1+1≥2? Norbornadiene-Azobenzene Molecules as Multistate Photoswitches

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By combination of two photochromic molecules as multistate photoswitches new properties regarding to molecular solar thermal (MOST) energy storage systems and information storage capacity of smart materials are expected. By fusing the azobenzene with the norbornadiene system, new multinary photoswitches were designed. A successful synthesis towards different analogues was developed via Suzuki coupling reaction as key step. The isomerization behaviour of these norbornadiene-azobenzene fusions was studied by UV-Vis and ^{1}H NMR spectroscopy in different solvents investigating the electronic communication within these multinary-photochromic systems.

1. Introduction

Photochromic molecules are defined by the ability to undergo a light-induced reversible change between two forms with different absorption spectra.[1] Nowadays those photoswitches exhibit increasing attention due to their diverse and versatile applications for example in photobiology,[2] information storage[3] or solar fuel applications.[4–5] For the latter, azobenzenes (AB) as well as the norbornadiene-quadricyclane system (NB/QC) are both potent lead structures for molecular solar thermal energy storage (MOST) systems.[6–7] Upon irradiation with UV-light of around 350 nm the thermodynamically more stable E-isomer of ABs converts into the less stable Z-isomer.[8] The thermodynamically more stable NB can undergo a [2+2]-cycloaddition to its corresponding metastable QC also by irradiation of around 300 nm in the presence of a photosensitizer.[9] The differences in energy from parent to metastable photoisomer can be exploited to design versatile MOST systems.[5]

Herein, the combination of AB and NB as a new candidate for MOST applications is presented: One disadvantage of NBs is their absorption of light in the UV-region. Although the absorption maximum can be red-shifted by introducing different substituents, the energy density as a consequence decreases due to the increase of the molecular mass.[10] Moreover, the half-lives of the photoisomers are influenced.[7] By adding the AB scaffold as a substituent to the NB moiety, not only the absorption maximum might be shifted but also the storage density should be increased due to the additional energy storage capability in the AB-moiety. The combination of different photochromic units in one system in general bears special challenges, however, with the potential to create new or better properties for 'smart' materials.[11–13] In this fundamental study, the isomerization behavior and electronic communication of AB-NB switches are investigated. To the best of our knowledge there is only one report by Dubonosov et al. of combining an AB with a NB. In this study two substituted NBs were both connected to an AB moiety in para-position (Scheme 1, 1, 2). Although the authors mention successful switching of the norbornadiene as well as the azobenzene moiety, a detailed analysis has not been provided.[14] Previously, it could be shown that π-conjugation in ortho- and para-bis-ABs significantly influences the compounds isomerization behavior. In contrast to that, in bis-ABs connected in meta-position both photochromic moieties behave almost independently due to less π-conjugation (the "meta-rule", Scheme 1, 4).[15,16] Combining these observations, novel meta- and para-connected AB-NB were designed and their isomerization and energetic behavior of both photochromic moieties connected in one molecule were investigated (Scheme 1, 6–11).

These NB-AB dyads contain both, the AB and the NB scaffold, in either meta- or para-connection (Scheme 1, 6–11).
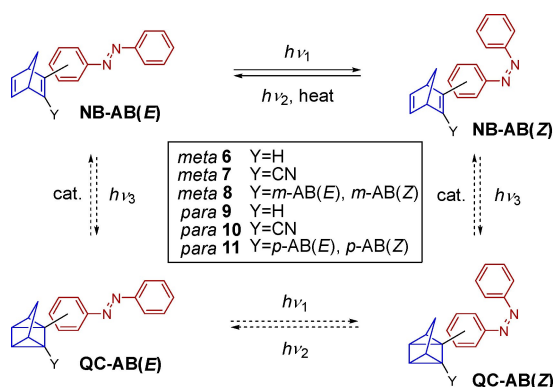
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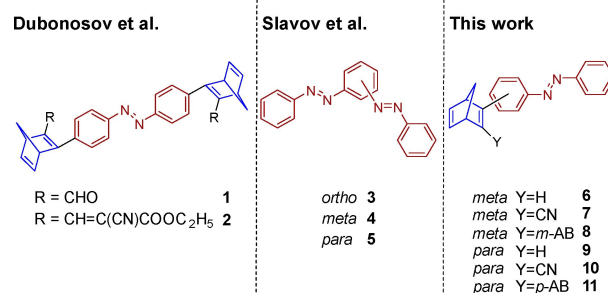
Scheme 1. Overview of previously reported NB-ABs **1** and **2**, bis-azobenzenes sharing one phenyl ring **3**–**5**, and NB-ABs investigated in this study **6**–**11**.[14,16]

