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# Synthesis of a Dual Clickable Fullerene Platform and Construction of a Dissymmetric BODIPY-[60]Fullerene-DistyrylBODIPY Triad

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*In memory of Jack Cousseau*

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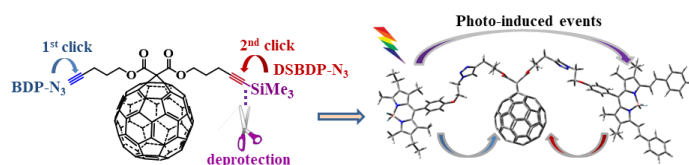
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## Graphical abstract



## Abstract

The synthesis of a methanofullerene platform bearing on one side an alkyne and on the other a protected alkyne is reported. This clickable fullerene building block was functionalized by two distinct BODIPY azido derivatives using a 1<sup>st</sup> CuAAC/alkyne deprotection /2<sup>nd</sup> CuAAC, sequence, through either stepwise or one-pot processes in an efficient manner. The triad displays strong absorption from 300 to 700 nm. The strong fluorescence quenching observed for the two BODIPYs within the triad is probably due to photo-induced energy and/or electron transfer events.

## Introduction

Fullerene [60] is a fascinating three dimensional nanostructure, with outstanding photophysical and electrochemical properties that has promising applications in material<sup>[1]</sup> and life sciences.<sup>[2]</sup> Chemical modification of the fullerene core not only increases the solubility of the resulting fullerene derivatives, but also allows the synthesis of sophisticated molecular assemblies, such as Donor-Acceptor systems.<sup>[1]</sup> The main strategy to prepare such derivatives is to functionalize the fullerene core in the final step of a given synthesis (direct approach)<sup>[3]</sup> while the post-functionalization of fullerene building blocks (indirect approach) has been more rarely considered. Nevertheless, a few research groups have investigated interesting coupling strategies including esterification,<sup>[4]</sup> amidation<sup>[5]</sup> and condensation<sup>[6]</sup> for post-functionalization of fullerene derivatives. More recently, the copper-catalyzed alkyne-azide cycloaddition (CuAAC), simultaneously discovered by Sharpless<sup>[7]</sup> and Meldal,<sup>[8]</sup> arose as an efficient way to functionalize fullerene derivatives,<sup>[9]</sup> and to prepare a large variety of new advanced materials<sup>[10, 11]</sup> and bioactive compounds.<sup>[12]</sup> The use of this reaction in fullerene chemistry has thus allowed the synthesis and isolation of discrete derivatives that would be difficult to access using the direct approach. The main strategy that has appeared relies on the use of mono- and multi-adducts of fullerene building blocks functionalized by identical reactive moieties, either azide or alkyne units.<sup>[9c-d, 13]</sup> The functionalization of fullerene building blocks bearing two different “clickable” moieties, has only been reported with hexa-adducts of C<sub>60</sub>, in which the fullerene core is used for its three dimensional structure.<sup>[12c, 14]</sup> To our knowledge, the functionalization of a mono-adduct of C<sub>60</sub> bearing two orthogonal CuAAC clickable moieties has not been described in the literature. This approach seems to be very appealing, since it could allow the preparation of fullerene derivatives with diverse appendages displaying different properties, while keeping the electrochemical and photophysical properties of fullerene C<sub>60</sub>. We have previously described a dual clickable fullerene, bearing two different functions (alkyne and maleimide), that could undergo sequential CuAAC and thiol-maleimide Michael addition reactions.<sup>[15]</sup> This strategy allowed the preparation of a set of photo- and/or electroactive fullerodendrimers and cysteine-functionalized fullerene assemblies.<sup>[16]</sup> However, this method displays some limitations: possible retro-Michael reactions of the adducts in solution,<sup>[17]</sup> and introduction of a chiral center resulting from the thiol-maleimide addition, which can be problematic if an enantiopure form is required.<sup>[18]</sup> To circumvent these limitations, we have decided to replace

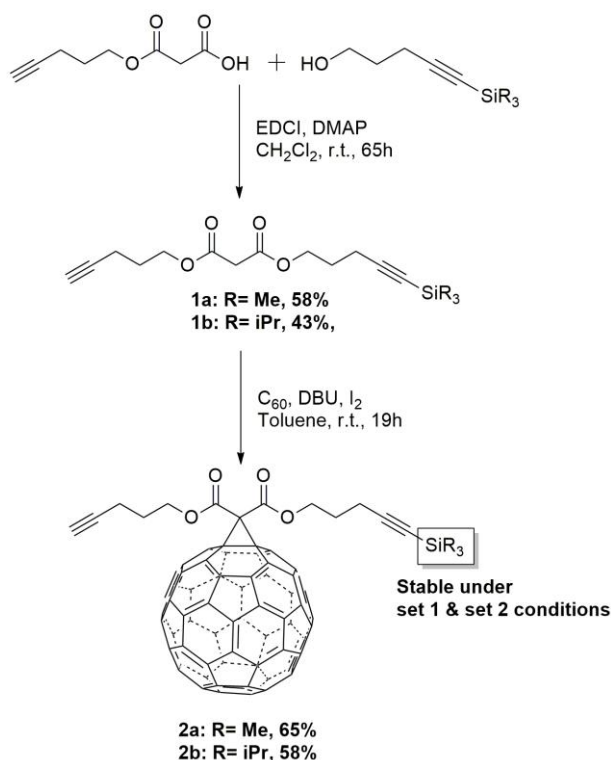
the maleimide moiety by a second clickable CuAAC function in a new methanofullerene platform. As azide-functionalized fullerene monoadducts are unstable in the solid state,<sup>[9b]</sup> a building block bearing two alkyne moieties, one terminal and one protected, was preferred. While the chemoselective formation of consecutive triazole linkages by two successive click reactions from derivatives incorporating both a terminal alkyne and a protected alkyne has been widely used with many different molecules, this strategy has never been reported with fullerene building blocks.<sup>[19]</sup>

In this article, we report the synthesis of a new methanofullerene platform that bears on one side an alkyne and on the other side a protected alkyne. We first investigated two alkyne protecting groups, trimethylsilyl (TMS) and tri-*iso*-propylsilyl (TIPS) for their stability under different CuAAC conditions, as it is known that TMS protected alkynes may undergo slow deprotection into terminal alkynes under CuAAC conditions, while the TIPS protected alkyne is stable.<sup>[19a-b]</sup> Once the stability of these protecting groups had been assessed, the reactivity of the new platform was examined in the following reaction sequence: a **1<sup>st</sup> CuAAC** reaction of the terminal alkyne, **deprotection** of the protected alkyne, and finally a **2<sup>nd</sup> CuAAC** reaction. In order to prepare C<sub>60</sub> derivatives with significant value from the viewpoint of synthetic and materials chemistry, we combined our new methanofullerene platform with light harvester/electron donor derivatives. Among the different families of donor chromophores that have been associated with C<sub>60</sub>, we have selected 4,4'-difluoro-4-bora-3a,4a-diaza-*s*-indacenes (referred to as BODIPYs), which display outstanding optical and photophysical properties, including high absorption coefficients and emission quantum yields. Their association, that gives rise to photo-induced energy transfer and/or electron transfer has been developed for different applications including artificial photosynthetic systems,<sup>[20]</sup> triplet-triplet annihilation up-conversion,<sup>[21]</sup> photocatalysis,<sup>[22]</sup> and more recently as an antimicrobial agent.<sup>[23]</sup> In addition, BODIPYs can be easily functionalized, resulting in the modulation of their optical and electrochemical features.<sup>[24]</sup> Two different azide BODIPYs, a BODIPY (BDP) and a distyryl-BODIPY (DSBDP) that absorb in different spectral ranges, were linked to the methanofullerene platform using either stepwise or one-pot processes, resulting in a BDP-C<sub>60</sub>-DSBDP triad that displays panchromatic light capture (from 300 to 700 nm). In this triad, the fullerene is placed between the two light harvester/electron donor derivatives, a different design than in previously reported BODIPYs-C<sub>60</sub> triads.<sup>[20h, 22c, 25]</sup> From this particular arrangement, one could expect that the photophysical behavior of this assembly should be as complex as that observed with a BODIPY-azaBODIPY-C<sub>60</sub> triad in a V-configuration<sup>[25b]</sup> with competitive light induced energy transfer and electron transfer events.

