

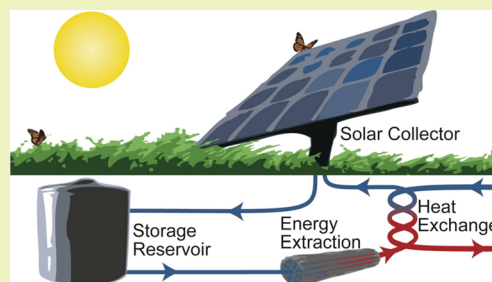
## Efficiency Limit of Molecular Solar Thermal Energy Collecting Devices

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**ABSTRACT:** As a larger fraction of energy is based on solar energy and other renewable energy sources, technologies for energy storage and conversion is becoming increasingly important. Molecular solar thermal (MOST) is a concept for long-term storage of solar energy in molecules and release of the energy as heat with full regeneration of the initial materials. The process is inherently closed cycle and emission free. No assessment of the fundamental efficiency limits of the technology has been made. In this report, efficiency limits and fundamental factors for molecular design of molecular solar thermal systems are discussed. Maximum efficiencies and potential temperature gradients are estimated using a number of basic assumptions on desired storage lifetimes and energy losses. The predicted maximum solar energy conversion efficiency is 10.6% at a  $S_1-S_0$  gap of 1.89 eV. At this  $S_1-S_0$  gap, the stored energy is able to create temperature differences of  $\sim 300$  °C. Several existing systems have an energy storage density in line with the predicted maximum one but do so at larger than optimal  $S_1-S_0$  gaps.

**KEYWORDS:** Molecular solar thermal, Energy efficiency, Energy storage, Solar thermal, Solar energy, Energy conversion, Maximum solar energy-conversion efficiency

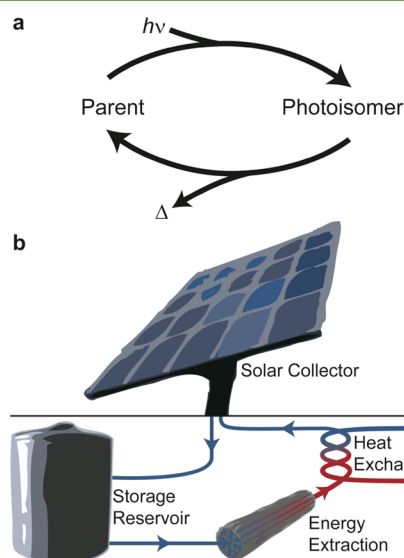


## INTRODUCTION

Development of renewable energy technologies are nowadays a focus point in the goal of reaching a sustainable world society. Hydropower and wind turbines are already implemented on a large scale, but limitations on their geographical location implies that these technologies alone cannot produce the needed energy output.<sup>1</sup> Solar energy technologies in the form of photovoltaics have seen an impressive development during the last decades, and it is estimated that the cost of solar energy for power production will be able to compete directly with fossil fuel technologies as early as 2016–2018.<sup>2</sup> As a larger fraction of the energy production stems from solar energy, storage of energy and load leveling is becoming increasingly important due to challenges with both intermittency in solar energy flux and variations in energy demand.<sup>3–8</sup> However, technologies for storing electrical energy have not been widely implemented on a large scale due to high cost, geographical constraints, and/or limited energy storage time.<sup>8–11</sup>

Collection of solar energy for storage in the form of energetic chemical bonds has the advantage that the harvesting and storage processes are collocated and combined in one entity. This approach is currently being studied in several variants, such as photoinduced water splitting, CO reduction, CO<sub>2</sub> reduction, and more biologically inspired approaches.<sup>12–16</sup> A less explored alternative is molecular solar thermal (MOST) systems where the absorption of light induces an isomerization reaction in a molecule, transforming it to a high-energy species, thus enabling storage of large amounts of heat.<sup>17</sup> In MOST systems, a photoactive molecule (the parent) is exposed to photons and is thus photochemically transformed into a high-energy photoisomer, which should ideally have a long lifetime. Using external stimuli such as heat or catalysis, the energy

stored in the photoisomer can be recovered in a controlled way along with regeneration of the parent molecule (Figure 1).



**Figure 1.** (a) The MOST cycle: The parent molecule is converted to a stable high-energy isomer upon absorption of a photon. The stored energy is released as thermal energy upon isomerization of the photoisomer back to the parent molecule. (b) A closed MOST system consisting of a solar collector, storage tank, heat extraction reactor, and heat exchanger.

