Supercritical carbon dioxide as a solvent for deposition of a tailored dye in dye sensitized solar cells

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Supporting Information

Experimental

General remarks

Compounds (**1**) and (**4**) were purchased from Aldrich. Anhydrous acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2), toluene, etc were obtained by passing them through columns of activated alumina or purchased from commercial suppliers (hexanes with a boiling range from 68–70 °C). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer at 400 and 100 MHz, respectively, or on a Bruker AV200 spectrometer at 200 and 50 MHz, respectively, using deuterated chloroform ($CDCl_3$), unless otherwise stated. Chemical shifts are reported relative to the resonances of residual $CHCl_3$ at δ = 7.26 ppm (H) and δ = 77.2 ppm (C). ^{13}C NMR spectra of fluorinated molecules are difficult to observe under conventional broad-band proton decoupling, thus chemical shifts of carbon that are adjacent to fluorine atom are not reported. Fluorine NMR spectra were recorded on a Bruker AV200 spectrometer at 200 MHz using $CFCl_3$ as the external reference at $\delta = 0$ ppm.

Melting points were recorded on an Electrothermal IA9300 digital melting point apparatus and are uncorrected.

Positive-ion EI mass spectra were run on a ThermoQuest MAT95XL mass spectrometer using an ionisation energy of 70 eV. Accurate mass measurements were obtained with a resolution of 5000-10000 using perfluorokerosene as the reference compound. High-resolution positive-ion electrospray mass spectra were acquired with a Micromass Q-TOF II mass spectrometer using a cone voltage of 50 V and a capillary voltage of 3.0 kV. The sample was introduced by direct infusion at a rate of 5 mL/min using PEG400 as an internal reference.

Unless otherwise indicated, column chromatography and rapid silica filtration was carried out by using Merck Kieselgel 60 silica gel. Rapid silica filtration chromatography involves a sintered glass funnel where the passage of solvents was accelerated through the silica bed by reduced rather than positive pressure.

Analytical TLC was conducted on Sigma–Aldrich silica gel coated aluminium sheets and visualised with UV/Visible radiation and/or by or potassium permanganate reagents.

Synthesis

Scheme S1. *Synthesis of the diamine precursors*

N,N-Bis(1H,1H,2H,2H-perfluorooctyl)benzylamine (2)

Following the procedure of Holczknecht,[1] a mixture of benzylamine (**1**) (0.90 g, 8.40 mmol), 1H,1H,2H,2H-perfluorooctyl iodide (18.0 g, 38.0 mmol), K_2CO_3 (5.50 g, 40 mmol) in anhydrous CH_3CN (20 mL) were heated in a Schlenk tube for 24 h at 80 °C. The suspension was cooled to RT, the solid was filtered and washed with CH_3CN (50 mL). The filtrate was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel using 10% EtOAc/*n*-hexane as eluent to give the *title compound* (**2**) as a pale yellow oil (3.00 g, 45%), R_f 0.92 (10% EtOAc/*n*-hexane). ^1H NMR (200 MHz) δ 7.36-7.28 (m, 5H, Aryl H), 3.65 (s, 2H, CH_2Ph), 2.85 (dd, 4H, J = 7.3, 7.3 Hz, NCH_2), 2.40-2.13 (m, 4H). ^{13}C NMR (50 MHz, partial) δ 138.2, 128.7, 128.7, 127.7, 58.7, 45.5, 29.2. ^{19}F NMR (200 MHz) δ -81.24 - -81.29 (m, 6F), -114.12 - -114.24 (m, 4F), -122.17 - -122.29 (m, 4F), -123.16 - -123.28 (m, 4F), -123.75 - -123.79 (m, 4F), -126.46 - -126.48 (m, 4F). LRMS (EI) *m/z* 799 (M^+, 10), 780 (5), 722 (10), 467 (15), 466 (62), 446 (4), 92 (10), 91 (100%). HRMS (TQ-MS-EI) *m/z* obsd $[M]^+$ 800.0791, calcd $C_{23}H_{15}F_{26}N$ $[M]^+$ 800.0868.

N,N-Bis(1H,1H,2H,2H-perfluorooctyl)amine (3)

Following the procedure of Rocaboy,[2] a mixture of (**2**) (3.00 g, 3.75 mmol) and 10% Pd/C (0.30 g, 0.28 mmol) in 50% EtOH/*n*-hexane (20 mL) were placed in a thick-walled high-pressure glass vessel. The vessel was purged with nitrogen and then evacuated. This step was repeated three times and then the vessel was filled with hydrogen and the mixture was stirred overnight at RT. After this period the reaction mixture was filtered through a pad of celite and the solvent was evaporated under reduced pressure to give the *diperfluorooctylamine* (**3**) as a colorless oil (2.58 g, 97%), R_f 0.21 (10% EtOAc/*n*-hexane). ^{1}H NMR (200 MHz) δ 2.97 (dd, 4H, J = 7.2, 7.2 Hz,), 2.42-2.16 (m, 4H). ^{13}C NMR (50 MHz, partial) δ 41.4, 31.7. ^{19}F NMR (200 MHz) δ -80.90 - -81.03 (m, 6F), -113.66 - -113.83 (m, 4F), -121.93 - -122.06 (m, 4F), -122.87 - -123.06 (m, 4F), -123.67 - -123.82 (m, 4F), -126.16 - -126.36 (m, 4F). LRMS (EI) *m/z* 707 (3), 690 (9), 377 (10), 376 (100%), 374 (3), 354 (3), 91 (3), 69 (4). HRMS (TQ-MS-EI) *m/z* obsd $[M-H]^+$ 708.0231, calcd $C_{16}H_9F_{26}N$ $[M-H]^+$ 708.0236.

Scheme S2. *Synthesis of* ***DOP(10)*** *and* ***DOFP (11)*** *perylene dyes.*

***N*-(2,5-Di-*tert*-butylphenyl)perylene-3,4-dicarboximide (6)**

The reaction conditions of Langhals[3] were followed with significant changes in the purification method. A mixture of perylene (**5**) (21.96 g, 60.0 mmol), 2,5-di-*tert*-butylaniline (6.98 g, 34.0 mmol), $Zn(OAc)_2.2H_2O$ (2.41 g, 11.0 mmol), imidazole (127 g, 1.86 mol) and water (72 mL) were placed in an autoclave equipped with a pressure gauge. The mixture was stirred at 190 °C that caused a gradual increase in pressure. After 20 h, the pressure gauge showed 15 bar and the reaction mixture was then cooled to RT. The mixture was diluted with $CHCl_3$ (1 L), then filtered through celite to remove any insoluble impurities. The filtrate was washed with water (3 × 50 mL), dried ($MgSO_4$) and evaporated under reduced pressure to afford a bright red solid. The crude material was dissolved in toluene (4 mL) and purified by column chromatography with gradient elution of increasing portions of CH_2Cl_2 in toluene. The relevant fractions were collected and the solvent evaporated to give a bright orange solid that consisted of the product and the bis-substituted perylene diimide. The mixture was then treated with EtOAc (100 mL) and the insoluble material was collected to yield the *title compound* (**6**) as a bright orange crystalline solid (5.37 g, 62%), m.p. 368-370 °C (lit.[3] m.p. >300 °C), R_f 0.27 (50% CH_2Cl_2/toluene). The NMR data was consistent with the reported data.[3] ^{1}H NMR (400 MHz) δ 8.59 (d, 2H, J = 8.1 Hz), 8.38 (d, 4H, J = 7.9 Hz), 8.36 (d, 2H, J = 7.9 Hz),7.87 (d, 2H, J = 8.1 Hz), 7.61 (d, 1H, J = 8.6 Hz),7.58 (d, 2H, J = 7.9 Hz), 7.46 (dd, 1H, J = 8.6, 2.0 Hz), 7.04 (d, 1H, J = 2.0 Hz), 1.35 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (50 MHz) δ 165.1, 150.1, 143.9, 137.5, 134.4, 133.2, 132.0, 131.0, 130.4, 129.3, 128.9, 128.0, 127.2, 126.3, 123.9, 121.4, 120.3, 35.8, 34.7, 31.9, 31.4. LRMS (EI) *m/z* 510 (5), 509 (M^+, 11), 454 (6), 453 (31), 452 (100%), 437 (6), 436 (13), 250 (3). HRMS (TQ-MS-EI) *m/z* $[M]^+$ obsd 509.2337, calcd $C_{36}H_{31}NO_2$ $[M]^+$ 509.2336.

9-Bromo-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (7)

The procedure of Langhals and co-workers was followed with modification in the purification method.[3] A mixture of perylene dicarboximide (**6**) (2.50 g, 4.91 mmol) and K_2CO_3 (2.45 g, 17.7 mmol) in chlorobenzene (50 mL) was heated to 40 °C and then treated rapidly with a solution of bromine (0.58 mL, 1.81 g, 22.6 mmol) in chlorobenzene (10 mL). The orange color of the solution immediately turned to wine-red and the mixture was stirred for 2.5 h at 45-50 °C. The solvent was evaporated and the crude mixture diluted with EtOAc (100 mL). The precipitate was collected, washed with cold EtOAc (100 mL), then recrystallized from EtOH to yield the *title compound* (**7**) as a red solid (2.73 g, 95%), m.p. 343 °C. (dec.) (lit.[3] m.p. >320 °C), R_f 0.67 (CH_2Cl_2). The NMR data was consistent with the reported data.[3] ^{1}H NMR (400 MHz) δ 8.63 (d, 1H, J = 7.8 Hz), 8.61 (d, 1H, J = 7.9 Hz), 8.40 (d, 1H, J = 7.9 Hz), 8.38 (d, 1H, J = 8.2 Hz), 8.33 (d, 1H, J = 8.1 Hz), 8.25 (d, 1H, J = 8.3 Hz), 8.14 (d, 1H, J = 8.3 Hz), 7.84 (d, 1H, J = 8.1 Hz), 7.67 (dd, 1H, J = 8.2, 7.8, Hz), 7.60 (d, 1H, J = 8.6 Hz), 7.46 (dd, 1H, J = 8.6, 2.2 Hz), 7.05 (d, 1H, J = 2.2 Hz), 1.34 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (50 MHz) δ 164.9, 150.2, 143.92, 136.8, 136.7, 133.1, 133.0, 132.1, 131.3, 130.2, 129.2, 128.9, 128.0, 126.7, 126.3, 124.5, 123.8, 121.8, 120.8, 120.5, 35.7, 34.4, 31.9, 31.4. LRMS (EI) *m/z* 589 (12), 587 (M^+, 11), 533 (32), 532 (100%), 531 (32), 530 (95), 516 (15), 514 (13). HRMS (TQ-MS-EI) *m/z* $[M]^+$ obsd 587.1451, calcd $C_{36}H_{30}BrNO_2$ $[M]^+$ 587.1454.

