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Platinum(II) Terpyridyl Acetylide Complexes on Platinized TiO_2: Toward the Photogeneration of H_2 in Aqueous Media

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New platinum(II) terpyridyl acetylide complexes having the ability to bind to TiO_2 have been synthesized and assayed in their ability to sensitize platinized titanium dioxide for the photogeneration of H_2 using visible light (λ > 410 nm). Specifically, the complexes [Pt(tpy-phen-COOH)($C{\equiv}C{-}C_6H_5$)]Cl (**1**), where tpy-phen-COOH = 4′-(4-carboxyphenyl)-[2,2′;6′,2″]terpyridine and $C{\equiv}C{-}C_6H_5$ = phenylacetylide, and [Pt(tpy-COOH)($C{\equiv}C{-}C_6H_5$)]Cl (**2**), where tpy-COOH = 4′-carboxy-2,2′;6′,2″-terpyridine, were prepared to investigate the effectiveness of attachment and proximity to the TiO_2 surface on hydrogen yield. Both complexes **1** and **2** sensitize the photogeneration of hydrogen, but produce fewer turnovers than the unbound chromophore, [Pt(ttpy)($C{\equiv}C{-}C_6H_5$)]PF_6 (**5**). On the basis of these observations and electrochemical data, a major limitation to the effectiveness of these chromophores is their instability upon oxidation. To attempt to remedy this problem, two donor-chromophore (D-C) dyads, [Pt(tpy-phen-COOH)-($C{\equiv}C{-}C_6H_4CH_2{-}PTZ$)]$PF_6$ (**3**), where $C{\equiv}C{-}C_6H_4CH_2{-}PTZ$ = *N*-(4-ethynylbenzyl)-phenothiazine and [Pt(tpy-COOH)($C{\equiv}C{-}C_6H_4CH_2{-}PTZ$)]Cl (**4**) were prepared to function as TiO_2-attached sensitizers. Transient absorption measurements have shown that the PTZ moiety reductively quenches the Pt center in several picoseconds. While the resultant PTZ^+ radical cation is capable of oxidizing rapidly the triethanolamine sacrificial electron donor, dyads **3** and **4** attached to platinized TiO_2 do not function to generate hydrogen upon irradiation, in contrast with results seen for **1** and **2**.

Introduction

The drive to convert solar energy into more usable forms of energy has been a powerful stimulus in transition metal photochemistry and photophysics. Many of these efforts have focused on the conversion of solar energy to electrical power through the use of semiconductor arrays and dye-sensitized semiconductors materials.[1−18] Pursued in parallel, but with less frequency, has been the conversion of

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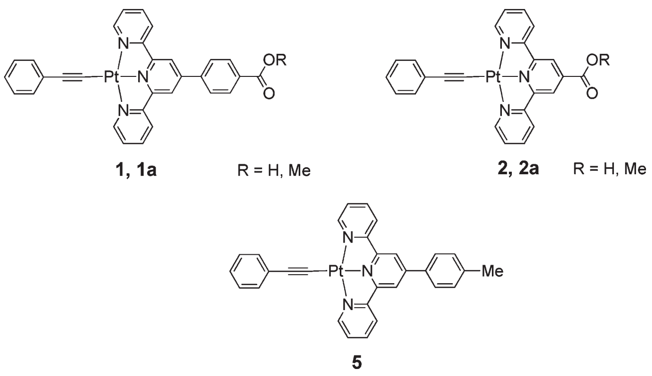
solar energy directly into chemical fuel by means of photoelectrochemical processes.[3,19−39] Within these reports, the light-driven reduction of water to H_2 has been a foremost objective because of hydrogen's high specific enthalpy of combustion as a fuel and the low environmental impact of its combustion product, water.

The strategy of using charge transfer chromophores to sensitize or inject electrons into the conduction band (CB) of TiO_2 has been pursued for more than three decades.[11−13,18] Moreover, if the TiO_2 is platinized (TiO_2−Pt), proton reduction to H_2 becomes possible when a sacrificial electron donor such as triethanolamine or another tertiary amine is also present.[26,35−40] While most of these studies have involved a d^6 Ru(II) tris diimine sensitizer, a few reports have examined d^8 Pt(II) diimine chromophores in this capacity. Recently, we described one of these systems with a Pt(II) bipyridyl dithiolate chromophore and TiO_2−Pt for electron separation and H_2 catalysis, and found that with $\lambda > 455$ nm light, the system was photostable as well.[40] This and other reports demonstrate that platinum chromophores are competent as dye sensitizers for TiO_2, and with TiO_2−Pt, are capable of the photogeneration of H_2.[41−44]

With the intention of making these systems more effective in producing H_2, efforts have been directed to the construction of integrated systems for hydrogen generation. Such a system would remove the constraint of diffusional quenching kinetics, and thereby eliminate the need for higher concentrations of quenching species to achieve efficient charge separation and productive photochemistry. However, the actual effects of chromophore attachment to TiO_2 in these constructions is often overlooked. In this paper, we describe the use of Pt(II) terpyridyl acetylide chromophores for the sensitization of TiO_2 in systems for the photogeneration of hydrogen (Figure 1). Complexes **1** and **2** possess carboxylate groups for attachment to platinized TiO_2 (Figure 2), and their effectiveness is compared to that of the parent chromophore **5**, which has no such anchoring group for TiO_2 binding.

Previous reports have shown that upon excitation of suitably anchored Ru(bpy) or Ru(tpy) derivatives, electron injection into the TiO_2 particle proceeds from the excited chromophore to the TiO_2 conduction band at a rate ranging from $\sim 10^2$ fs to picoseconds, depending on the distance between the chromophore and the particle.[11−13,18] In these systems, the nature of the excited state from which charge injection occurs is a metal-to-ligand charge transfer (MLCT), which is similar to that of the platinum terpyridyl acetylides exemplified by **5**.[45−53] For both sets of chromophores, the lowest unoccupied orbital is primarily the π^* orbital of a bpy or tpy ligand, and therefore, similar rates of charge injection from the excited state of the Pt(II) chromophore excited state into TiO_2 are expected.



1, 1a R = H, Me

2, 2a R = H, Me

5

Figure 1. Chromophores **1**, **2**, and **5** used for the sensitization of platinized titanium dioxide for the photogeneration of hydrogen, as well as the methyl ester precursors **1a** and **2a**.

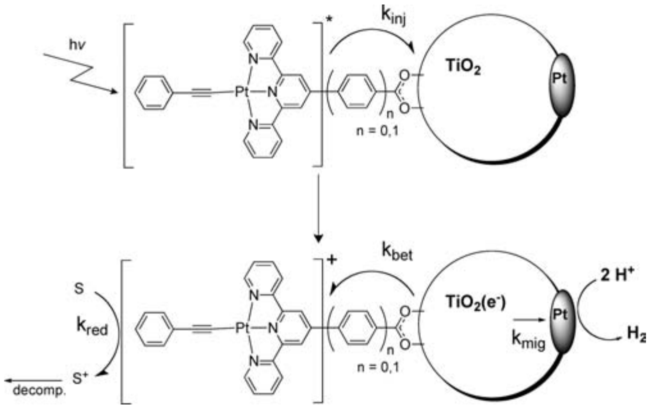


Figure 2. Schematic representation of a system for the photogeneration of hydrogen, using platinum terpyridyl acetylide chromophores **1** ($n = 1$) and **2** ($n = 0$) to sensitize platinized TiO_2. The processes of charge injection, back electron transfer, charge migration through the particle, and reduction by the sacrificial donor have rate constants denoted as k_{inj}, k_{bet}, k_{mig}, and k_{red}, respectively.

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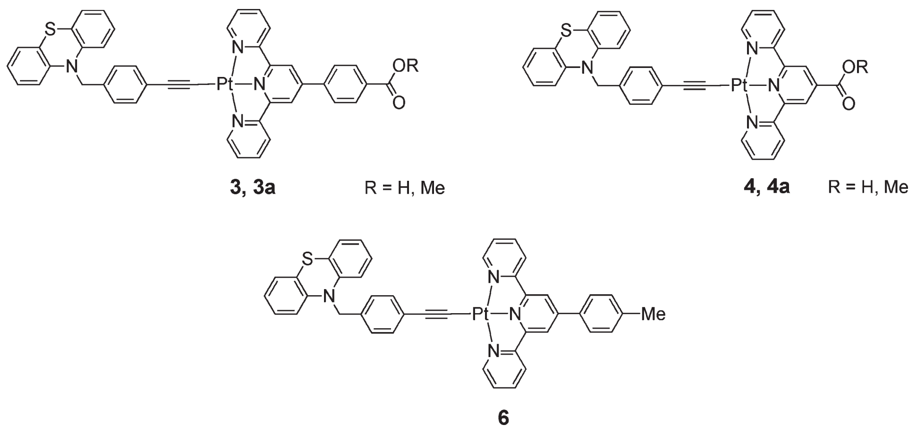

Figure 3. D-C dyads **3** and **4** used for the sensitization of platinized titanium dioxide for the photogeneration of hydrogen as well as the methyl ester precursors **3a** and **4a** and the previously reported D-C dyad **6**.

