

Supplementary Information

Thermal and Photoinduced Electron Transfer Reaction of Phthalocyanine Complexes of Zn(II) and Cu(II) in Acetonitrile

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Preparation of compounds.

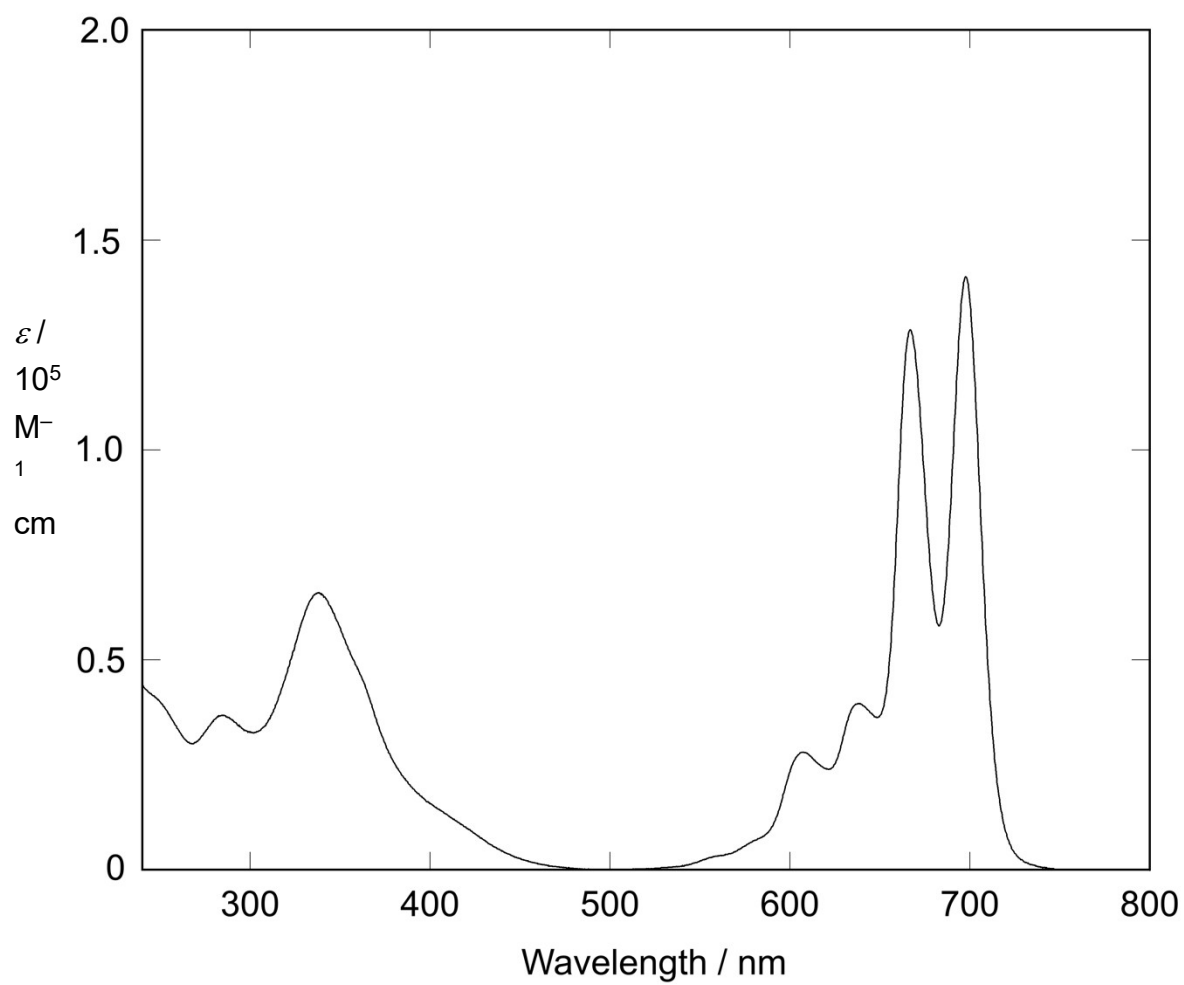


Figure S1. UV-visible absorption spectrum of the free base phthalocyanine in acetonitrile.

