Photophysical properties of non-homoconjugated 1,2-dihydro, 1,2,3,4-tetrahydro and 1,2,3,4,5,6-hexahydro-C_{60} derivatives

Khin K. Chin,[a] Shih-Ching Chuang,[a] Billy Hernandez,[b] Luis M. Campos,[a] Matthias Selke,[b] Christopher S. Foote†[a] and Miguel A. Garcia-Garibay*[a]

The photophysical properties of a novel series of non-homoconjugated 1,2-di-, 1,2,3,4-tetra-, and 1,2,3,4,5,6-hexasubstituted fullerenes (compounds **1**, **2**, and **3**, respectively) have been systematically investigated. In this report, we examine the effect of substitution pattern of non-homoconjugated derivatized fullerenes on the ground state UV-Vis absorption, triplet state properties (lifetime, quantum yield, extinction coefficient), and singlet oxygen quantum yield. The non-homoconjugated fullerene derivatives **1**–**3** exhibit higher singlet oxygen quantum yield than analogous homoconjugated Bingel adducts with the same number of saturated C=C bonds and exhibit decreasing quantum yield of singlet oxygen generation upon increasing the degree of functionalization on a single six member ring on the fullerene cage. This trend is similar for triplet quantum yield and triplet lifetime. The triplet extinction coefficient increases with functionalization. A detailed discussion comparing **1**, **2**, and **3** with functionalized homoconjugated systems and with other non-homoconjugated derivatives is presented.

Introduction

The synthesis of multiply functionalized fullerene derivatives possessing a specific addition pattern has been one of the most challenging areas of fullerene chemistry.[1] Elucidating the physical and photophysical properties of these isomers has been challenging due to difficult synthesis and rigorous chromatographic processes needed to obtain pure regioisomers. The separation of regioisomers synthesized by double additions of Bingel,[2] Diels–Alder,[3] Prato,[4] [2+2],[5] nitrene,[6] and carbene adducts of C_{60}[7] requires extensive purification prior to the characterization of their physical properties.

Our laboratories have been interested in understanding how the photophysical properties of fullerene derivatives are affected by their electronic structure. Although the photophysical properties of many fullerene derivatives have been reported,[8] there are several structures that have not been synthetically available. The absence of these regioisomers has thus limited a thorough elucidation of the relationship between photophysical properties and electronic structure. For example, the C_{3v} trisadduct derivative (all-*cis*-1) has only recently been synthetically available (Fig. 1)[9,11] for its photophysical properties to be documented.[10]

Recently, Rubin and coworkers demonstrated a stepwise synthetic approach to saturate three C=C bonds within a single six member ring of C_{60} by a double Diels–Alder reaction followed by an intramolecular radical addition.[11] Naturally, the perturbation caused by the saturation of three C=C bonds of a single six member ring should affect the extent of π-conjugation and electronic properties of C_{60} (Fig. 2).

[a]Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569, USA. E-mail: mgg@chem.ucla.edu
[b]Department of Chemistry and Biochemistry, California State University, Los Angeles, CA 90032, USA
† Deceased June 13, 2005.
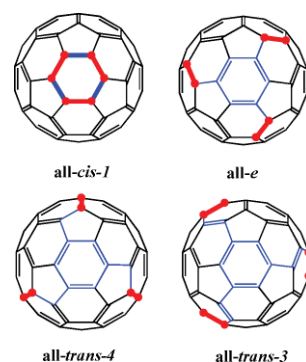
Fig. 1 Trisadducts of C_{60} with C_3 rotational axis. The sites of addition are indicated with a red bond and a dot. Different addition patterns carve out different π-chromophores.
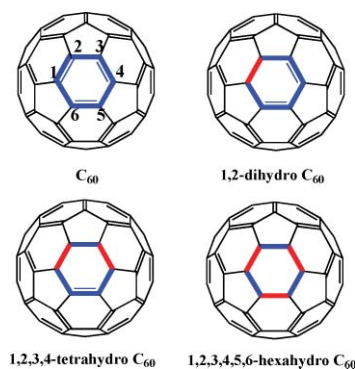
Fig. 2 Saturation of a single six-member ring on C_{60}. Derivatization at sequential positions on the six-member ring should affect the π-conjugation of C_{60} resulting in changes in photophysical properties.

To date, most studies of fullerene derivatives aimed at elucidating the relation between electronic structure and photophysical properties have used homoconjugated Bingel adducts.

However, the dependence of structural topology on the photophysical properties for non-homoconjugated systems has not been well studied due to the lack of synthetically available examples that can be systematically correlated.[12,18] Herein, we report triplet state properties and singlet oxygen photosensitization of a series of non-homoconjugated C_{60} derivatives with substitution at two, four, and all six carbons of a single six member ring.

