Electronic Supporting Information for:

Quantifying highly efficient incoherent energy transfer in perylene-based multichromophore arrays

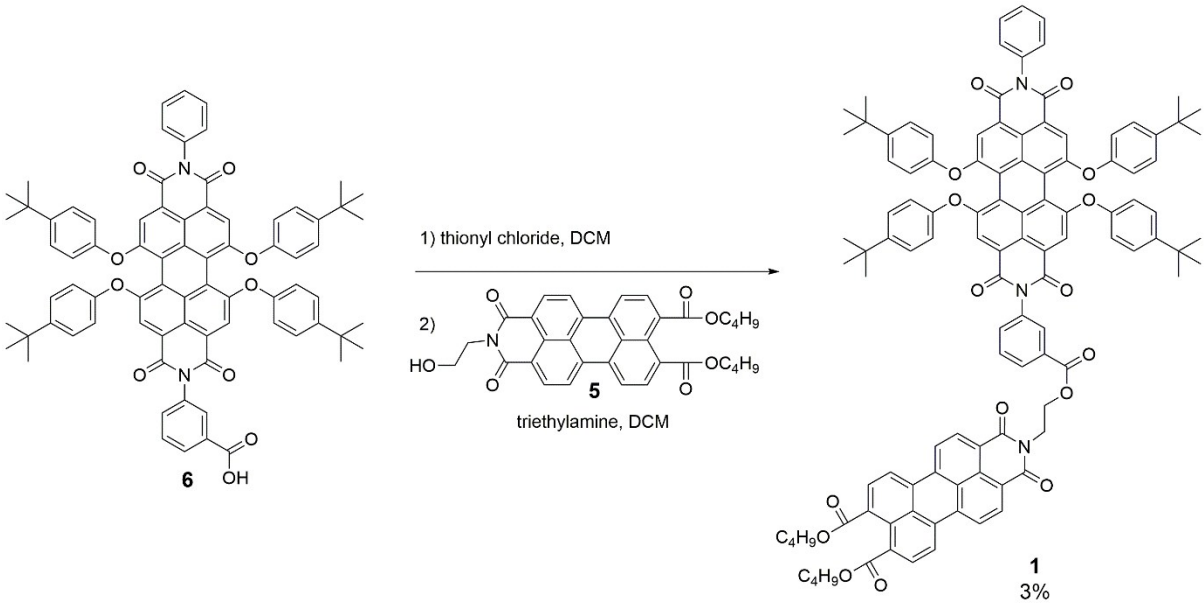
James E. A. Webb,[a] Kai Chen,[b] Shyamal K. K. Prasad,[b] Jonathan P. Wojciechowski,[a] Alexander Falber,[a] Pall Thordarson,[a] and Justin M. Hodgkiss[b]**

Synthesis

Materials:

All NMR spectra were obtained using either a BrukerAvance III 300 (300 MHz, ^{1}H; 75 MHz, ^{13}C) or BrukerAvance III 600 spectrometer (600 MHz, ^{1}H; 150 MHz, ^{13}C). Multiplicities are reported as singlet (s), doublet (d), triplet (t) and multiplet (m). Unless otherwise noted, all coupling constants (J) refer to proton-proton coupling and all ^{13}C NMR resonances are singlets. NMR spectra were processed using the Bruker TOPSPIN 3.1 software. For ^{1}H NMR, residual chloroform (δ 7.26 ppm) was used as the internal reference with coupling constants (J) quoted to the nearest 0.1 Hz. For ^{13}C NMR the central line of the deuterochloroform signal (δ 77.1 ppm) was used as an internal reference. IR spectra were recorded on an Agilent Technologies Cary 630 ATR(ZnSe)-FTIR spectrometer, signals are assigned as strong (s), medium (m), weak (w), broad (br) and shoulder (sh). UV-Vis spectra were recorded using an Agilent Technologies Cary 60 UV-Vis spectrophotometer using a quartz UV-Vis cuvette with 1 cm path length and fluorescence recorded using a Cary Eclipse fluorescence spectrophotometer using a quartz 1 cm path length fluorescence cuvette. Low resolution mass spectra were recorded on a Bruker UltrafleXtreme MALDI-TOF/TOF using *trans*-2-[3-(4-*t*-butylphenyl)-2-propyenylidene]malonitrile as the ionising matrix. High-resolution mass spectra were recorded using a Thermo Scientific LTQ Orbitrap XL. Analytical thin layer chromatography was performed using Merck silica gel plates, pre-coated with silica gel 60 F243 (0.2 mm). Flash chromatography employed 230–400 mesh silica gel. Reactions were conducted under a positive pressure of nitrogen. Commercially available chemicals were purified by standard procedures or used as purchased.

Array **1** (**D**-**A1**)



To a stirred solution of monobenzimide monoimido-m-be*n*zoic acid tetra(*p*-*t*Bu-phenoxy) perylene **6** (50 mg, 40 µmol) in dichloromethane (2 mL) was added thionyl chloride (300 µL, 4 mmol) and the reaction refluxed until TLC indicated complete formation of the acid chloride. The dichloromethane and residual thionyl chloride was removed by distillation and the remaining residue subjected to

high vacuum over 2 hours. Ethanolimide dibutylester perylene **5** (70 mg, 120 µmol) was then taken up in dichloromethane (1 mL) and added to the residue. To this was then added diisopropylethylamine (10 µL, 60 µmol) and stirred under nitrogen until TLC indicated completion. Solvent was then removed from the reaction mixture and residue subjected to high vacuum, then purified by preparative TLC yielding the perylene dimer as a purple film (2.4 mg, 1.4 µmol, 3% yield).

^{1}H NMR (300 MHz, $CDCl_3$, ppm (integration, splitting, J(Hz), [assignment])): 8.60 (2H, d, 8.0, appending perylene-H_{ar}), 8.40 (2H, d, 8.0, appending perylene-H_{ar}), 8.39 (2H, d, 8.1, appending perylene-H_{ar}), 8.26 (2H, s, dimer core-H_{ar}), 8.24 (2H, s, dimer core-H_{ar}), 8.07 (1H, m, benzimidocarboxylate-H_{ar}), 8.04 (2H, d, 8.1, appending perylene-H_{ar}), 7.91 (1H, m, benzimidocarboxylate-H_{ar}), 7.55-7.40 (7H, benzimide-H_{ar} and benzimidocarboxylate-H_{ar}), 7.22 (4H, d, 8.8, *p*-*t*Bu-phenoxy-H_{ar}), 7.21 (4H, d, 8.9, *p*-*t*Bu-phenoxy-H_{ar}), 6.85 (4H, d, 8.8, *p*-*t*Bu-phenoxy-H_{ar}), 6.83 (4H, d, 8.9, *p*-*t*Bu-phenoxy-H_{ar}), 4.69-4.64 (4H, O-[CH_2CH_2]-N), 4.33 (4H, t, 6.9, O-[CH_2]-CH_2CH_2), 1.77 (4H, m, OCH_2-[CH_2]-CH_2CH_2), 1.48 (4H, m, CH_2-[CH_2]-CH_3), 1.25 (18H, s, [*p*-*t*Bu]-phenoxy), 1.23 (18H, s, [*p*-*t*Bu]-phenoxy), 0.98 (6H, t, CH_2-[CH_3]).

ATR-FTIR: 2959 (w), 2929 (w), 2869 (w), 1703 (s), 1669 (m), 1584 (m), 1505 (m), 1457 (w), 1405 (m), 1379 (w), 1356 (w), 1341 (m), 1315 (m), 1293 (s), 1260 (s), 1219 (w), 1200 (w), 1174 (m), 1084 (s), 1017 (s), 969 (w), 939 (w), 924 (w), 906 (w), 883 (w), 835 (w), 801 (s), 749 (w), 704 (w), 689 (w), 667 (w).

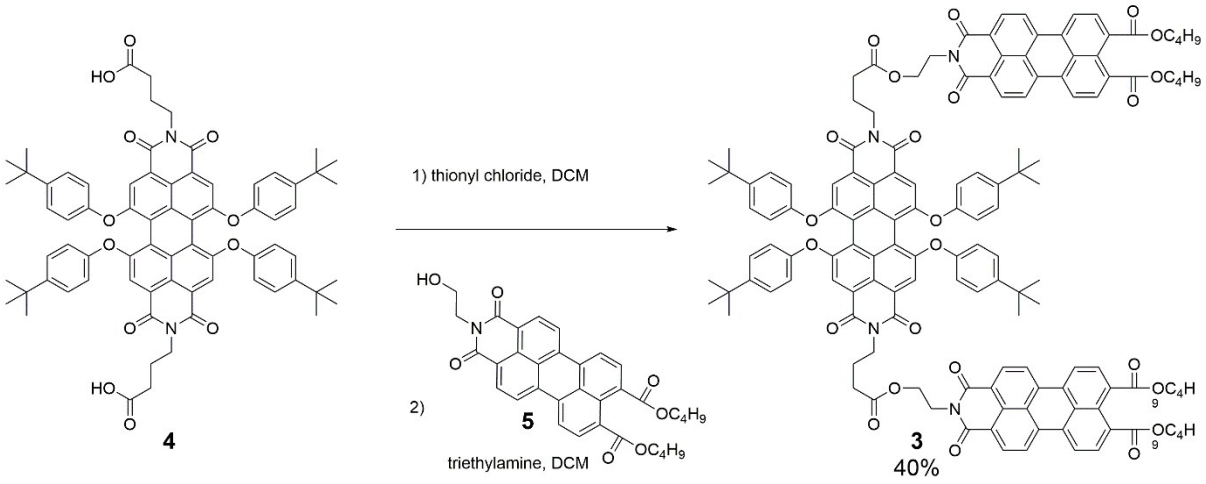
UV-Vis ($CHCl_3$, λ (log(ε)): 447 (4.52), 477 (4.69), 508 (4.77), 544 (4.46), 587 (4.67).

Fluorescence ($CHCl_3$, λmax): 618

MALDI (DCTB matrix): [$C_{111}H_{95}N_3O_{16}^+$] = [M^+], calc. 1725.67, found 1725.49.

HR-ESI: [$C_{111}H_{95}N_3O_{16}^+$] = [M^+], calc. 1726.6740, found 1726.6764

Array **2** (**D**-**A1**-**D**)



Tetraphenoxy diimidobutyric acid **4** (60 mg, 52 µmol) was refluxed for 15 min with thionyl chloride (2 mL, 27.6 mmol) in dichloromethane (3 mL). The reaction progress was tested by quenching small aliquots with absolute ethanol and subjected to TLC. Once complete by TLC, the solvent and residual thionyl chloride was removed by distillation and residue placed under high vacuum for 30 minutes. The acid chloride was then taken up in dichloromethane (1ml) and added dropwise into a stirred solution of monoethanolimide perylene **5** (120 mg, 212 µmol) with triethylamine (30 µL, 215 µmol)

in dichloromethane (4 mL). Stirred under nitrogen at room temperature, the reaction was worked up when TLC indicated completion. The reaction mixture was poured onto aqueous hydrochloric acid (0.5 M, 50 mL), extracted with chloroform (2 x 100mL) and washed with aqueous sodium hydrogen carbonate (sat., 50 mL), water (50mL), dried over sodium sulfate, filtered and solvent removed under reduced pressure. The residue was then purified by column chromatography with a neat chloroform to 2% methanol gradient, yielding the array **3** as a red-purple film (46 mg, 20 µmol, 40%).

