

Photophysics of π -conjugated metal–organic oligomers*

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Abstract: The optical absorption and photoluminescence properties of PPE-type π -conjugated oligomers that contain a 2,2-bipyridine-5,5'-diyl metal coordinating unit have been examined. The spectra of the free oligomers are compared with those that contain $-\text{Re}(\text{CO})_3\text{Cl}$ and $-\text{Ru}(\text{bpy})_2^{2+}$ chromophores chelated to the bpy-diyl unit.

INTRODUCTION

π -Conjugated polymers possess remarkable photophysical properties [1]. In a number of recent studies of polymer systems such as poly(phenylene vinylene) and poly(phenylene ethynylene) (PPV and PPE, respectively, see Fig. 1) it has been demonstrated that these polymers display strong fluorescence from the singlet excited state and long-lived transients which are attributed to triplet states that are formed in moderate quantum yields by intersystem crossing. The photophysics of π -conjugated polymers have been of interest in part due to the possibility that they may be useful as the active materials in optoelectronic devices such as light-emitting diodes (LEDs) and photodetectors [2].



Fig. 1 General structures of poly(phenylene vinylene) (PPV) and poly(phenylene ethynylene).

Inorganic photochemists have long been fascinated by the photophysics of transition-metal complexes such as $\text{Ru}(\text{bpy})_3^{2+}$ and its analogs [3]. These d^6 transition-metal complexes feature long-lived metal-to-ligand charge transfer (MLCT) excited states that are strongly luminescent, typically in the red region of the visible spectrum. In a one-electron approximation the MLCT excited states arise by photo-induced promotion of an electron from a metal-centered d -orbital to a π^* orbital localized on a bipyridine “acceptor” ligand.

In view of the rich and varied photophysical properties of π -conjugated materials and d^6 transition-metal complexes, it is of interest to combine these two molecular systems in order to produce new “hybrid” metal-organic π -conjugated systems that might have unusual and possibly useful optical and photophysical properties. Herein, we provide a preliminary report of the optical properties of a series of PPE-type conjugated oligomers that contain d^6 transition-metal polypyridine complex chromophores.

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STRUCTURES AND SYNTHESIS

Figure 2 illustrates the structures of the PPE oligomers and their metal complexes. These materials were synthesized according to methods described in previous papers [4,5]. PPE oligomers **2–4** and their metal complexes contain long alkyloxy chains to increase their solubility. The free oligomers and metal complexes are soluble in tetrahydrofuran and chlorinated hydrocarbons, but they are insoluble in polar solvents such as acetone and acetonitrile.

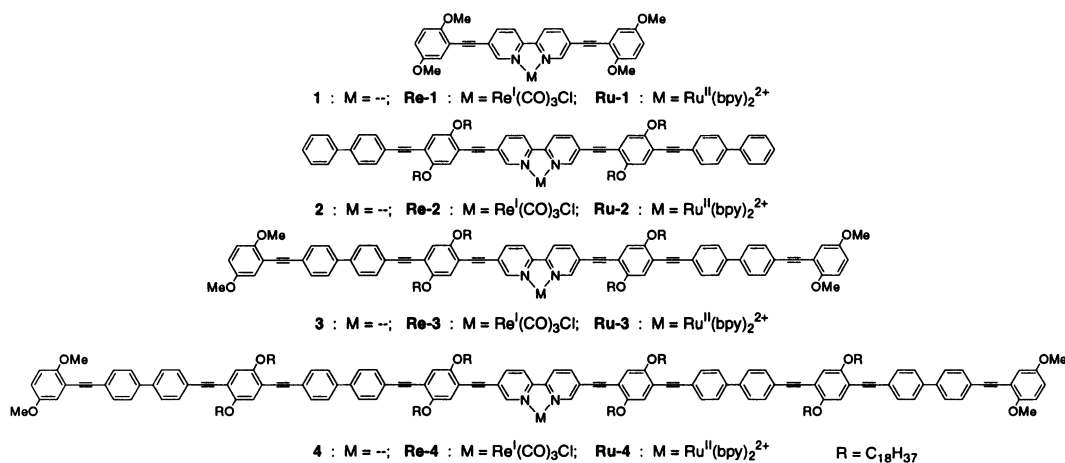


Fig. 2 Structures and acronyms for the oligomers and metal–oligomers.

