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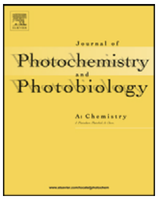

Photoinduced charge separation and recombination in solution and in gels of a Pt(II) terpyridyl–naphthalene diimide complex

Duraisamy Kumaresan, Kristi Lebkowsky, Russell H. Schmehl*

Tulane University, New Orleans, LA, United States

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ABSTRACT

Light induced electron transfer and subsequent recombination in a covalently linked terpyridyl Pt(II)/naphthalene diimide (ND) donor acceptor complex are discussed. The complex consists of the ND moiety covalently linked to a terpyridine ligand through a tolyl linkage (ND-tpy) with chloride serving as the fourth ligand of the Pt(II) center ([(ND-tpy)PtCl]). Photolysis of the complex in acetonitrile solution results electron transfer from the Pt(II) complex to the ND unit. This is followed by a significant structural change in the oxidized Pt complex/reduced ND that leads to formation of a charge separated species that decays by back electron transfer with a rate constant of $8 \times 10^4\ s^{-1}$, a much slower recombination rate than other Pt(II) donor/organic acceptor systems. The complex forms gels when concentrated DMSO solutions are heated and allowed to cool slowly. The gels have long tubular structures and the dried gels exhibit long range order of the Pt centers, as evidenced by X-ray powder diffraction. Photolysis of the gels suspended in solution leads to formation of long lived radical ions, formed presumably from self-exchange electron hopping between stacked donor and acceptor moieties in the gels.

1. Introduction

The development of photoactive materials for use in photovoltaic devices or other systems for net storage of solar energy has been an active area of research for many years [1–10]. Among the systems examined are those consisting of a chromophore covalently linked to one or more electron donors and/or acceptors [11–14]. Such supramolecular donor-chromophore, chromophore-acceptor or donor-chromophore-acceptor, systems generally give rise to transient charge separated species which recombine over time periods that depend on the free energy of the recombination reaction (generally highly exergonic), charge separation distance, electronic coupling and reorganization energy [15,16]. The energy stored in the intramolecular charge separated state is the sum of the ground state redox potentials required to form the one electron oxidized and one electron reduced species. Utilization of the energy stored in the charge separated species hinges on trapping the independent radical ions before they recombine, either intramolecularly or bimolecularly. One approach to utilization of the charge separated species involves electron transfer of one of the radical ions of the supramolecular complex with an electron or hole sink. An example is the attachment of supramolecular chromophoric systems to semiconductor electrodes that serve as traps for electrons generated in charge separated states [17].

Others have shown that self-assembly of chromophore-quencher ensembles can result in formation of aggregate structures having arrays of stacked electron donors and/or acceptors [18–22]. Charge hopping following photoinduced electron transfer leads to generation of long lived charge separated species. While such systems do not separate charge permanently, as do electron or hole sinks, it is possible that charge recombination half lives can be increased by several orders of magnitude, enhancing opportunities for charge utilization. Especially interesting examples of such systems can be found in the recent work of Wasielewski and coworkers; perylene diimide chromophores covalently linked to various electron donating amines or porphyrins aggregate to form stacks of the perylene diimide and charge hopping in the perylene diimide array is competitive with back electron transfer.

Recently square planar Pt(II) complexes have been shown to form aggregates in solution that can, in some cases, be employed to form extended structures such as gels and liquid crystals [23–25]. In addition, some aggregated complexes have been shown to be photoactive, exhibiting luminescence in the aggregate that can be linked to intermolecular interactions of individual chromophores. Square planar Pt(II) complexes having imine ligands (i.e. bipyridine or terpyridine) are known to exhibit luminescence from ligand-to-ligand (LLCT) or metal-to-ligand (MLCT) charge transfer states as monomers in dilute solution, but, upon dimerization of either

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* Corresponding author. Tel.: +1 504 8623566.
E-mail address: russ@tulane.edu (R.H. Schmehl).

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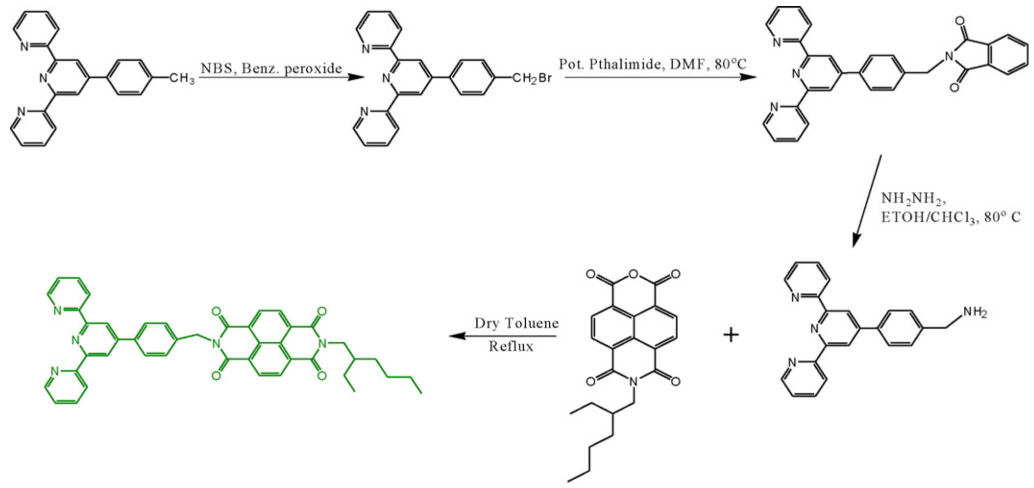


Scheme 1.

two ground states prior to excitation or the excited state with a ground state, a new state is formed that can best be described as a Pt_2 (dσ^*) to Pt_2 (pσ) associated with a transiently formed metal–metal bond [26]. This dσ^*–pσ state often exhibits luminescence at longer wavelength. Both the monometallic complex and the bimetallic excimer are capable of participating in photoinduced electron transfer reactions. Higher degrees of aggregation lead to the formation of extended structures which can ultimately result in macroscopic gels/precipitates.