## Results and discussions

### *Synthesis of methanofullerene platforms and stability of the alkyne protected groups under CuAAC conditions*

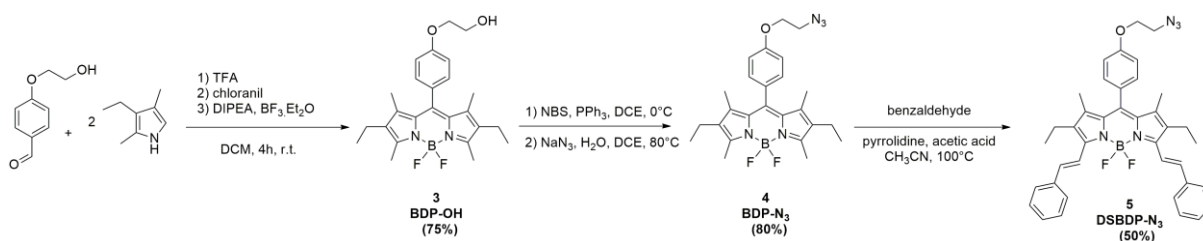
The synthesis of the two new methanofullerene platforms is presented in Scheme 1. We firstly prepared two non-symmetrical malonate derivatives with two different silyl protecting groups (**1a**: TMS, **1b**: TIPS) for the alkyne, by reacting the monoalkyl malonate with either commercially available 5-(trimethylsilyl)pent-4-yn-1-ol or 5-(tri-iso-propyl)pent-4-yn-1-ol<sup>[26]</sup> under EDCI/DMAP coupling conditions. The reaction of the malonates **1a** and **1b** with fullerene C<sub>60</sub> under Bingel reaction conditions provided the corresponding methanofullerene derivatives **2a** and **2b** in 65 and 58% yields respectively. These yields are comparable to those observed in similar cases. They can be explained by the formation of varying amounts of poly-adducts in the reaction mixture. The mono-adducts **2a** and **2b** were easily separated from the poly-adducts and the unreacted C<sub>60</sub> by column chromatography on silica gel. The stability of compounds **2a** and **2b** under two sets of CuAAC reaction conditions that we had previously<sup>[15-16]</sup> used for CuAAC coupling between an alkyne moiety part of a fullerene building block and an azide was then evaluated. The first set of conditions relies on the use of copper sulfate (CuSO<sub>4</sub>, 1 eq.) and sodium ascorbate (Na ascorbate, 2 eq.) in a mixture of dichloromethane/water (1/1) for 24 hours at room temperature.<sup>[15]</sup> The second experiment used a mixture of copper (I) bromide (CuBr, 1eq.) and *N,N*-diisopropylethylamine (DIPEA, 1 eq.) in dichloromethane at room temperature for 24 hours.<sup>[16]</sup> The stability of these compounds were assessed by TLC and proton NMR. As expected, compound **2b** with a TIPS protecting group was found to be stable under these conditions.<sup>[19b]</sup> Surprisingly, compound **2a** also appeared to be stable, and deprotection to a terminal alkyne was not observed under these conditions.



**Scheme 1.** Synthesis of the dual clickable methanofullerenes **2a** and **2b**. **Set 1:** CuSO<sub>4</sub> (1 eq.), Na ascorbate (2 eq.), DCM/water (1/1), 24 h, r.t., **Set 2:** CuBr (1eq.), DIPEA (1 eq.), DCM, 24h, r.t.

### *Synthesis and characterization of dissymmetric BDP-C60-DSBDP triad using CuAAC reactions*

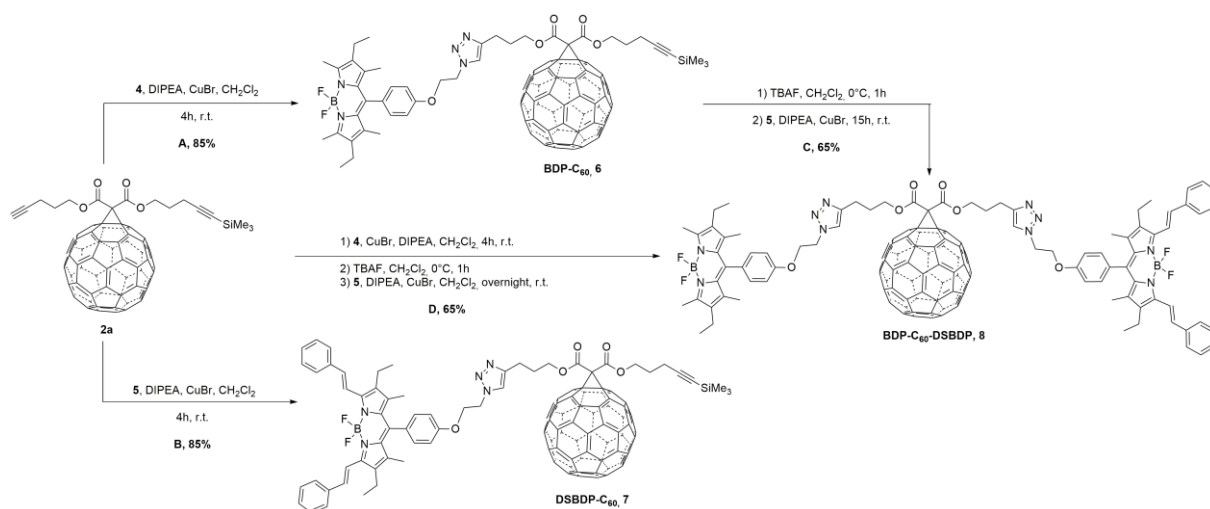
Once the stability of the alkyne protected groups on the fullerene platforms had been tested in different CuAAC conditions, we then investigated the grafting of BODIPY azides to the fullerene building blocks. For this study, the methanofullerene **2a** was chosen, since the TMS protecting group can be cleaved more easily than the TIPS group.<sup>[19b]</sup> The synthesis of the two BODIPY azides (BDP-N<sub>3</sub> **4** and DSBDP-N<sub>3</sub> **5**) is presented in Scheme 2.



**Scheme 2.** Synthesis of BDP-N<sub>3</sub> **4** and DSBDP-N<sub>3</sub> **5**.

Initially, the BODIPY **3** (BDP-OH) was synthesized using a three-step one-pot approach as described in the literature.<sup>[27]</sup> The corresponding BODIPY azide derivative was obtained by a

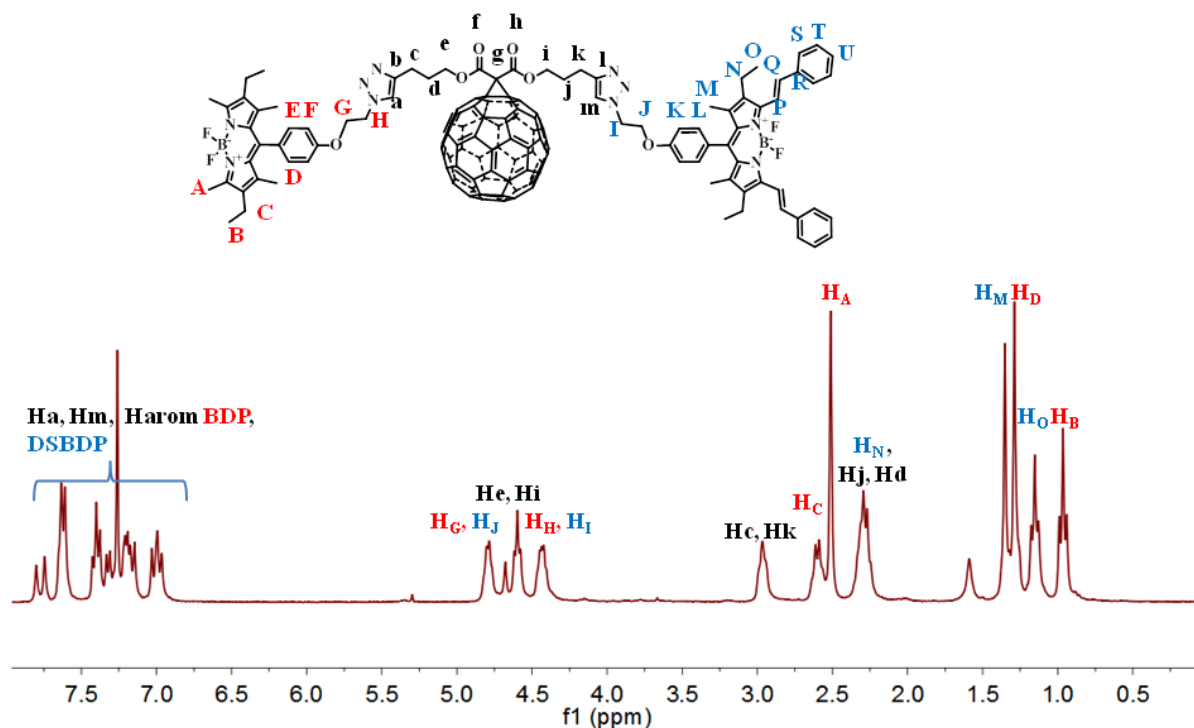
new one-pot procedure in 80% yield, by reacting **3** with N-bromosuccinimide (NBS) and triphenylphosphine (PPh<sub>3</sub>) in dichloroethane at 0°C for one hour, followed by an *in situ* reaction with sodium azide (NaN<sub>3</sub>) for 15 hours at 80°C. The distyryl-BODIPY **5** (DSBDP-N<sub>3</sub>) was then obtained in 50% yield through a Knoevenagel condensation of BDP-N<sub>3</sub> **4** with benzaldehyde. Next, the “click-deprotection-click” sequence between the methanofullerene **2a** and the BODIPY azides **4** and **5** was examined. The methanofullerene **2a** was reacted with 1.1 eq. of compounds **4** (Scheme 3, **A**) or **5** (Scheme 3, **B**) under our previously reported conditions, using equimolar amounts of CuBr and DIPEA at room temperature. The dyads **6** and **7** thereby obtained were isolated in high yields. The deprotection of the TMS alkyne in dyad **6** was attempted using classical conditions (TBAF in THF).<sup>[19b]</sup> Although the starting material was completely consumed within 15 minutes (monitored by TLC), no desired product was detected in the crude reaction mixture. We then attempted the deprotection with only a sub-stoichiometric quantity of TBAF, and changed the solvent from THF to dichloromethane. Under these conditions, the TMS-alkyne protected methanofullerene **6** was successfully deprotected, and the resulting product isolated in 85% yield. In subsequent experiments, the deprotection step was followed immediately by the second click reaction, without isolating the deprotected intermediate. Hence, compound **6** was subjected to deprotection using TBAF in anhydrous DCM, followed by the addition of **5**, CuBr and DIPEA at room temperature for 15 hours. The desired triad **8** was isolated in 65% yield after purification (Scheme 3, **C**). Finally, a one-pot process was carried out starting from the methanofullerene building block **2a** in order to reduce the number of work-up and purification operations. Thus, compound **2a** was firstly reacted with **4** in the presence of CuBr and DIPEA in dichloromethane for 4 hours. After complete conversion of the starting material (monitored by TLC), TBAF was added at 0°C to the crude mixture, followed by the addition of compound **5**, CuBr and DIPEA. The desired triad **8** was isolated in an efficient way in 65% yield (Scheme 3, **D**).



