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Review

Storing energy with molecular photoisomers

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SUMMARY

Some molecular photoisomers can be isomerized to a metastable high-energy state by exposure to light. These molecules can then be thermally or catalytically converted back to their initial state, releasing heat in the process. Such a reversible photochemical process has been considered for developing molecular solar thermal (MOST) systems. In this review, we introduce the concept, criteria, and state-of-the-art of MOST systems, with an emphasis on the three most promising molecular systems: norbornadiene/quadricyclane, *E*/*Z*-azobenzene, and dihydroazulene/vinylheptafulvene. After discussing the fundamental working principles, we focus on molecular design strategies for improving solar energy storage performance, remaining challenges, and potential focus areas. Finally, we summarize the current molecular incorporation into functional devices and conclude with a perspective on challenges and future directions.

INTRODUCTION

The global energy demand continues to grow as population and wealth increase and has been predicted to rise by 1.3% each year until 2040.[1] To address this challenge and achieve sustainability, one key is to further exploit renewable energy resources, which can relieve the pressure on conventional energy systems. It is projected that the renewable power capacity will expand globally by up to 50% between 2019 and 2024.[1] However, because of fluctuations in both supply and demand, renewable energy resources need to be complemented with load-leveling technologies. The sun is one of the most abundant sources of renewable energy, and the share of solar energy from renewable generation has steadily increased from 13% in 2013 to 26% in 2019.[2] Hence, solar energy storage solutions based on battery technologies or power-to-X technologies are attracting increasing attention. Although these technologies offer emission-free energy on demand, they also require, in most cases, rare or depletable raw materials.[3,4] In this context, it is intriguing to imagine alternative technologies that directly capture and store the energy from the sun, based entirely on earth-abundant raw materials, specifically organic molecules. Nature can store sunlight via photosynthesis with an efficiency between 0.1%–0.3%,[5] leading to biomass production. Artificially, solar energy can be stored as chemical energy, e.g., via electrochemical water splitting for hydrogen production. At the current stage, the highest artificial photosynthesis efficiency can reach 22.4%.[6] An alternative way of storing solar energy is to use photoswitchable molecules. This concept was first proposed in 1909 by Weigert,[7,8] who suggested using anthracene dimerization for solar energy storage. Since then, several molecular photoswitchable systems have been developed. Together, these systems have been referred to as molecular solar thermal systems (MOST) or solar thermal fuels.[9,10] In this review, we introduce the working principles of a MOST system and discuss the energy storage performance of the most

Context & scale

The global energy demand continues to grow both due to the increasing population and wealth. As one of the potential solutions, renewable energy resources can relieve the pressure on conventional energy sources. However, due to fluctuations in both supply and demand, they need to be complemented with load-leveling technologies. Since the sun is considered one of the most abundant renewable energy resources, solar energy storage solutions based on battery technologies or power-to-X technologies have attracted increasing attention. Such technologies offer emission-free energy on demand; they also require, in most cases, rare and depletable raw materials. In this context, it is stimulating to imagine alternative technologies that directly capture and store the energy from the sun, based entirely on earth-abundant raw materials, specifically organic molecules.

Some molecular photoswitches can absorb and transform sunlight into chemical energy, available for later release in the form of heat without any emission. We define their common properties as an innovative molecular system that can store solar energy into chemical bond strain and later release it on demand. Such

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studied molecular systems. Then, we show recent efforts to improve the solar energy storage performance. Finally, we discuss the challenges and future opportunities in this fascinating field.

Requirements: A vision facing practical challenges

Before introducing specific molecular structures and molecular design solutions, it is necessary to describe how a MOST system operates and to identify the ideal requirements (Figure 1). The energy storage cycle can be broken down into a series of four key processes (A–D) associated with two key quantities ($\Delta H_{storage}$ and $\Delta H^{\ddagger}$).

When a parent molecule is exposed to light, the incoming photon should be able to excite the molecule from the ground state (S_0) to an excited state ($S_{excited}$) via a photon absorption process (A). Afterward, the excited molecule undergoes a photoconversion process into the metastable high-energy photoisomer, with a certain probability—the photoisomerization quantum yield (φ_{iso}) (B). The molecule must remain in this high-energy isomerized state long enough to enable long-term storage, which is controlled by the barrier of thermal back-conversion ($\Delta H^{\ddagger}$). Additionally, the energy difference ($\Delta H_{storage}$) between the photoisomer and the parent molecule, representing the energy that can be stored by the system, should be significant. Later, to recover the uncharged molecule and collect the released heat, the back-conversion reaction can be initiated electrochemically, catalytically, or thermally (C). Finally, the system should not be susceptible to unintentional photochemical back-conversion through competing absorption (A′) and must sustain its performance over multiple operating cycles (D).

After a closer inspection of the energy diagram and all the processes involved, according to previous research and current conclusions, a criteria checklist can be established for an ideal MOST system:[11–13]

(1) Molecular absorption range (A): the solar irradiation spectrum with an air mass of 1.5 defines the incoming power to most countries on earth. It shows that more than 50% of photons lie between 300 and 800 nm. Therefore, the absorption spectrum of an ideal parent molecule should include a substantial part of this spectral region.[14]
(2) The photoisomerization quantum yield (φ_{iso}) (B): this unitless factor is qualified as the photoisomerization capacity of the switching molecule. Preferably, in order to make best use of the incoming photons from the sun, thus preventing the unexpected excitation → relaxation process, an ideal photoisomerization reaction should be triggered by a photon with a φ_{iso} as close to unity as possible. Thereby the shortest possible irradiation exposure time is required.
(3) The energy storage time (related to $\Delta H^{\ddagger}$): when the high-energy metastable isomer is formed, the thermal half-life ($t_{1/2}$) at room temperature (which is proportional to $e^{-\frac{\Delta H^{\ddagger}}{R\cdot 300K}}$) should be long enough to store energy for days ($\Delta H^{\ddagger} \geq$ 110 kJ mol^{-1}), months ($\Delta H^{\ddagger} \geq$ 120 kJ mol^{-1}), years ($\Delta H^{\ddagger} \geq$ 130 kJ mol^{-1}), or even longer.[14,15]
(4) The energy storage density ($\Delta H_{storage}$): as an energy storage fuel, the charged photoisomer should have a higher energy than its parent ground state. Previous research suggests that it should be at least 0.3 MJ kg^{-1}, exceeding conventional heat storage materials, such as salt hydrates ($\Delta H_{storage}$ up to ≈ 0.25 MJ kg^{-1}).[12,16]
(5) Energy release triggering agent (C): the energy release triggering agent must be efficient so that, when using a high-energy MOST material, the stored chemical energy can be released on demand.

photoisomers are referred to as molecular solar thermal energy storage systems (MOST), also known as solar thermal fuels (STF). In this review, we introduce the functional principles and criteria of a general MOST system, then introduce to a broad audience three key candidates and show the efforts made so far to achieve recent advances in results. Finally, we discuss the challenges and future opportunities that these dynamic molecular systems offer.

