Semiconducting End-Perfluorinated P3HT-Fullerenic Hybrids as Potential Additives for P3HT/$IC_{70}BA$ blends

S. Kakogianni,[a] M. A. Lebedeva,[b] G. Paloumbis,[c] A. K. Andreopoulou,[a,d] K. Porfyrakis,[b] and J. K. Kallitsis[a,d,*]

a. Department of Chemistry, University of Patras, 26504 Patras ,Greece

b. Department of Materials, University of Oxford, 16 Parks Road, Oxford, UK, OX1 3PH.

c. Advent Technologies SA, Patras Science Park, Stadiou str., Platani, GR-26504, Greece.

d. Foundation for Research and Technology Hellas/ Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Platani Str., Patras, GR26504, Greece.

1. Synthetic Procedures.

Ph-5FQ-N-C_{70}: Ph-5FQ-N_3 [1] (0.50 g, 1.06 mmol) and C_{70} (0.85 g, 1.06 mmol) were dissolved in *o*-DCB (40 mL), degassed with argon, and heated to 140 °C for 48 h. The solvent was then removed under reduced pressure, the solid re-dissolved in toluene (60 mL) and filtered to remove any insoluble residuals. The filtrate was then concentrated to the minimum volume (8 mL) and purified by column chromatography (silica gel loaded with petroleum ether, eluted with petroleum ether : toluene gradient mixtures 4:1, 1:1, 1:2, 1:6). The product containing fraction was then concentrated to dryness and dried under vacuum at 50 °C overnight to yield the product (0.82 g, 60%). ^{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): 154.3, 151.4, 151.3, 151.2, 151.1, 150.6, 150.5, 149.9, 149.4, 149.3, 149.2, 148.8, 148.6, 148.5, 148.4, 148.3, 148.2, 148.1, 148.0, 147.7, 147.6, 147.4, 147.3, 147.1, 146.9, 146.4, 146.3, 146.2, 146.1, 146.0, 145.7, 145.3, 145.1, 144.8, 144.7, 144.6, 144.4, 144.3, 144.1, 144.0, 143.9, 143.2, 143.1, 142.7, 142.5, 142.4, 141.2, 139.9, 136.2, 133.6, 132.3, 132.2, 131.9, 131.8, 131.4, 131.3, 131.1, 130.9, 130.6, 129.7, 129.4, 129.3, 129.1, 129, 128.2, 127.7, 127.6, 126.5, 126.3, 124.5, 124.0, 123.8, 123.6, 119.1. ^{19}F NMR (δ_F; $CDCl_3$): -136.1, -130.5. ^{15}N (δ_N; $CDCl_3$): 197.94.

$IC_{70}MA$: C_{70} (800 mg, 0.95 mmol) and indene (880 mg, 7.6 mmol) were dissolved in o-DCB (40 mL), and thoroughly degassed with N_2. The mixture was then refluxed at 180°C for 15 h, allowed to cool to RT, and added to a beaker containing MeOH (400 mL). The resulting mixture was kept at 0 °C for 1h, and filtered. The resulting precipitate was washed with hexane (3 x 50 mL), and MeOH (1 x 50 mL), and dried in air. The resulting solid was then purified twice by column chromatography (hexane/toluene 95:5) to isolate the desired monoadduct. Further purification was carried out by suspending it in MeOH (100 mL), filtering, washing with MeOH (50 mL), and drying in air to give the product (530 mg, 58%) as a dark brown solid. ^{1}H NMR (δ_H; $CDCl_3$; Me_4Si): 7.65 (d, 1H, J=7.2 Hz; ArH), 7.40-7.40 (m, 3H, ArH), 4.76 (s, 1H, CH), 4.30 (s, 1H, CH), 2.81 (d, 1H, J = 9.8 Hz, bridge C<u>H</u>H), 2.47 (d, 1H, J = 9.8 Hz, bridge CH<u>H</u>). MALDI-TOF MS (DCTB/MeCN, m/z): 956.1 (M^-).

end-($(P3HT)_n$-5) (low MW n=6 and medium MW, n=12): The low and medium MW *end*-$(P3HT\text{-}5F)_n$ were synthesized using the same synthetic procedure as described in the main manuscript for *high MW* polymer synthesis, with the exception of the following reagent quantities: diBr-(3-hexylthiophene) (0.0154 mol) and $Ni(dppp)Cl_2$ (0.3 mmol). Yield: 56%. R*egioregularity* 94% (calculated from ^{1}H NMR).

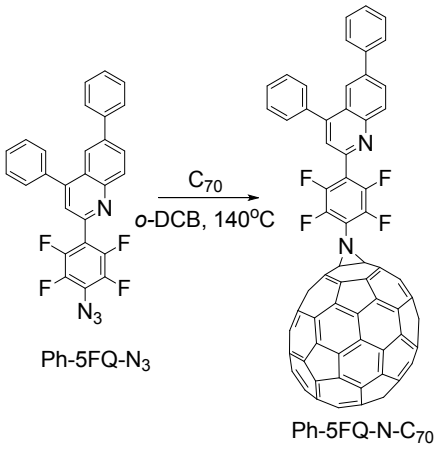
(P3HT)$_n$-5F-N-C$_{70}$: The *medium* and *high MW* C_{70}-containing hybrids were synthesized according to the procedure described for the *low MW* hybrid in the main manuscript, except for the following reagent quantities:

(P3HT)$_n$-5F-N$_3$	**C$_{70}$**	**Yield**
150 mg (*n=12)*	65 mg	60%
300 mg (*n=80)*	16 mg	65%

(P3HT)$_n$-5F-N-IC$_{70}$MA: The *high MW* $IC_{70}MA$-containing hybrid was synthesized according to the procedure described for the *medium MW* hybrid in the main manuscript, except for the following reagent quantities:

(P3HT)$_n$-5F-N$_3$	IC$_{70}$MA	Yield
200 mg (*n=80)*	13 mg	75%

2. Preparation and characterization of phenyl-perfluorophenyl-C$_{70}$ (Ph-5FQ-N-C$_{70}$) hybrid.



Scheme S1: Preparation of phenyl perfluorophenylquinoline-C_{70} (Ph-5FQ-N-C_{70}) hybrid.