^{1}H NMR (300 MHz, CDCl3, ppm (integration, splitting, J(Hz), [assignment])): 8.47 (4H, d, 8.1, appending perylene-H_{ar}), 8.29-8.24 (8H, appending perylene-H_{ar}), 8.09 (4H, s, trimer core perylene-H_{ar}), 7.94 (4H, d, 7.9, appending perylene-H_{ar}), 7.18 (8H, d, 8.9, trimer core perylene phenoxy-H_{ar}), 6.75 (8H, d, 8.9, trimer core perylene phenoxy-H_{ar}), 4.43 (8H, all N-[CH_2]-), 4.28 (8H, t, 6.9, COO-[CH_2]-CH_2), 4.06 (4H, t, 7.1, NCH_2-[CH_2]-O), 2.39 (4H, t, 7.2, OOC-[CH_2]-CH_2C), 1.97 (4H, quin, 7.1, NCH_2-[CH_2]-CH_2), 1.76 (8H, quin, 7.1, OCH_2-[CH_2]-CH_2CH_3), 1.47 (8H, sext, 7.4, OCH_2CH_2-[CH_2]-CH_3), 1.26 (36H, s, [*p*-*t*Bu]-phenoxy).

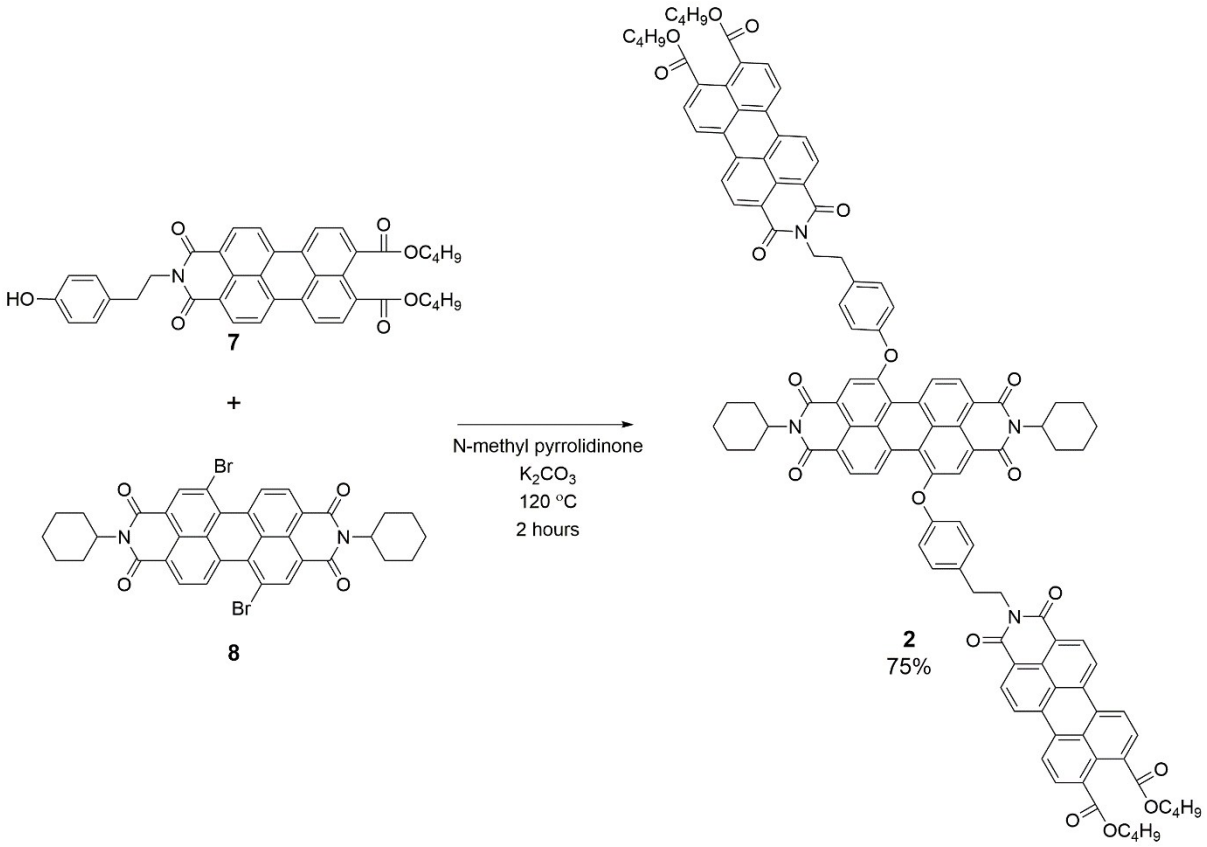
UV-Vis ($CHCl_3$, λ (log(ε)): 447 (4.66), 475 (4.86), 506 (4.91), 584 (4.53).

Fluorescence ($CHCl_3$, λmax): 611

MALDI (DCTB matrix): [$C_{140}H_{128}N4O_{24}^+$] = [M^+], calc. 2248.892, found 2248.444.

HR-ESI: [$C_{140}H_{128}N_4O_{24}^{2+}$] = [$M^{2+}$], calc. 1147.9368, found 1147.9374.

Array **3** (**D**-**A2**-**D**)



Tyrimide perylene **7** (75 mg, 117 µmol), was combined with 1,7-dibromo perylene dicyclohexylimide **8** (22 mg, 31 µmol) in N-methyl pyrrolidinone (1 mL) with potassium carbonate (17 mg, 123 µmol)

and placed in an oil bath at 120 °C for 2 hours. The reaction was then precipitated by addition to aqueous hydrochloric acid (2M, 3 mL). Filtration isolated the crude material which was then washed with hot ethanol (200 mL) and recrystallised from chloroform by the addition of methanol. Filtration isolated the trimer **2** as a dark red solid (43 mg, 24 µmol, 75%).

^{1}H NMR (300 MHz, $CDCl_3$, ppm (integration, splitting, J(Hz), [assignment])): 9.54 (2H, d, 8.7, core perylene-H_{ar}), 8.65 (4H, d, 8.0, peripheral perylene-H_{ar}), 8.55 (2H, d, 8.7, core perylene-H_{ar}), 8.49 (4H, d, 8.0, peripheral perylene-H_{ar}), 8.46 (4H, d, 7.8, peripheral perylene-H_{ar}), 8.27 (2H, s, core perylene-H_{ar}), 8.11 (4H, d, 7.8, peripheral perylene-H_{ar}), 7.47 (4H, d, 8.5, tyrimide-H_{ar}), 7.12 (4H, d, 8.5, tyrimide-H_{ar}), 5.00 (2H, m, N-[CH]-), 4.47 (4H, t, 7.8, N-[CH_2]-CH_2), 2.52 (4H, m, cyclohexyl CH_2-[CH_2]-CH_2), 1.90-1.35 (16H, m, cyclohexyl), 1.78 (8H, m, OCH_2-[CH_2]-CH_2), 1.49 (8H, m, -[CH_2]-CH_3), 1.01 (12H, t, 7.4, CH_2-[CH_3]).

ATR-FTIR: 2955 (w), 2903 (w), 2869 (w), 1695 (s), 1673 (m), 1655 (s), 1587 (s), 1561 (w), 1543 (w), 1524 (w), 1502 (m), 1476 (w), 1457 (w), 1405 (m), 1375 (w), 1353 (m), 1330 (m), 1308 (m), 1289 (m), 1256 (s), 1230 (s), 1211 (s), 1192 (s), 1166 (s), 1099 (s), 1077 (s), 1036 (m), 1010 (s), 965 (m), 935 (m), 906 (m), 872 (m), 842 (m), 824 (m), 805 (s), 745 (s), 697 (m), 674 (m), 656 (m).

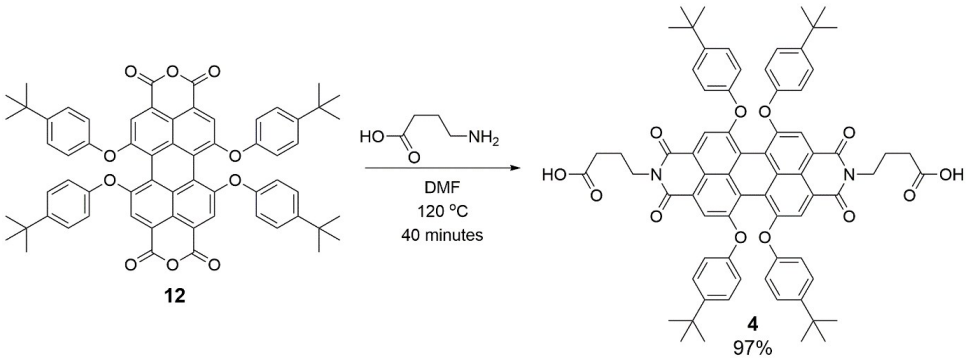
UV-Vis ($CHCl_3$, λ (log(ε)): 450 (4.61), 479 (4.93), 510 (5.09), 544 (4.70).

Fluorescence ($CHCl_3$, λmax): 572

MALDI (DCTB matrix): [$C_{116}H_{96}N_4O_{18}^+$] = [M^+], calc. 1832.672, found 1832.278.

HR-ESI [$C_{116}H_{96}N_4O_{18}$ + Na^+] = [M + Na^+], calc. 1856.6645, found 1856.6610.

1,6,7,12-tetra(*p*-*t*Butylphenoxy)-3,4,9,10-di(imidobutyric acid) perylene (**4**)



12 **4** 97%

Into a vial was combined 1,6,7,12-tetra(*p*-*t*Bu-phenoxy)-3,4,9,10-di(anhydride) perylene **12** (200 mg, 200 µmol) and 4-aminobutyric acid (200 mg, 1.9 mmol) in dimethylformamide (4 mL). The vial was sealed then placed in an oil bath at 120 °C for 40 minutes. The reaction was worked up by addition to hydrochloric acid (2M, aqueous, 20 mL), the precipitate, isolated by centrifuge, was then washed with water (25 mL) and twice with 20% water in methanol (25 mL). The precipitate was then filtered, air dried, taken up in dichloromethane, subjected to a silica plug firstly washed with dichloromethane, then eluted with 5% methanol in dichloromethane which, upon evaporation, yielded the desired 1,6,7,12-tetra(*p*-*t*Bu-phenoxy)-3,4,9,10-di(imidobutyric acid) perylene as a purple film (224 mg, 1.9 µmol, 97%)

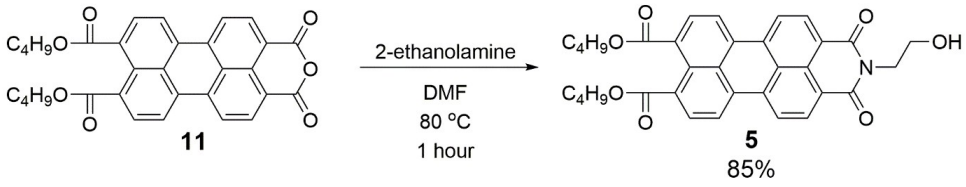
^{1}H NMR (300 MHz, $CDCl_3$, ppm (integration, splitting, J(Hz), [assignment])): 8.22 (4H, s, perylene-H_{ar}), 7.23 (8H, d, 9.0, *p*-*t*Bu-phenoxy-H_{ar}), 6.82 (8H, d, 9.0, *p*-*t*Bu-phenoxy-H_{ar}), 4.19 (4H, t, 6.7, N-[CH_2]-CH_2), 2.43 (4H, t, 7.3, CH_2-[CH_2]-COOH), 2.04 (4H, q, CH_2-[CH_2]-CH_2), 1.29 (36H, s, [*p*-*t*Bu]-phenoxy).

^{13}C NMR (150 MHz, $CDCl_3$, ppm): 175.2, 163.5, 155.9, 152.8, 147.3, 132.8, 126.6, 122.2, 120.6, 119.9, 119.4, 119.3, 39.7, 34.3, 31.4, 31.3, 23.3.

