Organization of single-walled carbon nanotubes wrapped with liquid-crystalline π-conjugated oligomers

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Received 17th October 2008, Accepted 28th November 2008
First published as an Advance Article on the web 22nd January 2009
DOI: 10.1039/b818352j

Two oligo(phenylenevinylene)s with cyanobiphenyl terminates were synthesized as non-covalent modifiers of single walled carbon nanotubes (SWNTs). The wrapping of SWNTs with synthesized oligomers enhanced the dispersibility in $CHCl_3$ by the dissociation of SWNT bundle structures. It was found that the addition of oligomers caused self-organized precipitation from a homogeneous dispersed solution of SWNT complexes. The self-organized precipitates exhibited thermotropic liquid-crystalline properties.

Introduction

Carbon nanotubes have received special attention owing to their unique mechanical and electronic properties.[1] Single-walled carbon nanotubes (SWNTs) are one-dimensional nanoscopic seamless fibers with diameters ranging from 0.7 nm to 5 nm and lengths of several micrometers; moreover, depending on their chirality and diameter, they can be metallic, semiconducting, or insulating.[2] The precise manipulation of SWNTs can create nanoscopic devices and circuitry as a result of their strong anisotropy of conductivity.[3] However, a strong intertube interaction among SWNTs results in the formation of insoluble aggregates. Non-controllable aggregation makes it difficult to manipulate and process them. Much effort has therefore been invested in recent years to improve their processability.[4] SWNTs have been modified by three methods: first, covalent functionalization of carboxylic acids with alcohols or primary amines at the open ends and side walls of SWNTs after oxidation; second, chemical modification of sidewalls by means of reactions such as nucleophilic substitutions and the addition of radicals on the sidewalls of SWNTs; and third, non-covalent functionalization of sidewalls with organic polymers and surfactants. The disadvantage of covalent modification is that the electronic and mechanical properties of SWNTs are altered by their partial destruction. In contrast, the non-covalent functionalization on the sidewalls of SWNTs with organic molecules through van der Waals or π–π interactions can modify their chemical and physical properties and improve their processability while still preserving their SWNT structure. Furthermore, this approach can also realize the possibility of being able to organize SWNTs into hierarchical molecular systems through controlled assembly processes of adsorbed organic molecules.

Many approaches to obtain large-scaled alignments of SWNTs, such as gas flow, liquid flow, magnetic/electronic fields, Langmuir–Blodgett, and layer-by-layer assembly, have been developed in recent years.[5] The alignment of carbon nanotubes can also be achieved by using liquid crystalline properties.[6] Song and Windle reported on lyotropic liquid-crystalline behavior of surface-treated multi-walled carbon nanotubes in acidic aqueous solution.[7] Dierking *et al.* reported orientation control of carbon nanotubes by dispersing them within nematic liquid crystals.[8] In the present study, we focus on the dynamic changes of organizations including SWNTs by exploiting the liquid crystalline properties of organic hosts. It was found that when SWNTs are dispersed into the thermotropic liquid-crystalline hosts, the self-organization of the hosts induces alignment of dispersed SWNTs and the alignment can be controlled by applying an external electric or magnetic field. This alignment control of SWNTs can switch the electronic conductivity by dynamically changing the orientation of SWNTs. In this context, we designed and synthesized novel liquid crystalline hosts **1** and **2** composed of oligo(phenylenevinylene) segments and cyanobiphenyl terminates, and we studied the formation of supramolecular complexes and the possibility of processing new classes of highly ordered nanostructured composite materials including SWNTs.

Results and discussion

Conjugated polymers such as poly(*m*-phenylene-*co*-*p*-phenylenevinylene)s (PmPV)[9] and poly(aryleneethynylene)s[10] interact with the sidewalls of carbon nanotubes (CNTs) and form stable dispersions of complexes in solvents. The *meta*-linkage in PmPV leads to dihedral angles in the chain and the conjugated polymer chain tends to form helical structures. The helical conformation of PmPV allows inclusion of CNTs through π–π interactions between the curved surface of CNTs and PmPV.[9] In this study, we focused on the repeating unit of PmPV and designed π-conjugated oligo(phenylenevinylene)s (OPVs) **1** and **2** as non-covalent modifiers of SWNTs (Scheme 1). The π-conjugated OPV segment was intended to interact non-covalently with the aromatic sidewall of SWNTs, and cyanobiphenyl terminates were designed to promote a spontaneous organization of complexes. OPVs **1** and **2** were synthesized by the coupling reaction of two precursors. Precursor **3** was synthesized by

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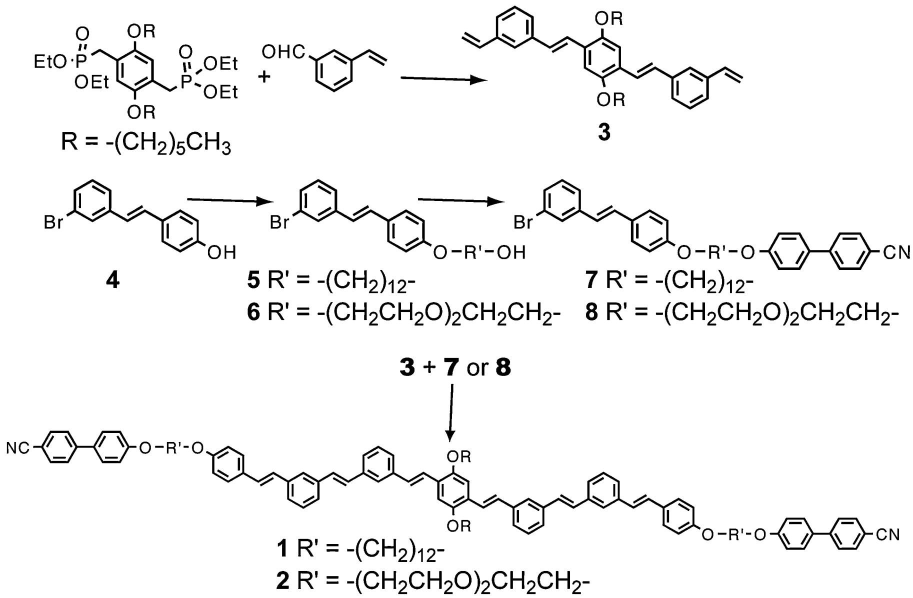

