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Supplementary information

Enhanced performance of dye-sensitized solar cells using carbazole-substituted di-chromophoric porphyrin dyes

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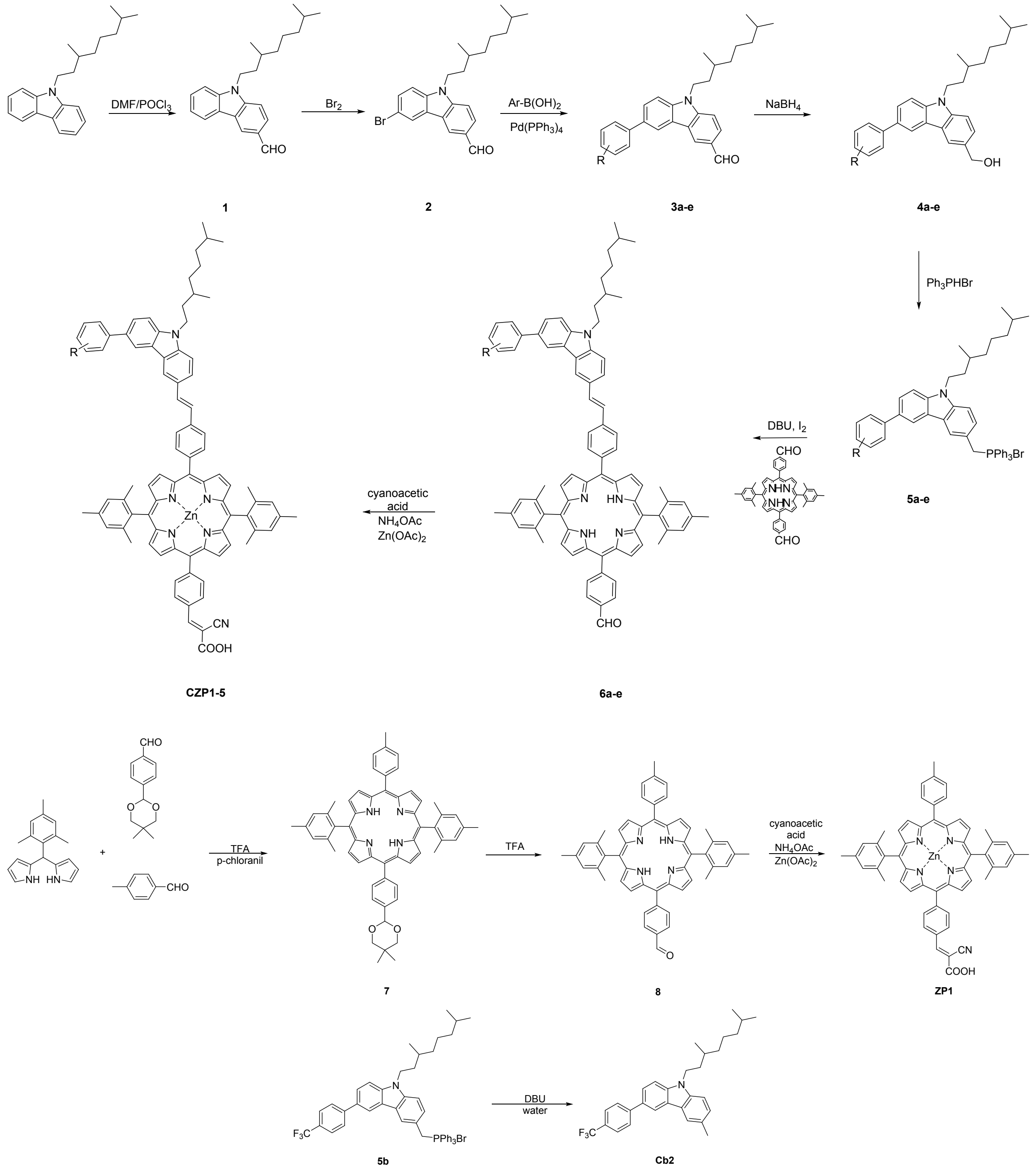
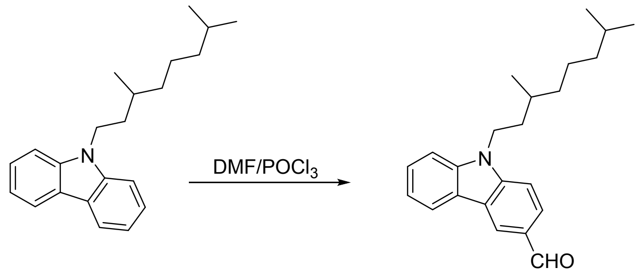
SI A. Synthesis



Scheme S1. The synthesis of investigated compounds.

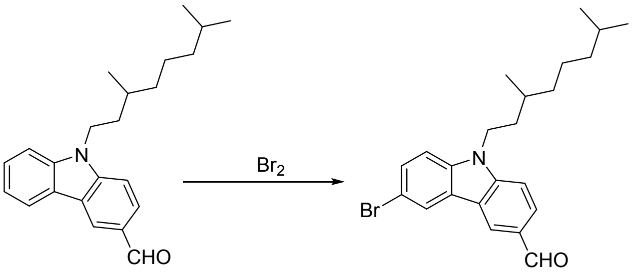
(9-(3,5-Dimethyloctyl)carbazole[1], 5,15-bis(4-formylphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin[2], 2,2’-(2,4,6-trimethylphenylmethylene)bispyrrol[3] and 4-(5,5,-dimethyl-1,3-dioxan-2-yl)benzaldehyde[4] were synthesised according to procedures reported before. All other chemicals were available commercially and used without additional purification, unless stated differently: phosphorous V oxychloride Aldrich 99%, sodium acetate BDH 99.0%, ethyl acetate Chem-Supply

99%, magnesium sulphate Scharlau 98%, dichloromethane Chem-Supply 99.8%, glacial acetic acid Ajax 99.7%, sodium hydrogencarbonate Ajax 99.7%,methanol Honeywell 99.9%, tetrahydrofuran Ajax 97%, sodium borohydride Aldrich 98.5%, toluene RCI Labscan 99.9, iodine Ajax 99.9%, cyanoacetic acid Aldrich 99%, ammonium acetate Chem-Supply 97%, 4-methylbenzaldehyde Sigma-Aldrich 97%, *p*-chloranil Fluka 97%, hexane Ajax 99%, ammonium hydroxide Ajax 28%, potassium carbonate Ajax 99.7%, hydrochloric acid RCI Labscan 32%, 1,8-diazabicyclo[5.4.0]undec-7-ene Aldrich 98%, tetrakis(triphenylphosphino)palladium (0) Sigma-Aldrich 99%, chloroform RCI Labscan 99.8%,sodium thiosulphate pentahydrate Chem-Supply 99.5%, triphenylphosphine hydrobromide, Sigma-Aldrich 97%, *p*-tolylboronic acid, Aldrich 97%, 4-methoxyphenylboronic acid Aldrich 95%, 4-(trifluoromethy)phenylboronic acid Aldrich 95%, 3-(trifluoromethy)phenylboronic acid Aldrich 95%, 4-(diphenylamino)phenylboronic acid Aldrich 95%. NMR spectra were recorded on Bruker Avance 400 spectrometer. The following abbreviations were used: s = singlet, d = doublet, dd = doublets of doublets, ddd = doublets of doublets of doublets, m = multiplet. All coupling constants J were measured in hertz (Hz). Chemical shifts are reported in parts-per-million (ppm). Tetramethylsilane was used as the internal reference. Mass spectra were recorded on Polaris Q or Hewlett Packard 5973. The synthetic procedures were not optimised.



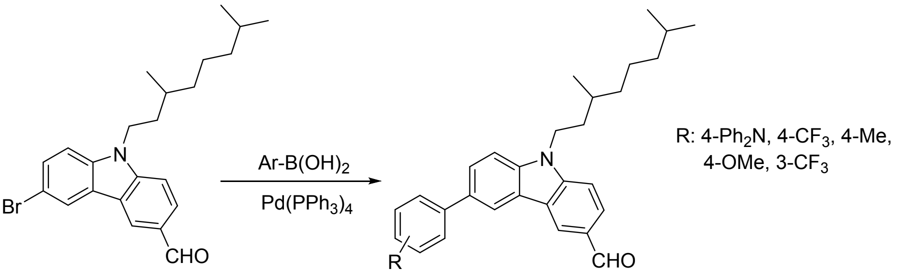
(9-(3,5-Dimethyloctyl)carbazole-3-carboxaldehyde (1): 9-(3,5-Dimethyloctyl)carbazole (10.18 g, 33 mmol) was dissolved in dry *N,N*-dimethylformamide (30 mL), then phosphorous oxychloride was added dropwise (6 mL, 24 mmol). The resulting mixture was stirred at 125°C for 1 h then poured into water solution of sodium acetate (60 mL, 20%). The mixture was extracted with ethyl acetate. The organic phase was separated, dried over magnesium sulphate and evaporated to dryness under reduced pressure at 50°C. The remaining viscous oil was purified on silica (dichloromethane) to give product as pale yellow oil (5.21 g, 47%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.09 (s, 1H, CHO), 8.61 (dd, 1H, J = 1.6 and 0.6 Hz, Carb-H4), 8.15 (ddd, 1H, J = 6.8, 1.2 and 0.6 Hz, Carb-H5), 8.00 (dd, 1H, J = 8.5 and 1.6 Hz, Carb H2), 7.53 (ddd, 1H, J = 8.2, 7.2 and 1.2 Hz, Carb-H6), 7.47-7.42 (m, 2H, Carb-H1, H7), 7.32 (ddd, J = 7.9, 7.2 and 1.0 Hz, Carb-H8), 4.42-4.27 (m, 2H, Alk), 1.93-1.83 (m, 1H, Alk), 1.74-1.63 (m, 1H, Alk), 1.61-1.51 (m, 2H, Alk), 1.42-1.09 (m, 6H, Alk), 1.04 (d, 3H, J = 6.6 Hz, CH_3), 0.85 (d, 3H, J = 6.7 Hz, CH_3), 0.84 (d, 3H, J = 6.7 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.7, 143.9, 141.1, 128.5, 127.2, 126.7, 124.0, 123.1, 123.0, 120.8, 120.3, 109,3, 108.8, 41.6, 39.2, 37.1, 35.6, 30.9, 27.9, 24.6, 22.6, 22.5, 19.7; HRMS (ESI, $(M+1)^+$): found: 336.2322, requires for $C_{23}H_{30}NO$: 336.2311.



6-Bromo-(9-(3,5-dimethyloctyl)carbazole-3-carboxaldehyde (2): (9-(3,5-Dimethyloctyl)carbazole-3-carboxaldehyde (5.20 g, 16 mmol) was dissolved in glacial acetic acid (35 mL) and cooled to 0°C then bromine (2.48 g, 16 mmol) dissolved in glacial acetic acid (10 mL) was added dropwise during 15 min. The resulting mixture was stirred at 0°C for additional 15 min. and afterwards evaporated to dryness under reduced pressure at 70°C. The remaining was dissolved in dichloromethane (50 mL) and washed with the saturated aqueous solution of sodium hydrogencarbonate. The organic layer was separated, dried over magnesium sulphate and filtered through pad of silica (dichloromethane). After solvent evaporation under vacuum at 50°C, product was obtained as pale yellow oil (5.72, 89 %) which solidified in the fridge.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.87 (s, 1H, CHO), 8.54 (dd, 1H, J = 1.6 and 0.6 Hz, Carb-H4), 8.26 (dd, 1H, J = 1.9 and 0.5 Hz, Carb-H5), 8.03 (dd, 1H, J = 8.6 and 1.6 Hz, Carb-H2), 7.61 (dd, 1H, J = 8.6 and 1.9 Hz, Carb-H7), 7.47-7.44 (m, Carb-H1), 7.31 (dd, 1H, J = 8.6 and 0.5 Hz, Carb-H8), 4.39-4.25 (m, 2H, Alk), 1.91-1.80 (m, 1H, Alk), 1.71-1.60 (m, 1H, Alk), 1.54-1.44 (m, 2H, Alk), 1.40-1.06 (m, 6H, Alk), 1.03 (d, 3H, J = 6.6 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.47, 144.08, 139.70, 129.45, 128.9, 127.5, 124.8, 124.4, 123.6, 122.1, 113.2, 110.7, 109.2, 41.8, 39.2, 37.1, 35.5, 30.9, 27.9, 24.6, 22.6, 22.5, 19.7; HRMS (ESI, $(M+1)^+$): found: 414.1405, requires for $C_{23}H_{29}BrNO$: 414.1427.