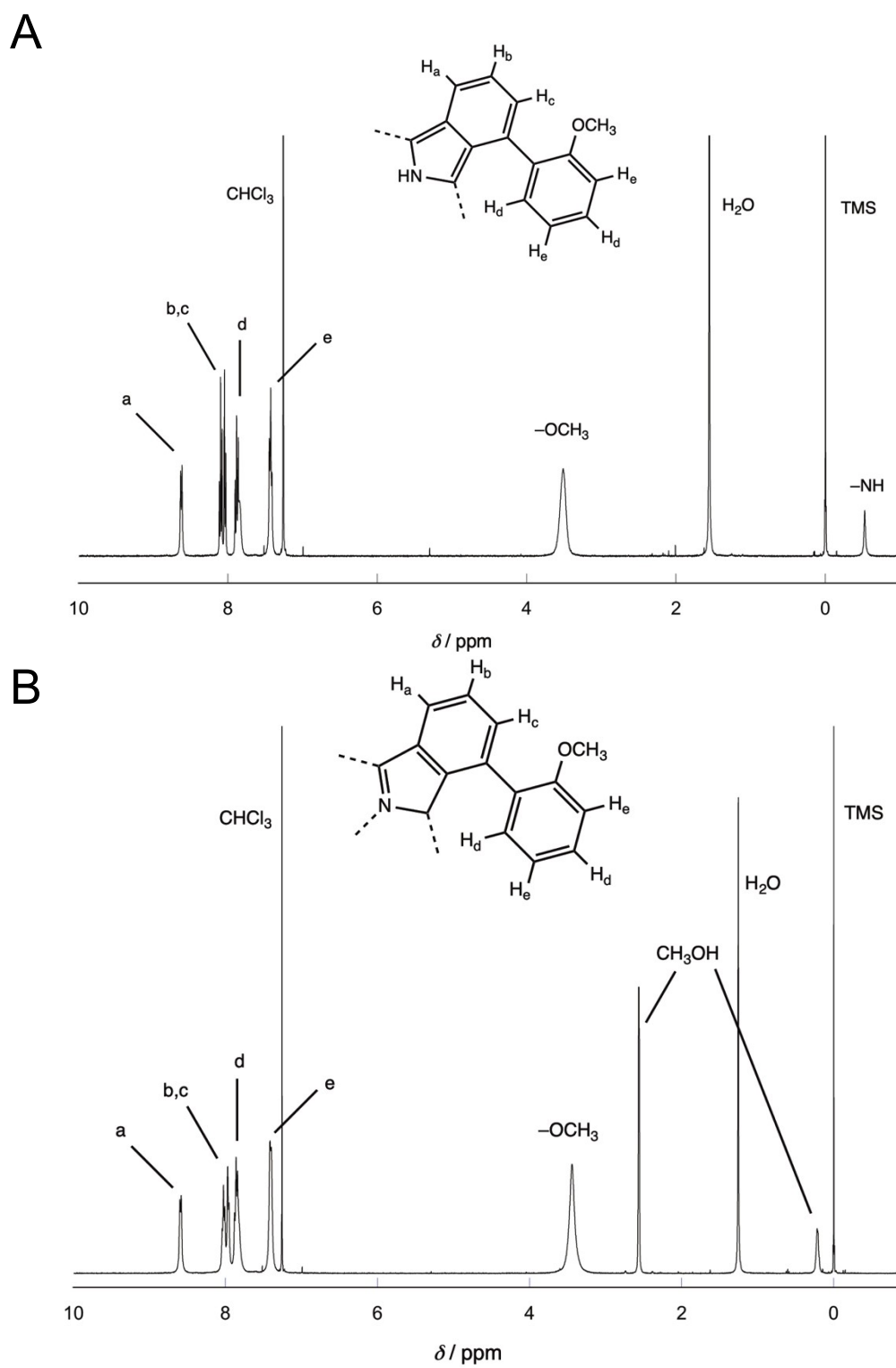


Figure S2. ^1H NMR spectra of the phthalocyanine (A) and its Zn(II) complex (B) in CDCl_3 .

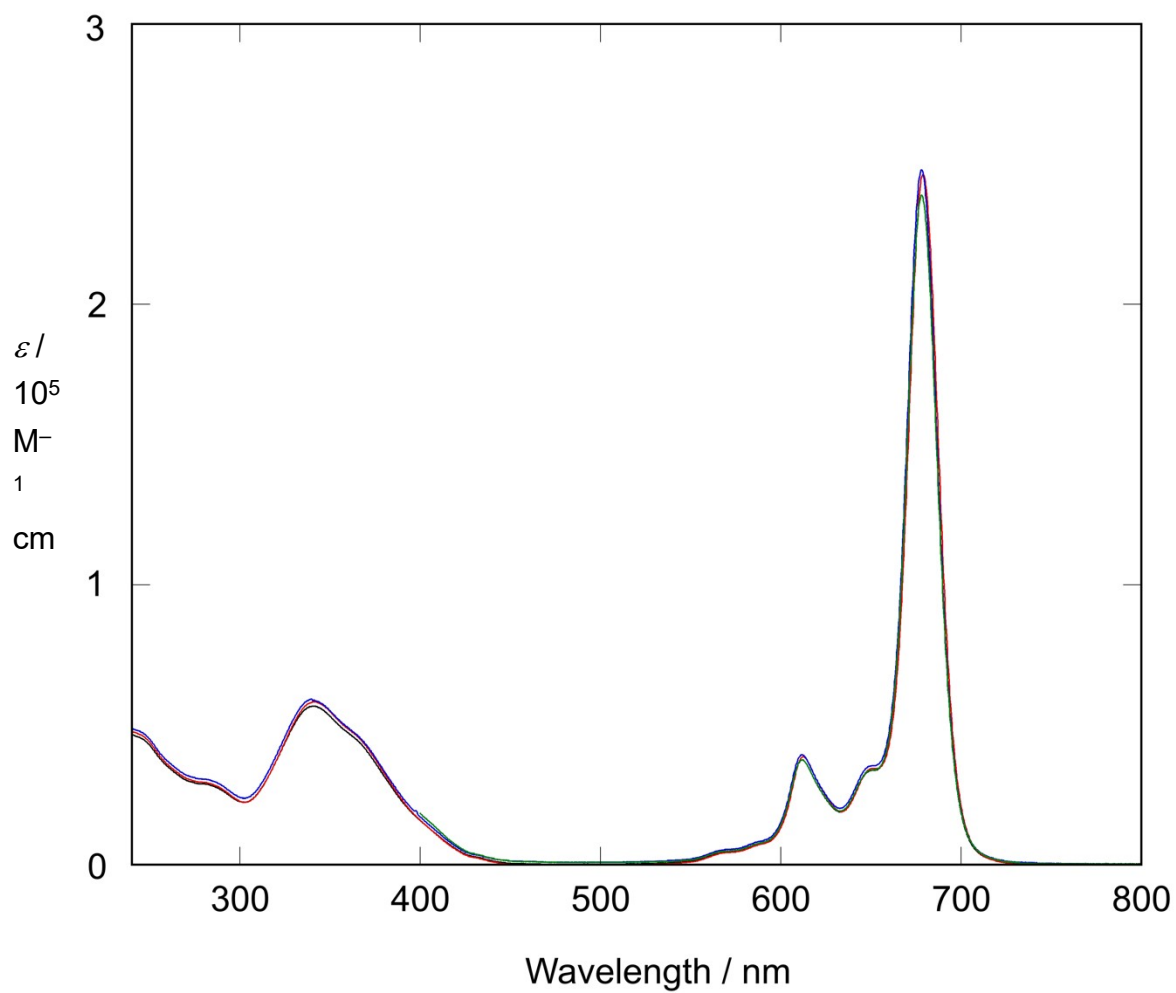


Figure S3. UV-visible absorption spectra of [Zn(Pc)] in acetonitrile. Concentration of [Zn(Pc)] is 1.50×10^{-6} M (green line), 8.33×10^{-6} M (blue line), 8.33×10^{-5} M (red line), and 1.43×10^{-4} M (black line).

