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# Long-Lived Charge Separation in a Dyad System Containing Cyclometalated Platinum(II) Complex and Ferrocene Donor

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A dyad system containing a cyclometalated platinum(II) complex and ferrocene donor,  $[\text{Pt}_2(\text{RC}^{\wedge}\text{N}^{\wedge}\text{N})_2(\mu\text{-DPPF})](\text{ClO}_4)_2$  (**1**,  $\text{HRC}^{\wedge}\text{N}^{\wedge}\text{N}$  = 4-tolyl-6-phenyl-2,2'-bipyridine, DPPF = 1,1'-bis(diphenylphosphino)ferrocene), has been synthesized in a reasonable yield simply by coordination of the phosphine ligand to the metal center. Spectroscopic characterization supports square planar coordination geometry with diphosphine ferrocene ligands, and the crystal structure confirms the symmetric butterfly-like assignment. Upon chemical or electrochemical oxidation, the ferrocene state of dyad **1** is able to convert to its ferrocenium state of **2**, accompanied by enhanced luminescent lifetime and intensity. Combined with steady-state and time-resolved emission/absorption spectra of the ferrocene state **1** and ferrocenium state **2** as well as the model complex **3**, we demonstrate that the photoinduced electron transfer (PET) from the ferrocene group to the platinum(II) chromophore in dyad **1** occurs with a rate constant and efficiency of  $1.9 \times 10^6 \text{ s}^{-1}$  and 87%, respectively, and the lifetime of the charge-separated (CS) state of dyad **1** is 9.4  $\mu\text{s}$  at room temperature. This performance is much better than the outstanding multistep PET processes of platinum(II) polyad systems that have been reported for artificial photosynthesis.

## Introduction

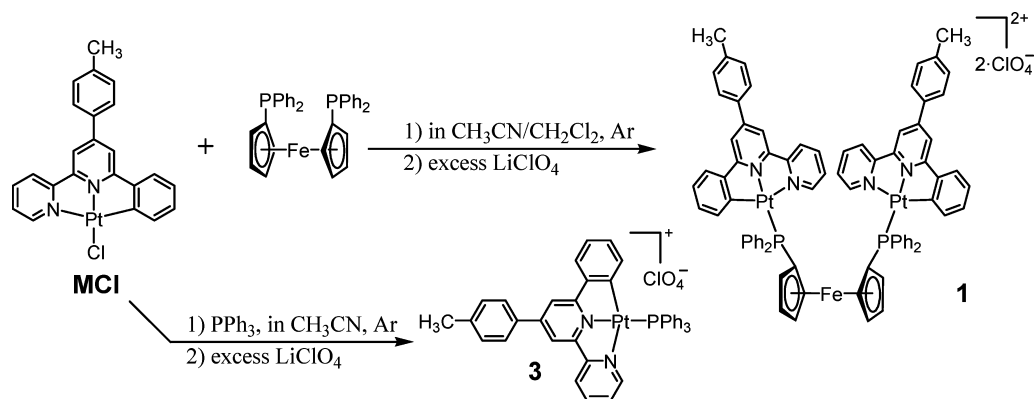
Photoinduced electron transfer (PET) is one of the most essential steps in photosynthesis, consisting of successive photon absorption and electron transfer processes, to attain the key final product of charge separation (CS). The formation of a long-lived CS state is crucial for the conversion of solar energy into chemical and electrical energies.<sup>1,2</sup> In an effort to understand the fundamental principles of the PET and CS processes and to develop artificial molecular systems for solar energy conversion and optoelectronic devices, much work has been done to construct dyads, triads, tetrads, and even pentads, which are comprised of a chromophore, electron donor(s), and/or acceptor(s).<sup>3–26</sup> The multistep PET from the spatially defined chromophore to the terminal electron acceptor through a series of electron mediators is well established to obtain fine-tuned and directed redox gradients along donor–acceptor linked arrays for the formation of the CS state with a long lifetime and high efficiency.<sup>3–12</sup> In this context, for instance, Gust, Moore, and Moore constructed an artificial photosynthesis array by using a porphyrin couple (P–P) as the chromophore, a carotenoid polyene (C) as the donor, and a diquinone moiety (QA–QB) as the acceptor, which is one of the most efficient pentads bearing a long-lived CS state of  $\text{C}^{+\bullet}\text{–P–P–QA–QB}^{\bullet-}$ .<sup>3a</sup> Imahori, Guldi, and Fukuzumi achieved an extremely long-lived CS state of 380 ms in a tetrad system, ferrocene–zinc porphyrin–free base porphyrin–fullerene ( $\text{Fc–ZnP–H}_2\text{P–C}_{60}$ ).<sup>7a</sup> Crossley and Fukuzumi built a ferrocene–zinc porphyrin–fullerene ( $\text{Fc–ZnP–C}_{60}$ ) system and obtained the longest CS lifetime of 630  $\mu\text{s}$  in ever reported triads at ambient temperature.<sup>8a</sup> Nevertheless, synthesis of such systems requires considerable effort and time. Although the long distance and thus weak electronic coupling between the terminal donor and acceptor prevent charge recombination (CR) efficiently, a

significant amount of the input energy will be lost during the multiple PET processes, thus leading to the relatively low-energy conversion efficiency. It is no doubt that a single-step and short-range ET process should distinctly minimize the loss of input photon energy,<sup>2</sup> but under the single-step PET conditions, the electronic coupling between the resulting donor radical cation and the acceptor radical anion is intense so that, in general, the CR takes place rapidly.

