

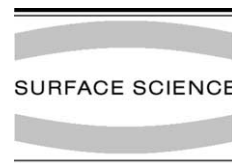


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# Influence of nanocrystals on the energy levels and luminescent properties of the polymer matrix in conjugated polymer–dielectric nanocomposites

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## Abstract

We report results of experimental investigations into the luminescent properties of conjugated polymers in which are embedded dielectric nanocrystals. In poly(*p*-phenylene vinylene), embedding nanocrystals results in a blue shift and broadening of luminescence spectra with a simultaneous disappearance of its vibronic structure. The same nanocrystals in poly(2-(6-cyano-6'-methylheptyloxy)-1,4-phenylene) cause a red shift and spectral broadening. The results are explained with reference to a model accounting for the change in the polarization component of carrier and exciton energy in the vicinity of nanocrystals. The polymer–dielectric nanocomposites demonstrated increased electroluminescence effectiveness compared with pure polymers.

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## 1. Introduction

Embedding semiconductor nanocrystals in a conjugated polymer matrix has previously been reported to result in a significant change in luminescent and photoelectric properties [1–3] of the composite material, which may be used to optimize the parameters of photonic devices. The effects described are due to the capture of non-equilibrium carriers into narrow-gap semiconductor inclusions and radiative recombination therein. To date, however, the influence of dielectric nanocrystals on the properties of *the polymer itself*

has been investigated much less. Though the band gap of dielectrics is much greater than the energies of the photons in question, the influence of the nanocrystals can be considerable due to changes in local polarizability. In conducting polymers, this is responsible for large energy shifts in molecular orbitals and exciton energies [4]. We present herein the results of our experimental and theoretical investigations of this problem.

## 2. Sample preparation

We worked with three types of polymer matrix materials: poly(*p*-phenylene vinylene) (PPV), poly(2-methoxy-5-(2-ethyl hexyloxy)-*p*-phenylene vinylene) (MEH-PPV) and poly(2-(6-cyano-6'-methylheptyloxy)-1,4-phenylene) (CN-PPP). For

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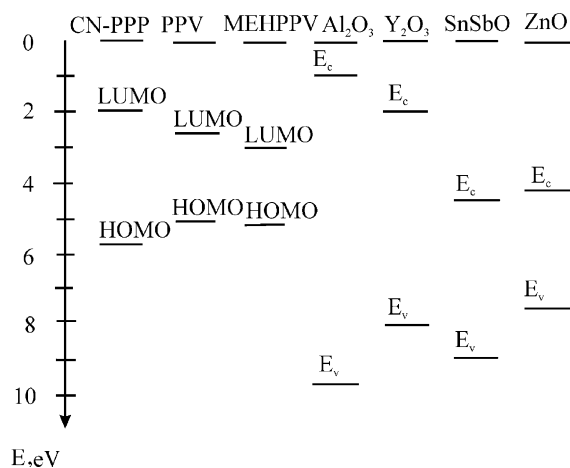


Fig. 1. Characteristic energy levels in nanocomposite components. Abbreviations LUMO and HOMO correspond, respectively, to the lowest unoccupied and highest occupied molecular orbitals in a polymer;  $E_c$  and  $E_v$  denote the edges of conduction and valence band in a dielectric.

dielectric inclusions we employed the following dielectric oxides:  $Y_2O_3$ ,  $Al_2O_3$ , ZnO and the antimony–tin oxide  $SnO_2/Sb_2O_3/Sb_2O_5$  (abbreviated throughout the present work as SnSbO). These nanocrystals were of average size 25 nm ( $Y_2O_3$ ), 38 nm ( $Al_2O_3$ ) and 54 nm (ZnO). The available values of band gap  $E_g$  and electron affinity  $\chi$  for these materials allow us to find relative positions of the band edges in all possible polymer–dielectric composites (Fig. 1). They show that type-I heterojunctions should exist between  $Al_2O_3$  and  $Y_2O_3$  and their host polymer (dielectric nanocrystals are antidots for both electrons and holes) whereas between SnSbO and ZnO and the host polymers, type-II heterojunctions with a staggered band diagram are formed.

Composite samples were prepared by mixing the nanocrystal powder with a polymer precursor followed by sonication for 1.5 h and spin-coating onto glass substrates. The samples were annealed for 2 h in an atmosphere of 95% Ar and 5%  $H_2$ .