9-Dioctylamino-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (8)

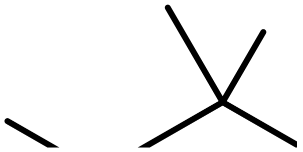
A stirred mixture of the bromide (**7**) (0.50 g, 0.85 mmol), dioctylamine (**4**) (0.23 g, 0.94 mmol), tri(dibenzylidenacetone)dipalladium(0) (39 mg, 0.04 mmol), tri(*tert*-butyl)phosphonium tetrafluoroborate (42 mg, 0.15 mmol) and sodium *tert*-butoxide (82 mg, 0.85 mmol) in anhydrous toluene (50 mL) was heated at 90 °C overnight. After this period the reaction mixture was cooled and the solvent was removed under reduced pressure. The crude material was dissolved in 50 % CH_2Cl_2/toluene (20 mL) and passed through a pad of silica gel. The filtrate was concentrated and purified by column chromatography on silica gel with constant elution with 50% CH_2Cl_2/toluene. The necessary fractions were collected and concentrated to give the *title compound* (**8**) as a purple solid (0.32 g, 50%) m.p. 140-142 °C, R_f 0.61 (50% CH_2Cl_2/toluene). The NMR data was consistent with the reported data.[4] ^{1}H NMR (400 MHz) δ 8.63 (d, 1H, J = 8.2 Hz), 8.62 (d, 1H, J = 8.3 Hz), 8.46 (d, 1H, J = 8.2 Hz), 8.42 (d, 1H, J = 8.3 Hz), 8.40 (d, 1H, J = 8.6 Hz), 8.33 (d, 1H, J = 8.2 Hz), 8.32 (d, 1H, J = 8.0 Hz), 7.61 (dd, 1H, J = 8.2, 8.0 Hz), 7.59 (d, 1H, J = 8.6 Hz), 7.44 (dd, 1H, J = 8.6, 2.2 Hz), 7.25 (d, 1H, J = 8.6,), 7.02 (d, 1H, J = 2.2 Hz), 3.28 (dd, 4H, J = 7.5, 7.3 Hz), 1.61-1.56 (m, 4H), 1.33 (s, 9H), 1.30 (s, 9H), 1.28-1.23 (m, 20H), 0.84 (t, 6H, 2 × CH_3). ^{13}C NMR (50 MHz) δ 164.3, 152.6, 150.1, 144.0, 138.5, 138.3, 133.5, 132.2, 132.0, 130.8, 130.6, 129.7, 128.8, 127.8, 126.9, 126.2, 126.0, 124.8, 124.3, 123.4, 121.0, 119.8, 118.9, 118.5, 54.0, 35.7, 34.4, 31.9, 31.9, 31.4, 29.5, 29.4, 27.4, 27.3, 22.8, 14.2. LRMS (EI) *m/z* 751 (17), 750 (57), 749 (M^+, 100%), 693 (8), 692 (15), 650 (9), 649 (18), 479 (8). HRMS (TQ-MS-EI) *m/z* $[M]^+$ obsd 748.4971, calcd $C_{52}H_{64}N_2O_2$ $[M]^+$ 748.4962.

9-Dioctylamino-perylene-3,4-dicarboxy anhydride (DOP) (10)

A mixture of dioctylamine perylene imide (**8**) (0.20 g, 0.27 mmol), potassium hydroxide (0.73 g, 13 mmol) and *tert*-butyl alcohol (50 mL) were heated at reflux overnight. After this period the reaction mixture was cooled to RT and poured into acetic acid (100 mL). The mixture was stirred at 40 °C for 4 h and then the solvent was removed under reduced pressure. The crude material was dissolved in $CHCl_3$ (50 mL), then washed with water (3 × 20 mL), dried ($MgSO_4$) and the solvent was removed under vacuum. This crude material was subjected to column chromatography with constant elution with 50% CH_2Cl_2/toluene to afford the *title compound* (**DOP**) (**10**) as a blue solid (0.10 g, 67%), m.p. 143-145 °C, R_f 0.12 (toluene). The NMR data was consistent with the reported data.[4] ^{1}H NMR (400 MHz) δ 8.28 (d, 1H, J = 8.0 Hz), 8.25 (d, 1H, J = 8.3 Hz), 8.26 (d, 1H, J = 8.2 Hz), 8.22 (d, 1H, J = 8.0 Hz), 8.20 (d, 1H, J = 8.4 Hz), 8.07 (d, 1H, J = 8.2 Hz), 7.98 (d, 1H, J = 8.3 Hz), 7.58 (dd, 1H, J = 8.0, 8.0 Hz), 7.18 (d, 1H, J = 8.4 Hz), 3.33 (dd, 4H, J = 7.6, 7.4 Hz), 1.65-1.59 (m, 4H), 1.35-1.24 (m, 20H), 0.85 (t, 6H, 2 × CH_3). ^{13}C NMR (50 MHz) δ 161.1, 161.0, 153.7, 139.5, 139.2, 133.4, 133.2, 132.8, 130.0, 129.5, 128.1, 126.4, 126.0, 125.6, 124.9, 122.0, 119.5, 118.6, 118.1, 115.9, 114.4, 53.9, 31.9, 29.6, 29.4, 27.4, 27.3, 22.8, 14.2. LRMS (EI) *m/z* 563 (9), 562 (42), 561 (M^+, 100%), 463 (20), 462 (59), 350 (12), 349 (7), 207 (8). HRMS (TQ-MS-EI) *m/z* $[M]^+$ obsd 561.3225, calcd $C_{38}H_{43}NO_3$ $[M]^+$ 561.3237. UV/Vis (CH_2Cl_2) λ_{max} 557 nm, ε 36250.

9-(*N*,*N*-Bis(1H,1H,2H,2H-perfluorooctyl)amino)-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (**9**)

A stirred mixture of the bromide (**7**) (0.50 g, 0.85 mmol), *N*,*N*-Bis(1H,1H,2H,2H-perfluorooctyl)amine (**3**) (0.72 g, 1.02 mmol), tri(dibenzylidenacetone)dipalladium(0) (26 mg, 0.03 mmol), tri(*tert*-butyl)phosphonium tetrafluoroborate (28 mg, 0.01 mmol) and sodium *tert*-butoxide (98 mg, 1.02 mmol) in dry toluene (50 mL) was heated at 90 °C overnight. After this period the reaction was cooled and the solvent was removed under reduced pressure. The crude material was dissolved in 50% CH_2Cl_2/toluene (50 mL) and passed through a pad of silica gel. The filtrate was concentrated and purified by column chromatography on silica gel with constant elution with 50% CH_2Cl_2/toluene. The necessary fractions were collected and concentrated to give the *title compound* (**9**) as cherry red solid (0.59 g, 57%), m.p. 99-100 °C, R_f 0.38 (50% CH_2Cl_2/toluene). ^{1}H NMR (400 MHz) δ 8.67-8.65 (m, 2H), 8.54 (d, 1H, J = 7.8 Hz), 8.49-8.46 (m, 2H), 8.42 (d, 1H, J = 8.2 Hz), 8.28 (d, 1H J = 8.4 Hz), 7.72 (dd, 1H J = 8.2, 7.8 Hz), 7.59 (d, 1H, J = 8.6 Hz), 7.46 (dd, 1H, J = 8.6, 2.2 Hz), 7.39 (d, 1H, J = 8.4 Hz), 7.03 (d, 1H, J = 2.2 Hz), 3.63 (dd, 4H, J = 7.7, 7.5 Hz), 2.42-2.29 (m, 4H), 1.33 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (50 MHz partial) δ 165.1, 150.2, 147.6, 144.0, 137.5, 137.3, 133.2, 131.4, 130.1, 128.0, 127.4, 126.9, 126.6, 126.3, 124.4, 124.6, 123.9, 121.6, 121.3, 120.5, 120.0, 119.8, 118.2, 46.3, 35.7, 34.4, 31.9, 31.4, 30.0. ^{19}F NMR (200 MHz) δ -80.82 - -80.93 (m, 6F), -113.57 - -113.75 (m, 4F), -121.91 - -121.93 (m, 4F), -122.90 - -122.94 (m, 4F), -123.21 - -123.29 (m, 4F), -126.09 - -126.28 (m, 4F). HRMS (TOF-MS-ES) *m/z* $[M+Na]^+$ obsd 1239.2415, calcd $C_{52}H_{38}F_{26}N_2O_2Na$ $[M+Na]^+$ 1239.2416.



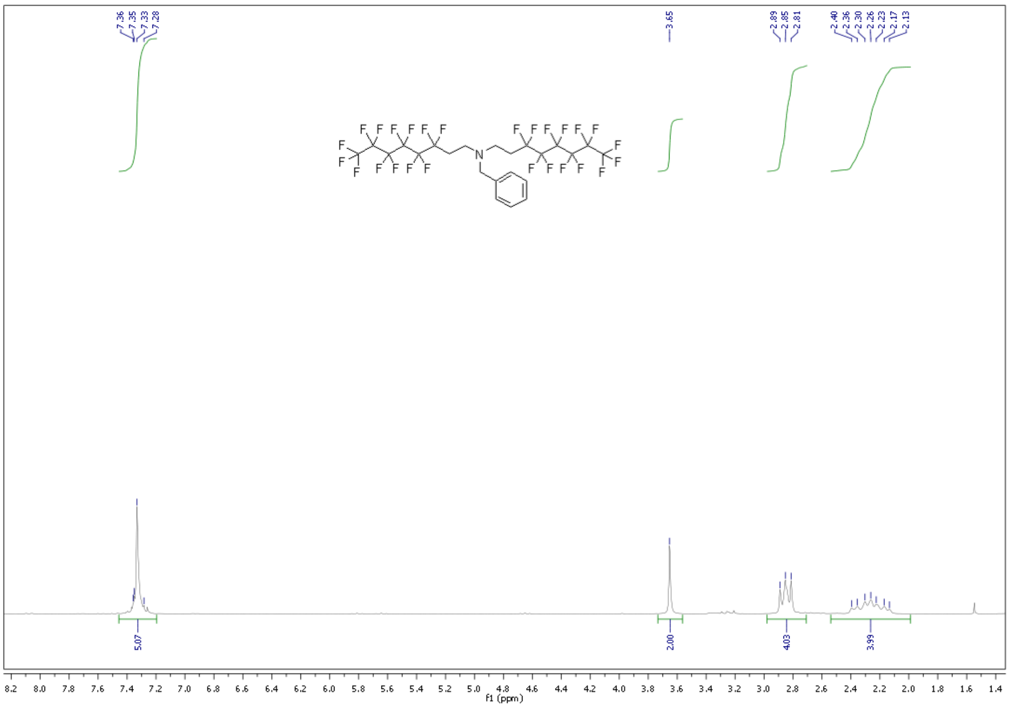
9-(*N*,*N*-Bis(1H,1H,2H,2H-perfluorooctyl)amino)-perylene-3,4-dicarboxy anhydride (DOFP) (11)

A mixture of bisperfluorooctylamine perylene imide (**9**) (0.36 g, 0.30 mmol), potassium hydroxide (0.82 g, 15 mmol) and *tert*-butyl alcohol (50 mL) was heated at reflux overnight. After this period the reaction mixture was cooled to RT and poured into acetic acid (100 mL). The mixture was stirred at 40 °C for 4 h and then the solvent was removed under reduced pressure. The crude material was dissolved in CH_2Cl_2 (50 mL), then washed with water (3 × 20 mL), dried ($MgSO_4$) and the solvent was removed under vacuum. This crude material was subjected to column chromatography with constant elution with 50% CH_2Cl_2/toluene to afford the *title compound* (**DOFP**) (**11**) as a purple solid (0.20 g, 65%), m.p. 183-184 °C, R_f 0.19 (50% CH_2Cl_2/toluene). ^{1}H NMR (200 MHz) δ 8.42 (d, 1H *J* = 7.8 Hz), 8.41-8.32 (m, 4H), 8.26 (d, 1H, *J* = 8.3 Hz), 8.21 (d, 1H, *J* = 8.2 Hz), 7.74 (dd, 1H, *J* = 8.2, 7.8 Hz), 7.37 (d, 1H, *J* = 8.2 Hz), 3.67 (dd, 4H, *J* = 7.8, 7.4 Hz,), 2.54-2.28 (m, 4H). ^{13}C NMR

(125 MHz, 50 °C, partial): δ 160.8, 148.8, 138.9, 138.7, 133.7, 131.6, 130.0, 129.7, 127.6, 127.2, 127.0, 126.1, 125.3, 124.8, 120.7, 120.2, 120.0, 117.2, 116.7, 46.4, 29.9, 29.3. ^{19}F NMR (200 MHz) δ -80.76 - -80.86 (m, 6F), -113.58 - -113.71 (m, 4F), -121.89 - -121.94 (m, 4F), -122.78 - -122.95 (m, 4F), -123.71 - -123.24 (m, 4F), -126.04 - -126.24 (m, 4F). LRMS (EI) *m/z* 1029 (M^+, 100%), 1010 (10), 696 (16), 349 (10), 204 (10), 169(33), 85 (46), 83 (75). HRMS (TOF-MS-ES) *m/z* $[M]^+$ obsd 1029.0776, calcd $C_{38}H_{17}F_{26}NO_3$ $[M]^+$ 1029.0793. UV-Vis (CH_2Cl_2) λ_{max} 514 nm, ε 37925.

