

# Dyads for Photoinduced Charge Separation Based on Platinum Diimine Bis(acetylide) Chromophores: Synthesis, Luminescence and Transient Absorption Studies

James E. McGarrah and Richard Eisenberg\*

Department of Chemistry, University of Rochester, Rochester, New York 14627-0216

Received January 13, 2003

The platinum diimine bis(acetylide) chromophore was utilized to explore photoinduced intramolecular reductive quenching with phenothiazine donors in chromophore–donor dyad complexes. Compounds of the general formula  $\text{Pt}(\text{X}_2\text{-bpy})(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{CH}_2(\text{D}))_2$  (where D = phenothiazine (PTZ) or trifluoromethylphenothiazine (TPZ) and X = <sup>t</sup>Bu or CO<sub>2</sub>Et) were synthesized from the corresponding  $\text{Pt}(\text{X}_2\text{-bpy})\text{Cl}_2$  and aryl acetylene by a CuI-catalyzed coupling reaction. Solvent dependence was explored for the system with X = <sup>t</sup>Bu in MeCN, CH<sub>2</sub>Cl<sub>2</sub>, EtOAc, and toluene. Electron transfer quenching of the <sup>3</sup>MLCT excited state of the platinum diimine bis(acetylide) takes place in MeCN leaving no intrinsic emission from the excited state, but in toluene both the PTZ and TPZ dyad complexes exhibit no emission quenching. Picosecond pump–probe transient absorption (TA) experiments were used to monitor decay of the <sup>3</sup>MLCT excited state and electron transfer to form the charge-separated (CS) state. Electrochemical measurements were used to estimate the driving force for charge recombination (CR), with  $\Delta E_{\text{CR}}$  based on the reduction potential corresponding to  $\text{Pt}(\text{X}_2\text{-bpy})(\text{C}\equiv\text{C}-\text{Ar})_2 \rightarrow \text{Pt}(\text{X}_2\text{-bpy}^{\bullet-})(\text{C}\equiv\text{C}-\text{Ar})_2$  and the oxidation corresponding to donor  $\rightarrow$  donor<sup>•+</sup>. Kinetic information from the TA measurements was used to correlate rate and driving force with the electron transfer reactions. Concomitant with the decay of the <sup>3</sup>MLCT excited state was the observation of a transient absorption at ca. 500 nm due to formation of the PTZ or TPZ radical cation in the CS state, with the rate of charge separation,  $k_{\text{CS}}$ , being  $1.8 \times 10^9$  to  $2 \times 10^{10} \text{ s}^{-1}$  for the three dyads explored in MeCN and 1:9 CH<sub>2</sub>Cl<sub>2</sub>/MeCN. The fastest rate of CR occurs for X = CO<sub>2</sub>Et and D = PTZ, the compound with smallest  $\Delta E_{\text{CR}} = 1.71 \text{ V}$ . The rate of CR for dyads with X = <sup>t</sup>Bu and D = PTZ or TPZ was estimated to be  $1.7\text{--}2.0 \times 10^8 \text{ s}^{-1}$  in MeCN. The slower rate corresponds to a greater driving force for CR,  $\Delta E_{\text{CR}} = 2.18$  and  $2.36 \text{ V}$  for D = PTZ and TPZ, respectively, suggesting that the driving force for charge recombination places it in the Marcus inverted region.

## Introduction

One of the fundamental steps in photosynthesis and light-to-chemical energy conversion is photoinduced charge separation. Toward this end, multicomponent molecules have been designed and constructed containing an electron donor, an electron acceptor, and a metal complex-based charge transfer chromophore.<sup>1–3</sup> The most commonly examined transition metal chromophores in this regard are octahedral d<sup>6</sup> diimine complexes having a <sup>3</sup>MLCT excited state such

as  $\text{Ru}(\text{diimine})_3^{2+}$  and  $\text{Re}(\text{diimine})(\text{CO})_3(\text{py})^+$ .<sup>2–17</sup> Numerous studies with these chromophores have used phenothiazine (PTZ) as the electron donor for reductive quench-

\* Author to whom correspondence should be addressed. E-mail: eisenberg@chem.rochester.edu.

(1) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435–461.

(2) Bignozzi, C. A.; Schoonover, J. R.; Scandola, F. *Prog. Inorg. Chem.* **1997**, *44*, 1–95.

(3) Schmehl, R. H.; Ryu, C. K.; Elliott, C. M.; Headford, C. L. E.; Ferrere, S. *Adv. Chem. Ser.* **1990**, *226*, 211–223.

(4) Daub, J.; Engl, R.; Kurzawa, J.; Miller, S. E.; Schneider, S.; Stockmann, A.; Wasielewski, M. R. *J. Phys. Chem. A* **2001**, *105*, 5655–5665.

(5) Imahori, H.; Yamada, H.; Guldi, D. M.; Endo, Y.; Shimomura, A.; Kundu, S.; Yamada, K.; Okada, T.; Sakata, Y.; Fukuzumi, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2344–2347.

(6) Bates, W. D.; Chen, P.; Dattelbaum, D. M.; Jones, W. E., Jr.; Meyer, T. J. *J. Phys. Chem. A* **1999**, *103*, 5227–5231.

(7) Pfennig, B. W.; Chen, P. Y.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 2898–2901.

(8) Gust, D.; Moore, A. L.; Moore, T. A. *Acc. Chem. Res.* **1993**, *26*, 198–205.

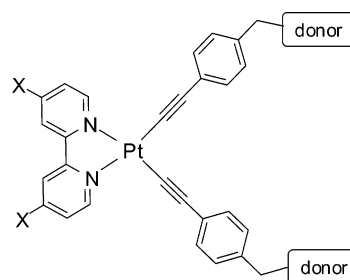
(9) Chen, P. Y.; Mecklenburg, S. L.; Meyer, T. J. *J. Phys. Chem.* **1993**, *97*, 13126–13131.

(10) Chen, P. Y.; Mecklenburg, S. L.; Duesing, R.; Meyer, T. J. *J. Phys. Chem.* **1993**, *97*, 6811–6815.

ing.<sup>6,7,11–13,18–21</sup> For  $\text{Re}(\text{bpy})(\text{CO})_3(\text{py-PTZ})^+$ , quenching of the  $^3\text{MLCT}$  emission is complete and a CS state is observed with a lifetime of 25 ns in acetonitrile.<sup>13</sup> Similar  $\text{Re}(\text{diimine})(\text{CO})_3(\text{py-PTZ})^+$  and  $\text{Re}(\text{diimine})(\text{CO})_3(\text{py-donor})^+$  dyads having different diimine ligands have also been studied extensively.<sup>6,11,13</sup> As part of these studies, charge recombination of the charge-separated state in these systems was probed by systematic variation of the diimine ligand which controls the driving force for charge recombination. In the chromophore, the LUMO is a  $\pi^*$  diimine orbital so that the reduction potential of the chromophore and hence the driving force for charge recombination correlate directly with the diimine LUMO energy.

Recent studies by us and others have shown that a relatively new transition metal chromophore, platinum diimine bis(acetylide), possesses a long-lived  $^3\text{MLCT}$  excited state.<sup>22–25</sup> The nature of this excited state is similar to the charge transfer excited states of  $d^6$  diimine chromophores discussed above. In the study reported here, chromophore–donor (C–D) dyad complexes utilizing  $\text{Pt}(\text{diimine})(\text{acetylide})_2$  and either PTZ or TPZ (trifluoromethylphenothiazine) as reductive quenchers are described. The motivation for this study was to better understand the factors influencing the longevity of charge separation in multicomponent systems containing this novel platinum diimine chromophore. Previously, we have reported a donor–chromophore–acceptor (D–C–A) triad for photoinduced charge separation that utilizes the platinum diimine bis(acetylide) chromophore.<sup>26</sup> In that system, an aromatic nitro group served as the acceptor moiety, a phenothiazine (PTZ) served as the donor, and the platinum diimine bis(acetylide) moiety functioned as the chromophore. Selective excitation of the chromophore generated within 10 ns the charge-separated state that decayed to

the ground state with a lifetime of 70 ns in both DMF and dichloromethane.



C–D Dyad

Phenothiazine and its derivatives serve as good intramolecular reductive quenchers because they have facile one-electron oxidations,  $E_{1/2}(\text{PTZ}^{+}/\text{PTZ})$  of ca. 0.32 V vs  $\text{Fc}^+/\text{Fc}$ , and the PTZ radical cation ( $\text{PTZ}^{+\cdot}$ ) is known to have a strong absorption in the visible.<sup>4,13</sup> This makes the identification of the charge-separated (CS) intermediate formed upon electron transfer from PTZ or TPZ to the  $^3\text{MLCT}$  excited state of the chromophore unambiguous. Furthermore, the photochemistry of PTZ has been extensively studied due to pharmacological effects of promazine, a complex that contains the PTZ moiety.<sup>27</sup>

In this paper we use synthetic modification and picosecond spectroscopy in order to explore photoinduced charge separation in the C–D dyads. The quenching of the  $^3\text{MLCT}$  excited state by electron transfer in the C–D dyads is dependent on the relative energies of the CS state and the  $^3\text{MLCT}$  excited state, which vary as a function of solvent. In more polar solvents, quenching is observed, whereas in the nonpolar solvent toluene, quenching does not occur. The results suggest that in toluene the CS state is destabilized relative to the  $^3\text{MLCT}$  state so that undiminished luminescence from the  $^3\text{MLCT}$  state is observed. Interestingly, in toluene solution, enhancements in the luminescence lifetime and quantum yield are found for the C–D dyads as compared to those of the chromophore by itself under these conditions.

