

Synthesis and excited state properties of a [60]fullerene derivative bearing a star-shaped multi-photon absorption chromophore†

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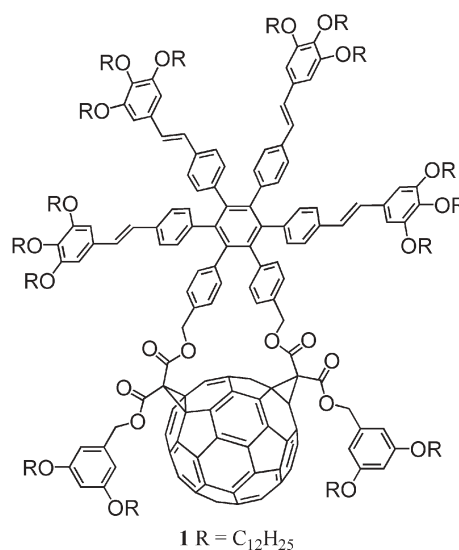
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The synthesis and excited state properties of a compound assembling C₆₀ with a new multi-photon absorption chromophore are reported.

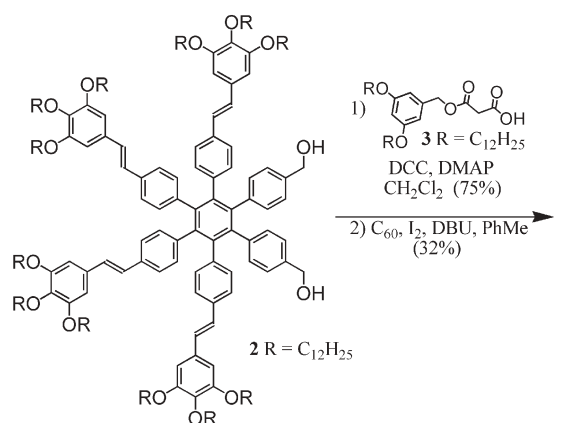
The past several years have seen a considerable interest in the development of photochemical molecular devices based on the combination of C₆₀ with π -conjugated oligomers.¹ In particular, such hybrid systems have shown interesting excited state properties and have found applications in the field of solar energy conversion.² Whereas the photophysical properties of a wide range of fullerene-(π -conjugated oligomer) dyads have been reported so far,¹ research focused on related assemblies combining C₆₀ and conjugated oligomers with strong multi-photon absorption (MPA) cross sections has been probed to a lesser degree.³ Such hybrid systems are however potentially interesting since they should be capable of generating singlet oxygen upon multi-photon absorption⁴ followed by energy transfer to the fullerene sensitizing unit.⁵ This could broaden the applicability of C₆₀ derivatives in photodynamic therapy⁶ which is currently highly limited by both the weak linear and the low induced absorptions of fullerene-based sensitizers in the 650–750 nm region. As part of our research on compounds combining C₆₀ with π -conjugated oligomers, we now report the synthesis and the excited state properties of compound **1** assembling C₆₀ with a new MPA chromophore. In the design of the MPA dye, we have selected a star-shaped system. Actually, whereas the optimization of MPA like TPA compounds has largely focused on 1-D structures, it has recently been shown that increased dimensionality and branched structures lead to highly effective multiphoton absorption.⁷

Compound **1** was prepared by taking advantage of the versatile regioselective reaction developed in the group of Diederich⁸ which led to C₆₀ bis-adducts by a cyclization reaction at the C sphere with bis-malonates in a double Bingel⁹ cyclopropanation. To this end, bis-malonate was prepared by the reaction of diol **2** with

malonic acid mono-ester **3** under esterification conditions using *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylamino pyridine (DMAP) in CH₂Cl₂ (Scheme 1). Treatment of the bis-malonate thus obtained with C₆₀, I₂, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded the desired cyclization product **1** in 32% yield.



Compound **1** was characterized by ¹H- and ¹³C-NMR, UV-vis and IR spectroscopies. In addition, the structure of **1** was confirmed by FAB mass spectrometry. The relative position of the two cyclopropane rings in **1** on the C₆₀ surface was determined



Scheme 1 Preparation of compound **1**.

