Electronic Supplementary Information

Supramolecular Nanostructures Constructed by Rod-Coil Molecular Isomers: Effect of Rod Sequence for Molecular Assembly

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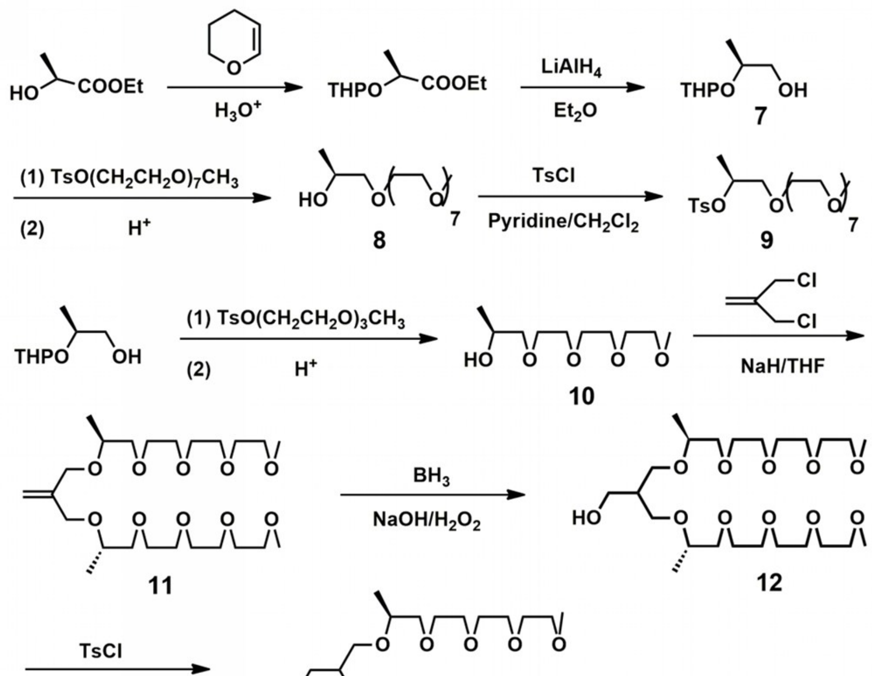
Synthesis



Synthesis of compounds 9-13.

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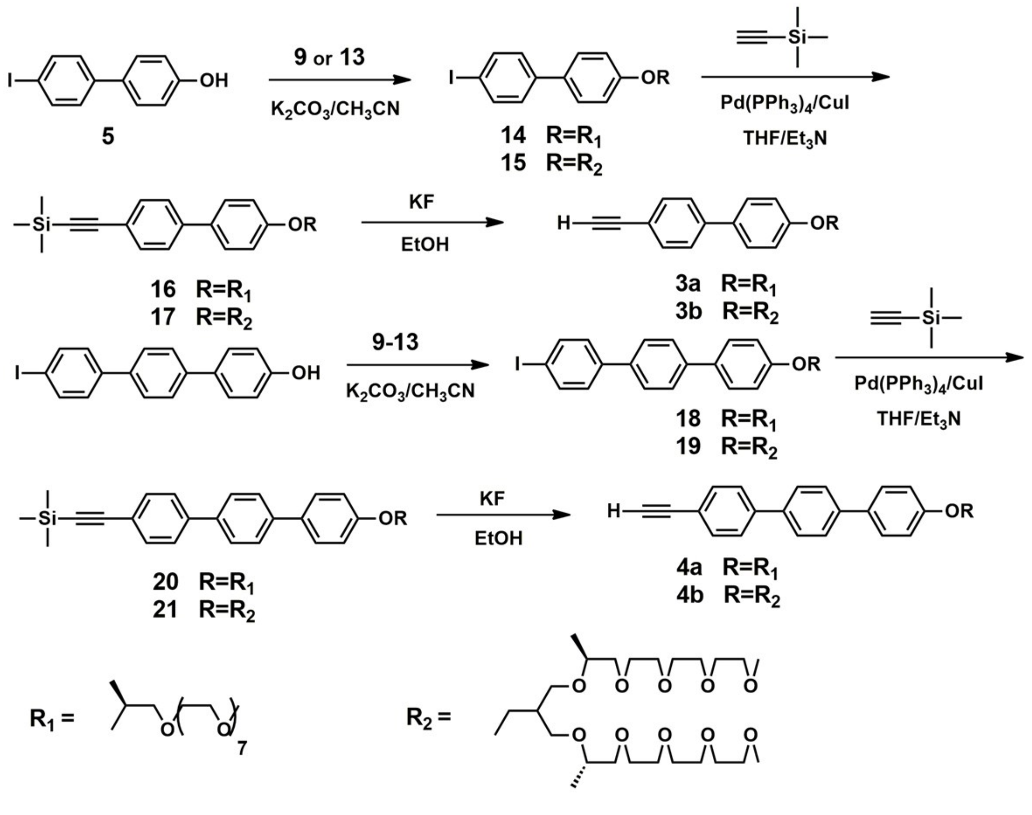
Compounds **9-13** was prepared according to the similar procedures reported previously and they gave the following spectroscopic data.[1,2]

Compound 9: yellow liquid yield: 77%. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.82-7.79 (d, J = 8.2 Hz, 2H), 7.35-7.32 (d, J = 8.2 Hz, 2H), 4.75-4.64 (m, 1H), 3.70-3.52 (m, 53H), 3.38 (s, 3H), 2.43 (s, 3H), 2.45 (s,1H), 1.29-1.27 (d, 3H).

Compound 12: yellow liquid: 75.2%. ^{1}H NMR (300MHz, CDCl$_3$, δ, ppm): 5.10 (s, 2H), 4.01 (s, 4H), 3.65-3.29 (m, 34H), 2.45 (s, 3H), 2.22-2.12 (m, 1H), 1.01-1.04 (m, 6H).

Compound 13: yellow liquid: 43%. ^{1}H NMR (300MHz, CDCl$_3$, δ, ppm): 7.78 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 4.11 (d, J = 5.9 Hz, 2H), 3.65-3.29 (m, 34H), 2.45 (s, 3H), 2.22-2.12 (m, 1H), 1.01-1.04 (m, 6H).



Scheme S1. Synthetic route of molecules **3a-4b**.

Synthesis of compounds 14 and 15

Compounds **14** and **15** were synthesized using the same procedure.[3] A representative example is described for **14**. Compound **9** (0.70 g, 1.26 mmol) and 4-hydroxy-4'-iodobiphenyl (0.45g, 1.52 mmol) were dissolved in acetonitrile (50mL) and then excess potassium carbonate was added to the solution. The mixture was heated at reflux for 24 hours with vigorous stirring. The solvent was removed in a rotary evaporator and the resulting mixture was poured into water and extracted with ethyl acetate, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel) using methylene dichloride /methanol (10:1 v/v) as eluent to yield a yellow ropy liquid (0.746 g, 88%). ^{1}H NMR (300MHz, $CDCl_3$, δ, ppm):7.73 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.65-4.55 (m, 1H), 3.73-3.53 (m, 30H), 3.38 (s, 3H). 1.34 (d, J = 6.3 Hz, 3H)

Compound 15: yellow ropy liquid (yield=79.9%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.72 (d, J = 4.2 Hz, 2H), 7.46 (d, J = 4.5 Hz, 2H), 7.28 (d, J = 4.2 Hz, 2H), 6.97 (d, J = 4.5 Hz, 2H), 4.07 (d, J = 3.0 Hz, 2H), 3.46-3.69 (m, 34H), 3.36 (s, 6H), 2.27-2.41 (m, 1H), 1.12-1.15 (m, 6H).

