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Forum

Platinum Chromophore-Based Systems for Photoinduced Charge Separation: A Molecular Design Approach for Artificial Photosynthesis

Soma Chakraborty,[†] Thaddeus J. Wadas,[†] Heidi Hester,[‡] Russell Schmehl,*,[‡] and Richard Eisenberg*,[†]

Department of Chemistry, University of Rochester, Rochester, New York 14627, and
Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

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Photoinduced charge separation is a fundamental step in photochemical energy conversion. In the design of molecularly based systems for light-to-chemical energy conversion, this step is studied through the construction of two- and three-component systems (dyads and triads) having suitable electron donor and acceptor moieties placed at specific positions on a charge-transfer chromophore. The most extensively studied chromophores in this regard are ruthenium(II) tris(diimine) systems with a common ^{3}MLCT excited state, as well as related ruthenium(II) bis(terpyridyl) systems. This Forum contribution focuses on dyads and triads of an alternative chromophore, namely, platinum(II) di- and triimine systems having acetylide ligands. These d^8 chromophores all possess a ^{3}MLCT excited state in which the lowest unoccupied molecular orbital is a π^* orbital on the heterocyclic aromatic ligand. The excited-state energies of these Pt(II) chromophores are generally higher than those found for the ruthenium(II) tris(diimine) systems, and the directionality of the charge transfer is more certain. The first platinum diimine bis(arylacetylide) triad, constructed by attaching phenothiazene donors to the arylacetylide ligands and a nitrophenyl acceptor to 5-ethynylphenanthroline of the chromophore, exhibited a charge-separated state of 75-ns duration. The first Pt(tpy)(arylacetylide)$^+$-based triad contains a trimethoxybenzamide donor and a pyridinium acceptor and has been structurally characterized. The triad has an edge-to-edge separation between donor and acceptor fragments of 27.95 Å. However, while quenching of the emission is complete for this system, transient absorption (TA) studies reveal that charge transfer does not move onto the pyridinium acceptor. A new set of triads described in detail here and having the formula [Pt(NO$_2$phtpy)(*p*-C≡C–C$_6$H$_4$CH$_2$(PTZ-R)](PF$_6$), where NO$_2$phtpy = 4′-{4-[2-(4-nitrophenyl)vinyl]phenyl}-2,2′;6′,2′′-terpyridine and PTZ = phenothiazine with R = H, OMe, possess an unsaturated linkage between the chromophore and a nitrophenyl acceptor. While the parent chromophore [Pt(ttpy)(C≡CC$_6$H$_5$)]PF$_6$ is brightly luminescent in a fluid solution at 298 K, the triads exhibit complete quenching of the emission, as do the related donor–chromophore (D–C) dyads. Electrochemically, the triads and D–C dyads exhibit a quasi-reversible oxidation wave corresponding to the PTZ ligand, while the R═H triad and related C–A dyad display a facile quasi-reversible reduction assignable to the acceptor. TA spectroscopy shows that one of the triads possesses a long-lived charge-separated state of ∼230 ns.

Introduction

Solar energy utilization for industrial, portable, and electrical energy represents one of the grand challenges for the 21st century, and within that challenge, photosynthesis will play a key role. For large-scale production of carbon-containing fuels based on biomass, natural photosynthesis serves as the means for conversion of light to chemical energy, while for a hydrogen-based technology, artificial photosynthesis may prove to be the basis for fuel generation, although alternatives exist such as the direct conversion of

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* To whom correspondence should be addressed. E-mail: russ@tulane.edu (R.S.), eisenberg@chem.rochester.edu (R.E.).

[†] University of Rochester.

[‡] Tulane University.

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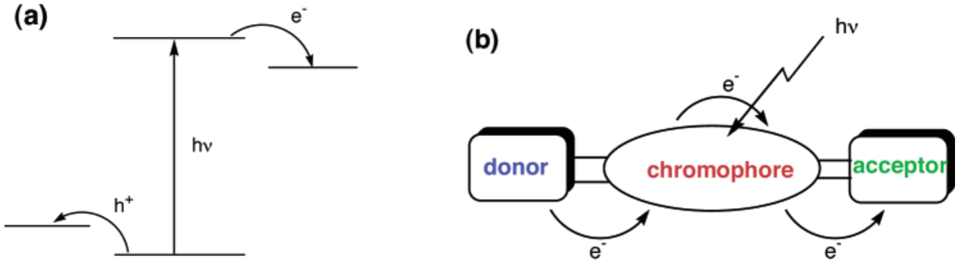

Figure 1. Simplified energetics (a) and arrangement (b) of a molecular photochemical device for photoinduced CS.

sunlight to electrical energy using photovoltaics followed by water electrolysis (such electrical energy, however, has been described as very expensive).[1−3] For artificial photosynthesis, the criteria that must be fulfilled for success parallel closely those addressed elegantly by nature in plants and algae. These include (1) visible-light-harvesting systems for the efficient capture of solar energy and its transfer to a photochemical reaction center, (2) a charge-transfer chromophore that effectively leads to the creation of an electron−hole pair from which all subsequent chemistry flows, (3) the separation of the electron−hole pair into oxidizing and reducing equivalents with its attendant work by an electron-transfer sequence, (4) the separate collection of reducing and oxidizing equivalents for chemical reactions because photochemical events are generally single-electron events, whereas the production of fuels proceeds normally by even electron chemistry, and (5) catalysis of the desired reactions for the formation of fuels and stable oxidants such as molecular oxygen.[1,4,5] Each of these points has fostered much study, and numerous articles, reviews, and volumes have been written about each of them. In this Forum contribution, we focus on only one aspect of artificial photosynthesis, namely, photoinduced charge separation (CS).

Molecular Triads for Photoinduced CS. In the design of molecularly based systems for light-to-chemical energy conversion, this step is approached by placement of suitable electron donor and acceptor moieties at specific positions on an absorber/chromophore to yield two- and three-component systems, i.e., dyads and triads.[5−65] The approach follows Balzani's formulation of a supramolecular photochemical device that can be diagrammed in terms of donor,

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acceptor, and chromophore redox couples in the ground and excited states as shown in Figure 1.[66,67] The excited state of the chromophore is sufficiently reducing to transfer an electron to the acceptor, while the oxidized chromophore is sufficiently oxidizing to accept an electron from the donor. In this scenario, the chromophore excited state is oxidatively quenched, but it is also possible to envision related systems that proceed via reductive quenching, with electron transfer to the chromophore occurring initially. The process of photoinduced CS such as that illustrated in Figure 1 represents the critical initial step following photon absorption from which productive chemistry can ensue, leading in principle to stored chemical energy in artifical photosynthesis.

During the past 15 years, numerous triads and associated or precursor dyads have been prepared and studied in an effort to facilitate photoinduced CS and maximize the lifetimes of the resultant CS states. Generally, in these molecularly designed systems, the chromophore is a Ru(II) d^6 tris(diimine) or a bis(terpyridyl) moiety with a ^{3}MLCT excited state (there is arguably no luminescent chromophore more extensively studied in transition-metal chemistry than the parent of these systems, $Ru(bpy)_3^{2+}$), while donors are most often readily oxidizable organic molecules and acceptors are either organic or metal complex components capable of facile reduction.[14,42,60,68−81] Two examples of such triads are shown as **1**[25] and **2**[82] (Chart 1). These systems, which have a chromophore linked to both a donor and an acceptor, can be referred to as D−C−A triads (for **2**, there are two acceptors and one donor). Alternative topologies for triads are possible in which, for example, the chromophore is linked to a primary acceptor that, in turn, is connected to a secondary acceptor for the creation of CS such as **3**.[83]

Systematic variation of donor and acceptor components for a given chromophore has fostered numerous studies on the driving force dependence of the sequential electron transfers for CS and charge recombination (CR). While CS represents the critical initial step in artificial photosynthesis following photon absorption, CR is one of the great obstacles that must be overcome to have an *efficient* light-driven

