# Photoinduced Electron Transfer in Platinum(II) Terpyridyl Acetylide Chromophores: Reductive and Oxidative Quenching and Hydrogen Production<sup> $\dagger$ </sup>

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A series of luminescent platinum(II) terpyridyl acetylide complexes, ( $[Pt(tpy)(C \equiv CPh)]ClO_4$  (1) and  $[Pt-CPh]ClO_4$  (1) (  $(ttpy)(C \equiv C_{-p}-C_{6}H_{4}R)$ ]ClO<sub>4</sub>, where tpy = terpyridine, ttpy = 4'-p-tolylterpyridine, R = H, Cl, Me) (2-4) were studied with regard to excited-state quenching by dialkylated bipyridinium cations as electron acceptors and triethanolamine (TEOA) as an electron donor and the photogeneration of hydrogen from systems containing the chromophore, the dialkylated bipyridinium cations, TEOA, and colloidal Pt as a catalyst. The dialkylated bipyridinium cations include methyl viologen (MV<sup>2+</sup>) and a series of diquats prepared from 2,2'-bipyridine or 4,4'-dimethyl-2,2'-bipyridine. The quenching rates for the diquats for one of the chromophores (2) are close to the diffusion-controlled limit. The most effective electron acceptor and relay for hydrogen evolution has been found to be 4,4'-dimethyl-1,1'-trimethylene-2,2'-bipyridinium (DQ4) which on photoreduction by the chromohore provides the strongest reducing agent of the diquats studied. The rate of hydrogen evolution depends in a complex way on the concentration of the bipyridinium electron relay, increasing with concentration at low concentrations and then decreasing at high concentrations. The rate of  $H_2$  photogeneration also increases with TEOA concentration at low values and eventually reaches a plateau. The most effective system examined to date consists of the chromophore 2 ( $2.2 \times 10^{-5}$  M), **DQ4** ( $3.1 \times 10^{-4}$  M), TEOA ( $2.7 \times 10^{-2}$  M), and Pt colloid (6.0  $\times$  10<sup>-5</sup> M), and has produced 800 turnovers of H<sub>2</sub> (67% yield based on TEOA as sacrificial electron donor) after 20 h of photolysis with  $\lambda > 410$  nm.

# Introduction

Artificial photosynthesis and the conversion of sunlight into stored chemical energy in the form of fuels represent one of science's great challenges in this century.<sup>1</sup> The particular reaction of paramount importance in this regard is water splitting into its constituent elements with hydrogen as the fuel. The subsequent, efficient recombination of H<sub>2</sub> and O<sub>2</sub> through a fuel cell then represents an ideal way in which to generate usable energy in a completely carbon-free way. The development of an artificial photosynthetic system for water splitting has been tackled over the last three decades in numerous ways, beginning with Fujishima and Honda's seminal work<sup>2</sup> on water splitting over irradiated large band gap semiconductors and the reports by Lehn,<sup>3</sup> Kagan,<sup>4</sup> and Grätzel<sup>5,6</sup> on a molecular approach to the problem, focusing on H<sub>2</sub> generation from aqueous protons and a sacrificial electron source. The latter are thus detailed molecular approaches to the reductive side of the water splitting reaction.

In the systems pioneered by Lehn, Kagan, and Grätzel, an approach represented in Scheme 1 was followed in which Ru- $(bpy)_3^{2+}$  was employed as a visible light photosensitizer, methyl viologen (MV<sup>2+</sup>) served as an oxidative quencher and electron relay, triethanolamine (TEOA) or ethylenediaminetetraacetic acid (EDTA) functioned as the electron source, and a colloidal Pt catalyst was used to generate the hydrogen. During the ensuing three decades, different steps and components of the various systems have been investigated in detail. For example, sensitizers have been extensively varied ranging from  $d^6$  Ru-

**SCHEME 1** 



(II) trisdiimine complexes to Zn(II) porphyrins,<sup>7–12</sup> cyclometalated [Ir(C<sup>N</sup>)<sub>2</sub>(N<sup>N</sup>)]Cl complexes,<sup>13,14</sup> methyl acridine orange,<sup>15</sup> and conjugated polymers.<sup>16</sup> Electron relays have been modified and extended to include other viologens,<sup>17,18</sup> various alkylated pyridines and diquats,<sup>19–21</sup> Rh diimine complexes,<sup>3</sup> cobalt(II) complexes,<sup>22,23</sup> and semiconductor particles.<sup>24,25</sup> Other system components have been studied as well.<sup>26–28</sup>

Solution-luminescent platinum(II) terpyridyl acetylide complexes were first reported in 2001 by Yam and co-workers.<sup>29</sup> Like the analogous Pt diimine bis(acetylide) complexes,<sup>30–33</sup> these cationic systems possess a <sup>3</sup>MLCT emissive state and undergo electron-transfer quenching with both donor and acceptor molecules. Since the initial report, papers from different laboratories have appeared dealing with these complexes and related derivatives with respect to (a) vapochromic behavior for selected volatile organic compounds,<sup>34</sup> (b) sensing capabilities for simple inorganic cations<sup>29,35,36</sup> and (c) photocatalysis of hydrogen generation from Hantsch dihydropyridines.<sup>37</sup> In 2006, we reported that complex 2 can be employed as part of a multiple component system containing a chromophore, a sacrificial electron donor, an electron relay, and a colloidal catalyst for the light-driven generation of H<sub>2</sub> from aqueous protons. The system has both advantages and disadvantages from previously reported multiple component mixtures for light driven hydrogen generation. In this paper, we describe details and

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Figure 1. Perspective drawing of complex 1 with atomic numbering scheme.

