Research Article

Novel Terthiophene-Substituted Fullerene Derivatives as Easily Accessible Acceptor Molecules for Bulk-Heterojunction Polymer Solar Cells

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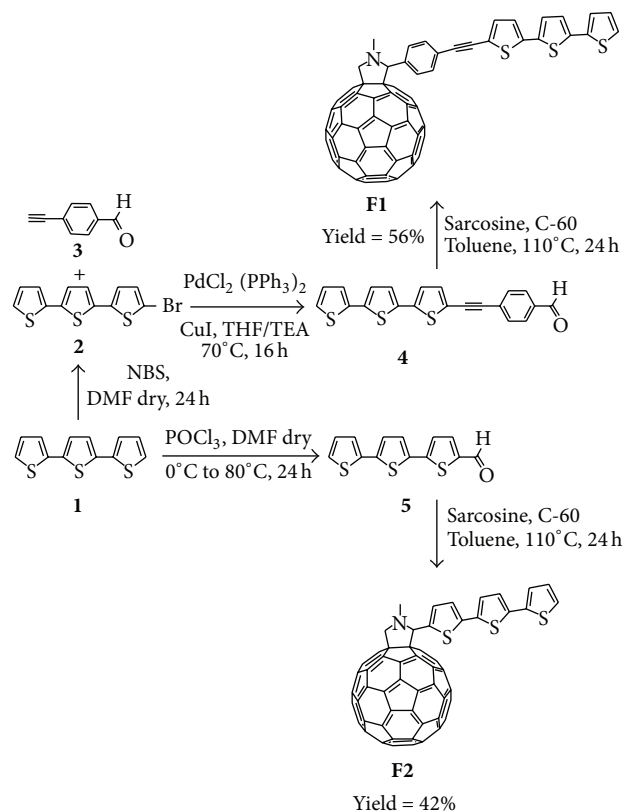Andrea Pellegrino; andrea.pellegrino@eni.com

Five fulleropyrrolidines and methanofullerenes, bearing one or two terthiophene moieties, have been prepared in a convenient way and well characterized. These novel fullerene derivatives are characterized by good solubility and by better harvesting of the solar radiation with respect to traditional PCBM. In addition, they have a relatively high LUMO level and a low band gap that can be easily tuned by an adequate design of the link between the fullerene and the terthiophene. Preliminary results show that they are potential acceptors for the creation of efficient bulk-heterojunction solar cells based on donor polymers containing thiophene units.

1. Introduction

The use of renewable energy sources instead of fossil fuel is a necessity for humanity. The Sun is a green and cheap source of energy: 10 minutes of solar irradiation onto the Earth's surface is equal to the total yearly human energy consumption [1, 2]. The world energy challenge can be won harnessing the Sun power with photovoltaic technologies. Organic photovoltaic devices (OPVs) based on conjugated polymers and oligomers have received a lot of attention because of their potential for lightweight, flexible, and low cost photovoltaic energy conversion [3–7]. Among them, the most common devices are bulk-heterojunction (BHJ) polymer solar cells made upon blending an electron donor conjugated polymer with an electron acceptor material such as fullerene derivatives [3–7]. Fullerene-based OPV can be fabricated via vapor deposition; however, considering the expected demand for enhancing cost performance by mass production in the near future, application of roll-to-roll processing (i.e., the solvent casting method) appears highly desirable [8]. Therefore, development of stable fullerene derivatives that show both high

power conversion efficiency and sufficient solubility in organic solvents is strongly desired [3–7]. Various types of fullerene derivatives for use as OPV acceptor materials have thus been developed. [6, 6]-Phenyl-C61-butyric acid methyl ester (PCBM) [9, 10] is known to be the best blending material among these derivatives as an acceptor with polythiophenes such as regioregular poly(3-hexylthiophene) (P3HT), which is a typical donor partner in polymer solar cells [3–7].

Although PCBM is the most popular acceptor material so far for BHJ polymer solar cells, it is important to explore new easily accessible C60 derivatives as acceptor partners for polymer donor materials with a huge diversity of chemical structures. Many efforts have been devoted to the modification of the PCBM skeleton by introducing substituents on the phenyl ring, exchanging methyl groups with long alkyl chains, an ethyleneoxy moiety, or a perfluoroalkyl chain to tune the miscibility, thermal properties, and energy levels, and the resulting methanofullerene derivatives have been used to control the film morphology, raise the open circuit voltage (V_{oc}), and improve the device stability [11–17]. A few years ago, a PCBM analogue containing a thiophene moiety,

Scheme 1: Synthesis of **F1** and **F2**.

Figure 1: Terthiophene-substituted fullerene derivatives studied in the present work.

