Fluorescence Quenching of Poly[2-methoxy-5-(2'-ethylhexoxy)-*p*-phenylene vinylene] (MEH-PPV) in Solutions

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Fluorescence quenching processes of poly[2-methoxy-5-(2'ethyl-hexoxy)-*p*-phenylene vinylene] (MEH-PPV) in solution by electron acceptors, O_2 and acid, have been studied. Static quenching of the fluorescence from MEH-PPV by an electron acceptor (DDQ or TCNE) occurs due to electron transfer from MEH-PPV to the electron acceptor and this electron transfer quenching can be promoted by chloroform. Photooxidation takes place in the MEH-PPV solution and singlet oxygen is an intermediate in the photooxidation, according to the results of ESR spectroscopy. Acid also plays an important role in the fluorescence quenching process of MEH-PPV, by the protonation of the alkoxy groups in the molecular chain.

Keywords   MEH-PPV, fluorescence quenching, electron acceptor, singlet oxygen, protonic acid

Introduction

Poly(1,4-phenylene vinylene) (PPV) has been the subject of explosive interest in these years. It has potential applications in light-emitting diode, light emitting electrochemical cell and plastic laser.[1-4] To improve its solubility and optical properties substituents are introduced to the PPV main chain.

Poly[2-methoxy-5-(2'-ethylhexoxy)-*p*-phenylene vinylene] (MEH-PPV) is one of derivatives with alkoxy groups on phenyl rings. It exhibits superior solubility in organic solvents and high luminescence quantum yield in solutions and neat film.[5-8]

The applications of the polymer devices at present are limited due to their shorter lifetime than that of the devices based on inorganic semiconductors.[9,10] In MEH-PPV, the substituents also introduce some active groups in the molecular chains besides improving its solubility. Two alkoxy groups for each units of the molecule change the electronic structure of the conjugation and the molecule is more reactive than PPV. To study the stability of the materials it is very important to explore the factors that can affect the luminescence properties. In this paper we report the experimental results of MEH-PPV reacting with other components and of the luminescence quenching processes due to the interactions.

Experimental

Poly[2-methoxy-5-(2'-ethylhexoxy)-*p*-phenylene vinylene] (MEH-PPV) sample was obtained from Prof. Fred Wudl with average molecular weight of 700000. Tetracyanoethylene (TCNE) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) were purchased from Acros. Chloroform and tetrahydrofuran (THF) were purified following standard methods before use. HCl gas was obtained by a reaction of H_2SO_4 and sodium chloride.

UV-visible absorption spectra were recorded on a Hitachi 557 spectro-photometer. Photoluminescence spectra were measured on a Hitachi F-4500 spectrophotometer and the lifetime of the luminescence was measured on a Horiba NAES 1100 time resolved fluorescence spectrometer. ESR spectra were registered by a Brucker ESP-300E spectrometer. The oxygen-saturated samples were irradiated under medium-pressure Hanovia Hg lamp (500 W) and a glass filter was used to cut off the irradiation below 380 nm.

The solutions were prepared under red light and stored in sealed vials in cool and dark place when they were not in use. All the experiments were performed at room temperature.

Results and discussion

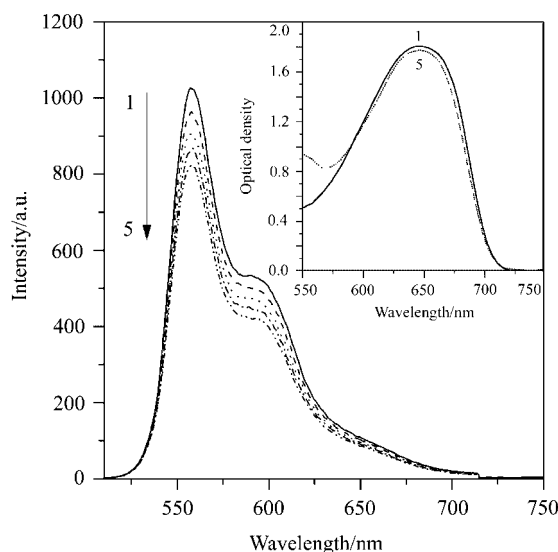### Fluorescence quenching of MEH-PPV by electron acceptors

