Supporting Information

Efficiency limitations in a low band-gap Diketopyrrolopyrrole-based polymer solar cell

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Sample Preparation:

For the spectroscopy measurements and SEM imaging, samples were spin-coated from the same solution and under identical processing conditions as for the OPV devices. 15 mm spectrosils were used as substrates for the spectroscopy measurements and ITO substrates were used for the SEM imaging.

SEM Imaging

To directly see the effect of DIO on the morphology, we used a scanning electron microscope (SEM). Because it is normally difficult to obtain a good contrast between two different organic materials with this technique, we selectively removed the $PC_{71}BM$ part from the films before the measurements. This was done using a slightly modified approach as reported by Friedel et al.[1] We identified methylenechloride as a solvent with high solubility for $PC_{71}BM$ and very poor solubility for the DPP-polymer. To further increase the solubility orthogonality of the two materials, we cooled both the solvent and the spin-coated blends to -20 °C before rinsing the sample for approximately 5-10 minutes at the same temperature [1]. Another trick used to slow down, and therefore better control the rinsing process was to dilute the methelynechloride with isopropanol by 2:3 ratio. By comparison of the absorption spectra taken before and after rinsing the film, we confirmed that over 95% of the $PC_{71}BM$ and less than 5% of the DPP-polymer was removed, as shown in Figure SI 1.

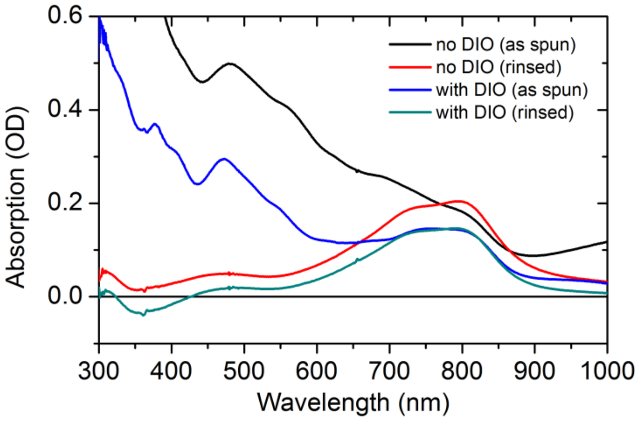


Figure SI 1: Absorption spectra of the films used for SEM imaging before and after rinsing off the $PC_{71}BM$. The intensity of the polymer absorption peak does not change, showing that the majority of the polymer part is maintained.

Morphology Investigation by X-Ray

To probe how the crystallinity and domain purity of the two materials in the blends are affected by the solvent additive, we performed bulk small angle X-ray measurements of drop casted samples. Combined SAXS and WAXS measurements were performed at beamline I22, at the Diamond Light Source at the Harwell Science and Innovation Campus in Didcot, U.K. The energy was set at E = 8 keV and the beam was focused to a size of 200 x 100 μm^2 at the sample position. The polymer/fullerene blend was dropcasted from solution onto a silicon wafer, dried, scratched off and filled into an Al sample holder with a 0.8 mm hole. A Pilatus 300k detector was used for WAXS and a Pilatus 2M for SAXS measurements. The measuring time was 20 s. Despite the large-scale phase separation between the polymer and the $PC_{71}BM$ in the blends without solvent additive, the polymer domains showed significantly reduced ordering as compared to the polymer only film. The size and crystallinity of the polymer domains decreased further under the addition of DIO. By contrast, the crystallinity of the $PC_{71}BM$ domains increased by processing with DIO. Similar findings have previously been attributed to the better solubility of $PC_{71}BM$ in DIO and the improved aggregation of $PC_{71}BM$ in this high boiling point solvent.[2,3].

