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Doping poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] with PbSe nanoparticles or fullerenes

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Abstract

The positions of the molecular orbitals of the conjugated semiconducting polymer, poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), relative to the Fermi level, shift when lead selenide (PbSe) quantum dots or the fullerene based molecule [(6)-1-(3-(methoxycarbonyl)propyl)-[(5)]-1-phenyl-[5,6]-C61, known as PCBM, are dispersed in the polymer host. This is evident from the consistent shifts of occupied molecular orbitals and the valence band edge to greater binding energies and a decrease in density of states near the Fermi level, as probed by photoemission. In the case of PbSe nanocrystal quantum dots, far smaller binding energy shifts were observed. This behavior seems more characteristic of a charge donor, though PbSe and PCBM should act as charge acceptors. In the case of both dopants, what doping does exist occurs only with small concentrations (<10%). MEH-PPV doped with a large-Z semiconducting material, such as PbSe nanocrystal quantum dots, is a candidate for use as a good gamma radiation detector.

1. Introduction

The doping of semiconducting polymers is a hugely active area of interest [1–5]. However, it is not clear whether nanoparticles dope a polymer in the conventional sense of acting as charge donors or acceptors, or merely act as particulates in a polymer matrix with a high surface area to volume ratio. In the latter case, doping can still occur due to the dipole layer at the nanoparticle interface [6]. Two such dopants command attention: lead selenide (PbSe) quantum dots and the fullerene based molecule [(6)-1-(3-(methoxycarbonyl)propyl)-[(5)]-1-phenyl-[5,6]-C61, known as PCBM. Polymer photodetectors based on poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-

phenylenevinylene] (MEH-PPV) and related PPV polymers, doped with lead selenide (PbSe) [7–9], lead sulfide (PbS) [10, 11], and cadmium selenide (CdSe) [12, 13] nanocrystal quantum dots have shown significant increases in quantum efficiencies. PCBM has also been used to dope MEH-PPV, with promising results [5, 14–16]. Fullerene derivatives have been used to dope other semiconducting polymers [1, 4, 17–27], sometimes in combination with other nanoparticle systems [28]. Certainly doping polymers with semiconducting nanoparticles or fullerene molecules is seen as a route to improving polymer solar cell performance [1, 4, 9, 29–32]. Recently Zhao *et al* reported that a composite of blue light emitting conjugated polymer

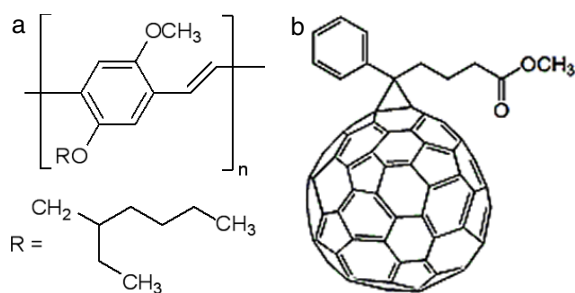


Figure 1. Schematics of (a) poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and (b) [6]-1-(3-(methoxycarbonyl)propyl)-[5,6]-C₆₁, known as PCBM.

polyfluorene, red light emitting dye, and a large- Z atom (Z is the atomic number) 1,3-diiodobenzene shows promising γ radiation detecting properties [33]. They confirmed the fluorescence resonance energy transfer between the polymer and the dye. The photoluminescence intensities respond linearly to γ -ray dosage. Campbell and Crone presented scintillation results of CdSe–ZnSe core–shell quantum dots and MEH-PPV composite for radiation-detection application [34]. They demonstrated the Forster excitation transfer from the quantum dots to the polymer and thus potential for gamma-ray, neutron, and charged-particle detection while having benefits of a low cost, easy processability, and large-area applications.

Both PbSe and PCBM accept excited electrons from MEH-PPV at extremely high charge transfer rates (time in picoseconds), aiding charge separation: but do they act as charge acceptors in the ground state? If not uniformly dispersed, there is also the issue of when nanoclusters cease to dope with increasing concentrations. The latter issue is of importance if PbSe, or like nanocrystal quantum dots, are added to the MEH-PPV matrix to make a composite suitable for gamma radiation detection; both to add a large- Z material to the polymer, thus increasing the cross-section, as well as to improve quantum efficiencies. Here we explore both questions.

2. Experimental details

Powdered MEH-PPV (Sigma Aldrich) from a single batch with the average molecular weight $86\,000\text{ g mol}^{-1}$ was dissolved in chlorobenzene. The chemical structure of the MEH-PPV is shown in figure 1(a). These solutions were heated to 80°C and stirred for 8 h, then filtered and spincoated onto coated glass substrates for the pristine MEH-PPV sample. The substrate was indium tin oxide (ITO) coated glass with sheet resistance of $\sim 10\ \Omega/\square$ (150 nm thick ITO) obtained from Delta Technologies.