In this work we would like to report the formation of long lived charge separated species following photolysis of gels formed from solutions of a terpyridyl Pt(II) chromophore (electron donor) complex covalently linked to a naphthalene diimide acceptor complex ($[ClPt(tpy\text{-}ND)]^+$, below). The results are interpreted in terms of charge separation via hole and electron migration in extended structures consisting of alternating columns of the Pt(II) donors and the naphthalene diimide acceptors.

2. Experimental

2.1. Syntheses

The ligand 4′-(*p*-tolyl)-2,2′,6′,2″-terpyridine was obtained from Aldrich chemical company and used without further purification. All solvents were used as received.

The ligand tpy-ND, was prepared by an adaptation of the procedure of Hammarstrom as shown in Scheme 1 below [27].

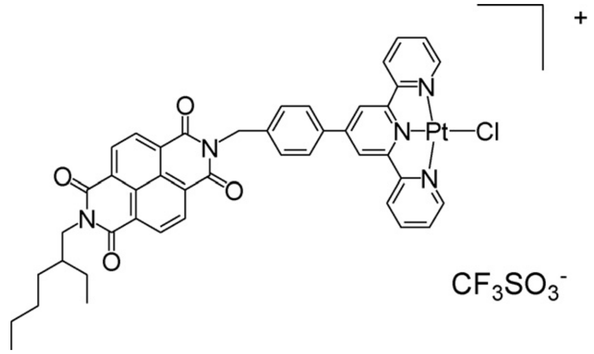
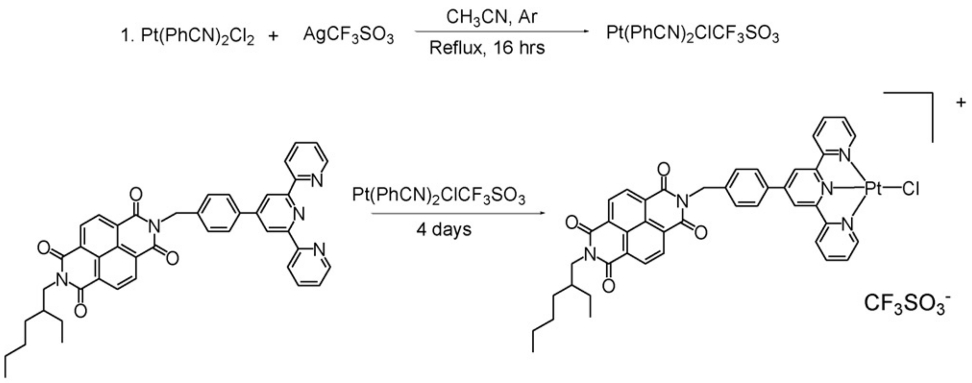


Fig. 1. $[ClPt(tpy\text{-}ND)]^+$.

The complex (Fig. 1) is prepared from reaction of the terpyridyl naphthalene diimide ligand and bis(benzonitrile)Pt(II) chloride in acetonitrile under Ar reflux as shown in Scheme 2. The product complex was characterized by ^1H NMR and ESI–TOF mass spectrometry at high resolution (see supplemental information).

2.2. Instrumentation and methods

^1H NMR spectra were obtained using a Varian Inova 400 MHz spectrometer equipped with a variable temperature probe. UV–vis absorption spectra were obtained using an HP 8452A diode array spectrophotometer. Luminescence spectra measured with a SPEX



Scheme 2.

Fluorolog photon counting spectrofluorimeter equipped with a 450 W Xe arc lamp and a Peltier cooled PMT housing. Spectra were not corrected for instrument response. Luminescence spectra were also obtained using the same spectrometer but using a CCD detector. 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, distilled from CaH_2 under N_2, with tetrabutylammonium hexafluorophosphate as supporting electrolyte and glassy carbon electrodes.

Scanning electron micrographs of dried gels were acquired using a Hitachi 4800 high-resolution SEM. Transmission electron micrographs of gels were obtained with a JEOL 2010 STEM. TEM samples were prepared by evaporation of gel containing DMSO solutions on carbon grid supports. X-ray powder diffraction was obtained using a Scintag XDS2000 powder diffractometer. Samples analyzed were from dried gels, mechanically ground to a fine powder.

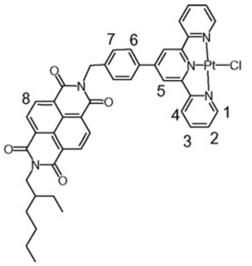
An Applied Photophysics LKS60 spectrometer was used in acquisition of transient absorption spectra. The excitation source was a Quantel Brilliant Nd:YAG laser equipped with 2nd and 3rd harmonics. Pulse widths averaged 4 ns and the output was used to pump an OPOTEK optical parametric oscillator that provided tunable output between 425 and 650 nm. Transient spectra were acquired on a point by point basis.

