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Self-assembly behaviors of the cholesteryl trimeric-phenylene vinylene derivative in the H_2O/THF system



Yu-Zhen Zhao ^a, Zhen-Lin Zhang ^a, Ying Li ^a, Xue-Qiang Liu ^b, Shi-Min Liu ^a, Jin-Ku Yu ^{a,*}, Hai-Quan Zhang ^{a,*}

^a State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China
^b College of Information Science and Engineering and Key Laboratory for Special Fiber and Fiber Sensor of Hebei Province, Yanshan University, Qinhuangdao 066004, China

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ABSTRACT

Cholesteryl trimeric phenylene vinylene (Chol-TPV) has been synthesized and characterized. The selfassembly behaviors of Chol-TPV in THF/H₂O system at different water content (water content: 40% and 80%) and different solute concentration (solute concentration: 1.0×10^{-5} mol/L and saturated concentration) were studied using UV–vis spectrophotometry, photoluminescence spectrophotometry, and circular dichroism spectroscopy. Based on an analysis of the UV–vis and photoluminescence spectra, Chol-TPV shows the typical H-type aggregation at saturated concentration in 80% aqueous THF. However, Chol-TPV shows the non-typical H-type aggregation under other conditions. The circular dichroism signal suggests that the Chol-TPV exists in the right handed helical architectures with high water content at a concentration of 1.0×10^{-5} mol/L, and a helix inversion was found at saturated concentration. © 2013 Jin-Ku Yu. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

1. Introduction

Mesoscopic order in π -conjugated systems is a significant topic, because it dictates the performance of the organic electronic devices [1]. Due to its favorable optical and electronic properties, self-assembly of linear π -conjugated molecules is at the center stage among different classes of π -conjugated systems and has been used in the design of organic electronic devices. Oligo (pphenylene vinylene)s (OPVs) are a preferred class of linear π conjugated molecules as their optical and electronic properties strongly depend upon their aggregated structures [2,3]. The hydrogen bonding and π - π stacking interactions are the main driving forces for the OPVs molecular self-assembly, which can adjust the structure of the molecular aggregations [4]. Cholesterol derivatives have been found to be efficient gelators due to their tendency to form one dimensional stack of the steroid units. There have been several reports on cholesteryl OPVS chromophoric systems that self-assemble to form the helical architectures [5,6]. However, the introduction of the cholesteryl groups into OPVs inhibits π - π interactions of the OPVs chromophores owing to strong van der Waals force of the steroid units. It is known that the aggregation of chiral molecules is initiated upon the addition of poor solvent in a good solvent system, and this molecular aggregation could lead to dramatic change of absorption, photoluminescence and circular dichroism spectra [7]. In order to understand the influence of van der Waals force and π - π interaction on the self-assembly behaviors of cholesteryl OPVs chromophores in good/poor solvent system, we designed a Chol-TPV compound and studied its self-assembly behaviors in THF/H₂O using spectroscopic methods.

2. Experimental

2.1. General

The ¹H NMR spectrum was recorded on an AVANCZ 500 spectrometer at 298 K in $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard. FT-IR spectra were recorded on a Perkin–Elmer spectrophotometer in the 400–4000 cm⁻¹ region using a powered sample on a KBr plate. UV–vis absorption spectra were recorded on an UV-3100 spectrophotometer. Photoluminescence measurements were carried out with a RF-5301PC. CD spectra were recorded on a Bio-kine32 V451-[Acquire spectra (MOS-450)] spectrophotometer.

2.2. Reagents

* Corresponding authors.

Potassium *tert*-butanolate (BuOK) and cholesteryl chloride were purchased from Aldrich Chemical Co. The *p*-xylene, CCl₄, *N*-

E-mail addresses: yujinku@ysu.edu.cn (J.-K. Yu), hqzhang@ysu.edu.cn (H.-Q. Zhang).

bromosuccinimide (NBS), K₂CO₃, triphenylphosphine, 4-hydroxybenzaldehyde, *N*,*N*'-dimethyl formamide (DMF) were purchased from Beijing Chemical Co.

