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Supporting information for: Energy Transfer in Pendant Perylene Diimide Copolymers

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Experimental Section

Materials: Starting materials 7-tridecanone and perylene-3,4,9,10-tetracarboxylic dianhydride were purchased from Sigma-Aldrich. Commercial solvents and reagents were used without further purification unless specified otherwise. 2,6,-Diisopropylaniline was purified by conversion to its hydrochloride salt (prepared by addition of concentrated hydrochloric acid to an ethanolic solution of the crude aniline), recrystallisation from ethanol and subsequent aqueous extraction into ether under basic conditions to liberate the pure aniline.[S1] Tetrahydrofuran (THF) was distilled from the sodium–benzophenone ketyl under N_2 to remove water and inhibitor (4-hydroxy-3,5-di-*tert*-butyltoluene). Liquid *tert*-butyl acrylate was passed over basic alumina prior to polymerisation to remove the inhibitor.

Methods: Ultraviolet-visible-near infrared (UV-Vis-NIR) absorbance spectra were recorded with a Varian Cary 4000 (900–200 nm). Steady state fluorescence measurements of solutions were carried out on a Varian Cary Eclipse Fluorescence Spectrophotometer, while steady-state solid fluorescence was measured using an Ocean Optic HR4000 Spectrophotometer with a fibre optic probe.

Low-resolution electrospray ionisation (ESI) mass spectra were recorded on a ThermoQuest Finnigan LCQ ion trap mass spectrometer. High-resolution matrix-assisted laser desorption/ionisation–fourier transform ion cyclotron resonance (MALDI-FTICR) mass-spectra were recorded on a Bruker 7T Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FTICR).

One-dimensional ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 200 (200 MHz) or DPX 500 (500 MHz) spectrometer. Samples were dissolved in deuterated chloroform, either as the neat solvent ($CDCl_3$) or containing 0.03% (v/v) tetramethylsilane ($CDCl_3$-TMS) as specified, or deuterated water (D_2O). Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., and stored away from light at room temperature. Deuterated chloroform was de-acidified by passage through basic alumina (Brockmann Grade

I) immediately prior to use. Samples were filtered through a plug of dry cotton wool directly into NMR tubes prior to analysis to remove any suspended solids. Where possible, the TMS peak at 0.00 ppm was used as an internal reference; otherwise the residual solvent peak was used. Signals are recorded in terms of chemical shift (in ppm), relative integral, multiplicity, and assignment, in that order. The following abbreviations for multiplicity are used: s, singlet; d, doublet; t, triplet; qt, quartet; qn, quintet; m, multiplet.

Column chromatography was carried out using flash chromatography on Davisil LC60A 4063 micron chromatographic silica. Analytical thin layer chromatography (TLC) analysis were performed on Merck silica gel 60 F254 precoated sheets (0.2 mM).

Molecular weight distributions of polymers were measured by analytical Gel Permeation Chromatography (GPC) on a Shimadzu LC-10AT liquid chromatography system fitted with a PLgel 5 μm MiniMIX-C (50 × 4.6 mm) guard column and two PLgel 5 μm MIXED-C (300 × 7.5 mm) columns. The system was equipped with a Shimadzu RID-10A differential refractive index detector and a Shimadzu SPD-10A UV-visible absorption detector. THF containing 1,4-hydroquinone (0.04 $\mathrm{g\,L^{-1}}$) was used as the mobile phase, eluting at $1.0\,\mathrm{mL\,min^{-1}}$ at 40 °C. Analyte samples were dissolved in THF spiked with 0.5 vol.% toluene as flow rate marker and filtered (polytetrafluoroethylene, 0.45 μm pore size) prior to injection (100 μL). Chromatograms were calibrated using linear polystyrene standards. Experimental molecular weight (M_n) and dispersity () values of the synthesised polymers were determined by conventional calibration using Cirrus software.

Synthesis of Sensitiser Monomer

1-Hexylheptylamine (1): Prepared according to the procedure of Holman *et al.*[S2] A 250 mL round-bottom flask was charged with 7-tridecanone(10.4 g, 52.5 mmol), NH_4OAc (40.1 g, 521 mmol), $NaBH_3CN$ (2.3 g, 38 mmol) and MeOH (75 mL), and the mixture stirred at room temperature (r.t.) for 48 h, until the starting material was absent by TLC. The reaction was quenched by dropwise addition of concentrated HCl (∼6 mL), and the solvents removed by rotary evaporation. The resulting white solid was redissolved in H_2O (500 mL) and adjusted to ~pH 10 with solid KOH, then extracted with $CHCl_3$ (3× 750 mL). The $CHCl_3$ extracts were combined and concentrated to give the product as a pale yellow oil (10.2 g, 97%). ^{1}H NMR (D_2O, 200 MHz): $\delta = 0.84$ (t, 6H, CH_3), 0.99–1.19 (m, 16H, 8 CH_2), 1.48 (m, 4H, 2 CH_2CHNH_2, 2.79 (qn, 1H, $CHNH_2$).