Dubonosov et al.	Slavov et al.	This work
R = CHO **1**	ortho **3**	meta Y=H **6**
R = CH=C(CN)COOC$_2$H$_5$ **2**	meta **4**	meta Y=CN **7**
	para **5**	meta Y=m-AB **8**
		para Y=H **9**
		para Y=CN **10**
		para Y=p-AB **11**

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Scheme 2. Possible photoisomers of AB-NB compounds **6–11**. QC-AB(*E*) and QC-AB(*Z*) were not observed in this study.
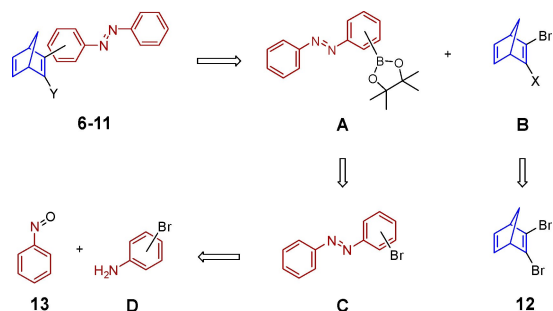
Because two photoswitchable moieties are combined, these compounds can be categorized as multinary-photoswitches. Therefore, molecules **6**, **7**, **9** and **10** can, in theory, adopt four different states [NB-AB(*E*), NB-AB(*Z*), QC-AB(*E*), QC-AB(*Z*)]; **8**, **11** in principle can switch between six different states of isomerization [NB-AB(*E*,*E*), NB-AB(*E*,*Z*), NB-AB(*Z*,*Z*), QC-AB(*E*,*E*), QC-AB (*E*,*Z*), QC-AB(*Z*,*Z*)] (Scheme 2).

Challenges of combining two or more photochromic systems are the proper energy match of the absorption wavelength of both moieties to induce switching of either both chromophores at the same time, or only one selectively. The combinations of photoswitchable units can lead to energy transfer if the two scaffolds are energetically coupled inhibiting the switching.[17,18] Another obstacle can be a low quantum yield for each of the individual processes.

2. Results and Discussion

2.1. Synthesis

A synthetic route towards all NB-ABs **6–11** was developed as outlined in Scheme 3. As a key step, a Suzuki coupling reaction was envisioned to form the necessary AB-NB-connection.[19] The boronic esters **A** could be obtained by borylation via Miyaura reaction of mono-bromo-substituted ABs **C**.[20–21] Those inter-
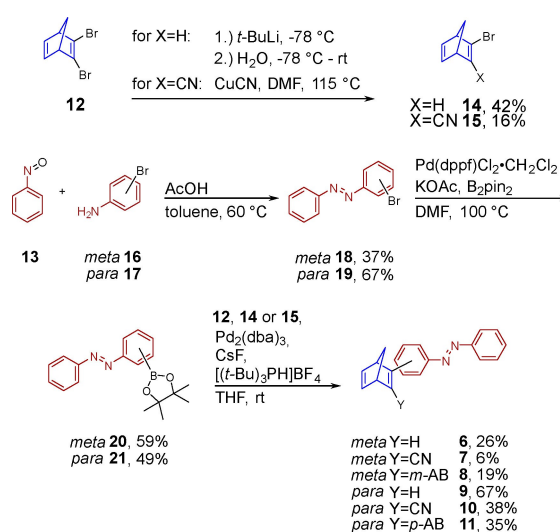
mediates could be synthesized by Baeyer-Mills coupling of nitrosobenzene (**13**) with the respective bromo-anilines **D** (Scheme 3).[22]