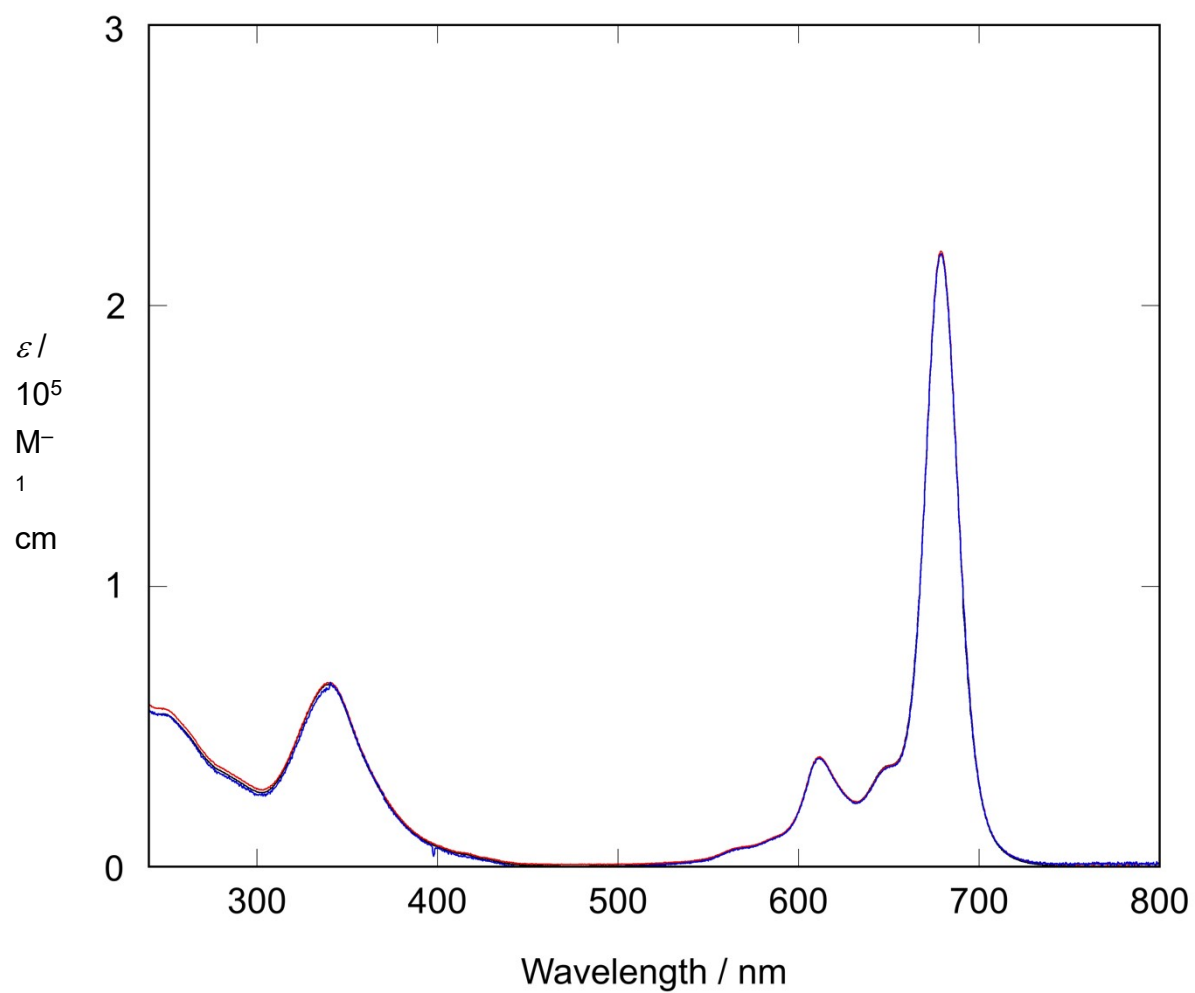


Figure S4. UV-visible absorption spectra of [Cu(Pc)] in acetonitrile. Concentration of [Cu(Pc)] is 6.00×10^{-7} M (blue line), 1.78×10^{-6} M (red line), and 2.06×10^{-5} M (black line).