ATR-FTIR: 3257 (w), 2959 (w), 2903 (w), 2873 (w), 2866 (w), 1744 (w), 1688 (s), 1647 (m), 1580 (s), 1502 (s), 1457 (w), 1438 (m), 1409 (m), 1394 (w), 1356 (m), 1338 (m), 1304 (s), 1289 (s), 1245 (m), 1215 (s), 1181 (s), 1166 (s), 1148 (s), 1107 (m), 1096 (m), 1073 (w), 1032 (w), 1014 (m), 999 (w), 976 (w), 935 (w), 909 (w), 883 (m), 861 (m), 831 (m), 820 (m), 801 (m), 790 (m), 760 (w), 745 (w), 730 (w), 701 (w).

MALDI (DCTB matrix) [$C_{72}H_{70}N_2O_{12}^{+}$] = [$M^{+}$] calc. 1154.493, found 1154.258.

3,4-ethanolimide-9,10-di(butyl carboxylate) perylene (**5**)



Into dimethylformamide (4 mL), was combined perylene monoanhydride dibutyl ester **11** (400 mg, 770 µmol), and ethanolamine (250 µL, 4 mmol). This was then placed in an oil bath and heated to 80 °C under nitrogen for 1 hour. The reaction was then removed from the heat, precipitation induced by addition of water and the precipitate isolated and washed with water by centrifuge, transferred, dried and subjected to a silica plug, washing with chloroform and then eluting with 2% methanol in chloroform. The solvent removed under educed pressure, taken up in a small amount of dichloromethane, and precipitated by addition to hexane with filtration isolating the monoethanolimide dibutylester perylene **5** as a red solid (371 mg, 660 µmol, 85%)

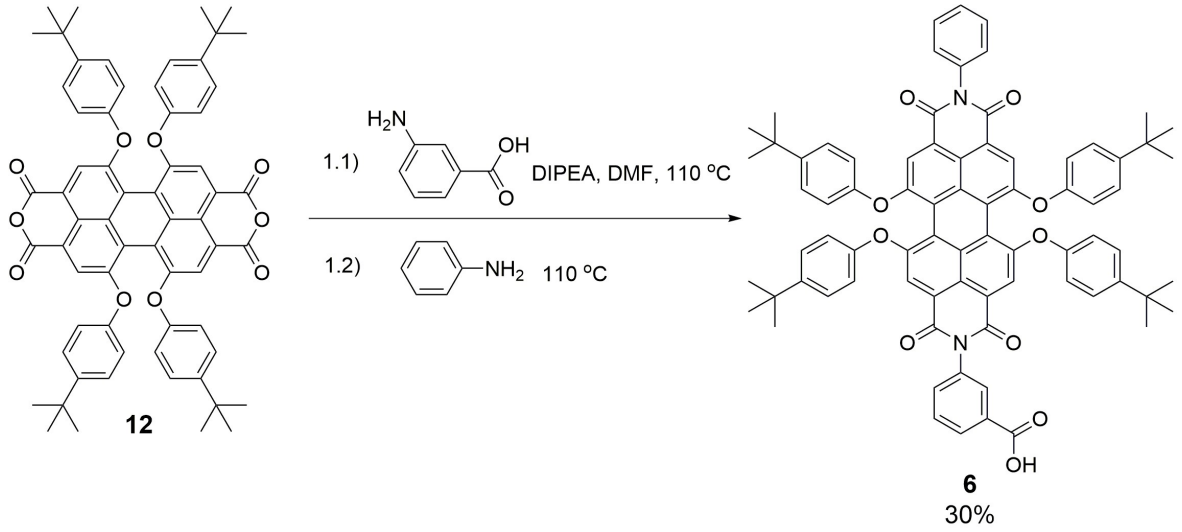
^{1}H NMR (300 MHz, $CDCl_3$, ppm (integration, splitting, J(Hz), [assignment])): 8.13 (2H, d, 7.7, perylene-H_{ar}), 7.87-7.79 (4H, perylene-H_{ar}), 8.09 (2H, d, 7.9, perylene-H_{ar}), 4.42-4.32 (4H, N-[CH_2]-CH_2 and O-[CH_2]-CH_2), 4.06 (2H, m, 5.2, NCH_2-[CH_2]-OH), 2.29 (1H, CH_2-[OH]), 1.84 (4H, quin, 7.1, CH_2-[CH_2]-CH_2), 1.54 (4H, sext, 7.3, CH_2-[CH_2]-CH_3), 1.04 (6H, t, 1.0, CH_2-[CH_3])

^{13}C NMR (75 MHz, $CDCl_3$, ppm): 168.1, 164.0, 134.8, 131.8, 131.2, 131.0, 130.0, 128.7, 128.4, 128.3, 125.0, 122.4, 121.3, 121.2, 65.6, 61.5, 42.8, 30.7, 19.3, 13.8

ATR-FTIR: 3566 (w, br), 2959 (w), 2933 (w), 2869 (w), 1718 (s), 1699 (s), 1669 (w), 1647 (s), 1636 (s), 1591 (s), 1576 (w), 1558 (w), 1539 (m), 1520 (w), 1505 (m), 1472 (w), 1457 (m), 1420 (w), 1375 (w), 1360 (w), 1308 (m), 1293 (s), 1260 (s), 1174 (s), 1081 (m), 805 (m), 745 (s).

MALDI (DCTB matrix) [$C_{34}H_{31}NO_7^{+}$] = [M^{+}], calc. 565.21, found 565.25.

1,6,7,12-tetra(*p*-*t*Butylphenoxy)-3,4-(*m*-carboxylic acid benzimide)-9,10-benzimide perylene (**6**)



1,6,7,12-tetra(*p*-*t*Bu-phenoxy)-3,4,9,10-di(anhydride) perylene **12** (250 mg, 250 µmol) was combined with *m*-amino benzoic acid (30 mg, 220 µmol) in dimethylformamide (5 mL) with diispropylethylamine (45 µL, 260 µmol) in a sealed vial and placed in an oil bath at 110 °C for 20 minutes. The vial was then removed from the heat, allowed to cool to room temperature, then to this was added aniline (75 µL, 800 µmol), the vial sealed and placed back into the oil bath at 110 °C for 30 minutes. The reaction was then removed from the oil, allowed to cool and worked up by addition of methanol (20 mL) with further precipitation induced by addition of hydrochloric acid (aq. 2M, 2 mL). The resultant mixture was then centrifuged, supernatant decanted, and the solid similarly centrifuge-washed with methanol twice. The resulting material was then dried and purified via column chromatography on silica using a chloroform/isopropanol gradient from 0-5%. After evaporation this yielded the 1,6,7,12-tetra(*p*-*t*Bu-phenoxy)-3,4-(*m*-carboxylic acid benzimide)-9,10-benzimide perylene **6** as a purple solid (72 mg, 61 µmol, 30% yield).

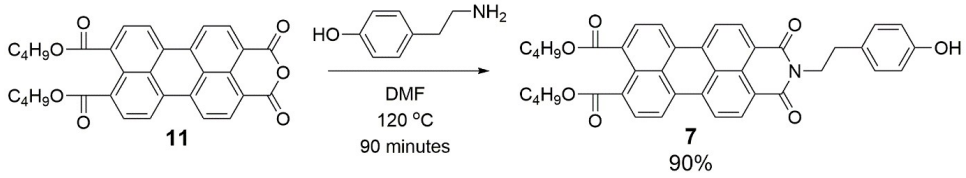
^{1}H NMR (300 MHz, $CDCl_3$, ppm (integration, splitting, J(Hz), [assignment])): 8.25 (2H, s), 8.24 (2H, s), 8.23 (1H, m), 8.17 (1H, m), 8.00 (1H, m), 7.61 (1H, t, 7.9), 7.55-7.40 (5H, m), 7.23 (8H, d, 8.7), 6.85 (8H, d, 8.7), 1.26 (36H, s).

^{13}C NMR (150 MHz, $CDCl_3$, ppm): 169.7, 163.6, 163.4, 156.2, 156.1, 152.8, 147.5, 135.5, 134.0, 133.2, 133.1, 130.7, 130.5, 129.4, 129.3, 128.7, 128.5, 126.9, 126.7, 122.6, 122.3, 121.0, 120.6, 120.3, 120.1, 119.8, 119.7, 119.4, 119.3, 34.4, 31.4.

ATR-FTIR: 3420 (m, br), 2959 (m), 2925 (m), 2854 (m), 1744 (w), 1733 (w), 1703 (s), 1669 (s), 1636 (m), 1584 (s), 1569 (s), 1543 (m), 1505 (s), 1457 (m), 1435 (m), 1405 (s), 1364 (m), 1341 (s), 1315 (s), 1289 (s), 1211 (m), 1174 (m), 1110 (w), 1081 (w), 1014 (w), 969 (w), 909 (w), 883 (w), 835 (w), 801 (w), 790 (w), 764 (w), 753 (w), 727 (w), 708 (w), 689 (w), 674 (w), 652 (w).

MALDI (DCTB matrix) [$C_{77}H_{66}N_2O_7^+$] = [M^+], calc. 1178.47, found 1178.31.

3,4-tyrimide-9,10-di(butyl carboxylate) perylene (**7**)



Tyramine (132 mg, 0.96 mmol) was combined with 3,4-anhydride-9,10-di(butyl carboxylate) perylene **11** (420 mg, 0.80 mmol) in a vial with dimethyl formamide (8 mL), sealed and placed in an oil bath at 120 °C for 90 minutes. This was then precipitated with methanol, filtered, precipitate washed with additional methanol, dissolved with dichloromethane and evaporated to dryness to yield the monotyrimide di(butylester) perylene **7** as a red solid (463 mg, 0.72 mmol, 90%).

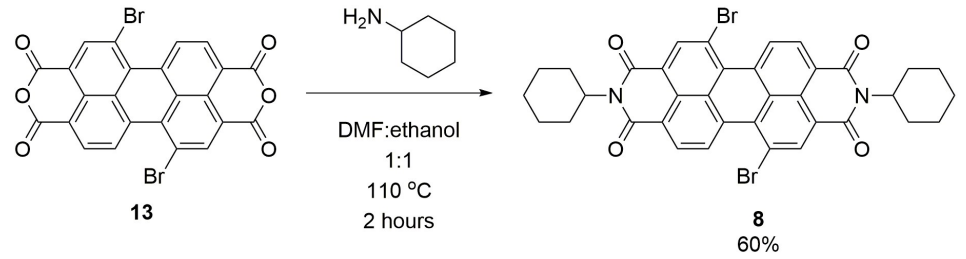
^{1}H NMR (300 MHz, $CDCl_3$, ppm (integration, splitting, J(Hz), [assignment])): 8.59 (2H, d, 8.1, perylene-H_{ar}), 8.43 (2H, d, 8.1, perylene-H_{ar}), 8.41 (2H, d, 8.0, perylene-H_{ar}), 8.09 (2H, d, 8.0, perylene-H_{ar}), 7.24 (2H, d, 8.5, tyrimide-H_{ar}), 6.79 (2H, d, 8.5, tyrimide-H_{ar}), 4.38 (2H, m, N-[CH_2]-CH_2), 4.36 (4H, t, 6.8, COO-[CH_2]-CH_2), 2.99 (2H, m, NCH_2-[CH_2]-C), 1.80 (4H, quin, 7.2, $COOCH_2$-[CH_2]-CH_2), 1.50 (4H, sext, 7.5, CH_2-[CH_2]-CH_3), 1.00 (6H, t, 7.4, CH_2-[CH_3]).

