

# Direct observation of the ultrafast energy transfer in a porphyrin and ruthenium dyad

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The luminescence dynamics of a polypyridyl ruthenium II  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  and 5,10,15,20-tetraphenylporphyrin ( $\text{H}_2\text{TPP}$ ) dyad have been measured by using time-resolved fluorescence spectroscopy. The transient luminescent spectra of the dyad show an ultrafast energy transfer within 300 ps after photoexcitation of the  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  at 453 nm. However, no energy transfer has been observed as the excitation wavelength is 400 nm, corresponding to the absorption peak of  $\text{H}_2\text{TPP}$ . The origin of the energy transfer from  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  to  $\text{H}_2\text{TPP}$  has been analyzed according to the Förster energy-transfer theory.

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The organic donor-bridge-acceptor (DBA) dyads have attracted much attention in recent years because of their potential application in the nano-molecular devices<sup>[1,2]</sup>. In these systems, the electron and energy transfer from D to A is dominant to decide the device performance<sup>[2-10]</sup>. Ultrafast dynamics have been widely studied by using ultrafast fluorescence spectroscopy<sup>[11-13]</sup>. Porphyrin and ruthenium are usually used as the model molecules to investigate the electron and energy transfer processes in these DBA systems<sup>[14-16]</sup>. Flamigni *et al.* studied the electron transfer in  $\text{PH}_2\text{-Ru}$  and  $\text{PZn-Ru}$  dyads. They estimated the electron transfer rate (about  $10^{10} \text{ s}^{-1}$ ) from porphyrin to Ru complex by the measurement of the luminescence lifetime of the porphyrin<sup>[3]</sup>. Harriman *et al.* measured the transient luminescence in two kinds of  $\text{PZn-Ru}$  dyads<sup>[17]</sup>. By fitting the luminescence decays by a two-exponential function and calculating the energy transfer rate, they suggested that the energy transfer from ruthenium to porphyrin existed after the photoexcitation of ruthenium molecules. The energy transfer rate  $k_{\text{et}}$  was about  $10^7 \text{ s}^{-1}$ <sup>[17]</sup>. Up to now, the energy transfer rate  $k_{\text{et}}$  is usually estimated by measuring the luminescence lifetimes of the free donor and the donor in DBA systems<sup>[3,18,19]</sup>. However, this may be inaccurate if there is other mechanism of the luminescence quenching<sup>[20,21]</sup>. In this letter, we report our investigation of the energy transfer in a polypyridyl ruthenium (II) ( $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$ ) and porphyrin monomer: 5,10,15,20-tetraphenylporphyrin ( $\text{H}_2\text{TPP}$ ) dyad, by measuring the luminescence dynamics. The time resolved luminescence spectra show the ultrafast energy transfer within 300 ps after photoexcitation of the  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  at 453 nm. However, no energy transfer is observed as the excitation wavelength is 400 nm, corresponding to the absorption peak of  $\text{H}_2\text{TPP}$ . The origin of the energy transfer from  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  to  $\text{H}_2\text{TPP}$  has been analyzed according to the Förster energy-transfer theory.

The method of the synthesis of the  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$

and  $\text{H}_2\text{TPP}$  dyad has been previously reported<sup>[22,23]</sup>. The structure of the  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  and  $\text{H}_2\text{TPP}$  dyad linked by a butyl chain is shown in Fig. 1. The sample solution in  $\text{CH}_2\text{Cl}_2$  was contained in a quartz cell with 1-mm thickness. The concentration was about  $2 \mu\text{mol/L}$ . The transient luminescence was measured by using the time-resolved fluorescence spectroscopy. The laser pulse was generated by a Nd:YAG laser (PL2143) and an optical parametric generation (OPG) system (PG401SH/DFG2-10) with a 22-ps pulse width, a repetition rate of 10 Hz, a pulse energy of  $160 \mu\text{J}$ , and a wavelength of 453 nm. The laser pulses selectively excited  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$ . The transient luminescences from the  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  and  $\text{H}_2\text{TPP}$  dyad through a pair of lenses and a spectrometer were recorded by a streak camera (Hamamatsu C1587), which has a resolution of 20 ps and a charge-coupled device (CCD, Hamamatsu C4742-95). The laser pulses from a Ti:sapphire laser (Spectra Physics) with a 130-fs pulse width, a power of  $17.5 \mu\text{W}$ , and a wavelength of 400 nm were used to excite  $\text{H}_2\text{TPP}$ . The emission from samples was recorded by a spectrometer (Hamamatsu C5094) and a streak camera (Hamamatsu C6860) with a resolution  $<5 \text{ ps}$  and a CCD (Hamamatsu C4742-95).