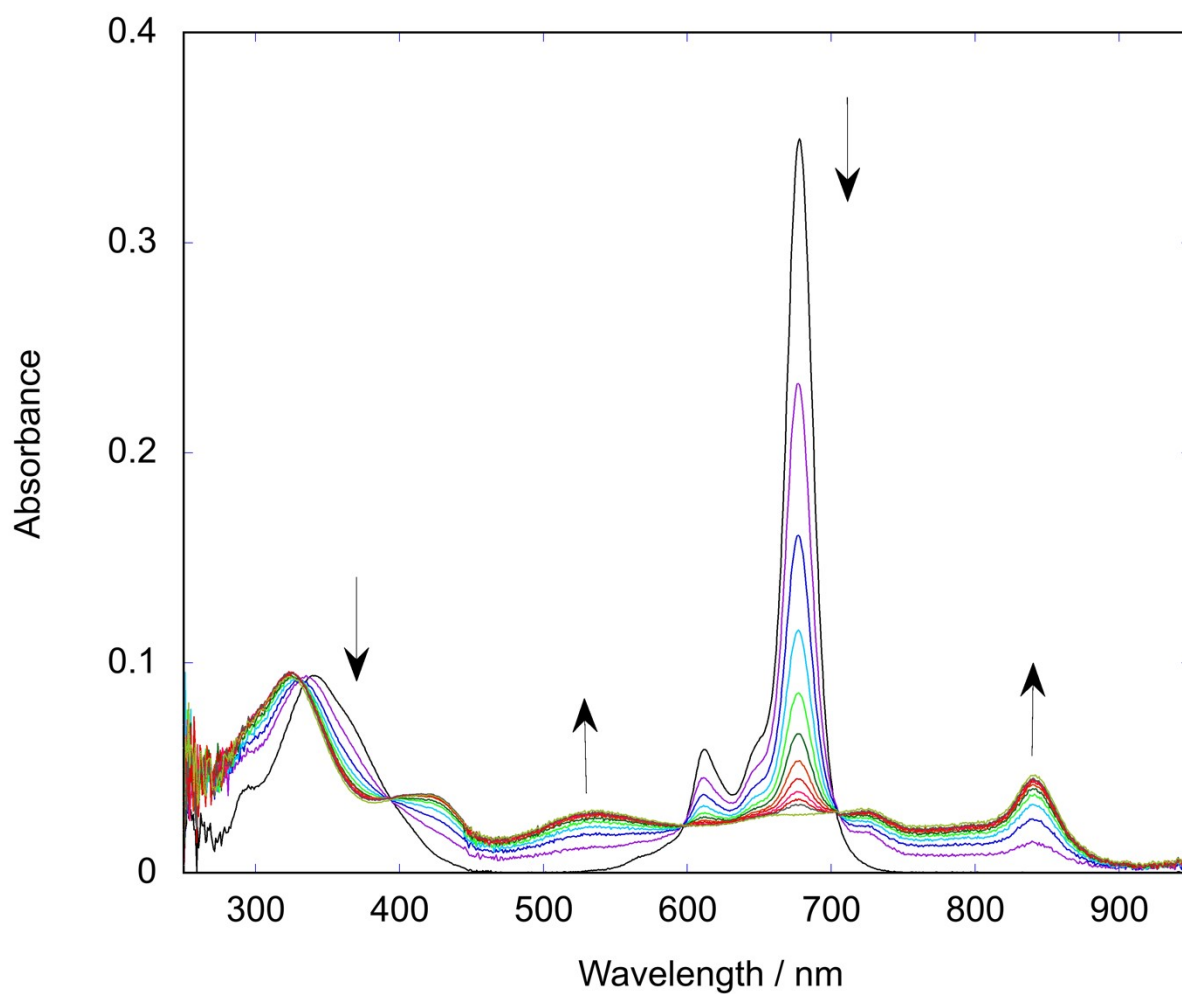


Figure S5. The spectral change in the UV-visible region for the reaction of the Zn(II) phthalocyanine complex with Cu²⁺ in acetonitrile. $C_{[\text{Zn}(\text{Pc})]} = 3.30 \times 10^{-6}$ M, $[\text{Cu}^{2+}] = 1.94 \times 10^{-4}$ M. Spectra were measured at every 8 ms interval.

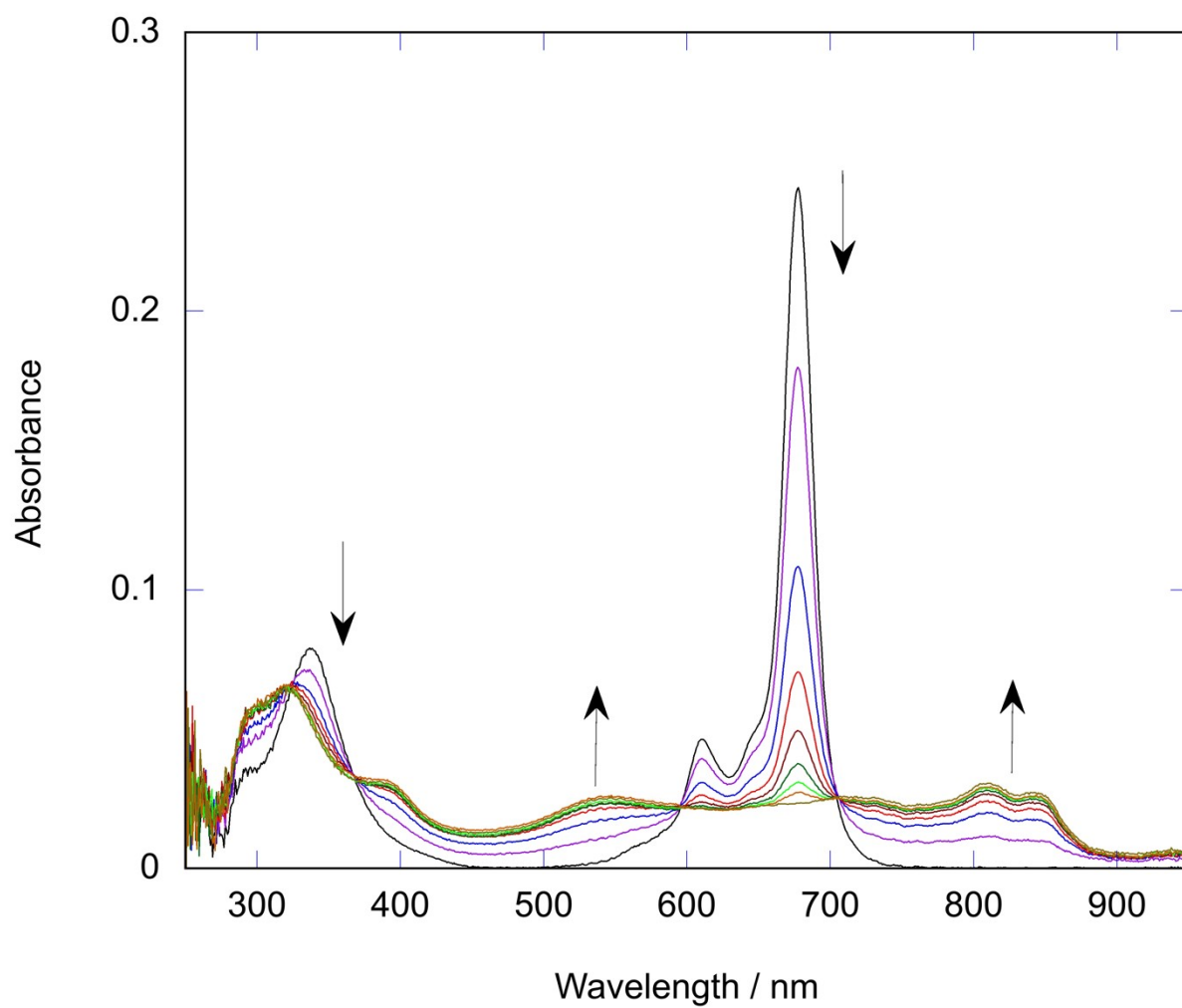


Figure S6. The spectral change in the UV-visible region for the reaction of the Cu(II) phthalocyanine complex with Cu²⁺ in acetonitrile. $C_{[\text{Cu}(\text{Pc})]} = 1.21 \times 10^{-6}$ M, $[\text{Cu}^{2+}] = 1.69 \times 10^{-4}$ M. Spectra were measured at every 20 ms interval.