Fluorescence from MEH-PPV in THF is quenched by DDQ and TCNE, as shown in Figure 1 and Figure 2, respectively. In the quenching process, there is no change in the shape of the fluorescence spectra. It means that there is no exciplex formed between MEH-PPV and DDQ or TCNE to emit in the solutions. The absorption (the inset of Figure 1 and Figure 2, respectively) also shows that there is no change in the main band of MEH-PPV, even in the presence of very high concentration of the DDQ or TCNE, indicating no ground state complex formation.
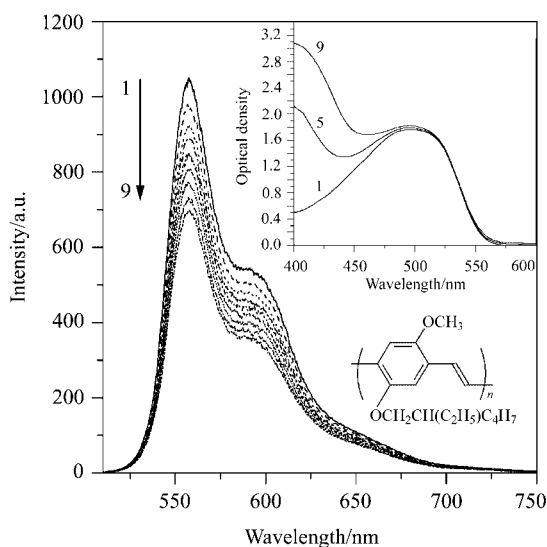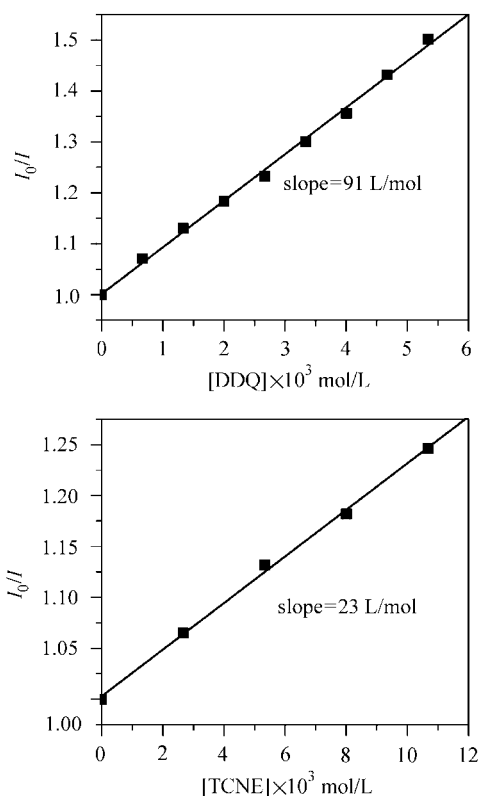

Figure 1 Fluorescence quenching of MEH-PPV $(7.3 \times 10^{-5}$ mol/L) by DDQ in THF. DDQ concentration (mol/L): (1) 0.0; (2) 6.7×10^{-4}; (3) 1.3×10^{-3}; (4) 2.0×10^{-3}; (5) 2.7×10^{-3}; (6) 3.3×10^{-3}; (7) 4.0×10^{-3}; (8) 4.7×10^{-3}; (9) 5.3×10^{-3}. Excitation wavelength: 500 nm. Inset: absorption spectra of MEH-PPV in THF during the fluorescence quenching.

