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Supporting Information

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

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1. Synthetic Procedures

Synthesis of Dodecyloxy-biphenyl-boronic acid

4-Bromo-4'-hydroxybiphenyl: A 100 mL round bottom flask, equipped with a reflux condenser and a magnetic stirrer, was degassed (flamed under vacuum) and filled with argon. 4-Bromo-4'-acetoxy biphenyl (21.00 g, 72.16 mmol), KOH 10N (360.82 mmol) and 80 mL THF were added and stirred for 3 days under Ar atmosphere. After cooling at 0 ^{o}C, HCl 10N was added and after removing the organic solvent the crude solid was filtered and washed with *n*-hexane. The light yellow solid was dried under vacuum at 40 ^{o}C overnight, Yield 97%.

Dodecyloxy-biphenyl bromide: A 250 mL round bottom flask, equipped with a reflux condenser and a magnetic stirrer, was degassed (flamed under vacuum) and filled with argon. 4-Bromo-4'-Hydroxybiphenyl (10.00 g, 40.16 mmol), dodecyl bromide ($C_{12}H_{25}Br$) (19.23 mL, 80.32 mmol), potassium carbonate (K_2CO_3) (16.63 g, 120.48 mmol) and 70mL acetone were added and the system was flushed with argon and the reaction mixture refluxed for 3 days. The solvent was rotary evaporated and water was added and stirred for 3 hr. The water phase was removed and the solid washed with EtOH 95% and dried under vacuum at 40 ^{o}C overnight, Yield 99.5%. ^{1}H NMR (δ_H; $CDCl_3$; Me_4Si): 7.52 (d, 2H), 7.47 (d, 2H), 7.41 (d, 2H), 6.96 (d, 2H), 3.99 (t, 2H), 1.81 (m, 2H), 1.46 (m, 2H), 1.2-1.4 (m, 16H), 0.89 (t, 3H).

Dodecyloxy-biphenyl-boronic acid: A predried flask 250 mL, equipped with a reflux condenser, a magnetic stirrer and an adding funnel was flamed under vacuum and filled with argon three times. Dodecyloxy-bisphenyl bromide (10.00 g, 23.98 mmol) and 80 mL of freshly distilled THF [THF(dry)] were added and the solution was cooled to -70 ^{o}C. At this temperature were added dropwise (29.97 mL, 47.96 mmol) of *n*-BuLi 1.6 N in *n*-hexane. The system was allowed to stir for 3 h, while maintaining the temperature at -40 ^{o}C. After the 3 h period, the system was cooled again to -70 ^{o}C and $B(OMe)_3$ (19.01 mL, 0.17 mol) was added dropwise. Afterwards the system is allowed warm up to room temperature. The next day, 80 mL of HCl 10% aqueous solution were added and allowed to stir for 4 h. The organic solvent was rotary evaporated and the solid was filtered and washed with water and *n*-hexane. The pure solid was dried at 40 ^{o}C under vacuum overnight, Yield 60%. ^{1}H NMR (δ_H; $CDCl_3$; Me_4Si): 7.79 (d, 2H), 7.66 (d, 2H), 7.58 (d, 2H), 7.01 (d, 2H), 4.04 (t, 2H), 1.86 (m, 2H), 1.50 (m, 2H), 1.2-1.4 (m, 16H), 0.91 (t, 3H).

Synthesis of 6-phenyl-(2-perfluorophenyl)-4-phenyl-quinoline, Ph-5FQ

A 100 mL round bottom flask, equipped with a reflux condenser and a magnetic stirrer, was degassed (flamed under vacuum) and filled with argon. Br-5FQ (4.00 g, 8.88 mmol), 4-phenylboronic acid (1.30 g, 10.65 mmol), potassium carbonate (K_2CO_3) (3.68 g, 26.64 mmol) in 2M aqueous solution, tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) (0.40 g, 0.33 mmol) and 100 mL toluene were added and the system was degassed and flushed with argon again. The flask was covered with aluminum foil and the reaction mixture refluxed for 3 days. Then the mixture was filtered from paper filter followed by the extraction of the organic layer with ethyl acetate (EtOAc) and distilled water. The organic part was stirred with anhydrous magnesium sulphate ($MgSO_4$), filtrated and the solvent was rotary evaporated. The solid was dried under vacuum at 40 ^{o}C overnight and then dispersed in methanol (MeOH) for further purification. The solid was then filtered and the obtained solid was vacuum dried at 40 ^{o}C overnight, Yield 80%. ^{1}H NMR (δ_H; $CDCl_3$; Me_4Si): 8.29 (d, 1H), 8.17 (d, 1H), 8.06 (dd, 1H), 7.67-7.35 (m, 11H). ^{13}C NMR (δ_C; $CDCl_3$; Me_4Si): 149.70, 148.13, 146.49, 140.56, 140.25, 137.34, 130.56, 129.91, 129.57, 128.97, 128.85, 128.82, 127.90, 127.51, 126.29, 123.50, 123.35, 115.71. ^{19}F NMR (δ_F; $CDCl_3$): -161.5, -153.4, -142.5. ^{15}N NMR (δ_N; $CDCl_3$): 122.91.

Synthesis of 6-(4-dodecyloxybiphenyl)-2-perfluorophenyl-4-phenyl-quinoline, $C_{12}(Ph)_2$-5FQ

A 100 mL round bottom flask, equipped with a reflux condenser and a magnetic stirrer, was degassed (flamed under vacuum) and filled with argon. Br-5FQ (1.50 g, 3.33 mmol), 4-(4-dodecyloxyphenyl) phenyl boronic acid (1.91 g, 4.99 mmol), K_2CO_3 (2.76 g, 19.98 mmol) in 2M aqueous solution, $Pd(PPh_3)_4$ (0.23 g, 0.19 mmol) and 40 mL toluene were added and the system was degassed and flushed with argon again. The flask was covered with aluminum foil and the reaction mixture was refluxed for 2 days. Then the mixture was filtered followed by the extraction of the organic layer with EtOAc and distilled water. The organic part was stirred with $MgSO_4$, filtrated and the solvent was rotary evaporated. The solid was dried under vacuum at 70 ^{o}C overnight. For further purification after washing with MeOH and hexane, the solid was vacuum dried at 70 ^{o}C overnight, Yield 40%. ^{1}H NMR (δ_H; $CDCl_3$; Me_4Si): 8.38 (d, 1H), 8.22 (d, 1H), 8.13 (dd, 1H),7.71-7.50 (m, 12H), 6.98 (d, 2H), 4.00 (t, 2H), 1.81 (m, 2H), 1.55-1.20 (m, 18H), 0.88 (t, 3H). ^{13}C NMR (δ_C; $CDCl_3$; Me_4Si): 159.01, 149.66, 148.17, 146.70, 140.57, 140.15, 138.38, 137.41, 132.64, 130.62, 129.76, 129.61, 128.85, 128.78, 128.03, 127.82, 127.22, 126.37, 123.71, 123.38, 123.24, 114.65, 68.15, 31.92, 30.92, 29.67-29.29, 26.07, 22.69, 14.12. ^{19}F NMR (δ_F; $CDCl_3$): -161.52, -153.39, -142.46. ^{15}N NMR (δ_N; $CDCl_3$): 123.46.

