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A Brief Review on Photochromism Based on [2.2] Paracyclophane Scaffold

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Abstract

A fascinating molecule among the many unique and intriguing structures of hydrocarbons is cyclophane. [2.2]Paracyclophane, which is of particular relevance in the cyclophane family, has two co-facial benzene rings where the interaction between the π -orbitals known as the "phane effect" occurs because of their close proximity (around 3 Å). Its derivatives have a broad area of application like, asymmetric organocatalyst, solar cell devices, photochromic molecues, OLEDs, etc. Here in this review, the photochromism of the derivatives of [2.2]paracyclophane is the main emphasis. It is anticipated that a broad scientific community will find the review to be very interesting.

Keywords: Photochromism, [2.2]Paracyclophane, Phane effect

Exploring the novel structure and related hidden special properties of molecules are of great thirst in scientific community. Like the allotropes of carbon starting from coal to graphite to fullerene and latest is graphene. Among various interesting and novel structures of hydrocarbons, cyclophane is one such fascinating molecule. In the cyclophane family [2.2]paracyclophane is of special interest as it contains two co-facial benzene rings where the interaction, which is popularly known as 'phane effect', between the π-orbitals takes place due to short distance (nearly 3 Å).[1] [2.2]paracyclophane was first discovered by Farthing and Brown in the year 1949 and was synthesized in laboratory by Cram and Steinberg in 1951.[2, 3] Since its discovery, the 'phane effect' of this novel molecule is nicely exploited in various derivatives of [2.2]paracyclophane and thus it become a very important scaffold for various functional materials, such as photochromic material,[4] sensor,[5] asymmetric organocatalyst,[6] solar cell,[7] light emitting devices,[8] chiroptical material,[9] etc. There are a large number of reports on paracyclophane based molecules used as various functional materials and describing those in a single place is quite difficult. Here the main focus is on the photochromism of [2.2]paracyclophane derivatives. Hope the review will be of great interest to a large scientific community.

[2.2]paracyclophane Scaffold Used in Photochromism: The first utilization of [2.2]paracyclophane scaffold in designing organic photochromic molecules was demonstrated by Jiro Abe and his co-workers in the year 2009. A novel photochromic molecule pseudogem-bisDPI[2.2]PC (**1**) was synthesized and the spectrokinetic properties were thoroughly investigated.[4] Hexaarylbiimidazole (HABI) was known to exhibit photochromism at room temperature. HABI, which is colourless, undergoes cleavage under various stimuli, such as heat, light, pressure to colouredtriarylimidazole radical (TPIR), which thermally recombine to produce HABI. Thus the photochromic behaviour is attributed to the homolytic bond cleavage of the C-N bond between two imidazole rings. If the photogenerated radicals are closely spaced then thermal recombination and hence fading of the colour will increase, which is the demand for better photochromic property in this system. In order to bring them close to each other Abe judiciously chosen [2.2]paracyclohane scaffold. The substitution of HABI in pseudogeminal position of [2.2]paracyclophane was unique as the two TPIRs are now very closely placed with respect to each other, and hence they can recombine to dimeric form (HABI) at a very faster rate. The C-N bond length between two imidazole moiety is around 1.48 Å, as found from X-ray determined crystal structure of **1**. Upon irradiation with UV light, this photochromic species, **1** undergoes colour change from colourless (**1**) to blue coloured pseudogem-bisDPIR[2.2]PC (**2**), both in the solid state and solution phase at room temperature (Figure 1). After reaching the photostationary equilibrium state when the irradiation is off, the absorption of **2** decreases rapidly following a monoexponential kinetics. Complete bleaching was observed within 200 ms in benzene at 25 °C. From the absorption spectra (Figure 1a) it is found that there are a sharp absoption band at 400 nm and a broad absorption band ranging from 500

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to 900 nm. Because of the formation of radical, compound **1** shows fast optical switching in both colour and spin states, which is generally not found in any other photochromic system. The novel molecule (**1**) built on [2.2]paracyclophane scaffold also retains its photochromic behaviour in amorphous film and in PMMA polymeric matrix, which has practical application in optical solid state devices.pseudogem-BisDPI[2.2]PC can also be used to real-time image processing at video frame rates. Building up photochromic molecule on[2.2]paracyclophane scaffold opened up a window of a new family of photochromic materials having extraordinary switching speeds and outstanding stabilities. This leads to evolve into solid-state photonic materials.