TABLE 1: Selected Bond Lengths (Å) and Angles (deg) for Complex 1

Pt(1)-N(2)	1.9652(15)	Pt(1)-N(3)	2.0211(15)
Pt(1) - N(1)	2.0231(15)	Pt(1) - C(1)	1.9734(19)
N(1)-C(9)	1.345(2)	N(1) - C(13)	1.379(2)
N(2)-C(18)	1.345(2)	N(2) - C(14)	1.345(2)
N(3)-C(23)	1.345(2)	N(3)-C(19)	1.381(2)
N(2) - Pt(1) - C(1)	178.74(7)	N(2) - Pt(1) - N(3)	80.65(6)
C(1) - Pt(1) - N(3)	99.78(7)	N(2) - Pt(1) - N(1)	80.70(6)
C(1) - Pt(1) - N(1)	98.87(7)	N(3) - Pt(1) - N(1)	161.35(6)
C(9) - N(1) - C(13)	119.05(15)	C(9) - N(1) - Pt(1)	127.66(12)
C(13) - N(1) - Pt(1)	113.28(12)	C(18) - N(2) - C(14)	123.69(16)
C(18) - N(2) - Pt(1)	118.24(12)	C(14) - N(2) - Pt(1)	117.95(12)

aspects of the earlier report and expand the scope of the study through variation of the chromophore, the electron relay, the concentration of sacrificial donor (TEOA) and the concentration of electron relay (diquats). The results lead to conclusions about different steps in the overall energy storing reaction and allow comparison between different systems used to carry it out.

#### **Results and Discussion**

The Platinum Terpyridyl Acetylide Chromophore: Structural Characterization. The synthesis and solution characterization of all of the Pt terpyridyl acetylide chromophores used in the present study (1-4) have been described in previous work, as have their absorption and emission spectra.38 The molecular structure of 1 obtained from a crystal grown by acetonitrile (MeCN) evaporation is shown in Figure 1 with important bond lengths and angles summarized in Table 1. A complete tabulation of distances and angles is found in the Supporting Information in CIF format. As anticipated, the Pt(II) coordination geometry is a square planar with modest distortion imposed by the constraint of the terpyridyl ligand (the cis N-Pt-N angles average 80.67 (6)° and the one trans N-Pt-N angle is 161.35  $(6)^{\circ}$ ). For the same reason, the bond distance from Pt to the central terpy N atom (Pt-N2 = 1.9652(15) Å) is slightly shorter than that to the other two nitrogen atoms (Pt-N1 = 2.0231-(15) Å, Pt-N3 = 2.0211(15) Å), which is consistent with the corresponding bond distances in [Pt(tpy)(C=C-C<sub>6</sub>H<sub>4</sub>-p-N(CH<sub>3</sub>)<sub>2</sub>)]-BF<sub>4</sub>.<sup>39</sup> The Pt-N2 distance of 1.9652(15) Å agrees well with the values of 1.956(4),<sup>39</sup> 1.969(5),<sup>35</sup> 1.97(10),<sup>40</sup> 1.961(13),<sup>41</sup> and 1.935(6) Å<sup>42</sup> in other related platinium(II) alkynyl complexes, while the Pt-C (acetylide) distance of 1.9734(19) Å corresponds

 TABLE 2: Photophysical Data of the Chromophores in Acetonitrile/Water (2:3, v/v) at Room Temperature

cmpd	$\lambda_{abs}$ (MLCT) ( $\epsilon$ /dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )	$ au^{ au}(\mu s)^a$	λ <sub>em</sub> (nm)	$\phi_{ m em}$	E <sub>oo</sub> (eV)
1	430 (4980)	1.9	597	0.010	2.46
2	420 (7700)	4.6	609	0.025	2.48
3	424 (6430)	4.7	591	$0.024 \\ 0.004$	2.48
4	433, 461 (5165)	0.8	625		2.46

<sup>*a*</sup> Taken from ref 38.

