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Review Article

THE VERSATILITY OF SPIROPYRAN AS MULTIRESPONSIVE COMPOUND

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ABSTRACT

Photoresponsive is a highly important system that leads to the development of photo-optical media, photo-switches, photo-mechanical systems, micropatterning, and non-linear optical media. It delivers external signals upon the irradiation of UV or visible light, which also can be reversed to original state. Spiropyrans is one of well-known group of photoresponsive compound, whose properties have been studied extensively. They are able to undergo conversion from closed spiropyran to open zwitterions merocyanine. The current concept of applying the SP as molecular switch is based on the overall consistency of reversibility, rapid response time and less interference. The adherence to those properties is therefore can lead to potential molecular devices, sensors and fluorescent switches. Therefore this review discussed on the background, external effects and the potential applications of photoresponsive spiropyran compounds.

Keywords: Photoresponsive, Spiropyran, Merocyanine, Photo-switches, Visible light

1. INTRODUCTION

There was once a saying by James Thurber, that there are two kinds of light-the glow that illumines and the glare that obscures. In other definition, a light holds a form of travelling energy which makes things visible or affords illumination. It is widely used as a predominant stimulus to control chemical reactions, special physical properties, and biological evolutions [1]. Hence, light is very crucial to the biological system in any creature. For instance, the photosynthesis system in a plant uses light as an energy source as well as optimising their life processes [2].

The importance of light in biological photoresponsive system initiated the idea of mimicking the process in nature and applying them to the molecular design of synthetic photoresponsive polymer. This approach enables the development of smart materials and devices [3]. Such devices include the reversible optical storage [4], polymer viscosity control [5], photomechanical transduction and actuation [6], bioactivity switching of proteins [7], tissue engineering and drug delivery [8]. Thus, the development of functional polymer that possesses photochromic units has become a cutting-edge area in the field of material science today.

In photochromic system, there are few photoreactions compound that are extensively being investigated, for example azobenzene [9], spiropyran [10], cinnamic acid [11], triphenylmethane [12] and other derivatives. Photoresponsive is dealing on how a system responds under light exposure. The observation of these works are widely distributed in nature, which can be seen in many systems of photoregulated biological process such as vision in animals, phototropism in plants and photomovements in microorganisms [13]. Nowadays, this nature concept is being mimicked for development of responsive smart materials.

The conception of the photo-switching molecules was riginally inspired even before 19th century [14]. There were based on an integration of photoactive element, which able to capture optical signals and convert them to physiochemical signals [15]. Upon absorption of light, reversible transformation of a single chemical species between two isomeric forms has been induced [16]. Moreover, the generated isomers differ not only in the absorption spectra but also in various physical and chemical properties such as refractive index, dielectric constant and geometrical structure [17]. These happened due to the various physico-chemical mechanisms involving the *cis*-trans photoisomerization of double bonds, oxidation-reduction photoreactions and homolytic or heterolytic photocleavage of the molecules [18].

Inspired by unique characteristics as mentioned above, variety of organic photoreversible compounds have been explored as such the chromophore groups including azobenzene, spiropyranes, trimephylmethane dyes and their derivatives as shown in Figure 1. These responsive compounds undergo reversible photochromic behavior; insisting by the light, able to transforminto their isomer. While, at different conditions (thermodynamically) or under different light irradiation reversion take place to form their initial form [19]. Hence, this review will concentrate on one of the photochromatic compounds, spiropyran. Although it has many abilities yet it possibly being overlooked as not many review discussed on this compound. The background, syntheses, external response that stimulates the compounds and also their applications has been outlined in this review.

