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Organoplatinum(II) Complexes with Chromophore–Acceptor Dyad Studied by Ultrafast Time-Resolved Absorption Spectroscopy

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Photoinduced electron-transfer (ET) reactions are fundamental steps in photosynthesis, and which have led to extensive investigations into charge-separated species in artificial mimics.[1] In the literature, many molecular systems based on d^6 metal-to-ligand charge transfer (MLCT) and porphyrin π–π^* chromophores have been developed for light-induced photocatalysis.[2] These chromophores have several advantages, including high absorptivity in the visible spectral region, favorable redox properties, and relatively long-lived excited states, the properties of which can be tuned by varying the auxiliary ligands.[3] Early developments in photoinduced ET catalysis focused on biomolecular reactions of triplet excited states of metal complexes. Studies on photoinduced multi-electron-transfer reactions of transition-metal complexes have led to many important observations, such as photoreduction of water using multicomponent systems, $[\mathrm{Ru(bpy)_3}]^{2+}$/EDTA/$\mathrm{MV}^{2+}$ (EDTA = ethylenediaminetetraacetic acid disodium salt) or [Pt(terpy)(arylacetylide)]$^+$/TEOA/MV^{2+} (terpy = 2,2′:6′,2″-terpyridine, TEOA = triethanolamine),[4] along with single-component system, EDTA/Ru-Pt^{2+}.[5] In the past decades, there have been extensive studies on the design of "chromophore-quencher" assemblies that comprise metal complex chromophores covalently linked to an organic electron donor or acceptor.[6,7] A key obstacle for light-to-chemical energy conversion is the efficient back electron-transfer reaction between the highly oxidized and reduced species generated by ET reactions of excited-state species. A way to minimize the back electron-transfer reaction is that the latter is in the Marcus inverted region, allowing the photochemically generated oxidized and reduced species to have sufficient lifetimes to undergo multi-electron-transfer reactions other than the back ET reaction.[8] Alternatively, the back ET reaction could be slowed down by the large reorganization energies required. Direct observation of inverted region behavior has been achieved by Gray and Winkler in a study of the back electron-transfer reactions between the products generated from the quenching of an electronically excited iridium(I) complex by pyridinium acceptors.[8a] Fukuzumi et al. also reported a long-lived charge-separated state with a lifetime of 10 μs involving the zinc(II) porphyrin-gold(III) porphyrin dyad in cyclohexane.[1f] In recent years, Eisenberg and coworkers have reported a class of dyads containing a cationic $[\mathrm{Pt(terpy)(C{\equiv}CAr)}]^+$ chromophore.[4d–g,9]

Herein we report the photoinduced ET reaction from $\mathrm{Pt^{II}}$ chromophore to viologen acceptor in a new [ClPt{C^N^N-(PhMV^{2+})}] (**1**; HC^N^N(PhMV^{2+}) = 4′-[*p*-(1-methyl-4,4′-bipyridinium-1′-yl)methylphenyl]-6-phenyl-2,2′-bipyridine) dyad (Scheme 1). Despite the large driving force, the backward electron-transfer reaction is around 10^3 times slower than the forward electron-transfer reaction.

For comparison, the Pt(diimine)-methylviologen bis(arylacetylide) dyad, $[\mathrm{Pt(MV\text{-}bpy)(C{\equiv}CPh)_2}](\mathrm{PF_6})_2$ (**3**; MV-bpy = 1-(4-(4′-methyl-2,2′-bipyridin-4-yl)butyl)-1′-methyl-4,4′-bipyridinediium), was synthesized, characterized, and examined for light-induced ET reaction (Scheme 2, and see the Supporting Information). Complexes [ClPt{C^N^N(PhMe)}] (**2**) and $[\mathrm{Pt(Me_2bpy)(C{\equiv}CPh)_2}]$ (**4**; $\mathrm{Me_2bpy}$ = 4,4′-dimethyl-2,2′-