Experimental

General methods

All reactions were performed under an argon atmosphere unless otherwise noted. Chemicals were used as purchased without further purification. Distilled solvents were dried as follows: THF from Na/benzophenone, and ODCB from CaH_2. ^{1}H and ^{13}C NMR spectra were recorded using Avance 500 MHz spectrometers. FTIR spectra were recorded using a Perkin-Elmer Paragon 1000 spectrometer. UV-Vis spectra were recorded using HP 8452 and 8453 diode-array single beam spectrometers. HRMS of non-C_{60} products were obtained after ionizing through EI. HRMS and LRMS of C_{60} derivatives were obtained after ionizing through MALDI. Column chromatography was carried out on silica gel 40–63 μm from EMD; thin layer chromatography was carried on glass plates coated with silica gel 250 μm from Sorbent Technologies. HOMO/LUMO and HOMO−1/LUMO+1 orbitals were computed using AM1 method using MacSpartan. Compounds 1, 2, and 3 are synthesized according to a reported procedure.[11]

Materials

2,3-Benzanthrancene (purity >99%), toluene (spectrophotometric grade), anthracene (purity >98%) and rubrene (98%) were purchased from Aldrich Chemical Company. Deuterated toluene was obtained from Cambridge Isotope Laboratories. C_{60} (>99.5%) was obtained from MER Corporation.[13] 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, 2, or 3 were prepared in spectrophotometric grade toluene with an absorbance at the excitation wavelength of A_{355} ≈ 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.[8f] Briefly speaking, 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^{-1}). 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, 2, and 3 and monitoring the decay kinetics using transient absorption. Solutions of adduct 1, 2, and 3 in toluene (A_{355} ≈ 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, 2, or 3 were 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, 2, or 3 were 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^{-1}, $\Delta\varepsilon_{T-T}$ (490) = 26000 M^{-1} cm^{-1}) and at 670 nm for 1, 2, or 3 in experiments to determine the triplet molar absorption coefficient.

Singlet oxygen quantum yield was determined by measuring the singlet oxygen near infrared luminescence using a cryogenic germanium photodiode detector (model 403 HS; Applied Detector Corp., USA) cooled by liquid nitrogen.[23] Air saturated samples of 1, 2, or 3 were dissolved in toluene-d_8 and excited at either 355 nm or 532 nm using anNd:YAG laser (model MiniLaseII/10 Hz; New Wave Research Inc., USA), with pulse energies of 2–5 mJ pulse^{-1}. Scattered laser light and other undesired radiation was eliminated using a series of filters, namely a Schott color glass filter (model RG850; cut-on 850 nm; Newport, USA) taped to the sapphire entrance of the detector. The port opening to the detector contains the remaining filters, a long wave pass filter (silicon filter model 10LWF∼1000; Newport, USA) which transmits in the range of 1100–2220 nm and blocks at 800–954 nm, and a band pass filter (model BP-1270-080-B*; CWL 1270 nm; Spectrogon, USA) with maximum transmission of 60% at 1270 nm. Singlet oxygen luminescence was measured orthogonal to laser excitation. The initial $^1O_2$ intensity was extrapolated to $t = 0$. The data points of the initial 0–5 μs were not used due to electronic interference signals from the detector. Signals were digitized on a LeCroy 9350 CM 500 MHz oscilloscope and analyzed using Origin software. Decay traces were averaged over 10–40 laser pulses.
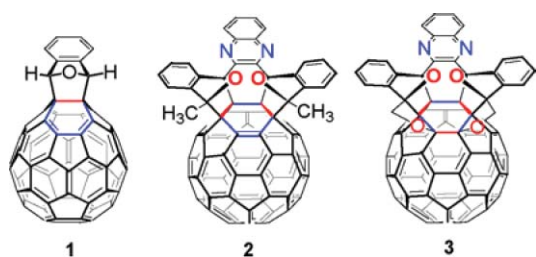
Results and discussion

UV-Vis spectroscopy

The ground state absorption spectra of derivatives **1**, **2**, and **3** reveal significant changes as compared to pristine C_{60}. The intensity of the characteristic UV absorption peak at *ca.* 330 nm decreases and becomes more red-shifted with increasing substitution (Fig. 3). The three isobenzofuran derivatives **1**, **2**, and **3** also display very different absorption features between 420–650 nm when compared to that of C_{60}. Increasing substitution from two to six carbons on a single six member ring also results in the appearance of a small absorption band at ~430 nm. The non-homoconjugated derivatives **1**, **2**, and **3** show absorption peaks at 434, 428 and 429 nm, respectively.
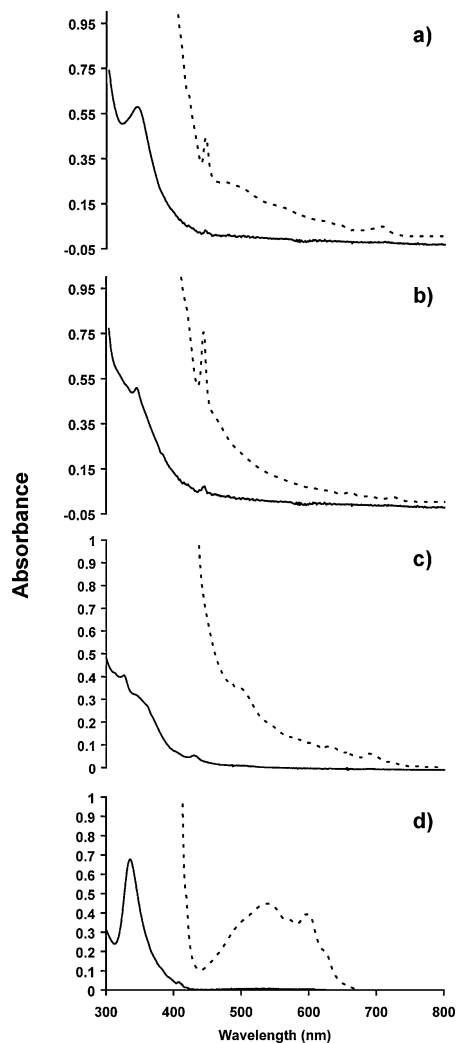
Fig. 3 UV-Vis absorption spectra of C_{60} derivatives a) 1,2-dihydro- (**1**), b) 1,2,3,4-tetrahydro- (**2**), c) 1,2,3,4,5,6-hexahydro-isobenzofuran (**3**), and d) C_{60} recorded in toluene.

