Solution Behavior of Dendrimer-Coated Rodlike Coordination Polymers

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ABSTRACT: We report here the synthesis and self-assembly behavior of a series of three coordination polymers (**1**–**3**) insulated with different generations and lengths of oligoether dendrons. Their self-assembly behavior in solutions was investigated according to the variation in generation of dendrons and solvent polarity by using spectroscopic measurements, molecular calculation, and transmission electron microscopy (TEM). In contrast, polymer **1** based on first-generation dendrons with diethylene oxide unit and polymers **2** and **3** based on higher volume fractions of dendrons are readily soluble in common organic solvents and H_2O. Polymer **2** based on first-generation dendrons with triethylene oxide unit was observed to self-assemble into nanorods consisting of two π-stacked polymer backbones in both nonpolar $CHCl_3$ solvent and film, whereas **2** exists as isolated single polymer chains in polar solvents. Polymer **3** based on second-generation dendrons with tetraethylene oxide units also exists as isolated single polymer chains in both solution and film states. Notably, the $CHCl_3$ solution of **2** at concentrations above 2 wt % was observed to be a nematic fluid, resulting from the formation of rigid polymer backbone driven by π-stacking, whereas the THF solution of **2** undergoes gelation at concentrations above 2 wt %. The primary driving force for this unique self-assembling behavior is proposed to be the solvation ability of solvent molecules to silver salts and the coverage ability of dendrons to insulate the conjugated backbones.

Introduction

A great deal of attention has been paid to the conjugated polymers because of their applications in optoelectronic devices such as light-emitting diodes, optical sensors, and photovoltaic cells.[1] However, because of their high conformational rigidity, these polymers have limited solubility and are difficult to process. On the other hand, from a photophysical point of view, the conjugated polymer chains have a high tendency for aromatic $\pi-\pi$ interactions, which lead to the formation of weakly emissive aggregated species in solution and in film states.[2] Therefore, extensive efforts have been made to develop soluble and isolated conjugated polymers for exploration of novel properties and functions.[3] One strategy for isolating conjugated polymer is to insulate the conjugated backbones with bulky dendritic chains. When the dendrimer size and coverage are large enough to give rise to site isolation of polymer core, the insulated polymer chain can be obtained by attaching dendrons laterally to a polymer chain. A number of dendronized conjugated polymers have been reported, including derivatives of polyphenylene, polyfluorene, poly(phenylenevinylene), poly(phenyleneethynylene), and polythiophene, insulated with poly(benzyl ether), polyphenylene, and aliphatic polyether dendrons.[4] The dendritic side groups can enhance transport properties and also alter the mechanical characteristics of the conjugated polymers. Furthermore, these insulated polymers can exhibit a strong increase in fluorescence efficiency with increase in dendron generation. However, the general synthesis of conjugated polymers by aromatic coupling such as Suzuki and Sonogashira reactions is considerably affected by steric hindrence of dendritic side chain and solubility of conjugated backbones to produce only limited lengths of polymer backbones.[5] Alternatively, strong directional interactions, such as complexation between linear conjugated ligands and transition-metal atoms that adopt a linear coordination geometry, can give rise to extended polymer chains with length up to several micrometers.[6] Previous publications from our laboratory have shown that extended polymeric chains formed from complexation between bent-shaped ligands and metal cations can give rise to helical polymers.[7]

Although conjugated systems consisting of rigid rod and flexible coil segments are excellent candidates for creating well-defined supramolecular structures via a process of spontaneous organization,[8] the recent study of synthesized conjugated polymer insulated with dendrons has been mainly focused on optical properties.[5] The rigidity contrast between stiff rodlike and flexible coil-like blocks is expected to greatly affect the details of molecular packing and thus the nature of thermodynamically stable supramolecular structures. In order to balance these competing blocks, rigid–flexible block molecules self-organize into a variety of supramolecular structures which can be controlled by variation of the rod to coil volume fraction.[9] Another interesting feature of rigid–flexible block systems is their amphiphilic characteristic that shows a strong tendency for their hydrophilic and hydrophobic segments to separate in space into distinct nanodomains.[10] Depending on the solvent content and polarity, amphiphilic molecules self-assemble into different aggregated structures via mutual interactions between segments and solvent.[11]

Therefore, one can imagine that both unique optical properties and aggregation behavior of rodlike conjugated polymers insulated with flexible dendrons can be found according to the variation of dendron volume fraction and solvent polarity. To corroborate this concept, we synthesized the coordination polymers insulated with polyether dendrons and investigated their aggregation behavior in both solution and film states. To construct the rodlike coordination polymers, we have designed linear-shaped ligands consisting of aromatic rod segments and flexible dendritic chains with different generation numbers, that is, first generation and second generation. The resulting conjugated polymers were investigated in solution and in film states by using UV/vis, fluorescence spectroscopies, molecular model-

