

Amplified quenching in metal–organic conjugated polymers†

Yao Liu, Shujun Jiang and Kirk S. Schanze*

Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, FL, USA.

E-mail: kschanze@chem.ufl.edu

Received (in Purdue, IN, USA) 22nd November 2002, Accepted 6th January 2003

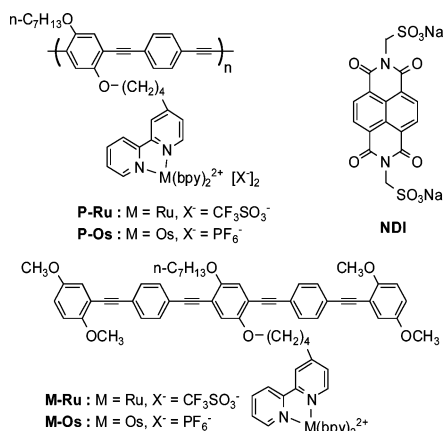
First published as an Advance Article on the web 11th February 2003

The luminescence from conjugated polyelectrolytes that contain pendant metal complex units is quenched very efficiently by oppositely charged electron acceptors.

The fluorescence of conjugated polyelectrolytes (CPEs) is quenched by charged electron and energy acceptors with remarkable efficiency.^{1–3} Stern–Volmer (SV) constants as large as 10^8 M^{-1} have been reported for CPE quenching, and studies of corresponding monomer model compounds show that amplification factors of 10^4 are typical. The amplified quenching effect has been attributed to two factors.^{1–4} First, the charged quenchers are believed to complex to the CPE chains by ion-pair interactions, effectively increasing the local concentration of the quencher. Second, the singlet exciton is believed to diffuse extremely rapidly along the CPE chain, an effect which increases the ‘quenching radius’ of the quencher.³

We have an interest in amplified quenching of CPEs in which the luminescent exciton is a triplet spin-state. Theoretical and experimental studies indicate that the triplet exciton in conjugated polymers is more strongly confined than the singlet.^{5,6} Owing to this difference, it is possible that the triplet exciton will diffuse more slowly than the singlet, and this may be reflected by attenuation of the amplified quenching.

In the present communication we report the results of photophysical and excited-state quenching studies of metal–organic polymers **P-Ru** and **P-Os** along with the corresponding monomeric model compounds **M-Ru** and **M-Os**. The metal–organic polymers are cationic polyelectrolytes because of the dipositive charge on the metal complex units. The polymers display a long-lived luminescent excited state that is quenched very efficiently by anionic electron transfer quenchers. Comparison of the Stern–Volmer (SV) quenching of the polymers with the corresponding monomers reveals that the polymers are quenched 75 and 20 times more efficiently than the models, for **M = Ru** and **Os**, respectively.



The polymers and model compounds were prepared by Sonogashira coupling reactions⁷ and the new materials were fully characterized by NMR and mass spectrometry (for the models).[‡] Photophysical data for the metal–organic materials are provided in Table 1. Polymers **P-Ru** and **P-Os** display intense absorption bands at 425 nm due to the long-axis polarized π, π^* transition of the PPE backbone. Weaker absorptions in the 450–500 nm region are due to $M \rightarrow 2,2'$ -bipyridine (bpy) metal-to-ligand charge transfer (MLCT). **P-Os** also features a weak ‘tailing’ band (530–700 nm) due to the spin-forbidden $S \rightarrow T$ MLCT transition. The absorption of the model compounds is very similar, Fig. 1, except that the π, π^* bands arising from the oligo(phenylene ethynylene) (OPEs) are slightly blue shifted relative to the polymers. The MLCT bands of the $M(\text{bpy})_3^{2+}$ chromophores are clearly visible in Fig. 1 (marked by arrows).

The Ru-containing materials feature a broad luminescence with $\lambda_{\text{max}} = 642 \text{ nm}$. This emission is believed to arise from the $\text{Ru} \rightarrow \text{bpy}$ MLCT excited state. The MLCT assignment is

Table 1 Photophysical properties and Stern–Volmer constants^a

	UV-vis $\lambda_{\text{max}}/\text{nm}$ (log ϵ)	$\lambda_{\text{max}}^{\text{em}}/\text{nm}$	ϕ_{em} (%)	$\tau_{\text{em}}/\mu\text{s}$	$K_{\text{SV}}/10^6 \text{ M}^{-1}$
P-Ru	425 (4.65)	642	1.0	1.2 ^b	1.6
	480 (4.10)				
M-Ru	390 (4.91)	643	6.0	1.3	0.021
	457 (4.20)				
P-Os	427 (4.85)	771	0.23	0.031 ^b	0.37
	487 (4.11)				
M-Os	382 (4.76)	766	0.28	0.033	0.018
	487 (4.04)				

^a All data for argon purged DMF solutions. ^b Multiexponential decay, median lifetime is reported (ref. 10b). ^c Stern–Volmer quenching by NDI.

