Supplementary Information

Structure Dependence of Intramolecular Electron Transfer Reactions of Simple Dyads of Zinc(II) Porphyrin Complex Bearing a Peripheral Bipyridine Moiety

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Supplementary Information

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Table S1. UV-visible absorption spectral data of the dyads in methanol.

Dyad	λ_{max} / nm (log (ε / M^{-1} cm^{-1}))		
1	421.6 (5.813)	557.0 (4.314)	596.4 (3.928)
2	421.4 (5.846)	556.0 (4.350)	596.0 (3.965)
3	421.4 (5.798)	556.4 (4.305)	595.6 (3.927)
4	421.4 (5.818)	556.8 (4.320)	596.6 (3.936)
5	421.4 (5.756)	556.4 (4.305)	595.6 (3.942)
6	421.8 (5.800)	556.2 (4.305)	596.0 (3.939)
7	422.0 (5.793)	556.8 (4.299)	596.8 (3.945)

Table S2. Quantum yield, Φ_f, for the fluorescence of the dyads in methanol, and the estimated values of the rate constant of the photoinduced intramolecular electron transfer reaction at the S_1 excited state, $k_{PIET(S1)}$.

Dyad	Φ_f	$k_{PIET(S1)}$ / s^{-1}
1	3.55×10^{-2}	1.0×10^{10}
2	3.43×10^{-2}	1.3×10^{9}
3	3.67×10^{-2}	1.1×10^{9}
4	3.55×10^{-2}	6.6×10^{8}
5	3.19×10^{-2}	1.3×10^{10}
6	3.84×10^{-2}	1.8×10^{9}
7	3.79×10^{-2}	3.9×10^{8}

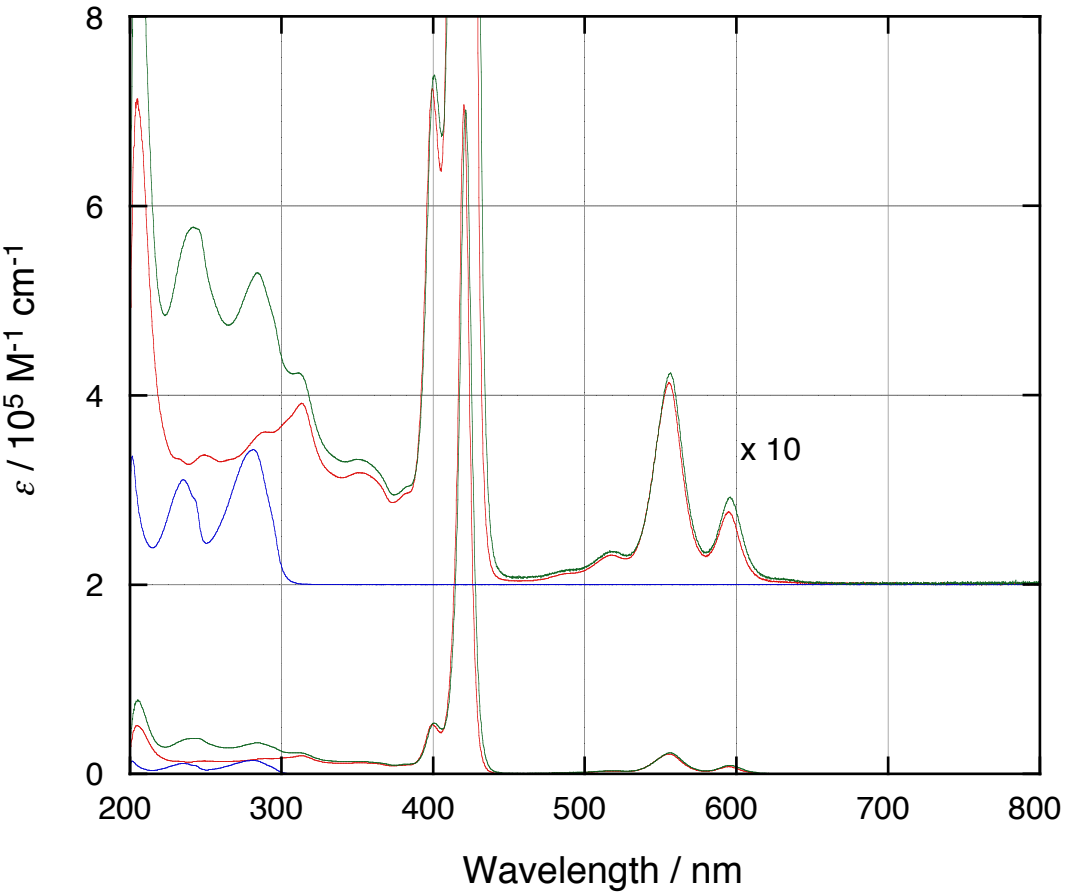

Figure S1. UV-visible absorption spectra of [Zn(TPP)] (red line), [Zn(TPP-NHCO-CH_2-bpy)] (green line), and 2,2'-bipyridine (blue line) in methanol.

