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# Fullerene as Spin Converter

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Elif Okutan

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<http://dx.doi.org/10.5772/intechopen.74541>

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## Abstract

It has now been more than 30 years since buckminsterfullerene became a real thing. An exclusive field of study called fullerene chemistry arises and is discovered to be unique in many respects. In a very short time, a great deal of effort has been devoted on the fullerene chemistry and properties of fullerene derivatives. The fields of fullerene and light-induced processes considerably overlapped, and now numerous wonderful examples are on exhibition. The large number of these systems has been designed to take advantage of the electron-accepting property of fullerene and broadcasts the fullerenes as universal spin converter advertising its perfect intersystem crossing (ISC) quantum yield where a spin converter can be identified as a chromophore that undergoes efficient ISC with a low first excited state ( $S_1$ ), but does not necessarily strongly harvest visible light. Thus, donor-acceptor systems in the field of light-induced processes within multicomponent fullerene arrays have been proposed as models for optical limiters, owing to the singlet oxygen production efficiency of  $C_{60}$  and the  $C_{60}$  derivatives in the field of medicinal chemistry.

**Keywords:** fullerene, spin converter, light harvesting, singlet oxygen, triplet-triplet annihilation

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## 1. Introduction

Transformation of known and the creation of new are always intrigued to synthetic chemists. Not long ago, elemental carbon was not even a figurant as starting material. This position promoted fiercely after the family of carbon allotropes enlarged by the welcoming new members to the core family “graphite and diamond.” Unlike to graphite and diamond, fullerenes are spherical molecules with solid-state structure and are soluble in various solvents that opened a new era for chemical manipulation of carbon-based materials [1].

Few discoveries like this are captured the attention of scientist and the general public alike as much as the discovery of these architecturally esthetic molecules. But the popularity of fullerenes in science is not merely due to esthetics. Years of intense research activity showed that  $C_{60}$  is a powerful building block to be used in materials science and medicinal chemistry [2, 3]. What put fullerenes in the heart of nanotechnology today is the association of several extreme properties, such as outstanding mechanical, thermal, electronic, and electrical properties, coupled with chemical robustness, which have spurred a broad range of applications that provides new research possibilities for scientists, particularly in terms of electron-acceptor proficiency, both in the solid state and in solution [4]. An entirely new discipline called as “fullerene chemistry” emerged [5–7].

## 2. Optical studies of fullerene

Fullerene structure facilitates ingrained synthetic methodologies that catalyzing the production of a wide variety of novel derivatives often encompasses many fields outside the traditional scope [8, 9]. One of the most exciting properties of fullerene chemistry is related to their excited-state properties [10, 11]. The most abundant representative of the family  $C_{60}$  can be identified via its strong absorptions between 190 and 410 nm (allowed  $^1T_{1u}-^1A_g$ ) as well as by some pale but significant transitions in the 410 and 620 nm (orbital forbidden singlet-singlet) region which is responsible for the purple color of  $C_{60}$  and the red color of  $C_{70}$  [12, 13].

The fullerenes, in particular  $C_{60}$ , exhibit a variety of remarkable photophysical properties, making them very attractive building blocks for the construction of photosynthetic antenna and reaction center models that result from their large pi electron system that cater dense manifolds of low-lying electronically excited states [14–17]. As it is given below, most photochemical and photophysical applications of fullerenes are likely be mediated by lowest of these energetic states which present triplet spin multiplicity (**Figure 1**).

The fullerenes can also be identified as useful optical limiters since the triplet-triplet absorptivities are higher than the ground-state absorptions [20, 21]. The singlet excited state (1.99 eV) of  $C_{60}$  efficiently decays to the lower lying triplet excited state (1.57 eV) via intersystem crossing [17]. The triplet quantum yields are very high. The triplet excited states are responsive to diverse processes for deactivation, such as ground-state quenching, triplet-triplet annihilation via molecular oxygen leading to  $^1O_2$ , and electron transfer to donor molecules [17]. The long-lived triplet states due to the ISC process of excited singlet states gave rise to a substantial interest for their prosperous applications, such as singlet oxygen generation for [22–26], enhancing photoinduced electric conductivity via formation of charge-separated state caused by the excited triplet state of fullerene [27–29] and in the applications of photovoltaics, photocatalysis, photoinduced charge separation, and molecular probes (**Figure 2**) [30–36].

