PAPER

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# Ethynyl-bridged fullerene derivatives: effect of the secondary group on electronic properties

Simon Rondeau-Gagné,<sup>a</sup> Antoine Lafleur-Lambert,<sup>a</sup> Armand Soldera<sup>b</sup> and Jean-François Morin<sup>\*a</sup>

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Eight new ethynyl-bridged fullerene derivatives with different substituents (referred to as the "secondary group") in the  $\alpha$ -position relative to the alkyne have been prepared in order to study the ability of the secondary group to modulate their electrochemical properties, especially the LUMO energy level, of C<sub>60</sub>. These new materials have been characterized using cyclic voltammetry, and the results have been compared to those obtained using DFT calculations. Unexpectedly, the introduction of an electron-rich group induced a decrease of the LUMO energy level of the C<sub>60</sub> cage, while an electron-poor group increased it. The newly prepared materials are electrochemically stable, opening the way to the use of these n-type materials in organic electronics.

# Introduction

 $C_{60}$  is one of the most promising n-type materials for the development of organic and molecular electronics due to its excellent ability to accommodate negative charges in a reversible way.<sup>1</sup> This particular property is attributed to the presence of a triply-degenerate LUMO molecular level that allows the addition of up to six electrons on a single cage.<sup>2</sup> For some applications, however, the LUMO energy level of pristine  $C_{60}$  is not ideal, and it becomes necessary to modulate it in order to optimize the performance of organic electronics devices, such as field-effect transistors and bulk heterojunction solar cells.<sup>3</sup> In this regard, we and other research groups have reported different strategies to address this issue with limited success, the biggest challenge being to establish electronic communication between the C<sub>60</sub> cage and substituents.<sup>4</sup> In fact, most of the substitution reactions reported so far to functionalize  $C_{60}$  involved the creation of two sp<sup>3</sup> carbon atoms between the substituent and the cage. This makes through-bond electronic communication between both halves very difficult to achieve.

Recently, we have reported the synthesis and electrochemical behaviour of a series of ethynyl-bridged  $C_{60}$  derivatives with different substituents attached to the alkyne.<sup>4a</sup> Our strategy to modulate the LUMO energy level of  $C_{60}$  relies on the fact that the ethynylation reaction on  $C_{60}$  produces only

<sup>b</sup> Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1. E-mail: armand.soldera@usherbrooke.ca; Fax: +1 819-821-8017; Tel: +1 819-821-7650



Scheme 1 Synthesis of  $C_{60}$  derivatives 1–8 through ethynylation reactions.

one sp<sup>3</sup> carbon atom between the substituent and the C<sub>60</sub> cage (Scheme 1), allowing better electronic communication between both moieties. However, this was not sufficient to induce significant changes to the electronic properties of C<sub>60</sub>. On the other hand, we have discovered that the secondary group (in the  $\alpha$ -position on the cage relative to the alkyne) introduced on the fullerene core to quench the anion formed during the ethynylation of C<sub>60</sub> could potentially be interesting for modulation purposes. For instance, an electron-withdrawing benzoyl group shifted the reduction peak by 26 mV toward more positive potentials.<sup>4a</sup>

We report herein the synthesis and electrochemical characterization of new ethynyl-bridged  $C_{60}$  derivatives bearing a 4-octyloxyphenylacetylene on the core and different

<sup>&</sup>lt;sup>a</sup> Département de chimie, Centre de recherche sur les matériaux avancés, Université Laval, 1045 Ave. de la Médecine, Québec, Canada G1V 0A6. E-mail: jean-francois.morin@chm.ulaval.ca; Fax: +1 418-656-7916; Tel: +1 418-656-2812

secondary groups designed to obtain further insight into their ability to influence the electronic properties of  $C_{60}$ . For stability reasons, no carbonyl-containing electrophiles were used to quench the  $C_{60}$  monoanion, since they undergo rearrangement and follow-up reactions in the electrochemical process.<sup>4a</sup> Moreover, DFT calculations using numerical basis sets were performed to calculate LUMO energies. The purpose of such calculations is firstly to show if the trend in the LUMO energies is correctly reproduced, since the calculation of unoccupied orbitals is not straightforward.<sup>5</sup> Accordingly, a comparison with experimental data was undertaken.

