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Synthesis and characterization of a new ethynyl-bridged C_{60} derivative bearing a diketopyrrolopyrrole moiety

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ABSTRACT

A new soluble C_{60} derivative bearing a diketopyrrolopyrrole (DPP) moiety has been synthesized by ethynylation reaction. Characterization by UV–visible spectrophotometry and cyclic voltammetry has been performed in order to study the influence of the DPP moiety on electronic and optical properties of the fullerene. Moreover, DFT calculations have been conducted on the derivative and its precursor in order to correlate the orbital geometry with experimental data.

Introduction

Fullerenes, particularly C_{60}, have attracted a lot of attention since their discovery by Harold, Kroto, and Smalley in 1985.[1] Through the combination of relatively low-cost production, ease of functionalization and astonishing electronic properties, C_{60} became one of the most promising *n*-type materials for optoelectronic application.[2] However, pristine C_{60} has poor solubility in common organic solvents, making large-scale processing difficult to achieve. This lack of solubility encouraged chemists to develop new reactions to covalently attach solubilizing groups on C_{60}, while keeping its good electronic properties. In this context, the ethynylation reaction has proven to be very convenient and efficient for many different linkers.[3] We have recently established that the introduction of an ethynyl-bridged substituent on the C_{60} cage can modify its LUMO energy level, which makes this functionalization strategy very useful for the development of new *n*-type materials for bulk heterojunction (BHJ) solar cells.[4]

In addition to improving charge transport ability, *n*-type materials used in BHJ solar cells should also have the capability of absorbing the sunlight efficiently in order to maximize charge separation in the active layer. However, C_{60} absorbs light mainly in the high-energy region of the sun spectrum, meaning that a low band-gap π-conjugated unit has to be installed on C_{60} in order to increase sunlight absorption.[5] Thus, an interesting strategy is to replace the electronically inert solubilizing substituent, commonly found in C_{60} derivatives used in BHJ solar cells, by an electro-active, light-harvesting moiety.

Herein we report the synthesis, electrochemical properties and DFT calculations of a new ethynyl-bridged C_{60} derivative bearing a 3,6-dithiophen-2-yl-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DT-DPP) moiety (**1**, Scheme 1). The DT-DPP unit has not only been chosen because of its relatively low band-gap and ease of functionalization, but also because of its high occurrence in recently prepared conjugated polymers for BHJ solar cells.[6] It is well accepted that small organic molecules provide better thin film morphology when blended with a polymer having structural compatibility.[7] To the best of our knowledge, this is the first report of the preparation of a monosubstituted, unsymmetrical DPP derivative for opto-electronic applications. It is worth mentioning that Janssen et al. recently reported the preparation of C_{60}-DPP derivatives.[8] However, the C_{60} units were attached at both ends of a symmetrical DPP unit using a Prato reaction.

Results and discussion

Synthesis

The synthesis of compound **1** is presented in Scheme 1. DT-DPP derivative was synthesized using a well-known procedure.[9] Starting from DT-DPP, an alkylation reaction using dodecylbromide and potassium carbonate was performed to afford compound **2** in good yield. It is noteworthy that the purification of compound **2** was rather difficult because the excess of dodecylbromide used for the alkylation reaction tends to co-elute with compound **2** during the column chromatography. A monobromination reaction