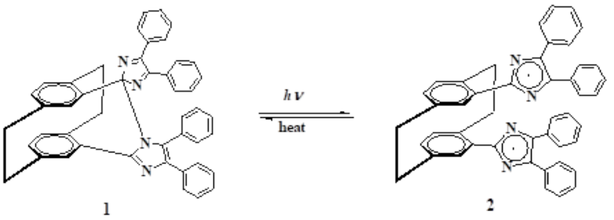

Figure 1. pseudogem-BisDPI[2.2]PC **1** undergoes colour change from colourless (**1**) to blue coloured pseudogem-bisDPIR[2.2]PC (**2**), both in the solid state and solution phase at room temperature.

In order to modify the rate of thermal back reaction Abe and coworker synthesized pseudogem-DPI-PI[2.2]PC (**3**), where there is one phenanthroimidazole group and diphenylimidazole (Figure 2).[10] This makes the colouredintermediate radical to bleach faster than **1** (half-lives of **1** and **3** are 33 ms and 35 µs respectively, at room temperature). Such molecules showing strong photocolouration and rapid thermal bleaching are potential materials for forthcoming fast light modulator application. The structural modification is done in light of Marcus theory. According to this theory the thermal bleaching rate would be accelerate by increasing ΔG^0, which is done by increasing the steric bulk by introducing phenanthroimidazole moiety in the paracyclophane scaffold. The steric repulsion between the phenanthroimidazole group and phenyl rings destabilizes the intermediate biradical pseudogem-DPIR-PIR[2.2]PC **4**. This study reveals that the stability of biradical is an important factor in controlling the thermal beaching rate of the photochromic paracyclophane-bridged imidazole dimer. Compare to other photochromic system, PC-bridged imidazole dimers are potential candidates for diverse molecular design. Also, the thermal decolouration rate is theoretically predictable. This result opened up a gateway of a wide variety of PC-bridged imidazole dimer derivatives by selecting proper aromatic 1,2-diketones.

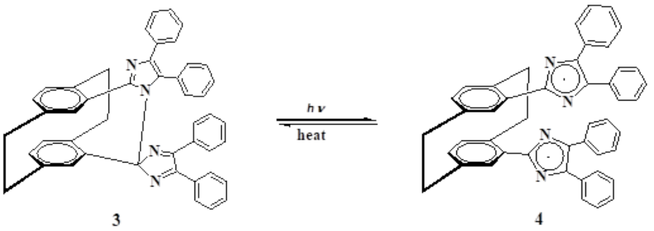

Figure 2. pseudogem-DPI-PI[2.2]PC, **3** undergoes colour change from colourless (**3**) to coloured pseudogem-DPIR-PIR[2.2]PC **4**

The author has outlined an effective approach to develop fast-photochromic molecules with enhanced sensitivity to solar UVA radiation, focusing on [2.2]paracyclophane-bridged imidazole dimers.[11] The photosensitivity of these dimers can be easily heightened by designing the phenyl rings attached to the imidazole rings appropriately. The versatility in molecular design and the simplicity of synthesis makes these photochromic molecules highly appealing for advanced ophthalmic plastic lenses. This study demonstrates that the photosensitivity of [2.2]PC-bridged imidazole dimers, displaying swift colouration upon UV light exposure and rapid fading in darkness (Figure 3), can be adjusted through thoughtful design of the phenyl rings linked to the imidazole rings. The research also reveals the predictability of UV-vis absorption spectra through theoretical calculations. While these molecules hold promise for high-performance ophthalmic plastic lenses and revolutionary optical switching devices, future investigations should prioritize exploring their potential in controlling other properties, such as thermal-bleaching rate and colouring.

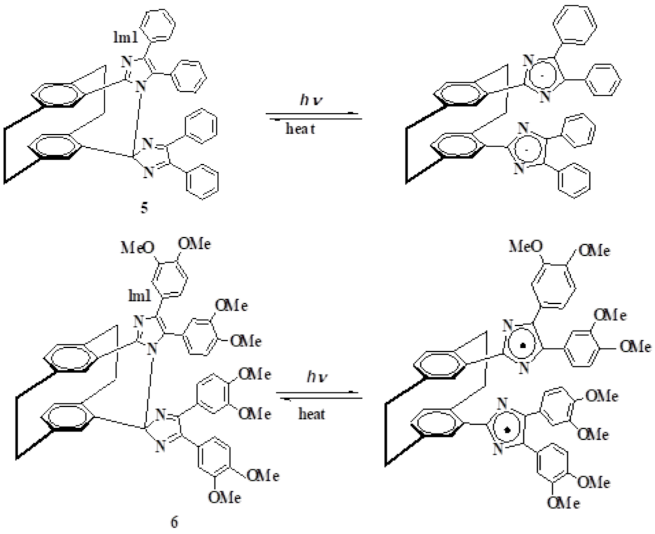

Figure 3. The photosensitivity of [2.2]PC-bridged imidazole dimers, **5** and **6**, displaying swift colouration upon UV light exposure and rapid fading in darkness.