## Experimental Section

**General Procedures and Materials.** Prior to use, BuLi was titrated using pivaloyl-*o*-toluidine according to the procedure by Suffert.<sup>28</sup> Phenothiazine (PTZ), cuprous iodide, 2-trifluoromethylphenothiazine (TPZ), and trimethylsilylacetylene (TMSA) were purchased from Aldrich and used without further purification. Purchased from Strem Chemical Company was 4,4'-( $\text{CO}_2\text{H}$ )<sub>2</sub>-2,2'-bipyridine. The complexes *cis*- $\text{PtCl}_2(\text{DMSO})_2$ ,<sup>29</sup>  $\text{PtCl}_2(\text{PhCN})_2$ ,<sup>30</sup>  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ ,<sup>31</sup>  $\text{Pt}(\text{dcbpy})\text{Cl}_2$ ,<sup>24,32</sup> **1**,<sup>24</sup> and 4,4'-( $\text{CO}_2\text{Et}$ )<sub>2</sub>-2,2'-bipyridine<sup>33</sup> were prepared according to literature procedures. Dichlo-

- (11) Chen, P. Y.; Duesing, R.; Graff, D. K.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 5850–5858.
- (12) Duesing, R.; Tapolsky, G.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5378–5379.
- (13) Chen, P.; Westmoreland, D.; Danielson, E.; Schanze, K. S.; Anthon, D.; Neveux, P. E., Jr.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1116–1126.
- (14) Anderson, P. A.; Keene, F. R.; Meyer, T. J.; Moss, J. A.; Strouse, G. F.; Treadway, J. A. *J. Chem. Soc., Dalton Trans.* **2002**, 3820.
- (15) Yonemoto, E. H.; Saupé, G. B.; Schmehl, R. H.; Hubig, S. M.; Riley, R. L.; Iverson, B. L.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 4786–4795.
- (16) Schanze, K. S.; Macqueen, D. B.; Perkins, T. A.; Cabana, L. A. *Coord. Chem. Rev.* **1993**, *122*, 63–89.
- (17) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, *158*, 73–149.
- (18) Treadway, J. A.; Chen, P. Y.; Rutherford, T. J.; Keene, F. R.; Meyer, T. J. *J. Phys. Chem. A* **1997**, *101*, 6824–6826.
- (19) Rutherford, T. J.; Keene, F. R. *Inorg. Chem.* **1997**, *36*, 2872–2878.
- (20) Fanni, S.; Keyes, T. E.; Campagna, S.; Vos, J. G. *Inorg. Chem.* **1998**, *37*, 5933.
- (21) Maxwell, K. A.; Sykora, M.; DeSimone, J. M.; Meyer, T. J. *Inorg. Chem.* **2000**, *39*, 71–75.
- (22) Chan, C.-W.; Cheng, L.-K.; Che, C.-M. *Coord. Chem. Rev.* **1994**, *132*, 87–97.
- (23) Hissler, M.; McGarrah, J. E.; Connick, W. B.; Geiger, D. K.; Cummings, S. D.; Eisenberg, R. *Coord. Chem. Rev.* **2000**, *208*, 115–137.
- (24) Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrah, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447–457.
- (25) Whittle, C. E.; Weinstein, J. A.; Geore, M. W.; Schanze, K. S. *Inorg. Chem.* **2001**, *40*, 4053–4062.
- (26) McGarrah, J. E.; Kim, Y.-J.; Hissler, M.; Eisenberg, R. *Inorg. Chem.* **2001**, *40*, 4510–4511.

- (27) Gupta, R. R. *Phenothiazines and 1,4-Benzothiazines in Bioactive Molecules*; Elsevier: Amsterdam, The Netherlands, 1988; Vol. 4.
- (28) Suffert, J. *J. Org. Chem.* **1989**, *54*, 509–510.
- (29) Kukushkin, V. Y.; Pombeiro, A. J. L. *Inorg. Synth.* **2002**, *33*, 189–195.
- (30) Uchiyama, T.; Toshiyasu, Y.; Nakamura, Y.; Miwa, T.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 181–185.
- (31) Four, P.; Guibe, F. *J. Org. Chem.* **1981**, *46*, 4439–4445.
- (32) Adams, C. J.; James, S. L.; Liu, X. M.; Raithby, P. R.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **2000**, 63–67.

romethane, THF, diethyl ether, acetonitrile, toluene, and hexane were purified by a solvent purification system first described by Grubbs.<sup>34,35</sup> Flash chromatography was performed using a Biotage Flash 40/12 system under 20 psi of nitrogen pressure.

**Characterization.** Infrared spectra were obtained from KBr pellets using a Mattson Galaxy 6020 FTIR spectrometer. <sup>1</sup>H NMR spectra were recorded on a Bruker AMX-400 spectrometer (400 MHz) with the residual protio signal of CDCl<sub>3</sub> referenced to  $\delta$  7.26; <sup>19</sup>F NMR spectra were recorded on a Bruker Avance 400 spectrometer (376.3 MHz) with the fluorine signal of CF<sub>3</sub>C<sub>6</sub>H<sub>5</sub> referenced to  $\delta$  0.00. Cyclic voltammetry experiments were conducted on an EG&G PAR 263 potentiostat/galvanostat using a three-electrode single-cell compartment. All samples were degassed with argon. A glassy carbon working electrode, Pt auxiliary electrode, and Ag/AgNO<sub>3</sub> in acetonitrile reference electrode were used. For all measurements, ferrocene was used as an internal reference and all redox potentials are reported relative to the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple.<sup>36</sup> Absorption spectra were recorded using a Hitachi U2000 scanning spectrophotometer (200–1100 nm).

**Transient Absorption Spectroscopy.** Nanosecond transient difference absorption spectroscopy was performed on a previously described system utilizing a Lambda Physik LEXtra XeCl excimer laser (FWHM  $\sim$  15 ns) to pump a Lambda Physik LPD 3000 dye laser.<sup>37</sup> Light of wavelengths 343, 405, and 440 nm were generated using PTP, DPS, and Coumarin 440 dyes purchased from Lambda Physik. Excitation of the sample was at 90° to the probe using a pulsed Xe lamp. Single-wavelength kinetics were collected using a single monochromator and a Hamamatsu R928 photomultiplier (PM). The signal was captured on a Tektronix TDS 620 digital oscilloscope and transferred to a program of local design for analysis. TA spectra were collected by focusing the analyzing light onto a fiber optic cable that passed through a 0.275 M Acton Research Corporation SpectraPro spectrograph and then imaged onto an Oriel INSTASPEC V CCD detector. Control of the delay and processing of the data was done using Oriel software. Picosecond transient difference absorption spectroscopy was performed using a previously described system with a few modifications.<sup>38</sup> The laser source was updated with a Continuum model Leopard D-20 Nd:YAG with a 20 ps at fwhm pulse at 1064 nm (30 mJ), 532 nm (14 mJ), and 355 nm (10 mJ). The controlling software was also updated using LabView to control the delay line and switching between diode array and PM tube detection. White light continuum generation ( $\lambda >$  420 nm) was achieved by passing 1064 nm light into a 10 cm path length cell containing 1:1 H<sub>2</sub>O/D<sub>2</sub>O. All samples were measured in a 10 mm  $\times$  8 mm flow cell with a 100 mL reservoir adjusted in concentration to give an OD between 0.4 and 0.6 at 355 nm. Excitation of the sample was kept below 3 mJ per pulse. The overlap of pump and probe ( $\sim$ 4 mm diameter for both at the sample) was maximized in the middle of the sample cell using a small angle ( $\sim$ 10°) between beams.

**Luminescence.** Luminescence spectra were obtained using a Spex Fluorolog-2 fluorimeter corrected for the spectral sensitivity

of the photomultiplier tube (Hamamatsu R929). Fluid solution emission samples were degassed either with argon or by several freeze–pump–thaw cycles using a vacuum of at least 10<sup>−4</sup> Torr. Samples were optically dilute (OD < 0.10) at the wavelength of excitation unless otherwise noted. Frozen glass emission samples were prepared in 3 or 4 mm quartz EPR tubes using a circular quartz-tipped immersion Dewar filled with liquid nitrogen. Lifetime measurements were made either using a described TCSPC spectrometer<sup>38</sup> or by nanosecond excitation using the previously described ns TA spectrometer. Quantum yields were measured relative to [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in degassed acetonitrile using a value of  $\phi = 0.062$ .<sup>39</sup>

**Syntheses. *p*-Iodobenzyl-*N*-phenothiazine, *p*-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(PTZ).** BuLi (4.4 mL of 2.26 M, 9.94 mmol) was slowly added to a solution of 1.4 mL of diisopropylamine (9.99 mmol) in 60 mL of THF at 0 °C. The solution was stirred for 20 min before the addition of 2.00 g of phenothiazine (10.0 mmol). The bright yellow solution was allowed to warm to room temperature, and 2.97 g of *p*-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br dissolved in 30 mL of THF was added via cannula to the stirring solution. Within a few minutes the solution turned a reddish-brown. The reaction was monitored by TLC and evaporated to dryness once all the reactants were consumed, 3 days. The residue was dissolved in 500 mL of dichloromethane and washed with 2  $\times$  200 mL of saturated aqueous NaCl and 100 mL of water, dried with MgSO<sub>4</sub>, filtered, and evaporated to dryness. The residue was dissolved in 1:1 dichloromethane/hexanes and filtered through a 1 cm pad of silica gel on a 60 mL medium-porosity glass sintered frit with 250 mL of 1:1 dichloromethane/hexanes. The filtrate was concentrated and purified using a flash chromatography Biotage Flash 40M cartridge (KP-Sil, 32–63  $\mu$ m, 60 Å) eluting with 1:4 dichloromethane/hexanes. *R*<sub>f</sub> = 0.40 (1:3 dichloromethane/hexanes on silica TLC). Yield: 2.6 g (63%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 5.02 (s, 2H), 6.59 (d, 2H, *J* = 8.1 Hz), 6.88 (t, 2H, *J* = 7.6 Hz), 6.99 (t, 2H, *J* = 8.0 Hz), 7.09 (t, 4H, *J* = 8.0 Hz), 7.64 (d, 2H, *J* = 8.3 Hz). MS (EI): *m/z* 415 (72%), 288 (100%). *M*<sub>r</sub>: 415.30

***p*-Ethynylbenzyl-*N*-phenothiazine, *p*-HC $\equiv$ CC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(PTZ).** To a Schlenk flask containing 3.0 mmol of *p*-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(PTZ), 0.15 mmol of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, and 0.30 mmol of CuI were added 50 mL of degassed benzene and 10 mL of freshly distilled triethylamine. To this solution was added a degassed solution of 4.5 mmol of (trimethylsilyl)acetylene in 10 mL of benzene. The solution was stirred for 6 h and assayed by mass spectrometry. The solution was evaporated to dryness, dissolved in 25 mL of 1:1 dichloromethane/hexanes, and filtered through a 2 cm pad of silica gel on a 60 mL medium-porosity frit eluting with 225 mL of 1:1 dichloromethane/hexanes. The filtrate was concentrated and was purified using flash chromatography with a Biotage Flash 40M cartridge (KP-Sil, 32–63  $\mu$ m, 60 Å) eluting with 1:4 dichloromethane/hexanes. *R*<sub>f</sub> = 0.45 (1:3 dichloromethane/hexanes on silica TLC). Characterization for *p*-(TMS)C $\equiv$ CC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(PTZ). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.34 (AA'BB', 4H, *J*<sub>AB</sub> = 8.4 Hz,  $\Delta\nu$  = 79.1 Hz.), 7.09 (d, 2H, *J* = 7.2 Hz), 6.95 (t, 2H, *J* = 8.0 Hz), 6.85 (t, 2H, *J* = 7.2 Hz), 6.57 (d, 2H, *J* = 8.0 Hz), 5.00 (s, 2H), 0.29 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 144.7, 137.8, 132.8, 127.7, 127.4, 127.1, 123.1, 115.8, 105.3, 94.7, 52.8, 0.5. FT-IR (KBr)  $\nu$ /cm<sup>−1</sup>: 2167 ( $\nu$ <sub>C $\equiv$ C</sub>), 1912 ( $\nu$ <sub>C=C</sub>). MS (EI): *m/z* 385.

