

# Optically Triggered Synchronous Heat Release of Phase-Change Enthalpy and Photo-Thermal Energy in Phase-Change Materials at Low Temperatures

Hao Liu, Junwen Tang, Liqi Dong, Hui Wang, Tianyu Xu, Wenchao Gao, Fei Zhai, Yiyu Feng,\* and Wei Feng\*

Phase-change materials (PCMs) are used in several energy recycling utilization systems due to their latent-heat-storage and -release ability. However, the inability of PCMs to release heat at temperatures below their freezing point limits their application in distributed energy utilization systems. This paper reports optically-triggered low-temperature heat release in PCMs based on a solid-liquid phase change (PC) controlled by the trans-cis (E-Z) photoisomerization of azobenzene. To achieve this, a photo-responsive alkyl-grafted Azo is incorporated into tetradecane (Ted) to create a photosensitive energy barrier for the PC. The Azo/Ted composite exhibits controllable supercooling (4.04-8.80 °C) for heat storage and achieves synchronous heat release of PC enthalpy and photo-thermal energy. In addition, the Azo reduces the crystallization of Ted by intercalating into its molecular alignment. Furthermore, under light illumination, the Azo/Ted composite releases considerable heat (207.5 J  $g^{-1}$ ) at relatively low temperatures (-1.96 to -6.71 °C). The temperature of the annular device fabricated for energy utilization increases by 4 °C in a low-temperature environment (-5 °C). This study will pave the way for the design of advanced distributed energy systems that operate by controlling the energy storage/release of PCMs over a wide range of temperatures.

Dr. H. Liu, Dr. J. Tang, Dr. L. Dong, Dr. H. Wang, Dr. T. Xu, Dr. W. Gao, Dr. F. Zhai, Prof. Y. Feng, Prof. W. Feng School of Materials Science and Engineering and Tianjin Key Laboratory of Composite and Functional Materials Tianjin University Tianjin 300350, P. R. China E-mail: fengyiyu@tju.edu.cn; weifeng@tju.edu.cn Prof. Y. Feng, Prof. W. Feng Key Laboratory of Advanced Ceramics and Machining Technology Ministry of Education Tianjin 300350, P. R. China Prof. Y. Feng, Prof. W. Feng Tianjin Key Laboratory of Composite and Functional Materials Tianjin 300072, P. R. China Prof. Y. Feng Key Laboratory of Materials Processing and Mold Ministry of Education Zhengzhou University Zhengzhou 450002, P. R. China

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.202008496.

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## **1. Introduction**

Phase-change materials (PCMs) are regarded as potential candidates for energy storage systems due to their ability to absorb, store, and release a large amount of latent heat over a defined temperature range when they go through changes in their physical state.<sup>[1]</sup> Phase change (PC) of a PCM occurs when it reaches its specific PC temperature during heating or cooling, and is usually accompanied by heat absorption or release.<sup>[2]</sup> Generally, heat storage or release by PCMs depends on the PC temperature and enthalpy.<sup>[3]</sup> For example, the storage of latent energy by PCMs occurs above their freezing point, whereas heat is spontaneously released at temperatures lower than the freezing point.<sup>[4]</sup> Consequently, the inability to control heat release and the narrow PC temperature range limit the application of PCMs in distributed energy utilization systems.<sup>[5]</sup>

Optically triggered energy release is

considered as one of the most promising methods to control the energy utilization of PCMs over a wide range of temperatures.<sup>[6]</sup> This method involves the incorporation of photochromic molecules into organic PCMs to enable photoinduced reversible structural transformation in a PCM to control the PC at specific temperatures.<sup>[7]</sup> In addition, this process depends on the PC of the photochromic molecules. This method offers the possibility to release the PC enthalpy and photo-thermal (PT) energy of PCMs simultaneously.<sup>[8]</sup> Among several photosensitive molecules,<sup>[9]</sup> azobenzene derivatives have been extensively explored and have been considered as ideal photochromic candidates for molecular regulation of structural transformation<sup>[10]</sup> owning to their reversible isomerization from the metastable cis (Z)-isomer to the stable trans (E)-isomer under UV and visible light illumination,<sup>[11]</sup> which has been widely used for light-induced thermal energy storage,<sup>[12]</sup> as well as having potential applications in data storage<sup>[13]</sup> and transmistor devices of fully photon operated logic circuits.<sup>[14]</sup> Therefore, when azobenzene molecules are introduced into organic PCMs, the effectiveness of the control over the heat release and the stability of heat storage



at different temperatures is determined by the isomerization (degree and speed) of azobenzene.

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However, despite the advantages of azobenzene molecules, their utilization for optically triggered release of latent heat (PC and PT) over a wide temperature range has not been achieved, due to the structural difference between azobenzene and organic PC molecules. For example, azobenzene and organic PC molecules exhibit significantly different PC temperatures, and the isomerization of azobenzene is, to some extent, affected by the steric hindrance and molecular interaction between the two molecules.<sup>[6b]</sup> Consequently, it is difficult to induce PC of azobenzene and PC molecules synchronously. Based on molecular interaction between azobenzene and PC molecules, there should be a partial similarity between the molecular structures of azobenzene and PC molecules to ensure uniform dispersion of azobenzene in PC molecules. Thus, an energy barrier is introduced for the PC by changing the molecular alignment for crystallization. This indicates that the crystallization temperature  $(T_c)$ and PC enthalpy ( $\Delta H$ ) of PCMs can be controlled by adjusting the amount and structure (substituents) of azobenzene.

Another limitation of organic PCMs is their inability to combine heat storage and release at very low temperatures, especially below  $T_c$ . Most organic PC molecules release heat (enthalpy) via solid-liquid PC at temperatures above 0 °C;<sup>[15]</sup> however, a further decrease in  $T_c$  usually reduces the  $\Delta H$ .<sup>[4]</sup> To overcome this limitation, supercooling has been introduced as an effective method to store the latent energy of PCMs at temperatures below  $T_c$ <sup>[16]</sup> The introduction of metastable photochromic molecules with a very low  $T_c$  significantly affects the crystallization of PC molecules, resulting in a supercooling state. Thus, the supercooling degree (the decrease in  $T_c$ ) is the minimum temperature limit for heat storage and release. However, an extremely low temperature usually impedes the photo-isomerization of Azo, thus inhibiting the release of PT energy. To date, only a few studies have reported the utilization of photochromic organic molecules for the synchronous release of PT energy and PC enthalpy at temperatures below 0 °C. The optimization of the molecular structure of photochromic and PC molecules to match their  $T_c$  at low temperatures induced by isomerization is critical for optically triggering heat output at a low temperature.

