Control of $Ia\overline{3}d$ Gyroid phase formation in aryloyl-hydrazine-based molecules by using two chemical modifications, introducing the side group and slight non-symmetry into the core moiety

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Control of the formation of $Ia\overline{3}d$ Gyroid phases and their nano-structures is critical to advance Gyroid materials chemistry. In the thermotropic liquid crystalline (LC) systems, antispindle shape favors the $Ia\bar{3}d$ LC phases, where both ends of the molecules, which are slightly expanded as compared to the central portion, causes the packing frustration on the side-by-side arrangement, resulting in the formation of two helical networks of opposite chiralities (ref. 1,2) (Figure 1). We have been investigating how various chemical modifications in the core portion of networks by side-by-side arrangethe aryloyl-hydrazine-based molecules change the thermotropic phase behavior (ref. 3).



Figure 1 Schematic illustration for the formation of two helical ment of antispindle-shaped molecules (ref. 1,2).

In this presentation, we reveal two chemical modifications in the core portion, introducing slight non-symmetry into the core portion (in 2-5) and attaching the methyl side-group (in 3-5), effectively lower and extend the $Ia \ \overline{3} d$ phase regions, and change the core aggregation mode from the double-layered core (in 1 and 2) to the single-layered core modes (in 3-5), as revealed by the X-ray diffraction



Figure 2 Structures and phase transitions of four aryloyl-hydrazine-based molecules 1-5 (R = C₂₂H₄₅) on heating; $I2_13$, the so-called $Im\overline{3}m$ -type chiral phase (ref. 4); Sm, smectic; Colh, hexagonal columnar phase. The electron density maps [green (medium) to red (high)] for the $Ia\overline{3}d$ phases indicate two core aggregation modes.

intensity analyses (Figure 2). We discuss that the methyl group can control and tune the intermolecular cohesive interaction governing the formation of the $Ia\bar{3}d$ LC phases.

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