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Perspective

Photoswitches and photochemical reactions for optically controlled phase transition and energy storage

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SUMMARY

Molecular solar thermal (MOST) energy storage materials enable the storage of photon energy within their chemical bonds and the release through external stimulation. Despite the discovery of various molecular systems that enable MOST energy storage, the intrinsic limitation of the low energy-storage density in common MOST compounds restricts their applications in the real world. To counter this limitation, methods have been implemented to increase the total energy storage capacity of the system through harnessing phase change energy involved in the energy storage and release processes. In this perspective, we highlight the recent advances to the designs of phase transition MOST energy storage compounds, the challenges of current designs, and the future directions.

INTRODUCTION

Molecular solar thermal (MOST) energy-storage materials are a class of compounds that store photon energy in chemical bonds upon photoconversion, which releases as heat during reversion when triggered by external stimulation.[1–3] MOST materials typically consist of photoswitches that isomerize between the thermodynamically stable and metastable states upon light absorption and store isomerization energy (ΔH_{iso}), including azo(hetero)arenes,[4,5] hydrazones,[6] fulvalene diruthenium,[7] norbornadiene (NBD)/quadricyclane (QC) couples,[8] and dihydroazulene/vinyl-heptafulvene systems.[9] The MOST systems have emerged as solar energy harvesting tools, displaying long energy-storage time (up to years) and releasing thermal energy on demand.[10,11] Compared with the established or emerging solar devices, such as inorganic solar cells[12] or solar-driven water splitting systems,[13,14] MOST materials offer a unique opportunity to directly store energy in the photoactive compounds without generating new products (e.g., electricity or solar fuels) that require independent storage units, such as electrical batteries or gas storage containers. Additionally, organic photoswitches present desirable features, including modular optical properties, processability, flexibility, and light weight, which can allow for new applications on windows, garments, and portable heating devices.

However, MOST applications have been limited either by the low chemical stability of photochromes (e.g., fulvalene diruthenium[15] and NBD/QC,[16] despite their large ΔH_{iso} greater than 100 kJ/mol[17,18] or up to 1,000 J/g^2) or the low energy-storage densities, notably that of azobenzene (ΔH_{iso} = 41 kJ/mol or 225 J/g)[19] that is instead chemically stable and cyclable. Therefore, molecular designs that modulate the relative degrees of intramolecular interactions in the thermodynamically stable and metastable states have been developed to enhance ΔH_{iso} of azobenzene system and have been explored both computationally and experimentally.[20–22]

THE BIGGER PICTURE

Challenges and opportunities:

- The intrinsic limitation of the low energy-storage density results in setbacks for the application of MOST materials, as well as opportunities for new methods of increasing the energy that can be harnessed in MOST materials.
- The integration of phase change (including crystal-to-liquid, crystal-to-amorphous, and crystal-to-crystal) and photo-isomerization enables an increase in the storage density of MOST materials by combining the resulting energy from the phase change with the inherent isomerization energy of photoswitches.
- The understanding gained from such advances in the molecular designs provides a pathway for the advancement in MOST applications and hope for the future of solar technologies.

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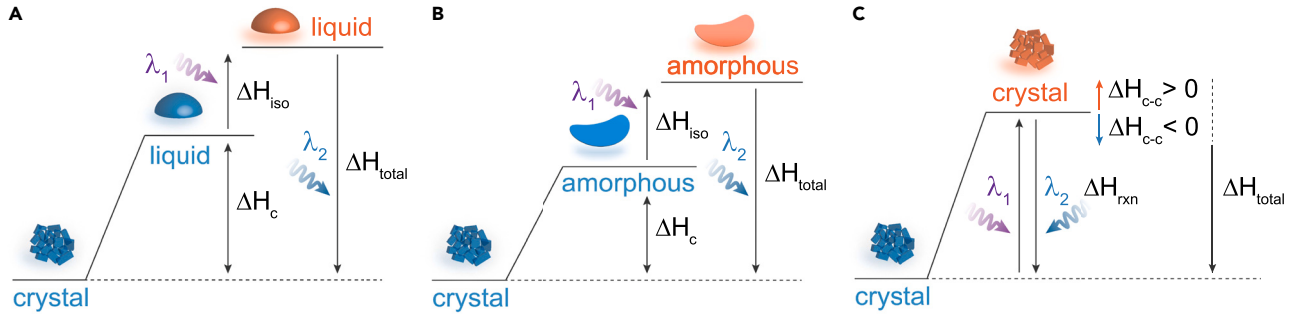

Figure 1. Energy storage and release diagrams

Photon and thermal energy storage during (A) crystal-to-liquid, (B) crystal-to-amorphous solid, and (C) crystal-to-crystal phase transitions under the irradiation at λ_1 and the energy release prompted by the irradiation at λ_2.

Blue and orange colors represent different chemical or isomeric states of photoresponsive compounds.

ΔH_c, crystallization energy; ΔH_{iso}, isomerization energy; ΔH_{rxn}, photochemical reaction energy; $\Delta H_{c\text{-}c}$, crystal-to-crystal phase transition energy; ΔH_{total}, total energy storage.

Alternatively, different degrees of intermolecular interactions in each isomeric state can be harnessed to improve the energy storage.[23,24] If the structure and polarity of isomers are significantly dissimilar, they result in different molecular packing and ultimately distinct phases.[25,26] Such photo-induced phase transitions of MOST compounds enable dual storage of phase transition energy and ΔH_{iso} in the metastable state, giving rise to a greatly increased total energy storage.

In recent years, the photo-induced crystal-to-liquid phase transition (Figure 1A) of various azobenzene and azoheteroarene derivatives has been reported, which allows for the storage of ΔH_{iso} and the phase transition energy, i.e., crystallization energy (ΔH_c). This strategy culminates in a functionalized derivative with a maximum storage density of 130 kJ/mol (368 J/g) that is comparable to the specific energy of commercial 18,650 Na-ion batteries, 50%–60% lower than their Li-ion counterpart.[27] Such photoswitches are designed to undergo a significant structural change, either through inversion or rotation of groups,[28,29] between a planar and a non-planar isomer. However, typical planar isomers are closely packed in the crystalline phase, hindering photo-isomerization due to the low conformational freedom. Judicious functionalization of azoheteroarene photoswitches that resulted in lower intermolecular interactions among the photochromes enabled their photo-isomerization and phase transition to liquid at room temperature.[30] A prominent challenge of crystal-liquid phase change materials (PCMs), however, is a potential leakage of liquid and its combustion, which necessitates the requirement of leakproof containers.

