JOURNAL OF Materials CHEMISTRY

An investigation of the emission solvatochromism of a fluorene–triarylamine copolymer studied by time resolved spectroscopy

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Received 16th February 1999, Accepted 28th April 1999

The hole transporting fluorene–triarylamine copolymer poly{9,9-dioctylfluorene-*co*-[*N*,*N*′-bis(4-methoxyphenyl)-*N*,*N*′-diphenyl-1,4-phenylenediamine]} [PFMO] has been investigated by absorption and emission spectroscopy as both spin-coated films and solutions. The peak wavelength of the steady-state photoluminescence emission and its decay time depend strongly on the dielectric constant of the solvent. The absorption spectrum is, however, largely insensitive to the choice of solvent. These observations suggest the presence of a strongly polar excited state with a charge-transfer character.

1. Introduction

Following the first reports of the potential of conjugated polymers for device applications (organic light emitting diodes [OLEDs],[1] field-effect transistors[2] and solar cells[3]) it has been established that they are of interest for a wide variety of uses that have previously been the reserve of inorganic semiconductors. For electroluminescence [EL] and most other applications, key processes that determine device performance are efficient injection of charge carriers from standard contact materials and their facile motion in the bulk material. Due to intense research in this area, there is now a range of materials available which combine these attributes. A further requirement for OLED application is a large photoluminescence quantum yield in order to provide a satisfactory overall EL emission efficiency. It is often not possible to combine the desired electronic and optical characteristics in a single material. This leads to an interest in multilayer device structures where different, purpose-synthesized materials are used for charge transport and emission.[4]

A new family of fluorene–triarylamine copolymers has recently been shown to possess both high positive carrier mobilities and low ionisation potentials [I_p].[5] Isotropic spin-coated films of the dialkylfluorene homopolymer poly(9,9-dioctylfluorene) [PFO] have a time-of-flight hole mobility of up to 4×10^{-4} cm^2 Vs^{-1} at a field of 5×10^5 V cm^{-1} at room temperature.[5] Typical hole mobilities for the copolymers are in the range from 3×10^{-4} to 3×10^{-3} cm^2 Vs^{-1} at a comparable field of 2.5×10^5 V cm^{-1} and also at room temperature. The I_p values of the copolymers fall in the range from 4.98 to 5.30 eV with the homopolymer I_p value significantly higher at 5.8 eV.[5] Poly{9,9-dioctylfluorene-*co*-[*N*,*N*′-bis(4-methoxyphenyl)-*N*,*N*′-diphenyl-1,4-phenylenediamine]} [PFMO] (see Fig. 1 for chemical structure) has a particularly low I_p value, namely 4.98 eV (from cyclic voltammetry) and should thus have a small barrier to hole injection from standard indium-tin-oxide [ITO] contacts (workfunction ≈ 4.8–5.0 eV). PFMO is therefore an interesting material both in terms of injection and charge transport properties.

This paper concerns a more detailed study of the emission properties of PFMO. The principal spectroscopic features have been investigated by absorption spectroscopy and both steady-state and time-resolved photoluminescence spectroscopy.

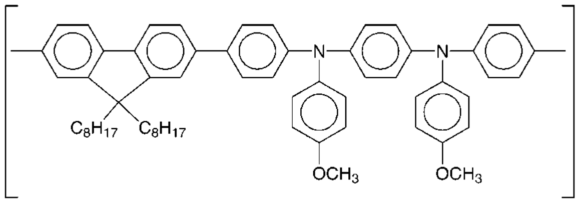

Fig. 1 The chemical structure of PFMO.

2. Experimental

PFMO solutions (20 mg ml^{-1} in toluene) were spin-coated onto Spectrosil B® discs, to yield films of typical thickness 45 nm. Dilute solutions (0.14 mg ml^{-1}) of PFMO in HPLC-grade toluene, 1,4-dioxane, tetrahydrofuran [THF] and dichloromethane [DCM] were also studied. Absorption spectra of solutions were measured in an Unicam® UV4 spectrophotometer using a 1 mm path length quartz cuvette.