Scheme 1

a Wittig–Horner coupling reaction of a phosphonate and 3-vinyl benzaldehyde.[11] The other precursors **7** and **8** were synthesized in three steps. The phenol group in **4**, which was synthesized through a Wittig–Horner coupling reaction of diethyl (3-bromobenzyl)phosphonate with 4-acetoxy benzaldehyde and hydrolysis of the acetoxy group, was reacted with 12-bromodecan-1-ol or 2-[2-(2-chloroethoxy)ethoxy]ethanol in the presence of K_2CO_3. The obtained products **5** and **6** were subsequently converted to **7** and **8** by performing a Mitsunobu reaction with 4-cyano-4′-hydroxybiphenyl using DEAD. In the final step, a Heck coupling reaction of **3** with **7** and **3** with **8** gave target compounds **1** and **2**. Both compounds **1** and **2** were fully characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, and MALDI-TOF-MS spectroscopy. The precursors and target compounds exhibit an IR absorption band around 960nm arising from wagging vibration of the *trans*-configured double bonds. UV-Vis spectra of **1** and **2** show two broad absorption bands at $\lambda_{max} = 308$ and 392 nm in CHCl$_3$ solution (Fig. 1). Compounds **1** and **2** exhibited a fluorescence band at 450 nm with a shoulder peak at 475 nm. The absorption and fluorescence spectra are quite different from those of linear OPVs,[12] suggesting the short π-system due to the *meta*-linkage of the OPV segment in **1** and **2**.

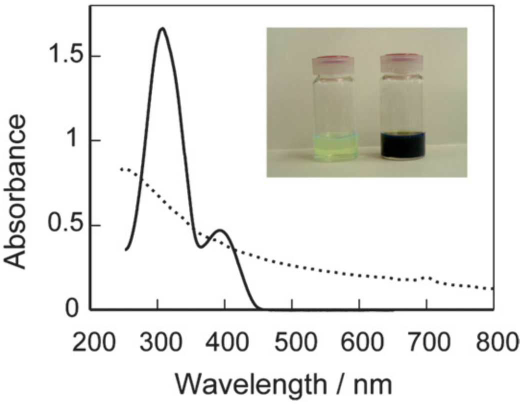

Fig. 1 UV-Vis spectra for **1** (solid line) and **1**-SWNTs complex (dotted line) in CHCl$_3$. The inset shows a photograph of CHCl$_3$ solutions of **1** and **1**-SWNTs complex.

To prepare the complexes **1**-SWNTs and **2**-SWNTs,[13] SWNTs were added to a solution of the oligomers **1** or **2** in CHCl$_3$, the mixture was sonicated for 1 h and the resulting suspension was centrifuged. The dark supernatant was carefully decanted and the isolated suspension was filtered through a 200 nm pore diameter PTFE membrane and washed with CHCl$_3$ to remove excess oligomers. The removal of oligomers was monitored by measuring the fluorescence of the filtrate. Washing of the black residue on the membrane with CHCl$_3$ and drying under vacuum yielded the **1**-SWNTs and **2**-SWNTs complexes. The complexes were peeled away from the PTFE membrane and added to 10 ml of CHCl$_3$, followed by sonication for 10 min to disperse the complexes. The complexes can be dispersed again into organic solvents such as CHCl$_3$, CH$_2$Cl$_2$ and THF by sonication and the dispersed solutions are stable over a period of several months. It was found that it is possible to produce a homogeneous and stable suspension of SWNTs by using **1** and **2** even after removal of the excess free oligomers (Fig. 1 inset). This finding indicates that the adsorbed oligomers do not desorb from the surface of SWNTs and that the non-covalent wrapping of SWNTs with conjugated oligomers prevents reaggregation of SWNTs into large bundles.

Fig. 1 also shows the UV-Vis spectra of **1** and **1**-SWNTs complex in CHCl$_3$. The solution of the **1**-SWNTs complex showed a broad absorption band from 250 nm to 800 nm together with a broad absorption band around 330 nm corresponding to **1** adsorbed onto SWNTs. The broad absorption around 600 and 800 nm reveals the band-to-band transition of pure SWNTs[14] and the shift and broadening of the absorption bands for **1** in the **1**-SWNTs complex can be ascribed to the π–π interactions between the SWNTs and the OPV segment in **1**.[9] The solubilities of SWNTs in the presence of **1** or **2** were estimated from the absorbance at 700 nm by using the reported specific extinction coefficient for SWNTs at 700 nm, $\varepsilon_{700} = 2.35 \times 10^4$ cm^2 g^{-1}.[15] The solubilities of SWNTs wrapped with **1** and **2** are 760 and 720 mg L^{-1}, respectively. Although the solubility of SWNTs wrapped with PmPV is reported to be about 100 mg L^{-1}, the short OPV segments in **1** and **2** make the insoluble SWNTs highly soluble in $CHCl_3$ through the stable adsorption of numerous discrete modifiers onto the side walls of SWNTs. The contents of oligomers in the complexes were determined by thermogravimetric analyses (TGA), which provided the weight fraction of organic oligomers in the complexes.[16] While the TGA profile of the free **1** showed a weight loss of 59% under a nitrogen atmosphere at 550 °C, the observed weight loss of the **1**-SWNTs complex was 23%. From the TGA analyses, the amounts of **1** and **2** in the complexes were found to be 39 and 40%, respectively.

