Transient DC Photocurrent Investigation of Charge Redistribution within Re(CO)₃Cl(2,2′-bipyridine): An Unexpected Decrease in Molecular Dipole Moment upon Emissive Excited-State Formation

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Introduction

The photophysics, photochemistry, and photoredox chemistry of an enormous number of diimine complexes with $4d^6$ and $5d^6$ metal ions have been investigated.[1] The attraction of the metal(d^6)/diimine(π^*) combination stems from the possibility, in a best case scenario, of simultaneously achieving (a) significant visible-region light absorption, (b) long excited-state lifetimes, (c) detectable visible-region luminescence, and (d) excellent photochemical stability. The available evidence indicates that the desired scenario can fairly reliably be achieved via strongly allowed singlet metal-to-ligand (diimine) charge transfer (MLCT) excitation, followed by intersystem crossing to a nominally triplet MLCT state, or states, provided that no further conversion to labile and/or rapidly deactivating excited states (e.g., ligand field states) can be avoided. Much of the interest in these compounds derives from potential applications in energy conversion (light-to-electricity or light-to-fuel),[2] luminescence-based chemical sensing,[3,4] light-initiated chemical catalysis,[5] or even light-initiated information storage.[6,7]

One of the first systems found that satisfied the series of photophysical requirements delineated above was *fac-*Re(CO)₃Cl(bpy) (bpy = 2,2′-bipyridine).[8] Notably, this success has inspired a very large number of extensions, variations, and amplifications of the chemistry,[9−12] as well as several sophisticated fundamental studies (e.g., resonance Raman,[13] excited-state Raman,[14] and transient infrared spectroscopy studies;[15] time-resolved luminescence and variable-temperature luminescence studies;[16] low-temperature emission/Franck−Condon fitting studies;[9] solvatochromic emission studies;[7,17,18] various emission-based micro-environmental studies;[19,20] etc.). Nevertheless, we reasoned that additional photophysical studies, focusing specifically on the *charge-transfer* characteristics of the emissive excited state of *fac-*Re(CO)₃Cl(bpy) (**1**) could prove informative. We report here on a study of **1** via transient DC photocurrent (TDCP).

TDCP is a technique developed by Braun and Smirnov to evaluate the change in the dipole moment of a neutral chromophore in solution upon photoexcited-state formation.[21] To the extent that a ground-state dipole moment, μ_{gr}, exists, the chromophore will be partially oriented by an externally applied, DC electric field. Upon the formation of a photoexcited state, μ typically changes, and the chromophoric molecule becomes either more strongly (increase of μ) or less strongly (decrease of μ) oriented in the field. The change in μ and the resulting reorientation cause a transient flow of charge at the electrodes. The flow, which can be monitored as a photovoltage, persists until the rotational reorientation is finished, and then it reverses when the chromophore returns to the ground state. Thus, the TDCP measurement provides information about the sign and magnitude of ground-state/excited-state dipole-moment changes ($\Delta\mu(\text{ex} - \text{gr})$). As noted below, this information, in turn, can be used to estimate one-electron transfer distances (internal charge distances) in a fashion that is highly complementary to alternative techniques such as electronic Stark-effect spectroscopy.

Experimental Section

*fac-*Re(CO)₃Cl(bpy) was synthesized via a method previously described in the literature.[9] The TDCP setup is similar to one described by Smirnov and Braun.[22] In a typical experiment, 1000 V was applied across the chromophore solution-filled gap of 0.5 mm separating the stainless steel electrodes comprising two of the four walls of the TDCP cell. Solutions of **1** in chloroform/toluene (1:1) were filtered through a 0.22 μm Teflon filter prior to use. The solution was excited with a 355 nm pulse of a Quantel YG-270 Nd:YAG laser. The pulse width is ∼6.5 ns.

