

The Dependence of Benzo-15-Crown-5 Ether-Containing Oligo Paraphenylene Vinylene (CE-OPV) Emission Upon Complexation with Metal Ions in Solution

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The effects of metal salts (NaCl, CaCl₂·2H₂O, EuCl₃·6H₂O and Eu(OAc)₃) on the steady state and time resolved fluorescence behaviour of poly(para phenylene vinylene) oligomers containing benzo-15-crown-5 ether units (CE-OPV) have been investigated. The presence of EuCl₃ causes a significant (8–9 fold) increase in the fluorescence emission intensity of the OPV segments, as compared to pure CE-OPV, in 99:1 methanol/chloroform solution and a small (~9 nm) red shift in the emission maximum. The presence of Na⁺ or Ca²⁺ results in less marked increases in fluorescence intensity compared to Eu³⁺. In the presence of Eu³⁺ and Na⁺, the fluorescence intensity increases approximately linearly with metal ion concentration up to a metal ion/CE-OPV molar ratio of ~10. The emission enhancement is not related to a simple 1:1 (CE-OPV:metal ion) complex formation process. In contrast, in acetonitrile, CE-OPV shows complex fluorescence *quenching* behaviour as a function of EuCl₃ concentration. This solvent dependence suggests that the emission changes with metal concentration are related to the formation of charge-transferred complexes. The marked changes in fluorescence quantum yield of the PPV backbone due to complexation with metal ions makes CE-OPV a sensitive fluorescent probe for metal ions, or may be exploited for improving the quantum yield of PPV-based devices.

KEY WORDS: Emission enhancement; fluorescence quenching; phenylene vinylene emission; metal ion sensing.

INTRODUCTION

Fluorescence detection is widely used as a transduction method in chemical and/or biosensing applications due to the inherent sensitivity of luminescence techniques. Fluorescence-based sensing applications can be established by exploiting changes in emission properties including intensity, variations in emission wavelength, excited state lifetimes and energy transfer efficiency [1].

The detection mechanism in fluorescence-based optical sensors most commonly involves monitoring a reduction in fluorescence intensity caused by the interaction between the fluorophore and the analyte. For such purposes, materials with maximised luminescence quantum yields are required to provide a high initial signal that is reduced in the presence of the analyte to improve detection limits.

Conjugated polymer-based chemical sensors, including those based on poly(paraphenylene vinylene)s (PPV), are evolving as new sensor systems of high sensitivity [2–5]. Advantages of using conjugated polymeric segments as the emissive species, as compared to single, simple organic probe molecules, include enhancement of chemosensor sensitivity by “wiring chemosensors in series” [6], the ability to tune excitation and emission wavelength with conjugation length, possible exploitation of electro- as

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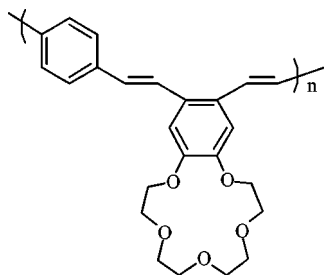
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well as photo-luminescence, the variety of transduction methods that modify the emission and conductivity [7], ease of synthesis and the ability to make sensor films. Some PPV-based conjugated polymers, however, do not have particularly high luminescent quantum yields. In addition, aggregation-induced fluorescence quenching has been reported by various researchers, in MEH-PPV-based systems [8–16]. Nguyen *et al.* [13,14] reported that the memory of the extent of aggregation of MEH-PPV in solution, responsible for luminescence quenching, is carried into the cast film. Therefore it is necessary to design a system with enhanced fluorescence efficiency.

The ability of crown ethers to complex with metal ions has been exploited, through chromic or emissive changes in dyes with crown ethers attached [17,18]. Crown ethers can also be substituted into PPV oligomers [19] and polymers [20] and serve at least two useful purposes of relevance to the present discussion. Firstly, through the incorporation of the crown ether groups, the conjugated polymer may be made soluble in common solvents, and secondly, crown ether groups are able to form complexes with metal ions [21]. Winkler *et al.* [19] reported the synthesis of PPV oligomers with benzo-15-crown-5 ether substituents (CE-OPV- Scheme I). Fluorescence efficiencies of 28–52% from chloroform solutions of copolymers prepared using varying proportions of PPV and benzo-15-crown-5 ether-containing PPV co-monomers, are much higher than those of homopolymers consisting of the CE-OPV monomeric unit alone, but lower than the quantum efficiencies of the homopolymer of PPV without the crown ether group [20].

As mentioned above fluorescence-based sensors usually involve the quenching of the fluorophore's emission. A more attractive method for many purposes would be to have an enhancement of emission intensity in the presence of the analyte, however, among the fluorescence based chemical sensors, only a few examples of low molecular weight fluorescence probes that contain crown ether groups showing fluorescence enhancement with metal ions have been reported [22,23].



Scheme 1. Structure of CE-OPV.