Once in the conduction band, these electrons are able to migrate to the catalytic sites of platinum metal and effect proton reduction. Rates of charge transport through single particles of TiO_2 are becoming increasingly well understood, and several physical models have been proposed to describe the mobility of electrons in these particles.[18,54-60] These rates have been found to depend on the energy of the injected electron as well as the density of trap sites in the particle.

With charge injection taking place on a picosecond time scale, it is unlikely that reductive quenching by a sacrificial donor will occur prior to electron injection. It is more probable that, after charge injection, the oxidized chromophore will be reduced by the sacrificial donor, or undergo back electron transfer with electrons in the conduction band, at a rate that is again affected by the distance and pathway between the chromophore and the particle. For oxidatively unstable chromophores, this scenario leads to "long-term" decomposition as a consequence of light driven electron injection into TiO_2. Recent work of Zhiyong et al., on the degradation of Methyl Orange dye on TiO_2 addresses this issue directly,[61] and a 2006 report by Grätzel describes this as one of the chief concerns in designing systems to achieve high turnovers in photovoltaic systems.[62]

To counter the issue of Pt chromophore oxidative instability and to expand the study of charge transfer complexes on TiO_2, donor-chromophore dyads **3** and **4** bearing the phenothiazine moiety (Figure 3) have also been synthesized and examined as sensitizers for the photogeneration of hydrogen (Figure 4). The results are also described herein and are compared to those obtained for **1** and **2**. Phenothiazine donors have previously been found to be effective reductive quenchers of MLCT excited states of Ru and Pt polypyridyl complexes, such as in the case of the donor-chromophore (D-C) dyad, [Pt(ttpy)($C{\equiv}C-C_6H_4CH_2-PTZ$)]$PF_6$ [**6**] (Figure 3) by transient absorption spectroscopy.[52] In similarly motivated efforts, donor-chromophore dyads have been explored for photocurrent production in Grätzel-type cells, though such systems are relatively uncommon compared to pure chromophore sensitizers.[16,63,64]

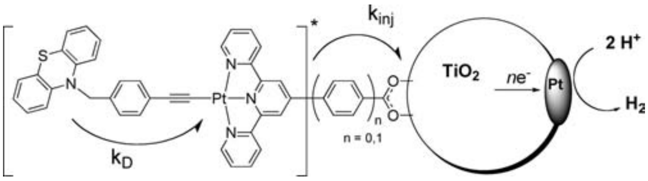

Figure 4. Schematic representation of D-C dyads **3** (n = 1) and **4** (n = 0) as sensitizers for the photogeneration of hydrogen. k_D is the rate constant for reductive quenching of the chromophore by the phenothiazine moiety.

Experimental Section

Materials. The chemicals *N*,*N*-dimethylformamide (DMF), acetonitrile (MeCN), tetrahydrofuran (THF), dimethylsulfoxide, copper(I) iodide, ammonium acetate, ammonium hexafluorophosphate (NH_4PF_6), 2-acetylpyridine, triethylamine, potassium hydroxide, 2-furaldehyde (Aldrich), electrochemical grade tetrabutylammonium hexafluorophosphate and potassium *tert*-butoxide (Fluka), potassium hexachloroplatinate, (Strem Chemical), and titanium dioxide P25 (Degussa) were used without further purification.

The synthesis of $Pt(DMSO)_2Cl_2$ was carried out according to a literature procedure.[52] [Pt(ttpy)($C{\equiv}C-C_6H_5$)]PF_6 (**5**) was used as previously prepared.[52] Platinized TiO_2 catalysts were prepared by the photodeposition method, using potassium hexachloroplatinate as the platinum source by a method previously described.[40] Syntheses were performed under nitrogen with solvents purified by passing the degassed solvent through columns containing activated molecular sieves and activated alumina.[65] All other reagents were of spectroscopic grade and used without further purification.

Characterization. ^1H NMR spectra were recorded on a Bruker Avance-500 spectrometer (500 MHz). Mass determinations were accomplished by electrospray ionization mass spectrometry (ESIMS) using a Shimadzu mass spectrometer equipped with a quadrupole mass filter. Mass spectrometric data for

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1−**4** are provided in the Supporting Information. Cyclic voltammetry experiments were conducted on an EG&G PAR 263A potentiostat/galvanostat using a three electrode single compartment cell, with DMF as the solvent. A glassy carbon working electrode, Pt wire auxiliary electrode, and Ag wire reference electrode were used. For all measurements, samples were degassed with nitrogen. Tetrabutylammonium hexafluorophosphate (0.10 M) was used as the supporting electrolyte while ferrocene was employed as an internal redox reference. All redox potentials are reported relative to NHE using the ferrocenium/ferrocene (Fc^+/Fc) couple (0.45 V vs SCE for DMF)[66] as an internal standard, and all scans were done at 100 mV/s. Absorption spectra were recorded using a Hitachi U2000 scanning spectrophotometer (300−800 nm). Emission spectra were obtained using a Spex Fluoromax-P fluorimeter. Monochromators were positioned with a 2 nm band-pass, and solution samples were degassed by sparging with N_2. Frozen glass samples were prepared in butyronitrile using NMR tubes in a circular quartz-tipped immersion Dewar filled with liquid nitrogen. Emission spectra were uncorrected for spectral response. Infrared spectra of titanium dioxide samples were obtained using a Shimadzu 8400 S FT-IR spectrometer in air with the background signal subtracted.

Femtosecond transient absorption measurements were performed with a regeneratively amplified titanium/sapphire laser producing 1.7 mJ 100 fs duration pulses at 800 nm with a 1 kHz repetition rate. The 400 nm pump pulse was generated by frequency doubling the Ti:sapph. fundamental, resulting in a ~120 fs pulse with 0.5−1 μJ per pulse. The probe continuum extended from 320 to 600 nm and was produced by focusing a small portion of the 400 nm pulse into a 2 mm thick CaF_2 crystal. The relative polarization of the pump and probe beams was 55°, to eliminate artifacts from molecular rotation. The sample was degassed with nitrogen and sealed in a 10 mm cuvette. After being focused through the sample with the pump pulse, the probe was collected, dispersed by a spectrograph (Acton 320 mm fl, 150 g/mm), and measured with a 1024 pixel diode array detector. Each transient absorption spectrum is the average of 1000 laser pulses, in which the alternating pump-off and pump-on spectra are compared in 100 ms exposures to produce the transient absorption spectrum for a single pump−probe time delay. The time delay was controlled by optically delaying the pump pulse and the time resolution was 250−300 fs, depending on wavelength.

For photoinduced hydrogen evolution experiments, each sample was prepared in a 50 mL round-bottom flask with a solution volume of 25 mL of acetonitrile/water (3:2 v/v). Typically, the sample contained 2.0×10^{-5} M photosensitizer, 25 mg platinized TiO_2 (TiO_2/Pt, Pt% = 0.05%), and triethanolamine (50−500 mg). The pH of the solution was adjusted to 7 with 10% HCl. The flask was sealed with a septum and degassed by bubbling nitrogen for 20 min under atmospheric pressure at room temperature. Following degassing, a gas syringe was used to remove 5 mL nitrogen from the flask headspace and 5 mL methane (760 Torr) was likewise injected into the flask, to serve as an internal standard. The samples were irradiated with a 200 W Mercury Xenon lamp. A long-pass filter ($\lambda > 410$ nm) was used to exclude higher energy light, capable of exciting the bandgap of TiO_2. The hydrogen generated by the system was measured by periodically withdrawing 0.1 mL of the headspace atmosphere of the reaction vessel and analyzing it with a GC-17A (Shimadzu) gas chromatograph equipped with a 5 Å molecular sieves column (30 m × 0.53 mm) and a thermal conductivity detector. Pre-purified nitrogen was employed as the carrier gas.

