COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Solvent tuned excited state configuration mixing in a π-conjugated metal–organic oligomer†

Shengxia Liu and Kirk S. Schanze*
Department of Chemistry, University of Florida, Gainesville, FL, 32611-7200, USA.
E-mail: kschanze@chem.ufl.edu

Received (in West Lafayette, IN, USA) 1st March 2004, Accepted 29th April 2004
First published as an Advance Article on the web 1st June 2004

The photophysical properties of a π-conjugated metal–organic oligomer vary smoothly with solvent composition. The variation is believed to arise from solvent-tuned configuration mixing of $^3\pi,\pi^*$ and ^{3}MLCT levels.

There is current interest in the optical properties of π-conjugated oligomers and polymers that contain transition metals that interact strongly with the π-conjugated electronic system.[1] These materials have potential for application in light-emitting diodes, solar cells, photoconductors and luminescent sensors.[2] In order to optimize these materials for opto-electronic applications, it is necessary to understand the factors that control their optical properties. To achieve this objective, we are exploring the excited state properties of π-conjugated oligomers and polymers that contain complexes of Re(I), Ru(II), Ir(III) and Pt(II) as part of the π-conjugated system.[3] These materials exhibit long-lived, luminescent triplet excited states that are derived either from π,π* transitions localized on the π-conjugated segment, or metal-to-ligand charge transfer transitions localized on the metal complex chromophores (*e.g.*, $^3\pi,\pi^*$ and ^{3}MLCT, respectively).

We recently designed several diblock π-conjugated oligomers that are end-capped with metal–bipyridine chromophores with the objective of determining whether it is possible to decouple the $^3\pi,\pi^*$ excitations from the ^{3}MLCT states that are localized on the metal chromophores. As part of this work T1–Ru (structure below) was prepared and its photophysical properties characterized. This oligomer features a π-conjugated core segment consisting of a 3-alkylthiophene that is linked to short oligo(arylene ethynylene) (OAE) segments. The oligomer is capped on both ends with (L)Ru(bpy)$_2^{2+}$ chromophores. It was anticipated that in this system there would be an energetically low lying $^3\pi,\pi^*$ state localized on the three ring π-system (phenyl–C≡C–thienyl–C≡C–phenyl) in the core of the oligomer. Because of the relatively large distance between the oligomer core segment and the (L)Ru(bpy)$_2^{2+}$ chromophores, it was anticipated that the ^{3}MLCT and $^3\pi,\pi^*$ states might be decoupled, and therefore could be separately observed by photoluminescence and/or transient absorption spectroscopy.

The present communication describes the effect of solvent on the excited state properties of T1–Ru.† As described in detail below, photoluminescence and transient absorption spectroscopy (PL and TA, respectively) suggest that in THF solution the lowest excited state is ^{3}MLCT, whereas in CH_2Cl_2 the oligomer-based $^3\pi,\pi^*$ state is lowest. The remarkable observation is that the excited state properties of T1–Ru vary smoothly in THF-CH_2Cl_2 solvent mixtures, from ^{3}MLCT in THF to $^3\pi,\pi^*$ CH_2Cl_2, i.e., there is not a distinct state "crossover" which occurs as the solvent is varied. This finding strongly suggests that when the two excited state manifolds are in close in energy they undergo configuration mixing,[4] and the photophysical properties that result are a composite of the two contributing configurations.