3. Results and discussion

3.1. Complex preparation and characterization

As mentioned above, the ligand ND-tpy was prepared by the procedure of Hammarstrom et al. [27]. The Pt(II) complex was then made by initial reaction of bis-benzonitrile platinum(II) dichloride [28] with silver triflate, to remove one of the chloride ligands, followed by reaction with the ligand in refluxing acetonitrile. The product triflate salt, [(ND-tpy)PtCl](OTf), was structurally characterized by ^{1}H NMR and mass spectrometry using an ESI–TOF spectrometer with a mass resolution in excess of 10,000. Mass spectral data, obtained from acetonitrile solutions of the complex, reveal the monocation as the principal species in solution along with a fragment that involved loss of the NDI (see supplementary information). Room temperature proton NMR spectra were complex. Fig. 2 shows ^{1}H NMR spectra in DMSO-d_6 at temperatures between room temperature and 90 °C.

The spectrum at room temperature exhibits many aromatic resonances; however, integration of the entire aromatic region is consistent with that expected based on the total integration of the aliphatic region. The implication is that some degree of aggregation is occurring in solution at room temperature. At higher temperatures the spectrum becomes simpler and COSY spectra obtained at 75 °C can be fully assigned as shown in the 1D spectrum of Fig. 2. Given that ESI mass spectral data indicate only a single Pt complex in solution (parent ion and one fragment), it is reasonable to assume that solutions of the complex do indeed contain a single species.



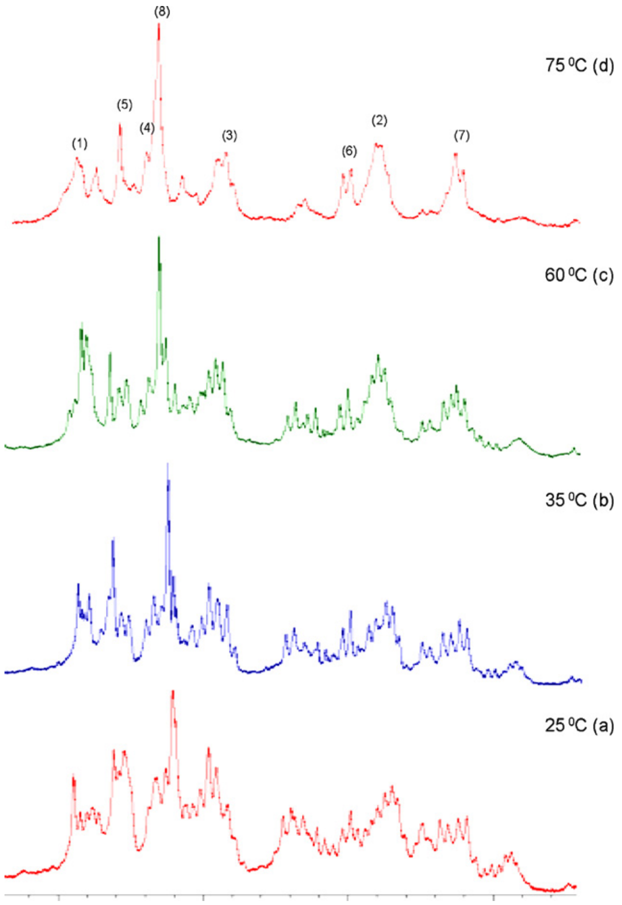


Fig. 2. ^{1}H NMR spectra of 1 mM [(ND-tpy)PtCl] in DMSO-d_6 at several temperatures.

3.2. Absorption and luminescence spectra

In solutions where aggregation of the ND-tpy ligand does not occur, such as for $[Zn(ND\text{-}tpy)_2]^{2+}$ in CH_3CN (Fig. 3A), absorption spectra exhibit three distinct absorption bands, including a tpy localized π–π^* transition at 280 nm and a relatively narrow π–π^* transition, localized on the ND chromophore, at 375 nm. All of the absorption transitions are ligand localized π–π^* transitions and there is no evidence of possible intraligand charge transfer transitions. A clear sign of aggregation of this dicationic chromophore is the broadening and disappearance of the 375 nm absorption band and inclusion into the broad, higher energy transition centered at 330 nm. Absorption spectra of $[(ND\text{-}tpy)PtCl]^+$ in acetonitrile, a 20/80 acetonitrile/chloroform mixture and in pure DMSO are shown in Fig. 3B and C. The spectrum in CH_3CN has features resembling those of the Zn^{2+} complex, but also exhibits a lower energy Pt(II) to tpy metal-to-ligand (MLCT) charge transfer transition similar to that observed in $[(tpy)PtCl]^+$ [29]. A key feature is the absorption feature at 380 nm that appears in the spectra in acetonitrile and, to a lesser extent, the $CH_3CN/CHCl_3$ solvent mixture; this band broadens considerably and disappears altogether when the naphthalene diimide aggregates in solution, as is the case in DMSO, where room temperature aggregation has been shown in ^{1}H NMR spectra.