Square platinum(II) polypyridyl complexes represent an important class of compounds that have the benefit of directionality in the charge transfer excitation from the metal to the polypyridyl ligand.<sup>16–26</sup> Compared with octahedral  $d^6$  polypyridyl metal complexes, such as ruthenium(II), osmium(II), and rhenium(I) systems,<sup>14,15</sup> the directionality of charge transfer in platinum(II) chromophores is more certain and can be exploited in the design of systems for PET and CS by incorporation of the electron donor and acceptor.<sup>16–26</sup> Pioneering work carried out by Eisenberg and others has proved that platinum(II) complex-based multicomponent systems are promising in PET and CS processes.<sup>24</sup> They, for example, developed a series of molecular dyads or triads based on platinum(II) polypyridyl complexes, in which triad  $[\text{Pt}(\text{NO}_2\text{phtpy})(p\text{-C}\equiv\text{C–C}_6\text{H}_4\text{CH}_2\text{–(PTZ)})](\text{PF}_6)_3$ , where  $\text{NO}_2\text{phtpy}$  = 4'-{4-[2-(4-nitrophenyl)vinyl]phenyl}-2,2';6',2''-terpyridine and PTZ = phenothiazine, was observed to form a fully CS state upon excitation with a lifetime of 230 ns in  $\text{CH}_3\text{CN}$  at room temperature, while the efficiency of CS state formation was determined as only 25%. More recently, Nozaki, Akiyama, and Okada reported a highly efficient photoproduction of CS states with the longest lifetime of 1.3  $\mu\text{s}$  in toluene at room temperature ever reported in platinum(II) complex-based systems,<sup>26</sup> which is, namely,  $\text{MTA–Pt}(\text{diimine})\text{–(M)NDI}$  triads, containing dimethoxydimethyltriphenyl amine (MTA) as the donor and naphthalene diimide [(M)NDI] as the acceptor. However, the long-lived CS

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## SCHEME 1: Syntheses of Platinum(II) Complexes 1 and 3



state of efficient and short-range donor–acceptor platinum(II) dyad systems is rare.

In this contribution, we report the formation of a long-lived CS state in a simple platinum(II) complex-based dyad **1**,  $[\text{Pt}_2(\text{RC}^{\wedge}\text{N}^{\wedge}\text{N})_2(\mu\text{-DPPF})](\text{ClO}_4)_2$  ( $\text{HRC}^{\wedge}\text{N}^{\wedge}\text{N}$  = 4-tolyl-6-phenyl-2,2'-bipyridine, DPPF = 1,1'-bis-(diphenylphosphino)-ferrocene). An electron-donating group of ferrocene was incorporated to the cyclometalated platinum(II) chromophore by facile coordination of the phosphine ligand to the metal center.<sup>20d,27</sup> The strongly  $\sigma$ -donating auxiliary phosphine ligands improve the solubility and photophysical property of platinum(II) polypyridyl complexes **1** and the model complex **3** remarkably. Upon chemical or electrochemical oxidation, the ferrocene state of dyad **1** is able to convert to its ferrocenium state of **2**, accompanied by enhanced luminescent lifetime and intensity. With the aid of steady-state and time-resolved emission/absorption spectroscopy, we demonstrate that the PET from the ferrocene group to the platinum(II) chromophore in dyad **1** occurs with a rate constant and efficiency of  $1.9 \times 10^6 \text{ s}^{-1}$  and 87%, respectively. The lifetime of the CS state via an intramolecular PET process in dyad **1** was determined as  $9.4 \mu\text{s}$  at room temperature. This performance is much better than the best results obtained in multistep PET processes of platinum(II) complex-based triad systems.

## Results and Discussion

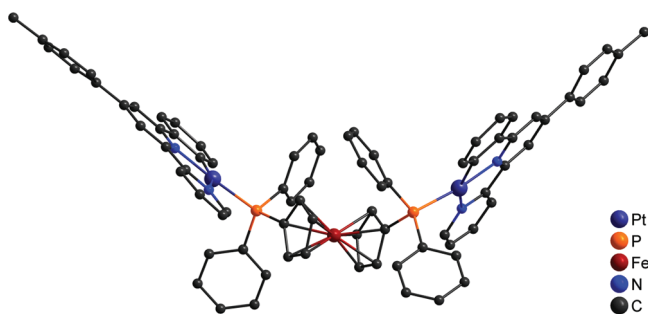
**Syntheses and Characterization.** Complex **1** was synthesized by facile displacement of the chloride group in **MCl** with the phosphine on the ferrocene ancillary ligand (DPPF) under an inert atmosphere (Scheme 1). For the contribution of the phosphine-tethered structure, platinum(II) complex **1** has a good solubility in various organic solvents, like  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CN}$ , and  $\text{CH}_3\text{COOC}_2\text{H}_5$ , and can be easily purified by column chromatography on silica gel to afford the desired product with a yield of ca. 60%. For comparison, the model complex **3** was also prepared analogously in a yield of 70% as well.<sup>18b</sup>

NMR spectroscopy, MS spectrometry, and satisfactory elemental analyses confirmed the identities of complexes **1** and **3**. The signals corresponding to  $(\text{M}^+)$  as well as the  $(\text{M}^+ + \text{ClO}_4^-)$  fragment were clearly observed in the positive MALDI-TOF mass spectrum of **1**. The methyl protons on the  $\text{RC}^{\wedge}\text{N}^{\wedge}\text{N}$  ligand of dyad **1** exhibit a single peak at 2.41 ppm, and the protons on the ferrocene moiety exhibit a double peak around 4.59 ppm, which suggest the symmetric structure of dyad **1**. Due to one-bond coupling between  $^{31}\text{P}$  and  $^{195}\text{Pt}$  satellites,<sup>18b</sup> only one typical triple signal in the  $^{31}\text{P}$  NMR spectrum of **1** and a comparable signal of model complex **3** were obtained.

