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Novel Functional Fullerene Materials: Fullerenes as Energy Acceptors

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Summary. Fullerene derivatives exhibit absorption throughout the UV/Vis region up to 750 nm. This feature is important for easy excitation. Once excited, fullerenes may become both electron and energy acceptors. The distinction between these two pathways depends strongly on the partner involved (donor) and on the conditions employed (solvent, *etc.*).

Keywords. Fullerenes; Electron transfer; Energy transfer; Fulleropyrrolidines.

Introduction

The discovery of C_{60} [1, 2] has offered new opportunities to the scientific community for exploring the chemical and physical properties of novel forms of carbon. As a result of the increased interest in this new field, an enormous number of studies related to fullerene and its derivatives has appeared in recent years, covering a wide range of different subjects including many fields of chemistry, physics, material sciences, and biology [3]. One of the most important properties of C_{60} and the higher fullerenes is their enhanced ability to act as electron acceptors [4–6]. This has led to a large number of fulleride salts, synthesized *via* reduction reactions, with fascinating solid state properties like ferromagnetism [7] and superconductivity [8, 9]. In addition, the chemical functionalization of fullerenes, using novel reactions as well as long-established synthetic methodologies [3, 10], has produced a wide variety of new molecules with potential applications in material sciences [11, 12], technology, and medicinal chemistry [13]. Another interesting and much promising field concerning fullerene and its derivatives is related to their excited state properties [14, 15]. The fullerene derivatives exhibit, in addition to the strong absorption bands in the UV region, weaker but significant bands in the visible region. This makes them very good candidates for applications concerning photoinduced electron transfer [4–6] and photodynamic therapy [13] due to the low-energy light required for their excitation. In this report, we present synthetic and photophysical studies associated with excited states of fullerene derivatives. In

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particular, we discuss the photosensitizing features of some novel functionalized fullerene materials.

Results and Discussion

N-*mTEG*-glycine (*mTEG* = triethyleneglycol monomethyl ether; **1**, Scheme 1) was synthesized according to Refs. [16, 17]. The *mTEG* group was chosen in order to increase the solubility of the resulting fulleropyrrolidine derivatives.

The cycloaddition of N-*mTEG*-glycine and paraformaldehyde to C_{60} was carried out in refluxing toluene [18, 19] (Scheme 2). The N-*mTEG*-3,4-fulleropyrrolidine **2** was isolated by flash chromatography in acceptable yields (35–40%). Similar experimental conditions were used for the synthesis of compounds **3**–**6**, using sarcosine or N-*mTEG*-glycine and pyrene aldehyde or sarcosine or N-*mTEG*-glycine and 4-pyridine aldehyde as the starting materials, respectively (Schemes 3, 4). The

$$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2OH \xrightarrow[TEA]{(COCl_2)_2,\ DMSO} CH_3OCH_2CH_2OCH_2CH_2OCH_2CHO$$

$$CH_3OCH_2CH_2OCH_2CH_2OCH_2CHO + H_2NCH_2COOCH_2Ph \xrightarrow[CH_3COOH]{NaBH_3CN}$$

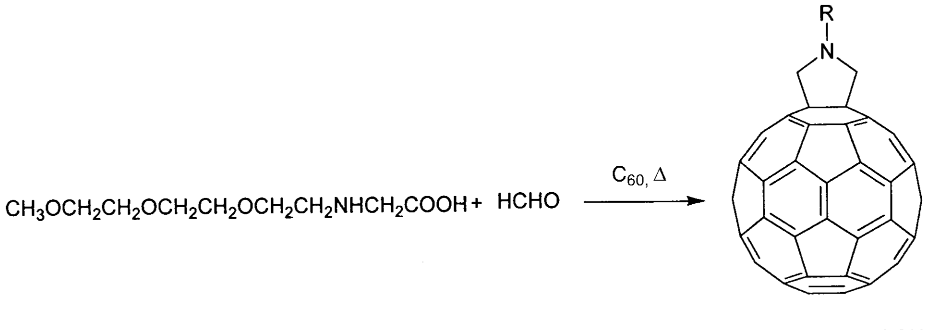
$$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2NHCH_2COOCH_2Ph \xrightarrow{ZCl,\ NaOH}$$

$$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2NZCH_2COOCH_2Ph \xrightarrow{H_2,\ Pd/C}$$