A fast photochromic polymer based on [2.2] paracyclophane scaffold (**7**) is developed by the same author and coworkers in the year 2010, in order to modify the photochromic properties. [12] This molecule **7** is prepared by a stepwise formation of two imidazole rings from benzil and methacrylate-benzil. So, the photochromic controlling unit and polymerisation unit are separately built up into paracyclophane scaffold. Just like the photochromic molecules mentioned above, this molecule **7** also shows rapid photochromism from colourless to blue or green (Figure 4). A characteristics absorption bands around 400 nm and a broad band from 500-1000 nm are observed. The decay also follows first order kinetics and the half-life of intermediate biradicals are 7.2 ms (A) and 52 ms (B). The influence of copolymerisation on the photochromism is studied by varying ratio of different monomers (MMA). The rate of fast photochromism remains almost same in solution state as well as solid film state. This type of molecules is classified into pendant type photochromic polymers. The photochromic behaviour is not affected by the surrounding environment of the photochromes and copolymerisation both in solution and solid film. This photochromic polymer can have application in various photo triggered modules into photo-oriented system.

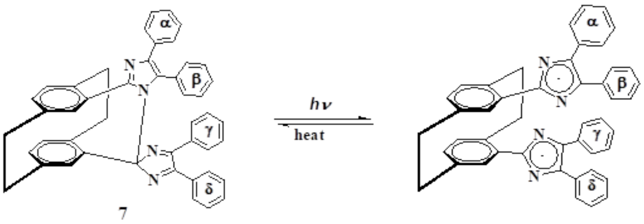

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Figure 4. Molecule **7** shows rapid photochromism from colourless to blue or green.

The growth of first photochromic materials is a major challenge for the photochemistry and material science due to their enormous applications in various field including solar protection lenses, smart windows, and decorative objects. The photosensitivity of photochromic material to solar ultraviolet A (UVA) radiation region is needed to be increased for the application in smart windows and ophthalmic lenses. Another way to increase the photosensitivity to UVA light based on the introduction of larger aromatic group as a sensitizing unit. Abe and coworker introduced a pyrenyl group on the 2 position of the imidazole ring of hexaarylbiimidazole was found to induce the CT-like transition from the frontier molecular orbitals delocalized over the pyrenyl moieties and **8** to the LUMO delocalized mainly in **9** on the basis of the TDDFT calculations (Figure 5).[13] As a result Pseudogem-PPI-DPI[2.2]PC shows an intense absorption band in the UVA light region but Pseudogem-bisDPI[2.2]PC did not. From this study it is concluded that the photochromic properties of HABI derivatives can be enhanced by the introduction of large aromatic group instead of phenyl ring that have higher sensitivity and an absorption band in the longer wave length region. The pyrenyl unit can also influences the dissociation reaction rate by modifying the surface crossing between the attractive potential surface of the locally excited state of pyrenyl moiety and the repulsive potential surface along the C-N bond elongation axis which was already proven with the help of the time-resolved transient absorption spectroscopy and fluorescence measurements. The incorporation of the pyrenyl moiety would affect the spin density distribution and intramolecular radical-radical interaction. Indeed, pseudogem-PPIR-DPIR[2.2]PC absorbs the longer-wavelength light than pseudogem-bisDPIR[2.2]PC. Intramolecular charge transfer from the electron-donating pyrenyl moiety to the 5 pi -electron imidazole ring is responsible for this transition. The introduction of pyrenyl moity can preserve the rapid thermal bleaching characteristic to the [2.2]PC bridge imidazole dimer as a result the thermal bleaching rate of pseudogem-PPIR-DPIR[2.2]PC is larger than that of pseudogem-bisTPIR[2.2]PC (33 ms in benzene at 298K). Because the pyrenyl moiety is also sterically bulky, the concept of the acceleration for the back reaction of the coloured species of pseudogem-DPI-PI[2.2]PC can be applied to that of pseudogem-PPI-DPI[2.2]PC.

