

Electronic Supplementary Information

5,15-Bis(di-*p*-anisylamino)-10,20-diphenylporphyrin: Distant and Intense Electronic Communication Between Two Amine Sites

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Materials. 5,15-dibromo-10,20-diphenylporphyrin^[1] and di-*p*-anisylamine^[2] were synthesized according to previous reports. THF was distilled over benzophenone ketyl. Dichloromethane and acetonitrile used for the series of measurements were distilled over CaH₂. Other materials were used as received unless otherwise stated: Dry pyridine, cesium carbonate, and zinc acetate dehydrate from Kanto Chemical; palladium acetate from Wako Pure Chemical Industries; (oxydi-2,1-phenylene)bis(diphenylphosphine) (DPEPhos) from Tokyo Chemical Industry; decamethylferrocene from Sigma-Aldrich.

Synthesis of H₂-1. Under an argon atmosphere, a mixture of 5,15-dibromo-10,20-diphenylporphyrin (50 mg, 0.081 mmol), di-*p*-anisylamine (90 mg, 0.39 mmol), cesium carbonate (37 mg, 0.11 mmol), palladium acetate (1.8 mg), DPEphos (6.5 mg) in THF (8 mL) was refluxed at 68°C for 10 h with shielding from light; the purple suspension turned into green. The crude product was then directly filtered through silica gel with a mixture of dichloromethane-ethyl acetate (95:5 v/v) as an eluent, in order to remove insoluble solids. The filtrate was evaporated, and the residue was washed with acetonitrile till unreacted di-*p*-anisylamine was removed. The residue was purified with column chromatography on silica gel, eluting with a mixture of dichloromethane and ethyl acetate (95:5 v/v). The third green fraction was collected, and concentrated to furnish dark-green solid of **H₂-1** (14 mg, 19%). Recrystallization from dichloromethane and hexane under an argon atmosphere with shielding from light gave **H₂-1** as dark-green needle crystals. ¹H NMR (500 MHz, [D₁]chloroform): δ=9.13 (d, *J*=4.7 Hz, 4H, β-pyrrole), 8.62 (d, *J*=4.8 Hz, 4H, β-pyrrole), 8.10-8.08 (m, 4H, Ph), 7.73-7.65 (m, 6H, Ph), 7.21 (d, *J*=9.1 Hz, 8H, *p*-anisyl), 6.73 (d, *J*=9.1 Hz, 8H, *p*-anisyl), 3.71 (s, 12H, methoxy), -2.02 ppm (brs, 2H, inner-NH); ¹³C NMR (150 MHz, [D₁]chloroform): δ=153.8, 152.9, 141.7, 142.0, 141.6, 135.3, 134.6, 128.4, 128.0, 126.9, 123.5, 123.1, 114.7, 112.9, 55.7; HR-FAB-MS: *m/z* 916.3740; calcd for C₆₀H₄₈N₆O₄, [M⁺]: 916.3737.

Synthesis of Zn-1. Under an Ar atmosphere, **H₂-1** (5.0 mg, 0.0054 mmol) was dissolved in dichloromethane (10 mL). To the green solution zinc acetate dehydrate (3.6 mg, 0.016 mmol) in methanol (0.27 mL) was added, and the mixture was stirred for 2 h at ambient temperature with shielding from light. The completion of the reaction was confirmed with TLC (silica gel, dichloromethane and pyridine (100:1 v/v) as an eluent). The reaction mixture was evaporated, and the residue was dissolved in dichloromethane. The solution was washed with water and then aqueous sodium hydrogen carbonate (5w%). The organic phase was collected, desiccated over sodium sulfate, evaporated, and the resulting residue was purified with column chromatography on silica gel, eluting with a mixture of dichloromethane, ethyl acetate, and pyridine (95:5:1 v/v/v). The single green fraction was collected, which was thoroughly evaporated in vacuo to obtain

dark-green solid of **Zn-1**. This conversion is almost quantitative. Recrystallization from dichloromethane and hexane under an argon atmosphere with shielding from light afforded dark-green needle crystals of **Zn-1**. ^1H NMR (600 MHz, $[\text{D}_1]$ chloroform): δ =9.24 (d, J =4.6 Hz, 4H, β -pyrrole), 8.74 (d, J =4.6 Hz, 4H, β -pyrrole), 8.11-8.10 (m, 4H, Ph), 7.72-7.65 (m, 6H, Ph), 7.19 (d, J =8.9 Hz, 8H, p -anisyl), 6.68 (d, J =9.1 Hz, 8H, p -anisyl), 3.65 ppm (s, 12H, methoxy); ^{13}C NMR (150 MHz, $[\text{D}_1]$ chloroform); δ =153.6, 153.2, 149.7, 147.2, 142.4, 134.4, 133.2, 130.7, 127.7, 126.7, 123.9, 123.3, 121.1, 114.7, 55.6; HR-FAB-MS: m/z 978.2871; calcd for $\text{C}_{60}\text{H}_{46}\text{N}_6\text{O}_4\text{Zn}$, $[\text{M}^+]$: 978.2782.

