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## High-contrast fluorescence switching using a photoresponsive dithienylethene coordination compound

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## ABSTRACT

A novel hybrid system (**Zn4**) containing a zinc bis(acylamidine) fluorescent dye covalently decorated with two photochromic dithienylethene (DTE) structures was prepared using a concise synthetic route. The photoregulated quenching of the fluorescence from the metal complex was achieved by reversibly switching the DTE component between its two isomers using UV and visible light. The fluorescence quenching can be attributed to intramolecular energy transfer, electron transfer or a combination of the two. Either process is only possible when the DTE is in its ring-closed form (**Zn4b**). The ring-open counterpart (**Zn4a**) lacks an absorption band in the visible region of the spectrum to accommodate energy transfer from the metallobis(acylamidine) to the photochromic DTE, and has an oxidation potential that is too large to match the reduction potential of the metal complex making electron transfer thermodynamically unfavourable. UV–vis absorption and emission spectroscopy demonstrated that the photoregulation of fluorescence has little effect on the photochromic process and the fluorescence could be turned “on” and “off” several times without the appearance of notable side products. The high contrast ratio (~100:1) between the bright and dark states combined with the excellent thermal bistability make the hybrid an excellent candidate for potential use in non-destructive read-out and biological labeling applications, although several limitations need to be overcome (speed of photoswitching, and stability and solubility in water).

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### 1. Introduction

Regulating fluorescence intensity is one of the most attractive uses for molecular photoswitches because of the high sensitivity, resolution, contrast and the fast response times provided by fluorescence technology. Introducing control mechanisms into fluorescence systems would, therefore, offer a convenient means to modulate this versatile optical property. The reversible cyclization reaction of the dithienylethene (DTE) architecture (Scheme 1) has attracted special attention from both fundamental and practical points of view owing to many beneficial properties [1,2]. UV and visible light can be used to toggle the basic structure back and forth (often with a high level of fatigue resistance) between two isomers, each having unique optical and electronic properties. The molecular backbone can be decorated with a wide range of modifying groups to fine-tune the optoelectronic properties of both isomers. This last feature is critical for effective regulation of fluorescence as should be obvious after reading this report.

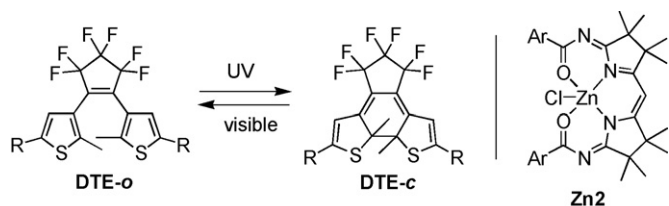
One application in which it would be useful to photoregulate fluorescence with DTEs is non-destructive data storage where the bright and dark states can be used to code binary information [3–8]. A fluorescent read-out signal offers high sensitivity (often down to the single molecule) and because excitation requires a small number of photons, few side effects are induced to spoil the digitalized signals [9,10].

Biological fluorescence labeling is another setting where regulating fluorescence can be potentially useful. Tracking of particular cell components and events will be facilitated by turning the fluorescent probe “on” and “off” on command [11]. For this application, reversibility and high contrast are critical aspects that must be satisfied. In a related application, better resolution in far-field confocal microscopy can be achieved with spatial resolution below the diffraction limit when photoresponsive DTE derivatives are used [12].

Typically, compounds based on the dithienylethene architecture tend to show very weak fluorescence and are not practical for applications that rely on modulating this optical property. The lack of intense fluorescence has been ascribed to the free rotation around the C–C bonds joining the two thiophene heterocycles to the central cyclopentene ring, which increase the rate of radiationless decay of the excited state [13–16]. Decorating

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**Scheme 1.** The reversible cyclization reaction of the dithienylethene architecture between its ring-open (**DTE-o**) and ring-closed (**DTE-c**) isomers using UV and visible light, and the highly fluorescent generalized zinc bis(acylamidine) structure **Zn2** used as the fluorescent dye in these studies.

the DTE backbone with a strongly fluorescent molecule overcomes this problem and has been the focus of several studies in which the intensity of emitted light is regulated by converting the DTE between its two isomers. Examples include molecular dyads (DTE–anthracene [17], DTE–diphenylbenzene [18], DTE–oligothiophene [19]), triads (DTE–anthracene–DTE, [20] oligothiophene–DTE–oligothiophene [7,21], porphyrin–DTE–porphyrin [3,4], and BODIPY–DTE–BODIPY [22]) and systems that combine several DTE components with a porphyrin macrocycle [23]. Although significant work has been done to improve the fluorescence quenching efficiency, many examples are restricted by the low fluorescence contrast ratios between the bright and dark states. This report describes the synthesis of a bistable fluorescent photochromic system (**Zn4a**) with a high fluorescence contrast ratio by covalently joining a highly fluorescent zinc bis(acylamidine) dye and two photoresponsive DTE compounds. The two components that make up the hybrid structure were chosen based on their complementary optical properties. As will be clearly demonstrated, the absorbance of only one isomer of the DTE backbone overlaps with the emission band of the metallobis(acylamidine) allowing effective energy transfer from the excited state of the dye to the photochromic component. This is a situation necessary for regulating the emission by toggling the DTE between a quenching and non-quenching isomer. Although the system was designed to harness energy transfer

