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Supporting Information

Self-Assembly of Coordination Polymers into Multi-Stranded Nanofibers with Tunable Chirality

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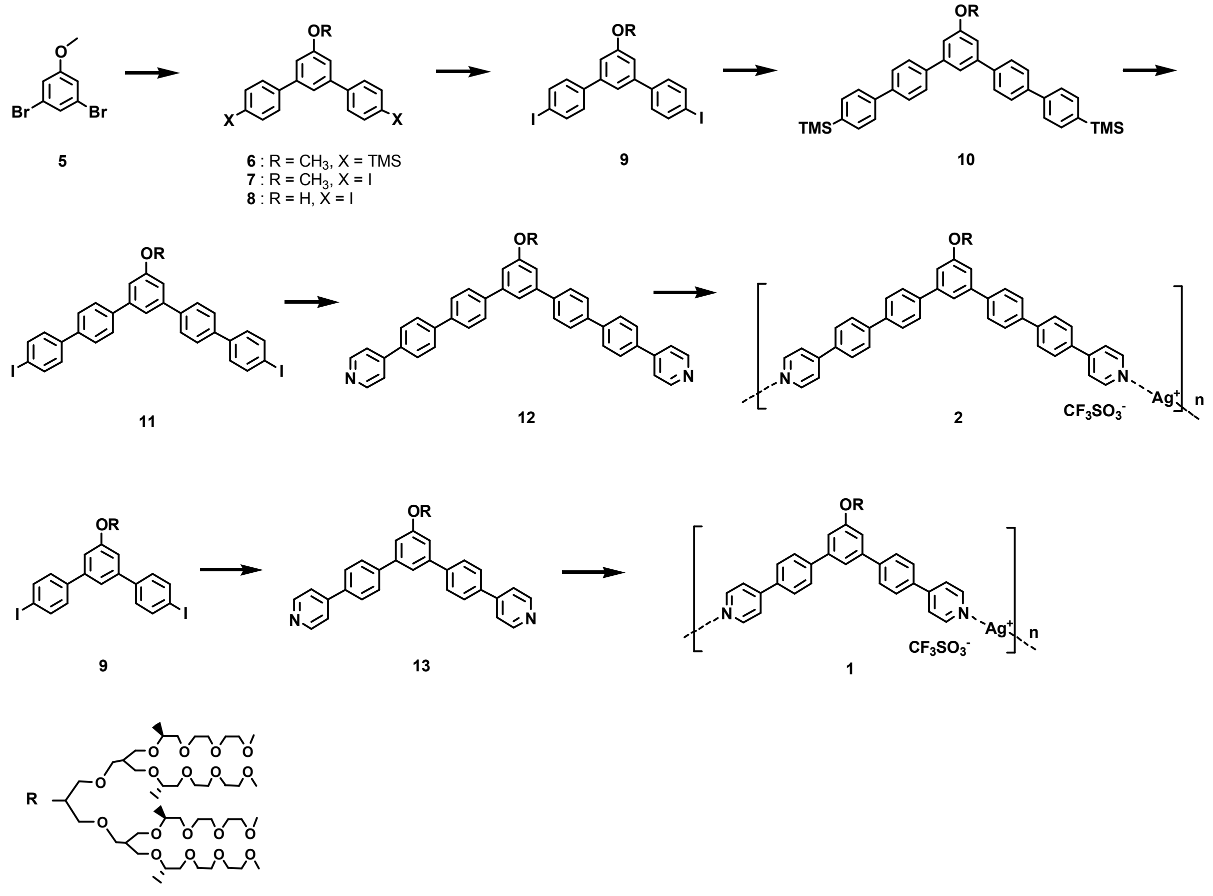
Experimental Section

