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An effective trigger for energy release of vinylheptafulvene-based solar heat batteries

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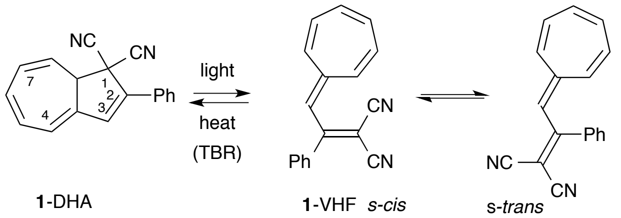
Stoichiometric copper(I) tetrakis(acetonitrile) is found to activate the thermal ring-closure reaction of a series of high-energy vinylheptafulvene isomers to the corresponding low-energy and photoactive dihydroazulenes, allowing the release of energy upon request.

The design of functional organic materials for solar energy conversion and storage has attracted the attention of scientists interested in actively facing the energy crisis and the imminent end of fossil fuel reserves. One such possibility is represented by photochromic molecules as candidates for harvesting and storing solar energy in metastable photoisomerisation products.[1-9] Such systems have been termed solar heat batteries. Among others, the dihydroazulene/vinylheptafulvene (DHA/VHF) pair is a photo/thermoswitch that has been purposely developed towards energy storage over the past few years.[10-13] Its key feature is being a system in which the two components can be interconverted by two different stimuli (T-type photoswitch). Indeed light triggers the ring-opening of **1**-DHA to the high energy photo-isomer **1**-VHF,[14,15] and a thermally induced retro-cyclization of **1**-VHF (TBR, thermal back reaction) regenerates **1**-DHA (Scheme 1) with half-lives ranging from 218 min (in CH_3CN), 545 min (in CH_2Cl_2) to 2333 min (in cyclohexane).[16] The TBR is also accompanied by a release of energy and an important challenge is to be able to prompt this process upon demand, ideally by applying a certain external stimulus. Recent functional modifications of the parent couple **1**-DHA/VHF have shown the ability to improve the performance of the system in terms of energy density and of tuning the lifetime of the corresponding VHF form by substitutions at positions 1, 3, 4 and 7 of the dihydroazulene *core* (see Scheme 1 for numbering).[17] In addition, both acyclic compounds and strained macrocycles bearing two DHA units have recently been explored.[13,23] Importantly, in the case of a strained macrocycle, one VHF unit reverted within hours back to DHA, which is interesting for immediate energy release, conversely, it took weeks for full discharge of the second VHF, potentially interesting for long-term needs.[13] To date, it has been possible to tune VHF half-lives from milliseconds to years, but for some of the long-lived VHFs, the main drawbacks are instability and the need to find an efficient trigger to release the energy of the system upon demand.

In a previous communication we reported on the effects of Lewis acids (LA) upon this reaction dynamic.[19] On one hand, a ring opening occurred when **1**-DHA was treated in the dark with a strong LAs such as $AlCl_3$, while the TBR was driven by addition of excessive amounts of LAs such as Zn(II) and Ag(I) salts in 1,2-dichloroethane (DCE). Here we bring the study a major step forward, showing the strong effect of copper(I) tetrakis(acetonitrile) salts on a series of DHA derivatives (Figure 1) for inducing the TBR and hence energy release from the VHF to the DHA form as a mean to address energy release upon demand. Gratifyingly, using stoichiometric amounts of the copper promoter turned out extremely efficient.



Scheme 1. Parent DHA/VHF photochromic system **1** and the two conformers of VHF (s-*cis* and s-*trans*).

