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Skov, Anders Bo; Vlasceanu, 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 Vlasceanu, 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 possible candidate.

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 photocromismization (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 norbornadiene – quadricyclane system). Furthermore, the half-life of the thermal reversion from VHF to DHA (self-discharge rate) is 218 min (MgCN), 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.

**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 (R1 - R5) have been introduced during assembly of the VHF scaffold (d), which can then be ring-closed to the DHA (g).

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

**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 protocols for functionalization of several positions have now been described, allowing fine-tuning of the system 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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**References**


