

Photophysical Studies on Terpyridyl Platinum(II) Chromophore - Electron Acceptor Dyads for the Photocatalytic Hydrogen Generation from Water

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Introduction

Generation of hydrogen(H_2) fuel using the visible light absorbing molecular systems in photochemical water splitting has long been an attractive topic of research. For molecular based system to carry out this reaction by visible light irradiation, key components include a metal complex sensitizer, an electron carrier such as viologen, a sacrificial electron donor, and a hydrogen producing catalyst that is usually colloidal platinum or $CoCl_2$. The metal complex sensitizers used for this conversion are based on octahedral Ru(II) bipyridyl,¹⁻³ Pt(II) polypyridyl,⁴⁻⁶ Zn(II) porphyrin,^{7,8} cyclometalated Ir-complexes^{9,10} and chromophores attached to platinumized TiO_2 particles.¹¹⁻¹³ Besides the Pt(II) metal complex sensitizers directly connected to an acceptor group as chromophore-acceptor dyads (C-A dyads) are investigated for this purpose.¹⁴ Our recent research in this field focuses the photophysical studies on square planar terpyridyl Pt(II) complexes to achieve photo-induced charge separated state¹⁵⁻¹⁷ and authentic systems for the photocatalytic activity. The terpyridyl Pt(II) chromophore MLCT transition absorbs in the visible region and has the nature to direct the energetic electron on the terpyridyl unit after ³MLCT excitation. This directionality can be exploited in designing systems to exhibit photo-induced charge separation when connected with suitable electron donating or accepting units. Once the charge separation is achieved it can be attached to catalysts to drive energy storage¹⁸⁻²⁰ and to improve efficiency in hydrogen evolution.²¹

In this regard, various chromophore-acceptor dyads **1-4** (Figure 1) were prepared from the ligands with an acceptor group in the terpyridyl unit via benzylic or phenyl linkage. The dyads **1-4** were prepared by following the straight forward multi-step synthetic processes. The details of the syntheses and characterizations of all these dyads were discussed in our previously published articles.¹⁵⁻¹⁷

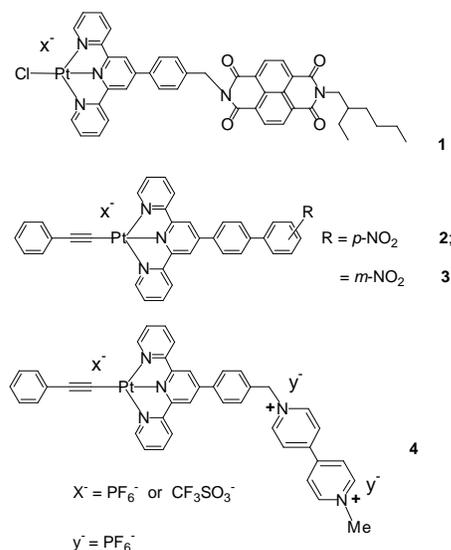


Figure 1. List of C-A dyads involved in the photophysical studies.

Among the dyads, the methyl viologen connected to terpyridyl platinum(II) chromophore **4** was found least stable due to its benzylic linkage hydrolyzed to form a platinum(II) terpyridyl benzyl alcohol and a viologen unit in basic conditions. Comparatively the dyad **1** was found more stable in air and in basic conditions. In general, the dyads are dissolving easily in DMF and in acetonitrile solvents which are chosen as solvents to study their transient behaviors using a nanosecond transient absorption instrument.

Experimental

The solvents acetonitrile and DMF were procured from Aldrich and used for all the experiments without further purification unless specified. The UV-visible absorption studies were done using an HP 8452A diode array spectrophotometer. Luminescence spectra were recorded with a SPEX Fluorolog emission spectrometer. Electroanalytical measurements (cyclic voltammetry and differential pulse voltammetry) were made with a CH Instruments model 650 C electrochemical analyzer. All voltammetric data were obtained in dry acetonitrile and in some cases dry DMF, with tetrabutylammonium hexafluorophosphate as supporting electrolyte and glassy carbon electrodes. Nanosecond flash photolysis studies were done in an Applied Photophysics LKS60 spectrometer. The excitation source was a Quantel Brilliant Nd:YAG laser equipped with 2nd and 3rd harmonics. Pulse widths averaged 4 ns and the output was used to pump an OPOTEK optical parametric oscillator that provided tunable output between 425 and 650 nm. Transient spectra were acquired on a point by point basis.

Results and Discussion

The absorption spectra of all the dyads were measured in acetonitrile exhibit features in the range of 280-800 nm. A naphthalene diimide acceptor connected dyad **1** showed strong absorption in the 280-375 nm and the metal to ligand charge transfer ($d\pi(Pt)-\pi^*(tpy)$) absorption at 410-500 nm. The strong absorption in higher energy region is identified as ligand localized $\pi-\pi^*$ transitions. The similar higher energy absorption of the dyads **2**, **3** and **4** in the region of 300-370 nm is assigned as intra-ligand transitions. There is no evidence of possible intra-ligand transition in the dyad **1**, but prominent sign of aggregation of the dyad is observed by the broadening and disappearance of the 375 nm band in solvents such as DMSO and ethanol. This aggregation behavior of dyad **1** is due to the $\pi-\pi$ interaction of naphthalene diimide moieties and the metal-metal interactions. However the sharp spectral band at 380 nm appeared in acetonitrile solution in lower concentrations shows no aggregation.

