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An Inorganic Application of Transient Direct Current Photoconductivity: Corroboration of a Charge-Transfer Assignment for the Luminescing States of Pt(dpphen)(ecda)[1]

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Introduction

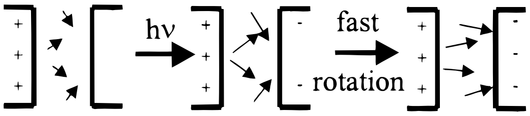
Transient direct current photoconductivity (TDCP) is an experimental technique capable of providing information about the sign and magnitude of differences in dipole moment, μ, for the ground state versus an excited state of an uncharged molecular chromophore in solution.[2] Briefly, the technique utilizes a static, external electric field to achieve partial orientation of dipolar molecules, as shown in Scheme 1. If photoexcitation leads to a change in dipole moment, the molecules will become either more completely (increase in μ) or less completely (decrease in μ) oriented by the field. In either case, the change, together with the accompanying rotational motion (see Scheme 1), is equivalent to a transient flow of positive charge toward a negative electrode and vice versa. The charge flow will persist until the rotational reorientation is finished, and then it will reverse when the molecule returns to its ground electronic state. The reorientation and associated buildup of charge can be tracked by monitoring the transient photovoltage generated across the TDCP cell. Braun and Smirnov, in particular, have shown how the TDCP methodology can be utilized to (a) evaluate the degree of photoinduced charge transfer, (b) measure net electron-transfer distances, and/or (c) monitor excited-state rotational correlation times for various light-absorbing organic compounds.[2] To the best of our knowledge, however, the technique has yet to be applied to inorganic systems. An illustrative application to a representative diimine, dithiolate complex of Pt(II) is the focus of this Note.

Experimental Section

Pt(dpphen)(ecda) was synthesized as described by Zuleta et al.[3] Solutions of Pt(dpphen)(ecda) in 1:1 toluene/chloroform were filtered through a 0.22 μm filter prior to use.

The cell is identical to cell II in ref 4. The solutions of Pt(dpphen)(ecda) were excited with 532 nm light from a Quantel YG-270 Nd:YAG laser. The laser has a pulse width of about 7 ns as monitored by an Electro-Optics Technology silicon PIN detector ET-2000. The pulse power hitting the sample is 120 μJ/shot. A 1000 V field was applied in the cell. The distance between the electrodes was 0.46 mm. The path length of the cell is 8.5 mm. No change in the absorption spectrum was observed after TDCP measurements.

Scheme 1



Luminescence lifetime measurements were performed using a PRA LN102 dye laser, pumped by a PRA LN1000 nitrogen laser. The exciting wavelength was 400 nm. The luminescence was monitored at 600 nm.

Experimental data for the Stark effect measurements are given in the Supporting Information.

Results and Discussion

The title compound, **1**, is one of several related Pt(II) complexes displaying an intense visible-region charge transfer (CT) absorption and a long-lived, emissive photoexcited state at ambient temperature in solution.[3,5] The CT transition has been assigned as an allowed singlet mixed metal/ligand-to-ligand transition.[5] We found via electronic Stark effect spectroscopy at 77 K that the visible-region absorption induces an absolute change in μ of ca. 7 D, consistent with a charge-transfer assignment (see Supporting Information). The complex was then examined via TDCP at 295 K in a 1:1 toluene/$CHCl_3$ solution. In contrast to Stark-effect spectroscopy, which probes the electronic structural changes accompanying initial light-induced excited-state formation,[6,7] TDCP generally reports on the changes associated with the lowest accessible excited state, since it probes excited-state properties in roughly the 1−10 ns time regime. Like other Pt(diimine)(dithiolate) compounds, **1** undergoes rapid intersystem crossing from the singlet state to a lower lying, evidently triplet, emissive state or states, **1***.[3,5] Evidence for intersystem crossing comes both from the enormous red shift in the luminescence spectrum relative to the absorption spectrum and from the comparatively long lifetime of the emissive state (68 ns).