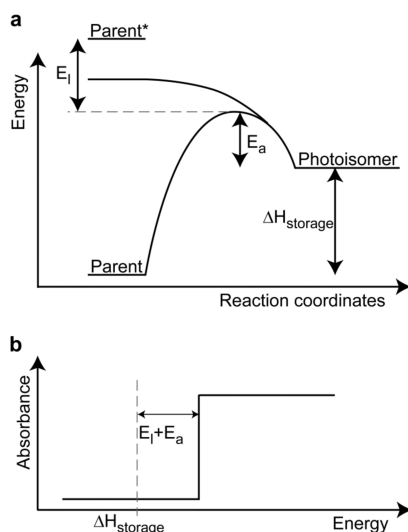
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Furthermore, because only an internal rearrangement of the active molecule is necessary in the energy storing process, the system can work in a closed system. This has many advantages to open systems (e.g., petrol combustion), such as ease of recycling material, negligible contamination of the environment, and that cycling of material allows for a higher material cost.<sup>17</sup>

Several chemical systems have been proposed as candidates for MOST energy storage, e.g., stilbene like molecules, fulvalene ruthenium complexes (Ru<sub>2</sub>Fv), and norbornadienes, which also have been incorporated into photoresponsive polymers (Figure 2).<sup>18–33</sup> However, a theoretical discussion



**Figure 2.** (a) Energy diagram explaining the enthalpy of energy storage ( $\Delta H_{\text{storage}}$ ), the activation energy of backisomerization ( $E_a$ ), and a loss term ( $E_l$ ). (b) Absorption of the material is modeled as a step function, absorbing all photons above the threshold energy.

governing the fundamental limits with regards to solar energy conversion efficiency and energy storage density has been absent. Efficiency limits, like the well-known Shockley and Queisser limit for silicon solar cells, provide a benchmark for working devices as well as indicating where improvement potential lies.<sup>34</sup> Here, we present an estimate of the maximum solar energy conversion efficiency of MOST devices and discuss the three most important device parameters which are solar energy conversion efficiency, energy storage density, and energy storage half-life. We will show that these properties are dependent on each other so that the intended application needs to be kept in mind when optimizing MOST systems.

### ESTIMATING THE MAXIMUM SOLAR ENERGY CONVERSION EFFICIENCY

In a molecular solar thermal storage and release system, the active molecule works both as a light collector and as an energy storage material. A consequence of this is that the active molecule needs to be in liquid phase, either by being a liquid at the operation temperature or dissolved in a solvent, so it can be pumped between a solar collector, a storage reservoir, and an energy extraction device (Figure 1).<sup>29</sup> To maximize the energy density, a very high concentration of the active molecule is necessary; preferably the molecule should be a low viscous liquid at room temperature. Furthermore, a sufficiently thick absorbing layer of the working fluid is needed in the solar

collector for the parent molecule to be able to absorb all incoming photons. The end product from the solar collector should consist primarily of the photoisomer to achieve as high energy density as possible but still contain a concentration high enough so that the parent molecule absorbs all incoming photons. A consequence of this demand is that the photoisomer needs to be optically transparent in the range of the solar spectrum.

To calculate the maximum solar energy conversion efficiency, we assume that all molecules act individually, i.e., do not affect each other, and that the active molecule absorbs all photons with energy higher than a threshold value and none below that value. Each absorbed photon results in one photoisomerization, i.e., the quantum yield of photoisomerization is unity. The stored energy in the system is the energy difference between the parent molecule and the photoisomer (Figure 2); excess photon energy is dissipated as heat. Two more modes of energy losses are taken into account in the model. The first one takes into account the energy loss due to the requirement of having an energy barrier toward the back reaction. Without this barrier, the photoisomer would immediately isomerize back to the parent compound dissipating the energy as heat and preventing it from storing the solar energy for any substantial amount of time. The required energy barrier ( $E_a$ ) can be estimated by applying chemical kinetics using the desired half-life ( $\tau_{1/2}$ ) as input.

