

Electronic Supplementary Information (ESI)

Control of supramolecular nanoassemblies by tuning the interactions of bent-shaped rod-coil molecules

Shengnan You,^{‡a} Keli Zhong,^{‡b} Long Yi Jin^{*a}

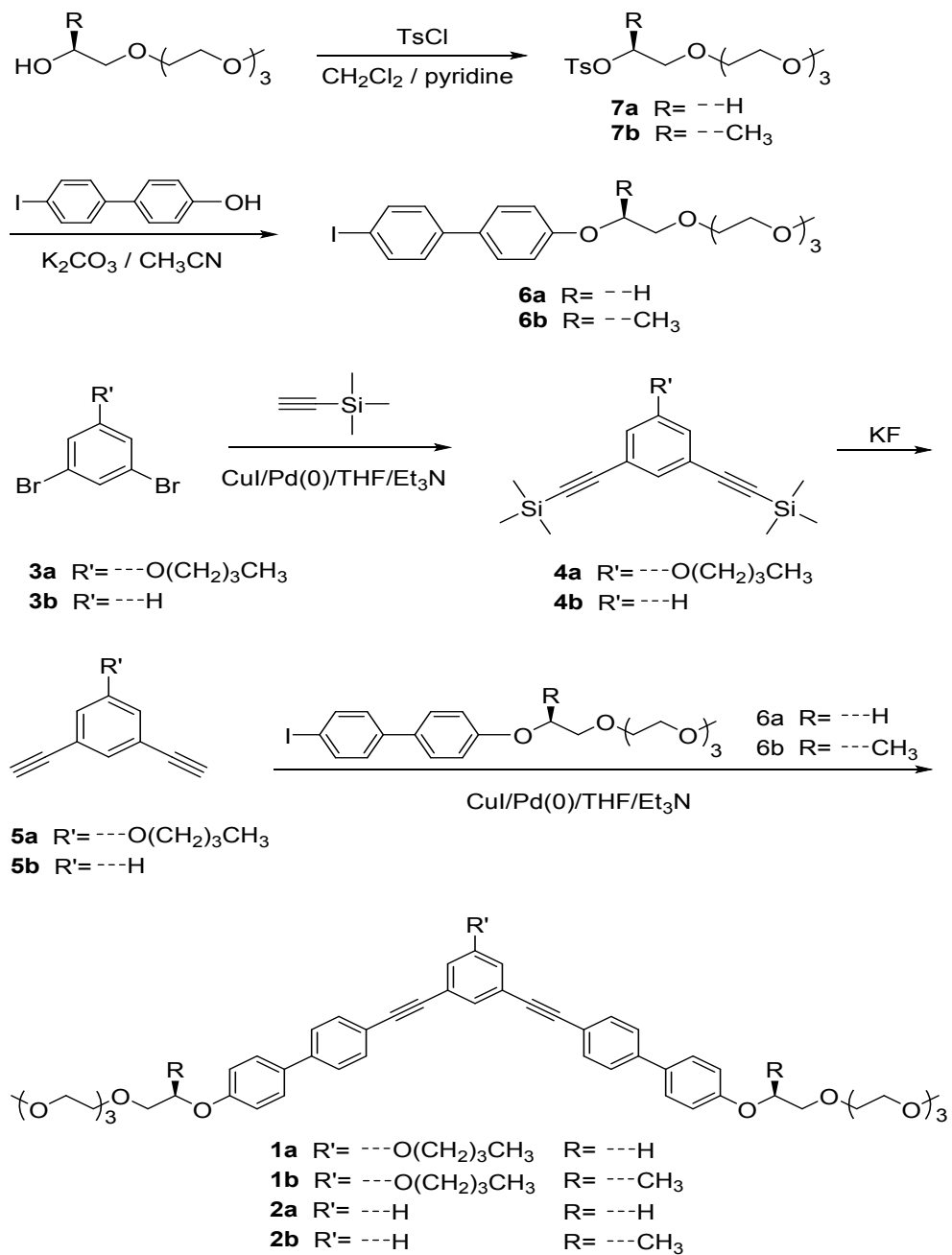
^aKey Laboratory for Organism Resources of the Changbai Mountain and Functional Molecules, Ministry of Education, and Department of Chemistry, College of Science, Yanbian University, Yanji 133002, China

^bCollege of Chemistry, Chemical Engineering and Food Safety, Bohai University, Jinzhou 121013, China

