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Triplet state properties of malonic acid C_{60} derivatives $C_{60}[C(COOR)_2]_n$; R = H, Et; *n* = 1–6

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Laser flash photolysis and pulse radiolysis have been used to determine properties of the lowest triplet state of a series of water-soluble malonic acid derivatives of C_{60}, $C_{60}[C(COOH)_2]_n$ with $n = 2–6$, in water at pH 7.4. Similar studies were carried out on the corresponding ethyl esters, $C_{60}[C(COOEt)_2]_n$ with $n = 1–6$, in the non-polar solvents, benzene or toluene. The properties include the T–T absorption spectra, the triplet molar absorption coefficients and the quantum yields of formation, Φ_T and Φ_Δ of the triplet and of singlet oxygen, respectively. This study shows a general tendency of the λ_{max} of the T–T absorption spectra, and of the Φ_Δ values to decrease with increasing number of addends. For regioisomers, the spectroscopic and photophysical parameters are modulated with the pattern of addition. The Φ_Δ quantum yields for the acids in aqueous solution are systematically lower than those of the ethyl esters in toluene. The lower Φ_Δ values observed for the acids in aqueous solution, and to a lesser extent for the esters in benzonitrile, can be interpreted as due to the presence of solute clusters in polar solvents.

Introduction

Knowledge of the photophysical properties of fullerenes and fullerene derivatives is critical to the design of certain artificial molecular systems mimicking photosynthetic reaction centres.[1] Such properties are also vital in the design of fullerene-containing photoelectrochemical systems,[2,3] as well as being important in the selective photocleavage of single- and double-stranded DNA by fullerene–oligonucleotide conjugates.[4,5] For the use of fullerenes in physiological media, an important requirement is their functionalisation with hydrophilic addends. Photophysical studies, in particular the determination of the triplet quantum yield, can provide useful diagnostic tools to investigate dimerisation and aggregation of such amphiphilic molecules.[6,7]

The objective of the present work is to compare the triplet properties of a series of water-soluble malonic acid C_{60} derivatives in aqueous solution with those of their corresponding ethyl esters in non-polar solvents. Measurements on nine malonic acid C_{60} derivatives based on $C_{60}[C(COOH)_2]_n$ ($n = 2$ to 6) and on the corresponding ethyl esters (also including the mono-adduct) have enabled us to investigate the influence of the number of addends, and of their pattern of addition, on their photophysical properties. The bis-adducts studied were *trans*-2-, *trans*-3-, *trans*-4- and *e*-$C_{60}[C(COOH)_2]_2$. The tris-adducts were *e*,*e*,*e*- and *t*333-$C_{60}[C(COOH)_2]_3$, the tetra-, penta- and hexa-adducts being the all-*e*-regioisomers.

Guldi *et al.*[8,9,10] have previously studied some photophysical properties of several of these multi-functional C_{60}-malonic esters, and here we provide further information on a wider range of derivatives and the corresponding acids. Fig. 1 shows the structures of the molecules studied (only the esters are shown). Using laser flash photolysis and pulse radiolysis, we have determined the triplet absorption spectra, including molar absorption coefficients, and the triplet state and singlet oxygen quantum yields, Φ_T and Φ_Δ of $C_{60}[C(COOH)_2]_n$ in water and of $C_{60}[C(COOEt)_2]_n$ in organic solvents. We discuss the influence of the number of addends, the pattern of addition and the solvent polarity on these parameters.

Experimental

The malonic acid derivatives $C_{60}[C(COOH)_2]_n$ ($n = 2–6$) and their corresponding ethyl esters ($n = 1–6$) were synthesized as described by Hirsch *et al.*[11–14] The aqueous solutions were buffered at pH 7.4 using 5.0×10^{-3} M phosphate buffer. Water was re-distilled over alkaline potassium permanganate under nitrogen. Perdeuterated water, D_2O (99.8% D) was from Janssen Chemicals (Beerse, Belgium). The pH measurements were made with a radiometer pH meter with a glass

