

Photophysical and Nonlinear Absorptive Optical Limiting Properties of [60]Fullerene Dimer and Poly[60]fullerene Polymer

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A systematic study of the photophysical properties and nonlinear absorptive optical limiting responses of the [60]fullerene dimer (C_{60} dimer) and poly[60]fullerene (poly- C_{60}) polymer in room-temperature solutions is reported. The results are compared with those of C_{60} and representative C_{60} derivatives. While the absorption, fluorescence (spectrum, quantum yield, lifetime), and photoinduced electron-transfer properties of the C_{60} dimer are somewhat different from those of C_{60} , they are qualitatively similar to those of other C_{60} derivatives. The triplet–triplet absorption of the C_{60} dimer is noticeably weaker than those of C_{60} and other C_{60} derivatives, corresponding to lower optical limiting responses of the C_{60} dimer at 532 nm. However, the photophysical and nonlinear absorptive optical limiting properties of the poly- C_{60} polymer are significantly different. The polymer solution shows much weaker fluorescence, barely detectable triplet-state absorption, and marginal optical limiting response. The different excited-state and nonlinear optical properties of the poly- C_{60} polymer are explained in terms of new excited singlet-state decay pathways in the polymer that are not available in monomeric and dimeric C_{60} molecules. In addition, the issue concerning significant excited-state fullerene cage–cage interactions in the C_{60} dimer and poly- C_{60} polymer is discussed.

Introduction

The electronic transitions and excited-state properties of fullerene molecules and derivatives, especially [60]fullerene (C_{60}) derivatives, have attracted much attention.^{1–3} It is now well-established that the low-lying electronic transitions in C_{60} are only weakly allowed due to the high degree of symmetry in the closed-shell electronic configuration. As a result, the observed C_{60} absorption band in the visible is weak, with the molar absorptivity at the band maximum of only $\sim 950 \text{ M}^{-1} \text{ cm}^{-1}$. The visible absorptions are somewhat stronger in C_{60} derivatives, as expected for the lowering of molecular symmetry upon a functionalization of the fullerene cage.^{4–6} Molar absorptivities of the visible absorption bands of several different classes of C_{60} derivatives have been determined recently for a systematic comparison.^{5,6} The results show that the transition probabilities in the visible region are rather similar not only for the derivatives in the same class (methano- C_{60} derivatives, for example) but also among different classes of C_{60} derivatives. A logical conclusion seems that the low-lying electronic transitions in C_{60} derivatives are dictated by the functionalized C_{60} cages and much less affected by the functional groups attached to the cages.^{5,6}

Fullerene molecules are only weakly fluorescent.^{7,8} For C_{60} in room-temperature toluene, the fluorescence quantum yield is 3.2×10^{-4} .^{8a,9} The weak fluorescence is due to the competition of efficient intersystem crossing to the excited triplet state, with an intersystem yield of unity according to the result of singlet molecular oxygen generation.¹⁰ The efficient intersystem crossing produces a high population of the excited triplet state. Because the triplet–triplet transient absorption cross sections are higher than the ground-state absorption cross sections,^{11,12} C_{60} in room-temperature solution exhibits excellent nonlinear absorptive optical limiting properties.^{13–16} In fact,

C_{60} is actively investigated as one of the best broad-band optical limiters for potential laser power limiting and optical switching applications.^{17,18} Similar excited-state properties have been observed for C_{60} derivatives.^{1–3,5,6,19–22} For example, it has been shown that the excited-state properties of different methano- C_{60} and pyrrolidino- C_{60} derivatives are rather similar.^{5,6,19,21,22} The derivatives are more fluorescent than the parent C_{60} , with fluorescence yields of the derivatives being larger by approximately a factor of 3 and fluorescence lifetimes being longer by approximately 25% (1.4–1.6 ns for the derivatives vs 1.2 ns for C_{60}).^{5,6} The intersystem crossing continues to be the dominating excited-singlet-state decay pathway in the C_{60} derivatives, again with unity intersystem yields according to results from singlet molecular oxygen generation measurements.^{1,19,23} The triplet–triplet transient absorption spectra of the C_{60} derivatives have spectral profiles similar to that of the parent C_{60} , but the spectra of the derivatives are slightly blue-shifted and have lower absorption cross sections.^{19,22,24} However, the nonlinear absorptive properties of the C_{60} derivatives as measured by optical limiting responses toward a nanosecond pulsed laser at 532 nm are only marginally different from those of the parent C_{60} in room-temperature solutions.^{6,25–27}

The derivatization of fullerene cages has been extended to the preparation of fullerene-containing polymers.^{3,28–34} Of particular interest are polyfullerenes, which are all-carbon polymers of covalently linked fullerene cages.^{31,32,34} The first successful preparation of polyfullerene oligomers/polymers was based on photochemical reaction in the solid state.³¹ In the preparation, oxygen-free fullerene solid films were irradiated with visible and ultraviolet light. According to results from laser desorption mass spectroscopy and other instrumental measurements, the phototransformed fullerene solid films contain linked fullerene species.^{31,35} A number of follow-up investigations of the phototransformed fullerene films have been

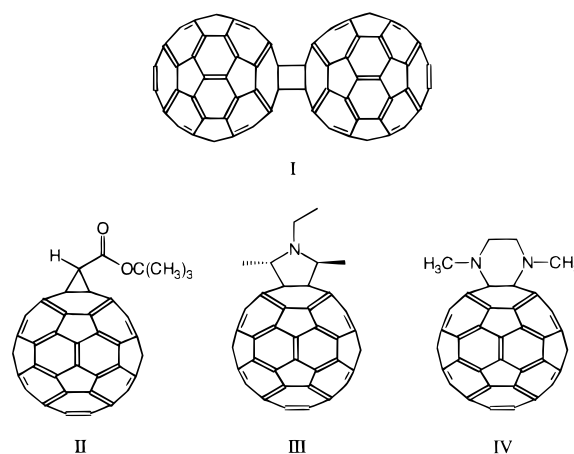
reported,³⁶ coupled with active computational studies of fullerene dimers and oligomeric species.³⁷ We have developed a solution-based method for the preparation of purified polyfullerene polymers in bulk quantity.^{34,38} The poly[60]fullerene (poly- C_{60}) polymer thus prepared is free from unreacted C_{60} and dimeric C_{60} species. Since the polymer has some limited solubility in a room-temperature solvent DMSO, it becomes possible to examine the photophysical and nonlinear optical properties of the poly- C_{60} polymer solution, which may be compared with those of C_{60} -containing copolymers. The limited solubility also makes available more experimental techniques for the structural characterization of the polymer.^{38,39}

It has been proposed that a preferred linking pattern in the fullerene oligomers/polymers is [2 + 2] cycloaddition between two neighboring fullerene cages.^{31,34–36} The proposal has much to do with the fact that there seems to be no better mechanism to account for the linking of neat fullerene cages into all-carbon polymers. Since the photochemical [2 + 2] cycloaddition is through the excited triplet state, the experimental results that suggest high sensitivities of both solid-state and solution-based photopolymerization reactions toward oxygen quenching are consistent with such a mechanism. In an effort to examine the oligomeric models of the poly- C_{60} polymer, we have tried without success the preparation of C_{60} dimers and trimers through controlled photochemical [2 + 2] cycloaddition reactions and by quenching the thermal decomposition of the poly- C_{60} polymer. Recently, however, a successful mechanochemical preparation of the dimeric C_{60} species **I** (C_{60} dimer) has been reported.⁴⁰ Results from a comparative FT-IR investigation show that the C_{60} dimer and poly- C_{60} polymer have similar vibrational absorption patterns, which may be regarded as an indication for their similar structural characteristics.⁴¹

In this paper, we report a systematic study of the photophysical properties and nonlinear absorptive optical limiting responses of the C_{60} dimer **I** and poly- C_{60} polymer in room-temperature solutions. The results are compared with those of C_{60} and representative C_{60} derivatives. The absorption, fluorescence (spectrum, quantum yield, lifetime), and photoinduced electron-transfer properties of the C_{60} dimer are qualitatively similar to those of other C_{60} derivatives. However, the triplet–triplet absorption of the C_{60} dimer is noticeably weaker than those of C_{60} and other C_{60} derivatives, corresponding to lower optical limiting responses of the C_{60} dimer at 532 nm. For the poly- C_{60} polymer, the photophysical and optical limiting properties are significantly different. The polymer solution shows much weaker fluorescence, barely detectable triplet-state absorption, and marginal optical limiting response. The different excited-state and nonlinear optical properties of the poly- C_{60} polymer are explained in terms of new excited-singlet-state decay pathways in the polymer that are not available in monomeric and dimeric C_{60} molecules. In addition, the issue concerning possible excited-state fullerene cage–cage interactions in the C_{60} dimer and poly- C_{60} polymer is discussed.

Experimental Section

Materials. C_{60} (purity >99.5%) was obtained from Bucky-USA. The sample purity was checked by UV/vis absorption, ^{13}C NMR, and matrix-assisted laser desorption ionization time-of-flight MS methods, and the sample was used without further purification. Hexane, toluene, *o*-xylene, acetonitrile, acetone, carbon disulfide, chlorobenzene, and *o*-dichlorobenzene (all spectrophotometry grade) were obtained from Burdick & Jackson. 1,2,4-Trimethylbenzene (98%), 1,2,3,5-tetramethylbenzene (85%) and the remaining being other isomers), 1-chlo-



ronaphthalene (90% and the remaining being 2-chloronaphthalene), and *N,N*-dimethylaniline (99%) were obtained from Aldrich. The solvents were used as received because there was no interference of possible impurities in the wavelength range of interest according to absorption and emission spectroscopic measurements of the solvents.

