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Stimuli-Responsive Organic Phase Change Materials: Molecular Designs and Applications in Energy Storage

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Cite This: *Acc. Mater. Res.* 2022, 3, 634−643

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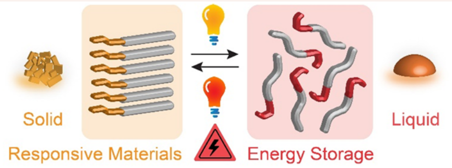


CONSPECTUS: Achieving a stable latent heat storage over a wide temperature range and a long period of time as well as accomplishing a controlled heat release from conventional phase change materials have remained prominent challenges in thermal energy control. Because the conventional phase change materials have the fixed phase transition temperatures under the standard ambient pressure, the latent heat storage is only viable at temperatures higher than their melting and crystallization points. Once the latent heat is stored in the liquid phase of materials, it is imperative to maintain the temperature of the system above its crystallization point to prolong the heat storage. Without the continuous energy input or extensive insulation, the crystallization of liquid occurs spontaneously, leading to the loss of latent heat and a short heat storage time. Thus, there exists a critical need to develop methods that enable the control over the phase transition of materials, unrestricted by the temperature of the surroundings. The successful development of such methods and materials in recent years has been viable through the incorporation of molecular switches that respond to external stimuli, notably light, electrochemical bias, and ions, by reversible structural changes. We have discovered novel functional organic material systems that exhibit solid-to-liquid phase transitions controlled by optical and electrical stimulation, along with other research groups. The development and optimization of such materials are enabled by the judicious molecular designs and syntheses.

In this Account, we will introduce the cutting-edge design principles of controllable phase change materials that have demonstrated the storage of thermal energy for up to a couple of months without crystallization over a wide temperature range, from subzero to over 100 °C, which addresses the major weakness of conventional phase change materials. In particular, materials that are controlled by solar irradiation and compounds that exhibit substantial gravimetric energy densities are presented, which will guide the further development of functional materials for practical energy storage applications. The controllable heat storage materials will not only recycle the wasted solar thermal energy but also ameliorate massive energy loss in industrial processes. In particular, the waste heat released at temperatures below 100 °C can be effectively absorbed and stored in organic phase change materials, which cannot be easily reclaimed by other energy conversion and storage systems, including thermoelectrics and electrical batteries. This complementary storage method will harness various sources of waste heat and reduce the consumption of fossil fuels by recycling the wasted energy, which will contribute to mitigating climate change.

1. INTRODUCTION

Phase transitions of organic and inorganic materials between solid and liquid phases are widely utilized for thermal energy storage, via endothermic melting and exothermic crystallization processes that occur in response to the changing temperature of environment. Various types of phase change materials (PCMs) ranging from inorganic salts and salt hydrates[1] to organic polyols,[2] sugar alcohols,[3] polyethylene glycols,[4] and aliphatics[5] are employed for thermal energy storage in different ranges of operation temperatures. Organic PCMs operate at a low-temperature range, typically spanning from 0 to 200 °C,[6] which makes them suitable for low-grade waste heat storage,[2] particularly the solar heat in the absence of a solar concentrator.[7] Therefore, organic PCMs have been considered for heating applications in the building sector, to control the indoor temperature conditions, along with thermochromic materials that are typically used in smart windows and coatings.[8] Thermochromic dyes change their optical density in response to temperature change, which controls the transmission or reflectance level of incident sunlight. One of the biggest challenges of latent heat storage in the PCMs, regardless of their types, is the difficulty in controlling their phase transition in an environment of changing temperature,[9] although monitoring the temperature change is feasible by the use of thermochromic dyes incorporated in the PCMs.

To develop a PCM system that can be controlled by different stimuli orthogonal to temperature change, stimuli-responsive materials have been considered. Most notably, a

Received: March 10, 2022
Revised: May 20, 2022
Published: May 27, 2022

https://doi.org/10.1021/accountsmr.2c00049

molecular system called photoswitch is a great candidate, because such molecule reversibly isomerizes between two isomers in response to irradiation and exhibits a drastic change in its optical and physical properties.[10−17] The light-induced phase transition of photoswitches has been explored for many other applications, such as photolithography,[18,19] optical memory,[20] photocontrolled adhesion,[21,22] and actuation.[23] Enabling a facile switching between solid and liquid states requires a careful design of molecular or polymeric systems, considering the type of photochromes, rigidity of molecular or polymeric scaffolds, and porosity of systems. The degree of conformational freedom of photoswitches in the condensed phase impacts the viability of their structural isomerization upon the absorption of light.[24] Also, their optical properties dictate the degree and rate of phase transition as well as the scale or quantity of materials that can be optically switched.[25]

Building upon the design principles of photoswitchable materials discovered in the other applications, we have pursued applying such systems in controllable heat storage in the recent years, along with other research groups.[26−29] Specific parameters that are critical in heat storage systems, such as overall heat storage density and heat storage period, are considered in designing such photoswitchable PCMs. In this Account, the detailed design principles of photochromic core and phase direction groups will be introduced, along with their impact on the figures of merit of heat storage systems. Furthermore, the challenges of the current state-of-the-art systems and the development of new methods that overcome such limitations will be illustrated, including an electrochemical switching that complements the photochemical processes.

2. MECHANISM OF CONTROLLED ENERGY STORAGE AND FIGURES OF MERIT

Figure 1a shows the phase transition of conventional organic phase change materials (PCMs) such as paraffins[30] and fatty acid esters[31] that undergo melting above their melting point (T_m) and crystallization below their crystallization point (T_c). For each PCM, the T_m and T_c are typically fixed, except for a slight variation that is typically derived by changing the speed of the heating and cooling processes. In the heat storage cycle, the solid PCMs absorb heat from external sources and store the latent heat in the liquid phase above T_m. However, the liquid phase needs to be kept at a temperature higher than T_c to preserve the stored latent heat. When the temperature drops below T_c, spontaneous crystallization of the liquid phase occurs, leading to the uncontrollable loss of the stored latent heat. Therefore, the heat storage time in the liquid phase is limited by the temperature change of the environment, which is difficult to control. This passive heat storage mechanism significantly hinders the efficient and controllable storage of waste heat and its utilization.