The broad absorption band of C_{60} spanning from 430 to 660 nm becomes featureless upon derivatization. The overall spectral differences in compounds **1**, **2** and **3** may result both from the progressive changes in the conjugation of the fullerene chromophore and the presence of a rigid and strained 1,4-epoxy

naphthalene moiety.[11,14] The absorption changes in **1**, **2**, **3** are similar to those of previously reported for non-homoconjugated pyrrolidinofullerene derivatives.[12b] In addition, derivatives, **1**, **2**, and **3** exhibit slight absorbance in the red portion of the spectrum. Since these compounds do not show any observable emission up to 900 nm at room temperature, or in glassy matrices at 77 K, the current study is restricted to the characterization of their triplet state photophysical properties by nanosecond laser flash photolysis.

Triplet state properties of compounds 1, 2, 3

Triplet–triplet absorption spectra

The triplet–triplet absorption spectra of the three fullerene derivatives recorded in toluene are shown in Fig. 4. The triplet–triplet absorption spectra were acquired with the laser flash photolysis setup described previously.[8f] The observed transients are attributed to the triplet state because they are readily quenched by triplet quenchers in argon purged solutions (*vide infra*) and by oxygen in air-saturated and oxygen-purged solutions.
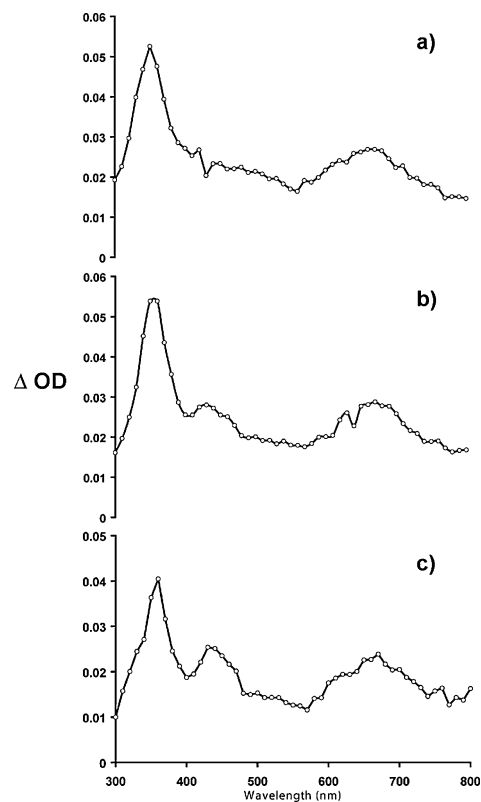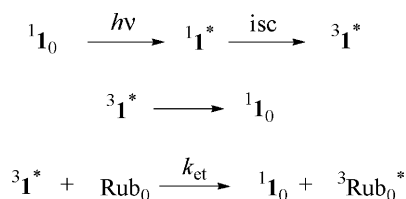

Fig. 4 Triplet–triplet absorption spectrum of a) 1,2-dihydro-, b) 1,2,3,4-tetrahydro-, c) 1,2,3,4,5,6-hexahydro-isobenzofuran C_{60} derivatives (**1**, **2**, and **3** respectively) recorded in toluene ($\lambda_{exc} = 355$ nm).

The triplet–triplet absorption of all three derivatives show a broad absorption band near 670 nm that is blue shifted by about 50 nm with respect to that of C_{60}. Non-homoconjugated derivatives **1**, **2**, and **3** also possess a weak absorption band at 430 nm. This band appears as a small shoulder for the 1,2-dihydro compound **1**, but increases in intensity for the 1,2,3,4-tetrasubstituted derivative **2** and shows more pronounced absorption with subsequent

This journal is © The Royal Society of Chemistry and Owner Societies 2008

Photochem. Photobiol. Sci., 2008, **7**, 49–55 | 51

functionalization exhibited by the 1,2,3,4,5,6-hexasubstituted **3**. A much more intense peak which is a common absorption for the triplet state of C_{60}, compounds **1–3**, and other multiply functionalized fullerenes, appears at *ca.* 360 nm.

Triplet extinction coefficient and triplet quantum yield

The triplet extinction coefficient of **1**, **2**, and **3** were determined by energy transfer experiments[15] using rubrene (Rub_0, Scheme 1) as an energy acceptor.

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

$$^3\mathbf{1}^* \longrightarrow {}^1\mathbf{1}_0$$

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

Scheme 1

The rate of energy transfer was measured by monitoring the triplet–triplet absorption of a donor in the presence of various concentrations of quencher. 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 absorption of the quencher. As energy transfer is monitored by triplet–triplet absorption, the donor and acceptor must not have significant overlapping transient absorption at the observed wavelengths. Laser excitation at 355 nm of argon-purged toluene solutions of fullerene derivative **1** ($A_{355} \sim 0.3$) results in the formation of the singlet excited state ($^1\mathbf{1}^*$), which efficiently undergoes intersystem crossing to form the triplet state ($^3\mathbf{1}^*$). Energy transfer from the triplet state of the fullerene derivative to rubrene, which has lower triplet energy, occurs by collisional quenching (Scheme 1).