6-Aryl-(9-(3,5-dimethyloctyl)carbazole-3-carboxaldehyde (3a-e): 6-Bromo-(9-(3,5-dimethyloctyl)carbazole-3-carboxaldehyde (1.00 g, 2.4 mmol) and a boronic acid (3.6 mmol) were dissolved in dimethoxyethane and degassed under sonication. Aqueous solution of potassium carbonate (20 mL, 1M) was added followed by tetrakis(triphenylphosphino)palladium (0) (0.10 g, 4% M). The resulting mixture was stirred under argon at 90°C for 5 hrs. Afterwards, the reaction mixture was cooled down and diluted with ethyl acetate (50 mL). The organic phase was separated, dried over magnesium sulphate and evaporated to dryness under reduced pressure at 50°C. The remaining was purified on silica (dichloromethane).

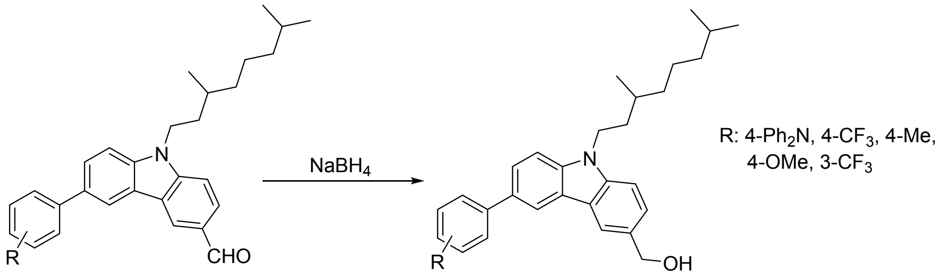
6-(4-(*N*,*N*-diphenylamino)phenyl)-(9-(3,5-dimethyloctyl)carbazole-3-carboxaldehyde (**3a, Cb1**): Yield: 95%; pale yellow amorphous solid; ^1H NMR (400 MHz, $CDCl_3$) δ: 10.10 (s, 1H, CHO), 8.64 (dd, 1H, J = 1.6 and 0.6 Hz, Carb-H4), 8.34 (dd, 1H, J = 1.9 and 0.6 Hz, Carb-H5), 8.02 (dd, 1H, J = 8.6 and 1.6 Hz, Carb-H2), 7.75 (dd, 1H, J = 8.5 and 1.9 Hz, Carb-H7), 7.60-7.56 (m, 2H, Ar), 7.50-7.45 (m, 2H, Carb-H1, H8), 7.31-7.25 (m, 4H, Ph), 7.22-7.14 (m, 6H, Ph, Ar), 7.07-7.01 (m, 2H, Ph), 4.44-4.29 (m, 2H, Alk), 1.97-1.85 (m, 1H, Alk), 1.78-1.64 (m, 1H, Alk), 1.57-1.44 (m, 2H, Alk), 1.43-1.09 (m, 6H, Alk), 1.06 (d, J = 6.5 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.6, 147.8, 146.8, 144.3, 135.7, 133.5, 129.3, 128.6, 127.9, 125.9, 124.3, 124.2, 124.1, 123.6, 123.3, 122.8, 118.7, 109.5, 109.0, 41.7, 39.2, 37.1, 35.6, 30.9, 27.9, 24.6, 22.6, 22.5, 19.7; HRMS (ESI, $(M+1)^+$): found: 579.3370, requires for $C_{41}H_{43}N_2O$: 579.3297.

6-(4-Trifluoromethylphenyl)-(9-(3,5-dimethyloctyl)carbazole-3-carboxaldehyde (3b): Yield: 86%; white-off waxy solid; ^1H NMR (400 MHz, $CDCl_3$) δ: 10.12 (s, 1H, CHO), 8.67 (dd, 1H, J = 1.6 and 0.6 Hz, Carb-H4), 8.38 (dd, 1H, J = 1.9 and 0.6 Hz, Carb-H5), 8.05 (dd, 1H, J = 8.6 and 1.6 Hz, Carb-H2), 7.82-7.80 (m, 2H, Ar), 7.78 (dd, 1H, J = 8.6 and 1.9 Hz, Carb-H7), 7.75-7.72 (m, 2H, Ar), 7.53 (dd, 1H, J = 8.6 and 0.6 Hz, Carb-H8), 7.51-7.48 (m, 1H, Carb-H1), 4.46-4.31 (m, 2H, Alk), 1.97-1.86 (m, 1H, Alk), 1.77-1.66 (m, 1H, Alk), 1.55-1.45 (m, 2H, Alk), 1.43-1.10 (m, 6H, Alk), 1.06 (d, 3H, J = 6.6 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.6, 141.0, 132.3, 128.9, 127.5, 127.4, 126.2, 125.8, 125.7, 124.1, 123.2, 119.5, 109.8, 109.1, 41.8, 39.2, 37.1, 35.6, 30.9, 27.9, 24.6, 22.6, 22.5, 19.8; HRMS (ESI, $(M+1)^+$): found: 480.2490, requires for $C_{30}H_{33}F_3NO$: 480.2509.

6-(4-Methylphenyl)-(9-(3,5-dimethyloctyl)carbazole-3-carboxaldehyde (**3c**): Yield: 86%; pale yellow oil which solidifies with time; ^1H NMR (400 MHz, $CDCl_3$) δ: 10.10 (s, 1H, CHO), 8.64 (dd, 1H, J = 1.6 and 0.6 Hz, Carb-H4), 8.34 (dd, 1H, 1.8 and 0.6 Hz, Carb-H5), 8.01 (dd, 1H, J = 8.6 and 1.6 Hz, Carb-H2), 7.56 (dd, 1H, J = 8.5 and 1.8 Hz, Carb-H7), 7.62-7-58 (m, 2H, Ar), 7.48 (dd, 1H, J = 8.6 and 1.6 Hz, Carb-H8), 7.48-7.45 (m, 1H, Carb-H1), 7.31-7.28 (m, 2H, Ar), 4.43-4.29 (m, 2H, Alk), 2.43 (s, 3H, Ar-CH_3), 1.96-1.85 (m, 1H, Alk), 1.75-1.64 (m, 1H, Alk), 1.55-1.46 (m, 2H, Alk), 1.44-1.09 (m, 6H, Alk), 1.06 (d, 3H, J = 6.6 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.7, 144.3, 140.4, 138.8, 136.6, 133.9, 129.6, 128.6, 127.2, 127.1, 126.1, 124.2, 123.3, 119.0, 109.5, 109.0, 41.7, 39.2, 37.1, 35.7, 31.0, 28.0, 24.6, 22.7, 22.6, 19.7; HRMS (ESI, $(M+1)^+$): found: 426.2814, requires for $C_{30}H_{36}NO$: 426.2791.

6-(4-Methoxylphenyl)-(9-(3,5-dimethyloctyl)carbazole-3-carboxaldehyde (**3d**): Yield: 98%; pale yellow oil which solidifies with time; ^1H NMR (400 MHz, $CDCl_3$) δ: 10.10 (s, 1H, CHO), 8.64 (dd, 1H, J = 1.6 and 0.5 Hz, Carb-H4), 8.31 (dd, 1H, 1.8 and 0.6 Hz, Carb-H5), 8.02 (dd, 1H, J = 8.5 and 1.6 Hz, Carb-H2), 7.73 (dd, 1H, J = 8.5 and 1.8 Hz, Carb-H7), 7.65-7-61 (m, 2H, Ar), 7.47 (dd, 1H, J = 8.5 and 1.8 Hz, Carb-H8), 7.47-7.45 (m, 1H, Carb-H1), 7.05-7.01 (m, 2H, Ar), 4.44-4.29 (m, 2H, Alk), 3.88 (s, 3H, OCH_3), 1.96-1.84 (m, 1H, Alk), 1.76-1.64 (m, 1H, Alk), 1.56-1.44 (m, 2H, Alk), 1.43-1.09 (m, 6H, Alk), 1.05 (d, 3H, J = 6.6 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.7, 159.0, 144.4, 140.2, 134.3, 128.7, 128.4, 127.2, 126.8, 126.0, 124.2, 123.6, 123.4, 118.8, 114.5, 109.5, 109.0, 55.4, 41.7, 39.2, 37.1, 35.7, 31.0, 28.0, 24.6, 22.7, 22.6, 19.8; HRMS (ESI, $(M+1)^+$): found: 442.2720, requires for $C_{30}H_{36}NO_2$: 442.2741.

6-(3-Trifluoromethylphenyl)-(9-(3,5-dimethyloctyl)carbazole-3-carboxaldehyde (**3e**): Yield: 91%; pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 10.12 (s, 1H, CHO), 8.67 (dd, 1H, J = 1.6 and 0.5 Hz, Carb-H4), 8.37 (dd, 1H, J = 1.8 and 0.5 Hz, Carb-H5), 8.05 (dd, 1H, J = 8.6 and 1.6 Hz, Carb-H2), 7.96-7.94 (m, 1H, Ar), 7.90-7.85 (m, 1H, Ar), 7.77 (dd, 1H, J = 8.5 and 1.8 Hz, Carb-H7), 7.64-7.57 (m, 2H, Ar), 7.53 (dd, 1H, J = 8.5 and 0.5 Hz, Carb-H8), 7.51-7.48 (m, 1H, Carb-H1), 4.46-4.31 (m, 2H, Alk), 1.98-1.85 (m, 1H, Alk), 1.78-1.65 (m, 1H, Alk), 1.56-1.45 (m, 2H, Alk), 1.43-1.09 (m, 6H, Alk), 1.06 (d, 3H, J = 6.6 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.6, 144.4, 142.4, 140.9, 132.3, 130.5, 129.3, 128.9, 127.4, 126.1, 124.2, 124.1, 124.0, 123.7, 123.4, 123.1, 119.4, 109.8, 109.1, 41.8, 39.2, 37.1, 35.6, 30.9, 27.9, 24.6, 22.6, 22.5, 19.8; HRMS (ESI, $(M+1)^+$): found: 480.2482, requires for $C_{30}H_{33}F_3NO$: 480.2509.



(6-Aryl-9-(3,7-dimethyloctyl)carbazol-3-yl)methanol (4a-e): 6-Aryl-(9-(3,5-dimethyloctyl)carbazole-3-carboxaldehyde (2.3 mmol) was dissolved in a mixture of tetrahydrofuran (15 mL) and methanol (5 mL), cooled to 0°C, and a solution of sodium borohydride (60 mg, 63.8 mmol) in aqueous sodium hydroxide (1.5 mL, 4%), was added dropwise. The resulting mixture was stirred at 0°C for 1hr then evaporated to dryness under vacuum at 50^{o}C. The remaining was filtered through pad of silica (dichloromethane) and evaporated to dryness under vacuum at 50^{o}C.