In our previous work,[19] we described how the addition of large excess (10-250 equiv.) of ethereal $ZnCl_2{}^{\cdot}(Et_2O)_2$ or AgOTf in DCE could enhance the rate of the TBR from **1**-VHF to **1**-DHA. However, $ZnCl_2$ tended to precipitate out of solution in complete absence of Et_2O and forced the use of complicated solvent mixtures. Hydrated AgOTf gave cloudy solutions, prevented only by the use of the presumably etherate form

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$Ag(Et_2O)_3OTf$. In addition, this enhancement of the TBR did not occur in polar solvents containing accessible lone pairs, such as acetonitrile, acetone, ethyl acetate and ethanol. We therefore turned our attention to other stable LAs, commercially available and of good solubility in polar solvents, and thus we selected $Cu(CH_3CN)_4BF_4$ and $Cu(CH_3CN)_4PF_6$, which were previously used extensively by Sauvage and co-workers for coordination with phenanthrolines and the template-assisted synthesis of mechanically interlocked molecules.[20]

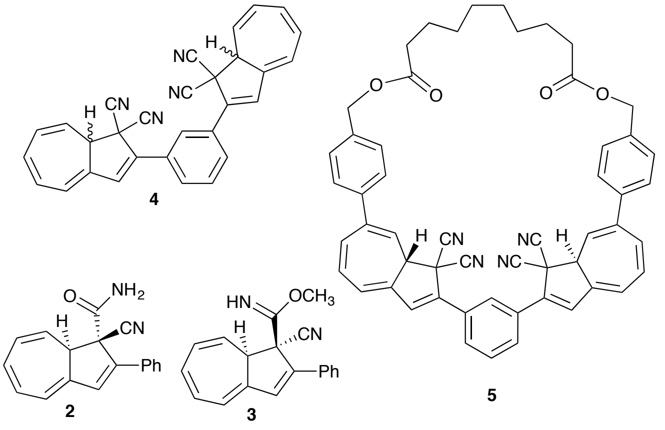

Figure 1. DHAs **2**-**5** studied in the present work in addition to **1** (**2**, **3** and **5** as racemic mixtures, **4** as mixture of diastereomers).

We initially switched the solvent of the studies from DCE to acetone, a more polar solvent that according to previous results should enhance the speed of the TBR,[16] and at the same time is containing two lone pairs on oxygen capable of interacting with copper. Solutions of **1**-DHA in acetone were irradiated at their absorption maximum (365 nm), resulting in a quantitative conversion to the corresponding **1**-VHF. Then UV-Vis absorption spectra were acquired under different conditions, *i.e.* at temperatures of 25°C and 35°C, and in or without the presence of 1-4 equivalents of a $Cu(I)(CH_3CN)_4$ salt.[21] The half-lives of the VHFs were determined by fitting the data with an exponential function. Control experiments were also run with $Ag(CH_3CN)_4BF_4$, in light of the previous studies reported with Ag(OTf). The results indicated a drop of the half-life in acetone from 422 min to 115 min at 25 °C with 1 equiv. of Cu(I) (Table 1), to 64 min at 35 °C still with 1 equiv. and to 49 min with 4 equiv. at 35 °C. The TBR is hence even faster than in the more polar solvent acetonitrile (half-life of 218 min).[16] Only a slight improvement was registered upon addition of more than a stoichiometric amounts of Cu(I) and no effect was recorded in the presence of $Ag(CH_3CN)_4BF_4$. Since it is known that Ag(I) can enhance the ring closure in DCE,[19] the absence of such an effect suggests that the nitriles may coordinate stronger to Cu(I).

Table 1. Half-lives ($t_{1/2}$) at 25 °C of the TBR (VHFs to DHAs) in neat solvent or in the presence of $Cu(CH_3CN)_4BF_4$ (1 equiv. per DHA unit (**1**-**4**), >2 equiv. per DHA unit (**5**)).

	$t_{1/2}$ (min)				
DHA/ VHF	Me_2CO	Me_2CO + Cu(I)	CH_2Cl_2	CH_2Cl_2 + Cu(I)	CH_3CN
1	422	115	545[16]	18-22	218[16]
2	15.1	0.9	1.1	< 0.5	2.5[22]
3	-	n.d.	-	n.d.	>4d[22]
4	675	70-75	346, 572[18]	5, 35-38	140, 160[18]
5	10% discharge in 24 h	10% discharge in 2-3 h	-	69, 534	77, 5455[13]