For the nanocrystal bearing films, PbSe nanocrystals in solution (obtained from Evident Technologies) were added to MEH-PPV solutions prepared as described above in appropriate volume to obtain the desired weight ratios. These PbSe crystals were 5–8 nm in diameter and suspended in hexane. PCBM bearing films were prepared from the same base MEH-PPV solution described above by adding powdered PCBM (Sigma Aldrich) in amounts needed to achieve the given

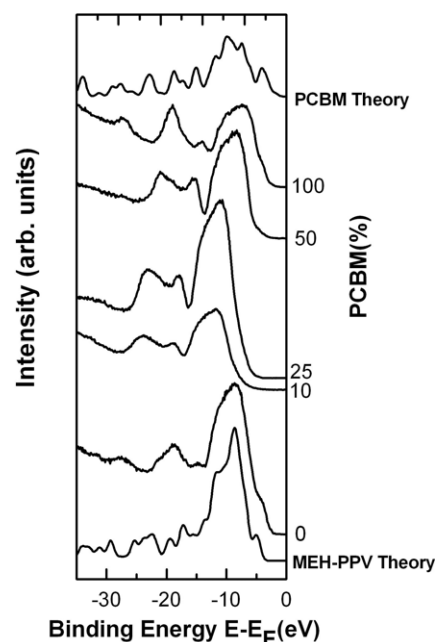


Figure 2. The occupied electronic structure of MEH-PPV polymer with increasing amounts of PCBM, as characterized by photoemission. The photoemission spectrum of pure MEH-PPV compared with model expectations (bottom curve) and the photoemission spectrum of pure PCBM films compared with model expectations (top curve). There is qualitative agreement with the calculated ground state molecular orbitals following a summation and using a 1 eV Gaussian applied to each molecular orbital. The photoemission spectra were taken at a photon energy of 62 eV with a light incidence angle of 45° relative to the surface normal with normal emission.

weight ratios. The schematics of the PCBM chemical structure is given in figure 1(b). These samples were dried, *in vacuo*, for 8 h at room temperature. Film thicknesses were measured to be 90 nm with good uniformity ($\pm 10\%$).

Angle resolved photoemission spectra were acquired using a 3 m toroidal grating monochromator [35, 36] at the Center for Advanced Microstructures and Devices (CAMD) in Baton Rouge, Louisiana [37]. Angle resolved measurements were made in a UHV chamber employing a hemispherical electron analyzer with an angular acceptance of $\pm 1^\circ$, using plane polarized synchrotron light dispersed by a 3 m toroidal grating monochromator as described elsewhere [35, 36]. The combined resolution of the electron energy analyzer and monochromator is 120–150 meV for high kinetic photon energies (50–120 eV), but higher resolution (about 80 meV) is obtained at lower photon energies of 15–40 eV. Throughout, all binding energies are referenced to a gold standard Fermi level, and angles are defined with respect to the substrate surface normal.

3. Results and discussion

While the electronic structure of MEH-PPV and PCBM have many similarities, as a composite, the electronic structure does change as expected from that predicted for MEH-PPV to that predicted for PCBM, as seen in figure 2. After

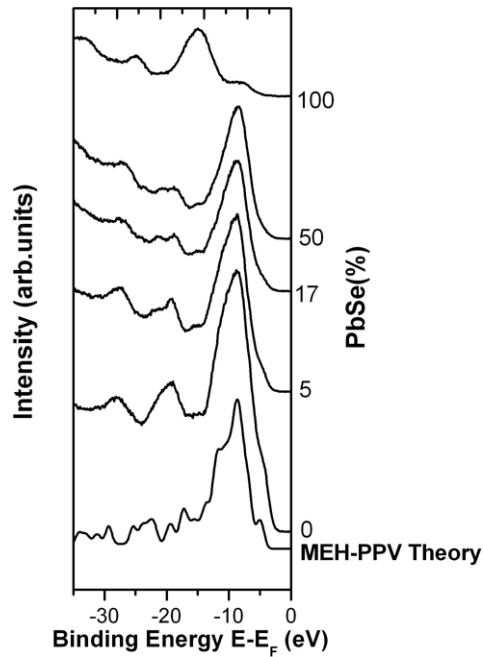


Figure 3. The occupied electronic structure of MEH-PPV polymer with increasing amounts of PbSe nanocrystals, as characterized by photoemission. The photoemission spectrum of pure MEH-PPV compared with model expectations (bottom curve). The photoemission spectra were taken at a photon energy of 66 eV with a light incidence angle of 45° relative to the surface normal with normal emission.

a shift of the calculated orbital energies by about 4.4 eV (roughly the expected work function), the experiment is seen to be in qualitative agreement with very simplistic calculated representation of the density of states based on the ground state molecular orbitals (NDO-PM3 or neglect of differential diatomic overlap, parametric model number 3) [38] for a single PCBM complex or a short chain of MEH-PPV, with a 1 eV width Gaussian envelope applied to each molecular orbital, without correcting for the substrate, final state or matrix element effects, as has been done elsewhere [39, 40]. Some changes are evident in the photoemission spectra as the composite concentration changes (figure 2). In the shape of the photoemission spectra, these changes are even more clear when PbSe nanocrystals are dispersed in MEH-PPV host (figure 3).

