J. Phys. Chem. A **1999,** *103,* 8173−8178

Photophysical Properties of Pseudo-Dihydro Derivatives of C_{70}

**Sarah Foley,[†] Mário N. Berberan-Santos,*[,†] Aleksandre Fedorov,[†] David J. McGarvey,[‡]
Célia Santos,[§] and Bárbara Gigante[§]**

Centro de Química-Física Molecular, Instituto Superior Técnico, 1049-001 Lisboa, Portugal; School of Chemistry and Physics, Keele University, Staffordshire ST5 5BG, UK; and INETI-IBQTA, Departamento de Tecnologia e Indústrias Químicas, Estrada do Paço do Lumiar, 1649-038 Lisboa, Portugal

Received: July 20, 1999

The first photophysical study of addition derivatives of C_{70} is reported. The spectroscopic and photophysical properties of the singlet and triplet states of these compounds have been determined using a combination of time-resolved and steady-state techniques, including picosecond single photon timing, laser flash photolysis, and low-temperature polarized fluorescence. Electronic absorption, fluorescence, and phosphorescence spectra are red-shifted with respect to those of C_{70}. As with the parent fullerene, the main deactivation channel of the excited singlet state is intersystem crossing, and the yield of singlet oxygen formation is close to unity. Most of the measured photophysical parameters such as the fluorescence lifetime, and fluorescence quantum yield, are similar, but not identical, to those of C_{70}. Fluorescence polarization shows that the emission transition moment is located in the *xy* plane, like in C_{70}, and that the effective fluorophore symmetry remains high.

Introduction

The discovery in 1985 of stable molecular carbon by Kroto and Smalley et al.[1] immediately generated great interest. The subsequent macroscopic synthesis of both [60-I_h]fullerene (C_{60}) and [70-D_{5h}]fullerene (C_{70})[2,3] allowed widespread investigation of the properties, reactivity, and possible applications of the fullerenes.[4−6] The photophysical and photochemical properties of the most abundant fullerenes, C_{60} and C_{70}, have been the subject of numerous studies.[6−8] It was established that intersystem crossing (ISC) is the dominant decay channel for the excited singlet state of both C_{60} and C_{70}, the quantum yield of triplet formation being close to unity. The fluorescence lifetime is short for both molecules (ca. 1.1 ns for C_{60} and 0.65 ns for C_{70}) and almost equal to the inverse of the singlet → triplet intersystem crossing rate constant. The fluorescence lifetimes and quantum yields are temperature-insensitive, showing that ISC is nonactivated for these compounds.[9,10] Consistent with the weakly allowed nature of the radiative process, the fluorescence radiative lifetimes are of the order of 1 μs, that is, 3−4 orders of magnitude higher than the actual lifetimes. The quantum yields of fluorescence are therefore low (ca. 3×10^{-4} for C_{60} and 6×10^{-4} for C_{70}).[7,8] However, under certain favorable conditions, the effective fluorescence quantum yield may increase 10−100-fold as a consequence of the singlet ← triplet back intersystem crossing, making these molecules reasonably fluorescent.[9,11] Another interesting aspect of both C_{60} and C_{70} is their ability to produce singlet oxygen, $O_2(^1\Delta_g)$, with almost unit efficiency.[7] This is explainable by the conjunction of several favorable factors: (i) quantum yield of triplet formation close to unity, (ii) efficient quenching of the fullerene triplet by ground-state oxygen, $O_2(^3\Sigma_g^-)$ (close to diffusion control[7]), and (iii) reverse process (i.e., quenching of singlet oxygen by ground-state fullerene) proceeding at a rate much smaller than diffusion control.[7] These facts, together with the necessarily low fluorescence quantum yield, make C_{60} and C_{70} very good photosensitizers.[7]

More recently, the photophysics of some addition derivatives of C_{60} was studied.[8,12−19] As regards monoadducts, and owing to the symmetry reduction induced by the addend, the radiative rate constant increases, in line with an increase of the electronic absorption coefficients. For the same reason, the fluorescence quantum yield is also higher than that of C_{60}. On the other hand, it is observed that the fluorescence lifetime remains almost unchanged, which implies that the ISC rate constant is little affected by substitution. Singlet oxygen is produced with almost unit efficiency, as with C_{60}. Thermal delayed fluorescence of a magnitude comparable to that of C_{60} is observed.[19]

In this work, we report the first photophysical study of C_{70} derivatives. Three different 1,2-monoadducts of C_{70} and levopimaric acid derivatives were studied. The spectroscopic and photophysical properties of the singlet and triplet states of these compounds were determined by several time-resolved and steady-state techniques, including picosecond single photon timing, laser flash photolysis, and low-temperature polarized fluorescence. Apart from red-shifted electronic absorption, fluorescence, and phosphorescence, the photophysical properties of the derivatives of C_{70} are much closer to those of the parent fullerene than in the case of C_{60}. Fluorescence polarization, in particular, shows that the effective fluorophore symmetry remains high.