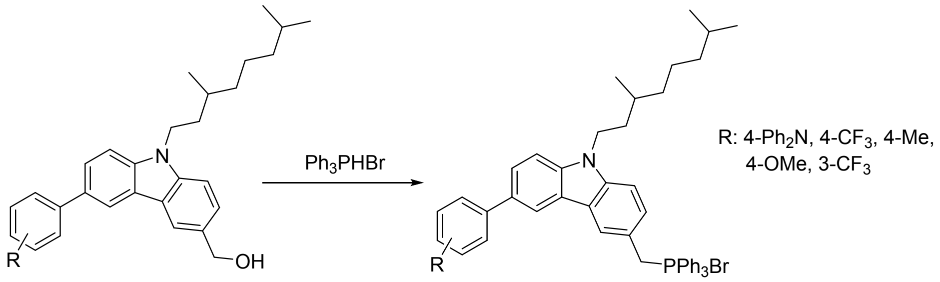
(6-(4-*N*,*N*-diphenylaminophenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)methanol (**4a**): Yield: 97 %, pale yellow amorphous solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (dd, 1H, J = 1.8 and 0.5 Hz, Carb-H4), 8.13 (dd, 1H, J = 1.6 and 0.6 Hz, Carb-H5), 7.69 (dd, 1H, J = 8.4 and 1.8 Hz, Carb-H2), 7.61-7.56 (m, 2H, Ar), 7.49 (dd, 1H, J = 8.4 and 1.6 Hz, Carb-H7), 7.43 (dd, 1H, J = 8.4 and 0.6 Hz, Carb-H1), 7.50-7.45 (m, 1H, Carb-H8), 7.31-7.25 (m, 4H, Ph), 7.21-7.13 (m, 6H, Ph, Ar), 7.05-7.01 (m, 2H, Ph), 4.86 (s, 2H, CH_2OH), 4.40-4.25 (m, 2H, Alk), 1.94-1.85 (m, 2H, Alk), 1.73-1.09 (m, 8H, Alk), 1.04 (d, J = 6.5 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.9, 146.4, 140.5, 140.0, 132.0, 131.6, 129.2, 127.9, 125.6, 125.0, 124.5, 124.2, 123.3, 123.2, 122.7, 119.5, 118.5, 108.9, 108.8, 66.2, 41.5, 39.2, 37.1, 35.6, 30.9, 27.9, 24.6, 22.7, 22.6, 19.8; HRMS (ESI, $(M+1)^+$): found: 581.3568, requires for $C_{41}H_{45}N_2O$: 581.3526.

(6-(4-Trifluoromethylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)methanol (**4b**): Yield: 91 %, colourless oil which solidifies with time; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (dd, 1H, J = 1.8 and 0.5 Hz, Carb-H4), 8.16 (dd, 1H, J = 1.7 and 0.6 Hz, Carb-H5), 7.83-7.78 (m, 2H, Ar), 7.75-7.68 (m, 3H, Carb-H2, Ar), 7.53 (dd, 1H, J = 8.5 and 1.7 Hz, Carb-H7), 7.51 (dd, 1H, J = 8.5 and 0.6 Hz, Carb-H1), 7.41 (dd, 1H, J = 8.4 and 0.5 Hz, Carb-H8), 4.88 (d, 2H, J = 5.6 Hz, CH_2OH), 4.42-4.27 (m, 2H, Alk), 1.95-1.83 (m, 1H, Alk), 1.74-1.63 (m, 1H, Alk), 1.55-1.44 (m, 2H, Alk), 1.42-1.09 (m, 6H, Alk), 1.05 (d, 3H, J = 6.6 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.6, 140.5, 131.9, 130.8, 127.3, 125.8, 125.7, 125.6, 125.2, 123.4, 123.0, 119.5, 119.2, 109.1, 109.0, 66.1, 41.5, 39.2, 37.1, 35.6, 30.9, 27.9, 24.6, 22.6, 22.5, 19.8; HRMS (ESI, $(M+1)^+$): found: 482.2650, requires for $C_{30}H_{35}F_3NO$: 482.2665.

(6-(4-Methylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)methanol (**4c**): Yield: 89 %, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (dd, 1H, J = 1.8 and 0.6 Hz, Carb-H4), 8.14 (dd, 1H, J = 1.8 and 0.6 Hz, Carb-H5), 7.70 (dd, 1H, J = 8.5 and 1.8 Hz, Carb-H2) 7.62-7.58 (m, 2H, Ar), 7.49 (dd, 1H, J = 8.4 and 1.8 Hz, Carb-H7), 7.44 (dd, 1H, J = 8.4 and 0.6 Hz, Carb-H1), 7.39 (dd, 1H, J = 8.5 and 0.6 Hz, Carb-H8), 7.31-7.26 (m, 2H, Ar), 4.87 (d, 2H, J = 5.9 Hz, CH_2OH), 4.40-4.25 (m, 2H, Alk), 2.42 (s, 3H, Ar-CH_3), 1.94-1.83 (m, 1H, Alk), 1.74-1.09 (m, 9H, Alk), 1.04 (d, 3H, J = 6.6 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 140.2, 138.7, 136.6, 133.8, 129.3, 128.3, 127.2, 127.0, 125.9, 124.0, 123.2, 119.0, 109.6, 109.5, 66.3, 41.7, 39.2, 37.1, 35.7, 31.0, 28.0, 24.6, 22.7, 22.6, 21.3, 19.7; HRMS (ESI, $(M+1)^+$): found: 428.2929, requires for $C_{30}H_{38}NO$: 428.2948.

(6-(4-Methoxylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)methanol (**4d**): Yield: 74 %, white-off amorphous solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (dd, 1H, J = 1.8 and 0.6 Hz, Carb-H4), 8.13 (dd, 1H, J = 1.6 and 0.5 Hz, Carb-H5), 7.67 (dd, 1H, J = 8.5 and 1.8 Hz, Carb-H2) 7.65-7.60 (m, 2H, Ar), 7.49 (dd, 1H, J = 8.4 and 1.6 Hz, Carb-H7), 7.43 (dd, 1H, J = 8.5 and 0.5 Hz, Carb-H1), 7.38 (dd, 1H, J = 8.5 and 0.5 Hz, Carb-H8), 7.04-7.00 (m, 2H, Ar), 4.86 (s, 2H, CH_2OH), 4.40-4.25 (m, 2H, Alk), 3.87 (s, 3H, OCH_3), 1.93-1.82 (m, 1H, Alk), 1.74-1.08 (m, 9H, Alk), 1.04 (d, 3H, J = 6.6 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.6, 139.8, 134.8, 132.2, 131.5, 128.7, 128.2, 128.1, 126.7, 126.6, 125.5, 125.1, 123.3, 123.2, 119.5, 118.5, 114.3, 114.2, 108.9, 108.8, 66.2, 55.4, 41.4, 39.2, 37.1, 35.6, 30.9, 27.9, 24.6, 22.7, 22.6, 19.8; HRMS (ESI, $(M+1)^+$): found: 444.2878, requires for $C_{30}H_{38}NO_2$: 444.2897.

(6-(3-Trifluoromethylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)methanol (**4e**): Yield: 93 %, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (dd, 1H, J = 1.8 and 0.6 Hz, Carb-H4), 8.17 (dd, 1H, J = 1.7 and 0.6 Hz, Carb-H5), 7.95-7.93 (m, 1H, Ar), 7.71 (dd, 1H, J = 8.5 and 1.8 Hz, Carb-H2), 7.59-7.56 (m, 2H Ar), 7.51 (dd, 1H, J = 8.5 and 1.7 Hz, Carb-H7), 7.47 (dd, 1H, J = 8.5 and 0.6 Hz, Carb-H1), 7.41 (dd, 1H, J = 8.4 and 0.5 Hz, Carb-H8), 4.88 (d, 2H, J = 5.2 Hz, CH_2OH), 4.41-4.27 (m, 2H, Alk), 1.94-1.83 (m, 1H, Alk), 1.73-1.09 (m, 9H, Alk), 1.04 (d, 3H, J = 6.6 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.9, 140.6, 140.5, 131.9, 130.9, 130.5, 129.2, 125.8, 125.2, 124.0, 123.9, 123.5, 123.1, 123.0, 119.6, 119.1, 109.2, 109.0, 66.1, 41.5, 39.2, 37.1, 35.6, 30.9, 28.0, 24.6, 22.7, 22.6, 19.8; HRMS (ESI, $(M+1)^+$): found: 482.2678, requires for $C_{30}H_{35}F_3NO$: 482.2665.



(6-Aryl-9-(3,7-dimethyloctyl)carbazol-3-yl)methyltriphenylphosphonium bromide (5a-e): (6-Aryl-9-(3,7-dimethyloctyl)carbazol-3-yl)methanol (2.2 mmol) was dissolved in dry toluene (15 mL) then triphenylphosphonium bromide was added (0.75 g, 2.2 mmol). The resulting mixture was stirred at room temp. for 24 hrs. After this time, the solvent was removed under vacuum at 60^{o}C. The remaining was dissolved in minimal amount of dichloromethane, adsorbed on silica and washed first with pure dichloromethane and then with 10% methanol in dichloromethane, then the solvent was removed under vacuum at 50^{o}C.

(6-(4-*N,N*-diphenylaminophenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)methyltriphenylphosphonium bromide (**5a**): Yield: 53 %, white amorphous solid; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 7.92 (dd, 1H, J = 1.8 and 0.4 Hz, Carb-H4), 7.76-7.67 (m, 10H, Ar), 7.65 (dd, 1H, J = 8.5 and 1.8 Hz, Carb-H2), 7.62-7.54 (m, 6H, Ar), 7.52-7.47 (m, 2H, Ar), 7.33 (dd, 1H, J = 8.5 and 0.4 Hz, Carb-H1), 7.31-7.23 (m, 3H, Ar, Carb-H5), 7.21-7.11 (m, 7H, Ar, Carb-H7), 7.06-6.98 (m, 3H, Ar, Carb-H8), 5.42 (d, 2H, J = 13.4 Hz, CH$_2$P), 4.15-4.00 (m, 2H, Alk), 1.82-1.67 (m, 1H, Alk), 1.61-1.42 (m, 3H, Alk), 1.37-1.06 (m, 6H, Alk), 0.97 (d, 3H, J = 6.6 Hz, CH$_3$), 0.85 (d, 3H, J = 6.6 Hz, CH$_3$), 0.84 (3H, J = 6.6 Hz, CH$_3$); HRMS (ESI, (M-Br)$^+$): found: 825.4382, requires for $C_{59}H_{58}N_2P$: 825.4332.