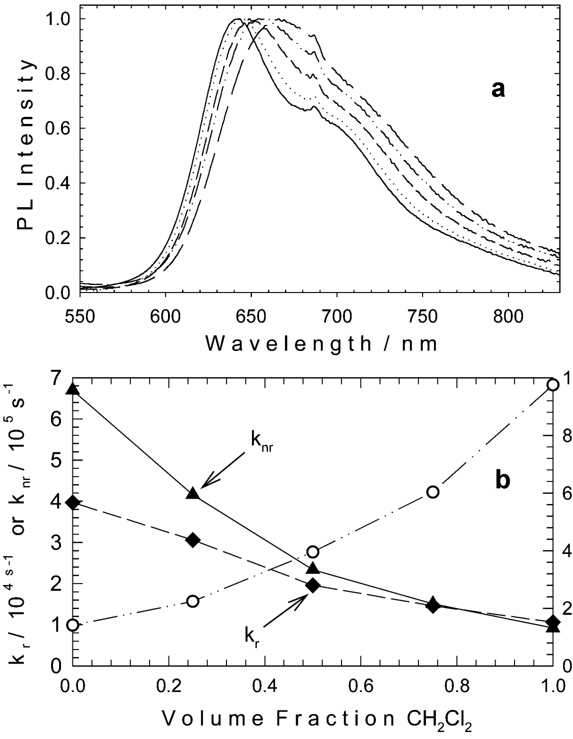
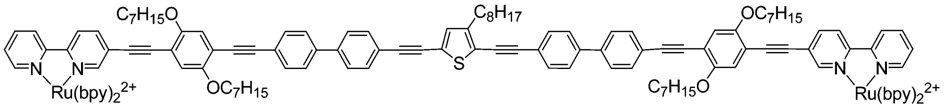


Fig. 1 (a) Photoluminescence spectra of T1–Ru in CH_2Cl_2, THF and CH_2Cl_2 solvent mixtures. Volume fraction of CH_2Cl_2 (in order of decreasing λ_{max}): 0, 0.25, 0.50, 0.75 and 1.0. (b) Plot showing k_{nr}, k_r and τ_{em} for T1–Ru in CH_2Cl_2/THF solvent mixtures. Note that the scale for k_r is 10^4 s^{-1}, whereas that for k_{nr} is 10^5 s^{-1}.

The absorption spectrum of T1–Ru is dominated by an intense transition with λ_{max} = 399 nm in THF and 392 nm in CH_2Cl_2 (ε_{max} in THF is 88,400 $M^{-1}cm^{-1}$). This transition arises from the long-axis polarized π,π* transitions of the OAE chromophore. The MLCT absorption for the (L)Ru^{II}(bpy)$_2^{2+}$ chromophores appears as a shoulder on the red side of the more intense π,π* band. In solution at ambient temperature T1–Ru displays a moderately intense red photoluminescence. While exploring the properties of the luminescence, it was noticed that its wavelength maximum ($\lambda_{max,PL}$) and bandshape is moderately solvent dependent (Fig. 1a). In particular, in CH_2Cl_2 $\lambda_{max,PL}$ = 640 nm and the emission features a well-defined vibronic shoulder, whereas in THF $\lambda_{max,PL}$ = 659 nm and the band is noticeably broader and the vibronic structure is less well-defined. On the basis of previous work, we suspected that the solvent-induced change in $\lambda_{max,PL}$ and band-shape might arise due to a switch in the lowest excited state.[3c,d] The blue-shifted, structured emission observed in CH_2Cl_2 has the characteristics



T1-Ru

---

† Electronic supplementary information (ESI) available: complete details of the synthesis and characterization of T1–Ru. See http://www.rsc.org/suppdata/cc/b4/b403084b/

DOI: 10.1039/b403084b

expected for $^3\pi,\pi^*$ luminescence, while the broad, structureless emission seen in THF is consistent with ^{3}MLCT emission. As shown in Fig. 1a, the solvent effect on $\lambda_{\mathrm{max,PL}}$ and the emission bandshape occurs progressively as the composition of the CH_2Cl_2/THF solvent mixture is varied.

