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Synthesis, characterization and DFT calculations of new ethynyl-bridged C_{60} derivatives

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ABSTRACT

A new series of soluble C_{60} derivatives for organic electronic application has been synthesized by ethynylation reaction using different electron-donating and electron-withdrawing groups of varying length.

1. Introduction

Fullerenes play a fundamental role in the development of organic electronics. The relative low cost, ease of functionalization and remarkable electrochemical properties of C_{60} has led it to become one of the most used *n*-type materials for the development of efficient and stable opto-electronic devices, especially for solar cells[1] and molecular electronic[2] applications. Because pristine C_{60} is difficult to process owing to its poor solubility in common organic solvents, solubilizing substituents have to be attached to it through covalent bond formation. In the past two decades, a lot of reactions have been developed to efficiently functionalize the C_{60} cage. These include, among others, direct arylation through organometallic precursors[3] and radical reactions,[4] cyclopropanation (Bingel reaction),[5] [2+2],[6] [3+2][7] and [4+2][8] cycloaddition.

In addition to increased the solubility of C_{60}, properly designed functional groups have the ability to modulate the electronic properties of C_{60}, particularly the LUMO energy level, either by through-bond[1d,9] or through-space interactions.[10] The ability of such functional groups to modulate the electronic density on the C_{60} cage strongly rely on the type of linker used to attach it to the C_{60}. For example, cyclopropanation and cycloaddition reactions, which lead to the formation of two sp^3 carbons between the substituent and the C_{60} cage, do not allow direct through-bond conjugation, making modulation of the electronic properties rather difficult.[1d,e] The modulation of the LUMO energy level of C_{60} is particularly important for organic electronic application (e.g., polymer solar cells) as a difference of few tenth of eV could have a significant impact on the device efficiency.[11] Thus, a synthetic strategy enabling the modulation of the electronic properties of C_{60} still needs to be developed.

Ethynylation reaction has proven to be very useful to bridge the C_{60} with different substituents in moderate to good yields.[12] This reaction has been used recently to prepare surface nanomachines,[13] electro- and photoactive materials[14] and NLO active molecules.[15] Although electrochemical characterization of few alkynyl-bridge C_{60} derivatives has been reported in the recent literature,[14a,15a] no systematic study of the influence of the nature of the alkyne derivatives on the electronic properties of C_{60} has been performed. For the purpose of the LUMO energy level modulation, ethynylation reaction is expected to be particularly interesting since the electron density can be tuned through the substituent bearing the terminal alkyne (R) but also through the electrophilic species (E) used to quench the reaction (Scheme 1). Moreover, an ethynyl moiety directly attached to the C_{60} participates in a through-space p-orbital overlapping, called 'periconjugation', thus indirectly increasing the electronic communication between C_{60} and the R group.[15a,16]

Herein we report the synthesis, optical and electrochemical properties and DFT calculations of a series of thirteen C_{60} derivatives prepared by ethynylation reaction using different

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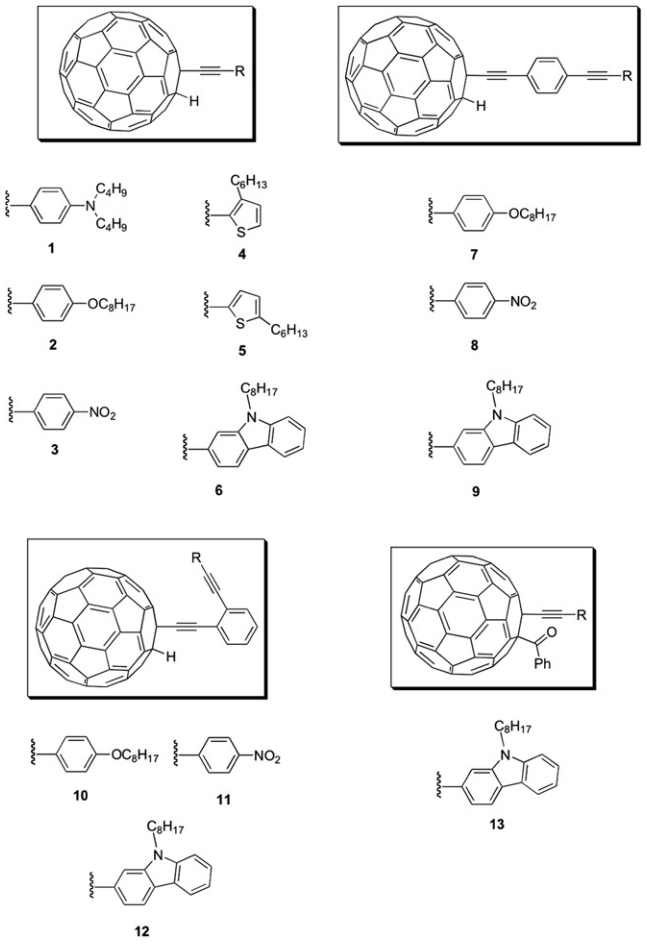


Scheme 1. Ethynyl-bridged C_{60} derivatives.

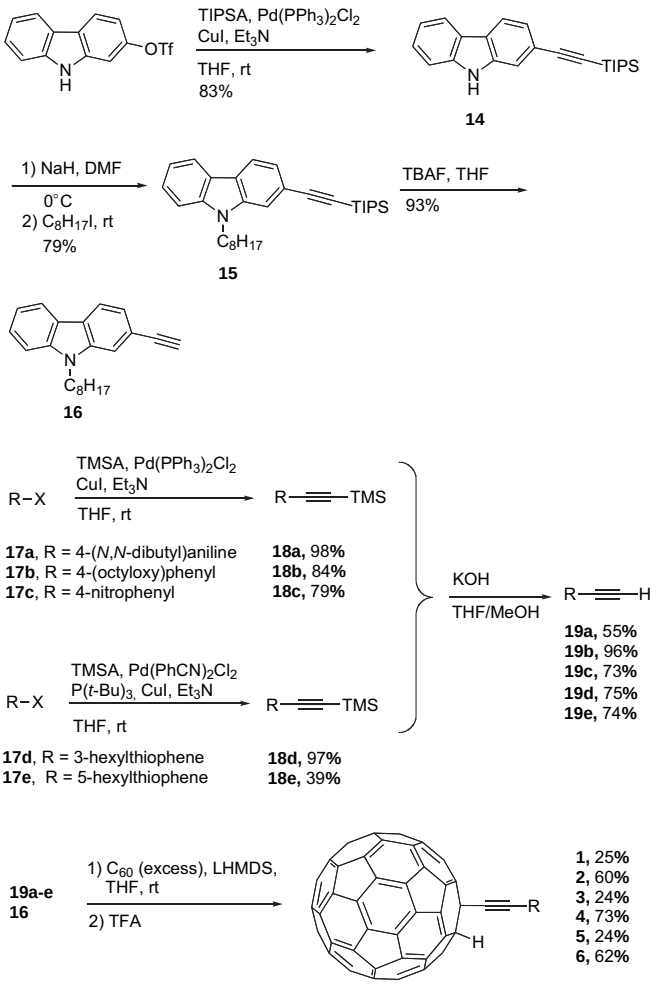
electron-donor and electron-acceptor groups in order to determine the ability of such groups to modulate the LUMO level of C_{60} using an ethynyl bridge (Scheme 1). This work is the first step of a project aiming at developing new C_{60} derivatives for solar cells application.

2. Results and discussion

All the C_{60} derivatives synthesized in this study are presented in Scheme 1. Different electron-donating and electron-withdrawing groups were used for the purpose of this study, namely substituted thiophene, carbazole and phenyl rings bearing heteroatoms (N, O). Thiophene and carbazole rings have been chosen because those are important building blocks in organic semiconductors, especially in conjugated polymers for solar cell application.[17] Phenyl group was used for its ease of functionalization in different positions. All these units have been substituted with alkyl chains to enhance the solubility of the resulting derivatives. As electrophiles, proton was used in all cases, except for **13** in which unsubstituted benzoyl group was used to study its effect on the LUMO energy level of C_{60}.

In order to study the conjugation path in ethynyl-bridged C_{60} derivatives, the substituents have been directly attached to the C_{60} (compounds **1**–**6**) or placed in a face-to-face configuration (*ortho* position) (compounds **10**–**12**) relative to the C_{60} cage. In the former case, a through-bond mechanism is expected to dominate while in the later case, a through-space interaction is more likely to take place. The effect of the substituents length has also been studied in the linear derivatives by adding a phenyl linker between the substituents and the C_{60} cage (compounds **7**–**9**). The synthesis of the precursors and their C_{60} derivatives is outlined in Scheme 2–5.

The starting aryl iodides (**17a**,**b**) have been prepared using well-established protocols[18,19] while derivatives **17c**–**e** were purchased. For the carbazole derivatives, the synthesis is depicted in Scheme 2. First, a standard Sonogashira coupling between triisopropylsilylacetylene (TIPSA) and the commercially available 2-(trifluoromethanesulfonyl)-carbazole was performed to provide compound **14** in good yield. It is noteworthy that TIPSA was used rather than trimethylsilylacetylene (TMSA) since the TMS-protected alkyne on carbazole is not stable enough under the alkylation conditions. Compound **14** was then alkylated with octyl iodide using sodium hydride (NaH) in DMF to give compound **15**. Then, the TIPS-protected alkyne was cleaved using tetrabutylammonium fluoride (TBAF) in THF to provide compound **16** in excellent yield.



Scheme 2. Synthesis of compounds **1**–**6**.

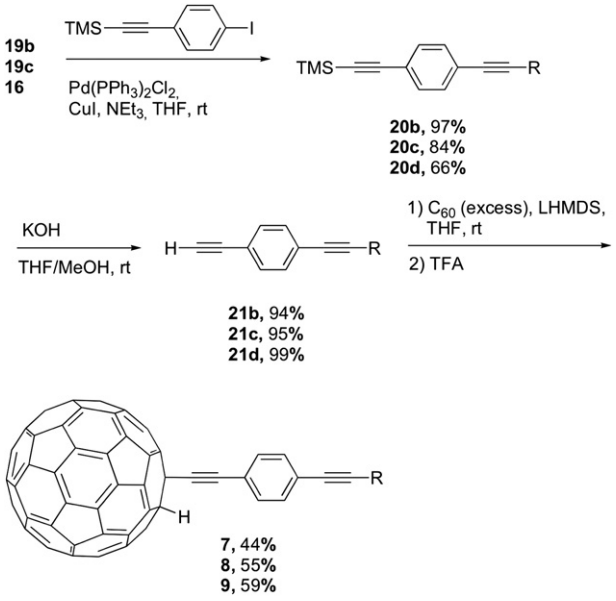
For the synthesis of compounds **18a**–**c**, the corresponding aryl iodides have been coupled to TMSA using standard Sonogashira coupling at room temperature with good to excellent yield (79–98%). For the 2-bromothiophene derivatives, the standard Sonogashira conditions lead to only very low yield of the desired product, even at high temperature (65 °C). Thus, we applied the conditions developed by Buchwald and co-workers using $PdCl_2(PhCN)_2$ and a hindered ligand ($P(t\text{-}Bu)_3$) specially designed for unactivated aryl bromides.[20] These conditions were very successful for the synthesis of **18d** (3-hexylthiophene) (97% yield) but not for the synthesis of **18e** (39% yield). This difference of reactivity has not been investigated in the course of this study. All the TMS-protected alkyne (**18a**–**e**) were then desilylated in basic

conditions in a mixture of THF and methanol to provide the terminal alkyne **19a–e** in moderate to excellent yields (55–93%). The lower yield for the *N*,*N*-dibutylaniline derivative (**19a**) can be explained by the poor stability of this compound. Partial decomposition has been observed during the purification by column chromatography on silica gel.

The ethynylation reactions on C_{60} were conducted using a slightly modified procedure reported by Tour and co-workers[14] Terminal alkyne precursor and C_{60} were added in dry THF and sonicated for three hours before LHMDS (lithium bis(trimethylsilyl)amide) was added. After few minutes of stirring at room temperature, the reaction was quenched with trifluoroacetic acid (TFA) and the solvent was immediately removed under vacuum. All the derivatives have been purified by usual column chromatography on silica gel. The success of the ethynylation reaction of C_{60} has been assessed by the appearance of a peak at around 7.1 ppm in the ^{1}H NMR, which corresponds to the presence of a proton directly attached to C_{60}.[15b] Moreover, a set of peaks appears between 140 and 160 ppm in the ^{13}C NMR spectra upon attachment of C_{60}, which corresponds to the carbon of the C_{60} cage.

