

REVIEW

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Solar energy conversion and storage by photoswitchable organic materials in solution, liquid, solid, and changing phases

Qianfeng Qiu, Yuran Shi and Grace G. D. Han *

This review illustrates various structural design principles for molecular solar thermal (MOST) energy storage materials based on photoswitches that operate under different conditions, e.g. solution state, neat liquid, and solid, or result in a solid–liquid phase transition during their photo-isomerization. The structural modifications of MOST compounds enable the formation of each phase, which also influences the important performance metrics of the photoactive energy materials: the energy storage density per molecule or gravimetric energy density. Other major optical and thermal properties are also modulated by the molecular designs and affect the energy storage period, efficiency of the system, and device structures that accommodate the solar energy storage in each form of the MOST compounds. The introduction of different strategies that enable the large density heat storage under specific phase conditions will help to facilitate the further development of efficient MOST systems that will be readily integrated to device-scale applications with a transformative impact on the renewable energy markets.

1. Introduction

Molecular solar thermal (MOST) materials, composed of photo-switching molecules that respond to light and isomerize into a metastable conformer, have been investigated as a promising candidate that stores photon energy in chemical bonds and releases the energy in the form of heat upon triggering. Among many of the novel photoswitching compounds developed to

undergo either *trans*–*cis* or ring opening-closing isomerization, four of the following compounds have been extensively studied for their energy storage capabilities: (1) dihydroazulene/vinylheptafulvene (DHA/VHF) couples,^{1–5} (2) fulvalene dimetal complexes, notably FvRu₂(CO)₄,^{6–8} (3) norbornadiene/quadracyclane (NBD/QC) couples,^{9,10} and (4) azobenzene systems.^{11,12} These molecular systems are reported to store a significant amount of energy in their metastable isomeric forms (on the right side of the equilibrium) obtained by the photo-irradiation of ground-state isomers (on the left side) as shown in Fig. 1. The phases in

Department of Chemistry, Brandeis University, 415 South Street, Waltham, MA 02453, USA. E-mail: gracehan@brandeis.edu



Qianfeng Qiu

Qianfeng Qiu received his BS degree in Chemistry from Ocean University of China in 2016 and an MS in Physical Chemistry at Sun Yat-sen University in 2019. He is currently pursuing his PhD under the supervision of Prof. Grace Han at Chemistry Department of Brandeis University. His research focuses on developing molecular solar thermal (MOST) energy storage compounds based on photoswitches including azobenzene. He also investigates the optically-induced phase transition of organic materials for various applications.



Yuran Shi

Yuran Shi graduated from Brandeis University with a BA/MA degree in Chemistry and a BA in Computer Science in 2021. He conducted three years of undergraduate research under the guidance of Prof. Grace Han, developing visible-light-responsive molecular photoswitches for energy applications. He is starting his PhD program in Chemistry at Stanford University in 2021, and his research interests range from soft materials to optoelectronic molecules.

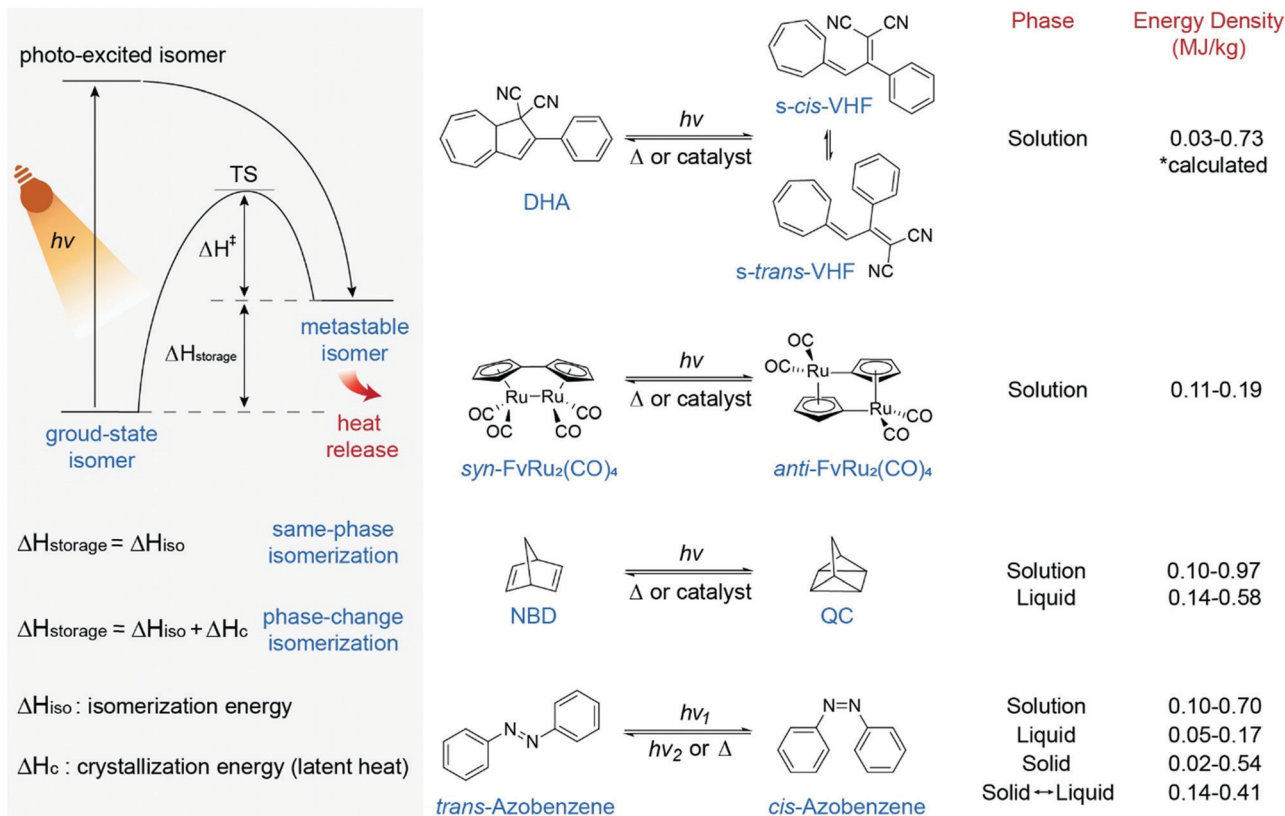


Fig. 1 Photon energy storage process, classes of MOST compounds, their isomerization reactions, and the range of their energy densities reported in the corresponding phases.

which the photo-activation is performed are described for each category of MOST systems, and the ranges of attainable energy density for each phase are shown. This illustrates the stages of development for each MOST system towards practical applications which span from solution-state or liquid-based flow systems for solar water heating¹³ and thermal control of

building environment^{9,14} to solid-state films for window coatings¹⁵ and polymeric fibers for the integration to smart fabrics.¹⁶ It is crucial to design MOST materials that operate in a certain phase that is required for each application, and thus there has been extensive research on the molecular designs that allow the compounds to form a desired phase, switch within the phase, or undergo phase transitions while switching. In this review, we primarily focus on the design strategies of MOST compounds that isomerize under various conditions (*i.e.* solution-state, neat liquid phase, solid phase, and solid-liquid phase transition) and how such molecular designs impact the energy storage in the respective MOST system.

We note that the MOST systems based on DHA/VHF report high energy densities up to 0.73 MJ kg⁻¹ according to the computational evaluation of their isomerization energy.¹ DHA undergoes a photo-activated ring opening to form VHF isomers that are under equilibrium between *s-cis* and *s-trans* conformation, and the heat release is triggered by the thermal activation or catalysis of the ring closure of VHF. The unidirectional photo-switching from DHA to VHF and the full back isomerization in the dark indicate a remarkable potential of the molecular system for photon energy storage.^{17,18} Various molecular design principles have been explored through the chemical modification of the DHA/VHF scaffold, which improves their optical properties, the thermal half-life of VHF, and the energy density of the system. The examples include the substitution of



Grace G. D. Han

Sciences. Her research interests span energy conversion and storage, molecular switch chemistry, phase transition of materials, and atomic-resolution molecular imaging.

