Photophysical Properties of a 1,2,3,4,5,6-Hexasubstituted Fullerene Derivative

Khin K. Chin,[†] Shih-Ching Chuang,[†] Billy Hernandez,[‡] Matthias Selke,[‡]
Christopher S. Foote,[†,§] and Miguel A. Garcia-Garibay*[,†]

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569, and
Department of Chemistry and Biochemistry, California State University, Los Angeles, California 90032

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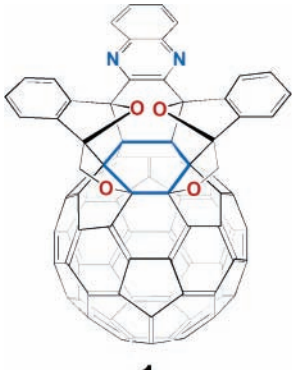
The photophysical properties of a novel 1,2,3,4,5,6-hexasubstituted fullerene derivative (**1**) are examined in this study. In addition to the ground state absorption spectrum of **1**, we report its triplet−triplet absorption spectrum and molar extinction coefficient ($\Delta\epsilon_{T-T}$), as well as the triplet quantum yield (Φ_T), lifetime (τ_T), and energy (E_T). The saturation of a single six-member ring on the fullerene cage results in significant changes in the triplet state properties as compared to that of pristine C_{60}. The triplet−triplet absorption spectrum shows a hypsochromic shift in long wavelength absorption, and both the triplet state lifetime and the triplet quantum yield are decreased. The triplet energy was found to be similar to that of C_{60}. In addition, the quantum yield (Φ_Δ) of singlet oxygen generated by **1** was calculated and is found to be significantly less than in the case of C_{60}.

Introduction

Functionalized fullerene derivatives have attracted much attention in recent years for their widespread application in photovoltaic devices and as potential photodynamic therapeutic agents.[1−5] The poor solubility of pristine C_{60} in polar solvents has made functionalized derivatives preferable alternatives in biological applications[6−15] and in materials science.[16−17] One of the strongest motivations for the functionalization of C_{60} comes from the rich photophysical and electrochemical properties that result by controlled manipulation of the conjugated fullerene core. The saturation of two carbons at a time exposes a wide variety of interesting chromophores with condensed and linearly conjugated π-electron topologies that possess the curvature of the C_{60} surface. Previous reports have shown that small perturbations in the π system give similar photophysical properties as those of pristine fullerene, but a larger number of substitutions result in more significant changes.[18−29] In light of the large number of applications for these novel compounds, there has been widespread effort to elucidate the relationship between the structure of these derivatives and their photophysical properties.[30−34]

Prat et al. have reported a homologous series of methanofullerenes, showing that the number of perturbations of the π system at different sites within the fullerene framework cause systematic changes in the triplet state properties.[30] Foley et al. have examined the effect of the pattern of substitution on photophysical properties with several water-soluble fullerene derivatives.[34] By measuring singlet oxygen production from a set of sequential functionalizations, Hamano et al. have also highlighted the effects of substitution patterns, as well as changes in photophysical properties due to the type of adduct.[33]



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In a recent report, Chuang et al. described the synthesis of the 1,2,3,4,5,6-hexasubstituted fullerene derivative, **1**, which is the first well-characterized example of a fullerene substituted at all carbons of a single six-member ring.[35] This novel fullerene architecture has a unique substitution pattern not examined in any previous reports, which formally represents the chromophore at the end of a nanotube. The structure of **1**, functionalized with a tris-σ-homobenzene moiety,[36−40] is a tris-adduct with all six carbons around a single six-member ring substituted. Several other tris-adducts with different architectures have been reported, and significant effects on the photophysical properties have been shown to depend on the type of substituents and their location on the fullerene cage. The C_3 (all *e*) adduct exists as an orange-red solid,[36b] the D_3 (all-*trans*-3) adduct is cherry-red,[36c] and the C_{3v} (all-*trans*-4) adduct has a unique olive-green color.[36d] Herein, we report the triplet state properties (Table 1) and singlet oxygen photosensitization of a dark-brown 1,2,3,4,5,6-hexasubstituted C_{60} derivative, with substitution at all carbons of a single six-member ring.