[6, 6]-thienyl-C61-butyric acid methyl ester (TCBM), has been reported to exhibit device performance close to PCBM with P3HT as the donor [11–17]. A series of TCBM analogues with different alkyl chains (methyl, hexyl, and ethylhexyl) at the 5 positions of the thiophene ring was then prepared [18]. Like methanofullerenes, fulleropyrrolidines are efficient acceptors for OPV devices and, recently, it was established that the introduction of a thiophene moiety on the pyrrolidine ring has a favorable effect on the power conversion energy (PCE) of a solar cell [19]. It was reported that 1-(2-(2-methoxyethoxy)ethyl)-2-(2-thiophen-2-yl)fulleropyrrolidine and related derivatives with bithiophene or terthiophene are efficient acceptor partners with P3HT, the compound bearing terthiophene being characterized by the highest V_{oc} but lower fill factor (FF) and short circuit current (J_{sc}) due to reduced solubility when compared to the mono- and bithiophene derivatives [19]. In fact the solubility of a fullerene derivative strongly affects the morphology of its composite with P3HT and therefore the efficiency of the cell [20, 21]. These interesting results prompted us to design novel soluble terthiophene-substituted fullerene derivatives as easily accessible acceptor molecules for BHJ polymer solar cells (Scheme 1). We prepared both terthiophene-substituted fulleropyrrolidines (**F1–F3**) and methanofullerenes (**F4-F5**), with the aim of obtaining soluble acceptor materials with a good affinity for donor polymers based on thiophene units (Figure 1). As our work was in progress, as expected, it was reported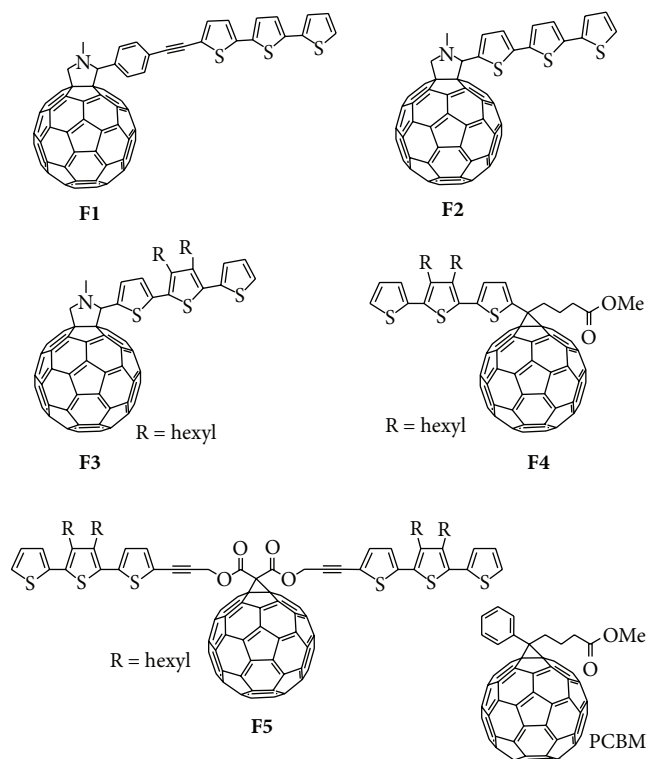 by Saravanan et al. that **F2** is a better electron acceptor than PCBM for the fabrication of P3HT based bulkheterojunction solar cells [22].

2. Materials and Methods

General Comments. Solvents were dried by standard procedures: tetrahydrofuran (THF) and toluene were freshly distilled from Na/benzophenone under nitrogen atmosphere; *N,N*-dimethylformamide (DMF) was dried over activated molecular sieves; triethylamine (Et_3N) was freshly distilled over KOH. All reagents were purchased from Sigma-Aldrich and were used without further purification (2,2′:5′,2″-terthiophene 99% purity, fullerene-C_{60} 99.5% purity, and 4-[(trimethylsilyl)ethynyl] benzaldehyde 97% purity). Reactions requiring anhydrous conditions were performed under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz on a Bruker AVANCE-400 instrument. Chemical shifts (δ) for ^{1}H and ^{13}C spectra are expressed in ppm relative to internal Me_4Si as standard. Signals were abbreviated as follows: *s*: singlet; bs: broad singlet; *d*: doublet; *t*: triplet; *q*: quartet; *m*: multiplet. Mass spectra were obtained by FT-ICR Mass Spectrometer APEX II & Xmass software (Bruker Daltonics) and 4.7 Magnet and Autospec Fission Spectrometer (FAB ionization). MALDI-TOF mass spectra were obtained using a MICROFLEX LT (Bruker) with dithranol (DHB) or *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. Absorption spectra were recorded at room temperature with a Perkin-Elmer Lambda 950 spectrophotometer. Samples were

prepared by dissolving the compounds in chlorobenzene solutions in cell with 10 mm optical path length. Thin layer chromatography (TLC) was carried out with precoated Merck F_{254} silica gel plates whereas flash chromatography (FC) was carried out with Macherey-Nagel silica gel 60 (230–400 mesh).

2.1. Preparation of Fullerene Derivatives F1–F3.
Fullerenes **F1** and **F2** were prepared according to Scheme 1, by using compounds **1–5** as intermediates, whereas **F3** was prepared according to Scheme 2 with compounds **6** and **7** as intermediates.

2.2. Synthesis of Compound 2.
Compound **2** was prepared as reported in the literature [23]. Under a nitrogen atmosphere, *N*-bromosuccinimide (NBS) (176.3 mg, 0.99 mmol, 1 equiv.) was added in small portions to a solution of commercial 2,2′:5′,2″-terthiophene (**1**) (245.7 mg, 0.99 mmol, 1 equiv.) in *N,N*-dimethylformamide (14.1 mL) and stirred for 24 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 (15 mL) and washed with water (2 × 50 mL): the organic layer was dried over Na_2SO_4 and evaporated to dryness. The product, isolated in quantitative yield (324 mg), was used without further purification. ^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.25 (td, 1H, J = 1.2 Hz, J = 3.6 Hz), 7.20-7.19 (m, 1H), 7.10-7.08 (m, 1H), 7.06-7.02 (m, 2H), 6.99 (d, 1H, J = 4 Hz), 6.93 (d, 1H, J = 3.6 Hz).

2.3. Synthesis of Compound 4.
The novel terthiophene derivative **4** was prepared following a procedure reported for related compounds [24]. To a solution of 4-ethynylbenzaldehyde (**3**) (42.2 mg, 0.32 mmol, 1.2 equiv.), obtained starting from 4-[(trimethylsilyl)ethynyl]benzaldehyde [25], and terthiophene derivative (**2**) (88.5 mg, 0.27 mmol, 1 equiv.) in degassed tetrahydrofuran (6 mL), [PdCl$_2$(PPh$_3$)$_2$] (7.6 mg, 4 mol%), CuI (3.1 mg, 6 mol%), and triethylamine (1.5 mL) were added, under a flow of nitrogen. The reaction mixture was left under stirring at 70°C overnight. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using dichloromethane/hexane 6/4 as eluant, to give **4** as a dark yellow solid (66.1 mg; yield 65%).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 10 (s, 1H), 7.89 (d, 2H, J = 8.4 Hz), 7.67 (d, 2H, J = 8.4 Hz), 7.27 (d, 2H, J = 3.6 Hz), 7.22 (d, 1H, J = 3.2 Hz), 7.14 (d, 1H, J = 3.6 Hz), 7.11 (t, 2H, J = 3.6 Hz), 7.06 (dd, 1H, J = 3.6 Hz, J = 5.2 Hz).