To access *meta-/para*-bromo-substituted ABs **18/19**, Baeyer-Mills coupling with either *meta*- or *para*-bromoaniline **16** or **17** in acidic media was performed. All reactions were done under nitrogen atmosphere and the bromoanilines **16–17** were degassed in toluene prior to the addition of nitrosobenzene (**13**). As nitroso compounds in general tend to be unstable, 1.5 eq. of nitrosobenzene (**13**) were used. This reaction generated *meta*- and *para*-bromo-substituted ABs **18** and **19** as red solids. For the implementation of *meta*- and *para*-boronic esters **20** and **21** a Miyaura reaction was performed according to the literature.[20,23] The borylation provided the starting material for the following Suzuki coupling in this route. Dissimilar from other Suzuki coupling reactions of NBs reported,[24] here, boronic esters instead of boronic acids were utilized. This choice was based on different advantages: Boronic esters are in general better soluble, more reactive and in most cases easily accessible via Miyaura coupling reaction of brominated aryl-compounds, while boronic acids tend to form anhydrides.[25] For the borylation bis(pinacolato)-diboron (B$_2$pin$_2$) was applied generating the desired products as red solids.

The different substitution patterns of the second NB building block provide a combinatorial-like access to various AB-NBs. In the following Suzuki-coupling reaction di-bromo-NB **12**, mono-bromo-NB **14** as well as cyano-NB **15** were employed as starting materials. Mono-bromo-NB **14** was prepared from di-bromo-NB **12** by monolithium-halogen exchange with *t*-BuLi. Trapping of this organolithium intermediate with water gave mono-bromo-NB **14** as yellowish oil.[26] cyano-NB **15** was obtained also as yellowish oil by nucleophilic attack of one equivalent of cyanide to di-bromo-NB **12** (Scheme 4).[27] With both building blocks, boronic esters **A** and NBs **B**, in hand Suzuki coupling reactions were performed. For this transformation, a catalyst system of CsF/Pd$_2$dba$_3$/ [(*t*-Bu)$_3$PH] BF$_4$ was utilized.[28] AB-NBs **6** and **9** turned out to be not very stable. Therefore, the reaction times in those cases were shortened to increase the yield of the products obtained as orange solids.

Scheme 3. Synthetic strategy towards AB-NBs **6–11**.

Scheme 4. Synthesis of AB-NBs **6–11**.

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Also, excess of NB starting material was avoided to prevent side reactions.

2.2. UV/Vis Absorption Spectroscopy

All AB-NBs **6–11** were investigated via UV-Vis spectroscopy. The spectra revealed a red-shift of the absorptions of *para*-connected compounds **9–11** compared to their *meta*-analogues and the parent AB and NB (Figure 1).[29] The absorption maximum of compound **8** is not shifted, while **6** shows a slight blue shift and **7** a slight red shift in comparison to unsubstituted AB in DMSO.[29] This observation can be explained by an elongated π-system due to higher π-conjugation of AB with NB in *para*- and less conjugation in *meta*-position (*meta*-rule).[16] The characteristic n-π* maximum of AB is located for *meta*-AB-NB **6**, *meta*-cyano-AB-NB **7** and *meta*-AB₂-NB **8** at around 450 nm, while for *para*-AB-NB **9**, *para*-cyano-AB-NB **10** and *para*-AB₂-NB **11** these maxima are not

or not fully visible. To examine the isomerization behavior of compounds **6–11**, the samples were irradiated with light of different wavelengths. Exemplary, the isomerization behavior for *para*-AB-NB compound **10** will be discussed (for **6**, **7**, **8**, **9** and **11** see SI). After irradiation with 365 nm in DMSO, the absorbance at around 364 nm decreased, while the n–π* absorption band showed a slight increase around 450 nm, representative for the the (*E*)→(*Z*) isomerization of AB. After irradiation with 302 nm, the shoulder at 290 nm decreased and the absence of an isosbestic point during the photoisomerization indicated decomposition.