Materials. NaH (60%), and *p*-toluenesulfonyl chloride (98%) from TCI and Tokyo Kasei were used as received. 4-pyridylboronic acid (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 chloride, 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 AM 250 spectrometer. ^{19}F-NMR spectra were recorded from D_2O solutions on a Bruker AVANCE 500 spectrometer. The chemical shifts were measured as upfield shifts relative to that of $CFCl_3$ as an external standard. 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. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 10C1 X-ray beam line at the Pohang Accelerator Laboratory (Korea). The films of **1** and **2** were prepared from multistep fast evaporation of aqueous solutions (0.5 wt%) on Kapton film, and then were held in an aluminum sample holder which were sealed with the window of 7 μm thick Kapton films on both sides. The MALDI-TOF mass spectra were performed on Perceptive Biosystems Voyager-DE STR using a 2,5-dihydroxy benzoic acid matrix. Dynamic light scattering (DLS) measurements were performed using an ALV/CGS-3 Compact Goniometer System. The UV/vis spectra and transmittance were obtained from a Shimadzu UV-1650PC spectrometer. The fluorescence spectra were obtained from a Hitachi F-4500 fluorescence spectrometer. Circular Dichroism (CD) and Linear Dichrosim (LD) spectra were obtained using Jasco J-810 spectropolarimeter. The transmission electron microscope (TEM) was performed at 120 kV using JEOL-JEM 2010. Molecular modeling and mechanical calculations were computated with Materials Studio Modeling 4.0 (Accelrys Inc.) software. Compounds were synthesized according to the procedure described Scheme 1 and then purified by silica gel column chromatography and prep. HPLC (Japan Analytical Instrument).

Synthesis



Scheme 1. Synthesis of the coordination polymers **1** and **2**.

Compound **6**: yield 96%. Compound **5** (835 mg, 3.14 mmol) and 4-trimethylsilyl-phenyl-boronic acid (1.34 g, 6.91 mmol) were dissolved in degassed THF (25 ml). Degassed 2.0 M aqueous Na_2CO_3 (20 ml) was added to the solution and then tetrakis(triphenylphosphine) palladium(0) (36 mg, 31 μmol) was added. The mixture was refluxed for 24 hrs with vigorous stirring under nitrogen. Cooled to room temperature, the layers were separated, the aqueous layer was washed twice with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed in a rotary evaporator, and the crude products was purified by column chromatography (silica gel, hexane : CH_2Cl_2 = 1 : 1) to yield 1.22 g of a white crystal. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) δ 7.61 (d, 8H, Ar-H), 7.41 (s, 1H, Ar-H, *p* to OCH_3), 7.12 (s, 2H, Ar-H, *o* to OCH_3), 3.92 (s, 3H, OCH_3).

Compound **7**: yield 97%. To a solution of compound **6** (1.22 g, 3.02 mmol) in CH_2Cl_2 (250 ml) at –78 °C was added 1.0 M solution of ICl in CH_2Cl_2 (10 ml). The reaction mixture was stirred over 2 hrs under nitrogen. 1.0

M aqueous $Na_2S_2O_5$ solution was added and stirred over 1 hr. The layers were separated, the aqueous layer was washed twice with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed in a rotary evaporator, and the crude products were purified by column chromatography (silica gel, CH_2Cl_2) to yield 1.49 g of a white crystal. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) δ 7.79 (d, 4H, Ar-H, *o* to I), 7.37 (d, 4H, Ar-H), 7.29 (d, 1H, Ar-H, *p* to OCH_3), 7.06 (s, 2H, Ar-H, *o* to OCH_3), 3.95 (s, 3H, OCH_3).

Compounds **8**: yield 96%. To a solution of compound **7** (0.50 g, 0.86 mmol) in CH_2Cl_2 at 0 ^{o}C was added 1.0 M solution of BBr_3 in CH_2Cl_2 (5 ml). The reaction mixture was stirred over 2 hrs under nitrogen. Methanol (10 ml) was added and stirred over 1 hr. The solvent was removed in a rotary evaporator, and the crude products was purified by column chromatography (silica gel, CH_2Cl_2 followed by ethyl acetate) to yield 0.42 g (90 %) of a brownish solid. ^{1}H-NMR (250 MHz, DMSO, δ, ppm) δ 7.82 (d, 4H, Ar-H, *o* to I), 7.45 (d, 4H, Ar-H), 7.33 (d, 1H, Ar-H, *p* to OH), 7.12 (s, 2H, Ar-H, *o* to OH).

