

## Photophysics of $\pi$ -Conjugated Polymers That Incorporate Metal to Ligand Charge Transfer Chromophores

Kevin D. Ley, C. Ed Whittle, Michael D. Bartberger, and Kirk S. Schanze\*

Department of Chemistry, University of Florida  
Gainesville, Florida 32611-7200

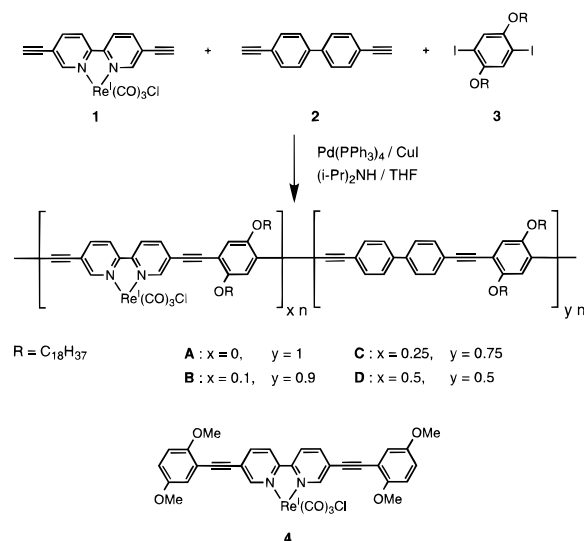
Received September 18, 1996  
Revised Manuscript Received February 10, 1997

Luminescent  $\pi$ -conjugated polymers have received attention owing to their potential for application in organic light-emitting diodes.<sup>1–4</sup> Considerable work has been carried out on all organic polymers; however, less attention has been given to  $\pi$ -conjugated polymers that incorporate a transition metal complex chromophore into the polymer backbone.<sup>5</sup> This is surprising given that charge transfer excited states of  $d^6$  transition metal complexes have been studied extensively owing to their unique properties which include tunable excited state energies, moderately efficient luminescence, and diverse excited state redox reactivity.<sup>6</sup>

We have initiated an effort to synthesize and characterize the excited state properties of soluble,  $\pi$ -conjugated polymers comprising the arylenethynylene architecture which incorporate  $d^6$  transition metals chelated to a 2,2'-bipyridyl site that is integral to the  $\pi$ -conjugated system. The present communication describes our initial findings on a series of polymers that contain the *fac*-(bpy)Re<sup>I</sup>(CO)<sub>3</sub>Cl (bpy = 2,2'-bipyridyl) chromophore. The Re(I) chromophore was selected because it features a well-defined Re  $\rightarrow$  bpy metal to ligand charge transfer (MLCT) excited state that is long-lived, luminescent, and redox active.<sup>7</sup>

Polymers **A–D** were synthesized from **1**, **2**, and **3** via Pd-mediated cross coupling (Scheme 1).<sup>3,8–10</sup> **A–D** vary in the mole ratio of **1** to **2** used in the coupling reaction mixtures, which ranged from 0:1 (**A**) to 1:1 (**D**).<sup>8</sup> FTIR spectra of **B**, **C**, and **D** confirm that the (bpy)Re<sup>I</sup>(CO)<sub>3</sub>Cl unit is incorporated into the polymers by the appearance of the  $\nu(1)$ ,  $\nu''$ , and  $\nu(2)$  carbonyl bands at 2024, 1930, and 1907 cm<sup>-1</sup>, respectively.<sup>11</sup> Quantitative analysis using the 2024 cm<sup>-1</sup> IR absorption band indicates that the mole fraction of (bpy)Re<sup>I</sup>(CO)<sub>3</sub>Cl containing

Scheme 1



repeat units ( $\chi_{Re}$ ) is 0.13, 0.25, and 0.33 in **B**, **C**, and **D**, respectively, in reasonable accord with the stoichiometry used in the polymerization reactions.<sup>10</sup>

Absorption spectra of **A–D** (Figure 1A) feature a strong band with  $\lambda_{max} \approx 398$  nm which is assigned to the  $\pi, \pi^*$  transition of the polymer backbone.<sup>3,4</sup> The presence of the (bpy)Re<sup>I</sup>(CO)<sub>3</sub>Cl unit in **B–D** is manifest by the appearance of a broad absorption band with  $\lambda_{max} \approx 460$  nm, the intensity of which increases (relative to the  $\pi, \pi^*$  transition) with  $\chi_{Re}$ . The long-wavelength absorption in the Re-containing polymers is very likely due to the  $d\pi(Re) \rightarrow \pi^*(poly)$  MLCT transition, where  $\pi^*(poly)$  refers to the lowest unoccupied  $\pi^*$  level of the polymer backbone. The delocalized nature of the  $\pi^*(poly)$  acceptor orbital in the polymers is evident by the significant red shift of the  $d\pi(Re) \rightarrow \pi^*(poly)$  transition relative to the position of the  $d\pi(Re) \rightarrow \pi^*(bpy)$  MLCT transition in model complex **4** ( $\lambda_{max} \approx 407$  nm).<sup>12</sup>

