

# “Click”-Functionalization of [60]Fullerene and Graphene with an Unsymmetrically Functionalized Diketopyrrolopyrrole (DPP) Derivative

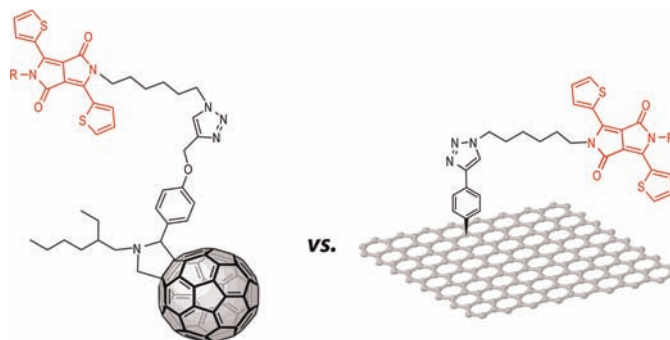
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## ABSTRACT



A synthetic strategy is developed that allows for the facile functionalization of carbon nanostructures thus providing the possibility of comparing the striking different optical and electrochemical properties of ensembles based on the diketopyrrolopyrrole (DPP) chromophore covalently attached to either [60]fullerene or graphene.

Recently, diketopyrrolopyrrole (DPP)-based materials have attracted much interest due to their promising performance as a subunit in OFETs,<sup>1</sup> organic photovoltaics (OPV),<sup>2</sup> organic light-emitting diodes (OLEDs),<sup>3</sup> chemosensors,<sup>4</sup>

two-photon absorption,<sup>5</sup> and solid-state dye lasers<sup>6</sup> among others.

For these purposes, both polymers<sup>7</sup> and small molecules<sup>8</sup> have been synthesized based on the DPP core. In this regard, because of the interesting photovoltaic properties observed in bulk heterojunction solar cells based on blends of fullerene and DPP derivatives,<sup>9</sup> very recently-dyads<sup>10</sup> and triads<sup>11</sup> based on covalently linked DPP derivatives and C<sub>60</sub> have received some attention with

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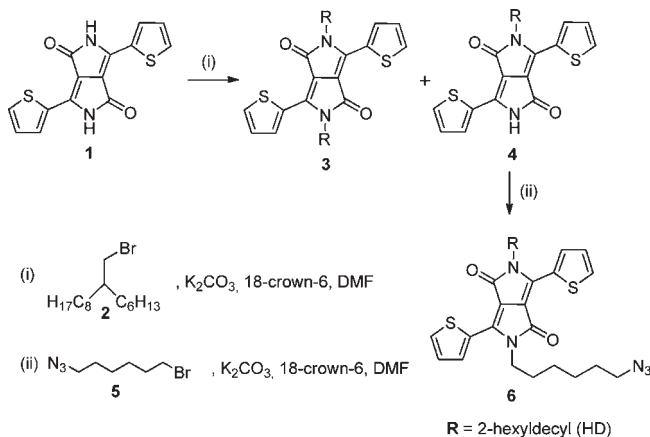
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the aim of investigating charge separation and photo-physical processes as well as their performance in photo-voltaic devices.

Here, we describe the synthesis of a novel unsymmetric DPP derivative bearing azide moieties only in one of the pyrrole units of the DPP core (**6**, Scheme 1). Additionally, we use an extended side chain [2-hexyldecyl (HD)] on the other nitrogen of the DPP moiety, to obtain processable materials. We show that this novel building block can be used for the facile functionalization of not only [60]fullerene but also other carbon nanostructures such as graphene by means of a click coupling through the Cu-catalyzed azide–alkyne cycloaddition (CuAAC) reaction.<sup>12</sup>

**Scheme 1.** Synthesis of Azido-Functionalized DPP Derivative **6**



Reaction of 3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]-pyrrole-1,4-dione (**1**)<sup>13</sup> with 1-bromo-2-hexyldecane (**2**) under stoichiometric control afforded a mixture of

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dialkylated (**3**)<sup>14</sup> and monoalkylated (**4**) derivatives in a 33% and 25% yield respectively. Both compounds can be separated chromatographically, and further reaction of **4** with 1-azido-6-bromohexane (**5**)<sup>15</sup> afforded the target unsymmetrical DPP derivative (**6**) with an azido functionality in a 36% yield (Scheme 1; see Supporting Information for further details).

