Efficient energy transfer from poly(N-vinyl-carbazole) to tetra-methylester of perylene-3,4,9,10-tetracarboxylicacid

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Organic electroluminescent (EL) devices based either on small molecules or on polymers are of great current interest due to their potential application in full color display panels covering a variety of emission colors from blue to red [1–4]. For polymer electroluminescent devices, to control and improve light emission, the commonly used concept is to blend a fluorescent dye into a proper polymer. Transfer of excitation from host to the guest is promoted by three processes: Forster transfer of singlet excitons generated on the host to the guest, Dexter transfer of both singlet and triplet excitons generated on the host to the dopant, and the direct generation of singlet and triplet excitons on the guest [5].

Forster transfer of energy from an absorbing host to an emitting guest has been used to realize different color emission. Also, it reduces self-absorbance by shifting the emission away from the absorption edge in blends. In general, a significant spectra overlap (overlap of the host emission spectrum and the dopant absorption spectrum) is a key requirement for efficient energy transfer. The transfer rate parameters are proportional to overlap area [6, 7]. In this letter we investigate energy transfer from the semiconducting polymer, poly(N-vinyl-carbazole) (PVK) to organic molecule tetra-methylester of perylene-3,4,9,10-tetracarboxylicacid (TMEP). We examine both the PL and EL spectra for a single layer made from PVK doped with TMEP.

Scheme 1a shows the chemical structure of TMEP. TMEP is liquid crystalline material in which the proximity of the electron-orbitals of adjacent molecules shows an ordered structure, it is a novel electron acceptor for plastic solar cells [8]. TMEP was synthesized according to the method described in [8]. PVK (obtained from Aldrich) is a widely used semiconducting polymer and it is used as the host material. The films of PVK and PVK doped with TMEP were made by spin-coating at 4000 rpm from a chloroform solution with a weight concentration of 5 kg/m^3. The organic layer was 90 nm in thickness (measured by a Dektak profilometer). PL spectra were measured by Hitachi Fluorescence spectrophotometer. UV-vis spectra were recorded for thin films on quartz substrates using a UV-VIS-NIR scanning spectrophotometer from Shimadzu. A chemical method was used to erode the ITO glass to our requirement. For EL devices, Al was used as the cathode by thermal evaporation of aluminum and the layer thickness was 100 nm. The active area was 2×2 mm^2. EL spectra were measured by Applied Photophysics monochromer.

For any device, surface quality of the organic layer is an important factor for high performance. To prove the high quality of the sample surface, we got the AFM surface graph of our solid thin-film made from TMEP/PVK 10% (5 kg/m^3) blend by spin-coating at 4000 rpm. Fig. 1 shows the three dimensional surface AFM image of the doped polymer. Surface rms-roughness is 2 nm and maximum roughness is 24 nm.

Fig. 2 shows the PL spectra of thin solid films of PVK, TMEP absorption spectra. According to the theory of Forster transfer, a large spectral overlap between the
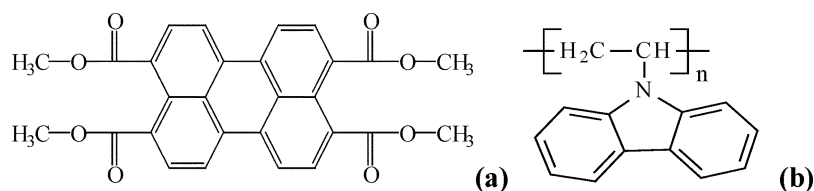
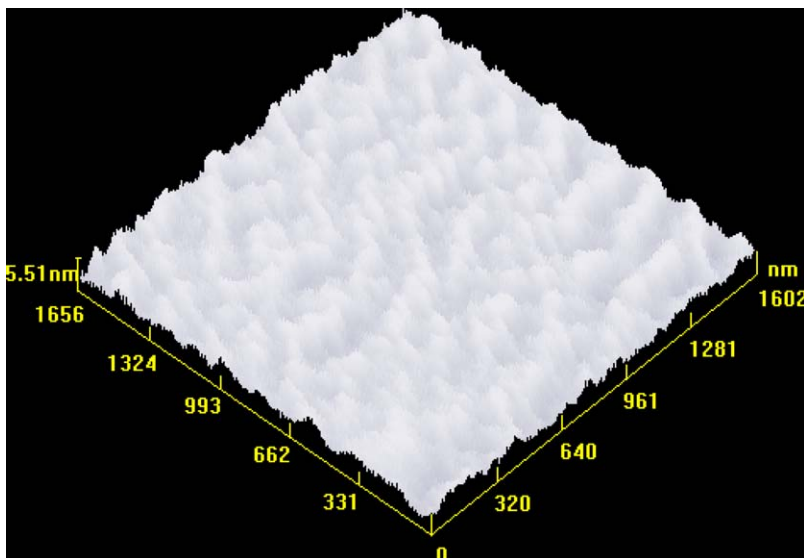*Scheme 1* The chemical structure of TMEP(a) and PVK(b).