A novel method that enables the storage and release of heat at variable temperatures, particularly at lower temperatures than the T_m and T_c of PCMs, has recently emerged, which incorporates molecular switches that respond to light by significant structural and polarity changes (Figure 1b).[32] The concept and operation mechanism of molecular switches will be elaborated in the section 3.1. The switches in their ground state are generally in a linear or planar shape (for example, the *E* isomer of azobenzene) that allows for facile packing among the molecules and the formation of solid. The activation of such switches by photoirradiation at λ_1 generates nonplanar isomers of switches in their metastable state (*Z* isomer of azobenzene) that are structurally unfavorable for packing, thus forming liquid. The solid-to-liquid transition under irradiation can occur at variable T_1, which can be either above or below the T_m of the ground-state switches. The liquid metastable state switches generally exhibit much lower T_m and T_c than those of the ground-state switches, even below room temperature. Thus, the liquid state and its latent heat storage can be preserved at variable T_2, unrestricted by the changing temperature of environment. The release of latent heat is then triggered by the reverse structural isomerization of switches, typically induced by the irradiation at a wavelength of light (λ_2) that is orthogonal to the activation wavelength (λ_1). Through this process, both the latent heat (ΔH_m) and isomerization energy (ΔH_{iso}) of the switches are released via the simultaneous reverse isomerization and liquid-to-solid phase transition (Figure 1c).

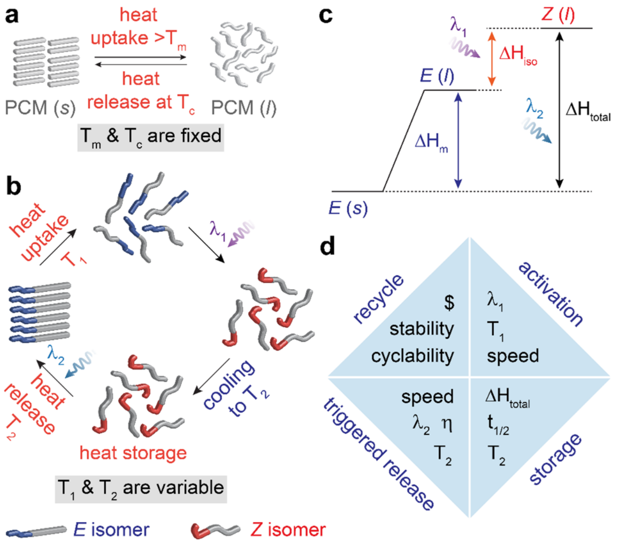


Figure 1. (a) Latent heat storage and release mechanism of conventional organic phase change materials (PCMs). (b) Optically controlled latent heat storage and release cycle of photoswitchable PCMs, which allows for the heat storage over a wide temperature range. Reproduced from ref 34. Copyright 2020 American Chemical Society. (c) Total energy storage in photoswitchable PCMs that undergo photoisomerization and concurrent phase transition. (d) Figures of merit of the optically controlled heat storage systems for each step of operation: activation wavelength (λ_1), activation temperature (T_1), total heat storage density (ΔH_{total}), heat storage temperature (T_2), half-life ($t_{1/2}$) of the metastable isomer, wavelength of light for photochemical reverse switching (λ_2), efficiency or degree of reverse switching (η), and heat release temperature (T_2).

The success of photocontrolled heat storage cycle is determined by various design parameters of the molecular systems and their properties (Figure 1d). The activation wavelength (λ_1) and temperature (T_1) at which the isomerization and phase transition occur can be tuned by molecular designs. T_1 dictates the operation conditions of the heat storage system and the types of viable heat sources. The speed of phase transition under the photoirradiation is an important figure of merit, which is determined by the optical properties (e.g., absorption coefficient, quantum yield of switching, and photostationary state (PSS) ratio of two isomers) and the quantity of materials as well as the intensity of incident light. The heat storage density (ΔH_{total}), temperature (T_2), and time that is determined by the half-life ($t_{1/2}$) of the metastable isomer are the key practical metrics for applications. The

