Demonstration of an azobenzene derivative based solar thermal energy storage system†

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Molecules capable of reversible storage of solar energy have recently attracted increasing interest, and are often referred to as molecular solar thermal energy storage (MOST) systems. Azobenzene derivatives have great potential as an active MOST candidate. However, an operating lab scale experiment including solar energy capture/storage and release has still not been demonstrated. In the present work, a liquid azobenzene derivative is tested comprehensively for this purpose. The system features several attractive properties, such as a long energy storage half-life (40 h) at room temperature, as well as an excellent robustness demonstrated by optically charging and discharging the molecule over 203 cycles without any sign of degradation (total operation time of 23 h). Successful measurements of solar energy storage under simulated sunlight in a microfluidic chip device have been achieved. The identification of two heterogeneous catalyst systems during testing enabled the construction of a fixed bed flow reactor demonstrating catalyzed back-conversion from cis to trans azobenzene at room temperature under flow conditions. The working mechanism of the more suitable catalytic candidate was rationalized by detailed density functional theory (DFT) calculations. Thus, this work provides detailed insights into the azobenzene based MOST candidate and identifies where the system has to be improved for future solar energy storage applications.

Introduction

The development of sustainable energy has been attracting increasing attention, due to the pressing environmental and social challenges linked to high dependency on fossil fuels in our modern society.1 As the most abundant energy source for Earth, the Sun can provide the energy needed for mankind for an entire year in only six hours.2 Various ways to take advantage of solar energy have been studied and developed over the last few decades, including photovoltaics,3 artificial photosynthesis,4 and solar thermal heating.5 In order to store sunlight for future use, molecular solar thermal storage techniques (MOST,6,7 also known as solar thermal fuels, STF8) focus on harvesting solar energy and storing it in photoswitchable materials. A parent molecule can be isomerized by solar irradiation to a metastable high energy photoisomer for a long storage period. When the energy is required, it can be thermally or catalytically back-converted to the parent state. Ideally, the stored energy should be released on demand as heat, thus operating as a closed-cycle system.

In order to realize the MOST concept, several features concerning the charge and discharge process need to be considered.7,8,10 (1) Since more than 50% of sunlight is distributed from 300 nm to 800 nm, the parent molecules should be able to absorb broadly in this spectral region. (2) The quantum yield of the photoisomerisation reaction should be as close to unity as possible. (3) The storage half-life at room temperature should be long enough to fulfill application-relevant storage times, such as daily, monthly, yearly or even longer storage requirements. (4) The energy of the metastable photoisomer should be significantly higher than the ground state of the parent isomer. (5) The system should ideally be able to operate over an infinite number of charging and heat releasing cycles. (6) Using a heterogeneous catalyst, the photoisomer should easily release the stored energy as heat. (7) For energy collection, storage, and bulk heating applications, MOST materials need to be pumped between solar collector, storage reservoir and heat extraction devices. As a consequence, the MOST system should be a liquid or highly soluble solid.
The MOST concept has been represented by many potential candidates, including norbornadiene/quadricyclane derivatives,\textsuperscript{7-9,14} dihydroazulene/vinylheptafulvene couples,\textsuperscript{15-21} difulvalenediruthenium complexes,\textsuperscript{4} anthracene dimers,\textsuperscript{22} Dewar isomers\textsuperscript{23} and azobenzene derivatives.\textsuperscript{24-43} The last systems have been in the spotlight recently due to the broad absorption spectrum, high robustness, daily storage half-life, tunable energy density (J mol\textsuperscript{-1}), and the low synthetic cost.\textsuperscript{40-42} AZO1 (see Fig. 1a) possesses many of the needed features described above; however it has not been tested in a full MOST operating cycle including energy capture, storage and release. Here, for the first time, we investigate the performance of AZO1 by studying its function through multiple energy storage and release cycles. In order to do so, we have identified and tested a heterogeneous catalyst system for the energy release step and constructed a flow system consisting of a solar collector and a fixed-bed catalytic converter. Furthermore, the functioning mechanism of the catalytic conversion is further proposed and rationalized using PCM-B3LYP-D3BJ/6-31G(d)+SDD(Cu) calculations.

