Supporting Information for

Morphological Control of Coil-rod-coil Molecules Containing *m*-terphenyl Group: Construction of Helical Fibers and Helical Nano-rings in Aqueous Solution

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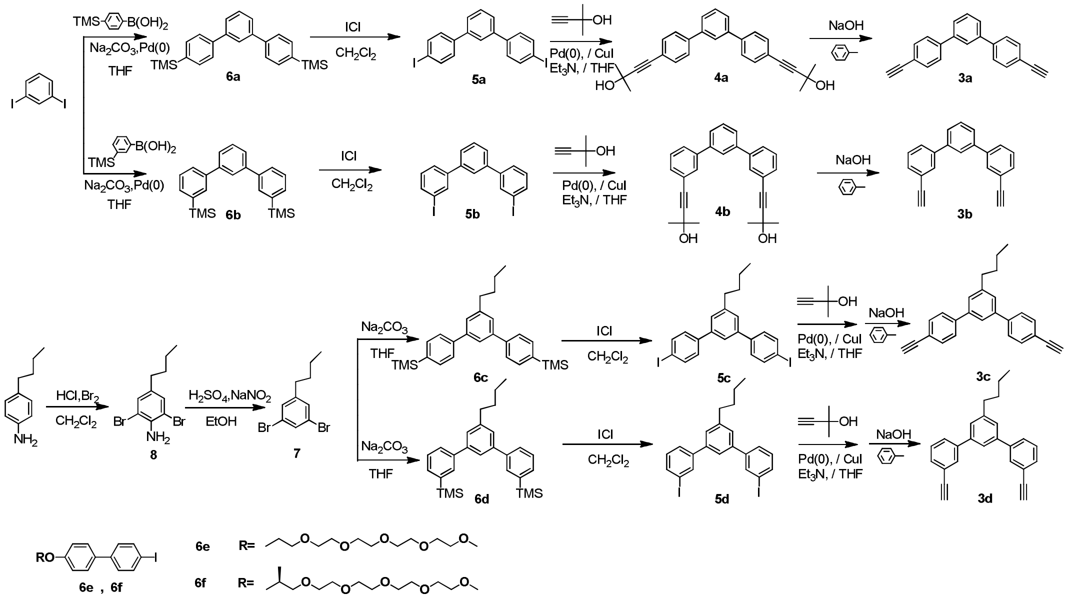
EXPERIMENTAL SECTION



Scheme S1. Synthetic route of molecules 1-2.

Synthesis

Synthesis of compounds 4a, 4b, 4c, 4d

Molecules were synthesized following a similar procedure. A representative example is described for compound **4a**. Compound **5a** (1.0 g, 2.074 mmol), 2-methyl-3-butyn-2-ol (0.52 g, 6.223 mmol), CuI (0.016 g, 0.083 mmol) and $Pd(PPh_3)_4$ (0.048 g, 0.041 mmol) were dissolved in dry THF (30 ml) and Et_3N (20 ml). The mixture was refluxed for 24 h under Ar, and then the solution was concentrated and washed by water. The mixture was extracted with CH_2Cl_2 and dried over anhydrous magnesium sulphate andfiltered. After the solvent was removed in a rotary evaporator, the crude product was purified by silica gelchromatography (CH_2Cl_2: PE, 1 : 3 as eluent) to yield 0.4 g of a yellow solid (48.9%). ^{1}HNMR (300 MHz, $CDCl_3$, δ, ppm): 7.77 (s, 1H), 7.49-7.61 (m, 11H), 1.71 (s, 2H), 1.65 (s, 12H).

Compound 4b, Yield:52%. ^{1}HNMR (300 MHz, $CDCl_3$, δ, ppm): 7.74 (d, J=15 Hz, 2H), 7.39-7.59 (m, 10H), 2.08 (s, 2H), 1.65 (s, 12H).

Compound 4c, Yield:50%. ^{1}HNMR (300 MHz, $CDCl_3$, δ, ppm): 7.59 (d, J=9 Hz, 5H), 7.50 (d, J=9 Hz, 4H), 7.39 (s, 2H), 2.73 (t, J=6 Hz, 2H), 1.65 (s, 12H), 1.38-1.48 (m, 2H), 1.24-1.28 (m, 2H), 0.96 (t, J=6 Hz, 3H).

Compound 4d, Yield:47%. ^{1}HNMR (300 MHz, $CDCl_3$, δ, ppm): 7.70 (s, 2H), 7.59 (d, J=9 Hz, 3H), 7.40 (d, J=6 Hz, 6H), 2.74 (t, J=6 Hz, 2H), 1.70-1.75 (m, 2H), 1.65 (s, 12H), 1.38-1.46 (m, 2H), 0.96 (t, J=6 Hz, 3H).