In response to this challenge, solid-state MOST compounds that undergo either crystal-to-amorphous solid (Figure 1B) or crystal-to-crystal (Figure 1C) phase transition under irradiation have emerged as favorable alternatives. For crystal-amorphous solid PCMs, the total stored energy is the combination of ΔH_{iso} and ΔH_c that is typically smaller than the ΔH_c involved in crystal-liquid phase transitions. For the crystal-to-crystal phase change, molecular transformations that require minor volume changes are generally investigated. Rather than the typical photo-isomerization, such as *E-Z* switching or ring opening-closing, intermolecular [2 + 2] or [4 + 4] cycloaddition reactions are chosen, which do not drastically alter the crystalline nature of compounds upon photo-dimerization. Historically, such single crystal-to-single crystal transitions have been primarily investigated as a novel synthetic method, as well as for the fundamental understanding of molecular

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packing in crystals.[31–33] Because the photo-dimerization reactions are the least explored for MOST applications, we introduce promising candidates and highlight two important parameters, ΔH_{rxn} (photochemical reaction energy) and $\Delta H_{c\text{-}c}$ (crystal-to-crystal phase transition energy; + or − term), which will combine to determine ΔH_{total} (total energy-storage density) of MOST compounds. Herein, we illustrate the molecular design strategies employed in achieving each type of phase transition upon photoirradiation, which will shed light on the relative advantages, as well as challenges of the compounds explored for MOST applications.

Photo-induced crystal-to-liquid phase change

Azo(hetero)arene photoswitches are known to reversibly switch between a planar *E* (thermodynamically stable state) and a non-planar *Z* configuration (metastable state), promoted by UV and visible light irradiation for $E \rightarrow Z$ and $Z \rightarrow E$ isomerization, respectively. As a result of significant planarity changes, the crystal-to-liquid transition is commonly observed during $E \rightarrow Z$ switching. Compared with the changes observed in azo(hetero)arene photoswitches, the planarity changes of hydrazones between *Z* (thermodynamically stable state) and *E* (metastable state) configurations are smaller, unless a cyclic linker is introduced to increase the disorder of *E* structure. Recent advances in phase change *E*-*Z* photoswitches and molecular design principles are discussed below.

Azo(hetero)arenes functionalized with alkyl chains

Azobenzenes and arylazopyrazoles functionalized with long alkyl chains or those bearing terminal alkene groups (Figure 2A) have been reported to undergo facile crystal-to-liquid phase transition upon $E \rightarrow Z$ isomerization. To improve the optical properties of azobenzene, functionalization at the *ortho* positions, with respect to the azo moiety, by F, Cl, or OMe groups[34] was performed, effectively red-shifting the n−π* transition band of the *E* isomer and separating it from the n−π* band of *Z*. This allows for the promotion of $E \rightarrow Z$ isomerization by visible light irradiation in the range from 530 to 625 nm instead of UV (365 nm) that induces π−π* transition. Such compounds with a tridecanoate group can undergo a simultaneous phase change and isomerization under filtered sunlight, storing up to 70 kJ/mol (150 J/g). Other derivatives bearing an arylazopyrazole core structure[35] and an alkyl ester group on the pyrazole ring exhibit similar phase transition behavior as azobenzene. Remarkably, the half-lives of the arylazopyrazole *Z* isomers in the liquid state extend to 2 weeks or longer due to the intramolecular C−H···π interactions that stabilize the metastable *Z* configuration in a T-shape, in contrast to an azobenzene *Z* isomer that displays a twisted shape and a shorter half-life of 4 days.[36] In addition, the uniquely T-shaped *Z* isomers of aryazopyrazoles exhibit a stable liquid phase even at subzero temperatures as low as −30 °C, enabling energy storage in an extremely cold climate without risking the crystallization of *Z* isomers. Arylazopyrazoles with a chain on the phenyl ring[37] also behave similarly, reporting half-lives of over 3 months and high energy densities up to 130 kJ/mol (368 J/g).

Cyclic hydrazones

Hydrazones exhibit desirable optical and thermal properties including high photostationary state (PSS) ratios, large quantum yields, and tunable thermal half-lives of metastable *E* isomers,[38,39] showing great promise for MOST applications. However, the ability of acyclic hydrazones to store photon energy is difficult to demonstrate due to the high activation energy barrier of $E \rightarrow Z$ thermal reversion and an intrinsically small energy gap between two isomeric states. By attaching a

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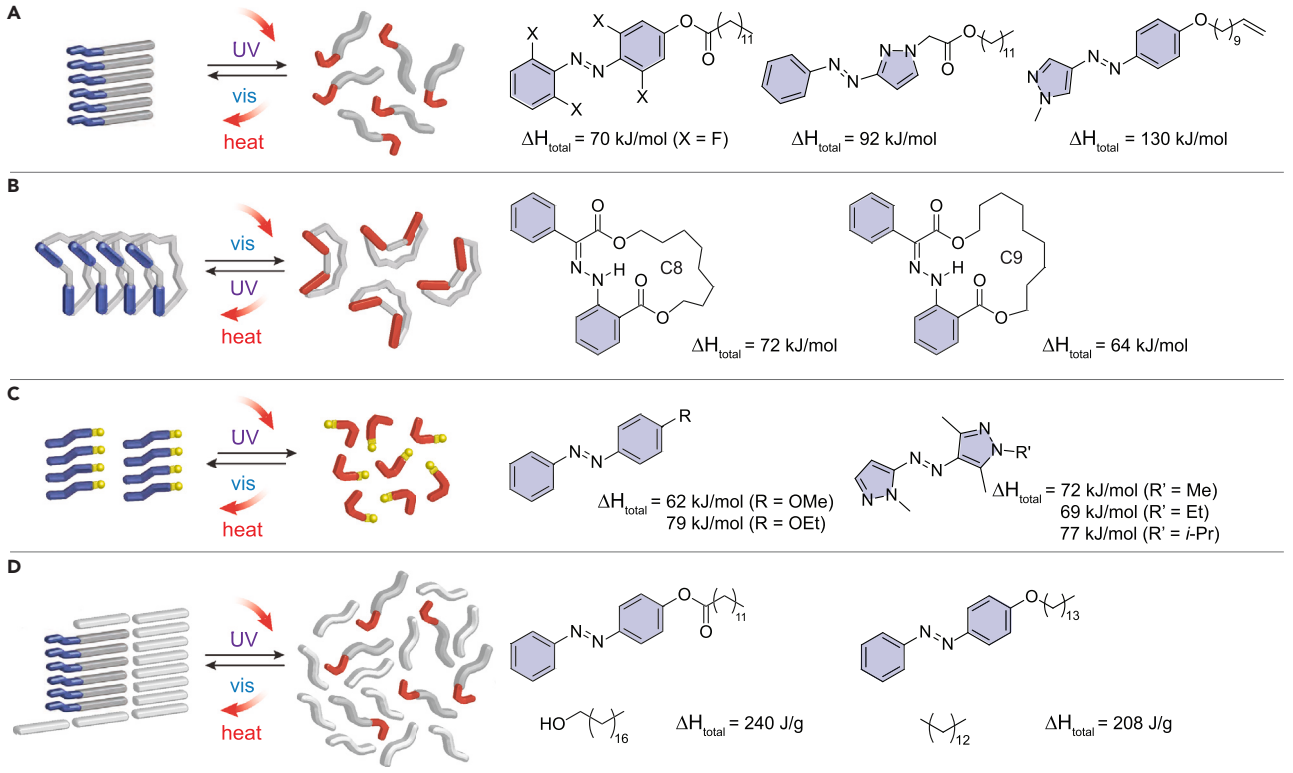

