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"Bicontinuous Cubic" Liquid Crystalline Materials from Discotic Molecules: A Special Effect of Paraffinic Side Chains with Ionic Liquid Pendants

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Liquid crystalline (LC) semiconductors attract increasing attention due to their potential utility for solution-processable and self-repairable organic electronics. Toward this goal, extensive studies have been made on the hexagonal columnar ($\mathrm{Col_h}$) assembly of discotic LC molecules, since their π-stacked columnar arrays are expected to serve for electrical conduction.[1] However, in a practical sense, macroscopic alignment of such conducting columns with a desired configuration requires further study.[2] From this point of view, discotic LCs with a bicontinuous cubic ($\mathrm{Cub_{bi}}$) geometry might work, if their three-dimensionally interconnected networks serve as π-electronic channels. However, reported studies[3] are highly limited and still in a preliminary stage.

Here we report triphenylene (TP) derivatives (Figure 1a) carrying paraffinic side chains with ionic liquid (IL)[4] termini form an LC mesophase with a $\mathrm{Cub_{bi}}$ geometry[5] over a wide temperature range including room temperature. In 2005, we reported that $\mathbf{1_{10}}$ forms an LC assembly with a $\mathrm{Col_h}$ geometry.[6] The phase sequence upon cooling displayed, after the $\mathrm{Col_h}$ mesophase (111−47 °C), an optically isotropic phase, which however was unidentifiable due to no clear diffractions with our conventional diffractometer for X-ray analysis (XRD). Quite recently, we reinvestigated the phase diagram of $\mathbf{1_{10}}$ using a synchrotron radiation beam and found that the optically isotropic phase is not amorphous but an LC mesophase with a $\mathrm{Cub_{bi}}$ geometry (Figure 1b). This unexpected observation prompted us to design 19 new TP derivatives with different paraffinic spacers and IL pendants (Figure 1a).[7] Noteworthy, two of them, having a long tetradecyl spacer between the TP core and IL pendants ($\mathbf{1_{14}}$ and $\mathbf{2_{14}}$), exclusively form a $\mathrm{Cub_{bi}}$ LC mesophase over a very wide temperature range (∼200 °C). Upon laser flash photolysis, compound $\mathbf{1_{10}}$ in the $\mathrm{Cub_{bi}}$ LC state displayed a transient microwave conductivity (FP-TRMC) comparable to that of a $\mathrm{Col_h}$ LC reference.

The optically isotropic phase of $\mathbf{1_{10}}$ at 30 °C in synchrotron radiation XRD displayed 14 distinct peaks in a small-angle region ($2\theta = 1.8°-5.6°$), along with a broad halo ($2\theta = 12°-19°$) due to the decyl side chains in the molten state. 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 space group $Ia\bar{3}d$ (Figure 1b).[7] 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.[7] As already reported,[6] these new peaks were indexed as (110), (200), and (210) diffractions of a $\mathrm{Col_h}$ mesophase (Figure 1b). Interestingly, the phase sequence of the $\mathrm{Cub_{bi}}$ and $\mathrm{Col_h}$ LC phases,[4a] thus observed, is opposite to those of the reported LC assemblies of discotic molecules.[3]

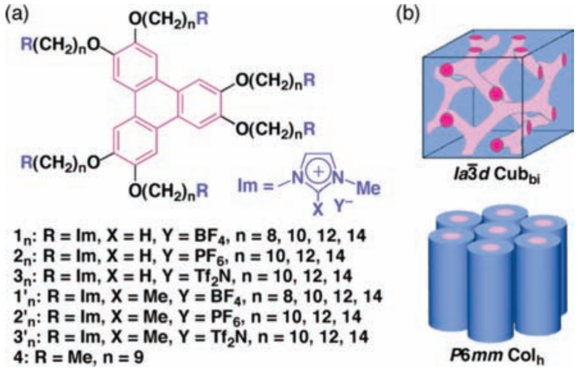

Figure 1. Schematic structures of (a) imidazolium ion-appended triphenylene derivatives (except **4**) and (b) bicontinuous cubic ($Ia\bar{3}d$) and hexagonal columnar ($P6mm$) liquid crystalline assemblies.