Grace Han was born in South Korea and graduated from POSTECH with BS in Chemistry. She obtained her PhD in Chemistry at MIT in 2015 and joined the Department of Materials Science and Engineering at MIT as a postdoctoral associate. Grace started her independent career as an assistant professor at the Department of Chemistry at Brandeis University in 2018 and was appointed to the Landsman Career Development Chair in the

various electron-donating and withdrawing groups on the photoswitch core,^{3,19–23} the conjugation of the DHA/VHF scaffold with other photoswitches such as diarylethene and norbornadiene,^{23,24} and controlling the aromaticity of the system,^{5,25} protonation–deprotonation process,²⁶ and strain of macrocycles containing DHA/VHF.²⁷ Although the synthesis of these compounds and their solution-state photoswitching and thermal reversion properties have been elucidated, the experimental measurement of their thermal energy storage densities has remained a challenge, primarily due to the concomitant melting and heat release process occurring at an increased temperature, which makes it difficult to quantify the exothermicity of the VHF-to-DHA isomerization. This review primarily focuses on the experimental demonstrations of the photo-switching in different phases and the measurement of thermal energy released from MOST systems in such phases. Therefore, the DHA/VHF compounds are not further illustrated here, and we direct the readership to a recent review that discusses the design strategies of DHA/VHF systems for enhancing MOST-relevant properties and calculated energy densities.²⁸ FvRu₂(CO)₄ systems undergo the cleavage and reformation of Ru–Ru and C–Ru bonds upon light irradiation, storing the photon energy in the metastable *anti* conformer which can be thermally reversed or catalyzed to release energy.^{6,29} Various solution-state studies have characterized the optical and thermal properties of FvRu₂(CO)₄ systems.^{7,8,30–34} NBD undergoes a photoinduced [2+2] cycloaddition to convert into its valence isomer QC.^{35–37} The strained QC molecules store a significant amount of energy up to 0.97 MJ kg^{−1} which can be released in the form of heat upon thermal activation or catalysis of QC-to-NBD reversion.³⁸ Both highly concentrated solutions and neat liquid phase of materials have been reported to show facile switching and heat release.^{13,39–41} Azobenzene derivatives exhibit reversible photo-isomerization between ground-state *trans* and metastable *cis* forms. Pristine azobenzene and many of its derivatives absorb in the UV range ($h\nu_1$) to promote *trans*-to-*cis* isomerization, and the reverse isomerization is generally triggered by visible light ($h\nu_2$) for releasing the energy.^{12,42} However, recent studies have successfully demonstrated the separation of the n- π^* absorption bands between *trans* and *cis* isomers in the visible light range, enabled by the covalent functionalization of the *ortho* positions of the photochrome, thus achieving a complete cycle of energy storage and release in the absence of UV sources.^{43,44} The energy storage in azobenzene and azoheteroarene systems has been successfully tested in solutions, neat liquid phase, and solid phase. Moreover, the isomerization-induced phase transition between solid (*trans*) and liquid (*cis*) phases has emerged as a novel strategy for enhancing the energy storage in materials, resulting from the phase transition enthalpy contributing to the total energy density in addition to the isomerization energy.¹²

In order to develop an ideal MOST system, the research community has pursued diverse approaches of fulfilling the following criteria:^{45,46} high quantum yields of isomerization, high photostationary state (PSS) ratios between ground-state and metastable-state isomers, significant overlap between

absorption spectra of photochromes and the solar spectrum, spectral separation between two isomers, high thermal stability of the metastable isomers (*i.e.* a long thermal half-life, $t_{1/2}$), *etc.* These optical and thermal parameters will be discussed along with the structural designs that enable the conformational change of molecules in each phase, particularly in condensed phases where the intermolecular interaction and steric hindrance play a significant role. Also, the molecular weight of a MOST system is an important factor that determines the gravimetric energy density (MJ kg^{−1}) of the system, which is defined as the total energy stored in the unit mass of the materials. Thus, the relative mass ratio between photoactive moieties (energy storage units) and photo-inactive structures (no energy storage; contribution to the total weight) is one of the major metrics that are optimized for MOST compounds. Further discussions on the molecular weight and efficient templating strategy are illustrated in Section 4.

The molecular designs related to some of these features will be highlighted in the examples that are categorized into four groups according to the phases in which the photon energy storage is performed (solution, condensed liquid, and solid state) as well as the phase that transforms along with photo-switching (between solid and liquid). In addition, the design principles of MOST compounds, which result in a particular phase of materials (liquid, solid, or reversible transition between those), will be described in the respective sections.

2. Solution-state MOST compounds

Solution-state MOST systems are photoswitching compounds investigated in a respective solvent, as illustrated in Table 1, where the photoactivation of the ground-state isomer and the photon energy storage occur. The metastable-state isomer obtained in the photo-irradiated solution is generally condensed by solvent removal, and then its isomerization energy is evaluated by a calorimetric tool such as differential scanning calorimetry (DSC) which measures the exothermicity of the reverse isomerization process from the metastable to ground-state form. The solution-state compounds undergo a facile isomerization within the dilute condition in the absence of steric hindrance which otherwise influences the photoswitching process particularly in condensed phases.⁴⁷ The solution-state MOST materials, if highly concentrated, could be integrated into a flow system for solar energy storage and heat release for various applications.^{8,48–50}

The pristine norbornadiene/quadracyclane (NBD/QC) couple, which undergoes reversible σ bond formation and dissociation, has a remarkable potential to store up to 0.97 MJ kg^{−1}, the highest gravimetric energy density experimentally measured so far for MOST systems. The pristine NBD, however, absorbs wavelengths below 250 nm in solution, which is a small fraction of the solar spectrum at sea level.³⁸ In order to utilize a wider range of the solar spectrum, Moth-Poulsen and co-workers developed NBD derivatives covalently functionalized with cyano and aromatic groups, which forms a push–pull

Table 1 Solution-state properties of MOST materials

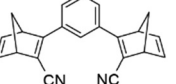
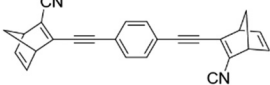
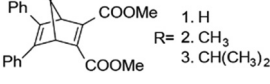
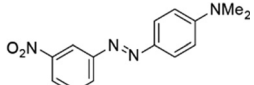
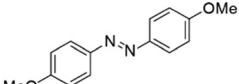
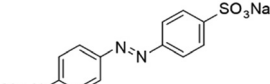
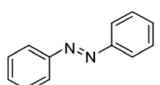
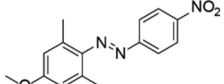
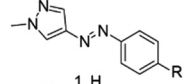
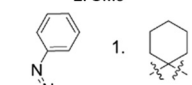
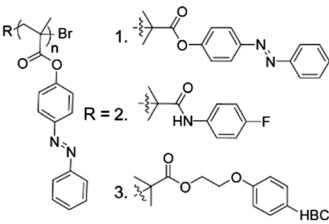
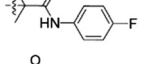
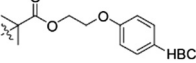
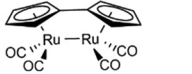
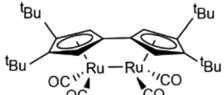
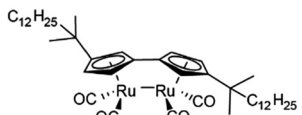
Chemical structure	MW (g mol ⁻¹)	Solvent	λ_{max} (nm)	$\Delta H_{\text{storage}}$ (kJ mol ⁻¹)	$\Delta H_{\text{storage}}$ (kJ mol ⁻¹)	$t_{1/2}$ 298 K	Ref.
	92	Benzene or isopentane	< 250	89	0.97	> 14 h (413 K)	38 and 45
	193 260	DCM DCM	309 398	122 103	0.63 0.40	55 d 5.0 h	39
	308	CDCl ₃	308	86 ^a	0.56	49 d (QC-QC)	40
	356	CDCl ₃	359	92 ^a	0.51	4.3 h (QC-QC)	
	244	Toluene	308	86	0.35	43 d	13
	360 388 445	Toluene Toluene Toluene	240 ~ 242 ~ 245	85 68 46	0.24 0.18 0.10	6.3 h 7.7 h 2.3 d	51
	270	Toluene	428	98	0.36	0.2 h	
	242	Toluene	358	80	0.38	9.6 h	
	327	Acetone	420	94	0.29	9.6 h	52
	182	<i>n</i> -Heptane	317	49	0.27	4.2 d	
	285	Acetone	377	30	0.10	1.9 h	
	186 216	Water Water	328 347	38 38	0.21 0.18	3.8 y 47 d	57
	444 430 404 458	DCM DCM DCM DCM	~ 325 ~ 325 ~ 325 ~ 325	55 ^a 49 ^a 44 ^a 45 ^a	0.25 0.23 0.22 0.20	— — 2.4 h (323 K) —	58