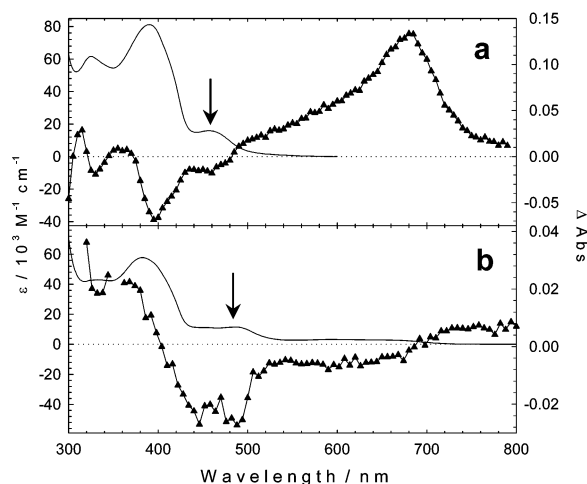


Fig. 1 Ground state absorption (solid lines, scale at left) and transient absorption (symbols, scale at right) spectra. TA spectra obtained immediately following 10 ns, 355 nm excitation pulse. (a) **M-Ru**; (b) **M-Os**.

† Electronic supplementary information (ESI) available: complete details concerning the synthesis and characterization of the new materials, NMR and electrospray mass spectra, absorption and emission spectra of **P-Ru** and **P-Os**, and Stern–Volmer plots. See <http://www.rsc.org/suppdata/cc/b2/b211575a/>

supported by the fact that the emission quantum yield (ϕ_{em}) and lifetime (τ_{em}) in **M-Ru** and **P-Ru** are similar to that of other Ru–polypyridyl systems.⁸ A red emission is also observed from **P-Os** and **M-Os**, but in this case it is shifted to considerably lower energy (≈ 770 nm). This shift is consistent with the emission emanating from an Os→bpy MLCT excited state, and this assignment is supported by the considerably reduced ϕ_{em} and τ_{em} values which are typical for Os–polypyridyl systems.⁹

While the UV absorption and luminescence properties of the metal–organic materials suggest that the lowest excited state in all cases arises from a M→bpy MLCT state, transient absorption (TA) spectroscopy provides clear evidence that the $^3\pi,\pi$ state from the PPE segment is also involved in the photophysics of **P-Ru** and **M-Ru**. Fig. 1 compares the TA difference spectra acquired on **M-Ru** and **M-Os** immediately following the 10 ns, 355 nm excitation pulse. (The TA spectra of the corresponding polymers are similar.) As shown in Fig. 1(a) the difference spectrum of **M-Ru** is characterized by a broad and intense absorption with $\lambda_{max} \approx 680$ nm, along with bleaching of the ground state absorption bands in the 400–500 nm region. The difference absorption features decay uniformly with $\tau = 1.2$ μ s, in agreement with the emission lifetime. The strong TA absorption band at 680 nm and bleach at 400 nm are clearly due to the $^3\pi,\pi^*$ state which is localized on the OPE segment. However, there is also bleaching in the ground-state Ru→bpy MLCT absorption band (marked by arrow) and excited state absorption in the 350–370 nm region. The latter features are hallmarks of the MLCT state.⁸ The MLCT TA features, coupled with the observation of MLCT emission, strongly suggest that in **M-Ru** (and by inference also in **P-Ru**), the MLCT and $^3\pi,\pi^*$ states are in equilibrium. This is consistent with previous studies which indicate that the $^3\pi,\pi^*$ state of OPEs and PPEs is 1.90 eV (650 nm), which is very close to the energy of the MLCT state.¹⁰

The TA difference spectrum of **M-Os** shown in Fig. 1(b) is essentially identical to that of the parent complex, Os(bpy)₃²⁺ which indicates that for the Os-containing materials the MLCT state is the only state populated at long times following excitation. The MLCT assignment for the TA spectrum is supported by the fact that the transient decays with $\tau = 27$ ns. The OPE triplet state is not populated because in the Os-systems the MLCT state is too low in energy.

Steady-state emission quenching was carried out on the polymers and model complexes ($c = 1$ μ M) using the anionic electron acceptor NDI, and the K_{SV} values are listed in Table 1. Interestingly, NDI quenches the polymers much more efficiently than the corresponding monomers. In addition, **P-Ru** is quenched approximately 4-fold more efficiently than **P-Os**, which reflects the fact that the excited state lifetime of the former is longer. Quenching studies carried out using time resolved emission demonstrate that for both polymers dynamic quenching is significant (see ESI†). The fact that ion-pairing between the polymers and NDI plays an important role in the quenching process is illustrated by the fact that **P-Ru** is quenched efficiently by anthraquinone-2,6-disulfonate ($K_{SV} = 1.4 \times 10^6$ M⁻¹), but much less efficiently by the neutral quencher 1,8-dichloroanthraquinone ($K_{SV} = 3.8 \times 10^4$ M⁻¹).