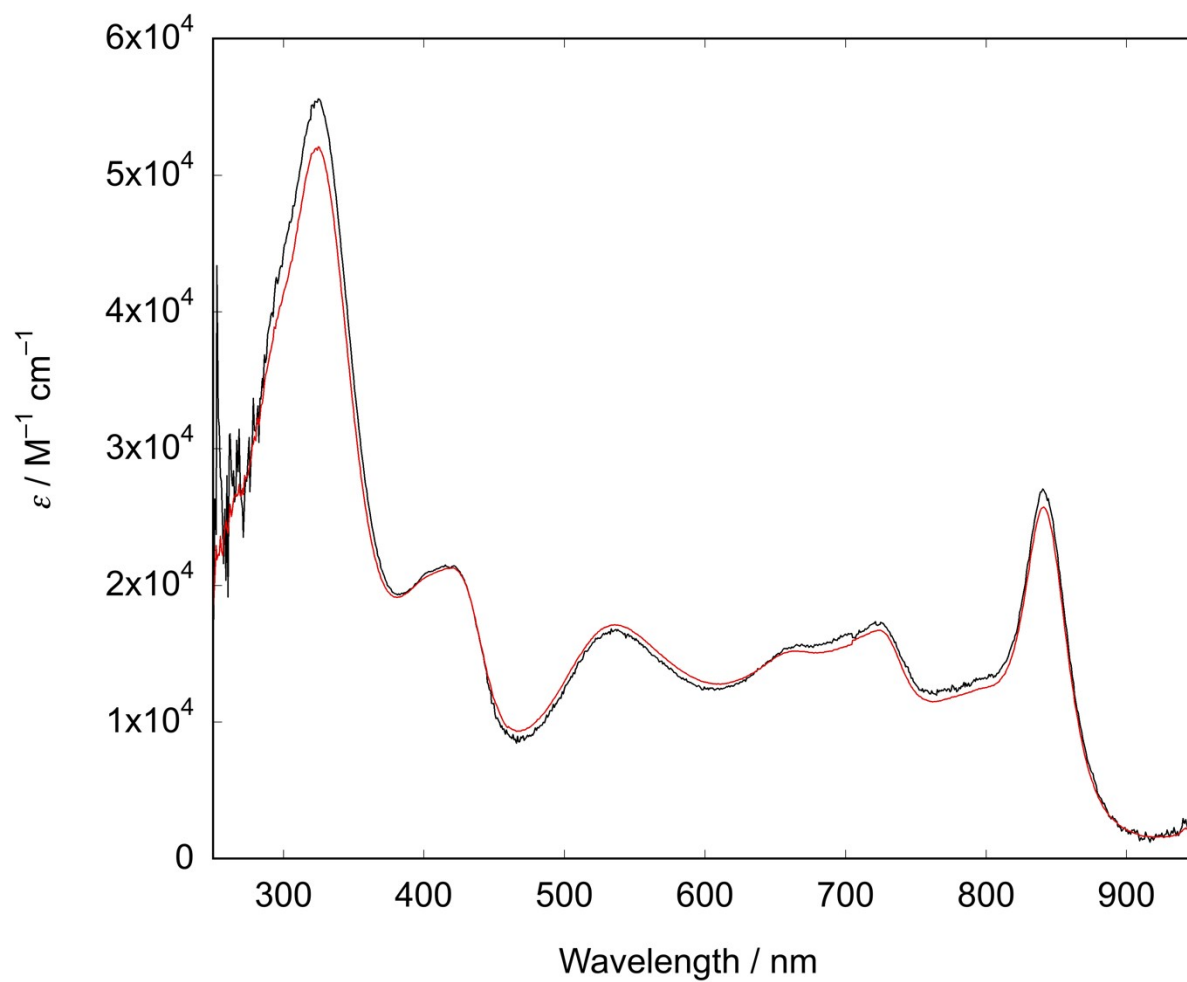


Figure S7. The UV-visible absorption spectra of the π -cation radical of the Zn(II) phthalocyanine complex given by the reaction with Cu^{2+} in acetonitrile. $C_{[\text{Zn(Pc)}]} = 1.65 \times 10^{-6}$ M (black line), 1.65×10^{-5} M (red line).

