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Luminescence Properties of End-Substituted Oligo(PhenyleneVinylene)s

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Abstract

We have used three soluble three-phenyl-ring oligo(phenylenevinylene)s (OPV(1)s) with poly(alkyleneoxy) electron-donors and hexylsulfonyl electron-acceptors to investigate the end-substitution effect. Besides the increase in solubility, the end-substitution is found effective in fine tuning the absorption and emission properties. Symmetrically substituted OPV(1)s, with the same donor or acceptor end-groups, show a small red-shift in their absorption and emission spectra as compared to the unsubstituted OPV(1). Asymmetrically substituted OPV(1), with a donor at one end and an acceptor at the other, shows a larger red-shift in both the absorption and emission spectra due to the increased π -electron delocalization associated with the "push-pull" effect of the donor and acceptor in the molecule.

1. Introduction:

Poly(phenylenevinylene) (PPV) and its derivatives have attracted considerable attention due to their potential use in light emitting devices (LEDs) ^{1,2} and nonlinear optical applications ^{3,4}. One of the main research efforts has been aimed at the modification of PPV's electronic and mechanical properties by introducing substituents in the molecular structure. For example, substitution on the phenyl ring of PPV with two alkoxy groups can reduce the PPV energy gap by nearly half an electron volt⁵, while providing greater solubility and better film-forming properties. Over the past few years, various soluble PPV derivatives and copolymers have been synthesized to tune the electronic and emissive properties and to enhance the solubility and processibility of these materials^{6,7}.

In order to modify a material in a rational way, it is essential to have a good understanding of the intrinsic geometric, electronic, and optical properties of the material. However, broad molecular weight distribution, and the possible presence of blocks with different conjugation length

in polymeric material can complicate the investigation. In this regard, oligomers of the PPV type are of great interest. Their well-defined chemical structure together with their improved solubility and processibility allow access to detailed interpretation of experimental measurements while providing insight into the physical properties of related polymers. In addition, it is well known that in oligo(phenylenevinylene)s (OPVs), the shorter conjugated segment improves the fluorescence yields and the electroluminescence efficiency, and that the wavelength for absorption and emission decreases with decreasing conjugated length. This is especially useful in the search for blue light emitting materials. For these reasons, a number of research groups have synthesized different types of OPVs to investigate their absorption, luminance and electronic properties ⁸⁻¹⁰. Recently, a series of highly soluble three-phenyl-ring (distyrylbenzenes) bearing poly(alkyleneoxy) electron-donor(s) and/or hexylsulfonyl electron-acceptor(s) has been synthesized by Wong et al¹¹. Unlike the lateral substitution, substituents attached at the ends of a molecule do not generally disrupt the co-planarity of the π -conjugated system. The effect of end-

substitution on absorption spectroscopic properties, third-order nonlinear optical properties and thermal behavior has been discussed by Wong et al¹¹. In this paper, we report our investigation of end-group substitution on photoluminescent (PL) and electroluminescent (EL) properties in these OPV(1)s.

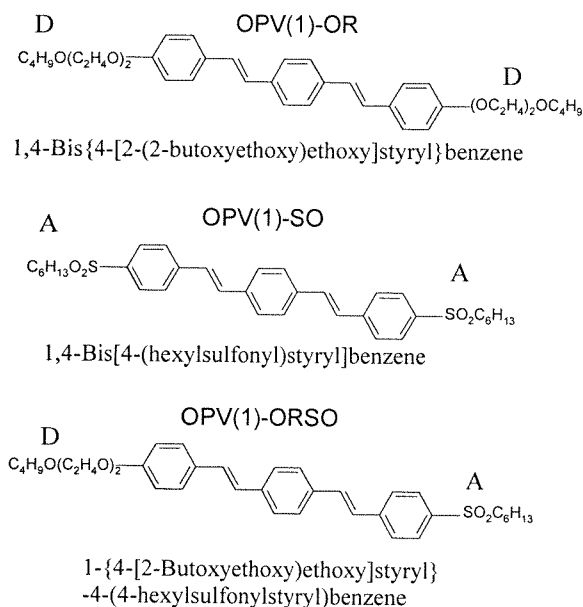


Figure 1. Three oligo(phenylenevinylene)s used in this study. The D and A represent donor and acceptor respectively.

