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Coupling a dendrimer and a fullerene chromophore: a study of excited state properties of C_{61}(poly(aryl)acetylene)$_2$

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Abstract

A new methanofullerene, C_{61}(poly(aryl)acetylene)$_2$, where the mono-adduct contains dendrimer units, has been studied with respect to its photophysical properties. The visible absorption and the emission spectra, the triplet molar extinction coefficient as well as the near unity value of the quantum yield of singlet oxygen production upon photoexcitation reveal characteristics in keeping with other methanofullerenes previously studied, where the addend species is not an electron donating group. The results indicate that, even when the methanofullerene is photoexcited, this large addend does not electronically communicate through the methano bridge neither through space. Photophysical properties of methanofullerenes can thus be preserved when they are functionalised with such addends. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The fullerenes and their derivatives have been the subject of much study with regard to their photophysical properties and potential use for applications in optoelectronics [1–4], biology and medicine [5]. C_{60} can be derivatised via a large number of known cage functionalisation methods [6,7]. Such functionalisation of fullerenes can alter their optical properties [8–10]. One important class of mono-functionalised C_{60} derivatives are the methanofullerenes which belong to the most widely studied class of functionalised [60]fullerenes (see for example [8,11–13]). These studies have shown that methanofullerenes retain most of the photophysical characteristics associated with C_{60}, except when the functionlised C_{60} contains an electron donating moiety. This includes the case of prophyrin-C_{60} [14,15], of aniline-C_{60} dyades [16] and of systems where methanofullerenes are linked to copper complexed rotaxanes [17], which all exhibit strong changes in the photophysical properties of the excited states of the fullerene units.

In this Letter, we report some photophysical properties of a novel methanofullerene, 61,61-bis[4-{3,5-bis[3,5-bis(3,5-di-*tert*-butylphenylethy-

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nyl)phenylethynyl]phenylethynyl}phenyl]-1,2-dihydro-1,2-methano[60]fullerene. In the following, we name this compound C_{61}(poly(aryl)acetylene)$_2$. Its synthesis and characterisation has been reported recently [18]. It has a single addend consisting of two poly(aryl)acetylene dendrimer branches containing two dendrimer generations (see Fig. 1 for a schematic representation). That these are apparently not electron donating groups for the C_{60} moiety in the ground state, has been demonstrated by cylic voltammetry [18]. With this molecule we test the influence of poly(aryl)acetylene addends on the excited state properties of methanofullerene. Further motivation arises from the fact that the addend possesses structural branching which is of interest for dendrimer and macromolecular chemistry [19]. Recent studies on a series of related phenylacetylene dendrimers have shown that these molecules can act as energy funnels similar to light harvesting antennas in green plants [20,21]. Therefore, connection of C_{60} to such a dendrimer could lead to a new class of molecules having interesting electronic properties.

We report ground and excited state absorption spectra of C_{61}(poly(aryl)acetylene)$_2$ in solution. Furthermore, using C_{60} as a reference [22], we have determined the quantum yield of singlet oxygen production (Φ_Δ), the quantum yield of singlet to triplet intersystem crossing (Φ_T) and the triplet molar absorption coefficient (ε_T) by laser flash photolysis and pulse radiolysis techniques. We also report laser induced emission spectra at low temperatures in toluene matrices.

2. Experimental

C_{61}(poly(aryl)acetylene)$_2$ was synthesised as outlined in a previous publication [18] and used following purification by HPLC. Ground state absorption measurements were made using a Cary 300 double beam spectrophotometer. Triplet state properties were studied in benzene solution using pulse radiolysis and laser flash photolysis techniques as previously described [13,23–26]. In the pulse radiolysis experiments, biphenyl in roughly 10^3 times higher concentration has been used as a triplet donor. In the laser flash photolysis experiment we use the frequency tripled fundamental of a Nd:YAG laser (Quantel YG 585 10G, $\lambda_{exc} = 355$ nm). The triplet–triplet absorption spectra have been recorded as described in [13]. Singlet oxygen

