Supplementary Material (ESI) for Chemical Communications

Supplementary Material for

A_2B_2–type *push-pull* porphyrins as reverse saturable and saturable absorbers

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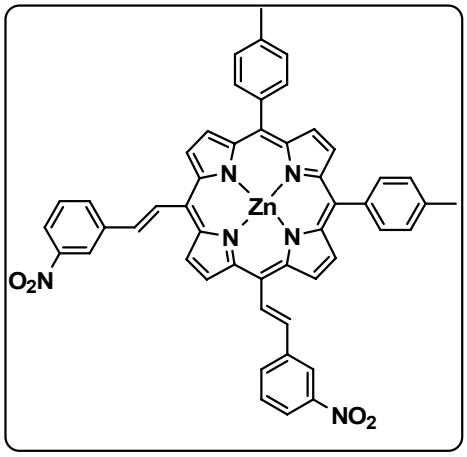
Instrumentation and Materials

All chemicals were of analytical grade, and were purified before use. Dichloromethane was dried over phosphorus pentoxide followed by distillation; THF was dried over sodium/benzophenone followed by distillation. The chemicals used for Suzuki and Heck coupling reactions were purchased from Aldrich, and boronic acids and esters were kindly supplied from Frontier Scientific. The preparation of 2,5-bis(hydroxymethyl)pyrrole, tripyrrane, 5,10-disubstituted porphyrins followed published procedures or minor modifications thereof.[1,2] All condensation reactions were carried out under argon atmosphere with the reaction flask shielded from ambient light. Silica gel 60 (Merck) was used for column chromatography. Analytical thin layer chromatography (TLC) was carried out using silica gel 60 plates (fluorescence indicator F_{254}; Merck). Melting points are uncorrected and measured with a Stuart SMP10 instrument. Proton NMR spectra were recorded at a frequency of 400 MHz or 600 MHz (Bruker), and the ^{13}C NMR spectra recorded at a frequency of 125 MHz. Chemical shifts are given in ppm and referenced to the TMS signal as internal standard. Assignment of the signals was confirmed by 2D spectra (COSY, HMBC, HMQC). Mass spectra were recorded using a Micromass/Waters Corp USA Quattro *micro*^{TM} for low resolution and a Micromass/Waters Corp USA liquid time-of-flight spectrometer equipped with electrospray for high resolution.

Preparation of {(*all-E*)-5,10-bis-[2-(3-nitro-phenyl)-vinyl]-15,20-bis(*p*-tolyl)-porphyrinato)}zinc(II) (3) *via* Heck coupling reaction

(5,10-Dibromo-15,20-bis(*p*-tolyl)porphyrinato)zinc(II) (100 mg, 0.140 mmol), was dissolved in DMF (50 mL) under a nitrogen atmosphere. The 3-nitrostyrene (1.36 mL, 9.8 mmol), sodium acetate (65 mg, 0.784 mmol), palladium acetate (3.14 mg, 0.014 mmol) and triphenylposphine (14.68 mg, 0.056 mmol) were added and the temperature was raised to 120 °C for 16 hours (TLC control). The crude product was extracted with dichloromethane and washed with water. The product was purified by silica gel column chromatography using CH_2Cl_2: *n*-hexane = 1:1 and gave 70 mg (0.082 mmol, 60 %) of desired compound after recrystallization from dichloromethane/methanol; mp > 300 °C; R_f = 0.12 (CH_2Cl_2: *n*-hexane = 1:1, v/v); ^{1}H-NMR (600 MHz, CD_2Cl_2, TMS): δ = 2.76 (s, 6H, -C*H*$_3$), 6.58 (d, 2H, *J* = 16 Hz, vinyl), 7.49 (d, 4H, *J* = 7.7 Hz, arom *H*), 7.69 (t, 4H, *J* = 7.7 Hz, arom *H*), 7.91 (d, 4H, *J* = 7.7 Hz, arom *H*), 7.93 (d, 2H, *J* = 7.7 Hz, arom *H*), 8.29 (d, 2H, *J* = 8.2 Hz, arom *H*), 8.65 (s, 2H, β-pyrrole-*H*), 8.71 (d, 2H, *J* = 16 Hz, vinyl), 8.88 (s, 2H, β-pyrrole-*H*), 8.93 (d, 2H, *J* = 4.4 Hz, β-pyrrole-*H*), 9.23 (d, 2H, *J* = 4.4 Hz, β-pyrrole-*H*); ^{13}C-NMR (125 MHz, CD_2Cl_2): δ = 150.38, 149.72, 148.92, 148.53, 146.90, 139.29, 138.67; UV/VIS (DMF): λ_{max} (log ε) = 445 (5.12), 584 (3.98), 630 (3.80).