Figure 2. Crystal-to-liquid phase change

Photo-induced crystal-to-liquid phase transition of photoswitches functionalized with (A) long alkyl chains, (B) cyclic linkers, and (C) small substituents. (D) Photoswitches doped in conventional phase change materials.

ΔH_{total}, total energy storage in a composite.

cyclic alkyl linker (C_8 and C_9) to a hydrazone core, the increased strain of the *E* isomers allowed for greater ΔH_{iso} and energy storage of the system.[40] In addition, the cyclization increased the structural disorder in the *E* isomeric form, resulting in the crystal-to-liquid phase transition upon the *Z* → *E* isomerization (Figure 2B). The total energy stored in the cyclic *E* hydrazones, i.e., the combination of ΔH_{iso} and phase transition energy, can reach quantities as large as 72 kJ/mol (183 J/g), comparable to the energy-storage density of phase change MOST compounds incorporating azoarene switches.

Azo(hetero)arenes with small substituents

In order to maximize the gravimetric energy density of MOST compounds, the molecular structures can be modified to reduce the molecular weight of photoswitches. Azobenzene[41] and azobispyrazole[30] cores functionalized with small alkyl or alkoxy groups (Figure 2C) show desirable photoswitching yields, thermal stabilities of *Z* isomers, facile solid-liquid phase transition, and large energy-storage densities, reaching or exceeding 300 J/g, which is a critical figure of merit for MOST applications. For example, an azobispyrazole core substituted with three methyl groups on its *ortho* positions with respect to the azo moiety shows effective *E* → *Z* photoswitching in solid and concomitant transition to liquid at room temperature. This is in sharp contrast to common MOST compounds that require the melting of *E* isomers before photoswitching due to their limited conformational freedom at room temperature. The liquefied *Z* isomers effectively solvate *E* solids and allow them to diffuse and convect under UV irradiation and maximize the photoswitching depths of

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condensed-phase materials up to 1,400 μm, which is nearly 500-fold enhanced from the static penetration depth of UV (3 μm).

Azobenzenes as dopants in conventional PCMs

Common organic PCMs, such as *n*-alkanes, fatty acids, and fatty alcohols, exhibit fixed sets of melting and crystallization points, which allows for the heat storage only at temperatures above those set points. Azobenzene derivatives with a tridecanoate functional group serve as effective photoswitch dopants in such conventional PCMs and provide optical control over the phase transition temperatures of composites (Figure 2D).[42] *E* → *Z* photoswitching of dopants in the composites reduces the crystallization points of PCMs by over 10 °C, enabling the storage of the liquid phase for 10 h at a temperature much lower than its original crystallization point.[43] Similarly, an azobenzene derivative functionalized with a tetradecyloxy group serves as a photoswitch dopant in tetradecane, an organic PCM, to optically control its phase transition with 10–30 mol % loading.[44] The composites with *Z* dopants display crystallization points below 0 °C, a few degrees lowered from the crystallization point of tetradecane, enabling the energy storage and release at subzero temperatures. This composite strategy can be further applied to various pairs of organic PCMs and photoswitch dopants that exhibit vastly different intermolecular interactions with each photoisomer.

Photo-induced crystal-to-amorphous phase change

Photoswitching between crystalline and amorphous solid phases is less commonly observed than between crystalline and liquid phases. Two key requirements for maintaining the solid state of photoswitches before and after isomerization are (1) the large molecular weights of compounds and (2) the presence of strong intermolecular interactions, including a large degree of H-bonding or dispersion force, which do not drastically weaken even after *E* → *Z* isomerization.

Azobenzene-functionalized diacetylenes

Linear molecules bearing diacetylene cores and H-bonding units such as amide groups are functionalized with terminal azobenzene groups and alkyl linkers (Figure 3A), which self-assemble into a crystalline phase via intermolecular π-interactions and H-bonds.[45] The *E* → *Z* switching of terminal azobenzene groups disrupts the self-assembly and crystalline packing of linear molecules, characterized by X-ray diffraction, while preserving the solid state of compounds. The investigation of an ester counterpart (n = 8), which undergoes solid-to-liquid phase transition upon *E* → *Z* photo-isomerization rather than solid-to-amorphous, demonstrates the significance of H-bonding units in maintaining the solid state of photoswitch materials. The phase transition and photo-isomerization together enable a large energy storage up to 222 J/g, which corresponds to 160 kJ/mol (per diacetylene compound) or 80 kJ/mol (per azobenzene unit), nearly a 100% increase from the energy density of an unfunctionalized azobenzene unit (i.e., 41 kJ/mol).[19] The *E* crystalline state is particularly stabilized by the strong interactions among the linear molecules, which maximizes the energy gap between the thermodynamically stable state (*E*) and the photoactivated state (*Z*). However, the photoswitching of azobenzenes in a crystalline solid is limited due to the close packing of molecules; therefore, the dispersion of crystalline compounds in solvents was employed to facilitate the *E* → *Z* isomerization.

