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Observation of Triplet Intraligand Excited States through Nanosecond Step-Scan Fourier Transform Infrared Spectroscopy

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Nanosecond step-scan Fourier transform infrared spectroscopy permits the observation of triplet intraligand (^{3}IL) character in the excited states of $[Ru(bpy)_2(PNI\text{-}phen)]^{2+}$ and $[Ru(PNI\text{-}phen)_3]^{2+}$ where PNI is 4-piperidinyl-1,8-naphthalimide. After pulsed 355-nm laser excitation, the two ground-state imide C═O bands in each compound are bleached and two substantially lower energy vibrations are produced; the lower energy feature appears as two distinct bands split by an overlapping transient bleach. Model studies confirm that the time-resolved vibrational data are consistent with photoinduced sensitization of the ^{3}IL excited state. Density functional theory calculations also support these assignments because localization of triplet electron density on the PNI moiety is expected to lead to red-shifted C═O vibrations of magnitude similar to those measured experimentally. The current results illustrate that triplet electron density can be directly tracked by time-resolved infrared measurements in metal–organic chromophores and that frequency shifts comparable to those observed in charge-transfer systems can be realized.

Time-resolved infrared (TRIR) spectroscopy continues to emerge as a powerful tool for interrogating and following the structural evolution of excited states.[1−8] This technique is particularly powerful when applied to photoinduced charge-transfer systems where electron density changes following light absorption are tracked either directly or indirectly by frequency shifts of IR chromophores strategically placed in structures of interest. In metal-to-ligand charge-transfer (MLCT) molecules, TRIR spectroscopy has proven quite successful in diagnosing the nature of the lowest excited states in various d^6 metal complexes.[1−6] In Ru^{II} systems, charge-transfer assignments are readily accessible, whereas triplet intraligand (^{3}IL) excited states have yet to be identified using TRIR methods. This limitation stems from the fact that most Ru^{II} molecules possessing ^{3}IL character lack appropriate IR-absorbing functionalities. In 2001, we performed a detailed photophysical study on Ru^{II} compounds bearing naphthalimide chromophores (**1** and **2**).[9] Luminescence and transient absorption methods revealed an excited state composed predominately of ^{3}IL (4-piperidinyl-1,8-naphthalimide, PNI) character thermally equilibrated with the emissive ^{3}MLCT manifold. This equilibrated excited state is easily accessed using any excitation wavelength between 355 and 550 nm.[9]

As each PNI subunit bears two strongly absorbing C═O functionalities, we anticipated that the production of the ^{3}IL excited state could be readily observed in nanosecond step-scan Fourier transform infrared (FT-IR) experiments. This is indeed the case, and comparison to an appropriate model system (**3**, ANI) strongly suggests that triplet electron density can be directly tracked in **1** and **2**. Importantly, C═O frequency shifts comparable to those observed in charge-transfer imide-containing systems are realized,[7,8] supporting the notion that TRIR methods can be successfully applied toward detecting ^{3}IL excited states.

Compounds **1**−**3** (Figure 1) are available from our previous study,[9] and TRIR experiments using 355-nm excitation at 1 mJ/pulse (Spectra Physics GCR Nd:YAG laser) were performed using instrumentation based on a Bruker IFS-55 FT-IR spectrometer with 8-cm^{-1} resolution.[10] All TRIR experiments were performed on compounds in

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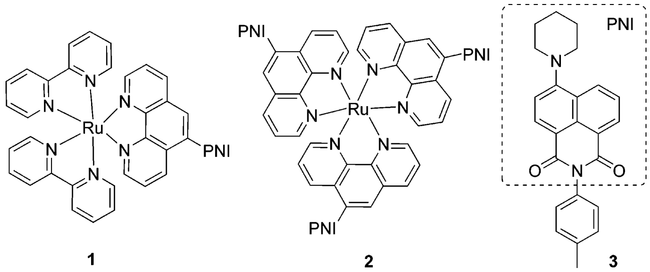

Figure 1. Structures of compounds **1**−**3**. The counterions in each Ru^{II} complex are PF_6^-.