C_{60} Dimer. The C_{60} dimer **I** was synthesized by following a procedure reported in the literature.⁴⁰ The dimerization of C_{60} was accomplished in a solid-state mechanochemical reaction of C_{60} with potassium cyanide by use of a vibration mill under nitrogen atmosphere. The C_{60} dimer was separated from the reaction mixture through silica gel column chromatography using first a hexane–toluene mixture and then a toluene–*o*-dichlorobenzene mixture as eluent. After careful purification, the C_{60} dimer was characterized by ^{13}C NMR using 1-chloronaphthalene with 10% (v/v) benzene- d_6 as solvent. The ^{13}C NMR results, δ 151.57 (8C), 147.16 (4C), 146.13 (8C \times 2), 146.02 (8C), 145.84 (8C), 145.51 (4C), 145.23 (8C), 144.27 (8C), 143.14 (4C), 142.90 (8C), 142.65 (8C), 142.07 (8C), 141.92 (8C), 140.82 (8C), 139.17 (8C), and 76.45 (4C) ppm, are in excellent agreement with those reported in the literature.⁴⁰ The C_{60} dimer sample was further purified for spectroscopic measurements by repeatedly washing with a solvent mixture of hexane and toluene on a silica gel column to remove any residual C_{60} .

Poly- C_{60} . The photochemical preparation, purification, and characterization of the poly- C_{60} polymer have been described elsewhere.^{34,38} Briefly, a suspension of C_{60} clusters with a total C_{60} concentration of 3×10^{-4} M was prepared in a solvent mixture consisting of 66% (v/v) toluene and 34% acetonitrile at room temperature.^{42,43} In the preparation, acetonitrile was rapidly poured into a toluene solution of C_{60} .⁴³ The average size of the C_{60} clusters is ~ 120 nm according to dynamic light scattering (photon correlation spectroscopy of quasi-elastic light scattering)⁴⁴ results. The suspension was deoxygenated by bubbling with dry nitrogen gas for ~ 1 h. Photoirradiation of the suspension was carried out using an immersion-well photochemical apparatus, which consists of a 450 W medium-pressure mercury lamp and a Pyrex filter. During photoirradiation, the suspension of C_{60} clusters in the reaction vessel was purged with a slow stream of dry nitrogen gas to prevent recontamination of oxygen. Upon completing the photoirradiation (~ 48 h), the solvents were removed on a rotary evaporator. The reaction mixture was extracted repeatedly using toluene to remove unreacted C_{60} and dimeric species, yielding dark brown poly- C_{60} solids. The photopolymerization yield under the experimental condition is $\sim 28\%$, estimated gravimetrically on the basis of the amount of poly- C_{60} sample

obtained from the polymerization reaction. The polymer sample is partially soluble in DMSO, which allows characterization using solution-based techniques. The FT-IR spectrum of the poly-C₆₀ polymer in KBr matrix shows that the most intense peak is at 526 cm⁻¹, similar to that in the spectrum of C₆₀.⁴¹ The generally weak IR signals relative to the peak at 526 cm⁻¹ are consistent with the poly-C₆₀ polymer being an all-carbon material. Results from the proton NMR measurement and elemental analysis show that the polymer sample is free from hydrogen-containing impurities. The solubility of the poly-C₆₀ polymer in DMSO is unlikely due to the presence of any polar groups in the polymer structure. It is probably a result of the high polarizability of the poly-C₆₀ polymer. The observed extreme polyelectrolyte effects in the gel permeation chromatography (GPC) measurements of the poly-C₆₀ polymer solution³⁹ are consistent with such an explanation. The GPC analysis of the soluble fraction of the poly-C₆₀ sample used in this study was carried out using DMSO with 0.2% (w/w) lithium bromide as mobile phase at 75 °C. An average molecular weight M_w of 14 000 and a polydispersity index of 3.6 were obtained for the poly-C₆₀ polymer sample in reference to linear poly(2-vinylpyridine) standards.

Measurements. Absorption spectra were obtained using a computer-controlled Shimadzu UV2101-PC spectrophotometer. Emission spectra were recorded on a Spex Fluorolog-2 photon-counting emission spectrometer equipped with a 450 W xenon source, a Spex 340S dual-grating and dual-exit emission monochromator, and two detectors for both visible and near-infrared sensitivities. Fluorescence 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.⁴⁵ The instrument response of the TCSPC setup has a fwhm of ~1.2 ns.⁶

Transient absorption spectra were recorded using nanosecond laser flash photolysis method. The third harmonic from a Continuum Surelite-I Q-switched Nd:YAG laser (355 nm, 4 ns pulse width, 10 Hz repetition) was used as the excitation source. The transient was probed by use of a 450 W xenon lamp through a water filter. The probing light was controlled with a mechanical shutter from Vincent Associates, which was synchronized with the laser excitation pulse by use of a timing control unit made in house. The probing light wavelength was selected through a Spex 1681B monochromator. The detector consists of a Hamamatsu R928 photomultiplier tube and a Tektronix TDS-350 digital oscilloscope interfaced to a personal computer. In the measurements, the signals were averaged over ~250 laser shots to improve the signal-to-noise ratio.

Optical limiting measurements were performed by use of the setup illustrated in Figure 1. It consists of a Continuum Surelite-I Q-switched Nd:YAG laser operated in the single-shot mode. The infrared fundamental was frequency-doubled to generate the second harmonic at 532 nm. It was isolated by use of a Surelite harmonic separation package. The maximum energy at 532 nm is 160 mJ/pulse with a 5 ns pulse width (fwhm). The laser output was varied in a range of 10–160 mJ/pulse by using a waveplate–polarizer combination. The laser beam has a diameter of 6 mm, corresponding to energy densities in the range 0.035–0.57 J/cm². A Galilean style telescope consisting of a plano-concave lens and a plano-convex lens was used to reduce the laser beam waist to 3 mm in diameter for higher energy densities up to 2.2 J/cm². A Scientech Mentor MC2501 calorimeter and a MD10 meter were

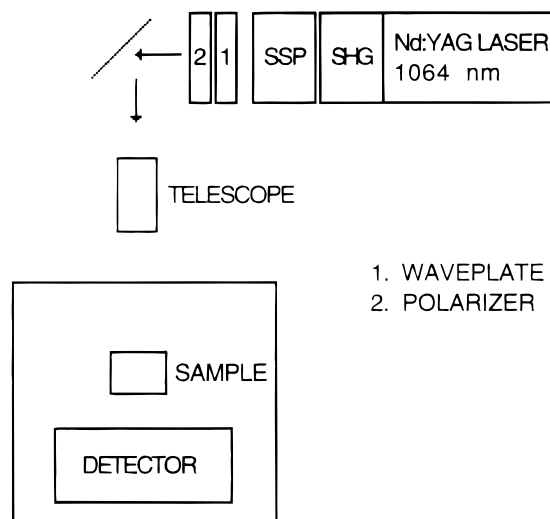


Figure 1. Experimental setup for optical limiting measurements.

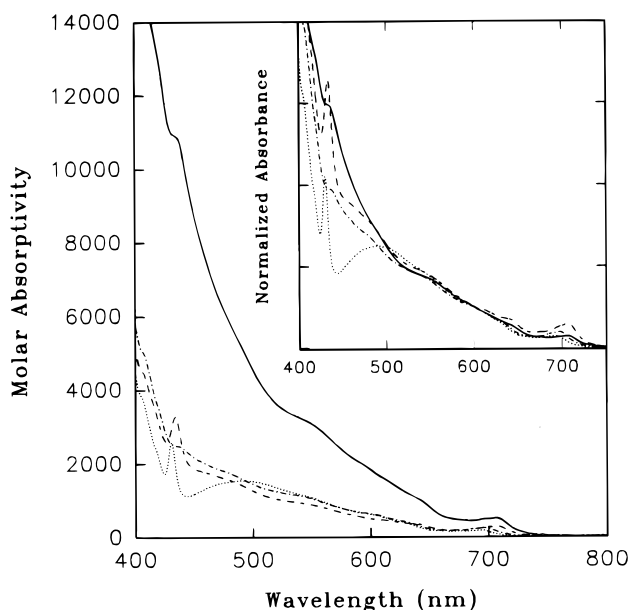


Figure 2. Absorption spectrum of the C₆₀ dimer **I** (—) is compared with the spectra of the methano-C₆₀ derivative **II** (···), pyrrolidino-C₆₀ derivative **III** (---), and amino-C₆₀ derivative **IV** (-·-) in room-temperature solutions. Shown in the inset is a comparison of the normalized absorption spectra.

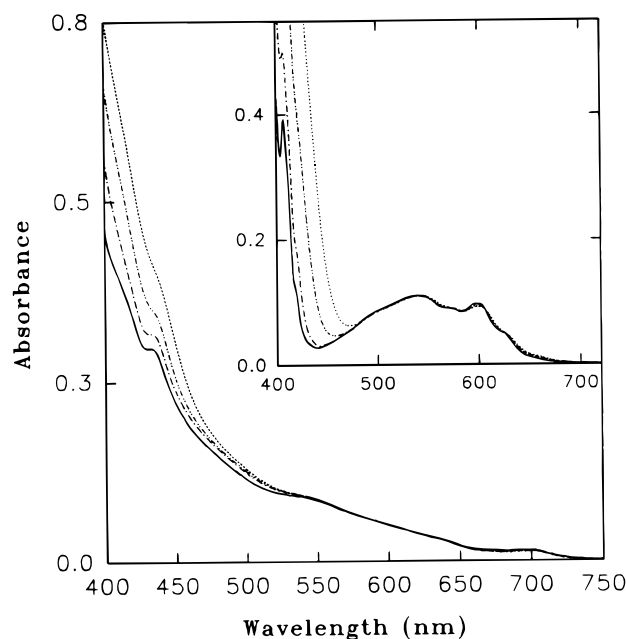
used as the detector. The solution samples were measured in a cuvette with 2 mm optical path length.

