Supporting Information for:

A 2,7-Linked Carbazole Based "Double Cable" Polymer with Pending Perylene Diimide Functional Groups: Preparation and Photovoltaic Properties

*David K. Mohamad[2], Achim Fischereder[1], Hunan Yi[1], Ashley J. Cadby[2], David G. Lidzey *[2] and Ahmed Iraqi.*[1]

[1] Department of Chemistry, University of Sheffield, Sheffield S3 7HF, United Kingdom.

[2] Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, United Kingdom.

1. Material preparation and analysis techniques.

Materials: 2,7-Dibromo-3,6-dimethyl-9-(2-hexyldecyl)-9*H*-carbazole [1], 5,5'-bis(tri-*n*-butylstannyl)-2,2'-bithiophene [2] were prepared according to established literature procedures. Tetrahydrofuran (THF) was distilled over sodium-benzophenone under inert nitrogen atmosphere. Toluene was dried and distilled over sodium under an inert argon atmosphere. Acetonitrile (HPLC grade) was dried and distilled over phosphorus pentoxide under an inert argon atmosphere, then stored over molecular sieves 3A.

Measurements: NMR spectra were recorded on Bruker 250 MHz, AMX400 400 MHz or DRX500 500MHz NMR spectrometers at 22 °C in chloroform-*d*$_1$ or acetone-*d*$_6$ solutions with TMS as the internal standard. IR absorption spectra were recorded on the Nicolet Model 205 FT-IR Spectrometer. Liquid samples were analysed neat, using NaCl–plate method and solid samples were analysed using the Diamond ATR attachment for solid samples. Melting points were obtained using Gallenkamp Melting Point Apparatus. MALDI-TOF spectra were recorded on a Bruker Reflex III in reflection positive ion mode with a DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) matrix. GPC curves were recorded on equipment consisting of a Hewlett Packard Model 1090 HPLC, a Hewlett Packard Model 1037 Differential Refractive Detector, two Polymer Labs PLgel 5μ Mixed C (300 mm x 7.5 mm) columns and a guard (50 mm x 7.5 mm). The oven was adjusted to 40 °C and CHCl$_3$ (HPLC grade) was used as the eluent at a rate of 1 cm^3 min^{-1}. Polymer samples were made up as solutions in chloroform (2.5 mg cm^{-3}) spiked with toluene as a reference. The GPC curves were obtained by the RI-detection method, which was calibrated with a series of polystyrene narrow standards (Polymer Laboratories). Elemental analyses were carried out by the Perkin Elmer 2400 CHN Elemental Analyzer for CHN analysis and by the

Schöniger oxygen flask combustion method for anion analysis. UV-visible absorption spectra were measured by Hitachi U-2010 Double Beam UV / Visible Spectrophotometer. The absorbance of polymers was measured in solution in spectrophotometric grade solvents (dichloromethane, tetrahydrofuran and toluene) at ambient temperature using rectangular quartz cuvettes (light path length = 10 mm). Thermogravimetric analysis curves (TGA) were obtained by Perkin Elmer TGA-7 Thermogravimetric Analyser at a scan rate of 10°C/minute under inert nitrogen atmosphere. Platinum pans were used as sample holder. The weights of the samples were approx. 5 mg. DSC curves were recorded on Perkin Elmer Pyris 1 Differential Scanning Calorimeter equipped with Perkin Elmer CCA7 Subambient Accessory at the scan rate of 10°C/minute under inert nitrogen atmosphere. Aluminium pans were used as sample pans. An empty aluminium pan was used as the reference. Cyclic voltammograms were recorded using a Princeton Applied Research Model 263A Potentiostat/Galvanostat. Measurements were carried out under argon at 25 ± 2 ºC. 10 cm^3 of tetrabutylammonium hexafluorophosphate solution in acetonitrile (0.1 mol dm^{-3}) was used as the electrolyte solution. A three electrode system was used consisting of an Ag/Ag$^+$ reference electrode (silver wire in 0.01 mol dm^{-3} silver nitrate solution in the electrolyte solution), a platinum working electrode (2 mm-diameter smooth platinum disc, area = 3.14×10^{-2} cm^2), and a platinum counter electrode (platinum wire). Polymer thin films were formed by drop casting 1.0 mm^3 of polymer solutions in chloroform (HPLC grade) (1 mg cm^{-3}) onto the working electrode, then dried in air. Ferrocene was employed as a reference redox system according to IUPAC's recommendation. [3] All reactions were carried out under inert nitrogen atmosphere.