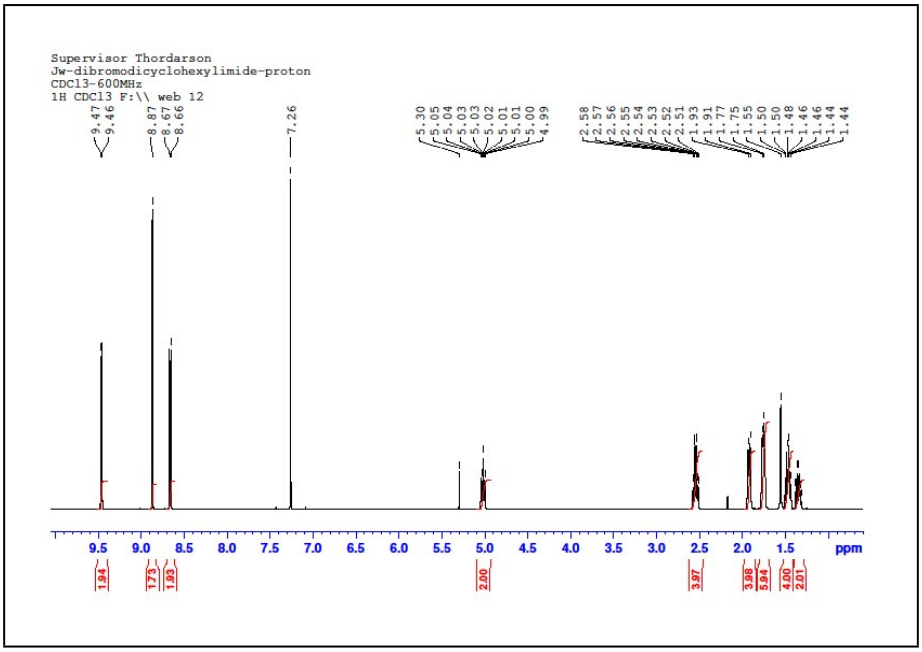
^{13}C NMR (150 MHz, $CDCl_3$, ppm): 168.3, 163.4, 154.4, 135.3, 131.8, 131.8, 131.3, 130.7, 130.2, 129.0, 128.9, 128.8, 125.7, 122.5, 121.8, 121.7, 115.4, 65.6, 41.9, 33.3, 30.6, 19.3, 13.8.

ATR-FTIR: 3443 (w), 2959 (w), 2936 (w), 2869 (w), 1692 (s), 1651 (s), 1610 (w), 1591 (s), 1509 (m), 1472 (w), 1457 (w), 1420 (w), 1375 (w), 1364 (w), 1349 (m), 1327 (w), 1293 (s), 1263 (s), 1233 (m), 1207 (m), 1192 (m), 1174 (m), 1163 (m), 1118 (m), 1103 (m), 1077 (m), 1010 (w), 846 (w), 824 (m), 805 (m), 745 (s).

MALDI (DCTB matrix) [$C_{40}H_{35}NO_7^+$] = [M^+] calc. 641.241, found 641.082.

1,7-dibromo-3,4,9,10-di(cyclohexylimide) perylene (**8**)





1,7-Dibromo-3,4,9,10-di(anhydride) perylene **13** (1.0 g, 1.8 mmol) was combined in a 1:1 mixture of ethanol and DMF (20 mL), to this was then added cyclohexylamine (830 µl, 9.7 mmol) and the reaction placed in an oil bath at 110 °C for 2 hours. To this was then added hydrochloric acid (2M, aq., 50 mL) and the precipitate isolated by filtration, washed with methanol and air dried to yield a red/bronze powder (770 mg, 1.1 mmol, 60%) which matched literature values.[1]

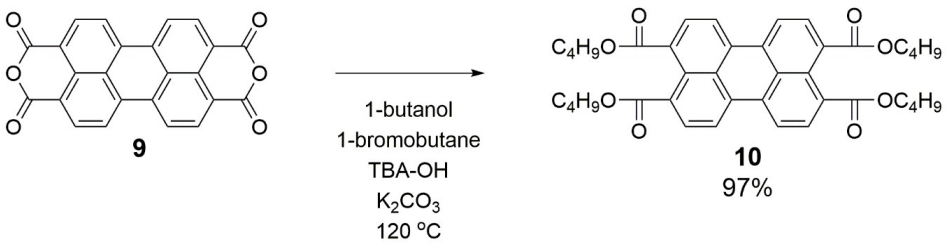
^{1}H NMR (600 MHz, $CDCl_3$, ppm (integration, splitting, J(Hz), [assignment])): 9.46 (2H, d, 8.1, perylene-H_{ar}), 8.87 (2H, s, perylene-H_{ar}), 8.66 (2H, d, 8.1, perylene-H_{ar}), 5.02 (2H, m, 12.1, 3.7, N-[CH]-$(CH_2)_2$), 2.55 (4H, m, cyclohexyl), 1.92 (4H, m, cyclohexyl), 1.76 (6H, m, cyclohexyl), 1.47 (4H, m, cyclohexyl), 1.34 (2H, m, cyclohexyl).

^{13}C NMR (150 MHz, $CDCl_3$, ppm): 169.7, 163.6, 163.4, 156.2, 156.1, 152.8, 147.5, 135.5, 134.0, 133.2, 133.1, 130.7, 130.5, 129.4, 129.3, 128.7, 128.5, 126.9, 126.7, 122.6, 122.3, 121.0, 120.6, 120.3, 120.1, 119.8, 119.7, 119.4, 119.3, 34.4, 31.4.

ATR-FTIR: 3420 (m, br), 2959 (m), 2925 (m), 2854 (m), 1744 (w), 1733 (w), 1703 (s), 1669 (s), 1636 (m), 1584 (s), 1569 (s), 1543 (m), 1505 (s), 1457 (m), 1435 (m), 1405 (s), 1364 (m), 1341 (s), 1315 (s), 1289 (s), 1211 (m), 1174 (m), 1110 (w), 1081 (w), 1014 (w), 969 (w), 909 (w), 883 (w), 835 (w), 801 (w), 790 (w), 764 (w), 753 (w), 727 (w), 708 (w), 689 (w), 674 (w), 652 (w).

MALDI (DCTB matrix) $[C_{36}H_{28}Br_2N_2O_4^+]$ = $[M^+]$, calc. 712.04, found 712.10.

3,4,9,10-tetra(butyl carboxylate) perylene (**10**)



Perylene-3,4,9,10-tetracarboxylic dianhydride **9** (10 g, 25.5 mmol) was suspended in butanol (44 mL) and tetrabutylammonium hydroxide (50-60%, 31 mL, 65.7 mmol) was added and stirred. Once all the solid had gone into solution, 1-bromobutane (40 mL, 370 mmol) and potassium carbonate (10 g, 70 mmol) and the reaction placed in an oil bath at 120 °C. After 3 hours the reaction was poured onto 200 mL chloroform, then extracted with water (3 x 100 mL) then sat. potassium hydrogen carbonate (2x 100 mL), then water once more (100 mL). The solvent was removed and the oily residue taken up in hexane with a small amount of ethylacetate and triturated. The yellow precipitate filtered off and washed with hexane, yielding the product as a yellow solid (16.16 g, 24.7 mmol, 97%) which matched lit. values.[2]

^{1}H NMR (300 MHz, $CDCl_3$, ppm (integration, splitting, J(Hz), [assignment])): 8.26 (4H, d, 8.0, perylene-H_{ar}), 8.02 (4H, d, 8.0, perylene-H_{ar}), 4.35 (8H, t, 6.8, COO-[CH_2]-CH_2), 1.78 (8H, quin, 7.2, $COOCH_2$-[CH_2]-CH_2), 1.48 (8H, sext, 7.5, $COOCH_2CH_2$-[CH_2]-CH_3), 0.99 (12H, t, 7.4, $COOCH_2CH_2CH_2$-[CH_3]).

^{13}C NMR (75 MHz, $CDCl_3$, ppm): 168.5, 132.9, 130.4, 130.4, 128.9, 128.7, 121.3, 65.3, 30.7, 19.3, 13.8.

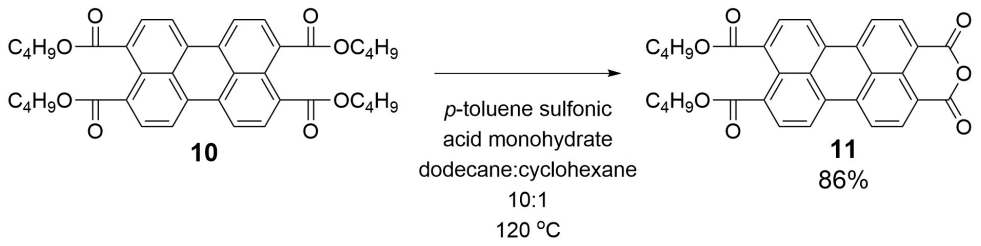
ATR-FTIR: 2955 (m), 2928 (m), 2899 (sh), 2869 (m), 1717 (s), 1702 (s), 1583 (m), 1509 (w), 1471 (m), 1408 (w), 1389 (w), 1375 (w), 1304 (m), 1263 (s), 1065 (m), 1032 (m), 1002 (m), 980 (m), 961 (s), 939 (s), 886 (m), 842 (s), 804 (s), 771 (m), 745 (s).

UV-Vis ($CHCl_3$, λ (log(ε)): 418 (4.21), 442 (4.52), 471 (4.60)

Fluorescence ($CHCl_3$, λmax): 487

MALDI (DCTB matrix) [$C_{40}H_{44}O_8^+$] = [M^+], calc. 652.30, found 652.18.

3,4-anhydride-9,10-di(butyl carboxylate) perylene (**11**)



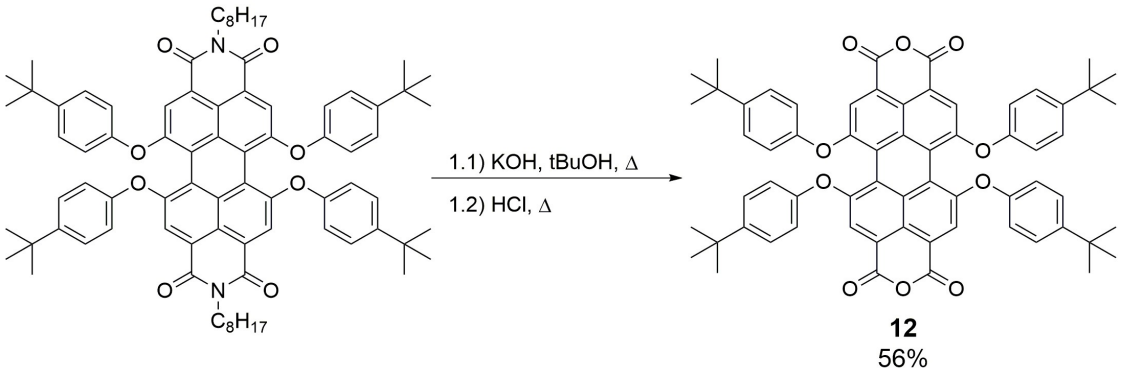
Perylene tetrabutyl-3,4,9,10-tetracarboxylate **10** (2.0 g, 3 mmol) was combined with *p*-toluene sulfonic acid monohydrate (580 mg, 3 mmol) in dodecane (5 mL) and cyclohexane (0.5 mL) in a sealed vial, then placed in an oil bath at 120 °C. The solid material went into solution, then precipitated out after approximately 20 minutes. The solid was then isolated by filtration, washed with boiling hexane then with acetonitrile to yield the dibutyl-3,4-dicarboxylate-9,10-carboxylic monoanhydride **11** as a bright red powdery solid (1.36 g, 2.6 mmol, 86%) which matched lit. values.[3]

^{1}H NMR (300 MHz, $CDCl_3$, ppm (integration, splitting, J(Hz), [assignment])): 8.67 (2H, d, 8.1, perylene-H_{ar}), 8.54 (2H, d, 7.3, perylene-H_{ar}), 8.52 (2H, d, 7.3, perylene-H_{ar}), 8.15 (2H, d, 8.1, perylene-H_{ar}), 4.36 (4H, t, 6.8, COO-[CH_2]-CH_2), 1.80 (4H, m, OCH_2-[CH_2]-CH_2), 1.51 (4H, m, CH_2-[CH_2]-CH_3), 1.00 (6H, t, 7.4, CH_2-[CH_3]).