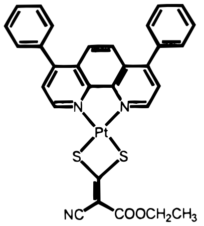


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Figure 1 shows the TDCP response engendered by formation of the emissive excited state. The signal is expected to look roughly like d[**1***]/d*t*.[2] Since the luminescence lifetime is relatively long compared to the laser pulse, the signal should resemble the laser excitation pulse intensity vs time profile, plus any correction for excited-state relaxation (radiative or nonradiative decay, net photochemistry, etc.). As shown by the simulation in Figure 1, the experimental curve indeed is fit well by the independently determined derivative of the integral of

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(1) dpphen = 4,7-diphenyl-1,10-phenathroline; ecda = 1-(ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolate.

(2) Smirnov, S. N.; Braun, C. L. *Rev. Sci. Instrum.* **1998**, *69*, 2875−2887 and references therein.

(3) Zuleta, J. A.; Burberry, M. S.; Eisenberg, R. *Coord. Chem. Rev.* **1990**, *97*, 47−64.

(4) Smirnov, S. N.; Braun, C. L. *J. Phys. Chem.* **1992**, *96*, 9587−9591.

(5) Zuleta, J. A.; Bevilacqua, J. M.; Rehm, J. M.; Eisenberg, R. *Inorg. Chem.* **1992**, *31*, 1332−1337.

(6) For a general review, see: Bublitz, G. U.; Boxer, S. G. *Annu. Rev. Phys. Chem.* **1997**, *48*, 213−242.

(7) For a review of applications to inorganic systems, see: Vance, F. W.; Williams, R. D.; Hupp, J. T. *Int. Rev. Phys. Chem.* **1998**, *17*, 307−329.

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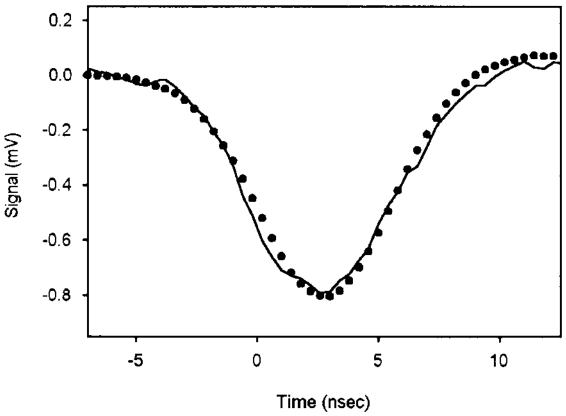

Figure 1. TDCP response from **1** (0.5 mM solution). A least-squares fit (dots) gives -120 ± 5 D^2 for $\mu_{exc}{}^2 - \mu_{gr}{}^2$.

the ca. 7 ns Nd:YAG laser pulse. Similar results were obtained in pure toluene as solvent. The observation of a finite TDCP signal is significant: it shows that a net charge transfer, with respect to the ground-state charge distribution, must exist in the emissive excited state. Two interpretations concerning the nature of the emissive state of **1** can be found in the extant literature. On the basis of low-temperature luminescence studies in a solvent glass in a magnetic field, Crosby and Kendrick[8] concluded that **1** exists as a weakly associated dimer and that **1*** emits from a triplet dσ*pσ excited state encompassing two platinum centers. In essence, the excited state is a Pt−Pt-bonded state featuring a bond order of 0.5. Relaxation to the ground state changes the bond order to zero, not unlike the photophysical behavior of the well-known $Pt_2(P_2O_5)_4{}^{4-}$ complex.[9] Zuleta and co-workers,[5] on the other hand, concluded that, at least at room temperature, emission in liquid environments comes from three triplet states in thermal equilibrium: a diimine-centered $\pi-\pi^*$ state and two mixed metal/dithiolate-to-diimine CT states.[10] Since only the charge-transfer states (or admixtures with these states) will yield a change in μ upon relaxation to the ground state and, therefore, only these states will yield a finite TDCP signal, the CT states must be responsible for the observed solution-phase emission.[11]

A more quantitative evaluation is possible based on measurements of the TDCP signal amplitude. The signal should scale as the dipole difference quantity, $\mu_{exc}{}^2 - \mu_{gr}{}^2$, where exc and gr denote excited and ground electronic states. As implied above, the signal also should scale with the number of photoexcited molecules generated or the number of photons absorbed.[2] For the closely related complex Pt(dpphen)(tbcda), Cummings et al.[12] report that μ_{gr} is 9 ± 1 D, a not unreasonable finding given the formal dipositive charge on the platinum atom and dinegative charge on the sulfur-containing ligand. In order to fit the data in Figure 1, we require a ground-state dipole moment of at least 10.95 D; this then yields an excited-state dipole moment of zero.