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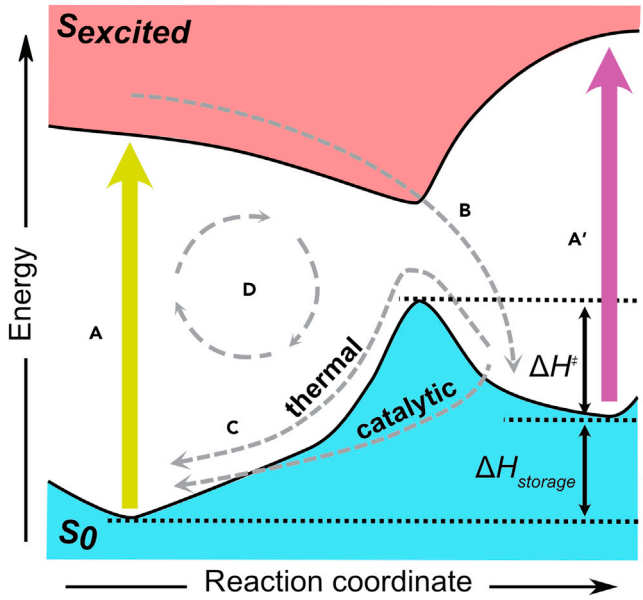

Figure 1. Schematic MOST cycle: S_0 and $S_{excited}$ represent the ground and excited state landscapes of the molecule, respectively

(A) Denotes the photo-excitation process.

(B) Represents the conversion process from parent molecule to its corresponding photoisomer along the excited state energy surfaces.

(C) Shows the back-conversion process along the ground state energy surface via either a thermal or catalytic trigger; $\Delta H^{\ddagger}$ and $\Delta H_{storage}$ represent the thermal energy barrier between photoisomer-parent states and effective storage enthalpy, respectively.

(A′) Indicates the photo-excitation process of the photoisomer, which can be potentially photo-back-converted to the parent state. Finally, the whole system must repeatedly pass through the entire cycle as indicated by (D).

(6) Cyclability (D): as a solar energy battery, the ideal MOST system should sustain a large number of charge and discharge cycles without showing molecular fatigue or degradation.
(7) Absorption spectrum difference between parent and photoisomer states (A and A′): the absorption spectrum of the parent state should not overlap with its converted form, in order to avoid photon absorption competition between these two states.
(8) From a sustainability perspective, MOST compounds are preferably environmentally benign and nontoxic.

Unfortunately, there is still no molecule that matches all the earlier-mentioned criteria since it is challenging to optimize all processes and parameters simultaneously because of their strong intersystem correlations. For instance, red-shifting the molecular absorption spectrum by introducing additional substituents will make it harder to maintain a high-energy density.[17,18]

In the following section, we introduce the molecular systems that are currently receiving the most attention and systematically focus on the most significant achievements that modify the three systems based on improvement of their solar match properties, energy density, energy storage time, back-conversion triggering techniques, and devices. Then, we seek to answer the deeper questions: how are the specific challenges of each system being addressed through molecular design, what is the chance of resolving residual challenges, how can the molecular systems be

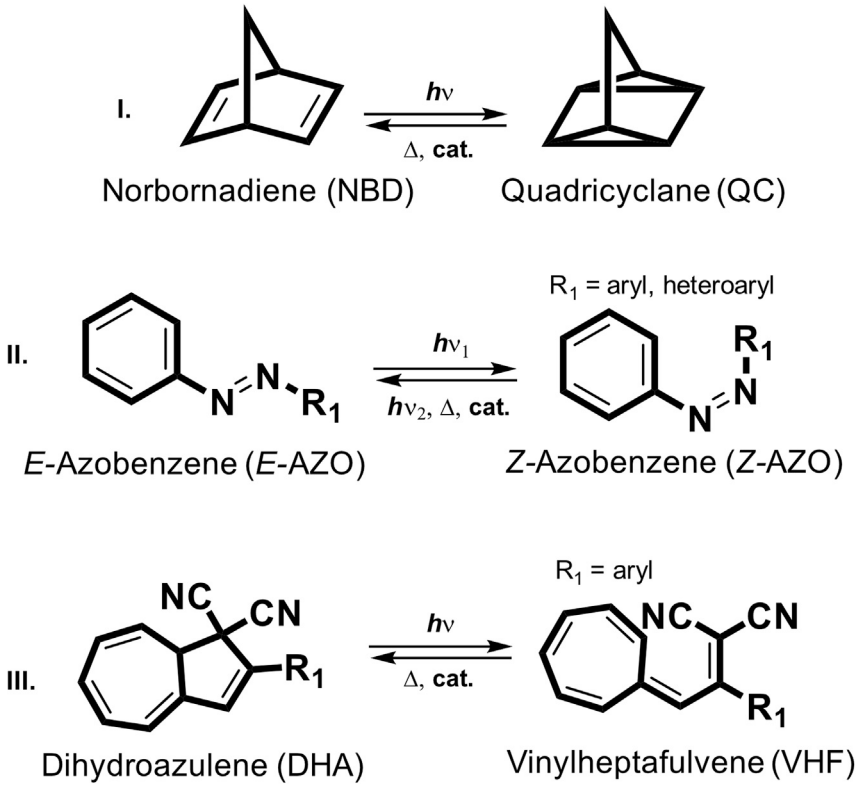

Figure 2. Common MOST systems
I. Norbornadiene/quadricyclane (NBD/QC); II. Azobenzene (*E*/*Z*-AZO); and III. Dihydroazulene/vinylheptafulvene (DHA/VHF)

incorporated into basic devices for energy storage and conversion, and which opportunities exist for further research?

MOLECULAR SYSTEMS

Various photoswitchable molecules have been proposed as MOST candidates, including anthracene,[19] stilbene,[20] dithienylethene,[21] Dewar benzene,[22] spiropyran,[23] Stenhouse adducts,[24] and fulvalene-tetracarbonyl-diruthenium.[9] Currently, three systems are receiving the most attention and in-depth molecular engineering: the norbornadiene/quadricyclane (NBD/QC) couple, the *E*/*Z*-azobenzene (*E*/*Z*-AZO) couple, and the dihydroazulene/vinylheptafulvene (DHA/VHF) couple.

Norbornadiene (NBD) to quadricyclane (QC) photoreactions (Figure 2, I) were first reported in 1958 for a dicarboxylic derivative[25] and in 1961 for its unsubstituted form.[26] The corresponding photoreaction consists of a [2+2] cycloaddition between the alkene moieties in NBD to yield photoisomer QC. The reaction can proceed through direct irradiation[26] or under sensitized conditions.[27] However, NBD absorbs only in the UV region and therefore is not appropriate for solar irradiation (Figure 2, I). Thus, much effort has been devoted to the functionalization of NBD to improve performance.

Azobenzene (*E*/*Z*-AZO, Figure 2, II) can be switched from the ground state *E*-isomer to the metastable higher-energy *Z*-isomer by photon absorption. In this case, irradiation into the strong π-π* transition band initiates excitation into a higher excited state, which will subsequently relax to the S_1 state. However, the back-conversion

of the *Z*-isomer to the *E*-isomer is also easily triggered by light. Hence, due to the competing photochemical reaction from *Z* to *E* form, such molecular switches will require a bandpass filter to reach full conversion under solar irradiation.

