

Supporting Information

Persistent Electron-Transfer State of a π -Complex of Acridinium Ion Inserted between Porphyrin Rings of Cofacial Bisporphyrins

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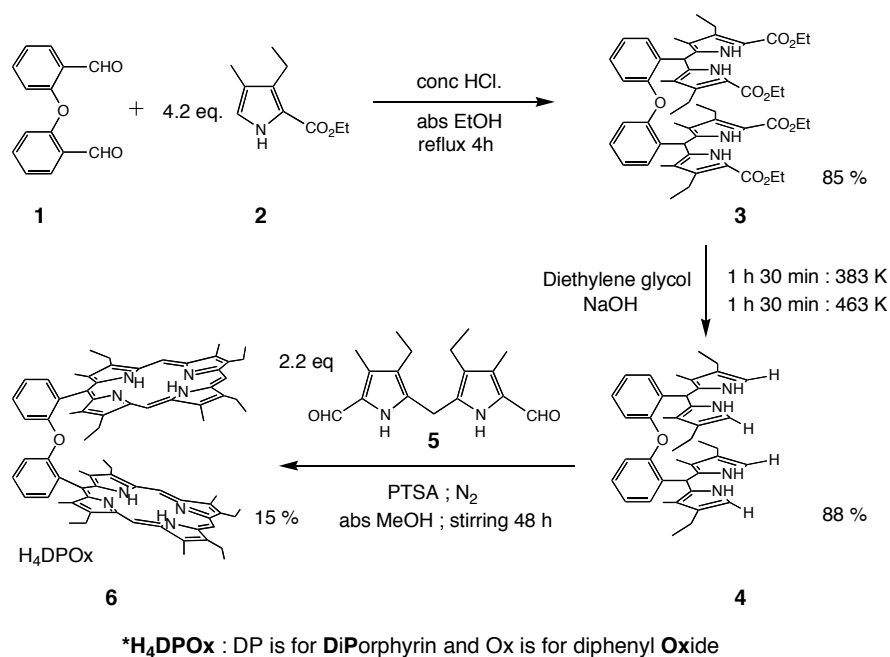
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Synthesis of H₄DPOx.

General Methods for Synthesis. The synthetic method of H₄DPOx is shown in Scheme S1. ¹H NMR spectra were recorded on a Bruker DRX-500 AVANCE transform spectrometer at the Centre de Spectrométrie Moléculaire de l'Université de Bourgogne; chemical shifts are expressed in ppm relative to chloroform (7.258 ppm). Microanalyses were performed at the Université de Bourgogne on a Fisons EA 1108 CHNS instrument. UV-visible spectra were recorded on a Varian Cary 1 spectrophotometer. Mass spectra were obtained on a Bruker ProFLEX III spectrometer in the MALDI / TOF mode using dithranol as a matrix.

Scheme S1



Silica gel (Merck; 70-120 μm) was used for column chromatography. Analytical thin layer chromatography was performed using Merck 60 F254 silica gel (precoated sheets, 0.2 mm thick). Reactions were monitored by thin-layer chromatography and

UV-visible spectroscopy. Bis(2-formylphenyl)ether **1** is commercially available and was used as received. Ethyl 3-ethyl-4-methyl-*1H*-pyrrole-2-carboxylate **2**¹ and 5,5'-diformyl-3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrrylmethane **5**² have been synthesized as already described.