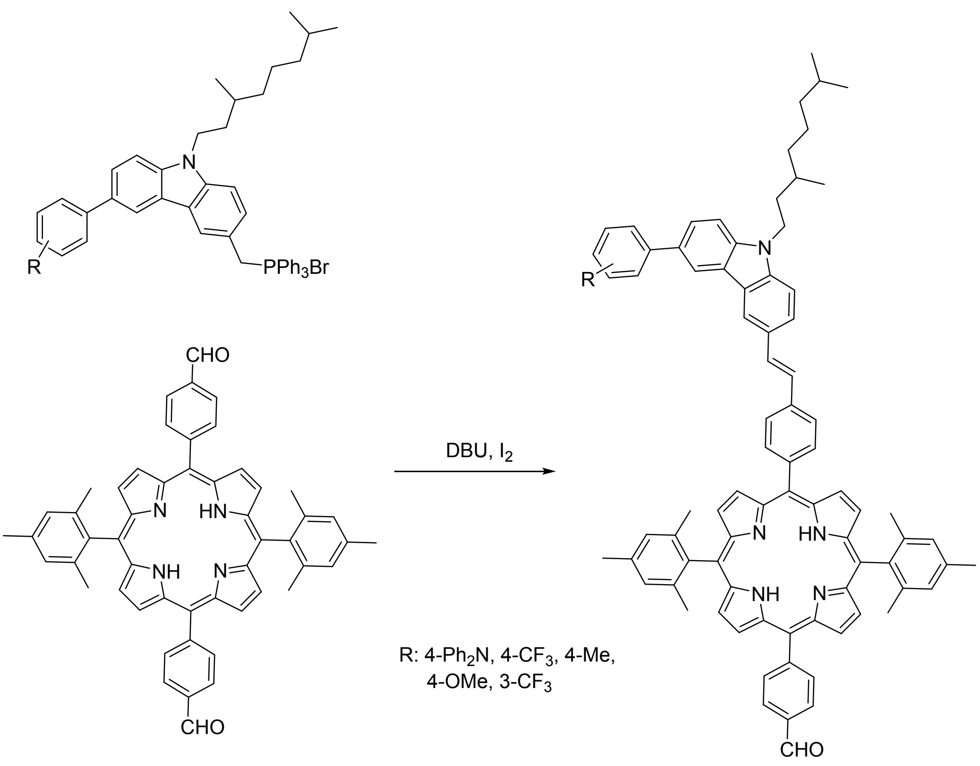
(6-(4-Trifluoromethylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)methyltriphenylphosphonium bromide (**5b**): Yield: 96 %, white amorphous solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.00 (dd, 1H, J = 1.7 and 0.5 Hz, Carb-H4), 7.84-7.59 (m, 21H, Ar, Carb-H2, H5), 7.40 (dd, 1H, J = 8.5 and 0.5 Hz, Carb-H1), 7.35 (dd, 1H, J = 8.5 and 1.7 Hz, Carb-H7), 7.11 (dd, 1H, J = 8.5 and 0.5 Hz, Carb-H8), 5.63 (m, 2H, CH$_2$P), 4.22-4.07 (m, 2H, Alk), 1.85-1.73 (m, 1H, Alk), 1.64-1.45 (m, 3H, Alk), 1.39-1.08 (m, 6H, Alk), 1.00 (d, 3H, J = 6.6 Hz, CH$_3$), 0.86 (d, 3H, J = 6.6 Hz, CH$_3$), 0.85

(3H, J = 6.6 Hz, CH_3); HRMS (ESI, $(M\text{-}Br)^+$): found: 726.3510, requires for $C_{48}H_{48}F_3NP$: 726.3471.

(6-(4-Methylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)methyltriphenylphosphonium bromide (**5c**): Yield: 45 %, white amorphous solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (dd, 1H, J = 1.8 and 0.5 Hz, Carb-H4), 7.80-7.70 (m, 9H, Ar, Carb-H5), 7.66 (dd, 1H, J = 8.5 and 1.8 Hz, Carb-H2), 7.64-7.57 (m, 6H, Ar), 7.55-7.51 (m, 3H, Ar), 7.36 (dd, 1H, J = 8.5 and 0.5 Hz, Carb-H1), 7.35 (dd, 1H, J = 8.5 and 1.8 Hz, Carb-H7), 7.30-7.27 (m, 2H, Ar), 7.11 (dd, 1H, J = 8.5 and 0.5 Hz, Carb-H8), 5.55 (m, 2H, CH_2P), 4.23-4.07 (m, 2H, Alk), 2.42 (s, 3H, Ar-CH_3), 1.83-1.72 (m, 1H, Alk), 1.62-1.42 (m, 3H, Alk), 1.37-1.07 (m, 6H, Alk), 0.99 (d, 3H, J = 6.6 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); HRMS (ESI, $(M\text{-}Br)^+$): found: 672.3719, requires for $C_{48}H_{51}NP$: 672.3754.

(6-(4-Methylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)methyltriphenylphosphonium bromide (**5d**): Yield: 80 %, white amorphous solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (dd, 1H, J = 1.8 and 0.5 Hz, Carb-H4), 7.83-7.45 (m, 19H, Ar, Carb-H2,H5), 7.37 (dd, 1H, J = 8.5 and 0.5 Hz, Carb-H1), 7.34 (dd, 1H, J = 8.5 and 1.8 Hz, Carb-H7), 7.13 (dd, 1H, J = 8.5 and 0.5 Hz, Carb-H8), 7.06-7.01 (m, 2H, Ar), 5.56 (m, 2H, CH_2P), 4.24-4.10 (m, 2H, Alk), 3.90 (s, 3H, Ar-OCH_3), 1.86-1.74 (m, 1H, Alk), 1.64-1.46 (m, 3H, Alk), 1.40-1.09 (m, 6H, Alk), 1.01 (d, 3H, J = 6.6 Hz, CH_3), 0.86 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); HRMS (ESI, $(M\text{-}Br)^+$): found: 688.3660, requires for $C_{48}H_{51}NOP$: 688.3703.

(6-(3-Trifluoromethylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)methyltriphenylphosphonium bromide (**5e**): Yield: 91 %, colourless viscous oil which solifies with time; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (dd, 1H, J = 1.8 and 0.5 Hz, Carb-H4), 7.86-7.71 (m, 11H, Ar), 7.66 (dd, 1H, J = 8.5 and 1.8 Hz, Carb-H2), 7.64-7.57 (m, 8H, Ar), 7.55 (dd, 1H, J = 1.8 and 0.5 Hz, Carb-H5), 7.42 (dd, 1H, J = 8.5 and 1.8 Hz, Carb-H7), 7.39 (dd, 1H, J = 8.5 and 0.5 Hz, Carb-H1), 7.13 (dd, 1H, J = 8.5 and 0.5 Hz, Carb-H8), 5.60 (m, 2H, CH_2P), 4.22-4.07 (m, 2H, Alk), 1.84-1.73 (m, 1H, Alk), 1.62-1.43 (m, 3H, Alk), 1.36-1.07 (m, 6H, Alk), 0.99 (d, 3H, J = 6.6 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); HRMS (ESI, $(M\text{-}Br)^+$): found: 726.3517, requires for $C_{48}H_{48}F_3NP$: 726.3471.



5-(4-Formylphenyl)-15-(4-(2-(6-aryl-9-(3,7-dimethyloctyl)carbazol-3-yl)ethenyl)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (6a-e): (6-Aryl-9-(3,7-dimethyloctyl)carbazol-3-yl)methyltriphenylphosphonium bromide (2.7 µmol) and 5,15-bis(4-formylphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (200 mg, 2.7 µmol) were dissolved in dry chloroform then 1,8-diazabicyclo[5.4.0]undec-7-ene (1.0 mL, 6.7 mmol) was added. The resulting mixture was stirred at room temp. for 1 h. Afterwards the mixture was washed by diluted hydrochloric acid (50 mL, 5%) and then with saturated aqueous solution of sodium hydrogencarbonate. The organic layer was separated, dried over magnesium sulphate and evaporated to dryness under vacuum at 50^{o}C. The remaining was purified on silica (dichloromethane) collecting the second major purple fraction. The crude (*E* and *Z* mixture) product was dissolved in dichloromethane (20 mL) and iodine (1.5 eq.) was added. The resulting mixture was stirred at room temperature for 24 hrs. Afterwards, the mixture was washed with saturated aqueous solution of sodium thiosulphate, dried over magnesium sulphate and evaporated to dryness under vacuum at 50^{o}C. The remaining was dissolved in minimal amount of dichloromethane and precipitated with methanol. The solid was collected and dried under vacuum at 60^{o}C.

5-(4-Formylphenyl)-15-(4-(2-(6-(4-*N*,*N*-diphenylaminophenyl-9-(3,7-dimethyloctyl)carbazol-3-yl)ethenyl)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (**6a**): Yield: 33 %, dark purple powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.41 (s, 1H, CHO), 8.95-8.91 (m, 2H, β-pyrrolic), 8.83-8.78 (m, 2H, β-pyrrolic), 8.77-8.71 (m, 4H, β-pyrrolic), 8.45 (dd, 1H, J = 1.7 and 0.5 Hz, Carb-H4), 8.41 (dd, 1H, J = 1.7 and 0.5 Hz, Carb-H4), 8.23-8.32 (m, 4H, Ar), 8.05-7.91 (m, 6H, Ar), 7.86 (dd, 1H, J = 8.5 and 1.7 Hz, Carb-H2), 7.76 (dd, 1H, J = 8.5 and 1.7 Hz, Carb-H7), 7.70-7.64 (m, 3H, Vinyl-H, Carb-H1, H8), 7.54-7.48 (m, 3H, Ar, Vinyl-H), 7.34-7.18 (m, 12H, Ar), 7.08-7.03 (m, 2H, Ar), 4.48-4.34 (m, 2H, Alk), 2.66 (s, 6H, Porph-Ar-CH_3), 2.01-1.92 (m, 1H, Alk), 1.88 (s, 12H, Porph-Ar-CH_3), 1.75-1.71 (m, 3H, Alk), 1.49-1.41 (m, 6H, Alk), 1.12 (d, 3H, J = 6.6 Hz, CH_3), 0.91 (d, 6H, J = 6.6 Hz, CH_3), -2.56 (br s, 2H, NH); HRMS (ESI, $(M+1)^+$): found: 1301.6847, requires for $C_{93}H_{85}N_6O$: 1301.6779.

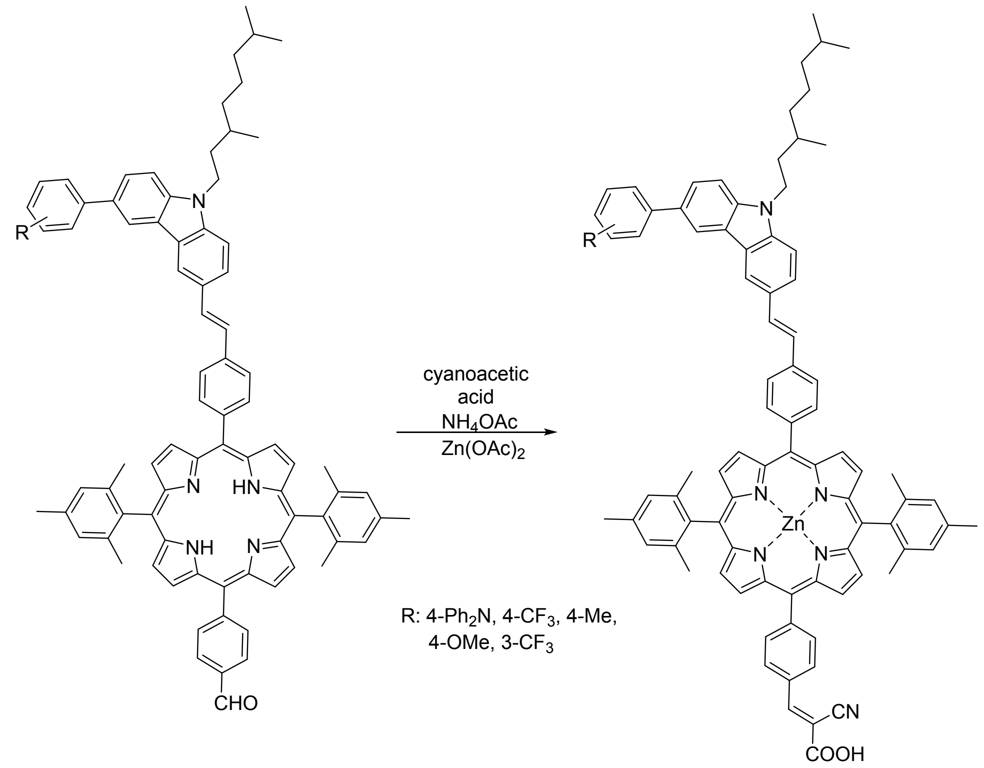
5-(4-Formylphenyl)-15-(4-(2-(6-(4-trifluoromethylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)ethenyl)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (**6b**): Yield: 30 %, dark purple powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.38 (s, 1H, CHO), 8.92-8.89 (m, 2H, β-pyrrolic), 8.74-8.70 (m, 6H, β-pyrrolic), 8.45-8.40 (m, 4H, Ar, Carb-H4, H5), 8.30-8.22 (m, 4H, Ar), 7.97-7.92 (m, 2H, Ar), 7.88-7.84 (m, 3H, Ar, Carb-H2), 7.78-7.73 (m, 3H, Ar, Carb-H7), 7.65 (d, 1H, J = 16.2 Hz, Vinyl-H), 7.54-7.47 (m, 3H, Ar, Vinyl-H), 7.29 (d, 4H, J = 0.6 Hz, Ar), 4.46-4.33 (m, 2H, Alk), 2.63 (s, 6H, Porph-Ar-CH_3), 2.01-1.92 (m, 1H, Alk), 1.85 (s, 12H, Porph-Ar-CH_3), 1.79-1.60 (m, 3H, Alk), 1.46-1.33 (m, 6H, Alk), 1.10 (d, 3H, J = 6.6 Hz, CH_3), 0.88 (d, 6H, J = 6.6 Hz, CH_3), -2.57 (br s, 2H, NH); HRMS (ESI, $(M+1)^+$): found: 1202.5883, requires for $C_{82}H_{75}F_3N_5O$: 1202.5918.