The trimethylsilyl protecting group was removed by dissolving in 100 mL of THF/MeOH (1:1) and stirring with 0.42 g of K<sub>2</sub>CO<sub>3</sub> for 4 h. The solution was quenched with 25 mL of water, and most of the organic solvent was removed by rotary evaporation. The mixture was extracted with 100 mL of dichloromethane, dried with

- (33) Elliott, C. M.; Hershenhart, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 7519–7526.  
 (34) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.  
 (35) Albiez, P. J. *Electrophilic Late Transition Complexes of Pt(II) and Ir(III): Rational Design, Synthesis, and Study*; University of Rochester: Rochester, 2001; p 233.  
 (36) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877–910.  
 (37) Chen, L.; Farahat, M. S.; Gaillard, E. R.; Farid, S.; Whitten, D. G. J. *Photochem. Photobiol. A: Chem.* **1996**, *95*, 21–25.  
 (38) Arnold, B. R.; Atherton, S. J.; Farid, S.; Goodman, J. L.; Gould, I. R. *Photochem. Photobiol.* **1997**, *65*, 15–22.

- (39) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583–5590.



MgSO<sub>4</sub>, and evaporated to an oil. The oil was purified by flash chromatography, Biotage Flash 40M cartridge (KP-Sil, 32–63 μm, 60 Å), eluting with 1:9 dichloromethane/hexanes. *R<sub>f</sub>* = 0.25 (1:4 dichloromethane/hexanes on silica TLC). Overall yield: 2.33 mmol (77.7%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.37 (AA'BB', 4 H, *J*<sub>AB</sub> = 8.2 Hz, Δ*ν* = 68.0 Hz), 7.09 (dd, 2H, *J* = 7.6 Hz, *J* = 1.5 Hz), 6.98 (t, 2H, *J* = 8.1 Hz), 6.87 (t, 2H, *J* = 7.5 Hz), 6.59 (d, 2H, *J* = 7.6 Hz), 5.09 (s, 2H), 3.06 (s, 1H). FT-IR (mull) *ν* (cm<sup>-1</sup>): 2105 (*ν*<sub>C≡C</sub>). Anal. Calcd for C<sub>21</sub>H<sub>15</sub>NS (fw = 313.42): C, 80.37; H, 4.91; N, 4.42. Found: C, 80.48; H, 4.82; N, 4.47.

***p*-Iodobenzyl-*N*-(2-trifluoromethyl)phenothiazine, *p*-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-(TPZ).** A procedure similar to the synthesis of *p*-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(PTZ) was used. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.65 (m, 2H), 7.20–7.06 (broad m, 5H), 7.02 (pseudo triplet, 1H), 6.91 (pseudo triplet, 1H), 6.80 (bs, 1H), 6.62 (dd, 1H, *J* = 8.1 Hz, *J* = 1.0 Hz), 5.02 (s, 2H). <sup>19</sup>F NMR (CF<sub>3</sub>C<sub>6</sub>H<sub>5</sub>) δ: -0.4 (s).

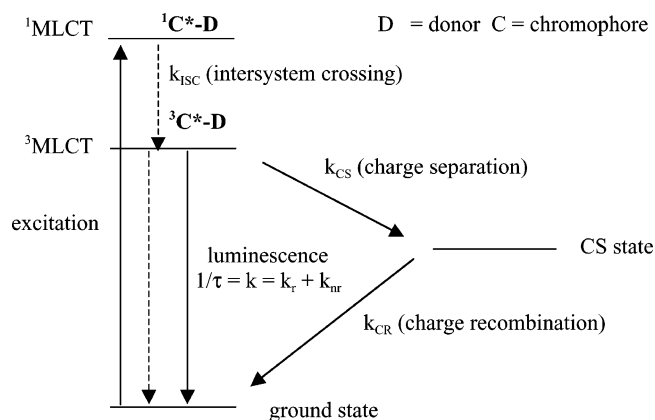
***p*-Ethynylbenzyl-*N*-(2-trifluoromethyl)phenothiazine, *p*-HC≡CC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(TPZ).** A procedure similar to that for 4-HC≡CC<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>(PTZ) was used to synthesize this compound. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.38 (AB quartet, 4H, *J*<sub>AB</sub> = 8.1 Hz, Δ*ν* = 61.2 Hz), 7.16–7.08 (m, 3H), 6.99 (pseudo triplet, 1H), 6.88 (pseudo triplet, 1H), 6.79 (d, 1H, *J* = 1.0 Hz), 6.63 (dd, 1H, *J* = 8.1 Hz, *J* = 1.0 Hz), 5.08 (s, 2H), 3.07 (s, 1H). <sup>19</sup>F NMR (CF<sub>3</sub>C<sub>6</sub>H<sub>5</sub>) δ: -0.3 (s).

**Pt((CO<sub>2</sub>Et)<sub>2</sub>bpy)Cl<sub>2</sub>.** In a Schlenk flask 4,4'-(CO<sub>2</sub>Et)<sub>2</sub>-bpy (600.0 mg, 2.0 mmol) and PtCl<sub>2</sub>(DMSO)<sub>2</sub> (844.2 mg, 2.0 mmol) were suspended in 30 mL of 1:1 MeOH/dichloromethane. The mixture was stirred at room temperature for 24 h to give an orange solid, which was collected by filtration. The orange solid was redissolved in dichloromethane, and the solution was filtered through Celite. The filtrate was concentrated and put in the freezer (-37 °C). The orange-red crystals were collected by filtration. Yield: 0.98 g; 86%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 9.75 (d, 2H, *J* = 6.0 Hz), 8.60 (d, 2H, *J* = 1.6 Hz), 8.07 (dd, 2H, *J* = 6.0 Hz, *J* = 1.6 Hz), 4.54 (q, 4H, *J* = 7.1 Hz), 1.51 (t, 6H, *J* = 7.1 Hz). *M<sub>r</sub>* = 566.29.

**Pt((CO<sub>2</sub>Et)<sub>2</sub>bpy)(C≡C-*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>, 2.** This compound has been previously reported.<sup>25</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 9.98 (d, 2H, *J* = 5.8 Hz), 8.62 (s, 2H), 8.08 (dd, 2H, *J* = 5.7 Hz, *J* = 1.6), 7.22 (AB quartet, 8H, *J*<sub>AB</sub> = 7.8 Hz, *ν* = 115.9 Hz), 4.47 (q, 4H, *J* = 7.1 Hz), 1.46 (t, 6H, *J* = 7.1 Hz).

**Pt((CO<sub>2</sub>Et)<sub>2</sub>bpy)(C≡C-*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(PTZ))<sub>2</sub>, 2-PTZ.** In a 50 mL Schlenk tube 150 mg of Pt(4,4'-(CO<sub>2</sub>Et)<sub>2</sub>-bpy)Cl<sub>2</sub> (0.265 mmol), 222 mg of *p*-HC≡CC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(PTZ) (0.583 mmol, 2.2 equiv), and 5 mg of CuI (0.026 mmol, 0.1 equiv) were degassed and dissolved in 19 mL of dichloromethane and 1 mL of triethylamine. The closed reaction was heated for 6 h at 45 °C, allowed to cool and stirred overnight. The reaction mixture was evaporated to dryness, dissolved in 20 mL of dichloromethane, and purified by flash chromatography, Biotage Flash 40M cartridge (Alumina, 40 μm, 60 Å), eluting with neat dichloromethane (*R<sub>f</sub>* = 0.3 in dichloromethane.) The pure fractions containing the product were concentrated to ~5 mL via rotary evaporation in the dark. The dark red solution was precipitated in 25 mL of cold pentane, filtered, washed with 3 × 5 mL of Et<sub>2</sub>O, and dried under vacuum. Yield: 250.8 mg, 85%. For elemental analysis and optical spectroscopy the compound was further purified by dissolution in a minimum of dichloromethane, reprecipitation and drying in vacuo. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 10.01 (d, 2H, *J* = 5.7 Hz), 8.67 (s, 2H), 8.12 (dd, 2H, *J* = 5.7 Hz, *J* = 1.5 Hz), 7.47 (d, 4H, *J* = 8.2 Hz), 7.33 (AB quartet, 8H, *J*<sub>AB</sub> = 8.2 Hz, *ν* = 112.0 Hz), 7.07 (dd, 4H, *J* = 7.6 Hz, *J* = 1.5 Hz), 6.98 (pseudo t, 4H, *J* = 7.8 Hz), 6.85 (pseudo triplet, 4H, *J* = 7.2 Hz), 6.65 (d, 4H, *J* = 8.1 Hz), 5.07 (s, 4H), 4.51 (q, 4H, *J* = 7.1 Hz), 1.47 (t, 6H, *J* = 7.1 Hz). FAB<sup>+</sup> (matrix):

Scheme 1



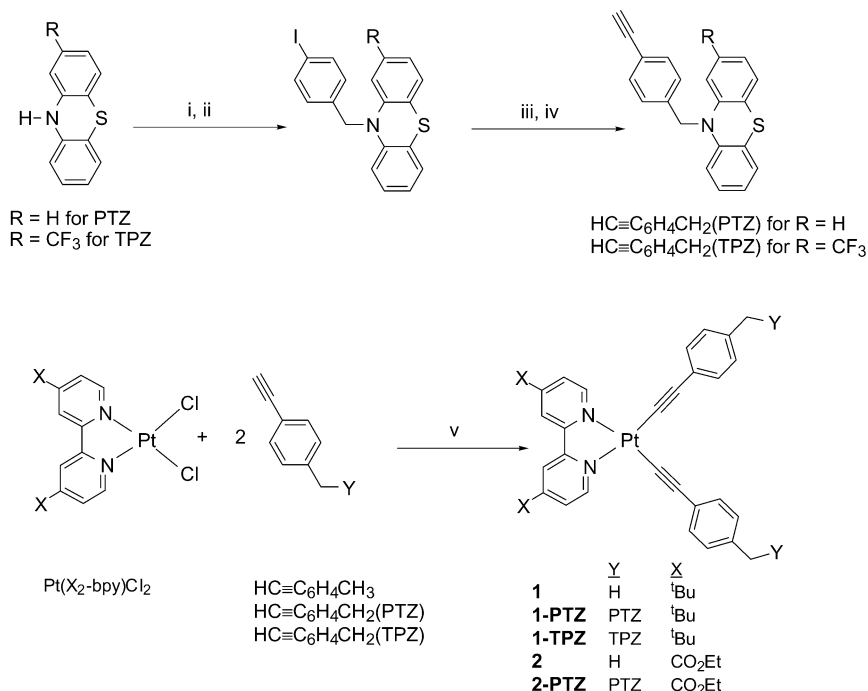
*m/z* 1119. FT-IR (KBr) *ν* (cm<sup>-1</sup>): 2115, 1729. Anal. Calcd for C<sub>58</sub>H<sub>44</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>Pt (*M<sub>r</sub>* = 1120.20): C, 62.15; H, 3.96; N, 5.00. Found: C, 62.10; H, 3.55; N, 4.86.

