Electronic Supplementary Information

for

Control of electron-transfer reduction by protonation of zinc octabutoxyphthalocyanine assisted by intramolecular hydrogen bonding

Tatsuhiko Honda, Takahiko Kojima,* and Shunichi Fukuzumi*

Experimental Section

Materials. Chemicals were purchased from commercial sources and used without further purification, unless otherwise noted. Benzonitrile (PhCN) used for spectroscopic and electrochemical measurements was distilled over phosphorus pentoxide prior to use.[1] $H_2(OBu)_8Pc$, $Zn(OBu)_8Pc$, and $Zn(SBu)_8Pc$, were synthesized according to the reported procedures.[2] $[Ru(bpy)_3](PF_6)_3$ was prepared from tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate by the oxidation with PbO_2.[3]

Synthesis of $[Zn(OBu)_8PcH](CH_3COO)$. The mixture of $Zn(OBu)_8Pc$ in $CHCl_3$ and excess amount of acetic acid was evaporated. The resulting solid was washed with hexane and dried *in vacuo* to give $[Zn(OBu)_8PcH](CH_3COO)$ as red-brown powder quantitatively. Elemental analysis (%) calcd for $C_{66}H_{84}N_8O_{10}Zn{\bullet}(H_2O)_{0.5}$: C 64.77, H 7.00, N 9.16; found: C 64.66, H 6.79, N 9.13.

Spectroscopic Measurements. UV-vis spectroscopy was carried out on a Shimadzu UV-3100PC spectrometer or a Hewlett Packard 8453 diode array spectrometer at room temperature using 1 cm cells. Equilibrium constants (log K) of the protonated phthalocyanines [Equation (1)] were determined by the Hill equation [Equation (2)], which analyzes changes of absorption spectra during the titration as a function of the concentration of added acids.[4]

$$\mathrm{Pc} + n\,\mathrm{HA} \overset{K}{\rightleftharpoons} \mathrm{PcH}_n{}^{n+} + n\,\mathrm{A}^- \qquad (1)$$

$$\log\,[(A_\mathrm{o} - A_\mathrm{i})/(A_\mathrm{f} - A_\mathrm{o})] = n \log\,[\mathrm{HA}] + \log K \qquad (2)$$

, where A_o is observed absorbance, A_i is an absorbance of Pc, A_f is an absorbance of $PcH_n{}^{n+}$, n is a number of proton to react, and [HA] denotes the concentration of acid, respectively.

^1H NMR spectra were recorded on a JEOL A-300 spectrometer and chemical shifts were determined relative to the residual solvent peaks. The fluorescence spectra were measured by using an absolute PL quantum yield measurement system (Hamamatsu photonics Co., Ltd., C9920-02) by excitation at 430 nm. Phosphorescence spectrum was measured by using a SPEX Fluorolog τ3 spectrophotometer.

The energy levels of singlet excited states of Zn(II)-phthalocyanines were determined on the basis of the averaged values (in eV) of their absorption and fluorescence maxima.

The energy levels of their tripled excited states were calculated by using the emission maxima of their phosphorescence spectra.

Time-Resolved Transient Absorption Measurements. Nanosecond time-resolved transient absorption measurements were performed using a laser system provided by UNISOKU Co., Ltd. Measurements of nanosecond transient absorption spectra were performed according to the following procedure. A deaerated solution was excited by a Panther optical parametric oscillator pumped by a Nd:YAG laser (Continuum, SLII-10, 4-6 ns fwhm) at $\lambda = 430$ nm. The photodynamics was monitored by continuous exposure to a xenon lamp (150 W) as a probe light and a photomultiplier tube (Hamamatsu 2949) as a detector. The equilibrium constant of monoprotonation at the triplet excited state (K^*) was determined from the observed rate constant of triplet decay by using Equation (3),[5]

$$(k_{\mathrm{obs}} - k_1)/(k_2 - k_{\mathrm{obs}}) = K^*[\mathrm{HA}] \quad (3)$$

where k_{obs} is the observed rate constant of the decay of the triplet excited state, k_1 is rate constant of that of $\mathrm{Zn(OBu)_8Pc}$, k_2 is rate constant of that of $\mathrm{Zn(OBu)_8PcH^+}$, and [HA] denotes the concentration of acid.

Electrochemical Measurements. Cyclic voltammetry (CV) was performed on an ALS 630B electrochemical analyzer and was conducted in deaerated PhCN containing 0.1 M $[(n\text{-Bu})_4\mathrm{N}]\mathrm{PF_6}$ ($\mathrm{TBAPF_6}$) as a supporting electrolyte at room temperature. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 $\mathrm{mm^2}$) and a platinum wire as the counter electrode. The Pt working electrode (BAS) was routinely polished with BAS polishing alumina suspension and rinsed with acetone before use. The potentials were measured with respect to the $\mathrm{Ag/AgNO_3}$ (0.01 M) reference electrode. All potentials (vs. $\mathrm{Ag/Ag^+}$) were converted to values vs. SCE by adding 0.29 V.[6] All electrochemical measurements were carried out under an atmospheric pressure of nitrogen.