Results and discussion

To characterize the physical properties of AZO1, it was first studied in toluene in terms of its absorptivity, half-life of energy storage and quantum yield of the photoisomerization reaction. Comparing these results with available data of AZO1 in methanol,\textsuperscript{23} the maximum in the absorption spectrum was observed to be slightly red shifted, indicating a low solvent polarity effect compared to, for instance, a DHA-MOST system\textsuperscript{18} (ca. 5 nm, $\varepsilon_{\text{Max},350\text{nm}} = 2.6 \times 10^4$ M\textsuperscript{-1} cm\textsuperscript{-1}, see Fig. 1b). Concerning the storage lifetime, a half-life from cis to trans state of 36.3 h in toluene can be extracted from the Eyring plot. The activation enthalpy was calculated as $\Delta H_{\text{therm}} = 93.7$ kJ mol\textsuperscript{-1}, together with an activation entropy $\Delta S_{\text{therm}} = -31.7$ J mol\textsuperscript{-1} K\textsuperscript{-1} (S2, ESIF). The quantum yield of the trans to cis photoisomerization reaction was determined to be 21% at 340 nm, using a literature procedure\textsuperscript{44} (S3, ESIF). In addition, it was observed that the AZO1-cis state can photoisomerise back to the trans form. The corresponding quantum yield of the cis to trans photoisomerisation was determined to be 23% at 455 nm, slightly higher than the reverse process. Due to this photo-induced two-way switch effect for AZO1, full conversion via full spectrum solar light can likely not be achieved and a band pass filter was used in the device conversion experiments.

Good cyclability is one of the most important criteria of MOST systems. To investigate the robustness of AZO1, a solution of ca. 10\textsuperscript{-5} M in toluene was prepared without degassing. Two controllable LED light sources were turned on and off alternatingly (340 nm with 100 s irradiation time and 455 nm with 300 s irradiation time) to charge and discharge the molecules back and forth. After 203 complete cycles (with a total operation time of 22.6 h), no significant signs of degradation were observed, thus demonstrating high robustness of AZO1, even in the presence of oxygen (see Fig. 1c).

To further demonstrate the functionality of the AZO1 system in a real device, a continuous flow system was built. For this lab-scale conversion test under an AM1.5 solar simulator, diluted solutions of AZO1 were used to collect data by UV-vis spectroscopy. Two concentrations of AZO1 solutions were pumped individually through a microfluidic chip,\textsuperscript{24-25} with varying residence time (33.9 mm\textsuperscript{3} inner volume with a channel depth of 100 $\mu$m, see Fig. 2a). Since AZO1-cis can be back-converted by visible light, an optical UV transmitting band pass filter (400 nm) was inserted in between the solar simulator and the microfluidic chip. The UV-Vis spectra of the AZO1 solution before and after pumping into the microfluidic chip were recorded. Eqn (1) was used to calculate the cis-to-trans conversion percentage (S4, ESIF):

$$\text{Conversion} \% = \frac{A_{\text{isomer},350\text{nm}}}{A_{\text{parent},350\text{nm}}} \times \frac{\varepsilon_{\text{iso},306\text{nm}}}{\varepsilon_{\text{parent},350\text{nm}}} \times \frac{\varepsilon_{\text{isomer},350\text{nm}}}{\varepsilon_{\text{isomer},350\text{nm}}}$$

where $A_{\text{iso},350\text{nm}}$ is the actual absorbance at 350 nm; $A_{\text{iso},306\text{nm}}$ and $\varepsilon_{\text{iso},306\text{nm}}$ correspond to the absorbance and absorptivity of the solution at its isosbestic point at 306 nm, respectively; and $\varepsilon_{\text{parent},350\text{nm}}$ and $\varepsilon_{\text{isomer},350\text{nm}}$ are the absorptivity of the AZO1-trans and AZO1-cis isomers at 350 nm, respectively. A maximum conversion of around 80% from the AZO1 trans to cis state was obtained from a solution of 2 $\times$ 10\textsuperscript{-4} M. This is likely due to the photo-stationary state of azobenzene trans-to-cis photoisomerization (see Fig. 2b). Concerning the energy storage efficiency, 0.88% of the solar energy could theoretically be stored in a neat sample (S5, ESIF). The highest efficiency that can be expected for a 5 $\times$ 10\textsuperscript{-4} M solution is 0.02%, and for a 2 $\times$ 10\textsuperscript{-4} M solution is 0.01%. With a band pass filter (SCHOTT,
theoretical maximum temperature difference was calculated as ca. 226 °C for a fully charged neat sample (see S7, ESI†).

