Supplementary Information for

The absorption and fluorescence emission spectra of meso-tetra(aryl)porphyrin dications with weak and strong carboxylic acids: a comparative study

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S1a: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data of the porphyrins

H_2TPP. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: -2.77 (2H, br, s, NH), 7.77-7.84 ($8H_m$ and $4H_p$, m), 8.26-8.27 ($8H_o$, d), 8.90 ($8H_\beta$, s); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 120.18 (C_{meso}), 142.20 (C_1), 134.60 (C_2, C_6), 126.73 (C_3, C_5), 127.75 (C_4), 131.5 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 417 (5.79), 513 (4.58), 548 (4.38), 590 (4.30), 647 (4.29).

H_2T(4-OMe)PP. ^{1}H NMR (400MHz, $CDCl_3$, TMS), δ/ppm: -2.72 (2H, br, s, NH), 7.29-7.32 ($8H_m$, d), 8.15-8.17 ($8H_o$, d), 8.89 ($8H_\beta$, s), 4.13 ($12H_{Me}$, s); ^{13}C NMR (~100MHz, $CDCl_3$, TMS), δ/ppm: 119.75 (C_{meso}), 134.67 (C_1), 135.62 (C_2, C_6), 112.20 (C_3, C_5), 159.39 (C_4), 131.34 (C_β), 55.61 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε)= 421 (5.61), 517 (4.32), 555 (4.22), 593 (4.06), 651 (4.11).

H_2T(2-Me)PP. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: -2.59 (2H, br, s, NH), 7.54-7.74 ($8H_m$ and $4H_p$, m, meta and para-position relative to C atom attached to meso position), 7.99-8.11 ($4H_o$, m, ortho-position relative to C atom attached to meso position), 8.70 ($8H_\beta$, s), 2.01-2.11 ($12H_{Me}$, m);); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 118.82 (C_{meso}), 139.54 (C_1), 139.63 (C_2), 128.38 (C_3), 129.22 (C_4), 124.21 (C_5), 133.90 (C_6), 141.48 (C_α), 129.22 (C_β), 21.37 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 416 (6.04), 512 (4.74), 545 (4.34), 589 (4.34), 645 (4.25).

H_2T(4-Me)PP. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: -2.76 (2H, br, s, NH), 7.55-7.58 ($8H_m$, d), 8.09-8.12 ($8H_o$, d), 8.86 ($8H_\beta$, s), 2.65 ($12H_{Me}$, s); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 120.47 (C_{meso}), 139.73 (C_1), 134.92 (C_2, C_6), 127.81 (C_3, C_5), 137.71 (C_4), 131.37 (C_β), 21.57 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 418 (5.89), 516 (4.54), 551 (4.34), 590 (4.18), 647 (4.20).

H_2T(2-Cl)PP. ^{1}H NMR (400MHz, $CDCl_3$, TMS), δ/ppm: -2.62 (2H, br, s, NH), 7.66-7.87 ($8H_m$ and $4H_p$, m, meta and para-position relative to C atom attached to meso position), 8.10-8.26 ($4H_o$, m, ortho-position relative to C atom attached to meso position), 8.72 ($8H_\beta$, s); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 116.76 (C_{meso}), 137.10 (C_1), 136.94 (C_2), 129.01 (C_3), 129.93 (C_4), 125.32 (C_5), 135.52 (C_6), 140.50 (C_α), 135.39 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 416 (5.64), 512 (4.47), 543 (4.07), 587 (4.15), 643 (3.96).

H_2T(4-Cl)PP. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: -2.83 (2H, br, s, NH), 7.77-7.79 ($8H_m$, d), 8.15-8.17 ($8H_o$, d), 8.87 ($8H_\beta$, s); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 119.01 (C_{meso}), 140.37 (C_1), 135.52 (C_2, C_6), 127.07 (C_3, C_5), 134.41 (C_4), 131.64 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 418 (5.79), 513 (4.52), 547 (4.25), 590 (4.16), 647 (4.10).

H_2T(thien-2-yl)P. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: -2.65 (2H, br, s, NH); 7.48-7.51(4H, m); 7.84-7.86 (4H, m); 7.907-7.920 (4H, m); 9.03 (8H, s, β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): (See ESI,† S3-1).

H_2T(4-SCH_3)PP. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 8.82 (s,8H,H_β), 8.07 (d, 8H, H_o), 7.58 (d, 8H, H_m), 2.70 (s,12H,CH_3), -2.84 (s,2H,NH); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): (See ESI,† S3-1).

H_2T(2-NO_2)PP. ^{1}H NMR (400 MHz, DMSO-d_6, TMS), δ/ppm: - 2.83 (s, 2H, NH), 8.61 (s, 8H, H_β), 8.30 (m, 4H, H_o), 8.45 (m, 8H, H_m), 7.98 (m, 4H, H_p); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): (See ESI,† S3-1).