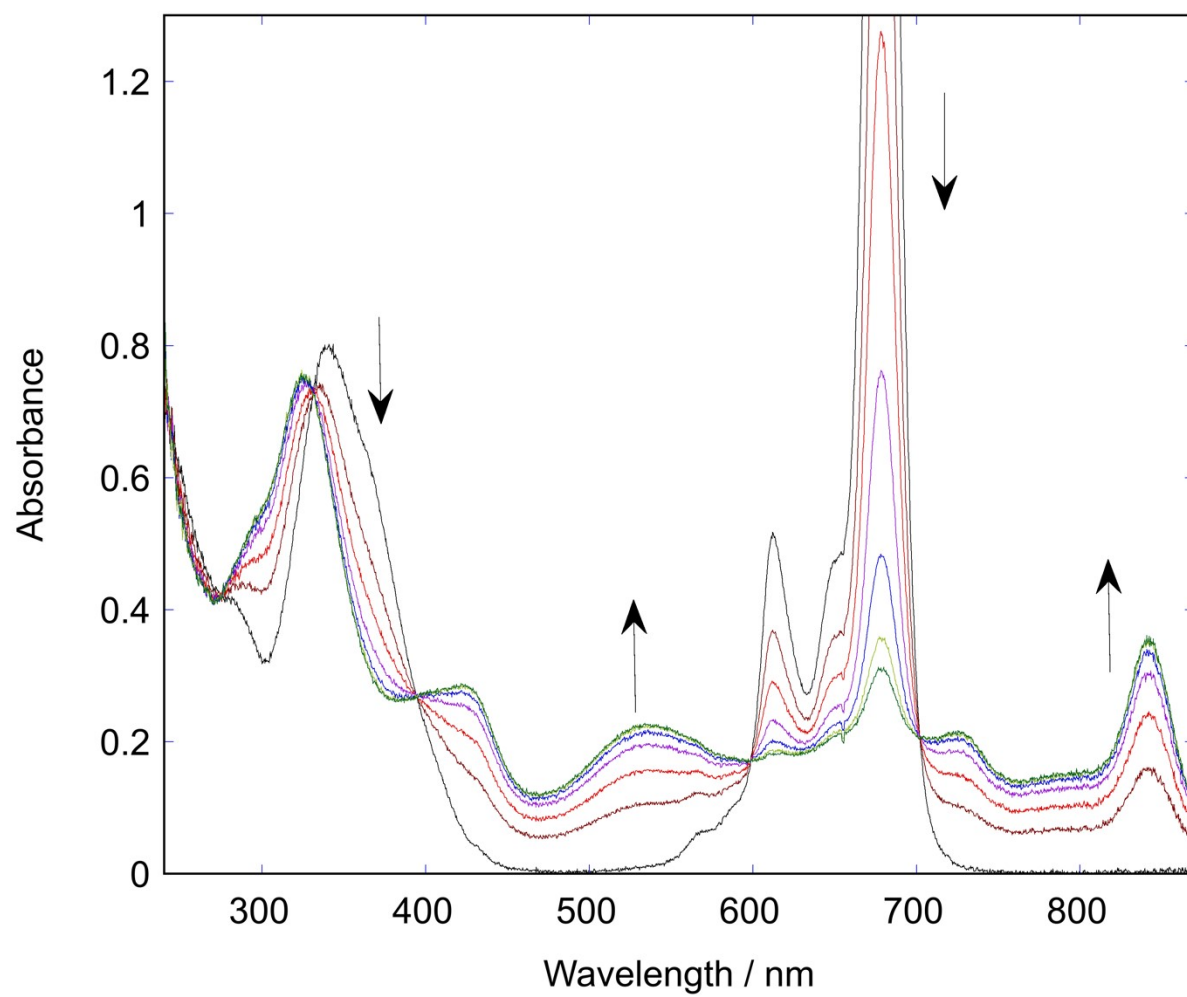


Figure S8. The spectral change in the UV-visible region for the electrochemical oxidation of the Zn(II) phthalocyanine complex in acetonitrile. The applied voltage was 0.38 V vs. $\text{Fc}^{+/0}$. $[\text{TBAP}] = 0.10 \text{ M}$.

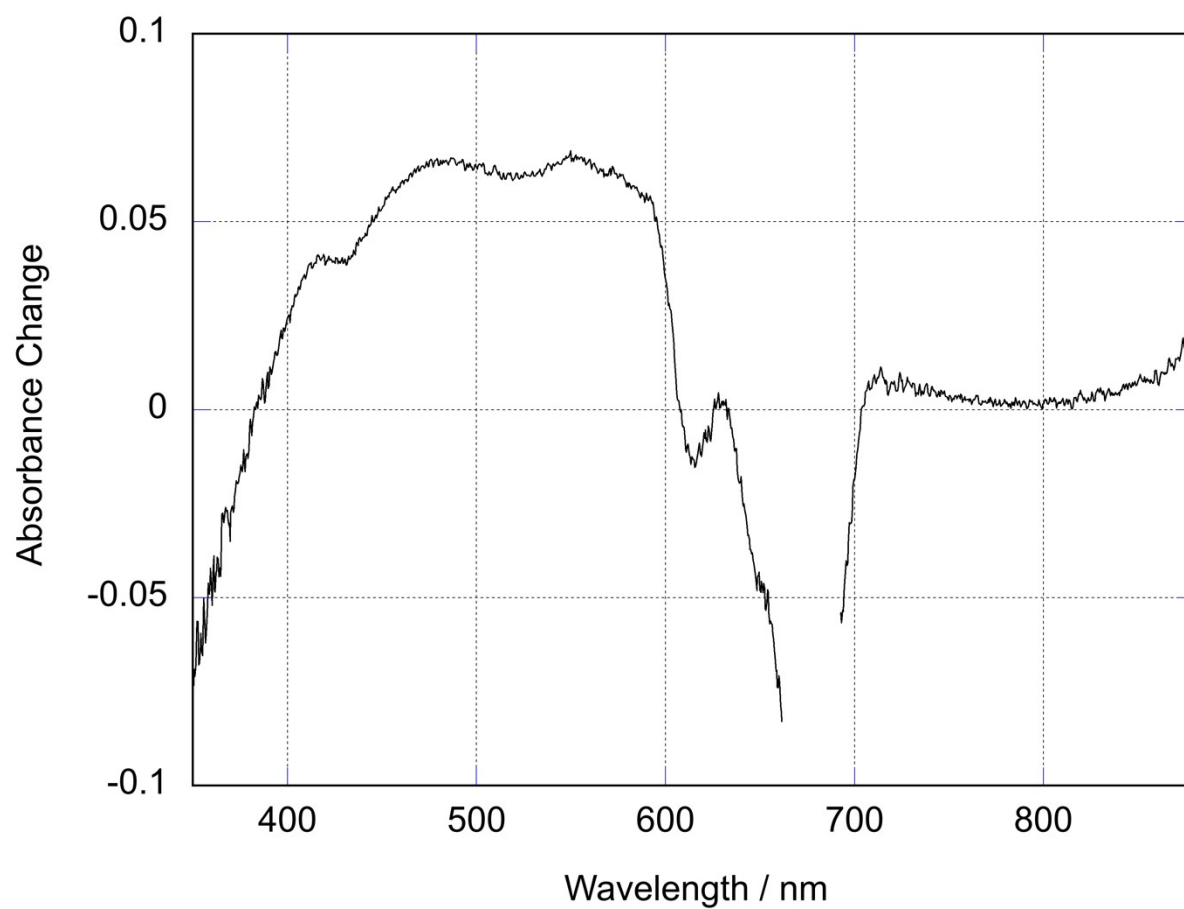


Figure S9. Transient absorption spectrum observed for the solution of [Zn(Pc)]. [Zn(Pc)] = 2.67×10^{-5} M. The spectra were recorded 1 μ s after a laser pulse under argon atmosphere.