$$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2NHCH_2COOH$$

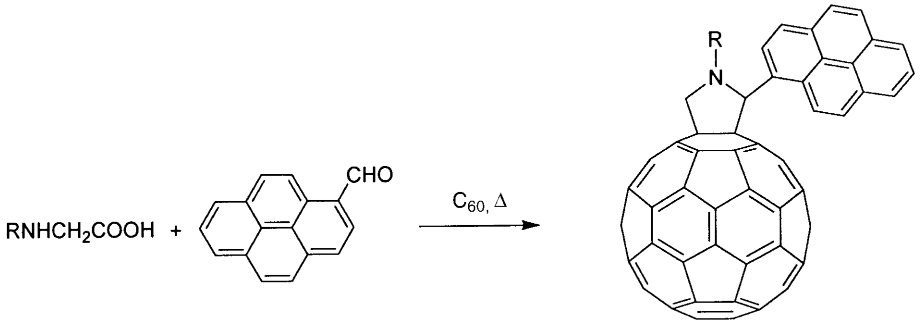
1

Scheme 1



2: $R = CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$

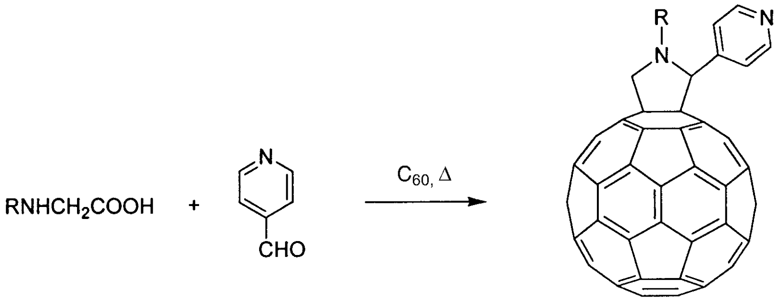
Scheme 2



3: $R = CH_3$

4: $R = CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$

Scheme 3



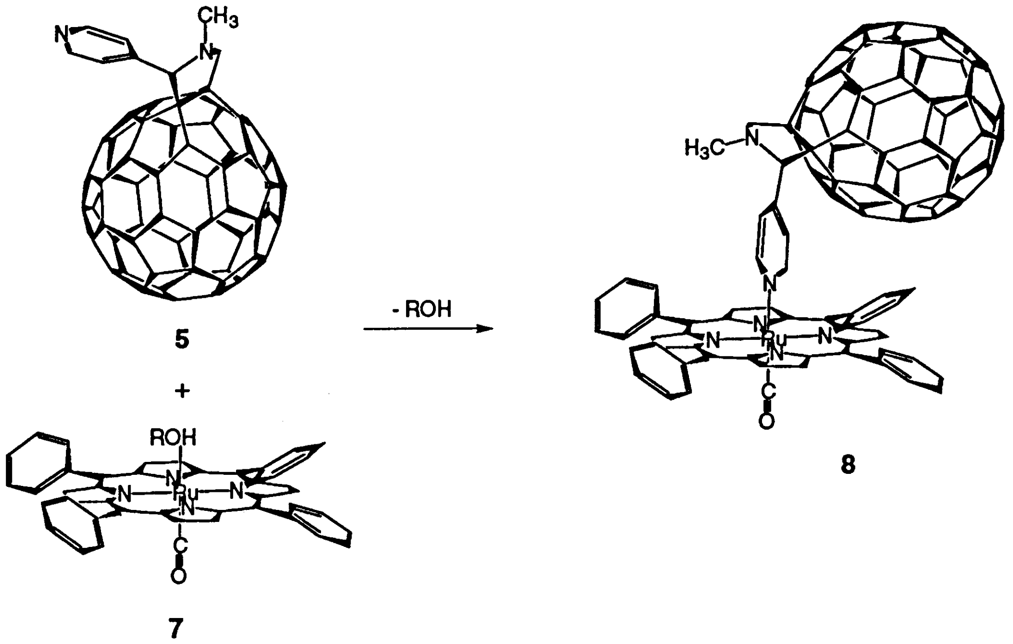
5: $R = CH_3$

6: $R = CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$

Scheme 4

Ru-porphyrin complex **8** was synthesized by reaction of **5** and the commercially available Ru(CO)*TPP* complex **7**. **7** contains an alcohol molecule that is very weakly bound to the metal and is immediately displaced by a stronger ligand, *e.g.* pyridine. The binding of **5** to **7** proceeds rapidly at room temperature, affording the new complex **8** in quantitative yield (Scheme 5). The formation of **8** can be easily monitored by ^{1}H NMR spectroscopy (shift of the pyridine protons from 8.7 ppm in **5** to 1.54 ppm in **8**). In addition, the UV/Vis absorption spectrum of **8** shows a superposition of the absorption bands of both the Ru-porphyrin complex **7** and the fullerene derivative **5**.