Next we changed the solvent to dichloromethane (DCM), a non-competitive medium, which had a drastic effect. Addition of 1-10 equiv. of Cu(I) to the orange solution of **1**-VHF (λ_{max} 475 nm in DCM) resulted in a colour change to pink-violet and a red-shift in the longest-wavelength absorption up to 520 nm (1 equiv.) or 545 nm (10 equiv.) was measured, strongly indicating complexation (Figure 2). Indeed the half-life of **1**-VHF in DCM shortened to 18-22 min at room temperature in the presence of 1 equiv. of Cu(I), while it was 545 min without the metal ions present (Table 1). Addition of catalytic (0.2 equiv.) Cu(I) furnished a half-life of 83-91 min, but if running a second cycle (*i.e.* irradiating the cuvette already in the presence of the Cu(I) promoter) the half-life increased to 223 min, suggesting a photo-degradation of the complex (see ESI).[23] The use of 10 equiv. of Cu(I) enhanced the speed of the ring-closure to 9 min. The strong complexation effect was also evidenced by the observation of very different irradiation times to fully convert the DHA to the VHF form, in the presence (5 min) or in the absence (2 min) of Cu(I). Therefore coordination presumably occurs to a significant degree in both DHA and VHF forms, although we expect the lone pair donor strength of the nitriles being much higher for the VHF on account of the electron donor properties of the vinylheptafulvene. Efforts to determine an accurate association constant for the complex **1**-VHF@Cu(I) using the UV-Vis dilution method were in vain, because the results were compromised both by the fast TBR, which is occurring within the dilution time scale, and by an extended overlap of the **1**-VHF and **1**-VHF+Cu(I) absorption spectra. For the TBR, it is particularly important to note that calculations have shown[24] that the $C(CN)_2$ in the transition state structure carries a significant negative charge and the seven-membered ring a positive charge. Thus, copper complexation may stabilize this state (see ESI).

Interestingly, the introduction of a copper-scavenger allowed the cycle to be repeated. Hence, upon addition of ethylenediamine to the solution of **1**-VHF with Cu(I) a visible naked-eye colour change occurred, from pink to orange (Figure 2), at the same time bringing back the rate of the TBR to the pre-copper level. If ethylenediamine is added after the TBR is completed (*i.e.* the "energy stored" has been released), the Cu(I) is seized and uncomplexed **1**-DHA recovered.

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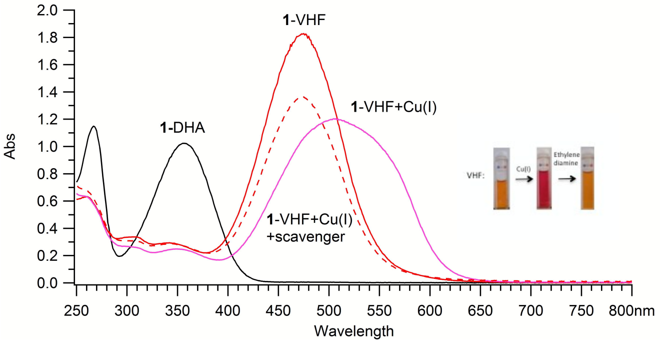

Figure 2. UV-Vis absorption spectra in CH_2Cl_2 at 25 °C of **1**-DHA (black curve, $6.2x10^{-5}$ M), **1**-VHF (red curve, $6.2x10^{-5}$ M), **1**-VHF+Cu(I) (pink curve, **1**-VHF: $4.3x10^{-5}$ M, Cu(I): $4.7x10^{-5}$ M), **1**-VHF+Cu(I)+ excess of ethylenediamine (red broken curve).

Recyclability experiments were performed to estimate whether the system efficiency was compromised by the demetallating agent, and to compare the kinetics of the TBR after some cycles. The VHF half-lives after consecutive cycles are reported in Figure 3. Every full cycle was constituted by four steps: (i) irradiation at 365 nm of **1**-DHA to **1**-VHF until no **1**-DHA is left, (ii) addition of ca. 1 equiv. of Cu(I) solution in DCM, (iii) recording of the UV-Vis absorption spectra of the TBR until no **1**-VHF is left, (iv) addition of a stoichiometric amount of ethylenediamine in DCM to bring the system back to the pre-copper status. After subsequent copper addition/demetallation cycles, the half-life of **1**-VHF did not change significantly (fluctuations likely originate from small variations in the exact amount of the added ethylenediamine, see ESI).

