Extending the Usable Temperature Range of Photo-Induced Melting in Acylhydrazone Crystals

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Photoisomerization associated with reversible crystal-to-liquid transitions has become an attractive research field for its potential applications to solar thermal fuels and self-healing materials.[1] Such photo-induced melting typically requires a photoswitching mechanism that leads to meta-stable isomer(s) with lower melting points. The changes in thermal properties associated with such structural transformations are closely related to crystal structures, posing challenges in molecular design for this phase transition. In this work, we aimed to extend the usable temperature range of the photo-induced melting by exploiting the eutectic point, which depends on the transient conformers during photoisomerization.

We synthesized various acylhydrazone derivatives[2] that have structural flexibility around the isomerization site (Figure 1(b)). Owing to the well-separated absorption band and thermal half-lives for as long as several months, both the *E*- and *Z*-isomers were successfully isolated. By mixing these isomers in arbitrary ratios, their eutectic points were determined. Based on this observation, we investigated the temperature dependence of photoinduced melting and found that two critical factors contribute to the extension of the usable temperature range:

1. The transient meta-stable conformer(s) of the *Z*-isomer generated during photoisomerization further lowers the eutectic point of the system.
2. The intramolecular interactions induced by a modifier (R) increase the energy cost of crystallization for the melt *Z*-isomer (Fig. 1(d)).

We will present new molecular designs to achieve low-temperature photoinduced melting utilizing eutectic mixing, together with experimental and theoretical examinations.

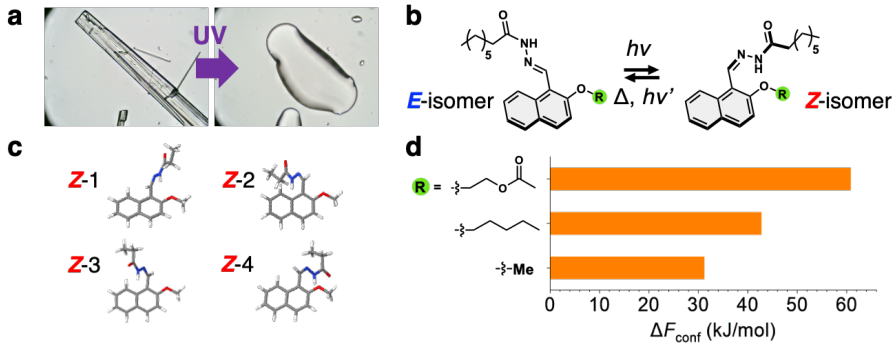

Fig. 1 (a) Microscopy snapshots of photo-induced melting. (b) Molecular structures of *E*/*Z* isomers of acylhydrazones (c) Examples of plausible transient conformers of the *Z*-isomer. (d) Free energy comparison among various R groups.

1) Qiu, et al., *J. Mater. Chem. 9*(2021)11444. 2) Koibuchi, et al. *J. Phys. Chem. Lett. 14*(2023)8320.