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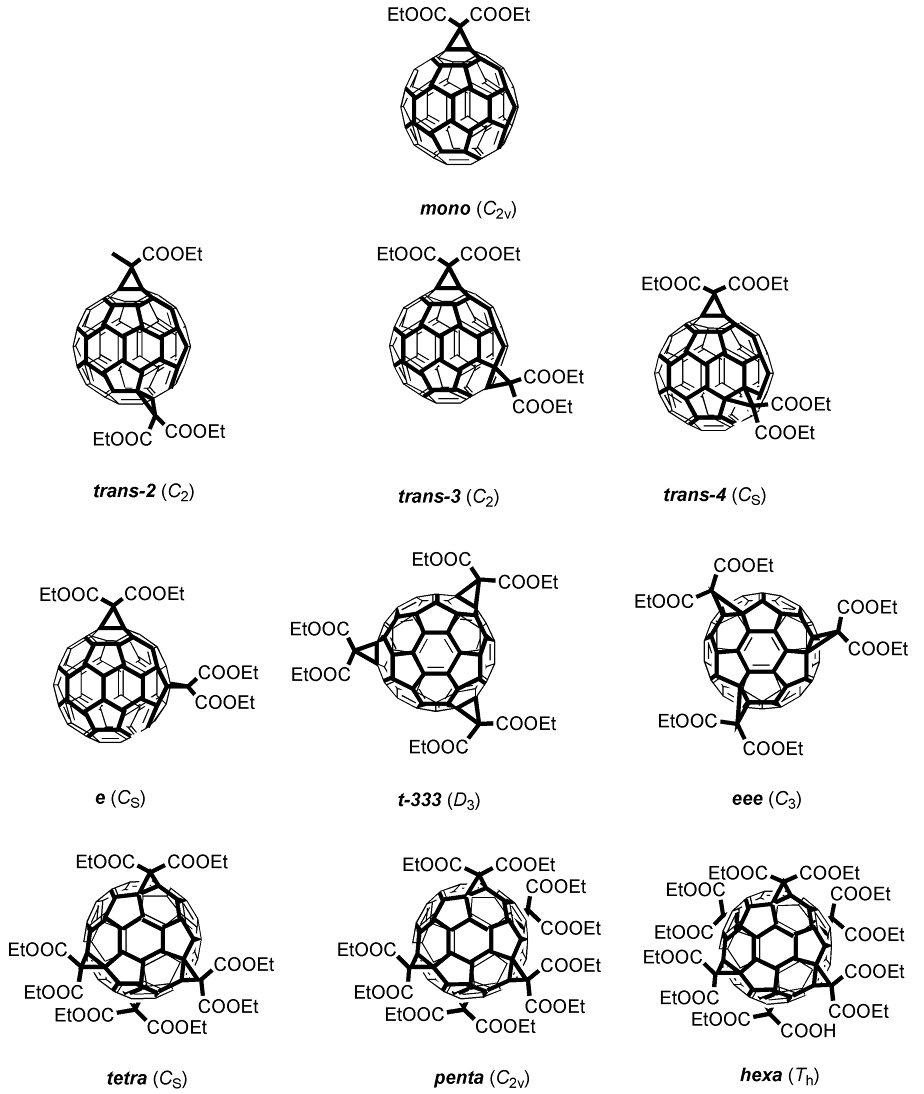
mono (C_{2v})

trans-2 (C_2)   *trans-3* (C_2)   *trans-4* (C_S)

e (C_S)   *t-333* (D_3)   *eee* (C_3)

tetra (C_S)   *penta* (C_{2v})   *hexa* (T_h)

Fig. 1 Structures of C_{60} $[C(COOEt)_2]_n$ ($n = 1–6$).

electrode and the pD were taken as the pH measured +0.4.[15] Toluene (BDH), benzene (Romil), cyclohexane (Aldrich) and benzonitrile (Aldrich) were all HPLC grade and used without further purification.

Solutions were excited at 355 or 532 nm, either with a JK Lasers System 2000 Nd/YAG laser[16] or a Spectron-Q-switched Nd/YAG laser.[17] Quantum yields of singlet oxygen O_2 ($^1\Delta_g$) production, Φ_Δ, were determined by photoexcitation of the $C_{60}[C(COOH)_2]_n$ ($n = 2$ to 6) in oxygenated D_2O at pH 7.4, and of the corresponding ethyl esters ($n = 1–6$) in air-equilibrated toluene or benzene using, respectively, peri-naphthenone in D_2O and C_{60} in toluene or benzene as standard reference sensitisers, for both of which Φ_Δ^{St} is unity.[18,19] The singlet oxygen phosphorescence signal, peaking at 1270 nm, was observed *via* laser flash photolysis using a liquid-nitrogen cooled germanium diode and amplifier supplied by Applied Detector Corporation (USA). Triplet molar absorption coefficients at λ_{max}, the wavelength of the principal T–T absorption band, were determined *via* laser flash photolysis using a comparative method,[20] with the assumption that the triplet quantum yield, Φ_T, is equal to the singlet oxygen quantum yield, Φ_Δ.