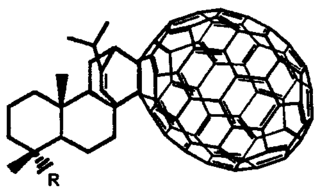
Results and Discussion

Nature of the Derivatives. Addition to adjacent carbon atoms in fullerenes, as in the Diels−Alder reaction ([4 + 2] cycloaddition), takes place preferentially at bonds joining two six-membered rings, or [6,6] bonds, which have higher double-bond character.[20] In C_{60}, all [6,6] bonds are equivalent, but in C_{70} there are four different [6,6] bond types. A simple reactivity criterion, based on the strain caused by neighboring five-membered rings, predicts, in agreement with experiment, that

---

[†] Instituto Superior Técnico.
[‡] Keele University.
[§] INETI.
[*] Corresponding author. E-mail: berberan@ist.utl.pt.

10.1021/jp992495o CCC: $18.00



1 R = COOMe
2 R = CH_2OH
3 R = CHO

Figure 1. Structure of the C_{70} derivatives (1,2-isomer in all cases).

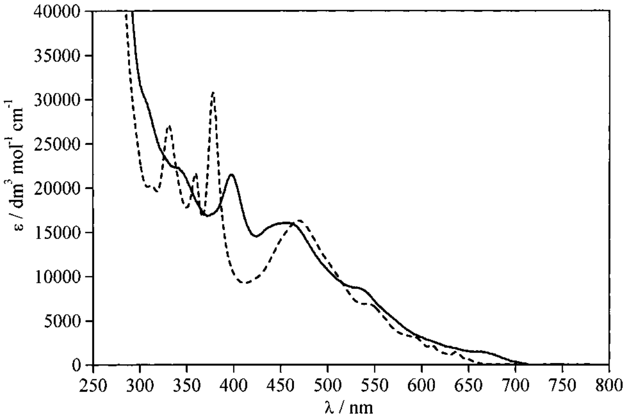


Figure 2. UV−vis absorption spectrum of C_{70} (- - -) and of **1** (—) in methylcyclohexane at room temperature. The absorption spectra of **2** and of **3** are identical to that of **1**.

the most reactive [6,6] bond (C(1)−C(2) or α bond) lies in the vicinity of the C_{70} "pole".[20] The next most reactive bond (C(5)−C(6) or β bond) is still close to the "pole".[20] Some cycloaddition reactions yield a mixture of 1,2- and 5,6-monoadducts resulting from addition to either an α bond or a β bond, respectively, the first product being usually predominant (e.g., in a ratio of ca. 2:1[21]). Addition to the remaining two "equatorial" [6,6] bond types (ϵ and κ[21]) usually has low to negligible yields. The three studied [2 + 4] adducts of C_{70} and levopimaric acid **1**, **2**, and **3**, illustrated in Figure 1, are structurally pseudo-dihydro fullerenes[13] predominantly resulting from α bond monoaddition and will be designated further in accordance with the functionality of the resin moiety, thus $C_{70}-CO_2Me$ **1**, $C_{70}-OH$ **2**, and $C_{70}-CHO$ **3** respectively for the ester, the alcohol, and the aldehyde derivatives. From the point of view of their photophysical properties, the three display identical behavior, as could be expected from an inspection of the chemical structures of the addends. Their joint study is nevertheless relevant, as it provides a stringent test to the data invariance.

Singlet State Photophysics. The electronic absorption spectrum of $C_{70}-CO_2Me$ **1** in methylcyclohexane is presented in Figure 2. A broad absorption band with a maximum around 460 nm seems to correlate with the 470 nm band in C_{70}. Similarly, the stronger absorption band at 400 nm should correlate with the 380 nm band in C_{70}. This correspondence is supported by the polarization data discussed below. A shoulder visible at 540 nm seems also to have a counterpart in C_{70}. Another, weaker shoulder is observed at 660 nm. Complete assignments must however await a high-resolution study, together with high-quality quantum calculations similar to those recently carried out for pristine C_{70}.[23] The absorption onset occurs at ca. 740 nm. In comparison with C_{70}, the absorption spectrum is generally red-shifted but has similar absorption coefficients; see Table 1. Comparison of the spectra and absorption coefficients with the published ones for three different monoadduct isomers of C_{70}[21] confirms that in the derivatives studied here addition to the α bond is largely dominant.

