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Azole-based diarylethenes as the next step towards advanced photochromic materials

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ABSTRACT

For a long time, starting from pioneering works of M. Irie in the late 80 s and early 90 s of the last century, photochromic diarylethenes were primarily associated with dithienylethenes – diarylethenes possessing thiophene groups. However, about 10 years ago, azole heterocycles (thiazole, oxazole, imidazole) started to be used as aryl moieties instead of common thiophenes, which contributed significantly to the development of diarylethene-based photochromes. In this review, we analyzed in detail the effects of substituting traditional thiophenes in diarylethenes by azoles and revealed amazing examples of functional molecules, materials, and devices based on azole-containing photochromic molecules.

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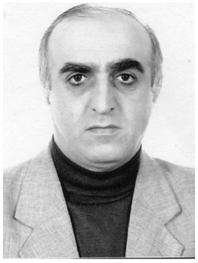
Marat M. Khusniyarov graduated from the Novosibirsk State University (Russian Federation) in 2002. He obtained his PhD in the group of Prof. Jörg Sundermeyer, Philipps-Universität Marburg (Germany), in 2006. As a postdoc, he joined the group of Prof. Karl Wieghardt at the Max Planck Institute for Bioinorganic Chemistry (Germany). In 2009, he was awarded a prestigious Liebig Fellowship and established an independent junior research group at the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU, Germany). Here, he accomplished his Habilitation mentored by Prof. Karsten Meyer in 2016. Since 2016, he is teaching as a Privatdozent and continue to lead his independent research group at the FAU. His research interests include photoactive and magnetic materials, molecular switches and sensors, molecular magnetism, applied spectroscopy, and theoretical calculations.

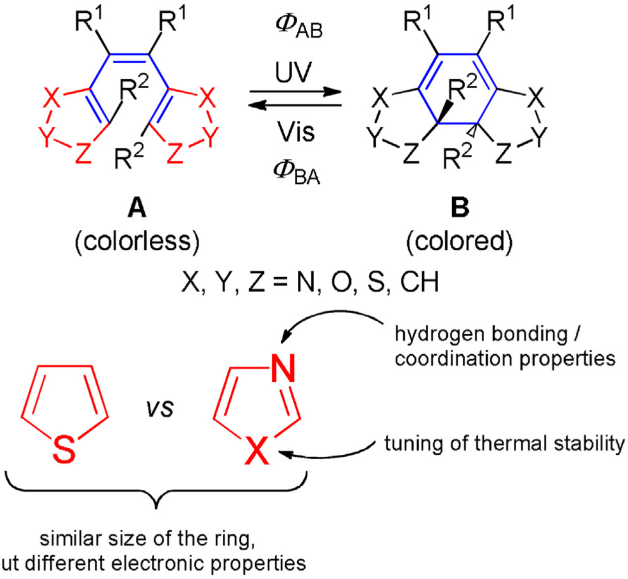


Valerii Z. Shirinian. Currently he is leading researcher at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences with expertise in Organic Chemistry, Photochemistry and Organic Synthesis; he received his PhD in Organic Chemistry (1992) and Doctor of Sciences in Chemistry (2010). His research focused on design and syntheses of novel functional photoactive compounds and dyes (diarylethenes, spiropyrans, spirooxazines and merocyanines), as well as spectral properties study of photosensitive compounds for memories and switches.

1. Introduction

Photochromism is the phenomenon of the reversible isomerization of molecules under the action of light. Photochromic diarylethenes (DAE's) with heterocyclic moieties show high thermal stability of photoinduced form, high resistance to fatigue, reversible switching in solution and in the solid state, and a large rearrangement of electronic distribution upon photoisomerization (Scheme 1) [1]. Due to these prominent photophysical properties, DAE's are the subject of extensive research aiming, for instance, the development of unprecedented photon-controlled functional materials/devices and realization of novel light-controlled processes [2]. Various applications of DAE's include the development of elements for organic electronics [3] and photocontrollable sensors [4], control of optical [5], magnetic [6], and fluorescence [7] properties of transition metal complexes, photoswitchable nanosystems.[8] DAE's are actively used in such emerging areas as spatiotemporal control of biological systems[9] and chemical reactions [10] as well as in photopharmacology [11].

Since the discovery of this class of photochromes by M. Irie in 1988 [12], thiophene derivatives were primarily used as aromatic moieties, which provided high thermal stability of photoinduced isomers. Although during the first 15 years after the discovery, some works dealing with DAE's featuring azole moieties (thiazole, oxazole, imidazole) appeared [13], crucial effects of these moieties on photochromic properties were not recognized. Only during the last 10–15 years, a number of works were published, where a great potential of azole derivatives has been revealed. Replacement of thiophenes by azoles in a number of cases significantly changed the properties of an initial open form **A** and a photoinduced form **B** due to particular electronic effects and non-covalent interactions (Scheme 1). On the other hand, due to their excellent photochemical properties, azole-containing DAE's became frequently used for the development of functional molecules, materials, and devices. Finally, on the basis of azole derivatives, irreversible photoinduced transformations were discovered, which opened new perspectives for preparative organic photochemistry.



Scheme 1. Photochromism of diarylethenes.

This paper is not a comprehensive review on azole-containing DAE's [14]. Our goal is to bring together highlights on azole-based DAE's and to demonstrate how these photochromes contributed to a significant expansion of the research field during the recent years.

2. Enhancement of photochromic performance

2.1. Spectral properties

Azoles (thiazole, oxazole, imidazole) strongly differ both from the thiophene and from each other in their electronic properties. For this reason, the introduction of various heterocycles allows the modulation of spectral properties of DAE's. This can be demonstrated by a series of symmetric DAE's with a perfluorocyclopentene bridge elaborated by M. Irie and coworkers (Fig. 1). In the series of DAE's with normal (β-substituted thiophene and 4-substituted azoles) heterocycles (**1** [15] **2** 13c] **3** [16]), the replacement of thiophenes with thiazoles or oxazoles leads to a strong hypsochromic shift of the absorption maxima of photoinduced isomers **B** (575, 525, and 462 nm, respectively). A similar pattern was observed for DAE's bearing inverse (α-substituted thiophene and 5-substituted azoles) moieties (**4** [17] **5** [13c] **6** [18]). In the case of inverse oxazoles, the absorption maxima become hypsochromically shifted into the UV region (353 nm). In addition to the unique "invisible" and negative photochromism, **6** differs from all other analogues by strong fluorescence of the initial isomer ($\Phi^{fl} = 19\%$), while the photocyclization leads to a decrease of emission intensity.

The strong dependence of spectral characteristics of DAE's on heterocycles was used to control the properties of functional photochromic materials. Thus, the use of thiophene and various azoles allowed to develop multicolor switchable mixed crystals (see section 3.1), and a mixed polymer consisting of monomers **7**–**9**, which can be painted in different colors (cyan, magenta, yellow, and their combinations) (Fig. 2) [19].