2,2'-Bis-(5,5'-(ethyloxycarbonyl)-4,4'-diethyl-3,3'-dimethyl-2,2'-dipyrrylmethyl)diphenylether (3). Mixtures of 1.20 g of bis(2-formylphenyl)ether **1** (5.30 mmol) and 4.03 g of ethyl 3-ethyl-4-methyl-*1H*-pyrrole-2-carboxylate **2** (22.3 mmol) were dissolved in 30 mL of hot ethanol. Concentrated hydrochloric acid (1 mL) was then added and the solution was stirred under reflux for 4 h. The mixture was cooled to room temperature and the resulting solid was filtered and washed by cold methanol, then dried to give the title product **3** (4.12 g, 85%). ¹H NMR (CDCl₃): δ 8.50 (brs, 4H, NH), 7.03 (m, 6H, ArH), 6.24 (d, *J* = 7.6 Hz, 2H, ArH), 5.74 (s, 2H, CH), 4.24 (q, *J* = 7.1 Hz, 8H, -CH₂-CH₃), 2.68 (q, *J* = 7.5 Hz, 8H, -CH₂-CH₃), 1.69 (s, 12H, -CH₃), 1.29 (t, *J* = 7.1 Hz, 12H, -CH₃), 1.05 (t, *J* = 7.5 Hz, 12H, -CH₃). MS (MALDI-TOF): *m/z* = 915.01 [M]⁺, 915.12 Calcd for C₅₄H₆₆N₄O₉.

2,2'-Bis-(4,4'-diethyl-3,3'-dimethyl-2,2'-dipyrrylmethyl)diphenylether (4). A suspension of 4.16 g of **3** (5.7 mmol) in diethylene glycol (150 mL) containing NaOH (15.0 g) was heated at 383 K under N₂ for 1 h 30 min and then at 463 K for another 1 h 30 min after which the solution was allowed to cool to room temperature. The mixture was poured into ice water (2 000 mL) and the resulting solid was filtered, washed with water and then dried to give compound **4** (2.50 g, 88%). ¹H NMR (CDCl₃): δ 7.40 (brs, 4H, NH), 7.02 (m, 6H, ArH) 6.37 (d, *J* = 7.6 Hz, 2H, ArH), 6.20 (br s, 4H, CH), 5.61 (s, 2H, CH), 2.39 (q, *J* = 7.5 Hz, 8H, -CH₂-CH₃), 1.76 (s, 12H, CH₃), 1.11 (t, *J* = 7.5 Hz, 12H, -CH₃). MS (MALDI-TOF): *m/z* = 626.38 [M]⁺, 626.87 Calcd for C₄₂H₅₀N₄O.

2,2'-Bis-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin-5-yl)diphenylether (H₄DPO_x, 6). To a solution of 2,2'-bis-(4,4'-diethyl-3,3'-dimethyldipyrromethan-5-yl)diphenylether **4** (2.49 g, 4.0 mmol) and 5,5'-diformyl-3,3'-

diethyl-4,4'-dimethyl-2,2'-dipyrrylmethane **5** (2.50 g, 8.8 mmol) in methanol (1 500 mL) was added 30 mL of a solution of *p*-toluene sulfonic acid (15 g, 79 mmol) in methanol during 18 h. The dark red solution was stirred at room temperature under Ar for 48 h. *o*-Chloranil (4.6 g) was added, and the solution was stirred in air for 1 h. The mixture was taken to dryness and redissolved in 250 mL of dichloromethane. A saturated methanolic solution of Zn(OAc)₂•2H₂O (10 mL) was added and the mixture was refluxed for 1 h. The organic phase was separated and washed 3 times with water (500 mL), then dried over MgSO₄. The zinc derivative was isolated by column chromatography on silica gel (CH₂Cl₂). Demetallation by 6 M HCl afforded the free base bisporphyrin, which was further purified by chromatography (silica gel, CH₂Cl₂/MeOH 100/0 to 95/5 in volume). Purple microcrystals of bisporphyrin were obtained in 15.0% yield (m = 420 mg). ¹H NMR (CDCl₃): δ 10.09 (s, 2H, meso), 8.52 (brs, 4H, meso), 8.09 (d, *J* = 7.3 Hz, 2H, ArH), 7.79 (m, 2H, ArH), 7.23 (m, 4H, ArH), 4.12-4.39 (m, 8H, -CH₂-CH₃), 3.39 (s, 12H, -CH₃), 2.06 (t, *J* = 7.7 Hz, 12H, -CH₃), 1.30-1.70 (m, 32H), -3.45 (s, 2H, NH), -3.90 (s, 2H, NH). MS (MALDI-TOF): *m/z* = 1123.67 [M]⁺, 1123.52 Calcd. for C₇₆H₈₂N₈O. UV-vis (CH₂Cl₂), λ_{max} (nm) (ε × 10⁻⁴, M⁻¹ cm⁻¹): 391 (58.9), 506 (5.5), 540 (3.1), 574 (3.0), 627 (1.3). Anal Calcd for C₇₆H₈₂N₈O: C, 81.25; H, 7.36; N, 9.97. Found: C, 81.56; H, 7.27; N, 9.69.

