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From Molecular Photoswitch to Solar-Thermal Battery Optimization of the DHA-VHF System

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The Dihydroazulene-Vinylheptafulvene (DHA-VHF) photoswitch has been functionalized at several positions, all of which can be used as handles for fine-tuning the absorption, storage and release of solar energy. High energy densities and slow self-discharge rates are essential if the system is to be used for long term solar energy storage.

Introduction

The Dihydroazulene-Vinylheptafulvene (DHA-VHF) system is a two-way molecular switch which can be interconverted between the closed (DHA) and open (VHF) forms by photo/thermal stimulation. Irradiation converts DHA to VHF, and VHF returns to DHA by a ground-state reaction, releasing heat. As the thermal conversion from the metastable VHF state to DHA is exothermic, the system has been proposed as a means of storing solar energy (a solar heat battery), and presents several advantages which make it a good candidate for this purpose.

As VHF is unable to switch back to DHA by irradiation, quantitative conversion from DHA to VHF is possible with a high quantum yield of photoisomerization (Φ > 0.5), allowing efficient use of the solar energy.

The system still presents several challenges that need to be overcome if it is to find application as a solar heat battery. The energy stored in the metastable state (energy density of the system) is approx. 0.1 MJ/kg, or roughly 10% of the energy density of the currently leading candidate (the norbornadiene – quadricyclane system). Furthermore, the half-life of the thermal reversion from VHF to DHA (self-discharge rate) is 218 min (MeCN), and thus too low for long-term energy storage. The optimal system for energy storage applications should thus exhibit a larger energy difference between DHA and VHF, as well as a larger energy barrier between the two. These two properties can be influenced by functionalization of the system at the various positions shown, each affecting the properties in a unique way. In order to find an optimal structure of the system, the effect of functionalizing each position with regard to energy storage and self-discharge rate must be mapped.

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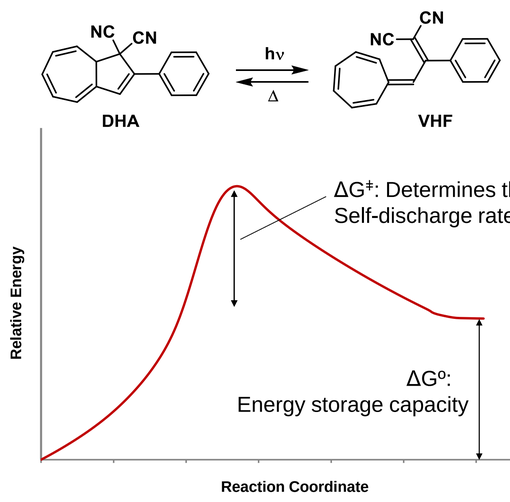
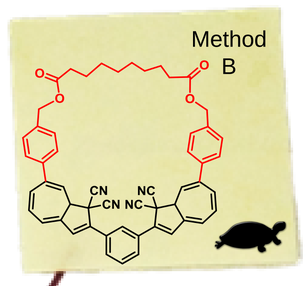
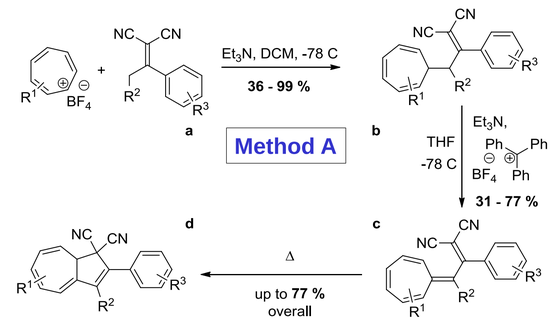




Synthetic approaches

Functionalization of the system can be divided into two overall methods:

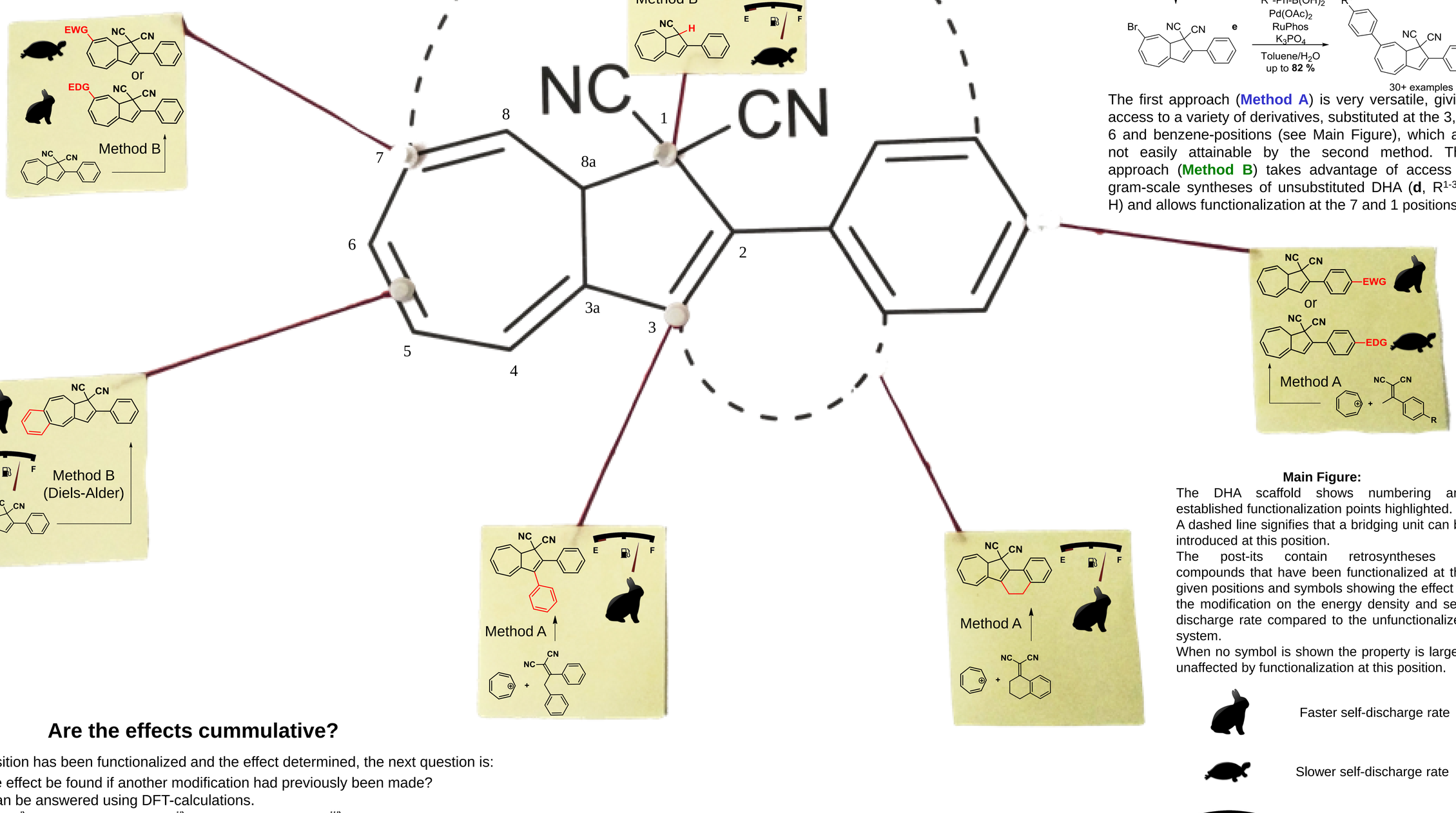
The first is an early-functionalization approach (**Method A**), where functional components (R^1 - R^3) have been introduced during assembly of the VHF isomer (**c**), which can then be ring-closed to the DHA (**d**).



The second is a late-stage functionalization approach (**Method B**), where modifications are introduced on to an already-assembled DHA scaffold (**d**), which can then be converted to the VHF.

Method B

The first approach (**Method A**) is very versatile, giving access to a variety of derivatives, substituted at the 3, 5, 6 and benzene-positions (see Main Figure), which are not easily attainable by the second method. This approach (**Method B**) takes advantage of access to gram-scale syntheses of unsubstituted DHA (**d**, R^{1-3} = H) and allows functionalization at the 7 and 1 positions.



Main Figure:

The DHA scaffold shows numbering and established functionalization points highlighted.
A dashed line signifies that a bridging unit can be introduced at this position.
The post-its contain retrosyntheses of compounds that have been functionalized at the given positions and symbols showing the effect of the modification on the energy density and self-discharge rate compared to the unfunctionalized system.
When no symbol is shown the property is largely unaffected by functionalization at this position.

Faster self-discharge rate

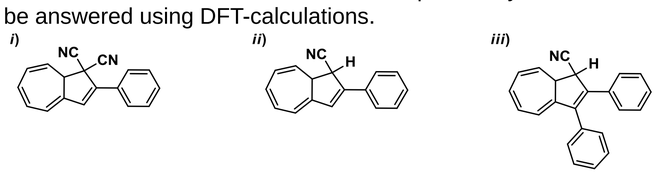
Slower self-discharge rate

Energy density increased

Energy density decreased

Are the effects cummulative?

Once a new position has been functionalized and the effect determined, the next question is:
Would the same effect be found if another modification had previously been made?
This question can be answered using DFT-calculations.



	i)	*ii*)	*iii*)
Calculated Energy Density*	61 kJ/kg (15.7 kJ/mol)	253 kJ/kg (58.5 kJ/mol)	211 kJ/kg (64.9 kJ/mol)
Calculated Half-life*	41 hrs	133 yrs	14 yrs
	Too fast Too little energy stored	Too slow Better storage capacity	Closer to optimal self-discharge rate Higher storage capacity but also higher mass

*Calculations were carried out in acetonitrile as solvent using the IEF-PCM model and M06-2x/6-311+G(d) method.

In the above case the system is modified at the 1-position (***ii***) to yield a higher storage capacity (relative to parent ***i***), but now the half-life is too high, and needs to be reduced. This can be done by an additional modification at the 3-position (***iii***), in which case the effects are maintained, and furthermore stack with the effects of modification on the 1-position, to yield a higher energy storage (which is counterbalanced by the higher weight) and a lower half-life. This ”stacking” of the individual effects allows us to fine-tune the properties until a ”sweet spot” is found.

Conclusion

If the DHA-VHF molecular switch is to be used in solar energy storage applications several properties have to be optimized. Foremost among these are the energy density and self-discharge rate, which can be modified by functionalization of the system.

Synthetic protocols for functionalization of several positions have now been described, allowing fine-tuning of the properties by combining several modifications. The synergy of the modifications can be probed by DFT-calculations, so that predictions can be made as to which combinations will have a favorable result on the properties in focus, and which approaches are to be avoided. The integration of DFT-calculations and an increasing number of functionalization protocols makes the DHA-VHF toolbox a versatile one, with which a future solar heat battery component may one day be realized.

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