The photoisomerization of DHA into photoisomer VHF occurs via a carbon-carbon bond-breaking event (Figure 2, III).[28] A recent theoretical study of the switching mechanism showed that planarization occurs upon DHA photo-excitation, which leads to ring-opening and subsequent decay of the molecule to the VHF ground state through an $S_1 \rightarrow S_0$ internal conversion process.[29] Similar to most variants of QC, VHF features photochemical inactivity under irradiation. Such a property can significantly improve photostationary states within MOST systems, inheriting a spectral overlap different from the AZO case and thus avoiding the photoinduced back-conversion under solar light. Yet, VHF itself has a strong absorption overlap with DHA and thus potentially competes for absorption.

Unfortunately, the three candidates are not very efficient at storing solar energy in their unsubstituted forms, because their performance in several of the design criteria presented here is very limited. In the next section, based on the three couples, we will describe the underlying mechanisms and means to overcome these challenges.

MOST CHALLENGES AND SOLUTIONS

Solar spectrum match

Solar irradiation on earth has a broad optical spectrum from ≈100 nm to 1 mm.[30] For MOST systems, it is desirable that the low-energy isomer can photoisomerize at longer wavelengths, because the solar flux of UV photons is relatively low, especially at wavelengths below 330 nm. Ideally, absorption occurs in the visible region where the solar spectrum is most intense. Therefore, efforts have been made to synthetically modify the structure by adding substituents that extend the onset of absorption of the parent molecule. So far, the major strategy is to extend the conjugation of the system and/or add an electron-donating and electron-accepting pair. As one practical example, including aryl groups on one side of the NBD C=C double bonds (C2–C3) can lead to a red-shift of the absorption that enables a better match with the solar spectrum and an increased photoreaction quantum yield. Using this handle, the parent NBD absorption of around 300 nm has been shifted toward 400 nm by simply expanding the π-conjugated system with two phenyl groups.[31] Besides, substitution with a donor-acceptor pattern is one of the most effective methods to lower the HOMO–LUMO gap of chromophores, red-shifting the major absorption band. Hence, another effective approach is to promote charge transfer through space—called homoconjugation (i.e., separation of two π-systems by a non-conjugated bridge)—by including different donor and acceptor substituents on both C=C double bonds (Figure 3, NBD-2). The through-space concept has led to several promising systems but has so far only been explored for systems where two donors have been introduced on one double bond (C2–C3) and two acceptors on the other (C5–C6). Previous work showed that introducing two cyano groups on positions C2 and C3 and three methyl groups on positions C1, C5, and C6 significantly increased the photoisomerization quantum yield (φ_{iso}) by up to 96%. Simultaneously, the absorption spectrum of the parent state is red-shifted to 360 nm.[11] We note that this factor (φ_{iso}) is very system dependent and may vary from less than 1% to near quantitative, and that no design solutions exist so far to optimize φ_{iso}. Another approach is to provide charge transfer through π-conjugated bonds (Figure 3, NBD-3, NBD-4). A wide variety of compounds with tunable optical properties have been prepared using this approach, not only for NBD but also for AZO and DHA units. For instance, the most red-shifted NBD molecules obtained via this approach have an onset of

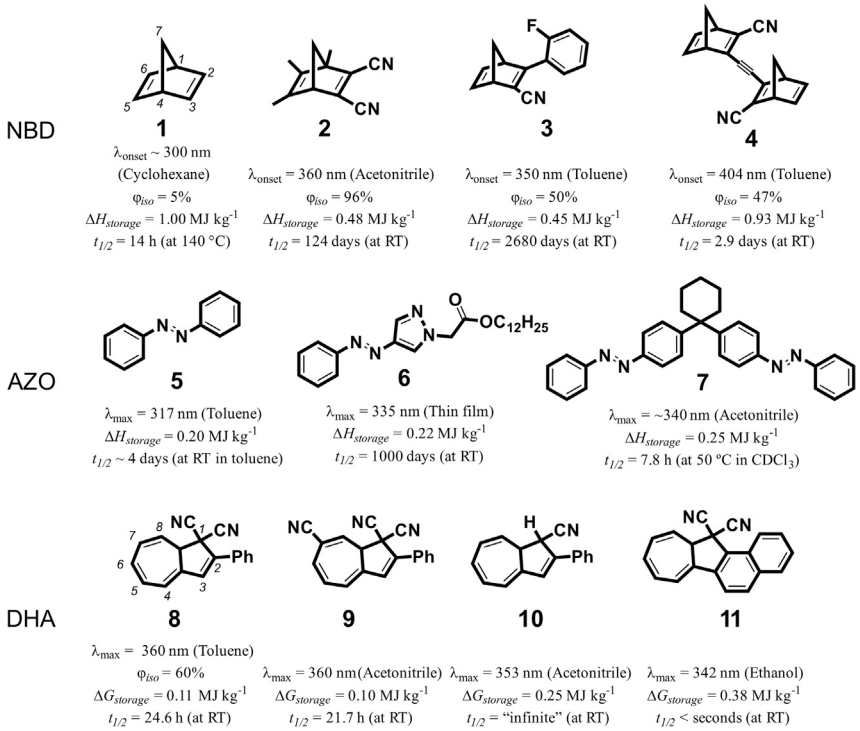

Figure 3. Selected examples of NBDs, AZOs, and DHAs with key properties listed.[11,36–46]
Room temperature is abbreviated as RT.

absorption of around 700 nm in methanol.[32] Substituents with donor-donor or donor-acceptor pairs can shift the absorption of the AZO *E*-isomer toward the center of the solar spectrum and drastically decrease the lifetime of the *Z*-isomer at the same time (Figure 3, AZO-6). Another example is that of AZO with a diethylaniline group as a donor and a nitro group as an acceptor unit, which has an onset of 489 nm.[33–35] Unfortunately, modifying chromophores by adding substituents comes at a cost as the added substituents increase the molecular weight and reduce the gravimetric energy storage density (Figure 3, AZO-7). Additionally, most examples for all three systems show that the red-shifted absorption is commonly accompanied by reduced activation barriers of the thermal back-conversion, which, in turn, reduces the energy storage time.[17]

The combination of different photoswitches is another approach for tuning absorption maxima, energy density, and/or lifetimes of metastable states. For example, DHA coupled with NBD has an absorption maximum at 392 nm, which is red-shifted relative to that of the parent DHA (Figure 3, DHA-8).[47] It was possible to first photoisomerize DHA into VHF and then NBD into QC by an initial irradiation at 450 nm followed by irradiation at 320 nm. Additional advantages of increasing energy density by using this approach will be discussed in the following section.