ATR-FTIR: 2951 (m), 2932 (m), 2869 (m), 1762 (s), 1721 (s), 1702 (s), 1587 (s), 1509 (m), 1457 (m), 1412 (m), 1281 (s), 1252 (s), 1170 (s), 1147 (s), 1121 s), 1103 (sh), 1082 (m), 1009 (s), 961 (m), 857 (m), 838 (m), 804 (s), 734 (s).

MALDI (DCTB matrix): $[C_{32}H_{26}O_7^+] = [M^+]$, calc. 522.17, found 522.13.

1,6,7,12-tetra(*p*-*t*Butylphenoxy)-3,4,9,10-di(anhydride) perylene (**12**)



12
56%

Tetra(p-tBu-phenoxy) di(octylimide) perylene (3.34 g, 3 mmol) was combined with ground potassium hydroxide (1.26 g, 32 mmol) in tert-butyl alcohol (90 mL). This was then refluxed under nitrogen for 4 hours, then the solvent evaporated, reducing the reaction mixture to a thick yellow oil, to which was added hydrochloric acid (aq., 2M, 300 mL), then the mixture heated to almost boiling, allowed to cool and precipitate filtered off. Washing the precipitate with water (400 mL) and drying yielded the crude tetra(p-tBu-phenoxy) perylene dianhydride, which was then recrystallised from cyclohexane yielding **12** as a purple solid (1.75 g, 1.7 mmol, 56%) and matched lit. values.[4]

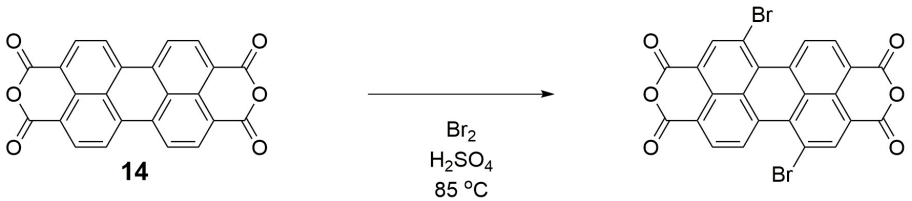
^{1}H NMR (300 MHz, CDCl3, ppm (assignment, J(Hz))): 8.21 (4H, s, perylene-H_{ar}), 7,27 (8H, d, 6.7, *p*-*t*Butylphenoxy-H_{ar}), 6.83 (8H, d, 6.7, *p*-*t*Butylphenoxy-H_{ar}), 1.30 (H36, s, [*p*-*t*Butyl]phenoxy).

^{13}C NMR (150 MHz, $CDCl_3$, ppm): 159.8, 156.4, 152.3, 148.1, 133.5, 126.9, 121.5, 121.4, 121.4, 119.4, 118.7, 34.5, 31.4.

ATR-FTIR: 2938 (m), 2899 (w), 2865 (w), 1770 (s), 1743 (s), 1581 (m), 1501 (s), 1406 (w), 1393 (m), 1360 (m), 1337 (s), 1285 (s), 1222 (s), 1173 (m), 1136 (w), 1110 (m), 1013 (m), 994 (s), 875 (w), 834 (w), 797 (w), 741 (w).

MALDI (DCTB matrix) $[C_{64}H_{56}O_{10}^+] = [M^+]$, calc. 984.39, found 984.18.

1,7-dibromo-3,4,9,10-di(anhydride) perylene (**13**)



14

13
regioisomers
95%

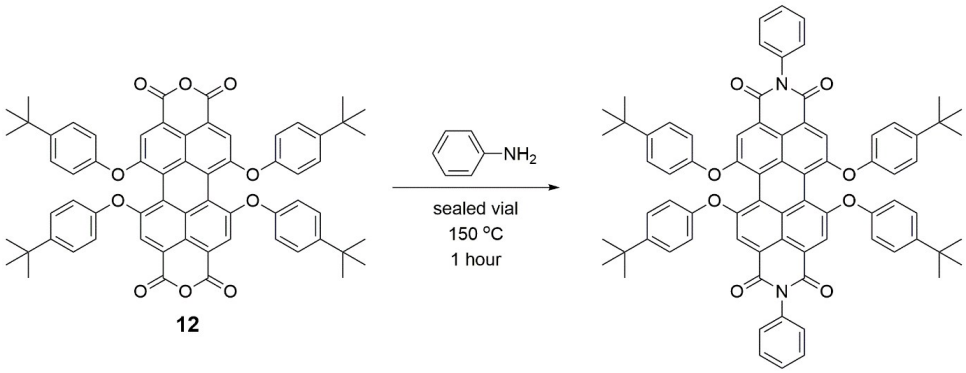
Perylene dianhydride **14** (10 g, 26 mmol) was stirred in concentrated sulfuric acid (160 mL) overnight at 55 °C under nitrogen. To this, over 1 hour, was then added bromine (3mL, 59 mmol) then iodine (240 mg, 1 mmol) and the reaction heated to 85 °C for 8 hours. The bromine was then removed by

passing a stream of nitrogen through one of the flask necks, pushing the bromine through a sodium sulfite bubbler over 4 hours. The reaction was then poured onto an ice-water slurry (40 mL), stirred for 30 minutes, then filtered. The precipitate was then washed with water, ethanol (E95) and acetone. The solid was then dried to yield **13** as a red powdery material (13.88 g, 25 mmol, 95%) and matched literature values.[5]

ATR-FTIR: 1766 (s), 1736 (m), 1722 (s), 1587 (s), 1558 (w), 1498 (w), 1375 (m), 1304 (m), 1282 (s), 1226 (m), 1211 (m), 1185 (w), 1163 (m), 1137 (s), 1047 (m), 1032 (s), 1021 (m), 954 (m), 920 (w), 909 (w), 857 (m), 824 (w), 801 (m), 753 (m), 730 (s), 689 (m), 667 (w).

MALDI (DCTB matrix) [$C_{24}H_6Br_2O_6^+$] = [M^+], calc. 547.853, found 547.788.

1,6,7,12-tetra(*p*-*t*Butylphenoxy)-3,4,9,10-di(benzimide) perylene (**15**)



12 **15**
74%

Into a vial was combined 1,6,7,12-tetra(*p*-*t*Bu-phenoxy)-3,4,9,10-di(anhydride) perylene **12** (200 mg, 200 µmol) with aniline (1 ml, 11 mmol). The vial was sealed and placed in an oil bath at 150 °C for one hour. The reaction was then precipitated by addition to hydrochloric acid (2M, aqueous, 10 mL) and centrifuged. The precipitate was then washed with hydrochloric acid (2M, aqueous, 20 mL), water (50 mL), methanol (20 mL) and air dried. The resultant solid was then subjected to a silica plug eluted with dichloromethane, which upon evaporation yielded the desired 1,6,7,12-tetra(*p*-*t*Bu-phenoxy)-3,4,9,10-di(benzimide) perylene **15** as a purple film (167 mg, 147 µmol, 74%).

1H NMR (300 MHz, CDCl3, ppm (integration, splitting, J(Hz), [assignment])): 8.24 (4H, s, perylene-H_{ar}), 7.54-7.38 (6H, m, benzimide m- and p-H_{ar}), 7.27-7.24 (2H, m, benzimide o-H_{ar}), 7.23 (8H, d, 9.0, phenoxy-H_{ar}), 6.85 (8H, d, 9.0, phenoxy-H_{ar}), 1.26 (36H, s, [*p*-*t*Bu]-phenoxy).

^{13}C NMR (150 MHz, $CDCl_3$, ppm): 169.7, 163.6, 163.4, 156.2, 156.1, 152.8, 152.8, 147.5, 135.5, 135.2, 134.0, 133.2, 133.1, 130.7, 130.5, 130.5, 129.4, 129.3, 128.7, 128.5, 126.9, 126.7, 126.7, 122.6, 122.3, 121.0, 120.6, 120.3, 120.1, 119.8, 119.7, 119.4, 119.3, 34.4, 31.4.

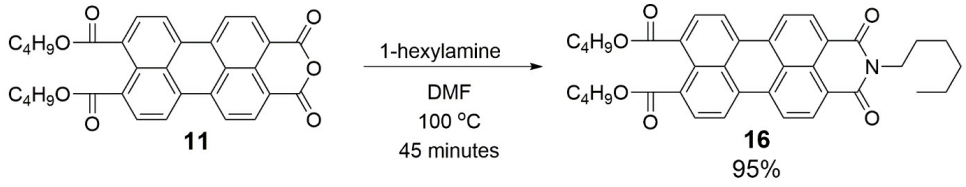
ATR-FTIR: 2955 (w), 2903 (w), 2866 (w), 1699 (s), 1666 (s), 1584 (s), 1498 (s), 1461 (w), 1405 (s), 1360 (w), 1338 (s), 1315 (s), 1282 (s), 1200 (s), 1170 (s), 1107 (m), 1081 (w), 1069 (w), 1014 (m), 987 (w), 958 (w), 939 (w), 906 (w), 879 (m), 831 (s), 820 (m), 801 (m), 779 (w), 753 (m), 738 (s), 704 (w), 689 (m), 671 (w), 663 (w), 652 (w).

UV-Vis ($CHCl_3$, λ (log(ε)): 456 (4.22), 546 (4.46), 586 (4.68).

Fluorescence ($CHCl_3$, λmax): 612

MALDI (DCTB matrix) [$C_{76}H_{66}N_2O_8^+$] = [M^+], calc. 1134.48, found 1134.40.

3,4-hexylimide-9,10-di(butyl carboxylate) perylene (**16**)



Into a vial was combined 3,4-anhydride-9,10-di(butyl carboxylate) perylene (200 mg, 380 µmol) with 1-aminohexane (0.5 mL, 3.8 mmol) and dimethylformamide (2mL). This was sealed and placed into an oil bath at 110 °C for 45 minutes. The reaction was then precipitated by addition to a 20% solution of hydrochloric acid (2M, aqueous) in methanol (10 mL). The precipitate was isolated by centrifuge, washed with 20% water in methanol (20 mL), air dried and subjected to a silica plug, eluted with dichloromethane, which after evaporation yielded the 3,4-hexylimide-9,10-di(butyl carboxylate) perylene as a red film (220 mg, 360 µmol, 95%).

^{1}H NMR (300 MHz, $CDCl_3$, ppm (integration, splitting, J(Hz), [assignment])): 8.30 (2H, d, 8.0, perylene-H_{ar}), 8.06 (2H, d, 8.0, perylene-H_{ar}), 8.01 (2H, d, 8.0, perylene-H_{ar}), 7.91 (2H, d, 8.0, perylene-H_{ar}), 4.37 (4H, t, 6.8, O-[CH_2]-CH_2), 4.14 (2H, t, 7.6, N-[CH_2]-CH_2), 1.83 (4H, m, OCH_2-[CH_2]-CH_2), 1.76 (2H, m, NCH_2-[CH_2]-CH_2), 1.53 (4H, m, OCH_2CH_2-[CH_2]-CH_3), 1.48-1.33 (6H, hexyl CH_2), 1.03 (6H, t, 7.3, butyl CH_3), 0.92 (3H, t, 7.0, hexyl CH_3).