To estimate quenching dynamics, the fluorescence quenching results were analyzed following Stern-Volmer (SV) relationship:[11] $I_0/I = 1 + K_{SV}[Q] = 1 + k_q\tau[Q]$. where I_0 and I are the fluorescence intensities in the absence and presence of the quenchers (Q), respectively. For these two electron acceptors, the I_0/I vs. [Q] plots were quite linear, as shown in Figure 3. Time-resolved fluorescence decay was measured to determine the mechanism of the quenching of the MEH-PPV by DDQ and TCNE. The fluorescence lifetime of MEH-PPV in THF is invariant with added quenchers ($\tau \sim 0.36$ ns, λ_{em} =555 nm), indicating that only static quenching occurs in the solutions. This result is in accordance with that of poly(2-methoxy-5-propyloxy sulfonate phenylene vinylene) (MPS-PPV) with N,N'-dimethyl-4,4'-bipyridinium (MV^{2+}) (methyl viologen). In that case static quenching of the MPS-PPV fluorescence by MV^{2+} was observed.[12]

In the chloroform solution, however, different phenomena were observed. Figure 4 presents the quenching

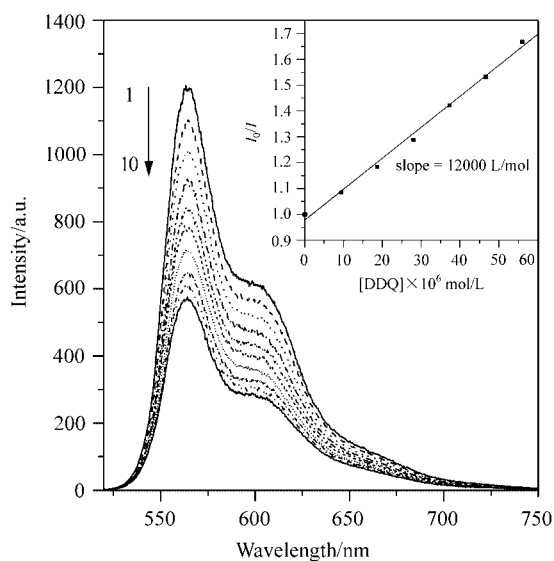
Figure 2 Fluorescence quenching of MEH-PPV $(7.3 \times 10^{-5}$ mol/L) by TCNE in THF. TCNE concentration (mol/L): (1) 0.0; (2) 2.7×10^{-3}; (3) 5.3×10^{-3}; (4) 8.0×10^{-3}; (5) 1.1×10^{-2}. Excitation wavelength: 500 nm. Inset: absorption spectra of MEH-PPV in THF during the fluorescence quenching.

Figure 3 Stern-Volmer plot of the fluorescence quenching of MEH-PPV by DDQ(A) and TCNE(B), respectively.

of MEH-PPV fluorescence by DDQ in chloroform with the SV plot in the inset. It can be seen that the quenching efficiency is much higher than that in THF with quenching constant of 12000 L/mol, whereas that in THF is only 91 L/mol. It is assumed that the chloroform takes part in or promotes the electron transfer process between MEH-PPV and DDQ.
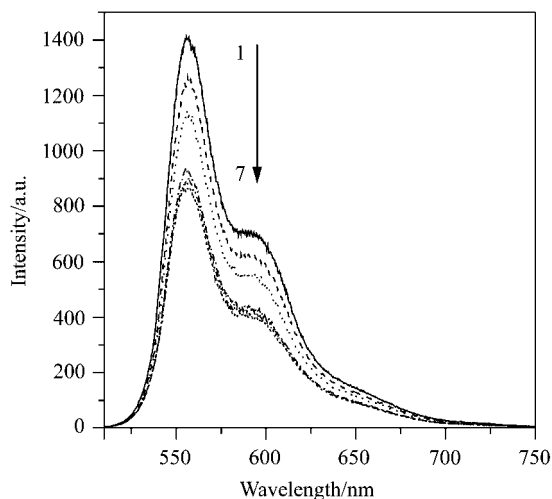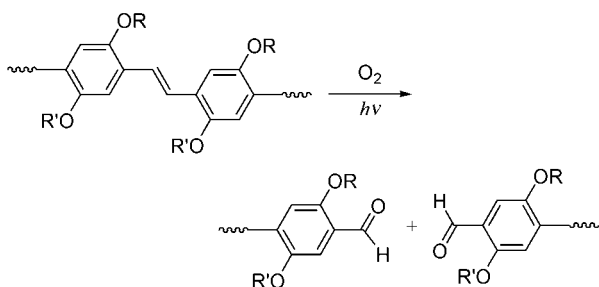
Figure 4 Fluorescence quenching of MEH-PPV $(7.3 \times 10^{-5}$ mol/L) by DDQ in CHCl$_3$. DDQ concentration (mol/L): (1) 0.0; (2) 8.4×10^{-5}; (3) 1.7×10^{-4}; (4) 2.5×10^{-4}; (5) 3.4×10^{-4}; (6) 4.2×10^{-4}; (7) 5.0×10^{-4}; (8) 5.9×10^{-4}; (9) 6.7×10^{-4}; (10)7.6 $\times 10^{-4}$. Excitation wavelength: 500 nm. Inset: The Stern-Volmer plot.

