Step-Scan FT-IR Time-Resolved Spectroscopy in the Solid State

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The use of KBr pellets as an interference-free matrix for performing time-resolved infrared (TR-IR) measurements on samples in their crystalline state is described and demonstrated. Step-scan Fourier transform infrared time-resolved spectroscopy (S²FT-IR TRS) is used to measure the infrared (IR) absorption difference (ΔA, excited state minus ground state) spectra of the long-lived charge-transfer excited states of polypyridine Ru(II) and Pt(II) complexes pressed into KBr pellets. A comparison of the difference spectra measured for the metal-to-ligand charge-transfer (³MLCT) state of the Ru(II) complex in a KBr pellet vs. acetonitrile (ACN) solution is used to validate the technique. The Pt(II) complex could not be analyzed in solution because of its extremely poor solubility. Thus, these results illustrate one of the significant advantages of performing TR-IR measurements on solid KBr sample pellets.

Index Headings: **KBr pellet; Time-resolved; Step-scan FT-IR; Polypyridine transition metal complexes; Solid state.**

INTRODUCTION

Polypyridine transition metal complexes have been the focus of an intense research effort for the past thirty years.[1-5] Much of the interest in this class of complexes arises from their useful excited-state properties: low-lying metal-to-ligand charge transfer (MLCT) excited states, long solution lifetimes, robust photostability, and wide tunability of photophysical properties through judicious choice of chromophoric and ancillary ligands.[6-10] Many of these compounds are useful as light-sensitizing agents (LSAs) for photovoltaic and photochemical devices[9,11,12] or as electron donors and acceptors for studying electron- and energy-transfer mechanisms.[13-16] Others are of interest for their potential nonlinear optical properties.[17,18] In the ongoing effort to better understand these materials, time-resolved infrared (TR-IR) spectroscopy has proven itself a valuable tool for relating the molecular structure of the complex to its excited-state properties. TR-IR provides detailed insight into the distribution of charge in these excited states and the kinetics of their decay by measuring the differences in ground- and excited-state vibrational frequencies for specific IR chromophores and by recording the temporal evolution of those transient spectral features.

Normally, samples used for these analyses are prepared in deoxygenated solvents such as acetonitrile (ACN) or 1,2-dichloroethane (DCE), which have relatively broad spectral windows in the mid-IR. However, some metal complexes, particularly the class of d^8 diimine dithiolate complexes, are not soluble to any appreciable degree in these solvents.[18] It has been found that the nanosecond regime TR-IR spectra of such complexes can be successfully measured in the solid state by use of step-scan Fourier transform infrared time-resolved spectroscopy (S²FT-IR TRS) and the standard KBr pellet technique. The use of KBr pellets for analyzing solid-state photochemistry was explored in the early 1960s,[19,20] but, surprisingly, there have been no recent applications of this sampling technique to fast TR-IR experiments.

In this report, results obtained on solid samples contained in a salt pellet are validated by comparing the TR-IR absorption difference (ΔA, excited state minus ground state) spectra of the octahedrally coordinated d^6 complex, [Ru(bpy)₂(4-COOEt-4′-CH₃bpy)]²⁺(PF₆⁻)₂ (**1**), measured in KBr matrix, to previously published spectra of this complex dissolved in de-oxygenated ACN (bpy is 2,2′-bipyridine).[21,22] Furthermore, the ΔA spectrum of a poorly soluble square planar d^8 Pt(II) diimine dithiolate complex, Pt(dpphen)(dcbdt) (**2**), prepared in a solid KBr matrix is also presented to highlight the significant advantages of this sample preparation technique for TR-IR spectroscopy when suitable solvents are not available (dpphen is 4,7-diphenyl-1,10-phenanthroline, and dcbdt is *N,N′*-dicyclohexyl-(1,1-dithiolatomethylene)barbituric acid).

