Norbornadiene–dihydroazulene conjugates

Martin Drøhse Kilde, Mads Mansø, Nicolai Ree, Anne Ugleholdt Petersen, Kasper Moth-Poulsen, Kurt V. Mikkelsen* and Mogens Brøndsted Nielsen*

Conjugates of norbornadiene (NBD) and dihydroazulene (DHA) photoswitches were synthesised and subjected to isomerisation studies.
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Norbornadiene–dihydroazulene conjugates†

Martin Drøhse Kilde,‡a Mads Mansø,‡b Nicolai Ree, id a Anne Ugleholdt Petersen,² a Kasper Moth-Poulsen, id b Kurt V. Mikkelsen id a* and Mogens Brøndsted Nielsen id a*²

The introduction of various photochromic units into the same molecule is an attractive approach for the development of novel molecular solar thermal (MOST) energy storage systems. Here, we present the synthesis and characterisation of a series of covalently linked norbornadiene/dihydroazulene (NBD/DHA) conjugates, using the Sonogashira coupling as the key synthetic step. Generation of the fully photoisomerized quadricyclane/vinylheptafulvene (QC/VHF) isomer was found to depend strongly on how the two units are connected – by linear conjugation (a para-phenylene bridge) or cross-conjugation (a meta-phenylene bridge) or by linking to the five- or seven-membered ring of DHA – as well as on the electronic character of another substituent group on the NBD unit. When the QC–VHF system could be reached, the QC-to-NBD back-reaction occurred faster than the VHF-to-DHA back-reaction, while the latter could be promoted simply by the addition of Cu(I) ions. The absence or presence of Cu(I) can thus be used to control whether heat releases should occur on different or identical time scales. The experimental findings were rationalized in a computational study by comparing natural transition orbitals (NTOs). Moreover, the calculations revealed an energy storage capacity of 106–110 kJ mol⁻¹ of the QC–VHF isomers, which is higher than the sum of the capacities of the individual, separate units. The major contribution to the energy storage relates to the energetic QC form, while the major contribution to the absorption of visible light originates from the DHA photochrome; some of the NBD–DHA conjugates had absorption onsets at 450 nm or beyond.

Introduction

With the increasing demand for energy in the world, environmentally friendly energy resources are a necessity. The Sun provides limitless energy although the major challenge is to store the energy and release it when needed. Photochromic molecules, which upon light irradiation convert from low-energy isomers to high-energy, metastable isomers, have attracted increasing interest in recent years as an opportunity for storing solar energy. Such molecular systems are often termed molecular solar thermal (MOST) systems or solar thermal fuels (STF).¹ This principle is to absorb the Sun’s radiant energy and store it as chemical energy in the chemical bonds of the metastable isomers that thermally convert back over time. Two important criteria for a functional system are to have absorbance matching the solar spectrum, ideally around 590 nm, and low molecular weight resulting in high energy density.²

Among the most studied photo-/thermoswitches for MOST applications are trans/cis-azobenzene (AZB),¹d,³ norbornadiene/quadricyclane (NBD/QC)²a,⁴ and dihydroazulene/vinylheptafulvene (DHA/VHF)⁵ couples (Scheme 1), but other systems have also been explored.⁶ Some of us have recently shown that covalently linking together several NBDs results in improved energy densities, redshifted absorptions, and the possibility

![Scheme 1](https://example.com/scheme1.png)  
for stepwise switching.\(^4\) Stepwise forward and/or backward switchings were also observed in acyclic and macrocyclic DHA dimers.\(^7\) In the macrocyclic structures, stepwise energy releases corresponded to an initially fast discharge, hypothetically addressing thermal applications on different time scales with an initial immediate energy release (hours), and a subsequent slow process (days or weeks). To explore the concept of multimode switching further and to harvest a broader region of UV-visible light, we decided to create a new class of hybrid MOST chromophore systems by the linkage of NBD and DHA photoswatches. This is a rare combination of traditional and inverse photochromes both capable of storing significant amounts of heat. Herein, we present the synthesis, physico-chemical characterisation and computational modelling of a series of six such conjugates expanding our knowledge of hybrid multichromophores for solar energy storage applications.

### Results and discussion

#### Synthesis

An array of NBD/QC–DHA/VHF conjugates was conveniently prepared from previously reported DHA derivatives \(1a, 1b, 1c, 1d, 1e, 1f\) and NBD derivatives \(2a, 2b, 2c\) (Schemes 2 and 3). First, NBD–DHAs \(3a\textsubscript{NBD–DHA}–5a\textsubscript{NBD–DHA}\) with a phenyl substituent on the NBD was synthesized according to Scheme 1. DHA \(1a\) was subjected to a well-established bromination-elimination protocol,\(^{15}\) providing a bromo-functionalized intermediate, which was used directly in a Sonogashira coupling with \(2a\) giving \(3a\textsubscript{NBD–DHA}\) in 9% yield over 3 steps. DHAs \(1b\) and \(1c\) were converted under similar coupling conditions into conjugates \(4a\textsubscript{NBD–DHA}\) and \(5a\textsubscript{NBD–DHA}\) in yields of 61% and 51%, respectively. The second series of NBD–DHAs \(3b\textsubscript{NBD–DHA}–5b\textsubscript{NBD–DHA}\) with a cyano group on the NBD was synthesized according to Scheme 3. First, the acetylenic DHAs \(1d\) and \(1e\) were desilylated using tetrabutyl-ammonium fluoride (TBAF) in AcOH and THF, and the terminal alkyne intermediate was then coupled with \(2b\), which resulted in products \(3b\textsubscript{NBD–DHA}\) and \(4b\textsubscript{NBD–DHA}\) in yields of 10% and 31%, respectively. DHA \(1f\) was subjected to identical coupling conditions providing \(5b\textsubscript{NBD–DHA}\) in a yield of 79%. In these coupling reactions, the homo-coupled dimers \(6–8\) were isolated as by-products.