Experimental Section

Materials. Synthesis of the 1,2,3,4,5,6-hexasubstituted C_{60} derivative (**1**) is reported elsewhere.[35] 2,3-Benzanthrancene (purity > 99%), toluene (spectrophotometric grade), anthracene (purity > 98%), and rubrene (98%) were purchased from Aldrich Chemical Co. Deuterated toluene was obtained from

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* Corresponding author. mgg@chem.ucla.edu.
[†] University of California, Los Angeles.
[‡] California State University.
[§] Deceased June 13, 2005.

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TABLE 1: Triplet State Properties of Hexasubstituted Fullerene 1

property	value[a]
E_T	33 kcal/mol ≤ E_T ≤ 38 kcal/mol
ϵ_T	$(22 \pm 0.1) \times 10^3$ $M^{-1}cm^{-1}$ (670 nm)[b]
τ_T	18 ± 1 μs
k_o	$(1.56 \pm 0.15) \times 10^9$ $M^{-1}s^{-1}$
Φ_T $^1O_2$ (355 nm)	0.67 ± 0.03[d]
Φ^1O_2 (355 nm)	0.65 ± 0.03[e]
Φ^1O_2 (532 nm)	0.55 ± 0.03[f]
S_Δ (355 nm)	0.97 ± 0.02[g]
k_q ($^1O_2$)	not measurable

[a] All experiments were conducted in spectrophotometric grade toluene or toluene-d_8 at room temperature and excited at 355 nm or 532 nm with a concentration of **1** where absorbance at the excitation wavelength is $A_{exc} \approx 0.3$. Reported values are averages of three or more measurements. [b] Determined using the energy transfer method with rubrene as a reference. [c] In argon-purged solutions and void of any quenchers. [d] Calculated using the comparison method with C_{60} as reference. [e] Determined in air-saturated conditions with sample concentrations from absorbance (OD) = 0.1−0.5, using C_{60} as standard. [f] Determined in air-saturated conditions with sample concentrations from absorbance (OD) = 0.05−0.2, using C_{60} as standard. [g] $S_\Delta = \Phi_\Delta/\Phi_T$. S_Δ is the fraction of the triplet state of **1** that forms singlet oxygen by energy transfer. [h] No observed quenching of singlet oxygen by **1** up to 2.98×10^{-5} M.

Cambridge Isotope Laboratories. C_{60} (>99.5%) was obtained from MER Corporation.[41] Perylene (98%) was obtained from Sigma Chemical Company. Benzo[*a*]pyrene (98%) was obtained from Fluka. All chemicals were used as received except for anthracene, which was recrystallized from acetone prior to use.

Measurements. Samples of **1** were prepared in spectrophotometric grade toluene, with an absorbance at the excitation wavelength of $A_{355} \approx 0.3$. Solutions were purged with argon for 30 min. There was negligible change in the concentration of the solution after purging and was verified by noting only a slight (~0.02) increase in absorbance at the excitation wavelength.

UV−vis absorption spectra were obtained using Hewlett-Packard 8453 and Beckman DU-650 spectrophotometers.

Time-resolved measurements, triplet decay kinetics, triplet−triplet spectra, triplet−triplet extinction coefficients, triplet quantum yields, and triplet energies, were obtained by transient absorption methods described previously.[42] Briefly, measurements were obtained by excitation of argon-purged solutions at 355 nm using a frequency tripled Quanta Ray DCR-2 Nd:YAG laser (3-20 mJ/pulse). Transient absorption was monitored using a probe beam from a Hanovia 100-W xenon lamp passed through a Jarrell-Ash 82-410 monochromator (250 μm slits) and detected using a Hamamatsu R928 PMT. Data output from the PMT was collected using a LeCroy 9350 oscilloscope coupled to a Macintosh G4 computer using Labview software. Kinetic curves were averaged over 30−70 laser pulses.