Electrochemistry. $n\text{Bu}_4\text{NPF}_6$ (TBAH) as a supporting electrolyte was recrystallized from EtOH, dried at 120°C , and then put in vacuo for 24h. A series of measurements was carried out under a nitrogen atmosphere in a standard one-component cell, using 3mm ϕ glassy carbon (BAS) as a working electrode, platinum wire as a counter electrode, and an Ag/AgNO₃ reference electrode (0.01M AgNO₃ in 0.1M-TBAP/acetonitrile, BAS). Solution resistances (R_u) of 2000 Ω and 2200 Ω were compensated for **H₂-1** and **Zn-1** respectively, when the voltammograms in Fig. 4 were recorded. As an internal standard, decamethylferrocene ($E^{\text{D}^{\text{D}}}$ = -550 mV vs Fc^+/Fc in 0.1M TBAH-dichloromethane) was added after each measurement.

UV/Vis/NIR spectroscopy for oxidized species.

1) in dichloromethane 1,1'-dichloroferrocenium hexafluorophosphate ($E^{\text{D}^{\text{D}}}$ = 399 mV vs Fc^+/Fc in 0.1M-TBAP/dichloromethane) was synthesized according to a previous report.^[3] All samples, including the solutions of the oxidant, were fabricated and tightly sealed in quartz cells (optical length: 1 cm) in a N₂ glove box. The concentrations of the samples of **H₂-1** and **Zn-1** (ca. 10^{-5}M) were determined with their UV/Vis/NIR spectra with the spectra shown in Fig. 3 as the standard. Those of the oxidant (ca. 10^{-3}M) were calculated from the absorbance at 705 nm (ϵ = $3.40 \times 10^2 \text{M}^{-1} \text{cm}^{-1}$). The oxidant solution was added to the porphyrin solution ($3.60 \times 10^3 \mu\text{L}$) with a microsyringe, then the mixture was gently shaken, and its spectrum was measured. The addition of the oxidant was iterated until there was no significant spectral change so as to complete the second oxidations (Fig. S6 and S7). The increase of the volume upon the additions of the oxidant/reductant is corrected. Molar extinction coefficients for the IVCT bands are calculated as follows: For **Zn-1** with quite large values of $\Delta E_{1/2}$ and comproportionation constant (K_c), the spectrum with the most intense IVCT band is adopted, assuming the completion of the conversion of **Zn-1** into **Zn-1⁺**. For **H₂-1** with rather small values of $\Delta E_{1/2}$ and K_c , a spectrum with 0.0725 eq of the oxidant is adopted in order to minimize the disproportionation as much as possible.

2) in a mixture of acetonitrile and dichloromethane Since the solubility of **Zn-1** and **H₂-1** in acetonitrile is quite low, here only qualitative observations were executed.

DFT calculation. The three-parameterized Becke-Lee-Yang-Parr (B3LYP) hybrid exchange-correlation functional^[4] was employed. As a basis set Lanl2DZ^[5] was used. The geometries were optimized with the *C_i* symmetry constraint. Solvent effects were not considered in the geometry optimizations. TD-DFT calculations were executed with the same condition listed above, except for consideration of the solvent effects with the polarized continuum model (PCM). This series of calculations was implemented with Gaussian 03 program.

Apparatus. Electrochemical data were recorded with a BAS ALS-620C voltammetric analyzer. UV/Vis/NIR spectra were measured with a Shimadzu UV-3100 spectrometer, ¹H NMR spectra with a Bruker DRX 600 (600 MHz) spectrometer, or a JEOL AL-500 (500 MHz) spectrometer.

References for Electronic Supplementary Information

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- [3] T. Horikoshi, K. Kubo, H. Nishihara, *J. Chem. Soc., Dalton Trans.* **1999**, 3355–3360.
- [4] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.
- [5] a) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270-283; b) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284-298; c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299-310.