H_2T(2,6-Cl)PP. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: -2.59 (2H, br, s, NH), 7.68 (12H, m, $H_{m,p}$), 8.66 (8H, s, H_β,); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): (See ESI,† S3-1).

S1b: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data of the porphyrins dications

H_4TPP($CF_3COO)_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 0.276 (4H, br, s, NH), 7.99-8.043 ($8H_m$ and $4H_p$, m), 8.616-8.652 ($8H_o$, m), 8.616-8.652 ($8H_\beta$, m); ^{13}C NMR (~100MHz, $CDCl_3$, TMS), δ/ppm: 122.77 (C_{meso}), 139.90 (C_1), 138.52 (C_2, C_6), 128.31 (C_3, C_5), 130.01 (C_4), 145.72 (C_α), 128.31 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 437 (5.83), 600 (4.46), 652 (4.93).

H_4T(4-OMe)PP($CF_3COO)_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 0.425 (4H, br, s, NH), 7.553-8.573 ($8H_m$, d), 8.527-8.562 ($8H_\beta$, $8H_o$, br), 4.195 ($12H_{Me}$, s); ^{13}C NMR (~100MHz, $CDCl_3$, TMS), δ/ppm: 122.09 (C_{meso}), 133.44 (C_1), 140.01 (C_2, C_6), 114.01 (C_3, C_5), 161.49 (C_4), 146.11 (C_α), 127.75 (C_β), 55.84 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 449 (5.77), 686 (5.07).

H_4T(2-Me)PP($CF_3COO)_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: -0.954 (4H, br, s, NH), 7.721-7.895 ($8H_m$ and $4H_p$, br, meta and para-positions relative to C atom attached to the meso position), 8.181-8.216 ($4H_o$, br, ortho-position relative to the C atom attached to the meso position), 8.651-8.682 ($8H_\beta$, s), 2.208-2.285 (H_{Me}, m); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm:

121.47 (C_{meso}), 138.33 (C_1), 140.86 (C_2), 128.41 (C_3), 129.08 (C_4), 125.39 (C_5), 136.62 (C_6), 145.51 (C_α), 130.54 (C_β), 21.87 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 432 (5.99), 583 (6.46), 633 (4.89).

$H_4T(4\text{-}Me)PP(CF_3COO)_2$. ^1H NMR (400MHz, $CDCl_3$, TMS), δ/ppm: 0.42 (4H, br, s, NH), 7.79-7.82 ($8H_m$, d), 8.46-8.49 ($8H_o$, d), 8.55 ($8H_\beta$, s), 2.67 ($12H_{Me}$, s); ^{13}C NMR (~100MHz,$CDCl_3$, TMS), δ/ppm: 122.60 (C_{meso}), 137.56 (C_1), 138.62 (C_2, C_6), 129.12 (C_3, C_5), 140.31 (C_4), 145.85 (C_α), 127.95 (C_β), 21.68 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 442 (5.85), 666 (5.01).

$H_2T(thien\text{-}2\text{-}yl)P(CF_3COO)_2$. ^1H NMR (400MHz, $CDCl_3$, TMS), δ/ppm: 1.53 (4H, br, s, NH); 7.78-7.814 (4H, dd); 8.26-8.28 (4H, d); 8.37-8.38 (4H, d); 8.58 (8H, s, β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): (See ESI,† S3-2).

$H_2T(4\text{-}SCH_3)PP(CF_3COO)_2$. ^1H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 8.77 (s,8H,H_β), 8.33 (d, 8H, H_o), 7.88 (d, 8H, H_m), 3.12 (s,12H,CH_3), 0.2 (s,4H,NH); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): (See ESI,† S3-2).

$H_2T(2\text{-}NO_2)PP(CF_3COO)_2$. ^1H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 1.25 (s, 4H, NH), 8.53 (s, 8H, H_β), 8.10 (m, 4H, H_o), 8.30 (m, 8H, H_m), 8.10 (m, 4H, H_p); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): (See ESI,† S3-2).

$H_2T(2,6\text{-}Cl)PP(CF_3COO)_2$. ^1H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 0.5 (4H, br, s, NH), 7.8-8.0 (12H, m, $H_{m,p}$), 8.79 (8H, s, H_{β},); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): (See ESI,† S3-2).

$H_4T(4\text{-}Cl)PP(HCOO)_2$. ^1H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.746 ($8H_m$, d), 8.4 ($8H_o$, d), 8.674 ($8H_\beta$, s); no signal was observed for the NH protons at 20 ^{0}C, but at -60 ^{0}C, the NH resonance was observed at δ 0.19 ppm[1].; ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 122.17 (C_{meso}), 138.09 (C_1), 139.59 (C_2, C_6), 129.19 (C_3, C_5), 137.54 (C_4), 145.66 (C_α), 128.94 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 442 (5.65), 662 (4.91).