Results and discussion

Triplet absorption spectra

The absorption profiles of the triplet-minus-ground state difference absorption spectra of the acids and ethyl esters obtained by laser flash photolysis are rather similar (Fig. 2(a) and (b)). The wavelength of maximum absorption in the principal absorption band of the T–T spectra, λ_{max}, shows little change on going from $n = 1$ to $n = 5$, but for $n = 6$ there is a significant shift to the blue.

The triplet–triplet absorption maxima of the acids in water (H_2O) are slightly blue-shifted relative to the corresponding ethyl esters, with the exception of the *eee* tris-adduct (Table 1).

The triplet–triplet absorption bands of these derivatives in the 700 nm region are most likely related to the $2\,^3G_u \leftarrow 1\,^3T_{2g}$ transition, corresponding to the strong 750 nm band of C_{60}.[21] Where comparison is possible, the positions of the triplet absorption band maxima for the esters broadly agree with those reported by Guldi *et al.*[8] However, Guldi *et al.* report a λ_{max} of 650 nm for the *eee* tris-adduct, which contrasts with our observation of λ_{max} at 725 nm for this derivative (Fig. 2(b), Table 1).

Determination of the quantum yields of singlet oxygen production, Φ_Δ, and of the corresponding triplet quantum yields, Φ_T

The sensitised production of singlet oxygen by the malonic acid derivatives $C_{60}[C(COOH)_2]_n$ ($n = 2–6$) in D_2O, and by their corresponding ethyl esters in toluene or benzene, was assessed by comparison of the slopes of linear plots of I_o (the amplitude of the time-resolved $^1O_2$ ($^1\Delta_g$) 1270 nm phosphorescence signal extrapolated to $t = 0$) *vs.* laser intensity, with