Results

Absorption Spectra. The absorption spectrum of the C₆₀ dimer **I** in CS₂ at room temperature (22 °C) is shown in Figure 2 and is compared with those of the methano-C₆₀ derivative **II**, pyrrolidino-C₆₀ derivative **III**, and amino-C₆₀ derivative **IV**, which are representatives of three commonly observed C₆₀ derivative classes. Similar to the other C₆₀ derivatives, the C₆₀ dimer has a weak 0–0 absorption peak at ~700 nm. However, the molar absorptivity of the C₆₀ dimer at the 0–0 absorption band is larger than those of the other C₆₀ derivatives by approximately a factor of 2 (Figure 2 and Table 1). Shown in the inset of Figure 2 is a comparison of the normalized absorption spectra of the C₆₀ dimer and the other C₆₀ derivatives. The absorption spectral profile of the dimer is similar to that of the amino-C₆₀ derivative **IV** such that their spectra are less

TABLE 1: Absorption and Fluorescence Properties of the C₆₀-Dimer and Poly-C₆₀ Polymer Compared with Those of Other Representative C₆₀ Derivatives

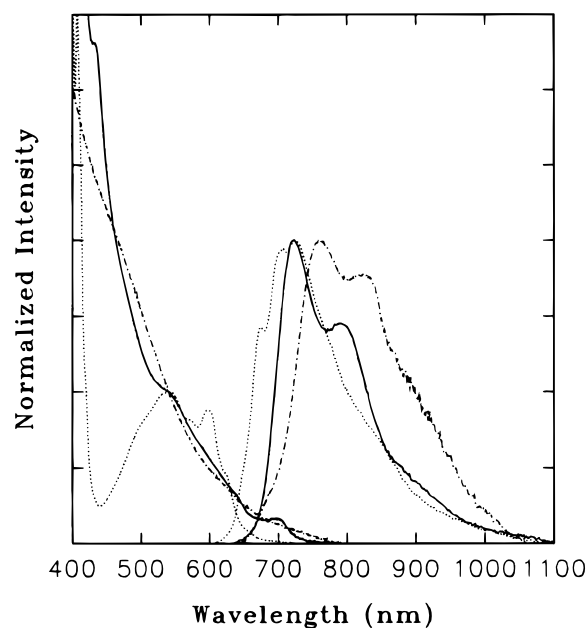
compound	solvent	ABS ₀₋₀ (nm)	ϵ_{0-0} (M ⁻¹ cm ⁻¹)	FLSC ₀₋₀ (nm)	τ_F (ns)	$\Phi_F (\times 10^4)$
C ₆₀	toluene				1.2	3.2
C ₆₀ dimer I	toluene	698	516	720	1.5	9.2
methano-C ₆₀ II ^a	toluene	695	244	720	1.5	11
pyrrolidino-C ₆₀ III ^b	toluene	707	300	726	1.5	10
amino-C ₆₀ IV ^a	toluene	694	246	713	1.3	9.1
poly-C ₆₀ polymer	DMSO			760	<i>c</i>	1.8

^a From ref 6. ^b From ref 5. ^c Nonexponential decay.**Figure 3.** Absorption spectra of the C₆₀-dimer in toluene (—), *o*-xylene (---), 1,2,4-trimethylbenzene (- · - ·), and 1,2,3,5-tetramethylbenzene (····). Shown in the inset are the absorption spectra of C₆₀ in the same solvents for comparison.

structured and that there is no sharp absorption peak in the 400–450 nm region, which has been considered as a fingerprint in the spectra of monofunctionalized methano- and pyrrolidino-C₆₀ derivatives.

Absorption spectra of the C₆₀ dimer were also measured in the solvent series of methyl-substituted benzenes including toluene, *o*-xylene, 1,2,4-trimethylbenzene, and 1,2,3,5-tetramethylbenzene and in other solvents including CS₂, chlorobenzene, *o*-dichlorobenzene, and 1-chloronaphthalene. As shown in Figure 3, there are systematic changes in the blue region of the absorption spectra in the solvent series of methyl-substituted benzenes. The changes are similar to those observed for C₆₀ in the same solvent series, namely, that the more intense blue absorption band undergoes red shift with increasing number of methyl groups in the substituted benzenes (Figure 3).⁵

The poly-C₆₀ polymer is insoluble in common organic solvents. However, a fraction of the polymer sample is slightly soluble in room-temperature DMSO, which allows the determination of the absorption spectrum. In the absorption spectral measurement, the polymer sample was dissolved in DMSO through sonication and the solution was carefully filtered through 0.2 μ m Teflon filters. As shown in Figure 4, the absorption spectrum of the poly-C₆₀ polymer in room-temperature DMSO is a structureless curve. A comparison of the normalized absorption spectra in Figure 4 shows that absorptivities in the blue region of the spectra are lower in the polymer than in the dimer.

**Figure 4.** Absorption and fluorescence spectra of the poly-C₆₀ polymer in DMSO (---), the C₆₀ dimer in toluene (—), and C₆₀ in toluene (····).

Fluorescence Spectra. The fluorescence spectrum of the C₆₀ dimer in room-temperature toluene (concentration $\sim 2.5 \times 10^{-5}$ M) is shown in Figure 4. The spectrum is different from that of C₆₀ but similar to those of other classes of C₆₀ derivatives (Figure 5). In addition to the 0–0 emission band at ~ 720 nm, there is a peak at ~ 790 nm and a shoulder at ~ 900 nm. The fluorescence spectrum of the dimer is rather inert to changes in solvent environment. The spectra are essentially the same in solvents of different polarities and polarizabilities, even in the solvent series of methyl-substituted benzenes including toluene, *o*-xylene, 1,2,4-trimethylbenzene, and 1,2,3,5-tetramethylbenzene (Figure 6).

The fluorescence spectrum of the poly-C₆₀ polymer was measured in room-temperature DMSO following the same experimental procedure as that for the absorption spectrum. As shown in Figure 4, the spectra of the poly-C₆₀ polymer and the C₆₀ dimer have similar vibrational profiles. However, the spectrum of the polymer is broader, with the 0–0 emission band ~ 40 nm red-shifted (Figure 4).

Fluorescence Quantum Yields. Fluorescence quantum yields of the C₆₀ dimer in room-temperature solutions were measured in reference to the yield of C₆₀ in toluene (3.2×10^{-4}), which was determined using rhodamine 101 in ethanol as a standard.^{8a} In toluene, the yield of the C₆₀ dimer is 9.2×10^{-4} , which is about 3 times higher than that of C₆₀ and is similar to those of other classes of C₆₀ derivatives.^{5,6}

Fluorescence quantum yields of the C₆₀ dimer in different solvents were also determined. Effects due to changes in solvent refractive index on fluorescence yield measurements were corrected.⁴⁶ The fluorescence yields are only weakly solvent

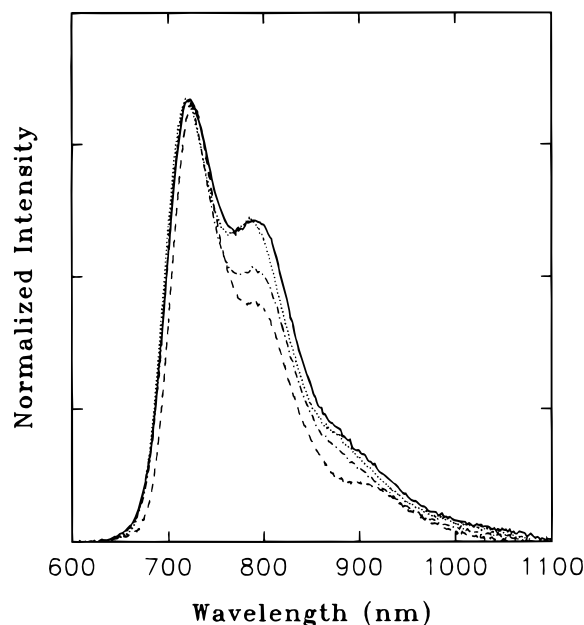


Figure 5. Fluorescence spectrum of the C_{60} dimer **I** (—) is compared with the spectra of the methano- C_{60} derivative **II** (···), pyrrolidino- C_{60} derivative **III** (---), and amino- C_{60} derivative **IV** (-·-) in room-temperature solutions.

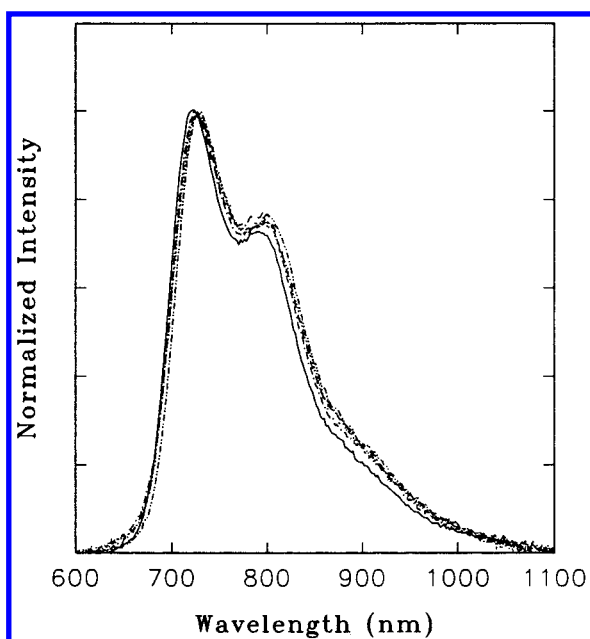


Figure 6. Fluorescence spectra of the C_{60} dimer in toluene (—), *o*-xylene (---), 1,2,3,5-tetramethylbenzene (···), CS_2 (-·-), and *o*-dichlorobenzene (-·-).

dependent. As shown in Table 2, the yields in different solvents vary in the range 7.8–9.2, and the $\Phi_{F,DIMER}/\Phi_{F,C_{60}}$ ratios vary in the range 2.4–3.1 (Table 2), with an average of 2.8. Interestingly, while the yields of the C_{60} dimer are noticeably smaller in CS_2 and larger in 1,2,3,5-tetramethylbenzene, the $\Phi_{F,DIMER}/\Phi_{F,C_{60}}$ ratios in the two solvents are actually close to the average 2.8.

