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Computational design of a molecular triple photoswitch for wavelength-selective control†

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A small single molecule with multiple photoswitchable subunits, selectively and independently controllable by light of different wavelengths, is highly attractive for applications in multi-responsive materials and biological sciences. Herein, triple photoswitches are presented consisting of three independent azobenzene (AB) subunits that share a common central phenyl ring: the *meta*-trisazobenzenes (MTA). It is the unique meta-connectivity pattern leading to decoupling of all azo-subunits although they do overlap spatially. Based on this pattern, we design a triple MTA photoswitch, as proof-of-principle, with three different, electronically independent AB branches on the computer, which can be individually photo-excited to trigger ultra-fast $E \rightarrow Z$ isomerization at the selected AB branch.

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1. Introduction

Azobenzene (AB) and its derivatives are by far the most popular molecular photoswitches with a wide range of application in the fields of photobiology, photochemistry and functional organic materials.^{1–7} Their attractive light-responsive properties are based on the ultra-fast photoisomerization between two long-lived *E*- and *Z*-configurations.^{1–13} In addition, their photochromic and isomerization properties and, in particular, their activation wavelength can be modulated on demand by suitable chemical modifications, *e.g.* by introduction of substituents to the benzene rings. Owing to their adjustable photochemical properties, AB-based compounds provide a versatile basis for numerous applications in data storage devices,³ optoelectronic devices,⁴ and molecular switches.⁵

Recently, multi-photochromic compounds containing more than one switching unit that can possibly be selectively and independently controlled by external stimuli are attracting much interest.^{14–17} A single molecule integrating multiple different AB subunits may exhibit such a multi-functional nature, and may be applicable in supramolecular stimuli-responsive systems, organic liquid crystal photonics, functional nanomaterials, and multi-responsive biological systems.^{2–5}

The photochromic behavior and the photoisomerization of AB and its derivatives have been intensively investigated so far,^{8–13} but only a few have recently demonstrated dual functionality. A general multi-addressable behavior of bisazobenzenes with two AB subunits was demonstrated, however, the individual AB subunits were not individually, *i.e.* selectively addressable.^{18–23} The switching behavior and the photochromic characteristics of four *para*-bisazobenzene derivatives connected by aryl–aryl linkers between two AB moieties were studied in an effort to optimize the photoswitching efficiency of linear multi-azobenzenes.¹⁹ Furthermore, other multi-photochromic compounds containing multiple switching subunits such as *cyclo*-trisazobenzene,^{24–26} *tris*-[4-(phenylazo)-phenyl]-amine^{27,28} on a surface, and other multi-photochromic compounds^{29–36} have been addressed to explore new multi-photochromic effects and light-induced functionalities as well. More recently, orthogonal and reversible control of two distinct types of photoswitches in a multifunctional molecular system has been reported, giving rise to impressive dual functionality.^{36,37} However, the design of multi-state multi-photochromic compounds with multiple functionalities still poses a great challenge, because, in general, wavelength selective control of individual components of a multi-photochromic compound requires selective addressability and independent functionalities of the single photochromic subunits.

The ultrafast dynamics and photochromic properties of *ortho*-, *meta*- and *para*-bisazobenzenes have been investigated systematically, and their properties and cooperative behavior have been found to strongly depend on their connectivity pattern.²¹ The two AB branches are uncoupled in *meta*-bisazobenzenes and the absorption spectrum is a superposition of the spectra of two individual AB subunits. In contrast, a substantial red-shift of the $\pi\pi^*$ absorption band occurs in *para*-

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Table 1 Comparison of the vertical excitation energies of the first eight low-lying excited states of MTA, 4'-SH-MTA, 2',4',6'-tri-CN-MTA and (2',4',6'-tri-CN-4''-SH)-MTA at the TD-DFT/BHHLYP level with the 6-31G* basis set. The values are given in eV, oscillator strength in parenthesis

State	MTA	4'-SH-MTA	2',4',6'-tri-CN-MTA	2',4',6'-tri-CN-4''-SH-MTA
S ₁	2.92 (0.00)	2.92 (0.00)	2.63 (0.00)	2.63 (0.00)
S ₂	2.93 (0.00)	2.93 (0.00)	2.92 (0.00)	2.92 (0.00)
S ₃	2.93 (0.00)	2.95 (0.00)	2.93 (0.00)	2.95 (0.00)
S ₄	4.15 (0.00)	3.95 (1.47)	3.52 (0.04)	3.40 (0.04)
S ₅	4.19 (1.41)	4.11 (0.04)	3.70 (1.02)	3.66 (1.02)
S ₆	4.19 (1.41)	4.19 (1.35)	4.21 (1.30)	3.95 (1.06)
S ₇	4.40 (0.00)	4.36 (0.12)	4.29 (0.43)	4.16 (0.70)
S ₈	4.93 (0.00)	4.85 (0.03)	4.29 (0.00)	4.30 (0.00)

corresponding relaxed potential energy surface scan (Fig. 5c). Hence, the computed potential energy curves suggest that excitation into the S₇ ($\pi\pi^*$) state at the unsubstituted AB branch will eventually lead to $E \rightarrow Z$ isomerization of that particular AB branch. Similar curves are found for excitation of the $\pi\pi^*$ states located at the SH-substituted (S₆) and the 2',4',6'-tri-CN substituted (S₅) branches (ESI[†]). Hence, our calculations suggest that indeed individual photoswitching of the different AB branches is in principle possible, when the AB branches are individually excited.