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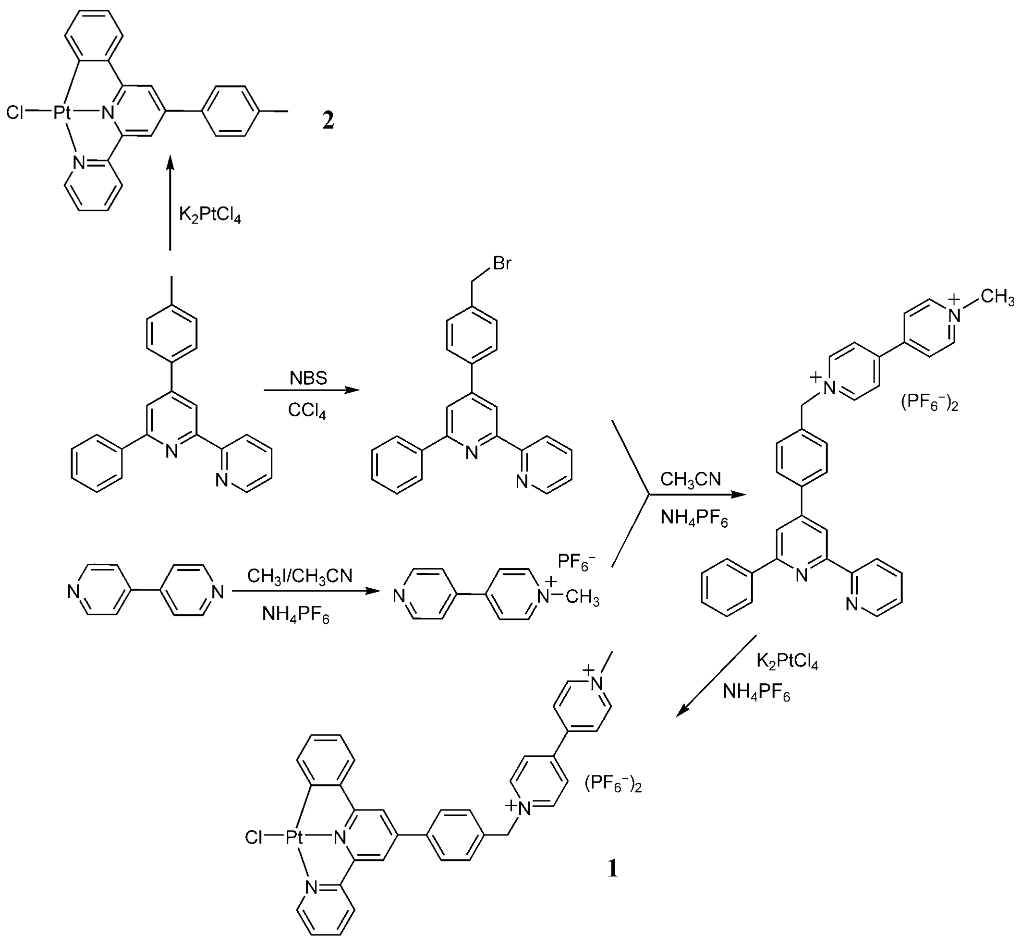
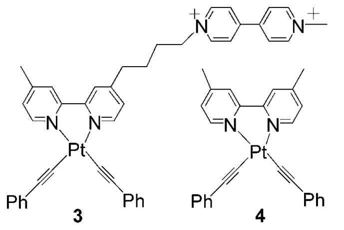


Scheme 1.



Scheme 2.

bipyridine) were prepared to model the photoinduced charge-transfer process for **1** and **3** respectively.

HC^N^N(PhMe) (4-(*p*-tolyl)-6-phenyl-2,2′-bipyridine) was prepared by the Kröhnke method,[10] and bromination was carried out in the presence of *N*-bromosuccinimide and a small amount of benzoyl peroxide in CCl_4. (1-Methyl-4,4′-bipyridinium)PF_6 was obtained by alkylation of 4,4′-bipyridine with CH_3I.[11] The MV^{2+}-appended 6-phenyl-2,2′-bipyridine ligand, HC^N^N($PhMV^{2+}$), was synthesized according to Scheme 1. Complex **1** and [ClPt{C^N^N(PhMe)}] (**2**) were synthesized according to literature methods.[12,13] The crystal structure of **1** was determined by X-ray crystallography (Figure 1).[14]

