



Review

Power of light – Functional complexes based on azobenzene molecules



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ABSTRACT

A significant amount of academic and industrial research efforts is devoted to design, synthesis and to investigate the important determinants of stabilizing/destabilizing photo-sensitive based complexes capable of undergoing repeated light-triggered conformation changes. In this review, we provide the readers with a deep and comprehensive knowledge concerning complexes formed with azobenzene molecules as the light-sensitive ligands. Azobenzene, reported for the first time 83 years ago, has been used as a photochromic unit in numerous complex structures and has played a key role in thousands of scientific publications. However, this review focuses on a representative group of palladium, zinc, iron, nickel, and copper complexes which have had noteworthy influence on breakthrough ideas and society. Particularly, in this review we show that the azobenzene-metal complexes demonstrated to be effective for DNA cleavage, they have formed the most significant part of molecular machines and they have been applied in catalysis, molecular biology, and medicine, as well as they have been used as chemosensors.

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1. Introduction

The development of functional materials has become an intensive area of research in recent years [1]. They have been designed for creation of “smart chemical systems”, whose functionality and/or properties are sensitive to external stimuli such as: heat, cation

addition, pH change, pressure, or light [2–4]. Light represents perhaps the most attractive external stimulus because in contrast to chemicals, which are used for regulating biological processes, photons do not cause contamination of the studied object and have low or negligible toxicity. Furthermore, light can be delivered with very high spatial and temporal precision, which is of importance for controlling the action of bioactive compounds. Moreover, light can be regulated in qualitative and quantitative manner by adjusting wavelength and intensity, respectively [5,6]. The development

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of such high-tech materials encouraged the growth of light-triggered chemical switches [7]. Furthermore, light activation has potential in photodynamic therapy, photothermal therapy, radiotherapy, protected delivery of bioactive moieties, anticancer drug delivery systems, and theragnostic (i.e., real-time monitoring and tracking combined with a therapeutic action to different diseases sites and organs) [8]. Admitting the importance and versatility of transition metal complexes, smart photo-responsive examples remain rather uncharted in comparison with the considerable number of well-known photo-sensitive organic switches [9,10]. In principle, photo-responsive metal complexes can be obtained by incorporation of organic photochromic units in the structure of their ligands [11]. These photo-sensitive ligands, rather than acting as typical spacers that change the properties of their complexes, transform them into dynamic smart entities able to provide a functional response to the external stimuli [12].

In the first part of this review, we discuss the photoisomerization processes of azobenzene molecules, as organic photochromic units, while in the second part we describe selected examples of palladium, zinc, iron, nickel, and copper complexes containing the UV-sensitive moieties in their structures. In this review, we focused particularly on these complexes due to their significant multidisciplinary uses and an important potential in real-life applications in: medicine, biotechnology, catalysis, and organic chemistry synthesis.

2. Azobenzene

Azobenzene, reported for the first time in 1834 by Prof. Mitscherlich [13], is probably the most frequently used photochromic unit for a construction of photo-triggered compounds. In 1856 azobenzene was investigated by Alfred Nobel as “yellowish-red crystalline flakes” [14], and since 1937, when Prof. Hartley [15] published an investigation concerning the influence of light on the configuration of N=N double bonds of azobenzene, the molecule has been widely studied experimentally and theoretically, both in fundamental and applied research areas [16–20]. At the basis of the functional behavior of azobenzene is the reversible *trans* (E)→*cis* (Z) isomerization of the N=N bond upon photo-excitation. The absorption spectrum of azobenzene has then long attracted attention. Its low-energy part displays two bands, a weak band in the visible region (~420–440 nm) associated with excitation of the formally dipole-forbidden $^1B_{2g}(n\pi^*)$ state and a strong band in the ultraviolet region (~316–320 nm) associated with absorption of the dipole-allowed $^1B_{1u}(\pi\pi^*)$ state [21,22].