Steady-state photoluminescence [PL] emission spectra were recorded under standard conditions: a Spectra Physics pulsed (12 ns), frequency tripled Nd:YAG laser ($\lambda_{ex}=355$ nm) was used as excitation source. The spectrum of the emitted light was detected with an Instaspec® charge coupled device after dispersion through a spectrograph.

For time-resolved photoluminescence decay measurements, time correlated single photon counting was used. The samples were excited with the frequency-doubled output of a Coherent 700 series dye laser, synchronously pumped by a frequency-doubled ($\lambda_{pump}=532$ nm), mode-locked (100 ps pulse width) Coherent Antares® Nd:YAG laser. Styryl 9 was used as the dye and IR 140 served as a saturable absorber. After frequency doubling the excitation wavelength was $\lambda_{ex}=390$ nm and the pulse duration was 5 ps. The light emitted from the sample was first dispersed by a monochromator and then detected with a microchannel plate detector (Hamamatsu R3809) operating in single photon counting mode. The instrument response function was recorded with the sample replaced by a ground glass scatterer. The time resolution of the system was ≈ 30 ps. The experimental data were numerically fitted to a convolution of the instrument function with a model decay function and the quality of fit was assessed *via* χ^2 values, time varying residuals and the autocorrelation function.

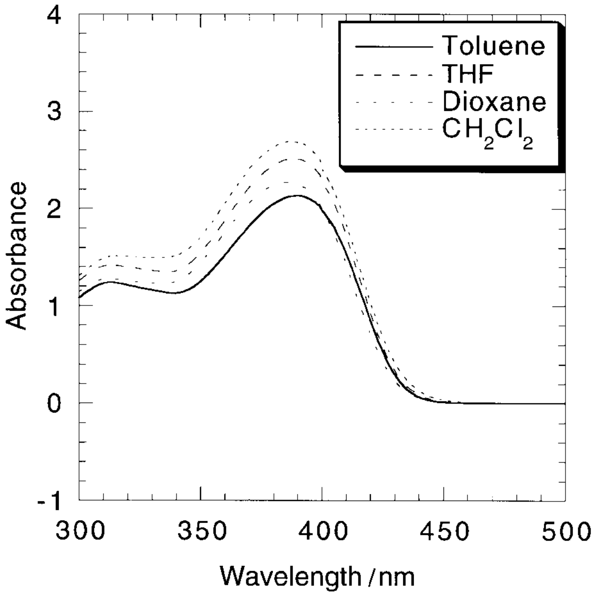

Fig. 2 Absorption spectra of PFMO solutions (0.14 mg ml^{-1} concentration) in toluene, THF, dioxane and DCM.

3. Results

The absorption spectra of solutions of PFMO in different solvents are shown in Fig. 2. The spectral position of the absorption maximum at $\lambda_{abs}=390$ nm does not depend to any significant degree on the solvent. This is in sharp contrast to the steady-state photoluminescence results. The corresponding PL spectra are displayed in Fig. 3 and show a strong solvatochromism of the emitted light, with a red shift of the peak emission wavelength by up to 50 nm. Note that in all cases these are good solvents such that the PFMO concentration can be increased by more than a factor of five hundred before precipitation is seen. Note also that the spectrum of the THF solution was unaltered by dilution to a fifty times lower concentration (not shown here). These observations strongly suggest that aggregation (inter-molecular) effects are not responsible for the red shift. The red shift does appear, however, to be correlated with the dielectric constant of the solvent. In a solvent with a low dielectric constant (*e.g.* toluene) PFMO exhibits a blue emission with resolved vibronic structure. As the solvent dielectric constant increases the structure is lost and a strong red shift occurs. In DCM solution, green PL with a broad featureless spectrum is observed. The emission spectrum of the spin-coated film is comparable to that of the solution in 1,4-dioxane.