In addition to direct chemical modification, different photophysical methods have also been explored, including the use of sensitizers[48–51] and more recently, the use of photon upconversion systems. The latter systems convert low-energy photons that otherwise cannot be absorbed by the molecules into higher-energy photons. One such process is triplet-triplet annihilation upconversion (TTA-UC), which can convert low-energy photons into photons that match the spectrum of MOST

systems.[52] This interesting alternative was demonstrated by a hybrid MOST device, where UV and visible light can be simultaneously absorbed using two different AZO-derivative polymers, each designed to harvest photons of different wavelengths.[53]

Extension of the energy storage time

The essential significance of MOST technology is its ability to store solar energy for on-demand energy release, alleviating the natural intermittency of solar supply. Energy storage time determines one of the key performances of such energy systems. The thermal stability of high-energy isomers must be sufficient at ambient temperatures to ensure the storage of energy for a reasonable period. The desirable storage time may vary depending on target applications. It has been suggested that the half-life should at least be 6–10 h to match the most basic day-night rhythm and months to years for longer-term storage applications.[14]

Unfortunately, even if the optical properties can be precisely tuned, other properties, including the energy storage time, are more challenging to control accurately. The height of the energy barrier is sensitive to substitution, leading to energy storage times from seconds to years.[18,36] Substituted AZOs show various thermal half-lives dependent on the functionalization pattern and the substituents introduced,[54] and very long *Z*-isomer half-lives have recently been achieved using some specific *ortho* substitution patterns or heteroaryl AZO-switches.[55,56] For the opposite direction, intramolecular London-dispersion interactions[57] or hydrogen bonds[58] forming in the *Z*-state have been used to markedly decrease the thermal $Z \rightarrow E$ isomerization of AZO, which, however, inevitably leads to reduced $\Delta H_{storage}$ due to lowered energy of the *Z*-isomers. AZO compounds can also be modified by altering the aromatic rings themselves. Replacement of a phenyl moiety with an aromatic heterocycle can strongly modify the isomerization properties.[59] An example is how five-membered heterocycles, such as pyrroles, pyrazoles, imidazoles, or thiophenes, can tune the thermal half-life from seconds to years (Figure 3, AZO-6).[39,55,60,61] Interestingly, AZO with pyrazolylazophenyl ethers represent a rare example where the conflict between storage time and energy density is resolved, providing a thermal half-life of 3 months and a $\Delta H_{storage}$ of 52 kJ mol^{-1}.[62] One possible explanation is the change of the electronic structure in which the incorporation of electron-rich rings leads to push-pull systems, which, in some cases, shorten the half-life of the *Z*-isomer dramatically. On the other hand, T-shaped C–H–π-interactions between the two aromatic rings can only occur in the *Z*-isomer and provide increased stability.

Besides the intrinsic molecular properties, solvents with different polarities can also affect the back-conversion of MOST systems.[63,64] The thermal back-reaction of VHF into DHA proceeds via the s-*Z* conformer with a half-life that is very solvent-dependent, with polar solvents usually accelerating the process. Hence, a zwitterionic transition state has been proposed for the VHF-to-DHA conversion.[43,65] The conversion can also be tuned by donor and acceptor groups at DHA positions 2, 3, and 7 (Figure 3, DHA-8); the half-life is, for instance, increased by adding a donor group at C2 and an acceptor group at C3 or C7.[66,67] By placing a cyano acceptor group at position C7, photoisomerization provides an exceptionally long-lived VHF that returns to DHA with a half-life of 21.7 h in acetonitrile at 25°C (*ca*. six times slower than for the parent system; Figure 3, DHA-9).[44] This functionalization does not significantly alter the energy density. However, the most decisive influence on the back-conversion has been observed by replacing one of the cyano groups at C1. Specifically, it was found that replacing one cyano group for a hydrogen atom can completely stop the back-reaction for VHF, while simultaneously doubling the energy density (Figure 3, DHA-10).[45]

A major discovery in recent years regarding half-life control was the introduction of intramolecular steric repulsion to transition states. This makes it possible to raise the activation barrier ($\Delta H^{\ddagger}$) without compromising other properties. For example, an *ortho* steric effect was demonstrated in NBD molecules, enabling long half-lives of up to 2,680 days with energy densities up to 0.45 MJ kg^{-1} (Figure 3, NBD-3). This result enables to break the otherwise strong correlation between the onset of absorption and the back-conversion barrier.[36] In the case of AZO, two *ortho*-substituents—which can be as small as a methyl group—have been added to impose a steric hindrance at the transition state of lone pair electrons on nitrogen atoms of AZO derivatives that potentially retards the $Z \rightarrow E$ relaxation, while preserving the intrinsic electronic structure of the ground states.[63,68]

Increasing energy density

The ability to store energy (Figure 3; C) depends not only on the molar storage energy ($\Delta H_{storage}$) but also on the gravimetric energy density (normally expressed in units of MJ kg^{-1}). Thus, to achieve a high energy density, the molecular weight should be as low as possible. Therefore, this topic has been subject to intensive research in recent years.[17] As one example, during efforts to develop low-molecular-weight but high-energy-density NBD derivatives, the cyano group—one of the smallest electron-accepting groups—showed attractive energy densities of 0.4–0.6 MJ kg^{-1} with molecular weights of 193–260 g mol^{-1}.[37]

For AZO-based compounds, energy storage is mainly increased via intra- or intermolecular interactions that stabilize the stable (*E* form) or destabilize the metastable isomer (*Z*-form). By analyzing a large set of AZO-switches through high-throughput simulations, it was shown that intramolecular hydrogen bonds or π-π stacking, which is present in the *E*-state but disrupted in the *Z*-state, can lead to a significant $\Delta H_{storage}$ increase.[69] Further studies revealed that even subtle intermolecular interactions, such as C–H–π London-dispersion interactions, can have a considerable stabilization effect on *E*-isomers, increasing energy storage in the AZO unit by more than 5.5 kJ mol^{-1} (Figure 3, AZO-7) compared with the parent azobenzene (36.3 kJ mol^{-1}).[40]

Regarding DHA, an intriguing approach to increasing the energy density is to connect the DHA-to-VHF conversion to the loss of aromaticity of an annellated benzene ring. Indeed, fusion to the C2–C3 bond of DHA provides a DHA/VHF couple with an energy density of 0.38 MJ kg^{-1}, i.e., four times higher than for the parent system (Figure 3, DHA-11).[46] However, this compound does not display the desired photoisomerization upon irradiation, instead undergoing light-promoted rearrangements to other dihydroazulene isomers. Yet, the DHA can be opened to VHF by chemical means ($AlCl_3$ followed by water treatment); although, the VHF form undergoes immediate thermal back-conversion. Although the same lack of photoactivity is observed upon benzannulation at C7–C8. Instead, benzannulation at C5–C6 provides, gratifyingly, DHA-to-VHF photoactivity, but the corresponding VHF returns immediately to DHA.[70] This last modification shows that benzannulation can in fact work in concert with photoactivity, although it compromises the storage time in this specific example.

In summary, two methods exist for increasing energy density. One is to increase the molar energy storage by stabilizing the parent molecule or destabilizing the photoisomer. The other method is to reduce the molecular weight—this has been done using small donor-acceptor components or, as we will see later, by combining several photoswitches around a central donor or acceptor moiety.