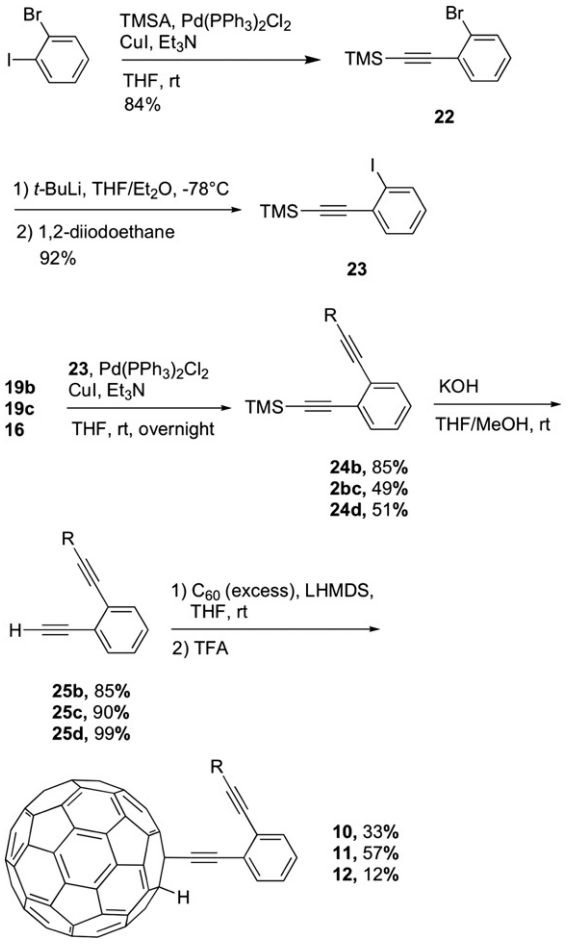
For the ethynylation reaction, the yield of reaction is very dependent on the solubility and ease of purification. For example, the reaction yields for **1** (25%) and **5** (24%) were found to be much lower than for **4** (73%) and **6** (62%) since they are much less soluble. Nonetheless, the reaction yields obtained for the soluble derivatives are slightly better than those published previously,[13–15] probably due to the better solubility of our derivatives but also to careful time monitoring for each reaction steps.

In order to study the influence of the length of the linker between the substituents and the C_{60} cage, oligo(phenylene ethynylene) (OPE) based on the alkoxyphenyl, carbazole and nitrophenyl have been synthesized and their preparation is outlined in Scheme 3. Compounds **19b–c** and **16** were coupled to 4-(trimethylsilylethynyl)iodobenzene[21] under standard Sonogashira conditions to provide **20b–d** in moderate to excellent yield (66–97%). Then, the alkyne were deprotected and coupled to the C_{60} using the same conditions described above to provide compounds **7–9** in moderate yields (44–59%).



Scheme 3. Synthesis of compounds **7–9**.

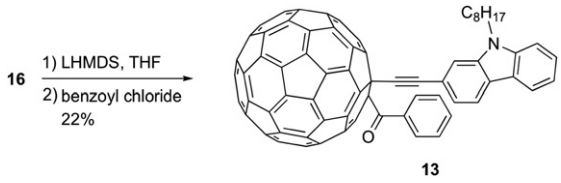
Derivatives in which the electron-rich or electron-poor substituent is facing the C_{60} cage owing to an *ortho* linker were also synthesized (Scheme 4). Starting from 2-iodobromobenzene, one



Scheme 4. Synthesis of compounds **10–12**.

TMSA group was selectively attached at the 2 position using standard Sonogashira coupling conditions to provide compound **22** in good yield. In order to ensure the regioselectivity of this coupling, the reaction was initiated at 0 °C before it was warmed at room temperature for several hours. Then, the bromine was changed to an iodine atom using *tert*-butyllithium followed by 1,2-diiodoethane to afford compound **23** in 92% yield. Although Sonogashira coupling can be performed directly on the bromine derivative under standard conditions, the replacement of the bromine by the iodine has been achieved in order to be able to perform the next step at room temperature since 1,2-dialkynyl benzene derivatives are known to be unstable at elevated temperature (required for Sonogashira coupling on a bromine derivative) because they can undergo radical-promoted cyclization.[22] Compound **23** was then coupled to **19b–c** and **16** using Sonogashira coupling in moderate to good yield (49–85%) and the alkyne were deprotected using KOH to afford the precursors **25b–d**. Those were then attached to the C_{60} as previously described in moderate to poor yield (12–57%). The lower yields obtained for the *ortho* derivatives can be attributed to the difficulty to form the acetylide using LHMDS compared to the other derivatives. In fact, more LHMDS was necessary to efficiently deprotonate the precursors of compounds **10–12** than usually required for other precursors (2 equiv).

For the benzoylation reaction (Scheme 5), compound **16** was dissolved in THF and treated with LHMDS before a large excess of benzoyl chloride was added. The low yield (22%) of this reaction is attributed to the formation of a significant amount of unknown polar side products.



Scheme 5. Synthesis of compound **13**.

UV-visible spectra of the phenylalkoxy-, carbazole and nitrobenzene derivatives with and without the C_{60} have been taken in dilute solution and the results are presented in Table 1 (see Supplementary data for all the spectra). All those compounds and their acetylenic precursors absorb light in the UV region (290–339 nm), which is consistent with other OPEs reported in the literature.[14a,23] Compared to compounds **2**, **3** and **6**, UV-visible spectra of compounds **7**, **8** and **9** were shifted bathochromically (13, 17 and 22 nm, respectively) because of the extended conjugation length (see example in Fig. 1). On the other hand, the *ortho* derivatives **10**–**12** are also red shifted compared to compounds **2**, **3** and **6**, but at a lesser extent. This can be attributed to a more efficient conjugation through a *para* linker.[24] Interestingly, the difference in the λ_{max} values for compounds **2** and **10** is only 2 nm, compared to 12 and 15 nm for the **3**/**11** and **6**/**12** pairs, respectively. This could be an indication that through-space ground state interaction takes place between the C_{60} cage and the octyloxyphenyl substituent in *ortho* position. Nierengarten and co-workers reported recently a bathochromic shift, related to an intramolecular through-space interaction, of the absorption band of OPEs lying close to a C_{60}.[25] However, UV-visible experiments cannot be used to study such interaction in our derivatives since the C_{60} and the OPE UV-visible bands overlap in the 300–340 region.

Table 1
Optical properties of compounds **2**, **3**, **6**–**12**

Compound	λ_{max}[a] (nm)	ε[b] ($mmol^{-1}$ cm^2)
2	263, 307	
3	259, 314	
5	261, 327	38,800
6	270, 315	
7	262, 320	
8	260, 333	
9	268, 337	10,780
10	260, 309	
11	260, 326	19,100
12	268, 330	

[a] The first value correspond to the most intense band in the spectrum while the second value correspond to the π–π* transition.
[b] Calculated in a 1 cm quartz cell with a concentration of $5{,}0\times10^{-6}$ mol/L at 25 °C.

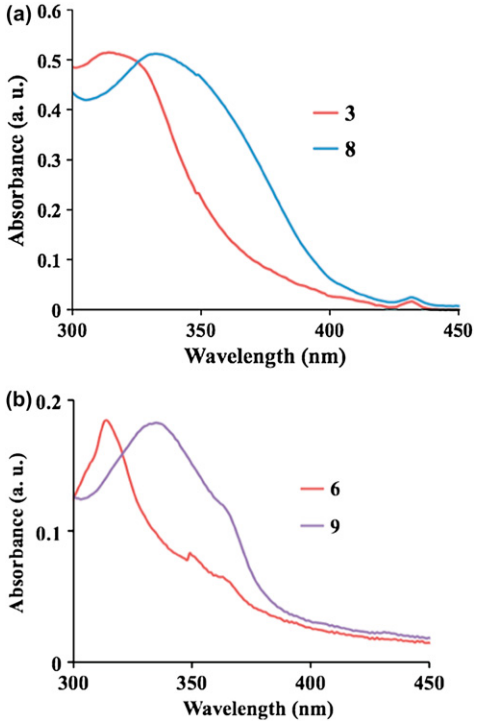


Figure 1. UV-visible spectra of (a) compounds **3** and **8** and (b) compounds **6** and **9** in chloroform (10^{-6} M).

To study the influence of electron-donating and electron-withdrawing units on the LUMO level of C_{60}, cyclic voltammetry measurements were performed in solution in cathodic regime and the results are summarized in Table 2 (see Supplementary data for all the CVs). All proton-substituted derivatives (compound **1**–**12**) show at least two quasi-reversible reduction waves between 0 and −2.5 V versus Fc/Fc^+ as usually observed for C_{60} derivatives. The

Table 2
Cyclic voltammetry data of C_{60}, PCBM and compounds **1**–**13**[a]

Compound	E^{red1} (V)	Exp. LUMO (eV)[b]	Theo. LUMO (eV)
C_{60}	−0.824	−3.980	−3.744
PCBM	−0.921	−3.880	−3.590
1	−0.873	−3.927	−3.630
2	−0.876	−3.924	−3.592
3	−0.847	−3.953	−3.810
4	−0.855	−3.945	−3.649
5	−0.877	−3.923	−3.620
6	−0.864	−3.936	−3.624
7	−0.862	−3.938	−3.620
8	−0.856	−3.944	−3.750
9	−0.854	−3.946	−3.636
10	−0.859	−3.941	−3.644
11	−0.845	−3.955	−3.740
12	−0.847	−3.953	−3.602
13	−0.838	−3.962	−3.624

[a] Potential versus ferrocene/ferrocinium measured with cyclic voltammetry at a scan rate of 200 mV/s in a degassed mixture of *o*-DCB/MeCN (4:1) containing Bu_4NPF_6 (0.1 M) as a supporting electrolyte. Platinum wires were used as working and counter electrodes and Ag/Ag^+ electrode was used as reference electrode.
[b] Values estimated using the following equation; $E_{LUMO}=-(E^{red1}+4.8)$ eV.[26]

LUMO levels of the C_{60} derivatives were calculated from the potential of the first reduction wave (E^{red1}) using the equation $E_{LUMO}=-(E^{red1}+4.8)$ eV.[26] It is noteworthy that the values of potential at the peak maximum give us much more better reproducibility than the values of the half-wave potential typically used for the calculation of the E_{LUMO}. Thus, our values are not absolute ones, but they are used to establish comparison between our derivatives and the well-studied [6,6] phenyl-C_{61}-butyric acid methyl ester (PCBM).

Compared to PCBM, the introduction of an ethynyl bridge between the substituents and C_{60} lowered the E_{LUMO} value. As expected, the highest LUMO levels have been calculated for compound **1** and **2** that contain strong electron-donating units in the *para* position relative to the alkyne, a dialkylamine (−3.927 eV) and an alkoxy (−3.924 eV), respectively (Fig. 2). In the opposite, compound **3** shows the lower E_{LUMO} value (−3.953 eV) owing to the presence of a strong electro-withdrawing nitro group (Fig. 2). Those results show that modulation of the LUMO energy level of C_{60} through an alkyne bridge is feasible, but not trivial. The modulation of 50 meV between different derivatives is in the same order of magnitude as that observed in other reports.[1] Interestingly the substitution pattern on the thiophene ring has a significant influence on the electrochemical properties of the C_{60} derivatives. In fact, the hexyl chain in position 3 of the thiophene ring makes the E_{LUMO} value of C_{60} lower (−3.945 eV) than its 5-hexylthiophene homologue (−3.923 eV). This small difference can be attributed to not only solvent effects but also to an electronic interaction between

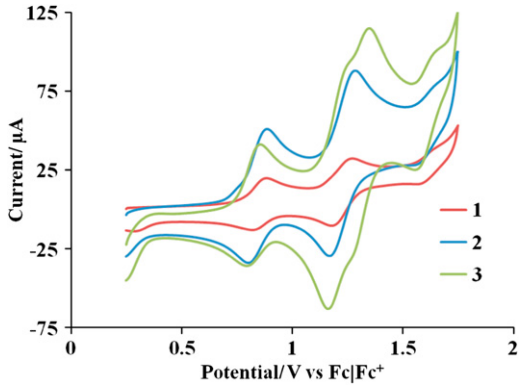


Figure 2. Cyclic voltamogram of compounds **1**, **2** and **3** in 0.1 M Bu_4NPF_6 at a scan rate of 0.1 V s^{-1} at room temperature.

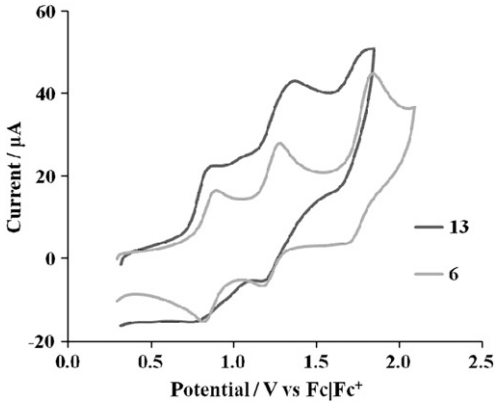


Figure 3. Cyclic voltamogram of compounds **6** and **13** in 0.1 M Bu_4NPF_6 at a scan rate of 0.1 V s^{-1} at room temperature.

the alkyl chain and the C_{60} cage. The DFT-optimized geometries of the derivatives showed that the alkyl chain in compound **4** (vide infra) is much more closer to the fullerene than in compound **5**, which translates into a significant smaller dipole. The δ^+ charge carried by this proximate alkyl chain has better ability to stabilize a negative charge on the C_{60} cage, thus decreasing the E^{red1} value.