The fullerene triplet ($^3\mathbf{1}^*$) was monitored at 670 nm and the rubrene triplet ($^3Rub^*$) was followed at 490 nm where $^3\mathbf{1}^*$ does not have significant triplet absorbance. Since rubrene has only negligible absorbance at the 355 nm excitation wavelength under the experimental conditions, the rubrene triplet ($^3Rub^*$) observed at 490 nm ($E_T = 26.0$ kcal mol^{-1}, $\Delta\varepsilon_{T-T}$ (490) = 26000 M^{-1} cm^{-1})[16] can be solely attributed to energy transfer from each fullerene derivative. The triplet molar absorption coefficient of the fullerene derivatives is given by eqn (1) where ΔOD is the signal intensity of the triplet at the monitoring wavelengths. The triplet coefficient was corrected for incomplete energy transfer. The probability of energy transfer (P_{tr}) from $^3\mathbf{1}^*$ to rubrene (Rub_0) was calculated using eqn (2), where [Rub] is the rubrene concentration, k_D is the intrinsic decay rate constant of **1**, and k_{et} is the rate constant of energy transfer from $^3\mathbf{1}^*$ to rubrene.

$$\Delta\varepsilon_{T-T,1} = \Delta\varepsilon_{T-T,Rub}\left(\frac{\Delta OD_1}{\Delta OD_{Rub}}\right)\left(\frac{1}{P_{tr}}\right) \tag{1}$$

$$P_{tr} = \frac{k_{et}[Rub]}{k_{et}[Rub] + k_D} \tag{2}$$

The triplet extinction coefficients of the non-homoconjugated systems increase with increasing saturation of the fullerene chromophore. The triplet coefficient of 1,2-dihydro compound

1, 14000 M^{-1} cm^{-1}, is much higher than that of a previously studied homoconjugated 1,2-dihydrofullerene, whose coefficient is 4200 M^{-1} cm^{-1}.[17] Subsequent functionalizations gave a triplet coefficient of 19800 M^{-1} cm^{-1} for the 1,2,3,4-tetrahydro-fullerene **2** and an even higher value of 21600 M^{-1} cm^{-1} for the 1,2,3,4,5,6-hexaadduct **3**.

Previous examples of homoconjugated and multiply functionalized fullerene derivatives have shown that the reported triplet extinction coefficients can vary widely, ranging from 4800 M^{-1} cm^{-1} to as high as 40042 M^{-1} cm^{-1}. The triplet extinction coefficient is dependent on the number of substituents, substitution pattern, and type of substituents.[18] The 1,2,3,4,5,6-hexaadduct **3** has a similar extinction coefficient as that of a tetrakis Bingel adduct, D_{2h}-all-*e*-C_{60}[C(COOEt)$_2$]$_4$ (20914 M^{-1} cm^{-1}) and a hexakis Bingel adduct, T_h-all-*e*-C_{60}[C(COOEt)$_2$]$_6$ (20871 M^{-1} cm^{-1}). In addition, the coefficient of 1,2-dihydrofullerene **1** is similar to that of a tris-substituted derivative, *e*-face, *e*-edge, *trans*-1-C_{60}[C(COOEt)$_2$]$_3$ (15085 M^{-1} cm^{-1}). This suggests that substitution by a non-homoconjugated addend has a greater effect on the triplet extinction coefficient of the fullerene chromophore than that of a homoconjugated addend (Bingel adduct). The results of the current study also indicate that for non-homoconjugated systems, the triplet extinction coefficient increases with sequential disruption of the fullerene core, in analogy to trends reported previously for homoconjugated systems.[12a,17]

The triplet quantum yields of fullerene derivatives **1**, **2**, and **3** were determined by the comparative method using C_{60} as a standard.[19] Under identical experimental conditions and with optically matched solutions ($A_{355} \sim 0.3$) of each derivative and C_{60}, the triplet quantum yield (ϕ_T) was calculated (eqn (3)). ΔOD is the initial intensity of the triplet absorbance and $\Delta\varepsilon_{T-T}$ is the triplet extinction coefficient determined above, at 670 nm for the fullerene derivatives and 740 nm for C_{60}.

$$\frac{\Delta\varepsilon_{T-T,1}\phi_{T,1}}{\Delta\varepsilon_{T,C_{60}}\phi_{T,C_{60}}} = \frac{\Delta OD_1}{\Delta OD_{C_{60}}} \tag{3}$$

The triplet quantum yields of fullerene derivatives **1**, **2**, and **3** are shown in Table 1 and shows progressive changes with increasing disturbance in the conjugation of the fullerene chromophore. The quantum yield decreases with increasing saturation of the C=C bonds in a six member ring. This is consistent with studies of homoconjugated fullerene derivative systems.[17] The quantum yield of monoadduct **1** is similar to that of a mono-Bingel adduct C_{60}[C(COOEt)$_2$] ($\Phi_T = 0.95$). The 1,2,3,4-tetrahydro adduct **2** displays a higher triplet quantum yield than a bis-Bingel adduct *e*-C_{60}[C(COOEt)$_2$]$_2$ ($\Phi_T = 0.79$). Hexaadduct **3** exhibits a similar quantum yield as a tris Bingel *e*-face, *e*-edge, *trans*-1-C_{60}[C(COOEt)$_2$]$_3$ adduct ($\Phi_T = 0.69$). Overall, the increased perturbation in the π conjugation of a single six-membered ring in a non-homoconjugated system results in a consistent decrease in triplet quantum yield and is similar to previous reports for homoconjugated systems.[12a,17]