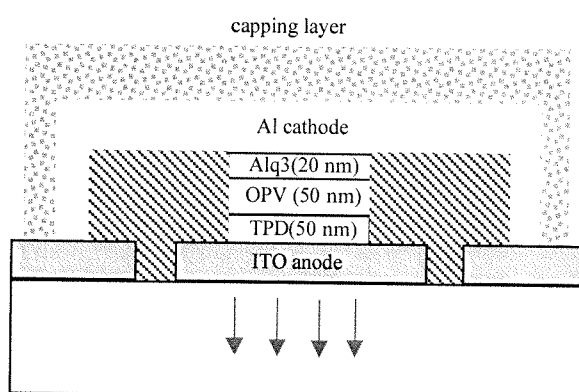


Figure 2. A typical OLED structure used in our electroluminescence study on OPV(1)s.

2. Experimental details

The OPV(1)s used in this work (Figure 1) were synthesized using the stereoselective Wadsworth-Emmons reaction as a key step. Details about the synthesis can be found in Wong et al¹¹. In these oligomers, the backbones are kept the same, but the end groups are substituted systematically. The difference in electronic properties of the substituents attached to the conjugated backbone will shift the highest occupied molecular orbital or HOMO level, the lowest unoccupied molecular orbital or LUMO level and the energy gap of the OPV(1)s, leading to different absorption and emission behavior. The result of the PM3 semi-empirical quantum mechanical calculations shows that the ground state optimized molecular geometries of the three OPV(1)s possess a good coplanarity of the π -conjugated system. The long chain nature of the substituents employed in our series is to enhance solubility during synthesis and purification as well as to prevent crystallization.

The solid thin films of the OPV(1)s were prepared by thermal evaporation in an Edwards Auto 306 coater equipped with a cryo-pump, using either tungsten or molybdenum boats. All depositions were performed at high vacuum (2×10^{-7} torr). A typical growth rate was 2 \AA/s and the substrates were all held at room temperature. The light emitting diodes used for EL study were prepared on commercial ITO coated glass substrates (Applied Films Corp.) with sheet resistance of 12 \Omega/ , and an ITO thickness of $\sim 120 \text{ nm}$. Before lithographical patterning, the ITO substrates were cleaned using cleanroom soap, acetone, and isopropanol. The anodes were formed by etching the patterned ITO substrates in a solution of HCl:HNO₃:H₂O (25:2:25). The patterned ITO substrates were treated in UV ozone for ten minutes before loading into the vacuum chamber. The device structures consisted of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) as hole transporting material, OPV(1)s as the emissive layer, tris(8-hydroxy-quinolate)-aluminum (Alq₃) as an electron transport material, and thermally evaporated aluminum as a cathode. A typical device structure is illustrated in Figure 2. A Varian Cary 1 Bio UV/vis spectrometer and a Spex Fluorolog-2 spectrometer were used for absorption and PL measurements for solution at a concentration less than 10^{-5} M . A Photo Research®-650 SpectraColori-meter was used to measure the electroluminescence spectra.

