

**Excitation energy flow control in
{Ru(2,2'-bipyridine)₂}-{pyridylporphyrin}₂ system**

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Electronic supplementary information

Experimental details

Table 1

Figures S1-S3

Experimental details.

Materials. Reagents were purchased from WAKO, Dojin, and Aldrich. All reagents were used without further purification unless noted. The ruthenium complex $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})_2](\text{PF}_6)_2^1$ and H_2PyP^2 have been prepared according to literature procedures. Tetra-*n*-butylammonium hexafluorophosphate, $[\text{n-Bu}_4\text{N}]\text{PF}_6$, was recrystallized twice from ethanol. Solvents for the electrochemical measurements were distilled from calcium hydride under argon. For the photophysical measurements, spectrograde solvents (Dojin) were used.

Preparation of $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{PyP})_2](\text{PF}_6)_2$ (1:2-H₂). The acetonitrile complex, $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ (50.0 mg, 0.064 mmol) and H_2PyP (90.0 mg, 0.137 mmol) were dissolved in 90 cm³ of chlorobenzene. The mixture was refluxed for 48 h under argon, and then cooled to room temperature. Purple precipitate was collected by filtration. This procedure affords analytical pure complex. For the spectral measurements recrystallized samples (acetone/H₂O) were used. Yield: 49.3 mg (38 %). Found: C, 66.38; H, 4.44; N, 9.44 %. Calcd. for $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{PyP})_2](\text{PF}_6)_2$: C, 66.63; H, 4.29; N, 9.71 %. FAB MS: $m/z = 2019$. ¹H NMR (δ , acetone-d₆) (ppm): 10.07 (d, 2H, bpy), 9.53 (d, 4H, py), 9.03 (d, 2H, bpy), 8.90 (d, 4H, β), 8.90 (d, 8H, β), 8.85 (d, 2H, bpy), 8.66 (br, 4H, β), 8.62 (d, 2H, bpy), 8.57 (t, 2H, bpy), 8.46 (d, 4H, py), 8.26 (t, 2H \times 2, bpy), 8.12 (d, 6H, tol), 8.06 (d, 6H, tol), 7.73 (t, 2H, bpy), 7.66 (d, 6H, tol), 7.61 (d, 6H, tol), 2.70 (s, 6H, tol), 2.66 (d, 12H, tol), -2.84 (s, 4H, por-NH).

Preparation of $[\text{Ru}(\text{bpy})_2(\text{ZnPyP})_2](\text{PF}_6)_2$ (1:2-Zn). The free base porphyrin complex, **1:2-H₂** (36.1 mg, 0.018 mmol) and excess zinc(II) acetate dihydrate (15.4 mg, 0.070 mmol) were dissolved in an acetone/H₂O (5:1 v/v, 60 ml) mixed solvent and stirred for 4 h at room temperature. The solution was concentrated to remove acetone and then precipitated the crude product. The crude product was filtered and

recrystallized from acetone/H₂O. Yield: 28.5 mg (76.7 %). Found: C, 59.65; H, 4.09; N, 8.56 %. Calcd. for [Ru(bpy)₂(ZnPyP)₂](PF₆)₂·6H₂O: C, 59.69; H, 4.20; N, 8.70 %. ¹H NMR (δ, acetone-d₆) (ppm): 10.07 (d, 2H, bpy), 9.45 (d, 4H, py), 9.03 (d, 2H, bpy), 8.91 (d, 2H, bpy), 8.84–8.90 (m, 12H, β), 8.72 (d, 4H, β), 8.66 (d, 2H, bpy), 8.57 (t, 2H, bpy), 8.39 (d, 4H, py), 8.26 (d, 4H, bpy×2), 8.07, 8.03 (d, 12H, tol), 7.61, 7.57 (d, 12H, tol), 2.70 (s, 6H, tol), 2.66 (s, 12H, tol).