EXPERIMENTAL

A crystalline powder of either complex **1** or **2** was ground in an agate mortar with a ~20:1 excess of oven-dried, finely divided KBr (Fischer Scientific). A KBr pellet was then prepared in a standard hydraulic press by using a pressure of 20 000 psi. The pressure was maintained for 5 min to improve the optical quality of the pellet. No attempts were made to exclude oxygen from the matrix during its preparation, but the results from these time-resolved experiments show no evidence of excited-state quenching due to ground-state triplets. The
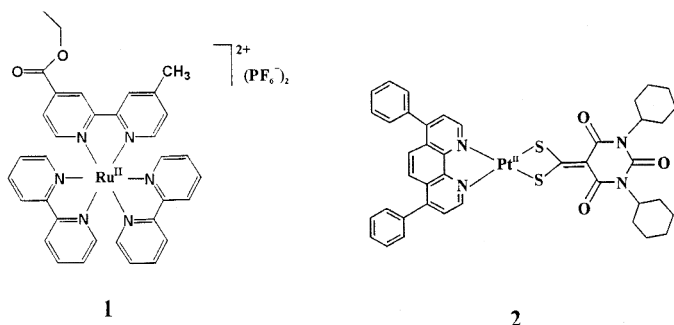
SCHEME I. [Ru(bpy)$_2$ (4-COOEt-4$'$-CH$_3$bpy]$^{2+}$(PF$_6^-$)$_2$ (**1**) and PT(dpphen)(dcbdt) (**2**).

high pressure of the pellet-fusing process generates a solid matrix essentially devoid of trapped gases. The circular pellet produced in this manner was 8 mm in diameter and approximately 0.5 mm thick. When examining the KBr sample under the bright field of a polarizing microscope, we could see small crystallites of the complex. However, under crossed polarizers, no overall birefringence was observed; that is, the pellets are macroscopically isotropic.

The ratio of the complex to KBr was adjusted so that the absorption of the largest intensity vibrational band of interest fell between 0.2 and 0.6 absorbance units in the finished pellet. The optical density of the sample at the pump laser's wavelength (532 nm) was observed to be approximately 0.4 absorbance units for both complexes, thus guaranteeing moderate, uniform excitation throughout the sample. Between successive measurements, samples were stored in a vacuum dessicator. For the samples used in these experiments, no photodegradation or loss of optical quality was observed even after several days of measurements.

The experimental details for measuring the ground-state and nanosecond regime ΔA spectra by using S^2 FT-IR TRS have been reported previously.[23] In the measurements presented here, the excited-state decay of the KBr sample was recorded with 10 ns time resolution, and the ΔA spectrum was created by averaging the spectra from the first 100 ns of that decay. The spectral resolution for the ground state and ΔA spectra for the KBr samples is 6 cm^{-1}.

The excited states of the metal complexes were generated by using the second harmonic of a pulsed Nd:YAG laser (532 nm, 10 ns, 4 mJ/pulse). A long-focal-length lens was used to slightly reduce the laser spot size in order to match the 8 mm diameter of the sample pellet. The source aperture of the Bruker IFS-88 was also set to 8 mm, so that the IR beam probed only those regions of the sample exposed to the laser pulse. The ΔA spectra in KBr are the average of 700 laser shots per interferogram position for **1** and 225 for **2**. These conditions led to data collection times of 7.1 and 4.6 h, respectively. The large discrepancy in data collection times is a result not only of the number of coadditions in each spectrum but also of differences in undersampling allowed by the optical filters used in each experiment.