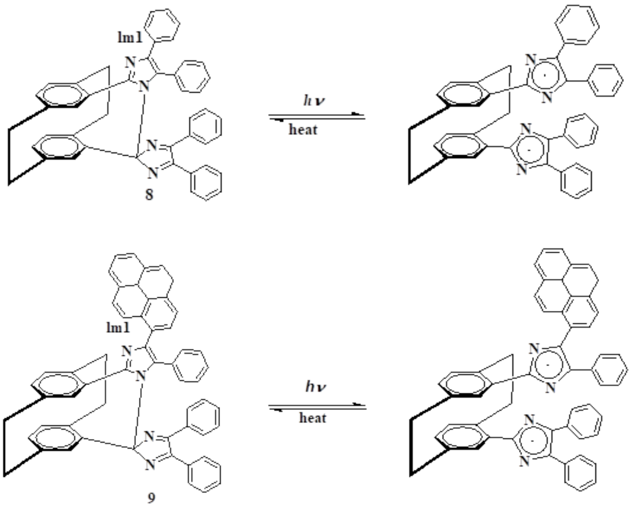

Figure 5. Photochromism of **8** and **9**.

The [2.2]paracyclophane-bridged imidazole dimers with photochromic properties exhibit immediate colouration when exposed to UV light and undergo rapid fading in darkness. This study presents experimental details on enhancing photosensitivity and elucidates the unique photoisomerization of newly designed [2.2]paracyclophane-bridged imidazole dimers (**10** and **12**).[14] The exploration of structure-property relationships reveals an effective strategy for crafting high-performance fast-photochromic molecules with heightened sensitivity to solar UVA radiation. The [2.2]paracyclophane-bridged imidazole dimer comprises two distinct imidazole rings, Im1 and Im2. Im1 possesses a 6π electron system with an electron-donating characteristic, while Im2 features a 4π electron system with an electron-withdrawing characteristic. The incorporation of electron-donating substituents into the phenyl rings attached to the electron-withdrawing Im2 has been proven to augment photosensitivity, facilitated by intramolecular charge transfer transitions. The study delves into the unique photoisomerization arising from alterations in the bonding arrangement between the two imidazole rings. This research underscores the significance of the electronic environment disparity between Im1 and Im2 in controlling the photosensitivity of [2.2]PC-bridged imidazole dimers. Skilful design of the phenyl rings linked to the imidazole rings allows for the enhancement of photosensitivity in the UVA radiation region (Figure 6). The introduction of electron-donating substituents into the phenyl rings connected to the electron-withdrawing Im2 is demonstrated to amplify photosensitivity through intramolecular charge transfer transitions. The diverse molecular design and straightforward synthesis make this category of photochromic molecules exceptionally appealing for revolutionary optical switching devices.

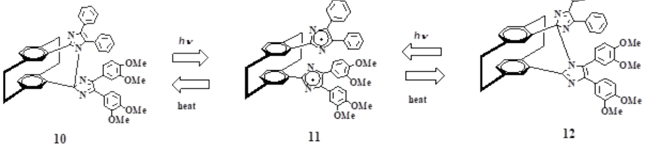

Figure 6. Skilful design of the phenyl rings linked to the imidazole rings allows for the enhancement of photosensitivity in the UVA radiation region.

A unique photochromic organogelator featuring a [2.2]paracyclophane-bridged imidazole dimer unit with four urea arms capable of hydrogen bonding was synthesized (**13** and **14**).[15] When benzene solution of the photochromic organogelator was exposed to UV light, rapid photochromism, transitioning from colourless to green, was observed (Figure 7). Transient vise-NIR absorption measurements revealed a distinctive absorption peak around 400 nm and a broad absorption spanning 500 to 1000 nm, corresponding to the coloured species. The half-life of the coloured species was determined to be 243 ms at 298 K. In cyclohexane, the formation of the organogel was confirmed through SEM observation and IR spectroscopy, displaying swift photochromism even in the gel phase. The author demonstrated that the inherently fast photochromic reactions, involving homolytic photocleavage of the CeN bond of the imidazole dimer unit and recombination between the photogenerated imidazolyl radicals, occurred seamlessly even within the gel phase. It is envisaged that modifying this system could enable the realization of simultaneous morphological and physicochemical control exclusively under light irradiation, paving the way for a novel class of photo-oriented intelligent materials systems.