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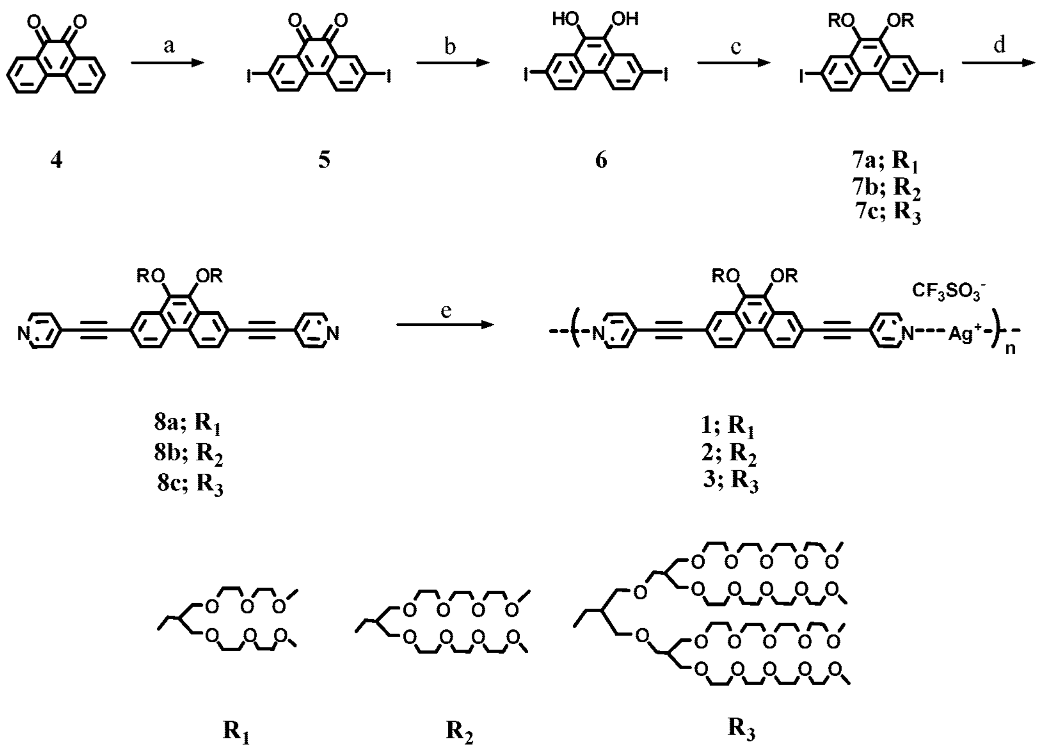
Scheme 1. Syntheses of 1−3[a]



[a] Reaction conditions: (a) NIS, CF_3COOH, rt, 86%; (b) $Na_2S_2O_4$, THF, rt, 94%; (c) TsOR, K_2CO_3, DMF, reflux, **7a**: 76%, **7b**: 72%, **7c**: 63%; (d) 4-ethynylpyridine hydrochloride, K_2CO_3, $Pd(0)(PPh_3)_4$, CuI, H_2O, DME, reflux, **8a**: 65%, **8b**: 62%, **8c**: 51%; (e) AgOTF, EtOH, rt.

ing calculation, and transmission electron microscopy (TEM), which demonstrates that the conjugated polymers can exist as an isolated single polymer or aggregated nanorods of two π-stacked polymers depending on the generation of dendrimer and solvent polarity.

Results and Discussion

Scheme 1outlines the synthesis of linear-shaped bipyridine ligands consisting of a phenanthrene moiety as a rigid aromatic segment and laterally attached oligoether dendrons as a flexible segment. The linear coordination polymers (**1**−**3**) were prepared by complexation of the synthesized ligands with silver triflate. The design of oligoether dendrons was focused on the construction of an aliphatic dendritic core with different lengths and generations, that is, first-generation dendrons based on a di- and tri(ethylene oxide) and second-generation dendrons based on tetra(ethylene oxide) units. The basic synthetic methodology to generate such oligoether dendrons employed a facile convergent route reported previously.[7] The synthesis of aromatic segment started with iodination of phenanthrenequinone to yield intermediate 2,7-diiodophenanthrenequinone (**5**), which was reduced to 2,7-diiodophenanthrene-9,10-diol (**6**) by sodium hydrosulfite.[12] The subsequent etherification of **6** with tosylated oligoether dendrons in the presence of potassium carbonate produced precursors of ligand molecules. The final ligands were prepared from the Sonogashira reaction with **7**- and 4-ethynylpyridine hydrochloride in the presence of Pd(0) catalysis. The resulting ligands were complexed with silver triflate to prepare coordination complexes **1**−**3**. The synthesized ligands and coordination polymers were characterized by ^1H NMR spectroscopy, elemental analysis, and MALDI-TOF mass spectrometry and were shown to be in full agreement with the expected chemical structures.

