

Title: Photocyclization of Fluorinated Acetophenones Unlocks an Efficient Way to Solar Energy Storage

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Abstract: The development of light-driven isomerization offers a promising avenue for energy storage applications. However, a persistent challenge lies in controlling the stability of the photoisomeric state and in catalyzing the thermal reversal effectively. In this work, we introduce the molecular pair *ortho*-methylacetophenone \rightleftharpoons benzocyclobutenol as a promising platform for long-term energy storage. To obtain an overall good performance, a trifluoromethyl group is strategically introduced. This group prevents unproductive reaction pathways during the photochemical cyclization, ensures stable photoisomers, and facilitates back-isomerization by critically lowering the pK_a of the benzocyclobutenol scaffold. Thus, efficient reversal using simple organic bases is achieved, which capitalizes on substantial rate differences for normal *vs.* anionic electrocyclic ring-openings. Ultimately, this discovery enables controlled heat release under ambient conditions.

Introduction: The utilization of solar energy is one of the key scientific challenges of the 21st century, offering significant potential for mitigating climate change.¹ In this regard, light-driven out-of-equilibrium isomerization offers an attractive pathway for harnessing photon energy and embedding it within chemical bonds.^{2,3} If a thermal back reaction can be triggered after photochemical isomerization, this tandem process offers a sustainable approach to heat generation, which currently accounts for more than 90% of the world's energy consumption (Figure 1A).⁴ In contrast to solar thermal collectors, heat generation by molecular solar thermal (MOST) systems offers a temporal separation between the time when the energy is generated and when it is released. This can be controlled, e.g., by the introduction of a suitable catalyst initiating back-isomerization. However, identifying compounds for MOST application is challenging due to the intricate interplay between the photochemical and thermal isomerization processes.⁵⁻⁸ In this context, a number of privileged compound pairs have been proposed, which include norbornadiene \rightleftharpoons quadricyclane,⁹ *E*-azobenzene \rightleftharpoons *Z*-azobenzene,¹⁰ and dihydroazulen \rightleftharpoons vinylheptafulven¹¹ (Figure 1B). Current research concentrates on improving the photophysical properties of the established systems¹²⁻¹⁵ as well as on identifying new isomer couples.¹⁶⁻²⁰ Important metrics for MOST optimization are high isomerization yields (>95%), significant back-isomerization energies ($\Delta H_{\text{iso}} > 300$ J/g), and a good overlap with the solar spectrum ($\lambda = 300$ -800 nm). A major challenge remains the improvement of the thermal stability of the photoisomer, which is a crucial factor for safe and long-term energy storage. This endeavor is further frustrated by the notion that higher thermal stability often correlates with a decrease in stored energy.^{21,22} The identification of effective catalysts that trigger heat release at stable photoisomers adds another hurdle for devising a reliable system.

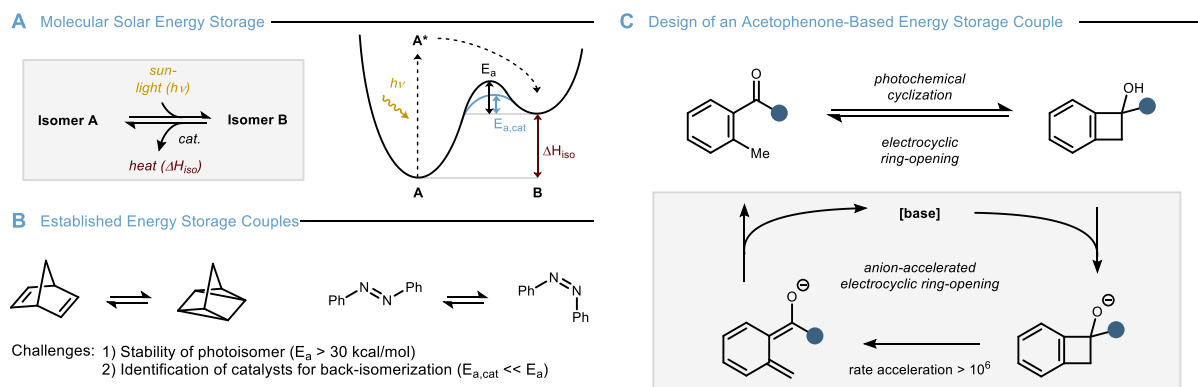


FIGURE 1. Storing solar energy with molecular isomers. (A) Schematic representation of a MOST system. (B) Representative examples of MOST systems. (C) Design of an energy storage couple based on the photocyclization and thermal reversion of *ortho*-methylacetophenones.