For the poly- C_{60} polymer in room-temperature DMSO, the fluorescence quantum yield was also measured in reference to the yield of C_{60} . As compared in Table 1, the polymer has a lower fluorescence quantum yield (1.8×10^{-4}) than both the C_{60} dimer and C_{60} .

Fluorescence Decays. Fluorescence decays were measured using the time-correlated single photon counting method. For

C_{60} in toluene, the fluorescence lifetime of 1.2 ns thus obtained is in excellent agreement with the results reported in the literature.^{4,7} For the C_{60} dimer in both toluene and *o*-dichlorobenzene at room temperature, the fluorescence decay curves can be deconvoluted well from the corresponding instrument response functions in terms of a monoexponential equation. The fluorescence lifetimes of the C_{60} dimer are 1.5 ns in toluene and 1.3 ns in *o*-dichlorobenzene, which are longer than that of C_{60} .

The fluorescence decay of the poly- C_{60} polymer in DMSO was measured in a similar fashion (Figure 7). However, the decay curve cannot be deconvoluted from the corresponding instrument response function by using a mono-, bi-, or triexponential equation. Qualitatively, it appears that the overall fluorescence decay of the poly- C_{60} polymer in DMSO is faster than those of the C_{60} dimer and C_{60} (Figure 7).

C_{60} Dimer Photostability. A solution of the C_{60} dimer in toluene was photoirradiated using a 450 W xenon lamp. Effects of photoirradiation on the solution were monitored in absorption and fluorescence measurements. The results show no meaningful changes in both absorption and fluorescence spectra of the dimer solution after 10 h of continuous photoirradiation. It may thus be concluded that the C_{60} dimer is photochemically stable.

Electron-Transfer Quenching and Exciplex Formation. Similar to C_{60} and C_{60} derivatives, the C_{60} dimer undergoes electron-transfer interactions with electron donor *N,N*-dimethylaniline (DMA) in both ground and excited singlet states. The formation of a ground-state charge-transfer complex requires high DMA concentrations. At low DMA concentrations (<0.3 M), the electron-transfer quenching of the excited singlet state and the formation of C_{60} dimer–DMA exciplex may be studied without the interference of ground-state complexation. As shown in Figure 8 for the C_{60} dimer in room-temperature toluene solutions containing different concentrations of DMA, fluorescence intensities are significantly quenched. However, when normalized (Figure 8, inset), the fluorescence intensities at longer wavelengths are relatively higher at higher DMA concentrations, which can be attributed to contributions of an emissive C_{60} dimer–DMA exciplex.

Optical Limiting. Optical limiting measurements were carried out at 532 nm using the setup illustrated in Figure 1. For the purpose of calibration, the optical limiting responses of C_{60} in toluene were determined, and the results are in excellent agreement with those reported in the literature.¹³ For the C_{60} dimer, optical limiting measurements were performed in toluene and *o*-dichlorobenzene solutions with a linear transmittance of 74%. As shown in Figure 9, the output fluence I_{OUT} is nonlinear with the input fluence I_{IN} and reaches a plateau at the input fluence I_{IN} of $\sim 0.6 \text{ J/cm}^2$. The saturated I_{OUT} value at the plateau is $\sim 0.24 \text{ J/cm}^2$ (Table 3). Apparently, the optical limiting responses of the C_{60} dimer are weaker than those of C_{60} at the same linear transmittance. The saturated I_{OUT} value at the plateau for C_{60} in toluene with the same linear transmittance of 74% is only $\sim 0.13 \text{ J/cm}^2$ (Figure 9).

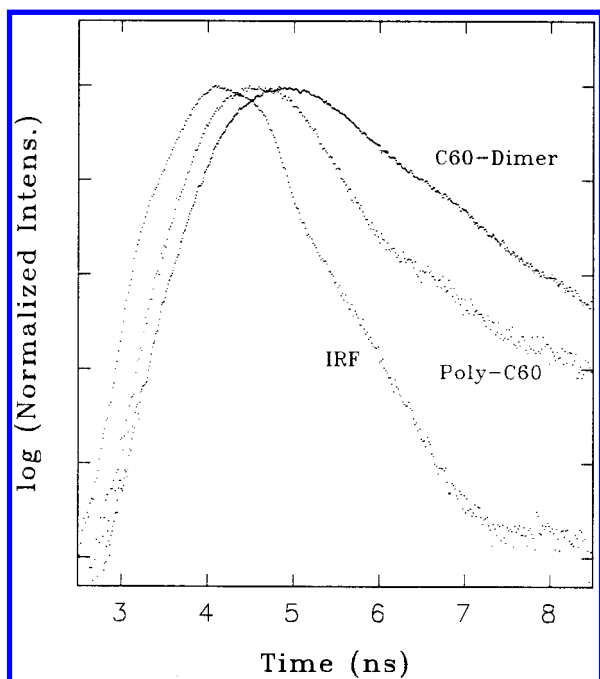
Optical limiting measurements were carried out in a similar fashion for the poly- C_{60} polymer in DMSO solution of 60% linear transmittance. As shown in Figure 10, the output light fluences do not follow the linear transmittance line with respect to input light fluences, which indicates some weak optical limiting responses. However, there is no plateau at input light fluences up to 0.75 J/cm^2 (Figure 10).

Triplet-State Properties. In a search for possible phosphorescence, the emission spectrum of the C_{60} dimer was measured in toluene at 77 K. The low-temperature spectrum is rather

TABLE 2: Fluorescence Quantum Yields of the C₆₀ Dimer in Different Solvents at Room Temperature^a

solvent	<i>n</i>	ε	Φ _{F,C₆₀} (×10 ⁴)	Φ _{F,DIMER} (×10 ^{−4})	Φ _{F,DIMER} /Φ _{F,C₆₀}
toluene	1.496	2.379	3.2	9.2	2.9
1:1 (v/v) toluene–hexane ^b	1.443	2.173		9.6	
5:1 (v/v) toluene–acetonitrile ^b	1.465	10.10		8.7	
<i>o</i> -xylene	1.506	2.568	2.9	9.1	3.1
1,2,4-trimethylbenzene	1.505	2.264	3.1	9.1	2.9
1,2,3,5-tetramethylbenzene	1.513	2.289	3.2	9.6	3.0
carbon disulfide	1.632	2.641	2.6	6.8	2.6
chlorobenzene	1.524	5.710	2.8	7.5	2.7
<i>o</i> -dichlorobenzene	1.552	9.930	3.0	7.9	2.6
1-chloronaphthalene	1.633		3.4	8.0	2.4

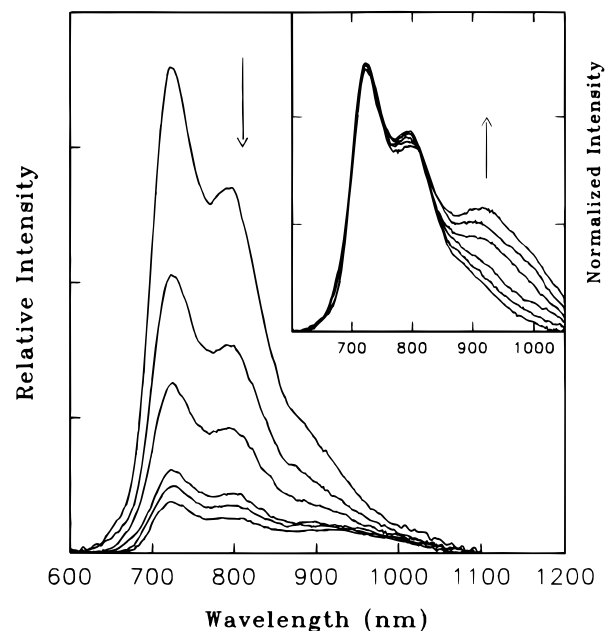
^a The Φ_F values were corrected for refractive index differences in different solvents. ^b The refractive index and dielectric constant of the binary solvent mixture were estimated by algebraic averaging based on mole fractions.

**Figure 7.** Fluorescence decays of the poly-C₆₀ polymer in DMSO and the C₆₀ dimer in toluene.

similar to the room-temperature spectrum, except for better structural resolution in the 700–800 nm wavelength region (Figure 11). The result seems to suggest no meaningful contribution from phosphorescence at 77 K.

Transient absorption spectra were measured using laser flash photolysis method. The sample solutions for the measurements were carefully degassed through repeated (up to 14 cycles) freeze–pump–thaw. The transient absorption spectrum of C₆₀ in toluene was recorded for the purpose of calibration, and the spectrum is in excellent agreement with those already reported in the literature (Figure 12).^{11a} For the C₆₀ dimer, a toluene solution of 20 μM concentration was used in the measurement, which corresponds to an optical density at the excitation wavelength 355 nm of ~1.0. The transient absorption spectrum of the C₆₀ dimer in toluene thus obtained is compared with those of C₆₀ and the methano-C₆₀ derivative **II** in Figure 12. The spectrum of the C₆₀ dimer is broad without clear structures. It is also significantly weaker than those of C₆₀ and the methano-C₆₀ derivative (Figure 12). While the main absorption peak in the spectrum of the methano-C₆₀ derivative is ~25 nm blue-shifted from that in the spectrum of C₆₀, the main absorption peak of the dimer remains unshifted at ~750 nm (Figure 12).