Besides their remarkable electron acceptor properties, fullerenes are also excellent energy acceptor moieties. In this context, the moderate energy levels of the singlet (1.99–1.76 eV) and triplet (1.57–1.50 eV) excited states play a crucial role to control the competing pathways, *i.e.* intramolecular energy transfer (photosensitization) *vs.* electron transfer. Prominent examples are fullerene-oligomer hybrids, in which both singlet-singlet energy transfer and intramolecular electron transfer were found to take place and, most importantly, to compete with each other [20].



Scheme 5

Owing to the efficient ISC process in fullerene-based materials, the above mentioned photosensitization effect seems particularly appealing. For instance, driven by their surface curvature, a strong spin-orbit coupling arises for fullerene, which in turn is responsible for triplet quantum yields as high as 100% in pristine yields. Most importantly, these fullerene triplet excited states have emerged as key intermediates for the quantitative generation of singlet oxygen in molecular systems [15].

$$C_{60} \xrightarrow{h\nu} {}^{1*}C_{60} \rightarrow {}^{3*}C_{60} \tag{1a}$$

$$ {}^{3*}C_{60} + O_2 \rightarrow C_{60} + {}^{1*}O_2 \tag{1b}$$

In the context of photosensitizing singlet oxygen, the weak absorption features of fullerenes, especially in the visible region, appear, however, to be a pragmatic concern. A practicable and, likewise, simple strategy to facilitate a more proficient singlet oxygen sensitization implies promoting the absorption cross section in the ultraviolet and visible range *via* linking strongly absorbing antenna molecules to the fullerene.

Generally, we would like to distinguish between antenna molecules having their strongest transitions in the ultraviolet or in the visible region. Promising candidates for the former category are pyrene and other polynuclear aromatic moieties [21, 22]. They are strong ultraviolet absorbers and exhibit singlet excited states with excellent donor properties (3.0–3.5 eV). On the other hand, their one-electron oxidation potentials are unfavourably high, precluding an intramolecular electron transfer.

Considering the close proximity of the pyrene moiety and the fullerene core in the C_{60}-pyrene dyad **4** it appears that an intramolecular energy transfer should take place instantaneously together with the initial excitation process of the chromophore (*i.e.* pyrene). In line with this purely structural assignment, the fluorescence quantum yield, employed as a sensitive marker for the deactivation of the pyrene singlet excited state (3.22 eV), is nearly quantitatively quenched in the C_{60}-pyrene dyad. A reference pyrene, for example, fluoresces quite strongly with a quantum yield of 0.65. Instead, the characteristic fluorescence spectrum of a functionalized fullerene derivative, with a characteristic ^{*0}–0 transition around 715 nm, was observed. To confirm the origin of the fullerene fluorescence, the excitation spectrum of the C_{60}-pyrene dyad was probed in toluene. Since the excitation spectrum unequivocally shows the attributes of the pyrene transition in the ultraviolet region with maxima at 335 nm and 360 nm, we conclude that an efficient and rapid singlet-singlet energy transfer governs the deactivation of the pyrene singlet excited state:

$$C_{60}\text{-pyrene} \xrightarrow{h\nu} C_{60}\text{-}^{1*}\text{pyrene} \rightarrow {}^{1*}C_{60}\text{-pyrene} \tag{2}$$

Time-resolved transient absorption measurements provided further evidence in support of the proposed energy transfer scenario and, thereby, corroborated the quantitative emission experiments. In particular, despite irradiating with an 18 ps laser pulse (355 nm) at the pyrene ground-state absorption, the fullerene singlet-singlet absorption around 880 nm appears nearly instantaneously after the completion of the laser pulse. Due to the instrumental limitations of our picosecond apparatus (18 ps) we can only estimate an upper limit for the development of the fullerene singlet excited state with an estimated time constant of 45 ps in toluene. On a larger time scale (*i.e.* up to 6 ns) the fullerene singlet excited state transforms into the triplet excited state with ISC dynamics ($\sim 5.0 \times 10^{-8}\,s^{-1}$) that are practically identical to those of a fullerene reference such as a fulleropyrrolidine.