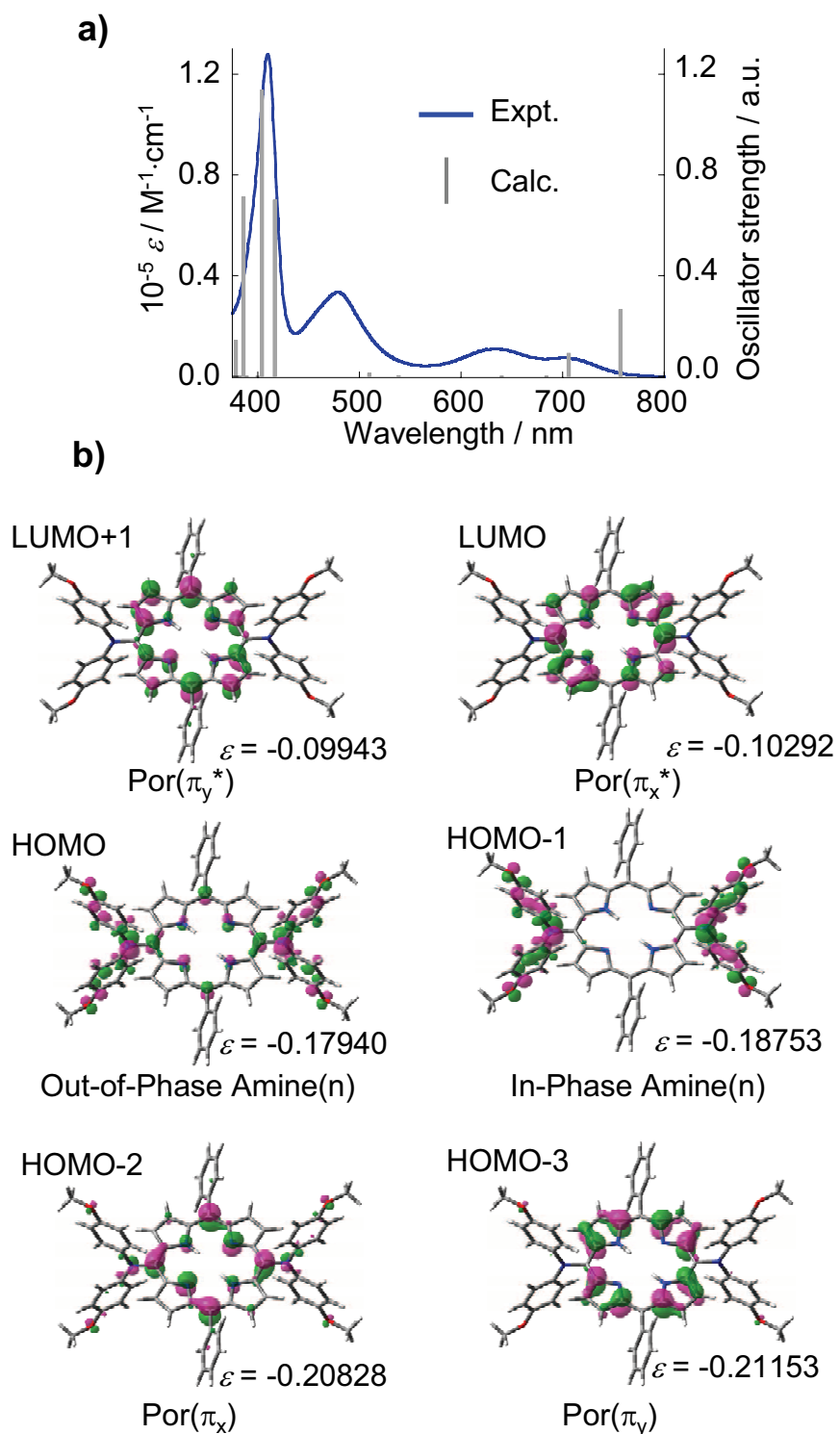
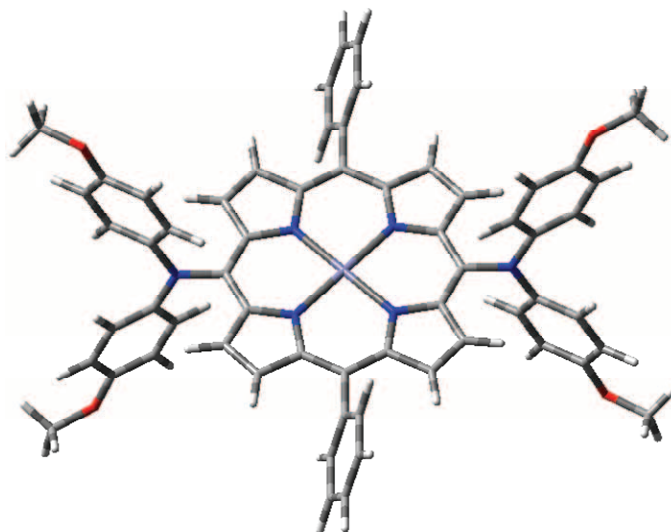


Fig. S1 a) Experimental and calculated (oscillator strength, DFT/B3LYP/LanI2DZ) electronic spectra of **H₂-1** in dichloromethane. b) Contour plots of frontier orbitals, assignments, and orbital energies (in Hartree) of **H₂-1**.

Top view



Side view

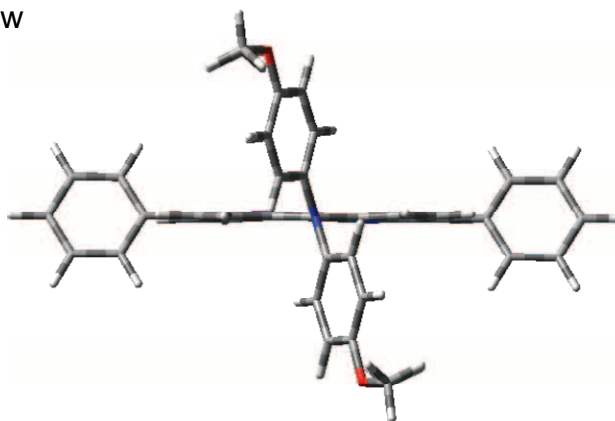


Fig. S2 Optimized structure of **Zn-1** by DFT/B3LYP/Lan12DZ. The dihedral angles between the plane defined by three C-N bonds, and the porphyrin macrocycle, or two *p*-anisyl groups are 73°, 33°, and 33°, respectively.