The solubility of coordination polymers in general solvents was investigated to gain some insight into the encapsulation of aromatic backbones by oligoether dendrons. **1** based on the first-generation dendrons with diethylene oxide units was insoluble in common organic solvents, suggesting that the incomplete coverage of short dendrons into aromatic backbones leads to strong π-aggregations between the polymer backbones. In contrast to **1**, **2** based on the longer dendritic chains with triethylene oxide units was readily dissolved in common organic solvents as well as H_2O. To investigate the solution state structure of polymer **2**, UV−vis and fluorescence spectroscopic experiments were performed in both organic and aqueous solutions (Figure 1). The absorption spectra of **2** in polar H_2O and THF solutions at 0.1−0.01 wt % exhibited maximum transitions at 295 and 307 nm, resulting from the conjugated aromatic segments. In this concentration range, absorption spectra showed the shape-persistent spectra, accompanied by obedience to Beer's law, indicating that there is no apparent intermolecular aromatic association. Notably, the absorption spectrum of **2** in $CHCl_3$ solution (0.1 wt %) was strongly

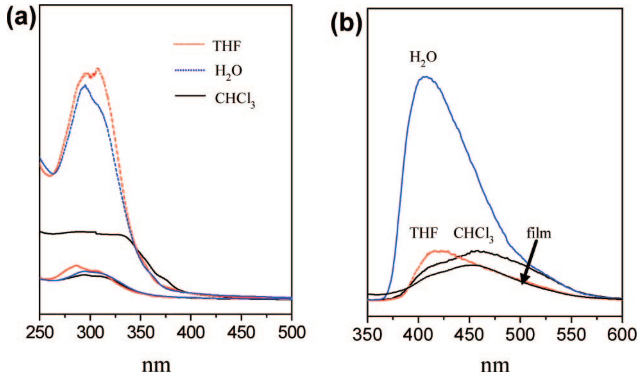


Figure 1. (a) UV/vis spectra of **2** in solutions (up, 0.1 wt %; bottom, 0.01 wt %). (b) Fluorescence spectra of **2** in solutions and in film (0.1 wt %, excited at 330 nm). The film was prepared by the spin-coating method from 0.1 wt % THF solution on the quartz substrates.

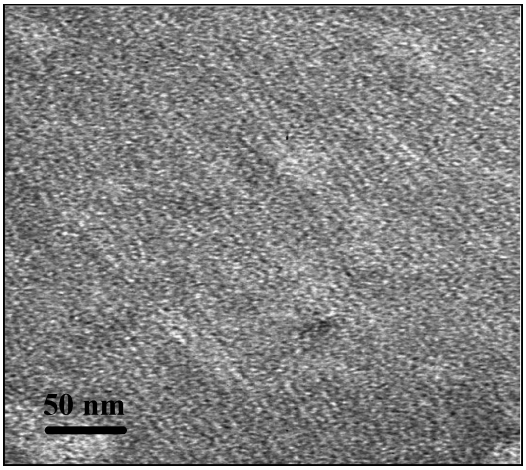


Figure 2. TEM image of **2** prepared in $CHCl_3$ solution (negatively stained with uranyl acetate).

quenched and broad as compared to those in polar solvents, which is attributed to aggregation of the conjugated aromatic segments (Figure 1a).[13] The aggregation behavior of **2** in $CHCl_3$ solution was further confirmed by fluorescence measurements. The emission spectrum of **2** in $CHCl_3$ solution exhibited λ_{max} at 460 nm, which is red-shifted by 40−50 nm with respect to that observed in H_2O and THF solutions (λ_{max}: 408 and 418 nm, respectively), indicative of aggregation of conjugated aromatic segments (Figure 1b).[14]

To further investigate the aggregation structure in $CHCl_3$, transmission electron microscopy (TEM) experiments have been performed with film prepared from a $CHCl_3$ solution of **2**. Figure 2 shows a representative micrograph obtained from a 0.01 wt % solution of **2** cast onto a TEM grid. The negatively stained sample with uranyl acetate clearly shows 1-dimensional nanorods with a uniform diameter of about 2 nm and lengths up to several micrometers. Considering the calculated molecular length and thickness, the diameter of about 2 nm indicates that the aggregated rods consist of two π-stacked polymer chains aligned parallel to each other (calculated diameter of 1.8 nm). This result can be further illustrated by a computer model in which the COMPASS empirical force-field calculation is used on the polymer **2** (Figure 3).[15] The optimized structure of a single polymer of **2** showed the incomplete coverage of first-generation dendrons with triethylene oxide units to encapsulate the conjugated backbones (Figure 3a). Although the dendrons of **2** could surround the phenanthrene units, their coverage is not enough for silver cations and counteranions. Therefore, the computer modeling is used on a cluster of two π-stacked polymer chains with aromatic distance of 4.5 Å. Energy minimization of the cluster suggested that the aggregated rod of two polymer chains are energetically favorable which is consistent with TEM results, and dendritic chains can fully encapsulate the aromatic backbone as well as silver salt (Figure 3b). On the basis of these results, the aromatic backbones of **2** in film and in $CHCl_3$ solution can be considered to self-assemble into discrete rodlike aggregates with laterally stacked bimolecules encapsulated by oligoether dendrons.