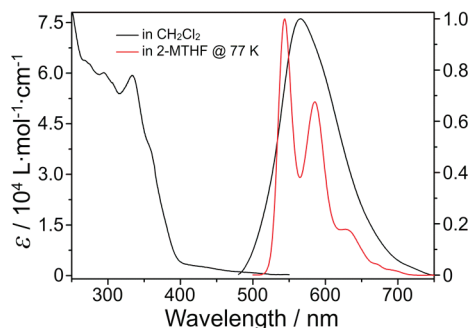
All these features indicate the presence of the  $\text{Pt}_2(\mu\text{-dppf})$  unit with chemically equivalent phosphorus atoms.

**X-ray Crystallography.** The crystal structure of **1** determined by X-ray diffraction is shown in Figure 1, which has a symmetric butterfly-like structure, belongs to the monoclinic crystal system, and contains three acetonitrile molecules in each unit (Supporting Information, Figure S1). The platinum(II) metal centers have four coordinates, arranging in an essentially square-planar geometry with some extent of torsions in the bond angles from orthogonality, probably due to the coordination constraints imposed by the  $\text{RC}^{\wedge}\text{N}^{\wedge}\text{N}$  ligand. The distance between two platinum(II) metal centers was found to be 9.91 Å, indicating the absence of intramolecular  $\text{Pt(II)}\text{--Pt(II)}$  or  $\pi\text{--}\pi$  interactions. The edge-to-edge distance between the ferrocene and platinum(II) metal center is 3.46 Å. The  $[\text{Pt}(\text{RC}^{\wedge}\text{N}^{\wedge}\text{N})]$  coordination plane and cyclopentadienyl ring on the ferrocene moiety are noncoplanar for the presence of the sterically bulky diphosphine auxiliary ligand, and the interplanar angle is  $64.52^\circ$ . These structural features would suppress the electronic interactions between the platinum(II) chromophore and the ferrocene donor in the ground state. The crystal packing diagram of dyad **1** was shown in Figure S1 (Supporting Information), in which the molecules are arranged in a screw configuration and extended along the *b* axis to form one-dimensional infinite chains with screw pitch of 21.98 Å.

**Electrochemistry.** To evaluate whether the ferrocene moiety could act as a suitable donor to build a highly efficient dyad system, the electrochemical property of dyad **1** as well as the model complex **3** were investigated in this work. Complex **1** exhibits a reversible oxidation process at +0.61 V (+0.59 V in  $\text{CH}_2\text{Cl}_2$ ) and an irreversible oxidation process at peak potential of ca. +1.29 V in  $\text{CH}_3\text{CN}$  (Supporting Information, Figures S2–3). The former is ascribed to the redox process of  $\text{Fc}^{+/0}$  on the ferrocene subunit of DPPF,<sup>27</sup> and the latter is tentatively



**Figure 1.** Perspective drawing of dyad **1**. Hydrogen atoms and solvent molecules were omitted for clarity.



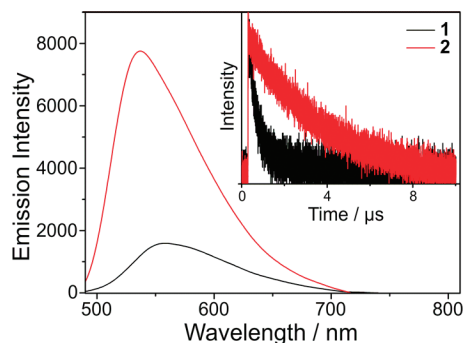
**Figure 2.** UV-vis absorption and emission spectra of dyad **1** in  $\text{CH}_2\text{Cl}_2$  at 298 K ( $\lambda_{\text{ex}} = 450$  nm) and in 2-MTHF at 77 K ( $\lambda_{\text{ex}} = 370$  nm).

assigned to the Pt(II)→Pt(III) oxidation. Owing to rapid solvolysis of the resultant platinum(III) species, the oxidation of square-planar complexes is generally irreversible.<sup>24</sup> Clearly, the ferrocene group on the DPPF ligand is reduction-active and capable of acting as an effective electron donor. On the other hand, dyad **1** displays a reversible reduction process at  $-1.51$  V ( $-1.54$  V in  $\text{CH}_2\text{Cl}_2$ ) and an irreversible reduction process at a peak potential of  $-2.10$  V in  $\text{CH}_3\text{CN}$ . Consistent with dyad **1**, model complex **3** shows a reversible reduction process at  $-1.58$  V and an irreversible reduction process at peak potential of  $-2.20$  V in  $\text{CH}_2\text{Cl}_2$ . The two sets can be therefore attributed to the successive one-electron reductions of the polypyridyl moiety, which is generally considered to be the electron localization on the RC<sup>^</sup>N<sup>^</sup>N<sup>^</sup> ligand.<sup>18c</sup> To convert the ferrocene state of dyad **1** to its corresponding ferrocenium state **2**,  $\text{Fe}(\text{ClO}_4)_3$  was used as an oxidant. It was noted that with the titration of  $\text{Fe}(\text{ClO}_4)_3$  into dyad **1** in  $\text{CH}_2\text{Cl}_2$  a newly formed reversible redox at  $+0.25$  V (vs  $\text{Fc}^{+/0}$ ) from  $\text{Fe}(\text{ClO}_4)_3/\text{Fe}(\text{ClO}_4)_2$  appeared and gradually increased, while the redox potential of the ferrocene group on dyad **1** simultaneously decreased at ca.  $+0.59$  V (Supporting Information, Figure S4). This result confirms that  $\text{Fe}(\text{ClO}_4)_3$  is sufficiently oxidative to obtain an electron from dyad **1**, leading to the formation of its ferrocenium state **2**.