#### UV-Vis absorption spectroscopy and switching studies

Fig. 1 summarizes the absorption properties of previously studied compounds. The unsubstituted NBD has an absorption onset at 267 nm and a maximum far in the UV region, which can be redshifted upon addition of functional groups across one of the double bonds as seen in compounds \(9\) and \(10\) (Fig. 1).\(^{14}\) DHA \(1a\) has an absorption onset at 452 nm (the onset is defined as \(\varepsilon = 100 \text{ M}^{-1} \text{ cm}^{-1}\)) and a maximum at 360 nm (toluene),\(^8\) hence redshifted relative to the unsubstituted NDB and derivatives \(9\) and \(10\). Its corresponding, non-photoactive VHF isomer has a characteristic absorption region of UV-visible light, we decided to create a new class of hybrid MOST chromophore systems by the linkage of NBD and DHA photoswatches. This is a rare combination of traditional and inverse photochromes both capable of storing significant amounts of heat. Herein, we present the synthesis, physico-chemical characterisation and computational modelling of a series of six such conjugates expanding our knowledge of hybrid multichromophores for solar energy storage applications.

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**Scheme 2** Synthesis of NBD–DHA conjugates \(3a\textsubscript{NBD–DHA}, 4a\textsubscript{NBD–DHA}\) and \(5a\textsubscript{NBD–DHA}\). Reagents and conditions (a) (1) Br\(_2\), CH\(_2\)Cl\(_2\), –78 °C, (2) LiHMDS, THF, 0 °C, (3) \(2a\). Pd(PPh\(_3\))\(_2\)Cl\(_2\) (10 mol%), Cu (10 mol%), (iPr\(_2\))NH/THF. (b) \(2a\). Pd(PPh\(_3\))\(_2\)Cl\(_2\) (10 mol%), Cu (11 mol%), (iPr\(_2\))NH/THF. (c) \(2a\). Pd(PPh\(_3\))\(_2\)Cl\(_2\) (45 mol%), Cu (49 mol%), (iPr\(_2\))NH/THF. LiHMDS = lithium hexamethyldisilazide.

**Scheme 3** Synthesis of NBD–DHA conjugates \(3b\textsubscript{NBD–DHA}, 4b\textsubscript{NBD–DHA}\) and \(5b\textsubscript{NBD–DHA}\). Reagents and conditions (a) (1) TBAF, AcOH, THF, (2) \(2b\). Pd(PPh\(_3\))\(_2\)Cl\(_2\) (10 mol%), Cu (13 mol%), (iPr\(_2\))NH/THF. (b) (1) TBAF, AcOH, THF, (2) \(2b\). Pd(PPh\(_3\))\(_2\)Cl\(_2\) (10 mol%), Cu (10 mol%), (iPr\(_2\))NH/THF. (c) \(2b\). Pd(PPh\(_3\))\(_2\)Cl\(_2\) (10 mol%), Cu (10 mol%), (iPr\(_2\))NH/THF.
Aromatic back-reactions were studied at 50 °C. A schematic analysis (vide infra) depicted in Fig. 1, and data are listed in Table 1. UV-Vis absorption spectra corresponding to all the photo-thermo-switching experiments can be found in the ESI.†

Initially, all the NBD-DHA systems were subjected to irradiation around the longest-wavelength absorption onset, corresponding to the onset of the respective DHA subunits (3a/bNBD-DHA, and 5a/bNBD-DHA, 400 nm, 4a/bNBD-DHA, 450 nm), ensuring photochemical conversion to the NBD-VHF states. All conjugates 3a/bNBD-DHA—5a/bNBD-DHA were found to easily undergo photochemically induced ring-opening of the DHA scaffold to generate the NBD-VHF form, as seen by the distinct VHF absorption band arising around 470 nm (close to that of 1aVHF at 464 nm (ref. 8)) accompanied by a decrease in the characteristic DHA absorption band around 360 nm. In addition, 1H NMR spectroscopic studies performed in toluene-d8 (at concentrations of 10−2−10−3 M) of all six DHA–NBD compounds verified that irradiation at the onset of the respective DHA subunits solely led to the conversion of the DHA subunit to the VHF and no conversion of the NBD subunit to QC (see ESI Fig. S25–S39†). The VHFs are not photo-active, but VHF-to-DHA ring-closures back to the initial NBD–DHA states were successfully achieved thermally. Both the ring-opening and ring-closure events appeared with isosbestic points in the absorption spectra, indicating that only one reaction occurs each way (however, small degrees of decomposition of the systems cannot be excluded). By following the decay of VHF absorbance at 50 °C (first-order kinetics), the rate of back-reaction was obtained by curve fitting the data with a single-exponential fit. For the NBD-VHFs 4bNBD-VHF and 5bNBD-VHF, the half-lives were similar (see Table 1), in the range of 50–70 min. For NBD-VHFs 3bNBD-VHF and 3bNBD-VHF, the half-lives were longer, reaching almost 600 min for 3bNBD-VHF. Thus, as seen before,11 an electron-withdrawing alkyne-linker placed on the seven-membered ring has a significant impact on the rate of ring-closure events.