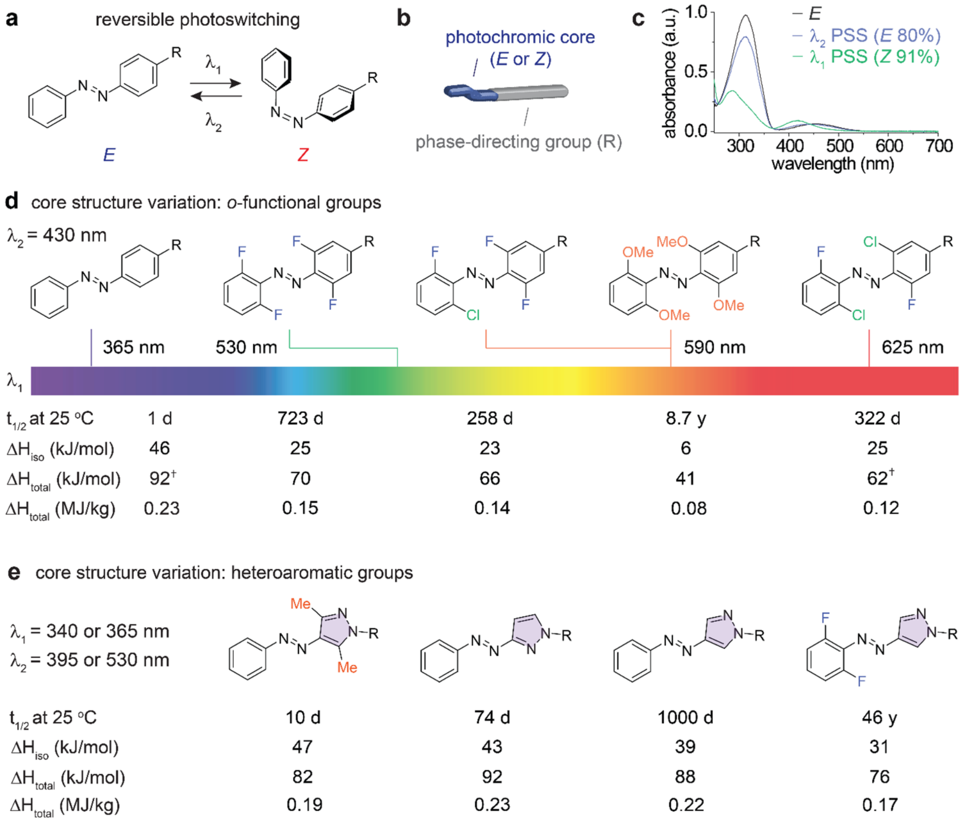


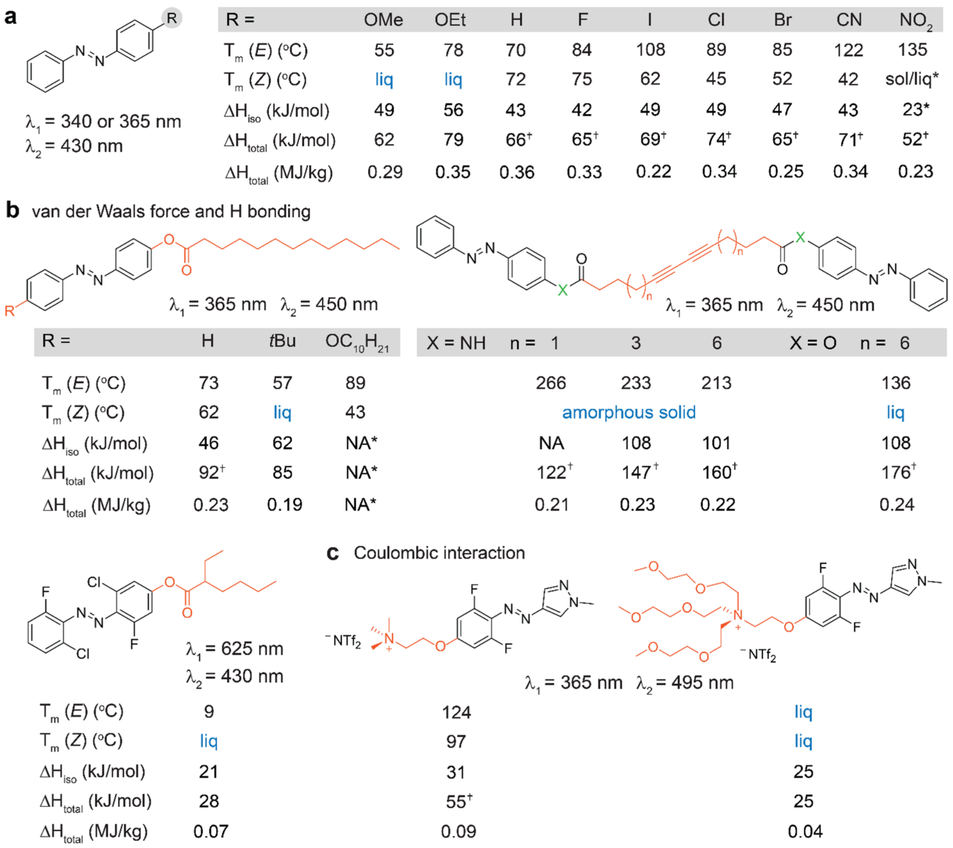
Figure 2. (a) Reversible structural changes of an azobenzene derivative upon the irradiation at different wavelengths. (b) A general structure of photoswitchable PCMs. (c) UV–vis absorption spectra of an azobenzene derivative (i.e., *o*-fluoroazobenzene in (d)) that illustrate the different absorbance features of *E* and *Z* isomers at each PSS. (d) Series of *o*-functionalized azobenzene derivatives that absorb a wide range of wavelengths of light for *E*-to-*Z* isomerization, their reversion kinetics, and thermal energy storage properties. (e) Series of arylazopyrazole derivatives that exhibit a wide spectrum of half-lives of metastable *Z* isomers and their thermal energy storage properties.[34] †Direct solid-to-liquid phase transition under the irradiation is not achievable and requires the solvation of molecules.

triggering conditions, including the wavelength of light for photochemical reverse switching (λ_2), efficiency or degree of reverse switching (η: the ratio of metastable isomers that are reverted to the ground state), and heat release temperature (T_2), can be also tuned by molecular designs. The speed of phototriggered crystallization dictates the time scale of heat release process, which can be tailored to each application. Lastly, the sustainable operation of the heat storage cycle requires the chemical and photochemical stability of the PCMs, repeatability of the photoswitching and phase transition for hundreds of cycles, and the reasonable cost of materials that will realize the levelized cost of energy storage at \$15/kWh level.[33]

3. MOLECULAR DESIGNS AND THEIR IMPLICATIONS IN ENERGY STORAGE PERFORMANCE

3.1. Photochromic Core Structures

The reversible photoisomerization of azobenzene, one of the most explored photoswitches, is illustrated in Figure 2a. The initial configuration of azobenzene, prior to any photoirradiation, is in its *E* or *trans* isomeric state that is typically planar and allows for facile packing among the molecules through strong $\pi-\pi$ interactions. The switch is turned on by the irradiation at λ_1, which induces the structural isomerization of *E* (*trans*) configuration to *Z* (*cis*) form. The nonplanar *Z* isomers experience a large steric hindrance, both intramolecularly and intermolecularly, thus exhibit a higher energy level than the *E* counterpart and the less effective packing of molecules. These two factors contribute to the formation of the liquid state of *Z* isomers that store both latent heat and isomerization energy of photoisomers (Figure 1c).[32] The photoswitchable PCMs are largely composed of two parts: a photochromic core, which reversibly changes the isomeric structure, and a phase-directing group (R) that does not undergo any structural change but determines the overall intermolecular interactions and the phase of molecules at room temperature (Figure 2b). In Figure 2c, typical absorbance spectra of an azobenzene derivative as the initial *E* isomer (black), upon the photoswitching to *Z* isomer by the irradiation at λ_1 (green) and after the reverse switching to *E* under the irradiation of λ_2 (blue), are displayed. The large absorption peak at around 315 nm represents the $\pi-\pi^*$ transition of azobenzene, whereas the smaller peak at around 450 nm shows the $n-\pi^*$ transition. The *E*-to-*Z* isomerization can be promoted either by the irradiation at the peak of $\pi-\pi^*$ band in the UV range or at the tail of $n-\pi^*$ band of *E* where the spectral overlap with that of *Z* is minimal. The *Z*-to-*E* isomerization is the most efficiently triggered by the irradiation at the peak of $n-\pi^*$ band of *Z*. The PSS ratio indicates the *E*/*Z* ratio in the mixture of isomers at the photodynamic equilibrium that is reached upon the irradiation at a specific wavelength. Thermogravimetric analysis (TGA) of azobenzene derivatives shows their thermal degradation temperatures near or above 200 °C, which ensures the high thermal stability of



