



Intermolecular hydrogen bonding-assisted high contrast fluorescent switch in the solid state



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ABSTRACT

We describe a convenient approach to achieve fluorescence modulation based on self-assembled complexes between photochromic diarylethenes and solid-emissive Boron–Fluorine dye. Photochromism of the self-assemblies results in slight modulation of the Boron–Fluorine dye's fluorescence in dilute solution, but high-contrast ON/OFF fluorescence switching in nanoparticles and in the solid state. During this process, intermolecular hydrogen bonds between the carboxyl units on diarylethenes and the imidazole ring on Boron–Fluorine dye play important role in the efficient fluorescence resonance energy transfer from Boron–Fluorine dye to closed isomer of diarylethenes. The excitation wavelength (405 nm) of the self-assembled complexes hardly induces photochromism of diarylethene molecules, providing non-destructive readout ability. This system represents a simple and efficient alternative to the covalent system to achieve fluorescent switch in the solid state, and it may be potentially applied in rewritable high-density optical storage.

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1. Introduction

Organic fluorescent and phosphorescent materials have been widely studied for potential applications in optoelectronic devices, sensors, bio-imaging, photodynamic therapy and etc [1–16]. For practical utilization in optoelectronic devices, like organic light-emitting diodes (OLEDs), luminescent materials are usually fabricated into thin film or other solid forms, which necessitates molecules displaying efficient fluorescence in the solid state. Most chromophores developed till now tend to aggregate in the solid state, leading to aggregate-induced fluorescence quenching (ACQ). However, the ACQ problem has been successfully solved by introduction of bulky substituents, inserting dye molecules into a core, construction of dyes with aggregation-induced emission enhancement (AIEE), J-aggregate formation [17–19]. Various solid-emissive dyes have been synthesized and characterized based on the above considerations, which promotes the study of switchable solid-state fluorescence.

The switching and tuning of the solid-state emission is of great interest both in the field of fundamental research and for practical applications in memory, molecular machine, and displaying

devices. The external stimuli are usually light, sound, electricity, and mechanical force, among which light-controllable mode is the most favorite one because of its convenience over other stimuli. Although many light-sensitive materials are utilized to fabricate memory devices, bistable photochromism of diarylethene (DTE) is considered as most promising due to DTE's various advantages over other photochromic systems, such as excellent fatigue resistance, fast response, high quantum yields, thermal irreversibility, large changes of the absorption wavelength between the two isomers, and facile synthesis [20–25]. Multifunctional fluorescent molecules combining DTE units have been successfully investigated with the aimed applications in optical memory. Combining the solid-state fluorescence of solid emitters and photochromism of DTE, ultrahigh-density storage may be realized, if the fluorescence of the chromophore matches the absorption of the close isomer of DTE. In 2004, Park et al. introduced AIEE cyano-substituted ethylene into DTE unit, and successfully realized the solid-state fluorescence switching [26,27]. Some other solid-emissive chromophores, such as tetraphenylethene [28], naphthalimide [29–31], perylenebisimide [32,33], can also be covalently linked to DTE to afford high contrast fluorescent switches in the solid state. However, covalent linking chromophore to DTE unit is synthetically tedious and arouses increased expense, which limits its practical applications. Instead, regulation of the chromophore's fluorescence through intermolecular Förster resonance energy transfer (FRET) is much

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easier. Simply mixing the chromophore with DTE molecules could provide the self-assembly (SA), and photochromism of DTE unit may reversibly regulate the emission of the chromophore. But some requisites should be met, namely spectral overlap and short distance to allow for efficient intermolecular FRET [34–36].

Recently, we developed a series of highly solid-emissive Boron–Fluorine dyes (BOPIM), with Boron 2-(2'-pyridyl)imidazole as the main chromophore [37]. Various intermolecular non-covalent bonds, such as hydrogen bond, halogen bond, are formed to promote non-parallel packing, thus inhibiting ACQ. On the other hand, their Stokes shifts are greatly enlarged due to an efficient intramolecular charge transfer (ICT). And we also found that the naked N atom on imidazole ring in BOPIM dye could form intermolecular hydrogen bond with the carboxyl group of another chromophore Rhodamine B (RhB). Therefore, intense red emission of RhB was observed in the solid state, due to efficient intermolecular FRET from BOPIM skeleton to RhB [38]. Based on the above results, reversible regulation of BOPIM's solid emission may be realized by light stimulus, through intermolecular FRET from BOPIM to closed isomer of DTE. Herein, we synthesized photochromic DTE derivatives (DTE1 and DTE2) containing a carboxyl group and investigated the self-assemblies of DTE molecules with BOPIM dye (Scheme 1). BOPIM emits intense green fluorescence centered at 513 nm, which matches the absorption of the closed isomer of DTE1 and DTE2 molecules. In order to shorten the intermolecular distance, intermolecular hydrogen bond is constructed between the precursors.