### 3. Photoluminescence spectra

Photoluminescence spectra of pure PPV and PPV-based nanocomposites are presented in Fig. 2.

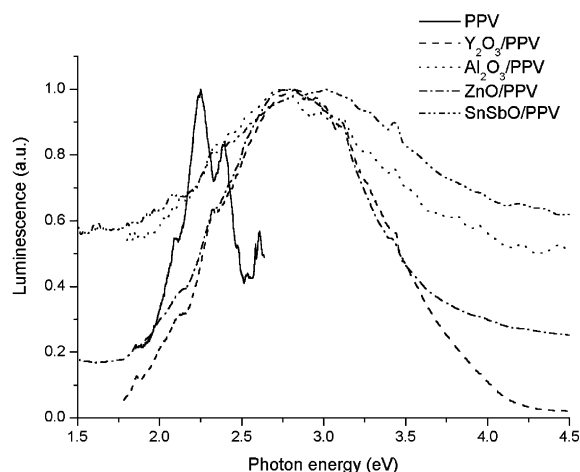


Fig. 2. Normalized photoluminescence spectra of pure PPV and PPV-based nanocomposites.

It is seen that, after embedding wide-gap nanocrystals, the luminescence maximum shifts to higher energies and broadens considerably. The spectra of the nanocomposites no longer exhibit the distinct vibronic structure typical of pure PPV. The exact position of the spectral maximum depends on the nanoparticle material. The maximum position in SnSbO/PPV is shifted towards higher energies relative to in other composites is equal to 3.0 eV, compared with 2.7–2.8 eV in  $Y_2O_3$ ,  $Al_2O_3$  and ZnO. The luminescence excitation spectrum in nanocomposites is also modified significantly. Instead of a maximum at 2.5–4.0 eV, wide absorption regions with spectral shapes different for different composites appear at higher energies.

Photoluminescence spectra of CN-PPP-based nanocomposites are modified by nanocrystals less noticeably than those of the PPV-based materials (Fig. 3). The luminescence maximum acquires a small red shift from 3.085 eV in pure CN-PPP to the values 3.05 eV (SnSbO), 3.06 eV (ZnO), 2.98 eV ( $Y_2O_3$ ), and 2.96 eV ( $Al_2O_3$ ) in the composites containing ~10% (by volume) of nanoparticles. The increase of nanoparticle volume up to 60% causes almost no change in the position of the maximum for SnSbO and ZnO, changes the maximum to 2.93 eV for  $Y_2O_3$  and to 2.84 for  $Al_2O_3$ , and noticeably broadens the spectrum and increases the intensity of luminescence at lower photon energies. The luminescence excitation

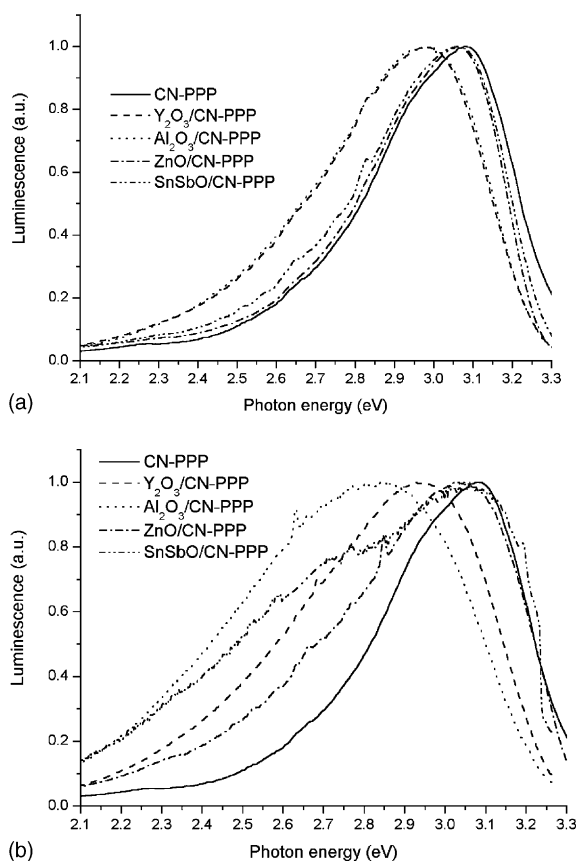


Fig. 3. Normalized photoluminescence spectra of pure CN-PPP and CN-PPP-based nanocomposites with volume fraction of a dielectric (a) 10% and (b) 60%.

spectra for composites with a high percentage of nanocrystals always contain a maximum at photon energies 3.43 eV ( $Y_2O_3$ ), 3.37 eV ( $Al_2O_3$ ), 3.45 eV ( $SnSbO$ ), and 3.67 eV ( $ZnO$ ). The latter value coincides with that for pure CN-PPP.