Molecular solar thermal systems are unimolecular, meaning that in most cases first-order kinetics will apply when modeling the rate of back conversion by thermal means. The half-life ( $\tau_{1/2}$ ) of the photoisomer (PI) with respect to its rate of backconversion ( $k$ ) is

$$\frac{d[\text{PI}]}{dt} = -k[\text{PI}] \quad (1)$$

$$\ln(0.5) = \ln \frac{[\text{PI}]}{[\text{PI}_0]} = -k\tau_{1/2} \quad (2)$$

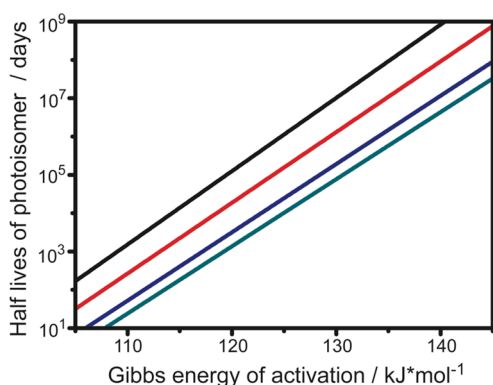
The Eyring equation was used to calculate the rate of backconversion as a function of Gibbs energy of activation ( $\Delta G^\ddagger$ ).

$$k = \frac{k_T \times T}{h} e^{-\Delta G^\ddagger/RT} \quad (3)$$

where  $k_T$  is Boltzmanns constant,  $h$  is Plancks constant,  $R$  is the gas constant, and  $T$  is the storage temperature. Combining eqs 2 and 3 gives an expression for the half-life of the photoisomer.

$$\frac{h \times \ln(2)}{k_T \times T \times e^{-\Delta G^\ddagger/RT}} = \tau_{1/2} \quad (4)$$

Half-lives as a function of storage temperatures and free energy of the backconversion reaction are shown in Figure 3. The storage time is very dependent on the Gibbs energy of activation. An increase of only 10 kJ/mol gives about the same effect on the attainable storage time as a decrease in temperature from ambient to zero degrees. At ambient temperature, an activation energy, and thus energy loss, of 120 kJ/mol is enough to receive a half-life of the photoisomer of 1400 days, a more than sufficient amount of time for seasonal energy storage. For day to night energy storage, an activation energy of 110 kJ/mol is enough. It is interesting to compare the possible storage time of a MOST system to that of batteries. For comparison, typical lithium ion batteries have a



**Figure 3.** Half-lives of photoisomer (in days) at different storage temperatures (black = 0 °C, red = 10 °C, blue = 20 °C, and green = 25 °C) with respect to Gibbs energy of activation of backconversion ( $\Delta G^\ddagger$ ).

self-discharge rate of 46% per year (2009).<sup>10</sup> This is a much higher rate than that of a MOST system having a free energy of backisomerization of 120 kJ/mol. Furthermore, the self-discharge rate of a MOST system can be made negligible by increasing the free energy of backisomerization by an additional 10 kJ/mol.

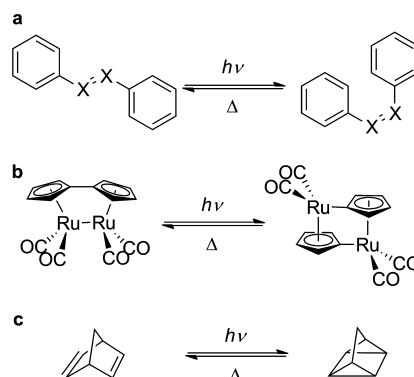
There might exist methods of increasing the storage time without increasing the energy barrier of backisomerization. For example, if the photoisomer is a solid at room temperature and precipitates from the working fluid when formed, it would efficiently be trapped in the high energy conformation. Even if this would be a method of significantly enhancing the energy collecting efficiency and energy storage density of the system, without affecting its storage half-life, it would (in our view) compromise how a MOST system could be designed, and it is therefore not taken into account here.

The second loss term compensates for different relaxation effects and the fact that the initial excited state might not be the electronically excited state from where the isomerization reaction occurs. For example, many photochemical reactions occur on the triplet surface, which means that the loss term,  $E_l$ , then would equal the energy difference between the  $S_1$  and  $T_1$  state.<sup>35</sup> This is a system-dependent parameter that should, if possible, be minimized. When calculating the maximum solar energy conversion efficiency, this parameter is set to zero, indicating that the isomerization reaction occurs at the singlet surface and that no relaxation occurs from the initially formed Franck–Condon state.