The fluorescence of **1** was quenched completely by the formation of a complex with SWNTs.[9] The fluorescence quenching is likely to be the result of photoinduced energy or electron transfer between the excited conjugated oligomers and the SWNTs, as previously reported for other complexes with π-conjugated molecules and polymers as non-covalent modifiers.[4,9,10] The ^{1}H NMR spectrum of the **1**-SWNTs complex in $CDCl_3$ indicates significant broadening in the resonances for protons of **1**, suggesting the presence of conductive SWNTs and ferromagnetic catalysts.[17] Furthermore, the proton resonances of phenylene and vinyl units in the OPV segment are shifted up-field compared with those of free **1**. Similar changes have been observed in non-covalent functionalizations of SWNTs with PmPV.[9] The florescence quenching and the ^{1}H NMR spectral change suggest that the OPV segment in **1** interacts strongly with SWNTs through the intermolecular π–π interactions. The flexible side chains in **1** and **2** adsorbed onto the surface of SWNTs result in the stable and homogeneous suspension of nanotubes in organic solutions. Fig. 2 shows the Raman spectra for the **1**-SWNTs complex obtained with a laser excitation wavelength of 514 nm. Raman spectroscopy of the complexes showed D- and G- bands at 1338 and 1590 cm^{-1}, respectively.[18] The peak positions of the D- and G-bands for the complexes remained unaltered from those for only SWNTs powder. The Raman intensity ratio between the G-band and the D band in the **1**-SWNTs complex is lower than that for SWNTs only, indicating a lack of chemical and physical damage to SWNTs and a low level of impurities. The radial breathing mode (RBM) for the **1**-SWNTs complex, which is related to the diameter of SWNTs or the formation of bundle structures, can be resolved as shown in Fig. 2. Although there are no peaks for **1** in the RBM region, the frequency in the RBM of SWNTs revealed a 6 cm^{-1} shift compared to that of SWNTs powder. This frequency shift in the RBM provides evidence of the dissociation of bundle structures by the functionalization of SWNTs with **1**.[19]

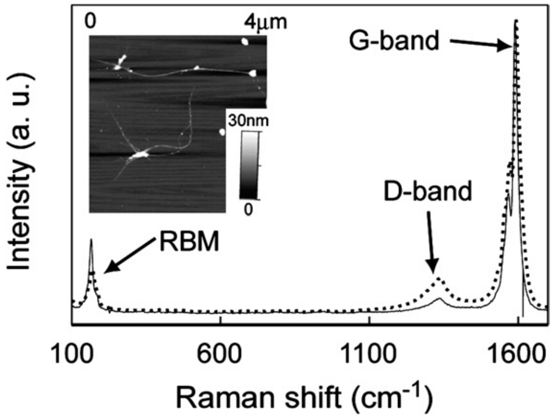

Fig. 2 Raman spectra for **1**-SWNTs complex (solid line) and SWNTs powder (dotted line). The inset shows the AFM image of **1**-SWNTs complex on mica.

We have investigated the structure of **1**-SWNTs complex by atomic force microscopy (AFM) and transmission electron microscopy (TEM). An AFM image of the **1**-SWNTs complex prepared by spin evaporation of one drop of its dispersion on mica shows small SWNT ropes with an average height of about 3.0nm and a length of several micrometers as shown in the inset of Fig. 2. A TEM image of **1**-SWNTs complexes on a TEM grid also reveals well-separated SWNT bundles. The average diameter of SWNTs in the TEM image was determined to be about 1.4 nm, which is almost coincident with the diameter of typical SWNTs. The AFM and TEM images are similar to those observed in dispersed solutions of SWNTs wrapped with non-covalent modifiers such as conjugated polymers and amphiphilic biopolymers.[9,20] These images indicate that the individual SWNT strands are twisted into the observed small ropes and these ropes are partially covered with organic molecules. From these results, we conclude that the sonication of SWNTs in $CHCl_3$ in the presence of **1** or **2** diminishes the aggregations among SWNTs by the covering of single SWNTs or small SWNT ropes with **1** or **2** in organic solvents.

Self-organization properties among mesogenic units in **1** and **2** coating the exterior surfaces of SWNTs can be used to control the alignment of SWNTs within the organizations. Whereas the dispersions of SWNTs wrapped with **1** or **2** are stable, the

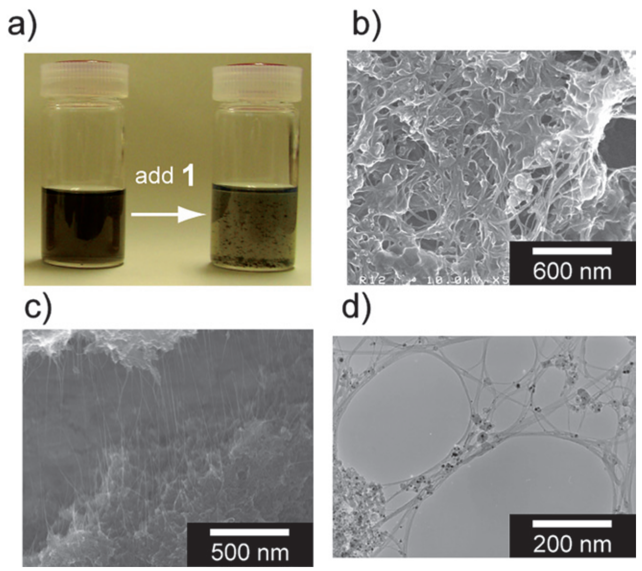

Fig. 3 A photograph of precipitate formation caused by the addition of **1** into a homogeneous dispersion of **1**-SWNTs complex (a), SEM (b and c) and TEM (d) images of the isolated precipitate.

