

Abstract

Index No: 195/18/Chem./26

Thesis title: “Synthesis and Photophysical Properties of Ferrocene and Dithienylethene Based Multi-responsive Organic Materials.”

The main aim of the research work is to synthesize photochromic dithienylethene (DTE) and redox active ferrocene based molecules, describing their photophysical and electrochemical properties and to study their various applications in material science. In order to accomplish this goal, a variety of photochromic molecules based on DTE have been designed and successfully synthesised by using several types of organic transformations. In every instance, the reactive position of the photoswitching DTE unit is connected either by redox active ferrocene molecules or by a wide variety of fluorophore molecules, such as quinoline, coumarin, naphthalimide, and so on. The structural architecture has been designed in such a way that their properties of isomerization process can be regulated in presence of light as a stimulus to make them an excellent candidate as an efficient photoswitch.

In **first work**, A C₂-symmetric photochromic molecule, containing dithienylethene (DTE) and ferrocene unit, represents the first probe where a metal (Hg²⁺) binds with the central DTE moiety. Remarkably, the inherent photo-isomerization property of DTE core remains unperturbed upon Hg²⁺ coordination, however with slower kinetics. The dynamic metal coordination between photoisomerized states was confirmed by experimental as well as quantum chemical calculations. Further, we have designed another ferrocene appended dithienylethene (DTE-Fc) in **second work**. The ferrocene appended dithienylethene (DTE-Fc) is highly π -conjugated photochromic material which displayed high photoreaction quantum yield and fatigue resistance property. It is a unique example of a “turn-on” mode fluorescent DAE without a traditionally known fluorophore or S,S-dioxide moiety. Furthermore, DTE-Fc is proven to be highly efficient in lithographic technique (erasable ink) and deciphering secret (QR/ Bar) codes. However, the extended conjugation at the reactive position of DTE restricts its optimum capability to show fast photoswitching. Therefore, to obtain good photoswitching speed, further development of photochromic fluorescent molecule was performed keeping the connection of DTE and fluorophore in a non-conjugated manner. In **third work**, demonstrated

DTE exhibits fluorescence photoswitching performance in solution, solid state, as well as in gel form through FRET mechanism. Taking advantage of high fluorescence photoswitching performance in solution as well as in solid state along with AIE, the developed DTE based material was applied in latent fingerprints (LFPs) and in anti-counterfeiting technology.

The work described in the 5th Chapter of thesis does not include any photochromic organic molecules and their specific applications in security technology (photochromic ink or photo-erasable writing of confidential information, light triggered generation of QR/bar code, latent fingerprint generator, and so on), rather, it is comprised of ferrocene and two fluorophores (quinoline and coumarin) and applied in cascaded molecular logic gates. In this work, a novel differentially selective electrochemical and fluorescent chemosensor, based on a ferrocene-appended coumarin-quinoline platform has been designed and synthesized. The probe is very specific toward Fe^{3+} via a reversible redox process, whereas it detects Cu^{2+} via irreversible oxidation. Interestingly, it exhibits differential affinity toward the Cu^+ ion via complexation. HRMS, ^1H NMR titration, and IR spectral studies revealed the formation of a bidentate Cu^+ complex involving an O atom of the amide group attached to the quinoline ring and a N atom of imine unit, and this observation was further supported by quantum-chemical calculations. Upon the addition of Fe^{3+} and Cu^{2+} ions, the fluorescence emission of the probe shows a “turn-on” signal due to inhibition of the photoinduced electron transfer (PET) process. The addition of sodium L-ascorbate (LAS) as a reducing agent causes fluorescence “turn off” for the Fe^{3+} ion but not for the Cu^{2+} ion because it oxidizes the ferrocene unit to a ferrocenium ion with its concomitant reduction to Cu^+ , which further complexes with the probe. A unique combination of Fe^{3+} , LAS, and Cu^{2+} ions has been used to produce a molecular system demonstrating combinational “AND-OR” logic operation.

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