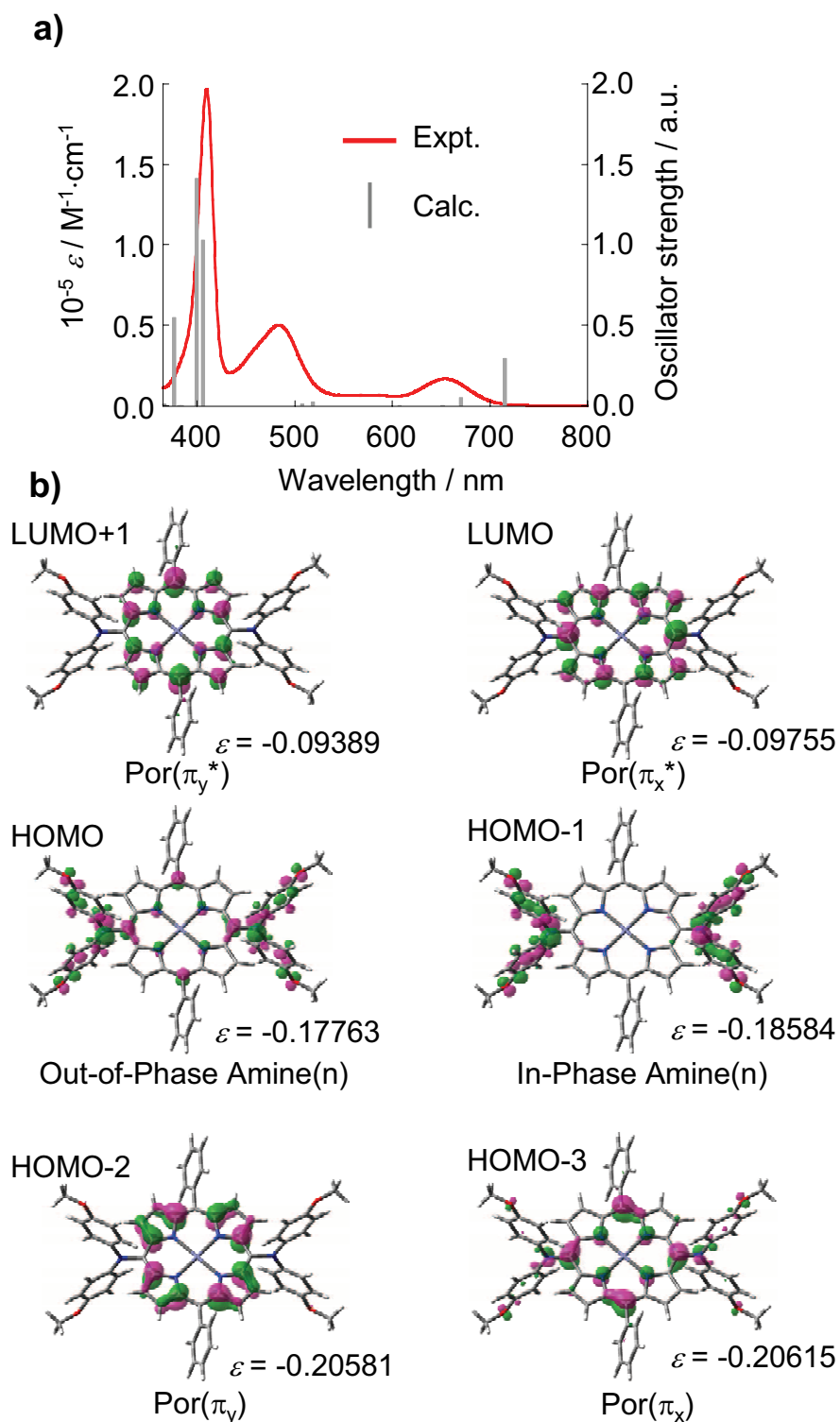


Fig. S3 a) Experimental and calculated (oscillator strength, DFT/B3LYP/LanI2DZ) electronic spectra of **Zn-1** in dichloromethane. b) Contour plots of frontier orbitals, assignments, and orbital energies (in Hartree) of **Zn-1**.

