Electronic Supplementary Information (ESI)

Self-organizing *p*-quinquephenyl building blocks incorporating lateral hydroxyl and methoxyl groups into supramolecular nano-assemblies

Zhaoyang Lu[a†], Keli Zhong[b†], Yang Liu[a], Zhaohua Li[a], Tie Chen[a*], Long Yi Jin[a*]

[a] Key Laboratory for Organism Resources of the Changbai Mountain and Functional Molecules, Ministry of Education and Department of Chemistry, College of Science, Yanbian University, No. 977 Gongyuan Road, Yanji 133002,

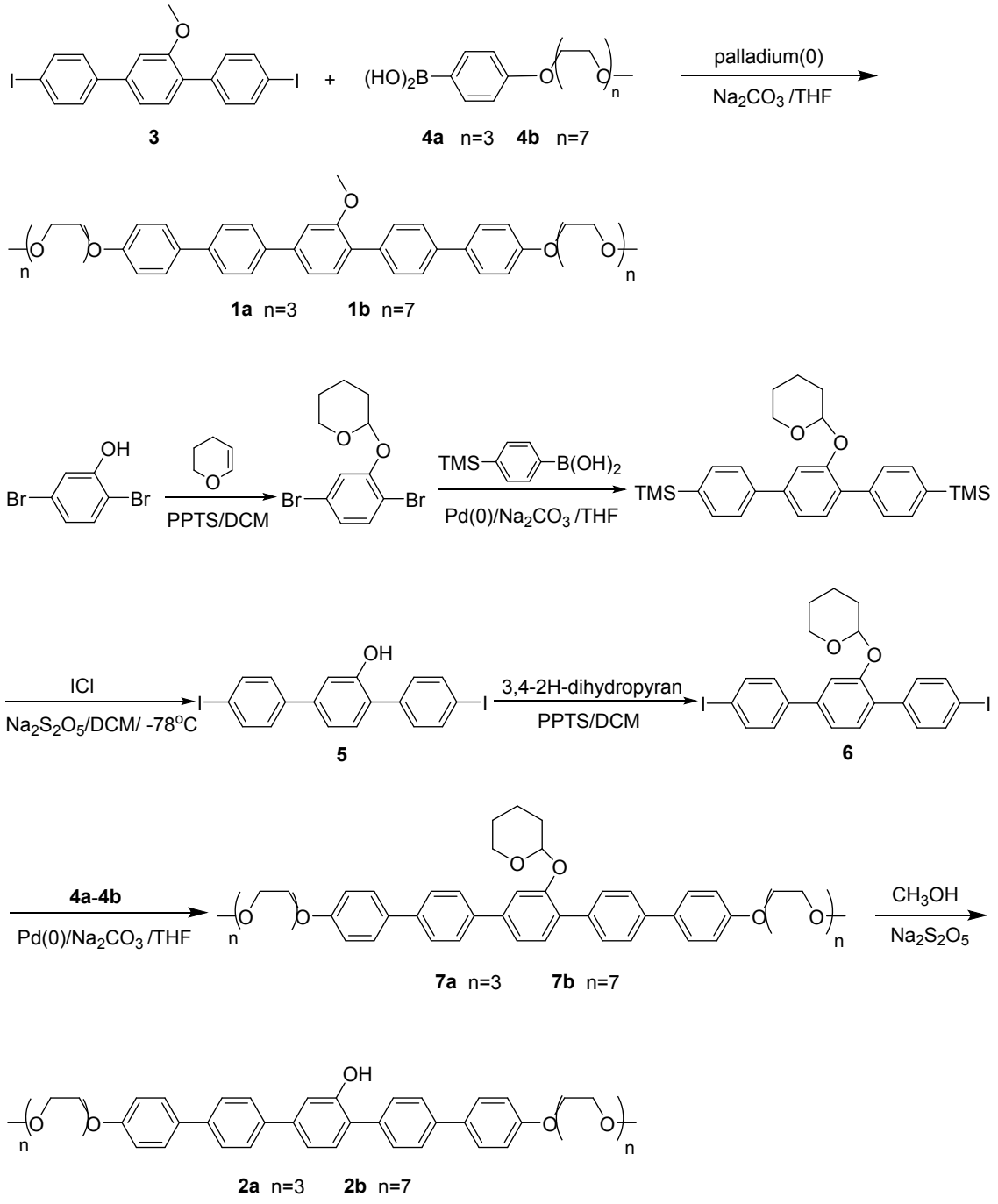
[b] College of Chemistry and Chemical Engineering, Bohai University, Jinzhou, Liaoning, 121013, China

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

† These authors contributed equally to this work.