References

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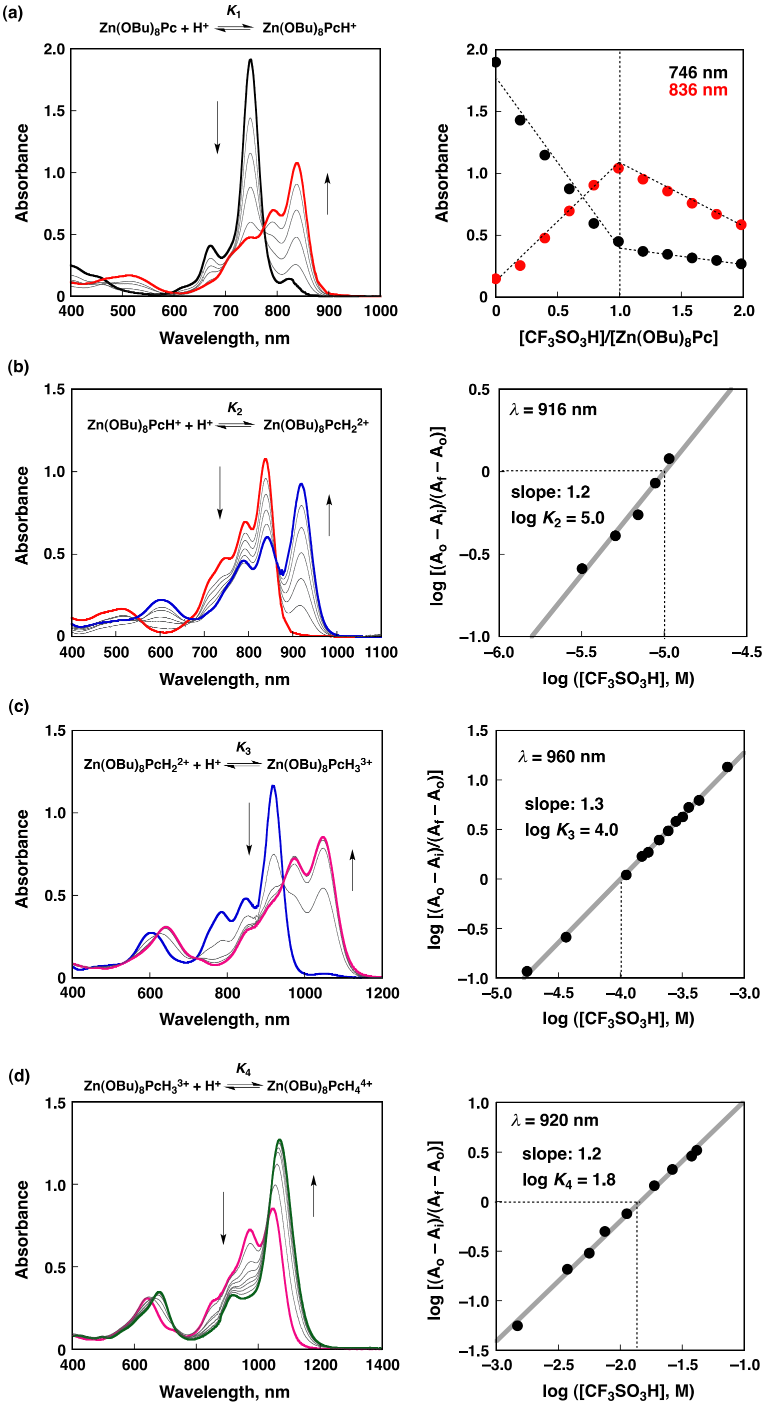


Fig. S1 Left column: Absorption spectral change in the course of titration of Zn(OBu)$_8$Pc (1.0×10^{-5} M) in PhCN with CF$_3$SO$_3$H. Right column: (a) Absorbance changes at 746 (black) and 836 nm (red). A Hill plot to determine the stoichiometry and the formation constant; (b) log K_2, (c) log K_3, and (d) log K_4.

