CF$_2$-bridged C$_{60}$ dimers and their optical transitions

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Fullerene dyads bridged with perfluorinated linking groups have been synthesized through a modified arc-discharge procedure. The addition of Teflon inside an arc-discharge reactor leads to the formation of dyads, consisting of two C$_{60}$ fullerenes bridged by –CF$_2$- groups. The bridging groups consisting of electronegative atoms, lead to different energy levels and to new features in the photoluminescence spectrum. A suppression of the singlet oxygen photosensitization, indicated that the radiative decay from singlet to singlet state is favoured against the intersystem crossing singlet to triplet transition.

Fullerene dimers [1] have been synthesized by utilizing various bridging groups that link the two buckyballs. A wide range of methods can be found in the literature, with examples including the dimerization of pristine C$_{60}$ [2] through high pressure treatment, mechanosynthesis using KCN and K$_2$CO$_3$ [3] or dipolar cycloaddition reactions. [4] Besides the [2+2] carbon linking between the two buckyballs, typical bridging groups include oxygen [5] and methylene units, as well as photo-switchable azobenzenes. [6] A dimerization of adjacent fullerenes inside carbon nanotube peapods occurs as well. A fullerene dimerization was monitored and distinguished between formations of dyads in the first stage with small nanotubes to be formed in subsequent stages through bond fusion. [7] Fullerene dimers provide a class of materials for applications in artificial photosynthesis and molecular electronic devices due to their richer energy level structure compared to the single cage fullerene counterparts. [8] Despite the number of fullerene dimers presented in the literature, the synthesis of -CF$_n$- bridged dimers has not been reported due to difficulties arising from the poor reactivity of the C-F bond. We achieved the synthesis of this unexpected dyad in the high temperature plasma conditions of an arc-discharge reactor by evaporating Teflon simultaneously with graphite. We also demonstrated their reactivity with a Bingel-Hirsch reaction. The fluorine addition could be beneficial in terms of optoelectronic applications since it has been demonstrated that the presence of the highly electronegative fluorine atoms in conjugated polymers leads to high-performing materials for field-effect transistors with a bright blue photoluminescence. [9]

![Figure 1](image)

**Figure 1.** a) HPLC traces of fullerene extract from scandium rods, without (black) and with (blue), Teflon and the proposed structure of the dyads (inset). b) MALDI-TOF analysis indicating the two systems and various other perfluorinated fullerenes with – CF$_3$ and/or –CF$_2$ groups. 19F NMR as inset. c) Fullerene monomers and dyad. Red arrow indicates a decrease in the yield and a green an increase after the addition of Teflon.

A modified arc-discharge procedure was used to synthesize the dyads. [10] Our initial target was the synthesis of perfluorinated empty cages and endohedral metallofullerenes. The decomposition of Teflon close to the arc resulted in reactive CF$_2n$ and C$_{2n}$ fragments as precursor molecules. Addition of the -CF$_2$- bridging dimers has not been reported due to difficulties arising from the poor reactivity of the C-F bond. We achieved the synthesis of this unexpected dyad in the high temperature plasma conditions of an arc-discharge reactor by evaporating Teflon simultaneously with graphite. We also demonstrated their reactivity with a Bingel-Hirsch reaction. The fluorine addition could be beneficial in terms of optoelectronic