In this work, we report a conceptually new MOST couple, which is founded in the photocyclization of *ortho*-methylacetophenones (Figure 1C).^{23,24} The corresponding benzocyclobutenols obtained after irradiation are recognized for their high level of strain yet remarkable stability, hinting at their potential for effective application in energy storage. Our strategy for back-isomerization builds on an electrocyclic ring opening of the corresponding benzocyclobutenolate, which, in turn, can be accessed from the respective benzocyclobutenol by deprotonation. This approach capitalizes on charge-acceleration within pericyclic reactions, an observation originally made by Evans and co-workers when studying oxy-Cope rearrangements.²⁵ Our endeavors in establishing a well-balanced isomer pair that meets the stringent photochemical and physicochemical prerequisites for MOST application are presented. Moreover, we detail our results in developing the anion-accelerated ring opening reaction, employing a simple organic base as the catalyst, which triggers heat release at ambient temperatures.

Results: A plausible mechanism for the photocyclization of *ortho*-methylacetophenones is outlined in Figure 2A.^{26,27} Excitation of the syn-conformer of *ortho*-methylacetophenone **1** gives access to the triplet ketone **31** via intersystem crossing (ISC). Subsequently, 1,5-hydrogen atom transfer (HAT) provides triplet biradical **32**, which undergoes another ISC to forge enol isomers *E*-**2** and *Z*-**2** simultaneously. The mechanistic foundation for this photoenolization process goes back to pioneering studies from the 1970s by the groups of Wagner²⁸ and Scaiano.²⁹ The *Z*-isomer *Z*-**2** is known to quickly reverse to the starting material, while the *E*-isomer *E*-**2** generally possesses a longer life-time. This principally sets the stage for a 4- π electrocyclization (EC) towards the desired benzocyclobutenol **3**. However, in the case of *ortho*-methylacetophenone **1a** (R = Me), the photocyclization is characterized by low yields and thus not suitable for the development of a MOST system (Figure 2B, Entry 1).³⁰ We presumed that the inefficiency of this process is based on a competitive 1,5-hydride shift of isomer *E*-**2a** (Figure 2B, grey box).³¹ For this reason, we initiated our optimization by hydrogen displacement to inhibit the unproductive reversion to starting material. Fluorine emerged as our favored option for this endeavor due to the enhanced stability of the C–F bond. Moreover, fluorine fulfills our aim to identify a low molecular weight candidate to uphold a high energy density. However, the introduction of one fluorine atom (**1b**) led to unsatisfactory results (Entry 2), which can be explained by slow keto-enol tautomerism of the photogenerated enol of **1b** (See pages S13-15 of the SI). In contrast, difluoroacetophenone **1c** and trifluoroacetophenone **1d** showed significantly better results, with a yield of 49% and 66%, respectively (Entries 3 and 4). Since benzocyclobutenols such as **3d** do not absorb light beyond 280 nm, the occurrence of a photostationary state is effectively obviated in this sequence. Thus, **3d** could be obtained in >99% yield by extending the reaction time (Entry 5). The reaction also performed well when

using a 370 nm light emitting diode (LED), displaying first order kinetics with no indications of side reactions or decomposition, as monitored by ^{19}F nuclear magnetic resonance (NMR) spectroscopy (See Figure S12 in the SI). X-ray analysis of the product revealed an elongated, newly-formed C–C σ -bond of 1.58 Å, highlighting the distorted character of the strained entity. To decipher the mechanism of the pivotal 4π electrocyclic ring closure towards **3d**, we synthesized trifluoroacetophenone **4** and subjected it to the optimized conditions (Figure 2C). Benzocyclobutenol **6** was obtained as a single diastereomer, signifying a conrotatory ring closure of *E*-**5**, consistent with a thermal reaction pathway. The subsistence of *E*-**5** as a reaction intermediate was validated through a trapping experiment with *N*-methylsuccinimide, yielding

