Toward a Molecular Photochemical Device: A Triad for Photoinduced Charge Separation Based on a Platinum Diimine Bis(acetylide) Chromophore

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Received June 26, 2001

One of the fundamental steps in photosynthesis after light absorption and electron−hole creation is charge separation. In the design of molecularly based artificial systems for light-to-chemical energy conversion, this is approached by the placement of donor and acceptor moieties at specific positions on the absorber or chromophore, leading to the construction of two- and three-component systems—i.e., dyads and triads.[1−17] A number of such three-component donor-chromophore-acceptor (D−C-A) systems have been reported including ones based on d^6 Ru(II) tris(diimine) and Re(I) diimine chromophores and longer-lived charge-separated excited states have been achieved.[10,15,18−20] The electronic influence of the connection between individual components in triad systems has also been examined,[2,21] and more complex systems have been constructed that are able to achieve energy storage, such as through the light-driven formation of ATP.[22,23] In the present communication, we describe the first D−C−A triad in which the chromophore is a Pt diimine center. Through extensive investigations during the past decade, the nature of the Pt diimine excited state has been established as a charge transfer-to-diimine in which the highest occupied or donor molecular orbital varies in composition.[24−27] For square planar Pt diimine bis(acetylide) complexes that are brightly emissive in solution, the HOMO is metal-based and the excited state is ^{3}MLCT.[24]

The triad described in this study, shown as **I**, has a phenothiazine (PTZ) donor and a nitrophenyl ($PhNO_2$) acceptor. On the basis of the direction of the excited-state charge transfer for the Pt diimine chromophore, the phenothiazine is attached to the acetylide ligands while the nitrophenyl acceptor is bound to the diimine. The synthesis of **I** is carried out via a multistep sequence illustrated in Scheme 1. The nitrophenyl-linked phenanthroline (**A**) is synthesized by two Pd-catalyzed Sonogashira/Hagihara couplings that serve to insert an ethynylene moiety between the diimine and the acceptor, while the PTZ-linked aryl acetylide ligand is formed as the neutral acetylene (**B**) by PTZ alkylation of *p*-bromobenzyl iodide followed by another Pd-catalyzed coupling. Once properly derivatized, the ligands are complexed stepwise to Pt(II) by diimine substitution into $PtCl_2(PhCN)_2$ to give **C** and CuI-catalyzed reaction of the deprotected acetylene with **C** to yield triad **I**. For comparison with **I**, two dyads, one without the *p*-nitro substituent (**II**) and the other without the PTZ donor (**III**), have also been prepared and characterized (see Supporting Information).

Electrochemical measurements show that triad **I** is in principle capable of functioning in its envisioned capacity. In 1:1 MeCN/DMF solution, **I** exhibits a pseudo-reversible reduction at −0.92V (SCE) and a reversible reduction at −1.20 V.[28] While the latter is similar in value to that seen for the model compound Pt(5-PhC≡Cphen)(C≡CPh)$_2$ and for other Pt diimine bis(acetylides),[24] the former is a more facile reduction associated with the nitrophenyl group. This assignment is supported by an observed reduction of 5-(*p*-nitrophenylethynyl)phenanthroline (**A**) at −1.03 V (SCE) in MeCN. Triad **I** also shows two irreversible oxidations at ca. 0.8 and 1.4 V in 1:1 MeCN/DMF. The latter is similar to values reported for Pt diimine bis(acetylides)[24] while the former, which is also seen for the D−C dyad **II**, corresponds to PTZ

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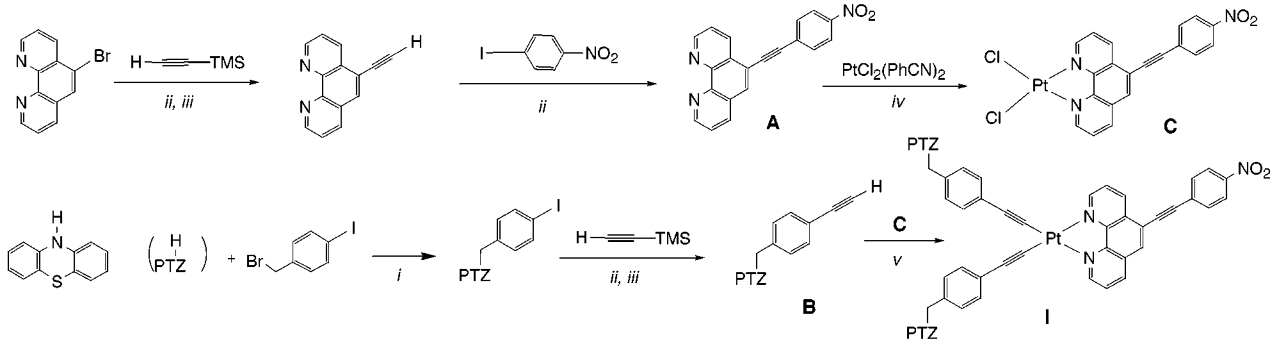
[28] CV was preformed using 0.10 M $TBAPF_6$ as an electrolyte in MeCN or 1:1 MeCN/DMF referenced to Fc/Fc$^+$ couple at 0.40 V (SCE).