Synthesis of Ph-5FQ-N_3

In a 50 mL round bottom flask (degassed and filled with argon) Ph-5FQ (1.00 g, 2.24 mmol), sodium azide (NaN_3) (0.17 g, 2.68 mmol) and 20 mL N,N-dimethylformamide anhydrous 99.8% [DMF(dry)] were stirred at 40 ^{o}C for 24 h. The reaction mixture was precipitated into deionized water. After filtration, the solid was washed with deionized water three times in order to remove unreacted NaN_3 and sodium fluoride (NaF). Finally the solid was dried under vacuum at 30°C overnight, Yield 90%. ^{19}F NMR (δ_F; $CDCl_3$): -151.59, -142.91. ^{15}N NMR (δ_N; $CDCl_3$): 183.05, 456.10.

Synthesis of $C_{12}(Ph)_2$-5FQ-N_3

In a 50 mL round bottom flask (degassed and filled with argon) $C_{12}(Ph)_2$-5FQ (300.00 mg, 0.42 mmol), NaN_3 (33.00 mg, 0.51 mmol) and 30 mL DMF(dry) were stirred at 40 °C for 24 h. The reaction mixture was precipitated into deionized water. After filtration the solid was washed with deionized water three times in order to remove unreacted NaN_3 and NaF and dried under vacuum at 30 °C overnight, Yield 71%. ^{19}F NMR (δ_F; $CDCl_3$): -151.5, -142.7. ^{15}N NMR (δ_N; $CDCl_3$): 311.06, 133.42.

Synthesis of homopolymer P5FQ

P5FQ was prepared according to the previously published procedure.[30] Herein, we provide the ^{19}F, ^{15}N NMR characterization of the homopolymer: ^{19}F NMR (δ_F; $CDCl_3$): -161.61, -153.21, -142.57. ^{15}N NMR (δ_N; $CDCl_3$): 123.47.

Synthesis of P5FQ-N_3

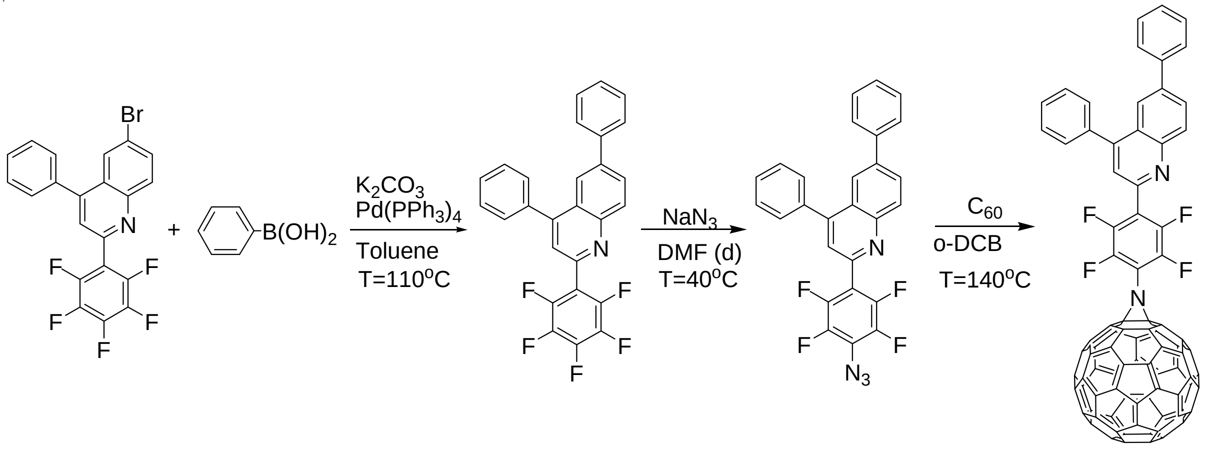
In a 50 mL round bottom flask (degassed and filled with argon) P5FQ (250.00 mg, 0.53 mmol), NaN_3 (38.00 mg, 0.58 mmol) and 5 mL DMF(dry) were stirred at 40 °C for 24 h. The reaction mixture was precipitated into a mixture of deionized water:methanol 1:1. After filtration, the solid was washed with deionized water three times in order to remove unreacted NaN_3 and NaF and was dried under vacuum at 30 °C overnight, Yield 85%. ^{19}F NMR (δ_F; $CDCl_3$): -151.81, -142.96. ^{15}N NMR (δ_N; $CDCl_3$): 375.33, 181.50.

2. Tables

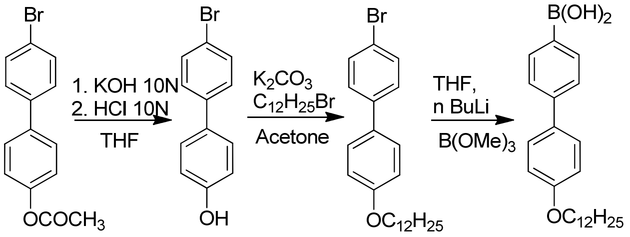
Table S1. Molecular characteristics of P3OT - P5FQ copolymers through GPC analysis and the feed ratio of the monomers used for the polymerization reaction.