Compounds **9**: Compound **8** (110 mg, 0.22 mmol), ROTs (200 mg, 0.183 mmol) and K_2CO_3 (126 mg, 0.915 mmol) were dissolved in CH_3CN (15 ml). The reaction mixture was refluxed 24 hrs under nitrogen. Cooled to room temperature, the water (30 ml) was added and the aqueous layer was washed twice with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed in a rotary evaporator. The crude products were purified by column chromatography (silica gel, ethyl acetate : methanol = 20 : 1) to yield 220 mg of a colorless oil; yield 86%. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) δ 7.73 (d, 4H, Ar-H, *o* to I), 7.32 (d, 4H, Ar-H), 7.29 (d, 1H, Ar-H, *p* to OCH_2), 7.07 (s, 2H, Ar-H, *o* to OCH_2), 4.11 (d, 2H, CCH_2O), 3.33-3.63 (m, 72H, OCH_2 and OCH_3), 2.35 (m, 1H, $CH(OCH_2)_3$), 2.03 (m, 2H, $CH(OCH_2)_3$), 1.03 (m, 12H, $CHCH_3$).

Compounds **10**: **9** (220 mg, 0.157 mmol), and 4-trimethylsilyl-phenyl-boronic acid (121.8 mg, 0.628 mmol) were dissolved in degassed THF (15 ml). Degassed 2.0 M aqueous Na_2CO_3 (10 ml) was added to the solution and then tetrakis(triphenylphosphine) palladium(0) (72 mg, 62 μmol) was added. The mixture was refluxed for 24 hrs with vigorous stirring under nitrogen. Cooled to room temperature, the layers were separated, the aqueous layer was washed twice with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed in a rotary evaporator, and the crude products was purified by column chromatography (silica gel, ethyl acetate : methanol = 20 : 1) to yield 218 mg of a colorless oil: yield 96%. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) δ 7.63-7.75 (m, 16H, Ar-H), 7.49 (d, 1H, Ar-H, *p* to OCH_2), 7.18 (s, 2H, Ar-H, *o* to OCH_2), 4.15 (d, 2H, CCH_2O), 3.33-3.63 (m, 72H, OCH_2 and OCH_3), 2.35 (m, 1H, $CH(OCH_2)_3$), 2.13 (m, 2H, $CH(OCH_2)_3$), 1.04 (m, 12H, $CHCH_3$), 0.29 (s, 18H, $(CH_3)_3Si$).

Compound **11**: To a solution of compound **10** (218 mg, 0.151 mmol) in CH_2Cl_2 (100 ml) at –78 °C was added 1.0 M solution of ICl in CH_2Cl_2 (0.9 ml). The reaction mixture was stirred over 2 hrs under nitrogen. 1.0 M aqueous $Na_2S_2O_5$ solution was added and stirred over 1hr. The layers were separated, the aqueous layer was washed twice with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed in a rotary evaporator, and the crude products were purified by column chromatography (silica gel, ethyl acetate : methanol = 20 : 1) to yield 226 mg of a colorless oil.: yield 97%. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) δ 7.62-7.80 (m, 12H, Ar-H), 7.46 (d, 1H, Ar-H, *p* to OCH_2), 7.37-7.40 (m, 4H, Ar-H), 7.16 (s, 2H, Ar-H, *o* to OCH_2), 4.13 (d, 2H, CCH_2O), 3.34-3.63 (m, 72H, OCH_2 and OCH_3), 2.35 (m, 1H, $CH(OCH_2)_3$), 2.13 (m, 2H, $CH(OCH_2)_3$), 1.04 (m, 12H, $CHCH_3$).

Compounds **12** and **13:** Compounds **12** and **13** were synthesized using the same procedure. A representative example is described for compound **12**. **11** (226 mg, 0.145 mmol), and 4-pyridylboronic acid (121.8 mg, 0.628 mmol) were dissolved in degassed dioxane (10 ml). Degassed 2.0 M aqueous Na_2CO_3 (7 ml) was added to the solution and then tetrakis(triphenylphosphine) palladium(0) (72 mg, 62 μmol) was added. The mixture was refluxed for 24 hrs with vigorous stirring under nitrogen. Cooled to room temperature, the layers were separated, the aqueous layer was washed twice with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed in a rotary evaporator, and the crude products was purified by column chromatography (silica gel, ethyl acetate : methanol = 15 : 1) to yield 67.8 mg of a colorless oil.