The purified hybrid material (Ph-5FQ-N-C_{70}) was thoroughly characterized by ATR, ^1H and ^{13}C NMR (Figure S1) spectroscopies. The ATR spectrum (Figure S1a) of the crude Ph-5FQ-N-C_{70} hybrid exhibits intense peaks of C_{70} fullerene which decrease significantly after the chromatographic purification. The ^{13}C NMR spectrum (Figure S1b) of the Ph-5FQ-N-C_{70} hybrid shows 42 peaks in the region 120-156 ppm, which are attributed to the functionalized C_{70} carbon cage. The Ph-5FQ-N-C_{70} hybrid was also characterized through UV-Vis and PL spectrospcopies in solution and in film form (Figures S2). The UV-Vis spectra of the small molecule Ph-5FQ-N-C_{70} hybrid recorded in toluene solution correspond to a sum of the characteristic peaks of its net counterparts, and the PL spectra upon excitation at the quinoline's absorption maximum (340 nm) presented no quenching of the photoluminecence. The UV-Vis spectra of the Ph-5FQ-N-C_{70} recorded in film form (Figure S3) presented a broad and nearly featureless absorption in the region of 200-800 nm, while upon excitation at 360 nm quenching of photoluminescence intensity was observed.

3. Spectroscopic characterization of Ph-5FQ-N-C_{70}.

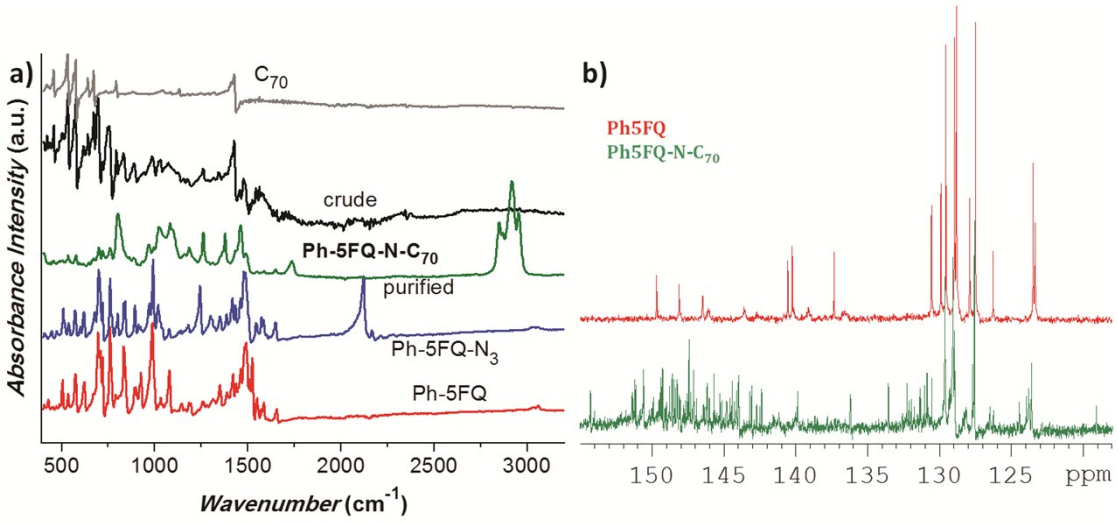


Figure S1: a) ATR spectra of the purified Ph-5FQ-N-C_{70} and the corresponding precursors and b) ^{13}C NMR spectra of the purified Ph-5FQ-N-C_{70} and the initial Ph-5FQ recorded in $CDCl_3$.

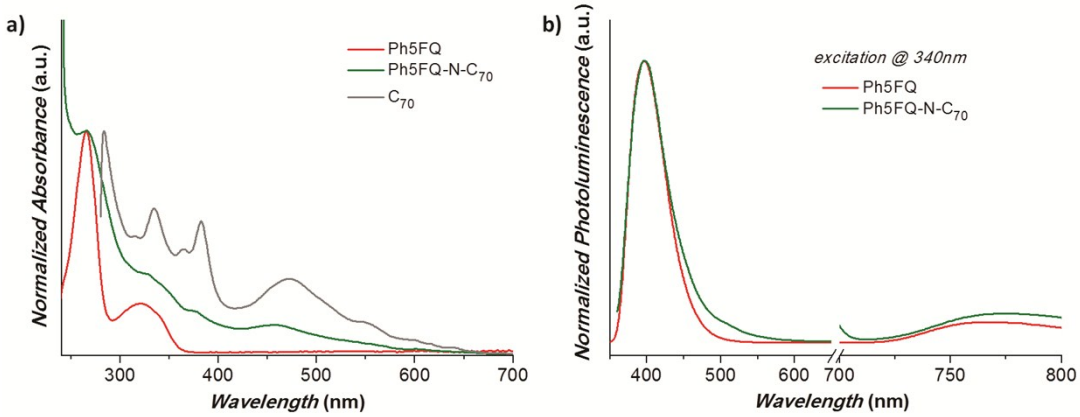


Figure S2: a) Normalized Absorption spectra of Ph-5FQ, Ph-5FQ-N-C_{70} hybrid and C_{70} and b) Photoluminescence spectra, upon excitation at 340 nm, of Ph-5FQ and Ph-5FQ-N-C_{70}, recorded in toluene solutions.

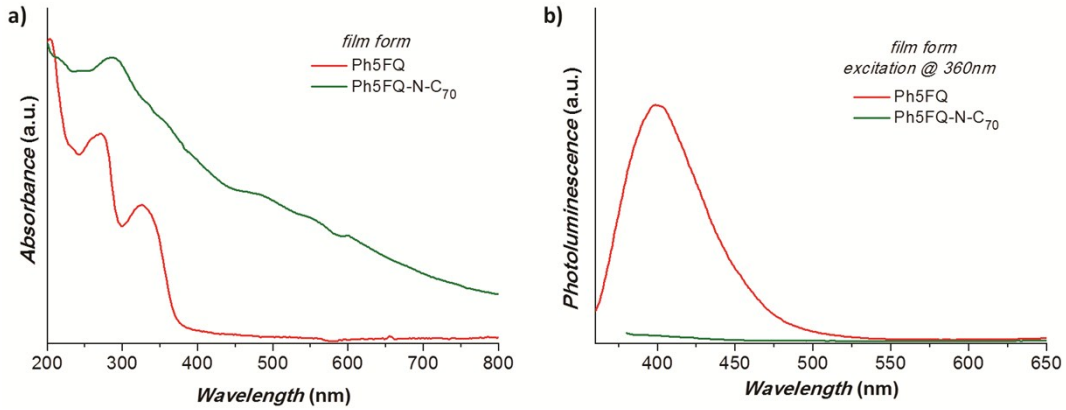


Figure S3: a) Absorption spectra of Ph-5FQ and Ph-5FQ-N-C_{70} hybrid and b) Photoluminescence spectra, upon excitation at 360 nm, of Ph-5FQ and Ph-5FQ-N-C_{70}, recorded in film form.