NMR spectra

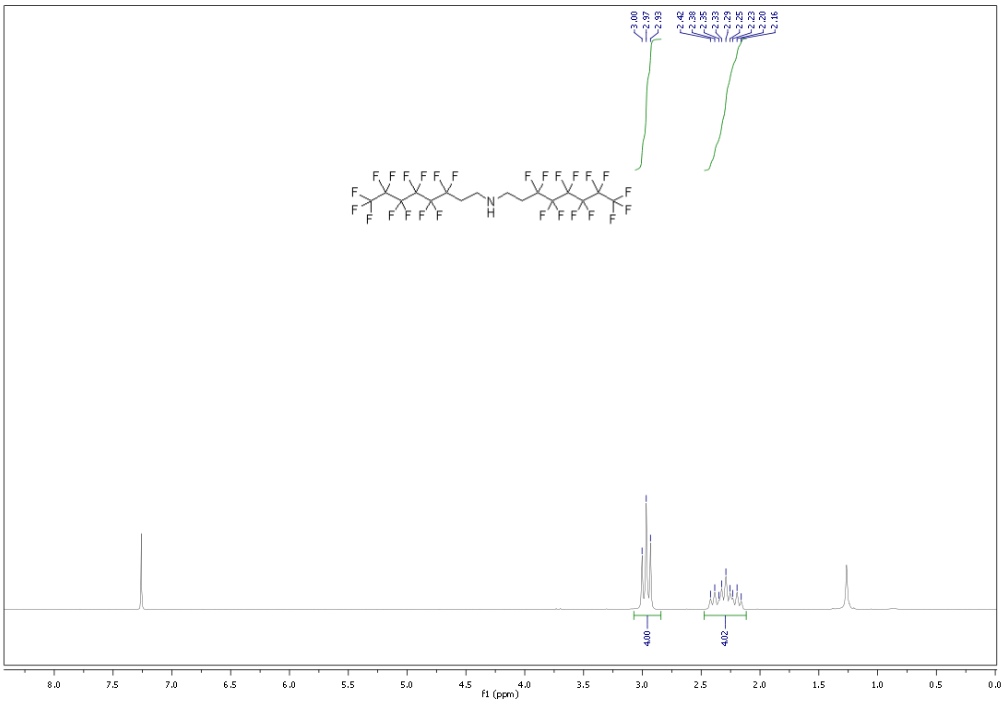
200 MHz ^{1}H NMR ($CDCl_3$) spectrum of *N*,*N*-bis(1H,1H,2H,2H-perfluorooctyl)benzylamine (**2**).



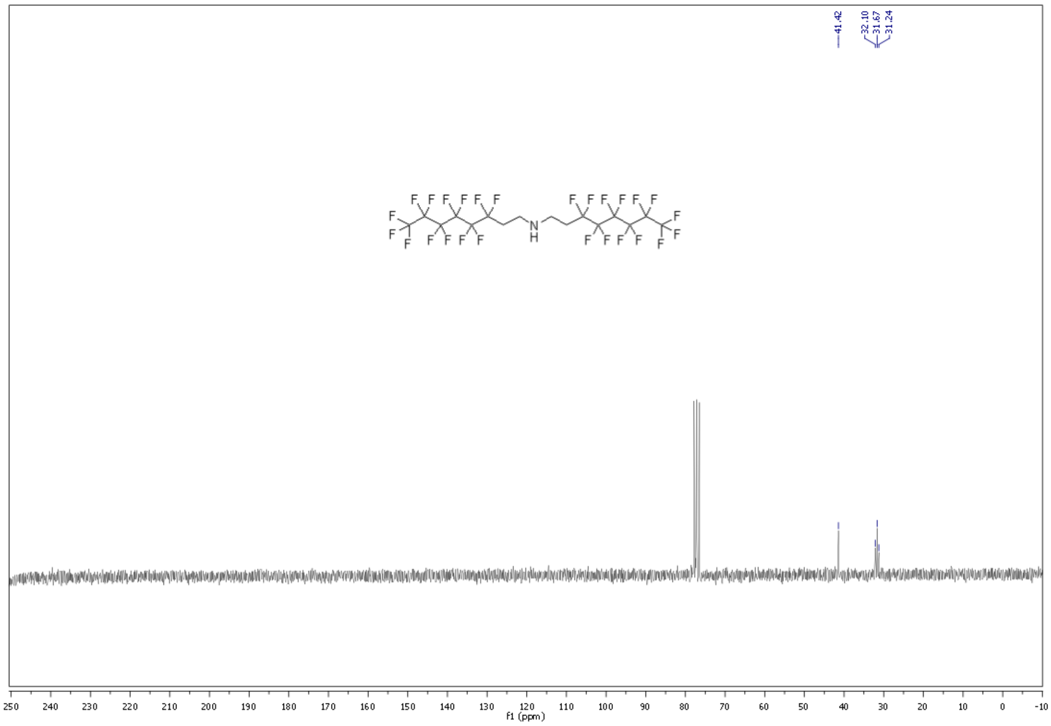
50 MHz ^{13}C NMR ($CDCl_3$) spectrum of *N*,*N*-bis(1H,1H,2H,2H-perfluorooctyl)benzylamine (**2**).

200 MHz ^{19}F NMR ($CDCl_3$) spectrum of *N*,*N*-bis(1H,1H,2H,2H-perfluorooctyl)benzylamine (**2**).

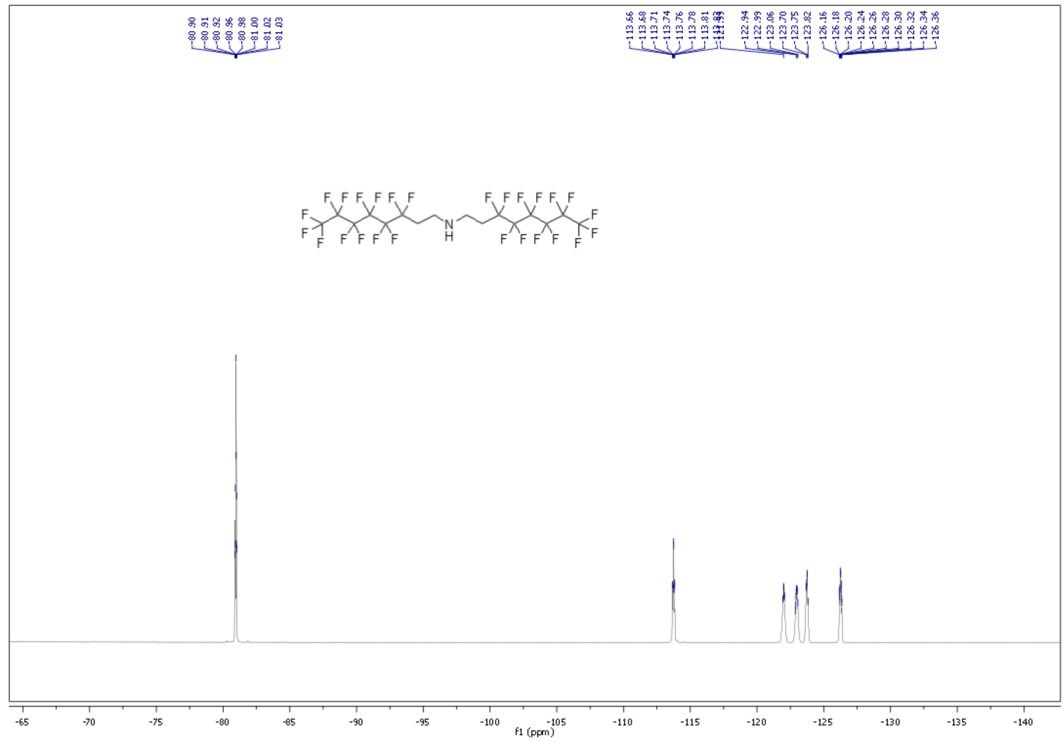
200 MHz ^{1}H NMR ($CDCl_3$) spectrum of bis(1H,1H,2H,2H-perfluorooctyl)amine (**3**).



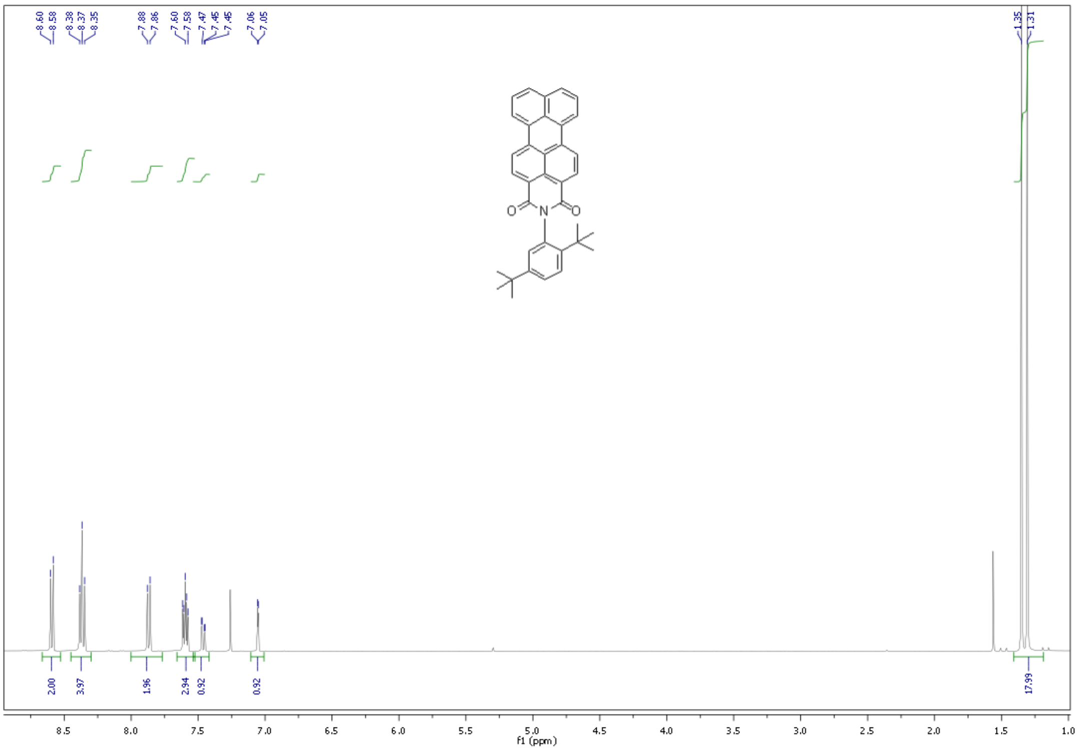
50 MHz ^{13}C NMR ($CDCl_3$) spectrum of bis(1H,1H,2H,2H-perfluorooctyl)amine (**3**).