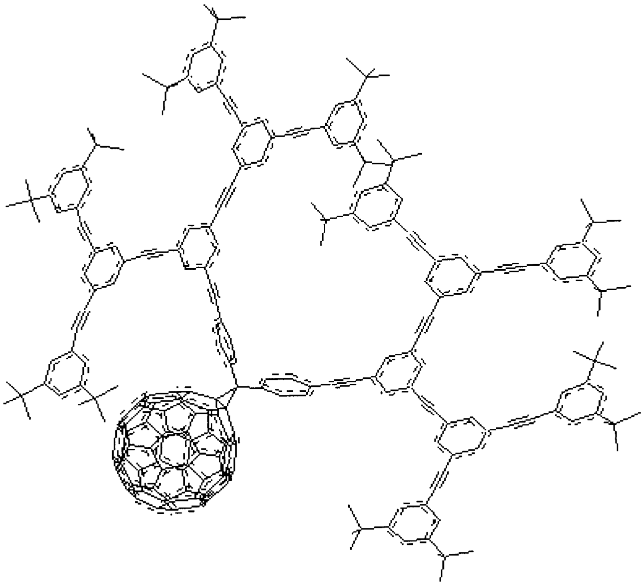

Fig. 1. Schematic representation of C_{61}(poly(aryl)acetylene)$_2$.

phosphorescence was observed at 1270 nm using a liquid nitrogen cooled germanium diode.

For emission studies, an Ar^+ laser (Spectra Physics, model 2016) was used for excitation at 514 nm. Dispersed fluorescence of C_{61}(poly(aryl)acetylene)$_2$ in toluene solution was detected using a HRB 600 monochromator (Jobin-Yvon, grating blazed at 750 nm) together with a photomultiplier (Hamamatsu R943-02), which provides good sensitivity in the red spectral region. No correction for the spectral response was attempted. Laser stray light was eliminated by colour filters placed in front of the monochromator. The sample was placed in the optical path sector of a liquid helium bath cryostat which has variable temperature facilities (SMC from Air Liquide). Experiments were carried out at four temperatures ($T = 300$, 185, 105 and 5 K). The cooling rates employed were 8 K h^{-1} between 300 and 200 K and 60 K h^{-1} between 200 and 5 K, respectively.

3. Results and discussion

3.1. UV/Vis absorption spectra

The absorption spectrum of C_{61}(poly(aryl)acetylene)$_2$ in cyclohexane solution is shown in Fig. 2 for three different dilutions. In the visible, we observe the sharp band at 430 nm which is characteristic of [6,6]-ring bridged methanofullerenes. Additional broad bands, peaking at 495, 660, 681 and 694 nm, are also observed in the visible part of the spectrum of C_{61}(poly(aryl)acetylene)$_2$. All of these features are also seen in a set of [6,6]-ring bridged methanofullerenes previously studied [13]. These were (61,61-bis[4-*tert*-butylbenzoate]-1,2-di-hydro-1,2-methano[60] fullerene, 61,61-bis [4-(*tert*-butyldiphenylsilyloxymethyl)phenyl]-1,2-di-hydro-1,2-methano[60]fullerene and 61-[(ethoxycarbonyl)methylcarboxylate]-1,2-di-hydro-1,2-methano[60]fullerene. The broad bands in the visible are also observed in the [6,6]-ring bridged methanofullerenes studied in [8,12]. Their origins have been discussed earlier [13]. The broad absorption centred at 495 nm is explained by comparison with the C_{60} absorption where similar features are seen arising from dipole forbidden transitions activated by Herzberg–Teller vibronic interactions [27]. The group of weak features between 660 and 694 nm may also be derived from orbitally forbidden transitions in C_{60} [27]. The similarity of the visible spectral features of C_{61}(poly(aryl)acetylene)$_2$ as compared to other methanofullerenes indicates that the mono-addend perturbation of the lowest-lying electronic states of the methanofullerene is relatively independent of the nature of the addend.