### Table 1  UV-Vis absorption data (longest-wavelength absorption maxima) at 25 °C and VHF/QC half-lives at 50 °C in toluene.

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<th>NBD-VHF</th>
<th>QC-VHF</th>
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<td>λmax [nm] (ε × 10^3 M⁻¹ cm⁻¹)</td>
<td>λmax [nm] (ε × 10^3 M⁻¹ cm⁻¹)</td>
<td>t₁ [min] (50 °C)</td>
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<tr>
<td>3a</td>
<td>sh 365 (15.9) 335 (21.7)</td>
<td>478 (33.5)</td>
<td>587</td>
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<tr>
<td>3b</td>
<td>406 (27.5)</td>
<td>459 (21.5)</td>
<td>59</td>
</tr>
<tr>
<td>4a</td>
<td>392 (34.1)</td>
<td>473 (24.2)</td>
<td>52</td>
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<tr>
<td>4b</td>
<td>361 (23.1)</td>
<td>467 (21.7)</td>
<td>70</td>
</tr>
<tr>
<td>5a</td>
<td>345 (23.7)</td>
<td>469 (27.5)</td>
<td>53</td>
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<tr>
<td>5b</td>
<td>355 (35.1)</td>
<td>473 (24.2)</td>
<td>52</td>
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Data obtained from a single exponential fit of the growth of absorption of the NBD-DHA λmax. | Data obtained from a single exponential fit of the decay of VHF absorption. | Data obtained from the sum of two exponential functions of the growth of the absorption of the NBD-DHA λmax locking the t₁ value (see eqn (1)) to that obtained from the decay of VHF absorption (of QC-VHF). | Data from the growth of absorbance at 355 nm could not be fitted with a single exponential fit (see ESI Fig. S47†).
back-reaction, and the “cyanoethylene” moiety present in 3b enhances the electron-withdrawing effect further. As previously reported\textsuperscript{11} for 7-substituted DHAs, E/Z isomerization around the exocyclic double bond of the VHF results in the accumulation of the 6-substituted isomer upon several photo/thermal cycles (see ESI Fig. S41\textsuperscript{†}). For all the NBD-DHAs 3a/bNBD-DHA—5a/bNBD-DHA, light irradiation at 290 nm in toluene (an absorption cut-off ~290 nm) resulted in selective isomerization of the DHA unit to form the NBD–VHF states. Changing the solvent to cyclohexane (an absorption cut-off ~190 nm) allowed for shorter wavelength (220–240 nm) light to be used. However, the formation of NBD–VHF isomers was obtained in all cases 3–5. In an attempt to reach the QC–VHF state, all of the formed NBD–VHFs were irradiated in toluene at the local maxima (3aNBD–VHF: 360 nm, 3bNBD–VHF: 332 nm, 4aNBD–VHF: 338 nm, 4bNBD–VHF: 320 nm, 5aNBD–VHF: 350 nm, 5bNBD–VHF: 330 nm). In this case, a gradual decrease in the characteristic absorptions at around 320 nm (4bNBD–VHF), 350 nm (5aNBD–VHF), and 330 nm (5bNBD–VHF) was observed for compounds 4bNBD–VHF, 5aNBD–VHF, and 5bNBD–VHF, corresponding to light-induced conversion from the NBD–VHF state to the QC–VHF state. Irradiation of the respective compounds 4aNBD–VHF (320 nm), 5aNBD–VHF (350 nm) and 5bNBD–VHF (330 nm) was performed until changes in the absorption spectrum were observed (corresponding to either full conversion to the QC–VHF state or a photostationary state between the QC–VHF and NBD–VHF states). For NBD–VHFs 3aNBD–VHF, 3bNBD–VHF, and 4aNBD–VHF, no sign of isomerization to the QC–VHF state was observed. Irradiation at various wavelengths between 290 nm and 400 nm resulted only in photodegradation of the three systems. For comparison, we also subjected a 1:1 mixture of DHA 1a and NBD 9 (10\textsuperscript{–2} M) to irradiation at 404 nm until the complete conversion of the 1aDHA into 1aVHF. Subsequently, 9NBD was successfully photoisomerized into 9QC by irradiation at 320 nm. In consequence, the lack of NBD–to–QC photoisomerization of 3aNBD–VHF, 3bNBD–VHF, and 4aNBD–VHF originates from an intramolecular effect rather than from an intermolecular effect. Subsequently, we followed the switching capabilities (the NBD–VHF state to the QC–VHF state) by NMR spectroscopy in toluene-d\textsubscript{4}. Firstly, a 1:1 mixture of DHA 1a and NBD 9 (10\textsuperscript{–2} M) was easily converted from 1aDHA into 1aVHF (with no change of NBD 9) using 415 nm light, and thereafter 9NBD was successfully converted into 9QC using 340 nm light. Secondly, after the formation of the NBD–VHF state of all compounds 3–5, we subjected these NMR samples to light irradiation at 340 nm. For 5bNBD–VHF, we estimate that roughly 70% was converted into 5bQC–VHF. For the other NBD–VHF compounds, no sign of isomerization could be observed in the \textsuperscript{1}H NMR spectra; only decomposition of the NMR samples was observed upon prolonged irradiation (see ESI Fig. S25–S39\textsuperscript{†}). We assign the lack of isomerization of 4aNBD–VHF and 5aNBD–VHF on the NMR scale to a combination of low NBD–to–QC photoisomerization quantum yields as well as to the increased concentrations required for the NMR studies compared to the UV-Vis studies (a difference of 2–3 orders of magnitude), where switchings of 4bNBD–VHF and 5aNBD–VHF were indeed observed.