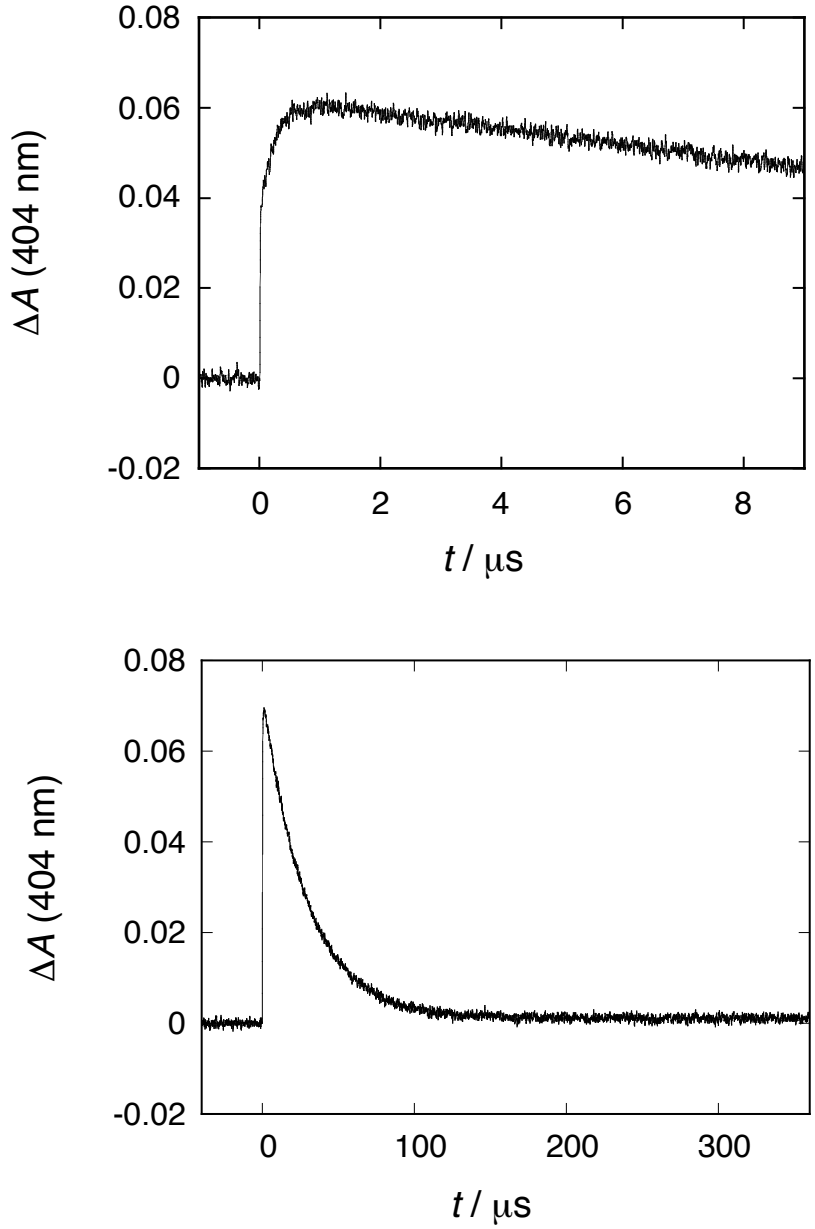

Figure S2. Time dependence of the absorbance change accompanying the photoexcitation of the methanol solution of **2**. $\lambda = 404$ nm. [**2**] = 1.64×10^{-6} M. [Cu^{2+}] = 1.42×10^{-4} M. $T = 298.2$ K.