$H_4T(2\text{-}Cl)PP(CF_3COO)_2$. ^1H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 1.5 (4H, br, s, NH), 7.77-7.938 ($8H_m$ and $4H_p$, m, meta and para-positions relative to the C atom attached to the meso position), 8.29 ($4H_o$, br, ortho-position relative to C atom attached to the meso position), 8.681 ($8H_\beta$, s); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 117.99 (C_{meso}), 137.39 (C_1), 137.72 (C_2), 129.58 (C_3, C_4), 125.88 (C_5), 136.75 (C_6), 146.16 (C_α), 131.04 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 431 (5.76), 580 (4.69), 632 (4.75).

$H_4T(4\text{-}Cl)PP(CF_3COO)_2$. ^1H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 0.392 (4H, br, s, NH), 8.026-8.046 ($8H_m$, d), 8.518-8.539 ($8H_o$, d), 8.635 ($8H_\beta$, s); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 121.73 (C_{meso}), 138.11 (C_1), 139.22 (C_2, C_6), 128.81 (C_3, C_5), 137.50 (C_4), 145.67 (C_α), 128.38 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 439 (6.06), 656 (5.16).

$H_4TPP(HCOO)_2$. ^1H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.777 ($8H_m$ and $4H_p$, d), 8.174 ($8H_o$, d), 8.828 ($8H_\beta$, s); no signal was observed for the NH protons at 20 ^{0}C, but at -60 ^{0}C, the NH resonance was observed at δ 0.49 ppm[1].; ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 123.26 (C_{meso}), 139.23 (C_1), 138.85 (C_2, C_6), 129 (C_3, C_5), 130.70 (C_4), 145.67 (C_α), 128.78 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 439 (5.75), 604 (4.42), 657 (4.89).

$H_4T(4\text{-}OMe)PP(HCOO)_2$. ^1H NMR (400MHz, $CDCl_3$, TMS), δ/ppm: 7.532 ($8H_m$, d), 8.547 ($8H_o$, d), 8.56 ($8H_\beta$, s), 4.162 ($12H_{Me}$, s); no signal was observed for the NH protons at 20 ^{0}C, but at -60 ^{0}C, the NH resonance was observed at δ 0.42 ppm[1].; ^{13}C NMR (~100MHz, $CDCl_3$, TMS), δ/ppm: 122.59 (C_{meso}), 132.67 (C_1), 140.31 (C_2, C_6), 114.62 (C_3, C_5), 162.13 (C_4), 145.99 (C_α), 128.46 (C_β), 55.89 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 452 (5.36), 695 (4.73).

$H_4T(2\text{-}Me)PP(HCOO)_2$. ^1H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.863-7.9 ($8H_m$ and $4H_p$, br, meta and para-position relative to C atom attached to meso position), 8.254-8.332 ($4H_o$, br, ortho-position relative to C atom attached to meso position), 8.73-8.76 ($8H_\beta$, br), 2.144-2.203 (H_{Me}, m); no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 121.69 (C_{meso}), 138.12 (C_1), 140.86 (C_2), 129.53 (C_3), 129.56 (C_4), 125.62 (C_5), 136.54 (C_6), 145.63 (C_α), 130.60 (C_β), 21.03 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 433 (5.79), 582 (4.49), 635 (4.69).

$H_4T(4\text{-}Me)PP(HCOO)_2$. ^1H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.88-7.91 ($8H_m$, d), 8.533-8.553 ($8H_o$, d), 8.7 ($8H_\beta$, s), 2.767 ($12H_{Me}$, s); no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 123.1 (C_{meso}), 136.87 (C_1), 138.86 (C_2, C_6), 129.63 (C_3, C_5), 141.34 (C_4), 145.75 (C_α), 128.68 (C_β), 21.62 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 443 (5.88), 672 (5.09).

$H_4T(2\text{-}Cl)PP(HCOO)_2$. ^1H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.92-7.95 ($8H_m$ and $4H_p$, br, meta and para-positions relative to the C atom attached to the meso position), 8.4-8.5 ($4H_o$, br, ortho-position relative to C atom attached to meso position), 8.78-8.826 ($8H_\beta$, br); no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (~100MHz, $CDCl_3$, TMS), δ/ppm: 119.24 (C_{meso}), 137.83 (C_1), 138.02 (C_2), 129.87 (C_3, C_4), 126.62 (C_5), 136.84 (C_6), 145.57 (C_α), 132.55 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 432 (5.65), 580 (4.41), 631 (4.52).

H_2T(thien-2-yl)P$(HCOO)_2$. ^{1}H NMR (400MHz, $CDCl_3$, TMS), δ/ppm: 7.81-7.83 (4H, dd); 8.38-8.39 (4H, d); 8.43-8.44 (4H, d); 8.69 (8H, s, β); no signal was observed for the NH protons at 20 ^{0}C[1]; UV-vis in CH_2Cl_2, λ_{max}/nm (logε): (See ESI,† S3-2).