Synthesis of Compound 3a, 3b, 3c, 3d

Molecules were synthesized following a similar procedure. A representative example is described for compound **3a**. Compound **4a** (0.2 g, 0.507 mmol) and NaOH (0.203 g, 5.07 mmol)were dissolved in toluene (50 ml) mixture was refluxed for 5 h under Ar, and then the solution was concentrated and washed by water. The mixture was extracted with CH_2Cl_2 and dried over anhydrous magnesium sulphate and filtered. After the solvent was removed in a rotary evaporator, the crude product was purified by silica gelchromatography (CH_2Cl_2: PE, 1 : 3 as eluent) to yield 113 mg of a yellow solid (80%). ^{1}HNMR (300 MHz, DMSO, δ, ppm): 7.96 (s, 1H), 7.83 (d, J=9 Hz, 4H), 7.72 (d, J=6 Hz, 2H), 7.59 (d, J=6 Hz, 5H), 4.29 (s, 2H).

Compound 3b, Yield:78%. ^{1}HNMR (300 MHz, DMSO, δ, ppm): 7.78 (s, 3H), 7.39 -7.64 (m, 9H), 3.12 (s, 2H).

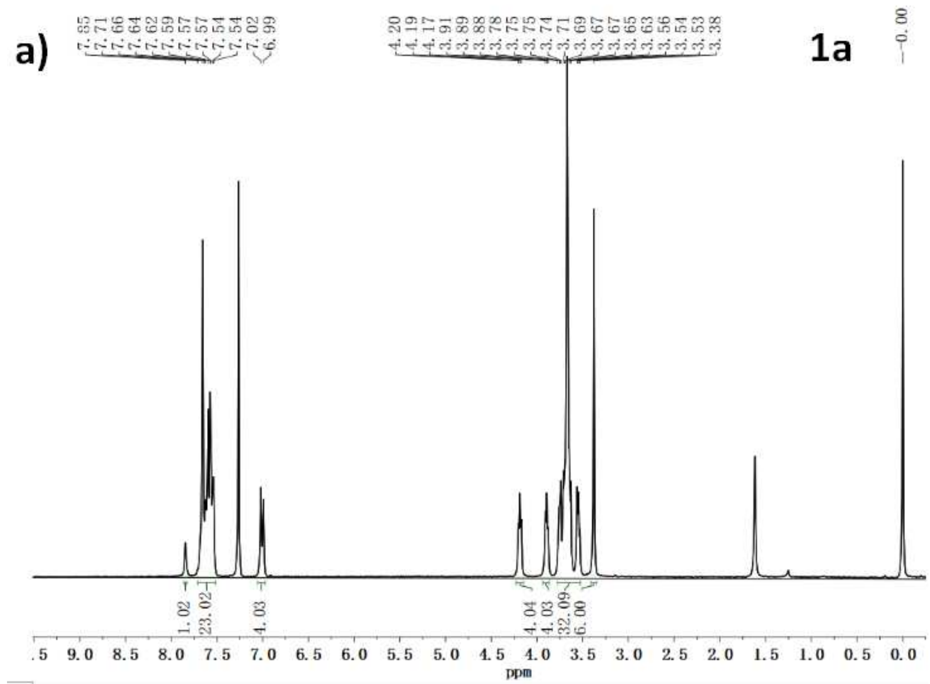
Compound 3c, Yield:72%. ^{1}HNMR (300 MHz, DMSO, δ, ppm): 7.79 (t, J=9 Hz, 5H), 7.56 (t, J=9 Hz, 6H), 4.28 (s, 2H), 2.73 (t, J=6 Hz, 2H), 1.60-1.71 (m, 2H), 1.30-1.42 (m, 2H), 0.92 (t, J=6 Hz, 3H).