The addition of a phenyl group between the electro-donating/withdrawing substituent and the C_{60} cage is responsible for a partial loss of the electronic communication between them. Indeed, there is almost no difference in the E_{LUMO} values between compounds **7** (−3.938 eV) and **8** (−3.944 eV) containing the alkoxyphenyl and the nitrophenyl group, respectively. Thus, the electro-donating/withdrawing units have to be close to the C_{60} cage to have influence on its electronic properties.

To study a possible through-space interaction between the C_{60} and the substituent, *ortho* OPEs were tested. By comparing compounds **10**, **11** and **12**, it is clear that the electronic nature of the substituent has little or no effect on the LUMO energy level of C_{60} with values ranging from −3.941 to −3.955 eV. Interestingly, the E_{LUMO} values calculated for the nitrophenyl derivatives substituted in *para* position (**3**) and that in *ortho* position (**11**) are almost identical (∼ −3.954 eV). This result is quite surprising given that compound **11** has one more phenyl group between the nitrophenyl and the C_{60} cage. Although it is too premature to attribute this to a direct through-space interaction, this hypothesis is the most likely in regard to the data collected so far. However, the through-space interaction in compounds **10**–**12** is expected to be minimal since the distance between the substituent and the C_{60} cage (calculated on the optimized geometries) is ca. 5.7 Å, which is too high to allow efficient intramolecular interaction.

As shown in Figure 3, the presence of an electron-withdrawing benzoyl group on the C_{60} (compound **13**) decreases the first reduction potential substantially (−0.838 V) with respect to its protonated counterpart (**6**, −0.864 V). Also, compound **13** is not as stable as the proton-substituted ones upon reduction as shown by the irreversibility of the reduction wave. Nonetheless, these results show that using different electrophilic species in the course of the reaction can significantly perturb the LUMO energy level of C_{60}.

The electronic structure of pristine C_{60}, PCBM, and the series of ethynyl-bridged C_{60} derivatives were investigated by performing extensive density functional theory (DFT) calculations. Our basic aim is to understand how different substituents modulate the levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which can be directly related to the optical and electrochemical properties of these materials. DFT calculations were performed using the B3LYP hybrid functional,[27] which mixes the Lee, Yang, and Parr functional for the correlation part and Becke's three-parameter functional for the exchange, as implemented in the Gaussian 03 code.[28] The B3LYP functional has become the standard method to study organic chemistry because it constitutes a good compromise between computational cost and accuracy in the prediction of a variety of molecular properties.[29] Moreover, Zhan and co-workers demonstrated that the ionization potentials, electron affinities and electronic excitation energies of a variety of organic and inorganic compounds can be linearly correlated with the HOMO, LUMO and HOMO/LUMO gap energies calculated at the B3LYP level.[30] Because of the size of the molecules, initial geometry optimizations and vibrational frequency analysis were performed at the B3LYP/STO-3 G level adopting all-*trans* conformations for the alkyl chains. After the structures were confirmed to be true minima, the geometries were refined using the split-valence double-zeta 6-31G(d) basis set, and subsequent single-point calculations used to evaluate HOMO and LUMO energies were performed adopting an enlarged split-valence triple-zeta 6-311+G(d,p) basis set.

An interesting result from our calculations is that HOMO energies along the series of ethynyl-bridged derivatives can be modulated over a significant range of ∼0.6 eV, while modulation of LUMO levels appears to be more moderate spanning a range of ∼0.2 eV. Thus, the differences predicted for the HOMO/LUMO gaps are largely originated by changes in the HOMO levels. A visual inspection of the molecular orbitals, as shown in Figure 4 for selected derivatives, explains this observation. Thus, while the LUMO orbitals reside exclusively in the fullerene cage, only in the compounds **1**, **3**, **4**, **8** and **11** we have localization of the HOMO on

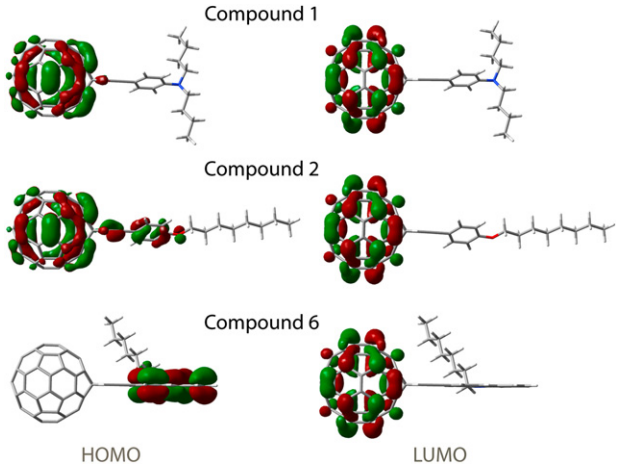


Figure 4. Visual representation of the HOMO and LUMO molecular orbitals for selected ethynyl-bridged C_{60} derivatives. The corresponding HOMO/LUMO orbital energies in eV are −6.125/−3.630 for compound **1**, −6.076/−3.592 for compound **2**, and −5.889/−3.624 for compound **6**.

the fullerene unit. In other derivatives, the HOMO is partially delocalized over the substituent (compounds **2** and **5**), and in most cases it completely resides in it. This degree of localization translates into HOMO levels over ~5.7–5.9 eV when the orbital resides in the substituent, whereas, a complete or partial localization over the fullerene cage translates into larger values (~6.0–6.3 eV) much closer to pristine C_{60} (6.45 eV) or PCBM (6.11 eV).

On the other hand, the ordering of HOMO levels follows reasonably well the electron-donating ability of the substituents: –Ph–NO_2<–Ph–NBu_2 ~ –hexyl-tiophene ~ –Ph–*O*–Oct<*N*-octyl-carbazole. The same ordering is observed for the LUMO levels, except that LUMO values from carbazole derivatives are in this case much closer to the energies obtained for the other molecules. Overall, the substitution of the C_{60} unit and the corresponding decrease in π-delocalization leads in general to a decrease in the absolute value of the LUMO levels and thus in the electron accepting ability of fullerene towards values closer to PCBM. This effect together with the strong modulation of the HOMO energies leads to a significant range of values ~2.11–2.50 eV for the HOMO/LUMO gaps, which are smaller than those predicted for pristine C_{60} (2.71 eV) or PCBM (2.52 eV).

Finally, we investigated the ability of our calculations to predict quantitatively the LUMO energy levels of the C_{60} derivatives. A least squares fit between experimental and theoretical LUMO energies ($E_{exp}^{LUMO} = A \bullet E_{DFT}^{LUMO} + B$) leads to a moderate degree of correlation (Pearson's coefficient r=0.43). However, restricting the fit to the compounds bearing a –H in the electron-withdrawing position (i.e., all except compound **13**), the results show to a better correlation (r=0.61). Moreover, if we focus the analysis on the structurally related compounds **1**–**6**, which differ only in the group connected to the terminal alkyne (R) and thus share the same basic skeleton, we obtain a significantly improved correlation between theory and experiment (r=0.83). This analysis suggests that DFT can be used as a useful tool to understand and qualitatively predict the changes in LUMO levels for structurally related C_{60} derivatives, but points also to the difficulties in correlating these changes when the differences between derivatives are not limited to a single group but affect the overall structure of the substituent.

3. Conclusion

In conclusion, a new series of soluble C_{60} derivatives for organic electronic application has been synthesized by ethynylation reaction using different electron-donating and electron-withdrawing groups of varying length. We show that electronic communication between the C_{60} and the substituent can take place via the alkyne bridge. We also show that depending on the electronic nature of the substituent attached to the C_{60}, materials with different absorption bands can be obtained. However, only slight modification of the LUMO energy level is observed when the electronic nature of the substituent is changed. DFT calculations of the LUMO energy level of the derivatives synthesized show good correlation with those measured by electrochemistry. Further experiments will include, among others, the attachment of new electrophiles (other than proton and benzoyl) to assess the ability of such groups to modulate the LUMO energy level through to the position next to the alkyne on the C_{60} cage. More electron-donating and electron-withdrawing units will also be synthesized to study a potential through-space interaction between the C_{60} cage and the substituent attached to it.

4. Experimental

4.1. General remarks

[60]Fullerene (99% pure) was used as received. Solvents used for organic synthesis (THF, CH_2Cl_2, DMF) were dried and purified with a Solvent Purifier System (SPS). Other solvents were used as received. Tetrahydrofuran (THF) and triethylamine (TEA) used for Sonogashira reactions were degassed 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 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 wavelength and/or aqueous sulfuric acid solution of ammonium heptamolybdate tetrahydrate (10 g/100 mL H_2SO_4+900 mL H_2O). Flash column chromatographies were performed on 230–400 mesh silica gel R10030B. Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz (^{1}H) and 100 MHz (^{13}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 (δ) relative to residual solvent peak. High-resolution mass spectra (HRMS) were recorded with 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^{-1}

4.2. General procedure for addition of C_{60} to terminal alkynes

To a round bottom flask equipped with a magnetic stir bar was added the terminal alkyne, C_{60} (2 equiv per terminal alkyne H) and THF (5 mM) under argon atmosphere. The reaction mixture was sonicated for 3 h and LHMDS (2 equiv per terminal alkyne H) was then added at room temperature to the greenish-brown solution formed after sonication. During the addition of LHMDS, small aliquots from the reaction were extracted and quenched with trifluoroacetic acid (TFA) for TLC analysis. After the addition of LHMDS, the reaction was stirred for 5 min and quenched with TFA (20 equiv). After removal of solvent under vacuo, the crude product was diluted with CH_2Cl_2 and the organic layer was filtered under vacuum to remove excess of unreacted C_{60}. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with a mixture of CS_2/hexanes to afford the desired compound.

*4.2.1. N,N-Dibutyl-4-iodoaniline(**17a**).* A 50 mL round bottom flask equipped with a magnetic stir bar was charged with 4-iodoaniline (2.00 g, 9.13 mmol), anhydrous DMF (18.2 mL) and NaH (650 mg, 27.1 mmol) under argon atmosphere. The reaction mixture was cooled to 0 °C, stirred for 30 min and butyl iodide (4.15 mL, 36.5 mmol) was then added. The temperature was raised to room temperature and the solution was stirred overnight. MeOH was carefully added, followed by H_2O and the mixture was extracted with CH_2Cl_2. The organic layer was washed with H_2O (4×), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel with hexanes as eluent to afford the desired compound **17a** (1.08 g, 35% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.40 (d, J=8.9 Hz, 2H), 6.40 (d, J=8.9 Hz, 2H), 3.21 (t, J=7.7 Hz, 4H), 1.53 (m, 4H), 1.32 (m, 4H), 0.94 (t, J=7.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): 147.6, 137.6, 114.0, 75.3, 50.7, 29.2, 20.3, 13.9; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{22}IN$ $[M+H]^+$: 332.0873, found 332.0873. FT IR (ATR): 2962m, 2593w, 2208w, 1605w, 1458m, 1264s, 764m.

*4.2.2. N,N-dibutyl-4-((trimethylsilyl)ethynyl)aniline(**18a**).* A 50 mL round bottom flask equipped with a magnetic stir bar was charged with **17a** (1.00 g, 3.02 mmol), THF (15 mL), triethylamine (1.66 mL,

12.1 mmol), $PdCl_2(PPh_3)_2$ (42 mg, 0.06 mmol), CuI (11.5 mg, 0.06 mmol) and trimethylsilylacetylene (0.85 mL, 6.04 mmol) under argon atmosphere. The reaction mixture was stirred overnight at room temperature, diluted in CH_2Cl_2, washed with NH_4Cl (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 1% EtOAc/hexanes as eluent to afford the desired compound **18a** (907 mg, 98% yield) as a dark orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.28 (d, *J*=8.6 Hz, 2H), 6.50 (d, *J*=8.7 Hz, 2H), 3.25 (t, *J*=7.6 Hz, 4H), 1.55 (m, 4H), 1.33 (m, 4H), 0.94 (t, *J*=7.3 Hz, 6H), 0.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 148.1, 133.3, 110.9, 108.5, 106.8, 90.8, 50.6, 29.3, 20.3, 14.0, 0.26; HRMS (APPI-TOF) *m*/*z* calcd for $C_{19}H_{31}NSi$ $[M+H]^+$: 302.2299, found 302.2317. FT IR (ATR): 2956m, 2897w, 2147s, 1605s, 1515s, 1367m, 1247m, 1186m, 839s, 760m.

