



Review

Recent advance of photochromic diarylethenes-containing supramolecular systems

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ABSTRACT

Photochromic diarylethenes were deemed to be one of the most promising molecular building blocks for photoresponsive materials. This review gives a brief summary to the recent progress of studies of diarylethenes in supramolecular systems, focusing on their applications in biological systems, photoresponsive mechanical materials and photoresponsive chemosensors.

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1. Introduction

Supramolecular chemistry [1] has been one of the most attractive research topic of modern chemistry, and is still receiving rapid progresses in multidisciplinary fields, such as supramolecular photochirogenesis [2,3], organic electronic devices [4,5] and biocompatible materials [6]. Stimuli-responsive supramolecular systems is particularly intriguing because they provides an attractive approach for creating novel materials that are capable of responding to environmental changes [7–9]. Comparing to temperature (*T*), pH and other stimulating factors [10–12], light is considered as the most useful external stimulus for dynamically controlling the morphology and functionality of supramolecular assemblies because of its non-invasivity and convenience for use.

Photochromism, known as a photoinduced reversible transformation between two isomers that have different absorption spectra, offers a fascinating tool for manipulating molecular and supramolecular geometry and photo- and electronic properties

[13]. Photochromism phenomenon is commonly found in inorganic compounds, organic compounds and many biologic systems [14]. Among the variety of synthetic organic photochromic compounds, such as azobenzenes, diarylethenes (DAEs), spiropyrans, thiophenfulgides and hemithioindigos [15–17], DAEs are particularly appealing because of their accessible modification, thermal stability, high fatigue resistance over many cycles of photo-switching and large changes in their optical and electronic properties upon photoisomerization [14,15]. The fundamental of the photochromism of diarylethenes is reversible photo-induced ring-opening and ring-closing isomerization. The substitution effects on the absorption spectra and quantum yields have been extensively investigated, which provides detailed information and guidance for designing novel photoswitches with properties desired [18]. Hence, photochromic diarylethenes compounds are the most promising candidates as photoresponsive molecular building blocks to assemble photoresponsive supramolecular systems.

This review will summarize recent studies on photoresponsive supramolecular systems with diarylethenes as photoswitching units, as well as the applications of such systems in different areas, including photoresponsive supramolecular systems in construction of artificial biological molecular systems, as “smart” materials exhibiting mechanic properties upon photo irradiation and as photoresponsive chemosensors.

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2. Diarylethenes as photoresponsive building blocks in supramolecular systems

The pioneering study concerning photochromic diarylethenes can be traced back to 1980s [19], and the excellent properties of this kind of compounds attracted significant attention from chemists. The photochromic properties of diarylethene derivatives correlated to their chemical structure have been thoroughly investigated over the 40 years development. Generally speaking, both open and closed forms are stabilized by the aromatic stabilization energy of the heterocyclic aromatic moiety, and the introduction of electron-withdrawing groups on the aromatic rings often decreases the thermal stability of the closed forms. The conversion ratio between the open- and closed-isomers in the photostationary states, a critical parameter for their applications, could be optimized by rationally choosing appropriate substituent(s) and frameworks to offer ideal conversion ratios of >95%, which makes it an excellent building block for stimuli responsive supramolecular architecture [14]. The construction of stimuli-responsive supramolecular self-assembly has recently attracted significant interest because these assemblies are promising candidates for smart materials that could find applications in chemistry, biology and material science [20–22]. By virtue of the significant difference of absorption spectra in open and closed forms, the morphology and chemical/physical properties of diarylethenes-based supramolecular assemblies, which are thermally irreversible, can be regulated by photoirradiation [23–26].