**Scheme 3.** Synthesis of BDP-C<sub>60</sub> **6** (Route A), DSBDP-C<sub>60</sub> **7** (Route B), BDP-C<sub>60</sub>-DSBDP **8** from **6** (Route C), and through a one-pot process from **2a** (Route D).

All the new compounds were fully characterized by NMR spectroscopy and by electrospray mass spectrometry. Examination of the <sup>1</sup>H NMR of the BDP-C<sub>60</sub> dyad **6** clearly indicates the disappearance of the alkyne moiety at 2.04 ppm while the peak of the TMS group remains intact (**Figure S40**, top). Furthermore, the typical singlet of the triazole unit appears at 7.68 ppm as well as the signals that correspond to the protons of the BDP derivative (**Figure S40**, middle). The same features were observed for the DSBDP-C<sub>60</sub> dyad **7** along with additional peaks from 7.00 to 7.80 ppm related to the distyryl moieties of the DSBDP (**Figure S40**, bottom). Finally, inspection of the <sup>1</sup>H NMR of the triad **8** shows the simultaneous disappearance of the TMS and terminal alkyne protons at 0.16 and 2.04 ppm, respectively. The signals related to the BDP and DSBDP moieties are clearly observed in the 7.00 to 8.00 ppm region, the singlet peaks corresponding to the two triazole protons are masked by the aromatic protons of DistyrylBODIPY (**Figure 1**). All these data confirm the occurrence of the “click-deprotection-click” sequence.





**Figure 1.**  $^1\text{H}$  NMR spectrum recorded (300 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) for: BDP- $\text{C}_{60}$ -DSBDP **8**.

### *Steady-State Absorption Spectra.*

**Figure 2** shows the absorption spectra of molecular dyads (BDP- $\text{C}_{60}$  **6**, and DSBDP- $\text{C}_{60}$  **7**) and molecular triad (BDP- $\text{C}_{60}$ -DSBDP **8**) in DCM. The spectra of parent chromophores BDP **4** and DSBDP **5**, in addition to the methanofullerene platform **2a** are also provided in this figure. The spectrum of the starting BDP **4** shows a narrow and intense absorption band at 525 nm attributed to the  $S_0 \rightarrow S_1$  transition and a much weaker and broader absorption band at 371 nm due to the  $S_0 \rightarrow S_2$  transition.<sup>[28]</sup> The spectrum of the DSBDP **5** exhibits an intense and large absorption band at 637 nm, this  $S_0 \rightarrow S_1$  transition is red-shifted compared to that of **4** owing to the extended conjugation of the BODIPY core.<sup>[29]</sup> The additional bands in the UV region of **5** are ascribed to the  $\pi$ - $\pi$  distyryl subunits (345 nm) along with a shoulder attributed to the  $S_0 \rightarrow S_2$  transition of the BODIPY backbone. The fullerene derivative **2a** displays typical signatures of a methanofullerene with a sharp band at 327 nm and a smaller band at 426 nm.<sup>[30]</sup> The absorption of the dyads **6** and **7** are respectively the sum of the absorption of fullerene **2a** and the BDP **4**, and of fullerene **2a** and DSBDP **5**. The same trend is observed in the absorption of the triad **8**, which is the superposition of the absorption of the three photoactive components (i.e.  $\text{C}_{60}$ , BDP and DSBDP). These findings suggest a negligible ground state interaction between the BODIPYs (BDP and/or DSBDP) and the fullerene entities in the dyads and the triad, respectively. Finally, owing to the presence of two

differently functionalized BODIPY derivatives on the same fullerene core, the triad **8** reveals good spectral coverage from 300 to 700 nm, which could be beneficial in the area of broadband capture.<sup>[20b, 31]</sup>

### Steady-State Fluorescence Spectra.

The fluorescence spectra of the parent BODIPYs **4** and **5**, the two dyads **6** and **7**, and the triad **8** were also recorded in DCM (**Figure 3-left** and **Figure S67**). The compounds were excited either at 495 nm or at 605 nm. At 495 nm, the absorption is mostly attributed to the BDP part ( $\epsilon$ -BDP **4** = 21500 L.mol<sup>-1</sup>.cm<sup>-1</sup>), as C<sub>60</sub> and DSBDP display very minor absorption ( $\epsilon$ -C<sub>60</sub> **2** = 1000 L.mol<sup>-1</sup>.cm<sup>-1</sup> and  $\epsilon$ -DSBDP **5** = 1400 L.mol<sup>-1</sup>.cm<sup>-1</sup>) at this wavelength (ratio of light absorbed BDP-**4**/C<sub>60</sub>-**2** = 21.5 and BDP-**4**/DSBDP-**5** = 15). At 605 nm, the absorption is mostly attributed to the DSBDP moiety ( $\epsilon$ -DSBDP **5** = 33500 L.mol<sup>-1</sup>.cm<sup>-1</sup>), as C<sub>60</sub> and BDP display very minor absorption ( $\epsilon$ -C<sub>60</sub> **2** = 220 L.mol<sup>-1</sup>.cm<sup>-1</sup> and  $\epsilon$ -BDP **4** = 350 L.mol<sup>-1</sup>.cm<sup>-1</sup>) at this wavelength (ratio of light absorbed DSBDP-**5**/C<sub>60</sub>-**2** = 150 and DSBDP-**5**/BDP-**4** = 95).