When calculating the efficiency limit of a MOST system, the quantum yield is assumed to be unity even at very low driving forces for photoisomerization. Furthermore, the parent compound and the photoisomer are in most cases very similar in structure. For example, isomerization of stilbenes and  $Ru_2Fv$  (Scheme 1) proceeds via internal rotations and rearrangements; no parameters that change the rigidity in the molecules are changed. Therefore, it is assumed that the entropy of the isomerization reaction is negligible compared to the enthalpy change, which means that the free energy equals the activation enthalpy in the above reasoning.

To calculate the number of absorbed photons at unit time and area ( $\dot{N}$ ) as a function of enthalpy difference between the parent molecule and the photoisomer, numerical integration of the AM 1.5 solar spectrum (ASTM G173-03) was performed.

**Scheme 1.** Three Examples of Molecular Solar Thermal Energy Storage Systems. (a) Cis–trans isomerization of stilbenes ( $X = C$ ) and azobenzenes ( $X = N$ ). (b) Isomerization of fulvalene ruthenium. (c) Intramolecular 2 + 2 cycloaddition of norbornadiene.

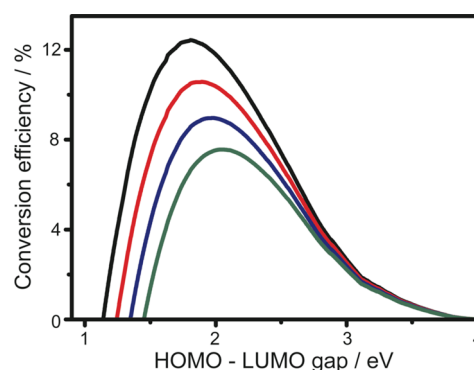


$$\dot{N} = \int_{E_{nm}}^0 \dot{N}_{\text{sun}}(nm) dn m \quad (5)$$

where  $\dot{N}_{\text{sun}}$  is the photon flux of solar radiation per unit area, time, and wavelength, and  $E_{nm}$  corresponds to the energy of the  $S_1$ – $S_0$  gap of the parent compound. The total solar energy conversion efficiency ( $P$ ) of the system as a function of the  $S_1$ – $S_0$  gap can then be calculated as

$$P(E_{nm}) = \frac{\dot{N}(E_{nm})(E_{nm} - E_a - E_l)}{\dot{E}_{\text{sun}}} \quad (6)$$

where  $\dot{E}_{\text{sun}}$  is the energy of solar radiation per unit area and time, reaching the surface of the Earth. Figure 4 shows the



**Figure 4.** Solar energy conversion efficiency ( $P$ , eq 6) as a function of  $S_1$ – $S_0$  gap of solar thermal devices having different amount of losses ( $E_a + E_l$ ) going from the electronically excited parent molecule to the photoisomer. Black:  $E_a + E_l = 110$  kJ/mol ( $\tau_{1/2} = 24$  days at 25 °C). Red:  $E_a + E_l = 120$  kJ/mol ( $\tau_{1/2} = 1.4 \times 10^3$  days). Blue:  $E_a + E_l = 130$  kJ/mol ( $\tau_{1/2} = 7.7 \times 10^4$  days). Green:  $E_a + E_l = 140$  kJ/mol ( $\tau_{1/2} = 4.3 \times 10^6$  days).

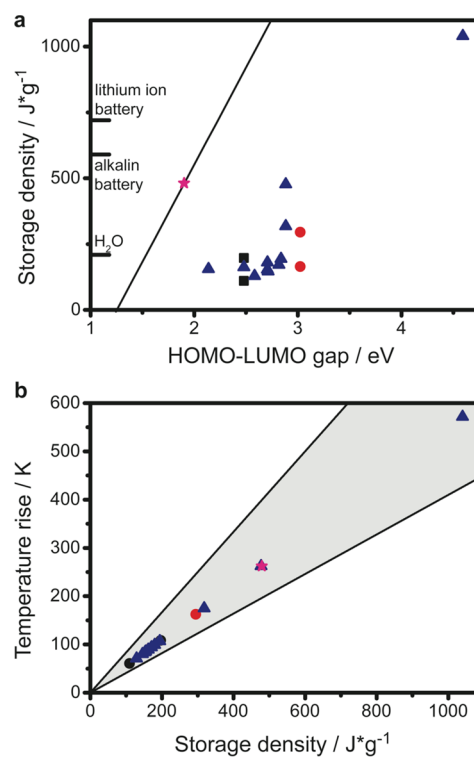
maximum collected energy as a function of lowest excitation energy of the parent compound, having different total energy losses ( $E_a + E_l$ ). The minimal amount of losses needed to form a photoisomer and trap it for a sufficient amount of time for use in seasonal energy storage is 120 kJ/mol ( $E_a = 120$  kJ/mol and  $E_l = 0$  kJ/mol) and for use in day to night energy storage is 110 kJ/mol, which gives a maximum energy conversion efficiency (solar energy to chemical energy for heat production) of 10.6% and 12.4% at a  $S_1$ – $S_0$  gap of 1.89 and 1.81 eV, respectively.