addition of excess oligomers into the dispersed solution induces the formation of aggregates (Fig. 3a). When **1** (5.0 mg) was dissolved into the dispersion of **1**-SWNTs complex (1.0 mg) in 1.0 ml $CHCl_3$, a black precipitate slowly formed and settled out of the solution. No solid formed upon the addition of 4-cyano-4′-*n*-pentylbiphenyl (5CB) and oligo(phenylenevinylene) lacking the terminate cyanobiphenyl segments into the dispersion. The content of **1** within the precipitate, analyzed by TGA, was about 70 wt%. Scanning electron microscopy (SEM) images of the precipitate reveal three-dimensional aggregates composed of SWNT ropes whose diameters are in the range 10–50 nm (Fig. 3b). The SEM image of the edge of the precipitate clearly shows that the precipitate contains numerous nanotubes as shown in Fig. 3c. The TEM image of the precipitate shows an extensive network structure of *ca.* 5 nm diameter SWNT ropes (Fig. 3d). The SWNT ropes in the network structure show bundles of individual SWNTs, which are highly aligned with the rope axis. These observations suggest that the additional liquid-crystalline oligomers act as a glue among complexes and the addition of the glue leads to the organization of SWNTs complexes through the interaction among mesogenic units.

A differential scanning calorimetry (DSC) thermogram of **1** was measured by heating and subsequent cooling over the range of 0 to 170 °C; it showed that **1** exhibited two endothermic peaks at 87 and 152 °C, corresponding to the phase transition from crystalline to liquid crystalline and the isotropic transition, respectively. When the isotropic liquid of **1** was cooled slowly, the birefringent optical texture appeared in the range of 80 to 150 °C under the temperature-controlled polarized optical microscope (TPOM) as shown in Fig. 4a. This focal-conic fan-shaped texture of **1** in the mesophase corresponds to a smectic liquid-crystalline phase. The precipitate, which was obtained from the homogeneous dispersion of **1**-SWNTs complex by the addition of **1**, also exhibited two DSC peaks at 82 and 153 °C. These transition points are almost the same as those of **1**. The TPOM image for the precipitate sample showed a birefringent optical texture consisting of numerous fibrous assemblies in the same temperature range (Fig. 4b), and the texture disappeared above 153 °C. The film was homogeneous and the aggregates of SWNTs were not observed during heating to 200 °C under optical microscopy, indicating the stable dispersion of SWNTs within the liquid crystalline host **1**. The XRD patterns at 120 °C remained unaltered in **1** and the **1**-SWNTs complex ($d = 3.61$, 1.86, and 0.87 nm), suggesting that the inclusion of SWNTs within the liquid-crystalline **1** does not affect its self-organized structure. The other oligomer **2** with triethylene glycol spacers between the phenylenevinylene segment and cyanobiphenyl terminates exhibited a glass transition temperature around 45 °C, a broad exothermic peak around 120 °C, and an endothermic peak at 138 °C upon heating (Fig. 4c), and **2** did not show any optical texture from room temperature to 140 °C under TPOM. On the other hand, the precipitate composed of SWNTs and **2** shows a sharp exothermic peak at 94 °C as well as a glass transition at 45 °C and a melting point at 141 °C. The sharp exothermic peak suggests that the mixing with SWNTs enhances the long-range organization of non-liquid-crystalline molecule **2**. A similar DSC change was observed in the case of composite gels composed of ionic liquids and SWNTs reported by Fukushima *et al.*[21] Interestingly, TPOM of this precipitate revealed a birefringent texture in the range of 96–141 °C (Fig. 4d) and fibrous assemblies containing SWNTs in a rapidly cooled sample were observed by SEM (Fig. 4e). Thus, the synthesized phenylenevinylene oligomers with cyanobiphenyl terminates can organize SWNTs with a high aspect ratio into micrometer-sized fibrous assemblies.