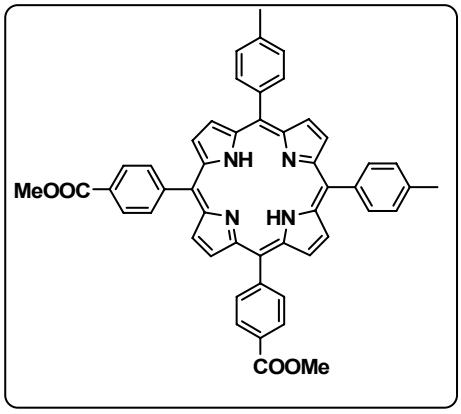
General procedure for preparation of compounds 4-10 *via* Suzuki coupling reaction.

A Schlenk flask was charged with K_3PO_4 (20 eq.) and anhydrous THF (60 mL) under an argon atmosphere, then porphyrin (1 eq.), arylboronic acid or arylboronic ester (10 eq.) and $Pd(PPh_3)_4$ (0.1 eq.) were added. The reaction was refluxed for 7-10 hours (monitored by TLC) and protected from light. After completion, the solvent was evaporated and the residue was dissolved in

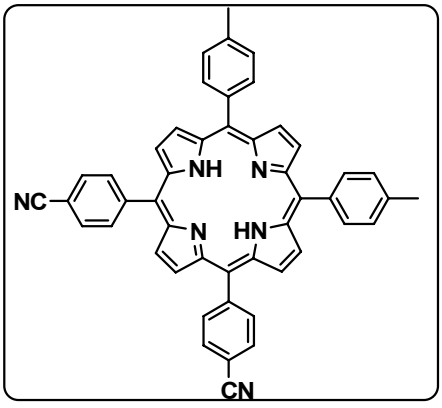
CH_2Cl_2. This mixture was washed with saturated $NaHCO_3$, H_2O, and brine and then dried over Na_2SO_4. The organic solvent was evaporated and the crude product was purified by flash chromatography using dichloromethane:*n*-hexane = 1:1, followed by recrystallization from dichloromethane/methanol to give the desired compound.

5,10-Bis-(4-methoxycarbonylphenyl)-15,20-bis(*p*-tolyl)porphyrin (4a).