Table 1 (continued)

Chemical structure	MW (g mol ⁻¹)	Solvent	$\lambda_{\max}$ (nm)	$\Delta H_{\text{storage}}$ (kJ mol ⁻¹)	$\Delta H_{\text{storage}}$ (kJ mol ⁻¹)	$t_{1/2}$ 298 K	Ref.
  	266 ^b 266 ^b 266 ^b	THF THF THF	320 — —	186 ^a 168 ^a 121 ^a	0.70 0.63 0.46	3.1 d — —	59
	442	THF	~400	83	0.19	—	6
	668	THF	~350	88	0.13	—	7
	863	Toluene or THF	333	99	0.11	—	8

^a Per unit energy density. ^b Repeating unit MW, HBC: hexa-*peri*-hexabenzocoronene, —: unreported.

conjugated system and leads to a significantly red-shifted light absorption compared to that of pristine NBD.³⁹ Among diverse electron-withdrawing groups, a cyano group was selected due to its low molecular weight which doesn't compromise the gravimetric energy storage density of the MOST system. On the side of the aromatic functional group, an ethynyl linker was introduced to further extend the conjugated system and red-shift the absorption wavelength to 398 nm. Despite the favorable optical property gained and the high isomerization energy ($\Delta H_{\text{storage}}$ per molecule) obtained from the functionalization, the gravimetric energy densities ($\Delta H_{\text{storage}}$ per weight) of the functionalized compounds were decreased due to the increased molecular weight, particularly from the incorporation of aromatic functional groups.

In the pursuit of resolving this issue, a strategy of coupling one aromatic group to multiple NBDs was developed.⁴⁰ This reduces the weight contribution of the shared donor (*i.e.* an aryl or ethynyl-aryl group) to the molecular weight per NBD unit. The electronically-coupled photoswitches exhibited similar thermal reversion barriers for QC–QC and QC–NBD isomeric states. The isomerization energy per photoswitch of either dimer was similar to that of the pristine NBD/QC couple, while the larger molecular weight of the extended structure contributed to lowering the gravimetric energy density of the dimeric form. Another molecular design which contains two phenyl substituents on the NBD unit also exhibited a similar level of red-shifted absorption and $\Delta H_{\text{storage}}$ per molecule, while the substantial weight of two aryl groups significantly reduced the gravimetric energy density of NBD.¹³

An interesting study investigated the impact of steric pressure within the photoswitch structure imposed by a varied substituent R (H, Me, and *i*-Pr) on the light absorption of

NBD and thermal stability of QC.⁵¹ The increased steric bulk would push the C=C bonds closer to each other, causing a slight red-shift of the absorption, reflected by both $\lambda_{\max}$ (240, 242, and 245 nm) and λ_{onset} (391, 403, and 414 nm) of the derivatives in the order of increasing level of steric pressure. The longer half-life of a more sterically hindered compound was attributed to the larger steric repulsion in the NBD isomer than in the QC for such a compound, and the *i*-Pr NBD derivative was tested in a flow device for effective photoisomerization to its QC isomer (Fig. 2a).

The isomerization of azobenzene derivatives and the associated energy change were first studied by Yee and coworkers in 1983 using photometric calorimetry.⁵² Various structures with electron donating and withdrawing substituents on the azobenzene scaffold were synthesized, demonstrating the red-shift of the π – π^* absorption band from $\lambda_{\max}$ of 317 nm (pristine azobenzene) up to 428 nm. The substituted structures exhibited

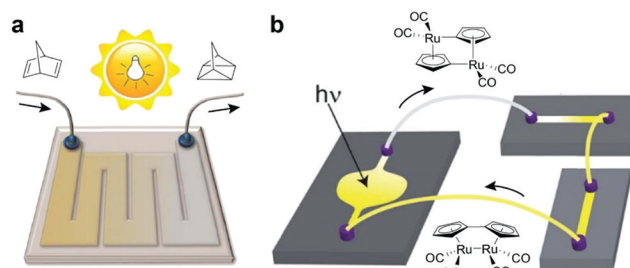


Fig. 2 A schematic illustration of flow systems developed for solution-state photon energy storage with (a) NBD/QC and (b) FvRu₂(CO)₄. Reproduced and adapted from ref. 8 and 51 with permission from The Royal Society of Chemistry.

a similar or greater energy storage density compared to pristine azobenzene, except for the *ortho*-dimethyl substituted structure, which has a low quantum yield of *E*–*Z* isomerization and results in a lower ΔH . Overall, the substituents contributed to decreasing the thermal half-life of the *cis* isomers by reducing the π electron density on the azo group through electron delocalization.

The substitution of a phenyl group by a heteroaryl ring was revealed to increase the PSS ratio between *trans* and *cis* isomers under photo-irradiation.^{53–55} For pristine azobenzene, there is a considerable overlap between the absorption of *trans* and *cis* isomers, leading to a suboptimal PSS for either *trans*-to-*cis* or *cis*-to-*trans* conversion processes (around 90%).⁵⁶ An arylazopyrazole photochrome, on the other hand, displays widely separated λ_{max} of *trans* (328 nm) and *cis* (275 nm), and its *para*-methoxy derivative also shows the parted λ_{max} of *trans* (347 nm) and *cis* (281 nm). This spectral separation between photoisomers leads to nearly quantitative photo-isomerization in both directions (greater than 98%). In addition, the half-lives of *cis* isomers were greatly prolonged to months and years, compared to those of azobenzene derivatives that span from hours to days. The remarkable thermal stability of *cis* arylazopyrazole isomers was attributed to the intramolecular C–H $\cdots \pi$ interaction between the orthogonal pyrazole C–H group and phenyl ring in the T-shaped *cis* conformation, which increases the reversion energy barrier. Furthermore, the methoxy-substituted arylazopyrazole exhibits photoswitching in aqueous solutions due to the increased polarity, which enables the potential application of thermal energy storage in a non-volatile and environmentally-friendly medium.⁵⁷

The impact of London dispersion force on the isomerization energy was studied by Wegner and coworkers, through the substitution of the bridging group between two azobenzene units.⁵⁸ Large cycloalkyl substituents were probed to increase the degree of London dispersion among *trans* isomers, which contributed to raising the ΔH per azobenzene unit as well as the gravimetric energy density of the MOST system.

Polymeric structures based on a poly(methacrylate) backbone and azobenzene side groups were also developed to explore the correlation between steric effect and energy storage of MOST systems.⁵⁹ The poly(methacrylate) displays a high syndiotacticity from radical polymerization, bearing *syn* ester side groups spaced apart by 5 Å. The favorable steric effect that increases the energy level of *cis* compared to *trans* state effectively enhanced the energy density of polymer (0.7 MJ kg^{−1}) by 3.8 times per azobenzene unit and 2.6 times per weight relative to the pristine azobenzene. The incorporation of a large end group, such as hexa-*peri*-hexabenzocoronene (HBC), was designed to facilitate the self-assembly of the polymer into cylindrical structures to further enhance the steric effect. However, the presence of photo-inactive end groups resulted in the significant reduction of gravimetric energy density as well as the isomerization energy per azobenzene unit.