#### Efficient PET and Long-Lived CS in the Dyad System.

The electronic absorption spectrum is shown in Figure 2 (left). Dyad **1** exhibits intense vibronic-structured absorption bands at wavelengths below 350 nm with extinction coefficients ( $\epsilon$ ) on the order of  $10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  and a moderately intense band in the region above 400 nm. These absorption properties were found to follow Beer's law in the range of  $10^{-6}$ – $10^{-3}$  M, suggesting the absence of significant aggregation within these common concentrations. With reference to the model complex **3** and literature reports,<sup>18b</sup> these two bands are ascribed to the intraligand (IL) and <sup>1</sup>MLCT [ $(5d)\text{Pt} \rightarrow \pi^*(\text{RC}^{\wedge}\text{N}^{\wedge}\text{N})$ ] state, respectively. Upon excitation at 450 nm, dyad **1** displayed a weakly broad emission at  $\lambda_{\text{max}}$  563 nm with a lifetime of 0.46  $\mu\text{s}$  in  $\text{CH}_2\text{Cl}_2$  at room temperature, whereas well-defined vibronic emission bands were detected at  $\lambda_{\text{max}}$  543, 584, and 631 nm in frozen 2-methyltetrahydrofuran (2-MTHF) at 77 K (Figure 2). The emission quantum yield was determined as 0.011 in  $\text{CH}_2\text{Cl}_2$  with degassed  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  acetonitrile solution as the reference ( $\Phi_{\text{r}} = 0.062$ ).<sup>28</sup> Similar to that of the model complex **3** (Supporting Information, Figure S5), the origin of the emission for dyad **1** is assigned to the <sup>3</sup>MLCT state in nature.

Since dyad **1** incorporated a redox-sensitive ferrocenyl group, spectroscopic changes are expected with either electrochemical oxidation or the addition of a chemical oxidant. As described above, dyad **1** features a weak and short-lived emission of the <sup>3</sup>MLCT state in  $\text{CH}_2\text{Cl}_2$  solution. When the oxidation potential



**Figure 3.** Emission spectra of **1** and **2** in  $\text{CH}_2\text{Cl}_2$  ( $\lambda_{\text{ex}} = 450$  nm). The insets show the decay profile of their corresponding emission.

was maintained at 1.10 V for 20 min, 100–200 mV more positive than that of the ferrocenyl subunit, the emission intensity was enhanced greatly (Supporting Information, Figure S6). This interesting phenomenon was also observed with the titration of  $\text{Fe}(\text{ClO}_4)_3$  into dyad **1**. Addition of 1 equiv of oxidant  $\text{Fe}(\text{ClO}_4)_3$  to the solution of dyad **1** results in the increment of emission intensity and lifetime. As shown in Figure 3 and Figure S7 (Supporting Information), the emission maximum was blue-shifted from 563 to 552 nm, and the corresponding lifetime was extended from 0.46  $\mu\text{s}$  for the ferrocene state **1** to 3.5  $\mu\text{s}$  for the ferrocenium state **2**. The blue-shift of the emission maximum caused by oxidation is possibly due to the difference of electronic effect for the ferrocene group in dyad **1** and the ferrocenium unit in **2**. Moreover, upon the titration of  $\text{Fe}(\text{ClO}_4)_3$  into the ferrocene state **1** in frozen 2-MTHF, the ferrocenium state **2** displayed vibronic emission bands at 504, 540, and 579 nm, the same as the model complex **3** (Supporting Information, Figure S8). In contrast, with either titration of  $\text{Fe}(\text{ClO}_4)_3$  or electrochemical oxidation the absorption spectrum of the ferrocenium state **2** is similar to that of the ferrocene state **1** in the low-energy region (Supporting Information, Figure S9). The observations indicate no significant interaction between the platinum(II) chromophore and the ferrocene electron donor in dyad **1** at the ground state but show that indeed such interaction does occur in the excited state.

Combining electrochemical and spectroscopic measurements, the excited-state energy level of the dyad system was estimated by eq 1. Here, the 0–0 transition energy ( $E_{0-0}$ ) at 2.29 eV was calculated from emission maximum at 77 K.  $E(\text{Pt}^{0/-})$  and  $E(\text{Pt}^{0/+})$  were directly read from the half-wave potentials of the one-electron redox in the cyclic voltammogram, and their corresponding values are  $-1.54$  and  $+0.59$  V (vs  $\text{Fc}^{+/0}$ ), respectively. Taken all together,  $E(\text{Pt}^{*/-})$  was calculated to be ca.  $+0.75$  V vs  $\text{Fc}^{+/0}$  ( $+0.35$  V vs NHE), while  $E(\text{Pt}^{*/+})$  was ca.  $-1.30$  V vs  $\text{Fc}^{+/0}$  ( $-1.70$  V vs NHE). Consequently, the driving force for intramolecular PET  $\Delta G_{\text{CS}}$  from the ferrocene donor to platinum(II) chromophore in dyad **1** was determined by the Weller equation<sup>29</sup> shown as eq 2 (top), where  $e$  is the charge of the electron,  $\epsilon_0$  is the permittivity of the vacuum,  $\epsilon$  is the relative dielectric constant of the solvent, and  $R_{\text{D-C}}$  of 5.37 Å from the crystal structure refers to the center-to-center distance between the ferrocene donor and platinum(II) chromophore. At the same time, the driving force for the intramolecular charge recombination of dyad **1**, namely, energy level of charge-separated state  $\Delta G_{\text{CR}}$ , was estimated as eq 2 (bottom).