Measurements. UV-visible absorption spectra were recorded on Hitachi U3000 spectrophotometers. ¹H NMR spectra were measured at room temperature with a JEOL JNM-EX270 spectrometer. Cyclic voltammograms were measured with a HOKUTO HZ-300 cyclic voltammetric analyzer at a scan rate of 100 mV/s. The working and counter electrodes were a platinum disk and a platinum wire, respectively. For the measurements, the sample solutions (ca. 0.001 M) in 0.1 M [*n*-Bu₄N]PF₆-CH₂Cl₂ were deoxygenated with a stream of argon gas. The reference electrode was Ag/AgCl against which the half-wave potential E_{1/2} of Fc⁺/Fc was 0.43 V. All values of redox potentials were referred to Ag/AgCl. For the measurement of emissive properties, the solutions were deoxygenated by purging with an argon gas stream for 15 min and sealed before the measurements. The emission and excitation spectra at room temperature were recorded on JASCO FP-6600 spectrofluorometer. The emission spectra and time-resolved emission spectra at 77 K were measured by using a multichannel photodetector (Hamamatsu, PMA-11) and a streak camera (Hamamatsu Photonics, C4334), respectively. Temperature of the solutions was controlled within ±1 °C by using a liquid N₂ cryostat (Oxford instruments, MODEL NO.010200). The laser flash at 400 nm was obtained from an Ti:sapphire laser (Coherent, Mira Model 900-F) for measurement of **1:2-H₂** and the laser flashes at 420 and 450 nm were obtained from an OPO laser (LOTIS TII, LT-2214/M) pumped by a Nd:YAG laser (355 nm, LOTIS TII, LS-2137/3) for **1:2-Zn**.

1. G. M. Brown, R. W. Callahan and T. J. Meyer, *Inorg. Chem.*, **1975**, *14*, 1915.
2. E. B. Fleischer and A. M. Shachter, *Inorg. Chem.*, **1991**, *30*, 3763.

Table S1 Oxidation and reduction potentials of the complexes in CH₂Cl₂. (/ V vs. Ag/AgCl)

Complexes	Ru component		Porphyrin component			
	Ru ^{II/III} (ΔE _p)	L ^{0/-} (ΔE _p)	Por ^{0/+} (ΔE _p)	Por ⁺²⁺ (ΔE _p)	Por ^{-/0} (ΔE _p)	Por ^{2-/-} (ΔE _p)
1:2-H₂	+1.47 (0.18)	-1.32 (0.09)	+1.02 (0.10)	+1.31 (0.12)	-1.12 (0.09)	-1.58 (0.08)
1:2-Zn	+1.46 (0.18)	-1.32 (0.10)	+0.83 (0.11)	+1.13 (0.11)	<-1.3	
[Ru(bpy) ₂ (py) ₂] (PF ₆) ₂	+1.41 (0.10)	-1.28 (0.08)				
H ₂ PyP			+1.00 (0.07)	+1.25 (0.06)	-1.21 (0.11)	-1.52 (0.10)

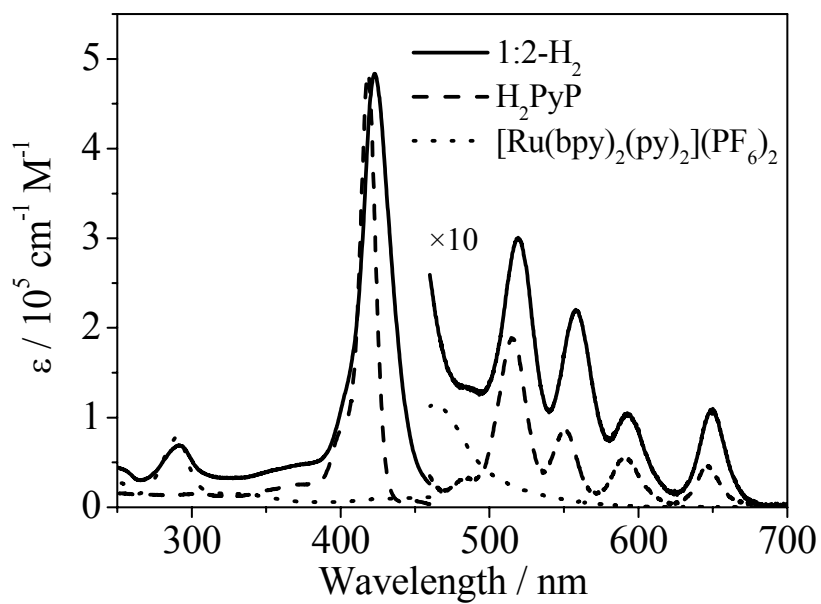


Fig. S1 UV-vis absorption spectra of **1:2-H₂** (solid line) and its component, H₂PyP (dashed line) and [Ru(bpy)₂(pyridine)₂](PF₆)₂ (dotted line) in CH₂Cl₂ at room temperature.