4′-(4-Methylcarboxyphenyl)-[2,2′;6′,2″]terpyridine (tpy-phen-COOMe). This ligand was prepared using standard methodology, but has not been previously reported by this procedure. Alternative procedures have been reported, with comparable yields.[67,68] A 500 mL flask was charged with potassium *tert*-butoxide (6.8 g, 59 mmol) and THF (60 mL). This was stirred vigorously until most of the base had dissolved. To this was added dropwise a solution of 2-acetyl pyridine (5.5 mL, 49 mmol) in THF (60 mL) over 1 h, yielding an off white suspension. A solution of 4-methylcarboxy-benzaldehyde (4 g, 24 mmol) in THF (60 mL) was then added dropwise over 1 h, and the resulting orange solution was left to stir for 3 h, during which it became dark red. A solution of ammonium acetate (10 g, excess) in methanol (50 mL) and glacial acetic acid (25 mL) was added, and the reaction stirred at reflux for 16 h. After removing volatiles by rotary evaporation, water was added to the green slurry, and the pH adjusted to 7 with sodium hydroxide. The resulting yellow precipitate was collected by filtration, washed with acetonitrile, diethyl ether, and dried in vacuo. Yield: 2.485 g (28%). Characterization data are consistent with those previously reported.

tpy-phen-COOH. A 25 mL flask was charged with tpy-phen-COOMe (0.200 g, 0.54 mmol), sodium hydroxide (200 mg, excess), acetonitrile (8 mL), and water (8 mL). The suspension was stirred at reflux for 16 h. The solution was neutralized with dilute HCl, and the white solid collected by precipitation, washed with THF/diethyl ether (1:1/v:v), and dried in vacuo. Yield: 0.170 g (89%). ^{1}H NMR data were consistent with those previously reported.[67]

[Pt(tpy-phen-COOMe)Cl]Cl. A 25 mL flask was charged with $Pt(DMSO)_2Cl_2$ (0.080 g, 0.20 mmol), tpy-phen-COOMe (0.080 g, 0.22 mmol), DMF (8 mL), and methanol (8 mL). The resulting suspension was stirred at reflux under N_2 for 16 h. A yellow suspension formed, and complete precipitation was effected by the addition of water. The solid was collected by filtration and washed with acetone and diethyl ether. Yield: 0.094 g (74%). ^{1}H NMR (DMSO-d_6): δ 9.12 (2H, s), 9.02 (2H, d, J = 5 Hz), 8.93 (2H, d, J = 8), 8.60 (2H, t, J = 8), 8.37 (2H, d, J = 8), 8.24 (2H, d, J = 8), 8.03 (2H, t, J = 7), 3.96 (3H, s).

[Pt(tpy-phen-COOMe)(C≡C−C_6H_5)]Cl (1a). A 10 mL flask was charged with [Pt(tpy-phen-COOMe)Cl]Cl (0.080 g, 0.13 mmol), ammonium hexafluorophosphate (0.100 g, excess), CuI (0.010 g, 0.06 mmol), and DMF (4 mL). Ammonium hexafluorophosphate was required to enhance the solubility of the complex and reduce reaction time (see Results and Discussion). The reaction flask was sealed with a septum, and the solution sparged with N_2. Phenylacetylene (0.10 mL, 0.9 mmol) and triethylamine (0.10 mL, 0.8 mmol) were added via syringe, and the reaction mixture was stirred in the dark for 48 h. A red precipitate that formed upon the addition of diethyl ether was collected by centrifugation and dissolved in acetonitrile. The addition of tetrabutylammonium chloride resulted in complete precipitation as the chloride salt, which was washed with acetone and diethyl ether, then dried in vacuo. Yield: 0.079 g (84%). ^{1}H NMR (DMSO-d_6): δ 9.21 (2H, d, J = 5 Hz), 9.14 (2H, s), 8.90 (2H, d, J = 8), 8.58 (2H, t, J = 8), 8.33 (2H, d, J = 8), 8.24 (2H, d, J = 8), 7.98 (2H, t, J = 8), 7.53 (2H, d, J = 7), 7.37 (2H, t, J = 7), 7.30 (1H, t, J = 7), 3.96 (3H, s). MS (positive-API-ES): m/z 663.10 $[M - Cl]^+$.

[Pt(tpy-phen-COOH)(C≡C−C_6H_5)]Cl (1). A test tube was charged with **1a** (0.030 g, 0.32 mmol), potassium hydroxide (0.060 g, 1 mmol), THF (1.0 mL), and water (1.0 mL). The tube was sealed with a septum, and the suspension was stirred for 2 days in the dark. The suspension was adjusted to pH 7 with dilute HCl, and additional water was added. The precipitate was collected by centrifugation and washed with water, acetone, and

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dried in vacuo. Yield: 0.020 g (90%). ^{1}H NMR (DMSO-d_6): δ 9.15 (2H, d, J = 5 Hz), 9.10 (2H, s), 8.88 (2H, d, J = 8), 8.55 (2H, t, J = 8), 8.28 (2H, d, J = 8), 8.20 (2H, d, J = 8), 7.95 (2H, t, J = 6), 7.50 (2H, d, J = 7), 7.36 (2H, t, J = 7), 7.29 (1H, t, J = 7). HRMS - ESI (exp; calc): m/z (648.11725, 649.12134; 648.1177, 649.1198) for [$^{194}PtC_{30}H_{20}N_3O_2$, $^{195}PtC_{30}H_{20}N_3O_2$]$^+$. Anal. Calcd for $PtC_{30}H_{20}N_3O_2Cl$: C, 52.63; H, 2.92; N, 6.14. Found: C, 49.35; H, 3.73; N, 5.66.

[Pt(tpy-phen-COOMe)($C{\equiv}C-C_6H_4CH_2-PTZ$)]Cl (3a). A 10 mL flask was charged with [Pt(tpy-phen-COOMe)Cl]Cl (0.040 g, 0.063 mmol), *N*-(4-ethynylbenzyl)-phenothiazine (0.049 g, 0.16 mmol), ammonium hexafluorophosphate (0.050 g, excess), CuI (0.010 g, 0.06 mmol), and DMF (4 mL). Ammonium hexafluorophosphate was required to enhance the solubility of the complex and reduce reaction time. The flask was sealed with a septum, and the solution sparged with N_2. Triethylamine (0.10 mL, 0.8 mmol) was added via syringe, and the reaction mixture was stirred in the dark for 48 h. A dark red precipitate formed upon the addition of diethyl ether, which was collected by centrifugation and dissolved in acetonitrile. The addition of tetrabutylammonium chloride resulted in complete precipitation as the chloride salt, which was washed with acetone and diethyl ether, then dried in vacuo. Yield: 0.043 g (74%). ^{1}H NMR (DMSO-d_6): δ 9.15 (2H, d, J = 5 Hz), 9.11 (2H, s), 8.87 (2H, d, J = 8), 8.54 (2H, t, J = 7), 8.32 (2H, d, J = 8), 8.23 (2H, d, J = 8), 7.92 (2H, t, J = 7), 7.45 (2H, d, J = 8 Hz), 7.33 (2H, d, J = 8 Hz), 7.20 (2H, d, J = 8 Hz), 7.13 (2H, t, J = 8 Hz), 6.96 (2H, t, J = 7 Hz), 6.86 (2H, d, J = 8 Hz), 5.18 (2H, s), 3.96 (3H, s). MS (positive-API-ES): m/z 874.20 [M − Cl]$^+$.

[Pt(tpy-phen-COOH)($C{\equiv}C-C_6H_4CH_2-PTZ$)]Cl (3). A test tube was charged with **3a** (0.020 g, 0.022 mmol), potassium hydroxide (0.060 g, 1 mmol), THF (1.0 mL), and water (1.0 mL). The tube was sealed with a septum, and the suspension was stirred for 2 days in the dark. The suspension was adjusted to pH 7 with dilute HCl, and additional water was added. The precipitate was collected by centrifugation and washed with water, acetone, and dried in vacuo. Yield: 0.010 g (49%). ^{1}H NMR (DMSO-d_6): δ 9.16 (2H, d, J = 5 Hz), 9.10 (2H, s), 8.90 (2H, d, J = 7), 8.55 (2H, t, J = 8), 8.24 (2H, d, J = 8), 8.16 (2H, d, J = 7), 7.93 (2H, t, J = 6), 7.46 (2H, d, J = 8), 7.33 (2H, d, J = 8), 7.19 (2H, d, J = 8), 7.13 (2H, t, J = 7), 6.96 (2H, t, J = 7), 6.86 (2H, d, J = 8), 5.18 (2H, s). MS (positive-API-ES): m/z 860.25 [M − Cl]$^+$. HRMS data were not obtained but the isotope pattern for the MS data is consistent with the formula of the cation (see Supporting Information). Anal. Calcd for $PtC_{43}H_{29}N_4O_2SCl$: C, 57.65; H, 3.24; N, 6.26. Found: C, 53.34; H, 3.39; N, 5.82.