**Pt(Bu<sub>2</sub>-bpy)(C≡C-*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(PTZ))<sub>2</sub>, 1-PTZ.** In a 50 mL Schlenk tube, 222 mg (0.415 mmol, 1 equiv) of Pt(Bu<sub>2</sub>-bpy)Cl<sub>2</sub>, 286 mg (0.913 mmol, 2.2 equiv) of *p*-HC≡CC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(PTZ), and 8 mg (0.042 mmol, 0.1 equiv) of CuI were degassed and dissolved in 19 mL of dichloromethane and 1 mL of triethylamine. The mixture was heated at 45 °C for 3 h with stirring and evaporated to dryness. The residue was dissolved in 15 mL of dichloromethane and purified by flash chromatography, Biotage Flash 40M cartridge (Alumina, 40 μm, 60 Å), eluting with neat 4:1 dichloromethane/hexanes. The fractions were evaporated, dissolved in dichloromethane, precipitated from cold hexanes, and dried in vacuo. Yield: 0.271 g, 60%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 9.68 (d, 2H, *J* = 6.0 Hz), 7.93 (d, 2H, *J* = 1.7 Hz), 7.55 (dd, 2H, *J* = 6.0 Hz, *J* = 1.9 Hz), 7.32 (AB quartet, 8H, *J*<sub>AB</sub> = 8.2 Hz, *ν* = 126.8 Hz), 7.06 (dd, 4H, *J* = 7.5 Hz, *J* = 1.5 Hz), 6.97 (pseudo triplet, 4H, *J* = 7.6 Hz), 6.85 6.97 (pseudo triplet, 4H, *J* = 7.4 Hz), 6.65 (d, 4H, *J* = 7.3 Hz), 5.05 (s, 4H), 1.43 (s, 18 H). FAB<sup>+</sup> (matrix): *m/z* 1087. FT-IR (KBr) *ν* (cm<sup>-1</sup>): 2111. Anal. Calcd for C<sub>60</sub>H<sub>52</sub>N<sub>4</sub>S<sub>2</sub>Pt (*M<sub>r</sub>* = 1088.29): C, 66.22; H, 4.82; N, 5.15. Found: C, 66.19; H, 4.73; N, 4.95.

**Pt(Bu<sub>2</sub>-bpy)(C≡C-*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(TPZ))<sub>2</sub>, 1-TPZ.** A procedure similar to that used for 1-PTZ was used. Yield: 253 mg, 40%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 9.65 (d, 2H, *J* = 6.0 Hz), 7.93 (d, 2H, *J* = 1.7 Hz), 7.54 (dd, 2H, *J* = 6.0 Hz, *J* = 1.9 Hz), 7.32 (AB quartet, *J*<sub>AB</sub> = 8.2 Hz, *ν* = 123.3 Hz), 7.06 (m, 8H), 6.88 (m, 4H), 6.68 (d, 2H, *J* = 8.1 Hz), 5.05 (s, 4H), 1.42 (s, 18H). <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ: -0.35 (s). FAB<sup>+</sup> (matrix): *m/z* 1223. Anal. Calcd for C<sub>62</sub>H<sub>50</sub>N<sub>4</sub>S<sub>2</sub>F<sub>6</sub>-Pt (FW = 1224.30): C, 60.82; H, 4.12; N, 4.58. Found: C, 60.90; H, 3.59; N, 4.52.

## Results and Discussion

Two Pt diimine bis(acetylide) complexes, **1** and **2**, and three phenothiazine related dyads, **1-PTZ**, **1-TPZ**, and **2-PTZ**, have been synthesized and investigated in this study. Compounds **1** and **2** were used as models to compare the luminescence and absorption properties of the three C–D dyads **1-PTZ**, **1-TPZ**, and **2-PTZ**. Scheme 1 illustrates the relative energies of the <sup>1</sup>MLCT, <sup>3</sup>MLCT CS, and ground states for the C–D dyads, and it presents a qualitative model on which to consider and analyze the observed photophysical processes. Following absorption of a photon by the Pt diimine

Scheme 2<sup>a</sup>


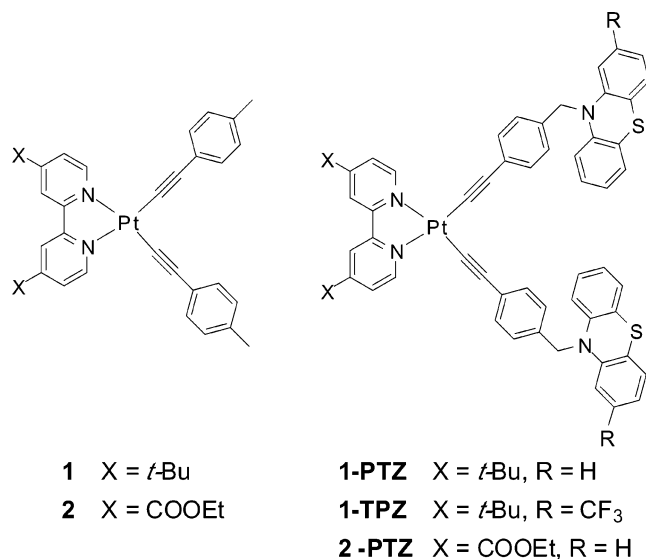
i. LDA, THF, -40 °C; ii. *p*-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br; iii. 5 mol % Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, 10 mol % CuI, benzene, NEt<sub>3</sub>, 1.2 eq. TMSA; iv. K<sub>2</sub>CO<sub>3</sub>, 1:1 MeOH/ THF; v. 10 mol % CuI, 19:1 CH<sub>2</sub>Cl<sub>2</sub>/NEt<sub>3</sub>

<sup>a</sup> (i) LDA, THF, -40 °C; (ii) *p*-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br; (iii) 5 mol % Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, 10 mol % CuI, benzene, NEt<sub>3</sub>, 1.2 equiv of TMSA; (iv) K<sub>2</sub>CO<sub>3</sub>, 1:1 MeOH/THF; (v) 10 mol % CuI, 19:1 CH<sub>2</sub>Cl<sub>2</sub>/NEt<sub>3</sub>.

bis(acetylide) chromophore in all of the compounds, the <sup>1</sup>MLCT excited state rapidly undergoes intersystem crossing to form its triplet counterpart, <sup>3</sup>MLCT. In the dyads, the <sup>3</sup>MLCT can either decay back to the ground state through radiative or nonradiative processes or undergo electron transfer to form the CS state. For electron transfer to occur, the CS state needs to lie at an energy near or below that of the <sup>3</sup>MLCT excited state. The CS state subsequently undergoes back electron transfer or charge recombination (CR) to re-form the ground state.

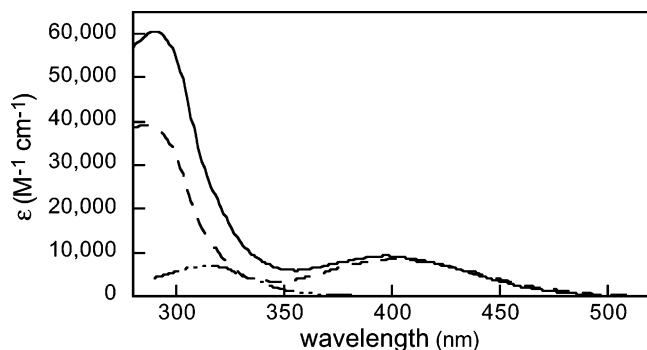
2. The first step involves the reaction of the lithium base of the phenothiazine, generated in situ using LDA, with *p*-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br to form *p*-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(PTZ) or *p*-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(TPZ) for R = H or CF<sub>3</sub>. For R = H, the Pd-catalyzed Sonogashira-Hagihara coupling,<sup>40</sup> corresponding to step iii in Scheme 2, with (trimethylsilyl)acetylene (TMSA) gave a yield of 75–80% after chromatography to form TMSC≡CC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(PTZ). Formation of the terminal alkyne, HC≡CC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(PTZ), was performed with K<sub>2</sub>CO<sub>3</sub> in anhydrous methanol/tetrahydrofuran. The yield for this step is nearly quantitative, and the overall yield for the PTZ donor ligand is 55%. The analogous preparation of the trifluoromethyl derivative gave an overall yield of the final product, HC≡CC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>(TPZ), of 45%.

Complexes **1** and **2** and dyads **1-PTZ**, **1-TPZ**, and **2-PTZ** were synthesized by the reaction of the previously reported complexes Pt(X<sub>2</sub>-bpy)Cl<sub>2</sub><sup>24,41–43</sup> (where X = CO<sub>2</sub>Et or <sup>t</sup>Bu) with the different arylacetylenes using the sequence and conditions shown in Scheme 2. Coordination of the acetylides was accomplished utilizing a CuI-catalyzed coupling reaction previously described.<sup>24,44,45</sup> Since problems were encountered

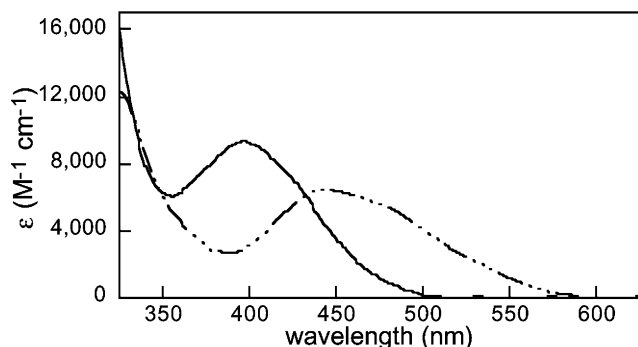


**Syntheses of Dyad Complexes.** The donor-linked acetylides were prepared according to the description in Scheme

- (40) Sonogashira, K.; Fujikura, Y.; Yatake, T.; Toyoshima, N.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *145*, 101–108.  
 (41) Cummings, S. D. *Platinum Diimine Dithiolates*; University of Rochester: Rochester, 1996.  
 (42) Kuimova, M. K.; Mel'nikov, M. Y.; Weinstein, J. A.; George, M. W. *J. Chem. Soc., Dalton Trans.* **2002**, 2857–2861.  
 (43) Cummings, S. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1996**, *118*, 1949–1960.  
 (44) Hissler, M.; Zissel, R. *J. Chem. Soc., Dalton Trans.* **1995**, 893–896.  
 (45) James, S. L.; Younus, M.; Raithby, P. R.; Lewis, J. *J. Organomet. Chem.* **1997**, *543*, 233–235.



**Figure 1.** UV-visible absorption spectra of  $2 \times p\text{-IC}_6\text{H}_5\text{CH}_2(\text{PTZ})$  (---), **1** (---), and **1-PTZ** (—) in dichloromethane. To show the electronic contribution of the PTZ moiety in **1-PTZ** the extinction coefficient is doubled for  $p\text{-IC}_6\text{H}_5\text{CH}_2(\text{PTZ})$ .



**Figure 2.** The UV-visible spectra for **1** and **2** in dichloromethane.

in the synthesis of  $\text{Pt}((\text{CO}_2\text{Et})_2\text{bpy})\text{Cl}_2$ , a new procedure was developed utilizing  $\text{Pt}(\text{DMSO})_2\text{Cl}_2$  as the starting material instead of  $\text{K}_2\text{PtCl}_4$ . Amounts of the diimine and  $\text{Pt}(\text{DMSO})_2\text{Cl}_2$  (1:1 stoichiometry) were suspended in a 1:1 mixture of MeOH and  $\text{CH}_2\text{Cl}_2$  which was stirred overnight. The suspension was filtered, yielding the platinum diimine dichloride complex in nearly quantitative yield.

