanze, K. S., Eds.; Marcel Dekker, New York, 1997; Vol. 1, p 325. (b) Sun, Y.-P.; Riggs, J. E.; Guo, Z.; Rollins, H. W. In *Optical and Electronic Properties of Fullerenes and Fullerene-Based Materials*; by Shinar, J., Vardeny, Z. V., Kafafi, Z. H., Eds.; Marcel Dekker, New York, 1999; p 43.
- (3) (a) Echegoyen, L.; Echegoyen, L. F. *Acc. Chem. Res.* **1998**, *31*, 593. (b) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075. (c) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40.
- (4) (a) Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695. (b) Guldi, D. M. *Chem. Soc. Rev.* **2002**, *31*, 22.
- (5) (a) Imahori, H.; Tkachenko, N. V.; Vehmanen, V.; Tamaki, K.; Lemmetyinen, H.; Sakata, Y.; Fukuzumi, S. *J. Phys. Chem. A* **2001**, *105*, 1750. (b) Hirayama, D.; Takimiya, K.; Aso, Y.; Otsubo, T.; Hasobe, T.; Yamada, H.; Imahori, H.; Fukuzumi, S.; Sakata, Y. *J. Am. Chem. Soc.* **2002**, *124*, 532. (c) Imahori, H. *J. Phys. Chem. B* **2004**, *108*, 6130.
- (6) (a) D'Souza, F.; Zandler, M. E.; Smith, P. M.; Deviprasad, G. R.; Arkady, K.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. A* **2002**, *106*, 649. (b) D'Souza, F.; Smith, P. M.; Zandler, M. E.; McCarty, A. L.; Itou, M.; Araki, Y.; Ito, O. *J. Am. Chem. Soc.* **2004**, *126*, 10700.
- (7) (a) Thomas, K. G.; Biju, V.; Kamat, P. V.; George, M. V.; Guldi, D. M. *ChemPhysChem* **2003**, *4*, 1299. (b) Schuster, D. I.; Cheng, P.; Jarowski, P. D.; Guldi, D. M.; Luo, C. P.; Echegoyen, L.; Pyo, S.; Holzwarth, A. R.; Braslavsky, S. E.; Williams, R. M.; Klihm, G. *J. Am. Chem. Soc.* **2004**, *126*, 7257.
- (8) Liddell, P. A.; Kodis, G.; Andreasson, J.; de la Garza, L.; Bandyopadhyay, S.; Mitchell, R. H.; Moore, T. A.; Moore, A. L.; Gust, D. *J. Am. Chem. Soc.* **2004**, *126*, 4803.
- (9) (a) Sawamura, M.; Kuninobu, Y.; Toganoh, M.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2002**, *124*, 9354. (b) Toganoh, M.; Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2003**, *125*, 13974. (c) Nishikawa, H.; Kojima, S.; Kodama, T.; Ikemoto, I.; Suzuki, S.; Kikuchi, K.; Fujitsuka, M.; Luo, H. X.; Araki, Y.; Ito, O. *J. Phys. Chem. A* **2004**, *108*, 1881.
- (10) Lawson, J. M.; Oliver, A. M.; Rothenfluh, D. F.; An, Y.-Z.; Ellis, G. A.; Ranasinghe, M. G.; Khan, S. I.; Franz, A. G.; Ganapathi, P. S.; Shephard, M. J.; Paddon-Row, M. N.; Rubin, Y. *J. Org. Chem.* **1996**, *61*, 5032.
- (11) (a) Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 4093. (b) Williams, R. M.; Koeberg, M.; Lawson, J. M.; An, Y.-Z.; Rubin, Y.; Paddon-Row, M. N.; Verhoeven, J. W. *J. Org. Chem.* **1996**, *61*, 5055.
- (12) Liu, S.-G.; Shu, L. H.; Rivera, J.; Liu, H. Y.; Raimundo, J.-M.; Roncali, J.; Gorgues, A.; Echegoyen, L. *J. Org. Chem.* **1999**, *64*, 4884.
- (13) Ohno, T.; Moriawaki, K.; Miyata, T. *J. Org. Chem.* **2001**, *66*, 3397.