Triplet energies

The triplet energy of the series of fullerene derivatives was estimated using bracketing experiments by the energy transfer method detailed in the Experimental section. The relative triplet energy of each fullerene derivative can be estimated by using

Table 1 Triplet state properties of compounds **1**, **2** and **3**

Property[a]	Compound **1**	Compound **2**	Compound **3**[i]
E_T/kcal mol^{-1}		$33 \leq E_T \leq 38$	
ε_T/M^{-1} cm^{-1b}	14000 ± 1000	19800 ± 1000	21600 ± 1000
τ_T/μs^c	25 ± 1	22 ± 1	18 ± 1
k_O/M^{-1} s^{-1}	$(1.7 \pm 0.09) \times 10^9$	$(2.3 \pm 0.2) \times 10^9$	$(1.56 \pm 0.15) \times 10^9$
$\Phi_T{}^d$	0.96 ± 0.02	0.89 ± 0.03	0.67 ± 0.03
Φ^1O_2 (355 nm)^e	0.95 ± 0.02	0.87 ± 0.03	0.65 ± 0.03
Φ^1O_2 (532 nm)^f	0.82 ± 0.02	0.70 ± 0.03	0.55 ± 0.03
S_Δ (355 nm)^g	0.99	0.98	0.97
$k_q(^1O_2)$	Not measurable^h		

^{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**, **2**, or **3** where absorbance at the excitation wavelength is $A_{exc} \approx 0.3$. Reported values are averages of 3 or more measurements. ^{b} Determined using the energy transfer method with rubrene as a reference.[15] ^{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**, **2**, or **3** that forms singlet oxygen by energy transfer (see text). ^{h} No observed quenching of singlet oxygen by **1**, **2**, or **3** up to 2.98×10^{-5} M. ^{i} Data taken from previous report.[10]

Table 2 Quenching rate constants (k_q) of the triplet states of **1**, **2** and **3** by various quenchers

Quencher	E_T/kcal mol^{-1}	**1**^{a}	**2**^{a}	**3**^{a}
O$_2$	22	1	1	1
Rubrene	26	0.46	0.51	0.58
2,3-Benzanthracene	29	0.26	0.23	0.25
Perylene	35	0.006	0.027	0.05
Benzo[a]pyrene	42	No quenching observed		
Anthracene	42	No quenching observed		

^{a} k_q ($\times 10^{10}$ M^{-1} s^{-1}).

quenchers of different triplet energies and measuring the rates of energy transfer.[15] The rate constants of quenching by various quenchers of the triplet state of each fullerene derivative are shown in Table 2. The triplet state of each derivative **1–3** is quenched at diffusion controlled rates by oxygen ($E_T = 22$ kcal mol^{-1})[15] in air and oxygen saturated solutions of toluene. Rubrene ($E_T = 26$ kcal mol^{-1})[15] and 2,3-benzanthracene ($E_T = 29$ kcal mol^{-1})[15] quench at slightly slower than diffusion controlled rates. Perylene ($E_T = 34$ kcal mol^{-1})[15] quenches the triplet of all three compounds **1–3** at significantly lower than diffusion controlled rates. This suggests that the approximate energies are close ($\sim$0–2 kcal mol^{-1}) to that of perylene. Benzo[a]pyrene ($E_T = 41.8$ kcal mol^{-1})[15] and anthracene ($E_T = 42.5$ kcal mol^{-1})[15] showed no quenching of any of the fullerene triplets. Reverse quenching experiments using each fullerene derivative as a quencher of the triplet of benzo[a]pyrene were conducted and gave results consistent with estimated triplet energies that were much lower than that of benzo[a]pyrene. From energy transfer experiments, we estimate that the triplet energies of the fullerene derivatives are similar to each other and close to that of perylene; i.e. 33 kcal mol^{-1} $\leq E_T$ (fullerene derivatives **1–3**) $\leq$ 38 kcal mol^{-1}.

The triplet energies of **1**, **2**, and **3** were also calculated by density functional theory at the B3LYP/6-31G*[20] and B3LYP/6-31G**//B3LYP/3-21G level of theory (Table 3).[21] The triplet energy values show a slight decrease upon consecutive saturation of double bonds on a single six-membered ring, from 36.2 kcal mol^{-1} to 35.2 kcal mol^{-1} and 33.6 kcal mol^{-1} for **1**, **2**, and **3**, respectively.

Table 3 Computed triplet energy (kcal mol^{-1}) of compounds **1–3**

Level of theory	1	2	3
B3LYP/6-31G*//B3LYP/6-31G*	36.2	35.2	33.6
B3LYP/6-31G**//B3LYP/3-21G	38.8	35.2	34.8

These values are comparable to the calculated triplet energy of C_{60} of 36.2 kcal mol^{-1}, which has been experimentally determined to be 36.0 kcal mol^{-1}.[22] The calculated triplet energy values are consistent with those estimated in the energy transfer experiments, confirming that the triplet energies of fullerene derivatives **1–3** are within ca. 0–2 kcal mol^{-1} of the triplet energy of perylene and the parent C_{60}.