In this account, we discuss some of the main achievements in this rapidly developing field and, in particular, the triplet photosensitizer (PS) phenomena associated with the excited triplet state of fullerenes that later used as catalysts in photochemical reactions. Triplet PSs as the name derived from the compounds, used to transfer energy to other, are used for not only

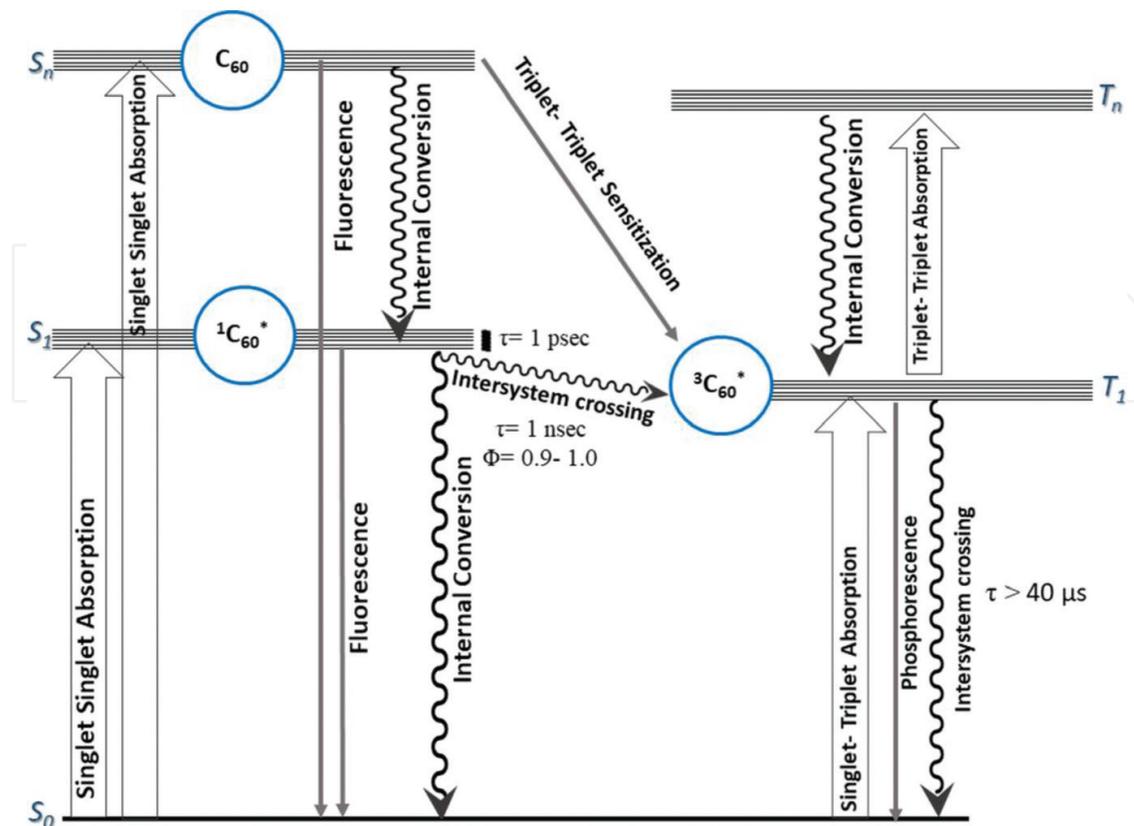


Figure 1. The Jablonski diagram: schematic depiction of the energy levels of typical compound (adapted from [18, 19]).