FvRu₂(CO)₄ was particularly studied for the application in flow systems (Fig. 2b). Vollhardt and coworkers designed the alkyl-functionalized compounds to increase the solubility of

FvRu₂(CO)₄: 22 g L^{−1} for pristine compound, 276 g L^{−1} with *t*-Bu substitution, and 400 g L^{−1} with dodecyl chains demonstrated in THF.⁸ Despite the successful design strategy for solubility enhancement, the large substituents compromised the gravimetric energy density of the system, as also shown in NBD/QC and azobenzene counterparts.

3. Condensed liquid-state MOST compounds

The removal of solvent molecules that do not participate in the photo-isomerization process would greatly enhance the energy storage density of the MOST system. Therefore, building upon the fundamental characterization of the optical and thermal properties of MOST compounds conducted in solution, the development of neat liquid phase MOST compounds has been pursued *via* structural designs that allow the compounds to exhibit melting points similar to or lower than room temperature. Generally, the liquid phase of MOST compounds can be achieved by reducing the stacking of aromatic units in photochromic cores, particularly for planar molecules such as *trans* azoarenes. A prominent strategy is to install a branched alkyl or branched ethylene glycol chain to one of the aromatic rings to generate asymmetric structures where the flexible and bulky chains hinder the facile stacking between adjacent aromatic cores (Fig. 3).^{60–62} Non-branched linear alkyl chains with a limited degree of freedom are prone to generate crystalline MOST compounds, which will be further illustrated in section 5, due to the planarity of alkyl-linked aromatic molecules and the well-ordered stacking among the alkyl chains as well as between aromatic cores.^{14,63–65} Therefore, it is essential to weaken both the π – π interaction and London dispersion force among the neighboring molecules to produce a stable liquid phase with a low melting point. For intrinsically non-planar photochromes, such as NBD, the presence of the flexible branched chain is less crucial, yet desirable for generating liquid phase.

While pristine NBD is a liquid, most of the derivatives with red-shifted light absorption are solids at room temperature, and their photoswitching properties have been primarily characterized in dilute solutions. The photoswitching of a few NBD derivatives has been performed in a neat liquid phase, as illustrated in Table 2.⁴¹ The molecular designs build upon

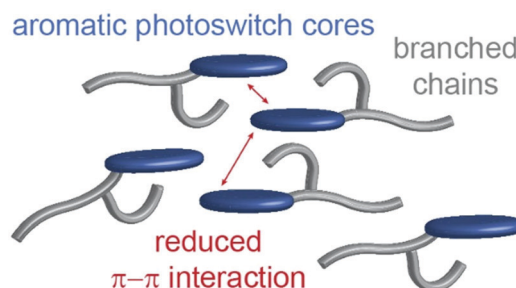
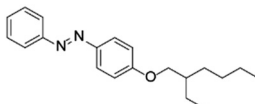
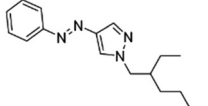
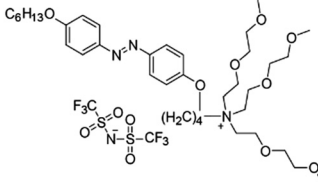


Fig. 3 A schematic illustration of a liquid-phase MOST compound design.

Table 2 Liquid-state properties of MOST materials

Chemical structure	MW (g mol ⁻¹)	λ_{max} (nm)	$\Delta H_{\text{storage}}$ (kJ mol ⁻¹)	$\Delta H_{\text{storage}}$ (MJ kg ⁻¹)	$t_{1/2}$ 298 K	Ref.
1. 						
2. 	264	323	152	0.58	3.0 d	41
3. 	290	342	103	0.35	5.3 d	41
4. 	292	323	49	0.17	3.5 d	41
5. 	318	326	48	0.15	2.0 d	41
	310	344	52	0.17	16 h	62
	284	328	41	0.14	128 d	60
	957	356	52	0.05	—	61

—: unreported.

the principles studied in the solution state, incorporating a push–pull structure across a C=C bond and a series of alkyl or cycloalkyl substituents on the NBD bridge, in order to red-shift the absorption spectrum and to improve thermal stability of QC isomers. Surprisingly, the half-lives measured in solution (2–5 days) were shortened to 2–205 min under neat liquid conditions, due to the internal thermal triggering of QC-to-NBD reversion and cascading isomerization in the condensed environment.

To achieve a liquid phase of azobenzene and arylazopyrazole at room temperature, the covalent attachment of a branched 2-ethylhexyl group was performed on phenyl and pyrazole rings.^{60,62} Such a branched alkyl chain in a racemic form drastically weakened the intermolecular interactions among the photochromic molecules, lowering their melting point for both *trans* and *cis* isomers and allowing for their facile isomerization in the liquid phase (Fig. 4). The 2-ethylhexyl group was also selected for its low molecular weight compared to longer

alkyl or ethyleneglycol chains.⁶⁰ The incorporation of these heavier groups was demonstrated in the structure of ammonium-based ionic compound, resulting in lowering its crystallinity due to the flexibility and bulkiness of functional groups which weakened the π – π stacking and Madelung energy of the structure. The counter anion Tf_2N^- , which exhibits the delocalized anionic charge, was selected to lower the electrostatic interactions. The resulting ionic liquid showed a similar level of ΔH per azobenzene unit despite a much lower gravimetric energy density attributed to the incorporated heavy substituents.⁶¹

4. Solid-state MOST compounds

The design of solid-state MOST compounds has been achieved by incorporating photoswitches onto several solid scaffolds (Table 3), such as nanocarbon materials (*i.e.* reduced graphene oxide, rGO, or carbon-nanotubes, CNTs),^{66–73} polymers,^{74–77} and metal organic frameworks (MOFs).⁷⁸ These extended 1D, 2D, and 3D templates allow the MOST compounds to maintain a solid phase, either as films, powders, or suspended solids, and enable the photoswitches to undergo isomerization while attached on the extended scaffold (Fig. 5). The templating strategy results in an array of orderly packed photochromes that experience significant intermolecular interactions, which often leads to the suppressed isomerization of photoswitches. Therefore, it is crucial to create a templated structure that allows for a facile conformational change of photoswitches by

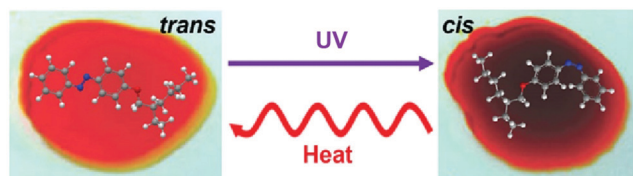


Fig. 4 Neat liquid state, reversible photo-isomerization of 2-ethylhexyl-substituted azobenzene. Reproduced and adapted from ref. 62 with permission from The Royal Society of Chemistry.