Following the general procedure 5,10-dibromo-15,20-bis-(*p*-tolyl)porphyrin (33 mg, 0.05 mmol), 4-methoxycarbonylphenyl boronic acid (90 mg, 0.5 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and K_3PO_4 (212 mg, 1 mmol) in THF (60 mL) gave 20 mg (0.02 mmol, 52 %) of purple solid after recrystallization from dichloromethane/methanol; R_f = 0.28 (CH_2Cl_2: *n*-hexane = 1:1); mp > 300 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = -2.76 (s, 2H, N*H*), 2.70 (s, 6H, -CH_3), 4.13 (s, 6H, -OCH_3), 7.59 (d, 4H, *J* = 7.6 Hz, arom *H*), 8.12 (d, 4H, *J* = 7.6 Hz, arom *H*), 8.32 (d, 4H, *J* = 8.19 Hz, arom *H*), 8.46 (d, 4H, *J* = 8.18 Hz, arom *H*), 8.80 (d, 2H, *J* = 4.68 Hz, β-pyrrole-*H*), 8.82 (s, 2H, β-pyrrole-*H*), 8.90 (s, 2H, β-pyrrole-*H*), 8.92 (d, 2H, *J* = 4.68 Hz, β-pyrrole-*H*); ^{13}C-NMR (125MHz, $CDCl_3$): δ = 166.89, 146.66, 138.54, 137.09, 134.10, 129.76, 129.12, 127.48, 127.03, 126.80, 120.85, 118.09, 52.37, 21.46; UV/VIS (DMF): λ_{max} (log ε) = 420 (4.92), 516 (4.27), 551 (4.08), 581 (3.87), 655 (3.97); HRMS (MS ES+) [$C_{50}H_{39}N_4O_4$] ($M+H^+$): calcd 759.2971, found 759.2941.

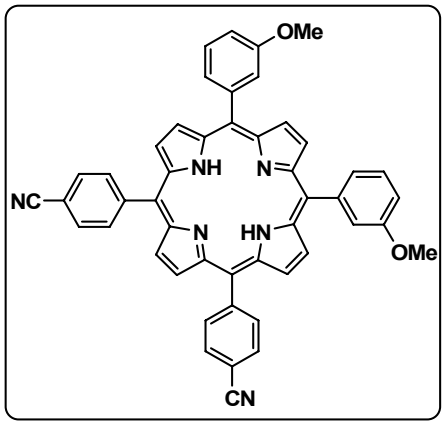


5,10-Bis-(4-cyanophenyl)-15,20-bis(*p*-tolyl)porphyrin (4b).



Following the general procedure 5,10-dibromo-15,20-bis-(*p*-tolyl)porphyrin (30 mg, 0.046 mmol), 4-cyanophenyl boronic acid (68 mg, 0.46 mmol), $Pd(PPh_3)_4$ (5.3 mg, 0.0046 mmol) and K_3PO_4 (196 mg, 0.925 mmol) in THF (50 mL) gave 15 mg (0.021 mmol, 47%) of purple solid after recrystallization from dichloromethane/methanol; mp > 300 °C; R_f = 0.34 (CH_2Cl_2: *n*-hexane = 1:1, v/v); ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = -2.79 (s, 2H, N*H*), 2.74 (s, 6H, -C*H*$_3$), 7.60 (d, 4H, *J* = 8.18 Hz, arom *H*), 8.10 (m, 8H, arom *H*), 8.36 (d, 4H, *J* = 8.18 Hz, arom *H*), 8.75 (d, 2H, *J* = 4.68 Hz, β-pyrrole-*H*), 8.78 (s, 2H, β-pyrrole-*H*), 8.92 (s, 2H, β-pyrrole-*H*), 8.95 (d, 2H, *J* = 4.68 Hz, β-pyrrole-*H*); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 146.55, 138.30, 137.28, 134.29, 130.13, 137.11, 121.13, 118.57, 111.51, 21.10; UV/VIS (DMF): λ_{max} (log ε) = 420 (4.94), 515 (3.79), 551 (3.62), 584 (3.44), 655 (3.68); HRMS (MS ES+) [$C_{48}H_{33}N_6$] ($M+H^+$): calcd 693.2767, found 693.2734.

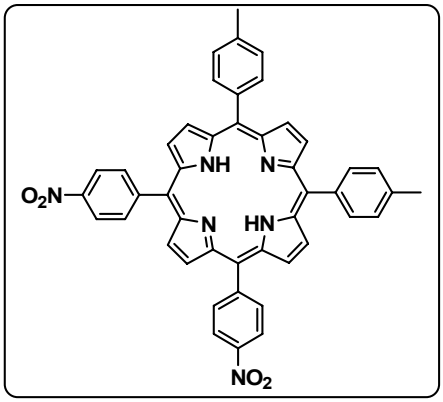
5,10-Bis-(4-cyanophenyl)-15,20-bis(3-methoxyphenyl)porphyrin (4c).