2. Monomer synthesis

N,N'-Bis(3-pentyl)-perylene-3,4:9,10-bis(dicarboximide) 1

Compound **1** was obtained by a modified literature procedure [4]. A dispersion of perylene-3,4,9,10-tetracarboxylic dianhydride (6.00 g, 15.3 mmol), zinc acetate (6.00 g, 32.7 mmol) in pyridine (40 cm^3) was degassed three times, followed by the addition of 1-ethylpropylamine (4.00 cm^3, 34.3 mmol). The mixture was heated to 80°C for 4 h and then refluxed overnight. Most of the pyridine was removed by vacuum-distillation and the slurry obtained was dissolved in CHCl$_3$ and washed with water and the organic fraction was concentrated *in vacuo*. The crude product was purified by column chromatography (95/5 V/V, CHCl$_3$/methanol) and then recrystallised from ethanol/CHCl$_3$ to yield **(1)** as dark red crystals (4.344 g, 53.5% yield). ^{1}H-NMR: (CDCl$_3$): δ_H/ ppm: 8.633 (d, 4H, J = 7.9 Hz); 8.536 (d, 4H, J = 8.0 Hz); 5.087 (m, 2H); 2.283 (m, 4H); 1.975 (m, 4H); 0.961 (t, 12H, J = 7.5 Hz). ^{13}C-NMR: (CDCl$_3$): δ_C/ ppm: 163.95, 134.24, 131.29, 129.44, 126.1, 123.45, 122.83, 57.74, 25.02, 11.41. FT-IR (ATR): ($\tilde{v}$ /cm^{-1}): 2964.1, 2932.3, 2874.0, 1696.7, 1646.1, 1591.0, 1575.9, 1506.0, 1482.8, 1456.3, 1432.6, 1404.1, 1330.2, 1299.7, 1246.6, 1207.0,

1195.9, 1175.6, 1158.6, 1120.5, 1085.7, 1036.7, 976.2, 959.4, 927.5, 906.9, 850.6, 803.4, 789.8, 781.7, 744.1. Anal. Calcd. for $C_{30}H_{22}N_2O_4$: C, 76.96%; H, 5.70%; N, 5.28%. Found: C, 77.05%; H, 5.73%; N, 5.20%.

N,N'-Bis(12-tricosanyl)-perylene-3,4:9,10-bis(dicarboximide) 2

Compound **2** was prepared according to a modified literature procedure [5]. A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (1.33g, 3.4 mmol), 1-undecyl dodecylamine [6] (2.9 g, 8.5 mmol) and imidazole (10 g) was heated to 140°C. After 4 h, the solution was cooled down to room temperature and the red solid was dispersed in ethanol (100 cm^3). This mixture was poured into 2M HCl (300 cm^3) and stirred overnight. The red precipitate was filtered and washed with H_2O until the washing was neutral and dried under vacuum for 6 h at 100 °C. The crude product was further purified by column chromatography on silica gel (100% $CHCl_3$) followed by flash vacuum chromatography on silica gel with a gradual change in the eluent polarity from 98/2 V/V petroleum ether/ethyl acetate to 60/40 petroleum ether/ethyl acetate. Finally the product was recrystallised from ethanol to obtain pure N,N'-bis(12-tricosanyl)-perylene-3,4:9,10-bis(dicarboximide) **2** (1.569 g, 44.6% yield). The product gave a single spot on TLC (100% chloroform) (R_f = 0.875). ^{1}H-NMR: (CDCl$_3$): δ_H/ ppm: 8.644 (m, 8H); 5.202 (m, 2H); 2.257 (m, 4H); 1.882 (m, 4H); 1.207 (m, 72H); 0.850 (t, 12H, J = 6.9 Hz). ^{13}C-NMR: (CDCl$_3$): δ_C/ ppm: 164.62, 163.54, 134.46, 131.86, 131.09, 129.57, 126.41, 123.93, 123.19, 122.97, 54.75, 32.35, 31.88, 31.74, 30.53, 29.59, 29.56, 29.52, 29.30, 28.64, 26.95, 22.64, 14.07. FT-IR (ATR): ($\tilde{v}$ /cm^{-1}): 2918.3, 2849.2, 1692.0, 1648.5, 1592.4, 1577.0, 1466.1, 1404.8, 1336.9, 1251.8, 1175.3, 812.2, 749.7, 721.6. Anal. Calcd. for $C_{70}H_{102}N_2O_4$: C, 81.19%; H, 9.93%; N, 2.71%. Found: C, 81.37%; H, 10.03%; N, 2.58%. MALDI-TOF MS *m/z* (matrix: DTCB) found 1036 (M + H$^+$).

N-(12-tricosanyl)-perylene-3,4-dicarboxyanhydride-9,10-dicarboximide 3

Compound **3** was obtained according to a modified literature procedure [7]. A mixture of N,N'-bis(12-tricosanyl)-perylene-3,4:9,10-bis(dicarboximide) **2** (5.97 g, 5.765 mmol) in *t*-BuOH (58 cm^3) was heated to 89°C before freshly ground KOH (1.368 g, 24.38 mmol) was added. The solution was stirred for 1.5 h before it was cooled down to room temperature to add 10% HCl (15 cm^3) slowly under stirring. After 40 min, 10% HCl (135 cm^3) was added again and the mixture extracted with CHCl$_3$. The organic fractions were washed with water until the washing was neutral and then concentrated. The crude product was purified by flash vacuum chromatography on silica gel (99% CHCl$_3$ / 1% acetic acid) followed by column chromatography on silica gel (100% CH_2Cl_2) to obtain the pure product (1.07g, 26% yield). The product gave a single spot on TLC (100% CHCl$_3$) (R_f = 0.20). ^{1}H-NMR: (CDCl$_3$): δ_H/ ppm: 8.692 (m, 8H); 5.197 (m, 1H); 2.249 (m, 2H); 1.887 (m, 2H);

