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Mechanically induced energy conversion by polymorphic single crystals of α -[(4-methoxyphenyl)methylene]-4-nitrobenzeneacetonitrile

Durga Prasad Karothu,^{1,2} Srujana Polavaram,¹ Ejaz Ahmed,¹ Zainab Alhaddad,¹ Panče Naumov^{1,2,3}

¹Smart Materials Lab, New York University Abu Dhabi (United Arab Emirates)

²Center for Smart Engineering Materials, New York University Abu Dhabi (United Arab Emirates)

³Molecular Design Institute, Department of Chemistry, New York University 100 Washington Square East, New York, NY, USA

dpk3@nyu.edu

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Single-crystal-to-single-crystal (SCSC) phase transitions are considered as direct structural transformations between single crystals in the solid state that occur without impairment of the crystal lattice. The SCSC transitions can be induced in organic, inorganic, metal-organic or organometallic crystalline materials by external stimuli such as heat, light, mechanical force, or electricity [1]. The respective crystalline materials have demonstrated potentials for applications in several fields, such as energy harvesting, sensors, actuators and artificial muscles [2–4]. In particular, SCSC transitions triggered by application of mechanical force that result in crystal motion [5,6], known as ‘mechanosolient effect’, are very rare deformations that occur by sudden release of energy [6,7] originating from the elastic strain accumulated in the crystal lattice. For example, single crystals of the metastable form I of terephthalic acid are known to be mechanosolient, and they move when subjected to localized mechanical stress [6,7]. Inspired by the extraordinary behavior of this material, we have now investigated another material which exhibits the mechanosolient effect. The compound, α -[(4-methoxyphenyl)methylene]-4-nitrobenzeneacetonitrile, is known to display concomitant polymorphism (forms I, II, III, and a *cis* form) and it can also crystallize as solvates [8–11]. The structures of forms II and III are non-centrosymmetric and are thus candidates as non-linear optical (NLO) material. Crystalline samples of form II obtained by crystallization from melt or deposition from vapor phase are mechanically unstable and undergo transformation to form III under mechanical stress [8]. However, this mechanical transformation has not been completely explained, and therefore it warrants further studies with respect to its mechanical, spectroscopic and structural aspects.

Here, we report the results from a detailed study of the mechanosolient effect in this compound. Single crystals of form II are metastable, and upon contact with a metal needle undergo a remarkable reshaping upon transformation to form III. The reversible transition (form III to form II) was performed by heating. Moreover, when they are exposed to mechanical pressure (form II to form III) and heating (form III to form II), the transformations are accompanied by change in color and fluorescence lifetime. The transitions induced by mechanical stimulation and heating were studied by thermal, mechanical, spectroscopic and crystallographic techniques. This material is a rare example of small molecule fluorescent crystal that undergoes a mechanosolient transition, and might be a promising candidate for the development of pressure-responsive materials.

- [1] Zheng, Y. S., Jia, X. D., Li, K., Xu, J. L. & Bu, X. H. (2021). *Adv. Energy Mater.* 2100324.
 [2] Dong, Y., Wang, J., Guo, X., Yang, S., Ozen, M. O., Chen, P., Liu, X., Du, W., Xiao, F., Demirci, U. & Liu, B. F. (2019). *Nat. Commun.* **10**, 4087.
 [3] Dattler, D., Fuks, G., Heiser, J., Moulin, E., Perrot, A., Yao, X. & Giuseppone, N. (2020). *Chem. Rev.* **120**, 310.
 [4] Abendroth, J. M., Bushuyev, O. S., Weiss, P. S. & Barrett, C. J. (2015). *ACS Nano* **9**, 7746.
 [5] Liu, G., Liu, J., Liu, Y. & Tao, X. (2014). *J. Am. Chem. Soc.* **136**, 590.
 [6] Karothu, D. P., Weston, J., Desta, I. T. & Naumov, P. (2016). *J. Am. Chem. Soc.* **138**, 13298.
 [7] Ahmed, E., Karothu, D. P., Warren M. & Naumov, P. (2019). *Nat. Commun.* **10**, 3723.
 [8] Vrcelj, R. M., Shepherd, E. E. A., Yoon, C. S., Sherwood J. N. & Kennedy, A. R. (2002). *Cryst. Growth Des.* **2**, 609.
 [9] Jha, K. K., Dutta, S. & Munshi, P. (2018). *Cryst. Growth Des.* **18**, 1126.
 [10] Cattoën, X., Kumar, A., Dubois, F., Vaillant, C., Matta-Seclén, M., Leynaud, O., Kodjikian, S., Hediger, S., De Paëpe, G. & Ibanez, A. (2022). *Cryst. Growth Des.* **22**, 2181.
 [11] Sanz, N., Baldeck, P. L., Nicoud, J. F., Fur, Y. L. & Ibanez, A. (2001). *Solid State Sci.* **3**, 867.

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