Synthesis of compounds 16 and 17

Compounds **16** and **17** were synthesized using the same procedure.[3] A representative example is described for **16**. Compound **14** (0.748 g, 1.11 mmol) and trimethylsilyl-acetylene (0.23 g, 2.35 mmol) were added to tetrahydrofuran (25 mL). Triethylamine (20 mL) was added and then tetrakis (triphenyl-phosphine) palladium (0) (26 mg, 0.02 mmol) and copper iodide (8.4 mg, 0.04 mmol) were added. The mixture was degassed and then heated at reflux for 24 hours with vigorous stirring under nitrogen. The solvent was removed in a rotary evaporator and the resulting mixture was poured into water and extracted with dichloromethane, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel) using ethyl acetate/methanol (10:1 v/v) as eluent to yield a yellow solid (0.715 g, 86.6%). ^{1}H NMR (300MHz, $CDCl_3$, δ, ppm): 7.57-7.46 (m, 6H), 6.99 (d, J = 8.7 Hz, 2H), 4.65-4.57 (m, 1H), 3.78-3.53 (m, 30H), 3.38 (s, 3H), 1.34 (d, J = 6.3 Hz, 3H). 0.26 (s, 9H).

Compound 17: yellow liquid (yield=35.2%). ^{1}H NMR (300MHz, $CDCl_3$, δ, ppm): 7.57-7.45 (m, 6H), 6.99 (d, *J* = 9.0 Hz, 2H), 4.11(d, *J* = 5.9 Hz, 2H), 3.65-3.29(m, 40H), 2.22-2.12 (m, 1H), 1.01-1.04 (m, 6H), 0.25 (s, 9H).

Synthesis of compounds 3a and 3b

Compounds **3a** and **3b** were synthesized using the same procedure.[4-6] A representative example is described for **3a**. Compound **16** (0.619 g, 0.96 mmol) and potassium fluoride (0.56 g, 9.64 mmol) were dissolved in ethanol (60 mL). The mixture was degassed and then heated at reflux for 16 hours with vigorous stirring under nitrogen. The solvent was removed in a rotary evaporator and the resulting mixture was poured into water and extracted with ethyl acetate, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel) using methylene dichloride / methanol (10:1 v/v) as eluent to yield a yellow solid (0.95 g, 96.9%). ^{1}H NMR (300MHz, CDCl$_3$, δ, ppm): 7.55-7.48 (m, 6H), 7.00 (d, *J* = 8.7 Hz, 2H), 4.66-4.56 (m, 2H), 3.77-3.50 (m, 30H), 3.38 (s, 3H), 3.12 (s, 1H), 1.34 (d, *J* = 6.0 Hz, 3H).

Compound **3b**: yellow liquid (yield=90.9%). ^{1}H NMR (300MHz, CDCl$_3$, δ, ppm): 7.61-7.45 (m, 6H), 7.01 (d, *J* = 6.0 Hz, 2H), 4.09 (d, *J* = 9.0 Hz, 2H), 3.72-3.38 (m, 40H), 2.42-2.34 (m, 1H), 1.23-1.16 (m, 6H).

Synthesis of compounds 18 and 19

Compounds **18** and **19** were synthesized using the same procedure.[7] A representative example is described for **18**. Compound **9** (0.37 g, 0.67 mmol) and 4-hydroxy-4'-iodoterphenyl (0.30g, 0.81 mmol) were dissolved in acetonitrile (50 mL) and then excess potassium carbonate was added to the solution. The mixture was heated at reflux for 24 hours with vigorous stirring. The solvent was removed in a rotary evaporator and the resulting mixture was poured into water and extracted with ethyl acetate, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel) using methylene dichloride / methanol (10:1 v/v) as eluent to yield a yellow ropy liquid (7.6 g, 76%). ^{1}H NMR (300MHz, CDCl$_3$, δ, ppm): 7.68-7.38 (m, 10H), 7.03 (d, *J* = 8.9 Hz, 2H), 4.23-4.11 (m, 1H), 3.78-3.48 (m, 30H), 3.37 (s, 3H), 1.35-1.33 (d, *J* = 6.0 Hz, 3H).

Compound 19: yellow liquid (yield=76.2%). ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm) 7.78 (d, *J* = 9.0 Hz, 2H), 7.66-7.54 (m, 6H), 7.38 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 4.11 (d, *J* = 5.9 Hz, 2H), 4.02-3.39 (m, 40H), 2.45 (m, 1H), 1.18-1.02 (m, 6H).

Synthesis of compounds 20 and 21

Compounds **20** and **21** were synthesized using the same procedure. A representative example is described for **20**. Compound **18** (0.51 g, 0.75 mmol) and trimethylsilyl-acetylene (0.16 g, 1.63 mmol) were added to tetrahydrofuran (25 mL). Triethylamine (20 mL) was added and then tetrakis (triphenyl-phosphine) palladium (0) (17 mg, 0.014 mmol) and copper iodide (6 mg, 0.032 mmol) were added. The mixture was degassed and then heated at reflux for 24 hours with vigorous stirring under nitrogen. The solvent was removed in a rotary evaporator and the resulting mixture was poured into water and extracted with dichloromethane, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel) using ethyl acetate/methanol (10:1 v/v) as eluent to yield a yellow solid (0.384 g, 69%). ^{1}H NMR (300MHz, CDCl$_3$, δ, ppm): 7.64-7.54 (m, 10H), 7.02(d, *J* = 8.7 Hz, 2H), 4.66-4.57 (m, 2H), 3.75-3.51 (m, 30H), 3.37 (s, 3H), 1.35 (d, *J* = 6.0 Hz, 3H). 0.27 (s, 9H).

Compound 21: yellow liquid (yield=76.2%). ^{1}H NMR (300MHz, CDCl$_3$, δ, ppm): 7.78 (d, *J* = 9.0 Hz, 2H), 7.67-7.53 (m, 6H), 7.40 (d, *J* = 6.0 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 4.11 (d, *J* = 9.0 Hz, 2H), 3.81-3.37 (m, 40H), 2.49-2.43 (m, 1H), 1.19-1.04 (m, 6H), 0.27 (s, 9H).

Synthesis of compounds 4a and 4b

Compounds **4a** and **4b** were synthesized using the same procedure. A representative example is described for **4a**. Compound **20** (0.384 g, 0.52 mmol) and potassium fluoride (0.30 g, 5.16 mmol) were dissolved in ethanol (60 mL). The mixture was degassed and then heated at reflux for 16 hours with vigorous stirring under nitrogen. The solvent was removed in a rotary evaporator and the resulting mixture was poured into water and extracted with ethyl acetate, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel) using methylene dichloride / methanol (10:1 v/v) as eluent to yield a yellow solid (0.347 g, 90%). ^{1}H NMR (300MHz, CDCl$_3$, δ, ppm): 7.68-7.54

(m, 10H), 7.02 (d, J = 8.9 Hz, 2H), 4.64-4.59 (m, 1H), 3.78-3.53 (m, 30H), 3.37 (s, 3H), 3.14 (s, 1H), 1.35 (d, J = 6.0 Hz, 3H).