A kinetic analysis of the transient decay trace yields a triplet-state lifetime of 10 μs for the C₆₀ dimer in room-temperature toluene. However, the triplet-state lifetime of C₆₀ in toluene

**Figure 8.** Fluorescence spectra of the C₆₀ dimer in room-temperature toluene at different DMA concentrations of (in the direction of the arrow) 0, 0.036, 0.075, 0.15, 0.19, and 0.25 M. Shown in the inset are the spectra normalized at the first emission peak.

obtained using the same experimental setup under the same conditions is ~70 μs, which is significantly shorter than the 133 μs result reported by Weisman and co-workers.⁴⁷ Despite much effort in the decay measurement, which includes the use of extremely dilute solutions and low excitation light intensity, we have not been able to reach the same optimization achieved by Weisman and co-workers.⁴⁷ Thus, it is likely that the observed triplet lifetime of 10 μs for the C₆₀ dimer represents the lower limit.

The triplet-state absorption of the poly-C₆₀ polymer in a carefully deoxygenated DMSO solution was investigated under the same experimental conditions as those for the C₆₀ dimer and C₆₀. However, the transient absorption signals are too weak to be distinguished clearly from the noise. According to the experimental results, it may be safely concluded that the triplet-state absorption in the poly-C₆₀ polymer is weaker than those in the C₆₀ dimer and C₆₀ by at least an order of magnitude.

Discussion

The absorption spectrum of the C₆₀ dimer **I** is apparently different from that of C₆₀ but similar to that of the amino-C₆₀ derivative **IV** (Figure 2, inset). Both spectra are broad and without the sharp absorption peak in the 400–450 nm region that is regarded as a fingerprint for mono-functionalized

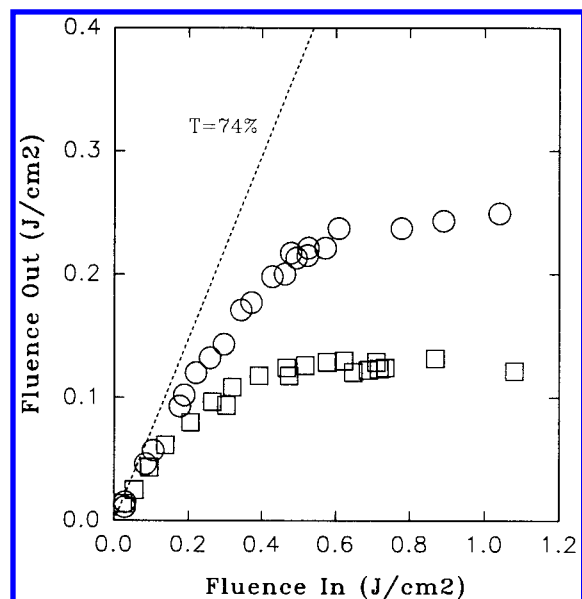


Figure 9. Optical limiting results of the C_{60} dimer in the solution with a linear transmittance of 74% at 532 nm are compared with those of C_{60} (\square) under the same experimental conditions.

TABLE 3: Optical Limiting Properties of the C_{60} Dimer and Poly- C_{60} Polymer Compared with Those of Other Representative C_{60} Derivatives

compound	solvent	I_{OUT} at saturation (J/cm^2)			
		$T = 74\%$	$T = 72\%$	$T = 70\%$	$T = 60\%$
C_{60}	toluene	0.13		0.1	~ 0.055
C_{60} dimer I	toluene	0.24			
	<i>o</i> -DCB	0.24			
methano- C_{60} II ^a	toluene			0.11	
pyrrolidino- C_{60} III ^b	toluene			0.11	
amino- C_{60} IV ^a	toluene		0.13		
poly- C_{60} polymer	DMSO				^c

^a From ref 6. ^b From ref 26. ^c No saturation at input light fluences up to 0.75 J/cm^2 .

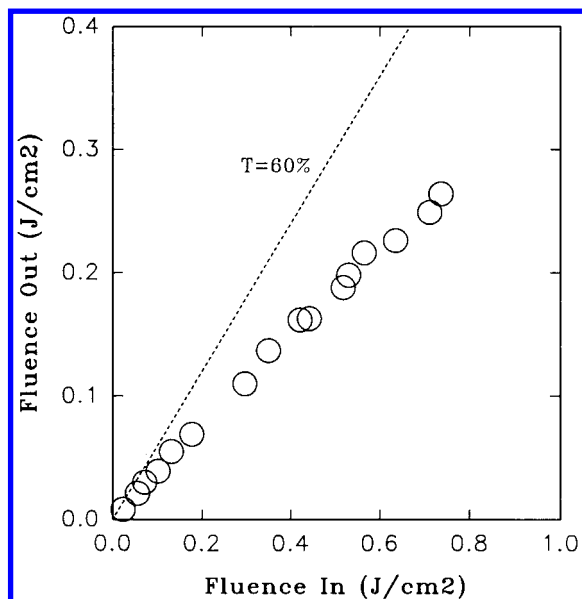


Figure 10. Optical limiting results of the poly- C_{60} polymer in DMSO solution with a linear transmittance of 60% at 532 nm.

methano- C_{60} and pyrrolidino- C_{60} derivatives. However, the similarity between the absorption spectral profiles of the dimer and the amino- C_{60} is unlikely due to any structural relationships between the two molecules. Since the absorption spectrum of

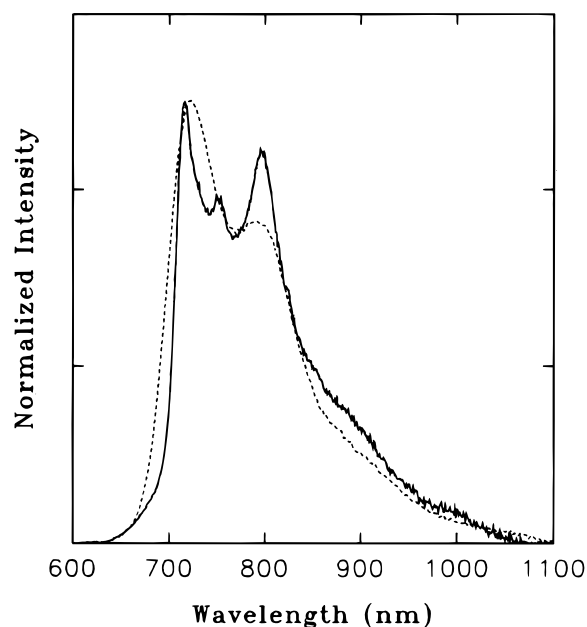


Figure 11. Emission spectrum of the C_{60} dimer in toluene at 77 K (—) is compared with the fluorescence spectrum in room-temperature toluene (---).

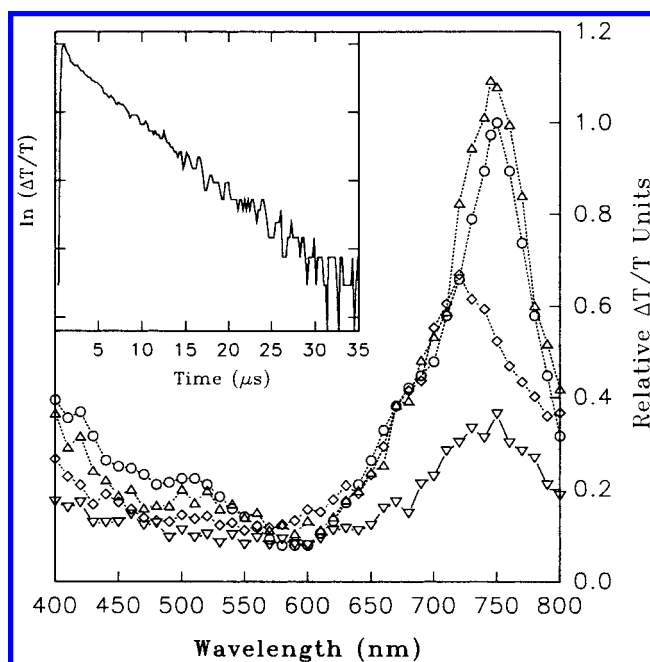


Figure 12. Transient absorption spectrum of the C_{60} dimer (∇) is compared with those of C_{60} (Δ , this work; \circ , ref 11a) and the methano- C_{60} derivative II (\diamond) in room-temperature solutions. The extinction coefficient at the C_{60} absorption peak (~ 750 nm) is 12 000 $M^{-1} cm^{-1}$ according to ref 11a, though other values have also been reported in the literature.¹² Shown in the inset is the excited-triplet-state decay trace of the C_{60} dimer monitored at 740 nm.

the dimer is already broad, it seems no surprise that the spectrum of the poly- C_{60} polymer is even broader to become a structureless curve (Figure 4) due to the inhomogeneity associated with the polymeric structure.

The lowest energy electronic transition in the C_{60} dimer is red-shifted from that in C_{60} . However, the 0–0 absorption band of the C_{60} dimer at 698 nm is close to those (694–707 nm) of other C_{60} derivatives. It has been shown^{5,6} that molar absorptivities are not dramatically different between C_{60} derivatives, even for derivatives in different classes. The observed molar

absorptivities of the C₆₀ dimer are much higher (Figure 2) simply because each mole of the dimer consists of 2 mol of C₆₀ cages. In fact, the absorptivities per mole of C₆₀ cages are quite similar between the C₆₀ dimer and other C₆₀ derivatives (Figure 2). It implies that the electronic structures of the two cages in the C₆₀ dimer are independent without substantial interactions with respect to electronic transitions. The comparison of 0–0 absorption energies and transition probabilities between the C₆₀ dimer and C₆₀ derivatives in different classes shows that the low-lying electronic transitions in the derivatized fullerene molecules are dictated by the electronic structures of the 1,2-functionalized fullerene cages and much less affected by the functional groups attached to the cages.^{5,6} In this regard, the C₆₀ dimer may be considered as two linked C₆₀ derivatives with a [6,6]-closed functionalization (1,2-addition) pattern. It is thus no surprise that the C₆₀ dimer exhibits similar absorption spectral changes to those observed for C₆₀ and methano- and pyrrolidino-C₆₀ derivatives in the solvent series of methyl-substituted benzenes (Figure 3).⁵ However, the nature of the apparently specific interactions between the fullerene cage and methyl-substituted benzenes remains to be understood.