Herein, we prepared photo-responsive organic PC composites (Azo/Ted) by mixing 1-phenyl-2-(4-(tetradecyloxy)phenyl)diazene (Azo) in tetradecane (Ted). The molecular interaction between the Azo and Ted affected the crystallization of Ted. The Z-rich Azo (Z-Azo) with a  $T_c$  similar to that of Ted introduced a photoresponsive energy barrier for the PC, thus inducing a supercooling state. In addition, the supercooling degree, PT energy, and PC enthalpy of the Azo/Ted composite were controlled by adjusting the molar ratios of Azo in the composite in accordance with the change in the crystallization and isomerization. After exposure to UV illumination, the Z-Azo/Ted composite synchronously combined heat storage at a low temperature and optically triggered heat release of PC enthalpy and PT energy under blue-light illumination. Finally, an annular device was fabricated for energy utilization, including light absorption, low-temperature storage, and optically triggered heat release. The temperature was tracked using a high-resolution IR thermal imaging camera. The results revealed that the photo-responsive Azo/Ted composite can be utilized for designing an advanced distributed energy system by optimizing its low-temperature storage and photo-induced heat release.

## 2. Results and Discussion

## 2.1. Basic Properties of Azo

The low-temperature heat storage and controllable heat release of PCMs is significant for the utilization of their energy. However, the synchronous release of PT energy and PC enthalpy in PCMs is challenging due to the difference between the  $T_c$  of azobenzene and PC molecules. To overcome this limitation, based on molecular design, we incorporated an alkyl-grafted Azo into Ted to realize photo-induced isomerization, as well as the PC of both Azo and Ted. According to Table S1, Supporting Information, compared with Azo13 and Azo15 (azobenzene with chain length of 13 and 15), Azo shows the suitable crystallization temperature (-3.4 °C), which is close to that of Ted (0.11 °C) and similar alkyl chains (14 carbon) to Ted. And the molecular interaction (van der Waals force among alkyl chains) between Azo and Ted facilitated the intercalation of Azo into the molecular alignment of Ted (Figure 1a). After the E-to-Z isomerization, the  $T_{c-Z}$  (-3.4 °C Figure 1b) of the liquid Z-Azo decreased to a temperature close to that of Ted ( $T_c = 0.11$  °C) due to reduced crystallization. This effect induced a supercooling state in Azo/ Ted composite. By adjusting the Azo content in the Azo/Ted composite, the  $T_{c,Z}$  for heat release was regulated. The obtained photo-responsive Azo/Ted composite exhibited considerable potential for the synchronous release of PC energy and PT heat for energy utilization at a low temperature.

Fourier transform infrared (FTIR) (Figure S1, Supporting Information) and <sup>1</sup>H NMR (Figure S2, Supporting Information) spectroscopy were performed to investigate the chemical structure of the Azo. The characteristic peak of Azo was observed at 1602 cm<sup>-1</sup>, which can be attributed to the stretching vibration of -N=N-.<sup>[9b,17]</sup> An additional peak was observed at 1500 cm<sup>-1</sup>, which can be attributed to the -C=C- stretching vibration of benzene. Furthermore, multiple peaks were observed from 1251 cm<sup>-1</sup> to 1022 cm<sup>-1</sup>; these can be assigned to -C-O-C-. The chemical structure of Azo was also examined via <sup>1</sup>H NMR. The photoisomerization of the Azo was tracked using its absorption spectra (Figure 2a). Before irradiation, the Erich Azo (E-Azo) showed an intense peak of  $\pi$ - $\pi$ \* transition at 349 nm and a weak broad peak at around 437 nm, which can be attributed to the  $n-\pi^*$  transition. After UV irradiation (365 nm), there was a continuous decrease in the  $\pi$ - $\pi$ \* transition peak and a slight increase in  $n-\pi^*$  transition due to the E-to-Z photoisomerization.<sup>[18]</sup> As shown in the <sup>1</sup>H NMR spectra (Figure 2b; Equation (S1), Supporting Information), a photoisomerization degree of 81% was achieved after UV irradiation for 30 min. In addition, the Z-Azo achieved a thermodynamically stable state that it takes 156 h to finish Z-to-E isomerization in darkness. This process was controlled and accelerated using blue-light (420 nm) irradiation (Figure S3, Supporting Information). More importantly, as shown in Figure 2c, the planar E-Azo exhibited satisfactory crystallization with prominent diffraction peaks at 6°, 21°, and 24°, due to the strong van



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Figure 1. a) Chemical structure of Ted and Azo; b) Schematic of solid–liquid PC (yellow solid–red liquid) under UV and blue-light irradiation controlled via molecular alignment of Ted and affected by isomerization of Azo at different temperatures.

der Waals forces among them compared with those of amorphous Z-isomer. Consequently, the Z-Azo (Figure 2d) exhibited a remarkable decrease in its melting point ( $T_{m-Z}$ , 47.7 °C) and  $T_{c-Z}$  (-3.4 °C) due to its poor crystallization compared with that of *E*-Azo (80.5 °C and 63.8 °C). These results indicate that Azo undergoes photo-induced PC and isomerization over a wide range of temperatures (from -3.4 to 102.1 °C). In addition, the  $T_{c-Z}$  of Azo (-3.4 °C) matched up that of Ted ( $T_{c-Ted}$ , 0.11 °C) and can also be tuned by controlling the isomerization degree. The overlapping  $T_c$  indicates that synchronous release of PT enthalpy and PC energy can be achieved in the Azo/Ted composite.