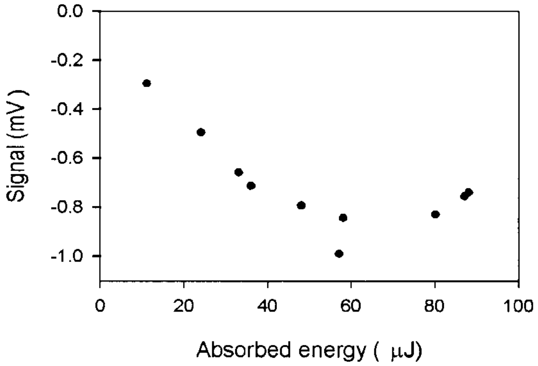

Figure 2. Plot of TDCP signal vs amount of optical absorbed energy by solutions of **1**.

If μ_{gr} is as large as 11.0 D, then the experimental fit yields an excited-state dipole moment of 1 ± 2 D and, of course, a $\Delta\mu$(exc−gr) of −10 D or −2.1 e Å (or if μ_{gr} is, say, 11.5 D, $\Delta\mu$ is −8 D).[13] These estimates of the change in dipole moment upon formation of the *triplet* excited state are smaller than what one might naively expect for transfer of a unit electronic charge from the metal ion or the sulfur atoms to the center of the diimine ligand (ca. 2.8 or 4.4 Å, respectively; 1 e Å $\approx$ 4.8 D). They are consistent, however, with the $|\Delta\mu|$ value inferred above from Stark experiments for formation of the corresponding *singlet* CT excited state. In any case, there is now considerable evidence from other studies that self-polarization, partial electronic delocalization, and other effects can conspire to make effective one-electron-transfer distances much smaller than simple “geometric” charge-transfer distances.[14,15]

As shown in Figure 2, at low concentrations the TDCP signal increases linearly with the number of absorbed photons, as expected from theory.[2] At the highest accessible concentrations, however, the signal plateaus and ultimately decreases. Because the intensity depends on the number of excited-state molecules present during the roughly 10 ns interval comprising the experiment, any concentration-dependent phenomenon that results in a substantial decrease in the lifetime of the excited state could lead to a signal attenuation effect. At the highest chromophore concentration examined (1.5 mM), we find that the lifetime of **1*** is indeed slightly shortened ($\tau = 56$ ns), but by too little to account for the observed loss of TDCP signal intensity.[16,17] A second interpretation is that dimers form in the ground state and that the emissive state is now the ^{3}dσ*pσ state. The fraction emitting from this state would experience zero change in dipole moment and would contribute zero intensity to the TDCP signal. The roll off in signal intensity with increasing chromophore concentration would be attributed

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(8) Crosby, G. A.; Kendrick, K. R. *Coord. Chem. Rev.* **1998**, *171*, 407−417.

(9) Roundhill, D. M.; Gray, H. B.; Che, C. M. *Acc. Chem. Res.* **1989**, *22*, 55−61 and references therein.

(10) It is known that the closely related complex Pt(dpphen)(tbcda) (tbcda = 1-(*tert*-butoxycarbonyl)-1-cyanoethylene-2,2-dithiolate) emits from an exciplex state at low temperatures, whereas monomer emission is observed at room temperature (See: Paw, W.; Cummings, S. D.; Mansour, M. A.; Connick, W. B.; Geiger, D. K.; Eisenberg, R. *Coord. Chem. Rev.* **1998**, *171*, 125−150).

(11) The solution-phase TDCP findings do not rule out the alternative assignment in solid-state environments.

(12) Cummings, S. D.; Cheng, L.-T.; Eisenberg, R. *Chem. Mater.* **1997**, *9*, 440−450.

(13) Note that $(10.95^2 - 0^2) = (11^2 - 1^2) = (11.5^2 - 3.5^2) = 120$.