Concerning related catalysts, several candidates, including mineral acids like perchloric acid, Cu(II) salts (CuCl₂/Cu(OAc)₂), gold nanoparticles which involve a redox mechanism, as well as electrocatalytic methods have been reported to induce the back-conversion of azobenzene derivatives. However, for a closed cycle system which can be operated in devices, a heterogeneous catalyst that can be fixed in a reaction centre is required. Based on this fact, a heterogeneous catalyst or an insoluble homogeneous catalyst needs to be developed. For AZO1, two potential catalysts, cobalt(II) phthalocyanine physisorbed on the surface of activated carbon (CoPc@C) and [Cu(CH₃CN)₄]PF₆, fulfill the described physical properties and thus, they were tested individually. Both showed a positive effect on reducing the back-conversion half-life at room temperature. [Cu(CH₃CN)₄]PF₆ has a very low solubility in toluene, being active for various MOST systems, including norbornadiene/quadricycle derivatives and dihydroazulene/vinylheptafulvene couples. For the AZO1-cis compound, a back-conversion reaction rate of up to 30 s⁻¹ was calculated at room temperature of 25 °C (up to 6 × 10⁶ times higher than a reaction rate of 5 × 10⁻⁶ s⁻¹ without the catalyst at 25 °C; see Fig. 3a, S7, ESI†). CoPc@C was produced following a reported procedure; however it had a risk of leaching from its solid support. Therefore, the [Cu(CH₃CN)₄]PF₆ salt was chosen to be incorporated into the catalytic device for further testing. With this result in mind, a small-sized reaction centre was built. 5 mg of Cu(II) salt was inserted into a Teflon tube which has a 1 mm inner diameter (see Fig. 3b). 5 × 10⁻⁷ M 79% AZO1-cis solution from the microfluidic chip experiments was then flowed through the catalytic bed with a speed of 1 mL h⁻¹. As result, 48% of AZO1-cis was successfully back-converted to the corresponding trans state. Thus, the described continuous fluidic chip experiments can achieve the requirements for the complete application of the MOST concept including photon capture/storage and energy release processes.

To further understand the mechanism of back-conversion with [Cu(CH₃CN)₄]PF₆, a detailed study within the framework of the density functional theory (DFT) was performed. A simplified AZO1 system was used replacing the ethylenedimoiety with a methyl group at the PCM-B3LYP-D3BJ/6-31G(d)++SDD(Cu) level of theory (S8, ESI†). Among the different coordination options, the CH₃CN ligands could be displaced by the new ligand (the cis isomer of the azobenzene moiety, in this case). Four different coordination possibilities were considered to ensure a good modelling of the experimental conditions. In all cases, the formation of the new complex is slightly endergonic (1-5 kcal mol⁻¹). As the azobenzene derivative is not symmetric, two sets of coordination alternatives arise. Coordination through the nitrogen atom directly linked to the photoisomer was considered, i.e. when the concentration approaches neat conditions, \( 1 - \frac{cM_w}{\rho_{AZO1}} \) approaches zero. This correction is reasonable for all MOST heat release estimations with close to neat conditions. In the case of AZO1, the theoretical maximum temperature difference was calculated as ca. 226 °C for a fully charged neat sample (see S7, ESI†). After solar capture/storage, energy release is the second fundamental process for the MOST concept. To estimate the adiabatic heat release as a function of concentration, a modified equation from a previous study was used (eqn (2)):

\[
\Delta T = \frac{c M_w \Delta H_{\text{storage}}}{\rho_{AZO1} C_{p,AZO1}} + 1 - \frac{c M_w}{\rho_{AZO1}} \rho_{\text{solvent}} C_{p,\text{solvent}}
\]

where \( c \) is the concentration of AZO1, \( M_w \) represents its molecular weight; \( \Delta H_{\text{storage}} \) corresponds to the DSC measured energy storage capacity of AZO1-cis which equals to 167.5 J g⁻¹; \( \rho_{AZO1} \) is the volumetric mass density of AZO1 supposed to be 1.09 g mL⁻¹; \( C_{p,AZO1} \) is the specific heat capacity of AZO1 in J g⁻¹ K⁻¹, assumed similar to that of unsubstituted azobenzene; and \( \rho_{\text{solvent}} \) and \( C_{p,\text{solvent}} \) address the volumetric mass density in g L⁻¹ and the specific heat capacity in J g⁻¹ K⁻¹ of the solvent, respectively (which are equal to 867 g L⁻¹ and 1.7 J g⁻¹ K⁻¹). In this approach, the volume load factor of the solvent and
unsubstituted phenyl ring (path b, S8, ESI† and Fig. 4a) is favored (by ca. 2.3 kcal mol\(^{-1}\)) as compared to the methoxyphenyl linked nitrogen atom (path a). Isomerization of azobenzenes is very dependent on substitution and reaction conditions.\(^{58}\) In this case, different pathways were considered and rotation and inversion mechanisms of the isomerization were explicitly evaluated. As in the not catalyzed thermal reaction,\(^{46}\) the inversion transition states (TS1a–TS1b) were found to be preferred.