12: yield 32%. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) δ 8.68 (d, 4H, Py_α), 7.76 (m, 16H, Ar-H), 7.53 (d, 4H, Py_β), 7.49 (d, 1H, Ar-H, *p* to OCH_2), 7.20 (s, 2H, Ar-H, *o* to OCH_2), 4.13 (d, 2H, CCH_2O), 3.34-3.63 (m, 72H, OCH_2 and OCH_3), 2.35 (m, 1H, $CH(OCH_2)_3$), 2.13 (m, 2H, $CH(OCH_2)_3$), 1.08 (m, 12H, $CHCH_3$). Anal. Calcd for $C_{84}H_{116}N_2O_{19}$: C, 69.21; H, 8.02; N, 1.92. Found: C, 69.08; H, 7.97; N, 1.95. MALDI-TOF-MS m/z $(M+H)^+$ 1457.81.

13: yield 37%. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) δ 8.68 (d, 4H, Py_α), 7.77 (m, 8H, Ar-H), 7.56 (d, 4H, Py_β), 7.46 (d, 1H, Ar-H, *p* to OCH_2), 7.19 (s, 2H, Ar-H, *o* to OCH_2), 4.13 (d, 2H, CCH_2O), 3.34-3.63 (m, 72H, OCH_2 and OCH_3), 2.35 (m, 1H, $CH(OCH_2)_3$), 2.13 (m, 2H, $CH(OCH_2)_3$), 1.08 (m, 12H, $CHCH_3$). Anal. Calcd for

$C_{72}H_{108}N_2O_{19}$: C, 66.23; H, 8.34; N, 2.15. Found: C, 66.28; H, 8.33; N, 2.13. MALDI-TOF-MS m/z $(M+H)^+$ 1305.31.

Complexation of **12** and **13** with silver triflates and tetrafluoroborates: Complexes were prepared using the same procedure. A representative example is described for **2**. **12** (30 mg, 0.021 mmol) and silver triflate (5.39 mg, 0.021 mmol) were dissolved in dry EtOH solvent (10 ml) and stirred under N_2 for 3 hrs at 25 °C, and the solvent was then removed in a rotary evaporator to yield dimly yellow solid of **2**. **1**: Anal. Calcd for $C_{73}H_{108}AgF_3N_2O_{22}S$: C, 56.11; H, 6.97; N, 1.79. Found: C, 56.20; H, 6.99; N, 1.77. MALDI-TOF-MS m/z $(M+Ag)^+$ 1412.95. **2**: Anal. Calcd for $C_{85}H_{116}AgF_3N_2O_{22}S$: C, 59.54; H, 6.82; N, 1.63. Found: C, 59.52; H, 6.84; N, 1.60. MALDI-TOF-MS m/z $(M+Ag)^+$ 1565.91. **1** (BF_4): Anal. Calcd for $C_{72}H_{108}AgBF_4N_2O_{19}$: C, 57.64; H, 7.26; N, 1.87. Found: C, 56.90; H, 7.19; N, 1.82. MALDI-TOF-MS m/z $(M+Ag)^+$ 1412.75. **2** (BF_4): Anal. Calcd for $C_{84}H_{116}AgBF_4N_2O_{19}$: C, 61.05; H, 7.08; N, 1.70. Found: C, 60.72; H, 7.01; N, 1.65. MALDI-TOF-MS m/z $(M+Ag)^+$ 1565.53.

Computation: Simulations were conducted with Materials Studio Modeling 4.0 (Accelrys Inc.) software according to the following procedure. First, a coordination polymer consisting of 15 ligands and silver triflates was built using the MS Visualizer. The potential energy of helical polymer was then minimized until root-mean square derivative 1.0 (kcal/mo)/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 100000. The interatomic interactions were modeled with the COMPASS force field.

Density Calculation: $N = (\rho \times A \times N_A \times l) / M$; ρ = density (estimated from hexane and CCl_4 solution), A = cross-sectional area of the column (calculated from XRD data), N_A = avogadro' number, l = height of a tilted ligand against central axis (calculated from molecular modeling), M = molecular weight. **2**: $n = (1.301\text{g} \times 10^{-21}\text{nm}^3 \times 14.92\text{nm}^2 \times 6.02 \times 10^{23}/\text{mol} \times 2.55\text{nm}) / (1714\text{g/mol}) = 17.50$.