 TABLE 3: Excited State Energy, Rate of Quenching, and
 Electrochemical Data<sup>a</sup> of the Pt Chromophores

cmpd	$k_{ m q}$ (by TEOA) <sup>b</sup> $ imes$ 10 <sup>9</sup> M <sup>-1</sup> s <sup>-1</sup>	$k_{ m q}~({ m by}~{ m MV^{2+}})^b \  imes~10^9~{ m M^{-1}~s^{-1}}$	$E^{2+/+}$	$E^{{\scriptscriptstyle +}{\scriptscriptstyle /}{\scriptscriptstyle 0}}$
1	2.4	5.1	$+1.49^{\circ}$	$-0.63, -1.16^{d}$
2	1.4	3.3	$+1.34^{\circ}$	$-0.59, -1.07^{d}$
3	1.4	3.4	$+1.41^{c}$	$-0.61, -1.09^{e}$
4	1.5	0.4	$+1.50^{\circ}$	$-0.59, -1.05^{e}$

<sup>*a*</sup> Electrochemical data were obtained in degassed DMF solution with 0.10 M *n*Bu<sub>4</sub>NPF<sub>6</sub> (TBAH) as supporting electrolyte at room temperature; scan rate 100 mV s<sup>-1</sup>. Potentials (vs NHE) converted from internal Fc<sup>+/0</sup> using ref 55. <sup>*b*</sup> Measured in acetonitrile/water (2:3 v/v). <sup>*c*</sup> Irreversible oxidation peak estimated vs NHE. <sup>*d*</sup> Reversible reductions measured with Fc<sup>+/0</sup> as an internal standard and adjusted to NHE. <sup>*e*</sup> Taken from ref 38.

well to values of  $1.977(6)^{39}$  and  $1.98(1)^{40}$  for  $[Pt(tpy)(C \equiv C - C_6H_4-p-N(CH_3)_2)]BF_4$  and  $[Pt(tpy)(C \equiv CPh)]PF_6$ , respectively. The crystal structure of **1** shows the cations pack in pairs with head-to-tail stacking and a nearest intermolecular Pt···Pt distance of 3.4143(2) Å.

Steady-State Absorption and Emission Spectra. The electronic spectra of 1-4 have been reported previously in dichloromethane solutions.<sup>38</sup> However, since all of the reactions for light-driven hydrogen production presented here were carried out in a 2:3 acetonitrile/water mixture, the steady-state absorption and emission spectra of the chromophores were remeasured in this solvent system (see Figures 2 and 3). As in dichloromethane solutions, all of the complexes exhibit vibronicstructured absorption bands at high energy ( $\lambda < 350$  nm) with extinction coefficients ( $\epsilon$ ) on the order of 10<sup>4</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> that are attributable to intraligand transitions.<sup>35,36,38</sup> A less intense, solvatochromic band corresponding to a  $d\pi(Pt)-\pi^*$ -(terpy) metal-to-ligand charge transfer (MLCT) transition is seen for all of the complexes in the range of 375-520 nm with  $\epsilon$  on the order of  $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . For **2** as an example, Figure 2 reveals that the MLCT absorption maximum in acetonitrile/ water occurs at 23 800 cm<sup>-1</sup>, which is ca. 700 cm<sup>-1</sup> higher in energy than that in methylene chloride (23 100 cm<sup>-1</sup>). Similar solvatochromism of the MLCT band has been reported previously for the Pt(diimine)(C=CAr)<sub>2</sub> complexes<sup>30</sup> and related Pt-(diimine)(dithiolate) complexes,<sup>43</sup> consistent with a highly polar ground state, an MLCT state of reduced (and possibly inverted) polarity, and increasing solvent stabilization of the former with increasing solvent dielectric constant.

The [Pt(terpyridyl)(acetylide)]<sup>+</sup> complexes 1–4 exhibit strong photoluminescence with  $\lambda_{max}$  ranging from 595 to 625 nm and relative emission quantum yields,  $\phi_{em}$ , given in Table 2. Complexes 2 and 3 give higher quantum yields, 0.025 and 0.024, respectively, than complexes 1 and 4. The values of  $\phi_{em}$  were obtained using [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in degassed MeCN as the reference solution ( $\phi = 0.062$ ).<sup>44</sup> The excited-state energy of the <sup>3</sup>MLCT emissive state,  $E_{oo}$ , can be estimated most directly from the onset of the emission at 77 K.<sup>45</sup> In this way, complexes 2 and 3 were found to have the same  $E_{oo}$  of 2.48 eV while 1 and 4 were determined to have  $E_{oo}$  of 2.46 eV. These values



Figure 2. Absorption spectra of the Pt chromophores in acetonitrile/water (v/v = 2:3) at  $1.0 \times 10^{-5}$  M.



Figure 3. Normalized emission spectra of the Pt chromophores in acetonitrile/water (v/v = 2:3) at  $1.0 \times 10^{-5}$  M.

compare well with  $E_{oo}$  estimates obtained in the same way for Pt(diimine)(arylacetylide)<sub>2</sub> complexes having similar substituents. The excited-state energies  $E_{oo}$  of the latter systems were also estimated independently by Whittle et al., using a single mode analysis,<sup>33</sup> yielding values that, while 5–7% lower, were essentially in agreement given the estimated errors on these measurements.