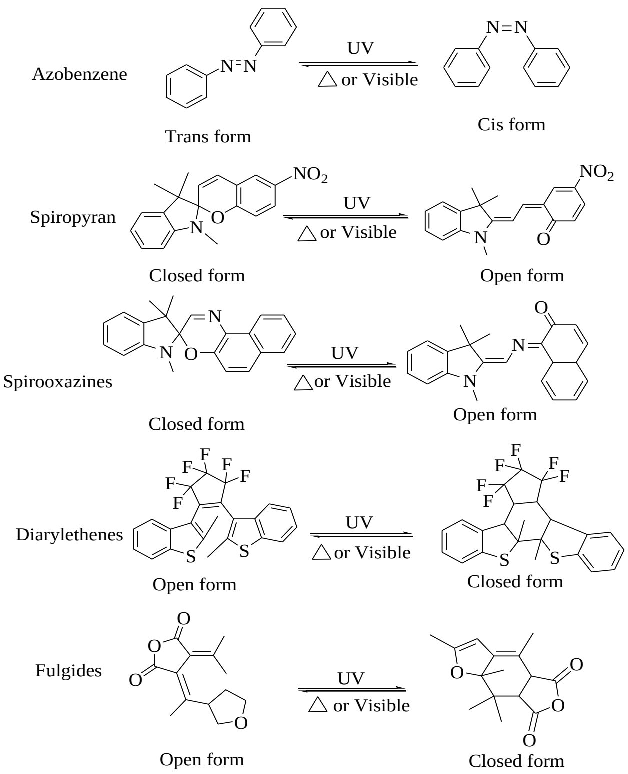

Fig. 1: Photochromic compounds that commonly used in light responsive system [20]

2. SPIROPYRAN

Spiropyran and spriroxazine derivatives as shown in Figure 2are one of the most notable and important photochromic materials. These organic photochromes have been extensively studied over the past several decades due to their high photosensitivity, very clear colourchange and rapid switching kinetics between the two isomers [21]. The capability of existing in two thermodynamically stable states in different conditions had promoted the used in various fields such as in molecular electronic [22], photonics [23], sensors [24] and computing [25].

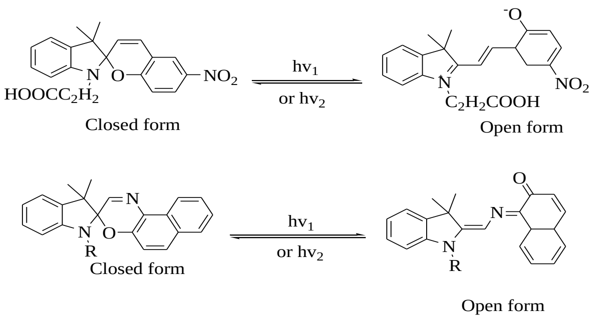

Fig. 2: Photochromic isomers of spiropyran and spirooxazines at open and close form when ultraviolet light is applied [26].

The excellent performance of spiropyran (spiro[2H-1-benzopyran-2,2@-[2,3]-dihydroindole]s in general, is due to the presence of two heterocyclic parts attached by a tetrahedral sp^3spiro carbon atom (Figure 3). Itexisted as a closed, non polar, orthogonal and spiropyran form. These two halves also posited in orthogonal planes. Moreover, when spiropyran is exposed to 530nm of UV light, it will undergo isomerization that produces an open, polar, planar, conjugated and coloredmerocyanine form (MC) [27].

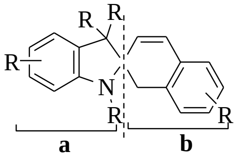

Fig. 3: Schematic representative of the spirobenzopyranindoline moiety. The structure showing the indoline part (a) is linked in a spiro manner through an insulating tetrahedral carbon to a 2H-benzopyran ring (b)

The mechanism of spiropyran based photochromic reaction involves a heterocyclic cleavage that triggers the ring opening reaction [28]. The single bond of the pyran ring (sp^3 hybridization) was cleaved and followed by the rotation of the two halves of the molecules to give planarzwitterionic forms (open form). The open form also called photomerocyanine, which is a resonance hybrid of a zwitterionic structure and neutral structure (Figure 4).

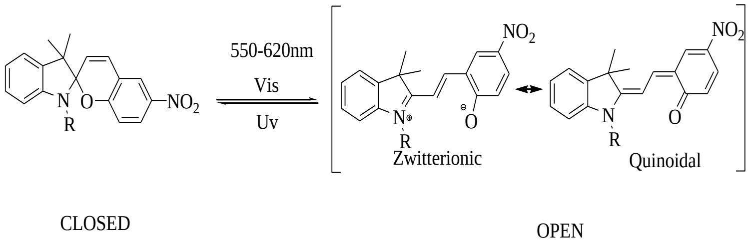

Fig. 4: Molecular structure of nitrospiropyran in the closed and open forms. In the "open form" zwitterionic and neutral reasonance contribute to the merocyanine structure

This zwitterionic structure is a largely influences to the structure of the open state form because of the lost of aromaticity of the oxygen-bearing ring in neutral form [29]. Thus, the molecules may be switched back to closed form with visible light (or thermally in nonpolar solvents) once spiro carbon atom become sp^3 again [30]. This process is also accompanied by a colour change (colourless to red) through physical appearance. It is due to the spiro form lacks conjugation whereas the planar photo produced zwitterionic species are in fact merocyanine dyes [31].