***N,N′*-Bis(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylbisimide (2):** Prepared according to the procedure of Holman *et al.*[S2] In a 500 mL RBF, perylene-3,4,9,10-tetracarboxylic dianhydride (4.0 g, 10 mmol) and **(1)** (4.4 g, 22 mmol) in imidazole (15.2 g) were stirred at 180 °C for 5 h. The reaction mixture was cooled to r.t., dissolved in ethanol (100 mL), treated with aqueous HCl (2 M, 400 mL), and stirred overnight. The resulting dark red precipitate was filtered and rinsed thoroughly with water, then dried *in vacuo* at 130°C to give the product as a dark red powder (7.5 g, 98%). ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.88$ (t, 12H, CH_3), 1.11–1.44 (m, 32H, 16 CH_2), 1.87 (m, 4H, 2 CH_2CHN,), 2.21 (m, 4H, 2 CH_2CHN-), 5.19 (m, 2H, 2 CH_2CHN), 8.69 (m, 8H, perylene-H).

***N*-(1-Hexylheptyl)perylene-3,4,9,10-tetracarboxyl-3,4-anhydride-9,10-imide(3):** Prepared according to the procedure of Holman *et al.*[S2] In a 500 mL RBF, **(2)** (6.4 g, 8.5 mmol) was suspended in *t*-BuOH (150 mL) and treated with solid KOH (1.5 g, 28 mmol). The reaction mixture was heated at reflux with vigorous stirring until the solution turned dark red/purple in colour (~30 min). The mixture was cooled to r.t., treated with acetic acid (80 mL) and aqueous HCl (2 M, 40 mL), and stirred overnight. The dark red precipitate was filtered, washed with distilled water (400 mL) and dried *in vacuo* at 130°C. Once dry, the red solid (7.2 g) was suspended in aqueous K_2CO_3 (10% *w/v*, 150 mL) and heated at reflux for 30 min, whereupon any remaining perylene-3,4,9,10-tetracarboxylic dianhydride was drawn into solution as the bright green tetrapotassium tetracarboxylate. The mixture was cooled and filtered, the filter cake rinsed with aqueous K_2CO_3 (10% {emphw/v) at 70°C until the filtrate was colourless (120 mL), rinsed with aqueous HCl (2 M, 2×100 mL), then rinsed thoroughly with water (200 mL) and dried *in vacuo* at 130°C. The dried solid (4.1 g) was then suspended in 100 mL boiling water, and Et_3N was added until a dark red solution of the desired product formed. Remaining starting material was removed by filtration and the dark red filtrate acidified with 2 M HCl and allowed to stir overnight. The resulting red precipitate was filtered, rinsed thoroughly with water, and dried *in vacuo* at 130°C. This material was similarly treated once more with water/Et_3N to remove any remaining traces of starting material, and upon precipitation and drying yielded the desired product as an amorphous red solid (2.3 g, 46%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.86 (t, 6H, CH3), 1.13–1.41 (m, 16H, 8 CH_2), 1.93 (m, 2H, -CH_2CHN-), 2.29 (m, 2H, -CH_2CHN-), 5.21 (m, 1H, $(CH_2)_2$CHN), 8.73 (dd, 8H, perylene).

***N*-(1-Hexylheptyl)-*N′*-(hexanol)perylene-3,4,9,10-tetracarboxylbisimide (4): (3)** (2.0 g, 3.5 mmol), 6-aminohexan-1-ol (0.6 g, 5.2 mmol) and imidazole (7.5 g) were combined in a 100 mL RBF, and the reaction mixture stirred at 180°C for 5 h. The reaction mixture was cooled to r.t., dissolved in ethanol (40 mL), treated with HCl (2 M, 200 mL) and stirred overnight. The dark red precipitate was filtered and rinsed thoroughly with water, then dried *in vacuo* at 130 °C to yield the desired product as a red solid (2.3 g, 98%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.84 (t, 2H, CH_3), 1.11–1.42 (m, 16H, 8 CH_2), 1.52–1.87 (m, 8H, 4CH_2), 2.21 (m, 4H, 2 -CH_2CHN-), 3.67 (m, 4H, 2 -CH_2N-), 4.24 (t, 2H, -CH_2O), 5.17 (m, 1H, -OH), 8.61 (m, 8H, perylene).