Sample	**Feed Ratio** P3OT : P5FQ	***Mn***	***Mw***
P3OT-P5FQ(i)	1:10	15320	19560
P3OT-P5FQ(ii)	1:10	21735	27840
P3OT-P5FQ(iii)	1:8	22370	28240
P3OT-P5FQ(iv)	1:6	22740	31080
P3OT-P5FQ(v)	1:5	25010	29930
vinylP3OT	-	21265	25660

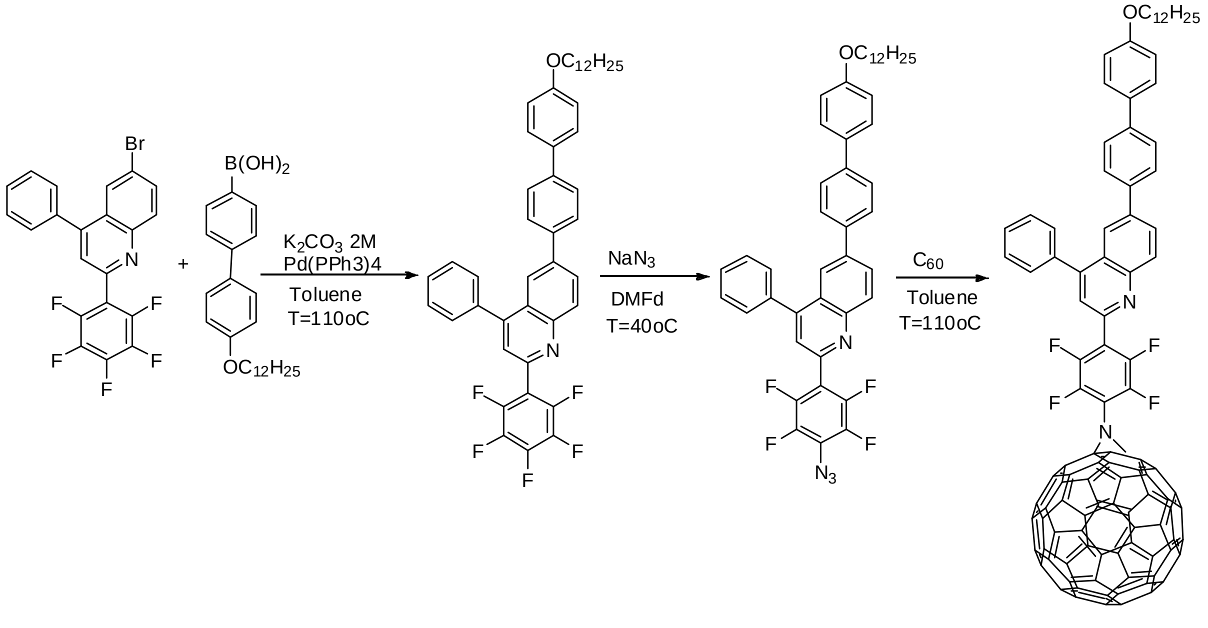
3. Schemes



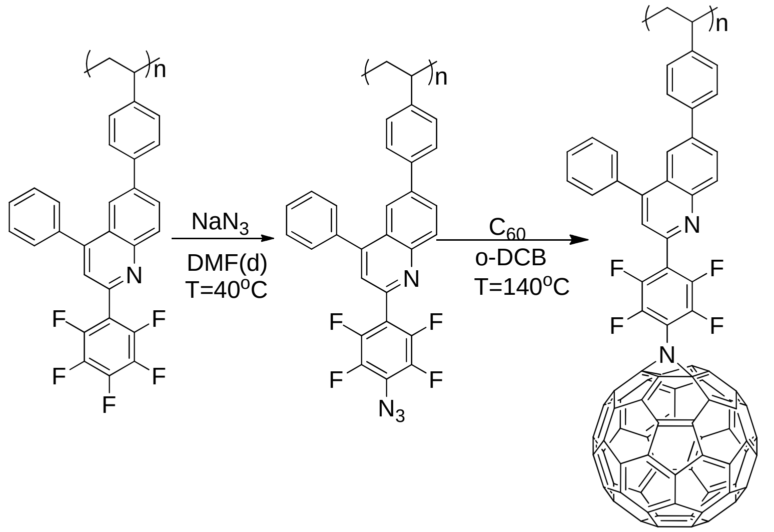
Scheme S1: Synthetic route of Ph-5FQ-N-C_{60}



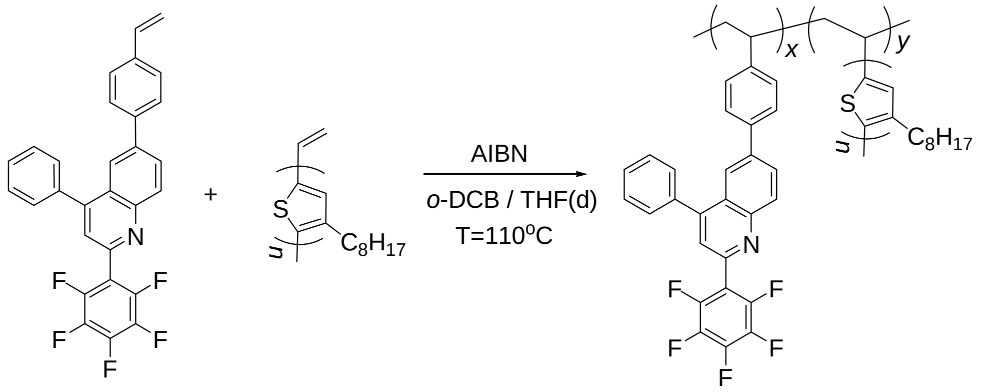
Scheme S2: Synthetic route of dodecyloxy-biphenyl-boronic acid



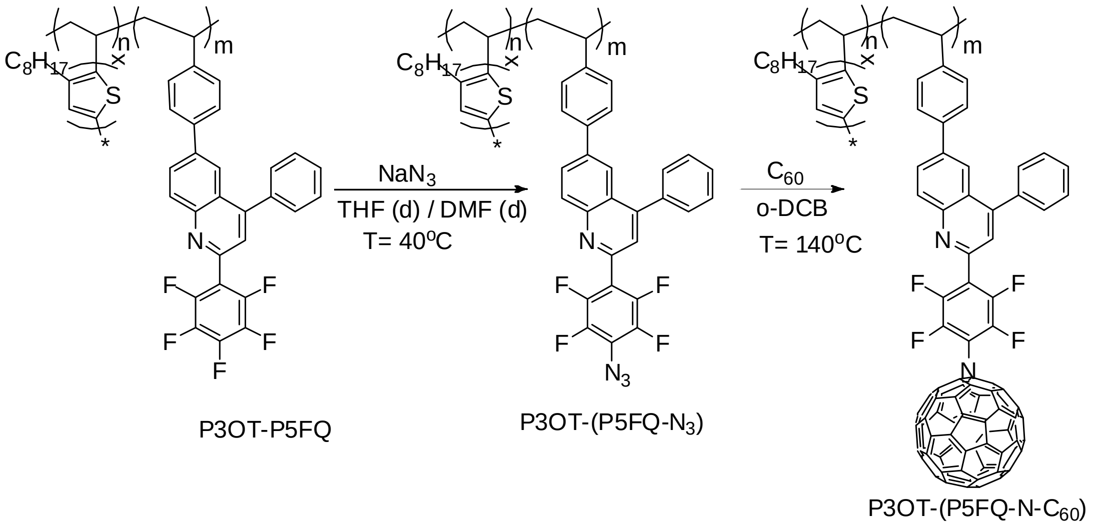
Scheme S3: Synthetic route of dodecyloxy-biphenyl-perfluorophenylquinoline C_{60} hybrid, $C_{12}(Ph)_2$-5FQ-N-C_{60}.



