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Spectral Properties of Porphyrin Doped MEH-PPV as Films and in Chloroform Solutions

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Abstract: The spectral properties of different mass percentages of the porphyrin(5,10,15,20-tetra-p-tolyl-21H, 23H-porphine, TTP) doped poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) were studied by UV-Vis absorption and fluorescent emission spectra in this paper. The absorption spectra of the blended systems as both films and chloroform solutions show the same behaviors. Meanwhile, the aggregation of polymer chains for MEH-PPV was found under the both cases and the absorption of TTP at 420 nm increase with increasing TTP in the blends. However, the emission spectra from the films are different from those in chloroform solutions. Förster energy transfer from MEH-PPV to TTP occurs in the films and chloroform solutions. Moreover, the splits of emission peak of MEH-PPV induced by energy transfer in chloroform solutions with high TTP doping levels are observed. The phenomenon is disappeared when the solution is diluted, indicating an enlarged distance between the energy donor and acceptor at that time. Furthermore, the rate of energy transfer was obtained at $1 \times 10^8 \text{ mg} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$.

Key words: UV-Vis absorption; photoluminescence; conjugated polymer; energy transfer

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1 Introduction

The conjugated polymers have been paid much attention due to their broad prospects as organic light-emitting diodes (OLEDs) in display^[1-4]. The full color display requires the emission region at red, green and blue. However, achieving pure-red emission has proved relatively challenging. Rare earth complexes with europium (III) have been used as emitters in OLEDs for red emission^[5,6]. They have very narrow emission bands and give pure chrominance. On the other hand, porphyrins are very extensively used dyes which emit lights at the range of red. Some researches have reported for using porphyrins in OLEDs^[7]. Most of them are blended as mixtures with conjugated polymers and emitted redlight via the Förster energy transfer process from the host polymers to porphyrins. Thus, the color of emission can be changed by combination of a dye

with a polymer. Although porphyrin involved red-emission OLEDs have been reported, few papers were published on the features of Förster energy transfer of blends as films and in solutions and the spectral properties of the blends with different concentrations have not been reported yet. Recently, we reported OLEDs of TTP doped poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) blended emitter^[8,9]. For further understanding the mechanism of the luminescence, the spectral properties of TTP in thin MEH-PPV films and chloroform solutions were studied in this paper and Förster energy transfer induced spectral changes were discussed. Although the overlap between the absorption band of TTP and the emission band of MEH-PPV is small, the significant energy transfer can be observed. The results will be helpful to understanding the mechanism of energy transfer and further the luminescent rules for OLEDs.

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2 Experiments

TTP was purchased from Aldrich Company and used without further treatment. MEH-PPV was synthesized according to the literature method^[10]. The blends were prepared by mixing the appropriate amounts of TTP and MEH-PPV in chloroform. The amount of TTP is in from 0.5% ~ 8.0% in mass fraction. Optical absorption and photoluminescence (PL) of the blends were measured in films deposited by spin coating and in chloroform solutions. The PL spectra were measured by a Hitachi F-4500 luminescence spectrophotometer. UV-Vis spectra were recorded by a Perkin Elmer Lambda 25 spectrophotometer.

3 Results and Discussion

3.1 UV-Vis Spectra of Blends as Films

The UV-Vis absorption spectra of TTP dispersed in PMMA, neat MEH-PPV and TTP doped MEH-PPV films are shown in Fig. 1. In Fig. 1 (a), the peak of absorption for TTP at 420 nm is the band of Soret ($S_0 \rightarrow S_2$) and ones at 518, 522, 595 and 650 nm are the bands of Q ($S_0 \rightarrow S_1$)^[11]. In Fig. 1 (b), a broad peak around 500 nm is caused by energy absorption of MEH-PPV. On the other hand, Fig. 1 (c) illustrates the absorption spectrum of a film of 3% TTP doped MEH-PPV. From Fig. 1 (c), we can see that two significant peaks at 420 nm and 480 nm represent the absorption of TTP and MEH-PPV, respectively. Meanwhile, we observed during the experiment that the absorption of TTP at 420 nm

increases with increasing the TTP doping level in blends. Moreover, the absorption peak of MEH-PPV has a blue-shifted with the increasing of TTP absorption at 420 nm. The range for the shifting is between the wavelength of 500 nm and 470 nm. This result indicated the aggregation of polymer chains in neat MEH-PPV film^[12]. However, the co-existence of TTP may reduce the molecular aggregation.

