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Preferential solvation of an ILCT excited state in bis(terpyridine–phenylene–vinylene) Zn(II) complexes

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The excited state of terpyridine derivatives of phenylene–vinylene fragments chelating Zn(II) show a strong solvatochromism (up to 56 nm) upon preferential solvation by polar solvents of an intraligand charge transfer state.

A large number of poly- and oligo-phenylene vinylene (PPV and OPV) derivatives have been prepared that fluoresce from a singlet π–π* excited state with a variety of colors. PPVs and OPVs have potential as emitting chromophores and electron transport layers in organic light emitting devices (OLEDs).[1] Modification of OPVs with electron accepting moieties at the terminus causes the emitting excited state to acquire charge transfer character, thus broadening the emission range of the material.[2] In addition, Wasielewski *et al.* have shown that OPV and PPV derivatives with covalently attached 2,2′-bipyridyl (attached in the 4 position) have emission that is sensitive to the presence of metal ions.[3] Coordination of particular ions (*e.g.* Zn(II)) serves to increase electron delocalization on the polymer backbone, causing a red shift in the emission. In these systems the emissive excited state of the Zn(II) complex was also suggested to have charge transfer character. In this work we wish to report the luminescence behavior of the terpyridine substituted OPV derivatives **tvvpp** and **tvvOR** (Fig. 1). The Zn(II) complexes of the ligands exhibit clearly defined charge transfer luminescence that is highly solvent dependent. In addition, both complexes exhibit evidence for significant preferential solvation of the charge transfer state in mixed polar (PS)/nonpolar (NPS) solvents.

The two ligands **tvvpp** and **tvvOR**,[4] that have been chosen for this study, differ in that the number and location of alkoxy substituents, factors important in influencing the energy[5] and transition dipole of potential charge transfer transitions localized on the ligand. Both ligands are fluorescent with the emission maximum of **tvvpp** (λ_{max}^{em} = 509 nm in chloroform (Chl)) being at higher wavelength than that of **tvvOR** (494 nm).

The bis-chelated Zn(II) complexes of the **tvvpp** and **tvvOR** ligands, **Zn(tvvpp)$_2^{2+}$** and **Zn(tvvOR)$_2^{2+}$**, are prepared *in situ* by adding an excess of $Zn(H_3CCOO)_2$ to the ligands in chloroform. ^1H NMR spectra allow definitive characterization of the complexes.[6] The lowest-energy absorption band of the free ligand is red-shifted upon complexation by Zn(II): for **tvvpp** the maximum in chloroform shifts from 409 to 420 nm and for **tvvOR** from 377 to 388 nm. This complexation is also reflected by changes in the emission spectra. The emission maximum is strongly red-shifted for **tvvpp**, from 509 to 572 nm (in chloroform), and for **tvvOR**, from 494 to 556 nm. In addition, the vibrational structure of the emission of **tvvpp** and **tvvOR** completely disappears upon complexation by Zn(II). The emission quantum yields are high and essentially the same for the two Zn(II) complexes.

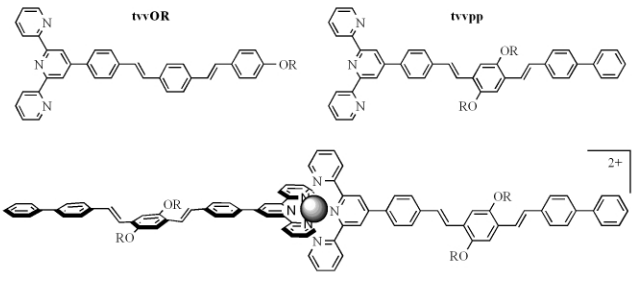

Fig. 1 Representation of (top) **tvvOR** and **tvvpp** ligands, R = $-C_8H_{17}$; (bottom) **Zn(tvvpp)$_2^{2+}$**.

The luminescence of both of the Zn(II) complexes exhibits significant solvatochromism. The addition of fractional amounts of higher polarity solvents to chloroform solutions of **Zn(tvvpp)$_2^{2+}$** or **Zn(tvvOR)$_2^{2+}$** induces a large red shift in the luminescence of the complexes. The ground state absorption exhibits only small changes.[7] For example, when dichloromethane (DCM) is added to a chloroform solution of either complex, the emission maximum shifts steadily as the mole fraction x of DCM is increased (Fig. 2). This shift is linear up to x = 0.8, where it reaches the maximum observed in pure DCM. The shifts are substantial and reach 41 nm for **Zn(tvvpp)$_2^{2+}$** (from 578 to 619 nm) and 43 nm for **Zn(tvvOR)$_2^{2+}$** (from 554 to 597 nm).

