



Interplay between fluorescence and morphology in composite MEH-PPV/PCBM nanoparticles studied at the single particle level

Daeri Tenery, Andre J. Gesquiere *

NanoScience Technology Center, Department of Chemistry and CREOL, The College of Optics and Photonics, University of Central Florida, 12424 Research Parkway Suite 400, Orlando, FL 32826, United States

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ABSTRACT

We report the study of the photoluminescence properties of composite conjugated polymer (MEH-PPV)/ fullerene (PCBM) nanoparticles as a function of PCBM doping level. The emission properties of individual nanoparticles were studied by Single Particle Spectroscopy (SPS), and distinct changes in vibronic structure with nanoparticle composition were observed. These changes are found to be due to the presence of domains in the nanoparticles with two distinct types of optical signatures, one with molecular and one with aggregate character, for which the abundance and morphology is found to change with PCBM doping levels. Interestingly, highly delocalized structures with a large extent of exciton migration are formed at low PCBM doping levels, while at high PCBM doping levels the exciton collapses into highly localized structures. Furthermore, at very high doping levels phase separation within the MEH-PPV/PCBM nanoparticles is found, even though the reported nanoparticles are only a few tens of nanometers in diameter.

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1. Introduction

Conjugated polymer material properties have been found to vary strongly with preparation conditions, which has been related to the enormous conformational disorder that exists for conjugated polymers due to the sensitivity of the morphology of conjugated polymer materials to processing parameters [1]. In particular, the photophysics and optical properties of conjugated polymer materials have been found to strongly depend on the morphology and interactions of the corresponding conjugated polymers [2]. As a result, the spectroscopic and optoelectronic properties of conjugated polymer materials have been extensively studied with respect to the relationship between properties and morphology of the bulk material [3–5]. Findings such as changes in spectral properties and fluorescence anisotropy decay during the lifetime of the excited state have been related to exciton migration, during which the exciton hops over a set of chromophores with increasing conjugation length via an energy transfer mechanism [6,7]. Furthermore, aggregation of conjugated polymer molecules leads to the formation of interchain excitations at low energy aggregate sites in the conjugated polymer materials that have a low quantum yield and act as exciton traps [8,9]. This combination of properties is found to typically result in red shifted spectroscopy of the conjugated polymer even in poor solvents where the conjugated

backbone can be severely kinked and bended, thereby reducing the effective conjugation length for absorption [10].

Aggregation can also alter the relative intensities of emission bands in fluorescence spectra thereby modifying the apparent vibronic structure, as reported in recent literature for fluorescence spectra of bulk conjugated polymer films [6,11–16]. The intensities of emission bands can be evaluated based on the Franck–Condon factors, which are generally expressed as

$$\prod_i \frac{e^{-S_i} S_i^{n_i}}{n_i!} \quad (1)$$

for vibronic progressions between the 0th and n_i th vibrational levels, and can be found by considering the overlap of the harmonic oscillator eigenfunctions for the 0th and n_i th vibrational levels. The parameter S_i in Eq. (1) is the Huang–Rhys factor for the i th mode, and represents the strength of electron–phonon interaction [17]. In addition, the Huang–Rhys factor has been shown to represent the extent of exciton migration, conformational disorder and conjugation length in conjugated polymers [6,18,19]. This will be discussed in detail later on in this paper. Specifically for the conjugated polymer poly[2-methoxy-5-(2-ethylhexyl-oxy)-p-phenylenevinylene] (MEH-PPV) it is generally accepted that the fluorescence spectra of its neat films can be simulated by a two-emitter Franck–Condon model. In this model the overall emission spectrum is considered to be the superposition of two Franck–Condon vibronic progressions where one emitter has aggregate (intermolecular) character and the other emitter has isolated molecule (intramolecular/excitonic) character, and the 0–0 vibronic peak of

* Corresponding author. Tel.: +1 407 454 1317; fax: +1 407 882 2819.
E-mail address: andre@mail.ucf.edu (A.J. Gesquiere).

the aggregate emitter virtually coincides with the 0–1 vibronic peak of the molecular emitter [12,15,16]. However, for conjugated polymer blended materials this matter has not received as much attention, and investigations have been limited to MEH-PPV blends with PBD (2-(4-biphenyl)-5-(4-tertbutylphenyl)-1,3,4-oxadiazole) and polystyrene, and poly(p-phenylenevinylene) (PPV) blends with polyvinyl alcohol and silica nanoparticles [18,20–22]. In all of these cases fluorescence spectra were fitted with the two-emitter Franck–Condon model.

We recently reported on the fabrication of composite nanoparticles of the conjugated polymer MEH-PPV and the fullerene 1-(3-methoxycarbonylpropyl)-1-phenyl-[6,6]C₆₁ (PCBM) [23]. This material system is commonly used as an active layer in Bulk Heterojunction Organic Photovoltaic Devices (BH-OPV) [24]. The nanoparticles have bulk properties but contain only a limited number of molecules, which alleviates to a large extent the complexity of bulk conjugated polymer materials brought about by their conformational disorder. This approach allows us to study effects of morphology and intermolecular interaction on optical properties from a molecular perspective, and has recently gained a broad interest [25–30].