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C60-CF2-C60. In the mass spec of the C60-CF2-C60 we distinguished two fragments, the C60-CF2 and C60 at m/z=771 and m/z=720, respectively. The C60-(CF2)2-C60 dimer is not subject to fragmentation. We suspect this is due to the rigid structure of its bridge consisting of two linking CF2 groups. The m/z=50 difference between the dyads, hints to the presence of CF2-groups. The presence of fluorine is further confirmed by NMR spectroscopy with the 19F NMR spectra providing evidence for the presence of fluorine atoms, (Fig. S3a). The (C60)2-CF2 dyads is showing a peak located at -67.04 ppm. [11] As a comparison, the 19F spectrum of (C60)2-(CF2)2 presents two peaks at -67 ppm and -66.55 ppm, due to different environment of the fluorine atoms with respect to the carbon cage. The 13C NMR is shown in Fig. S4b. The spectrum for the (C60)2-(CF2)2, demonstrates weak signals for fullerene sp2 carbons, seen in the expected region for a C60 dimer, 140-152 ppm. [12] A signal for sp3 carbon environment was also seen at 29.1 ppm. The signal for the sp3 CF2 carbon was not observed as it was obscured by residual solvent peaks. The FTIR spectra (Fig. S3c) provide a strong indication on the presence of perfluorinated groups from the appearance of the very strong antisymmetric and symmetric C-F vibration fingerprint peaks at 1092 and 1031 cm⁻¹ in both samples. Fig. S3d-f also shows the Raman spectra of C60 and of the two dyads revealing the presence of all eight vibration modes. The symmetry groups representing them are given above each peak. The A_g(1) represents an in and out of plane vibration and while it is quite strong in the pristine C60, it nearly disappears in both dyads. The Hg(8) hexagon shear mode [13] appears with increased intensity in the dimers. The pentagonal pinch A_g(2) and the pentagon shear mode, assigned to the isolated pentagon ring, both remain strong and relatively strong in all samples with a blue shift in the dyads compared to pristine fullerene, something expected for polymerized or functionalized C60. The five-fold degenerate, Hg(1) mode shifts from 33.4 meV (269 cm⁻¹) for pristine C60 to 30.5 meV (246 cm⁻¹) for the dyads. Due to change of symmetry, a peak appears at 15 meV (122 cm⁻¹). These low energy features originate from inter-ball vibrational modes. In previous studies on C120, two peaks at 127 and 139 cm⁻¹ were observed, in relative agreement with the work herein. [13] The materials exhibit a limited reactivity with Lewis acids such as TiCl4, something that is indicating that the oxidation potentials are expected to be close to the threshold of 0.62-0.72 V vs Fc/Fc+. [14] The mass spectra after the Lewis acid reaction are shown in Fig. S4. Since the surface functionalization of fullerenes is a necessary step for their utilization in various applications, the reactivity of the dimers was tested through a Bingel-Hirsch reaction. The MALDI-TOF analysis revealed the presence of mono-, bis-, tris-, tetra-, and penta-malonate adducts. All peaks were separated by m/z=158, the value assigned to each malonate (Fig.2). A more careful analysis of the mass spectrum reveals fragments at m/z=878 and m/z=1036 of the mono- and bis-adducts of C60.
This dual fluorescence is reminiscent of other ultra-small carbon nanomaterials. The size of our materials is very close to the mean diameter of the dual fluorescent carbon dots rnanoscale carbon nanomaterials. The size of our materials is very close to the mean diameter of the dual fluorescent carbon dots, hence the data presented here are for an agglomeration of fullerenes as standard. These high quantum yields closely resemble fullerene S1 excitation-dependent photoluminescence maps for c) (C60)2-CF2 d) (C60)2-(CF2)2 e) Bingel derivative of (C60)2-CF2. f) Bingel derivative of (C60)2-(CF2)2. Concentration: 0.025 mg/ml.

In Fig.3 and Fig. S6 we present the excitation-dependent PL maps for the dyads and their Bingel derivatives recorded in CS2 a) UV-Visible spectra recorded in toluene b) UV-visible spectra for the dyads and their Bingel derivatives recorded in CS2 Excitation-dependent photoluminescence maps for c) (C60)2-CF2 d) (C60)2-(CF2)2 e) Bingel derivative of (C60)2-CF2. f) Bingel derivative of (C60)2-(CF2)2. Concentration: 0.025 mg/ml.

Figure 3. a) UV-Visible spectra recorded in toluene b) UV-visible spectra for the dyads and their Bingel derivatives recorded in CS2 Excitation-dependent photoluminescence maps for c) (C60)2-CF2 d) (C60)2-(CF2)2 e) Bingel derivative of (C60)2-CF2. f) Bingel derivative of (C60)2-(CF2)2. Concentration: 0.025 mg/ml.

The dyads exhibit similar emission patterns with a quantum yield of 2 % for the (C60)2-CF2 and 14 % for (C60)2-(CF2)2 using pyrene as standard. These high quantum yields closely resemble carbogenic quantum dots which are synthesized in the range of 2-20 nm and have an emission maximum in the range of 430-480 nm with an optimum excitation range: 320-380 nm. The fullerene S1→S0 transition appears at λexc=476 nm with λem=709 nm, while for the pristine C60 it is λexc=495 nm with λem=715 nm. This dual fluorescence is reminiscent of other ultra-small nanoscale carbon nanomaterials. The size of our materials is very close to the mean diameter of the dual fluorescent carbon dots reported by Zhou et al. The second emission at 700-720 nm is coming from the fullerene core. Methods for making carbon dots include synthesis from chemical oxidation and ring opening of C60, pyrolysis of small molecules and surface passivation of nanographite. Chua et al reported the formation of highly fluorescent carbon dots by fullerene fragmentation through acid treatment and they called them graphene quantum dots. However, since fullerene contains a pentagon ring, these clusters cannot be considered as analogues of graphene. The coronene moiety with an isolated pentagon ring surrounded with hexagons is the core of the fullerene and upon surface functionalization it is fluorescent with 57 % QY; a value 8 times higher than the parent coronene. Furthermore, fluorinated conjugated systems have lower HOMO-LUMO and bright electrogenerated chemiluminescence with a series of perfluorinated compounds behaving as n-type semiconductors with blue emissions and QY value of 68 %. In general, the electronaffine fluorinated groups have been considered to lower the HOMO-LUMO levels and to open the HOMO-LUMO gap compared to non-fluorinated polymers with similar backbones. The dominant red emission after green excitation in pristine fullerenes arises from the fivefold degenerate h1u to the three-fold degenerate t1u. In order to clarify the presence of aggregation dependent optical properties, we recorded the PL spectra in different concentrations (Fig. S6). No spectral differences where observed over a broad concentration range.