$H_2T(4\text{-}SCH_3)PP(HCOO)_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 8.67 (s,8H,H_β), 8.5 (b, 8H, H_o), 8.31 (b, 8H, H_m), 2.73 (s,12H,CH_3); no signal was observed for the NH protons at 20 ^{0}C[1]; UV-vis in CH_2Cl_2, λ_{max}/nm (logε): (See ESI,† S3-2).

$H_2T(2\text{-}NO_2)PP(HCOO)_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 8.76 (s, 8H, H_β), 8.57-8.67 (m, 4H, H_o), 8.71-8.73 (m, 8H, H_m), 8.19-8.23 (m, 4H, H_p); no signal was observed for the NH protons at 20 ^{0}C[1]; UV-vis in CH_2Cl_2, λ_{max}/nm (logε): (See ESI,† S3-2).

$H_2T(2,6\text{-}Cl)PP(HCOO)_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.87-7.90 (12H, m, $H_{m,p}$), 8.95 (8H, s, H_{β},); no signal was observed for the NH protons at 20 ^{0}C[1]; UV-vis in CH_2Cl_2, λ_{max}/nm (logε): (See ESI,† S3-2).

S2 The UV-Vis spectral data of the free base porphyrins in CH_2Cl_2[a]

Porphyrins		Bands					$\Delta\nu_{Q(0,0), Soret}$ (cm^{-1})
		Soret	IV	III	II	I	
H_2TPP	λ (nm)	417	513	548	590	647	8525
	logε	5.79	4.58	4.38	4.30	4.29	
	f	1.734	0.112	0.035	0.024	0.015	
	$f_{Soret}/f_{Q(0,0)}$	115.6					
H_2T(4-OMe)PP	λ (nm)	421	517	555	593	651	8392
	logε	5.61	4.32	4.22	4.06	4.11	
	f	1.510	0.068	0.037	0.014	0.014	
	$f_{Soret}/f_{Q(0,0)}$	107.9					
H_2T(2-Me)PP	λ (nm)	416	512	545	589	645	8535
	logε	6.04	4.74	4.34	4.34	4.25	
	f	2.210	0.173	0.039	0.043	0.018	
	$f_{Soret}/f_{Q(0,0)}$	122.8					
H_2T(4-Me)PP	λ (nm)	418	516	551	590	647	8467
	logε	5.89	4.54	4.34	4.18	4.20	
	f	2.710	0.218	0.091	0.050	0.037	
	$f_{Soret}/f_{Q(0,0)}$	73.2					
H_2T(2-Cl)PP	λ (nm)	416	512	543	587	643	8486
	logε	5.64	4.47	4.07	4.15	3.96	
	f	1.590	0.094	0.014	0.024	0.005	
	$f_{Soret}/f_{Q(0,0)}$	318.0					
H_2T(4-Cl)PP	λ (nm)	418	513	547	590	647	8467
	logε	5.79	4.52	4.25	4.16	4.10	
	f	2.560	0.190	0.062	0.045	0.022	
	$f_{Soret}/f_{Q(0,0)}$	116.4					

[a] Oscillator strength; $f = 4.32 \times 10^{-9} \int \varepsilon_\nu d\nu$

S3-1 The UV-Vis spectral data of some electron-rich and electron-deficient free base porphyrins and their dications with CF_3COOH in CH_2Cl_2[a]

Porphyrins		Bands					$\Delta\nu_{Q(0,0), Soret}$ (cm^{-1})
		Soret	IV	III	II	I	
H_2T(thien-2-yl)P[b]	λ (nm)	424	521	560	596	660	8433
	logε	5.39	4.40	4.28	4.24	4.24	
	f	1.130	0.054	0.021	0.011	0.005	
	$f_{Soret}/f_{Q(0,0)}$	204					
H_4T(thien-2-yl)P$(CF_3COO)_2$[b]	λ (nm)	459	-	-	-	723	7955
	logε	5.53	-	-	-	4.9	
	Δν [c]	-1798	-	-	-	-1320	
	f	1.25	0.112	0.035	0.024	0.27	
	$f_{Soret}/f_{Q(0,0)}$	4.6					
H_2T(4-SMe)PP[b]	λ (nm)	422	517	555	594	651	8336
	logε	5.64	4.55	4.46	4.32	4.39	
	f	1.260	0.058	0.035	0.015	0.010	
	$f_{Soret}/f_{Q(0,0)}$	120					
H_4T(4-SMe)PP$(CF_3COO)_2$[b]	λ (nm)	461	-	-	-	692	7241
	logε	5.53	-	-	-	4.99	
	Δν [c]	-2005	-	-	-	-910	
	f	1.57	-	-	-	0.35	
	$f_{Soret}/f_{Q(0,0)}$	4.5					
$H_2T(2-NO_2)PP$[b]	λ (nm)	420	516	550	593	650	8425
	logε	5.57	4.66	4.44	4.40	4.27	
	f	1.28	0.095	0.029	0.023	0.005	
	$f_{Soret}/f_{Q(0,0)}$	264.5					
$H_4T(2-NO_2)PP(CF_3COO)_2$[b]	λ (nm)	431	-	536	583	635	7454
	logε	5.62	-	4.47	4.52	4.67	
	Δν [c]	-608	-	475	289	363	
	f	1.27	-	0.057	0.046	0.073	
	$f_{Soret}/f_{Q(0,0)}$	17.4					
H_2T(2,6-Cl)PP[d]	λ (nm)	417	512	-	606	630	8108
	logε	5.24	4.55	-	4.59	4.51	
	f	0.722	0.057	-	0.088	0.033	
	$f_{Soret}/f_{Q(0,0)}$	21.9					
H_2T(2,6-Cl)PP$(CF_3COO)_2$	λ (nm)	429	-	-	580	612	8467

