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Synthesis and photochromic properties of triazole-bridged dithienylethene compounds with pyrene units

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ABSTRACT

Three new triazole-bridged dithienylethene compounds with pyrene or benzene units were synthesized using the azide alkyne Huisgen cycloaddition reaction. Their structures were well characterized by NMR spectroscopy and mass spectrometry. UV/Vis absorption spectra and fluorescence spectra indicated that these dithienylethene compounds displayed obvious photochromism and fluorescent switch properties. The open-ring isomer of compound **1** with two pyrene subunits showed intramolecular pyrene excimer fluorescence which arises from intramolecular association of two pyrene units, in contrast to compound **2** with one pyrene subunit.

Photochromism refers to a reversible change in the properties of a molecule in response to light. Among the various photochromic compounds, dithienylethenes are gaining increasing attention in the field of photoelectronics, such as optical memory media and photo-switching devices, due to their high thermal stability, excellent fatigue resistance, and characteristic bistability.[1] A current key process is the development of novel backbones with reversible photochemical isomerization and entirely different properties for respective isomeric forms. An effective method used in this process is modulation of the structure of the group R in Figure 1.[2]

Excimer fluorescence forms the basis of many analytical probes and can also be used to monitor close interactions between aromatic units.[3] The most popular fluorophore is pyrene, and innumerable examples of inter- and intramolecular excimer formation involving pyrene residues have been reported.[4] In particular, intramolecular excimer fluorescence is a strong indicator of the spatial proximity of the relevant subunits given that such emission occurs solely from folded rotamers.[5]

In the present study, triazole-bridged dithienylethene compounds with pyrene or benzene units **1**–**3** were synthesized via the azide alkyne Huisgen cycloaddition reaction. These dithienylethene compounds displayed obvious photochromism and fluorescent switch properties. The open-ring isomer of compound **1** with two pyrene subunits showed intramolecular pyrene excimer fluorescence which arises from intramolecular association of two pyrene units, in contrast to compound **2** with one pyrene subunit.

The backbone of dithienylethene was synthesized via the McMurry coupling reaction using previously reported methods.[6] Compounds **1**–**3** were synthesized via the azide alkyne Huisgen cycloaddition reaction which is also called the click reaction (Scheme 1). It requires simple reaction conditions including readily available starting materials and reagents, no solvent or the use of a solvent that is benign or easily removed (preferably water), and provides simple product isolation by non-chromatographic methods (crystallization or distillation). All the target compounds were characterized by standard analytical techniques, such as NMR and mass spectrometry.

The photochromic behavior of dithienylethenes **1**–**3** induced by photoirradiation in CH_2Cl_2 was measured at room temperature. The photochromic behavior of **1**, **2,** and **3** in different solvents was shown in Figure S1. Reversible photoisomerizations between **1o**–**3o** (open-ring isomer) and **1c**–**3c** (closed-ring isomer) of dithienylethenes were demonstrated by alternating between irradiation with UV light ($\lambda = 302$ nm) and visible light ($\lambda > 402$ nm), as illustrated in Figure 2. As shown in Figure 3A, the absorption maximum of compound **1** in CH_2Cl_2 was observed

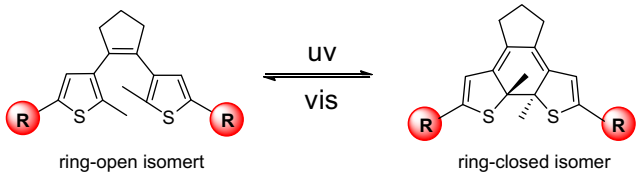

Figure 1. Ring-opening and ring-closing photoisomerization of dithienylethenes.

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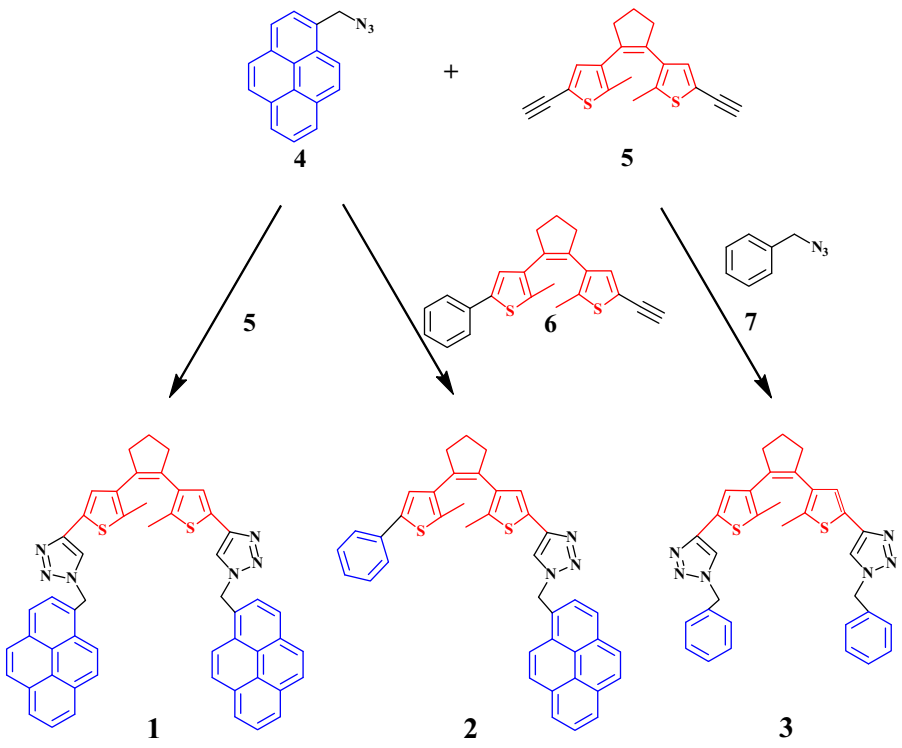