Scheme S4: Synthetic route of poly(perfluorophenyl-quinoline) C_{60} hybrid, P5FQ-N-C_{60}.



Scheme S5: Synthetic route of the random copolymer P3OT-P5FQ.



Scheme S6: Synthetic route of the hybrid copolymer P3OT-(P5FQ-N-C_{60})

4. Figures

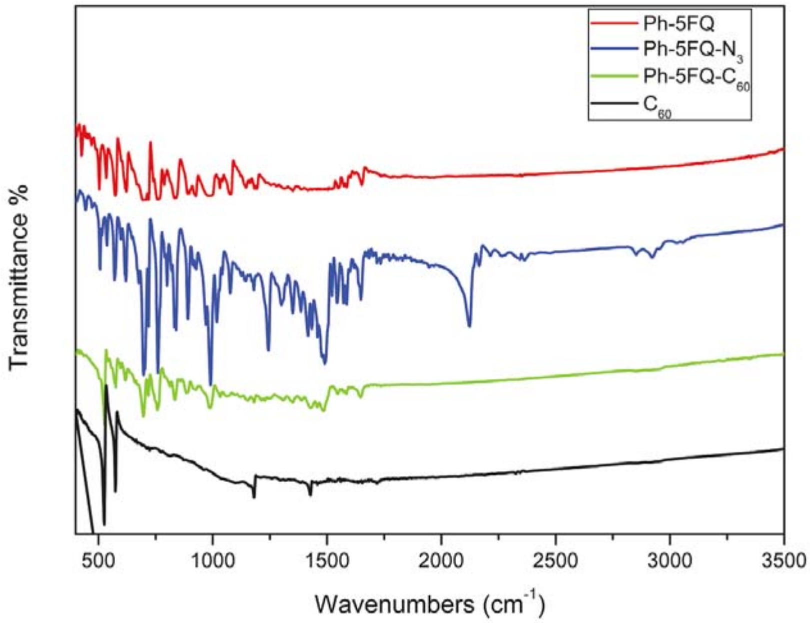


Figure S1. FT-IR transmittance of Ph-5FQ, Ph-5FQ-N$_3$, Ph-5FQ-N-C$_{60}$ and C$_{60}$

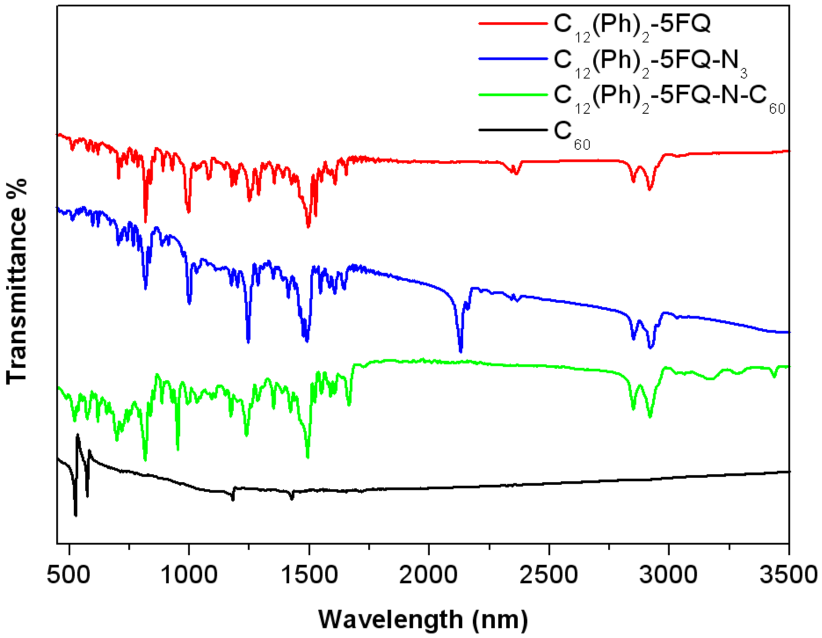
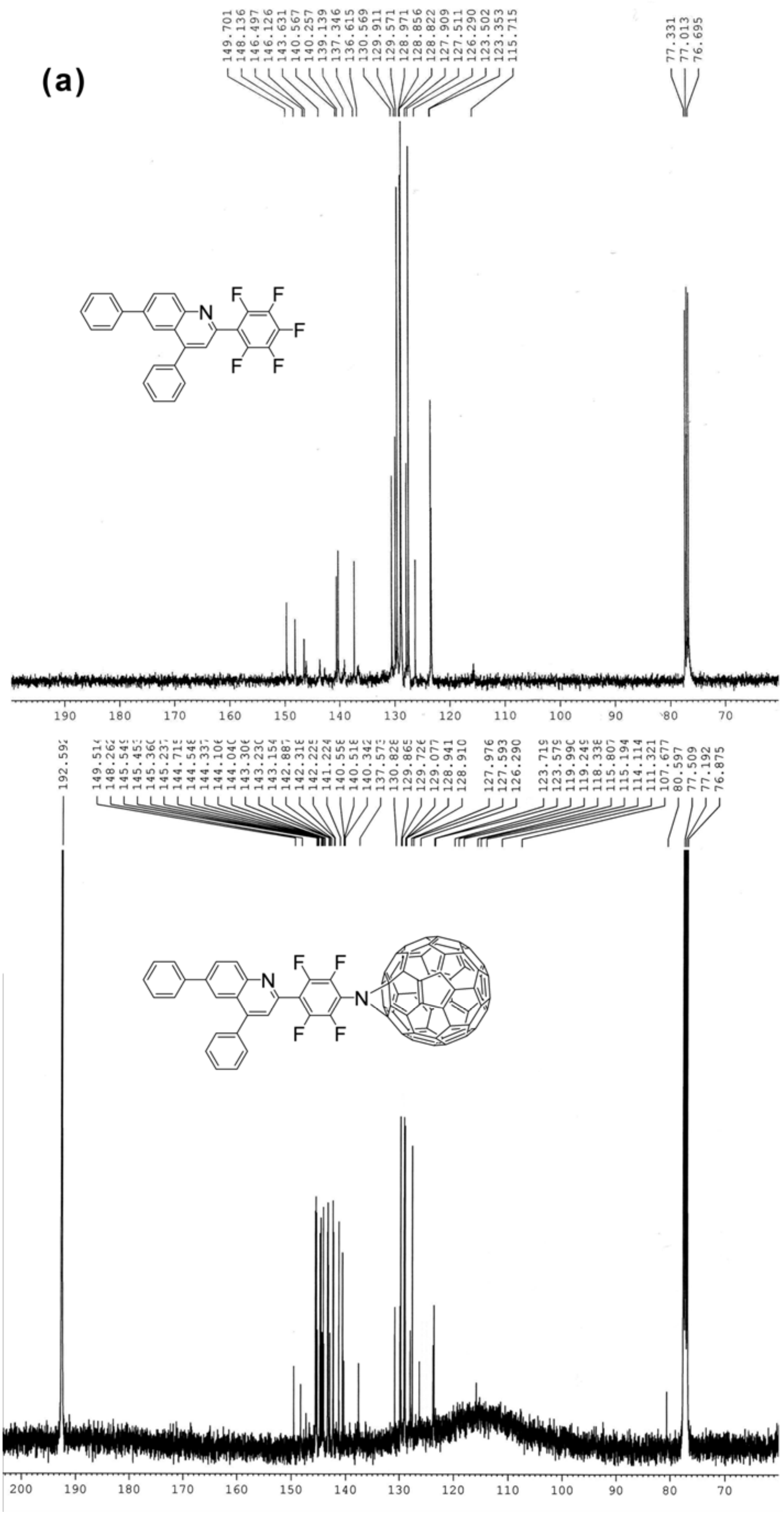