**Absorption Spectra.** Absorption spectra for the C–D complexes show that within experimental error they are the sum of spectra for the isolated platinum diimine bis(acetylide) complex and the donor. This is shown in Figure 1 for **1-PTZ** with **1** and  $p\text{-IC}_6\text{H}_5\text{CH}_2(\text{PTZ})$ . The methylene bridge that separates the donor (PTZ or TPZ) from the chromophore (**1** or **2**) is a saturated  $\text{sp}^3$  carbon atom which inhibits strong electronic coupling that would alter the electronic spectra of the donor and chromophore moieties in the dyads.

The  $^1\text{MLCT}$  absorption of **2** ( $\text{X} = \text{CO}_2\text{Et}$ ) is shifted to lower energy relative to that of **1** ( $\text{X} = t\text{-Bu}$ ). This is shown in Figure 2. As noted previously, the donating (or electron-withdrawing) ability of substituents on the diimine greatly affects the  $^1\text{MLCT}$  transition energy.<sup>24,25,46</sup> In addition, there is a slight shift of the MLCT absorption of the C–D dyad complexes to higher energy relative to that found for the unsubstituted model compounds **1** and **2**.

**Electrochemistry.** Compounds **1-PTZ**, **1-TPZ**, **2-PTZ**, and appropriate models were investigated by cyclic voltammetry. The results are reported in Table 1. The first oxidation for the dyads corresponds to the oxidation of PTZ to  $\text{PTZ}^{+\bullet}$  or TPZ to  $\text{TPZ}^{+\bullet}$ . Likewise, the first reduction corresponds

**Table 1.**  $E_{1/2}$  Reduction Potentials (V versus  $\text{Fc}^+/\text{Fc}$ )

compound	donor <sup>+0</sup> ( $\Delta E$ , mV) <sup>d</sup>	$\text{Pt}(\text{X}_2\text{-bpy})^{0-}$ ( $\Delta E$ , mV) <sup>d</sup>
$\text{HC}\equiv\text{CC}_6\text{H}_4\text{CH}_2(\text{PTZ})^a$	0.35 (84)	
$\text{HC}\equiv\text{CC}_6\text{H}_4\text{CH}_2(\text{TPZ})^b$	0.46 (241) <sup>c</sup>	
<b>1</b> <sup>a</sup>		−1.82
<b>1-PTZ</b> <sup>a</sup>	0.41 (77) <sup>c</sup>	−1.77 (107)
<b>1-TPZ</b> <sup>a</sup>	0.57 (110)	−1.79 (77)
<b>2-PTZ</b> <sup>b</sup>	0.27 (96)	−1.44 (120)

<sup>a,b</sup> Measured using 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) in either <sup>a</sup> acetonitrile or <sup>b</sup> dichloromethane. <sup>c</sup> Quasireversible. <sup>d</sup>  $\Delta E = E_{\text{max}}(\text{cathodic}) - E_{\text{max}}(\text{anodic})$ .

to the one-electron reduction of  $\text{X}_2\text{-bpy}$  to  $\text{X}_2\text{-bpy}^{\bullet-}$  coordinated to  $\text{Pt}(\text{II})$ .<sup>24,43</sup> The moieties on the C–D dyad that undergo the easiest one-electron reduction and oxidation lead to the CS state consisting of  $\text{Pt}(\text{X}_2\text{-bpy}^{\bullet-})$  and the donor radical cation.

The first oxidation for the dyads occurs more easily than the irreversible oxidation of  $\text{Pt}(\text{II})$  to  $\text{Pt}(\text{III})$  observed at 0.78 V vs  $\text{Fc}^+/\text{Fc}$  (ferrocenium/ferrocene) for model compound **1**.<sup>24</sup> The oxidation is quasireversible and is assigned to the one-electron oxidation of the donor moiety (PTZ or TPZ). For comparison, 10-methylphenothiazine (10-MePTZ) and 10-phenylphenothiazine (10-PhPTZ) oxidize reversibly between 0.31 and 0.33 V versus the  $\text{Fc}^+/\text{Fc}$  couple in 0.1 M TBAH/THF.<sup>4</sup> The electrochemical reduction potentials for the oxidation of PTZ in a number of  $\text{Re}(\text{I})$  and  $\text{Ru}(\text{II})$   $d^6$  polypyridyl PTZ dyads and triads are reported to be between 0.72 and 0.83 V vs SCE in 0.1 M TBAH/acetonitrile.<sup>13,19,21</sup> The values in Table 1 can be adjusted to SCE in order to compare the literature values measured against SCE.<sup>36</sup> They range from 0.73 to 0.81 V (SCE), which agrees well with the reported values.

**Solvent Effects.** Luminescence quenching in the C–D dyad complexes with  $\text{X} = t\text{-Bu}$  is solvent dependent. Solutions of **1-PTZ** and **1-TPZ** in acetonitrile are approximately 1000 times less luminescent than that of **1**, whereas in toluene they are as luminescent as **1**. Quenching in the more polar solvents of acetonitrile and dichloromethane is due to electron transfer from the  $^3\text{MLCT}$  excited state to the CS state (vide infra).

The quantum yields and lifetimes of luminescence for compounds **1**, **1-PTZ**, and **1-TPZ** were determined in acetonitrile, dichloromethane, ethyl acetate and toluene, and are given in Table 2 along with the ratios of these quantities for the dyads relative to those of model compound **1**. In dichloromethane, the emission of **1-PTZ** is completely quenched, but luminescence is observed for **1-TPZ**, although somewhat diminished relative to **1** (Figure 3). Unexpectedly, room temperature solutions of **1-PTZ** and **1-TPZ** in toluene possess quantum yields and lifetimes that are greater and longer-lived than **1**, the model chromophore! (See Table 2.) The band shape and energy of the luminescence from **1-PTZ** and **1-TPZ** are very similar to those of **1**. It is evident that attachment of the donor has only a minor electronic effect on the chromophore, with the  $^3\text{MLCT}$  emission and  $^1\text{MLCT}$  absorption for **1-PTZ** and **1-TPZ** occurring at slightly higher energies than those for **1**.

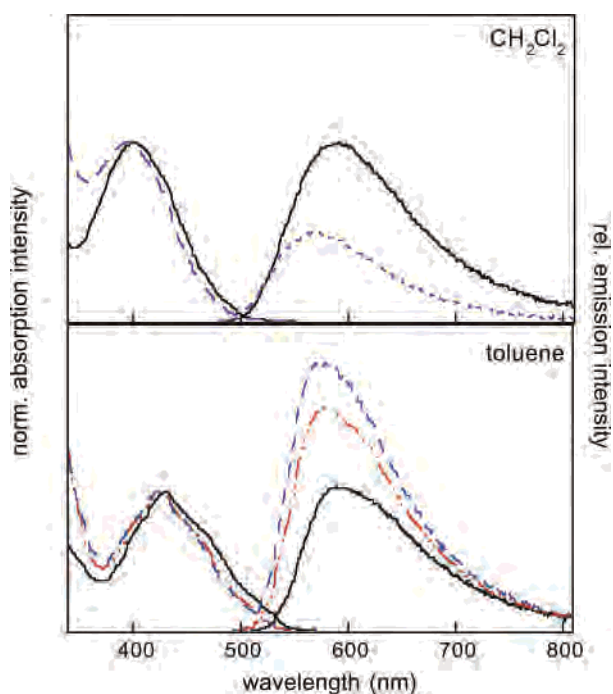
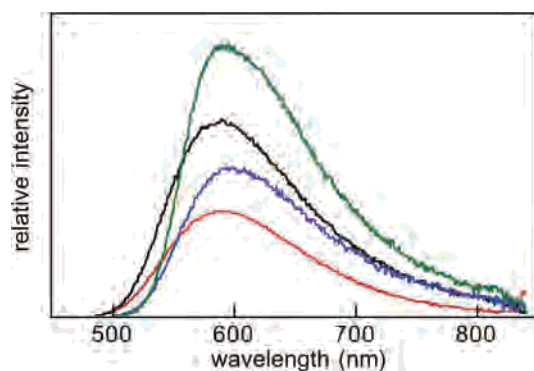
(46) Cummings, S. D.; Eisenberg, R. *Inorg. Chem.* **1995**, *34*, 3396–3404.



**Table 2.** Luminescent Quantum Yields and Lifetimes for **1**, **1-PTZ**, and **1-TPZ** and Ratios of Quantum Yields and Lifetimes for Dyads **1-PTZ** and **1-TPZ** versus **1** in Different Solvents<sup>a</sup>

solvent ( $\epsilon_s$ ) <sup>b</sup>	$\phi_{\text{lum}} (\tau)$			$\phi_{1\text{-PTZ}}/\phi_1$ ( $\tau_{1\text{-PTZ}}/\tau_{1a}$ )	$\phi_{1\text{-TPZ}}/\phi_1$ ( $\tau_{1\text{-TPZ}}/\tau_1$ )
	<b>1</b>	<b>1-PTZ</b>	<b>1-TPZ</b>		
MeCN (37.5)	0.070 (440 ns)	$\sim 10^{-4}$ ( $< 1$ ns)	$\sim 10^{-4}$ ( $< 1$ ns)	$\sim 10^{-3}$	$\sim 10^{-3}$
CH <sub>2</sub> Cl <sub>2</sub> (8.9)	0.13 (660 ns)	$\sim 10^{-4}$ ( $< 1$ ns)	0.063 (250 ns)	$\sim 10^{-3}$	0.48 (0.38)
EtOAc (6.0)	0.099 (520 ns)	0.0025 (12.6 ns)	0.17 (720 ns)	0.025 (0.024)	1.74 (1.38)
toluene (2.4)	0.18 (690 ns)	0.21 (960 ns)	0.33 (1140 ns)	1.16 (1.39)	1.83 (1.65)

<sup>a</sup> Luminescent quantum yields were determined relative to optically dilute solutions of [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in acetonitrile,  $\phi_o = 0.062$ . Lifetimes less than 50 ns were determined by TCSPC with excitation at 360 nm. Lifetimes less than 1 ns are multiexponential. <sup>b</sup>  $\epsilon_s$  = dielectric constant.

**Figure 3.** Room temperature absorption and emission spectra of (—) **1** and (---) **1-TPZ** in dichloromethane (top panel) and (—) **1**, (---) **1-PTZ**, and (---) **1-TPZ** toluene (bottom panel).**Figure 4.** Luminescence spectra of **1** in (green —) toluene, (black —) dichloromethane, (blue —) ethyl acetate, and (red —) acetonitrile at ambient temperature.