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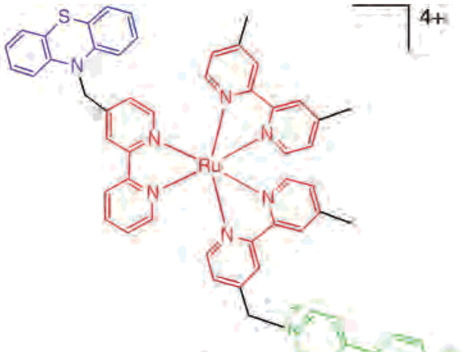
Chart 1



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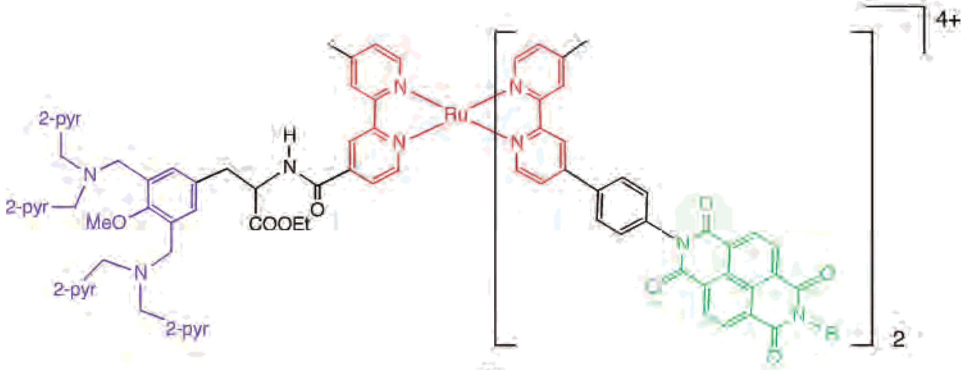

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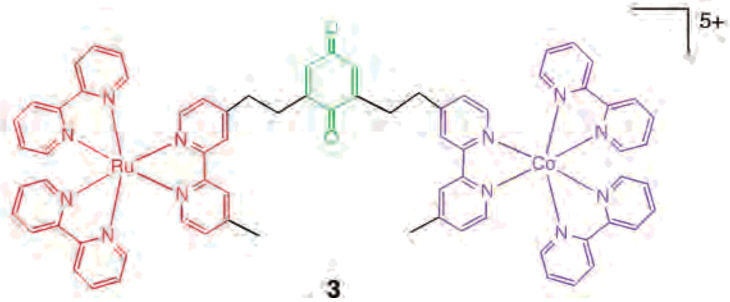

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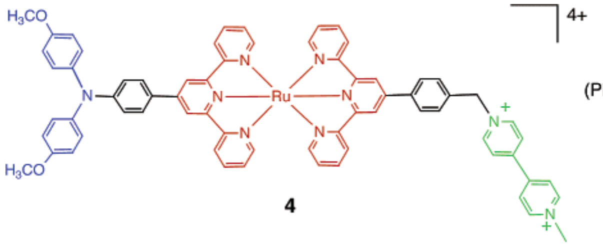
energy-storing reaction. For a comprehensive analysis of the dynamics and relative rates of CS and CR from an energetics standpoint, it is essential to know the redox potentials of the donor, the acceptor, and the chromophore in both its ground and excited states.

For CS, it is desirable to have only a minimum thermodynamic driving force ΔG sufficient to give essentially complete quenching of the excited state because additional free energy consumed in the quenching reaction becomes unavailable for subsequent energy-storing reactions. The dependence of the activation energy $\Delta G^{\ddagger}$ for electron transfer on the driving force of the reaction ΔG is given by the well-known equation from Marcus shown as eq 1, where ΔG relates to the electrochemical potential ΔE of the reaction and λ corresponds to the reorganization energy of reactants and solvent. As ΔE for the quenching reaction increases, $\Delta G^{\ddagger}$ for the reaction decreases until $\Delta G^{\circ} = -\lambda$. at which point the reaction is activationless and after which the Marcus inverted region is encountered in which the rate decreases with increasing driving force. For efficient CS, one wants to retard CR (or the "back" reaction) relative to the forward or CS reaction. Equation 1 suggests that this may be done by placing CR firmly in the Marcus inverted region; this notion would also necessitate a modest driving force at best for the CS reaction because the sum of $\Delta G_{\mathrm{CS}} + \Delta G_{\mathrm{CR}}$ is limited by the excited-state energy of the chromophore. These energetic considerations are most often based on measured and calculated redox potentials for the electroactive components of the triad.

$$\Delta G^{\ddagger} = (\Delta G^{\circ} + \lambda)^2/4\lambda \qquad (1)$$

In the construction of D−C−A triads, many different connections between the components differing in rigidity and distance have been employed to further probe the path dependence and dynamics of the electron transfers in these systems. The D−C−A triads shown as **1** and **2**, for example, have been found to have charge-separated states that exist with lifetimes of 115 and 27 ns, respectively, and transiently stored energy of approximately 1.14 and 1.59 eV based on simple electrochemical analyses of donor oxidation and acceptor reduction potentials. Analyses of the dynamics of systems such as **1** and **2** are complicated, however, by the existence of different positional isomers for component attachment that leads to a range of separations between the donor and acceptor. Moreover, if the particular triad possesses a flexible linker between the chromophore and redox-active component, the separation within a given isomer is really an average over all possible conformations.

Indeed, it was to remove some of the uncertainty in the separation of D and A, as well as to maximize that separation, that led to the creation of triads based on the Ru(tpy)$_2^{2+}$ chromophore despite the fact that its excited state is much shorter lived than Ru(bpy)$_3^{2+}$. In these elegantly constructed Ru(tpy)$_2^{2+}$ systems, the existence of positional isomers is removed and the redox-active components are connected along the principal chromophore axis. One such example is **4**,[32] which in light of **1** is found to have a disappointingly short CS state of <100 ns. It is also found that whereas CS into a phenothiazene donor occurs readily for the ruthenium tris(diimine)-based triads, it does not occur in the case of the [PTZ-Ru(tpy)$_2$-MV]$^{4+}$ triad (PTZ = phenothiazene; MV = methylviologen) analogous to **4**. Differences in the redox potentials of the different Ru chromophores clearly affect the efficacy of both donors and acceptors to achieve CS. This is just one example.



4

The use of porphyrins as the chromophore in triads and higher multicomponent systems for photoinduced CS is extensive and beyond the scope of what we can cover in this Article. However, the existence of such constructions is important to recognize, and their success in achieving relatively long-lived charge-separated states is notable. The following two examples are illustrative.[84−87] In the first, Gust et al. have prepared a series of molecular pentads based on a porphyrin dyad (P−P), a carotenoid polyene (C), and a diquinone moiety (QA−QB) as an acceptor.[88] All of the pentads undergo photoinduced electron transfer from the C−*P−P−QA−QB singlet state, with one of them generating a final charge-separated state of C$^{•+}$−P−P−QA−QB$^{•−}$ with a quantum yield of 0.83 and a CS state lifetime of 55 μs. In this system, about half of the initial porphyrin excited singlet state energy is preserved as chemical potential, with the remainder going into CS. In the second example reported by Guldi et al., an extremely long-lived (1.6 s at 163 K) charge-separated state has been successfully obtained in a tetrad consisting of a ferrocene, a pair of zinc porphyrins and a fullerene (Fc−ZnP−ZnP−C60) with a quantum yield of 0.34.[89] This work follows an earlier study on a related Fc−ZnP−H2P−C60 system that also exhibited long-lived photoinduced CS.