Strongly fluorescent emission in the solid state could find broad potential applications, such as fluorescent biological labels, sensors

and light-emitting diodes [27]. However, many organic chromophores and polymers that can emit strong fluorescence in dilute solutions usually show drastically reduced fluorescence efficiency in the solid state because of “concentration quenching”. In order to solve the “concentration quenching” problem, Yi and coworkers have designed a series of switchable supramolecular self-assemblies based on the hydrogen bonding interaction between pyridine-containing diarylethene BTEPy and carboxylic acids [23] (Fig. 1). By adapting this strategy, fluorescence enhancement of BTEPy was observed in solution, solid state and as nanoparticle assembly. Especially, when BTEPy interacts with a carboxyl-containing Bodipy dye (Fig. 1), which is an attractive chromophore been extensively used for light-harvesting molecular arrays and fluorescent molecular probes [28], the “concentration quenching” in the solid state can be alleviated due to the hydrogen bond formation and energy transfer process [23].

The use of phototriggered conformational change of diarylethenes has been used to tune the physical properties of self-assembled supramolecular systems. Yagai and coworkers [24] reported merocyanine–diarylethene multi-chromophore complex between **2a** and chiral diarylethene derivative **3**, formed by hydrogen bonding interaction (Fig. 2), which cause a J-type aggregation of **2a**. Switching between monomer and J-type aggregation is controlled through the photoisomerization of diarylethene component, and subsequently switching of the absorption band, the circular dichroism (CD) signals and fluorescence can be controlled by light input. When **2b** is incorporated to the binary system of **2a** and **3**, H aggregation due to the assembly of **2b** and **3** is formed. Photoisomerization of the ternary system

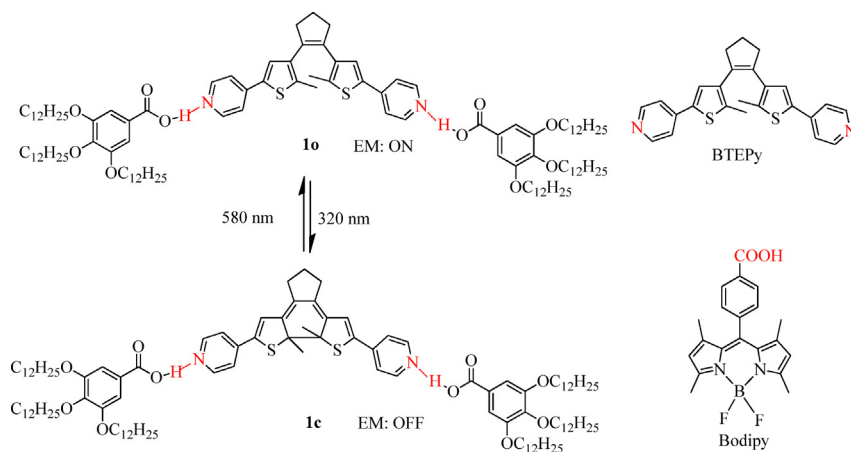


Fig. 1. Photochromic process of self-assembled complex **1** and structures of compound BTEPy and Bodipy.

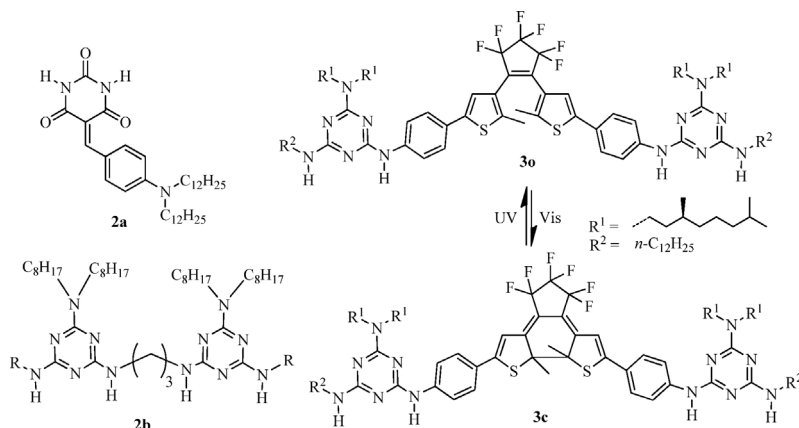


Fig. 2. Structures of merocyanine **2** and diarylethene component **3**.

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