Synthesis

Compounds **3** and **5** were prepared according to a method previously reported.[1]



Scheme S1 Synthetic route of molecules **1a-1b** and **2a-2b**.

Synthesis of compound 6.

Compound **5** (218 mg, 0.44 mmol) was dissolved in dichloromethane, 3,4-2H-dihydropyran (368 mg，4.38 mmol) and pyridinium 4-Toluenesulfonate (11 mg，0.044 mmol)were added to a 100 mL round bottom flask. The reaction mixture was

stirred at room temperature for 36 hours. 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. The solid was collected by filtration, and further purified by flash chromatography using petroleum ether / dichloromethane (3:1 v/v) as eluent to yield a white solid (145 mg，57%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.73(m, 4H), 7.38-7.28(m, 5H), 7.42(d, *J*=1.8 Hz, 1H), 7.17(dd, *J*=8.4, 1.8 Hz, 1H), 5.14(s, 1H), 4.06-3.96(m, 1H), 3.58-3.51(m, 1H), 2.23-1.75(m, 6H).

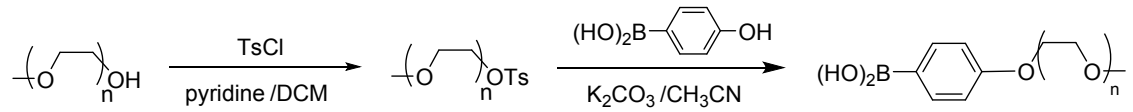
Synthesis of compound 7a and 7b.

A representative example is described for **7a**. Compound **6** (145 mg, 0.25 mmol), and compound **4a** (156 mg, 0.55 mmol) were dissolved in degassed tetrahydrofuran (20 mL). Degassed 2 M aqueous Na_2CO_3 (20 mL) was added to the solution and then tetrakis-(triphenylphosphine) palladium(0) (7 mg, 0.0055 mmol) was added. The mixture was heated at reflux for 48h with vigorous stirring under nitrogen. Cooled to room temperature, the aqueous layer was washed with methylene chloride. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silical gel) using methylene chloride/ethyl acetate (2:1 v/v) as eluent to yield a white solid (102 mg, 51%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.71-7.53(m, 13H), 7.39-7.35(m, 1H), 7.32-7.29(m, 1H), 7.04-7.00(m, 4H), 5.56-5.53(m, 1H), 5.41-5.37(m, 1H), 4.20(t, *J*=4.8 Hz, 4H), 3.90(t, *J*=4.8 Hz, 4H), 3.79-3.55(m, 16H), 3.39(s, 6H), 1.75-1.56(m, 6H).

Compound **7b**：white solid (56%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.71-7.47(m, 13H), 7.40-7.29(m, 2H), 7.04-7.00(m, 4H), 5.57-5.51(m, 1H), 4.93-4.87(m, 1H), 4.19(t, *J*=4.2 Hz, 4H), 3.90(t, *J*=4.2 Hz, 4H), 3.76-3.53(m, 48H), 3.38(s, 6H), 1.83-1.64(m, 6H).

Synthesis of compound 4a and 4b.