**Reductive Quenching.** Complexes 1–4 were all found to undergo reductive quenching by triethanolamine (TEOA) which had been used as a sacrificial electron donor in earlier reported  $Ru(bpy)_3^{2+}$ -based systems for light-driven hydrogen generation (Table 3). For all of the chromophores, quenching studies were conducted by measurements of steady-state emission intensities. The quenching of eq 1 is dynamic in nature and was well modeled by the Stern–Volmer equation<sup>46</sup> (eq 2), where  $I_0$  is the integrated MLCT emission intensity in the absence of quencher,  $\tau_o$  is the excited-state lifetime in the absence of quencher, I and  $\tau$  are the corresponding values in the presence of quencher,  $k_q$  is the bimolecular quenching rate constant, and [Q] is the quencher concentration. Linear plots of  $I_0/I$  vs [Q] together with excited-state lifetimes for the Pt chromophores yielded values of the quenching rate constants  $k_q$  that for 2, 3, and 4 were approximately 1.4  $\times$  10  $^9~M^{-1}~s^{-1}$  and for 1 was slightly greater at 2.4  $\times$  10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>.

\*[Pt(terpyridyl)(acetylide)]<sup>+</sup> + TEOA  $\rightarrow$ \*[Pt(terpyridyl)(acetylide)] + TEOA<sup>+</sup> (1)

$$I_{o}/I = \tau_{o}/\tau = 1 + k_{q}\tau[Q]$$
<sup>(2)</sup>

The reductive quenching of 3 in acetonitrile has recently been studied by Schmehl and co-workers47 who determined a good estimate of its excited-state reduction potential as +1.4 V vs SCE (+1.6 V vs NHE) using a series of reductive quenchers including triphenylamine (TPA), diphenylamine (DPA), triethylamine (TEA), and diisopropylamine (DIPA), diethyl-1,4dihydro-2,6-dimethyl-3,5-pyridinecarboxylate (DHP), N,N,N',N'tetramethylphenylenediamine (TMPD), N-methylphenothiazine (MPTH) and N, N, N', N'-tetramethylbenzidine. The determined value for the excited-state reduction potential indicates that 3 and the other chromophores are strong excited-state oxidants. Because 1-4 undergo irreversible oxidations, only an estimate of the excited-state oxidation potential can be made using the value of the observed oxidation wave and the excited-state energy  $E_{00}$ . When written as a formal reduction, the estimate for the excited-state potential E (complex<sup>2+/+\*</sup>) for chromophores 1-4 are -0.97, -1.14, -1.07, and -0.96 V, respectively, versus NHE where the potential E (complex<sup>2+/</sup>  $^{+*}$  = E (complex<sup>2+/+</sup>) - (the excited-state energy  $E_{oo}$  in eV). Please note that no correction is given for the work term in this simple estimation.

The related Pt(diimine)(C=CAr)<sub>2</sub> complexes are also known to undergo reductive electron-transfer quenching, and they have also been studied quantitatively in this regard.<sup>32,48</sup> In the case of Pt(dbbpy)(C=CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, for example, 10-methylphenothiazine and *N*,*N*,*N'*,*N'*-tetramethylbenzidine were found to give essentially diffusion-controlled  $k_q$  values of 9.6 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> and 1.3 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively. Phenothiazine and *N*,*N'*dimethylaniline gave similar results. It is noteworthy that the



**Figure 4.** Formation of MV<sup>+•</sup> upon irradiation by visible light in the presence of  $2.2 \times 10^{-5}$  M **2**,  $3.1 \times 10^{-4}$  M MV<sup>2+</sup>, and  $6.0 \times 10^{-5}$  M Pt colloid.

quenching rate constants for these Pt chromophores is around 3 orders of magnitude faster with these quenchers than are found with  $Ru(bpy)_3^{2+}$  (6.5 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>).<sup>5</sup>

**Oxidative Quenching.** We previously reported that **2** undergoes oxidative quenching by  $MV^{2+}$  with a rate constant  $k_q$  of  $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in acetonitrile/water (3:2). This result was in accord with earlier reported studies of related Pt diimine bis(acetylide) complexes that exhibit oxidative as well as reductive quenching of their respective excited states. In those earlier studies,<sup>30</sup> the rates of quenching using 4-nitrobenzalde-hyde and dinitrobenzene were essentially diffusion controlled with  $k_q$  values of  $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , while the rate using nitrobenzene was slightly slower with a  $k_q$  value of  $5.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .

In the present study, the potential electron relays **DQ1–DQ4** in addition to  $MV^{2+}$  were examined. Specifically, these dicationic diquat systems were found to give essentially diffusion controlled quenching rates of  $\sim 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  with complex 2. While the oxidative quenching of complexes 1, 3–4 *was* not examined quantitatively for **DQ1–DQ4** in the present study, similar quenching rate constants may be expected on the basis of the similar reaction chemistry seen in subsequent studies, particularly with regard to hydrogen generation (vide infra).