The ligand ND-tpy exhibits fluorescence in aerated CH_3CN solution at room temperature with a maximum of 405 nm. The emission maximum is independent of excitation wavelength. Following coordination to Pt, distinct changes are observed in the luminescence behavior. If the $[(ND\text{-}tpy)PtCl]^+$ complex is excited at 370 nm (or shorter wavelengths), weak luminescence, presum-

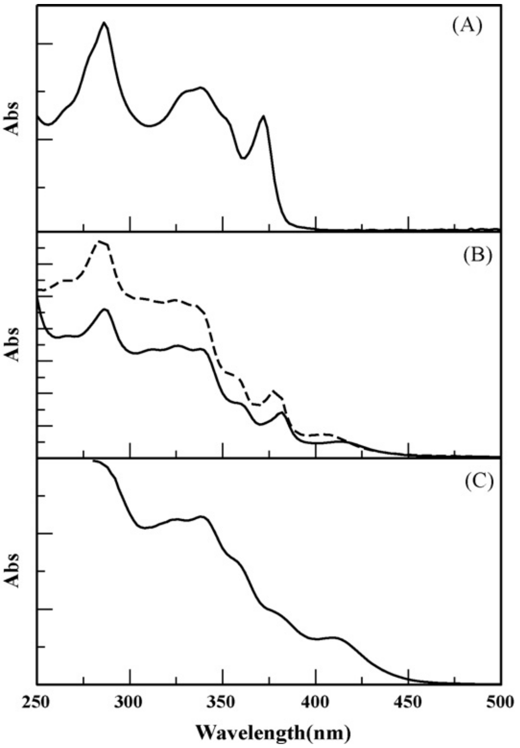


Fig. 3. Absorption spectra of (A) $[Zn(ND\text{-}tpy)_2]^{2+}$ (100 μM) in CH_3CN, (B) $[(ND\text{-}tpy)PtCl]^+$ (50 μM) in CH_3CN (- - -) and 20/80 $CH_3CN/CHCl_3$ (–) and (C) $[(ND\text{-}tpy)PtCl]^+$ (50 μM) in DMSO.

ably localized on the ND-tpy ligand, is observed at 435 nm. The red shift in ligand localized luminescence is not clear, but may be the result of a change in electronic interactions of the terpyridyl substituent following coordination to Pt. A second, even weaker and broad (FWHM = 100 nm) emission is observed at 590 nm when excitation was at 370 nm. Excitation of the complex into the Pt(II) to tpy (π^*) MLCT transition (410 nm) results in luminescence only at 590 nm, supporting the potential assignment of the emission as arising from the Pt to tpy ^{3}MLCT state. However, Rogers and Kelly reported 610 nm phosphorescence of a closely related naphthalene diimide derivative [30], observed for 77K samples doped with methyl iodide. For the 590 nm emission to be ND localized, it would require that the yield of triplet states is excitation wavelength dependent. In all cases the emission is very weak and no attempt was made to measure the emission quantum yields, but the yields were certainly less than 10^{-3}. We were not able to measure luminescence lifetimes with N_2 laser excitation and direct detection of the decays following dispersion through a monochromator; however, transient spectral decays were obtained using time resolved absorption (*vide infra*).

3.3. *Intramolecular photoinduced charge separation and recombination in acetonitrile*

From the luminescence data presented above and employing the data of Rogers et al. [31] for a closely related naphthalene diimine derivative, it appears that the lowest energy MLCT and ND localized triplet excited states are nearly isoenergetic at slightly more than 2.0 eV. In considering possible photoredox products, a reaction involving reduction of the terpyridyl Pt(II) species and oxidation of the ND unit can be excluded since the first one electron reduction potential of the terpyridyl Pt(II) center is −1.5 V vs. SCE (from cyclic voltammetry in supplementary information) and the one electron oxidation of the ND is more positive than 1 V (not observed in voltammetry); the sum of the potentials exceeds the energy of either the triplet MLCT state of the Pt chromophore or the ND triplet. However, either of the states could serve as sensitizer for an intramolecular electron transfer from the terpyridyl Pt(II) complex to the ND. The first one electron reduction of the ND is −0.64 V vs. SCE and, while the Pt(III/II) process is not observed by cyclic voltammetry, it is very likely less than the approximately +1.4 V vs. SCE necessary for the light induced intramolecular electron transfer process to be exergonic (for instance, oxidative addition with Cl_2 occurs) [32].

The transient spectroscopic behavior observed in acetonitrile has three different time domains. Fig. 4 shows transient spectra of [(ND-tpy)PtCl] at different times following laser pumped OPO excitation into the Pt to tpy MLCT absorption at 425 nm. Initially the complex exhibits broad absorption over the 400–650 nm range (Fig. 4A). This gives way to a transient with maxima at 360, 420 and 480 nm that reacts over a period of approximately 10 μs (Fig. 4B) to a transient with absorption maxima at 360 and 470 nm. This transient decays to the ground state with a lifetime of 13 μs. The initial transient observed can be explained as a juxtaposition of the Pt(II) to tpy MLCT and ND intraligand transients, almost certainly existing in equilibrium since the lifetime of the transient far exceeds that of the ^{3}MLCT state of $[(tpy)PtCl]^+$. Fig. 5 shows spectra obtained for the two "parent" chromophores: $[(tpy)PtCl]^+$ (Fig. 5A) and *N*,*N*′-di(2-ethyl-hexyl)-naphthalene diimide (ND, Fig. 5B). The lifetime of the excited state of $[(tpy)PtCl]^+$ is approximately 1 ns and the transient spectrum displayed actually represents spectra obtained within the lifetime of the excitation pulse at 415 nm (note that the points at 410 and 420 nm are missing, since they appear as strong scattering signals). The excited state exhibits broad absorption between 550 and 700 nm. The ND triplet spectrum was obtained in acetonitrile solution in the presence of a small amount of trifluoroacetic acid which serves to disrupt aggregation. The ND has excited state absorption between 400 and 525 nm, complimenting the $[(tpy)PtCl]^+$ chromophore. It is clear that a weighted sum of the two transients could yield the spectrum observed in the first several hundred nanoseconds following excitation of $[(ND\text{-}tpy)PtCl]^+$ (Fig. 4A), provided the MLCT and ND localized triplet excited states are in equilibrium (*vide infra*).