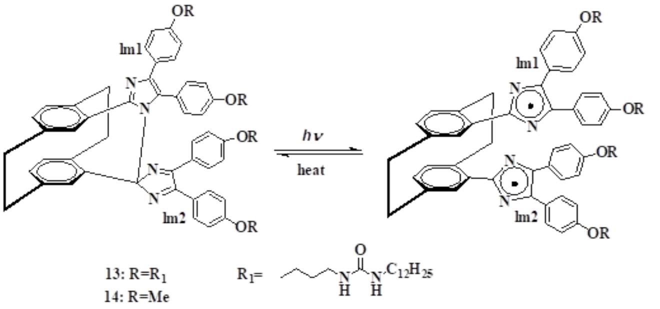

Figure 7. Transitioning from colourless to green of **13** and **14**.

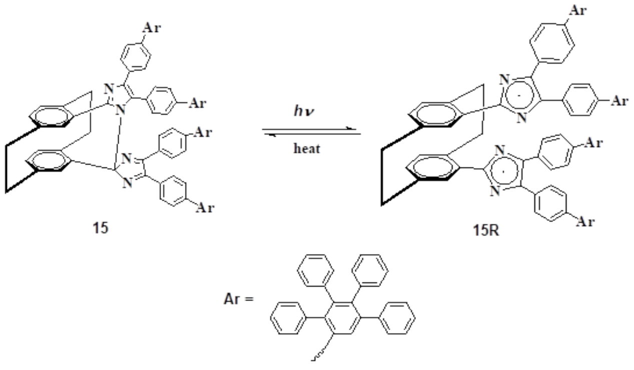

Figure 8. [2.2]paracyclophane-bridged imidazole dimer, having 3′,4′,5′-triphenyl-1,1′:2′,1″-terphenyl substituents, **15**.

A [2.2]paracyclophane-bridged imidazole dimer, featuring 3′,4′,5′-triphenyl-1,1′:2′,1″-terphenyl substituents (**15**), was synthesized and subjected to investigation of its photochromic properties (Figure 8).[16] Upon UV irradiation of the parent imidazole dimer, the coloured species exhibited a short half-life of 1.0 ms at 298 K in benzene. Despite the introduction of bulky substituents, a rapid thermal backreaction akin to other [2.2]paracyclophane-bridged imidazole dimers was observed. The enthalpy and entropy of activation energies ($\Delta H^\ddagger$ and $\Delta S^\ddagger$, respectively) for the thermal back-reaction of this molecule were compared with those of other [2.2]paracyclophane-bridged imidazole dimers. This comparison aimed to explore the general applicability and limitations of the molecular design of photochromic imidazole dimers, elucidating the correlation between substituent bulkiness and the rate constant of the thermal back-reaction. Additionally, a new method for controlling the rate constant of the thermal back-reaction of [2.2]paracyclophane-bridged imidazole dimers was proposed. To delve deeper into the fast photochromism, compound 4, a fast photochromic molecule with bulky substituents on the [2.2]paracyclophane-bridged imidazole dimer, was prepared. Notably, it exhibited a relatively slow thermal back-reaction compared to pseudogem-DPI-PI[2.2]PC at 298 K in benzene.

Thorough investigation of the thermodynamic parameters for the thermal back-reaction of **15**, spanning temperatures from 278 to 313 K, revealed interestingly that the sluggish thermal back-reaction was attributed to a large negative $\Delta S^‡$. The presence of a specific bulky substituent, while typically hindering fast biradical recombination due to steric hindrance, did not significantly alter the activation enthalpy $\Delta H^‡$ for 4 compared to pseudogem-DPI-PI[2.2]PC. Instead, the marked difference in overall free energy $\Delta G^‡$ was attributed to the large negative entropy $\Delta S^‡$ for 4. The study proposed that introducing a substituent with diverse conformations on the [2.2]paracyclophane-bridged imidazole dimer restricts molecular conformations in the transition state, causing entropic unfavorability. Consequently, the rate constant of the thermal back-reaction is decreased, primarily influenced by the activation entropy. In summary, this research demonstrated the potential to control the rate constants of the thermal back-reaction of photochromic [2.2]paracyclophane-bridged imidazole dimer derivatives through enthalpy and/or entropy effects. The systematic control of the thermal back-reaction in thermally reversible photochromic compounds opens avenues for custom-made molecular design.

Abe and coworker synthesized paracyclophane based photochromic polymer film, which exhibits rapid colouration upon UV irradiation and fast thermal bleaching within 10 milli second at room temperature (Figure 9).[17] This molecule (**16**) shows potential application in development of real-time dynamic holographic material. Here the photoinduced changes in diffraction efficiency are caused by the photochemical changes in the paracyclophane based photochromic molecule. The faster bleaching of colour makes this new type of molecule important for designing real time dynamic holographic material and opens up a scope of future development of 3D display.