[‡]equally contributed to this work

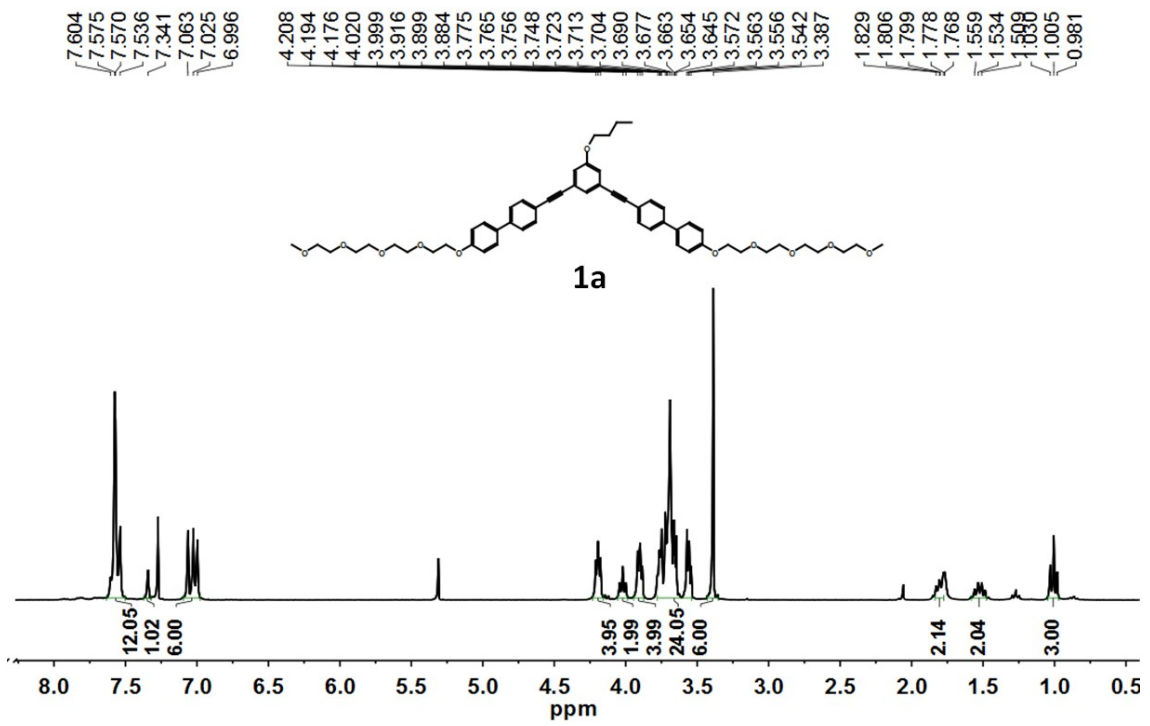
**Corresponding author. E-mail address: lyjin@ybu.edu.cn (L. Y. Jin)*

1. Synthetic method



Scheme S1. Synthetic route of molecules from **7a-7b** to **1a-1b**.

2. Characterization of compounds 1a-1b and 2a-2b



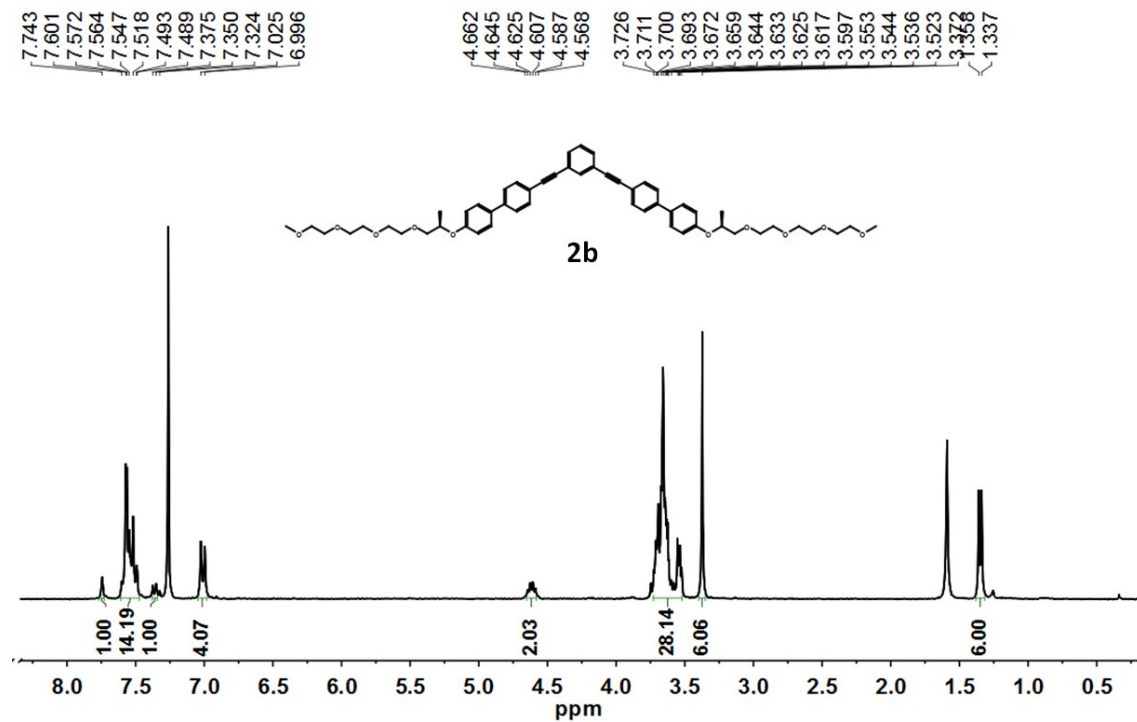
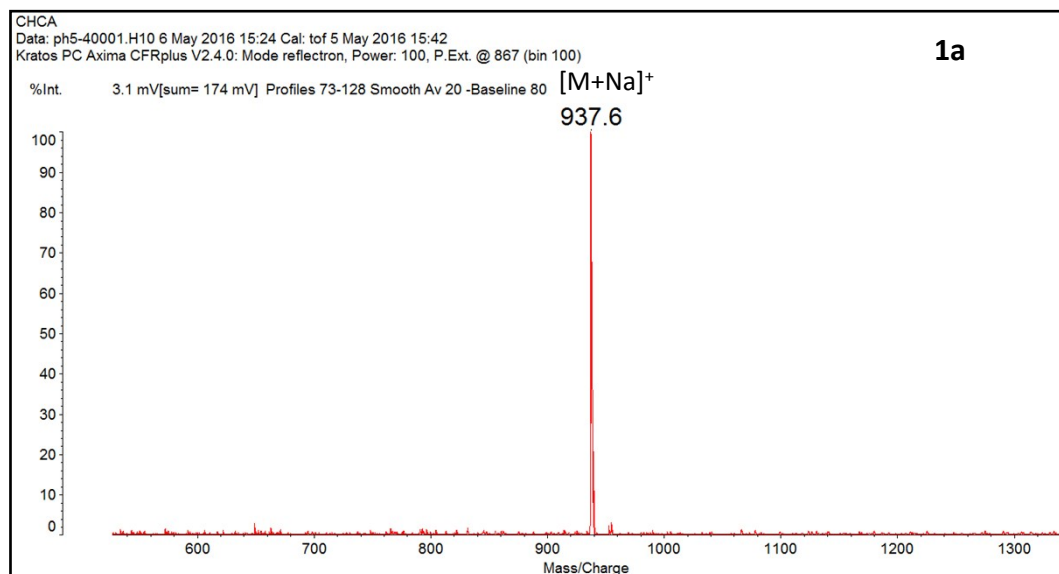