A remaining question to discuss is the quantum yield of photoswitching of the individual AB branches. In principle, every crossing encountered during the initial relaxation process corresponds to a potential loss channel, because the excited molecules could switch to another excited state. However, the states crossed are located at the other branches, *i.e.* spatially separated, and hence a non-radiative decay into these states would correspond to an energy transfer from one branch to another. The efficiency of energy transfer on the other hand depends on the coupling strength between the electronic states

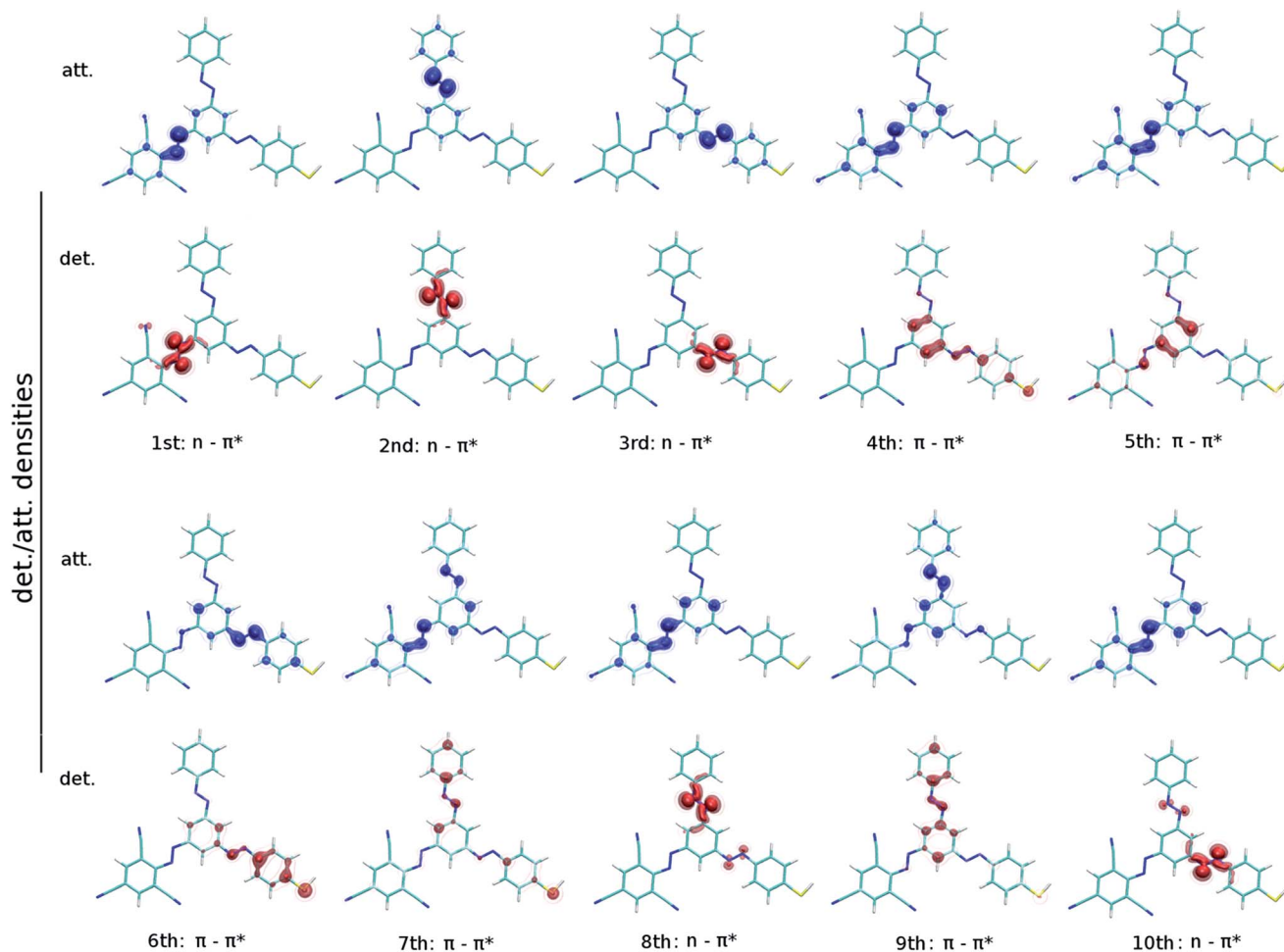


Fig. 4 Detachment (red) and attachment (blue) densities for the energetically lowest ten excited singlet states S₁ to S₁₀ of (2',4',6'-tri-CN-4''-SH)-MTA at the BHHLYP/6-31G* level of theory.