The absorbance of C_{61}(poly(aryl)acetylene)$_2$ in the UV region is very strong due to the large π-electron-conjugated system of the two poly(aryl) acetylene dendrimer addends. Broad bands are observed at 310, 301, 293, 276 and 262 nm (see Figs. 2 and 3). Adopting a molar absorptivity of about 1800 M^{-1} cm^{-1} for the 495 nm methanofullerene band (compare [8]) and assuming that the 495 nm band is not altered significantly by the presence of the dendrimer addends, we can estimate the absorptivity at 310 nm to be of the order of 700 000 M^{-1} cm^{-1} for our compound. In view of the very strong absorptivity in the UV of C_{61}(poly(aryl)acetylene)$_2$ as compared to C_{60} [28], as well as to other methanofullerenes [13] of even lower UV absorptivity than C_{60}, we conclude that the cage electronic states contribute only insignificantly to the absorption in this spectral region. This is confirmed when comparing the UV spectrum of C_{61}(poly(aryl)acetylene)$_2$ to the UV spectrum of diphenylacetylene [29] which is the building block of the dendrimer addend (Fig. 3).

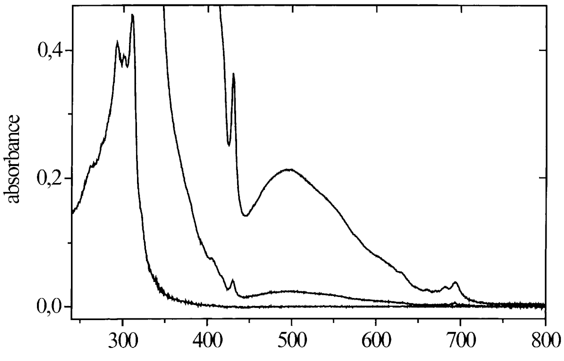

Fig. 2. Absorption spectra of C_{61}(poly(aryl)acetylene)$_2$ in cyclohexane solution at three different dilutions.

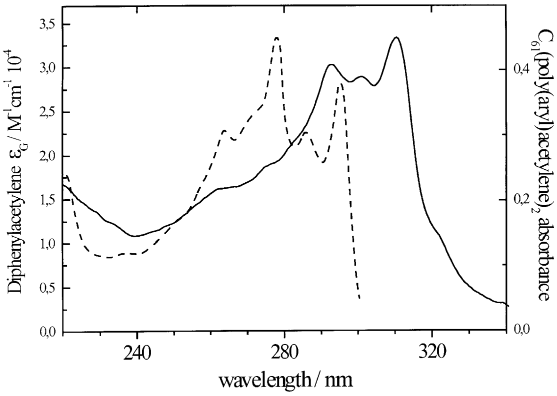

Fig. 3. UV absorption spectra of diphenylacetylene (molar extinction coefficient ε_G, dotted line) and C_{61}(poly(aryl) acetylene)$_2$ (absorbance, solid line).

The two spectra are very similar. Apparently, the UV bands of diphenylacetylene become shifted to the red by approximately 15 nm when diphenylacetylene blocks are joined to form the large π-electron-conjugated system of the second generation dendrimer addend of C_{61}(poly(aryl)acetylene)$_2$.