Figure S2. FT-IR transmittance of C$_{12}$(Ph)$_2$-5FQ, C$_{12}$(Ph)$_2$-5FQ-N$_3$, C$_{12}$(Ph)$_2$-5FQ-N-C$_{60}$ and C$_{60}$


(a)
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146.126
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129.571
128.971
128.856
128.822
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127.511
126.290
123.502
123.353
115.715
77.331
77.013
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F
F
F
F
F
190
180
170
160
150
140
130
120
110
100
90
80
70
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145.549
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145.237
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144.548
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129.865
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80.597
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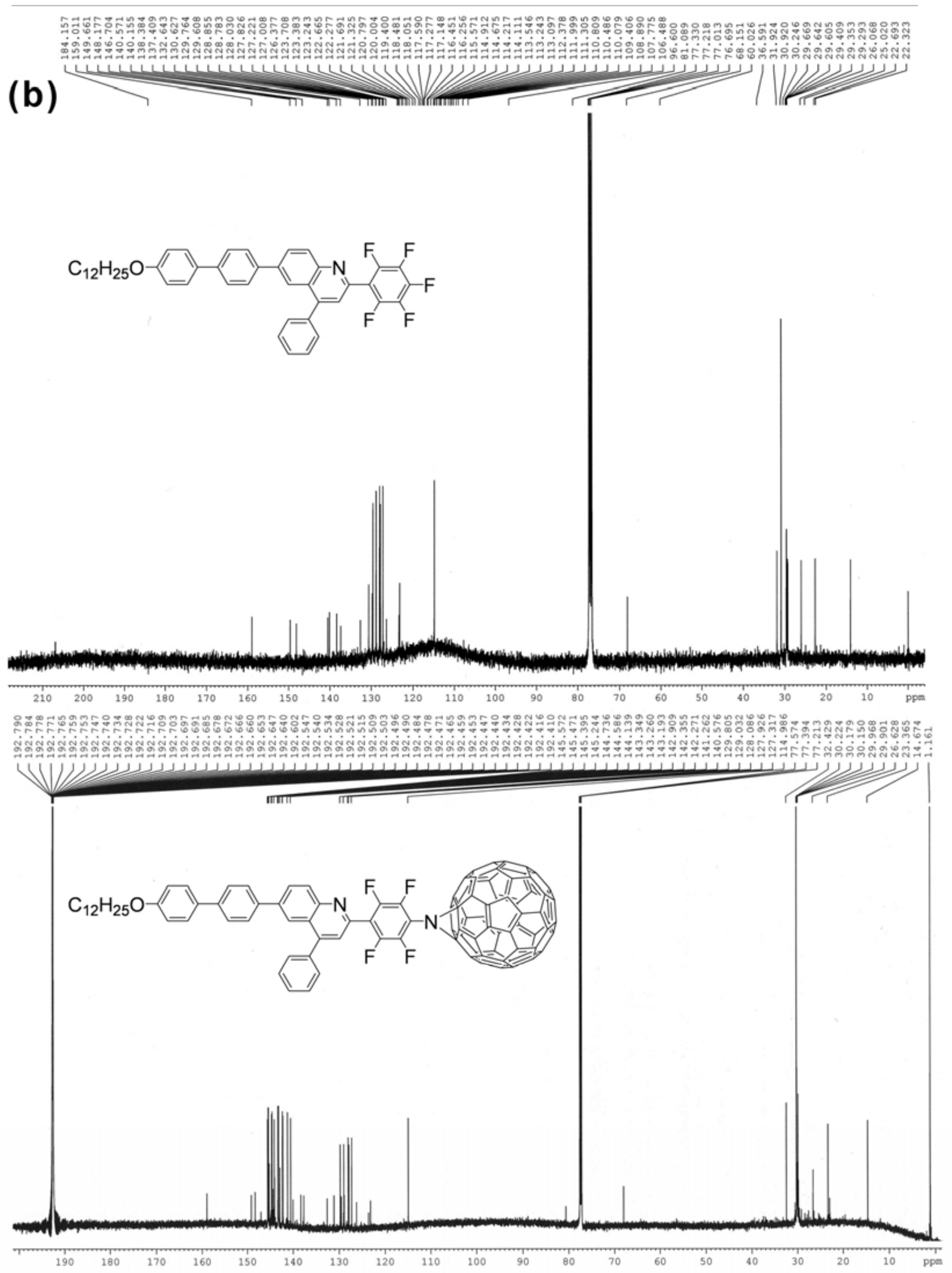

Figure S3. Comparison of the ^{13}C NMR spectra (a) of Ph-5FQ (top) and of Ph-5FQ-N-C_{60} (bottom), and (b) of $C_{12}(Ph)_2$-5FQ (top) and of $C_{12}(Ph)_2$-5FQ-N-C_{60} (bottom). The organic molecules' NMR spectra were recorded in $CDCl_3$ and those of the hybrids in a $CDCl_3$:CS_2 3:1 mixture.