**Photoreduction of MV^{2+}.** While  $MV^{2+}$  is an effective quencher of chromophores 1-4, the characteristic blue color of MV<sup>+•</sup> is not observed during simple quenching experiments, presumably because of rapid back-electron transfer. However, when the sacrificial electron donor TEOA is also present in the photolysis solutions, the blue color of MV<sup>+•</sup> develops within 2 min and continues to increase in intensity up to a limiting value after ca. 50 min. Time dependence of the MV<sup>+•</sup> concentration in a system containing  $5.6 \times 10^{-3}$  M TEOA,  $2.2 \times 10^{-5}$  M of 2 and 3.1  $\times$  10<sup>-4</sup> M MV<sup>2+</sup> under visible light irradiation ( $\lambda$  > 410 nm) is shown in Figure 4. When irradiation is stopped, the blue color persists under an inert atmosphere but dissipates upon exposure of the solution to air within 1-2 min. The persistence of MV<sup>+•</sup> in solution as judged by the solution's blue color when TEOA is present is due to the fact that upon oxidation, TEOA undergoes decomposition leading to di(ethanol)amine and glycolaldehyde, along with transfer of a second, highly reducing electron to another MV<sup>2+</sup>.

When  $MV^{2+}$  as the oxidative quencher and electron relay is replaced by the diquats **DQ1–DQ4** (Scheme 2), similar quenching is observed with a decrease in the photoluminescence of **2**, and in the presence of TEOA, the formation of persistent solution colors characteristic of the corresponding diquat radical cations (green, tan, yellow-green, and pink for **DQ1–DQ4**, respectively).



**Figure 5.** Comparison of hydrogen production using different chromophores at  $2.2 \times 10^{-5}$  M (together with  $3.1 \times 10^{-4}$  M MV<sup>2+</sup>,  $5.6 \times 10^{-3}$  M TEOA, phosphate pH 7 buffer, and  $6.0 \times 10^{-5}$  M Pt colloid).

**SCHEME 2** 



Hydrogen Production Using Platinum(II) Terpyridyl Acetylide Chromophores. In a preliminary communication, we reported that photolysis of [Pt(ttpy)(C=CPh)]ClO<sub>4</sub> (2) in MeCN/  $H_2O$  in the presence of  $MV^{2+}$ , TEOA, and colloidal Pt leads to the photogeneration of H2.49 With a cutoff filter that allows only  $\lambda > 410$  nm, initial results yielded up to 84 turnovers and a 34% yield based on the initial amount of TEOA used as the electron donor. The reported yield is a lower limit estimate since unreacted TEOA remains in solution, as determined by liquid chromatography-mass spectrometry (LCMS). This multiple component system closely paralleled earlier ones based on Ru-(II) tris diimine sensitizers,<sup>5,6</sup> but with some mechanistic differences. The success of 2 as a chromophore for the photogeneration of H<sub>2</sub> is thought to relate to the long-lived (4.6  $\mu$ s) <sup>3</sup>MLCT excited-state of **2**, its energy (2.48 eV, Table 2), and its ability to undergo both oxidative and reductive quenching. The reduction potentials of excited-state redox processes for 2 can be estimated as -1.14 and +1.89 V (vs NHE) for oxidation and reduction, respectively. From quenching studies using a graded series of electron-donor quenchers, Schmehl has shown that **3** is a strong excited-state oxidant, albeit at a slightly lower excited-state reduction potential (ca. +1.4 V vs SCE or 1.65 V vs NHE).47

In the present study, the scope of the earlier work has been enlarged. A series of experiments using chromophores 1-4 have been carried out employing similar irradiation conditions ( $\lambda > 410$  nm) and the following concentrations: chromophore, 2.2  $\times 10^{-5}$  M; TEOA,  $5.6 \times 10^{-3}$  M; MV<sup>2+</sup>,  $3.1 \times 10^{-4}$  M; and colloidal Pt catalyst,  $6.0 \times 10^{-5}$  M in acetonitrile/water (2:3 v/v). Quantitative determination of generated H<sub>2</sub> was conducted by GC analysis with added methane as an internal standard. Figure 5 shows the time dependence of hydrogen production in this reaction system for the different Pt chromophores. The plot shows that hydrogen generation follows the order 2 > 1 > 3 > 4, which is dependent on both the absorptivities of the chromophores and their quenching rate constants. The molar



Figure 6. Comparison of hydrogen production using different diquat electron relays at  $3.1 \times 10^{-4}$  M (together with  $2.2 \times 10^{-5}$  M 2,  $5.6 \times 10^{-3}$  M TEOA, phosphate pH 7 buffer, and  $6.0 \times 10^{-5}$  M Pt colloid).



Figure 7. Comparison of hydrogen production under different concentration of DQ4 (together with  $2.2 \times 10^{-5}$  M 2,  $5.6 \times 10^{-3}$  M TEOA, phosphate pH 7 buffer, and  $6.0 \times 10^{-5}$  M Pt colloid).