The observed behavior is consistent with a change in the orbital parentage of the emitting excited state of each ligand upon complexation of Zn(II). In the absence of Zn(II), the structured luminescence of the ligands is very similar in energy and vibronic spacing to that of other known oligo-phenylenevinylene derivatives and is assigned as arising from a π–π* state.[8] The unstructured absorption and emission of the Zn(II) complexes and the significant solvatochromism suggest the emitting state has significant charge transfer character. Since a Zn(II) to terpyridine metal-to-ligand charge transfer can be

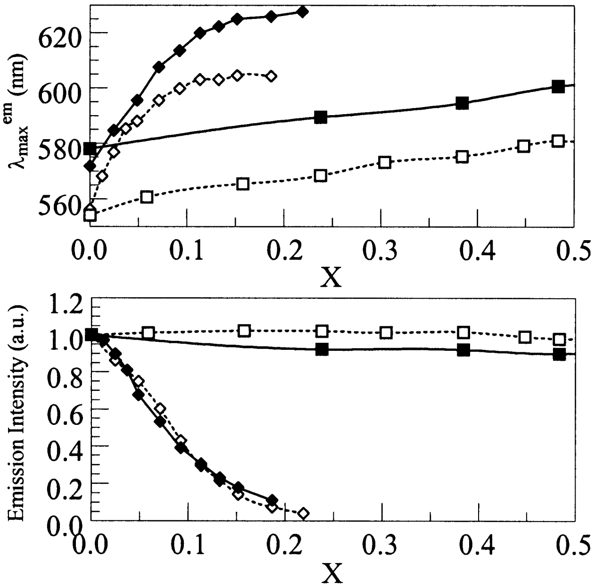

Fig. 2 Emission properties of **Zn(tvvpp)$_2^{2+}$** (full symbols) and **Zn(tvvOR)$_2^{2+}$** (open symbols) as a function of the mole fraction x, in chloroform, of acetonitrile (diamonds; non linear variation) and dichloromethane (squares; linear variation): (a) emission maxima; (b) emission intensities.

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Table 1 Shifts of λ_{max}^{em} at $x = 0.1$ ($\Delta\lambda_{0.1}$), and maximum shifts ($\Delta\lambda_{max}$) obtained for **Zn(tvvpp)$_2^{2+}$** and **Zn(tvvOR)$_2^{2+}$** in different solvent mixtures; $x_{1/2}$ is the value of x at which half of the variation of λ_{max}^{em} has occurred.

	Zn(tvvpp)$_2^{2+}$			**Zn(tvvOR)$_2^{2+}$**		
	$\Delta\lambda_{max}$/ nm	$\Delta\lambda_{0.1}$/ nm	$x_{1/2}$	$\Delta\lambda_{max}$/ nm	$\Delta\lambda_{0.1}$/ nm	$x_{1/2}$
Chl/MeCN	56	45	0.06	48	45	0.03
Chl/DMSO	50	47	0.03	43	43	0.03
Chl/Me$_3$CCN	38	30	0.04	43	39	0.03
Chl/MeOH	54	34	0.07	47	29	0.06
Chl/DCM	41	5	0.43	43	9	0.38

excluded, it is more likely that the observed behavior arises from an intra-ligand charge transfer (^{1}ILCT) state, occurring from the phenylene–vinylene moiety to the Zn(II) coordinated terpyridine. Consistent with this is the expected positive shift in the one-electron reduction potential of terpyridine ligands upon coordination of Zn(II). In addition, a similar ILCT assignment has been postulated recently for Zn(II) bipyridyl pyrene complexes.[9] Solvatochromic ILCT states have also been reported for OPVs containing a central alkoxyphenyl moiety and electron withdrawing goups on the peripheral phenyls.[10]

