



Research paper

Solvent tuning configurational conversion of lycopene aggregates in organic-aqueous mixing solvent

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ABSTRACT

In general cases, carotenoid aggregates are prepared in organic-water mixing solvent depending on its hydrophobic character. It is well-known that one of carotenoids, lycopene, is more likely to form typical H-aggregates. In this study, new type lycopene J-aggregates were prepared in DMSO-water mixing solvent with small amount of toluene, which was observed for the first time. We proposed a potential structure model combining with exciton model to interpret the mechanism of spectra changes. Our finding has provided new methods and novel ideas for controlling carotenoid aggregates formation.

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1. Introduction

Carotenoids are a kind of omnipresent pigments which can be found in most organisms [1–3]. It can act as a light-harvesting material that absorbs blue-green light, or perform as a quencher to protect the organisms from destroying by the singlet oxygen and other reactive radicals [4–7]. In general cases, carotenoid aggregates are prepared in organic-water mixing solvent depending on its hydrophobic character. And the types of aggregates are commonly classified into H-aggregates and J-aggregates. The strongly coupled H-aggregates are interpreted as a “card-packed” structure, which can cause a hypsochromic shift of the absorption relative to carotenoid monomers [8,9]. In contrast, the loosely coupled J-aggregates are interpreted as a “head-to tail” structure, which can cause a bathochromic shift of absorption relative to carotenoid monomers [8,9]. One important member of carotenoids, lycopene, is always known to form typical H-aggregates [10,11], although coexistence of H- and J-aggregates of lycopene has been suggested and reported in the study of Langmuir-Blodgett films [12,13]. However, typical J-aggregates of lycopene have never been found before.

By Ultraviolet-visible (UV-vis) absorption spectroscopy, we investigated the lycopene aggregates formation in acetone-water, isopropanol-water and DMSO-water mixing solvents, respectively, under various temperature and toluene addition conditions. The

results show that the formation of lycopene J-aggregates can be controlled and even prevalent as typical J-aggregates in DMSO-water mixing solvent with small amount of toluene addition. Furthermore, the resonance Raman analysis also supports the J-aggregates configuration. Our finding has provided new methods and novel ideas for controlling carotenoid aggregates formation.

The lycopene aggregates prepared in acetone-water, isopropanol-water and DMSO-water mixing solvents at 0 °C are distinguished from the monomer by their absorption spectra (Fig. 1). As for the monomer in DMSO, the maxima in the spectrum at 524, 489 and 462 nm are attributed to 0 → 0, 0 → 1 and 0 → 2 vibrational transitions, respectively. As for the aggregates, we could find that lycopene tends to form typical H-aggregates in acetone-water and isopropanol-water mixing solvents, since there is a strong hyperchromic absorption band around 350 nm [13,14]. On the other hand, the small bathochromic-shifted absorption band around 560 nm can be assigned to the J-aggregates of lycopene, which are formed by the head-to-tail aggregation between neighboring layers [10,12–14].

However, when it comes to DMSO-water mixing solvent, the absorbance peak of H-aggregates is significantly decreased, nearly equal to the absorbance peak of J-aggregates, and the wavelength of H- and J-peak has red-shifted to 389 and 566 nm relatively to the aggregates in acetone-water and isopropanol-water mixing solvents. This phenomenon has been attributed to stronger dispersion effect of DMSO on carotenoids than the other two solvents [15,16]. The calculated polarizability by Lorenz-Lorenz equation is $8.0 \times 10^{-24} \text{ cm}^3$, $6.3 \times 10^{-24} \text{ cm}^3$, and $6.9 \times 10^{-24} \text{ cm}^3$ for DMSO,

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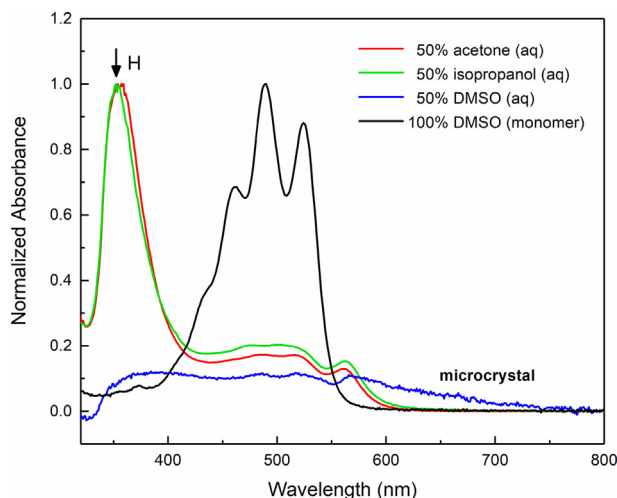


Fig. 1. UV-vis absorption spectra of lycopene monomer in DMSO (black line), H-aggregates in 50% acetone (red line), 50% isopropanol (green line) and 50% DMSO (blue line)-water mixing solvents. All spectra were normalized at the individual maxima absorbance except of the 50% DMSO-water mixing solvent. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

acetone and isopropanol, respectively [17]. One generally accepted model of carotenoid aggregates is that carotenoid molecules aggregate in several parallel two-dimensional layers [18]. The carotenoid molecules located in each layer are aligned in the same direction. The twist of neighboring layers and slip angle in each layer both decide the formation of H- and J-aggregates. Dislike lutein or lutein diacetate aggregates which have regular twist angle between adjacent layers [8,19], lycopene aggregates are arranged at a random tilt angle due to the lack of chiral centers [13]. In general cases, lycopene tends to form typical H-aggregates, since the arrangement of this carotene in each layer is a “card-packed” structure [11]. In DMSO-water mixing solvent, the strong dispersion effect from DMSO shifts the molecular centers of lycopene molecules in each layer of aggregates greatly [16], therefore it undermines the H-type interactions and yields spectra with nearly equal absorbance peak of H- and J-aggregates [19]. Moreover, it is also worth noting that the S/N ratio of UV spectra in DMSO-water mixing solvent is low and a red absorption tail appears between 600 and 800 nm. This is due to the formation of lycopene microcrystals, i.e. the bigger size of aggregates.

