

A versatile approach for creating hybrid semiconducting polymer–fullerene architectures for organic electronics†

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A novel methodology, through which fullerenes are effectively introduced directly onto semiconducting species, is presented herein. Electron accepting perfluorophenyl-quinolines either as small molecules, as homopolymers, or as random copolymers with regioregular poly(3-alkyl thiophene), have been synthesized and further employed for the preparation of hybrid materials with C₆₀ or PCBM. More specifically, *via* this route one of the fluorine atoms of the perfluorophenyl ring is transformed into an azide that undergoes [3+2]-cycloaddition onto the fullerene's surface, producing 1,6-azo bridged carbon nanostructure–organic semiconducting hybrids.

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Introduction

Efficient bulk heterojunction (BHJ) organic photovoltaic (OPV) solar cells comprised of bicontinuous, nanophase separated active layers that remain stable over time and environmental conditions are of utmost importance for their commercialization.^{1–3} Parameters such as the chemical structure of the donor and the acceptor, the conditions for mixing and depositing the active layer as well as post-deposition treatment and device architecture have been exhaustively investigated.^{4–13} Numerous new and “exotic” materials have appeared over time with continuous enhancement of the OPV performance.^{14–16} Nevertheless, the still most commonly employed system, especially when it comes to large area devices, remains the rr-poly(3-hexylthiophene) and [6,6]-phenyl C₆₁-butyric acid methyl ester binary mixture (P3HT–PCBM). The introduction of a hybrid compatibilizer, bearing both an electron donating polymer and electron accepting fullerene units, has been effective at enhancing the stability of this blend but in almost every case, compatibilizers require multiple and laborious post-polymerization synthesis steps.^{17–29}

Recently, we reported our efforts towards the development of polymeric or hybrid electron acceptors based on the perfluorophenyl-quinoline entity.³⁰ The optoelectronic properties

of the polymeric and the hybrid molecules proved the potential of these molecules as electron acceptors in OPVs. However, it is well known that polymeric and even small organic electron acceptors greatly suffer from low charge carrier mobility. For that reason we have already prepared hybrid structures by functionalizing single wall carbon nanotubes (SWCNTs) with different quinoline species bearing electron accepting groups.³¹ The combination of SWCNTs with semiconducting polymers offers an attractive route to reinforce the macromolecular compounds as well as to introduce novel electronic properties based on electronic interactions and/or morphological alterations between the two constituents. And also this method suffers from the limited SWCNT content allowed into the photovoltaic active layer. Thus, an ideal solution would be to couple the processability and good electron accepting properties of perfluorophenyl-quinolines with the even greater electron accepting and transporting properties of fullerenes, and also ensure the applicability of the final hybrid materials in the active layer of an OPV.

As already mentioned, the idea to connect semiconducting polymeric species onto carbon nanostructures, like CNTs or fullerenes, has been demonstrated by various research groups. However, in all cases a non-conjugated connecting bridge has been employed for the organic part fixation onto the carbon nanostructure's surface.^{11,12,32–34} Instead, a conjugated interconnecting part through the direct attachment of the semiconductor onto the carbon nanostructure could enhance electronic interactions between the two counterparts possibly creating novel hybrid systems with unique integrated properties.

Working in this direction we employed an efficient methodology for the attachment of fullerene species onto perfluorophenyl-quinolines, either polymeric or monomeric ones, using one of the fluorine atoms of the perfluorophenyl ring

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which can be easily transformed into an azide. This undergoes [3+2]-cycloaddition with fullerene species in a simple and straightforward reaction,^{35–39} producing 1,6-azo bridged fullerene based hybrids. Through this route polymeric as well as small molecule perfluorophenyl-quinoline C₆₀ hybrids were created. Taking this a step further, we developed electron donor-acceptor copolymers comprising rr-poly(3-alkyl-thiophene) and poly(perfluorophenyl-quinoline) blocks. On the perfluorophenyl rings of the quinoline block we then attached fullerene units, either C₆₀ or PCBM ones.⁴⁰ These hybrid materials are designed so as to be used as compatibilisers of typical P3HT:PCBM blends in BHJ OPVs. Work in this direction is currently under way.

Experimental

Materials

Fullerene, carbon 60, 99.5% was purchased from SES research. [60]PCBM 99% was purchased from Solenne b.v. Tetrahydrofuran was purchased from Aldrich and was distilled with benzophenone and metallic sodium [THF(dry)]. *N,N*-Dimethylformamide, purchased from Aldrich, was dried over CaH₂ and distilled under reduced pressure [DMF(dry)]. All other solvents and reagents were purchased from Aldrich, Alfa Aesar or Across and were used without further purification unless otherwise stated. Bromo phenyl perfluoroquinoline (Br-5FQ),³⁰ perfluorophenyl-vinylphenyl-quinoline (5FQ),³⁰ polymeric perfluorophenylquinoline (P5FQ),³⁰ 2-vinyl terminated regioregular poly(3-octylthiophene)⁴¹ and 4-bromo-4'-acetoxy biphenyl⁴² were synthesized according to the reported procedures.