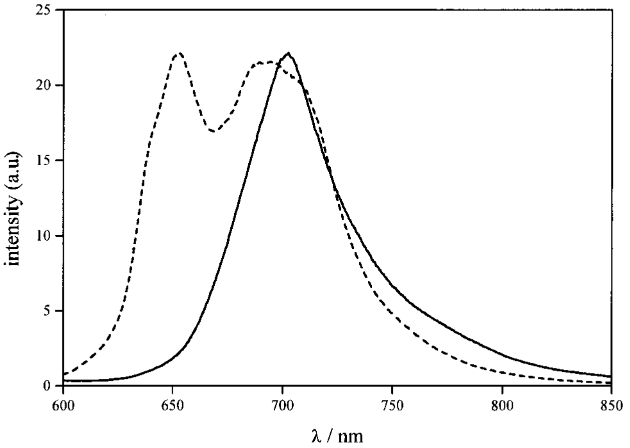


Figure 3. Fluorescence spectra of C_{70} (- - -) and of **3** (—) in methylcyclohexane at room temperature (excitation wavelength was 460 nm, excitation and emission slit widths were 27 and 9 nm, respectively).

The fluorescence spectrum of $C_{70}-CHO$ **3** in methylcyclohexane is displayed in Figure 3 and shows broad emission between 650 and 750 nm, with little vibronic structure and with a maximum at ca. 700 nm. As with the absorption, the emission is red-shifted by about 50 nm with respect to C_{70}. The determined fluorescence quantum yield in cyclohexane at room temperature is 7×10^{-4}, only marginally higher than that of C_{70} ($\phi_F = 6 \times 10^{-4}$ in methylcyclohexane[22]). The zero−zero transition lies at approximately 698 nm, corresponding to a singlet energy of 170 kJ mol^{-1}.

The decay of fluorescence for $C_{70}-OH$ **2** in methylcyclohexane at room temperature is shown in Figure 4. It is close to a single exponential with a lifetime of 1.1 ns. This lifetime is consistent with values measured for the other two derivatives in hydrocarbon solvents at room temperature and is in agreement with efficient intersystem crossing as the main deactivation path for the S_1 state. The measured singlet lifetime is higher than that of C_{70} (0.65 ns). From the fluorescence lifetime and from the fluorescence quantum yield, the computed radiative and nonradiative decay constants are respectively $k_r = 6 \times 10^5$ s^{-1} and $k_{nr} = 9 \times 10^8$ s^{-1}. For C_{70} these constants are $k_r = 9 \times 10^5$ s^{-1} and $k_{nr} = 2 \times 10^9$ s^{-1}. Thus, unlike what happens with C_{60} vs C_{60} monoadducts, where the major change is an almost 10-fold increase of the radiative rate constant upon addition, whereas the nonradiative one is practically unaffected, here both

TABLE 1: Singlet State Properties of C_{70} and C_{70} Monoadducts[a]

	λ_{max}(abs)/ nm	ϵ_{max}/dm^3 mol^{-1} cm^{-1}	λ_{max}(fl)/ nm	$\phi_F/10^{-4}$	τ_F/ns	k_r/s^{-1}	k_{nr}/s^{-1}	ref
C_{70}	381	29 400	650	6	0.65	9×10^5	2×10^9	7, 8, 10, 45
	470	16 000						
1, **2**, **3**	400	24 000	702	7	1.1	6×10^5	9×10^8	this work
	460	18 000						

[a] In hydrocarbon solvents at room temperature.

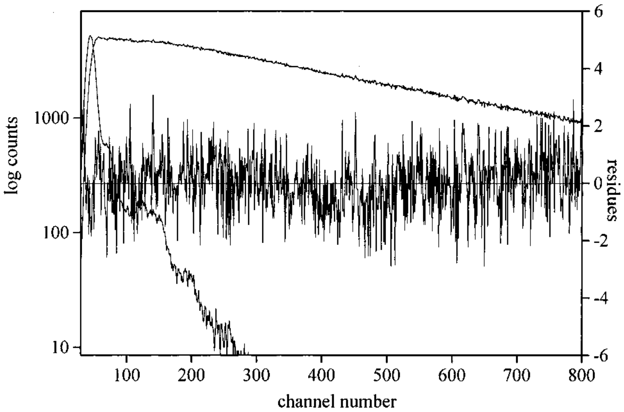


Figure 4. Fluorescence decay of **3** in methylcyclohexane at room temperature. The excitation and emission wavelengths were 300 and 690 nm, respectively. The time scale was 2.76 ps/channel. The decay is well fitted to the sum of two exponentials (reduced chi-squared = 1.1), with $\tau_1 = 1.1$ ns (99%) and $\tau_2 = 0.03$ ns (1%).