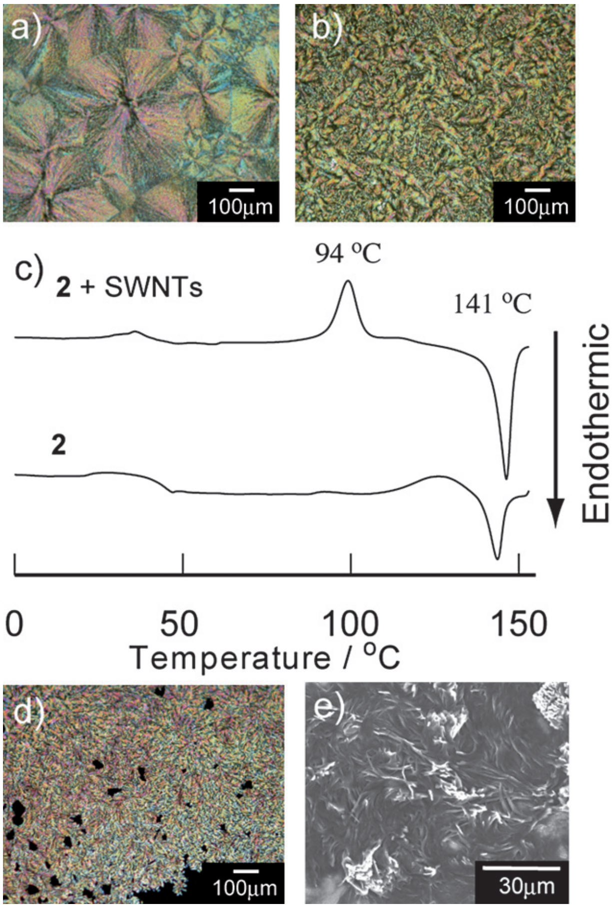

Fig. 4 Polarized optical micrographs of **1** (a) and the precipitate composed of **1** and SWNTs (b) at 120 °C after cooling from the isotropic phase. DSC diagrams for the second heating of **2** and the precipitate composed of **2** and SWNTs at 10 °C/min (c). Polarized optical micrograph (d) and SEM (e) of the precipitate composed of **2** and SWNTs at 120 °C after cooling from the isotropic phase.

Experimental

General

^1H NMR spectra were measured on a Bruker AVANCE 400 FT-NMR spectrometer. Mass spectral data were obtained using a PerSeptive Biosystems Voyager DE-Pro spectrometer with dithranol as a matrix. FT-IR spectra were obtained using a Shimazu FTIR-8400 spectrometer. UV-Vis and fluorescence spectra were measured on a Shimazu MultiSpec-1500 spectrophotometer and a JASCO FP-750, respectively. Differential scanning calorimeter (DSC) thermograms were recorded on a SII Exstar6000 DSC 6200. Raman spectra were obtained on a HaloLab 5000 spectrophotometer at an excitation wavelength of 532 nm. Scanning electron microscope (SEM) images were obtained on a Keyence VE-8800. Transmission electron microscope (TEM) images were obtained on a JEOL JEM-2010 electron microscope at an acceleration voltage of 200 kV without any staining. The specimens for TEM were prepared by the drop casting of the solution onto amorphous carbon-coated copper grids (400 mesh). Temperature-controlled polarizing optical microscopy (TPOM) was carried out using an Olympus BX-50 with a Mettler Toledo FP82HT hot stage.

Materials

All chemicals were purchased from commercial suppliers and used without purification. All solvents were distilled before each procedure. Purified HiPco-SWNTs were purchased from Carbon Nanotechnologies, Inc. The purification of product was carried out by the combination of adsorption column chromatography (silica gel, Wakogel C-200) and recycling preparative HPLC (Japan Analytical Industry, Model LC-908). Analytical thin-layer chromatography was performed on commercial Merck plates coated with silica gel 60 F_{254}.

(*E*,*E*)-2,5-Bis(3-vinylstyryl)-1,4-hexyloxybenzene (3)

A solution of 3-vinyl benzaldehyde (0.85 ml, 6.65 mmol) and 1,4-bis(diethylphosphonate-methyl)-2,5-hexyloxybenzene (1.54 g, 2.66 mmol) in dry THF (10 ml) was added dropwise to a THF solution of potassium *t*-butoxide (0.9g, 7.98 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 3 h at room temperature and poured into cooled water. After addition 2 ml of 2M HCl aqueous solution, the aqueous phase was extracted with CH_2Cl_2. The combined organic layer was washed with three 100 ml potions of water and then dried over $MgSO_4$. After filtration, the solvent was reduced by rotary evaporation. The product was purified by column chromatography (silica gel) using $CHCl_3$/n-hexane (v/v = 1:1, $R_f = 0.65$) as an eluent to give a pale yellow solid. Yield: 1.1g (78%). ^{1}H NMR ($CDCl_3$, 400.13MHz): δ (ppm) = 7.54 (2H, s, Ar*H*), 7.49 (2H, d, *J* = 16.4Hz, ArC*H*=CH), 7.42–7.45 (2H, m, Ar*H*), 7.30–7.32 (4H, m, Ar*H*), 7.14 (2H, d, *J* = 16.4Hz, ArC*H*=CH), 7.12 (2H, s, Ar*H*), 6.75 (2H, dd, *J* = 6.7Hz, –C*H*=CH_2), 5.80 (2H, d, *J* = 16.8Hz, –CH=CH_2), 5.28 (2H, d, *J* = 11.2Hz, –CH=CH_2), 4.05 (4H, t, *J* = 6.4Hz, –OCH_2–), 1.85–1.89 (4H, m, –OCH$_2$CH_2–), 1.37–1.58 (12H, m, –CH_2–), 0.92 (6H, t, *J* = 6.8 Hz, –CH_3); ^{13}C NMR ($CDCl_3$, 100.61MHz): δ (ppm) = 151.2, 138.2, 137.9, 136.8, 128.8, 128.6, 126.9, 125.8, 125.2, 124.6, 123.8, 114.0, 110.7, 69.6, 31.6, 29.5, 26.0, 22.6, 14.0.

(*E*)-4-(3-Bromostyryl)phenol (4)

A solution of diethyl (3-bromobenzyl)phosphonate (1.23g, 4.0 mmol) and 4-acetoxy benzaldehyde (0.79g, 4.8 mmol) was added dropwise to a THF solution of potassium *t*-butoxide (1.34g, 12.0 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 3 h at room temperature and poured into cooled water. After addition 2 ml of 2M HCl aqueous solution, the precipitate was collected and washed with 100 ml water. The crude product was purified by column chromatography (silica gel) using $CHCl_3$ ($R_f = 0.12$) as an eluent to give a white solid. Yield: 0.75g (68%). FT-IR (ATR): 3230 cm^{-1} (νOH); ^{1}H NMR ($CDCl_3$, 400.13MHz): δ (ppm) = 7.63 (1H, s, Ar*H*), 7.33–7.40 (4H, m, Ar*H*), 7.19 (1H, t, *J* = 7.6Hz, Ar*H*), 7.03 (1H, d, *J* = 16.4 Hz, ArC*H*=CH), 6.85 (1H, d, *J* = 16.4 Hz, ArC*H*=CH), 6.82 (2H, s, Ar*H*), 4.87 (1H, s, –O*H*).