In contrast to the $CHCl_3$ solution, **2** exists as an isolated single polymer in polar solvents as described earlier. The solvation of dendrons and the ionic character of silver salt are believed to play an important role in the existence as a single polymer chain. In nonpolar solvents, the solubility of dendrons decreases and the attractions between ionic silver salts increase, resulting in the aggregation of the polymer chains. However, the better solvation of the dendrons and ionic silver salts in polar solvent increases the solubility of polymer **2** to be molecularly dissolved.

To investigate the effect of dendron size for construction of rod with two π-stacked polymer chains, spectroscopic measurements were performed with **3**. Similar to **2** in polar solvents, the absorption spectra of polymer **3** obeyed a Beer's law at 0.1−0.01 wt % in all solution states. In addition, its emission spectra exhibited the maxima at 405−420 nm, which is consistent with the results of an isolated single polymer **2** (Figure 4). Considering the same structure of conjugated chromophore of **2** and **3**, the emission λ_{max} of **3** demonstrated that the intermolecular aromatic associations between polymer backbones are lacking. This is attributed to the fully encapsulation of aromatic backbones and silver salts by second-generation dendrons. This result is also illustrated by a computer model. The optimized structure of a single polymer **3** showed that second-generation dendrons fully insulate the aromatic backbones and silver salts, preventing the conjugated backbones from interchain $\pi-\pi$ stacking interactions (Figure 3c).

Another interesting point to be noted is that the formation of aggregates formed through π-stacking interactions of two polymer chains can lead to the formation of macroscopic ordering due to their stiff rodlike characteristic. Stiff rodlike molecules consisting of a rigid rod block with a flexible coil block is well-known to provide an ordered structure because the anisometric molecular shape and stiff rodlike conformation of the rod segment impart orientational organization.[16] Consequently, a significant difference in macroscopic properties can be expected to occur by the presence of intermolecular π-stacking interactions which lead to enhanced stiffness of aromatic backbones. Accordingly, the polarized photofluorescence experiments were conducted on the macroscopically aligned film by the rubbing technique.[17] Figure 5 shows polarized fluorescence of the aligned film of polymers, in which the polarizer was placed parallel or perpendicular to the rubbing direction. The polarized emission of polymer **2** at 460 nm under excitation at 330 nm in the parallel direction ($I_{\parallel}$) was much larger than that in the perpendicular one ($I_{\perp}$), which yields a polarization ratio (defined as $I_{\parallel}/ I_{\perp}$) of 8.0 (Figure 5a). This value indicates that the transition dipoles of the conjugated polymers are aligned parallel to the long axis of the rod and thus emit polarized light with polarization parallel to the plane of the film.[18] In contrast to **2**, the observed polarization ratio of **3** decreases to 2.4 at 460 nm, suggesting the polymers **3** are not efficiently aligned parallel to each other (Figure 5b). This difference in polarization ratio demonstrates that the anisotropic interactions of rigid rods formed from two π-stacked polymers are much stronger relative to those of single polymer chains. This difference is most probably because the dendrons laterally attached to phenanthrene segments of **3** are able to freely rotate along the C−C bonds in aromatic backbones. These free rotations of dendrons in polymer backbones induce the conformationally flexible aromatic segments which give rise to the reduction of anisotropic interactions between polymer chains, whereas the aromatic backbones of **2** are fixed through $\pi-\pi$ interactions to prevent the free rotation of the aromatic segments. Subsequently, the fixed aromatic rotation leads to the formation of a uniform cylinder with regular position of dendrons, which enhances the rigidity of the rods. This can give rise to the self-assembling of rigid polymers to be more oriented states.

A property inherent to the presence of elongated stiff rods is the possibility of forming nematic liquid crystals. To confirm liquid crystalline behavior, the chloroform solutions were investigated with polarized optical microscopy. The solutions at concentrations above 2 wt %, indeed, revealed a typical nematic texture (Figure 6).[19] The formation of a nematic liquid crystal indicates that the anisotropic interactions of π-stacked polymers lead to the formation of stiff rodlike objects.