Comparing with the maximum efficiency of silicon photovoltaics, the maximum energy conversion efficiency of a molecular solar thermal device is somewhat lower. However, other upcoming solar collecting technologies have theoretical maximum efficiencies close to that of the MOST system. Concentrated solar thermoelectric generators have an estimated maximum power conversion efficiency of 15.9%, and dye sensitized solar cells employing  $I_3^-/I^-$  as the electrolyte have an estimated maximum power conversion efficiency of 13.4%.<sup>36,37</sup> It should be noted that the MOST system stores the energy as heat and not electricity and is thus not as versatile as solar power-producing devices. The  $S_1-S_0$  gap at which the maximum solar energy conversion efficiency is achieved for MOST systems is higher than the corresponding bandgap for photovoltaic devices (1.34 eV).<sup>38</sup> This should make it easier to construct an optimized molecular solar thermal system than an organic photovoltaic device because a  $S_1-S_0$  gap of 1.89 eV (656 nm) is much easier to obtain in a molecular system than 1.34 eV (925 nm). Furthermore, an increase of the  $S_1-S_0$  gap to 2.1 eV (590 nm) in the solar thermal system, which is a readily available molecular HOMO–LUMO energy separation, only results in a lowering of the maximum efficiency from 10.6% to 9.9%.

The maximum solar energy conversion efficiency is highly dependent upon the energy separation between the electronically excited state of the parent isomer and the photoisomer ( $E_1 + E_a$ ; Figure 2). Each additional 10 kJ/mol of energy separation reduces the maximum efficiency of the device by two percentage points, pointing at reduction of this loss as a key improvement parameter on which to focus. Another possible way of increasing the efficiency of a MOST system could be to implement it together with triplet–triplet annihilation upconversion, which lately has begun to show some potential.<sup>39–44</sup>

## ENERGY DENSITY

The energy density of the working fluid needs to be high compared to other possible storage systems delivering heat, such as hot water. Water with an elevated temperature compared to an ambient temperature of 50 K has an energy storage density of 209 J/g.<sup>45</sup> For MOST systems, the energy density depends on the energy difference between the parent molecule and the photoisomer ( $\Delta H_{\text{storage}}$ ) and, thus, indirectly on the  $S_1-S_0$  gap of the parent molecule. The  $S_1-S_0$  gap must, thus, be a compromise between achieving maximum solar energy conversion efficiency ( $S_1-S_0$  gap of 1.89 eV) and achieving highest possible energy density. The lightest molecule proposed as a MOST candidate is the norbornadiene–quadricyclane system, having a molecular weight in the basic unsubstituted form of 92 g/mol. This is a very small molecule, which can store a significant amount of energy, but it predominantly absorbs in the UV region of the electromagnetic spectra. It is hard to believe that the absorption can be extended to 600–700 nm without increasing the molecular weight by adding functional groups. It has therefore been stated that a minimum molecular weight of a MOST candidate that is capable of absorbing visible light lies in the region of 130 g/mol.<sup>17</sup> Assuming an energy loss of 120 kJ/mol, going from the LUMO of the parent molecule to the photoisomer, the maximum solar energy conversion efficiency is achieved at a  $S_1-S_0$  gap of 1.89 eV, which results in an energy storage density of 480 J/g (Figure 5). This value is significantly lower than the measured storage density of the unsubstituted norbornadiene–