Reference

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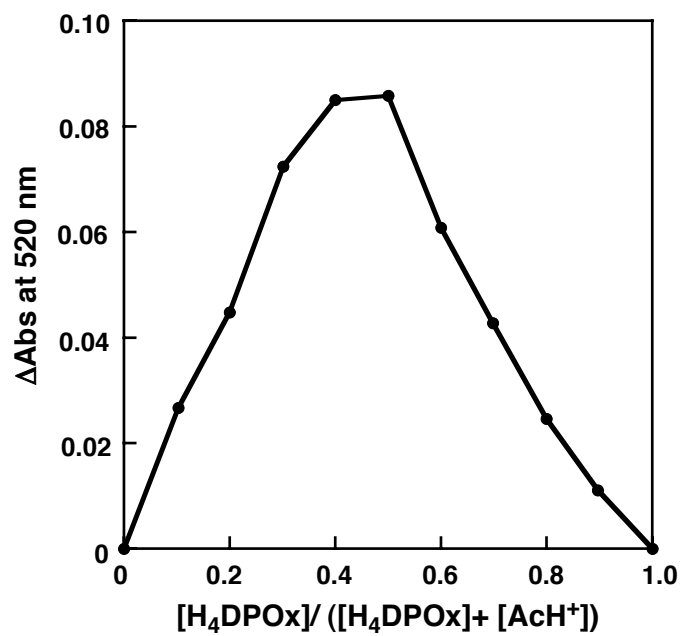
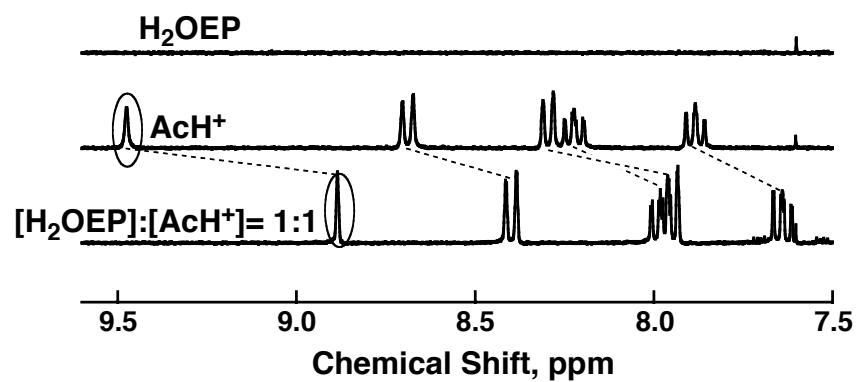


Figure S5. Job's plot obtained by absorption band at 520 nm for the complex formation between H_4DPOx and AcH^+ in PhCN ($[\text{H}_4\text{DPOx}] + [\text{AcH}^+] = 2.5 \times 10^{-5} \text{ M}$).