Platinum Diimine and Terpyridyl Chromophores. Another class of chromophores for possible use in photoinduced CS and artificial photosynthesis consists of d^8 Pt(II) complexes containing diimine or terpyridyl ligands. These systems have been studied by us and others over the past decade and a half in terms of their photophysical properties, the nature of their emitting states, their ability to undergo electron-transfer quenching, and their incorporation into dyads and triads for CS.[90−135] The diimine-based systems

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have the general formula Pt(diimine)L_2, where the diimine corresponds to 2,2′-bipyridine, 1,10-phenanthroline, or a derivative thereof and L_2 is a dianionic chelate or two monoanionic ligands. For these chromophores, the lowest unoccupied molecular orbital (LUMO) is localized on a π^* orbital of the diimine ligand, while the nature of the highest occupied molecular orbital (HOMO) varies with the ancillary ligands L. For systems with L_2 = dithiolate, the HOMO possesses mixed-metal and dithiolate character, while for the bis(arylacetylide) complexes ($L = C{\equiv}CAr$), the HOMO consists predominantly of a Pt d orbital. For the acetylide complexes, the resultant ^{3}MLCT state is intensely luminescent in fluid solution with high emission quantum yields and excited-state lifetimes between 0.1 and 3.0 μs.

The cationic platinum terpyridyl acetylide systems display bright solution emission with a microsecond-lived excited state.[116,117,120] As with the diimine bis(acetylide) chromophore, the excited state responsible for the luminescence is a ^{3}MLCT transition originating from a Pt d orbital to a π^* (terpyridine) orbital.[116,117,119] In addition to having all of the inherent properties similar to the platinum diimine bis(acetylide) chromophore, the cationic platinum terpyridyl acetylide system has the potential advantage of providing better solubility based on its positive charge for dyads and triads containing it in polar organic media.

Both the platinum diimine bis(acetylide) and platinum terpyridine acetylide systems undergo facile electron-transfer quenching with both electron-transfer donors and acceptors.[104,105] Despite the ease of quenching in which the metal center is reduced or oxidized, the complexes are only photostable under reductive quenching conditions, i.e., in the presence of an electron donor. In the presence of an electron acceptor, the complexes exhibit slow decomposition upon irradiation. This is in contrast to the Ru(II) chromophores related to $Ru(bpy)_3^{2+}$, which generally undergo oxidative quenching while maintaining photostability.

In view of the fact that the platinum diimine (arylacetylide)$_2$ and cationic platinum terpyridyl arylacetylide complexes undergo electron-transfer quenching, it is useful to estimate excited-state reduction and oxidation potentials for these systems, which can be done simply by using eqs 2 and 3, respectively. The E_{00} transitions are estimated using either the 77 K emission maximum or the room-temperature emission maximum adjusted to reflect the fact that the room-temperature maximum does not correspond exactly to E_{00} (it is not uncommon to estimate E_{00} using the high-side energy of the emission band at 10−20% of its maximum intensity). For calculation of the excited-state reduction potentials, the first diimine/terpyridine reduction wave, which is reversible or quasi-reversible in all cases, is used, while for estimation of the excited-state oxidation potentials, the irreversible Pt(II) → Pt(III) oxidation waves of the complexes are employed. The irreversible oxidation waves, while not rigorously correct for use in a thermochemical cycle, provide a good measure within the series of complexes of the relative ease of oxidation, and therefore the estimates of excited-state oxidation potentials can be made for internal comparison.

$$E(\mathrm{Pt}^{*/-}) = E_{00} + E(\mathrm{Pt}^{0/-}) \qquad (2)$$

$$E(\mathrm{Pt}^{*/+}) = E_{00} - E(\mathrm{Pt}^{+/0}) \qquad (3)$$

The excited-state energies of the Pt(II) chromophores are generally higher than those found for the ruthenium(II) tris(diimine) systems, although both sets of chromophores have ^{3}MLCT excited states with a HOMO primarily of metal d-orbital character and a LUMO localized on a π^* orbital of the diimine or heterocyclic aromatic ligand. For use in multicomponent systems for photoinduced CS, the Pt chromophores need to operate in a reductive quenching mode for reasons of long-term photostability. Estimates of excited-state reduction potentials for the platinum diimine bis(acetylide) complexes of ~1.0−1.3 V versus NHE obtained using eq 2 show them to be moderately good photooxidants.[105]

Platinum Diimine Chromophore-Based Triad. The directional nature of the excited-state charge transfer in the platinum diimine and terpyridyl complexes made the placement of donor and acceptor moieties clear for photoinduced CS in triads. The acceptor functionality was to be connected to the heterocyclic aromatic ligand, a π^* orbital of which serves as the LUMO in the chromophore, whereas the donor

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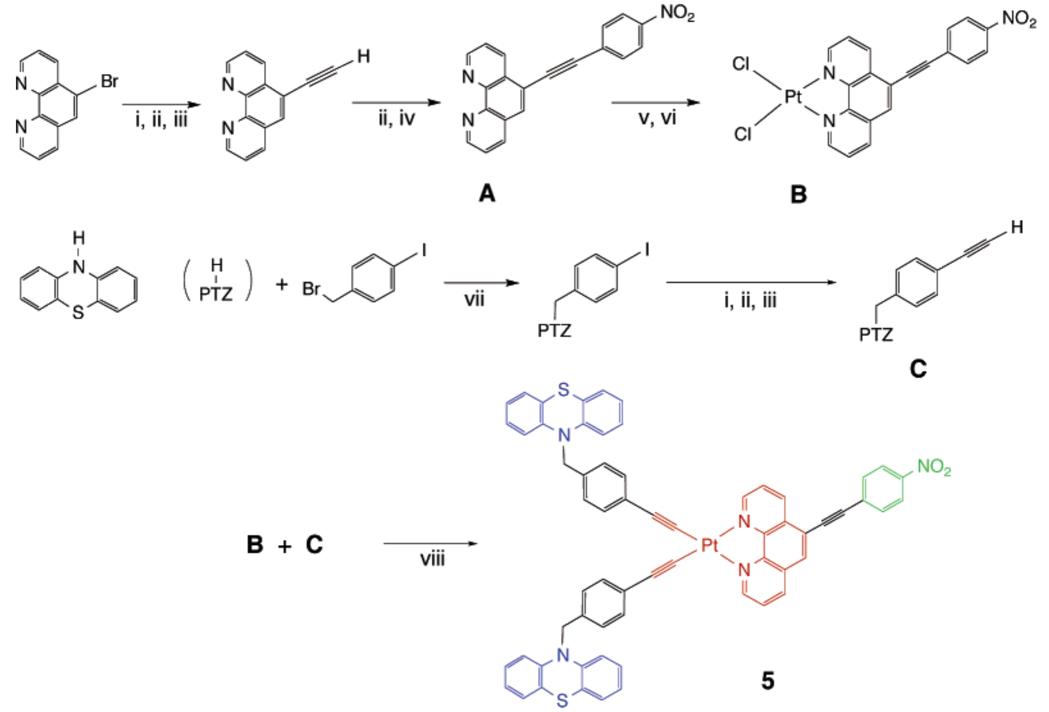
Scheme 1 [a]



[a] (i) TMSCCH. (ii) Pd(PPh$_3$)$_2$Cl$_2$ (5−10 mol %), CuI (5−10 mol %), NR$_3$. (iii) K$_2$CO$_3$, MeOH. (iv) *p*-I(C$_6$H$_4$)NO$_2$. (v) PtCl$_2$(PhCN)$_2$. (vi) CHCl$_3$, 70 °C. (vii) LDA, THF, −78 °C, RT. (viii) CuI (10 mol %), CH$_2$Cl$_2$, NEt$_3$.

entity was to be linked to the Pt center through the acetylide ligand. The first Pt-based triad, shown as **5**, was synthesized following this strategem via the multistep sequence shown in Scheme 1, in which several Sonogashira/Hagihara couplings were employed. The donor in **5** was PTZ, while the acceptor was nitrophenyl. For comparison with **5**, two dyads, one without the *p*-nitro substituent and the other without the PTZ donor, corresponding to D−C and C−A dyads, respectively, were also prepared and studied.

Electrochemical measurements showed that **5** was capable of achieving photoinduced CS with both a more facile oxidation (for PTZ) and a more facile reduction (for nitrobenzene) than were found for the Pt chromophore alone. With regard to electronic spectroscopy, triad **5** and both associated dyads exhibited characteristic MLCT absorption bands centered around 400 nm characteristic of the platinum diimine bis(acetylide) chromophore. However, in contrast with the bright luminescence of platinum diimine bis(acetylide) complexes in a fluid solution, triad **5** and the D−C dyad were found to be nonemissive, while the C−A dyad was seen to be weakly luminescent.