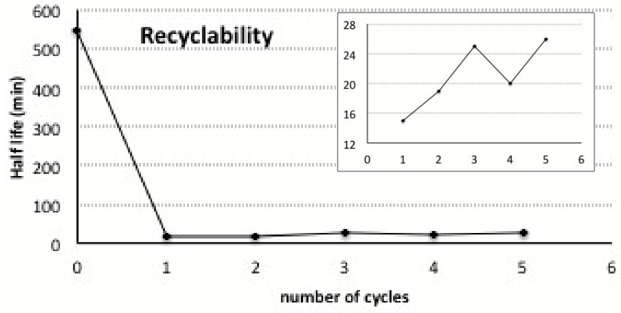

Figure 3. Recyclability of the system (irradiation, Cu(I) addition, TBR, ethylenediamine addition) reported as half-life of **1**-VHF *vs* cycle. At “cycle zero”, the half-life is reported without addition of Cu(I) promoter.

Then we focused our interest towards a selection of previously reported DHAs **2**-**5**,[13,18,22] for elucidating the influence of different functional groups and the number of DHA units with the possibility for multiple nitriles to coordinate simultaneously. We investigated the effect of the Cu(I) additive on the TBR both in acetone and DCM. In acetone only a slight change in the absorption maxima (<4 nm) of the DHA and VHF forms was detected in the presence or absence of Cu(I), except for **2**-VHF, whose absorption maximum red-shifted from 413 nm to 450 nm with Cu(I) (1-3 equiv.) in acetone, evidencing a strong complexation effect. Nevertheless it was not possible to evaluate the binding constant of the **2**-VHF@Cu(I) complex due to the extremely fast TBR. The half-life was barely measurable at ambient temperature, changing from 15 min in neat acetone to 0.9 min in the presence of Cu(I). In this case, both a nitrile and an amide offer potential binding groups for complexation with copper,[25] but we do not have any experimental evidence on which is the one driving the effect. On going experiments are focusing on chelating the amido group instead of the nitrile, to expand the research on this promising candidate for the development of fast responsive materials. Results became even more interesting when moving to DCM as the solvent. An unexpected value of TBR of 1.1 min was recorded for **2**-VHF in neat DCM, which when compared to 2.5 min in CH_3CN and 15.1 min in acetone suggests a different ring-closure mechanism from that of the **1**-VHF. Indeed for the electrocyclic cyclization from **1**-VHF to **1**-DHA a zwitterionic TS was hypothesized and supported by an empirical linear correlation between the logarithm of the rate constant and the Dimroth-Reichardt solvent polarity parameter,[16] as well as by Hammett correlations obtained from variously substituted VHFs.[26] Further studies are on going on this substrate, but addition of 1 equiv. of Cu(I) to a solution of **2**-VHF gave an instantaneous and complete TBR (full recovery of **2**-DHA within less than 30 s after the copper addition).

On the other hand, when the amide is replaced by an imidate group, as it is for compound **3**, we neither succeeded to induce a complete TBR, nor to limit the decomposition previously reported.[22] Besides, an extended overlapping of the UV-Vis absorption spectra of **3**-VHF and **3**-DHA prevents the possibility of selected irradiation and likely provokes other photo-induced processes. Still a blue-shift was detected upon addition of Cu(I), but no TBR to a DHA form was evidenced neither in acetone nor in DCM.