***N*-(1-Hexylheptyl)-*N′*-(hexylacrylate)perylene-3,4,9,10-tetracarboxylbisimide (5):** In a 50 mL RBF, a solution of **(4)** (250 mg, 0.37 mmol) and Et_3N (38 mg, 0.37 mmol) in THF (10 mL) was cooled to 0°C. Acryloyl chloride (34 mg, 0.37 mmol) in THF (5 mL) was added dropwise over 20 min, then the solution was stirred for 1 h at 0 °C before stirring for another 2 h at r.t. THF was removed under reduced pressure and the resulting solid was dissolved in $CHCl_3$ (50 mL) and washed with H_2O (3 × 50 mL) and brine (2 × 25 mL). The organic solvent was removed by rotary evaporation, giving the desired perylene monomer as a red powder (268 mg, 99%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.82 (t, 6H, 2 CH_3), 1.09-1.40 (m, 10H, 5 CH_2), 1.63 (m, 2H, CH_2CH_2O), 1.72 (m, 2H, CH_2CH_2N), 1.81 (m, 4H, 4CH_2CH$_2$CHN-), 2.17 (m, 4H, 2 CH$_2$CHN-), 4.09 (t, 2H, -CH$_2$O), 4.16 (t, 2H, CH$_2$N)), 5.15(CH$_2$CHN) (m, 1h, 5.83 (d, 1H, -COHCCHH), 6.11 (d, 1H, -COHCCHH), 6.52 (d, 1H, -COHCCHH), 8.64 (d, 8H, perylene). ^{1}3C NMR (CDCl$_3$-TMS, δ): 14.40, 22.73, 25.87, 26.75, 26.91, 27.082, 28.13, 28.67, 29.37, 31.91, 40.66, 54.97, 64.72, 123.15, 123.28, 124.44, 124.67, 126.73, 128.78, 129.65, 129.75, 130.57, 131.26, 131.59, 132.05, 134.47, 134.94, 163.56, 164.98, 166.65. MS (MALDI-FTICR): *matrix*: 4CCA 10 mg/mL in CH$_3$CN:H$_2$O (4:1). Sample 0.5 mg/mL in THF:sample (4:1), (m/z): found 727.373, calculated 727.374.

Syntheis of Acceptor Monomer

***N*-(1-Diisopropylaniline)-*N*′-(hexanol)-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylbisimide (6):** In a 500 mL RBF, 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic dianhydride, (8.7 g, 16.5 mmol) in 100 mL *N*-methyl-2-pyrrolidone (NMP) was stirred under argon at r.t. for 30 min. Diisopropylaniline (2.9 g, 17 mmol) and 6-aminohexan-1-ol (1.9 g, 17 mmol) were added to the solution, which was subsequently heated at 180 °C and stirred under argon for 18 h until the reaction was complete by TLC (DCM). The reaction mixture was added to aqueous HCl (1 M, 500 mL), resulting in the formation of an orange precipitate, which was filtered and washed with water (500 mL). The orange solid was dried overnight *in vacuo* at 130°C, yielding 12 g of the crude product. The three major products where separated by column chromatography (DCM:MeOH, 20:1), giving 3.2 g (23%) of *N,N*'-bis(1-diisopropylaniline)-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylbisimide. ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 1.19 (d, 24H, 8 CH$_3$), 2.74 (m, 4H, 2 CH(CH$_3$)$_2$), 7.38 (d, 4 H, 2 CHCHCH), 7.51 (t, 2H 2 CHCHCH), 8.75 (s, 4H, perylene); 4.4 g (34%) of N,N'-bis(hexanol)-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylbisimide, ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 1.39–2.02 (m, 12H, 6CH$_2$), 2.28 (m, 4H, 2 CH_2CH$_2$-N), 3.54 (m, 2H, CH$_2$-N), 4.41 (t, 2H, CH$_2$-O), 5.11 (s, 2H, OH), 8.67 (s, 4H, perylene); and 4.2 g (31%) of the desired N-(1-diisopropylaniline)-N'-(hexanol)1,6,7,12-tetrachloro-perylene-3,4,9,10-tetracarboxylbisimide ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 1.17 (d, 12H, 4 CH_3), 1.34 -1.92 (m, 6H, 3CH_2), 2.28 (m, 2H, CH_2CH_2-N), 2.71 (m, 2H, $CH(CH_3)_2$), 3.53 (t, 2H, CH_2-N), 4.41 (t, 2H, CH_2-O), 5.11 (s, 1H, OH), 7.36 (d, 2H, C*H*CHC*H*), 7.50 (t, 1H, CHC*H*CH), 8.76 (D, 4H, perylene).

***N*-(1-Diisopropylaniline)-*N′*-(hexanol)-1,6,7,12-tetra(phenoxy)perylene-3,4,9,10-tetracarboxylbisimide (7):** In a 100 mL RBF **(6)** (1.7 g. 2.2 mmol), phenol (3.3 g, 36 mmol) and K_2CO_3 (5.0 g, 36 mmol) were stirred under argon in NMP (50 mL) at 130 °C for 16 h. The reaction mixture was then poured into aqueous HCl (1 M, 500 mL) and stirred for 1 h at r.t. The precipitate was collected by vacuum filtration and washed with H_2O (500 mL). The purple solid was dried at 130 °C *in vacuo*, yielding 2.7 g (92%) of the desired product. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.10 (d, 12H, 4 CH_3), 1.33 -1.84 (m, 6H, 4CH_2), 2.27 (m, 2H, CH_2CH_2-N) 2.69 (m, 2H, $CH(CH_3)_2$), 3.53 (m, 2H, CH_2-N), 4.41 (m, 2H, CH_2-O), 5.09 (s, 1H, -OH), 6.77–7.29 (m, 20H, 4 (Phenol (5H))), 7.34 (d, 2H, C*H*CHC*H*), 7.49 (t, 1H, CHC*H*CH), 8.22 (d, 4H, perylene).