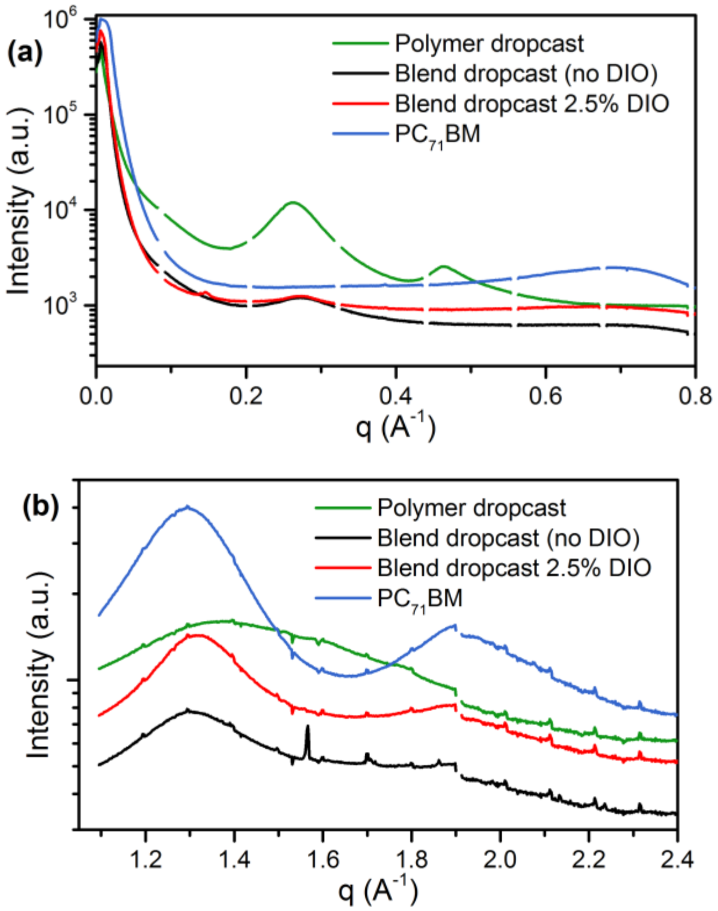


Figure SI 2: Small angle (a) and wide angle (b) X-ray diffraction of the polymer PTDPPQz, $PC_{71}BM$ and its respective blends without and with additive showing the crystallinity of both components. a) shows the ordering within the polymer refering to a side-main chain type crystallisation and b) shows the aggregation of $PC_{71}BM$

Film Formation Process

Figure SI 3 shows an illustration of the film formation process of the blends with the use of a single solvent (left) and when 2.5 volume % of DIO is used as a solvent additive (right).

When only chlorobenzene (CB) is used as a single solvent, the polymer, which has a lower solubility, pre-aggregates as the concentration increases during the evaporation of the solvent. Because of the tendency to phase-separate, the polymer and $PC_{71}BM$ form large domains as seen in Figure 4 a). The tendency to phase separate and the only low solid state solubility of $PC_{71}BM$ within the polymer has been confirmed in crystallisation experiments with different contents of $PC_{71}BM$ (see supporting information).

The film formation process changes entirely when 2.5 volume % DIO is added to the solution. During spin-coating the CB evaporates much faster (within seconds) than the DIO (which can stay in the device for hours), therefore gradually increasing the volume fraction of DIO. After the main solvent has evaporated, a binary, non-miscible system is left behind in which the polymer is no longer soluble but still swollen in the remaining DIO.

The important role of the DIO is therefore to act as a compatibilizer and to allow the $PC_{71}BM$ to diffuse into the polymer domains while the film is swollen by DIO, leading to the formation of a much finer morphology. Therefore the additive is required rather to act as a compatibilizer then as a solvent which enhances $PC_{71}BM$ aggregation.

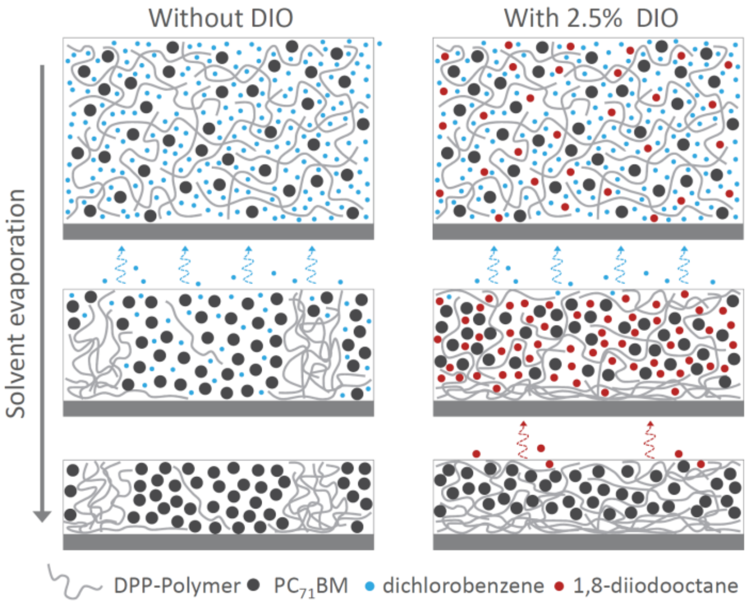


Figure SI 3 Illustration of the envisioned film formation processes during spin-coating for a solution containing only dichlorobenzene (blue dots, left) and containing a small amount of DIO solvent additive (red dots, right).