3. PHOTOCHROMIC BEHAVIOUR OF SPIROPYRAN

Recent advances in spiropyran family and derivatives have allowed the design of a wide range of stimulus-responsive amphiphiles that undergo spontaneous self-assembly in aqueous solution in response to external stimuli such as solution solvent,pH, metal ions, temperatureand light irradiation [21]. These photo-, thermo-, solvato- and ionochromic behavior of spiropyran-merocyanine state derivatives in various media has lead to different photochromic responses.

3.1. Solvents

One of the stimuli that allow the switch of spiropyran is also dependent on the solvents used. This phenomenon known as solvatochromism effect that can be defined as variation of the electronic spectroscopic properties (absorption bands) of a compound induced by variation polarity of the solvent medium used [32]. Previous work [33] reported that the solvatochromic behavior of spiropyran involves in a change of the position, intensity and shape of absorption band when measured in different types of solvents.

In general, most spiropyrancompound will likely undergo solvatochromism where in general, the maximum absorbance shifts to a shorter wavelength (*hypsochromic*or blue shift) when the environment are highly polar [34]. Moreover, previous work [35] described that the polar media can also stabilize and favour the formation of the zwitterions structure of the merocyanine open form over the quinoidal isomer. On the other hand, as the polarity decreases, it promotes the conversion to the spiropyran form instead [36]. Thus results in maximum absorbance shift toward longer wavelength (*bathochromic* or red shift) as shown in Figure 5.

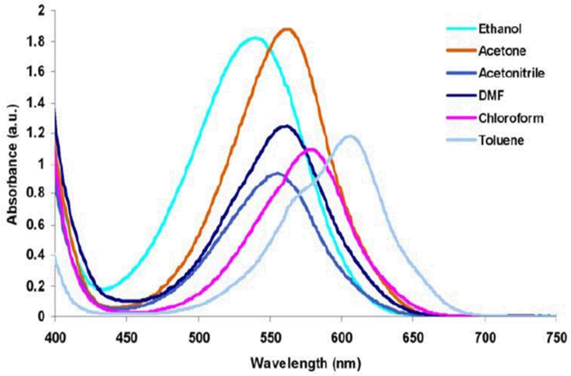

Fig. 5: Absorbance spectra of nitro spiropyran in different solvents.

All the absorption changes mentioned are also related to the intermolecular between the solute-solvent which able to modify the energy gap between the ground and excited state of the absorbent (Scarmagnani 2010). This can be explained by the illustration in Figure 6 where it showed the energy differences between the ground and the excited state of the MC form in both polar and non-polar solvents. This imply that the ground state of the coloured MC form are better solvated than their first electron excited state and larger than those of the excited state. While in non-polar solvents, ground state was slightly higher in energy level that make the energy differences between both ground and excited state much lower [21].

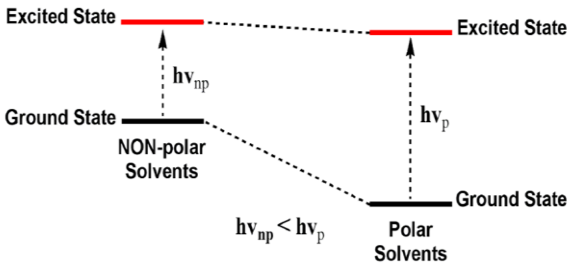

Fig. 6: Schematic representation of the energy difference between the ground and theexcited state of the MC form in polar and non-polar solvents

3.2. pH

External stimuli such pH solution cause changes in photochromic behavior of particular compound. These changes of behavior will allow in creations of many other new perspectives for the development of multiresponsive materials for biological and environmental applications. However it does not pose any particular system because the system provided is quite similar to the ionochromic phenomenon. Despite the similarity, this external stimuli was mostly connected to the three-state molecular switch that were first introduced by Raymo and co-worker [37].

The system definition mainly concerns the three-state molecular switch that can give out responds which are ultraviolet light, visible light and H^+ inputs [20]. In the initial state, the spiropyranexisted as colourless solution and after exposure under ultraviolet light, this photochrome undergo isomerization to merocyanine. The process was confirmed by the appearance of a band at 563 nm in the absorption spectrum. Nevertheless, the colorless open spiropyran will be protonated in the presence of acid and yield a positively charged form of molecules (**MEH**). Moreover, the whole state could be switched back to the original **SP** either thermally (visible light) or addition of base (releasing H^+). Figure 2.7 has shown the interconversion of three states mentioned, **SP**, **MC** and **MEH** state accompanied by irradiation, base and acid solution [38].