$$\begin{aligned} E(\text{Pt}^{*/-}) &= E_{0-0} + E(\text{Pt}^{0/-}) \\ E(\text{Pt}^{*/+}) &= E(\text{Pt}^{0/+}) - E_{0-0} \end{aligned} \quad (1)$$



$$\begin{aligned}
 -\Delta G_{\text{CS}} &= E_{0-0} - (E_{\text{ox}} - E_{\text{red}} + \Delta G_{\text{S}}) \\
 \Delta G_{\text{CR}} &= E_{\text{ox}} - E_{\text{red}} + \Delta G_{\text{S}} \\
 -\Delta G_{\text{S}} &= e^2/(4\pi\epsilon_0\epsilon_{\text{R}}R_{\text{D-C}})
 \end{aligned}
 \quad (2)$$

Calculation of the driving force  $\Delta G_{\text{CS}}$  (−0.45 eV) and  $\Delta G_{\text{CR}}$  (+1.84 eV) in this dyad system suggests that the ET from the ferrocene donor to the  $^3\text{MLCT}$  excited state of the platinum(II) chromophore is thermodynamically feasible. Given the improved luminescence capability, i.e., emission intensity and lifetime, with the oxidation of the ferrocene subunit to ferrocenium, it is reasonable to consider that the shorter lifetime and the weaker emission of dyad **1** is due to the *intramolecular* PET from the ferrocene group to the platinum(II) chromophore (Scheme 2). According to eq 3, the rate constant ( $k_{\text{ET}}$ ) and efficiency ( $\Phi_{\text{ET}}$ ) for dyad **1** were determined to be  $k_{\text{ET}} = 1.9 \times 10^6 \text{ s}^{-1}$  and  $\Phi_{\text{ET}} = 87\%$ , respectively, in which the PET efficiency is remarkable among the ever reported platinum(II) polyads.<sup>16,23–26</sup>

$$\begin{aligned}
 k_{\text{ET}} &= (1/\tau_{\text{dyad1}}) - (1/\tau_{\text{dyad2}}) \\
 \Phi_{\text{ET}} &= 1 - \tau_{\text{dyad1}}/\tau_{\text{dyad2}}
 \end{aligned}
 \quad (3)$$

Time-resolved spectroscopic techniques were further introduced to trace the formation of the CS state in this dyad system. Transient absorption spectra of the ferrocene state **1**, the ferrocenium state **2**, and the model complex **3** were recorded at 298 K in  $\text{CH}_2\text{Cl}_2$  solution (Figure 4). Evidently, upon excitation by 355 nm light, the ferrocene state **1** showed a broad absorption in the region of 400–850 nm (Figure 4a), while the ferrocenium state **2** (Figure 4b) exhibited totally different curves from that of the ferrocene state **1** but quite similar to that of the model complex **3** (Figure 4c). The decays of the ferrocenium state **2** throughout the absorption region and the recovery of the bleach occur on the same time scale and can be described by a monoexponential function. The lifetime of 3.2  $\mu\text{s}$  obtained from the decays of the absorption transients as well as from the bleach recoveries is in quantitative agreement with that of the luminescence (3.5  $\mu\text{s}$ ). On the basis of the above observations, the subsequent transient absorption of the ferrocenium state **2** is attributed to the typical  $^3\text{MLCT}$  excited state of the platinum(II) complex. Since no obvious change could be observed in the transient spectra of the model complex **3** with the addition of

$\text{Fe}(\text{ClO}_4)_3$  (Supporting Information, Figure S10), it is believed that the oxidation of the ferrocene state **1** to the ferrocenium state **2** restores the luminescent capability of the platinum(II) chromophore by preventing the PET process in the ferrocene state **1**.

With the aid of electrochemical spectroscopy, we assigned the transient species of the ferrocene state **1**. In UV–vis spectroelectrochemical study, the ground state absorption spectrum of the ferrocene state **1** was defined as the reference, hence any changes associated with bulk reduction of **1** can be regarded as differences in the absorption ( $\Delta A$ ). Note that with one-electron reduction of the ferrocene state **1** in 0.1 M  $^n\text{Bu}_4\text{NPF}_6$  solution of  $\text{CH}_2\text{Cl}_2$  the generated species displays new absorption bands at 400, 433, 485, and 519 nm (Supporting Information, Figure S11). It is therefore reasonable to think that the species absorbing over 400–600 nm corresponds to the radical anion of the  $[\text{RC}^-\text{N}^-\text{N}^-]$  ligand. The broad envelope from 650 to 850 nm is also from the  $[\text{RC}^-\text{N}^-\text{N}^-]$  radical anion according to the documented spectroscopic works of platinum(II) complexes.<sup>22–25</sup> Regarding the oxidized donor counterpart, the weak absorption feature at  $\sim 620 \text{ nm}$  for the ferrocenium radical cation<sup>30</sup> is submerged by the strong and broad absorption of the  $[\text{RC}^-\text{N}^-\text{N}^-]$  radical anion. From the kinetics probed at 400, 430, and 480 nm (Supporting Information, Figure S12), a fast rise phase followed by a rather slow decay suggests the formation (Figure 4, bottom) and the disappearance (Figure 4, top) of the CS in dyad **1**. The rise grows quickly with the forward ET rate constant ( $k_{\text{ET}}$ ) of  $1.3 \times 10^6 \text{ s}^{-1}$ , consistent with that obtained by the time-resolved luminescence spectroscopy ( $1.9 \times 10^6 \text{ s}^{-1}$ ). On the other hand, the rate of the back CR ( $k_{\text{CR}}$ ) derived from the decay phase is  $1.05 \times 10^5 \text{ s}^{-1}$  (9.4  $\mu\text{s}$ ) at room temperature, which is considerably longer than most of the ever reported platinum(II) polyads.<sup>16,23–26</sup>