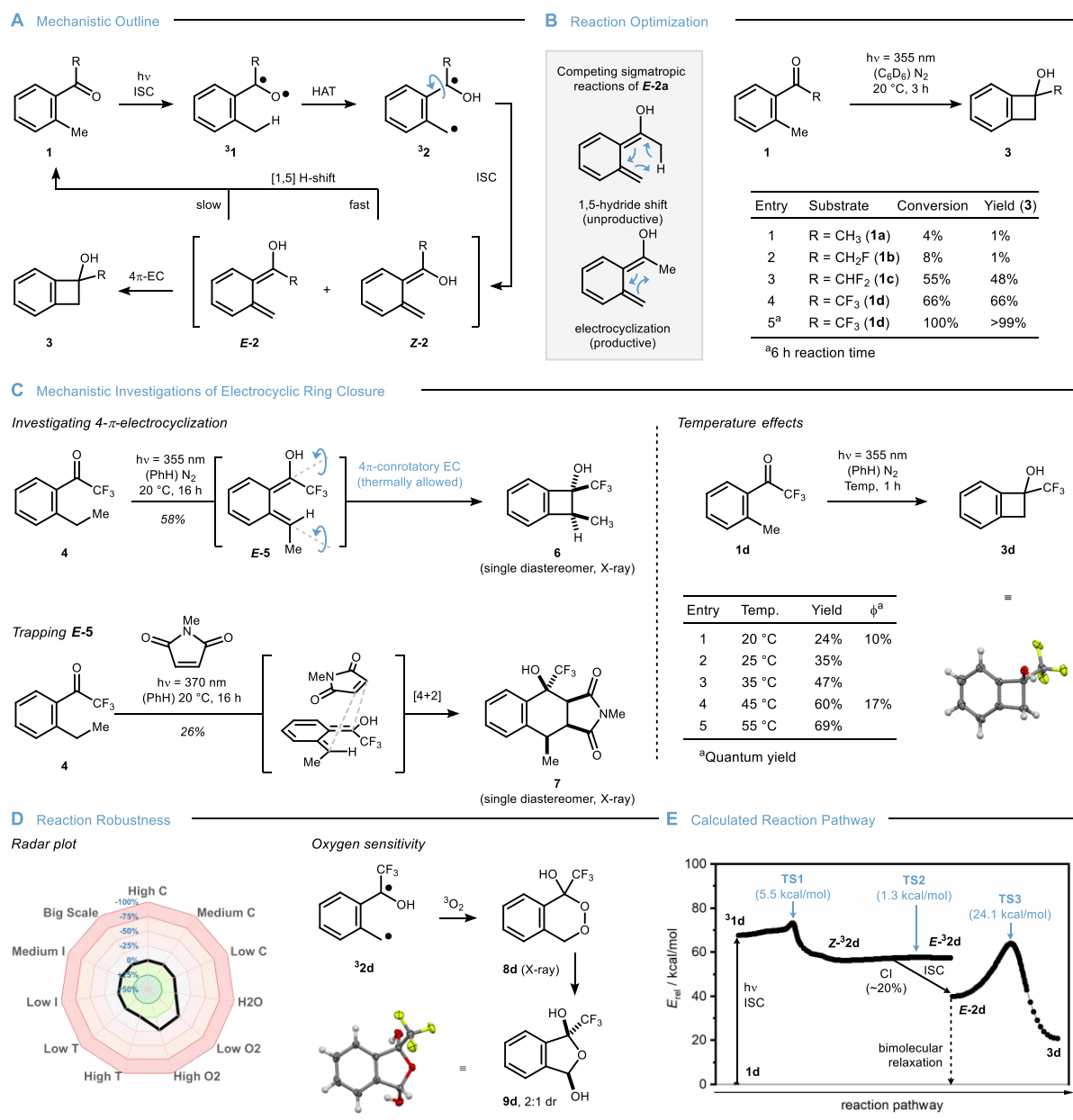


FIGURE 2. Development of an efficient photoisomerization of *ortho*-methylacetophenones. (A) Mechanistic considerations and current limitations for the photocyclization of *ortho*-methylacetophenones. (B) Reaction optimization addressing the acetyl liability. (C) Mechanistic investigations uncovering key factors for cyclization efficiency. (D) Assessing the reaction robustness. (E) Calculated reaction pathway using DFT. All calculated intermediates were also detected (directly or indirectly) by NMR and transient absorption spectroscopy.