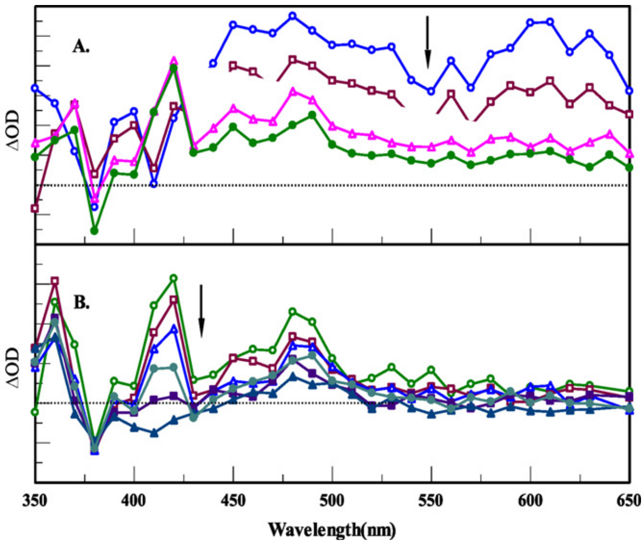


Fig. 4. Transient absorption spectra of $[(ND\text{-}tpy)PtCl]^+$ in N_2 purged CH_3CN at (A) 73 ns (open circles), 120 ns (open squares), 240 ns (open triangles) and 309 ns (closed circles) following 425 nm excitation and (B) 293 ns (open circle), 613 ns (open squares), 1200 ns (open triangles), 2300 ns (closed circles), 6000 ns (closed squares) and 13,000 ns (closed triangles) after excitation.

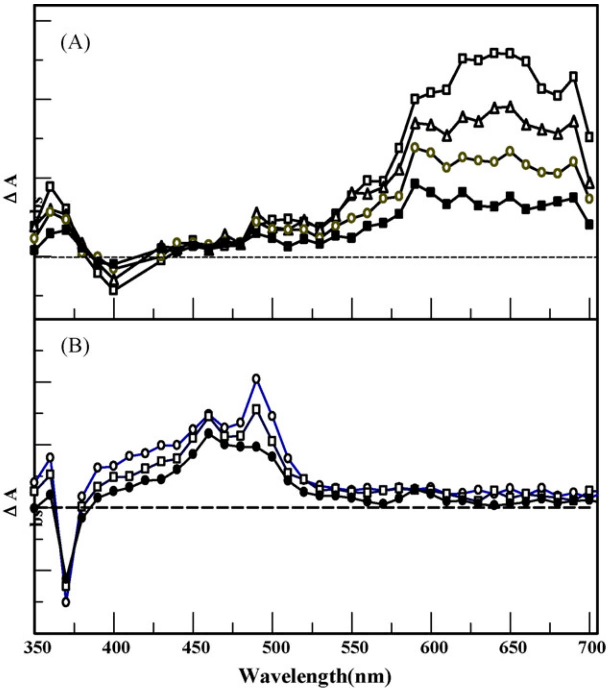


Fig. 5. Transient spectra of (A) [(tpy)PtCl]$^+$ in CH_3CN at several times during the 4 ns excitation pulse at 415 nm and (B) *N*,*N*′-di-(2-ethyl-hexyl)-naphthalene diimide at 650 ns (open circles), 2.9 μs (open squares) and 12 μs (filled circles) following 355 nm excitation.

Over the first few hundred nanoseconds an intermediate transient species appears with maxima at 360, 420 and 480 nm. This intermediate transient is difficult to assign definitively. One possibility is that this species represents the electron transfer product [(ND$^-$-tpy)Pt(III)Cl]$^+$. The intramolecular photoinduced electron transfer is anticipated to be favorable since the excited state energy is approximately 2.1 eV (based on the observed weak luminescence), the Pt(III/II) potential for the closely related [Pt(tpy)Cl]$^+$ has been estimated to be +1.1 V vs. SCE [33], the ND(0/−1) potential is −0.65 V vs. SCE and the overall photoredox reaction would be exergonic by 0.35 V. The energy of the charge separated state should be approximately 1.7 V. The final spectrum of Fig. 4B exhibits transient absorption at 360 and 470 nm and bleaching between 370 and 450 nm. The absorption at 470 nm and the bleaching minimum at 380 correspond closely to absorption changes observed upon one electron reduction of ND in acetonitrile (disappearance of the absorption at 380 nm and the appearance of a strong absorption at 470 nm). Obtaining spectra of one electron oxidized terpyridyl Pt(II) complexes has proved to be elusive and, as far as we are aware, no definitive reports exist in the literature. Electrochemical oxidation is both kinetically and chemically irreversible. As a result, we are not able to generate a calculated transient spectrum from the spectra of the expected radical ions and the bleached ground state spectrum. Nonetheless the spectrum observed 13 μs after the pulse does resemble the reduced ND of the complex and our postulate is that the final species decaying back to the ground state is a form of [(ND$^-$-tpy)Pt(III)Cl]$^+$ in which the coordination environment of the Pt(III) may be greater than four.