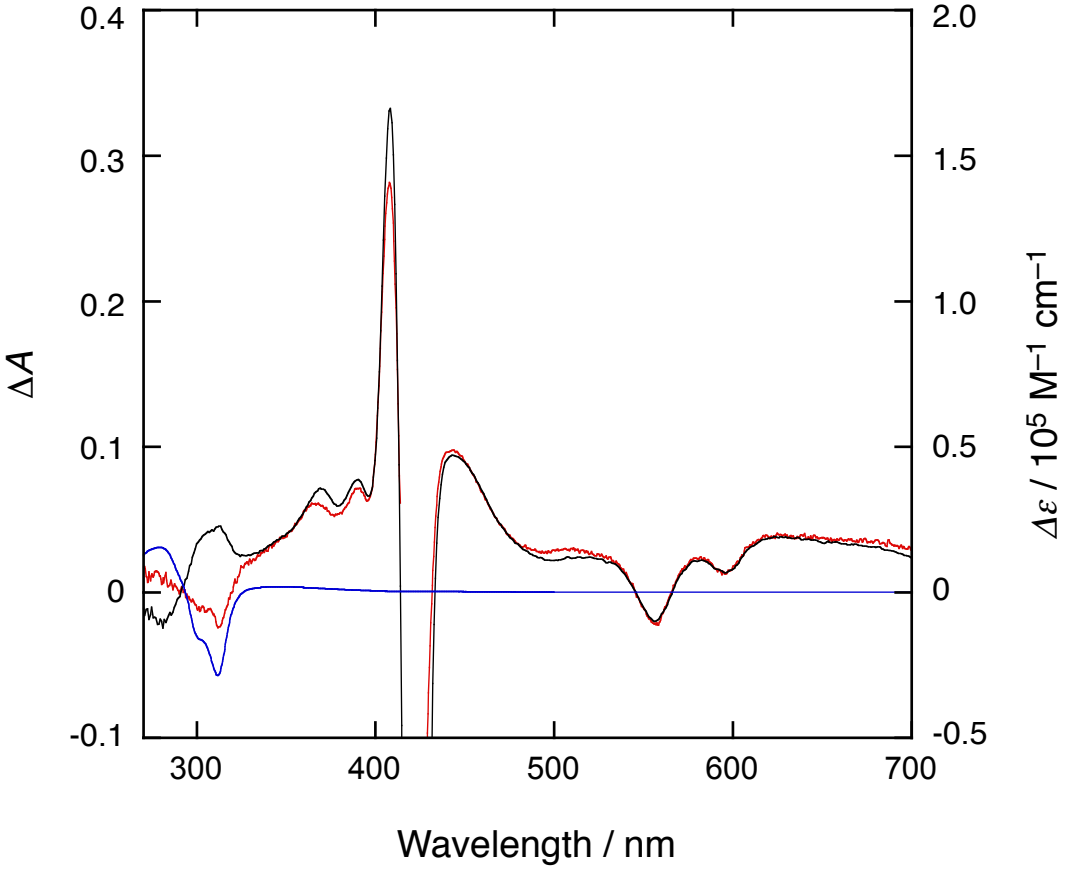

Figure S3. Comparison of the transient absorption spectrum observed at 1 μs after a laser irradiation for the methanol solution of [Zn(TPP-NHCO-CH_2-bpy)] (**2**) in the presence of Cu^{2+} (red line) with the difference between the spectrum of the π-radical cation of **2** and that of **2** in acetonitrile (black line). The π-radical cation of **2** was produced by the reaction of **2** with Cu^{2+} in acetonitrile. Spectrum shown in blue line is the sum of two difference spectra; one is the difference spectrum between Cu(I)-bpy (1:1 ratio) complex and Cu(II)-bpy complex (1:1 ratio), and another is that between 2,2'-bipyridine and Cu(II)-bpy complex (1:1 ratio) (See Figure S4).

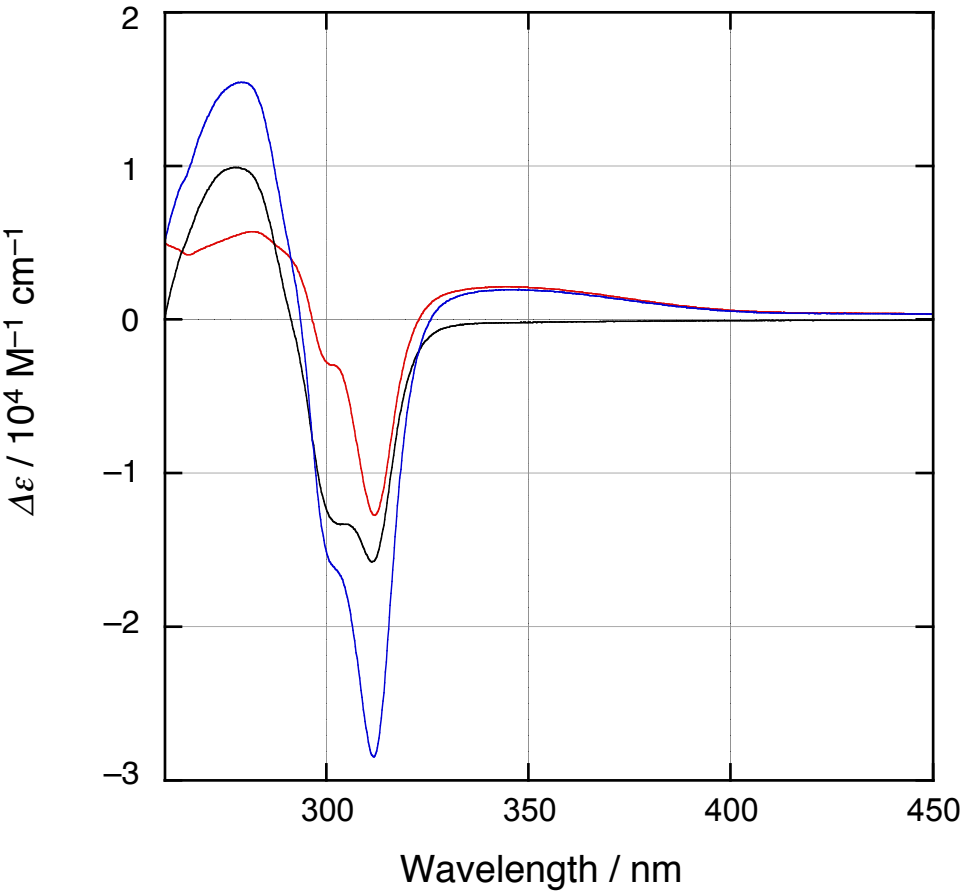

Figure S4. The difference spectrum between Cu(I)-bpy complex (1:1 ratio) and Cu(II)-bpy complex (1:1 ratio) and that 2,2'-bipyridine and Cu(II)-bpy complex (1:1 ratio) are shown by red and black lines, respectively. The spectrum shown by a blue line is the sum of these two spectra. The transient absorption spectrum of **2** shown by a red line in Figure S3 is a difference between [Zn($TPP^{+\bullet}$-NHCO-CH_2-bpy•Cu^{+})] and [Zn(TPP-NHCO-CH_2-bpy•Cu^{2+})], and the difference spectrum shown by a black line in Figure S3 is that between [Zn($TPP^{+\bullet}$-NHCO-CH_2-bpy•Cu^{2+})] and [Zn(TPP-NHCO-CH_2-bpy)]. The difference between these two spectra in the UV-region corresponds to the above spectrum shown by a blue line.