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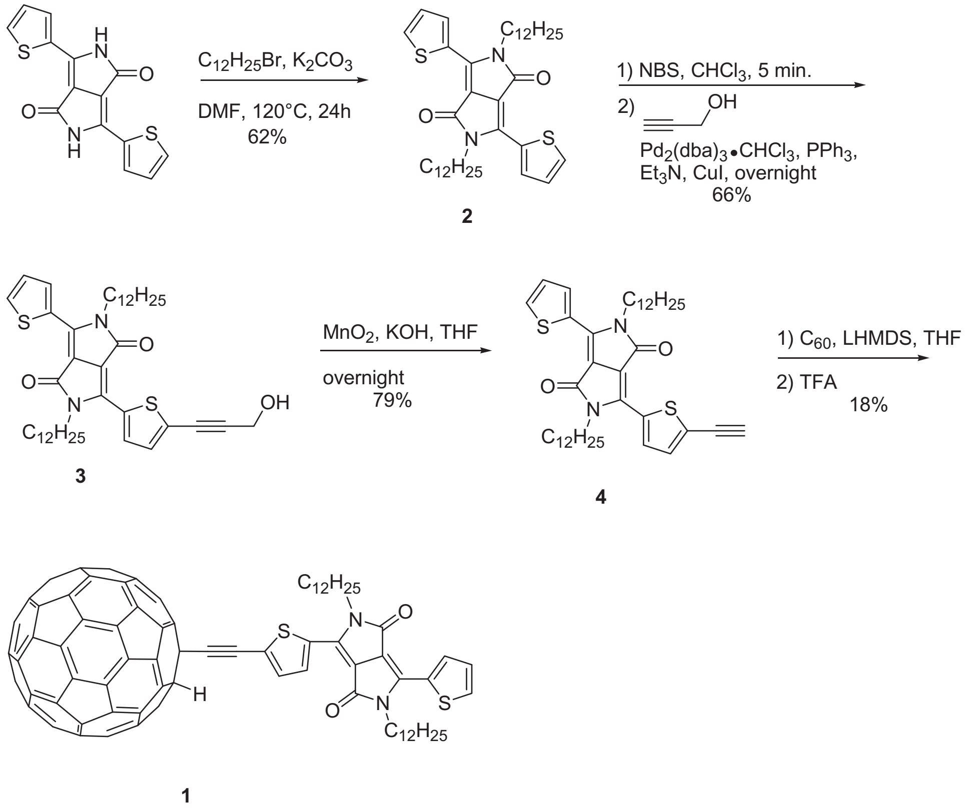


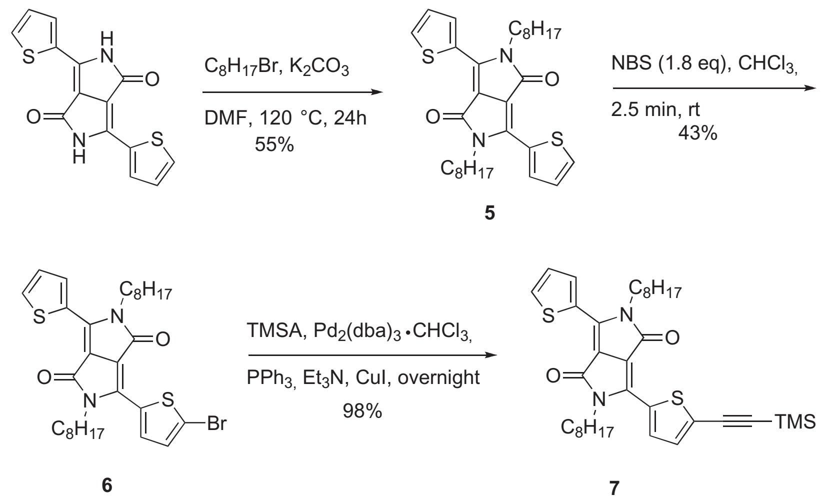
Scheme 1. Synthetic pathway to compound **1**.

was then performed by adding *N*-bromosuccinimide (NBS) (2.1 equiv) to a solution of compound **2** in chloroform, followed by the addition of distilled water after 5 min of reaction. Although this short reaction time limits the formation of the bisbrominated adduct, a significant amount of it was formed and all the purification techniques attempted to separate it from the monobrominated adduct failed. Thus, a Sonogashira coupling was carried out on the mixture using standard conditions with propargyl alcohol as the alkyne to give compound **3** in 66% yield over two steps**.** An alcohol-terminated alkyne was selected in the aim of increasing the polarity of the coupling products, thus enabling the purification of the monoadduct by standard column chromatography. Oxidative cleavage of the propargyl alcohol using activated manganese oxide under anhydrous basic conditions[10] was then conducted to afford the terminal alkyne precursor **4** in good yield.

