Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Optically-Regulated Thermal Energy Storage in Diverse Organic Phase-Change Materials

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Experimental Section

All phase-change materials (PCMs) were purchased commercially and used without purification. The synthesis of azobenzene additive was conducted following the previous report.[1] The composites were prepared by dissolving the relative fractions of the PCM and azobenzene additive mixed in dichloromethane which was evaporated at 40 °C. The dried samples (2–3 mg) were then transferred to glass substrates (3 cm by 3 cm), spread thin by a spatula (1–2 cm wide, less than 1 mm thick) and heated at temperatures 1–2 °C higher than the melting point of PCM on a hotplate while being irradiated by a Blak-Ray B-100AP/R (UVP) high intensity UV lamp (365 nm, 100 W, unfocused) that was placed 25 cm above the samples. After 1 h of charging, the samples were transferred to DSC pans in the dark for measurements. For solution-state charging, the azobenzene compound was dissolved in dichloromethane and illuminated by the UV lamp while being stirred at a room temperature. The charged solutions were then dried under reduced pressure in the dark to prepare DSC samples. DSC analysis was conducted on a Q series DSC Q20 (TA Instruments) with the RCS40 component. ^{1}H NMR spectra were taken on Varian Inova-500 spectrometers. Chemical shifts were reported in ppm and referenced to residual solvent peaks (CD_2Cl_2: 5.33 ppm for ^{1}H).

Supporting Note 1. Calculation of Heat Storage Capacities in Composites

ΔH_{comp} in Figure 1b is the heat released from liquid (cis) → solid (trans) transition of the composite upon triggering with visible light. The optimized composites which contain azobenzene dopants (e.g. $\chi = 0.5$ for 50 wt% doping) store the fractional latent heat of the PCM (ΔH_f, various among PCMs), that of trans-Azo dopants ($\Delta H_{trans-Azo}$= 118 J/g), as well as the fractional isomerization energy of the metastable cis-Azo (ΔH_{iso}= 116 J/g).

$$\Delta H_{comp} = \chi\, \Delta H_f + (1-\chi)\, \Delta H_{trans-Azo} + (1-\chi)\, \Delta H_{iso}$$

Due to the exothermic cis-to-trans conversion which occurs during the visible-light triggering of PCM crystallization, the total heat storage capacity of the composite systems is similar to the neat PCM's. A quantitative measurement of ΔH_{comp} is challenging due to the difficulty in decoupling the heat release from the composite and the heat absorption from the light source for optical triggering during the DSC measurement. However, assuming at least 50% cis-to-trans conversion, the expected heat release is comparable to pristine PCM's heat of fusion. When PCM's intrinsic heat of fusion is over 236 J/g, the ΔH_{comp} becomes smaller than ΔH_f.

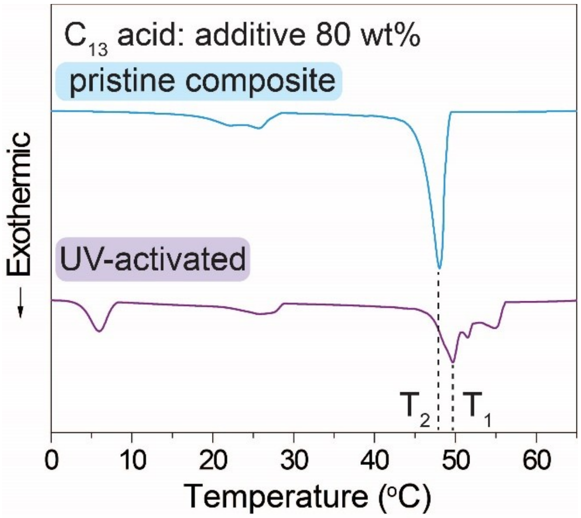

Fig. S1. DSC plots of C_{13}-acid composite containing excess (80 wt%) azobenzene dopant, before and after UV activation, measured at a cooling rate of 10 ^{o}C/min.

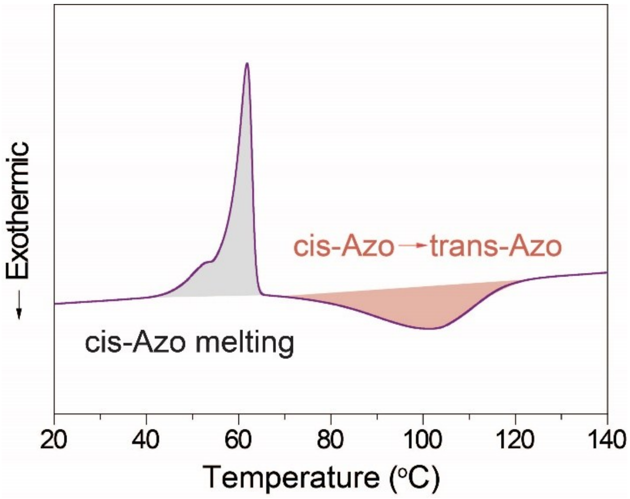

Fig. S2. A DSC plot of cis-Azo while heating at a rate of 10 ^{o}C/min. After melting, the reverse isomerization (cis→trans) occurs at a range of 70–120 ^{o}C due to thermal triggering.

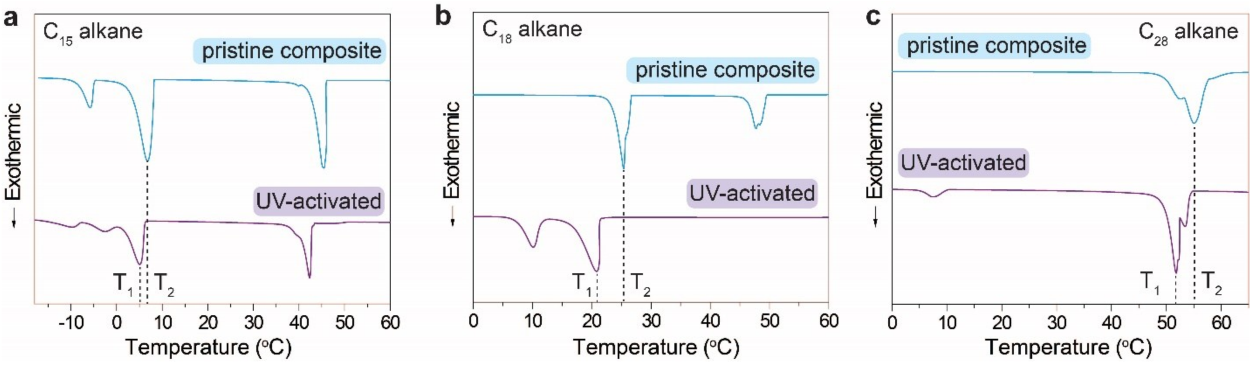

Fig. S3. DSC traces of various n-alkane composites containing (a) $C_{15}H_{32}$, (b) $C_{18}H_{38}$, and (c) $C_{28}H_{58}$.

References

1. G. G. D. Han, H. Li and J. C. Grossman, *Nat. Commun.*, 2017, **8**, 1446.