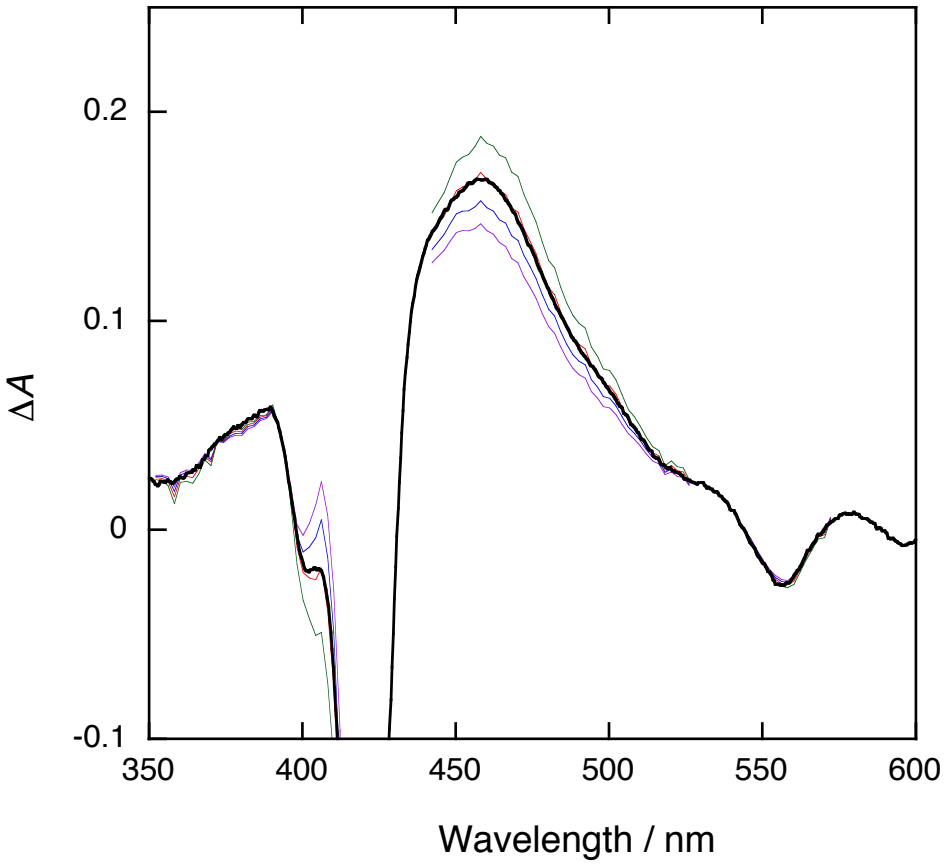

Figure S5. Simulated transient absorption spectrum of the species A_1 in the case of **4**. Purple, blue, red, and green lines correspond to the initial conditions where the intermediate observed just after a laser irradiation consisting of 100%, 90%, 80%, and 70% of A_1, respectively. The transient absorption spectrum of the T_1 excited state of **4** is shown by the black line. These findings indicate that 20% of the S_1 excited state undergoes the intramolecular electron transfer to give the charge-separated state and the rest changes to the T_1 excited state via an intersystem crossing during irradiation by a 5-ns pulse laser.

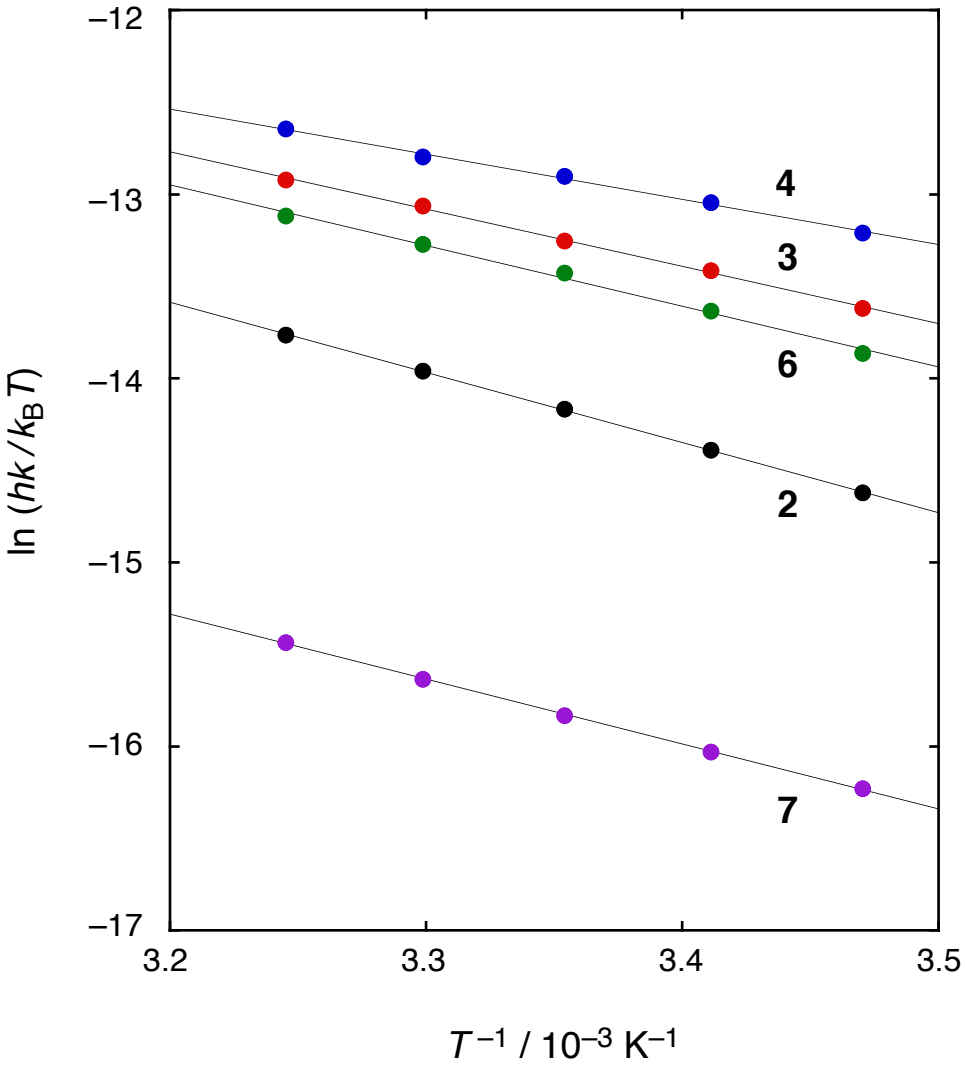

Figure S6. Temperature dependence of the rate constant for the intramolecular electron transfer reaction in the T_1 excited state.