Alternative strategies to improve overall performance

Although the parent systems and some of the modifications described earlier may help toward fulfilling some basic requirements, the systems will likely need to be further improved in several aspects. Notably, one needs to consider the molecular performance under real conditions, such as highly concentrated media or a solid state. The function of the entire system eventually needs to be taken into account. This includes solvents, additives, nanotemplates, or polymer matrices that do not contribute to energy storage but in practice limit the performance of the system as a whole. Furthermore, side reactions and competitive absorption of photons by different molecules in the devices become more pronounced when the concentration of the photoactive species is increased. One way to study these effects while working toward future applications is to use fluidic devices.[9] Operating the systems in a liquid state requires, in most cases, the use of solvents with high concentrations of the active molecules. This necessitates engineering of the molecular properties, e.g., using solubilizing side chains. Solvent-free liquids have been developed for photoswitches to avoid solvent dilution altogether. For example, AZO was engineered to a molecular liquid by introducing a branched alkyl chain, which was reversibly photoisomerizable in the neat state.[71] On the other hand, the maximum achievable energy density was still only 0.17 MJ kg^{-1}, partially because the substituent was too large. Recently, AZO-based soft matter systems have also shown high potential to store solar energy, for example, an absolute heat release temperature of up to 6.5°C has been experimentally demonstrated using an asymmetric arylazopyrazole-based dendrimer.[72] Several NBD-QC liquids have been developed with energy densities up to 0.58 MJ kg^{-1}. But they showed low chemical stability due to intermolecular degradation reactions and fast thermal reversion rates with half-lives of minutes.[73] Although these studies demonstrate the potential of liquid MOST systems, they also illustrate a need for further development.

An alternative strategy is to combine solar energy from photoisomerization with latent heat from phase transitions. Using this approach, MOST systems can also absorb thermal energy from the local environment in addition to the stored solar energy. This strategy provides a promising avenue for significant improvement of energy storage densities without compromising other photophysical properties. In this context, photochemical crystal-to-liquid transitions (PCLTs; Figure 4A), where molecular crystals of the stable isomers are transformed into amorphous liquid-metastable isomers, have received the most attention.[74–77] The exploitation of PCLT for improving the energy density was first reported using photo-liquefication of AZO-containing crystals (*E*-state) into liquids (*Z*-state).[78] Because of the high-crystallization enthalpy, the exothermicity more than doubled from 46 to 97 kJ mol^{-1} ($\Delta H_{storage} = \Delta H_{Z\text{-}E} + \Delta H_{Crystal\text{-}Liquid}$); yet, the gravimetric energy density was only 0.13 MJ kg^{-1} because of the heavy substituents.[78] In another example, it was shown that in AZO-functionalized (poly)diacetylenes, the amorphous *Z*-form, can store up to 0.24 MJ kg^{-1} of heat relative to its crystalline *E* form, benefiting from the extra phase transition enthalpy of up to 94 kJ kg^{-1}.[79] However, PCLT photoconversion was not achieved in the neat state and an auxiliary solvent was needed.[79] The lowest-weight AZO compound known so far that can undergo PCLT is 4-methoxyazobenzene, which can provide a theoretical energy density of > 0.3 MJ kg^{-1}. However, only about 0.20 MJ kg^{-1} of energy was stored in practice, probably due to low photoconversion yield.[80] Later on, using a series of further optimized phase-change AZO systems a maximum energy storage density up to 0.3 MJ kg^{-1} was achieved, showing that the molecular size and polarity can also significantly affect the energy storage capacity.[81] Recently, arylazopyrazole-based photoswitches were reported to undergo efficient PCLT with nearly complete photoconversion (~97%) at room

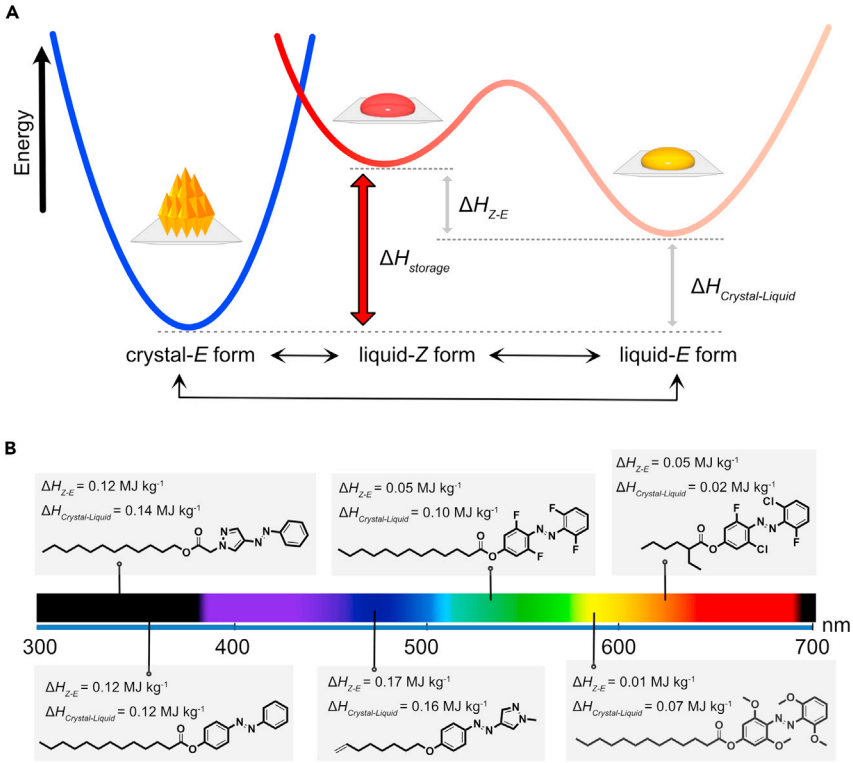

Figure 4. Energy diagram and structures of some selected phase change MOST molecules.
(A) Schematic diagram of a photoinduced crystal-to-liquid phase transition and its associated enthalpy change. Black arrows represent conversion routes between different liquid/crystal-*Z*/*E* form.[86]
(B) A few selected phase-change AZO compounds that can cover different ranges of the solar irradiation spectrum.[55,62,82,83]

temperature.[62] High energy densities of 0.32–0.37 MJ kg^{-1} were achieved after combining 0.16–0.19 MJ kg^{-1} of photochemical energy and 0.14–0.21 MJ kg^{-1} of latent heat stored during $E \rightarrow Z$ isomerization and crystal melting, respectively. Similar studies have captured thermal energy in a series of arylazopyrazoles, which can almost cover all the visible light area from the solar irradiation spectrum and release the stored energy by optically triggered crystallization at various temperature ranges (Figure 4B).[55,62,82,83,84] This concept has also been applied to develop AZO-based dendrimers as advanced soft matter systems, with some interesting switchable adhesive properties in addition to solar energy storage purpose.[85]

Until now, we have mostly discussed systems where substituents have been used to improve solar spectrum match, solubility, and thermal stability. All substituents reduce energy density one way or the other, so how can this influence be minimized? A very attractive strategy in this respect is to link two or more chromophores by one functional moiety (e.g., donor, acceptor, aromatic ring), which leads to a lower molecular weight per photoswitch unit, thereby increasing the energy density. This concept is used in NBD-based multiswitches, where the electron donor units are shared between two or three NBD units, leading to energy densities up to 0.9 MJ kg^{-1} together with a red-shifted absorption spectrum (Figure 3, NBD-4).[87] This concept has also been successfully used to form AZO-based polymers with energy densities up to 0.7 MJ kg^{-1}.[88] Furthermore, it is also possible to incorporate two or more photoswitches into macrocyclic structures where the macrocycle strain