***N*-(1-Diisopropylaniline)-*N′*-(hexylacrylate)-1,6,7,12-tetra(phenoxy)perylene-3,4,9,10-tetra-carboxylbisimide (8):** In a 50 mL RBF, **(7)** (380 mg, 0.40 mmol) and Et_3N (38 mg, 0.40 mmol) in THF (10 mL) was cooled to 0°C. A solution of acryloyl chloride (33 mg, 0.4 mmol) in THF (5 mL) was added dropwise over 20 min, then the solution stirred at 0°C for 1 h before stirring for another 2 h at r.t. The THF was removed under reduced pressure and the resulting solid dissolved in $CHCl_3$ (100 mL), washed with H_2O (3×100 mL) then brine (2× 50 mL). The organic phase was removed under reduced pressure, yielding 375 mg of the desired perylene monomer as a purple powder (95%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.08 (d, 12H, 4 CH_3), 1.28–1.78 (m, 6H, 3CH_2), 2.28 (m, 2H, CH_2CH_2-N), 2.71 (m, 2H, 2 $CH(CH_3)_2$), 3.51 (m, 2H, CH_2-N, 4.18 (m, 2H, CH_2-O), 5.79 (d, 1H, -COHCC*H*H), 6.17 (d, 1H, -CO*H*CCHH), 6.34 (d, 1H, -COHCCH*H*), 6.81–7.17 (m, 2H, 4 (Phenol (5H)),7.31 (d, 2H, C*H*CHC*H*), 7.40 (t, 1H, CHC*H*CH), 8.20 (d, 4H, perylene). ^{1}3C NMR ($CDCl_3$-TMS, δ): 1.01, 7.97, 12.85, 17.42. 21.50, 25.65, 26.46, 26.80, 29.08, 40.45, 51.41, 53.10, 53.83, 60.68, 64.52, 67.87, 70.95, 72.96, 114.48, 116.49, 119.59, 121.69, 127.50, 128.60, 139.35, 129.54, 130.00, 154.61, 155.28, 155.32, 155.78, 155.91, 163.19, 166.29. MS (MALDI-FTICR): 4CCA 10 mg/mL in CH_3CN:H_2O (4:1) Matrix. Sample 0.5 mg/mL in THF:sample (4:1), (m/z): found 1073.399, calculated 1073.400.

Polymers

SP20:1:0 : (5) (0.10 g, 0.13 mmol), *t*BA (0.35 g, 2.8 mmol) and AIBN (6 mg, 0.04 mmol) in 0.55 mL toluene was degassed *via* bubbling of N_2 gas. The solution was stirred at 70°C for 5 h, then AIBN (3 g, 0.02 mmol) was added followed by further degassing and the solution was heated at 70°C for a further 8 h until polymerisation was shown to be complete by NMR. The crude product was dissolved in THF and precipitated into H_2O:MeOH (1:1) at 0°C. The solid was recovered by vacuum filtration and dried over phosphorus pentoxide, giving 0.43 g of the pure product. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.77–0.96 (M, 2.46 H, CH_3)), 1.10–2.04 (m, 14.57 H, CH_2)), 2.07–2.48 (m, 2H, CH_2CH_2$-N), 3.99–4.27 (m, 2.01 H, CH_2N), 4.54–5.19 (m, 8.85H, $COCH_2$), 8.55–8.88 (m, 1H, perylene). M_n = 6730 g mol^{-1}, M_p = 14740 g mol^{-1}, Đ = 2.64.

AP20:0:1 : (9) (30 mg, 0.021 mmol), *t*BA (72 mg, 0.56 mmol) and AIBN (2 mg, 0.014 mmol) in 0.2 mL toluene was degassed *via* bubbling of N_2 gas. The solution was stirred at 70°C for 5 h, then AIBN (2 mg, 0.02 mmol) was added followed by further degassing and the solution was heated at 70°C for a further 8 h until polymerisation was shown to be complete by NMR. The crude product was dissolved in THF and precipitated into H_2O:MeOH (1:1) at 0°C. The pure product was filtered and dried over phosphorus pentoxide, giving 89 mg of the pure product. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.68–1.01 (M, 1.79 H, CH_3)), 1.01–1.95 (m, 20.69 H, CH_2)), 2.06–2.58 (m, 2.24 H, $C\mathit{H}_2CH_2$-N), 3.98–4.24 (m, 1.68 H, CH_2N), 5.11–5.22 (m, 0.30 H, $COCH_2$), 6.89–7.32 (m, 10.97 H, benzylic), 8.11–8.35 (m, 1H, perylene). M_n = 3770 g mol^{-1}, M_p = 17450 g mol^{-1}, Đ = 5.31.

CP150:5:1 : (5) (15 mg, 0.021 mmol), **(9)** (5 mg, 0.004 mmol), *t*BA (80 mg, 0.63 mmol) and AIBN (2 mg, 0.013 mmol) 0.2 mL toluene was degassed *via* bubbling of N_2 gas. The solution was heated at 70°C for 4 h, then AIBN (2 mg, 0.02 mmol) was added followed by further degassing and the solution was heated at 70°C for a further 8 h until polymerisation was shown to be complete by NMR. The crude product was dissolved in THF and precipitated into H_2O:MeOH (1:1) at 0°C. The pure product was filtered and dried over phosphorus pentoxide, yielding 74 mg of the pure product. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.74–1.01 (M, 0.22 H, CH_3)), 1.09–1.96 (m, 27.98 H, CH_2)), 2.13–2.61 (m, 3.60 H, $C\mathit{H}_2CH_2$-N), 3.94–4.28 (m, 0.91 H, CH_2N), 5.04–5.27 (m, 0.35 H, $COCH_2$), 6.87–7.42 (m, 0.48 H, benzylic), 8.10–8.93 (m, 1H, perylenes). $M_\mathrm{n} = 2180\,\mathrm{g\,mol^{-1}}$, $M_\mathrm{p} = 5540\,\mathrm{g\,mol^{-1}}$, $Đ = 3.22$.

