Experimental section for compounds 7, 14 and 16.

General. All commercially available reagents were purchased and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker spectrometers at 300 MHz and 50 MHz. Absorption spectra were collected in CH_2Cl_2 or $CHCl_3$ at room temperature. Infrared spectra were mesured on a *Perkin Elmer* FTIR 1600 spectrometer.

Preparation of *meso*-(4-acetoxyphenyl)dipyrromethane (7): 4-formylphenyl acetate (2mmol, 1 eq.) was added to 40 mL of freshly filtered pyrrole and degased (argon for 10 min). $BF_3{\cdot}Et_2O$ (0.2 mmol, 0.1 eq.) was added to the mixture and the solution was stirred for 2h at r.t. under argon. The reaction mixture was evaporated to dryness and the dark residue was dissolved in $CHCl_3$ and washed with 50 mL of 0.1 M NaOH aqueous solution. The organic phase was dried over $MgSO_4$, filtrated and concentrated under reduced pressure. The resulting crude product was purified by column chromatography (silica gel, PE/EtOAc 4:1, % NEt_3) affording the desired product as a yellow solid in 76% yield.
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.94 (brs, 2H, NH), 7.20 (AA'BB', m, 2H, Ar*H*), 7.02 (AA'BB', m, 2H, Ar*H*), 6.69 (m, 2H), 6.15 (dd, $^{3}J_{HH}$ = 6.04 Hz, $^{4}J_{HH}$ = 2.74 Hz, 2H), 5.91 (m, 2H), 5.47 (s, 1H, *meso*H), 2.29 (s, 3H, $COCH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 169.5, 149.5, 139.6, 132.2, 129.4, 121.6, 117.3, 108.4, 107.3, 60.4, 43.4. IR [cm^{-1}]: 3431, 3380, 1727, 1561, 1502, 1428, 1369, 1236, 1196, 1159, 1111, 1082, 1026, 1015, 923, 882, 864, 790, 776, 764, 595, 565, 510.

General method for the synthesis of Porphyrins 14 and 16: The corresponding dipyrromethane (2 mmol, 1 eq.) and 4-pyridylaldehyde (2 mmol, 1 eq.) were dissolved in 200 mL of CH_2Cl_2 and degassed (argon). After 15 min TriFluoroacetic Acid (TFA) (6 mmol, 3 eq.) was added and the mixture stirred for 1h. The reaction completion was monitored by TLC (SiO_2, CH_2Cl_2/Aceton 9:1). After all the starting material was consumed 35 mL of THF were added followed by NEt_3 (6 mmol, 3 eq.) and DDQ (3 mmol, 1.5 eq.) dissolved in 10 mL of THF. The reaction mixture was stirred over night at r.t. The reaction mixture was filtered over a silica pad and washed with ~100 mL CH_2Cl_2/Aceton 9:1. The filtrate was evaporated to dryness under reduced pressure. The crude product was purified by column chromatography (silica gel, CH_2Cl_2/Aceton 9:1, % NEt_3). The desired product was obtained as a purple solid.

***meso*-5,15-di(4-pyridyl)-10,20-di(4-acetoxyphenyl)porphyrin (14):** Purple solid. Yield 4%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 9.05 (d, $^{3}J_{HH}$ = 5.85 Hz, 4H, *H*-pyridyl), 8.94 (d, $^{3}J_{HH}$ = 4.94 Hz, 4H, *H*-β-pyrrol), 8.83 (d, $^{3}J_{HH}$ = 4.94 Hz, 4H, *H*-β-pyrrol), 8.21 (d, $^{3}J_{HH}$ = 8.60 Hz,

4H, *o*-(acetoxyphenyl)), 8.17 (d, $^3J_{HH}$ = 4.39 Hz, 4H, *H*-pyridyl), 7.53 (d, $^3J_{HH}$ = 8.42 Hz, 4H, *m*-(acetoxyphenyl)), 2.50 (s, 6H, *H*-CH_3), -2.87 (s, 2H, *H*-internal pyrrole). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 169.5, 150.8, 148.3, 139.1, 135.3, 131.8, 130.7, 129.4, 120.0, 119.9, 117.2, 113.8. UV/VIS [λ_{max} nm, in $CHCl_3$, (ε*10^{-4})] = 418 (48.50), 514 (2.04), 549 (0.69), 589 (0.58), 645 (0.29) nm. Infrared spectrum [cm^{-1}]: 3446, 3313, 3077, 1754, 1593, 1501, 1407, 1368, 1201, 1166, 1067, 1019, 969, 911, 882, 801, 729.

Single crystals of **14** were obtained by slow evaporation of a solution of **14** in $CHCl_3$.

Crystal data : $C_{49}H_{35}Cl_9N_6O_4$, M = 1090.88, *Triclinic,* space group *P-1*, a = 9.7555(2), b = 13.5546(3), c = 20.0154(4) Å, a = 78.3190(10)°, β = 76.7100(10)°, g = 77.1790(10)°, V = 2479.38(9) Å^3, T = 173(2) K, Z = 2, Dc = 1.461 g.cm^{-3}, μ = 0.559 mm^{-1}, 26849 collected reflections, 4342 independent (Rint = 0.0851), GooF = 1.021, R_1 = 0.0809, wR_2 = 0.2037 for I>2σ(I) and R_1 = 0.1163, wR_2 = 0.2310 for all data.

***meso*-5,15-di(4-pyridyl)-10,20-di(4-trifluoromethylphenyl)porphyrin (16):** Purple solid. Yield 5%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 9.06 (d, $^3J_{HH}$ = 5.67 Hz, 4H, *H*-pyridyl), 8.85 (s, 8H, Ar*H*), 8.34 (d, $^3J_{HH}$ = 8.23 Hz, 4H, *H*-β-pyrrol), 8.17 (d, $^3J_{HH}$ = 5.85 Hz, 4H, *H*-pyridyl), 8.06 (d, $^3J_{HH}$ = 8.42 Hz, 4H, *H*-β-pyrrol), -2.88 (s, 2H, *H*-internal pyrrole). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 150.4, 147.7, 145.1, 145.0, 134.4, 130.5, 130.1, 129.7, 129.6, 129.5, 127.7, 126.1, 123.7, 122.5, 119.2, 117.5, 117.1. UV/VIS [λ_{max} nm, in CH_2Cl_2, (ε*10^{-4})] = 416 (41.90), 512 (1.55), 547 (0.33), 587 (0.34), 643 (0.13) nm.

Infrared spectrum [cm^{-1}]: 3424, 3313, 2922, 1612, 1594, 1402, 1325, 1166, 1126, 1107, 1067, 1019, 967, 801,735, 635.

Single crystals of **16** were obtained by slow vapour diffusion of diethyl ether into a solution of **16** in $CHCl_3$.

Crystal data: $C_{44}H_{26}F_6N_6$, M = 752.71, *Monoclinic,* space group *C2/c*, a = 32.844(16), b = 18.240(9), c = 11.775(6) Å, a = g = 90°, β = 99.463(6)°, V = 6958(6) Å^3, T = 173(2) K, Z = 8, Dc = 1.437 g.cm^{-3}, μ = 0.109 mm^{-1}, 13895 collected reflections, 7657 independent (Rint = 0.0674), GooF = 1.044, R_1 = 0.0894, wR_2 = 0.2267 for I>2σ(I) and R_1 = 0.2267, wR_2 = 0.2726 for all data.