Figure 2 shows the absorption spectra of  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$ ,  $\text{H}_2\text{TPP}$ , and the dyad.

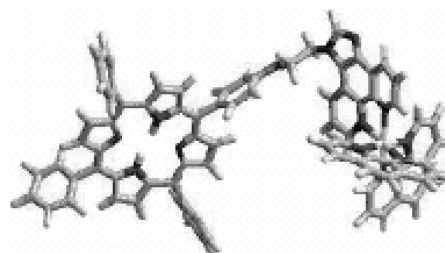


Fig. 1. Structure of the  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  and  $\text{H}_2\text{TPP}$  dyad.

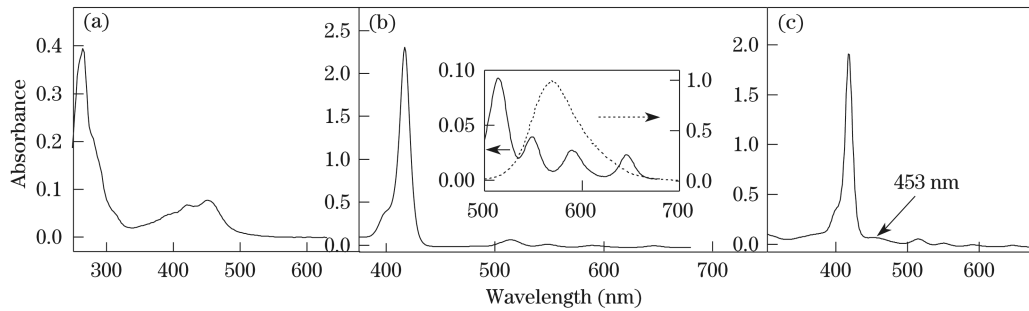


Fig. 2. Absorption spectra of (a)  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$ , (b)  $\text{H}_2\text{TPP}$ , and (c) the  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  and  $\text{H}_2\text{TPP}$  dyad. The inset of (b) shows the overlap of the  $\text{H}_2\text{TPP}$  absorption (solid line) and the  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  emission (dashed line).

$[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  shows a wide absorption peak at 453 nm, which is due to the metal-to-ligand charge-transfer (MLCT)<sup>[24,25]</sup>.  $\text{H}_2\text{TPP}$  exhibits a strong absorption at 417 nm (B band) and four weak peaks at 514, 549, 590, and 646 nm (Q band)<sup>[25]</sup>. The inset of Fig. 2(b) shows the overlap of the  $\text{H}_2\text{TPP}$  absorption spectra and the  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  emission spectra. The absorption spectrum of the  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  and  $\text{H}_2\text{TPP}$  dyad exhibits the linear addition of the absorptions of  $\text{H}_2\text{TPP}$  and  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$ , which indicates a weak interaction between the  $\text{H}_2\text{TPP}$  and  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  in the dyad<sup>[22]</sup>.

Figures 3(a) and (b) show the luminescence spectrum of a 1:1 molar mixture of  $\text{H}_2\text{TPP}$  and  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  and the time-integral luminescence spectrum of the  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  and  $\text{H}_2\text{TPP}$  dyad, respectively, excited at 453 nm. The mixture shows a strong luminescence at 575 nm from  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$ <sup>[24]</sup> and a weak peak at 650 nm from  $\text{H}_2\text{TPP}$ <sup>[18–25]</sup> due to its weak absorption at 453 nm<sup>[3]</sup>. However, the dyad exhibits a strong luminescence peak at 650 nm and a weaker peak at 575 nm. This suggests that the intramolecular energy transfer from  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  to  $\text{H}_2\text{TPP}$  occurs.