Instruments and measurements

¹H, ¹³C, ¹⁹F, ¹⁵N and 2D NMR (HMBC) spectra were recorded on Bruker Advance DPX 400.13, 100.6 and 376.5 MHz spectrometers, respectively, with CDCl₃ as solvent containing TMS as internal standard. Gel permeation chromatography (GPC) measurements were carried out using a Polymer Lab chromatographer equipped with two PLgel 5 μm mixed columns and a UV detector using CHCl₃ as eluent with a flow rate of 1 mL min⁻¹ at 25 °C and polystyrene standards. Sonication was done on a Branson (Branson), ultrasonic cleaner 2510 model. Thermogravimetric analysis (TGA) was carried out on ~8 mg samples contained in alumina crucibles in a Labsys TM TG apparatus of Setaram under nitrogen and at a heating rate of 10 °C min⁻¹. UV-Vis spectra were recorded using a Hitachi U-1800 spectrophotometer. Continuous wave photoluminescence was measured on a Perkin Elmer LS45B spectrofluorometer. FT-IR spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer. Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM2100 operating at 200 kV. Sample preparation for TEM examination involved the preparation of dilute solutions of the samples in THF or *o*-DCB and filtration through a 0.45 μm filter. A drop of the solution was placed on 3 mm carbon coated copper grids (Electron Microscopy Sciences) and the samples were dried in air for 2 days.

Synthesis procedures

The synthesis procedures for dodecyloxy-biphenyl-boronic acid, Ph-5FQ, C₁₂(Ph)₂-5FQ, Ph-5FQ-N₃, C₁₂(Ph)₂-5FQ-N₃ and P5FQ-N₃ are given in the ESI.†

Synthesis of the phenyl-perfluorophenylquinoline C₆₀ hybrid, Ph-5FQ-N-C₆₀. A 100 mL round bottom flask equipped with a reflux condenser and a magnetic stirrer was degassed (flamed under vacuum) and filled with argon. Ph-5FQ-N₃ (0.50 g, 1.06 mmol), C₆₀ (0.80 g, 1.11 mmol) and 40 mL 1,2-dichlorobenzene (*o*-DCB) were added and the system was degassed and flushed with argon again. The reaction mixture was stirred at 140 °C for 48 h. After evaporation of the solvent, the solid was dissolved in toluene, filtered to remove any undissolved residuals and chromatographed through silica gel loaded with petroleum ether using petroleum ether, petroleum ether:toluene 1:1 and 1:2 mixtures, and finally toluene. The second fraction contained the desired Ph-5FQ-N-C₆₀ hybrid material, which was rotary evaporated and the solid was dried under vacuum at 50 °C overnight, yield 60%. ¹³C NMR (δ_C; CS₂: CDCl₃ 1:3; Me₄Si): 149.51, 148.26, 147.35, 145.55, 145.45, 145.36, 145.24, 144.72, 144.55, 144.34, 144.11, 144.04, 143.31, 143.23, 143.15, 142.89, 142.32, 142.23, 141.22, 140.56, 140.52, 140.34, 137.57, 130.83, 129.87, 129.73, 129.08, 128.94, 128.91, 127.98, 127.59, 127.01, 126.29, 123.72, 123.58, 115.81, 80.60. ¹⁵N (δ_N; CS₂: CDCl₃ 1:3): 311.15, 378.85. ¹⁹F NMR (δ_F; CS₂: CDCl₃ 1:3): -147.70, -163.95.

Synthesis of the dodecyloxy-biphenyl-perfluorophenylquinoline C₆₀ hybrid, C₁₂(Ph)₂-5FQ-N-C₆₀. A 100 mL round bottom flask equipped with a reflux condenser and a magnetic stirrer was degassed (flamed under vacuum) and filled with argon. C₁₂(Ph)₂-5FQ-N₃ (182.71 mg, 0.25 mmol), C₆₀ (180.16 mg, 0.25 mmol) and 25 mL toluene were added and the system was degassed and flushed with argon again. The reaction mixture was stirred at 110 °C for 48 h. After evaporation of the solvent, the solid was stirred in *n*-hexane for 2 days at 40 °C in order to remove most of the unreacted C₆₀. Column chromatography using silica gel was performed in order to remove any remaining traces of C₆₀, using petroleum ether-toluene gradient mixtures, providing pure C₁₂(Ph)₂-5FQ-N-C₆₀ as the second fraction. The obtained solid was dried under vacuum at 50 °C overnight, yield 55%. ¹³C NMR (δ_C; CS₂: CDCl₃ 1:3; Me₄Si): 158.99, 149.20, 148.33, 147.05, 145.57, 145.47, 145.40, 145.24, 144.86, 144.74, 144.59, 144.38, 144.14, 144.09, 143.35, 143.26, 143.19, 142.91, 142.36, 142.27, 141.26, 140.58, 140.55, 140.07, 138.36, 137.73, 132.64, 131.15, 129.81, 129.56, 129.11, 129.03, 128.93, 128.09, 127.92, 127.32, 126.27, 123.63, 123.22, 114.97, 80.65, 68.03, 32.43, 30.22, 30.18, 30.15, 30.07, 29.90, 29.83, 29.79, 26.63, 23.36, 14.67. ¹⁵N (δ_N; CS₂: CDCl₃ 1:3): 311.02, 373.5. ¹⁹F NMR (δ_F; CS₂: CDCl₃ 1:3): -161.80, -145.90.