#### 2.2. Photoisomerization of Azo/Ted

The solid–liquid PC of the Azo/Ted composite controlled by photo-isomerization is shown in Figure S4, Supporting Information. The color change (yellow to red) of the Azo/Ted composite indicates the solid–liquid PC; the Azo/Ted-1 is a yellow solid powder ( $T_{c-E} = 63.8 \text{ °C}$ ,  $T_{m-E} = 80.5 \text{ °C}$ ) at room temperature, and it gradually changed to a red viscous liquid under UV irradiation for 10 min. The PC can be attributed to the formation of *Z*-Azo with a low  $T_{c-Z}$  of -3.4 °C, which also decreased  $T_{c-Ted}$ .

However, this photo-induced PC is reversible. For example, after blue-light irradiation for 16 min, the red liquid changed to a yellow agglomerated powder, which can be peeled off from the substrate. The Azo/Ted-2 and Azo/Ted-3 composites underwent a similar reversible PC between yellow powder and light red liquid under UV irradiation for a longer time.

The photo-isomerization (degree and speed) of Azo in the Azo/Ted composite is crucial for the PC of Azo and Ted. Thus, it determines the possibility of the synchronous release of PC enthalpy and PT energy at specific temperatures. We investigated the effect of the Azo content on the E-Z isomerization of Azo/Ted. As shown in Figure 3a,b and Figure S5, Supporting Information, all the Azo/Ted composites enabled Eto-Z isomerization under UV light; however, when the molar ratio of Azo was increased from 10% to 50%, the time taken to reach the photostationary state increased from 10 to 25 min, which was faster than that for the pure Azo (30 min). This result indicates that the molecular interaction (van der Waals force) between Azo and Ted favors the steric transformation of Azo. This is because the flexible tetradecyl ether of the planar E-Azo successfully intercalated into the lamellar alignment of Ted, leading to weak intermolecular  $\pi$ -stacking between two adjacent Azo,<sup>[19]</sup> thus facilitating isomerization. However, the intermolecular  $\pi$ -stacking between two adjacent Azo increased







**Figure 2.** a) Time-evolved UV-vis absorption spectra of Azo from Z- (uncharged) to E-isomer (charged) under UV irradiation; b) <sup>1</sup>H NMR spectra, c) XRD patterns, and d) DSC plots of the Z- (vellow dotted line) and E- (red solid line) Azo. The cooling and heating rates were 10 °C min<sup>-1</sup>.

with an increase in the Azo content in the Azo/Ted composites. Consequently, the time taken to achieve the photostationary state increased with an increase in the Azo content. This result was also confirmed by the Z-to-E reversion. Under blue-light irradiation, the times required for the Z-Azo/Ted-1, Z-Azo/Ted-2 and Z-Azo/Ted-3 to recover original the E-isomer were 16, 24, and 36 min, respectively (Figure 3c,d; Figure S6, Supporting Information), compared with 92, 115, and 126 h, respectively, in darkness (Figure S7, Supporting Information). In addition, both processes were faster in Azo/Ted than in pure Azo (50 min and 156 h, respectively). Furthermore, the velocity of the Z-to-E reversion in the Azo/Ted composite continuously decreased with an increase in the Azo content due to the reduced intermolecular interaction. This effect was observed under blue-light irradiation and in darkness. Based on the calculation using Equation (S2) (Figure S8, Supporting Information), the first-order kinetic constant of the *Z*-to-*E* isomerization of Azo/Ted-1 was  $1.01 \times 10^{-5}$  s<sup>-1</sup>, which is one order of magnitude higher than that of pure Azo  $(3.49 \times 10^{-6} \text{ s}^{-1})$ .

The degree of photo-isomerization was also investigated in this study. According to <sup>1</sup>H NMR calculations, under UV irradiation, the *E*-to-*Z* isomerization degree of all the Azo/Ted composites (Figure 2e) was approximately 83% at the photostationary state (Table S2, Supporting Information), regardless of the molar ratios of Azo; this is competitive with the findings of previous studies.<sup>[20]</sup> In addition, the recovery of the *Z*-Azo in the Azo/Ted composites to its original *E*-isomer occurred at different speeds. This result indicates that the Azo/Ted-1 with reversible isomerization exhibits considerable potential for storing and releasing high-density PT energy. Particularly, at low temperatures, this process can be accelerated using blue light irradiation. Consequently, the optically triggered heat output favors fast energy accumulation with a significant increase in temperature, which reduces the influence by severe heat transfer to the low-temperature environment. The cyclic performance of the isomerization of Azo in the Azo/Ted composite was also investigated by alternately irradiating the composites with UV (365 nm) and blue light (420 nm). As shown in Figure S9, Supporting Information, the Azo/Ted-1 exhibited excellent cyclic performance for up to 20 cycles.

In addition, the *E*- and *Z*-Azo exhibited different  $T_{m-E}$  and  $T_{c-Z}$  values due to the difference in their crystallization. The crystallization of *E*-Azo, *Z*-Azo, and the Azo/Ted composites was investigated via X-ray diffraction (XRD). According to previous studies,<sup>[21]</sup> molecules with long alkyl chains are prone to forming lamellar structures through intermolecular van der Waals forces, and the change in molecular interaction leads to a change in crystallization. As shown in Figure 3f, compared with Ted (the peak at 19°) and *E*-Azo (peaks at 6°,21°, and 24°), all the Azo/Ted composites exhibited the typical crystallization peak of both Ted and *E*-Azo at different intensities. The *E*-Azo induced by high temperature (70 °C) showed the same peaks of that induced by blue-light irradiation (Figure S10, Supporting Information). Results indicate that PC of both Azo and Ted can be regulated by *trans-cis* isomerization induced by blue light







**Figure 3.** Time-evolved UV–vis absorption spectra of Azo/Ted-1 and Azo/Ted-3 under irradiation with a,c) UV light (365 nm) and b,d) blue light (420 nm) after they reached the photostationary state. e) Isomerization degrees of Azo/Ted-1, Azo/Ted-2, Azo/Ted-3, and Azo under irradiation for different times. f) XRD patterns of Ted, *E*-Azo/Ted-1, *E*-Azo/Ted-2, *E*-Azo/Ted-3, *Z*-Azo/Ted-1, *Z*-Azo/Ted-2, and *Z*-Azo/Ted-3.