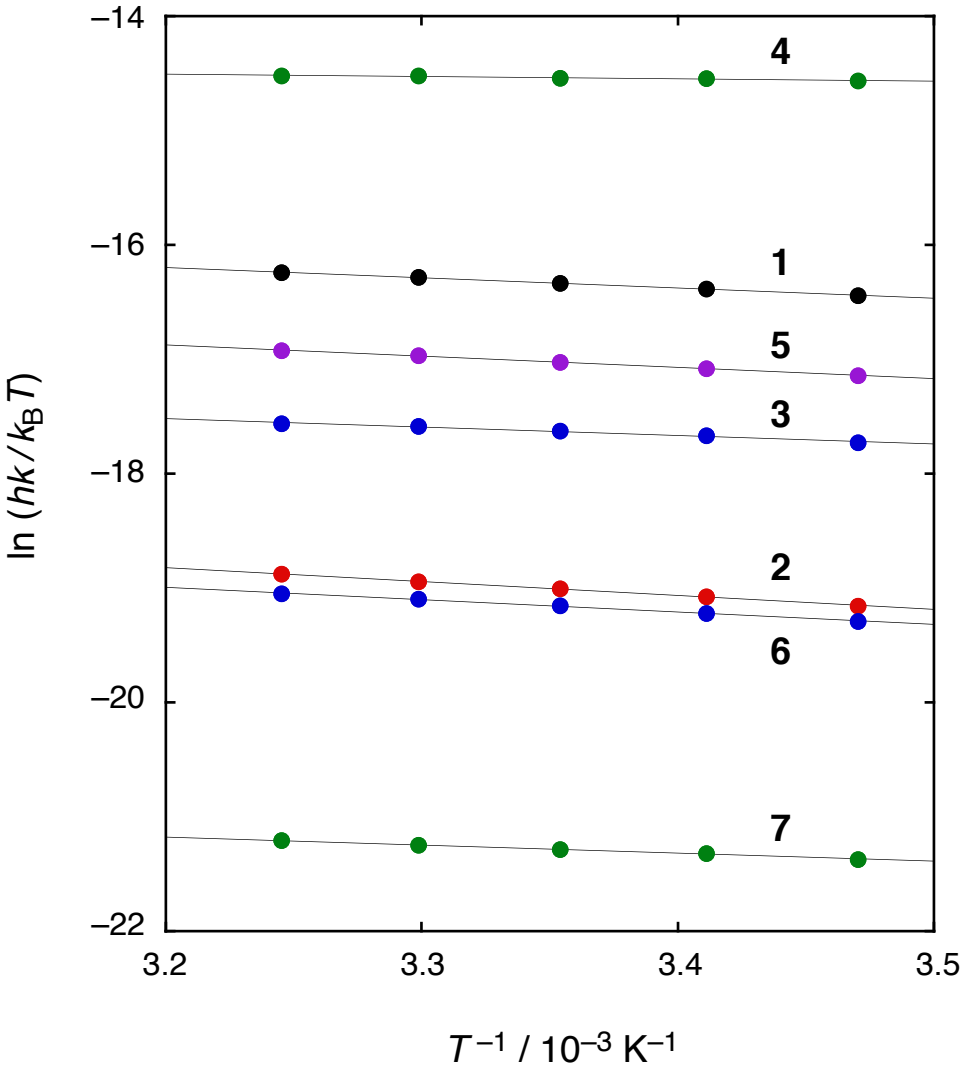

Figure S7. Temperature dependence of the rate constant for the charge recombination reaction.

Synthesis

Synthesis of 2,2'-bipyridine-4-acetic acid 2,2'-Bipyridine-4-acetic acid was prepared by the following procedures. To a dry THF (40 cm^3) solution of 4-methyl-2,2'-bipyridine (1.86g, 10.9 mmol) was added a solution of 1.26 M LDA in dry THF 8.50 cm^3 at –78 °C under Ar. The mixture was stirred at –78 °C for 4 h. Dimethyl carbonate (1.00 cm^3, 11.9 mmol) was added to the mixture and stirred at –78 °C for 2 h, then stirred at room temperature for 14 h. The reaction mixture was treated with water and extracted with CH_2Cl_2. The organic phase was dried over magnesium sulfate. The solvent was evaporated to dryness, and the residue was purified by column chromatography on silica gel eluted with CH_2Cl_2 : acetone (3:1) to give methyl (2,2'-bipyridin-4-yl)acetate (1.76 g, 7.71 mmol, 70.7 %). To a methanol solution (20 cm^3) of methyl (2,2'-bipyridin-4-yl)acetate (1.76g) was added an aqueous solution (15 cm^3) of NaOH (0.191 g, 4.78 mmol), then stirred at 50 °C for 15 h. The solvent was removed, and the residue was washed with CH_2Cl_2. Reprecipitation from the mixture of ethanol and *n*-hexane gave the white product, which was dried under vacuum (0.890 g, 3.71 mmol, 77.6 %). Anal. Calcd for $C_{12}H_{9.4}N_2NaO_{2.2}$: C, 60.10; H, 3.95; N, 11.68. Found: C, 60.08; H, 4.17; N, 11.67. ^{1}H NMR (400 MHz, CD_3OD): δ 3.62 (s, 2H, CH2), 7.42 (m, 1H, H_5), 7.42 (ddd, 1H, $H_{5'}$, 7.5, 4.8, 1.3 Hz), 7.93 (ddd, 1H, $H_{4'}$, 8.0, 7.5, 1.8 Hz), 8.24 (ddd, 1H, $H_{3'}$, 8.0, 1.3, 1.00 Hz), 8.26 (m, 1H, H_3), 8.53 (d, 1H, H_6, 5.0 Hz), 8.65 (ddd, 1H, $H_{6'}$, 4.8, 1.8, 1.00 Hz).