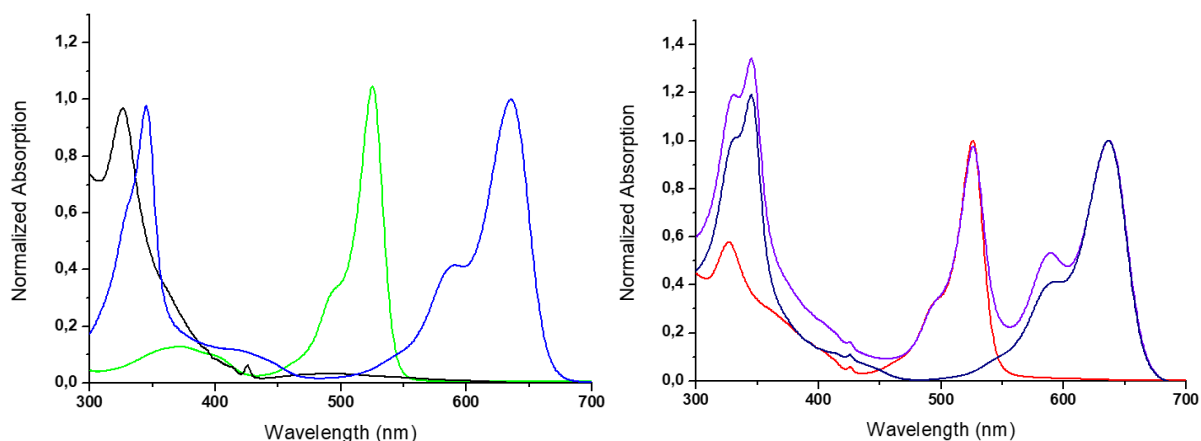
BDP **4** and DSBDP **5** exhibited strong fluorescence at 536 nm ( $\lambda_{exc}$ =495 nm) and 651 nm ( $\lambda_{exc}$ =605 nm) with high fluorescence quantum yields (Table 1). However, in the dyads **6** and **7**, the intensities of the BDP and DSBDP emission bands were found to be quenched by over 98% and 94%, respectively. The quenching of the fluorescence observed in these dyads indicates the presence of intramolecular quenching events, such as electron-transfer (ET) and/or energy transfer (EnT) processes. Energy transfer in the BDP-C<sub>60</sub> dyad cannot be excluded due to the spectral overlap between BDP emission and methanofullerene absorption.<sup>[20j]</sup> As far as the DSBDP-C<sub>60</sub> dyad is concerned, a similar system combining the same chromophores was described in which electron transfer was demonstrated,<sup>[32]</sup> while energy transfer was excluded. However, energy transfer cannot be totally discounted<sup>[22a]</sup> in our system even though the spectral overlap between DSBDP emission and methanofullerene absorption is minimal.

Furthermore, when the BDP-C<sub>60</sub>-DSBDP triad **8** was excited at 495 nm, the emission band of the BDP moiety was also found to be quenched by over 99%, with the appearance of a new peak at around 650 nm corresponding to DSBDP emission (**Figure S67**). This suggests the occurrence of singlet-singlet energy transfer from the excited <sup>1</sup>BDP\* to the DSBDP. The excitation spectrum of the triad was then recorded at 670 nm (emission of <sup>1</sup>DSBDP \*). This spectrum revealed excitation peaks of both BDP and DSBDP, confirming the occurrence of

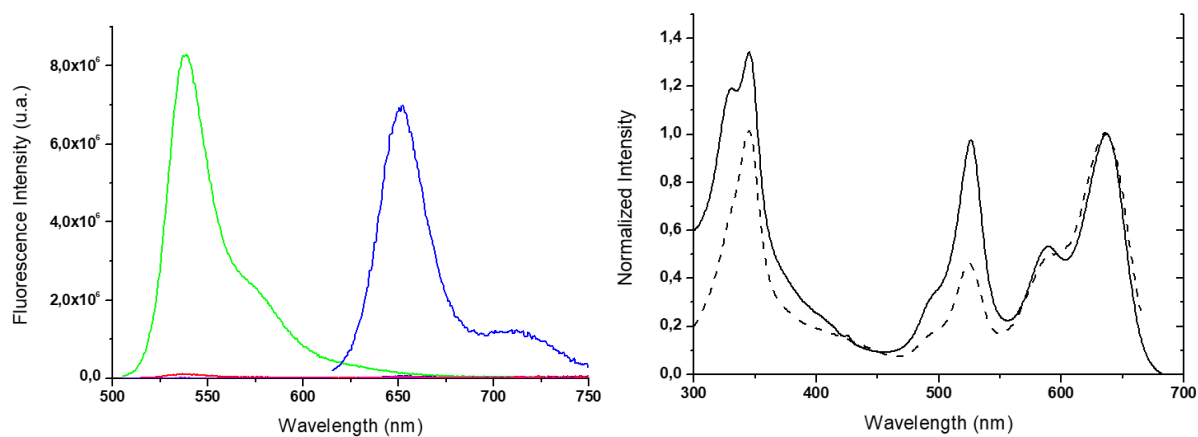
an energy transfer process (**Figure 3-right**). In addition, the excitation spectrum does not perfectly match the absorption spectrum in the BDP region. This indicates the occurrence of additional photochemical events in the triad when the BDP was excited, most likely from  $^1\text{BDP}^*$  to the  $\text{C}_{60}$  as observed in the BDP- $\text{C}_{60}$  dyad. Finally, when the triad was also excited at 605 nm, the emission band of DSBDP was found to be quenched by over 95%, suggesting a likely photo-induced electron transfer process from the  $^1\text{DSBDP}^*$  to the  $\text{C}_{60}$  as proposed for the dyad DSBDP- $\text{C}_{60}$ .

We have also performed the absorption and emission spectra of the dyads (**6** and **7**), of the triad **8** and of the parent compounds (**4** and **5**) in toluene (**Figures S68-S71** and **Table S1**). These measurements show a similar quenching effect in toluene as compared to dichloromethane.

To decipher the exact nature of the photophysical processes in the dyads **6** and **7** and the triad **8**, transient absorption measurements will be performed, but we consider that these analyses go beyond the scope of this work.<sup>[33]</sup>



**Figure 2.** **Left**) Normalized absorption spectra of BDP-N<sub>3</sub> **4** (green, [C] = 15.5  $\mu\text{M}$ ), DSBDP-N<sub>3</sub> **5** (blue, [C] = 9.7  $\mu\text{M}$ ), and C<sub>60</sub> platform **2a** (black, [C] = 32.1  $\mu\text{M}$ ) in dichloromethane. **Right**) Normalized absorption spectra of BDP-C<sub>60</sub> **6** (red, [C] = 13.9  $\mu\text{M}$ ), DSBDP-C<sub>60</sub> **7** (navy blue, [C] = 10.1  $\mu\text{M}$ ), and DSBDP-C<sub>60</sub>-BDP **8** (violet, [C] = 14.1  $\mu\text{M}$ ) in dichloromethane.



**Figure 3. Left)** Emission spectra in dichloromethane of BDP-N<sub>3</sub> **4** (green,  $\lambda_{exc}$  = 495 nm), DSBDP-N<sub>3</sub> **5** (blue,  $\lambda_{exc}$  = 605 nm), BDP-C<sub>60</sub> **6** (red,  $\lambda_{exc}$  = 495 nm, see Figure S67), DSBDP-C<sub>60</sub> **7** (navy blue,  $\lambda_{exc}$  = 605 nm, see Figure S67), and DSBDP-C<sub>60</sub>-BDP **8** (violet,  $\lambda_{exc}$  = 495 nm ; pink,  $\lambda_{exc}$  = 605 nm, see Figure S67). **Right)** Comparison of the UV-vis absorption (solid line) and fluorescence excitation spectra (dotted line,  $\lambda_{em}$  = 670 nm) of DSBDP-C<sub>60</sub>-BDP triad in dichloromethane.

**Table 1.** Absorption and fluorescence data of the investigated compounds.

Compound	$\lambda_{abs}$ , nm ( $\epsilon$ , M <sup>-1</sup> .cm <sup>-1</sup> )	$\lambda_{em}$ , nm	$\Phi$ , % $\pm$ 5 %
<b>4</b>	525 (67500)	535	>95 <sup>a</sup>
<b>5</b>	637 (76000)	650	91 <sup>b</sup>
<b>2a</b>	330 (29000)	-	-
<b>6</b>	330 (41500), 525 (73500)	535	1.3 <sup>a</sup>
<b>7</b>	330, 345 (103500), 637 (87000)	650	4.9 <sup>b</sup>
<b>8</b>	330, 345 (73500), 525 (53000), 637 (55000)	535 650	0.6 <sup>a</sup> 4.6 <sup>b</sup>

<sup>a</sup> Rhodamine 6G used as standard ( $\lambda_{exc}$  = 495 nm,  $\phi$  = 0.95 in ethanol). <sup>b</sup> Oxazine 1 used as standard ( $\lambda_{exc}$  = 605 nm,  $\phi$  = 0.11 in ethanol).

