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Towards photochromic and thermochromic biosensing

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ABSTRACT

Photochromism and thermochromism are interesting physicochemical phenomena applied in the chemistry, health and biology fields and others. Nonetheless, exploiting these chromo-switchable properties in biosensing remains unexplored, and very few results have been reported in the scientific literature. Along these lines, the rich mature knowledge of these phenomena supports the challenge of facing the development of photo- and thermochromic bioanalytical systems. This work discusses potential approaches to exploit photochromism and thermochromism for biosensing, and it reviews the state-of-the-art of these phenomena in the surrounding areas of biosensing in order to plot a stimulating scenario for innovation.

Contents

1. Introduction

Photochromism and thermochromism are phenomena by which matter switches its colour as a response to electromagnetic radiation and thermal stimuli, respectively. These processes are driven by compounds that lead to light- and heat-induced changes between two states with different absorption spectra [1]. Photochromism and thermochromism can be found in nature. For instance, chameleon diamonds (high nitrogen content natural diamonds) undergo a thermally induced colour switch that reverses under darkness conditions [2]. Besides, in living organisms, visible light absorption of retinal bound to opsin proteins gives rise to a photochromic isomerisation that triggers the enzymatic pathway of the vision cycle [3].

Intense research has focused on the design and synthesis of photo- and thermochromic systems, which have provided broad knowledge in this field [4]. Moreover, the development of smart functional materials by integrating these switchable compounds into different environments has had a significant impact on industry. Thus many commercial products based on these technologies can be found in applications that range from ornamentation to data storage [5].

From the analytical chemistry point of view, many studies have addressed the development of chemical sensors based on photochromism, mostly for sensing inorganic ions [6]. However, photo- and thermochromism in biosensing remain unexplored. Some works that used these phenomena in biological systems and medical

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applications are found in the bibliography, but they rarely point to biosensing or claim specific potential in this field. Indeed very few studies that directly deal with photo- and/or thermochromic biosensing systems have been reported.

The physicochemical phenomena involved in transduction strongly determine the application field of a sensor system and the nature of the analytical information that can be obtained from the sample under study. From this perspective, exploring biosensing capabilities of photo- and thermochromism is an interesting challenge, whose potential is supported by the scientific and industrial relevance of these chromo-switchable systems.

This paper focuses on thermo- and photochromism for biosensing. In addition to reviewing works that have directly dealt with these phenomena for bioanalysis, an overview of the studies that report chemical sensors (non-biosensors), biological systems, medical applications and technological developments is presented. Moreover, new strategies are proposed and discussed throughout, including experimental results and significant bibliographic references that support the potential of these approaches. The criteria followed in this review seek to include relevant studies and strategies from different scientific areas in order to plot a scenario from which to outline a trend towards the development of photochromic and thermochromic biosensors.

The manuscript contains two sections: molecular and supramolecular systems; photochromic and thermochromic technologies. The first part offers a brief introduction to the main chemical and biochemical approaches of photochromism chemistry, and surveys on studies into biosensing surroundings. The second part reviews different thermo- and photochromic technological approaches, and highlights their bioanalytical capabilities.

2. Molecular and supramolecular systems

The design of photochromic molecules is an active scientific area that typically involves several families of compounds, such as azobenzenes, spiropyrans and diarylethenes [7]. These molecules switch between two isomeric forms with a different absorption spectrum under UV and visible light exposure (Fig. 1A). Moreover, assembling photochromes and fluorescent structures in the same molecule leads to photochromic compounds in which the light-activated isomerisation of the photochrome modulates the fluorescent behaviour of the fluorophore [9,10].

By linking specific receptors that modify photochromic behaviour after analyte binding, these photochromes have applications in chemical sensing. Table 1 lists representative examples of photochromic chemical sensors for different kinds of analytes. Along these lines, several papers address the review of molecular photochromic compounds for chemical sensing, including a in-depth description of the mechanisms involved in these systems [1,6,7]. From the analytical point of view, it is worth highlighting a recent review by Song and coworkers, which comprises an interesting section about multi-analyte discrimination [20].

Photochromic sensors have been widely studied to determine metal ions by modifying photochromes with moieties for selective recognitions [11,12], typically electron-rich groups (containing N, O or S atoms), crown ethers and calixarenes [6,20]. Moreover, many studies have addressed photochromic molecular sensors for inorganic anions. Structural changes in spiropyran derivatives after CN^- nucleophilic addition [14] or after pyrophosphate (PPi) cooperative ligation interactions [15] are some examples of the chemical mechanisms that take place in these systems.

