

Supporting Information for:
**Photophysical Properties and Electronic Structure of Porphyrins
 Bearing Zero to Four *meso*-Phenyl Substituents:
 New Insights into Seemingly Well Understood Tetrapyrroles**

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1. Complete citation for one truncated reference

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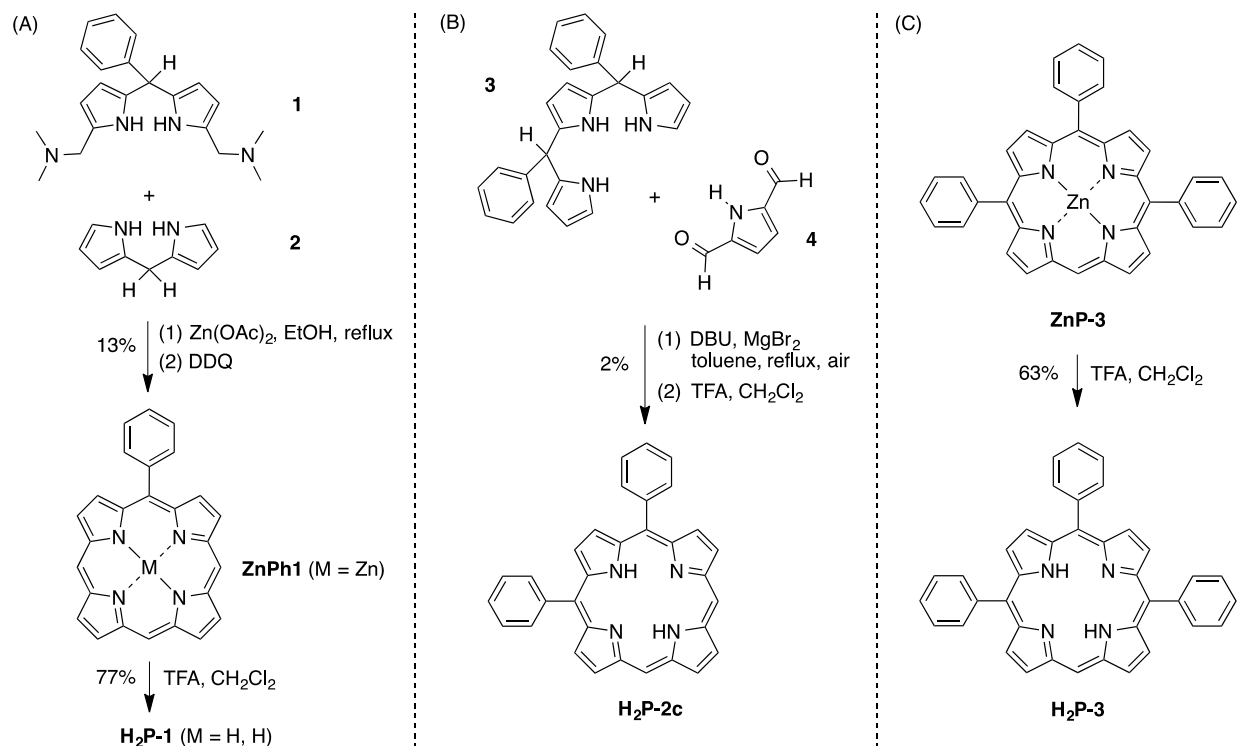
2. Synthesis results

5-Phenylporphyrin (**H₂P-1**) was first reported by Therien and co-workers who carried out studies of absorption, fluorescence, and EPR spectroscopy, but without delineation of synthetic procedures.¹⁴ Later, Senge and co-workers synthesized **H₂P-1** via three different approaches; (a) [2 + 1 + 1] mixed condensation reaction of benzaldehyde, pyrrole-2-carboxaldehyde, and dipyrromethane, (b) [3+1] mixed condensation reaction of 5,10-diphenyltripyrane, pyrrole, and benzaldehyde (as a result of scrambling), (c) nucleophilic substitution of porphine.¹⁵ In each case, the reaction resulted mixture of porphyrins requiring elaborate purifications. Here, the [2 + 2] condensation²⁰ of 1,9-bis(*N,N*-dimethylaminomethyl)-5-phenyldipyrromethane (**1**)²⁰ and dipyrromethane (**2**)¹⁰ upon treatment with zinc acetate in refluxing ethanol followed by oxidation

with DDQ afforded 5-phenylporphyrin (**ZnP-1**) in 13% yield (Scheme S1, panel A). Demetalation of **ZnP-1** afforded **H₂P-1**.