3.2 PL of Blends as Films

PL spectra of MEH-PPV and TTP are shown in Fig. 2. The emission peak from MEH-PPV is at 582 nm and ones from TTP are at 660 nm and 722 nm, respectively. The small overlap between the emission spectrum of MEH-PPV and the absorption band of TTP causes Förster energy transfer. In order to clarify the details of Förster energy transfer in the blended systems, the PL spectra of films with varying mass fraction of TTP doped MEH-PPV were measured. The excitation wavelength was selected at 420 nm and 500 nm, respectively. The former is for the excitation of TTP and the later is for MEH-PPV. Fig. 3 illustrates the PL spectra of the blended systems in the case that different excitation wavelengths were used. The spectra placed in the upper part were recorded with $\lambda_{\text{ex}} = 420$ nm and those in the lower were recorded with $\lambda_{\text{ex}} = 500$ nm.

From Fig. 3, it can be seen clearly that the emission of TTP increases with increasing the TTP doping level in the both cases. Furthermore, the emission of TTP is higher by excitation at 420 nm than that by 500 nm indicating that the emission under the excitation wavelength of 500 nm is mostly from the energy transfer of MEH-PPV. Meanwhile,

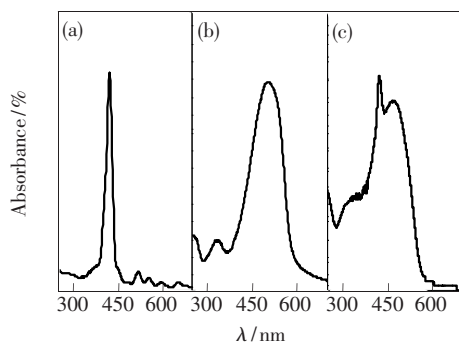


Fig. 1 UV-Vis absorption spectra of the films for TTP dispersed in PMMA (a), MEH-PPV (b) and 3% TTP doped MEH-PPV (c).

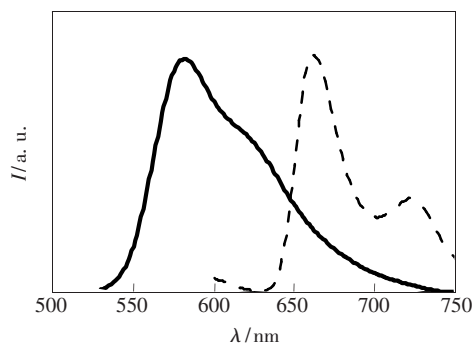


Fig. 2 Emission spectra of (solid) MEH-PPV ($\lambda_{\text{ex}} = 500$ nm) and (dash) TTP ($\lambda_{\text{ex}} = 420$ nm)

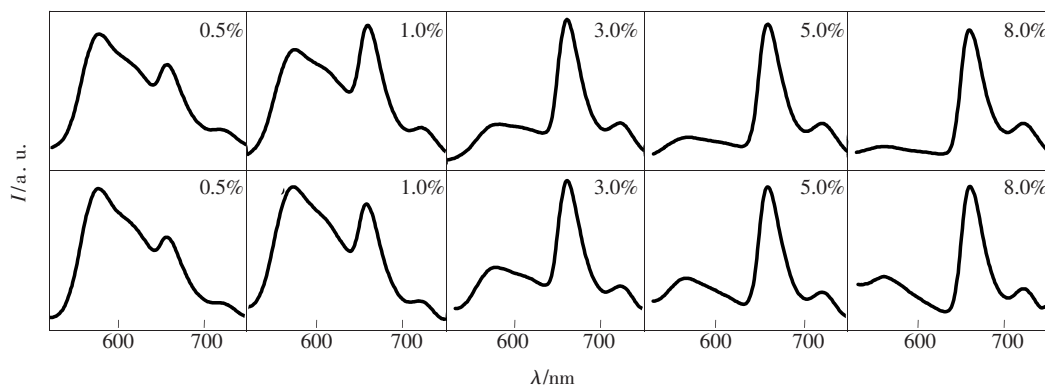


Fig. 3 Emission spectra of varying TTP doped MEH-PPV films with $\lambda_{ex} = 420$ nm (upper part) and 500 nm (lower part)

although TTP does not absorb at 500 nm, the emission intensity at 660 nm increases and dominates the spectrum above the doping level of 3.0%, showing that energy transfer from MEH-PPV to TTP occurs in the blended systems again. Generally, Förster energy transfer occurs in the case that the emission band of donor and the absorption band of acceptor overlap obviously. In this study, the emission band of MEH-PPV overlaps with several small absorption peaks of TTP. A strong red emission from TTP still can be observed. This result may help to select optimum materials for OLEDs.