tricycle **7** as the sole product.^{32–34} Based on these results, we hypothesized that raising the reaction temperature will facilitate the EC and thus improve the conversion to benzocyclobutenol **3d**. Indeed, we observed an increase in rate when gradually raising the reaction temperature of the photocyclization (Figure 2C, right). Notably, this improvement correlated well with the measured quantum yields (ϕ) of the isomerization process, which were determined at the excitation wavelength of 355 nm with a combined laser flash photolysis (LFP)-NMR technique (See pages S27-33 of the SI). To explain this temperature-dependent quantum yield, we assume that the EC is more drastically facilitated by the temperature change than the unproductive reversion to starting material via bimolecular processes. An improved quantum yield at elevated temperatures is a valuable asset for large scale MOST applications, where heating can be a side effect due to intense photoirradiation or insufficient cooling.

Next, we evaluated the reaction's robustness. While the reaction yield was insensitive to changes in temperature, light intensity, water-content, or scale, aerobic conditions led to drastically reduced performance as indicated by the radar diagram depicted in Figure 2D.³⁵ Oxygen is a known interferent of reaction intermediates during photoenolization.³⁶ When performing the reaction under air or oxygen atmosphere, peroxide **8d** was formed, which slowly decomposed to hemiacetals **9d** explaining the sluggish reaction outcomes. Control experiments suggest that **8d** is formed by a spin-allowed quenching of the triplet biradical **³2d** by ³O₂ (see SI for further details). We further studied the impact of modifications to the *ortho*-substituent and electronic perturbations of the aromatic ring on the reaction outcome. While we were able to access 12 previously unknown benzocyclobutenols, the parent compound **3d** remained the best candidate for MOST application based on its good energy density, high reaction rate, and absence of side reactions (see Figure S30 in the SI for further details). When it comes to solvent selection, benzene proved to be the most effective, enabling the consistent generation of multigram quantities at up to 1 M concentrations (see SI for further details).

To further validate the key mechanistic steps proposed in Figure 2A, an in-depth LFP analysis was conducted for **1d** at 355 nm, which allowed the detection of photoenol **Z-2d** as a short-lived intermediate ($\tau \sim 0.50 \mu\text{s}$) and photoenol **E-2d** as a relatively long-lived intermediate. Assuming similar difference extinction coefficients, the ratio of **Z-2d** and **E-2d** formed after the laser pulse is estimated to be $\sim 80:20$. This is in good accordance with the measured quantum yield of 17% under the prerequisite that only **E-2d** undergoes efficient EC. To confirm this assumption, density functional theory (DFT) calculations were performed, highlighting an energetically favorable 1,5-hydride shift for **Z-2d** (See pages S51-54 in the SI). In addition, the productive reaction pathway including the relative energies of the intermediates and respective transition states during the formation of **3d**, was calculated using the nudged elastic band formalism with transition state optimization (NEB-TS) at B3LYP/6-311+G(d,p) level of theory (see Figure 2E). The HAT from **³1d** \rightarrow **³2d** was found to be thermodynamically favorable by 11.4 kcal/mol and readily occurs via a low energy barrier of 5.5 kcal/mol (**TS1**). A small distance between the singlet potential energy surface and the triplet potential energy surface at **TS2**, or a possible conical intersection (CI), enables efficient ISC, leading to the formation of **Z-2d** and **E-2d**.³⁷ The ratio of **Z-2d** and **E-2d** is ultimately dictated by the geometry at which the CI is localized. Finally, exothermic EC of **E-2d** furnishes benzocyclobutenol **3d** via **TS3** (24.1 kcal/mol), which aligns with the experimental findings. Importantly, all key intermediates studied computationally have been detected spectroscopically or via trapping experiments providing a solid mechanistic framework for the photochemical isomerization part of this MOST system.