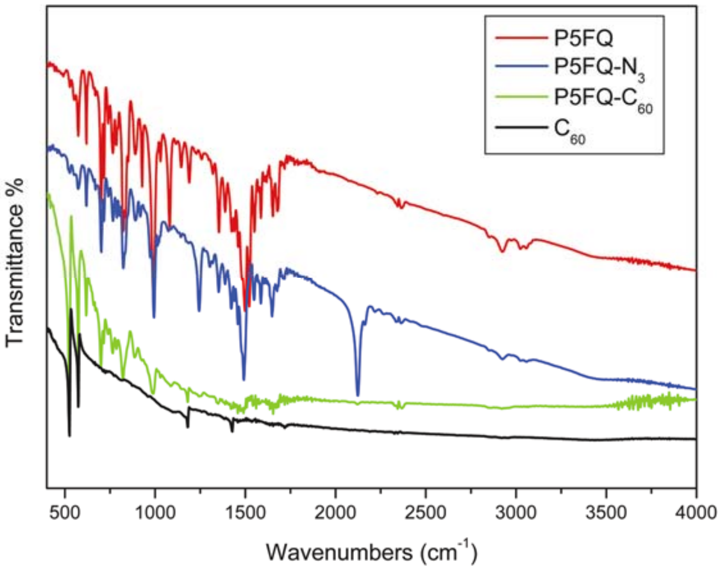

Figure S4. FT-IR transmittance of P5FQ, P5FQ-N$_3$, P5FQ-N-C$_{60}$ and C$_{60}$

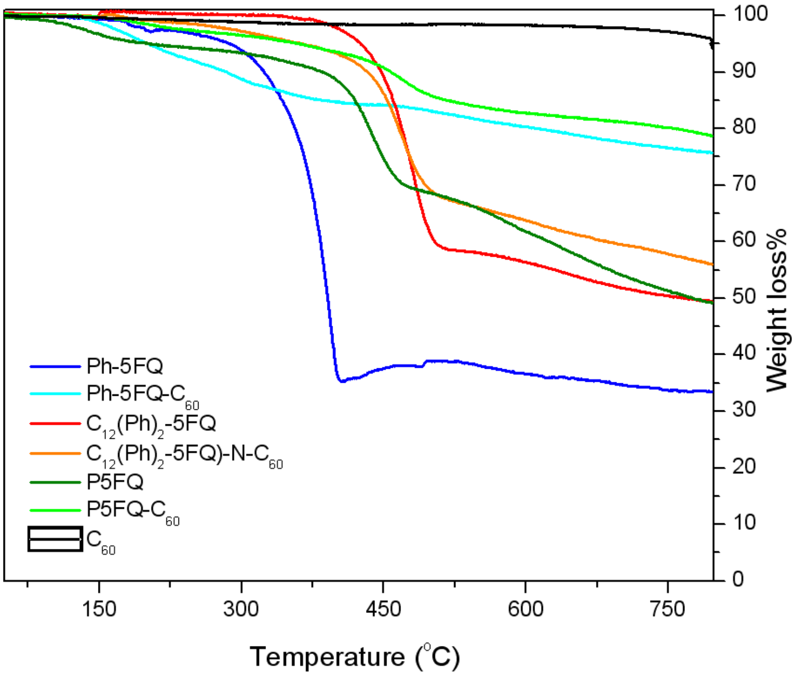

Figure S5. Thermogravimetric analysis of Ph-5FQ, Ph-5FQ-N-C$_{60}$, C$_{12}$(Ph)$_2$-5FQ, C$_{12}$(Ph)$_2$-5FQ-N-C$_{60}$, P5FQ, P5FQ-N-C$_{60}$ and C$_{60}$

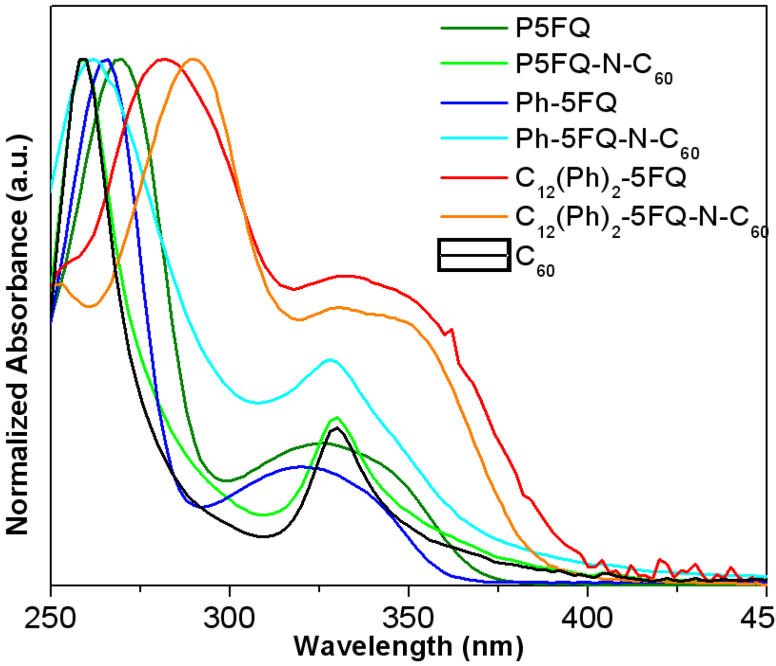

Figure S6. Uv-vis spectra of Ph-5FQ, Ph-5FQ-N-C_{60}, $C_{12}(Ph)_2$-5FQ, $C_{12}(Ph)_2$-5FQ-N-C_{60}, and C_{60} in THF solutions and of P5FQ and P5FQ-N-C_{60} in $CHCl_3$ solutions.