It is interesting to consider the mechanism for the amplified quenching. Fig. 2 shows a cartoon in which several possible mechanisms are considered. In all of the mechanisms it is

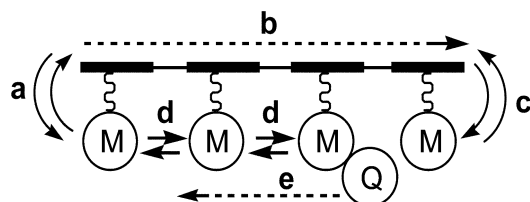


Fig. 2 Schematic diagram of exciton diffusion. See text for details.

assumed that the anionic quencher (Q) is ion-paired to a metal complex unit (M). Quenching involves diffusion of the exciton to a quencher ‘trap’ site (see below) and/or diffusion of the quencher along the chain (path e) to the exciton. We cannot rule out the latter pathway, and in any event it is likely to play a role, since earlier work has shown that polyelectrolytes accelerate reactions by allowing oppositely charged reactants to diffuse to a reaction site by ‘directed diffusion’.¹¹

Two possible mechanisms for exciton diffusion along the polymer chains can be envisioned for **P-Ru**. In the first (path a→b→c), the triplet exciton transfers from a Ru(bpy)₃²⁺ unit to the PPE chain (by Dexter exchange transfer), the triplet exciton diffuses along the backbone, and then undergoes exchange transfer to another Ru(bpy)₃²⁺. The second mechanism involves ‘self-exchange hopping’ of the MLCT exciton between adjacent Ru(bpy)₃²⁺ chromophores (path d). Indeed, in recent work on non-conjugated polymers that contain pendant Ru(bpy)₃²⁺ and Os(bpy)₃²⁺ moieties, it was shown that such MLCT state self-exchange hopping occurs, $k \approx 10^9$ s⁻¹.¹²

The exciton diffusion mechanism that involves the PPE $^3\pi,\pi^*$ state (a→b→c) is infeasible in **P-Os**, because in this case the MLCT state is at too low an energy to equilibrate with the PPE-based triplet state. Because amplified quenching also occurs in **P-Os**, we conclude that the most likely mechanism for exciton diffusion in both polymers involves self-exchange hopping between the M(bpy)₃²⁺ chromophores.

In summary, the results demonstrate that amplified quenching occurs in metal–organic polymers where the lowest excited state has triplet spin character. Analysis of the quenching data suggests that diffusion of the $^3\pi,\pi^*$ state along the PPE backbone is not kinetically competitive with alternate pathways for quenching, including self-exchange exciton hopping and/or directed diffusion of the quencher along the polyelectrolyte chain. Comparison of these results with those obtained on fluorescent CPes, where amplified quenching involves a singlet exciton,^{1–3} hints that diffusion of the triplet exciton is slow.

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

Notes and references

‡ The polymers were soluble only in DMF and DMSO solution, and due to the limited solubility molecular weight determination by GPC was not possible. GPC analysis of model PPE polymers synthesized under identical conditions as **P-Ru** and **P-Os** reproducibly showed $M_n \approx 20$ kD ($X_n \approx 20$, ca. 20 metal units and 40 phenylene rings).

- L. Chen, D. W. McBranch, H.-L. Wang, R. Helgeson, F. Wudl and D. G. Whitten, *Proc. Natl. Acad. Sci. USA*, 1999, **96**, 12287.
- (a) B. S. Harrison, M. B. Ramey, J. R. Reynolds and K. S. Schanze, *J. Am. Chem. Soc.*, 2000, **122**, 8561; (b) C. Tan, M. R. Pinto and K. S. Schanze, *Chem. Commun.*, 2002, 446.
- D. L. Wang, J. Wang, D. Moses, G. C. Bazan and A. J. Heeger, *Langmuir*, 2001, **17**, 1262.
- T. M. Swager, *Acc. Chem. Res.*, 1998, **31**, 201.
- (a) D. Beljonne, H. F. Wittmann, A. Köhler, S. Graham, M. Younus, J. Lewis, P. R. Raithby, M. S. Khan, R. H. Friend and J. L. Brédas, *J. Chem. Phys.*, 1996, **105**, 3868; (b) A. Köhler, J. S. Wilson, R. H. Friend, M. K. Al-Suti, M. S. Khan, A. Gerhard and H. Bässler, *J. Chem. Phys.*, 2002, **116**, 9457.
- Y. Liu, S. Jiang, K. Glusac, D. H. Powell, D. F. Anderson and K. S. Schanze, *J. Am. Chem. Soc.*, 2002, **124**, 12412.
- U. W. E. Bunz, *Chem. Rev.*, 2000, **100**, 1605.
- A. Juris, V. Balzani, F. Barigelli, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.
- E. M. Kober, J. V. Caspar, R. S. Lumpkin and T. J. Meyer, *J. Phys. Chem.*, 1986, **90**, 3722.
- (a) K. A. Walters, K. D. Ley and K. S. Schanze, *Chem. Commun.*, 1998, **10**, 1115; (b) 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.
- S. K. C. Elmroth and S. J. Lippard, *Inorg. Chem.*, 1995, **34**, 5234.
- C. N. Fleming, K. A. Maxwell, J. M. DeSimone, T. J. Meyer and J. M. Papanikolas, *J. Am. Chem. Soc.*, 2001, **123**, 10336.