Helical *H*-type aggregation of trimeric *p*-phenylene vinylene with chiral ester groups

HAIQUAN ZHANG*, YING LI and PENG WANG

State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China

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Abstract. Self-assembly properties of the trimeric *p*-phenylene vinylene derivative containing symmetrical end-groups of *R*-(+)-2-methylbutyric acid ester (ChTPV) in H₂O/THF mixed solvents were studied by absorption, photoluminescence and circular dichroism (CD) spectra. The results indicate that ChTPV exhibits helical *H*-type nano-aggregates in 80% H₂O/THF mixed solvents, and the negative exciton coupling suggests that the chromophoric dipoles are oriented in a counter-clockwise direction.

Keywords. Light scattering; *H*-type aggregation; cotton effects; exciton coupling effect.

1. Introduction

The oligo(*p*-phenylene vinylene) and its derivatives have been widely investigated to understand the photophysics properties of corresponding polymers, while it is also a luminescent material in itself (Ruiz *et al* 2000; Lange *et al* 2001; Ryu *et al* 2002). It is known that the supramolecular order plays a critical role in device performance, as both charge mobility and luminescent efficiency are influenced by molecular aggregation. However, it is very difficult to control the nanoscale aggregated structure of rod-like conjugated molecules. Self-assembly is regarded as a practical and promising approach for building a wide variety of functional, ordered nanostructures. In recent years, the multitudinous oligo(*p*-phenylene vinylene) derivatives were synthesized and used to investigate self-assembly properties. For example, Matmour *et al* (2008) reported the self-assembly of oligo(*p*-phenylene vinylene)–peptide hybrid amphiphile in solution and at the solid–liquid interface. Iwaura *et al* (2006) described the molecular level helical stack of nucleotide appended oligo(*p*-phenylene vinylene) derivatives by supramolecular self-assembly. However, the chemical structures of these oligo(*p*-phenylene vinylene) derivatives which are used to investigate self-assembly properties are generally complicated so it is difficult to synthesize them. In our previous work, we reported synthesis and liquid crystalline properties of the oligo(*p*-phenylene vinylene) containing *R*-(+)-2-methylbutyric acid ester (figure 1) (Zhang *et al* 2009). Here we discuss its self-assembly properties in H₂O/THF mixed solvents.

2. Experimental

2.1 Preparation of H₂O/THF mixed solvents

ChTPV was dissolved in H₂O/THF mixed solvents with different water contents, and the water volume percentages were found to be 0%, 40% and 80%, respectively. In order to compare the self-assembly properties of ChTPV in different water contents, the concentration of ChTPV in mixed solvents was fixed at 10 μM.

2.2 Measurements

UV-vis absorption spectra of ChTPV solution was recorded on a UV-3000 spectrophotometer. Photoluminescence measurements were carried out by using a Hitachi F-4500 fluorescence spectrophotometer. CD spectra was recorded on Bio-kin32 V4.51-[Acquire spectra (MOS-450)] spectrophotometer. The specimen for TEM observation were prepared using carbon support films. TEM images of the specimen were obtained by using a JEM-2010 microscope with an accelerating voltage of 80 kV.

3. Results and discussion

The UV-vis absorption spectra of ChTPV in H₂O/THF mixed solvents with different water contents are shown in figure 2a. The absorption spectra of ChTPV in pure THF is similar to that in 40% H₂O/THF mixed solvents, and maximal absorption peak appears at 357 nm. When 80% water is added into THF solution of ChTPV, the absorption maximum blue-shifts from 357 nm to 314 nm, and half peak wide evidently decreases. According to the molecular exciton model,

* Author for correspondence (hqzhang@ysu.edu.cn)

Figure 1. Molecular structure of ChTPV.

Figure 2. (a) Absorption spectra of ChTPV in $\text{H}_2\text{O}/\text{THF}$ mixed solvents with different water contents and (b) TEM image of ChTPV aggregates in $\text{H}_2\text{O}/\text{THF}$ mixed solvents with 80% water content (concentration of ChTPV in solvent mixtures: $10 \mu\text{M}$).