Azobenzene-functionalized adamantanes

Another molecular scaffold that enables the photo-induced crystal-to-amorphous phase transition is an adamantane core that can effectively separate four

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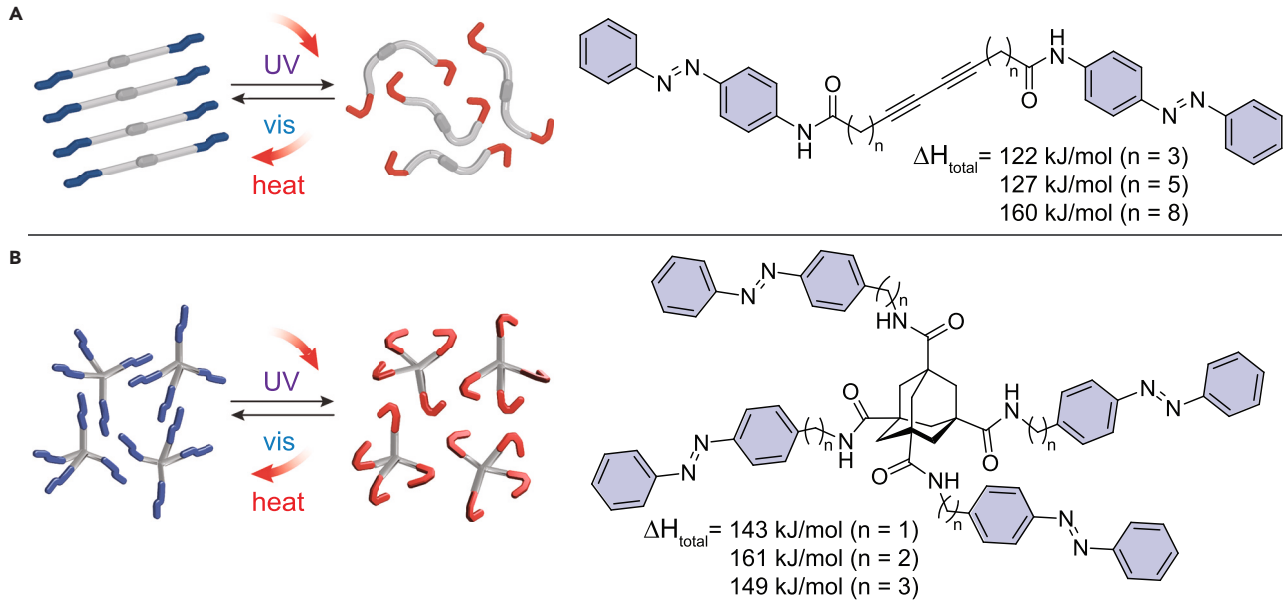

Figure 3. Crystal-to-amorphous phase change
Photo-induced crystal-to-amorphous phase transition of azobenzene-functionalized (A) diacetylene and (B) adamantane scaffolds.

azobenzene substituents and arrange them in a tetrahedral geometry (Figure 3B).[46] The spatial separation of azobenzene units reduces the π-interactions between the photochromes, allowing for $E \rightarrow Z$ photoswitching at room temperature in a crystalline phase. Upon isomerization, the disordered network of tetrahedral molecules with *Z* azobenzene units still forms a solid phase due to the presence of rigid and large adamantane core moieties, as corroborated by the loss of X-ray diffraction in the solid *Z* compounds. Unlike the diacetylene designs (Figure 3A), the tetrahedral network of molecules does not provide a large stabilization effect on the *E* isomeric state, thus limiting the energy storage up to 161 kJ/mol (141 J/g) of the adamantane compound with four azobenzene units. Despite the insignificant enhancement of energy-storage density compared with the unfunctionalized azobenzene, the azobenzene-functionalized adamantane designs achieve the primary aim to store and release solar photon energy in exclusively solid-state MOST materials under ambient conditions.

Photo-induced crystal-to-crystal phase change

Photoactive molecules that undergo crystal-to-crystal phase transitions upon irradiation have been commonly investigated for the development of novel synthetic procedures but have rarely been studied for their potential as MOST compounds. The compounds that successfully undergo photochemical reaction or photo-isomerization in a crystalline phase are classified into two groups: one that results in a negligible volume change upon the photo-induced transformation and the other that requires a larger change, hence an additional structure that increases the conformational freedom of molecules. A major advantage of investigating the compounds that undergo crystal-to-crystal phase change is the ability to elucidate their structural changes induced upon photoirradiation by crystallography.

[2 + 2] and [4 + 4] photocycloadducts

Photo-induced cycloaddition of compounds occurring in a crystalline phase has been widely investigated as a synthetic method for generating strained chemical

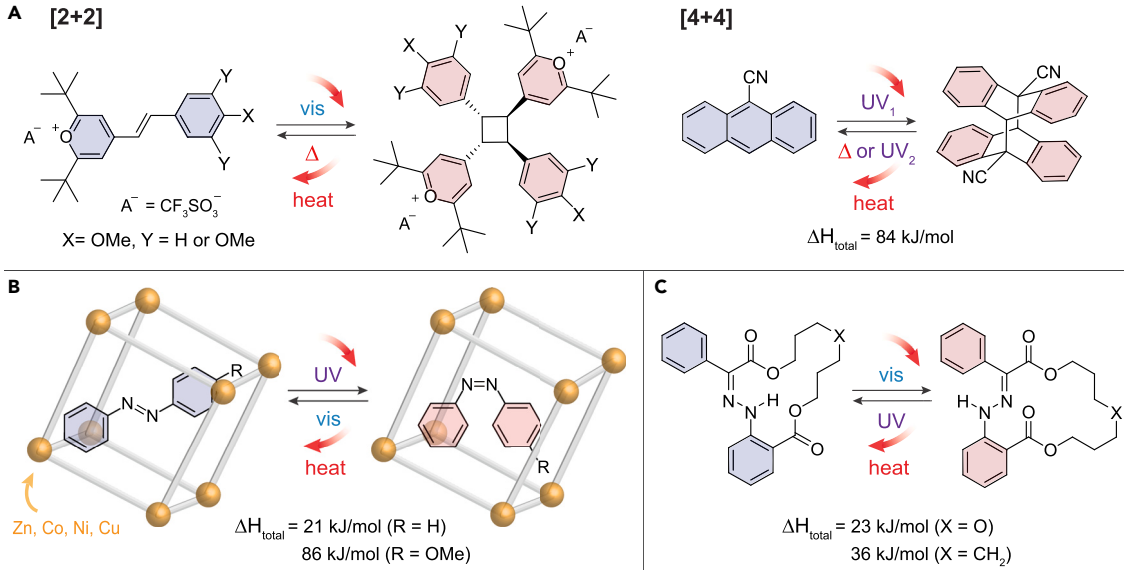

Figure 4. Crystal-to-crystal phase change

Photo-induced crystal-to-crystal phase transition of (A) styrylpyrylium and 9-cyanoanthracene that undergo reversible [2 + 2] and [4 + 4] photocycloaddition, respectively, (B) metal-organic frameworks incorporating azobenzene guests, and (C) cyclic hydrazones with shorter alkyl linkers.

moieties.[47–49] As a result of the strain present in the cycloadduct structures and their elevated energy state, the photo-induced cycloaddition reactions can be used to store photon energy that can be released as heat upon triggered cycloreversion, analogous to NBD/QC MOST systems. Beyond intramolecular [2 + 2] cycloaddition of NBD, the photochemical [2 + 2] or [4 + 4] reactions have been rarely explored for successful MOST applications due to the facile photo-induced oxidation that produces phenanthrene from stilbene and anthraquinone from anthracene.[50–52]