Synthesis of the Porphyrin dyads Porphyrin dyads **2** - **7** were synthesized by the procedure similar to that of **1**, using 5-(4-aminophenyl)-10,15,20-triphenylporphyrin and corresponding carboxylic acid derivatives of 2,2'-bipyridine. The dyads synthesized in the present study contain various amounts of solvent molecules of crystallization, and the amount was confirmed based on the peak area of the ^{1}H NMR spectra of each solvent molecule except for H_2O molecule.

The dyad **2** was prepared by mixing 5-(4-aminophenyl)-10,15,20-triphenyl-porphyrin (0.153 g, 0.218 mmol), (2,2'-bipyridin-4-yl)acetic acid (0.076 g, 0.35 mmol), 2-chloro-1-methylpyridinium iodide (0.20 g, 0.78 mmol), and 4-dimethylaminopyridine (0.26 g, 2.1 mmol) in DMF (15 cm^3), and the mixture was heated at 80°C for 3 h under Ar. After cooling the reaction mixture, 15 cm^3 of dichloromethane was added and the mixture was washed with water for three times. The organic phase was dried using sodium sulphate and then the solvent was evaporated to dryness. The residue obtained was purified by column chromatography (silica gel) using dichloromethane containing 2 % methanol as an eluent. The compound obtained was recrystallized from the mixture of chloroform, ethanol, and *n*-hexane.

The resulting dark violet precipitate was collected by filtration and dried *in vacuo* (Yield: 40 %, 0.079 g). Anal. Calcd for $C_{56}H_{37}N_7OZn \cdot 2.2H_2O$: C, 72.40; H, 4.49; N, 10.55. Found: C, 72.36; H, 4.15; N, 10.33. ^{1}H NMR (400 MHz, DMF-d_7): δ 4.12 (2H, s, bridging CH_2); 7.51 (1H, dd, *J* = 7.9, 4.9 Hz, bpy-4'H); 7.64 (1H, d, *J* = 5.2 Hz, bpy-5H); 7.82-7.85 (9H, m, *m*-, *p*-phenyl); 8.02 (1H, t, *J* = 7.9 Hz, bpy-5'H); 8.19 (2H, d, *J* = 8.4 Hz, *o*-phenyl); 8.22 (2H, d, *J* = 8.4 Hz, *m*-phenyl); 8.26-8.29 (6H, m, *o*-phenyl); 8.54 (1H, d, *J* = 7.9 Hz, bpy-6'H); 8.68 (1H, s, bpy-3H); 8.75 (1H, d, *J* = 5.2 Hz, bpy-6H); 8.78 (1H, d, *J* = 4.9 Hz, bpy-3'H); 8.86 (2H, d, *J* = 4.8 Hz, pyrrole); 8.87 (4H, s, pyrrole); 8.94 (2H, d, *J* = 4.8 Hz, pyrrole); 10.90 (1H, s, -NHCO-).

The dyad **3** was prepared by mixing 5-(4-aminophenyl)-10,15,20-triphenyl-porphyrin (0.025 g, 0.036 mmol), 3-(2,2'-bipyridin-4-yl)propionic acid (0.020 g, 0.086 mmol), 2-chloro-1-methylpyridinium iodide (0.036 g, 0.14 mmol), and 4-dimethylaminopyridine (0.044 g, 0.36 mmol) in DMF (5 cm^3), and the mixture was heated at 80°C for 3 h under Ar. After cooling the reaction mixture, 5 cm^3 of dichloromethane was added and the mixture was washed with water for three times. The organic phase was dried using sodium sulphate and then the solvent was evaporated to dryness. The residue obtained was purified by column chromatography (silica gel) using dichloromethane containing 5 % methanol as an eluent. The compound obtained was recrystallized from the mixture of chloroform, dichloromethane, methanol, and *n*-hexane. The resulting dark violet precipitate was collected by filtration and dried *in vacuo* (Yield: 59 %, 0.026 g). Anal. Calcd for $C_{57}H_{39}N_7OZn \cdot 1.1CH_3OH \cdot 0.4CH_2Cl_2$: C, 72.24; H, 4.58; N, 10.08. Found: C, 72.43; H, 4.75; N, 10.18. ^{1}H NMR (400 MHz, DMF-d_7): δ 3.05 (2H, t, *J* = 7.8 Hz, bridging CH_2); 3.29 (2H, t, *J* = 7.8 Hz, bridging CH_2); 7.50 (1H, dd, *J* = 7.9, 4.8 Hz, bpy-4'H); 7.52 (1H, d, *J* = 5.0 Hz, bpy-5H); 7.82-7.86 (9H, m, *m*-, *p*-phenyl); 8.01 (1H, t, *J* = 7.9 Hz, bpy-5'H); 8.16 (2H, d, *J* = 8.8 Hz, *o*-phenyl); 8.20 (2H, d, *J* = 8.8 Hz, *m*-phenyl); 8.26-8.30 (6H, m, *o*-phenyl); 8.52 (1H, d, *J* = 7.9 Hz, bpy-6'H); 8.54 (1H, s, bpy-3H); 8.69 (1H, d, *J* = 5.0 Hz, bpy-6H); 8.78 (1H, d, *J* = 4.8 Hz, bpy-3'H); 8.87 (2H, d, *J* = 4.8 Hz, pyrrole); 8.87 (4H, s, pyrrole); 8.93 (2H, d, *J* = 4.8 Hz, pyrrole); 10.53 (1H, s, -NHCO-).