[Pt(tpy-phen-COOH)Cl]PF_6. A 25 mL flask was charged with $Pt(DMSO)_2Cl_2$ (0.053 g, 0.13 mmol), tpy-phen-COOH (0.050 g, 0.14 mmol), DMF (8 mL). The resulting suspension was stirred at reflux under N_2 for 16 h. A yellow suspension formed, and complete precipitation was effected by the addition of excess of NH_4PF_6 in water. The solid was collected by filtration and washed with tetrahydrofuran/diethyl ether (1:1/v:v), diethyl ether, and dried in vacuo. Yield: 0.047 mg (49%). ^{1}H NMR (DMSO-d_6, with added drop HCl): δ 9.12 (2H, s), 9.02 (2H, d, J = 5 Hz), 8.93 (2H, d, J = 8), 8.60 (2H, t, J = 8), 8.37 (2H, d, J = 8), 8.24 (2H, d, J = 8), 8.03 (2H, t, J = 7).

4′-(2-furyl)-2,2′;6′,2″-terpyridine (tpy-furyl). This ligand was synthesized by the same method as described for tpy-phen-COOMe, and differs from reported literature methods.[69,70] A 500 mL flask was charged with potassium *tert*-butoxide (10.00 g, 89.3 mmol) and THF (80 mL). A solution of 2-acetylpyridine (8.0 mL, 71.4 mmol) in THF (80 mL) was added dropwise. A solution of 2-furaldehyde (3.0 mL, 36.2 mmol) in THF (80 mL) was then added dropwise to the white suspension over the course of 1 h becoming dark red after an additional 2 h of stirring. A solution of ammonium acetate (10 g, excess) in ethanol (50 mL) and glacial acetic acid (25 mL) was added. The resultant solution was heated at reflux for 48 h. Volatiles were removed by rotary evaporation and distilled water was added to yield a brown solid. This was collected by filtration and washed with water, 50% aqueous ethanol, diethyl ether, then dried in vacuo. Yield: 5.420 g (50%). ^{1}H NMR data were consistent with those previously reported.

4′-Carboxy-2,2′;6′,2″-terpyridine (tpy-COOH). This ligand was synthesized from tpy-furyl by a reported method without significant modification.[16] During workup, it was observed that precipitation of the product from this filtrate after adjusting to pH 4 with HCl was slow, taking several hours to complete. ^{1}H NMR data were consistent with those previously reported.

4′-Methylcarboxy-2,2′;6′,2″-terpyridine (tpy-COOMe). A flame-dried 25 mL flask was charged with tpy-COOH (0.800 g, 2.9 mmol), K_2CO_3 (0.800 g, 6.0 mmol), and dry, anhydrous THF. The flask was sealed with a septum, and stirred vigorously for 2 h. At this time, iodomethane (0.70 mL, 11 mmol) was delivered to the suspension via syringe. The mixture was allowed to stir overnight. Water was added, and the resulting white precipitate was collected by filtration. This was washed with water and dried in vacuo. Yield: 0.372 g (44%). ^{1}H NMR (DMSO-d_6): δ 8.91 (2H, s), 8.80 (2H, d, J = 4 Hz), 8.70 (2H, d, J = 7), 8.08 (2H, t, J = 8), 7.58 (2H, t, J = 5), 4.02 (3H, s).

[Pt(tpy-COOMe)Cl]Cl. A 25 mL round-bottom flask was charged with tpy-COOMe (0.080 g, 0.27 mmol), $Pt(DMSO)_2Cl_2$ (0.100 g; 0.24 mmol), 8 mL DMF, and 4 mL MeOH. The mixture was stirred at reflux for 16 h. Acetone was added to the resulting yellow suspension, and the yellow precipitate was collected by filtration and washed with acetone and diethyl ether before drying in vacuo. In some instances, solvatochromism (red, purple) was observed upon precipitation with acetone. Repeated washing with acetone gave a yellow solid. Yield: 0.088 g (58%). ^{1}H NMR (DMSO-d_6): δ 9.08 (2H, s), 9.05 (2H, d, J = 5 Hz), 8.99 (2H, d, J = 8), 8.57 (2H, t, J = 8), 8.05 (2H, t, J = 5), 4.08 (3H, s).

[Pt(tpy-COOMe)($C{\equiv}C-C_6H_5$)]Cl (2a). A 10 mL flask was charged with [Pt(tpy-COOMe)Cl]Cl (0.080 g, 0.14 mmol), CuI (0.010 g, 0.06 mmol), and DMF (4 mL). Ammonium hexafluorophosphate was required to enhance the solubility of the complex and reduce reaction time (see Results and Discussion). The reaction flask was sealed with a septum, and the solution sparged with N_2. Phenylacetylene (0.10 mL, 0.9 mmol) and triethylamine (0.10 mL, 0.8 mmol) were added via syringe, and the reaction mixture was stirred in the dark for 48 h. A red precipitate formed upon the addition of diethyl ether, was collected by centrifugation, washed with a mixture of acetonitrile/diethyl ether (1:1/v:v) followed by pure diethyl ether, and dried in vacuo. Yield: 0.079 g (93%). ^{1}H NMR (DMSO-d_6): δ 9.25 (2H, d, J = 6 Hz), 9.18 (2H, s), 8.98 (2H, d, J = 8 Hz), 8.56 (2H, t, J = 8 Hz), 8.00 (2H, d, J = 8 Hz), 7.55 (2H, d, J = 8), 7.39 (2H, t, J = 8), 7.31 (1H, t, J = 8), 4.08 (3H, s).

[Pt(tpy-COOH)($C{\equiv}C-C_6H_5$)]Cl (2). A test tube was charged with **2a** (0.020 g, 0.032 mmol), potassium hydroxide (0.040 g, 1 mmol), THF (1.0 mL), and water (1.0 mL). The tube was sealed with a septum, and the suspension was stirred for 2 days in the dark. The suspension was adjusted to pH 7 with dilute HCl, and acetone was added. The precipitate was collected by centrifugation, washed with water followed by acetone, and dried in vacuo. Yield: 0.011 g (56%). ^{1}H NMR (DMSO-d_6): δ 9.18 (2H, d, J = 6 Hz), 9.02 (2H, s), 8.89 (2H, d, J = 8 Hz), 8.51 (2H, t, J = 8 Hz), 7.96 (2H, t, J = 6 Hz), 7.52 (2H, d, J = 7), 7.38 (2H, t, J = 8), 7.30 (1H, t, J = 7). HRMS - ESI (exp; calc): m/z (572.08478, 573.08911; 572.0864, 573.0885) for [$^{194}PtC_{24}H_{16}N_3O_2$, $^{195}PtC_{24}H_{16}N_3O_2$]$^+$. Anal. Calcd for

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$PtC_{24}H_{16}N_3O_2Cl$: C, 47.37; H, 2.63; N, 6.91. Found: C, 45.09; H, 2.73; N, 6.65.

[Pt(tpy-COOMe)(C≡C−$C_6H_4CH_2$−PTZ)]Cl (4a). A 10 mL flask was charged with [Pt(tpy-COOMe)Cl]Cl (0.040 g, 0.072 mmol), *N*-(4-ethynylbenzyl)-phenothiazine (0.045 g, 0.14 mmol), CuI (0.010 g, 0.06 mmol), and DMF (4 mL). This was sealed with a septum, and sparged with N_2. Triethylamine (0.10 mL, 0.8 mmol) was added via syringe, and the reaction mixture was stirred in the dark for 48 h. A dark red precipitate which formed upon the addition of diethyl ether was collected by centrifugation, washed with acetonitrile/diethyl ether (1:1/v:v) followed by diethyl ether, and dried in vacuo. Yield: 0.043 g (71%). ^{1}H NMR (DMSO-d_6): δ 9.18 (2H, d, J = 5 Hz), 9.09 (2H, s), 8.93 (2H, d, J = 8), 8.52 (2H, t, J = 8), 7.96 (2H, t, J = 8), 7.47 (2H, d, J = 7), 7.35 (2H, d, J = 7), 7.19 (2H, d, J = 8), 7.13 (2H, t, J = 7), 6.96 (2H, t, J = 7), 6.87 (2H, d, J = 8), 5.19 (2H, s), 4.05 (3H, s).