and/or heat. Moreover, with an increase in the molar ratios of Azo, the crystallization peak of *E*-Azo became sharp, while that of Ted became weak. This is because the flexible tetradecyl ether of the planar *E*-Azo intercalated into the lamellar alignment of Ted via van der Waals forces, thereby mitigating the crystallization of Ted. In addition, this effect was enhanced with an increase in the *E*-Azo content, while the increase in the crystallization of Azo was due to strong  $\pi$ -stacking. The crystallization of Ted was completely destroyed by the sterically curved *Z*-Azo liquid because of its low  $T_{c.Z}$ . In addition, the viscous *Z*-Azo liquid inhibited the ordered molecular alignment of Ted, which resulted in a broad peak at 14–24°. The ability to control the crystallization is beneficial for matching  $T_{c.Z}$  with  $T_{c.Ted}$  for optically triggered heat release.

#### 2.3. Thermal Performance of Azo/Ted

 $T_{\rm c-Z}$  determines the temperature necessary for optically triggered heat release, which is also the lower temperature limit of heat storage. One of the limitations of the photo-induced synchronized release of PC enthalpy and PT energy is the  $T_{\rm c}$  mismatch between photo-chromic molecules and PCMs. Thus, we tuned the  $T_{\rm c-Z}$  of the Z-Azo/Ted ( $T_{\rm c-Z/Ted}$ ) to match  $T_{\rm c-Ted}$  for heat release. As shown in Figure 4a, all the *E*-Azo/Ted composites exhibited two exothermic peaks. The peak observed at approximately 2 °C ( $T_{\rm c-Ted}$  in the composite) can be attributed to the enthalpy release of Ted, which is close to  $T_{\rm c-Ted}$  (0.11 °C). The slight increase in the  $T_{\rm c-Ted}$  (from 0.11 to 2 °C) of the *E*-Azo/Ted can be attributed to the increase in the energy absorbed by Ted molecules for







**Figure 4.**  $T_c$  and heat release of Azo/Ted composite at different molar ratios of Azo. a) DSC curves of Z-Azo/Ted (solid line) and E-Azo/Ted (dotted line) at a cooling rate of 10 °C min<sup>-1</sup>; b)  $T_{c-Z/Ted}$  (red line) and  $T_{c-E/Ted}$  (yellow line).  $T_0$  (blue point) is equal to  $T_{c-Ted}$ . The shaded region represents the temperature range for the optically triggered heat release; c)  $\Delta T_c$  of the Azo/Ted composites under UV irradiation for different times; d) DSC exothermic curve of the Z-Azo/Ted composite and Z-Azo from 60 to 140 °C at a heating rate of 10 °C min<sup>-1</sup>; e) Total amount of released heat ( $\Delta H_{total}$ ) including the  $\Delta H_{PC}$  and  $\Delta H_{PT}$ , and f) the corresponding  $E_{PC}$ % and  $E_{PT}$ % of Ted ( $\blacksquare$ ), Azo/Ted-1 ( $\blacklozenge$ ), Azo/Ted-2 ( $\bigstar$ ), Azo/Ted-3 ( $\blacklozenge$ ).

crystallization due to the intercalation of *E*-Azo. This was confirmed by the decrease in  $T_{c-E}$  in the Azo/Ted composites compared with that in the *E*-Azo (63.8 °C). The additional peaks observed between 30 and 65 °C correspond to the  $T_{c-E}$  in the composite ( $T_{c-E/Ted}$ ). However,  $T_{c-E/Ted}$  significantly decreased from 58.3 to 35.1 °C with an increase in the molar ratio from 10% to 50% due to the decreased crystallization. This result indicates that the Ted significantly affected the crystallization of the planar *E*-Azo/ Ted composite due to the van der Waals forces between them, which is consistent with the XRD results (Figure 3f). However, the large gap between  $T_{c-Ted}$  and  $T_{c-E}$  impedes the enthalpy release of both Azo and Ted at specific temperatures during cooling.

This problem was solved via the photo-isomerization of Azo in Ted. As shown in Figure 4a, after the irradiation,  $T_{c-Z}$  overlapped with  $T_{c-\text{Ted}}$  to become  $T_{c-Z/\text{Ted}}$ , which was the only broad exothermic peak of the Z-Azo/Ted composites during cooling.  $T_{c-Z/\text{Ted}}$  was further tuned in the range of -6.71 °C ( $T_{c-Z}$  of Z-Azo/Ted-3) to 0.11 °C ( $T_{c-\text{Ted}}$ ) by controlling the molar ratio of Azo. The overlapped  $T_{c-Z/\text{Ted}}$  is significant for the synchronous release of PC enthalpy and PT energy. Moreover, the overlapped  $T_{c-Z/\text{Ted}}$  enables the Z-Azo/Ted composites to store and release latent energy at temperatures lower than  $T_{c-\text{Ted}}$ . This effect introduced an energy barrier for the PC of Ted for supercooling. The supercooling ( $\Delta T_c$ ) is defined as shown in Equation (1):

$$\Delta T_c = T_{c-E/Ted} - T_{c-Z/Ted} \tag{1}$$

With an increase in the molar ratio of Azo, the  $T_{c-Z/Ted}$  of the Azo/Ted composites decreased significantly, from

–1.96 to –6.71 °C; however,  $T_{c-E/Ted}$  increased from 2.08 to 2.13 °C (Figure 4b). Consequently,  $\Delta T_c$  increased from 4.04 to 8.8 °C, resulting in a high-supercooling state, which is listed in Table S3, Supporting Information.

