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Conformation-Controlled Diplatinum(II)-Ferrocene Dyad to Achieve Long-Lived Charge-Separated State

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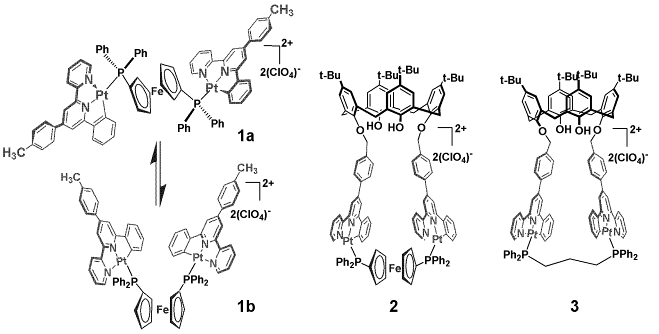
Abstract: Square-planar polypyridyl platinum(II) complexes possess a rich range of structural and spectroscopic properties that is ideal for designing artificial photosynthetic centres. Taking advantage of the directionality in the charge transfer excitation from the metal to the polypyridyl ligand, we describe here diplatinum(II)-ferrocene dyads, open-butterfly like dyad 1 and closed-butterfly like dyad 2, to understand the conformation and orientation effects to prolong the lifetime of charge-separated state. In contrast to the open-butterfly like dyad 1, the closed-butterfly like dyad 2 shows three times long lifetime of charge separated state upon photoexcitation, demonstrating that the orientation in the rigid structure of dyad 2 is a very important issue to achieve long-lived charge separated state.

Photosynthesis in nature provides a blue-print for the conversion of sunlight to chemical energy by a chain of photoinduced electron transfer (PET) process.[1] The success and importance stimulate scientists to construct artificial molecular systems, such as dyads, triads, tetrads, and even pentads, which upon photoexcitation give rise to long-lived charge-separated (CS) states to convert solar energy into chemical and electrical energies.[2-5] The multistep PET from the chromophore donor to the acceptor through a series of electron mediates is an ideal way to form a CS state with a long lifetime because the long distance and weak electronic coupling between the terminal donor and acceptor prevent charge recombination (CR) efficiently.[6-8] However, a long-lived CS state under single-step PET condition is not often obtained because the electronic coupling between the resulting donor radical cation and acceptor radical anion is so strong that the CR in general, takes place rapidly.[9-11]

Square-planar polypyridyl platinum(II) complexes represent an important class of compounds that possess a rich range of structural and spectroscopic properties.[12-13] Some of them have been exploited in the design of PET systems by incorporating electron donor and/or acceptor.[14-15] Pioneering work by Eisenberg and others has demonstrated that platinum(II) complex-bonded multi-component systems are promising in the PET process.[15] They obtained a fully CS state with lifetime of 230 ns in CH_3CN upon excitation of a triad, $[Pt(NO_2phtpy)(p\text{-}C{\equiv}C\text{-}C_6H_4CH_2\text{-}(PTZ)](PF_6)$, where NO_2phtpy = 4'-{4-[2-(4-nitrophenyl)vinyl] phenyl}-2,2';6',2''-terpyridine and PTZ = phenothiazine.[15a] Nozaki, Akiyama and Okada found that the molecular triad, MTA-Pt(diimine)-(M)NDI, dimethoxy dimethyl triphenyl amine (MTA) as the donor and naphthalene diimide [(M)NDI] as the acceptor underwent highly efficient photo-production of a CS state at room temperature with lifetime of 1.3 µs in toluene.[14d] Benefiting from the directionality in the charge transfer excitation from the metal to the polypyridyl ligand, we found a long-lived CS state in a simple platinum(II) complex-based dyad **1**, $[Pt_2(RC^{\wedge}N^{\wedge}N)_2(\mu\text{-DPPF})](ClO_4)_2$ (**1**, RC^N^N = 4-tolyl-6-phenyl-2,2'-bipyridine, DPPF = 1,1'-bis-(diphenylphosphino)-ferrocene). The single crystal structure of **1** revealed that the two cyclometalated platinum(II) coordination planes and cyclopentadienyl ring on the ferrocene moiety are actually noncoplanar holding an open-butterfly like structure, with the edge-to-edge distance being 3.5 Å between the ferrocene and platinum(II) metal center. The lifetime of CS state of dyad **1** was determined as 9.4 µs at room temperature.[16a] The result implied the potential of well-designed platinum(II) complex to obtain long-lived CS state, even via single-step PET process.



Scheme 1. Structure of dyad **1**, **2** and the reference **3**.