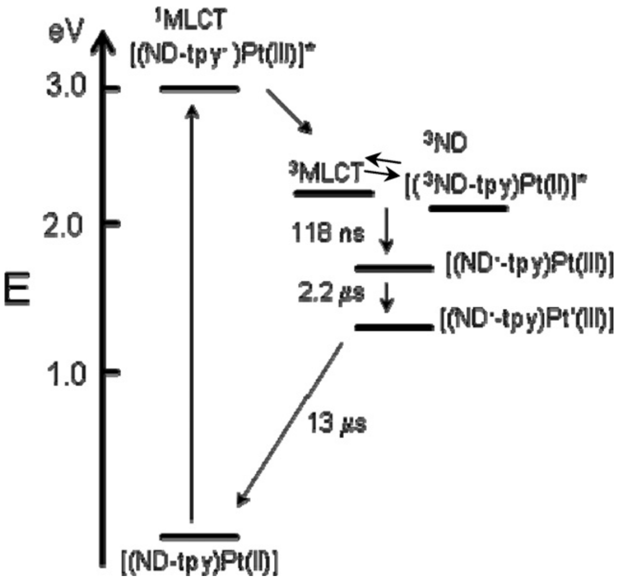


Fig. 6. State diagram for the species involved in the light induced intramolecular electron transfer in [(ND-tpy)PtCl]$^+$.

An energy level diagram summarizing the confirmed and postulated results is shown in Fig. 6. In transient absorption experiments excitation is into the Pt(II) to tpy (π^*) MLCT absorption at 420 nm. Intersystem crossing to the triplet manifold follows within less than a nanosecond and is thus within the laser excitation pulse in our experiments. This is followed by intramolecular electron transfer from the initial equilibrated excited states (^{3}MLCT and ^{3}ND). The fact that the ^{3}MLCT state is observed (transient absorbance between 600 and 700 nm) over the 118 ns lifetime of the initially observed transient species is evidence for equilibration of the ^{3}MLCT and ^{3}ND states; otherwise, the ^{3}MLCT state would not be observed at times beyond the excitation pulse. The initial electron transfer process yields a transient with maxima at 360, 420 and 480 nm which is followed by disappearance of the 420 nm transient in a first order process on the 2–5 μs timescale (Fig. 7). Our postulate is that this spectral change corresponds to evolution of the initially formed Pt(III) species, assumed to absorb at this wavelength, to a species having a different coordination environment (for example, solvation of the initially formed species to yield a five coordinate intermediate). The resulting transient species decays, in a first order back electron transfer process with a lifetime of 13 μs (k_{bet} ~$8 \times 10^4\ \mathrm{s}^{-1}$), to the starting complex. The back electron transfer rate constant is remarkably slow for this system and stands in contrast to other Pt(II) containing systems exhibiting intramolecular photoinduced electron transfer. For instance, in collaboration with Eisenberg's group, we have observed very rapid back electron transfer in chromophore–acceptor complexes in which the chromophore is a terpyridyl Pt(II) acetylide and the acceptor is either a nitrophenyl moiety (k_{bet} ~$5 \times 10^7\ \mathrm{s}^{-1}$) [34] or

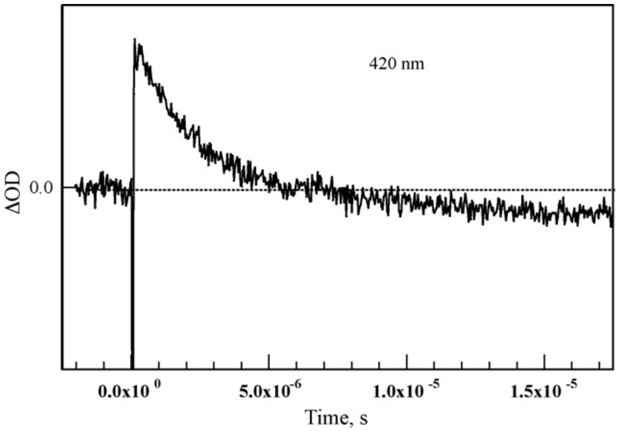


Fig. 7. Transient absorbance of [(ND-tpy)PtCl]$^+$ at 420 nm following 425 nm excitation.

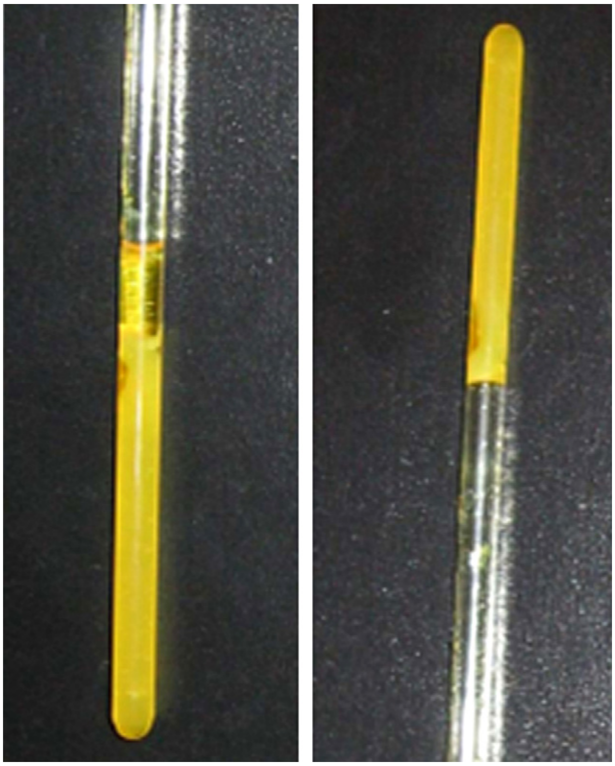


Fig. 8. Photograph of NMR tube containing [(ND-tpy)PtCl]$^+$ in DMSO following cooling after heating to 90 °C. The right hand image is the inverted tube showing the gel.