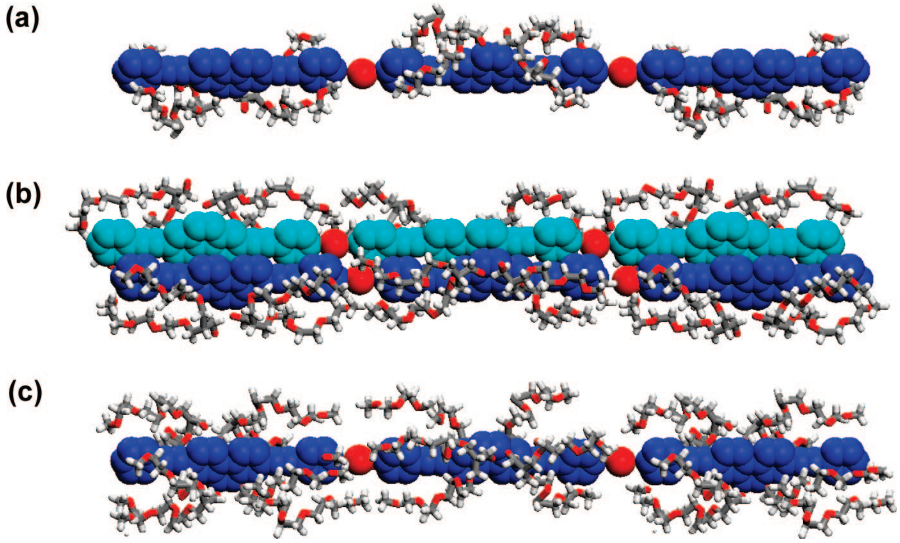


Figure 3. Chemical structures by molecular modeling of (a) **2** of a single chain, (b) **2** of two π-stacked chains, and (c) **3** of a single chain.

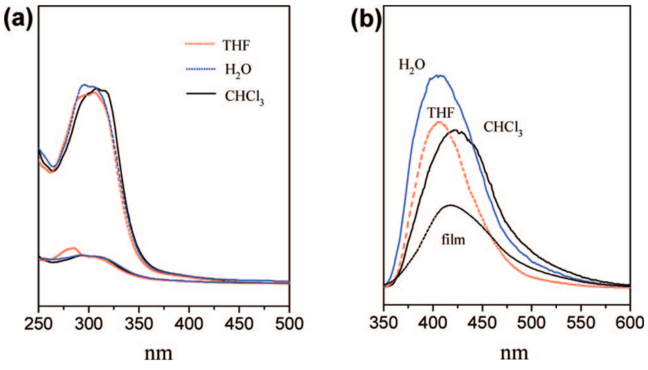


Figure 4. (a) UV/vis spectra of **3** in solutions (up, 0.1 wt %; bottom, 0.01 wt %). (b) Fluorescence spectra of **3** in solutions and in film (0.1 wt %, excited at 330 nm). The film was prepared by the spin-coating method from 0.1 wt % THF solution on the quartz substrates.

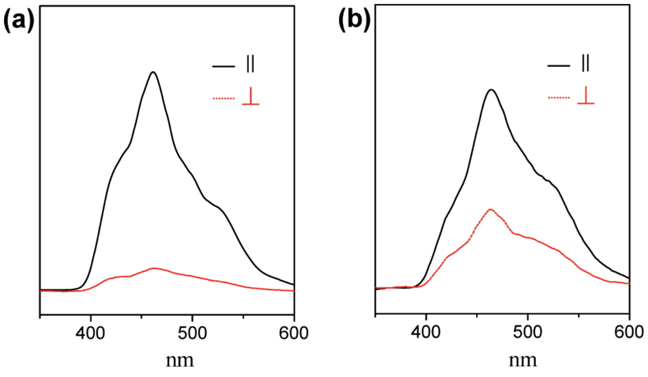


Figure 5. Polarized fluorescence spectra of (a) **2** and (b) **3** in oriented film states (excited at 330 nm). The spectra were obtained with polarizers oriented parallel (solid black line) and perpendicular (dashed red line) to the long axis orientation of the conjugated polymers.

In great contrast to the $CHCl_3$ solutions, the aqueous solution of **2** exhibited only an isotropic state in this concentration range, indicating that the formation of a nematic fluid requires lateral association of the polymer backbones. Notably, **2** underwent spontaneous isotropic gelation at concentrations above 2 wt % in THF solution. The isotropic gelation suggests that interconnections between the isolated single polymers occur to form 3-D networks.[20] The emission intensities of **2** in both $CHCl_3$ and THF solutions were strongly quenched compared to that in aqueous solution, suggesting that the interconnection or association of polymers occur in these solutions (Figure 7). However, the quenched emission intensity in THF shows to be with a lack of band shift, indicative of no apparent $\pi-\pi$ stacking interactions. Therefore, the polymer chains in THF can be considered to exist as isolated single polymers consisting of dendronized phenanthrene uints

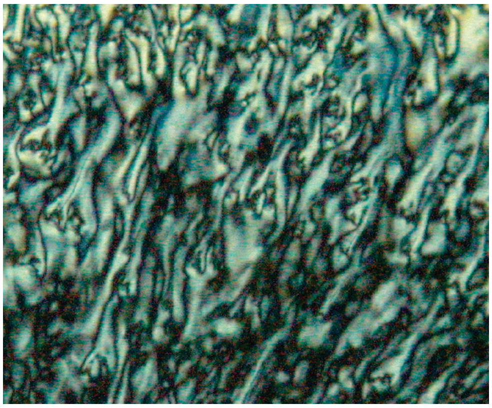


Figure 6. Polarized optical micrograph of nematic fluid of **2** in 10 wt % $CHCl_3$ solution.