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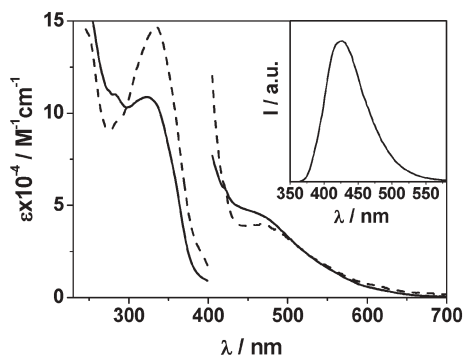
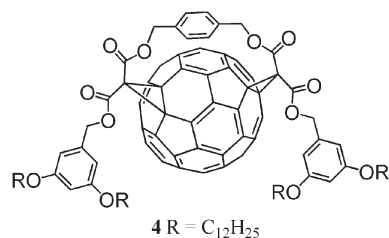


Fig. 1 A comparison of the absorption spectrum of the dyad **1** (–) in CH_2Cl_2 with that of the summation (---) of the absorption spectra of the reference compounds **2** and **4** in CH_2Cl_2 . The inset shows the fluorescence spectrum of **2** in CH_2Cl_2 .

based on the molecular symmetry (C_1) deduced from the ^1H - and ^{13}C -NMR spectra. The absorption spectrum of dyad **1** in CH_2Cl_2 is shown in Fig. 1, along with the profile obtained by summing the spectra of its component units **2** and **4**. This comparison suggests substantial ground state interactions between the fullerene and π -conjugated units in dyad **1**, with the main absorption band of chromophore **2**, centered at around 335 nm, being reduced in intensity. The ground state interactions in dyad **1** may be explained by the close proximity of the two subunits as already observed for a bis(phenanthroline)Cu(I) derivative substituted with cyclic C_{60} bis-adduct moieties.¹⁰ However, small conformational changes in the hexasubstituted benzene chromophore resulting from the cyclic structure involving two of its aromatic units may also explain, at least in part, the observed differences.



The fluorescence spectrum of **2** in CH_2Cl_2 is shown in Fig. 1. It displays a broad band with a maximum at 425 nm. The corresponding singlet lifetime was measured to be 1.5 ± 0.2 ns and the fluorescence quantum yield is 0.53 in CH_2Cl_2 . Direct excitation of the star-shaped organic moiety in dyad **1** at 335 nm results in a 200-fold decrease of its emission intensity in toluene, CH_2Cl_2 and benzonitrile, when compared to **4** under the same conditions. Clear evidence on whether this process is followed by sensitization of the fullerene moiety in dyad **1** cannot be obtained because some residual emission from the appended fragment is still present above 650 nm, and this is enough to mask the weak fullerene fluorescence ($\Phi = 0.0004$). Monitoring the luminescence of sensitized singlet oxygen allows us to indirectly evaluate the relative yield of formation of the lowest triplet excited state of C_{60} .¹¹ Fig. 2 shows the singlet oxygen emission spectra recorded for fullerene **4** compared to dyad **1** under the same conditions in toluene and benzonitrile and at two different excitation wavelengths (355 and 500 nm). These data provide the following information: (a) Dyad **1** is always a poorer sensitizer of singlet

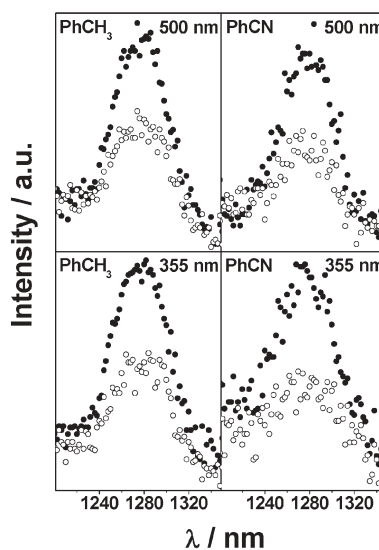


Fig. 2 Sensitized singlet oxygen luminescence of dyad **1** (○) and the fullerene **4** (●) in toluene (left) and benzonitrile (right) and while exciting at 500 nm (top) and 355 nm (bottom).

oxygen than fullerene **4**; (b) irrespective of solvent polarity or excitation wavelength, the relative quantum yield of singlet oxygen of dyad **1** is the same, pointing to identical yields of fullerene triplet formation. The absence of any solvent effect on the yield of C_{60} triplet tends to discard any major role of electron transfer in the cascade of photoinduced processes. Furthermore, no C_{60} anion features were found in the NIR region down to 1200 nm, neither for **1** nor during bimolecular quenching experiments between **2** and **4** in toluene and benzonitrile, down to a 20 ns timescale. Therefore an occurrence of long-lived charge separated states is excluded. These data suggest that quenching of the star-shaped organic conjugated moiety is likely due to singlet–singlet energy transfer to the fullerene fragment, followed by intersystem crossing to generate the fullerene triplet, as observed for similar C_{60} arrays.¹¹ The lifetime of the quenched fluorescence could not be determined since it is shorter than our instrumental resolution (200 ps). However, from the fluorescence quenching data,¹¹ the rate constant of the energy transfer process can be estimated as $\geq 1.3 \times 10^{11} \text{ s}^{-1}$ in all solvents.