Singlet oxygen quantum yield

This series of fullerene derivatives **1–3** gives us the opportunity to examine the effect of substitution pattern on the singlet oxygen quantum yield. Singlet oxygen is generated by energy transfer from the triplet state of each fullerene derivative to ground state molecular oxygen. The quantum yield of $^1O_2$ generation (Φ_Δ) can be expressed using the following equation.

$$\Phi_\Delta = \Phi_T P_{T,O_2} f_{T,\Delta} \qquad (4)$$

Here Φ_T is the quantum yield of triplet formation, P_{T,O_2} the proportion of triplet quenched by $^3O_2$ [$P_{T,O_2} = 1 - (\tau_{air}/\tau_{N_2})$], and $f_{T,\Delta}$ is the fraction of triplet quenched by $^3O_2$ leading to formation of $^1O_2$. The product $P_{T,O_2}f_{T,\Delta}$ is often referred to as

S_Δ, i.e. the fraction of the triplet state that forms singlet oxygen by energy transfer. The values of k_q, and S_Δ (Table 1) are consistent with the classic scheme by Gijzeman et al.[23,24] for generation of singlet oxygen by energy transfer. Diffusion-controlled quenching of excited triplet sensitizers (T_1) by triplet dioxygen ($^3\Sigma$) should initially lead to an excited ($T_1{}^3\Sigma$) encounter-complex. Of the nine different spin configurations possible for this encounter-complex, only one [$^1(T_1{}^3\Sigma)$] should lead to energy transfer and singlet oxygen formation. Thus, a value of unity is often observed for $f_{T,\Delta}$ when the rate of quenching of the triplet excited sensitizer by triplet oxygen (k_q) is 1/9 k_{diff}. At 355 nm, the singlet oxygen quantum yields are identical (within limits of error) to the quantum yields of triplet formation for all three derivatives. This implies values of near unity for both P_{T,O_2} and $f_{T,\Delta}$ at 355 nm, and consequently for S_Δ. The quenching rates of the triplet states of derivatives **1**, **2**, and **3** by triplet oxygen are indeed near 1/9 k_{diff}, thus providing strong evidence for a simple mechanism of singlet oxygen generation by energy transfer. Table 1 shows the singlet oxygen quantum yield of compound **1**, **2**, and **3** excited at 355 nm and 532 nm. The singlet oxygen quantum yield decreases with increasing functionalization for excitation at 355 nm, where mono-functionalized 1,2-dihydrofullerene **1** is 0.95, tetra-hydrofullerene **2** is 0.87 and hexa-hydrofullerene **3** is 0.65. Previous reports on singlet oxygen generated by multifunctionalized derivatives have also shown that disruption in the π-conjugation causes a decrease of quantum yield for singlet oxygen generation.[8,12,17,18] Comparing results obtained by excitation at the same wavelength (355 nm), it can be found that the quantum yield from disruption of one C=C bond by a non-homoconjugated addend (compound **1**, Φ^1O_2 (355 nm) = 0.95) is comparable to that of homoconjugated analogs.[17] The second addition of a non-homoconjugated addend at the adjacent C=C bond (cis-1 position) preserves more π-conjugation than the second addition of a homoconjugated addend at the e-position in a second aromatic ring, correlating with a larger quantum yield with compound **2** (Φ^1O_2 (355 nm) = 0.87) than with the homoconjugated derivative e-$C_{60}[C(CO_2Me)_2]_2$ (Φ^1O_2 (355 nm) = 0.79). This trend also applies to a third addition as compound **3** has a higher quantum yield for singlet oxygen generation than a tris-Bingel adduct e-face, e-edge, trans-1-$C_{60}[C(COOEt)_2]_3$, which perturbs conjugation in three different benzene rings.[17]

In agreement with the systematic decrease in the triplet quantum yields as a function of π-conjugation detailed previously, consecutive disruption in the local conjugation of a single six-membered ring by one, two, and three double bonds on the fullerene cage consistently shows a small, but progressive decrease in singlet oxygen quantum yield. However, consecutive addition to a single isolated benzene ring produces a smaller effect than consecutive addition of homoconjugated adducts to separated benzene rings around the fullerene core.

Conclusions

We have reported a systematic study on the photophysics of the non-homoconjugated 1,2-dihydro, 1,2,3,4,-tetrahydro, 1,2,3,4,5,6-hexahydro fullerene derivatives. The synthetic availability for this series of adducts offers us the opportunity to carry out an insightful investigation of the photophysical properties of non-homoconjugated systems. Saturation of C=C bonds by a non-homoconjugated addend at adjacent positions preserves more π-conjugation than the derivatives with delocalized addends. This is reflected in measurements of triplet energy, triplet quantum yield, and singlet oxygen quantum yield. Progress toward the understanding of the effects of electronic structure on the photophysical properties of non-homoconjugated systems is made in the current study.