ZINDO-1 calculations were performed on *fac-*Mn(CO)₃Cl(bpy) using the software package HyperChem.[23] The atomic coordinates for *fac-*Mn(CO)₃Cl(bpy) were taken from the crystal structure determination by Horn et al.[24]

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 (1) For a review see: Juris, A.; Balzani, V.; Barigeletti, F.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85−277, and references therein.
 (2) For example: O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737−740.
 (3) For example: MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 6108−6110.
 (4) For a review of recent applications, see: Keefe, M. H.; Benkstein, K. D.; Hupp, J. T. *Coord. Chem. Rev.*, in press.
 (5) For example: Bruce, M. R. M.; Megehee, E.; Sullivan, B. P.; Thorp, H. H.; O'Toole, T. R.; Downard, A.; Pugh, J. R.; Meyer, T. J. *Inorg. Chem.* **1992**, *31*, 4864−4873.
 (6) For example: O'Toole, T. R.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 5699−5706.
 (7) See also: Zhang, H.-T.; Subramanian, P.; Fussa-Rydel, O.; Bebel, J. C.; Hupp, J. T. *Solar Energy and Solar Cells* **1992**, *25*, 315−325.
 (8) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952−957.
 (9) Representative work: Worl, L. A.; Duesing, R.; Della Ciana, L.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849−858.
(10) Shaw, J. R.; Schmehl, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 389−394.
(11) Stoeffler, H. D.; Thornton, N. B.; Temkin, S. L.; Schanze, K. S. *J. Am. Chem. Soc.* **1995**, *117*, 7119−7128.
(12) Slone, R. V.; Benkstein, K. D.; Bélanger, S.; Hupp, J. T.; Guzei, I. A.; Rheingold, A. L. *Coord. Chem. Rev.* **1998**, *171*, 221−243.
(13) For example: Rossenaar, B. D.; Stufkens, D. J.; Vlcek, A. *Inorg. Chem.* **1996**, *35*, 2902−2909.

(14) For example: Waterland, M. R.; Simpson, T. J.; Gordon, K. C.; Burrell, A. K. *J. Chem. Soc., Dalton Trans.* **1998**, 185−192.
(15) Schoonover, T. R.; Strouse, G. F. *Chem. Rev.* **1998**, *98*, 1335−1355 and references therein.
(16) Rossenaar, B. D.; Lindsay, E.; Stufkens, D. J.; Vlcek, A. *Inorg. Chim. Acta* **1996**, *250*, 5−14.
(17) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998−1003.
(18) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888−2897.
(19) McKiernan, J.; Pouxviel, J. C.; Dunn, B.; Zink, J. I. *J. Phys. Chem.* **1989**, *93*, 2129−2133.
(20) Kotch, T. G.; Lees, A. J.; Fuerniss, S. J.; Papathomas, K. I.; Snyder, R. W. *Inorg. Chem.* **1993**, *32*, 2570−2575
(21) Smirnov, S. N.; Braun, C. L. *Rev. Sci. Instrum.* **1998**, *69*, 2875−2887 and references therein.
(22) Smirnov, S. N.; Braun, C. L. *J. Phys. Chem.* **1992**, *96*, 9587−9591.
(23) HyperChem release 4 by Hypercube, Inc., 419 Phillip St., Waterloo, Ontario, Canada N2L 3X2.
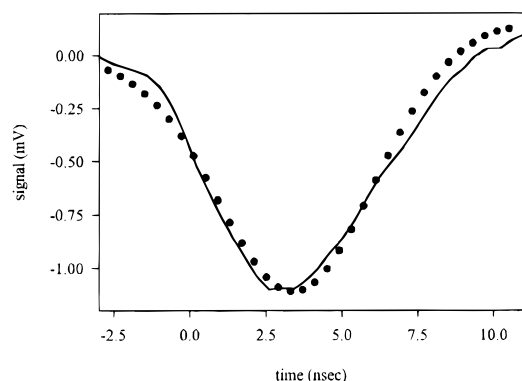(24) Horn, E.; Snow, M. R.; Tiekink, E. R. T. *Acta Crystallogr.* **1987**, *C43*, 792−794.

Figure 1. TDCP response from a chloroform/toluene solution of Re(CO)$_3$Cl(bpy) solution. A least-squares fit (dots) gives -90 ± 5 D^2 for $\mu_{ex}^2 - \mu_{gr}^2$.
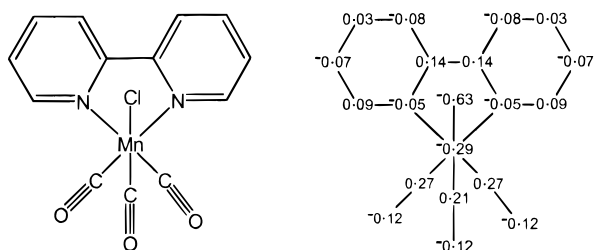

Figure 2. Charge distribution in the ground state for Mn(CO)$_3$Cl(bpy).