To the best of our knowledge, no monobromination of a DT-DPP unit has never been reported in literature. By the time that the paper was under review, a paper describe a different way of preparing monosubstituted Dt-DPP derivative.[11] Thus, another strategy to brominate the DT-DPP unit was attempted in order to obtain the monobrominated adduct in pure form in good yield. The strategy is depicted in Scheme 2. First, alkylation using standard basic conditions with *n*-octylbromide was conducted. In this case, octyl chains were chosen to substantially decrease the co-elution phenomenon during the purification process by column chromatography. After compound **5** was obtained, monobromination was conducted using 1.8 equiv of NBS (instead of 2.1 equiv) and the time of reaction was reduced to 2.5 min. These simple modifications helped significantly in reducing the amount of bisbrominated adducts, thus enabling the purification by column chromatography. It is noteworthy that the work-up procedure must be carried out very quickly since reactive NBS remains in the mixture even after chloroform/water liquid extractions. Compound **6** was obtained as analytically pure material in moderate yield (43%). Sonogashira coupling using standard conditions was then conducted with trimethylsilylacetylene (TMSA) to afford compound **7** in good yield.

The ethynylation reaction on C_{60} was conducted using slightly modified conditions reported by Tour et al.[12] Compound **4** and C_{60} were added in dried and degassed THF and sonicated for 3 h before lithium hexamethyldisilylamide (LHMDS) was added dropwise to the mixture to give a red–purple solution (characteristic of the DT-DPP unit and the C_{60} anion mixture). After few minutes of stirring at room temperature, trifluoroacetic acid was added to the mixture and the solvent was immediately removed under reduced pressure. A proton was used to quench the C_{60} anion because it is more reactive than any of the electrophiles previously reported to quench this reaction.[4,3c] Moreover, previously published ethynyl-bridged C_{60} derivatives bearing a proton on the C_{60} cage in alpha position relative to the alkyne showed very good chemical and thermal stability.[4] Compound **1** was purified by standard column chromatography on silica gel. The success of the ethynylation reaction was assessed by ^{1}H NMR. As expected, a peak at around 7.1 ppm, corresponding to the proton directly attached to the C_{60} core, appeared and the peak at 3.59 ppm, corresponding to the terminal alkyne of compound **4,** disappeared. Furthermore, a set of peaks between 130 and 145 ppm were observed by ^{13}C NMR, which correspond to the carbon atoms of the C_{60} core.

In order to study the influence of the DT-DPP moiety on the LUMO energy level of the C_{60}, cyclic voltammetry measurements were performed on thin film of compounds **1**, **4,** and the well-studied PCBM (C_{61}-butyric methylester) for the sake of comparison. Results are shown in Figure 1 and summarized in Table 1. For the thin film formation, a saturated solution of the sample to analyze was deposited on the working electrode. LUMO levels were calculated using the following equation: $E_{\mathrm{LUMO}} = -(E^{\mathrm{onset}} + 4.7\ \mathrm{eV})$.[13] It is noteworthy that our values are not absolute ones, but they were used to establish comparison between our derivatives.



Scheme 2. Improved strategy for the synthesis of a monofunctionalized DPP derivative.