Compound 4b: yellow liquid (yield=89.3%). ^{1}H NMR (300MHz, $CDCl_3$, δ, ppm): 7.80 (d, J = 7.5 Hz, 2H), 7.68-7.54 (m, 6H), 7.38 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.9 Hz, 2H), 4.11 (d, J = 5.9 Hz, 2H), 3.65-3.29 (m, 40H), 2.22-2.12 (m, 1H), 1.20-1.03 (m, 6H).

Table S1. Thermal transitions of molecules **1a-2b** (data are from the second heating and the first cooling scans).

		Phase transition temperature (°C)	
Molecule	f_{coil}	Heating	Cooling
1a	0.61	HPL 199.16 Col_{ob} 223 i	i 215 Col_{ob} 180.3 HPL
2a	0.61	L 204.51 HPL 228 i	i 222 HPL 198.3 L
1b	0.67	M_{tet} 130 i	i 117.5 M_{tet}
2b	0.67	Col_{hex} 164.5 i	i 149.2 Col_{hex}

f_{coil} : volume fraction of coil to rod-coil molecule. L: Lamellar phase, HPL: hexagonal perforated lamellar phase, Col_{ob}: oblique columnar phase, Col_{hex}: hexagonal columnar phase, M_{tet}: body-centered tetragonal micellar, i: isotropy.

Table S2. Small-Angle X-ray diffraction data for the structure of **1a** in the bulk state.

Mesophase (lattice constant)	Reflections/nm		Miller indices
	q_{obsd}	q_{calcd}	(h k l)
HPL at H30 °C a=6.14 nm c=10.14 nm	1.1820	1.1828	1 0 0
	1.2390	1.2459	0 0 2
	1.3387	1.3435	1 0 1
	2.1360	2.1334	1 1 1
Col_{ob} at C210 °C a=6.76 nm b=5.63 nm γ=60°	1.0681	1.0670	1 0 0
	1.2959	1.2959	0 1 0
	2.2499	2.2429	2 1 1
	2.5774	2.5730	1 2 1
	2.7908	2.7845	1 1 2

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections, HPL: hexagonal perforated lamellar phase, Col_{ob}: oblique columnar phase.

Table S3. Small-Angle X-ray diffraction data for the structure of **2a** in the bulk state.

Mesophase (lattice constant)	Reflections/nm		Miller indices
	q_{obsd}	q_{calcd}	(h k l)

HPL at H220 °C a=6.37 nm c=12.19 nm	0.9481	0.9542	0 0 2
	1.0379	1.0396	1 0 0
	1.9009	1.8940	2 0 0
	2.8474	2.8474	0 3 0

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections, HPL: hexagonal perforated lamellar phase.

Table S4. Small-Angle X-ray diffraction data for the structure of **1b-2b** in the bulk state.

Mesophase (lattice constant)	Reflections/nm		Miller indices
	q_{obsd}	q_{calcd}	(h k l)
M_{tet} (**1b**) at H120 °C a=9.45 nm c=8.56 nm	0.94	0.93	1 1 0
	1.32	1.32	2 0 0
	1.61	1.60	1 0 2
	2.08	2.09	1 2 2
	2.28	2.30	1 0 3
	2.63	2.66	2 1 3
Col_{hex} (**2b**) at H150 °C a=5.57 nm	1.30	1.31	1 0 0
	2.24	2.24	1 1 0
	2.58	2.59	2 0 0

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections, Col_{hex}: hexagonal columnar phase, M_{tet}: body-centered tetragonal micellar.

Note: In Table S2-S4, a, b, c (nm) and γ (characteristic angle) denote lattice constant. The following equations are used to calculate the cell parameters of various supramolecular nanostructures.

The lattice plane spacing: $d = \frac{2\pi}{q(hkl)}$

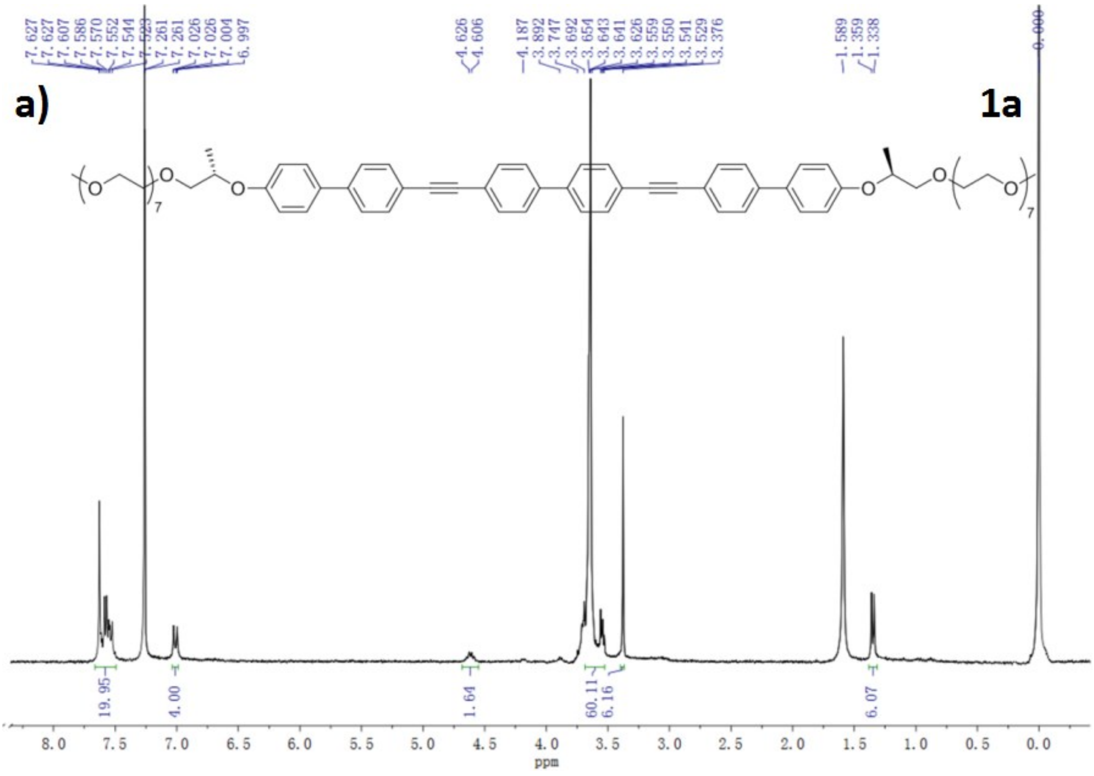
The hexagonal perforated lamellar lattice: $\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$