Triplet energies and triplet extinction coefficients were determined by energy transfer experiments. Energy transfer was observed by quenching the triplet state of **1** and monitoring the decay kinetics using transient absorption. Solutions of adduct **1** in toluene ($A_{355} \approx 0.3$) were placed in 1 cm quartz cuvettes with a selected quencher at increasing concentrations. The solutions were purged under argon for 30 min and were measured under identical experimental conditions and laser power. The quenching rate constant was determined using a Stern−Volmer analysis, where the transient absorption traces were curve fitted to a monoexponential decay using Igor Pro 3.1 software. Compound **1** was excited at 355 nm in the presence of quenchers rubrene, benzo[*a*]pyrene, perylene, and 2,3-benzanthracene. The quenching rate of the triplet of **1** was monitored at a local maximum in the triplet−triplet absorption at 365 nm. The absorbance (ΔOD) of the triplet of rubrene was measured at 490 nm (E_T = 26.0 kcal/mol, $\Delta\epsilon_{T-T}$ (490) = 26 000 $M^{-1}cm^{-1}$)[43] and at 670 nm for **1** in experiments to determine the triplet molar absorption coefficient.

Singlet oxygen quantum yield was determined by measuring the singlet oxygen near-infrared luminescence at 1268 nm using a North Coast liquid nitrogen cooled germanium photodiode.[44] Air saturated samples of **1** were dissolved in toluene-d_8 and excited at either 355 nm or 532 nm using the laser photolysis setup described above. Scattered laser light was eliminated using a silicon cutoff filter at 1100 nm and a 1270 nm interference filter. Singlet oxygen luminescence was measured orthogonal to laser excitation. Data output from the detector was collected using a LeCroy 9350 oscilloscope coupled to a Macintosh G4 computer using Labview software. Decay traces were averaged over 20−40 laser pulses.

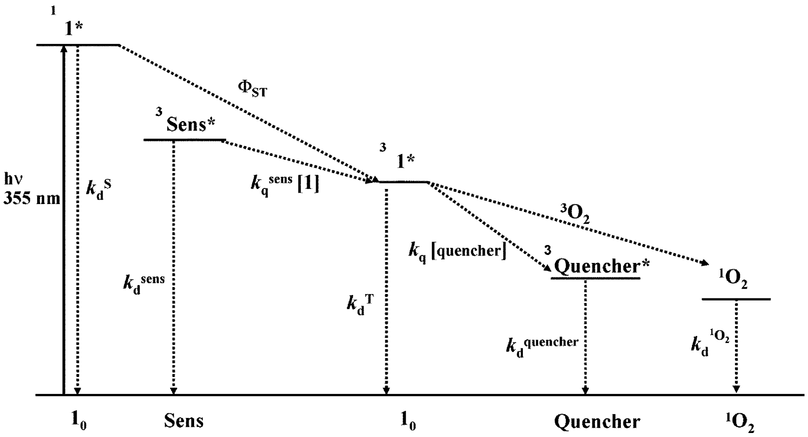
Results and Discussion

The photophysical processes relevant to **1** are summarized in Scheme 1. Excitation of **1** with UV light generates the singlet excited state (^{1}**1***), which is followed by intersystem crossing to the lower lying triplet state (^{3}**1***) and a relatively efficient internal conversion to the ground state (k_d^S). The triplet state can be deactivated by decay to the ground state (**1_0**) or it can transfer its energy to a lower triplet energy quencher (Q_0) by collisional energy transfer.[45] The triplet state, (^{3}**1***) can also transfer its energy to triplet molecular oxygen ($^3O_2$) to generate singlet oxygen ($^1O_2$). The triplet state of **1** can be selectively attained through energy transfer by excitation of an external photosensitizer (Sens) with higher triplet energy. Similar to other fullerene derivatives, the main pathway of deactivation of the singlet excited-state is population of the triplet state by intersystem crossing ($\Phi_{ST} = 0.67 \pm 0.03$). Given that there is no observable fluorescence, the quantum yield of internal conversion is estimated as $\Phi_d^S \approx 0.33$. In this study we have focused on the characterization of the triplet state photophysical properties by nanosecond laser flash photolysis.