Materials with maximised luminescence quantum yields are also required for improved brightness in PPV-based photoluminescence devices (e.g. displays). It has been hypothesized that maximum attainable electroluminescent device efficiency is directly proportional to the fluorescence quantum yield, with a correction factor for spin statistics of injected carrier recombination [24–26].

In this work we report an example of a PPV-based crown ether-containing polymer that exhibits a marked enhancement of the polymer backbone emission in the presence of metal ions such as Eu^{3+} , Na^+ and Ca^{2+} . This is the first report on enhanced fluorescence of solutions of benzo-15-crown-5 ether-containing PPV oligomers upon metal complexation. The marked increase in fluorescence quantum yield of the PPV backbone may be exploited for both metal sensing applications or improving the quantum yield of PPV-based devices.

EXPERIMENTAL DETAILS

Materials

The synthesis of CE-OPV has been reported by Winkler *et al.* [19] and the samples used in the present study were sourced from the original synthesis batch. Typical values of $M_w = 3,900 \text{ g}\cdot\text{mol}^{-1}$ and $M_w/M_n \sim 1.8$ (corresponding to ~ 5.5 monomeric units per oligomer chain) were reported [19]. The structure of CE-OPV is given in Scheme I.

The solvents methanol, chloroform and acetonitrile, benzo 15-crown-5 ether (Aldrich) and metal salts sodium chloride (NaCl (BDH)), calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (BDH)), europium (III) chloride ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (Aldrich)), europium (III) acetate ($\text{Eu}(\text{OAc})_3$ (Aldrich)) and ammonium chloride (NH_4Cl (BDH)) were of AR grade and were used without further purification. These salts were selected for our studies since the cation radii approximately match the radius of the cavity of benzo 15-crown-5 ether to achieve a stable complex [21] (ionic radii of $\text{Eu}^{3+} = 0.95 \text{ \AA}$, $\text{Ca}^{2+} = 1.0 \text{ \AA}$ and $\text{Na}^+ = 1.02 \text{ \AA}$ and the radius of cavity of 15-crown-5 ether is $0.86\text{--}0.92 \text{ \AA}$). Furthermore, this choice of salts allows the effect of the anion and cation to be assessed.

For all the experiments the metal salts were weighed accurately and dissolved in known volumes of the appropriate solvent. The solutions of oligomer were prepared by dissolving appropriate amounts of these materials in 1 ml of chloroform and further diluting to 100 mL using methanol. For experiments in acetonitrile, CE-OPV was dissolved directly in the solvent. The concentrations of CE-OPV solutions used in these studies were based on the molecular weights of monomeric units present in

the oligomer. UV-Vis absorption measurements were carried out on a UV-3101 spectrophotometer from Shimadzu. Photoluminescence (PL) measurements were recorded on a LS-50 spectrophotometer from Perkin Elmer. The excitation wavelength used in all the steady-state photoluminescence studies was 370 nm. Corrected emission spectra were recorded on a Varian Eclipse fluorimeter with correction curves generated both by use of a calibrated lamp method [27] and by using the published corrected emission intensities of *N,N'*-dimethylamino-*m*-nitrobenzene and 4-dimethylamino-4'-nitrostilbene [28].

Time-resolved photoluminescence decay studies were carried out using the time correlated single photon counting method. The excitation source employed was the frequency doubled output of a mode-locked titanium:sapphire laser (Coherent Mira 900F, $\lambda_{\text{exc}} = 400$ nm, $\lambda_{\text{em}} = 480$ nm) pumped by a 12.5 W Ar⁺ laser. This system provided pulses of approximately 90 fs duration at 76 MHz. The laser pulse repetition rate was reduced to 4 MHz with a home made single pass pulse picker based on a TeO₂ Bragg Cell driven by a CAMAC CD 5000 electronics unit. The detection electronics have been described elsewhere [29].

The quantum yield of CE-OPV in 99:1 methanol-chloroform (non-degassed), determined relative to a degassed solution of 9,10 dimethyl anthracene in ethanol at 20°C following excitation at 350 nm ($\phi_f \sim 0.89$) [30], was found to be $\sim 6\%$. It should be noted that this fluorescence quantum yield is in marked disagreement with the value of 80% reported previously [19]. The previ-

ously reported value is clearly erroneous, and this may be due to the use of an impure 9,10-diphenylanthracene reference sample or use of a non-degassed reference solution. The relative fluorescence quantum yield of CE-OPV in methanol is 60% that in acetonitrile when excited at 370 nm.

Solutions of different metal ion to CE-OPV concentration ratios were prepared by varying the concentration of metal ions. The concentration of CE-OPV oligomer was kept constant to ensure that the change in photoluminescence intensity was due only to complexation of the crown ether with the metal ion and not CE-OPV concentration effects. All the measurements were carried out in solution at room temperature (25°C) and without degassing of solutions.