5-(4-Formylphenyl)-15-(4-(2-(6-(4-methylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)ethenyl)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (**6c**): Yield: 26 %, dark purple powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.38 (s, 1H, CHO), 8.92-8.89 (m, 2H, β-pyrrolic), 8.74-8.70 (m, 6H, β-pyrrolic), 8.44-8.38 (m, 4H, Ar, Carb-H4, H5), 8.30-8.21 (m, 4H, Ar), 7.96-7.92 (m, 2H, Ar), 7.83 (dd, 1H, J = 8.5 and 1.6 Hz, Carb-H2), 7.74 (dd, 1H, J = 8.5 and 1.7 Hz, Carb-H7), 7.68-7.62 (m, 3H, Ar, Vinyl-H), 7.52-7.45 (M, 3H, Carb-H1,H8, Vinyl-H), 7.33-7.24 (m, 6H, Ar), 4.46-4.30 (m, 2H, Alk), 2.63 (s, 6H, Porph-Ar-CH_3), 2.43 (s, 3H, Ar-CH_3), 1.99-1.89 (m, 1H, Alk), 1.85 (s, 12H, Porph-Ar-CH_3), 1.84-1.71 (m, 3H, Alk), 1.48-1.32 (m, 6H, Alk), 1.09 (d, 3H, J = 6.6

Hz, CH_3), 0.88 (d, 6H, J = 6.6 Hz, CH_3), -2.57 (br s, 2H, NH); HRMS (ESI, $(M+1)^+$): found: 1148.6236, requires for $C_{82}H_{78}N_5O$: 1148.6201.

5-(4-Formylphenyl)-15-(4-(2-(6-(4-methoxylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)ethenyl)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (**6d**): Yield: 25 %, dark purple powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.38 (s, 1H, CHO), 8.92-8.89 (m, 2H, β-pyrrolic), 8.73-8.69 (m, 6H, β-pyrrolic), 8.43-8.40 (m, 3H, Ar, Carb-H4), 8.35-8.21 (m, 4H, Ar, Carb-H5, H2), 7.96-7.93 (m, 2H, Ar), 7.83 (dd, 1H, J = 8.5 and 1.6 Hz, Carb-H7), 7.74-7.67 (m, 4H, Ar, Carb-H1, H8), 7.65 (d, 1H, J = 16.2 Hz, Vinyl-H), 7.51-7.45 (m, 3H, Ar, Vinyl-H), 7.28 (d, 4H, J = 0.6 Hz, Ar), 7.07-7.02 (m, 2H, Ar), 4.46-4.29 (m, 2H, Alk), 3.89 (s, 3H, Ar-OCH_3), 2.63 (s, 6H, Porph-Ar-CH_3), 2.00-1.88 (m, 1H, Alk), 1.85 (s, 12H, Porph-Ar-CH_3), 1.80-1.72 (m, 3H, Alk), 1.49-1.30 (m, 6H, Alk), 1.09 (d, 3H, J = 6.6 Hz, CH_3), 0.89 (d, 6H, J = 6.6 Hz, CH_3), -2.58 (br s, 2H, NH); HRMS (ESI, $(M+1)^+$): found: 1163.6129, requires for $C_{82}H_{78}N_5O_2$: 1164.6150.

5-(4-Formylphenyl)-15-(4-(2-(6-(3-trifluoromethylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)ethenyl)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (**6e**): Yield: 27 %, dark purple powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.38 (s, 1H, CHO), 8.94-8.87 (m, 2H, β-pyrrolic), 8.76-8.69 (m, 6H, β-pyrrolic),8.46 (dd, 1H, J = 1.5 and 0.5 Hz, Carb-H4), 8.46 (dd, 1H, J = 1.5 and 0.5 Hz, Carb-H5), 8.43-8.40 (m, 2H, Ar), 8.29-8.21 (m, 4H, Ar), 8.03-7.91 (m, 4H, Ar), 7.86 (dd, 1H, J = 8.5 and 1.5 Hz, Carb-H2), 7.75 (dd, 1H, J = 8.5 and 1.5 Hz, Carb-H7), 7.65 (d, 1H, J = 16.4 Hz, Vinyl-H), 7.62-7.59 (m, 2H, Ar), 7.54-7.47 (m, 3H, Carb-H1, H8, Vinyl-H), 7.29 (d, 4H, J = 0.6 Hz, Ar), 4.48-4.32 (m, 2H, Alk), 2.63 (s, 6H, Porph-Ar-CH_3), 2.00-1.93 (m, 1H, Alk), 1.85 (s, 12H, Porph-Ar-CH_3), 1.80-1.63 (m, 3H, Alk), 1.47-1.31 (m, 6H, Alk), 1.00 (d, 3H, J = 6.6 Hz, CH_3), 0.88 (d, 6H, J = 6.6 Hz, CH_3), -2.57 (br s, 2H, NH); HRMS (ESI, $(M+1)^+$): found: 1201.5885, requires for $C_{82}H_{75}F_3N_5O$: 1202.5918.



5-(4-(2-Cyano-2-carboxyethenyl)phenyl)-15-(4-(2-(6-aryl-9-(3,7-dimethyloctyl)carbazol-3-yl)ethenyl)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinato zinc(II) (CZP1-5): 5-(4-Formylphenyl)-15-(4-(2-(6-aryl-9-(3,7-dimethyloctyl)carbazol-3-yl)ethenyl)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (1.0 µmol) was dissolved in mixture of tetrahydrofuran (4.5 mL) and glacial acetic acid (4.5 mL), then cyanoacetic acid (83 mg, 1.0 mmol), ammonium acetate (77 mg, 1 mmol) and zinc acetate (66 mg, 6.0 µmol) was added and the resulting mixture was stirred at 65°C under argon, for 6 hrs. Afterwards water (50 mL) was added, the reaction mixture was cooled to room temp. and the resulting solid was filtered off. The solid was washed several times with water then dried under vacuum at 50°C.

5-(4-(2-Cyano-2-carboxyethenyl)phenyl)-15-(4-(2-(6-(4-*N*,*N*-diphenylaminophenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)ethenyl)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinato zinc(II) (**CZP1**): Yield: 99 %, dark purple powder; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.83 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.74 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.67 (dd, 1H, J = 1.5 and 0.5 Hz, Carb-H4), 8.60 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.59 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.56 (dd, 1H, J = 1.7 and 0.5 Hz, Carb-H5), 8.45-8.40 (m, 4H, Ar), 8.23-8.19 (m, 2H, Ar), 8.04-7.99 (m, 2H, Ar), 7.95 (s, 1H, CH), 7.89 (dd, 1H, J = 8.5 and 1.5 Hz, Carb-H2), 7.79 (dd, 1H, J = 8.5 and 1.7 Hz, Carb-H7), 7.78-7.74 (m, 2H, Ar), 7.74 (d, 1H, J = 16.2 Hz, Vinyl-H), 7.69-7.65 (m, 2H, Carb-H1,H8), 7.63 (d, 1H, J = 16.2 Hz, Vinyl-H), 7.36-7.31 (m, 8H, Ar), 7.17-7.04 (m, 8H, Ar), 4.54-4.43 (m, 2H, Alk), 2.59 (s, 6H, Porph-Ar-CH_3), 2.09-2.01 (m, 1H, Alk), 1.80 (s, 12H, Porph-Ar-CH_3), 1.70-1.04 (m, 9H, Alk), 1.02 (d, 3H, J = 6.6 Hz, CH_3), 0.83 (d, 6H, J = 6.6 Hz, CH_3), 0.82 (d, 6H, J = 6.6 Hz, CH_3); HRMS (ESI, (M+1)$^+$): found: 1430.5886, requires for $C_{96}H_{84}N_7O_2Zn$: 1430.5972.

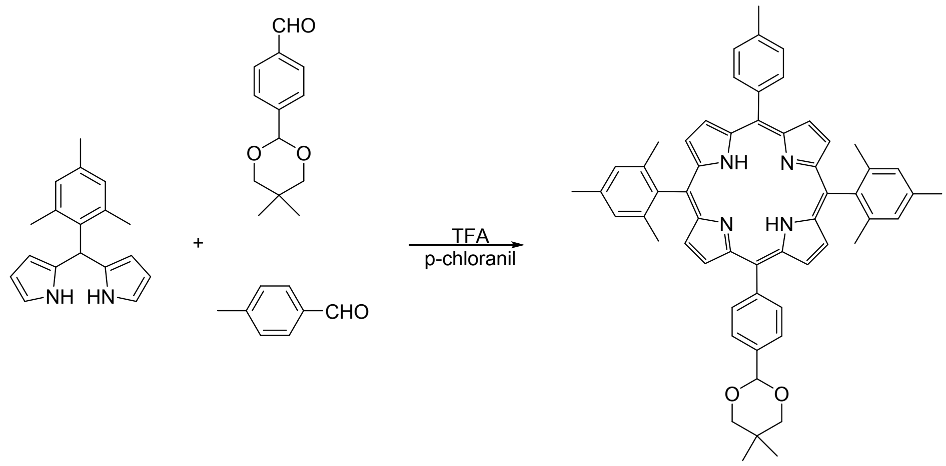
5-(4-(2-Cyano-2-carboxyethenyl)phenyl)-15-(4-(2-(6-(4-trifluoromethylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)ethenyl)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinato zinc(II) (**CZP2**): Yield: 99 %, dark purple powder; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.84 (d, 2H, J = 4.6 Hz, β-pyrrolic), 8.74 (d, 2H, J = 4.6 Hz, β-pyrrolic), 8.72-8.69 (m, 2H, Carb-H4, H5), 8.60 (d, 2H, J = 4.6 Hz, β-pyrrolic), 8.59 (d, 2H, J = 4.6 Hz, β-pyrrolic), 8.44-8.36 (m, 4H, Ar), 8.25-8.19 (m, 2H, Ar), 8.10-8.00 (m, 4H, Ar), 7.95 (s, 1H, CH), 7.92 (dd, 1H, J = 8.5 and 1.5 Hz, Carb-H2), 7.91 (dd, 1H, J = 8.5 and 1.5 Hz, Carb-H7), 7.89-7.84 (m, 2H, Ar), 7.75 (d, 1H, J = 16.1 Hz, Vinyl-H), 7.75 (dd, 1H, J = 8.5 and 0.5 Hz, Carb-H1), 7.70 (dd, 1H, J = 8.5 and 0.5 Hz, Carb-H1), 7.64 (d, 1H, J = 16.1 Hz, Vinyl-H), 7.32 (s, 4H, Ar), 4.55-4.47 (m, 2H, Alk), 2.59 (s, 6H, Porph-Ar-CH_3), 2.10-2.00 (m, 1H, Alk), 1.80 (s, 12H, Porph-Ar-CH_3), 1.71-1.04 (m, 9H, Alk), 1.03 (d, 3H, J = 6.6 Hz, CH_3), 0.82 (d, 6H, J = 6.6 Hz, CH_3), 0.81 (d, 6H, J = 6.6 Hz, CH_3); HRMS (ESI, (M+1)$^+$): found: 1331.5161, requires for $C_{85}H_{74}F_3N_6O_2Zn$: 1331.5111.