The potential of push-pull styrylpyrylium derivatives for reversible cycloaddition and photon energy storage was first probed in 1985 by Hünig et al., who qualitatively reported the thermally induced reversion of two cycloadducts of styrylpyryliums bearing methoxy substituents (Figure 4A).[53] However, the quantity of stored energy, energy-storage time, photochemical reversion and energy release, or impact of counter-anions and functionalization patterns on the energy-storage-release process remain unexplored. Another report in 1993 by Enkelmann et al. only described the photo-induced, single-crystal-to-single-crystal conversion of styrylpyrylium to its cycloadduct without any analysis of their potential as reversible energy-storage materials.[54] Given the favorable absorption of visible light, for example, at 530 nm, by the push-pull styrylpyryliums and their facile [2 + 2] cycloaddition in crystalline solid, the system is likely to serve as a promising MOST material.[55] Thus, there exists a critical need to unravel the design rules of styrylpyrylium derivatives to achieve a solid-state MOST system and study how the crystal-to-crystal phase transition affects the energy-storage density.

Anthracenes undergo [4 + 4] photo-cycloaddition to dianthracenes through UV irradiation at wavelengths greater than 350 nm, and dianthracenes revert to anthracenes either by thermal activation or by the irradiation of shorter wavelengths of UV less than 300 nm. Such reversible photo-cycloaddition is typically studied in the solution state, whereas an example of solid-state cycloaddition and thermally induced exothermic cycloreversion was demonstrated with 9-cyanoanthracene, storing up to

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84 kJ/mol (206 J/g) of dianthracene (Figure 4A).[56] The solid-state reactions, enabled by the engineering of molecular packing in crystals, significantly reduce the side reactions with atmospheric oxygen, resulting in high yields of products. In addition, the large energy-storage densities and easy synthesis of anthracene derivatives are favorable qualities of MOST compounds. Further investigation of this system, particularly the extension of absorption wavelengths to visible light and the impact of crystal-to-crystal phase transition on energy storage, will shed light on the potential of solid-state [4 + 4] cycloaddition for energy storage.

Metal-organic frameworks incorporating photoswitches

As previously mentioned, photoswitches that undergo large structural changes during isomerization, including azobenzene, have difficulty switching in a crystalline state due to the limited conformational freedom of molecules. To address this issue and enable *E-Z* isomerization in a crystalline state, metal-organic frameworks (MOFs) can be employed as a host to photoswitch guests, rendering the space around photochromes needed for isomerization (Figure 4B).[57] Azobenzene encapsulated in $[Zn_2^{II}(BDC)_2(DABCO)]$ (BDC = 1,4-benzenedicarboxylate, DABCO = 1,4-diazabicyclo[2.2.2]octane) undergoes 40% $E \rightarrow Z$ switching at PSS under 365 nm irradiation. At a larger extent of guest loading, the framework expands and allows for a more facile switching of azobenzene. The type of metal node (Zn, Co, Ni, or Cu) is revealed to affect the flexibility of frameworks and switching of guests, resulting in various energy-storage densities: Zn (29 J/g), Co (28 J/g), Ni (23 J/g), and Cu (12 J/g).[58] Notably, the half-life of *Z* azobenzene increases from days to years, as a result of the encapsulation and interactions in the framework.

The optimization of MOFs-photoswitch system was achieved by the incorporation of 4-methoxyazobenzene as the guest in $[Zn_2^{II}(BDC)_2(DABCO)]$, which markedly increased the PSS of azobenzene to 98% and energy density to 86 kJ/mol (101 J/g).[59] This was enabled by the significant redshift of the π–π^* absorption of 4-methoxyazobenzene, effectively separating the absorptions of the *E* and *Z* isomers.

Cyclic hydrazones with shorter linkers

The cyclization method applied to hydrazones increases their ΔH_{iso} and phase transition energy associated with $Z \rightarrow E$ isomerization, as shown in Section 1.2.[40] The type of phase transition is revealed to depend on the length of linker group, which determines the degree of disorder; the identical hydrazone core functionalized with either a C_7 alkyl linker or C_6O_1 linker displays crystal-to-crystal phase transition upon photo-isomerization (Figure 4C). These derivatives with a lower disorder in the *E* configuration, compared with those with longer linkers, maintain a crystalline phase regardless of the isomeric state. Compared with the total energy storage achieved by the C_8 functionalized hydrozone (72 kJ/mol or 183 J/g) that undergoes crystal-to-liquid phase transition (Section 1.2), the total energy storage for the hydrazones with the C_7 and C_6O_1 linkers is reduced to 36 kJ/mol (95 J/g) and 23 kJ/mol (60 J/g), respectively. This highlights the tradeoff between achieving a large energy-storage density and exclusively solid-state MOST materials. The lower phase change energy involved in crystal-to-crystal transition ($\Delta H_{c\text{-}c}$), compared with that of crystal-to-liquid transition (ΔH_c), contributes to the lower total energy storage in the solid-state hydrazone derivatives. Despite the limited storage density, the availability of diverse hydrazones, their wide range of absorption wavelengths and half-lives, as well as their ability to undergo solid-state isomerization in the absence of frameworks, suggest the potential for achieving novel solid-state MOST materials based on *E-Z* isomerization.

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CONCLUSIONS AND OUTLOOK

MOST energy-storage research has rapidly transitioned from the fundamental investigation of photoswitch properties in solution state to their functions in condensed phases to achieve practical energy-storage applications with large gravimetric energy densities. The isomerization of compounds is drastically affected by the crowded environment of condensed phases, particularly in the crystalline state, which prompted the investigation of molecular engineering to allow for the facile switching in solid. The effective strategies for such modifications and the resultant phase change, i.e., crystal-to-crystal, crystal-to-amorphous, and crystal-to-liquid, induced by the isomerization are reviewed for each class of phase change MOST compounds. The total energy-storage densities enhanced by the photo-induced phase transition are also highlighted. Lastly, an emerging class of [2 + 2] and [4 + 4] photo-cycloadducts as promising solid-state MOST compounds is showcased, and the development of exclusively crystalline MOST materials will be an important topic for future investigations.