Scheme 1. Synthesis of dithienylethenes **1**–**3**. Regents and conditions: vitamin C, solution of copper sulfate, tert-butyl alcohol–water, reflux.

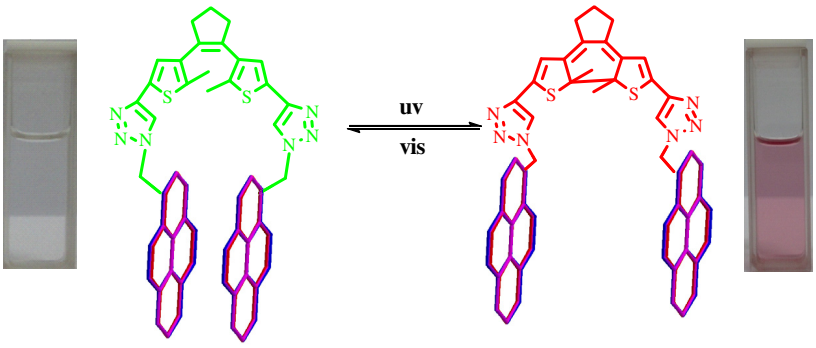

Figure 2. Photochromism and photograph of the color of compound **1** in CH_2Cl_2 (2.0×10^{-5} mol/L).

at 272 nm ($\varepsilon = 8.2 \times 10^4$ L mol^{-1} cm^{-1}) and 342 nm ($\varepsilon = 5.8 \times 10^4$ L mol^{-1} cm^{-1}) as a result of a π–π* transition.[7] The photostationary state was attained by irradiation with 302 nm light. This colorless solution turned pink and a new absorption band centered at 510 nm ($\varepsilon = 0.98 \times 10^4$ L mol^{-1} cm^{-1}) appeared. Due to π-electrons delocalizing and extending to the two thiophene rings, the absorption of the open-ring isomer at a shorter wavelength decreased gradually and the absorption of the closed-ring isomer at a longer wavelength increased gradually, which is in agreement with a previous report.[8] On irradiation with visible light ($\lambda > 402$ nm), the colored **1c** underwent a cycloreversion reaction to the initial colorless open-ring isomer **1o**. Simultaneously, the photochromic process demonstrated by **1** has been characterized by means of NMR spectrometry (see Supporting Information: Fig. S2). In the open-ring state, compound **1** showed signals at 1.75 (methyl-H) and 6.90 (thiophene–H) ppm. When the $CDCl_3$ solution of **1** underwent UV light irradiation and achieved a photostationary state, the CH_3–H and thiophene–H showed the 0.04 and 0.35 ppm downfield shifts, respectively, as a result of the changes of structural configuration between the two isomers. Furthermore, from the integrated area of the thiophene–H signals, the photocyclization yield was calculated to be 33%.[1n] Similar ^{1}H NMR spectral changes were also observed for solutions of **2** and **3** (Fig. S2). As shown in Figure 3B and C, compounds **2** and **3** showed excellent photochromic properties similar to that of compound **1**. The absorption characteristics and the photochromic quantum yields of the open-ring (φ_{o-c}) and closed-ring isomers (φ_{c-o}) of the compounds are summarized in Table 1.

The fluorescence change in dithienylethenes **1** and **2** induced by photoirradiation in CH_2Cl_2 was investigated at room temperature. As shown in Figure 4A and D, the emission of monomer (I_M) at 395 nm, and emission of the excimer at 475 nm (I_E) were observed in compound **1**, respectively. The value of I_E/I_M for compound **1** was 1.50. The open-ring isomer of compound **1** showed intramolecular pyrene excimer fluorescence which arises from intramolecular association of two pyrene units. These observations suggest the spatial proximity of two pyrenes in the open-ring isomer of compound **1**, and the presence of the facing π–π stacking of