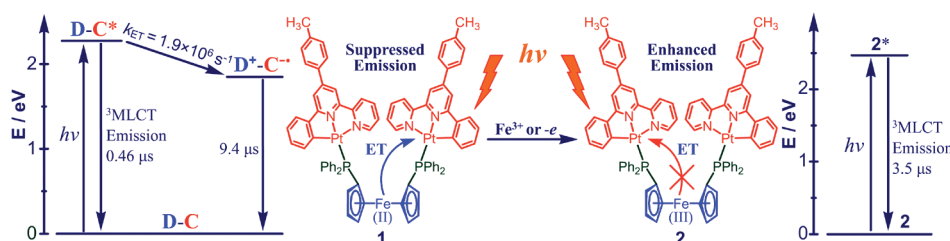
It is known that platinum(II) complex-based systems generally employ multistep PET processes to achieve long-lived CS states.<sup>23–26</sup> The CS formation efficiency was estimated as 10–30% in some cases with a lifetime of 75–230 ns.<sup>24</sup> In the case of dyad **1**, light absorbed by the platinum(II) chromophore gives its  $^3\text{MLCT}$  excited state ( $\text{D-C}^*$ ), which lies  $\sim 2.29 \text{ eV}$  above the ground state (Scheme 2). The PET reaction takes place from the ferrocene unit to the platinum(II) chromophore in its  $^3\text{MLCT}$  state and yields the products of the ferrocenium radical

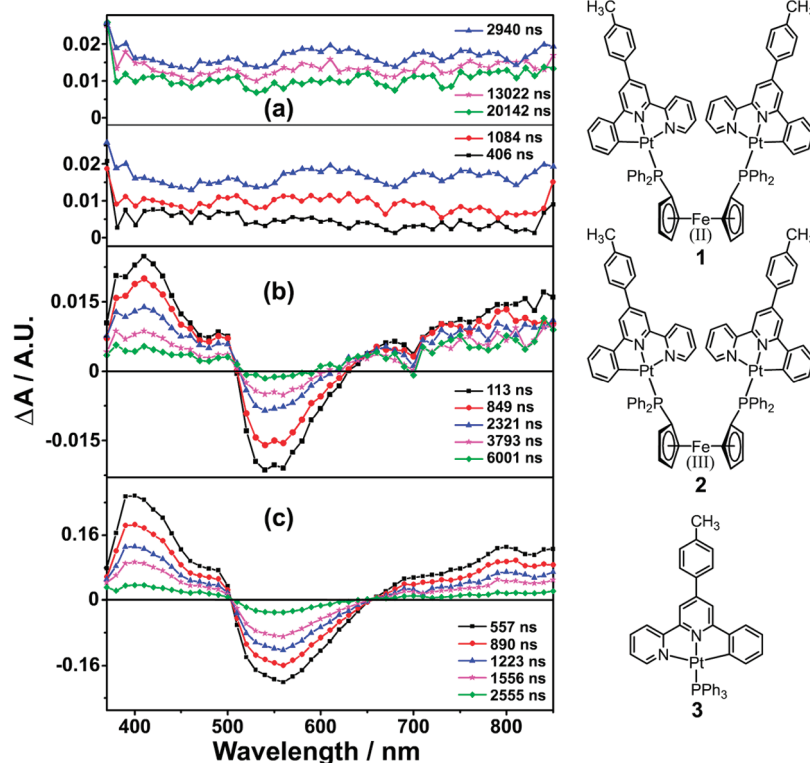
**TABLE 1: Absorption and Emission Characteristics as Well as Electrochemical Properties of the Ferrocene State of **1**, the Ferrocenium State of **2**, and the Model Complex **3****

entry	$\lambda_{\text{abs}}/\text{nm}^a$ ( $\epsilon/\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ )	$\lambda_{\text{em}}^a$ (nm)	$\Phi_{\text{f}}^a$	$\tau^a$ ( $\mu\text{s}$ )	$\lambda_{\text{em}}^b$ (nm)	$E_{\text{red}}$ (V) <sup>c</sup> vs $\text{Fc}^{+/0}$	$E_{\text{ox}}$ (V) <sup>c</sup> vs $\text{Fc}^{+/0}$
<b>1</b>	272(62 800), 296(59 800), 334(59 500), 432(2 300)	563	0.011	0.46	543 <sub>max</sub> , 584, 631	−1.54; <sup>a,d</sup> −1.51, <sup>d,e</sup> −2.10 <sup>f</sup>	+0.59; <sup>a,d</sup> +0.61, <sup>d,e</sup> +1.29 <sup>f</sup>
<b>2</b>	271, 294, 336, 430	532	0.043	3.49	504 <sub>max</sub> , 540, 579	–	–
<b>3</b>	270(20 300), 296(20 300), 334(21 200), 432(1 000)	538	0.065	0.51	502 <sub>max</sub> , 540, 577	−1.58; <sup>d</sup> −2.20 <sup>f</sup>	–