2.4. Synthesis of Compound 5.
The known terthiophene derivative **5** [19] was prepared following a procedure reported for related compounds [26]. To a solution of 2,2′:5′,2″-terthiophene (**1**) (100.7 mg, 0.40 mmol, 1 equiv.) in *N,N*-dimethylformamide (3 mL), under nitrogen and cooled to 0°C, was added, in small portions, phosphoryl trichloride (75.1 mg, 0.49 mmol, 1.2 equiv.). The cool bath was then removed and the mixture was stirred for 24 h at 80°C. After cooling to room temperature, the reaction mixture was neutralized with NaOH (2 mL, 1.25 M) and then diluted with CH_2Cl_2 and washed with water: the organic layer was dried
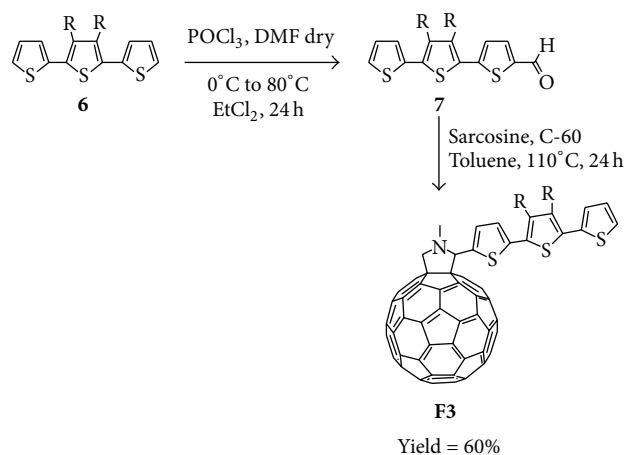
SCHEME 2: Synthesis of **F3**.

over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography, using dichloromethane as eluant, to give **5** as a dark solid (77.4 mg; yield 70%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 9.88 (s, 1H), 7.69 (d, 1H, J = 3.6 Hz), 7.30 (t, 2H, J = 4 Hz, J = 2 Hz), 7.25 (t, 2H, J = 4 Hz, J = 3.2 Hz), 7.15 (d, 1H, J = 4 Hz), 7.07 (dd, 1H, J = 3.6 Hz, J = 5.2 Hz).

2.5. Synthesis of Compound 6.
The terthiophene derivative **6** was prepared according to the literature [27]. To a solution of 2,5-dibromo-3,4-dihexylthiophene (523.4 mg, 1.27 mmol, 1 equiv.) and 2-tributylstannylthiophene (1.18 g, 3.17 mmol, 2.5 equiv.) in degassed tetrahydrofuran (8.5 mL), under a flow of nitrogen, [PdCl$_2$(PPh$_3$)$_2$] (71 mg, 8 mol %) and KF (581 mg, 10 mmol, 7.9 equiv.) were added. The reaction mixture was left under stirring at 70°C overnight. The solvent was removed under reduced pressure and the residue was diluted with CH_2Cl_2 and washed with water: the organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography, using hexane as eluant, to give **6** as a dark green oil (370 mg; yield 70%). ^{1}H-NMR data are fully consistent with data reported in the literature [27].

2.6. Synthesis of Compound 7.
The terthiophene derivative **7** was prepared following a procedure reported for related compounds [26]. To a solution of 3′,4′-dihexyl-2,2′:5′,2″-terthiophene (**6**) (257 mg, 0.62 mmol, 1 equiv.) and *N,N*-dimethylformamide (49.7 mg, 0.68 mmol, 1.1 equiv.) in dichloroethane (6.2 mL), under nitrogen and cooled to 0°C, was added, in small portions, phosphoryl trichloride (104.3 mg, 0.68 mmol, 1.1 equiv.). The cool bath was then removed and the mixture was stirred overnight at 80°C. After cooling to room temperature, the organic solvent was removed and the residue was dissolved in chloroform. A solution of NaOH 1.25 M was added and stirred for 2 h. The organic layer was washed with water, dried over Na_2SO_4, and concentrated. The crude product was purified by flash chromatography, using chloroform as eluant, to give pure **7** (207 mg; yield 75%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 9.91

(s, 1H), 7.72 (d, 1H, $J = 4$ Hz), 7.38 (dd, 1H, $J = 1.2$ Hz, $J = 5.2$ Hz), 7.24 (d, 1H, $J = 4$ Hz), 7.19 (dd, 1H, $J = 0.8$ Hz, $J = 3.6$ Hz), 7.10 (dd, 1H, $J = 3.6$ Hz, $J = 1.6$ Hz), 2.82 (bt, 2H, $J = 8$ Hz, $J = 8.4$ Hz), 2.74 (bt, 2H, $J = 8$ Hz, $J = 8.4$ Hz), 1.63-1.53 (m, 4H), 1.48-1.39 (m, 4H), 1.36-1.33 (m, 8H), 0.91 (bd, 6H). MS (FAB$^+$): m/z 376.

2.7. Synthesis of the New Fulleropyrrolidines F1–F3.
Fulleropyrrolidines **F1–F3** were prepared by using the Prato cycloaddition procedure [28, 29]. A mixture of the suitable aldehyde (1 equiv.), fullerene C-60 (1 equiv.), and sarcosine (8 equiv.) was refluxed for 24 h in anhydrous toluene under a nitrogen atmosphere. After cooling to room temperature, the solvent was evaporated under vacuum and the residue was purified by flash chromatography, as indicated in each case.