TABLE 4: Quenching of 2 by Different Diquat ElectronRelays Acetonitrile/Water (2:3, v/v)

cmpd	E <sub>1/2</sub> (V vs NHE)	$k_{ m q} ({ m by}  {f 2}) \ ( imes  10^9  { m M}^{-1}  { m s}^{-1})$	$\Delta E^{\circ} \ \mathrm{V}^{a}$
MV <sup>2+</sup>	-0.44	3.3	0.67
DQ1	-0.37	10.0	0.74
DQ2	-0.55	7.1	0.56
DQ3	-0.65	6.1	0.46
DQ4	-0.70	7.0	0.41

<sup>*a*</sup> Electrochemical driving force for the quenching reaction estimated using an excited-state oxidaiton potential of -1.14 V.

extinction coefficients ( $\epsilon$ ) of the MLCT maxima of these complexes exist in the order of  $2 > 1 > 3 \approx 4$ . The observation that **4** is least effective for hydrogen generation may relate to the smallest quenching rate constant it has for oxidative quenching by  $MV^{2+}$  of the four chromophores. The slight induction periods in Figure 5 relate to charging of the Pt colloid through transfer of multiple electrons before the onset of H<sub>2</sub> generation as well as to instrument sensitivity at low H<sub>2</sub> levels.

In a second series of experiments, the nature of the electron relay was probed by using different diquats (**DQ1–DQ4**) in place of  $MV^{2+}$ . These experiments were all conducted using **2** as the chromophore with similar concentrations and conditions to those given above in the previous experiments. The results in terms of H<sub>2</sub> production are shown in Figure 6. The rate of hydrogen generation is greatest for **DQ4** with the overall order being **DQ4** > **DQ2**  $\approx$  **DQ3** > MV<sup>2+</sup> > **DQ1**. In Table 4 both the reduction potential and the quenching rate constant with **2** are shown for each electron relay. There exists an obvious correlation between the reduction potentials of **DQ1–DQ4** and MV<sup>2+</sup> and the respective rates of H<sub>2</sub> photogeneration. **DQ4**, which is the most difficult to reduce, exhibits the fastest rate of H<sub>2</sub> generation, while **DQ1**, which is most easily reduced, shows the slowest rate.

No such correlation, however, exists between the quenching rate constants and the rates of H<sub>2</sub> generation. The excited-state oxidation potential of 2 estimated above as -1.14 V vs NHE from  $E_{00}$  and the irreversible oxidation found for the complex by cyclic voltammetry indicates that the excited chromophore 2\* is capable of reducing all of the diquats. It is evident, however, that factors other than simple driving force dependence go into determining the quenching rates in light of the absence of such a correlation. If in fact the driving force dependence of the quenching reaction were the dominant factor in determining the rate of H<sub>2</sub> production, the order shown in Figure 6 would be reversed. Instead, it appears that both the effectiveness of DQ4 and the observed order for H<sub>2</sub> production for the diquats relate to the reducing ability of the corresponding radical cation  $(DQ4^{+\bullet} \text{ is most reducing and } DQ1^{+\bullet} \text{ is least})$ . This suggests that electron transfer from the radical cation of the electron relay to the Pt colloid may in fact be a limiting step in the system.

In a study of the effect of viologen and diquat electron relays on the photogeneration of H<sub>2</sub> using Zn(II) meso-tris(sulfonatophenyl)porphyrin (Zn(TPPS<sub>3</sub>) as the sensitizer, Okura et al., found that the largest rates of H<sub>2</sub> production were obtained with diquats that were most difficult to reduce, as we find in the present study.<sup>9</sup> The reaction conditions in Okura's study were adjusted so that an excess of the hydrogen evolving catalyst (hydrogenase) was present to make the photoreduction of the electron relay rate-determining, but further examination showed that the competitive back reaction and forward electron transfer to the hydrogenase catalyst were clearly involved in determining the effectiveness of the system for the photogeneration of H<sub>2</sub>. The results we describe in this paper, while in accord with those earlier conclusions, show even more clearly that the rate of H<sub>2</sub> photogeneration correlates most closely with the reducing power of the diquat radical anion generated by quenching or a subsequent reduction.



**Figure 8.** Comparison of hydrogen production under different concentrations of TEOA (together with  $2.2 \times 10^{-5}$  M **2**,  $3.1 \times 10^{-4}$  M MV<sup>2+</sup>, phosphate pH 7 buffer, and  $6.0 \times 10^{-5}$  M Pt colloid).