Figure S2. $^1\text{H-NMR}$ spectra of molecules **2a-2b** in CDCl_3 .



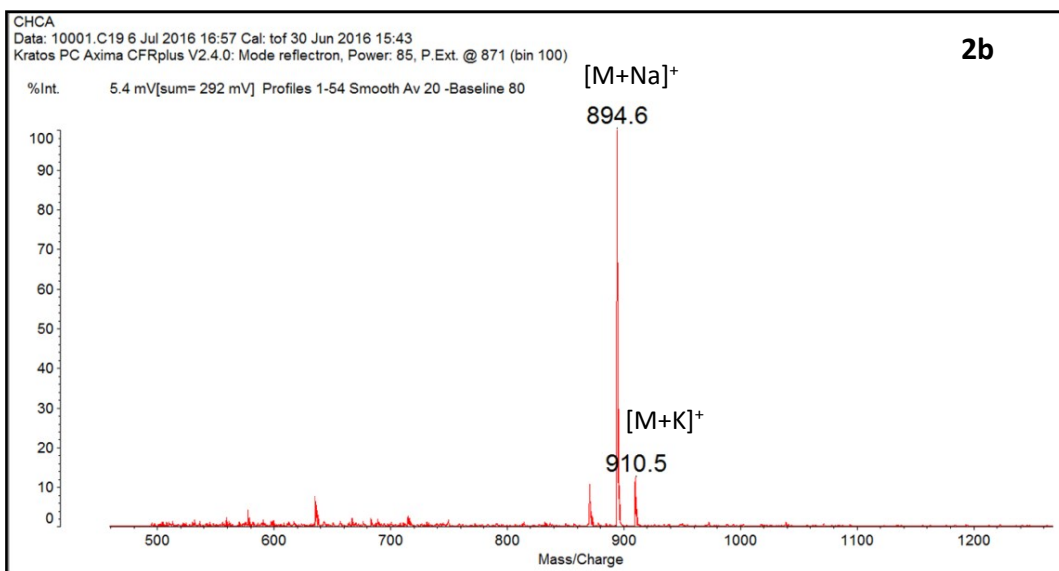
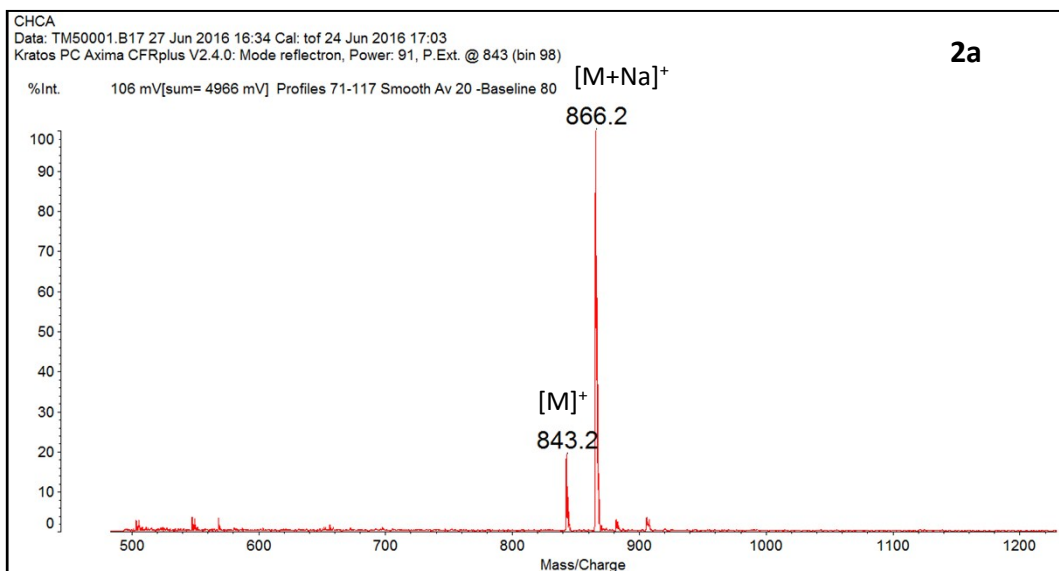
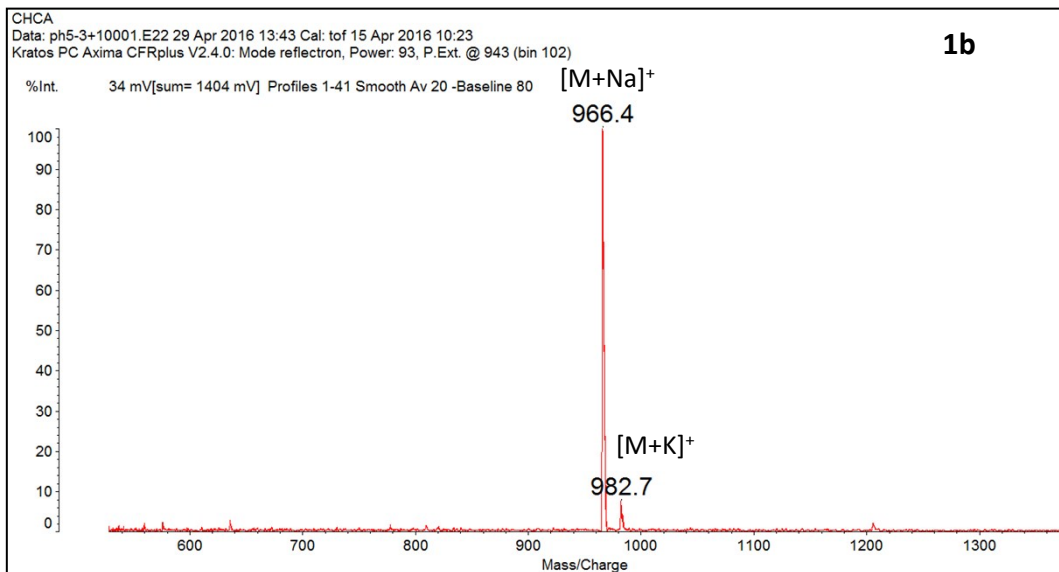