# **Results and discussion**

# Synthesis

All the  $C_{60}$  derivatives synthesized in this study are presented in Scheme 1. A number of different electron-rich and electronpoor secondary groups were used in this study, namely substituted thiophene and various phenyl rings bearing heteroatoms (S) or halogens (Br, F). All of the materials employed in this study contained 1-ethynyl-4-(octyloxy)benzene<sup>4a</sup> to enhance the solubility of the resulting derivatives.

In a typical procedure,<sup>4a,6</sup> 1-ethynyl-4-(octyloxy)benzene and C60 were added to dried and de-gassed THF, and sonicated for at least 3 h before lithium bis(trimethylsilyl)amide (LHMDS) was added at room temperature. After 5 min, an excess of the electrophile was added to the dark green solution, and the resulting mixture was allowed to stir at room temperature for 16 h. The solvent was then evaporated and the crude product purified using standard column chromatography (see the Experimental section). All the derivatives were obtained in a pure form in low to moderate yield (7-43%)and all were very soluble in the usual organic solvents such as THF, chloroform, toluene, acetone and dichloromethane. The low yield obtained for compound 8(7%) can be explained by the important steric hindrance of the electrophile. Usually, when the electrophile is added to a reaction mixture, the solution rapidly goes from green to brown, meaning that the anion has been quenched. In the case of compound 8, this colour transition was never reached and many unknown side products were recovered. For compounds 4-6, the low yields can be explained by the poor electrophilic nature of the reagent used to quench the ethynylation reaction. On the other hand, when non-sterically hindered (-CH<sub>3</sub>, compound 2) or electron-deficient (-CH2PhF5, compound 7) groups are used, a moderate yield (ca. 40%) can be obtained. The better yield obtained for compound 7 compared to compound 3 illustrates the importance of having an electron-withdrawing substituent on the carbon bearing the halogen.

#### Electrochemistry

To study the influence of the secondary group on the LUMO level of  $C_{60}$ , cyclic voltammetry measurements were performed in solution in a cathodic regime. The results are summarized in Table 1. All the derivatives (compounds **1–8**) show at least two quasi-reversible reduction waves between 0 and -2.5 V vs. Fc/Fc<sup>+</sup>, as usually observed for C<sub>60</sub> derivatives. The LUMO energy levels of C<sub>60</sub> derivatives were calculated from the

Table 1Cyclic voltammetry data of  $C_{60}$ , PCBM and compounds $1-8^a$ 

Compound	$E^{ m red1}/ m V$	LUMO/eV <sup>b</sup>
C <sub>60</sub>	-0.82	-3.98
PCBM	-0.92	-3.88
1	-0.87	-3.93
2	-0.90	-3.90
3	-0.92	-3.88
4	-0.89	-3.91
5	-0.93	-3.87
6	-0.86	-3.94
7	-0.96	-3.84
8	-0.85	-3.96

<sup>*a*</sup> Potential *vs.* Fc/Fc<sup>+</sup> measured by cyclic voltammetry at a scan rate of 200 mV s<sup>-1</sup> in a de-gassed mixture of *o*-DCB: MeCN (4:1) containing Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) as a supporting electrolyte. Platinum wires were used as working and counter electrodes, and an Ag/Ag<sup>+</sup> electrode was used as a reference electrode. <sup>*b*</sup> Values estimated using the following equation:  $E_{LUMO} = -(E^{red1} + 4.8) \text{ eV}.^7$ 

potential of the first reduction wave  $(E^{\text{red1}})$  using the equation  $E_{\text{LUMO}} = -(E^{\text{red1}} + 4.8) \text{ eV.}^7$  It is noteworthy that the potential values at the peak maximum give us a much better reproducibility than the values of the half-wave potential typically used for the calculation of  $E_{\text{LUMO}}$ . Thus, our values are not absolute ones, but they are used to establish a comparison between our derivatives and well-studied [6,6]phenyl- $C_{61}$ -butyric acid methyl ester (PCBM). As shown in our previous report, the introduction of an alkynyl bridge to  $C_{60}$  lowers the LUMO energy level compared to PCBM, but increases it compared to pristine  $C_{60}^{4a}$ .