In the preliminary communication describing part of the present study, it was noted that the rate of H<sub>2</sub> evolution in controlled photolysis varied in nonmonotonic ways for both MV<sup>2+</sup> concentration and solution pH. The results were explained based on a reaction scheme in which MV<sup>2+</sup> and proton-transfer entered into two or more elementary steps. Examination of the concentration dependence of the most effective diquat, **DQ4**, was also carried out and is shown in Figure 7. While the rate of H<sub>2</sub> evolution increases with increasing **DQ4** concentration below  $1 \times 10^{-4}$  M, it appears to reach a limiting value in the range  $3 \times 10^{-4}$ -1.5  $\times 10^{-3}$  M, after which the rate declines as DQ4 concentration increases further. This finding is similar to what we reported for MV<sup>2+</sup> as the electron relay. Possible reasons for the decline in H<sub>2</sub> production rate at higher concentrations of MV<sup>2+</sup> included possible association complexes such as  $(MV)_2^{3+\bullet}$  of diminished reducing ability<sup>50,51</sup> and destructive hydrogenation of the viologen<sup>52,53</sup> when colloidal Pt is employed as the H<sub>2</sub> generating catalyst. Both factors may be at work in the system having **DQ4** as the electron relay. The optimal value of the diquat concentration found for the system composed of 2/TEOA/DO4 was found to be  $3.1 \times 10^{-4}$ M at pH 7. With this system and an initial concentration of TEOA of 5.6  $\times$  10<sup>-3</sup> M, 64 turnovers of H<sub>2</sub> relative to 2 were generated after 180 min of irradiation with  $\lambda > 410$  nm compared with the corresponding MV<sup>2+</sup> system that yielded 32 turnovers.

Examination of the influence of TEOA concentration on the rate of H<sub>2</sub> production was also examined. As shown in Figure 8, the rate increases up to a value of  $\sim 2.7 \times 10^{-2}$  M, beyond which the rate levels off, which is comparable to the system photocatalyzed by Ru(bpy)<sub>3</sub><sup>2+,52</sup> When the TEOA concentration was 0.11 M, photolysis led to more than 300 turnovers, and in the absence of a phosphate buffer with a TEOA concentration of  $2.7 \times 10^{-2}$  M, 800 turnovers were achieved with a yield of 67% based on TEOA. A reason for the increased turnover number in the absence of buffer is unclear and requires testing but may relate to buffer anion binding to the colloidal Pt surface thus decreasing the catalyst's effectiveness.

#### Conclusions

The platinum(II) terpyridyl acetylide chromophores 1-4 exhibit fast reductive quenching with TEOA and near diffusioncontrolled oxidative quenching with  $MV^{2+}$  and a series of diquats **DQ1–DQ4**. In the simple oxidative quenching experiments, no evidence of the photochemically reduced radical cation of the dialkylated bipyridinium electron acceptor is seen, but when TEOA is also present, the color of the respective radical cation appears within minutes. When a colloidal platinum catalyst is also added to the system, hydrogen is evolved. The most effective electron acceptor and relay for hydrogen evolution has been found to be DQ4 (4,4'-dimethyl-1,1'-trimethylene-2,2'-bipyridinium) which is also the hardest to reduce and which on photoreduction provides the strongest reducing agent. The rate of hydrogen evolution depends in a complex way on the concentration of the bipyridinium electron relay, increasing with concentration at low concentrations and then decreasing at high concentrations. The rate of H<sub>2</sub> photogeneration also increases with TEOA concentration at low values and eventually reaches a plateau. The most effective system examined to date consists of the chromophore 2 (2.2  $\times$  10<sup>-5</sup> M), **DQ4** (3.1  $\times$  10<sup>-4</sup> M), TEOA ( $2.7 \times 10^{-2}$  M), and Pt colloid ( $6.0 \times 10^{-5}$  M) in pH 7 acetonitrile/water (2:3 v/v) adjusted with concentrated HCl, and has produced 800 turnovers of H<sub>2</sub> (67% yield based on TEOA as sacrificial electron donor) after 20 h of photolysis with  $\lambda > \lambda$ 410 nm.

### **Experimental Section**

**Chemicals.** All of the chromophores were synthesized following details reported previously<sup>49</sup> by the reaction of [Pt-(R-terpy)Cl]Cl with different arylacetylenes in the presence of CuI as the catalyst in triethylamine/DMF and were characterized by <sup>1</sup>H NMR and ESI-MS spectroscopies. The perchlorate salts were obtained by exchange of chloride with potassium perchlorate. Warning: Perchlorate salts of metal complexes are known to be explosive and should therefore be handled with extreme care and proper protection. Methyl viologen (MV<sup>2+</sup>) dichloride and triethanolamine (TEOA) were used as purchased (Aldrich). The diquat salts (**DQ1–DQ4**) were prepared as published.<sup>54</sup> HPLC grade acetonitrile was purchased from Fisher and used without further purification.

Physical Measurements. Absorption spectra were recorded using a Hitachi U2000 scanning spectrophotometer (200-1100 nm). Emission spectra were obtained using a Spex Fluoromax-P fluorimeter corrected for instrument response. Monochromators were positioned with a 2-nm band-pass, and solution samples were degassed by at least three freeze-pump-thaw cycles. The 77 K frozen glass samples (1:4 MeOH/EtOH) were prepared in NMR tubes using a circular quartz-tipped immersion Dewar filled with liquid nitrogen for measuring the emission spectra and estimating the excited-state energy of chromophores. Cyclic voltammetry experiments were conducted on an EG&G PAR 263A potentiostat/galvanostat using a three-electrode singlecompartment cell. A glassy carbon working electrode, a Pt wire auxiliary electrode, and a Ag wire reference electrode were used. For all measurements, samples were dissolved in DMF and degassed with argon. Tetrabutylammonium hexafluorophosphate (Fluka) was used as the supporting electrolyte (0.1 M), and ferrocene (ROC/RIC) was employed as an internal redox reference. All redox potentials were reported relative to the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple (0.45 V vs SCE<sup>55</sup> and SCE vs NHE = 0.24 V). All scans were done at 100 millivolts per s.