[Pt(tpy-COOH)(C≡C−$C_6H_4CH_2$−PTZ)]Cl (4). A test tube was charged with **4a** (0.030 g, 0.032 mmol), potassium hydroxide (0.060 g, 1 mmol), THF (1.0 mL), and water (1.0 mL). The tube was sealed with a septum, and the suspension was stirred for 2 days in the dark. The suspension was adjusted to pH 7 with dilute HCl, and additional water was added. The precipitate was collected by centrifugation, washed with water and acetone, and dried in vacuo. Yield: 0.011 g (36%). ^{1}H NMR (DMSO-d_6): δ 9.22 (2H, d, J = 6 Hz), 9.07 (2H, s), 8.94 (2H, d, J = 8), 8.53 (2H, t, J = 8), 7.97 (2H, t, J = 8), 7.48 (2H, d, J = 8), 7.34 (2H, d, J = 8), 7.18 (2H, d, J = 7), 7.12 (2H, t, J = 7), 6.94 (2H, t, J = 7), 6.85 (2H, d, J = 8), 5.18 (2H, s). MS (positive-API-ES): *m*/*z* 785.15 $[M - Cl]^+$. HRMS data were not obtained but the isotope pattern for the MS data is consistent with the formula of the cation (see Supporting Information). Anal. Calcd for $PtC_{37}H_{25}N_4O_2SCl$: C, 54.21; H, 3.05; N, 6.84. Found: C, 51.44; H, 3.26; N, 6.18.

Results and Discussion

Syntheses and Characterization. All of the compounds were synthesized using standard methodology.[52,53,71−76] It was observed that having a carboxylic acid on the terpyridine ligand impeded the copper-catalyzed ligand exchange of acetylide for chloride in the final step. Thus, these reactions took much longer than usual, and required purification to remove any remaining chloride complex. Alternatively, if the terpyridyl ligand contained the methyl ester, acetylide coordination proceeded smoothly, and the esters could be subsequently hydrolyzed in strong aqueous base without degradation of the chromophores. Therefore, the latter method was employed in the syntheses of compounds **1**−**4**.

In addition, attempts to substitute chloride by acetylide ligands in the complex [Pt(tpy-phen-COOMe)Cl]Cl were slow and frequently stopped short of completion because of poor solubility of the chloride salt of the cationic Pt(II) complex. Therefore, NH_4PF_6 was added to the reaction solution to improve solubility. After reaction, conversion back to the chloride salt was effected by the addition of tetrabutylammonium chloride to solutions of the hexafluorophosphate salt.

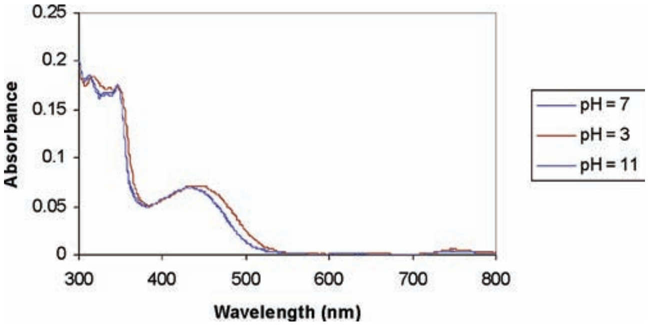

Figure 5. Room temperature absorption spectra of **2** in DMF/H_2O (1:1) at 1×10^{-5} M, adjusted to various pH values.

^{1}H NMR data for all of the compounds are consistent with the assigned structures and previously reported compounds of this type.[52,53,71−76] All of the ligands and complexes have distinct, well-resolved patterns in their aromatic proton resonances, which are attributable to the protons of the pyridine rings and phenyl substituents. The pyridine resonances (δ 7.8−9.4 ppm) are particularly informative, as they shift substantially upon coordination of the Pt(II) metal ion and upon exchange of chloride for acetylide, particularly the protons nearest the acetylide moiety. Hydrolysis of the methyl esters was easily followed by monitoring the proton resonance of the methyl ester group.

Mass spectrometry is particularly informative in analyzing platinum containing compounds, as platinum gives a characteristic isotopic pattern. Analysis by mass spectrometry gave data consistent with the proposed formulas and included the expected isotope pattern for Pt containing complexes. However, elemental analyses of the platinum terpyridyl acetylide complexes reported here were always unsatisfactory in carbon for which experimental results were always low. Poor elemental analyses for compounds of this type have been noted previously by us and others working on these systems despite high purity of samples as determined by other characterization methods, the most notable of which is ^{1}H NMR spectroscopy.

Absorption and Emission Spectra. Dimethylformamide/water (1:1 v/v) was used as the "mixed" solvent for characterization of complexes **1** and **2** because of the complexes' poor solubility in other solvents. All of the complexes exhibit features in the range of 300−800 nm which are consistent with previously studied platinum terpyridyl acetylide complexes.[45−53] The higher energy absorptions (300−370 nm) are assigned as intraligand transitions, while the broad, less intense absorptions ($\varepsilon \sim$ 7000−9000 M^{-1} cm^1) at lower energies (410−500 nm) are assigned to MLCT (dπ(Pt)-π^*(tpy)) transitions.

The electronic absorption spectrum of compound **2** was found to be dependent on the pH of the solution, red shifting at lower pH as the carboxylate group is protonated (Figure 5). The observed red shift at lower pH is consistent with the MLCT assignment, as −COOH is a stronger electron withdrawing group, lowering the energy of the lowest unoccupied molecular orbital (LUMO) which is π^*(tpy). Similar behavior has been observed previously in platinum bipyridyl dithiolate complexes

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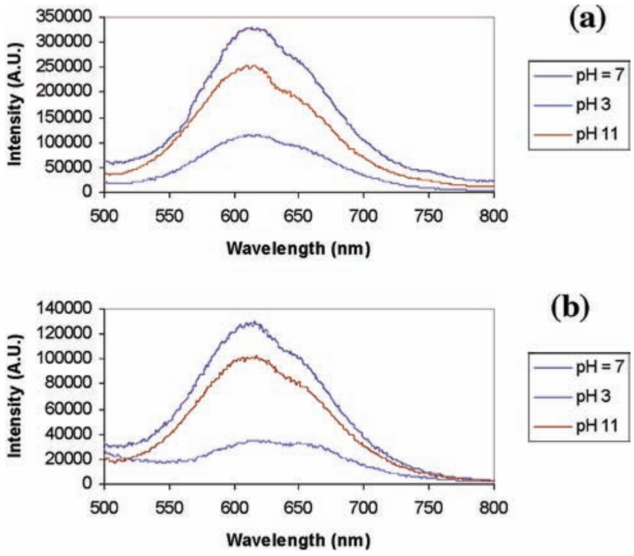

Figure 6. Room temperature emission spectra of complexes **1** (a) and **2** (b) in DMF/H_2O (1:1) at 1×10^{-5} M, adjusted to various pH values. Excitation wavelength 420 nm.

with carboxylic acid moieties on the bipyridyl ligand.[40] Additionally, the spectrum of the methyl ester derivative **2a** is similar to that observed for **2** at low pH. In contrast, the electronic spectrum of compound **1** is *not* very sensitive to pH, which may be expected given the increased distance of the carboxylic acid moiety from the terpyridyl ligand (Supporting Information, Figure S1). This increased distance and the fact that the central tpy ring and the attached *p*-benzoate ring will not be coplanar lead to poorer electronic communication between the tpy ligand and the carboxylic acid or carboxylate substituent.

The absorption spectra of complexes **3** and **4** are similar to those of **1** and **2**, with slight broadening and red-shifting of the MLCT transitions, similar to what has been observed for dyad **6** (Figure 7).[52] Dyad **4** also exhibits a pH sensitivity regarding its absorption spectrum that resembles that seen with complex **2**.

Emission studies were conducted on compounds **1** and **2** and both were found to be weakly emissive, with luminescence profiles typical of platinum terpyridyl acetylide complexes, that is, broad, structureless emissions at $\lambda_{\text{max}} \sim 610$ nm.[51−53,77] The quantum yields for emission for **1** and **2** were found to be 0.011 and 0.004, respectively, using Ru(bpy)_3^{2+} as a standard with an emission quantum yield ϕ_{em} of 0.062.[78] There appears to be some dependence of the emission intensity of these compounds upon pH, although this effect may be due to changes in the solvent (Figure 6). The emission properties of the methyl esters **1a** and **2a** were also examined. These were found to be similar to the acids with low quantum yields of 0.0048 and 0.0017, respectively.