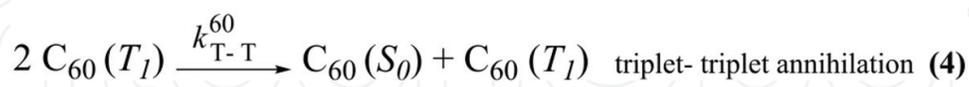
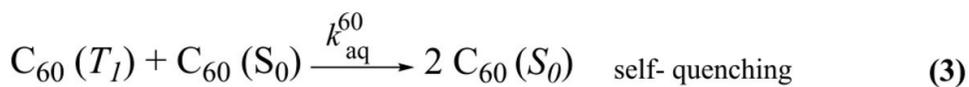
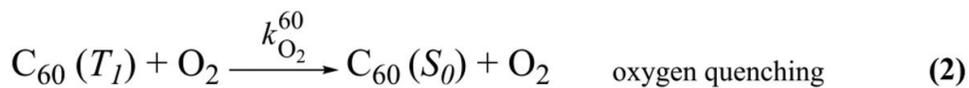


Figure 2. Main decay channels that control the lifetime of triplet C<sub>60</sub> in solution [37]. (reprinted by permission of ACS Publications).

energy transfer but also for photovoltaic reactions such as photodynamic therapy (PDT), photo-induced hydrogen production from water, and triplet-triplet annihilation (TTA) upconversion systems. The photosensitizing properties of some relevant classes of functionalized fullerene-based materials are surveyed.

Even in the early reports on excited states of fullerene prepared via light excitation, researchers were concerned with the persistence of long-lived excited and low triplet states. A number of

researches addressed the decay kinetics of fullerenes ( $C_{60}$  and  $C_{70}$ ), and the unimolecular triplet state lifetimes are found to be significantly longer than recognized [22, 38–45]. In the bimolecular triplet state processes, there are various deactivation mechanisms including oxygen quenching, triplet-triplet annihilation, triplet energy exchange, and self-quenching. The deactivation of organic triplet states by dissolved oxygen is reported by numerous researchers, and oxygen quenching constants for  $C_{60}$  and  $C_{70}$  are recorded in room temperature [22, 23] and were persistent with previous results [37]. Triplet-triplet annihilation occurs between two clashing triplet states considering the deactivation of one molecule, while exposure of the other in a highly excited state that will quickly convert to first singlet excited state ( $S_1$ ) (**Figure 2**). The reported  $k_{TT}$  values are  $5.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in room temperature which should be considered to be high and kept in mind to eliminate contributions from this channel while measuring excited state kinetics such as studying with low concentration [37, 46]. In another scenario triplet energy may flow between two species in solution [46]. If one species  $T_1$  state is significantly lower than the other, the second specimen will collect the energy and behave as a triplet quencher. On another scenario, the two  $T_1$  states might be separated by several  $k_{TT}$ . In this case, reverse energy transfer may also be occurred, and results showed that reversible energy transfer between triplet states  $C_{60}$  and  $C_{70}$  is a fast and efficient process [47]. Also, even though no mechanism was proposed for self-quenching mechanisms, the ground-state concentration dependence refers to the encounter of a molecule on  $T_1$  state with ground-state molecule. Studies showed that fullerene displays strong self-quenching over organic triplet states [48, 49].

Fullerene exhibits unique C–C single and double bonds. The deficiency of high-energy C–H and O–H vibrations makes these materials very interesting in photonics. The usual materials such as polymers have absorption in the near infrared because of the overtones of the abovementioned vibrations. No such absorption is observed in fullerenes while exhibiting narrow electronic bands and resonances [50, 51]. Fullerene's large number of conjugated double bonds lead to large nonlinear polarizabilities. The third-order optical polarizability,  $\gamma$ , is always symmetry allowed, while the second-order polarizability,  $\beta$ , is reported to be zero for  $C_{60}$  and  $C_{70}$  since they have centrosymmetric structures [51]. By preparing charge-transfer complexes (fullerene as electron acceptor), the center of symmetry is interrupted, and second-order optical nonlinearity is induced [52]. Specifically, the optical limiting in fullerene based on the reverse saturable absorption which takes place when the excited state absorption cross section is bigger than that of the ground state. This effect was reported for  $C_{60}$  and for  $C_{70}$  under 532 nm and 1064 nm excitations where optical limiting performance of  $C_{60}$  is bigger than  $C_{70}$  since the latter exhibits a higher linear state absorption coefficient [53].