To verify the low solid state miscibility of the polymer and the $PC_{71}BM$ we have carried out crystallisation experiments where polymer- $PC_{71}BM$ blends with different mixing ratios were heated on a hot-plate at 175 °C for 30 minutes under nitrogen environment. At this temperature the mobility of the $PC_{71}BM$ molecules in greatly enhanced and the formation of macroscopic $PC_{71}BM$ crystal was observed for all polymer-$PC_{71}BM$ blends.

If the fullerene molecules can intercalate between the polymer side-chains or in case of a high solid state miscibility of the two materials, no phase separation or PCBM crystallisation will be expected, as shown by Kohn et al. [4] for P3HT-$PC_{60}BM$ blends. However, in the materials system studied here we observed clear $PC_{71}BM$ crystallization for all blend rations, clearly suggesting a very weak solid state miscibility.

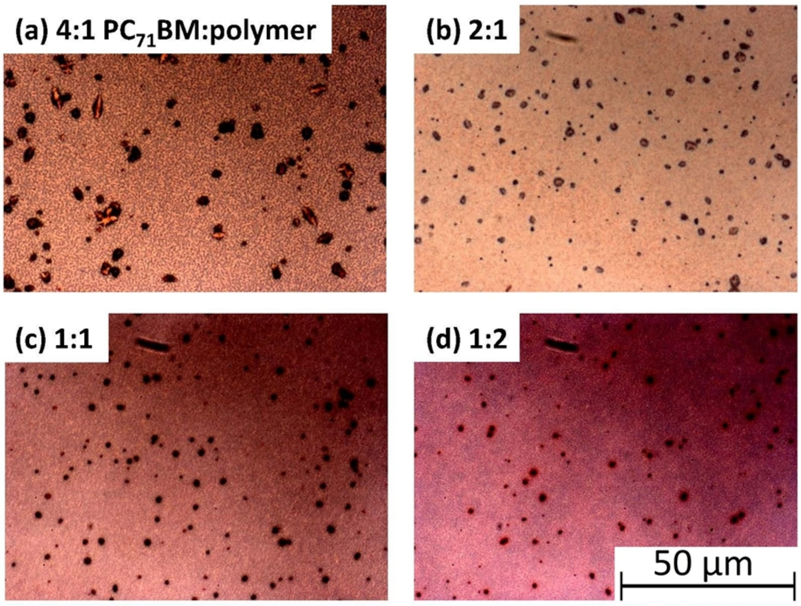


Figure SI 4: Microscopy images of DPP-polymer:PC$_{71}$BM blends with different mixing ratios after annealing on a hot-plate at 175 °C for 30 minutes under nitrogen environment. The dark areas represent the PC$_{71}$BM crystals. All images were taken with the same magnification.

To probe the exciton lifetime of the PC$_{71}$BM singlet excitons, time-correlated single photon counting measurements (TCSPC) were carried out on PC$_{71}$BM films under 10^{-5} mbar vacuum. For these measurements the samples were excited with a pulsed ps-laser at 470 nm and the photoluminescence was probed at 720 nm. The obtained decay kinetics and a mono-exponential decay fit with 660 ps are shown in Figure SI 5.