Dyads **3** and **4** were found to be non-emissive in fluid solution, consistent with previous observations made with the closely related dyad **6**.[52] The methyl ester analogues, **3a** and **4a**, were also found to be non-emissive. Low-temperature emission studies at 77 K could not be conducted with compounds **3** and **4** because of their poor solubility in butyronitrile. Therefore, compounds **3a** and **4a** were examined. Both were found to be brightly emissive in frozen butyronitrile (Figure 7). The low temperature emission spectrum of **3a** is similar to those observed for related complexes, with both exhibiting evidence of vibronic progression, similar to that previously reported for closely related dyad **6**.[51−53,77] The spectrum of **4a** is red-shifted relative to **3a** because of lowering of the terpyridyl π* orbital by the electron-withdrawing ester in the former. That complexes **3a** and **4a** are emissive in a frozen glass but are non-emissive in a room temperature solution is consistent with a thermally activated non-radiative decay process such as solvent reorganization that is inhibited in a rigid matrix.

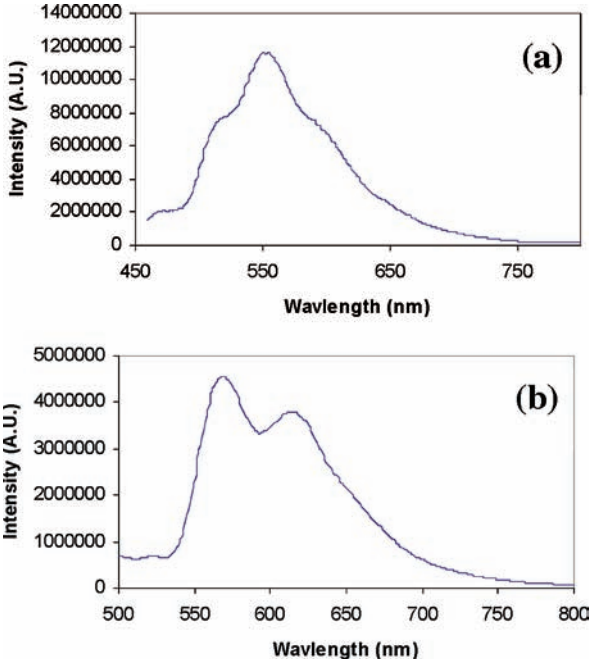

Figure 7. 77 K emission spectra of (a) **3a** and (b) **4a** at 1×10^{-5} M in butyronitrile. Excitation wavelength 480 nm.

Quenching Studies. The emission intensities of compounds **2** and **2a** were too weak to allow reliable quantification of reductive quenching by triethanolamine. On the other hand, the emission intensities of **1** and **1a** were sufficient to allow Stern−Volmer analyses of quenching by triethanolamine. Linear plots of (I_o/I) versus [TEOA] yielded K_{SV} values of 1×10^5 M^{-1} and 3×10^5 M^{-1} for **1** and **1a**, respectively, with no evidence of static quenching from absorption spectra in the presence of increasing amounts of TEOA. If one assumes that the excited state lifetime for these complexes is the same as that for the parent chromophore **5** (~1 μs), then the resultant quenching rate constants k_q are calculated to be greater than diffusion controlled rates (~1×10^{11} M^{-1} s^{-1} and ~3×10^{11} M^{-1} s^{-1} respectively), which means that the actual emission lifetimes of **1** and **1a** must be shorter than that of chromophore **5**.

Electrochemistry. The methyl esters **1a**−**4a** were found to be more amenable to electrochemical characterization than the free acids **1**−**4** because of their superior solubilities and the absence of acidic protons to complicate analysis. However, even the methyl esters exhibited weak,

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Table 1. Electrochemical Data ($E_{1/2}$) for Pt Complexes **1a**−**4a**

compound	oxidation $E_{1/2}$/V	reduction $E_{1/2}$/V
1a	1.30[a]	−0.61, −1.05
3a	1.05[b], 1.33[a]	−0.54, −1.03
2a	1.03[a], 1.26[a]	−0.66
4a	0.92[a], 1.05[b], 1.39[a]	−0.62

[a] Irreversible under experimental conditions. [b] Quasi-reversible with Au working electrode and scan limited to 1.1 V. Potential is given in volts vs NHE as determined using the ferrocenium/ferrocene (Fc^+/Fc) couple (0.45 V vs SCE for DMF)[66] as an internal standard.

broad redox waves in most cases. All of the complexes exhibit a reversible reduction at ∼−0.62 V based on NHE as determined using the ferrocenium/ferrocene (Fc^+/Fc) couple (0.45 V vs SCE for DMF)[66] as an internal standard, with **1a** and **3a** showing a second reduction at ∼−1.05 V (Table 1). These reductions have been assigned in earlier studies to be tpy-based.[52,53] Most importantly, the complexes all exhibit irreversible oxidation waves that in previous studies were assigned as Pt-based. Square planar Pt(II) compounds are well-known to undergo irreversible oxidation processes, but the nature of possible Pt(III) species and ultimate degradation products is unknown. The Pt(II) oxidations in compounds **1**−**4** appear near 1.3 V, similar to values found for previously studied platinum terpyridyl acetylides.[52,53] Additionally, the dyads **3a** and **4a** show quasi-reversible oxidations attributable to the phenothiazine moiety at ∼1 V, while both **2a** and **4a** exhibit one additional oxidation wave each.

Transient Absorption Spectroscopy. The phenothiazine-attached ligand employed in this work has been reported previously and established as a good reductive quencher of the excited state of the platinum terpyridyl acetylide chromophore.[52] To obtain values for the rate of this reductive quenching, the previously reported dyad **6** was studied with transient absorption spectroscopy as shown in Figure 8. This dyad was more convenient to study than dyads **3** and **4** because of the higher solubility of **6**. It is anticipated that the rates of reductive quenching are similar for all three dyads.

The transient absorption spectrum (Figure 8a) clearly shows the initial formation of the chromophore excited state, apparent as the broad absorption at 600 nm, and the subsequent rapid formation of the phenothiazine radical cation, with a distinctive absorption band at 510 nm. The electron transfer thus occurs by the reductive quenching of the chromophore excited state, and is consistent with previous observations described for this dyad.[52] The signal assigned to the PTZ radical cation appears in the transient spectrum less than 50 ps after excitation. Kinetic analysis of the risetime at 510 nm and the decay time at 600 nm (Figure 8b) reveals that the cation forms in less than 6 ps. The latter result sets a lower limit for the rate constant for *intra*molecular reductive quenching of the chromophore by PTZ of $k > 10^{11}\ s^{-1}$. The transient signals then decay with time-constants of 1.1 and 1.5 ns for the 600 nm and 510 nm signals, respectively, indicating charge recombination on this time scale. The negative signal observed at 400 nm is due to scattering from the excitation pulse.

Reduction of the PTZ Radical Cation. It has been previously shown that trialkylamines can reduce the phenothiazine cation radical.[79] Triethanolamine was also demonstrated to function in this capacity. A solution of the phenothiazine ligand was made in MeCN, to which was added a small amount (0.1 equiv) of ceric ammonium nitrate in MeCN in air.[80] This produced a rapid color change from nearly colorless to bright red, indicative of formation of the PTZ radical cation. When a small amount of neat triethanolamine was added, this color dissipated rapidly, leaving the solution nearly colorless, confirming that triethanolamine can transfer an electron rapidly to the phenothiazine radical cation.

Binding to TiO_2 and Platinized TiO_2 (TiO_2−Pt). To quantify the degree of binding of the complexes to the TiO_2 nanoparticles, solutions were analyzed by UV/vis spectroscopy before and after stirring with TiO_2. After stirring, the supernatant solution was separated from the TiO_2 suspensions by centrifugation and filtered 2−4 times through glass fiber filter paper until clear, before analysis. It was observed that binding of the complexes to TiO_2−Pt depends on the treatment applied to the sample after the photodeposition of platinum metal, as well as the solvent used for the binding study. All binding studies were conducted with quantities of the chromophore falling well below the saturation limit of the TiO_2 (∼50 μmol/g), which was predicted on the basis of previous studies verified by independent analysis of the saturation limit of tpy-phen-COOH on TiO_2.[81]

Specifically, when TiO_2−Pt was prepared using the photoreduction method, heat treatment following the photoreduction was found to be important to remove byproducts capable of inhibiting chromophore binding. A thorough investigation of this process and the effect of heat treatment on the activity of platinized TiO_2 has recently been reported by Millon et al.[82] Briefly, in the photoreduction method, an alcohol (methanol in the present case) serves as the reductant. This leads to the formation of formic acid and formaldehyde, which bind to the free surface of the TiO_2. This can be seen clearly in the IR spectrum of a sample of platinized TiO_2 freshly prepared by this method, and subjected only to washing with ethanol and drying overnight in vacuo. This is compared with the spectrum of the same sample, heated to 500 °C in vacuo for 3 h (Figure 9).

