

Novel H-bonded Bent-core Liquid Crystals and Supramolecular Nanocomposites

Ferroelectric and antiferroelectric liquid crystals become more important due to their fast response of electrooptical properties by applying external electric fields. Because of switchable behavior of the achiral bent-core (banana-shaped) mesogen, the mesomorphic and electrooptical properties of many kinds of bent-core liquid crystals have been intensively studied. Novel banana-shaped hydrogen-bonded liquid crystals and polymers are developed to demonstrate that various smectic phases and ordered alignments of nanoparticles are achieved in their nanocomposites by the template of liquid crystals hosts under ac and dc electric fields.

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The concept of supermolecules bearing noncovalent bond segments (e.g. H-bonds) was investigated and developed because of its functional properties and extensive availabilities by the self-assembled phenomena through molecular recognition between complementary constituents. Interestingly, supramolecular approaches have been employed recently in mesomorphic studies to establish self-assembled molecules, such as H-bonded mesogens. Ferroelectric and antiferroelectric liquid crystals (FLCs and AFLCs) become more important due to their fast response of electrooptical properties by applying external electric fields. Since the first example of the achiral bent-core (banana-shaped) mesogen possessing switchable behavior was explored, many kinds of bent-core liquid crystals have been synthesized to examine their mesomorphic and electrooptical properties.

Previously, novel banana-shaped H-bonded symmetric trimers (with two H-bonds) and asymmetric heterodimers (with one H-bond) were self-assembled by appropriate molar ratios of proton donors (H-donors) and acceptors (H-acceptors). The influences of H-bonded linking positions and aromatic ring num-

bers (4-8 aromatic rings in the rigid cores) as well as the flexible chain lengths on the mesomorphism and the switching behavior of the bent-core supramolecules were evaluated. Except for the supramolecular structures with longer rigid cores or shorter flexible chains possessing the rectangular columnar (Colr or B1) phase, the $SmC_A P_A$ phase was revealed in most supramolecular asymmetric heterodimers and switched to the $SmC_S P_F$ phase by applying electric fields. The polar smectic C phase was dominated for those with H-bonded sites apart from the core center. Interestingly, the SmA and nematic phases were observed in H-bonded asymmetric dimers with H-bonded sites close to the core center, which theoretically proved that the polar smectic C phase was disfavored due to an unfavourable bend angle (smaller than the lower limit of 110°) in the lowest-energy H-bonded conformer. Compared with the fully covalently bonded analogue, lower transition temperatures and lower threshold voltages were developed in the H-bonded asymmetric dimers with the polar smectic C phase, and the existence of polar switching behavior in the polar smectic C phase of asymmetric heterodimers was proven to be associated with their configurations with higher dipole moments and suitable bend

angles.¹

In addition, supramolecular side-chain banana-shaped LC polymer complexes bearing various molar ratios of H- and covalent-bonded bent-core components were acquired by the free radical polymerization, where the H-bonded structures were executed via mixing equimolar portions of proton donor (H-donor) polymers (homopolymers/copolymers) and pyridyl proton acceptor (H-acceptor) bent cores (small molecules). The influences of the molar ratios of bent-core H-bonded components in side-chain banana-shaped LC polymers and their corresponding polymer complexes on mesomorphic and electro-optical properties were first investigated. Surprisingly, a novel enantiotropic polar smectic ($SmCP_A$) phase was introduced in some bent-core side-chain polymer complexes by copolymerization proper molar ratios of bent-core covalent- and H-bonded monomers without the $SmCP$ phase.²

Recently, three analogous bent-core molecules (see Fig. 1), i.e. a H-bonded complex and a covalent-bonded compound with branched siloxane units (**H-SiO** and **C-SiO**, respectively) and a H-bonded complex with an