CP300:10:1 : (5) (17 mg, 0.023 mmol), **(9)** (3 mg, 0.002 mmol), *t*BA (90 mg, 0.70 mmol) and AIBN (4 mg, 0.02 mmol) in 0.2 mL toluene was degassed *via* bubbling of N_2 gas. The solution was heated at 70°C for 4 h, then AIBN (2 mg, 0.014 mmol) was added followed by further degassing and the solution was heated at 70°C for a further 8 h until polymerisation was shown to be complete by NMR. The crude product was dissolved in THF and precipitated into H_2O:MeOH (1:1) at 0°C. The pure product was filtered and dried over phosphorus pentoxide, giving 94 mg of the pure product. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.73–1.05 (M, 4.82 H, CH_3)), 1.03–1.95 (m, 32.02 H, CH_2)), 2.07–2.59 (m, 6.39 H, $C\mathit{H}_2CH_2$-N), 3.98–4.27 (m, 1.40 H, CH_2N), 5.12–5.28 (m, 0.23 H, $COCH_2$), 6.88–7.41 (m, 0.53 H, benzylic), 8.11–8.94 (m, 1H, perylenes). $M_\mathrm{n} = 4050\,\mathrm{g\,mol^{-1}}$, $M_\mathrm{p} = 16290\,\mathrm{g\,mol^{-1}}$, $Đ = 4.76$.

Supplementary information Figures

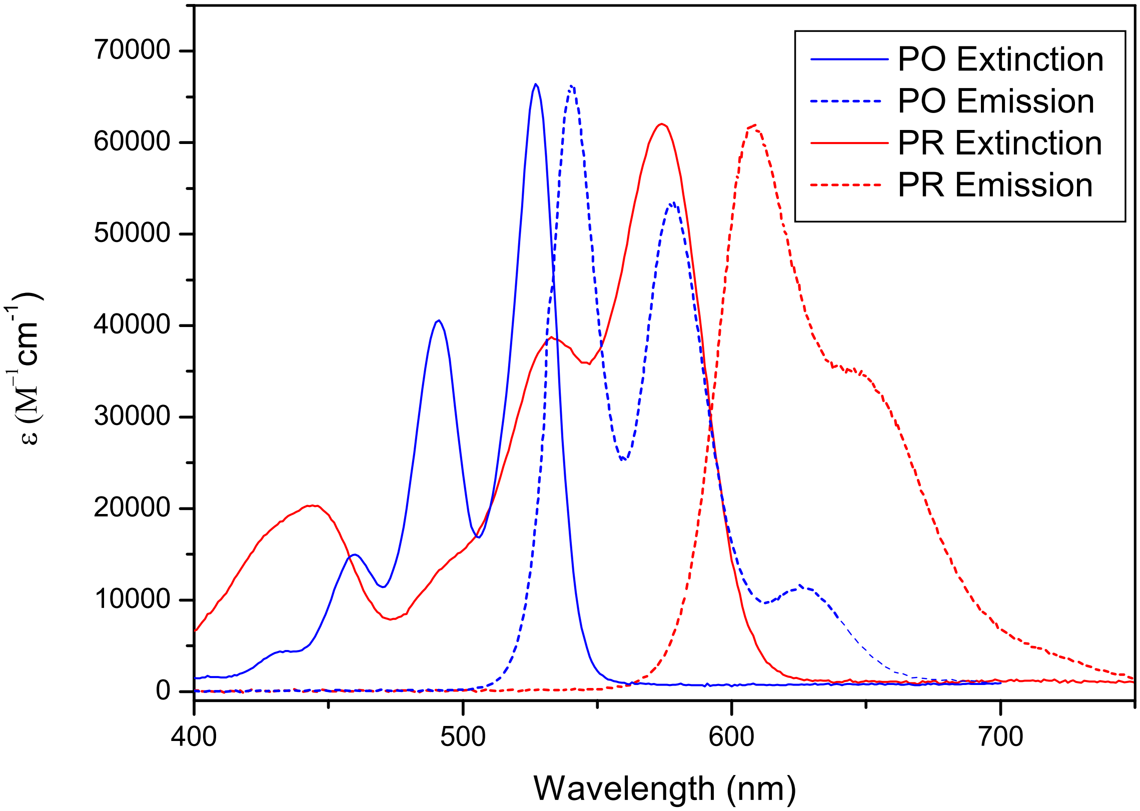

Figure S1: Absorbtion and emission spectra of Perylene Orange (PO) and Perylene Red (PR). Emission spectrum is in arbitrary units and normalised to peak excitation.