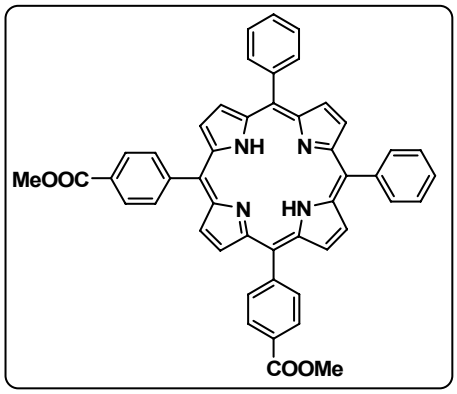
Following the general procedure 5,10-dibromo-15,20-bis(3-methoxyphenyl)porphyrin (30 mg, 0.044 mmol), 4-cyanophenyl boronic acid (64 mg, 0.44 mmol), $Pd(PPh_3)_4$ (5 mg, 0.0044 mmol) and K_3PO_4 (186 mg, 0.88 mmol) in THF (60 mL) gave 15 mg (0.020 mmol, 47 %) of purple solid after recrystallization from dichloromethane/methanol; mp > 300 °C; R_f = 0.3 (CH_2Cl_2: *n*-hexane = 1:1, v/v); ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = -2.82 (s, 2H, N*H*), 4.02 (s, 6H, -OC*H*$_3$), 7.38 (m, 2H, arom *H*), 7.69 (t, 4H, *J* = 8.18 Hz, arom *H*), 7.81 (m, 4H, arom *H*), 8.10 (d, 4H, *J* = 8.18 Hz, arom *H*), 8.36 (d, 4H, *J* = 7.6 Hz, arom *H*), 8.77 (d, 2H, *J* = 4.68 Hz, β-pyrrole-*H*), 8.79 (s, 2H, β-pyrrole-*H*), 8.94 (s, 2H, β-pyrrole-*H*), 8.97(d, 2H, *J* = 4.68 Hz, β-pyrrole-*H*); ^{13}C-NMR (125 MHz, $CDCl_3$): δ

= 157.55, 146.47, 142.51, 134.51, 130.14, 127.19, 120.56, 118.53, 117.18, 115.85, 113.19, 111.58, 55.07; UV/VIS (DMF): λ_{max} (log ε) = 419 (4.90), 513 (3.56), 547 (3.25), 592 (3.16), 643 (3.18); HRMS (MS ES+) [$C_{48}H_{33}N_6O_2$] (M+H^+): calcd 725.2655, found 725.2641.

5,10-Bis-(4-nitro-phenyl)-15,20-bis(*p*-tolyl)porphyrin (4d). Following the general procedure 5,10-dibromo-15,20-bis(*p*-tolyl)porphyrin (30 mg, 0.0462 mmol), 4-nitrophenylboronic acid pinacol ester (116 mg, 0.462 mmol), $Pd(PPh_3)_4$ (5.3 mg, 0.00462 mmol) and K_3PO_4 (196 mg, 0.925 mmol) in THF (50 mL) gave 16 mg (0.021 mmol, 47 %) of purple solid after recrystallization from dichloromethane/methanol; mp > 300 °C; R_f = 0.5 (CH_2Cl_2: *n*-hexane = 1:1, v/v); ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = -2.76 (s, 2H, N*H*), 2.74 (s, 6H, -CH_3), 7.60 (d, 4H, *J* = 7.6 Hz, arom *H*), 8.11 (d, 4H, *J* = 7.6 Hz, arom *H*), 8.42 (d, 4H, *J* = 8.19 Hz, arom *H*), 8.67 (d, 4H, *J* = 8.18 Hz, arom *H*), 8.76 (d, 2H, *J* = 4.67 Hz, β-pyrrole-*H*), 8.80 (s, 2H, β-pyrrole-*H*), 8.92 (s, 2H, β-pyrrole-*H*), 8.96 (d, 2H, *J* = 4.68 Hz, β-pyrrole-*H*); ^{13}C-NMR (125MHz, $CDCl_3$): δ = 148.53, 147.31, 138.25, 137.33, 134.66, 127.12, 121.48, 116.47, 21.09; UV/VIS (DMF): λ_{max} (log ε) = 421 (4.90), 516 (3.64), 552 (3.46), 584 (3.34), 655 (3.60).; HRMS (MS ES+) [$C_{46}H_{32}N_6O_4$] (M+H^+): calcd 733.2563, found 733.2573.