For the isomerization of the other AB-NB compounds **6**, **7**, **8**, **9** and **11** a similar behavior compared to in DMSO was observed. In contrast to that, the photoisomerization of AB-NB compound **10** in acetonitrile, methanol, and cyclohexane showed a clear isosbestic point, but no signs of NB-QC isomerization could be observed (Figure 2, left). Changing the solvent to dimethyl formamide (DMF) or toluene, also decomposition was observed.
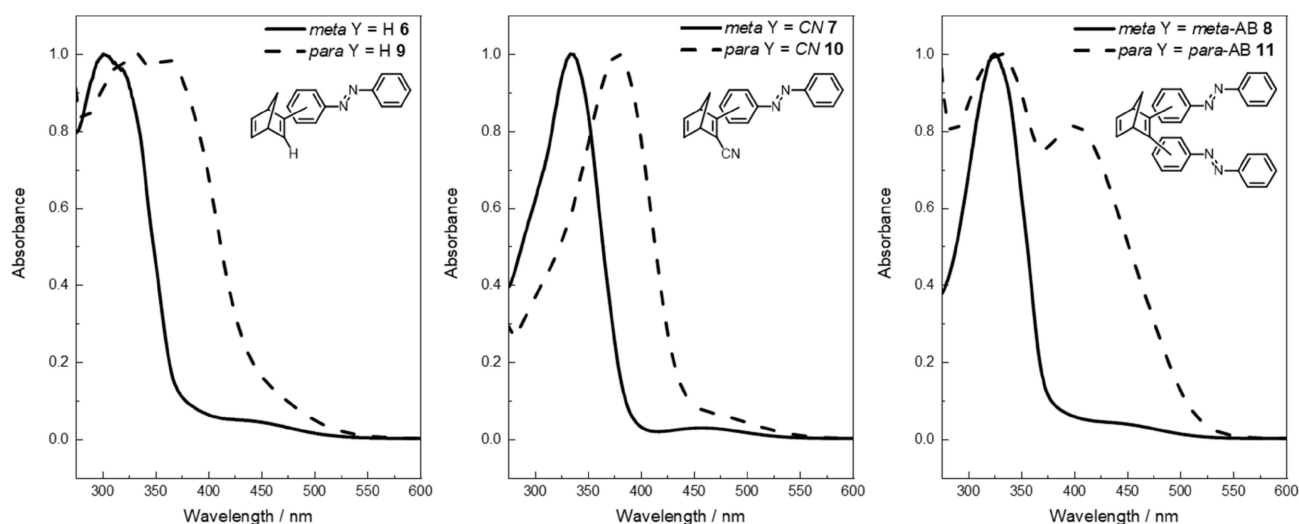

Figure 1. Normalized UV/Vis absorption spectra of compounds **6–11** in DMSO. (**7,8,10**: 2×10⁻⁵ mol/L; **11**: 2×10⁻⁵ mol/L; **6,9**: 4×10⁻⁵ mol/L, for detailed information see the Supporting Information).
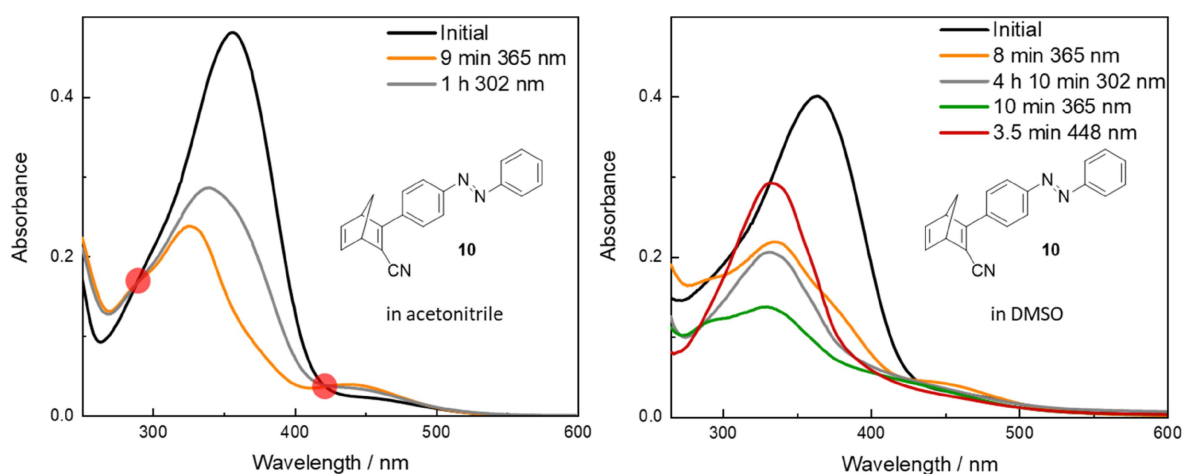

Figure 2. Isomerization behavior of AB-NB **10** [2×10⁻⁵ mol/L in acetonitrile (left) and DMSO (right)]. Isosbestic points are highlighted in red.