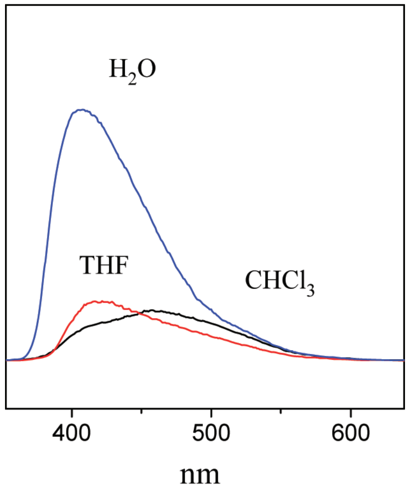


Figure 7. Fluorescence spectra of **2** in various solutions (2 wt %, excited at 330 nm).

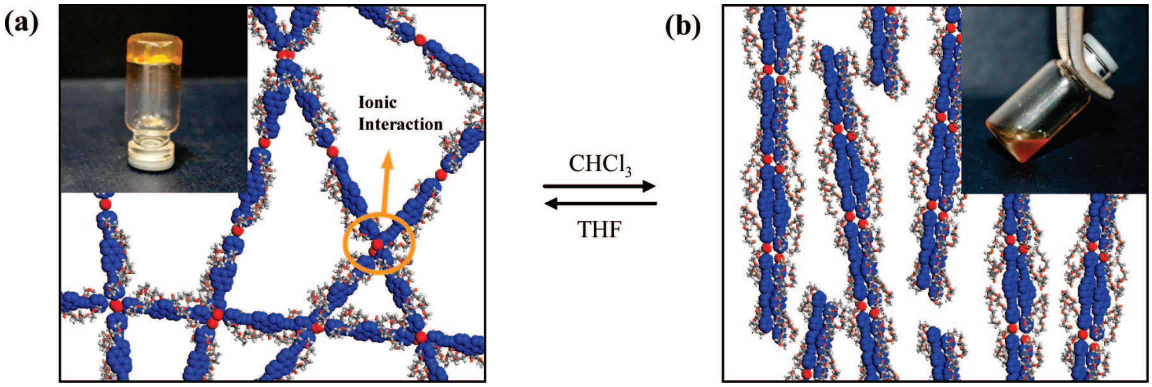


Figure 8. Schematic representation and photogragh (inset) of (a) an isotropic gel and (b) a nematic fluid of **2**.

and naked silver salts to external environment. However, the polarity of THF is not strong enough to solvate the ionic components, leading to energetic penalty associated with the contact between the ions and solvent molecules. To reduce the energetic penalty, the silver cations and counteranions begin to contact with each other, leading to the interconnections between randomly placed single polymer chains, giving rise to the formation of isotropic gels (Figure 8). On the other hand, the nonpolar CHCl$_3$ induces the aggregation of polymer backbones into stiff elongated rods consisting of two π-stacked polymer chains with fully encapsulated ionic components to prevent direct contact with external solvent molecules, leading to a fluid nematic solution.

Conclusions

The linear coordination polymers insulated by laterally attached oligoether dendrons were synthesized through a compexation of linear aromatic ligands and silver triflate, and their photophysical property and aggregation behavior in both solution and in film states were investigated according to the variation in generation of dendrons and solvent polarity. In contrast, polymer **1**, which is insoluble due to its short oligoether dendrons, and polymers **2** and **3** are readily soluble in common organic solvents and H$_2$O. Polymer **2** based on a first-generation dendron with triethylene oxide unit was observed to self-assemble into nanorods consisting of two π-stacked polymers in nonpolar CHCl$_3$ solution and in film states, whereas **2** exists as an isolated single polymer in polar solvents. **3** with a further increase in the generation and length of the dendrons (second-generation dendrons based on tetraethylene oxide) gives rise to an isolated single polymer in polar as well as nonpolar solvents. This aggregation behavior seems to originate from a consequence of the delicate balance between the coverage ability of flexible dendrons to rigid aromatic backbones and the solvation effect of solvent molecules on dendrons and silver triflate. Notably, the aggregation of the aromatic polymer chains in CHCl$_3$ leads to macroscopic orientation and the formation of a nematic liquid crystal due to enhanced stiffness of 1-D objects. With solvent exchange from CHCl$_3$ to THF, the aggregates of **2** disassemble into single polymer chains that interconnect to each other through ionic interactions to form isotropic gels. These results suggest that construction of 1-D coordination polymers encapsulated by dendritic chains offers a strategy to manipulate the optical properties together with fluidity of polymer solutions.

