

Photoswitch designs for molecular solar thermal energy storage

Junichi Usuba¹ and
Grace G.D. Han ^{1,*}

Recent advances in the design of molecular photoswitches have opened up opportunities for storing solar energy in strained isomeric structures and releasing heat on demand, culminating in molecular solar thermal (MOST) energy storage densities over 0.3 MJ kg⁻¹ and validating the potential for achieving thermal battery applications.

Photoisomerization of molecular switches and the corresponding energy level changes enable the storage of photon energy in metastable-state isomers. The energy difference between the ground- and metastable-state, or isomerization energy (ΔH_{iso}), is stored then released during the reverse isomerization triggered by irradiation, thermal activation, redox process, catalysis, or other mechanisms (Figure 1A). This optically controllable energy storage-release cycle in a closed system has emerged as a complementary photon harvesting tool to photovoltaics, particularly attractive for portable applications.

For molecular solar thermal (MOST) systems, the energy storage density, energy conversion efficiency, and energy storage time are the major figures of merit, which can be optimized by the judicious molecular designs and fine-tuning their optical and thermal properties (Figure 1B). A large energy storage density can be acquired by designing switches of small molecular weights, which operate in condensed phases. Other desirable parameters, including a large photostationary-state

(PSS) ratio, high quantum yield of photoisomerization (Φ_{iso}), absorption of visible light (λ_{abs}), and long half-life ($t_{1/2}$) of metastable isomer are also achieved by the design of switches. Fulfilling all parameters in any intrinsic photoswitch system is challenging, hence a variety of structural modifications have been pursued. We also note that such structural modifications often improve the target parameters at the expense of other parameters. Therefore, the pursuit of a molecular system with a complete set of optimized properties is an ongoing effort and we highlight a series of successful design principles applied to each class of photoswitches. A recent review by Moth-Poulsen and colleagues [1] offers a comprehensive list of MOST compounds that are applied to solar thermal energy storage devices and the relevant parameters such as energy conversion efficiency and energy storage density.

The MOST quartet

Among four representative photoswitch systems investigated for MOST applications, azobenzenes display high photostability and large *E-Z* PSS ratios, while $t_{1/2}$ of pristine *Z* isomer is reported to be only ~4 days, which limits the energy storage time (Figure 1C). Arylazoheteroarene derivatives were discovered to extend $t_{1/2}$ significantly, for example to 1000 days [2], enabling long-term energy storage. Other design strategies, including the functionalization of aryl or heteroaryl groups, attachment of photoswitches on nanocarbon scaffolds, and incorporation of phase-directing groups have resulted in fine-tuning the intra- and intermolecular interactions of azo-switches, improving their optical properties, $t_{1/2}$, and energy storage densities. (Fulvalene)tetracarbonyl-diruthenium [3] undergoes a *syn-anti* isomerization and exhibits a long $t_{1/2}$ of *anti* isomer and a substantial energy storage density, while its small Φ_{iso} hampers an efficient energy storage (Figure 1D). Pentamethyl substitution of one cyclopentadiene was revealed

to facilitate the bond dissociation, thereby improving Φ_{iso} . Additionally, replacement of ruthenium with a more abundant metal will be desired for large-scale applications.

Norbornadiene (NBD)/quadricyclane (QC) couple offers a remarkable energy storage density due to the high strain in QC structure (Figure 1E) [4]. However, NBD typically absorbs UV, due to the short conjugation, which hinders solar harvesting. The red-shifted λ_{abs} of NBD in the visible light range was achieved by the donor-acceptor functionalization [5]. Dihydroazulene (DHA)/vinylheptafulvene (VHF) couple exhibits an excellent Φ_{iso} and a suboptimal ΔH_{iso} , which is improved by the functionalization that provides an additional aromatic stabilization to DHA structure (Figure 1F) [6].

Emerging photoswitches

Beyond the four classes of photoswitches, other compounds that exhibit favorable photoswitching characteristics have emerged as new candidates. For example, hydrazones that undergo a photo-induced *Z-E* isomerization, analogous to azobenzenes, have demonstrated their remarkable switching properties in both solution and solid state, despite the unknown energy storage capacity. Acyclic hydrazones, such as HZ1 (Figure 2A, top), typically display extraordinary $t_{1/2}$ and energy barriers for thermal reversion (*E*→*Z*), based on which ΔH_{iso} is predicted to be negligible.

