

## Towards non-substituted blue emitting PPV: Experiments and Simulation

A. D. Faceto (1)\*, F. C. B. Maia (1), F. E. G. Guimarães (1)

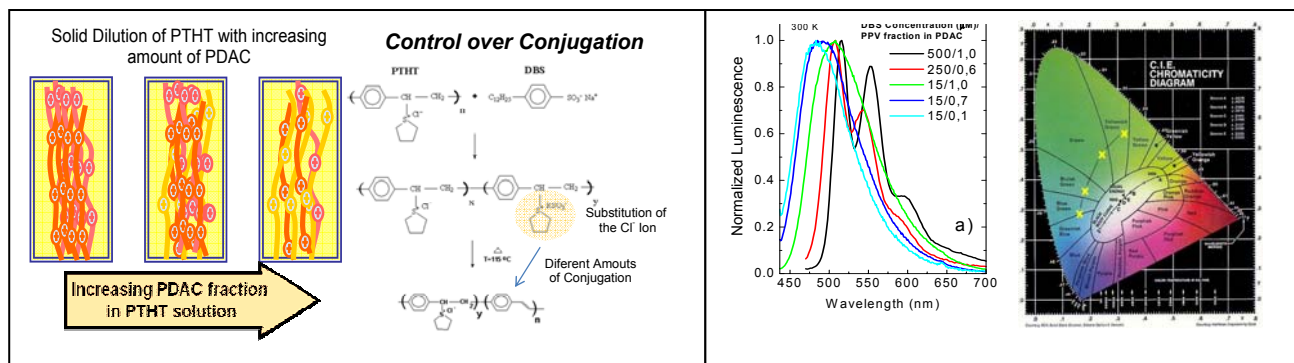
(1) Instituto de Física de São Carlos/Universidade de São Paulo, São Carlos – SP – Brasil e-mail: [faceto@ifsc.usp.br](mailto:faceto@ifsc.usp.br)

**Abstract** –The control the emission properties of a material is an important, but difficult task for light emitting organic semiconductors. PPV (poly(p-phenylene vinylene)) generally emit a yellowish-green fluorescence. Here, we report the greenish-blue photoluminescence for non-substituted PPV just by controlling both the migration processes and the final emissive density of states. This effect is confirmed by Monte Carlo simulation.

Devices based on PPV generally emit a yellowish-green fluorescence and derivatives obtained by direct substitution of a radical pendant along the molecular backbone are required to produce different colors. We demonstrate the possibility of the tuning emission region for a particular light emitting organic material just by controlling the migration processes and the final emissive density of states. A shift from the usual yellowish-green to a greenish-blue photoluminescence for the non-substituted PPV can be accomplished by doing a dilution of the PPV chain in a solid matrix of an optically inert polymer and/or by changing the effective conjugation. The PPV molecules were separated with Poly (diallyldimethylammonium chloride) (PDAC) by using Layer by Layer (LbL) technique. The conjugation length was achieved through molecular engineering by intercalating non-conjugated units in a copolymer (Figure 1) based on a PPV precursor (PTHT), by incorporating a long chain dodecylbenzenesulfonate ion (DBS) along the chain, followed by low temperature treatment (Figure 1).

In order to study the excited state dynamic of a wide range of polymeric materials in a matrix having length distribution, we have developed a molecular model and performed Monte Carlo simulations in such disordered polymeric system. The molecular model considers the material as a sequence of conjugated subunits having electronic states with distinct HOMO-LUMO gap and an associated vibrational progression with characteristics of the most effective phonon. We used three distribution functions (Gauss, Poisson and Lorentz) in order to describe different aspects of molecular conformation and sample preparation. After light absorption, the excitation dynamics are the result of a competition among the radiative emission, the internal intra-molecular vibrational relaxation and inter-molecular incoherent energy transference via Förster mechanism.

The step-by-step migration and relaxation processes of the excited state were simulated by Monte Carlo for different fractions of PPV in an inert matrix or along the chain. Static and dynamic luminescence, as well as excitation and absorption spectra obtained from simulation were compared with those of real world samples consisting of layered structures prepared with the LbL technique. Figure 2 shows the normalized PL for films in which PPV conjugated units were separated along or between the chains by changing both PDAC and DBS concentrations. As the amount of PDAC and DBS increased, a blue-shift of the PL was observed as demonstrated by the luminescence spectra or in a chromatic diagram in Figure 2. The simulated luminescence spectra show a very good agreement in terms of the characteristic spectral blue shift and line broadening for diluted PPV as well as for the PPV copolymer.



**Figure 1:** Schematic illustration for dilution of the PPV chain in a solid matrix of an inert polymer and for the change of the effective conjugation length.

**Figure 2:** Blue emission of PPV demonstrated spectrally or by the position in a chromatic diagram (yellow crosses).