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Review

Light controlled receptors for heavy metal ions

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ABSTRACT

This review focuses on the recent growth in the photo triggered molecular receptors for heavy metal ions. The photochromic unit in such molecular receptors performs as a trigger unit to allow control over a range of the properties through an external stimulus. This review opens up with the new opportunities for the development of host molecular motifs for heavy metal ion sensing applications. The photochromic switches based on a chemical structure like spiropyran, chromenes and spirooxazines tagged with appropriate chromogenic or fluorogenic unit reported till date have been summarized and categorized by the selectivity of metal ion to achieve the suitable optical response. The review has relevance for designing new photoreversible switches with the interesting optical response for environmentally important heavy metal ions.

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1. Introduction

Photoswitches, in general, are tools that function in accordance with light sources [1–4]. The mechanism that plays a bigger role, while working at the interface of switches and sensors, is normally based on photochromism [5–7]. It was Fritzsche, who first reported the phenomenon of photochromism in 1867 [8]. He observed the disappearance of an orange color solution of tetracene in broad daylight and appearance of color in the dark. Later, Hirshberg and Hebd in 1950 explored the synthesis of photochromic molecules and provided an insight into the mechanistic aspects of photochromism (The Greek term "phos" means 'light' and "chroma" means 'color') [9]. Since then, photochemistry has gone through major advancement, particularly during last six decades. The initial exploration by Hirshberg led to the development of many new classes of photochromic compounds with reversible response [10,11].

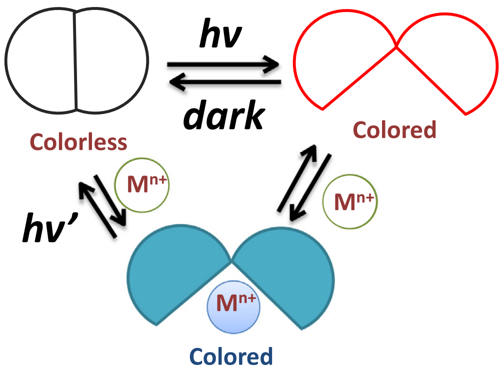
In most of the photochromic processes, rearrangement between two different species occurs with the induction of suitable light sources. Reversibility serves as the important role model for most of the photochromic phenomena. The comprehensive definition of photochromism deals mainly with the reaction processes, where progress in forward or backward directions can be triggered by an external agent called "light" or "metal ion" (Scheme 1). The observance of significantly different absorption or emission or color enables clear identification of different species [12]. The photochromic phenomena in systems such as spiropyrans, spirooxazines, oxazines, benzopyrans etc. generally deals with the photo-induced conversion of the closed form (colorless) into an open form (colored) or vice versa. The open form is generally referred to as the merocyanine form, while the closed form is also called as spiro form. The conversion of open form to closed form occurs thermally or sometimes photochemically [13,14]. The open merocyanine form further isomerizes into several different stereoisomeric forms through *cis–trans* isomerization of the double bonds [15]. However, in case of both photochromic and thermochromic systems such as naphthopyran, the photochemical reaction at low temperature yields a single product instead of several photoproducts. The decrease in temperature often transforms the dual response (thermo- and photo-reversible) of naphthopyran into only photoreversible nature [16]. In most instances, systems like spiropyrans, chromenes or spirooxazines proceeds through thermal induced reverse reaction [17,18]. Another type of photoswitchable frameworks developed by Favaro et al. on irradiation with suitable light source produced two different colored forms via rotation around C—C bond (*cisoid* and *transoid*). A photoswitchable system developed by Favaro et al. also displayed thermoreversible response [19]. It has been demonstrated that the rate of thermal bleaching increases with an increase in the temperature, which in turn decreases the light-induced coloration [16]. The systems like fulgides or diarylethenes proceed through the photochemical bleaching reaction in most cases [20–22]. The photochromism in the systems described here can be classified as positive or negative photochromism depending upon the coloration and decoloration response in different solvents [23].

One of the chief rationales behind photochromic (or photoactive) systems to display photochromism is the competency at which the physical and chemical properties can be reversibly controlled at the behest of an external agent. Light as an external input seems practical in this case since its action is convenient to monitor precisely, substantially flexible for specific action and can be switched with regard to our convenience [24,25]. In photochromic molecules like naphthopyrans, spiropyrans, spirooxazines, oxazine etc. the photocleavable $C_{sp3\text{-}pyran}$—O bond plays a crucial role in determining the photochromic index [15].

The interconversion processes involve structural as well as electronic modifications. The absorption signature difference can be modulated at the molecular and supramolecular level. Similarly, the sensitivity of the systems can be enhanced by attaching fluorescent or chromogenic tags to the original molecule.

2. Classification of photoactive receptors

The structural alteration in the photoactive receptors proceeds through a single step electrocyclic transformation during light irradiation (Fig. 1). Several examples of photoactive molecules exist in the literature till date [26]. Out of several photochromic species; naphthopyrans, spiropyrans, and spirooxazines display enhanced activation in response to metal chelation [27–30]. Another class of photoswitches has also been reported in the literature such as acylhydrazones developed by Hecht and co-workers [31]. Such small molecule switches exhibit excellent fatigue resistance with more than 100 nm band separation between E and Z isomers. Hecht and co-workers have also revamped the fatigue resistance of diarylethenes by introducing electron withdrawing groups such as trifluoro methyl substituents into the core system [32]. Bragg and Katz and co-workers have developed visible light triggered 1,2-dicyanoethene substituted blinkers, which can undergo reversible transformation between *cis* and *trans* geometries [33,34]. The excellent electronic nature of reversible dicyanoethenes bears the potential to act as an electron carrier in novel sunlight responsive semiconductor materials.



Scheme 1. A typical transformation in the photochromic systems induced by metal ion or light.