Figure 1 AFM image of the surface of organic doped polymer layer (TMEP/PVK 10%).
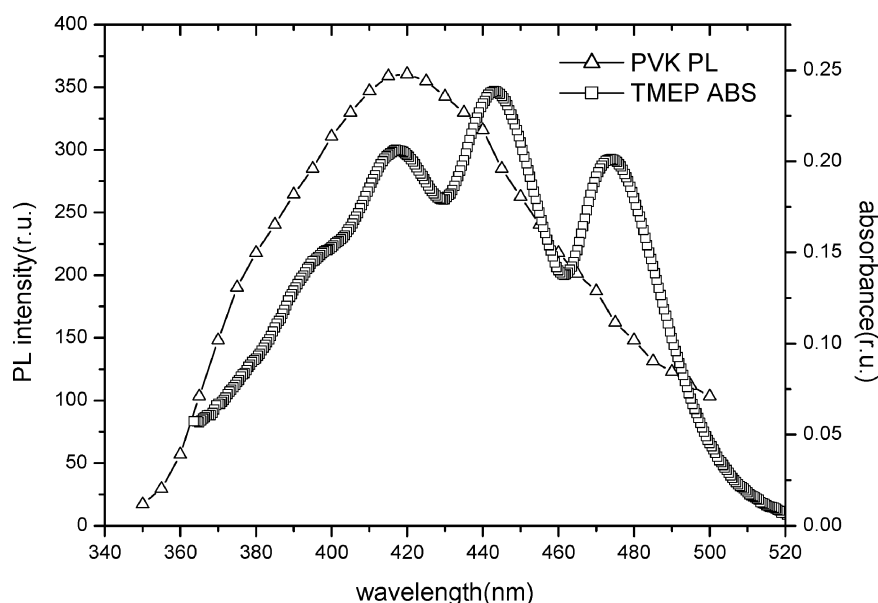

Figure 2 PVK PL spectrum and TMEP absorption spectrum.

emission of the host and the absorption of the guest is necessary for efficient Forster transfer [5]. From Fig. 2, it can be seen that the spectra overlap area between TMEP absorption spectrum and PVK emission spectrum is large, showing that it is possible for efficient energy transfer from PVK to TMEP.

The excitation spectra of PVK and 10% TMEP/PVK blend thin films are shown in Fig. 3. The excitation spectra of TMEP/PVK blend is very similar to that of PVK, and they reach their maxima at 295.5 nm.

Fig. 4 shows the PL spectra of thin solid films of TMEP/PVK blended at varying weight ratios. PVK PL spectra and TMEP PL spectra were used as references. The PL spectra of the TMEP/PVK blends were recorded at an excitation wavelength of 295.5 nm, where mainly PVK is excited because the absorption of PVK at this wavelength is much stronger than that of TMEP (shown in Fig. 3). Under the excitation of 295.5 nm the emission of pure TMEP is not observed. Combined with the excitation spectra, we conclude that