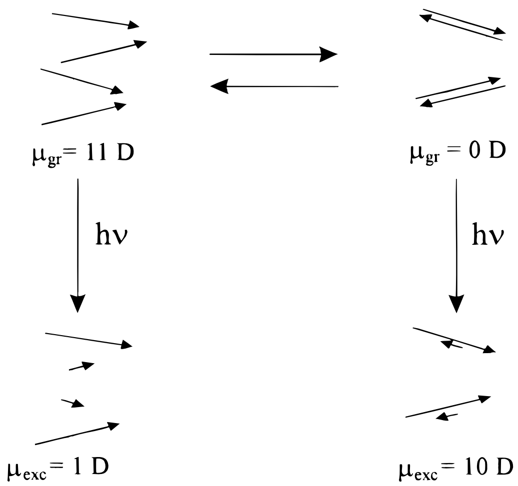
(14) See, for example: Shin, Y. K.; Brunschwig, B. S.; Creutz, C.; Sutin, N. *J. Phys. Chem.* **1996**, *100*, 8157−8169.

(15) See also: Vance, F. W.; Karki, L.; Reigle, J. K.; Hupp, J. T.; Ratner, M. A. *J. Phys. Chem. A* **1998**, *102*, 8320−8324.

(16) The shorter lifetime can be interpreted as being due to an excited-state self-quenching reaction (see: Connick, W. B.; Geiger, D.; Eisenberg, R. *Inorg. Chem.* **1999**, *38*, 3264−3265). Assuming a diffusion-limited quenching rate constant of 1×10^{10} M^{-1} s^{-1} and a concentration of 1.5 mM, self-quenching is anticipated to give an additional decrease of excited-state population of only 15% after 10 ns. However, the observed TDCP signal is at least 60% lower than expected.

(17) Excessive absorption of laser light before it reaches the detection region of the cell would also cause a roll off in the signal. However, the solution with the highest concentration has an absorbance of 0.6, well below a desired optical density of 1 (see ref 2). Therefore the roll off and decrease of the TDCP signal are not attributable to an absorption “artifact”.

Scheme 2



simply to shifts in the monomer ⇄ dimer equilibrium. This explanation by itself, however, is incapable of accounting for the *decrease* in TDCP signal at yet higher concentration.

A third explanation, which could, in principle, account for both the roll off and the decrease, is again a ground-state dimer formation, but with retention of the charge-transfer character of the emissive state. As illustrated in Scheme 2, a dimer adopting an antiparallel configuration would possess a dipole moment of zero in the ground state, but ca. +10 D in the emissive excited state. The value of $\mu_{exc} - \mu_{gr}$ for the dimeric species, therefore, would be equal but opposite in sign to the value for the monomer. While admittedly speculative, we favor this interpretation.[18] If changes in τ are neglected, the data in Figure 2 yield a monomer ⇄ dimer equilibrium constant of 1.5 mM^{-1}; if changes in τ are included (assuming Stern−Volmer behavior), the data yield an equilibrium constant of 1.4 mM^{-1}.[19]

To summarize, the TDCP technique has been successfully employed to corroborate the charge-transfer assignment for the emissive excited state of **1** at ambient temperature in solution. We are currently seeking to extend the methodology to related compounds with the aim of understanding relationships between effective one-electron-transfer distances and molecular structural properties.

Acknowledgment. We thank Dr. Youngjin Kim, Dr. Keith Stevenson (Northwestern University), and, especially, Prof. Sergei Smirnov (New Mexico State University) for many helpful suggestions. Financial support by the Swiss National Science Foundation (postdoctoral fellowship for F.W.M.V) and the U.S. Department of Energy, Office of Science (Grant DE-FG02-87ER13808), is gratefully acknowledged.

Supporting Information Available: Stark data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] A crystal structure showing the postulated antiparallel stacking for a Pt (diimine)(dithiolate) complex has been reported: Zuo J.-L.; Xiong, R.-G.; You, X.-Z.; Huang, X.-Y. *Inorg. Chim. Acta* **1995**, *237*, 177−180.

[19] Connick et al.[15] report that aggregation of several analogues of **1** is undetected via absorption or emission spectroscopy at concentrations up to 5 × 10^{-4} M in CH_3CN or CH_2Cl_2 as solvent. These findings are not inconsistent with the inference here of modest association (ca. 45%) of **1** at the same concentration; the lower polarity of the solvent used in the TDCP studies (toluene/$CHCl_3$) should favor greater association of **1**.