Excitation of THF solutions of **A–D** at 298 K into the  $\pi, \pi^*$  transition produces an intense emission at  $\lambda_{max} = 435$  nm (2.85 eV). This emission is similar to that observed from related arylenethynylene polymers and, on that basis it is assigned to the  $^1\pi, \pi^*$  fluorescence of the polymer backbone.<sup>3,4</sup> The quantum yield and lifetime of the fluorescence decrease with increasing  $\chi_{Re}$ , indicating that the metal chromophore quenches the  $^1\pi, \pi^*$  state (**A**,  $\Phi_f = 0.28$ ,  $\langle \tau \rangle = 1.1$  ns; **B**,  $\Phi_f = 0.16$ ,  $\langle \tau \rangle = 0.71$  ns; **C**,  $\Phi_f = 0.11$ ,  $\langle \tau \rangle = 0.44$  ns; **D**,  $\Phi_f = 0.073$ ,  $\langle \tau \rangle = 0.37$  ns).<sup>13</sup> The parallel decrease in  $\Phi_f$  and  $\langle \tau \rangle$  with increasing  $\chi_{Re}$  is consistent with a model in which the diffusing  $^1\pi, \pi^*$  exciton is dynamically quenched by (bpy)Re<sup>I</sup>(CO)<sub>3</sub>Cl traps. However, quenching of the  $^1\pi, \pi^*$  fluorescence is inefficient even when  $\chi_{Re}$  is large, suggesting that intrachain diffusion of the  $^1\pi, \pi^*$  exciton is slow compared to its lifetime and/or that trapping of the exciton by Re(I) sites is nonadiabatic.

Emission spectroscopy carried out at 80 K in 2-MTHF glasses provides additional information concerning the excited state

(12) Semiempirical molecular orbital calculations (Gaussian 94, AM1 parameter set) on model arylenethynylene oligomers that contain 5,5'-diethynyl-2,2'-bipyridyl units suggest that the  $\pi^*$  LUMO (the dominant acceptor orbital for the MLCT transition) is strongly delocalized over the adjacent dialkoxyphenylethynyl units and partly into the biphenylethynyl units. However, the biphenyl units are twisted  $\sim 40^\circ$  out-of-plane, and this disrupts the conjugation. LUMO eigenvalues and plots of the basis AO coefficients for four model oligomers are provided as Supporting Information.

(13) The fluorescence decays of the polymer solutions required two or three exponential terms for adequate simulation.<sup>10</sup> The reported values are median lifetimes computed from the multiexponential data according to  $\langle \tau \rangle = \sum \alpha_i \tau_i$ , where  $\alpha_i$  and  $\tau_i$  are, respectively, the normalized amplitude and lifetime of the  $i$ th decay component.

(1) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539. (b) Baigent, D. R.; Hamer, P. J.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1995**, *71*, 2175.

(2) (a) Green, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36. (b) Greenham, N. C.; Brown, A. R.; Bradley, D. D. C.; Friend, R. H. *Synth. Met.* **1993**, *55–57*, 4134.

(3) (a) Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886. (b) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593.

(4) Davey, A. P.; Elliott, S.; O'Connor, O.; Blau, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1433.

(5) (a) Peng, Z.; Yu, L. *J. Am. Chem. Soc.* **1996**, *118*, 3777. (b) Rasmussen, S. C.; Thompson, D. W.; Singh, V.; Petersen, J. D. *Inorg. Chem.* **1996**, *35*, 3449. (c) Maruyama, T.; Yamamoto, T. *Synth. Met.* **1995**, *69*, 553.

(6) (a) Meyer, T. J. *Prog. Inorg. Chem.* **1983**, *30*, 389. (b) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belsler, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

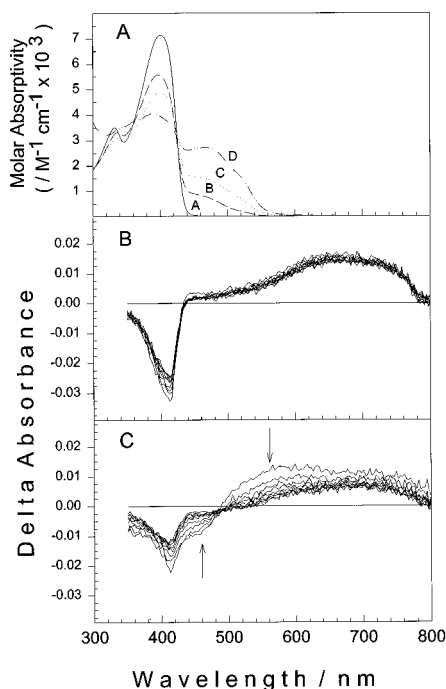
(7) (a) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (b) Schanze, K. S.; MacQueen, D. B.; Perkins, T. A.; Cabana, L. A. *Coord. Chem. Rev.* **1993**, *122*, 63.