To address the challenge, a new strategy of cyclization was employed (Figure 2A, bottom), which induces torsional, transannular, and large-angle distortion strains in the *E* isomer, thus significantly decreasing $t_{1/2}$ of *E*. The cyclic hydrazone HZ2 also displays a reversible phase transition between *Z* (crystalline) and *E* (liquid), which allows for the storage of latent heat in addition to ΔH_{iso} (Figure 2B) [7]. The total energy storage density (ΔH_{total}) of 72 kJ mol⁻¹ is comparable to that of conventional MOST compounds. The cyclization strategy

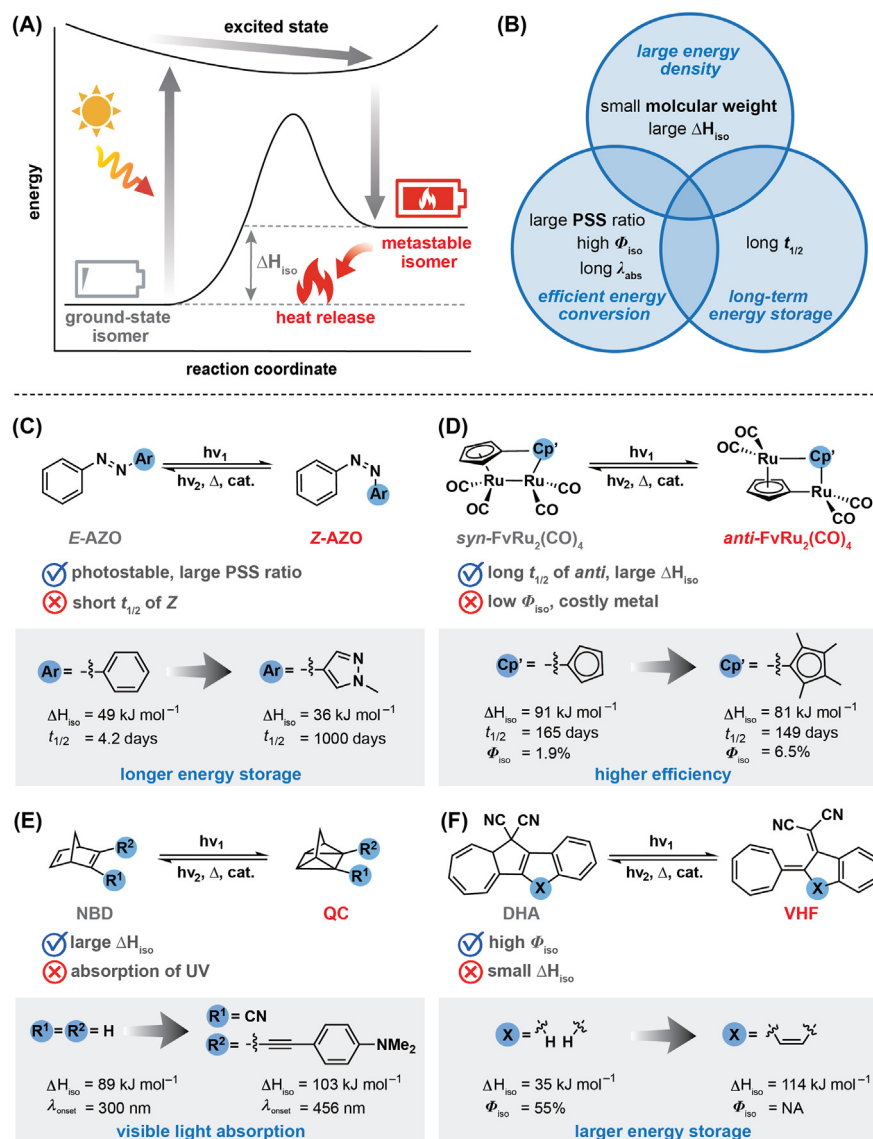


Figure 1. Molecular solar thermal (MOST) energy storage mechanism and the conventional photoswitches. (A) An energy diagram of photoisomerization and heat storage/release process. (B) Figures of merit for MOST systems. (C–F) major classes of photoswitches explored as conventional MOST compounds. Abbreviations: DHA, dihydroazulene; ΔH_{iso} , isomerization energy; λ_{abs} , absorption wavelength; NBD, norbornadiene; Φ_{iso} , quantum yield of photoisomerization, PSS, photostationary state; QC, quadricyclane; $t_{1/2}$, half-life of metastable isomer; VHF, vinylheptafulvene.