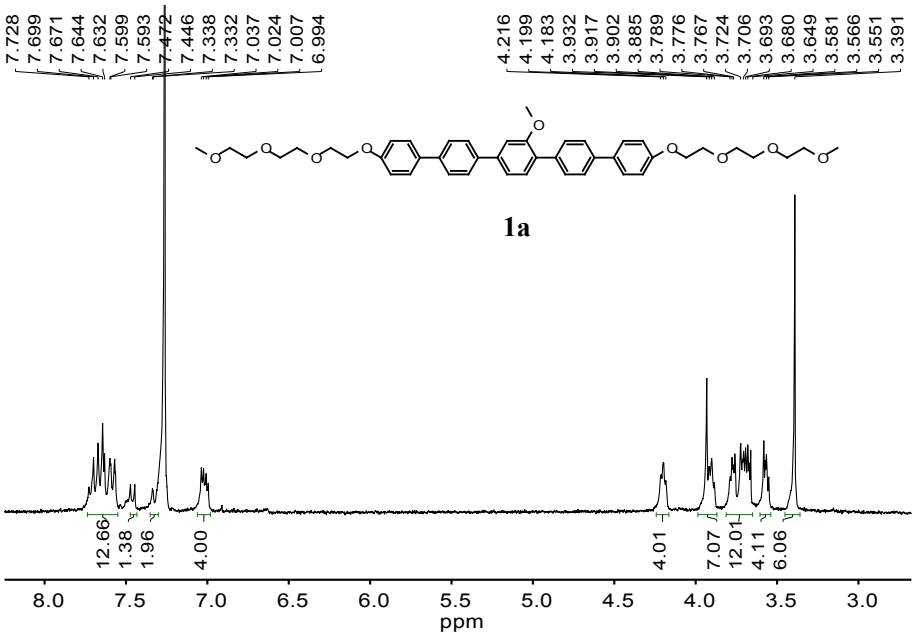
Compounds **8a**, **8b** and **9a**, **9b** were prepared according to the similar procedures reported previously.[2] A representative example is described for **4a**.



8a n=3 **8b** n=7 **9a** n=3 **9b** n=7 **4a** n=3 **4b** n=7

Compound **9a** (1.91 g, 6 mmol) and 4-hydroxybenzeneboronic acid (1.00 g, 7.2 mmol) were dissolved in acetonitrile (40 mL) and then excess potassium carbonate (2.48 g, 18 mmol) 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 and methylene dichloride, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness. The crude product was purified by column chromatography using ethyl acetate as eluent to yield a slightly red liquid (408 mg, 24%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.74(d, *J*=8.7 Hz, 2H), 6.97(d, *J*=8.7 Hz, 2H), 4.18 (t, *J*=4.5 Hz, 2H), 3.88 (t, *J*=4.5 Hz, 2H), 3.54-3.77(m, 8H), 3.38 (s, 3H).

Compound **4b**: yellow liquid (30%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 8.13 (d, *J*=8.7 Hz, 1H), 7.73(d, *J*=8.7 Hz, 1H), 7.00(d, *J*=8.7 Hz, 1H), 6.91(d, *J*=8.7 Hz, 1H), 4.13-4.27 (m, 2H), 3.82-3.94 (m, 2H), 3.52-3.77(m, 34H), 3.37(s, 3H).