4. Evaluation of the purification procedure P3HT-5F-N-C_{70} and P3HT-5F-N-IC_{70}MA hybrids by ATR spectroscopy.

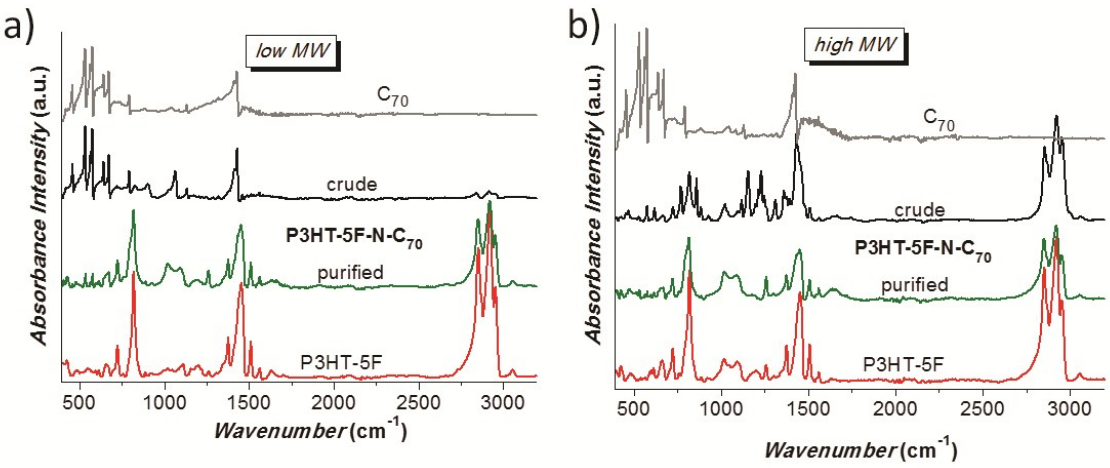


Figure S4: ATR spectra of a) *low* and b) *high MW* crude and purified *end* P3HT-5F-N-C_{70} hybrids and the corresponding *end* P3HT-5F precursors.

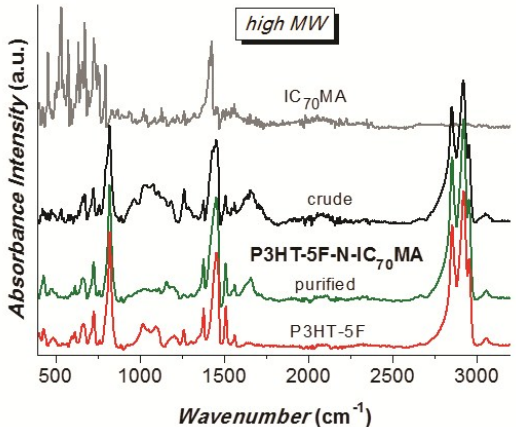


Figure S5: ATR spectra of *high MW* crude and purified *end* P3HT-5F-N-IC_{70}MA hybrid and the initial P3HT-5F and fullerene derivative, respectively.

5. HPLC purification.

The medium MW P3HT-5F-N-IC_{70}MA hybrid was additionally purified by high performance liquid chromatography (HPLC) in toluene (**Figure S6**). 40 mg of P3HT-5F-N-IC_{70}MA (n=12) were dissolved in 10 mL of HPLC grade toluene, and purified by HPLC over 5 injections (2 mL per injection). The hybrid polymer appeared on HPLC as a long tail of weak intensity from 3.8 min to 60 min, the eluted material was collected until the eluted solution became colourless (25 mg were collected in total). The first fraction eluted at 2-3.8 min (~10 mg) appeared to be the unreacted fullerene-free polymeric precursor *end* P3HT-5F-N_3, as was confirmed by the absence of the IC_{70}MA signal in MALDI, the absence of the fullerene reduction peaks in cyclic voltammetry, and the absence of the characteristic fullerene absorption in the UV-Vis spectra. (Note: The relative peak area on the HPLC trace is not quantitative, and does not represent the unreacted IC_{70}MA – polymer hybrid ratio, as the extinction coefficient of the fullerene at the detector wavelength (312 nm) is much higher than that of the P3HT containing fractions).

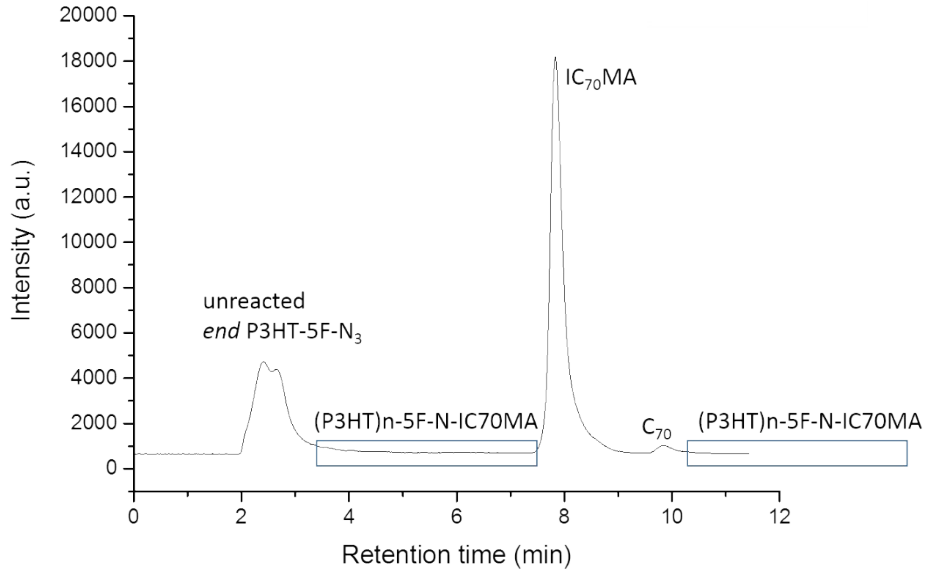


Figure S6: HPLC trace of *medium MW* crude P3HT-5F-N-IC_{70}MA.