When attempts were made to assess the efficacy of chromophore binding to these samples of TiO_2−Pt, DMSO was initially chosen as the solvent, to avoid complications due to the low solubility of complexes **1** and **2**. It was clear from the visible spectrum of the supernatant DMSO solutions that binding to TiO_2−Pt not subjected to heat treatment was incomplete, even after stirring for several hours. After filtration, absorbance spectra of the supernatant solutions from these experiments would exhibit features characteristic of the chromphore. In contrast, binding to TiO_2−Pt that had

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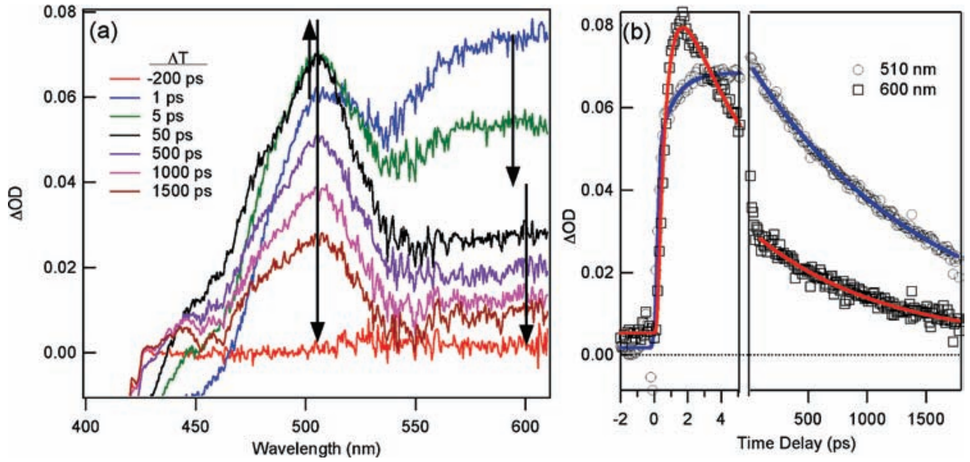

Figure 8. (a) Transient absorption spectra of dyad **6** in acetonitrile, collected at various intervals after excitation. (b) Kinetics of the photoinduced absorption changes at 510 and 600 nm showing the rapid loss of absorption at 600 nm and the long-time decay of both signals in 1−1.5 ns. The excitation wavelength was 400 nm.

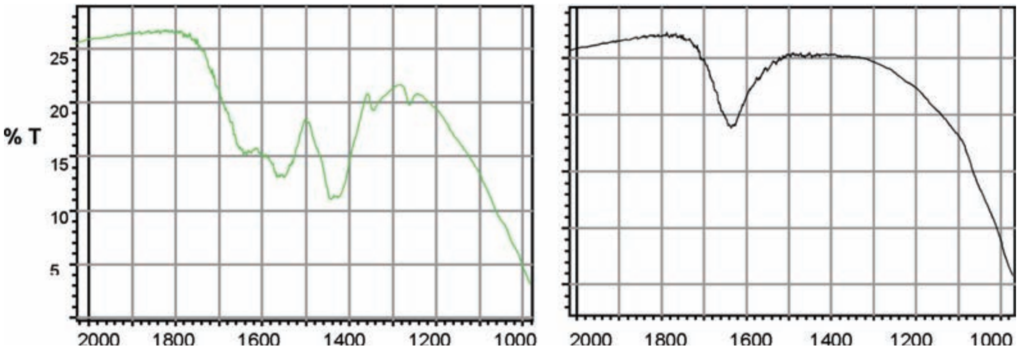

Figure 9. Transmission FTIR spectra of pellets of platinized TiO_2 (5% Pt) prepared by the photodeposition method before heat treatment (left) and after heating at 500 °C in vacuo for 3 h (right). Spectral window 2000−1000 cm^{-1}.

been heated was complete after 1 h, and no absorbance due to the chromophore was detected in solution.

Upon a change to an acetonitrile/water solvent (3:2 v/v), it was found that the complexes bind strongly to TiO_2−Pt, including samples that had not undergone heat treatment. This solvent effect is possibly due to an increased exchange rate with surface bound species in aqueous media versus DMSO, and is consistent with the predicted increase of the pK_a of the carboxylic acid group (and decreased acidity) in DMSO versus $MeCN/H_2O$.

Evidence of Electron Injection into TiO_2. To demonstrate that both the bound and free chromophores are able to inject electrons into TiO_2, solutions of **1** and **5** (5 mL at 1×10^{-4} M) were added in different experiments to 0.100 g TiO_2 in a flask to which 0.500 g TEOA, 10 mL H_2O, and 10 mL of MeCN were added. The flasks were sealed with septa and the suspensions sparged with N_2. Upon irradiation with a Hg lamp (λ > 410 nm), the suspensions were observed to change in color from yellow or orange to blue-gray. When briefly exposed to air, this blue-gray color would rapidly dissipate, and the original yellow or orange color would return, suggesting that the color observed was due to reduced titanium dioxide.[83−85] However, after several cycles, a gray color would persist indefinitely. Upon washing and drying of the TiO_2 from these experiments, the gray color was similar to platinized TiO_2 prepared by the photodeposition method. These last observations are consistent with the notion of slow photodecomposition of Pt terpyridyl complexes to form colloidal Pt when irradiated with λ > 410 nm for several hours.[27] As discussed previously, the mechanism for this decomposition subsequent to oxidation has yet to be determined.

Hydrogen Production. Previously we reported that the Pt tpy acetylide complex **5** promotes the photogeneration of H_2 in a system containing TiO_2−Pt and TEOA as the sacrificial electron donor when irradiated with λ > 410 nm.[86,87] Experiments were done to compare the effectiveness of TiO_2-bound chromophores **1** and **2** with that of **5** for the photogeneration of H_2 under the same conditions. The platinum metal loading on the TiO_2 employed was 0.05% Pt wt/wt, and the resultant material was nearly white, allowing for visual confirmation of chromophore binding. The activity of the TiO_2 platinized at 0.05 wt %/wt loading of metal yielded activity very similar to that of

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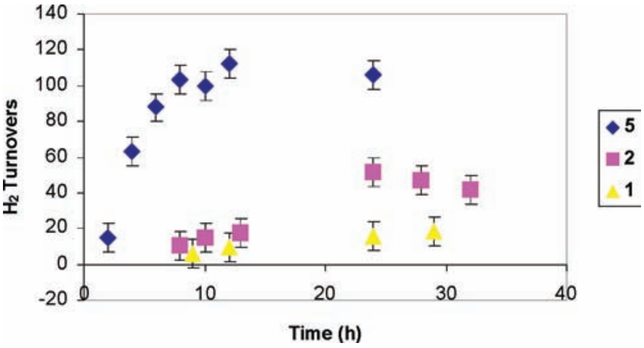

Figure 10. Hydrogen turnovers as a function of irradiation time in systems containing chromophores **1**, **2**, or **5**. Error bars are approximate.