Results and Discussion

Figure 1 shows, as a solid line, the TDCP response of **1**. For an excited state that is long-lived in comparison to the width of the laser pulse (the case here), the signal is expected to evolve as approximately the first derivative of the integral of the pulse.[21] As illustrated by the dotted line in Figure 1, the experiment does agree reasonably well with the simulated signal shape, based on the independently characterized laser-pulse intensity versus time profile and the excited-state decay time. Notably, the sign of the TDCP signal at short and intermediate times is negative, indicating that the absolute value of the excited-state dipole moment, $|\mu_{ex}|$, is less than $|\mu_{gr}|$. A more quantitative analysis is possible, based on a least-squares fit of the amplitude of the TDCP signal (Figure 1). The amplitude depends on the number of photons absorbed, the magnitude of the external electric field, and the magnitude of the difference quantity, $\mu_{ex}^2 - \mu_{gr}^2$. For **1**, the analysis gives -90 ± 5 D^2 for $\mu_{ex}^2 - \mu_{gr}^2$.

The observation of a decrease in μ^2, upon ^{3}MLCT excited-state formation, was initially puzzling: The decrease implies a corresponding decrease of charge separation within **1**, despite the conversion of the Re^I-bpy^0 fragment (ground state) into a formally Re^{II}-bpy$^-$ fragment ("charge-separated" excited state). The observation further implies the existence of a very substantial ground-state dipole moment, that is, a $|\mu_{gr}|$ value of at least $(90 \pm 5$ D$^2)^{1/2}$ or 9.5 D.

Some insight is provided by semiempirical electronic structure calculations (ZINDO-1) on *fac*-Mn(CO)$_3$Cl(bpy). The manganese compound was substituted for **1** because of the unavailability of semiempirical parameters for rhenium. As shown in Figure 2, calculations for the ground electronic state place significant negative charge on the three oxygen atoms, the manganese atom, and especially the chlorine atom. They place positive charge on the carbon atoms within the CO ligands. Combining the atomic charges, we obtain a ground-state dipole moment of 10.5 D, with the moment approximately aligned with the Mn−Cl bond (26° deviation), that is, largely orthogonal to
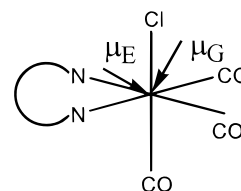

Figure 3. Ground-state and excited-state dipole moment for Mn-(CO)$_3$Cl(bpy) as calculated by a ZINDO-1 calculation.

the metal−bipyridine plane. Extending the analysis to **1**, and using the charge distributions in Figure 2 for the Mn(I) complex as a reference point, the much greater propensity of Re(I) to engage in π back bonding would almost certainly lead to a shift of electron density from the metal center to the atoms comprising the carbonyl ligands. If the effect were not fully offset by a transfer of additional electron density from the chloride ligand to the metal center (a distinct possibility, given the slightly higher electronegativity for rhenium in comparison to manganese), the ground-state dipole moment for **1** could be even greater than the 10.5 D value that was calculated for the manganese complex.

Additional calculations (again using ZINDO-1) were carried out for various excited states of *fac*-Mn(CO)$_3$Cl(bpy). The calculations indicate, in contrast to the experimental results for **1**, that the lowest excited state is not a charge-transfer state.[25] Nevertheless, calculations for the first upper state that does exhibit predominantly MLCT character suggests: (a) a dipole moment (μ_{ex}) slightly smaller than μ_{gr} and (b) a net dipole vector directed roughly midway between the metal−bpy plane and the metal−chloride axis (see Figure 3). The first finding, that the molecular dipole moment decreases upon ^{3}MLCT excited-state formation, is qualitatively consistent with the experimental observation for the corresponding rhenium compound, **1**. The second finding implies that metal−bpy charge transfer and metal−chloride charge differences, roughly equally contribute to the excited-state dipole moment, at least in the manganese model compound.