6. NMR spectra.

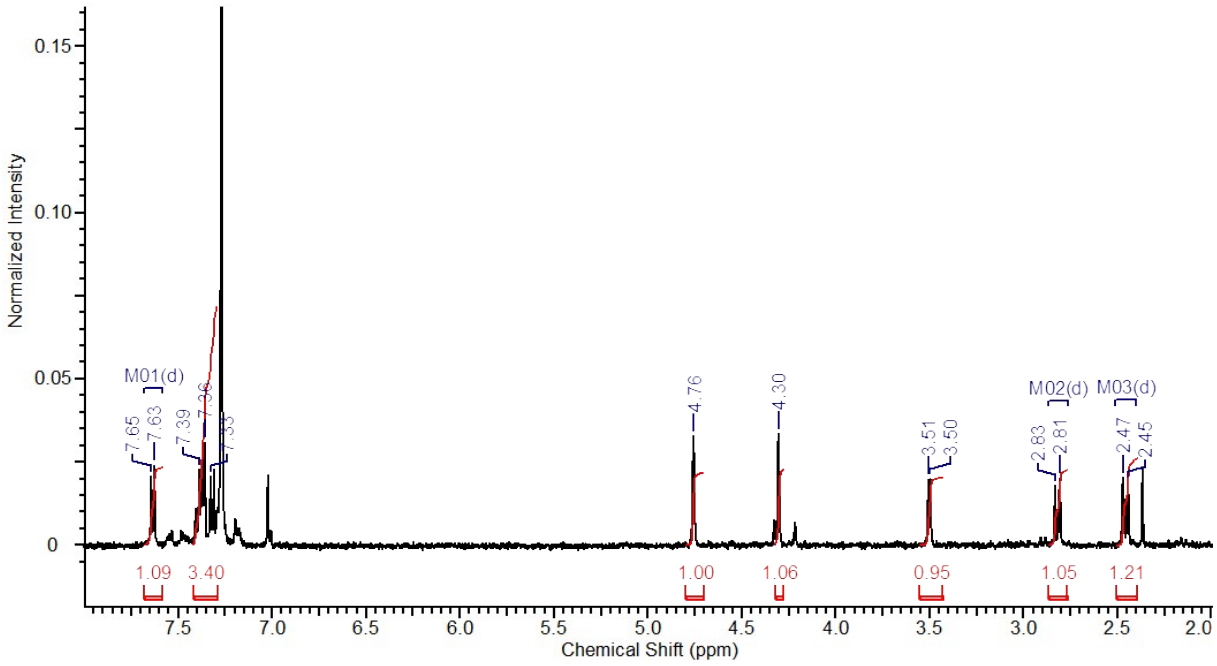


Figure S7: ^{1}H NMR spectrum of IC_{70}MA recorded in $CDCl_3$.

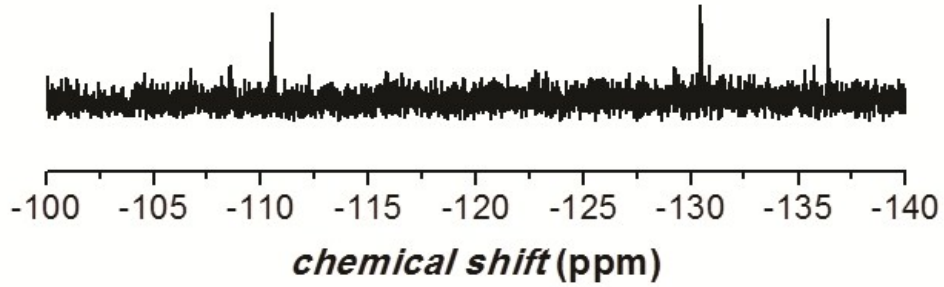


Figure S8: ^{19}F NMR spectrum of the *end*-$(P3HT)_n$-5F recorded in $CDCl_3$.

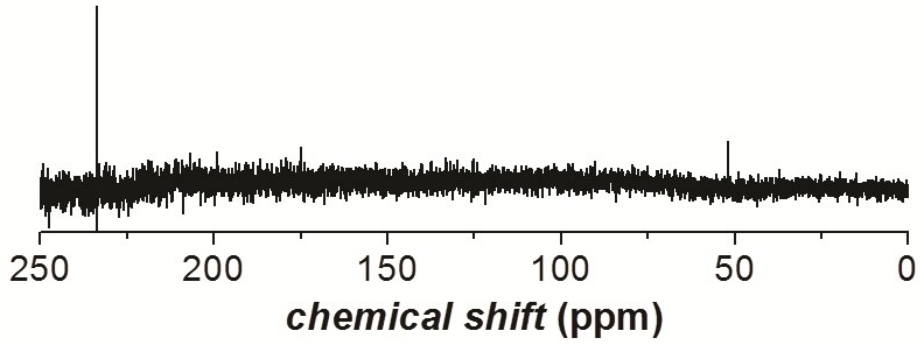


Figure S9: ^{15}N NMR spectrum of the end-(P3HT)*n*-5F-N_3 medium MW (*n=12*) recorded in $CDCl_3$.

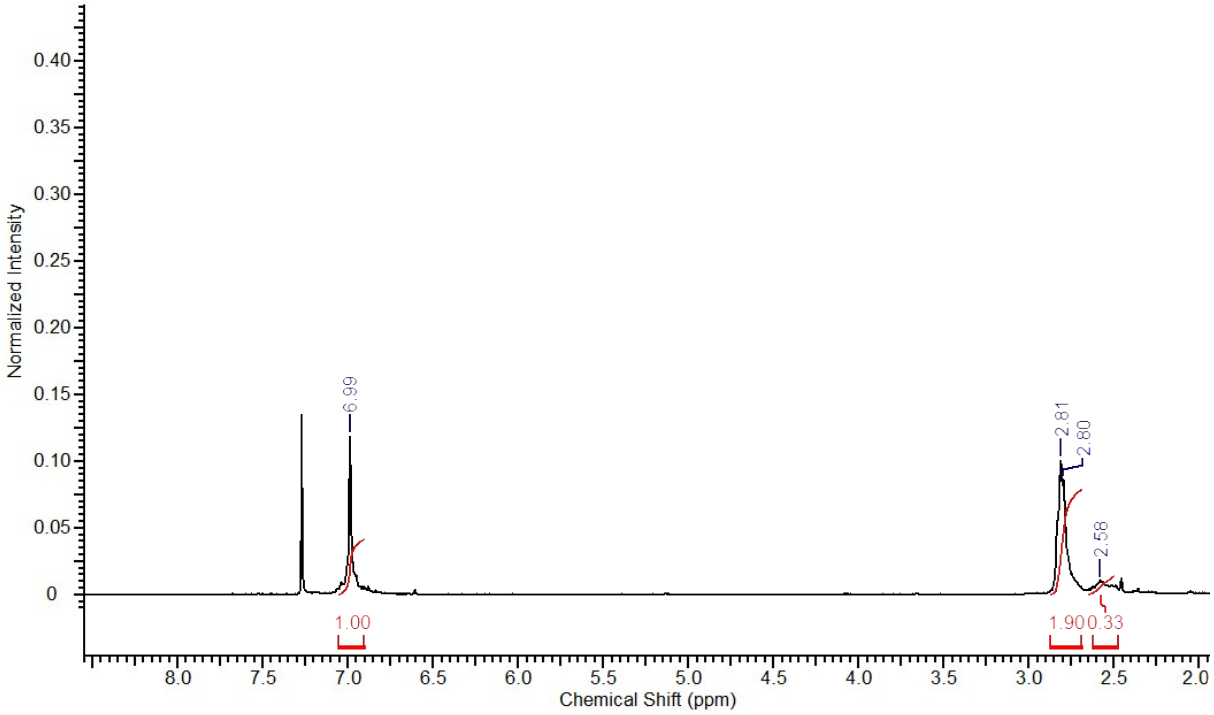


Figure S10: ^{1}H NMR spectrum of *low MW* P3HT-5F-N-C_{70} (*n=6*) recorded in $CDCl_3$.