As for the dimeric system **4**-VHF-VHF, the half-life in acetone is reduced from 675 min to 70-75 min (with 1-4 equiv. of Cu(I)); moreover, in acetone only one half-life is detected, while in acetonitrile two distinct and sequential ring-closures were previously observed, but not differing drastically.[22] In DCM the half-lives of the first and the second TBR were determined to 346 min and 572 min, respectively. Upon addition of 0.5-2.5 equiv. of Cu(I) per DHA unit, the absorption maximum of **4**-VHF-VHF was redshifted from 470 nm to 495-515 nm. The irradiation times for DHA to VHF ring-openings changed, from 2 min (first ring opening to DHA-VHF) and ca. 10 min (second ring opening to VHF-VHF), to 4 min and more than 30 min in the presence of the copper salt. As expected, the copper effect on the TBR was extremely strong also on this substrate. Two distinct half-lives, described by a double exponential decay, were always detected when varying the equivalents of Cu(I) per DHA unit from 0.5 to 2.5. Thus by addition of 0.5 equiv. of Cu(I) per DHA unit, we measured two distinct half-lives of 9 min and 66 min; by addition of 1.3 equiv. of Cu(I) per DHA unit the half-lives decreased to 5 min and 37 min, and by addition of 2.5 equiv. of Cu(I) per DHA unit to 5 min and 23 min.

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Finally we investigated the effect of Cu(I) on the switching properties of macrocycle **5**, constituted by a conformationally constrained double-DHA, which has shown interesting charge/discharge properties (fast and ultraslow TBRs for the two VHFs) if compared to the corresponding acyclic structural analogue **4**.[13] The decay that describes the TBR of the **5**-VHF-VHF structure turned out to be very complex in the presence of Cu(I), suggesting the presence of multiple equilibria in solution (DHA-DHA, DHA-VHF, VHF-VHF and corresponding complexes with copper), and the data are difficult to fit with a simple model. Although the very first part of the decay appeared as a mono-exponential function in acetone, only a qualitative evaluation of the "discharge" of the system was possible (*i.e.* percentage reduction of the absorbance of VHF within time). A 10% discharge was obtained in acetone in the absence of Cu(I) within 24 h, while the presence of Cu(I) (3 equiv.) induced 10% discharge within only 2-3 h. Moreover, after 24 h in the presence of Cu(I) a 35% discharge of the system was recorded. No additional significant information could be extrapolated from the TBR data in acetone. On the contrary, when macrocycle **5** was investigated in DCM with 2-3 equiv. of Cu(I) per DHA unit, recovery of more than 75% of **5**-DHA-DHA was possible already after 22 h at 25 °C (Figure 5). This result should be compared to half-lives in the polar solvent acetonitrile (promoting the TBR) of 77 min and 5455 min (91 h). In the presence of Cu(I), the decay was modelled through a double exponential decay giving half-lives of 69 min and 534 min. Thus, we were able to activate the second TBR of **5**, which was "on pause" for energy storage, and to release it upon demand. Addition of ethylenediamine restored the pre-copper system (see video in ESI).

In conclusion, we have shown that the ring-closure of VHFs to DHAs can be very well activated by stoichiometric Cu(I) ions both in acetone, a competitive Lewis basic solvent, and even more effectively in dichloromethane upon complexation of the VHF form. Importantly, we have proved that this complexation is reversible and also allows a faster release of energy in the case of the long-lived VHFs of macrocycle **5**. This is a significant step forward for triggering energy release in the DHA/VHF solar heat battery system.

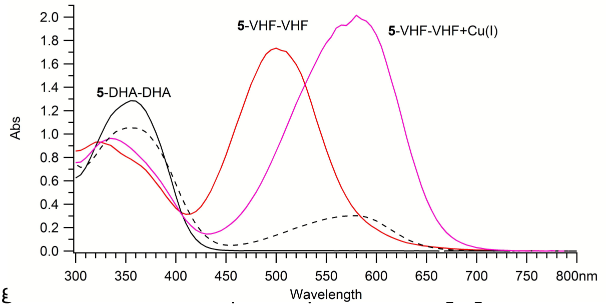

Fig f **5**-DHA-DHA (black curve, 5.7x10^{-5} M), **5**-VHF-VHF (red curve, 5.7x10^{-5} M), **5**-VHF-VHF+Cu(I) (pink curve, **5**-VHF-VHF: 5.5x10^{-5} M, Cu(I): 15.3x10^{-5} M), spectrum after 22 h (broken black curve, >75% of **5**-DHA-DHA recovered).

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