- (14) Sandanayaka, A. S. D.; Sasabe, H.; Araki, Y.; Furusho, Y.; Ito, O.; Takata, T. *J. Phys. Chem. A* **2004**, *108*, 5145.
- (15) (a) Eckert, J. F.; Nicoud, J. F.; Nierengarten, J. F.; Liu, S. G.; Echegoyen, L.; Barigelletti, F.; Armaroli, N.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *J. Am. Chem. Soc.* **2000**, *122*, 7467. (b) Yamazaki, M.; Araki, Y.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. A* **2001**, *105*, 8615. (c) Saha, A.; Nayak, S. K.; Chattopadhyay, S.; Mukherjee, A. K. *J. Phys. Chem. A* **2004**, *108*, 8223. (d) Delgado, J. L.; de la Cruz, P.; Lopez-Arza, V.; Langa, F.; Kimball, D. B.; Haley, M. M.; Araki, Y.; Ito, O. *J. Org. Chem.* **2004**, *69*, 2661. (e) Kang, S. H.; Ma, H.; Kang, M. S.; Kim, K. S.; Jen, A. K. Y.; Zareie, M. H.; Sarikaya, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1512. (f) Guldi, D. M.; Luo, C. P.; Swartz, A.; Gomez, R.; Segura, J. L.; Martin, N. *J. Phys. Chem. A* **2004**, *108*, 455.
- (16) Sension, R. J.; Szarka, A. Z.; Smith, G. R.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1991**, *185*, 179.
- (17) Seshadri, R.; Rao, C. N. R.; Pal, H.; Mukherjee, T.; Mittal, J. P. *Chem. Phys. Lett.* **1993**, *205*, 395.
- (18) Sun, Y.-P.; Bunker, C. E.; Ma, B. *J. Am. Chem. Soc.* **1994**, *116*, 9692.
- (19) (a) Lawson, G. E.; Kitaygorodskiy, A.; Ma, B.; Bunker, C. E.; Sun, Y.-P. *Chem. Commun.* **1995**, 2225. (b) Bunker, C. E.; Rollins, H. W.; Sun, Y.-P. *J. Chem. Soc., Perkin Trans 2* **1996**, 1307.
- (20) Xie, Q. S.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978.
- (21) (a) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 5. 157. (b) Hirsch, A. *Top. Curr. Chem.* **1999**, *199*, 1. (c) Diederich, F.; Kessinger, R. *Acc. Chem. Res.* **1999**, *32*, 537. (d) Nakamura, Y.; O-kawa, K.; Nishimura, J. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 865.
- (22) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364.
- (23) (a) Djojo, F.; Herzog, A.; Lamparth, I.; Hampel, F.; Hirsch, A. *Chem. Eur. J.* **1996**, *2*, 1537. (b) Irngartner, H.; Fettel, P. W. *Tetrahedron* **1999**, *55*, 10735. (c) Mas-Torrent, M.; Rodríguez-Mias, R. A.; Solà, M.; Molins, M. A.; Pons, M.; Vidal-Gancedo, J.; Veciana, J.; Rovira, C. *J. Org. Chem.* **2002**, *67*, 566.
- (24) Sun, Y.-P.; Huang, W. J.; Guduru, R.; Martin, R. B. *Chem. Phys. Lett.* **2002**, *353*, 353.
- (25) Despite repeated effort, we were unsuccessful in the synthesis and separation of a **R₆** compound.
- (26) (a) Janssen, R. A.; Hummelen, J. C.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 544. (b) González, R.; Hummelen, J. C.; Wudl, F. *J. Org. Chem.* **1995**, *60*, 2618.
- (27) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, *254*, 1186.
- (28) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 5829.
- (29) Hummelen, J. C.; Knight, B. W.; Le Peq, F.; Wudl, F. *J. Org. Chem.* **1995**, *60*, 532.
- (30) Sun, Y.-P.; Guduru, R.; Lawson, G. E.; Mullins, J. E.; Guo, Z. X.; Quinlan, J.; Bunker, C. E.; Gord, J. R. *J. Phys. Chem. B* **2000**, *104*, 4625.
- (31) One explanation for the saturation might be that after the reduction of C₆₀ to C₆₀^{•-} by one DMA equivalent, the further reduction to C₆₀²⁻ is beyond the reach of the remaining intramolecular DMA unit(s).