RESULTS AND DISCUSSION

The absorption and emission spectra of CE-OPV in MEOH:chloroform mixture are very similar to those reported in acetonitrile [19], although marked spectral shifts are observed in polymer film matrices. No significant differences can be seen in the UV-visible spectra of CE-OPV in the absence or presence of the metal ions investigated (Na⁺, Ca²⁺ and Eu³⁺) in solution, although slight changes in the absorption intensities are observed in the low wavelength region (Fig. 1). The lack of significant spectral difference as a function of metal ion indicates that the complexation of the metal ion into the crown ether ring is not

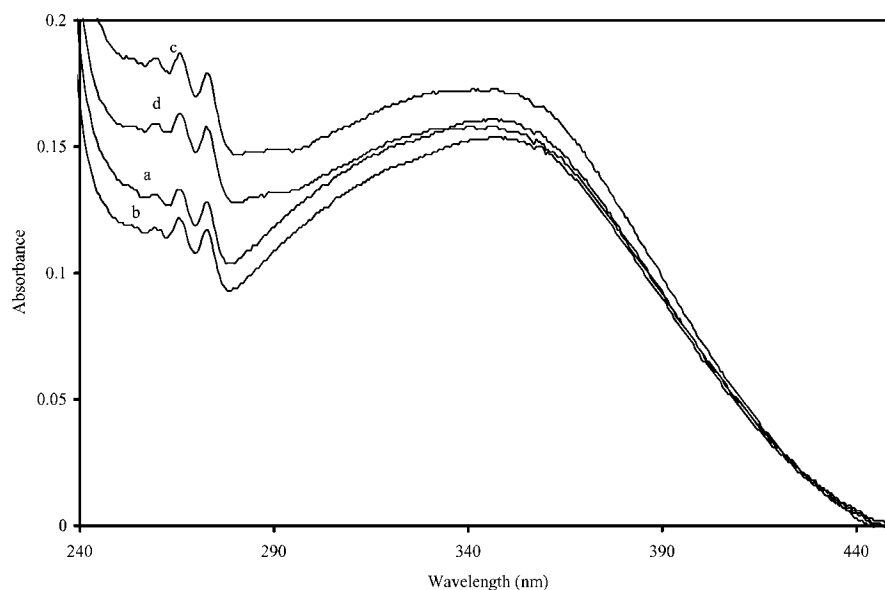


Fig. 1. UV-visible absorption spectra of CE-OPV (3.3×10^{-5} M) in the absence (a) and presence of metal ions (in a 1:4 molar ratio) ((b) Na⁺, (c) Ca²⁺ and (d) Eu³⁺).

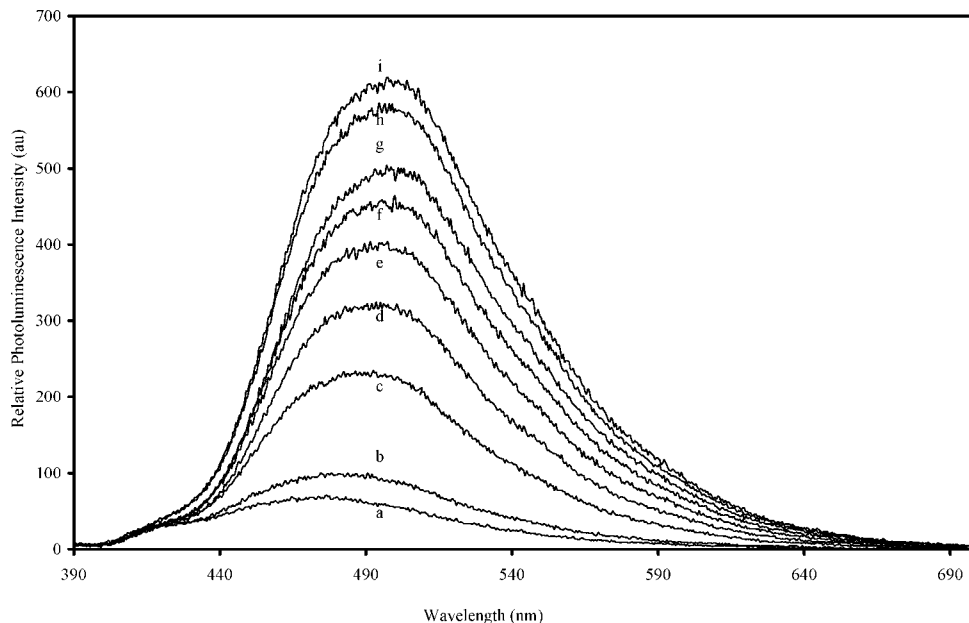


Fig. 2. Photoluminescence spectra of CE-OPV (8.13×10^{-7} M) in the presence of Eu^{3+} ions as a function of $[\text{Eu}^{3+}]/[\text{CE-OPV}]$ mole ratio: (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, (f) 6, (g) 7, (h) 9 and (i) 10.

perturbing the conjugation length of the conjugated backbone to any large degree.

Figure 2 shows the steady state photoluminescence spectra of CE-OPV in the presence of EuCl_3 at various $\text{Eu}^{3+}/\text{CE-OPV}$ molar ratios. It can be seen that the relative photoluminescence intensity of CE-OPV increases markedly as a function of the metal ion to CE-OPV molar ratio. Metals ions are more commonly observed to quench

rather than enhance emission, and it is this unusual observation that forms the basis behind the potential of CE-OPV for metal ion sensing applications and for photoluminescence enhancement of the polymer.