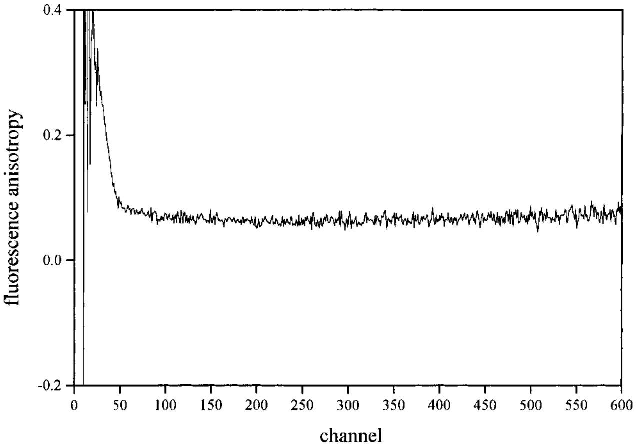


Figure 5. Experimental fluorescence anisotropy decay of **2** in the MT glass at 110 K. The excitation and emission wavelengths were 590 and 690 nm, respectively. The time scale was 2.76 ps/channel. It is seen that after the impulse duration the anisotropy value has a nearly constant value (0.085 ± 0.005).

constants slightly decrease, with the variation being more pronounced for the nonradiative one and diminishing by no more than approximately 50%. The near invariance of the radiative and nonradiative rate constants shows that the C_{70} fluorophore is much less affected by the addition of a group to a [6,6] bond than C_{60}.

The decay of fluorescence anisotropy for **2** in MT glass is illustrated in Figure 5. The decay shows a very fast component previously identified as polarized Raman scattering, followed by a constant plateau where $r = 0.085 \pm 0.005$, and is constant over the whole time range. Given the excitation wavelength used (590 nm), this value is consistent with that found from the steady-state excitation polarization spectrum recorded under identical conditions (Figure 6). The minimum at 400 nm coincides with a strong absorption band (see Figure 2). These results are very similar to those previously obtained[10] for C_{70}, showing that the first electronic transition of **1**, **2**, and **3** is again polarized in the *xy* ("equatorial") plane, while the 400 nm transition is predominantly *z* axis polarized. The surprising aspect is the absolute value of anisotropy measured near the absorption onset, close to 0.1 as in C_{70} and indicative of degenerate moments in the *xy* plane.[10] It thus appears that addition to a [6,6] bond located near the "pole" (α or β) does not significantly affect the effective fluorophore symmetry, which seems to remain D_{5h}, as in C_{70}. This lack of strong perturbation is in agreement with the previously noted near constancy of the radiative and nonradiative rate constants. These aspects, which should reflect the π-electron delocalization pattern in both ground[24−26] and excited states, certainly deserve further attention.

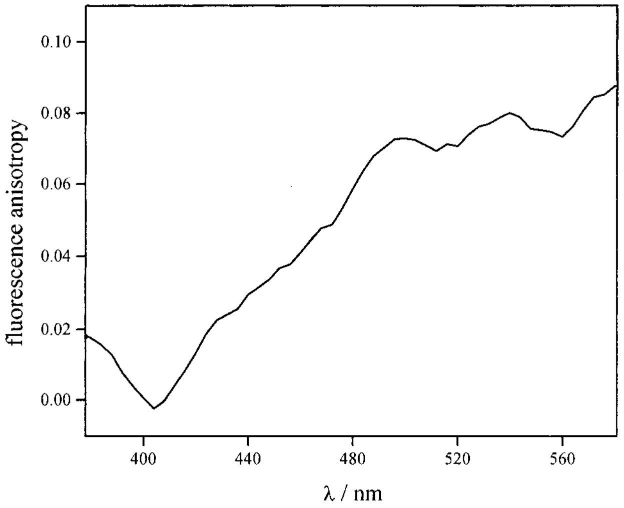


Figure 6. Steady-state anisotropy of **2** in the MT glass at 110 K. The emission wavelength was 700 nm. The excitation and emission bandwidths were 27 and 18 nm, respectively. A Schott RG695 cutoff filter was employed in the emission.

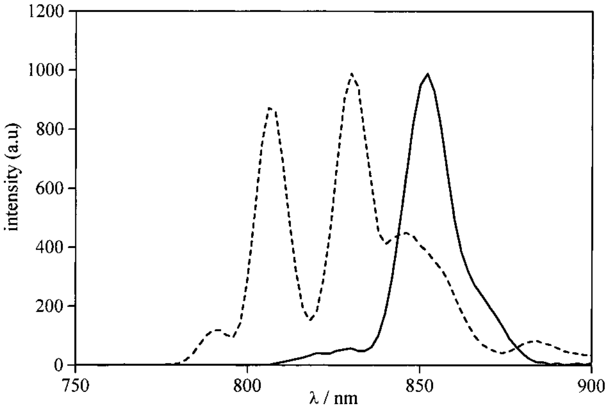


Figure 7. Phosphorescence spectrum of C_{70} (- - -) and of **1** (—) in MT glass at 110 K (excitation wavelength was 460 nm, excitation and emission slit widths were 27 and 9 nm, respectively).