logε	5.24	-	-	4.76	4.58
Δν [c]	-608	-	-	740	647
f	0.8	-	-	0.15	0.12
$f_{Soret}/f_{Q(0,0)}$	6.7				

[a] See the footnotes of S2. [b] See the Tables and supporting information of [2]. [c] $\Delta\upsilon$ (cm^{-1}) = $10^7(1/\lambda_1 - 1/\lambda_2)$; ($\lambda_1$ = the wavelength of the band of the free base porphyrin; λ_2 = the wavelength of the corresponding band of the dication). [d] Prepared and purified according to the literature.[3]

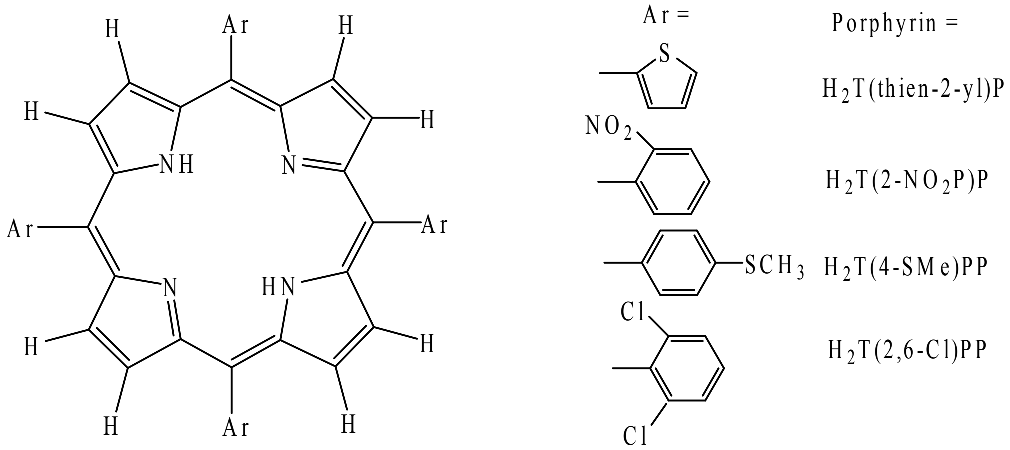
S3-2 The UV-Vis spectral data of some electron-rich and electron-deficient free base porphyrins and their dications with HCOOH in CH_2Cl_2[a,b]

Porphyrins		Bands					$\Delta\nu_{Q(0,0), Soret}$ (cm^{-1})
		Soret	IV	III	II	I	
H_2T(thien-2-yl)P	λ (nm)	424	521	560	596	660	8433
	f	1.130	0.054	0.021	0.011	0.005	
	$f_{Soret}/f_{Q(0,0)}$	204					
H_4T(thien-2-yl)P$(HCOO)_2$	λ (nm)	460	-	-	-	732	8078
	logε	5.53	-	-	-	4.93	
Δν [b]		-1846	-	-	-	-1490	
	f	1.566	-	-	-	0.33	
	$f_{Soret}/f_{Q(0,0)}$	4.74					
H_2T(4-SMe)PP	λ (nm)	422	517	555	594	651	8336
	f	1.260	0.058	0.035	0.015	0.010	
	$f_{Soret}/f_{Q(0,0)}$	120					
H_4T(4-SMe)PP$(HCOO)_2$	λ (nm)	465	-	-	-	706	7341
	logε	5.45	-	-	-	5.04	
	Δν [b]	-2191	-	-	-	-1197	
	f	1.35	-	-	-	0.35	
	$f_{Soret}/f_{Q(0,0)}$	3.9					
$H_2T(2\text{-}NO_2)PP$	λ (nm)	420	516	550	593	650	8425
	f	1.28	0.095	0.029	0.023	0.005	
	$f_{Soret}/f_{Q(0,0)}$	264.5					
$H_4T(2\text{-}NO_2)PP(HCOO)_2$	λ (nm)	431	-	546	582	636	7454
	logε	5.63	-	4.47	4.52	4.68	
	Δν [b]	-608	-	133	319	339	
	f	1.53	-	0.066	0.047	0.039	
	$f_{Soret}/f_{Q(0,0)}$	39					
H_2T(2,6-Cl)PP	λ (nm)	417	512	-	606	630	8108
	f	0.722	0.057	-	0.088	0.033	
	$f_{Soret}/f_{Q(0,0)}$	21.9					
H_2T(2,6-Cl)PP$(HCOO)_2$	λ (nm)	425	-	-	594	628	8467
	logε	5.11	-	-	4.52	4.41	
	Δν [b]	-451	-	-	333	50	