## Electrochemistry

The electrochemical properties of the parent BODIPYs **4-5**, of the dyads **6-7** and the triad **8** were studied by cyclic voltammetry (CV). All experiments were performed at room temperature in dichloromethane solutions using tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) as supporting electrolyte and ferrocene (Fc) as internal reference. The half-wave potentials (V vs Fc<sup>+</sup>/Fc) of all derivatives (**4-8**) are collected in Table 2. The cyclic voltammograms of these compounds are also presented in **Figure 4**. The parent chromophore **4** displays the typical behavior of a BODIPY derivative, with a one-electron reversible oxidation wave at 0.58 (V vs Fc<sup>+</sup>/Fc) corresponding to the formation of the BODIPY  $\pi$ -radical cation (BDP<sup>+</sup>) and a one-electron quasi-reversible reduction wave at -1.78 (V vs Fc<sup>+</sup>/Fc) due

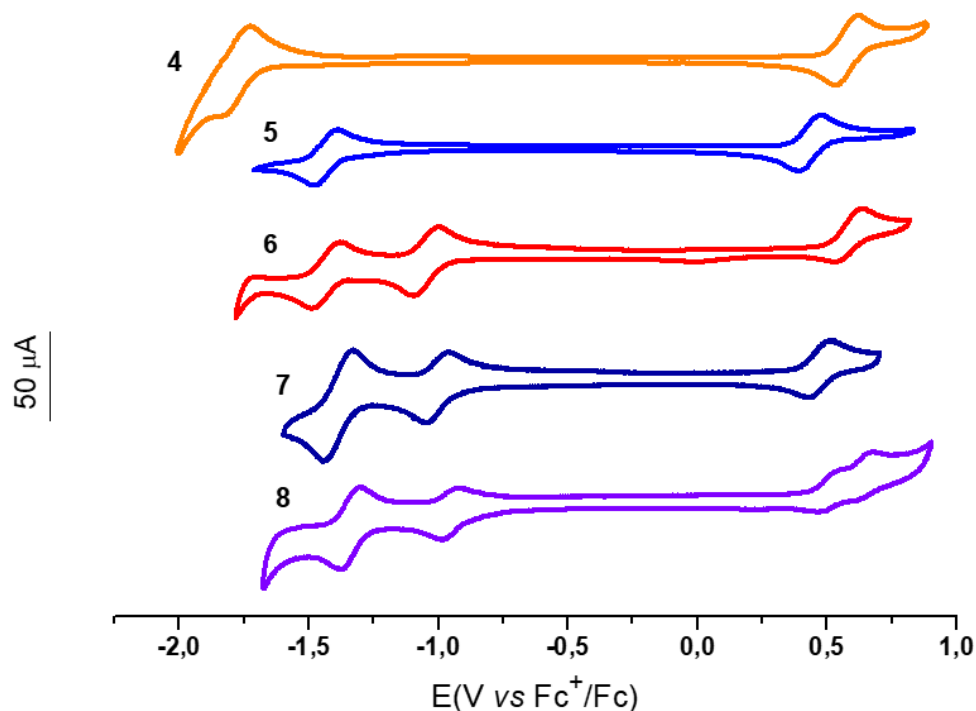
to the formation of the BODIPY  $\pi$ -radical anion ( $\text{BDP}^{\bullet-}$ ).<sup>[34]</sup> In the voltammogram of **5**, the presence of the two styryl groups added to the BODIPY core affects both oxidation and reduction potentials, the DSBDP derivative is more easily reduced and oxidized.<sup>[20b]</sup> Thus in the cathodic region, the reduction of the BODIPY core to  $\text{DSBDP}^{\bullet-}$  is reversible and anodically shifted by 340 mV in **5** relative to **4**. In the anodic region, the oxidation of the BODIPY core to  $\text{DSBDP}^{+\bullet}$  is also reversible and cathodically shifted by 140 mV in comparison with **4**.

Dyad **6** shows two reversible reduction processes at -1.05 V and -1.43 V that are attributed to the successive reduction of the fullerene core into the radical anion ( $\text{C}_{60}^{\bullet-}$ ) and dianion ( $\text{C}_{60}^{2-}$ ).<sup>[16]</sup> The reduction of the BODIPY core in this dyad was not investigated due to the instability of the methanofullerene moiety after several reductions processes, known as the retro-Bingel reaction.<sup>[35]</sup> In the anodic region, the one-electron reversible oxidation wave observed at 0.6 V was attributed with certainty to the  $\text{BDP}^{+\bullet}$  in agreement with the CV of **4**.

Cyclic voltammogram of dyad **7** shows two reversible reduction waves in the cathodic region. The first one-electron process at -1.00 (V vs  $\text{Fc}^+/\text{Fc}$ ) was assigned to the formation of  $\text{C}_{60}^{\bullet-}$ . The following one-electron reduction process at -1.39 (V vs  $\text{Fc}^+/\text{Fc}$ ) is due to two overlapping reductions, one corresponding to the second reduction of  $\text{C}_{60}$  and the other to the first reduction of DSBDP. Furthermore, the one-electron reversible oxidation process observed at 0.47 (V vs  $\text{Fc}^+/\text{Fc}$ ) is attributed to the  $\text{DSBDP}^{+\bullet}$  in agreement with the CV of **5**.

Triad **8** shows in the cathodic region similar reduction processes than dyad **7**, with two reversible reductions waves at -0.96 V and -1.34 (V vs  $\text{Fc}^+/\text{Fc}$ ) based on the  $\text{C}_{60}$  core (1<sup>st</sup> red) and two overlapping reductions based on the  $\text{C}_{60}$  core (2<sup>nd</sup> red) and the DSBDP unit (1<sup>st</sup> red). In the anodic region, the two reversible oxidations processes observed at 0.50 V and 0.64 (V vs  $\text{Fc}^+/\text{Fc}$ ) are assigned to the oxidation of the DSBDP and the BDP moieties, respectively.

Finally, on the basis of the similar redox potential analysis, we can conclude that no significant electronic interactions are found within the dyads and the triad in the ground state.



**Figure 4.** Cyclic voltammograms of the parent chromophores BDP **4** (orange) and DSBDP **5** (blue), of the dyads BDP- $C_{60}$  **6** (red) and DSBDP- $C_{60}$  **7** (navy blue) and of the triad DSBDP- $C_{60}$ -BDP **8** (violet) in anhydrous and oxygen-free dichloromethane, 0.1M of  $n\text{-Bu}_4\text{NPF}_6$ , pseudo-reference electrode: Ag wire, working electrode: Pt, auxiliary electrode: Pt, scanning rate:  $100\text{mV}\cdot\text{s}^{-1}$ .

**Table 2.** Electrochemical Half-Wave Potentials (V vs  $\text{Fc}^+/\text{Fc}$ ) of the parent chromophores BDP **4** and DSBDP **5**, the dyads BDP- $C_{60}$  **6**, DSBDP- $C_{60}$  **7**, and the triad DSBDP- $C_{60}$ -BDP **8**.

Compound	Potential (V vs $\text{Fc}^+/\text{Fc}$ )					
	BDP $^{0/+}$	DSBDP $^{0/+}$	$C_{60}^{0/-}$	$C_{60}^{-/2-}$	DSBDP $^{0/-}$	BDP $^{0/-}$
BDP- $N_3$ , <b>4</b>	0.58					-1.78
DSBDP- $N_3$ , <b>5</b>		0.44			-1.44	
BDP- $C_{60}$ , <b>6</b>	0.58	-	-1.05	-1.43		
DSBDP- $C_{60}$ , <b>7</b>	-	0.47	-1.00	-1.39	-1.39	
DSBDP- $C_{60}$ -BDP, <b>8</b>	0.64	0.50	-0.96	-1.34	-1.34	

## Conclusion

In summary, we have reported for the first time the synthesis of a new clickable methanofullerene platform that bears on one side an alkyne and on the other a protected alkyne. Two alkyne protecting groups, trimethylsilyl (TMS) and tri-*iso*-propylsilyl (TIPS), were investigated in this study. The use of the TIPS group was motivated by the well-known instability of the TMS group under CuAAC reaction conditions. Firstly, two sets of CuAAC conditions currently used in fullerene chemistry were used to assess the stability of the

protecting groups in this platform. The TIPS protecting group was found to be stable, but unexpectedly the TMS group also withstood these conditions. Once this stability had been demonstrated, the new methanofullerene platform bearing the TMS-alkyne unit was combined with two azido BODIPYs derivatives, used as light harvester/electron donors derivatives. These derivatives were associated separately to the fullerene platform in an efficient way allowing the synthesis of two dyads, BDP-C<sub>60</sub> and DSBDP-C<sub>60</sub>. Then, both BODIPYs were grafted onto the fullerene building block using the sequence *1<sup>st</sup> CuAAC/ alkyne deprotection /2<sup>nd</sup> CuAAC* through either stepwise or one-pot processes. Both approaches allowed the synthesis of a BDP-C<sub>60</sub>-DSBDP triad in good yields. Owing to the presence of the two BODIPYs units including the distyryl-BODIPY with its extended conjugation, the triad displayed absorbance well into the near-infrared region, covering a 300-700 nm spectral range. The strong fluorescence quenching observed in the two dyads BDP-C<sub>60</sub> and DSBDP-C<sub>60</sub> are evidence of intramolecular events such as energy transfer (EnT) and/or electron-transfer (ET) between the <sup>1</sup>BDP\* and C<sub>60</sub>, and <sup>1</sup>DSBDP\* and C<sub>60</sub>, respectively. The photochemical behavior in the triad should be more complex owing to the presence of the two BODIPYs derivatives as well as to its geometry. The same intramolecular events observed in the dyads are likely to be responsible for the deactivation of the <sup>1</sup>BDP\* and <sup>1</sup>DSBDP\* by C<sub>60</sub> in the triad. In addition, from steady-state fluorescence, a singlet-singlet energy transfer from the <sup>1</sup>BDP\* to the DSBDP was also demonstrated in the triad.