TABLE 2: Triplet State Related Properties of C_{70} and C_{70} Monoadducts

	$\lambda_{max}(ph)^a$/nm	τ_P/ms^a	ϕ_T	ϕ_Δ	ref
C_{70}	830	46	0.994	0.82 ± 0.15	7−9, 45
1, **2**, **3**	850	6.2	≥ 0.8	0.91 ± 0.10^b	this work

[a] In MT at 77 K. [b] Relative to phenalenone.

Triplet State Photophysics. The high-energy portion of the phosphorescence spectrum of the ester derivative **1** is shown in Figure 7. As with the absorption and emission, a red shift of ca. 50 nm is apparent, the wavelength of maximum intensity being 850 nm. The triplet energy is therefore calculated to be ca. 140 kJ mol^{-1} and the singlet−triplet gap to be about 30 kJ mol^{-1}. The phosphorescence lifetime recorded in MT at 77 K was 6.2 ms and was thus lower that of C_{70} in similar conditions;[9,27] see Table 2.

Laser excitation of **1**, **2**, and **3** gives rise to a transient absorption in both the visible and infrared region of the spectrum which is identified as the triplet state, since it is quenched by

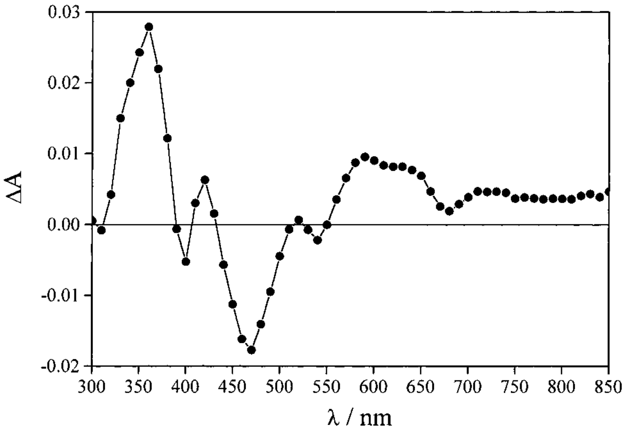


Figure 8. Triplet minus singlet difference absorption spectrum for **1** in degassed toluene at room temperature.

molecular oxygen giving singlet oxygen. In Figure 8 the triplet minus singlet difference absorption spectrum for $C_{70}-CO_2Me$ **1** in toluene is shown. Positive peaks at 360, 420, 590, and 710 nm are apparent, as well as negative peaks at 400, 460, and 540 nm, indicating depletion of the ground state (cf. Figure 2).

The intrinsic lifetimes of long-lived triplet states in fluid solutions are notoriously difficult to measure accurately,[28] on account of bimolecular processes such as impurity quenching, ground-state quenching, and triplet−triplet annihilation. Evidence has previously been given showing that the triplet state lifetimes vary depending on fullerene concentration and also laser intensity.[29,30] Assuming a single-exponential decay law, the measured triplet state lifetime of **1**, **2**, and **3** in degassed toluene at room temperature is ca. 45 μs with a relatively low laser energy of 5 mJ pulse^{-1}. Even under these conditions triplet−triplet annihilation is still present, as evident by deviations to a first-order exponential fit. A second-order decay rate constant of ca. 2×10^9 dm^3 mol^{-1} s^{-1} due to the triplet−triplet annihilation reaction is obtained from a more general fit incorporating the possibility of a second-order process. Such a rate constant is similar to the values previously reported[29,30] for C_{60} and C_{70}. The triplet lifetime obtained from the same fit is 250 μs. Using the reported rate constant for self-quenching of C_{70} in room-temperature toluene,[30] $k = 1.2 \times 10^8$ dm^3 mol^{-1} s^{-1}, and an intrinsic triplet lifetime of 6 ms, one obtains a lifetime of 390 μs for the concentration used (2×10^{-5} mol dm^{-3}), in good agreement with experiment, considering the approximations made. (Exact agreement is obtained with $k = 1.9 \times 10^8$ dm^3 mol^{-1} s^{-1}.)

Quenching of the triplet state of **1**, **2**, and **3** by ground-state molecular oxygen results in the formation of singlet oxygen. In room-temperature toluene the quenching rate constants were 1.6×10^9 dm^3 mol^{-1} s^{-1} and compare well with those reported in the literature[29−32] for C_{60} and C_{70}. The common value of ϕ_Δ for **1**, **2**, and **3** is collected in Table 2 and is close, but somewhat lower than, unity (0.9 ± 0.1). Exactly identical values were obtained for C_{60}, in agreement with reports of ϕ_T[11,33,34] and ϕ_Δ[32,35] slightly smaller than unity for this compound. Since ϕ_Δ can only be smaller than or equal to the quantum yield of triplet formation ϕ_T, this means that the ϕ_T values for **1**, **2**, and **3** are equal to or higher than 0.8. In all experiments the emission of singlet oxygen, observed at 1270 nm, decayed exponentially with a solute independent rate constant. The average lifetime $\tau_\Delta = 28$ μs is comparable with the published value of 27−29 μs.[36]

Using the comparative method, it is possible to estimate the molar extinction coefficients of the triplets of the C_{70} derivatives. The maximum transient absorbances of the triplet of **1**, **2**, and **3** at 590 nm were plotted as a function of laser intensity, and the gradients were compared to that of the standard employed which was taken as benzophenone in benzene whereby $\Delta\epsilon_T = 7220$ dm^3 mol^{-1} cm^{-1} at 530 nm.[37] The $\Delta(\epsilon_T - \epsilon_S)$ values obtained at 590 nm are ca. 1200 dm^3 mol^{-1} cm^{-1} for all derivatives.