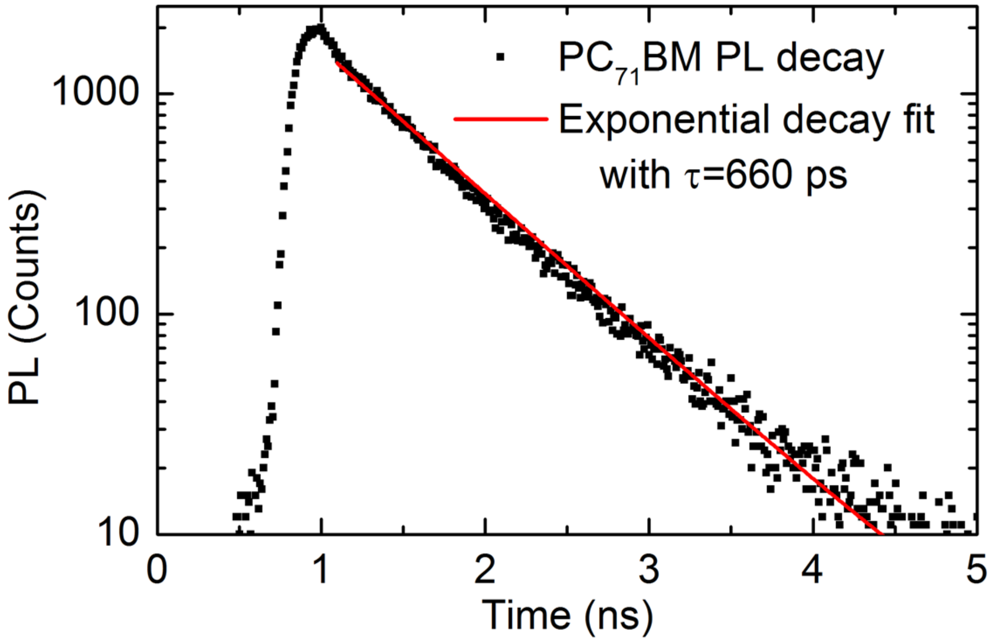


Figure SI 5: Time correlated single photon counting measurements from the PC$_{71}$BM fluorescence, probed at 720 nm. The red solid line shows an exponential decay fit with a lifetime of 660 ps.

Polymer synthesis and characterization

Measurements and general methods:

Monomers and compounds 1-3 were synthesised by previously reported literature procedures.[5,6] Thiophene 2-carbonitrile, *n*-butyllithium (1.6 M solution in hexane), potassium tertiary butoxide, ($Pd_2(dba)_3$) and P(*o-tol*)$_3$ were obtained from Aldrich. The other materials were common commercial level and used as received. Copolymer has been synthesized by Suzuki coupling reaction. All reactions were carried out under nitrogen atmosphere.

^{1}H NMR spectra were obtained from a Bruker 400 MHz NMR (^{13}C NMR on a 100 MHz) spectrometer. Chemical shifts were given in parts per million with respect to the internal standard TMS.

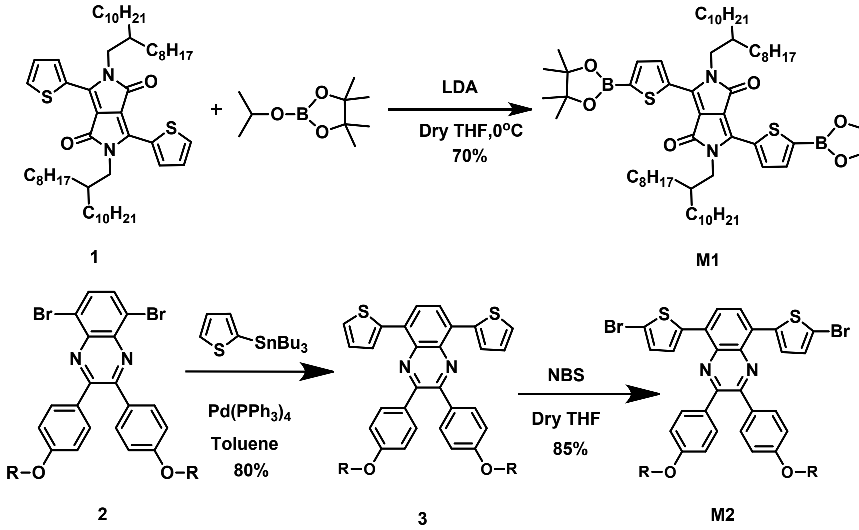
Thermogravimetric analysis (TGA) measurements were performed on a Mettler Toledo TGA SDTA 851 apparatus at a heating rate of 10 °C/min under a nitrogen atmosphere. The absorption and photoluminescence spectra were characterized using a Perkin Elmer (Lambda 35) UV–visible Spectrometer and Jobin Yvon Fluorolog3, respectively. Spectroscopic measurements were performed in standard quartz cells (1 cm X 1 cm). All the measurements were carried out at room temperature. All the spectra in solution were recorded in $CHCl_3$ and spectra in the solid state were recorded from films of compounds spin coated on quartz substrates.

Average molecular weights (M_w, M_n) were determined by Gel permeation chromatography (GPC) against polystyrene standards. THF was used as eluent with a flow rate of 1 mL/min.

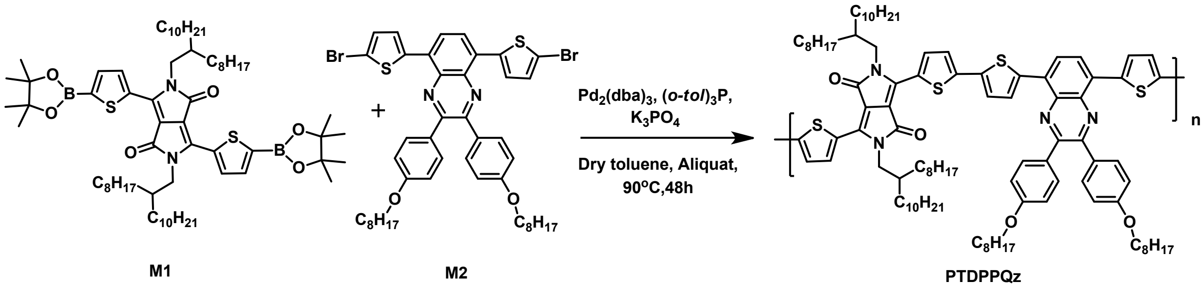
Synthesis:

Synthesis of monomers (M1 and M2) and copolymer (PTDPPQz)

Synthesis of 2,5-Bis(2-octyldodecyl)-3,6-bis[5-(4,4,5,5-tetramethyl-1,3,2- dioxoborolan-2-yl) thiophene-2-yl]-2,5-dihydropyrrolo[3,4- c]pyrrole-1,4-dione (M1)[5] **{Bürckstümmer, 2011 #55}**



Scheme SI 1: Synthetic scheme for the monomers M1 and M2



Scheme SI 2: Synthesis of the copolymer PTDPPQz

Diisopropylamine (700 mg, 0.98 mL, 6.94 mmol) was taken in 15 mL of dry THF and n-Butyllithium in *n*-hexane (2.55 mL, 6.38 mmol) was added slowly to this at 0 °C under argon atmosphere. The freshly prepared LDA solution was added slowly at -25 °C to a 15 mL THF solution of 2,5-bis(2-octyldodecyl)-3,6-dithiophene-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (2.0 g, 1 mmol) and 2-isopropoxy- 4,4,5,5-tetramethyl-1,3,2-dioxoborolane (1.64 g, 1.80 mL, 8.79 mmol). This reaction mixture was stirred at 0 °C for 2 h and quenched with 10 mL of 1 M HCl solution. After extraction with chloroform (3 X 20 mL) the combined organic fractions were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was dissolved in 2 mL of dichloromethane, and the solution was precipitated into 200 mL of cold acetone under vigorous stirring. The precipitate was filtered off and washed with cold acetone to afford 1.74 g as a pink solid.

Yield: 1.74 g (78 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.91 (d, *J* = 3.7 Hz, 2H), 7.71 (d, *J* = 3.8 Hz, 2H), 4.05 (d, *J* = 7.6 Hz, 4H), 1.89 (s, 2H), 1.37 (s, 24H), 1.31 – 1.16 (m, 64H), 0.86 (m, *J* = 6.7 Hz, 12H)

^{13}C NMR (100 MHz, $CDCl_3$,): δ (ppm) 162.17, 140.94, 138.08, 136.58, 136.08, 109.14, 85.01, 46.67, 38.19, 32.35, 32.31, 31.68, 30.45, 30.06, 30.02, 29.95, 29.79, 29.72, 26.75, 25.20, 23.12, 23.09, 14.56

Elemental analysis: Anal. Calcd for $C_{66}H_{110}B_2N_2O_6S_2$: C, 71.20; H, 9.96; B, 1.94; N, 2.52; O, 8.62; S, 5.76 Found: C, 71.50; H, 9.19; N, 3.21; S, 6.71
Melting point: 90 °C

Synthesis of 2,3-Bis(4-(2-ethylhexyloxy)phenyl)-5,8-bis[5'-bromo-dithien-2-yl-quinoxaline, (M2)

2, 3-bis(4-(2-ethylhexyloxy)phenyl)-5,8-dithien-2-yl-quinoxalines (2) (1.35 g, 1.92 mmol) was dissolved in THF, and NBS (N-bromosuccinimide) (752 mg, 4.22 mmol) was added in one portion. After the mixture was stirred at room temperature for 3 h, it was poured into methanol and the precipitate was filtered off. The precipitate was washed with methanol several times and the product was dried under vacuum at 50 °C to obtain an orange powder.

Yield: 1.49 g, 90 %

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.04 (s, 1H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 4.0 Hz, 1H), 7.12 (d, *J* = 4.0 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 4.03 (t, *J* = 6.5 Hz, 2H), 1.89 - 1.74 (m, 2H), 1.49 (d, *J* = 7.8 Hz, 2H), 1.32 (dd, *J* = 22.3, 13.6 Hz, 9H), 0.91 (t, *J* = 6.2 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$,): δ (ppm) 158.17, 155.94, 140.33, 138.01, 131.58, 130.08, 126.02, 117.14, 69.01, 38.67, 37.20, 29.79, 26.72, 23.09, 14.56, 11.61

Elemental analysis: Anal. Calcd for $C_{44}H_{48}Br_2N_2O_2S_2$: C, 61.39; H, 5.62; Br, 18.57; N, 3.25; O, 3.72; S, 7.45 Found: C, 61.84; H, 6.14; N, 3.64; S, 6.36