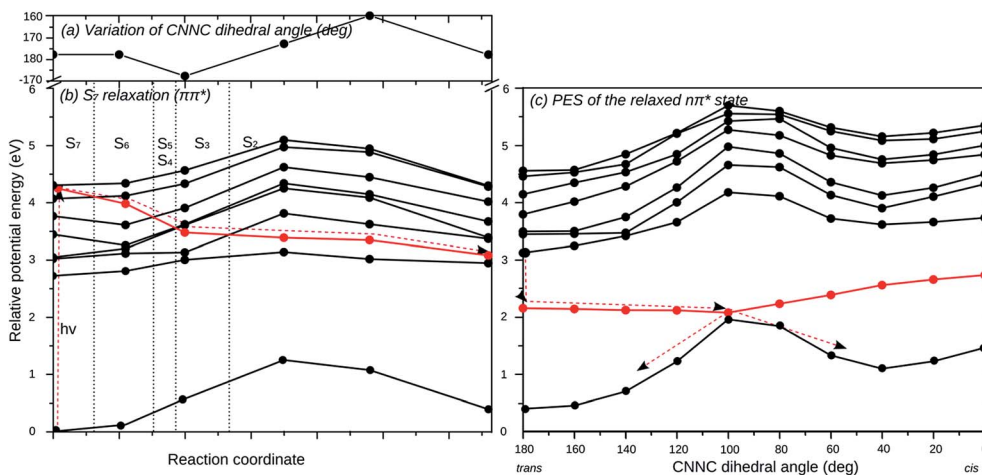


Fig. 5 Relaxed scans of the potential energy surfaces along the isomerization pathway of the unsubstituted AB branch of (2',4',6'-tri-CN-4''-SH)-MTA. (a) Variation of CNNC dihedral angle (deg) along the unconstrained relaxation of S_7 starting at the ground state equilibrium geometry. (b) Potential energy curves along the unconstrained relaxation of S_7 , the $\pi\pi^*$ excited state of the unsubstituted AB branch, to decay non-radiatively into S_2 , the $n\pi^*$ state of the unsubstituted AB branch. (c) Potential energy surface scan of the relaxed $\pi\pi^*$ excited state of the unsubstituted AB branch along the CNNC dihedral angle. The red line corresponds to the state, which is optimized, and the vertical dotted lines in (b) separate the regions where the optimized state is S_7, S_6 , etc. down to S_2 .

located at the different AB branches, and this is negligible, as we have demonstrated above. Therefore, energy transfer can be expected to be slow, at least much slower than the well-known ultra-fast $E \rightarrow Z$ isomerization of azobenzene, which occurs in about 200 fs. In summary, we expect the quantum yields of switching the individual AB branches in MTAs to be similar to the ones of the corresponding isolated ABs.

5. Summary and outlook

In summary, we have successfully designed a multi-photochromic compound *in silico* based on a meta-connectivity principle applied to multi-azobenzenes. The smallest trisazobenzene consists of three azobenzene (AB) branches, which share the central phenyl ring. We have shown the low-lying excited electronic states of the three AB branches to be electronically decoupled despite of the large spatial overlap. It is highly astonishing that four phenyl rings are sufficient to build a photoswitch that exhibits the properties of three independent azobenzene molecules.

(2,4,6-CN;4-SH)-meta-trisazobenzene served as representative example and proof-of-principle for a triple photoswitch, in which all AB-branches can be, in principle, selectively excited because the individual $\pi\pi^*$ bands are energetically well separated. In addition, computation of the isomerization pathways of individually excited AB branches demonstrated selective excitation to lead to selective photoswitching.

We believe the meta-connectivity principle to be generally applicable for the construction of multi-photoswitchable systems, as it leads to maximally uncoupled individual subsystems retaining their individual photochemistry. A general limitation of course are the timescales of photoswitching compared to other non-radiative and radiative decay channels. In particular, excitation energy transfer from one subunit to

another can significantly interfere. However, as long as the switching process is fast enough, the other deactivation pathways do not play a relevant role.

While in this work static quantum chemical calculations are sufficient to demonstrate the concept of meta-connectivity and the computational design of a first triple-photoswitch based on azobenzene, in general nuclear quantum dynamics are required to study the efficiency of photoswitching and to determine timescales and relevant loss channels. In the future we plan to synthesize and spectroscopically investigate the suggested meta-trisazobenzene derivatives in analogy to previous works.⁴⁹⁻⁵¹ This work indeed paves the way for future development of selectively photoswitchable control systems being used in advanced materials and nano-electronic devices.

Conflicts of interest

There are no conflicts to declare.

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