1.208 (m, 36H); 0.852 (t, 6H, J = 6.9 Hz). (CDCl$_3$): δ_C/ ppm: ^{13}C-NMR: (CDCl$_3$): δ_C/ ppm: 164.32, 163.20, 159.81, 136.23, 133.42, 131.88, 131.68, 131.12, 129.39, 126.60, 126.37, 124.71, 123.97, 123.84, 123.02, 118.85, 54.90, 32.29, 31.86, 29.57, 29.55, 29.51, 29.23, 26.93, 22.63, 14.07. FT-IR (ATR): ($\tilde{v}$/cm^{-1}): 2920.3, 2850.9, 1769.2, 1733.4, 1698.7, 1657.7, 1592.2, 1576.8, 1466.1, 1456.3, 1404.5, 1354.2, 1313.9, 1260.0, 1246.0, 1199.3, 1178.0, 1152.4, 1139.8, 1123.4, 1012.9, 862.4, 846.0, 808.2, 794.5, 776.2, 752.4, 735.2. Anal. Calcd. for C$_{47}$H$_{55}$NO$_5$: C, 79.07%; H, 7.76%; N, 1.96%. Found: C, 78.70%; H, 7.84%; N, 1.82%. Mass (EI); (m/z): 713 (100 %), 714 (52%), 715 (14%) (M$^{•+}$).

N-(12-tricosanyl)-N'-(6-hydroxyhexyl)perylene-3,4:9,10-bis(dicarboximide) 4

Compound **4** was prepared according to a modified literature procedure [8]. A solution of 6-aminohexanol (0.049 g, 0.418 mmol) and zinc acetate (0.001 g, 0.006 mmol) in N,N-dimethylacetamide (4 cm^3) was heated to 110°C before N-(12-tricosanyl)-perylene-3,4-dicarboxyanhydride-9,10-dicarboximide **3** (0.199 g, 0.278 mmol) was added. This solution was stirred for 3 h at 110°C before the temperature was increased to 160°C for 15 h. The excess solvent was distilled off under vacuum and the slurry obtained was dissolved in CHCl$_3$ and washed with H$_2$O (3 x 50 cm^3). The collected organic layers were concentrated under vacuum and the crude product was purified by column chromatography on silica gel (99/1 V/V, CHCl$_3$/acetic acid) to give **4** as a red solid (123.7 mg, 54.6% yield). The product gave a single spot on TLC (99/1 V/V, CHCl$_3$/acetic acid) (R$_f$ = 0.35). ^{1}H-NMR: (CDCl$_3$): δ_H/ ppm: 8.571 (m, 8H); 5.202 (m, 1H); 4.204 (t, 2H, J = 7.46 Hz); 3.689 (t, 2H, J = 6.36 Hz); 2.277 (m, 2H); 1.906 (m, 2H); 1.800 (m, 2H); 1.646 (m, 2H); 1.507 (m, 4H); 1.214 (m, 36H); 0.852 (t, 6H, J = 6.85 Hz). ^{13}C-NMR: (CDCl$_3$): δ_C/ ppm: 163.37, 162.30, 162.03, 133.18, 132.84, 130.55, 129.96, 129.79, 128.29, 127.95, 124.945, 124.91, 123.00, 122.25, 121.86, 121.78, 121.66, 61.74, 53.87, 39.40, 31.58, 31.36, 30.88, 28.61, 28.58, 28.31, 26.94, 26.03, 25.70, 24.28, 21.64, 13.07. FT-IR (ATR): ($\tilde{v}$/cm^{-1}): 3519.4, 2920.2, 2851.2, 1692.5, 1644.1, 1593.7, 1576.7, 1464.7, 1439.3, 1403.6, 1340.2, 1253.3, 1177.7, 1074.8, 1053.7, 859.9, 809.5, 794.7, 745.6, 721.0. Anal. Calcd. for C$_{53}$H$_{68}$N$_2$O$_5$: C, 78.29%; H, 8.43%; N, 3.45%. Found: C, 77.74%; H, 8.48%; N, 3.24%. MALDI-TOF MS *m/z* (matrix: DTCB) found 813 (M + H$^+$).

N-(12-tricosanyl)-N'-(6-tosyloxyhexyl)perylene-3,4:9,10-bis(dicarboximide) 5

A solution of *p*-toluenesulfonyl chloride (0.4685 g, 2.457 mmol) in CH$_2$Cl$_2$ (3 cm^3) was cooled down to 0 - 5°C and added to a solution of trimethylamine hydrochloride (0.0605 g, 0.633 mmol), N-(12-tricosanyl)-N'-(6-hydroxyhexyl)perylene-3,4:9,10-bis(dicarboximide) **4** (0.4617 g, 0.5678 mmol), Et$_3$N (0.5 mL) in CH$_2$Cl$_2$ (3 cm^3) at 0 – 5°C. This mixture was stirred for 1.5 h at 0 – 5°C