According to Förster theory, the rate for energy transfer is^[13]

$$k = (1/\tau_0)(R_0/R)^6,$$

where τ_0 is the fluorescence lifetime of the donor (MEH-PPV), in the absence of the acceptor (TTP). R_0 is called the characteristic transfer distance, which is related to the spectral overlap between emission of donor and the absorption of acceptor, and a complex geometric factor. The spectral overlap between the emission of MEH-PPV in the region of 550 ~ 700 nm and TTP absorption in the region of 550 ~ 680 nm is enough for the efficient energy transfer. According to the literature^[7], the transfer distance, R_0 , for MEH-PPV and porphyrin is 2.5 nm. Of course, in the case of films both molecules are contacted intimately. Therefore, Förster energy transfer is feasible in the blended films.

3.3 UV-Vis Spectra of Blends in Chloroform Solutions

In the case of the blends in chloroform, the

spectral behaviors of absorption are the same as those in films. The absorption of TTP at 420 nm increases with increasing the TTP doping level in the blended systems. On the other hand, the absorption peak of MEH-PPV is blue-shifted from 498 nm to 468 nm in pure chloroform solution with increasing the TTP doping level, indicating the aggregation of polymer chains in solutions^[14].

3.4 PL of Blends in Chloroform Solutions

The emission spectra of the blended systems in chloroform solutions are quite different from those in films. Meanwhile, the profiles of the spectra change with doping concentration. Fig. 4 shows the emission spectra with TTP different doping levels at the excitation wavelengths of 420 nm (left part) and 500 nm (right part). The concentration of MEH-PPV is chosen at $2 \text{ mg} \cdot \text{mL}^{-1}$ in this measurement. It is clearly to see that the emission of pure MEH-PPV is about 610 nm. However, several new peaks appear gradually with the addition of TTP, such as at 580, 620, 660 and 720 nm with the TTP doping level of 8.0%. As we knew that the later two peaks are from the emission of TTP, but the former two should split from the emission of MEH-PPV. On the other hand, at the excitation wavelength of 420 nm at which TTP has the maximum adsorption, the emission of TTP at 660 nm increases as increasing the TTP level. Comparing with the emission at the excitation wavelength of 500 nm, the TTP part in the spectra is larger. At the same time, we can see that the emission of MEH-PPV splits at the TTP doping level over 3.0% and reduces with increasing the amount of TTP.

Regarding the split of the emission for MEH-PPV, seeing Fig. 5, the spectra of TTP absorption and emission of 5.0% TTP doped MEH-PPV at the excitation wavelength of 420 nm, shows the reason. From Fig. 5, it is clearly that the Q-band of TTP at 592 and 642 nm absorb the emission from MEH-PPV. The maximum absorption wavelengths of Q-band are well matched the valleys of the split region of MEH-PPV. This phenomenon is getting severely with the increasing of TTP doping level. It is a powerful evidence for supporting energy transfer in chloroform. However, the reason for the spectral split

in chloroform solutions rather than in films is that the emission region of fluorescence from the films and solutions is different. When the excitation light irradiated on the surface of the films, the emission light is recorded by the detection system directly, whereas in the case of solutions the excitation light irradiated into the center of cell and the emission is initiated from the central part in the solutions. If the concentration of solution is higher (>1 mg/mL), the molecular distance between MEH-PPV and TTP is short. The emission of MEH-PPV should pass through the region which contained TTP before the detection, so caused the spectral split of MEH-PPV. This is also called the inner filter effect in solution^[15]. The phenomenon is getting weakly as the dilution process as shown in Fig. 7.