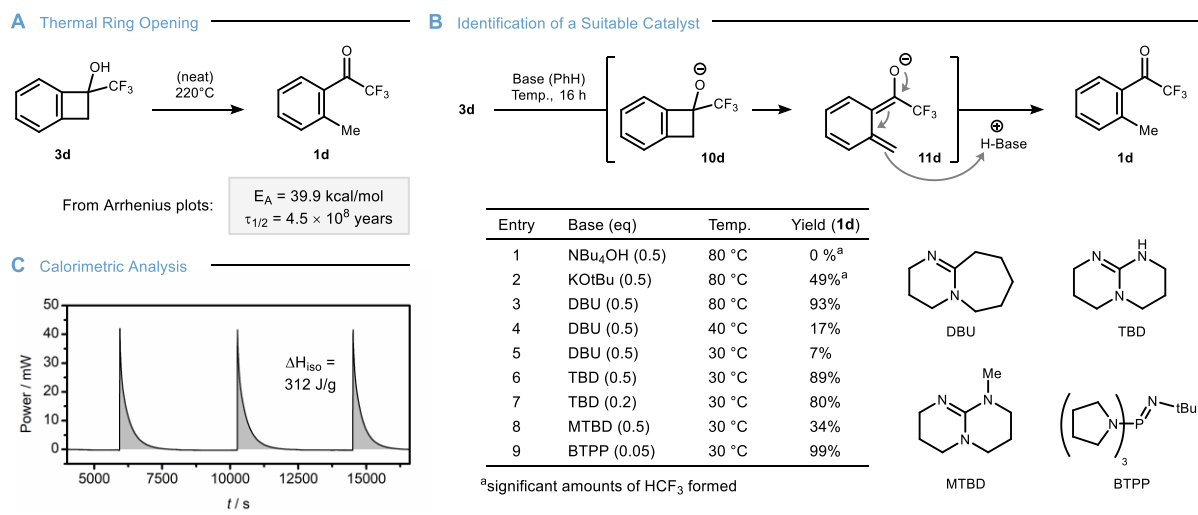


FIGURE 3. Establishing back-isomerization through catalysis. (A) Thermal ring-opening based on 4- π electrocyclic ring opening. (B) Identification of catalysts based on anionic rate-acceleration. (C) Calorimetric analysis of the ring opening event.

Having a promising candidate in hand, we started looking at the electrocyclic ring opening. Benzocyclobutenol **3d** exhibited an exceptional thermal stability showing no signs of decomposition even after extended heating at 150 °C. This result is in stark contrast to other benzocyclobutenols, which are known to undergo electrocyclic ring opening at 100-110 °C.^{38,39} However, when heating **3d** to 220 °C in a closed vial, clean back-isomerization to the starting material was observed (Figure 3A). An activation barrier of 41.1 kcal/mol was derived from a conversion-time-plot of the ring-opening event correlating well with the calculated TS energy from Figure 2E (43.0 kcal/mol for **3d** \rightarrow **E-2d**). This characteristic makes **3d** attractive for long-term energy storage and safe transportation with an extrapolated thermal half-life of 5.5×10^8 years at room temperature, clearly distinguishing it from other MOST systems. As opposed to the high stability of benzocyclobutenol **3d**, its anion readily underwent ring opening (Figure 3B, **10d** \rightarrow **11d**).^{40,41} The torqueselectivity of the process is known to follow outwards rotation of the hydroxy group based on pioneering computational studies by Houk and coworkers.⁴² When potassium *tert*-butoxide was used as a base at 90 °C, 49% of acetophenone **1d** was obtained along with minor amounts of decomposition materials (Figure 3B, Entry 1). Hydroxyl bases were not suitable as they triggered a consecutive haloform reaction as evidenced by fluoroform evolution (Entry 2, see SI for further details). However, the progression to organic superbases resulted in a notable improvement.⁴³ 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) catalyzed a clean and high yielding ring-opening reaction (Entry 3). Moreover, fine-tuning of the organic base, catalyst loading, and reaction time allowed us to maintain good conversion while dropping the reaction temperature to 30 °C (Entries 5-9). Optimal results were achieved by either using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) or *tert*-butylimino-tri(pyrrolidino)phosphoran (BTPP) as bases and correspond to a rate acceleration of 10^6 - 10^7 compared to the uncatalyzed ring opening of **3d**. Interestingly, a transition from first order kinetics for the thermal ring opening to zero order kinetics for the catalyzed process was witnessed. This change is advantageous for MOST application due to the uniform heat release within a zero-order reaction paradigm. Subsequently, we analyzed the thermochemistry of the catalytic process using a reaction calorimeter (Figure 3C). We obtained an average of 14.4 kcal/mol (312 J/g) of heat release for the opening event, significantly surpassing the heat stored in solar-warmed water ($\Delta T = 50$ °C, $\Delta H = 209$ J/g). The high energy density is also confirmed by our DFT calculations. Although the stored energy is somewhat lower than the archetypal quadricyclane \rightleftharpoons norbornadiene pair (14.4 kcal/mol vs. 21.2 kcal/mol in toluene),⁴⁴ the latter