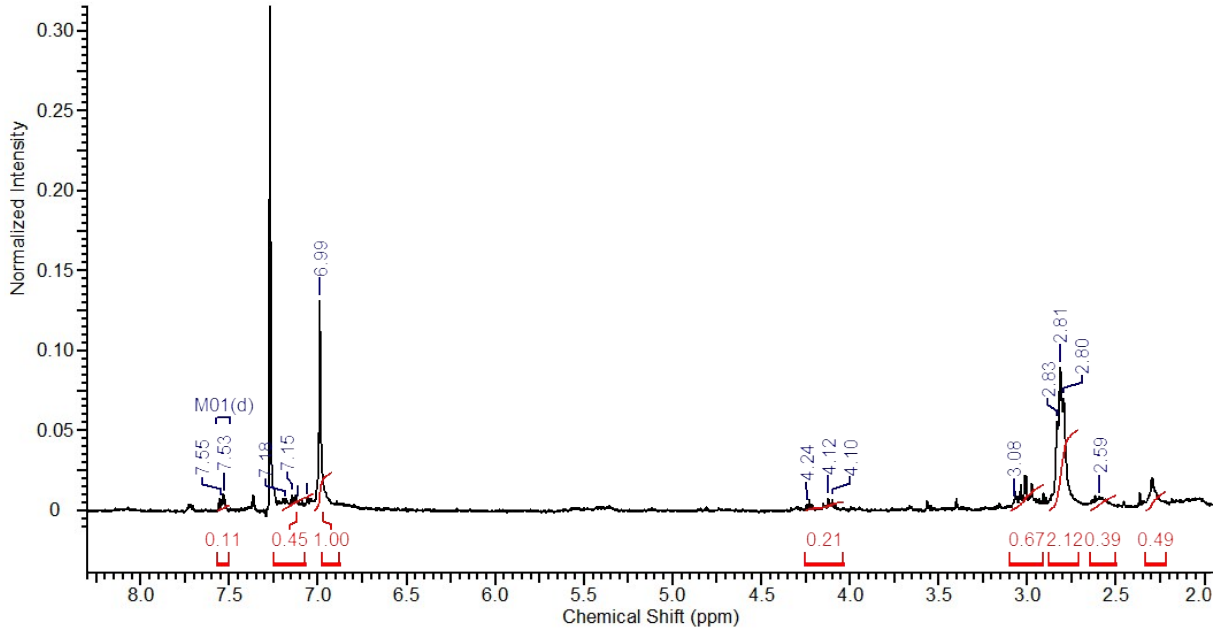


Figure S11: ^{1}H NMR spectrum of *medium MW* P3HT-5F-N-IC$_{70}$MA (*n=12*, HPLC purified) recorded in $CDCl_3$.

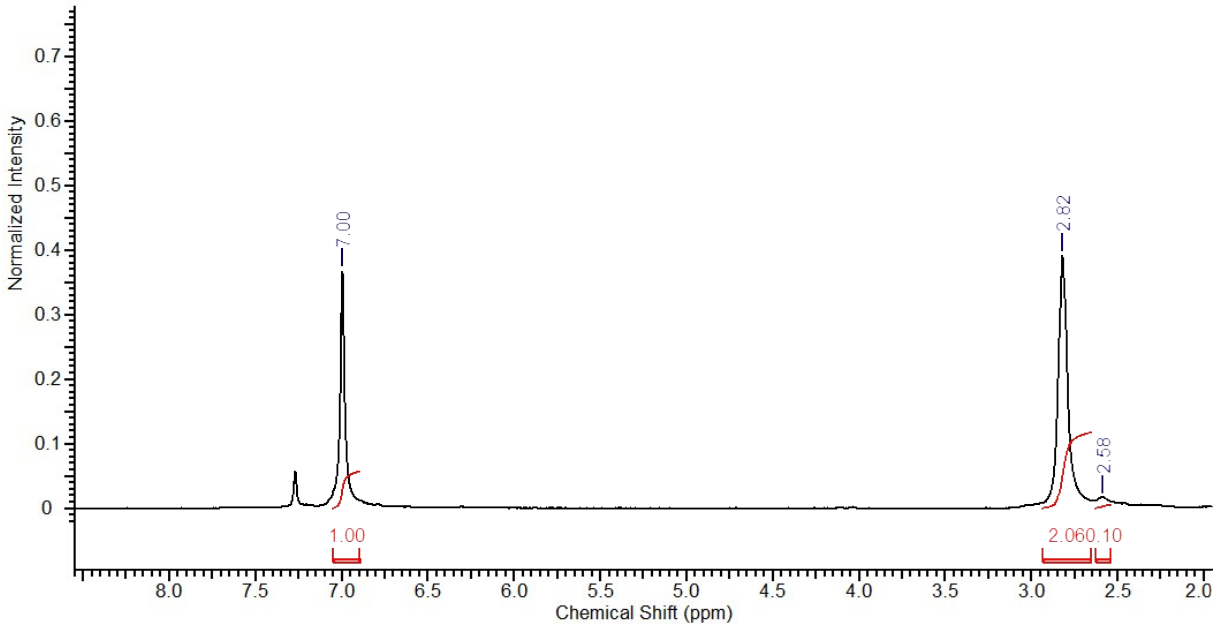


Figure S12: ^{1}H NMR spectrum of *high MW* P3HT-5F-N-IC$_{70}$MA (*n=80*) recorded in $CDCl_3$.

7. Optoelectronic spectroscopy.

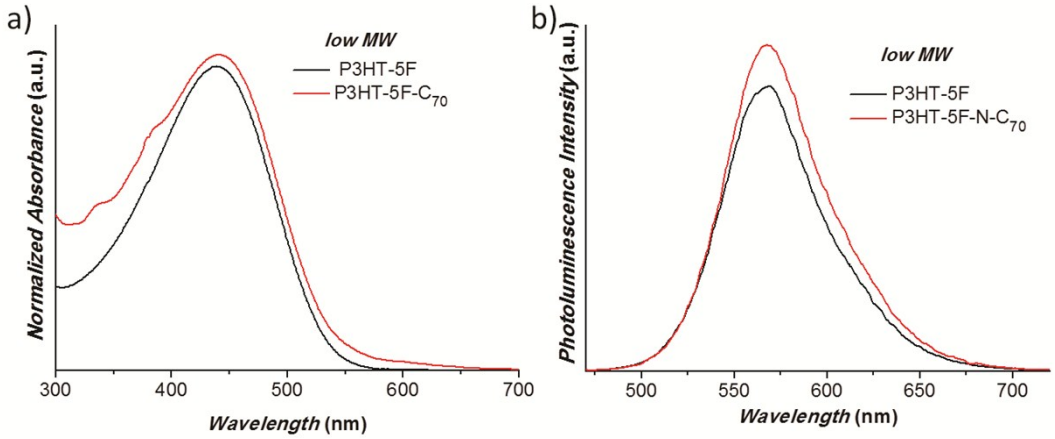


Figure S13: (a) Normalized absorption spectra and (b) Photoluminescence spectra upon excitation at 440 nm of the *low MW end* P3HT-5F and its hybrid with C_{70}, recorded in toluene solutions.