UV−Vis Spectroscopy. The ground state absorbance spectrum of **1** exhibits drastic differences compared to the UV−vis absorption spectrum of C_{60} (Figure 1). The characteristic peak at 330 nm and the forbidden transition between 420 and 650 nm exhibited by pristine C_{60} are no longer present in the spectrum of **1**. The broad absorption bands with maxima at ~550 and ~600 nm are absent. Compound **1** exhibits small absorption bands at 430 and 480 nm. In contrast to the absence of long wavelength absorptions by C_{60}, **1** also shows some absorbance in the red portion of the spectrum. The absorbance spectrum of **1** shows spectral similarities to a C_{3v} tris-epoxidated fullerene derivative, $C_{60}O_3$, reported by Tajima et al., which is proposed to be substituted at all six carbons on a single six-member ring of the fullerene cage.[46] Specifically, both **1** and the tris-epoxidated derivative show a sharp absorption at 430 nm, a small shoulder at 480 nm, and some long wavelength absorption. The ground state absorbance spectrum of **1** is also similar to a tris-substituted methanofullerene reported by Foote et al.[30] and a 1,2,3,4-tetrahydrofullerene reported by Bensasson et al.[27] Saturation of a single six-member ring of the fullerene cage results in significant differences from the ground state absorption of pristine C_{60} but is not much different from spectra exhibited by other multifunctionalized derivatives.[27,29−34]

Triplet−Triplet Absorption Spectrum. The triplet−triplet absorption spectrum of **1** is shown in Figure 2. The transient

SCHEME 1



observed is attributed to the triplet state of **1** because it is readily quenched by oxygen in air-saturated solutions and by triplet quenchers in argon-purged solutions (see below). The triplet−triplet absorption of **1** is similar to those of other fullerene derivatives having two resolved UV absorbing peaks at 360 and 430 nm. The long wavelength absorption bands are blue-shifted compared to those in C_{60} with a broad peak at 670 nm. This significant blue shift in the long wavelength absorption is consistent with previous reports of multifunctionalized derivatives.[28−34] A tris-substituted methanofullerene reported by Guldi and Asmus[28] and an *o*-quinodimethane bisadduct by Nishimura et al.[32] show hypsochromic shifts of long wavelength absorption with respect to pristine C_{60} having peaks at 650 and 690 nm, respectively.

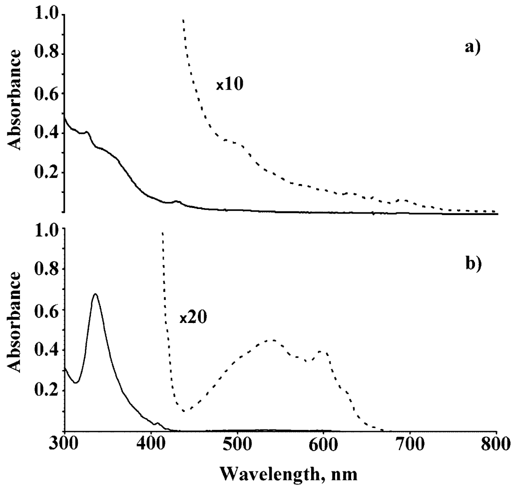


Figure 1. UV−vis absorption spectra of (a) hexasubstituted C_{60} derivative, **1**, and (b) C_{60} recorded in toluene.

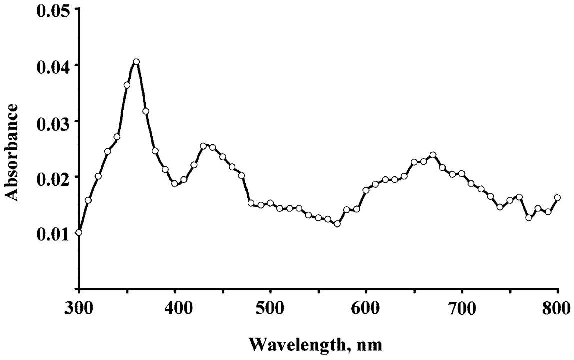


Figure 2. Triplet−triplet absorption spectrum of hexasubstituted C_{60} derivative, **1**, in toluene (λ_{exc} = 355 nm).

