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Highly Efficient Photoproduction of Charge-Separated States in Donor−Acceptor-Linked Bis(acetylide) Platinum Complexes

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In the 21st century, research in pure and applied science has mainly been focused on discovering artificial systems that mimic natural photosynthetic systems.[1] Recently, considerable advancements in multichromophoric systems, including multistep electron transfer, have been made.[2] However, these systems do not always exhibit efficient, long-lived charge-separated (CS) states. The most promising strategy is a spin-control approach using a chromophore undergoing rapid intersystem crossing.[3] Metal (Ru, Ir, Pt) complexes that exhibit intense phosphorescence at room temperature via strong spin−orbit coupling (SOC) are desirable for this purpose.[4] Such complexes provide a new route for generating triplet dyes, as has been recently demonstrated.[5] This approach can be applied to CS systems.[6] Eisenberg and co-workers showed that some D−Pt−A complexes, in which Pt is linked with an electron donor (D) and acceptor (A), undergo photoinduced charge separation to produce the CS state $D^+{-}Pt{-}A^-$.[7] The CS-state formation efficiency was estimated as 10−30% in some cases,[7b] with a lifetime of 75−230 ns.[7] This low efficiency was attributed to the occurrence of rapid electron back-transfers in partial CS states ($D^+{-}Pt^-{-}A$ or $D{-}Pt^+{-}A^-$).[7b] Further, the identification of the spin state of $D^+{-}Pt{-}A^-$ has not been reported. Here we report a highly efficient system ($\Phi_{CS} = 0.96{-}0.97$) with clear identification of the long-lived CS state.

The new triads MTA−Pt−MNDI (**1**) and MTA−Pt−NDI (**2**) contain dimethoxydimethyltriphenylamine (MTA) as the donor and a naphthalene diimide [(M)NDI] as the acceptor. These chromophores were bonded to the Pt moiety through highly twisted phenylene ethynylene linkages. MTA$^+$ and (M)NDI$^-$ exhibit strong, well-characterized absorptions in different wavelength regions (see below); this enables the detection and quantification of the CS states.

1 and **2** exhibit comparable spectral and redox properties. The UV−vis spectrum of **1** in toluene shows the longest absorption band (MMLL′CT,[8] $\lambda_{max} = 430$ nm) attributed to the Pt chromophore (Figure 1). The shorter absorption bands are attributed to MTA ($\lambda_{max} = 300$ nm) and MNDI ($\lambda_{max} = 380$ nm). These absorptions were almost superimposed with those of their components (D, A, and Pt), suggesting negligible electronic interactions between them in the ground state. The model compound **3** shows strong phosphorescence ($\lambda_{em} = 560$ nm) at room temperature in solution under deaerated conditions, while **1** shows considerably weaker phosphorescence (Figure 1, inset), suggesting that fast electron or energy transfer from the locally excited triplet state of the Pt chromophore ($^3LE_{Pt}$) occurs.

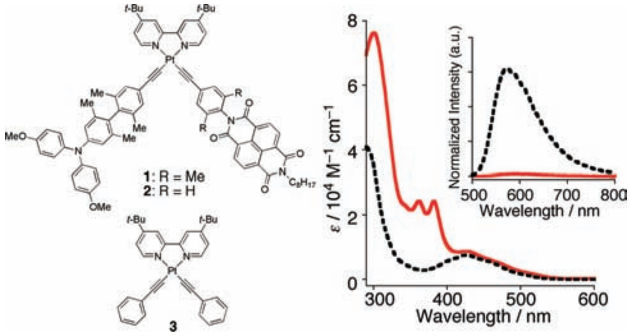

Figure 1. Molecular structures of **1**, **2**, and **3** and UV−vis and (inset) phosphorescence spectra of **1** (red line) and model complex **3** (black dashed line) in toluene at room temperature.

1 showed the following redox potentials (in V vs Fc/Fc$^+$) in CH_2Cl_2: $E_{1/2}(MTA/MTA^+) = +0.16$; $E_p(Pt/Pt^+) = +0.92$; $E_{1/2}(MNDI/MNDI^-) = -1.06$; $E_{1/2}(MNDI^-/MNDI^{2-}) = -1.51$; $E_p(Pt/Pt^-) = -1.89$. The CS state energies (E_{CS}) in solvents of different polarities were evaluated as follows using the dielectric continuum model:[9] 1.87 eV in toluene; 1.18 eV in THF; 0.95 eV in butyronitrile (Tables S1 and S2 and Figure S1 in the Supporting Information). The energy of $^3LE_{Pt}$ estimated from the 0−0 transition in the phosphorescence spectrum of **3** in glassy MTHF (2.48 eV, Figure S2) is higher than that of $^3LE_{MNDI}$ (~2.0 eV)[6c,10] but lower than that of $^3LE_{MTA}$ (2.88 eV).[11]

Figure 2a shows transient absorption spectra of **1** in toluene at room temperature under 400 nm laser-pulse excitation (400 fs fwhm). Immediately after excitation (1 ps), a broad peak with $\lambda_{max} = 650$ nm was observed. A similar 650 nm absorption was observed in the transient spectra of **3** (Figure S3); this indicates that the 650 nm absorption corresponds to the T−T absorption of $^3LE_{Pt}$ induced by very fast intersystem crossing in $^1LE_{Pt}$. Within 1 ns, the initially observed 650 nm absorption disappeared, and new absorptions with maxima at 470, 610, and 750 nm appeared. The 470 and 610 nm absorptions are assigned to MNDI$^-$, while the 750 nm absorption is assigned to MTA$^+$; these radical ions were independently generated by electrochemical reduction and oxidation of **1** (Figure S4). Thus, the transient spectrum after 1 ns is clearly assigned to the CS state.

