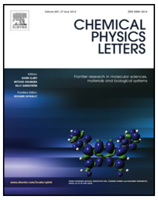
Chemical Physics Letters 614 (2014) 67–71

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett



Temperature resolved aggregate states in dialkoxyphenylene-thiophene oligomer

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ARTICLE INFO

Article history:
Received 10 July 2014
In final form 8 September 2014

ABSTRACT

Aggregate formation in dialkoxyphenylene-thiophene oligomers were investigated experimentally by atomic force microscopy, absorption and by steady-state photoluminescence at room and at low temperatures. Aggregate features were observed to occur in solutions and solid state films. Depending on the solvent, temperature and excitation power, aggregate bands at different wavelength ranges appear in the emission spectra, indicating that different aggregate species are involved. Despite many experimental results involving aggregated states in the literature, in this work the experimental results are shown to have a direct correlation with theoretical achievements.

1. Introduction

Organic materials, such as conjugated polymers, constitute very complex molecular structures where inter- and intra-molecular interactions, electron-vibrational coupling and the presence of disorder or defects must be taken into account to better understand their optical and transport properties. Even in a solid-state film of a simple conjugated polymer, this molecular complexity can be found, which would be dependent on the concentration and solvent used in the solution and on the fabrication method of the film. Effects of molecular aggregation can then occur as a result of this molecular complexity, involving different molecular conformations and packing conditions. Such effects in conjugated polymers represent a prominent field of research from the theoretical [1–3] as well as the experimental [4–6] points of view. Theoretically, you can consider a single-type of aggregate, ideally formed in a solid-state film and study its optical or transport properties through a relatively “simplistic” model. However, from the experimental point of view, it seems a little more complicated, once you can have aggregated and non-aggregated domains coexisting in the same film, which can be still separated from each other by distances allowing excitonic energy transfer or charge transfer. In addition, different aggregated species, dimers, trimmers, H-aggregates (π-stacking face to face intermolecular interaction) [1] and J-aggregates (head to tail intermolecular interaction) [1] are possible to be formed in the film, demanding a much more careful analysis. In this work we studied the (1-(10-(4-methoxy-2,5-di(thiophen-2-yl)phenoxy)decyl)-2,3-dimethyl-1H-imidazol-3-ium chloride) (TBT25) oligomer in solutions and in solid state films. Atomic force microscopy (AFM) was used to study solid-state film morphologies. Aggregate features were observed to be dependent on the solvent type and were investigated at low temperatures and different excitation laser powers.

2. Samples and experimental details

Two solutions of the TBT25 oligomer were made, one diluted in chloroform ($CHCl_3$) and the other diluted in ethanol (C_2H_5OH) with the same 7 mg/mL concentration. Very diluted solutions of TBT25 (0.007 mg/mL) in $CHCl_3$ and C_2H_5OH were also made for complementary sake. All these solutions were left to stir for more than 24 h before producing spin-coating films and measuring them. The films of TBT25 from the 7 mg/mL solutions in $CHCl_3$ and in C_2H_5OH were made on top of glass substrates at the same (1000 rpm) spin velocity. The films were made inside a glove-box in an inert atmosphere to avoid photo-oxidation effects. The time duration of the spin-coating process was 180 s. After that, each film was left to dry naturally at room temperature inside the glove-box during 30 min to further remove the correspondent solvent.

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http://dx.doi.org/10.1016/j.cplett.2014.09.022

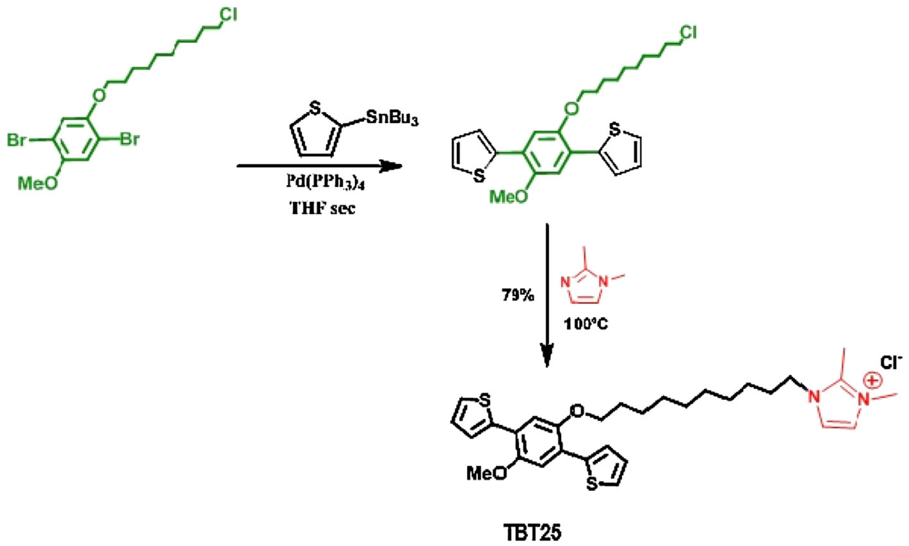

Figure 1. The reaction scheme for the synthesis of the TBT25 oligomer molecule performed in two steps: by a Stille pallado-catalyzed reaction of the dibrominated monomer followed by an exchange reaction of the chloride atom by the imidazol group.