Establishment of CS in **5** was demonstrated using transient absorption (TA) spectroscopy experiments. The TA spectra were obtained at room temperature from CH$_2$Cl$_2$ and DMF solutions with excitation at 405 nm. Several transient features including a strong absorption at 525 nm, weaker absorptions between 390 and 500 nm, a pronounced bleach at ca. 360 nm, and a weak absorption at ∼800 nm were observed and found to decay exponentially with a single time constant (70 ± 5 ns in DMF; 75 ± 5 ns in CH$_2$Cl$_2$), indicating that they belong to a single species. An isosbestic point at 385 nm was also seen. The strong absorption at 525 nm corresponds to the PTZ$^{\bullet+}$ radical cation, while the broad feature between 390 and 500 nm overlaps with the reported signal of the nitrophenyl radical anion at ∼455 nm in DMF.[136] The bleach at 360 nm correlates with depletion of the ground-state nitrophenyl moiety upon excitation. All of the results were thus consistent with the formation of the charge-separated D$^{\bullet+}$−C−A$^{\bullet-}$ species for **5** upon excitation.

From the standpoint of energetics, the difference between the ground and excited states of **5** was estimated from the 77 K emission band for the triad in frozen CH$_2$Cl$_2$/toluene to be 2.46 eV. On the basis of the respective electrochemical oxidation and reduction of the PTZ and PhNO$_2$ moieties, the charge-separated state in **5** (D$^{\bullet+}$−C−A$^{\bullet-}$) can be estimated to transiently store 1.67 eV. Because only the decay of the charge-separated state of the triad (D$^{\bullet+}$−C−A$^{\bullet-}$) to the ground state was observed in the TA experiments on a nanosecond time scale, we conclude that the lifetimes of the species leading to its formation, i.e., D−C*−A and D$^{\bullet+}$−C$^{\bullet-}$−A, were less than 15 ns.

In a separate study,[112,137] D−C dyads were prepared and studied in which 4,4′-di(ethoxycarbonyl)bipyridine and 4,4′-di-*tert*-butylbipyridine were the diimine ligands, while PTZ and 2-(trifluoromethyl)phenothiazine functioned as the one-electron donors. When the diimine was 4,4′-di-*tert*-butylbipyridine, the emission intensity was observed to be solvent-dependent, with significant luminescence quenching occurring in polar solvents but not in nonpolar solvents. Intramolecular electron transfer was observed by TA spectroscopy, and analysis of the photophysical and electrochemical data

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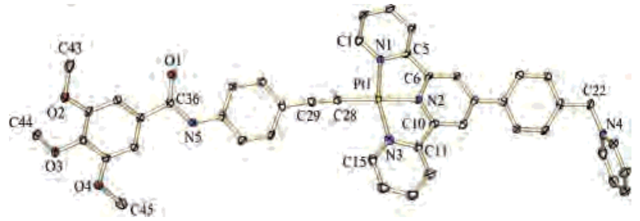
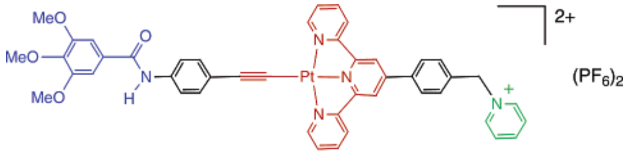


Figure 2. Crystal structure of the complex dication of **6** at 50% probability ellipsoids. Hydrogen atoms and solvent molecules of crystallization have been omitted for clarity.

suggested that while CS appeared to be in the Marcus normal region, CR was found to be in the inverted region.

Synthesis and Characterization of New Pt(tpy)-Based Dyads and Triads. The first triad based on the platinum terpyridyl arylacetylide chromophore is [Pt(pytpy)(*p*-C≡C-*p*-C_6H_4−NH−CO−$C_6H_2(OMe)_3$]$(PF_6)_2$ (**6**), where pytpy = 4′-(4-pyridin-1-ylmethylphenyl)-2,2′;6′,2″-terpyridine. The 3,4,5-trimethoxybenzamideacetylide ligand was synthesized by the reaction of trimethoxybenzoyl chloride with *p*-ethynylaniline, while the acceptor-functionalized terpyridyl ligand was prepared by bromination of tolylterpyridine (ttpy) followed by refluxing of the bromo derivative in neat pyridine. The molecular structure of triad **6**, shown in Figure 2, reveals the anticipated arrangement of a distorted square-planar geometry around the Pt(II) center, with three coordination sites occupied by the terpyridyl ligand and the fourth taken up by the acetylide donor. The edge-to-edge separation between the donor and acceptor fragments in this triad system is ca. 28 Å.

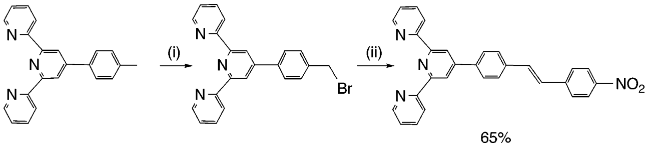


6

While the parent chromophore is strongly emissive, the D−C−A triad **6**, as well as the related D−C dyad, exhibits complete quenching of emission, consistent with efficient reductive quenching of the excited state. On the other hand, the corresponding C−A dyad was found to be emissive with a lifetime similar to that of the chromophore. The TA results for these systems are totally consistent with the quenching observations: the TA spectra of the D−C−A triad and D−C dyad are essentially identical, as are those of the C−A dyad and the parent chromophore. The results clearly show that the pyridinium acceptor is not involved in charge transfer in these systems and indicate the need for a change in either acceptor or acceptor linkage to achieve effective CS. Similar failures in terms of CS have been noted with different donors in Ru-based triads and underscore some of the factors that must be taken into consideration in the design of such systems.

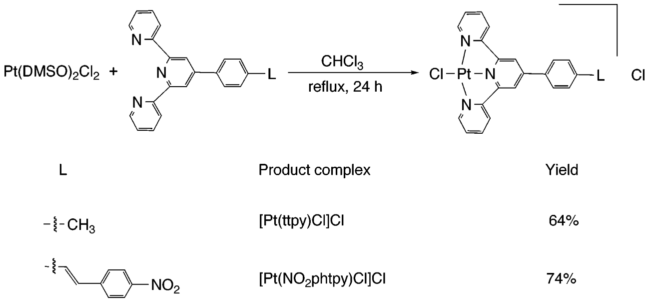
As part of this Forum contribution, we describe here a new set of dyads and triads based on the cationic platinum terpyridyl acetylide chromophore **7**. In addition to their syntheses and spectroscopic and electrochemical characterization, we report photophysical studies including TA spectra of the D−C−A triads and the related D−C and C−A dyads that show one of the triads to have a relatively long-lived CS state ($D^{\bullet+}$−C−$A^{\bullet-}$).

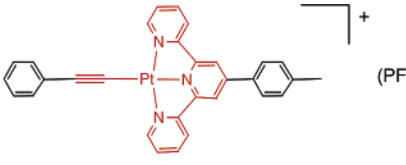
Scheme 2 [a]



[a] (i) *N*-Bromosuccinamide, dibenzoyl peroxide, CCl_4, 100 °C. (ii) $P(OEt)_3$, 120 °C, 1 h; *p*-nitrobenzaldehyde, K(*t*-BuO), THF, RT, 2 h.