R =	OMe	OEt	H	F	I	Cl	Br	CN	NO$_2$
T$_m$ (*E*) (°C)	55	78	70	84	108	89	85	122	135
T$_m$ (*Z*) (°C)	liq	liq	72	75	62	45	52	42	sol/liq*
ΔH$_{iso}$ (kJ/mol)	49	56	43	42	49	49	47	43	23*
ΔH$_{total}$ (kJ/mol)	62	79	66†	65†	69†	74†	65†	71†	52†
ΔH$_{total}$ (MJ/kg)	0.29	0.35	0.36	0.33	0.22	0.34	0.25	0.34	0.23

R =	H	*t*Bu	OC$_{10}$H$_{21}$
T$_m$ (*E*) (°C)	73	57	89
T$_m$ (*Z*) (°C)	62	liq	43
ΔH$_{iso}$ (kJ/mol)	46	62	NA*
ΔH$_{total}$ (kJ/mol)	92†	85	NA*
ΔH$_{total}$ (MJ/kg)	0.23	0.19	NA*

	X = NH n = 1	3	6	X = O n = 6
T$_m$ (*E*) (°C)	266	233	213	136
T$_m$ (*Z*) (°C)	amorphous solid			liq
ΔH$_{iso}$ (kJ/mol)	NA	108	101	108
ΔH$_{total}$ (kJ/mol)	122†	147†	160†	176†
ΔH$_{total}$ (MJ/kg)	0.21	0.23	0.22	0.24

T$_m$ (*E*) (°C)	9	124	liq
T$_m$ (*Z*) (°C)	liq	97	liq
ΔH$_{iso}$ (kJ/mol)	21	31	25
ΔH$_{total}$ (kJ/mol)	28	55†	25
ΔH$_{total}$ (MJ/kg)	0.07	0.09	0.04

Figure 3. (a) Azobenzene derivatives functionalized with a variety of small groups on the *para* position and their thermal properties.[40] (b) Azobenzene derivatives functionalized with linear[9] or branched alkyl,[35] diacetylene,[41] and H-bonding groups,[41] which control the noncovalent intermolecular interactions among the molecules and their thermal properties. (c) Arylazopyrazole derivatives[42] functionalized with ionic groups that vary the Coulombic interactions among the molecules in the condensed phase. *Because of the fast thermal reversion of *Z* under the photoirradiation condition, the enrichment of *Z* isomers is not achieved. †Direct solid-to-liquid phase transition under the irradiation is not achievable and requires the solvation of molecules.

the compounds during the typical heat absorption process occurring at below 100 °C.[9]

The chemical modification of the photochromic core has a significant implication in changing the absorbance profiles of PCMs, achieving diverse activation wavelengths (λ_1) as shown in Figure 2d.[35] The unmodified azobenzene is primarily activated by the UV irradiation that promotes the π−π* transition. However, the *o*-functionalized azobenzene derivatives display a substantial red shift of their n−π* band, as exemplified in Figure 2c, which enables the visible light activation of *E*-to-*Z* isomerization. The *o*-functional groups stabilize different frontier molecular orbitals of *E* and *Z* isomers, which leads to the red and blue shift of their n−π* bands, respectively.[36] The *o*-fluoroazobenzene switches from *E* to *Z* by the irradiation at 530 nm (green), and other compounds that are functionalized with mixed fluoro and chloro groups as well as methoxy groups exhibit further red-shifted n−π* bands of *E* isomers, enabling the switching at 590 nm (orange) and 625 nm (red). All of the switches were triggered for the *Z*-to-*E* isomerization at 430 nm (blue), which promotes the n−π* bands of *Z* isomers. The *o*-functionalization of azobenzene therefore realizes a reversible switching of molecules by the irradiation solely within the visible light range, opening up opportunities to operate the heat storage system using the natural or filtered sunlight in the absence of any artificial light sources. The *o*-functionalized azobenzene cores, appended with a tridecanoate chain (R) on their *para* position, have been demonstrated to absorb the filtered sunlight of low irradiance and to undergo *E*-to-*Z* switching and concomitant phase transition in a greenhouse. The crystallization was then triggered by the irradiation with a blue LED or filtered sunlight through a blue bandpass filter.

The *o*-functional groups also significantly stabilize the energy of *Z* isomers, which translates to their half-lives and heat storage time that are significantly longer than those of unfunctionalized azobenzene. The spontaneous thermal reversion of *Z* isomers at room temperature or at any storage temperature (T$_2$) limits the heat storage period, which can be effectively resolved by the *o*-functionalization of azobenzene. A drawback of such design, however, is the reduced isomerization energy (ΔH_{iso}) compared to that of unfunctionalized azobenzene. This is attributed to the lowered *Z* isomer energy of *o*-fluoro or chloroazobenzene[36] and the raised *E* isomer energy of *o*-methoxyazobenzene,[37,38] both of which substantially reduces the energy gap between the *E* and *Z* isomers, compared to that of unfunctionalized azobenzene. The compound with the longest half-life of *Z*, i.e., *o*-methoxyazobenzene, exhibits the lowest ΔH_{iso}, followed by the other *o*-functionalized azobenzenes. Total energy storage densities (ΔH_{total}) of these compounds are in the range 41−70 kJ/mol. The unfunctionalized azobenzene with the identical R group, i.e., tridecanoate, however, has a larger ΔH_{iso} and results in 92 kJ/mol of total energy storage. However, the molecule in its planar *E* structure displays a high T_m (73 °C),[9] which hinders the direct photoinduced phase transition from the crystalline *E* to liquid *Z* at room temperature. At an elevated temperature close to its T_m, the molecules gain conformational freedom, but the UV irradiation cannot enrich *Z* isomers because of the facile thermal reversion at the high temperature. Therefore, the tridecanoate-functionalized azobenzene requires the solution-state isomerization to acquire *Z* isomers, which also applies to the di-*o*-fluoro-di-*o*-chloroazobenzene derivative in Figure 2d with a T_m of 78 °C (marked by † sign).