(*E*)-1-(3-Bromostyryl)-4-(12-hydroxydodecyloxy)benzene (5)

4 (0.75g, 2.73 mmol) and 12-bromodecan-1-ol (0.88g, 3.3 mmol) were dissolved in 100 ml acetone and K_2CO_3 (1.88g, 13.7 mmol) was added to this solution. The mixed solution was stirred under reflux over one night. Subsequently, the mixture was cooled to room temperature and the precipitate was filtered off. The filtrate was evaporated to dryness and the crude mixture was purified by column chromatography (silica gel) using $CHCl_3$ ($R_f = 0.24$) as an eluent. Recrystallisation from 2-methoxyethanol yielded **5** as a white solid. Yield: 0.40g (32%). ^{1}H NMR ($CDCl_3$, 400.13MHz): δ (ppm) = 7.63 (1H, s, Ar*H*), 7.43 (2H, d, *J* = 8.8Hz, Ar*H*), 7.37 (1H, d, *J* = 7.2 Hz, Ar*H*), 7.34 (1H, d, *J* = 7.2Hz, Ar*H*), 7.17 (1H, t, *J* = 8.0Hz, Ar*H*), 7.04 (1H, d, *J* = 16.0 Hz, ArC*H*=CH), 6.88 (1H, d, *J* = 16.0 Hz, ArC*H*=CH), 6.87 (2H, d, *J* = 8.6Hz, Ar*H*), 3.98 (2H, t, *J* = 6.4Hz, –OCH_2–), 3.66, (2H, t, *J* = 6.8Hz, –CH_2OH), 1.76–1.80 (2H, m, –CH_2CH$_2$O–), 1.54–1.58 (2H, m, –CH_2CH$_2$OH), 1.21–1.47 (16H, m, –CH_2–).

(*E*)-1-(3-Bromostyryl)-4-(2-[2-(2-hydroxyethoxy)ethoxy]ethoxystyryl)benzene (6)

This was synthesized from **4** (1.65g, 6.0mmol) and 2-[2-(2-chloroethoxy)ethoxy]ethanol (1.74ml, 12.0mmol) following the same procedure as for **5**. The crude product was purified by column chromatography (silica gel) using $CHCl_3$ ($R_f = 0.10$) as an eluent to give a white solid. Yield 55%. ^{1}H NMR ($CDCl_3$, 400.13MHz): δ (ppm) = 7.62 (1H, s, Ar*H*), 7.44 (2H, d, *J* = 8.8Hz, Ar*H*), 7.37 (1H, d, *J* = 7.2 Hz, Ar*H*), 7.34 (1H, d, *J* = 7.2Hz, Ar*H*), 7.18 (1H, t, *J* = 8.0Hz, Ar*H*), 7.04 (1H, d, *J* = 16.0 Hz, ArC*H*=CH), 6.88 (1H, d, *J* = 16.0 Hz, ArC*H*=CH), 6.87 (2H, d, *J* = 8.6Hz, Ar*H*), 4.14–4.17 (2H, m, ArOCH_2–), 3.87–3.88 (2H, m, ArOCH$_2$CH_2O–), 3.70–3.75 (6H, m, –OCH_2), 3.61–3.63 (2H, m, –CH_2OH), 2.48 (1H, br, –O*H*).

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To a mixture of 4-cyano-4′-hydroxybiphenyl (0.125g, 0.64mmol), **5** (0.245g, 0.533mmol) and triphenylphosphine (PPh_3) (0.183g, 0.695 mmol) in dry THF (50ml) cooled to 0 °C with an iced bath was added dropwise a solution of diethyl azodicarboxylate (DEAD) in THF under N_2. The reaction was allowed to warm to room temperature and stirred for 3 h. The reaction was stopped by the addition of water, and THF was removed under reduced pressure. The resulting aqueous solution was extracted with diethyl ether. The organic layers were combined, washed with a 1.0 M aqueous solution of NaOH, washed with water, dried over $MgSO_4$ and filtered. The filtrate was evaporated and the crude product was purified by column chromatography (silica gel) using $CHCl_3$ ($R_f = 0.8$) as an eluent. Recrystallisation from 2-methoxyethanol yielded **7** as a white solid. Yield: 0.30g (89%). ^{1}H NMR ($CDCl_3$, 400.13MHz): δ (ppm) = 7.75 (2H, d, *d* = 8.0 Hz, Ar*H*), 7.64 (2H, d, *J* = 8.0Hz, Ar*H*), 7.63 (1H, s, Ar*H*), 7.52 (2H, d, *J* = 8.8Hz, Ar*H*), 7.42 (2H, d, *J* = 8.8Hz, Ar*H*), 7.37 (1H, d, *J* = 7.8Hz, Ar*H*), 7.34 (1H, d, *J* = 8.8Hz, Ar*H*), 7.17 (1H, t, *J* = 7.8Hz, Ar*H*), 7.04 (1H, d,

J = 16.0 Hz, ArCH=CH), 6.98 (2H, d, J = 8.8Hz, ArH), 6.88 (2H, d, J = 8.6Hz, ArH), 6.87 (1H, d, J = 16.0 Hz, ArCH=CH), 3.95–4.02 (4H, m, –OCH_2–), 1.78–1.82 (2H, m, –CH_2CH$_2$O–), 1.30–1.47 (16H, m, –CH_2–); ^{13}C NMR (CDCl$_3$, 100.61MHz): δ (ppm) = 159.6, 158.6, 145.2, 139.9, 132.6, 130.1, 129.9, 129.7, 129.5, 128.9, 128.3, 127.9, 127.0, 124.9, 119.0, 115.1, 114.7, 110.1, 68.0, 29.2, 25.9; MALDI-TOF-MS for $C_{39}H_{42}BrNO_2$: m/z calcd, 635.24; found 636 [M + H]$^+$.