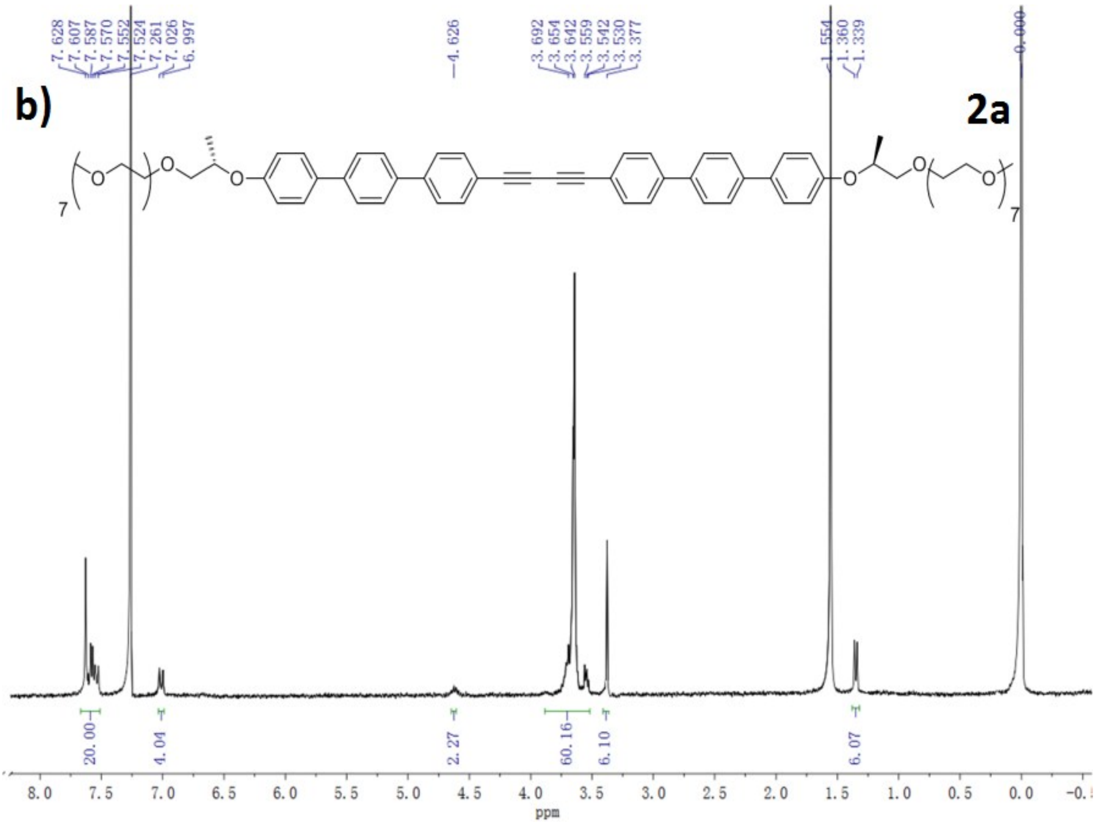
The oblique columnar lattice (a, b):

$$\frac{1}{d^2} = \frac{1}{sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2 sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

M_{tet}: body-centered tetragonal micellar lattice: $\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$ (where h, k, and l are the Miller indices)

Hexagonal columnar phase: a= d(100)/sin60^{o}, for molecule **2b** a=1.31/(√3/2)=5.6.





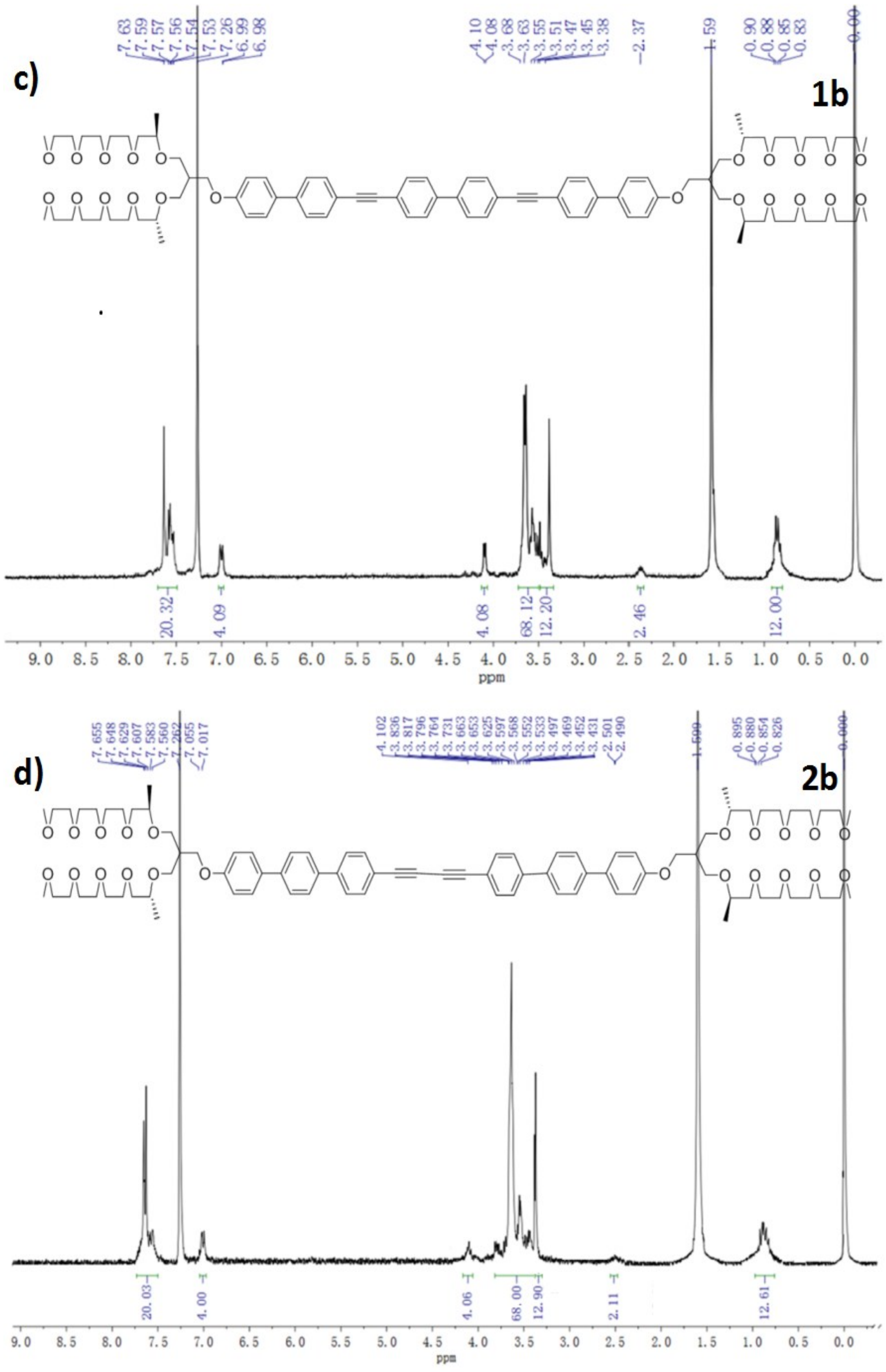
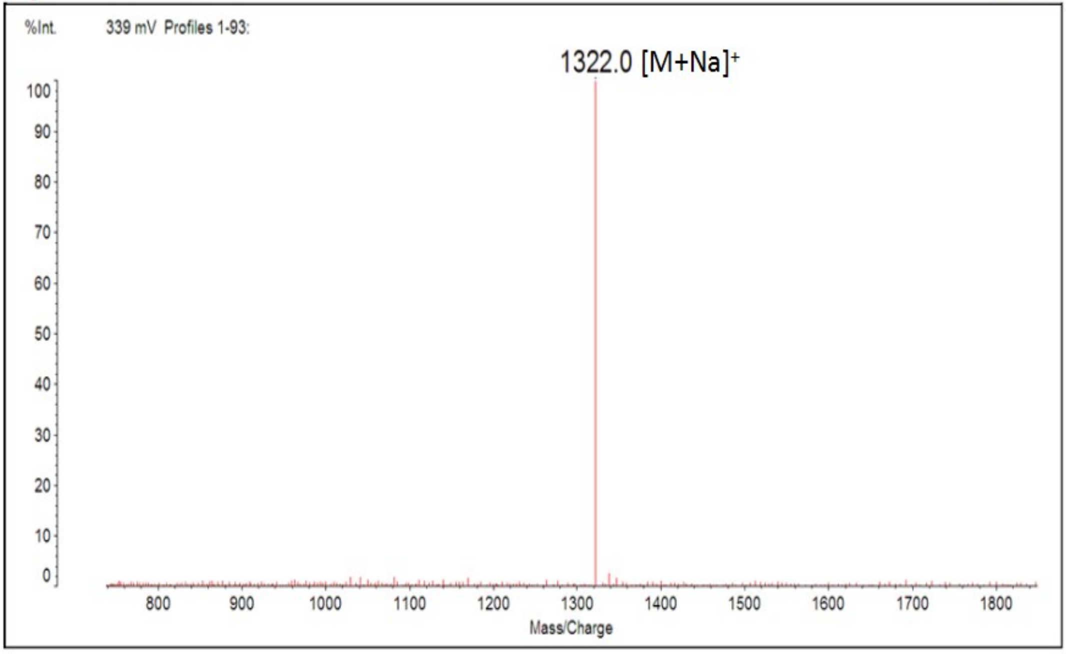