Table 3 Solid-state properties of MOST materials

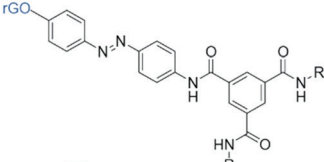
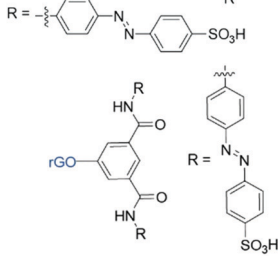
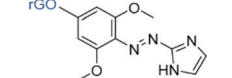
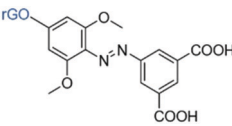
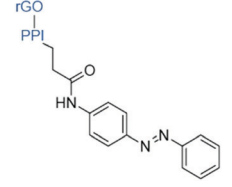
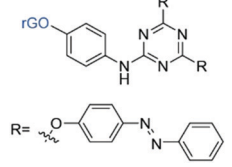
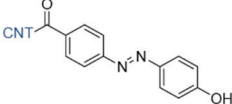
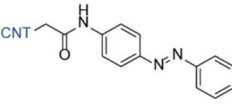
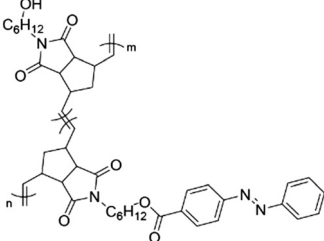
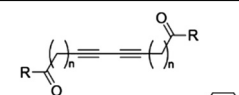
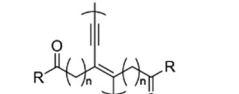
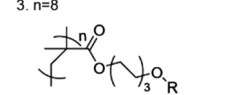
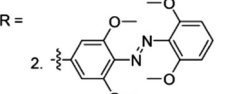
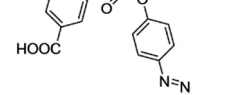
Chemical structure	Per unit MW (g mol ⁻¹)	λ_{max} (nm)	$\Delta H_{\text{storage}}$ (kJ mol ⁻¹)	$\Delta H_{\text{storage}}$ (MJ kg ⁻¹)	State (F/S/P)	$t_{1/2}$ 298 K	Ref.
	~ 573	380	224 310	0.39 0.54	F (20–30 μm) S (MeCN)	52 d	66
	~ 618	374	216 290	0.35 0.47	F (15–35 μm) S (MeCN)	— 37 d	67
	~ 507	410	193	0.38	F (100 μm)	12 d	68
	~ 533	391	266	0.50	S (MeCN)	52 d	69
	~ 251	360	94	0.37	S (DCM)	80 h	70
	~ 582	338	168	0.29	S (DMF)	55 d	71
	~ 598	354	132 173	0.22 0.29	F (~ 30 μm) S (EtOH)	— 16 h	72
	~ 457	350	91	0.20	S (MeCN)	33 h	73
	763	320	137	0.18	F (100 μm)	0.25 h	77

Table 3 (continued)

Chemical structure	Per unit MW (g mol ⁻¹)	λ_{max} (nm)	$\Delta H_{\text{storage}}$ (kJ mol ⁻¹)	$\Delta H_{\text{storage}}$ (MJ kg ⁻¹)	State (F/S/P)	$t_{1/2}$ 298 K	Ref.
 1. $n=3$ R = 2. $n=5$ 3. $n=8$	290 318 360	360 360 360	61 73 80	0.21 0.23 0.22	S (DCM)	— — 28 h	76
 1. $n=3$ R = 2. $n=5$ 3. $n=8$	290 318 360	~360 ~360 ~360	45 51 59	0.15 0.16 0.16	S (DCM)	— — —	76
 1. $n=3$ R = 2. $n=5$ 3. $n=8$	~380 ~486	351 323	48 8	0.12 0.02	F (35 nm) F (20 nm)	12 h 16 h	74
 1. $n=3$ R = 2. $n=5$ 3. $n=8$	~296	325	27	0.09	F (~250 nm)	75 h	75
 1. $n=3$ R = 2. $n=5$ 3. $n=8$	575 799 879	347 350 350	77 87 88	0.13 0.11 0.10	F (400–600 h)	—	81
$\text{Zn}_2(\text{BDC})_2(\text{DABCO})(\text{AB})_1$	761	441	22	0.029	P	4.5 y	78

rGO: reduced graphene oxide, CNT: carbon nanotube, PPI: poly(propylene imine) dendrimer, F: film, S: suspension, P: powder, —: unreported, BDC: 1,4-benzenedicarboxylate, DABCO: 1,4-diazabicyclo[2.2.2]octane, AB: azobenzene.

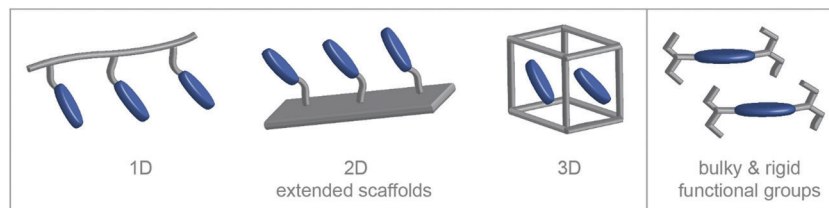


Fig. 5 A schematic illustration of a solid-phase MOST material design.

providing conformational freedom that is carefully designed and implemented. This has been accomplished by fine-tuning the grafting density of azobenzene units on the scaffolds.

However, lowering the grafting density has implications, notably a lowered gravimetric energy density of the MOST system. Polymeric backbones and carbon templates do not

participate in the photon energy storage, while significantly contributing to the overall mass of the material systems. This leads to the development of strategies that optimize the loading density of photoactive species on the polymer or carbon templates, which still enables the unhindered photo-switching, induces favorable intermolecular interactions among the photoswitch side groups, and mitigates the suboptimal gravimetric energy density lowered by the inclusion of large templates. It is indeed a challenging quest to achieve a solid-state MOST system that exhibits a large isomerization energy, a long half-life of *cis* isomer, and a high PSS ratio under illumination. Nevertheless, many rGO or CNT-based MOST systems have been developed with an optimized grafting density and reported to store up to 0.54 MJ kg^{-1} level of energy density.⁶⁶ Moreover, the impact of the chromophore size and the presence of intermolecular H-bonds on the half-life of *cis* isomers has been investigated.

In the absence of extended 1D, 2D, and 3D templates, it requires a different strategy to fine-tune the spatial separation between the photoswitches in a condensed solid, since small aromatic molecules are prone to crystallize, limiting the conformational freedom of switches. In order to accomplish a MOST system based on small molecules operating in solid form, the formation of an amorphous phase is essential, enabled by the covalent functionalization of photoswitches with bulky and rigid substituents (Fig. 5). This strategy will be further discussed later in this section.

Feng and coworkers demonstrated the templated photochrome assembly on rGO with various sizes of photochromic moieties.⁶⁶ The largest group contains three azobenzene units linked to a central 1,3,5-benzenetricarboxamide, and such a bulky structure was grafted onto rGO at a density of 1:68 (one group per 68 carbons) to achieve the highest energy density. It showed over 70% isomerization at PSS in a suspended solid state, a high energy density (0.54 MJ kg^{-1}), and a long half-life of *cis* isomer (52 days). The facile isomerization in the suspended solid state is attributed to the sufficient free volume around each photochrome, supported by the decreased PSS ratio for a higher density sample at a 1:60 grafting ratio. The functionalized rGO MOST materials were deposited on substrates as thin films and irradiated with UV, which led to a lower degree of isomerization compared to the suspension state

due to the increased steric hindrance in solid materials without solvation. Another functional group with two azobenzene units linked to a 1,3-benzene dicarboxamide moiety was functionalized onto rGO, which exhibited a reduced energy density than the larger trimer counterpart.⁶⁷ The lower grafting density and the less steric interaction among the photoswitches resulted in the suboptimal energy density as well as a shorter half-life of *cis* isomers. The UV-irradiated films were monitored by IR thermography during the thermally-activated reverse isomerization and the heat release. Compared to the identical film without UV irradiation, the *cis*-rich sample exhibited $\sim 14^\circ\text{C}$ higher temperature, demonstrating the significant heat release from the isomerization (Fig. 6).