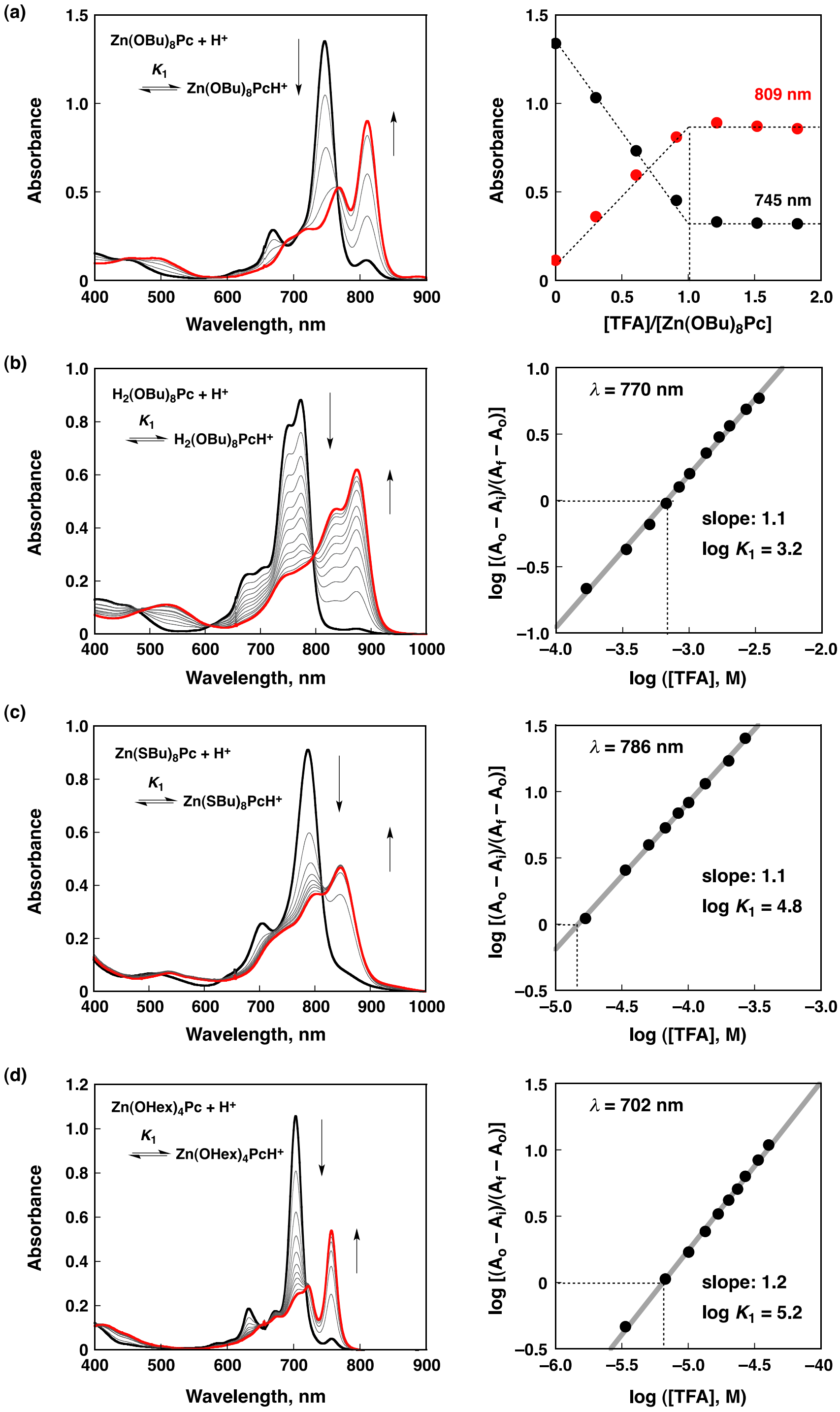


Fig. S2 Left column: Absorption spectral change in the course of titration of (a) $Zn(OBu)_8Pc$, (b) $H_2(OBu)_8Pc$, and (c) $Zn(SBu)_8Pc$ in PhCN with TFA. Right column: (a) Absorbance changes at 745 (black) and 809 nm (red). A Hill plot to determine the stoichiometry and the formation constant (log K_1) of (b) $H_2(OBu)_8PcH^+$, and (c) $Zn(SBu)_8PcH^+$.

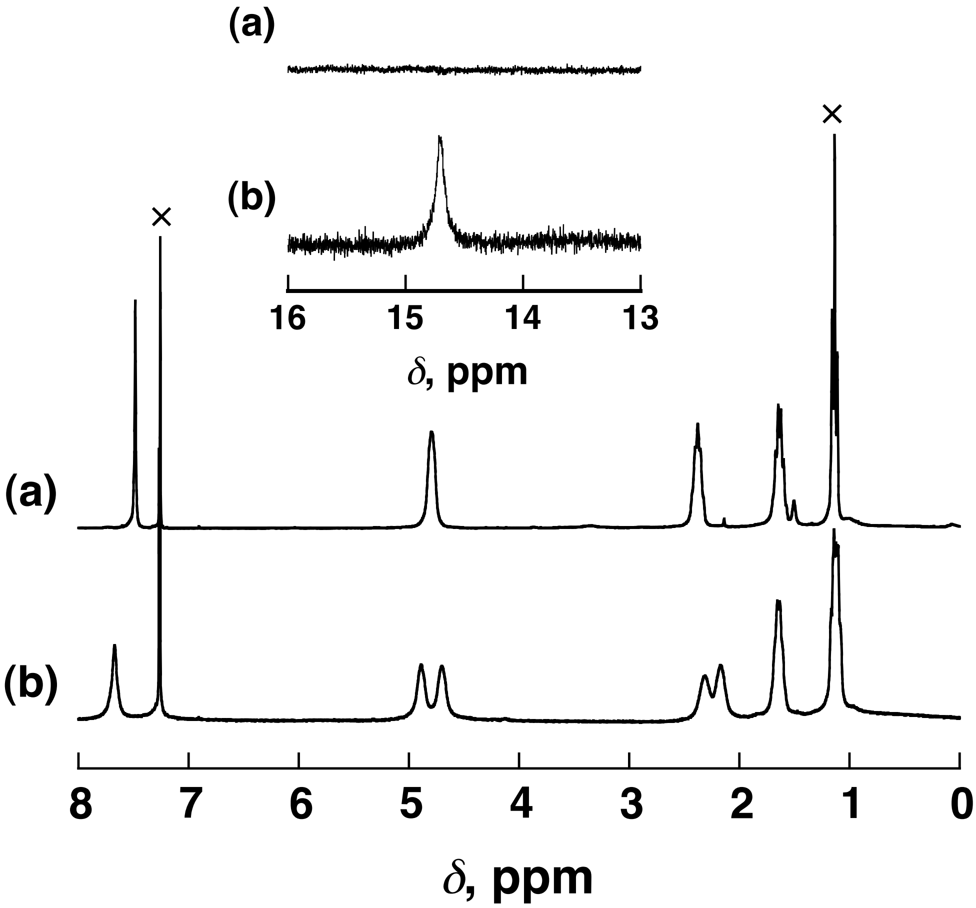


Fig. S3 ^{1}H NMR spectra of (a) Zn(OBu)$_8$Pc and (b) Zn(OBu)$_8$Pc with 2 equiv of TFA in CDCl$_3$ at 243 K. The symbol × denotes the signal derived from solvent molecules.