*4.2.3. N,N-Dibutyl-4-ethynylaniline (**19a**).* A 25 mL round bottom flask equipped with a magnetic stir bar was charged with **18a** (750 mg, 2.49 mmol), KOH (558 mg, 9.95 mmol), THF (6.0 mL), MeOH (6.0 mL) and water (1.0 mL). The reaction mixture was stirred for 2 h, diluted with CH_2Cl_2, washed with H_2O (3×) and dried over Na_2SO_4. The solvent were removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 1% EtOAc/hexanes as eluents to afford compound **19a** (311 mg, 55% yield) as a dark orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.32 (d, *J*=8.4 Hz, 2H), 6.53 (d, *J*=8.5 Hz, 2H), 3.26 (t, *J*=7.6 Hz, 4H), 2.95 (s, 1H), 1.53 (m, 4H), 1.34 (m, 4H), 0.95 (t, *J*=7.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): 148.2, 133.3, 111.0, 107.4, 85.1, 74.4, 50.7, 29.3, 20.3, 13.9; HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{23}N$ $[M+H]^+$: 230.1903, found 230.1905. FT IR (ATR): 3305w, 2956m, 2896w, 2099m, 1606s, 1514s, 1366m, 1180m, 812s.

Compound **1**. See the general procedure for addition of C_{60} to terminal alkynes. The materials used were **19a** (50 mg, 0.22 mmol), C_{60} (314 mg, 0.43 mmol), THF (87 mL), LHMDS (0.5 mL, 0.42 mmol) and TFA (0.3 mL, 4.36 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 20% CS_2/hexanes as eluents to afford compound **1** (51 mg, 25% yield) as a brown powder: mp>300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.63 (d, *J*=8.1 Hz, 2H), 7.13 (s, 1H), 6.69 (d, *J*=8.4 Hz, 2H), 3.35 (t, *J*=7.1 Hz, 4H), 1.64 (m, 4H), 1.41 (m, 4H), 1.00 (t, *J*=7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): 152.2, 151.9, 148.3, 147.6, 147.3, 146.7, 146.4, 146.2, 145.9, 145.6, 145.5, 145.4 (2C), 144.7, 144.6, 143.2, 143.0, 142.5, 142.2, 142.0 (2C), 141.7, 141.6, 140.4, 140.2, 136.3, 135.0 (27 signals from sp^2-C in the C_{60} core), 133.4 (–C═, Ar), 111.3 (–C═, Ar), 107.7 (–C═, Ar), 90.1 (–C≡), 85.2 (–C≡), 62.1 (CH in the C_{60} core), 55.4 (quaternary sp^3-C in the C_{60} core), 50.7 (CH_2), 29.4 (CH_2), 20.5 (CH_2), 14.1 (CH_3); HRMS (APPI-TOF) *m*/*z* calcd for $C_{76}H_{23}N$ $[M+H]^+$: 950.1903, found 950.1910. FT IR (ATR): 2920m, 2852m, 2212w, 1603s, 1515s, 1363m, 1185s, 830s, 766s.

*4.2.4. 2-((Trimethylsilyl)ethynyl)-3-hexylthiophene (**18d**).* A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 2-bromo-3-hexylthiophene (750 mg, 3.03 mmol), THF (10 mL), triethylamine (1.7 mL, 12.1 mmol), $PdCl_2(PhCN)_2$ (35 mg, 0.09 mmol), CuI (12 mg, 0.06 mmol), P(*t*-bu)$_3$ (0.09 mL, 0.09 mmol) and trimethylsilylacetylene (0.8 mL, 6.07 mmol) under argon atmosphere. The reaction mixture was stirred overnight at room temperature, diluted in CH_2Cl_2, washed with NH_4Cl (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes as eluent to afford compound **18d** (779 mg, 97% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.05 (d, *J*=5.1 Hz, 1H), 6.77 (d, *J*=5.1 Hz, 1H), 2.67 (t, *J*=7.6 Hz, 2H), 1.59 (m, 2H), 1.30 (m, 6H), 0.88 (t, *J*=6.5 Hz, 3H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 148.9, 128.3, 126.1, 118.6, 100.8, 97.9, 31.9, 30.4, 29.7, 29.2, 22.9, 14.4, 0.29; HRMS (APPI-TOF) *m*/*z* calcd for $C_{15}H_{24}SSi$ $[M+H]^+$: 265.1441, found 265.1436. FT IR (ATR): 2925w, 2856w, 2143w, 1248m, 836s, 757m.

*4.2.5. 2-Ethynyl-3-hexylthiophene (**19d**).* A 25 mL round bottom flask equipped with a magnetic stir bar was charged with **18d** (750 mg, 2.84 mmol), KOH (796 mg, 14.2 mmol), THF (7.0 mL), MeOH (7.0 mL) and water (1.0 mL). The reaction mixture was stirred for 2 h, diluted with CH_2Cl_2, washed with water (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes as eluent to afford compound **19d** (488 mg, 75% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.14 (d, *J*=5.1 Hz, 1H), 6.84 (d, *J*=5.1 Hz, 1H), 3.42 (s, 1H), 2.70 (t, *J*=7.6 Hz, 2H), 1.60 (m, 2H), 1.31 (m, 6H), 0.88 (t, *J*=6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 149.1, 128.0, 126.2, 116.9, 83.1, 31.6, 30.2, 29.4, 28.9, 22.6, 14.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{12}H_{16}S$ $[M+H]^+$: 193.1045, found 193.1050. FT IR (ATR): 3309m, 2924s, 2855s, 2100w, 1664m, 1465m, 1410s, 1294w, 838m.

Compound **4**. See the general procedure for addition of C_{60} to terminal alkynes. The materials used were **19d** (40 mg, 0.21 mmol), C_{60} (300 mg, 0.42 mmol) THF (83 mL), LHMDS (0.5 mL, 0.42 mmol) and TFA (0.3 mL, 4.36 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 10% CS_2/hexanes as eluent to afford compound **4** (140 mg, 73% yield) as a brown powder: mp>300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.28 (d, *J*=5.0 Hz, 1H), 7.07 (s, 1H), 6.96 (d, *J*=5.2 Hz, 1H), 2.95 (t, *J*=7.6 Hz, 2H), 1.80 (m, 2H), 1.35 (m, 6H), 0.87 (t, *J*=6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 151.3, 151.1, 149.1, 147.5, 147.3, 146.5, 146.3, 146.1, 145.7, 145.6, 145.5, 145.4, 145.3, 145.2, 144.6, 144.4, 143.1, 142.9, 142.5, 142.0, 141.9 (2C), 141.8, 141.6, 141.5, 140.4, 140.3, 136.0, 135.1 (29 signals from sp^2-C in the C_{60} core), 128.3 (–C═, Ar), 126.8 (–C═, Ar), 117.4 (–C≡), 98.1 (–C≡), 61.7 (CH in the C_{60} core), 53.3 (quaternary sp^3-C in the C_{60} core), 31.8 (CH_2), 30.5 (CH_2), 29.9 (CH_2), 29.2 (CH_2), 22.9 (CH_2), 14.4 (CH_3); HRMS (APPI-TOF) *m*/*z* calcd for $C_{72}H_{16}S$ $[M+H]^+$: 913.1045, found 913.1055. FT IR (ATR): 2915s, 2848s, 2327w, 2213w, 1717m, 1426s, 1181s, 1013s, 805m, 767s.

*4.2.6. 2-((Trimethylsilyl)ethynyl)-5-hexylthiophene (**18e**).* A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 5-bromo-2-hexylthiophene (500 mg, 2.02 mmol), THF (7 mL), triethylamine (1.1 mL, 8.10 mmol), $PdCl_2(PhCN)_2$ (23 mg, 0.06 mmol), CuI (8 mg, 0.04 mmol), P(*t*-Bu)$_3$ (0.06 mL, 0.06 mmol) and trimethylsilylacetylene (0.6 mL, 4.05 mmol) under argon atmosphere. The reaction mixture was stirred overnight at room temperature, diluted in CH_2Cl_2, washed with NH_4Cl (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes as eluent to afford compound **18e** (208 mg, 39% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.03 (d, *J*=3.6 Hz, 1H), 6.59 (d, *J*=3.5 Hz, 1H), 2.74 (t, *J*=7.6 Hz, 2H), 1.63 (m, 2H), 1.31 (m, 6H), 0.87 (t, *J*=6.5 Hz, 3H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 148.6, 132.9, 124.2, 120.7, 98.4, 97.9, 31.8, 30.4, 28.9, 22.8, 14.3, 0.17; HRMS (APPI-TOF) *m*/*z* calcd for $C_{15}H_{24}SSi$ $[M+H]^+$: 265.1441, found 265.1441. FT IR (ATR): 3308m, 2927s, 2855m, 2107w, 1459m, 1378w, 799s.

*4.2.7. 2-Ethynyl-5-hexylthiophene (**19e**).* A 25 mL round bottom flask equipped with a magnetic stir bar was charged with **18e** (350 mg, 1.32 mmol), KOH (371 mg, 6.62 mmol), THF (3.0 mL), MeOH (3.0 mL) and water (1.0 mL). The reaction mixture was stirred for 2 h, diluted with CH_2Cl_2, washed with water (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes as eluent to afford compound **19e** (223 mg, 74% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.07 (d, *J*=3.5 Hz, 1H), 6.61 (d, *J*=3.5 Hz, 1H), 3.27 (s, 1H), 2.75 (t, *J*=7.6 Hz, 2H), 1.64 (m, 2H), 1.29 (m, 6H), 0.88 (t, *J*=6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$,

100 MHz): 148.6, 133.1, 123.9, 119.2, 80.4, 77.5, 31.5, 30.1, 28.7, 22.6, 14.1; HRMS (APPI-TOF) *m/z* calcd for $C_{12}H_{16}S$ $[M+H]^+$: 193.1045, found 193.0973. FT IR (ATR): 3311m, 2927s, 2858s, 2108w, 1664m, 1466m, 1412m, 1295w, 836m.

Compound **5**. See the general procedure for addition of C_{60} to terminal alkynes. The materials used were **19e** (40 mg, 0.21 mmol), C_{60} (300 mg, 0.42 mmol), THF (83 mL), LHMDS (0.5 mL, 0.42 mmol) and TFA (0.3 mL, 4.16 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 10% CS_2/hexanes as eluents to afford compound **5** (45 mg, 24% yield) as a brown powder: mp>300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.39 (d, *J*=3.7 Hz, 1H), 7.11 (s, 1H), 6.80 (d, *J*=3.3 Hz, 1H), 2.89 (t, *J*=7.5 Hz, 2H), 1.74 (m, 2H), 1.36 (m, 6H), 0.90 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 151.6, 151.3, 149.3, 147.7, 147.6, 146.7, 146.4, 146.3 (2C), 145.9, 145.8, 145.7, 145.5, 145.4, 144.8, 144.6, 143.3, 142.7, 142.6, 142.2, 142.1 (2C), 141.9, 141.7, 140.4 (2C), 136.1, 135.3 (28 signals from sp^2-C in the C_{60} core), 133.4 (–C═, Ar), 124.4 (–C═, Ar), 119.5 (–C≡), 95.1 (–C≡), 61.7 (CH in the C_{60} core), 55.4 (quaternary sp^3-C in the C_{60} core), 31.6 (2C, CH_2), 30.3 (CH_2), 28.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3); HRMS (APPI-TOF) *m/z* calcd for $C_{72}H_{16}S$ $[M+H]^+$: 913.1045, found 913.1021.FT IR (ATR): 2914m, 2844m, 2325w, 1670w, 1425m, 1180m, 1034m, 794s, 767s.

*4.2.8. 2-((Triisopropylsilyl)ethynyl)-9H-carbazole (**14**).* A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 9*H*-carbazol-2-yl trifluoromethanesulfonate (500 mg, 1.59 mmol), DMF (8 mL), triethylamine (0.9 mL, 6.34 mmol), $PdCl_2(PPh_3)_2$ (45 mg, 0.06 mmol), CuI (6 mg, 0.03 mmol) and triisopropylsilylacetylene (0.7 mL, 3.17 mmol) under argon atmosphere. The reaction mixture was stirred overnight at 100 °C, cooled to room temperature, diluted in CH_2Cl_2, washed with NH_4Cl (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 6% EtOAc/hexanes as eluents to afford compound **14** (455 mg, 83% yield) as a colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.99 (d, *J*=8.1 Hz, 1H), 7.93 (d, *J*=8.1 Hz, 1H), 7.79 (s, 1H), 7.45 (s, 1H), 7.36 (q, *J*=6.5 Hz, 2H), 7.29 (d, *J*=8.1 Hz, 1H), 7.20 (t, *J*=8.1 Hz, 1H), 1.17 (s, 21H); ^{13}C NMR ($CDCl_3$, 100 MHz): 140.2, 138.9, 126.3, 123.7, 123.3, 122.9, 120.5, 120.4, 120.0, 119.7, 114.2, 110.7, 108.3, 89.9, 18.7, 11.4; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{29}NSi$ $[M+H]^+$: 348.2142, found 348.2147. FT IR (ATR): 2961w, 2866w, 2149w, 1460w, 1325w, 1264s.

