MS066.O03

Crystal jumping of alkyl acridone and its dicyanomethylenated derivatives

Takashi Takeda[1], Tomoyuki Akutagawa[1]
[1]*Institute Of Multidisciplinary Research For Advanced Materials, Tohoku Univ., Sendai, Japan*
E-mail: takeda@tagen.tohoku.ac.jp

Physically responsible molecular systems through the external stimuli are interesting from the view point of molecular mechanical devices such as sensor, actuator, electronic materials etc. Recently, the thermosalient effect, which has been referred to the "crystal jumping phenomenon", has been attracted much attention due to its potential application for future functional materials.[1] Since there have been only a dozen of sporadic reports on thermosalient molecular crystals, the development/discovery of new thermosalient crystal is necessary to understand and obtain the molecular design strategy for the thermosalient crystals.

We have been developed functional molecular materials based on the cooperative molecular motion in the (liquid) crystals. During the course of the development of electrochromic system based on quinacridone,[2] we found that simple alkyl acridone 1 and its dicyanomethylenated derivatives 2 showed the crystal jumping behavior (Figure).[3] The variable temperature X-ray diffraction analyses revealed that the anisotropic dissociation of pi-stacking in dimer structure was important for inducing crystal jumping phenomena for 1b, whereas the collective fluctuation/flipping motion of a dicyanomethylene unit induced the crystal jumping phenomena in 2 (Figure d). We also demonstrated that the systematic chemical modification was effective to investigate and understand the crystal/molecular design of the thermosalient crystals. The subtle change of alkyl chain length of 1 and 2 influenced the packing arrangements and flexibilities of molecules in the crystals, which critically affected the activity of the crystal jumping properties.

[1] Naumov, P. et al. (2015) Chem. Rev. 115, 12440-12490 and references cited therein.
[2] Takeda, T. et al. (2014) J. Org. Chem. 79, 9669-9677.
[3] Takeda, T.; Akutagawa, T. (2016) Chem. Eur. J. 22, 7763-7770.

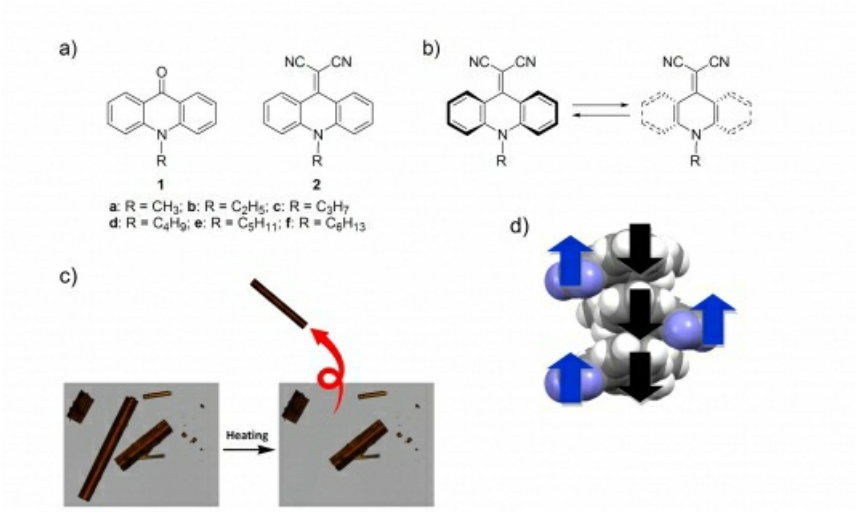

Figure a) Molecular structures of alkylacridones **1** and their dicyanomethylenated derivatives **2**. b) Dynamic equilibrium between twisted molecular structures of **2** c) Crystal jumping of **2d** upon heating. d) Molecular packing of **2b** viewed from the bc plane. Blue and black arrows indicate the direction of the flipping/fluctuation of a dicyanomethylene unit and a twisted acridone π unit, respectively.

Keywords: Crystal Jumping, Molecular Motion, Acridone