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Photophysical process of MEH-PPV solution

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Abstract

The solvent, temperature and concentration-dependent fluorescences of MEH-PPV solutions were examined. The aliphatic and aromatic solvents have different effects on the emission spectra of MEH-PPV solutions because of the different interaction mechanisms between MEH-PPV and different solvents at excited states. With the increase of the polarity of the solvents, the emission spectra show blue and red shift at 77 K and room temperature, respectively. With the decrease of the temperature, the emission spectra of MEH-PPV in xylene show red-shift and the fluorescence intensities increase. The concentration-dependent emission spectra remarkably changed with the increase of the concentration because of the existence of the aggregate states and the interchain interactions in concentrated solutions.

Keywords: MEH-PPV; Energy transfer; Aggregate state; Interchain interaction

1. Introduction

Recent years, the study of poly (1,4-phenylene vinylene) (PPV) as active media in a variety of optoelectronic devices, such as light emitting diodes [1], photodiodes, light emitting electrochemical cells [2] and plastic laser [3], has been an active area in both theoretical and practical research. The introduction of alkoxy groups can reduce the oxidation potential and also improve the solubility remarkably. So poly(2-methoxy,5-(2′-ethylhexloxy)-*p*-phenylene-vinylene) (MEH-PPV) particularly draws the attention of chemists because of its high quantum yield of fluorescence and good solubility in common organic solvents. To study the photophysical process of MEH-PPV solution is helpful for better understanding the nature of the excited state in solid films. However, extensive studies of the fluorescence of MEH-PPV solution have not reached, so some uncertainty about the photophysical process of MEH-PPV solution still leave over.

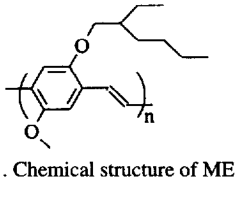
The fluorescences of MEH-PPV solution in different solvents and different concentrations are reported in this paper and the temperature dependence of emission spectra in MEH-PPV solution are also discussed.

2. Experimental

MEH-PPV (Scheme 1) was synthesized in this laboratory according to the reported method [4] and characterized by elemental analysis, IR, NMR etc. The molecular weight is about 200,000 determined by GPC (polystyrene as a standard).

Xylene, benzene, tetrahydrofuren (THF), chlorobenzene (CB), dichloromethane (CH_2Cl_2) and cyclohexanone were all purchased from Beijing Chemical Plant without further purification prior to use except THF, which was purified according to the routine method. Interference fluorescence was not observed under the experimental conditions for all the reagents used. The concentration of MEH-PPV solutions in different solvents is 3.8×10^{-5} M. The polymer film was obtained by gradually evaporating the concentrated THF solution in a 1 mm quartz cell in air.

The UV–visible absorption spectra were taken on a Hitachi 340 UV-VIS spectrometer. The steady-state emission and excitation spectra were obtained on a Hitachi MPF-4 fluorescence spectrophotometer. The measurements of fluorescent spectra in different concentrations were obtained in front face.



Scheme 1. Chemical structure of MEH-PPV.

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3. Results and discussion

3.1. Solvent effects

The absorption and fluorescence spectra of MEH-PPV dilute solutions (3.8×10^{-5} M) were investigated in different solvents and all results are listed in Table 1. Table 1 shows that, although no much difference was observed for the absorption spectra in different solvents because the absorption bands are broader and not well defined, and consequently it is difficult to exactly find the $\lambda_{ab}{}^{max}$, the trend that there are slight red shift of absorption spectra in aromatic solvents compared with that in aliphatic solvents which have same polarity is obvious. This means that the aromatic solvents and aliphatic solvents have different effect on the absorption of MEH-PPV. It is known that an absorption spectrum of conjugated polymer depends on its molecular conformation due to changing conjugation length of the polymer. So we thought that this polymer might have different conjugation length in different solvents. This different effect can be observed more clearly from the emission spectra which are narrower and well-defined.

Generally, the emission spectra of chromophore red shift with the increase of the solvents polarity due to the dipole–dipole interaction of the excited state. However, from Table 1 we can see that the aromatic solvents and aliphatic solvents also have different effect on the fluorescence of MEH-PPV. The emission spectra in aromatic solvents are more red-shifted than that in aliphatic solvents which have same polarity. We suppose that this difference may partly be the result of differences in π–π interactions between the polymer chains and the different solvents. Both MEH-PPV and aromatic solvents have aromatic ring. π–π stacking interactions between them may exist except the general dipole–dipole effect. We agree with that the chains of MEH-PPV may be more rigid in aromatic solvents than that in aliphatic solvents [5]. Consequently, the effective conjugation length of MEH-PPV have increased. This was consistent with the findings of Diaz-Garcia et al. [5] that the photophysics of MEH-PPV polymer films cast from different solvents are different.

Aliphatic solvents, such as THF provide a much different chemical environment from the aromatic solvents. The interaction of MEH-PPV and solvents are mainly caused by the dipole–dipole interaction. THF is a fairly polar solvent, so it is likely that weak-polar polymer is more kinked in these polar solvents. This also can be explained by the strong interaction between the alkoxy groups and the polar solvents that twist the backbone of MEH-PPV and prevent better packing of the conjugated chains. Therefore, the effective conjugation length of MEH-PPV decreases due to twisting. Further research toward a better understanding of this effect is currently in progress.