Experimental Section

Materials. NaH (60%) and *p*-toluenesulfonyl chloride (98%) from TCI and Tokyo Kasei were used as received. Phenanthrenquinone and 4-ethynylpyridine hydrochloride (98%) from Aldrich were used as received. Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Lancaster, and TCI, etc.) and were used without purification. Methylene choride and ethyl acetate were distilled before use. Visualization was accomplished with UV light and iodine vapor. Flash chromatography was carried out with silica gel 60 (230−400 mesh) from EM Science. Dry THF was obtained by vacuum transfer from sodium and benzophenone.

Techniques. ^{1}H NMR spectra were recorded from CDCl$_3$ solutions on a Bruker Advance DRX 400 NMR spectrometer. The purity of the products was checked by thin layer chromatography (TLC; Merck, silica gel 60). Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer at Organic Research Center, Sogang University. MALDI-TOF mass spectra were performed on Perceptive Biosystems Voyager-DE STR using a 2,5-dihydroxybenzoic acid matrix. The UV/vis spectra were obtained from a Shimadzu UV-1650PC spectrometer. The fluorescence spectra were obtained from a Hitachi F-4500 fluorescence spectrometer. The transmission electron microscope (TEM) was performed at 120 kV using a JEOL-JEM 2010. Compounds were synthesized according to the procedure described in Scheme 1 and then purified by silica gel column chromatography and prep. Molecular modeling and mechanical calculations were computated with Materials Studio Modeling 4.0 (Accelrys Inc.) software.

Synthesis. Compound **5**: yield 86%. Phenanthrenequinone (3.00 g, 14.4 mmol) was placed in a round-bottom flask under nitrogen. Trifluoromethanesulfonic acid (12.71 mL, 14.4 mmol) was added to the flask followed by cooling to 0 °C. *N*-Iodosuccinimide (10.81 g, 3.0 mmol) was added slowly over 10 min, and the reaction was allowed to gradually warm to room temperature. After 6 h at room temperature the reaction was poured onto ice, filtered, and dried to afford **5** (5.7 g, 12.4 mmol) as a red solid; mp >250 dec. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): δ 8.49 (s, 2 H), 8.05 (d, 2 H), 7.71 (s, 2 H).

Compound **6**: yield 94%. 2,7-Diiodophenanthrenequinone **5** (2.00 g, 4.35 mmol) and Na$_2$S$_2$O$_4$ (2.61 g, 15 mmol) were dissolved into a mixture of THF (150 mL) and H$_2$O (50 mL). The mixture was stirred for 6 h and then extracted with THF. The crude product was dried over anhydrous magnesium sulfate and filtered to afford **6** (1.88 g, 4.09 mmol). ^{1}H NMR (400 MHz, DMSO, δ, ppm): δ 9.31 (s, 2H, ArOH), 8.50 (s, 2H, Ar−H), 8.48 (d, 2H, Ar−H), 7.80 (d, 2H, Ar−H).

Compounds **7a**−**c**: Compounds **7a**−**c** were synthesized using the same procedure. A representative example is described for compound **7a**. **6** (300 mg, 0.649 mmol), TsOR$_1$ (753 mg, 1.62 mmol), and K$_2$CO$_3$ (966 mg, 7.00 mmol) were dissolved in DMF (25 mL). The mixture was heated at reflux for 18 h and then cooled to room temperature. Solvent was removed in a rotatory evaporator, and the resulting mixture was poured into water and extracted with methylene chloride. The methylene chloride solution was washed with water dried over anhydrous magnesium sulfate and filtered.

The crude products were purified by column chromatography to yield 410 mg of yellow oil.

7a: yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): δ 8.23 (s, 2H, Ar−H), 7.74 (d, 2H, Ar−H), 6.80 (d, 2H, Ar−H), 4.03 (d, 4H, CCH_2O), 3.22−3.63 (m, 52H, OCH_2 and OCH_3), 1.93 (m, 2H, $CH(OCH_2)_3$).

7b: yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): δ 8.22 (s, 2H, Ar−H), 7.75 (d, 2H, Ar−H), 6.80 (d, 2H, Ar−H), 4.03 (d, 4H, CCH_2O), 3.25−3.60 (m, 68H, OCH_2 and OCH_3), 1.95 (m, 2H, $CH(OCH_2)_3$).

7c: yield 63%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): δ 8.27 (s, 2H, Ar−H), 7.83 (d, 2H, Ar−H), 6.88 (d, 2H, Ar−H), 4.05 (d, 4H, CCH_2O), 3.18−3.63 (m, 184H, OCH_2 and OCH_3), 2.12 (m, 6H, $CH(OCH_2)_3$).

Compounds **8a−c**: Compounds **8a−c** were synthesized using the same procedure. A representative example is described for compound **8a**. **7a** (300 mg, 0.287 mmol), 4-ethynylpyridine hydrochloride (120 mg, 0.860 mmol), $Pd(PPh_3)_4$ (116 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol), and K_2CO_3 (238 mg, 1.72 mmol) were added to a mixture of DME (10 mL) and H_2O (7 mL). The mixture was degassed and then stirred at 60 °C for 24 h. Solvent was removed in a rotatory evaporator, and the resulting mixture was poured into water and extracted with methylene chloride. The methylene chloride solution was washed with water dried over anhydrous magnesium sulfate and filtered. The crude products were purified by column chromatography (silica gel, MeOH:ethyl acetate = 1:20) to yield 185 mg of a yellow oil.

