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Visible Light Switching of a BF_2-Coordinated Azo Compound

Yin Yang, Russell P. Hughes, and Ivan Aprahamian*

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, United States

Supporting Information

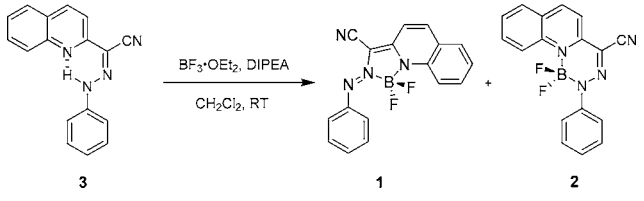
ABSTRACT: Here we report the synthesis and characterization of a BF_2–azo complex that can be induced to isomerize without the need of deleterious UV light. The complexation of the azo group with BF_2, coupled with the extended conjugation of the N=N π-electrons, increases the energy of the n–π^* transitions and introduces new π-nonbonding (π_{nb}) to π^* transitions that dominate the visible region. The well separated π_{nb}–π^* transitions of the *trans* and *cis* isomers enable the efficient switching of the system by using only visible light. The complexation also leads to a slow *cis* → *trans* thermal relaxation rate ($t_{1/2}$ = 12.5 h). Theoretical calculations indicate that the absorption bands in the visible range can be tuned using different Lewis acids, opening the way to a conceptually new strategy for the manipulation of azo compounds using only visible light.

Azobenzene has been the focus of intense research[1] since it was first reported by Alfred Nobel in 1856.[2] Because of its unique photophysical properties, azobenzene has been used in various applications ranging from industrial dyes,[3] to actuators,[4] nonlinear optical devices,[5] molecular switches and machines,[6] ion channel modulators,[7] and so forth. The π-system of azo compounds can be easily modified through the use of substituents that lead to changes in its absorption profile and more importantly its reversible *trans*/*cis* isomerization process. These properties have been extensively studied leading to the categorization of azobenzene derivatives into three groups: azobenzene, aminobenzene, and pseudo stilbene type molecules, based on the relative energetic order of their n–π^* and π–π^* transitions.[1] Recently, there has been a thrust[8] to develop azobenzene photoswitches that can be toggled between the *trans* and *cis* states by using only visible light.[9] The reason behind this is that the use of UV light, which is required for the *trans* → *cis* isomerization can lead to complications (i.e., photodamage)[9a] especially for *in vivo* applications (e.g., strong scattering[10] and apoptosis[11]). Various strategies,[1,9] which rely on the separation of the n–π^* bands in the visible range, pushing the π–π^* transition to that region, or using metal-to-ligand charge transfer (MLCT) to red-shift the activation wavelength,[12] have been used to accomplish this goal, including: (i) the incorporation of electron-withdrawing or -donating groups in the ortho and para positions, (ii) the use of push–pull substituents, (iii) protonation, (iv) the use of bridgehead derivatives, and (v) the incorporation of metal complexes. In certain cases, these approaches have led to the desired red-shift in the absorption profiles but they were also accompanied by very fast *cis* → *trans* thermal isomerization,[7c,13] which is undesirable for certain applications (e.g., protein probes,[14] molecular machines[6]), side reactions as is the case with protonation,[15] and relatively low isomerization ratios as is the case with the MLCT systems.[12] Nonetheless, Herges, Woolley and Nishihara have successfully developed a handful of systems[9,12c] that can be activated by visible light in both directions, without the accompanied enhancement in thermal isomerization rate. This behavior results either from the separation of the n–π^* bands or interligand CTs.

An interesting but a much less explored pathway to shifting the π–π^* transitions in azo compounds to the visible range is by coordinating the azo group's n-electrons with Lewis acids. Some early reports have looked at this effect;[16] however, none to the best of our knowledge took advantage of it to make switchable systems that can be fully modulated in the visible range. Here we wish to report the photoswitching of a BF_2–azo complex (**1**), which demonstrates a highly efficient *trans*/*cis* isomerization process that can be fully controlled using visible light. The system also undergoes a slow *cis* → *trans* thermal isomerization, the rate of which can be modulated using molecular oxygen. On the basis of theoretical analysis, the complexation of BF_2 with the azo group's nitrogen lone-pair electrons, coupled with the extended π-system in **1**, results in the reversal of the position of the n–π^* and π_{nb}–π^* transitions on the energy scale (similar to the pseudo stilbene type systems). This phenomenon leads to two isomers with extraordinarily well separated π_{nb}–π^* bands that have large molar extinction coefficients in the visible range.