Synthesis of the poly(perfluorophenyl-quinoline) C₆₀ hybrid, P5FQ-N-C₆₀. A 50 mL round bottom flask equipped with a reflux condenser and a magnetic stirrer was degassed (flamed under vacuum) and filled with argon. P5FQ-N₃ (0.22 g, 0.43 mmol), C₆₀ (0.30 g, 0.43 mmol) and 20 mL *o*-DCB were added and the system was degassed and flushed with argon again. The reaction mixture was stirred at 140 °C for 48 h. After evaporation of

the solvent, the solid was stirred in *n*-hexane for 2 days at 40 °C and in toluene for another 2 days at 40 °C in order to remove unreacted C₆₀ traces, filtered and the obtained solid was dried under vacuum at 50 °C overnight, yield 60%. Unfortunately, the low solubility of this hybrid and the strong coupling of the carbon to fluorine atoms of the fluorinated phenyl ring did not allow its successful NMR characterization.

Synthesis of the random copolymer regioregular-poly(3-octylthiophene)-*r*-poly(perfluorophenylquinoline), P3OT-P5FQ. A 10 mL round flask equipped with a reflux condenser and a magnetic stirrer was degassed and filled with argon. Vinyl-5FQ (250.00 mg, 0.53 mmol), vinyl terminated rr-P3OT (25.00 mg, 0.13 mmol), azobisisobutyronitrile (AIBN) (8.70 mg, 0.05 mmol), 3 mL THF(dry) and 2 mL *o*-DCB were added and the flask was degassed and flushed with argon again. The reaction mixture was stirred at 110 °C for 72 h. The mixture was precipitated into methanol and after filtration the obtained solid was washed with diethyl ether and EtOAc. The solid was dried under vacuum at 40 °C overnight affording 130.00 mg of the final copolymer. ¹H NMR (δ_H; CDCl₃; Me₄Si): 8.40–7.70 (broad, 3H-P5FQ), 7.70–7.00 (broad, 8H-P5FQ), 6.98 (s, 1H-P3OT), 6.95–6.3 (broad, 2H-P5FQ), 2.80 (t, 2H-P3OT), 1.69 (m, 2H-P3OT), 1.47–1.20 (two broad, 6H-P3OT), 0.87 (t, 3H-P3OT). ¹³C NMR (δ_C; CDCl₃; Me₄Si): 150.72, 146.08, 139.80, 136.71, 133.74, 130.55, 130.54, 129.43, 129.41, 128.74, 128.59, 127.4, 127.15, 126.45, 126.10, 117.29, 115.42, 31.92, 30.55, 29.57, 29.47, 29.32, 22.70, 14.12. ¹⁹F NMR (δ_F; CDCl₃): –161.58, –153.27, –142.58. ¹⁵N NMR (δ_N; CDCl₃): 234.76.

Table S1† presents the various copolymers prepared along with their molecular characteristics from GPC analyses.

Synthesis of the copolymer P3OT-(P5FQ-N₃). A 50 mL round bottom flask with a reflux condenser and a magnetic stirrer was degassed and filled with argon. Copolymer P3OT-P5FQ (100.00 mg, 0.15 mmol), NaN₃ (36.80 mg, 0.59 mmol), 4 mL THF(dry) and 6 mL DMF(dry) were stirred at 40 °C for 24 h under argon. The reaction mixture was precipitated into a mixture of deionized water–methanol (1 : 1). After filtration the solid was washed with deionized water three times and dried under vacuum at 30 °C overnight affording the final azide in quantitative yield. For P3OT-(P5FQ-N₃) ATIR spectroscopy was used for the confirmation of the successful azide introduction.

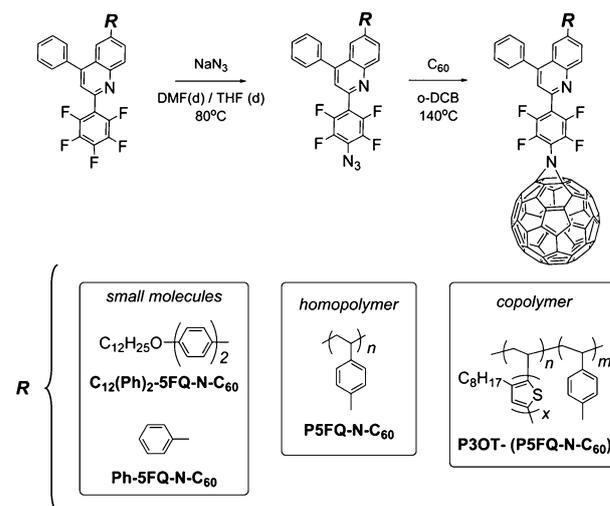
Synthesis of the hybrid copolymer P3OT-(P5FQ-N-C₆₀). A 50 mL round bottom flask equipped with a reflux condenser and a magnetic stirrer was degassed (flamed under vacuum) and filled with argon. P3OT-(P5FQ-N₃) (80.00 mg), C₆₀ (40.00 mg, 0.06 mmol), and 10 mL *o*-DCB were added and the system was degassed and flushed with argon again. The reaction mixture was stirred at 140 °C for 72 h. After evaporation of the solvent, the solid was stirred in *n*-hexane and then in toluene each for 3 days at 40 °C in order to remove traces of unreacted C₆₀. The mixture was filtered and the obtained solid was dried under vacuum at 50 °C overnight affording 100.00 mg. Due to the low solubility of this hybrid material in CDCl₃ NMR spectroscopy evaluation was not successful even after the addition of CS₂ to improve the solubility of the fullerene part.