The luminescence spectra in MEH-PPV-based nanocomposites (Fig. 4) are also broadened compared to a pure polymer. With the experimental accuracy, their maximum shows no systematic shift.

The observed influence of nanocrystals on the composite spectra may be accounted for in terms of the difference in polarization properties between the dielectric inclusions and polymer matrix. In conducting polymers, polaron effects shift the energy levels [5], decreasing the HOMO–LUMO gap and reducing the luminescence energy. The polaron shift  $W$  arises due to interactions between an

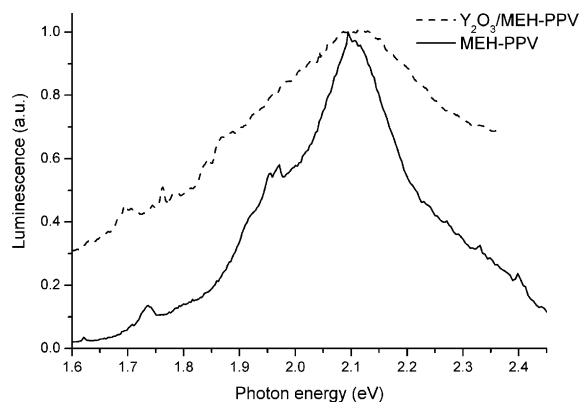


Fig. 4. Normalized photoluminescence spectra of pure MEH-PPV and MEH-PPV-based nano-composites.

electron and not only its nearest neighbors, but also atoms from higher coordination spheres. If inclusions have smaller polarizability than the matrix (expected in PPV-based composites), these decrease the polaron shift of energy levels and hence increase the energy of the luminescence line. For inclusions with higher polarizability the effect is the opposite. These qualitative conclusions were confirmed by theoretical estimates.

An extra mechanism contributing to a blue shift in the luminescence maximum in PPV may be related to changes in the conjugated length. In the sites where the bonds between a polymer chain and nanocrystal are formed, the electronic configuration in the polymer chain changes,  $s$ – $p$ -hybridization occurs [6], and the overlapping of  $\pi$ -orbitals diminishes, decreasing the conjugation length.

The disappearance of vibronic structure may be attributed to the formation of bonds between polymer chains and nanocrystals, changing randomly the vibration modes. In addition, different nanocrystals may have different sizes and masses. These factors together smear out the initially discrete phonon structure and the related vibronic spectra.

#### 4. Luminescence kinetics

To obtain additional information on the properties of non-equilibrium carriers in our nanocomposites, time-resolved measurements were also

performed, using the Photon Technology International spectrofluorometer C-60 for optical excitation ranging in wavelength from 220 to 400 nm. The standard stroboscopic measurement scheme was used with a 10 Hz series of 364 nm wavelength, 2 ns duration excitation pulses produced by a dye laser.

The qualitative features of the measured kinetics were the same in all samples investigated. For this reason we present in Fig. 5 only the results for two different polymers (PPV and CN-PPP) and one dielectric ( $Y_2O_3$ ). Time-resolved measurements reveal kinetics of photoluminescence containing three characteristic times. In PPV/ $Y_2O_3$ , for example, these are equal to 0.35, 3.5 and 12 ns. The component with the largest decay time (12 ns) has amplitudes one order of magnitude smaller than fast components.