Synthesis of 5,10-diphenylporphyrin (**H₂P-2c**) was first described by Briñas and Brückner via [2 + 2] condensation of 1-benzoyl-5-phenyl-9-formyldipyrromethane and dipyrromethane.¹⁶ **H₂P-2c** was also prepared via two methods [described above as routes (b) and (c)].¹⁵ The former method by Briñas and Brückner requires elaborate precursor preparation, while latter methods by Senge and co-workers require chromatographic separation of porphyrins. Here, we carried out a [3 + 1] condensation of 5,10-diphenyltripyrane (**3**)⁹ + 2,5-diformylpyrrole (**4**)²¹ (Scheme S1, panel B). The reaction conditions were applied from established methods for the synthesis of meso-substituted magnesium porphyrins by [2 + 2] condensation of two 1-acyldipyrromethanes (identical or non-identical) under basic condition (in the presence of DBU), where magnesium bromide serves as a template to facilitate porphyrinic macrocycle formation.²² The intermediate porphyrin **MgP-2c** was formed (not isolated) without detectable scrambling upon analysis of the crude reaction mixture by MALDI-MS. Treatment of the reaction mixture with TFA demetalated **MgP-2c** to give the desired free base porphyrin **H₂P-2c**. The drawback of this method was a low yield (2%) was offset by the ready availability of the starting materials and the absence of a mixture of porphyrins.

5,10,15-Triphenylporphyrin (**H₂P-3**) was first prepared upon nucleophilic substitution of 5,10-diphenylporphyrin (**H₂P-2t**) by Senge and co-workers.¹⁷ We previously carried out the preparation of zinc(II) 5,10,15-triphenylporphyrin **ZnP-3** by standard [2 + 2] condensation of a 1,9-dibenzoyldipyrromethane + a dipyrromethane, followed by zinc metalation.¹⁹ Here, demetalation of **ZnP-3** with TFA afforded **H₂P-3** in 63% (Scheme S1, panel C).



Scheme S1. Synthesis of phenylporphyrins.

3. Synthesis experimental section

Zn(II)-5-Phenylporphyrin (ZnP-1). Following a standard procedure for the synthesis of mono-*meso*-substituted-porphyrins,²⁰ a solution of 1,9-bis(*N,N*-dimethylaminomethyl)-5-phenyldipyrrromethane²⁰ (**1**, 84.1 mg, 0.250 mmol) and dipyrrromethane¹⁰ (**2**, 36.5 mg, 0.250 mmol) in ethanol (25 mL) at room temperature was treated with Zn(OAc)₂ (459 mg, 2.50 mmol). The mixture was heated to reflux. After 2 h, the reaction mixture was allowed to cool to room temperature. A sample of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 170 mg, 0.75 mmol) was added, and the mixture was stirred for 15 min. Triethylamine (175 μ L, 1.25 mmol) was added, and the reaction mixture was concentrated to dryness. Column chromatography [silica, hexanes/CH₂Cl₂ (1:1)] afforded a red solid (14.8 mg, 13%): ¹H NMR (300 MHz, THF-*d*₈) δ 7.75–7.82 (m, 3H), 8.21–8.29 (m, 2H), 9.05 (d, *J* = 4.3 Hz, 2H), 9.44 (d, *J* = 4.3 Hz, 2H), 9.50–9.55 (m, 4H), 10.29 (s, 1H), 10.31 (s, 2H); ESI-MS obsd *m/z* = 449.07392, calcd 449.07333 [(M + H)⁺, M = C₂₆H₁₆N₄Zn]; λ_{abs} (toluene) 406 (100), 532 (4.7), 565 (1.0) nm; λ_{ems} (toluene) 568, 623 nm, Φ_{f} = 0.034.

5-Phenylporphyrin (H₂P-1). A solution of **ZnP-1** (11.2 mg, 0.0250 mmol) in anhydrous CH₂Cl₂ (10 mL) was treated with TFA (190 μ L, 2.50 mmol) at room temperature for 16 h. The reaction mixture was quenched by the addition of 10% aqueous NaHCO₃ (10 mL), and then extracted with CH₂Cl₂. The organic extract was washed with water, dried (Na₂SO₄), and filtered. The filtrate was concentrated. Column chromatography [silica, hexanes/CH₂Cl₂ (1:1)] afforded a purple solid (7.4 mg, 77%): ¹H NMR (300 MHz, THF-*d*₈) δ –3.61 to –3.46 (br, 2H), 7.78–7.86 (m, 3H), 8.22–8.30 (m, 2H), 9.05 (d, *J* = 4.7 Hz, 2H), 9.46 (d, *J* = 4.7 Hz, 2H), 9.50–9.57 (m, 4H), 10.33 (s, 1H), 10.40 (s, 2H); ESI-MS obsd *m/z* = 387.16084, calcd 387.16042 [(M + H)⁺, M = C₂₆H₁₈N₄]; λ_{abs} (toluene) 402 (100), 496 (5.7), 527 (0.8), 569 (1.8) nm; λ_{ems} (toluene) 626, 692 nm.