Strikingly different behavior is observed when more polar solvents are added (see Table 1). Fig. 2 illustrates the case where acetonitrile (ACN) is added to chloroform. No further changes in the emission maximum are observed above $x_{ACN} = 0.2$ and the total emission shift is 56 nm for **Zn(tvvpp)$_2^{2+}$** and 48 nm for **Zn(tvvOR)$_2^{2+}$**. It is remarkable that more than 85% of the variation in wavelength occurs from $x = 0$ to 0.11. A very strong decrease in emission intensity at λ_{max} occurs with a very similar trend. This prevents analysis of the emission at higher molar fractions of AN and other polar solvents. Similar results have been obtained for various organic dyes in nonpolar/polar solvent mixtures (NPS/PS) and the behavior has been attributed to *preferential solvation* of the excited state by the PS.[11–14] To observe preferential solvation, a change of the dipole moment of the solute (in our case the Zn(II) complex) upon excitation is required. Both **Zn(tvvpp)$_2^{2+}$** and **Zn(tvvOR)$_2^{2+}$** do not have net dipole moments in the ground state since local dipole moments associated with the ligands oppose one another. In solvent mixtures, the complex in the ground state is thus solvated by NPS and PS molecules in proportions reflecting the molar fraction, and the absorption is only weakly affected.

Formation of an emissive charge transfer state in these systems explains the observed solvatochromism of the emission. When the Zn(II) complex is excited, the symmetry is lost since a dipole change occurs on only one of the ligands due to a charge transfer from the alkoxyphenyl moiety to the terpyridine. In order to stabilize the excited state dipole, which has a lifetime of 2.5 ns in chloroform, PS molecules diffuse to the newly formed dipole. The degree of PS solvation of the excited state that can occur depends on the excited state lifetime (diffusion distance) and the concentration of PS in solution. The relation between mole fraction and emission maximum clearly shows that preferential solvation occurs and that the proportion PS/NPS in the solvation sphere does not merely represent that of the bulk solution (Fig. 3). The ratio PS/NPS in the solvation sphere changes the emission properties of both **Zn(tvvpp)$_2^{2+}$** and **Zn(tvvOR)$_2^{2+}$**. The emission maximum increases with the number of PS molecules in the solvation sphere, and the observed spectra are probably a superposition of several emission spectra due to different degrees of solvation by PS and NPS molecules. In fact, the full width at half maximum of the emission bands increases as the mole fraction of PS increases.

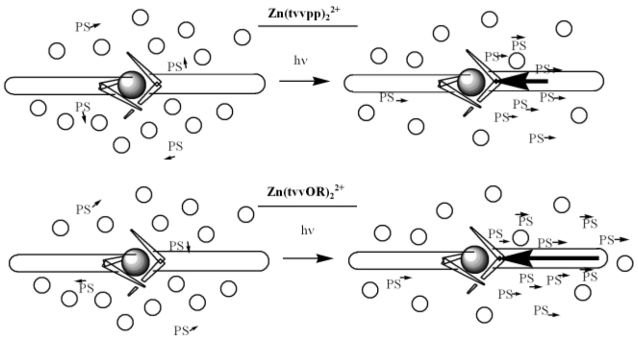

Fig. 3 Schematic representation of the preferential solvation of **Zn(tvvpp)$_2^{2+}$** (top) and **Zn(tvvOR)$_2^{2+}$** in chloroform (circles)/polar solvent (PS) mixtures upon excitation. The black arrow represents the dipole due to the alkoxyphenyl to terpyridine ILCT.

A final point relates to the relative magnitude of the excited state dipole of the two species. The slope of λ_{max} *vs.* x is larger for **Zn(tvvOR)$_2^{2+}$** than **Zn(tvvpp)$_2^{2+}$**. This suggests that preferential solvation is more important for **Zn(tvvOR)$_2^{2+}$**. The implication is that the excited state dipole is larger for **Zn(tvvOR)$_2^{2+}$**. This can be reasonably associated with a charge transfer state involving alkoxyphenyl to terpyridine charge transfer.

In conclusion, the ILCT excited state of **Zn(tpy-PV)$_2^{2+}$** complexes exhibits preferential solvation of unexpected magnitude with a variety of polar solvents. This behavior may be useful in the design of medium sensitive luminescent sensors and potentially in the development of electroluminescent chromophores having emission that can be tuned by subtle changes in the medium.

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