before water was added. The water layer was extracted with CH_2Cl_2 and the collected organic phases were washed with water then concentrated. The crude product was dissolved in a minimum amount of Et_2O followed by the addition of methanol until a red solid precipitated out. The mixture was cooled overnight and the pure product collected by centrifugation (0.370 g; 67.2 % yield). The product gave a single spot on TLC (60/40 V/V petroleum ether/ethyl acetate) (R_f = 0.72). ^{1}H-NMR: ($CDCl_3$): δ_H/ ppm: 8.635 (m, 8H); 7.814 (d, 2H, J = 8.31 Hz); 7.373 (d, 2H, J = 8.07 Hz); 5.204 (m, 1H); 4.172 (t, 2H, J = 7.38 Hz); 4.053 (t, 2H, J = 6.48 Hz); 2.472 (s, 3H); 2.266 (m, 2H); 1.895 (m, 2H); 1.718 (m, 4H); 1.421 (m, 4H); 1.212 (m, 36H); 0.854 (t, 6H, J = 6.85 Hz). ^{13}C-NMR: ($CDCl_3$): δ_C/ ppm: 164.51, 163.41, 163.18, 144.62, 134.49, 134.10, 133.21, 131.71, 131.21, 130.93, 129.81, 129.42, 129.18, 128.87, 126.24, 126.14, 124.02, 123.26, 123.00, 122.96, 122.83, 70.48, 54.81, 40.30, 32.35, 31.87, 29.60, 29.58, 29.54, 29.30, 28.72, 27.81, 26.97, 26.43, 25.10, 22.63, 21.62, 14.07. FT-IR (ATR): ($\tilde{v}$ /cm^{-1}): 2921.1, 2851.6, 1692.9, 1652.1, 1593.9, 1578.0, 1463.7, 1437.4, 1403.9, 1338.6, 1251.3, 1187.9, 1172.6, 1095.7, 953.4, 922.0, 850.1, 809.2, 795.1, 745.2, 722.2. Anal. Calcd. for $C_{60}H_{74}N_2O_7S$: C, 74.50%; H, 7.71%; N, 2.90%; S, 3.31%. Found: H, 73.98%; H, 7.68%; N, 2.80%; S, 3.28%. MALDI-TOF MS m/z (matrix: DTCB) found 968 (M + H$^+$).

N-(12-tricosanyl)-N'-(6-(2,7-dibromo-3,6-dimethyl-carbazol-9-yl)-hexyl)perylene-3,4:9,10-bis(dicarboximide) 6

A solution of N-(12-tricosanyl)-N'-(6-tosyloxyhexyl)perylene-3,4:9,10-bis(dicarboximide) **5** (0.270 g, 0.279 mmol) in DMSO (6 cm^3) and THF (5 cm^3) was added dropwise to a mixture of 2,7-dibromo-3,6-dimethyl-9*H*-carbazole (0.152 g, 0.466 mmol) and freshly ground KOH (0.06 g, 1.07 mmol) in DMSO (3 cm^3). The obtained solution was stirred for 16 h before THF was removed under high vacuum. Et_2O (200 cm^3) was then added followed by H_2O (500 cm^3) and the water layer separated then extracted with Et_2O (2 x 200 cm^3). To improve the phase separation NaCl was added to the water. The collected organic layers were concentrated and the crude product was purified by column chromatography on silica gel (99/1 V/V, $CHCl_3$/acetic acid) followed by a recrystallisation from ethanol/$CHCl_3$ to give **6** as a dark purple solid (0.155 mg, 48% yield). ^{1}H-NMR: ($CDCl_3$, 9 mg/ml): δ_H/ ppm: 8.602 (m, 8H); 7.788 (s, 2H); 7.516 (s, 2H); 5.204 (m, 1H); 4.199 (t, 2H, J = 7.38 Hz); 4.131 (t, 2H, J = 7.38 Hz); 2.583 (s, 6H); 2.261 (m, 2H); 1.98 − 1.69 (m, 6H); 1,480 (m, 4H); 1.2084 (m, 36H); 0.852 (t, 6H, J = 6.9 Hz). ^{13}C-NMR: ($CDCl_3$): δ_C/ ppm: 163.57, 162.48, 162.32, 138.84, 133.61, 133.30, 130.78, 130.35, 130.03, 128.49, 128.28, 126.82, 125.37, 125.29, 122.99, 122.24, 122.08, 122.02, 121.87, 121.41, 120.60, 120.36, 111.30, 53.78, 52.39, 42.30, 39.30, 31.35, 30.87, 28.58, 28.56, 28.52, 28.30, 27.65, 26.84, 25.96, 25.86, 25.74, 21.95, 21.64, 13.07. FT-IR (ATR): ($\tilde{v}$ /cm^{-1}): 2920.6, 2850.6, 1694.1, 1653.9, 1593.6, 1578.2, 1453.3, 1436.8, 1404.0, 1337.6, 1300.3, 1248.2, 1174.4, 1165.5, 1080.9, 1040.0, 995.9, 955.3, 924.8, 864.8, 850.3, 835.4, 809.8,

746.0, 721.9. Anal. Calcd. for $C_{67}H_{77}Br_2N_3O_4$: C, 70.09%; H, 6.76%; N, 3.66%; Br, 13.92%. Found: C, 69.92%; H, 6.61%; N, 3.51%; Br, 14.18%. MALDI-TOF MS m/z (matrix: DTCB) found 1147 (M + H$^+$).