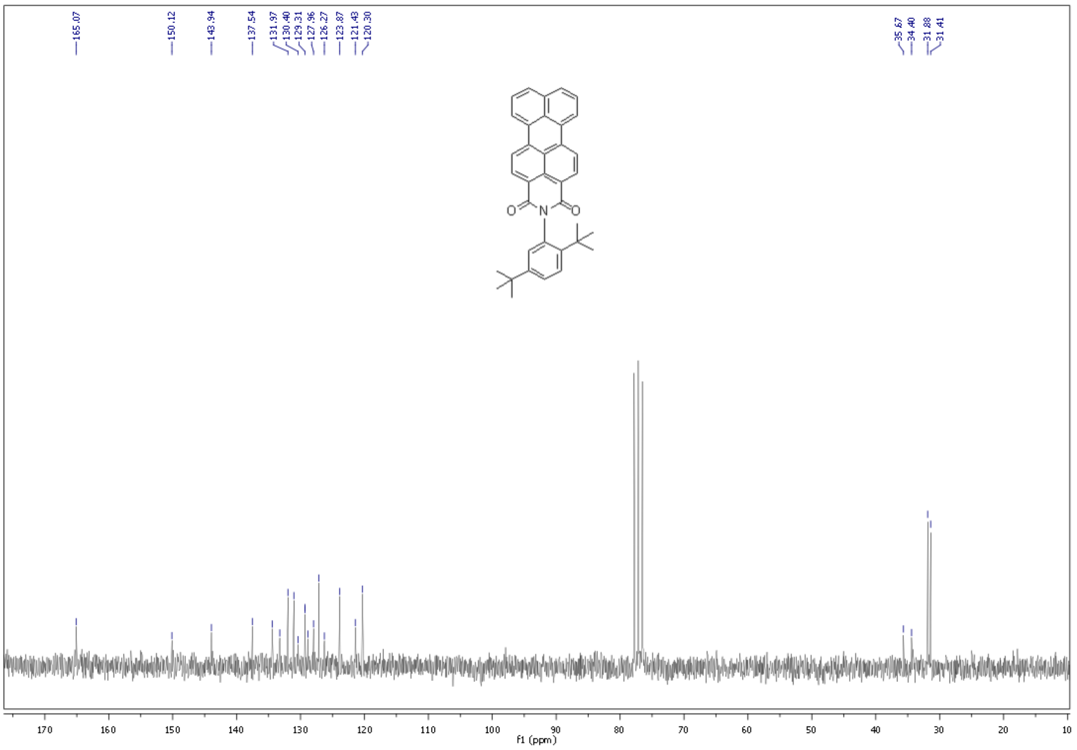
200 MHz ^{19}F NMR ($CDCl_3$) spectrum of bis(1H, 1H, 2H, 2H-perfluorooctyl)amine (**3**).



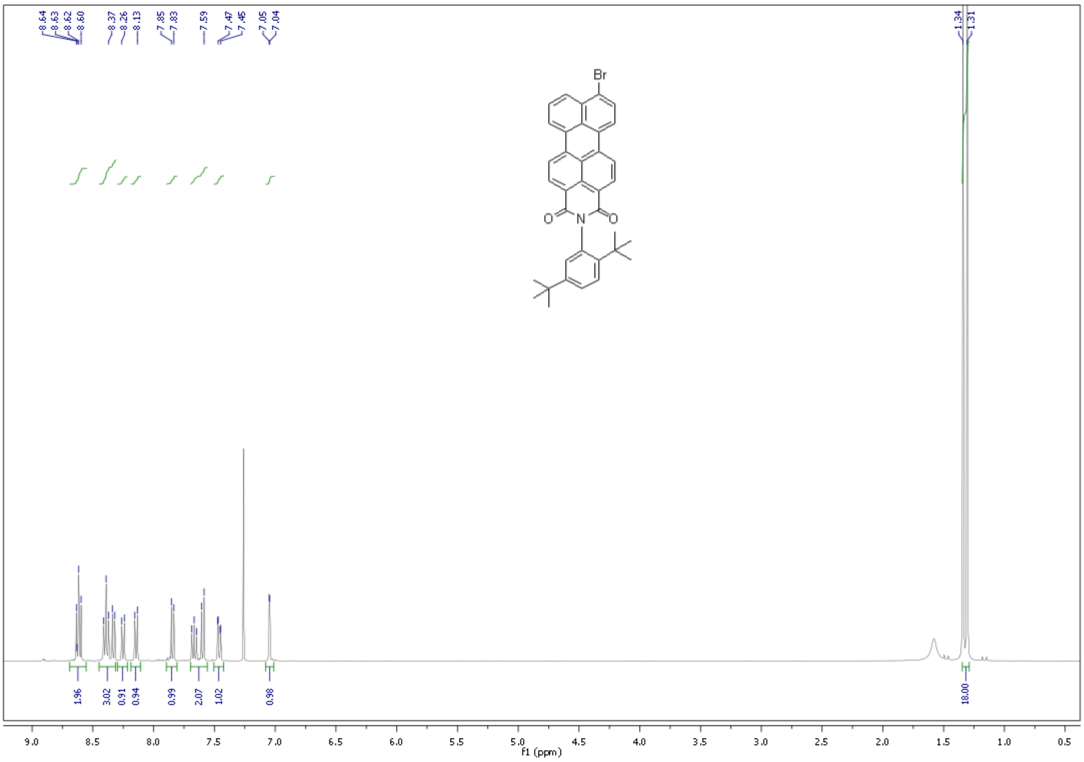
400 MHz ^{1}H NMR ($CDCl_3$) spectrum of *N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboxImide (**6**).



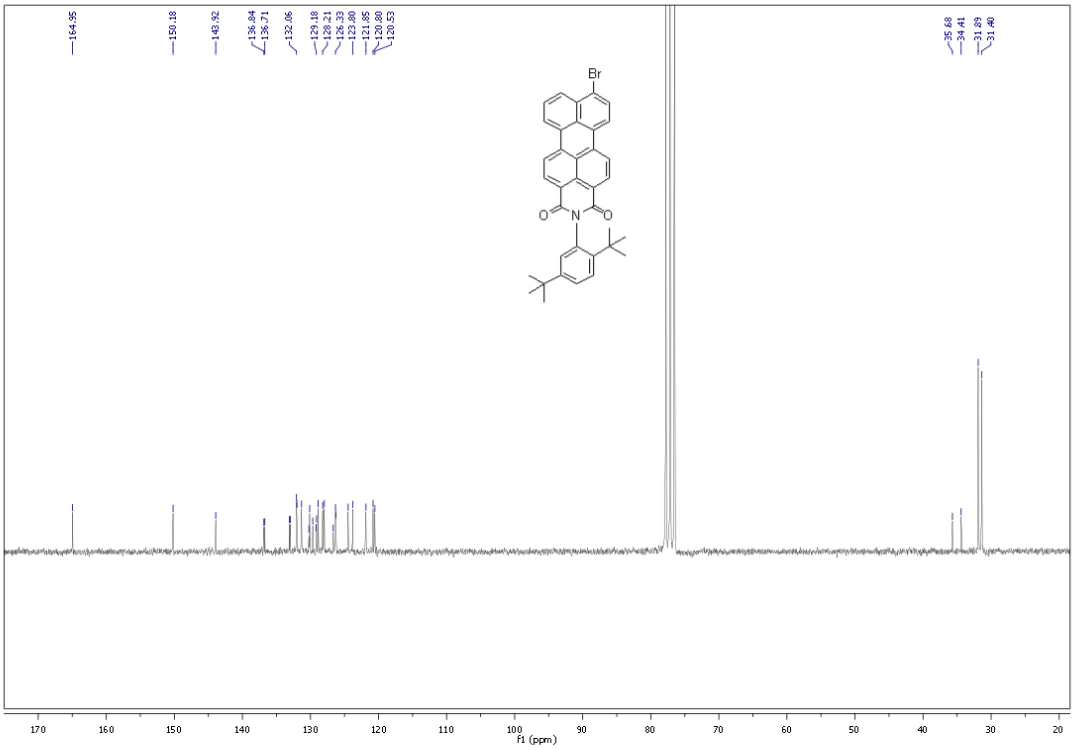
50 MHz ^{13}C NMR ($CDCl_3$) spectrum of *N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (**6**).



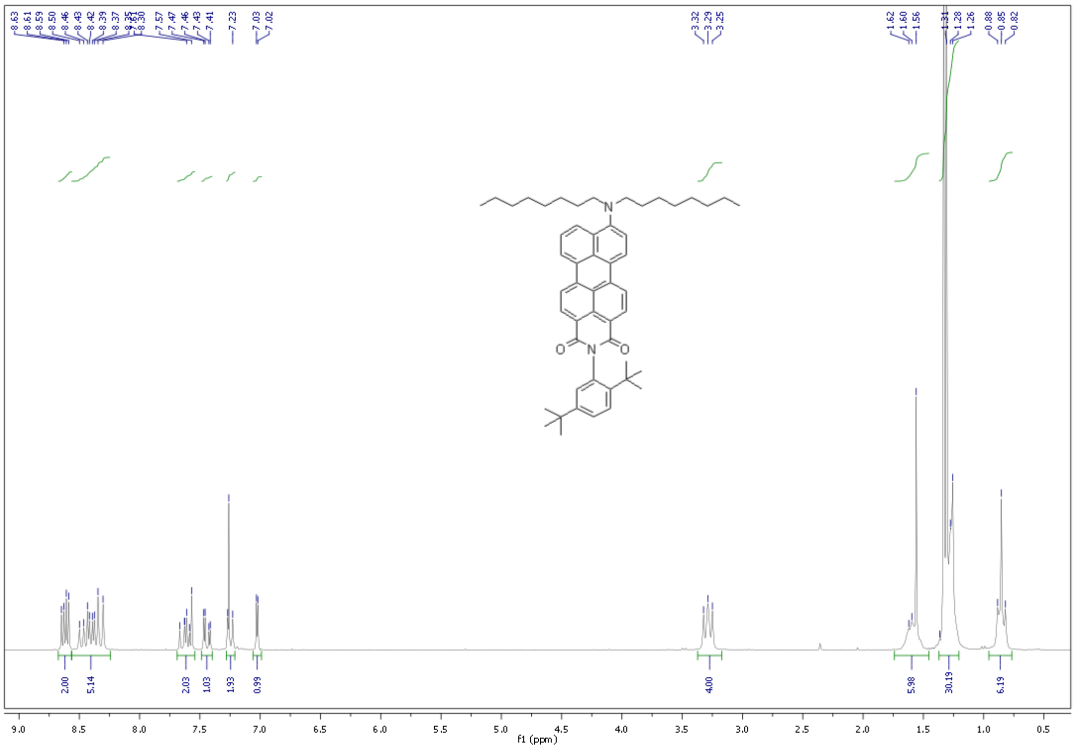
400 MHz ^{1}H NMR ($CDCl_3$) spectrum of 9-bromo-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (**7**).