The fluorescence spectrum of the C₆₀ dimer again supports the notion that the dimer may be considered as a pair of 1,2-functionalized C₆₀ derivatives. There are only small differences between the fluorescence spectra of the C₆₀ dimer and other C₆₀ derivatives (Figure 5). The fluorescence and absorption results are consistent with respect to the conclusion that the low-lying electronic transitions in C₆₀ derivatives are dictated by the electronic structures of the 1,2-functionalized fullerene cages and much less affected by the functional groups attached to the cages.^{5,6}

With the two linked fullerene cages, the C₆₀ dimer may be considered as a bichromophoric system. For many arene-based bichromophoric molecules in which two arene species are linked by a single bond (9,9'-bianthryl, for example), the formation of a twisted intramolecular charge transfer (TICT) state is a commonly observed decay pathway in the excited singlet state.^{48,49} The TICT state formation is typically extremely dependent on the solvent polarity and, in most cases, observed only in a polar solvent environment.^{48,49} Fluorescence properties of the C₆₀ dimer in solvents of different polarities apparently do not suggest such an excited-singlet-state decay process. The photoexcited C₆₀ cage is easily reduced by an electron donor to form a relatively more stable radical anion, hard to be oxidized to form a radical cation. As a result, it is difficult to form an intramolecular radical ion pair in the C₆₀ dimer. The linkage of the two fullerene cages through two single bonds in the C₆₀ dimer also hinders the excited-state intramolecular twisting, which is often necessary for the electron transfer in arene-based bichromophoric systems because of the twisting related "sudden polarization" phenomenon.⁴⁸ Thus, it is understandable that there is no intramolecular electron-transfer process in the C₆₀ dimer following photoexcitation.

According to the cyclic voltammetry results, reduction potentials of the C₆₀ dimer are similar to those of C₆₀.⁴⁰ As in C₆₀ and methano- and pyrrolidino-C₆₀ derivatives, the excited singlet state in the C₆₀ dimer is quenched efficiently through electron transfer by DMA. The quenching in room-temperature toluene is accompanied by the formation of an emissive exciplex (Figure 8). For C₆₀, the exciplex emission is observable only in an aliphatic hydrocarbon solvent such as hexane or methylcyclohexane, but not in a more polarizable solvent such as toluene. However, an emissive exciplex between the methano-C₆₀ derivative **II** or the pyrrolidino-C₆₀ derivative **III** and DMA

was observed in both aliphatic and aromatic hydrocarbon solvents.⁵ The C₆₀ dimer is apparently different from C₆₀ but similar to the C₆₀ derivatives with respect to the formation and decay of an emissive exciplex with DMA. Again, the C₆₀ dimer behaves as a pair of 1,2-functionalized C₆₀ derivatives.

As discussed above, the absorption properties of the C₆₀ dimer suggest no substantial interactions between the ground-state electronic structures of the two fullerene cages with respect to electronic transitions. Thus, the photoexcitation is likely localized at one of the two fullerene cages in the C₆₀ dimer. The possibility of significant intramolecular interactions between the photoexcited fullerene cage and the ground-state fullerene cage in the C₆₀ dimer should be considered. The consequence of such interactions may include excited-state quenching and the formation of an excimer-like excited state. In a classical excimer system such as pyrene, the excited pyrene molecule is quenched by ground-state pyrene (self-quenching) to form a singlet excimer with a sandwich-like structural arrangement between the two pyrene molecules.⁵⁰ The pyrene–pyrene distance in the sandwich-like excimer structure is ~3.5 Å, which allows an effective overlap between the π orbitals of the two pyrene molecules.⁵⁰ For C₆₀ in room-temperature solution, there is no intermolecular self-quenching of the excited singlet state. The observed fluorescence lifetimes of a dilute solution of C₆₀ in toluene and a nearly saturated solution of C₆₀ in *o*-dichlorobenzene are essentially the same.⁵¹ The absence of concentration-dependent self-quenching of the C₆₀ excited singlet state is likely due to the short fluorescence lifetime, which makes the contribution of self-quenching relatively insignificant even in the saturated *o*-dichlorobenzene solution of C₆₀ with diffusion-controlled quenching rate constant ($k_d[C_{60}]$). However, self-quenching is known to be a dominant decay pathway of the C₆₀ excited triplet state in fairly dilute solutions.⁴⁷ For the C₆₀ dimer, results from our semiempirical MNDO calculations show that the intercage C–C bond length is ~1.58 Å in the gas phase, which is longer than the C(sp³)–C(sp³) bonds in ordinary hydrocarbons. The results are consistent with those obtained from X-ray crystallography analyses of the C₆₀ dimer in the solid state.⁴⁰ The center-to-center distance between the two fullerene cages in the C₆₀ dimer is ~9 Å. Despite the close distance between the excited-state and ground-state fullerene cages intramolecularly, the fluorescence results of the C₆₀ dimer seem to suggest no meaningful intramolecular quenching of the excited singlet state. The intramolecular self-quenching rate constant must be too small to make the process competitive within the fluorescence lifetime.

For the excited triplet state of the C₆₀ dimer, the observed lifetime is somewhat shorter than those of other C₆₀ derivatives.²² The possible effect of intramolecular intercage quenching may be evaluated in a more quantitative fashion. With the assumption that the observed excited-triplet-state lifetime τ_T is already affected by the intramolecular self-quenching and the intrinsic excited-triplet-state lifetime without the quenching effect is τ_T^0 , there is the following relationship:

$$\tau_T^0/\tau_T = 1 + k_q\tau_T^0 \quad (1)$$

where k_q is the intramolecular fullerene excited-triplet-state self-quenching rate constant. Since τ_T is available experimentally, eq 2 can be rearranged as follows.

$$\tau_T^0 = (1/\tau_T - k_q)^{-1} \quad (2)$$

Obviously, $1/\tau_T - k_q > 0$ is required for a nonnegative τ_T^0 value. Thus,

$$k_q < 1/\tau_T \quad (3)$$

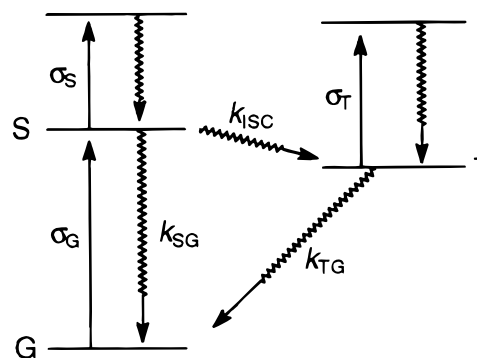
For the C₆₀ dimer, the shorter limit of the excited-triplet-state lifetime τ_T is 10 μ s, as reported in the Results section. It follows that the upper limit for k_q is 10⁵ s⁻¹. The result shows that the intramolecular intercage quenching of the excited triplet state in the C₆₀ dimer is inefficient, comparable at best to the intermolecular self-quenching in a C₆₀ solution of moderate concentration.⁴⁷

With the cage structure, fullerene molecules apparently cannot achieve the kind of sandwich arrangement as pyrene molecules in the excimer formation. Thus, the issue concerning fullerene excimers is particularly interesting. It has been reported that the self-quenching of C₇₀ excited triplet state is accompanied by the formation of a triplet C₇₀ excimer.⁵² The C₇₀ excimer formation may have something to do with the fact that the excited triplet state of C₇₀ is very long-lived (>12 ms).⁵² Structural details of the fullerene excimer remain to be understood. However, there is no formation of triplet C₆₀ excimer under similar experimental conditions. The results of the C₆₀ dimer also show no intramolecular excimer of C₆₀ cages.

The photostability of the C₆₀ dimer suggests that there is no meaningful excited singlet- or triplet-state ring-opening reaction, which is the reverse of the [2 + 2] photocycloaddition reaction. The result is significant to the mechanistic understanding of fullerene photopolymerization. Existing methods for the preparation of polyfullerenes are based on photochemistry in the solid state (fullerene solid films)³¹ or solidlike state (suspension of fullerene clusters).³⁴ A mechanism of [2 + 2] photocycloaddition through the fullerene excited triplet states has been proposed for the fullerene photopolymerization.^{31,34–36} However, an interesting question is why the same excited-triplet-state photocycloaddition does not happen in carefully deoxygenated solutions with fullerene concentrations varying over a wide range.^{2,53} In fact, according to the results concerning fullerene intermolecular self-quenching and triplet excimer formation,^{47,52} there should be substantial interactions between excited triplet and ground-state fullerene molecules under the experimental conditions for photopolymerization reactions in solutions. Since [2 + 2] cycloaddition is a reversible process in photoexcited states, one may argue that the lack of fullerene photopolymerization in solutions is due to the reaction conditions being unfavorable to the cyclobutane ring formation and that the conditions become more favorable in solid-state or solidlike-state fullerene photoreactions. With such an argument we would then expect an efficient photochemical ring-opening reaction in the C₆₀ dimer, which results in the breaking of intercage bonds. The observed photostability of the C₆₀ dimer obviously suggests otherwise. The result thus raises more questions on the proposed excited-triplet-state [2 + 2] cycloaddition mechanism for the fullerene photopolymerization.

The photophysical properties of the poly-C₆₀ polymer are obviously different from those of the C₆₀ dimer and C₆₀. Of particular interest are the fluorescence parameters. The fluorescence quantum yield of the poly-C₆₀ polymer in room-temperature DMSO is lower than that of C₆₀ and much lower than that of the C₆₀ dimer. The lower fluorescence yield of the polymer must be due to decay processes that are not available in the excited singlet states of the C₆₀ dimer and C₆₀. The unique decay processes in the polymer also compete with intersystem crossing, resulting in a lower triplet-state population. In fact, the triplet–triplet transient absorption of the poly-C₆₀ polymer is hardly detectable under the same experimental conditions as those for the C₆₀ dimer and C₆₀ (Figure 12). Mechanistic details of the unique decay processes in the polymer

SCHEME 1



remain to be understood. One possibility is intramolecular self-quenching of the excited fullerene cage by surrounding ground-state fullerene cages in the polymer structure. Intrapolymer excited-state quenching and excimer formation have been observed in many poly(vinylarene) polymers such as polystyrene and poly(vinylanthracene).⁵⁴ However, as discussed above, such a quenching mechanism apparently contributes little to the photophysics of the C₆₀ dimer. Another possibility for the weaker fluorescence of the poly-C₆₀ polymer is the presence of excited-state decay pathways associated with the more floppy polymer structure.

