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Effect of alkoxy side chains on intra and interchain exciton coupling in PPE-PPV copolymers solution

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ABSTRACT

The effects of alkoxy side chains on the optical and morphological properties of five *poly* (*p-phenylene-ethylene*)-*alt-poly* (*p-phenylene-vinylene*)s (PPE-PPVs) solutions are investigated. By steady-state and time-resolved photoluminescence spectroscopy combined with Franck-Condon analyses, we show that the introduction of symmetrical side chains onto the PPE-PPV backbone increases the π–π stacking between the polymer chains leading to interchain interactions hence H-aggregate domains. Total dissymmetrical side chains lead to J-aggregate domains through intrachain interactions. On the other hand partial dissymmetrical side chain configurations lead to H and HJ-aggregate domains.

1. Introduction

Conjugated polymers have emerged as promising materials in optoelectronic device applications such as organic photovoltaic cells (OPVs) [1] because of their photophysical and electronic properties in combination with their flexibility and solution processability [2–6]. In the production of these devices, these materials are cast from a highly concentrated solution into a thin film [7]. In solution, the conjugated macromolecules tend to be rather flexible due to the torsional motion of their monomer units [8]. They can adopt then different arrangements and packing leading to a diverse range of microstructure and morphology such as aggregates.

Aggregates exhibit two classes of intermolecular interactions; inter and intrachain interactions leading to H and J-aggregate types, respectively. These two types of fundamental electronic interactions are distinguished by the intensity difference between the 0-0 electronic transition and the 0-1 -vibronic one. When the interchain interaction is dominant, the 0-0 electronic transition is forbidden by symmetry and less intense than the 0-1 transition. In contrast, when the intrachain interaction is dominant, the 0-0 transition is allowed and more intense than the 0-1- [9–11]. This classification is a key development in understanding the relationship between morphology and photophysical properties [12]. Because the degree of aggregation in solution can be preserved through casting process and affect the morphology of the thin film, studies of aggregates in solution are directly relevant to understanding thin film characteristics [7,13].

Aggregation in solution is greatly dependent on the concentration, the aromaticity of solvent and the temperature. Panzer et al. have shown, through the temperature-dependent photoluminescence measurements in poly (3-hexythiophene) (P3HT) solution, the presence at 5 K of two H- aggregates with planar polymer backbones yet different degree of order regarding their side chains [14]. The effect of solvent on the formation of aggregation has been

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studied by Guo et al. in poly(4,8-bis alkyloxybenzo[1,2-*b*:4,5-*b*'])-dithiophene-2,6-diyl-alt-(alkylthieno[3,4-*b*]thiophene2carboxylate])-2,6-diyl (PBDTTT) solution. They compared the PBDTTT/chlorobenzene to the PBDTTT/chloroform solutions and they concluded that the easier aggregation of polymer chains is observed in aromatic solvent. In fact, the open chain conformation adopted in aromatic solvent leads to increased overlapping of the π- orbitals of adjacent chains. Furthermore, they concluded that the highly concentrated solution exhibits more aggregation [15].

On the other hand, the nature, the position and the size of the side chains attached to the conjugated polymer backbone can affect the intermolecular packing then the aggregation. Shin et al. have studied this effect in two polymers with an asymmetric alkoxythienyl side chains and a symmetric alkoxyphenyl side chains. They found that the introduction of the symmetric side chains to the conjugated backbone increases the intermolecular packing between chain, which improves both the light-harvesting of the polymer and its charge carrier mobility [16]. Moreover, Tinti et al. have shown, through studying the charge carrier mobility in a series of anthracene-containing poly (*p*-phenylene-ethylene)-alt-poly (*p*-phenylene-vinylene)s (AnE-PVs) differing by the alkoxy side chains, that the polymer with a long linear dodecyl side chains has a detrimental effect on mobility due to a less compact molecular packing between chains [17].

Recently Chakraborty et al. have shown, using time-resolved measurements, that the long lived emission in poly (2-methoxy-5-(2-ethylhexyloxy)-1, 4-phenylenevinylene) (MEH-PPV), is from H-aggregates [18].

In the present work, we combine steady-state and time-resolved optical spectroscopy in order to study the intra- and interchain interactions in a series of five PPE-PPVs concentrated solutions with an aromatic solvent chlorobenzene. The PPE-PPV polymers named P18/8, P8/18, P18/18-8, P 8/18-8 and P18-8/18-8, whose chemical structures are given in Fig. 1, are an interesting class of materials [6,19,20]. They combine the properties of poly (*p*-phenylene-ethylene) (PPE) and poly (*p*-phenylene-vinylene) (PPV) in the same conjugated backbone, but they differ by the position and nature of grafted alkoxy side chains.