Conclusions

In this work, we report the first photophysical study of C_{70} derivatives, three different monoadducts having been studied. The spectroscopic and photophysical properties of the singlet and triplet states of these compounds, determined by several time-resolved and steady-state techniques, showed that, apart from red-shifted electronic absorption, fluorescence, and phosphorescence, the photophysical properties of the derivatives of C_{70} are much closer to those of the parent fullerene than in the case of C_{60}. As with the parent fullerene, the main deactivation channel of the excited singlet state is intersystem crossing, and the yield of singlet oxygen formation is close to unity. The measured photophysical parameters such as the fluorescence lifetime, and fluorescence quantum yield, are similar, but not identical, to those of C_{70}. Fluorescence polarization shows that even the effective fluorophore symmetry is surprisingly high, a symmetry axis of at least 3-fold symmetry being required to produce the observed polarization.

Apart from the electronic absorption spectrum,[21] the only previously available studies on the properties of C_{70} monoadducts concern their redox behavior in the ground state.[38] It was found that their electrochemical characteristics are quite close to those of C_{70}. In this work, it was shown that the same is true, to a great extent, with respect to the photophysical properties.

Experimental Section

Materials. C_{60} (>99.9%) and C_{70} (>99.9%) were obtained from Stefan Kaesdorf (Munich, Germany) and used as received. C_{70} (>99%) was obtained from Hoechst AG (Frankfurt am Main, Germany) and levopimaric acid (99%) from Helix Biotech (Toronto, Canada), and both were used as received. Phenalenone (Aldrich) was recrystallized from cyclohexane, and benzophenone (Aldrich) was recrystallized twice from petroleum ether. All solvents used in spectroscopic and photophysical studies were of spectroscopic grade. For low-temperature fluorescence measurements the solvent mixture, methylcyclohexane−toluene (7:2, v/v), which is denoted MT was used. Oxygen and nitrogen used in the triplet studies were from British Oxygen Co.

Synthesis. The three [2 + 4] adducts of C_{70} and levopimaric acid **1**, **2**, and **3** were synthesized by a Diels−Alder reaction, as described for the corresponding C_{60} adducts.[39] The detailed synthesis, purification, and structural characterization will be described elsewhere:[40]

*Methyl [70]fullerepimarate, **1***. UV/vis ($CHCl_3$, 3.64×10^{-5} M): λ_{max} (ϵ) 374 (18 800), 398 (23 700), 424(16 300), 456 (17 800). MALDITOF-MS (DCTB): m/z 1156 ($MH^{\bullet -}$), 840 ($C_{70}^{\bullet -}$, base peak).

*[70]Fullerepimarol, **2***. UV/vis ($CHCl_3$, 3.68×10^{-5} M): λ_{max} (log ϵ) 374 (19 100), 398 (24 500), 424(17 400), 458 (18 200). MALDITOF MS (m/z): 1128 ($M^{\bullet -}$), 840 ($C_{70}^{\bullet -}$, base peak).

*[70]Fullerepimaral, **3***. UV/vis ($CHCl_3$, 3.68×10^{-5} M): λ_{max}(ϵ) 374 (19 700), 398 (25 300), 424(16 800), 456 (19 000). MALDITOF MS (m/z): 1126 ($M^{\bullet -}$), 840 ($C_{70}^{\bullet -}$, base peak).

Instrumentation. Kinetic absorption measurements were made using the third harmonic (355 nm) of a Spectron Qswitched Nd:YAG laser as described previously.[41] Laser energies were measured with a Gentec ED200 pyroelectric joulemeter. Time-resolved singlet oxygen luminescence was detected via the (0,0) phosphorescence band centered at 1270 nm using a Judson germanium diode (G-050, active diameter = 0.5 cm) equipped with a silicon cutoff filter and coupled to a Judson preamplifier. Time-resolved picosecond fluorescence intensity decays were obtained by the single photon timing method with laser excitation as previously described.[10] Decay data analysis was performed with the Globals Unlimited software package (Laboratory for Fluorescence Dynamics, University of Illinois, Urbana, IL). Low-temperature phosphorescence lifetimes were measured by the modulation method, using a CW argon ion laser (512 nm), whose beam was passed through a mechanical chopper to produce equally spaced (typical period: 200 ms) square pulses with a width of 5 ms. The emitted luminescence was passed through a RG 695 filter before detection by a fast photodiode coupled to an oscilloscope.

