

Discotic ionic liquid crystals as excellent dispersants for single-walled carbon nanotubes

A variety of soft electrical conductors have been developed by doping carbon nanotubes (CNTs) into organic and polymeric materials, where better electrical properties are realized by the dispersion of a larger amount of CNTs. Recently, liquid crystalline (LC) materials have attracted increasing attention for hybridization with CNTs, since LC materials have the potential to orient CNTs for anisotropic electrical conduction. However, the reported LCs possess rather low miscibility with pristine CNTs of less than 0.01 wt%. Here we report that discotic ionic liquid crystals (ILCs) of triphenylene (TP) derivatives, ILC_{col} and ILC_{cub} (Fig. 1(a)) [1,2] bearing six imidazolium ion pendants, serve as excellent dispersants for pristine single-walled CNTs (SWNTs) [3]. The resultant composite materials can maintain their LC properties up to the SWNT content of ~8 wt%, which is 2–3 orders of magnitude greater than those reported previously. Of further interest, the ILC composites, when sheared, display anisotropic conducting properties, since SWNTs are oriented along the shear direction. This orientation is kept for at least half a year.

In 2003, we reported that imidazolium ion-based ionic liquids (ILs), when being ground with SWNTs, are transformed into physical gels (bucky gels), where SWNTs are highly dispersed by a p-cation/p-electronic interaction and eventually form a 3D network structure associated with an interionic interaction of ILs [4]. As reported previously [1,2], the discotic ionic liquid crystals ILC_{col} and ILC_{cub} (Fig. 1(a)), utilized for the present study, assemble into hexagonal columnar (Col_h , 134–18°C on cooling) and cubic (Cub, 221–18°C on cooling) mesophases, respectively, over a

wide temperature range including room temperature [2].

As a typical example of the hybridization of ILCs with SWNTs, pristine HiPco SWNTs were added at 150°C to ILC_{col} (isotropic melt) with an SWNT content of 5 wt%, and the mixture was ground with a pestle for 30 min (Fig. 1(b)), whereupon it turned to a viscous black paste (Fig. 1(b), inset). As observed by optical and cross-sectional transmission electron microscopy, only a very small amount of SWNT agglomerates was detected in the black paste. Similar black pastes were obtained when the SWNT contents employed were in the range of 3–15 wt%. However, upon further increase in the doping level to 30 wt%, the mixture lost its fluidity and became semisolid. Although doped SWNTs affected the phase diagram of ILC_{col} to a certain extent, the LC clearing temperature decreased only by 18°C (134 → 116°C) when ILC_{col} was doped with even 5 wt% SWNTs. Likewise, SWNTs dispersed very well in ILC_{cub} , where the resulting composite again displayed only a marginal decrease in the LC clearing temperature (221 → 205°C on 5 wt% SWNT doping). Of interest, the effects of doped SWNTs on the X-ray diffraction (XRD) profiles of ILC_{col} and ILC_{cub} , observed at **BL44B2**, were essentially different from one another (Fig. 2). In the case of ILC_{cub} , as the doping level of SWNTs was higher, the diffraction peaks shifted toward a lower 2θ region (Fig. 2(b), inset). In contrast, the diffraction peaks of ILC_{col} hardly shifted upon increment of the content of SWNTs (Fig. 2(a), inset). These contrasting observations indicate that ILC_{cub} incorporates SWNTs into its cubic lattice, whereas ILC_{col} prefers to maintain its original 2D hexagonal lattice without incorporating SWNTs.

In the course of the above studies, we noticed that the discotic LC columns of ILC_{col} , upon being doped with SWNTs, align homeotropically with respect to the substrate surface, while SWNTs are randomly oriented just as they are in the isotropic melt. However, a shear treatment of the ILC/SWNT composites induces a horizontal orientation of SWNTs with respect to the substrate surface. Accordingly, shear treatment in combination with annealing gave rise to three different states **States 1–3** in terms of the orientations of the LC columns and SWNTs (Fig. 3). Namely, the ILC_{col} /SWNT composite, upon shear treatment, gave **State 1**, where both LC columns and SWNTs were coaxially oriented horizontally with respect to the glass plates. Subsequent short annealing of the sheared composite for 5 min gave **State 2**, where the LC columns were oriented homeotropically, while maintaining the horizontal orientation of SWNTs. Further annealing

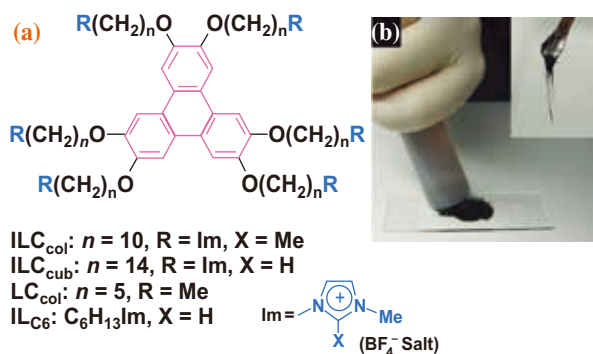


Fig. 1. (a) Molecular structures of ionic liquid crystals ILC_{col} and ILC_{cub} , together with those of nonionic liquid crystal LC_{col} and monovalent ionic liquid ILC_6 as references. (b) Pictures of an ILC_{col} /SWNT composite.