Gratifyingly, as mentioned above, irradiation of the para-linked 4aNBD–VHF and both of the meta-linked NBD–VHFs 5aNBD–VHF and 5bNBD–VHF at their local maxima resulted in full or partial isomerization to their corresponding QC–VHFs when followed by UV-Vis absorption spectroscopy at concentrations of 10\textsuperscript{–5} M. This could be seen by a decrease in absorbance at the local maximum while the VHF absorbance remained unchanged. After cyclization to the QC–VHFs, the thermal back-reaction to the NBD–DHAs was followed. The half-life of VHF-to-DHA in the three QC–VHF systems (4bQC–VHF, 5aQC–VHF, and 5bQC–VHF) could be easily obtained by following the decay of VHF-absorbance, as there are no interfering absorbance bands in this region (around 470 nm). When following the
decay of VHF-absorbance in the QC–VHF states, similar half-lives were obtained to that for the NBD–VHFs. Thus, the rate of VHF back-reaction seems to be independent of the NBD/QC state.

The half-life of QC-to-NBD in the three QC–VHF systems (4bQC–VHF, 5aQC–VHF and 5bQC–VHF) is more challenging to obtain as the NBD and DHA absorption bands are overlapping. However, as we know the rate of DHA formation (from the VHF decay rate), it is possible to estimate the kinetics of the QC-to-NBD conversions. For all the QC–VHF systems, an approximate half-life for the conversion of the QC moiety was obtained by following the growth of the absorbance peak around 340 nm (4b: 368 nm, 5a: 355 nm, 5b: 326 nm). The growth of absorbance in time, $A(t)$, was fitted as the sum of two exponential functions (eqn (1); where $c_1$ and $c_2$ are constants; $k_1$ and $k_2$ are the rate constants for VHF-to-DHA and QC-to-NBD conversions, respectively, and $A_\infty$ is the absorbance at an infinite time). In this fitting procedure, the $k_1$ rate constants were kept fixed as the numbers obtained from the decay of VHF absorbance (corresponding to VHF half-lives of ca. 53, 70, and 57 min for 4b, 5b, and 5a, respectively). Thereby, QC-to-NBD conversions were found to occur with half-lives of ca. 11–12 min (4b, 5a) and ca. 32 min (5b).

Fitting the growth of the absorbance peak at around 340 nm with only one exponential function gives overall half-lives for the conversion of QC–VHF into NBD–DHA of ca. 45 min for 4b and 5b.

$$A(t) = c_1 e^{-k_1 t} + c_2 e^{-k_2 t} + A_\infty \quad (1)$$

### Copper promoted back-reaction

To reach the QC–DHA selectively, it was attempted to accelerate the back-reaction of the VHF moiety of the QC–VHF state. Lewis acids have shown to have a pronounced effect on the reversible switching of DHA/VHF systems. Hence, a strong Lewis acid such as AlCl₃ promotes ring-opening¹⁶ (DHA-to-VHF), while a Cu(i) salt (Cu(MeCN)₄BF₄) greatly induces ring-closure¹⁷ (VHF-to-DHA; data for 1a are included in Table 2). Similarly, cobalt-based catalyst systems for the effective triggering of the QC-to-NBD conversion have been reported in the literature.¹⁸ Furthermore, it was of interest to test whether the NBD/QC scaffold would show stability towards the Cu(i) salt, as an analogous NBD has shown instability in the presence of similar Cu(i) salts.¹⁸ Compound 5a was chosen (devoid of a cyano group at NBD), as it is postulated that the catalytic effect of the Cu(i) salt is mediated by coordination to the vinlylic cyano groups of VHF. For comparison with the earlier studies

![Fig. 2 UV/Vis absorption spectra recorded at 25 °C in toluene at concentrations of 10⁻⁵ M. Top: Spectra of NBD–DHA systems: 3aNBD–DHA (magenta), 3bNBD–DHA (cyan), 4aNBD–DHA (black), 4bNBD–DHA (red), 5aNBD–DHA (blue), 5bNBD–DHA (green). Middle: Spectra of NBD–VHF systems: 3aNBD–VHF (magenta), 3bNBD–VHF (cyan), 4aNBD–VHF (black), 4bNBD–VHF (red), 5aNBD–VHF (blue), 5bNBD–VHF (green). Bottom: Spectra of QC–VHF systems (or a photostationary state between the QC–VHF and NBD–VHF): 4bQC–VHF (red), 5aQC–VHF (blue), 5bQC–VHF (green).](image)

### Table 2 Kinetics data for VHF-to-DHA and QC-to-NBD conversions at 25 °C in CH₂Cl₂ with and without the addition of Cu(MeCN)₄BF₄