5,10-Diphenylporphyrin (H₂P-2c). Following a procedure for synthesis of *cis*-AB-porphyrins,²² a solution of 5,10-diphenyltripyrane⁹ (**3**, 94.4 mg, 0.250 mmol) and 2,5-diformylpyrrole²¹ (**4**, 30.8 mg, 0.250 mmol) in toluene (2.5 mL) was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 375 μ L, 2.50 mmol) and anhydrous MgBr₂ (138 mg, 0.750 mmol) at reflux for 16 h. The MALDI-MS analysis of the crude reaction mixture indicated the formation of magnesium(II) 5,10-diphenylporphyrin [**MgP-2c**, *m/z* = 484.0, calcd 484.2 (M = C₃₂H₂₀N₄Mg)]. The reaction mixture was concentrated under vacuum, then treated with anhydrous CH₂Cl₂ (5 mL) and TFA (100 μ L) at room temperature for 15 min. The reaction mixture was quenched by the addition of 10% aqueous NaHCO₃ (10 mL), and then extracted with CH₂Cl₂. The organic extract was washed with water, dried (Na₂SO₄), and filtered. The filtrate was concentrated. Column chromatography [silica, hexanes/CH₂Cl₂ (1:1)] afforded a purple solid (1.9 mg, 2%): ¹H NMR (300 MHz, THF-*d*₈) δ –3.31 to –3.27 (br, 2H), 7.74–7.83 (m, 6H), 8.19–8.28 (m, 4H), 8.89 (s, 2H), 8.98 (d, *J* = 4.7 Hz, 2H), 9.42 (d, *J* = 4.7 Hz, 2H), 9.52 (s, 2H), 10.34 (s, 2H); ESI-MS obsd *m/z* = 463.19238, calcd 463.19172 [(M + H)⁺, M = C₃₂H₂₂N₄]; λ_{abs} (toluene) 408 (100), 502 (5.4), 532 (0.7), 577 (1.5) nm; λ_{ems} (toluene) 635, 700 nm.

5,10,15-Triphenylporphyrin (H₂P-3). A solution of **ZnP-3** (6.0 mg, 0.010 mmol) in anhydrous CH₂Cl₂ (5 mL) was treated with TFA (77 μ L, 1.0 mmol) at room temperature for 12 h. The reaction mixture was quenched by the addition of 10% aqueous NaHCO₃ (10 mL), and then extracted with CH₂Cl₂. The organic extract was washed with water, dried (Na₂SO₄), and filtered. The filtrate was concentrated. Column chromatography [silica, hexanes/CH₂Cl₂ (1:1)] afforded a purple solid (3.4 mg, 63%): ¹H NMR (300 MHz, THF-*d*₈) δ –2.95 to –2.91 (br, 2H),

7.71–7.85 (m, 9H), 8.19–8.29 (m, 6H), 8.81–8.90 (m, 4H), 8.98 (d, $J = 4.7$ Hz, 2H), 9.41 (d, $J = 4.7$ Hz, 2H), 10.32 (s, 1H); ESI-MS obsd $m/z = 539.22329$, calcd 539.22302 $[(M + H)^+]$, $M = C_{38}H_{26}N_4$; λ_{abs} (toluene) 414 (100), 508 (4.8), 542 (1.4), 584 (1.4), 639 (0.6) nm; λ_{ems} (toluene) 643, 709 nm.

4. MO properties of porphyrins from DFT calculations

Table S1. MO properties of porphyrins from DFT calculations (eV).^a

Cmpd	H-1	H	L	L+1		L – H	(L+1) – (H-1)	L – (H-1)	(L+1) – H		ΔE_{avg}	ΔE_{dif1}	ΔE_{dif2}
H₂P-0	-7.059	-7.006	-1.290	-1.288		5.72	5.77	5.77	5.72		5.74	0.06	0.05
H₂P-1	-7.055	-6.938	-1.315	-1.280		5.62	5.77	5.74	5.66		5.70	0.15	0.08
H₂P-2c ^b	-7.046	-6.897	-1.307	-1.301		5.59	5.74	5.74	5.60		5.67	0.15	0.14
H₂P-2c' ^c	-7.047	-6.895	-1.306	-1.303		5.59	5.74	5.74	5.59		5.67	0.15	0.15
H₂P-2t	-7.055	-6.867	-1.343	-1.277		5.52	5.78	5.71	5.59		5.65	0.25	0.12
H₂P-3	-7.043	-6.818	-1.332	-1.300		5.49	5.74	5.71	5.52		5.61	0.26	0.19
H₂P-4	-7.034	-6.790	-1.324	-1.318		5.47	5.72	5.71	5.47		5.59	0.25	0.24

^a DFT calculations were performed for the structures shown in Chart 2 in toluene. The MOs are abbreviated as HOMO–1 (H–1), HOMO (H), LUMO (L), and LUMO+1 (L+1). The last three columns are defined for use in the four-orbital model as follows: $\Delta E_{avg} = [(E_L - E_H) + (E_{L+1} - E_{H-1})]/2 = [(E_{L+1} - E_H) + (E_L - E_{H-1})]/2$; $\Delta E_{dif1} = (E_{L+1} - E_{H-1}) - (E_L - E_H)$; $\Delta E_{dif2} = (E_L - E_{H-1}) - (E_{L+1} - E_H)$.

^b The 5,10-diphenyl rings do not encompass the proton axis (see Figure 9).

^c The 5,10-diphenyl rings encompass the proton axis (see Figure 9).