2.8. Synthesis of F1.
The crude product was purified by flash chromatography, using hexane/toluene from 4/6 to 3/7 as eluant. Yield is 56%. ^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.98 (bs, 2H), 7.63 (d, 2H, $J = 8$ Hz), 7.25 (bd, 1H, $J = 4$ Hz), 7.20-7.17 (m, 2H), 7.10 (q, 2H, $J = 4$ Hz, $J = 7.2$ Hz), 7.06 (d, 1H, $J = 4$ Hz), 7.04 (dd, 1H, $J = 4.8$ Hz, $J = 3.6$ Hz), 5.31 (s, 1H), 5.26 (bs, 1H), 4.46 (d, 1H, $J = 10$ Hz), 3.02 (s, 3H). MALDI-TOF MS: m/z 1122.9 (C$_{83}$H$_{17}$NS$_3$ requires 1123.1, matrix DCTB).

2.9. Synthesis of F2.
The crude product was purified by flash chromatography, using hexane/toluene from 1/1 to 3/7 as eluant. Yield is 42%. ^{1}H-NMR (400 MHz, CDCl$_3$ + CS$_2$): δ 7.38 (bs, 1H), 7.23 (d, 1H, $J = 5.2$ Hz), 7.17 (d, 1H, $J = 3.6$ Hz), 7.13 (d, 1H, $J = 3.6$ Hz), 7.11 (d, 1H, $J = 4$ Hz), 7.08 (d, 1H, $J = 3.6$ Hz), 7.03 (dd, 1H, $J = 3.6$ Hz, $J = 4.8$ Hz), 5.29 (s, 1H), 5.05 (d, 1H, $J = 9.6$ Hz), 4.31 (d, 1H, $J = 9.6$ Hz), 2.99 (s, 3H). MALDI-TOF MS: m/z 1022.8 (C$_{75}$H$_{13}$NS$_3$ requires 1023, without matrix).

2.10. Synthesis of F3.
The crude product was purified by flash chromatography, using hexane/toluene 1/1 as eluant. Yield is 60%. ^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.37 (d, 1H, $J = 3.6$ Hz), 7.32 (bd, 1H, $J = 5.2$ Hz), 7.20-7.18 (m, 1H), 7.14-7.13 (m, 1H), 7.08-7.06 (m, 1H), 5.28 (s, 1H), 5.02 (d, 1H, $J = 9.6$ Hz), 4.28 (d, 1H, $J = 9.6$ Hz), 2.97 (s, 3H), 2.72-2.64 (m, 4H), 1.48-1.44 (m, 2H), 1.40-1.37 (m, 2H), 1.32-1.27 (m, 12H), 0.91-0.85 (m, 6H). MALDI-TOF MS: m/z 1192.6 (C$_{87}$H$_{37}$NS$_3$ requires 1191.2, matrix DHB).

2.11. Preparation of Fullerene F4.
Fullerene **F4** was prepared from compounds **8–10** as shown in Scheme 3.

2.12. Synthesis of Compound 9.
The novel compound **9** was prepared as follows. To a solution of 3′,4′-dihexyl-2,2′:5′,2″-terthiophene (**6**) (409.6 mg, 0.98 mmol, 1 equiv.) and methyl 5-chloro-5-oxopentanoate (**8**) (161.7 mg, 0.98 mmol, 1 equiv.) in toluene (1.6 mL), under nitrogen and cooled to 0°C, was added, in small portions, tin tetrachloride (255.3 mg, 0.98 mmol, 1 equiv.) and stirred for 2 h. The reaction mixture was diluted with CH$_2$Cl$_2$ and washed with water: the organic layer was dried over Na$_2$SO$_4$ and concentrated. The crude

product obtained was purified by flash chromatography, using dichloromethane as eluant, to give **9** as a pure product (347 mg; yield 65%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.67 (d, 1H, $J = 4$ Hz), 7.36 (dd, 1H, $J = 0.8$ Hz, $J = 5.2$ Hz), 7.18-7.15 (m, 2H), 7.09 (dd, 1H, $J = 3.6$ Hz, $J = 5.2$ Hz), 3.71 (s, 3H), 2.99 (t, 2H, $J = 7.2$ Hz), 2.81 (bt, 2H), 2.71 (bt, 2H), 2.48 (t, 2H, $J = 7.2$ Hz), 2.15-2.08 (m, 2H), 1.58-1.53 (m, 2H), 1.47-1.39 (m, 4H), 1.36-1.29 (m, 8H), 0.92 (bd, 6H, $J = 6.8$ Hz).

2.13. Synthesis of Compound 10.
The novel compound **10** was prepared as follows. A mixture of **9** (165 mg, 0.3 mmol, 1 equiv.) and p-toluenesulfonyl hydrazide (68 mg, 0.36 mmol, 1.2 equiv.) was refluxed in MeOH (0.5 mL) for 18 h. After cooling to room temperature, the organic solvent was removed under reduced pressure and the residue was dissolved in dichloromethane and washed with water. The organic layer was dried over Na$_2$SO$_4$ and concentrated. The residue was purified by flash chromatography, using hexane/ethyl acetate 7 : 3 as eluant, to give **10** as a pure product (148 mg; yield 75%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.97 (s, 1H), 7.94 (d, 2H, $J = 8$ Hz), 7.35-7.30 (m, 2H), 7.16 (d, 1H, $J = 1.2$ Hz), 7.14 (d, 1H, $J = 4$ Hz), 7.09 (dd, 1H, $J = 3.6$ Hz, $J = 4.8$ Hz), 7.01 (d, 1H, $J = 3.6$ Hz), 3.82 (s, 3H), 2.77-2.69 (m, 4H), 2.62 (t, 2H, $J = 7.6$ Hz, $J = 8$ Hz), 2.45 (s, 3H), 2.35 (t, 2H, $J = 5.2$ Hz, $J = 6.4$ Hz), 1.58-1.54 (m, 4H), 1.45-1.42 (m, 4H), 1.37-1.29 (m, 8H), 0.92 (bd, $J = 6.4$ Hz). MS (FAB$^+$): m/z 712.