Beyond the current scope of studies that have successfully developed condensed-phase MOST applications with practical levels of energy densities over 300 J/g, there are other critical challenges that should be addressed to materialize large-scale MOST devices. Most of the photoactive molecular systems being discussed for energy storage exhibit micron-scale light penetration depths in condensed phases, due to the overlap between the absorption profiles of two isomeric/molecular states. Despite the meaningful improvement of light penetration depths achieved thus far,[30,34] particularly for the forward isomerization or molecular transformation that results in photon energy storage, the spectral separations between two states of molecules are still suboptimal. Molecules that display a negative photochromism, e.g., spiropyrans,[60] donor-acceptor Stenhouse adducts,[61] and styrylpyryliums,[62] can be thus attractive candidates that further enhance the penetration of incident visible light irradiation. However, we note that it is still extremely challenging to find a molecular system that also exhibits a large penetration depth of an orthogonal wavelength, which is required to trigger the reverse isomerization/molecular transformation and to effectively release energy in condensed phases.

Due to the difficulties in achieving an efficient energy release via photochemical triggering, alternative (electro)catalytic triggering methods have been explored in recent years, employing redox processes,[63,64] acid catalysts,[65] heterogeneous transition metal complexes,[66] and (electro)catalytic metal surfaces.[67,68] Translation of the chemical processes, evaluated in solutions or at the surface of heterogeneous catalysts or electrodes, to bulk condensed phases is not a straightforward quest. The dense molecular packing and strong intermolecular interactions present in condensed materials will likely change the efficacy of triggering methods, as showcased in a recent report on the electrochemical triggering of $Z \rightarrow E$ isomerization of an arylazopyrazole in condensed films.[69] The electrocatalytic efficiency of conversion was improved in condensed phases, compared with that of solution state, whereas the rate of conversion was substantially lowered. The application of other triggering methods that utilize acids, heterogeneous catalysts, or metal surfaces to condensed liquid or solid materials will require an efficient cascade process of molecular transformations, through proton or electron transfer, to yield a complete and rapid energy release.

In summary, the advances in MOST research that improve the energy-storage densities, light absorption properties, condensed-phase switching, and efficiencies of

energy release will require the judicious designs of new photoswitches and photochemical reactions. In addition, the ability to design MOST compounds with desired phase properties and phase transitions during the energy storage and release cycles will be critical to construct scalable solar energy conversion devices.

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AUTHOR CONTRIBUTIONS

G.G.D.H. conceptualized the topic. X.L., S.C., J.W., and G.G.D.H. wrote the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

1. Moth-Poulsen, K., Ćoso, D., Börjesson, K., Vinokurov, N., Meier, S.K., Majumdar, A., Vollhardt, K.P.C., and Segalman, R.A. (2012). Molecular solar thermal (MOST) energy storage and release system. Energy Environ. Sci. *5*, 8534–8537.

2. Wang, Z., Erhart, P., Li, T., Zhang, Z.-Y., Sampedro, D., Hu, Z., Wegner, H.A., Brummel, O., Libuda, J., Nielsen, M.B., et al. (2021). Storing energy with molecular photoisomers. Joule *5*, 3116–3136.

3. Sun, C.-L., Wang, C., and Boulatov, R. (2019). Applications of photoswitches in the storage of solar energy. ChemPhotoChem *3*, 268–283.

4. Bandara, H.M., and Burdette, S.C. (2012). Photoisomerization in different classes of azobenzene. Chem. Soc. Rev. *41*, 1809–1825.

5. Weston, C.E., Richardson, R.D., Haycock, P.R., White, A.J.P., and Fuchter, M.J. (2014). Arylazopyrazoles: azoheteroarene photoswitches offering quantitative isomerization and long thermal half-lives. J. Am. Chem. Soc. *136*, 11878–11881.

6. Shao, B., and Aprahamian, I. (2020). Hydrazones as new molecular tools. Chem *6*, 2162–2173.

7. Kanai, Y., Srinivasan, V., Meier, S.K., Vollhardt, K.P.C., and Grossman, J.C. (2010). Mechanism of thermal reversal of the (fulvalene) tetracarbonyldiruthenium photoisomerization: toward molecular solar–thermal energy storage. Angew. Chem. Int. Ed. Engl. *49*, 8926–8929.

8. Dubonosov, A.D., Bren, V.A., and Chernoivanov, V.A. (2002). Norbornadiene–quadricyclane as an abiotic system for the storage of solar energy. Russ. Chem. Rev. *71*, 917–927.

9. Wang, Z., Udmark, J., Börjesson, K., Rodrigues, R., Roffey, A., Abrahamsson, M., Nielsen, M.B., and Moth-Poulsen, K. (2017). Evaluating dihydroazulene/vinylheptafulvene photoswitches for solar energy storage applications. ChemSusChem *10*, 3049–3055.

10. Dong, L., Feng, Y., Wang, L., and Feng, W. (2018). Azobenzene-based solar thermal fuels: design, properties, and applications. Chem. Soc. Rev. *47*, 7339–7368.

11. Mansø, M., Petersen, A.U., Wang, Z., Erhart, P., Nielsen, M.B., and Moth-Poulsen, K. (2018). Molecular solar thermal energy storage in photoswitch oligomers increases energy densities and storage times. Nat. Commun. *9*, 1945.

12. Ballif, C., Haug, F.-J., Boccard, M., Verlinden, P.J., and Hahn, G. (2022). Status and perspectives of crystalline silicon photovoltaics in research and industry. Nat. Rev. Mater. *7*, 597–616.

13. Luo, Y., Zhang, Z., Chhowalla, M., and Liu, B. (2022). Recent advances in design of electrocatalysts for high-current-density water splitting. Adv. Mater. *34*, e2108133.

14. Tao, X., Zhao, Y., Wang, S., Li, C., and Li, R. (2022). Recent advances and perspectives for solar-driven water splitting using particulate photocatalysts. Chem. Soc. Rev. *51*, 3561–3608.

15. Lennartson, A., Lundin, A., Börjesson, K., Gray, V., and Moth-Poulsen, K. (2016). Tuning the photochemical properties of the fulvalene-tetracarbonyl-diruthenium system. Dalton Trans. *45*, 8740–8744.

16. Dreos, A., Wang, Z., Udmark, J., Ström, A., Erhart, P., Börjesson, K., Nielsen, M.B., and Moth-Poulsen, K. (2018). Liquid norbornadiene photoswitches for solar energy storage. Adv. Energy Mater. *8*, 1703401.

17. Boese, R., Cammack, J.K., Matzger, A.J., Pflug, K., Tolman, W.B., Vollhardt, K.P.C., and Weidman, T.W. (1997). Photochemistry of (fulvalene)tetracarbonyldiruthenium and its derivatives: efficient light energy storage devices. J. Am. Chem. Soc. *119*, 6757–6773.

18. Usuba, J., and Han, G.G.D. (2023). Photoswitch designs for molecular solar thermal energy storage. Trends Chem. https://doi.org/10.1016/j.trechm.2022.12.010.

