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Short communication

Photo-controllable and aggregation-induced emission based on photochromic bithienylethene

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ABSTRACT

In this article a series of photochromic bithienylethenes containing coumarin fluorescent unit were synthesized and their properties including photochromic behavior and fluorescent properties were also investigated. One compound not only exhibited photochromic behaviors but also had aggregation-induced emission characteristics. The fluorescence could also be enhanced continuously by the photo-isomerization reaction. As ring-closed isomer formed, the rigid structure of compound enhanced the aggregation so that the nanoparticle in the solution increased constantly. Thus, this may provide a novel approach for preparing a new family with AIE characteristics and photochromic properties which may have the potential application in the optical memory and nonlinear optics.

Photochromic compounds as photo-responsive functional materials have been widely investigated due to their potential applications in many fields such as optical memory [1] and optical switches [2]. During the reversible photoisomerization, their photochemical and photophysical properties such as absorption spectra [3], photo luminescence [4] and geometrical structure [5] maybe changed upon photo excitation. In particular, bithienylethene derivatives are the most promising compounds because of their excellent fatigue resistant and thermal irreversible properties [6]. Recently, the design and synthesis of novel complex systems based on bithienylethenes that integrate several switchable functional units into a single molecule is a main aspect in the progress of molecular switches [7].

Coumarin derivatives, another kind of optical active material, are widely used in the fields of biology, medicine and polymer science [8]. The combination of coumarin with dithienylethene should not only involve a multi-addressed memory system, but also entail the possibilities drug release mechanism [9]. In the present study, we designed and prepared a complex multi-addressable compound containing both coumarin and diarylethene. Moreover, this novel structure represents a unique example of aggregation-induced emission (AIE) [10]. To the best of our knowledge, the phenomenons of dithienylethene derivatives linked to coumarin fluorescent unit based on AIE characteristics have been rarely reported. In this letter, we have prepared a series of photochromic bithienylethenes named as B2C and B1C to investigate their AIE behavior (Scheme 1).

Although with the fluorescent group coumarin linked, compound B2C could emit very weak fluorescence in any organic solvent. After water was added into the THF solution of B2C, the fluorescence began to appear. With the increasing of the water content in the solution, the fluorescence increased strongly. After irradiated by the UV light, the color of this solution changed from colorless to purple due to the formation of closed ring isomer. Also the fluorescence would be enhanced continuously because of the photo-isomerization reaction. The possible mechanism was proposed. Due to the hydrophobic interactions, the photochromic molecules aggregated to nanoparticles when water added, which led to the fluorescence emission. After UV irradiation, the ring closed isomer formed, and the rigid structure enhanced the aggregation so that the nanoparticle in the solution increased constantly.

The compound B2C was prepared by simple esterification reaction of carboxyl bithienylethene and 7-Hydroxycoumarin, and the synthetic route is shown in Scheme S1 (ESI). The absorption

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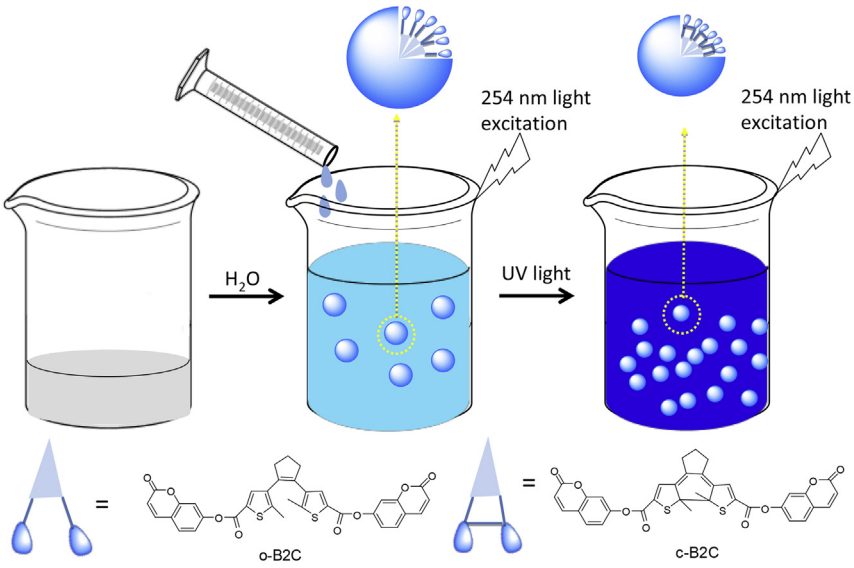

Scheme 1. Schematic representation of the morphology and fluorescence transition by water addition and UV light irradiation.

spectrum of B2C is illustrated in Fig. 1. The maximum absorption of compound **o-B2C** is observed at 315 nm. Upon irradiation with 254 nm UV light, the colorless solution of **B2C** gradually turns purple due to the appearance of a new visible absorption band centered at 562 nm, which is attributed to the formation of the closed-ring form **c-B2C**. The photo-stationary state is attained after about 4 min UV light irradiation. Alternatively, the purple solution could be bleached to colorlessness upon irradiation with visible light ($\lambda > 550$ nm), indicating that **c-B2C** returned to the initial state **o-B2C**.