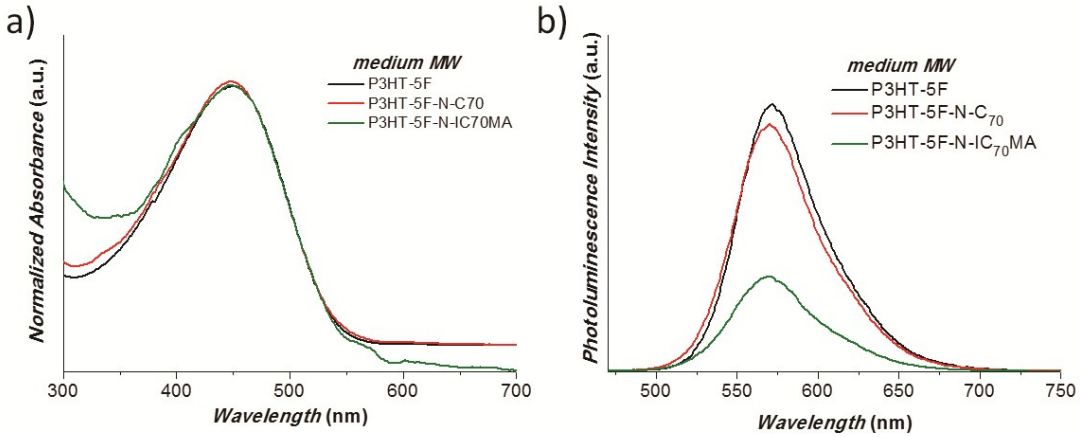


Figure S14: (a) Normalized absorption spectra and (b) Photoluminescence spectra upon excitation at 440 nm of the *medium MW end* P3HT-5F and its hybrids with C_{70} and $IC_{70}MA$, recorded in toluene solutions.

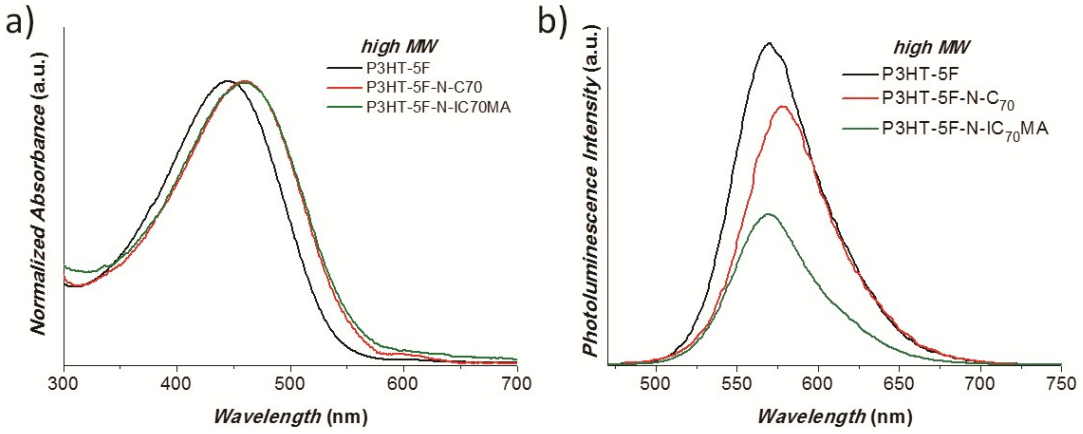


Figure S15: (a) Normalized absorption spectra and (b) Photoluminescence spectra upon excitation at 440 nm of the *high MW end* P3HT-5F and its hybrids with C_{70} and $IC_{70}MA$, recorded in toluene solutions.

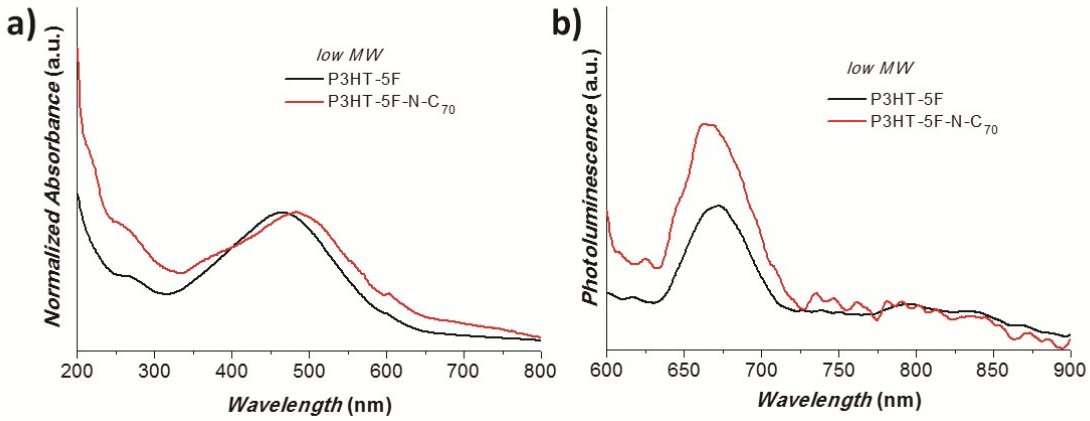


Figure S16: (a) Normalized absorption spectra and (b) Photoluminescence spectra, upon excitation at 520 nm, of the *low MW end* P3HT-5F and its hybrid with C_{70}, recorded in film form.