Finally, we believe that the use of this dual clickable fullerene platform, easily functionalized by two successive CuAAC reactions, could have a significant impact in the field of fullerene chemistry. Indeed, while this triad could be prepared using classical fullerene chemistry, by pre-forming a bis-triazole malonate and then grafting on C<sub>60</sub> (direct approach), this method would have the disadvantage of the formation of undesired poly-adducts due to the multifunctional nature of the fullerene, resulting in the loss of the BODIPYs precursors and the recovery of the target in low yield.

The approach developed in this work should allow a straightforward access to fullerene derivatives that could be of interest in the fields of materials science. We are planning to combine light harvester/electron donor and helical peptides to this platform with the goal of developing photoelectrochemical devices. This work is currently underway in our laboratory.

## Experimental Section

**General Information.** All organic reagents and solvents were purchased from commercial suppliers (Sigma-Aldrich, TCI, and others) and were used as received. Fullerene C<sub>60</sub> (purity 99.5+%) was purchased from MTR Ltd. DCM was dried on CaCl<sub>2</sub> and distilled over CaH<sub>2</sub> prior to use. Toluene was distilled over NaH prior to use. Column chromatography was performed using silica gel 60 (0.040-0.063mm). Thin layer chromatography (TLC) was performed on aluminium sheets coated with silica gel 60 F<sub>254</sub>.

NMR spectra were performed in CDCl<sub>3</sub> at 25 °C on a Bruker Avance AM300 spectrometer. Chemical shifts were referenced to this internal solvent (7.26 for <sup>1</sup>H and 77.16 ppm for <sup>13</sup>C). Coupling constants (J values) are given in hertz (Hz). Splitting patterns are designated as s (singlet), bs (broad signal), d (doublet), t (triplet), q (quartet), and m (multiplet). High Resolution ESI-Mass spectra were recorded with a Waters Xevo Q-ToF instrument. Optical measurements were performed in 10 mm path length quartz cuvettes. Absorption spectra were recorded using a Shimadzu UV-visible spectrophotometer UV-2600 in transmission mode. The emission spectra were recorded on diluted solutions (to avoid reabsorption artefacts), using a Fluoromax-4 spectrofluorimeter (Jobin-Yvon; Horiba). Corrected signals from lamp fluctuations and apparatus response functions were measured.

**Pent-4-ynyl mono malonate**<sup>[36]</sup> and **5-(tri-iso-propyl)pentyn-4-yn-1-ol**<sup>[26]</sup> were prepared according to procedures reported in the literature. Azido-Bodipy **4** and azido-distyrylBodipy **5** were prepared using a modification of the synthetic route reported in the literature.<sup>[37]</sup>

**Compound 1a:** In a three neck round bottomed flask, **pent-4-ynyl mono malonate** (1.32 g, 7.76 mmol) and 5-(trimethylsilyl)-4-pentyn-1-ol (1.08 g, 6.90 mmol) were dissolved in 50 mL anhydrous DCM. Then, EDCI.HCl (1.46 g, 7.60 mmol) and DMAP (0.84 g, 6.90 mmol) were added at 0°C. The reaction mixture was stirred for 30 mins at 0°C and then for 65 hours at room temperature. After purification by column chromatography on silica gel (DCM), 1.24 g of a light pink oil was obtained (yield= 58%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ=0.12 (s, 9H; H<sub>n</sub>), 1.82-1.96 (m, 4H; H<sub>d</sub>, H<sub>j</sub>), 1.97 (t, J=2.6 Hz, 1H; H<sub>a</sub>), 2.25-2.32 (m, 4H; H<sub>c</sub>, H<sub>k</sub>), 3.36 (s, 2H; H<sub>g</sub>), 4.20-4.26 ppm (m, 4H; H<sub>e</sub>, H<sub>i</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ=0.2 (C<sub>n</sub>), 15.2 (C<sub>c</sub>), 16.6 (C<sub>k</sub>), 27.4, 27.6 (C<sub>d</sub>, C<sub>j</sub>), 41.6 (C<sub>g</sub>), 64.1, 64.2 (C<sub>e</sub>, C<sub>i</sub>), 69.3 (C<sub>a</sub>), 82.8 (C<sub>b</sub>), 85.6 (C<sub>m</sub>), 105.5 (C<sub>l</sub>), 166.5 ppm (C<sub>f</sub>, C<sub>h</sub>); HRMS (ESI): m/z calcd for C<sub>16</sub>H<sub>24</sub>O<sub>4</sub>SiNa<sup>+</sup>: 331.1342 [M+Na]<sup>+</sup>; found: 331.1334.



**Compound 1b:** In a three-neck round bottomed flask, **pent-4-ynyl mono** malonate (1.32 g, 7.76 mmol) and 5-(tri-iso-propyl)pent-4-yn-1-ol (1.66 g, 6.90 mmol) were dissolved in 50 mL of anhydrous DCM. Then, EDCI.HCl (1.46 g, 7.60 mmol) and DMAP (0.84 g, 6.90 mmol) were added at 0°C. The reaction mixture was stirred for 30 minutes at 0°C and then for 65 hours at room temperature. After purification by column chromatography on silica gel (DCM), 1.17 g of a light pink oil was obtained (yield= 43%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ=1.04-1.05 (bs, 21H; H<sub>n</sub>, H<sub>o</sub>), 1.83-1.92 (m, 4H; H<sub>d</sub>, H<sub>j</sub>), 1.97 (t, *J*=2.3 Hz, 1H; H<sub>a</sub>), 2.29 (td, *J*=2.4 Hz, *J*=6.9 Hz 2H; H<sub>c</sub>), 2.35 (t, *J*=7.0 Hz, 2H; H<sub>k</sub>), 3.38 (s, 2H; H<sub>g</sub>), 4.26 ppm (t, *J*=6.2 Hz, 4H; H<sub>e</sub>, H<sub>i</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ=11.4 (C<sub>n</sub>), 15.2 (C<sub>c</sub>), 16.6 (C<sub>k</sub>), 18.7 (C<sub>o</sub>), 27.5, 28.0 (C<sub>d</sub>, C<sub>j</sub>), 41.6 (C<sub>g</sub>), 64.1, 64.3 (C<sub>e</sub>, C<sub>i</sub>), 69.3 (C<sub>a</sub>), 81.5 (C<sub>m</sub>), 82.9 (C<sub>b</sub>), 107.1 (C<sub>l</sub>), 166.5 ppm (C<sub>f</sub>, C<sub>h</sub>); HRMS (ESI): *m/z* calcd for C<sub>22</sub>H<sub>36</sub>O<sub>4</sub>SiNa<sup>+</sup>: 415.2281 [M+Na]<sup>+</sup>; found: 415.2291.

**Compound 2a:** Fullerene C<sub>60</sub> (400 mg, 0.55 mmol) was dissolved in 400 mL of dry toluene. After 3 hours of stirring, compound **1a** (143 mg, 0.46 mmol) in 5 mL of dry toluene was added to the fullerene solution and argon was then bubbled through the solution for 30 minutes. To this oxygen-free solution were added successively I<sub>2</sub> (140 mg, 0.55 mmol), and DBU (138 μL, 0.92 mmol). The resulting reaction mixture was stirred at room temperature for 19 h under argon and then evaporated to dryness. Purification of the brown residue by column chromatography (SiO<sub>2</sub>, toluene/cyclohexane 8/2) gave 285 mg of **2a** as a black solid (yield= 60%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ=0.17 (s, 9H; H<sub>n</sub>), 2.04-2.12 (m, 5H; H<sub>a</sub>, H<sub>d</sub>, H<sub>j</sub>), 2.39-2.46 (m, 4H; H<sub>c</sub>, H<sub>k</sub>), 4.58-4.64 ppm (m, 4H, H<sub>e</sub>, H<sub>i</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ=0.3 (C<sub>n</sub>), 15.3 (C<sub>c</sub>), 16.7 (C<sub>k</sub>), 27.4, 27.7 (C<sub>d</sub>, C<sub>j</sub>), 52.2 (C<sub>g</sub>), 65.9, 66.0 (C<sub>e</sub>, C<sub>i</sub>), 69.9 (C<sub>a</sub>), 71.6 (C<sub>60</sub>, C<sub>sp3</sub>), 82.5 (C<sub>b</sub>), 86.1 (C<sub>m</sub>), 105.2 (C<sub>l</sub>), 139.1, 139.2, 141.1, 142.0, 142.3, 143.12, 143.15, 143.2, 144.0, 144.7, 144.8, 145.0, 145.22, 145.25, 145.3, 145.4 (C<sub>60</sub>, C<sub>sp2</sub>), 163.62, 163.64 ppm (C<sub>f</sub>, C<sub>h</sub>); IR:  $\tilde{\nu}$  = 1741 cm<sup>-1</sup> (C=O), 524 (C<sub>60</sub>); HRMS (ESI): *m/z* calcd for C<sub>76</sub>H<sub>22</sub>O<sub>4</sub>SiNa<sup>+</sup>: 1049.1185 [M+Na]<sup>+</sup>; found: 1049.1219.