Synthesis of the hybrid copolymer P3OT-(P5FQ-N-PCBM). A 50 mL round bottom flask equipped with a reflux condenser

and a magnetic stirrer was degassed (flamed under vacuum) and filled with argon. P3OT-(P5FQ-N₃) (70.00 mg), PCBM (65.00 mg, 0.07 mmol), and 20 mL *o*-DCB were added and the system was degassed and flushed with argon again. The reaction mixture was sonicated for 20 min and then was stirred at 140 °C for 72 h. After evaporation of the solvent, the solid was stirred in *n*-hexane at 40 °C for 3 days with a view to remove any traces of unreacted PCBM. The mixture was filtered and the solid was washed with *n*-hexane, toluene several times and finally with *n*-hexane. TLC of the hybrid copolymer on silica gel plates using toluene as eluent was used to confirm the absence of free PCBM in the final hybrid. The obtained solid was dried under vacuum at 50 °C overnight affording 105.80 mg. ¹H NMR (δ_H; CDCl₃; Me₄Si): 8.4–8.0 (broad, 3H-P5FQ), 7.92 (d, 2H-PCBM), 7.8–7.2 (broad, 8H-P5FQ), 7.57–7.53 (m, 2H-PCBM), 7.48 (d, 1H-PCBM), 6.98 (s, 1H-P3OT), 3.68 (s, 3H-PCBM), 2.93–2.89 (m, 2H-PCBM), 2.79 (t, 2H-P3OT), 2.55–2.51 (t, 2H-PCBM), 2.23–2.15 (m, 2H-PCBM), 1.68 (m, 2H-P3OT), 1.5–1.2 (broad, 6H-P3OT), 0.88 (broad, 3H-P3OT). ¹³C NMR (δ_C; CDCl₃; Me₄Si): 173.46, 148.83, 148.36, 147.83, 145.87, 145.21, 145.17, 145.09, 145.06, 144.81, 144.68, 144.64, 144.53, 144.44, 144.03, 143.78, 143.14, 143.02, 142.95, 142.25, 142.20, 142.15, 141.01, 140.80, 138.05, 137.59, 136.75, 134.55, 132.62, 132.11, 130.55, 128.45, 128.26, 127.72, 119.73, 79.89, 51.87, 51.66, 33.89, 33.69, 31.91, 30.7, 29.55, 29.46, 29.30, 22.68, 22.39, 14.13. ¹⁵N NMR (δ_N; CDCl₃): 234.32, 209.97. ¹⁹F NMR (δ_F; CDCl₃): –152.50, –110.78.

Results and discussion

In this work the previously reported perfluorophenyl-vinyl-phenylquinoline monomer and its homopolymer (P5FQ)²⁷ as well as the newly synthesized small monomolecular phenyl-(Ph-5FQ) and dodecyloxybiphenyl-(C₁₂(Ph)₂-5FQ) substituted perfluorophenyl-quinolines (Schemes S1 and S3,† respectively) were employed for the initial screening and the optimization of the reaction conditions for the development of the hybrid fullerene based materials. Additionally, the electron donating–



Scheme 1 Synthesis of C₆₀ based hybrids.

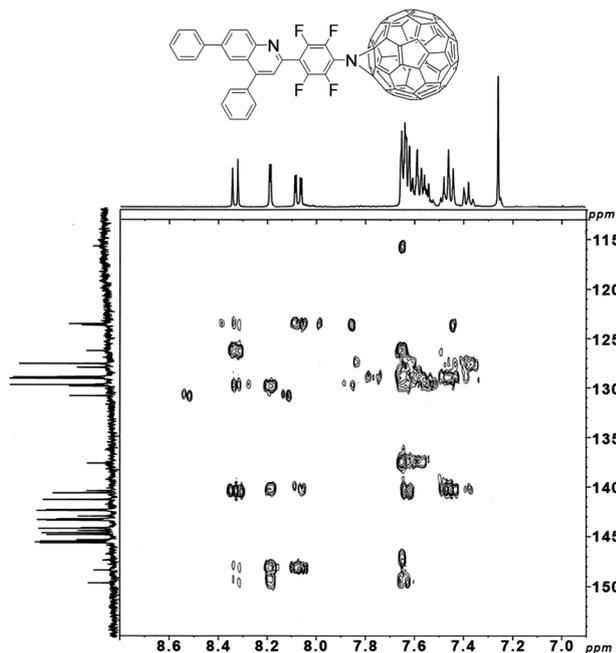


Fig. 1 ^1H , ^{13}C -HMBC 2D NMR spectra of Ph-5FQ-N- C_{60} in the CDCl_3 - CS_2 3 : 1 mixture.

electron accepting random copolymer P3OT-P5FQ was prepared through free radical polymerization (FRP) of the allyl-terminated rr-poly(3-octyl thiophene) macromonomer³⁴ and the

vinylc perfluorophenylquinoline monomer²⁷ (Scheme S5, Table S1†). Scheme 1 presents the general reaction sequence employed for the preparation of perfluoroquinoline- C_{60} hybrids.