SCHEME 2

$$^{1}1_0 \xrightarrow{h\nu} {}^{1}1^* \xrightarrow{isc} {}^{3}1^*$$

$$^{3}1^* \xrightarrow{k_D} {}^{1}1_0$$

$$^{3}1^* + Rub_0 \xrightarrow{k_{et}} {}^{1}1_0 + {}^{3}Rub^*$$

Triplet Extinction Coefficient and Triplet Quantum Yield. The triplet coefficient of **1** was determined by energy transfer experiments[45] using rubrene (Rub_0, Scheme 2) as the energy acceptor. The rate and extent of energy transfer was determined by selective excitation at 355 nm using the Nd:YAG laser photolysis setup. Excitation of **1** to the excited singlet state (^{1}**1***) is followed by intersystem crossing to the triplet state (^{3}**1***). The triplet state of **1** can transfer its energy to rubrene, which has a lower triplet energy, by collisional quenching (Scheme 2).

The triplet of rubrene (^{3}Rub*) observed at 490 nm (E_T = 26.0 kcal/mol, $\Delta\epsilon_{T-T}$ (490) = 26 000 $M^{-1}cm^{-1}$)[43] can be attributed to energy transfer from **1** because rubrene does not have significant absorbance at the 355 nm excitation wavelength. The triplet state of **1** (^{3}**1***) was measured at 670 nm, and the appearance of the rubrene triplet (^{3}Rub*) was followed at 490 nm, where ^{3}**1*** does not have significant triplet absorbance. The triplet coefficient was calculated and corrected for incomplete energy transfer. The probability of energy transfer (P_{tr}) from ^{3}**1*** to rubrene (Rub_0) can be calculated using eq 1, where k_{et} is the rate constant of energy transfer from ^{3}**1*** to rubrene, [Rub] is the concentration of added rubrene,[45] and k_D is the decay rate constant of **1** in the absence of any quenchers. The triplet molar absorption coefficient of **1** is given by eq 2, where ΔOD is the signal intensity of the triplet at the observed wavelengths, 670 and 490 nm for ^{3}**1*** and ^{3}Rub*, respectively.

$$P_{tr} = \frac{k_{et}[Rub]}{k_{et}[Rub] + k_D} \qquad (1)$$

$$\Delta\epsilon_{T-T,\mathbf{1}} = \Delta\epsilon_{T-T,Rub}\left(\frac{\Delta OD_1}{\Delta OD_{Rub}}\right)\left(\frac{1}{P_{tr}}\right) \qquad (2)$$

Figure 3 shows a Stern−Volmer analysis of the quenching of triplet **1** by rubrene. The change in the rate of decay of triplet **1** (inset a, Figure 3) was analyzed with respect to the amount of added rubrene. When the concentration of rubrene (Rub) is added so that there is 96% energy transfer, the observed triplet

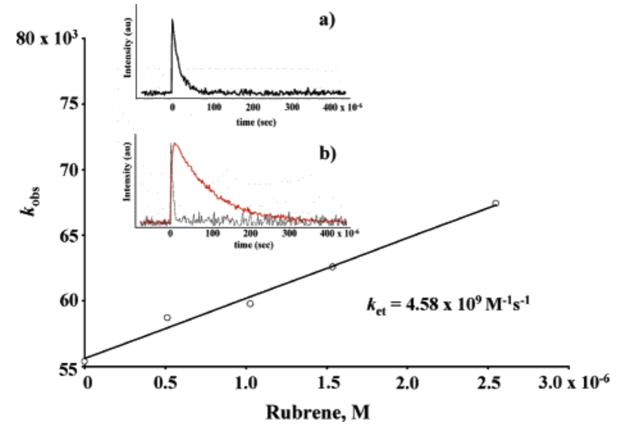


Figure 3. Stern−Volmer quenching analysis of the triplet state of **1** in the presence of rubrene. Inset: Decay traces observed at local maxima in the triplet−triplet absorption spectra of (a) **1** in the absence of rubrene measured at 670 nm and (b) rubrene triplet generated by energy transfer measured at 490 nm. Overlaid is the decay trace of a nearly completely quenched triplet of **1** (670 nm) to show the efficiency of energy transfer in the presence of rubrene.

of **1** at 670 nm is almost completely quenched (short-lived transient, inset b, Figure 3), and the triplet of rubrene is clearly observed (long-lived transient, inset b, Figure 3).

