

Discovery of 'bicontinuous cubic' liquid crystalline mesophase from discotic molecules

Liquid crystalline (LC) semiconductors have attracted increasing attention owing to their potential use in solution-processable and self-repairable organic electronics. Toward this goal, extensive studies have been performed on hexagonal columnar (Col_h) assembly of discotic LC molecules, since their π -stacked columnar arrays are expected to serve in electrical conduction. However, in a practical sense, the macroscopic alignment of such conducting columns with a desired configuration requires much effort to realize. From this point of view, discotic LCs with a bicontinuous cubic (Cub_{bi}) geometry might work, if their three-dimensionally interconnected networks serve as π -electronic channels.

Here, we report that triphenylene (TP) derivatives (Fig. 1(a)) carrying paraffinic side chains with ionic liquid (IL) termini form an LC mesophase with a Cub_{bi} geometry over a wide temperature range including room temperature. In 2005, we reported that 1_{10} (see Fig. 1) forms an LC assembly with a Col_h geometry [1]. The phase sequence upon cooling displayed, after the Col_h mesophase (111–47°C), an optically isotropic phase, which however was not identified because of the lack of clear diffractions obtained in our conventional diffractometer for X-ray analysis (XRD). Recently, we have reinvestigated the phase diagram of 1_{10} using a synchrotron radiation beam (BL02B2 and BL44B2) and found that the optically isotropic phase is not amorphous but an LC mesophase with a Cub_{bi} geometry (Fig. 1(b)) [2]. This unexpected observation prompted us to design 19 new TP derivatives with different paraffinic spacers and IL pendants (Fig. 1(a)). Interestingly, two of them with a long tetradecyl spacer between the TP core and IL pendants, i.e., 1_{14} and 2_{14} , exclusively form a

Cub_{bi} LC mesophase over a very wide temperature range (~200°C).

The optically isotropic phase of 1_{10} at 30°C displayed 14 distinct diffraction peaks in a small-angle region ($2\theta = 1.8$ – 5.6° , Fig. 2(a)). The reciprocal spacing ratios of these diffraction peaks ($\sqrt{6}:\sqrt{8}:\sqrt{14}:\sqrt{16}:\sqrt{20}:\sqrt{22}:\sqrt{24}:\sqrt{26}:\sqrt{30}:\sqrt{32}:\sqrt{38}:\sqrt{42}:\sqrt{46}:\sqrt{50}$) agreed well with those expected for the cubic symmetry with the space group $la\bar{3}d$. Upon heating to 87°C, these peaks disappeared completely, and instead, a set of new diffractions with d -spacings of 17.0, 14.7, and 11.2 Å appeared (Fig. 2(b)). As previously reported [1], these new peaks were indexed as the (110), (200), and (210) diffractions of a Col_h mesophase (Fig. 1(b)). As summarized in Fig. 3, the phase transition behaviors of the other TP derivatives (Fig. 1(a)) on heating were likewise determined by synchrotron radiation XRD analysis. Ten TP derivatives formed a Cub_{bi} mesophase, which in every case appeared in a lower temperature range than the Col_h mesophase. In the comparison of 1_{10} with 1_8 , 1_{12} , and 1_{14} with BF_4^- counterions, note that their phase behaviors are highly dependent on the length of the paraffinic side chains. Compound 1_8 with the shortest side chains among the family showed only a glass-to-isotropic transition (Fig. 3(a)). On the other hand, analogously to 1_{10} , 1_{12} with dodecyl chains exhibited a bicontinuous $la\bar{3}d$ cubic phase, although, in a much wider temperature range (16–160°C, on heating) than that observed for 1_{10} . To our surprise, a further increase in the side-chain length from dodecyl (1_{12}) to tetradecyl (1_{14}) resulted in the exclusive formation of a Cub_{bi} mesophase from 24 up to 221°C. To the best of our knowledge, there are no LC molecules that form a Cub_{bi} mesophase in

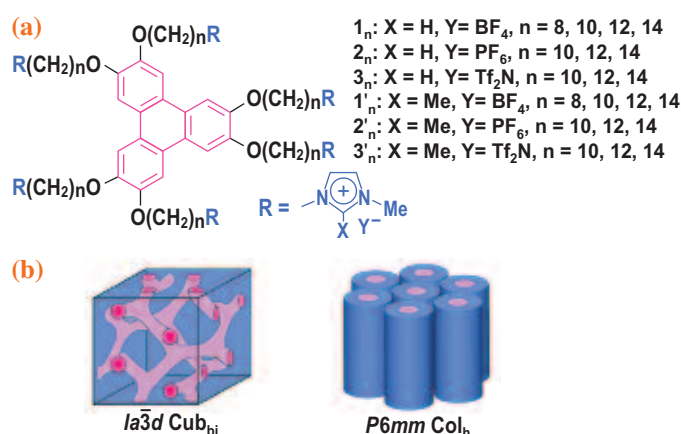


Fig. 1. Schematic structures of (a) imidazolium ion-appended triphenylene derivatives and (b) bicontinuous cubic ($la\bar{3}d$) and hexagonal columnar ($P6mm$) liquid crystalline assemblies.