Due to the importance of the molecular vibration in the conjugated polymers, which plays a crucial role in exciton migration [21], FC analysis is usually involved in modelling the PL spectra. We use a single intrachain (or a modified) FC progression, to reproduce the experimental PL spectra.

In what follows, we find that the aggregate type is related to the nature and the position of the side chains. Finally, from the time-resolved PL measurements, we have determined the PL lifetimes for the different substituted PPE-PPVs, in order to confirm the influence of the side chains on the aggregate type.

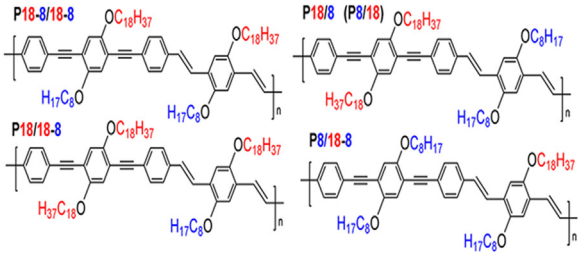

Fig. 1. Molecular structure of the PPE-PPV copolymers [6].

2. Experiments

The material was synthesized as described elsewhere [6]. In spectroscopic studies, we have used a chlorobenzene solution prepared at 10 mg/1.5 ml. PL spectra were recorded with a PTI Quanta Master 400 Spectrofluorimeter with a continuous Xenon arc lamp (75 W) light source in the emission range 185–680 nm.

Time resolved PL measurements were performed using time-correlated single photon counting (TCSPC) based on picoseconds diode laser PDL 800-B with 404 nm laser head running at 40 MHz repetition rate. The driver box PDL is physically separate from the actual laser head, which is attached via flexible lead. The laser head is also fixed at the FluoTime 100. The light is directed at the sample, and then filtered out from scattered excitation light by means of an optical cut off filter. After, it is detected and amplified by photomultiplier tubes. All of those optical instruments are localized in the FluoTime 100. The electrical signal obtained from the detector is led to a pre-amplifier, then to the TCSPC electronics, called Time Harp 200, via a standard 50 Ω coax cable. The TCSPC

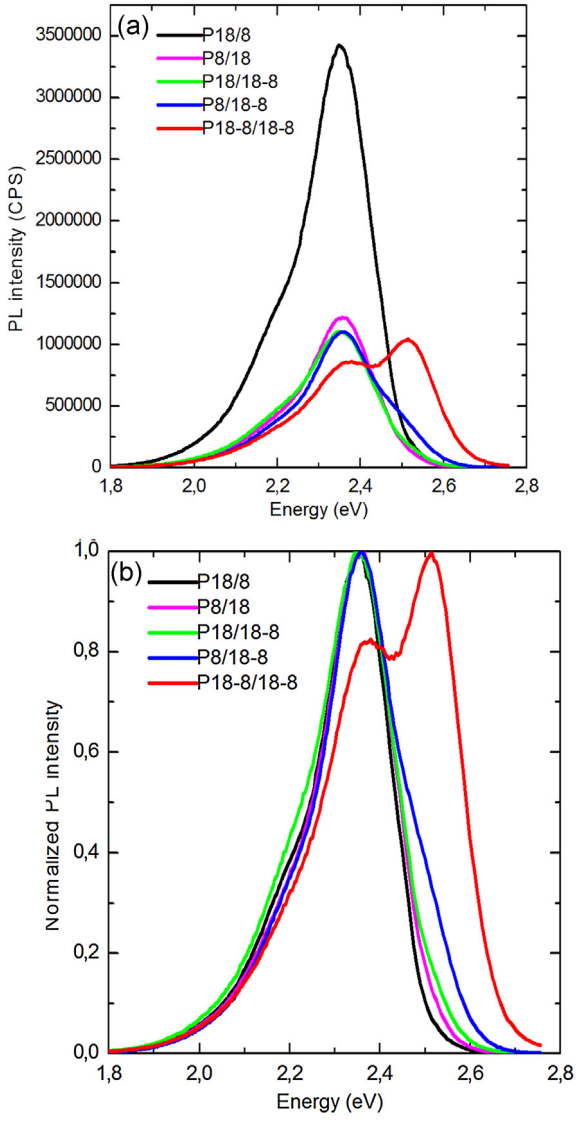

Fig. 2. (a) PL spectra from P18/8, P8/18, P18/18-8, P8/18-8 and P18-8/18-8 solutions recorded at room temperature and obtained using excitation energy equal to 3.06 eV. (b) Normalized PL spectra.