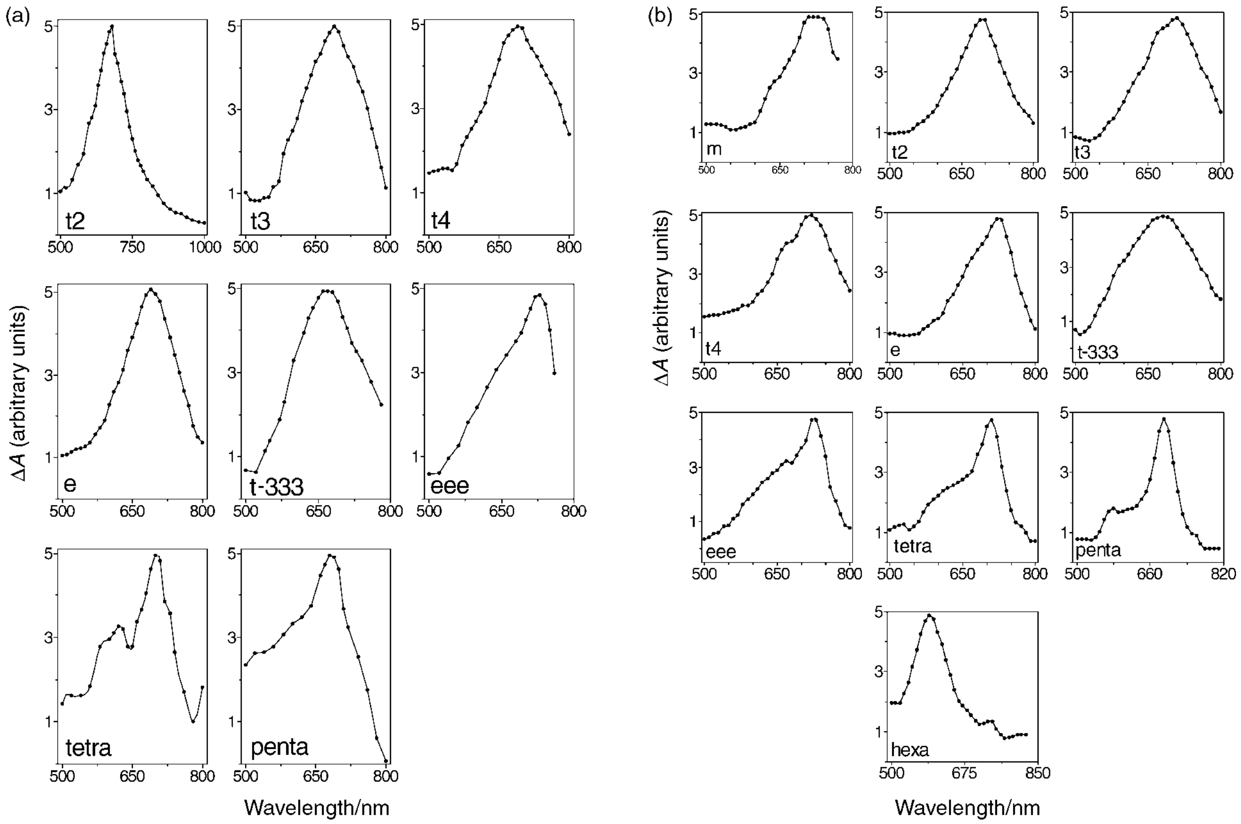

Fig. 2 (a) Triplet spectra of C_{60} $[C(COOH)_2]_n$ (n = 2–6) in water at pH 7.4 and (b) C_{60} $[C(COOEt)_2]_n$ (n = 1–6) in toluene.

the slopes obtained for optically-matched solutions of the reference compounds. The ratio of the slopes, α^F, of $^1O_2$ production sensitised by the fullerene derivatives F as a function of the laser intensity, to the corresponding slopes, α^{St}, determined for $^1O_2$ production sensitised by the reference as a function of the laser intensity, allows the determination of the quantum yield of singlet oxygen production by the fullerene derivatives from the slope ratio, after correction for any small differences in the fraction of light absorbed by the solutions at the laser excitation wavelength, λ_{exc} (eqn. (1)).

$$\Phi_\Delta^F = \Phi_\Delta^{St} \frac{\alpha^F}{\alpha^{St}} \frac{1 - 10^{-A^{St}_{\lambda_{exc}}}}{1 - 10^{-A^F_{\lambda_{exc}}}} \qquad (1)$$

In this equation, $A^{St}_{\lambda_{exc}}$ and $A^F_{\lambda_{exc}}$ are the absorbances for the standard and for the fullerene solutions at the excitation

Table 1 Triplet molar absorption coefficients (±20%)/M^{-1} cm^{-1} and λ_{max}/nm

Fullerene derivative	$C_{60}[C(COOEt)_2]_n$ (toluene)	$C_{60}[C(COOH)_2]_n$ (H_2O, pH 7.4)
C_{60}	20 200(750)[a]	—
Mono-adduct	12 200(710) 900(720)[c]	720[b]
trans-2 (bis-adduct)	16 700(690) 15 300(690)[d] 8200(690)[c]	11 000(680)
trans-3 (bis-adduct)	10 700(700) 11 400(700)[d] 8000(705)[c]	8900(700)
trans-4 (bis-adduct)	11 200(720)	6800(700)
e (bis-adduct)	15 400(710) 9700(710)[c]	15 000(690)
trans-333 (tris-adduct)	8700(730)	11 200(670)
eee (tris-adduct)	10 900(725) 7500(650)[c]	8900(730)
All *e* (tetra-adduct)	15 000(710)	7400(710)
All *e* (penta-adduct)[e]	8000(690)	4950(680)
All *e* (hexa-adduct)[e]	7700(590)	—

[a] From ref. 21. [b] Observed for $C_{60}[C(COONa)_2]$ in water, and complexed with γ-cyclodextrin in water.[27] [c] From ref. 8. Dr D. Guldi has informed us that "the measurements of the triplet absorption coefficients reported in ref. 8 were performed *via* the comparative method, with the assumption that the triplet molar absorption coefficient of C_{60}, chosen as standard, is 16 000 M^{-1} cm^{-1} at 750 nm and that the triplet quantum yields for all these esters are unity". [d] *Via* pulse radiolysis. [e] In benzene.