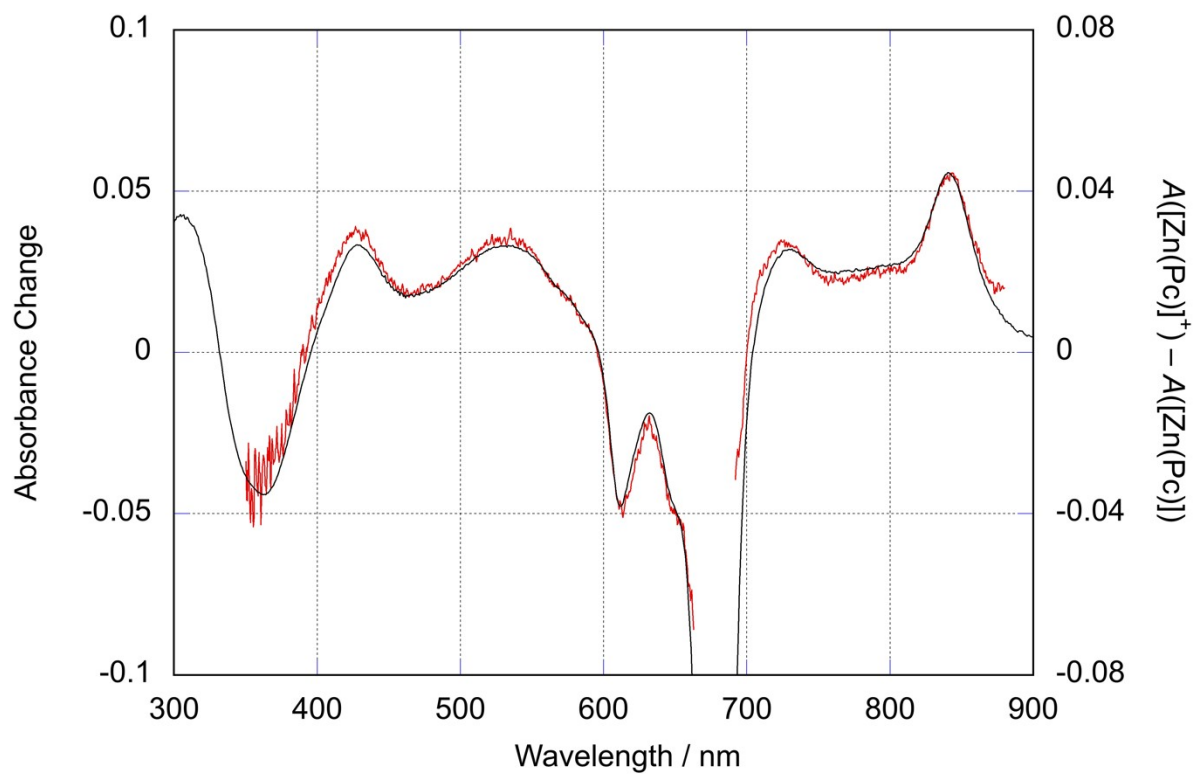


Figure S10. Comparison of the transient absorption spectrum observed for the solution of [Zn(Pc)] in the presence of [VO(salen)]⁺ recorded 15 μs after a laser pulse (red line) and the difference spectrum between the π-cation radical [Zn(Pc)]⁺ and [Zn(Pc)] (black line).

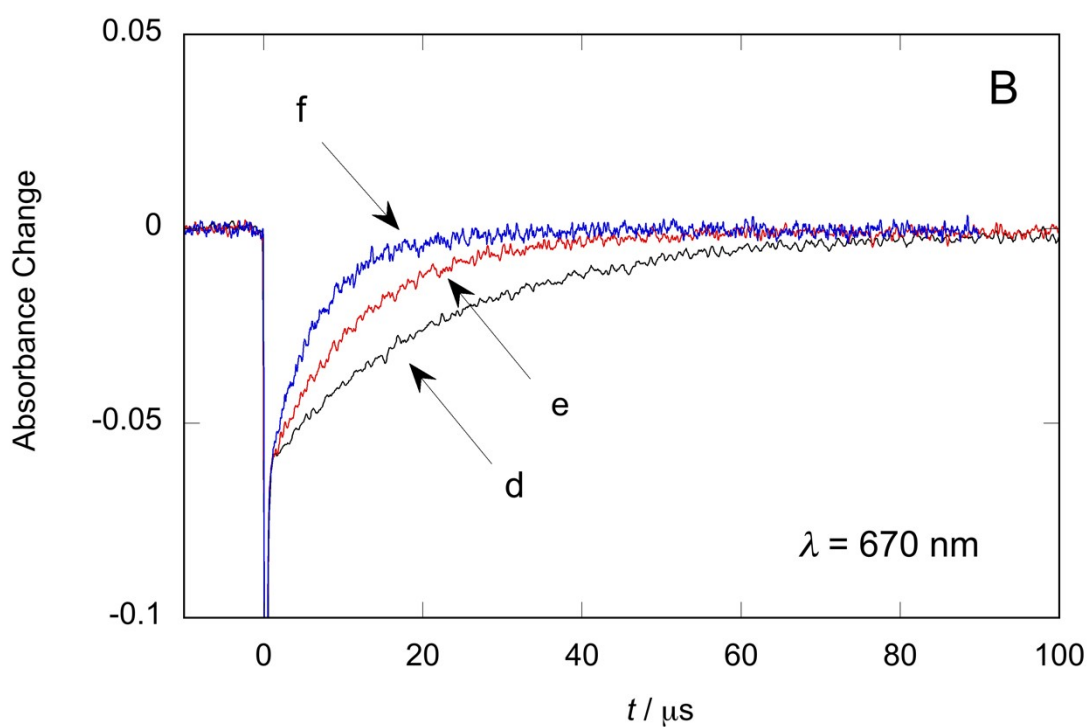
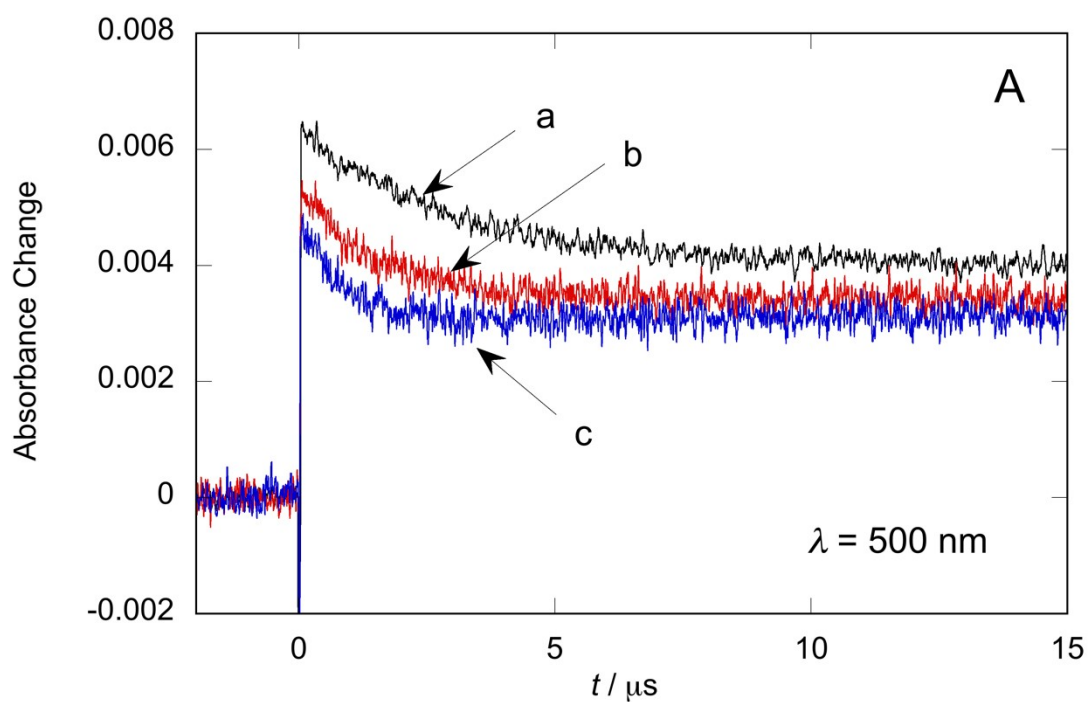
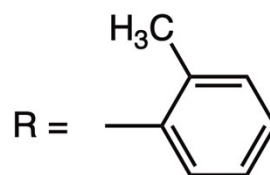
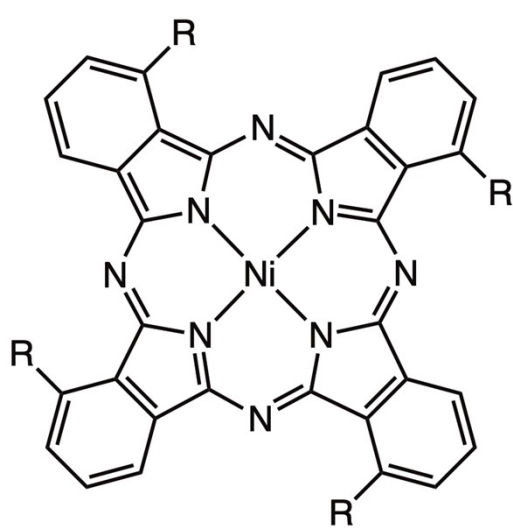
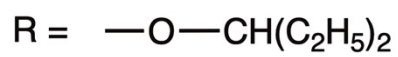