19. Corruccini, R.J., and Gilbert, E.C. (1939). The heat of combustion of *cis*- and *trans*-azobenzene. J. Am. Chem. Soc. *61*, 2925–2927.

20. Cho, E.N., Zhitomirsky, D., Han, G.G.D., Liu, Y., and Grossman, J.C. (2017). Molecularly engineered azobenzene derivatives for high energy density solid-state solar thermal fuels. ACS Appl. Mater. Interfaces *9*, 8679–8687.

21. Liu, Y., and Grossman, J.C. (2014). Accelerating the design of solar thermal fuel materials through high throughput simulations. Nano Lett. *14*, 7046–7050.

22. Schweighauser, L., Strauss, M.A., Bellotto, S., and Wegner, H.A. (2015). Attraction or repulsion? London dispersion forces control azobenzene switches. Angew. Chem. Int. Ed. Engl. *54*, 13436–13439.

23. Kunz, A., Heindl, A.H., Dreos, A., Wang, Z., Moth-Poulsen, K., Becker, J., and Wegner, H.A. (2019). Intermolecular London dispersion interactions of azobenzene switches for tuning molecular solar thermal energy storage systems. ChemPlusChem *84*, 1145–1148.

24. Feng, Y., Liu, H., Luo, W., Liu, E., Zhao, N., Yoshino, K., and Feng, W. (2013). Covalent functionalization of graphene by azobenzene with molecular hydrogen bonds for long-term solar thermal storage. Sci. Rep. *3*, 3260.

25. Le, M., and Han, G.G.D. (2022). Stimuli-responsive organic phase change materials: molecular designs and applications in energy storage. Acc. Mater. Res. *3*, 634–643.

26. Zhou, H., Xue, C., Weis, P., Suzuki, Y., Huang, S., Koynov, K., Auernhammer, G.K., Berger, R., Butt, H.J., and Wu, S. (2017). Photoswitching of

glass transition temperatures of azobenzene-containing polymers induces reversible solid-to-liquid transitions. Nat. Chem. *9*, 145–151.

27. Abraham, K.M. (2020). How comparable are sodium-ion batteries to lithium-ion counterparts? ACS Energy Lett. *5*, 3544–3547.

28. Tan, E.M.M., Amirjalayer, S., Smolarek, S., Vdovin, A., Zerbetto, F., and Buma, W.J. (2015). Fast photodynamics of azobenzene probed by scanning excited-state potential energy surfaces using slow spectroscopy. Nat. Commun. *6*, 5860.

29. Gámez, J.A., Weingart, O., Koslowski, A., and Thiel, W. (2012). Cooperating dinitrogen and phenyl rotations in *trans*-azobenzene photoisomerization. J. Chem. Theory Comput. *8*, 2352–2358.

30. Gonzalez, A., Odaybat, M., Le, M., Greenfield, J.L., White, A.J.P., Li, X., Fuchter, M.J., and Han, G.G.D. (2022). Photocontrolled energy storage in azobispyrazoles with exceptionally large light penetration depths. J. Am. Chem. Soc. *144*, 19430–19436.

31. Chen, J.M., Hou, Y.X., Zhou, Q.K., Zhang, H., and Liu, D. (2017). UV-induced single-crystal-to-single-crystal conversion from a coordination ladder to a two-dimensional network through an intermolecular carbon–carbon coupling reaction. Dalton Trans. *46*, 9755–9759.

32. Wang, R., Liu, H., Li, J., Tian, J., Li, Z., and Zhao, Y. (2018). Solid-state photodimerization of azaanthracene derivative based on a [4+4] cycloaddition. Asian J. Org. Chem. *7*, 906–909.

33. Hu, F., Bi, X., Chen, X., Pan, Q., and Zhao, Y. (2021). Single-crystal-to-single-crystal transformations for the preparation of small molecules, 1D and 2D polymers single crystals. Chem. Lett. *50*, 1015–1029.

34. Shi, Y., Gerkman, M.A., Qiu, Q., Zhang, S., and Han, G.G.D. (2021). Sunlight-activated phase change materials for controlled heat storage and triggered release. J. Mater. Chem. A *9*, 9798–9808.

35. Gerkman, M.A., Gibson, R.S.L., Calbo, J., Shi, Y., Fuchter, M.J., and Han, G.G.D. (2020). Arylazopyrazoles for long-term thermal energy storage and optically triggered heat release below 0 °C. J. Am. Chem. Soc. *142*, 8688–8695.

36. Liu, H., Feng, Y., and Feng, W. (2020). Alkyl-grafted azobenzene molecules for photo-induced heat storage and release via integration function of phase change and photoisomerization. Compos. Commun. *21*, 100402.

37. Zhang, Z.Y., He, Y., Wang, Z., Xu, J., Xie, M., Tao, P., Ji, D., Moth-Poulsen, K., and Li, T. (2020). Photochemical phase transitions enable coharvesting of photon energy and ambient heat for energetic molecular solar thermal batteries that upgrade thermal energy. J. Am. Chem. Soc. *142*, 12256–12264.

38. Zheng, L.Q., Yang, S., Lan, J., Gyr, L., Goubert, G., Qian, H., Aprahamian, I., and Zenobi, R. (2019). Solution phase and surface photoisomerization of a hydrazone switch with a long thermal half-life. J. Am. Chem. Soc. *141*, 17637–17645.

39. Shao, B., Qian, H., Li, Q., and Aprahamian, I. (2019). Structure property analysis of the solution and solid-state properties of bistable photochromic hydrazones. J. Am. Chem. Soc. *141*, 8364–8371.

40. Qiu, Q., Yang, S., Gerkman, M.A., Fu, H., Aprahamian, I., and Han, G.G.D. (2022). Photon energy storage in strained cyclic hydrazones: emerging molecular solar thermal energy storage compounds. J. Am. Chem. Soc. *144*, 12627–12631.

41. Qiu, Q., Gerkman, M.A., Shi, Y., and Han, G.G.D. (2021). Design of phase-transition molecular solar thermal energy storage compounds: compact molecules with high energy densities. Chem. Commun. (Camb) *57*, 9458–9461.

42. Han, G.G.D., Deru, J.H., Cho, E.N., and Grossman, J.C. (2018). Optically-regulated thermal energy storage in diverse organic phase-change materials. Chem. Commun. (Camb) *54*, 10722–10725.

43. Han, G.G.D., Li, H., and Grossman, J.C. (2017). Optically-controlled long-term storage and release of thermal energy in phase-change materials. Nat. Commun. *8*, 1446.