More insight into the solvent effect on the photophysics of T1–Ru comes from examination of the radiative and non-radiative decay rates (k_r and k_{nr}, respectively) determined by measuring the emission lifetime and quantum yield (τ_{em} and ϕ_{em}, respectively) of the complex as a function of solvent composition.‡ Fig. 2 shows plots of τ_{em}, k_r and k_{nr} *vs.* volume fraction of CH_2Cl_2 (f_{MeCl}) in the THF/CH_2Cl_2 solvent mixture. It is evident that these parameters vary smoothly with solvent composition. The lifetime increases monotonically from $\approx$ 1 μs in THF to $\approx$ 10 μs in CH_2Cl_2. The increase in lifetime arises because k_{nr} and k_r decrease with increasing f_{MeCl}. Importantly, the decay parameters observed for T1–Ru in THF are comparable to those of Ru–polypyridine complexes in which ^{3}MLCT is the lowest excited state (*e.g.*, for $Ru(bpy)_3{}^{2+}$ in CH_2Cl_2: τ_{em} = 488 ns, $k_r = 5.9 \times 10^4\ s^{-1}$ and $k_{nr} = 3.5 \times 10^5\ s^{-1}$)[5] By contrast, the values of the decay parameters observed for the complex in CH_2Cl_2 solution are comparable to those of transition metal complexes in which the lowest excited state is based on an intraligand $^3\pi,\pi^*$ configuration.[6] Notably, for T1–Ru in CH_2Cl_2 solution $k_r < 10^4\ s^{-1}$; the low radiative rate constant suggests a decreased contribution of spin–orbit coupling, which likely arises due to a decrease in the contribution of metal-based orbitals in the excited state configuration (*i.e.*, less ^{3}MLCT character).

Taken together, the emission spectra and decay parameters strongly suggest that the nature of the emissive excited state in T1–Ru varies smoothly from ^{3}MLCT in THF solution to $^3\pi,\pi^*$ in CH_2Cl_2. Additional evidence for this transition comes from UV/visible/near-IR transient absorption (TA) spectroscopy experiments on T1–Ru in THF, CH_2Cl_2 and in 1 : 1 THF/CH_2Cl_2 (Fig. 2). In each case strong TA is observed and its decay kinetics match those of the emission, indicating that the TA arises from the excited state. It is notable that there are significant differences among the TA spectra in the three solvent compositions. In CH_2Cl_2 the transient bleach is broad (*i.e.*, through the entire ground state π,π^* absorption band) and the broad transient absorption extends from 500 nm out to 1600 nm in the near-IR. By contrast, in THF the bleach is narrower (*i.e.*, only the red side of the ground state absorption is bleached) and the transient absorption is mainly in the visible and features two distinct maxima at 510 and 645 nm. In the solvent mixture, the TA spectrum is intermediate to those in the pure solvents. In previous work we have characterized the TA difference spectra of metal-containing π-conjugated oligomers,[3] and on the basis of this work we conclude that the TA difference spectrum of T1–Ru in CH_2Cl_2 is characteristic of an oligomer-based $^3\pi,\pi^*$ excited state, while that observed in THF is characteristic of a ^{3}MLCT state localized on one of the $(L)Ru(bpy)_2{}^{2+}$ units. It is important to emphasize that the TA difference spectrum of T1–Ru in CH_2Cl_2 exhibits a broad near-IR excited state absorption that is believed to be the signature of the $^3\pi,\pi^*$ exciton in OAE systems.[3a,b,d,6] By contrast, the narrow transient bleach, and structured visible transient absorption bands are characteristic of an MLCT configuration.[3c,d]