With the objective to probe the properties of the fullerene triplet excited state in the C_{60}-pyrene dyad **4** we measured the quantum yields and the intermolecular reaction with O_2 in solvents of different polarity. High triplet quantum yields, with values of 0.83 and 0.81 in toluene and benzonitrile, respectively, sustain again the efficiency of the process, regardless of the solvent polarity. On the other hand, an intermolecular quenching rate constant between the fullerene triplet excited state and molecular oxygen of $1.16 \times 10^9\,M^{-1}s^{-1}$ (in toluene) underlines the reactivity of the photosensitized fullerene triplet. In conclusion, the short-lived and moderately redox-active singlet excited state of, for example, pyrene is transformed into the highly reactive fullerene triplet excited state in non-polar and polar solvents.

Considering, however, an excitation in the visible part of the spectrum, where human tissue is translucent, metalloporphyrins are the chromophores of choice. They display intense ground-state absorption in the visible region and can act not only as electron donors but also as photosensitizers. Though porphyrins are currently among the most studied substrates for photodynamic therapy, it should be noted that singlet oxygen quantum yields *via* metalloporphyrins are far less than unity, mostly due to strong emission from the porphyrin excited states.

The photophysical behavior of the ruthenium-based tetraphenylporphyrin complex coordinated to a fullerene-pyridine ligand (Ru*TPP*-C_{60}, **8**) is fundamentally different from that of the compounds considered above (*i.e.* pyrene). Due to the heavy nucleus of the ruthenium center the underlying spin-orbit coupling responsible for the spin-forbidden transformation of the singlet to the triplet excited state is quite fast (faster than our time resolution) and yields the long-living triplet excited state. Thus, the differential absorption changes recorded immediately after the 18 ps laser pulse (532 nm) with maxima at 370, 470, 590, and 870 nm are ascribed to the triplet excited state features of the porphyrin antenna. In toluene, these triplet absorptions decay readily and are accompanied by the concomitant evolution of a new transition. A distinct maximum at 700 nm and a shoulder at 800 nm characterize the latter state. Since these features match those reported for the triplet-triplet absorption of the fullerene core in monofunctionalized fullerene derivatives, its formation arises presumably from the following intramolecular triplet-triplet energy transfer:

$$\mathrm{Ru}\mathit{TPP}\text{-}\mathrm{C}_{60} \xrightarrow{h\nu} {}^{3*}\mathrm{Ru}\mathit{TPP}\text{-}\mathrm{C}_{60} \rightarrow \mathrm{Ru}\mathit{TPP}\text{-}{}^{3*}\mathrm{C}_{60} \tag{3}$$

The fullerene triplet excited state in the Ru*TPP*-C_{60} dyad exhibits decay dynamics which are linearly dependent on the oxygen concentration. From this dependence we derived an intermolecular rate constant of $1.4 \times 10^9\,M^{-1}\mathrm{s}^{-1}$ in toluene. This intermolecular reaction involves the photosenitization of cytotoxic singlet oxygen as independently confirmed by the corresponding $(^1\Delta_g)$ O_2 phosphorescence at 1270 nm. In particular, we determined a moderate quantum yield of 0.63 for oxygen-saturated toluene solutions of the Ru*TPP*-C_{60} dyad.

Although the quantum yield deviates from unity, it is nevertheless higher than that found for the Ru*TPP* reference complex alone. This in turn points to the efficient interaction of photoexcited fullerenes with molecular oxygen.

In polar solvents, this intramolecular triplet-triplet energy transfer is replaced by an electron transfer process, yielding the one-electron reduced fullerene π-radical anion and the porphyrin π-radical cation. This change in direction can easily be rationalized by inspecting the free energy changes which are associated with an intramolecular electron transfer. Whereas in toluene formation of the charge-separated radical pair is only slightly exothermic ($-\Delta G = -0.14\,\mathrm{eV}$), it becomes highly exothermic, for example, in benzonitrile ($-\Delta G = -0.71\,\mathrm{eV}$). In contrast, the driving force for an intramolecular triplet-triplet energy transfer remains nearly unaffected by the solvent polarity ($-\Delta G = -0.23\,\mathrm{eV}$).

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