3. Polymer synthesis

Polymer P1

A solution of **6** (0.228 g, 0.1987 mmol), 5,5'-bis(tri-*n*-butylstannyl)-2,2'-bithiophene (0.148 g, 0.1987 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.0036 g, 0.0040 mmol) and tri-*o*-tolylphosphine (0.0048 g, 0.0159 mmol) in toluene (6.3 cm^3) was heated to 95°C. This solution was stirred for 22 h before it was cooled to room temperature, followed by the addition of 2-(tributylstannyl)-thiophene (0.076 g, 0.2047 mmol). The solution was heated to 97°C again and stirred overnight. After addition of toluene (10 cm^3) the hot solution (100°C) was precipitated in methanol. The collected polymer was subjected to Soxhlet extraction with methanol (48 h), acetone (24 h), toluene (48 h) and CHCl$_3$ (48 h). The chloroform fraction was concentrated to c.a. ~ 20 cm^3 and added to methanol (500 cm^3) to provide a first fraction of the polymer after filtration (0.079 g, 34% yield). The insoluble residue left in the thimble was put into CHCl$_3$ and stirred to reflux for 6 h before the solution was filtered, concentrated to c.a. ~ 40 cm^3 and the polymer precipitated in methanol (500 cm^3) to afford a second fraction of the polymer after filtration (0.088 g, 37% yield). GPC (CHCl$_3$) - first fraction of polymer: M_n = 13,100; M_w = 28,800; PD = 2.2. GPC (CHCl$_3$) - second fraction of polymer: M_n = 26,300; M_w = 46,900; PD = 1.8. ^{1}H-NMR: (C$_2$D$_2$Cl$_4$ at 100 °C): δ_H/ppm: 8.54 - 8.08 (m, 4H); 7.790 (br.s, 2H); 7.399 (br.s, 2H); 7.192 (br.s, 2H); 7.039 (br.s, 2H); 5.088 (br.s, 1 H); 4.204 (bs, 2H); 4.l00 (br.s, 2H); 2.556 (br.s, 6H), 2.173 (br.s, 2H); 1.884 (br.s, 4H); 1.748 (br.s, 2H); 1.517 (br.s, 4H); 1.35 - l.11 (m, 36 H); 0.790 (br.s, 6H). For second fraction of polymer: Anal. Calcd. for $C_{75}H_{81}N_3O_4S_2$: C, 78.15%; H, 7.08%; N, 3.65%; S, 5.56%; Br, 0%. Found: C, 76.03%; H, 6.69%; N, 3.31%; S, 6.27%; Br, 2.02%.

Poly[N-(2-hexyldecyl)-3,6-dimethyl-2,7-carbazole-alt-2,2'-(5,5'-bithienylene)] P2

Toluene (10 cm^3) was added to a mixture of 2,7-dibromo-3,6-dimethyl-9-(2-hexyldecyl)-9*H*-carbazole (0.5774 g, 1.0 mmol), 5,5'-bis(tri-*n*-butylstannyl)-2,2'-bithiophene (0.7443 g, 1.0 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.0183 g, 0.02 mmol) and tri(*o*-tolyl)phosphine (0.0244 g, 0.08 mmol). The solution was heated to 95°C for 92 h before it was cooled down to room temperature to add 2-(tributylstannyl)-thiophene (0.370 g, 0.99 mmol). The mixture was then refluxed for 2.5 h before bromobenzene (0.313 g, 1.99 mmol) was added. The mixture was heated to reflux for 2 hours, before toluene (10 cm^3) and CHCl$_3$ (16 cm^3) were added and the mixture kept at 60 °C to solubilise the polymer. The hot solution was precipitated in methanol (500 cm^3) and the

precipitate was filtered and subjected to Soxhlet extraction with methanol (24 h), acetone (24 h), hexane (18 h). It was then extracted with $CHCl_3$ and the chloroform solution concentrated to 30 cm^3 and the polymer precipitated in methanol. The yellow solid was collected by filtration and dried under vacuum. (0.322 g, 55.4 % yield). GPC Mn = 27,100; Mw = 59,800, PD = 2.2. ^{1}H-NMR: ($CDCl_3$): δ_H/ ppm: 7.996 (s, 2H); 7.481 (s, 2H); 7.295 (d, 2H, J = 3.18 Hz); 7.126 (d, 2H, J = 2.94 Hz); 4.169 (bs, 2H); 2.692 (s, 6H); 2.201 (s, 1H); 1.54 – 1.11 (m, 24 H); 0.869 (m, 6H). ^{13}C-NMR: ($CDCl_3$): δ_C/ ppm: 143.39, 140.24, 137.11, 131.68, 127.30, 126.51, 123.67, 122.18, 122.04, 110.55, 47.67, 37.83, 31.92, 31.79, 30.06, 29.75, 29.65, 29.39, 26.48, 22.72, 21.58, 14.17. Anal. Calcd. for $C_{38}H_{47}NS_2$: C, 78.43; H, 8.14; N, 2.41; S, 11.02; Br, 0. Found: C, 77.15; H, 8.04; N, 2.23; S, 11.66.