UV-visible absorption spectra were collected on a Hewlett-Packard 8452 diode array spectrometer. Luminescence decay measurements were collected as described previously.[24]
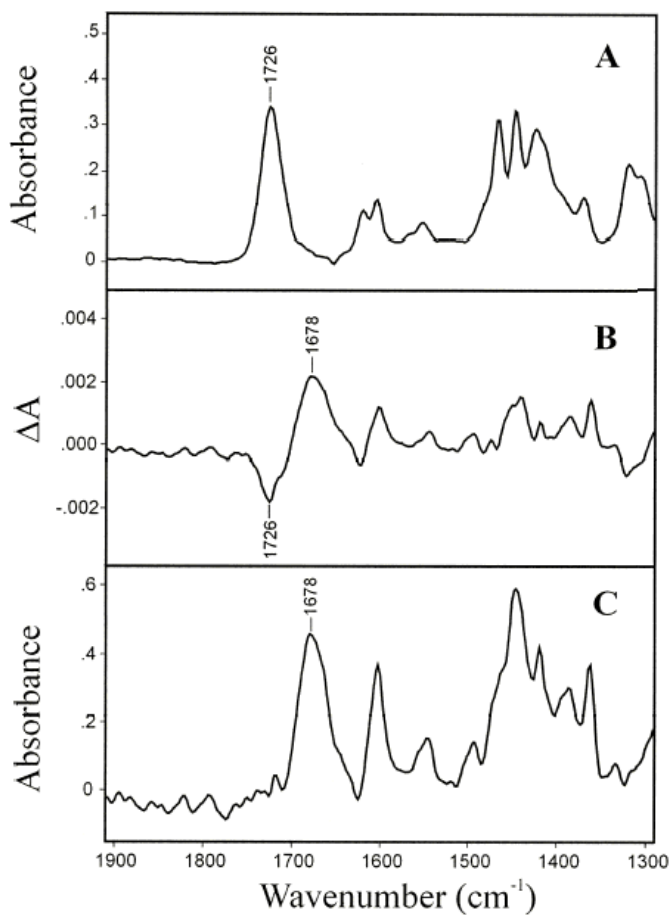

FIG. 1. Ground-state (**A**) and time-resolved difference spectra (**B**) of **1** in a KBr pellet at room temperature. An approximation of the ^{3}MLCT excited-state spectrum is presented in **C** as the sum of the ground-state spectrum and 200× the measured difference spectrum.

RESULTS

Ru(bpy)$_2$(4-COOEt-4$'$-CH$_3$bpy)$^{2+}$. Figure 1 shows the room-temperature ground-state (Panel A) and ΔA spectra (Panel B) of microcrystallites of the PF$_6$ salt of **1** pressed into a KBr pellet. This ΔA spectrum is consistent with previously reported TR-IR spectra of the ^{3}MLCT state of **1** in ACN.[21,22] The ester νC=O mode of the substituted bipyridine ligand downshifts in the excited state from 1726 to 1678 cm^{-1}, a total shift of 48 cm^{-1}. The additional bands below 1650 cm^{-1} in the ground-state and ΔA spectra can be ascribed to bipyridine modes of the substituted and unsubstituted ligands.[25]

A weighted sum of the ground-state and ΔA spectra ($A_{GS} + 200\Delta A$) is presented in Fig. 1C as an approximation of the excited-state spectrum. The ΔA coefficient was chosen as the maximum factor that produced an excited-state spectrum without negative bands. This construction makes it clear that there is a single ester νC=O band in the excited state of **1**. In particular, there is no residual intensity on the high-energy side of the ground-state ester νC=O band that would be indicative of an MLCT state in which the electron was transferred to one of the unsubstituted bpy ligands.

The temporal trace of the integrated intensity of the excited-state ester νC=O band is shown in Fig. 2. With the use of nonlinear regression, these data were fit to the
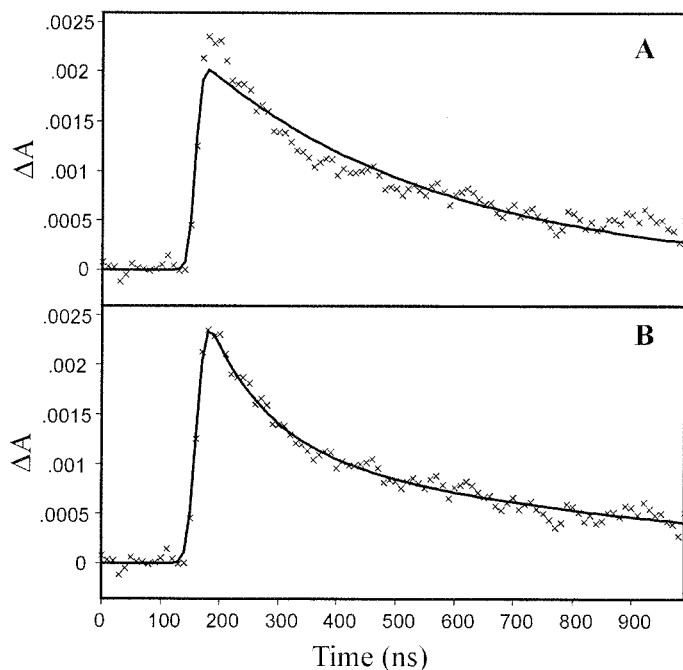
FIG. 2. Monoexponential (A) and biexponential (B) fits to the integrated intensity of the excited-state ester νC=O band of **1** as a function of time. The parameters for the monoexponential fit were $A_1 = 8.15 \times 10^{-5} \pm 1.46 \times 10^{-5}$, $t_0 = 156.7 \pm 1.8$ ns, $w = 13.2 \pm 2.4$ ns, $\tau_1 = 412.3 \pm 19.0$ ns. The parameters for the biexponential fit were $A_1 = 4.53 \times 10^{-5} \pm 5.13 \times 10^{-6}$, $A_2 = 3.85 \times 10^{-5} \pm 4.95 \times 10^{-6}$, $t_0 = 160.0 \pm 1.1$ ns, $w = 16.4 \pm 1.4$ ns, $\tau_1 = 99.7 \pm 15.8$ ns, $\tau_2 = 746.5 \pm 102.8$ ns.