The relative photoluminescence intensity versus the metal ion to CE-OPV concentration ratio is plotted in Fig. 3 for the three metal chlorides studied in this work (Na^+ , Ca^{2+} and Eu^{3+}). It can be seen that the relative

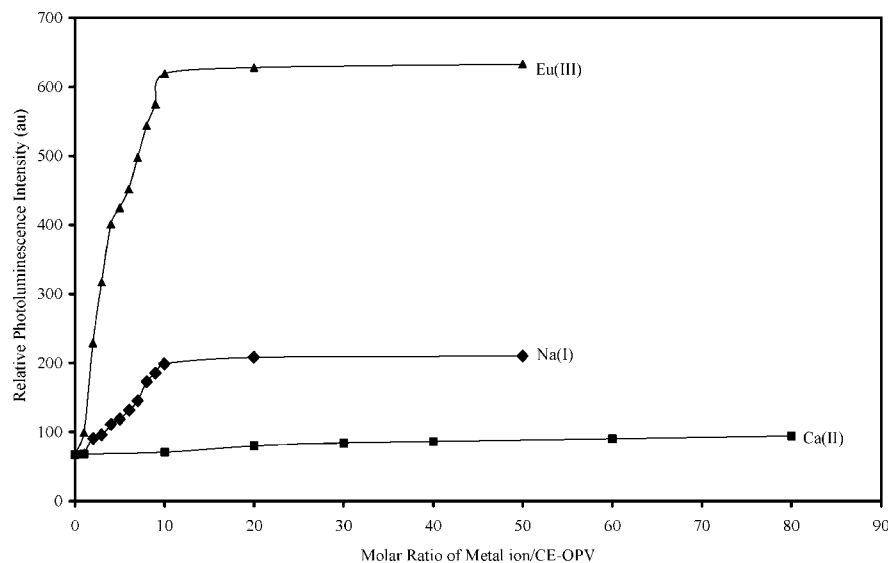


Fig. 3. Variation of relative photoluminescence intensity as a function of $[\text{metal ion}]/[\text{CE-OPV}]$ molar ratio at 8.13×10^{-7} M CE-OPV.

photoluminescence intensity of CE-OPV increases as the metal chloride to CE-OPV concentration ratio increased up to ~ 10 and attains saturation level at higher metal chloride to CE-OPV concentration ratios. It is also seen that the enhancement of luminescence is more marked with Eu^{3+} than the other two ions. The presence of the metal chloride also causes a slight (~ 9 nm) red shift in the photoluminescence emission maximum, despite the complexation of CE-OPV with metal ions not showing any significant change in UV-visible absorption spectrum.

It should be noted that the Eu^{3+} ion in methanol is itself luminescent far to the red of the CE-OPV emission (with a sharp peak at ~ 616 nm) [31]. However, such a peak is not visible in even the corrected emission spectra at the Eu^{3+} concentrations ($< 10^{-4}$ M) employed in our studies (Fig. 2) showing that the particular crown ether present in the current CE-OPV polymer is not an effective photoluminescent sensitizer for Eu^{3+} chloride in solution [31]. This is in contrast to the work of Valeur and co-workers in which efficient transfer of incident light energy was found to occur from quinoxalione and diquinoxalione 15-crown-5 and 18-crown-6 crown ethers to lanthanide ions [32]. Also, we have not observed any increase in

photoluminescence in the related polymer, MEH-PPV or from the benzo-15-crown-5 ether moiety, in the presence of Eu^{3+} , Ca^{2+} or Na^{+} ions. These observations, together with the fact that complexation of CE-OPV with metal ions does not cause any significant change in the UV-Visible absorption spectrum, indicate that the photoluminescence of CE-OPV in the presence of metal ions still originates from the conjugated segments only, and that the observed increase in photoluminescence is associated with interactions between the metal ion-crown ether complex and the conjugated backbone.

The CE-OPV polymer was also tested for luminescence enhancement with different counter ions. As shown in Fig. 4, the addition of Eu-acetate rather than EuCl_3 did produce an increase in PPV emission but this increase was less concentration dependent than that observed for EuCl_3 . The effect of other charged species such as NH_4^+ (which is known to be complexed by 15-crown-5 ether) in the absence of Eu^{3+} was also investigated. The change in fluorescence intensity as a function of NH_4^+ concentration is insignificant.