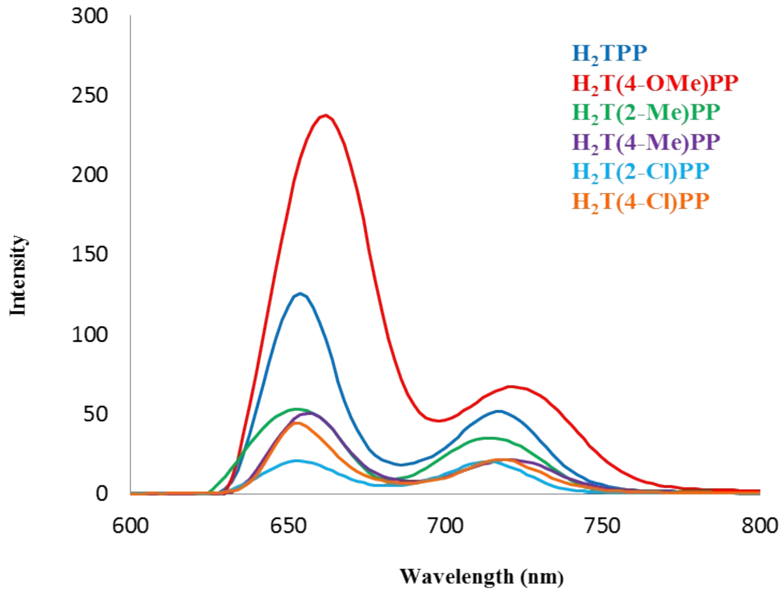
f	0.81	-	-	-	0.02
$f_{Soret}/f_{Q(0,0)}$	40.5				

[a,b] See the footnotes of S2 and S3. [c] See S3-3 for the structre of the porphyrins.

S3-3 The structure of porphyrins of S3-1 and S3-2.