Figure S3. MALDI-TOF-MS spectra of **1a** (m/z $[M]^+$ 915.1), **1b** (m/z $[M]^+$ 943.2), **2a** (m/z $[M]^+$ 843.2) and **2b** (m/z $[M]^+$ 871.5), matrix: CHCA.

3. Synthesis of compounds 3-7

Molecules **3a-7a** and **3b-7b** were synthesized using similar procedures. A representative example is described for **3a-7a**. The molecule **3b** was purchased from TCI and used as received.

Synthesis of compound 3a

Excess K_2CO_3 (5.48 g, 39.7 mmol), 3,5-Dibromophenol (2 g, 7.94 mmol) and 1-Bromobutane (2.2 g, 15.88 mmol) were dissolved in absolute acetonitrile (70 mL) in a 250 mL single-neck round bottom flask. The mixture was refluxed for 24 h. The solvent was removed in a rotary evaporator and washed by water, and then the mixture was extracted with ethyl acetate and dried over anhydrous magnesium sulfate and filtered. After the solvent was removed in a rotary evaporator, the black crude product was purified by silica gel chromatography (PE as eluent) to yield 2.4 g of colorless liquid (98%).

Molecule **3a**: 1H -NMR (300 MHz, $CDCl_3$, δ ppm) 7.219 (t, 1H, $J=1.5$ Hz), 6.977 (d, 2H, $J=1.8$ Hz), 3.911 (t, 2H, $J=6.3$ Hz), 1.789-1.696 (m, 2H), 1.529-1.405 (m, 2H), 0.967 (t, 3H, $J=7.2$ Hz).

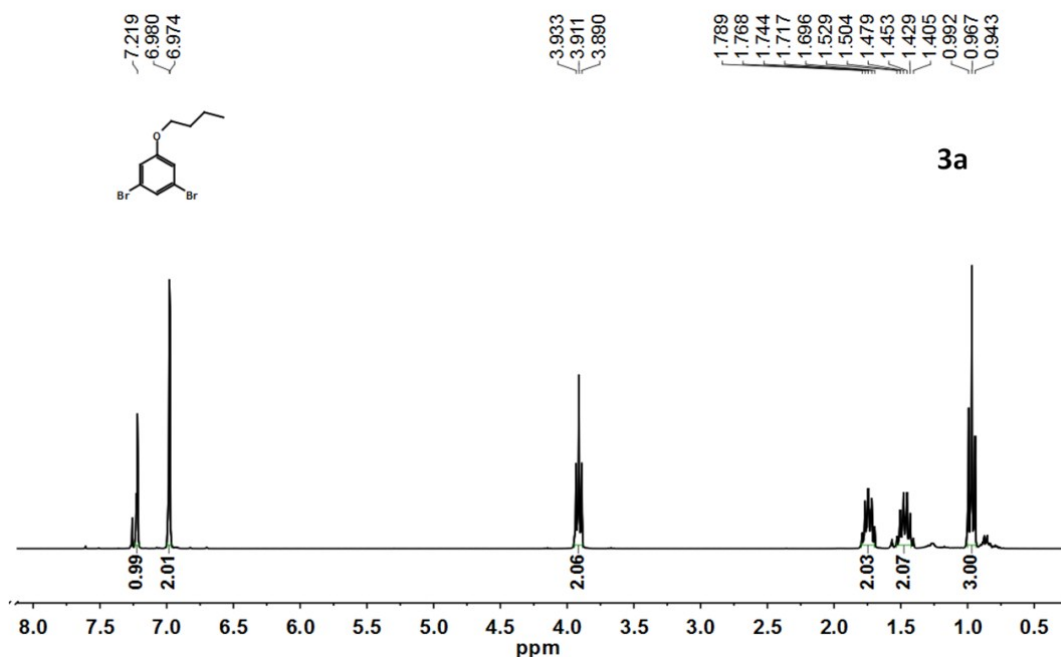


Figure S4. $^1\text{H-NMR}$ spectra of molecule **3a** in CDCl_3 .