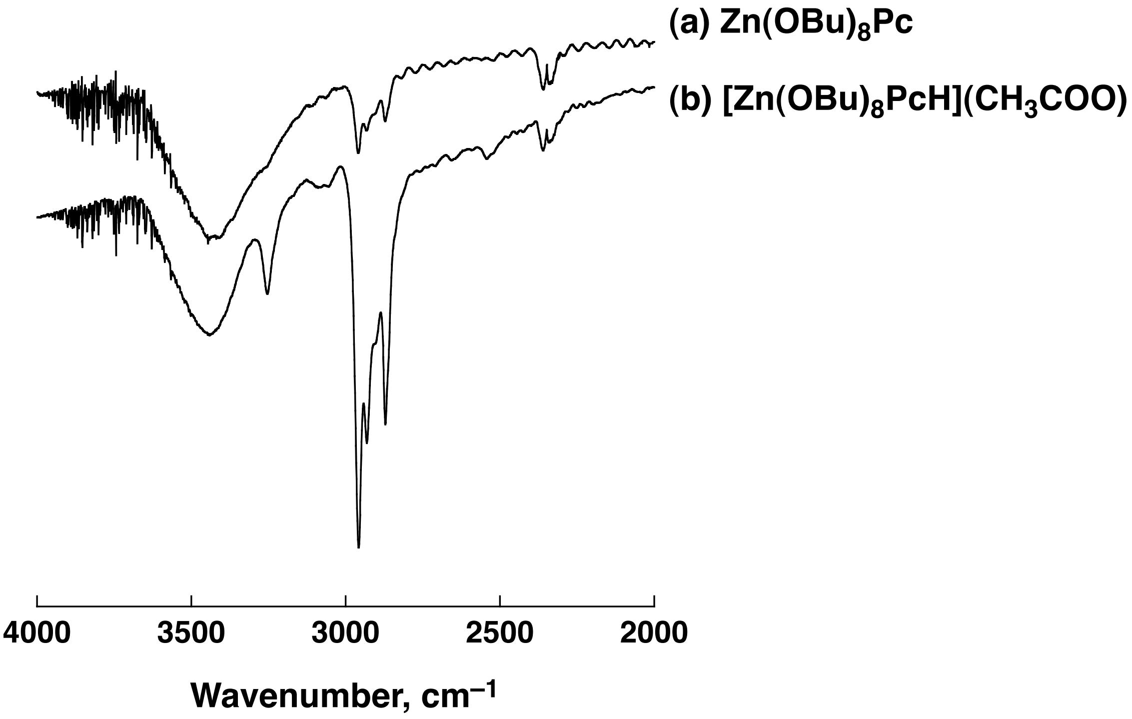


Fig. S4 IR spectra (in KBr pellet) of (a) $Zn(OBu)_8Pc$ and (b) $[Zn(OBu)_8PcH](CH_3COO)$.