Fig S1. ^{1}H-NMR spectra of molecules **1-2** in $CDCl_3$.

a) **1a**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90
80
70
60
50
40
30
20
10
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800
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1000
1100
1200
1300
1400
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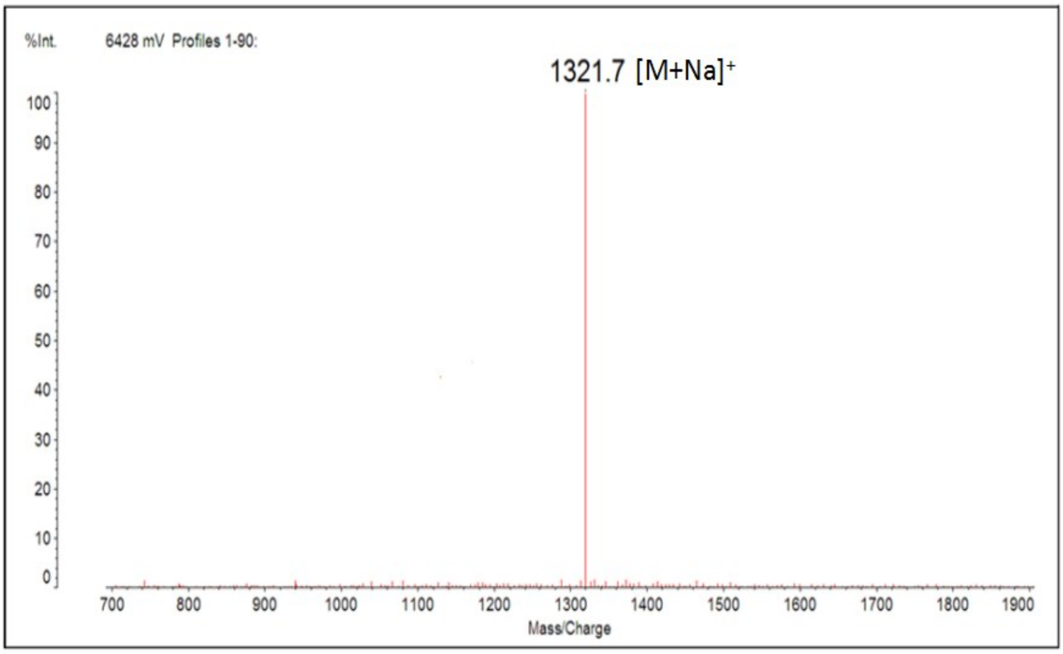
1600
1700
1800
Mass/Charge

b) **2a**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6428 mV Profiles 1-90:
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1900
Mass/Charge