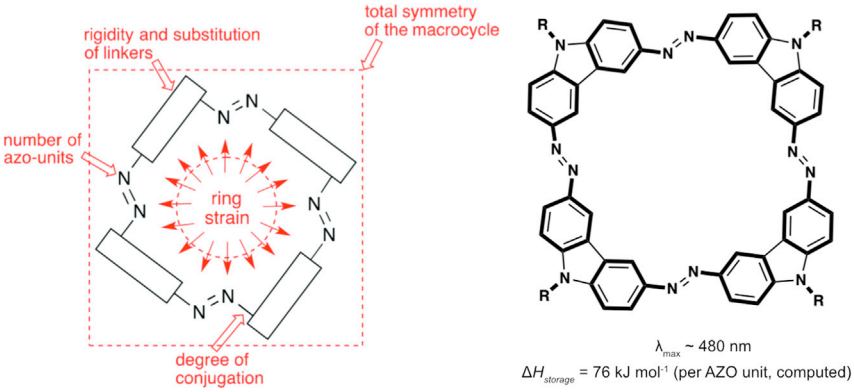

Figure 5. Incorporation of MOST structures in macrocycles: design parameters for AZO macrocycles (left); cyclotetraazocarbazole (right).
Adapted from Schweighauser et al.[91] with permission from The Royal Society of Chemistry.

may influence the energetics of the system as well. One example of this is cyclic systems with multiple AZO units, where both storage energy and storage time are augmented because of the cyclic arrangement (Figure 5).[89] Through a suitable combination of size and linker, the molecular ring can be engineered such that the *Z*-state suffers more strain; thus, it is more destabilized than the *E*-state, leading to a higher isomer energy difference than that of isolated AZO. During the thermal back-reaction, the conversion of one *Z*-unit to its transition state structure puts additional strain on both the transition state unit and the remaining *Z*-units in the ring framework, which increases the total energy of the transition state and thus the activation barrier. Computational results predicted that such AZO macrocycles might have storage densities up to 0.6 MJ kg^{-1} and half-lives of more than 1 year.[90] Although this concept is very intriguing, the specific compound did not show the predicted properties in reality.[90] Yet, in a macrocyclic system containing azo-carbazole moieties, the storage density per AZO unit has a theoretical increase of over 60% by this approach.[91] In this example, the rigidity of carbazoles has to be paid for by altering photophysical properties of the AZO units: the *E*- and the *Z*-isomers absorb at very similar wavelengths, thereby preventing selective switching. In the future, clever design of the connecting structure might maintain the separation of *E*- and *Z*-absorption, while introducing the rigidity necessary to build strain in the storage state at the same time. The cyclic arrangement offers the unique advantage to optimize these parameters without adding additional molecular weight. Additionally, the dramatic structural changes upon isomerization allow to control also intermolecular interactions, adding extra design options. Similarly, molecular bond strain has also been explored in a series of DHA-dimer macrocycles, which increased the VHF half-life.[92–94] Macrocycles incorporating two DHA units were found to undergo stepwise DHA-to-VHF photoisomerization and VHF-to-DHA energy releases on a fast and a slow timescale. Furthermore, by decreasing the macrocyclic ring size, it was possible to tune the half-life of the VHF-to-DHA conversion.[92]

Long-term stable energy storage can also be accomplished using photoswitches on nanoscale templates to enforce intermolecular interactions.[10,95,96] This approach has been demonstrated successfully by grafting azobenzenes on carbon nanotubes and graphenes.[97,98] When densely packed together, the planar *E*-isomers can be stabilized by favorable intermolecular attractive forces, whereas the twisted *Z*-isomers are destabilized by steric repulsion. This resembles a phase transition and can significantly increase the amount of energy stored per azobenzene unit.

Meanwhile, the thermal isomerization kinetics can also be significantly retarded because of the limited degree of freedom of molecules in such constrained environments. By optimizing the structure of the hybrid materials, high energy densities up to 0.5 MJ kg^{-1} and thermal half-lives of up to thousands of hours have been achieved.[41] However, their application potential is limited by a sluggish photocharging process due to the crowded environment in these dense films that greatly reduces $E \rightarrow Z$ isomerization quantum yield and competing light absorption of nanocarbons.

In addition to chemically modifying the molecular structure, material crafting is another option for improving solar energy capture and storage performance. By implementing MOST systems in thin-film devices, photoswitches have also been incorporated into flexible materials and fabrics.[99–101] Under such circumstances, the mass fraction of the photoswitch in the material is an essential factor affecting the practical energy density. For example, several NBD molecules with high energy densities of 0.35–0.48 MJ kg^{-1} were embedded into polystyrene matrices, which afforded very low-energy densities of only 30–52 kJ kg^{-1} because the NBD loading amount was limited (8–15 weight-%).[101] In the future, materials should be developed that contain a high-mass fraction of photoswitches while retaining good component compatibility and processability.

Controlling energy release

For the MOST energy storage system to be practical, we need to control when and how the stored energy is released. Several possible routes have been explored, such as thermal activation,[15] optical activation,[41] electrocatalytic,[102] and catalytic activation.[12]

For NBD/QC couples, different metallic catalysts have been tested to release the stored energy. Compounds based on Rh,[103] Ag,[104] Cu,[105] Sn,[105] and Co,[106] have been reported to recover NBD from QC. Fundamental understanding of these complex processes can be obtained by surface science studies in ultra-high vacuum (UHV).[107] In recent years, this approach was used to study energy release from the NBD/QC couple on Pt(111)[108,109] and Ni(111).[110,111] It was found that Pt(111) is significantly more active for triggering the energy release than Ni(111).[108,110] On clean Pt(111), a monolayer of QC is immediately back-converted to NBD even at cryogenic temperatures (125 K). The formed NBD chemisorbs onto the metal surface and was observed to be decomposed via a norbornadienyl intermediate at elevated temperatures. In contrast, QC is stable in frozen multilayer films without direct contact to Pt.[108,112]

Another intriguing concept is releasing energy from the metastable high-energy isomer with an electrochemical trigger. In the case of NBD/QC, we note that the overall conversion is not a redox reaction; yet, it can be initiated by oxidation of QC to a $QC^{+\bullet}$ intermediate (Figure 6A), which triggers a chain reaction converting QC to NBD. In this process, the electrode potential controls the concentration of radical cations and, thereby, the rate of the back-conversion.[102] By infrared (IR) reflection absorption spectroscopy,[113] it was possible to monitor the complete storage cycle and obtain quantitative information on the reversibility. For non-functionalized NBD/QC couples, a high (initial) selectivity of ~95% is reached for both the photochemical conversion and the electrochemically triggered back-conversion at Pt(111) electrodes. Recently, a more robust NBD derivative, 2-cyano-3-(3,4-dimethoxyphenyl)-norbornadiene was used,[36] the donor-acceptor ligands red-shift the light absorption and at the same time, the cyano group acts as a marker for IR