Surprisingly, the introduction of an electron-rich group (compounds 4 and 6) as the secondary group decreases the LUMO energy level, while an electron-poor group (compound 7) increases it when compared to compound 1 (R = H). In fact, compound 7, which contains five electron-withdrawing fluorine atoms ( $E^{\text{red1}} = -0.96 \text{ V}$ ), was expected to enhance the electron affinity of the C<sub>60</sub> cage compared to an "electronically inert" moiety such as a proton (compound 1,  $E^{\text{red1}} = -1.042 \text{ V}$ ) or a methyl group (compound 2,  $E^{\text{red1}} = -1.070 \text{ V}$ ). Likewise, the electron-donating 2-thiophene group (compound 6,  $E^{\text{red1}} = -1.030 \text{ V}$ ) that was expected to decrease the electron affinity compared to compounds 1 and 2, actually increased it. The increasing order of electron affinity is thus as follows: 7 < 5 < 3 < 2 < 4 < 1 < 6 < 8. Clearly, these results demonstrate that it is possible to significantly modulate the LUMO energy level of C<sub>60</sub> by functionalization.

One way to explain these unexpected results is to look at the electrostatic interaction between the secondary group and the  $C_{60}$  cage. On one hand, the pentafluorobenzene group, in which all the fluorine atoms bear a partial negative charge  $(\delta-)$ , destabilizes the negative charges added on the cage upon electrochemical reduction, making it more difficult to reduce (higher  $|E^{\text{red}1}|$  value). On the other hand, the sulfur atom on the thiophene group bears a partial positive charge  $(\delta+)$ , thus stabilizing the negative charge added to the  $C_{60}$ . The difference in  $E^{\text{red}1}$  values between the two derivatives bearing a thiophene group (compounds **5** and **6**) could be explained by the proximity of the sulfur atom to the  $C_{60}$  cage. Indeed, the sulfur atom in compound **6** is closer to the  $C_{60}$  cage compared

to compound **5**, thus increasing its ability to stabilize the negative charges added to the  $C_{60}$ . Such a proximity effect has been observed in the first series of derivatives we reported earlier.<sup>4a</sup> To yield a better insight into this phenomenon, DFT calculations were performed on all the derivatives.

#### Calculations

Evaluation of the LUMO energies was performed using  $DMol^3$  code from Accelrys. The use of numerical basis functions offers the opportunity to describe long range interactions. However, the global orbital cutoff depends upon the elements present in the structure. Two cutoff values were considered depending on the kind of atoms present in the structure: 3.7 and 4.0 Å.<sup>8</sup> Details of these calculations will be published separately.<sup>9</sup> The PBE functional has been considered, and the stemming data are compared to experimental measurements in Table 2. In order to take into account the accuracy of the procedure, data are reported in a graphical form in Fig. 1.

From Table 1, it is clear that the LUMO energy for  $C_{60}$  is not accurately described using the PBE functional. To obtain an accurate value of the LUMO energy, the BLYP functional was used, yielding -3.973 eV, which is clearly approaching the experimental data. However, the addition of any substituent greatly affects the accuracy of such a functional, and values of the LUMO computed using the PBE functional are closer to

Table 2 Experimental and computed LUMO energies (eV) for  $C_{60}$ , PCBM and compounds 1–8

Compound	Experimental	PBE
C <sub>60</sub>	-3.98	-4.213
PCBM	-3.88	-4.054
1	-3.93	-4.005
2	-3.90	-3.962
3	-3.88	-3.926
4	-3.91	-4.039
5	-3.87	-4.056
6	-3.94	-4.056
7	-3.84	-4.045
8	-3.96	-4.09



**Fig. 1** Graphical representation of the LUMO energies in Table 2;  $\bullet$  and — correspond to the BPE functional and the experimental data, respectively.  $\blacksquare$  corresponds to the LUMO energy for compound **4** when the phenyl is in a perpendicular position.

