Title:	Chiral Bent-Shaped Molecules Exhibiting Unusually Wide Range of Blue Liquid-Crystalline Phases and Multistimuli-Responsive Behavior
Authors:	Punjani, V. (/jspui/browse?type=author&value=Punjani%2C+V.) Mohiuddin, G. (/jspui/browse?type=author&value=Mohiuddin%2C+G.) Kaur, Supreet (/jspui/browse?type=author&value=Kaur%2C+Supreet) Choudhury, A.R. (/jspui/browse?type=author&value=Choudhury%2C+A.R.) Pal, S.K. (/jspui/browse?type=author&value=Pal%2C+S.K.)
Keywords:	Liquid crystals Mechanochromism Phase transitions Single crystals Thermochromism
Issue Date:	2020
Publisher:	Wiley-VCH Verlag
Citation:	Chemistry - A European Journal, 26(26), pp.5859-5871.
Abstract:	Recently, an unprecedented observation of polar order, thermochromic behavior, and exotic mesophases in new chiral, bent-shaped systems with a −CH3 moiety placed at the transverse position of the central core was reported. Herein, a homologous series of compounds with even-numbered carbon chains from n=4 to 18 were synthesized, in which −Cl was substituted for −CH3 at the kink position and a drastic modification in the phase structure of the bent-shaped molecule was observed. An unusual stabilization of the cubic blue phase (BP) over a wide range of 16.4 °C has been witnessed. Two homologues in this series (1-12 and 1-14) exhibit an interesting phase sequence consisting of BPI/II, chiral nematic, twist grain boundary, smectic A, and smectic X (SmX) phases. The higher homologues (1-16 and 1-18) stabilize the SmX phase enantiotropically over the entire temperature range. Crystal structure analysis confirmed the bent molecular architecture, with a bent angle of 148°, and revealed the presence of two different molecular conformations in an asymmetric unit of compound 1-4. A DFT study corroborated that the −Cl moiety at the central core of the molecule led to an increase in the dipole moment along the transverse direction, which, in turn, facilitated the unusual stabilization of frustrated structures. Crystal polymorphism has been evidenced in three homologues (1-10, 1-12, and 1-14) of the series. On the application of mechanical pressure through grinding, compound 1-10 transformed from a bright yellow crystalline solid to a dark orange–green amorphous solid, which reversed upon dropwise addition of dichloromethane, indicating reversible mechanochromism in this class of compounds. In addition, excellent thermochromic behavior has been observed for compound 1-10 with a controlled temperature–color combination.
Description:	Only IISERM authors are available in the record.
URI:	https://chemistry-europe.onlinelibrary.wiley.com/doi/full/10.1002/chem.201905707 (https://chemistry-europe.onlinelibrary.wiley.com/doi/full/10.1002/chem.201905707) http://hdl.handle.net/123456789/3482 (http://hdl.handle.net/123456789/3482)
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