Acknowledgements

Notes and references

1 (a) S. Anderson, H. L. Anderson and J. K. M. Sanders, Expanding roles for templates in synthesis, Acc. Chem. Res., 1993, **26**, 469–475; (b) L. Isaacs, R. F. Haldimann and F. Diederich, Tether-directed remote functionalization of buckminsterfullerene: regiospecific hexaadduct formation, Angew. Chem., Int. Ed. Engl., 1994, **33**, 2339–2342; (c) S. Sergeyev and F. Diederich, Regio- and stereoselective tether-directed remote functionalization of C_{60} with derivatives of the Tröger base, Angew. Chem., Int. Ed. Engl., 2004, **43**, 1738–1740; (d) I. Lamparth, C. Maichle-Mössner and A. Hirsch, Reversible template-directed activation of equatorial double bonds of the fullerene framework: regioselective direct synthesis, crystal structure, and aromatic properties of T_h–C_{66}(COOEt)$_{12}$, Angew. Chem., Int. Ed. Engl., 1995, **34**, 1607–1609; (e) F. Diederich and M. Gomez-Lopez, Supramolecular fullerene chemistry, Chem. Soc. Rev., 1999, **28**, 263–277; (f) U. Reuther, T. Brandmüller, W. Donaubauer, F. Hampel and A. Hirsch, A highly regioselective approach to multiple adducts of C_{60} governed by strain minimization of macrocyclic malonate addends, Chem.–Eur. J., 2002, **8**, 2261–2273; (g) W. Qian and Y. Rubin, Convergent, regioselective synthesis of tetrakisfulleroids from C_{60}, J. Org. Chem., 2002, **67**, 7683–7687; (h) C. Thilgen and F. Diederich, Tether-directed remote functionalization of fullerenes C_{60} and C_{70}, C. R. Chim., 2006, **9**, 868–880.
2 (a) A. Hirsch, I. Lamparth and H. R. Karfunkel, Fullerene chemistry in three dimensions: isolation of seven regioisomeric bisadducts and chiral trisadducts of C_{60} and di(ethoxycarbonyl)methylene, Angew. Chem., Int. Ed. Engl., 1994, **33**, 437–438; (b) C. Bingel, Cyclopropanierung von fullerenen, Chem. Ber., 1993, **126**, 1957–1959.
3 (a) S. R. Wilson and Q. Lu, 2,6-Dimethoxyanthracene - a directing group for regioselective bisaddition to C_{60}, Tetrahedron Lett., 1995, **36**, 5707–5710; (b) A. Duarte-Ruiz, T. Müller, K. Wurst and B. Kräutler, The bis-adducts of the [5,6]-fullerene C_{60} and anthracene, Tetrahedron, 2001, **57**, 3709–3714.
4 (a) M. Maggini, G. Scorrano and M. Prato, Addition of azomethine ylides to C_{60}: synthesis, characterization, and functionalization of fullerene pyrrolidines, J. Am. Chem. Soc., 1993, **115**, 9798–9799; (b) S. R. Wilson, Y. Wang, J. Cao and X. Tan, Amino acids as precursors for N-unsubstituted fulleropyrrolidine derivatives, Tetrahedron Lett., 1996, **37**, 775–778; (c) Q. Lu, D. I. Schuster and S. R. Wilson, Preparation and characterization of six bis(N-methylpyrrolidine)-C_{60} isomers: magnetic deshielding in isomeric bisadducts of C_{60}, J. Org. Chem., 1996, **61**, 4764–4768.
5 (a) Y. Nakamura, N. Takano, T. Nishimura, E. Yashima, M. Sato, T. Kudo and N. Nishimura, First isolation and characterization of eight regioisomers for [60]fullerene-benzyne bisadducts, Org. Lett., 2001, **3**, 1193–1196; (b) F. Diederich and R. Kessinger, Templated regioselective and stereoselective synthesis in fullerene chemistry, Acc. Chem. Res., 1999, **32**, 537–545.
6 (a) F. Djojo, A. Herzog, I. Lamparth, F. Hampel and A. Hirsch, Regiochemistry of two-fold additions to [6,6] bonds in C_{60}: influence of the addend-independent cage distortion in 1,2-monoadducts, Chem.–Eur. J., 1996, **2**, 1537–1547; (b) G. Shick, A. Hirsch, H. Mauser and T. Clark, Opening and closure of the fullerene cage in cis-bisimino adducts of C_{60}: The influence of the addition pattern and the addend, Chem.–Eur. J., 1996, **2**, 935–943.

7 M. W. J. Beulen, J. A. Rivera, M. A. Herranz, B. Illescas, N. Martín and L. Echegoyen, Reductive electrochemistry of spiromethanofullerenes, *J. Org. Chem.*, 2001, **66**, 4393–4398.

8 (*a*) T. Hamano, K. Okuda, T. Mashino, M. Hirobe, K. Arakane, A. Ryu, S. Mashiko and T. Nagano, Singlet oxygen production from fullerene derivatives: effect of sequential functionalization of the fullerene core, *Chem. Commun.*, 1997, (1), 21–22; (*b*) F. Prat, R. Stackow, R. Bernstein, W. Y. Qian, Y. Rubin and C. S. Foote, Triplet-state properties and singlet oxygen generation in a homologous series of functionalized fullerene derivatives, *J. Phys. Chem. A*, 1999, **103**, 7230–7235; (*c*) Y. Nakamura, M. Taki, S. Tobita, H. Shizuka, H. Yokoi, K. Ishiguro, Y. Sawaki and J. Nishimura, Photophysical properties of various regioisomers of [60]fullerene-*o*-quinodimethane bisadducts, *J. Chem. Soc., Perkin Trans. 2*, 1999, **1**, 127–130; (*d*) P. F. Coheur, D. A. dos Santos, J. Cornil, P. R. Birkett, J. Liévin, J. L. Brédas, D. R. M. Walton, R. Taylor, H. W. Kroto and R. Colin, Photophysical properties of hexa-functionalized C_{60} derivatives: Spectroscopic and quantum-chemical investigations, *J. Chem. Phys.*, 2000, **112**, 8555–8566; (*e*) S. Foley, S. Bosi, C. Larroque, M. Prato, J. M. Janot and P. Seta, Photophysical properties of novel water soluble fullerene derivatives, *Chem. Phys. Lett.*, 2001, **350**, 198–205; (*f*) J. W. Arbogast and C. S. Foote, Photophysical properties of C_{70}, *J. Am. Chem. Soc.*, 1991, **113**, 8886–8889.

