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Skov, Anders Bo; Vlaseanu, Alexandru; Broman, Søren Lindbæk; Cacciarini, Martina; Nielsen, Mogens Brøndsted

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

Anders B. Skov, Alexandru Vlaseanu, Søren L. Broman, Martina Cacciarini, and Mogens Brøndsted Nielsen

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 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 potential candidate for such a system.

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/g, or roughly 10% of the energy density of the currently leading candidate (the nortrobirane – quazicyclone 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.

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.

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 approaches

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

The first is an early-functionalization approach (Method A), where functional components (F1 – F4) 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 scaffold shows numbering and established functionalization points highlighted. A dashed line signifies that a tetratomic unit can be introduced at this position. The post to contain retinocycles of compounds that have been functionalized at the green 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.

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References


Calculations were carried out in acetone/ tetrahydrofuran 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 d), 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 (d), 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.