the emission of TMEP comes from the excitation of PVK. At the TMEP/PVK 1% circumstance, we can clearly see the PL emission from PVK at 410 nm and the TMEP emission at 530 nm. When the ratio increases from 1 to 10%, the intensity of PVK emission at 410 nm decreases, while the intensity of TMEP emission at 530 nm increases. For TMEP doping concentrations above 10% TMEP, PVK emission component in the PL spectrum has nearly vanished, and PL spectra are dominated by green TMEP emission due to complete energy transfer from PVK to TMEP. For TMEP doping concentration increasing from 10 to 15%, TMEP emission at 530 nm begins to decrease, it means that energy transfer from PVK to TMEP can be maximized at the appropriate mixing ratio. Forster energy transfer theory is used to explain energy transfer from PVK to TMEP. For efficient Forster energy transfer, we have demonstrated the large overlap area between PVK PL spectra and TMEP absorption spectra [6, 7]. When PVK is excited, it will transfer energy to the nearby molecule
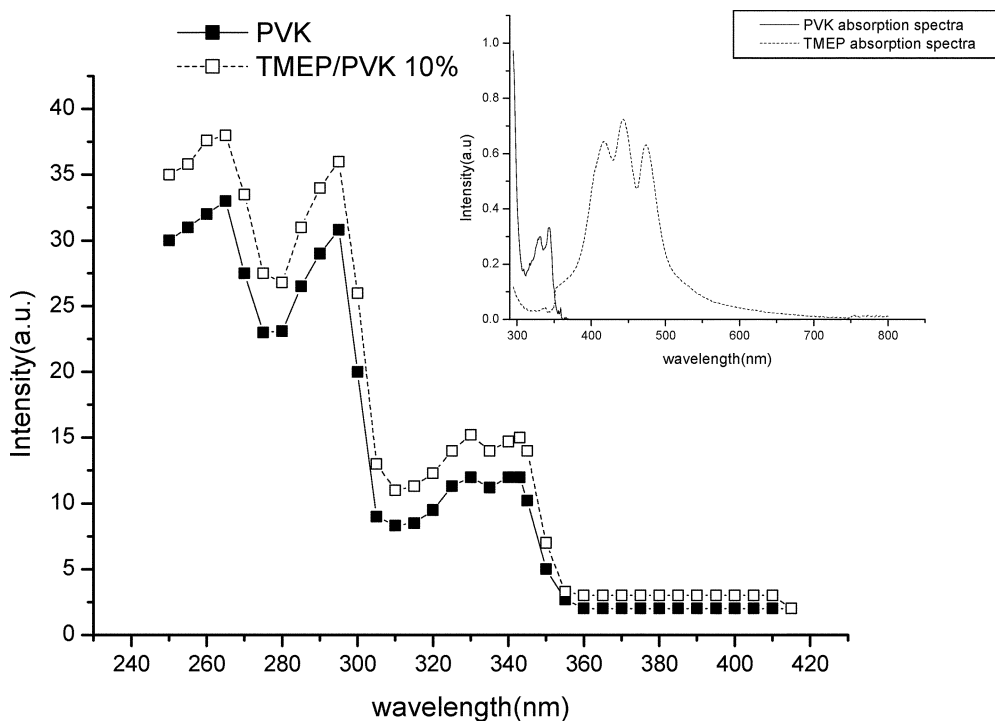
Figure 3 The excitation spectra of PVK and TMEP:PVK blend. Inset: TMEP and PVK absorption spectra.
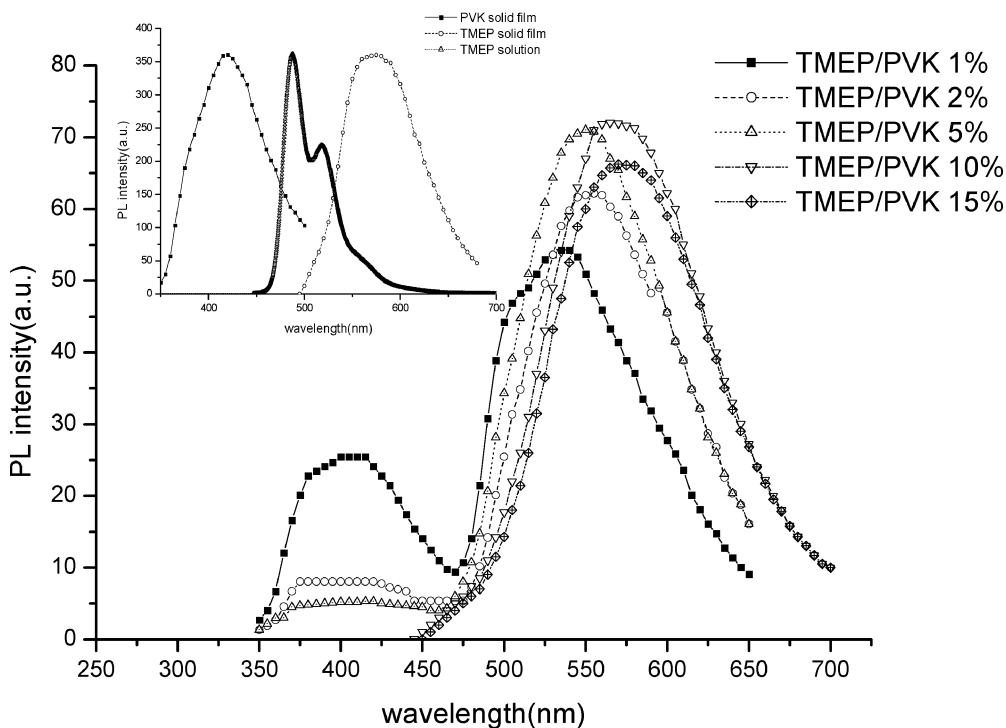

Figure 4 PL spectra of TMEP doped PVK at varying weight ratios. Inset: PL spectra for PVK and TMEP film, and PL spectra for TMEP solution.