Next, the fluorescent property of compound B2C was also investigated by fluorescence spectrophotometer (Fig. 2). The fluorescent emission behaviors of compound B2C were measured in different solvents. In the THF aqueous solution the strong fluorescence was found. Since THF is a good solvent and water is poor solvent of B2C, the molecules must aggregate in the aqueous mixtures with high water fractions. The phenomenon shows this compound may be with AIE behaviors.

For further study the fluorescent emission behavior of B2C in aqueous solutions, the fluorescence of B2C with different water content was investigated (Fig. 3). With the increasing of the water

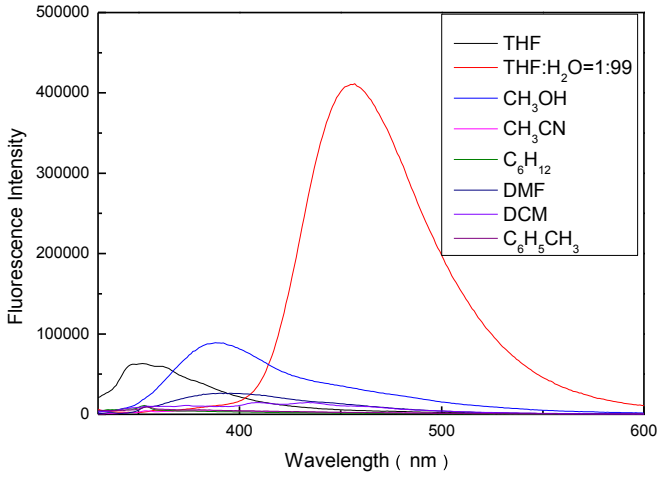

Fig. 2. Fluorescence spectral changes of the compound **B2C** in different solvents.

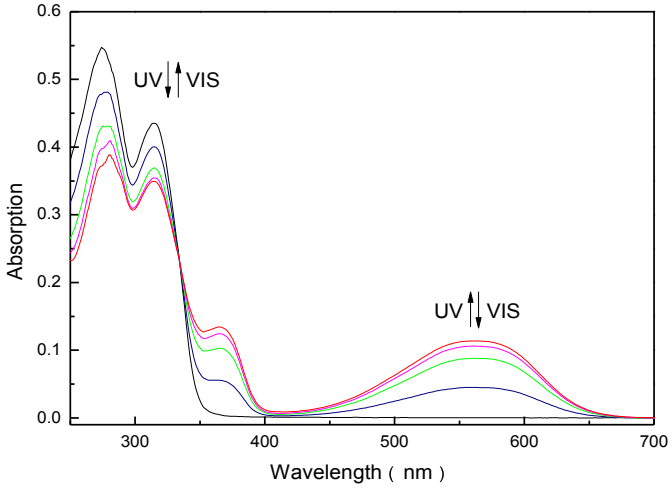

Fig. 1. UV–vis spectral changes of the compound **B2C** upon 254 nm light irradiation in THF (1.0×10^{-5} M) at 25 °C.

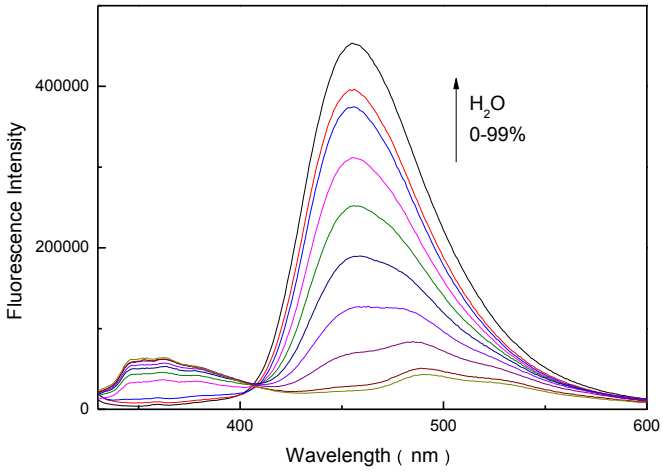

Fig. 3. Fluorescence spectral changes of the compound **B2C** with different water content.