The dyad **4** was prepared by mixing 5-(4-aminophenyl)-10,15,20-triphenyl-porphyrin (0.101 g, 0.146 mmol), 4-(2,2'-bipyridin-4-yl)butanonic acid (0.070 g, 0.29 mmol), 2-chloro-1-methylpyridinium iodide (0.14 g, 0.54 mmol) and 4-dimethylaminopyridine (0.18 g, 1.4 mmol) in DMF (10 cm^3), and the mixture was heated at 80°C for 3 h under Ar. After cooling the reaction mixture, 10 cm^3 of dichloromethane was added and the mixture was washed with water for three times. The organic phase was dried using sodium sulphate and

then the solvent was evaporated to dryness. The residue obtained was purified by column chromatography (silica gel) using dichloromethane containing 5 % methanol as an eluent. The compound obtained was recrystallized from the mixture of chloroform, DMF, and *n*-hexane. The resulting dark violet precipitate was collected by filtration and dried *in vacuo* (Yield: 73 %, 0.098 g). Anal. Calcd for $C_{58}H_{41}N_7OZn \cdot 1.3DMF \cdot 0.3CHCl_3 \cdot 2H_2O$: C, 68.90; H, 5.06; N, 10.72. Found: C, 68.88; H, 4.91; N, 10.65. ^{1}H NMR (400 MHz, DMF-d_7): δ 2.24 (2H, quintet, J = 7.6 Hz, bridging CH_2); 2.69 (2H, t, J = 7.6 Hz, bridging CH_2); 2.96 (2H, t, J = 7.6 Hz, bridging CH_2); 7.46 (1H, d, J = 4.8 Hz, bpy-5H); 7.49 (1H, dd, J = 7.9, 4.6 Hz, bpy-4'H); 7.82-7.86 (9H, m, *m*-, *p*-phenyl); 8.01 (1H, t, J = 7.9 Hz, bpy-5'H); 8.18 (2H, d, J = 8.8 Hz, *o*-phenyl); 8.21 (2H, d, J = 8.8 Hz, *m*-phenyl); 8.26-8.30 (6H, m, *o*-phenyl); 8.47 (1H, s, bpy-3H); 8.52 (1H, d, J = 7.9 Hz, bpy-6'H); 8.68 (1H, d, J = 4.8 Hz, bpy-6H); 8.77 (1H, d, J = 4.6 Hz, bpy-3'H); 8.87 (4H, s, pyrrole); 8.87 (2H, d, J = 4.8 Hz, pyrrole); 8.95 (2H, d, J = 4.8 Hz, pyrrole); 10.46 (1H, s, -NHCO-).

The dyad **5** was prepared by mixing 5-(4-aminophenyl)-10,15,20-triphenyl-porphyrin (0.050 g, 0.072 mmol), (E)-3-(2,2'-bipyridin-4-yl)acrylic acid (0.070 g, 0.28 mmol), 2-chloro-1-methylpyridinium iodide (0.036 g, 0.14 mmol), and 4-dimethylaminopyridine (0.087 g, 0.71 mmol) in DMF (5 cm^3), and the mixture was heated at 80°C for 3 h under Ar. After cooling the reaction mixture, 5 cm^3 of dichloromethane was added and the mixture was washed with water for three times. The organic phase was dried using sodium sulphate and then the solvent was evaporated to dryness. The residue obtained was purified by column chromatography (silica gel) using dichloromethane containing 5 % methanol as an eluent. The compound obtained was recrystallized from the mixture of dichloromethane, methanol, and *n*-hexane. The resulting dark violet precipitate was collected by filtration and dried *in vacuo* (Yield: 76 %, 0.049 g). Anal. Calcd for $C_{57}H_{37}N_7OZn \cdot 0.2C_6H_{14} \cdot 0.4CH_3OH \cdot 0.1CH_2Cl_2 \cdot 0.3DMF \cdot 2H_2O$: C, 71.74; H, 4.82; N, 10.25. Found: C, 71.71; H, 4.73; N, 9.97. ^{1}H NMR (400 MHz, DMF-d_7): δ 7.51 (1H, d, J = 16.0 Hz, bridging C_2H_2); 7.56 (1H, dd, J = 7.7, 4.8 Hz, bpy-4'H); 7.77 (1H, d, J = 4.8 Hz, bpy-5H); 7.83-7.86 (9H, m, *m*-, *p*-phenyl); 7.92 (1H, d, J = 16.0 Hz, bridging C_2H_2); 8.06 (1H, t, J = 7.7 Hz, bpy-5'H); 8.27-8.35 (10H, m, *o*-phenyl (2H), *m*-phenyl (2H), *o*-phenyl (6H)); 8.55 (1H, d, J = 7.7 Hz, bpy-6'H); 8.80 (1H, s, bpy-3H); 8.837 (1H, d, J = 4.8 Hz, bpy-3'H); 8.85 (1H, d, J = 4.8 Hz, bpy-6H); 8.88 (4H, s, pyrrole); 8.89 (2H, d, J = 4.8 Hz, pyrrole); 8.98 (2H, d, J = 4.8 Hz, pyrrole); 10.98 (1H, s, -NHCO-).