To investigate the effect of ambient temperature on lycopene aggregates formation in various mixing solvents, absorption spectra of aggregates in three mixing solvents were measured at 0 °C, 30 °C and 60 °C. The results are shown in Fig. 2. When the temperature reaches 30 °C, the characteristic H-aggregates absorbance between 320 and 400 nm is suppressed, while the spectral characteristics of monomer between 400 and 550 nm, and that of J-aggregates formation between 600 and 800 nm increase slightly. Further rise of the temperature to 60 °C causes the decrease of H-aggregates absorbance more significantly, accompanying with a pronounced rise of J-aggregates absorbance and monomer absorption characteristics at the same time. These phenomena can be explained as that the increase of temperature promotes the thermal motion among lycopene molecules, consequently the tightly packed H-aggregates are loosened and correspondingly J-aggregates and monomer increase. In DMSO-water mixing solvent, the spectra changes are relatively small comparing to acetone-water and isopropanol-water mixing solvents. This is due to that the strong dispersion effect of DMSO has exerted great influence on aggregates, thus the spectra changes caused by the temperature effect are relatively less obvious.

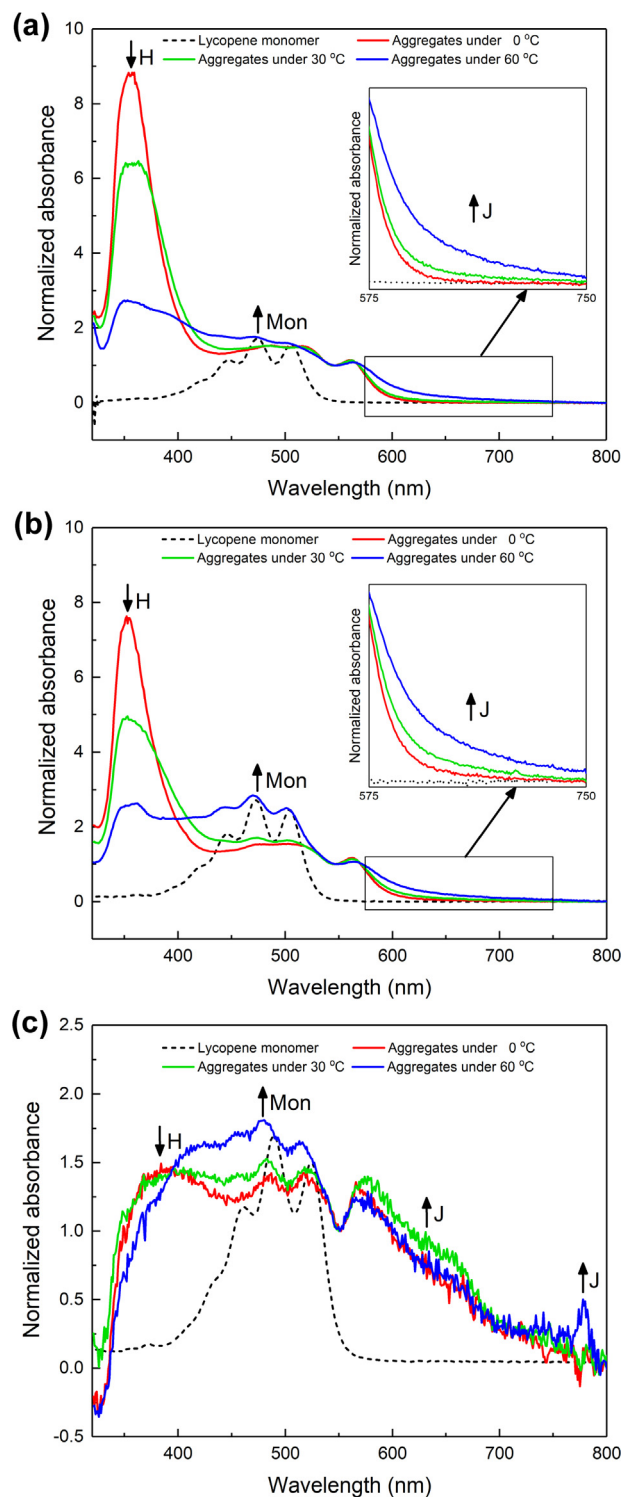


Fig. 2. UV-vis absorption spectra of lycopene aggregates formed in acetone-water (a), isopropanol-water (b) and DMSO-water (c) mixing solvents at 0 °C (red line) and heated to 30 °C (green line) and 60 °C (blue line). The spectrum of lycopene monomer (black dashed line) in pure solvent is also displayed for comparison. The spectra of lycopene aggregates were normalized by the intensity at around 546, 549 and 551 nm, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The fitted vibrational peaks of monomeric lycopene in mixing solvents and in pure solvent were listed in Table 1 from low to high energy. The spectral peaks of lycopene monomers in mixing solvents are obviously different from those in pure solvent, which is

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