Instead of functionalizing the azobenzene core, the substitution of a phenyl group by a heteroaromatic moiety generates a new series of photoswitchable PCMs based on an arylazopyrazole core (Figure 2e).[34] As initially discovered by Fuchter et al., the presence of C−H bond on the pyrazole ring that is positioned *ortho* to the azo group unlocks the intramolecular C−H···π interaction with the phenyl group, forming a T-shaped *Z* isomer.[39] This effectively stabilizes the energy of *Z* isomers and prolongs the half-life of the metastable state, leading to the longer heat storage time. The presence of difluoro group on the phenyl ring further stabilizes the *Z* isomer, which yields an incredibly long half-life of 46 years. The substitution of *ortho* positions on the pyrazole ring by methyl groups, on the contrary, substantially reduces the half-life of the *Z* isomer because of the absence of the C−H···π interaction. The ΔH_{iso} of each compound reflects the relative stability of the *Z* isomers; the least stable *Z* isomer of methyl-functionalized arylazopyrazole is correlated with the largest energy gap between the *E* and *Z* (ΔH_{iso}). All four compounds are capable of switching under the irradiation in the condensed phase, and the methylated arylazopyrazole undergoes a facile switching from crystalline *E* to liquid *Z* at room temperature, despite its $T_m \sim 67$ °C. The other three compounds with a higher T_m (91, 71, and 61 °C) also successfully achieve the light-induced phase transition and isomerization at an elevated temperature around their T_m, because of the exceptionally high thermal stability of their *Z* isomers.[34] The *Z*-to-*E* thermal reversion temperatures of those three arylazopyrazoles, measured by differential scanning calorimetry (DSC), range from 137 to 179 °C, which are much greater than those of azobenzene derivatives (102−120 °C).[9,35]

Notably, most of the newly designed compounds in Figure 2d,e exhibit an extremely enhanced stability of *Z* liquid phase over a wide range of temperatures from −40 °C up to their thermal isomerization temperatures. This remarkable property paves a way to generate a material system that stores and releases the latent heat even at subzero temperatures. The stable and long-term storage of light-activated liquid phase for months at variable temperatures is ideal for small, portable devices that are not perfectly insulated for temperature control. The PCM-based heat storage devices can overcome challenges of conventional battery- or fuel-powered heating devices that are difficult to function in an extremely cold climate.

3.2. Phase-Directing Groups

The R group, typically on the *para* position of an azobenzene core, is designed to control the degree of intermolecular interactions among the PCMs, their phase in each isomeric state, and their thermal properties including heat storage temperature (T_2) and heat storage density. Unlike the *ortho* functional groups shown in Figure 2d, the monofunctional group on the *para* position of azobenzene does not significantly alter its absorption profile or the half-life of *Z* isomers, unless the R group substantially extends the conjugation length of azobenzene. Figure 3a illustrates a series of azobenzene derivatives[40] with a variety of small functional groups on the *para* position, which is designed to probe the impact of size and polarity of the functional group (R) on the phase and heat storage density of the photoswitchable PCMs. The absorption profiles of the functionalized azobenzenes were similar to that of unfunctionalized azobenzene (R = H), thus UV (340 or 365 nm) and 430 nm light were used for inducing the reversible photoisomerization.

Most notably, the methoxy and ethoxy groups on the *para* position enable the formation of very stable *Z* liquid at the room temperature. These two compounds behave similarly to the *o*-functionalized azobenzenes[35] (Figure 2d) and arylazopyrazole derivatives[34] (Figure 2e) in that their liquid *Z* isomers are preserved over a wide range of temperatures spanning from −40 °C to their isomerization onset temperature above 60 °C. This exceptional liquid stability is attributed to the ability of the nonplanar functional groups on azobenzene to prevent the stacking of *Z* isomers. The reduced planarity of *E* isomers decreases their $\pi-\pi$ interaction in the crystalline phase, enabling the facile photoswitching of *E* isomers to form liquid *Z* at room temperature. These compounds exhibit considerable energy densities per mole (62 and 79 kJ/mol) and remarkable gravimetric energy densities near or exceeding 0.3 MJ/kg, which is attributed to their low molecular weights compared to those of tridecanoate-functionalized azobenzenes[9] or dodecanoate-appended arylazopyrazole derivatives[34] (Figure 2d,e; 0.12−0.23 MJ/kg). Other monofunctionalized azobenzenes in Figure 3a were suboptimal for practical heat storage, because of the crystallization of their *Z* isomers at room or lower temperatures and/or the less complete *E*-to-*Z* activation at temperatures above their relatively high T_m (marked by † sign).

The role of intermolecular van der Waals interactions on the phase of *E* and *Z* isomer was further explored by installing a long alkyl functional group on one *para* position of azobenzene and substituting the other *para* position with either sterically bulky group (e.g., *tert*-butyl) or another long alkyl chain (e.g., dodecyloxy) in Figure 3b.[9] The monofunctionalized azobenzene with a tridecanoate group exhibits crystallinity for both *E* and *Z* isomers at room temperature because of the combination of intermolecular $\pi-\pi$ interaction among the core structures and van der Waals forces among the alkyl chains. The additional *tert*-butyl group effectively lowers the T_m of *E* and results in the formation of liquid of *Z* isomer, because of the intermolecular stacking perturbed by the sterically bulky *tert*-butyl group. The dodecyloxy group, in contrast, further strengthens the van der Waals interaction among the molecules and increases the T_m of compound to 89 °C. This property prevents the photoswitching of *E* to *Z* in condensed phases, because of the rapid thermal reversion of *Z* during the irradiation performed at high temperatures close to the T_m. The incomplete *E*-to-*Z* conversion challenges the accurate measurement of ΔH_{iso} by DSC, as the exotherm of *Z*-to-*E* thermal reversion and the endotherm of the residual *E* melting overlap (marked by † sign).