We subsequently investigated the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of the DPP derivative **6** with both [60]fullerene (**7**)<sup>16</sup> and graphene (G-ALK)<sup>17</sup> derivatives endowed with alkyne functionalities (Scheme 2). The reaction with the [60]fullerene derivative (**7**) was carried out by using the conditions previously described by some of us, i.e. with (CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> in THF for 3 days at rt in the presence of 1 equiv of Cu powder.<sup>16</sup> The resulting sample was separated on silica gel in a relatively straightforward fashion to obtain DPP-C<sub>60</sub> in a 32% yield. The <sup>1</sup>H NMR spectrum of **6** is characterized by the typical singlet of the 1,2,3-triazole unit at 7.50 ppm as well as by the signal corresponding to the CH<sub>2</sub>-triazole protons at 4.31 ppm. The conversion of the azido to 1,2,3-triazole groups is also confirmed by the disappearance of the strong azido band at 2092 cm<sup>-1</sup> in **6** and the appearance of the C–C double bond stretching vibration of the triazole ring at 1504 cm<sup>-1</sup> in DPP-C<sub>60</sub> (Figure S1). The structure of DPP-C<sub>60</sub> has also been confirmed by MALDI-TOF mass spectrometry showing the expected molecular ion peak at *m/z* 1656.5.

Having succeeded in the reaction between the stable DPP-azide building block **6** and the [60]fullerene derivative, we further investigated the reactivity of **6** with an alkyne-modified graphene (G-ALK) by taking advantage of our recently developed strategy to produce this type of graphene derivative.<sup>17</sup> The presence of the modified alkyne moiety on the graphene surface significantly improves solubility (e.g., in DMF) which allows the click reaction to take place in an homogeneous phase.

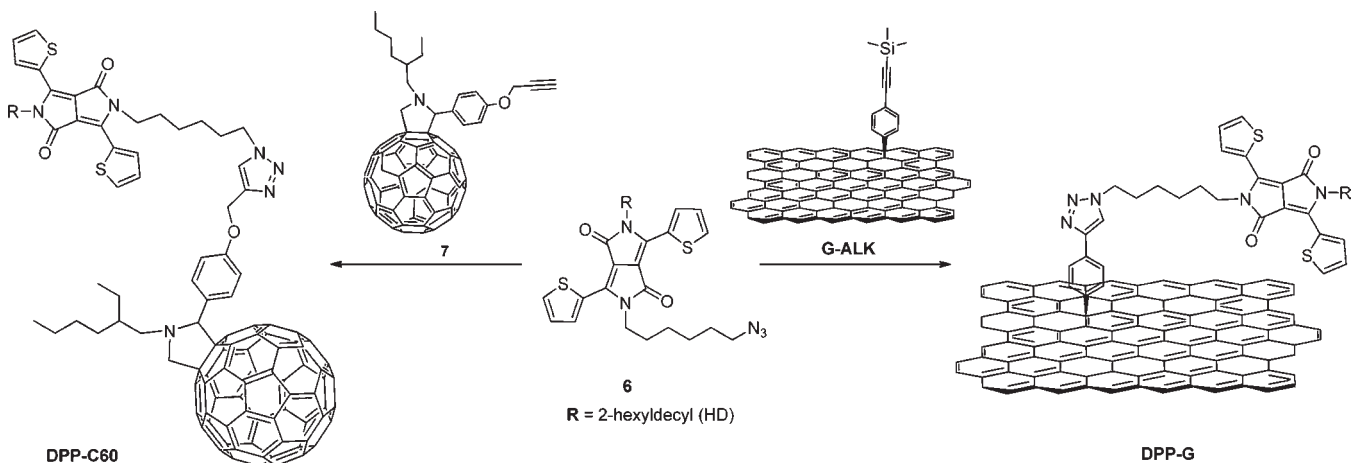
The existence of click linkage between DPP and graphene was confirmed by complementary FTIR and Raman spectroscopies. While the FTIR allows following changes in the vibrational spectrum of the organic dye, Raman spectroscopy is very sensitive to the presence of graphitic species, even though some remaining fluorescence of DPP can worsen the quality of the spectrum. Thus, the FTIR spectrum of DPP-G, obtained by ATR microspectroscopy, shows the almost complete disappearance of the azide band around 2100 cm<sup>-1</sup> and the presence of new bands at 1488 and 1160 cm<sup>-1</sup> corresponding respectively to the C=C and C–N stretching vibrations of the triazole ring (Figure S3).<sup>17</sup> In addition, the originally symmetric band due to the C=O in the DPP (at 1663 cm<sup>-1</sup>) becomes wider and asymmetric and shifts to higher frequency (1690 cm<sup>-1</sup>) in DPP-G because it now has contributions from the carbonyl group of DPP as well