The transient emission spectra of the dyad after

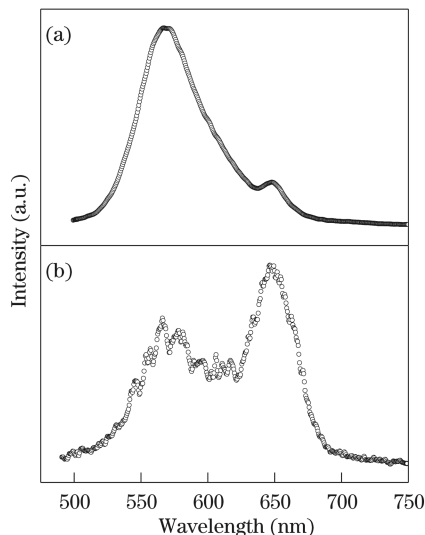


Fig. 3. (a) luminescence spectrum of a 1:1 molar mixture of  $\text{H}_2\text{TPP}$  and  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  and (b) time-integral luminescence spectrum of  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  and  $\text{H}_2\text{TPP}$  dyad excited at 453 nm.

photoexcitation of  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  at 453 nm are shown in Fig. 4(a). It is significant that at the initial delay time, the luminescence of the dyad is mainly from  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$ , while the luminescence from  $\text{H}_2\text{TPP}$  becomes more and more strong with the evolution of the delay time. At 0.29 ns, the luminescence of  $\text{H}_2\text{TPP}$  is significantly stronger than that of  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$ . Figure 4(b) shows the time evolutions of the transient luminescence of the dyad and the monomer  $\text{H}_2\text{TPP}$  at

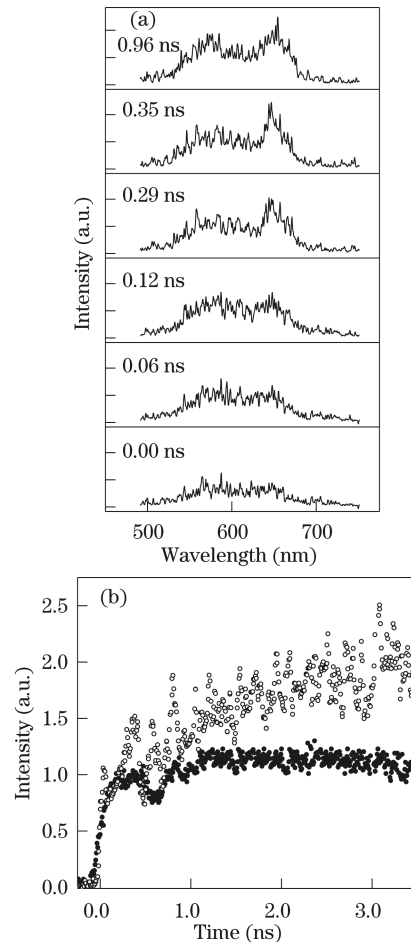


Fig. 4. (a) Transient emission spectra of the dyad excited at 453 nm and (b) luminescence decay of the  $[\text{Ru}(\text{phen})_2(\text{ip})]^{2+}$  and  $\text{H}_2\text{TPP}$  dyad (dots) and the  $\text{H}_2\text{TPP}$  monomer (circles) at 650 nm.

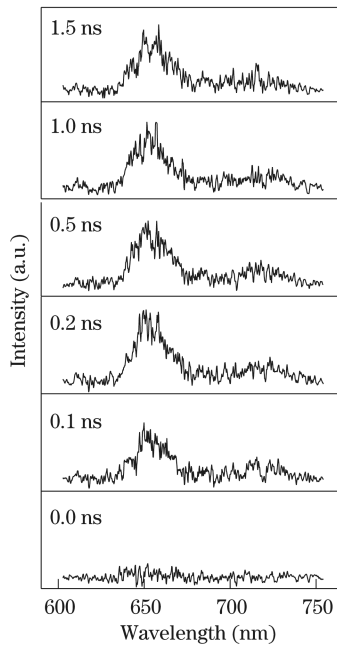


Fig. 5. Transient emission spectra of the dyad excited at 400 nm.

650 nm. The transient luminescence from H<sub>2</sub>TPP in the dyad is significantly enhanced due to the energy transfer from [Ru(phen)<sub>2</sub>(ip)]<sup>2+</sup> compared with the monomer. Figure 5 shows the transient luminescent spectra of the dyad as the excitation wavelength is 400 nm, which is the same as that of the monomer porphyrin molecule<sup>[24,25]</sup>, suggesting no energy transfer from H<sub>2</sub>TPP to [Ru(phen)<sub>2</sub>(ip)]<sup>2+</sup>.