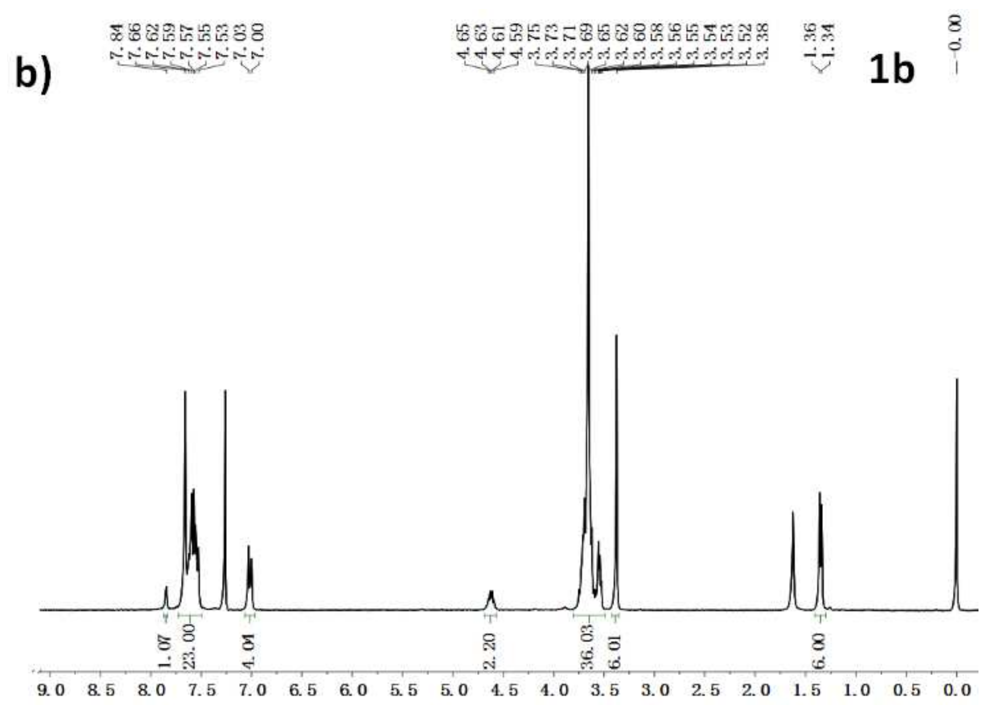
Compound 3d, Yield:77%. ^{1}HNMR (300 MHz, $CDCl_3$, δ, ppm): 7.77 (s, 2H),7.61 (t, J=9 Hz, 3H), 7.49 (d, J=6 Hz, 2H), 7.41 (t, J=6 Hz, 4H), 3.12 (s, 2H), 2.74 (t, J=6 Hz, 2H), 1.64-1.74 (m, 2H), 1.36-1.48 (m, 2H), 0.96 (t, J=6 Hz, 3H).

Compound 6a-5a, 6e, 6f, 8-7, 6b-5b were synthesized by the same procedure from literature.[1-4]

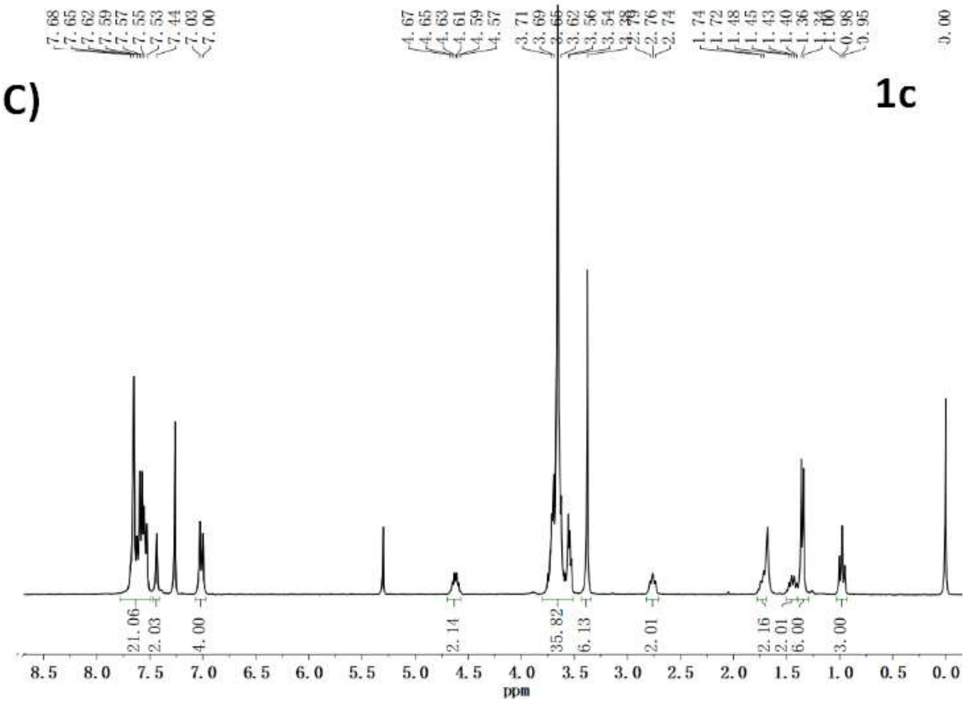
Preparation of aqueous solutions

In a 20 mL flask, 1 mg of molecule and 10 mL distilled water were added. The flask was sonicated for 3~5 minutes at 25 ^{o}C in KQ-250E ultrasonicator (250W), until the molecule was dissolved in water. Then, the flask was further sonicated for 40 minutes at 25 °C in KQ-100KDE ultrasonicator (60 W). Finally, the solution is allowed to stand for 1 hour to prepare samples of AFM or TEM.