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**Scheme 2.** “Click” Reactions for the Synthesis of **DPP-C<sub>60</sub>** and **DPP-G**

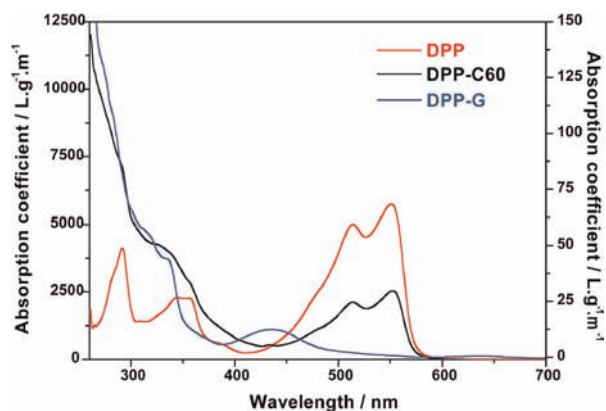


as the remaining carboxylic groups in graphene. Furthermore, the Raman spectrum of a **DPP-G** thin film onto Si/SiO<sub>2</sub> displays only two strong signals at 1598 and 1356 cm<sup>-1</sup>. As widely known these signals correspond to the G and D modes of graphitic structures, related to the sp<sup>2</sup> carbon network and structural defects on it, respectively (Figure S3).

UV/vis absorption spectra of the symmetric **DPP** derivative **3** and the corresponding dyad **DPP-C<sub>60</sub>** are given in Figure 1. The absorption of the dyad resembles a superposition of the spectra of the separate **DPP** and *N*-methylfulleropyrrolidine **7**. Absorption peaks at 547, 511, 356, 339, and 292 nm correspond to the **DPP** derivative overlapping with a broad absorption below 400 nm corresponding to fullerene. No significant electronic interactions (e.g., charge-transfer absorptions) can be observed in the absorption spectrum of the dyad **DPP-C<sub>60</sub>** in agreement with that previously observed for other **DPP**-fullerene ensembles.<sup>18</sup> In the cyclic voltammogram (CV) of the symmetric **DPP** derivative **3** two reversible oxidations and one reversible reduction can be observed (Figure 2a). From the onsets of oxidation and reduction, the electrochemical band gap of **3** can be calculated as 2.04 eV which is in good agreement with the optical band gap. On the other hand, dyad **DPP-C<sub>60</sub>** gives rise, in addition to the redox processes observed for the **DPP** derivative **6**, to three quasireversible one-electron reduction waves that reflect the first three one-electron reduction steps of the fullerene core. This behavior is another indication of the lack of significant interactions between both moieties in the ground state.

Concerning the emission properties of the dyad **DPP-C<sub>60</sub>**, a significant quenching of the characteristic fluorescence of the **DPP** derivative **1** was observed which is a strong fluorophore with an emission quantum yield as high as 0.62 (Figure S2). As in other previously reported

**DPP**-[60]fullerene ensembles this quenching is due to the very fast decay of the S1 state of the **DPP** moiety, by either energy transfer to the C<sub>60</sub> units or electron transfer from the **DPP** to the C<sub>60</sub>.<sup>18</sup>



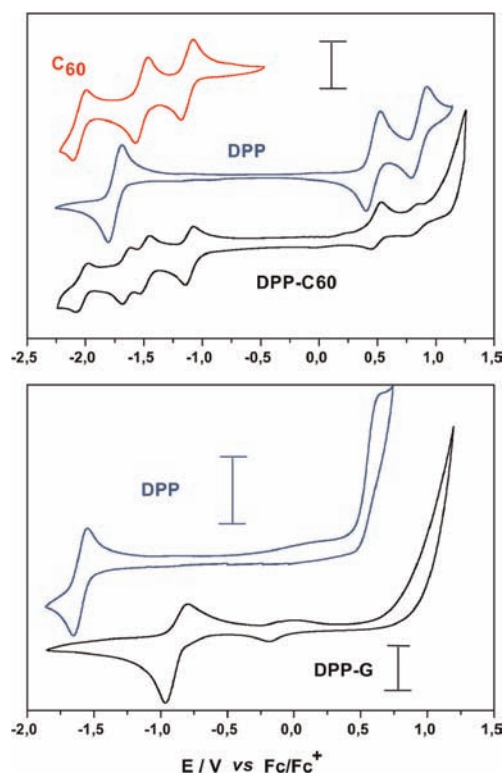
**Figure 1.** UV/vis absorption spectra of **DPP**, **DPP-C<sub>60</sub>** (left y-axis), and **DPP-G** (right y-axis) in *N*-methyl-2-pyrrolidone (NMP) solutions.