The room temperature luminescence studies of the dyads **1-4** were done in degassed acetonitrile solutions in low concentrations (1×10^{-5} M). The dyads **1-3** were found emissive; the emission maximum appeared in 600 nm is characterized as the luminescence from terpyridyl platinum(II) chromophore and the dyad **4** was weakly emissive in this region in solution because of the charge transfer quenching of ³MLCT state by the viologen acceptor unit. Further the ³MLCT platinum chromophore and the triplet state of the naphthalene diimide in the dyad **1** were appeared to be isoenergetic. For the emission to be naphthalene diimide centered, it may require the yield of triplet states is excitation wavelength dependant. But the emissions from both MLCT and ND localized triplet excited states of **1** were found very weak. The emission properties of the dyads **2** and **3** resembled their parent platinum(II) chromophore emission without any changes.

The electrochemical measurements of all the dyads were done in either acetonitrile or DMF with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. All of the redox

potentials are reported relative to NHE based on the Fc/Fc⁺ couple used as an internal standard. For the dyad **1** the reduction at -0.4 V is assigned as the first reduction of naphthalene diimide and its second reduction appeared at -0.88 V is overlapped with the first reduction of terpyridyl unit appearing at -0.61 V. The dyads **2** and **3** showed three ligand reduction potentials at -0.54, -0.82 and -1.11 V. These reduction potentials for the dyads **2** and **3** are almost similar regardless of their *meta*- and *para*- position of the nitro group. The dyad **4** showed the reduction at -0.12 V which is assigned as the first viologen reduction. The second reduction of the viologen appeared at -0.76 along with broad terpyridine first reduction onset starting at -0.46 V. For all the dyads an irreversible oxidation at 1.5-1.6 V represents the Pt(II) to Pt(III) oxidation. More details on these redox values are given in our previous articles.^{15, 16}

Transient absorption studies. To study the photo-induced electron transfer processes in these dyads, nanosecond transient absorption studies were performed on dyads **1-4** in acetonitrile. The dyad **1** shows several absorptions in various time scales after the excitation at 425 nm. The initial spectrum obtained immediately after the laser excitation pulse exhibits broad absorption over the 400-700 nm range; this fades in 118 ns to produce the transient maxima at 360, 420 and 470 nm (Figure 2A). These transient maxima are assigned as naphthalene diimide radical anion (ND⁻) formation as a result of photo-induced charge separation. The initial broad transient absorption is assigned as intraligand transients which may be coming from the isoenergetic triplet MLCT and triplet naphthalene diimide states. A similar initial transients observed in the parent chromophores (TpyPtCl and ND) of the dyad **1** discloses the equilibrium between MLCT and ND localized triplet excited states. Further the transient maximum at 420 nm decays with a lifetime of 2.2 μs is assigned as solvent coordinated TpyPt(III) species. This species decays in a first order back electron transfer process with a lifetime of 13 μs to the starting complex. The back electron transfer rate constant is surprisingly slow for this system and stands in contradiction of other Pt(II) containing systems showing the photo-induced electron transfer. The transient absorption spectra of the

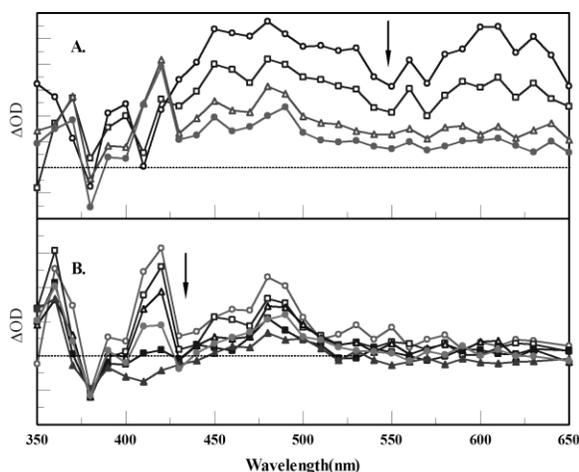


Figure 2. Transient absorption spectra of dyad **1** in acetonitrile at (A) 73(○), 120(□), 240(Δ) and 309(●) ns and (B) 293(○), 613(□), 1200(Δ), 2300(●), 6000(■) and 13000(▲) ns traces after the laser excitation at 425 nm.

dyads **2** and **3** are virtually same as their parent chromophore TpyPt(acetylde) and no influences observed from the nitro substitu-