and photo-induced phase transition could be applied to emerging photoswitches and improve their MOST energy storage.

Analogous to NBD/QC system, compounds that undergo photo-induced

reversible [2+2] or [4+4] cycloaddition, for example, stilbene (Figure 2C, left) and anthracene (Figure 2C, right), could be investigated for MOST applications. A prominent challenge in both systems is the photo-induced oxidation that produces phenanthrene and anthraquinone

[8]. The irreversible oxidation is prevalent in solutions, in the presence of atmospheric oxygen. Therefore, solid-state switching would ameliorate the challenge and crystal engineering of molecules would determine the efficiency of intermolecular cycloadditions.

For example, stilbenes that incorporate an electron-rich and -deficient aryl group are reported to adopt a head-to-tail packing in crystals and undergo a facile photo-induced dimerization [9]. Pristine anthracene forms a herringbone packing structure, as a result of C–H $\cdots\pi$ interactions in crystals, which hinders solid-state cycloaddition [10]. However, 9-anthracenecarboxylic acid adopts a face-centered stacking, allowing for reversible cycloaddition [11]. The quantitative photo-induced cycloaddition and cycloreversion in the solids, appreciable reaction enthalpies, and substantial light penetration depths will be the key parameters desired for successful MOST applications.

Also analogous to DHA/VHF system, photoswitches that undergo ring-opening/closing isomerization could be considered. Spiropyran/merocyanine couple is a well-known photochromic system used for actuation, sensing, drug delivery, and other applications (Figure 2D, left) [12], and donor–acceptor Stenhouse adducts (DASA) are recently developed photoswitches with tunable λ_{abs} in the visible/near-infrared range (Figure 2D, right) [13]. Both systems exhibit well-separated spectra of photoisomers, but their PSS ratio, λ_{abs} , and $t_{1/2}$ are solvent-dependent [14,15], implying that energy storage would be significantly influenced by the intermolecular interactions in a condensed phase. Furthermore, the large structural change associated with isomerization would be hindered in solid state, requiring substituents that increase the conformational freedom of photoswitches in a crowded environment. Unraveling the potential of such systems in energy storage