Our interest in hydrazone-based switches[17] has led us to the development of BF_2–hydrazone complexes[18] that display aggregation induced emission.[19] As part of our efforts to optimize the properties of these solid-state dyes, we serendipitously discovered that the reaction of boron trifluoride with hydrazone **3** (Scheme 1) yields **1** as the main product (68%) instead of the expected BF_2–hydrazone **2** (10%). On the other hand, carrying out the reaction at elevated temperatures (60 °C) instead of RT yields **2** as the

Scheme 1. Synthesis of Compounds 1 and 2



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predominant compound. Both of these complexes were isolated, purified using chromatography, and characterized using NMR spectroscopy, mass spectrometry and X-ray crystallography (see SI).

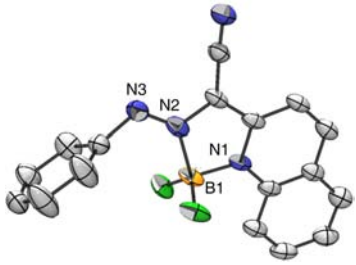
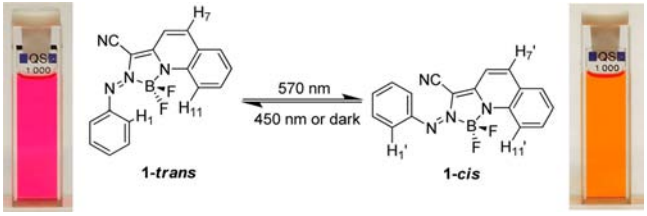


Figure 1. ORTEP drawing (50% probability ellipsoids) of the crystal structure of **1**. The hydrogen atoms and disorder in the phenyl ring have been removed for clarity.

Analysis of the crystallographic data (Figure 1 and Figure S15) reveals that **1** crystallizes in the *trans* form with a N(2)═N(3) bond length of 1.278(3) Å that is almost identical to that of azobenzene (average 1.25 Å).[20] Moreover, the X-ray structure shows that the coordination of BF_2 with one of the azo group nitrogens (N2) along with the quinolinyl nitrogen (N1) forms a five-membered ring having B−N bond lengths of 1.632(3) and 1.568(3) Å, respectively.[21] The ^{1}H NMR spectrum (Figure S10) of an equilibrated CH_2Cl_2 solution (in the dark) shows two sets of signals in the ratio of 87:13 assigned to the *trans* and *cis* isomers, respectively. A full assignment of the ^{1}H NMR signals using COSY and NOESY spectroscopies (Figures S4 and S5) revealed that the well resolved signals at 8.42 and 8.33 ppm belong to proton H7 of the *cis* and *trans* isomers of **1** (Scheme 2), respectively. These

Scheme 2. Visible Light-Induced Trans/Cis Isomerization of 1



signals were subsequently used as probes to quantitatively follow the *trans*/*cis* isomerization process in **1**. The ^{19}F NMR spectrum also showed two quartets at −142.72 and −150.60 ppm that were assigned to the *trans* and *cis* isomers, respectively.

The photoisomerization of **1** was studied extensively by UV/vis (Figure 2) spectroscopy. When stored in the dark, **1** adopts its thermodynamically stable *trans* form that has an absorption maximum (λ_{max}) at 530 nm (ε = 8026 M^{-1} cm^{-1}). Upon irradiation at 570 nm, the *cis* form (λ_{max} = 480 nm; ε = 7792 M^{-1} cm^{-1}) becomes dominant, accompanied by a sharp color change of the solution from bright purple to light orange (Scheme 2).[22] The process is also accompanied by changes in the intensity of bands at higher energies (λ_{max} = 340 and 264 nm). Irradiation at 450 nm drives the system back to its *trans* form. The isosbestic points (λ = 499, 399, 330, and 257 nm) in the UV/vis spectra demonstrate that only two species are