convolution of a Gaussian pulse shape with either 1 or 2 exponential decays according to

$$y = \sum_{n}^{N_{exp}} A_n w \, \exp\left[\frac{-(t - t_0)}{\tau_n}\right] \times \exp\left[\left(\frac{w}{4\tau_n}\right)^2\right]\left(1 - \mathrm{erf}\left[\frac{w}{2\tau_n} - \frac{(t - t_0)}{w}\right]\right)$$

where A_n is the amplitude of each decay component, w is the Gaussian pulse width, t_0 is the center of the Gaussian pulse, and τ_n is the e^{-1} decay time. The best fit of a single exponential, $\tau_1 = 412 \pm 16$ ns (convoluted with a Gaussian pulse of 13.2 ± 2.4 ns width), is shown in Fig. 2A. It is clear from the systematic deviation of the residuals that a single exponential gives a poor fit to these data. On the other hand, a biexponential decay with $\tau_1 = 100 \pm 16$ ns and $\tau_2 = 747 \pm 103$ ns (convoluted with a Gaussian pulse of 16.4 ± 1.4 ns width) fits the data very well, as shown in Fig. 2B. Within experimental error, the amplitudes of the τ_1 and τ_2 decays are of the same magnitude. Although two exponentials were necessary to describe the observed decay, a comparison of the time-resolved ΔA spectra before and after the τ_1 decay revealed no discernible spectral differences throughout the measured bandwidth, 1150 to 2250 cm^{-1}. Similar analysis of the excited-state ester νC=O band of **1** in deoxygenated ACN revealed a monoexponential decay with $\tau = 484 \pm 43$ ns.

Pt(dpphen)(dcbdt). Figure 3 shows the room-temperature ground-state (top) and ΔA spectra (bottom) of complex **2** prepared in a KBr pellet. The band of highest
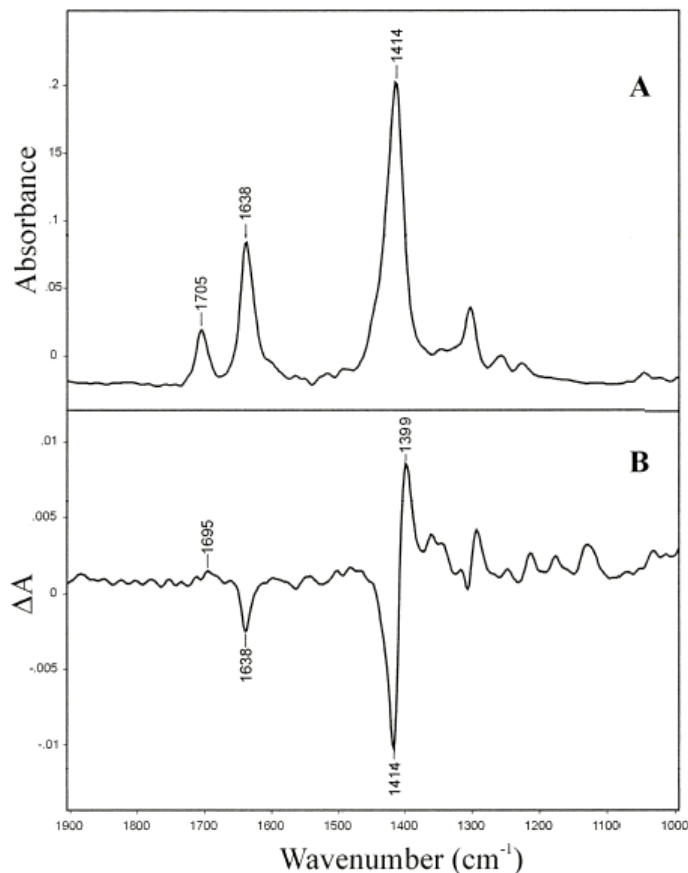