**Compound 2b:** Fullerene C<sub>60</sub> (500 mg, 0.7 mmol) was dissolved in 400 mL of dry toluene. After 3 hours of stirring, compound **1b** (230 mg, 0.58 mmol) in 5 mL of dry toluene was added to the fullerene solution and argon was then bubbled through the resulting solution for 30 minutes. To this oxygen-free solution were added successively I<sub>2</sub> (175 mg, 0.7 mmol), and DBU (175 μL 1.17 mmol). The resulting reaction mixture was stirred at room temperature for

19 h under argon and evaporated to dryness. Purification of the brown residue by column chromatography (SiO<sub>2</sub>, toluene/cyclohexane 8/2) gave 374 mg of **2b** as a black solid (yield=58%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ=1.07 (bs, 21H; H<sub>n</sub>, H<sub>o</sub>), 2.03-2.12 (m, 5H; H<sub>a</sub>, H<sub>d</sub>, H<sub>j</sub>), 2.41 (td, *J*=2.3 Hz, *J*=6.8 Hz, 2H; H<sub>c</sub>), 2.47 (t, *J*=7.0 Hz, 2H; H<sub>k</sub>), 4.60-4.65 ppm (m, 4H; H<sub>e</sub>, H<sub>i</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ=11.4 (C<sub>n</sub>), 15.3 (C<sub>c</sub>), 16.7 (C<sub>k</sub>), 18.8 (C<sub>o</sub>), 27.4, 28.1 (C<sub>d</sub>, C<sub>j</sub>), 52.2 (C<sub>g</sub>), 65.9, 66.0 (C<sub>e</sub>, C<sub>i</sub>), 69.9 (C<sub>a</sub>), 71.6 (C<sub>60</sub>, C<sub>sp3</sub>), 82.0 (C<sub>m</sub>), 82.5 (C<sub>b</sub>), 106.8 (C<sub>l</sub>), 139.2, 141.1, 142.0, 142.3, 143.14, 143.16, 143.2, 144.0, 144.8, 144.84, 145.0, 145.25, 145.28, 145.3, 145.4 (C<sub>60</sub>, C<sub>sp2</sub>), 163.6, 163.7 ppm (C<sub>f</sub>, C<sub>h</sub>); IR:  $\tilde{\nu}$  = 1740 cm<sup>-1</sup> (C=O), 524 (C<sub>60</sub>); HRMS (ESI): *m/z* calcd for C<sub>82</sub>H<sub>34</sub>O<sub>4</sub>SiNa<sup>+</sup>: 1133.2124 [M+Na]<sup>+</sup>, found: 1133.2180.

**Compound 6:** To a 25 mL flask under argon was added compound **2a** (220 mg, 0.18 mmol) in dry DCM (10 mL). Argon was bubbled through the solution for 30 minutes, then BDP-N<sub>3</sub> **4** (100 mg, 0.21 mmol), DIPEA (30  $\mu$ L, 0.18 mmol), and CuBr (32 mg, 0.18 mmol) were added. The mixture was stirred for 4 hours at room temperature under argon. Then, the solution was washed twice with 20 mL of an aqueous solution of EDTA (0.05 M), then with 20 mL of water. The organic phase was dried over anhydrous MgSO<sub>4</sub>, then filtered, and finally concentrated under reduced pressure. After purification by column chromatography on silica gel (DCM/Et<sub>2</sub>O 100/5), 220 mg of **6** as a red solid was obtained (yield= 85%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ=0.15 (s, 9H; H<sub>n</sub>), 0.97 (t, *J*=7.5 Hz, 6H; H<sub>B</sub>), 1.29 (s, 6H; H<sub>D</sub>), 2.01-2.15 (m, 2H; H<sub>j</sub>), 2.25-2.32 (m, 6H; H<sub>C</sub>, H<sub>d</sub>), 2.45-2.51 (m, 8H; H<sub>k</sub>, H<sub>A</sub>), 3.00 (t, *J*=7.1 Hz, 2H; H<sub>c</sub>), 4.45 (t, *J*=4.7 Hz, 2H; H<sub>H</sub>), 4.54-4.65 (m, 4H; H<sub>e</sub>, H<sub>i</sub>), 4.85 (t, *J*=4.6 Hz, 2H; H<sub>G</sub>), 6.98 (d, *J*=8.5 Hz, 2H; H<sub>E</sub> or H<sub>F</sub>), 7.17 (d, *J*=8.5 Hz, 2H; H<sub>E</sub> or H<sub>F</sub>), 7.68 ppm (s, 1H, H<sub>a</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ=0.3 (C<sub>n</sub>), 12.1 (C<sub>D</sub>), 12.6 (C<sub>A</sub>), 14.8 (C<sub>B</sub>), 16.9 (C<sub>k</sub>), 17.2 (C<sub>C</sub>), 22.1 (C<sub>c</sub>), 27.8 (C<sub>d</sub>, C<sub>j</sub>), 52.2 (C<sub>g</sub>, C<sub>H</sub>), 66.1 (C<sub>e</sub>, C<sub>i</sub>), 66.6 (C<sub>G</sub>), 71.6 (C<sub>sp3-C60</sub>), 86.3 (C<sub>m</sub>), 105.3 (C<sub>l</sub>), 115.2 (C<sub>E</sub> or C<sub>F</sub>), 129.9 (C<sub>E</sub> or C<sub>F</sub>), 131.1, 132.9, 138.3 (C<sub>BDP</sub>, C<sub>sp2</sub>), 139.1 (C<sub>60</sub>, C<sub>sp2</sub>), 139.14, 139.8, 141.12, 140.14, 141.9, 142.1, 142.3, 142.33, 143.12, 143.17, 143.2, 143.9, 144.0, 144.6, 144.80, 144.84, 145.0, 145.1, 144.2, 145.34, 145.39, 145.42 (C<sub>60</sub>, C<sub>sp2</sub>), 153.8, 158.3 (C<sub>BDP</sub>, C<sub>sp2</sub>), 163.72, 163.75 ppm (C<sub>f</sub>, C<sub>h</sub>); <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>): δ=-145.68 ppm (q, *J*= 34.4 Hz); <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>): δ=0.80 ppm (t, *J*=34.5 Hz); IR:  $\tilde{\nu}$  = 1740 cm<sup>-1</sup> (C=O), 524 (C<sub>60</sub>); HRMS (ESI): *m/z* calcd for C<sub>101</sub>H<sub>53</sub>BN<sub>3</sub>O<sub>5</sub>F<sub>2</sub>Si<sup>+</sup>: 1492.3877 [M+H]<sup>+</sup>; found: 1492.3911.

**Compound 7:** To a 25 mL flask under argon was added compound **2a** (30 mg, 0.03 mmol) in dry DCM (5 mL). Argon was bubbled through the solution for 30 minutes, then DSBDP-N<sub>3</sub> **5**

