Supplementary materials

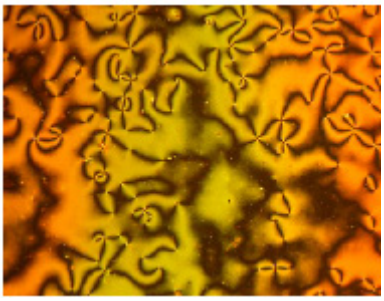


Figure S1. POM image (209 × 158 px) under crossed polarizers of the nemtic phase upon heating of 20 mol % of **I6a /II6a** system at 200 °C.

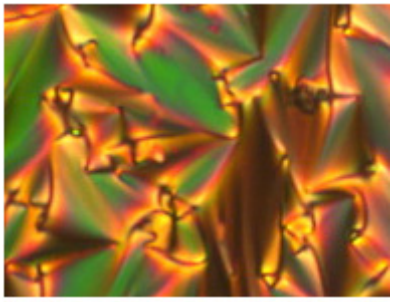
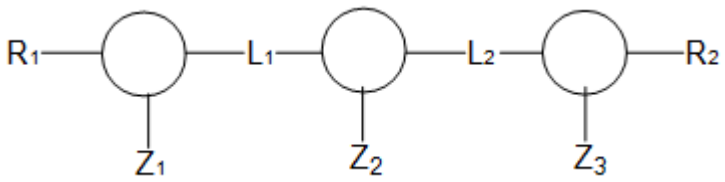


Figure S2. POM image (209 × 158 px) under crossed polarizers of the smectic A phase upon heating of 40 mol % of **III6e /IV6e** system at 120 °C.

Illustration of mechanisms to control mesogenic behaviors:

Most of the rod-like liquid crystalline compounds consist of two or more rings, which are bonded directly to one another or connected by linking groups (L), and may have terminal (R) and lateral (Z) substituents. The chemical structure of many mesogens can be represented by the general formula **1**.



(1)

The rings, represented in **1** by circles, and the linking groups L form the coreof the compound. The core is usually a relatively stiff unit, compared to the terminal substituents, which in most cases are

flexible moieties such as alkyl groups. Thelateral substituents Z are, in most cases, small units such as halogens, methyl group and -CN group. The major anisotropy of the molecules, which is necessary for their mesogenity, results from the cores, which are also the cause of the relatively high melting temperatures. The competition between the clearing temperature and the melting temperature of a compound controls the possibility of observing the mesogenic properties. In principle, anisotropic molecules of all shapes are mesogenic; however, in many cases, because of too high melting temperatures the mesogenic properties cannot be detected. In many of the latter cases the isotropic melts can be supercooled, which offers the possibility of observing monotropic liquid crystalline phases. The systematic decrease in the melting temperatures by the attachment of flexible terminal groups to the cores is therefore very important. Lateral substituents can also have the same effect.

Characterizations:

A Q20 Differential Scanning Calorimeter from TA Instruments Co. was used to conduct the calorimetric experiments (DSC; USA). Using the melting point and enthalpy of indium and lead, the DSC was calibrated. DSC analysis was done on little samples (2–3 mg) in aluminum pans. In an inert atmosphere of nitrogen gas, all measurements were made at a heating rate of 10°C/min, with all transitions being recorded from the second heating scan.

Using a standard polarized optical microscope POM (Wild, Germany) connected to a homemade hot-stage, transition temperatures were verified and the kind of mesophase was identified for all chemicals synthesized.