Azobenzene derivatives linked to a diacetylene moiety through alkyl spacers are also studied to measure the influence of van der Waals forces on the relative packing of molecules in *E* and *Z* forms.[41] Because of the presence of a diacetylene moiety which promotes the effective self-assembly of molecules, those with *E* azobenzene groups exhibit crystallinity with T_m as high as 266 °C. The crystal structure of molecules bearing *E* azobenzene termini shows the presence of H-

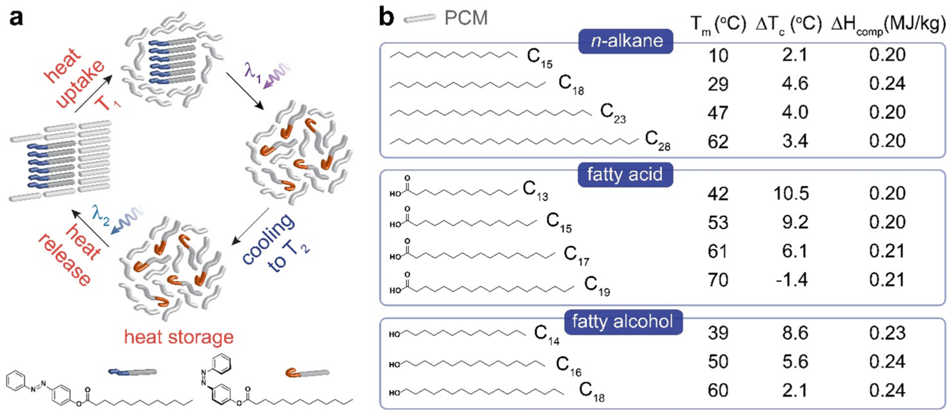


Figure 4. (a) Optically controlled heat storage and release cycle in a composite of conventional and photoswitchable PCMs.[5] (b) Classes of conventional organic PCMs and their operation temperatures (T_m). Degree of supercooling achieved by UV activation (ΔT_c) and the latent heat storage capacity of composite (ΔH_{comp}) containing 50 wt % of photoswitchable PCMs. Reproduced with permission from ref 5. Copyright 2018 Royal Society of Chemistry.

bonding among the neighboring amide groups. As the alkyl spacers get longer, the T_m of *E* isomer decreases, presumably because of the increased flexibility of alkyl groups and weakened H-bonding. The substitution of the amide linkage by an ester group drastically lowers the T_m of *E* isomer to 136 °C, which signifies the role of intermolecular H-bonding in enhancing the crystallinity of linear molecules. Surprisingly, *Z* isomers of all compounds lost crystallinity, displaying either amorphous solid or liquid phase at room temperature. This is attributed to the significant structural and polarity change of two azobenzene terminal groups, which prevents the packing of linear molecules. The thermal activation of *Z* isomers by DSC reveals the concomitant *Z*-to-*E* reverse isomerization and the crystallization of *E*, resulting in a large amount of heat released from the molecules (122−176 kJ/mol), which is also significant per azobenzene moiety (61−88 kJ/mol). Because the direct measurement of ΔH_{iso} is not viable because of the coupled isomerization and crystallization processes during the thermal activation, the separate measurement of the latent heat of *E* isomers and the subtraction of it from ΔH_{total} indirectly quantify ΔH_{iso} (51−54 kJ/mol per azobenzene moiety). Because of the extremely high T_m of the molecule with the shortest alkyl spacer (266 °C), its thermal degradation occurs while melting, making it difficult to characterize its latent heat and indirectly assess its ΔH_{iso}. The series of diacetylene−azobenzene compounds with exceptionally high crystallinity and T_m for *E* isomers require solvation for photoswitching (marked by † sign), similar to the case for other azobenzene derivatives with high T_m, including halide-substituted azobenzenes (Figure 3a). Powder X-ray diffraction (PXRD) analysis of diacetylene−azobenzene derivatives confirms the phase transition between the crystalline *E* and liquid *Z* isomers.[41] An in situ variable-temperature X-ray analysis will enable monitoring the thermal reverse isomerization (*Z* to *E*) and simultaneous crystallization.

The design of an azobenzene derivative with a branched alkyl chain, on the contrary, significantly weakens the intermolecular interactions among the photochromic cores.[43,44] The *E* isomer is more crystalline than the *Z* counterpart, showing a low T_m, whereas the *Z* isomer is a stable liquid even at subzero temperatures. Despite the low ΔH_{total}, the compound achieves the optically controlled storage and release of latent heat at low temperatures. Attaching an ionic group to a photochromic core introduces new intermolecular interaction through Coulombic forces that play a role in directing the phase of photoswitchable PCMs (Figure 3c).[42] The bulky substituents contribute to lowering the intermolecular interactions between molecules and forming a liquid state more easily than the compact counterpart. The compact molecule with a high T_m cannot photoswitch in its ionic crystalline phase without any solvation (marked by † sign), whereas the bulky molecule exhibits a stable ionic liquid state at room temperature for both *E* and *Z* isomers, allowing for unhindered photoisomerization. The photoinduced phase transition between an ionic liquid (*Z*) and an ionic crystal (*E*) has been reported by Kimizuka et al., and such compounds have been investigated for photoswitching of their conductivity in films.[28]