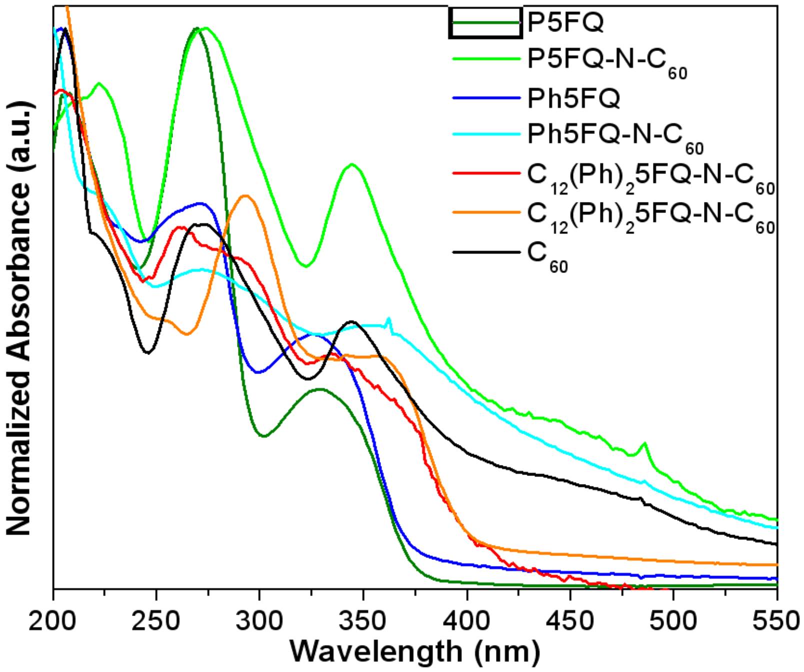

Figure S7. Uv-vis spectra of Ph-5FQ, Ph-5FQ-N-C_{60}, $C_{12}(Ph)_2$-5FQ, $C_{12}(Ph)_2$-5FQ-N-C_{60}, P5FQ, P5FQ-N-C_{60} and C_{60} in film form.

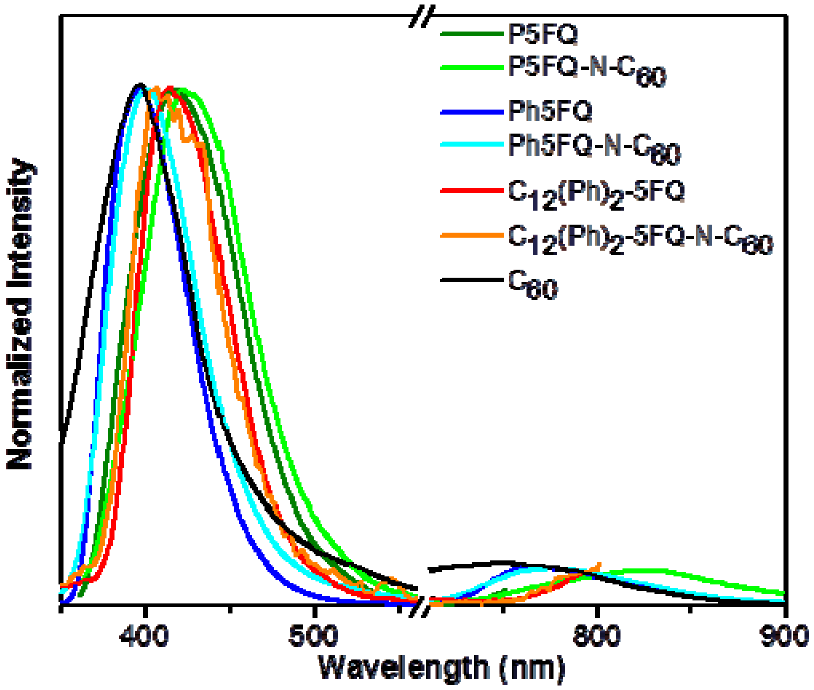

Figure S8. PL spectra of Ph-5FQ, Ph-5FQ-N-C_{60} (excitation at 320 nm), $C_{12}(Ph)_2$-5FQ, $C_{12}(Ph)_2$-5FQ-N-C_{60}, P5FQ, P5FQ-N-C_{60} and C_{60} (excitation at 340 nm) in THF solutions.

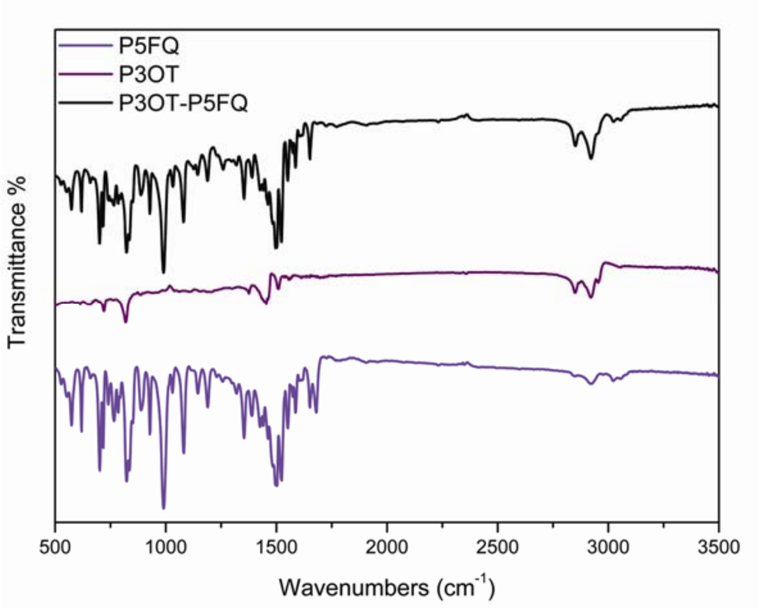

Figure S9. FT-IR transmittance of homopolymer P5FQ, homopolymer P3OT and copolymer P3OT-P5FQ

