

Thermo-responsive single-component organic materials: Iso-symmetric phase transition, polymorphism and negative thermal expansion

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Due to their vast applications in science and technology, the thermo-responsive materials have always been the forefront of the materials science. Usually, materials expand upon heating but the negative thermal expansion (NTE) materials are unusual because they contract along one or more directions with increasing temperature.⁴ Although the NTE effects are not uncommon effect are rarely observed in organic materials and especially in single-component all-organic systems.¹ Recently focus has been shifted to develop the pure organic materials due to their benign nature and flexibility. Moreover, existence of both positive thermal expansion (PTE) and NTE in organic molecular systems are extremely rare.^{1b} Materials with NTE property finds immense applications in modern technologies² and lightweight, environmentally benign and easily tunable organic materials have plenty to offer in this niche area.^{2,3} In an effort to discover unusual PTE and NTE in organic materials, we have studied a series of imidazoline derivatives, where 2-(4-bromophenyl)-4,5-dihydro-1*H*-imidazole has shown a prominent NTE effect compared to its other derivative. This unique system not only undergoes solvent mediated polymorphic modifications to form centrosymmetric (**1C**, space group $P2_1/c$) and non-centrosymmetric (**1N**, space group Cc) structures but each of the forms experiences single-crystal to single-crystal reversible yet isosymmetric phase transition at ~ 210 K upon cooling. While form **1C** transforms to a structure with space group $P2_1/n$, the form **1N** converts to a new structure but without changing the space group. Interestingly, upon cooling, across the phase transition temperature at ~ 210 K, **1N** undergoes colossal PTE to NTE transition along the *a*-axis but NTE to PTE along the *b*-axis while *c*-axis experiences almost zero thermal expansion. Whereas, **1C** exhibits PTE to NTE only along the *b*-axis and only PTE along the other two axes. These anisotropic unusual thermal expansions, which is mainly due to the scissor like motion that molecules are undergoing upon temperature stimuli. Given these unusual properties, this novel all-organic material, which is analogous to a known molecular ferroelectric,⁴ may find potential applications in future organic electronics.

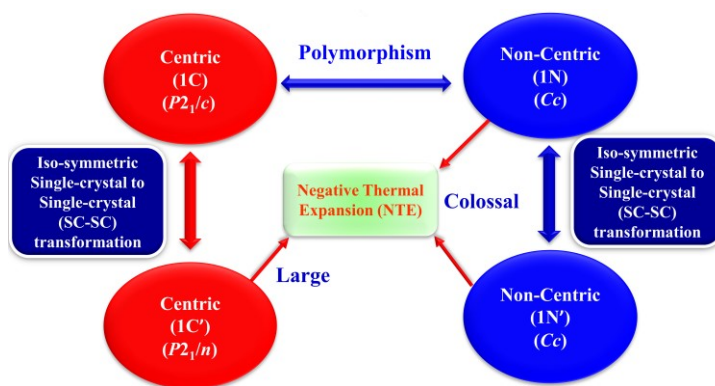


Figure 1. The detail flow chart

- [1] a) Z. Liu, Q. Gao, J. Chen, J. Deng, K. Lin and X. Xing, *Chem. Commun.*, 2018, **54**, 5164–5176, b) L. Negi, A. Shrivastava and D. Das, *Chem. Commun.*, 2018, **54**, 10675–10678.
- [2] a) J. Chen, L. Hu, J. Deng and X. Xing, *Chem. Soc. Rev.*, 2015, **44**, 3522–3567, b) K. Takenaka, *Sci. Technol. Adv. Mater.*, 2012, **13**, 013001.
- [3] K. M. Hutchins, R. H. Groeneman, E. W. Reinheimer, D. C. Swenson and L. R. MacGillivray, *Chem. Sci.*, 2015, **6**, 4717–4722.
- [4] S. Dutta, V. Vikas, A. Yadav, R. Boomishankar, A. Bala, V. Kumar, T. Chakraborty, S. Elizabeth and P. Munshi, *Chem. Commun.*, 2019, **55**, 9610–9613.

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