Absorption spectroscopy

Figure 3 illustrates the absorption spectra of the series of free oligomers **1–4**, along with the spectra of the corresponding (L)Re(CO)₃Cl and (L)Ru(bpy)₂²⁺ complexes (**Re-1–Re-4** and **Ru-1–Ru-4**, respectively). The absorption spectra of all of these materials are dominated by π,π^* transitions. First, as seen in Fig. 3a, the free oligomers exhibit a very strong absorption that is centered at approximately 400 nm. This absorption band does not red-shift significantly with increasing oligomer length, indicating that the conjugation length of the PPE-type oligomers is comparatively short. However, the oscillator strength of the π,π^* transition increases substantially with increasing oligomer length. Similar observations have been reported recently with structurally similar PPE oligomers and polymers [6–8].

Introduction of a metal ion at the bpy-diyl unit induces a red-shift of the lowest energy π,π^* transition. Thus, as seen in Figs. 3b and 3c, all of the metallated oligomers feature an absorption band with $\lambda_{\text{max}} \approx 440$ nm. The oscillator strength of this transition is relatively constant across the series of metallated oligomers, regardless of whether the metal center is $-\text{Re}(\text{CO})_3\text{Cl}$ or $-\text{Ru}(\text{bpy})_2^{2+}$. This conservation in the intensity and position of the transition indicates quite clearly that the band is comprised mainly of π,π^* type transitions based on the PPE oligomer. Furthermore, it seems likely that the low-energy π,π^* transition in the metallated oligomers originates from the oligomer “segment” that contains the metallated bipy-diyl unit. The red-shift that occurs upon metallation likely arises because the metal forces the bipyridine chromophore into a planar conformation, thereby increasing the effective conjugation length in the oligomer “core” [9].

An important feature with respect to the metallated oligomers is that the MLCT absorption bands are not discernable in the spectra, presumably because of their relatively low oscillator strength compared to that of the oligomer-based π,π^* transitions. Nonetheless, we believe that the MLCT transitions exist, and that they are merely obscured by the stronger, more intense π,π^* bands.

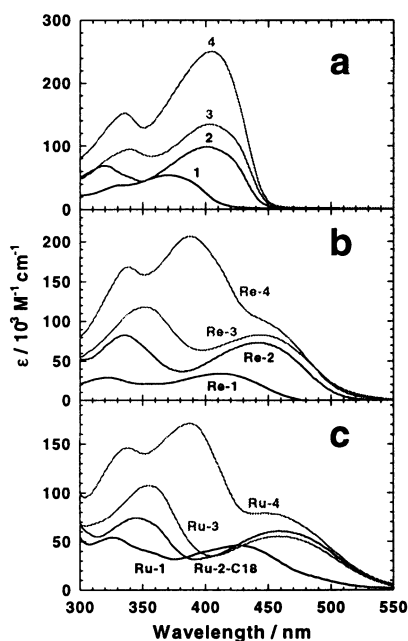


Fig. 3 UV–vis absorption spectra of PPE oligomers in THF solution. (a) **1–4**. (b) **Re-1–Re-4**. (c) **Ru-1–Ru-4**.

Photoluminescence spectroscopy

Figure 4 shows a series of variable temperature photoluminescence spectra obtained on the metallated oligomers, **Re-1–Re-4** (left panels) and **Ru-1–Ru-4** (right panels) as dilute solutions in 2-methyl-tetrahydrofuran. In all cases, the metallated oligomers feature photoluminescence in the red region of the visible spectrum (note wavelength axes in Fig. 4). The fluorescence characteristic of the free oligomers in the blue region of the spectrum is absent in the metallated oligomers. This fact indicates that the $^1\pi,\pi^*$ state of the PPE backbone is completely quenched by the transition-metal center.