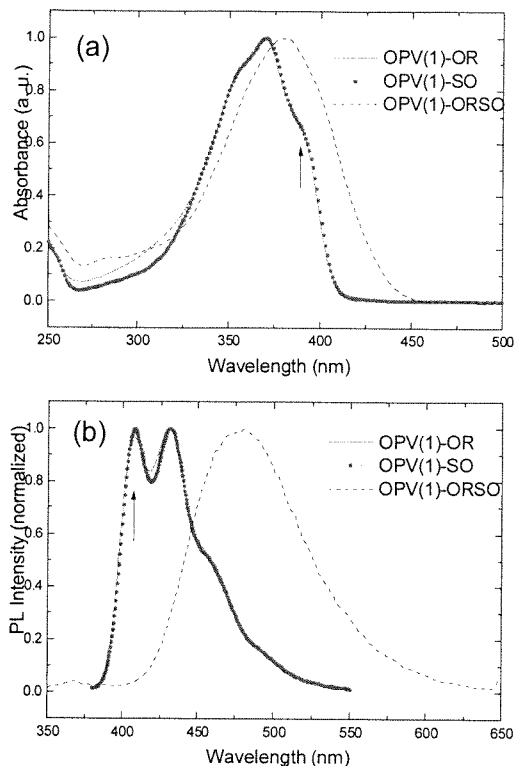


Figure 3. The UV-vis absorption spectra (a) and photoluminescence spectra (b) of OPV(1)s in chloroform. The arrows indicate the 0-0 phonon transition both in absorption and emission.

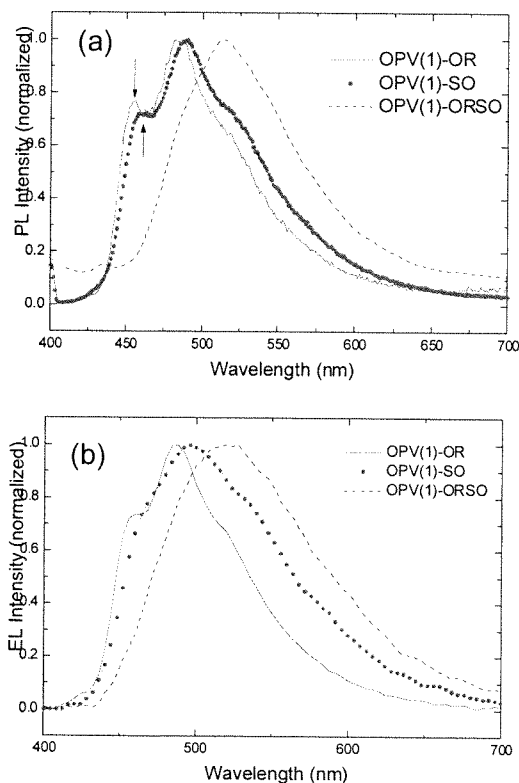


Figure 4. The PL spectra of solid OPV(1) thin films (a), and EL spectra (b) of OPV(1)s.

3. Results and Discussion

The UV-vis absorption spectra of OPV(1)s in chloroform are shown in Figure 3 (a). The symmetrically substituted OPV(1)s, OPV(1)-OR (acceptor groups at two ends) and OPV(1)-SO (donor groups at two ends), show no difference in their UV absorption spectra. Their 0-0 phonon absorption peaks are clearly visible at 390 nm (3.18 eV), the absorption maxima are at 367 nm (3.49 eV), and are red shifted by ~ 0.11 eV as compared to the unsubstituted OPV(1)⁸. Such a red shift is consistent with the fact that the donating and withdrawing substituents at the para-position of distyrylbenzene enhance the π -electron delocalization along the entire unsaturated system. The asymmetrically substituted OPV(1)-ORSO shows a significant shift towards longer wavelengths, and its vibronic features are not clearly visible. The OPV(1)-ORSO is an asymmetrically (donor-acceptor) substituted conjugated system, and the excitation is generally dominated by the intra-molecular charge-transfer excitation which gives a strong and intense absorption in the UV-vis spectrum. It is usually featureless and rather symmetrical. The absorption maximum of OPV(1)-ORSO is at 380 nm (3.26 eV). Its red-shift can be explained by the interaction between the donor (OR) and the acceptor (SO) groups at the extremities of the molecules, a so-called push-pull effect, which effectively enhances π -electron delocalization asymmetrically.