44. Liu, H., Tang, J., Dong, L., Wang, H., Xu, T., Gao, W., Zhai, F., Feng, Y., and Feng, W. (2021). Optically triggered synchronous heat release of phase-change enthalpy and photo-thermal energy in phase-change materials at low temperatures. Adv. Funct. Mater. *31*, 2008496.

45. Han, G.D., Park, S.S., Liu, Y., Zhitomirsky, D., Cho, E., Dincă, M., and Grossman, J.C. (2016). Photon energy storage materials with high energy densities based on diacetylene–azobenzene derivatives. J. Mater. Chem. A *4*, 16157–16165.

46. Li, X., Cho, S., and Han, G.G.D. (2023). Light-responsive solid–solid phase change materials for photon and thermal energy storage. ACS Mater. Au *3*, 37–42.

47. Ehrenberg, M. (1968). The crystal structure of the dimer of 9-anthraldehyde. Acta Crystallogr. B Struct. Crystallogr. Cryst. Chem. *24*, 1123–1125.

48. Takegoshi, K., Nakamura, S., and Terao, T. (1998). Solid-state photodimerization of 9-methylanthracene as studied by solid-state ^{13}C NMR. Solid State Nucl. Magn. Reson. *11*, 189–196.

49. Stevens, B., Dickinson, T., and Sharpe, R.R. (1964). Photodimerization in crystalline 9-cyanoanthracene. Nature *204*, 876–877.

50. Lefebvre, Q., Jentsch, M., and Rueping, M. (2013). Continuous flow photocyclization of stilbenes – scalable synthesis of functionalized phenanthrenes and helicenes. Beilstein J. Org. Chem. *9*, 1883–1890.

51. Jørgensen, K.B. (2010). Photochemical oxidative cyclisation of stilbenes and stilbenoids—the Mallory-reaction. Molecules *15*, 4334–4358.

52. Sugiyama, N., Iwata, M., Yoshioka, M., Yamada, K., and Aoyama, H. (1969). Photooxidation of anthracene. BCSJ *42*, 1377–1379.

53. Hesse, K., and Hünig, S. (1985). Mehrstufige reversible redoxsysteme. XLII. [2 + 2]-photocycloadditionen von α-styrylpyrylium-Salzen zu 4,4′-(1,3-cyclobutandiyl)bis(pyrylium)-salzen sowie deren thermische und baseninduzierte cycloreversionen. Liebigs Ann. Chem. *1985*, 715–739.

54. Novak, K., Enkelmann, V., Wegner, G., and Wagener, K.B. (1993). Crystallographic study of a single crystal to single crystal photodimerization and its thermal reverse reaction. Angew. Chem. Int. Ed. Engl. *32*, 1614–1616.

55. Lange, R.Z., Hofer, G., Weber, T., and Schlüter, A.D. (2017). A two-dimensional polymer synthesized through topochemical [2 + 2]-cycloaddition on the multigram scale. J. Am. Chem. Soc. *139*, 2053–2059.

56. Donati, D., Guarini, G., and Sarti-Fantoni, P. (1972). Thermal behaviour and monomerization kinetics of 9-CN anthracene and 9-CN, 10-acetoxy anthracene dimers in the solid state. Mol. Cryst. Liq. Cryst. *17*, 187–195.

57. Griffiths, K., Halcovitch, N.R., and Griffin, J.M. (2020). Long-term solar energy storage under ambient conditions in a MOF-based solid–solid phase-change material. Chem. Mater. *32*, 9925–9936.

58. Griffiths, K., Halcovitch, N.R., and Griffin, J.M. (2021). Effect of transition metal substitution on the flexibility and thermal properties of MOF-based solid–solid phase change materials. Inorg. Chem. *60*, 12950–12960.

59. Griffiths, K., Halcovitch, N.R., and Griffin, J.M. (2022). Efficient solid-state photoswitching of methoxyazobenzene in a metal–organic framework for thermal energy storage. Chem. Sci. *13*, 3014–3019.

60. Klajn, R. (2014). Spiropyran-based dynamic materials. Chem. Soc. Rev. *43*, 148–184.

61. Helmy, S., Oh, S., Leibfarth, F.A., Hawker, C.J., and Read de Alaniz, J. (2014). Design and synthesis of donor–acceptor Stenhouse adducts: a visible light photoswitch derived from furfural. J. Org. Chem. *79*, 11316–11329.

62. Novak, K., Enkelmann, V., Köhler, W., Wegner, G., and Wagener, K.B. (1994). Homogeneous photodimerization and thermal back reaction of a styrylpyrylium triflate. Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A *242*, 1–8.

63. Goulet-Hanssens, A., Utecht, M., Mutruc, D., Titov, E., Schwarz, J., Grubert, L., Bléger, D., Saalfrank, P., and Hecht, S. (2017). Electrocatalytic $Z \rightarrow E$ isomerization of azobenzenes. J. Am. Chem. Soc. *139*, 335–341.

64. Franz, E., Kunz, A., Oberhof, N., Heindl, A.H., Bertram, M., Fusek, L., Taccardi, N., Wasserscheid, P., Dreuw, A., Wegner, H.A., et al. (2022). Electrochemically triggered energy release from an azothiophene-based molecular solar thermal system. ChemSusChem *15*, e202200958.

65. Gibson, R.S.L., Calbo, J., and Fuchter, M.J. (2019). Chemical *Z*–*E* isomer switching of arylazopyrazoles using acid. ChemPhotoChem *3*, 372–377.

66. Wang, Z., Roffey, A., Losantos, R., Lennartson, A., Jevric, M., Petersen, A.U., Quant, M., Dreos, A., Wen, X., Sampedro, D., et al. (2019).

Macroscopic heat release in a molecular solar thermal energy storage system. Energy Environ. Sci. *12*, 187–193.

67. Franz, E., Stumm, C., Waidhas, F., Bertram, M., Jevric, M., Orrego-Hernández, J., Hölzel, H., Moth-Poulsen, K., Brummel, O., and Libuda, J. (2022). Tunable energy release in a reversible molecular solar thermal system. ACS Catal. *12*, 13418–13425.

68. Eschenbacher, R., Xu, T., Franz, E., Löw, R., Moje, T., Fromm, L., Görling, A., Brummel, O., Herges, R., and Libuda, J. (2022). Triggering the energy release in molecular solar thermal systems: norbornadiene-functionalized trioxatriangulen on Au(111). Nano Energy *95*, 107007.

69. Greenfield, J.L., Gerkman, M.A., Gibson, R.S.L., Han, G.G.D., and Fuchter, M.J. (2021). Efficient electrocatalytic switching of azoheteroarenes in the condensed phases. J. Am. Chem. Soc. *143*, 15250–15257.