3.3. Composite Strategy

Another strategy to control the phase transition and heat storage of organic PCMs is to make a composite of conventional PCMs such as *n*-alkanes, fatty acids, and fatty alcohols with photoswitch dopants (Figure 4a,b).[5] The structural and polarity changes of the photoswitches impact the overall phase of the composite; the polar and nonplanar *Z* isomers prevent the crystallization of conventional PCMs even at temperatures below their crystallization points. This degree of supercooling (ΔT_c) represents the window of temperatures within which the latent heat is stored and controllably released by optical stimulus, and it varies depending on the % of azobenzene dopants in the composite as well as the type of conventional PCMs. Generally, the longer PCMs with higher T_m are more difficult to supercool (i.e., smaller ΔT_c) by the UV activation of photoswitch dopants, because of the strong van der Waals interactions among the PCMs and the tendency to crystallize upon cooling from the molten phase. ΔT_c increases with more polar PCMs, because they strongly interact with *Z* isomers of photoswitchable dopants in the molten state and form a stable supercooled liquid at lower temperatures. The *Z*-to-*E* isomerization of dopants rapidly generates the *E* isomer crystals that act as nucleation seeds for the composite, promoting the crystallization of the PCMs and concurrent heat release. The total energy storage density of a composite is expressed as gravimetric density in the unit of MJ/kg, instead of molar storage density (kJ/mol), because of the convoluted contribution of multiple parameters to the total

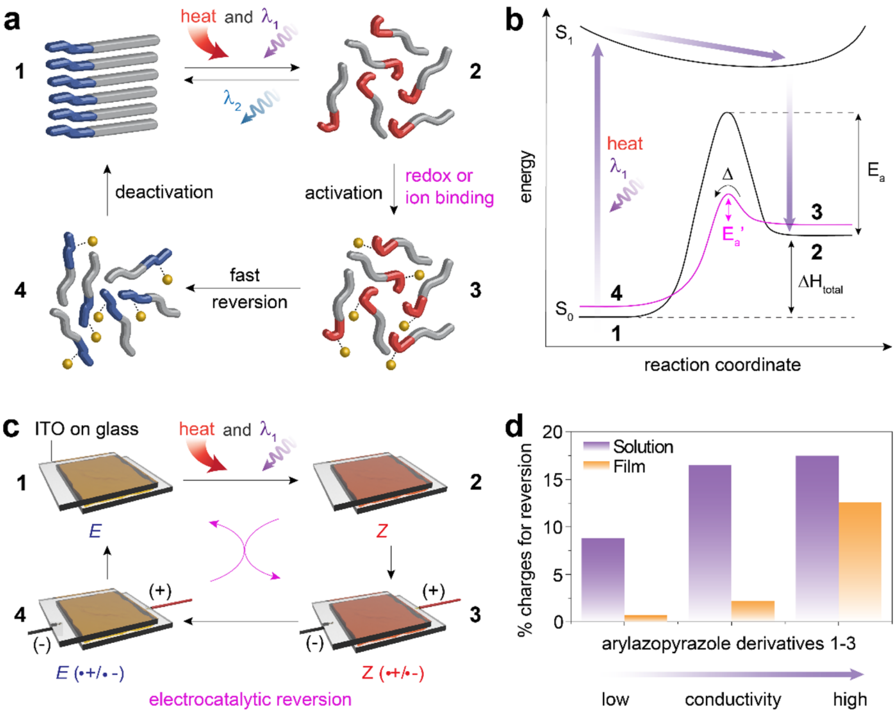


Figure 5. (a) Heat storage in photoswitchable PCMs and heat release triggered by either photochemical or alternative methods: electrochemical or ion binding mechanism. (b) Energy diagram of photoisomerization process and the reduced activation barrier for the reverse isomerization by the redox or ion binding activation of the metastable isomer. Reproduced with permission from ref 45. Copyright 2020 Elsevier. (c) Condensed-phase photoswitching of ionic PCMs and electrochemical triggering of *Z*-to-*E* isomerization via electrocatalytic mechanism. Reproduced from ref 42. Copyright 2021 American Chemical Society. (d) Substoichiometric number of charges used for catalytic *Z*-to-*E* reversion in solution and film state.

energy storage (i.e., fractional ΔH_m of PCMs, fractional ΔH_m of photoswitches, and fractional ΔH_{iso} of photoswitches). The mass ratio between two components are varied to maximize ΔT_c, and typically 50:50 wt % mixtures result in the largest ΔT_c for various PCM mixtures.

The composite strategy can be advantageous over the heat storage in single-component photoswitches, because of the lower usage of photoswitch compounds. The penetration depth of light (λ_1 and λ_2) through the condensed phase is substantially larger for the composite compared to that through single-component photoswitches, as a result of the lower concentration of photochromes. The long penetration depth of light enables the facile activation and the triggered crystallization of a large volume of materials. Because the incident photon energy (energy input) is greater than the heat storage density (energy output), the lower absorption of light by the azobenzene dopants in the composite can contribute to increasing the overall energy conversion efficiency of the system. Also, the conventional PCMs are sourced from inexpensive petroleum residue; thus the cost of the composite is lower than that of the 100% synthesized photochrome system. The major disadvantage of the composite, however, is the limited degree of supercooling of the composite (max. $\Delta T_c \sim 10$ °C), which is mostly dictated by the type of PCMs. The heat storage and release temperature (T_2) of the *Z* composite is therefore kept above room temperature, which renders it difficult to store latent heat around or below room temperature. This is in contrast to some of the optimal photoswitches presented in Figures 2 and 3 that are capable of storing heat over a wide temperature range from −40 to over +100 °C.

4. ALTERNATIVE SWITCHING METHODS

Photochemical switching between *E* and *Z* isomers effectively controls the phase of materials and the heat storage, provided that a high PSS ratio is obtained at each irradiation wavelength. Typically, *E*-to-*Z* isomerization yields a high PSS ratio above 90%, whereas *Z*-to-*E* isomerization is less complete because of the significant overlap between the n−π* bands of both isomers. In particular, some of the functionalized azoarene structures including the arylazopyrazole derivatives display a suboptimal reversion of *Z* to *E* upon photochemical triggering (η = 15−83%).[34,42] This leads to an incomplete crystallization and energy release from the PCMs. Alternatively to the photochemical triggering, redox[46,47] and ion binding[48,49] methods have been demonstrated to generate intermediates that lower the energy barrier for the *Z*-to-*E* isomerization in solutions (Figure 5a,b). This allows the quantitative *Z*-to-*E* reversion to occur at room temperature, which is in contrast to the high temperature needed to thermally revert *Z* species, typically in the range 80−100 °C for azobenzenes[35] and up to 147 °C for arylazopyrazoles[34] in the absence of electrochemical or photochemical stimuli.