2.14. Synthesis of F4.
The new methanofullerene **F4** was prepared following procedures reported for related compounds [18, 30, 31]. A mixture of **10** (55.3 mg, 0.084 mmol, 1.2 equiv.), sodium methoxide (4.5 mg, 0.084 mmol, 1.2 equiv.), and dry pyridine (0.84 mL) was stirred at room temperature for 30 min. Then a solution of fullerene C-60 (50.3 mg, 0.07 mmol, 1 equiv.) in o-dichlorobenzene (4.1 mL) was added, and the homogeneous reaction mixture was stirred at 75°C under nitrogen overnight. Then the mixture was refluxed for 24 h (180°C); after cooling to room temperature the solvent was evaporated at reduced pressure, and the residue was purified by column chromatography on silica gel with toluene/hexane 6 : 4 as eluent to give **F4** as a pure product (yield 55%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.46 (d, 1H, $J = 4$ Hz), 7.33 (dd, 1H, $J = 4.4$ Hz, $J = 0.8$ Hz), 7.18 (dd, 1H, $J = 4.4$ Hz, $J = 0.8$ Hz), 7.15 (d, 1H, $J = 4.4$ Hz), 7.10 (dd, 1H, $J = 3.6$ Hz, $J = 5.2$ Hz), 3.72 (s, 3H), 3.01 (bt, 2H, $J = 8$ Hz), 2.79 (bt, 2H, $J = 8.4$ Hz, $J = 8$ Hz), 2.73 (bt, 2H, $J = 8.4$ Hz, $J = 8$ Hz), 2.63 (t, 2H, $J = 7.2$ Hz), 1.63-1.56 (m, 4H), 1.45-1.40 (m, 4H), 1.35-1.28 (m, 8H), 0.91 (bd, 6H, $J = 6.8$ Hz). MALDI-TOF MS: m/z 1248.9 (C$_{90}$H$_{40}$O$_2$S$_3$ requires 1248.2, matrix DCTB).

2.15. Preparation of Fullerene F5.
Fullerene **F5** was prepared from compounds **11–13** as shown in Scheme 4.

2.16. Synthesis of Compound 11.
Under a nitrogen atmosphere, N-bromosuccinimide (NBS) (408.6 mg, 0.98 mmol, 1 equiv.) was added in small portions to a solution of 3′,4′-dihexyl-2,2′:5′,2″-terthiophene (**6**) (147.7 mg, 0.98 mmol, 1 equiv.) in N,N-dimethylformamide (14 mL, 0.07 M) and
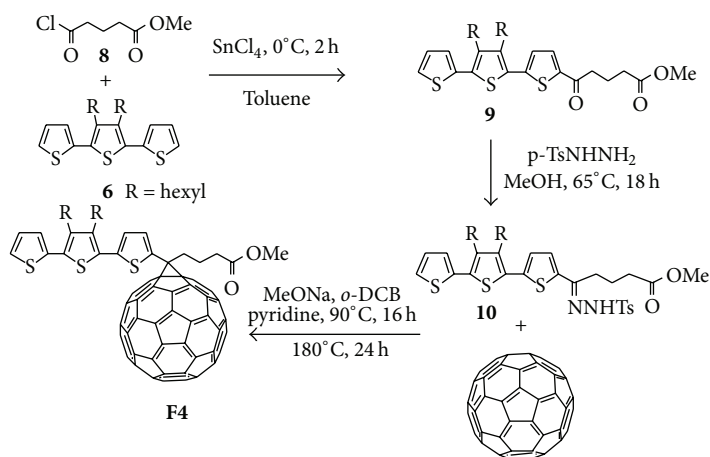
Scheme 3: Synthesis of **F4**.
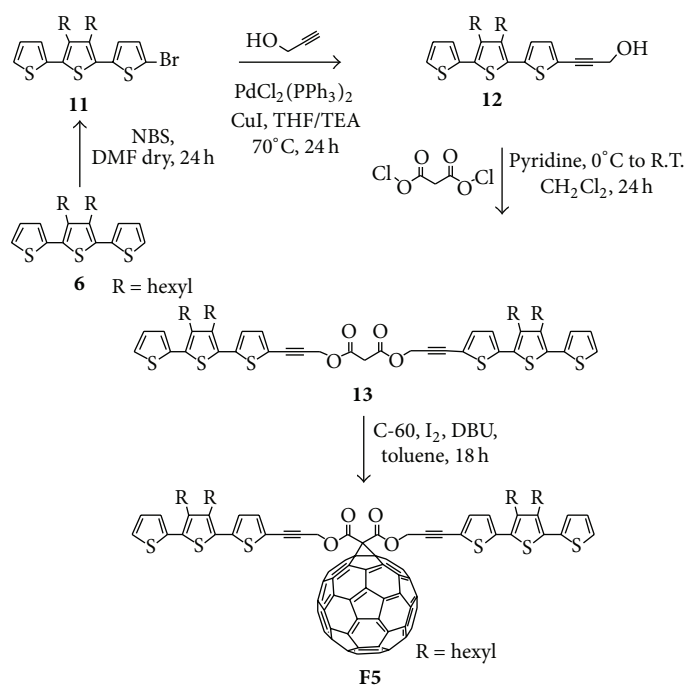
Scheme 4: Synthesis of **F5**.

stirred for 24 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 (15 mL) and washed with water (2 × 50 mL): the organic layer was dried over Na_2SO_4 and concentrated. The product, isolated in quantitative yield (485 mg), was used without further purification. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40-7.32 (m, 1H), 7.14 (d, 1H, $J = 2.4$ Hz), 7.08 (dd, 1H, $J = 3.6$ Hz, $J = 5.2$ Hz), 7.04-7.01 (m, 1H), 6.89-6.87 (m, 1H), 2.75-2.64 (m, 4H), 1.63-1.56 (m, 4H), 1.44-1.40 (m, 4H), 1.34-1.28 (m, 8H), 0.90 (bd, 6H, $J = 6.8$ Hz).