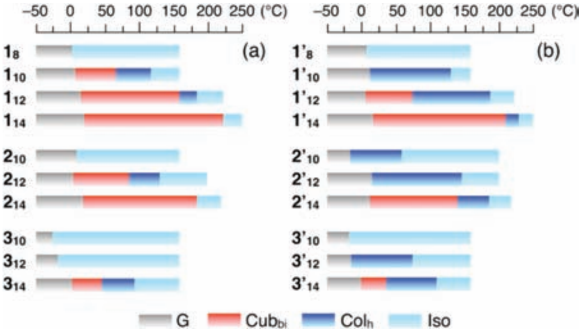

Figure 2. Phase transition behaviors of imidazolium ion-appended triphenylene derivatives on heating. G: glass, $\mathrm{Cub_{bi}}$: bicontinuous cubic, $\mathrm{Col_h}$: hexagonal columnar, Iso: isotropic liquid. Compound $\mathbf{1'_{14}}$ showed a $Pn\bar{3}m$ cubic-to-$Ia\bar{3}d$ cubic transition at 129 °C.[7]

As summarized in Figure 2, phase transition behaviors of other TP derivatives (Figure 1a) on heating were likewise determined by synchrotron radiation XRD in conjunction with differential scanning calorimetry (DSC) and polarized optical microscopy

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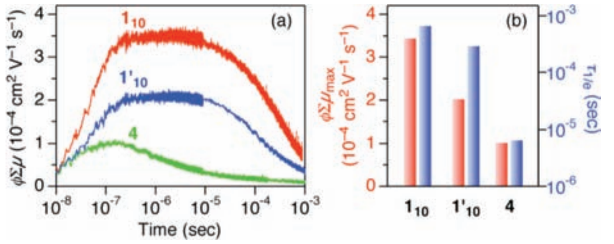

Figure 3. (a) FP-TRMC profiles at 25 °C of $\mathbf{1_{10}}$ (Cub$_{bi}$), $\mathbf{1'_{10}}$ (Col$_h$), and **4** (crystalline). (b) $\phi\Sigma\mu_{max}$ (red) and $\tau_{1/e}$ (blue) of $\mathbf{1_{10}}$, $\mathbf{1'_{10}}$, and **4**.

(POM).[7] Noteworthy, 10 TP derivatives formed a Cub$_{bi}$ mesophase, and in every case, it appeared in a lower temperature range than the Col$_h$ mesophase. In comparing $\mathbf{1_{10}}$ with $\mathbf{1_8}$, $\mathbf{1_{12}}$, and $\mathbf{1_{14}}$ having BF$_4^-$ counterions, one may notice that their phase behaviors are highly dependent on the length of the paraffinic side chains. Compound $\mathbf{1_8}$ with the shortest side chains among the family showed only a glass-to-isotropic transition (Figure 2a).[7] On the other hand, analogous to $\mathbf{1_{10}}$, compound $\mathbf{1_{12}}$ with dodecyl chains exhibited a bicontinuous $Ia\bar{3}d$ cubic phase, though, over a much wider temperature range (16−160 °C, on heating) than that observed for $\mathbf{1_{10}}$. To our surprise, further increase in the side-chain length from dodecyl to tetradecyl resulted in the exclusive formation of a Cub$_{bi}$ mesophase from 24 up to 221 °C.[7] To the best of our knowledge, no LC molecules have been reported that form a Cub$_{bi}$ mesophase over such an extremely wide temperature range (∼200 °C) from room temperature. When the counteranions were changed from BF$_4^-$ to a larger one such as PF$_6^-$ (**2**), an essentially identical side-chain dependency for the phase transition emerged, where $\mathbf{2_{14}}$ exclusively formed a Cub$_{bi}$ LC mesophase over a very wide temperature range (21−177 °C, on heating). Nonetheless, $\mathbf{2_{10}}$ with decyl chains, in contrast with its BF$_4^-$ analogue ($\mathbf{1_{10}}$), does not form an LC assembly. When much larger counteranions such as bis(trifluoromethanesulfonyl)imide (Tf$_2$N$^-$) were employed, no LC assembly was obtained from $\mathbf{3_{12}}$ carrying dodecyl side chains, and even $\mathbf{3_{14}}$ with the longest side chains among the family was unable to form only a Cub$_{bi}$ mesophase but also gave a Col$_h$ mesophase. Nevertheless, as an overall tendency, TP with larger counteranions (BF$_4^-$ → PF$_6^-$ → Tf$_2$N$^-$) requires longer paraffinic side chains (decyl → dodecyl → tetradecyl) to form the Cub$_{bi}$ mesophase. With this trend in mind, we also investigated the phase behaviors of $\mathbf{1'{-}3'}$ carrying bulkier imidazolium ion pendants than those of $\mathbf{1{-}3}$. As shown in Figure 2b, only 4 TP derivatives displayed, though not exclusively, a Cub$_{bi}$ LC mesophase. With respect to the effects of paraffinic side chains and counteranions, the trend observed for $\mathbf{1'{-}3'}$ appears to be similar to those for $\mathbf{1{-}3}$. Possibly due to the larger IL pendants in $\mathbf{1'{-}3'}$, the formation of the Cub$_{bi}$ LC assembly required much longer paraffinic side chains than in the case of $\mathbf{1{-}3}$. Typically, $\mathbf{1'_{10}}$ and $\mathbf{2'_{12}}$, in contrast to $\mathbf{1_{10}}$ and $\mathbf{2_{12}}$, did not display a Cub$_{bi}$ mesophase but only a Col$_h$ mesophase between the glassy and melt states.