Absorption spectra were recorded using either a Perkin-Elmer Lambda-2 UV−vis spectrophotometer or a JASCO 560V UV−vis spectrophotometer. Fluorescence measurements were made using a SPEX F112 spectrofluorimeter. Low-temperature measurements were performed using an Oxford cryostat with quartz windows.

Fluorescence Polarization. Steady state fluorescence polarization measurements were made as previously described.[42] Briefly, fluorescence excitation spectra were taken with the emission and excitation polarizers set in either the vertical or horizontal position. For each wavelength recorded the integration time was 15 s. Electronic thermal noise was recorded under identical conditions and subtracted from the polarized components. Time-resolved picosecond fluorescence intensity decay measurements were made by an alternating collection of impulses and decays with the emission polarizer set at the vertical, horizontal, and magic angle positions. A cutoff filter was used to effectively remove all the excitation light. The G factor for the system is unity.[10]

Singlet Oxygen Quantum Yield Measurements (ϕ_Δ). Air-equilibrated solutions of **1**, **2**, and **3** were optically matched at the laser excitation wavelength, along with that for the reference standard for which the singlet oxygen quantum yield has previously been determined. All solutions were prepared in 1 × 1 cm quartz cells with optically matched absorbances of 0.5 at 355 nm. For the determination of ϕ_Δ values time-resolved luminescence at 1270 nm was recorded using laser excitation. At each laser excitation energy the recorded luminescence trace was obtained by signal-averaging 10 single shots. The averaged traces were fitted to a biexponential, whose slower component was extrapolated to $t = 0$. Plots of I_0 (the extrapolated signal intensity at $t = 0$) versus laser intensity were found to be linear up to a laser intensity of 0.6 mJ pulse^{-1}. Since the gradients of I_0 versus laser intensity are proportional ϕ_Δ, the values of ϕ_Δ may be obtained by comparison with the gradient obtained for the reference standard.

Two standards were employed: C_{60} in air-equilibrated toluene for which ϕ_Δ is reported to be between 0.92 ± 0.05[32] and 0.98 ± 0.05;[33] phenalenone in air equilibrated toluene for which $\phi_\Delta = 1.0$.[43]

Oxygen Quenching Rate Constant (k_q) Measurements. The rate constants (k_q) for the oxygen quenching of the triplet states of the C_{70} derivatives were determined in toluene by kinetic absorption measurements on various O_2/N_2 mixtures. Six single shot kinetic absorption traces were signal averaged for each measurement, and good single-exponential fits were obtained for **1**, **2**, and **3**. The oxygen concentration in air-saturated toluene was taken to be[44] 1.8×10^{-3} mol dm^{-3}.

Acknowledgment. This work was supported by the TMR program of European Union (research network contract ERB FMRX-CT 98-0192 DG 12 - DLCL) and by the program Praxis XXI (contract PCEX/P/QUIM/106/96, FCT, Portugal). Dr. Luftmann (Institute of Organic Chemistry, University of Muenster, Germany) is thanked for the MALDITOF-MS spectra.

References and Notes

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162−163.

(2) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354−358.

(3) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167−170.

(4) Kroto, H. W., Fischer, J. E., Cox, D. E., Eds. *The Fullerenes*; Pergamon: Oxford, 1993.

(5) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, 1996.

(6) Kadish, K. M., Ruoff, R. S., Eds. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Electrochemical Society: Pennington, NJ, 1998; Vol. 6.

(7) Foote, C. S. *Top. Curr. Chem.* **1994**, *169*, 347−363.

(8) Sun, Y.-P. Photophysics and Photochemistry of Fullerene Materials. In Ramamurthy, V., Schanze, K. S., Eds. *Molecular and Supramolecular Photochemistry*; Marcel Dekker: New York, 1997; Vol. 1 (Organic Photochemistry).

(9) Berberan-Santos, M. N.; Garcia, J. M. M. *J. Am. Chem. Soc.* **1996**, *118*, 9391−9394.

(10) Fedorov, A.; Berberan-Santos, M. N.; Lefèvre, J.-P.; Valeur, B. *Chem. Phys. Lett.* **1997**, *267*, 467−471.

(11) Salazar, F. A.; Fedorov, A.; Berberan-Santos, M. N. *Chem. Phys. Lett.* **1997**, *271*, 361−366.

(12) Anderson, J. L.; An, Y.-Z.; Rubin, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1994**, *116*, 9763−9764.

(13) Bensasson, R. V.; Bienvenue, E.; Janot, J.-M.; Leach, S.; Seta, P.; Schuster, D. I.; Wilson, S. R.; Zhao, H. *Chem. Phys. Lett.* **1995**, *245*, 566−570.

