

Single-crystal-to-single-crystal phase transition of biphenyl-type Schiff bases

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We synthesized biphenyl-type disalicylaldehyde Schiff bases, **bis-SARs** (Fig. 1a), and examined their crystal structures and chromic properties. The fluorine-bearing **bis-SAF** crystal was found in three polymorphs. Form I was prepared via CHCl₃/MeOH vapor diffusion, while form III was obtained through CHCl₃/Hexane vapor diffusion. Form II was generated through cold crystallization of the melt. The **bis-SAF** crystal exhibited a single-crystal-to-single-crystal (SCSC) phase transition upon heating from form I to form III around 150 °C (Fig. 1b). After the SCSC phase transition, the dihedral angle (θ) of the biphenyl group changed and the crystal packing rearranged (Fig. 1c, d). Differential scanning calorimetry was used to quantify their thermal behavior: form I showed an exothermic phase transition at 146 °C, and forms II and III melted at around 182 °C and 211 °C, respectively. Photoluminescence spectroscopy revealed that form I showed an emission maximum at 592 nm, while form II showed a peak at 594 nm with a shoulder at 631 nm. Under UV irradiation, form III showed no emission and instead an increasing absorbance in the 450–600 nm range, namely photochromism. Quantum chemical calculations using molecular clusters explained the origin of the changes in chromic properties on the basis of their crystal structures.

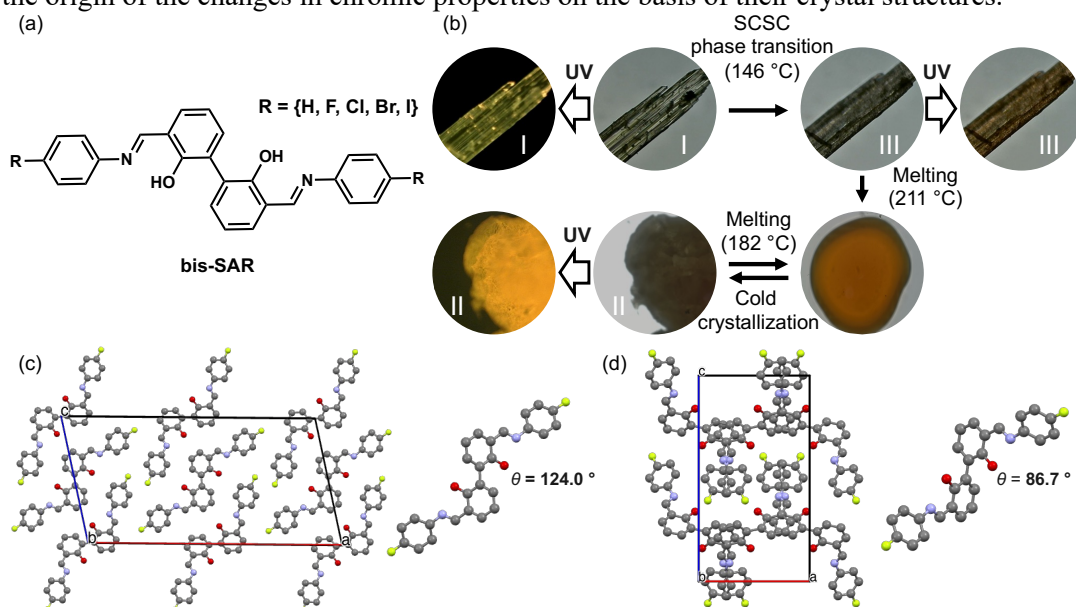


Fig.1 (a) Chemical structure of **bis-SAR**; (b) Microscopy images of **bis-SAF** crystals in form I, II, and III; crystal structures of **bis-SAF** in (c) form I and (d) form III.