(22 mg, 0.035 mmol), DIPEA (4  $\mu$ L, 0.03 mmol), and CuBr (4 mg, 0.03 mmol) were added. The mixture was stirred for 4 hours at room temperature under argon. Then, the solution was washed twice with 20 mL of an aqueous solution of EDTA (0.05 M), then with 20 mL of water. The organic phase was dried over anhydrous  $MgSO_4$ , then filtered, and finally concentrated under reduced pressure. After purification by column chromatography on silica gel (DCM/Et<sub>2</sub>O 100/5), 43 mg of **7** as a green solid was obtained (yield= 86%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =0.16 (s, 9H; H<sub>n</sub>), 1.16 (t,  $J$ =7.5 Hz, 6H; H<sub>B</sub>), 1.35 (s, 6H; H<sub>D</sub>), 2.01-2.14 (m, 2H; H<sub>j</sub>), 2.23-2.37 (m, 2H; H<sub>d</sub>), 2.44 (t,  $J$ =6.8 Hz, 2H; H<sub>k</sub>), 2.60 (q,  $J$ =7.5 Hz, 4H; H<sub>C</sub>), 2.97 (t,  $J$ =7.1 Hz, 2H; H<sub>c</sub>), 4.45 (bs, 2H; H<sub>H</sub>), 4.58-4.64 (m, 4H; H<sub>e</sub>, H<sub>i</sub>), 4.81 (bs, 2H; H<sub>G</sub>), 7.01 (d,  $J$ =8.5 Hz, 2H; H<sub>E</sub> or H<sub>F</sub>), 7.15-7.22 (m, 3H; H<sub>E</sub> or H<sub>F</sub>, H<sub>dist</sub>), 7.27-7.46 (m, 6H; H<sub>BDP-arom</sub>), 7.62 (m, 5H; H<sub>BDP-arom</sub>, H<sub>a</sub>), 7.77 ppm (d,  $J$ =16.8 Hz, 2H; H<sub>dist</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =0.3 (C<sub>n</sub>), 12.0 (C<sub>D</sub>), 14.2 (C<sub>B</sub>), 16.8 (C<sub>k</sub>), 18.5 (C<sub>C</sub>), 22.1 (C<sub>c</sub>), 27.8, 28.3 (C<sub>d</sub>, C<sub>j</sub>), 49.8 (C<sub>H</sub>), 52.3 (C<sub>g</sub>), 66.0 (C<sub>e</sub>, C<sub>i</sub>), 66.5 (C<sub>G</sub>), 71.6 (C<sub>sp3-C60</sub>), 86.2 (C<sub>m</sub>), 105.2 (C<sub>l</sub>), 115.3 (C<sub>E</sub> or C<sub>F</sub>), 120.2 (C<sub>a</sub>), 122.6, 127.5, 128.7, 128.8 (C<sub>BDP</sub>, C<sub>arom</sub>), 129.2 (C<sub>BDP</sub>, C<sub>sp2</sub>), 130.1 (C<sub>E</sub> or C<sub>F</sub>), 133.4, 134.0, 136.0, 137.4, 138.4 (C<sub>BDP</sub>, C<sub>sp2</sub>), 139.0, 139.1 (C<sub>60</sub>, C<sub>sp2</sub>), 141.11, 141.14, 141.9, 142.0, 142.30, 142.32, 143.10, 143.12, 143.17, 143.2, 143.9, 144.0, 144.6, 144.78, 144.83, 145.0, 145.1, 145.21, 145.25, 145.3, 145.40, 145.41 (C<sub>60</sub>, C<sub>sp2</sub>), 150.5, 158.4 (C<sub>BDP</sub>, C<sub>sp2</sub>), 163.72, 163.75 ppm (C<sub>f</sub>, C<sub>h</sub>); <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>):  $\delta$ =-138.81 ppm (q,  $J$ = 34.4 Hz); <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>):  $\delta$ =1.20 ppm (t,  $J$ = 34.5 Hz); IR:  $\tilde{\nu}$  = 1741 cm<sup>-1</sup> (C=O), 524 (C<sub>60</sub>); HRMS (ESI):  $m/z$  calcd for C<sub>115</sub>H<sub>60</sub>BN<sub>5</sub>O<sub>5</sub>F<sub>2</sub>Si<sup>+</sup>: 1666.4461[M<sup>+</sup>]; found: 1666.4480.

**Compound 8 – one pot approach:** To a 25 mL flask under argon was added compound **2a** (50 mg, 0.048 mmol) in dry DCM (10 mL). Argon was bubbled through the solution for 30 minutes, then BDP-N<sub>3</sub> **4** (22 mg, 0.048 mmol), DIPEA (8  $\mu$ L, 0.048 mmol), and CuBr (7 mg, 0.048 mmol) were added. The mixture was stirred overnight at room temperature under argon. After the complete conversion of the starting materials (monitored by TLC), TBAF (1M in THF, 14  $\mu$ L) was added at 0° C. The reaction temperature was then brought to room temperature, and the mixture was stirred for 30 minutes. When the corresponding deprotected compound started to be formed (monitored by TLC), DSBDP-N<sub>3</sub> **5** (30 mg, 0.048 mmol), DIPEA (8  $\mu$ L, 0.048 mmol), CuBr (7 mg, 0.048 mmol), and TBAF (1M in THF, 14  $\mu$ L) were added at 0° C. The mixture was stirred overnight at room temperature under argon. Then, the solution was washed twice with 20 mL of an aqueous solution of EDTA (0.05 M), then with 20 mL of water. The organic phase was dried over anhydrous  $MgSO_4$ , then filtered, and finally concentrated under reduced pressure. After purification by column chromatography on

silica gel (DCM/MeOH 100/2), 60 mg of **8** as a blue solid was obtained (yield= 65%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ=0.97 (t, *J*=7.5 Hz, 6H; H<sub>B</sub> or H<sub>O</sub>), 1.15 (t, *J*=7.5 Hz, 6H; H<sub>B</sub> or H<sub>O</sub>), 1.29 (s, 6H; H<sub>D</sub> or H<sub>M</sub>), 1.35 (s, 6H; H<sub>D</sub> or H<sub>M</sub>), 2.17-2.41 (m, 8H; H<sub>d</sub>, H<sub>j</sub>, H<sub>C</sub> or H<sub>N</sub>), 2.51 (s, 6H; H<sub>A</sub>), 2.55-2.68 (m, 4H; H<sub>C</sub> or H<sub>N</sub>), 2.88-3.04 (m, 4H; H<sub>c</sub>, H<sub>k</sub>), 4.34-4.50 (m, 4H; H<sub>H</sub>, H<sub>I</sub>), 4.60 (t, *J*=6.1 Hz, 4H; H<sub>e</sub>, H<sub>i</sub>), 4.73-4.86 (m, 4H; H<sub>G</sub>, H<sub>J</sub>), 6.92-7.08 (m, 4H, H<sub>BDP-arom</sub>), 7.08-7.21 (m, 4H, H<sub>BDP-arom</sub>), 7.30-7.49 (m, 6H, H<sub>BDP-arom</sub>, H<sub>dist</sub>), 7.53-7.69 (m, 6H, H<sub>BDP-arom</sub>, H<sub>a</sub>, H<sub>m</sub>), 7.77 ppm (d, 2H, H<sub>dist</sub>, *J*= 16.8 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ=12.0 (C<sub>D</sub>), 12.09 (C<sub>M</sub>), 12.6 (C<sub>A</sub>), 14.3 (C<sub>B</sub>), 14.8 (C<sub>O</sub>), 17.2 (C<sub>N</sub>), 18.5 (C<sub>C</sub>), 22.2 (C<sub>c</sub>, C<sub>k</sub>), 28.3 (C<sub>d</sub>, C<sub>j</sub>), 49.8 (C<sub>H</sub>, C<sub>I</sub>), 52.3 (C<sub>g</sub>), 66.5 (C<sub>G</sub>, C<sub>J</sub>), 66.6 (C<sub>e</sub>, C<sub>i</sub>), 71.6 (C<sub>sp3-C60</sub>), 115.2 (C<sub>BDP-arom</sub>), 115.3 (C<sub>BDP-arom</sub>), 120.2 (C<sub>dist</sub>), 122.8 (C<sub>a</sub>), 127.5, 128.80, 128.89, 129.1 (C<sub>BDP</sub>, C<sub>arom</sub>), 129.2 (C<sub>BDP</sub>, C<sub>sp2</sub>), 129.9 (C<sub>BDP-arom</sub>), 130.1, 131.2, 132.9, 133.4, 134.0, 136.0, 137.4, 138.2, 138.4, 138.5 (C<sub>BDP</sub>, C<sub>sp2</sub>), 139.1 (C<sub>60</sub>, C<sub>sp2</sub>), 141.14, 141.9, 142.3, 143.1, 143.20, 143.26, 144.0, 144.6, 144.7, 144.8, 145.0, 145.1, 145.2, 145.3, 145.4, (C<sub>60</sub>, C<sub>sp2</sub>), 150.5, 153.8, 158.3, 158.5 (C<sub>BDP</sub>, C<sub>sp2</sub>), 163.8 ppm (C<sub>f</sub>, C<sub>h</sub>); <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>): δ=-145.67 (q, *J*= 34.4 Hz), -138.83 ppm (q, *J*= 34.4 Hz); <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>): δ=2.41 ppm (dt, *J*= 34.5 Hz); IR:  $\tilde{\nu}$  = 1741 cm<sup>-1</sup> (C=O), 525 (C<sub>60</sub>); HRMS (ESI): *m/z* calcd for C<sub>137</sub>H<sub>82</sub>O<sub>6</sub>N<sub>10</sub>B<sub>2</sub>F<sub>4</sub>: 2058.6614[M]<sup>+</sup>; found: 2058.6655.

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## Keywords

Fullerene C60 • boron dipyrromethenes • donor-acceptor systems • Click Chemistry • CuAAC reaction

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