TEM experiments: For study of self-assembled structures of coordination polymers in aqueous solutions, a drop of solution (0.02 wt% aqueous solution) was placed on a carbon-coated copper grid and allowing the solution evaporate under ambient conditions. For study of gel structures in aqueous solution, a drop of aqueous solution of samples was placed on a grid, and dried at 50 ^{o}C in oven. The samples were stained by depositing a drop of 2 wt% uranyl acetate aqueous solution onto the surface of the sample-loaded grid. After 2 min, excess solution was wicked off by filter paper. The dried specimen was observed with a JEOL-JEM 2010 instrument operating 120 kV.

DLS spectroscopy: Dynamic light scattering measurements were performed using UNIPHASE He-Ne laser operating at 632.8 nm. The scattering was kept at 90^o during the whole experiment. The maximum operating power of the laser was 30 mW. The detector optics employed optical fibers coupled to an ALV/SOSIPD/DUAL detection unit, which employed an EMI PM-28B power supply and ALV/PM-PD preamplifier/discriminator. The signal analyzer was an ALV5000/E/WIN multiple digital correlator with 288 exponentially spaced channels. The hydrophobic radius (R_H) was determined from the DLS autocorrelation functions by the cumulants and the CONTIN methods using the software provided by the manufacturer.

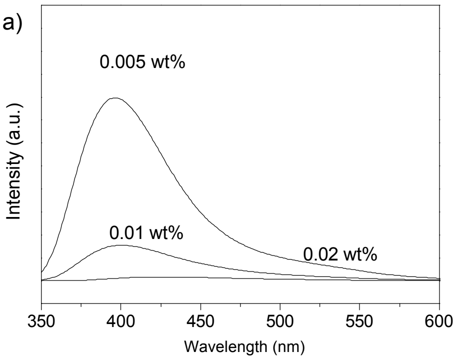


Figure S1. Fluorescence spectra of (a) **1** and (b) **2** in aqueous solutions (25 °C, excited at 285 and 305 nm, respectively) with concentration variation. This result indicates that the aggregation concentrations of **1** and **2** are 0.02 wt%.

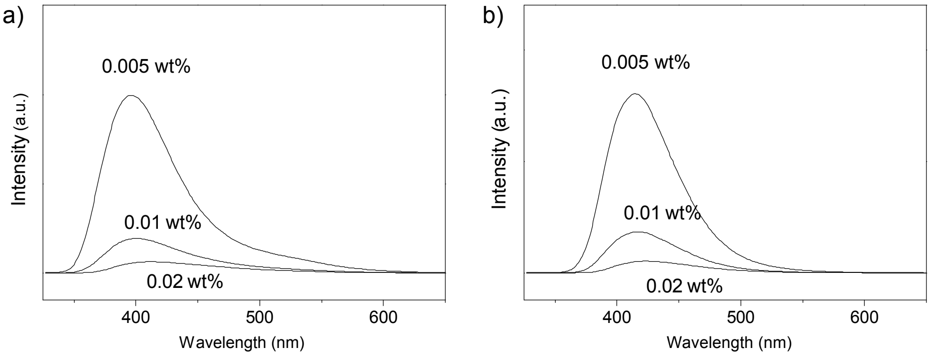


Figure S2. Fluorescence spectra of (a) **1** and (b) **2** (BF_4^-) in aqueous solutions (25 °C, excited at 285 and 305 nm, respectively) with concentration variation. This result indicates that the aggregation concentration of coordination polymers is 0.02 wt%.