The luminescence energy of **1** does not vary significantly with solvent (Figure 4), although the emission quantum yield does exhibit a significant variation. In acetonitrile,  $\phi_{\text{lum}}$  is

0.070, while in toluene, it is 0.18. The magnitude of this variation with solvent has been observed for other chromophores, such as Ru(bpy)<sub>3</sub><sup>2+</sup>.<sup>39</sup>

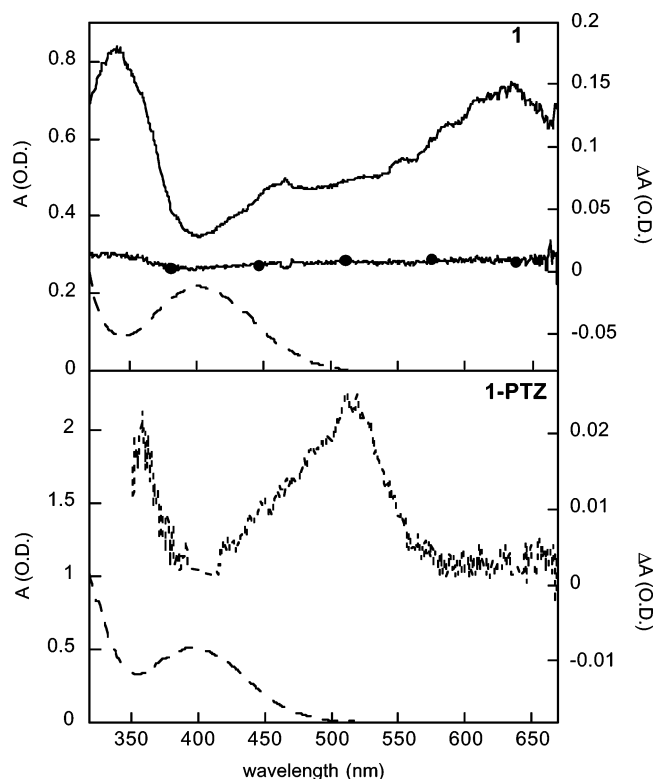
The luminescence lifetimes and quantum yields of **1** and **2** were compared against values reported by Schanze.<sup>25</sup> The luminescence quantum yield and lifetime are found to be  $\phi_{\text{lum}} = 0.0063$  and  $\tau_{\text{lum}} = 40.7$  ns for **2** in dichloromethane (measured by TCSPC) compared with respective values of 0.0046 and 20 ns reported by Schanze and co-workers.<sup>25</sup> There is a similar difference for **1** in dichloromethane, with values of  $\phi_{\text{lum}} = 0.113$  and  $\tau_{\text{lum}} = 800$  ns reported by Schanze compared with values of  $\phi_{\text{lum}} = 0.130$  and  $\tau_{\text{lum}} = 660$  ns measured in the present study (Table 2). These differences, which are relatively minor, may result from the different instrumentation employed in the measurements. In particular, sizable errors should be estimated for the nanosecond lifetimes reported previously owing to specific PMT response. The nonradiative and radiative rates can be calculated for **1** and **2** from eqs 1 and 2 leading to  $k_r(\mathbf{1}) = 2.0 \times 10^5 \text{ s}^{-1}$ ;  $k_r(\mathbf{2}) = 1.6 \times 10^5 \text{ s}^{-1}$ ;  $k_{\text{nr}}(\mathbf{1}) = 1.3 \times 10^6 \text{ s}^{-1}$ ; and  $k_{\text{nr}}(\mathbf{2}) = 2.4 \times 10^7 \text{ s}^{-1}$ . It is notable that  $k_{\text{nr}}(\mathbf{2})$  is 18 times greater than  $k_{\text{nr}}(\mathbf{1})$ . These values are essentially the same as those reported by Schanze with the exception of  $k_{\text{nr}}(\mathbf{2})$ , which is only half as large as the previously reported value.<sup>25</sup>

**TA Studies Characterizing the CS State.** Intramolecular charge transfer is the apparent mechanism by which the excited state is quenched; nanosecond and picosecond TA spectroscopy was used to characterize the quenching of the excited state, formation of the CS state, and recombination of the CS state back to the ground state. Preliminary investigations probed dyads **1-PTZ** and **2-PTZ** by nanosecond TA spectroscopy. No signal ascribable to the PTZ<sup>•+</sup> radical cation was observed for dyad **1-PTZ** in acetonitrile or for **2-PTZ** in dichloromethane. In contrast, **1-PTZ** in dichloromethane does show absorptions at 360 nm due to metal-coordinated 'Bu<sub>2</sub>-bpy<sup>•+</sup><sup>25,47</sup> and at 500 nm due to PTZ<sup>•+</sup><sup>4,13</sup> (Figure 5). It decays rapidly with the transient signal no longer present 50 ns after excitation.

Since nanosecond TA spectroscopy was unable to follow charge recombination in acetonitrile for the dyads adequately, picosecond TA studies were performed to monitor the return of the CS state back to the ground state. Figure 6 shows transient absorption spectra in acetonitrile at various delays after the flash (355 nm, 20 ps at fwhm) for the C–D dyads. **1-PTZ** and **2-PTZ** have very similar TA signals at ca. 500 nm due to the absorption of the PTZ<sup>•+</sup>. At 1 ns after excitation, solutions of **1-TPZ** have a transient absorption in the 500 nm region of the spectrum due to TPZ<sup>•+</sup>. Unlike the PTZ<sup>•+</sup> absorption, the TPZ<sup>•+</sup> absorption is broader and absorbs at slightly higher energy.

The results given in Figures 5 and 6 thus show that, under relatively polar solvent conditions, charge separation from the <sup>3</sup>MLCT excited state is observed for **1-PTZ**, **1-TPZ**, and **2-PTZ**. According to Scheme 1, the <sup>1</sup>MLCT excited state is formed upon excitation and then undergoes rapid intersystem

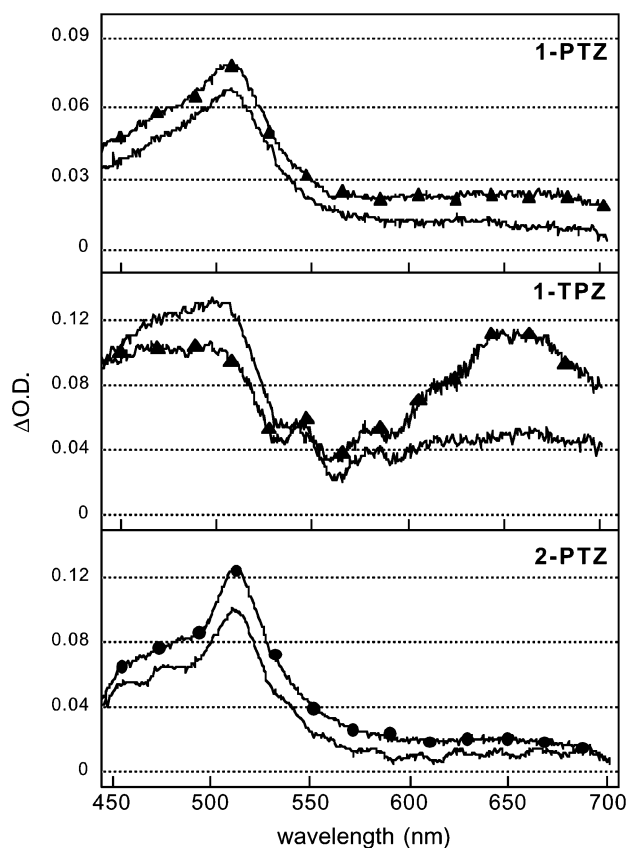
(47) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: New York, 1992.



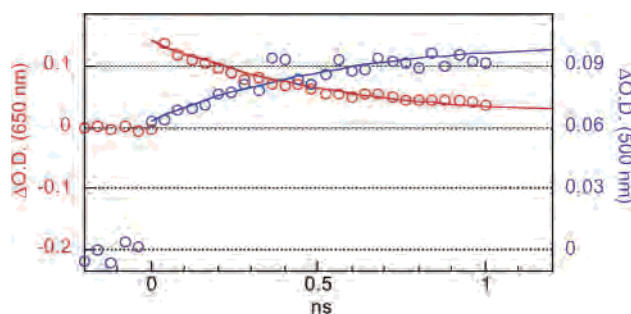
**Figure 5.** Transient absorption difference spectra and (---) absorption spectra for **1** and **1-PTZ** in dichloromethane collected at ambient temperature. For **1**, spectra were acquired following 440 nm excitation at (—) 0.06  $\mu\text{s}$  and (—●—) 2.06  $\mu\text{s}$  after the flash collected over a 50 ns time window. For **1-PTZ**, the spectrum was acquired immediately (<20 ns) following excitation at 405 nm, collected over a 20 ns time window.

crossing ( $\tau_{\text{isc}} < 1 \text{ ps}$ )<sup>48</sup> to form the <sup>3</sup>MLCT excited state. From there, the <sup>3</sup>MLCT excited state can either decay to the ground state or undergo electron transfer to form the CS state. TA spectra at earliest times after excitation show the <sup>3</sup>MLCT excited state for the C–D dyads based on absorptions at 350–370 nm (due to  $\text{Pt}(\text{X}_2\text{-bpy})^{*+}$ ) and 450–750 nm, with **1** and **2** having the greatest intensity at ca. 650 nm.<sup>25</sup> For **1-TPZ** it was possible to follow the transient decay of the <sup>3</sup>MLCT excited state at 650 nm and compare that against the transient formation of the CS state by monitoring at 500 nm on the picosecond time scale. Figure 6 (middle panel) shows spectra of **1-TPZ** at 200 ps and 1 ns after excitation. In the 200 ps spectrum, there is considerable signal at ca. 650 nm; this is interpreted as being due to the <sup>3</sup>MLCT excited state (cf., the TA spectrum of **1** due to the <sup>3</sup>MLCT excited state in the top panel of Figure 5). Figure 7 compares the intensity of the TA signals in time at 650 nm (<sup>3</sup>MLCT excited state) and 500 nm (CS state) for **1-TPZ** within the first nanosecond after excitation. There are two key features to Figure 7. The first is that the rise in signal at 500 nm has an instantaneous component and a slow component, and the second is that the slow component has the same time constant as the decay in signal at 650 nm. This latter feature suggests that the <sup>3</sup>MLCT excited state converts directly to the CS state. The time constant for charge separation ( $\tau_{\text{CS}}$ ) is estimated

(48) Yeh, A. T.; Shank, C. V.; McCusker, J. K. *Science* **2000**, 289, 935–938.



**Figure 6.** Picosecond transient absorption difference spectra for acetonitrile solutions of **1-PTZ** and **1-TPZ** and for 1:9 dichloromethane/acetonitrile solution of **2-PTZ** at room temperature following 355 nm excitation. Spectra acquired at the following time increments: (—●—) 100 ps, (—▲—) 200 ps, and (—○—) 1 ns.