2.3. Synthesis and structural characterizations

1,4-Bis-bromomethylbenzene: p-Xylene (6.2 mL, 50 mmol) and N-bromosuccinimide (NBS) (21.3 g, 110 mmol) were added to a solution of CCl₄ (100 mL) in a 250 mL three-necked flask. After the temperature reached to 80 °C, BPO (0.1 mg) was added into the flask. The mixture was vigorously stirred for 8 h at 80 °C under N₂. The residue was cooled and the filtrate was concentrated, subsequently recrystal by absolute ethyl alcohol. 1,4-*bis*-bromomethylbenzene was obtained as white powder in 84% yield. FT-IR (KBr, cm⁻¹): 1516, 1456 (γC =C); 750 (γC -Br). ¹H NMR (500 MHz, CDCl₃): δ 7.55–7.36 (m, 4H, Ph-H); 3.81–3.74 (m, 4H, –CH₂Br).

4,4'-Bis (triphenylphosphonium-bromide emethyl) benzene: A mixture of 1,4-bis-bromomethylbenzene (7.93 g, 10 mmol) and triphenylphosphine (17.29 g, 66 mmol) were dissolved in DMF (100 mL). The mixture was vigorously stirred for 24 h at 176 °C in a round-bottom flask. The residue was cooled and filtrated gave to 4,4'-bis(triphenylphosphonium-bromide emethyl) benzene as white power with yield 72%. FT-IR (KBr, cm⁻¹): 3354 (PPh₃). ¹H NMR (500 MHz, CDCl₃): δ 7.76–7.60 (30 H, Ph-H); 6.92–6.91 (4H, Ph-H); 5.38 (4 H, –CH₂Br).

Synthesis of compound 1: A mixture of p-hydroxybenzaldehyde (10 mmol), kalium iodide (1 mmol), potassium carbonate (30 mmol) and cholesteryl chloride (10 mmol) were dissolved in DMF (200 mL). Then, this mixture was heated to reflux for 180 min. After the reaction mixture was cooled to room temperature, the solvent was removed in vacuum, the residue was dissolved in ether (200 mL), and the ether solution was washed with water (100 mL), organic layer is dried using MgSO₄, and concentrated. The product was chromatographied on silica gel column using petroleum ether/ethyl acetate (10/2) as eluent. Compound 1 was obtained as white solid in 58.6% yield. FT-IR (KBr, cm⁻¹): 3081, 2933, 2867, 2729, 1703, 1597, 1516, 1457, 1318, 1250, 1153, 1003, 837, 607, 503; ¹H NMR (500 MHz, CDCl₃): δ 9.87 (s, 1H, CHO); 7.81–7.80 (d, 2H, Ph-H); 7.00–6.99 (d, 2H, Ph-H); 5.22 -5.21 (m, 1H, -C=CH-); 3.72 -3.71 (m, 1H, -OCH-); 2.34 -1.64 (m, 28H, -CH-, -CH₂-); 0.99-0.97 (m, 15H, -CH₃). Elemental analysis calcd. (%) for C₃₄H₅₀O₂ (490.38): C 83.21, H 10.27, O 6.52; found: C 83.23, H 10.26, O 6.51.

Synthesis of Chol-TPV: 4,4'-Bis(triphenylphosphonium-bromide emethyl) benzene (0.16 g, 0.2 mmol) and cholesterol ester benzaldehyde (0.2 g, 0.4 mmol) were dissolved in THF (15 mL). The anhydrous THF containing the potassium *tert*-butoxide (BuOK) (0.0672 g, 0.6 mmol) was added dropwise into the foregoing mixture at the speed of one drop every three seconds. The resulting solution was stirred at 0 °C for 24 h and the reaction environment was protected by N₂. The solvent was evaporated and the residue was chromatographied on silica gel column using petroleum ether/ ethyl acetate (10/1) as eluent. Chol-TPV was obtained as yellowgreen solid in 58.6% yield. FT-IR (KBr, cm⁻¹): 2925, 2853, 965, 549, 510; ¹H NMR (500 MHz, CDCl₃): δ 7.47–7.46 (d, 4H, Ph-H); 7.45– 7.447(d, 4H, Ph-H); 7.08–7.07 (d, 4H, Ph-H); 5.22–5.21 (m, 2H, – CH₂=CH₂); 3.72–3.71 (m, 2H, –CH); 2.38–1.72 (m, 56H, –CH); 1.51–0.96 (m, 34H, –CH). Elemental analysis calcd. (%) for C₇₆H₁₀₆O₂ (1050.82): C 86.80, H 10.16, O 3.04; found: C 86.81, H 10.15, O 3.02.

Preparation of H₂O/THF mixed solvents: Chol-TPV was dissolved in THF, and then added H₂O to prepare THF/H₂O mixed solution, the water volume percentages were found to be 0, 40% and 80%, respectively. The concentration of Chol-TPV in mixed solvents was at 1.0×10^{-5} mol/L and saturated solution.

