

Supramolecular liquid crystals for paintable ferroelectrics

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Recently, we have discovered a novel ferroelectric liquid crystal (ferroelectric columnar LC: FCLC) phase in a self-organized supramolecular system of polar stacks of tapered-paraffinic-wedge molecules based on a phthalonitrile core structure. Its molecular design allows hydrogen bonding among amide groups to connect the umbrella-like conical units of molecules, where the spontaneous polarization is stabilized because phthalonitriles possessing a strong permanent dipole moment are pushed up along the columnar axis by strong binding force of the hydrogen bonding. Unlike the conventional ferroelectrics including the crystalline inorganic solids of barium titanate (BTO) and lead zirconate titanate (PZT), and polymer films of polyvinylidene fluoride (PVDF), supra-molecular LCs easily self-organize into large uniform ferroelectric domains in painted films or LC bulks as well as variety of forms such as nano-/micro-fibers and gels (Fig.1), which makes possible easy-fabrication of devices such as high-density memories, ferroelectric field-effect transistors, and organic photovoltaic cells.

Ferroelectricity in these wet-processed films was visualized with a relatively new nonlinear optical imaging technique, phase-sensitive second-harmonic generation (SHG) microscopy, enabling the mapping of the distribution of the spontaneous polarization as well as its directional sense. Besides, detailed switching behavior of the system was discussed with SHG response together with classical electric measurements. Stabilization mechanism of the spontaneous polarization and molecular dynamics of the ferroelectric switching have been investigated also with a nonlinear optical technique, infrared-visible sum-frequency generation (IV-SFG) spectroscopy which can probe resonant vibrational modes of molecular moieties packed in a non-centrosymmetric manner hereby contributing the ferroelectricity. Hereby this study, we found that both of the phthalonitriles and the amides are responsible for the ferroelectric switching. A plausible molecular dynamics for the ferroelectric response was proposed: the reversal of the hydrogen-bonding through the rotation of the amides and flipping up-and-down of the phthalonitriles are necessarily associated with each other upon a field reversal. These results are very important for further molecular design, particularly towards practical application.

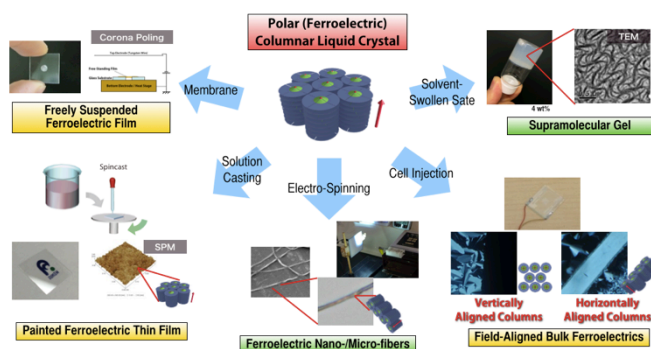


Fig. 1. Various ferroelectric forms created by the FCLC system.

Acknowledgment

Authors are grateful for Shimadzu Corporation, Tokyo Instruments, and Ekspla for technical assistance.

References

1. D. Miyajima, F. Araoka, H. Takezoe, J. Kim, K. Kato, M. Takata, and T. Aida, *Science*, 336, 209 (2012).
2. F. Araoka, S. Masuko, A. Kogure, D. Miyajima, T. Aida, and H. Takezoe, *Adv. Mater.*, 25, 4014 (2013).
3. F. Araoka and H. Takezoe, *Jpn. J. Appl. Phys.*, 53, 01AA01-1 (2014).
4. H. Takezoe and F. Araoka, *Liq. Cryst.*, 41, 393 (2014).
5. F. Araoka, M. Isoda, D. Miyajima, I. Seo, M. Oh-e, T. Aida, and H. Takezoe, to be submitted.