*4.2.9. 9-Octyl-2-((triisopropylsilyl)ethynyl)-9H-carbazole (**15**).* A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **14** (800 mg, 2.30 mmol), DMF (6 mL) and NaH (110 mg, 4.60 mmol) under argon atmosphere. The reaction mixture was cooled to 0 °C, stirred for 30 min and octyl iodide (0.9 mL, 4.83 mmol) was then added. The temperature was raised to room temperature and the mixture was stirred overnight. MeOH was carefully added, followed by H_2O and the mixture was diluted with CH_2Cl_2. The organic layer was washed with H_2O (4×), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel with hexanes to 2% EtOAc/hexanes as eluents to afford compound **15** (834 mg, 79% yield) as a colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.97 (d, *J*=8.1 Hz, 1H), 7.91 (d, *J*=8.1 Hz, 1H), 7.46 (s, 1H), 7.38 (t, *J*=7.6 Hz, 1H), 7.33 (d, *J*=7.6 Hz, 1H), 7.26 (d, *J*=7.6 Hz, 1H), 7.16 (t, *J*=7.4 Hz, 1H), 4.11 (t, *J*=7.2 Hz, 2H), 1.74 (m, 2H), 1.18 (m, 33H), 0.85 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): 141.1, 139.8, 126.0, 123.1, 122.9, 122.5, 120.5, 120.2, 120.0, 119.0, 112.1, 108.8, 108.7, 89.5, 42.9, 31.8, 31.6, 29.3, 29.2, 28.9, 27.2, 22.7, 18.8, 14.1, 11.5; HRMS (APPI-TOF) *m/z* calcd for $C_{31}H_{47}NSi$ $[M+H]^+$: 460.3394, found 460.3397. FT IR (ATR): 2926s, 2863s, 2148m, 1599m, 1456s, 1326s, 882m.

*4.2.10. 2-Ethynyl-9-octyl-9H-carbazole(**16**).* A 10 mL round bottom flask equipped with a magnetic stir bar was charged with **15** (500 mg, 1.09 mmol), tetrabutylammonium fluoride (1.6 mL, 1.63 mmol) and THF (5.4 mL). The reaction mixture was stirred for 30 min, diluted with CH_2Cl_2, washed with water (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 1% EtOAc/hexanes as eluents to afford compound **16** (308 mg, 93% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.01 (d, *J*=7.9 Hz, 1H), 7.96 (d, *J*=7.9 Hz, 1H), 7.51 (s, 1H), 7.42 (t, *J*=7.5 Hz, 1H), 7.32 (t, *J*=8.7 Hz, 2H), 7.18 (t, *J*=7.4 Hz, 1H), 4.14 (t, *J*=7.3 Hz, 2H), 3.11 (s, 1H), 1.76 (m, 2H), 1.19 (m, 10H), 0.84 (t, *J*=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 141.0, 139.8, 126.2, 123.3, 122.8, 122.3, 120.6, 120.2, 119.1, 118.6, 112.5, 108.8, 85.1, 76.5, 43.0, 31.8, 29.3, 29.1, 28.9, 27.2, 22.6, 14.1; HRMS (APPI-TOF) *m/z* calcd for $C_{22}H_{25}N$ $[M+H]^+$: 304.2060, found 304.2060. FT IR (ATR): 3308m, 3290m, 2954m, 2926s, 2854m, 2104w, 1598w, 1455s, 1441m, 1326s.

Compound **6**. See the general procedure for addition of C_{60} to terminal alkynes. The materials used were **16** (50 mg, 0.17 mmol), C_{60} (238 mg, 0.33 mmol), THF (66 mL), LHMDS (0.4 mL, 0.33 mmol) and TFA (0.3 mL, 4.16 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 30% CS_2/hexanes as eluents to afford compound **6** (105 mg, 62% yield) as a brown powder: mp>300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): 8.16 (q, *J*=7.7 Hz, 2H), 7.86 (s, 1H), 7.70 (d, *J*=6.8 Hz, 1H), 7.49 (m, 2H), 7.25 (m, 2H), 4.37 (s, 2H), 1.96 (s, 2H), 1.27 (m, 10H), 0.87 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 152.0, 151.9, 147.9, 147.1, 146.9, 146.7, 146.6, 146.5, 146.2, 146.1, 145.9, 145.8, 145.7, 145.6, 145.1, 145.0, 144.8, 143.5, 142.8, 142.4, 142.3 (2C), 142.0, 141.9, 141.5, 140.7, 140.6, 140.3 (28 signals from sp^2-C in the C_{60} core), 126.7 (–C═, Ar), 123.3 (–C═, Ar), 122.7 (–C═, Ar), 121.1 (–C═, Ar), 120.8 (–C═, Ar), 119.5 (–C═, Ar), 119.2 (–C═, Ar), 112.8 (–C═, Ar), 110.0 (–C═, Ar), 109.2 (–C≡), 85.3 (–C≡), 62.3 (CH in the C_{60} core), 55.7 (quaternary sp^3-C in the C_{60} core), 43.6 (CH_2), 32.1 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 27.6 (CH_2), 22.9 (CH_2), 14.4 (CH_3); HRMS (APPI-TOF) *m/z* calcd for $C_{82}H_{25}N$ $[M+H]^+$: 1024.2060, found 1024.2057. FT IR (ATR): 2916m, 2846m, 2213w, 1719w, 1595m, 1322s, 1119m, 998s, 808s, 763s.

*4.2.11. 1-Iodo-4-(octyloxy)benzene (**17b**).* A 50 mL round bottom flask equipped with a magnetic stir bar was charged with 4-iodophenol (2.00 g, 6.80 mmol), DMF (22.7 mL), octyl bromide (1.8 mL, 10.2 mmol) and K_2CO_3 (2.8 g, 20.5 mmol). The temperature was raised to 80 °C and the solution was stirred overnight. The reaction mixture was diluted with CH_2Cl_2, the organic layer was washed with H_2O (4×), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel with hexanes as eluent to afford the desired compound **17b** (3.14 g, 98% yield) as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.54 (d, *J*=8.9 Hz, 2H), 6.66 (d, *J*=9.4 Hz, 2H), 3.91 (t, *J*=6.5 Hz, 2H), 1.76 (m, 2H), 1.33 (m, 10H), 0.89 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 158.2, 132.1 (2C), 116.2 (2C), 112.5, 68.2, 31.8, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1; HRMS (APPI-TOF) *m/z* calcd for $C_{14}H_{21}IO$ $[M]^{*+}$: 332.0632, found 332.0632. FT IR (ATR): 2923m, 2853m, 1586w, 1485s, 1281m, 1240s, 1173m, 998w, 817s.

*4.2.12. 1-(Octyloxy)-4-((trimethylsilyl)ethynyl)benzene (**18b**).* A 50 mL round bottom flask equipped with a magnetic stir bar was charged with **17b** (2.5 g, 7.53 mmol), THF (38 mL), triethylamine (4.14 mL, 30.1 mmol), $PdCl_2(PPh_3)_2$ (106 mg, 0.15 mmol), CuI (28 mg, 0.15 mmol) and trimethylsilylacetylene (2.13 mL, 15.1 mmol) under argon atmosphere. The reaction mixture was stirred overnight at room temperature, diluted in CH_2Cl_2, washed with NH_4Cl (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes as eluent to afford the desired compound **18b** (1.91 g, 84% yield) as dark orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.38 (d, *J*=8.8 Hz, 2H), 6.79 (d, *J*=8.8 Hz, 2H), 3.93 (t, *J*=6.6 Hz, 2H), 1.76 (m, 2H), 1.32 (m, 10H), 0.89 (m, 3H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$,

100 MHz): 159.3, 133.4 (2C), 115.0, 114.3 (2C), 105.3, 92.2, 68.0, 31.8, 29.3, 29.2, 29.1, 26.0, 22.7, 14.1, 0.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{19}H_{30}OSi$ $[M+H]^+$: 303.2140, found 303.2140. FT IR (ATR): 2955w, 2926w, 2870w, 2155w, 1604w, 1505m, 1245s, 862m, 820s, 758m.

*4.2.13. 1-Ethynyl-4-(octyloxy)benzene (**19b**).* A 25 mL round bottom flask equipped with a magnetic stir bar was charged with **18b** (1.5 g, 4.96 mmol), KOH (1.13 g, 19.8 mmol), THF (6.0 mL), MeOH (6.0 mL) and water (1.0 mL). The reaction mixture was stirred for 2 h, diluted with CH_2Cl_2, washed with water (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes as eluent to afford compound **19b** (1.09 g, 96% yield) as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.41 (d, *J*=8.9 Hz, 2H), 6.82 (d, *J*=8.9 Hz, 2H), 3.93 (t, *J*=6.6 Hz, 2H), 2.98 (s, 1H), 1.77 (m, 2H), 1.32 (m, 10H), 0.89 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 159.5, 133.5 (2C), 114.4 (2C), 113.8, 83.8, 75.6, 68.0, 31.8, 29.3, 29.2, 29.1, 26.0, 22.7, 14.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{22}O$ $[M+H]^+$: 231.1740, found 231.1740. FT IR (ATR): 2920m, 2850m, 2346w, 1603m, 1505s, 1287m, 1240s, 1168s, 820s, 764m.

Compound **2**. See the general procedure for addition of C_{60} to terminal alkynes. The materials used were **19b** (50 mg, 0.22 mmol), C_{60} (313 mg, 0.43 mmol), THF (87 mL), LHMDS (0.5 mL, 0.43 mmol) and TFA (0.3 mL, 4.16 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** (125 mg, 60% yield) as a brown powder: mp>300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.74 (d, *J*=8.5 Hz, 2H), 7.13 (s, 1H), 6.99 (d, *J*=8.8 Hz, 2H), 4.04 (t, *J*=6.6 Hz, 2H), 1.84 (m, 2H), 1.32 (m, 10H), 0.91 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 159.8, 151.8, 147.7, 146.8, 146.5, 146.3, 145.9, 145.8, 145.7, 145.5, 145.4, 144.8, 144.6, 143.3, 142.7 (2C), 142.2, 142.1, 142.0, 141.9, 141.7, 141.6, 140.4, 140.3, 136.2, 135.2, 133.7 (27 signals from sp^2-C in the C_{60} core), 114.7 (–C═, Ar), 114.1 (–C═, Ar), 90.9 (–C═, Ar), 83.7 (–C≡), 68.2 (–C≡), 61.9 (CH in the C_{60} core), 31.8 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 14.1 (CH_3); HRMS (APPI-TOF) *m*/*z* calcd for $C_{76}H_{22}O$ $[M+H]^+$: 951.1743, found 951.1742. FT IR (ATR): 2903w, 2843w, 2328w, 2200w, 1724w, 1597m, 1504s, 1238s, 1167s, 1030s, 823s, 763m.

*4.2.14. 1-Bromo-2-ethynylbenzene (**22**).* A 50 mL round bottom flask equipped with a magnetic stir bar was charged with 1-bromo-2-iodobenzene (2.0 g, 7.07 mmol), THF (35 mL), triethylamine (3.88 mL, 28.3 mmol), $PdCl_2(PPh_3)_2$ (99 mg, 0.14 mmol), CuI (27 mg, 0.14 mmol) and trimethylsilylacetylene (1.05 mL, 7.42 mmol) under argon atmosphere. The reaction mixture was stirred overnight at room temperature, diluted in CH_2Cl_2, washed with NH_4Cl (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes as eluent to afford the desired compound **22** (1.51 g, 84% yield) as dark orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.58 (d, *J*=8.1 Hz, 1H), 7.49 (dd, J_1=7.76 Hz, J_2=1.42 Hz, 1H), 7.24 (t, *J*=7.6 Hz, 1H), 7.16 (t, *J*=7.6 Hz, 1H), 0.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 133.8, 132.5, 129.7, 127.0, 125.9, 103.2, 99.8, 0.15; HRMS (APPI-TOF) *m*/*z* calcd for $C_{11}H_{13}BrSi$ $[M]^{*+}$: 251.9954, found 251.9970. FT IR (ATR): 2959w, 2162w, 1465m, 1248m, 1045w, 860s, 836s.

