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Highly efficient energy and charge transfer in thin self-assembled multilayered polymer films

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Abstract

We report the synthesis and characterization of multilayer self-assembled polymer films made from a water-soluble conjugated polymer, poly(2,5-methoxy-propyloxy sulfonate phenylene vinylene) (MPS-PPV). We observe a red shift of both the absorption and fluorescence spectra with increasing numbers of active MPS-PPV layers. We attribute this red shift to changing polymer conformation and efficient energy transfer. Upon adding a water-soluble C_{60} or C_{60}-VBA copolymer top layer, the luminescence spectrum is strongly quenched due to charge transfer. The estimated charge transfer quantum efficiency from PL quenching is ~95%. We discuss in detail the unidirectional energy transfer followed by charge transfer in the self-assembled multilayered films.

Keywords: Self-assembly, Poly(phenylene vinylene) derivative, Photoluminescenc, Fullerene and derivatives

1. Introduction:

There has been a great deal of interest in orgainc thin films developed by self-asembly of alternating layers of positively and negatively charged polyelectrolytes[1]. In this paper, we described the synthesis and characterization of highly luminescent polyelectrolyte multilayer thin films made from the water-soluble conjugated polymer, MPS-PPV. Poly(propylenimine), a generation 3.0 dendrimer, poly(ethylenimine) (PEI), and poly(diallyldimethylammonium cloride) (PDDA) are used as cationic binders. These thin films exhibit unidirectional energy transfer from the inner stack (close to the substrate) to the outer stack. After capping with a C_{60} layer on top of this self-assembled multilayered thin film, we observe almost complete quenching of the fluorescence due to efficient charge transfer from MPS-PPV (donor) to C_{60} (acceptor).

2. Experimental

The experimental details of fabrication of polyelectrolyte multilayered films is described elsewhere[2]. UV-Vis spectra were obtained using a Perkin-Elmer Lamda-9 spectrometer. Fluoresence spectra were measured using a Spex fluorimeter.

3. Results and discussion

In this work, we use several polycations, combined with the anionic conjugated polymer MPS-PPV to fabricate self-assembled multilayer films. Fig.1 shows the absorption spectra of a MPS-PPV/dendrimer multilayered film as increasing numbers of bilayers are added to the film. The data show reproducible linear adsorption of

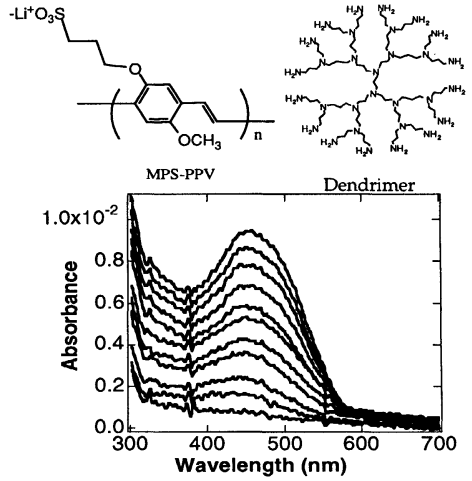

Figure 1 Linear absorption spectra for MPS-PPV/dendrimer multilayer as increasing number of layers

MPS-PPV onto the glass substrate due to electrostatic interaction. The molecular structures of the ionic building blocks are also shown in Fig. 1. Comparing the absolute absorbance for films prepared using two of the aforementioned cationic binders (dendrimer and PEI), it is clear that approximately 5 times greater optical density is

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achieved for each anionic MPS-PPV layer when PEI is used as the cationic binder. This is attributed to the highly branched structure of PEI, which results in more polymer entanglement between two oppositely charged polymers[3].