The supercooling of the Z-Azo/Ted composites can also be controlled through the E-to-Z isomerization degree of the Z-Azo. As shown in Figure 4c, the  $\Delta T_c$  of the Z-Azo/Ted composites increased with an increase in the Z-Azo content. In addition, at the same isomerization degree, the  $\Delta T_c$  of the Z-Azo/Ted-3 composite was higher than those of the Azo/ Ted-1 and Azo-Ted-2 composites. Furthermore, a large temperature gap (from 2.09 to -6.71 °C) was observed in the Azo/ Ted-3 composite when the isomerization degree was increased to 83%, compared with the gaps for the Azo/Ted-1 (4.04 °C) and Azo/Ted-2 (5.93 °C) composites. Previous studies reported that the inhibited supercooling of traditional PCMs due to nucleators is beneficial for inducing heterogeneous nucleation and promoting crystallization.<sup>[22]</sup> E-Azo and Z-Azo had different effects on the  $T_c$  of Ted. The planar *E*-Azo with a high  $T_c$  acted as an effective nucleating agent for Ted due to its isomorphous structure, whereas the sterically curved Z-Azo facilitated lowtemperature crystallization of Ted through strong molecular interaction. This effect introduced a photo-responsive energy barrier for the PC of Ted, causing an evident supercooling. The photo-controllable supercooling enabled optically triggered heat release over a wide temperature range (the shadow region, from -6.71 to 2.13 °C).

The energy density of the heat released by Azo/Ted determines its heat output capacity for energy utilization. Generally, SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com

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in spite of the energy barrier for supercooling and controllable release, the incorporation of photo-chromic molecules into PCMs decreases the energy density due to the reduced crystallization. Interestingly, as summarized in Table S4, Supporting Information, Z-Azo/Ted-1 achieved a maximum  $\Delta H_{\text{total}}$ of 207.5 J g<sup>-1</sup>, which is 1.7% higher than that of Ted (204 J g<sup>-1</sup>). Energy density ( $\Delta H_{\text{total}}$ ) is the sum of PC enthalpy ( $\Delta H_{\text{PC}}$ ) and PT energy ( $\Delta H_{\rm PT}$ ). The  $\Delta H_{\rm PC}$  ( $\Delta H_{\rm PC-Azo}$  and  $\Delta H_{\rm PC-Ted}$ ) of the Ted and the Z-Azo/Ted composites was measured via differential scanning calorimetry (DSC) at a cooling rate of 10 °C/ min. The integration of the exothermic area of the Z-Azo/Ted at approximately 2 °C in Figure 4a indicates that the  $\Delta H_{PC}$  of the Z-Azo/Ted composites decreased with an increase in the molar ratios of Azo. Particularly, the  $\Delta H_{PC}$  of the Azo/Ted-1 composite (191.1 J  $g^{-1}$ ) was 93.7% of that of Ted (204 J  $g^{-1}$ ); in contrast, the  $\Delta H_{PC}$  of the Azo/Ted-3 (77.5 J g<sup>-1</sup>) composite was only 38% of that of Ted. In addition, the  $\Delta H_{PC}$  of liquid Z-Azo/ Ted  $(\Delta H_{Z,PC})$  was higher than that of solid E-Azo/Ted  $(\Delta H_{E,PC})$ due to isomerization-induced PC. And  $\Delta H_{Z-E}$  (Equation (S3), Supporting Information) showed a steady increase with the increasing Azo molar ratios (Figure S11, Supporting Information). The increasing PC enthalpy is contributed by a large amount of Z-Azo in the composite. This result demonstrates that the  $\Delta H_{PC}$  of the composites consists of both Ted ( $\Delta H_{PC-Ted}$ ) and Azo ( $\Delta H_{PC-Azo}$ ). The  $\Delta H_{PT}$  values of the Z-Azo/Ted composites at different molar ratios of Azo were also measured via DSC (Figure 4d) at a heating rate of 10 °C/ min. The latent heat release of Z-Azo occurred when the temperature was increased to 70 °C, due to the thermal-induced Z-to-E isomerization. The integral of the broad exothermic peak represents the PT energy storage capacity of Z-Azo. The  $\Delta H_{\rm PT}$  values of the Z-Azo/Ted-1, Z-Azo/Ted-2, and Z-Azo/Ted-3 composites were 16.4, 45.3, and 70.6 J  $g^{-1}$ , respectively, which are 14%, 40%, and 62% of that of Z-Azo (113.6 J g<sup>-1</sup>), respectively (Table S4, Supporting Information). Thus, the high  $\Delta H_{\text{total}}$  of the Z-Azo/Ted-1 composite can be attributed to the higher increase in the  $\Delta H_{\rm PT}$  compared with the decrease in  $\Delta H_{PC.}$ 

 $\Delta H_{\text{total}}$  being controlled by  $\Delta H_{\text{PC}}$  (blue rectangle,  $\Delta H_{\text{PC-Azo}} + \Delta H_{\text{PC-Ted}}$  and  $\Delta H_{\text{PT}}$  (yellow rectangle) is shown in Figure 4e. The  $\Delta H_{\text{total}}$  of the Z-Azo/Ted-1 composite (207.5 J g<sup>-1</sup>) was considerably higher than those of Z-Azo/Ted-2 (172.4 J  $g^{-1}$ ) and Z-Azo/Ted-3 (148.1 J g<sup>-1</sup>) because the decrease in the  $\Delta H_{PC}$ of the Z-Azo/Ted-1 composite was higher than the increase in  $\Delta H_{\rm PT}$ . This indicates that the  $\Delta H_{\rm total}$  of Azo/Ted decreased significantly with an increase in the molar ratio of Azo above 10%. The proportions of the  $\Delta H_{PC}$  ( $E_{PC}$ %) and  $\Delta H_{PT}$  ( $E_{PT}$ %) in  $\Delta H_{total}$ at different molar ratios of Azo are plotted in Figure 4f; the proportions were calculated using Equation (S4), Supporting Information. As shown in Figure 4f, with an increase in the molar ratio of Azo, the  $E_{\rm PT}$ % of the composites increased, while the  $E_{\rm PC}$ % decreased. However,  $\Delta H_{\rm total}$  decreased with increasing  $E_{\rm PT}$ %. When  $E_{\rm PC}$ % decreased to 52.3%, the  $\Delta H_{\rm total}$  values of the Azo/Ted-3 (148.1 J g<sup>-1</sup>) and Z-Azo/Ted-1 (207.5 J g<sup>-1</sup>) composites were 72.6% and 71.4% of that of Ted (204 J  $g^{-1}$ ), respectively. The decrease in  $\Delta H_{\rm PC}$  can be attributed to the decrease in  $\Delta H_{\rm PC-Ted}$ . These results indicate that the introduction of Z-Azo severely affected the crystallization of Ted via the intercalation of Azo into the molecular alignment of Ted, which was confirmed by the supercooling (Figure 4c).