4. P1 Steady-state polaron yield

We can relate the PA signal to the density of photoexcited states using $-\Delta T/T \approx nd\sigma$ as described by Lanzani et al. [9]. Here, n is the density of excited states, σ is their absorption cross-section and d is the thickness of sample. It is more appropriate to use the penetration depth of the pump laser, or $1/\alpha_L$, as this is the effective thickness in which most of the laser is absorbed. We can quantify the polaron density measured in Figure 7(a) using the fact that the absorption cross-section of singlets and polarons are believed to be comparable [10]. For a randomly oriented bulk polymer, $\sigma = \alpha_{max}/N$ where α_{max} is the maximum absorption coefficient, N is the density of ground states or monomeric segments given by $N = \rho N_A/m_W$ where ρ is the density, N_A is Avagadro's number and m_W is the molecular weight of the repeat unit. We can thus estimate the polaron absorption coefficient (σ_p) using

$$\sigma_p \approx m \frac{m_W \alpha_{max}}{\rho N_A} \tag{1}$$

Using values of $m_W \sim$ 1200g/mol, $\rho \sim$ 1g/cm^3 and $\alpha_{max} \sim 7.5 \times 10^4 cm^{-1}$ in **P1**, we find $\sigma_p = 1.5 \times 10^{-16} cm^2$; a value that is consistent with other work on the polymer m-LPPP [11]. The **P1** polaron density can now be calculated using

$$n_p = \Delta T/T\left(1/d\sigma_p\right) \tag{2}$$

with the modulus of symbol $\Delta T/T$ at 1.72eV being 2.2×10^{-4}. Using a value of α_L as 48,780 cm^{-1}, we estimate that the penetration depth of the laser is $\sim$ 200 nm. Combining the polaron cross-section, differential transmission and penetration depth, we deduce a polaron density in **P1** thin-films under our measurement conditions to be $7.3 \times 10^{16} cm^{-3} s^{-1}$.

To better understand the recombination mechanism of the excited species in the material systems studied, both the dependence of the PA signal on pump intensity and the applied modulation frequency have been studied as shown in Fig. S3. We find that **P1** is characterized by dispersive dynamics [12] resulting from a distribution of excited state lifetimes. Typically, rather than the $N_I \sim \omega^{-2}$ form expected for the in-phase PA signal in the case of a uniform recombination rate, these systems display a gentle, high-frequency roll-off of the form $N_I \sim \omega^{\alpha}$ where $0 < \alpha < 1$, with lower values of α implying a more disperse distribution of lifetimes. For **P1** we determine a polaron lifetime $\tau = 0.56\text{ms}$ with $\alpha = 0.65$. Having fit to the modulation data (*see* Fig. S3), we can calculate the polaron density that we might expect under steady-state conditions. In particular we estimate by extrapolation from the PA measurements (performed at a chopping frequency of 135Hz), that the polaron density expected at quasi steady-state values will increase by 2.7 times, suggesting a value of $n_p^{0} = 2.0 \times 10^{17} \text{cm}^{-3}$.

We can relate the steady-state polaron density to a generation yield, η_p, by solving the rate equation

$$\frac{dn_p}{dt} = \frac{\eta_p \alpha_L N_0}{2}(1 + \cos \omega t) - \frac{n_p}{\tau} \tag{3}$$

Here, N_o is the number of photons incident on the film per unit area per second, ω is the chopping frequency, α_L is the film attenuation coefficient at the laser wavelength and τ is the polaron lifetime. Note, that this analysis ignores any saturation effects and assumes that the polarons undergo monomolecular recombination with a rate given by n_p/τ. We can calculate N_0 using $N_0 = P/(h\upsilon A)$ where P is the laser power, $h\upsilon$ the pump excitation photon energy and A the cross-sectional area of the laser-beam. The depth averaged excitation density is thus $N_0\alpha_L$, a value that is fixed at $1.2 \times 10^{17} \text{cm}^{-2}\text{s}^{-1}$ in our PA experiments. In the steady state, equation (3) can be solved to express the polaron yield as