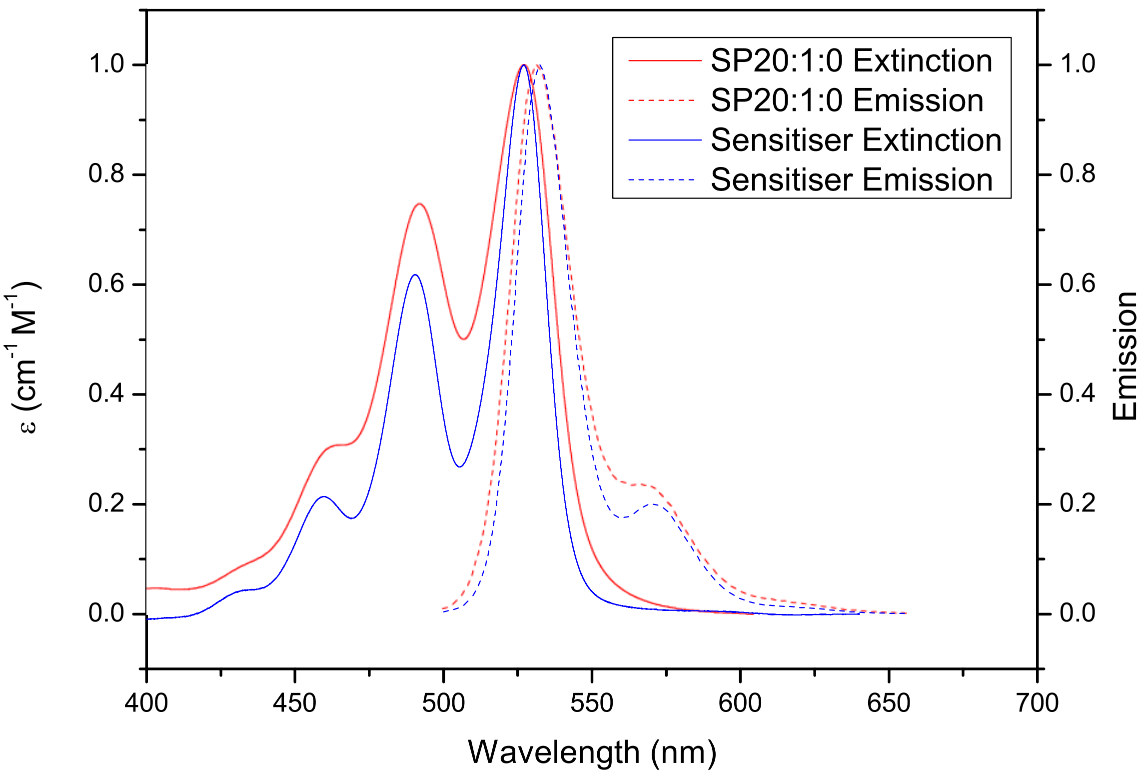

Figure S2: Normalised absorbtion and emission spectra of sensitiser monomer and SP:20:1:0

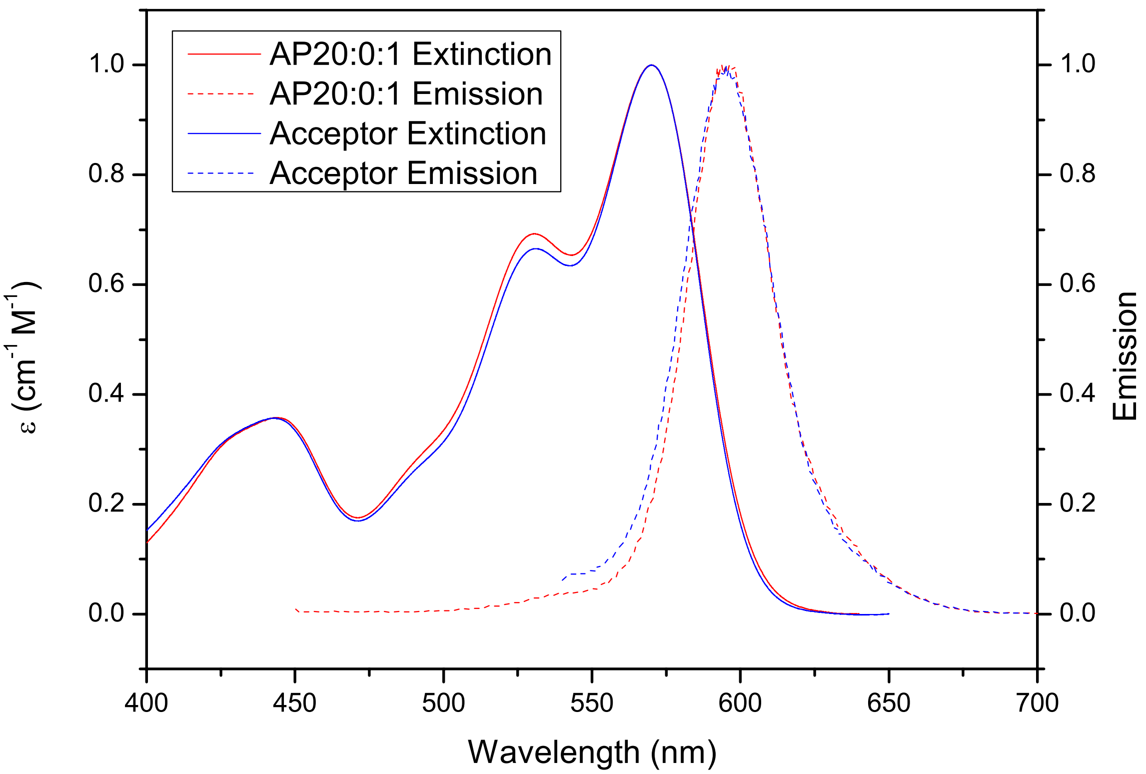

Figure S3: Normalised absorbtion and emission spectra of acceptor monomer and AP:20:0:1