#### 2.4. Annular Device for Distributed Energy Utilization

An annular device was designed and fabricated for distributed energy utilization, wherein the latent energy can be delivered and released via optically triggered heat output. The Azo/Ted-1 (**Figure 5**a) composite was loaded into a sealed quartz tube with dimensions of  $1.2 \times 1 \times 0.3$  cm (length × width × wall thickness). As shown in Figure 5a, before the charge (no UV light irradiation), the solid *E*-Azo/Ted-1 did not flow into the tube. Figure 5b shows a schematic illustration of the distributed energy utilization, with four steps: i) UV-light charging, ii) lowtemperature storage (red liquid, *Z*-isomer), iii) blue-light irradiation for latent heat release, and iv) yellow solid (*E*-isomer) at low temperature.

Figure S12, Supporting Information, showed the timeevolved temperature of Azo/Ted-1 at the stage of i) UV-light charging and ii) low-temperature storage. E-Azo/Ted in the device absorbed UV light to undergo the isomerization at room temperature (27 °C), leading to a temperature increase by 3-5 °C in 10 min. Before moving it to low-temperature environment, the temperature is not high enough to induce cisto-trans reversion immediately. The yellow solid E-Azo/Ted-1 changed into a transparent red liquid ( $T_{c-Z/Ted}$  of -1.96 °C) by storing both  $\Delta H_{\rm PT}$  and  $\Delta H_{\rm PC}$ . After the tube was rotated using a mechanical machine, the liquid flowed to the other side of the tube due to gravity. Simultaneously, the environment temperature decreased to -5 °C, while the temperature of the tube was maintained at –0.3 °C, which is higher than  $T_{c-Z/Ted}$  (–1.96 °C). The charged Z-Azo/Ted-1 showed a stable heat storage with no obvious temperature change after 10 min. When irradiated with blue light for 10 min, the red Z-Azo/Ted-1 liquid at the R area (Figure 5b) gradually changed to a yellow E-Azo/Ted-1 solid by releasing both the  $\Delta H_{\rm PT}$  and  $\Delta H_{\rm PC}$  via Z-to-E isomerization. After the stored energy was released, the temperature of the tube gradually decreased to -0.3 °C. The closed cycle of energy utilization was completed when the environment temperature returned to 27 °C. Energy can be recycled and distributed to any part of the tube due to the high fluidity of the charged liquid. The Z-Azo/Ted-1 composite successfully performed optically triggered heat release at a temperature range of -1.9 to 2.08 °C. The recyclability and controllability of the heat storage and release is significant for the distributed energy utilization.

The effect of the blue-light irradiation on the change in the temperature ( $T_R$ ) of the R point (the sample position) was tracked using a high-resolution infrared (IR) thermal imaging camera (Figure 5c). We also added the same weight of *E*-Azo/ Ted (Figure 5d) and Ted (Figure 5e) into the tube for comparison, respectively. The  $T_R$  of the tube with charged *Z*-Azo/Ted-1, uncharged *E*-Azo/Ted-1, Ted and with no sample (Figure S13, Supporting Information) was investigated to demonstrate the effect of the *Z*-Azo/Ted-1 on the heat release. Before the



**Figure 5.** a) Optical image of sealed quartz tube for annular device with solid *E*-Azo/Ted-1; b) Schematic illustration of the distributed energy utilization system using an annular device. A closed cycle of i) UV-light charging, ii) low-temperature storage (red liquid, *Z*-isomer), iii) blue-light irradiation for latent heat release, and iv) yellow solid (*E*-isomer) at low temperature. Time-evolved IR thermal imaging of the device with c) *Z*-Azo/Ted-1, d) *E*-Azo/Ted-1, and e) Ted for one cycle including blue-light irradiation (blue arrow) for 10 min and darkness (black arrow) for the next 5 min. The temperature gradient of the R area ( $D_0$ – $D_{160}$ ) was tracked ( $D_n$  indicates that the distance from  $D_0$  is *n* mm).

blue-light irradiation, the temperature of the L point  $(T_{L0})$  and  $T_{\rm R0}$  were -0.3 °C. The  $T_{\rm R}$  of the tube with the charged Z-Azo/ Ted-1 increased when the tube was irradiated with blue light, whereas no significant change was observed in  $T_{\rm I}$ . In addition, there was a significant increase in the temperature of the tube containing Z-Azo/Ted-1 (Figure 5c). As shown in Figure 6a, the difference  $(\Delta T_{\rm R})$  between  $T_{\rm R}$  and the temperature before irradiation  $(T_{R0})$ , calculated using Equation (2), gradually increased from –0.3 °C and reached a maximum ( $\Delta T_{\text{R-max}}$ ) of 4 °C under the blue-light irradiation for 10 min, which is much higher than that of *E*-Azo-Ted-1 (1.5 °C), Ted (0.7 °C) and empty tube (0.1 °C). The isomerization reversion of Z-Azo/Ted-1 in the annular device was also investigated. The cis-to-trans isomerization rate (Figures S14 and S15, Supporting Information) of Azo was significantly reduced in a low temperature environment in comparison of that in Figure 3c and e. Specifically, it took 40 min to recover from Z-Azo to E-Azo in the composites at -5 °C, which is much longer than that (16 min) at room temperature (27 °C). According to Figure 3, the molecular interaction between Azo and Ted favors the steric transformation of Azo. Thus, the slow isomerization at a relatively temperature (-5 °C) is mainly attributed to the limited movement of molecular chains, thereby impeding structural transformation. Besides, some blue light is also reflected by U-shaped tube, leading to the decrease in energy absorbed by *Z*-Azo/Ted-1 in the device. This result also indicates that the rise in temperature of the device is caused by isomerization-induced PC of *Z*-Azo/Ted-1.