Melting point: 101 °C

Synthesis of the copolymer PTDPPQz

2,5-Bis(2-octyldodecyl)-3,6-bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxoborolan-2-yl) thiophene-2-yl]-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M1**) (1 mmol) and 2,3-Bis(4-(2-ethylhexyloxy) phenyl)-5,8-bis[5'-bromo-dithien-2-yl-quinoxaline (**M2**) (1 mmol) were taken in degassed dry toluene (40 mL) and two drops of aliquat336 were added. The reaction container was loaded with the ligand (*o-tol*)$_3$P (20 mg), catalyst precursor $Pd_2(dba)_3$ (10 mg) and purged with nitrogen for 10 min to remove dissolved oxygen. Degassed aqueous solution of K_3PO_4 (1 mL) was added through syringe and the mixture was purged again with nitrogen for 10 min. Then the reaction mixture was refluxed at 90 ˚C for 48 h under dark condition. Reaction mixture was cooled to room temperature, washed with water, extracted with $CHCl_3$ and passed through anhydrous Na_2SO_4. The organic layer was evaporated and the concentrated polymer solution was precipitated by slowly adding into vigorously stirring methanol. Dark green precipitate was collected by filtration and then washed with hot methanol, hexane and acetone by Soxhlet extraction to remove low molecular weight oligomers. The polymer was dried overnight under vacuum.

Yield: 170 mg (66 %)

^{1}H NMR: ($CDCl_3$, 400 MHz): δ (ppm) 8.0-7.7 (br), 7.19-6.9 (br), 4.4-3.8 (br), 2.1-0.7 (m)

Elemental analysis: Anal. Calcd for $C_{84}H_{126}N_4O_4S_4$: C, 72.89; H, 9.18; N, 4.05; S, 9.27. Found: C, 71.85; H, 8.63; N, 4.01; S, 9.33