S4 The emission spectra of the free base porphyrins in CH_2Cl_2

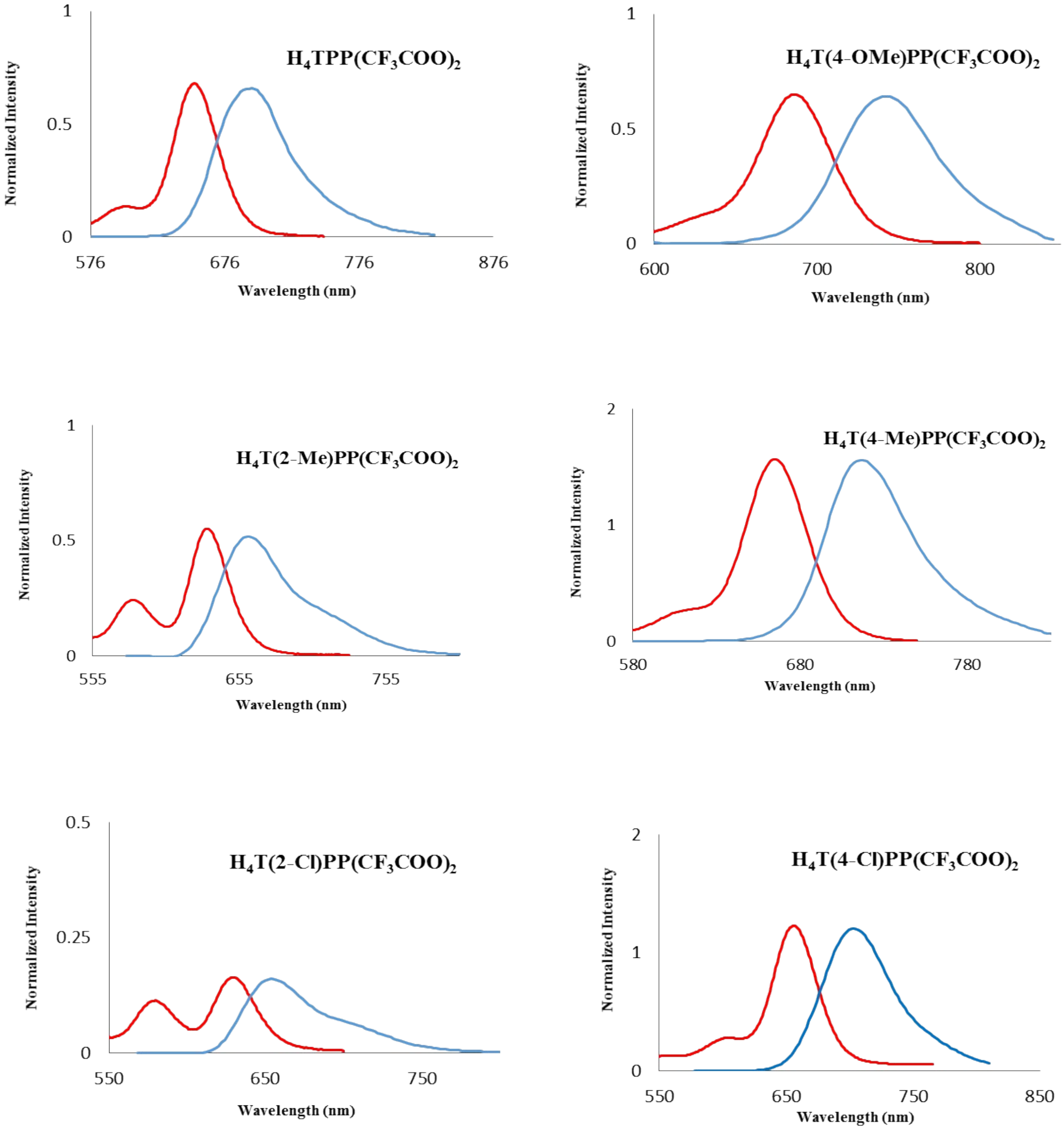


S5 The fluorescence spectral data of the free base porphyrins in CH_2Cl_2

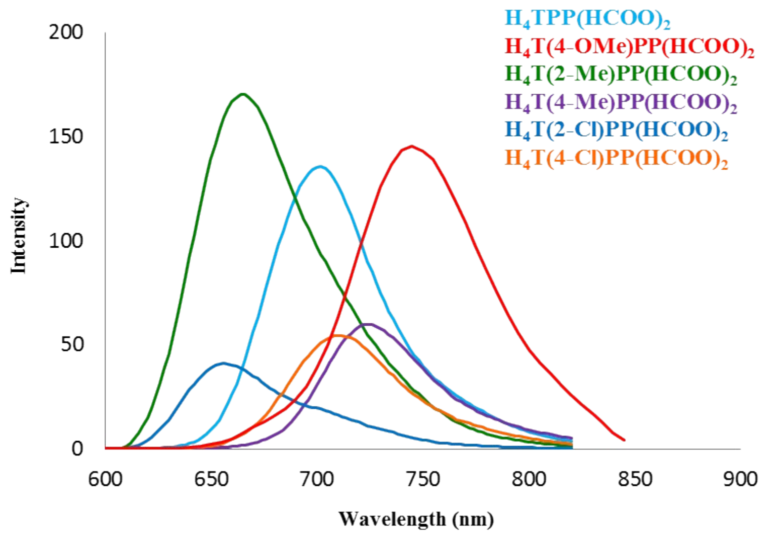
Porphyrins	H_2TPP	$H_2T(4\text{-}OMe)PP$	$H_2T(2\text{-}Me)PP$	$H_2T(4\text{-}Me)PP$	$H_2T(2\text{-}Cl)PP$	$H_2T(4\text{-}Cl)PP$
Absorption						
Q_{X10} (λ/nm)	590	593	589	590	587	590
Q_{X00} (λ/nm)	647	651	645	647	643	647
Splitting ($\Delta\nu_1$/cm^{-1})[a]	1493	1502	1474	1493	1484	1493
Emission						
Q^*_{X00} (λ/nm)	654 (2.21)	662 (3.55)	652 (1.57)	656 (2.05)	654 (1.07)	652 (1.81)
$\Delta\nu_{1/2}$ (cm^{-1})	606	822	798	603	700	513
Q^*_{X01} (λ/nm)	716 (1.00)	722 (1.00)	714 (1.00)	720 (1.00)	712 (1.00)	718 (1.00)
$\Delta\nu_{1/2}$ (cm^{-1})	684	945	785	722	632	662
Splitting ($\Delta\nu_2$/cm^{-1})[b]	1324	1255	1332	1355	1246	1410
$\Delta\nu_3 = \Delta\nu_1 - \Delta\nu_2$ (cm^{-1})	169	247	142	138	238	83
E_{00} (eV)[c]	1.91	1.89	1.91	1.90	1.91	1.91
Stokes shift ($\Delta\nu$/cm^{-1})	165	255	166	212	262	118
Φ_f[d]	0.130	0.280	0.073	0.050	0.031	0.043
τ_1 (ns)[e]	34.42	57.04	22.26	17.86	40.95	20.57
τ_2 (ns)[f]	153.57	309.70	89.65	90.33	171.42	101.7
τ_3 (ns)[g]	79.35	130.18	52.12	41.55	98.89	48.03
Σk_1 (× 10^{-6}s^{-1})[h]	29	17	45	56	24	48
Σk_2 (× 10^{-6} s^{-1})[i]	6	3	11	11	6	10
Σk_3 (× 10^{-6} s^{-1})[j]	13	8	19	24	10	21
k_{r1} (× 10^{-6} s^{-1})[k]	3.8	4.9	3.4	2.8	0.7	2.1
k_{r2} (× 10^{-6} s^{-1})[l]	0.8	0.9	0.8	0.6	0.2	0.4
k_{r3} (× 10^{-6} s^{-1})[m]	1.7	2.1	1.4	1.2	0.3	0.9
k_{nr1} (× 10^{-6} s^{-1})[n]	25.2	12.6	41.7	53.2	23.3	45.9
k_{nr2} (× 10^{-6} s^{-1})[o]	6.1	2.3	10.2	10.4	5.6	9.4
k_{nr3} (× 10^{-6} s^{-1})[p]	11.3	5.5	17.6	22.8	9.7	20.1