Earlier studies have shown that the energy transfers in a DBA system is due to the short and long distance dipole-dipole interaction, which is well explained by the Dexter and the Förster theory<sup>[2]</sup>, while in a dyad with a flexible bridge, the energy transfer from D to A mainly arises from the Förster interaction<sup>[2,26]</sup>. We calculated the distance between the center of D and the center of A in H<sub>2</sub>TPP and [Ru(phen)<sub>2</sub>(ip)]<sup>2+</sup> dyad. The average and the lowest potential energy distances are 1.593 and 1.745 nm, respectively. Since the distance for the Dexter energy transfer is usually within 1 nm, the Dexter energy transfer in our DBA system can be neglected.

According to the Förster theory, energy transfer is usually due to the overlap of the luminescence spectra of D and the absorption spectra of A. In the [Ru(phen)<sub>2</sub>(ip)]<sup>2+</sup> and H<sub>2</sub>TPP dyad, the overlap of the [Ru(phen)<sub>2</sub>(ip)]<sup>2+</sup> emission spectra and the H<sub>2</sub>TPP absorption spectra is significant at about 575 nm, as shown in the inset of Fig. 2(b). We calculated the Förster energy transfer rate  $k_{et}$  according to

$$k_{et} = \frac{1}{\tau_D} \left( \frac{R_0}{R} \right)^6, \quad (1)$$

$$R_0^6 = \frac{9000 \ln(10) \phi_D \kappa^2}{128 \pi^6 n^4 N} \int_0^\infty dv \frac{f_D(v) \varepsilon_A(v)}{v^4}, \quad (2)$$

where  $\tau_D$  is the luminescence lifetime of the free donor, which is about 340 ns<sup>[27]</sup>;  $R$  is the distance between D

and A (we calculated the distance of about 1.593 nm based on the molecular dynamic modulation);  $R_0$  is the critical distance and can be calculated according to the spectrum overlap<sup>[28]</sup>. In Eq. (2),  $\phi_D$  is the donor fluorescence quantum yield;  $\kappa^2$  is the orientation factor (which is 2/3 for randomly distributed free donors and acceptors);  $n$  is the refractive index;  $N$  is the Avogadro's constant;  $v$  is the frequency in  $\text{cm}^{-1}$ ;  $f_D(v)$  is the donor fluorescence intensity normalized to unit area; and  $\varepsilon_A(v)$  is the molar extinction coefficient of the acceptor with the unit  $\text{L}/(\text{mol}\cdot\text{cm})$ . The calculated value of  $k_{et}$  is about  $2.8 \times 10^9 \text{ s}^{-1}$  which is similar to the experimental observation (about  $3 \times 10^9 \text{ s}^{-1}$ ).

When the excitation wavelength is chosen at 400 nm, no energy transfer is expected because of the absence of the overlap between the H<sub>2</sub>TPP emission spectra and the [Ru(phen)<sub>2</sub>(ip)]<sup>2+</sup> absorption spectra.

In conclusion, the luminescence dynamics of [Ru(phen)<sub>2</sub>(ip)]<sup>2+</sup> and H<sub>2</sub>TPP dyad have been measured by using time-resolved fluorescence spectroscopy. The transient luminescent spectra of the dyad show an ultrafast energy transfer from [Ru(phen)<sub>2</sub>(ip)]<sup>2+</sup> to H<sub>2</sub>TPP within 300 ps after photoexcitation of [Ru(phen)<sub>2</sub>(ip)]<sup>2+</sup> at 453 nm. No energy transfer was observed from H<sub>2</sub>TPP to [Ru(phen)<sub>2</sub>(ip)]<sup>2+</sup> as the excitation wavelength is 400 nm. The energy transfer from [Ru(phen)<sub>2</sub>(ip)]<sup>2+</sup> to H<sub>2</sub>TPP is mainly due to the Förster interaction arising from the overlap of the H<sub>2</sub>TPP emission spectra and the [Ru(phen)<sub>2</sub>(ip)]<sup>2+</sup> absorption spectra. We calculated the energy transfer rate  $k_{et}$  from [Ru(phen)<sub>2</sub>(ip)]<sup>2+</sup> to H<sub>2</sub>TPP according to the Förster theory. The result is similar to the experimental observation. Further study on the mechanism of the energy transfer in the porphyrin and ruthenium dyad is underway.

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