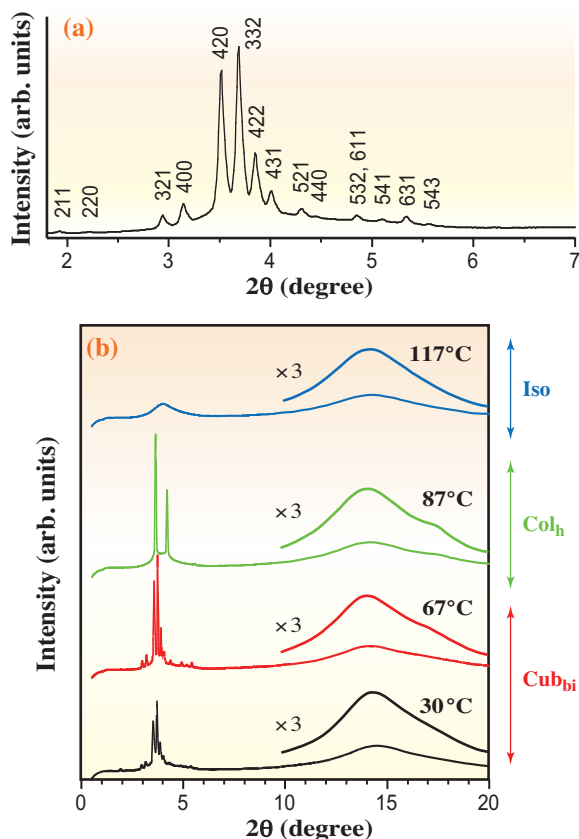


Fig. 2. (a) XRD pattern of 1_{10} at 30°C . The numbers indicate the Miller indices. (b) Temperature-dependent XRD patterns of 1_{10} on heating in 2θ ranges of $0\text{--}20^\circ$. The wavelength of the X-ray was set at 1.08 \AA .

such an extremely wide temperature range ($\sim 200^\circ\text{C}$) from room temperature. When the counteranions were changed from BF_4^- to larger ones such as PF_6^- (2), an essentially identical side-chain dependence of the phase transition emerged, where 2_{14} exclusively formed a Cub_{bi} LC mesophase over a very wide temperature range ($21\text{--}177^\circ\text{C}$, upon heating). Nonetheless, 2_{10} with decyl chains, in contrast to its BF_4^- analogue (1_{10}), did form no LC assembly. When much larger counteranions such as bis(trifluoromethanesulfonyl)imide (Tf_2N^-) were employed, no LC assembly was obtained from 3_{12} with dodecyl side chains, and even 3_{14} with the longest side chains among the family formed not only Cub_{bi} mesophase but also gave Col_{h} mesophase. Nevertheless, as an overall tendency, TP with larger counteranions ($\text{BF}_4^- \rightarrow \text{PF}_6^- \rightarrow \text{Tf}_2\text{N}^-$) requires longer paraffinic side chains (decyl \rightarrow dodecyl \rightarrow tetradecyl) to form the Cub_{bi} mesophase. Having this trend in mind, we also investigated the phase behaviors of $1'\text{--}3'$ with bulkier imidazolium ion pendants than $1\text{--}3$. As shown in Fig. 3(b), only four TP derivatives showed, though not exclusively, the Cub_{bi} LC mesophase. With respect to the effects of paraffinic

side chains and counteranions, the trends observed for $1'\text{--}3'$ appear to be similar to those for $1\text{--}3$. Possibly owing to the larger IL pendants in $1'\text{--}3'$, the formation of the Cub_{bi} LC assembly required much longer paraffinic side chains than that in the case of $1\text{--}3$. Typically, $1'_{10}$ and $2'_{12}$, in contrast to 1_{10} and 2_{12} , showed no Cub_{bi} mesophase, only a Col_{h} mesophase, between the glassy and melt states.

Overall, both Col_{h} and Cub_{bi} LC mesophases are most likely composed of π -stacked TP columns. We consider that (1) the π -stacking of the discotic core and (2) the interionic interaction of IL pendants are two major parameters for determining the phase diagram. When the paraffinic chains are sufficiently long, LC mesophases result, where the core and IL pendants can undergo π -stacking and interionic interactions, respectively. Meanwhile, when the paraffinic chains are rather short, LC mesophases hardly emerge unless the IL pendants are sufficiently small, since the columnar π -stacking of the discotic core is sterically disturbed. Semiconducting Cub_{bi} LC materials, unveiled in the present work, are quite attractive for many applications.

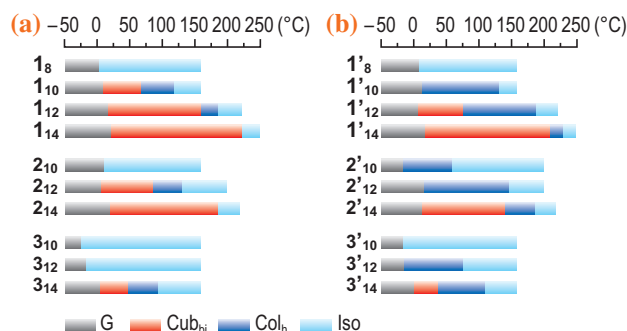


Fig. 3. Phase transition behaviors of imidazolium ion-appended triphenylene derivatives upon heating. G: glass, Cub_{bi} : bicontinuous cubic, Col_{h} : hexagonal columnar, and Iso: isotropic liquid. Compound $1'_{14}$ showed a $Pn\bar{3}m$ cubic-to- $Ia\bar{3}d$ cubic transition at 129°C .

Yohei Yamamoto

Graduate School of Pure and Applied Sciences,
University of Tsukuba

E-mail: yamamoto@ims.tsukuba.ac.jp

References

- [1] J. Motoyanagi *et al.*: Chem. Commun. (2005) 101.
- [2] M.A. Alam, J. Motoyanagi, Y. Yamamoto, T. Fukushima, J. Kim, K. Kato, M. Takata, A. Saeki, S. Seki, S. Tagawa, T. Aida: J. Am. Chem. Soc. **131** (2009) 17722.