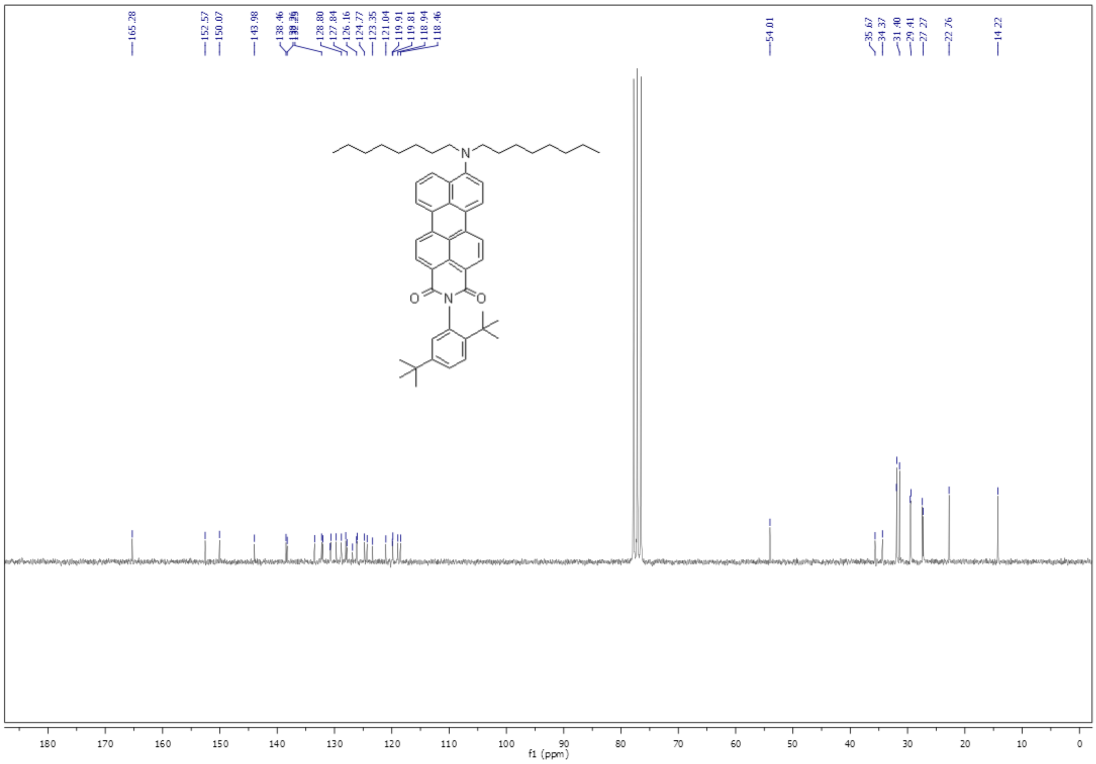
50 MHz ^{13}C NMR ($CDCl_3$) spectrum of 9-bromo-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (**7**).



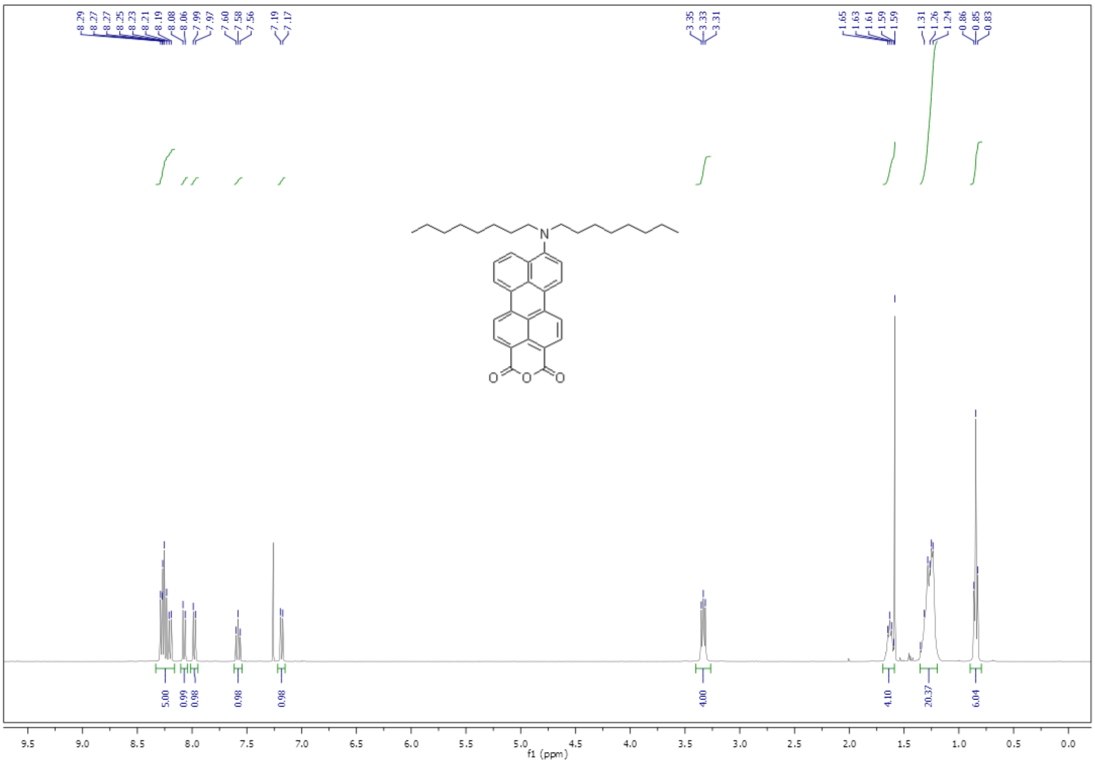
400 MHz ^1H NMR ($CDCl_3$) spectrum of 9-dioctylamino-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (**8**).



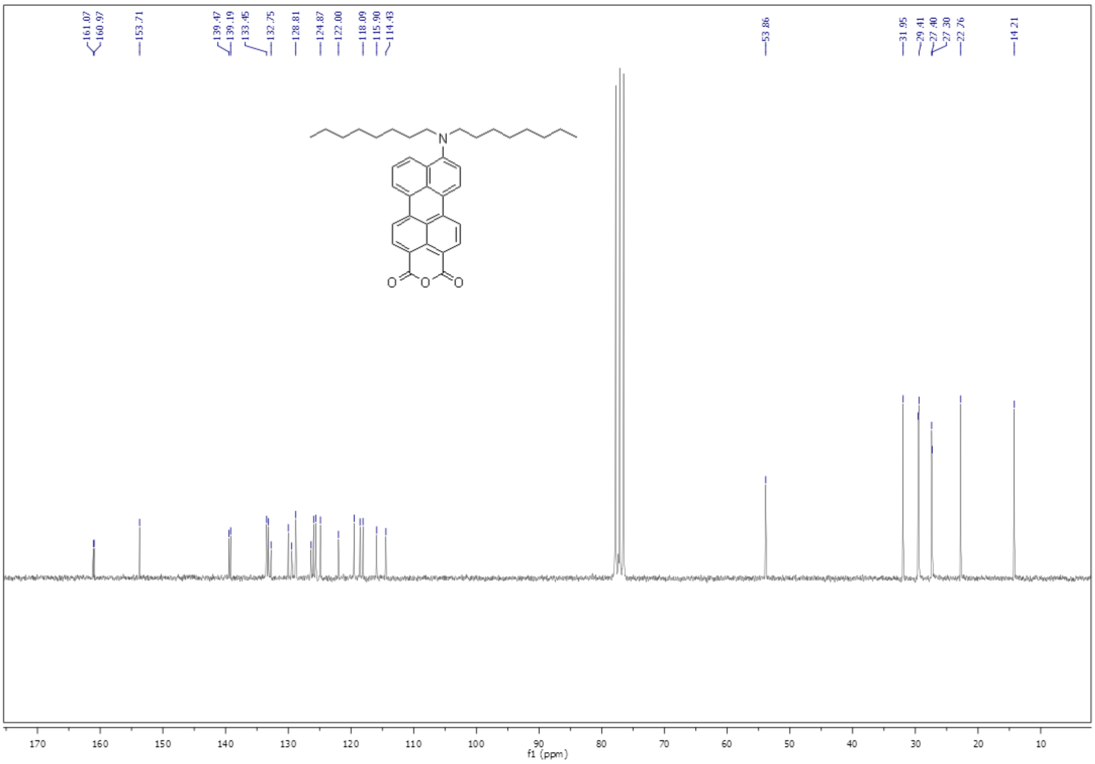
50 MHz ^{13}C NMR ($CDCl_3$) spectrum of 9-dioctylamino-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (**8**).



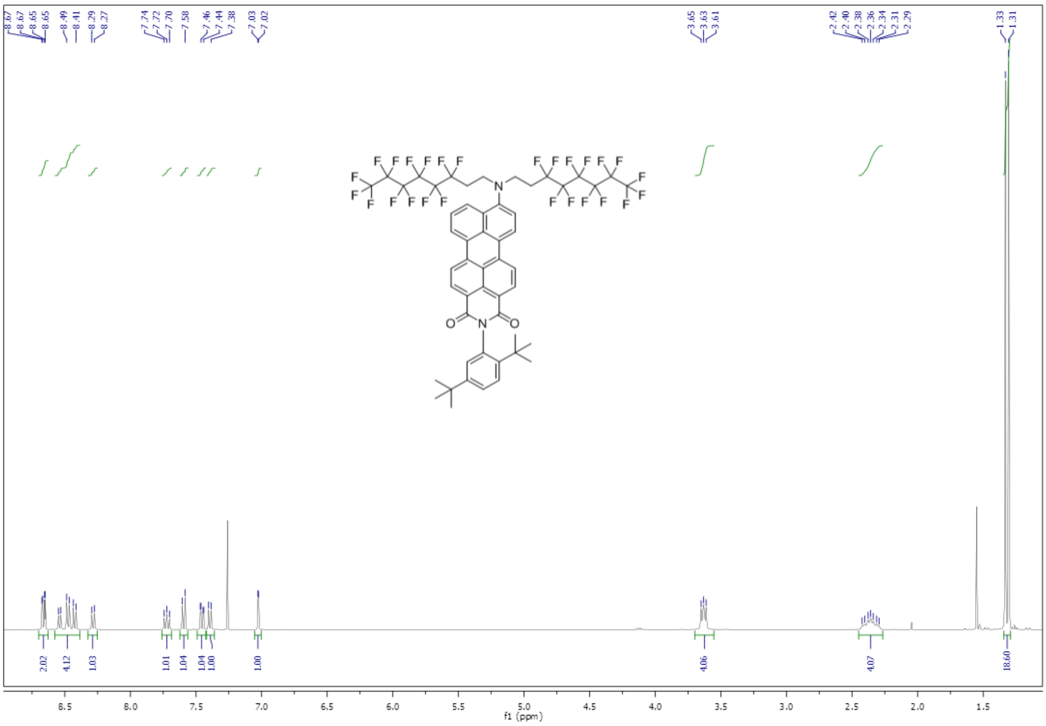
400 MHz ^{1}H NMR ($CDCl_3$) spectrum of 9-dioctylamino-perylene-3,4-dicarboxy anhydride (**DOP**) (**10**).



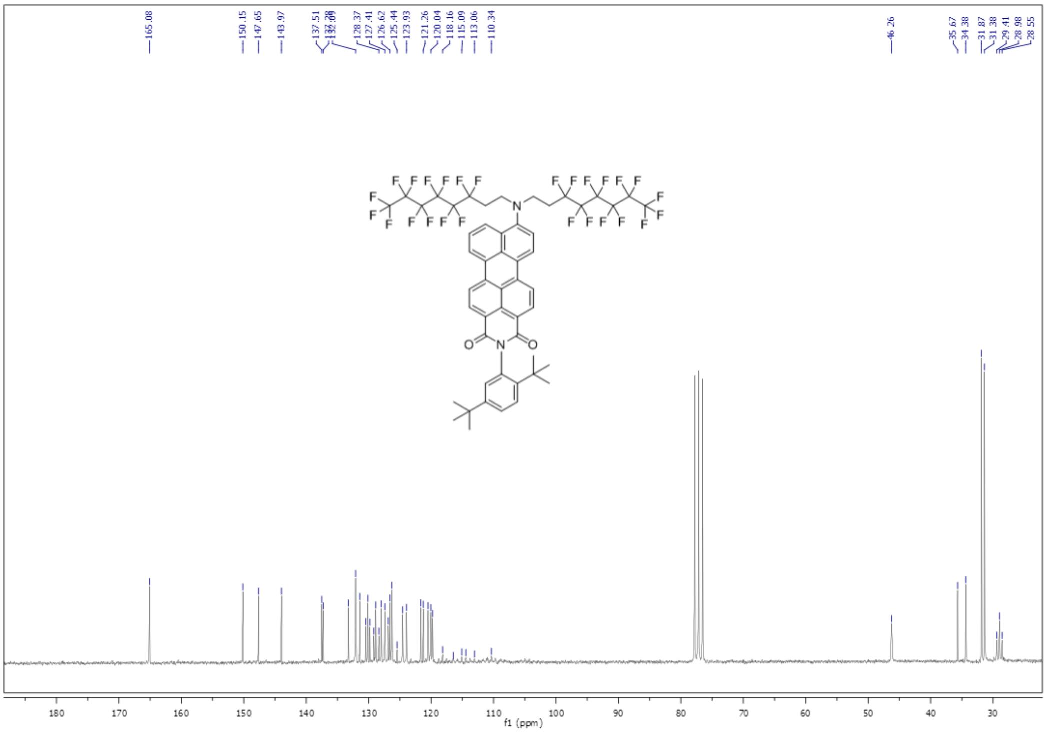
50 MHz ^{13}C NMR ($CDCl_3$) spectrum of 9-dioctylamino-perylene-3,4-dicarboxy anhydride (**DOP**) (**10**).