Table 1
The maximum of absorption and emission of MEH-PPV in different solvents

Solvent	Dielectric constant	$\lambda_{ab}{}^{max}$/nm	$\lambda_{em}{}^{max}$/nm (RT)
Benzene	2.28	492	558, 594 (sh)
Xylene	2.36	495	560, 594 (sh)
Chlorobenzene	5.59	498	565, 602 (sh)
THF	7.35	486	556, 590 (sh)
CH_2Cl_2	9.08	494	559, 594 (sh)
Cyclohexanone	15.2	495	560, 595 (sh)

3.2. Temperature effects

In order to examine the properties of MEH-PPV in the excited state, temperature effects on the fluorescence of MEH-PPV in xylene and THF were studied. The temperature-dependent emission spectra of MEH-PPV solution in xylene are shown in Fig. 1. Fig. 1 shows that the fluorescence intensity increased and red shifted with the decrease of the temperature. Additionally, the most structured emission spectra were observed at 77 K, which suggest an excitonic emission. The increase of the intensity with the decrease of the temperature is due to the decrease of non-radiative decay rate at low temperature. The bathochromic shift of emission spectra upon cooling indicates that cooling could improve the stability of conjugated segment by suppressing the conformational change which may be induced from the folding of segment [6]. At 77 K, MEH-PPV is in the form of frozen state, and the inhibition of the rotation of side chains and main chains causes the backbone of MEH-PPV more rigid, so the effective conjugation length increases upon cooling. The effect of temperature on the fluorescence of MEH-PPV solution in THF is similar to that in xylene.

3.3. Concentration effects

The excitation spectra of MEH-PPV solutions with different concentration have changed little and do not depend on the wavelength of emission. Similarly, no dependence of fluorescence emission upon excitation wavelength has been observed in the same concentration. However, the emission spectra changed dramatically with different concentrations. Fig. 2 shows the emission spectra of MEH-PPV solution in THF with different concentration. The peak of emission in

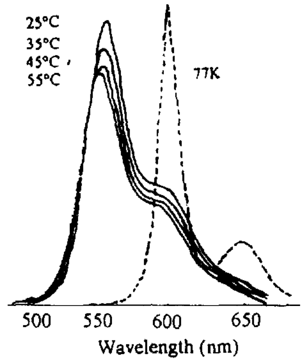

Fig. 1. Fluorescence of MEH-PPV in xylene at different temperature (the concentration is 3.8×10^{-5} M).

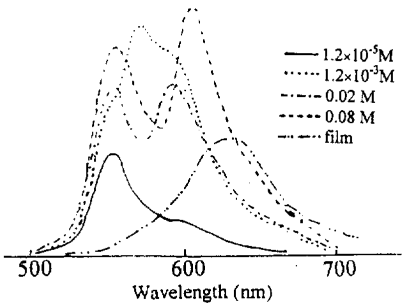

Fig. 2. Emission spectra of MEH-PPV solution in THF with different concentration.

dilute solution is at about 556 nm with a shoulder at about 590 nm, which may be ascribed to the process of energy transfer prior to emission. As the concentration increased, the peak at longer wavelength (590 nm) is gradually improving and red shift at same time. This demonstrated the presence of additional emission centers in concentrated solution. Such centers could be fluorescent dimers or other aggregate states with different degree of overlap between the different polymer chains or the separated conjugation segments on the same chains. The ratio between the intensities at 556 nm and 590 nm can be used to estimate the relative concentration of excimer-like components and the normal fluorescences. The result could be explained by the following two reasons. First, the energy transfer is easier in concentrated solution because of the aggregate states. There are more rapid and effective energy transfer to the emission centers having the lowest energy prior to emission [7]. Second, it is known that the shape of the emission spectrum is determined by the nature of the emitting species. The emission at 556 nm stems from an excitonic state whereas the emission of long wavelength at 590 nm can be attributed to aggregates [8], which formed between subunits of the polymer chains or the excimeric state [9]. The excimeric state is a resonant dimer between two (or possible more) polymer chains which is lower in energy than the exciton state where the excitation is confined to one chain. In dilute solution, where the existence of interchain species is unlikely due to large chain separation, intrachain excitation emission is responsible for the luminescence. However, in the very concentrated solution and in neat films, the formation of the interchain excimers suppresses the generation of emissive intrachain excitons.

Our results show that interchain interactions can have a strong effect on luminescence in conjugated polymers and must be considered for the design of new luminous materials.

4. Conclusion

The emission spectra of MEH-PPV red shifts slightly with the increase of the polarity of solvents. The aliphatic and aromatic solvents have different effects on the absorption and fluorescence of MEH-PPV solution because of the different interaction mechanisms. The temperature-dependent fluorescence of MEH-PPV solution showed the red shift emission line and the increase of emission intensity as temperature increased. As the concentration increased, the shape of the emission spectra have changed remarkably. The improvement and red-shift of the emission in longer wavelength with the increase of concentration could be attributed to the aggregate states or interchain excimeric states.

Acknowledgements

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