$$\Delta T_{\rm R} = T_{\rm R} - T_{\rm R0} \tag{2}$$

Further increase in  $\Delta T_{\rm R}$  was inhibited by heat transfer to the environment. In contrast, the  $\Delta T_{\rm R}$  of the tube containing the uncharged *E*-Azo/Ted-1 decreased to 1.5 °C due to the photo-thermal effect (phonon absorption). As shown in Figure 6b, the R area for irradiation also showed a clear temperature gradient with the highest temperature ( $T_{\rm R-max}$ ) at the irradiation center (D<sub>60</sub>-D<sub>80</sub>), and the temperature decreased with an increase in the distance to the irradiation center. The energy distribution







**Figure 6.** a) Change in temperature at the R point ( $\Delta T_R$ ) with time; b) Temperature gradient from D<sub>0</sub> to D<sub>160</sub> in the R area; c) Temperature gap ( $\Delta T_{RL}$ ); d)  $\Delta T_R$  upon five cycles of energy utilization.

of the incident light (UV and blue light) on R area was shown in Figure S16, Supporting Information. Thus, the uncharged *E*-Azo/Ted-1 far from the irradiation center stored and released only a small amount of heat due to a low-degree isomerization because it absorbed a relatively low amount of light energy.

To avoid the photothermal effect, the difference  $(\Delta T_{RL})$  between  $T_R$  and  $T_L$ , which was calculated using Equation (3), is also shown in Figure 6c.

$$\Delta T_{\rm RL} = T_{\rm R} - T_{\rm L} \tag{3}$$

The tube with Z-Azo/Ted-1 exhibited a  $\Delta T_{\rm RL}$  of 2.1 °C, which is 162%, 425% and 950% higher than those of the tubes *E*-Azo/ Ted (0.8 °C), Ted (0.4 °C) and no sample (0.2 °C) (Table S5, Supporting Information). In addition, the  $T_{\rm L}$  values of the tubes containing both Azo/Ted samples and that of the empty tube were similar. Thus, the increase in  $\Delta T_{\rm RL}$  can be attributed to the heat release by the Z-Azo/Ted-1 at the R area. These results indicate that the optically-triggered heat release with an increase in the  $\Delta T_{\rm R}$  up to 4 °C at a low-temperature environment was due to the controllable high-density heat release of Z-Azo/Ted-1, which is better than those of previously reported PCMs, whose heat release at temperatures lower than the  $T_{\rm c}$ cannot be controlled.

In darkness, the tube containing *Z*-Azo/Ted-1 showed a low-rate spontaneous heat release due to slow *Z*-to-*E* isomerization (Figure 3a). Consequently, the  $T_{\rm R}$  of the tube containing *Z*-Azo/Ted-1 returned to  $T_{\rm R0}$  at approximately 0 °C

within 1.5 min, which was slightly longer than that for the E-Azo/Ted-1-containing tube (1 min) and Ted-containing tube (0.5 min). This result indicates that the increasing temperature of the R area was due to the controllable heat release of the Z-Azo/Ted-1, rather than photothermal effect. Before returning to  $T_{R0}$ , the average  $T_R$  of the tube containing Z-Azo/ Ted-1 was 2.8 °C, which was higher than those of the tube containing E-Azo/Ted-1 (1.0 °C) and the empty tube (0 °C). This closed-cycle energy utilization exhibited excellent cycling performance for the temperature change with a  $\Delta T_{\text{R-max}}$  of 3.8–4 °C over five cycles (Figure 6d) due to the high degree of isomerization by Azo/Ted-1 during energy utilization cycling (Figure S17, Supporting Information). Through the calculation by Equation (S5), Supporting Information, the energy conversion efficiency ( $\eta$ ) of Azo/Ted-1 based energy utilization device was in the range from 9.2% to 9.8% with the average of 9.2% in five cycles (Table S6, Supporting Information).

This result indicates that Z-Azo/Ted can store and release both PT energy and PC enthalpy under alternate irradiation to induce reversible temperature change. In addition, the energyutilization process can be suitably controlled by controlling the low-temperature (supercooling) storage and optically-triggered heat output. The Z-Azo/Ted-1 composite is an ideal candidate for thermal management materials in distributed energy utilization systems owing to their ability to store/release heat at low temperatures. The device using Z-Azo/Ted can be further developed for an advanced distributed energy utilization system to perform tasks such as thermal management and thermal control.



## 3. Conclusion

In this study, we designed and prepared a series of Azo/ Ted composites for optically triggered low-temperature heat release of PT energy and PC enthalpy. The incorporation of Azo into Ted not only affected the crystallization of Ted but also accelerated the trans-cis (E-Z) photo-isomerization of the Azo by reducing the intermolecular  $\pi$ -stacking. This introduced a photo-responsive energy barrier for the PC for Azo/ Ted to achieve supercooling (4.04-8.80 °C) for heat storage. In addition, after UV charging,  $T_{c-Z}$  (-3.4 °C) and  $T_{c-Ted}$  (0.11 °C) overlapped to become  $T_{c-Z/Ted}$  (-6.71 to 1.96 °C), which can be tuned by adjusting the molar ratios of Azo in the Azo/Ted composite. This effect enables photo-induced release of PT energy and PC enthalpy. Furthermore, under blue-light illumination, Z-Azo/Ted-1 released high-density (207.5 J g<sup>-1</sup>) heat that included  $\Delta H_{PC}$  and  $\Delta H_{PT}$ , at a relatively low temperature (-1.96 to -6.7 °C); this heat release was 1.7% higher than that of Ted (204 J g<sup>-1</sup>). We also fabricated an annular device for energy utilization, including light absorption, low-temperature storage, and optically triggered release. The temperature of the device achieves a significant increase in 4 °C in a low-temperature environment (-5 °C) due to the optically-triggered heat release. Thus, this study will pave the way for the design of advanced distributed energy systems that operate by controlling the energy storage/release of PCMs over a wide temperature range.