Synthesis of compounds **4a-4b**

Compound **3a** (2.4 g, 7.8 mmol), Trimethylsilylacetylene (98%, 3.82 g, 38.96 mmol), Tetrakis(triphenyl-phosphine)Palladium (99%, 0.9 g, 0.78 mmol), Copper(I) Iodide (98%, 0.297 g, 1.56 mmol) were dissolved in THF (60 mL) and Et_3N (20 mL) in a 250 mL single-neck round bottom flask, extracted oxygen of the system, kept in dark place and refluxed for 24 h under the atmosphere of nitrogen. The solvent was removed using a rotary evaporator and washed by water, and then the mixture was extracted with ethyl acetate and dried over anhydrous magnesium sulfate and filtered. After the solvent was removed in a rotary evaporator the crude product was purified by column chromatography on silica gel as eluent to yield 1.7 g of yellow oily liquid (63%).

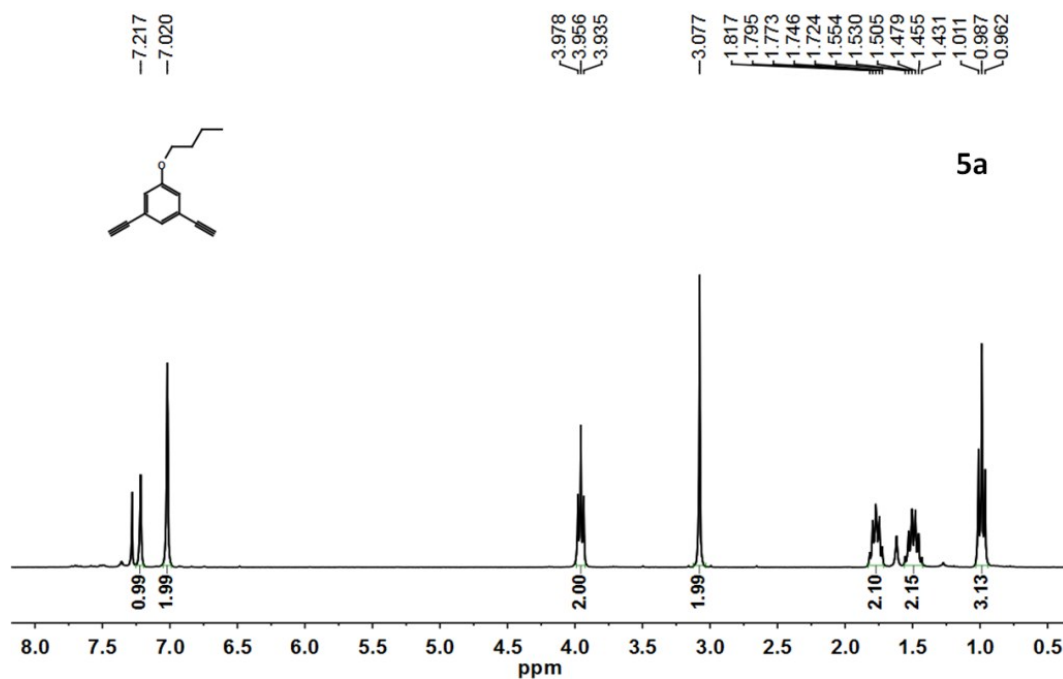
Molecule **4a**: $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm) 7.175 (s, 1H), 6.937 (s, 2H), 3.925 (t, 2H, $J=6.3\text{Hz}$), 1.781-1.688 (m, 2H), 1.523-1.400 (m, 2H), 0.959 (t, 3H, $J=7.2\text{Hz}$), 0.233 (s, 18H).

Molecule **4b**: $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm) 7.649 (s, 1H), 7.452 (d, 2H, $J=7.5\text{Hz}$), 7.295 (d, 1H, $J=7.5\text{Hz}$), 0.303 (s, 18H).

h, and then the solvent was removed using a rotary evaporator and washed by water, then the mixture was extracted with ethyl acetate and dried over anhydrous magnesium sulfate and filtered. After the solvent was removed in a rotary evaporator the crude product was purified by column chromatography on silica gel using PE as eluent to yield 0.28 g of yellow oily liquid (48.4%).

Molecule **5a**: $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm) 7.217 (s, 1H), 7.020 (s, 1H), 3.956 (t, 2H, $J=6.6\text{Hz}$), 3.077 (s, 2H), 1.817-1.724 (m, 2H), 1.554-1.431 (m, 2H), 0.987 (t, 3H, $J=7.2\text{Hz}$).

Molecule **5b**: $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm) 7.628 (s, 1H), 7.478 (d, 2H, $J=7.8\text{Hz}$), 7.309 (d, 1H, $J=7.2\text{Hz}$), 3.099 (s, 2H).