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</tbody>
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<sup>a</sup> In the presence of 1 equiv. of Cu(MeCN)₄BF₄. <sup>b</sup>In the presence of 8 equiv. of Cu(MeCN)₄BF₄. <sup>c</sup> Obtained from exponential growth of 5aNBD–DHA at 355 nm after the 16<sup>th</sup> minute of back-reaction (see ESI Fig. S31). <sup>d</sup>Obtained from exponential growth of the absorption of the NBD–DHA at 355 nm after the 16<sup>th</sup> minute of back-reaction (see ESI Fig. S31). <sup>e</sup>Data obtained from a single exponential fit of the decay of the Cu(i)VHF absorption. <sup>f</sup>Data from exponential fits of the growth of absorption of the NBD–DHA. <sup>g</sup>Obtained from exponential growth of the absorption of the NBD–DHA. <sup>h</sup>Obtained from exponential growth of the absorption of the NBD–DHA.
on 1a,17 CH2Cl2 at 25 °C was used as the solvent. Firstly, the switching properties of 5a in this solvent were investigated (see Table 2). Irradiation of 5a into DHA at 400 nm resulted in isomerization to 5a-NBD-VHF. The decay of VHF absorbance was then followed and fitted with a single exponential fit, which provided a VHF-to-DHA half-life of 428 min. Complete photoisomerization to 5a-NBD-VHF could be obtained by irradiation of 5a-NBD-VHF at 347 nm. Interestingly, the QC scaffold had a significantly increased rate of back-reaction in CH2Cl2 at 25 °C, resulting in a half-life of only 3 min (compared to 11 min in toluene at 50 °C). The VHF moiety in 5a-QC-VHF had a similar half-life to that in 5a-NBD-VHF.

Addition of 1 equiv. of Cu(MeCN)4BF4 to 5a-NBD-VHF in CH2Cl2 at 25 °C resulted in an almost 20-fold increase in the rate of the VHF-to-DHA back-reaction (Table 2). Thus, a half-life of 26 min was obtained, similar to that reported for 1a.17 Addition of 8 equiv. of the Cu(i) salt resulted in an almost 60-fold decrease in the VHF half-life (Scheme 5). Due to the markedly increased rate of back-reaction of the VHF moiety upon addition of 8 equiv. of the Cu(i) salt, these conditions were applied in the case of 5a-QC-VHF in an attempt to reach the 5a-QC-DHA state. However, owing to the fast rate of back-reaction of the QC moiety, 5a-QC-DHA could not be reached. The half-life of the VHF moiety was obtained from a single exponential fit from the decay of the VHF absorption band. Unfortunately, it was not possible to obtain any conclusive results about the half-life of the QC moiety with the addition of 8 equiv. of the Cu(i) salt. However, an overall half-life (5a-QC-VHF-to-5a-NBD-DHA) of 9 min was obtained from the growth of the absorption band at 355 nm fitted by a single exponential function. Nevertheless, we suspect that the half-life of the QC subunit in 5a-QC-VHF is 3 minutes or less.

**Computational study**

To understand why some NBD-VHFs (4b-NBD-VHF, 5a-NBD-VHF and 5b-NBD-VHF) could be fully photoconverted, while other conjugates could not (3a-NBD-VHF, 3b-NBD-VHF and 4a-NBD-VHF), we performed a computational study using time-dependent density functional theory (TD-DFT) at the CAM-B3LYP/6-311+G (d) level of theory in a dielectric medium of toluene (details are provided in the Experimental section). Fig. 3 shows the calculated natural transition orbitals (NTOs) and simulated UV-Vis absorption spectra of the lowest-energy conformers of 4a, 4b, 5a, and 5b, while calculated absorption spectra for 3a and 3b are shown in the ESI.† Gibbs free energies of the lowest-energy conformers of all compounds are also listed in the ESI.† The NTOs are the highest occupied transition orbitals (HOTOs) and the lowest unoccupied transition orbitals (LUTOs) that correspond to the transitions (labeled I and II) shown in the UV-Vis absorption spectra. The NTOs of the para-substituted system 4a-NBD-VHF (green box) show that transition II is not localized on the NBD unit, but it involves the VHF unit to a large extent. This perturbation of the photochromic unit may explain its reluctance to undergo NBD-to-QC conversion; the system should not be considered to be isolated NBD and VHF units, with local excitations, but rather as a new chromophore. The NTOs of 4b-NBD-DHA (blue box, top) show some extension of the DHA chromophore part, but as we see from the experiments, this more limited extension does not destroy the DHA-to-VHF photoactivity. For 4a-NBD-VHF (green box, middle), transition II also involves part of the VHF unit, but not to the same significant degree as that observed for 4a-NBD-VHF and, indeed, this compound was able to undergo the NBD-to-QC conversion.

The NTOs of the meta-substituted systems (5a and 5b) show that the HOTOs and LUTOs are more localized on the two different chromophores for all the various forms. Indeed, these compounds were able to undergo both DHA-to-VHF and NBD-to-QC conversions. Decoupling of individual photoswitches using the meta-connectivity principle has also been recently explored in experimental and computational studies on meta-substituted bis- and trisazo-benzenes.19 The two transitions I and II of 5a-NBD-DHA and 5b-NBD-DHA (blue boxes), corresponding to the NBD-to-QC and DHA-to-VHF photoisomerizations, are rather close in energies. This agrees with the experimental finding that the NBD-to-QC conversion could not be done without an accompanying DHA-to-VHF conversion. Moreover, excitation of NBD may lead to energy transfer to DHA, inducing its photoisomerization into VHF. However, experimentally, the DHA-to-VHF conversion was in fact achieved selectively, which is not so easy to rationalize. Overall, the NTOs give a good qualitative picture of the switching capabilities of the individual systems that are in good agreement with the experimental findings, but, of course, the reaction progress on the excited-state energy surfaces is more complicated than the simplified picture we have used here to rationalize our experimental findings.