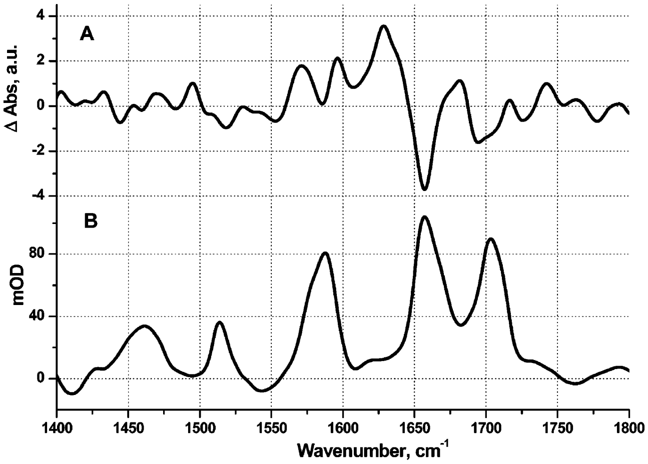

Figure 2. (A) TRIR difference spectrum of **3** taken 1 μs after a 355-nm pulse. (B) FT-IR spectrum of **3** in $CHCl_3$.

argon-deaerated $CHCl_3$ using two CaF_2 windows configured as a flow cell (10 mL/min). Additional experimental details are available as Supporting Information.

Prior to discussing the FT-IR and TRIR spectra of the Ru^{II} complexes (**1** and **2**), it is useful to first discuss the relevant spectra of model chromophore **3**. We know from previous studies that the singlet excited state of ANI dominates its photophysics (τ = 8.5 ns; Φ = 0.91),[11] so any long-delay-time photophysical processes result from triplet-state formation.[9,12] Figure 2 presents the ground- and excited-state difference spectra obtained in the mid-IR for **3**. There are three strong IR bands observed between 1550 and 1725 cm^{-1} in the ground-state spectrum, Figure 2B. The two bands centered at 1657 and 1705 cm^{-1} are assigned as imide C═O vibrations. The other band positioned at 1585 cm^{-1} is complex but originates predominately from imide naphthalene ring vibrations. Density functional theory (DFT) calculations performed on this model chromophore substantiate the assignments.[13] Table 1 lists the FT-IR and TRIR experimental values as well as their assignments together with pertinent frequencies calculated by DFT for the ground state and the lowest triplet state of **3**.

Table 1. C═O Vibration Frequencies Observed for **3** by TRIR before (GS) and after (TR) 355-nm Excitation[a]

experiment	GS, cm^{-1}	TR or TS, cm^{-1}	Δ, cm^{-1}
TRIR	1705[c]	1636[c]	69
	1657[d]	1570, 1598[d]	59, 87
	1585[e]		
DFT[b]	1713[c]	1645[c]	68
	1682[d]	(1595, 1590, 1585, 1582)[f]	(87, 92, 97, 100)
	1565[e]	1505[e]	60

[a] The DFT line collects the frequencies calculated for the ground (GS) and excited triplet state (TS) of **3**. The difference between TR and GS or TS and GS is denoted as $\Delta\nu$. [b] B3LYP 6-31G(d), scaled by 0.96. [c] Symmetrical C═O stretching vibrations. [d] Antisymmetrical C═O stretching vibrations. [e] C−H aromatic vibrations. [f] Four modes of C═O stretching vibrations weakly coupled with aromatic C−H vibrations (see the Supporting Information for details).

The TRIR spectrum of **3** at a 1-μs delay time contains a combination of bleached ground-state vibrations along with positive OD transients associated with the ANI triplet state. The two C═O bands at 1657 and 1705 cm^{-1} are bleached, and three red-shifted transient absorptions are produced (1570, 1598, and 1636 cm^{-1}). These experimental observations reveal a reduction of the force constant (and bond order) in the C═O substituents in the excited state, consistent with triplet-state production in **3**. The carbonyl vibration associated with the 1705-cm^{-1} ground-state band shifts to 1636 cm^{-1} ($\Delta\nu$ = 69 cm^{-1}). However, the fate of the 1657-cm^{-1} band is not as straightforward because the associated transient should emerge somewhere in the vicinity of the two low-energy bands observed experimentally. Concomitantly, the 1585-cm^{-1} ground-state bleach appears as a dip between the excited-state transients. Therefore, we believe the 1570- and 1596-cm^{-1} excited-state bands are simply a single C═O band split into two parts by ground-state bleaching of the 1585-cm^{-1} naphthalene ring mode. This assignment renders the transient corresponding to the 1657-cm^{-1} C═O vibration somewhere in the vicinity between 1570 and 1598 cm^{-1}, yielding a red shift between 59 and 87 cm^{-1}, largely in agreement with that observed for the higher energy C═O band. DFT calculations predict well the red shift of C═O vibrations in the triplet excited state of **3** compared to its ground state (Table 1). The transient associated with the 1585-cm^{-1} mode is likely masked by solvent absorptions because we do not observe any transients below 1550 cm^{-1}. We note that DFT calculations predict the triplet-state vibration corresponding to the 1585-cm^{-1} mode as centered near 1505 cm^{-1}, outside of our experimental window.