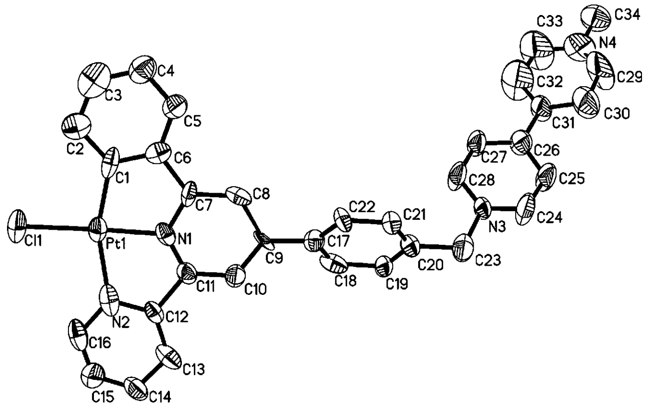


Figure 1. Structure of the dication of **1**, with H atoms omitted for clarity (30% probability ellipsoids). Selected bond lengths (Å) and angles (°): Pt1-C1 1.978(2), Pt1-N1, 1.944(1), Pt1-Cl1 2.325(4); C1-Pt1-N2 160.5(6), N1-Pt1-C1 81.9(6), N1-Pt1-Cl1 176.8(5).

The electronic absorption spectra of **1**, **2**, and MV^{2+} in CH_3CN are depicted in Figure 2. Complex **2** exhibits intense multiple ligand-centered (LC) absorption bands in the UV region, and a moderately intense metal-to-ligand charge transfer (MLCT) band at $\lambda_{max} = 425$ nm, with tailing extend-

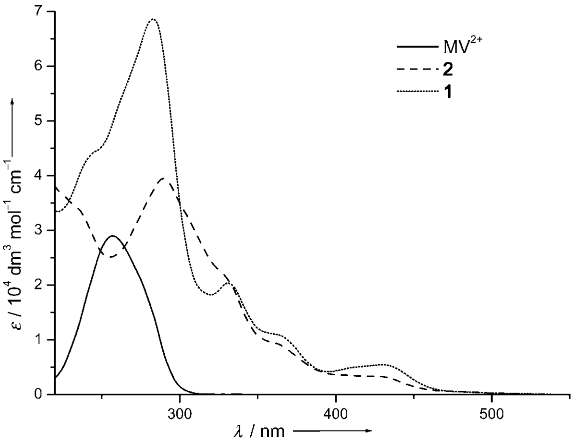


Figure 2. Absorption spectra of **1**, **2**, and MV^{2+} in CH_3CN at room temperature.

ed to ca. 550 nm. The absorption spectrum of **1** is approximately the summation of the spectra of **2** and MV^{2+}.

Complex **2** displays an emission at 556 nm in CH_3CN and at 562 nm in CH_2Cl_2 solution, the latter emission is much more intense.[12] The 556 nm emission of **2** in CH_3CN is quenched by MV^{2+} following Stern–Volmer behavior with a k_q value of $6.3\times10^9\,\text{M}^{-1}\text{s}^{-1}$ (Figures S1 and S2 in the Supporting Information). Complex **1** is non-emissive in CH_3CN solution at room temperature, presumably owing to rapid quenching of the ^{3}MLCT excited state of the [Pt(C^N^NPh)]$^+$ chromophore by MV^{2+}.

Energy transfer from the ^{3}MLCT state of [Pt(C^N^NPh)]$^+$ to the appended MV^{2+} in **1** is unfavorable in view of the lack of spectral overlap between the emission of **2** and absorption spectrum of MV^{2+} (Figure 2). To elucidate the rationale for the rapid intramolecular quenching, the cyclic voltammograms of **1**, **2**, and MV^{2+} were recorded in CH_3CN and the data are summarized in Table 1. Complex **2** displays an irreversible oxidation wave with $E_{pa}=+0.46$ V and a reversible reduction wave with $E_{1/2}=-1.70$ V. For **1**, similar irreversible oxidation with $E_{pa}=+0.55$ V and reversible reduction with $E_{1/2}=-1.69$ V were recorded. The consecutive reductions of the MV^{2+} moiety in **1** are reversible and occur at $E_{1/2}=-0.71$ and -1.15 V vs. Ag/AgNO$_3$.