The design of new structures with high first hyperpolarizability ( $\beta$ ) can be made via two state models in which  $\beta$  is expressed with the dipole moment difference, the transition dipole moment, and the energy difference between the key charge-transfer excited state and the ground electronic state [54]. The charge-transfer complexes can be characterized by the absorption cross section for an excited state of the organic moiety, which is significantly greater than that for the ground state [53]. Thus, these nanomaterials offer the optical limiting phenomena, particularly in the IR range. Fullerene-induced sensitization also favors bathochromic shift in the absorption spectra of related structures and activate transition in the near- and middle-IR

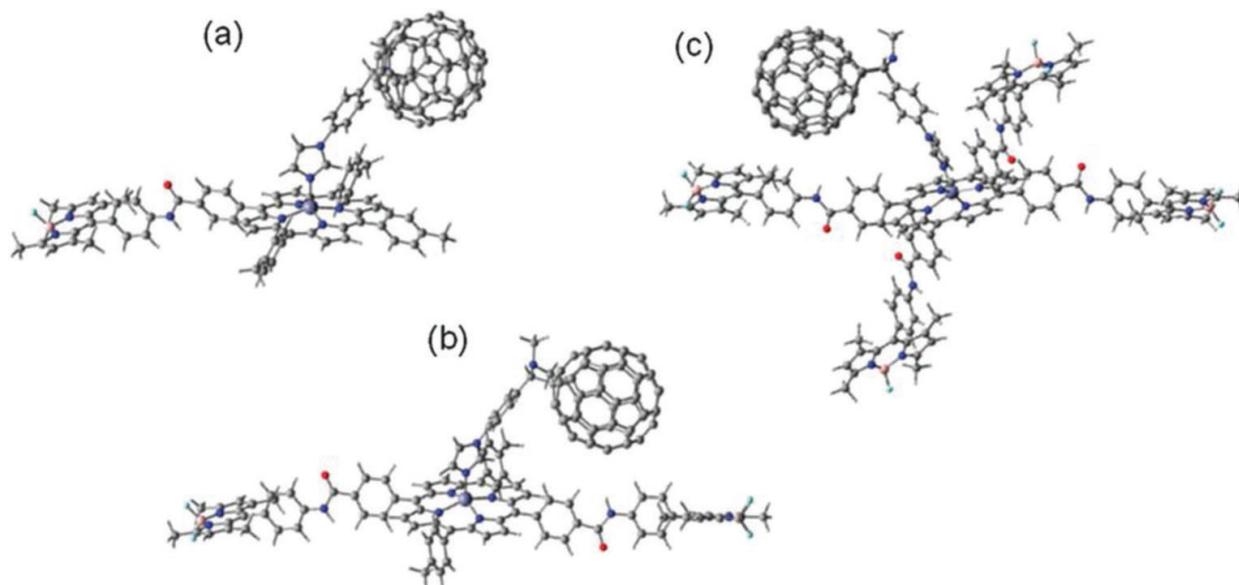
range [55]. During the charge transfer, an additional electric field gradient is reported to be formed as substitute from the intramolecular donor to fullerene rather than to the intramolecular acceptor. Consequently, the nanomaterial offers high-frequency Kerr effect and exhibits high value of nonlinear refraction and nonlinear third-order permeability [56, 57]. In general, photoinduced electron transfer in donor-acceptor dyads in solution is reported to be related to free energy change for charge separation  $\Delta G_{CS}$ , which depends on the energies for oxidation, reduction, and excitation and also to the Coulomb interaction and solvation of the radical ions [58]. The rate for electron transfer is obtained from the charge transfer and the electronic coupling of donor and acceptor in the excited state barrier. Also, energy transfer processes dipole-dipole (Förster) and exchange (Dexter) mechanisms are generally used to explain the deactivation of the initial photoexcited state.