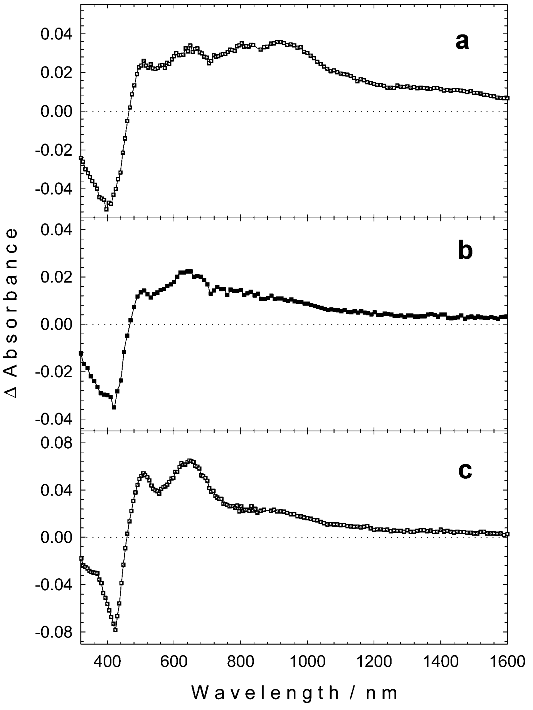


Fig. 2 Transient absorption difference spectra of T1–Ru obtained 50 ns following 355 nm excitation. Solvent: (a) CH_2Cl_2; (b) CH_2Cl_2 : THF (1 : 1 v:v); (c) THF.

All of the available evidence points to the fact that for T1–Ru in THF the long lived excited state is ^{3}MLCT, whereas in CH_2Cl_2 it is an OAE based $^3\pi,\pi^*$ state. The most interesting feature, however, is that in intermediate solvent mixtures, the photophysical properties vary smoothly between those of pure ^{3}MLCT and $^3\pi,\pi^*$ character. This effect is believed to arise because the lowest excited state in these complexes is derived from configuration mixing between states having pure ^{3}MLCT and OAE-based $^3\pi,\pi^*$ character. It is likely that variation of solvent changes the energy gap between the two pure configurations, leading to variation in the extent of the configuration mixing. This finding is significant in the context of transition metal containing π-conjugated systems, because it clearly demonstrates that the photophysical properties of the systems will be a composite of those of the π-conjugated system and the metal-complex localized charge transfer states. In addition, it suggests that when the two excited state manifolds have similar energies the photophysical properties of the system may be strongly dependent upon the environment.

We acknowledge the US National Science Foundation for support of this work (grant No. CHE-0211252).

Notes and references

‡ For all solvent compositions the emission and transient absorption decays are strictly first-order (*i.e.*, they follow single exponential kinetics).

1 R. P. Kingsborough and T. M. Swager, *Prog. Inorg. Chem.*, 1999, **48**, 123.
2 (*a*) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2001, **123**, 4304; (*b*) Q. Wang and L. Yu, *J. Am. Chem. Soc.*, 2000, **122**, 11806.
3 (*a*) K. A. Walters, K. D. Ley, C. S. P. Cavalaheiro, S. E. Miller, D. Gosztola, M. R. Wasielewski, A. P. Bussandri, H. van Willigen and K. S. Schanze, *J. Am. Chem. Soc.*, 2001, **123**, 8329; (*b*) K. A. Walters, D. M. Dattelbaum, K. D. Ley, J. R. Schoonover, T. J. Meyer and K. S. Schanze, *Chem. Commun.*, 2001, 1834; (*c*) Y. Wang, S. Liu, M. R. Pinto, D. M. Dattelbaum, J. R. Schoonover and K. S. Schanze, *J. Phys. Chem. A*, 2001, **105**, 11118; (*d*) K. D. Glusac, S. Jiang and K. S. Schanze, *Chem. Commun.*, 2002, 2504; (*e*) Y. Liu, Y. Li and K. S. Schanze, *J. Photochem. Photobiol. C: Photochem. Rev.*, 2002, **3**, 1.
4 Y. Ohsawa, S. Sprouse, K. A. King, M. K. DeArmond, K. W. Hanck and R. J. Watts, *J. Phys. Chem.*, 1987, **91**, 1047.
5 J. V. Caspar and T. J. Meyer, *J. Am. Chem. Soc.*, 1983, **105**, 5583.
6 (*a*) J. R. Shaw and R. H. Schmehl, *J. Am. Chem. Soc.*, 1991, **113**, 389; (*b*) J. A. Simon, S. L. Curry, R. H. Schmehl, T. R. Schatz, P. Piotrowiak, X. Jin and R. P. Thummel, *J. Am. Chem. Soc.*, 1997, **119**, 11012.