Figure S11. Absorbance-time traces for the photoinduced electron transfer reaction (A) and the back electron transfer reaction (B). Conditions: (A) $[\text{Zn(Pc)}] = 4.48 \times 10^{-6} \text{ M}$, $[\text{VO(salen)}^+] = 5.08 \times 10^{-5} \text{ M}$ (a), $1.02 \times 10^{-4} \text{ M}$ (b), $2.03 \times 10^{-4} \text{ M}$ (c); (B) $[\text{Zn(Pc)}] = 3.39 \times 10^{-6} \text{ M}$, $[\text{VO(salen)}^+] = 2.20 \times 10^{-4} \text{ M}$, $[\text{VO(salen)}] = 5.06 \times 10^{-5} \text{ M}$ (d), $1.01 \times 10^{-4} \text{ M}$ (e), $2.03 \times 10^{-4} \text{ M}$ (f).



(ref. 32)



(ref. 63)

Figure S12. The molecular structure of the phthalocyanine complexes mentined in the article.

Preparation of compounds.

Synthesis of phthalocyanine. To the mixture of 0.24 g of 3-(2-methoxyphenyl)-phthalonitrile (1.02 mmol) and 5.0 mL of 1-pentanol (Nacalai Tesque) was added 0.053 g of lithium (7.6 mmol), and the mixture was heated to 130 ° C under argon atmosphere for 1 hour. After the reaction mixture was allowed to cool, 6.5 mL of methanol and 1.5 mL of concentrated hydrochloric acid was slowly added with stirring and the mixture was cooled in a refrigerator overnight. The precipitated product was collected by suction filtration, washed with methanol, and then vacuum dried for 1 hour. The obtained solid was purified by silica gel column chromatography eluting with chloroform containing 5% hexane. The main band was collected, and the product was recrystallized from the mixture of chloroform and methanol (3:4) to obtain fine blue-green crystals (0.046 g, 49 μ mol, 19%). ^1H NMR (400 MHz, CDCl_3): δ / ppm : 8.62 (4H, d, $J = 7.5$ Hz, ArH), 8.02-8.12 (8H, m, ArH), 7.78-7.92 (8H, m, ArH), 7.36-7.48 (8H, m, ArH), 3.51 (12H, br, $-\text{OCH}_3$), -0.53 (2H, s, $-\text{NH}$).

Synthesis of the Zn(II) phthalocyanine complex. 15 mL of the methanol solution containing 0.201 g of zinc(II) acetate (1.15 mmol) was added to the chloroform solution (30 mL) of 0.046 g of the phthalocyanine (49 μ mol) and the mixture was heated to 75 ° C under argon atmosphere for 5 hours. The solvent was evaporated to dryness. The obtained solid was purified by silica gel column chromatography eluting with dichloromethane containing 2% methanol. The main band was collected, and the product was recrystallized from the mixture of chloroform and methanol (1:2) to obtain fine deep-blue crystals (0.041 g, 41 μ mol, 84%). ^1H NMR (400 MHz, CDCl_3): δ / ppm : 8.59 (4H, d, $J = 7.0$ Hz, ArH), 7.93-8.05 (8H, m, ArH), 7.80-7.90 (8H, m, ArH), 7.37-7.43 (8H, m, ArH), 3.44 (12H, br, $-\text{OCH}_3$), 2.56 (6.32H, s, CH_3OH), 0.21 (2.13H, s, CH_3OH). Anal. Calcd for $\text{C}_{60}\text{H}_{40}\text{N}_8\text{O}_4\text{Zn} \cdot 2\text{CH}_3\text{OH} \cdot 1.5\text{H}_2\text{O}$: C, 68.10; H, 4.70; N, 10.25. Found: C, 68.03; H, 4.46; N, 10.36.

Synthesis of the Cu(II) phthalocyanine complex. 7 mL of the methanol solution containing 0.052 g of copper(II) acetate (0.26 mmol) was added to the chloroform solution (20 mL) of 0.022 g of the phthalocyanine (23 μ mol) and the mixture was heated to 60 ° C under argon atmosphere for 2 hours. The solvent was evaporated to dryness. The obtained solid was purified by silica gel column chromatography eluting with dichloromethane

containing 20% hexane. The main band was collected, and the product was recrystallized from the mixture of chloroform and methanol (1:1) to obtain fine blue-purple crystals (0.020 g, 20 μ mol, 87%). Anal. Calcd for $C_{60}H_{40}N_8O_4Cu \cdot H_2O$: C, 70.75; H, 4.16; N, 11.00. Found: C, 70.92; H, 4.09; N, 11.01.