*4.2.15. 1-Iodo-2-ethynylbenzene (**23**).* A 50 mL round bottom flask equipped with a magnetic stir bar was charged with **22** (300 mg, 1.19 mmol), THF (11.9 mL) and Et_2O (11.9 mL). The temperature was cooled to −78 °C and *t*-BuLi (1.4 mL, 2.37 mmol) was added slowly. The reaction mixture was stirred for one hour and 1,2-diiodoethane was added (500 mg, 1.78 mmol). The reaction mixture was stirred overnight at room temperature, diluted in CH_2Cl_2, washed with H_2O (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes as eluent to afford the desired compound **23** (326 mg, 92% yield) as dark orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.84 (d, *J*=7.8 Hz, 1H), 7.47 (d, *J*=7.12 Hz, 1H), 7.28 (t, *J*=7.1 Hz, 1H), 6.97 (t, *J*=7.4 Hz, 1H), 0.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 138.9, 132.9, 129.8, 129.7, 128.4, 127.9, 106.7, 101.4, 0.18; HRMS (APPI-TOF) *m*/*z* calcd for $C_{11}H_{13}ISi$ $[M+H]^+$: 300.9904, found 300.9902. FT IR (ATR): 2957w, 2160w, 1458m, 1247m, 1016m, 858s, 836s.

*4.2.16. 4-(Octyloxy)-1-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)-benzene (**24b**).* A 25 mL round bottom flask equipped with a magnetic stir bar was charged with **23** (300 mg, 0.99 mmol), THF (5 mL), triethylamine (0.6 mL), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), CuI (4 mg, 0.02 mmol) and **19b** (460 mg, 2 mmol) under argon atmosphere. The reaction mixture was stirred overnight, diluted in CH_2Cl_2, washed with NH_4Cl (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 7% CH_2Cl_2/hexanes as eluents to afford compound **24b** (341 mg, 85% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.5 (m, 4H), 7.31 (t, *J*=7.6 Hz, 1H), 7.25 (t, *J*=5.7 Hz, 1H), 6.87 (d, *J*=8.8 Hz, 2H), 3.97 (t, *J*=6.6 Hz, 2H), 1.79 (m, 2H), 1.45 (m, 2H), 1.29 (m, 8H), 0.89 (m, 3H), 0.29 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 133.4, 133.3, 131.8, 128.7, 126.7, 125.5, 115.4, 114.6, 103.8, 98.6, 93.9, 87.1, 68.3, 32.1, 29.5, 29.4, 22.9, 14.4, 0.24; HRMS (APPI-TOF) *m*/*z* calcd for $C_{27}H_{34}OSi$ $[M+H]^+$: 403.2452, found 403.2456. FT IR (ATR): 2953w, 2921m, 2853w, 2161w, 1602m, 1505m, 1287m, 1246s, 1175m, 997m, 842s, 829s, 754s.

*4.2.17. 1-Ethynyl-2-((4-(octyloxy)phenyl)ethynyl)benzene (**25b**).* A 10 mL round bottom flask equipped with a magnetic stir bar was charged with **24b** (340 mg, 0.84 mmol), KOH (190 mg, 3.38 mmol), THF (1.1 mL), MeOH (1.1 mL) and water (0.5 mL). The reaction mixture was stirred for 15 min, diluted with CH_2Cl_2, acidified with HCl 10%, washed with water (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 7% CH_2Cl_2/hexanes as eluents to afford compound **25b** (236 mg, 85% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.5 (m, 4H), 7.31 (t, *J*=7.6 Hz, 1H), 7.25 (t, *J*=5.7 Hz, 1H), 6.87 (d, *J*=8.8 Hz, 2H), 3.97 (t, *J*=6.6 Hz, 2H), 3.35 (s, 1H), 1.79 (m, 3H), 1.45 (m, 2H), 1.29 (m, 8H), 0.89 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 133.5, 132.8, 131.8, 128.7, 127.7, 126.9, 124.6, 114.8, 86.8, 85.1, 82.6, 81.2, 68.3, 32.1, 29.6, 29.5, 29.4, 26.3, 22.9, 14.3; HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{26}O$ $[M+H]^+$: 331.2056, found 331.2058. FT IR (ATR): 3284w, 2936w, 2919w, 2850w, 1605m, 1509s, 1282m, 1247s, 998m, 836s, 763m.

Compound **10**. See the general procedure for addition of C_{60} to terminal alkynes. The materials used were compound **25b** (70 mg, 0.21 mmol), C_{60} (305 mg, 0.42 mmol), THF (85 mL), LHMDS (1.0 mL, 0.85 mmol) and TFA (0.3 mL, 4.2 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 30% CS_2/hexanes as eluents to afford compound **10** (73 mg, 33% yield) as a brown powder. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.81 (m, 1H), 7.65 (m, 1H), 7.52 (d, *J*=8.7 Hz, 2H), 7.43 (t, *J*=3.6 Hz, 2H), 7.18 (s, 1H), 6.73 (d, *J*=8.7 Hz, 2H), 3.86 (t, *J*=6.5 Hz, 2H), 1.71 (m, 2H), 1.39 (m, 2H), 1.26 (m, 8H), 0.87 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 159.4, 151.6, 151.4, 147.6, 147.4, 146.7, 146.5, 146.4 (2C), 146.2 (2C), 145.8, 145.7, 145.6, 145.4, 145.3, 144.7, 144.5, 143.2, 142.6, 142.5, 142.1, 142.0 (2C), 141.9, 141.7, 141.6, 140.4, 136.1, 135.3 (30 signals from sp^2-C in the C_{60} core), 133.3 (–C═, Ar), 133.2 (–C═, Ar), 132.0 (–C═, Ar), 131.6 (–C═, Ar), 128.7 (–C═, Ar), 127.8 (–C═, Ar), 127.3 (–C═, Ar), 124.9 (–C═, Ar), 114.9 (–C═, Ar), 114.6 (–C═, Ar), 96.2 (–C═, Ar), 94.5 (–C≡), 87.2 (–C≡), 82.7 (–C≡), 68.0 (–C≡), 62.0 (CH in the C_{60} core), 31.9 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 26.4 (CH_2), 23.1 (CH_2), 14.5 (CH_3); HRMS (APPI-TOF) *m*/*z* calcd for $C_{84}H_{26}O$ $[M+H]^+$: 1051.2056, found 1051.2060. FT IR (ATR): 2916w, 2849w, 2050w, 1601w, 1506m, 1246s, 1014m, 946w, 827s, 756s.

*4.2.18. 4-(Octyloxy)-1-((4-((trimethylsilyl)ethynl)phenyl)ethynyl)-benzene **(20b)**.* A 10 mL round bottom flask equipped with a magnetic stir bar was charged with 1-iodo-4-[2-(trimethylsilyl)ethynyl]-benzene (300 mg, 1.00 mmol), THF (5.0 mL), triethylamine (0.6 mL), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), CuI (4 mg, 0.02 mmol) and **19b** (460 mg, 2.00 mmol) under argon atmosphere. The reaction mixture was stirred overnight, diluted in CH_2Cl_2, washed with NH_4Cl (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 8% CH_2Cl_2/hexanes as eluents to afford compound **20b** (393 mg, 97% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.43 (m, 6H), 6.86 (d, *J*=8.8 Hz, 2H), 3.97 (t, *J*=6.5 Hz, 2H), 1.79 (m, 2H), 1.46 (m, 2H), 1.29 (m, 8H), 0.89 (m, 3H), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 133.4, 133.2, 132.1, 131.4, 127.4, 121.8, 115.6, 114.8, 114.7, 113.8, 105.9, 104.9, 96.2, 32.0, 31.9, 29.6, 29.5, 29.4, 29.3, 26.3, 22.9, 11.2, 0.24; HRMS (ESI-TOF) *m*/*z* calcd for $C_{27}H_{34}OSi$ $[M+H]^+$: 403.2452, found 403.2454. FT IR (ATR): 2954w, 2920w, 2851w, 2153w, 1596w, 1515m, 1248m, 864m, 830s, 757m.

*4.2.19. 1-Ethynyl-4-((4-(octyloxy)phenyl)ethynyl)benzene(**21b**).* A 10 mL round bottom flask equipped with a magnetic stir bar was charged with compound **20b** (350 mg, 0.87 mmol), KOH (195 mg, 3.48 mmol), THF (1.1 mL), MeOH (1.1 mL) and water (0.5 mL). The reaction mixture was stirred for 15 min, diluted with CH_2Cl_2, acidified with HCl 10%, washed with water (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 7% CH_2Cl_2/hexanes as eluents to afford compound **21b** (269 mg, 94% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.44 (m, 6H), 6.86 (d, *J*=8.6 Hz, 2H), 3.95 (t, *J*=6.7 Hz, 2H), 3.15 (m, 1H), 1.77 (m, 2H), 1.44 (m, 2H), 1.29 (m, 8H), 0.89 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 159.4, 133.1, 132.0, 131.3, 124.2, 121.4, 114.7, 114.5, 91.7, 87.5, 83.4, 78.7, 68.0, 31.9, 29.4, 29.2, 28.1, 26.0, 22.7, 14.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{26}O$ $[M+H]^+$: 331.2056, found 331.2055. FT IR (ATR): 3269w, 2921m, 2852w, 1607w, 1514m, 1250m, 1109w, 1024w, 824s.

Compound **7**. See the general procedure for addition of C_{60} to terminal alkynes. The materials used were compound **21b** (70 mg, 0.21 mmol), C_{60} (305 mg, 0.42 mmol), THF (85 mL), LHMDS (0.48 mL, 0.42 mmol) and TFA (0.3 mL, 3.9 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 30% CS_2/hexanes as eluents to afford compound **7** (97 mg, 44% yield) as a brown powder. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.79 (d, *J*=8.1 Hz, 1H), 7.62 (d, *J*=8.1 Hz, 1H), 7.50 (d, *J*=8.5 Hz, 1H), 7.45 (m, 3H), 7.14 (s, 1H), 6.90 (d, *J*=8.5 Hz, 1H), 6.87 (d, *J*=8.9 Hz, 1H), 3.98 (m, 2H), 1.79 (m, 2H), 1.46 (m, 2H), 1.30 (m, 8H), 0.89 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 151.8, 151.7, 151.3, 147.7, 147.3, 146.7, 146.5 (2C), 146.3, 145.9, 145.8, 145.7, 145.5 (2C), 145.4, 144.8, 144.6, 143.3, 143.1, 142.7, 142.6, 142.2, 142.1, 142.0, 141.9, 141.8, 141.7, 140.5, 140.4, 140.3, 136.1, 135.3 (32 signals from sp^2-C in the C_{60} core), 133.2 (–C═, Ar), 133.1 (–C═, Ar), 132.1 (–C═, Ar), 132.0 (–C═, Ar), 131.6 (–C═, Ar), 131.3 (–C═, Ar), 93.8 (–C═, Ar), 91.6 (–C═, Ar), 87.7 (–C≡), 83.4 (–C≡), 78.7 (–C≡), 68.1 (–C≡), 61.8 (CH in the C_{60} core), 33.6 (CH_2), 31.8 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 26.0 (CH_2), 22.7 (CH_2), 14.1 (CH_3); HRMS (APPI-TOF) *m*/*z* calcd for $C_{84}H_{26}O$ $[M+H]^+$: 1051.2056, found 1051.2069. FT IR (ATR): 3269w, 2920m, 2849, 1595w, 1511m, 1242m, 1106w, 826s.

*4.2.20. 9-Octyl-2-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)-9H-carbazole (**24d**).* A 10 mL round bottom flask equipped with a magnetic stir bar was charged with **23** (371 mg, 1.24 mmol), THF (4.1 mL), triethylamine (0.5 mL), $PdCl_2(PPh_3)_2$ (12 mg, 0.02 mmol), CuI (3 mg, 0.02 mmol) and compound **16** (250 mg, 0.83 mmol) under argon atmosphere. The reaction mixture was stirred overnight, diluted in CH_2Cl_2, washed with NH_4Cl (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 8% CH_2Cl_2/hexanes as eluents to afford the desired compound **24d** (198 mg, 51% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.05 (t, *J*=7.0 Hz, 2H), 7.59 (s, 1H), 7.56 (d, *J*=6.9 Hz, 1H), 7.52 (d, *J*=7.0 Hz, 1H), 7.44 (t, *J*=7.5 Hz, 2H), 7.35 (d, *J*=8.1 Hz, 1H), 7.23 (m, 3H), 4.22 (t, *J*=7.3 Hz, 2H), 1.82 (m, 2H), 1.22 (m, 10H), 0.85 (t, *J*=6.9 Hz, 3H), 0.32 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 141.1, 132.3, 128.2, 127.7, 126.1, 125.4, 123.0, 122.8, 122.5, 120.6, 120.2, 119.1, 111.9, 108.8, 95.0, 43.2, 31.8, 29.4, 29.2, 29.0, 27.3, 22.6, 14.1, 0.12; HRMS (APPI-TOF) *m*/*z* calcd for $C_{33}H_{37}NSi$ $[M+H]^+$: 476.2768, found 476.2770. FT IR (ATR): 3060w, 2926s, 2854m, 2208w, 2159w, 1598m, 1471m, 1326s, 1248m, 864s, 842s, 759s.