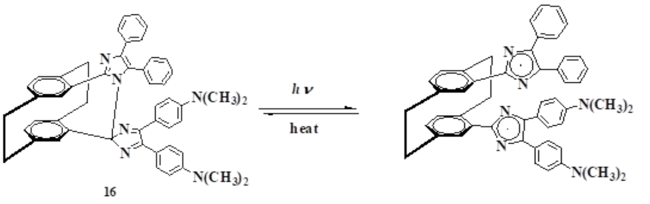

Figure 9. The photochromic behaviour of **16**.

Recently, Abe and colleagues have developed a series of rapid photochromic imidazole dimers featuring a [2.2]paracyclophane (PC) moiety that connects diphenylimidazole units, successfully accelerating the thermal decolouration rate.[18] The colourless [2.2]paracyclophane ([2.2]PC)-bridged imidazole dimers exhibit a photoinduced homolytic bond cleavage of the C−N bond between the imidazole rings upon UV light irradiation, resulting in a pair of coloured imidazolyl radicals. Subsequently, a radical−radical coupling reaction forms the initial C−N bond between the imidazole rings. The decolouration reaction to restore the initial imidazole dimer occurs solely through thermal means. The photochromic reaction boasts a high quantum yield close to unity and a substantial extinction coefficient for the radical, ensuring both a high optical density at the photostationary state and rapid switching speed. The application of these imidazole dimers to rapid fluorescence switching has been explored, aiming to develop a novel type of photochromic fluorescence switching molecule suitable for super-resolution microscopy. The broad absorption spectrum of the coloured radical, spanning from 500 nm to 900 nm, facilitates efficient quenching of the excited electronic state of fluorophores through Förster resonance energy transfer (FRET) from the fluorophores to the radical moiety. A [2.2]paracyclophane-bridged imidazole dimer with a fluorescein moiety as a fluorescence unit was successfully developed. This photochromic dye exhibits swift photochromism, generating a pair of imidazolyl radicals that quench fluorescence from the fluorescent unit via the FRET mechanism. The fluorescence intensity can be rapidly switched through the fast photochromism. The researchers demonstrated fluorescence switching based on the rapid photochromism of the newly designed [2.2]PC-bridged imidazole dimer. The radical moiety effectively quenches the excited electronic state of the fluorescent moiety through FRET, and the intensity quickly recovers within the thermal back reaction of the radical. While quantifying switching efficiency and photochromic reaction yield remains challenging and is an ongoing endeavour involving ultrafast time-resolved techniques, the system's potential in high-resolution fluorescence microscopy, such as dSTORM and SOFI, is evident. Despite the current limitation of a low radical population at room temperature due to the fast thermal back reaction, the combination of a few-millisecond back reaction with photo-switching, even by the fluorophore's excitation, presents significant potential in microscopy techniques like dSTORM and SOFI, where only one laser source is needed to probe and switch the fluorophore in the millisecond dark state, unlike PALM experiments that require two laser sources. Consequently, future developments will likely focus on a more rational molecular design to enhance the photochromic quantum yield for classical fluorescence imaging microscopy, along with the introduction of fatigue-resistant fluorescence units, such as perylene, for achieving high-resolution fluorescence imaging. These innovative systems hold great promise as fast switchable fluorescent probes for light-switching microscopy and high-resolution localization microscopy, shaping the future landscape of such developments.

Abe and his research group have advanced the field by creating a photochromic polymer film tailored for real-time dynamic holography. This film is engineered using a plasticized polymer infused with a swift photochromic molecule. The incorporation of a plasticizer into the conventional polymer has proven effective in enhancing the photochromic performance of the film. This particular fast photochromic molecule induces instantaneous colouration upon exposure to UV light and rapid fading in the dark. The use of plasticized photochromic polymers allows for real-time manipulation of holographic grating, showcasing superior recording sensitivity compared to alternative organic holographic materials. The addition of a plasticizer offers control over the colouration and thermal fade speeds of the photochromic pseudogem-bisTMDPI[2.2]PC within PMMA.[19] This technique, augmenting the sweeping volume for photochromic molecules in polymers, extends beyond fast photochromic compounds and holds applicability for diverse photochromic molecules, contributing to the development of high-performance photochromic materials. Low glass transition temperature (T_g) plasticized polymers, infused with the fast photochromic molecule, emerge as promising candidates for modulating the refractive index and transmittance exclusively within regions exposed to light. The rapid response to light exposure allows for recording and updating interference patterns constructed by reference and object beams. Notably, the photochromic polymer P-8 exhibits heightened recording sensitivity and faster erasing times when compared to other holographic materials. Consequently, this fast photochromic polymer stands as a significant advancement for deployment in real-time dynamic holographic displays. The advent of such photochromic polymers, founded on swift photochromism, marks an exciting direction in the ongoing development of real-time dynamic holographic displays.