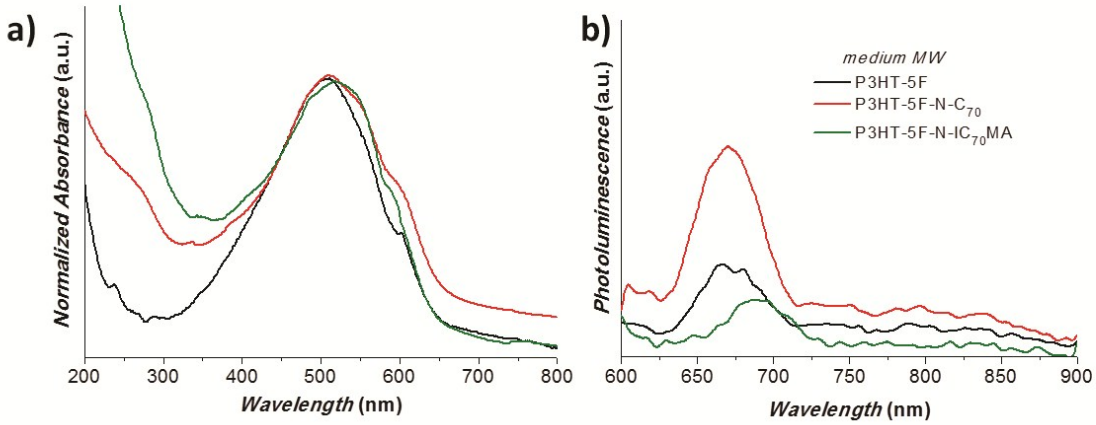


Figure S17: (a) Normalized absorption spectra and (b) Photoluminescence spectra, upon excitation at 520 nm, of the *medium MW end* P3HT-5F and its hybrids with C_{70} and $IC_{70}MA$, recorded in film form.

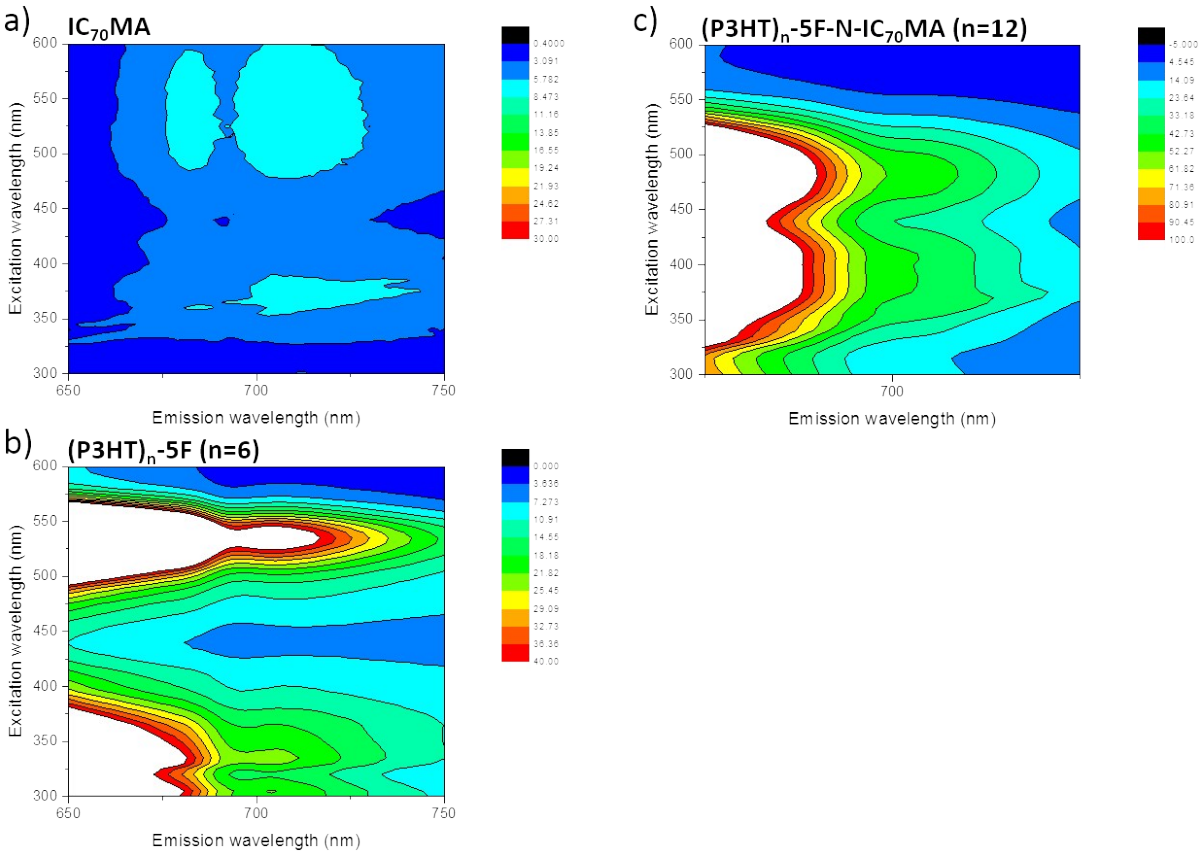


Figure S18: Photoluminescence maps of (a) $IC_{70}MA$, (b) $(P3HT)_n$-5F (n=6), and (c) $(P3HT)_n$-5F-N-$IC_{70}MA$ (n=12) recorded in toluene solutions showing the emission region of 650-750 nm.

8. Cyclic voltammetry.

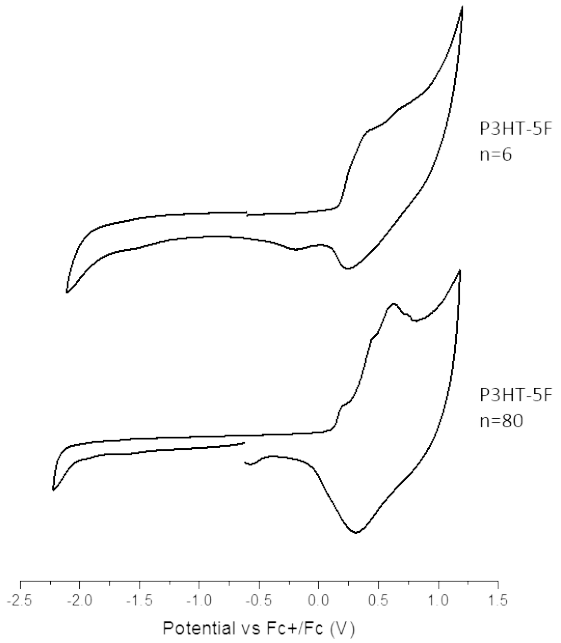


Figure S19: Cyclic voltammograms of the *low MW* (n=6), top, and *high MW* (n=12, bottom) P3HT-5F recorded in o-DCB containing 0.2 M [$^{n}Bu_4N$][BF_4] as supporting electrolyte at 0.1 V/s.