Table 1. Electrochemical data[a] of **1**, **2**, and MV^{2+} in CH_3CN at 298 K.

Cmpd	$E_{pa}(Pt^{3+}/Pt^{2+})$ [V]	$E_{1/2}(MV^{2+}/MV^{+})$ [V]	$E_{1/2}(MV^{+}/MV^{0})$ [V]	$E_{1/2}(L/L^{-})$[b] [V]
MV^{2+}		-0.78	-1.22	
2	0.46			-1.70
1	0.55	-0.71	-1.15	-1.69

[a] Measured in CH_3CN containing 0.1 M nBu$_4$NPF$_6$ as supporting electrolyte. Solutions were ca. 1×10^{-3} mol dm^{-3} in complex, and potentials were obtained with reference to Ag/AgNO$_3$ electrode, scan rate = 50 mV s^{-1}. The $E_{1/2}(Cp_2Fe^+/Cp_2Fe)$ value is 0.07 V. [b] L = C^N^N(PhMe) for **2** or C^N^N(PhMV^{2+}) for **1**.

We attribute the oxidation wave of **1** with $E_{pa}=+0.55$ V to the oxidation of Pt^{II} to Pt^{III}, whereas the reversible reduction wave at -1.69 V is attributed to the reduction of the cyclometalated ($^-$C^N^NPh) ligand. The ΔG_{FET} value for the intramolecular oxidative quenching in **1** can be estimated by the Rehm–Weller equation:[15]

$$\Delta G_{FET} = E_{ox}(D) - E_{red}(A) - E_{00} - CSE \qquad (1)$$

As **1** is non-emissive, **2** was used as a model for the estimation of the excited-state energy (E_{00}), which is 2.51 eV according to the method by McMillin.[16] E_{ox}(D) and E_{red}(A) are the potential for $E_{1/2}(Pt^{3+}/Pt^{2+})$ and $E_{1/2}(MV^{2+}/MV^{+})$, respectively. The $E_{1/2}(Pt^{3+}/Pt^{2+})$ of **1** is estimated to $(0.55-0.08)$ V = 0.47 V, according to the difference in potentials (160 mV) between E_{pa} and E_{pc} of the Cp_2Fe^+/Cp_2Fe couple. CSE is the coulombic stabilization energy of the charge-separated species, being 0.06 eV in polar solvent. Thus, ΔG_{FET} of **1** was estimated to be -1.39 eV (Table 1), revealing that electron transfer from the ^{3}MLCT excited state of the Pt^{II} chromophore to MV^{2+} is thermodynamically feasible.

To better understand the photoinduced excited-state ET process, time-resolved absorption (TA) spectral measurement upon flashing a degassed CH_3CN or CH_3OH solution of **1** at room temperature was conducted. For **1** in degassed CH_3CN only, nanosecond laser flash photolysis revealed no spectral change. However, in the presence of methanol, the characteristic absorptions of $MV^{+\cdot}$ at 395 and 605 nm were found in the TA difference spectrum, suggesting that the solvent scavenged the photogenerated oxidized [Pt(C^N^NPh)]$^+$ chromophore (Figure 3).