Scheme 3





7, [Pt]

Details of the syntheses and characterizations of new compounds reported in this paper can be found in the Supporting Information. In these new systems, the acceptor is the nitrophenyl moiety and its attachment to the terpyridyl ligand is accomplished by a Horner−Emmons−Wadsworth reaction as shown in Scheme 2. The coordination of both the ttpy and NO_2phtpy ligands to give the respective complexes [Pt(ttpy)Cl]Cl and [Pt(NO_2phtpy)Cl]Cl was accomplished by a modification of a previously reported procedure in refluxing $CHCl_3$ and is shown in Scheme 3.[138−140]

As the donor moiety in these new Pt-tpy-based systems, both PTZ and its 5-methoxy derivative (MPZ) were employed. The synthesis of the different arylacetylide dyads and triads was accomplished by a CuI-catalyzed chloride-to-acetylide exchange[119,141−144] that was employed previously

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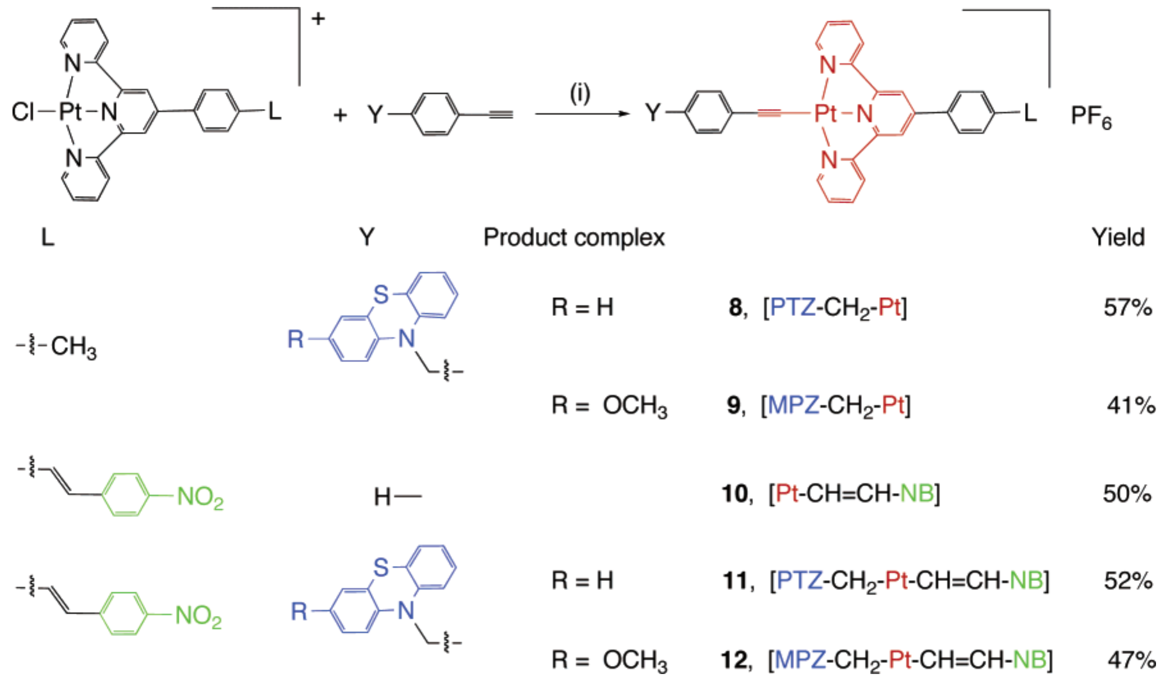
Scheme 4 [a]



[a] (i) CuI (10 mol %), DMF, NEt_3, NH_4PF_6.

to synthesize **5** and related dyads,[104,112] as well as other platinum acetylide complexes (Scheme 4).[145,146]

Complexes **8**−**12** were characterized by ^1H NMR and Fourier transform infrared spectroscopies, electrospray ionization mass spectrometry, and high-resolution mass spectrometry (HRMS), but valid and consistent elemental analytical data were difficult to obtain. Repeated attempts on dried, spectroscopically pure samples of compounds **8**−**12** led to highly variable results that were always low in C and occasionally low in N, so the chemical composition of the new systems was confirmed by HRMS, as summarized in the Experimental Section (see the Supporting Information). The spectroscopic data support the assignment of these complexes as monocationic with a geometry similar to that reported for **6** in which the Pt(II) center is surrounded by the terpyridyl ligand and the acetylide donor in a distorted square-planar arrangement.

While the NO_2phtpy ligand exhibits the expected ^1H NMR spectrum with two vinylic protons in a trans orientation ($J = 16.4$ Hz), the vinylic resonances merge into a distinct singlet upon coordination in **10**−**12** as well as in the precursor complex [Pt(NO_2phtpy)Cl]Cl. These unexpected singlets most likely result from an accidental degeneracy of the chemical shifts of the vinylic protons upon coordination. Evidence in support of this notion is provided by the ^1H NMR spectrum of triad **11** at 150 °C (Figure S1 in the Supporting Information) in which a splitting in the vinyl resonance is seen as the chemical shift degeneracy is lifted at higher temperature. Also, in the ^1H NMR spectra, the protons adjacent to the methoxy substituent of the MPZ ligand of **9** and **12** exhibit distinct 3- and 4-bond H−H coupling (8.45 and 2.4 Hz).

Table 1. Quantum Yield Values and Electrochemical Data[a] ($E_{1/2}$[b] Values for Reductions and Oxidation Waves) for Pt Dyads and Triads

compound	λ_{em} (nm)[c]	λ_{em} (nm)[d]	ϕ_{em}[e]	oxidation E (V)	reduction E (V)
7	630	550	0.022	1.68[f]	−0.55, −1.06
8		555	0.033×10^{-2}	1.05, 1.74[f]	−0.55, −1.06
9		548	0.024×10^{-2}	0.99, 1.75[f]	−0.53, −1.05
10	630	590	<0.001	1.64[f]	−0.56, −0.75, −1.07
11		548	0.04×10^{-3}	1.07, 1.63[f]	−0.56, −0.76, −1.07
12		552	0.02×10^{-3}	0.99, 1.66[f]	−0.56, −0.74, −1.06
NO_2phtpy					−0.57, −0.76, −1.23
Ttpy					−0.55

[a] Measured using 0.1 M tetrabutylammonium hexafluorophosphate in 1:1 DMF/MeCN at 50 mV/s at 293 K. Potentials in volts are versus NHE as calibrated using the ferrocene/ferrocenium couple at 0.40 V versus SCE (see the Experimental Section). [b] $E_{1/2} = 1/2[E_{max}(\text{cathodic}) + E_{max}(\text{anodic})]$. [c] Measured at room temperature in MeCN. [d] Measured at 77 K in 1:4 MeOH/EtOH. [e] Determined using $Ru(bpy)_3^{2+}$ as a standard in MeCN at room temperature. [f] Irreversible under experimental conditions.

Electrochemically, triads **11** and **12** and the associated dyads show the expected number of oxidation and reduction waves as obtained by cyclic voltammetry (Table 1, with redox potentials given relative to NHE using the Fc/Fc^+ couple as an internal standard). Prior studies of the electrochemistry of the Pt(tpy)(acetylide) complexes by Tung and Wu had shown the systems to undergo an irreversible oxidation and two reversible tpy-based reductions,[119] and in the present study, the chromophore is found to exhibit identical behavior, although the irreversible oxidation is seen at somewhat higher potential (1.68 V) than that previously reported (1.10 V versus SCE). The new triads and associated dyads all exhibit this same irreversible Pt-centered oxidation at 1.63−1.75 V, but in addition, the systems having a PTZ-based donor (**8**, **9**, **11**, and **12**) show a less anodic, quasi-reversible oxidation at 0.99−1.07 V assignable to the

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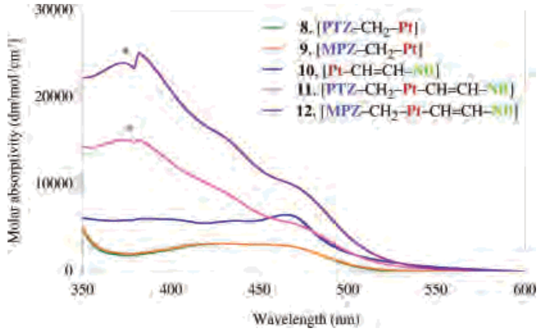

Figure 3. Room-temperature absorption spectra of the D−C dyads (**8** and **9**), C−A dyad (**10**), and D−C−A triads (**11** and **12**) in MeCN. An asterisk denotes an instrumental artifact.

donor.[73,74,112,147] The observed potentials for the latter correlate with the electron-donating ability of the PTZ donors, shifting to less positive potentials from those having the parent PTZ donor in **8** and **11** to those of the more strongly donating 5-methoxyphenothiazene derivatives (**9** and **12**).