Although the solution-state reversion of *Z* by the application of electrochemical potential and ion binding has been demonstrated for azobenzene derivatives, the translation of the principle to a condensed phase requires a new experimental design. Also, new parameters such as molecular conductivity impact the degree of electrochemical switching in the condensed phase. The arylazopyrazoles functionalized with *o*-fluoro groups on the phenyl ring as shown in Figure 2e and Figure 3c represent the class of switches that show suboptimal photochemical reversion, only reaching 38−47% *E* under the irradiation at 395 nm and 24−83% at 495 nm.[42] The quaternary ammonium group with a counteranion, bistriflimide, attached to an arylazopyrazole group increases the electrical conductivity of compound (Figure 3c). The compact ammonium group with short substituents such as methyl group gives rise to a higher conductivity (ca. 0.2 μS/cm at 35 °C) of the compound than that of neutral arylazopyrazole compound (0.01 μS/cm at 35 °C). The bulkier ammonium-substituted photochrome exhibits the highest conductivity (ca. 22 μS/cm at 35 °C) because of the increased mobility of molecules in the condensed phase.

The arylazopyrazole derivatives with varying conductivity were melt-pressed between two ITO-coated glass substrates to form thin films that were then irradiated with UV to switch to *Z* isomers, as shown in Figure 5c. When applied with electrical bias, the *Z* liquid films gradually switch to *E* isomers at room temperature, via the formation of radical intermediates ($Z^{\bullet +/\bullet -}$) that rapidly revert to *E* radical species ($E^{\bullet +/\bullet -}$). The radicals are then transferred to unreacted neutral *Z* molecules to catalyze further *Z*-to-*E* isomerization. Because of the electrocatalytic nature of the process, the number of charges used to complete the molecular reversion is much smaller than the total number of reverted molecules. The substoichiometric numbers of charges, compiled in Figure 5d, show that photoswitches with a lower conductivity consume less charge for redox-induced switching. A neutral arylazopyrazole with a dodecanoate chain (Figure 2e) requires less than 1% charge for the reversion in films, whereas the photochromes with ionic moieties (Figure 3c) undergo less efficient redox switching, because of the charges transported through the ionic moieties in the films. In general, the redox switching is far more efficient in the condensed phases than in solutions, because the radical species are terminated and quenched by solvents or electrolytes in solutions.

This first demonstration of the condensed-phase electrochemical switching sheds light on a new pathway to control the heat release from switchable PCMs, particularly for those that undergo an unfavorable photochemical reversion. The design principles discovered in this work guide the further development of photoswitchable PCMs that are controlled by multiple external stimuli. We note that other types of molecular switches, e.g., thermochromic compounds[8] that undergo significant configurational changes upon heat absorption, could offer an alternative method of controlling the phase of materials. Our recent work shows the spiropyran-to-merocyanine isomerization that occurs upon melting results in an extensive supercooling of the isomeric mixture. The supercooled liquid could be potentially triggered by other external stimuli to crystallize and release the stored thermal energy.[50]

5. CONCLUSIONS

The photoswitchable PCMs that exhibit a wide range of heat storage temperature (−40 to over +100 °C) and a substantial heat storage time over a couple of months have been successfully developed through the molecular design of photochromic cores and phase-directing groups. Now the heat storage in such organic PCMs can be optically controlled by various wavelengths of visible light, enabling to harness solar irradiation rather than depending on artificial UV light sources. The fundamental understanding of the intra- and intermolecular interactions in condensed phases and their impact on the melting and crystallization processes of materials, acquired in the studies, can be translated to comprehending other photocontrolled systems such as photoswitchable adhesives[21,22] and actuators.[51] The current systems are mostly tested in a small scale, from a few milligrams to hundreds of milligrams in the laboratory, to confirm the design principles. The application of such molecular systems in a large device would require further development and optimization of the molecules, particularly to facilitate the full activation of photoswitches in thick materials, which is often limited by the low light penetration depths (currently a maximum of ∼300 μm is reported).[35] Therefore, the studies on molecular designs that can drastically increase the light penetration through optically dense materials will be highly desired and critical for the practical application of controllable PCMs. For example, a variety of negative photochromes such as spiropyran−merocyanine, the donor−acceptor Stenhouse adduct, and hydrazone are considered as promising candidates.[10,11,14]

Additionally, achieving a high gravimetric energy density of PCMs will be crucial in the application stage where the size and weight of devices would determine the cost and portability of the technology. The current state of the art gravimetric energy density of the azobenzene-based PCMs is around 0.3 MJ/kg, which was achieved by reducing the size of phase-directing groups and the overall molecular weight. Further studies on improving energy densities will involve enhancing both ΔH_{iso} and ΔH_{m} of compact molecular systems through chemical modifications. These main figures of merit of the optically controlled heat storage systems are compared between the ideal benchmarks and the state of the art in Table 1. Finally, the switching of isomers by other methods, such as ion binding or mechanical triggering, have not been demonstrated in a condensed phase, particularly on a bulk scale. The translation of the solution-state or thin-film properties of molecules to bulk condensed phase with a substantial thickness would require a system engineering and design that enables the propagation of external stimuli throughout the bulk materials and ensures the complete switching of molecules in a large quantity.

Table 1. Figure of Merit Comparison between the Benchmarks and the State of the Art[a]

	T_2 (°C)	λ (nm)	δ (μm)	$\Delta H_{\mathrm{total}}$ (MJ/kg)
Benchmark	<0 to >100	400-800	10^3-10^4	>300
State-of-the-art	✓	✓	300	✓
Ref.	26, 34, 35	35	35	26, 40

[a] Heat storage temperature (T_2), irradiation wavelengths for reversible switching (λ), light penetration depth (δ), total heat storage density ($\Delta H_{\mathrm{total}}$).

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The authors declare no competing financial interest.

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■ ACKNOWLEDGMENTS

This work is supported by NSF CAREER award (DMR-2142887). We also thank Brandeis NSF MRSEC Bioinspired Soft Materials (DMR-2011846) and SPROUT award (2021-029) from the Brandeis Office of Technology Licensing.

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