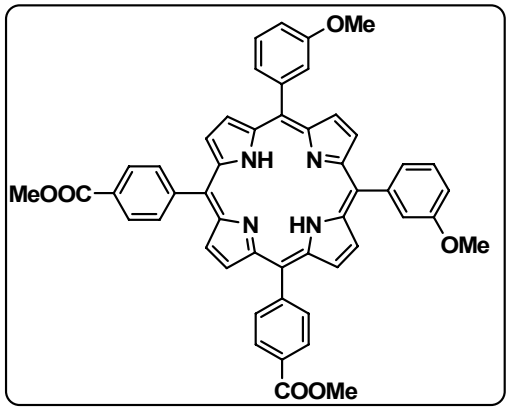


5,10-Bis-(4-methoxycarbonylphenyl)-15,20-diphenyl-porphyrin (4e). Following the general procedure 5,10-dibromo-15,20-diphenylporphyrin (30 mg, 0.048 mmol), 4-methoxycarbonylphenylboronic acid (86 mg, 0.48 mmol), $Pd(PPh_3)_4$ (5.5 mg, 0.0048 mmol) and K_3PO_4 (205 mg, 0.967 mmol) in THF (50 mL) gave 10 mg (0.013



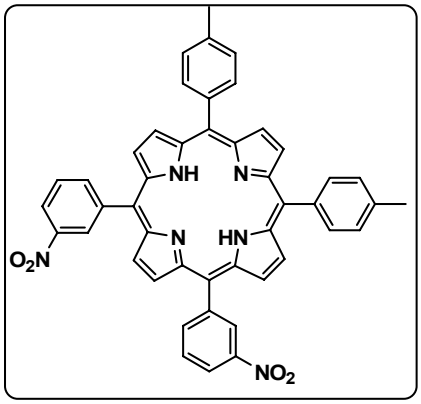
mmol, 30 %) of purple solid after recrystallization from dichloromethane/methanol; mp > 300°C; R_f = 0.5 (CH_2Cl_2: *n*-hexane = 1:1, v/v); ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = -2.76 (s, 2H, N*H*), 4.14 (s, 6H, -CH_3), 7.79 (d, 4H, *J* = 7.6 Hz, arom *H*), 8.24 (d, 4H, *J* = 8.18 Hz, arom *H*), 8.33 (d, 4H, *J* = 8.19 Hz, arom *H*), 8.47 (d, 4H, *J* = 8.18 Hz, arom *H*), 8.82 (m, 4H, β-pyrrole-*H*), 8.90 (m, 4H, β-pyrrole-*H*); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 166.85, 146.45, 141.47, 134.07, 129.19, 127.44, 126.29, 118.30, 51.99, 45.57; UV/VIS (DMF): λ_{max} (log ε) = 418 (4.94), 514 (3.80), 548(3.61), 588 (3.34), 646 (3.32); HRMS (MS ES+) [$C_{48}H_{35}N_4O_4$](M+H$^+$): calcd 731.2658, found 731.2625.

5,10-Bis-(4-methoxycarbonylphenyl)-15,20-bis(3-methoxyphenyl)porphyrin (4f).