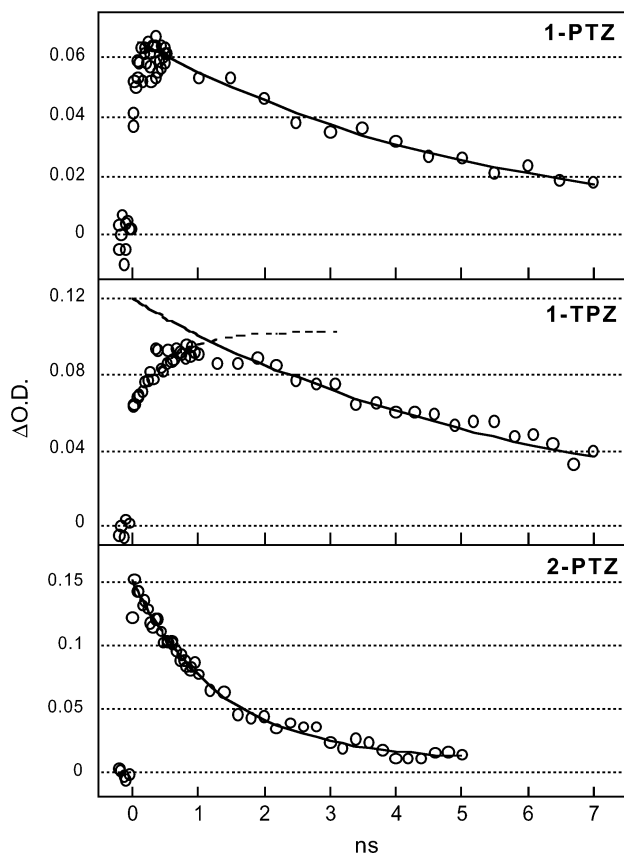


**Figure 7.** Transient different absorption kinetics at (blue —) 500 and (red —) 650 nm for **1-TPZ** in a dichloromethane solution following excitation at 355 nm. Both decay and rise are fit to the same time constant,  $\tau = 556 \text{ ps}$ .

to be 560 ps; this makes  $k_{\text{CS}}(\mathbf{1-TPZ})$ , the rate of charge separation for **1-TPZ**, equal to  $1.8 \times 10^9 \text{ s}^{-1}$ .

From the intensity of signal at ca. 500 nm, it was possible to compare the rates of charge separation ( $k_{\text{CS}}$ ) and charge recombination ( $k_{\text{CR}}$ ) for the C–D dyads. At ca. 500 nm, the formation and decay of the donor radical cation can be clearly observed for all three dyads, Figure 8. In all three data sets, the first TA signal was collected 40 ps after excitation. All three dyads show significant transient absorption signal at 40 ps. For **1-PTZ** and **1-TPZ**, this can be readily explained; while the <sup>3</sup>MLCT state has some transient absorption at ca. 500 nm (Figure 6), the rest of the signal grows in reaching a maximum within 1 ns for **1-TPZ** and 200–300 ps for





**Figure 8.** Kinetic profiles of the transient absorption difference spectra at 515 nm for **1-PTZ**, 500 nm for **1-TPZ**, and 510 nm for **2-PTZ** following 355 nm excitation in acetonitrile. Best fits to the decays (—) are shown, and for **1-TPZ** the best fit of the rise (---) is shown.

**1-PTZ.** For **2-PTZ** the TA signal grows in much faster. It reaches a maximum at 80 ps after excitation; thus, the formation of the CS state is faster for **2-PTZ** than for the other two dyads. The relative rates of charge separation for the dyads are  $k_{CS}(\mathbf{2-PTZ}) > k_{CS}(\mathbf{1-PTZ}) > k_{CS}(\mathbf{1-TPZ})$ .

The decay in TA signal for the dyads, shown in Figure 8, represents the conversion of the CS state back to the ground state. Because of instrumental constraints, the decay could be followed for only 7 ns after the excitation. The decay of the CS states for **1-PTZ** and **1-TPZ** are approximately the same, with the time constants being 5–6 ns. For **2-PTZ**, the CS decay rate can be determined more accurately because it completely decays within the 7 ns window of the instrument. The time constant for decay of **2-PTZ** was fit to a single exponential with  $\tau$  of 1.4 ( $\pm 0.1$ ) ns. The rate of charge recombination for **2-PTZ** is approximately 4 times faster than those of **1-PTZ** and **1-TPZ**.

Chromophores **1** and **2** are equally good sensitizers for intramolecular photoinduced charge separation. The maximum in the TA signal at ca. 500 nm for **1-TPZ** and **2-PTZ**, due to the donor radical cations, is approximately the same with collection conditions being nearly identical (excitation wavelength, power, and absorbance). This is despite the fact that the luminescence quantum yields for **1** and **2**, the respective model compounds, differ greatly ( $\phi_{lum}(\mathbf{2}) = 0.0063$  and  $\phi_{lum}(\mathbf{1}) = 0.130$  in dichloromethane). It was noted above that the radiative rates of decay for **1** and **2** in dichloro-

methane are roughly the same,  $k_r = (1-2) \times 10^5 \text{ s}^{-1}$ , but that the nonradiative rate of decay for **2** is ca. 18 times greater than that for **1** (vide supra). The TA results thus suggest that formation of the CS state must be roughly quantitative in both dyads and that charge separation occurs rapidly compared to the natural (radiative and nonradiative) decay of the  $^3\text{MLCT}$  excited state (see Scheme 1).

**Rate of Charge Separation.** The rates of charge separation can be rationalized in terms of the excited state reduction potential of the chromophore,  $E(\text{Pt}^{*/-})$ , and the reduction potential of the donor radical cation,  $E(\text{D}^{+/0})$ . The electrochemical potential between the CS state and the excited state,  $\Delta E_{CS}$ , which corresponds to the electrochemical driving force for CS state formation, can be calculated from eq 1. The

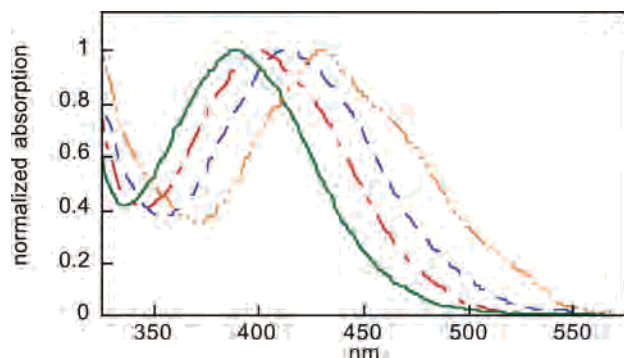
$$\Delta E_{CS} = E(\text{Pt}^{*/-}) - E_{1/2}(\text{D}^{+/0}) \quad (1)$$

difference in rate of CS formation between **1-PTZ** and **1-TPZ** is attributed to the difference in the reduction potential for the donor radical cation because the chromophores are the same ( $X = t\text{-Bu}$ ). The rate of charge separation for **1-PTZ** is faster than for **1-TPZ** because PTZ is a better one-electron donor than TPZ by ca. 160 mV. On the other hand, the difference in the rate of charge separation between **2-PTZ** and **1-PTZ** results from the difference in  $E(\text{Pt}^{*/-})$  of the two chromophores with that for **2** being greater than that for **1**. This result is rationalized by the fact that the more electron donating ligand ( $X = t\text{-Bu}$ ) raises the energy of the half-filled HOMO of the platinum diimine bis(acetylide) excited state relative to that of the less donating ligand ( $X = \text{CO}_2\text{-Et}$ ).<sup>24</sup> Therefore, the driving force for reductive quenching is greater for **2-PTZ** than for **1-PTZ**. Since the driving forces for charge separation are relatively small, the rates of charge transfer lie in the Marcus normal region where increasing the driving force increases the rate of electron transfer.

**A Qualitative Argument for Solvent Dependence in Charge Separation for C–D Dyads.** The relative energies of the CS state, the ground state, and the MLCT excited state vary as a function of solvent polarity. All three of these states correspond to polar electronic distributions. The CS state has a large dipole moment because formally it is zwitterionic with a separation of 12–14 Å between the two charges, a radical anion centered on the diimine and a radical cation centered on the nitrogen atom of the phenothiazine donor.<sup>49</sup> The ground state has a significant dipole moment because the two negatively charged acetylide ligands are coordinated in a cis geometry on one side of the platinum(II) metal center. The  $^3\text{MLCT}$  state is the least polar of the three because the dipole moment due to the cis coordination of the acetylide ligands is vectorially opposed to the dipole moment change created by the platinum-to-diimine charge transfer.

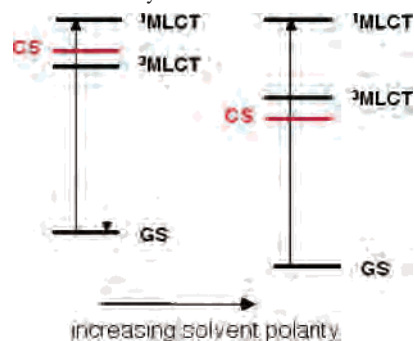
The change in dipole moment  $\Delta\mu$  from the ground state to the  $^1\text{MLCT}$  excited state of the platinum diimine bis(acetylide) chromophore can be seen in the solvent dependence of the charge transfer absorption which has been discussed previously.<sup>24</sup> Figure 9, which shows the solvent

(49) Domelsmith, N. L.; Munchhausen, L. L.; Houk, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 6506–6514.



**Figure 9.** Solvent dependent UV–visible absorption spectra for **1** in (green —) acetonitrile, (red - - -) dichloromethane, (blue - · -) ethyl acetate, and (orange · · · ·) toluene at room temperature.

**Scheme 3.** Qualitative Depiction of the Relative Energies of States as a Function of Solvent Polarity



dependence of **1**, reveals that the  $^1\text{MLCT}$  absorption maximum in toluene is  $2400\text{ cm}^{-1}$  lower in energy than that in acetonitrile. Similar solvatochromism has been reported for related Pt(diimine)(dithiolate) complexes.<sup>43,50</sup> A more direct measure of the large change in dipole moment upon  $^1\text{MLCT}$  excitation has recently been reported by Hupp and co-workers for the diimine dithiolate complex Pt(dpphen)(ecda) (dpphen = 4,7-diphenyl-1,10-phenanthroline; ecda = ethyl-2-cyano-1,1-dithiolatoacrylate).<sup>51</sup> This complex was found to have a large ground state dipole moment of  $\sim 10\text{ D}$  and a very small excited state dipole moment, which may or may not be opposite in direction to that of the ground state dipole.

Lowering the dielectric constant of the solvent has a destabilizing effect on the energy of polar states. The  $2400\text{ cm}^{-1}$  red shift in absorption energy is attributed to destabilization of the ground state relative to the MLCT excited state which remains essentially unchanged in energy because it is less polar than the ground state. The energy of the CS state is likewise destabilized relative to the MLCT states in solvents with low dielectric constants. Based on this view, an explanation for the solvent dependence of electron transfer quenching with C–D dyads can be formulated. Specifically, it appears that the relative energy ordering of the CS state and the less polar  $^3\text{MLCT}$  state changes in going from polar solutions of acetonitrile to nonpolar solutions of toluene. This is depicted in Scheme 3.