3. Results and discussion

The synthetic route for the Chol-TPV is outlined in Scheme 1. On the basis of a detailed analysis of IR, ¹H NMR, elemental analyses, and mass spectra, the structure was found to be consistent with the Chol-TPV structure.

UV-vis absorption spectra of Chol-TPV in THF/H₂O are shown in Fig. 1. The absorption spectra in THF and 40% THF/H $_2$ O with a solute concentration of 1.0×10^{-5} mol/L shows same features and maximum peak (369 nm), indicating the TPV chromophore did not demonstrate excitonic coupling. That implies that the distance (d) of the adjacent TPV chromophores is greater than the distance required to produce an excitonic coupling effect of TPV chromophores (~0.5 nm) [8]. The Chol-TPV molecular self-assemble is initiated with the addition of water, leading to a dramatic spectral blue-shift. The value of maximal peak is decreased with higher water content and solute concentration. As shown in Fig. 1, the maximal peak appeared at 341 nm in water content of 80% with a Chol-TPV concentration of 1.0×10^{-5} mol/L (Fig. 1a), and maximal peak appeared at 305 nm in water content of 80% with a saturated Chol-TPV concentration (Fig. 1b). Furthermore, maximal peak appeared at 344 nm in water content of 40% with a saturated Chol-TPV concentration. These spectral characteristics indicate that the excitonic coupling occurred between the TPV chromophores. In other words, the nearest distance (d) in adjacent TPV chromophores is smaller than that 0.5 nm under these condition. At the saturated Chol-TPV concentration, when water content increase to 80% the strong light absorption appeared at the long wavelength region ($\lambda > 410 \text{ nm}$) [9] (Fig. 1b).

The Photoluminescence spectra of Chol-TPV in THF/H₂O system are shown in Fig. 2. The maximum emission peak of Chol-TPV had a light red-shift in 40% THF/H₂O compared with that in THF with the solute concentration of 1.0×10^{-5} mol/L (Fig. 2a). When the water content increases to 80%, a marked blue-shift was found. However, an entirely different phenomenon was found in 40% (the maximum emission peak appeared at 372 nm, and the fine structure of emission spectrum became indistinct.) or 80% THF/H₂O (the maximum emission peak appeared at 456 nm and 484 nm,



Scheme 1. Synthetic routes of Chol-TPV.



Fig. 1. Absorption spectra of Chol-TPV in THF/H₂O. (a) Concentration of 1.0×10^{-5} mol/L and (b) saturated solution.



Fig. 2. Photoluminescence spectra of Chol-TPV in THF/H₂O. (a) Concentration of 1.0×10^{-5} mol/L and (b) saturated solution; excition wavelength: 360 nm; the excition wavelength is 340 nm in 40% H₂O saturated solution.

respectively.) saturated solution compared with that in THF with a Chol-TPV concentration of 1.0×10^{-5} mol/L (Fig. 2b). Combined with absorption spectra and the photoluminescence spectra, the Chol-TPV shows the spectral characteristic of the typical H-aggregation in 80% THF/H₂O saturated concentration (blue shift in the intense absorption, red shift in photoluminescence) [10]. Under other condition, the Chol-TPV shows the spectral characteristic of the no-typical H-aggregation (blue shift in the intense absorption and Photoluminescence).

The CD spectra of Chol-TPV in the THF/H₂O system with different water content and different solute concentration are shown in Fig. 3. The solution of Chol-TPV in THF is circular dichroism-inactive. However, the CD spectrum of Chol-TPV in 40% THF/H₂O and 80% THF/H₂O with the solute concentration of 1.0×10^{-5} mol/L showed an excition-coupled bisignate signal with negative (λ_{max} = 338 nm and 292 nm) and positive (λ_{max} = 366 nm and 317 nm) Cotton effects. This behavior is characteristic of a right-handed helical bias of the



Fig. 3. CD spectra of Chol-TPV in THF/H₂O system. (a) Concentration of 1.0×10^{-5} mol/L and (b) saturated solution.