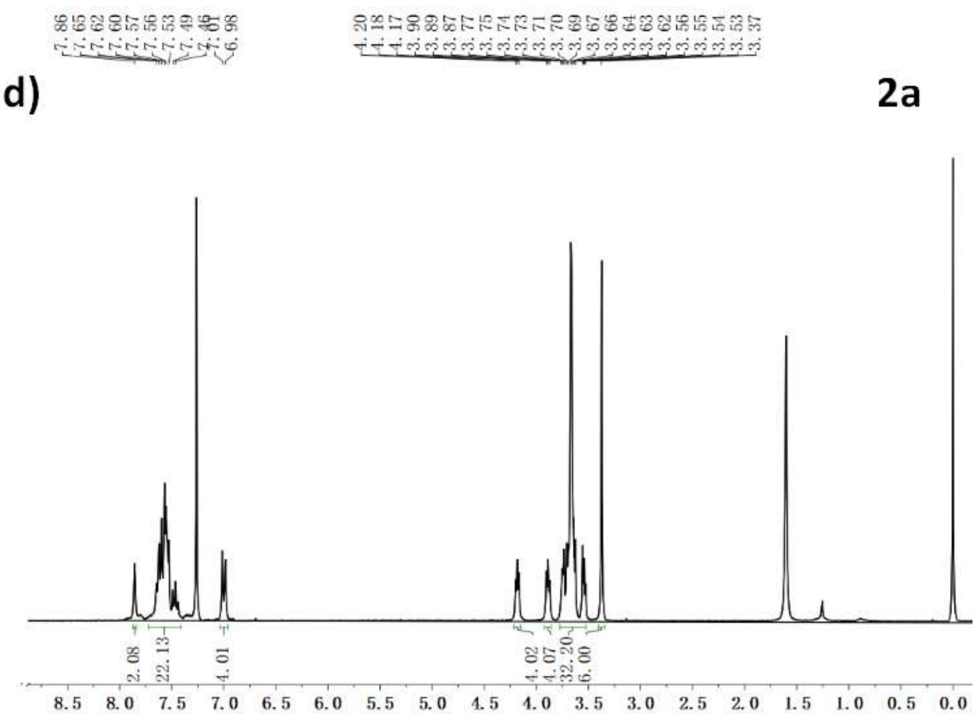


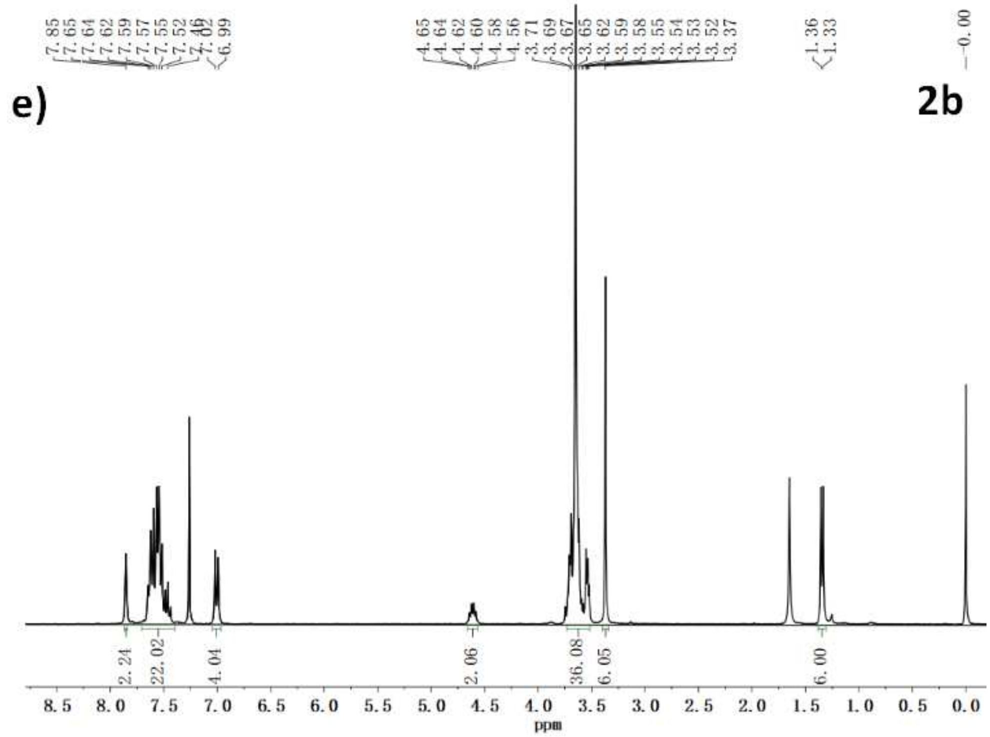


c) 1c



d) 2a





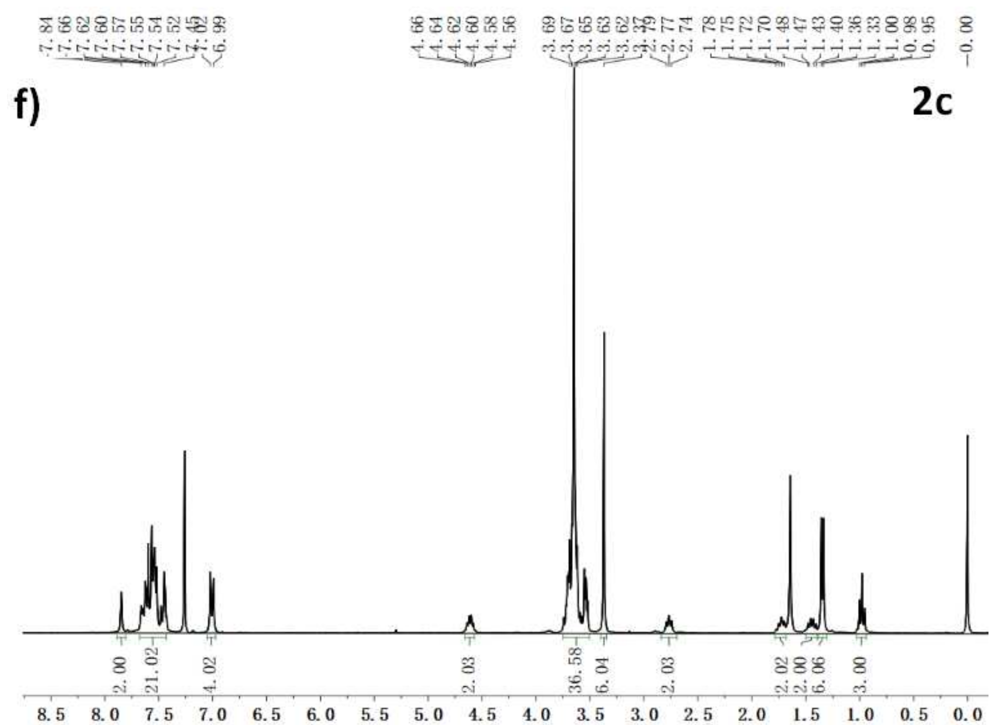