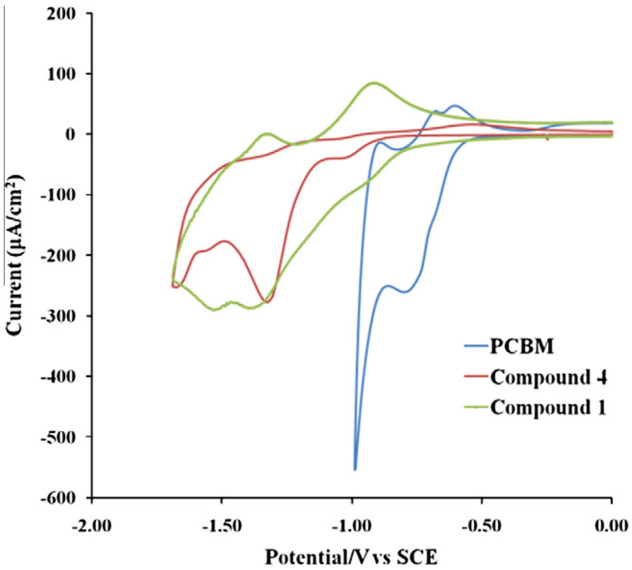


Figure 1. Cyclic voltammograms for compounds **1**, **4** and PCBM as recorded on thin film coated on a platinum wire in 0.1 M $TBABF_4$ in MeCN.

Table 1
Cyclic voltammetry data for compound **1**, **4** and PCBM

Compounds	E_{ox}/E_{red} (V)[a]	HOMO/LUMO (eV)
PCBM	n.d/−0.81	n.d/−4.20
4	0.96/−1.06	−5.66/−3.95
1	1.78/−0.93	−6.59/−4.08

[a] Potential versus SCE measured by cyclic voltammetry at a scan rate of 100 mV/s. Measurements performed on a thin film of compound coated on a platinum wire. Tetra-*n*-butylammonium tetrafluoroborate 0.1 M in MeCN was used as the electrolyte.

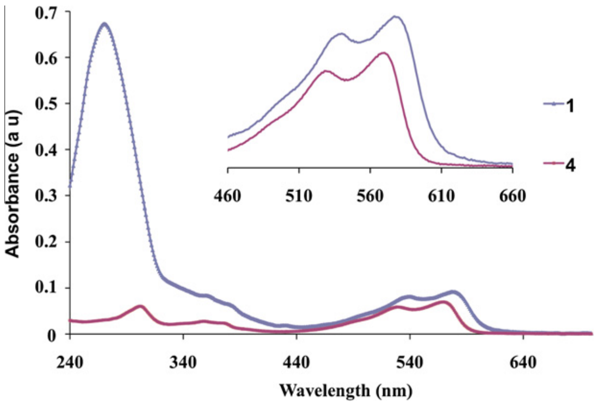


Figure 2. UV–visible spectra of compound **1** and **4**.

As shown in Table 1, compound **1** presents a higher LUMO level than PCBM, meaning that the electronic density onto the C_{60} cage in compound **1** is higher than in PCBM. This can be attributed to the electron-rich nature of the thiophene unit directly attached to the C_{60} cage. The increase of the LUMO energy level compared to the widely used PCBM should be very beneficial for the BHJ solar cells application since the efficiency of the device is directly related to the energy difference between the HOMO energy level of the donor (e.g., conjugated polymers) and the LUMO energy level of the acceptor (compound **1**).[14] Interestingly, the inductive effect between the C_{60} cage and the DT-DPP unit also affects the HOMO energy level of DT-DPP. As shown in Table 1, the addition of C_{60} on the terminal alkyne of compound **4** increased its oxidation potential by 0.82 V (from 0.96 V for **4** to 1.78 V for **1**), indicating a significant decrease of the electronic density on the DT-DPP unit. This result is in perfect line with the results obtained in the cathodic regime. Together, these results show that it is possible to modulate, to some extent, the energy levels of C_{60} using the alkynyl bridge.