The polymeric, copolymeric and small organic molecules carrying the perfluorophenyl ring were converted to azides and then reacted with C_{60} providing the final C_{60} -based hybrids (Schemes S1, S3, S4 and S6†). A systematic NMR investigation of the C_{60} -based small molecular hybrids was performed. In all C_{60} hybrid cases, no alterations in their ^1H NMR spectra were observed in comparison to the initial organic counterpart. As an example the ^1H , ^{13}C -2D HMBC (Heteronuclear Multiple Bond Correlation) NMR spectrum of Ph-5FQ-N- C_{60} in the CDCl_3 - CS_2 3 : 1 mixture is presented in Fig. 1 through which the quinoline carbon peaks can be distinguished from those of C_{60} . In the ^{13}C -NMR spectrum, the appearance of the substituted fullerene peaks at the region 141–146 ppm demonstrates the attachment of C_{60} onto the quinoline moieties. Specifically, 16 well resolved resonances are detected as is expected for [6,6]-closed aziridinofullerene structures.^{35,43–45} Moreover, in Fig. S3† the ^{13}C NMR spectra of Ph-5FQ-N- C_{60} and $\text{C}_{12}(\text{Ph})_2$ -5FQ-N- C_{60} are directly compared to the initial Ph-5FQ and $\text{C}_{12}(\text{Ph})_2$ -5FQ, respectively, showing the distinct alteration of the hybrids' ^{13}C NMR spectra. The peak at about 80.6 ppm observed in the spectra of the hybrids is attributed to the bridgehead carbon atom.^{35,43–45}

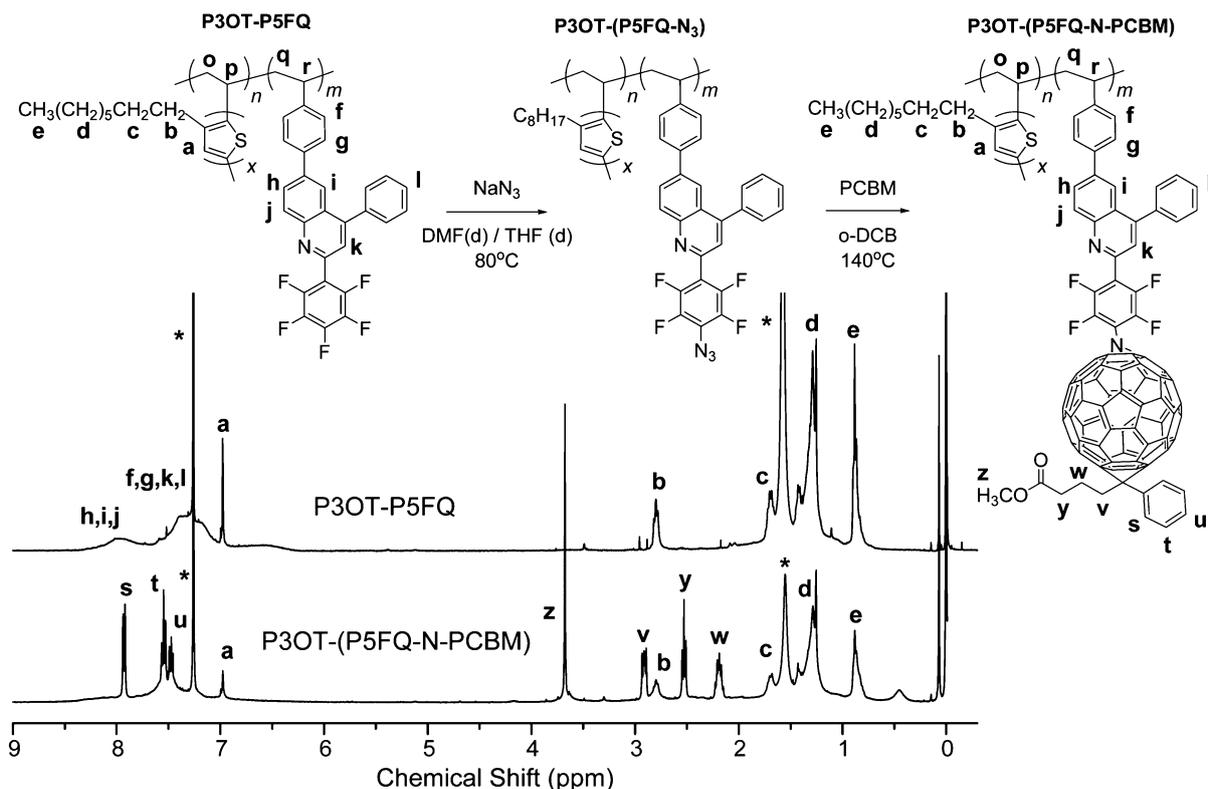


Fig. 2 Synthesis route toward rr-poly(3-octyl thiophene)-co-[poly(perfluorophenyl-quinoline)-PCBM] hybrids and ^1H NMR spectra of the P3OT-P5FQ(iii) copolymer and the P3OT-(P5FQ-N-PCBM) hybrid, both in CDCl_3 .