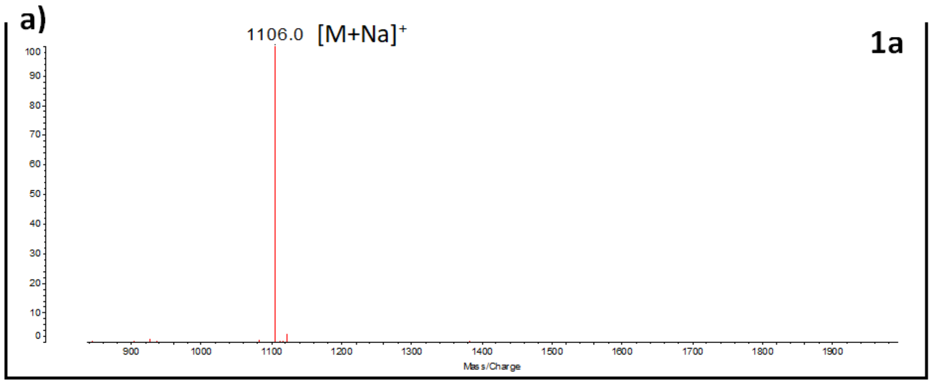
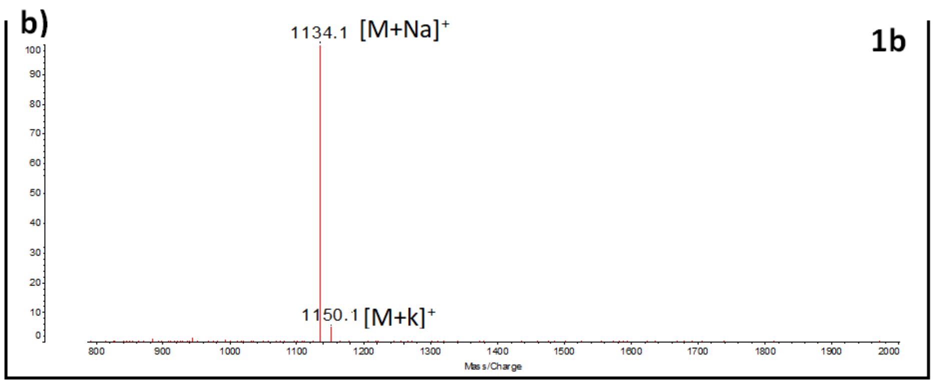
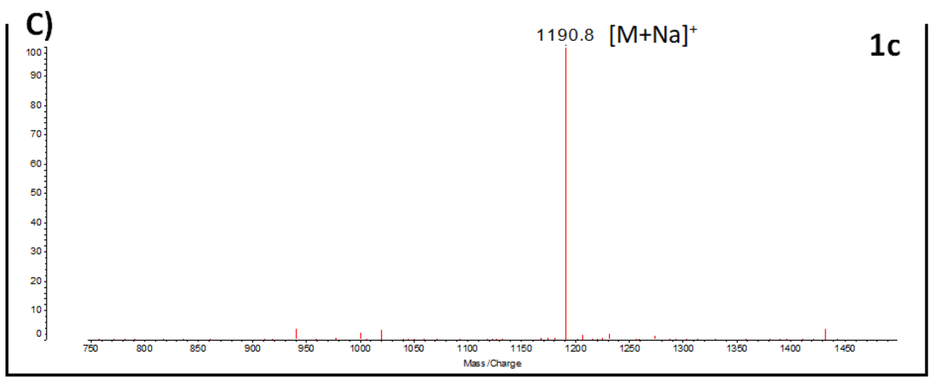
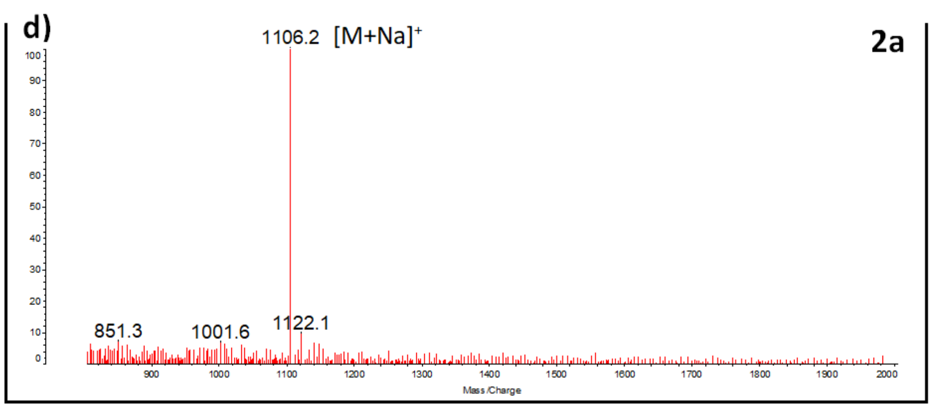