To evaluate the possibility of using compound **1** as a *n*-type light-harvesting material in BHJ solar cells, the UV–visible absorption spectra of compound **1** and its free alkyne precursor (compound **4**) were recorded**.** UV–vis spectrum of compound **1** was recorded in a diluted solution (2.7×10^{-6} M) in chloroform and the results are presented in Figure 2. The spectrum of compound **1** shows a band centered at 270 nm (27,200 $mmol^{-1}$ cm^2) attributed to the C_{60} cage and another one at 571 nm (33,100 $mmol^{-1}$ cm^2) with a shoulder at 540 nm (29,400 $mmol^{-1}$ cm^2) attributed to the $\pi \rightarrow \pi^*$ transition originating from the DT-DPP moiety. As observed by others and ourselves, the attachment of a C_{60} cage onto compound **4** leads to a slight bathochromic shift of the $\pi\pi^*$ transition (9 nm) due to an extension of the effective conjugation length.[4,15] This interesting property is expected to provide increased photon absorption of the conjugated polymer/fullerene derivative blends that could potentially lead to better BHJ solar cell efficiencies.[5]

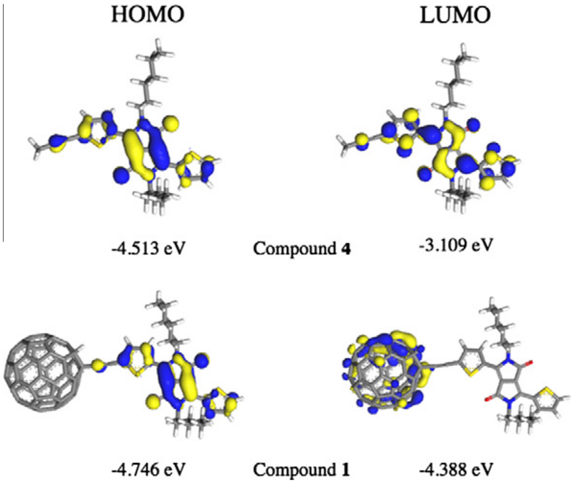


Figure 3. Calculated molecular orbitals for compounds **1** and **4**.

In the aim of investigating the electronic structure of compounds **1** and **4** in a more detailed fashion, Density Functional Theory (DFT) calculations were performed using DMol^3 from Accelrys, using the BLYP functional. The physical wave functions were expanded in terms of double numerical polarized basis set with an orbital cutoff of 4.0 Å in the DMol^3 method.[4b] This numerical basis set is equivalent in size and quality to the more current 6-31G** basis set. Becke exchange and Lee–Yang–Parr 1988 correlation functional (BLYP)[16] were used at the generalized gradient approximation (GGA) level. Results are shown in Figure 3. As expected, the HOMO on compound **1** is fully localized on the DT-DPP unit while the LUMO is fully localized on the C_{60} cage. This result suggests that there is only weak electronic communication between the DT-DPP and the C_{60} cage and this correlates well with the electrochemical and UV–vis results. These calculations strengthened our hypothesis suggesting that the influence of the DT-DPP unit on the LUMO energy level of C_{60} is likely to be attributed to an electron-donating inductive effect.

Conclusions

In summary, we report the synthesis of a monosubstituted 3,6-dithiophen-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione derivative bearing a C_{60}. This new material exhibits interesting electrochemical and optical properties and an increased LUMO energy level compared to the well-known PCBM. This last feature makes this material very promising for the further development of efficient BHJ solar cells and testing in such devices using this material in combination with π-conjugated polymers is underway.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.07.029.