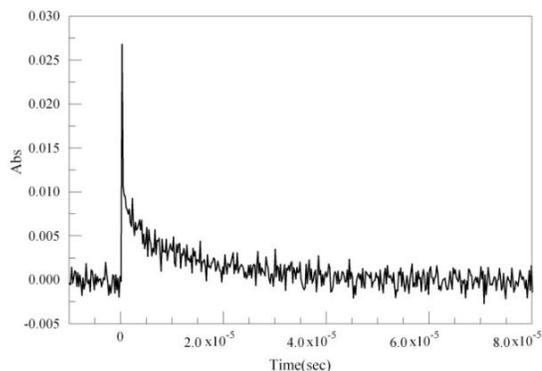


Figure 3. Transient kinetics recorded for the charge recombination step of dyad **1** after the laser excitation ($\lambda_{ex} = 425$ nm)

ent when connected in *meta*- or *para*- positions to the biphenyl unit of its terpyridine ligand. Both the dyads showed transient absorption maxima at 360 nm and broad absorption between 520-800 nm and a bleach at 450 nm regardless of its excitation wavelength. This indicates the nitro phenyl moiety does not accept an electron from the excited chromophore. These results are matching with the emissions observed from the dyads without any electron transfer quenching. So it becomes obvious that there is no occurrence of photo-induced electron transfer processes in dyads **2** and **3** wherever it excited. In contrast, the viologen connected dyad **4** shows transient absorption maximum at 400 nm for the viologen radical cation species with the same parent chromophore TpyPt(acetylde). However this transient absorption features decayed very fast ($k \sim 10^8$ s⁻¹). Transient absorption for the reduced viologen species (radical cation) normally appears at 397 and 610 nm. For the dyad **4**, the weak absorption at 610 nm is enveloped by the greater yield of terpyridine radical anion which normally appears at 550-800 nm. Another reason for the poor transient signals of dyad **4** is accounted to the easy hydrolysis of benzylic linkage to the viologen unit though viologen can oxidatively quenches excited state of the terpyridyl platinum chromophore. Therefore, the dyad **4** can successfully perform photo-induced electron transfer processes but poorly stable in solutions.

The dyads having successful formation of charge separated species with a slow back electron transfer rates are in principle suitable candidate to act as light induced electron transfer catalytic systems. The dyads **1** and **4** are performing the photo-induced charge transfer in solutions and can undergo reductive quenching reaction with

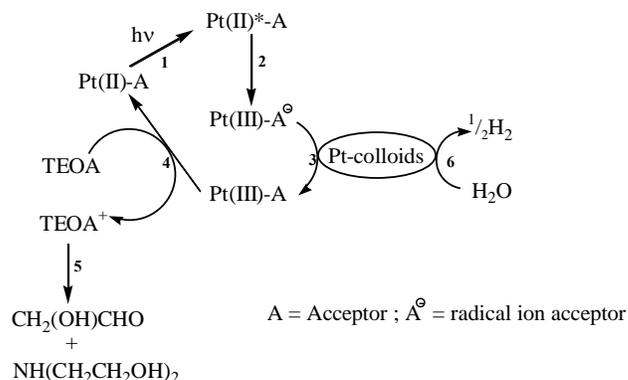


Figure 3. Generalized catalytic scheme for the hydrogen evolution using charge separated state of dyads **1** and **4**.

triethanolamine (TEOA) upon photolysis. Remarkably the dyad **1**+TEOA in degassed acetonitrile or **1**+DMSO solution color is changed from yellow to pale brown immediately after the flash photolysis experiment. This is a clear indication of charge separated species reacting with sacrificial donors. Similar experiments are not tested with dyad **4** because of its poor stability. However it is known that the viologen unit has propensity to readily react with TEOA in photolysis.^{5, 22} In general, the photo-induced charge separated (PCS) state can assist the hydrogen evolution in photochemical water splitting by following possible steps proposed in the catalytic scheme in figure 4. Similar catalytic steps are followed in other dyads having platinum(II) chromophore and viologen acceptor¹⁴ or ruthenium complex donor.²¹ In all the schemes charge separated state must be sufficiently living to transfer the electron to the Pt-colloidal catalyst through the acceptor (step 3). Later the oxidized platinum chromophore in the PCS state gains its electron from the decomposition of TEOA which eventually produces glycolaldehyde and diethanolamine (step 5).³ Electron transfer from the reduced acceptor (typically in the radical ion form) to platinum catalyst helps the proton reduction at Pt-surfaces (step 6).

Conclusions

The terpyridyl platinum(II) chromophore connected to various electron accepting group as chromophore-acceptor dyads **1-4** are analyzed for their properties to catalyze light-induced generation of H₂. The photoinduced charge separated state (PCS) is formed only in the dyads **1** and **4**. The dyads **2** and **3** are not forming PCS state. In both **1** and **4**, the PCS state formed were decayed at different rate constants $8 \times 10^4 \text{ s}^{-1}$ and $\sim 10^8 \text{ s}^{-1}$. The dyad **1** has super long lived PCS state compared to dyad **4**. This feature can be exploited to make more robust catalytic systems. Further studies are in progress to optimize and modify the functional groups in **1** to have better soluble, more visible light absorbing and fast PCS state forming catalytic system for the efficient photochemical generation of hydrogen.

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