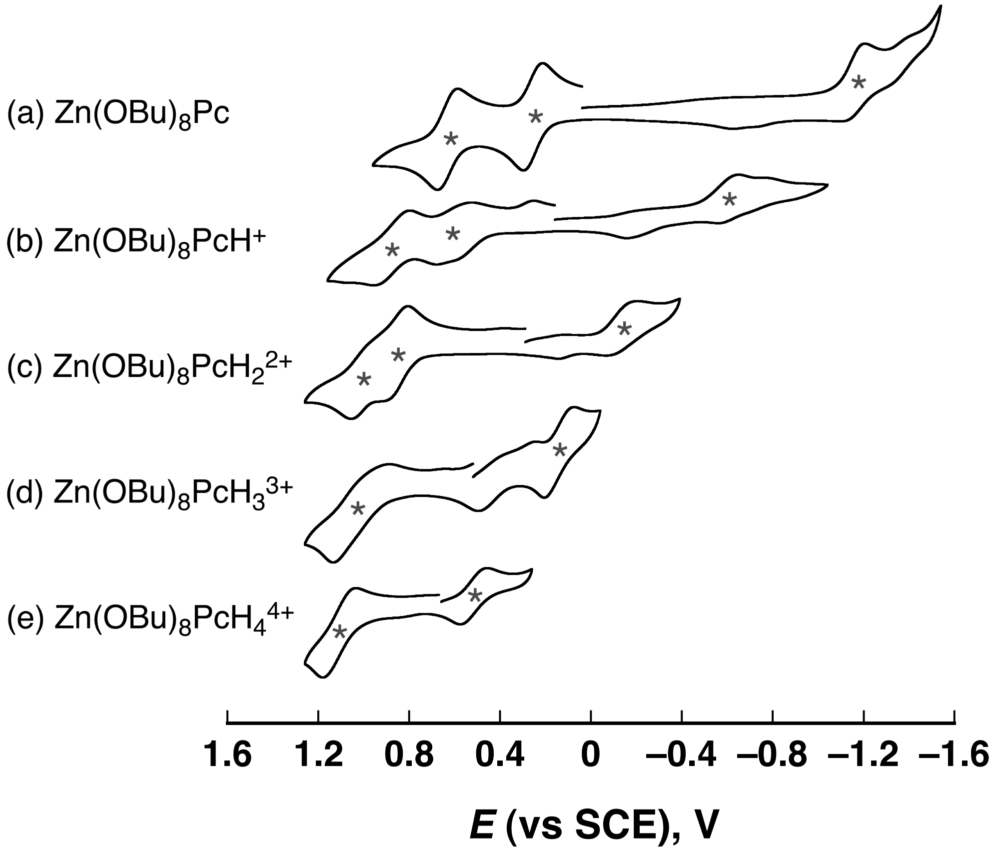


Fig. S5 Cyclic voltammograms of (a) $Zn(OBu)_8Pc$, (b) $Zn(OBu)_8PcH^+$ ($[CF_3SO_3H] = 2.5 \times 10^{-3}$ M), (c) $Zn(OBu)_8PcH_2{}^{2+}$ ($[CF_3SO_3H] = 5.0 \times 10^{-3}$ M), (d) $Zn(OBu)_8PcH_3{}^{3+}$ ($[CF_3SO_3H] = 1.0 \times 10^{-2}$ M), and (e) $Zn(OBu)_8PcH_4{}^{4+}$ ($[CF_3SO_3H] = 2.5 \times 10^{-2}$ M) in PhCN. The concentration of $Zn(OBu)_8Pc$ is 2.5×10^{-3} M. Measurements were performed under N_2 at room temperature in the presence of 0.1 M $[(n\text{-}Bu)_4N]PF_6$ as an electrolyte. Asterisk indicates the center of the redox couple.