FIG. 3. Ground-state (A) and time-resolved difference spectra (B) of **2** in a KBr pellet at room temperature.

intensity, centered at 1414 cm^{-1} in the ground-state spectrum, has contributions from both the dithiolate alkene and a ring mode of dpphen. The two bands at higher energy, 1705 and 1638 cm^{-1}, are assigned to the urea carbonyl and the two amide carbonyls, respectively.[26]

A component of the largest band shifts to lower energy upon excitation (1414 to 1399 cm^{-1}). This shift may represent either a perturbation of the dpphen ring or the dithiolate alkene. The amide carbonyl modes respond in an opposite fashion, moving to higher energy in the excited state (1638 to 1695 cm^{-1}). No corresponding transient signal for the urea carbonyl can be seen. Other IR bands and transient features appear in the ΔA spectrum in the region from 1400 to 1000 cm^{-1} and can be attributed to additional ring modes of the diimine and dithiolate ligands in the ground and excited states.

The ΔA features were all found to respond in an identical temporal fashion, decaying to the baseline in ~400 ns. A kinetic analysis of the temporal trace for the strongest excited-state band (1399 cm^{-1}) reveals a lifetime of 129 ± 14 ns for **2** in the solid state. In this case, the addition of a second exponential did not improve the fit. While the poor solubility of **2** meant that we could not use TR-IR to measure the excited-state lifetime in solution, measurement of the luminescence decay permitted calculation of a very similar lifetime (150 ns) for **2** in CH$_2$Cl$_2$.

DISCUSSION

Ru(bpy)$_2$(4-COOEt-4$'$-CH$_3$bpy)$^{2+}$. The time-resolved ΔA spectrum of the excited state of **1** in the solid state,

measured as microcrystallites embedded in a KBr matrix (Fig. 1B), matches very well the previously reported ΔA spectrum of the ^{3}MLCT state of **1** in ACN solution.[21,22] The ground-state νC=O frequency is only 5 cm^{-1} lower in KBr than in ACN and the excited-state shift is 48 cm^{-1} in KBr compared to 46 cm^{-1} in ACN. These similarities lead us to conclude that the degree and nature of charge transfer in the ^{3}MLCT state of **1** are very similar in the solid state and solution.

Solution samples of transition metal polypyridine complexes are normally deoxygenated, either by sparging with argon or by undergoing several freeze/pump/thaw cycles, to avoid quenching of the excited state by molecular oxygen. However, we find no evidence of quenching by O_2 in the TR-IR measurements of KBr pellet samples. The decay times of $\tau_1 = 100 \pm 16$ ns and $\tau_2 = 747 \pm 103$ ns measured for **1** in an air-exposed KBr pellet are comparable to the lifetime measured in deoxygenated ACN, 484 ± 43 ns. Molecular oxygen may have been excluded from the salt matrix during the high-pressure fusing process, or it may have not been mobile enough in the KBr matrix to effectively quench the ^{3}MLCT state.