The synthesis of the TBT25 oligomer was performed in two steps: by a Stille pallado-catalyzed reaction of the dibrominated monomer followed by an exchange reaction of the chloride atom by the imidazol group. The respective reaction schemes are shown in Figure 1. Precise experimental synthetic procedures will be given elsewhere.

The absorption (ABS) spectra were obtained using a Shimadzu 3600 spectrophotometer. The steady-state photoluminescence (PL) measurements of the films were performed at different temperatures using a liquid He or N_2 immersion cryostat and temperature controller. The films were either in contact with the cold He or N_2 gas at atmospheric pressure or under vacuum when at room temperature to avoid any photo-oxidation effects. The PL detection was made by an Ocean Optics USB4000 mini-spectrometer at an angle of 45° to the normal of the film surfaces. For the solutions, the PL measurements were made using a cuvette at room temperature. The scattered emission light after the laser beam passing through the solution was focused into the mini-spectrometer located at 90° from the laser beam. For the excitation of solutions and films it was used a 375 nm line from a CW diode laser.

The solid-state TBT25 films spin-coated on top of Si-substrates were directly investigated by atomic force microscopy (AFM) using a Nanoscope V MultiMode 8 SPM, from Bruker, operating in the PeakForce Tapping mode. ScanAsyst – Air cantilevers, from Bruker AFM Probes, with nominal spring constant of 0.4 N/m, nominal radius of curvature of 10 nm and resonant frequency between 20 and 80 kHz were employed throughout this work for AFM imaging. All AFM measurements were carried out in air.

3. Results and detailed discussion

Firstly, the relatively well diluted solutions (0.007 mg/mL) of TBT25 in C_2H_5OH and in $CHCl_3$ were investigated. The respective PL spectra obtained at room temperature are shown in Figure 2. The excitation for both solutions was made by a CW 375 nm laser line with an excitation power of 182 μW. The $CHCl_3$ solvent is relatively less polar than C_2H_5OH, conferring to it a condition of worse solvent due to the more polar chemical structure (Figure 1) of TBT25. It is worth noticing that the polar C_2H_5OH is also a protic solvent that can participate in hydrogen bonding, a relatively powerful intermolecular force. The first strong indication of the aggregate states formation [7,8] using $CHCl_3$ solvent was provided by the appearance of a clear redshifted band (labeled as **1**), around 490 nm, in the PL spectrum of the TBT25 in $CHCl_3$ solution (Figure 2). The pure electronic and vibronic states coming from TBT25, at lower wavelengths (Figure 2), will be referred as bulk states throughout the letter.

The formation of aggregated states in polymer solutions or solid state films constitutes a loss source for the PL emission of conjugated polymers [6]. Π-stacked dimers can decrease the photoluminescence quantum yield (PLQY) of conjugated polymers. The electronic transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in a dimer is symmetrically forbidden, which implies in a weaker photoluminescent emission in comparison to that from isolated molecules [9–11] Although detrimental for electroluminescent devices, the formation of aggregate states were observed to increase nanostructural order, in-plane π–π orientation, and field-effect hole mobilities [12]. In addition, exciton energy transfer

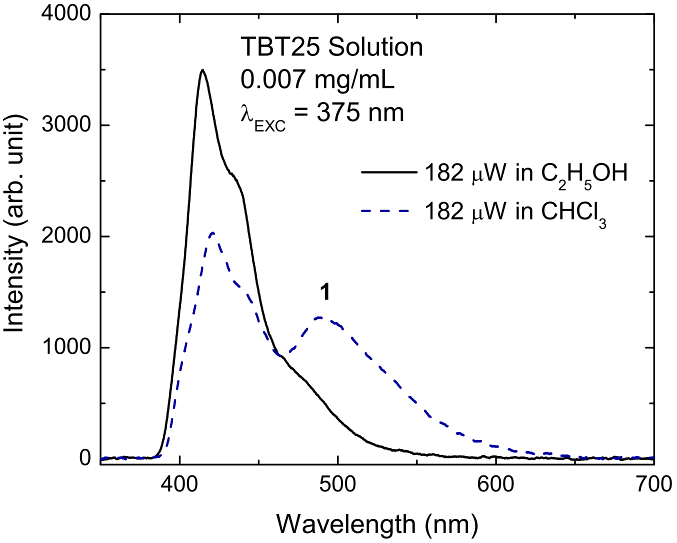

Figure 2. Room temperature photoluminescence spectra of diluted TBT25 solutions (0.007 mg/mL) in $CHCl_3$ (dashed line) and in C_2H_5OH (full line). The excitation was made by the same 375 nm CW laser line and laser power of 182 μW. The label **1** was given to the new band around 490 nm in the $CHCl_3$ solution spectrum. This redshifted band is associated to the emission of aggregated states.