<sup>a</sup> In  $\text{CH}_2\text{Cl}_2$  at room temperature. <sup>b</sup> In 2-MTHF at 77 K. <sup>c</sup> CV in 0.1 M  $^n\text{Bu}_4\text{NPF}_6$  as supporting electrolyte; scan rate, 50 mV/s; reference electrode, 0.1 M Ag/AgNO<sub>3</sub> in  $\text{CH}_3\text{CN}$ . <sup>d</sup> Reversible peak. <sup>e</sup> In  $\text{CH}_3\text{CN}$ . <sup>f</sup> Irreversible peak.

**SCHEME 2: Energy Diagrams of the Ferrocene State **1** and the Ferrocenium State **2****





**Figure 4.** (a) Transient absorption spectra of dyad **1** in  $\text{CH}_2\text{Cl}_2$  at 298 K ( $\lambda_{\text{ex}} = 355 \text{ nm}$ ). (b) Transient absorption spectra of **2** in  $\text{CH}_2\text{Cl}_2$  at 298 K. (c) Transient absorption spectra of **3** in  $\text{CH}_2\text{Cl}_2$  at 298 K.

cation and the  $[\text{RC}^+\text{N}^-\text{N}^{\cdot-}]$  radical anion ( $\text{D}^{++}-\text{C}^{\cdot-}$ ) that lies 1.84 eV above the ground state. This means that the excitation energy of the platinum(II) chromophore loses only 0.45 eV to reach the CS state of dyad **1**. In contrast to the ferrocene state **1**, the ferrocenium state **2** displays an enhanced emission for preventing the PET by oxidation of the ferrocene in dyad **1**. The fast single-step PET ( $k_{\text{ET}} = 1.9 \times 10^6 \text{ s}^{-1}$  and  $\Phi_{\text{ET}} = 87\%$ ) from the ferrocene unit to the platinum(II) chromophore in dyad **1** and the slow CR ( $k_{\text{CR}} = 1.05 \times 10^5 \text{ s}^{-1}$ ) are of advantage to effective light-energy conversion.

## Conclusion

A novel dyad system **1** with cyclometalated platinum(II) chromophore and ferrocene donor has been designed and synthesized to investigate PET and CS processes under the single-step conditions. The X-ray crystal structure of **1** reveals that the edge-to-edge distance between the ferrocene and platinum(II) metal center is 3.46 Å, in which the cyclometalated platinum(II) coordination plane and cyclopentadienyl ring on the ferrocene moiety are noncoplanar for the presence of the sterically bulky diphosphine auxiliary ligand. Spectroscopic and electrochemical studies demonstrate that the ferrocene state of dyad **1** is able to convert to its ferrocenium state of **2**, accompanied by enhanced luminescent lifetime and intensity. The ferrocene state **1** exhibits a suppressed emission for the available PET from the ferrocene donor to platinum(II) chromophore, while the ferrocenium state **2** shows an enhanced emission for preventing the PET process in the dyad **1**. By steady-state and time-resolved techniques, the PET process from the ferrocene group to the platinum(II) chromophore in dyad **1** has been well evidenced with the rate constant and efficiency of  $1.9 \times 10^6 \text{ s}^{-1}$  and 87%, respectively. The CS state of dyad **1** was locked-in by kinetic traces as compared with the ferrocenium state **2** and the model complex **3** as well. The

lifetime of the CS state via the single-step PET process of dyad **1** was determined as 9.4  $\mu\text{s}$  at room temperature. This performance is much better than the outstanding multistep PET processes of platinum(II) polyad systems that have been reported for artificial photosynthesis.

## Experimental Section

**Materials and Instrumentation.** 4-Tolyl-6-phenyl-2,2'-bipyridine ( $\text{RC}^+\text{N}^-\text{N}$ ) was prepared via Kröhnke syntheses,<sup>31</sup> and the mononuclear platinum(II) complex  $\text{Pt}(\text{RC}^+\text{N}^-\text{N})\text{Cl}$  (**MCI**) was made according to the literature method.<sup>18b</sup> 1,1'-Bis(diphenylphosphino)ferrocene,  $\text{K}_2\text{PtCl}_4$ , and other reagents were purchased from commercial sources and used as received without further purification. Solvents for photophysics and electrochemistry were treated following the standard procedures.<sup>32</sup> NMR spectra were measured on a Bruker-400 spectrometer with TMS ( $^1\text{H}$ ), 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) as the internal reference. The MALDI-TOF mass spectra were conducted on a Bruker BIFLEX III mass spectrometer. Elemental analyses were performed on a Carlo Erba 1106 analyzer. Electrochemical experiments were performed on a computer-controlled Princeton Applied Research model 283 Potentiostat/Galvanostat under an argon flow in deoxygenated  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_3\text{CN}$  using tetra-*n*-butylammonium hexafluorophosphate ( $^n\text{Bu}_4\text{NPF}_6$  0.1 M) as supporting electrolyte. All these measurements were carried out in a three-compartment electrolytic cell, where a plumbago disk was used as the working electrode, a platinum wire as the auxiliary electrode, and  $\text{Ag}/\text{AgNO}_3$  (0.1 M in  $\text{CH}_3\text{CN}$ ) as the reference electrode. Potentials were referenced to the ferrocenium/ferrocene ( $\text{Fc}^{+/0}$ ) couple by using ferrocene as an internal standard.<sup>33</sup>