In pursuit of lowering the *cis*-to-*trans* reverse isomerization energy barrier that requires high temperature triggering conditions (over 100°C for thermal reversion), prevalent in rGO-templated MOST compounds, a push-pull azoheteroarene with an imidazole ring was synthesized.⁶⁸ This design significantly reduces the half-life of the *cis* isomer to 12 days, due to the electron transfer from the methoxy groups to the imidazole ring, which decreases the bond order of $\text{N}=\text{N}$ and facilitates the molecular rotation. Similar rGO-templated azobenzene units with methoxy and carboxylic acid functional groups, on the other hand, exhibited a much longer half-life (52 days) caused by the intermolecular H-bonds among the neighboring COOH groups.^{68,69}

rGOs grafted with three-layer dendritic hyperbranched poly(propylene imine) containing azobenzene units were also developed to increase the loading density of photoactive species in the MOST system.⁷⁰ The energy density of 0.37 MJ kg^{-1} was achieved due to the increased intermolecular interactions among azobenzene units. Similarly, rGOs grafted with 1,3,5-triazine branches functionalized two azobenzene units were developed to increase the loading density of photoswitches. Due to the high grafting density and bundling effect, the *cis* isomers are greatly stabilized, displaying a long half-life of 55 days.⁷¹

A push-pull structured azobenzene was also grafted on CNTs,⁷² exhibiting an appreciable energy density and cyclability, with a shortened half-life of *cis* isomer compared to the pristine azobenzene on CNT structures.⁷³ The steric strain generated by the CNT-templated structure provides a high

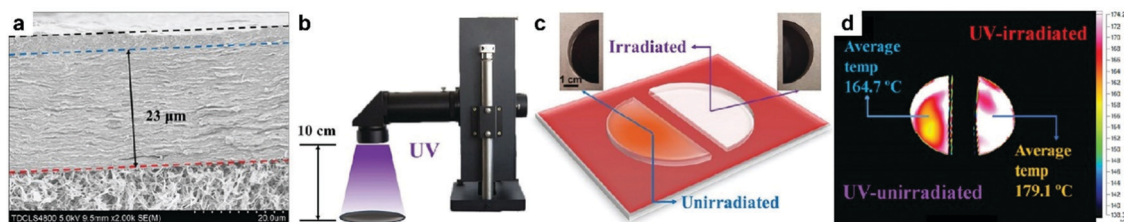


Fig. 6 (a) A cross-sectional SEM image of a film made of rGO-templated bisazobenzenes, (b) a schematic illustration of the UV irradiation setup, (c) irradiated and unirradiated samples, (d) comparative IR thermographs of macroscopic heat release from the irradiated and unirradiated samples upon thermal triggering. Permission is granted subject to an appropriate acknowledgement given to X. Zhao *et al.*, controlling heat release from a close-packed bisazobenzene-reduced-graphene-oxide assembly film for high-energy solid-state photothermal fuels, Wiley. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

degree of intermolecular interactions between the azobenzene units, effectively increasing the ΔH per azobenzene. However, due to the large template structure, the gravimetric energy density remained in the range of 0.2–0.3 MJ kg⁻¹. In thin film experiments, the *cis*-rich and *trans*-rich samples showed a temperature difference of 10 °C upon thermal triggering.

Polymer structures bearing photoswitch side groups are widely used to generate solid-state MOST systems. Compared to the nanocarbon scaffold, polymer backbones are more flexible, causing a lower degree of template-enforced steric interaction and more facile isomerization in the solid state. In addition, non-conjugated polymer backbones do not strongly absorb visible light, as opposed to CNTs and rGO, which generally increases the isomerization ratio at PSS. A poly(norbornene) containing azobenzene side chains, for example, achieves a fair degree of *trans*-to-*cis* isomerization (72%) at PSS.⁷⁷ The flexible polymeric MOST materials were stretched to generate more free volume, leading to a higher PSS ratio (85%), a high ΔH per azobenzene unit (137 kJ mol⁻¹), and more rapid *cis*-to-*trans* reverse isomerization under visible light irradiation (T_{max} reached in ~ 10 min) compared to the unstretched films. The thermal half-life of the polymer measured in the dark is 0.25 h at room temperature, which is much shorter than the half-lives of other solid-state MOST materials.

Symmetric diacetylenes decorated with azobenzene side groups and their photo-polymerized forms are crystalline solids that are insoluble in common organic solvents except for DMF, due to the strong intermolecular interactions including H-bonds through amide linkages and π - π interactions between azobenzene groups.⁷⁶ The solids suspended in organic solvents undergo photo-switching and simultaneous dissolution into solvents, following the generation of polar *cis* isomers with weakened intermolecular interactions. A much higher

gravimetric energy density was achieved with diacetylene-based MOST, compared to the poly(norbornene) counterpart,⁷⁷ due to the compact template structure and the high loading of photochromes in the materials. The polydiacetylenes obtained by the UV-induced topochemical polymerization of diacetylenes exhibit reduced energy densities compared to the monomers, due to the restricted conformational change of azobenzene units anchored in the rigid polymer backbones. It is notable that the role of H-bonding moiety, the amide linkage, is essential in generating insoluble solids, corroborated by a control experiment where the replacement of the amide group by an ester linkage drastically increased the solubility of diacetylene and polydiacetylene MOST materials.

Poly(methyl methacrylate) structures decorated with azobenzene (PAzo) and *ortho*-methoxy functionalized azobenzene side chains (PmAzo) were developed by Wu and coworkers to achieve a stacked device structure which harvests a large fraction of the solar spectrum.^{74,79,80} Equipped with a blue-to-yellow down-converter filter as a top layer, which suppresses the unwanted *cis*-to-*trans* reversion, the underlying layer of PmAzo effectively stores photon energy in the visible light range. Another layer of UV pass filter allows the selective passage of UV photons to the bottom layer of the polymer with unfunctionalized azobenzene side chains for energy storage. A considerable PSS ratio in the solid state was achieved for PmAzo (73%) comparable to that of solution-state photoswitching (72%), despite the decreased PSS ratio of PAzo in solid (24%) compared to that of a solution state (65%).

The challenge of depositing uniform films of MOST materials and controlling film thickness was addressed by the design of an ionic copolymer based on a poly(methyl methacrylate) backbone and side groups of azobenzene and benzoic acid (Fig. 7a).⁷⁵ This allows for the electrodeposition of a

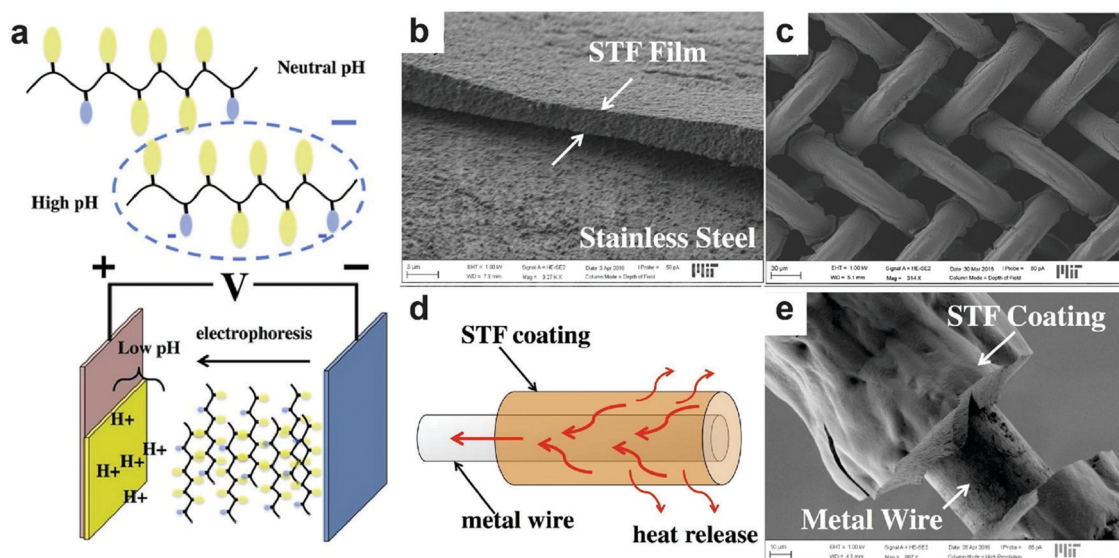


Fig. 7 (a) A schematic illustration of the electrodeposition of a copolymer with azobenzene and benzoic acid side groups. (b) A cross-sectional SEM image of an electrodeposited MOST (*i.e.* STF) film on a stainless steel substrate. (c) SEM image of 25 μm mesh coated with the MOST polymer. (d) Concept of the stored heat released into a metal wire. (e) SEM image of an electrodeposited film atop a 50 μm fiber. Reproduced and adapted with permission from ref. 75. Copyright 2016 American Chemical Society.

deprotonated polymer on conductive substrates, such as metal plates and wire meshes (Fig. 7b and c). The coated substrates enable the facile heat transfer from the MOST films to metallic components (Fig. 7d and e). Under thin-film conditions, 43% of the PSS ratio was achieved through direct irradiation on solid-state materials.