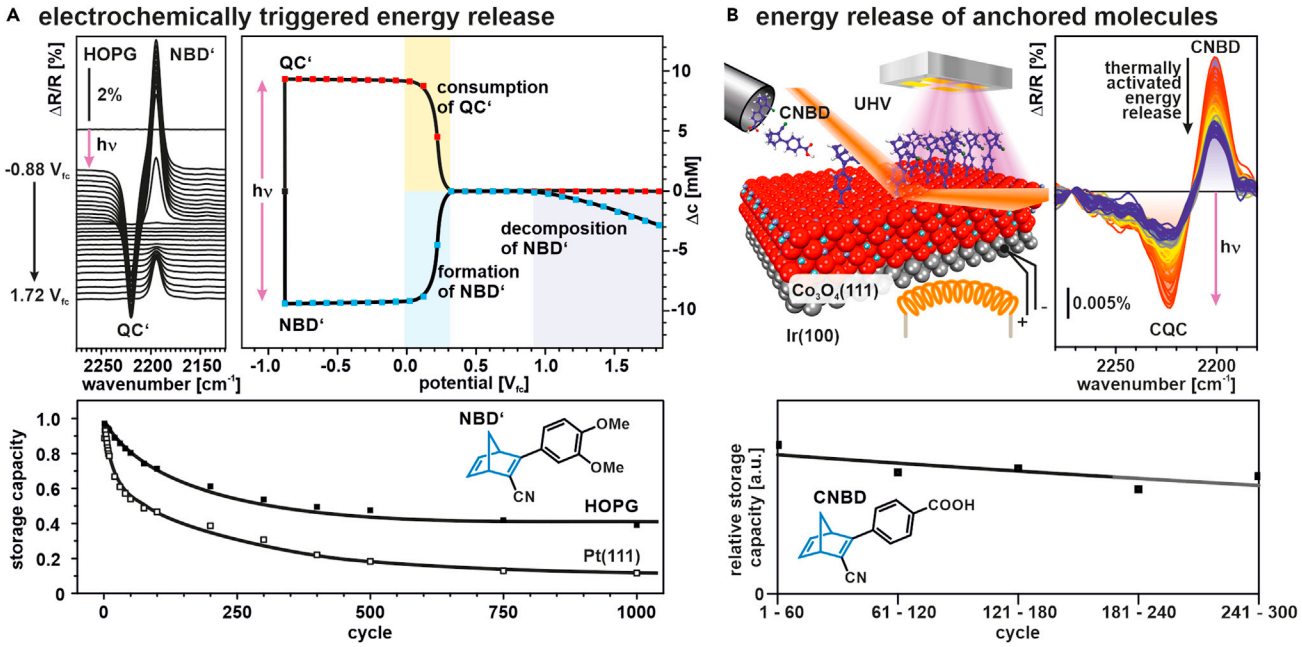

Figure 6. Energy release in the NBD/QC system as monitored by in-situ IR spectroscopy

(A) Electrochemically triggered energy release from QC′; (top left) IR spectra recorded during photochemical conversion and subsequent back-conversion as a function of the electrode potential (HOPG electrode); (top right) concentrations as a function of electrode potential; (bottom) long-term stability tests on HOPG and Pt(111) electrodes;

(B) Energy release from an anchored QC derivative on Co_3O_4(111) in UHV; (top) conversion and back-conversion at 350 K; (bottom) long-term stability tests at 370 K; all reference spectra were measured before irradiation.

(A) Is adapted from Waidhas et al.[115] with permission from The Royal Society of Chemistry.

(B) Is adapted with permission from Schuschke et al.[118], Copyright 2019 Springer Nature.

spectroscopy. In long-term experiments, up to 1,000 storage cycles and a reversibility of >99% were achieved.[114] It was identified that a limiting factor was electrode fouling at the Pt(111) electrode and uncontrolled catalytic back-conversion. In fact, both side reactions can be further mitigated by using more inert electrode materials. At highly oriented pyrolytic graphite (HOPG) electrodes, reversibility of up to 99.8% was achieved.[115] Electrocatalytically triggered *Z* to *E* back-conversion of AZOs has also been demonstrated via reductive radical cascade. By inducing electron transfer, the resulting $Z^{\bullet-}$ to $E^{\bullet-}$ AZO isomerizes 10^{13} times faster on the radical anion potential energy surface than normal *Z* to *E* conversion.[116] In addition, arylazopyrazoles-based AZO variants can be electrocatalytically back-converted to the condensed phase, showing an improved efficiency over an order of magnitude compared with the dissolved state.[117] Such electrocatalytic heat generation from MOST can potentially be used for applications such as car windshield de-icing.

Although the earlier-mentioned concepts focus on releasing the stored chemical energy in the form of thermal energy only, another scenario has been envisioned in which part of the energy is released in the form of electric power.[102] This idea is inspired by the working principle of dye-sensitized solar cells,[119] with the advantage that the solar energy would not only be converted but also stored chemically at open circuit potential.[102] To control the charge transfer and to suppress undesired intermolecular side reactions, the NBD/QC molecules can be linked to the electrode. Related model studies were performed using a Co_3O_4(111) surface with an atomically defined structure.[118,120–123] Monolayer films of NBD derivatives with a carboxylic acid functionality were prepared in which the carboxylic acid group serves as an

anchor and binds to the surface Co^{2+} ions by forming a chelating surface carboxylate.[120] Using the NBD-derivative 2-cyano-3-(4-carboxyphenyl)norbornadiene (CNBD), the authors prepared a hybrid interface with an anchored QC derivative on Co_3O_4(111) in UHV (Figure 6B). Photochemical conversion and thermally activated back-conversion were possible even in monolayer films, and photochemical IR spectroscopy experiments in UHV showed high reversibility (98.5%). Importantly, the anchoring reaction does not have a measurable effect on the activation barrier for back-conversion (~100 kJ mol^{-1}).[118] The same hybrid interface prepared in UHV was also tested in an electrochemical environment. Although the anchored NBD derivative was photochemically converted to the QC derivative under potential control, the back-conversion could not be triggered electrochemically because decomposition of the compounds competed with the electrochemically triggered energy release.[121] In the future, this limitation may be overcome by using anchor groups that are more resistant to electrochemical oxidation.

Cycling properties

Finally, long-term stability, including the absence of side reactions, is necessary for use as a rechargeable energy storage system. Several NBD systems with push-pull substituents allow a higher number of cycles in solution (maximum degradation rate of 0.14% per cycle).[124–126] In addition, embedded oligo (phenylene ethynylene) arms end-capped with thioacetate groups NBD show excellent reversibility of up to 99.9995% in toluene.[127] However, neat samples degrade after just a few cycles.[73] Solvent selection may affect cyclability. Some solution tests have revealed a remarkable stability of DHA in toluene with less than 0.01% degradation per cycle (corresponding to 70 complete photothermal cycles). In polar solvents, such as ethanol and acetonitrile, a molecular loss per cycle of 0.28% and 0.18%, respectively, was observed. Most likely, the major degradation channels involve the formation of fully unsaturated azulenes.[43,128] Another practical approach is to increase stability in solid state by embedding MOST materials in polymers, leading to stable conversion of the NBD system over thousands of cycles.[129]

In general, AZO compounds show excellent cyclability and several studies have reported more than 200 energy storage cycles with little or no degradation.[62,82,130]

FROM LAB DEMONSTRATION TO DEVICE

In order to quantify the amount of solar power that a MOST system can store, the solar energy storage efficiency over the whole process needs to be estimated, which includes consideration of optical absorption of both isomers and integration over the full solar spectrum.[12] The estimated maximum energy storage efficiency for an ideal MOST system can reach more than 15% depending on the height of the energy barrier ($\Delta H^{\ddagger}$) and the model considered.[14,131] Unfortunately, these numbers are challenging to achieve in practice, partially because photoswitchable couples might absorb photons in the same optical range as each other.[124,125,128,130]

