

Photophysics of phenyleneethynylene metal–organic oligomers. Probing the lowest excited state by time-resolved IR spectroscopy

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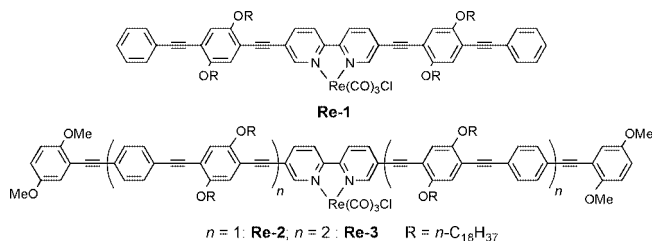
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The long-lived excited state in a series of metal–organic phenyleneethynylene oligomers is probed by UV-visible and infrared transient absorption spectroscopy.

There has been considerable recent interest in the optical and electronic properties of π -conjugated polymers that contain d^6 transition metal polypyridine complexes of Ru(II), Os(II) and Re(I) as integral components of the π -conjugated backbone.^{1–3} We have been investigating the photophysical properties of d^6 metal complexes derived from several series of mono-disperse oligomeric phenyleneethynylenes (OPEs) that contain the 2,2'-bipyridine-5,5'-diyl (bpy) metal binding site.^{3,4} These metal–OPEs serve as models for the structurally-related polymers and provide a detailed understanding of the nature of the long-lived excited states that are produced by photoexcitation of these systems. In the present communication we report the photophysical properties of the series of metal–OPEs **Re-1–Re-3**. These oligomers feature two energetically low-lying excited states: (1) a $d\pi(\text{Re}) \rightarrow \pi^*$ OPE metal-to-ligand charge transfer (MLCT) state, and (2) a ${}^3\pi,\pi^*$ state localized on the OPE.



Absorption spectra for metal–OPEs **Re-1–Re-3** and the corresponding free oligomers **1–3** are illustrated in Fig. 1.† The absorption of the free OPEs is dominated by an intense band with $\lambda_{\text{max}} \approx 400$ nm arising from the long-axis polarized π,π^* transition. The absorption of the metal–OPEs is red-shifted: each complex features a band with $\lambda_{\text{max}} \approx 440$ nm in addition to more intense absorptions that extend into the near-UV region. All of the absorption bands in the metal–OPE spectra are also assigned to π,π^* transitions.^{3,4,‡} The red-shift is attributed to a reduction in the HOMO–LUMO gap, which is caused by the effect of the electrophilic metal on the π and π^* energy levels.^{1,5} The constant energy of the low-energy absorption band in **Re-1–Re-3** implies that this transition arises from a chromophore that is conserved across the series of metal–OPEs. This observation leads us to conclude that the low energy π,π^* transition is localized in the bpy ‘core’ of the metal–OPEs.⁴

Free oligomers **1–3** feature a strong, short-lived blue fluorescence ($\lambda_{\text{max}} \approx 450$ nm and $\tau \approx 800$ ps).^{4,6§} In metal–OPEs **Re-1–Re-3** the blue fluorescence is quenched and replaced by a weak luminescence ($\phi_{\text{em}} < 0.005$) with $\lambda_{\text{max}} \approx 650$ nm and $\tau \approx 150$ ns.^{4,6} At room temperature, the emission appears as a broad band with a vibronic shoulder on the low-energy side. The metal–OPE emission intensity increases modestly with decreasing temperature, and for $T < 200$ K a

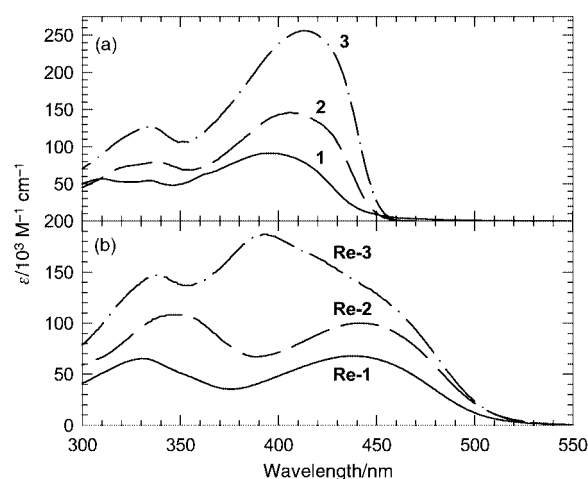


Fig. 1 UV-visible absorption spectra for THF solutions. (a) Free oligomers **1–3**. (b) Metal-oligomers **Re-1–Re-3**.