the experimental data (Fig. 1). Considering the simple insertion of the 1-ethynyl-4-(octyloxy)benzene group, compound 1, the PBE functional gives a value that approaches the experimental one. By adding methyl (compound 2) and benzyl (compound 3) groups, the increase in the LUMO energy is accurately depicted, revealing the correct representation of the electron affinity. However, from an experimental viewpoint, extending the chain by introducing a methyl sulfide group (compound 4) weakly increases the LUMO energy, while computationally it slightly increases it. This difference may be due to the fact that calculations are performed at 0 K without any neighbours, and this can affect the position of the phenyl group. More specifically, the position of the phenyl group supporting the methyl sulfide group, parallel to the fullerene (dihedral angle,  $\varphi$ , from Fig. 2 equals 90°), corresponds to the lowest energy, and its LUMO energy is -4.039 eV. However, when this phenyl group is perpendicular to the fullerene ( $\varphi = 0^{\circ}$ ), the LUMO energy increases to -3.993 eV (Fig. 1), in agreement with the difference between the calculated and experimental LUMO energies of compounds 1, 2 and 3. Considering compound 3, the difference between the two positions of the phenyl group is low, in the order of 0.010 eV.

To specifically address the effect of the phenyl position on the value of the LUMO energy level, the dihedral angle related to the bond linked to the phenyl group of compound 7 (Fig. 2) was varied, and the LUMO energy levels reported vs. this torsional angle.

Interestingly, the LUMO energy is greatly dependent on the position of the pentafluorophenyl group relative to the fullerene cage. In fact, when fluorine atoms in an *ortho* position relative to the methyne group are pointing in the direction of the C<sub>60</sub> ( $\varphi = 10^{\circ}$  in Fig. 2), the highest LUMO energy level (-3.71 eV) is obtained. By rotating the phenyl group until the *ortho* fluorine atoms are at the most distant point, a much lower LUMO energy level (-4.05 eV) is obtained. This difference of 10% between the two values can be directly attributed to the  $\delta$ - character of fluorine atoms, confirming the electrochemical results. It is noteworthy that a fluorine-C<sub>60</sub> interaction within a crystal structure has been previously reported.<sup>10</sup> Although we do not have direct proof



Fig. 2 LUMO energy calculated for compound 7 with respect to dihedral angle  $\varphi$ .

of such an interaction in solution, we expect this to somehow have a role in increasing the LUMO energy level of  $C_{60}$ compared to other "electronically inert" secondary groups. As a comparison, the LUMO energy of compound **3** shows only a slight dependence on the dihedral angle (in the order of 0.010 eV), meaning that the presence of hydrogen atoms close to the cage does not affect the electronic properties of  $C_{60}$ . More derivatives are being prepared to study in more detail the influence of the electronic properties of the secondary group on the electronic properties of  $C_{60}$ .

# Conclusions

The present study shows that the secondary group added into the  $C_{60}$  cage to quench the ethynylation reaction can help modulate the LUMO energy level of ethynyl-bridged  $C_{60}$ derivatives. In light of the electrochemical results and DFT calculations, it is concluded that the modulation of the electronic properties of  $C_{60}$  is not achieved by means of through-bond interactions, but presumably *via* a throughspace interaction. However, additional characterization and calculations on these derivatives will be needed to assess the validity of this hypothesis. Future work will involve the development of ethynyl-bridged derivatives with strongly polarized secondary groups to better understand the nature of the electronic effects of secondary groups on the fullerene surface and to modulate the  $C_{60}$  LUMO energy over a wider range of values.

# **Experimental section**

## General remarks

[60]Fullerene (99% pure) was used as received. Solvents used for organic synthesis (THF, CH<sub>2</sub>Cl<sub>2</sub>, DMF) were dried and purified with a solvent purifier system (SPS). Other solvents were used as received. Tetrahydrofuran (THF) used for ethynylation reactions was de-gassed for 30 min prior to use. LHMDS (1 M solution in THF) was used. All anhydrous and air sensitive reactions were performed in oven-dried glassware under a positive argon pressure. Analytical thin layer chromatography was performed with silica gel 60  $F_{254}$ , 0.25 mm pre-coated TLC plates. Compounds were visualised using 254 nm and/or 365 nm UV wavelengths and/or aqueous sulfuric acid solutions of ammonium heptamolybdate tetrahydrate (10 g/100 mL  $H_2SO_4 + 900$  mL  $H_2O$ ). Flash column chromatography was performed on 230-400 mesh silica gel R10030B. Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz (<sup>1</sup>H) and 100 MHz (<sup>13</sup>C). Signals are reported as m (multiplet), s (singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quadruplet) and br s (broad singlet), and coupling constants are reported in hertz (Hz). The chemical shifts are reported in ppm ( $\delta$ ) relative to the residual solvent peak. High resolution mass spectra (HRMS) were recorded using an apparatus equipped with an ESI or APPI ion source. IR spectra were recorded using a Nicolet Magna 850 Fourier transform infrared spectrometer (Thermo Scientific, Madison, WI) with a liquid nitrogen-cooled narrow band mercury cadmium telluride (MCT) detector and a