The calculated triplet molar absorption coefficient for **1** is 21 600 $M^{-1}cm^{-1}$ at 670 nm, which is considerably higher than that of C_{60} at 740 nm ($\Delta\epsilon_{T-T}$ (740) = 12 000 $M^{-1}cm^{-1}$).[43] Bensasson et al. have reported dihydro- and tetrahydrofullerene derivatives with triplet molar absorption coefficients of 10 500 $M^{-1}cm^{-1}$ and 4800 $M^{-1}cm^{-1}$, respectively.[27] A series of multifunctionalized fullerene derivatives reported by Foote et al. had triplet molar absorption coefficients ranging from 15 100 $M^{-1}cm^{-1}$ to as high as 40 000 $M^{-1}cm^{-1}$, demonstrating the relatively large variation of the triplet molar absorption coefficient with different functionalization patterns.[30]

The triplet quantum yield of **1** was determined by the comparative method and using the triplet coefficient determined as described above.[27] The initial intensity of the triplet absorbance (ΔOD) of optically matched solutions of **1** and C_{60} were measured under identical experimental conditions and laser power. The triplet quantum yield (ϕ_T) of **1** was calculated using C_{60} ($\Delta\epsilon_{T-T}$ (740) = 12 000 $M^{-1}cm^{-1}$, $\phi_T = 1$)[43] as a reference (eq 3)

$$\frac{\Delta\epsilon_{T-T,1}\phi_{T,1}}{\Delta\epsilon_{T-T,C_{60}}\phi_{T,C_{60}}} = \frac{\Delta OD_1}{\Delta OD_{C_{60}}} \qquad (3)$$

The triplet quantum yield of **1** was calculated to be 0.67 ± 0.03. This quantum yield is consistent with other reports of multifunctionalized fullerene derivatives that show a decrease in triplet quantum yield with a decrease in π conjugation within the fullerene cage.[29,30,32−34]

Triplet Energies. The triplet energy of **1** was estimated by energy transfer experiments. By monitoring the triplet−triplet absorption of a donor in the presence of increasing concentrations of quencher, one can measure the rate of energy transfer. The quenching rate was determined by measuring the changes in the rate of decay of the triplet state of the donor. Energy transfer was confirmed by observation of the triplet state absorption of the quencher. Because energy transfer is monitored by triplet−triplet absorption, the donor and acceptor must not have significant overlapping transient absorption at the observed wavelengths. The rate of energy transfer depends on the relative triplet energies of donor and quencher. By selectively using quenchers of varying triplet energies and measuring the rates of energy transfer, one can bracket the approximate triplet energy of **1**. The triplet state of **1** is efficiently quenched at a diffusion controlled rate by oxygen in air saturated solutions of toluene. Compound **1** is quenched at slightly lower than diffusion controlled rates by rubrene (E_T = 26.0 kcal/mol)[43] and 2,3-benzanthracene (E_T = 29.3 kcal/mol)[43] with rate constants of (4.6 ± 0.3) × 10^9 $M^{-1}s^{-1}$ and (2.6 ± 0.2) × 10^9 $M^{-1}s^{-1}$, respectively. The rate of energy transfer to perylene (E_T = 35.4 kcal/mol)[43] is significantly lower, with a rate constant of (5.8 ± 0.35) × 10^7 $M^{-1}s^{-1}$. Because the rate constant of quenching is about 2 orders of magnitude below a diffusion-controlled value, it can be estimated that **1** has a triplet energy within 0−2 kcal/mol of perylene, that is, 33 kcal/mol ≤ E_T **(1)** ≤ 38 kcal/mol.[42] Benzo[*a*]pyrene (E_T = 41.8 kcal/mol)[43] and anthracene (E_T = 42.5 kcal/mol)[43] showed no quenching of triplet **1**. Reverse quenching experiments using **1** as a quencher of the triplet of benzo[*a*]pyrene gave a quenching rate of (2.9 ± 0.2) × 10^9 $M^{-1}s^{-1}$. From the results of these quenching studies, we conclude that the approximate triplet energy of **1** is 33 kcal/mol ≤ E_T **(1)** ≤ 38 kcal/mol, which is close to that of C_{60} (E_T = 35 kcal/mol) and well below that of anthracene and benzo[*a*]pyrene.[43,47−49]