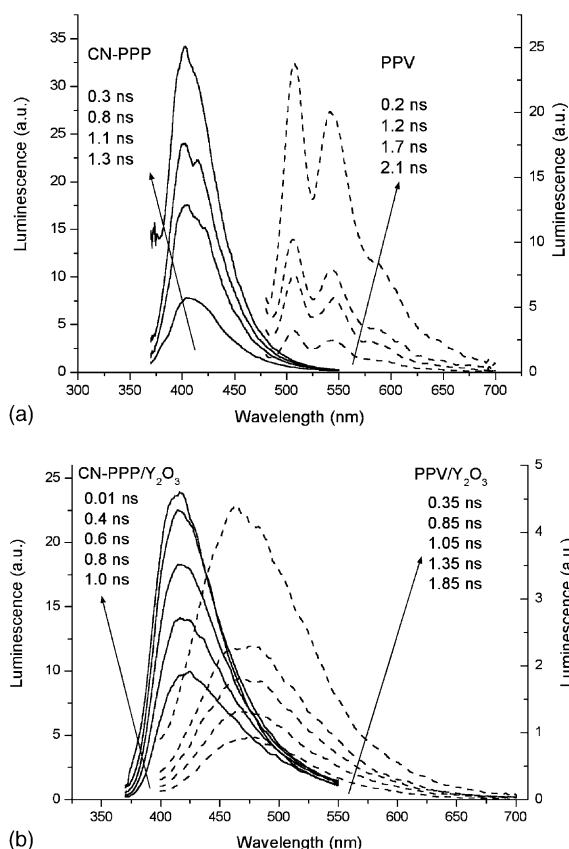


Fig. 5. Time-resolved photoluminescence spectra in (a) pure polymers and (b) nanocomposites polymer/ $Y_2O_3$ .

Each of these characteristic times is attributable to a distinct recombination mechanism. Two larger times are presumably related to capture of charges by dielectric inclusions followed by escape into the polymer matrix. The shortest time may relate to transitions inside the matrix and is very close to the reported recombination time in pure PPV,  $\tau = 0.4$  ns [7]. A slight decrease of  $\tau$  in the composite samples may relate to additional recombination at the polymer–dielectric interface.

## 5. Electroluminescence

The photoluminescence measurements described above allowed us to understand better the physics of observed process. However, for applications in light-emitting devices, the electro-, rather than photo-, luminescence is of primary importance. Its features were investigated as well and showed no considerable difference in luminescence spectra as compared with photoluminescence. The most important experimental fact consists in the increase of electroluminescence efficiency for a given injected current density in samples with dielectric nanocrystals shown in Fig. 6.

We propose a few possible explanations of this experimental observation. In the presence of dielectric inclusions, the current density in the sam-

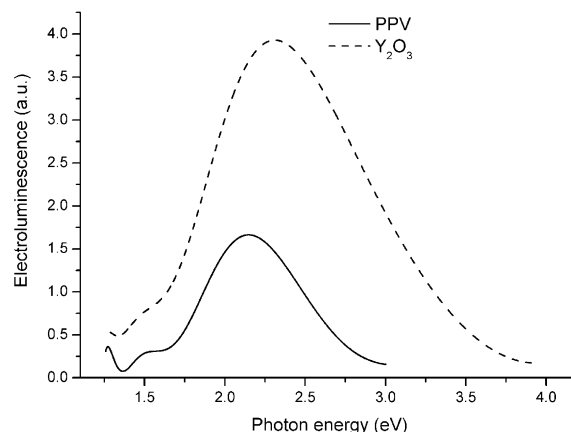


Fig. 6. Electroluminescence spectra for (1) pure and (2) nanocomposite/ $Y_2O_3$ .

ple is distributed non-uniformly. In the presence of dielectric particles, some film regions become thinner than in uniform film [8]. As a result, the current density and hence the light output increase [9]. Another mechanism of luminescence intensity increase may relate to the increase in cathode area caused by the nanocrystal-related surface roughness, increasing the injection effectiveness [10]. We may also imagine a growth of optical matrix element accompanying the nanocrystal-induced changes in the polymer energy spectrum discussed above. Additional investigations aimed to elucidate and maximize the growth of electroluminescence in nanocomposites are now in progress.

## 6. Conclusions

Experimental investigations of different polymer–dielectric nanocomposites show that embedding of dielectric nanocrystals may noticeably change the spectrum, intensity, and kinetics of photo- and electroluminescence. The character of the spectra modification may be qualitatively different depending on the matrix and inclusion materials and is presumably related to the modification of the matrix near the polymer–inorganic

interface. Non-uniform spatial distribution of the current density in composite structure results in a considerable increase of the intensity of electroluminescence of particular interest in polymer-based light-emitting devices.

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