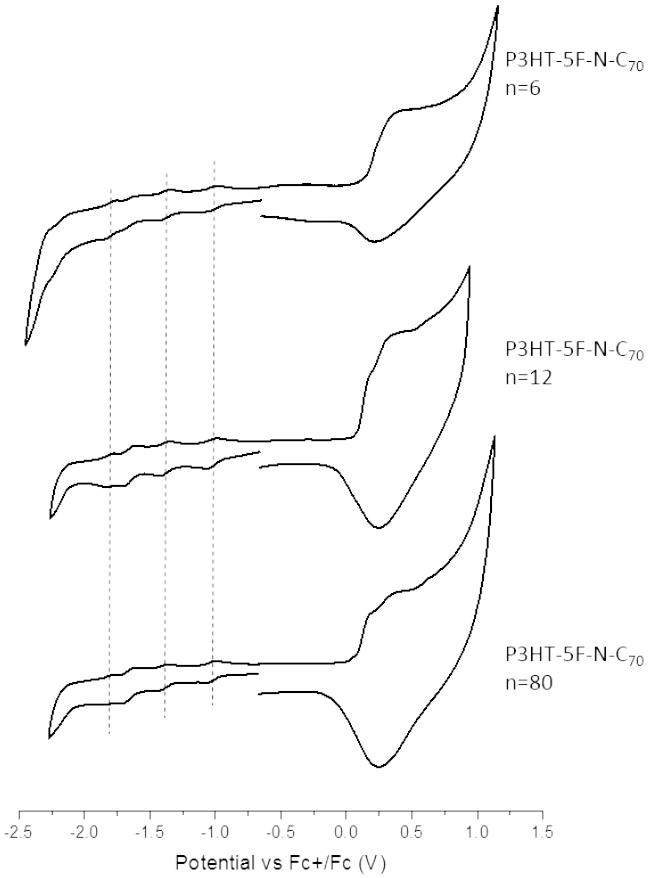


Figure S20: Cyclic voltammograms of the $(P3HT)_n$-5F-N-C_{70} (n=6, top, n=12, middle, and n=80, bottom) recorded in o-DCB containing 0.2 M [$^{n}Bu_4N$][BF_4] as supporting electrolyte at 0.1 V/s. Dashed lines indicate the similarity of the position of the fullerene reduction processes.

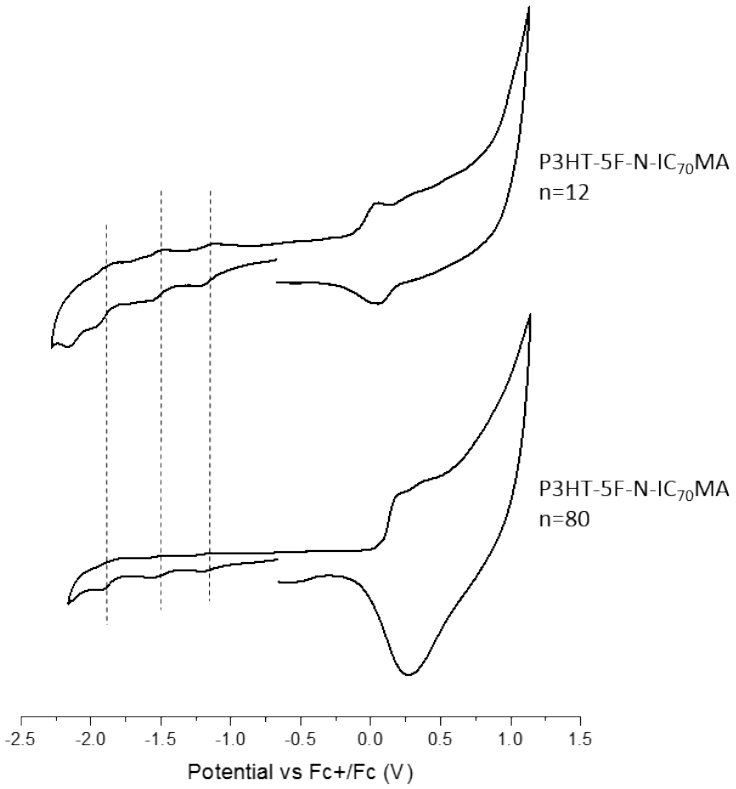


Figure S21: Cyclic voltammograms of the HPLC purified *medium MW* $(P3HT)_n$-5F-N-$IC_{70}MA$ (n=12, top) and the *high MW* $(P3HT)_n$-5F-N-$IC_{70}MA$ (n=80, bottom) recorded in o-DCB containing 0.2 M $[^nBu_4N][BF_4]$ as supporting electrolyte at 0.1 V/s. Dashed lines indicate the similarity of the position of the fullerene reduction processes.

9. Morphology Characterisation.

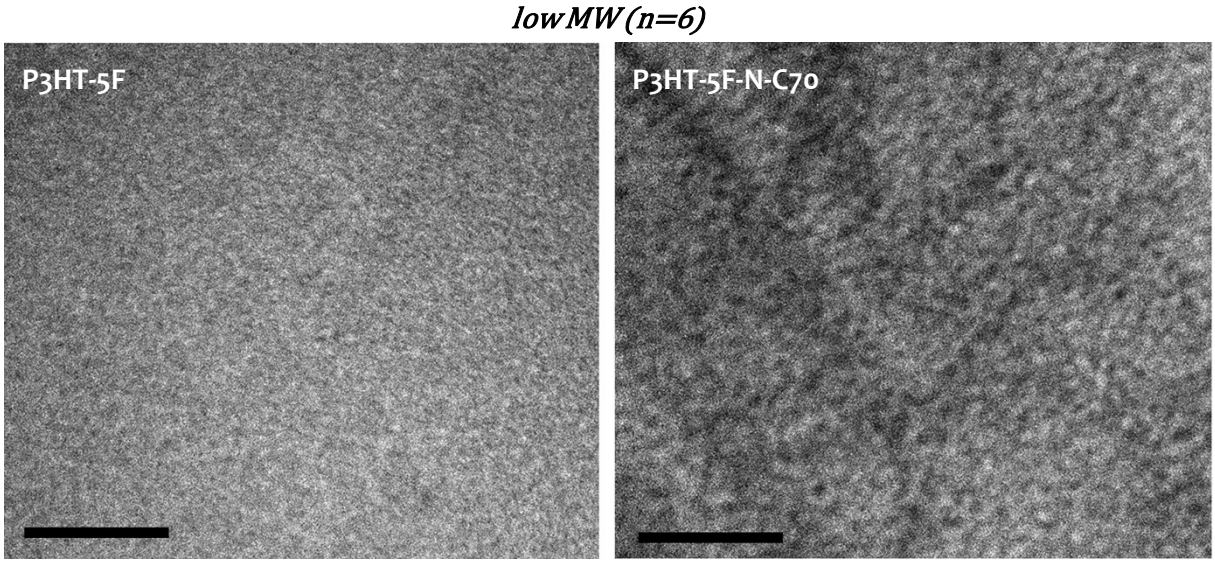


Figure S22: TEM images for low MW end P3HT-5F and P3HT-5F-N-C_{70} without thermal treatment. The scale bar is 50 nm in all images.

10. References.

[1] S. Kakogianni, S.N. Kourkouli, A.K. Andreopoulou, J.K. Kallitsis, *J. Mater. Chem.* A, **2014**, *2*, 8110–8117.