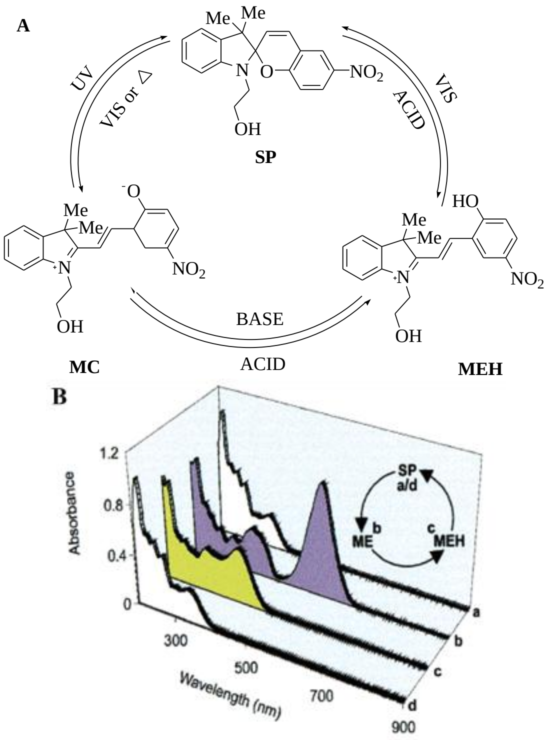

Fig. 7: Figure shows: A) Switching cycle associated with three states, SP, MC and MEHB) absorption spectra [38].

3.3. Metal ions

Bistable compound such as spiropyran can be converted under the presence of metal ions, hence introduced to the elegant synthetic design of receptor ligands. It was first demonstrated in near end of 19th century, the photoinduced of quinolinospiropyranindoline-metal complex in aqueous solution [39]. This finding was critical in helping some environmental monitoring works and development of rapid and reliable method for the detection and estimation of an important metal ion such as cyanine, zinc and aluminium [40]. Hence, most research focused on applying photochromes materialsto simultaneously binds metal ion and gives out responses.

The stabilization of spiropyran compound to form complexes with metal ion could be used as reversible sensor that can be switched between passive and active state and not just for concurrent detection of metal ions [41]. This is due to the merocyanine structure having the reasonance hybrid between two forms, the changed zwittterion form and quinodal form. Hence, the merocyanine is able to bind through the negatively charged phenol group of the zwitterions ion forms. This process is expressed on the Figure 8.

Great number of metal ions especially with certain d- and f-elements was being explored by many researchers. As example, previous work [41] have successfully synthesized a photoreversiblespiropyran "real-time" of aluminium ion sensor with great sensitivity and selectivity. Their research mentioned that the SP can be transformed into MC form when irradiated at 365nm which also chelated with Al^{3+}resulted colour changes. The study also demonstrated the Al^{3+}- MC was reversed back to spiropyran form by irradiation at visible light.

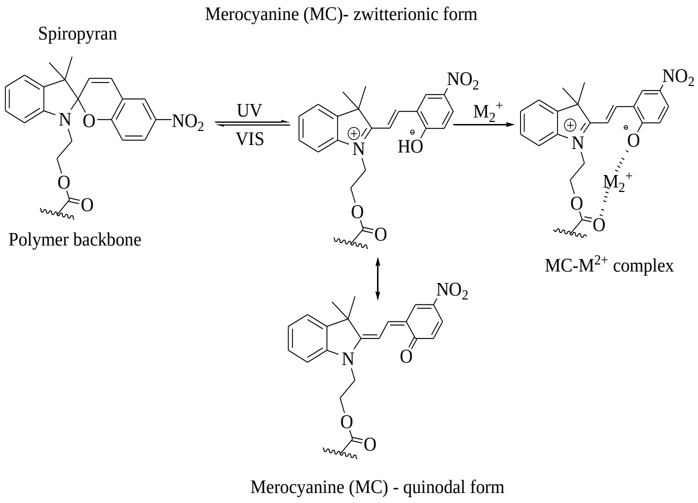

Fig. 8: Isomeric structure of Spiropyran (SP) and Merocyanine (MC) and the MC-M^{2+} complex

Other example of established metal ion includes the chemically and photochemically reversible Zn^{2+} ion chelating that can be detected with range up to part per billion [24]. This finding introduced a new extension based complex that have greater sensitivity and lower fatigue rates. While other works recognized other SP-metal binding complex such as Co^{2+}, Cd^{2+}, Ni^{2+}, Mg^{2+}, Fe^{2+}, Ag^{2+}, Na^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} can be isomerized into MC metal complex [42]. In addition, a complete mechanism study of spiropyran bearing nitro group with complexation of metal ions in solution had been published elsewhere [43].