Afterward, fullerene chemistry allowed researchers to open a new door to link fullerenes to photoactive species, and the work to date suggests that the first excited state can be populated by singlet-singlet energy transfer from attached dye and in the appropriate conditions can be quenched by triplet energy acceptors. Thus, fullerenes hold a significant promise, and the study on these materials will be a scientific endeavor [37, 43, 59–67].

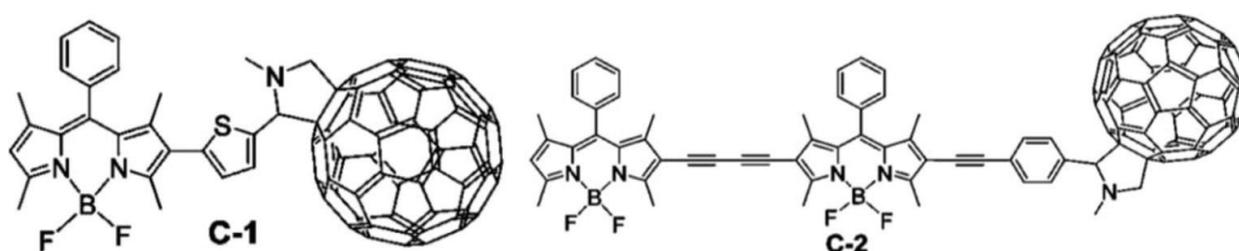
On the account of simple organic molecules, the triplet manifold is rarely reached by direct stimulation of the organic molecule, unless advertised spin-orbit coupling effect is populated by a heavy atom [68, 69]. The triplet manifold may be reached via indirect secondary routes such as intersystem crossing from the first excited state ( $S_1$ ) and charge separation and recombination between radical ions [70–73]. This kind of recombination may require orbital contact via flexible link or by a rigid spacer [74–79]. Ziessel et al. described results of photophysical properties of a closely spaced molecular dyad comprising terminal BODIPY dye and a fullerene. They investigated the driving force for light-induced electron abstraction by the  $S_1$  state of  $C_{60}$  from BODIPY unit and displayed the dependence to solvent polarity. In nonpolar solvents, fast excitation energy transfer was declared, while electron transfer became laborious. Polar solvents play a critical role switching on light-induced electron transfer [68].

Artificial photosynthetic systems to mimic natural systems for global energy demand are important not only to understand nature but also for environmental issues. Various synthetic models were designed and constructed based on tetrapyrroles as energy harvesting antennae due to their structural resemblance to natural chlorophylls [80–83]. Owing to fullerene's facile reduction and low reorganization energy, fullerene lessened the use of 2D electron donor-acceptor systems such as quinone and methyl viologen and was successfully demonstrated in studies as "antenna-reaction center." Maligaspe et al. developed supramolecular triads to mimic these issued antenna-reaction center systems designing boron dipyrin (BODIPY) entities as antenna that linked to zinc porphyrin (P) as electron donor and then coordinate to fullerene as electron acceptor (**Figure 3**) [84]. Similarly, BODIPY-ZnPc-fullerene system, where BODIPY unit located on peripheral position on Pc was designed, demonstrates a sequence of energy and electron transfer reactions upon photoexcitation [85]. An interesting example of distyryl-BODIPY-fullerene donor-acceptor system was also reported by Liu et al [86].

Upconversion systems are used in photovoltaics, photocatalysis, nonlinear optics, and luminescent molecular probes [87]. To facilitate upconversion one or two methods are deployed for



**Figure 3.** Optimized structures of BODIPY-ZnPc- $C_{60}$  triads [85]. (Reprinted by permission of RSC).



**Figure 4.** Structure of the  $C_{60}$ -based dyads as organic triplet sensitizers for triplet-triplet annihilation upconversions [36] (Reprinted by permission of ACS).