second broad emission feature emerges on the high-energy side of the main emission band. Very similar dual emission was recently reported for a related series of metal–OPEs that contain the $-\text{Re}(\text{CO})_3\text{Cl}$ chromophore.^{4,6} In the previous study, the dual emission was attributed to the ${}^3\pi,\pi^*$ and MLCT states which are believed to be very close in energy in the metal–OPEs.

In order to probe the nature of the long-lived luminescent excited state in more detail, ns– μs transient absorption spectroscopy (TAS) was carried out on **Re-1–Re-3** and free oligomers **1–3**. Generally similar results were obtained for the two sets of OPEs, and therefore only the data for **2** and **Re-2** is presented herein.⁶ First, 355 nm excitation of free oligomer **2** affords a very long lived transient ($\tau > 300$ μs) that features the difference absorption spectrum shown in Fig. 2. This transient absorption spectrum is very similar to the triplet–triplet difference spectra observed for structurally similar OPEs and poly-(phenyleneethynylenes), and on this basis it is assigned to the ${}^3\pi,\pi^*$ state.^{3,4} Excitation (355 nm) of metal–OPE **Re-2** affords a strongly absorbing transient ($\tau \approx 150$ ns) that has a difference spectrum also illustrated in Fig. 2. The spectrum is characterized by a bleach in the region of the lowest energy π,π^* transition and excited state absorption that extends from the visible into the near-IR.

The similarity of the emission and TA decay lifetimes for **Re-1–Re-3** suggests that the emission arises from the same excited state that gives rise to the transient absorption. However, because both emission and TAS give rise to relatively broad spectroscopic features, these techniques do not provide definitive evidence regarding the electronic structure of the excited state. In particular, while it is clear that the long-lived state observed for the free oligomers is ${}^3\pi,\pi^*$, based on the emission and TAS it is not possible to unequivocally determine whether the long-lived state is ${}^3\pi,\pi^*$ or MLCT in **Re-1–Re-3**.

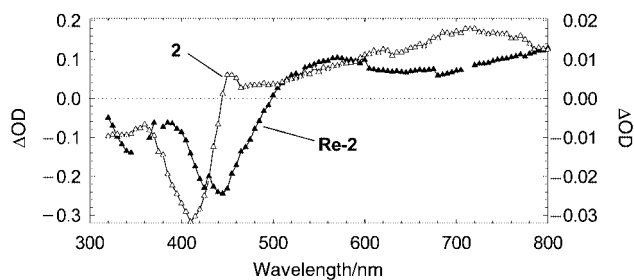


Fig. 2 Transient absorption difference spectra obtained on THF solutions following 355 nm pulsed excitation (10 ns pulsewidth, 5 mJ pulse⁻¹). (Δ): Free ligand **2**, 10 μs delay, scale at right. (▲): Metal-oligomer **Re-2**, 40 ns delay, scale at left.

Time-resolved, step-scan Fourier transform infrared spectroscopy (TRIR) is uniquely suited to establish the electronic structure of excited states in metal complexes that contain C≡O ligands.^{7,8} In particular, because the CO vibration has a large oscillator strength and its frequency is very sensitive to electron density at the metal center, it is possible to use TRIR to distinguish between intraligand and MLCT states.⁸ Directly relevant to the present study are TRIR studies of complexes of the type (diimine)Re^I(CO)₃(L) which indicate the following.⁸ (1) When the lowest excited state is Re → diimine MLCT, in the excited state the three CO bands are shifted to higher frequency by 30–60 cm⁻¹. (2) When the lowest excited state is intraligand ³π,π*, the CO bands broaden but shift only slightly to lower frequency.