While chromophore **7** and D−C dyads **8** and **9** exhibit two tpy-based reductions at −0.53 and −1.00 V, triads **11** and **12** and the C−A dyad **10** all undergo three quasi-reversible reductions (Table 1). In an analogous way under the same conditions, free tolylterpyridine shows one tpy-based reduction at −0.55 V, while the acceptor-functionalized ligand NO$_2$phtpy exhibits three reversible reductions. For CS in the acceptor-linked systems, the first reduction couple should correspond to a nitrophenyl-based reduction while the second and third should be tpy-based. However, because of the similarity in the first reduction potentials of those systems without a nitrophenyl moiety (**7**−**9**) and those with (**10**−**12**), definitive assignment of the first and second reductions for the latter is not possible in the absence of other data. It should be noted, however, that in **10**−**12** the acceptor group may be more like nitrostilbene than nitrophenyl and thus more easily reduced.

Absorption and Emission Spectroscopy of New Pt(tpy)-Based Dyads and Triads. The room-temperature absorption spectra of triads **11** and **12** and the associated dyads (**8**−**10**) in MeCN all exhibit multiple absorptions between 200 and 600 nm (Figure 3). While the higher energy absorptions (λ < 350 nm; $\epsilon \sim 10^4$ dm^3 mol^{-1} cm^{-1}) are mainly intraligand-based transitions originating within the acetylide and terpyridyl ligands, as well as a charge-transfer transition involving the Pt−C≡CR part of the molecules,[119,148] transitions with $\lambda > 400$ nm ($\epsilon \sim 10\,000$ dm^3 mol^{-1} cm^{-1}) correspond to a ^{3}MLCT transition involving dπ(Pt) → π*(tpy).[117−120,149−152] The dyad and triad systems having the nitrophenyl acceptor (**10**−**12**) possess an additional nitrophenyl-based transition[112] around 370 nm that is absent in the parent chromophore and the D−C dyads.

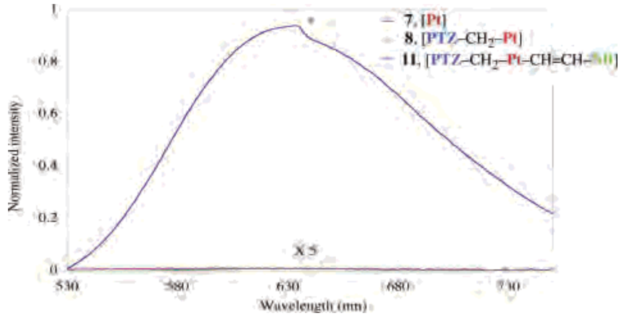

Figure 4. Room-temperature emission spectra of complexes **7**, **8**, and **11** taken in degassed MeCN. The asterisk denotes an instrumental artifact.

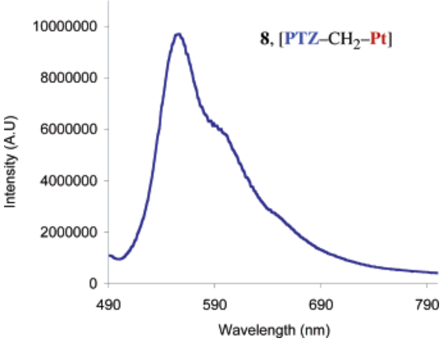

Figure 5. Emission spectrum of complex **8** in methanol/ethanol (1:4) glass at 77 K.

The room-temperature emission spectra of all of the complexes were measured in degassed MeCN (Figure 4). Whereas the chromophore is strongly emissive with a microsecond excited-state lifetime,[116,119] triads **11** and **12** and the corresponding dyads **8** and **9** are found to be nonemissive in a fluid solution, indicative of efficient reductive quenching of the chromophore ^{3}MLCT excited state. In contrast, the C−A dyad **10** is weakly emissive at room temperature in MeCN with a quantum yield of 0.002 (using Ru(bpy)$_3^{2+}$ as a standard with $\phi_{\mathrm{rel}}^{\mathrm{em}} = 0.062$) and a 200-ns excited-state lifetime. While the lifetime of the emission has not been determined directly, the TA results discussed below indicate that the excited state in the C−A dyad decays to the charge-separated species within 30 ns. Either the observed weak emission of dyad **10** corresponds to this short-lived species or else it may be the result of an undetected impurity in the C−A sample.

Despite the emission quenching of the D−C dyads and triads in a fluid solution, all of the complexes are luminescent in a rigid matrix (4:1 EtOH/MeOH glass) at 77 K (Table 1). Figure 5 displays the glass emission spectrum of complex **8**. All of the complexes demonstrate an emission profile that is consistent with the tpy-based vibronic progression reported earlier.[116,119]

TA Spectroscopy. To study charge transfer and the nature of CS in the parent chromophore and the dyads and triads, TA spectra were obtained for all of the samples at 298 K in MeCN and are shown in Figures 6−9. The TA spectrum of the parent chromophore **7** (Figure 6) shows positive absorp-

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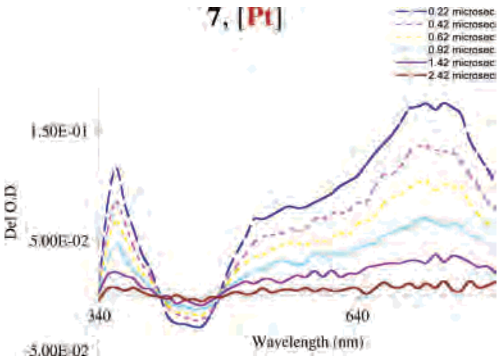

Figure 6. TA spectra of the chromophore **7** (0.08 mM) in MeCN at room temperature (λ_{ex} = 355 nm). The spectra are developed by measurement of the decays each 10 or 20 nm.

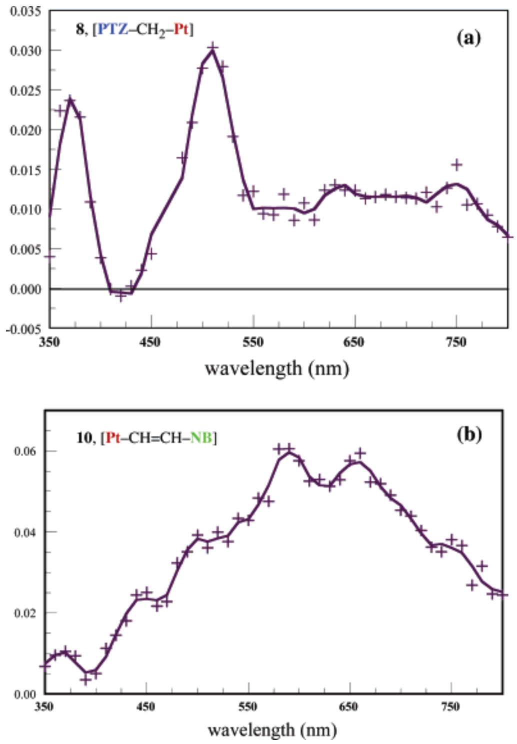

Figure 7. TA spectra at room temperature of (a) the donor−chromophore dyad **8** (0.08 mM) and (b) the chromophore−acceptor dyad **10** in MeCN 20 ns after pulsed excitation (λ_{ex} = 355 nm). The spectra are built from decays obtained each 10 or 20 nm.