9 U. Reuther, T. Brandmüller, W. Donaubauer, F. Hampel and A. Hirsch, A highly regioselective approach to multiple adducts of C_{60} governed by strain minimization of macrocyclic malonate addends, *Chem.–Eur. J.*, 2002, **8**, 2261–2273.

10 K. K. Chin, S.-C. Chuang, B. Hernandez, M. Selke, C. S. Foote and M. A. Garcia-Garibay, Photophysical properties of a 1,2,3,4,5,6-hexasubstituted fullerene derivative, *J. Phys. Chem. A*, 2006, **110**, 13662–13666.

11 (*a*) S.-C. Chuang, M. Sander, T. Jarrosson, S. James, E. Rozumov, S. I. Khan and Y. Rubin, Approaches to open fullerenes: synthesis and kinetic stability of Diels–Alder adducts of substituted isobenzofurans and C_{60}, *J. Org. Chem.*, 2007, **72**, 2716–2723; (*b*) M. Sander, T. Jarrosson, S.-C. Chuang, S. I. Khan and Y. Rubin, Approaches to open fullerenes: synthesis and thermal stability of *cis*-1 bis(isobenzofuran) Diels–Alder adducts of C_{60}, *J. Org. Chem.*, 2007, **72**, 2724–2731; (*c*) S.-C. Chuang, F. R. Clemente, S. I. Khan, K. N. Houk and Y. Rubin, Approaches to open fullerenes: a 1,2,3,4,5,6-hexaadduct of C_{60}, *Org. Lett.*, 2006, **8**, 4525–4528.

12 (*a*) D. M. Guldi and K.-D. Asmus, Photophysical properties of mono- and multiply-functionalized fullerene derivatives, *J. Phys. Chem. A*, 1997, **101**, 1472–1481; (*b*) K. George Thoma, V. Biju and M. V. George, Excited-state interactions in pyrrolidinofullerenes, *J. Phys. Chem. A*, 1998, **102**, 5341–5348.

13 The MER Corp., 7960 S. Kolb Road, Tucson, AZ 85706.

14 (*a*) R. N. Warrener, Isolation of isobenzofuran, a stable but highly reactive molecule, *J. Am. Chem. Soc.*, 1971, **93**, 2346–2348; (*b*) W. Friedrichsen, *Adv. Heterocycl. Chem.*, 1980, **26**, 135–241; (*c*) R. Rodrigo, Progress in the chemistry of isobenzofurans: Applications to the synthesis of natural products and polyaromatic hydrocarbons, *Tetrahedron*, 1988, **44**, 2093–2135; (*d*) B. Rickborn, in *Advances in Theoretically Interesting Molecules*, ed. R. P. Thummel, JAI Press Inc., Greenwich, CT, 1989, vol. I, pp. 1–134; (*e*) C. W. Bird, *Prog. Heterocycl. Chem.*, 1990, **2**, 87–101; (*f*) O. Peters and W. Friedrichsen, *Trends Heterocycl. Chem.*, 1995, **4**, 217–259.

15 I. Carmichael and G. L. Hug, Triplet-triplet absorption spectra of organic molecules in condensed phases, *J. Phys. Chem. Ref. Data*, 1986, **15**, 1–250.

16 S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker, New York, 1993.

17 J. L. Anderson, Y.-Z. An, Y. Rubin and C. S. Foote, Photophysical characterization and singlet oxygen yield of a dihydrofullerene, *J. Am. Chem. Soc.*, 1994, **116**, 9763–9764.

18 F. Prat, R. Stackow, R. Bernstein, W. Y. Qian, Y. Rubin and C. S. Foote, Triplet-state properties and singlet oxygen generation in a homologous series of functionalized fullerene derivatives, *J. Phys. Chem. A*, 1999, **103**, 7230–7235.

19 R. V. Bensasson, E. Bienvenue, J. M. Janot, S. Leach, P. Seta, D. I. Schuster, S. R. Wilson and H. Zhao, Photophysical properties of three hydrofullerenes, *Chem. Phys. Lett.*, 1995, **245**, 566–570.

20 (*a*) C. Lee, W. Yang and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785–789; (*b*) A. D. Becke, Density-functional thermochemistry. III. The, role of exact exchange, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

21 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, 2004.

22 W. Qian, M. D. Bartberger, S. J. Pastor, K. N. Houk, C. L. Wilkins and Y. Rubin, C_{62}, a non-classical fullerene incorporating a four-membered ring, *J. Am. Chem. Soc.*, 2000, **122**, 8333–8334, and references therein.

23 C. Schweitzer and R. Schmidt, Physical, mechanisms of generation and deactivation of singlet oxygen, *Chem. Rev.*, 2003, **103**, 1685–1757.

24 O. L. Gijzeman, F. Kaufman and G. Porter, Oxygen, quenching of aromatic triplet states in solution, *J. Chem. Soc. Faraday Trans. 2*, 1973, **69**, 708–720.