(8) Subscripts  $x$  and  $y$  in Scheme 1 reflect the mole ratios of **1** and **2** used in the coupling reaction mixtures.

(9) Gel permeation chromatography of **A–D** (CHCl<sub>3</sub> solution, polystyrene standards) yielded weight average molecular weight ( $M_w$ ) values of 20 600, 29 600, 124 000, and 74 200, respectively. As expected for step growth polymerization, the polymers exhibit rather broad molecular weight distributions.

(10) Further details are available in the Supporting Information.

(11) Gamelin, D. R.; George, M. W.; Glyn, P.; Grevels, F.-W.; Johnson, F. P. A.; Klotzbücher, W.; Morrison, S. L.; Russell, G.; Schaffner, K.; Turner, J. J. *Inorg. Chem.* **1994**, *33*, 3246.



**Figure 1.** (A) Absorption spectra of polymers **A–D** in THF solution. The spectra are plotted normalized to the concentration of the repeat units in the polymers. Concentrations were determined using the weighted average molecular mass of the two repeat units in each sample. (B) Transient absorption difference spectrum of **A** in THF solution at delay times ranging from 20 to 500 ns following a 355 nm excitation pulse. (C) Transient absorption difference spectrum of **C** in THF solution at delay times ranging from 20 to 500 ns following a 355 nm excitation pulse. Arrows indicate the direction of the change in absorption with time.

properties of the Re-containing polymers. First, **A** exhibits only  $^1\pi,\pi^*$  fluorescence at 80 K. By contrast, in addition to the fluorescence, polymers **B**, **C**, and **D** exhibit two other emission bands at lower energy. One of the low-energy emissions is a sharp band at  $\lambda_{\max} = 643$  nm ( $E = 1.92$  eV,  $\text{fwhm} \approx 400$   $\text{cm}^{-1}$ ), and the other is a broad band with onset at 625 nm and with  $\lambda_{\max} \approx 700$  nm ( $1.98$  eV  $> E > 1.77$  eV). The intensity of these bands relative to the  $^1\pi,\pi^*$  fluorescence increases along the series **B**  $<$  **C**  $<$  **D**, suggesting that the luminescence is associated with the presence of the metal complex sites. We assign the sharp 1.92 eV emission to phosphorescence from the  $^3\pi,\pi^*$  state<sup>14–17</sup> and the broad luminescence band to the  $d\pi(\text{Re}) \rightarrow \pi^*$  (poly) MLCT state. Excitation spectra obtained while monitoring the 700 nm band assigned to the MLCT state establish that excitation of the  $^1\pi,\pi^*$  state produces the long-wavelength emission, confirming that  $^1\pi,\pi^* \rightarrow \text{MLCT}$  energy transfer occurs.

Nanosecond laser flash photolysis was used to probe the long-lived excited states produced by excitation of **A–D** and model complex **4** at 298 K in fluid solution. First, 355 nm excitation of polymer **A** in degassed solution produces a long-lived transient ( $\tau = 4$   $\mu\text{s}$ ) characterized by bleaching of the  $\pi,\pi^*$

absorption and a broad absorption band that extends from the mid-visible into the near-IR (Figure 1B). The transient is quenched by  $\text{O}_2$  ( $k_q \approx 10^9$   $\text{M}^{-1} \text{s}^{-1}$ ), and on that basis it is assigned to the  $^3\pi,\pi^*$  state of the polymer backbone.<sup>18</sup> Polymers **B–D** display a similar transient absorption for the  $^3\pi,\pi^*$  state, but in addition, these materials feature a short-lived transient absorption with an intensity that increases with  $\chi_{\text{Re}}$ . Figure 1C illustrates the time-resolved spectrum of polymer **C**, which is representative for the Re-containing polymers. At early times the spectrum features bleaching of both the  $\pi,\pi^*$  and  $d\pi(\text{Re}) \rightarrow \pi^*$  (poly) absorptions along with enhanced absorption in the 500–700 nm region. The early time spectrum evolves ( $\tau = 100$  ns) into the spectrum of the  $^3\pi,\pi^*$  state ( $\tau = 7$   $\mu\text{s}$ ). The short-lived transient absorption in the spectrum of polymer **C** is assigned to the  $d\pi(\text{Re}) \rightarrow \pi^*$  (poly) MLCT state, an assignment which is supported by the observation of a very similar excited state difference absorption spectrum for model complex **4**. Quantitative transient absorption experiments indicate that the yield of the long-lived  $^3\pi,\pi^*$  state decreases along the series **A**  $>$  **B**  $>$  **C**  $>$  **D**.<sup>10</sup> Interestingly, the relative decrease in the yield of the  $^3\pi,\pi^*$  state along the series closely parallels the relative decreases in  $\Phi_{\text{fl}}$  and  $\langle \tau \rangle$ .<sup>10</sup> This correspondence indicates that the decreasing yield of the  $^3\pi,\pi^*$  state with increasing  $\chi_{\text{Re}}$  is due to quenching of  $^1\pi,\pi^*$  by the metal complex and that MLCT  $\rightarrow$   $^3\pi,\pi^*$  energy transfer does not occur.<sup>17</sup>