a viologen (k_{bet} ~$10^8\ \mathrm{s}^{-1}$; Jarosz, P. et al., *Energy and Environmental Science*, in press) covalently linked through the terpyridyl ligand. The nitophenyl is linked to the terpyridyl via an ethene bridge and is therefore more strongly coupled to the Pt complex than the ND acceptor examined here. The viologen, however, has a methylene bridge, essentially identical to that of [(ND-tpy)PtCl]$^+$. The rationale for the difference in back reaction rate constants may be related to (a) thermodynamic factors or (b) large differences in the reorganizational energy of back electron transfer. The one electron reduction potential of the ND is 200 mV more negative than that of the viologen, but the overall thermodynamic difference for the back electron transfer reactions cannot be assessed because the one electron oxidation potentials cannot be readily measured for either of the Pt complexes because of their electrochemical irreversibility. If the intermediate transient species observed for [(ND-tpy)PtCl]$^+$ does evolve to a solvento species in the 2.2 μs process (Fig. 7), it is likely that the back electron transfer reaction could have a large reorganizational barrier and that k_{bet} would be much slower for the complex with the ND acceptor because of differences in the reactivity of the chloro and acetylide complexes toward coordination of additional ligands following oxidation of the metal center. We are working hard to obtain definitive one electron oxidation potentials and spectra of the one electron oxidized species for terpyridyl Pt(II) complexes; without this information, a detailed description of the intermediate species involved is not possible.

3.4. Gel formation and characterization

Following acquisition of variable temperature ^{1}H NMR spectra, it was found that the solution in the cooled NMR sample tube formed a gel. Fig. 8 shows the yellow, opaque gel that was obtained. Gel formation only occurs for solutions having concentrations greater than 2 mM. In addition, gels are not observed without temperature cycling to 90 °C, but the incubation time at this temperature can be as short as 5–10 min. Also, gels do not form in any other solvent that is capable of dissolving the complex.

In an attempt to characterize the gels, both scanning electron micrograph (SEM) and transmission electron micrograph (TEM) were obtained for gels dried in a vacuum oven. Thus far we have been unable to obtain SEM of frozen gels. Fig. 9 shows typical TEM data illustrating the presence of strands of 200–350 nm in width and several microns in length. SEM images were similar, although thicker gel strands were observed; representative SEM images are provided with supplementary information. EDX analysis of gel strands in SEM clearly showed the presence of Pt and Cl, consistent with the presence of the complex in the gels.

A further measure of the degree of organization of the Pt(II) centers in the dried gels was obtained by X-ray powder diffraction. The dried gels reproducibly exhibited a remarkably simple powder diffraction pattern; an example is shown in Fig. 10. The three peaks can be evaluated as first, second and third order scattering, presumably from layers of Pt atoms with a spacing of 1.48 nm. This spacing of Pt atoms can be represented in a relatively small number of ways; the image shown in Fig. 11, with an approximate 1.5 nm spacing between columns of Pt centers, illustrates one structure that results from alternate stacking of terpyridyl Pt centers and naphthalene diimide moieties. The structure can be extended through interleaving of either the terpyridyl Pt(II) units, or the naphthalene diimide substituents; this provides the possibility for growth into three dimensional networks with extended structures. The packing also serves to block metal–metal interactions in stacking of Pt centers since each terpyridyl Pt center is alternated with an alkyl chain from the neighboring [(ND-tpy)PtCl]$^+$ molecules. While such a representation is speculative, it does illustrate one possibility for stacking that could result in macroscopic structures such as those shown in the electron micrographs.

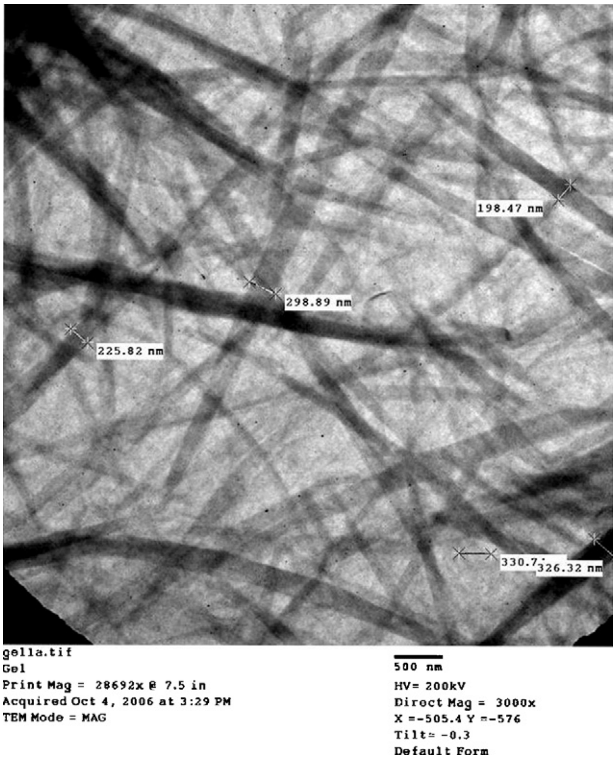


Fig. 9. TEM image of dried gel of [(ND-tpy)PtCl](ClO_4) in DMSO showing range of thicknesses of gel strands.