5-(4-(2-Cyano-2-carboxyethenyl)phenyl)-15-(4-(2-(6-(4-methylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)ethenyl)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinato zinc(II) (**CZP3**): Yield: 99 %, dark purple powder; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.84 (d, 2H, J = 4.6 Hz, β-pyrrolic), 8.75 (d, 2H, J = 4.6 Hz, β-pyrrolic), 8.70-8.66 (m, 2H, Carb-H4, H5), 8.61 (d, 2H, J = 4.6 Hz, β-pyrrolic), 8.60 (d, 2H, J = 4.6 Hz, β-pyrrolic), 8.59-8.54 (m, 2H, Ar), 8.47-8.39 (m, 4H, Ar), 8.24-8.20 (m, 2H, Ar), 8.05-8.00 (m, 2H, Ar), 7.96 (s, 1H, CH), 7.90 (dd, 1H, J = 8.6 and 1,5 Hz, Carb-H2), 7.80 (dd, 1H, J = 8.6 and 1.5 Hz), Carb-H7), 7.75 (d, 1H, J – 16.4 Hz, Vinyl-H), 7.77-7.65 (m, 4H, Ar, Carb-H1, H8), 7.65 (d, 1H, J = 16.4 Hz, Vinyl-H), 7.35-7.31 (m, 4H, Ar), 4.54-4.46 (m, 2H, Alk), 2.60 (s, 6H, Porph-Ar-CH_3), 2.44 (s, 3H, Ar-CH_3), 2.09-1.99 (m, 1H, Alk), 1.81 (s, 12H, Porph-Ar-CH_3), 1.70-1.04

(m, 9H, Alk), 1.03 (d, 3H, J = 6.6 Hz, CH_3), 0.83 (d, 6H, J = 6.6 Hz, CH_3), 0.82 (d, 6H, J = 6.6 Hz, CH_3); HRMS (ESI, $(M+1)^+$): found: 1331.5366, requires for $C_{85}H_{77}N_6O_2Zn$: 1277.5394.

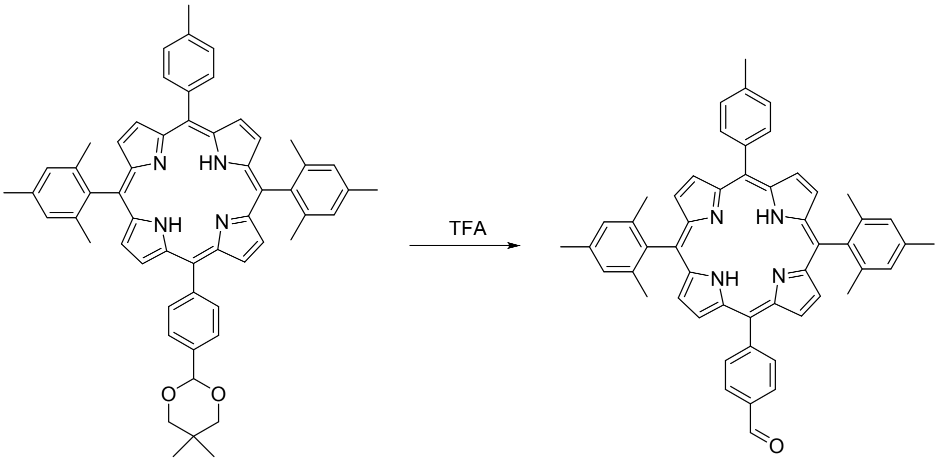
5-(4-(2-Cyano-2-carboxyethenyl)phenyl)-15-(4-(2-(6-(4-methoxylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)ethenyl)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinato zinc(II) (**CZP4**): Yield: 99 %, dark purple powder; ^1H NMR (400 MHz, DMSO-d_6) δ: 8.84 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.75 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.69-8.66 (m, 2H, Carb-H4, H5), 8.60 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.59 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.53-8.50 (m, 2H, Ar), 8.43-8.36 (m, 4H, Ar), 8.23-8.19 (m, 2H, Ar), 8.04-8.00 (m, 2H, Ar), 7.98 (s, 1H, CH), 7.89 (dd, 1H, J = 8.5 and 1.5 Hz, Carb-H2), 7.78-7.71 (m, 3H, Carb-H7, 2 x Vinyl-H), 7.69-7.63 (m, 2H, Carb-H1, H8), 7.32 (s, 4H, Ar), 7.11-7.07 (m, 2H, Ar), 4.54-4.46 (m, 2H, Alk), 3.83 (s, 3H, Ar-OCH_3), 2.69 (s, 6H, Porph-Ar-CH_3), 2.07-1.98 (m, 1H, Alk), 1.80 (s, 12H, Porph-Ar-CH_3), 1.75-1.05 (m, 9H, Alk), 1.02 (d, 3H, J = 6.6 Hz, CH_3), 0.82 (d, 6H, J = 6.6 Hz, CH_3), 0.81 (d, 6H, J = 6.6 Hz, CH_3); HRMS (ESI, $(M+1)^+$): found: 1293.5298, requires for $C_{85}H_{77}N_6O_3Zn$: 1293.5343.

5-(4-(2-Cyano-2-carboxyethenyl)phenyl)-15-(4-(2-(6-(3-trifluoromethylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)ethenyl)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinato zinc(II) (**CZP5**): Yield: 99 %, dark purple powder; ^1H NMR (400 MHz, DMSO-d_6) δ: 8.84 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.74 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.74-8.71 (m, 2H, Carb-H4, H5), 8.60 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.59 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.44-8.36 (m, 4H, Ar), 8.24-8.19 (m, 2H, Ar), 8.17-8.13 (m, 2H, Ar), 8.05-8.00 (m, 3H, Ar, CH), 7.91 (dd, 1H, J = 8.5 and 1.5 Hz, Carb-H2), 7.90 (dd, 1H, J = 8.5 and 1.5 Hz, Carb-H7), 7.79-7.68 (m, 5H, Ar, Carb-H1, H8, Vinyl-H), 7.65 (d, 1H, J = 16.4 Hz, Vinyl-H), 7.32 (s, 4H, Ar), 4.59-4.45 (m, 2H, Alk), 2.59 (s, 6H, Porph-Ar-CH_3), 2.10-2.00 (m, 1H, Alk), 1.80 (s, 12H, Porph-Ar-CH_3), 1.71-1.04 (m, 9H, Alk), 1.03 (d, 3H, J = 6.6 Hz, CH_3), 0.83 (d, 6H, J = 6.6 Hz, CH_3), 0.82 (d, 6H, J = 6.6 Hz, CH_3); HRMS (ESI, $(M-1)^-$): found: 1329.5003, requires for $C_{85}H_{72}F_3N_6O_2Zn$: 1329.4966.



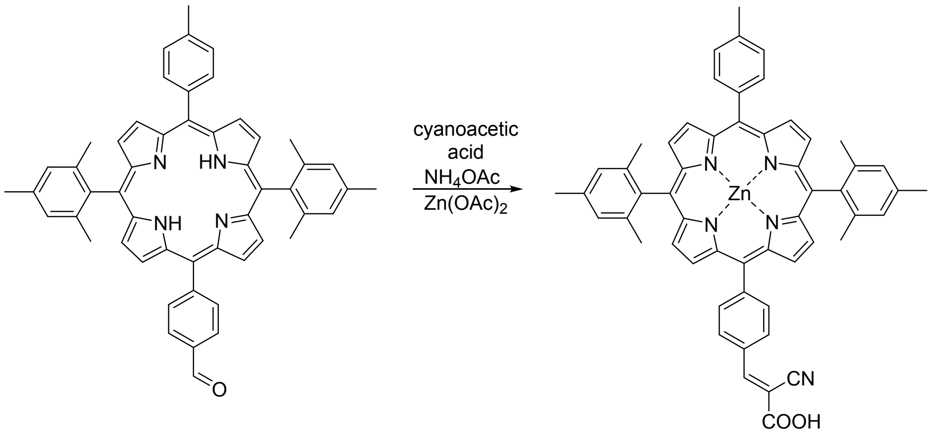
5-(4-(5,5,-dimethyl-1,3-dioxan-2-yl)phenyl)-15-(4-methylphenyl-10,20-bis(2,4,6-trimethylphenyl)porphyrin (7): 2,2’-(2,4,6-trimethylphenylmethylene)bispyrrol (0.79 g, 3.0 mmol), 4-methylbenzaldehyde (0.18 g, 1.5 mmol) and 4-(5,5,-dimethyl-1,3-dioxan-2-yl)benzaldehyde (0.33 g, 1.5 mmol) were dissolved in dichloromethane (300 mL), stirred for 5 minutes under argon then trifluoroacetic acid (0.42 mL, 3 mmol) was added in period of 30 sec. The resulting mixture was stirred for 1h at room temp., then p-chloranil (1.18 g, 4 mmol) was added and the mixture was gently refluxed for additional hour. The acid was neutralized by small excess of triethylamine, concentrated under vacuum at 50 ^{o}C and filtered through pad of silica (dichloromethane). The filtrate was evaporated to dryness and purified on silica (dichloromethane/hexane 7:3). After evaporation the resulting solid was dissolved in minimal amount of dichloromethane and precipitated with methanol to give purple solid (0.13 g, 11%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.81 (d, 2H, J = 4.8 Hz, β-pyrrolic), 8.78 (d, 2H, J = 4.8 Hz, β-pyrrolic), 8.67 (d, 2H, J = 4.8 Hz, β-pyrrolic), 8.65 (d, 2H, J = 4.8 Hz, β-pyrrolic), 8.24 (m, 2H, Ar), 8.10 (m, 2H, Ar), 7.90 (m, 2H, Ar), 7.54 (m, 2H, Ar), 7.28 (d, J = 0.7 Hz, 4H, Ar), 5.76 (s, 1H, CH), 3.96 (d, 2H, J = 11.0 Hz, CH_2), 3.85 (d, 2H, J = 11.0 Hz, CH_2), 2.69 (s, 3H, Ar-CH_3), 2.63 (s, 6H, Ar-CH_3), 1.83 (s, 12H, Ar-CH_3), 1.47 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), -2.63 (br s, 2H, NH); HRMS (ESI, $(M+1)^{+}$): found: 827.4314, $C_{57}H_{55}N_4O_2$ requires: 827.4320.