2.17. Synthesis of Compound 12. The new terthiophene derivative **12** was prepared according to the following procedure. To a solution of propargyl alchol (36.5 mg, 0.65 mmol, 1.1 equiv.) and **11** (247.8 mg, 0.59 mmol, 1 equiv.) in degassed tetrahydrofuran (14.7 mL), under a flow of nitrogen, were added $[PdCl_2(PPh_3)_2]$ (16.6 mg, 4 mol %), CuI (6.7 mg, 6 mol%), and triethylamine (3.7 mL). The reaction mixture was left under stirring at 70°C overnight. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, using chloroform as eluant, to give **12** (152 mg; yield 55%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, 1H, $J = 4.8$ Hz, $J = 0.8$ Hz), 7.18 (d, 1H, $J = 4.8$ Hz), 7.15 (dd, 1H, $J = 3.6$ Hz, $J = 0.8$ Hz), 7.09 (dd, 1H, $J = 3.6$ Hz, $J = 5.2$ Hz), 7.01 (d, 1H, $J = 3.6$ Hz), 4.55 (s, 2H), 2.74-2.68 (m, 4H), 1.59-1.55 (m, 4H), 1.44-1.41 (m, 4H), 1.36-1.29 (m, 8H), 0.92 (bd, 6H, $J = 6.8$ Hz).

2.18. Synthesis of Compound 13. The new terthiophene derivative **13** was prepared as follows. Malonyl dichloride (1.75 mL, 18 mmol, 1 equiv.) was added to a solution of terthiophene **12** (142 mg, 0.3 mmol, 2 equiv.) and pyridine (23.7 mg, 0.3 mmol, 2 equiv.) in dichloromethane (2.1 mL) at 0°C under nitrogen. After 1 h, the mixture was allowed to warm up to room temperature and then stirred for 18 h, filtered, and evaporated. The residue was purified by flash chromatography, using dichloromethane/hexane 8/2 as eluant, to give **13** (106 mg; yield 70%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.34 (d, 2H, J = 5.2 Hz), 7.21 (d, 2H, J = 4 Hz), 7.14 (dd, 2H, J = 3.6 Hz, J = 1.2 Hz), 7.08 (dd, 2H, J = 3.6 Hz, J = 5.2 Hz), 7.01 (d, 2H, J = 3.6 Hz), 5.05 (s, 4H), 3.57 (s, 2H), 2.73-2.67 (m, 8H), 1.58-1.54 (m, 8H), 1.46-1.41 (m, 8H), 1.35-1.29 (m, 16H), 0.93 (m, 12H). MS (FAB$^+$): m/z 1008.

2.19. Synthesis of F5. The new methanofullerene **F5** was prepared following procedures reported for similar compounds [32, 33]. 1,8-diazabicyclo[5.4.0]undec-7-ene (19.3 mg, 0.125 mmol, 2.5 equiv.) was added under nitrogen at room temperature to a stirred solution of fullerene C-60 (39 mg, 0.05 mmol, 1 equiv.), I$_2$ (19 mg, 0.075 mmol, 1.5 equiv.), and **13** (55 mg, 0.05 mmol, 1 equiv.) in toluene (39 mL) at room temperature. The resulting solution was stirred for 12 h and then filtered through a short plug of silica (CH$_2$Cl$_2$) and evaporated. The residue was purified by flash chromatography, using hexane/toluene 6/4 as eluant, to give **F5** (yield 52%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.33 (dd, 2H, J = 5.2 Hz, J = 1.2 Hz), 7.20 (d, 2H, J = 4 Hz), 7.13 (dd, 2H, J = 3.6 Hz, J = 1.2 Hz), 7.07 (dd, 2H, J = 3.6 Hz, J = 4.8 Hz), 6.98 (d, 2H, J = 4 Hz), 5.38 (s, 4H), 2.73-2.68 (m, 8H), 1.56-1.54 (m, 8H), 1.43-1.38 (m, 8H), 1.34-1.28 (m, 16H), 0.92 (m, 12H). MALDI-TOF MS: m/z 1729.3 (C$_{117}$H$_{66}$O$_4$S$_6$ requires 1727.3, matrix DCTB).

2.20. Electrochemical Characterization. The cyclovoltammetric (CV) characterization was carried out with an Autolab PGSTAT 128N potentiostat, run by a PC with GPES software. The working cell included a Glassy Carbon (GC) disk embedded in Teflon (Amel, surface 0.071 cm^2) as the working electrode, a Platinum counter electrode (Metrohm), and an aqueous saturated calomel electrode (SCE, Amel) as the reference electrode. The sample was dissolved in o-dichlorobenzene ($\approx$0.5 mg/mL) and drop coated from a capillary on the GC electrode. The electrolytic solution was acetonitrile (Carlo Erba, HPLC grade) with 0.1 M tetrabutylammonium tetrafluoroborate TBATFB (Fluka, electrochemical grade). The solution was degassed with argon purging. The scan rate was 200 mV s^{-1}. According to IUPAC recommendations the data have been referred to the Fc$^+$/Fc redox couple (ferrocenium/ferrocene).

E_{HOMO} and E_{LUMO} values were extrapolated from the onset peaks potential.

2.21. Preparation and Characterization of Solar Cells. Solar cells were fabricated on patterned ITO-coated glass substrates previously cleaned with detergent and water and then ultrasonicated in acetone and isopropyl alcohol for 15 min each.

A PEDOT : PSS (Clevios P VP AI 4083) layer was spin-coated at 3000 rpm onto air plasma cleaner ITO-coated substrates to a thickness of around 40 nm and then baked in an oven at 120°C for 10 min. Fullerenes and P3HT were dissolved separately in chlorobenzene (20 mg/mL) (Carlo Erba, HPLC grade), mixed 1 : 1 w/w obtaining a total concentration of 10 mg/mL, and then stirred overnight at 70°C. The blend solutions were spin-coated at 600 and 1200 rpm in glove box onto the ITO/PEDOT : PSS substrates. The thickness of the active layers, measured with a Veeco Dektak 150 profilometer, ranged between 50 nm and 130 nm. Then the samples were completed with the thermal evaporation of the Al (80 nm) cathode at a base pressure of 10^{-6} mbar. The active device area was 25 mm^2. The devices were postproduction thermal annealed in glove box (nitrogen filled) at 150°C for 10 min. The device electrical characterization was carried out at room temperature in glove box. Solar cells were illuminated using a solar simulator (Sun 2000, Abet Technologies) and the light power intensity was calibrated at AM1.5 illumination conditions (100 mW cm^{-2}) using a certified silicon solar cell. The current-voltage curves were taken with a Keithley 2602 source measure.