Fig. 4. Probable mode of self-assembly of Chol-TPV in THF/H₂O under different water content and different concentration.

supramolecular chirality. Surprisingly, the CD spectrum of saturated Chol-TPV in 80% THF/H₂O showed a strange behavior with first a positive (λ_{max} = 304 nm) followed by two negative (λ_{max} = 360 nm and 412 nm) Cotton effects. The non-bisignate exciton couplet with opposite signals indicates the possibility of different chiral dispositions. A helix inversion is reasonable because the initially formed 1D aggregate with a right-handed twist may wind in the opposite direction during the higher-order assembly to result in an ultimate left-handed twist [5].

Based on the observations on the differences of the photophysical and chiroptical properties of the Chol-TPV in different water content and different solute concentration, the selfassembly behaviors of the Chol-TPV molecule in THF/H₂O system can be described as follows (A mode of the molecular selfassembly in THF/H₂O system with different water content and solute concentration is shown in Fig. 4.): The cholesteryl groups in adjacent molecules approach each other as the water content increases. When the water content is close to 40% with the Chol-TPV concentration of 1.0×10^{-5} mol/L, the molecules form chiral aggregates due to strong van der Waals interactions among the steroid units. But data of the UV-vis spectra suggest that the chromophore did not show excitonic coupling under this condition, indicating the interactions among TPV chromophores are very weak (Fig. 4b). When water content is close to 80% with the Chol-TPV concentration of $1.0\times 10^{-5}\,mol/L$, the maximum absorption and emission spectra shows a marked blue shift, suggesting TPV chromophores form strong excitonic coupling (Fig. 4c). When the concentration of Chol-TPV increased from 1.0×10^{-5} mol/L to the saturated concentration, a helix inversion occurred (Fig. 4d).

4. Conclusion

In this paper, we designed and synthesized cholesteryl trimeric phenylene vinylene in order to understand the influence of van der Waals force and π - π interactions on its self-assembly behaviors in the THF/H₂O system. With different water content and the solute concentration, the cholesteryl trimeric *p*-phenylene vinylene forms different aggregated structures, leading to the dramatically different spectral characteristic. Cholesteryl trimeric phenylene vinylene vinylene in THF/H₂O forms right-handed helical architectures and changes into left-handed helical architectures at higher concentrations.

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References

- G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor heterojunctions, Science 270 (1995) 1789–1791.
- [2] J.F. Hulvat, M. Sofos, K. Tajima, S.I. Stupp, Self-assembly and luminescence of water soluble oligo(*p*-phenylene vinylene) amphiphiles, J. Am. Chem. Soc. 127 (2005) 366–372.
- [3] K.H. Ding, X. Ge, M. Zhang, S.C. Yuan, Synthesis and characterization of X-shaped oligo(para-phenylene) derivatives functionalized with fluorene ethynylene, Chin. Chem. Lett. 21 (2010) 1374–1377.
- [4] F.J. Hoeben, P. Jonkheijm, E.W. Meijer, A.P. Schenning, About supramolecular assemblies of π-conjugated systems, Chem. Rev. 105 (2005) 1491–1546.
- [5] A. Ajayaghosh, C. Vijayakumar, R. Varghese, S.J. George, Cholesterol-aided supramolecular control over chromophore packing: twisted and coiled helices with

distinct optical, chiroptical, and morphological features, Angew. Chem. Int. Ed. 45 (2006) 456–460.

[6] W.L. He, T. Liu, Z. Yang, et al., Facile synthesis and characterization of novel thermo-chromism cholesteryl-containing hydrogen-bonded liquid crystals, Chin. Chem. Lett. 20 (2009) 1303–1306.

- [7] H.Q. Zhang, Y. Li, P. Wang, Helical H-type aggregation of trimeric *p*-phenylene vinylene with chiral ester groups, Bull. Mater. Sci. 34 (2011) 1049–1051.
 [8] F. Zsila, Z. Bikádi, Z. Keresztes, J. Deli, M. Simonyi, Investigation of the self-
- [8] F. Zsila, Z. Bikadi, Z. Keresztes, J. Deli, M. Simonyi, Investigation of the selforganization of lutein and lutein diacetate by electronic absorption, circular

dichroism spectroscopy, and atomic force microscopy, J. Phys. Chem. B 105 $\left(2001\right)\,9413-9421.$

- B.Z. Tang, H.Y. Xu, J.W.Y. Lam, et al., C-60-containing poly(1-phenyl-1-alkynes): synthesis, light emission, and optical limiting, Chem. Mater. 12 (2000) 1446-1455.
- [10] D.G. Whitten, Photochemistry and photophysics of trans-stilbene and related alkenes in surfactant assemblies, Acc. Chem. Res. 26 (1993) 502–509.