Fig.2 shows the PL quantum efficiency (PLQE) spectra, obtained by normalizing the PL sepectra of the multilayers by the absorbance at the PL excitation wavelength (400 nm). All the self-assembled MPS-PPV/polycation multilayer films show some degree of PL quenching. For example, MPS-PPV/PEI exhibits complete quenching when the numbers of bilayers reaches 5 or more (see Fig. 2a). The MPS-PPV/dendrimer multilayer films show less than 50% quenching. However, we are able to eliminate the quenching effect by inserting

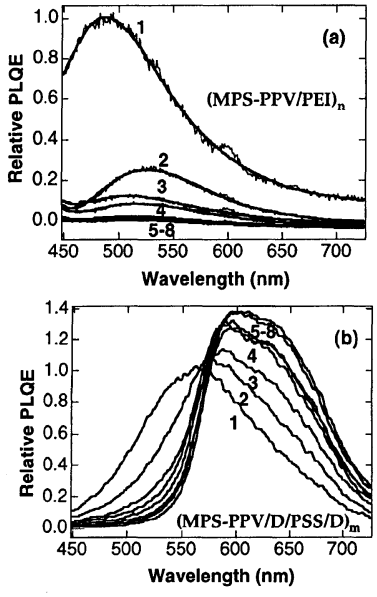

Figure 2 PLQE spectra for (MPS-PPV/PEI)m (a) and (MPS-PPV/D/PSS/D)m (b)

additional spacer layers between two MPS-PPV layers. The multilayer configuration is $(MPS\text{-}PPV/D/PSS/D)_m$, where D denote dendrimer, PSS is polystyrene sulfonate, and m is the number of MPS-PPV layers (see Fig. 2b). Since the formation of PL-quenching excimers on adjacent chains requires a coherent electronic state between two chains, this results implies that adding additional spacer layers results in isolation of MPS-PPV layers, from the standpoint of direct overlap of electronic wavefunctions. On top of this highly luminescent multialyer polyelectrolyte film $(MPS\text{-}PPV/D/PSS/D)_m$, m=15), a layer of water-soluble (sulfonated) C_{60} was added. We observe almost complete PL quenching in these multilayer films. We believe this is due to the photoinduced charge transfer from the MPS-PPV multilayers (donor) to the C_{60} (acceptor). Judging from the difference in the PL spectra before and after C_{60} is added, the quantum efficiency of charge transfer is estimated at ~95% (see Fig.3). The charge transfer rate is measured using ultrafast spectroscopy, and is determined to be ~1ps.

A question remains as to whether this is a highly

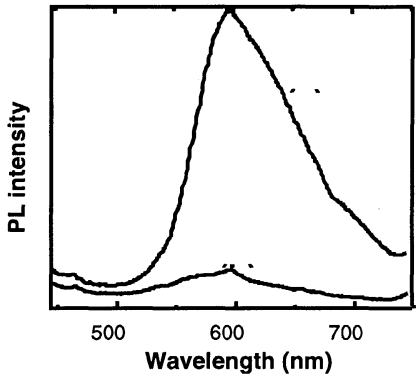

Figure 3 PL of MPS-PPV/dendrimer film (a) with C_{60} top layer (b).

efficient charge transfer process from the MPS-PPV multilayers to the C_{60} (undirectional energy transfer from the inner layer to the outer layer, followed by charge transfer to the C_{60} layer) or is due to penetration of C_{60} to the deeper layers. To answer this question, we synthesized a water-soluble C_{60} copolymer to use as the capping layer on top of the MPS-PPV multilayered film, $(MPS\text{-}PPV/D/PSS/D)_m$, m=15 and measured the charge transfer rate and quantum efficiency. Preliminary results are similar to that of the C_{60} capped multilayer films,[4] demonstrating that penetration of the C_{60} molecules into the deeper layers is not a dominant charge transfer mechanism.

4. Conclusion:

We have demonstrated highly efficient energy and charge transfer in self-assembled multilayer polyelectrolyte films. Energy transfer from the inner stack (close to the substrate) to the outer stack (close to the surface) is likely due to the slow transition of polymer conformation from a more coiled conformation to a more extended conformation. Capping a C_{60} or C_{60} copolymer layer on top of these highly luminescent multilayer films results in quenching of the photoluminescence with ~95% efficiency. The combination of efficient energy transfer and high quantum efficiency charge transfer suggests the potential application of these thin films in artificial photosynthesis and photovoltaic cells.

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