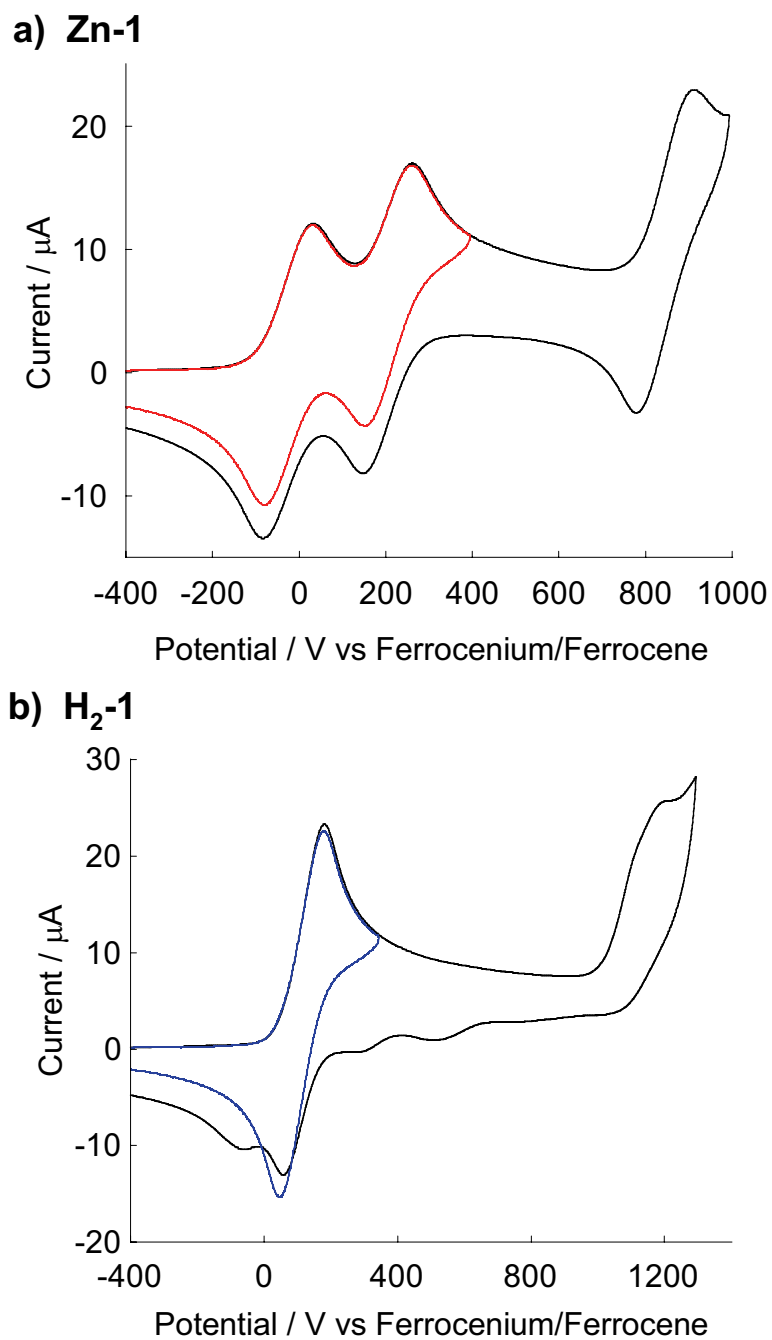


Fig. S4 Cyclic voltammograms in 0.1M TBAH-dichloromethane at a sweep rate of 100 mVs^{-1} : a) **Zn-1** (0.9 mM); b) **H₂-1** (0.9 mM).

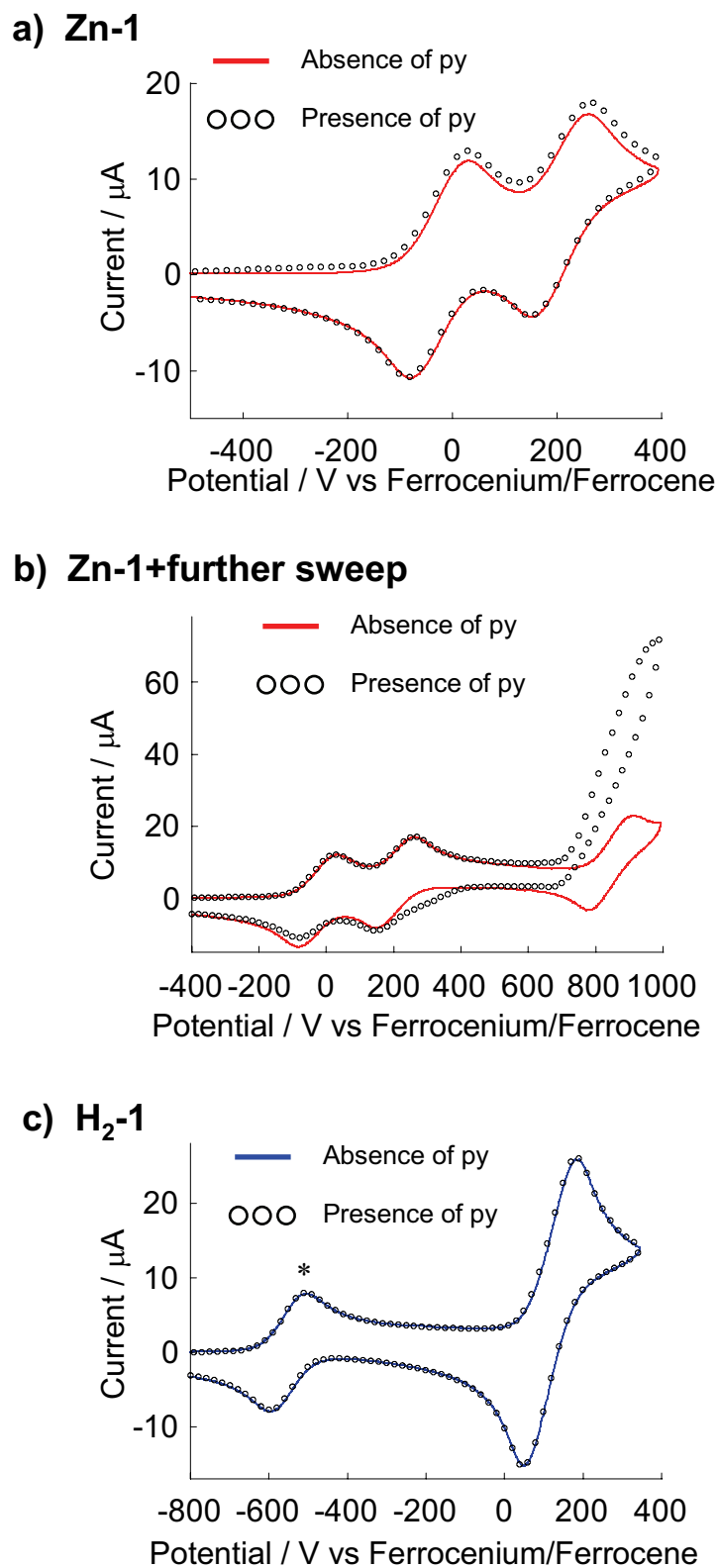


Fig. S5 Cyclic voltammograms in 0.1M TBAH-dichloromethane in the absence or presence of pyridine (ca. 20 equiv) at a sweep rate of 100 mVs^{-1} : a,b) **Zn-1** (0.9 mM); c) **H₂-1** (0.9 mM). The asterisk in c) indicates a redoxwave of decamethylferrocene as an internal standard.