In the absence of nanocarbon or polymeric scaffolds, small molecules based on an azobenzene moiety tend to crystallize due to the strong aromatic stacking interactions. The functionalization of pristine azobenzene with bulky substituents was demonstrated to effectively prevent the crystal packing and form an amorphous solid state of photoswitching materials.¹² A *meta* position of each phenyl group was functionalized with bulky aromatic substituents and an *ortho* position was methyl-functionalized.⁸¹ The molecules were able to reversibly photo-switch in thin films upon the exposure to photo-irradiations, exhibiting a high PSS *cis* ratio of 60% for compound 1, 80% for compound 2, and 74% for compound 3, as a result of increased free volume around the photochromes. In addition to the role of being spacer moieties, the bulky functional groups increased the isomerization energy, ΔH per azobenzene unit, by imposing a large intramolecular steric repulsion in a *cis* form, which raises the energy level of *cis* isomer and increases the energy difference between the *trans* and *cis* states. The ΔH per azobenzene unit increases with larger substituents (phenyl < ^tBu phenyl < biphenyl), while the gravimetric energy density decreases due to the high molecular weight of the larger molecules.

Metal-organic frameworks (MOFs) have been investigated as a porous medium that can incorporate various photoswitches as guest molecules, side groups, or a part of the framework backbones, primarily to create photo-responsive sensing materials, optoelectronics, and erasable inks.^{82–87} A recent report from Griffin and coworkers illustrated a solid-state MOST based on a MOF scaffold with a chemical formula of $\text{Zn}_2(\text{BDC})_2(\text{DABCO})(\text{AB})_x$ where x denotes an average number of azobenzene loaded per unit cell.⁷⁸ Upon UV irradiation, 40% of the azobenzene guest was switched to *cis* conformation, and 21 kJ mol^{−1} of thermal energy is calculated to be released by the triggered *cis*-to-*trans* isomerization process ($x = 1$). An extremely long half-life (4.5 years) of azobenzene *cis* isomer was obtained in the confined environment, which is unique for a pristine azobenzene structure.

5. Phase transition MOST compounds

A recently developed strategy for increasing the energy storage in MOST systems involves a design of photoswitches that undergo phase transitions during the structural isomerization. All of the reported examples thus far incorporate azobenzene or azoheteroarene structures, which display a solid phase in the ground state (*trans*) and liquid phase in the metastable state (*cis*) due to the increased polarity and sterics of the twisted *cis* isomeric form. In order to achieve a distinct phase for each isomeric form, a significant structural change should occur

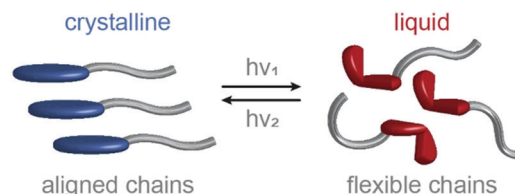


Fig. 8 A schematic illustration of a phase-transition MOST compound design.

during photo-isomerization that induces crystalline packing in one isomer and disrupts the packing in the other isomeric form. This requires the incorporation of a flexible, yet crystallizable, functional group to an aromatic photoswitch system and has been primarily achieved with long alkyl functionality attached to an azoarene core (Fig. 8). Long alkyl chains crystallize at low temperatures due to the London dispersion force, which scales with the length of the chain, and melt at increased temperatures to gain flexibility and interact with non-planar aromatic cores.^{14,63–65} Other functional groups that display

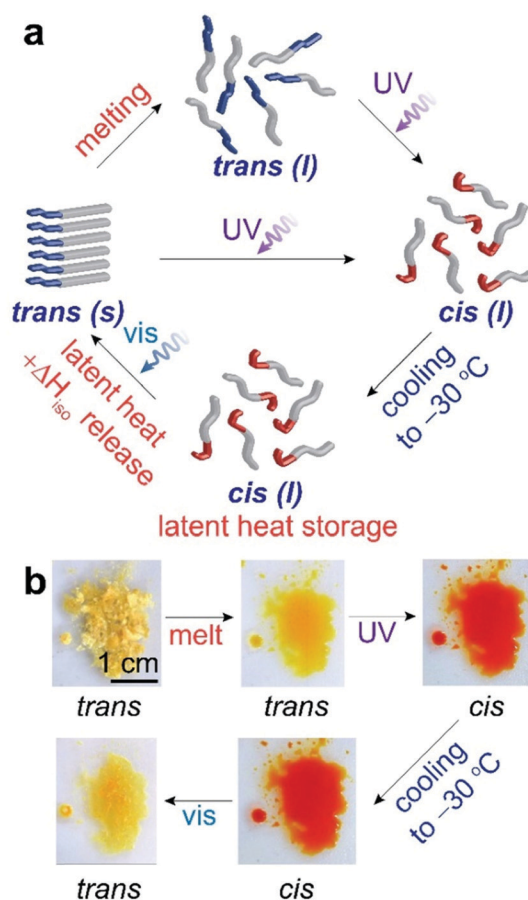
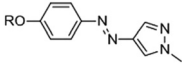
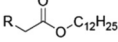
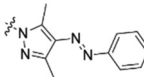
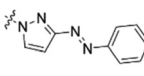
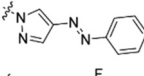
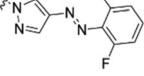
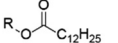
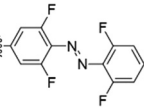
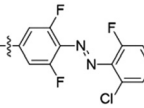
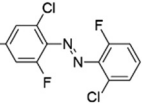
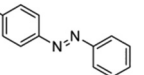
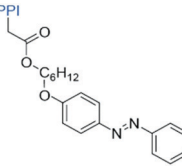
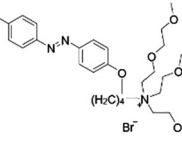


Fig. 9 (a) A schematic illustration of latent heat and photon energy absorption by a phase change MOST, the energy storage in the liquid phase, and the triggered release. (b) Series of optical images of a phase change MOST material that undergoes melting, UV irradiation, cooling, and visible-light-induced crystallization. Reproduced and adapted with permission from ref. 65. Copyright 2020 American Chemical Society.

Table 4 Thermal properties of phase transition MOST materials

Chemical structure	$T_m(\text{trans})$ (°C)	$T_m(\text{cis})$ (°C)	MW (g mol ⁻¹)	ΔH_{iso} (MJ kg ⁻¹)	ΔH_c (MJ kg ⁻¹)	ΔH_{total} (MJ kg ⁻¹)	ΔH_{total} (kJ mol ⁻¹)	$t_{1/2}$ 298 K	Ref.
	93 82	27 25	286 284	0.18 0.19	0.15 0.14	0.33 0.33	94 94		
R =  1. m=6									
2. n=6	83	35	298	0.18	0.16	0.34	101		
3. n=7	83	19	312	0.17	0.16	0.33	103	~90 d	14
4. n=8	88	28	340	0.16	0.18	0.34	116		
5. n=10	92	37	354	0.16	0.20	0.36	127		
6. n=11									
									
1. 									
2. 	67 91	Liq 53	427 398	0.11 0.11	0.08 0.12	0.19 0.23	82 92	—	65
3. 	71 61	Liq Liq	398 434	0.10 0.07	0.12 0.10	0.22 0.17	88 76		
4. 									
									
1. 	45	−36	466	0.05	0.10	0.15	70	2.0 y	
2. 	56	−42	483	0.05	0.90	0.14	66	258 d	
3. 	78	Liq	499	0.05	0.07	0.12	62	322 d	63
	81 84	31 40	380 409	0.13 0.12	0.04 0.08	0.17 0.20	65 81	—	64
R = 1. -OC ₁₃ H ₂₇ 2. -OC ₁₅ H ₃₁									
	65	—	713	0.18	0.03	0.21	151	32 h	88
	87	Liq	756	0.07	0.07	0.14	97	—	61

PPI: poly(propylene imine) dendrimer, —: unreported.

such characteristics are anticipated to produce phase transition MOST compounds.^{61,88}

A schematic of the energy storage and release process is shown in Fig. 9a, which involves the absorption of thermal and

photon energy by *trans* isomers in the process of generating a stable liquid state of *cis* isomers. The unique feature of the phase change MOST materials is that the crystallization energy is released concurrently with the release of isomerization energy during the triggered *cis*-to-*trans* reverse transformation. Therefore, the total energy storage density (ΔH_{total} in Table 4) is calculated as the sum of isomerization energy and the crystallization energy of a *trans* isomer. To maximize the total energy density, the molecular designs that increase the crystallinity of the *trans* isomer while maintaining the stable liquid phase of the *cis* isomer under varied temperature conditions were investigated.