Regarding biosensing, some works have dealt with the modification of photochromes for sensing molecules involved in biological processes. For instance, Yang and coworkers reported a spiropyran that was modified with nitro groups for glutathione (GSH) sensing [17]. The thiol group of the peptide undergoes nucleophilic substitution and induces the isomerisation of the photochrome, which generates a spectral change from slightly yellow to orange-yellow. As an example of biomacromolecules detection, Tao et al. designed an electrochemical sensor for β-galactosidase (β-gal) by including a galactose molecule in the spiropyran structure [18]. This

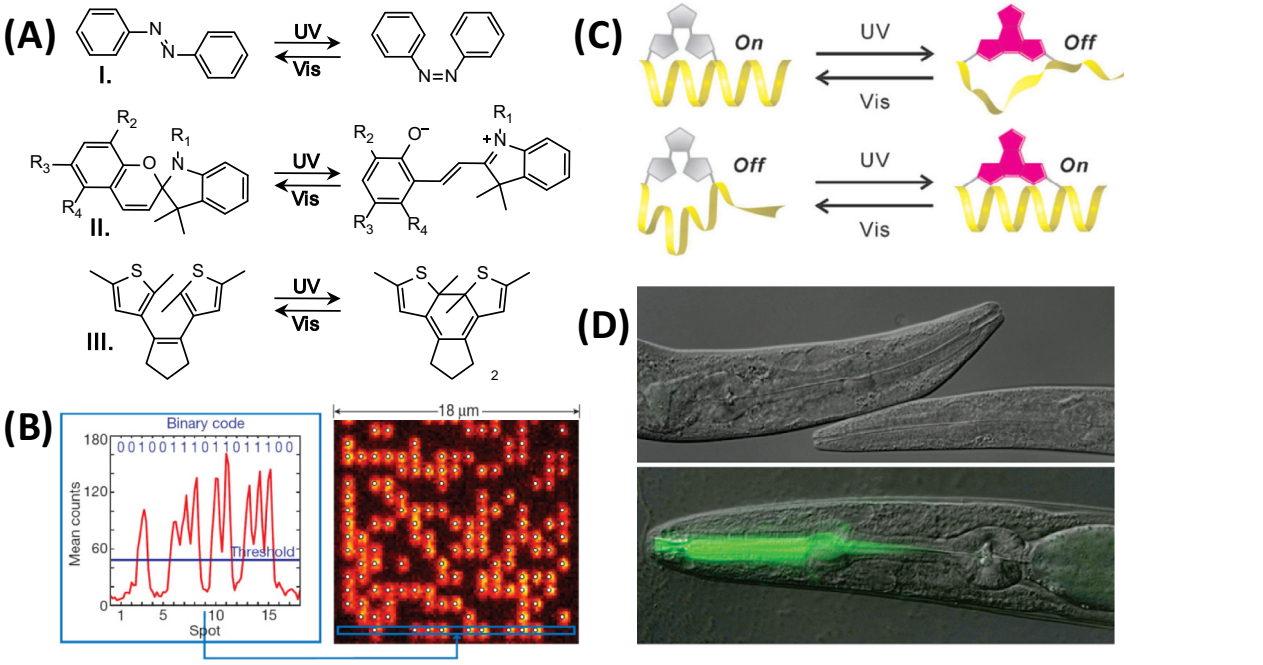

Fig. 1. (A) Chemical structures and photochromic switches of azobenzenes (I), spyropirans (II) and diarylethenes (III). (B) Data storage system based on the photoswitching properties of the photochromic green fluorescent protein. Reprinted by permission from Macmillan Publishers Ltd: [Nature] [8], copyright (2011). (C) Scheme of the photochromic control of the conformational state of a peptide. Reprinted by permission from Wiley-VCH Verlag GmbH&CO (*Chem. Eur. J.* 2012, 18, 9834–9840), copyright (2012). (D) Images of *Caenorhabditis elegans* biological control by photochromism. Adapted with permission from (*J. Am. Chem. Soc.* 2009, 131, 15966–15967). Copyright (2009) American Chemical Society.