A priori, two routes of for CS-state formation are possible: (A) electron transfer via a triplet state of the acceptor ($^3LE_{Pt} \rightarrow {}^3LE_{MNDI}$

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10.1021/ja904241r CCC: $40.75

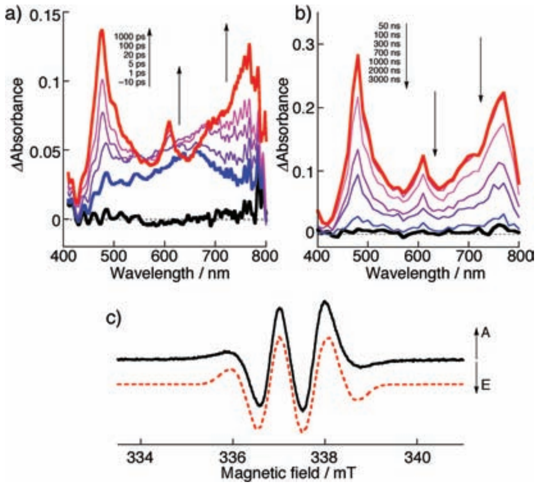

Figure 2. (a) Picosecond and (b) nanosecond transient spectra of **1** in toluene. (c) Time-resolved EPR spectrum recorded in direct detection mode (A, absorption; E, emission) after laser-pulse irradiation (442 nm) of **1** in MTHF at room temperature; the red dashed line is the simulated spectrum for the SCRP state.

→ CS) and (B) sequential electron transfer via a partial CS state ($^3LE_{Pt}$ → [D−Pt$^+$−A$^-$ or D$^+$−Pt$^-$−A] → CS).

Interestingly, the formation rates of MNDI$^-$ and MTA$^+$ are different and solvent-dependent. In toluene, $\tau_{470} = 220$ ps and $\tau_{750} = 250$ ps (Figure 2a). In butyronitrile, $\tau_{470} = 126$ ps and $\tau_{750} = 21$ ps. In THF, there are two-component rises: $\tau_{470}(1) = 146$ ps (77%), $\tau_{470}(2) = 829$ ps (23%); $\tau_{750}(1) = 77$ ps (62%), $\tau_{750}(2) = 615$ ps (38%). These results are best explained by assuming route B for the CS-state formation in polar solvents, because route A involves the simultaneous formation of MNDI$^-$ and MTA$^+$. MTA$^+$ is formed faster than MNDI$^-$ in butyronitrile and THF, whereas MNDI$^-$ is formed slightly faster in toluene. Similar trends were observed for **2** (Table S3).

Figure 2b shows nanosecond transient spectra of **1** under 355 nm excitation.[12] The lifetime was determined to be $\tau_{470} = 839$ ns (single exponential) in toluene. Shorter lifetimes were observed in polar solvents as double exponentials: 64 ns (34%) and 123 ns (66%) in butyronitrile; 40 ns (49%) and 124 ns (51%) in THF. The lifetimes of the CS state in **2** were as follows: $\tau_{470} = 1340$ ns (100%) in toluene; 105 ns (100%) in butyronitrile; 48 ns (63%) and 181 ns (37%) in THF. The double-exponential decays observed in the polar solvents could be due to conformational isomers that may form around the acetylene bonds (Figure S5). Surprisingly, the CS states in the rigid MTHF matrix are very long lived at low temperature (90 K): $\tau = 35$ μs (46%) and 135 μs (54%) for **1**; $\tau = 46$ μs (57%) and 248 μs (43%) for **2**.

The CS-state formation efficiency was determined from the molar absorptivities of the radical ions and photon numbers of the excitation light, which were estimated using a chemical actinometer, $[Ru(bpy)_3]^{2+}$, by our previously reported procedure.[13] The quantum yield for CS-state formation was determined to be $\Phi_{CS} = 0.96$ for **1** and 0.97 for **2** in toluene.

The time-resolved electron paramagnetic resonance (EPR) technique was successfully applied to the present system. Under 442 nm laser-pulse excitation in MTHF at room temperature, **1** showed a polarized spectrum characteristic of the spin-correlated radical pair (SCRP) state[14] with an AEAEAE pattern (Figure 2c; Figure S6 shows the spectra in other solvents). The observed phase pattern was reproduced by assuming a triplet precursor ($^3LE_{Pt}$) of the SCRP state, a positive exchange interaction ($J = +0.05$ mT)[15] in the CS state, and the following radical ion parameters: $g = 2.0035$ for MNDI$^-$ [16] and 2.0032 for MTA$^+$; $a^N = 0.9$ mT.[17]

In conclusion, we have developed a highly efficient CS system with a long lifetime for the CS state (SCRP state) using D−Pt−A complexes with highly twisted π linkers; this approach allows efficient formation of D$^+$−Pt−A$^-$, in which the SOC effect is minimized by the elimination of the unpaired electron from the Pt moiety, giving rise to a long-lived CS state. Further studies, including temperature and medium effects on the lifetime of the CS states and molecular design to control the SOC effect, are in progress.

Acknowledgment. This work was partially supported by a Grant-in-Aid (20750034) from MEXT, Japan.

Supporting Information Available: Detailed synthetic methods for **1** and **2**, Tables S1−S3, and Figures S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA904241R