10.1021/ic015559u CCC: $20.00

Scheme 1 [a]



[a] (i) LDA, THF, −78 °C, RT. (ii) $Pd(PPh_3)_2Cl_2$ (10 mol %), CuI (10 mol %), $HN(^iPr)_2$, RT. (iii) K2CO3, THF, MeOH, RT. (iv) $CHCl_3$, 70 °C. (v) CuI (10 mol %), CH_2Cl_2, NEt_3.

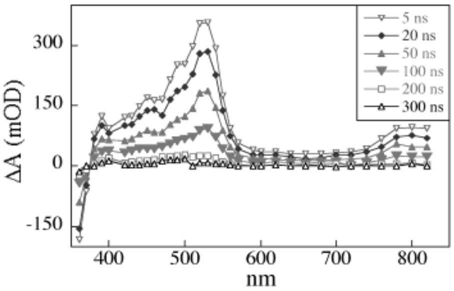


Figure 1. TA spectra with time delays of 5−300 ns for 0.07 mM **I** in DMF at room temperature with excitation at 405 nm.

oxidation.[18] For comparison, *p*-ethynylbenzyl(N-phenothiazine) (**B**) exhibits a reversible oxidation at 0.75 V.

Like previously reported Pt diimine bis(acetylide) complexes, **I**−**III** exhibit characteristic MLCT absorption bands centered around 400 nm with ϵ of ca. 12000−14000 M^{-1} cm^{-1} in DMF. In addition, triad **I** and dyad **III**, which both contain the *p*-nitrophenyl moiety, show an absorption at 360 nm in DMF that is assignable to it, whereas dyad **II** gives no evidence of such an absorption. In contrast with the bright luminescence of platinum bis(acetylide) complexes in fluid solution, triad **I** and dyad **II** are nonemissive, while dyad **III** is weakly luminescent. The emission from **III**, which appears at 625 nm in DMF, is approximately 20 times weaker than that found for the model compound Pt(5-PhC≡Cphen)(C≡CPh)$_2$ (λ_{em} of 595 nm in DMF).[24]

To establish that charge separation was indeed occurring in **I** upon excitation, transient absorption (TA) experiments were conducted. TA spectra were obtained at 298 K using previously described instrumentation.[29] The TA spectrum of a 0.07 mM solution of **I** in DMF (Figure 1) shows several features including a strong absorption at 525 nm, a weaker set of absorptions between 390 and 500 nm with intensity of ca. 150 mOD, a strong bleach of 200 mOD at ca. 360 nm, and an isosbestic point at 385 nm. There is also a weak absorption at ~800 nm. All of the features decay exponentially with a single time constant of 70 ± 5 ns in DMF, indicating that they correspond to a single species. The strong absorption at 525 nm corresponds to the $PTZ^{+\cdot}$ radical cation based on other studies of intermolecular charge transfer.[18−20] The broad feature between 390 and 500 nm overlaps the reported signal of the nitrobenzene radical anion at ~455 nm in DMF,[30] while the bleach at 360 nm correlates with depletion of ground-state nitrophenyl upon excitation. All of the results are thus consistent with the formation of the charge separated $D^+{-}C{-}A^-$ species for **I** upon excitation. For neither of the dyads **II** and **III** was a transient signal seen, indicating that any charge separation achieved on irradiation had a lifetime of less than 15 ns.

In CH_2Cl_2 similar results are obtained with 95% of the signal decaying exponentially with a single time constant 75 ± 5 ns. A minor, long-lived (ms) component is also seen at ~550 nm, but its nature has not yet been determined. Throughout the TA spectra in either DMF or CH_2Cl_2, no formation kinetics were observed, indicating that formation of the charge-separated species occurs within 15 ns.

The difference in energy between the excited state and the ground state was estimated from the onset of emission at 504 nm (2.46 eV, 19 840 cm^{-1}) in the luminesence spectrum of **I** in a 1:3 mixture of CH_2Cl_2/toluene at 77 K (see Supporting Information). On the basis of the respective electrochemical oxidation and reduction of PTZ and $PhNO_2$ moieties, the charge separated state in **I** ($D^+{-}C{-}A^-$) transiently stores 1.67 V. From estimates of the excited-state redox potentials of the Pt diimine bis(acetylide) chromophore, the charge separated intermediates $D{-}C^+{-}A^-$ and $D^+{-}C^-{-}A$ can be calculated to be ca. 2.3 and 1.95 V higher in energy than the triad ground state, respectively, but neither is observed directly, indicating rapid charge transfer to form the charge-separated triad ($D^+{-}C{-}A^-$) from either $D{-}C^+{-}A^-$ or $D^+{-}C^-{-}A$.

Our study has thus shown that triads using a Pt diimine bis(acetylide) chromophore such as **I** can be constructed and that the chromophore ^{3}MLCT excited state can be utilized for photoinduced charge-transfer processes. Efforts to increase the lifetime and otherwise utilize the charge separated state in such systems are in progress.

Acknowledgment. We wish to thank the Department of Energy, Division of Chemical Sciences, for support of this research. Y.-J.K. thanks Kangnung National University for financial support during 2000 for sabbatical study.

Supporting Information Available: Characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

IC015559U

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