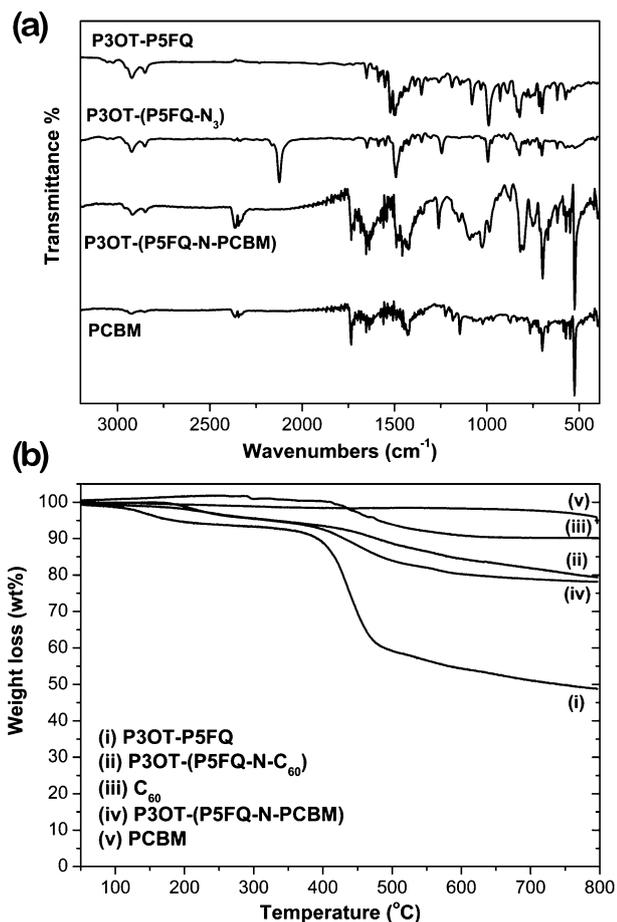


Fig. 3 (a) FT-IR spectra and (b) TGA thermograms of the P3OT-P5FQ copolymer, its C₆₀ and PCBM hybrid analogues and of the neat fullerene derivatives.

The same synthesis procedure for the development of C₆₀ based hybrid electron accepting or electron-donating–electron-accepting materials was also employed for the insertion of PCBM ([6,6]-phenyl-C₆₁-butyric acid methyl ester) moieties along the poly(perfluorophenylquinoline) block of the random copolymer P3OT-P5FQ. Fig. 2 analytically depicts the reaction conditions for the preparation of the P3OT-(P5FQ-N-PCBM) copolymeric hybrid along with a direct comparison of the ¹H NMR spectra of the initial P3OT-P5FQ(iii) random copolymer and its respective PCBM hybrid. The initial P3OT-P5FQ(iii) copolymer presented 50% contents for the P3OT and the P5FQ blocks, respectively. Peak integration at 3.67 ppm, owing to the CH₃O protons of PCBM and at 2.8 ppm due to the CH₂ protons neighboring the thiophene ring, and by keeping the ratio of P3OT to P5FQ as in the initial copolymer, provides a 25% content of PCBM in the hybrid copolymer, 37% for P3OT and 38% for P5FQ. Since the copolymer was exhaustively cleaned with *n*-hexane at 40 °C and then with toluene and no azide functionalities could be detected from FTIR, as explained below, we can conclude with certainty that no free PCBM remained in the final hybrid copolymer. Moreover, TLC performed in typical silica gel plates using toluene as eluent did not

reveal a spot due to free PCBM, other than a diffuse broad spot at the base owing to the copolymeric hybrid.

Additional evidence of the successful introduction of the fullerene derivatives to the organic materials is provided through infrared spectroscopy, Fig. 3a, and thermogravimetric analyses, Fig. 3b.

The FTIR spectra of P3OT-P5FQ are a sum of the respective individual blocks (Fig. S9†). As evident in Fig. 3a the P3OT-(P5FQ-N₃) copolymer shows an intense peak at 2124 cm⁻¹ attributed to the azide functionality, which disappears completely after its cycloaddition to PCBM. The final hybrid P3OT-(P5FQ-N-PCBM) exhibits the 524, 572 and 1429 cm⁻¹ peaks assigned to fullerene and the characteristic peak of the C=O group at 1740 cm⁻¹. For all the C₆₀ bearing molecules FTIR spectroscopy also revealed the disappearance of the azide peak and intense ones at 524 and 572 cm⁻¹ due to the attachment of the C₆₀ units. Even though the 1427 cm⁻¹ peak of C₆₀ was overlapped from the quinoline peaks, the one at 1180 cm⁻¹ was clearly identified (Fig. S1, S2 and S4†).

TGA analysis of the P3OT-P5FQ copolymer and its C₆₀ and PCBM hybrids, Fig. 3b, revealed the anticipated higher carbon residue of the hybrid materials compared to the initial copolymer. For the P3OT-(P5FQ-N-C₆₀) hybrid at 800 °C, a 79.5% residue was obtained while for P3OT-(P5FQ-N-PCBM), a 78% one was obtained compared to the 49% residue of the P3OT-P5FQ copolymer.

The PL spectra in solution after excitation at the quinolines' absorption maxima, ~340 and ~440 nm, showed luminescence peaks owing to the P5FQ segments. For all the C₆₀ hybrids of Scheme 1, the UV-Vis and PL spectra in solution and the film form are presented in Fig. S6–S8.† Noticeably, one common feature which dominates the photoluminescence in the film form of all hybrid cases, monomeric, polymeric, or copolymeric ones, is the quenching of the quinoline's luminescence after the attachment of the fullerene derivatives, as can be seen in Fig. 4.