Figure 3 presents the ground- and excited-state difference spectra obtained in the mid-IR for **1**. Because the corresponding ground- and excited-state difference spectra of **1** and **2** are identical within experimental error (see the Supporting Information), the following discussion applies to both Ru^{II} chromophores. Just as was observed in model **3**, there are three strong IR bands observed between 1550 and 1725 cm^{-1} in the ground-state spectrum of **1**, Figure 3B. Accordingly, all three bands correspond to the same features as those seen in **3**, although there are minor energy differences within our experimental uncertainty. The TRIR spectrum of **1** contains the same combination of bleached ground-state vibrations along with transients attributed to the

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(13) Selected DFT output files and simulated IR spectra of the ground state and lowest triplet state of **3** are provided as Supporting Information.

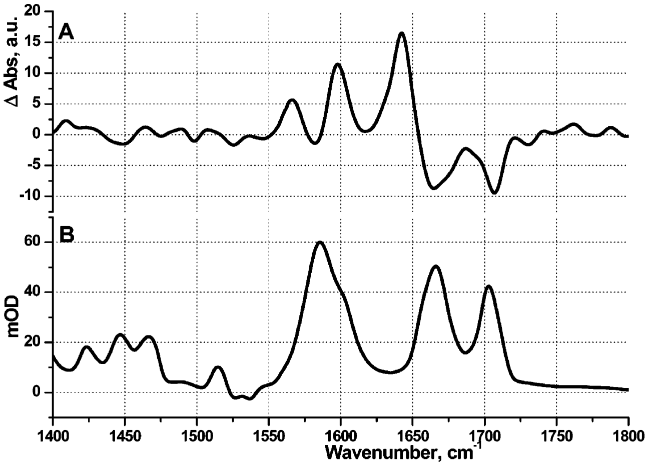

Figure 3. (A) TRIR difference spectrum of **1** taken 1 μs after a 355-nm pulse. (B) FT-IR spectrum of **1** in $CHCl_3$.

PNI-localized triplet state, just as was observed in model chromophore **3**. Specifically, two C═O bands at 1668 and 1705 cm^{-1} are bleached, and three red-shifted transient absorptions are produced (1567, 1597, and 1643 cm^{-1}). The difference spectrum can be interpreted in precisely the same manner as that described above for **3**. The higher energy carbonyl is red-shifted in the excited state to 1643 cm^{-1}. The appearance of two lower energy excited-state bands results from a single C═O vibration being cut into two portions by the ground-state bleaching of the 1585-cm^{-1} band. Therefore, the true peak of the lower energy excited-state carbonyl vibration can be found between 1567 and 1597 cm^{-1}. The limit imposed by the solvent window prevents observation of the transient associated with the 1585-cm^{-1} ground-state vibration. The pertinent ground- and excited-state C═O frequencies measured for compounds **1**−**3** in addition to their respective differences are collected in Table 2.

Table 2. C═O Vibration Frequencies Observed for **1**−**3** in the Ground State (GS) and Transients Observed after (TR) 355-nm Excitation[a]

compound	GS, cm^{-1}	TR, cm^{-1}	$\Delta\nu$, cm^{-1}
1	1705	1643	62
	1668	1567, 1597[b]	71, 101
2	1705	1645	60
	1668	1568, 1600[b]	68, 100
3	1705	1636	69
	1657	1570, 1596[b]	61, 87

[a] The difference between TR and GS is denoted as $\Delta\nu$. [b] Two bands result from a single peak that is split by a ground-state bleach. The true peak of the vibration lies between these energies.

In summary, we have applied nanosecond step-scan FT-IR measurements to detect ^{3}IL excited states in Ru^{II} complexes bearing PNI subunits. Our data show that the two C═O vibrations are substantially red-shifted following laser excitation, a direct consequence of sensitizing the PNI-localized triplet excited state. The time-resolved FT-IR step-scan experiment is essentially a supra-nanosecond technique mandating the use of compounds with long-lived excited states. We believe that the current study illustrates that this method can be extended to inorganic molecules with low-lying ^{3}IL states bearing appropriate IR-absorbing chromophores. The current results also demonstrate that triplet-state electron density can be directly tracked by TRIR in these chromophores and that frequency red shifts comparable to those observed in charge-transfer imide-bearing systems[7,8] can be realized.

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Supporting Information Available: Experimental details, DFT calculations, and additional spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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