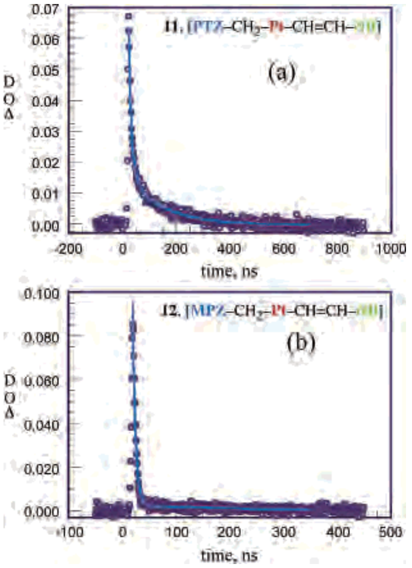

Figure 8. Transient decays (610 nm) for the donor−chromophore−acceptor triads **11** (a) and **12** (b) in room-temperature acetonitrile (λ_{ex} = 355 nm).

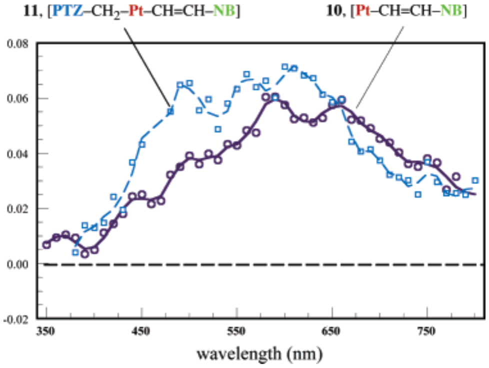

Figure 9. TA spectra at room temperature of the donor−chromophore−acceptor triad **11** in blue (0.08 mM in MeCN) 35 ns after pulsed excitation (λ_{ex} = 355 nm) and the chromophore−acceptor dyad **10** in black (0.08 mM in MeCN) 85 ns after pulsed excitation (λ_{ex} = 355 nm). The spectra are developed from decays obtained each 10 or 20 nm.

tion at 360 nm, a broad absorption between 520 and 800 nm with a maximum at 740 nm, and a bleach at 420−460 nm. The broad envelope between 520 and 800 nm corresponds at least in part to the absorption expected for the ttpy$^{\bullet-}$ radical anion generated in the ^{3}MLCT excited state.[32,42] The increased conjugation of the terpyridine ligand with the tolyl group serves to shift the ttpy$^{\bullet-}$ absorption to lower energy. The bleach corresponds to the disappearance of the ground-state MLCT absorption upon formation of the excited state. All of the features decay exponentially with a lifetime of 0.7 μs, which is somewhat short relative to the previously reported value of τ = 4.6 μs;[119] however, the faster decay observed in the present study was measured in MeCN, a coordinating solvent, while the longer lifetime was obtained in CH_2Cl_2. Dynamic interactions between the chromophore and the more coordinating solvent can serve to increase nonradiative decay, thereby decreasing the excited-state lifetime of the chromophore. Additionally, MeCN may help to facilitate exciplex formation, which has been shown to lead to excited-state quenching in Pt(II) heteroaromatic complexes.[128−130,132,153,154]

Both donor−chromophore dyad complexes exhibit TA spectra with distinct absorbance maxima due to the radical cation of the donor at 510 nm for the unsubstituted PTZ donor **8** (Figure 7a) and 560 nm for the MPZ (methoxy phenothiazine) derivative, **9**.[60,112,155,156] The red shift in moving from **8** to **9** results from the more electron-rich MPZ donor in the latter compared to PTZ. The $D^{\bullet+}$−$C^{\bullet-}$ transients of both dyads have short lifetimes (less than 20 ns). While

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detailed pictures of the dynamics of these complexes are not possible using a nanosecond TA apparatus, the data show that quenching *and* back electron transfer are complete within 20−30 ns.

In contrast, the chromophore−nitrophenyl acceptor dyad **10** has a TA signal that decays biexponentially with faster and slower components of 30 and 200 ns lifetimes, respectively. The slower component exhibits a small positive TA throughout the visible region (Figure 7b) that results from overlap of the absorptions due to the terpyridyl nitrostilbene radical anion and the oxidized Pt complex. The nitrostilbene radical anion absorbs at ∼ 450 nm but may be shifted to lower energy in the NO_2phtpy ligand upon coordination to the metal center.[157−159] On the basis of its TA spectrum, we assign the slower decaying component to be the charge-separated species, $C^{\bullet+}-A^{\bullet-}$, and its decay to be the return of the system to its ground state. The TA signal of the faster component is not as well characterized, but its decay can be followed through the disappearance of ΔOD in the range of 350−390 nm within 30 ns. The logical assignment for the short-lived component in the TA spectrum of **10** consistent with the observed results corresponds to the excited dyad $C^{*}-A$ that is generated within the laser pulse undergoing oxidative quenching and CS to form $C^{\bullet+}-A^{\bullet-}$.

For both triads, the PTZ−chromophore−nitrostilbene derivative **11** and the MPZ−chromophore−nitrostilbene derivative **12**, transient decays, shown in Figure 8, consist of a major rapid component with a lifetime of approximately 10 ns followed by a much smaller, longer-lived component, which, for **11**, has a lifetime of 230 ± 25 ns. Figure 9 shows the spectrum of the longer-lived transient of **11** along with that of the charge-separated $C^{\bullet+}-A^{\bullet-}$ species seen for **10**. The similarity between the two spectra is evident, but the former shows an additional signal between 480 and 520 nm due to the PTZ^{+} radical cation. The longer-lived transient of **11** is thus assigned to the fully charge-separated species $D^{\bullet+}-C-A^{\bullet-}$ that was one of the objectives in the new results presented here.

At present, however, we have not determined the *efficiency* of formation of the fully charge-separated state (CSS) of **11**, although on the basis of the transient decay plot of Figure 8a, it appears to be relatively low. A rough estimate is that only 25−30% of excited triad **11** leads to the fully charge-separated state $D^{\bullet+}-C-A^{\bullet-}$, and for triad **12**, the efficiency of CSS formation is even worse, with less than 10% of the excited triad leading to full CS (Figure 8b). Because of the very small signal obtained for the charge-separated products observed in triad **12**, it was not possible to obtain a reliable measure of the CR rate constant.

While TA measurements at shorter time scales need to be performed for both triads in order to achieve a fuller understanding of processes leading to the formation of the fully charge-separated state, it is possible, based on both electrochemical and photophysical data given above, to analyze the overall energetics and dynamics for photoinduced CS in these Pt(tpy)-based triads. However, because the electrochemical and photophysical measurements were obtained in different solvent systems (1:1 MeCN/DMF for the former and pure MeCN for the latter), the analysis will be semiquantitative at best. Regarding energetics of these systems, we estimate the E^{00} value for the chromophore in one of two ways: (a) from the higher energy value of the 298 K emission for the parent chromophore at 10% of its maximum intensity and (b) from the 77 K emission of triad **11** in MeOH/EtOH glass (1:4). The values thus obtained are experimentally the same and correspond to 2.26 eV (18 250 cm^{-1}, 548 nm). We use this value as the MLCT excited-state energy for triads **11** and **12**, while for the charge-separated $D^{\bullet+}-C-A^{\bullet-}$ state, the relative energy is determined from electrochemical data for either PTZ or MPZ oxidation and nitrophenyl reduction to be 1.63 or 1.55 eV, respectively. In these calculations, it is assumed that the first reduction wave of the triad corresponds to nitrophenyl reduction. A summary of the energetics and relaxation dynamics of triad **11** is given in Figure 10.

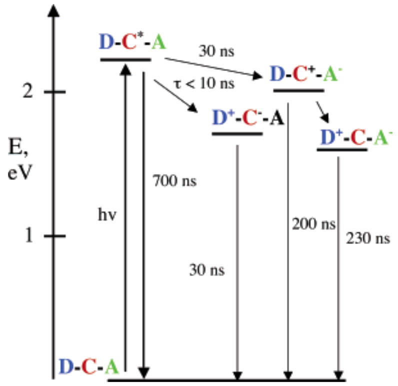

Figure 10. Energy diagram of a D−C−A triad.