**Photophysical Measurements.** UV-vis absorption spectra were measured by a Shimadzu UV-1601 PC spectrophotometer. Steady-state emission spectra were recorded on a Hitachi F-4500

spectrophotometer. Time-resolved luminescent profiles and transient absorption spectra were obtained by Edinburgh LP 920 using the third harmonic (355 nm) of a pulse Nd:YAG laser as the excitation source. Solution samples with proper concentrations were prepared by optical dilution for steady-state photoluminescence ( $OD < 0.05$ ) and emission lifetime determination, which were deoxygenated for 20 min in a 10-mm path-length quartz cell prior to measurements. The values of lifetime were calculated by exponential function fitting with luminescence spectrometer software L900. The experimental errors in determination of the PET rate constant and the CR rate constant are  $\pm 10\%$ . Low-temperature (77 K) emission spectra for glassy and solid-state samples were recorded in 5 mm diameter quartz tubes, which were placed in a liquid-nitrogen Dewar equipped with quartz windows, and 2-MTHF was used as the medium.

**Syntheses of 1.** A mixture of MCl (110.4 mg, 0.2 mmol) and DPPF (55.4 mg, 0.1 mmol) in  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  (10/10 mL) was stirred for 18 h under an argon atmosphere. Excess  $\text{LiClO}_4$  was added as a solid (**Caution! Perchlorate salts are potentially explosive and should be handled with care and in small amounts**). After filtration and removal of the solvents, the crude product was purified by silica gel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COOC}_2\text{H}_5 = 1/1$ ) to give the desired product as an orangish-red crystalline solid (107 mg, yield 60%). MALDI-TOF MS:  $m/z = 1587$  ( $\text{M}^+$ ), 1686 ( $\text{M}^+ + \text{ClO}_4$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.41 (s, 6H), 4.59 (d, 8H,  $J = 16.4$  Hz), 6.37 (d, 2H,  $J = 7.6$  Hz), 6.60 (t, 2H,  $J = 7.6$  Hz), 6.81 (s, 2H), 6.95–7.03 (m, 4H), 7.34 (d, 4H,  $J = 8.0$  Hz), 7.46–7.54 (m, 14H), 7.77 (d, 4H,  $J = 8.0$  Hz), 7.83 (s, 2H), 7.89 (q, 8H,  $J = 7.6$  Hz), 8.05 (s, 2H), 8.19 (s, 2H), 8.47 (d, 2H,  $J = 7.6$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 14.93 ( $J(\text{PtP}) = 4055$  Hz). Anal. Calcd for  $\text{C}_{80}\text{H}_{62}\text{N}_4\text{O}_{12}\text{Cl}_2\text{P}_2\text{Pt}_2$ : C, 53.79; H, 3.50; N, 3.14. Found: C, 53.28; H, 3.60; N, 3.09.

**Syntheses of 3.** A mixture of MCl (110.4 mg, 0.2 mmol) and  $\text{PPh}_3$  (52.4 mg, 0.2 mmol) was resolved in 20 mL of  $\text{CH}_3\text{CN}$  and stirred for 18 h under an argon atmosphere.<sup>18b</sup> Excess  $\text{LiClO}_4$  was added as a solid (**Caution! Perchlorate salts are potentially explosive and should be handled with care and in small amounts**). After filtration, the resultant solution was evaporated to ca. 5 mL. A precipitate was formed with the addition of  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  and further rinsed with  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  to afford the product as a yellow solid (123 mg, yield 70%). MALDI-TOF MS:  $m/z = 778$  ( $\text{M}^+$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$ : 2.45 (s, 3H), 6.37 (d, 1H,  $J = 7.2$  Hz), 6.54 (d, 1H,  $J = 5.6$  Hz), 6.66 (t, 1H,  $J = 7.2$  Hz), 7.06 (t, 1H,  $J = 7.2$  Hz), 7.24 (t, 1H,  $J = 4.8$  Hz), 7.48 (d, 2H,  $J = 8.0$  Hz), 7.58–7.62 (m, 6H), 7.66–7.69 (m, 3H), 7.89–7.94 (m, 6H), 8.03 (d, 1H,  $J = 8.0$  Hz), 8.14 (d, 2H,  $J = 8.0$  Hz), 8.27 (t, 1H,  $J = 7.6$  Hz), 8.58 (s, 1H), 8.74 (s, 1H), 8.86 (d, 1H,  $J = 8.0$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 25.80 ( $J(\text{PtP}) = 4015$  Hz).

**X-ray Crystallography.** A single crystal of dyad **1** was obtained by vapor diffusion of  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  into a  $\text{CH}_3\text{CN}$  solution. Crystal data were collected on a Bruker Smart 1000 X-ray diffractometer using graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71070$  Å) at 113 K. Cell refinement and data reduction were done using SAINT. An empirical absorption correction was applied using SADABS based on the multiple measurements of equivalent reflections. The structures were solved by direct methods and refined by full-matrix least-squares and difference Fourier techniques with SHELX-97. Perspective drawing and crystal aggregation diagram was performed using the program Diamond 2.1e. The details of data collection and crystal structure refinement are summarized in Table S1

(Supporting Information). Selected bond lengths and angles for dyad **1** are collected in Table S2 (Supporting Information). Crystallographic data for dyad **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC No. 772514.

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**Supporting Information Available:** The CIF of **1** and the detailed spectroscopic spectra of **1**, **2**, and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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