When TEOA was used, net formation of $MV^{+\cdot}$ radical was readily observed upon photolysis of **1**+TEOA. Figure 4 depicts typical spectral changes observed during irradiation of **1**+TEOA (1:10) in degassed CH_3CN with a 200 W Hg lamp (using a filter with cut-off wavelength at 400 nm). The solution changed from a pale yellow to blue-green. In the solution containing TEOA and ligand HC^N^N(PhMV^{2+}) without the Pt^{II} complex, similar photochemical reaction

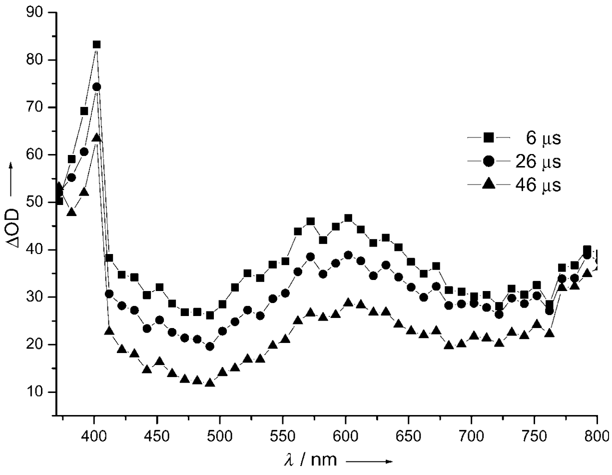


Figure 3. Transient absorption spectra of **1** monitored after 120 ns pulsed excitation at 355 nm in degassed CH_3OH at room temperature.

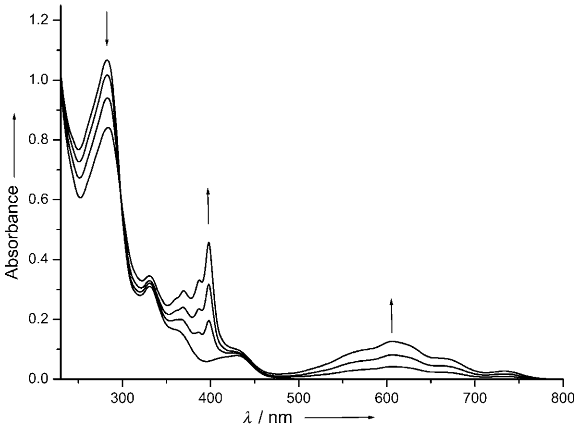
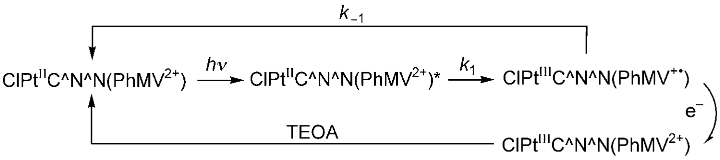


Figure 4. UV/vis spectra recorded during the irradiation of **1**+TEOA (1:10) solution in degassed CH_3CN at $\lambda > 400$ nm.

was not observed. The development of the absorption maxima at 395 and 605 nm could be attributed to the formation of methyl viologen radical cation as a result of oxidative decomposition of TEOA (Figure S3 in the Supporting Information). The concentration of $MV^{+\cdot}$ increased with the irradiation time and reached saturation after 40 min. Upon exposure to air, the blue-green color quickly faded and the absorbance of the MLCT absorption band at 430 nm was restored to the original value, revealing that no net photodecomposition of **1** had occurred (Figure S4 in the Supporting Information).

Femtosecond time-resolved absorption spectral measurement of **1** showed that upon excitation at 260 nm, the formation of the charge-separated species (Scheme 3) at the highest concentration was recorded at $t < 1$ ps (estimated time is ca. 400 fs) after the laser flash, revealing that the forward reaction rate constant k_1 is about 10^{12} s^{-1}. The charge-separated species $ClPt^{III}\{C^\wedge N^\wedge N(PhMV^{+\cdot})\}$ back decayed to the ground state via a unimolecular process with a rate constant (k_{-1}) of 1.6×10^9 s^{-1}. The results are depicted in Figures 5 and 6. The slower back electron-transfer process compared with the more rapid rate of formation (k_1) of the charge-separated species is striking as the driving force for the back reaction is around 1.18 V, whereas the driving force for the forward reaction is 1.39 V.



Scheme 3.