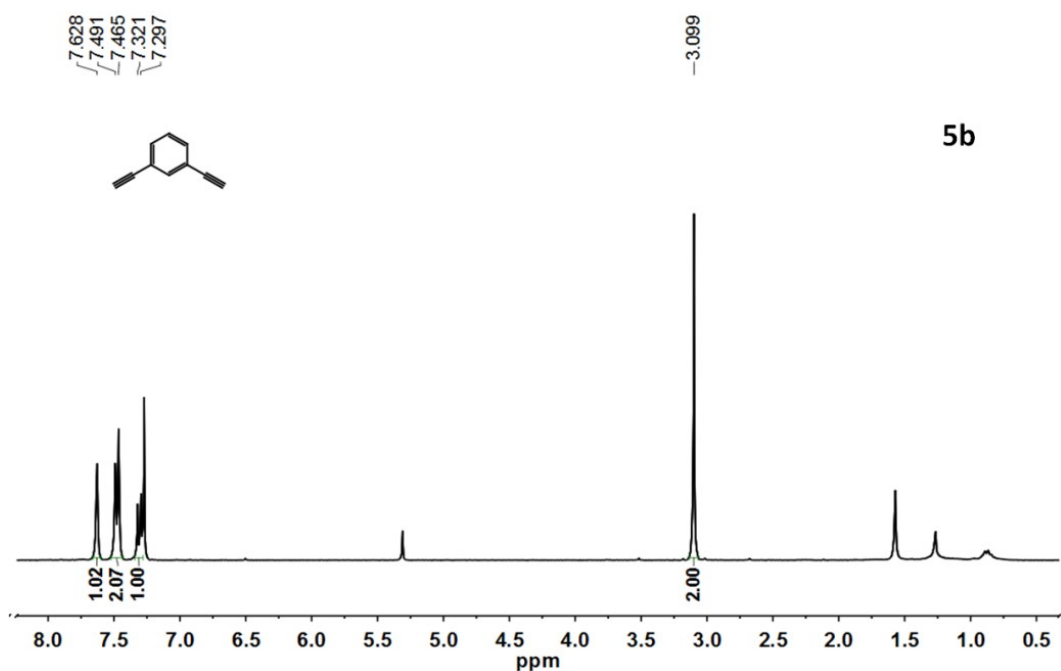


Figure S6. ¹H-NMR spectra of molecules **5a-5b** in CDCl₃.

Synthesis of compounds **7a-7b** [2]

A mixture of poly(ethylene glycol)methyl ether (4.16 g, 0.02 mol) was dissolved in refined dichloromethane (100 mL) and then pyridine (10 mL) was poured in a 250 mL single-neck round bottom flask. Toluene-*p*-sulfonyl chloride (TsCl, 98%, 5.715 g, 0.03 mol) were added into the flask. The reaction mixture was further stirred at room temperature for 12h. Then water (30 mL) was poured into the transparent solution in the flask and stirred for 1h, the diluted hydrochloric acid was added into the flask and acidified to pH<7 and stirred for half hour. The resulting solution was extracted with methylene dichloride. The organic solution was dried (MgSO₄) and filtered, the solvent was removed in a rotary evaporator to give **7a** as colorless liquid. The crude product was purified by silica gel chromatography (ethyl acetate as eluent) to yield 6.25 g (89.5%).

Synthesis of compounds **6a-6b**

Excess K₂CO₃ (3.41 g, 24.72 mmol), 4-Hydroxy-4'-iodobiphenyl (98+%, 2.2 g, 7.42 mmol) and **7a** (2.24 g, 6.18 mmol) were dissolved in absolute acetonitrile (80 mL) in a 250 mL single-neck round bottom flask, added 18-crown-6 (0.33 g, 1.24 mmol) as

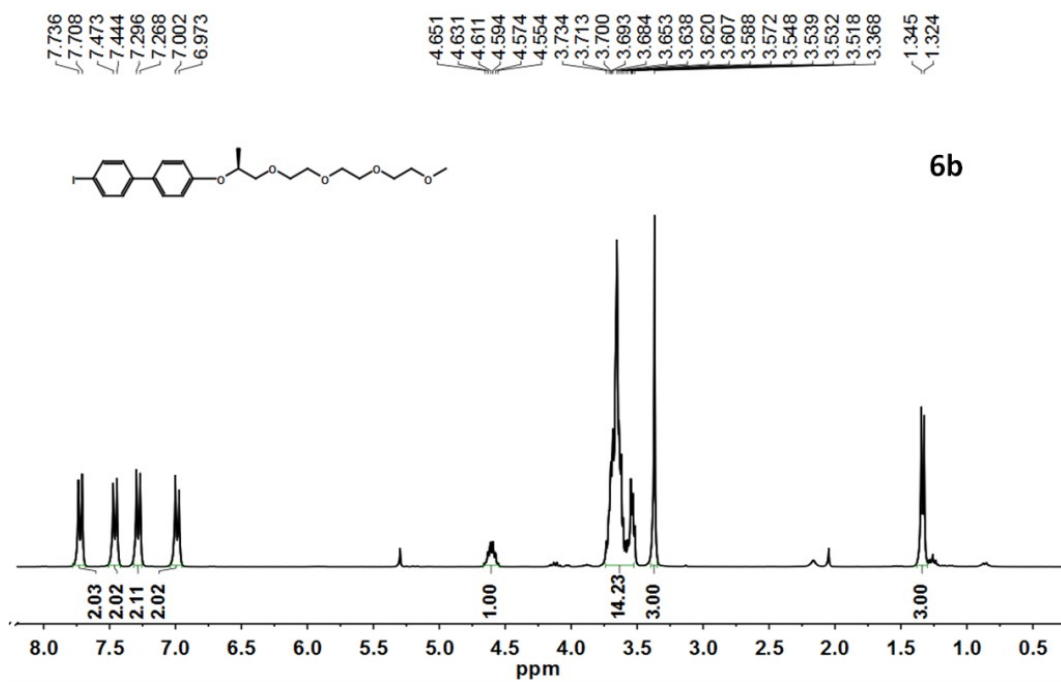


Figure S7. $^1\text{H-NMR}$ spectra of molecules **6a-6b** in CDCl_3 .

4. Small-angle X-ray diffraction data of 1a, 1b and 2a, 2b

Table S1. Small-angle X-ray diffraction data for columnar structure for molecule **1a**

(measured at room temperature, $\gamma=64.3^\circ$, $a = 4.38$ nm, $b = 3.40$ nm)

q_{obsd}	q_{calcd}	h	k	l
2.051	2.051	0	1	0
2.951	2.947	2	1	0
3.186	3.189	2	0	0
3.960	3.958	2	2	0

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections ($\lambda = 0.154$ nm).