In a solution of MEH-PPV in THF with DDQ, an efficient quenching of the fluorescence was observed when increasing the amount of chloroform in the solution, as shown in Figure 5. It indicates evidently that chloroform can promote the electron transfer from MEH-PPV to DDQ. Other studies have shown that heavy-atoms including halogens contribute to the formation of triplet state in the electron transfer system, accordingly help to quench the fluorescence.[13] Thus in the MEH-PPV and DDQ system triplet state plays an important role in the fluorescence quenching process of MEH-PPV.
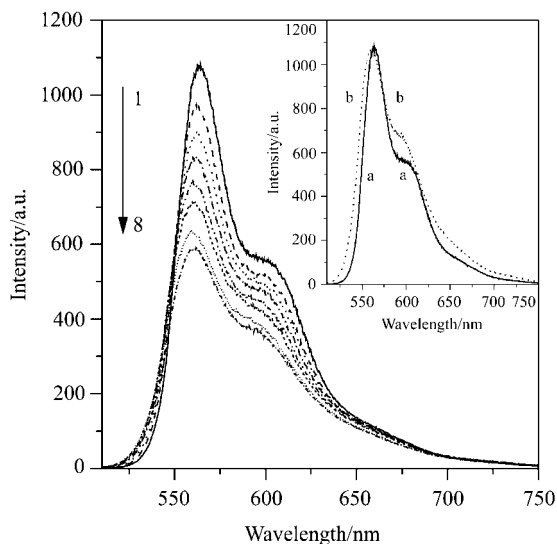
Photooxidation of MEH-PPV

Photoluminescent spectra of MEH-PPV in chloroform with photooxidation process are shown in Figure 6. With increasing exposing time of MEH-PPV to oxygen under irradiation by a Hg lamp, the band in higher energy shows a blue-shift. It can be seen clearly in Figure 6 with normalization. The variation of the emission spectrum indicates that the conjugation of the molecular chain is broken when photooxidation occurs (Scheme 1).

Scheme 1

Figure 5 Fluorescence quenching of MEH-PPV by CHCl$_3$ in the presence of DDQ in THF (0.02 mol/L). The volume of CHCl$_3$ added to the total 3 mL solution (μL): (1) 0; (2) 20; (3) 40; (4) 60; (5) 80; (6) 100; (7) 120.
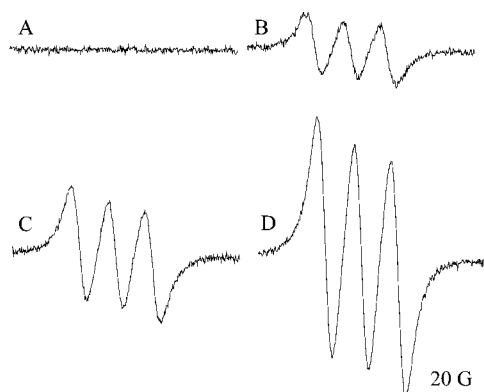

Figure 6 Fluorescence spectra of MEH-PPV in CHCl$_3$ with photooxidation. The time exposing to oxygen (min): (1) 0; (2) 20; (3) 40; (4) 60; (5) 80; (6) 100; (7) 120; (8) 140. Inset: Normalized spectra of MEH-PPV with exposing time to oxygen for 0 (a) and 140 min (b).

Hence shorter conjugated chains emit at shorter wavelength and the blue shift of the emission is observed.