If energy transfer from MEH-PPV to TTP equals to a process of fluorescence quenching for MEH-PPV, the quenching should obey Stern-Volmer quenching kinetics and can be described as the following equation^[16]

$$(I_0/I_x - 1) = k\tau_0 [\text{TTP}],$$

where I_0 and I_x are defined as the fluorescence intensity of MEH-PPV in solution when $[\text{TTP}] = 0$ and x ; k and τ_0 are defined above. The fluorescent intensity at 620 nm with different TTP doping levels in MEH-PPV is measured using the excitation wavelength of 500 nm when the concentration of MEH-PPV is $1.0 \text{ mg} \cdot \text{mL}^{-1}$. The values of I_0/I_x at different concentrations of TTP are calculated and listed in Table 1. The linear relationship between I_0/I_x and $[\text{TTP}]$ is plotted as shown in Fig. 6. Therefore, the energy transfer belongs to a process of fluorescence quenching. From the line illustrated in Fig. 6 the value of slope, $k\tau_0$, is obtained and if the lifetime of MEH-PPV in chloroform is 360 ps ^[17], the rate of energy transfer, k , can be gotten as $1 \times 10^8 \text{ mg} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$.

Table 1 The ratios of fluorescence intensity for neat MEH-PPV to that at different doping levels of TTP

[MEH-PPV] (mg · mL ⁻¹)	1.0					
[TTP] × 10 ⁻² (mg · mL ⁻¹)	0.0	0.5	1.0	3.0	5.0	8.0
I_0/I_x	1	1.27	2.54	5.48	6.05	11.58

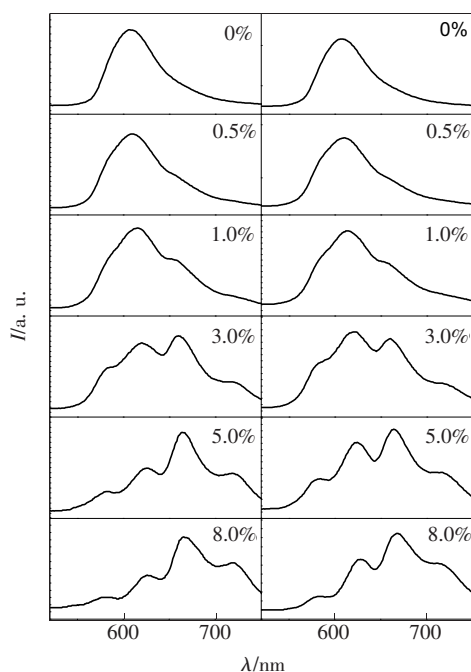


Fig. 4 Emission spectra of varying TTP doped MEH-PPV in chloroform with $\lambda_{\text{ex}} = 420 \text{ nm}$ (left part) and 500 nm (right part). The concentration of MEH-PPV is $2 \text{ mg} \cdot \text{mL}^{-1}$.

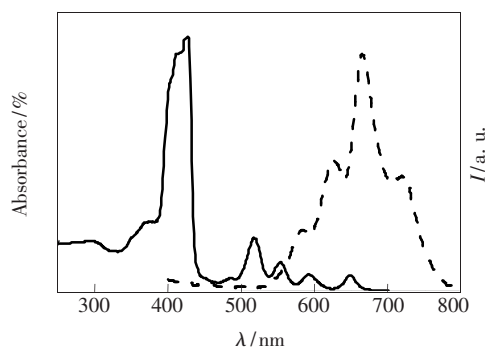


Fig. 5 UV-Vis absorption spectrum of TTP (solid) and emission spectrum of 5% TTP doped MEH-PPV (dash) in chloroform with $\lambda_{\text{ex}} = 420 \text{ nm}$

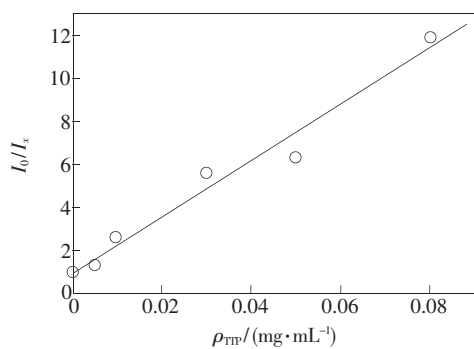


Fig. 6 The relationship between I_0/I_x and concentration of TTP

As we know from the discussion above, the Q-band of TTP at 592 and 642 nm with higher concentration will cause split of the emission spectrum of MEH-PPV. In the following research we will explore the emission of the blended systems at different concentrations.