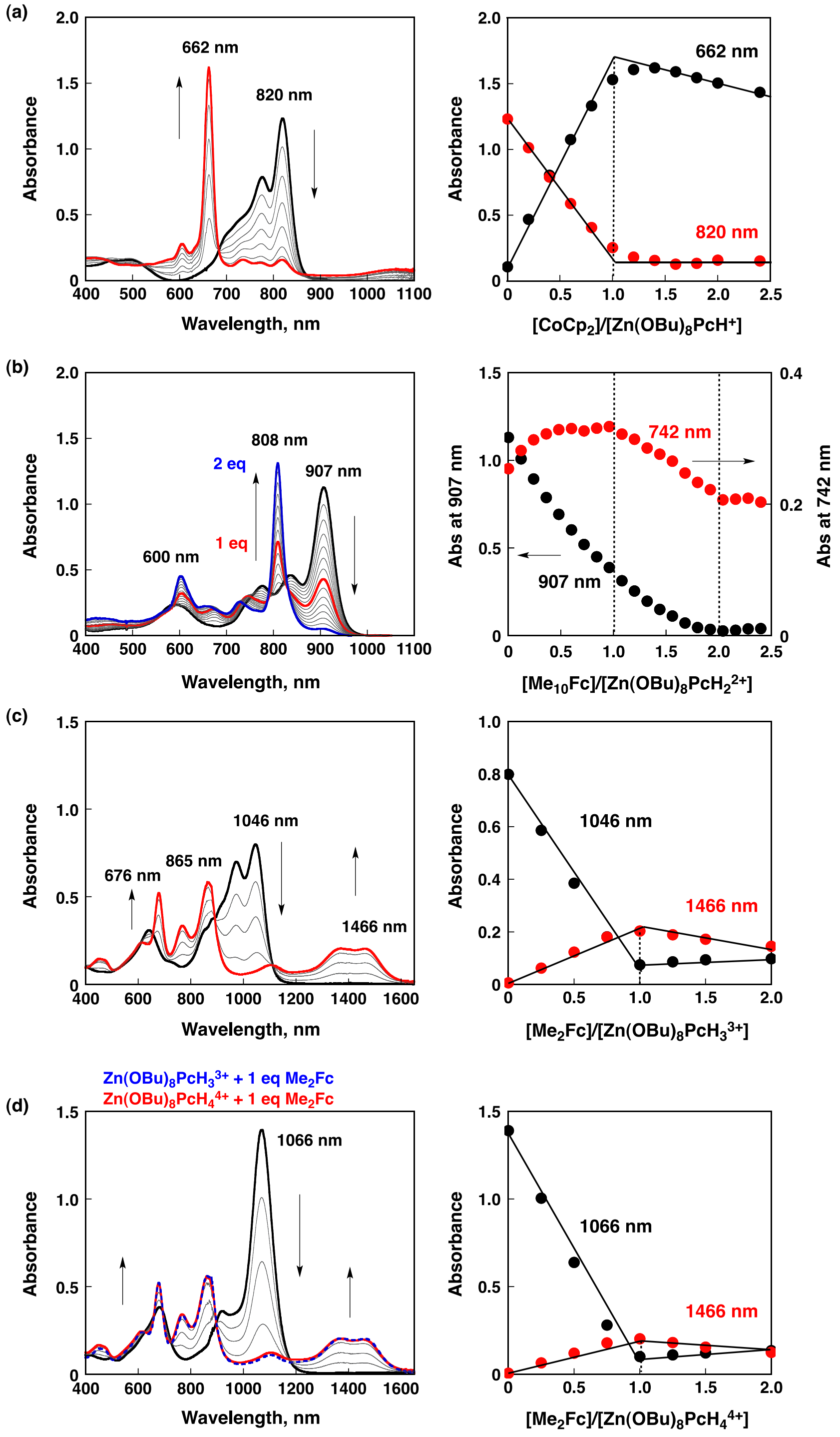


Fig. S6 Absorption spectral change in the course of titration of (a) $Zn(OBu)_8PcH^+$ ([Benzoic acid] = 2.0×10^{-4} M) with cobaltocene ($CoCp_2$), (b) $Zn(OBu)_8PcH_2^{2+}$ ([TFA] = 1.0×10^{-3} M) with decamethylferrocene ($Me_{10}Fc$), (c) $Zn(OBu)_8PcH_3^{3+}$ ([CF_3SO_3H] = 2.0×10^{-4} M) with 1,1'-dimethylferrocene (Me_2Fc), (d) $Zn(OBu)_8PcH_4^{4+}$ ([CF_3SO_3H] = 1.0×10^{-2} M) with Me_2Fc in PhCN. The concentration of $Zn(OBu)_8Pc$ is 1.0×10^{-5} M.

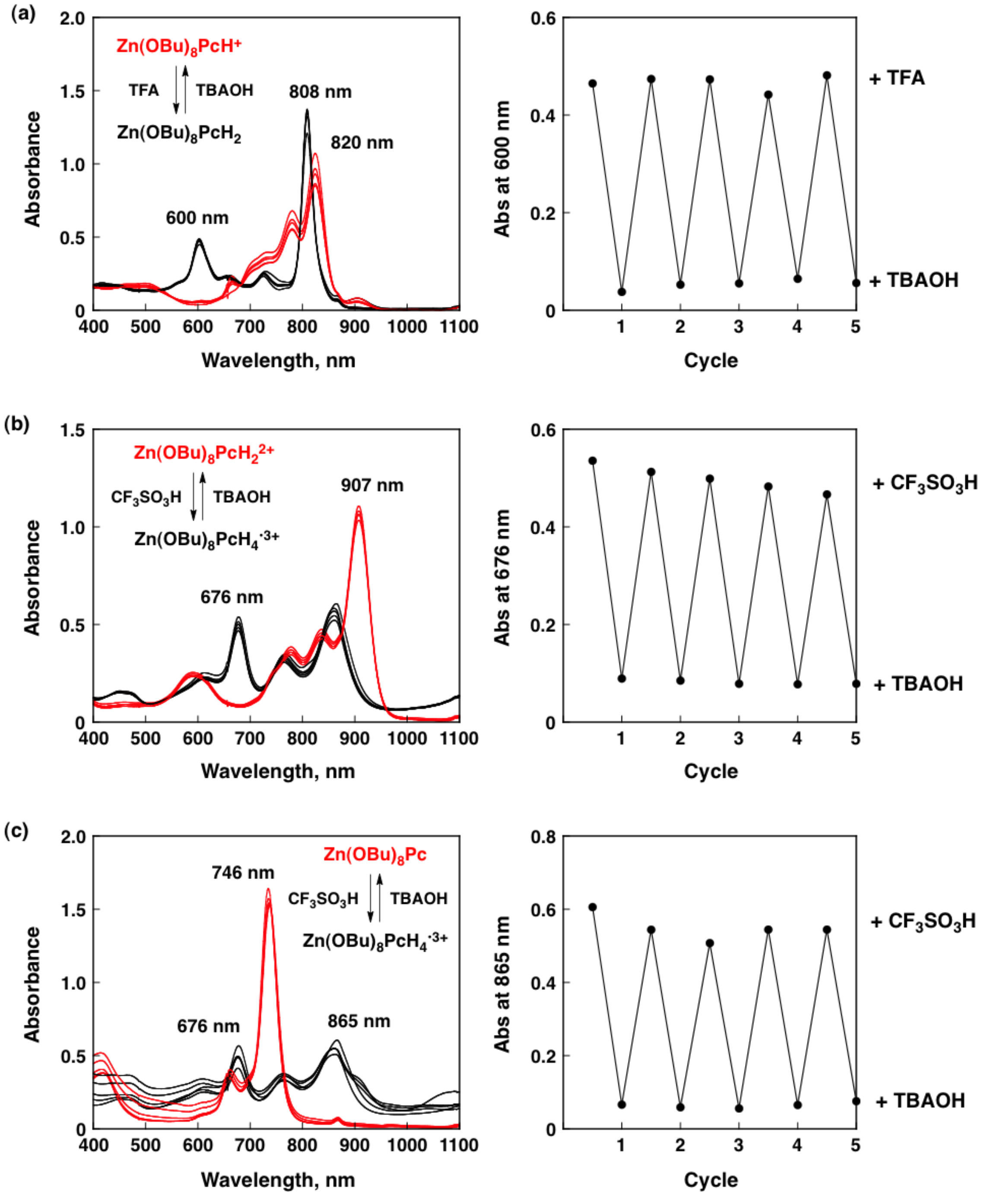


Fig. S7 Cyclical absorption spectral change in the course of alternate addition of (a) TBAOH (1.0×10^{-3} M) and TFA (1.0×10^{-3} M) to a solution of $Zn(OBu)_8PcH_2$ (1.0×10^{-5} M), (b) TBAOH (2.0×10^{-4} M) and CF_3SO_3H (2.0×10^{-4} M) to a solution of $Zn(OBu)_8PcH_4^{\bullet 3+}$ (1.0×10^{-5} M), and (c) TBAOH (1.0×10^{-2} M) and CF_3SO_3H (1.0×10^{-2} M) to a solution of $Zn(OBu)_8PcH_4^{\bullet 3+}$ (1.0×10^{-5} M) in PhCN under Ar flow.