It is reported that the photodegradation of poly(2, 5-bis(5,6-dihydro-cholestanoxy)-1,4-phenylenevinylene) (BCHA-PPV) involves singlet oxygen, O$_2$(a$^1\Delta$g).[14] To ascertain whether or not singlet molecular oxygen was an intermediate in the photooxidation of MEH-PPV, ESR spectrum of MEH-PPV solution in CHCl$_3$ after irradiation was measured. As shown in Figure 7, after irradiation with oxygen ESR spectrum of MEH-PPV exhibits a typical hyper fine structure of singlet oxygen and the intensity of the signal increases with increasing

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exposing time to oxygen. The results illustrate that the singlet oxygen is a reactive intermediate in the photo-oxidative decomposition of MEH-PPV in the solution.

Figure 7   ESR spectra of oxygen-saturated MEH-PPV in THF containing TEMP (5 mmol/L) under irradiation. Irradiation time (min): (A) 0; (B) 8; (C) 18; (D) 32.

### Fluorescence quenching of the MEH-PPV by acid

In our experiments it was found that MEH-PPV faded its color when dissolved in the chloroform that was not freshly purified. It is well known that chloroform is not stable under O_2 or light and can produce carbonyl chloride and HCl. So it is inferred that acid like HCl may influence or break the emissive conjugation of MEH-PPV. Figure 8 shows the fluorescence spectra of MEH-PPV in CH_2Cl_2 when exposed to HCl. With increasing time of exposition, the fluorescence of MEH-PPV is greatly quenched.
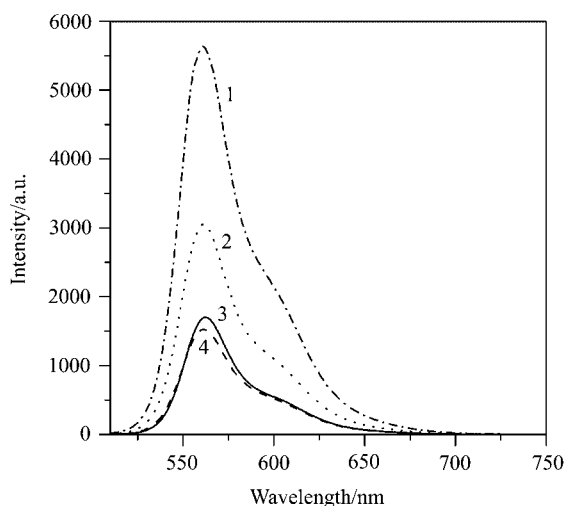
Figure 8   Fluorescence spectra of MEH-PPV in CH_2Cl_2 when bubbled with HCl. Bubbled time (min): (1) 0; (2) 5; (3) 10; (4) 15.

There are two ether side chains for each monomer unit in MEH-PPV. The ether groups are easier to be protonated with H^+ (Scheme 2).

Scheme 2
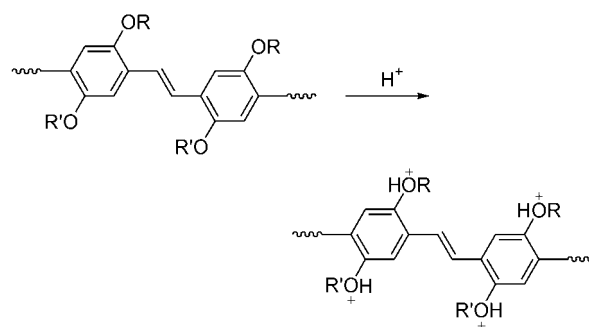
As a result the conjugation of the molecular chain is changed and meanwhile the protonated group is a possible additional pathway for the deactivation of excited states.

Conclusions

Some reagents such as electron acceptor, oxygen and acid can quench the light emitting of MEH-PPV greatly. In solutions the electron transfer quenching from MEH-PPV to electron acceptor is a static process and the molecules with halogen can promote the quenching process greatly. Singlet oxygen is proved to be an intermediate in the photooxidation of MEH-PPV in the liquid solution. Acid can also quench the emission of the MEH-PPV significantly. It illustrates that to control these factors well and carefully may conduce to the improvement of the light emitting efficiency of MEH-PPV when it is used to manufacture LED devices.

Acknowledgements

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