Examples of enhanced emission upon metal ion complexation have been reported, but are rare. The following equation is discussed by Lakowicz [28] and has been

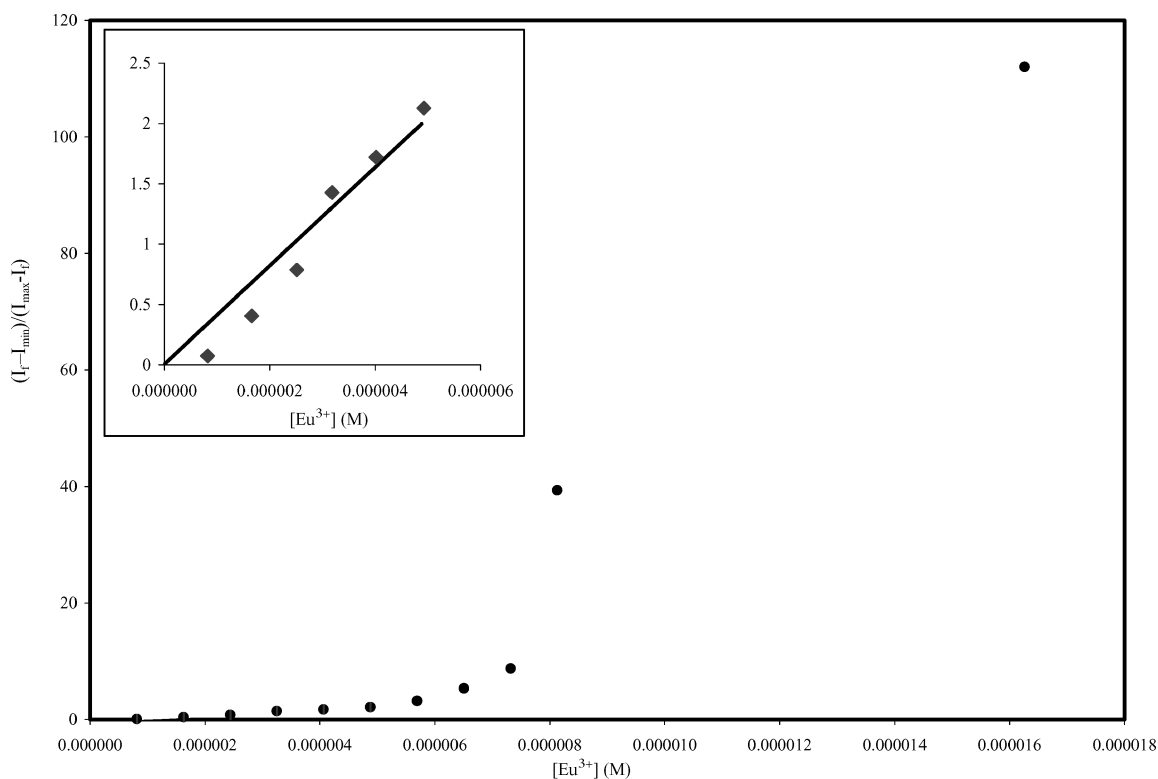


Fig. 4. Plot of $(I_f - I_{\min})/(I_{\max} - I_f)$ vs $[\text{Eu}^{3+}]$ (M) (Equation 1) at $[\text{CE-OPV}] = 8.13 \times 10^{-7}$ M. Inset shows a linear fit to the low Eu^{3+} concentration data.

employed to model cases of enhanced luminescence upon complexation [22].

$$(I_f - I_{\min}) / (I_{\max} - I_f) = K[M] \quad (1)$$

where I_f is the observed photoluminescence intensity at a given concentration of metal ion ($[M]$), I_{\max} is the saturated photoluminescence intensity, I_{\min} is the photoluminescence intensity of CE-OPV in the absence of any metal ion and K is the complexation equilibrium constant. Fig. 4 is a representative plot of the ratio of intensities given in Equation 1 versus Eu^{3+} concentration. The strong deviation of the data in Fig. 4 from linearity suggests that the enhancement mechanism in CE-OPV is not a simple 1:1 complex formation, as is assumed in the derivation of Equation 1. The approximately linear, low Eu^{3+} concentration region (Fig. 4) provides a complexation equilibrium constant of $\sim 4.1 \times 10^5 \text{ M}^{-1}$ whereas at higher Eu^{3+} concentrations (above $\sim 7 \mu\text{M}$) this increases to $\sim 10^7 \text{ M}^{-1}$.

These findings are in contrast with the behaviour reported by Kollmannsberger *et al.* [22] for crown ether-bound dyes in the presence of various alkali and alkaline-earth metal ions. These authors reported complexation constants of between ~ 160 – $25,000 \text{ M}^{-1}$ and suggested that in all cases studied complexes of well-defined 1:1 stoichiometry were formed. Non-linear fluorescence behaviour has been observed recently in the fluores-

cence *quenching* of the photoluminescence of conjugated macromolecules [33,34]. In that work static quenching by charge transfer was assumed to dominate and a linear region at low quencher concentration provided Stern-Volmer quenching constants of $\sim 10^6 \text{ M}^{-1}$. At higher quencher concentrations the Stern-Volmer plot exhibited strong up-sloping non-linear behaviour that was referred to as a “superlinear” region, implying the onset of an additional quenching process that was described by a “sphere-of-action” mechanism accounting for the fact that at high concentrations there are always quencher molecules within a charge transfer distance from one of the conjugated molecules. A similar mechanism may be operating here but is unclear why an enhancement in photoluminescence is observed in the CE-OPV in methanol case compared to fluorescence quenching in the work of Heeger *et al.* [33,34].

