

Supramolecular polymerization in liquid crystalline media enables modular approach to multifunctional core–shell columnar coassembly

Supramolecular polymerization offers an enormous opportunity to develop soft materials with a dynamic, adaptive, reconfigurable, and recyclable nature [1]. These characteristics are derived from noncovalently connected monomeric units that can be associated and dissociated, reversibly triggered by external environments such as heat, light, and chemicals. While recent progress in the field of supramolecular polymerization has been mainly made in solutionphase studies, we were interested in the use of liquid crystalline (LC) phases as media for supramolecular polymerization. When a disk-shaped chiral monomer, OCBDisk_{NH}* (Fig. 1), is noncovalently polymerized in a nematic LC medium comprising rod-shaped molecules of 4-cyano-4'-pentyloxybiphenyl (5OCB) (Fig. 1), the nematic LC phase undergoes "structural order-increasing" mesophase transition into a highly elaborate, single columnar mesophase having a discrete core-shell geometry (Fig. 2(a)) [2].

^{OCB}**Disk**_{NH}* (Fig. 1) is the derivative of a chiral benzenetricarboxamide (BTA), which is known to form one-handed helical supramolecular polymers in solution via amide-mediated triple hydrogen bonds (H-bonds). The hydrocarbon side chains of ^{OCB}**Disk**_{NH}* are appended with an oxycyanobiphenyl (OCB) terminus. This terminal OCB serves as a compatibilizer with 5OCB molecules (Fig. 1), since disks and rods are generally incompatible in coassembly: the former tends to pile up in a face-to-face manner, while the latter tends to orient parallel to one another. Such compatibilizing units are the key to integrating the supramolecular polymer of ^{OCB}**Disk**_{NH}* with the nematic LC medium of 5OCB.

A mixture of OCB DiskNH* and 50CB (molar ratio, 1/6) was heated to its isotropic melting temperature and then allowed to cool, where 50CB is integrated with supramolecularly polymerized ^{OCB}Disk_{NH}*. Figure 2(d) shows the synchrotron X-ray diffraction (XRD) profile obtained at SPring-8 BL44B2. It exhibits sharp and intense peaks in the low-angle region, while the high-angle region exhibits only a broad diffraction peak. This profile can be assigned to a columnar LC phase with a centered rectangular c2mm symmetry. Together with spectroscopic studies, we revealed that each column comprises helical stacks of H-bonded polymeric ^{OCB}Disk_{NH}* in its core, wrapped by a helical shell consisting of self-assembled 5OCB (Fig. 2(a)).



monomers and rod-shaped LC molecules.

Our core-shell columnar LC material showed unique dynamic behaviors in response to an applied electric field (E-field). In contrast to conventional single-component columnar LC phases that are rigid and barely orientable by electrical stimuli, our disk/ rod multicomponent columnar LC material rapidly responded electrically, resulting in unidirectional columnar ordering (Fig. 3(a)). Despite its rapid E-field responsiveness, the unidirectional order was maintained for several days after turning off the applied



Fig. 2. (a, b, c) Schematic representations of the supramolecular polymerization of disk-shaped monomers in LC medium comprising rod-shaped molecules, resulting in a "structural order-increasing" mesophase transition into columnar LC phases with a helical core-shell geometry. (d, e, f) Synchrotron XRD profiles of columnar LC materials with core-shell geometries.

E-field. The columnar orientation could also be redirected between parallel and perpendicular to the direction of applied direct-current (DC) and alternatingcurrent (AC) E-fields, respectively (Fig. 3(a)). Figures 3(b) and 3(c) show two-dimensional XRD profiles obtained at SPring-8 BL45XU, where two distinct diffraction arcs, indexed as the (200) and (400) planes of the rectangular columnar geometry, appeared in the equatorial direction under the DC E-field (Fig. 3(b)), whereas they appeared meridionally under the AC E-field (Fig. 3(c)). These profiles indicate the parallel and perpendicular orientations of the core-shell columns relative to the DC and AC E-field directions, respectively. We proposed that such rapid electrical reorganization occurs through electrical reconstruction, where the LC columns can dynamically dissociate into the core- and shell-forming molecules and reconfigure into the columns in their electrically preferred direction. Note that our core-shell columnar LC material simultaneously exhibits both high structural order and high stimuli responsiveness, which is highly desirable for sophisticated functional materials.

Furthermore, this system is flexible and adaptive enough to incorporate molecules other than 5OCB to form multifunctional core-shell columnar LCs. When this supramolecular polymerization of OCBDiskNH* was carried out in a nematic LC medium composed of a rod-shaped azobenzene derivative, 4-butyl-4'-methoxy azobenzene (BMAB) (Fig. 1), a core-shell columnar LC material with a rectangular geometry, as revealed by XRD at SPring-8 BL44B2, having a photoisomerizable shell was formed (Figs. 2(b) and 2(e)). This modularly obtained columnar mesophase was responsive not only electrically but also optically; it underwent a reversible phase transition between columnar and isotropic phases when photoirradiation was turned off and on. The optoelectrically responsive columnar LC material was incorporated into an LC-based rewritable "AND" logic gate device, where the columnar structure can be guickly reorganized only when the E-field and UV light are simultaneously applied (Fig. 3(d)).

The potential of our modular synthetic approach to multifunctional core-shell columnar LC materials was further extended by utilizing a monomer of ^{NO}Disk_{NH}*, which bears a sterically bulky nitroxyl radical in its side chains (Fig. 1) [3]. Similar to the case of ^{OCB}Disk_{NH}* and 5OCB, the supramolecular polymerization of monomeric ^{NO}Disk_{NH}* in nematic 5OCB afforded a single mesophase with a core-shell columnar geometry (Figs. 2(c) and 2(f)). The columnar orientation of this single LC phase can be redirected electrically and magnetically into parallel and perpendicular directions, respectively, to the applied fields. The abovementioned examples demonstrated that we can easily replace either the core or shell part of the core-shell columnar

LC coassemblies with different molecular components by simple mixing. Such a unique feature is conferred by the multicomponent coassembly of functional molecules by supramolecular polymerization in an LC medium. This design principle will shed light on the exploration of supramolecular soft materials with advanced functions and emergent properties.



Functional Liquid Crystalline Device Logically Operable by E-Field and Light Inputs

Fig. 3. (a) Schematic representations and (b, c) 2D-XRD profiles of electrical reconstruction behaviors of $^{\rm OCB}$ **Disk**_{NH}*/5OCB, where the core-shell LC columns can be oriented parallel and perpendicular to the directions of applied DC and AC E-fields, respectively. (d) Polarized optical micrographs of LC-based optoelectrically rewritable "AND" logic gate operation based on $^{\rm OCB}$ **Disk**_{NH}*/BMAB upon application of a DC E-field and/or upon irradiation with UV light with a lattice-patterned photomask. Dashed squares represent areas exposed to UV light, whereas the entire area was exposed to the E-field.

Keiichi Yano^a, Yoshimitsu Itoh^{a,*} and Takuzo Aida^{a,b}

- ^a Department of Chemistry and Biotechnology,
- The University of Tokyo
- ^bRIKEN Center for Emergent Matter Science/Wako

*Email: itoh@macro.t.u-tokyo.ac.jp

References

- [1] T. Aida et al.: Science 335 (2012) 813.
- [2] K. Yano, Y, Itoh, F. Araoka, G. Watanabe, T. Hikima and
- T. Aida: Science 363 (2019) 161.
- [3] K. Yano et al.: J. Am. Chem. Soc. 141 (2019) 10033.