Time-resolved photoluminescence decay measurements have been performed for all four solvents at several detection wavelengths. The results follow the trend that is illustrated by the two extreme solvent dielectric constants, the data for which are shown in Fig. 4 along with the results of the fitting procedure (note that the PL data are offset vertically for clarity). The red shift caused by the solvent is accompanied by an overall increase in the PL decay time. The decays for the toluene solution at the two representative emission wavelengths, $\lambda_{em}=460$ nm (Fig. 4a) and $\lambda_{em}=550$ nm (Fig. 4b), are fitted well by a single exponential. For the DCM solution at $\lambda_{em}=550$ nm (Fig. 4b) a single exponential decay is also seen, but with a significantly longer decay time than for the toluene solution. At $\lambda_{em}=460$ nm (Fig. 4a), the DCM solution shows a short time rapid decay spike followed by a quasi-single-

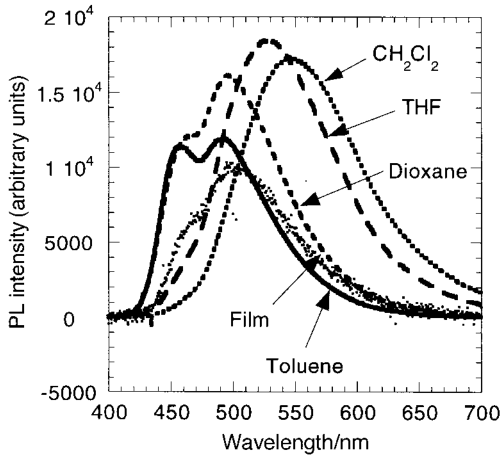

Fig. 3 Steady-state photoluminescence spectra of PFMO solutions (0.14 mg ml^{-1}) and a spin-coated film on a Spectrosil substrate. The excitation wavelength for all measurements was $\lambda_{ex}=355$ nm.

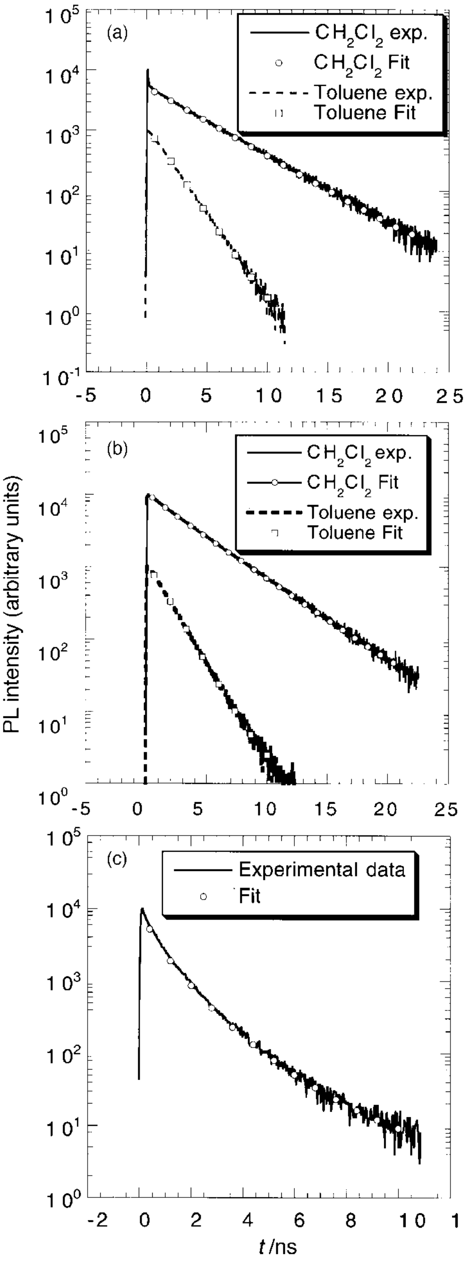

Fig. 4 Time-resolved photoluminescence decays for solutions of PFMO in toluene and DCM at detection wavelengths of (a) $\lambda_{em}=460$ nm and (b) $\lambda_{em}=550$ nm. Fig. 4c shows the decay for a spin-coated film on a Spectrosil substrate with $\lambda_{em}=460$ nm. In each case, $\lambda_{ex}=350$ nm. The results of fits (see text for details) to the data are also shown and the fit parameters are summarised in Table 1.