3.2. Triplet absorption spectra

A set of transient triplet absorption spectra at different delay times are shown in Fig. 4 as obtained by pulse radiolysis in argon saturated benzene solution. Here, biphenyl is used as a triplet sensitiser. The decay rate of the triplet state of C_{61}(poly(aryl)acetylene)$_2$ is $k = 3.79 \times 10^{-4}$ s^{-1} in our experimental conditions. The absorption maximum is at 720 nm. It is accompanied by a side band at around 800 nm. These two features, as well as the general shape of the absorption band between 550 and 820 nm are also observed in the triplet absorption spectra of the three methanofullerenes studied in [13]. The large blue shift of the maximum of the triplet–triplet absorption spectrum as compared to C_{60}, whose absorption maximum is located at 750 nm [22] has been discussed previously [13]. The bands of the methanofullerene derivative have been related to optically allowed $2^3Gu \leftarrow 1^3T_{2g}$ and $^3Hu \leftarrow 1^3T_{2g}$ C_{60}-transitions [13]. This parentage assignment appears to hold here since the large dendrimer addends do not show any influence on the TT-spectrum as compared to the methanofullerenes studied [13].

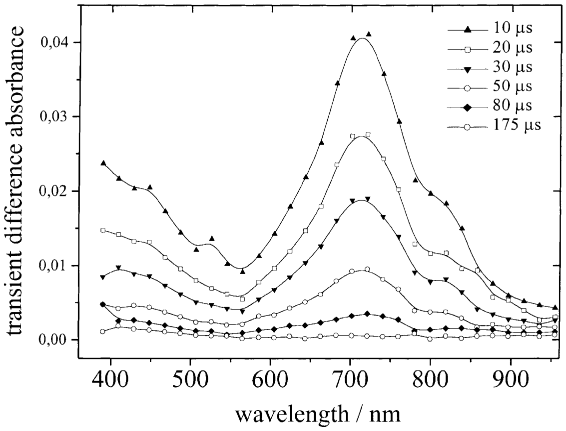

Fig. 4. Decay of the triplet absorptin of C_{61}(poly(aryl) acetylene)$_2$ in benzene solution. Shown are transient difference spectra at a series of detection intervals following pulse radiolysis using biphenyl as a triplet donor.

3.3. Quantum yield of singlet oxygen formation (Φ_Δ) and triplet molar absorption coefficient (ε_T)

Singlet oxygen production, sensitised by the triplet of C_{61}(poly(aryl)acetylene)$_2$, was quantified by recording the amplitude of $^1O_2$ ($^1\Delta_g$) phosphorescence at 1270 nm following laser excitation at $\lambda_{exc} = 355$ nm. It was compared to C_{60} sensitised $^1O_2$ ($^1\Delta_g$) phosphorescence. Φ_Δ has been determined, as outlined for example in [13], to be $\Phi_\Delta = 0.91 \pm 0.1$ for C_{61}(poly(aryl)acetylene)$_2$. Taking into account the experimental error, this value can be regarded as equal to those observed for other methanofullerenes ([13], Φ_Δ near unity). Since Φ_Δ must be smaller or equal to Φ_T the quantum yield of singlet to triplet intersystem crossing, Φ_T can be assumed to be also near unity. This is significant as it indicates that the presence of the dendrimer branches does not reduce the triplet yield of the compound, even if these addends contribute to the ground state absorption at the excitation wavelength. A reduced triplet yield has been found upon photoexciting compounds, where C_{60} is linked to electron donor addends [15–17]. This has been explained by a competitive electronic deactivation leading to the formation of a charge-separated state. We conclude that in our novel compound, a photoinduced intramolecular electron transfer process does not appear upon photoexcitation at $\lambda = 355$ nm.

From our laser flash photolysis study using the comparative method with C_{60} as a standard and assuming $\Phi_\Delta = \Phi_T$, we determine the triplet molar extinction coefficient, ε_T, of the methanofullerene derivative to be about $(13\,800 \pm 1000)$ M^{-1} cm^{-1} at $\lambda = 720$ nm. An independent estimate is obtained from the pulse radiolysis experiment. It yields a similar result ($(13\,000 \pm 1500)$ M^{-1} cm^{-1} at $\lambda = 720$ nm). As expected, ε_T of C_{61}(poly(aryl) acetylene)$_2$ is in the same range as that for the methanofullerenes studied in [13].