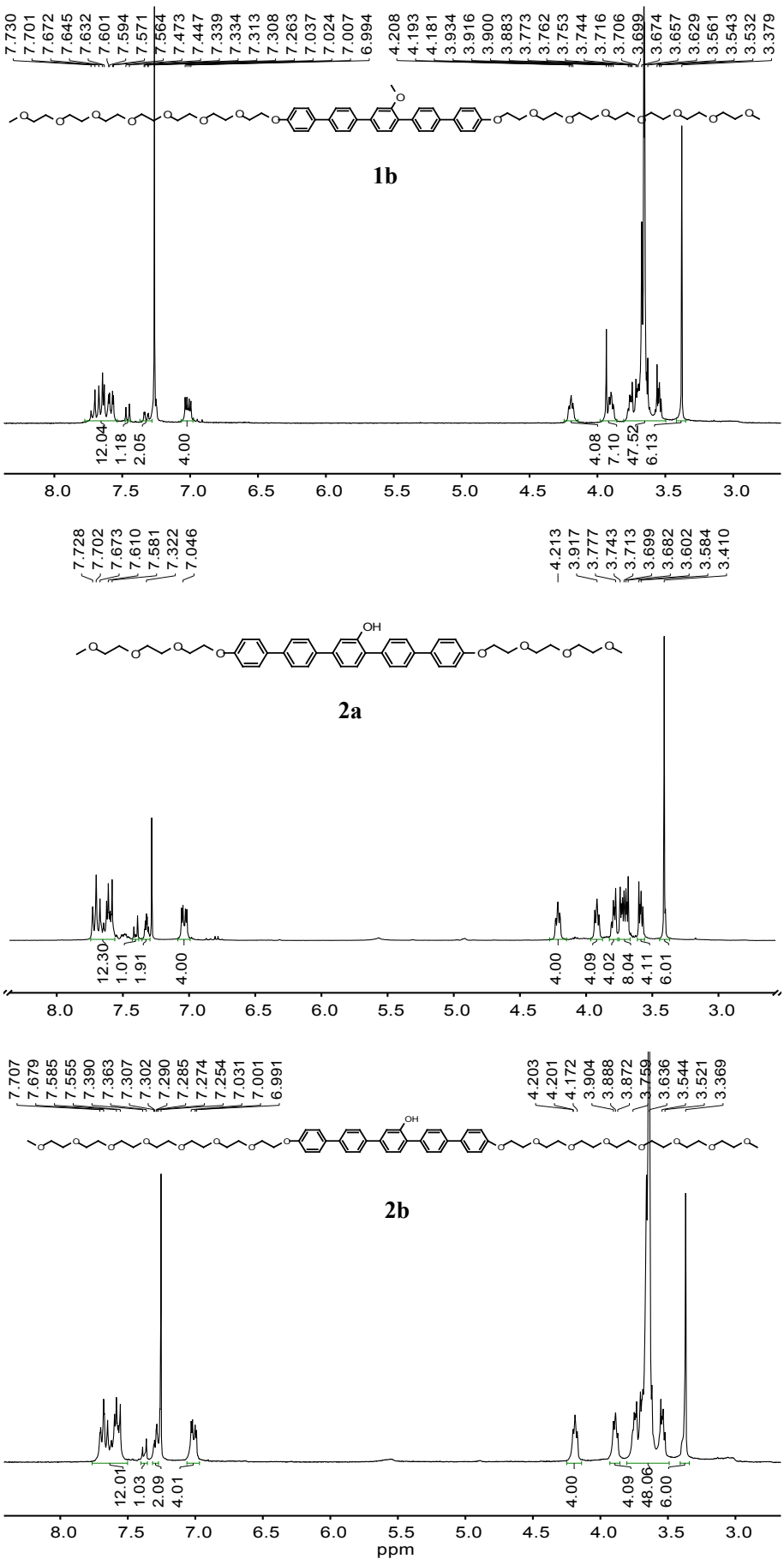


Fig. S1 ^{1}H NMR spectra of molecules **1a, 1b** and **2a, 2b** in $CDCl_3$.