Time-resolved photoluminescence measurements can help differentiate between static and dynamic emission quenching (or enhancement) processes. Dynamic processes result in a change in the steady-state emission intensity that is accompanied by a proportional change in the integrated area under the emission decay profile, whereas static processes result in emission intensity changes that are not accompanied by such a change. Time-resolved photoluminescence decay profiles from CE-OPV ($8.1 \times 10^{-7} \text{ M}$) in the absence and presence of EuCl_3 ($\text{EuCl}_3/\text{CE-OPV}$ molar ratios 0–10) are shown in Fig. 5.

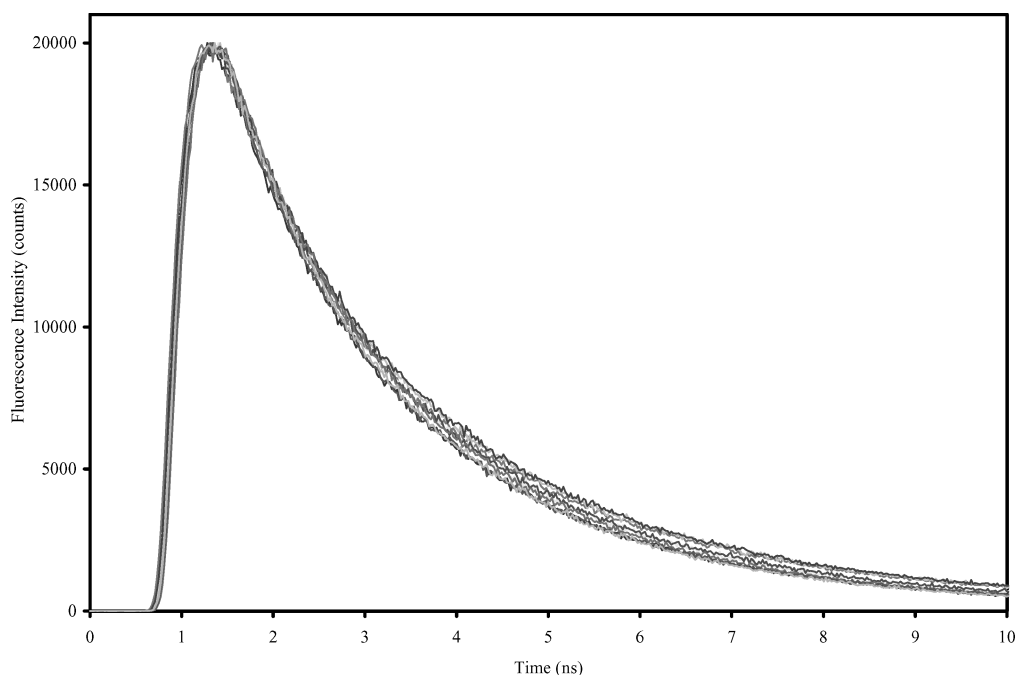


Fig. 5. Time-resolved photoluminescence decay profiles of CE-OPV ($8.1 \times 10^{-7} \text{ M}$) in the absence and presence of Eu^{3+} with $[\text{Eu}^{3+}]/(\text{CE-OPV})$ molar ratios of 0–10.

The emission does not decay in a simple exponential manner, but can be parameterised by the sum of two (or three) exponential component fits (with decay constants of ~ 1.3 ns and ~ 3 ns), but we have not attempted to assign discrete decay constants to any particular species. The integrated areas under the decays are essentially invariant with Eu^{3+} concentration in contrast to the increases observed in the steady-state spectra. The lack of significant change in the emission decay profile as a function of metal ion concentration confirms a mainly static emission enhancement process is dominant, which is somewhat of a disadvantage for sensing devices, since time-resolved detection can add an extra element of sensitivity and discrimination to the sensor.

The time-resolved emission decay results can be compared to those reported by Wasielewski *et al.* [35] in which the photoluminescence decay profiles of a metal-chelated PPV polymer were reported to lengthen significantly on addition of Zn^{2+} , Ni^{2+} and Fe^{3+} . The photoluminescence decays were reportedly described adequately by bi-exponential decay functions with a metal-dependent fast component ranging from a few picoseconds to several hundred picoseconds, and a metal-independent slow component with a time constant of ~ 2 ns. The long component for the metal free polymer was ~ 1 ns.

The emission decay profiles of CE-OPV in the absence of metal ion, as a function of CE-OPV concen-

tration (2×10^{-8} M to 2.3×10^{-5} M), are displayed in Fig. 6 and show a significant lengthening of the time-scale of the emission with increasing CE-OPV concentration. Both PPV backbones and crown ether rings are known to aggregate [12–14], so the observed changes in photoluminescence decay may possibly be attributed to aggregation. Conjugated polymer film studies [12] and single chain spectroscopy [36] have shown that aggregation in PPV-containing macromolecules leads to the formation of weakly emissive, but long-lived interchain excimeric species that significantly reduce the quantum yield of thin film devices. In CE-OPV the emission intensity increases proportionally with concentration suggesting that aggregation is not the dominant mechanism contributing to the observed fluorescence intensity changes.