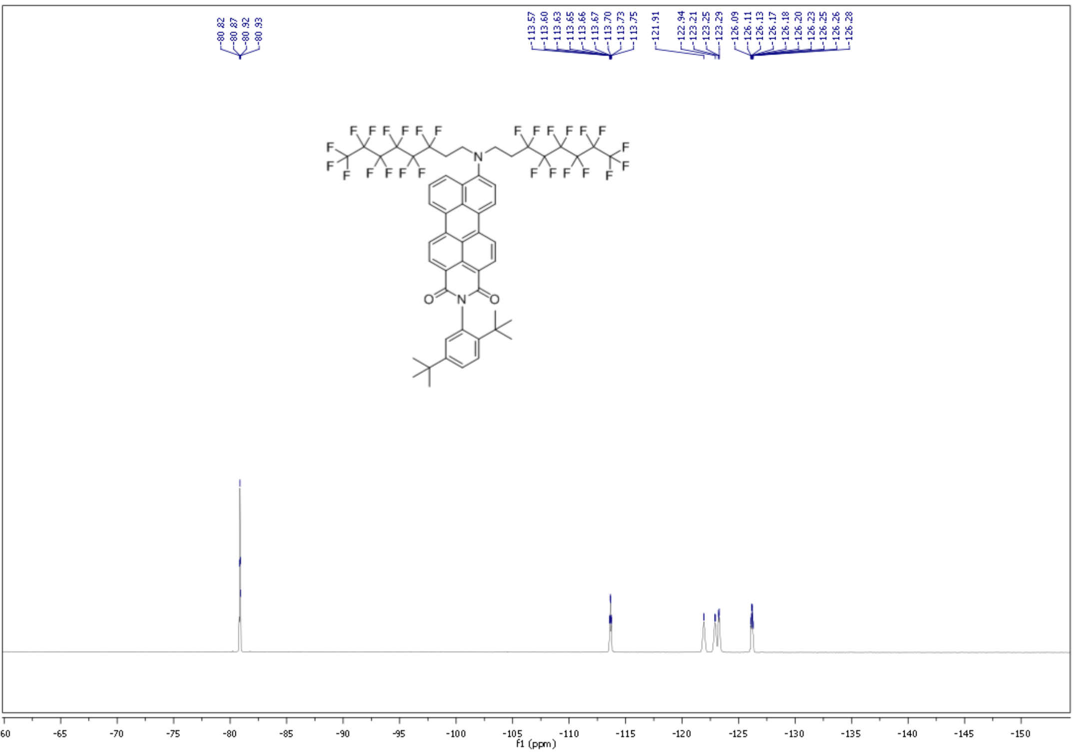
400 MHz ^{1}H NMR ($CDCl_3$) spectrum of 9-(*N*,*N*-di(1H,1H,2H,2H-perfluorooctyl)amino)-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (**9**).



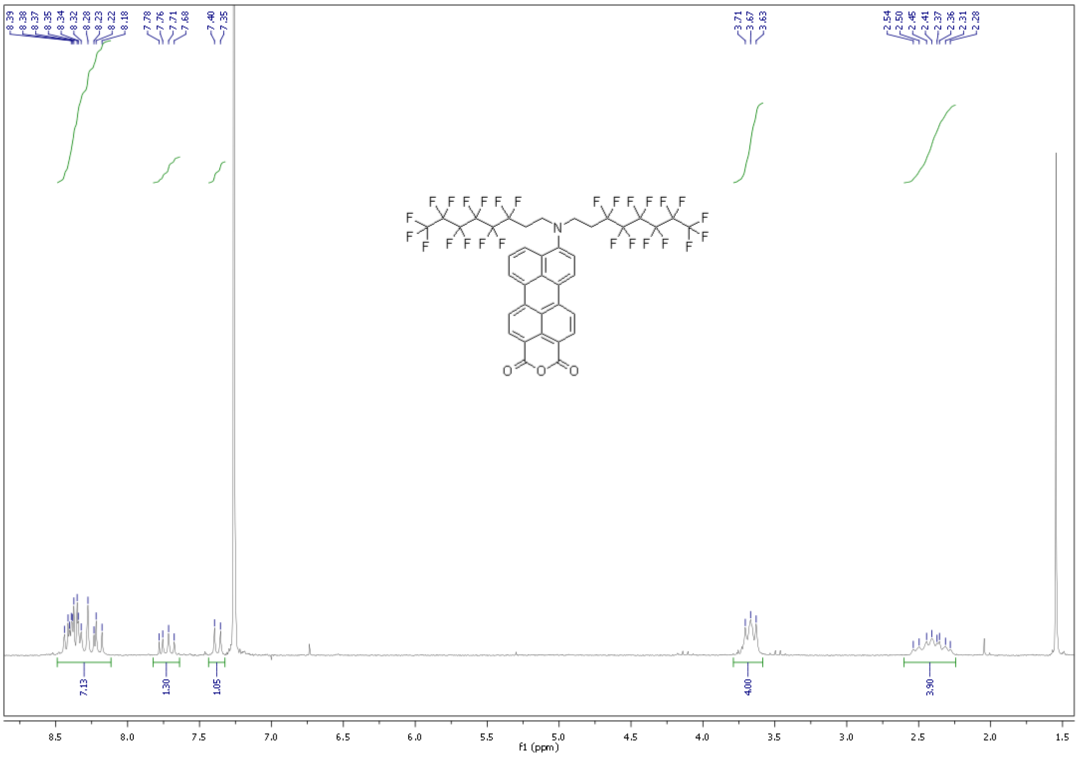
50 MHz ^{13}C NMR ($CDCl_3$) spectrum of 9-(*N*,*N*-di(1H,1H,2H,2H-perfluorooctyl)amino)-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (**9**).



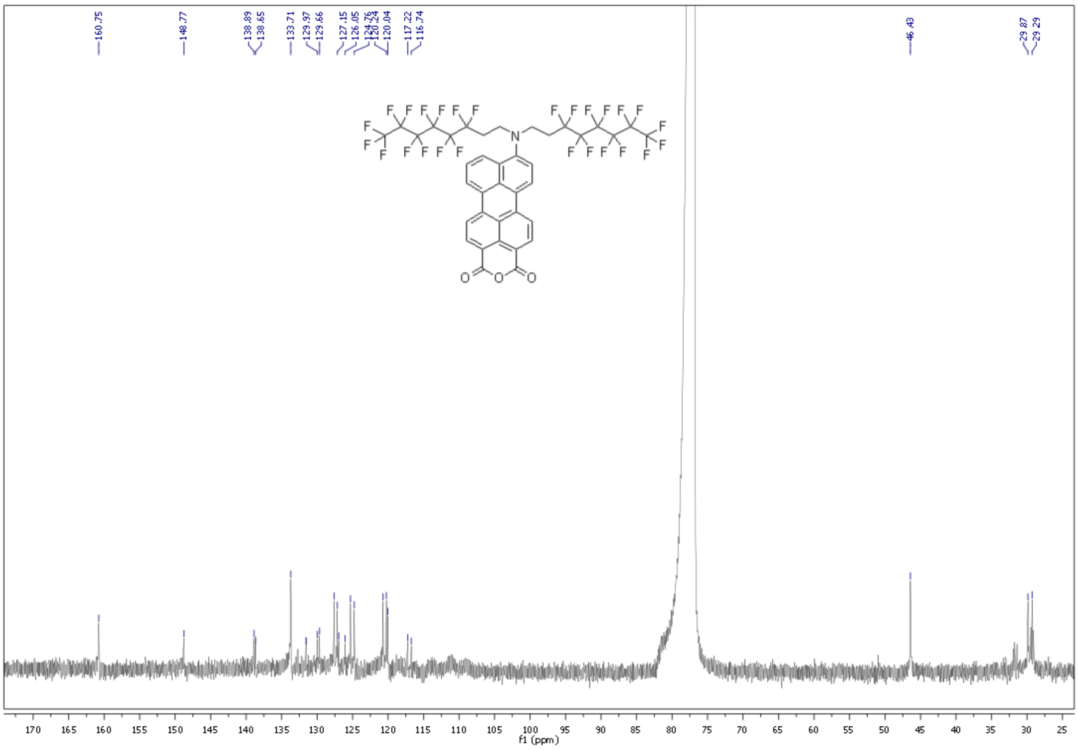
200 MHz ^{19}F NMR ($CDCl_3$) spectrum of 9-(*N*,*N*-di(1H,1H,2H,2H-perfluorooctyl)amino)-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (**9**).



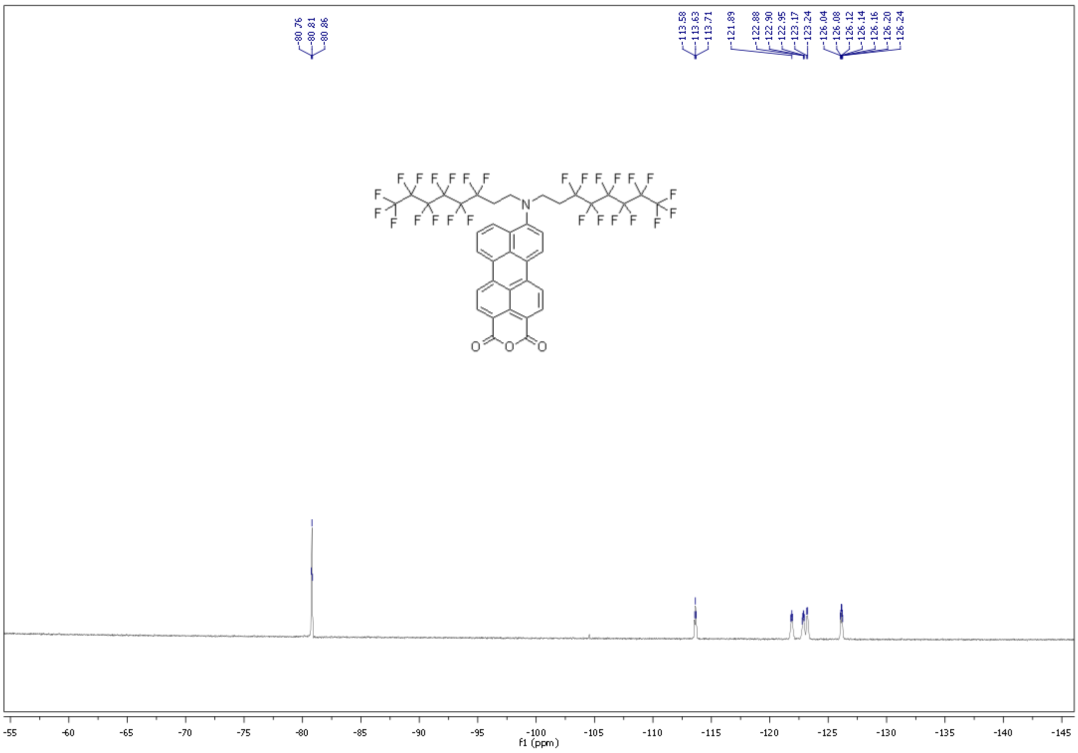
200 MHz ^{1}H NMR ($CDCl_3$) spectrum of 9-(*N*,*N*-di(1H,1H,2H,2H-perfluorooctyl)amino)-perylene-3,4-dicarboxy anhydride (**DOFP**) (**11**).