The issue of fatigue resistance towards the switching SP complex was said to be improved when binding with Co^{2+}, Ni^{2+} and Cu^{2+} ions. This is due to its intramolecular energy transfer to the lower positioned energy level of the metal ions. While, the spiropyran bearing group can also enhance the binding constant between spiro unit and metal ion which crowned spiropyran greater complexation stabilization as compared to mono-spiropyran unit [44]. Thus, photoswitchable metal complexes using spiropyran derivatives are depending on the types of analyte and spriopyranderivates [27].

3.4. Temperature

The last reserve conversion in photochromes is defined as thermochromism. This particular term mean its ability of "remote" sensing of medium temperature where leads to isomerization in photochromes compound [45]. This organic photochromism, based on the themoresponsive isomerization had established the temperature-gated molecular switch based on the ensemble of photochromic property of spiropyran [46]. It is known that there are several factors that photoinduced energy transfer depends on, such as the distance between the energy donor and energy acceptor and intramolecular energy transfer process. Plus, the distance in spiropyran-fluorescein dyed can be modulated by controlling temperature [27].The reported fluorescence spectra of spiropyran derivatives were measured at 25°C, 50°C and 70°C suggested that the energy transfer process between excited state of fluorescein and merocyanine would be reduced by increasing temperature. As a result, the modulation degree for the fluorescence intensity of the complex was reduced at high temperature compared to room temperature [47]. This proved that a thermally driven fluorescence switch may be useful as the fluorescence thermometer after further research.

As for another research on the same particular response was opposed to the previouswork [48] which mentioned that the thermal spiropyran and merocyanine isomerization accelerates at elevated temperature. The repeated change of temperature in between 10°C and 60°C shows an absorbance change of the same MC. This is due to the decrease in ground state energy of the MC form via the stabilization of the MC form by hydrogen bonding interaction. Nevertheless of the results obtained, the application of temperature sensing real samples presented in both findings may contribute to the development of efficient and useful molecular-based temperature indicators.

4. APPLICATIONS

The ability of spiropyran compounds to response in a various photochemical stimuli discussed above has motivated many researchers to utilize these system provided towards various applications. Tremendous potential in sensor device fabrication of metal ions and biological applications were the main focused in this study.

Up to now, there have been a number of spiropyran-based receptors have been reported. However, even most of the known spiropyran-based receptors are tailored to bind metal ions, all have been working using the nitro-funtionalizedspiropyran [49]. There are far less reports on other funtionalizedspiropyran especially spiro bearing hydroxyl group. Thus construction of new spiropyran-based receptor introduces the immobilization with polymer or inorganic microbeads. Having flexible solid support had tremendously been used in widow coating [50], optical switches [51], optical memories [50] and metal ion detection [52] which in turn enhanced their application. For instance, in polymer work polymethyl methylene (PMMA) was commonly used because of their ability to increase the affinity of the dye and matrix and improve total chemical durability [53].

Furthermore, there has been a rapid growth of research towards the biological application of the spiropyran compounds [54]. With the problem of low specificity faced by the chemotherapeutical methods of many existing drug, it encouraged the used of photo-active molecule in selectively target the specific tissue or tumour [55]. This system is most likely to be a new potential for cancer treatment that are rarely been exposed. In addition, it may also fill the inadequate data on the toxicological information of attributed molecules.

5. CONCLUSION

Spiropyrans is one of well-known group of photoresponsive compound, whose properties have been studied extensively. They are able to undergo conversion from closed spiropyran to open zwitterions merocyanine. The current concept of applying the SP as molecular switch is based on the overall consistency of reversibility, rapid response time and less interference. The adherence to those properties is therefore can lead to a potential molecular devices, sensors and fluorescent switches. Overall, this review intends to discuss the synthesize photochromic spiropyran compound as it can facilitate generation of derivatives, which could ultimately lead to the identification of structure with improved photophysical ability. Furthermore, the introduction of a simple and efficient multi-addressable switching system was performed to show its application for detection of various activity using the provided system.

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