Figure S1. ^{1}H-NMR spectra of molecules **1-2** in $CDCl_3$.


a)
1106.0 [M+Na]+
1a
Mass/Charge


b)
1134.1 [M+Na]+
1b
1150.1 [M+k]+
Mass/Charge


C)
1190.8 [M+Na]+
1c
Mass/Charge


d)
1106.2 [M+Na]+
2a
851.3
1001.6
1122.1
Mass/Charge

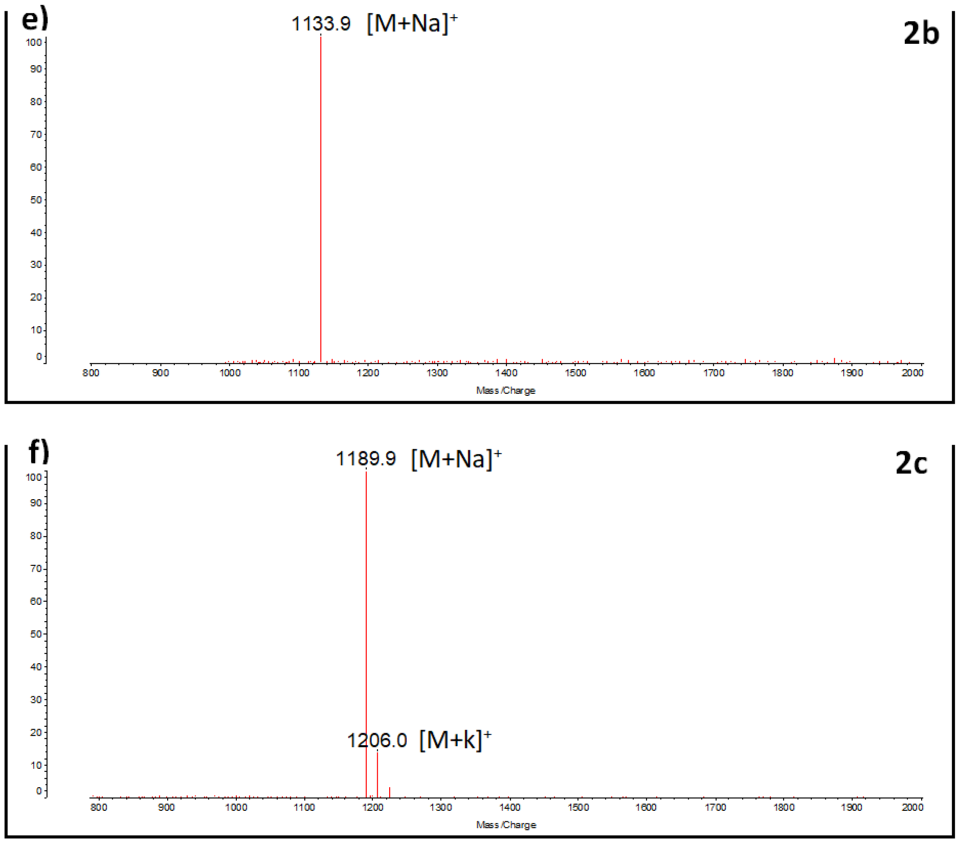


Figure S2. MALDI-TOF-Mass spectra of molecules **1-2** (matrix: CHCA).