125 MHz ^{1}H NMR ($CDCl_3$, 50 °C) spectrum of 9-(*N,N*-di(1H,1H,2H,2H-perfluorooctyl)amino)-perylene-3,4-dicarboxy anhydride (**DOFP**) (**11**).

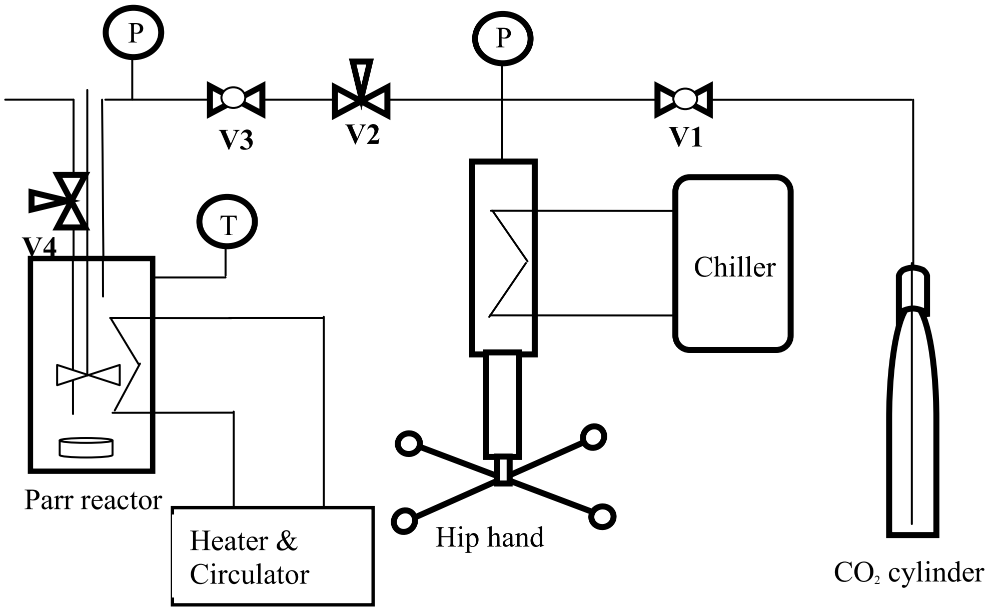


200 MHz ^{19}F NMR ($CDCl_3$) spectrum of 9-(*N,N*-di(1H,1H,2H,2H-perfluorooctyl)amino)-perylene-3,4-dicarboxy anhydride (**DOFP**) (**11**).



CO_2 Solubility Studies

The solubilities of the dyes (N3, N719, **DOP** (**10**) and **DOFP** (**11**)) in carbon dioxide were measured using a Static Precise Mass Measuring method[5] at 14 and 20 MPa and 50 °C (***Scheme S3***). A mass of dye (**DOP** (**10**), 56.166 mg and **DOFP** (**11**), 15.249 mg) was weighed into a sample pan with an accuracy of 0.001 mg (Mettler MT5, Mettler, Switzerland). The sample pan was then covered by a pan cover and placed inside a 50 mL pressure vessel (Parr Instrument Co, USA). The pan and pan cover were made in-house from glass and have diameters of 15 and 22 mm, respectively. The pan cover is 12 mm in height and has arches on its sides to allow CO_2 to diffuse in and out. A schematic of the experimental set-up is shown in the figure below:



Scheme S3. *Apparatus for measuring solubility in CO_2*

The temperature in the pressure vessel was raised to the desired value by recycling heated water through the jacket of the vessel (Tecam circulator C-40). Carbon dioxide (≥ 99.9% v/v, liquid withdrawal, BOC, UK) passed through a drying tube containing molecular sieve 5A to remove any water and was pumped into the vessel using a manual pressure generator (HIP 62-6-10, High Pressure Equipment Company USA**)** to the desired pressure value. The pressure was recorded using a transducer (Druck PTX 1400) with a dedicated display to within 0.1 bar, and the temperature was recorded to within 0.1 °C using a J-type thermocouple. A stirrer (RZR2020, Heidolph Instruments GmbH & Co. KG, Germany) was fitted to the pressure vessel and was operated at 130 rpm. This enabled CO_2 to contact the sample by passing through the arch of the pan cover. After a 4 hour equilibration, the CO_2 became saturated with the dye solute. The stirrer was turned off and the CO_2 vented and measured using a wet test meter (Model DM3A, Alexander Wright, UK). The pan containing dye that had not been solubilised was removed from the vessel and weighed. The mass loss from the dye was calculated, and hence its solubility in CO_2. During depressurisation most of the dissolved sample will precipitate in the vessel, however, the special pan cover allows the dissolved sample to precipitate on top of it, but prevents the precipitate from returning into the sample pan.

The solubility data at 50 °C for the four dyes and reference compound, *p*-tolylboronic acid (*p*TBA) are shown in the table below. The data are expressed as mg solute/Kg CO_2.

Dye	**Solubility of dye in $scCO_2$ (mg/kg)**
	14 (MPa)
N3	*
N719	*
DOP	0.1
DOFP	3.3
pTBA	40.5

* no recordable solubility

***Table S1**. $scCO_2$ solubility data measured at 14 and 20 MPa at 50 °C*

At constant temperature the solubility of **DOFP** increases with an increase of pressure. This behaviour can be attributed to higher CO_2 density which increased from 0.672 to 0.784 g/cm^3 at the respective pressures, and therefore would have led to higher solute loading in the CO_2. The density of CO_2 was obtained from NIST.[6]

UV-Visible Data

UV/Visible spectra are measured using a UV-Vis-NIR Cary 5E Varian Spectrophotometer in spectroscopic grade solvents.

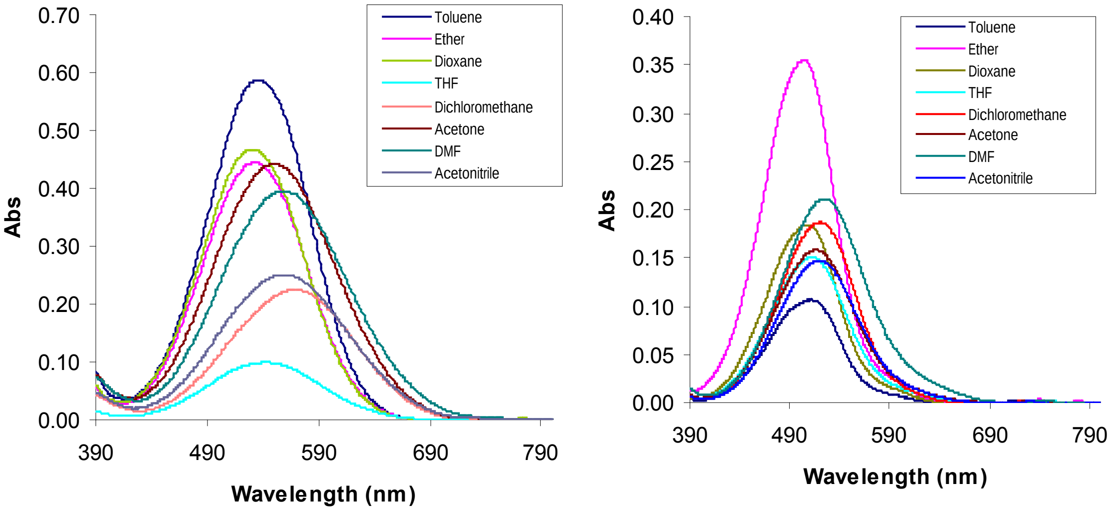


Figure S1. *Absorption spectra of* ***DOP (10)*** *(left) and* ***DOFP (11)*** *(right) in various organic solvents (0.12 mM).*

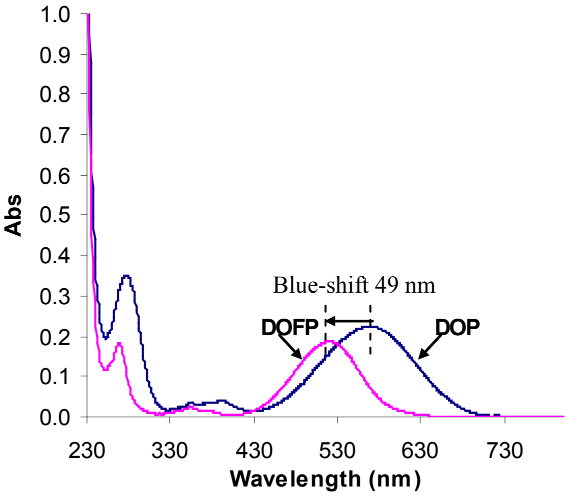


Figure S2. *Example of absorption spectra of* ***DOP (10)*** *and* ***DOFP (11)*** *in CH_2Cl_2 at 0.12 mM.*

Solvent	**DOP**		**DOFP**	
	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)
Toluene	536	4892	511	887
Ether	532	3700	503	2957
Dioxane	530	3884	509	1537
THF	539	820	511	1255
CH_2Cl_2	570	1870	521	1556
Acetone	552	3676	516	1319
DMF	559	3283	523	1759
CH_3CN	558	2092	519	1226

Table S2. *Spectroscopic data of* ***DOP*** *(**10**) and* ***DOFP*** *(**11**) in various organic solvents*

UV-Vis spectra of **DOP** (**10**) and **DOFP** (**11**) in various solvents showed a solvatochromic effect (Figure S1) and the λ_{max} values are summarized in Table 1. All the spectra show a peak at 500-570 nm which is assigned to the $\pi \rightarrow \pi^*$ transition.

Electrochemical Data

Cyclic voltammetry (CV) was performed on a Powerlab ML160 potentiostat interfaced via a Powerlab 4/20 controller to a PC running Echem for Windows. Measurements were run in argon-purged dichloromethane (CH_2Cl_2) with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) as the supporting electrolyte. The voltammograms were recorded at room temperature by utilizing glassy carbon (2.0 mm diameter) as the working electrode, platinum (1.5 mm diameter) as the counter electrode and silver wire pseudoreference electrode internally calibrated with ferrocene/ferrocenium (Fc/Fc^+). The silver wire was cleaned in concentrated nitric acid and then in concentrated hydrochloric acid to generate the Ag/Ag^+ reference. Voltammograms were recorded between 2000 and -1900 mV at different scan rates (50–200 mV/s) and some typical voltammograms, recorded at a scan rate 100 mV/s are shown. The half-wave reduction or oxidation potential $E_{1/2}$ for the compounds were calculated by averaging the corresponding anodic and cathodic peak potentials listed, $E_{1/2} = E_{1/2ox/red} - E_{1/2\ Fc/Fc+}$. The HOMO and LUMO energy levels, and band gap were determined from $E_{HOMO} = -[(E_{1/2ox} - E_{1/2\ Fc/Fc+}) + 4.80]$ eV, $E_{LUMO} = -[(E_{1/2red} - E_{1/2\ Fc/Fc+}) + 4.80]$ and $E_{LUMO} = E_{HOMO} + E_g$ respectively.