In the context of MOST systems, the energy storage capacity is an important parameter, that is, the energy difference between the low- and high-energy isomers. For systems 3–5, an initial DHA-to-VHF isomerization causes a rather small increase in Gibbs free energy of 8–10 kJ mol⁻¹ in toluene (based on the most stable s-trans-VHF conformer), while the second isomerization (NBD-to-QC) causes an additional, much

![Scheme 5](image-url)
larger increase of 96–101 kJ mol\(^{-1}\). The storage capacity of the DHA-to-VHF isomerization is comparable to calculations at the same level of theory for the parent DHA/VHF system in a dielectric medium of cyclohexane (\(\varepsilon_{\text{st}} = 2.017\) and \(\varepsilon_{\text{op}} = 2.035\)) with a storage capacity of 10 kJ mol\(^{-1}\).\(^{20}\) More surprisingly, the storage capacity of the NBD-to-QC isomerization is higher than that of the unsubstituted NBD/QC photothermal switch (see Scheme 1), which has a storage capacity of 88 kJ mol\(^{-1}\) at the same level of theory in a dielectric medium of toluene (see ESI Tables S1–S6\(^\dagger\)). These findings, therefore, prove the possibility...
of linking the two photochromic units without losing their individual energy storage capacities (in kJ mol$^{-1}$), but in fact increase the overall capacity to more than the sum of the individual units, and moreover with the ability to enhance the solar spectrum match. When taking molecular weights into account, we get energy storage capacities for 4b, 5a, and 5b (all of which could experimentally be converted into QC–VHF forms) of 0.27, 0.24, and 0.27 MJ kg$^{-1}$ (in toluene); the number for 5a is slightly lower on account of its higher molecular weight.

**Experimental section**

**General procedures (experimental work)**

All reagents and solvents were obtained from commercial suppliers and used as received unless otherwise stated. THF was collected from an IT (Innovative Technology) installation of model PS-MD-05. All air and moisture sensitive reactions were carried out under an inert atmosphere (argon gas). All handling of photochromic compounds was done in the dark. Purification by column chromatography was carried out on silica gel (flash column, SiO$_2$ 40–63 μm). For purification of DHA compounds, all glassware was wrapped in tin foil to exclude compounds from light. Thin-layer chromatography (TLC) was carried out using commercially available aluminum sheets pre-coated with silica gel (silica 60) with a fluorescence indicator and visualized under UV light at 254 or 365 nm; color change from yellow to red upon irradiation with UV light (40–63 μm, CH$_2$Cl$_2$) and then subjected to repeated flash column chromatography (1) (SiO$_2$ 40–63 μm, 60% toluene/heptane to 80% toluene/heptane), (2) (SiO$_2$ 40–63 μm, 20% EtOAc/heptane), (3) (SiO$_2$ 40–63 μm, 20% THF/heptane) which afforded 3aNBD-DHA (243 mg, 0.54 mmol, 9%) as an orange solid. R$_f$ (80% toluene/heptane) = 0.55. R$_f$ (20% EtOAc/heptane) = 0.33. R$_f$ (20% THF/heptane) = 0.20. m.p.: 73–76 °C. 1H NMR (500 MHz, CDCl$_3$) δ 7.81–7.73 (m, 4H), 7.52–7.42 (m, 4H), 7.38 (t, J = 7.7 Hz, 2H), 6.91 (dt, J = 5.0, 2.6 Hz, 1H), 6.89 (s, 1H), 6.86 (dt, J = 5.0, 2.6 Hz, 1H), 6.63 (dt, J = 11.8, 6.1 Hz, 1H), 6.56 (d, J = 11.3 Hz, 1H), 6.34–6.30 (m, 1H), 6.16 (t, J = 4.5 Hz, 1H), 4.05 (m, 1H), 3.87 (td, J = 4.5, 1.7 Hz, 1H), 3.77 (m, 1H), 2.24–2.20 (m, 1H), 2.12 (br d, J = 6.5 Hz, 1H) ppm. 13C NMR (126 MHz, CDCl$_3$) δ 159.4, 159.3, 143.0, 141.3, 141.0, 140.5, 135.6, 135.6, 132.2, 132.1, 131.8, 131.8, 131.5, 131.4, 130.4, 130.4, 129.5, 129.0, 128.6, 128.0, 126.5, 126.0, 123.8, 123.7, 123.6, 123.6, 120.6, 120.6, 115.1, 115.0, 112.8, 112.7, 99.2, 99.2, 88.3, 88.3, 70.0, 70.0, 57.3, 57.2, 53.4, 52.4, 51.1, 45.1, 45.0 ppm. HR-MS (MALDI + FT-ICR, dithranol): m/z = 447.1856 [M + H$^+$], calcd for [C$_{40}$H$_{33}$N$_4$]$: m/z = 447.18558$.