## 4. Experimental Section

*Materials*: Unless otherwise noted, the reagents were obtained from commercial sources and used as-received without purification. All other chemicals, including 4-hydroxyazobenzene, were purchased from TCI Development Co. Ltd., China.

*Synthesis of Azo*: Details on the experimental process can be found in the Supporting Methods within the Supporting Information (Figure S18, Supporting Information).

A round-bottom flask was charged with 4-hydroxyazobenzene (1.98 g, 10 mmol) and excess anhydrous potassium carbonate (1.73 g, 13 mmol). Then, 35 ml of ultra-dry DMF was added to the flask. Subsequently, 1-bromotetradecane (1.58 g, 6 mmol) was slowly dropped into the mixture. The reaction mixture was heated at reflux (120 °C) for about 4 h under vigorous stirring and was then poured into a 200-ml KOH (33.6 g, 0.6 mol) aqueous solution. The precipitated solid was filtered and purified using column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) to obtain 14-Azo as a yellow powder (2.1 g, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\partial$ ): 7.92 (dd, J = 15.4, 8.1 Hz, 4H), 7.49 (dt, J = 27.1, 7.2 Hz, 3H), 7.03 (d, J = 8.9 Hz, 2H), 4.07 (t, J = 6.6 Hz, 2H), 1.85 (p, J = 6.7 Hz, 2H), 1.50 (q, J = 7.2 Hz, 2H), 1.29 (s, 20H), 0.91 (t, J = 6.8 Hz, 3H). HRMS m/z: [M + H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>38</sub>N<sub>2</sub>O, 395.30; found, 395.31.

*Preparation of Azo/Ted*: First, tetradecane (Ted, 60 mg) was placed in a petri dish. Subsequently, an appropriate amount of Azo was dissolved in 5 ml of dichloromethane at molar ratios of 1:9, 3:7, and 1:1 (Azo: Ted). After the azobenzene was completely dissolved, the three groups of solutions were dropped separately into petri dishes filled with Ted. The color of the mixed solution changed from light yellow to orange with an increase in the Azo content. Then, the mixed solutions were dried at room temperature for 12 h to enable complete evaporation of the solvent to obtain phase change composites (Azo/Ted) with 10%/ 30%/50% azo molar ratios, denoted as Azo/Ted-1, Azo/Ted-2 and, Azo/Ted-3, respectively (**Table 1**).

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Table 1.	The molar	and w	veight	ratio	of Azo	in Azo	/Ted.
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Samples	Molar ratio of Azo [%]	Weight ratio of Azo [%]
Azo/Ted-1	10	18
Azo/Ted-2	30	46
Azo/Ted-1	50	67

Analysis of Chemical Structure, Optical Absorption, and Heat Release: The chemical structure of the Azo was characterized using Fourier transform infrared (FTIR) spectroscopy recorded on a Tensor 27 spectrometer (Bruker, USA) with a disc of KBr. <sup>1</sup>H NMR spectra were collected using a 400-MHz spectrometer (INOVA, Varian) with trimethylsilyl as an internal standard. High-resolution mass spectrometry (HRMS) was performed on an APEXIV 4.7 T Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonics, USA).

Thermal analysis was performed using a thermogravimetric analyzer (TGA; STA 449C, NETZSCH, Germany) protected by 50 mL min<sup>-1</sup> nitrogen purging at a heating rate of 5 °C min-1 from 30 to 800 °C. The time-evolved UV-vis absorption spectra of the phase-change composite (1 cm path length quartz cUVettes, CHCl<sub>2</sub>) was measured using a UV-vis spectrophotometer (330, Hitachi, Japan). The phasechange composite was irradiated using a 500-W mercury lamp (Beijing Changtuo Technology Company, China) with a filter set at 365 or 420 nm. The light source was placed 10 cm above the samples at 27 °C. The cisto-trans thermal reversion process was investigated using a UV-vis spectrophotometer after the samples had been stored in darkness and covered with foils. The samples were alternately irradiated with 420-nm visible light at room temperature. The heat flow of the charged samples was evaluated using differential scanning calorimetry (DSC; TA Q20, TA Instruments). The samples were then transferred to a hermetically sealed DSC pan. The heat release was analyzed using the following process: equilibration at 70 °C; cooling to -20 °C at a rate of 10 °C min<sup>-1</sup>; heating to 150 °C at a rate of 10 °C min<sup>-1</sup>; and re-cooling to -20 °C at a rate of 10 °C min<sup>-1</sup>. Finally, the samples were reheated to 150 °C at a rate of 10 °C min<sup>-1</sup>

Fabrication of Device for Energy Utilization: First, the Azo/Ted-1 (70 mg) was added into a quartz U-shaped tube with a size of  $1.2 \times 1 \times 0.3$  cm (length × width × wall thickness). Then, the U-shaped tube was bonded to another empty U-shaped tube with the same size to form an annular device. An empty ring device was also fabricated for comparison. The device was placed on a plate for energy utilization including light absorption, storage, and heat release.

- UV-light irradiation: The annular device was irradiated with UV light (365 nm, 80 mW cm<sup>-2</sup>) at room temperature (27 °C).
- Low-temperature storage: The sample (Azo/Ted-1) gradually turned into red liquid (Z-isomer) via E-to-Z isomerization. The annular device was rotated by 90°, and the liquid flowed in the circular tube due to gravity. Meanwhile, the temperature was reduced to ~0 °C.
- 3. Blue-light irradiation: The red liquid stored latent heat and PT energy for a long time. The device was irradiated with blue light (420 nm, 60 mW cm<sup>-2</sup>). The liquid was converted back to yellow solid via Z-to-E isomerization followed by heat release. The temperature change caused by the heat release was measured using an IR thermal imaging camera (Fluke TiX640 Expert HD, USA). Subsequently, the ambient temperature returned to room temperature (27 °C) without a change in the color of the yellow solid. A closed cycle of energy utilization was thus accomplished.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.



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## **Conflict of Interest**

The authors declare no conflict of interest.

## **Keywords**

controlled heat-release, distributed energy system, energy recycling, phase-change material

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