A relaxed scan along the rotation coordinate (CNNC dihedral) (see Fig. 4b) reveals a possible \(S_0\)–\(T_1\)–\(S_0\) mechanism accessible by coordination of the nitrogen atom of AZO1-cis to copper, which reveals a MLCT (metal-to-ligand charge transfer). In turn, this implies the participation of a \(\pi^*\) orbital of the azobenzene allowing rotation along the \(N=\text{N}\) with participation of the \(T_1\) state. At relative high torsion angles, the triplet state becomes less energetic and this path yields a barrier of around 20 kcal mol\(^{-1}\). This alternative mechanism allows for the bypassing of the more energetic inversion TS in the ground state (30 kcal mol\(^{-1}\)) and it should be available at room temperature.

Thus, copper coordination yields a decrease in the isomerization barrier of ca. 6 kcal mol\(^{-1}\) (computed barrier decreases from 25.4 kcal mol\(^{-1}\) for free azobenzene to 19.4 kcal mol\(^{-1}\)). This relatively small decrease in the energy barrier is enough to allow the isomerization process to occur in a few minutes instead of some days, thus accelerating the isomerization by 4 orders of magnitude, resulting in good agreement with experiments (energy difference of 8 kcal mol\(^{-1}\), from 23.5 kcal mol\(^{-1}\) for the free AZO1 to 15.6 kcal mol\(^{-1}\) for the copper activated reaction). Overall, while [Cu(CH\(_3\)CN)\(_4\)]PF\(_6\) is useful to increase the reaction rate notably, there is still great potential for improvement in the design of the energy release step. This could be done, for instance, favoring the MLCT or stabilizing the MECP between singlet and triplet states to increase the efficiency of the crossing. In both cases, this could lead to a decrease in the energy barrier and a subsequent acceleration of the back-conversion.

**Conclusions**

An AZO1-MOST charging/discharging cycle has been successfully demonstrated, including the study of the photophysical properties and back-conversion of the photoisomer. The AZO1 system features strong absorption (\(f_{\text{Max}}@350\text{ nm} = 2.6 \times 10^4\text{ M}^{-1}\text{ cm}^{-1}\)) and long thermal half-life (36.3 h). The optical cyclability test for a diluted solution shows no significant degradation in the presence of oxygen, allowing the use of AZO1 in toluene in application. For MOST application purposes, the conversion quantum yield at 340 nm was determined to be 21%
which is similar to the quantum yield of back-conversion of 23% at 455 nm. This implies that even diluted samples cannot be fully converted under sunlight. The estimated maximum energy storage efficiency for \textit{AZO1} in the neat state was calculated to be 0.88%. To experimentally demonstrate the functionality of this liquid azobenzene for MOST applications, conversion experiments were performed at different concentrations of \textit{AZO1} in a continuous microfluidic chip system. The measured maximum energy storage efficiency for a 5 × 10⁻⁴ M solution can reach close to 0.009%, close to reach the theoretical prediction of 0.02% at such a concentration. This, unfortunately, showed a strong photo-stationary effect between \textit{AZO-cis} and \textit{AZO-trans}, therefore highlights the need to further develop the azobenzene system by altering the optical properties.\textsuperscript{51-53} Further improvement to increase quantum yields and diminish the absorption of photoisomer, as well as differentiate the spectral difference between \textit{cis} and \textit{trans} states, would be certainly required. To estimate the theoretical heat release temperature difference, a corrected formula was introduced to account for the change from the diluted solution to the neat sample. A maximum temperature increase of 226 °C can be theoretically achieved by using eqn (2) with a correction term for a neat MOST sample. Furthermore, two new catalysts have been identified to allow the back-conversion of \textit{AZO1-cis} and a reaction centre based on a Cu(i) salt has been prepared as a proof of concept for the energy release process. With a concentration of 5 × 10⁻⁴ M and a flow speed of 1 mL h⁻¹, 48% of the \textit{cis} state isomer was successfully converted back to the \textit{trans} state. However, the reaction rate was still too low to be used for macroscopic heat release purposes. Finally, a detailed theoretical study of the mechanism has been proposed to further understand the discharge process using a Cu(i) salt. This could help in the future design of new azobenzene derivatives and the corresponding catalysts. In addition, results shown here could be extended to the control of azobenzene derivatives for different applications.

Conflicts of interest

There are no conflicts to declare.

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Notes and references