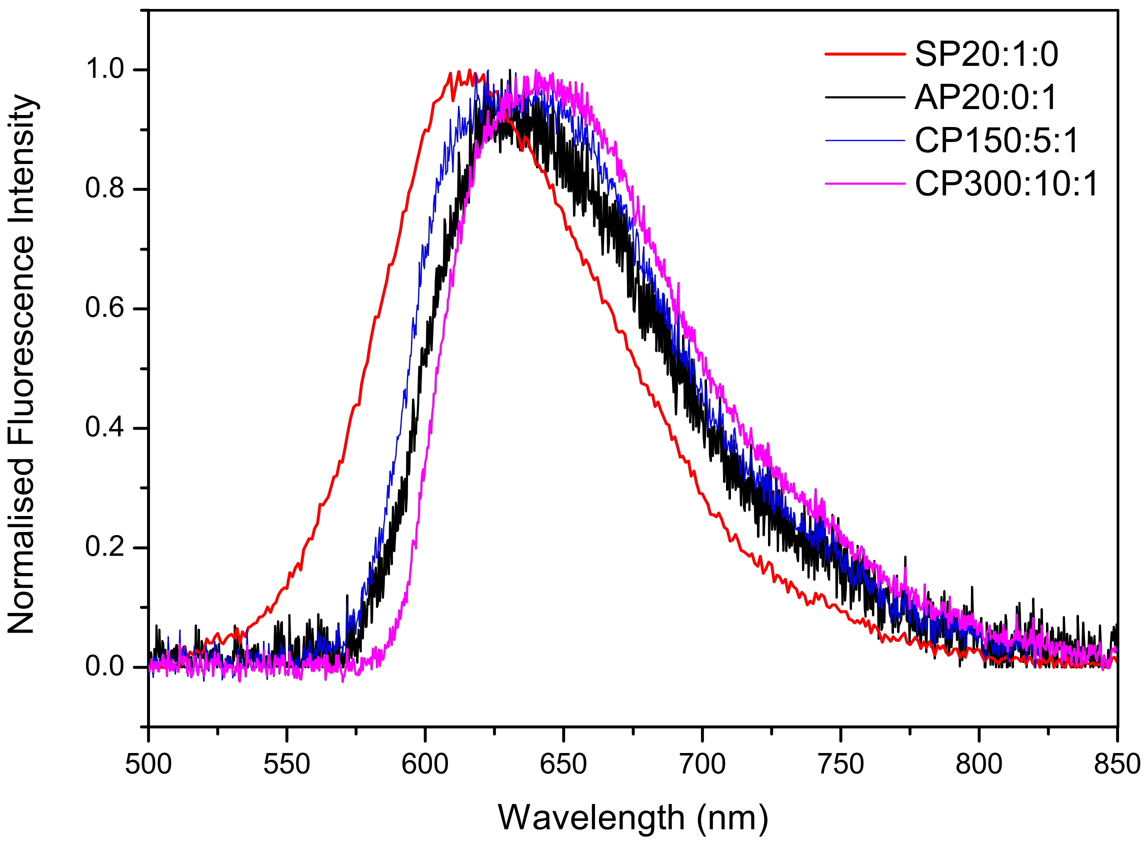

Figure S4: Comparison of the emission spectra of polymer films SP20:1:0, AP20:0:1, CP150:5:1 and CP300:10:1.