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2.3. NMR Spectroscopy

^{1}H NMR isomerization experiments were performed to further support these observations. AB-NB **10** was irradiated with light of 302 nm in MeCN-d_3 providing a mixture of AB(E)-NB and AB(Z)-NB [Figure 3, b)]. Subsequent irradiation with light of 365 nm preserved the AB moiety mostly as AB(Z) [Figure 3, c)]. By irradiation with light of 448 nm back isomerization occurred and as a consequence mostly AB(E)-NB was present [Figure 3, d)]. Those results in accordance to the UV-Vis analysis revealed only AB(E/Z) isomerization (Figure 3). Changing the solvent to DMSO-d_6, decomposition upon irradiation with 302 nm was observed (see ^{1}H-NMR spectra in DMSO-d_6 in SI). Additionally, the decomposition of compound **10** was supported by HPLC analysis. It has been shown before that the quantum yields of the NB-QC isomerization are solvent dependent and rather low in acetonitrile, but high in toluene.[30] In contrast, the isomerization-ability of AB is not as much affected by the solvent. Hence, both photoswitching units should be able to isomerize when changing the solvent to toluene. However, no isomerization of NB to QC was observed in toluene. Another explanation for the absent NB-QC isomerization could be an energy transfer between both photochromic units. Such a process as result of conjugation between the NB and AB moiety could inhibit the switching ability of NB to QC. This case of excitonic coupling was also observed in other cases of combined photochromic systems.[17] To support this assumption, an equimolar mixture of AB **22** and NB **23** was irradiated under the previous NMR isomerization conditions. It was found that both photoswitches isomerized in acetonitrile-d_3, substantiating the proposal of intramolecular electronic coupling of AB-NB **6–11** preventing switching of the NB moiety (Figure 4).

3. Conclusion

Multinary photochromic systems consisting of AB and NB **6–11** have been successfully synthesized to investigate the interaction within switching processes. Isomerization experiments revealed that (E)→(Z) isomerization of AB can be induced, but the [2+2]-cycloaddition of the NB-QC switch does not occur due to energy transfer. In different solvents, DMSO, DMF, toluene, acetonitrile, cyclohexane and methanol it was only possible to isomerize the AB- but not the NB-moiety, accessing only two of the possible states. Concerning this, similar challenges of accessing the QC in other combined photochromic units were observed.[12,13] These fundamental results provide the basis for alternative designs so that in the future the molecules might be used as MOST systems or in data storage devices.