cannot operate under sunlight conditions due to its weak absorptivity in the UVA spectral region.

The progression to sunlight irradiation and the establishment of a cyclable process are important criteria for the evaluation of MOST systems. In accordance, we subjected trifluoroacetophenone **1d** to sunlight irradiation (Figure 4A, top). An average yield of 87% was obtained after 4 hours with no signs of material deterioration or side reactions, underpinning the reaction's robustness (For detailed experimental procedures and set-ups, please refer to page S71 in the SI). To initiate back-isomerization and heat release, we established a protocol using a polystyrene (PS)-immobilized TBD base, which can be conveniently removed through simple filtration after the reaction has stalled (Figure 4A, bottom). An average yield of 90% was obtained when using the polymer-bound TBD base, which performed equally well as its low-molecular weight counterpart enabling a material recovery of >99% after this cycle. Importantly, re-exposing acetophenone **1d** to sunlight irradiation was successful ensuring the system's applicability at ambient conditions. To further study the cyclability, we had to establish a slightly modified closed-loop system using pentadecane as the solvent and heat for a time-efficient ring-opening. Although being slightly less efficient than the catalyzed approach under optimized conditions, this set-up showcases the reversibility and high reaction yields of the MOST system (Figure 4B).

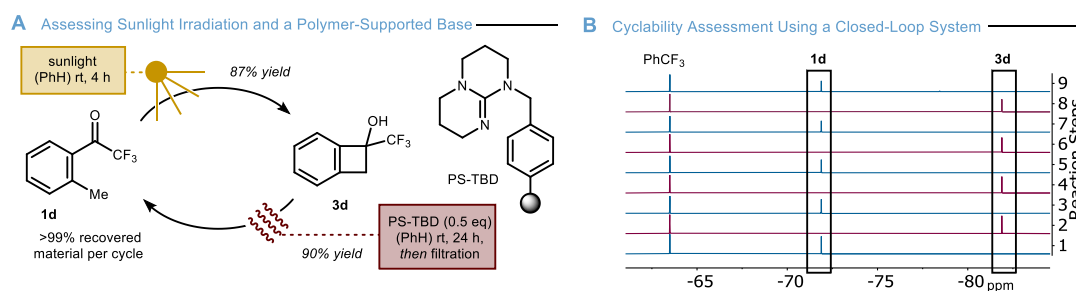


FIGURE 4. Investigating the applicability of the MOST system. (A) Performance under sunlight irradiation and by using an immobilized base for ring-opening. (B) Studying a closed-loop system using iterative irradiation and heating steps in pentadecane as the solvent.

Conclusions. Within this study, a robust, scalable, and efficient process for solar energy storage based on the photocyclization and subsequent ring-opening of *ortho*-methyltrifluoroacetophenone was achieved, with yields exceeding 99% for both forward and reverse reactions. This system offers long and safe energy storage times ($t_{1/2} > 10^8$ years) and ensures efficient heat release under ambient conditions (rate acceleration $> 10^6$). The overall good performance is based on the strategically placed trifluoromethyl group, which ensures high yield during the photochemical cyclization while maintaining a significant energy density of 312 J/g. The trifluoromethyl group also improves the stability of benzocyclobutenols and facilitates anionic electrocyclic ring-opening by critically lowering the pKa, allowing the use of simple organic bases as catalysts. To showcase the applicability of this small molecule energy storage system, a reaction set-up that uses sunlight irradiation and an immobilized catalyst was realized, which achieves high cyclability with >99% material recovery at high conversion rates (~90%).

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