3.4. Emission studies

Laser excited emission spectra have been recorded in toluene solution at four different temperatures (Fig. 5). At 300 K, the maximum of fluorescence spectrum is found at 708 nm with a side band at 778 nm. These spectral features are also observed in the fluorescence spectra of other methanofullerenes [8,11,12] indicating that also in the case of C_{61}(poly(aryl)acetylene), fluorescence only takes place from the lowest lying singlet state S_1. Mirror image characteristics are observed as is the case for other methanofullerenes (see for example [11]). The lowest lying electronic states of the compound, which are believed to be localised on the cage are not differently perturbed by the presence of the dendrimer addends as compared with other methanofullerenes. Again, the addend appears not to electronically communicate with the fullerene moiety via the sp^3 carbon atom in the methano bridge. This carbon atom is not conjugated either to the addend or to the fullerene cage. We note further that density functional theory (DFT) calculations by Curioni et al. [30] on the methanofullerene $C_{61}H_2$ and C_{60} show that the presence of the addend only effects states derived from configurational transitions beyond the LUMO t_{1u} orbital. It thus appears that the dendrimer addend perturbs significantly only LUMO + 1 states.

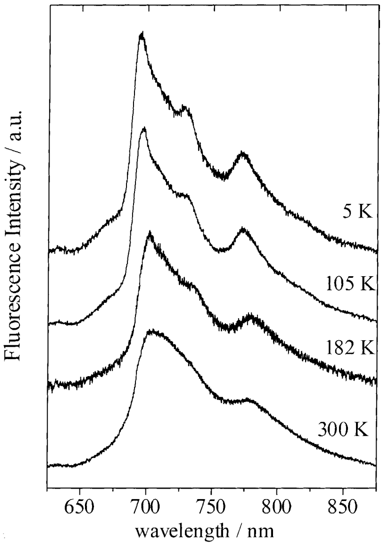

Fig. 5. Emission spectra of C_{61}(poly(aryl)acetylene)$_2$ in toluene solution (1–5 × 10^{-4} mol/l) solution at four different temperatures ($\lambda_{exc} = 514$ nm).

The emission spectra recorded at lower temperatures show the appearance of new features not observed in the room temperature spectrum. The spectrum recorded at 5 K shows broad band features at 695, 728 and 773 nm. The broadness of the bands in the solid toluene solution indicates that the emitting species are in a glassy environment. Reduction in temperature results in a blue shift in the band maxima, but the general emission characteristics remain unchanged, indicating that in the solid toluene solution the electronic states of the emitting species are not altered by the environment.

4. Conclusion

The excited state properties of a new methanofullerene, C_{61}(poly(aryl)acetylene)$_2$, combining the C_{60} cage with two large dendrimer chromophores, have been investigated. The visible absorption and the emission spectra, the singlet oxygen yield Φ_Δ as well as the triplet molar extinction coefficient ε_T of the new compound are very similar to those of methanofullerenes with smaller and different nonelectron donor addends.

The UV absorption of C_{61}(poly(aryl)acetylene)$_2$ is particularly strong and is mainly attributed to transitions located on the two dendrimer branches of the molecule, thus making these addends efficient photon antennae.

The results of our study show that no electron transfer takes place on excitation and that the dendrimer addend does not electronically communicate with the fullerene through the methano bridge upon photoexcitation at $\lambda \geqslant 355$ nm. The reasons for this can be explained by referring to the sp^3 carbon atom in the methano bridge, which is not conjugated to the addends or to the fullerene cage. Our results are thus in contrast to other supramolecular systems involving methanofullerenes [14–17] where steric interactions, as well as favourable redox potentials are the reasons for the strong intercomponent interaction observed following photoexcitation.

Our study demonstrates that it is possible to preserve the excited state properties of a methanofullerene when this molecule is functionalised with large poly(aryl)acetylene addends acting as photon antennae. This ability could be of interest for future molecular electronic applications.

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