The optical properties in the film form of P3OT-(P5FQ-N-C₆₀) and P3OT-(P5FQ-N-PCBM) are depicted in Fig. 5 in comparison

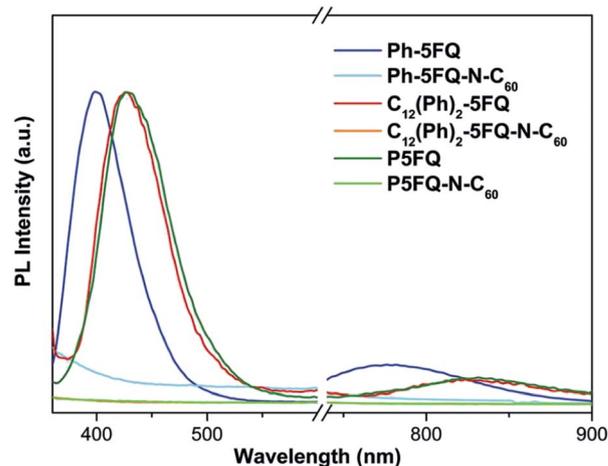


Fig. 4 PL spectra, excitation at 340 nm, of Ph5FQ, C₁₂(Ph)₂5FQ and P5FQ and their respective hybrids with C₆₀, in a film form cast from THF solutions.

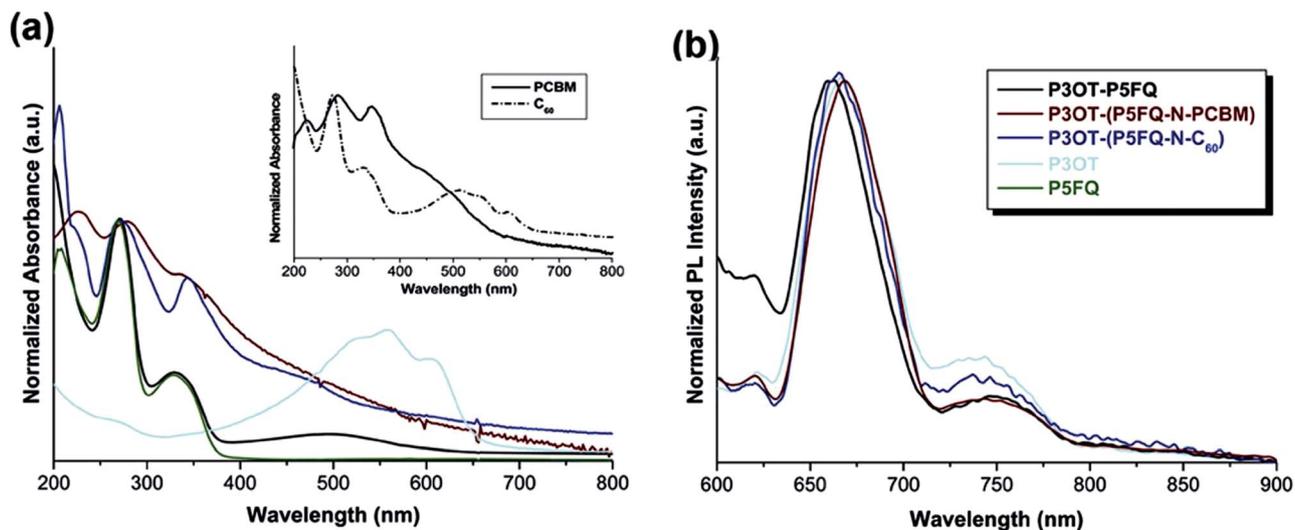


Fig. 5 (a) UV-Vis and (b) PL spectra, excitation at 520 nm, of the P3OT-P5FQ copolymer, its C_{60} and PCBM hybrids and of the net P3OT and P5FQ counterparts, in a film form cast from THF solutions.