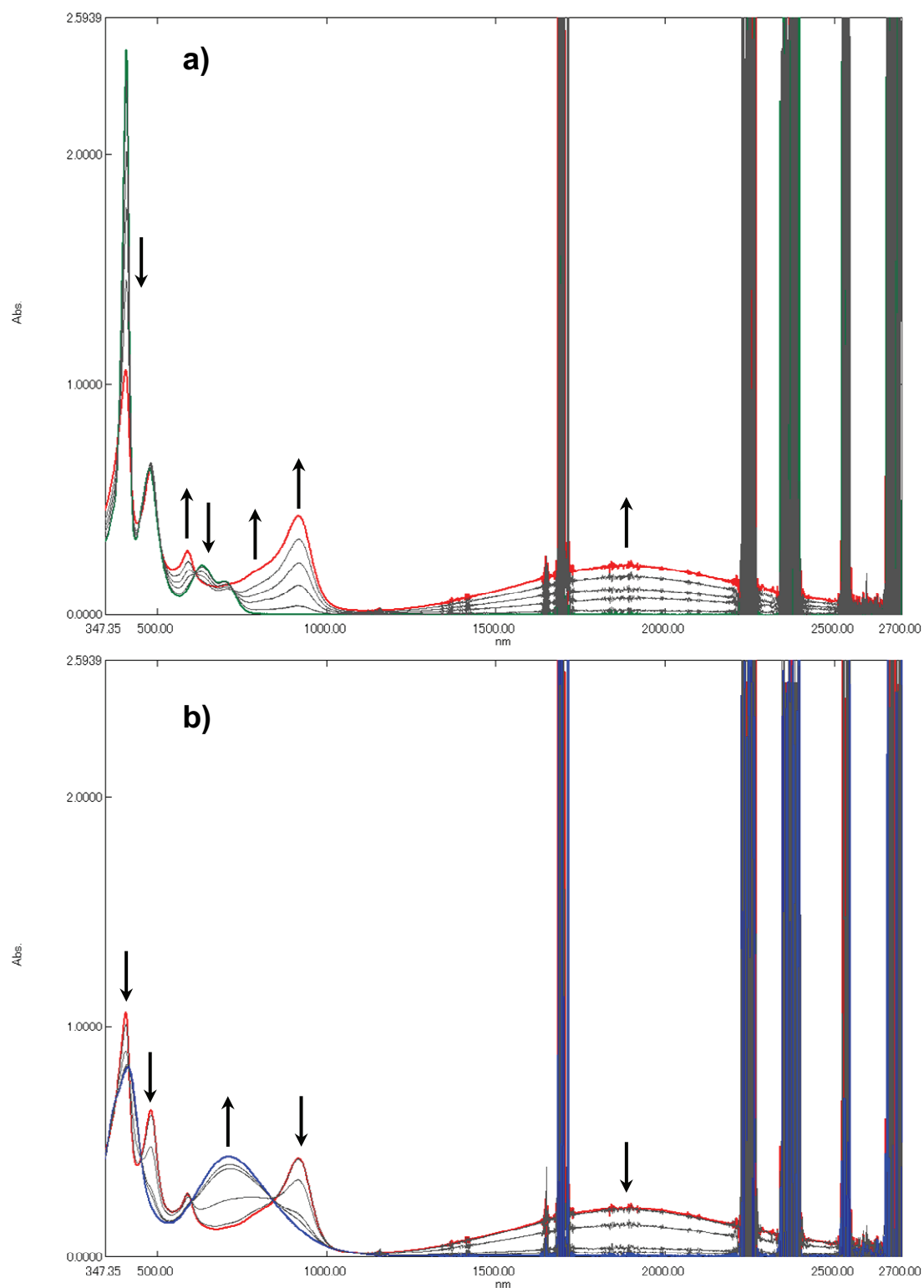


Fig. S6 UV/Vis/NIR spectral changes (raw data) of **H₂-1** upon additions of the oxidant in dichloromethane: a) **H₂-1** (green)→ **H₂-1⁺** (red, probably contaminated with **H₂-1²⁺** to some extent due to the small comproportionation constant); b) **H₂-1⁺** (red)→ **H₂-1²⁺** (blue). Several data are omitted for clarity. We note that these spectra contain slight contributions from 1,1'-dichloroferrocene, which has only small absorptivities in the shown region.