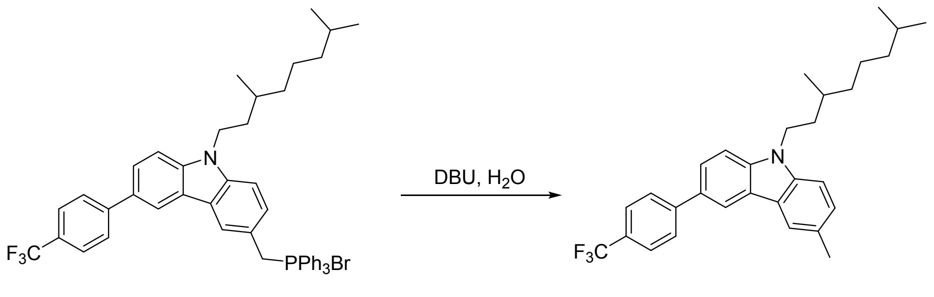


5-(4-formylphenyl)-15-(4-methylphenyl-10,20-bis(2,4,6-trimethylphenyl)porphyrin (8): 5-(4-(5,5,-dimethyl-1,3-dioxan-2-yl)phenyl)-15-(4-methylphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (1 mmol) was dissolved in dichloromethane (15 mL) then trifluoroacetic acid (9 mL) was added followed by water (3 mL). The resulting green solution was vigorously stirred for 30 min. then quenched by water (100 mL). The acid was neutralized by concentrated aqueous ammonia and the organic phase was separated, dried over magnesium sulphate, filtered through pad of silica (dichloromethane) and evaporated to dryness under reduced pressure at 50°C. The resulting solid was dissolved in minimal amount of dichloromethane and precipitated with methanol to give purple solid (78 mg, 85 %).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.22 (s, 1H, CHO), 8.95 (d, 2H, J = 4.8 Hz, β-pyrrolic), 8.81 (d, 2H, J = 4.8 Hz, β-pyrrolic), 8.72 (d, 2H, J = 4.8 Hz, β-pyrrolic), 8.66 (d, 2H, J = 4.8 Hz, β-pyrrolic), 8.14 (d, 2H, J = 3.8 Hz, Ar), 8.09 (m, 2H, Ar), 8.00 (d, 2H, J = 3.8 Hz, Ar), 7.55 (m, 2H, Ar), 7.28 (d, 4H, J = 0.7 Hz, Ar), 2.70 (s, 3H, Ar-CH_3), 2.63 (s, 6H, Ar-CH_3), 1.84 (s, 12H, Ar-CH_3), -2.56 (br s, 2H, NH); HRMS (ESI, $(M+1)^+$): found: 741.3546, $C_{52}H_{45}N_4O$ requires: 741.3588.



5-(4-(2-Cyano-2-carboxyethenyl)phenyl)-15-(4-methylphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinato zinc(II) (**ZP1**): Yield: 99 %, dark purple powder, ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.73 (d, 4H, J = 4.7 Hz, β-pyrrolic), 8.62 (s, 1H, CH), 8.59 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.56 (d, 2H, J = 4.7 Hz, β-pyrrolic), 8.40 (m, 4H, Ar), 8.07 (m, 2H, Ar), 7.58 (m, 2H, Ar), 7.31 (d, 4H, J = 0.7 Hz, Ar), 2.66 (s, 3H, Ar-CH_3), 2.58 (s, 6H, Ar-CH_3), 1.78 (s, 12H, Ar-CH_3), HRMS (ESI, $(M+1)^+$): found: 870.2766, $C_{55}H_{44}N_5O_2Zn$ requires: 870.2781.



9-(3,7-dimethyloctyl)-6-methyl-3-(4-trifluoromethylphenyl)carbazole (Cb2): (6-(3-Trifluoromethylphenyl)-9-(3,7-dimethyloctyl)carbazol-3-yl)methyltriphenylphosphonium bromide (0.50 g, 6.2 μm)were dissolved in dichloromethane (10 mL), two drops of water was added followed with 1,8-diazabicyclo[5.4.0]undec-7-ene (0.5 mL, 3.4 mmol). The resulting mixture was stirred at room temp. for 30 min. then filtered through pad of silica (dichloromethane). After solvent evaporation under reduced pressure at 50°C pale yellow oil was obtained

(0.26 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (dd, 1H, J = 1.8 and 0.5 Hz, Carb-H4), 7.95 (dd, 1H, J = 1.7 and 0.6 Hz, Carb-H5), 7.81-7.79 (m, 2H, Ar), 7.72-7.67 (m, 3H, Carb-H2, Ar), 7.56 (dd, 1H, J = 8.5 and 1.7 Hz, Carb-H7), 7.55 (dd, 1H, J = 8.5 and 0.6 Hz, Carb-H1), 7.43 (dd, 1H, J = 8.4 and 0.5 Hz, Carb-H8), , 4.43-4.25 (m, 2H, Alk), 2.55 (s, 3H, Carb-CH_3) 1.95-1.83 (m, 1H, Alk), 1.74-1.63 (m, 1H, Alk), 1.56-1.43 (m, 2H, Alk), 1.41-1.09 (m, 6H, Alk), 1.05 (d, 3H, J = 6.6 Hz, CH_3), 0.85 (d, 3H, J = 6.6 Hz, CH_3), 0.84 (3H, J = 6.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.3, 140.6, 132.0, 130.7, 127.1, 125.9, 125.5, 125.4, 125.3, 123.4, 123.1, 119.6, 119.4, 109.0, 108.9, 41.6, 39.1, 37.1, 35.6, 31.0, 27.8, 24.4, 22.4, 22.7, 21.6,19.6; HRMS (ESI, $(M+1)^+$): found: 466.3750, $C_{30}H_{35}F_3N$ requires: 466.2716.

SI B. Oscillator strength in different solvents

Table S1. Oscillator strength (f) of UV-visible absorption spetra of porphyrins (Fig. 1) in both DCM and DMF solvents.

Dyes	(f)# in DCM		(f) # in DMF		(DMF-DCM)/DCM	
	380-500 nm	520-630 nm	380-500 nm	520-630 nm	380-500 nm	520-630 nm
ZP1	1.52	0.08	1.56	0.10	5%	30%
CZP1	1.88	0.12	1.92	0.13	4%	16%
CZP2	2.07	0.12	2.07	0.14	2%	14%
CZP3	1.77	0.10	1.90	0.13	9%	40%
CZP4	1.91	0.12	1.98	0.13	6%	21%
CZP5	1.81	0.10	1.92	0.12	8%	19%
Max.	38%	56%	34%	38%	(CZP2-ZP1)/ZP1	
Min.	18%	23%	23%	22%*	(CZP3-ZP1)/ZP1	
#calculated by $4.32\times10^{-9}\times$A, where A=integrated area of the absorption band in each solution. Using the plot of molar extinction coefficient (ε, $M^{-1}cm^{-1}$) versus wavenumbers (cm^{-1}) to obtain the A[5]. *calculated by (CZP5-ZP1)/ZP1						

SI C. Differential pulse voltammetry plots

Table S2. Electrochemical properties of the compounds and bandgap calculation

Dye	Peak Potential vs. Fc/Fc$^+$		Onset Potential vs. Fc/Fc$^+$		$^a\Delta E_1$ /eV	$^b\Delta E_2$ /eV
	E_{Re} /V	E_{Ox}/V	E_{RO} /V	E_{OO} /V		
ZP1	-1.89	0.28	-1.78	0.18	2.17	2.00

	-2.20	0.59	-2.08	0.49		
CZP1	-1.86	0.34	-1.75	0.21	2.21	2.00
	-2.19	0.64	-2.09	0.51		
CZP2	-1.86	0.29	-1.76	0.18	2.15	1.98
	-2.18	0.51	-2.06	0.45		
	-	0.61	-	0.50		
	-	0.79	-	0.68		
CZP3	-1.86	0.33	-1.75	0.23	2.19	1.99
	-2.18	0.53	-2.06	0.47		
	-	0.67	-	0.54		
CZP4	-1.86	0.28	-1.76	0.18	2.13	1.99
	-2.20	0.47	-2.07	0.42		
	-	0.61	-	0.51		
	-	0.95	-	0.84		
CZP5	-1.86	0.32	-1.75	0.22	2.18	1.98
	-2.19	0.56	-2.10	0.49		
	-	0.64	-	0.53		
	-	0.82	-	0.72		
Cb1	-	0.42	-	0.32	-	3.04
	-	0.75	-	0.66		
Cb2	-	0.77	-	0.65	-	3.31
	-	1.05	-	0.96		

Notes: [a] Band gap from DPV, $\Delta E_1 = E_{Ox}^{1st} - E_{Re}^{1st}$; [b] Band gap from UV-vis absorption spectrum in DCM, $\Delta E_2 = 1243/\lambda_{onset}$, where λ_{onset} is onset wavelength.