Table 1 Solvent relative permittivities, peak emission wavelengths, λ_{em}, and dominant (long-time) single-exponential emission decay times for solutions of PFMO. Decay times were determined from exponential or double-exponential fits at $\lambda_{em} = 550$ nm except for THF where the detection wavelength was $\lambda_{em} = 530$ nm. The excitation wavelength was $\lambda_{ex} = 350$ nm in all cases

Solvent	ε_r	Peak λ_{em}/nm	Decay time/ns
Toluene	2.38[a]	491	1.5
1,4-Dioxane	2.21[a]	496	2.15
THF	8.20[b]	528	3.16
DCM	9.08[a]	547	3.7

[a] Reference 6. [b] Reference 7.

exponential decay at times longer than 1 ns. The fast component of the $\lambda_{em} = 460$ nm decay in DCM solution was fitted to an exponential with a decay time ≈70 ps that is close to the experimental time resolution. In THF there is a weaker fast component with a decay time ≈115 ps and in dioxane the fast component is very small and can be fitted with a decay time ≈190 ps. For toluene a single exponential gives a good fit but if a double exponential is forced, the fast component is ≈405 ps.

Fig. 4c shows the time resolved PL decay at $\lambda_{em} = 460$ nm for a PFMO spin-coated film on a Spectrosil substrate. The decay is clearly non-exponential and was fitted best with a distribution of exponentials with a mean decay constant of 650 ps and a distribution width of 460 ps. Even at a detection wavelength of $\lambda_{em} = 600$ nm (not shown here) the decay is still strongly non-exponential and considerably faster than in solution.

The exponential decay times in the long-time limit for all four solutions are displayed in Table 1 together with the peak emission wavelengths and relative permittivity (ε_r) values taken from the literature.[6,7] The decays were recorded at a wavelength of $\lambda_{em} = 550$ nm for toluene, dioxane and DCM solutions and at $\lambda_{em} = 530$ nm for the THF solution. The clear trend is that solvents causing a strong red shift in emission also lead to a large increase in decay time. Solutions in toluene have a 1.5 ns decay whilst those in DCM have a 3.7 ns decay. We note that this increase in decay time is much too large to be explained simply in terms of the expected $(1/\lambda_{em})^3$ variation with emission wavelength.[8] From the ratio of the peak emission energies in toluene and DCM solutions, and taking into account the weak changes in absorption strength, we estimate that the observed peak shift from 490 nm to 550 nm should only change the decay time by a factor of 1.14. Experimentally, however, we find that the decay time in DCM is a factor of 2.5 times longer than that in toluene.

4. Discussion

Conjugated polymers often show a time-dependent red shift of their fluorescence.[9] This is typically explained on the basis of a quasi-continuous energetic relaxation process that involves energy transfer through a gaussian density of exciton states broadened by inhomogeneities in physical and chemical structure. A similar observation, albeit on a different time scale, has been made for the decay of phosphorescence in molecular glasses.[10] The observation of a fast non-exponential decay at the higher energy end of the emission spectrum compared to a slower single exponential decay in the lower energy part is typical for systems that undergo a cascaded energy transfer between different emitting sites. In toluene solution energy transfer appears to be negligible for PFMO since single exponential fits with very similar decay times describe emission at both 460 and 550 nm. In the more polar DCM solution, there is a very fast component in the decay that might suggest rapid energy transfer on a *ca.* 50 ps time scale (comparable to the experimental time resolution). The rapidity of the process could explain why no corresponding build up in population of the red end emission was detected. Solution concentration effects, however, argue against this proposal. An alternative explanation for the fast decay component is that it is a consequence of solvation dynamics. It is not, however, obvious that the relaxation times for toluene, THF, dioxane and DCM should decrease in the sequence 405 ps, 190 ps, 115 ps and 70 ps. Further investigations are needed to fully explain this behaviour.

We note that the emissive state in solution appears to be well defined in energy since a single exponential decay is seen. Any broad energetic distribution that gives rise to a density of states function of significant width, results in a corresponding distribution of decay times that would become evident by the observation of a non-exponential decay. This is exactly what is seen for the decay measured for spin-coated films. The highly non-exponential film PL decay is considerably faster than in solution, and is consistent with the presence of a much broader energetic distribution of states amongst which fast energy transfer to energetically lower lying states is much more likely. Not all states decay radiatively but can instead also participate in further transfer steps or act as non-radiative recombination centres. This heterogeneity gives rise to the non-exponential decay that can only be fitted with a broad distribution of exponentials.