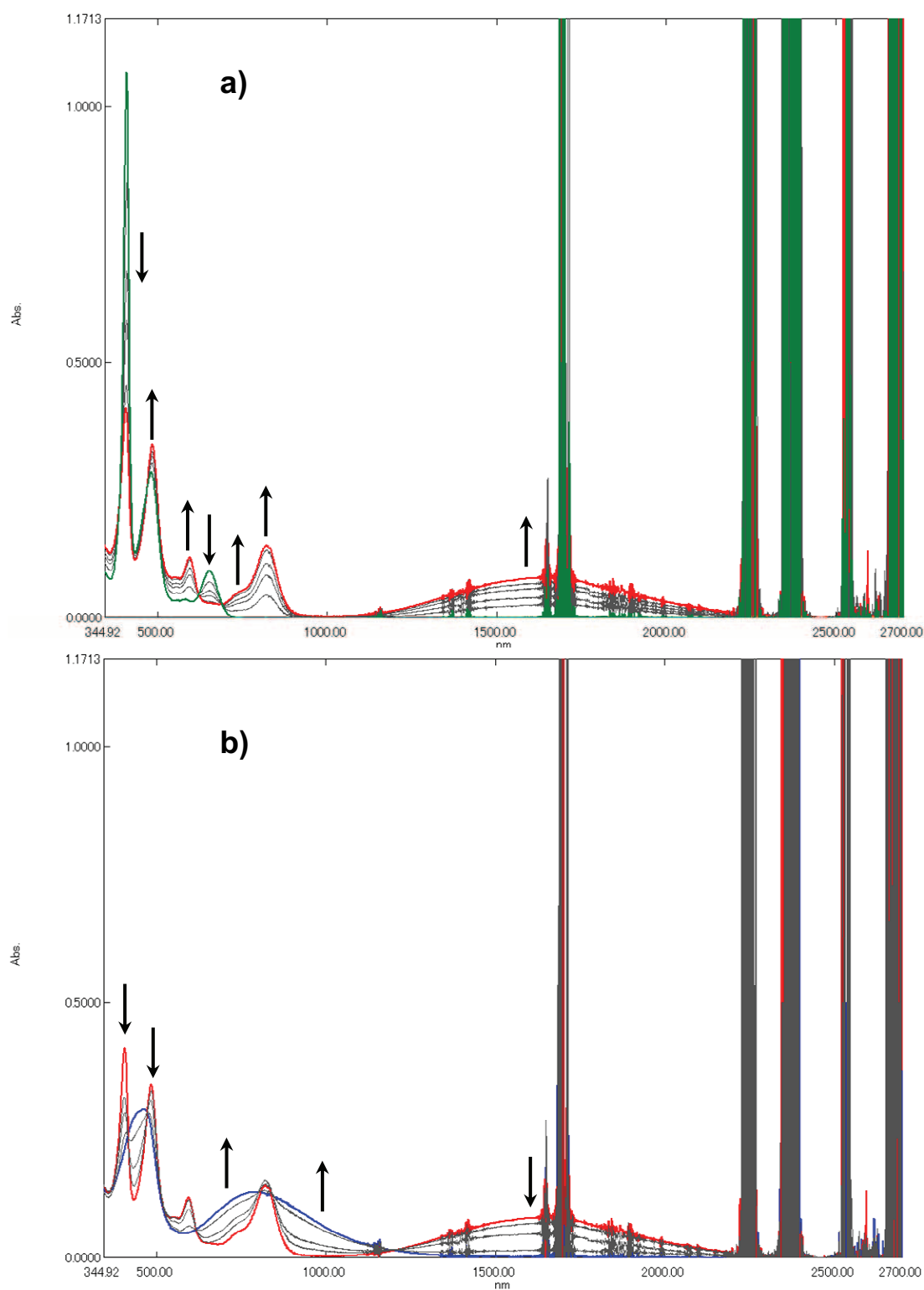


Fig. S7 UV/Vis/NIR spectral changes (raw data) of **Zn-1** upon additions of the oxidant in dichloromethane: a) **Zn-1** (green)→ **Zn-1⁺** (red); b) **Zn-1⁺** (red)→ **Zn-1²⁺** (blue). Several data are omitted for clarity. We note that these spectra contain slight contributions from 1,1'-dichloroferrocene, which has only small absorptivities in the shown region.

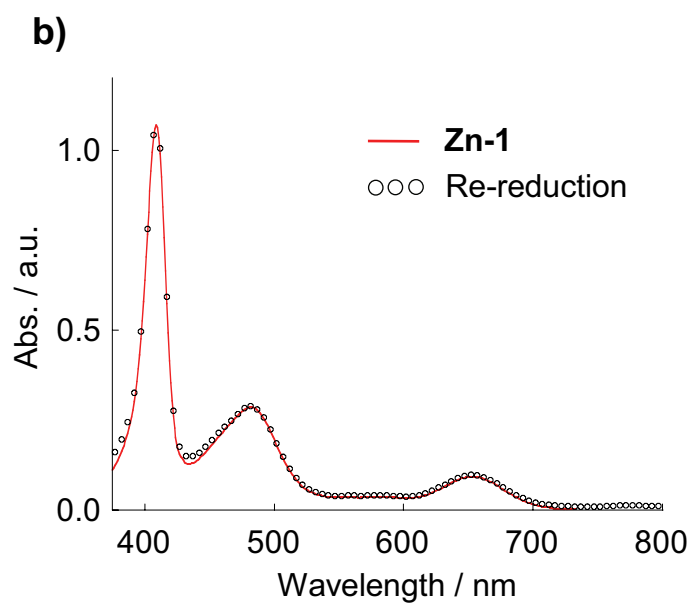
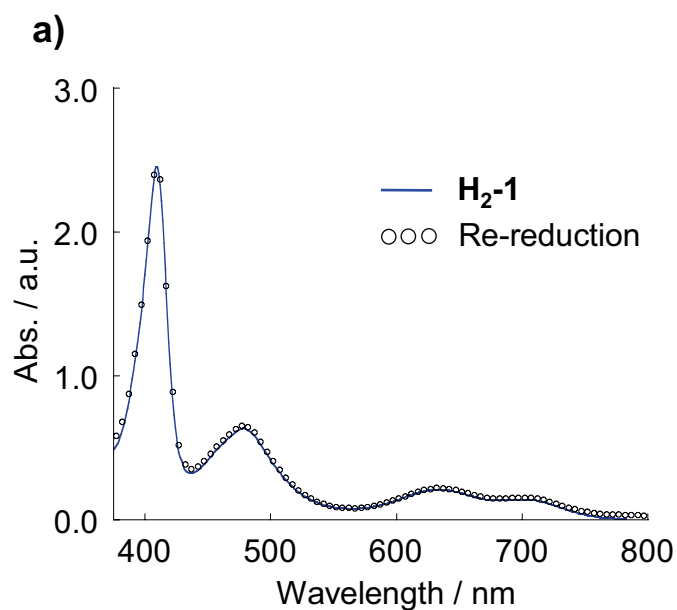