Unlike reported Cub$_{bi}$ assemblies of discotic LC molecules,[3] the Cub$_{bi}$ assemblies of some of the TP derivatives showed a diffraction peak with a d-spacing of ∼3.5 Å,[7] which is rather broad but suggests the presence of π-stacked TP columns in the Cub$_{bi}$ mesophase. To explore if Cub$_{bi}$ LC assemblies of π-conjugated molecules have the potential for carrier transport, we measured FP-TRMC profiles of $\mathbf{1_{10}}$ at 25 °C.[7] This electrodeless method not only allows for comparison of Cub$_{bi}$ with Col$_h$ in terms of transient conductivity but also excludes a possible contribution of ion conduction due to a high resonant frequency (∼9.1 GHz) of the microwave employed.[8] As shown in Figure 3, the Cub$_{bi}$ LC mesophase of $\mathbf{1_{10}}$ indeed displayed a TRMC signal, where the maximum transient conductivity ($\phi\Sigma\mu_{max} = 3.5 \times 10^{-4}$ cm^2 V^{-1} s^{-1}) was comparable to that of the Col$_h$ mesophase of $\mathbf{1'_{10}}$ (2.0×10^{-4} cm^2 V^{-1} s^{-1}) and even better than that of a crystalline sample of nonionic **4** (Figure 1a, $\phi\Sigma\mu_{max} = 1.0 \times 10^{-4}$ cm^2 V^{-1} s^{-1}). Of further interest to note is that the charge carriers, generated in these Cub$_{bi}$ and Col$_h$ mesophases, were long-lived, with lifetimes ($\tau_{1/e}$ = 0.64 and 0.27 ms for $\mathbf{1_{10}}$ and $\mathbf{1'_{10}}$, respectively) 2 orders of magnitude longer than that of **4** (0.004 ms) (Figure 3b). We have reported that paraffinic ester side chains show a similar elongation effect on carrier lifetime.[9]

Overall, both Col$_h$ and Cub$_{bi}$ LC mesophases are most likely composed of π-stacked TP columns. We consider that (1) π-stacking of the discotic core and (2) interionic interaction of the IL pendants are two major parameters to determine 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 columnar π-stacking of the discotic core is sterically disturbed. While better understanding of the phase behaviors of the TP derivatives awaits further studies, semiconducting Cub$_{bi}$ LC materials, unveiled in the present work, are quite attractive for many applications, considering their extremely wide temperature windows and capability of forming long-lived charge carriers.

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Supporting Information Available: Materials and methods, XRD, DSC, and POM data. This material is available free of charge via the Internet at http://pubs.acs.org.

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