Some discussion concerning the nature of the process leading to the enhancement of the emission intensity and the increased lifetime of complexed CE-OPV is warranted. An increase in emission intensity can arise through several processes. The enhanced emission observed, for example upon adsorption of a dye to a surface, at low temperature or in a more rigid solvent environment such as a polymer matrix, is often attributed to a reduction in the degrees of freedom of the fluorophore due to impaired vibrational motion through increased molecular rigidity. If non-radiative deactivation is so reduced, and the rates of all other deactivation pathways are unaltered, more

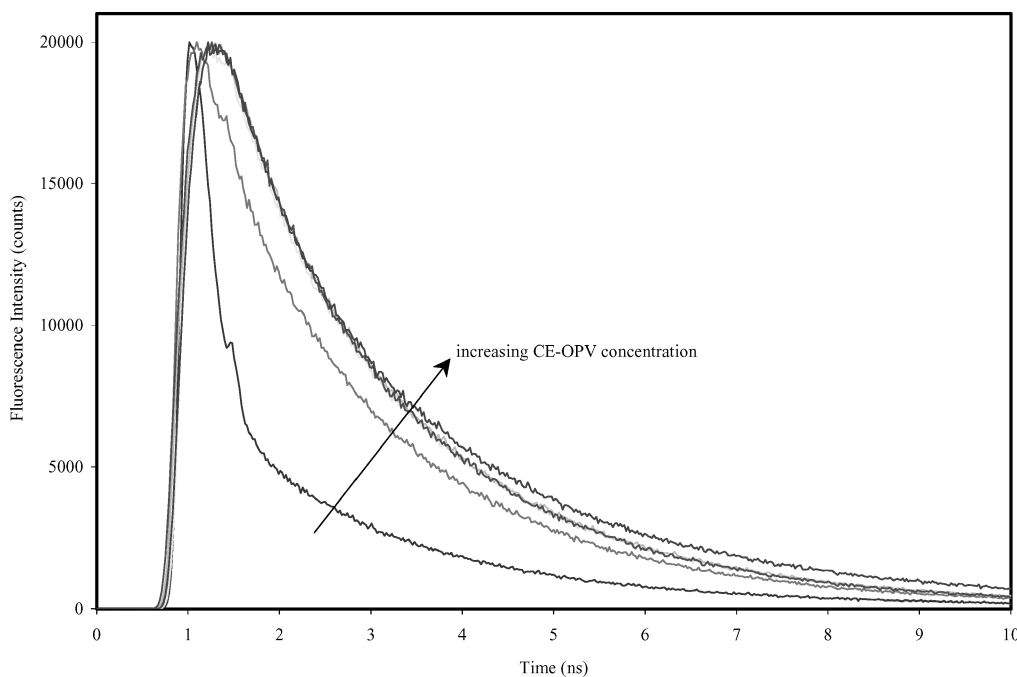


Fig. 6. Time-resolved photoluminescence decay profiles of CE-OPV in the absence of metal ions as a function of CE-OPV concentration (2×10^{-8} M to 2.3×10^{-5} M).

energy is channelled through the radiative pathway resulting in a higher fluorescence quantum yield and a longer fluorescence lifetime. As mentioned, both PPV backbones and crown ether rings are known to aggregate, and aggregation may induce some increased rigidity to the molecular system. The metal ions may even aid the aggregation by bridging chains together. It seems unlikely, however, that such aggregation leads to the marked increases in luminescence intensity observed in the CE-OPV/metal ion systems here, since aggregation occurs in the absence of metal ions and produces significant increases in the decay times (Fig. 6), contrary to our observations shown in Fig. 5 for the variation in metal ion concentration.

Emission may also be enhanced within a system if some pathway for deactivation of the excited state, from which the emission emanates, is removed in some way. A possible pathway that may be switched off upon complexation could be the presence of a closely lying level such as a triplet state. Intersystem crossing to this state would compete with the radiative pathway reducing the potential luminescence quantum yield. Triplet states of some PPV polymers have been reported following both pulse radiolysis and photo-excitation [37–40]. If, in the presence of metal ions, the energy of either the singlet state is reduced slightly or the energy of the triplet is increased slightly so that the triplet level is higher than that of the singlet, then deactivation through the triplet would be switched off and excitation energy would be channelled

through the radiative pathway. We have attempted to detect the presence of triplet state formation by nanosecond flash photolysis/transient absorption measurements monitoring at ~ 520 nm, but to date these measurements have failed to detect any transient absorption from the triplet state of CE-OPV. Measurements on more rapid time scales are planned. These measurements were carried out in undegassed solution and so the lack of evidence for CE-OPV triplet state formation might be unsurprising. However, since the enhancement of the luminescence was observed in undegassed solutions, were this explanation for the luminescence enhancement to be valid, we would also expect to see the triplet in undegassed solutions.