Figure 3. (a) Emission (excitation wavelength: 320 nm) and (b) excitation spectra of ChTPV (excitation wavelength: 414 nm for 0% and 40% $\text{H}_2\text{O}/\text{THF}$; 476 nm for 80% $\text{H}_2\text{O}/\text{THF}$) in $\text{H}_2\text{O}/\text{THF}$ mixed solvents with different water contents (concentration of ChTPV in solvent mixtures: $10 \mu\text{M}$).

the formation of parallel aggregates (i.e. *H*-aggregate structure) causes the spectrum of the monomer to broaden and blue-shift (Whitten 1993). In addition, the strong light absorption in the long wavelength region ($\lambda > 400 \text{ nm}$) is accompanied by light scattering of nano-aggregates, which can be confirmed by TEM images of aggregates of ChTPV in 80% $\text{H}_2\text{O}/\text{THF}$ mixed solvents (figure 2b) (Tang *et al* 2000; Chen *et al* 2004). The particle structures with a width of ca 70–120 nm are abundantly observed in TEM images.

The emission and excitation spectra of ChTPV in $\text{H}_2\text{O}/\text{THF}$ mixed solvents with different water contents are

presented in figure 3. Compared with ChTPV in pure THF, the shape of emission band and wavelength of maximal emission in 40% $\text{H}_2\text{O}/\text{THF}$ mixed solvents have no change, and their maximal emission peaks appear at 391 nm, 414 nm with a shoulder of 440 nm. When water content increases to 80%, the maximal emission peaks red-shift from 391 nm and 414 nm to 448 nm and 478 nm, respectively, and PL intensity approximately decreases 5 times. These results suggest further the formation of *H*-type aggregation of ChTPV in 80% $\text{H}_2\text{O}/\text{THF}$ mixed solvents (Kim *et al* 2007). Interestingly, the relative emission intensity of the second vibronic

Figure 4. (a) CD spectra of ChTPV in H₂O/THF mixed solvents with different water contents (concentration of ChTPV in solvent mixtures: 10 μ M) and (b) schematic illustration of helical *H*-type aggregation.

band (0–1) is markedly decreased. Furthermore, corresponding emission bands of single molecule still appear at 391 nm and 414 nm, which indicates that a small quantity of single ChTPV molecules still exist in 80% H₂O/THF mixed solvents. In contrast with ChTPV in 0 or 40% H₂O/THF mixed solvents, the excitation spectra of ChTPV in 80% H₂O/THF mixed solvents shows a broad band covering the long and short wavelength regions (figure 3b). This result indicates that the excitation band of the short wavelength region is mainly attributed to aggregates emission in 80% H₂O/THF mixed solvents.

In order to obtain valuable insight into the structure of aggregates, CD spectra study for ChTPV in H₂O/THF mixed solvents is performed in figure 4a. When ChTPV is dissolved in pure THF and 40% H₂O/THF mixed solvents, no CD signals are observed at wavelengths longer than 270 nm. However, a CD signal of ChTPV is observed in 80% H₂O/THF mixed solvents and the strong Cotton effects appear at 301 and 335 nm. The CD spectrum shows a $[\theta] = 0$ value at 317 nm, which is close to its absorption maximum (314 nm), implying an exciton coupling effect (Tong *et al* 2007). The isolated molecules of ChTPV in pure THF and 40% H₂O/THF mixed solvents are CD-inactive in the wavelength region of 270–550 nm, but the unambiguous CD signal was observed in 80% H₂O/THF mixed solvents, this result indicated that the CD signal was correlative with ChTPV aggregation at higher water content. The driving force which induces ChTPV to form aggregation is from the assembly of the chromophoric skeletons induced by the chiral end-groups and the π – π interaction of chromophoric skeletons. In combination with the analysis of the absorption

and emission spectra of ChTPV, we can conclude that the ChTPV molecules may form left-handed helical *H*-type aggregation in 80% H₂O/THF mixed solvents (figure 4b).

4. Conclusions

In conclusion, ChTPV shows the helical stack in 80% H₂O/THF mixed solvents and strong *H*-type aggregation. Particle structures with a width of ca 70–120 nm are observed.

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