(14) Lin, S.-K.; Shiu, L.-L.; Chien, K.-M.; Luh, T.-Y.; Lin, T.-I *J. Phys. Chem.* **1995**, *99*, 105−111.

(15) Bensasson, R. V.; Hill, T. J.; Land, E. J.; Leach, S.; McGarvey, D. J.; Truscott, T. G.; Ebenhoch, J.; Gerst, M.; Rüchardt, C. *Chem. Phys.* **1997**, *215*, 111−123.

(16) Guldi, D. M.; Asmus, K.-D. *J. Phys. Chem. A* **1997**, *101*, 1472−1481.

(17) Luo, C.; Fujitsuka, M.; Watanabe, A.; Ito, O.; Gan, L.; Huang, Y.; Huang, C.-H. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 527−532.

(18) Bensasson, R. V.; Bienvenue, E.; Fabre, C.; Janot, J.-M.; Land, E. J.; Leach, S.; Leboulaire, V.; Rassat, A.; Roux, S.; Seta, P. *Chem. Eur. J.* **1998**, *4*, 270−278.

(19) Berberan-Santos, M. N.; Salazar, F. A.; Garcia, J. M. M.; Santos, C.; Fonseca, T.; Marcelo Curto, M. J.; Gigante, B. *Electrochem. Soc. Proc.* **1998**, *98−8*, 319−327.

(20) Thilgen, C.; Herrmann, A.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2268−2280.

(21) Herrmann, A.; Diederich, F.; Thilgen, C.; ter Meer, H.-U.; Müller, W. H. *Helv. Chim. Acta* **1994**, *77*, 1689−1706.

(22) Ma, B.; Sun, Y.-P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2157−2162.

(23) Negri, F.; Orlandi, G. *J. Chem. Phys.* **1998**, *108*, 9675−9684.

(24) Krygowski, T. M.; Ciesielski, A. *J. Chem. Inf. Comput. Sci.* **1995**, *35*, 1001−1003.

(25) Van Lier, G.; Benasser, S.; Geerlings, P. *J. Chem. Soc., Perkin Trans. 2* **1998**, 349−354.

(26) Van Lier, G.; Geerlings, P. *Chem. Phys. Lett.* **1998**, *289*, 591−601.

(27) Wasielewski, M. R.; O'Neil, M. P.; Lykke, K. R.; Pellin, M. J.; Gruen, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 2774−2776.

(28) Linschitz, H.; Steel, C.; Bell, J. A. *J. Phys. Chem.* **1962**, *66*, 2574−2576.

(29) Fraelich, M. R.; Weisman, R. B. *J. Phys. Chem.* **1993**, *97*, 11145−11147.

(30) Etheridge, H. T.; Weisman, R. B. *J. Phys. Chem.* **1995**, *99*, 2782−2787.

(31) Palit, D. K.; Sapre, A. V.; Mittal, J. P.; Rao, C. N. R. *Chem. Phys. Lett.* **1992**, *195*, 1−6.

(32) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. L.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *95*, 11−12.

(33) Biczok, L.; Linschitz, H.; Walter, R. I. *Chem. Phys. Lett.* **1992**, *193*, 339−346.

(34) Bensasson, R. V.; Hill, T.; Lambert, C.; Land, E. J.; Leach, S.; Truscott, T. G. *Chem. Phys. Lett.* **1993**, *201*, 326−335.

(35) Terazima, M.; Hirota, N.; Shiginohara, H.; Saito, Y. *J. Phys. Chem.* **1991**, *95*, 9080−9085.

(36) Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 663−1021.

(37) Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9−14.

(38) Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Herrmann, A.; Rüttiman, M.; Crassous, J.; Cardullo, F.; Echegoyen, L.; Diederich, F. *J. Am. Chem. Soc.* **1998**, *120*, 7860−7868.

(39) Gigante, B.; Santos, C.; Fonseca, T.; Curto, M. J. M.; Luftmann, H.; Bergander, K.; Berberan-Santos, M. N. *Tetrahedron* **1999**, *55*, 6175−6182.

(40) Gigante, B.; Santos, C.; Luftmann, H.; Bergander, K.; Berberan-Santos, M. N., manuscript in preparation.

(41) Tinkler, J. H.; Tavender, S. M.; Parker, A. W.; McGarvey, D. J.; Mulroy, L.; Truscott, T. G. *J. Am. Chem. Soc.* **1996**, *118*, 1756−1761.

(42) Berberan-Santos, M. N.; Valeur, B. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2623−2625.

(43) Schmidt, R.; Tanielian, C.; Dunsbach, R.; Wolff, C. *J. Photochem. Photobiol. A* **1994**, *79*, 11−17.

(44) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993.

(45) Bensasson, R. V.; Hill, T.; Lambert, C.; Land, E. J.; Leach, S.; Truscott, T. G. *Chem. Phys. Lett.* **1993**, *206*, 197−202.