[2.2]Paracyclophane bridged imidazole dimers, renowned for their distinctive fast photochromism, hold significant potential for diverse industrial applications. However, for practical implementation, it is imperative to develop various types of imidazole dimers with distinct characteristics such as colour, reaction rate, and sensitivity. Introducing substituents and sensitizers is a common method for modulating the optical properties of these dimers. Yet, estimating the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels via optical spectroscopy poses challenges, particularly due to the optical inactivity of the LUMO in imidazole dimers. In this study, electrochemistry and density functional theory are employed to elucidate the impact of substituents on the electronic states of imidazole dimers. The HOMO and LUMO are found to be localized over only one of the imidazole rings within the dimer.[20] A comparison between the measured LUMO energies of imidazole dimers and the calculated LUMO energies of various visible sensitizers reveals which sensitizers are effective in imidazole dimer systems. These fundamental insights not only enhance our understanding of the electronic structures of imidazole dimers but also offer a strategic approach to designing novel fast photochromic molecules activated by visible light. The energy levels of HOMO and LUMO are demonstrated to be influenced by appropriate substituents on the phenyl rings attached to the imidazole rings, with the theoretically calculated LUMO energies showing a strong correlation with experimentally obtained reduction potentials. The proposal emerges that a visible sensitizer for the photochromic reaction of imidazole dimers can be tailored to have a higher LUMO energy level than the target imidazole dimer. These foundational insights not only provide valuable information for comprehending the electronic structures of [2.2]PC-bridged imidazole dimers but also serve as a guide for molecular design in creating visible sensitizers for imidazole dimer photochromic reactions. Furthermore, they offer a strategic pathway for designing innovative imidazole dimers, initiating photochromism through visible light activation.

The deliberate design of a [2.2]paracyclophane bridged bis(imidazole dimer) **17,** introduces a molecule with two photochromic units that can absorb photons in a stepwise fashion, offering both efficient light harvesting and valuable insights into novel photochemical sciences (Figure 10). Upon absorbing the first photon, a short-lived biradical species is formed, with a half-life of 88 ms at 298 K. Subsequent absorption of an additional photon by this biradical species triggers a photochromic reaction, resulting in the creation of a long-lived quinoid species. The short-lived biradical species and the long-lived quinoid species exhibit distinct absorption spectra and thermal back reaction rates.[21] Importantly, the stepwise two-photon excitation process in this photochromic system can be initiated even by incoherent continuous wave light irradiation, indicating its high efficiency. The [2.2]paracyclophane-bridged bis(imidazole dimer) unit is envisioned to be a promising candidate for multi-photon gated optical materials. Although the photogenerated biradical species (**17BR**) rapidly reverts to its initial colourless form, similar to observations in the [2.2]PC-bridged imidazole dimer, further photochemical reactions lead to the formation of the long-lived coloured species (**17Q**). This highly efficient stepwise two-photon process can be initiated with the incidence of incoherent continuous wave light, as the photochromic reaction of **17** depends on the re-excitation of the reversibly generated biradical species **17BR**. These experiments highlight the potential of the bridged bis(imidazole dimer) as a promising candidate for use as a multi-photon gated optical material, paving the way for the development of new functional photochromic molecules.

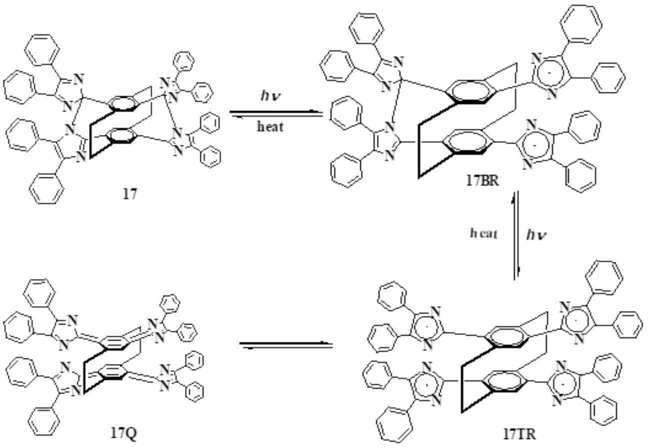

Figure 10. A molecule **17,** with two photochromic units that can absorb photons in a stepwise fashion.