Molecular weight details: M_n = 24.1 kg/mol; M_w = 86.8 kg/mol PDI = 3.59

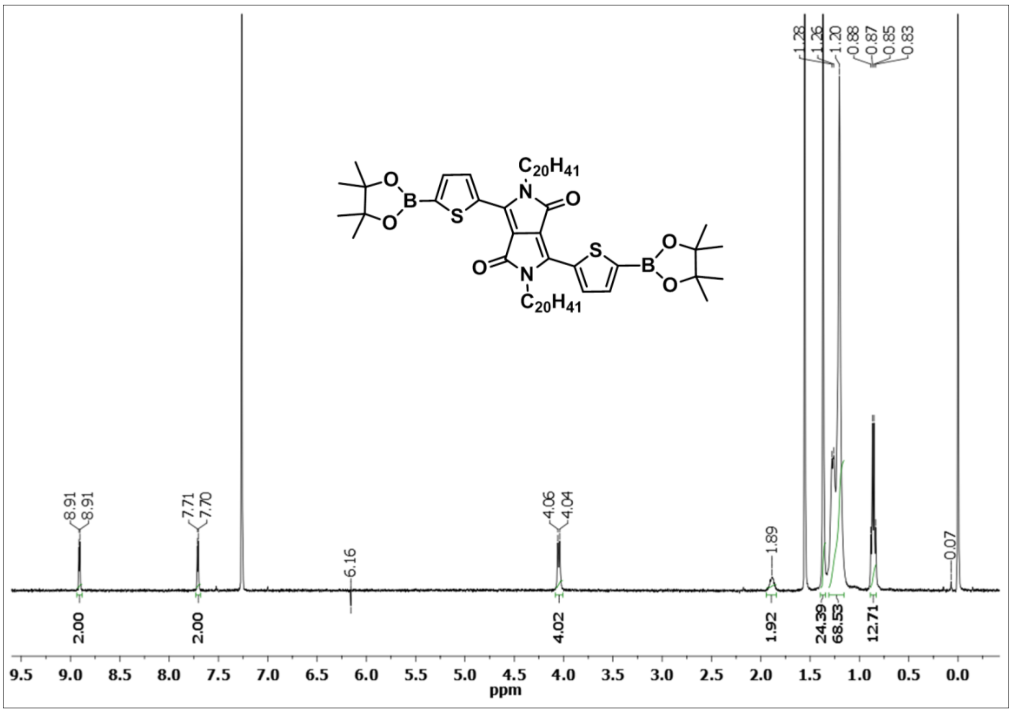


Figure SI 6: ^{1}H NMR spectrum of M1 in $CDCl_3$

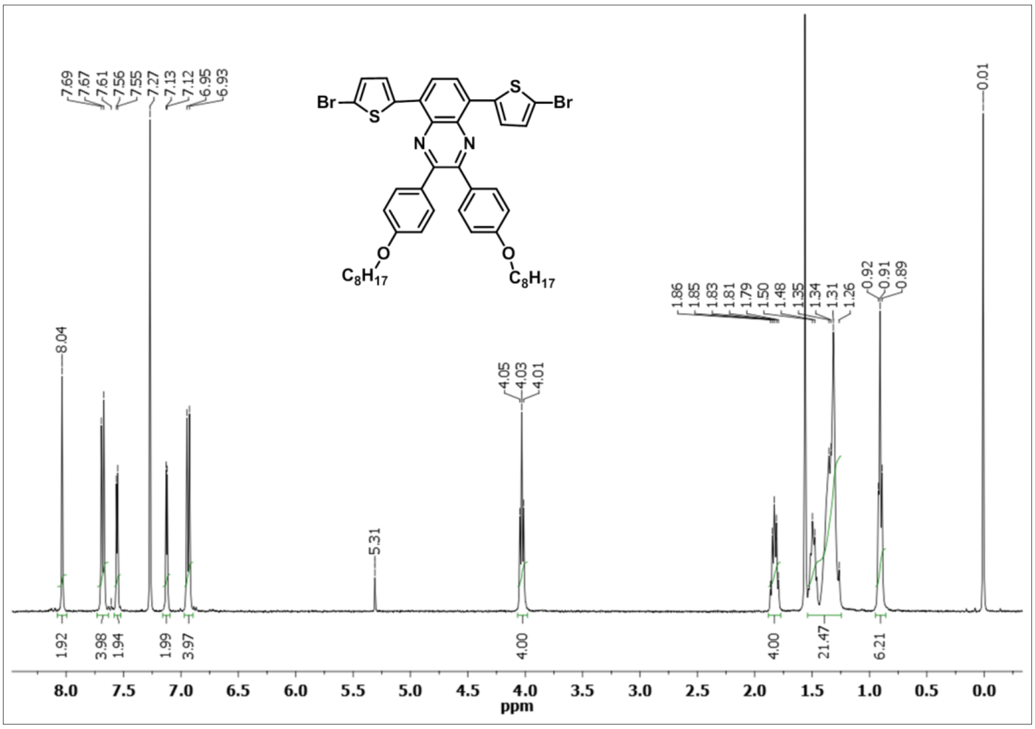


Figure SI 7: ^{1}H NMR spectrum of M2 in $CDCl_3$

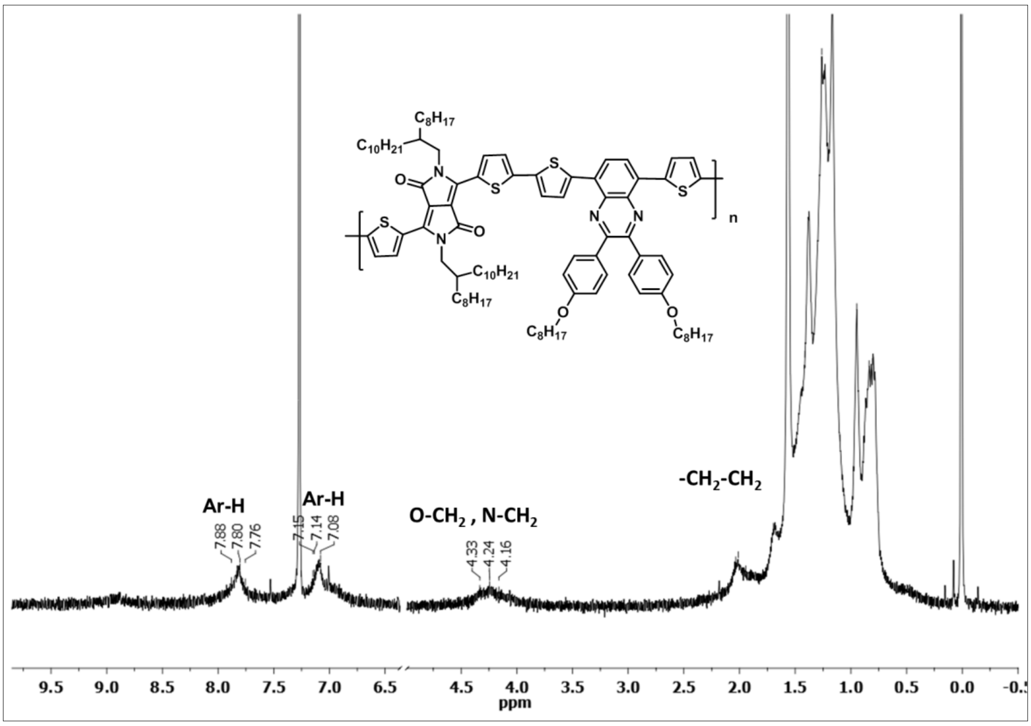


Figure SI 8: ^{1}H NMR Spectrum of PTDPPQz in $CDCl_3$

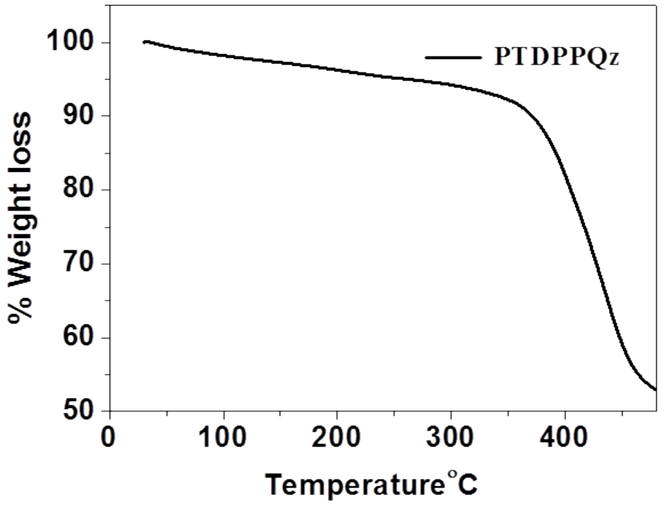