In this paper, we extend our Single Particle Spectroscopy (SPS) study of this composite nanoparticle system, in which the optical properties of individual nanoparticles are studied, to further investigate the fluorescence properties as a function of PCBM doping level with respect to material morphology at the molecular level. Through a detailed Franck–Condon analysis on an ensemble of emission spectra composed from emission spectra of individual composite MEH-PPV/PCBM nanoparticles with various PCBM doping levels we find that single particle emission spectra consist of contributions from two types of emitters in the conjugated polymer nanoparticles, consistent with reported literature. However, the SPS approach also reveals a unique distribution of properties within samples of a given composition as well as between samples of different composition in terms of Huang–Rhys factors and aggregation behavior. The disorder introduced by PCBM doping clearly affects exciton migration for the excitonic (molecular) emitters, while exciton migration to aggregate sites is limited by either removal of the aggregate sites themselves or by reduction in the extent of exciton migration to aggregate sites, i.e. the availability of aggregate sites is reduced. Nevertheless, if present or populated by exciton migration the aggregate emitters appear to be nearly unaffected by the presence of PCBM, while a broad distribution of aggregate morphologies is found due to variations in polymer chain folding and stacking at the aggregate sites. The reported results thus show how blending conjugated polymers with fullerenes at various doping levels brings changes in interchain interactions and population of aggregate sites even at length scales under a few tens of nanometers.

2. Experimental section

The fabrication, characterization and fluorescence imaging of composite MEH-PPV/PCBM nanoparticles has been previously reported [23]. In short, nanoparticles were fabricated via the reprecipitation method resulting in a nanoparticle suspension in water as shown in Fig. 1. For nanoparticle fluorescence imaging and spectroscopy, a drop of this nanoparticle suspension in water was added to a 4 wt% polyvinylalcohol (PVA, Sigma Aldrich) solution in water, followed by spin coating at 2000 rpm for 60 s on glass cover slides. To avoid adverse effects of photobleaching on the experimental observations, the samples were protected from the atmosphere by a 200 nm aluminum film deposited on top of the PVA/nanoparticle films by thermal evaporation. Single particle fluorescence imaging and spectroscopy were completed using a home built sample-scanning confocal microscope under 488 nm laser excitation [23]. Undoped (0 wt% PCBM) MEH-PPV nanoparticle samples were typically excited with 0.72 W/cm² laser power, while doped nanoparticles (5, 25, 50, 75 wt% PCBM) were studied with a 10-fold larger laser power (7.2 W/cm²). For the Franck–Condon analysis a home written Matlab (The MathWorks Inc., Natick, Massachusetts) program was used. During modeling of the data, we used two vibrational modes with three vibrational quanta ($n = 0, 1$ and 2) and the following assumptions were made for the emitters: each stick spectrum for a given emitter is broadened by a Gaussian that has the same width σ for each vibrational mode, each vibrational mode has the same Huang–Rhys factors (S) for the vibrational quanta, and the emitters are coupled with vibrational modes in the 1000–1600 cm⁻¹ region. All parameters were allowed to vary freely during non-linear least-squares fitting of model to the data.

3. Results and discussion

3.1. Franck–Condon analysis of single particle spectra

With Single Particle Spectroscopy the emission spectra of individual nanoparticles were collected for composite MEH-PPV/PCBM nanoparticle samples with 0, 5, 25, 50, and 75 wt% PCBM doping levels, where the 50 and 75 wt% PCBM doping levels are typically used in BH-OPV [31,32]. The resulting single particle ensemble spectra, which were constructed by averaging the single particle spectra for each of the nanoparticle compositions we studied, are shown in Fig. 2. Two observations can be made from these data. First, upon doping with PCBM the single particle ensemble spectra show a blue-shift that is attributed to interruption of intermolecular interactions of the MEH-PPV chains by PCBM. However, at the highest doping level (75 wt%) the emission maximum shifts back

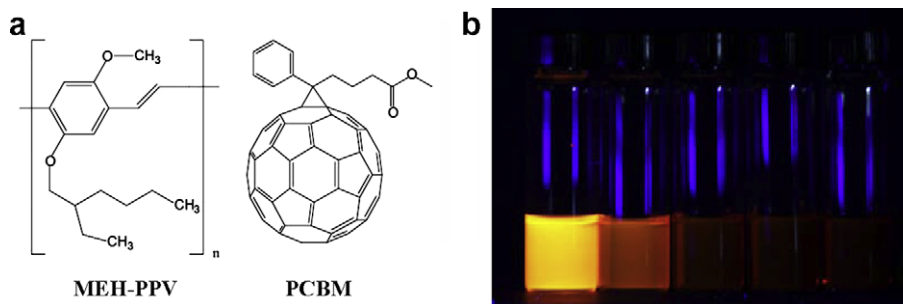


Fig. 1. (a) Sketch of the molecular structures of poly[2-methoxy-5-(2-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV) and the fullerene 1-(3-methoxycarbonylpropyl)-1-phenyl-[6,6]C₆₁ (PCBM). (b) Nanoparticle suspensions in water are shown under UV illumination. Composite MEH-PPV/PCBM nanoparticle suspensions represented in the photograph are 0, 5, 25, 50, 75 wt% PCBM from left to right, respectively. Due to the increasing PCBM content the fluorescence of the nanoparticles is clearly quenched due to charge transfer from MEH-PPV to PCBM.

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