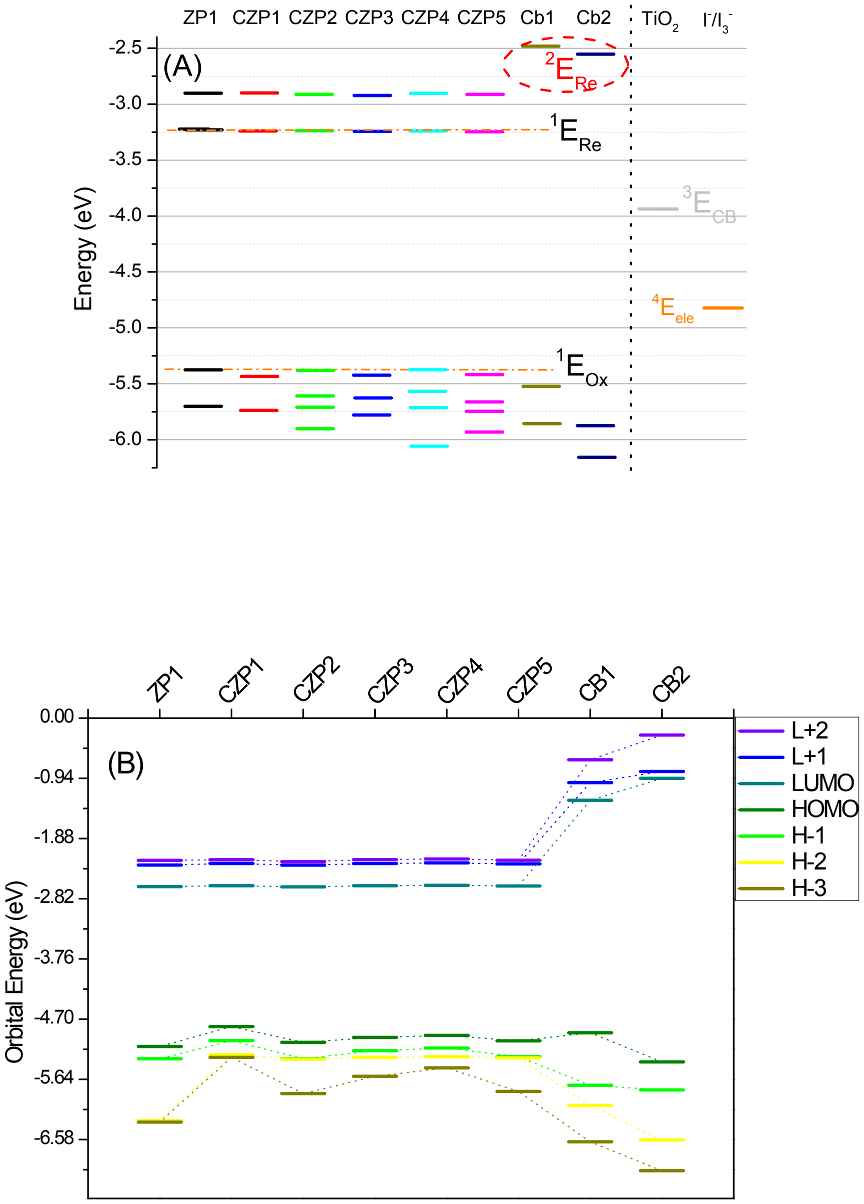


Figure S1A. Energy level diagram of the compounds. [1] The energy levels of oxidation (E_{Ox}) and the energy levels of reduction (E_{Re}) were calculated from the peak potentials of oxidation ($E_{Ox\text{ vs. }Fc/Fc^+}$) and reduction ($E_{Re\text{ vs. }Fc/Fc^+}$) as $E_{Ox} = -(E_{Ox\text{ vs. }Fc/Fc^+} + 5.1)$ (eV) and $E_{Re} = -(E_{Re\text{ vs. }Fc/Fc^+} + 5.1)$ (eV), respectively. The potential of the Fc/Fc$^+$ redox couple was assumed to be -5.1 eV vs. vacuum[6]. [2] E_{Re} of Cb1 and Cb2 were calculated from UV-vis absorption spectra by the equation $E_{Re} = \Delta E + E_{Ox}$, where the band gap ($\Delta E$) can get from the absorption of onset wavelength (λ_{onset}) by the equation $\Delta E = 1243/\lambda_{onset}$. [3] E_{CB} was adopted from Ref.[7]. [4] The I^-/I_3^- redox couple potential (E_{ele}) was adopted from Ref.[8]. Both values of [3] and [4] were calibrated to the absolute energy based on the assumption $E_{Fc/Fc+}$ =+0.63 V vs. NHE. Figure S1B. Energy level diagram of the molecular orbitals calculated from TD-DFT of each of the systems.

SI D. Device fabrication and characterization

Table S3. Averaged performance of thin film devices with porphyrin dyes compared with N719

Dye	Thickness /μm	J_{SC} mA/cm^2	V_{OC} mV	FF	η %	Note	Γ mol/cm^3
ZP1	2.2±0.1	6.0±0.2	690±10	0.62±0.01	2.6±0.1	After light soaking 20 mins	1.2×10^{-4}
CZP1		7.0±0.4	770±10	0.60±0.03	3.3±0.2		1.2×10^{-4}
CZP2		7.0±0.3	730±10	0.63±0.03	3.2±0.1		1.0×10^{-4}
CZP3		6.9±0.2	740±10	0.64±0.01	3.3±0.1		1.4×10^{-4}
CZP4		7.3±0.4	750±10	0.63±0.02	3.4±0.1		1.2×10^{-4}
CZP5		7.1±0.5	750±10	0.63±0.01	3.4+0.2		1.1×10^{-4}
N719	2.2±0.1	7.2±0.1	800±10	0.67±0.02	3.9±0.1	As-prepared	0.9×10^{-4} [9]

Electrolyte: 0.6 M DMPII, 0.1 M LiI, 0.05 M I_2, 0.5 M t-BP in AN:VN=85:15 (Vol.), where AN was acetonitrile, VN was valeronitrile; porphyrin dye solutions condition: 0.2 mM in THF; N719 dye solution condition: 0.4 mM in AN:TBA=1:1 (Vol.), where TBA was tert-Butanol.

Table S4. Performance of ~17.5 μm thick film devices with porphyrin dyes compared with N719

Dye	Thickness/μm	J_{SC} mA/cm^2	V_{OC} mV	FF	η %	Note
ZP1	17.7	10.81	605	0.68	4.44	After light soaking 20 mins
	16.6	11.25	605	0.63	4.26	
CZP1	17.4	13.76	710	0.64	6.23	
	16.7	12.56	705	0.65	5.72	
CZP2	17.7	12.84	715	0.65	6.01	
	17.2	12.94	710	0.66	6.05	
CZP3	17	11.42	660	0.67	5.01	
	17.4	12.70	675	0.65	5.59	
CZP4	17.7	11.54	685	0.67	5.28	
	17	12.23	685	0.65	5.46	
CZP5	17.4	12.59	695	0.64	5.57	
	17	12.42	685	0.67	5.69	
N719	18	15.84	735	0.69	8.01	As-

	18	16.66	735	0.69	8.44	prepared

Electrolyte condition: same as Table S3.

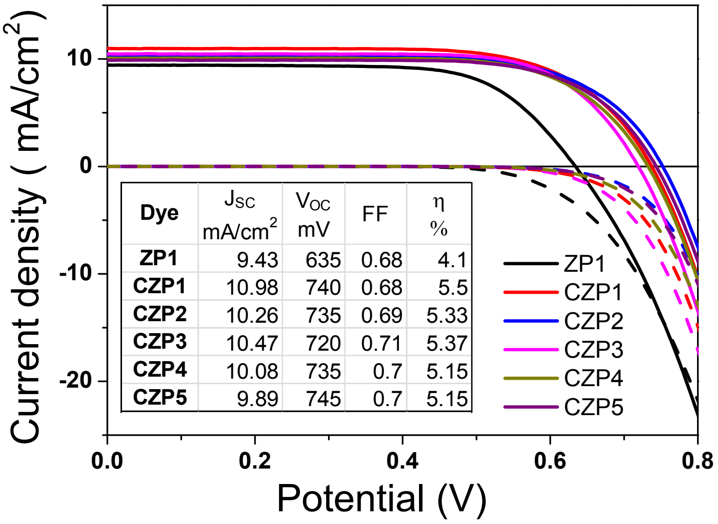


Figure S2. Current density-voltage (J-V) curves of DSSCs with the porphyrin dyes fabricated using 6 μm transparent + 3.2 μm scattering TiO_2, under AM 1.5 illumination (solid lines) and in the dark (dashed lines). The inset shows the photovoltaic performance for each device.

Table S5. J-V performance and dye loading of CZP3 compared to ZP1 in different solvent conditions

Solvent	Dye	J_{SC} mA/cm^2	V_{OC} mV	FF	η %	Dye loading Γ/ mol/cm^3
2mM CDCA in THF	ZP1	5.32	620	0.67	2.21	0.9×10^{-4}
	CZP3	6.55	695	0.67	3.03	1.2×10^{-4}
2mM CDCA in ethanol	ZP1	6.75	685	0.67	3.08	0.8×10^{-4}
	CZP3	8.42	765	0.66	4.23	1.3×10^{-4}
Pure ethanol	ZP1	6.27	700	0.58	2.53	1.2×10^{-4}
	CZP3	8.41	750	0.58	3.63	1.4×10^{-4}
Film thickness:2.7±0.1 μm; dye concentration 0.2 mM;						

SI E. Dyes in different solvents with high concentration

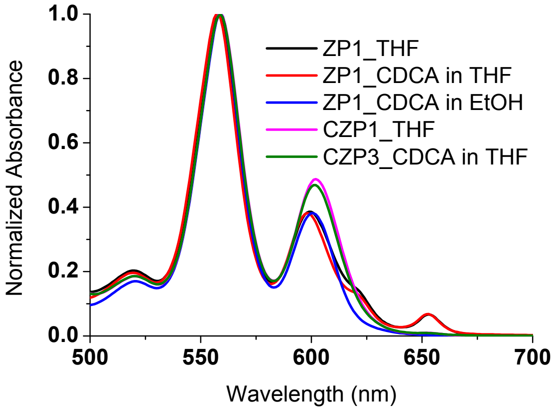
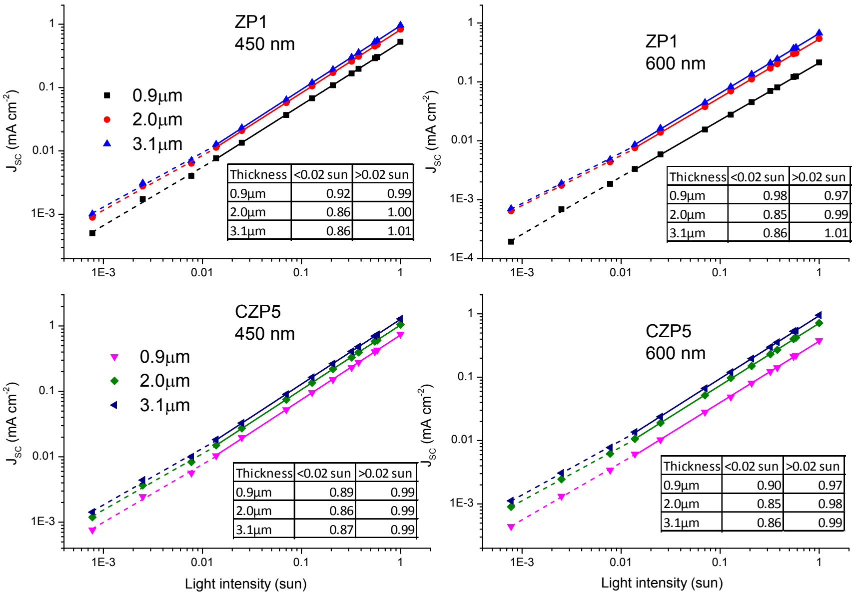


Figure S3. Normalized visible absorption spectra of some porphyrins in different solvents. Dye concentration: 30 μM.

SI F. J_{SC} dependence upon light intensity



ZP1, 450 nm

Thickness	<0.02 sun	>0.02 sun
0.9μm	0.92	0.99
2.0μm	0.86	1.00
3.1μm	0.86	1.01

ZP1, 600 nm

Thickness	<0.02 sun	>0.02 sun
0.9μm	0.98	0.97
2.0μm	0.85	0.99
3.1μm	0.86	1.01

CZP5, 450 nm

Thickness	<0.02 sun	>0.02 sun
0.9μm	0.89	0.99
2.0μm	0.86	0.99
3.1μm	0.87	0.99

CZP5, 600 nm

Thickness	<0.02 sun	>0.02 sun
0.9μm	0.90	0.97
2.0μm	0.85	0.98
3.1μm	0.86	0.99

Figure S4. Short circuit current (J_{SC}) dependence upon light intensity of ZP1 and CZP5. The fitted lines with two different light intensity ranges (split at ~0.02 sun) using power law are shown. Band filters were used to achieve 450±10 nm and 600±10 nm, representing for the Soret band and the Q band, respectively. The inset table shows the power numbers of the fitting.

The power numbers at <0.02 sun showed bigger deviation from 1, especially when the thickness increased, indicating charge collection losses would happen.

SI G. Quantification of the increased J_{SC} (ΔJ_{SC})

Table S6. Photocurrent deduced from IPCE in terms of five spectral ranges

Specification	Dye relationship	Wavelength range/nm					Totally
		315~380	385~440	445~510	515~540	545~700	
ΔJ_{SC} mA/cm^2	CZP1-ZP1$^{\#}$	0.14	0.12	0.62	0.1	0.83	1.81
	CZP3-ZP1$^{\#}$	0.12	0.12	0.69	0.14	0.97	2.04
	CZP3-ZP1*	0.1	0.08	0.54	0.19	1.01	1.92
Percentage %	CZP1-ZP1$^{\#}$	8	7	34	6	46	100
	CZP3-ZP1$^{\#}$	6	6	34	7	48	100
	CZP3-ZP1*	5	4	28	10	53	100

$^{\#}$ THF as solvent; * 2 mM CDCA in ethanol as solvent.

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