Tailoring liquid crystalline self-assembly, the first azulene de Vries materials and a SmA re-entrant phase

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Azulene is a non-alternant isomer of naphthalene and consists of a five-membered and a seven-membered ring showing a zwitterionic resonance structure with a permanent dipole moment. Azulenes electronic and optoelectronic properties make it a potential candidate for a wide range of applications such as near infrared emitters, LCDs and analytical chemistry. Furthermore, azulene-based liquid crystals display self-aligning properties which are favourable for high-performing devices.
The derivatization of the azulene motif starting from 2,6-dibromoazulene is straightforward.[1] The electron-poor seven-membered ring can be substituted with nucleophilic aromatic substitution and a Suzuki-Miyaura coupling can be performed on the electron-rich five-membered ring. Electron-withdrawing (EWG) substituents can be introduced at the lateral position, influencing the electronic structure (Fig. 1a).

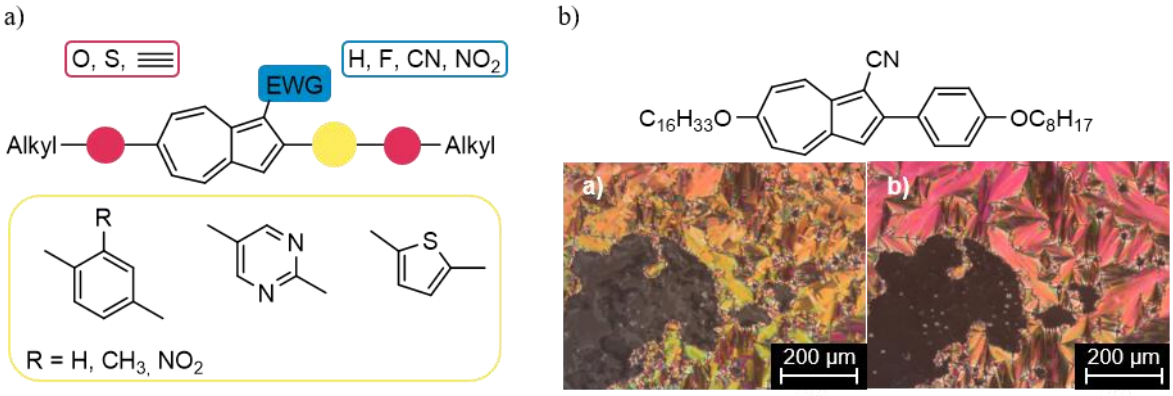

Figure 1. a) The azulene core motif with possible structure modifications and b) SmA re-entrant phase in cooling of derivative ***16O-AzCN-PhO8****.*[1, 2]

The polar aromatic motif of azulene improves translational order in smectic phases which can cause higher-order phases like the soft crystalline SmE phase to occur regularly.[2] One derivative exhibits an orthogonal SmA re-entrance phase below the tilted SmC phase, which has not been observed for achiral calamitic molecules before (Fig.1b). In addition, de Vries behavior with exceptionally small layer shrinkage at the SmA to the SmC transition was observed in some compounds. This could be beneficial in LCDs due to defect formation at the phase transition being prevented.

References

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