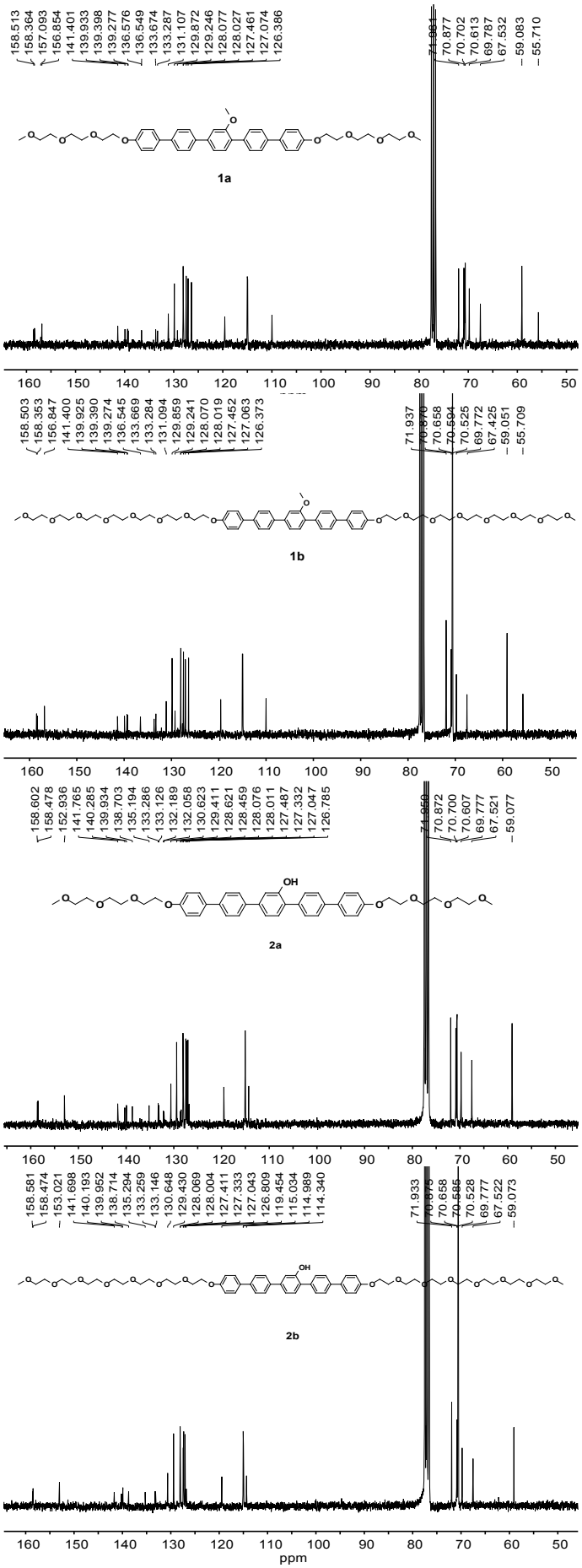


Fig. S2 ^{13}C NMR spectra of molecules **1a, 1b** and **2a, 2b** in $CDCl_3$.