The most likely explanation at this stage for the observed changes in fluorescence intensity as a function of metal ion concentration is variation in the efficiency of formation of a charge transfer state. Such states have been implicated in related studies [22,33,34]. Kollmannsberger *et al.* [22] postulated that a charge transfer state formed rapidly within crown-substituted dyes in the absence of the metal ion, and resulted in a cation-dependent enhancement of the locally excited state population caused through inhibition of the charge transfer process upon coordination with the cation, leading to a dramatic increase in the fluorescence intensity and decay times. In the work of Heeger *et al.* [33,34] charge transfer between conjugated macromolecules and cationic electron acceptors resulted in emission quenching that was observed to follow

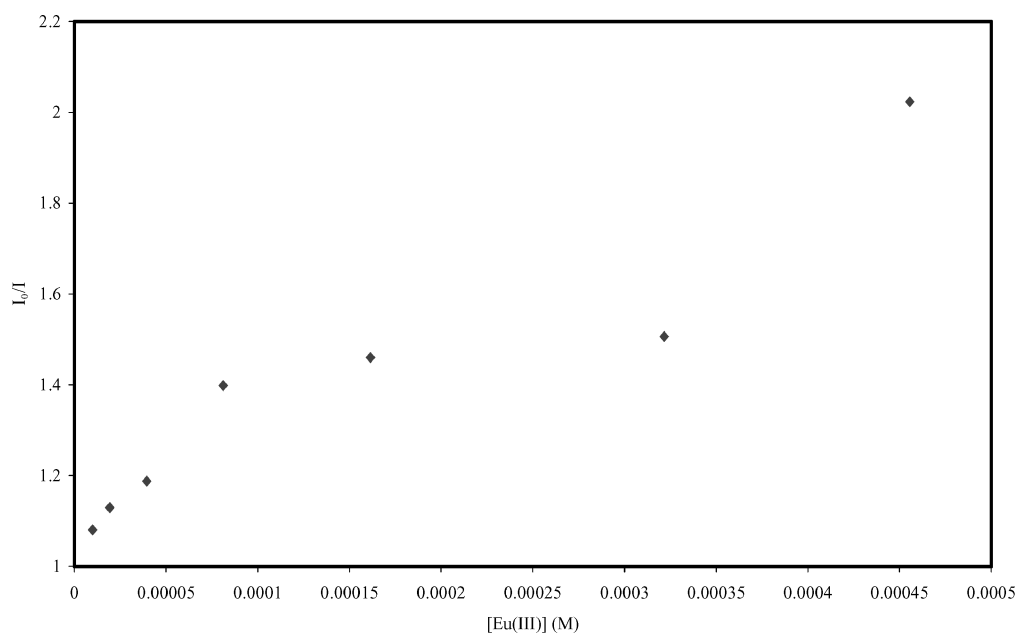


Fig. 7. Stern-Volmer plot of the fluorescence quenching of CE-OPV in the presence of Eu(OAc)₃ in acetonitrile [CE-OPV] $\sim 1 \times 10^{-6}$ M.

non-Stern-Volmer behaviour. We see no clear spectral evidence for a charge transfer state, however, the minor (~ 9 nm) red shift in the emission spectrum may possibly be due to some underlying charge transfer emission band.

We also note here that in acetonitrile, the emission intensity of CE-OPV is *quenched* as a function of EuCl_3 concentration (Fig. 7) in contrast to the emission *enhancement* observed in the methanol/water solvent mixture. The observed emission quenching does not follow Stern-Volmer behaviour, but rather is unusually complex, resembling that reported for acrylamide quenching of glyceraldehyde-3-phosphate dehydrogenase in the absence of a cofactor [41]. In that work, the complex quenching behaviour was attributed to heterogeneity of sites, with some being accessible and some inaccessible to quenching, and a conformational change induced by one of the buffers used. While we cannot, at this stage, identify the cause of the observed complex quenching behaviour in the CE-OPV/acetonitrile system, it seems reasonable to assume that it also be related to similar phenomena, with conformational changes altering the accessibility of the Eu ions (and the solvent) to the conjugated segments.

CONCLUSIONS

We have shown that CE-OPV in methanol/water solution can be used as a sensor to detect the presence of metal ions, through a marked and unusual enhancement of photoluminescence intensity occurring upon complexation with ions such as Na^+ , Ca^{2+} and particularly Eu^{3+} . The complexation-induced emission enhancement process is static in nature and appears to be more complicated than a simple 1:1 complex formation process since the intensity ratio is non-linearly related to metal ion concentration. In acetonitrile, $\text{Eu}(\text{OAc})_3$ causes complex quenching of the CE-OPV emission. The nature of these emission intensity changes has not yet been ascertained, but appears to be related to changes in the efficiency of some charge transfer state formation that is dependent upon the solvent. The enhancement of photoluminescence upon metal ion complexation may make it possible to increase the efficiency in electroluminescent devices with the CE-OPV metal complex as the active emitting layer.

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