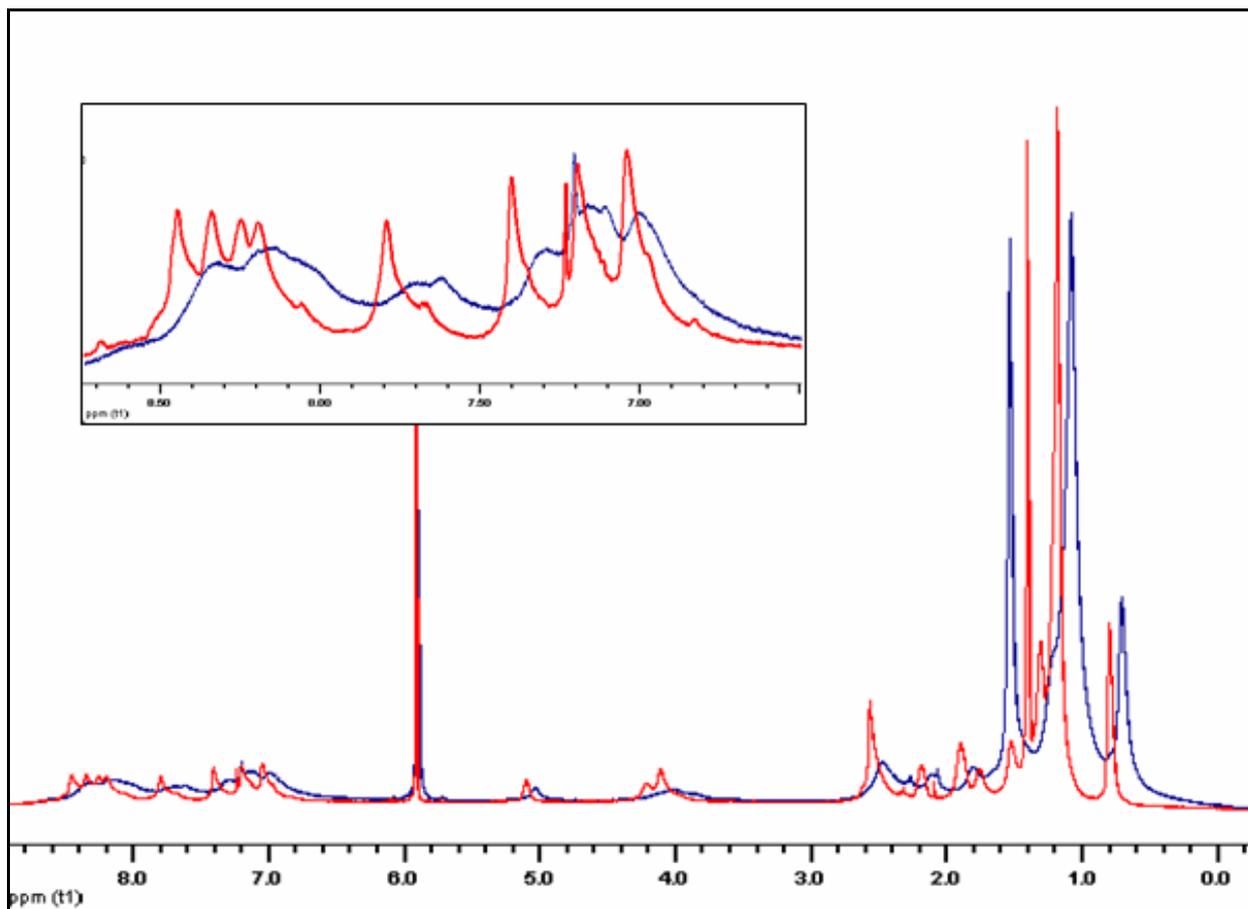$$\eta_p = \frac{n_p}{\alpha_L N_0 \tau} \tag{4}$$