(a)



(b)

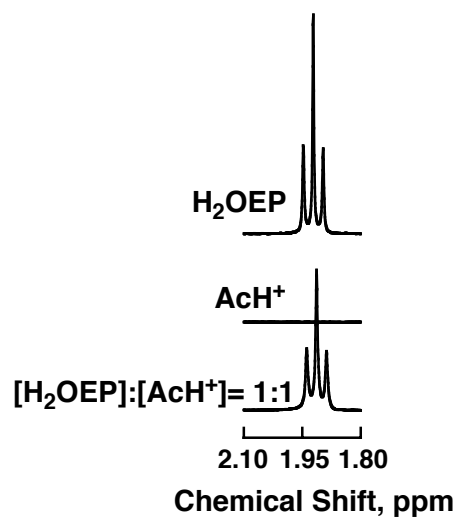


Figure S6. (a) ^1H NMR spectra of H_2OEP , AcH^+ , $[\text{H}_2\text{OEP}]:[\text{AcH}^+]=1:1$, in CDCl_3 . (b) Change in the chemical shift of the porphyrin moiety.

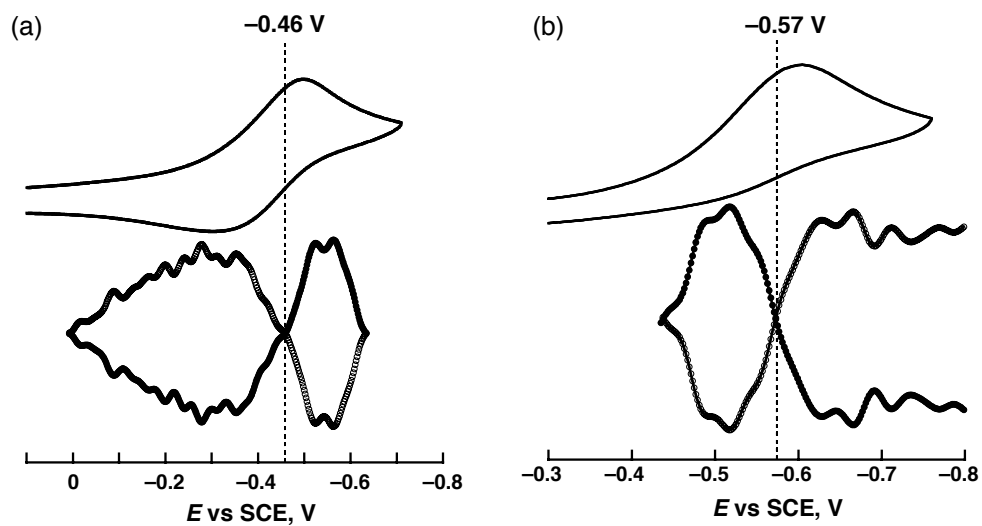


Figure S7. (a) CV and SHACV of AcH⁺ (3.0×10^{-3} M) and (b) AcH⁺ (3.0×10^{-3} M) in the presence of H₄DPOx (3.6×10^{-3} M) in deaerated PhCN. Sweep rate: 0.1 V s^{-1} for CV and 4 mV s^{-1} for SHACV.

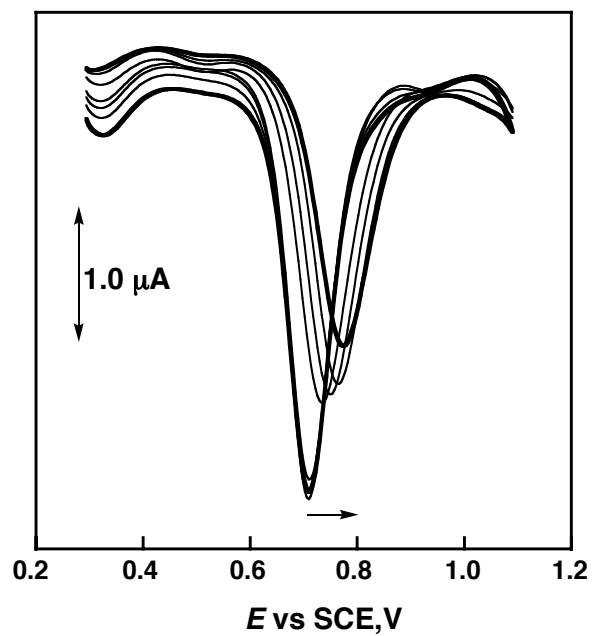


Figure S8. DPV of H₂OEP (5.3×10^{-4} M) in the presence of various concentrations of AcH⁺ (0 to 8.2×10^{-3} M) in PhCN. The arrows indicate the direction of change.

