



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

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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 ($[(\text{ND-tpy})\text{PtCl}]$). 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 $8 \times 10^4 \text{ s}^{-1}$, 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.

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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 sys-

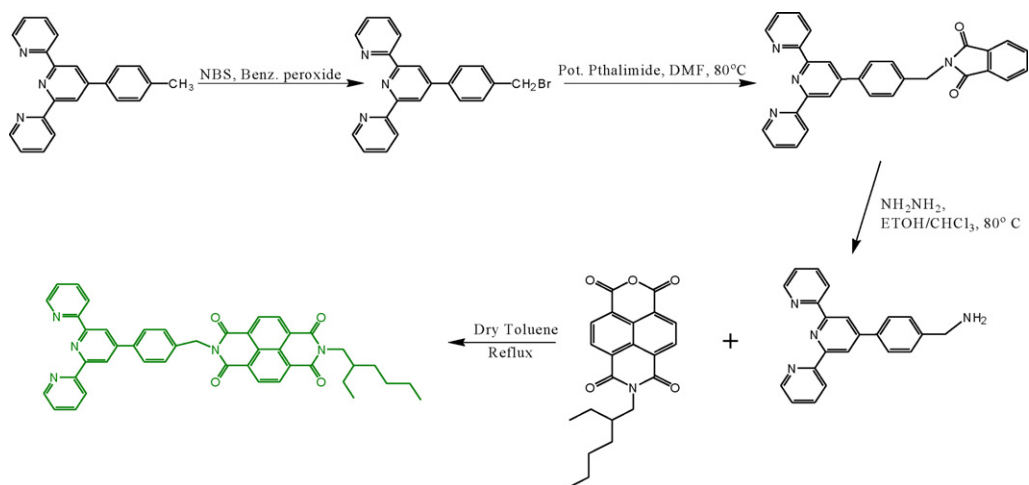
tems to semiconductor electrodes that serve as traps for electrons generated in charge separated states [17].

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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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 $Pt_2 (d\sigma^*)$ to $Pt_2 (p\sigma)$ associated with a transiently formed metal–metal bond [26]. This $d\sigma^*-p\sigma$ 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.

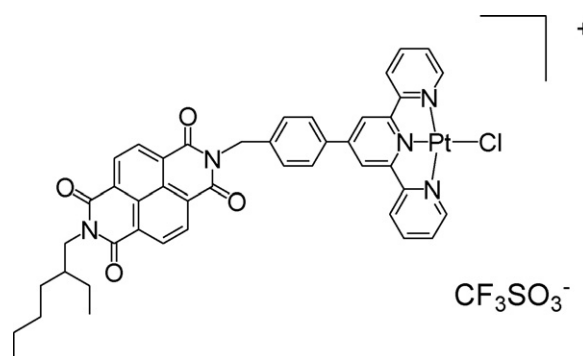
In this work we would like to report the formation of long lived charge separated species following photolysis of gels formed from solutions of a terpyridyl Pt(II) chromophore (electron donor) complex covalently linked to a naphthalene diimide acceptor complex ($[ClPt(tpy-ND)]^+$, below). The results 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.

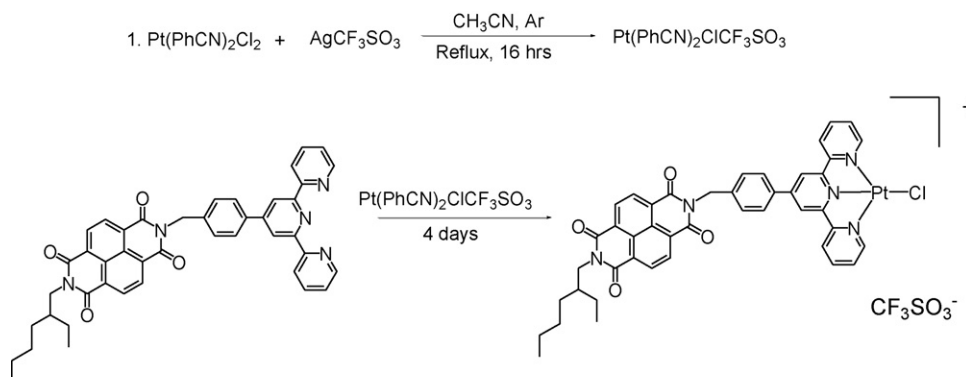
The ligand tpy-ND, was prepared by an adaptation of the procedure of Hammarstrom as shown in Scheme 1 below [27].

Fig. 1. $[ClPt(tpy-ND)]^+$.

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.

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