3. Results and Discussion

Terthiophene is an interesting π-conjugated electron-releasing substituent group that can influence both the light absorbing behavior and charge separation process of fullerenes. Interestingly, it was reported that 1-(2-(2-methoxyethoxy)ethyl)-2-(terthiophene)fulleropyrrolidine is an efficient acceptor partner with P3HT, being characterized by a higher V_{oc} but lower fill factor and shorter circuit current with respect to related compounds bearing thiophene or bithiophene instead of the terthiophene moiety, attributed to its lower solubility [19]. These interesting results prompted us to design novel soluble terthiophene-substituted fullerene derivatives as easily accessible acceptor molecules for BHJ polymer solar cells (Scheme 1). We prepared both terthiophene-substituted fulleropyrrolidines (**F1–F3**) and methanofullerenes (**F4-F5**), with the aim of obtaining soluble acceptor materials with a good affinity for donor polymers based on thiophene units.

The novel terthiophene-substituted fulleropyrrolidines (**F1**, **F3**) and the known **F2** [22] were prepared following a method similar to that originally developed by Prato and Maggini and coworkers (Schemes 1 and 2) [28, 29]. Sarcosine was treated with [C60]-fullerene in the presence of a suitable terthiophene-substituted aldehyde, in toluene, and the mixture was heated under reflux for 24 h under a nitrogen atmosphere.

The novel terthiophene-substituted methanofullerene **F4** was prepared following the procedure reported for other methanofullerenes [18, 30, 31], by reaction of the *p*-tosylhydrazone **10** with sodium methoxide and fullerene C-60 (Scheme 3), whereas **F5** was synthesized by the Bingel reaction [32, 33] treating the novel bisterthiophenylmalonate **13** with iodine, fullerene, and 1,8-diazabicyclo[5.4.0]undec-7-ene (Scheme 4).
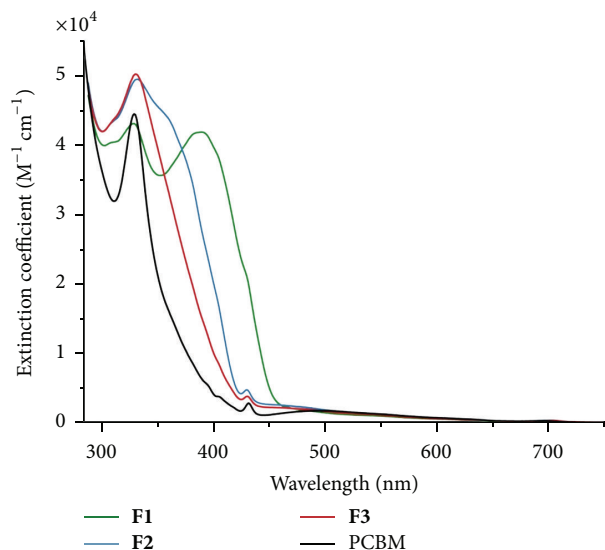
FIGURE 2: UV-visible absorption spectra of **F1–F3** and PCBM in chlorobenzene.

FIGURE 3: UV-visible absorption spectra of **F4, F5,** and PCBM in chlorobenzene.

All fulleropyrrolidines and methanofullerenes were purified by silica gel flash chromatography and characterized by elemental analyses, ^{1}H NMR and UV-visible spectroscopies, mass spectrometry, and cyclovoltammetry (see Section 2).

Figures 2 and 3 show the UV-visible absorption spectra of fullerenes **F1–F5** along with that of PCBM in chlorobenzene solution.

The fulleropyrrolidine **F2** shows a broad absorption band between 350 and 400 nm, as expected for a terthiophene moiety [22]. This band is red shifted in compound **F1**, in agreement with the presence of a π-delocalized bridge between the pyrrolidine and the terthiophene moiety, and blue shifted in compound **F3**, due to the presence of the hexyl chains, responsible of the tilting of the structure and the final reduced conjugation.

Red shifting is observed in the compounds **F4** and **F5** in comparison with PCBM. Interestingly also a large enhancement in the ε of the peak at 330 nm (assigned to the fullerene) is obtained. Theoretically this enhancement can benefit the performance of the solar cells being the absorption in this region complementary to P3HT. In fact, it was reported that fullerenes' derivatives with a better light absorption can lead to a better power conversion efficiency since more photons are available to be converted into electricity [34].

The electrochemical properties of the various fullerenes were examined by cyclic voltammetry (CV). Current potential profiles are shown in Figures 4 and 5.