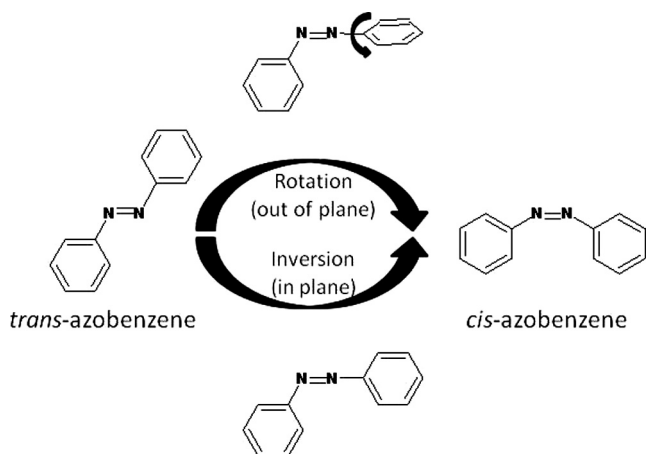


Fig. 1. Mechanisms of azobenzene *trans-cis* photo-isomerization.

Theoretically, isomerization in azobenzene can take place along two different pathways: one that involves torsional motion around the N=N double bond, and another in which in-plane inversion about one of the nitrogen centers takes place (Fig. 1) [23]. By use of quantum chemical methods has been calculated that *trans* isomer ~ 12 kcal·mol⁻¹ is more stable than the *cis* one [24]. The energy barrier of the photo-excited state is ~ 23 kcal·mol⁻¹, therefore the *trans* isomer predominates in darkness at room temperature. The *trans* form effortlessly isomerizes to the *cis* form by irradiation of the *trans* form of azobenzene with UV light (λ 320–365 nm). The isomerization is reversible and the *trans* isomer is recovered by exposure of the *cis* isomer to blue light with a wavelength range of 400–450 nm, or heated. For many azobenzenes, the two photochemical conversions occur on the scale of picoseconds; however, it has been reported the thermal relaxation of the *cis* isomer to the *trans* isomer is much slower (milliseconds to days) [23]. The photo-triggered isomerization of azobenzenes drastically changes the geometry of the molecule, its polarity, and electronic properties [25]. The isomerization process involves a decrease in the distance between the two carbon atoms in position 4 of the aromatic rings of azobenzene, from 9.0 Å in the *trans* form to 5.5 Å in the *cis* form. The *trans*-azobenzene is almost flat and has no dipole moment, whereas the *cis* isomer presents an angular geometry and a dipole moment of 3.0 D [26]. Because of these high changes in response upon photo-switching from their *trans* to *cis* configuration, azobenzene-base ligands and its derivatives have been the candidates of choice to design new photo-sensitive complexes for different applications such as: hydrogen generation, catalysis (including: C–H activation, C–C activation, C–C coupling, N=N bond cleavage, electron transfer reaction, hydroxylation, etc.), chemosensors with high selectivity and sensitivity for heavy and/or transition metals, anticancer therapy [27,28]. Fig. 2 provides various bonding modes of azobenzenes with metals.

3. Azobenzene-based photo-sensitive complexes

3.1. Azobenzene-palladium complexes

Because azobenzene-palladium complexes are one of the first azobenzene-metal systems reported in literature, we decided to introduce them to this review as the first examples. For the first time, in 1969 Murray [29] published structures of two azobenzene-palladium complexes: (C₆H₅N=NC₆H₅)₂PdCl₂ and (C₆H₅N=NC₆H₅)₃Pd₂Cl₆, in which bonding from azobenzene to metal occurs only via a nitrogen lone pair. Generally, palladium(II) is a better complexation agent for N-bases than 3d-metals, such as Ni(II), Co(II) and Mn(II). However, the tetraacetate bridging system is rather strong (providing a very short, ~ 2.5 Å, Pd–M distance and difficult approachability of Pd(II) atom), whereas the axial position of the co-metal coordination sphere is rather labile and easily accessible to a nucleophilic attack. Cyclopalladation is an intramolecular reaction in which a palladium atom, coordinated by a ligand, covalently binds to a carbon atom of the same ligand so that the newly formed Pd–C bond closes a ring (palladacycle). Cyclopalladation is an example of the cyclometalation reactions with d-block transition metals. Mostly, with palladium, the ligand donor atom is nitrogen, the size of the palladacycle is 5 and the carbon atom bound to Pd is sp²-aromatic. The cyclopalladated compounds frequently display catalytic activity, although it is usually assigned not to the complexes themselves but to elementary palladium particles produced from them. Cyclopalladation is generally important as a C–H bond activation reaction [30]. Since 1965 when Cope and Siekman [31] for the first time reported an activation of azobenzene with PdCl₂/K₂PtCl₄ by isolating cyclometallated dinuclear compounds a variety of organometallic compounds of

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