References and notes

1. (a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162–163; (b) Wudl, F. *J. Mater. Chem.* **2002**, *12*, 1959–1963.
2. (a) Frechet, J. M. J.; Thompson, B. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 58–77; (b) Backer, S. A.; Sivula, K.; Kavulak, D. F.; Fréchet, J. M. J. *Chem. Mater.* **2007**, *19*, 2927–2929; (c) Kooistra, F. B.; Knol, J.; Kastenberg, F.; Popescu, L. M.; Verhees, W. J. H.; Kroon, J. M.; Hummelen, J. C. *Org. Lett.* **2007**, *9*, 551–554.
3. (a) Anderson, H. L.; Faust, R.; Rubin, Y.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1366–1368; (b) Anderson, H. L.; Boudon, C.; Diederich, F.; Gisselbrecht, J.-P.; Gross, M.; Seiler, P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1628–1632; (c) Murata, Y.; Motoyama, K.; Komatsu, K. *Tetrahedron* **1996**, *52*, 5077–5090.
4. (a) Rondeau-Gagne, S.; Curutchet, C.; Grenier, F.; Scholes, G.; Morin, J.-F. *Tetrahedron* **2010**, *66*, 4230–4242; (b) Rondeau-Gagne, S.; Lafleur-Lambert, A.; Soldera, A.; Morin, J.-F. *New J. Chem.* **2011**, *35*, 942–947.
5. Anthony, J. E. *Chem. Mater.* **2011**, *23*, 583–590.
6. For representative examples, see: (a) Bijleveld, J. C.; Karsten, B.; Mathijssen, S.; Wienk, M. M.; de Leeuw, D. M.; Janssen, R. J. *J. Mater. Chem.* **2011**, *21*, 1600–1606; (b) Jo, J.; Gendron, D.; Najari, A.; Moon, J. S.; Cho, S.; Leclerc, M.; Heeger, A. J. *Appl. Phys. Lett.* **2010**, *97*, 203303; (c) Zou, Y.; Gendron, D.; Badrou-Aïch, R.; Najari, A.; Tao, Y.; Leclerc, M. *Macromolecules* **2009**, *42*, 2891–2894; (d) Wienk, M. M.; Turbiez, M.; Gilot, J.; Janssen, R. A. J. *Adv. Mater.* **2008**, *20*, 2556–2560.
7. Russell, D. M.; Newsome, C. J.; Li, S. P.; Kugler, T.; Ishida, M.; Shimoda, T. *Appl. Phys. Lett* **2005**, *87*, 222109/1–222109/3; (a) Smith, J.; Hamilton, R.; Qi, Y.; Kahn, A.; Bradley, D.; Heeney, M.; McCulloch, I.; Anthopoulos, T. D. *Adv. Funct. Mater.* **2010**, *20*, 2330–2337.
8. Karsten, B. P.; Bouwer, R. K. M.; Hummelen, J. C.; Williams, R. M.; Janssen, R. A. J. *Photochem. Photobiol. Sci.* **2010**, *9*, 1055–1065.
9. (a) Iqbal, A.; Jost, M.; Kirchmayr, R.; Pfenninger, J. A.; Rochat, A.; Wallquist, O. *Bull. Soc. Chim. Belg.* **1988**, *97*, 615–643; (b) Yamamoto, H.; International Patent, 2004, WO2004/090046.
10. Yang, J.; Ng, M.-K. *Synthesis* **2006**, 3075–3079.
11. Loser, S.; Bruns, C. J.; Miyauchi, H.; Ortiz, R. P.; Facchetti, A.; Stupp, S. I.; Marks, T. J. *J. Am. Chem. Soc.* **2011**, *133*, 8142.
12. (a) Shirai, Y.; Zhao, Y.; Cheng, L.; Tour, J. M. *Org. Lett.* **2004**, 2129–2132; (b) Shirai, Y.; Sasaki, T.; Guerrero, J. M.; Yu, B.-C.; Hodge, P.; Tour, J. M. *ACS Nano* **2008**, *2*, 97–106.
13. Ashraf, R. S.; Shahid, M.; Klemm, E.; Al-Ibrahim, M.; Sensfuss, S. *Macromol. Rapid Commun.* **2006**, *27*, 1454–1459.
14. Brabec, C. J.; Cravino, A.; Meissner, D.; Sariciftci, N. S.; Fromherz, T. M.; Rispens, T.; Sanchez, L.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 374–380.
15. Zhao, Y.; Shirai, Y.; Slepkov, A.; Cheng, L.; Alemany, L.; Sasaki, T.; Hegmann, F.; Tour, J. M. *Chem. Eur. J.* **2005**, *11*, 3643–3658.
16. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.