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STUDIES ON THE SOLID STATE PHOTOCHROMIC PROPERTIES OF A FULGIDE MIXED CRYSTAL

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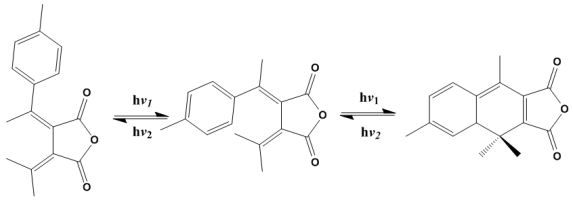
Photochromism is a reversible transformation between two isomers having different absorption spectra by photoirradiation. Photochromic compounds such as fulgides (bis[methylene]succinic anhydrides) have gained interest recently due to their potential applications in optical electronic devices such as optical memories and optical switches. Even though several photochromic compounds have been synthesized, it is very rare to find their photochromic properties in the crystalline state.



Scheme 01: Photochromic reaction of a fulgide

In this study (*E*)-p-methylacetophenylisopropylidenesuccinic anhydride (**1A**) and (*E*)-p-chloroacetophenylisopropylidenesuccinic anhydride (**1B**) were newly synthesized using Stobbe condensation method and they were used to obtain a photochromic mixed crystal (**MIX**) composed of these two fulgides using a simple solvent evaporation co-crystallization technique. Mixed crystal formation was confirmed usingSingle Crystal X-ray diffraction method by analyzing crystal structures for **1A, 1B** and **MIX**. Melting points of **MIX**, **1A** and **1B** are 134-136 ^{0}C, 156-158 ^{0}C and 136-138 ^{0}C respectively. λ_{max} values of solid state UV-Visible spectra of **MIX**, **1A** and **1B** are 536.0 nm, 516.5 nm and 547.5 nm respectively. Fatigue resistance of **1A**, **1B** and **MIX** was studied using solid state UV-Visible spectroscopyand theirthermal stability was qualitatively studied. Fatigue resistance of **1A**, **1B** and **MIX** was studied using solid state UV-Visible spectroscopyand theirthermal stability was qualitatively studied.

Photochromism of three crystals was observed by irradiating with 365nm UV light. Upon irradiation, yellow colour crystals of **1A**, **1B** and **MIX** turned to pink, orange and dark pink colours respectively by forming closed-ring isomer in the crystalline phase. The colour was reversed to the initial state while irradiating with visible light (λ>450nm). Higher fatigue resistance and higher thermal stability were observed for the mixed crystal compared to the other two pure compounds. This behaviour can be explained by considering their respective crystal structures. It was found that two carbon atoms involving in the cyclization reaction to form C-form of fulgide, are closer in distance to each other in **MIX** (3.344 Å) than in pure fulgides **1A** (3.375 Å), **1B** (3.380 Å). Therefore photo colouration and photo bleaching can easily be achieved with minimum atomic movements in the solid state.

Thus, it was possible to enhance the photochromic properties of **1A** and **1B**along with different colours by forming mixed crystals.

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