Table 2 Singlet oxygen quantum yields Φ_Δ (±10%)

Fullerene derivative	$C_{60}[C(COOEt)_2]_n$ (toluene)	$C_{60}[C(COOH)_2]_n$ (D_2O, pH 7.4)
C_{60}	1[a]	—
Mono-adduct	0.97	—
trans-2 (bis-adduct)	0.94	0.68
trans-3 (bis-adduct)	0.84	0.36
trans-4 (bis-adduct)	0.80	0.29
e (bis-adduct)	0.85	0.31
trans-333 (tris-adduct)	0.70	0.51
eee (tris-adduct)	0.55	0.30
All *e* (tetra-adduct)	0.30	0.21
All *e* (penta-adduct)	0.13[b]	0.12
All *e* (hexa-adduct)	0.13[b]	0.06

[a] From ref. 18. [b] Measured *vs.* C_{60} in benzene.

wavelength. The measured Φ_Δ values are given in Table 2. For these determinations the same solvent was used for the fullerene derivative and the standard, since the radiative properties of singlet oxygen are dependent on the solvent.[22]

The singlet oxygen quantum yields of the acids in aqueous solution are systematically lower than those of the ethyl esters in toluene or benzene (see Table 2). The lower values observed in aqueous solution can be interpreted as due to the presence of clusters. It is well known that the singlet to triplet intersystem crossing quantum yields decrease as a consequence of dimerisation or aggregation for aromatic hydrocarbons[23,24] porphyrins[25] and certain other fullerenes.[7,26] Some Φ_Δ measurements were also made in cyclohexane and benzonitrile. The values found for $C_{60}[C(COOEt)_2]_n$ ($n = 1$–6) in cyclohexane were identical, within experimental error, to the values found in toluene or benzene. However, the yields in benzonitrile (a more polar solvent) were intermediate between the toluene/benzene–ester results and the acid results in water (D_2O), implying some aggregation in benzonitrile.

In the case of the mono-adduct acid derivative, Guildi *et al.*[27] have deduced the presence of clustering in water on the basis of a short triplet state lifetime ($t_{1/2} \sim 0.4$ μs) as compared to that for the γ-cyclodextrin encapsulated mono-adduct ($t_{1/2} \sim 55$ μs). In the case of $C_{60}[C(COOH)_2]_n$, ($n = 2$–6) studied here, triplet state lifetimes in water ranging from 10–50 μs were obtained, and are similar to the lifetimes found for the corresponding esters in toluene.

The quantum yields of singlet oxygen production for $C_{60}[C(COOH)_2]_n$ ($n = 2$–6) in D_2O and their corresponding ethyl esters in toluene and benzene, can be employed in the estimation of the corresponding Φ_T, using eqn. (2).

$$\Phi_T = \frac{\Phi_\Delta}{S_\Delta S_Q} \qquad (2)$$

S_Δ is the fraction of triplet states quenched by oxygen leading to formation of singlet oxygen and S_Q is the fraction of triplet states quenched by oxygen.[28] Under the experimental conditions employed, the value of S_Q is close to unity for all the compounds studied, since the triplet lifetime decreases by at least one order of magnitude in the presence of oxygen. The S_Δ value is unity for the fullerenes studied to date, including C_{60} as well as C_{60} methanofullerenes,[29] since independently measured Φ_Δ and Φ_T are near unity for these molecules. It should be noted that the S_Δ value is 0.9 ± 0.1 for many aromatic ππ* triplet states without electron-donating groups.[30] Thus, if we assume the S_Δ value is unity for these fullerene derivatives, the Φ_T values are approximately equal to the Φ_Δ values (Table 2). This is verified below for two of these fullerenes.

Determination of triplet molar absorption coefficients

(i) Laser flash photolysis. Using a comparative method,[31,32] it is possible to estimate the triplet state molar absorption coefficients of the malonic acid derivatives *via* a knowledge of their triplet quantum yields. Linear plots of the extrapolated $t = 0$ absorbance changes at appropriate monitoring wavelengths *vs.* laser intensity are constructed for optically matched solutions of the fullerene derivative and the standard (C_{60} in benzene or toluene for which $(\varepsilon_T - \varepsilon_G)^{St} = 20\,200$ M^{-1} cm^{-1} at 750 nm[21] and $\Phi_T^{St} \sim 1$.[18,21]). In contrast to the determination of Φ_Δ, it is not necessary, for transient absorption studies, to use the same solvent for standard and unknown. The triplet molar absorption coefficients may be deduced using eqn. (3), where β^F and β^{St} represent the respective slopes of the plots described above.