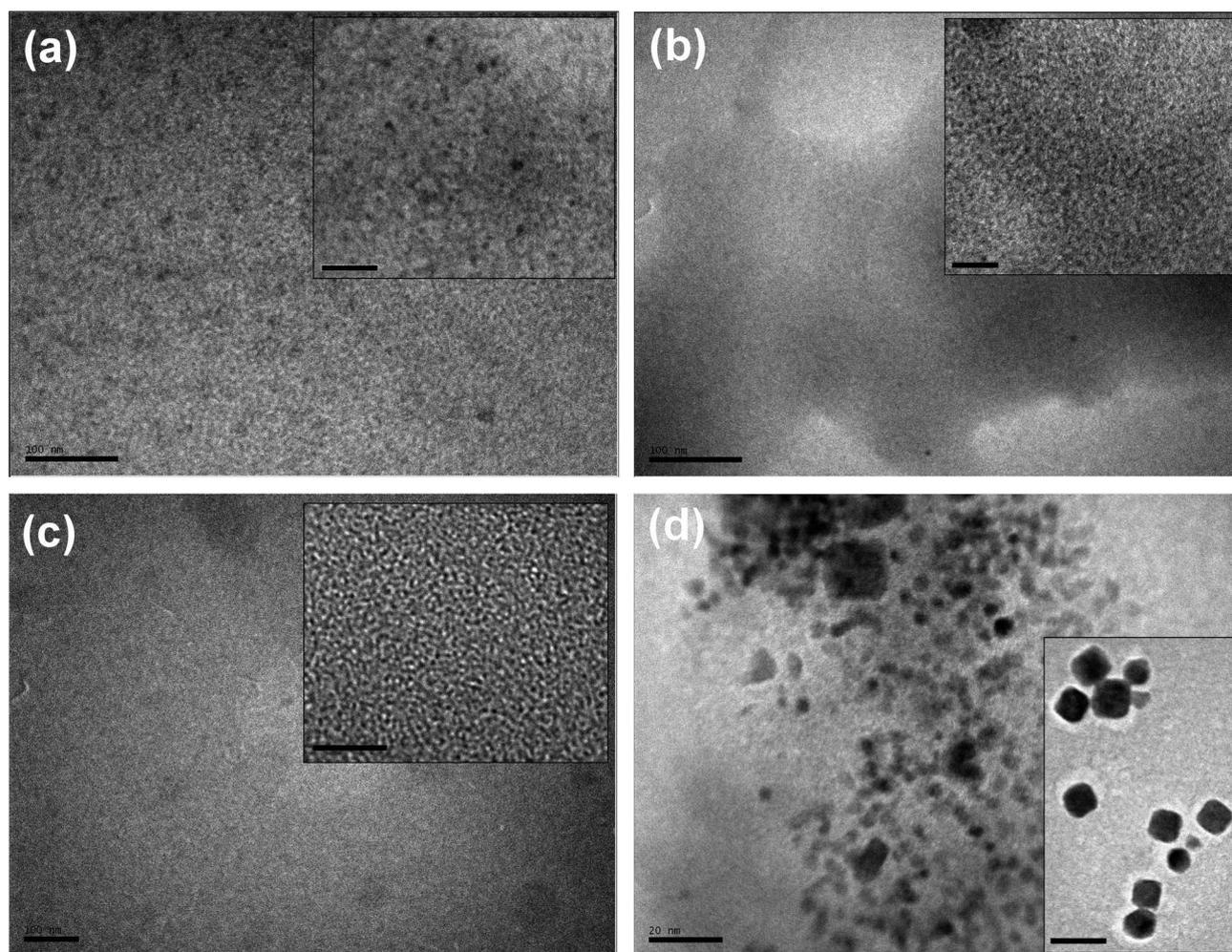


Fig. 6 TEM images of unstained P3OT-(P5FQ-N-PCBM) (a) using THF and (b) using *o*-DCB; (c) P3OT-PF5FQ using *o*-DCB (scale bar 100 nm). The insets in (a)–(c) show higher magnifications with the scale bar corresponding to 20 nm; (d) the TEM image of a P3OT-P5FQ/PCBM blend and of the net PCBM (inset, 20 nm scale bar), both using *o*-DCB.

to the initial electron donor–acceptor copolymer P3OT-P5FQ and to the neat P3OT and P5FQ polymers. The inset shows the absorption of the fullerene derivatives also in the film form. The UV-Vis spectra of the hybrids are a sum of their net counterparts' individual spectrum. The PL spectra of the hybrid materials after excitation at 520 nm, corresponding to the P3OT's absorption maximum, showed the characteristic photoluminescence peaks of the poly(thiophene) segments. The optical properties of these hybrid copolymers in THF solutions (Fig. S10–S13†) also showed the coexistence of P3OT, P5FQ and the fullerene derivative.

The morphology of the hybrid P3OT-(P5FQ-N-PCBM) and the initial P3OT-P5FQ copolymers was investigated by transmission electron microscopy (TEM), Fig. 6. Fig. 6a and b present the TEM images of the hybrid copolymer with PCBM using THF and *o*-DCB, respectively, without any thermal treatment of the samples. Fig. 6c shows the TEM images of the neat P3OT-P5FQ copolymer using *o*-DCB, while it should be noted here that films obtained from THF solutions showed exactly the same morphology. The insets depict higher magnifications with the scale bars corresponding to 20 nm. Uniform films were obtained in all cases. As can be seen in Fig. 6b films of P3OT-(P5FQ-N-PCBM) prepared using *o*-DCB presented smaller nano-phase segregated domains than those from THF (Fig. 6a) owing to the enhanced solubility of the polymeric and the fullerene moieties. For comparison reasons, we also prepared a blend comprising P3OT-P5FQ and PCBM in *o*-DCB. The two components' P3OT-P5FQ:PCBM weight ratio in the blend was 75 : 25 in order to resemble their ratio in the P3OT-(P5FQ-N-PCBM) hybrid. The morphology of the blend (Fig. 6d), in contrast to that of the hybrid copolymer, showed clear PCBM aggregates as well as crystallites similar to those obtained from neat PCBM cast from *o*-DCB, which is depicted in the inset of Fig. 6d at the same magnification of 20 nm.

Conclusions

In conclusion, we have synthesized new perfluorophenyl-quinoline–fullerene hybrids, monomeric, polymeric or copolymeric ones, as electron acceptors or electron donor–acceptors aiming at their application in organic photovoltaics. A straightforward methodology has been employed through which one of the fluorine atoms is quantitatively transformed into an azide that undergoes [3+2]-cycloaddition with fullerene species. All new materials were characterized through various complementary techniques providing evidence of the successful incorporation of the fullerenes and the purity of the final hybrids. Ultimately, this is a general synthetic methodology applicable to the direct attachment of fullerenes of any carbon atom number, and also to all other carbon nanostructures of sp²-hybridization *e.g.* single or multiwall carbon nanotubes and graphenes.

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