An important application of fullerene is their use as photosensitizers with regard to the very high yield of the reactive singlet oxygen state, generated through an energy transfer from their triplet state to oxygen. However, singlet oxygen can be detrimental to other biomedical applications due to its high reactivity and toxicity. The formation of an intermediate between the photosensitizer, that is subsequently deactivated, results in a phosphorescence at 1270 nm corresponding to the O2(Δg)→O2(Ωg) decay. We recorded the NIR emission of C60 and the dimers in CS2, since toluene is quenching the singlet oxygen due to formation of toluene radicals. The Bingel (C60)2-CF2 is showing a weak photosensitization (Fig. 4), while for the Bingel derivative of (C60)2-(CF2)2 the singlet oxygen phosphorescence is almost completely absent (see Fig.S8) following the same trend with the QY (Fig.4c). Notice that for the optimum singlet oxygen generation, the λexc=400 nm for the (C60)2-(CF2)2 is significantly blue shifted compared to pristine C60 (λexc=550 nm, see Ref.22). Fullerenes have a notoriously weak fluorescence, due to the intersystem crossing that leads to a long lived and weak decay from T1 to the S0 state and a subsequent energy transfer to oxygen. As such, there is an unambiguous correlation between the increased fluorescence quantum yields and the singlet oxygen generation. Since this photocycle is suppressed, the predominant transition is radiative relaxation from S1 to the ground S0 and results to the high quantum yield. Similar suppression of the singlet oxygen generation has been previously observed in fullerene functionalized with electrophotoreactive oxygen, for example C60O3, C60O4, C60O5 and dyads with pyrene. In order to elucidate the differences between the photophysical properties of these new dimers and conventional fullerenes, we functionalized C60 with the same malonate unit (Fig.S9). The photosensitization efficiency of the malonates with two CF2 bridging groups (Fig. 4) was tested and compared with the behavior of a C60 functionalized with one malonate unit. The singlet oxygen generation is weaker in the dyads signaling a quenching through the predominant S0-S1 transition. The optimum is λexc = 473 nm for the Bingel (C60)2-CF2 with a weaker feature at 550 nm and at 400 nm for the (C60)2-(CF2)2. For the pristine C60 the optimum λexc is 550 and 600 nm, significantly red
shifted. Both the pristine dyad, $(C_{60})_2$-CF$_2$, and the malonate $(C_{60})_2$-(CF$_2$)$_2$, exhibit a biexponential time resolved fluorescence with one long and one short lifetime component (Fig. 4b). The lifetimes derived from the biexponential decays are 0.53±2.85 ns for 420 nm, 0.73±3.24 ns for 440 nm, 0.84±3.58 ns; for 460 nm, 1.4 ns for 480 nm.

In summary, two novel C$_{60}$ dyads bridged with the electron withdrawing -CF$_2$- can be synthesized through an arc-discharge procedure. The structure of the dimers has been determined by $^{19}$F NMR, $^{13}$C NMR, mass spec and Raman/FTIR. HPLC analysis shows that the addition of Teflon alters the thermodynamics of the systems, suppresses specific classes of fullerences and stabilizes these unusual dyads. Detailed fluorescence studies indicated the similarity of their optical transitions compared to pristine and malonate C$_{60}$, resulting in reduced intensity of the singlet oxygen generation compared to conventional fullerences. Malonate derivatives exhibited similar optical properties albeit with a more pronounced singlet oxygen sensitization. These materials represent a new class of carbon nanostructures that combine the versatile surface functionality of fullerences with the photoluminescence properties of carbogenic dots.

Experimental Section

Graphite rods were vaporized in an arc-discharge reactor where Teflon tubes have been added. The arc-discharge took place under 80 mbar of constant helium flow and a dc current of 500 amps. The carbon soot was Soxhlet extracted with toluene. Bingel reaction: 0.05 mg of the $(C_{60})_2$-(CF$_2$)$_2$ were dissolved in 0.1 ml of CS$_2$. Solutions of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and diethyl bromomalonate were prepared accordingly: 0.005 ml of DBU in 4.995 ml toluene and 0.0057 ml diethyl malonate in 4.994 ml toluene. 0.01 and 0.0114 ml of the DBU and malonate solutions were added after 4 1/2 hours. A C$_{60}$ monomer functionalized with the same malonate unit was synthesized through 1:1:1 C$_{60}$: DBU: bromomalonate molar ratio.

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Supporting information section: HPLC curves, Raman/FTIR spectra, $^{19}$F/$^{13}$C NMR, photosensitization studies are available free of charge via the internet.

Keywords: Fullerene dyads • Fluorescence • Photosensitization

References


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Page No. – Page No.

–CF₂- bridged C60 dimers and their optical transitions