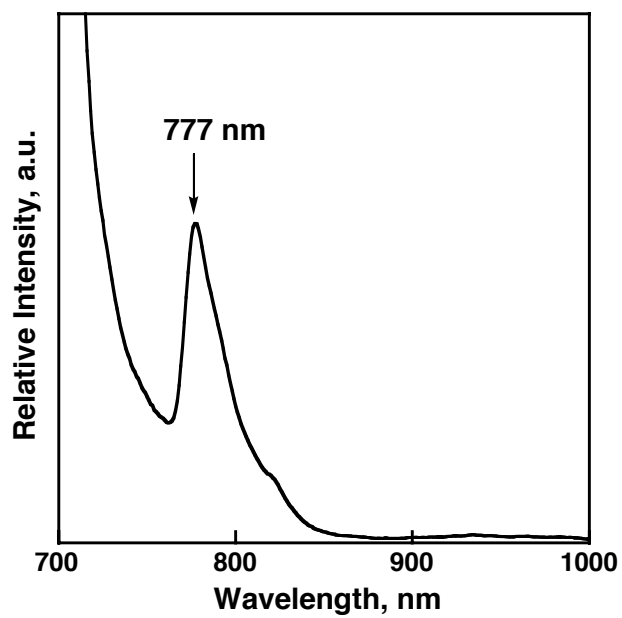


Figure S9. Phosphorescence spectrum of H₄DPOx in 50% EPA/ 50% ethyl iodide at 77 K.

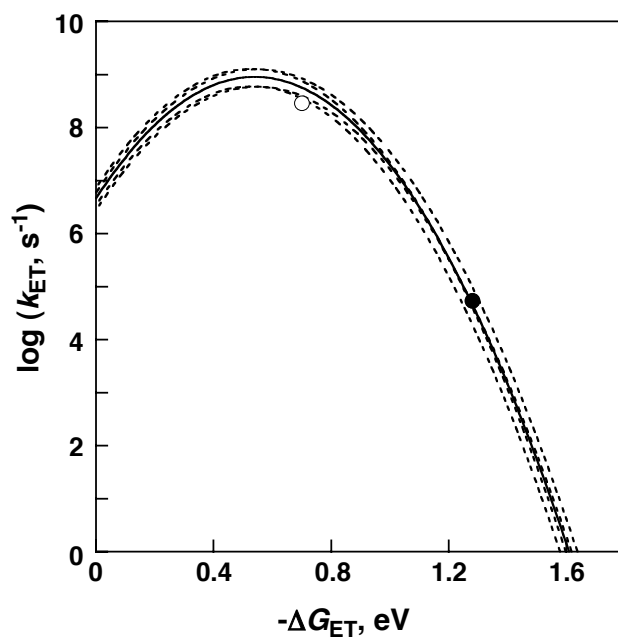


Figure S10. Marcus driving force ($-\Delta G_{\text{ET}}$) dependence of intramolecular ET rate constants ($\log k_{\text{ET}}$) using eq 2 with the λ (0.54 ± 0.01 eV) and V (1.6 ± 0.3 cm $^{-1}$) values, derived from the temperature dependence of k_{BET} in Figure 11, including the experimental values for photoinduced ET (○) and BET (●) in deaerated PhCN at 298 K. The broken curves indicate the error limit derived from uncertainty of the λ value and the V value.