The observed fluorescence spectrum of the poly-C₆₀ polymer is probably a distribution of emissions, which is consistent with the result that the observed fluorescence decay is nonexponential. While the possibility of multiple emissions in the observed fluorescence spectrum is best studied by systematically examining the excitation wavelength dependence, the low fluorescence quantum yield of the poly-C₆₀ polymer makes it very difficult to carry out such experiments.

The optical limiting properties of C₆₀ may be explained in terms of a reverse saturable absorption mechanism.^{13,14} A five-level model (Scheme 1) has been used to describe the reverse saturable absorption in fullerenes and organic dyes.^{14,17,18} Reverse saturable absorption occurs when the excited-state cross sections are larger than the ground-state cross section, $\sigma_{\text{EFF}}/\sigma_G > 1$, where σ_{EFF} includes a weighted average of σ_S and σ_T .¹⁸ This is certainly the case for C₆₀, with both σ_S and σ_T significantly larger than σ_G at 532 nm. Because of the nanosecond intersystem crossing rate constant, the optical limiting responses of a C₆₀ solution toward 5–10 ns laser pulses are due predominantly to the strong excited-triplet-state absorption. Thus, the factor $\sigma_{\text{EFF}}/\sigma_G$ for evaluating the nonlinear absorption is reduced to $\Phi_{\text{ISC}}\sigma_T/\sigma_G$, where Φ_{ISC} denotes the intersystem crossing quantum yield. For C₆₀, Φ_{ISC} is unity.

The optical limiting properties of the C₆₀ dimer may similarly be explained in terms of the reverse saturable absorption mechanism (Scheme 1). Since the fluorescence lifetime of the C₆₀ dimer is only slightly longer than that of C₆₀, the optical limiting responses of the C₆₀ dimer toward the nanosecond pulsed laser are likely dominated again by the contribution of the excited-triplet-state absorption. In this regard, the noticeably weaker optical limiting responses of the C₆₀ dimer than those of C₆₀ at 532 nm may be attributed to the fact that the C₆₀ dimer has a lower triplet–triplet absorption cross section (Figure 12).

The poor optical limiting performance of the poly-C₆₀ polymer may be discussed in a similar fashion. The intersystem crossing yield for the polymer is probably much less than unity, which might be largely responsible for the very weak triplet absorption signals. In fact, because of the hardly detectable triplet–triplet absorption of the C₆₀ polymer, and consequently

$\Phi_{ISC}\sigma_T/\sigma_G < 1$, it is surprising that the poly- C_{60} polymer exhibits any optical limiting at all. The observed weak optical limiting responses of the poly- C_{60} polymer solution are probably due to a mechanism other than the nonlinear absorption.

Conclusion

The photophysical properties of the C_{60} dimer are qualitatively similar to those of methano-, pyrrolidino-, and amino- C_{60} derivatives. Thus, as far as the photophysics is concerned, the C_{60} dimer is essentially a pair of linked C_{60} derivatives with each of them having a [6,6]-closed functionalization (1,2-addition) pattern. More quantitatively, there are greater similarities between the C_{60} dimer and other C_{60} derivatives in the absorption and excited-singlet-state properties than in the excited-triplet-state properties. Consequently, since the nonlinear absorptive optical limiting responses in the fullerene molecules are due predominately to the excited-triplet-state absorptions, the C_{60} dimer is a weaker optical limiter than C_{60} and the other C_{60} derivatives at 532 nm. Despite the close distance between the two covalently linked fullerene cages in the C_{60} dimer, there are no substantial intramolecular intercage interactions in both ground and excited states. The intramolecular self-quenching of the excited singlet state is absent, and the self-quenching of the excited triplet state is weak at best, with an excimer or charge-transfer state formation.

The poly- C_{60} polymer is very different from the C_{60} dimer with respect to their excited-state properties and nonlinear absorptive behavior. The great differences may be attributed to additional excited-singlet-state decay processes in the polymer that are not available in the dimer, though there is always the question whether the C_{60} dimer is indeed a structural model for the poly- C_{60} polymer. In addition, the C_{60} dimer excited-state properties and the photostability in particular raise interesting questions on the proposed excited-triplet-state $[2 + 2]$ mechanism for the fullerene photopolymerization. Further investigations are needed.

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References and Notes

- (1) (a) Foote, C. S. In *Topics in Current Chemistry, Electron-Transfer I*; Mattay, J., Ed.; Springer-Verlag: Berlin, 1994; p 347. (b) Foote, C. S. In *Light-Activated Pest Control*; ACS Symp. Ser. 616; Heitz, J. R., Downum, K. R., Eds.; American Chemical Society: Washington, DC, 1995; p 17.
- (2) Sun, Y.-P. In *Molecular and Supramolecular Photochemistry, Vol. I*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 1997; p 325.
- (3) (a) Leach, S. In *Physics and Chemistry of the Fullerenes*; Prassides, K., Ed.; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1994; p 117. (b) Jensen, A. W.; Wilson, S. R.; Schuster, D. I. *Bioorg. Med. Chem.* **1996**, *4*, 767.
- (4) Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 4093.
- (5) Ma, B.; Bunker, C. E.; Guduru, R.; Zhang, X.-F.; Sun, Y.-P. *J. Phys. Chem. A* **1997**, *101*, 5626.
- (6) Sun, Y.-P.; Lawson, G. E.; Riggs, J. E.; Ma, B.; Wang, N.-X.; Moton, D. K. *J. Phys. Chem. B* **1998**, *102*, 2, in press.
- (7) (a) Kim, D.; Lee, M.; Suh, Y. D.; Kim, S. K. *J. Am. Chem. Soc.* **1992**, *114*, 4429. (b) Catalán, J.; Elguero, J. *J. Am. Chem. Soc.* **1993**, *115*, 9249.
- (8) (a) Ma, B.; Sun, Y.-P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2157. (b) Sun, Y.-P.; Wang, P.; Hamilton, N. B. *J. Am. Chem. Soc.* **1993**, *115*, 6378.
- (9) The fluorescence yield was determined from the complete spectrum obtained by using a near-infrared-sensitive emission spectrometer (up to 1150 nm).^{8a} The quantum yield value is $\sim 33\%$ larger than the earlier values obtained from the fluorescence spectra in the wavelength region to only 850 nm.^{4,8a}
- (10) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Whetten, R. B. *J. Phys. Chem.* **1991**, *95*, 11.
- (11) (a) Dimitrijevic, N. M.; Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 4811. (b) Sension, R. J.; Phillips, C. M.; Szarka, A. Z.; Romanow, W. J.; McGhie, A. R.; McCauley, Jr., J. P.; Smith III, A. B.; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 6075. (c) Biczok, K.; Linschitz, H.; Walter, R. I. *Chem. Phys. Lett.* **1992**, *195*, 339. (d) Kajii, Y.; Nakagawa, T.; Suzuki, S.; Achiba, Y.; Obi, K.; Shibuya, K. *Chem. Phys. Lett.* **1991**, *181*, 100. (e) Watanabe, A.; Ito, O.; Watanabe, M.; Saito, H.; Koishi, M. *J. Chem. Soc., Chem. Commun.* **1996**, 117. (f) Sauve, G.; Dimitrijevic, N. M.; Kamat, P. *J. Phys. Chem.* **1995**, *99*, 1199. (g) Ebbeson, T. W.; Tanigaki, K.; Sadanori, K. *Chem. Phys. Lett.* **1991**, *181*, 501. (h) Lee, M.; Song, O.-K.; Seo, J.-C.; Kim, D. *Chem. Phys. Lett.* **1992**, *196*, 325. (i) Arbogast, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 8886.
- (12) Bensasson, R. V.; Hill, T.; Lambert, C.; Land, E. J.; Leach, S.; Truscott, T. G. *Chem. Phys. Lett.* **1993**, *201*, 326.
- (13) Tutt, L. W.; Kost, A. *Nature* **1992**, *356*, 225.
- (14) McLean, D. G.; Sutherland, R. L.; Brant, M. C.; Brandelik, D. M. *Opt. Lett.* **1993**, *18*, 858.
- (15) (a) Gvishi, R.; Bhawalkar, J. D.; Kumar, N. D.; Ruland, G.; Narang, U.; Prasad, P. N. *Chem. Mater.* **1995**, *7*, 2199. (b) Prasad, P. N.; Gvishi, G. R.; Kumar, N. D.; Bhawalkar, J. D.; Narang, U. *Proc. SPIE-Int. Soc. Opt. Eng.* **1995**, *2530*, 128.
- (16) Kost, A.; Tutt, L.; Klein, M. B.; Dougherty, T. K.; Elias, W. E. *Opt. Lett.* **1993**, *18*, 334.
- (17) Tutt, L.; Boggess, T. F. *Prog. Quantum Electron.* **1993**, *17*, 299.
- (18) Perry, J. W.; Mansour, K.; Lee, I.-Y. S.; Wu, X.-L.; Bedworth, P. V.; Chen, C.-T.; Ng, D.; Marder, S. R.; Miles, P.; Wada, T.; Tian, M.; Sasabe, H. *Science* **1996**, *273*, 1533.
- (19) Anderson, J. L.; An, Y.-Z.; Rubin, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1994**, *116*, 9763.
- (20) Williams, R. M.; Koeberg, M.; Lawson, J. M.; An, Y.-Z.; Rubin, Y.; Paddon-Row, M. N.; Verhoeven, J. M. *J. Org. Chem.* **1996**, *61*, 5055.
- (21) Lin, S.-K.; Shiu, L.-L.; Chien, K. M.; Luh, T.-Y.; Lin, T.-I. *J. Phys. Chem.* **1995**, *99*, 105.
- (22) (a) Guldi, D. M.; Hungerbuehler, H.; Asmus, K.-D. *J. Phys. Chem.* **1995**, *99*, 9380. (b) Guldi, D. M.; Asmus, K.-D. *J. Phys. Chem. A* **1997**, *101*, 1472. (c) Guldi, D. M.; Hungerbuehler, H.; Asmus, K.-D. *J. Phys. Chem.* **1995**, *99*, 13487. (d) Guldi, D. M.; Hungerbuehler, H.; Asmus, K.-D. *J. Phys. Chem. A* **1997**, *101*, 1783.
- (23) Sun, Y.-P.; Bunker, C. E.; Lawson, G. E.; Wang, N.-X.; Dabestani, R., manuscript in preparation.
- (24) (a) Nakamura, Y.; Minowa, T.; Hayashida, Y.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Chem. Soc., Faraday Trans.* **1996**, *377*. (b) Imahori, H.; Cardoso, S.; Tatman, D.; Lin, S.; Noss, L.; Seely, G. R.; Sereno, L.; De Silbert, J. C.; Moore, T. A.; Moore, A. L.; Gust, D. *Photochem. Photobiol.* **1995**, *62*, 1009.
- (25) Smilowitz, L.; McBranch, D.; Klimov, V.; Robinson, J. M.; Koskelo, A.; Grigorova, M.; Mattes, B. R.; Wang, H.; Wudl, F. *Opt. Lett.* **1996**, *21*, 922.
- (26) Sun, Y.-P.; Riggs, J. E. *Chem. Mater.* **1997**, *9*, 1268.
- (27) Sun, Y.-P.; Riggs, J. E. *Proc. SPIE-Int. Soc. Opt. Eng.* **1997**, *3142*, 83.
- (28) (a) Fischer, J. E. *Science* **1994**, *264*, 1548. (b) Hirsch, A. *Adv. Mater.* **1993**, *5*, 859. (c) Geckeler, K. E. *Trends Polym. Sci.* **1994**, *2*, 355.
- (29) (a) Cao, T.; Webber, S. E. *Macromolecules* **1995**, *28*, 3741. (b) Cao, T.; Webber, S. E. *Macromolecules* **1996**, *29*, 3826. (c) Camp, A. G.; Lary, A.; Ford, W. T. *Macromolecules* **1995**, *28*, 7959. (d) Bunker, C. E.; Lawson, G. E.; Sun, Y.-P. *Macromolecules* **1995**, *28*, 3744. (e) Sun, Y.-P.; Lawson, G. E.; Bunker, C. E.; Johnson, R. A.; Ma, B.; Farmer, C.; Riggs, J. E.; Kitaygorodskiy, A. *Macromolecules* **1996**, *29*, 8441.
- (30) (a) Geckeler, K. E.; Hirsch, A. *J. Am. Chem. Soc.* **1993**, *115*, 3850. (b) Hawker, C. J. *Macromolecules* **1994**, *27*, 4836. (c) Patil, A. O.; Schriver, G. W.; Carstensen, B.; Lundberg, R. D. *Polym. Bull.* **1993**, *30*, 187. (d) Liu, B.; Bunker, C. E.; Sun, Y.-P. *J. Chem. Soc., Chem. Commun.* **1996**, 1241.
- (31) Rao, A. M.; Zhou, P.; Wang, K.-A.; Hager, G. T.; Holden, J. M.; Wang, Y.; Lee, W.-T.; Bi, X.-X.; Eklund, P. C.; Cornett, D. S.; Duncan, M. A.; Amster, I. J. *Science* **1993**, *259*, 955.
- (32) Iwasa, Y.; Arima, T.; Fleming, R. M.; Siegrist, T.; Zhou, O.; Haddon, R. C.; Rothberg, L. J.; Lyons, K. B.; Carter, H. L., Jr.; Hebard, A. F.; Tycko, R.; Dabbagh, G.; Krajewski, J. J.; Thomas, G. A.; Yagi, T. *Science* **1994**, *264*, 1570.
- (33) Pekker, S.; Jánossy, A.; Mihály, L.; Chauvet, O.; Carrard, M.; Forró, L. *Science* **1994**, *265*, 1077.
- (34) Sun, Y.-P.; Ma, B.; Bunker, C. E.; Liu, B. *J. Am. Chem. Soc.* **1995**, *117*, 12705.
- (35) (a) Cornett, D. S.; Amster, I. J.; Duncan, M. A.; Rao, A. M.; Eklund, P. C. *J. Phys. Chem.* **1993**, *97*, 5036. (b) Zhou, P.; Dong, Z.-H.; Rao, A.