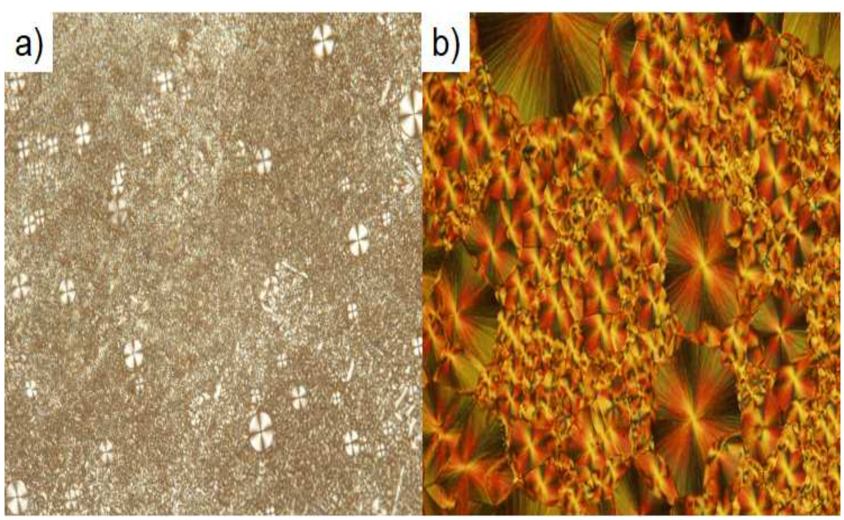


Figure S3. Representative optical polarized micrographs (40×) of the oblique columnar structures: molecules **1b** for (a), **1c** for (b).

Table S1. Thermal transitions of molecules **1-2** (data are from the second heating and the first cooling scans). a= volume fraction of coil to rod-coil molecule.

		Phase transition (^{o}C) and corresponding enthalpy changes (KJ·mol^{-1})	
Molecule	**f_{coil}^{a}**	**Heating**	**Cooling**
1a	**0.49**	**L221.7 Col_{ob} 265.9 i**	**i 275.0 Col_{ob} 239.3 L**
1b	**0.50**	**Col_{ob} 217.5 i**	**i 207.6 Col_{ob}**
1c	**0.53**	**Col_{ob} 56.8 i**	**i 53.9 Col_{ob}**
2a	**0.49**	**Col_{ob} 111.6 i**	**i 91.5 Col_{ob}**

L= Lamellar phase, Col_{ob}= oblique columnar phase.

Table S2. Small-Angle X-ray diffraction data for the structure of **1a** in the liquid crystalline phase at 265 ^{o}C.

The oblique columnar structure of **1a** in the liquid crystalline phase		
hkl	q_{obsd} (nm^{-1})	q_{calcd} (nm^{-1})
100	1.362	1.367
010	2.355	2.350
210	2.707	2.705
300	4.084	4.086

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections for oblique columnar structure with lattice parameters a=5.13nm, c=2.97 nm, γ =64°, respectively.

Table S3. Small-Angle X-ray diffraction data for the structure of **1b** in the crystalline phase at 150 ^{o}C.

The oblique columnar structure of **1b** in the crystalline phase		
hkl	q_{obsd} (nm^{-1})	q_{calcd} (nm^{-1})
100	1.440	1.438
010	1.681	1.680
210	1.953	1.951
120	2.456	2.463
200	2.883	2.876
310	3.103	3.246

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections for oblique columnar structure with lattice parameters a = 6.66 nm, b =5.70 nm, γ =41°.

Table S4. Small-Angle X-ray diffraction data for oblique columnar structure of molecule **1c** at 35 °C.

The oblique columnar structure of **1c** in the crystalline phase		
hkl	q obsd (nm^{-1})	q calcd (nm^{-1})
100	1.413	1.410
010	2.120	2.122
200	2.826	2.819
120	3.435	3.431

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections for the oblique columnar structure with lattice parameters a = 7.40 nm, b= 4.69 nm, γ= 37°.

Table S5. Small-Angle X-ray diffraction data for oblique columnar structure of molecule **2a** at 30 °C.

The oblique columnar structure of **2a** in crystalline phase		
hkl	q obsd (nm^{-1})	q calcd (nm^{-1})
100	1.794	1.794
010	2.566	2.563
210	3.425	3.417
200	3.588	3.588

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections for oblique columnar structure with lattice parameters a=3.86 nm, b=2.70 nm, γ=65°.

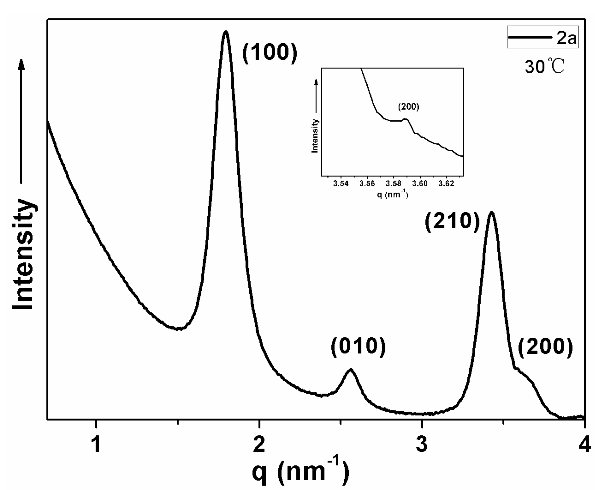


Figure S4. Small-angle X-ray diffraction patterns of **2a** measured in solid state (oblique columnar phase for **2a** at 30 °C).