Following the general procedure 5,10-dibromo-15,20-bis(3-methoxyphenyl)porphyrin (20 mg, 0.0293 mmol), 4-methoxycarbonylphenylboronic acid (52 mg, 0.293 mmol), $Pd(PPh_3)_4$ (94 mg, 0.00293 mmol), K_3PO_4 (124 mg, 0.587 mmol) in THF (50 mL) gave 9 mg (0.011 mmol, 32%) of purple solid after recrystallization from dichloromethane/methanol; mp > 300 °C; R_f = 0.3(CH_2Cl_2: *n*-hexane = 1:1, v/v); ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = -2.78 (*s*, 2H, N*H*), 4.01 (*s*, 6H, -OCH_3), 4.14 (s, 6H, -OCH_3), 7.37 (d, 2H, *J* = 8.18 Hz, arom *H*), 7.67 (t, 2H, *J* = 8.18 Hz, arom *H*), 7.82 (d, 4H, *J* = 7.6 Hz, arom *H*), 8.33 (d, 4H, *J* = 7.6 Hz, arom *H*), 8.47 (d, 4H, *J* =7.6 Hz, arom *H*), 8.82 (m, 4H, β-pyrrole-*H*), 8.93 (m, 4H, β-pyrrole-*H*); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.18, 157.80, 146.74, 143.06, 134.40, 129.48, 127.81, 120.35, 118.79, 113.46, 55.37, 52.33 ; UV/VIS (DMF): λ_{max} (log ε) = 419 (4.96), 514 (3.74), 549 (3.47), 588 (3.34), 646 (3.36) ; HRMS (MS ES+) [$C_{50}H_{39}N_4O_6$] (M+H$^+$): calcd 791.2870, found 791.2865.

5,10-Bis(3-nitrophenyl)-15,20-bis(*p*-tolyl)porphyrin (4g).



Following the general procedure 5,10-dibromo-15,20-bis(*p*-tolyl)porphyrin (33 mg, 0.05 mmol), 4-methoxycarbonylphenyl boronic acid (90 mg, 0.5 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol), K_3PO_4 (212 mg, 1 mmol) in THF (60 mL) gave 10 mg (0.013 mmol, 30 %) of purple solid after recrystallization from dichloromethane/methanol; mp > 300 °C; R_f = 0.3 (CH_2Cl_2: *n*-hexane = 1:1, v/v); ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = -2.77 (s, 2H, N*H*), 2.74 (s, 6H, -C*H*$_3$), 7.60 (d, 4H, *J* = 7.6 Hz, arom *H*), 7.99 (t, 2H, *J* = 7.6 Hz, arom *H*), 8.13 (d, 2H, *J* = 7.01 Hz, arom *H*), 8.57 (m, 2H, arom *H*), 8.72 (d, 4H, *J* = 8.19 Hz, arom *H*), 8.79 (d, 2H, *J* = 4.67 Hz, β-pyrrole-*H*), 8.93 (s, 2H, β-pyrrole-*H*), 8.96 (d, 2H, *J* = 4.68 Hz, β-pyrrole-*H*), 9.11 (s, 2H, β-pyrrole-*H*); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 146.84, 143.64, 139.69, 138.62, 137.61, 134.38, 128.20, 127.66, 127.44, 122.88, 121.52, 116.46, 29.59; UV/VIS (DMF): λ_{max} (log ε) = 421 (4.90), 516 (3.64), 551 (3.46), 589 (3.34), 646 (3.16); HRMS (MS ES+) [$C_{44}H_{32}N_4O_4$] ($M+H^+$): calcd 733.2563, found 733.2540.

References:

1. S. Taniguchi, H. Hasegawa, S. Yanagiya, Y. Tabeta, Y. Nakano, M. Takahashi, *Tetrahedron* 2000, **57**, 2103.
2. S. Hatscher, M. O. Senge, *Tetrahedron Lett.* 2003, **44**, 157.