- M.; Eklund, P. C. *Chem. Phys. Lett.* **1993**, *211*, 337. (c) Wang, Y.; Holden, J. M.; Dong, Z.-H.; Bi, X.-X.; Eklund, P. C. *Chem. Phys. Lett.* **1993**, *211*, 341. (d) Wang, Y.; Holden, J. M.; Bi, X.-X.; Eklund, P. C. *Chem. Phys. Lett.* **1994**, *217*, 413. (e) Wang, Y.; Holden, J. M.; Rao, A. M.; Eklund, P. C.; Venkateswaran, U. D.; Eastwood, D.; Lidberg, R. L.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev. B* **1995**, *51*, 4547. (f) Rao, A. M.; Menon, M.; Wang, K.-A.; Eklund, P. C.; Subbaswamy, K. R.; Cornett, D. S.; Duncan, M. A.; Amster, I. J. *Chem. Phys. Lett.* **1994**, *224*, 106.
- (36) (a) Rao, C. N. R.; Govindaraj, A.; Aiyer, H. N.; Seshardi, R. *J. Phys. Chem.* **1995**, *99*, 16814. (b) Sundar, C. S.; Sahu, P. C.; Sastry, V. S.; Rao, G. V. N.; Sridharam, V.; Premila, M.; Bharati, A.; Hariharan, Y.; Radhakrishnan, T. S. *Phys. Rev. B* **1996**, *53*, 8180. (c) Nunez-Regueiro, M.; Marques, L.; Hodeau, J. L.; Bethoux, O.; Perroux, M. *Phys. Rev. Lett.* **1995**, *74*, 278. (d) Onoe, J.; Takeuchi, K. *Phys. Rev. B* **1996**, *54*, 6167.
- (37) (a) Adams, G. B.; Page, J. B.; Sankey, O. F.; Keeffe, M. *Phys. Rev. B* **1994**, *50*, 17471. (b) Porezag, D.; Pederson, M. R. *Phys. Rev. B* **1996**, *52*, 14963. (c) Springborg, M. *Phys. Rev. B* **1995**, *52*, 2935. (d) Surján, P. R.; Udvardi, L.; Németh, K. *Synth. Met.* **1996**, *77*, 107.
- (38) Ma, B.; Lawson, G. E.; Sun, Y.-P. In *Fullerenes, Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1996; Vol. 3, p 783.
- (39) (a) Bunker, C. E.; Rollins, H. W.; Sun, Y.-P. *Fullerene Sci. Technol.* **1997**, *5*, 1579. (b) Ma, B.; Sun, Y.-P., unpublished results.
- (40) Wang, G.-W.; Komatsu, K.; Murata, Y.; Shrio, M. *Nature* **1997**, *387*, 583.
- (41) (a) Ma, B.; Milton, A. M.; Sun, Y.-P. In *Fullerenes, Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1997; Vol. 5, p 526. (b) Ma, B.; Milton, A. M.; Sun, Y.-P. *Chem. Phys. Lett.* **1998**, in press.
- (42) Sun, Y.-P.; Bunker, C. E. *Nature* **1993**, *365*, 398.
- (43) Sun, Y.-P.; Bunker, C. E. *Chem. Mater.* **1994**, *6*, 578.
- (44) (a) Phillies, G. D. J. *Anal. Chem.* **1990**, *62*, 1049A. (b) Weiner, B. B. In *Modern Methods of Particle Size Analysis*; Barth, H. G., Ed.; John Wiley & Sons: New York, 1984; Chapter 3.
- (45) O'Connor, D. V.; Phillips, D. *Time-Correlated Single Photon Counting*; Academic Press: New York, 1984.
- (46) Parker, C. A. *Photoluminescence of Solutions*; Elsevier: Amsterdam, 1968.
- (47) (a) Fraelich, M. R.; Weisman, R. B. *J. Phys. Chem.* **1993**, *97*, 11145. (b) Etheridge, H. T., III; Averitt, R. D.; Halas, N. J.; Weisman, R. B. *J. Phys. Chem.* **1995**, *99*, 11306.
- (48) (a) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971. (b) Lippert, E.; Rettig, W.; Bonačić-Koutecký, V.; Heisel, F.; Miché, J. A. *Adv. Chem. Phys.* **1987**, *68*, 1.
- (49) Bhattacharyya, K.; Chowdhury, M. *Chem. Rev.* **1993**, *93*, 507.
- (50) (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970. (b) Birks, J. B. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: London, 1975; Vol. 2, Chapter 9.
- (51) Bunker, C. E. Ph.D. Dissertation, Clemson University, 1997.
- (52) Etheridge, H. T., III; Weisman, R. B. *J. Phys. Chem.* **1995**, *99*, 2782.
- (53) Ma, B.; Guduru, R.; Sun, Y.-P., unpublished results.
- (54) (a) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469. (b) Ghiggino, K. P.; Haines, D. J.; Smith, T. A.; Wilson, G. J. *Can. J. Chem.* **1995**, *73*, 2015.