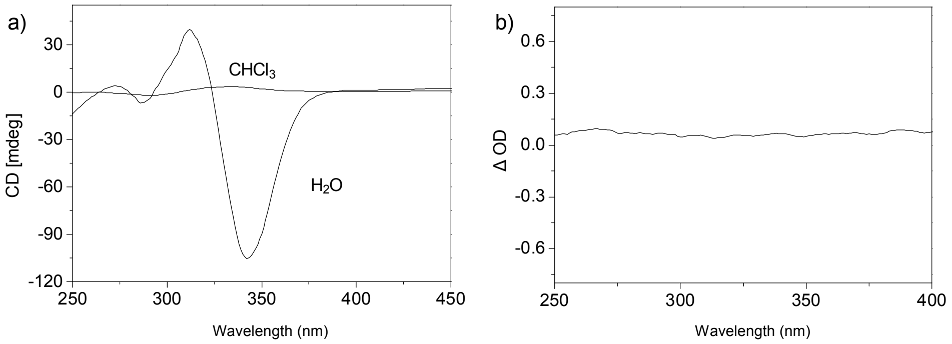


Figure S3. (a) CD spectra of **2** in chloroform and aqueous solution (25 °C, 0.1 wt%). (b) LD spectra of **2** in aqueous solution (0.1 wt%). The value of CD in $CHCl_3$ and the value of LD in aqueous solution are negligibly small, indicating that the CD signals of **2** in aqueous solution come from molecular assemblies.

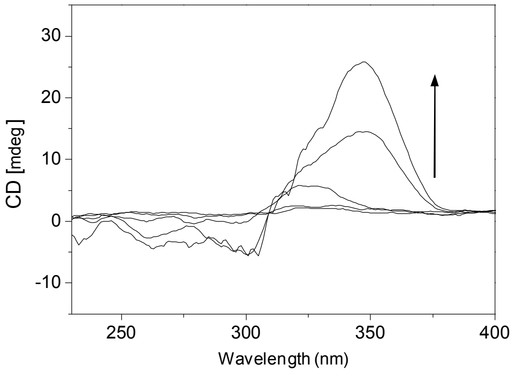


Figure S4. CD spectra of **2** (BF_4^-) in aqueous solution with concentration variation at 25 °C. The arrow indicates CD changes upon increasing concentration from 0.01 to 0.1 wt%.

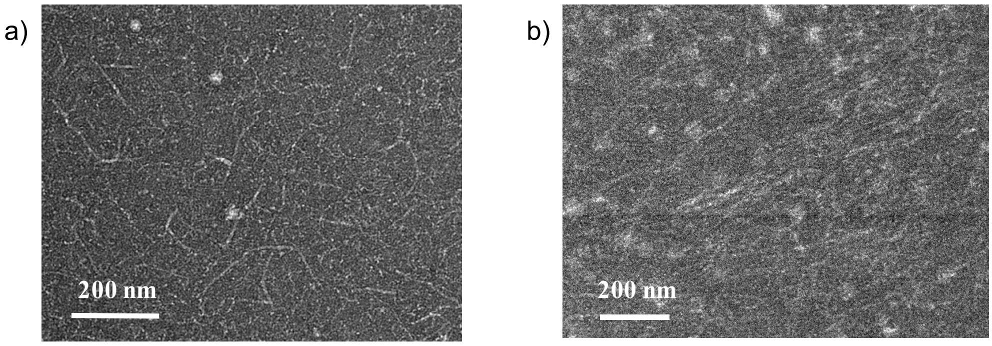


Figure S5. TEM images of (a) **1** and (b) **2** (BF_4^-) prepared from evaporation of aqueous solution.

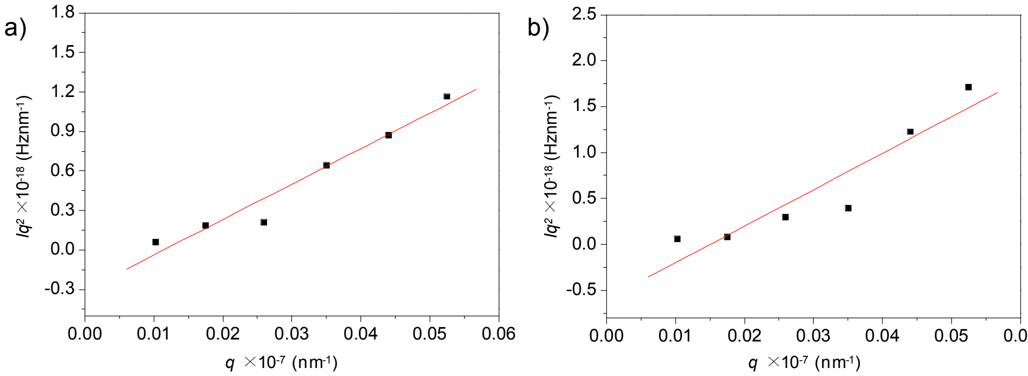


Figure S6. Kratky plots and linear fit of a) **1** and b) **2** in aqueous solution (0.1 wt %) at room temperature. These results indicate that coordination polymers **1** and **2** form 1D cylindrical shaped objects.[S1]