^{13}C NMR (75 MHz, $CDCl_3$, ppm):168.2, 163.3, 134.9, 131.8, 131.7, 130.9, 130.1, 129.0, 128.7, 125.5, 122.3, 121.9, 121.5, 65.6, 40.6, 31.6, 30.7, 28.1, 26.9, 22.6, 19.3, 14.1, 13.8.

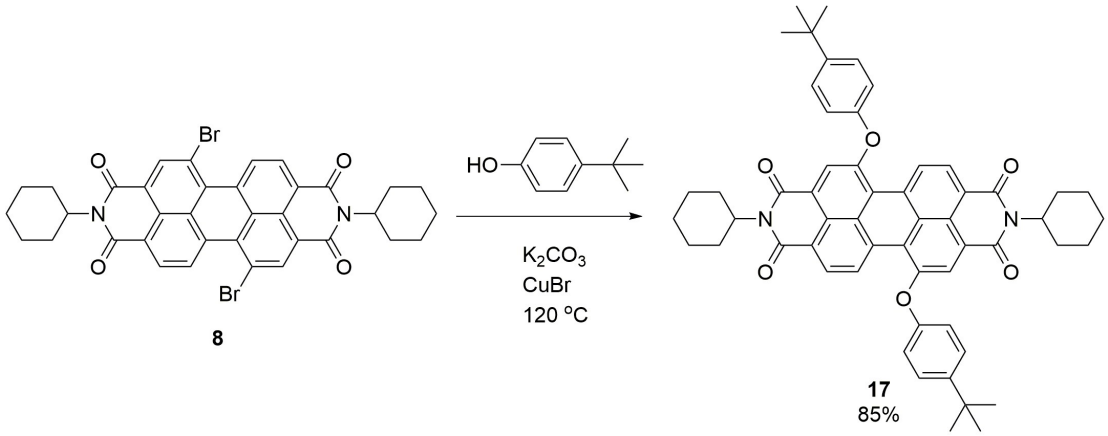
ATR-FTIR: 2951 (m), 2925 (m), 2866 (w), 2858 (w), 1706 (m), 1684 (m), 1643 (s), 1587 (s), 1509 (w), 1457 (w), 1427 (w), 1412 (w), 1348 (m), 1289 (m), 1248 (s), 1192 (m), 1158 (s), 1088 (m), 1069 (s), 1013 (m), 838 (m), 801 (s), 741 (s).

UV-Vis ($CHCl_3$, λ (log(ε)): 450 (4.20), 476 (4.53), 508 (4.64).

Fluorescence ($CHCl_3$, λmax): 524.

MALDI (DCTB matrix) [$C_{38}H_{39}NO_6^+$] = [M^+], calc. 605.28, found 605.23.

1,7-bis(*p*-*t*Butylphenoxy)-3,4,9,10-di(cyclohexylimide) perylene (**17**)



Into a vial was combined 1,7-dibromo-3,4,9,10-di(cyclohexylimide) perylene (10 mg, 14 µmol) with *p*-*t*Bu-phenol (480 mg, 3.2 mmol), potassium carbonate (10 mg, 72 µmol) and copper(I) bromide (5 mg, 35 µmol). This was then sealed and placed in an oil bath at 120 °C for 5 minutes. The reaction was then quenched by the addition of 20% hydrochloric acid (2M, aqueous) in ethanol (5 mL), filtered and washed with 20% water in ethanol (20 mL). The solid was air dried, taken up in dichloromethane and subjected to a silica plug in dichloromethane. This was then evaporated to yield the 1,7-di(*p*-*t*Bu-phenoxy)-3,4,9,10-di(cyclohexylimide) perylene as an orange-red film (10 mg, 12 µmol, 85%).

^{1}H NMR (300 MHz, $CDCl_3$, ppm (integration, splitting, J(Hz), [assignment])): 9.60 (2H, d, 8.4, perylene-H_{ar}), 8.57 (2H, d, 8.4, perylene-H_{ar}), 8.31 (2H, s, perylene-H_{ar}), 7.47 (4H, d, 9.0, *p*-*t*Bu-phenoxy-H_{ar}), 7.06 (4H, d, 9.0, *p*-*t*Bu-phenoxy-H_{ar}), 4.99 (2H, tt, 12.6, 2.3, N-[CH]-$(CH_2)_2$), 2.50 (4H, m, cyclohexyl), 1.88 (6H, m, cyclohexyl), 1.5-1.2 (6H, m, cyclohexyl), 1.37 (18H, s, [*p*-*t*Bu]-phenoxy).

^{13}C NMR (75 MHz, $CDCl_3$, ppm): 163.8, 163.5, 155.5, 152.6, 148.1, 133.4, 130.1, 129.3, 128.8, 127.4, 125.1, 124.3, 123.7, 123.6, 122.7, 119.2, 54.0, 34.5, 31.5, 29.1, 26.5, 25.4.

ATR-FTIR: 2955 (w), 2929 (w), 2910 (w), 2847 (w), 1695 (m), 1651 (s), 1595 (s), 1569 (w), 1543 (w), 1502 (m), 1476 (w), 1453 (w), 1405 (m), 1390 (m), 1360 (w), 1327 (s), 1312 (s), 1256 (s), 1245 (s), 1219 (s), 1192 (s), 1170 (s), 1133 (m), 1110 (m), 1062 (w), 1032 (m), 1010 (m), 984 (m), 969 (w), 928 (m), 913 (m), 898 (m), 876 (w), 853 (m), 831 (s), 809 (s), 775 (w), 760 (m), 745 (m), 727 (m), 708 (m), 697 (w), 678 (w), 667 (w).

UV-Vis ($CHCl_3$, λ (log(ε)): 402 (4.05), 507 (4.62), 543 (4.79).

Fluorescence ($CHCl_3$, λmax): 572

MALDI (DCTB matrix) [$C_{56}H_{54}N_2O_6^+$] = [M_+], calc. 850.40, found 850.37.

UFF Modelling structures

Universal Force Field molecular modelling of arrays **1**, **2** and **3**, acceptors **15** and **17** and donor **16** were performed using ArgusLab 4.0.1. Geometry optimisation was performed until geometry optimisation converged. Phenoxy groups and protons have been removed for clarity.

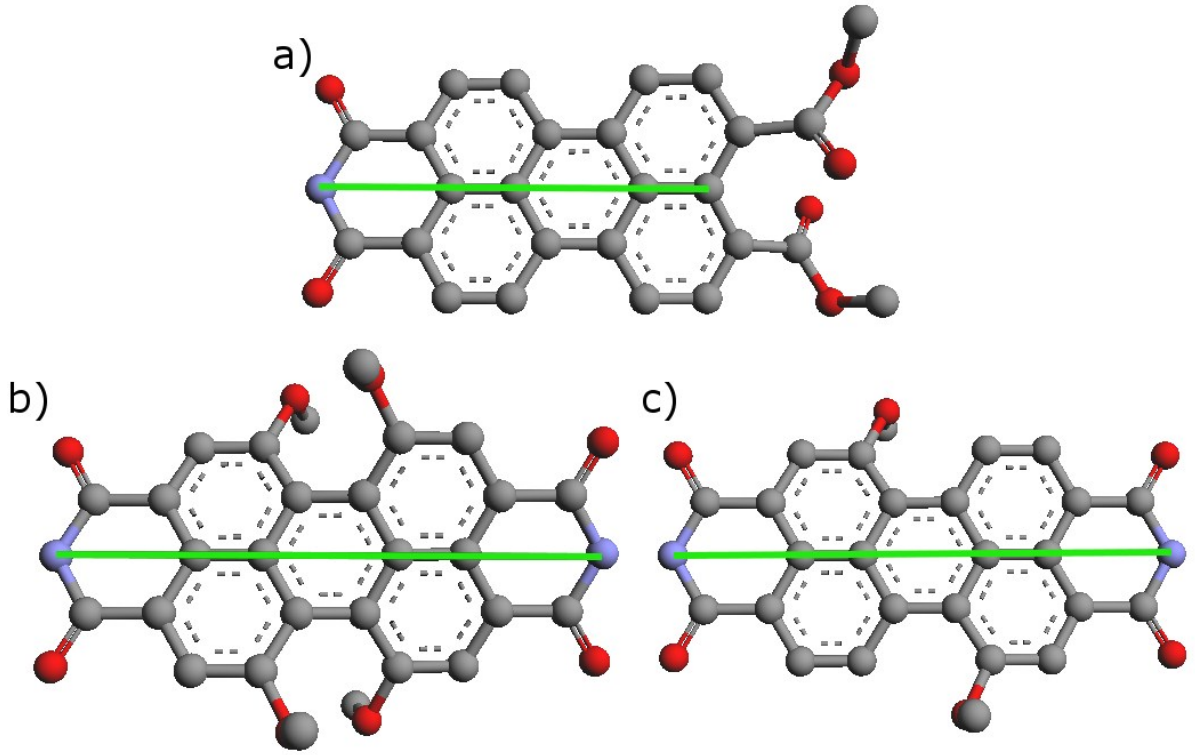


Figure 1 UFF molecular modelling structures of the (a) Donor, (b) A1 acceptor and (c) A2 acceptor. Distances measured are indicated in green. a) 0.88 nm, b) 1.15 nm, c) 1.16 nm.

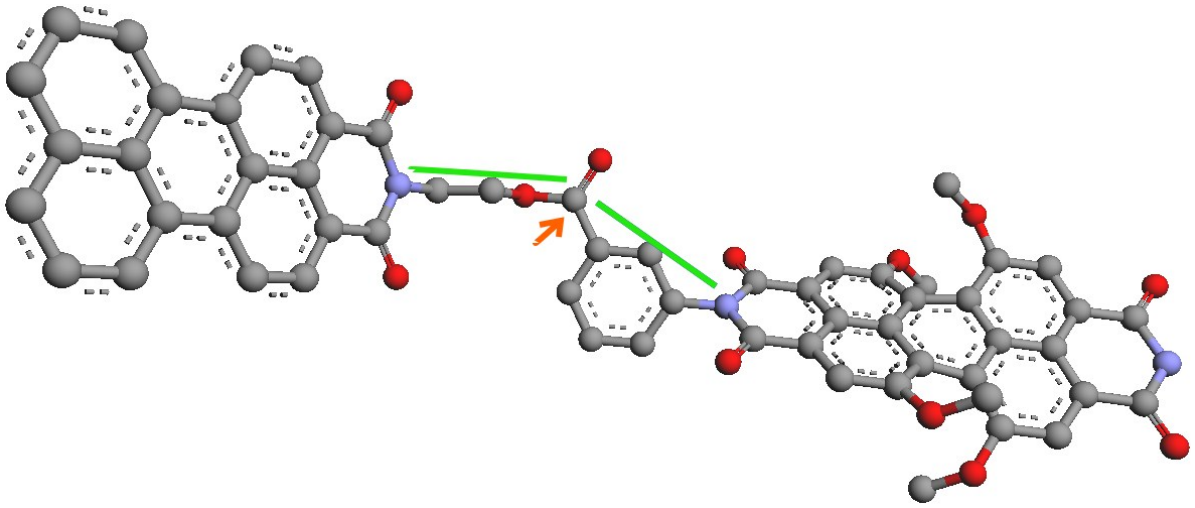


*Figure 2 UFF modelling structure of Array **1**. In green are the two 0.47 nm hinge lengths, and marked in orange is the hinge point.*