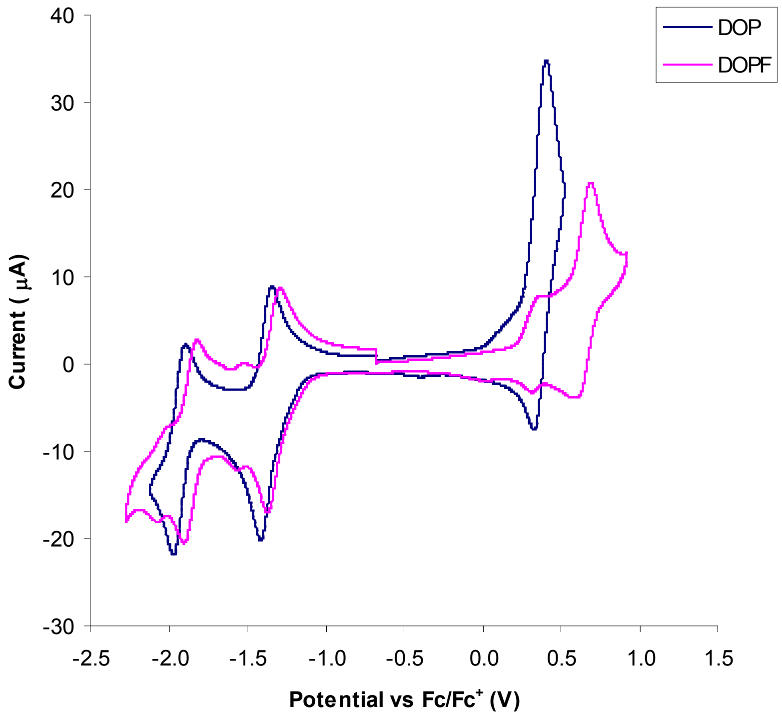


Figure S3. *Cyclic voltammograms of **DOP (10)** and **DOFP (11)** perylene dyes.*

Dye	$E_{1/2}$[a]				HOMO (eV)[b]	E_g (eV)[d]	LUMO (eV)[c]
	E_{ox}^{1}	E_{ox}^{2}	E_{red}^{1}	E_{red}^{2}			
DOP	0.37	-	-1.32	-1.93	-5.17	1.69	-3.48
DOFP	0.31	0.63	-1.39	-1.86	-5.11	1.70	-3.41

[a] Half wave potential determined as the average of the anodic and cathodic peak potentials vs ferrocene; [b] $E_{HOMO} = -[(E_{1/2ox} - E_{1/2\ Fc/Fc+}) + 4.8]$ eV; [c] $E_{LUMO} = -[(E_{1/2red} - E_{1/2\ Fc/Fc+}) + 4.8]$;[7] [d] $E_{LUMO} = E_{HOMO} + E_g$; E_{ox}^{1} and E_{ox}^{2}, first and second half wave oxidation potentials respectively; E_{red}^{1} and E_{red}^{2}, first and second half wave reduction potentials respectively (see Supporting Information).

Table S3. *Cyclic voltammetry data for **DOP (10)** and **DOFP (11)**.*

Fabrication and Characterization of DSSC

Commercially available Dyesol (MS001610) fluorine doped-tin oxide (FTO) glass substrate with pre-sintered nanocrystalline titanium dioxide (TiO_2) semi-conductor layer (photoanode dimension - 8 mm × 11 mm, 0.88 cm^2, 13-14 μm thick) were used.

Two methods were employed to deposit dyes onto the TiO_2 photoanodes; conventional method using commercial organic solvents and liquid/supercritical carbon dioxide ($scCO_2$). An average of two or more cells were obtained for each experiment.

***Conventional method**:* the pre-sintered titania photoanodes were reactivated by heating at 450 °C for 30 minutes in air, before cooling and immersing into a solvent containing the dye (0.5 mM) for 15 hours in the dark. The photoanode was removed after this period, rinsed with CH_3CN and dried with a stream of nitrogen gas.

***Caution!* All high pressure supercritical carbon dioxide ($scCO_2$) reactions should be carried out with adequate containment and with extreme caution.**

***Supercritical carbon dioxide ($scCO_2$)**:* generally the titania photoanodes were used as obtained from the manufacturer without heating, unless otherwise stated in the communication. A specific amount of dye (5-20 mg) was placed at the bottom of the reaction vessel and the titania photoanodes were placed in a vertical position on a stainless steel platform. The reaction vessel was charged with liquid CO_2, and using a controller the temperature and pressure were raised to set conditions (i.e. 50 °C and 14 MPa) to achieve supercritical conditions. After exposure for a defined time, the reaction vessel is switched off, left to rest and then the vessel slowly vented, while still at temperatures above 40 °C (it is still at supercritical when vented) to minimize disruption of the contents within the reactor. This $scCO_2$ reaction vessel (Model 4596 Pressure Reaction Apparatus, 25 mL Parr Micro Reactor fitted with rupture disc 5000 psi) has a sapphire windows that enable inspection of the TiO_2 photoanodes and color of the subcritical and supercritical $scCO_2$ solvent.

Carbon dioxide (BOC >99.5% - further purified over an Oxisorb catalyst) was delivered to the reaction using a Jasco PU-2080 CO_2 Plus air driven pump at the desired pressure. Heating of the reaction was achieved by using heating mantels fitted on the vessel. To allow elevated heating, the vessel is equipped with cooling water. The system pressure was measured by a pressure transducer (A105, RDP Electronics) and displayed on a digital display (E308, RDP Electronics). The internal temperature was monitored with thermocouple (Type J, RS Electronics) and displayed on a Parr 4836 Series Controller. The reaction was stirred at 330 rpm using a magnetic stirrer bar controlled by a laboratory stir/hot plate.

Sandwich-type dye sensitised solar cells were constructed using the dye coated titania photoanode and platinum (20 nm) on indium-tin oxide (ITO) glass as counter electrodes. To prepare the counter electrode, the ITO glass (Part No. CB-50IN-1511) was first cut into 2.5 × 2.0 cm^2 pieces. A small hole was drilled through the glass using an electric-powered drill fitted with a dental burst. The ITO glasses was cleaned with several solutions aided with sonication in the following order; a 1:1 mixture of 32% ammonia solution:hydrogen peroxide solution, 10% aqueous Decon 90 and finally distilled water at 20 minutes for each cycle, and then dried. The ITO glass was then coated with platinum using a sputter coater.

A 25 μm thick, polymer film (SX 1170-25, Solaronix) was placed between the TiO_2 photoanode and the platinum counter electrode. These components were then placed on a hotplate, with the platinum counter electrode face down, at a temperature of ~120 °C so that the polymer spacer melts and seals the electrodes together.

The electrolyte was filled under vacuum through the small hole in the platinum counter electrode and closed by heat sealing with the 25 μm polymer film (SX 1170-25, Solaronix) and glass cover slip.

Electrolyte that was used: 0.6 M tetrabutylammonium iodide (98%, Aldrich), 0.1 M LiI (Hopkin & Williams Ltd), 0.05 M I_2 (99.8%, Aldrich) and 0.5 M 4-*t*-butylpyridine (99%, Aldrich) in CH_3CN.

The DSSC sample was placed in the dark for 24 hours, before taking the photovoltaic measurements. The DSSCs were tested using a 1000 W Solar simulator (Newport Ltd) equipped with an AM 1.5 G filter (Newport Ltd). The light intensity was adjusted to 100 mW cm^{-2} using a calibrated Si photodetector (PECSI01, Peccell Technologies, Inc.). A black mask with open area 1.30 cm^2 was attached to the photoanode facing the solar simulator. The current voltage curves are recorded using a source-measure unit (2400, Keithley Instruments), controlled by a custom-made Labview program. The voltage is swept from 850 mV to -30 mV in 5 mV steps. The settling time is 40 ms between each measurement point. Characterisation parameters, fill factor (FF), short circuit current (J_{sc}), open circuit voltage (V_{oc}) and energy conversion efficiency (ECE) were collected. The spectral response (IPCE) was measured using a 150 W Xenon lamp (Oriel) fitted with a monochromator (Cornerstone 260) as the monochromatic lights source. The illumination spot size was chosen to be smaller than the active area of the DSSC test cells. IPCE photocurrents were recorded under short-circuit conditions using a source-measure unit (2400 Keithley Instruments).

$scCO_2$ Batch Mode

a)

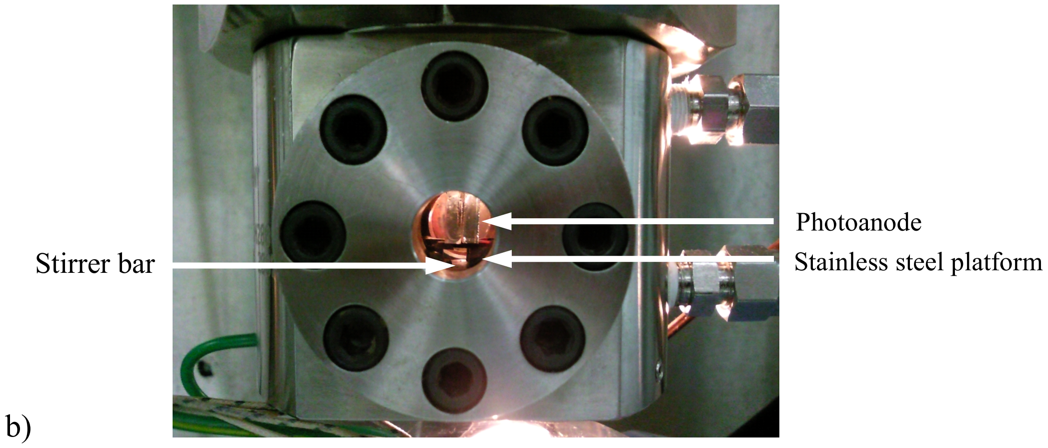


Figure S4. *a) Setup of the reactor for dye deposition, b) supercritical carbon dioxide ($scCO_2$) reactor with sapphire windows to observe the reaction.*

DSSC Performance Data

Dye	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	ECE (%)	Normalized Efficiency
DOP	535 ± 10.0	4.27 ± 0.09	0.54 ± 0.02	1.24 ± 0.04	1.00
DOFP	563 ± 7.5	4.03 ± 0.02	0.62 ± 0.01	1.41 ± 0.007	1.14

Table S4. *DSSC performance parameters of **DOP (10)** and **DOFP (11)** in conventional solvent deposition method.*

Dye	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	ECE (%)
DOFP	575 ± 2.5	3.70 ± 0.09	0.58 ± 0.01	1.25 ± 0.03

Table S5. *DSSC performance parameters of **DOFP (11)** in scCO$_2$ deposition method.*

Photoanode treatment	Solvent	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	ECE (%)	Normalised efficiency
Non pre-heated	CH_2Cl_2	2.97 ± 0.49	503 ± 12.5	0.57 ± 0.01	0.84 ± 0.15	1.00
Pre-heated	CH_2Cl_2	3.96 ± 0.01	515 ± 0.0	0.60 ± 0.01	1.22 ± 0.01	1.45
Non pre-heated	scCO$_2$	3.64 ± 0.09	548 ± 2.5	0.63 ± 0.01	1.24 ± 0.03	1.00
Pre-heated	scCO$_2$	3.56 ± 0.06	570 ± 5.0	0.63 ± 0.00	1.26 ± 0.04	1.02

Table S6. *DSSC performance parameters of **DOFP (11)** in conventional and scCO$_2$ deposition methods on pre-heated and non pre-heated photoanodes.*

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