Conflict of Interest

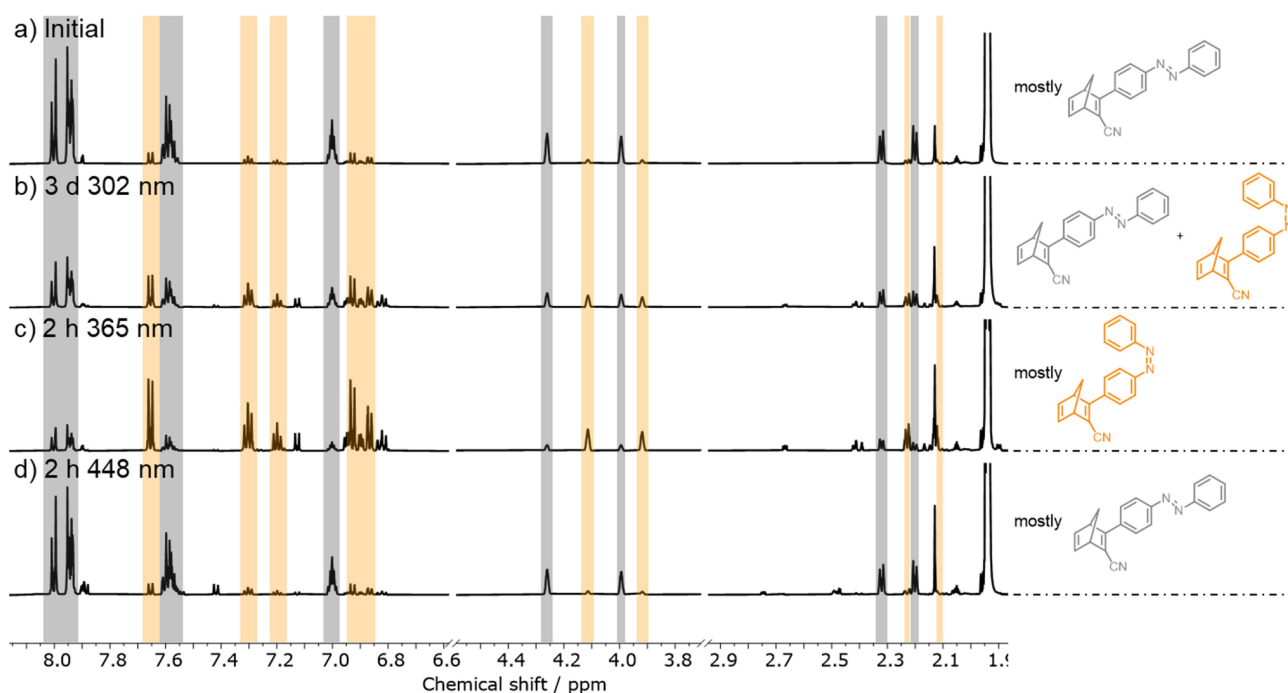The authors declare no conflict of interest.

Figure 3. Isomerization of AB-NB **10** monitored by 1H NMR spectroscopy (600 MHz, acetonitrile-d_3, N$_2$ atmosphere, −10 °C). grey = AB(E)-NB, orange = AB(Z)-NB.

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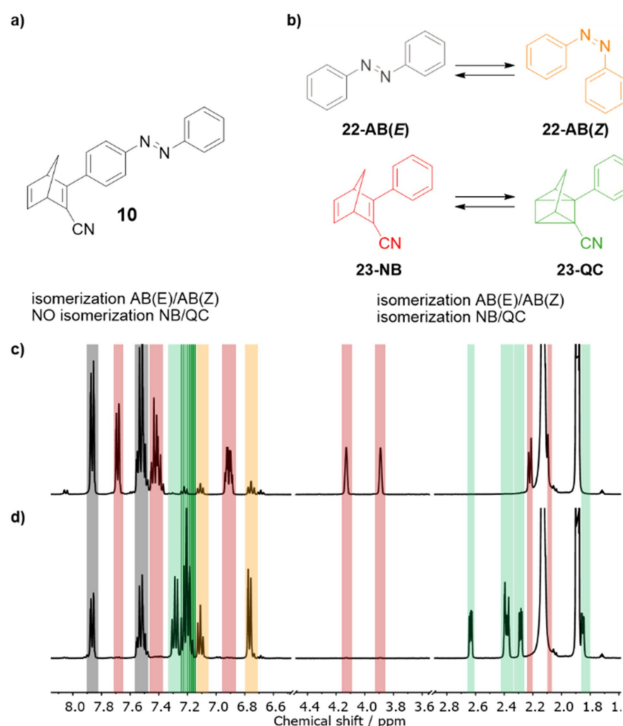European Chemical
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Figure 4. Top: a) Energetically coupled system NB-AB **10**, in which the AB moiety can be switched, but the NB-QC isomerization is prevented.
b) Control system of a mixture of AB **22** together and cyano-phenyl-NB **23**, in which both separated molecules in one solution can be isomerized. Bottom: ¹H NMR isomerization experiment of equimolar solution of AB **22** together with cyano-phenyl-NB **23** (400 MHz, each 8.5×10^{-3} mol/L in acetonitrile-d_3). grey = AB(E), orange = AB(Z), red = NB, green = QC. c) Initial spectrum, in which AB **22** is mostly present as AB(E) and cyano-phenyl-NB **23** as NB. d) After irradiation with light of 302 nm, AB(E/Z) isomerization as well as complete isomerization of cyano-phenyl-NB **23** from NB to QC could be observed.

Keywords: azo compounds · energy transfer · isomerization · norbornadiene · photoswitches

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