The need for the development of fluorescence switchable molecules in various polar and nonpolar environments has arisen to facilitate fluorescence imaging of nanostructures. A crucial category for achieving reversible light-triggered fluorescence switching is photochromic molecules. Despite numerous studies on fluorescence switching using photochromic reactions, there has been a limited exploration of photochromic molecules displaying reversible turn-on mode fluorescence switching. This study introduces naphthalimide units as a green fluorophore within the context of negative photochromism, wherein the absorption spectrum shifts to a blue wavelength after irradiation compared to the pre-irradiation state (Figure 11).[22] Specifically, these units are incorporated into a binaphthyl-bridged imidazole dimer exhibiting negative photochromic behaviour. In the initial coloured isomer **18** and **19**, the fluorescence of the naphthalimide unit is efficiently quenched (fluorescence quantum yield: $\Phi_{\text{fluo.}} = 0.01$) through Förster resonance energy transfer. However, in the transient isomer formed by the negative photochromic reaction, the fluorescence quantum yield increases to 0.75. The fluorescence intensity decreases upon thermal back reaction, returning to the original stable coloured form. These findings suggest that negative photochromic molecules are well-suited for turn-on mode fluorescence switches, offering valuable insights for the development of reversible fluorescence switching molecules. The absorption band at 500 nm in the stable orange form is ideal for quenching the fluorescence of 4-(N,N′-dimethylamino)-1,8-naphthalimide through Förster resonance energy transfer. Visible light irradiation causes the initial orange form to isomerize into the transient yellow form, eliminating the absorption band at 500 nm and leading to a significant activation of fluorescence from the naphthalimide unit. This negative photochromic switch is compatible with fluorophores emitting at 500 nm, such as fluorescein, rhodamine, Alexa Fluor, and BODIPY derivatives. The fluorescence state thermally reverts to the initial dark state, enabling efficient single-wavelength irradiation for fluorescence intensity switching. This characteristic represents an advantage of thermally reversible photochromic molecules for applications in superresolution fluorescence imaging techniques like PALM and STORM.

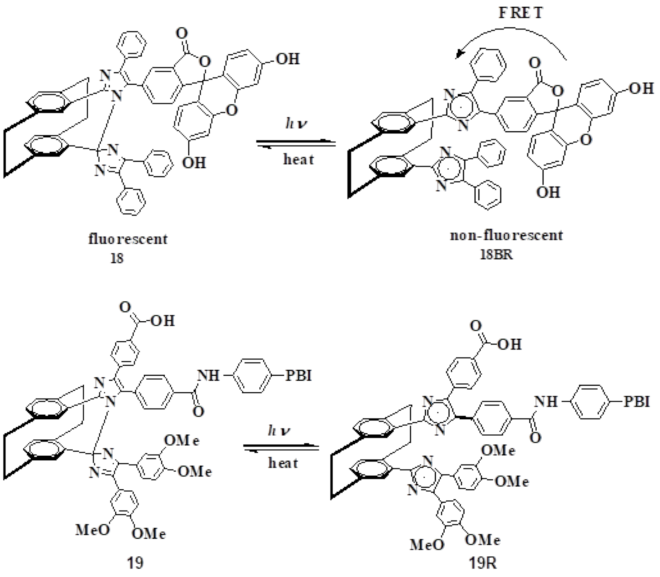

Figure 11. Photochromic reaction scheme of **18** and **19**.

In summary the novel photochromism based on [2.2]paracyclophane is discussed here. A variety of photochromic molecules are designed in order to modify the spectrokinetic properties. It is also shown that how the substituents can influence in the absorption behaviour of the photochromic molecules and affect their stability of coloured intermediates. The 'phane' effect in paracyclophane moiety is the key factor in determining the absorption and stability of the derivatives. These photochromic molecules have tremendous applications in different fields such as in eye wear technology, data storage devices, smart optics, etc. There are huge future scopes in designing a variety of derivatives based on [2.2]paracyclophane scaffold and their applications in areas like photochromic material, sensor, asymmetric organocatalyst, solar cell, light emitting devices, chiroptical material, etc.

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