such as rare-earth materials or two-photon absorption fluorescent dyes [88, 89]. These conventional upconversion methods come with the disadvantages of weak absorption, low upconversion quantum yield, or requirement of consistent high-power density excitation source. New upconversion method based on triplet photosensitizer and triplet accelerator become popular where triplet photosensitizers are responsible for light harvesting and enhancement of triplet excited state by intersystem crossing (ISC) [90]. The previously reported triplet photosensitizers are usually transition-metal complexes, such as PtII/PdII porphyrin complexes, IrIII/RuII complexes, or heavy-atom derivatives of organic fluorophores since ISC is facilitated by the heavy atom spin-orbital coupling effect [91–93]. Designing these systems via chemical derivatization of a known heavy atom-free organic triplet photosensitizer is not a decisive way to prepare new organic triplet photosensitizers because even simple derivatization of the chromophore may diminish ISC [25, 26]. Heavy atom-free organic triplet photosensitizers with absorption in visible range are highly desired and remained rare for TTA upconversion system (**Figure 4**) [36, 87, 94]. An intramolecular spin converter is used to overcome the aforementioned challenges. Both  $C_{60}$  and  $C_{70}$  were also used to construct heavy atom-free triplet photosensitizer, both red-to-green and green-to-blue upconversions [36, 95, 96].

Lim et al. also reported a supramolecular tetrad bearing covalently linked ferrocene-zinc porphyrin-BODIPY system coordinated to fullerene that proposed as photosynthetic antenna reaction center mimicked by performing systematic spectral, computational, and electrochemical studies to evaluate the role of each entity in the photochemical reactions [97].

Even the early studies on evaluation of using fullerene derivatives to generate singlet oxygen. Even if there was little quantitative data at that time displayed the singlet oxygen generation by dissolving  $C_{60}$  in polyvinylpyrrolidone (mutagenic for *Salmonella* strains TA102, TA104, and YG3003) in the presence of rat liver microsomes followed by the irradiation with visible light [98]. Singlet oxygen efficiency dependence on the kind and number of addends was also studied during the early period of fullerene chemistry. The results suggested that efficiency easy independent from the kind of addends but decreased with an increasing number of the substituent [99]. A strong correlation was also reported by Prat et al. between triplet properties and the topology of the fullerene core [100]. Since fullerene chemistry evolved during that time, several fullerene derivatives were prepared to effectively generate singlet oxygen for numerous applications [101–104]. For their possible application in photodynamic therapy, a prototype macromolecule bearing a distyrylbenzene dimer as TPA unit and a [60] fullerene moiety for singlet oxygen generation endowed with a high two-photon absorption (TPA) cross section and a high singlet oxygen quantum yield were reported by Collini et al. (Figure 5) [105]. The singlet oxygen generation and photoinduced charge separation of zinc phthalocyanine-fullerene dyad bearing tetra polyethylene glycol moieties were also reported for PDT application [106].

In organic synthesis, oxidation is one of the primary reactions; thus, there has been an extensive research interest devoted on the use of singlet oxygen as photocatalysis in photooxidation reactions [25, 26, 107, 108]. Huang et al. used energy funneling for the first time with  $C_{60}$ -BODIPY triads and tetrads as dual functional photocatalysis for two different photocatalytic reactions. They produce juglone via photooxidation of naphthol and superoxide radical ion by photocatalytic aerobic oxidation of aromatic boronic acids to produce phenol. Reaction time was also reduced reasonably with this strategy [109]. Novel heavy atom-free triplet photosensitizers to generate singlet oxygen contain one and two light-harvesting antennas as well as