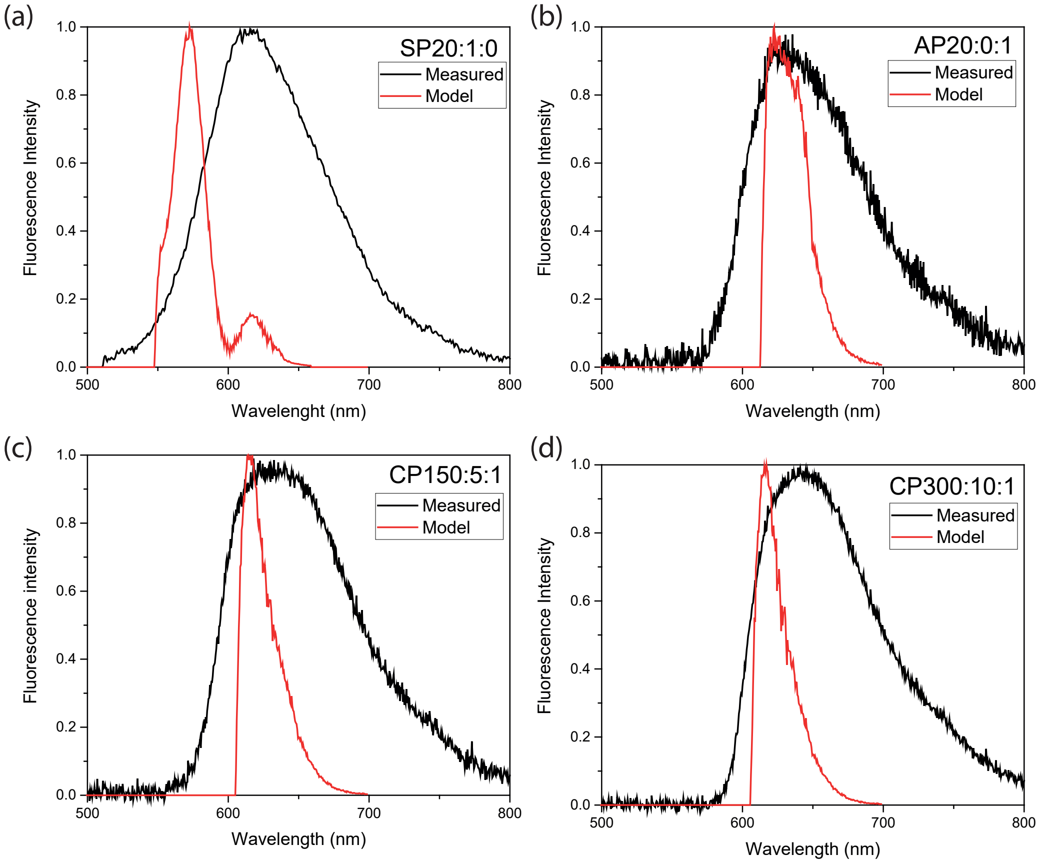

Figure S5: Emission (black) and modeled emission (red) of the polymer samples (a)-(d). Model emission was produced by attenuation the sensitiser or acceptors emission by the absorption of the sensitiser or acceptor monomers.

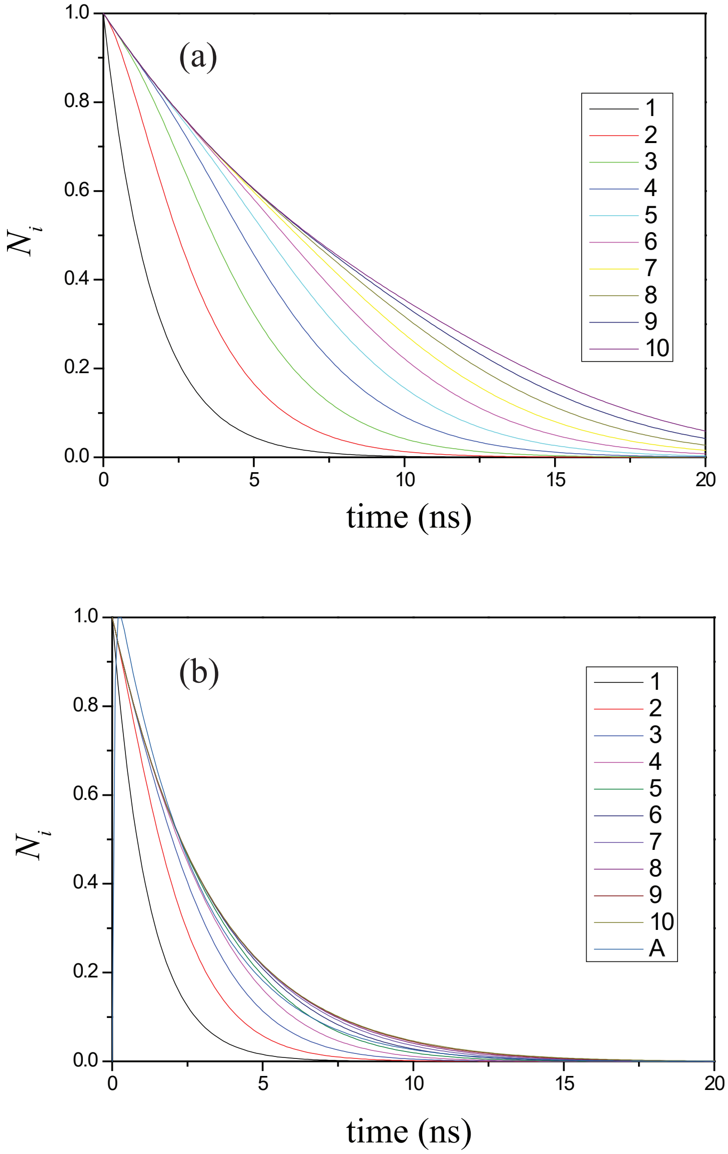

Figure S6: The populations of 10 connected states as described in the main text. (a) 10 states which decay from state i to state $i+1$, and radiate. (b) 10 states which can decay and radiate; and also transfer to state A, which also radiates.

References

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(S2) Holman, M. W.; Liu, R.; Adams, D. M. *J. Am. Chem. Soc.* **2003**, *125*, 12649–54.