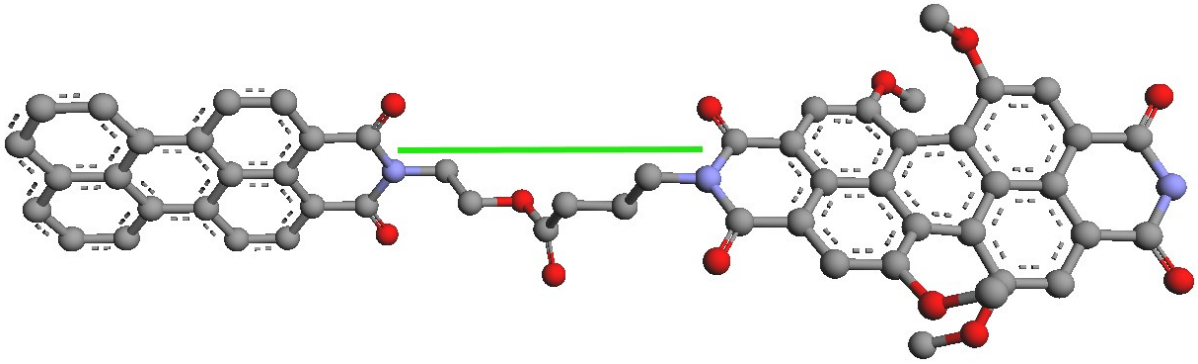


*Figure 3 UFF modelling of Array **2**, in green is the nitrogen to nitrogen distance of 0.86 nm.*

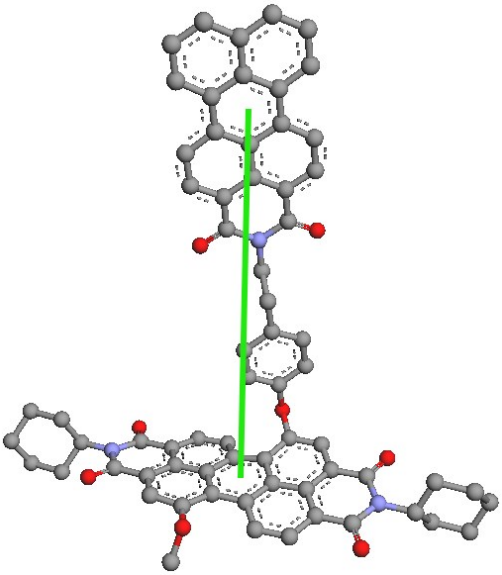
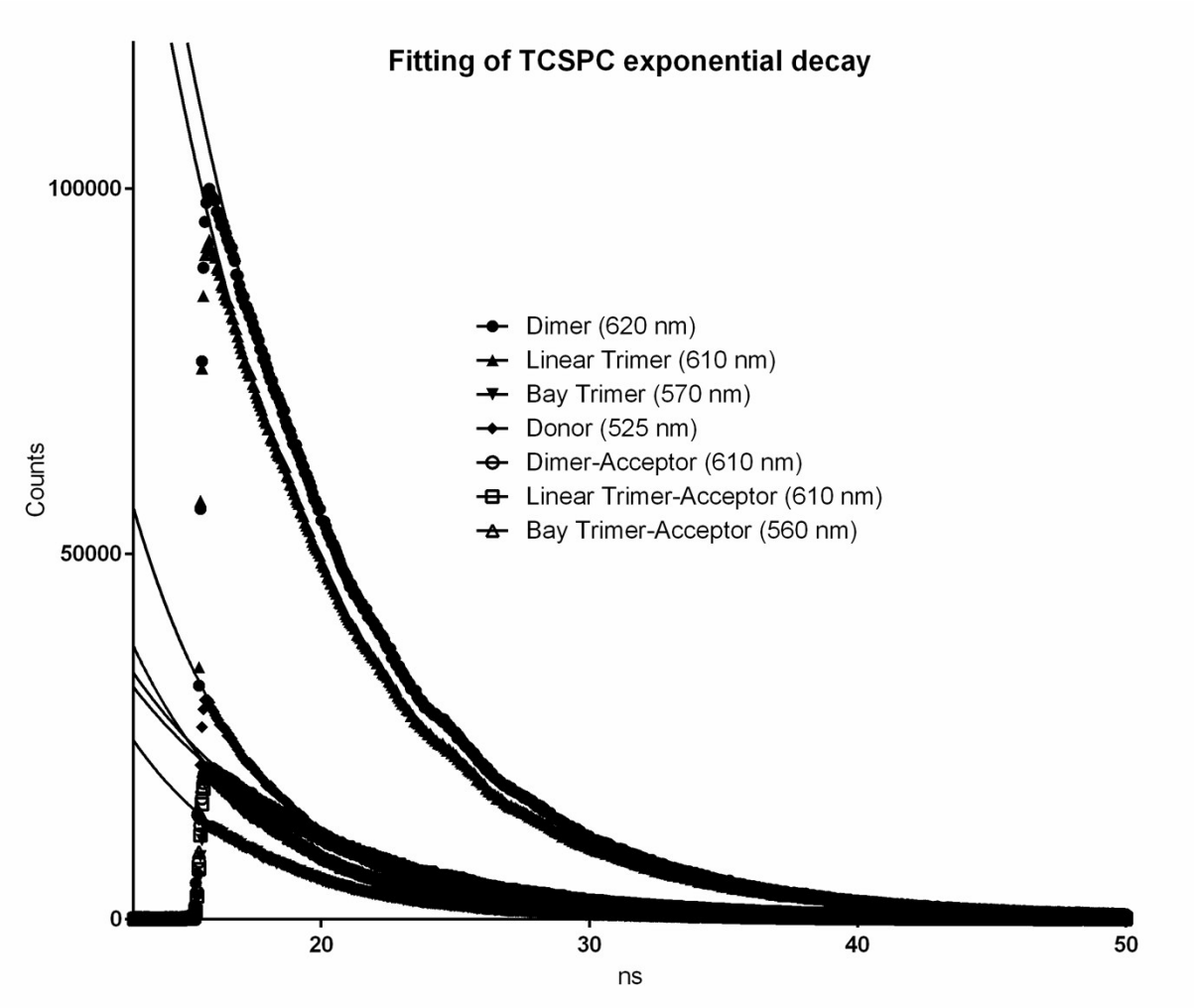


*Figure 4 UFF modelling of Array **3**, in green is the centroid to centroid distance of 1.72 nm.*

Time Correlated Single Photon Counting



	Em(nm)	T1	95% confidence (±)
Array **1** (480nm ex)	620	6.35	0.02
tetraphendibenzimide	610	6.38	0.02
monoimide diester	525	4.45	0.01
Array **2** (480nm ex)	610	6.19	0.02
tetraphenoxy dioctylimide	620	6.73	0.02
monoimide diester	525	4.45	0.01
Array **3** (480nm ex)	570	4.62	0.01
bisphenoxydiimide	560	4.78	0.02
monoimide diester	525	4.45	0.01

Ultrafast time resolved spectroscopy

An amplified Ti:Sapphire laser (Spectra Physics, Spitfire) was used as a source for 100 fs pulses with a repetition rate of 3 kHz. Half the output was sent to an optical parametric amplifier (TOPAS) to generate excitation pulses centred at 505 nm. The remaining details are measurement specific and described below.

Ultrafast transient absorption spectroscopy

The 505 nm excitation pulses were attenuated to 12 - 14 nJ/pulse and chopped at ω/2 (1500 Hz) so that every second pulse was blocked. To generate the visible continuum, which acts as the probe, a portion of the fundamental 800 nm output was focused inside a continuously translated 3 mm CaF_2 window. The excitation and probe were overlapped at the sample with the polarization set at the magic angle (54.7°). Differential absorption spectra were obtained by recording the transmission of the probe through the sample and comparing the fractional change of sequential pairs. This was achieved using a free space coupled prism (quartz) and a linear photodiode array read out at 3 kHz photodiode array (Entwicklungsbuero Stresing). 2000 shots were averaged per time point with a series of 65 time points spanning the -10 to 10 ps delay range. Delay was achieved by varying a mechanical delay to adjust the path length of the excitation pulse. An exponential spacing was used at 1 ps – 10 ps, and linear space between other delay times. Differential transmission was calculated and averaged with LabVIEW, each dataset contained spectra at each time point. Each sample was scanned 3 times without delay between scans.

Ultrafast time resolved photoluminescence spectroscopy

The same as TA, the excitation wavelength from the TOPAS was set to 505 nm, and the excitation intensity was 1.7 nJ/pulse. A half-waveplate and a linear polarizer were used to set the excitation polarization state. After the sample, the collected PL passes through a vertically orientated wire grid polarizer (PFU04, Moxtex). To eliminate depolarization effects for the population kinetics, the polarization state of the excitation is set at magic angle to the wire grid polarizer. For the TRPL anisotropy, measurements with vertically and horizontally polarized excitation are undertaken separately. The ultrafast TRPL is based on transient grating PL spectroscopy (TGPLS), which uses transient grating as an optical gate. The transient grating is generated by focusing and overlapping two vertically polarized 800 nm gate beams on a 1 mm thickness UV fused silica window (FS). To easily separate PL and diffracted PL signals, the gate beams and PL are arranged as BOXCAR geometry. The gated PL is guided to a spectrometer (SP2300 by Princeton Instruments) equipped with an intensified CCD (PIMAX3 by Princeton Instruments). A long pass filters and a short pass filter remove the scattering of the 505 nm excitation and 800 nm gate before the spectrometer. The iCCD is operated under gated mode and 10 ns intensifier gate width to accumulate 30000 shots for a single time-resolved spectra. By varying the mechanical time delay between the excitation and gate pulses, the broadband PL dynamics can be resolved. For each measurement, at least four scans were averaged. In post-data processing, spike-like noises are suppressed by a numerical median filter, and the system backgrounds are removed by subtracting signals collected at the negative time.

Global fitting (transient absorption, time-resolved photoluminescence)

All fitting and calculations were carried out in MATLAB, for non-linear fitting the 'trust-region-reflective' algorithm was used, while linear fitting was done via matrix division. Determination of rate constants was done via Equation 1.1, k_1 and k_2 determined by non-linear fitting. A_1 and A_2 are decay associated spectra (DAS) determined by linear weightings of the decays at each wavelength. Equations 1.2 were then used to model the individual component spectra with alpha determined by linear combination of the DAS to best fit steady state photoluminescence (PL) or transient absorption (TA) spectra of TA reference monomers. In all cases k_2 was determined to be significantly longer than the time range recorded.

$$S(\lambda,t) = A_1(\lambda)e^{-k_1 t} + A_2(\lambda)e^{-k_2 t} \quad 1.1$$

$$Species\ 1\ (\lambda,t) = A_3(\lambda)(1-\alpha)e^{-k_1 t} \quad Species\ 2\ (\lambda,t) = A_4(\lambda)(e^{-k_2 t} - (1-\alpha)e^{-k_1 t}) \quad 1.2$$

The residuals for each of the fits are shown below, in all cases the residuals are lacking in structure and therefore well fit by the extracted kinetic and spectral components.

Anisotropy correction

To correct for direct excitation of the acceptor the ratio of excitation was calculated using a linear decomposition of the absorption spectra. The contribution of signal intensity from the directly excited acceptor was calculated using data collected at the magic angle. This was separated into contributions from parallel and perpendicular components. The direct excitation intensity was removed to give the anisotropy decay that can be attributed to energy transfer between the donor and acceptor.