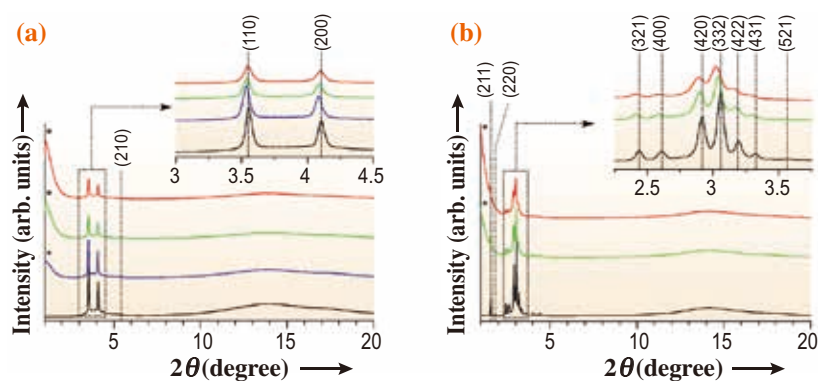


Fig. 2. XRD patterns (25°C) of ILC_{col} (a) and ILC_{cub} (b) alone (black), and their composites doped with 1 (blue), 3 (green), and 5 (red) wt% SWNTs. An X-ray beam with a wavelength of 1.08 Å was used. The asterisked diffraction at $2\theta < 2$ degrees in each XRD pattern is due to scattering by SWNTs.

of the composite for 1 h gave **State 3**, where SWNTs were oriented randomly in the homeotropically oriented LC columns. The horizontal orientation of SWNTs, once generated by the shear treatment, was maintained for at least half a year at room temperature unless the material was heated. Namely, thermal reorientation of SWNTs occurs much less rapidly than that of the LC columns.

The orientation of SWNTs is a dominant factor for charge-carrier transport properties of the ILC_{col} /SWNT composite (Fig. 3). When ILC_{col} doped with 1 wt% SWNTs was sandwiched by indium tin oxide

(ITO) electrodes, the DC conductivity across the film at 25°C in **State 1** (red circles) was nearly two orders of magnitude smaller than that in **State 3** (black squares). In contrast, **State 1** and **State 2** (blue rhomboids) were comparable to one another in terms of DC conductivity, indicating a negligibly small contribution of the LC columns to the observed conduction profile. On the other hand, at higher doping levels of SWNTs (3 and 5 wt%), the three states showed a much smaller difference (~20 times) in their DC conductivities, possibly owing to an increased probability of carrier hopping between SWNTs.

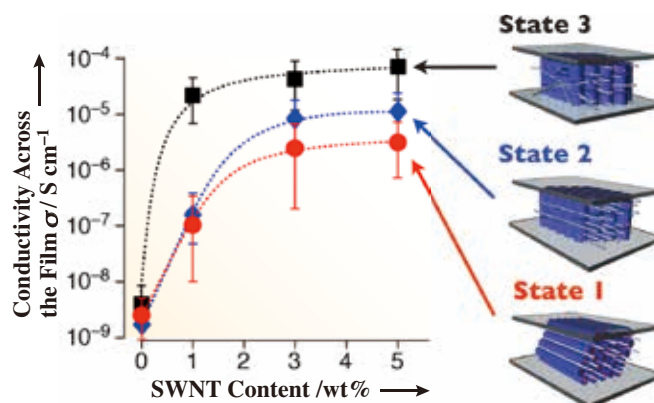


Fig. 3. Plots of conductivities across the film of States 1–3 at 25°C of ILC_{col} films doped with 0, 1, 3, and 5 wt% SWNTs, sandwiched by ITO electrodes with a separation of 12.5 μm.

Jeongho Jay Lee^a and Yohei Yamamoto^{b,*}

^aDepartment of Chemistry and Biotechnology, The University of Tokyo

^bDivision of Materials Science and TIMS, University of Tsukuba

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*Email: yamamoto@ims.tsukuba.ac.jp