Crystal Structure Determination of  $[Pt(tpy)(C \equiv CPh)]$ -CIO<sub>4</sub>. Crystals were grown by slow evaporation of a concentrated acetonitrile solution. A crystal  $(0.32 \times 0.32 \times 0.28 \text{ mm}^3)$ was placed onto the tip of a glass fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for data collection at 100.0(1) K. A preliminary set of cell constants and an orientation matrix were calculated from 876 reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. The data collection was carried out using Mo K $\alpha$  radiation (graphite monochromator) with a frame time of 5 s and a detector distance of 5.03 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.50° steps in  $\omega$  at four different  $\phi$  settings and a detector position of  $-33^{\circ}$  in  $2\theta$ . The intensity data were corrected for absorption. Final cell constants were calculated from the *xyz* centroids of 3975 strong reflections from the actual data collection after integration. Additional crystal and refinement information can be obtained from the CIF file deposited as Supporting Information.

Quenching Experiments. For all of the quenching experiments, stock solutions of the chomophores were made in acetonitrile/water (2:3 v/v) containing 5 mg of the particular complex. Samples with known quencher concentrations were prepared by adding an appropriate amount of solid quencher to 10 mL volumetric flasks containing the diluted Pt chromophore stock solutions ( $1.0 \times 10^{-5}$  M). The solutions were deaerated by three freeze-pump-thaw cycles. Steady-state luminescence spectra were then collected for each sample. UV-vis spectra were taken for each experiment to inspect potential photochemical products. In the simple bimolecular quenching reactions, there was no evidence of any change in absorption spectra under all experimental conditions. However, in the presence of both TEOA and MV<sup>2+</sup> reagents, visible excitation of the Pt chromophore generated the blue methyl viologen radical cation, which was detected by UV-vis spectra.

Details of Hydrogen Generating Experiments. For photoinduced hydrogen evolution, each sample was made in a 50 mL round-bottom flask with a volume of 25 mL in acetonitrile/ water (2:3 v/v). Typically, the sample contained  $2.2 \times 10^{-5}$  M Pt chromophore,  $6.0 \times 10^{-5}$  M Pt colloids, and  $3.1 \times 10^{-4}$  M electron carrier. Phosphate buffer (0.20 M) was used to maintain the pH, and the Pt colloids were stabilized using sodium polyacrylate polymer.<sup>56</sup> The flask was sealed with a rubber septum and degassed by bubbling nitrogen for 15 min under atmospheric pressure at room temperature, after which 5 mL of nitrogen was removed from the flask and replaced with 5 mL of methane (760 Torr) to serve as the internal standard. The samples were irradiated under a 200 W Mercury Xexon lamp. A cutoff filter was used to remove light with  $\lambda < 410$ nm. The amount of H2 generated was determined by GC analysis using a chromatograph (Shimadzu) with a molecular sieve 5 Å column (30 m  $\times$  0.53 mm) and thermal conductivity detector.

To investigate concentration effects of the different Pt chromophores, electron relays, the sacrificial donor, and the solution pH, one of the reaction components was varied while the others were held constant. General reaction conditions and concentrations included  $2.2 \times 10^{-5}$  M Pt chromophore,  $5.6 \times 10^{-3}$  M TEOA,  $6.0 \times 10^{-5}$  M Pt colloid,  $3.1 \times 10^{-4}$  M MV<sup>2+</sup> or diquat, and pH 7. When examining the reductive quenching effects on H<sub>2</sub> production for chromophore **2**, concentrations of TEOA were varied in the range  $5.6 \times 10^{-3} - 0.11$  M. Likewise, for oxidative quenching effects on H<sub>2</sub> production for Pt chromophore **2**, concentrations of the electron relay **DQ4** were varied in the range  $1 \times 10^{-4} - 6.2 \times 10^{-3}$  M.

**Determination of Rate Constants from Quenching Experiments.** In all samples, quenching rate constants ( $k_q$ ) were evaluated from steady-state luminescence experiments. Addition of quenchers to the Pt(II) compounds resulted in concentrationdependent luminescence intensity quenching. Bimolecular quenching was well-modeled by the Stern–Volmer equation<sup>46</sup> (eq 2), where  $I_o$  is the integrated MLCT emission intensity in the absence of quencher,  $\tau_0$  is the excited-state lifetime in the absence of quencher, *I* and  $\tau$  are the corresponding values in the presence of quencher,  $k_q$  is the bimolecular quenching rate constant, and [Q] is the molar concentration of the quencher.

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**Supporting Information Available:** X-ray crystallographic data of complex **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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