TiO_2−Pt with higher loadings, consistent with the observations of others.[88]

Both **1** and **2** promote the photogeneration of hydrogen when bound to platinized TiO_2 upon $\lambda > 410$ nm irradiation in the presence of triethanolamine. For both of these systems, as well as for the one using unbound chromophore **5**, hydrogen production decreases and eventually stops, at which point the suspensions were changed in color from yellow or orange to gray, similar to that observed when a higher loading of Pt metal (0.5−1%) is present on TiO_2. Additionally, when the gray material thus produced was used in place of TiO_2−Pt prepared by the photodeposition method, hydrogen was produced without an induction period upon irradiation of a system also containing chromophore **5** and TEOA, supporting the conclusion that the product of decomposition was colloidal Pt, similar to what we have noted previously.[27]

When the three chromophores were compared directly in their ability to produce hydrogen upon irradiation, the result was unexpected (Figure 10). The highest rate and overall yield were achieved with the unbound chromophore **5**. While the system with **5** yielded 115 turnovers after 12 h of irradiation, the system with bound chromophore **2** generated only 16 turnovers after 13 h of photolysis. Chromophore **2** produced hydrogen more effectively than **1**, which may be due to its closer proximity to and superior electronic communication with TiO_2. The apparent but slight decline in turnover numbers at longer irradiation times for **5** and **2** may be due to leakage through the septa of the reaction vessels, but the relative ability of the two chromophores for promoting the photogeneration of hydrogen is clear. While the observed turnover numbers for the TiO_2-anchored systems are modest, particularly when compared to the unattached multiple component systems, they are similar to other reported integrated systems for hydrogen production. A recent example of such a system based on a porphyrin sensitizer and a hydrogenase model compound is reported by Li et al., in which 16 turnovers were achieved.[89]

For the excited unbound chromophore **5**, the rate of bimolecular electron injection into TiO_2 is much slower than those for the anchored chromophores **1** and **2**, and hence photoexcited **5** is much more likely to undergo reductive quenching by TEOA *prior* to possible charge injection into the TiO_2. Electrochemical analysis shows that the first reduction of **5** and related platinum(II) terpyridyl acetylides is reversible, indicating that the complexes are at least moderately stable when reduced. Thus, a system involving unbound chromophore in which reductive quenching by TEOA is faster than oxidative quenching by electron transfer into TiO_2 may be expected to achieve a greater number of turnovers than if only the latter were operative. In contrast, chromophores **1** and **2** achieve H_2 generation through a mechanism that involves oxidative quenching by photoinjection of an electron from the chromophore into TiO_2. That these bound chromophores, **1** and **2**, exhibit lower rates of H_2 generation and achieve fewer H_2 turnovers than **5** supports the notions that (a) an oxidative quenching path is less efficient for H_2 photogeneration, possibly because of rapid back reaction, and (b) these TiO_2-anchored chromophores undergo oxidative decomposition as suggested by the electrochemical data and other observations.

In an attempt to increase the rates of reductive quenching and reduction of the oxidized chromophore, the concentration of TEOA was increased. This change in the system yielded a substantially greater number of turnovers in the system containing complex **1** as the sensitizer. In a trial where the concentration of TEOA was set to 1.3×10^{-1} M, 231 turnovers were achieved after 25 h irradiation, compared to 16 turnovers achieved by a system otherwise identical with the concentration of TEOA being 1.3×10^{-2} M.

In contrast with the results observed with **1** and **2**, dyads **3** and **4** do not produce H_2 when used as the photosensitizer, despite the fact that phenothiazine has been shown to reductively quench the chromophore.[52] The results of transient absorption spectroscopy demonstrate that this reductive quenching is very rapid. Despite the evidence that electron transfer reaction between the phenothiazine radical cation and the triethanolamine occurs readily to reduce the PTZ radical cation, back electron transfer between the reduced chromophore and PTZ radical cation is also very rapid. The decay rate for PTZ radical cation from the TA experiment study of dyad **6** is $> 1 \times 10^{9}$ s^{-1}. This decay is due to charge recombination, and the rate of this recombination is likely very similar in dyads **3** and **4**. This result suggests that while attachment of the PTZ moiety to the sensitizer may stabilize the latter to photodecomposition, the strategy is also counter-productive to the photogeneration of H_2 by anchored dyads because back electron transfer will be competitive with the processes that lead to hydrogen production.

Geometry on the Surface and Exchange Reactions with [Pt(tpy-phen-COOH)Cl]PF_6. In the course of investigating dyads **3** and **4** as sensitizers for the photogeneration of hydrogen, it was proposed that the complexes may adopt an arrangement in which the dyads lie flat on the surface of the TiO_2, as shown in Figure 4, making them unreactive for *net* electron transfer. The orientation of chromophores and complexes on the surface can influence the rates of charge transfer in ways that will affect the desired photocatalysis. Evidence for such geometry dependent behavior has been observed in other dye-sensitized systems.[15]

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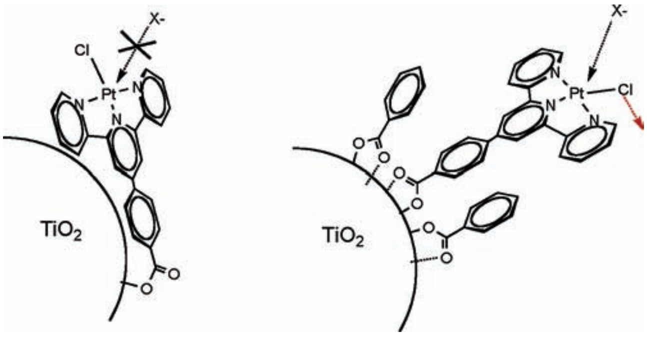

Figure 11. Depiction of the possible orientations of an adsorbed platinum species in the absence (left) and presence (right) of coadsorbate, and the effect on displacement of the chloride ligand by an incoming nucleophile, X.

Support for this hypothesis is provided in observations that involve ligand exchange reactions with [Pt(tpy-phen-COOH)Cl]PF_6 bound to the surface of TiO_2. In fluid solution, exchange of the chloride ligand for a thiophenolate is very rapid at room temperature, and is accompanied by a rapid color change from yellow to dark purple. Similar observations have been made of other platinum(II) terpyridyl chloride complexes.[90,91]

However, when anchored to TiO_2 at ~20% monolayer coverage (20% = 10 μmol/g TiO_2),[81] there is no evidence of color change upon the addition of a solution of sodium thiophenolate to the material, even after prolonged stirring. However, if benzoic acid or 4-*tert*-butyl-benzoic acid is added as a coadsorbate on the TiO_2 surface (50 μmol acid/g TiO_2), a color change (yellow to purple) is observed upon the addition of thiophenolate. It seems likely that the addition of the coadsorbate forces the bound complex PtCl(tpy-phen-COO−)$^+$ to adopt a geometry more perpendicular to the TiO_2 surface, thereby enabling the ligand exchange, which may occur through an associative mechanism as illustrated below (Figure 11).

With this result, attempts were made to utilize coadsorbates to manipulate the geometry of the D-C dyads on the surface, to enable the photocatalysis. However, even with coadsorbates added, neither of the dyads were found to be capable of producing hydrogen in the system.

Another hypothesis for the inability of **3** and **4** to promote the photogeneration of hydrogen may reside in the slow kinetics of charge transfer between the triethanolamine and the PTZ radical cation. No definitive rate constants have yet been determined for the electron transfer between trialkylamines and the PTZ radical cation. Other sacrificial donors were tried in the system, which have been shown to undergo electron transfer reactions with the PTZ radical cation. These include diisopropylethylamine and ascorbate.[79,92] However, systems employing these sacrificial donors were not observed to generate hydrogen upon irradiation.

Conclusions

Two new platinum(II) complexes, [Pt(tpy-phen-COOH)-($C\equiv C-C_6H_5$)]Cl (**1**) and [Pt(tpy-COOH)($C\equiv C-C_6H_5$)]Cl (**2**) have been prepared and characterized. These were used as sensitizers in a system with platinized titanium dioxide nanoparticles for the photogeneration of hydrogen. The ability of these complexes to act as sensitizers in this capacity is limited in the long term by decomposition upon oxidation. When compared to the related chromophore [Pt(ttpy)-($C\equiv C-C_6H_5$)]PF_6 (**5**) which does not possess an anchoring group for attachment to TiO_2, the unbound chromophore achieved a greater number of turnovers than **1** or **2**, consistent with the notion that **5** undergoes reductive quenching by TEOA to a greater extent than either **1** or **2**. Instead, **1** and **2** by virtue of their attachment to TiO_2 undergo oxidative quenching with electron injection into TiO_2 preferentially. To probe this hypothesis, the concentration of the sacrificial donor was increased, and this modification led to a greater number of turnovers of H_2. In further efforts to address the problem of oxidative instability, D-C dyads [Pt(tpy-phen-COOH)($C\equiv C-C_6H_4CH_2-$PTZ)]PF_6 (**3**) and [Pt(tpy-COOH)($C\equiv C-C_6H_4CH_2-$PTZ)]Cl (**4**) were prepared for use as sensitizers in the photogeneration of hydrogen. Despite evidence of rapid reductive quenching of the excited state of the chromophore and of an electron transfer reaction occurring between phenothiazine radical cation and triethanolamine, these dyads were unable to function for hydrogen production. There is some evidence that this may be due to an unfavorable orientation on the surface of TiO_2, although it may also be due to slow kinetics of the reaction between triethanolamine and the phenothiazine radical cation.

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Supporting Information Available: Plots of the absorption spectra of the Pt chromophores; cyclic voltammograms of **1a** and **2a**; mass spectrometric data for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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