An additional quenching mechanism that must be considered in the solid state is triplet–triplet annihilation. Recent luminescence studies of [Ru(bpy)$_3$]$^{2+}$ salts in the solid state have shown that, by energy transfer, ^{3}MLCT states may diffuse through the crystal and quench one another by electron transfer.[27] The lifetimes of the oxidized and reduced sites produced by this mechanism in the crystal were found to be ~100 ps, much too short for any significant accumulation of these species on the 10 to 100 ns time scale of the ΔA spectra presented in this report. While not affecting the measured spectra, significant triplet–triplet annihilation would be expected to affect the kinetic traces measured in a KBr pellet (Fig. 2) by producing a burst in the amplitude of the ^{3}MLCT state that decays within the Gaussian pulse width. However, a biexponential fit to the measured ester νC=O trace of **1** in KBr was sufficient without the inclusion of a burst-phase term. In addition, the luminescence decay of [Ru(bpy)$_3$](PF$_6$)$_2$ in KCl, measured at laser excitation intensities below the threshold for triplet–triplet annihilation, was previously fit to a biexponential decay with time constants of 125 and 500 ns, corresponding, respectively, to sites in the bulk and on the surface of the microcrystallites embedded in the alkali halide matrix.[27] Thus, the biexponential ^{3}MLCT decay observed for **1** in the solid state is similarly assigned to bulk and surface sites in the crystals.

While the kinetics are somewhat altered, we have shown through a comparison of the ΔA spectra of the excited states of **1** in solution and the solid state that the environment of the KBr matrix does not significantly perturb the nature of this ^{3}MLCT state. Thus, one can confidently correlate the ΔA spectra of the excited states of kinetically inert transition metal complexes measured in KBr pellets to the same charge-transfer states populated in solution.

Pt(dpphen)(dcbdt). Complex **2** is insoluble in ACN and DCE at the concentrations required for TR-IR analysis. Moreover, it is only sparingly soluble in less spectroscopically useful solvents such as benzene and dichloromethane. Interest in the lowest-lying excited state of this class of d^8 transition metal diimine complexes arises from the potential use of these compounds as solid-state photocatalysts, sensors, and nonlinear optical materials.[8,17] To access the photophysical information normally supplied by TR-IR analyses in solution, the spectra of this poorly soluble complex can be collected only by using a solid-state sampling technique such as the KBr pellet technique used in this report.

Complex **2** has an intense solvatochromic visible absorption band, centered between 400 to 500 nm, indicative of a charge transfer (CT) transition, similar to that of several other Pt(diimine)(dithiolate) complexes.[28–30] Below 400 nm, there are several additional bands that correspond to $\pi \rightarrow \pi^*$ transitions of the diimine and dithiolate ligands. By using a pump wavelength of 532 nm, we have excited directly into the CT transition of **2**. From low-temperature emission studies, the long-lived luminescent state of complexes with 1,1-dithiolatomethylene ligands is a thermally equilibrated mixture of triplet states, consisting of a pair of spin-orbit split components of a ^{3}CT state and a higher energy diimine $^3(\pi-\pi^*)$ state.[29] Regardless of excitation wavelength, the excited complex is expected to quickly relax into this thermally equilibrated mixture of states, much faster than the 10 ns time scale of the TR-IR measurements. On the basis of the low-temperature emission energies, we expect the mixture present in the room-temperature TR-IR experiments to be overwhelmingly ^{3}CT due to the higher energy of the $^3(\pi-\pi^*)$ state in this class of complexes.

The nature of the charge transfer transition in this class of d^8 diimine complexes has been difficult to assign unequivocally.[8,18,28–30] The diimine chelates are known to be the more easily reduced ligands; therefore, they are generally accepted as the ultimate electron receiver in the excited state. The participation of the metal and dithiolate ligand in the electron-donating molecular orbital (MO) is less certain. For a series of M(diimiine)(dithiolate) complexes with very similar solvatochromic CT absorption bands, the energy of the CT absorption was found to be dependent on the nature of the dithiolate ligand, indicating participation of the dithiolate ligand in the highest-occupied molecular orbital (HOMO).[30] However, complexes with saturated dithiolate ligands were found to have similar CT absorption bands, although there was no dithiolate π orbital to contribute to the charge transfer. On the basis of these observations, the transition in these complexes has been attributed to an electron being transferred from a combined Pt(d)S(p) orbital to an orbital localized largely on the dpphen ligand. However, for any individual complex in this series, it is not clear to what extent the metal and dithiolate participate in the charge transfer, particularly the conjugated π system in unsaturated ligands.