The dyad **6** was prepared by mixing 5-(4-aminophenyl)-10,15,20-triphenyl-porphyrin (0.100 g, 0.145 mmol), 4-(2,2'-bipyridin-4-yl)benzoic acid (0.077 g, 0.28 mmol), 2-chloro-1-methylpyridinium iodide (0.15 g, 0.57 mmol), and 4-dimethylaminopyridine (0.18

g, 0.15 mmol) in DMF (10 cm^3) , and the mixture was heated at 80°C for 3 h under Ar. After cooling the reaction mixture, 10 cm^3 of dichloromethane was added and the mixture was washed with water for three times. The organic phase was dried using sodium sulphate and then the solvent was evaporated to dryness. The residue obtained was purified by column chromatography (silica gel) using dichloromethane containing 5 % methanol as an eluent. The compound obtained was recrystallized from the mixture of chloroform and *n*-hexane. The resulting dark violet precipitate was collected by filtration and dried *in vacuo* (Yield: 86 %, 0.118 g). Anal. Calcd for $C_{61}H_{39}N_7OZn \cdot 0.2C_6H_{14} \cdot 0.1CH_3OH \cdot 0.5H_2O$: C, 76.29; H, 4.44; N, 10.00. Found: C, 76.38; H, 4.29; N, 9.93. ^{1}H NMR (400 MHz, DMF-d_7): δ 7.55 (1H, dd, *J* = 7.5, 4.2 Hz, bpy-4'H); 7.83-7.87 (9H, m, *m*-, *p*-phenyl); 7.97 (1H, d, *J* = 5.6 Hz, bpy-5H); 8.06 (1H, t, *J* = 7.5 Hz, bpy-5'H); 8.20 (2H, d, *o*- or *m*-phenyl (2H)); 8.27-8.33 (8H, m, *o*-phenyl (6H) and *o*- or *m*-phenyl (2H)); 8.45 (4H, d, *o*- or *m*-phenyl (2H) and *o*- or *m*-phenyl (2H)); 8.58 (1H, d, *J* = 7.5 Hz, bpy-6'H); 8.87 (1H, d, *J* = 4.2 Hz, bpy-3'H); 8.87-8.91 (6H, m, pyrrole (4H), bpy-3H, and bpy-6H); 8.90 (2H, d, *J* = 4.4 Hz, pyrrole); 9.00 (2H, d, *J* = 4.4 Hz, pyrrole); 10.91 (1H, s, -NHCO-).

The dyad **7** was prepared by mixing 5-(4-aminophenyl)-10,15,20-triphenyl-porphyrin (0.104 g, 0.150 mmol), 4'-(2,2'-bipyridin-4-yl)-4-biphenylcarboxylic acid (0.101 g, 0.287 mmol), 2-chloro-1-methylpyridinium iodide (0.15 g, 0.57 mmol), and 4-dimethylaminopyridine (0.18 g, 0.15 mmol) in DMF (10 cm^3), and the mixture was heated at 100°C for 3 h under Ar. After cooling the reaction mixture, 10 cm^3 of dichloromethane was added and the mixture was washed with water for four times. The organic phase was dried using sodium sulphate and then the solvent was evaporated to dryness. The residue obtained was purified by column chromatography (silica gel) using dichloromethane containing 3 % methanol as an eluent. The compound obtained was recrystallized from the mixture of DMF and methanol. The resulting dark violet precipitate was collected by filtration, washed with chloroform and *n*-hexane, and dried *in vacuo* (Yield: 54 %, 0.084 g). Anal. Calcd for $C_{67}H_{43}N_7OZn \cdot 0.5H_2O \cdot 0.2C_6H_{14}$: C, 77.73; H, 4.48; N, 9.30. Found: C, 77.58; H, 4.58; N, 9.15. ^{1}H NMR (400 MHz, DMF-d_7): δ 7.55 (1H, dd, *J* = 7.6, 4.3 Hz, bpy-4'H); 7.84-7.87 (9H, m, *m*-, *p*-phenyl); 7.94 (1H, d, *J* = 5.0 Hz, bpy-5H); 8.06 (1H, t, *J* = 7.6 Hz, bpy-5'H); 8.08-8.16 (6H, m, bridging biphenyl); 8.27-8.32 (8H, m, *o*-phenyl); 8.40 (2H, d, *J* = 8.4 Hz, bridging biphenyl); 8.45 (2H, d, *J* = 8.4 Hz, *m*-phenyl); 8.57 (1H, d, *J* = 7.6 Hz, bpy-6'H); 8.81 (1H, d, *J* = 4.3 Hz, bpy-3'H); 8.85 (1H, d, *J* = 5.0 Hz, bpy-6H); 8.88 (4H, s, pyrrole); 8.89 (1H, s, bpy-3H); 8.90 (2H, d, *J* = 5.2 Hz, pyrrole); 9.01 (2H, d, *J* = 5.2 Hz, pyrrole); 10.86 (1H, s, -NHCO-).