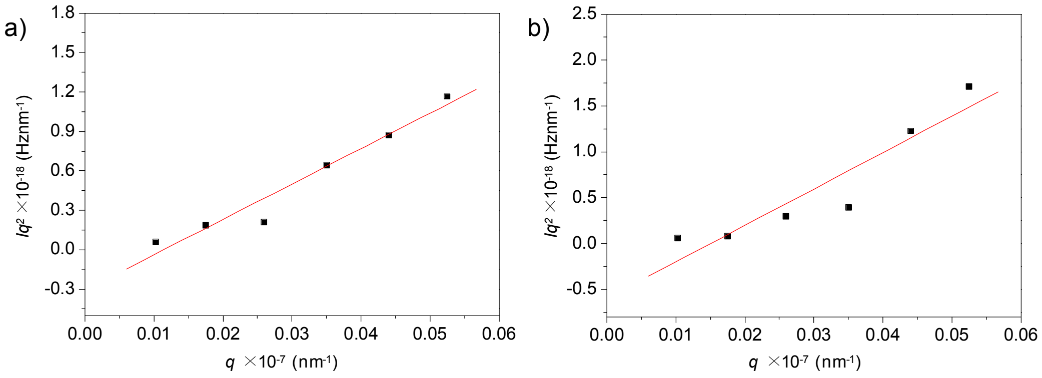


Figure S7. Kratky plots and linear fit of a) **1** and b) **2** in aqueous solution (0.1 wt %) at room temperature. These results indicate that coordination polymers **1** and **2** form 1D cylindrical shaped objects.[S1]

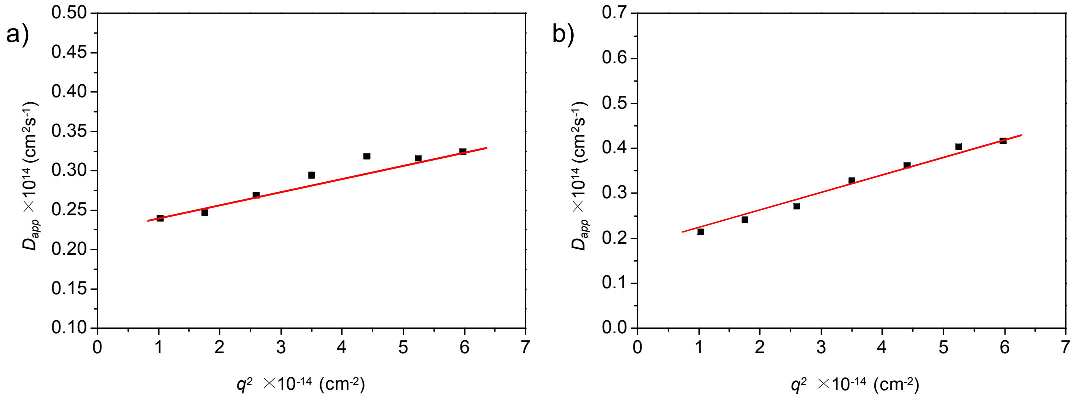


Figure S8. Angular dependence of the apparent diffusion coefficient for a) **1** and b) **2** in aqueous solution (0.1 wt %) at room temperature. The slopes of angular dependence of **1** and **2** were observed to be 0.03 and 0.05, respectively. These results indicate that coordination polymers **1** and **2** form 1D cylindrical shaped objects.[S1]

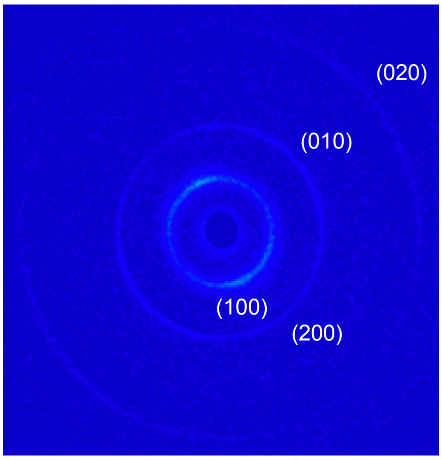


Figure S9. 2D X-ray diffraction pattern obtained from **1** prepared by slow evaporation of aqueous solution. The diffraction pattern shows 2D lamellar structure with in-plane order of $d_{(010)}$ = 1.97 nm with a layer thickness of $d_{(001)}$ = 3.95 nm.