[a] Energy difference between the Q_{X10} and Q_{X00} bands. [b] Energy differences between the Q^*_{X00} and Q^*_{X01} bands. [c] Midpoint of Q_{X00} and Q^*_{X00} maxima. [d]Based on a reported value of 0.13 for Q_f of TPP in CH_2Cl_2[4]. [e] $\tau_1^{-1} = 2.880 \times 10^{-9} n^2 \frac{g_l}{g_u} \langle \nu^2 \rangle \int \varepsilon(\nu) d\nu$. [f] $\tau_2^{-1} = 2.880 \times 10^{-9} n^2 \frac{g_l}{g_u} \int \frac{(2\nu_0 - \nu)^3}{\nu} \varepsilon(\nu) d\nu$. [g] $\tau_3^{-1} = 2.880 \times 10^{-9} n^2 \frac{g_l}{g_u} \langle \nu_f^{-3} \rangle_{av}^{-1} \int \frac{\varepsilon(\nu)}{\nu} d\nu$ and $\langle \nu_f^{-3} \rangle_{av}^{-1} = \frac{\int F(\nu) d\nu}{\int F(\nu) \nu^{-3} d\nu}$[5-7]. [h] $\Sigma k_1 = \tau_1^{-1}$. [I] $\Sigma k_2 = \tau_2^{-1}$. [j] $\Sigma k_3 = \tau_3^{-1}$. [k] $k_{r1} = Q_f \times \Sigma k_1$. [l] $k_{r2} = Q_f \times \Sigma k_2$. [m] $k_{r3} = Q_f \times \Sigma k_3$. [n] $k_{nr1} = \Sigma k_1 - k_{r1}$. [o] $k_{nr2} = \Sigma k_2 - k_{r2}$. [p] $k_{nr3} = \Sigma k_3 - k_{r3}$8[7].

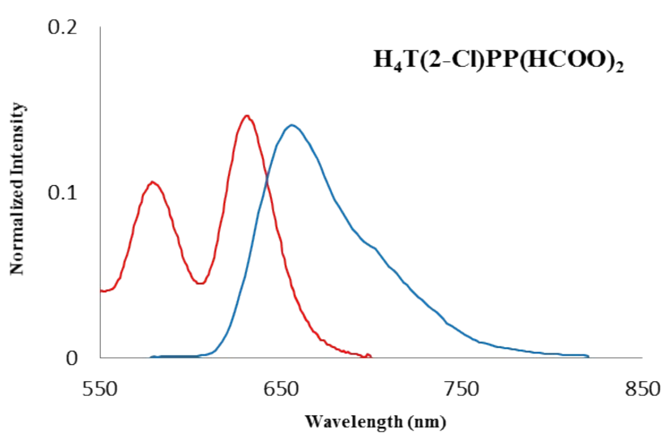
S6 Absorption (Q region) and emission spectra of the porphyrin dications with CF_3COOH in CH_2Cl_2 solutions normalized to each other at their respective Q maxima



S7 The emission spectra of the porphyrin dications with HCOOH in CH_2Cl_2



S8 Absorption (Q region) and emission spectra of the $H_4T(2\text{-}Cl)PP(HCOO)_2$ in CH_2Cl_2 solution normalized to it's Q maxima.



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