*4.2.21. 2-((2-Ethynylphenyl)ethynyl)-9-octyl-9H-carbazole (**25d**).* A 10 mL round bottom flask equipped with a magnetic stir bar was charged with compound **24d** (190 mg, 0.40 mmol), KOH (90 mg, 1.60 mmol), THF (1.0 mL), MeOH (1.0 mL) and water (0.5 mL). The reaction mixture was stirred for 15 min, diluted with CH_2Cl_2, acidified with HCl 10%, washed with water (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 8% CH_2Cl_2/hexanes as eluents to afford compound **25d** (183 mg, quantitative yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.06 (d, *J*=7.8 Hz, 1H), 8.03 (d, *J*=8.1 Hz, 1H), 7.64–7.52 (br m, 3H) 7.46 (m, 2H), 7.37 (d, *J*=8.2 Hz, 1H), 7.32 (t, *J*=7.6 Hz, 1H), 7.29–7.19 (br m, 2H), 4.24 (t, *J*=7.0 Hz, 2H), 3.40 (s, 1H), 1.84 (m, 2H), 1.40–1.16 (br m, 10H), 0.85 (t, *J*=6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 141.1, 139.9, 132.6, 131.7, 128.6, 127.7, 126.6, 126.2, 124.5, 123.1, 122.7, 122.5, 120.6, 120.2, 119.7, 119.1, 112.0, 108.8, 95.2, 87.4, 82.4, 81.1, 43.1, 31.8, 29.3, 29.2, 28.9, 27.3, 22.6, 14.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{30}H_{29}N$ $[M+H]^+$: 404.2373, found 404.2376. FT IR (ATR): 3286w, 3058w, 2924s, 2852m, 2206w, 1598m, 1454s, 1325s, 1225m, 850m, 814m, 756s.

Compound **12**. See the general procedure for addition of C_{60} to terminal alkynes. The materials used were compound **25d** (100 mg, 0.25 mmol), C_{60} (357 mg, 0.49 mmol), THF (99 mL), LHMDS (4.5 mL, 4.5 mmol) and TFA (0.4 mL, 4.9 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 40% CS_2/hexanes as eluent to afford compound **12** (33 mg, 12% yield) as a brown powder. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.98 (d, *J*=7.9 Hz, 1H), 7.92 (d, *J*=7.6 Hz, 1H), 7.86 (m, 1H), 7.75 (m, 1H), 7.67 (s, 1H), 7.53 (d, *J*=7.9 Hz, 1H), 7.48 (m, 2H), 7.42 (m, 1H), 7.32 (d, *J*=8.3 Hz, 1H), 7.18 (m, 2H), 4.18 (t, *J*=7.3 Hz, 2H), 1.82 (m, 2H), 1.25 (m, 10H), 0.84 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 151.5, 151.3, 146.5, 146.3, 146.2, 146.1, 145.7, 145.6, 145.3 (2C), 144.6, 144.4, 143.1, 143.0, 142.5, 142.0, 141.9, 141.8, 141.6, 141.0, 140.2, 139.9, 135.9, 135.2 (24 signals from sp^2-C in the C_{60} core), 131.9 (–C═, Ar), 131.7 (–C═, Ar), 128.8 (2C, –C═, Ar), 128.1 (–C═, Ar), 127.2 (–C═, Ar), 126.6 (–C═, Ar), 126.2 (–C═, Ar), 125.3 (–C═, Ar), 122.3 (–C═, Ar), 120.6 (–C═, Ar), 120.4 (–C═, Ar), 119.2 (–C═, Ar), 111.9 (–C═, Ar), 108.7 (–C≡), 96.5 (–C≡), 95.8 (–C≡), 88.1 (–C≡), 62.0 (CH in the C_{60}), 43.2 (CH_2), 31.9 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 29.1 (CH_2), 27.4 (CH_2), 22.7 (CH_2), 14.2 (CH_3); HRMS (APPI-TOF) *m*/*z* calcd for $C_{90}H_{29}N$ $[M+H]^+$: 1124.2373, found 1124.2375. FT IR (ATR): 2917s, 2847s, 2203w, 1596m, 1458s, 1324s, 1181m, 810s, 754s.

*4.2.22. 9-Octyl-2-((4-((trimethylsilyl)ethynyl)phenyl)ethynyl)-9H-carbazole(**20d**).* A 10 mL round bottom flask equipped with a magnetic stir bar was charged with 1-iodo-4-[2-(trimethylsilyl)ethynyl]benzene (312 mg, 1.04 mmol), THF (3.5 mL), triethylamine (0.4 mL), $PdCl_2(PPh_3)_2$ (10 mg, 0.01 mmol), CuI (3 mg, 0.01 mmol) and compound **16** (210 mg, 0.69 mmol) under argon atmosphere. The reaction mixture was stirred overnight, diluted in CH_2Cl_2, washed with NH_4Cl (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 8%

CH_2Cl_2/hexanes as eluents to afford compound **20d** (215 mg, 66% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.06 (d, *J*=7.8 Hz, 1H), 8.03 (d, *J*=8.2 Hz, 1H), 7.57 (s, 1H), 7.51 (d, *J*=8.2 Hz, 2H), 7.47 (m, 3H), 7.38 (d, *J*=7.8 Hz, 2H), 7.22 (t, *J*=7.5 Hz, 1H), 4.25 (t, *J*=7.2 Hz, 2H), 1.85 (m, 2H), 1.27 (m, 10H), 0.85 (t, *J*=6.9 Hz, 3H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 141.4, 140.2, 132.2, 131.6, 126.5, 123.9, 123.4, 122.9, 122.7, 122.6, 120.9, 120.6, 119.8, 119.4, 112.2, 112.1, 109.1, 105.0, 96.5, 93.2, 88.9, 43.4, 32.1, 29.6, 29.4, 29.2, 27.6, 22.9, 14.4, 0.22; HRMS (APPI-TOF) *m*/*z* calcd for $C_{33}H_{37}NSi$ $[M+H]^+$: 476.2768, found 476.2770. FT IR (ATR): 3050w, 2917m, 2851w, 2149 m, 1599w, 1471m, 1326m, 1219m, 856s, 831s, 814s, 760s.

*4.2.23. 2-((4-Ethynylphenyl)ethynyl)-9-octyl-9H-carbazole(**21d**).* A 10 mL round bottom flask equipped with a magnetic stir bar was charged with compound **20d** (200 mg, 0.42 mmol), KOH (94 mg, 1.68 mmol), THF (1.3 mL), MeOH (1.3 mL) and water (0.5 mL). The reaction mixture was stirred for 15 min, diluted with CH_2Cl_2, acidified with HCl 10%, washed with water (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 8% CH_2Cl_2/hexanes as eluents to afford compound **21d** (170 mg, quantitative yield) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.05 (t, *J*=9.0 Hz, 2H), 7.57 (s, 1H), 7.53 (d, *J*=8.3 Hz, 2H), 7.48 (t, *J*=8.0 Hz, 3H), 7.38 (m, 2H), 7.22 (d, *J*=7.4 Hz, 1H), 4.26 (t, *J*=7.3 Hz, 2H), 3.17 (s, 1H), 1.85 (m, 2H), 1.24 (br m, 10H), 0.86 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 141.1, 139.9, 132.1, 131.4, 126.2, 124.1, 123.1, 122.5, 122.5, 121.6, 120.6, 120.3, 119.4, 119.1, 111.9, 108.8, 93.0, 88.4, 83.3, 78.8, 43.1, 31.8, 29.4, 29.2, 28.9, 27.3, 22.6, 14.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{30}H_{29}N$ $[M+H]^+$: 404.2373, found 404.2376. FT IR (ATR): 3301w, 3048w, 2917m, 2853m, 1491w, 1470m, 1325m, 844s, 831s, 813s, 766m.

Compound **9**. See the general procedure for addition of C_{60} to terminal alkynes. The materials used were **21d** (80 mg, 0.20 mmol), C_{60} (284 mg, 0.39 mmol), THF (79 mL), LHMDS (0.45 mL, 0.4 mmol) and TFA (0.3 mL, 3.9 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 30% CS_2/hexanes as eluents to afford compound **9** (130 mg, 59% yield) as a brown powder. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.10 (m, 2H), 7.83 (d, *J*=7.9 Hz, 2H), 7.71 (d, *J*=7.9 Hz, 2H), 7.64 (s, 1H), 7.44 (br m, 4H), 7.15 (s, 1H), 4.33 (t, *J*=7.2 Hz, 2H), 1.91 (m, 2H), 1.27 (br m, 10H), 0.86 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 151.4, 151.1, 147.6, 146.6, 146.4, 146.3, 146.2 (2C), 145.8, 145.7, 145.6, 145.5, 145.4, 145.3, 144.7, 144.5, 143.2, 143.0, 142.6 (2C), 142.2, 142.1, 142.0, 141.8, 141.7, 141.6, 141.0, 140.4 (2C), 139.9, 136.1, 135.2 (32 signals from sp^2-C in the C_{60} core), 132.1 (–C═, Ar), 131.7 (–C═, Ar), 126.3 (–C═, Ar), 123.2 (–C═, Ar), 122.6 (–C═, Ar), 121.9 (–C═, Ar), 120.6 (2C, –C═, Ar), 120.3 (–C═, Ar), 119.5 (–C═, Ar), 119.3 (–C═, Ar), 111.9 (–C═, Ar), 108.8 (–C═, Ar), 93.9 (–C≡), 88.8 (–C≡), 61.8 (CH in the C_{60} core), 43.2 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 27.5 (CH_2), 22.8 (CH_2), 14.2 (CH_3); HRMS (APPI-TOF) *m*/*z* calcd for $C_{90}H_{29}N$ $[M+H]^+$: 1124.2373, found 1124.2354. FT IR (ATR): 3683w, 3313w, 3051w, 2312m, 2854m, 2327m, 2202m, 1596m, 1426s, 1323s, 1180s, 832s, 808s, 763m.

*4.2.24. 1-Nitro-4-((trimethylsilyl)ethynyl)benzene (**18c**).* A 25 mL round bottom flask equipped with a magnetic stir bar was charged with 4-iodonitrobenzene (1.0 g, 4.02 mmol), THF (13 mL), triethylamine (2.2 mL, 16.1 mmol), $PdCl_2(PPh_3)_2$ (31 mg, 0.08 mmol), CuI (15 mg, 0.08 mmol) and trimethylsilylacetylene (1.1 mL, 8.03 mmol) under argon atmosphere. The reaction mixture was stirred overnight at room temperature, diluted in CH_2Cl_2, washed with NH_4Cl (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 2% acetone/hexanes as eluents to afford the desired compound **18c** (695 mg, 79% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.17 (d, *J*=8.7 Hz, 2H), 7.59 (d, *J*=8.5 Hz, 2H), 0.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 147.4, 132.9, 130.3, 123.8, 102.9, 100.9, 0.30; HRMS (APPI-TOF) *m*/*z* calcd for $C_{11}H_{13}NO_2Si$ $[M+NH_4]^+$: 237.1054, found 237.1060. FT IR (ATR): 2952w, 2160w, 1591w, 1516m, 1345m, 1247m, 1106w, 837s, 763m.

*4.2.25. 1-Ethynyl-4-nitrobenzene (**19c**).* A 25 mL round bottom flask equipped with a magnetic stir bar was charged with **18c** (500 mg, 2.28 mmol), KOH (512 mg, 9.12 mmol), THF (6.5 mL), MeOH (6.5 mL) and water (0.5 mL). The reaction mixture was stirred for 15 min, diluted with CH_2Cl_2, acidified with HCl 10%, washed with water (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 2% acetone/hexanes as eluents to afford product **19c** (243 mg, 73% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.20 (d, *J*=8.2 Hz, 2H), 7.64 (d, *J*=8.8 Hz, 2H), 3.36 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 132.9, 128.9, 123.6, 82.3, 81.6. Compound **19c** was not observed by mass spectrometry analysis. FT IR (ATR): 3247m, 3105w, 2105w, 1591m, 1506m, 1339m, 1287m, 1105w, 964w, 850s.