Fig. 7 shows the PL emission of 5% TTP doped MEH-PPV in chloroform with dilution at different excitation wavelengths. The original concentrations for MEH-PPV and TTP are 2 and $0.01 \text{ mg} \cdot \text{mL}^{-1}$, respectively. Then, the concentration of the solutions is diluted by chloroform to 15 times at least and each time the concentration can be reduced to $1/2$. We can learn from Fig. 7 that the emission from TTP is getting weak with the process of dilution. The emission peak at 660 nm from TTP is annexed into MEH-PPV spectrum gradually due to the dilution induced low concentration. Meanwhile, at the very beginning, the emission of MEH-PPV is divided into two peaks at 580 and 620 nm, respectively. Then, the peak at 580 nm increases gradually with the dilution and finally influence caused by TTP disappears. On the other hand, if the excitation wavelength is at 500 nm, seeing the spectra in the right side of Fig. 7, we can not observe the emission from TTP after 4 times of dilution, showing that Förster energy transfer can not occur at that time due to the large distance between the molecules of MEH-PPV and those of TTP. Meanwhile, if the excitation wavelength is at 420 nm, the emission of TTP at 660 nm is still remained until the solution is diluted up to 15 times. The concentrations of MEH-PPV and TTP at the moment are 6×10^{-5} and $3 \times 10^{-7} \text{ mg} \cdot \text{mL}^{-1}$, respectively.

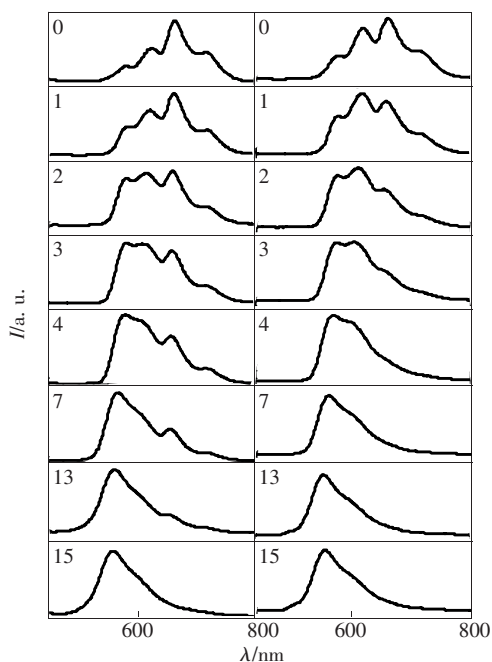


Fig. 7 Emission spectra of 5.0% TTP doped MEH-PPV in chloroform with dilution at different excitation wavelengths. The number in each grid shows the diluted time. Left: $\lambda_{\text{ex}} = 420 \text{ nm}$; right: $\lambda_{\text{ex}} = 500 \text{ nm}$.

4 Conclusion

We studied the spectral properties of varying mass percentage of TTP doped MEH-PPV as films and in chloroform solutions. The significant Förster energy transfer occurs from MEH-PPV to TTP, although the absorption of TTP and emission of MEH-PPV overlapping is very small. However, the emission spectra of the blends in chloroform are quite different from those of the films. The emission peak of MEH-PPV splits when the concentration of TTP in a blend with chloroform is higher and the details are discussed in the investigation, too. The kinetics of energy transfer shows that the rate for energy transfer is $1 \times 10^8 \text{ mg} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$. The research may be helpful to understanding the mechanism of energy transfer and select the materials for OLEDs as color-tunable emitters. It also clues us on what occurs in the polymer solution. This is one of the particular examples on the kinetics study concerning photo-physical processes for composite materials and further attention should be paid to the investigation on transient process of the system.

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卟啉掺杂的 MEH-PPV 薄膜和氯仿溶液的光学性质

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摘要: 研究了不同质量浓度卟啉(TTP)掺杂的 MEH-PPV 的紫外吸收和荧光发射光谱。这种掺杂体系在膜中和氯仿溶液中的吸收光谱具有同样的行为,同时,在这两种情况下发现了 MEH-PPV 链的聚集,以及 TTP 在 420 nm 的吸收随掺入量的增加而增加。但是,膜的发射光谱与氯仿溶液中的有所不同。因 TTP 的吸收带与 MEH-PPV 发射带的重叠,在膜和氯仿溶液中的高浓度掺杂体系中存在从 MEH-PPV 到 TTP 的 Förster 能量转移,但是在高 TTP 掺杂下的氯仿溶液中能量转移导致 MEH-PPV 发射峰的劈裂,而当溶液被稀释时,这种现象消失,表明此时能量给体和受体的距离扩大,这种能量转移的速率为 $1 \times 10^8 \text{ mg} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$ 。

关键词: 紫外-可见吸收; 发光光谱; 共轭聚合物; 能量转移

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