Given the strong interest in developing artificial photosynthetic systems for solar energy conversion,[1e,13] we wondered whether we could achieve a longer CS state of the platinum(II) molecular dyads by locking arrangement that can in principle further constrain the relative rotations of the two platinum(II) moieties. Toward this end, we designed and synthesized a relatively rigid dyad **2**, $[Pt_2L(\mu$-

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DPPF)]$(ClO_4)_2$, where (**2**, L = 5,11,17,23-tetra-tert-butyl-25,27-di[methoxy(4-phenyl)- (C^N^N)]-26,28-dihydroxy calix[4]arene, HC^N^N = 6-phenyl-2,2'-bipyridine, DPPF = 1,1'-bis-(diphenylphosphino)-ferrocene) (Scheme 1). Herein, calix[4]arene is introduced to attach cyclometalated platinum(II) complexes so as to lock the system by bridging the Pt(II) sites with a bis-(diphenyl phosphino)ferrocene. As a result, an artificial molecular dyad **2** of platinum complex with constrained closed-butterfly like structure is achieved. Importantly, the orientation and rotation of the platinum(II) chromophores and ferrocene electron donor in dyad **2** are different from those of dyad **1**, which greatly influence the PET and CR processes. As will be discussed later, upon photo excitation of dyad **2**, the PET takes place from the ferrocene electron donor to the platinum(II) chromphore with the formation of long-lived CS state up to 27.4 μs, three times higher than that found in dyad **1**.

The synthesis of complexes **1-3** is summarized in Scheme S1 (Scheme S1). They all have good solubility in common organic solvents and were well characterized by MS, NMR (^{1}H & ^{31}P) and elemental analysis (Figure S1). The crystal structure of **2** shows a symmetric closed-butterfly like structure belonging to the monoclinic crystal system (Table S1, Figure S2). In contrast to the symmetric open-butterfly like structure of **1**, dyad **2** exhibits a cone conformation anchoring a pair of square-planar polypyridyl platinum(II) units in a face-to-face manner. Through double-point bonding of phosphine ferrocene ligand (DPPF), the twin polypyridyl platinum(II) branches are pinched together. The distance between the two platinum(II) metal centers was found to be 4.26 Å, indicating the absence of intramolecular Pt(II)-Pt(II) interaction. The closest distance between the two interplanar polypyridyl ligands is 3.40 Å but both ring systems are distorted from planarity imposed by the geometrical constraints, and thereby lessening the possibility of a strong π-π interaction. More strikingly, the platinum(II) units and ferrocene electron donor adopt almost perpendicular arrangement with the edge-to-edge distance between ferrocene and platinum(II) metal center being 2.80 Å. Clearly, the incorporation of calix[4]arene reorganized the platinum(II) units and ferrocene donor, leading to the orientation of the chromophore and electron donor in dyad **2** far from that in dyad **1**.

To examine whether the ferrocene group could be an effective electron donor, the electrochemical properties of dyad **2** and its reference **3** were studied by cyclic voltammetry in CH_2Cl_2. (Figure. S3). Dyad **2** exhibits a reversible oxidation process at +0.63 V and an irreversible oxidation process at a peak potential of +1.11 V in CH_2Cl_2. The former is ascribed to the redox process of $Fc^{0/+}$ on the ferrocene subunit,[17] and the latter is tentatively assigned to the rapid solvolysis of the resultant platinum(II) species. Evidently, the ferrocene group in dyad **2** is reduction active and capable of acting as a powerful electron donor. On the other hand, dyad **2** displays a reversible process at -1.43 V and can be therefore attributed to the one-electron reduction of the polypyridyl moiety.

Table 1. Photophysical and electrochemical data of **1** and **2** in CH_2Cl_2.

	λ_{abs} /nm^a (ε/L·mol^{-1}·cm^{-1})	λ_{em}^{a} (nm)	λ_{em}^{b} (nm)	$E^{1/2}_{red}$^{a,c} *vs Fc*$^{0/+}$	$E^{1/2}_{ox}$^{a,c} *vs Fc*$^{0/+}$
1	272(62800), 296(59800) 334(59500), 432(2300)	563	543_{max}, 584, 631	-1.54	+0.59
2	292(67000), 335(5560) 307(58000), 425(2100)	-	543_{max}, 585, 630	-1.43	+0.63 +1.11
3	291(68400), 332(42300) 375(15900), 437(1200)	543	524_{max}, 557, 604	-1.43	+1.08

[a] In CH_2Cl_2 at room temperature. [b] In 2-MTHF at 77 K. [c] CV in 0.1 M $^nBu_4NPF_6$ as supporting electrolyte; scan rate, 50 mV/s; reference electrode, 0.1 M Ag/$AgNO_3$.