Compound **3**. See the general procedure for addition of C_{60} to terminal alkynes. The materials used were compound **19c** (30 mg, 0.20 mmol), C_{60} (294 mg, 0.41 mmol), THF (82 mL), LHMDS (0.51 mL, 0.41 mmol) and TFA (0.3 mL, 3.9 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 40% CS_2/hexanes as eluents to afford **3** (42 mg, 24% yield) as a brown powder. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.37 (d, *J*=8.3 Hz, 2H), 7.99 (d, *J*=8.9 Hz, 2H), 7.14 (s, 1H); ^{13}C NMR ($CDCl_3$/CS_2 1:1, 100 MHz): 151.0, 150.4, 147.7, 147.6, 147.4, 146.6, 146.5, 146.4, 146.3, 145.8, 145.6 (2C), 145.5, 145.4, 144.7, 144.5, 143.3, 143.0, 142.7, 142.6, 141.1, 141.0, 141.7 (3C), 140.5, 140.4, 135.9, 135.4 (29 signals from sp^2-C in the C_{60} core), 133.0 (–C═, Ar), 132.9 (–C═, Ar), 129.3 (–C═, Ar), 123.8 (–C═, Ar), 97.3 (–C≡), 81.6, (–C≡), 61.5 (CH in the C_{60} core), 55.1 (quaternary sp^3-C in the C_{60} core); HRMS (APPI-TOF) *m*/*z* calcd for $C_{68}H_5NO_2$ $[M+H]^+$: 868.0393, found 867.0307. FT IR (ATR): 2918w, 2849w, 2323w, 1592m, 1515m, 1340s, 1184w, 1106w, 852m.

*4.2.26. 4-Nitro-1-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)-benzene(**24c**).* A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **23** (765 mg, 2.55 mmol), THF (8.5 mL), triethylamine (0.9 mL), $PdCl_2(PPh_3)_2$ (24 mg, 0.03 mmol), CuI (6 mg, 0.03 mmol) and compound **19c** (250 mg, 1.70 mmol) under argon atmosphere. The reaction mixture was stirred overnight, diluted in CH_2Cl_2, washed with NH_4Cl (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 8% CH_2Cl_2/hexanes as eluents to afford compound **24c** (268 mg, 49% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.22 (d, *J*=8.9 Hz, 2H), 7.68 (d, *J*=8.9 Hz, 2H), 7.53 (m, 2H), 7.33 (m, 2H), 0.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 132.4, 132.2, 131.9, 130.2, 128.8, 128.3, 125.9, 124.7, 123.6, 102.9, 99.2, 93.4, 91.2; HRMS (APPI-TOF) *m*/*z* calcd for $C_{19}H_{17}NO_2Si$ $[M+H]^+$: 320.1121, found 320.1101. FT IR (ATR): 2958w, 2219w, 2157w, 1594w, 1516m, 1338s, 1248w, 837s, 755s.

*4.2.27. 1-Ethynyl-2-((4-nitrophenyl)ethynyl)benzene(**25c**).* A 10 mL round bottom flask equipped with a magnetic stir bar was charged with compound **24c** (250 mg, 0.78 mmol), KOH (176 mg, 3.13 mmol), THF (1.9 mL), MeOH (1.9 mL) and water (0.5 mL). The reaction mixture was stirred for 15 min, diluted with CH_2Cl_2, acidified with HCl 10%, washed with water (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 8% CH_2Cl_2/hexanes as eluents to afford compound **25c** (175 mg, 90% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.23 (d, *J*=6.8 Hz, 2H), 7.70 (d, *J*=6.8 Hz, 2H), 7.57 (m, 2H), 7.37 (m, 2H), 3.39 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 147.1, 132.7, 132.4, 131.9, 130.0, 128.9, 128.7, 125.0 (2C), 123.6, 92.9, 91.4,

81.8, 81.7; HRMS (APPI-TOF) *m/z* calcd for $C_{16}H_9NO_2$ $[M]^{*+}$: 247.0628, found 247.0635. FT IR (ATR): 3369m, 2218w, 1592m, 1507s, 1333s, 1305m, 1101m, 850m, 759m.

Compound **11**. See the general procedure for addition of C_{60} to terminal alkynes. The materials used were compound **25c** (50 mg, 0.20 mmol), C_{60} (292 mg, 0.41 mmol), THF (81 mL), LHMDS (0.46 mL, 0.46 mmol) and TFA (0.3 mL, 3.9 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 40% CS_2/hexanes as eluents to afford compound **11** (110 mg, 57% yield) as a brown powder. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.23 (d, *J*=8.4 Hz, 2H), 7.70 (m, 2H), 7.57 (m, 3H), 7.35 (m, 2H); ^{13}C NMR ($CDCl_3/CS_2$ 1:1, 100 MHz): 151.2, 146.5 (2C), 146.4, 145.7, 145.6, 145.5 (3C), 145.4, 144.7, 144.5, 144.2, 143.0, 142.6 (2C), 142.2, 142.1, 141.8, 141.7, 141.4, 135.2 (22 signals from sp^2-C in the C_{60} core), 134.6 (–C═, Ar), 132.4 (–C═, Ar), 132.3 (–C═, Ar), 132.2 (–C═, Ar), 129.2 (–C═, Ar), 129.0 (–C═, Ar), 128.8 (–C═, Ar), 127.6 (–C═, Ar), 127.0 (–C═, Ar), 124.7 (–C═, Ar), 124.3 (–C═, Ar), 123.6 (–C═, Ar), 120.3 (–C═, Ar), 120.0 (–C≡), 65.2 (–C≡), 61.8 (CH in the C_{60} core), 55.3 (quaternary sp^3-C in the C_{60} core); HRMS (APPI-TOF) *m/z* calcd for $C_{76}H_9NO_2$ $[M+H]^+$: 968.0706, found 968.0670. FT IR (ATR): 3300w, 2323w, 1712w, 1592m, 1513s, 1446m, 1337s, 1098w, 849m, 759m.

*4.2.28. 4-Nitro-1-((4-((trimethylsilyl)ethynyl)phenyl)ethynyl)-benzene(**20c**).* A 10 mL round bottom flask equipped with a magnetic stir bar was charged with 1-iodo-4-[2-(trimethylsilyl)ethynyl]-benzene (224 mg, 0.75 mmol), THF (3.4 mL), triethylamine (0.3 mL), $PdCl_2(PPh_3)_2$ (10 mg, 0.01 mmol), CuI (3 mg, 0.01 mmol) and compound **19c** (100 mg, 0.68 mmol) under argon atmosphere. The reaction mixture was stirred overnight, diluted in CH_2Cl_2, washed with NH_4Cl (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes to 1.5% CH_2Cl_2/hexanes as eluents to afford the desired compound **20c** (182 mg, 84% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.22 (d, *J*=9.0 Hz, 2H), 7.65 (d, *J*=8.5 Hz, 2H), 7.48 (s, 4H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 147.2, 132.4, 132.1, 131.8, 130.1, 124.2, 123.8, 122.1, 104.4, 97.2, 94.3, 89.4, 0.11; HRMS (APPI-TOF) *m/z* calcd for $C_{19}H_{17}NO_2Si$ $[M+H]^+$: 320.1101, found 320.1038. FT IR (ATR): 3255m, 2210w, 1589m, 1498s, 1334s, 1103m, 830s.

*4.2.29. 1-Ethynyl-4-((4-nitrophenyl)ethynyl)benzene(**21c**).* A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **20c** (450 mg, 1.41 mmol), KOH (316 mg, 5.60 mmol), THF (6.5 mL), MeOH (3 mL) and water (0.5 mL). The reaction mixture was stirred for 15 min, diluted with CH_2Cl_2, acidified with HCl 10%, washed with water (3×) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with CH_2Cl_2 as eluent to afford compound **21c** (330 mg, 95% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.23 (d, *J*=8.6 Hz, 2H), 7.67 (d, *J*=8.6 Hz, 2H), 7.51 (s, 4H), 3.21 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 147.1, 132.3, 132.2, 131.7, 129.9, 123.7, 123.0, 122.5, 93.9, 82.9, 79.6; HRMS (APPI-TOF) *m/z* calcd for $C_{16}H_9NO_2$ $[M+H]^+$: 248.0706, found 248.0674. FT IR (ATR): 3255m, 2210w, 1589s, 1498s, 1355s, 1104s, 838s.

Compound **8**. See the general procedure for addition of C_{60} to terminal alkynes. The materials used were compound **21c** (50 mg, 0.20 mmol), C_{60} (292 mg, 0.41 mmol), THF (81 mL), LHMDS (1.51 mL, 1.50 mmol) and TFA (0.3 mL, 3.9 mmol). The crude product was purified by flash chromatography on silica gel with hexanes to 50% CS_2/hexanes as eluents to afford compound **8** (108 mg, 55% yield) as a brown powder. ^{1}H NMR ($CDCl_3/CS_2$ 1:1, 400 MHz): 8.25 (d, *J*=8.7 Hz, 2H), 7.83 (d, *J*=8.2 Hz, 2H), 7.71 (d, *J*=8.2 Hz, 2H), 7.66 (d, *J*=7.7 Hz, 2H), 7.14 (s, 1H); ^{13}C NMR ($CDCl_3/CS_2$ 1:1, 100 MHz): 151.3, 150.9, 147.6, 147.4, 147.1, 146.6, 146.5, 146.4, 146.2, 145.8, 145.7, 145.6, 145.5 (2C), 145.3, 144.7, 144.5, 143.2, 142.7 (2C), 142.1, 142.0 (2C), 141.8, 141.7, 141.6, 140.4, 136.0, 135.2 (29 signals from sp^2-C in the C_{60} core), 133.3 (–C═, Ar), 133.2 (–C═, Ar), 131.9 (–C═, Ar), 129.8 (–C═, Ar), 123.7 (–C═, Ar), 123.4 (–C═, Ar), 122.7 (–C═, Ar), 94.7 (–C≡), 94.2 (–C≡), 89.8 (–C≡), 83.0 (–C≡), 61.7 (CH in the C_{60} core), 55.2 (quaternary sp^3-C in the C_{60} core); HRMS (APPI-TOF) *m/z* calcd for $C_{76}H_9NO_2$ $[M]^{*+}$: 967.0628, found 967.0636. FT IR (ATR): 3098w, 2920w, 2324w, 2212w, 1918w, 1589m, 1510s, 1335s, 1102m, 832s.

Compound **13**. A 50 mL round bottom flask equipped with a magnetic stir bar was charged with compound **6** (75 mg, 0.07 mmol) and THF (29 mL) under argon atmosphere. The reaction mixture was sonicated for 10 min and LHMDS (0.2 mL, 0.15 mmol) was then added at room temperature to the brownish solution formed after sonication. After the addition of LHMDS, the reaction was stirred for 5 min, quenched with benzoyl chloride (0.85 mL, 7.32 mmol) and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel with hexanes to CH_2Cl_2/CS_2/hexanes 3:1:1 as eluent to afford compound **13** (19 mg, 22% yield) as a brown powder: mp>300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): 8.50 (d, *J*=7.9, 2H), 7.99 (d, *J*=7.9 Hz, 1H), 7.78 (d, *J*=7.9 Hz, 1H), 7.73 (d, *J*=7.9 Hz, 1H), 7.62 (m, 3H), 7.48 (m, 3H), 7.33 (t, *J*=7.9 Hz, 1H), 7.22 (m, 1H), 4.09 (t, *J*=7.4 Hz, 2H), 1.72 (m, 2H), 1.25 (m, 10H), 0.84 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 151.9, 150.4, 149.6, 147.6, 147.4, 147.2 (2C), 145.9, 145.8, 145.7, 145.6 (2C), 145.2, 145.1, 144.6, 144.5 (2C), 144.4 (2C), 144.2, 144.0, 143.9, 143.6, 143.5, 143.1, 136.7 (26 signals from sp^2-C in the C_{60} core), 133.8 (–C═, Ar), 133.7 (–C═, Ar), 129.6 (–C═, Ar), 126.7 (–C═, Ar), 123.6 (–C═, Ar), 122.5 (–C═, Ar), 121.0 (–C═, Ar), 120.9 (–C═, Ar), 120.3 (–C═, Ar), 110.8 (–C═, Ar), 110.0 (–C═, Ar), 109.1 (–C═, Ar), 71.5 (C/Bz in the C_{60} core), 43.3 (CH_2), 32.2 (CH_2), 32.0 (CH_2), 29.9 (CH_2), 29.4 (CH_2), 27.5 (CH_2), 24.0 (CH_2), 14.4 (CH_3); HRMS (ESI-TOF) *m/z* calcd for $C_{89}H_{29}NO$ $[M+H]^+$: 1128.2322, found 1128.2302. FT IR (ATR): 2917s, 2848s, 1666m, 1594m, 1430s, 1324s, 1221s, 998m, 900m.

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Supplementary data

Detailed description of the experimental method, ^{1}H and ^{13}C NMR spectra for all new compounds, and a table reporting the theoretical HOMO, LUMO, HOMO/LUMO gaps and dipole moments obtained from DFT calculations for all compounds. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.03.092.

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