Data in Fig. 2 suggest that the fullerene moiety in **1** has an inherently different yield of singlet oxygen sensitization, probably related to its own structure where the organic conjugated fragment is close to the carbon cage. This might lead to some protective effects towards oxygen quenching as previously found in bismethanofullerene dendrimers.¹² The transient absorption spectra of **1** and **4** (Fig. S1)† compare well with triplet spectra of bismethanofullerenes reported earlier, however they are not fully superimposable to each other ($\Delta\lambda_{\text{max}}$ ca. 10 nm). This could be related to intramolecular interactions, as suggested above. Notably, the fullerene triplet lifetimes of dyad **1** (557 ns and 39 μs in air-equilibrated and air-free toluene solutions, respectively) are substantially longer than that of **4** (362 ns and 15 μs , Fig. S2).† This confirms that the triplet features of the fullerene are inherently different in **1** and **4** and protective effects of the organic fragment toward quenching of O_2 (see triplet lifetime in air-equilibrated solutions) or solvent impurities (deaerated samples) could at least partly explain this trend.¹²

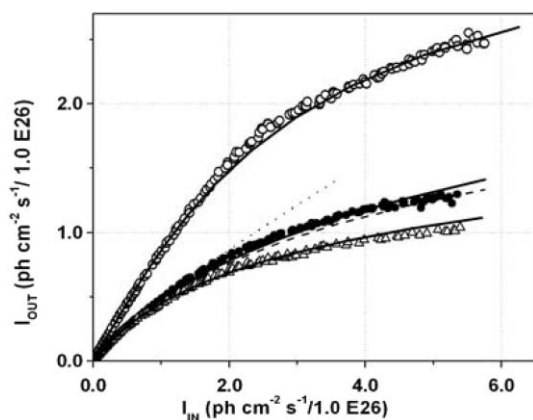


Fig. 3 Optical limiting of **2** (○), **4** (●) and **1** (△) in benzonitrile solutions using 9 ns pulses at 532 nm. Straight lines starting from the axis origin would indicate a linear behaviour. Non linear absorptions are observed as deviations from straight lines. Fitting of the data is obtained with models for the excited state dynamics (see text).

Fig. 3 shows the results of optical limiting measurements of benzonitrile solutions of the two separated moieties **2** and **4**, and of dyad **1**, using 9 ns pulses of a duplicated Nd : YAG at 532 nm. It is well known that fullerene is a reverse saturable absorption system with a greater absorption at high intensities due to the population of triplet states.¹³ However, Fig. 3 shows that also **2** has a non linear behaviour which should be considered in evaluating the behaviour of **1**. A model which accounts for the non linear behaviour of **2** is a sequential three photon absorption in which, similarly to other cases,¹⁴ a first one-photon transition populates an excited state of the molecule and then a two-photon absorption from this excited state occurs (ES-TPA). The fitting is reported on the figure and was obtained by solving coupled equations for the population dynamics of excited states.¹⁵ We found a cross section for the ES-TPA, $\sigma^{(2)} = 1.58 \times 10^{-43} \text{ cm}^4 \text{ s ph}^{-1} \text{ mol}^{-1}$, which is three to four order of magnitude larger than values found for ground state TPA, and is characteristic of excited states with very polarizable electronic states¹⁴ (other fitting parameter values are reported in the electronic supplementary information).†

The non linear behaviour of **4** is characteristic of a fullerene derivative. In this case the fitting of the low intensity behaviour can be obtained with a four level system with two singlet states and two triplet states which absorb more than the singlet states.¹⁶ The best fitting, using this model, is reported as a dotted curve in Fig. 3. One finds that it fails to reproduce the large intensities data. The simplest model, which accounts for the experimental data, must take into account that another one-photon transition can occur from the excited triplet state (values of the fitting are reported in Table S1).† In this case, we obtain a good fitting which also accounts for the high intensity region (continuous line over full circles). By combining the separated non linear behaviour of **2** and **4**, we are able to obtain an overall non linear response which is reported as a dashed line in Fig. 3. A small difference is found with respect to the fullerene behaviour, but the experimental data of **1** are not reproduced. This is another clear indication for an excited state interaction between the two moieties in **1**. However the

transient spectra (Fig. S1)† show that other excited states such as charge transfer are not involved in the process and that an energy transfer between singlet states occurs. Accordingly, the fitting of the experimental data of **1** can be obtained only with variation of the parameter values of the fullerene. The fitting is reported in Fig. 3 and the values of the fitting parameters in Table S1.† In particular, one finds larger excited states absorption cross sections most probably due to the protective effect resulting from the large substituent on the fullerene sphere in **1**, but the overall picture remains the same as deduced above.

In conclusion, the combination of C₆₀ with a MPA chromophore leads to improved optical limiting properties and owing to the intercomponent photoinduced energy transfer, the excited state deactivation dynamics is dominated by the fullerene chromophore. These findings pave the way towards the design of new efficient fullerene-based singlet oxygen sensitizer for photodynamic therapy applications.

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