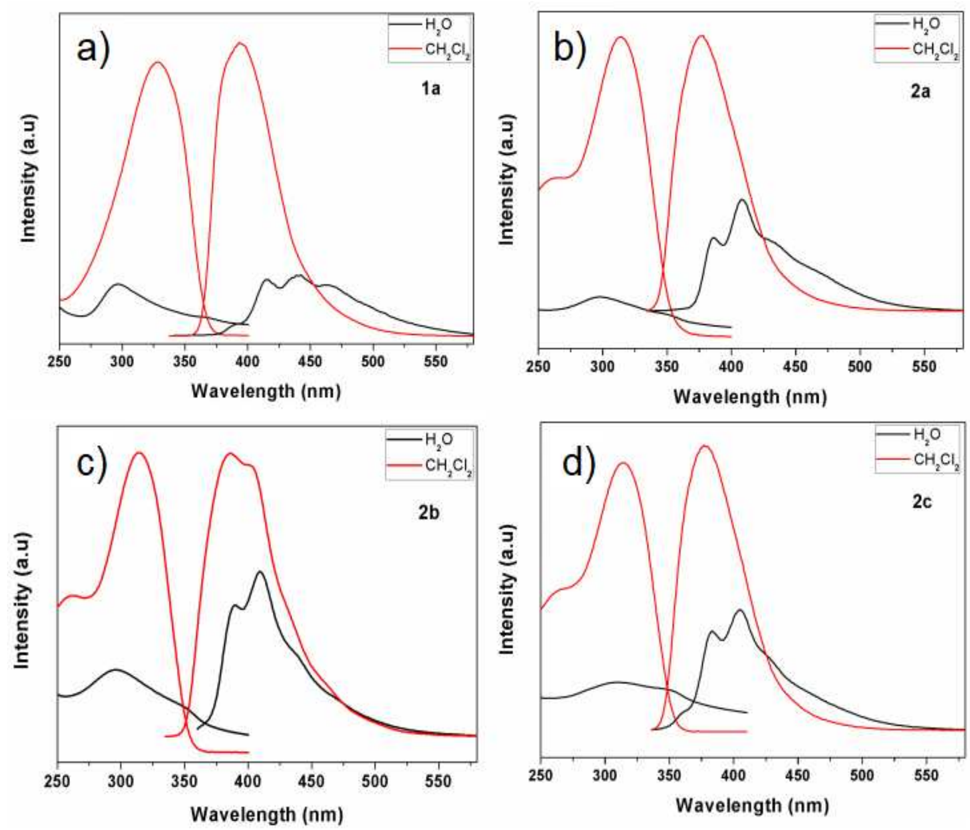


Figure S5. Absorption and emission spectra of **1a** and **2a-2c** (0.002 wt%) in dichloromethane and aqueous solution.

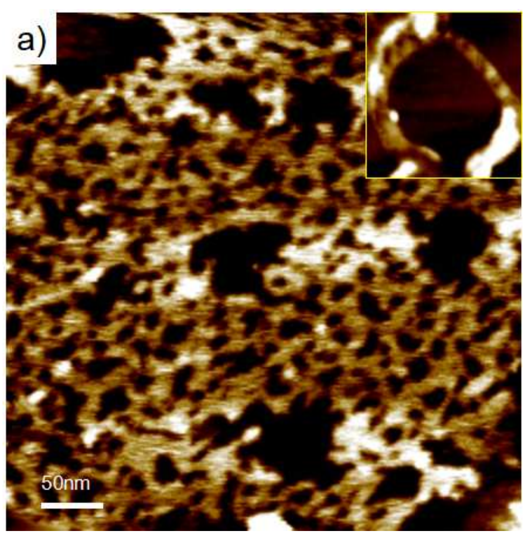


Figure S6. AFM phase image (inset, amplifying AFM image) of **2c** from 0.01 wt % aqueous solution.

References for Supporting Information

[1] Kokado, K.; Tokoro, Y.; Chujo, Y. *Macromolecules* **2009**, 42, 9238-9242.
[2] Yang, Y.; Cui, J.; Li, Z.; Zhong, K.; Lee, M.; Jin, L. *Macromolecules* **2016**, 49, 5912–5920.
[3] Shua, L.; Mayor, M. *Chem. Commun.* ***2*006**, 0, 4134-4136.
[4] Kim, J-K.; Lee, E.; Kim, M-C.; Sim, E.; Lee, M. J. Am. Chem. Soc. **2009**, 131, 17768-17770.