TMEP (within a separation of 3–5 nm). The transfer is highly feasible because there is much overlap between PVK PL spectra and TMEP absorption spectra [9].

From the PL spectra we can find the emission peak systematically shifting to longer wavelengths with ratios increasing from 1 to 15%. We believe it results from excimer formation [10, 11]. To verify our conclusion, PL spectra of solid TMEP film were measured, and they shifted to a longer-wavelength region (single peak at 577 nm), compared with the two emission peaks at 490 and 520 nm obtained from TMEP solution. It is

evident that the redshift is sensitive to the composition due to the excimer.

Two classes of excitation mechanism are possible in EL: energy transfer(by Forster) and charge trapping, and often both are operative in a single device [12]. TMEP has four electron-withdrawing ester groups, which makes it suitable for charge transport. As shown in Fig. 5, EL spectra TMEP/PVK at the ratio 1% showed PVK emission at 420 nm and TMEP emission at 530 nm. Emission peak at 420 nm diminished when the TMEP concentration increased to 10%. Comparing
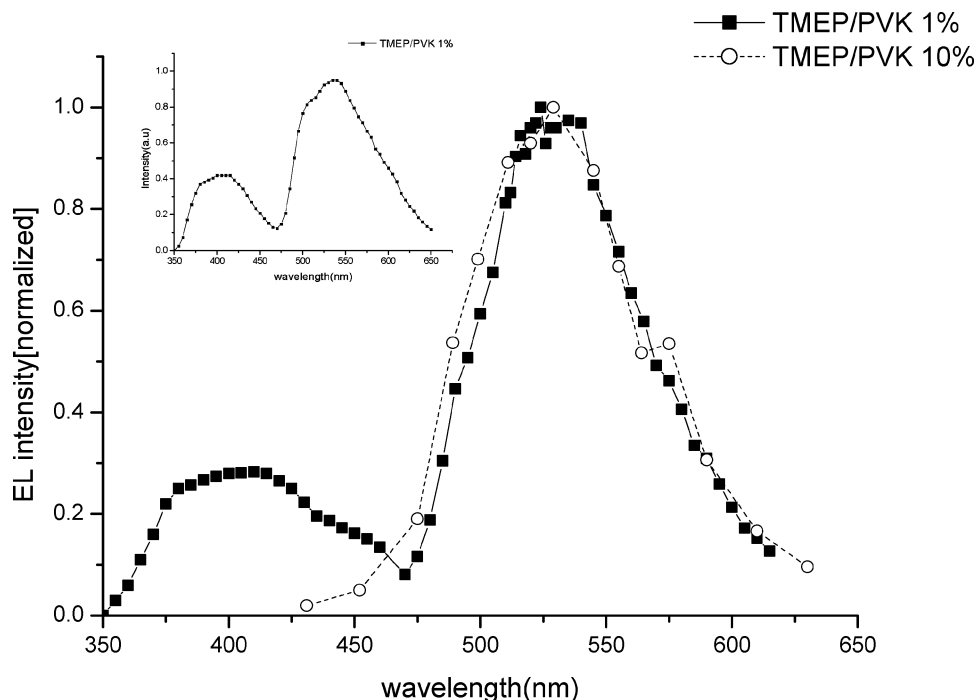
Figure 5 Normalized EL spectrum at TMEP doped ratios 1 and 10%. Inset: PL spectrum at TMEP doped ratio 1%.

EL spectrum with PL spectrum at TMEP doping concentration 1%, EL spectrum showed a slight decrease ratio at 420 nm compared with PL spectra. We attribute these observations to both Forster energy transfer from PVK to TMEP and charge trapping by TMEP molecules [12].

In summary this study demonstrated energy transfer from polymer PVK to small molecule TMEP. Both the EL and PL spectra were measured to confirm Forster energy transfer from PVK to TMEP. We found a slight redshift in PL spectra with increase of ratio of TMEP and attributed it to excimer formation. The EL spectrum is somewhat different from the PL spectrum at certain doping concentrations due to charge trapping by TMEP.

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