**Compound 3bNBD-DHA (isolated as a mixture of diastereoisomers).** To a solution of 1d (701 mg, 1.99 mmol) in THF (70 mL) was added acetic acid (1.2 mL, 21 mmol) by tetrabutylammonium fluoride (4.0 mL, 1 M in THF, 4.0 mol) and water. The mixture was stirred for 17 h at rt. The reaction mixture was diluted with EtO (200 mL) and quenched with sat. aq. NH$_4$Cl (100 mL). Organic phase was separated and extracted with sat. aq. NH$_4$Cl (3 × 100 mL), dried with MgSO$_4$, filtered, and concentrated in vacuo. The residue was redissolved in THF (60 mL); then 2b (610 mg, 4.02 mmol) was added, and the mixture was stirred for 17 h at rt. The mixture was filtered with argon. Pd(PPh$_3$)$_2$Cl$_2$ (139 mg, 0.198 mmol), Cul (47 mg, 0.25 mmol) and (iPr)$_2$NH (0.40 mL, 4.0 mmol) were added before the mixture was stirred overnight. The reaction mixture was passed through a plug of silica (40–63 μm, CH$_2$Cl$_2$) and then subjected to flash column...
chromatography (SiO₂ 40–63 μm, 80% toluene/heptane to 100% toluene), which afforded 6 (32 mg, 0.057 mmol, 6%) as a brown oil and 3b₉NBD-DHA (82 mg, 0.21 mmol, 10%) as a dark yellow solid. Compound 3b₉NBD-DHA: Rₜ (toluene) = 0.33. ¹H NMR (500 MHz, CDCl₃) δ 7.77–7.73 (m, 2H), 7.51–7.44 (m, 3H), 6.91–6.89 (m, 1H), 6.89–6.81 (m, 2H), 6.70–6.63 (m, 1H), 6.55 (d, J = 11.3 Hz, 1H), 6.36–6.32 (m, 1H), 6.26–6.20 (m, 1H), 3.90–3.87 (m, 1H), 3.87–3.84 (m, 1H), 3.83–3.79 (m, 1H), 2.32–2.27 (m, 1H), 2.21 (ddd, J = 7.1, 3.4, 1.7 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 153.7, 153.2, 142.2, 142.2, 141.6, 141.5, 140.3, 132.2, 132.2, 131.7, 131.4, 131.4, 130.6, 130.3, 129.6, 129.5, 129.5, 125.9, 125.9, 122.3, 122.3, 120.7, 116.2, 114.8, 112.7, 105.8, 105.8, 83.1, 73.1, 73.0, 57.3, 57.2, 54.3, 54.3, 51.2, 44.9 ppm. HR-MS (MALDI + FT-ICR, dithranol): m/z = 396.14949 [M + H⁺], calcd for [C₂₈H₁₈N₃⁺]: m/z = 396.14952. By-product: 6 (isolated as a mixture of diastereoisomers). Rₜ (toluene) = 0.52. ¹H NMR (500 MHz, CDCl₃) δ 7.76–7.72 (m, 4H), 7.51–7.44 (m, 6H), 6.89 (s, 2H), 6.64 (ddd, J = 11.4, 6.2 Hz, 2H), 6.50 (d, J = 11.4 Hz, 2H), 6.33 (br, d, J = 6.2 Hz, 2H), 6.26 (d, J = 4.8 Hz, 2H), 3.83 (ddd, J = 4.8, 2.2, 1.2 Hz, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 141.6, 140.2, 132.12, 131.2, 131.2, 130.6, 130.2, 129.5, 127.2, 126.5, 121.8, 120.6, 114.8, 112.6, 80.4, 80.4, 73.8, 73.8, 51.1, 44.9 ppm. HR-MS (MALDI + FT-ICR, dithranol): m/z = 559.19266 [M + H⁺], calcd for [C₄₀H₂₂N₄Na⁺]: m/z = 559.19172.

Compound 4b₉NBD-DHA (isolated as a mixture of diastereoisomers). To a solution of 9 (466 mg, 1.76 mmol) in THF/MeOH (20 mL, 1:1, v/v) was added K₂CO₃ (710 mg, 5.14 mmol). The mixture was stirred at rt for 1 h providing 2a after which the reaction mixture was passed through a plug of silica (40–63 μm, CH₂Cl₂). The mixture was almost concentrated in vacuo, then THF (50 mL) was added, and the mixture was again concentrated to 20 mL in vacuo. Compound 4b₉NBD-DHA (331 mg, 0.741 mmol, 62%, based on 1h) as an orange solid. Rₜ (70% toluene/heptane) = 0.40. M.p.: Turns sticky at 84 °C, melts fully at 115 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.88–7.84 (m, 2H), 7.71 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 1H), 6.96 (dd, J = 5.0, 3.0 Hz, 1H), 6.90 (s, 1H), 6.91–6.89 (m, 1H), 6.57 (ddd, J = 11.2, 6.4 Hz, 1H), 6.49 (d, J = 11.2, 6.4 Hz, 1H), 6.36 (d, J = 6.4 Hz, 1H), 6.32 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.83 (dd, J = 10.2, 3.8 Hz, 1H), 4.09 (s, 1H), 3.85 (d, J = 2.1 Hz, 1H), 3.80 (dt, J = 3.8, 2.1 Hz, 1H), 2.28 (dt, J = 6.6, 1.5 Hz, 1H), 2.16 (dt, J = 6.6, 1.5 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 153.7, 153.2, 135.6, 135.6, 132.2, 131.2, 131.2, 129.8, 129.1, 128.6, 128.1, 127.9, 126.3, 126.2, 125.8, 121.5, 119.6, 115.2, 112.8, 100.5, 91.1, 70.0, 57.4, 53.5, 51.3, 45.2 ppm. HR-MS (ESI + FT-ICR): m/z = 447.18548 [M + H⁺], calcd for [C₃₂H₂₃N₅⁺]: m/z = 447.18558.
starting from a comprehensive conformer search. All calculations were performed using Gaussian 16,23 and structures resulting from geometry optimizations were confirmed as true energy minima through harmonic frequency analyses by the absence of imaginary frequencies. Furthermore, the Gibbs free energy calculations, described in the following, include the zero-point vibrational energy and thermal contributions evaluated at a temperature of 298.15 K and a pressure of 1.00 atm.