We note further that the observed red shift of the PL emission from PFMO occurs in rather dilute solutions. The polymer concentration employed is equivalent to 1.6×10^{-4} mol l^{-1} on the basis of the molecular weight of the PFMO repeat unit. This is substantially below that used by *e.g.* Birks and Christophorou[11,12] to demonstrate the formation of excimers in pyrene solutions. Those authors found that excimer emission is negligible at a concentration of 10^{-4} mol l^{-1} or less even though pyrene has a long singlet lifetime that favours excimer formation. In addition, the emission from spin-coated films is relatively little shifted from the toluene solution spectrum. The obvious conclusion is that interchain (or intersegment) excimer states are not the cause of the changes in emission for PFMO. The absence of any changes in spectra for a fifty times more dilute THF solution of PFMO also gives strong support to the proposal that the emission from PFMO is due to intrachain rather than interchain processes.

This is in clear distinction to results reported for a cyano-substituted poly(*p*-phenylenevinylene) [cyano-PPV]. Samuel *et al.* compared the emission from solid films and a solution[13] and then compared the emission from the polymer dissolved in different solvents.[14] They found that films of cyano-PPV show a deep-red, featureless emission band with a decay time of 5.6 ns while solutions in toluene emit a green–orange spectrum with a much shorter decay time of 0.9 ns. Changing from a good solvent to a poor one led to long-lived, red shifted emission. The observed effects were attributed to the formation of aggregate sites that can form excimers. Their experimental observations differ in two main respects from our results. The first difference is that as noted above the PL decays in PFMO films are markedly shorter than in solution and display only a moderate red shift. The second difference is that all of the solvents used here are excellent solvents for PFMO. The polymer can be dissolved in DCM, toluene and THF at concentrations of the order of 100 g l^{-1}. The solubility in 1,4-dioxane is only slightly lower. These two observations confirm that it is the presence of a polar environment rather than aggregation that is responsible for the red shifted emission of PFMO solutions. Samuel *et al.*[13,14] clearly showed, however, that the polarity of the solvent does not play an important role in the photophysics of cyano-PPV.

The classical interpretation for absorption and emission solvatochromism is the presence of a strongly polar charge-transfer [CT] state. The relative solvent dependent shift of absorption and emission maxima allows the dipole moment difference between the ground and excited states to be calculated.[6] The results presented in the preceding section show, however, that the solution absorption spectrum of PFMO does not noticeably shift as the solvent is varied. In contrast, the emission spectra show a large solvent shift. One explanation for this would be that whilst the ground state is non-dipolar, there is a low lying excited state that possesses a large CT component. Absorption involves a Franck–Condon transition from the non-dipolar ground state and is little altered since the ground state does not shift with increasing solvent dielectric constant. The CT state, in contrast, is stabilized by high dielectric constant solvents and thus red shifts. Whether there is a single emissive singlet excited state that red shifts or whether the CT state only becomes the lowest lying singlet as a consequence of solvent stabilization remains to be determined. The evolution of the steady state PL spectra from a vibronically structured emission band in toluene to a featureless band in THF and DCM is suggestive that the latter is correct. Time resolved spectral data should help to answer this question. In addition, electroabsorption studies may prove revealing since they should allow a CT state to be resolved from superposed transitions in the absorption spectrum.

In summary, we have reported a spectroscopic study of the solution and solid film emission properties of the fluorene–triarylamine copolymer PFMO. We find that the PFMO emission is strongly dependent on the dielectric constant of the solvent and undergoes a large red shift and loss of vibronic structure as the dielectric constant increases. The red shift is accompanied by a strong increase in decay time. The data indicate the presence of an excited state with a strong CT character. Further investigations are planned to more fully elucidate the nature of this state and its relation to the chemical structure of the copolymer.

Acknowledgements

The Sheffield group thanks the European Commission for funding *via* the Training and Mobility of Researchers Network project EUROLED (ERBFMRXCT970106). We also thank the Dow Chemical Company for their support of this work.

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Paper 9/01264H