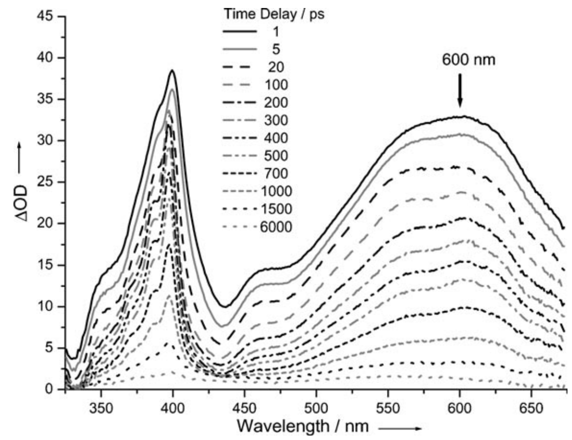


Figure 5. Transient absorption spectra of **1** monitored after 1 ps pulsed excitation at 266 nm in degassed CH_3CN at room temperature.

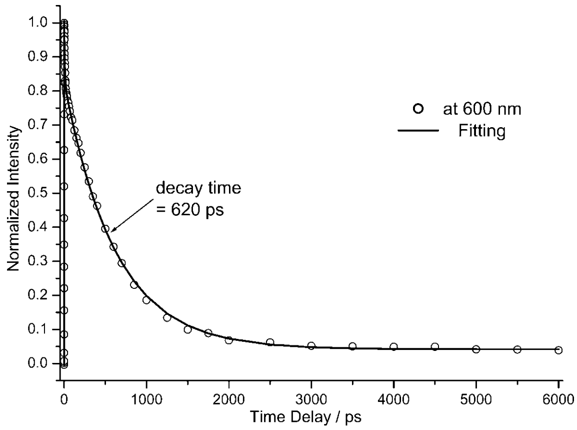


Figure 6. Decay traces of transient absorption spectra of **1** at $\lambda = 600$ nm in degassed CH_3CN at room temperature.

Importantly, we found that the slower back ET reaction than the forward light-induced ET reaction can also be observed in the Pt^{II} diimine-methylviologen bis(arylacetylide) system. The electronic absorption and emission spectra of both **3** and **4** in acetonitrile at 298 K are given in Figure 7, and the photophysical properties of **3**–**4** are described in the Supporting Information. The intramolecular charge-separated species $[Pt^{III}\text{-}MV^+]$ generated from **3** was detected by femtosecond time-resolved absorption spectroscopy ($\lambda_{max} =$

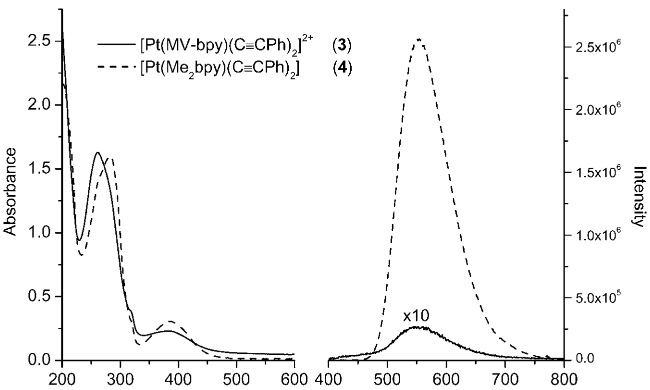


Figure 7. Absorption (left) and emission (right; $\lambda_{ex} = 380$ nm) spectra of **3** and **4** in acetonitrile at 298 K.

605 nm). The formation of charge-separated species for **3** occurred at ca. 40 ps after the laser flash; therefore the forward rate constant was estimated to be $2.5\times10^{10}\,s^{-1}$. The back ET monitored by decay of MV^+ absorption was a first-order process with a rate constant of $5.3\times10^{9}\,s^{-1}$ for **3** in CH_3CN solution at 298 K (Figure 8).