The TR-IR results shown here for **2** can be used to elucidate the degree of participation of the dithiolate ligand in the proposed Pt(d)S(p) $\rightarrow$ dpphen(π^*) charge-transfer luminescent state. The similarity of the luminescence decay kinetics of **2** in CH$_2$Cl$_2$ solution and the decay kinetics of its TR-IR features in the solid state indicates that the ΔA spectrum presented in Fig. 3 corresponds to the long-lived emitting state(s). In contrast to the results for **1**, there is no discernible difference in

the decay kinetics of surface and bulk crystalline species of **2**.

The observed transient features are consistent with electron depletion of a dithiolate ligand-centered orbital that is antibonding across each of the amide carbonyl groups. In the ΔA spectrum of Fig. 3, the amide carbonyl stretching band at 1638 cm^{-1} makes a large positive shift (+57 cm^{-1}) to 1695 cm^{-1}, consistent with strengthening these bonds. Interestingly, no change in the urea-stretching frequency (1705 cm^{-1}) is detected in the ΔA spectrum. The additional large ΔA feature, a shift of the 1414 cm^{-1} band to 1399 cm^{-1}, may represent a perturbation of a ring mode upon the addition of electron density to a dpphen π^* orbital. Alternatively, it could represent a weakening of the dithiolate alkene bond in the luminescent CT state. Additional measurements of Pt(diimime)(dithiolate) complexes with saturated dithiolates will be necessary to resolve this uncertainty.

Although a detailed analysis of these results is beyond the scope of this initial report, the ΔA spectrum of **2** reveals a contribution of the conjugated dithiolate ligand in the charge-transfer excited state. Depletion of electron density from this extensive molecular orbital and transfer of that charge to the diimine ligand should result in an extremely large excited-state dipole and highly polarized molecule. The hyperpolarizability of this class of d^8 transition metal complexes supports their development for use as nonlinear optical materials as well as LSAs.

The S^{2}FT-IR TRS technique in conjunction with standard KBr pellet samples has been shown to be a valid method for collecting excited-state IR spectral information for transition metal complexes in the solid state. The KBr pellet method was chosen as a solution to insolubility problems and as a model for the solid-state environment in which many LSAs are designed to operate. This latter application is highlighted by the growing number of reports that describe photovoltaic cells designed with transition metal LSAs applied directly to nanocrystalline films of a metal oxide semiconductor.[12,31–34] The KBr sample described here closely approximates the environment in which these compounds will be required to operate as dyes on a semiconductor surface. These pellets do not, however, suffer from IR opacity in the excited state due to electron injection into the conduction band of the substrate, a phenomenon known to occur in dye-sensitized TiO$_2$.[32] The KBr technique also allows TR-IR spectroscopy to be used in the study of numerous solid-state photophysical phenomena such as rigidochromism[35–37] and localization/delocalization of excited states in homoleptic polypyridine transition metal complexes.[38]

In addition, the KBr pellet technique offers numerous other advantages for TR-IR experiments. The pellets provide an extremely wide spectral window (40 000 to 400 cm^{-1}) that places few restrictions on either the pump laser or the spectral regions that may be probed. The robust stability of the KBr samples coupled with the permanence of the salt matrix allows their storage and reuse in later experiments. (The KBr pellet of **1** was subjected to over 250 000 laser flashes without any apparent degradation in its spectra.) The KBr pellet samples do not require the long sparging times or numerous freeze/pump/thaw cycles needed to eliminate molecular oxygen from solution samples, which otherwise would quench the excited state.

In summary, the use of KBr pellets for TR-IR measurements is easier and less time consuming and offers numerous spectroscopic advantages over samples prepared in traditional IR solvent systems. Current efforts in this laboratory are focused on determining the suitability of this technique for a wide array of metal carbonyls and substituted-polypyridine complexes as well as the investigation of numerous solid-state photophysical phenomena.

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