8a: yield 65%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): δ 8.63 (d, 4H, Py-Hα), 8.19 (s, 2H, Ar−H), 7.70 (d, 2H, Ar−H), 7.41 (d, 4H, Py-Hβ), 7.20 (d, 2H, Ar−H), 4.13 (d, 4H, CCH_2O), 3.26−3.65 (m, 52H, OCH_2 and OCH_3), 2.03 (m, 2H, $CH(OCH_2)_3$). Anal. Calcd for $C_{56}H_{72}N_2O_{14}$: C, 66.43; H, 7.87; N, 2.28. Found: C, 66.08; H, 7.93; N, 2.33. MALDI-TOF-MS *m*/*z* $(M + H)^+$ 997.49.

8b: yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): δ 8.63 (d, 4H, Py-Hα), 8.19 (s, 2H, Ar−H), 7.70 (d, 2H, Ar−H), 7.41 (d, 4H, Py-Hβ), 7.20 (d, 2H, Ar−H), 4.13 (d, 4H, CCH_2O), 3.26−3.67 (m, 68H, OCH_2 and OCH_3), 2.05 (m, 2H, $CH(OCH_2)_3$). Anal. Calcd for $C_{64}H_{88}N_2O_{18}$: C, 65.51; H, 7.56; N, 2.39. Found: C, 65.88; H, 7.33; N, 2.31. MALDI-TOF-MS *m*/*z* $(M + H)^+$ 1173.23.

8c: yield 51%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): δ 8.65 (d, 4H, Py-Hα), 8.17 (s, 2H, Ar−H), 7.68 (d, 2H, Ar−H), 7.43 (d, 4H, Py-Hβ), 7.22 (d, 2H, Ar−H), 4.10 (d, 4H, CCH_2O), 3.23−3.63 (m, 184H, OCH_2 and OCH_3), 2.05 (m, 2H, $CH(OCH_2)_3$). Anal. Calcd for $C_{124}H_{208}N_2O_{46}$: C, 60.47; H, 8.51; N, 1.14. Found: C, 60.08; H, 8.65; N, 1.09. MALDI-TOF-MS *m*/*z* $(M + H)^+$ 2462.42.

Complexation of **8a−c** with silver triflate: **1−3** were prepared using the same procedure. A representative example is described for **1**. **8a** (19.4 mg, 0.0195 mmol) and silver triflate (5.00 mg, 0.0195 mmol) were dissolved in dry EtOH solvent (10 mL) and stirred under N_2 for 3 h at 25 °C, and the solvent was then removed in a rotary evaporator to yield dimly yellow solid of **1**. **1**: Anal. Calcd for $C_{57}H_{72}AgF_3N_2O_{17}S$: C, 54.59; H, 5.79; N, 2.23. Found: C, 54.21; H, 5.69; N, 2.11. **2**: Anal. Calcd for $C_{65}H_{88}AgF_3N_2O_{21}S$: C, 54.58; H, 6.20; N, 1.96. Found: C, 55.12; H, 6.04; N, 1.93. MALDI-TOF-MS *m*/*z* $(M + Ag)^+$ 1281.03. **3**: Anal. Calcd for $C_{125}H_{208}AgF_3N_2O_{49}S$: C, 55.20; H, 7.71; N, 1.03. Found: C, 55.02; H, 7.65; N, 1.05. MALDI-TOF-MS *m*/*z* $(M + Ag)^+$ 2570.22.

Computation. Simulations were conducted with Materials Studio Modeling 4.0 (Accelrys Inc.) software according to the following procedure. First, a coordination polymer consisting of three ligands and two silver triflate was built using the MS Visualizer. The potential energy of helical polymer was then minimized until root-mean-square derivative 1.0 (kcal/mol)/Å or less. The constant temperature and density condition (NVT ensemble) was performed on the minimized structure. The structural energy minimization of a coordination polymer was carried out for 100.0 ps at 298 K, a time step of 0.001 ps, and number of steps of 100 000. The interatomic interactons were modeled with the COMPASS force field.

Polarized Fluorescence Measurements. The polarized emission spectra generated from the shear aligned films were obtained using a Hitachi F-4500 fluorescence spectrometer equipped with a NT47-216 polarizer. The macroscopic alignment of polymer films was performed by the rubbing technique.[21] The polymers on the quartz plates were rubbed by a quartz rod and were aligned parallel to the rubbing direction. The polarization of the fluorescence was determined by taking two consecutive images with both excitation and detection polarizations either horizontal (0°) or vertical (90°) orientation with respect to the image and calculating the polarization ratio: $R = I_{VER}/I_{HOR}$.

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