Golden Gate ATR accessory (Specac Ltd., London, UK). Each spectrum was obtained from 64 scans at a resolution of 4 cm<sup>-1</sup>. 2-(Bromomethyl)thiophene,<sup>11</sup> 3-(bromomethyl)-thiophene<sup>11</sup> and compound 1<sup>4a</sup> were prepared as previously reported.

#### General procedure for the addition of C<sub>60</sub> to terminal alkynes

To a round-bottomed flask equipped with a magnetic stirrer bar was added 1-ethynyl-4-(octyloxy)benzene,<sup>4a</sup> C<sub>60</sub> (2 equiv.) and THF (5 mM) under an argon atmosphere. The reaction mixture was sonicated for 3 h, and LHMDS (2 equiv.) then added at room temperature to the greenish-brown solution formed after sonication. After the addition of LHMDS, the reaction was stirred for 5 min and quenched with the electrophile (20 equiv., unless otherwise stated). After removal of the solvent under a reduced pressure, the crude product was diluted with CH<sub>2</sub>Cl<sub>2</sub> and the organic layer filtered under vacuum to remove excess unreacted C<sub>60</sub>. The solvent was removed under a reduced pressure and the crude product purified by flash chromatography on silica gel with a mixture of CS<sub>2</sub>/hexanes to afford the desired compound.

#### Synthesis of compound 2

See the general procedure for the addition of  $C_{60}$  to terminal alkynes. The materials used were 1-ethynyl-4-(octyloxy)benzene (50 mg, 0.22 mmol), C<sub>60</sub> (313 mg, 0.43 mmol), THF (86.8 mL), LHMDS (0.54 mL, 0.43 mmol) and methyl iodide (3.54 mL, 56.9 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 30%  $CS_2$ /hexanes as eluents to afford compound 2 (89 mg, 43%) yield) as a brown powder: mp > 300 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 7.71 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 4.03 (t, J = 6.5 Hz, 2H), 3.51 (s, 3H), 1.83 (m, 2H), 1.31 (m, 10H), 0.89 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 159.9, 157.5, 154.1, 148.2, 148.1, 146.8, 146.7, 146.6, 146.5, 146.3, 145.8, 145.7, 145.6 (2C), 145.4, 145.1, 145.0, 143.5, 142.9 (2C), 142.5, 142.4 (2C), 142.3, 141.9, 141.8, 140.5 (2C) (28 signals from the C<sub>60</sub> core), 134.7 (-C=, Ar), 133.8 (-C=, Ar), 115.0 (-C=, Ar), 114.64 (-C=, Ar), 86.9 (-C≡), 85.6 (-C≡), 68.4 (CH<sub>2</sub>-Ar), 62.0 (C-Ar in the C<sub>60</sub> core), 33.2 (C-CH<sub>3</sub>), 32.0 (O-CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.5 (2C) (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 22.9 (2C) (CH<sub>2</sub>), 14.4 (CH<sub>3</sub>); HRMS (APPI-TOF): m/z calc. for  $C_{77}H_{24}O[M + H]^+$ : 965.1900, found 965.1882.

## Synthesis of compound 3

See the general procedure for the addition of  $C_{60}$  to terminal alkynes. The materials used were 1-ethynyl-4-(octyloxy)benzene (40 mg, 0.17 mmol),  $C_{60}$  (250 mg, 0.35 mmol), THF (69.5 mL), LHMDS (0.39 mL, 0.35 mmol) and benzyl bromide (4.12 mL, 34.7 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 40% CS<sub>2</sub>/hexanes as eluents to afford compound **3** (39 mg, 22% yield) as a brown powder: mp > 300 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 7.72 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.24 (d, J = 7.3 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 5.23 (s, 2H), 4.03 (t, J = 6.7 Hz, 2H), 1.83 (m, 2H), 1.31 (m, 10H), 0.89 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 160.0, 154.4, 154.3, 148.0, 147.9, 146.8, 146.7 (2C), 146.6, 146.5, 146.2,