The Re-containing polymers display photophysical properties characteristic of the two chromophoric units comprising the structure. The unusual feature is that the two chromophores appear not to be strongly coupled. Thus, although energy transfer occurs from  $^1\pi,\pi^*$  to the  $d\pi(\text{Re}) \rightarrow \pi^*$  (poly) MLCT state, the latter does not sensitize formation of the  $^3\pi,\pi^*$  exciton. Furthermore,  $^1\pi,\pi^* \rightarrow \text{MLCT}$  energy transfer occurs with modest efficiency even when  $\chi_{\text{Re}}$  is large. One explanation for the weak communication between the two chromophoric units may be that the copolymers consist of blocks comprising mainly **1** and **3** and blocks comprising mainly **2** and **3**. An alternative possibility is that the unusual photophysics arise because energy transfer between the  $\pi,\pi^*$  excitons and the metal-localized MLCT states is inefficient. Förster dipole–dipole energy transfer from  $^1\pi,\pi^*$  to MLCT may be inefficient because intrachain migration of the  $^1\pi,\pi^*$  exciton is slow compared to its lifetime and/or because the transition dipoles for the  $^1\pi,\pi^*$  and MLCT states are exactly perpendicular. Inefficient energy transfer between the  $^3\pi,\pi^*$  exciton and the MLCT manifold is likely due to the fact that the two excited states are close in energy. Slow internal conversion between intraligand  $^3\pi,\pi^*$  and MLCT states has been reported to occur in polypyridyl  $d^6$  metal complexes when the intraligand and MLCT states are nearly degenerate.<sup>19</sup>

**Acknowledgment.** We gratefully acknowledge the National Science Foundation for support of this work (Grant No. CHE-9401620).

**Supporting Information Available:** Experimental procedures and compound characterization; tabular listings of quantitative FTIR analysis and fluorescence lifetime and relative triplet yield data; figures illustrating FTIR spectra of **B**, **C**, **D**, and **4**, and low-temperature emission spectra of **A**, **B**, **D**, and **4**; and results of semiempirical molecular orbital calculations on model aryleneethynylene oligomers (18 pages). See any current masthead page for ordering and Internet access instructions.

JA963278T

(14) The 1.92 eV luminescence assigned to phosphorescence from the  $^3\pi,\pi^*$  state is very similar in energy and band shape compared to the phosphorescence of other  $\pi$ -conjugated polymers (very few reports are available).<sup>15</sup> Furthermore, the singlet–triplet splitting (2.85–1.92 eV) is consistent with singlet–triplet splittings for pyridyl-containing PPP and PPV type polymers calculated by semiempirical theory.<sup>16</sup>

(15) (a) Wittman, H. F.; Fuhrmann, K.; Friend, R. H.; Khan, M. S.; Lewis, J. *Synth. Met.* **1993**, 55–57, 56. (b) Xu, B.; Holdcroft, S. *Adv. Mater.* **1994**, 6, 325.

(16) Blatchford, J. W.; Gustafson, T. L.; Epstein, A. J. *J. Chem. Phys.* **1996**, 105, 9214.

(17) The observation of  $\pi,\pi^*$  phosphorescence in the Re-containing polymers is likely due to an increase in the rate of  $T_0 \rightarrow S_0$  radiative decay due to the heavy atom effect.

(18) The  $^3\pi,\pi^*$  excited state of a poly(*p*-phenylenevinylene) features a very similar transient absorption spectrum; see: Scurlock, R. D.; Wang, B.; Ogilby, P. R.; Sheats, J. R.; Clough, R. L. *J. Am. Chem. Soc.* **1995**, 117, 10194.

(19) (a) Sacksteder, L.; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1990**, 29, 4335. (b) Taffarel, E.; Chirayil, S.; Kim, W. Y.; Thummel, R. P.; Schmehl, R. H. *Inorg. Chem.* **1996**, 35, 2127.