In considering the dynamics of photoinduced CS, we focus on the PTZ triad **11** and its associated dyads. The analysis put forward is consistent with the results obtained to date and involves two different competitve electron-transfer steps. The first is upon excitation and corresponds to reductive versus oxidative quenching of the chromophore. After that step, the second electron-transfer branch point is forward electron transfer to achieve full CS ($D^{\bullet+}-C-A^{\bullet-}$) versus back electron transfer to return to the ground state. The reductive quenching path of the chromophore ^{3}MLCT excited state to form $D^{\bullet+}-C^{\bullet-}-A$ is energetically more favorable than oxidative quenching, which yields $D-C^{\bullet+}-A^{\bullet-}$ (ΔE for the respective reactions of ca. 0.4 and <0.1 V). From the TA measurements of the dyads **8** and **10**, it would appear that reductive quenching is kinetically more favorable as well, with the formation of $D^{\bullet+}-C^{\bullet-}$ occurring within 10 ns versus the formation of $C^{\bullet+}-A^{\bullet-}$, which takes place with a 30-ns lifetime. However, the TA result for PTZ dyad **8** also shows that return to the ground state is extremely rapid as well, despite the large driving force that would place the reaction in the Marcus inverted region. This means that, although reductive quenching predominates for **11** upon excitation, forward electron transfer to generate the fully

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charge-separated species does not happen by this route. The rapid return to the ground state following reductive quenching in **8** is consistent with the fast decay component of the photoexcited triad **11***. In contrast, slower and less efficient oxidative quenching (30 vs <10 ns for reductive quenching) leads to D−C$^{\bullet+}$−A$^{\bullet-}$, which then rapidly advances to the fully charge-separated species rather than undergoing back reaction to the ground state. The TA result for dyad **10** that has the slow component (200 ns) corresponding to C$^{\bullet+}$−A$^{\bullet-}$ → C−A lends support to this view. The TA spectrum of the triad at shorter time scales (<10 ns) should provide additional support for this interpretation because we will be able to follow the time evolution of the transient spectrum that will allow more definitive assignments of the different species seen.

From the decay rate constants of the charge-separated states in the tpy-containing triad **11** and the related diimine triad **5**, we can assert that the fully charge-separated state D$^{\bullet+}$−C−A$^{\bullet-}$ in **11** is 3 times longer-lived. Both the larger donor−acceptor separation in triad **11** relative to that in **5** and the cationic charge of the former that makes for more effective solvation may account for the observed difference in the CR rate constants for these triads. On the basis of the oxidation and reduction potentials for the respective donor and acceptor in triad **11** and assuming the first reduction wave corresponds to the nitrophenyl reduction, it can be estimated that **11** transiently stores approximately 1.6 eV, which is comparable to the transiently stored energy of the previously reported platinum diimine bis(acetylide) triad **5** (1.67 eV) having the same donor and a similar acceptor group.[112]

Conclusions

Photoinduced CS is a key step in photosynthesis that in the design of a molecularly based system for light-to-chemical energy conversion is accomplished by the linking of electron donor and acceptor moieties to the charge-transfer chromophore. To achieve this goal, two- and three-component systems, i.e., dyads and triads, have been constructed having suitable electron donor and acceptor moieties at specific positions on the chromophore. Numerous multicomponent systems containing transition-metal centers have been synthesized with this objective in mind, and many have shown elements of success in achieving a long-lived charge-separated state upon irradiation. Increasing the lifetimes of the charge-separated states while transiently storing most of the incident photon energy for subsequent chemistry is a current objective. While most of the research in this area has employed Ru(II) heterocyclic aromatic chromophores, the research presented here has concentrated on related platinum(II) diimine and terpyridyl systems. These complexes have ^{3}MLCT excited states with a mainly Pt d orbital as the HOMO and a π^* orbital of the heterocyclic aromatic ligand as the LUMO. The Pt(II) chromophores generally have higher excited-state energies as well as a better defined directionality of charge transfer that clearly delineates the arrangement for more efficient CS.

The first Pt(II)-based triad (**5**) was synthesized by attaching PTZ-based donors to the anionic side and a nitrophenyl acceptor to the diimine side of a platinum phenanthroline bis(arylacetylide) chromophore. TA studies showed generation of a charge-separated species D$^{\bullet+}$−C−A$^{\bullet-}$ in good yield. The charge-separated state of **5** has a lifetime of 75 ns and transiently stores 1.67 eV. More recently, we have developed new systems using the cationic platinum terpyridine arylacetylide chromophore for better solubility in polar media and improved separation of charge. Triad **6**, [Pt(pytpy)(*p*-C≡C-*p*-C_6H_4−NH−CO−$C_6H_2(OMe)_3$]$(PF_6)_2$, having a trimethoxybenzene donor and a pyridinium acceptor was synthesized and structurally characterized. The edge-to-edge separation between the donor and acceptor fragments in this system was determined to be ca. 28 Å. While the parent chromophore is strongly emissive, the emission was observed to be completely quenched upon attachment of the donor group to the chromophore. However, TA studies indicated that a truly charge-separated state, i.e., D$^{\bullet+}$−C−A$^{\bullet-}$, was not achieved because the intermediate D$^+$−C$^-$−A species did not react further to yield the reduced pyridinium acceptor.

In this contribution, a new set of triads and associated dyads based on the cationic platinum terpyridyl arylacetylide chromophore have been described. The D−C−A triads are [Pt(NO_2phtpy)(p−C≡C−$C_6H_4CH_2$(PTZ)](PF_6) (**11**) and [Pt(NO_2phtpy)(*p*-C≡C−$C_6H_4CH_2$(MPZ)](PF_6) (**12**), and the relevant D−C and C−A dyads are **8**−**10**. While the parent chromophore (**7**) is brightly luminescent in a fluid solution, all of the D−C dyads and triads exhibit complete quenching of emission in solution. TA studies indicate the formation of the D$^{\bullet+}$−C−A$^{\bullet-}$ charge-separated species for triads **11** and **12**, and simple electrochemical analyses indicate that ca. 1.6 eV is transiently stored. Triad **11** exhibits a CS state lifetime of 230 ns, which is considerably longer-lived than that of **5** reported earlier. The increase in the CS lifetime from that of the previously reported platinum phenanthroline bis(arylacetylide) triad having the same donor and acceptor moieties may arise because of an increased donor−acceptor separation, as well as better solvation resulting from the cationic charge on the complex. While the CS state of **11** is longer-lived than that of **5**, we also find from TA studies that it is formed inefficiently as a proposed result of competing electron-transfer reactions in both quenching and CS steps. Both the CS state lifetime and the efficiency of its formation underscore subtle but important factors in the design of molecularly based systems for photoinduced CS. Also important is the fact that the yield of charge-separated products for **11** is greater than that for **12**; reasons for this are not entirely clear, but one may relate to the driving force dependence of the back reaction in D$^{\bullet+}$−C−A$^{\bullet-}$.[160] We envision that, with appropriate synthetic modifications, the lifetime of the fully charge-separated state for the Pt(tpy)-

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(160) The only significant difference between triads **11** and **12** is the fact that the free energy for charge recombination in the intermediate D$^{\bullet+}$−C$^{\bullet-}$−A is larger for complex **11** than for **12**; if the recombination of this intermediate falls in the Marcus inverted region, then recombination for **12** should be faster than that for **11**, and this would lead to a smaller yield of the fully charge-separated species D$^{\bullet+}$−C−A$^{\bullet-}$ for **12**.

based triad systems can be increased further so that subsequent bimolecular chemistry can become competitive with back electron transfer and that the efficiency of CS can be improved to make the construction of triads and further multicomponent systems a viable strategy for the conversion of light to stored chemical energy in a molecularly designed system for artificial photosynthesis.

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Supporting Information Available: Experimental details of the synthesis and characterization of new compounds **8**−**12** and the ^{1}H NMR spectrum of triad **11** including variable-temperature spectra of the vinylic resonances. This material is available free of charge via the Internet at http://pubs.acs.org.

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