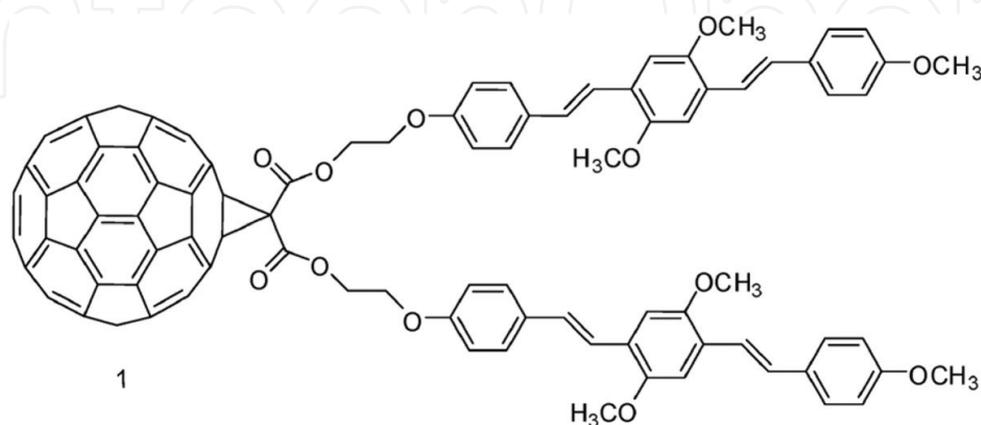
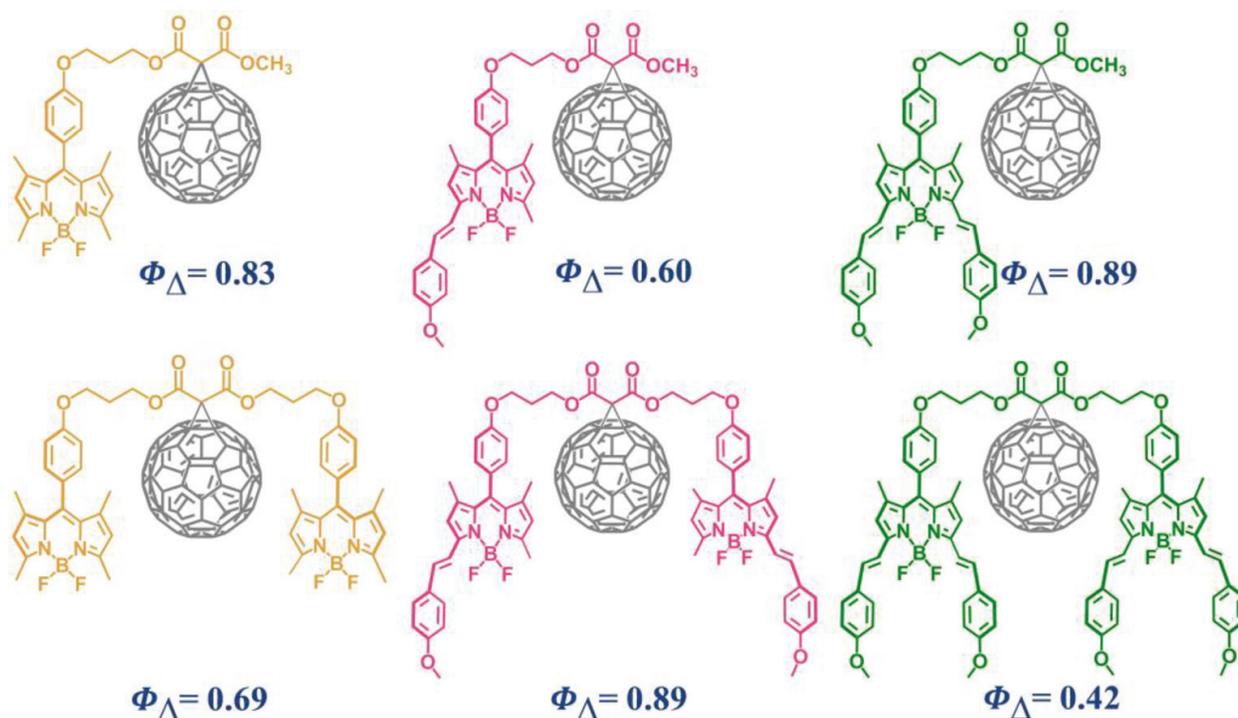


Figure 5. Fullerene-distyrylbenzene conjugate [105] (Reprinted by permission of RSC).



**Figure 6.** Heavy atom-free BODIPY-fullerene triplet photosensitizers [25, 26].

associated with different absorption wavelengths were successfully designed and synthesized in our laboratory (**Figure 6**).

## Acknowledgements

The author would like to thank to Gebze Technical University.

## Conflict of interest

There is no conflict of interest.

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