**Figure 5.** (a) Energy storage density as a function of the  $S_1-S_0$  gap for an optimal MOST device (line: magenta star indicates maximum solar energy -conversion conditions), inserted is the storage densities for various MOST systems ( $S_1-S_0$  gap taken as onset of absorption; black,  $Ru_2Fv$ ; red, stilbene derivatives; and blue, norbornadienes),<sup>18,20,23,29,30,32</sup> water ( $\Delta T = 50$  °C), and some common electrochemical batteries. (b) Temperature rise as a function of storage densities of a pure MOST molecule, assuming a heat capacity in between that of ethanol ( $c_p = 2.44$  J/K g lower line) and dichloromethane ( $c_p = 1.20$  J/K g, upper line). Present systems are indicated by black squares ( $Ru_2Fv$ ), red circles (stilbene like) and blue triangles (norbornadienes), and an optimal MOST system at maximum energy conversion conditions is indicated by a magenta star.

quadricycle system. However, norbornadiene only absorbs in the far UV end of the solar spectrum, which together with an extremely low molecular weight (92 g/mol) results in a very high energy storage density. There exist norbornadiene derivatives having attached electron donating and accepting groups that absorb light up to 500 nm that can store 160 J/g (norbornadienes absorbing at longer wavelength have so far a too fast rate of back-reaction for being practically useful).<sup>32</sup> As evident from Figure 4, the larger the energy losses in the MOST system the larger is the  $S_1-S_0$  gap required to achieve maximum solar energy conversion efficiency of the device. This means that a molecule having a total energy loss from the excited state to the photoisomer of 140 kJ/mol still has a high energy storage density (420 J/g) at the  $S_1-S_0$  gap giving maximum solar energy conversion efficiency. The fact that the storage density is not very dependent on energy losses means that the storage density and storage half-life are not very dependent on each other.

The energy storage density of a MOST device having an optimal solar energy conversion efficiency is about twice as high as water ( $\Delta T = 50$  K). Furthermore, the lower heat capacity of organic molecules compared to water results in a relative higher  $\Delta T$  for the MOST system compared to water (Figure 5).

It is clear from Figure 5 that existing MOST candidates can store a significant amount of energy, an energy that can be used to form a substantial temperature gradient. Furthermore, the size of the temperature gradient created when extracting the stored heat scale linearly with the heat capacity of the substance. This means that a low heat capacity of MOST systems is of value because it will enable higher generated temperatures. The possibility to form large temperature gradients is a great advantage of this system compared to water heating storage because a high temperature gradient is important for the energy transformation efficiency through the Carnot cycle. For example commercial plants using the organic Rankine cycle display an efficiency of 10–13% using a temperature gradient of slightly over 100 °C.<sup>46</sup> However, it should be noted that the temperature rise for the existing systems shown in Figure 5b are calculated for pure substances (and assumed heat capacities). A requirement for a MOST candidate is that it must be in a liquid state at room temperature. Dissolving it in a solvent severely limits its energy storage density and thus usability, if a very high solubility is not achieved.<sup>29</sup>

## CONCLUSION

Existing MOST systems are not close to optimal. We show here that the internal energy losses together with the coverage of the solar spectrum are the least optimized parameter in present systems. The majority of the systems absorb in the UV region or in the bluish part of the solar spectrum, quite far from the optimal  $S_1-S_0$  gap at 656 nm, which severely limits the solar energy conversion efficiency of all known systems. However, increasing the  $S_1-S_0$  gap from 656 to 590 nm (2.1 eV) only lowers the maximum solar energy conversion efficiency by 7%. The maximum attainable storage density depends on the molecular weight. It is harder to construct small molecules having a low  $S_1-S_0$  gap than a high  $S_1-S_0$  gap, so 2.1 eV might be an appropriate  $S_1-S_0$  gap to pursue. Today, there exist systems having storage enthalpies comparable to modern batteries, resulting in a potential of creating temperature gradients of over 100 degrees, enough to generate electrical power in organic Rankine cycles. Furthermore, systems exist that are stable over years of storage, which is much more stable than for example lithium ion batteries that have a self-discharge rate of 46% per year.<sup>10</sup> The energy stored in the MOST system is that of latent heat, which means that a possible application lies in areas where heat on demand is the preferred form of energy. This heat could in turn be converted to power with the inherent energy losses associated with the Carnot efficiency. The energy storage potentials of existing systems are in line with the optimal one, but the photon absorption must be red-shifted to achieve an efficient solar conversion without compromising the storage enthalpy and storage half-life. We hope that this work will invoke inspiration for the optimization of MOST systems in the quest for sustainable power generation and storage.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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