8

8 was synthesized from **6** (1.0g, 2.48mmol) and 4-cyano-4′-hydroxybiphenyl (0.73g, 3.72mmol) following the same procedure as for **7**. The crude product was purified by column chromatography (silica gel) using CHCl$_3$ (R$_f$ = 0.15) as an eluent. Recrystallisation from 2-methoxyethanol yielded **8** as a white solid. Yield 0.9 g (62%). ^{1}H NMR (CDCl$_3$, 400.13MHz): δ (ppm) = 7.67 (2H, d, J = 8.8Hz, ArH), 7.62 (1H, s, ArH), 7.61 (2H, d, J = 8.4Hz, ArH), 7.49 (2H, d, J = 8.8Hz, ArH), 7.40 (2H, d, J = 8.8Hz, ArH), 7.34–7.38 (2H, m, ArH), 7.19 (1H, t, J = 8.0Hz, ArH), 7.02 (1H, d, J = 16.0 Hz, ArCH=CH), 6.99 (2H, d, J = 8.8Hz, ArH), 6.88 (2H, d, J = 8.8Hz, ArH), 6.85 (1H, d, J = 16.0Hz, ArCH=CH), 4.15 (4H, t, J = 6.4Hz, –OCH_2–), 3.88 (4H, t, J = 4.8Hz, –OCH_2–), 3.77 (4H, s, –OCH_2); ^{13}C NMR (CDCl$_3$, 100.61MHz): δ (ppm) = 159.5, 158.8, 145.1 139.8, 132.6, 130.1, 130.0, 129.7, 129.6, 128.9, 128.3, 127.9, 127.0, 125.0, 119.0, 115.2, 114.9, 110.2, 70.9, 69.8, 67.6, 67.5; MALDI-TOF-MS for $C_{33}H_{30}BrNO_4$: m/z calcd, 583.14; found 584 [M + H]$^+$.

1

Tributylamine (0.26ml, 1.0mmol) was added to a solution of **3** (0.11g, 0.20mmol), **7** (0.3g, 0.47mmol), Pd(OAc)$_2$ (2.6mg, 11.6μmol) and tri(o-tolyl phosphine) (13mg, 42.6μmol) in dry DMF (4ml). The solution was bubbled with N$_2$ for 20min and then the reaction mixture was heated to 90 °C under N$_2$ for 48h. After cooling, the mixture was poured into methanol. The precipitated solid was purified by column chromatography (silica gel) using CHCl$_3$ (R$_f$ = 0.80) as an eluent and recycling preparative HPLC to obtain **1** as a yellow solid. Yield 0.22g (67%). ^{1}H NMR (CDCl$_3$, 400.13MHz): δ (ppm) = 7.69 (4H, d, J = 8.6Hz, ArH), 7.62–7.64 (6H, m, ArH and ArCH = CH), 7.51–7.55 (6H, m, ArH and ArCH = CH), 7.46 (4H, d, J = 8.6Hz, ArH), 7.33–7.42 (10H, m, ArH and ArCH=CH), 7.14–7.20 (8H, m, ArH and ArCH=CH), 7.12 (2H, d, J = 16.1Hz, ArCH=CH), 7.00 (2H, d, J = 16.0Hz, ArCH=CH), 6.98 (4H, d, J = 8.8Hz, ArH), 6.90 (4H, d, J = 8.7Hz, ArH), 4.09 (4H, t, J = 6.4Hz, –OCH_2–), 4.02 (8H, m, –OCH_2–), 1.85–1.88 (12H, m, –CH_2–), 1.56–1.59 (12H, m, –CH_2–), 1.40–1.42 (8H, m, –CH_2–), 1.30–1.35 (24H, m, –CH_2–), 0.91–0.94 (6H, m, –CH_3); ^{13}C NMR (CDCl$_3$, 100.61MHz): δ (ppm) = 159.5, 158.6, 151.2, 145.1, 138.0, 137.7, 132.6, 129.0, 128.9, 128.8, 128.7, 128.5, 128.3, 127.7, 127.0, 126.5, 125.4, 124.9, 124.5, 123.9, 119.0, 115.2, 114.9, 110.1, 68.0, 31.9, 29.6, 26.1, 22.7, 14.1; MALDI-TOF-MS for $C_{116}H_{128}N_2O_6$: m/z calcd, 1646.27; found 1647 [M + H]$^+$.