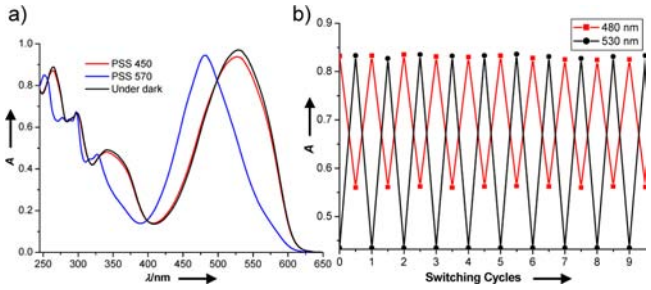


Figure 2. (a) The UV/vis spectral changes upon the photoisomerization of **1** in deoxygenated CH_2Cl_2 (0.1 mM). The black trace is of **1** equilibrated in the dark (mainly *trans*), which upon irradiation at λ = 570 nm gives the *cis* PSS (blue trace), which when irradiated at λ = 450 nm gives the *trans* PSS (red trace). (b) Multiple isomerization cycles of **1** (0.1 mM) in CH_2Cl_2 (not deoxygenated) after alternative irradiation at λ=570 (red trace) and 450 nm (black trace).

exchanging during the isomerization process (Figure 2a). What is remarkable is that the *trans*/*cis* isomerization can be activated solely by the use of visible light and there is no need for UV light. Furthermore, as shown in Figure 2b, the system shows very good reversibility as no degradation of **1** was observed during the entire photoisomerization studies that lasted for more than a month.

The isomerization process was also studied extensively using NMR spectroscopy (Figures S5−S10). The 2D heteronuclear ^{1}H−^{19}F NOESY spectrum of 1 (*trans* dominant) shows (Figure S8) as expected a correlation between the BF_2 fluorine atoms and protons H11 and H1 (Scheme 2). On the other hand, only one correlation is observed for the *cis* isomer, between the BF_2 fluorine atoms and proton H11′ (Figure S7). This indicates that the phenyl ring is moving away from the BF_2 group upon isomerization. The ^{1}H NMR spectrum of a 1:1 mixture of **1** does not change when pyridine is added to the solution (Figure S9). This indicates that the boron atom is not available for coordination with pyridine, that is, it is tetracoordinated in both isomers. These experiments rule out the light-induced B−N bond cleavage observed in other systems,[21] and show that the observed phenomenon in **1** is indeed the *trans*/*cis* isomerization process.

The photoswitching performance of **1** in deoxygenated dichloromethane was evaluated by measuring its photostationary state (PSS) and photoisomerization quantum yield (Figures S10−S13). The irradiation of a *trans*-dominant NMR sample of **1** at 570 nm for 5 min yields 97% of the *cis* isomer at the PSS, as determined by the signal intensity of protons H7 and H7′. Using the change in integration of protons H7 and H7′ as a function of irradiation time and knowing the light intensity at 570 nm (see SI), the quantum yield for the *trans* → *cis* isomerization ($\Phi_{trans\rightarrow cis}$) was calculated to be 48 ± 6%.[23] Similarly, irradiation at 450 nm for 30 min produced 80% of the *trans* isomer at the PSS, with a $\Phi_{cis\rightarrow trans}$ of 67 ± 8%. The thermal *cis*→*trans* isomerization of **1** was monitored using UV−vis spectroscopy (Figure S14), and the half-life at 294 K was determined to be 12.5 h, which is very long compared to pseudo stilbene type azo systems that are in the millisecond domain![1] Significantly, we found that the rate of thermal *cis* → *trans* isomerization is sensitive to the presence of oxygen in the solvent: when regular dichloromethane (not deoxygenated) was used for the measurements, the half-life went down to 30 min. Such a dependency of the isomerization rate on oxygen

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concentration is atypical for azo compounds.[1] The nature of the effect and its consequence on the isomerization mechanism in our system is under investigation.

The coordination of BF_2 with the n-electrons of the azo nitrogen in **1** is expected to reverse the position of the n−π^* and π−π^* transitions on the energy scale, as with pseudo stilbene type azobenzenes.[1] Recent reports[24] have indicated, however, that this energy reversal might not be a universal one in these systems. To understand the effect of Lewis acid coordination on the photophysical properties of azo compounds, we conducted computational modeling of the *trans* and *cis* isomers of **1**. Structures were optimized by density functional theory (DFT) using the B3LYP hybrid functional[25,26] and the 6-311++G** basis set,[27] as implemented in Jaguar;[28] this combination of method and basis set is appropriate for such systems.[9c] The optimized structure of *trans*-**1** matches well with its crystal structure (Figures S17 and S18). Calculations of the UV/vis spectra of the optimized structures were carried out in ADF[29] using time-dependent DFT (TDDFT)[30] using the B3LYP functional and a triple-ζ basis with two added polarization functions (TZ2P). These calculations were also successful in predicting the UV/vis spectra of the *cis* and *trans* isomers of **1** (Figures S31 and S32), and show that the absorption bands in the visible range (Figure 3, Table S2 and Figures S37−S41) stem from π-nonbonding to