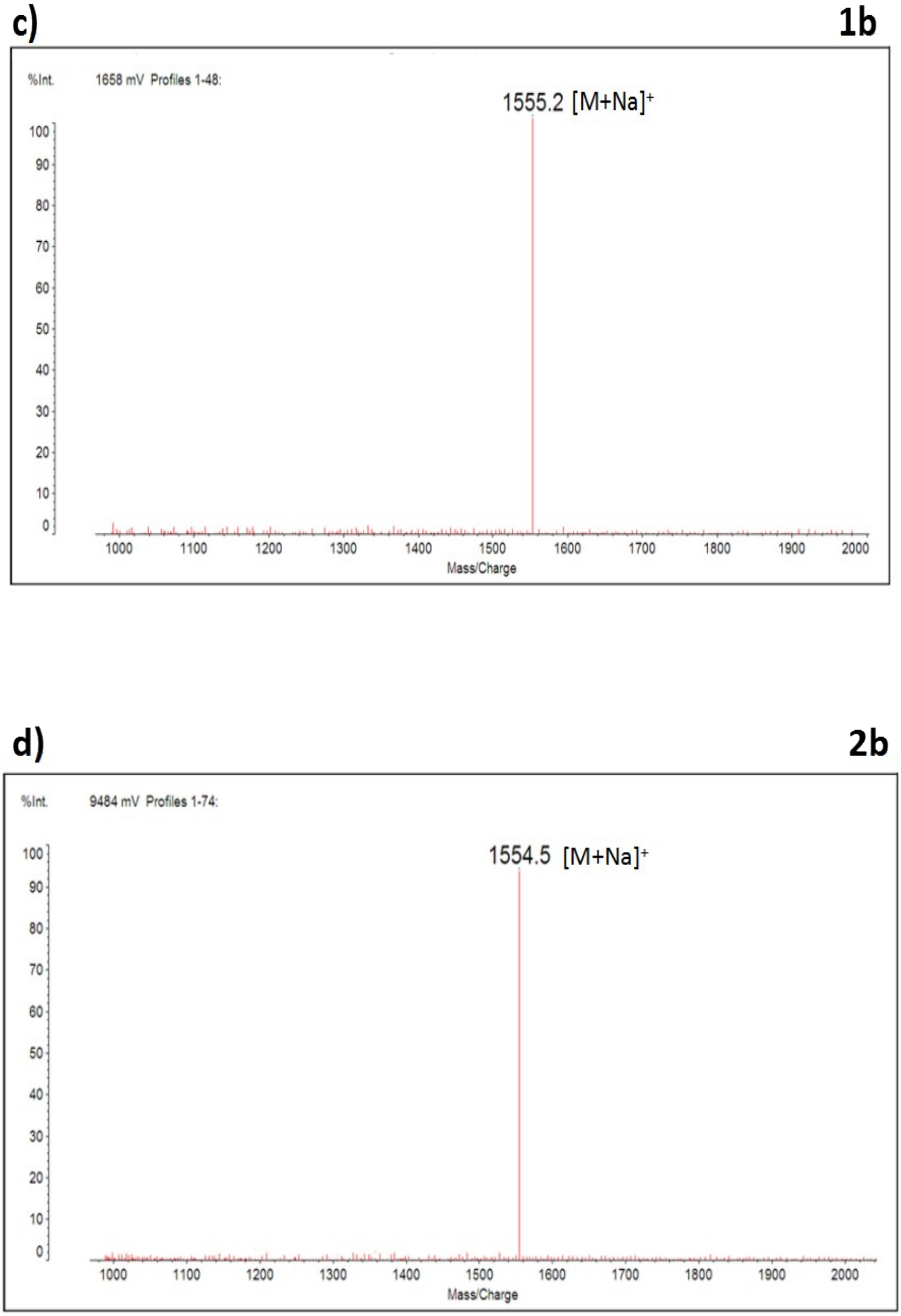
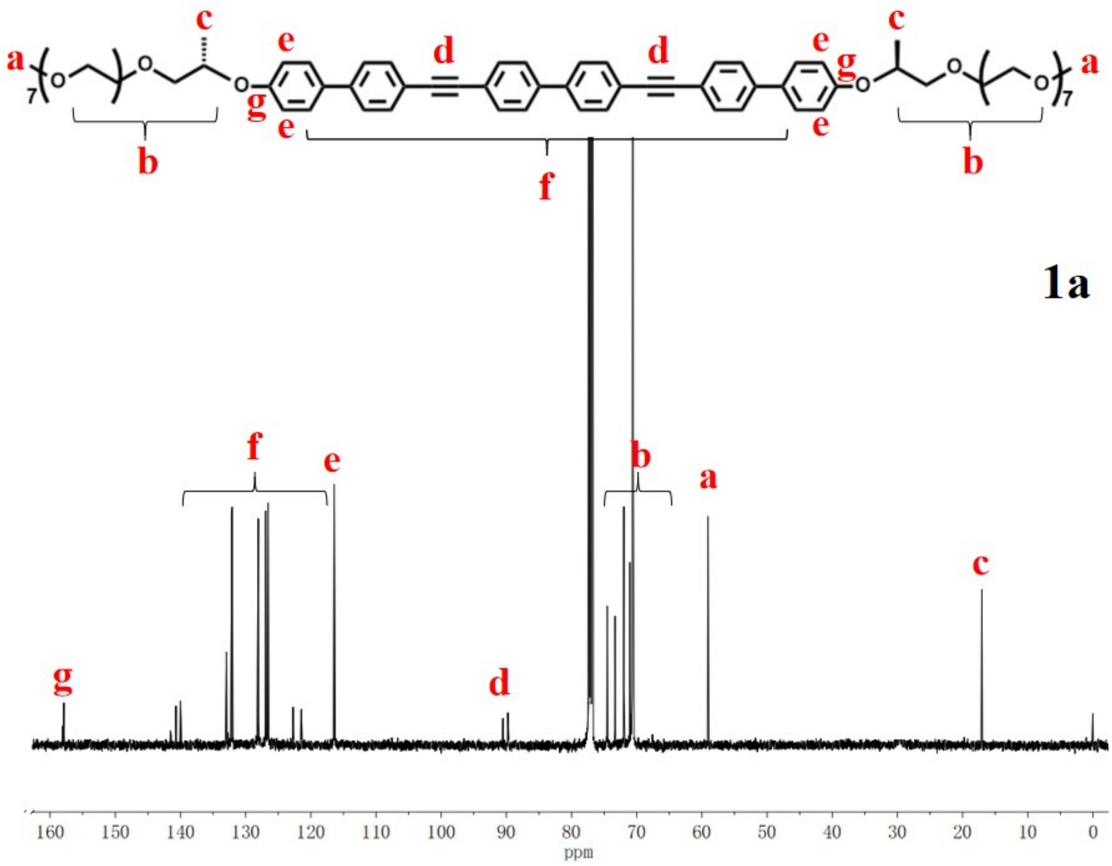


Fig S2. MALDI-TOF-Mass spectra of molecules **1-2** (matrix: CHCA).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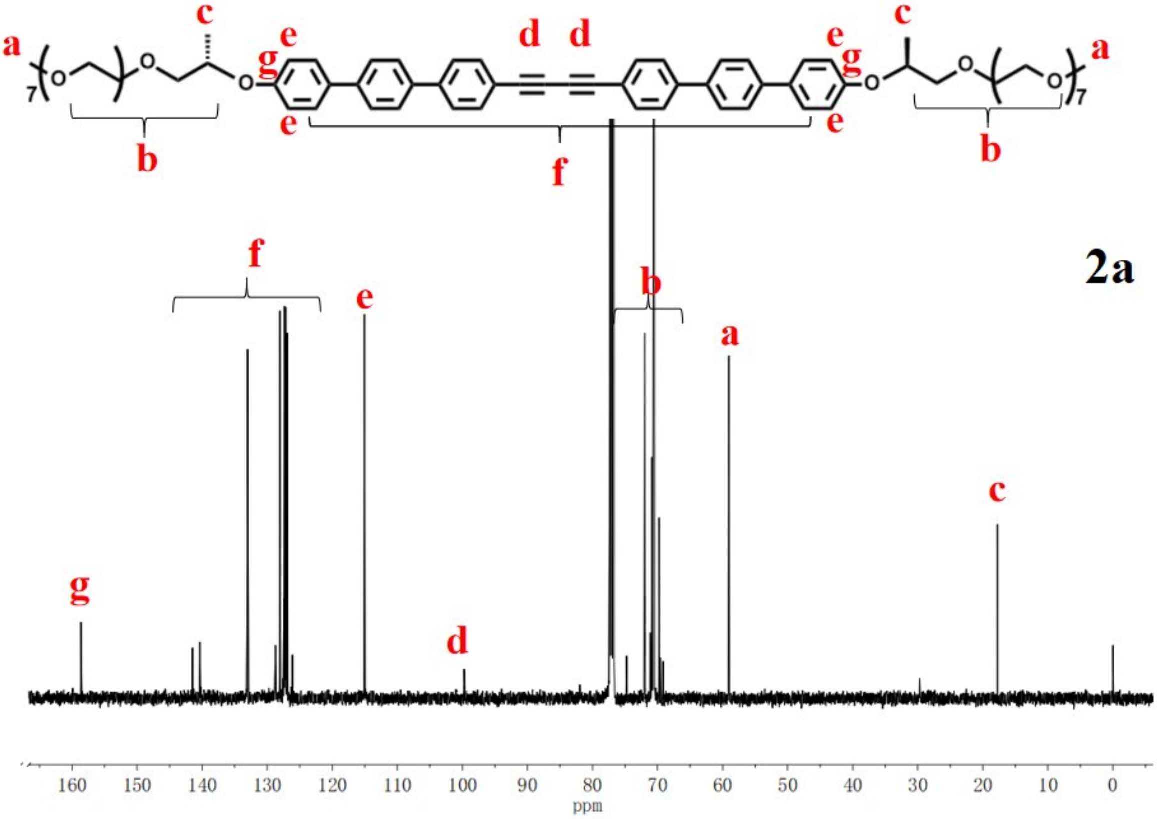
1a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ppm

