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Optimization of the DHA-VHF System

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The Dihydroazulene-Vinylhexafulvene (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-Vinylhexafulvene (DHA-VHF) system is a two-way molecular switch which can be interconverted between the closed (DHA) and open (VHF) forms by photothermal 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 possible candidate for a solar thermal battery.

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 photosimomization (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/g, or roughly 10% of the energy density of the currently leading candidate (the norbornadene – quinazoline 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. Two of these 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 evaluated.

Are the effects cumulative?

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.

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 (FR - FF) have been introduced during assembly of the VHF scaffold (d), 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.

Main Figure:

The DHA-VHF molecular switch can 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 blocka a versatile one, with which a future solar heat battery component may one day be realized.

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.

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References


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*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 (d) to yield a higher storage capacity (relative to parent a), 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 (b), 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.