145.7 (2C), 145.6, 145.5, 144.9 (2C), 143.4, 142.9, 142.8, 142.5, 142.4, 142.3, 142.1, 142.0, 141.5, 140.6, 138.9, 137.5 (29 signals from the C<sub>60</sub> core), 135.0 (–C=, Ar), 134.5 (–C=, Ar), 133.9 (–C=, Ar), 132.3 (–C=, Ar), 128.4 (–C=, Ar), 127.4 (–C=, Ar), 115.0 (–C=, Ar), 114.5 (–C=, Ar), 87.0 (–C=), 85.9 (–C=), 68.5 (CH<sub>2</sub>–Ar), 68.4, 66.8 (C-Ar in the C<sub>60</sub> core), 61.1, 50.4, 32.6 (O–CH<sub>2</sub>), 32.1 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 22.9 (CH<sub>2</sub>), 14.4 (CH<sub>3</sub>); HRMS (APPI-TOF): *m/z* calc. for C<sub>83</sub>H<sub>28</sub>O [M + H]<sup>+</sup>: 1041.2213, found 1041.2213.

# Synthesis of compound 4

See the general procedure for the addition of  $C_{60}$  to terminal alkynes. The materials used were 1-ethynyl-4-(octyloxy)benzene (50 mg, 0.22 mmol), C<sub>60</sub> (313 mg, 0.43 mmol), THF (86.8 mL), LHMDS (0.49 mL, 0.43 mmol) and 4-(methylthio)benzyl bromide (1.89 g, 8.68 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 40% CS<sub>2</sub>/hexanes as eluents to afford compound 4 (22 mg, 10% yield) as a brown powder: mp > 300 °C; <sup>1</sup>H NMR  $(CDCl_3, 400 \text{ MHz})$ : 7.69 (d, J = 8.6 Hz, 2H), 7.43 (d, J =8.6 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 5.17 (s, 2H) 4.01 (t, J = 6.5 Hz, 2H), 2.44 (s, 3H), 1.82 (m, 2H), 1.30 (m, 10H), 0.90 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 154.3, 154.2, 146.8, 146.7, 146.6, 146.5, 146.2, 145.7 (3C), 145.4, 145.0, 143.4, 143.0, 142.9 (2C), 142.5, 142.4, 142.3, 142.1, 142.0, 141.6, 140.6 (23 signals from the C<sub>60</sub> core), 139.1 (-C=, Ar), 135.1 (-C=, Ar), 134.5 (-C=, Ar), 133.9 (-C=, Ar), 132.6 (-C=, Ar), 129.8 (-C=, Ar), 126.8 (-C=, Ar), 126.2 (-C=, Ar), 115.0, 114.5, 87.0 (-C=), 68.4 (CH<sub>2</sub>-Ar), 67.0, 66.8 (C-Ar in the C<sub>60</sub> core), 49.9 (S-CH<sub>3</sub>), 32.1 (O-CH<sub>2</sub>), 29.7 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 23.0 (CH<sub>2</sub>), 15.9 (CH<sub>2</sub>), 14.4 (CH<sub>3</sub>); HRMS (APPI-TOF); m/z calc. for  $C_{84}H_{30}OS [M + H]^+$ : 1087.2090, found 1087.2106.