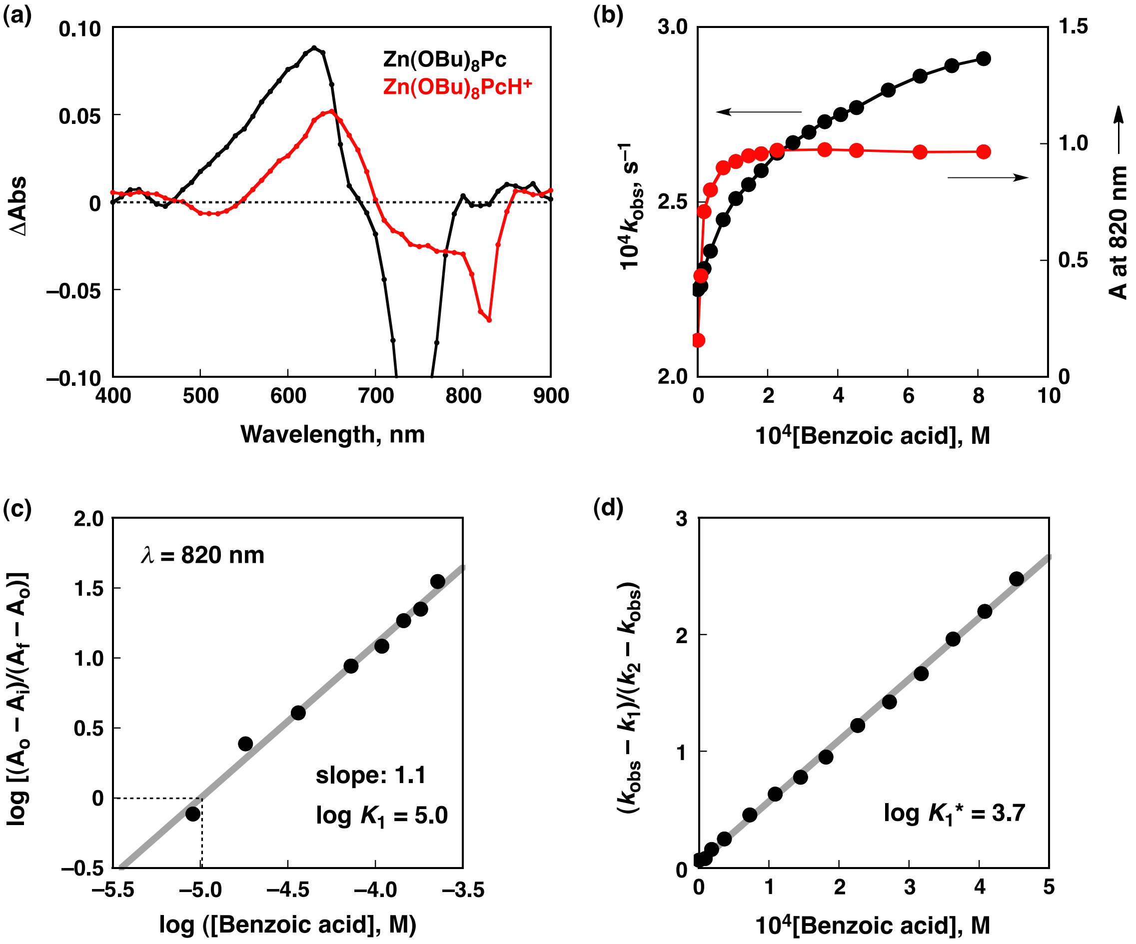


Fig. S8 (a) Nanosecond transient absorption spectra of $Zn(OBu)_8Pc$ (black) and $Zn(OBu)_8PcH^+$ (red, [TFA] = 1.0×10^{-5} M) in PhCN with photoirradiation at 430 nm. The concentration of $Zn(OBu)_8Pc$ is 1.0×10^{-5} M. (b) The observed rate constant at 650 nm (black, left) and absorbance changes at 820 nm (red, right) upon addition of benzoic acid to a PhCN solution of $Zn(OBu)_8Pc$ (1.0×10^{-5} M). (c) A Hill plot to determine the stoichiometry and the formation constant (log K_1). (d) A plot to determine the formation constant of monoprotontion at the triplet excited state (log K_1^*).