With increased PCBM doping, to about 10%, PCBM does not act much like an electron acceptor, but more like an electron donor. In the picture of band filling, the introduction of extra electrons to the MEH-PPV system fills any empty states near the Fermi level E_F and increases the binding energies of all the molecular orbitals [40]. The subtraction of electrons from the MEH-PPV system should lead to a decrease in binding energy of all the bands. To a concentration of about 10%, PCBM (figure 2), and to a lesser extent PbSe (figure 3), appear to act as electron donor, when added to the MEH-PPV system. This is because the addition of these nanocluster components leads to greater binding energies of the occupied molecular orbitals valence bands and the valence band maximum (relative to the Fermi level) and a decrease in density of states near E_F as seen in similar doped polymer systems [40].

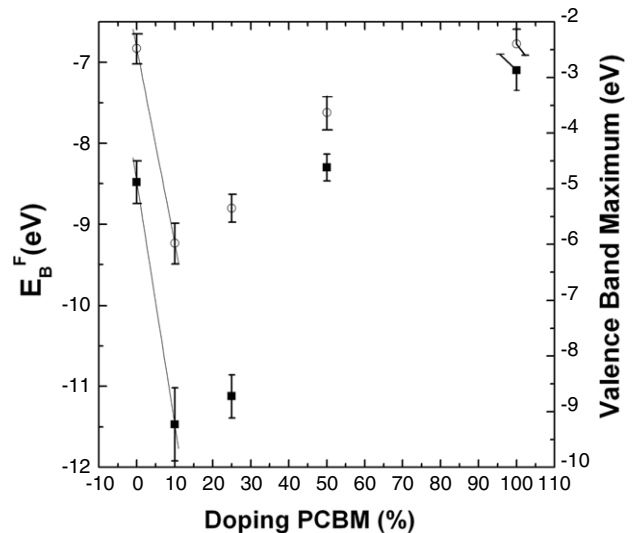


Figure 4. The binding energy of the main photoemission feature (■) and the binding energy of the valence band maximum (○) of MEH-PPV with increasing amounts of PCBM as characterized by photoemission.

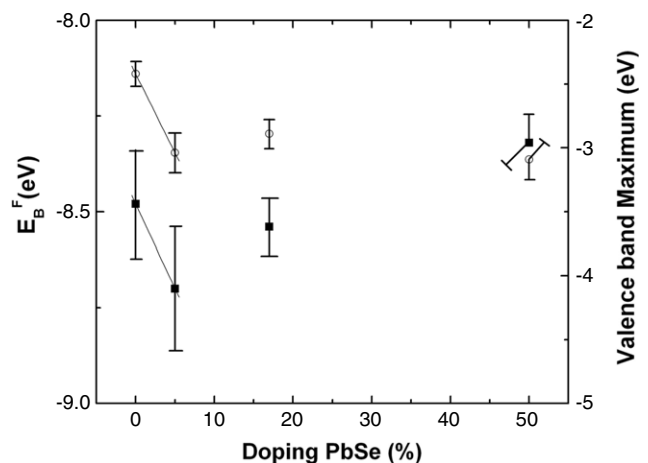


Figure 5. The binding energy of the main photoemission feature (■) and the binding energy of the valence band maximum (○) of MEH-PPV with increasing amounts of PbSe nanocrystals, as characterized by photoemission.

This influence of increasing concentrations of PCBM, resulting in a decrease in the density of states at the Fermi level and an increase in binding energies of the features due to the occupied molecular orbitals, is not as evident with increasing concentrations of PbSe nanocrystals, and does not extend to the very high doping concentrations. We have plotted the binding energies of the valence band maximum and the most prominent photoemission for both composites with PCBM (figure 4) and PbSe (figure 5). These increases in binding energies occur either because of band filling, that occurs in the case of PCBM, or due to charging. To a far lesser extent this also seems true for composites with PbSe nanoclusters. This means that the doped MEH-PPV material likely remains a good dielectric for loading concentrations of 10–25%. This is valuable because it provides a route for high loading values of PbSe, while

retaining properties that make the material a good gamma-ray scintillation detector.

For PCBM concentrations above 10%, the valence band maximum and density of states is restored, and to a far lesser extent with PbSe nanocluster inclusion. This restoration of the valence band maximum closer to the Fermi level tends to indicate that, at the higher concentrations, neither PbSe nor PCBM effectively dope MEH-PPV, but rather cluster or agglomerate, so that doping occurs only at the interface between the two mixed components. Clearly some structural studies are needed to establish whether the composites are phase separated or component materials separated.

4. Conclusion

The positions of the molecular orbitals of the semiconducting polymer MEH-PPV, relative to the Fermi level, shift with the doping of MEH-PPV by either PbSe nanocrystal quantum dots, or fullerene based molecule PCBM. The effect is more dramatic with PCBM than with PbSe and results in a decrease in density of states near Fermi level and shifts to greater binding energies of the occupied molecular orbitals and the valence band edge as probed by photoemission. Phase or component segregation seems likely for dopant concentrations greater than 10%. The composite of MEH-PPV and a large-Z material such as PbSe nanocrystal quantum dots is a potential gamma-detection material.

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