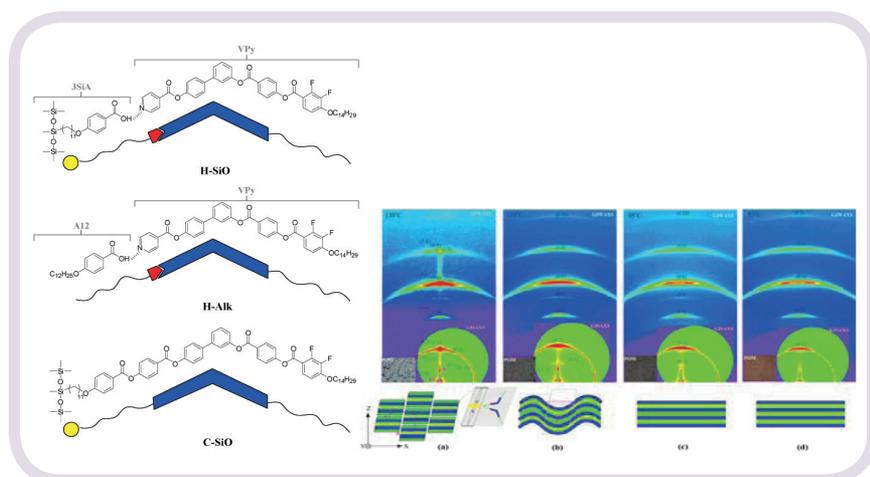


Fig. 1: Chemical structures of the hydrogen-bonded complex and covalently bonded compound with siloxane units (**H-SiO** and **C-SiO**, respectively) and the hydrogen-bonded complex lacking a siloxane unit (**H-Alk**). Combined GISAXS and GIWAXS patterns of the surface-aligned sample of the hydrogen-bonded complex **H-SiO** at various temperatures: (a) modulated ribbon structure (SmCG_2) at 130 °C; (b) undulated bilayer structure (USmCG_2) at 110 °C; (c) bilayer structure (SmCG_2) at 95 °C; (d) monolayer structure (SmCG) at 85 °C. Model: yellow, green and blue lines indicate oligosiloxane units, alkyl chains and aromatic cores, respectively. The light gray part of inset in (a) shows the molecular organization at a side view along the direction **a** (right) and front view along the normal direction of the **a-c** plane (left).³

alkyl unit (**H-Alk**), were investigated the effects of the hydrogen bonding and branched siloxane terminal units on their mesomorphic properties. The covalently bonded compound **C-SiO** and H-bonded complex **H-Alk** exhibited typical SmCP phases; in contrast, H-bonded complex **H-SiO** exhibited a series of general tilt smectic (SmCG) phases with highly ordered layer structures (i.e. SmCG_2P_F - USmCG_2P_A - SmCG_2P_F - SmCGP_F upon cooling). During the SmCG -type phase transition process, a 2D-modulated ribbon structure transferred into highly ordered layers via undulated layers, as the H-bonding strength increased with reduced temperatures. As the SmCG domains were aligned under dc electric fields, a gradual decrease in the leaning angle from ca. 60 to 50 (while the tilt angle kept at ca. 31) could be determined by in situ wide-angle X-ray scattering (WAXS). Combined with Fourier transform infrared and Raman spectroscopic data, our results suggest that the change in the leaning angle was

governed by the competition of the H-bonds and microsegregation of siloxane units within the bilayer structure of the hydrogen-bonded complex **H-SiO**. Besides, the ferroelectric-(antiferroelectric)-ferroelectric transitions proven by the switching current responses in the SmCG -type phases of **H-SiO** reveal that the polar switching occurred through collective rotations around the long axis of **H-SiO**. Therefore, novel SmCG phases with a series of highly ordered 2D-structures were induced by the effects of the H-bonding and branched terminal siloxane unit in the bent-core H-bonded LC complex **H-SiO**.³ Moreover, due to the interaction and alignment of the bent-core LC host **VPy-SiA** under dc/ac electric fields, the well-organized smectic layer packings of surface-modified gold nanoparticles **AuNPs-S** were obtained in nanocomposite **VPy-SiA/AuNPs-S** (see Fig. 2), where the TEM images perfectly match the d-spacing of 5.5 nm obtained in XRD measurements and the ferro- or antiferroelectric properties of nanocom-

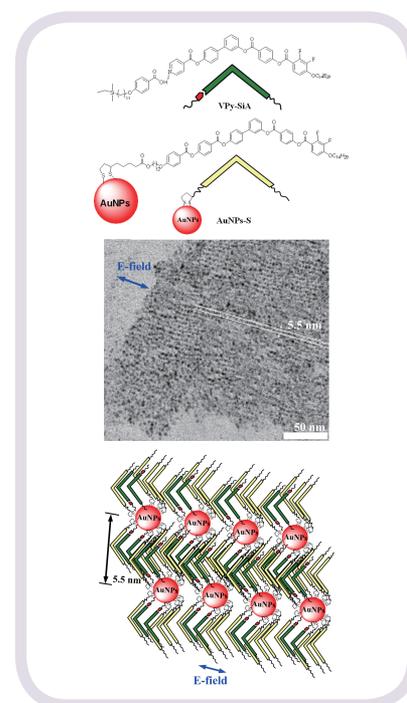


Fig. 2: Chemical structures of the H-bonded bent-core LC host **VPy-SiA** (containing H-bonded acceptor **VPy** and H-bonded donor **SiA**) and the surface-modified gold NPs **AuNPs-S** presenting the covalently bonded bent-core surfactant **S**. TEM morphology shows the smectic layer alignments of gold NPs under electric fields.⁴

posite **VPy-SiA/AuNPs-S** could be adjusted by the concentration of the gold nanoparticles **AuNPs-S**.⁴

Beamlines 17A1, 23A1, and 01C2 PXRD and SWAXS end stations

References

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