To experimentally realize a lab device demonstration, various experiments have been carried out. Heat release from MOST systems can be verified on a milligram scale by differential scanning calorimetry. When moving to larger-scale devices, one possibility is to trigger the energy release in molecular isomers using heterogeneous catalysts in flow reactors. This approach enables straightforward catalyst separation, as well as direct and precise control of the energy release rate. In the 1980s, it was already demonstrated that heat release from QC-derivative solutions can lead to temperatures above 50°C in principle.[132,133] Recently, using a fully charged

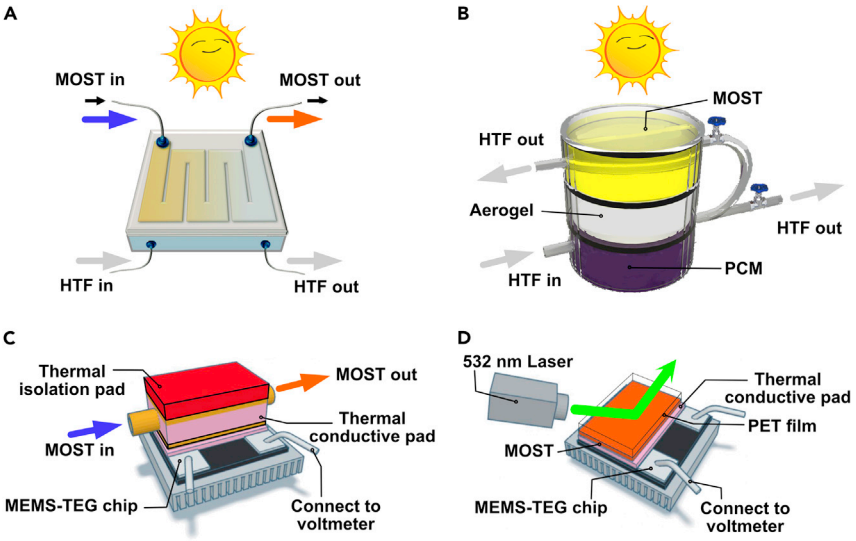

Figure 7. Recent exploited MOST hybrid systems for energy capture and release

Blue and red arrows indicate the direction of MOST flow before and after conversion, respectively. Gray arrows show the heat transfer fluid direction (HTF) in devices.

(A) MOST water heating hybrid system[124];

(B) MOST phase-change material hybrid system[134];

(C) Power generation using liquid form of MOST-TEG. The heat released by the MOST solution is captured by a TEG chip for electric power generation[126];

(D) Power generation using neat form of MOST-TEG. Charged neat form MOST material is coated on top of the TEG chip and a laser trigger is used to release heat for further power generation.[126]

push-pull QC compound dissolved at 1.5 M concentration in a low specific-heat capacity solvent toluene (ca. 1.6 J g^{-1} °C^{-1}), temperature changes of up to 63 K (85°C absolute temperature) were obtained after less than 1 min of reaction time.[125]

MOST systems can also be coupled with other solar technologies. One example is a two-layer device with MOST fluid in a transparent microfluidic collector on top of a thermal water heating system (Figure 7A).[124] By passing an NBD-based solution through the upper layer, sunlight converts NBD to QC, and the light that is not absorbed by the NBD layer is transmitted and absorbed by water flowing in the bottom layer. Thus, the upper part of the system successfully harvests solar energy as stored chemical energy in the MOST material with an efficiency of 1.1%. The combined device has a total solar energy capture efficiency of around 80%.[124] Further conceptional development has also focused on combining MOST with a phase-change storage material in a multilayer device. This advanced hybrid system can potentially deliver solar energy 24/7 (Figure 7B).[134]

Another coupled MOST device was recently used to generate electricity. By combining a microelectromechanical-systems-based thermoelectric generator (MEMS-TEG)[135–137] with a NBD derivarive[36] (in solution) (Figure 7C) or an AZO derivative[62] (neat coating) (Figure 7D), the hybrid device illustrates a proof-of-principle functional solar-electrical battery. Such integrated devices were able to continuously generate power densities of up to 1.3 W m^{-3}, showing that, on a small scale, opportunities exist for local solar energy storage and power production beyond traditional photovoltaic-electrochemical cell technologies.[126] The heat gradients achievable in current MOST systems are insufficient to drive a traditional heat engine system; however, the novel development of a MEMS-TEG chip

has demonstrated the feasibility of continuously generating electrical power from these systems. We note that this concept has generated a new type of solar cell that is independent of time and geographical restrictions and dramatically extends the application range of MOST systems.

OUTLOOK

In this review, we have summarized the state-of-the-art in MOST technology and discussed three well-studied classes of candidate materials, including their intrinsic properties and how their energy storage and release performance have been improved. We have also described the applications of MOST technology, as well as the remaining challenges and directions for future study. The parameters and discovery routes we reviewed here for each system will hopefully inspire future molecular and device design.

Regarding MOST molecules, it is unfortunately difficult to design a perfect switching couple that fulfills all criteria. As mentioned by Sun et al.[138,139] it is important to understand the key structure-property relations, and in this context, it is perhaps easier to set a specific goal (such as optimum absorption properties, high photoisomerization quantum yield, or high energy density) to guide molecular structure design toward its target. To overcome these challenges, one could consider combining several MOST systems, each optimized for specific wavelengths, into one system. This might allow us to combine advantages from different systems, as well as increase the energy storage density per molecule. An alternative direction could be to focus on polymerization of MOST monomers, thus having a cascading energy storage effect where absorption of one photon leads to several photoconversion events. Besides, molecular behavior could also be improved by other photochemical methods. For instance, light energy transfer technology has the potential to generate new opportunities for "red-shifting" MOST systems.[51] In this context, advanced triplet sensitizers promise to radically enhance efficiency as near-infrared to ultraviolet, and near-infrared to visible photon upconversion systems can use a larger part of the solar spectrum.[140–142] From a more general and optimistic perspective, the AI technology that is currently being developed[143] can potentially scan billions of possible molecular structures based on established DFT calculation benchmarks,[17,18,69,144] hence predicting the most optimal molecular structures to prepare. Automated flow chemistry machines, such as robot chemists,[145] can also reduce the cost of manual retrieval. A similar molecular manufacturing strategy is already summarized by de Almeida et al. for selection and synthesis of compounds in synthetic chemistry.[146]

It can further be envisioned that some features of MOST, such as structural flexibility and optical transparency, may allow us to integrate this technology into non-traditional applications. The transparency may be useful in applications, such as energy efficient windows,[101] and the structural flexibility may be useful in functional fabrics with thermal control and energy transfer functions.[147] The opportunity to store energy in a compact, local way and to release it on demand as heat may also lead to new hybrid systems for power production without the need for traditional batteries. Although up to 1.1% solar energy conversion efficiency has been demonstrated for MOST system in its current state,[124] it is still far from the performance of more traditional energy storage systems. For instance, today's commercial photovoltaic panels feature conversion efficiencies of well over 20%. However, due to the versatility of the systems and the large space of variability of organic materials, we have confidence that, with future advances, considering the discussed possible development

directions presented in this review, MOST systems may find practical use in a broad range of applications where thermal energy storage technologies today are not even imagined.

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