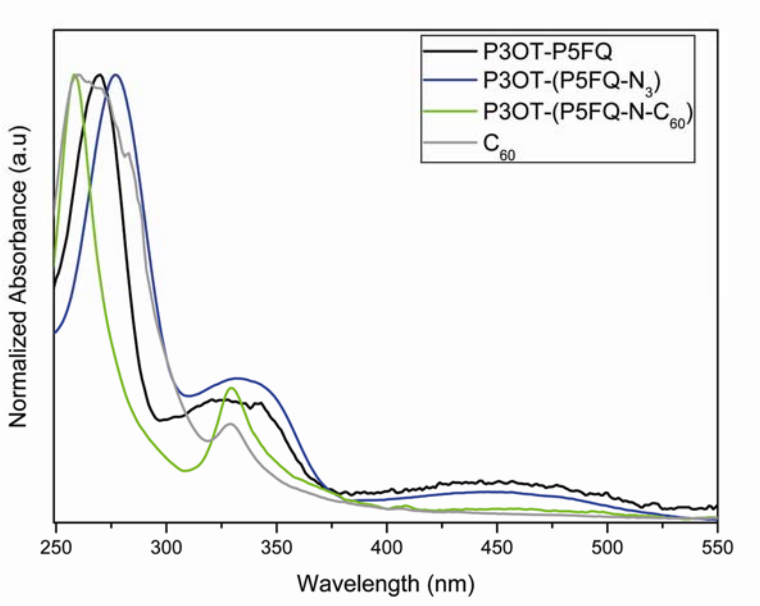

Figure S10. Uv-vis spectra of copolymer P3OT-P5FQ, copolymer P3OT-(P5FQ-N$_3$), hybrid copolymer P3OT-(P5FQ-N-C$_{60}$) and C$_{60}$ in THF solution

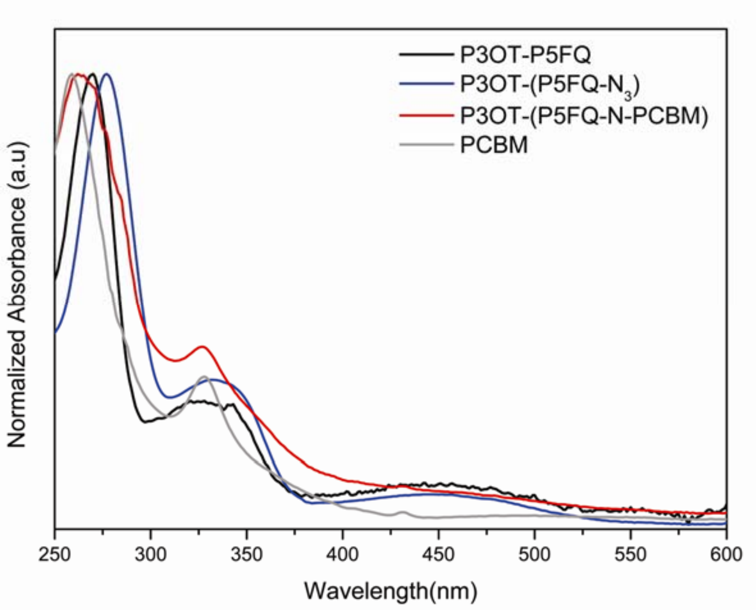

Figure S11. Uv-vis spectra of copolymer P3OT-P5FQ, copolymer P3OT-(P5FQ-N$_3$), hybrid copolymer P3OT-(P5FQ-N-PCBM) and PCBM in THF solution.

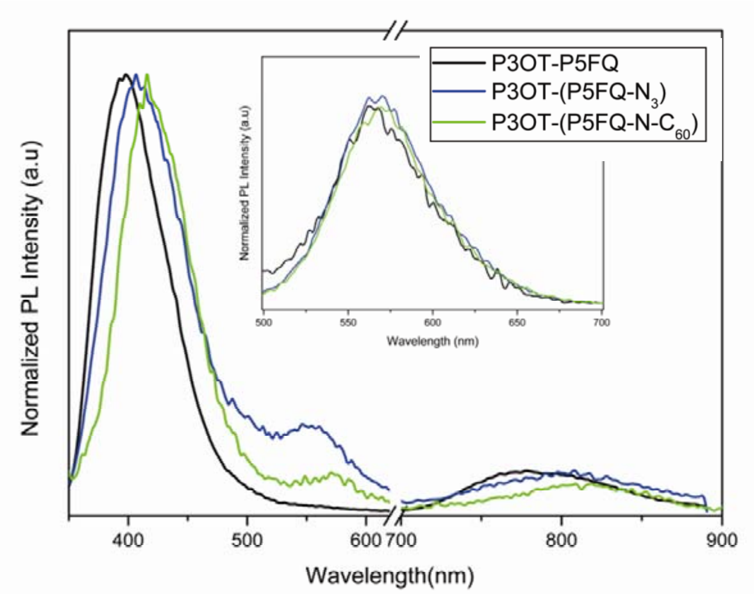

Figure S12. PL spectra of copolymer P3OT-P5FQ, copolymer P3OT-(P5FQ-N$_3$) and hybrid copolymer P3OT-(P5FQ-N-C$_{60}$) in THF solution after excitation at 340nm. The inset shows the respective PL spectra after excitation at 450nm.

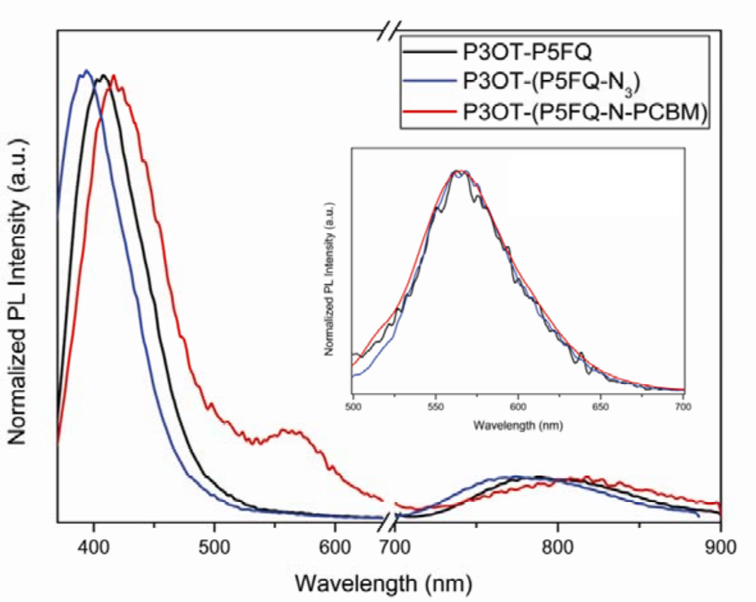

Figure S13. PL spectra of copolymer P3OT-P5FQ, copolymer P3OT-(P5FQ-N$_3$) and hybrid copolymer P3OT-(P5FQ-N-PCBM) in THF solution, after excitation at 330nm. The inset shows the respective PL spectra after excitation at 440nm.