The PL spectra of the OPV(1)s in chloroform are shown in Figure 3(b). The PL spectra of OPV(1)-OR and OPV(1)-SO are also very similar, and the peak shapes are similar to that of PPV, with visible structures due to vibronic levels in the ground state. The 0-0 phonon emission peaks are at 408 nm (3.04 eV) as marked by an arrow on the plot. The PL maxima are at 431 nm (2.88 eV). The PL emission of OPV(1)-ORSO shows more red-shift. The PL maximum is at 478 nm (2.60 eV). No vibronic features are in the spectra. One possibility for the peak broadening is due to the dipole-dipole interaction among the polar molecules and interaction with the solvent.

The PL spectra of solid OPV(1)s thin films are shown in Figure 4(a). The OPV(1)-OR and OPV(1)-SO thin films show a larger red-shift compared to their spectra in solution, which is usually the case for solution and solid state spectra. For OPV(1)-OR, the emission maximum is at 483 nm (2.57 eV) and its 0-0 phonon emission peak is at 455 nm (2.73 eV).

The emission maximum for OPV(1)-SO is at 489 nm (2.49 eV), and its 0-0 phonon emission peak is at 461 nm (2.69 eV). The PL spectra of OPV(1)-ORSO film show a more significant red-shift. Again the PL peak of OPV(1)-ORSO is quite broad and featureless. The emission maximum of OPV(1)-ORSO is at 514 nm (2.41 eV).

The EL emission spectra were measured in OLEDs using OPV(1)s as emitting materials. The turn-on voltages for these devices vary between 5 and 10 V, and the luminance is ~ 8 cd/m² at 12 volts. The EL spectra are shown in Figure 4(b). The EL spectrum of OPV(1)-OR is nearly identical to its thin film PL spectrum, indicating that the EL emission originates from the OPV(1)-OR. Its maximum is at 486 nm (2.55 eV). The EL spectrum of OPV(1)-SO is identical to the thin film PL spectrum at low wavelength, but it is broadened in the high-wavelength tail. The reason for this broadening is not clear, but one possible explanation is the packing effect, which leads to a red shift. Another possibility is the interaction of the excited states of the molecule with the strong electric field during device operation¹², considering the long-chain character of the molecule. The EL emission from OLEDs with a structure of ITO/TPD/OPV(1)-SO/Al is identical to the one using Alq₃ as an electron transport layer, which excludes the possibility of Alq₃ emission in the OPV(1)-SO EL spectra. OLEDs using OPV(1)-ORSO as emitter were prepared using a similar structure as shown in Figure 2, but without the Alq₃ layer. The EL emission maximum is at 521 nm (2.38 eV). The peak is rather broad (FWHM=120 nm) with no vibronic features. It shows a red-shift ($\Delta\lambda=7$ nm) in the emission maximum as compared to its PL spectrum. The peak shape of the EL emission spectra is independent of applied voltage in the measured range (5-15 V). The interaction between the strong electric fields (10^6 V/cm) in the OLED and the molecular dipoles is likely to have a role in this red-shift.

In conclusion, we have investigated the photoluminescent and electroluminescent properties of end-substituted oligo(phenylenevinylene)s. Besides the increase in solubility, the end-substitution is found effective in fine tuning the absorption and emission properties. The UV-vis absorption peak was red shifted up to 26 nm (0.24 eV), and the PL emission (in chloroform) peak was red shifted up to 64 nm (0.41 eV) as compared to the unsubstituted OPV(1). The EL emission from OLEDs using OPV(1)s as emitters shows similar

red shifts. Further investigation is required to clarify whether the interaction between molecular dipoles affects the absorption and emission properties of OPV(1)-ORSO, and to determine to what extent the interaction of strong electric fields with molecular dipoles during device operation affects the electroluminescent properties.

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