2a

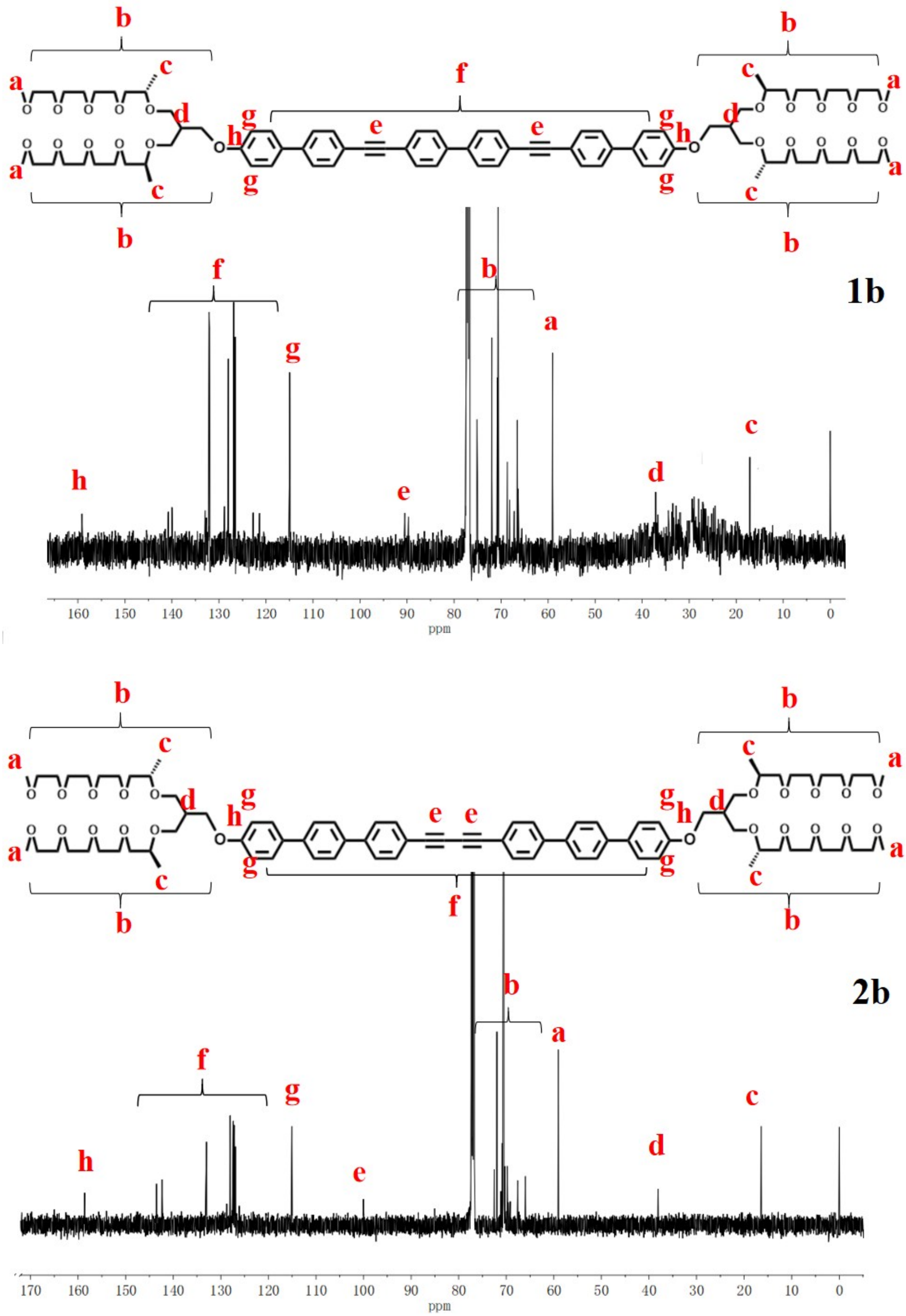

Fig S3. ^{13}C-NMR spectra of molecules **1-2** in $CDCl_3$ (75 MHz).

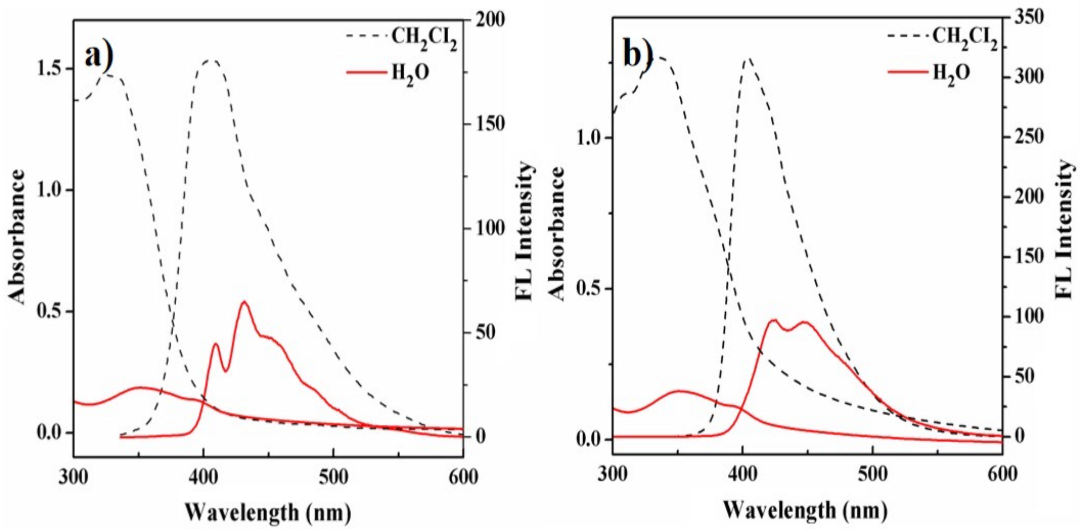

Fig S4. Absorption and emission spectra of **1b** (c)and **2b** (d) in methylene chloride and aqueous solution (2×10^{-5} M).