Figure 1 shows UV-vis absorption spectra of platinum(II) complexes **1-3** in CH_2Cl_2, all of which exhibit intense absorption bands at wavelengths below 360 nm and a weak absorption band at ~420 nm. With reference to spectroscopic work on platinum(II) complexes,[12,16] the two absorption bands at $\lambda < 360$ nm and $\lambda > 400$ nm are assigned to the intralignd (IL) and the [d(Pt)→π*(RC^N^N)] MLCT state. The incorporation of a ferrocene group into the platinum(II) complex caused no change in the characteristic absorption of ^{1}MLCT state of dyads **1** and **2** as well as reference **3**, implying no significant electronic interaction between the ferrocene electron donor and the platinum(II) chromophore in the ground state.

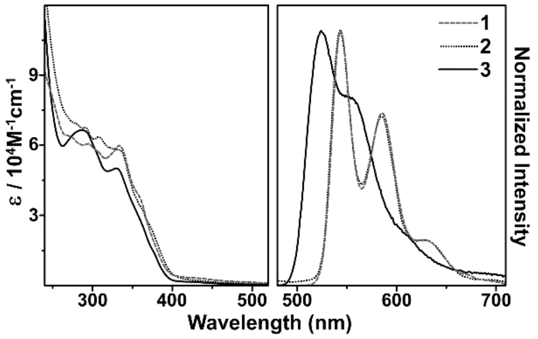

Figure 1. UV-vis absorption and emission spectra of complexes **1-3** in CH_2Cl_2 at room temperature, and in 2-MTHF at 77K (λ_{ex} = 425 nm)

In contrast, the emission behaviour of dyad **2** is quite different from that of reference **3**. Excitation of the ^{1}MLCT absorption at around 425 nm led to maximal emission at 543 nm for reference **3**, while no emission could be detected in dyad **2** at room temperature. Upon cooling to 77 K, dyad **2** became emissive with vibronic-structured emission at 543 nm (Figure.1). The vibrational spacing of 1300 cm^{-1} corresponding to the skeletal stretching of (RC^N^N) ligand suggests that the origin of the emission is derived from the ^{3}MLCT excited state in nature. As shown in Figure 1, the open butterfly-like dyad **1** displays a weak emission at λ_{max} = 563 nm with quantum yield of 0.011 in CH_2Cl_2, where degassed $Ru(bpy)_3(PF_6)_2$ in CH_3CN was used as the reference (Φ_r = 0.062).[18] Furthermore, the emission of dyad **2** was completely quenched in CH_2Cl_2 although its reference **3** was highly emissive. Evidently, there is intramolecular quenching of the excited platinum(II) chromophore by the ferrocene electron donor in dyads **1** and **2**. The greater quenching extent for dyad **2** than dyad **1** suggests a more efficient intramolecular quenching efficiency of dyad **2**. Since dyad **2** incorporated a redox-sensitive ferrocene group, spectroscopic changes were expected with the addition of an oxidant. Figure S4-S5 shows the UV-vis absorption and emission spectra changes of dyad **2** at various concentrations of $[Fe(ClO_4)_3]$ in CH_2Cl_2 at room temperature. Upon addition of $Fe(ClO_4)_3$ into solution, the emission of dyad **2** was gradually enhanced with a maximum at 552 nm, similar in energy to the typical ^{3}MLCT emission of reference **3**, but its absorption in the low-energy region remained unchanged. The results further confirm that there is no much interaction between the platinum(II) chromophore and ferrocene donor in dyad **2** in the ground state, but such interaction does occur in the excited state. Therefore, it is reasonable to consider that the intramolecular PET from the ferrocene group to the platinum(II) chromophore is responsible for the complete emission quenching.