We use the first oxidation and reduction potentials to estimate the HOMO and LUMO energy levels by means of equations $E_{HOMO}(eV) = -(E_{OX} + 4.8)$ and $E_{LUMO}(eV) = -(E_{RED} + 4.8)$, which involve the use of the internal ferrocene standard value of -4.8 eV with respect to the vacuum level [35, 36]. The results are summarized in Table 1. Interestingly, all the novel fullerene derivatives have an enhanced LUMO level with respect to PCBM, possibly improving the V_{oc}. In fact,
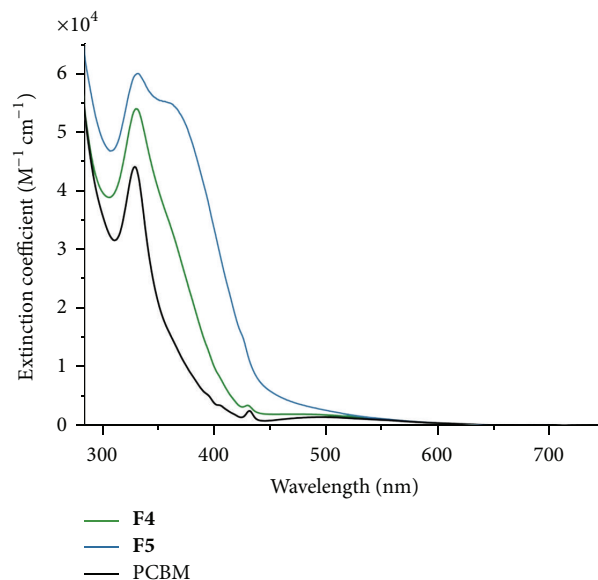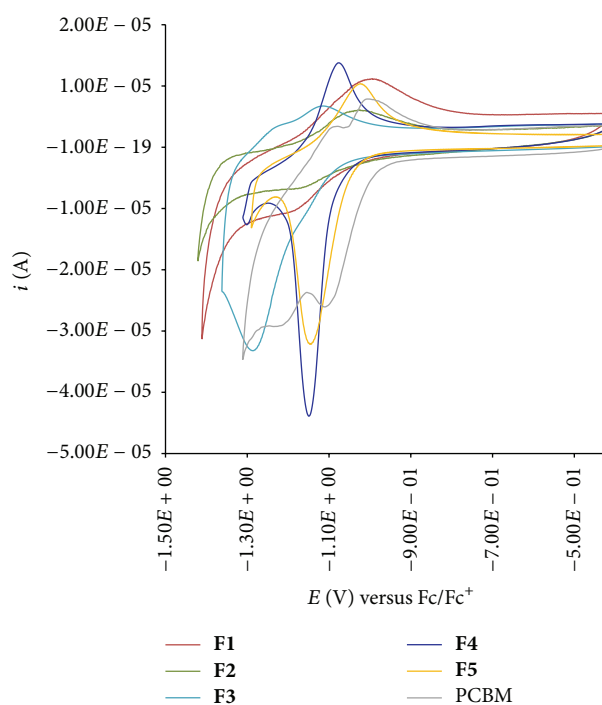

FIGURE 4: Synopsis of cathodic part of cyclovoltammograms for fullerenes **F1–F5** and PCBM.

Kim and coworkers reported that the V_{oc} of an OPV device is determined by the difference between the HOMO level of the p-type semiconductor and the LUMO level of the n-type conductor [37]. Fullerenes **F1–F3** and **F5** are characterized by a remarkably low band gap due to a relatively high HOMO level.
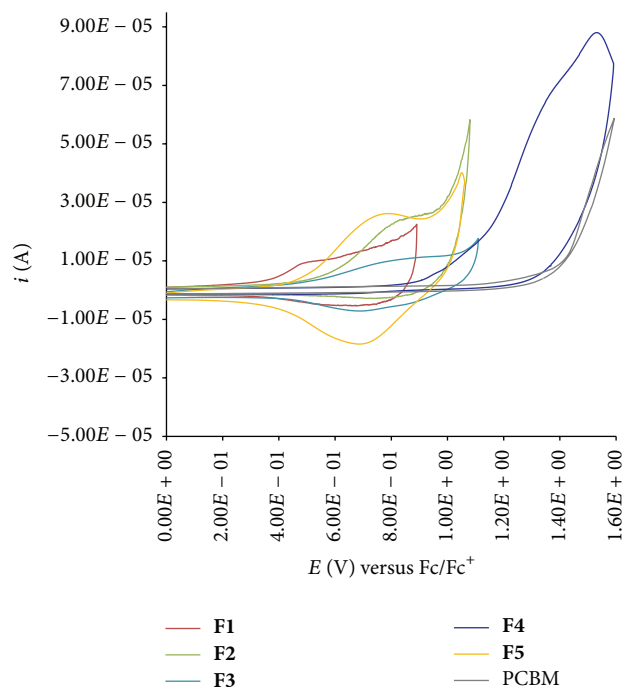
FIGURE 5: Synopsis of anodic part of cyclovoltammograms for fullerenes **F1**–**F5** and PCBM.

TABLE 1

Fullerene derivative	E_{HOMO} (eV)	E_{LUMO} (eV)	Band gap (eV)
F1	−5.15	−3.78	1.37
F2	−5.27	−3.78	1.49
F3	−5.29	−3.74	1.55
F4	−5.67	−3.75	1.92
F5	−5.26	−3.79	1.47
PCBM	−6.01	−3.83	2.18

The use of fullerenes **F1**, **F3**, and **F4** as acceptor molecules for bulk-heterojunction polymer solar cells was investigated in a preliminary way using P3HT as donor polymer. However, up to now the highest power conversion efficiency, reached with **F4**, was 0.46% only, although acceptable FF (0.30) and V_{oc} (0.48 Volt) were obtained. A wider screening of solvents and thickness in order to optimize morphology and performance is in progress in our laboratories.

4. Conclusions

In summary, we have prepared five interesting soluble fulleropyrrolidines and methanofullerenes, bearing one or two terthiophene moieties, as potential acceptors for the creation of efficient bulk-heterojunction solar cells based on donor polymers containing thiophene units. These novel fullerene derivatives are characterized by a better harvesting of the solar radiation with respect to traditional PCBM. In addition, they have a relatively high LUMO level and a low

band gap that can be easily tuned by an adequate design of the link between the fullerene and the terthiophene.

Besides, it is worth pointing out that the new fullerene derivatives prepared in the present work are also of interest as new molecular building blocks for materials with nonlinear optical (NLO) properties [38–43]. In particular, because the methanofullerene **F4** is an excellent candidate as second-order NLO chromophore due to the presence of the highly polarizable electron acceptor C60-fullerene system linked to the donor terthiophene through a cyclopropane group, its quadratic hyperpolarizability is under study in our laboratories.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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