Using our measured parameters, we determine a singlet-exciton to polaron yield of $\eta_p = 6\%$.
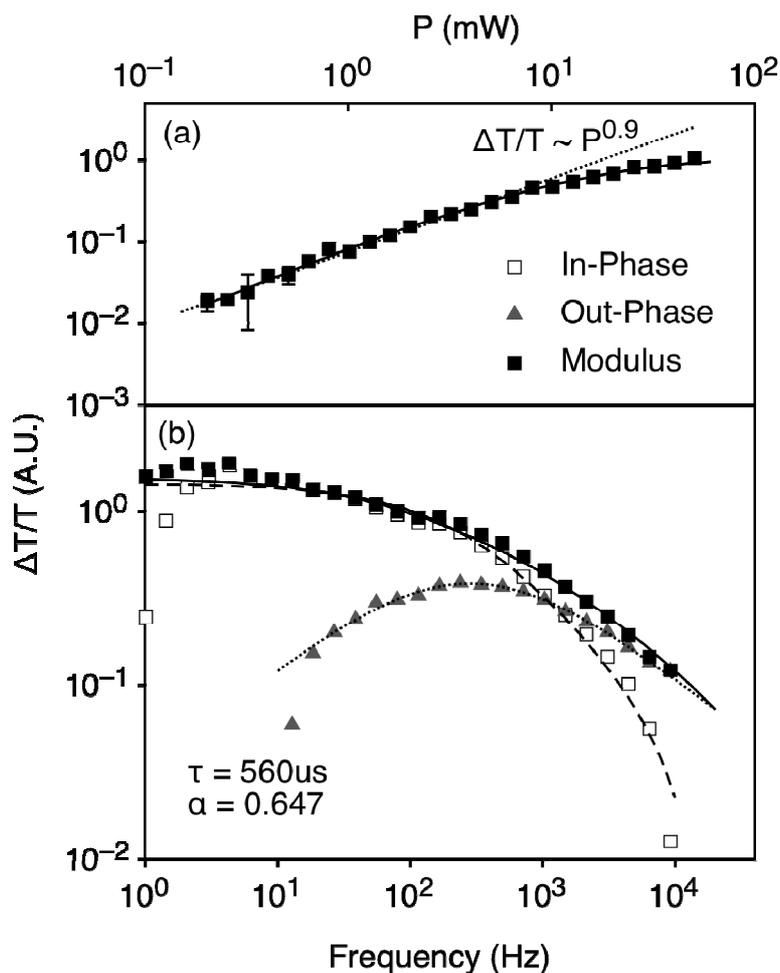
Figure S1
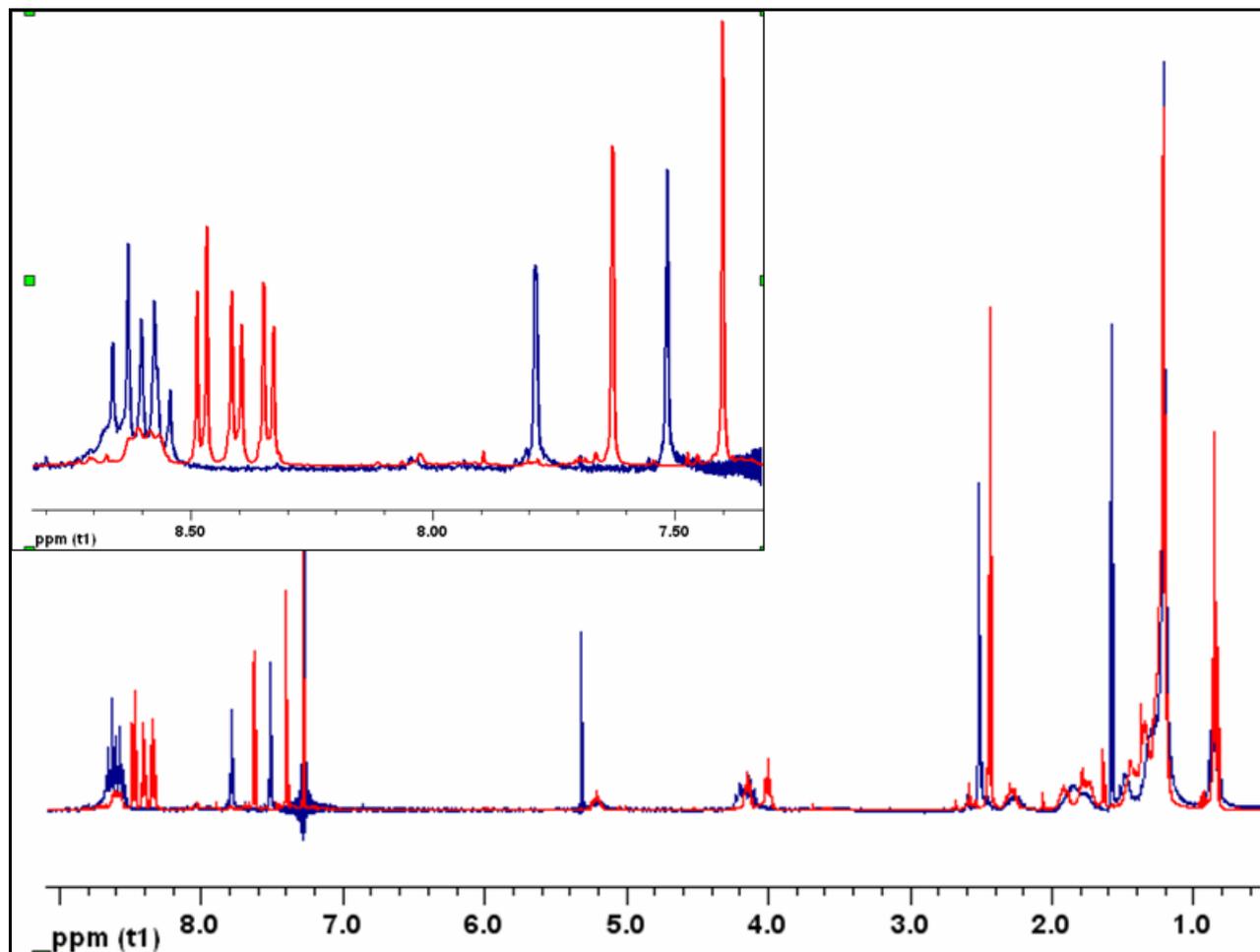
Fig S1. Overlay of two ^{1}H-NMR spectra from two different concentrations of compound (6); red: approx. 37 mg/ml; blue: approx. 9 mg/ml

Figure S2

Fig. S2. ^{1}H-NMR spectra of P1 in $C_2D_2Cl_4$ at room temperature (blue) and at 100 °C (red)

Figure S3

Fig. S3. PA dynamics of the 1.72eV polaronic feature of **P1** under 488nm illumination at 77K. (a)

Intensity dependence of the transmission difference on pump intensity at 135Hz modulation fitted

with a power law with exponent 0.9 (dotted line) and a trap modified MR model [13], (b)

Modulation dependence of the transmission difference fitted with the dispersive model proposed by

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