Table S2. Small-angle X-ray diffraction data for body-centred tetragonal structure for molecule **1b** (measured at room temperature, $a = 4.40$ nm, $c = 4.31$ nm)

q_{obsd}	q_{calcd}	h	k	l
2.018	2.022	1	1	0
2.849	2.848	0	2	0
2.918	2.919	0	0	2
3.539	3.545	1	1	2

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections ($\lambda = 0.154$ nm).

Table S3. Small-angle X-ray diffraction data for Hexagonal perforated lamellar (HPL) structure for molecule **2a** (measured at 90°C , $a = 9.51$ nm, $c = 10.10$ nm)

q_{obsd}	q_{calcd}	h	k	l
0.989	0.982	0	1	1
1.245	1.239	0	0	2

1.316	1.324	1	1	0
1.531	1.524	2	0	0
2.116	2.108	2	1	1
2.489	2.492	0	0	4
2.642	2.649	2	2	0

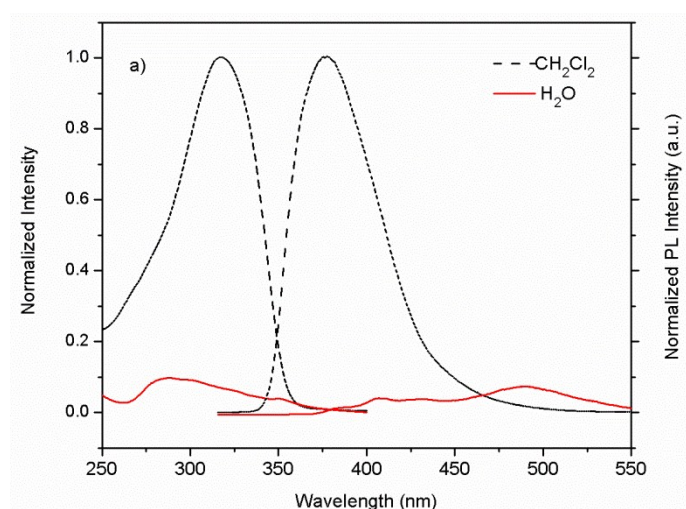
q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections ($\lambda = 0.154$ nm).

Table S4. Small-angle X-ray diffraction data for columnar structure for molecule **2b** (measured at 50 °C, $\gamma = 68.5^\circ$, $a = 4.58$ nm, $b = 3.00$ nm)

q_{obsd}	q_{calcd}	h	k	l
1.475	1.481	1	0	0
2.186	2.193	1	1	0
2.251	2.250	0	1	0
2.992	2.990	2	1	0

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections ($\lambda = 0.154$ nm).

5. Aggregation behavior of 1a, 1b and 2a, 2b in aqueous solution



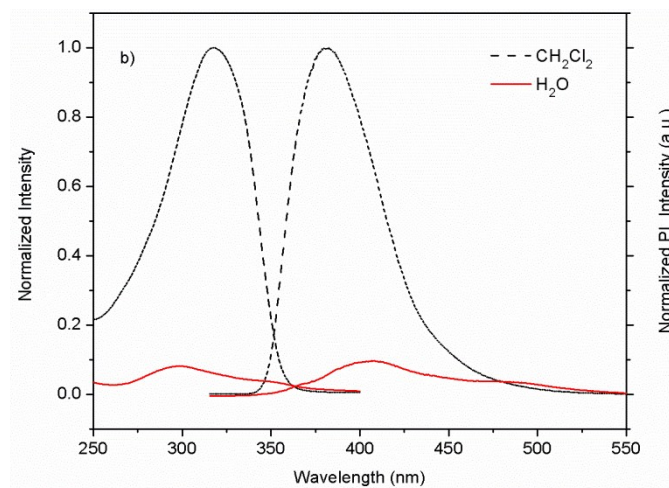


Figure S8. Absorption and emission spectra of a) **2a** and b) **2b** in methylene chloride and aqueous solution (0.02 wt%).

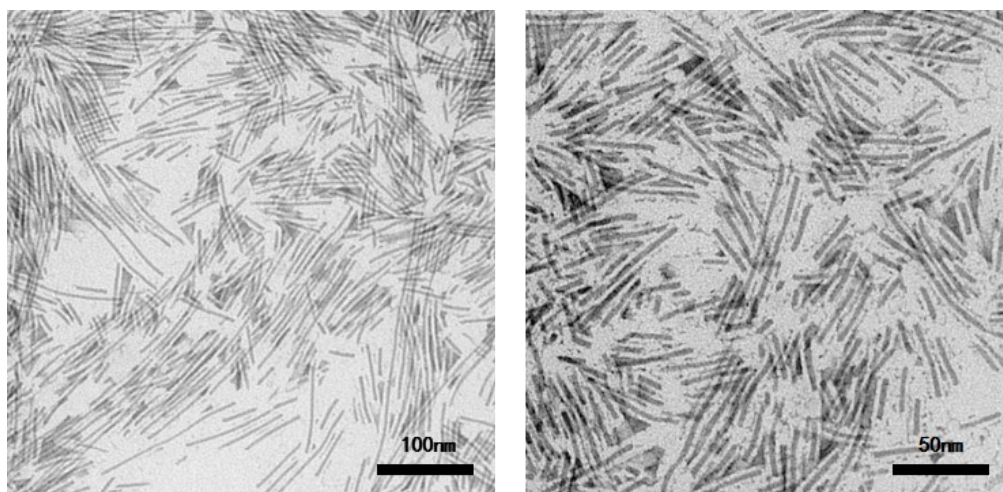


Figure S9. TEM images of negatively stained nanoaggregates of **1a** (0.02 wt%, negatively stained with sodium phosphotungstate).