The observation that the excited-state dipole moment for **1** is smaller than the ground-state dipole moment provides a reasonable explanation for the negative solvatochromism often encountered for MLCT absorption by Re(CO)$_3$Cl(diimine) complexes.[9,17,18] The negative solvatochromism has previously been attributed to an unusual strong influence of solvent polarity upon the internal structure, in particular, Re−N bond lengths, of **1** and related compounds.[18] Sullivan, however, has pointed out that for related compounds, a large ground-state dipole moment and noncollinearity for μ_{gr} and μ_{ex} can yield negative solvatochromism as well.[26]

Finally, because the TDCP technique has only rarely been applied to inorganic chromophores,[27] it may be useful to compare the technique with related, but perhaps more familiar, electronic Stark-effect spectroscopy methods.[28,29] Briefly, TDCP can provide information about the sign of the change in dipole

(25) Density functional theory calculations for *fac*-Mn(CO)$_3$Cl(bpy), however, suggest that the lowest transition is largely Mn−Cl to bpy charge transfer in character: Stor, G. J.; Stufkens, D. J.; Vernooijs, P.; Baerends, E. J.; Fraanje, J.; Goublitz, K. *Inorg. Chem.* **1995**, *34*, 1588−1594.
(26) Sullivan, B. P. *J. Phys. Chem.* **1989**, *93*, 24−26.
(27) Vanhelmont, F. W. M.; Johnson, R. C.; Hupp, J. T. *Inorg. Chem.* **2000**, *39*, 1814−1816.
(28) For a recent review of Stark-effect spectroscopy, see: Bublitz, G. U.; Boxer, S. G. *Annu. Rev. Phys. Chem.* **1997**, *48*, 213−242.
(29) For a review of the applications to inorganic systems, see: Vance, F. W.; Williams, R. D.; Hupp, J. T. *Int. Rev. Phys. Chem.* **1998**, *17*, 307−329.

moment accompanying excited-state formation and charge redistribution but not of the magnitude of the change (unless μ_{gr} is known independently). For example, the value of $-90 \pm 5 \text{ D}^2$, for the difference quantity, $\mu_{ex}^2 - \mu_{gr}^2$, would correspond to a $\Delta\mu$ (excited − ground) of -9.5 D, if μ_{gr} is 9.5 D, but it would be only -4.4 D if the correct value for μ_{gr} is $+12.5$ D. Stark spectroscopy, on the other hand, yields no sign information for isotropic samples, but it does provide accurate absolute values for $\Delta\mu(ex-gr)$ without the need to establish μ_{gr} independently. Second, Stark absorption spectroscopy provides $|\Delta\mu|$ data for the particular transition being excited. TDCP, on the other hand, generally reports on the lowest accessible excited state, even if that state is silent in the absorption spectrum. Third, TDCP compares μ_{ex}^2 and μ_{gr}^2 without regard to dipole orientations. Stark-effect spectroscopy, on the other hand, reports on the net difference between μ_{ex} and μ_{gr} as *vector* quantities. If μ_{ex} and μ_{gr} are oriented identically, the distinction is not meaningful. If, instead, the dipoles have differing orientations (as implied, for example, by Figure 3), only the Stark experiment will account for vector cancellations or partial cancellations. The distinction is particularly significant if one is seeking to derive effective one-electron transfer distances from measurements of dipole-moment changes; the adiabatic transfer distance can be directly equated under all conditions with $\Delta\mu(\text{Stark})/e$ (e is the unit electronic charge).[30] The quantity $\Delta\mu(\text{TDCP})/e$, however, can be directly equated with the one-electron transfer distance only when μ_{ex} and μ_{gr} are collinear. Fourth, Stark-effect spectroscopy, but not TDCP, can provide information about the degree of alignment of the change-in-dipole-moment vector ($\Delta\mu(ex-gr)$) with the transition dipole moment vector (essentially, the "light absorption" vector). Often, the two are collinear. The discussion surrounding the TDCP response of **1**, however, suggests that here, the two vectors likely deviate substantially from collinearity.

Derivatives of **1** that display better resolved MLCT absorption bands[9,31] would be interesting targets for combined TDCP and Stark-effect studies. The combined studies would take advantage of the complementary nature of the dipole-change information provided by the two techniques. We hope to report on the outcome of such studies soon.[32]

(30) Cave, R. J.; Newton, M. D. *Chem. Phys. Lett.* **1996**, *249*, 15−19.

(31) ^{1}MLCT and $^1\pi-\pi^*$ transitions in **1** overlap significantly, suggesting that a quantitatively reliable interpretation of absorption-based Stark-effect data would be difficult.

(32) Initial TDCP measurements on derivatives of **1** suggest that adding electron withdrawing substituents to the bpy ligand differentially increases μ_{ex}, thereby making $\Delta\mu$ and the TDCP signal smaller.