2

2 was synthesized from **3** and **8** following the same procedure as for **1**. The crude product was purified by column chromatography (silica gel) using CHCl$_3$ (R$_f$ = 0.22) as an eluent and recycling preparative HPLC to obtain **2** as a yellow solid. Yield 0.20g (71%). ^{1}H NMR (CDCl$_3$, 400.13MHz): δ (ppm) = 7.62–7.69 (6H, m, ArH and ArCH=CH), 7.59 (4H, d, J = 8.1Hz, ArH), 7.53 (2H, d, J = 16.0Hz, ArCH=CH), 7.49 (4H, d, J = 8.3Hz, ArH), 7.46 (4H, d, J = 8.2Hz, ArH), 7.32–7.44 (10H, m, ArH), 7.14–7.20 (8H, m, ArH and ArCH=CH), 7.10 (2H, d, J = 16.1Hz, ArCH=CH), 6.97–7.00 (6H, m, ArH and ArCH=CH), 6.92 (4H, d, J = 8.7Hz, ArH), 4.14–4.17 (8H, m, –OCH_2–), 4.09 (4H, t, J = 6.4Hz, –OCH_2–), 3.87–3.90 (8H, m, –OCH_2–), 3.77 (8H, s, –OCH_2–), 1.90–1.92 (4H, m, –OCH$_2$–), 1.52–1.58 (4H, m, –OCH$_2$–), 1.39–1.40 (8H, m, –OCH$_2$–), 0.91–0.94 (6H, m, –CH_3); ^{13}C NMR (CDCl$_3$, 100.61MHz): δ (ppm) = 159.5, 158.6, 151.2, 145.1, 138.0, 137.7, 132.6, 129.0, 128.9, 128.8, 128.7, 128.5, 128.3, 127.7, 127.0, 126.5, 125.4, 124.9, 124.5, 123.9, 119.0, 115.2, 114.9, 110.1, 70.9, 69.8, 69.7, 69.6, 67.6, 67.5, 31.7, 29.5, 26.0, 22.7, 14.0; MALDI-TOF-Ms for $C_{104}H_{104}N_2O_{10}$: m/z calcd, 1541.95; found 1542 [M + H]$^+$.

Dispersion of SWNTs

1 or **2** (18mg) and SWNTs (10mg) were added into 20 ml CHCl$_3$ and mixed solution was sonicated in a bath-type sonicator for 1 h. After sonication, the samples were centrifuged at 3000 rpm and the supernatant was then carefully decanted. The suspension was filtered through a 200 nm pore diameter PTFE membrane filter (Millipore Co) and washed with CHCl$_3$ several times. The residue was collected and re-suspended in 5 ml CHCl$_3$ by sonication for 10 min at room temperature.

Conclusion

Two novel phenylenevinylenes having cyanobiphenyl terminates were successfully synthesized and characterized. Synthesized conjugated oligomers **1** and **2** were found to form stable supramolecular complexes with SWNTs through strong π–π interactions between the sidewall of SWNTs and phenylenevinylene segment and wrapping around the SWNTs, imparting excellent solubility in organic solvents. The addition of excess **1** or **2** into the dispersed solution induces the formation of precipitates and the precipitates exhibited thermotropic liquid crystalline phases (Fig. 5). Birefringent optical textures consisting of numerous fibrous assemblies appeared in the mesophase range, indicating that the dispersion of SWNTs within liquid-crystalline hosts affects the organized structures in the thermotropic liquid-crystalline phase. We believe that the dispersion of SWNTs within liquid-crystalline hosts provides new opportunities for dynamically changing the orientation of SWNTs. The construction of liquid-crystalline composites containing SWNTs will be of importance in the development of nanoscopic smart devices such as electrical switches and circuits through the orientation control of SWNTs in response to the external stimulus inputs. Fabrication of devices using liquid crystalline composite materials composed of **1** or **2** with SWNTs is in progress.

Acknowledgements

This work was supported by projects for “Innovation Creative Center for Advanced Interdisciplinary Research Areas” in Special Coordination Funds for Promoting Science and

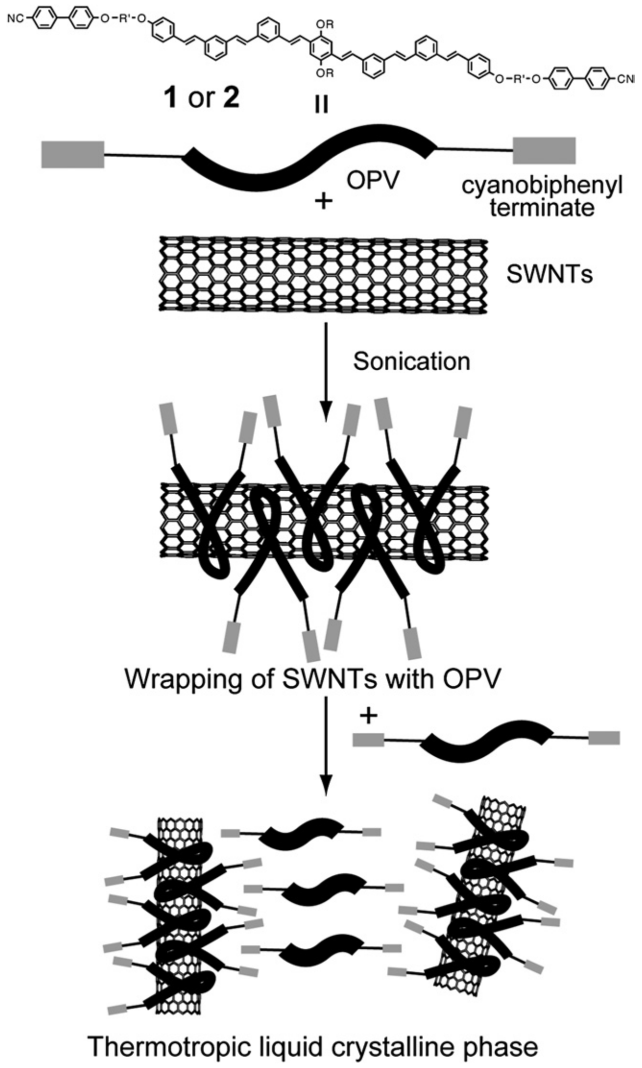

Fig. 5 Schematic illustration of self-organizing processes for the composite of liquid crystalline oligomers and SWNTs.

Technology from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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