In comparison with the **DPP**-[60]fullerene dyad **DPP-C<sub>60</sub>** it is noted that the absorptions of the **DPP** derivative at 511 and 547 nm in **DPP-G** are broadened, weakened, and blue-shifted to 435 nm (Figure 1). The weakening of the absorption is due to the strong  $\pi$  plasmon absorption of graphene that partially masks the **DPP** transitions.<sup>19</sup>

The blue shift of the **DPP** absorption in **DPP-G** can be rationalized in terms of a strong  $\pi$ - $\pi$  stacking between the planar **DPP** moiety and the flat surface of graphene that

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**Figure 2.** (a) CV of **DPP**, **C<sub>60</sub>**, and **DPP-C<sub>60</sub>** recorded in  $\text{Cl}_2\text{CH}_2/0.1$  M tetrabutylammonium hexafluorophosphate (TBAHFP) electrolyte. Scale bars for all curves correspond to  $3 \mu\text{A}$ . (b) CV of **DPP** and **DPP-G** in  $\text{NMP}/0.1$  M TBAHFP electrolyte. Scale bars correspond to  $3.5$  and  $20 \mu\text{A}$  for **DPP** and **DPP-G**, respectively.

may render an effective intermolecular orbital overlap. This is facilitated by the long flexible alkyl chain used as a linker between the **DPP** and graphene moieties.

Regarding the electrochemical behavior, the presence of graphene remarkably alters the CV of **DPP**, further highlighting the differences with the **DPP-C<sub>60</sub>** system. Despite the fact that bands at potentials higher than  $1.1$  V cannot be observed due to the limited electrochemical windows of NMP, the reduction bands of **DPP** shift dramatically to less cathodic potentials (over  $900$  mV) suggesting a strong communication between graphene and **DPP** (Figure 2b). This large displacement has already been observed for other  $\pi$ -conjugated electroactive moieties covalently attached to carbon nanotubes<sup>20</sup> and non-covalently assembled with graphene.<sup>21</sup> Qualitatively, this

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may be attributed to the fact that  $\pi$ - $\pi$  stacking may render an effective intermolecular orbital overlap. This orbital overlap between the LUMO level of the **DPP** and the graphene work function accounts for a splitting of the empty level<sup>22</sup> translating into a larger LUMO bandwidth which is in agreement with the anodic shift of the reduction potential of the **DPP** moiety. Given that the orbital overlap depends on the intermolecular distance and orientation,<sup>23</sup> a densely packed structure may be responsible for an efficient orbital overlap and therefore a pronounced effect observed for the sample with graphene.

Finally, the emission of the **DPP-G** system shows no emission under visible excitation at  $433$  nm, as occurred with **DPP-C<sub>60</sub>** (Figure S4).

In summary, we have developed a synthetic strategy that allows for the facile functionalization of carbon nanostructures thus providing the possibility of comparing the striking different optical and electrochemical properties of ensembles based on either [60]fullerene or graphene. The differences in dimensions and shape of the two different carbon nanostructures account for the more efficient intramolecular contact and effective interactive cross-section between the planar **DPP** moiety and the flat graphene. The **DPP** clicked to [60]-fullerene, even in its most stable configuration, can only interact with a small part of the curved **C<sub>60</sub>** surface, whereas in **DPP-G** the organic molecule is surrounded by large amounts of carbonaceous surface with which to interact (Figure S5). This synthetic strategy can be extended to molecular and polymeric **DPP** derivatives with lower band gaps. Work is in progress to further investigate the photophysical behavior of this kind of novel ensemble and to explore their performance in photovoltaic devices.

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**Supporting Information Available.** Complete experimental details, spectroscopic characterization, and energies of HOMOs/LUMOs and band gaps of click products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The authors declare no competing financial interest.