The structures shown in Scheme 4 (considering only the $R$-enantiomers of DHA) were initially constructed using GaussianView 6,23 and the geometries were optimized using the hybrid functional B3LYP24 and the Pople-style 6-311+G(d) basis set.25 Systematic rotations of 40.0° around the acetylenic part of the two chromophores were then performed, generating 9 distinct conformers of each structure. Subsequently, conformational samplings of the aforementioned conformers were carried out by employing the Confab algorithm implemented using Open Babel 2.4.126 with an energy cutoff of 50.0 kcal mol$^{-1}$ and a RMSD cutoff of 0.3 Å. All conformers were then optimized in a vacuum using the semi-empirical PM7 Hamiltonian as modified by Throssel and Frisch. An in-house script ensured that the s-cis-VHF and s-trans-VHF conformers were correctly categorized, since the two structures mix as a result of the conformer search. The distinct conformers were then identified using a Boltzmann cut-off of 5% and RMSD calculations using the Kabsch algorithm with a tolerance of 0.3 Å.

In order to study the photochromic properties of the molecules, we employed the range-separated hybrid functional CAM-B3LYP28 and the Pople-style 6-31+G(d) basis set as deemed appropriate in previous benchmark studies29 and work on similar systems.30,20,30 Furthermore, the IEF-PCM continuum solvation model31 was used to describe polarization effects of toluene through a static and an optical dielectric constant ($\varepsilon_{st} = 2.374$ and $\varepsilon_{op} = 2.238$, respectively). Thus, geometry optimizations and frequency calculations of the distinct conformers allowed us to construct an energy diagram of the different structures, and subsequent TD-DFT calculations of the first 15 excited states enabled us to simulate the UV-Vis spectra (cf. ESIT). For the lowest-energy conformers, natural transition orbital (NTO) calculations32 (an orbital transformation technique) of the strongest transitions were performed, which allowed us to produce more compact illustrations of the orbitals involved in the photoexcitation process.

Conclusions

In conclusion, a series of NBD–DHA conjugates, substituted with phenyl or cyano groups on the NBD, were prepared by Sonogashira couplings of known DHA and NBD starting materials. Linking the two photochromic compounds using a linearly conjugated phenylethynylene linker resulted in a red-shifted absorption maximum. All the systems effectively underwent isomerization to the NBD–VHF isomer upon irradiation of the NBD–DHA. The position of the linker unit

**Computations – methods**

The photochromic properties of the norbornadiene–dihydroazulene conjugates were theoretically studied by density functional theory (DFT) and its time-dependent analogue (TD-DFT)
and substituent on the NBD showed to have remarkable effects on the switching properties of the NBD–VHF isomer. Hence, connection through the 7-membered ring resulted in the loss of the photochromism of the NBD moieties in 3a and 3b. Interestingly, for the linearly conjugated para-linked systems 4a and 4b, only the cyano-substituted system 4b underwent photoisomerization to the QC–VHF isomer. Contrarily, cross-conjugation through the linker (meta-phenylene) between NBD and VHF resulted in a possible photoisomerization to the QC–VHF isomers of both the phenyl-substituted 5a and cyano-substituted 5b. These findings were rationalized by computational studies by looking at the calculated natural transition orbitals. Moreover, the computational study revealed NBD–VHF conjugates to be (8–10 kJ mol\(^{-1}\)) more energetic than NBD–DHA conjugates, while the second isomerization into QC–VHF increased the energy further by 96–101 kJ mol\(^{-1}\). Interestingly, the conjugates exhibit higher energy storage capacities than that corresponding to the sum of the individual photochromic units.

For none of the systems 3–5, conversion to the QC–DHA isomer could be obtained, as irradiation always resulted in the conversion of DHA into VHF; this, together with the computational study illustrates the need for both NBD and VHF chromophores to be independently optically addressable in order to be able to reach all four different states of the multichromophoric system.

The half-life of the QC moieties was found to be dependent on the solvent, going from 11 min in toluene at 50 °C to only 3 min in CH\(_2\)Cl\(_2\) at 25 °C. The fast back-reaction rate of QC in CH\(_2\)Cl\(_2\) is in line with our recently observed solvent effects of a related NBD/QC system.\(^{21}\) It proved impossible to reach the QC–DHA isomer using a previously published Cu(i)-mediated VHF-to-DHA conversion method. However, the addition of Cu (i) changed the VHF-to-DHA back-reaction to occur on the same time scale as that of the QC-to-NBD conversion. The absence or presence of Cu(i) is thus a convenient way of tuning heat release rates on different or identical time scales of QC–VHF conjugates.

The synthesis presented here, using the Sonogashira reaction in the key coupling step, allows for great modularity in the molecular design and enables the design of future multichromophoric systems with optimised solar capture efficiencies and application-optimized thermal energy release rates.

### Conflicts of interest

**Q6**

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### Notes and references