$$(\varepsilon_T - \varepsilon_G)^F = (\varepsilon_T - \varepsilon_G)^{St}\left(\frac{\Phi_T^{St}}{\Phi_T^F}\right)\left(\frac{\beta^F}{\beta^{St}}\right)\left(\frac{1 - 10^{-A^{St}_{\lambda exc}}}{1 - 10^{-A^F_{\lambda exc}}}\right) \qquad (3)$$

For all the fullerene derivatives studied, ε_G is negligible compared to ε_T at the triplet absorption maxima.

Using the above expression, the triplet molar absorption coefficients of the acids, $C_{60}[C(COOH)_2]_n$, in water, as well as

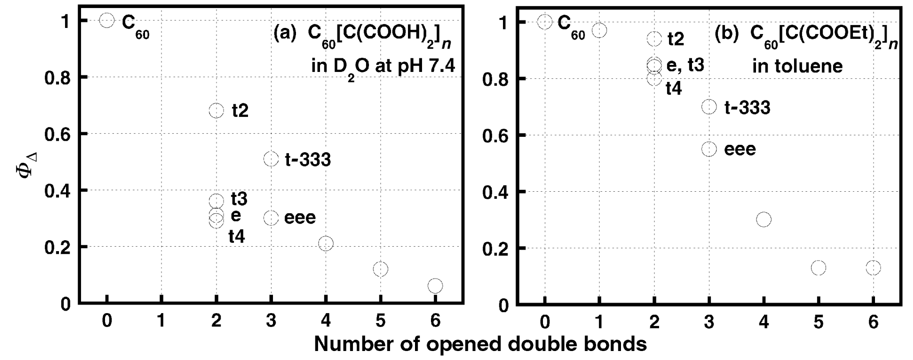

Fig. 3 Plots of quantum yields of singlet oxygen O_2 ($^1\Delta_g$) formation (Φ_Δ) (a) for C_{60} $[C(COOR)_2]_n$, R = H, $n = 2$–6 and (b) R = Et, $n = 1$–6 *vs.* the number of addends (n), *i.e.* the number of opened double bonds.

the corresponding ethyl esters $C_{60}[C(COOEt)_2]_n$ in toluene or benzene, have been determined, and are reported in Table 1. Guldi *et al.*[8] have determined triplet molar absorption coefficients for the mono, *trans*-2, *trans*-3, *e* bis- and *eee* tris-adduct ester derivatives and these values are also included in Table 1. The values of Guldi *et al.*[8] are all significantly lower than the values reported here and the reasons for this are indicated in a footnote to Table 1.

(ii) Pulse radiolysis. Pulse radiolysis was used to make measurements of the triplet molar absorption coefficients of the ethyl esters, *trans*-2 and *trans*-3 in toluene *via* a comparative method that exploits quantitative triplet energy transfer.[32] The triplet states of each ethyl ester were produced in benzene by energy transfer from the triplet state of biphenyl, for which ε_T is 27 100 M^{-1} cm^{-1} at 365 nm.[33] These measurements yield estimates of ε_T (*trans*-2) at 690 nm of 15 300 M^{-1} cm^{-1} and ε_T (*trans*-3) at 700 nm of 11 400 M^{-1} cm^{-1}. These values are in reasonable agreement with the molar absorption coefficients obtained from the laser flash photolysis measurements. This agreement confirms the validity of the assumption that $\Phi_T = \Phi_\Delta$ for these compounds.

Structural influences on photophysical properties

The results of this study reveal a trend; the values of Φ_Δ (Fig. 3(a) and (b) and Table 2), and the triplet molar absorption coefficient (Table 1) show a tendency to decrease with increasing number of addends. This effect of the extent of functionalisation on the photophysical properties of fullerenes (C_{60} and C_{70}) derivatives has already been reported.[34–38] For the different bis- and tris-regioisomers, the spectroscopic and photophysical parameters are dependent on the pattern of addition. There are evidently underlying effects of the specific addition pattern on the electronic structures governing the molecular spectra and photophysical properties of these fullerenes derivatives, in particular the interstate coupling factors, including electronic, vibrational and spin–orbit parameters. Theoretical studies on individual compounds are required to determine the quantitative aspects of these factors.

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