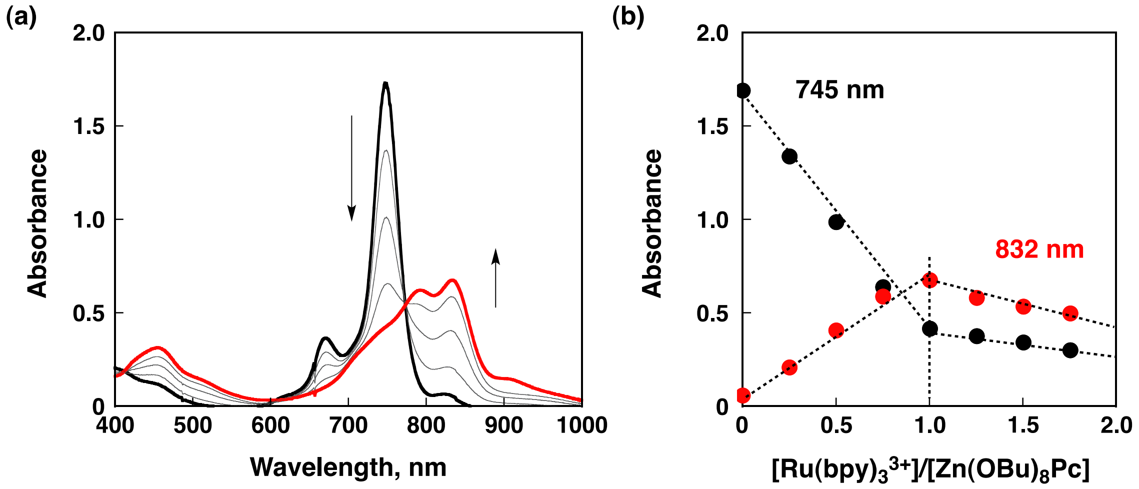


Fig. S9 (a) Absorption spectral change in the course of titration of $Zn(OBu)_8Pc$ (1.0×10^{-5} M) with $[Ru(bpy)_3](PF_6)_3$ in PhCN. (b) Absorbance changes at 745 (black) and 832 nm (red).

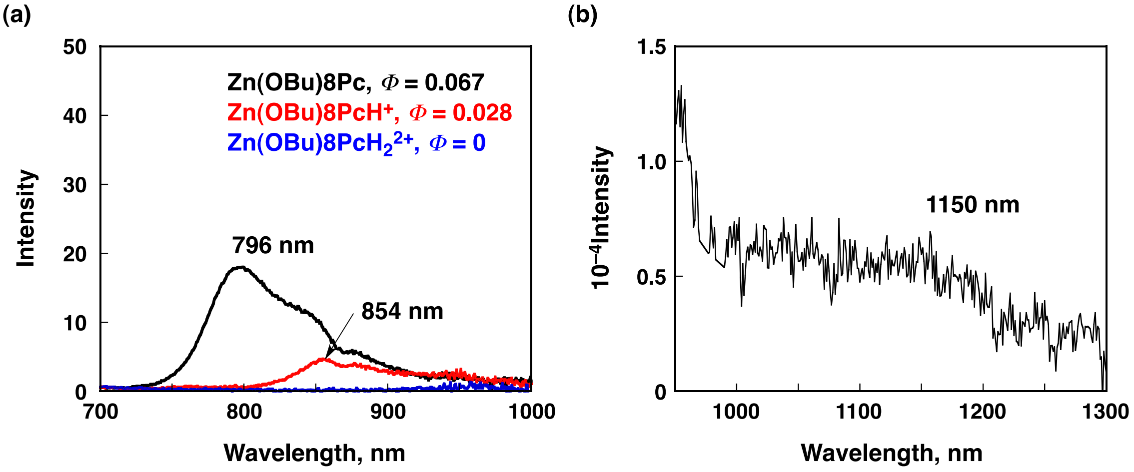
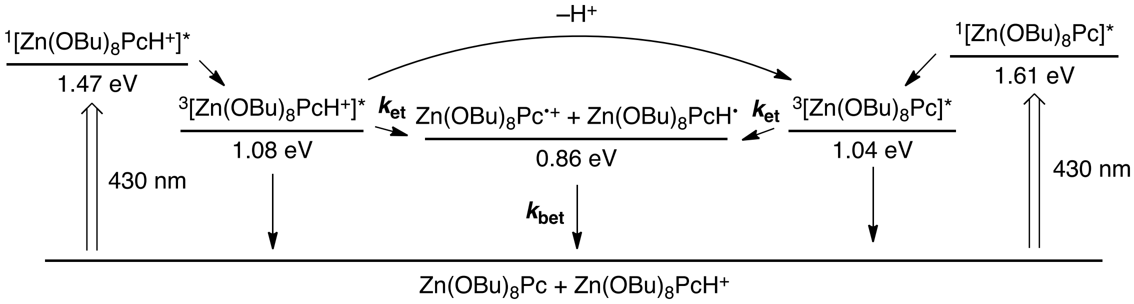


Fig. S10 (a) Fluorescence spectra of $Zn(OBu)_8Pc$ (black), $Zn(OBu)_8PcH^+$ (red, [TFA] = 1.0×10^{-5} M), and $Zn(OBu)_8PcH_2^{2+}$ (blue, [TFA] = 1.0×10^{-4} M) in PhCN photoirradiated at 430 nm ([$Zn(OBu)_8Pc$] = 1.0×10^{-5} M). (b) Phosphorescence spectrum of $Zn(OBu)_8PcH^+$ ([$Zn(OBu)_8Pc$] = 1.0×10^{-5} M, [TFA] = 1.0×10^{-5} M) in 2-MeTHF at 77 K with photoirradiation at 450 nm.



Scheme S1 Energy diagram of intermolecular photoinduced electron transfer and back electron transfer in a mixture of $Zn(OBu)_8Pc$ and $Zn(OBu)_8PcH^+$ in PhCN.