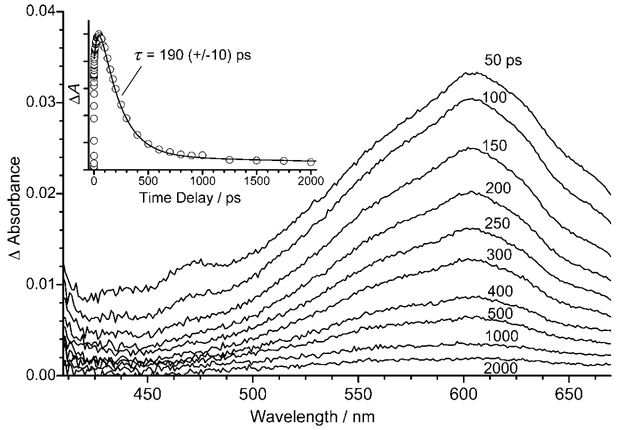


Figure 8. Room-temperature transient absorption spectra of **3** monitored after 50 ps pulsed excitation at $\lambda = 400$ nm in acetonitrile solution. Inset: decay traces of transient absorption spectra of **3** at $\lambda = 605$ nm.

The platinum(II) systems described in this work can catalyze light-induced generation of H_2. For example, in a solution mixture of **1** (2×10^{-5} M), TEOA (0.1 M), and colloidal platinum (5×10^{-5} M) in $MeCN/H_2O$ (4:1 v/v), H_2 gas was identified by GC analysis after 3 h of irradiation with a 500 W xenon lamp with excitation wavelength greater than 400 nm. Replacement of colloidal Pt by $CoCl_2$ in the photolysis gave H_2 generation in reduced amount (five turnovers after 4.5 h irradiation).

In summary, new platinum(II) chromophore–acceptor dyads have been synthesized. The back ET reaction rate constants of the two platinum(II) systems are slower than the forward electron-transfer reactions, despite the large driving force. Efforts to harness the slow back ET reactions of Pt^{II} chromophore–acceptor systems for light-induced multi-electron-transfer catalysis are in progress.

Experimental Section

Complexes **1** and **2** were prepared according to the literature method.[12] Characterization data for **1**: Yield: 30%; ^1H NMR (400 MHz, CD_3CN, TMS): $\delta = 4.40$ (s, 3H, CH_3), 5.92 (s, 2H, CH_2), 7.05 (m, 2H), 7.42 (d, $J = 6.9$ Hz, 1H), 7.46 (d, $J = 6.8$ Hz, 1H), 7.64 (d, $J = 8.2$ Hz, 2H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.73 (s, 1H), 7.95 (s, 1H), 8.00 (d, $J = 8.2$ Hz, 2H), 8.13 (t, $J = 8.0$ Hz, 1H), 8.19 (d, $J = 8.0$ Hz, 1H), 8.38 (d, $J = 6.9$ Hz, 2H), 8.44 (d, $J = 6.9$ Hz, 2H), 8.79 (d, $J = 6.2$ Hz, 1H), 8.85 (d, $J = 6.8$ Hz, 2H), 9.05 ppm (d, $J = 7.0$ Hz, 2H). Elemental analysis (%) calcd for $C_{34}H_{27}N_4ClF_{12}P_2Pt$ (1012.06): C 40.35, H 2.69, N 5.54; found: C 39.94, H 2.80, N 5.60. Vapor diffusion of diethyl ether into an acetonitrile solution of **1** afforded yellow-brown crystals suitable for X-ray crystallography.

For photoinduced hydrogen generation, each reaction solution was prepared in a test tube ($d = 25$ mm $\times$ $h = 150$ mm) with a volume of 10 mL in $MeCN/H_2O$ (4:1 v/v). The sample contained 2×10^{-5} M platinum(II) complex, 5×10^{-5} M colloidal platinum, and 0.1 M TEOA. A magnetic stir bar was placed in the test-tube, which was sealed with a rubber septum and degassed by bubbling N_2 for at least 15 min at room temperature in the dark. The test tube was immersed in a 500 mL water bath to maintain the reaction at about 20 °C. The reaction solution was irradiated with a 500 W xenon lamp, and cut-off filters were used to remove light with $\lambda <$ 400 nm. The amount of H_2 generated was identified by GC analysis using a 5 Å molecular sieve column, thermal conductivity detector, and argon carrier gas.

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Keywords: chromophores · electron transfer · hydrogen · platinum · viologen

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[14] CCDC 638117 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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