2. Experimental

2.1. Materials and measurements

All starting materials were obtained from commercial suppliers and used as received. Moisture sensitive reactions were performed under an atmosphere of nitrogen, and the solvents were treated according to standard methods. ^1H NMR and ^{13}C NMR were recorded on Bruker 400 NMR spectrometers. Chemical shifts are reported in ppm with CDCl_3 as reference (7.26 ppm for ^1H NMR). IR measurements were performed on Nicolet 360 FT-IR. UV–vis and fluorescent spectra were obtained on Hitachi U-3010 and F-4500, respectively. Solid fluorescent quantum yields were measured by using a Labsphere IS-080 (80), which contained an integrating sphere coating on the inside with barium sulfate as the reflecting material, and the diameter of the integrating sphere was 8 inches. The excitation wavelength was 374 nm, and the fluorescence wavelength range studied was 400–700 nm. Confocal fluorescence imaging was performed with a Leica TCS SP5 inverted microscope

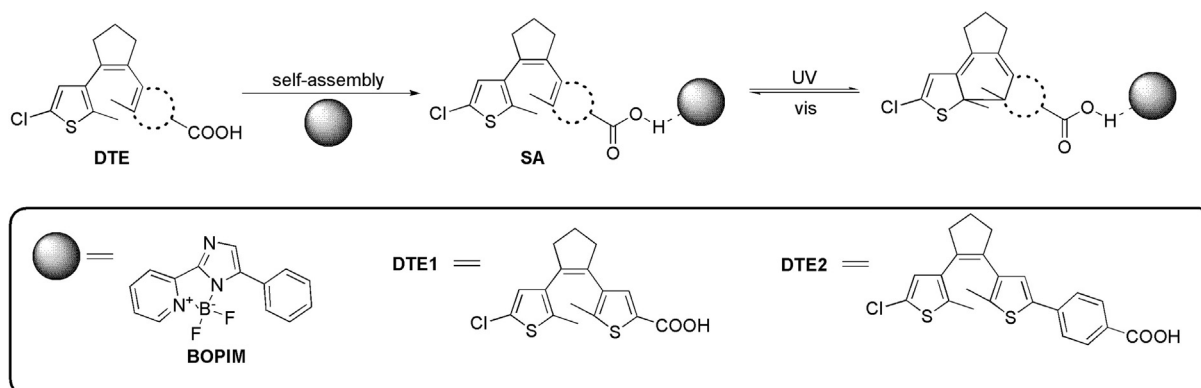
(DMI 6000B, Solms, Germany). A 63 oil-immersion objective lens was used. Transmission electron microscope (TEM) images were obtained using a H-7500 (Hitachi) transmission electron microscope.

2.2. Synthesis

The synthesis and characterizations of precursor BOPIM dye have been reported by our group [37]. Photochromic DTE1 and DTE2 were synthesized according to previous reports [39]. The two-component assembled composites were yielded by dissolving and stirring a mixture of photochromic DTEs and BOPIM dye with a 1:1 molar ratio in anhydrous THF. After half an hour's stirring, the obtained solution was evaporated under vacuum to provide the SA1 and SA2 as light yellow powders. The solutions of the self-assembled composites were prepared by re-dissolving the solid powders in THF solvent. The fluorescent nanoparticles of the self-assemblies SA1 and SA2 were obtained by reprecipitation method: a concentrated THF solution (10^{-2} M, 0.01 mL) was slowly injected into water (10 mL) under vigorous stirring to provide a suspension with a concentration of 10^{-5} M. The self-assembled solid films were obtained by coating the concentrated solution (10^{-3} M in THF) onto a quartz plate.

3. Results and discussion

Formation of intermolecular hydrogen bond would change the molecules' electronic environments on some level, which can be elucidated by ^1H NMR. The NMR measurement was conducted in CDCl_3 , because it is a good solvent to promote the hydrogen bond formation. Fig. 1 shows the resonances corresponding to the aromatic protons in the molecules. The signals of protons from carboxylic acid units were not observed due to fast proton exchange with water minority present in solution. Normally intermolecular hydrogen bond would induce marked chemical shift changes for the protons close to the hydrogen bond, which is the case for the self-assemblies between BOPIM dye with RhB [38]. And for the self-assemblies SA1 and SA2 described here, similar phenomenon was observed. The most significant chemical shift difference is found for the H(3) on pyridine ring. The $\Delta\delta$ is calculated as 0.236 ppm for SA1, and 0.204 ppm for SA2. These are comparatively large changes for hydrogen bond formation, manifesting the important role of the hydrogen bond. In comparison, the $\Delta\delta$ of H(3) for the self-assemblies of BOPIM dye with RhB is no more than 0.03 ppm. This may be due to the fact that SA1 and SA2 have higher association constants because of the smaller steric hindrance of the carboxyl units on DTE molecules. Another position close to the



Scheme 1. Self-assembly of photochromic DTEs and BOPIM dye.

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