## Synthesis of compound 5

See the general procedure for the addition of  $C_{60}$  to terminal alkynes. The materials used were 1-ethynyl-4-(octyloxy)benzene (50 mg, 0.22 mmol), C<sub>60</sub> (313 mg, 0.43 mmol), THF (86.8 mL), LHMDS (0.49 mL, 0.43 mmol) and 3-(bromomethyl)thiophene<sup>11</sup> (1.54 g, 8.68 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 40% CS<sub>2</sub>/hexanes as eluents to afford compound 5 (46 mg, 20% yield) as a brown powder: mp > 300 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 8.00 (s, 1H), 7.50 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 1.6 Hz, 1H), 7.32 (m, 1H), 6.88 (d, J =8.6 Hz, 2H), 5.00 (s,2H), 3.96 (t, J = 6.5 Hz, 2H), 1.74 (m, 2H), 1.26 (m, 10H), 0.87 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 160.3, 155.5, 154.2, 147.6 (2C), 146.4, 146.3, 146.2, 146.1 (2C), 145.8, 145.4, 145.3, 145.2, 145.0, 144.6, 144.5 (2C), 143.1, 142.6, 142.2, 142.1, 141.6, 141.5 (2C) (25 signals from the  $C_{60}$  core), 139.6 (-C=, Ar), 138.8 (-C=, Ar), 137.5 (-C=, Ar), 136.1 (-C=, Ar), 134.8 (-C=, Ar), 134.5 (-C=, Ar), 131.0 (-C=, Ar), 130.9 (-C=, Ar), 130.8, 125.8, 125.4, 124.4, 114.5, 68.2 (CH<sub>2</sub>-Ar), 67.9 (C-Ar in the C<sub>60</sub> core), 31.8 (O-CH<sub>2</sub>), 29.7 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 25.0 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.2 (CH<sub>3</sub>); HRMS

(APPI–TOF): m/z calc. for  $C_{81}H_{26}OS$   $[M + H]^+$ : 1047.1777, found 1047.178.

# Synthesis of compound 6

See the general procedure for the addition of  $C_{60}$  to terminal alkynes. The materials used were 1-ethynyl-4-(octyloxy)benzene (50 mg, 0.22 mmol), C<sub>60</sub> (313 mg, 0.43 mmol), THF (86.8 mL), LHMDS (0.49 mL, 0.43 mmol) and 2-(bromomethyl)thiophene<sup>11</sup> (1.54 g, 8.68 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 40% CS<sub>2</sub>/hexanes as eluents to afford compound 6 (27 mg, 12% yield) as a brown powder: mp > 300 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 7.97 (s, 1H), 7.47 (d, J = 8.6 Hz, 2H), 7,29 (d, J = 5.6 Hz, 1H), 7.05 (t, J = 4.2 Hz, 1H), 6.88 (d, J = 8.6 Hz, 2H), 5.18 (s, 2H), 3.95 (t, J = 6.5 Hz, 2H), 1.73(m, 2H), 1.25 (m, 10H), 0.86 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 160.3, 155.4, 154.4, 147.9 146.7 146.6, 146.5 (2C), 146.4, 146.0, 145.7, 145.6, 145.3, 144.8 (2C) 143.3 (2C), 142.9 (2C), 142.5, 142.4, 141.9, 141.8, 141.7 (2C) (25 signals from the C<sub>60</sub> core), 139.8 (-C=, Ar), 139.4 (-C=, Ar), 139.1 (-C=, Ar), 136.1 (-C=, Ar), 135.4 (-C=, Ar), 134.7 (-C=, Ar), 131.3 (-C=, Ar), 131.3 (-C=, Ar), 130.3, 127.2, 127.1, 126.0, 125.5, 125.1,124.4, 114.7, 77.6, 77.3, 77.0, 69.5, 68.5 (CH<sub>2</sub>-Ar), 68.2, 32.1 (O-CH<sub>2</sub>), 29.7 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 23.0 (CH<sub>2</sub>), 14.4 (CH<sub>3</sub>); HRMS (APPI-TOF): m/z calc. for  $C_{81}H_{26}OS [M + H]^+$ :1047.1777, found 1047.1765.