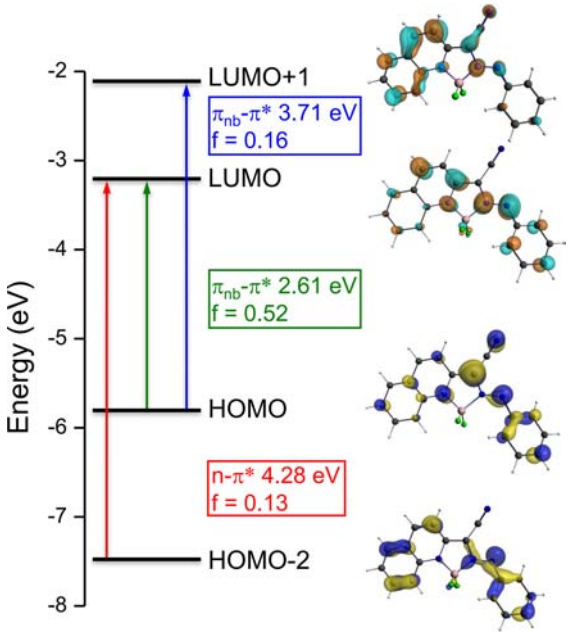

Figure 3. The calculated (B3LYP/6-311++G**) molecular orbital energy levels, transition energies and oscillator strengths of the n−π^* and π_{nb}−π^* transitions of the *trans* isomer of **1**.

π^*-antibonding transitions (HOMO → LUMO). Moreover, the calculations predict correctly the separation between the *cis* (λ_{max} = 482 nm) and *trans* bands (λ_{max} = 510 nm). Another set of π_{nb}−π^* transitions (HOMO to LUMO+1) is also predicted at a higher energy level (λ_{max} = 376 and 353 nm for *trans* and *cis*, respectively) where a smaller band is clearly visible in the UV/vis spectrum (Figure 2a), whereas the n−π^* transition is, as predicted, at an even shorter wavelength (λ_{max} = 338 nm for *trans*).[31] Relative to azobenzenes, binding to BF_2 drastically lowers the energy of the n-electrons, while additional conjugation in the N-C-C-N-N skeleton provides a higher energy π_{nb} molecular orbital which serves as the HOMO (Figures S37−S41). This in turns leads to the strong absorption band in the visible range that enables the manipulation of **1** using only visible light. Significantly, the BF_2 group is not unique in promoting this effect. As a proof of concept, we replaced it with Na^+ (*in silico*), which also resulted in red-shifted UV/vis absorption spectra (Figures S33 and S34). Intriguingly, the *trans* and *cis* isomers have a λ_{max} of 466 and 472 nm, respectively, implying that the absorption profile of the system can be manipulated using different Lewis acids! Moreover, the calculations predict that replacing the CN group with π-electron donating groups (Figures S35 and S36) and/or substituting the phenyl ring with such groups (based on the HOMO in Figure S29) will lead to a red shift in the absorption band, opening the door for further manipulations of the photophysical properties of the azocompound.

In conclusion, we have shown that the coordination of BF_2 with an azo group's nitrogen lone-pair, coupled with the extended conjugation of the N=N π-electrons, leads to a reconfiguration of its electronic structure, and a reversal of the n−π^* and π_{nb}−π^* transitions on the energy scale. Significantly, unusually well separated and strong π_{nb}−π^* transitions are observed for the *trans* and *cis* isomers in the visible range, which enable the switching of the system using only visible light. The high photoconversion, and photoisomerization quantum yields (which are higher than in azobenzene)[1] combined with the slow thermal relaxation and tunability of the photophysical properties make this conceptually new Lewis acid complexation strategy a viable pathway to the development of visible-light actuated functional materials.[4]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, NMR spectra of key compounds, photoisomerization studies, kinetic measurements, computational details and X-ray crystallography data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

ivan.aprahamian@dartmouth.edu

Notes

The authors declare no competing financial interest.

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