

Review

Recent advances in the use of photochromic dyes for photocontrol in biomedicine

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ABSTRACT

Light can play important roles in controlling biochemical processes. Owing to their high spatiotemporal resolution and non-invasive nature, light can be utilized as smart triggers to mediate the biological activities of substances. In this review, we summarize important photochromic dye based photoswitchable substances that have been developed in recent years. Additionally, the basic principles involved in the design of the photochromic biomaterials, and insights into how to expand applications of these light activated agents and the key challenges that need to be considered are discussed.

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1. Introduction

Nature contains numerous examples of organisms that respond to external stimuli, which operate to perform various biological functions with high degrees of spatial and temporal

control [1,2]. Because of its intrinsic spatiotemporal resolution and non-invasive nature [3–5], light is an ideal external control element that can be employed along with photochromic dyes (PDs) for remotely manipulating biological functions. The phenomenon of photochromism was first reported by Fritzsche in 1867 [8]. PDs [6,7] are a special class of compounds, which under light irradiation conditions, generate chemically and physically (including light absorption or color) different

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products through processes that can be reversed thermally or by using light.

To date, a considerable effort has been devoted to the use of PDs for light promoted control in biomedicine, especially for bioactivity mediation, and cell or tissue imaging. A diverse number of PDs have been explored in this context including azobenzenes, diarylethenes, spiropyrans, stilbenes, hydrazines, acylhydrazones, hemi-indigos, naphthopyrans, spirooxazines, dihydropyrenes, coumarins, naphthalenes, anthracene and styrylpyrene. However, the optimized use of these substances is limited by the fact that photochromic biomaterials most often require activation by using short wavelength (high energy) light and/or display toxicity in biological systems. In light of these issues, a number of new, visible or infrared light stimulated PDs have been developed. Moreover, several other effective solutions to these problems have been devised, such as those that rely on the use of multi-photon excitation processes [9], upconversion nanoparticles (UCNPs) [10–13] and metal to ligand charge transfer (MLCT) materials [14,15].

Many types of photoswitches have been linked to bioactive molecules, including proteins, nucleotides and peptides, to make them susceptible to photocontrol [16–19]. In addition, photoactivated chemotherapy regimes have been developed as mild methods for controlling the specificity of drug-action [20–22]. During the past few decades, many reports have described the use of PDs for photoactivation control in biomedicine. In the current review, we focus attention on PDs that have been devised to serve as photoactivatable control elements in a variety of biotechnologies, including biological imaging, on-demand cell attachment, photopharmacological chemotherapy and drug delivery, as well as for the conformational control of biomacromolecule. The basic principles involved in the design and application of photochromic biomaterials used in these areas along with suggestions about how to expand their utility are also presented.

2. Types and characteristics of photochromic dyes

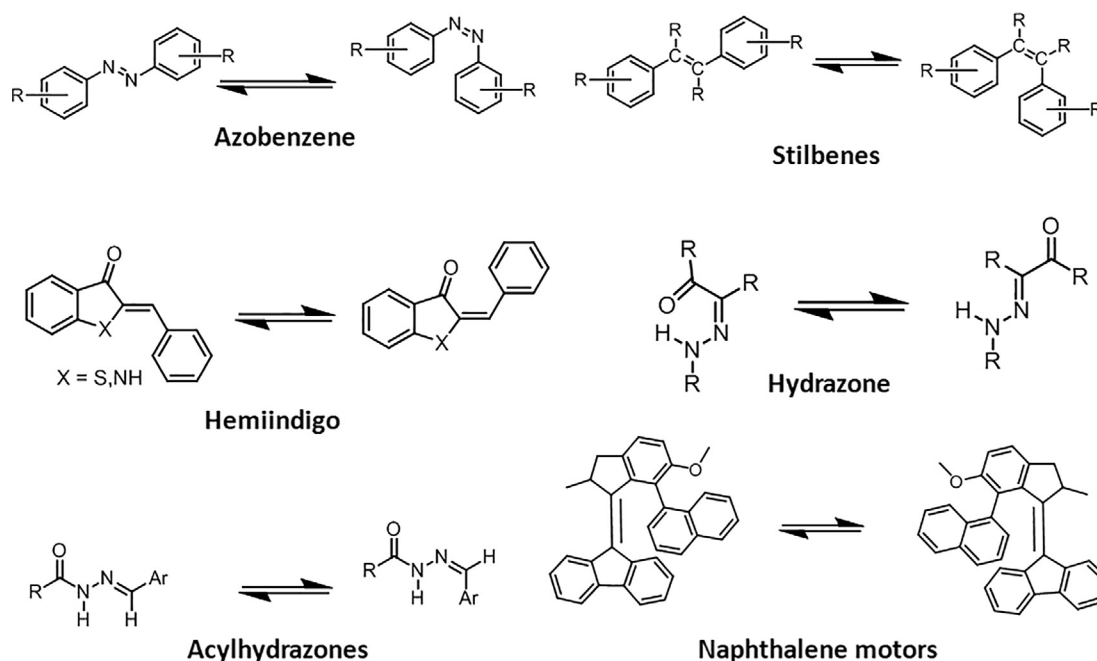
PDs undergo photoirradiation promoted, in most cases reversible (thermally or photochemically), chemical reactions that produce color changes (photochromism) [23–26]. The

rearrangements of chemical bonds and electron distributions occurring in these reactions cause structural as well as electronic changes in the PDs [27]. Traditional PDs are classified as being T-type (thermally reversible) and P-type (thermally irreversible) photochromic molecules, which differ in the way in which the reverse color changing process takes place [28]. Irradiation of a T-type PDs photochromic molecule, such as azobenzenes [29,30] and spiropyrans [31], generates a product, which is thermally unstable at room temperature and, as a result, it will undergo reverse color changing reaction in the dark. On the other hand, the photogenerated species can be thermally stable at room temperature and, consequently, not produce the original structure in the dark. Examples of these P-type PDs are furylfulgides [32] and diarylethenes [28,33].

Many families of PDs have been developed over the past decades that differ mainly by the type of photochemical reaction driving the color change. Consequently, PDs can be subcategorized by photoreaction pathway they follow, including *trans-cis* isomerization, photocleavage of bonds, electrocyclization and cycloreversion reactions and intermolecular cycloaddition and cycloreversion reactions.

2.1. *Trans-cis* isomerization

Azobenzenes and stilbenes undergo well-known reversible N=N and C=C *trans-cis* isomerization reactions upon irradiation with suitable wavelengths of light [30,34]. These processes result in large changes in molecular planar nature of and π -conjugation in molecules (Scheme 1) [30,35,36]. Hemiindigo, which has been used as a dye for more than 100 years, is comprised of a double bonded indigo and stilbene units. Importantly, substituted hemiindigos constitute a greatly promising new group of PDs for applications in biology. Very recently, Dube et al. designed and synthesized a series of hemiindigo derivatives that absorb light in the visible region (Scheme 1) [37]. In 2017, Feringa and coworkers described a naphthalene motor type PD that exhibits four-stage unidirectional rotation through light-driven unidirectional one step C=C bond rotation upon irradiation (Scheme 1) [38]. Hydrazones, another family of PDs that operate by C=N bond *trans-cis*



Scheme 1. *Trans-cis* isomerization type photochromic dyes.

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