(50) Zuleta, J. A.; Bevilacqua, J. M.; Eisenberg, R. *Coord. Chem. Rev.* **1992**, *111*, 237–248.

(51) Vanhelsmont, F. W. M.; Johnson, R. C.; Hupp, J. T. *Inorg. Chem.* **2000**, *39*, 1814–1816.

There are examples of other electron transfer acceptor–donor dyads (with porphyrins) where luminescence quenching is observed in polar solvents but not in nonpolar solvents.<sup>1,52</sup> This occurs with neutral dyads where the energies of the zwitterionic ( $\text{A}^{\bullet-}-\text{D}^{\bullet+}$ ) CS state and the excited state are comparable in solvents with high dielectric constants.<sup>1</sup> Coulombic effects due to the separation of charge in the CS state are used to explain and roughly quantify the relative energies of the excited state and the CS state.<sup>1,52</sup> The Coulombic terms used to adjust the energy of the CS state are sensitive to the distance between charges, the radii of the charges, and the dielectric constant. Similarly, the C–D dyads examined in the present study are neutral complexes where the energies of the  $^3\text{MLCT}$  and the CS states are nearly equivalent (vide infra). Therefore, it is not surprising that quenching of the excited state does not take place in less polar solvents.

**Energy of the Excited State.** There are several approaches to estimating the  $\Delta E_{00}$  energy of the  $^3\text{MLCT}$  excited state where  $\Delta E_{00}$  is the difference in energy between the zero vibrational levels of the ground and excited states. For a number of transition metal chromophores with diimine ligands, such as  $\text{Ru}(\text{diimine})_3^{2+}$  and  $\text{Re}(\text{diimine})(\text{CO})_3\text{X}$ , single-mode Franck–Condon expressions have been used to fit the luminescence and derive values for  $\Delta E_{00}$ . Schanze and co-workers employed this approach to estimate  $\Delta E_{00}$  of 2.13 and 1.84 eV for **1** and **2**, respectively, in dichloromethane at room temperature.<sup>25</sup> An alternative but formally less rigorous approach uses the highest energy emission maximum of the 77 K frozen glass solution to estimate  $\Delta E_{00}$ . Through the use of this procedure, we obtain excited state energies for **1-PTZ** (toluene) and **2-PTZ** (1:3 dichloromethane/toluene), which are emissive at 77 K, of 2.4 eV (512 nm) and 2.2 eV (556 nm), respectively.

**Energy of the Charge-Separated State.** The quantity  $\Delta E_{\text{CR}}$  is the electrochemical potential energy of the CS state relative to the ground state in the solvent used to measure  $E_{1/2}(\text{Pt}(\text{X}_2\text{-bpy})^{0/-})$  and  $E_{1/2}(\text{PTZ}^{+/0})$ . It is related to the free energy change of charge recombination,  $-\Delta G_{\text{CR}}$ , through inclusion of the electrostatic work term,  $w$ , in eq 2. The work term,  $w$ , is an approximate correction for the Coulombic energy interaction<sup>11</sup> between  $\text{Pt}(\text{X}_2\text{-bpy}^{\bullet-})$  and the donor radical cation of the CS state. The electrochemical potentials given in Table 1 are used to determine  $\Delta E_{\text{CR}}$  according to eq 3 in which  $E_{1/2}(\text{Pt}(\text{X}_2\text{-bpy})^{0/-})$  corresponds to the ground state reduction potential for the chromophore. These values are reported in Table 3 based on electrochemical measurements in either dichloromethane or acetonitrile. The calcu-

$$-\Delta G_{\text{CR}} = \Delta E_{\text{CR}} - w \quad (2)$$

$$\Delta E_{\text{CR}} = E_{1/2}(\text{PTZ}^{+/0}) - E_{1/2}(\text{Pt}(\text{X}_2\text{-bpy})^{0/-}) \quad (3)$$

lated values for the work term are small in acetonitrile (0.03 eV for  $\epsilon_s = 37.5$ ) and dichloromethane (0.12 eV for  $\epsilon_s =$

(52) DeGraziano, J. M.; Macpherson, A. N.; Liddell, P. A.; Noss, L.; Sumida, J. P.; Seely, G. R.; Lewis, J. E.; Moore, A. L.; Moore, T. A.; Gust, D. *New J. Chem.* **1996**, *20*, 839–851.

**Table 3.** Electrochemical Potentials for Charge Separation Based on Potentials for Chromophore Excited State Reduction and Charge Recombination<sup>a</sup>

$\Delta E_{CR}$	$\Delta E_{00}^b$	$E(\text{Pt}^{*/-})^b$	$\Delta E_{CS}^b$
2.18	2.1/2.4	0.4/0.6	-0.1/+0.2
2.36	2.1/2.4 <sup>c</sup>	0.3/0.6	-0.2/0.0
1.71	1.8/2.2	0.4/0.8	0.1/0.5

<sup>a</sup> All values are in volts. <sup>b</sup> The estimated error for  $\Delta E_{00}$  is  $\pm 0.1$  V. The first number is based on determination of  $\Delta E_{00}$  using the Franck–Condon single-mode analysis, and the second number is based on determination of  $\Delta E_{00}$  using the highest energy 77 K emission maximum. <sup>c</sup> Estimated value is that for **1-PTZ** since the chromophore is unchanged.

8.9) (dichloromethane),<sup>53</sup> thus making little contribution to  $\Delta G_{CR}$  in these solvents.

From a simple thermodynamic cycle using  $\Delta E_{CR}$  and  $\Delta E_{00}$ , it is possible to estimate the potential energy for charge separation,  $\Delta E_{CS}$ , according to eq 4. The values of  $\Delta E_{CS}$  and the excited state reduction potential  $E_{1/2}(\text{Pt}^{*/-})$  estimated from eq 5 are reported in Table 3. The values calculated from eqs

$$\Delta E_{CS} = \Delta E_{00} - \Delta E_{CR} \quad (4)$$

$$E_{1/2}(\text{Pt}^{*/-}) = \Delta E_{00} + E_{1/2}(\text{Pt}(\text{X}_2\text{-bpy})^{0/-}) \quad (5)$$

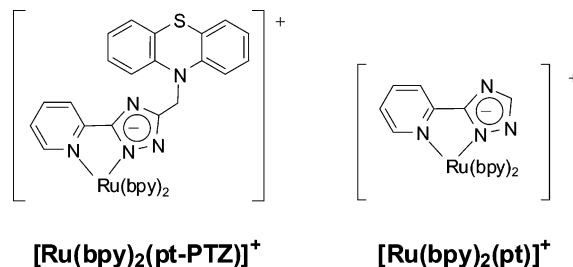
3–5 given in Table 3 indicate that the <sup>3</sup>MLCT and CS states in polar solutions (acetonitrile and dichloromethane) are close in energy. Based on the Franck–Condon single mode analysis,  $\Delta E_{CS}$  is slightly negative, whereas with the use of the 77 K emission data to estimate  $\Delta E_{00}$ , this quantity is slightly positive. For **1-TPZ**, only *partial* quenching is observed in dichloromethane, suggesting that  $\Delta E_{CS}$  is close to zero for this system and that as a consequence  $\Delta E_{CR}$  is close in value to  $\Delta E_{00}$ . A more detailed and quantitative analysis of  $\Delta E_{CS}$  appears warranted for C–D dyads of the type featured here and will require more accurate assessments of excited state energies and electrochemical measurements in the solvents studied.

**Another Observation of Enhancement in Quantum Yield and Lifetime.** In ethyl acetate and toluene, the <sup>3</sup>MLCT lifetime and quantum yield are enhanced for **1-TPZ** compared to **1**. The <sup>3</sup>MLCT excited state for **1-TPZ** is more energetic than **1** by ca. 0.06 eV. While one might suggest that the greater lifetime and luminescence quantum yield for **1-TPZ** can be explained by the energy gap law, the small difference in energy appears insufficient to explain the 83% enhancement in  $\phi_{lum}$  and the 65% increase in  $\tau_{lum}$ .

Interestingly, a similar enhancement in  $\phi_{lum}$  and  $\tau_{lum}$  from a <sup>3</sup>MLCT excited state has been reported previously for  $[\text{Ru}(\text{bpy})_2(\text{pt-PTZ})]^+$  in dichloromethane and acetonitrile versus a related model chromophore,  $[\text{Ru}(\text{bpy})_2(\text{pt})]^+$ .<sup>20</sup> In that report, thermodynamic estimates predict that the CS state is higher in energy than the <sup>3</sup>MLCT excited state by  $\sim 0.1$  eV analogous to what is suggested here. The authors did not note, however, any energetic differences in the excited state

(53) The work term (eV) is equal to  $-14.43(\epsilon_s)^{-1}(R)^{-1}$  where  $\epsilon_s$  is the solvent dielectric constant and  $R$  is in Å.

of the dyad versus the model compound and merely say that an “explanation for this behavior [i.e., the enhanced luminescence quantum yield and lifetime] is by no means simple, and any hypothesis advanced at the moment would be purely speculative.” Likewise, we offer no speculation for the observed enhancement in lifetime and quantum yield observed for **1-TPZ** and **1-PTZ** relative to **1**. The energy gap law argument by itself does not give a satisfactory explanation for the *magnitude* of the effect.



## Conclusions

Intramolecular electron transfer quenching has been observed via TA spectroscopy for the three dyads in the present study, **1-PTZ**, **1-TPZ**, and **2-PTZ**, in more polar solvents. Charge separation appears to be in the Marcus normal region since  $k_{CS}$  increases as  $\Delta E_{CS}$  increases. In contrast charge recombination appears to be in the Marcus inverted region, since  $k_{CR}$  decreases with increasing  $\Delta E_{CR}$ . The CS state is formed just as efficiently for **2-PTZ** as it is for **1-PTZ** or **1-TPZ** despite the luminescence quantum yield for **2** being 18 times less than that for **1**. The quantum yield for formation of the CS state does not appear to depend on the luminescence quantum yield,  $\phi_{lum}$ , leading to the conclusion that  $k_{CS}$  is greater than  $k_r$  and  $k_{nr}$ . These observations have considerable impact on the further design of triads and multiads for photoinduced charge separation.

Luminescence from dyads in nonpolar solvents represents an interesting observation. Dyads **1-PTZ** and **1-TPZ** both show electron transfer quenching to form the CS state in polar solvents, but in nonpolar solvents electron transfer quenching does not occur and indeed an enhancement in the luminescence quantum yield and lifetime is seen as compared to model compound **1**. It is not clear whether the enhancement in luminescence lifetime and quantum yield is a consequence of the slightly more energetic excited state of the dyads as suggested by the energy gap law or is due to some other factor. Further investigation is needed in order to further elucidate the solvent dependence and enhancement in luminescence.

**Acknowledgment.** We wish to thank the Department of Energy, Division of Chemical Sciences, for support of this research. We also gratefully acknowledge the help of Drs. Cavaan Fleming and Steve Atherton in the TCSPC and picosecond TA experiments, and Dr. Muriel Hissler in providing original samples of **1** and **1-PTZ**.

IC034026D