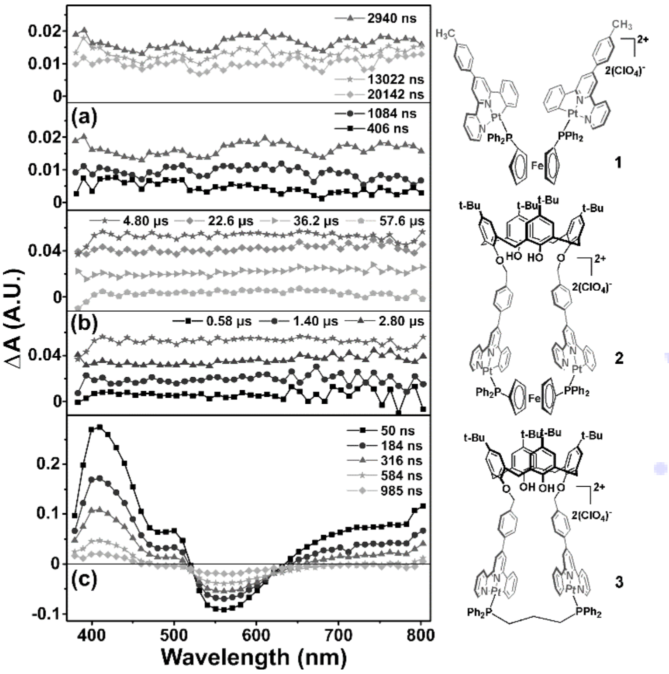

Figure 2. Transient absorption spectra of dyad **1** -**3** in CH_2Cl_2 at 298 K (λ_{ex} = 355 nm).

Table 2. Free energy changes of the PET and CR processes of dyad **1** and **2** in CH_2Cl_2.

Entry	$R_{D\text{-}C}$ (Å)^a	$E^{1/2}_{red}$	$E^{1/2}_{ox}$	E_{00} (eV)^c	ΔG_S (eV)^d	ΔG_{ET} (eV)^d	ΔG_{CR} (eV)^d	λ (eV)^d	k_{ET} s^{-1}	k_{CR} s^{-1}
1	5.37	-1.54	+0.59	2.29	- 0.30	- 0.46	-1.83	0.275	1.9×10^6	1.1×10^5
2	4.44	-1.42	+0.63	2.29	- 0.36	- 0.60	-1.69	0.165	8.3×10^5	3.6×10^4

[a] The value was directly obtained from the single crystal structure. [b] CV in 0.1 M $^nBu_4NPF_6$ as supporting electrolyte; scan rate, 50 mV/s; reference electrode, 0.1 M $Ag/AgNO_3$ in CH_3CN. Reversible peak. Irreversible peak. [d] Calculated from equations S1-S3 (supporting information), where E_{red} and E_{ox} refer to reduction and oxidation potential of the platinum(II) chromophore and the ferrocene group. E_{00} was the excited state energy of the platinum(II) chromophore, reading from the emission maximum at 77 K, $R_{D\text{-}C}$ refers to center to center distance between the donor and acceptor. r^+ and r^- are the radii of the oxidized donor and the reduced acceptor, respectively. *e* is the charge of the electron, ε_0 is the permittivity of the vacuum, ε_s is the relative dielectric constant of the solvent, *n* is the refractive index of the solvent.

The PET process in dyad **2** was directly observed by a flash photolysis experiment at room temperature. Figure 2 shows the time resolved absorption spectra of dyads **1**, **2** and **3**, respectively, in CH_2Cl_2 solution. Upon excitation by using 355 nm laser light, a strong transient absorption of the ^{3}MLCT state for reference **3** emerged immediately. The decay throughout the absorption region and recovery of the bleaching occurs on the same time scale, and can be well described by a mono-exponential function. The lifetime of 580 ns obtained from either the decays of the absorption or the bleaching recoveries is in agreement with that of the emission quenching. Dyad **2** displayed totally different decay curves from that of complex **3** but similar to the behavior of the open-butterfly like dyad **1**. According to the documented spectroscopic works on platinum(II) complexes,[13e,16a] The broad envelope from 400 to 600 nm, and 650 to 850 nm is originated from the radical anion of $[RC^{\wedge}N^{\wedge}N]^{-\bullet}$ ligand. The weak absorption feature at ~620 nm for the ferrocenium radical cation is submerged by the strong and broad absorption of the $[RC^{\wedge}N^{\wedge}N]^{-\bullet}$ radical anion.[19] Evidently, the electron transfer from the ferrocene group to the excited platinum(II) chromophore in dyad **1** and **2** operates. From the kinetics probed at 400 nm, a fast rise phase followed by a slow decay suggested that the PET led to the formation and the disappearance of the CS state in dyad **2** (Figure. S6). In comparison to that of dyad **1**, slower forward ET rate constant of 8.3×10^5 s^{-1} and much slower back CR rate (k_{CR}) of 3.6×10^4 s^{-1} were obtained in dyad **2** under the same conditions, which meant that the obtained lifetime of CS state is three-times higher than that in dyad **1**.