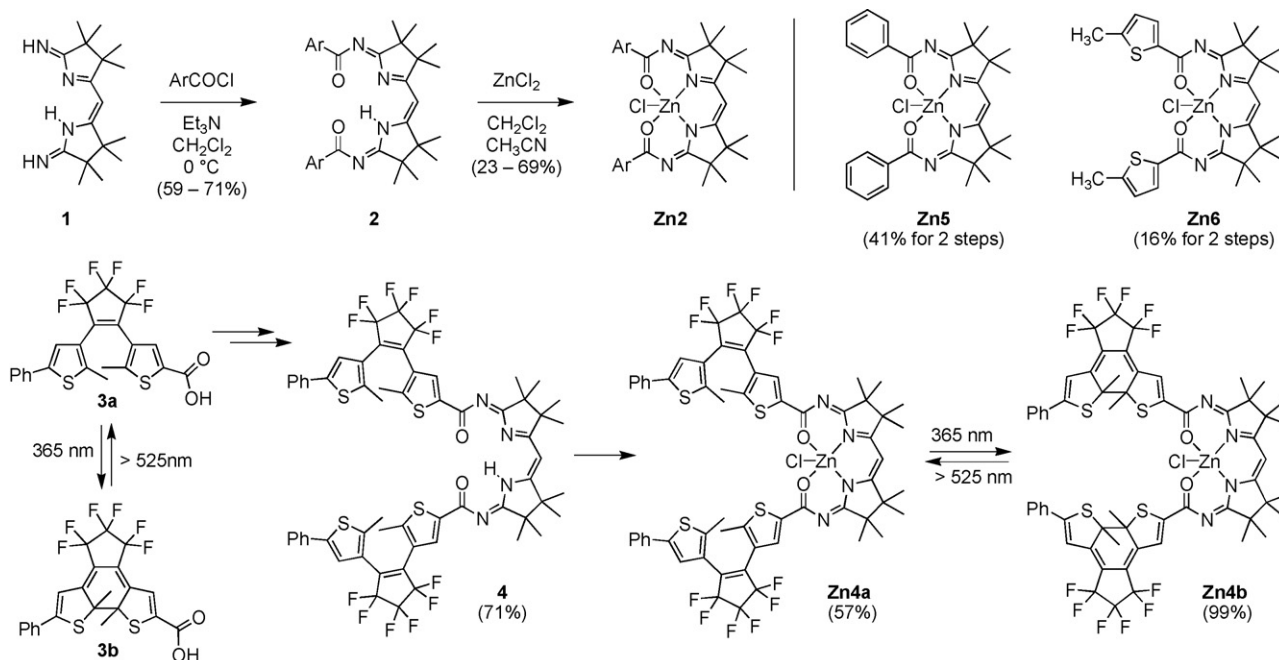
as the quenching mechanism, the possibility of electron transfer should not be excluded as will be discussed in this report. Another critical feature for an effective system is a clear separation of the absorption bands of the two DTE isomers and the fluorescence dye so that each component can be excited without affecting the others. This is also satisfied with hybrid compound **Zn4**.

## 2. Results and discussion

### 2.1. Synthesis of bis(DTE), bis(phenyl) and bis(thienyl) coordination compounds **Zn4a**, **Zn5** and **Zn6**

**Scheme 2** shows how all the compounds described in this paper are prepared. In all cases, the key component is the bis(acylamidine) **1**, [24] which can be coupled to aromatic carboxylic acid chlorides to afford the generalized bis(acylated) structure **2**. Metal insertion to produce the neutral zinc complex **Zn2** is achieved by treating ligand **2** with  $\text{ZnCl}_2$  in the presence of base [25]. These two synthetic steps are used to prepare the photoresponsive coordination compound **Zn4a** (from the acid chloride of DTE **3**, [26] as well as the non-photoactive compounds **Zn5** (from benzoyl chloride) and **Zn6** (from the acid chloride of 5-methyl-thiophene-2-carboxylic acid), which are used for comparative purposes. The preferred method to purify coordination compounds **Zn4a**, **Zn5** and **Zn6** is by recrystallization. Column chromatography is not appropriate because the imines are easily hydrolysed during purification. All new compounds have been characterized by means of  $^1\text{H}$  and  $^{13}\text{C}$  NMR, FT-IR, UV–vis spectroscopy, mass spectrometry and elemental analysis, and the results are consistent with the structures illustrated in **Scheme 2**.

Care must be taken when treating the metallobis(acylamidine) in subsequent studies. Although they all show high stability when dissolved in  $\text{CH}_2\text{Cl}_2$ , they do not exhibit equivalent stability in other solvents such as  $\text{CH}_3\text{CN}$  and EtOH even when stored in the dark. New bands are observed in both the UV–vis absorption and  $^1\text{H}$  NMR spectra, [27] changes that are not observed for equivalent  $\text{CH}_2\text{Cl}_2$  solutions of **Zn4a** or **Zn5** or for the equivalent free-base ligands. The structures produced in these solutions have yet to be isolated and characterized.



**Scheme 2.** Synthesis and photoreactions of the compounds reported in this paper.

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