First, we discuss the photoluminescence of the $-\text{Re}(\text{CO})_3\text{Cl}$ complexes (**Re-1–Re-4**, left panels of Fig. 4). In each case, the emission of the complexes is very weak—at ambient temperature the luminescence quantum yields are <0.001 . The photoluminescence of **Re-2–Re-4** is qualitatively similar, appearing as a broad band with $\lambda_{\text{max}} \approx 650$ nm. At cryogenic temperatures, the emission appears to consist of two overlapping bands; one band is structured with $\lambda_{\text{max}} \approx 650$ nm and a vibronic “shoulder” at $\lambda \approx 700$ nm, and the other band is broad and structureless with $\lambda_{\text{max}} \approx 580\text{--}590$ nm. The lifetimes of the photoluminescence for the $-\text{Re}(\text{CO})_3\text{Cl}$ complexes are approximately 150 ns at ambient temperature, and they increase up to several microseconds at cryogenic temperatures (lifetimes are shown in Fig. 4). We believe that the weak photoluminescence characteristic of the $-\text{Re}(\text{CO})_3\text{Cl}$ complexes may emanate from two excited states. The structured emission is believed to arise from the PPE oligomer-based $^3\pi,\pi^*$ state, and the broad structureless band arises from the $\text{Re} \rightarrow \text{bpy-diyI}$ MLCT state.

Next, we discuss the photoluminescence from the $-\text{Ru}(\text{bpy})_2^{2+}$ complexes (**Ru-1–Ru-4**), which are shown in the right panel of Fig. 4. First, in general, the photoluminescence from these complexes is considerably stronger than that for the $-\text{Re}(\text{CO})_3\text{Cl}$ complexes. The luminescence quantum yields for **Ru-1–Ru-4** at ambient temperature are in the range of 0.01–0.05. The emission spectra of the $-\text{Ru}(\text{bpy})_2^{2+}$ complexes all feature a vibronic structure that is very well resolved in the longer oligomers, especially **Ru-3**. The emission lifetimes are approximately 1 μs at ambient temperature and

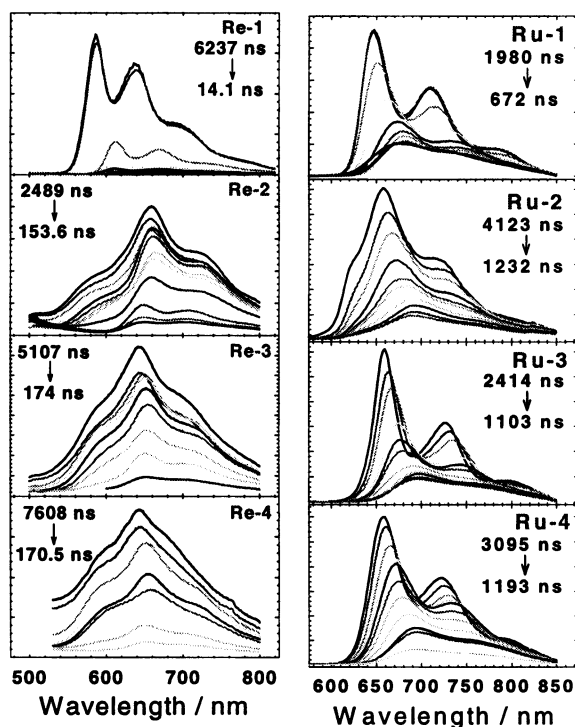


Fig. 4 Photoluminescence spectra of **Re-1–Re-4** (left panels) and **Ru-1–Ru-4** (right panels) in 2-methyltetrahydrofuran (80–298 K range). Decay times at 80 K and 298 K are shown in each panel.

increase to several μs at cryogenic temperatures (Fig. 4). Unlike the emission from the $-\text{Re}(\text{CO})_3\text{Cl}$ counterparts, the emission spectra of the $-\text{Ru}(\text{bpy})_2^{2+}$ complexes seem to be dominated by a single state, which is believed to be the $\text{Ru} \rightarrow \text{bpy-diyI MLCT}$ state.

CONCLUSION

This paper provides an overview of recent work that has focused on synthesis and photophysical characterization of metal–organic π -conjugated PPE oligomers. These compounds feature a rich manifold of excited states based on the π -conjugated electron systems, as well as charge-transfer excited states arising from the transition metal–bipyridine chromophores. In all of the metal–organic complexes, long-lived (i.e., ns– μs) photoluminescent excited states are observed. Careful analysis of the properties of these long-lived states suggests that they can be assigned either to the $^3\pi, \pi^*$ or $^3\text{MLCT}$ manifolds, or in special cases to an equilibrium distribution of these two excited states.

Future experiments are planned to use the fundamental information gained through this basic research to design new metal–organic materials having possible application in metal–organic LEDs, photodetectors, and luminescence-based oxygen sensors.

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