Based on this literature precedent, we applied TRIR to complexes **Re-1–Re-3** in an effort to unequivocally establish the identity of the long-lived excited state.¶ Essentially identical results were obtained for all three metal–OPEs, and thus we provide only the data for **Re-2** here. Fig. 3 illustrates the ground state FTIR spectrum of **Re-2** in CCl₄ solution in the 1850–2200 cm⁻¹ region. The spectrum features the three CO bands characteristic of the *fac*-(diimine)Re^I(CO)₃(L) chromophore.^{7,8} Near-UV photoexcitation of **Re-2** affords the TRIR difference spectrum also shown in Fig. 3. The difference spectrum is dominated by bleaching in all three CO bands. The appearance of the difference spectrum in the low-frequency region indicates that in the excited state the CO bands are broadened, but they are not shifted significantly from their position in the ground state. By contrast, in the excited state the high frequency band, which is assigned to the A'(1) mode, is clearly broadened and shifted to lower frequency by 6–8 cm⁻¹.

The excited state TRIR difference spectra of the metal–OPEs are virtually identical to that of the complex (dppz)Re(CO)₃(PPh₃)⁺ (dppz is dipyrido[3,2-*a*:2',3'-*c*]phenazine), which is known to feature a lowest excited state based on the ³π,π* (dppz) intraligand configuration.^{8,10} This similarity in the TRIR data leads us to conclude that the lowest excited state in metal–OPEs **Re-1–Re-3** is an intraligand ³π,π* state based on the bipyridyl–phenylene–ethynylene chromophore. The TRIR data also lends further insight into the electronic structure of the ³π,π* excited state in the metal–OPEs. First, the low frequency shift of the A'(1) band in **Re-1–Re-3** is essentially identical to that observed for (dppz)Re(CO)₃(PPh₃)⁺.⁸ This implies that in the metal–OPEs the ³π,π* excitation is localized in the bpy core of the OPE and not delocalised into the periphery of the oligomers. This conclusion is substantiated by photoluminescence and time resolved photoacoustic studies of structurally similar metal–OPEs which indicate that the energy of the lowest ³π,π* state is relatively independent of oligomer length.^{4,6} Moreover, the fact that the TRIR spectra are identical for complexes **Re-1–Re-3** reinforces the notion that the electronic

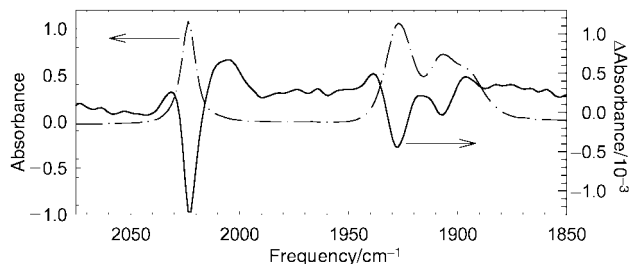


Fig. 3 Infrared spectra of **Re-2** in CCl₄. (—): Infrared spectrum of ground state complex. (---): Time-resolved step-scan difference spectrum obtained 50 ns following 355 nm excitation.

structure of the ³π,π* state is invariant with oligomer length, which further suggests that the excitation is localized in the oligomer core. This concept is consistent with theoretical studies which indicate that triplet excitons are more localized compared to their singlet counterparts in π-conjugated systems.¹¹

In summary, metal–OPE oligomers **Re-1–Re-3** feature a long-lived, luminescent excited state that can be observed by UV-visible and TRIR spectroscopy. TRIR indicates that the excited state is dominated by a ³π,π* intraligand configuration based on the OPE π-conjugated system. The TRIR spectra for the metal–OPEs are indistinguishable, which implies that the triplet exciton is localized in the bipyridine core of the OPE.

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Notes and references

† In free oligomers **1–3** the bipyridine moiety is not coordinated to a metal.

‡ Importantly, the MLCT absorptions are not resolved, presumably because these are weaker compared to the strongly allowed π,π* transitions.

§ Copies of Ph.D. dissertations are available in Adobe pdf format upon request to: kschanze@chem.ufl.edu.

¶ See ref. 9 for a description of the TRIR instrumentation.

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