Two phase-change MOST structures based on the arylazopyrazole with alkyl functional groups were recently reported by multiple research groups of Li, Moth-Poulsen, Fuchter, and Han.^{14,65} The alkyl group was functionalized on either the *para* position of the phenyl ring or on a nitrogen atom in the pyrazole group, and the length of the alkyl chain as well as other functional groups on the photochrome were varied to modulate the phase transition enthalpy and the melting point of *cis* isomers. The crystallization energy of *trans* isomers increases with the longer alkyl chains (with or without an alkene end group) attached on the phenyl ring, which contributes to enhancing the total energy storage density up to 0.36 MJ kg⁻¹. The series of compounds display much lowered melting points of *cis* isomers compared to *trans* counterparts, and one compound ($n = 8$) in particular showed a reversible photo-induced phase transition between solid (*trans*) and liquid (*cis*) at room temperature due to the low melting point of the *cis* isomer (19 °C).¹⁴ The other series of arylazopyrazole with the ester-linked alkyl chains on the pyrazole ring showed an extremely stable liquid phase of *cis* isomers (*i.e.* no melting or crystallization in the range of -50 to 90 °C; marked as 'Liq' in Table 4), as a result of the functionalization. These three compounds were demonstrated to store the liquid phase and the latent heat at temperatures much lower than 0 °C for a long-term storage up to a month, followed by the optically-triggered heat release at temperatures as low as -30 °C (Fig. 9b). This shows the potential of recycling waste heat and the triggered release of the stored latent heat at an extremely cold climate.

A recent report demonstrated the design of a series of phase-change MOST compounds that exhibit red-shifted $n-\pi^*$ absorption through the *ortho*-functionalization of an azobenzene moiety.⁶³ The fluorine, methoxy, and mixed halogen groups on the *ortho* positions of photochromes, appended to a tridecanoate group, enabled the solid-to-liquid transition of materials upon the exposure to low irradiance visible light, particularly sunlight through 530 nm, 590 nm, and 625 nm bandpass filters. Despite the lower gravimetric energy densities, which arise from the low ΔH_{iso} of *ortho*-functionalized azobenzenes, these new materials prove the concept of solar heat and photon dual energy storage in phase change materials, accomplished under ambient or greenhouse conditions in the absence of artificial UV light sources.

A similar design of azobenzene derivatives with an ether-linked long alkyl chain was shown to undergo photo-isomerization and

concomitant phase transition at room temperature, displaying a similar level of total energy density as the arylazopyrazole derivatives.⁶⁴ Poly(propylene imine)-based dendrimers functionalized with azobenzene terminal groups also exhibited a photo-induced solid-to-liquid phase transition which enabled the total energy storage of 0.21 MJ kg⁻¹.⁸⁸ An ammonium-based ionic derivative of azobenzene with a bromide counter anion showed an ionic crystalline phase as a *trans* isomer and its transition to ionic liquid phase upon UV irradiation.⁶¹ This shows the impact of the coulombic interaction between the azobenzene-linked cation and the anion on the phase of materials. The equivalent cationic compound with a larger anion with delocalized charge (Tf₂N, see Table 2) was shown to form a liquid phase even as a *trans* isomer, thus its photo-isomerization was performed in a neat liquid phase. The ionic crystal-liquid phase crossover led to storing a significant amount of thermal energy despite the large molecular weight of the structure.

All of the examples that we have illustrated here are single-component phase transition MOST materials, while there is another class of MOST composite materials that incorporate azobenzene derivatives as dopants in conventional phase change materials such as paraffins, fatty acids, and fatty alcohols. The photo-responsive dopant molecules reversibly control the phase transition of the composites, modulating the crystallization point of organic phase change materials and extending the latent heat storage time of their liquid phase. The photo-regulation of the supercooling of materials shows a unique way in which photo-switches are applied to control the thermal energy storage in another material through intermolecular interactions.⁸⁹⁻⁹¹

6. Conclusions and future directions

The remarkable discoveries of MOST systems operating in diverse phases open up the opportunities to apply a desired photoswitch system to an application that requires a specific phase of materials. The design principles were established for *trans*-*cis* isomers and ring-opening-closing photoswitches to result in the formation of liquid or solid phase, as well as the photo-induced phase transitions. In general, the incorporation of large scaffolds such as nanocarbon or polymeric backbone and bulky substituents leads to lower gravimetric energy densities despite the increased isomerization energy per each photoswitch unit. Nevertheless, such functionalization tools are essential for the generation of a particular phase that is desired for a flow system or film-based thermal energy storage applications, which require the absence of volatile organic solvents or photo-inactive components for maximizing the energy storage density. Other functional groups on photochromes were investigated to alter the optical properties, notably by red-shifting the absorption band from the UV to visible light range, and to modulate the thermal half-life of metastable isomers, which determines the energy storage time and the temperature at which the thermally-activated reversion occurs.

The experimental MOST investigations thus far focused on NBD/QC, azobenzene, and fulvalene dimetal complexes, and there is increasing attention on developing novel photoswitches that expand the scope of the current toolbox of MOST. For example, other photoswitch systems including donor-acceptor Stenhouse adducts,^{92–99} hydrazones,^{100–104} hemiindigos,^{105–107} and spiropyrans^{108–112} have shown outstanding success in applications such as sensing, liquid crystal modulation, photo-responsive actuation, and cargo delivery, building upon the thoroughly investigated optical properties in solutions and dispersions in a flexible medium.^{113–117} The thermal characteristics of these switches are less explored than conventional MOST compounds, partly due to the preliminary challenges including thermal decomposition or insufficient isomerization energy of some candidates. Despite the challenges, the application of strategies developed to overcome similar issues to pristine NBD or azobenzene, primarily the covalent functionalization of photochromes with electron donating, withdrawing, or bulky substituents, would potentially resolve the sub-optimal thermal characteristics of other switches with incredible potentials. In particular, the intrinsic absorption of light in the visible range as well as the negative photochromism of some photoswitches indicate great potential as MOST materials that harvest direct solar spectrum. Additionally, the experimental demonstration of energy storage in DHA/VHF systems is anticipated, based on their high isomerization energy theoretically calculated.

Moreover, various design strategies applied to solution-state MOST materials will be translated into neat liquid or solid phase systems, such as functionalization patterns that optimize the light absorption, isomerization kinetics, or the degree of London dispersion forces, in order to achieve devices with maximized solar spectrum harnessing, long-term energy storage, and gravimetric energy density in the absence of solvents. Small azobenzene derivatives bearing diverse electron donating or withdrawing groups, primarily studied in solutions for early research in the 1980s, are also expected to show interesting phase characteristics while maintaining a high level of gravimetric energy densities due to their relatively low molecular weights. Lastly, the integration of MOST systems into device structures will be considered when selecting a phase of MOST materials for applications. In a device that utilizes inorganic catalysts or electrochemical triggering methods, which assist the heat releasing process, the circulation of liquid phase or solution-state MOST compounds over immobilized catalysts or the electrode surface will be essential for charging and discharging a large volume of materials. Photoactive thin-film coatings on windows, windshields, or fabrics would require MOST materials that are insoluble in aqueous or common organic solvents while displaying a significant light penetration depth through the coating thickness. These specific requirements are currently explored to achieve practical MOST applications that will be complementary tools to conventional solar energy conversion technologies such as photovoltaics and solar fuel generations.

Conflicts of interest

There are no conflicts to declare.

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