Figure SI 9: TGA curve of the polymer PTDPPQz with a heating rate of 10 °C/min.

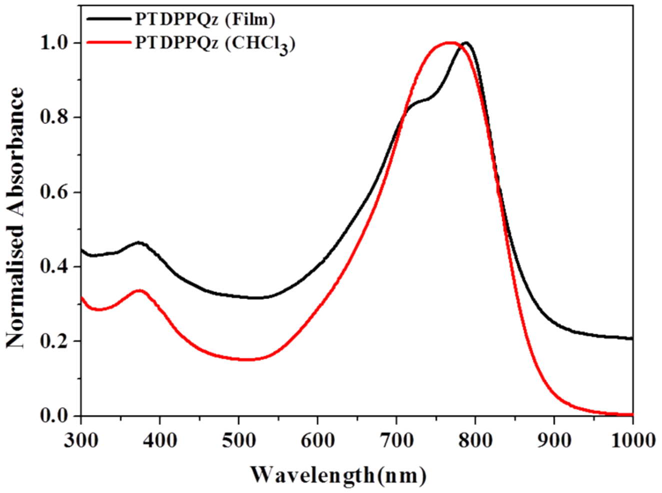
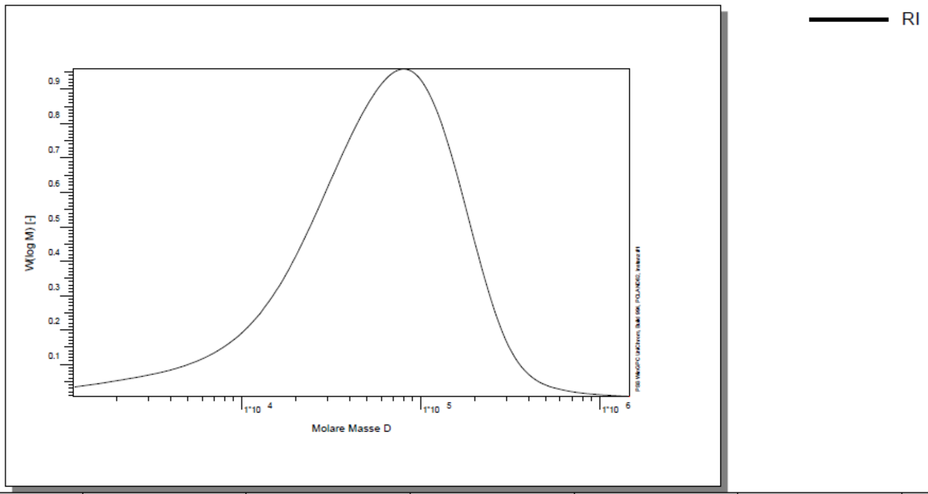


Figure SI 10: UV-vis absorption of PTDPPQz in $CHCl_3$ and as thin film.

Molecular weight distribution:



Name	Mn	Mw	D	Vp	Mp	Area
RI	24175,70	86896,50	3,59	7,30	81752,20	0,12

Figure SI 11: GPC Chromatogram of the polymer PTDPPQz in THF

SI – List of References

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