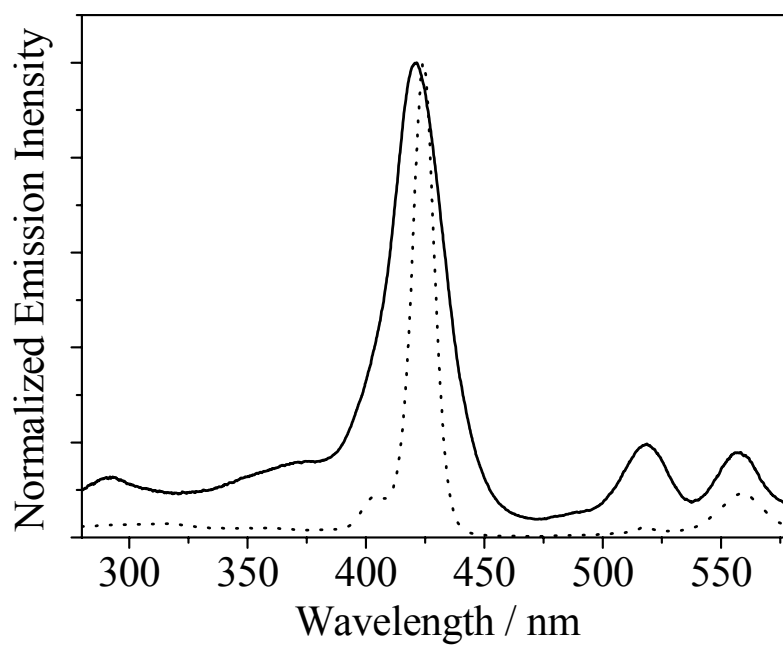


Fig. S2 Excitation spectra of **1:2-H₂** (solid line, $\lambda_{em} = 650$ nm) and **1:2-Zn** (dotted line, $\lambda_{em} = 610$ nm) in EtOH at room temperature.

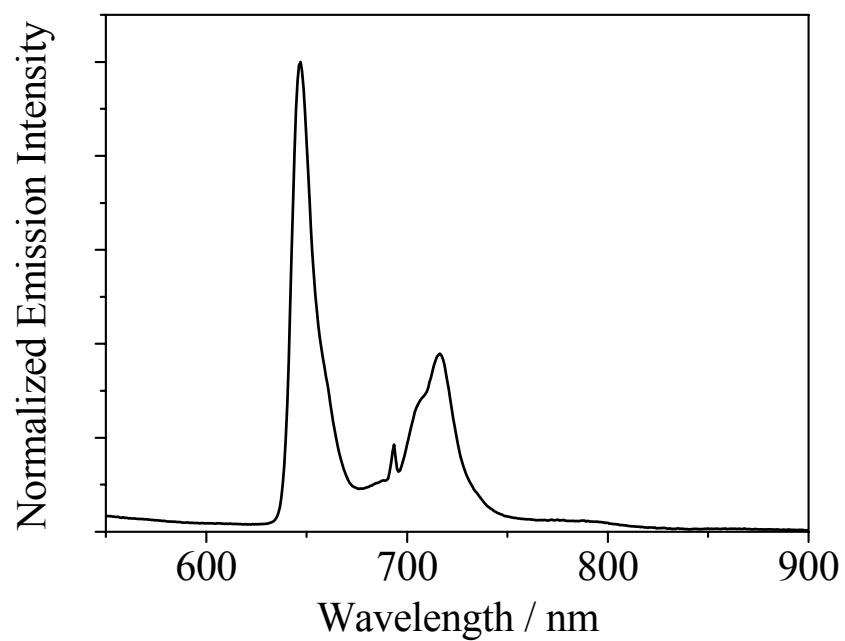


Fig. S3 Emission spectrum of **1:2-H₂** at 77 K in EtOH/MeOH = 4:1. The excitation wavelength is 400 nm. The small and sharp band at 690 nm is derived from scattered light.