Fig. S8 UV/Vis spectra in dichloromethane before the titration experiments shown in Fig. S6 and S7, and upon re-reduction after the titration experiments: a) $\text{H}_2\text{-1}$; b) Zn-1 . Re-reduction was conducted with excess equivalent of decamethylferrocene. We note that these spectra contain slight contributions from 1,1'-dichloroferrocene, decamethylferrocene, and decamethylferrocenium hexafluorophosphate, all of which have only small absorptivities in the shown region.

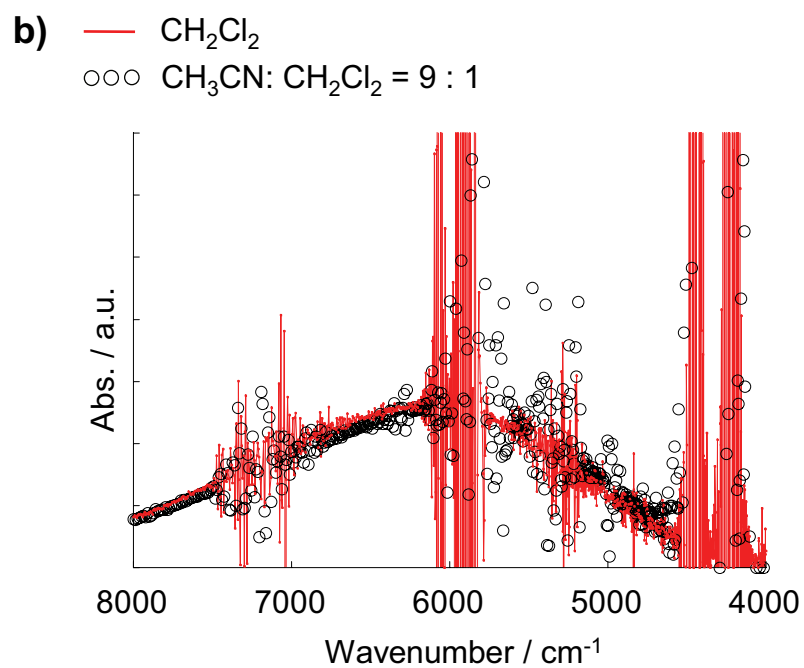
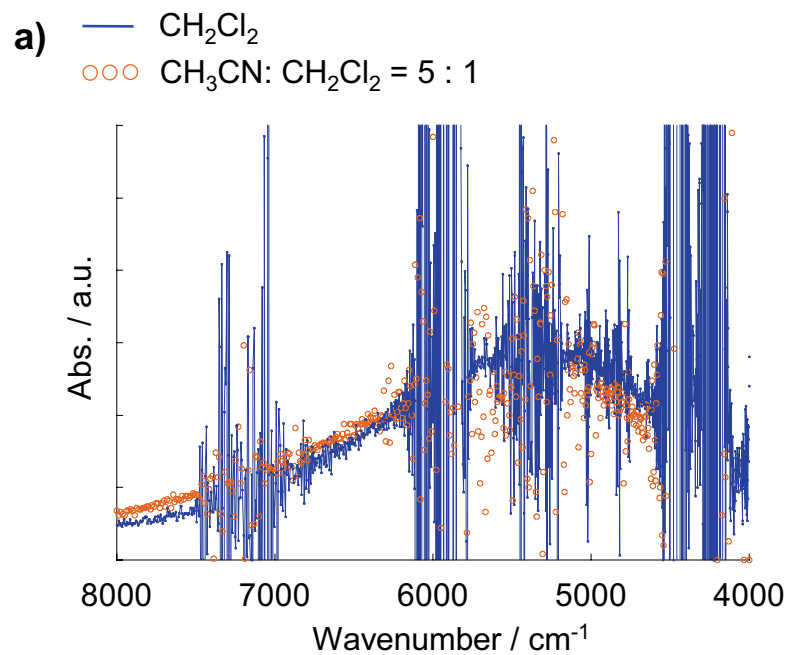


Fig. S9 NIR spectra in a mixture of acetonitrile and dichloromethane upon additions of the oxidant: a) **H₂-1**; b) **Zn-1**.