# Synthesis of compound 7

See the general procedure for the addition of  $C_{60}$  to terminal alkynes. The materials used were 1-ethynyl-4-(octyloxy)benzene (50 mg, 0.22 mmol), C<sub>60</sub> (312 mg, 0.43 mmol), THF (86.8 mL), LHMDS (0.49 mL, 0.43 mmol) and pentafluorobenzyl bromide (1.31 mL, 8.68 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 20% CS<sub>2</sub>/hexanes as eluents to afford compound 7 (97 mg, 40% yield) as a brown powder: mp > 300 °C; <sup>1</sup>H NMR  $(CDCl_3, 400 \text{ MHz})$ : 7.74 (d, J = 8.6 Hz, 2H), 6.98 (d, J =8.6 Hz, 2H), 5.31 (s, 2H), 4.03 (t, J = 6.6 Hz, 2H), 1.83 (m, 2H), 1.31 (m, 10H), 0.89 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 153.5, 152.8, 146.8 (2C), 146.6, 146.5, 146.2, 145.8, 145.7, 145.2, 145.1, 145.0, 144.8, 143.5, 143.3, 142.9, 142.6, 142.4, 142.3, 142.0, 141.9, 141.6, 140.6, 139.5 (24 signals from the C<sub>60</sub> core), 134.4 (-C=, Ar), 133.9 (-C=, Ar), 115.0 (-C=, Ar), 114.1 (-C=, Ar), 87.3 (-C=), 86.3 (-C=), 68.5 (CH2-Ar), 65.2 (C-Ar in the C60 core), 36.8 (O-CH2), 32.1 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 22.9 (CH<sub>2</sub>), 14.4 (CH<sub>3</sub>); <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz): -139.4 (dd,  $J_1 = 14.8 \text{ Hz}, J_2 = 7.8 \text{ Hz}, 2\text{F}$ , -153.7 (t, J = 21.3 Hz, 1F), -161.5 (m, 2F); HRMS (APPI-TOF) m/z calc. for C<sub>83</sub>H<sub>23</sub>F<sub>5</sub>O  $[M + H]^+$ : 1131.1742, found 1131.1722.

## Synthesis of compound 8

See the general procedure for the addition of  $C_{60}$  to terminal alkynes. The materials used were 1-ethynyl-4-(octyloxy)-benzene (50 mg, 0.22 mmol),  $C_{60}$  (312 mg, 0.43 mmol), THF (86.8 mL), LHMDS (0.49 mL, 0.43 mmol) and pentabromobenzyl bromide (3.0 g, 5.4 mmol). The crude product was

purified by flash chromatography on silica gel with hexanes to 40% CS<sub>2</sub>/hexanes as eluents to afford compound 8 (20.3 mg, 7% yield) as a brown powder: mp > 300 °C; <sup>1</sup>H NMR  $(CDCl_3, 400 \text{ MHz})$ : 7.75 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 6.07 (s,2H), 4.03 (t, J = 6.4 Hz, 2H), 1.82 (m, 2H), 1.30 (m, 10H), 0.90 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz); 159.9, 153.8, 153.4, 147.9, 147.8, 146.6, 146.4, 146.3, 146.3, 145.9, 145.7, 145.5, 145.4, 145.0, 144.9 (2C), 144.7, 144.6, 143.3, 142.7, 142.5, 142.2, 142.1, 141.9, 141.7, 141.3, 141.2, 140.2 (28 signals from the C<sub>60</sub> core), 139.1 (-C=, Ar), 135.6 (-C=, Ar), 134.3 (-C=, Ar), 133.7 (-C=, Ar), 129.9 (-C=, Ar), 129.0 (-C=, Ar), 114.8 (-C =, Ar), 113.9 (-C =, Ar), 87.1 (-C =), 86.4 (-C =),68.2 (CH<sub>2</sub>), 65.6 (C-Ar in the C<sub>60</sub> core), 61.3 (CH<sub>2</sub>), 53.5 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 26.0 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>); HRMS (APPI–TOF): m/z calc. for C<sub>83</sub>H<sub>23</sub>Br<sub>5</sub>O  $[M + H]^+$ : 1435.7626, found 1435.7657.

### Calculations

All the calculations, optimizations and electronic properties were carried out using the DFT algorithm implemented in DMol<sup>3</sup> code through the Materials Studio 5.0 environment from Accelrys Inc. The physical wavefunctions were expanded in terms of double numerical polarized basis sets with an orbital cutoff of 3.7 Å in the DMol<sup>3</sup> method.<sup>12</sup> Becke exchange and the Lee–Yang–Parr 1988 correlation functional (BLYP),<sup>13</sup> and PBE<sup>14</sup> were used at the generalized gradient approximation (GGA) level. A Fermi smearing of 0.005 Hartree and a real-space cutoff of 3.7 or 4.0 Å, depending on the kind of atoms present in the structure, were used to improve computational performance. A self-consistent field procedure was carried out with a convergence criterion of  $10^{-6}$  Hartree, and optimization of the structure stopped when the change in energy was less than  $10^{-5}$  Hartree.

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