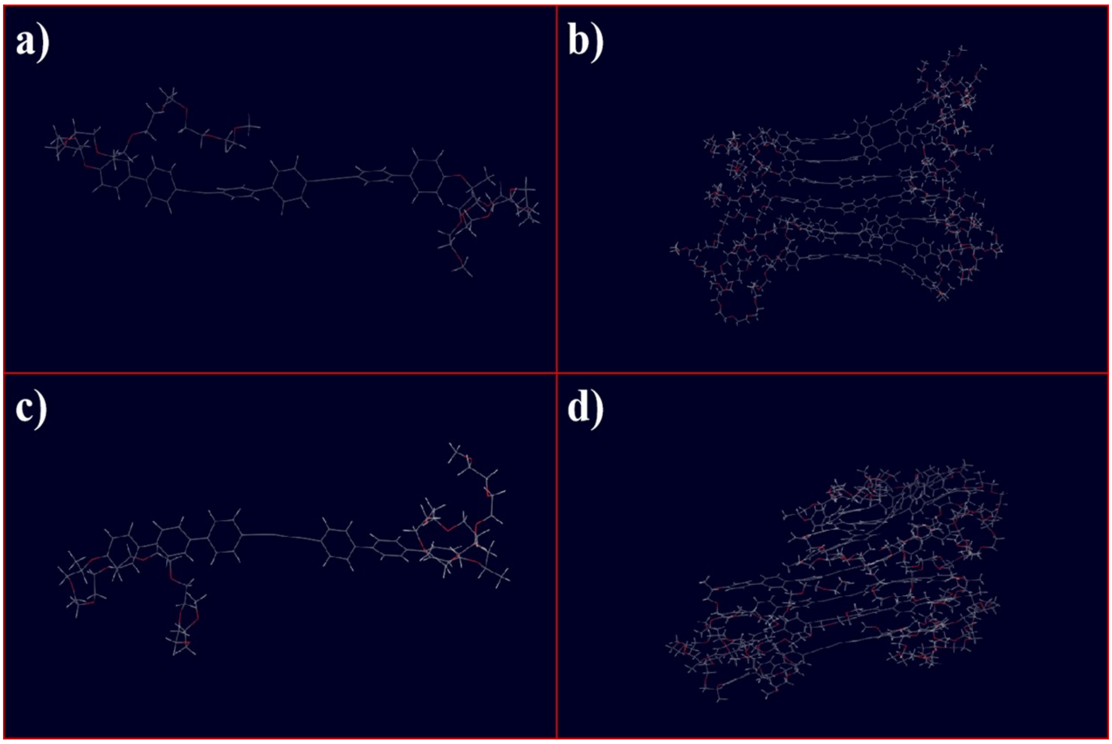

Fig S5. Molecular dynamic simulations results of (a) and (b) for **1a**, (c) and (d) for **2a** in water environment at 300 K by Maestro (SCHRÖDINGER 2015-4).

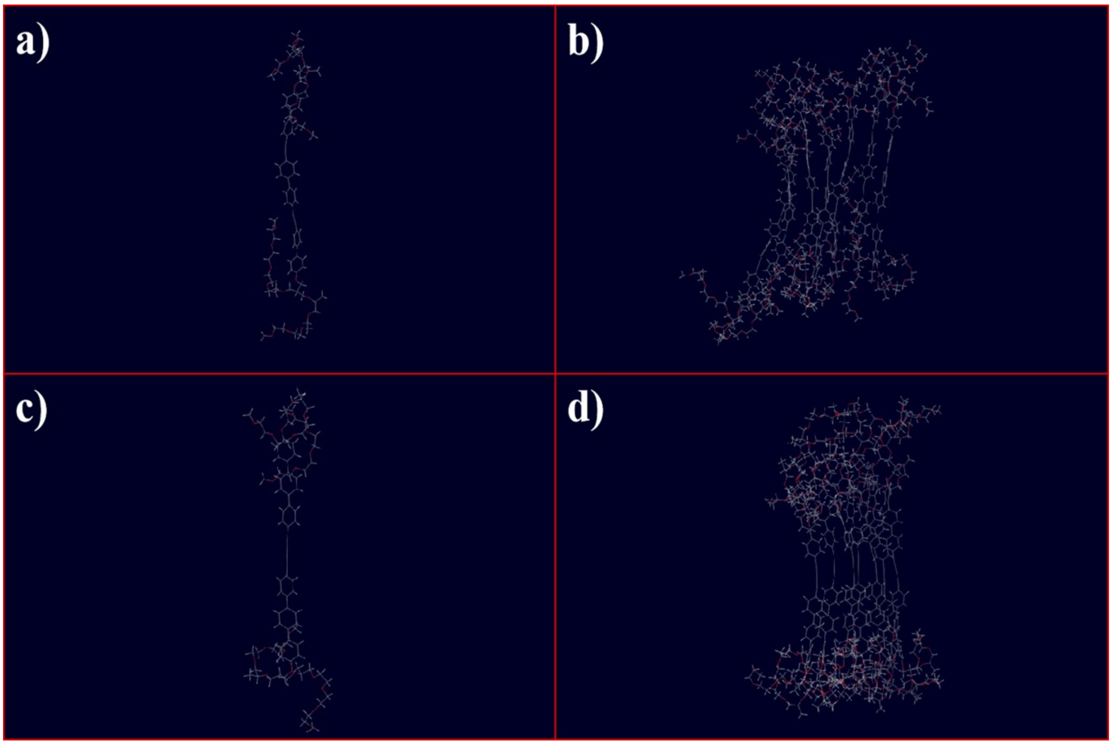

Fig S6. Molecular dynamic simulations results of (a) and (b) for **1b**, (c) and (d) for **2b** in water environment at 300 K by Maestro (SCHRÖDINGER 2015-4).

Note: When molecules aggregate into H-stacking, shows blue-shift in Uv-vis spectrum, while, adopting j-stacking, exhibits red-shift. Compare with molecules **1a** and **2a**, molecules **1b** and **2b** with dendritic oligoether chains have a more cross section areas than molecules **1a** and **1b** containing linear oligoether chains. This give arise to diverse molecular arrangement for molecules **1** and **2**. For molecules **1b** and **2b**, the rod building blocks prefer to stack into some tiled fashion caused by relatively bulky dendron groups, which is further confirmed by simulation of molecular assembly (packing of the rod block) in water environment shown in Fig. S5 and S6.

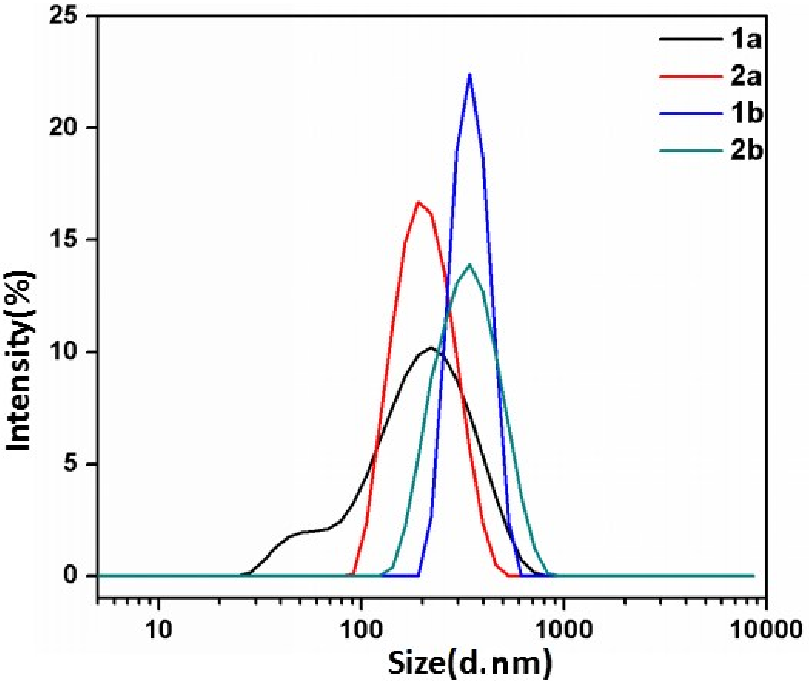

Fig S7. Size distribution graphs of aqueous solutions of molecules **1-2** (2×10^{-5} M) from DLS measurements.

References

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