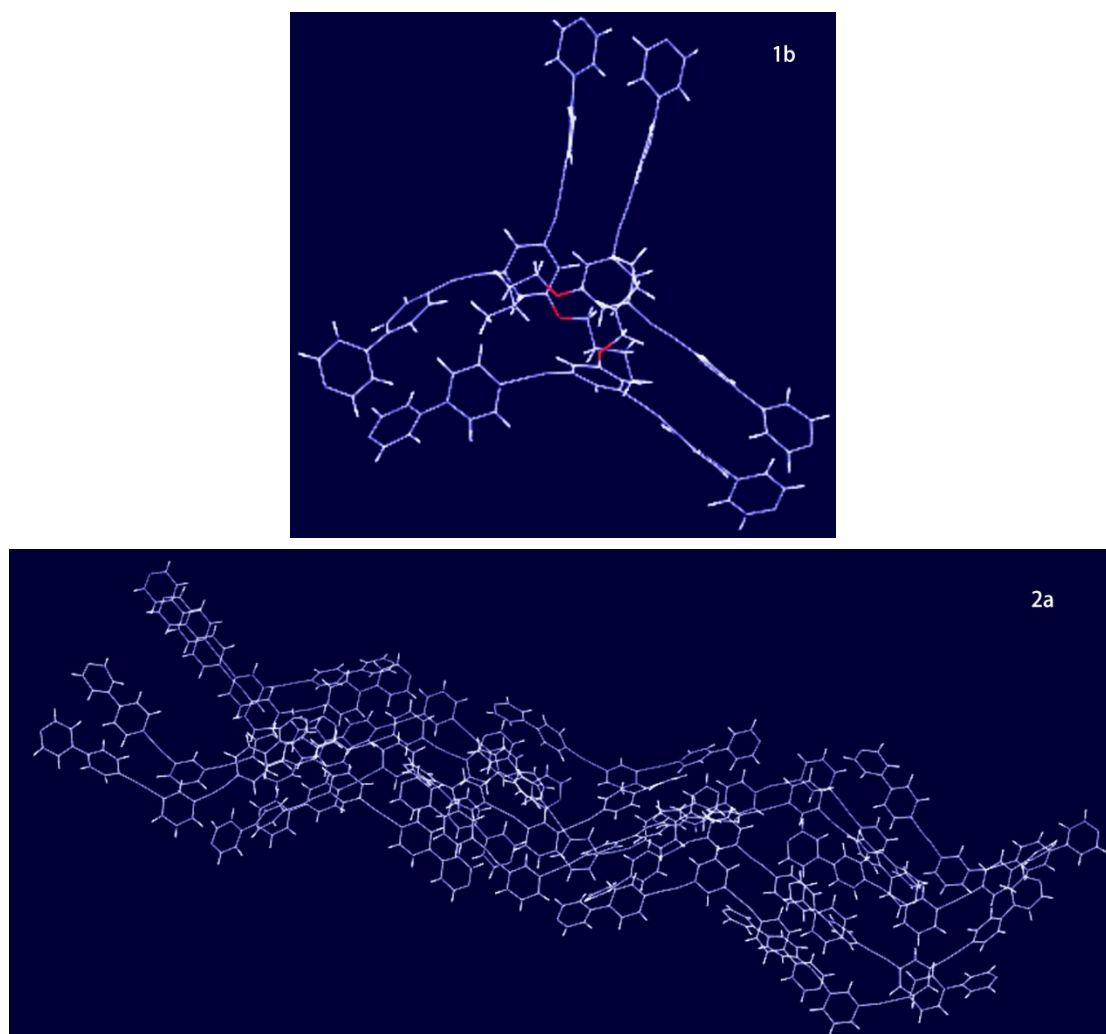


Figure S10. Molecular dynamic simulation results of **1b** and **2a** in aqueous environment.

6. General methods.

The products were purified by flash column chromatography on silica gel (200–300 mesh). Thin-layer chromatography (TLC) was performed on precoated aluminum-backed plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm) or by treating the plates with iodine. All compounds are subjected to $^1\text{H-NMR}$ analysis to confirm $\geq 95\%$ sample purity. Chemical shifts were reported in ppm relative to the tetramethyl silane peak (TMS, 0 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Molecular dynamic simulations were performed using Macro Model and Desmond modules from Schrödinger Suites (Schrödinger K.K.).

7. Molecular Simulations

The molecular dynamics simulations were calculated through Macro Model and Desmond module from Schrödinger Suites. The preliminary geometry of the molecules was optimized through the following parameters; force field: OPLS_2005, solvent: water, cutoff: Van der Waals (8.0) / electrostatic (20.0) / H-bond (4.0), minimization method: PRCG, maximum iterations: 2500, converge on: gradient, convergence threshold: 0.05, simulation temperature: 300.0 K. The energy-minimized structure of three molecules was subjected to perform molecular dynamics simulations through Desmond module with the following parameters; solvent model: SPC, simulation time: 10 ns, ensemble class: NVT, temperature: 300K, thermostat method: Nose-Hoover chain, Columbus short range method: cutoff (cutoff radius: 9.0), columbus long range method: smooth particle mesh Ewald, Ewald tolerance: 1e-09.

References

- S1. Y. Yang, J. Cui, Z. Li, K. Zhong, L. Y. Jin & M. Lee. *Macromolecules* **2016**, *49*, 5912–5920.
- S2. Y. Liu, K. L. Zhong, Z. H. Li, Y. Q. Wang, T. Chen, M. Lee and L. Y Jin, *Polym Chem.* **2015**, *6*, 7395–7401.