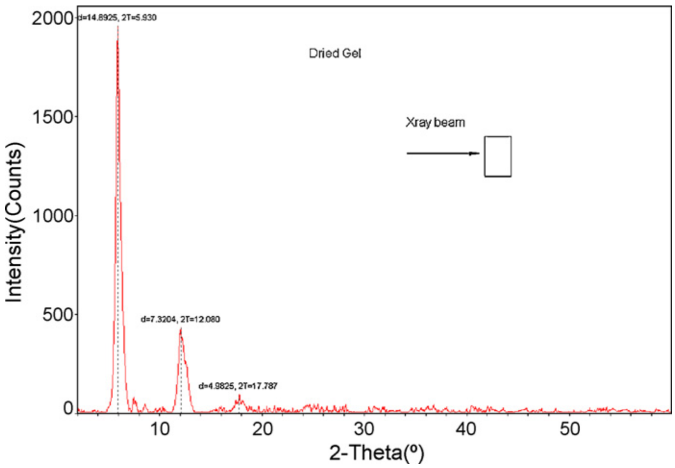


Fig. 10. Powder X-ray diffraction of dried gel of [(ND-tpy)PtCl](ClO$_4$).

3.5. Photophysical behavior of the gels

Direct photophysical examination of the gels was not possible because of the turbidity (see Fig. 8). Nonetheless, it was found that the gels could be suspended in DMSO solution and the suspensions could be investigated by nanosecond laser flash photolysis. The transient spectrum obtained resembles that of the ND anion radical. There is a 10 μs rise time for the transient signal at all wavelengths. Various explanations for this are possible; it may be that the gel serves as a near solid matrix that extends the excited state lifetimes of the chromophores and slows the intramolecular electron transfer rate. The resulting transient species formed decay on a time scale orders of magnitude slower than the recombination of the non-aggregated [(ND$^-$-tpy)Pt(III)Cl]$^+$ radical ion pair in acetonitrile. The Fig. 12 inset shows that the decay does not follow first order kinetics, the half life for the decay is greater than 1 ms and a portion of the radical ions has a very long lifetime (tens to hundreds of milliseconds). An explanation for the much slower charge recombination kinetics relates to the nature of stacking of the electron donating Pt(II) complex centers and the electron accepting ND centers. Following intramolecular photoinduced electron transfer, charge migration in the aggregated assembly may occur by self-exchange electron hopping between stacked ND units or between stacked Pt centers. The charge migration serves to uncouple the electron–hole pairs and result in long lived charge separated species that would recombine slowly as the electrons and holes encountered one another. Such enhanced charge separation has been observed in other self-organizing systems that provide the opportunity for electron and/or hole migration [35–37].

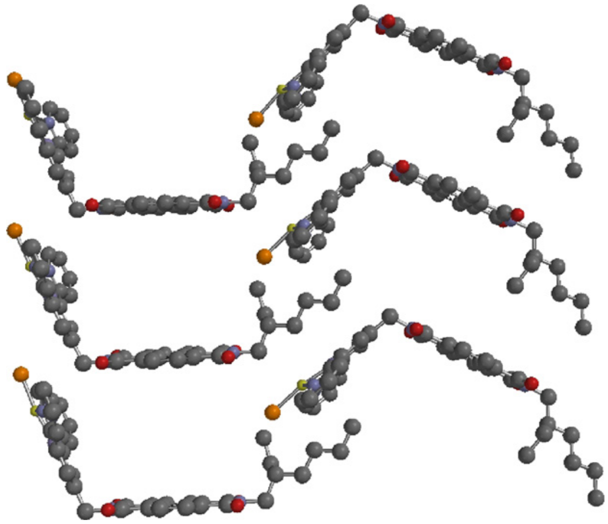


Fig. 11. Representation of potential stacking of naphthalene diimide and terpyridyl Pt(II) units of gels, providing a 1.5 nm separation of columns of Pt atoms.

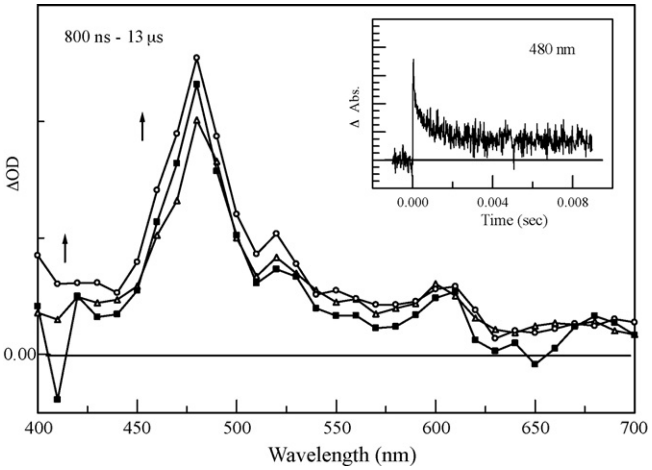


Fig. 12. Transient absorption spectra of suspended gels of [(ND-tpy)PtCl]$^+$ in acetonitrile solution between 800 ns and 13 μs. Inset: decay of transient signal at 480 nm.

4. Summary and conclusions

This work presents an overview of light induced electron transfer in a covalently linked terpyridyl Pt(II)/naphthalene diimide (ND) donor acceptor complex. Photolysis of the complex in the absence of aggregation in acetonitrile solution results electron transfer from the Pt(II) complex to the ND unit. This is followed by a significant structural change in the oxidized Pt complex/reduced ND that leads to formation of a charge separated species that decays by back electron transfer with a rate constant of 8×10^4 s^{-1}. The complex forms gels when concentrated DMSO solutions are heated and allowed to cool slowly. The gels have long tubular structures and the dried gels exhibit long range order of the Pt centers, as evidenced by X-ray powder diffraction. Photolysis of the gels suspended in solution leads to formation of long lived radical ions, formed presumably from self-exchange electron hopping between stacked donor and acceptor moieties in the gels.

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Seeking new insights

Emanating from the sun

H. Inoue thrives

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.03.013.

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