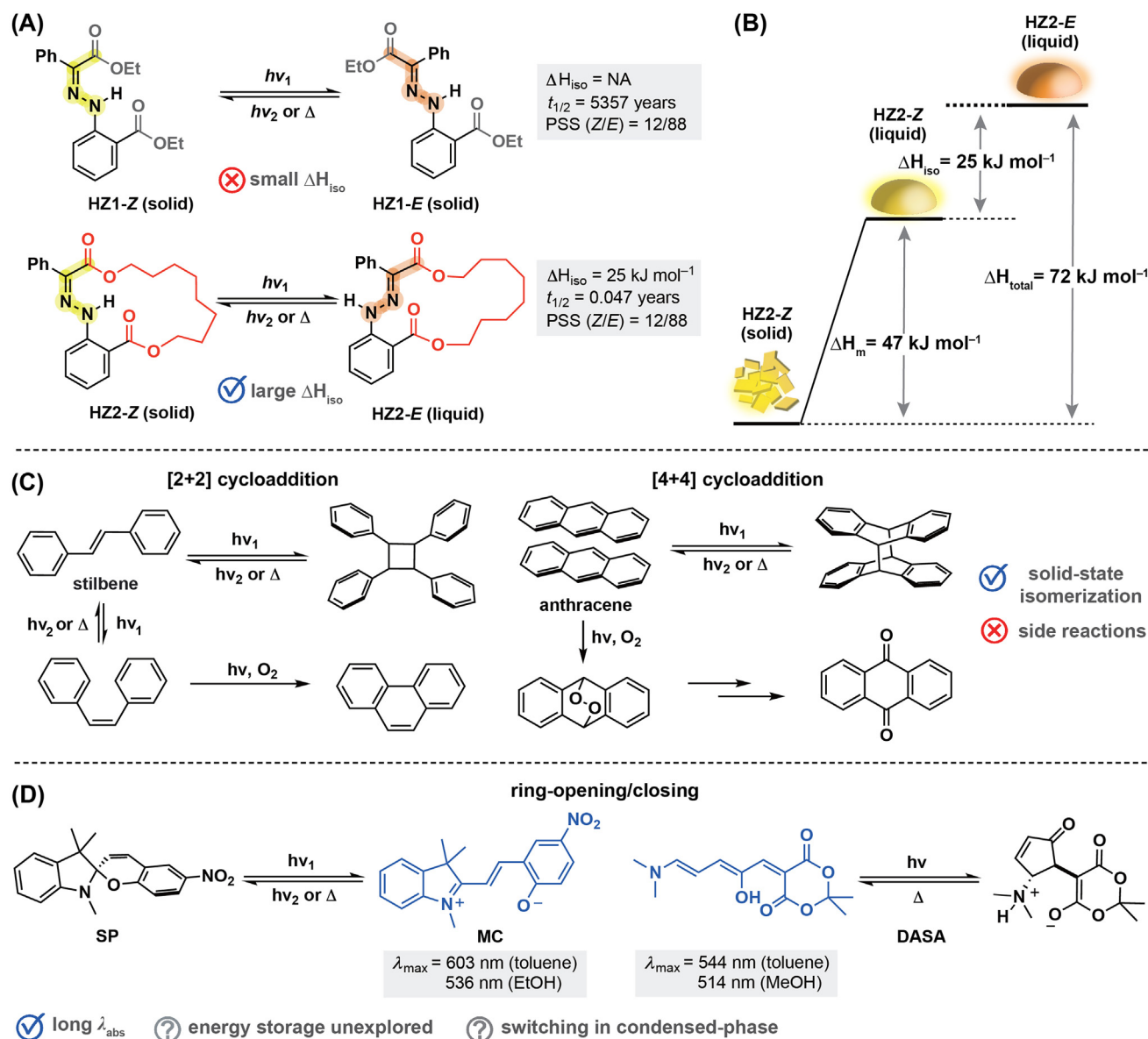


Figure 2. Emerging molecular solar thermal (MOST) compounds. (A) Acyclic (HZ1) and cyclic (HZ2) hydrazones and their isomerization; (B) schematic energy diagram of HZ2 isomerization. The total energy storage (ΔH_{total}) is the sum of latent heat (ΔH_{m}) and isomerization energy (ΔH_{iso}); (C) cycloaddition reaction of stilbene and anthracene; (D) ring opening-closing isomerization of photoswitches. Abbreviations: DASA, donor-acceptor Stenhouse adducts; MC, merocyanine; PSS, photostationary state; SP, spiropyran.

will be an important objective of the research field.

In summary, the MOST photoswitch designs have rapidly evolved in the past decade, revealing critical design principles that enhance the energy storage density,

efficiency, or time for each class of switches. The continuous development of new generation switches has resulted in the optimized systems that store over 0.3 MJ kg^{-1} of energy. Alternative systems, both cycloaddition and ring-opening compounds, have been rarely explored for

MOST, which presents an exciting opportunity to investigate their potential for solar energy storage. The large spectral separation between isomers and solid-state switching properties will offer unprecedented opportunities to achieve large-scale and solid-state thermal battery

applications. The solar thermal batteries based on MOST compounds will enable a solar-chargeable, off-grid, and long-term energy storage in light-weight organic materials that are easily produced from low-cost feedstocks, complementing the state-of-the-art energy conversion and storage technologies.

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Declaration of interests

No interests are declared.

¹Department of Chemistry, Brandeis University, 415 South Street, Waltham, MA, 02453, USA

*Correspondence:

gracehan@brandeis.edu (G.G.D. Han).

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