To shed light on the slower PET and CR processes, the free energy change Δ*G* and the reorganization energy λ of dyad **2** was estimated and compared with dyad **1** (Table 2).[18] Calculation revealed that the reorganization energy λ of 0.165 eV for dyad **2** is smaller than that of 0.275 eV for dyad **1** even though the donor acceptor distance ($R_{D\text{-}C}$) in dyad **2** is a shorter, a result of the introduction of calix[4]arene in the backbone. See from Table 2, the PET free energy changes ΔG_{ET} were determined to be -0.46 eV for dyad **1** and -0.60 eV for dyad **2**, and the charge recombination free energy changes ΔG_{CR} was -1.83 eV for dyad **1** and -1.69 eV for dyad **2**. Dyad **2** exhibited a much slower CR process than dyad **1** under the same condition probably due to a smaller λ in the relatively rigid structure. Moreover, the much smaller reorganization energy λ values than the negative ΔG_{ET} and ΔG_{CR} values for both dyad **1** and **2** indicated that the PET process and CR process both occurred in the Marcus inverted region.

On the basis of the above results, it could be speculated that the orientation of platinum(II) chromophore and the ferrocene electron donor plays an important role in the PET and CR processes. In the case of dyad **1**, the platinum(II) and ferrocene units are arranged in an open-butterfly like structure with interplanar angle of 64.52° and edge-to-edge distance of 3.46 Å. With the aid of calix[4]arene, dyad **2,** however, exhibits constrained closed-butterfly like conformation with the same chromophore and electron donor, in which the two polypyridyl platinum(II) units and ferrocene donor adopt almost perpendicular arrangement and the edge-to-edge distance between ferrocene and platinum metal center is 2.80 Å. Even in such a short distance, light absorbed by the platinum(II) chromophore gives its ^{3}MLCT excited state, which lies at 2.29 eV above the ground state. The PET reaction takes place from the ferrocene electron donor to the excited platinum(II) chromophore and yields the final products of CS state that lies 1.69 eV above the ground state. This means that the excitation energy of platinum(II) chromophore loses only 0.6 eV to reach the CS state of dyad **2** under the single-step PET condition. The close proximity of the second polypyridine unit on the inactive side of the dyad, which although not noticeably π-π coupled might also be providing a local electric and magnetic field effect similar to that known to be important in the case of the inactive M branch of photosynthetic reaction centres.[1,2a] Nature has optimized the charge separation process and developed a successful strategy to limit CR processes. The relative orientation of the reaction centre chromophores is highly conserved across a range of different species from trees to bacteria. The simplest way to set up a redox gradient would set up a co-facial array but the relative arrangement of the chromophores is quite complex highlighting the importance of orientation between the successive active chromophores of the natural CS apparatus.

In summary, a new calix[4]arene-based dinuclear platinum(II)-ferrocene dyad has been designed to demonstrate that subtle conformation constraint to alter the relative orientation of chromophores can have a significant influence on the PET and CR processes. The lifetime of 27.4 μs for charge separation state in dyad **2** is nearly three times longer than that in the reported butterfly-like structure of dyad **1** in which the same electron donor and chromophore was applied. The modulation of ET and CR rates by change in relative orientation of donor-acceptor pairs seen in this work suggests that orientation effects can be used to prolong the CS lifetimes in other artificial photosynthetic systems.

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Keywords: Orientation effect • PET • Long-lived charge separation • Platinum-ferrocene dyad • Calix[4]arene

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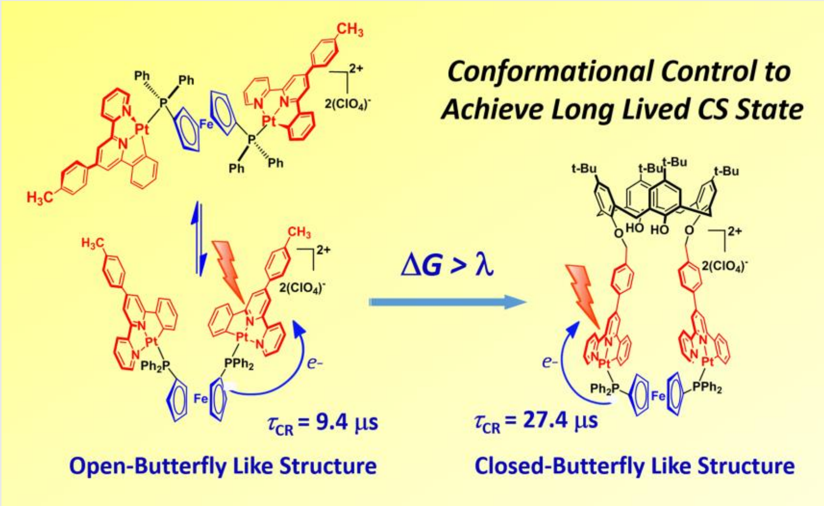

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