Singlet Oxygen Quantum Yield. The quantum yield of singlet oxygen generated by most fullerene derivatives is lower than that of C_{60}, which is unity. Singlet oxygen is generated by energy transfer from the triplet state of **1** to ground state molecular oxygen and it gives a lower limit of the triplet quantum yield of **1**.[50] Previous reports on the photophysical properties of multifunctionalized derivatives have shown that disruption in the π conjugation system causes a decrease in the singlet oxygen quantum yield.[29,30,32−34] Several reported dihydrofullerenes have shown that substitution on two carbons results in only a slight decrease in singlet oxygen generation. This decrease in singlet oxygen quantum yield is fairly systematic, with increasing substitution resulting in decreasing singlet oxygen quantum yield. Compound **1** gives us the opportunity to study the effect of saturating all six carbons on one six-member ring of the fullerene cage. The near-infrared phosphorescence of singlet oxygen at 1268 nm was measured using a germanium photodiode detector and the Nd:YAG laser photolysis setup described previously.[42] Compound **1** produces singlet oxygen in toluene-d_8, with a quantum yield of Φ_Δ = 0.65 ± 0.03 (355 nm) and 0.55 ± 0.03 (532 nm). At 355 nm, the fraction of triplet **1** that photosensitizes singlet oxygen, $S_\Delta = \Phi_\Delta/\Phi_T$ is nearly unity (S_Δ = 0.97). Therefore, the triplet state of **1** is an efficient photosensitizer of singlet oxygen, and it is the efficiency of intersystem crossing of **1** that limits singlet oxygen generation. There was no measurable quenching of singlet oxygen by **1**. When tetraphenylporphine (TPP) was used as a photosensitizer of singlet oxygen and excitation at 532 nm, where **1** only has slight absorbance at the concentrations of **1** tested, no quenching was observed even when adding **1** up to a concentration of 2.98 × 10^{-5} M.

Conclusions

It is well-documented that increased perturbation of the conjugated π system results in systematic changes in the photophysical properties of fullerene derivatives.[18−34] These properties are affected by the number, structure, and substitution pattern of the addends.[30−34] Saturation of a single six-member ring results in a large local perturbation in the π system of C_{60}. The triplet state photophysics of the first example of a 1,2,3,4,5,6-hexasubstituted C_{60} derivative examined in this study show that disruption of the π system of a single six-member ring results in significant changes in triplet state properties, including a systematic decrease in the triplet state lifetime, triplet quantum yield, and singlet oxygen quantum yield as compared to those of pristine C_{60}. The studied hexa-adduct shows a similar blue shift in long wavelength triplet−triplet absorption and decreases in triplet quantum yield; these are similar to previous reports on the photophysical properties of tris-adducts having different substitution patterns.[26,30] Although the triplet energy of **1** was approximately the same as that of C_{60} and similar to an *e*,*e*,*e* derivative determined by pulsed radiolysis, the quantum yield of singlet oxygen generated by **1** is greater than those of other reported tris-adducts where the addends are located in nonadjacent positions.[26] This notion has suggested that a local disturbance of the π-system preserves the electronic properties of C_{60}. An unusual pattern, the *e*-face, *e*-edge, trans-1 exhibits an exceptionally low quantum yield for the generation of singlet oxygen, which is an irregularity among all studied tris-adducts. This derivative, however, shows a much higher triplet energy, determined by phosphorescence at 77 K, than **1**.[30] Our study of **1** lends further evidence, showing that the location of the addend significantly affects photophysical properties. Future studies of the relationship between addition patterns and photophysical properties will be necessary to address this interesting issue.

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