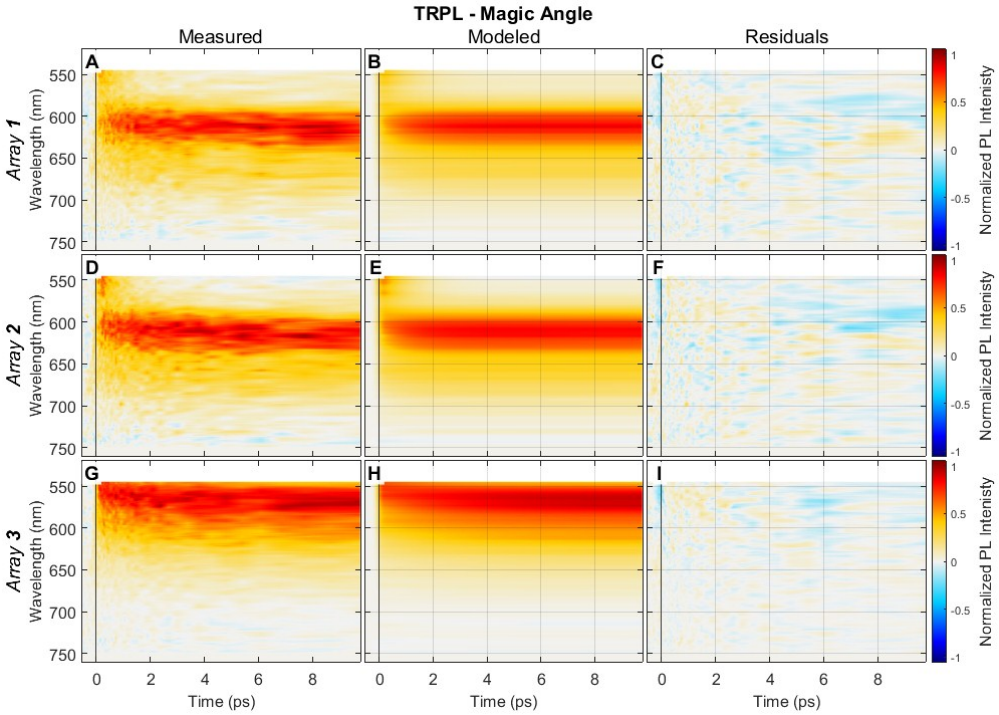


Figure S5. Fitting results of time resolved photoluminescence (TRPL) collected with excitation and measured intensity collected at the magic angle. ***A,D,G*** *contain the measured TRPL for array* ***1-3*** *respectively. These are fitted with time constants (main text section Table* ***2****) which generate the modelled surface (****B,E,H****) with residuals (****C,F,I****). Surfaces are displayed with each set (measured, modelled, and residual) normalized by measured surface.*

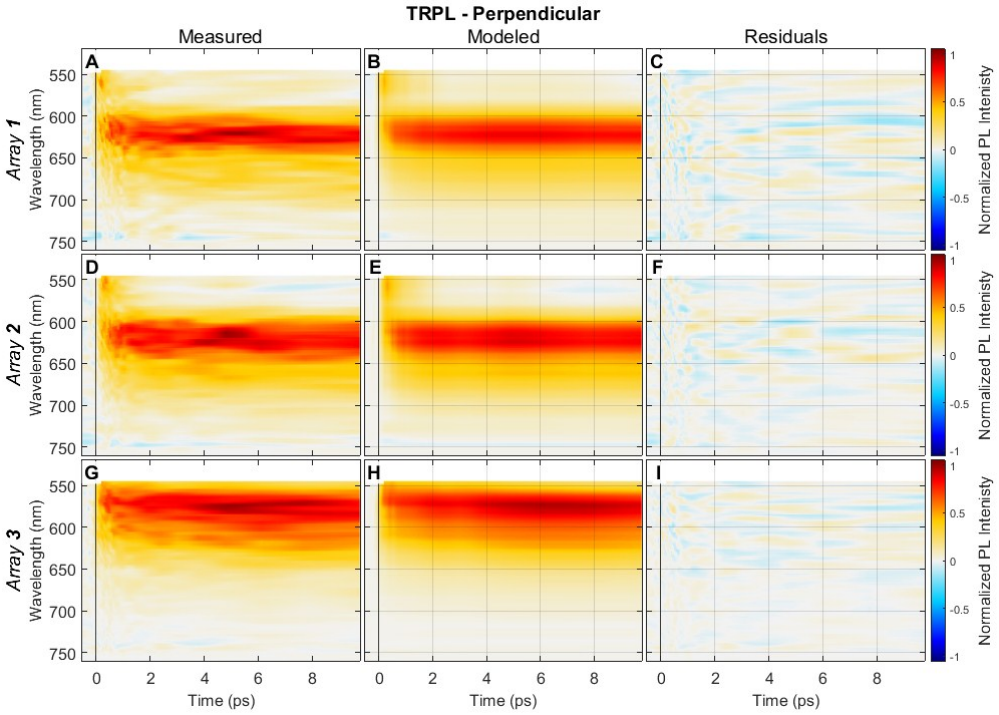


*Figure S6. Fitting results of time resolved photoluminescence (TRPL) collected with excitation and measured intensity collected perpendicular. **A**,**D**,**G** contain the measured TRPL for array **1-3** respectively. These are fitted with time constants (main text section Table **2**) which generate the modelled surface (**B**,**E**,**H**) with residuals (**C**,**F**,**I**). Surfaces are displayed with each set (measured, modelled, and residual) normalized by measured surface.*

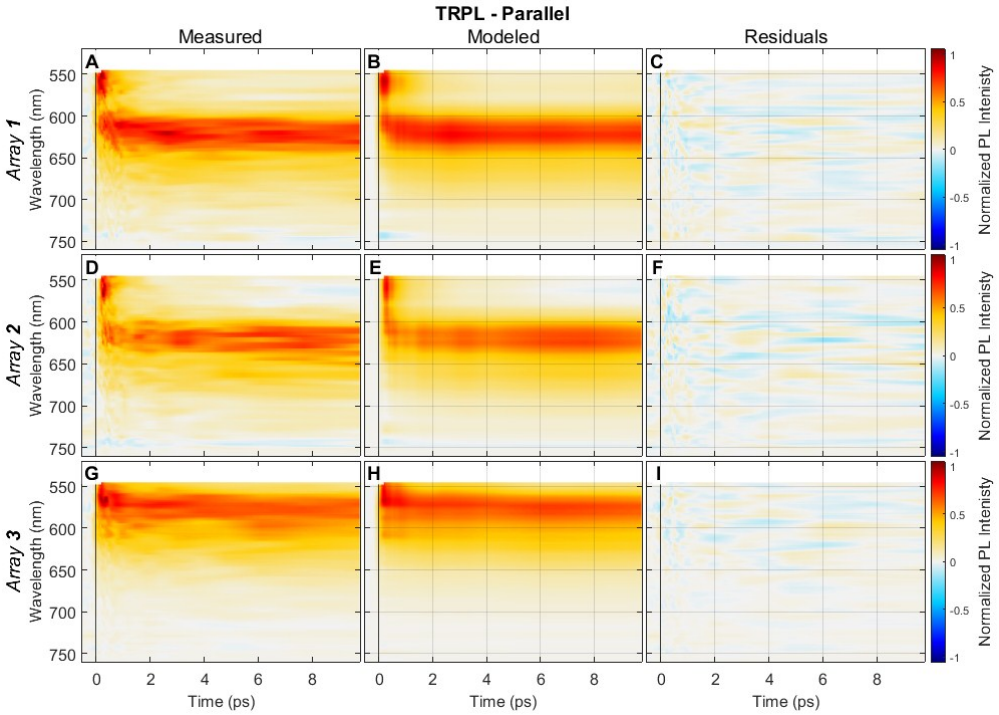


*Figure S7. Fitting results of time resolved photoluminescence (TRPL) collected with excitation and measured intensity collected parallel. **A**,**D**,**G** contain the measured TRPL for array **1-3** respectively. These are fitted with time constants (main text section Table **2**) which generate the modelled surface*

*(**B**,**E**,**H**) with residuals (**C**,**F**,**I**). Surfaces are displayed with each set (measured, modelled, and residual) normalized by measured surface.*

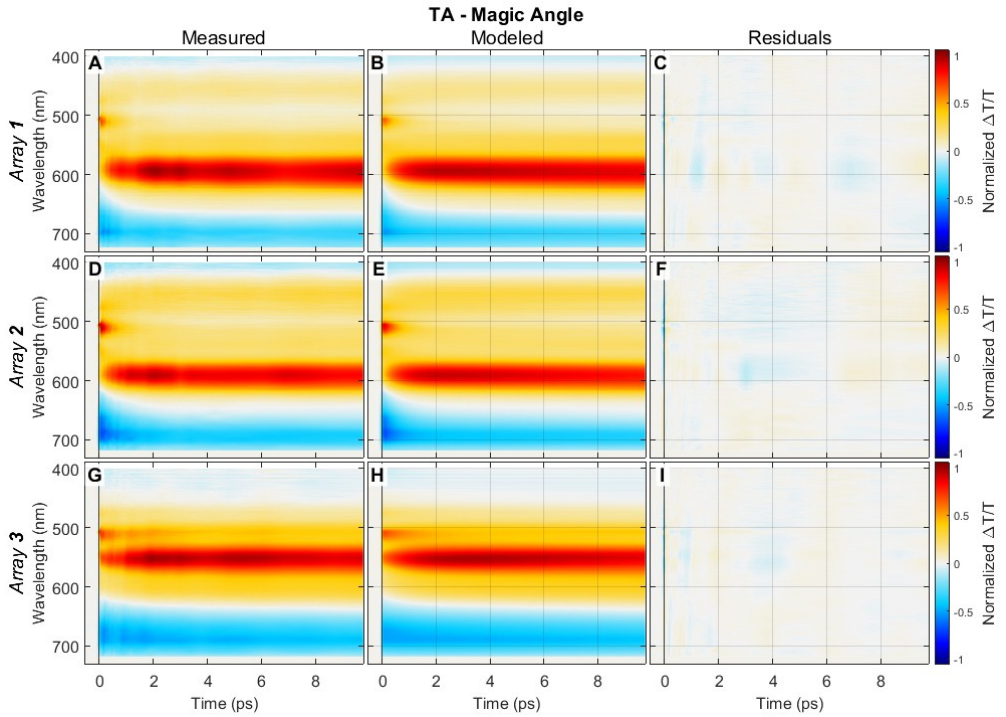


*Figure S8. Fitting results of transient absorption (TA) collected with excitation and measured intensity collected at the magic angle. **A**,**D**,**G** contain the measured TA for array **1-3** respectively. These are fitted with time constants (main text section Table **2**) which generate the modelled surface (**B**,**E**,**H**) with residuals (**C**,**F**,**I**). Surfaces are displayed with each set (measured, modelled, and residual) normalized by measured surface.*

References:

1. J. Ma, L. Yin, G. Zou and Q. Zhang, *Eur. J. Org. Chem.*, 2015, **2015**, 3296-3302.
2. S. Sengupta, R. K. Dubey, R. W. Hoek, S. P. van Eeden, D. D. Gunbas, F. C. Grozema, E. J. Sudholter and W. F. Jager, *J. Org. Chem.*, 2014, **79**, 6655-6662.
3. R. Wang, Z. Shi, C. Zhang, A. Zhang, J. Chen, W. Guo and Z. Sun, *Dyes Pigments*, 2013, **98**, 450-458.
4. D. K. Panda, F. S. Goodson, S. Ray, R. Lowell and S. Saha, *Chem. Commun.*, 2012, **48**, 8775-8777.
5. P. Singh, L. S. Mittal, V. Vanita, R. Kumar, G. Bhargava, A. Walia and S. Kumar, *Chem. Commun.*, 2014, **50**, 13994-13997.