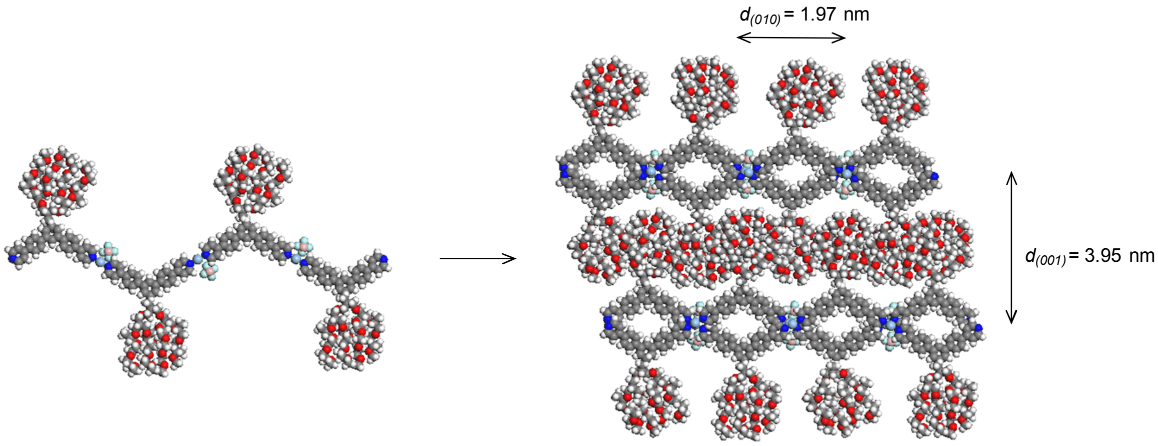


Figure S10. Molecular modeling for the formation of lamellar structure of **1**.

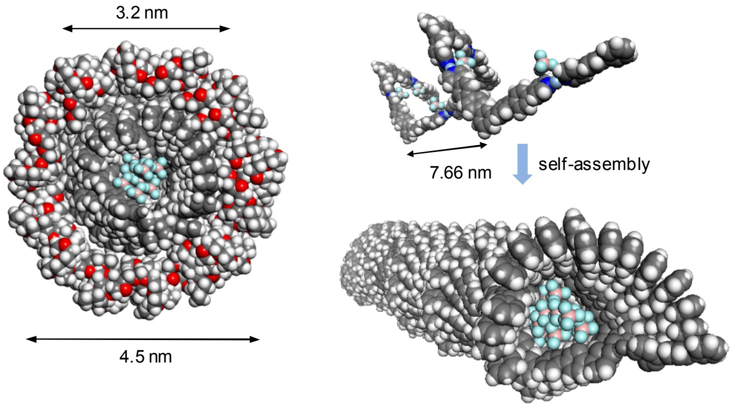


Figure S11. Molecular modeling for the formation of multi-stranded nanofibers of **2**. Top view (left) and perspective view at 45° (right).

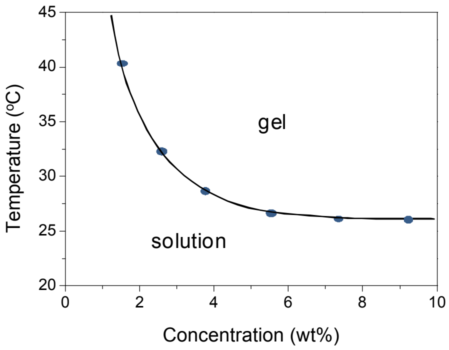


Figure S12. Phase diagram plotted in terms of the temperature versus the concentration of **2** in aqueous solution.

References

S1. (a) Massey, J.; Power, K. N.; Manners, I.; Winnik, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 9533-9540. (b) Boersma, J. *J. Chem. Phys.* **1981**, *74*, 6989-6990. (c) Bockstaller, M.; Köhler, W.; Wegner, G.; Vlassopoulos, D.; Fytas, G. *Macromolecules* **2000**, *33*, 3951-3953.