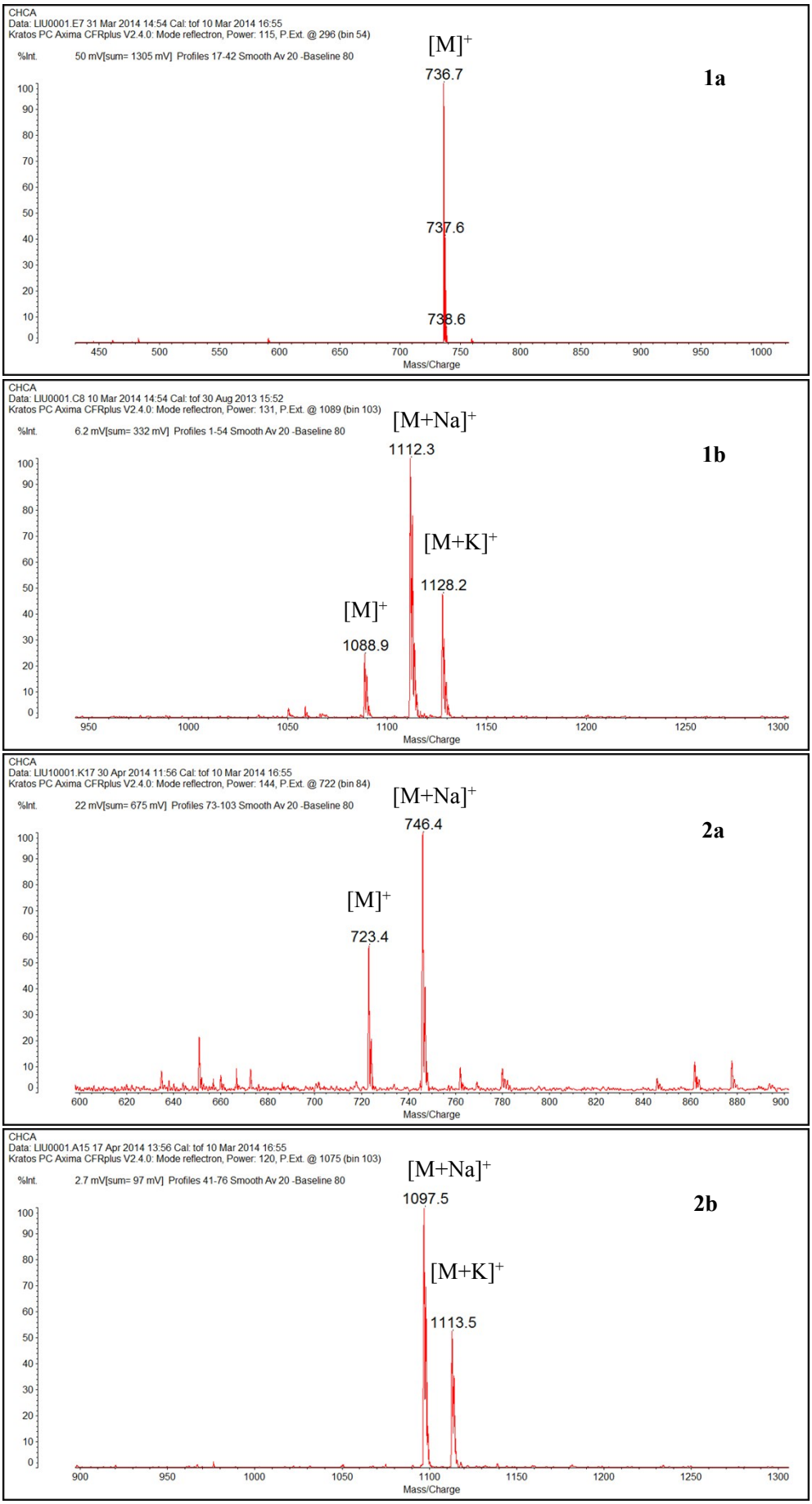


Fig. S3 MALDI-TOF-MS spectra of **1a, 1b** and **2a, 2b** (matrix: CHCA)

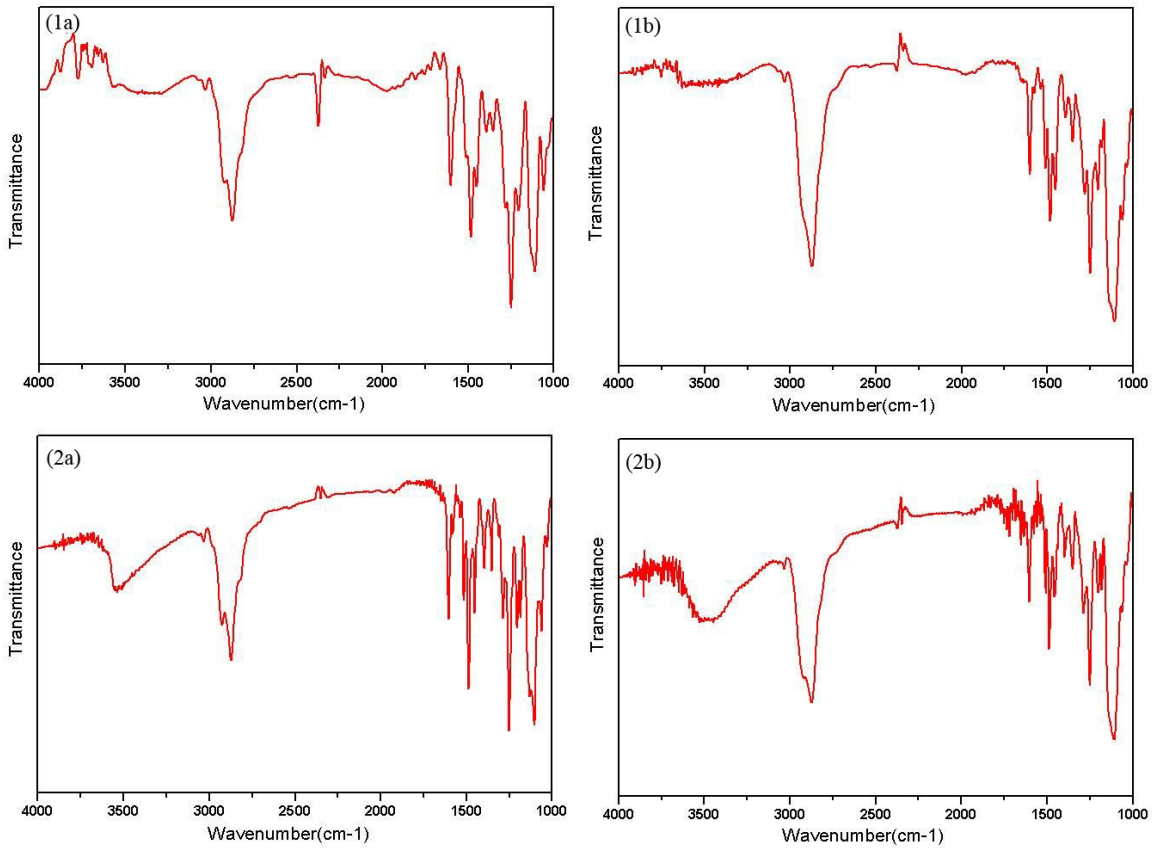


Fig. S4 FT-IR spectroscopy of molecules **1a, 1b** and **2a, 2b**.

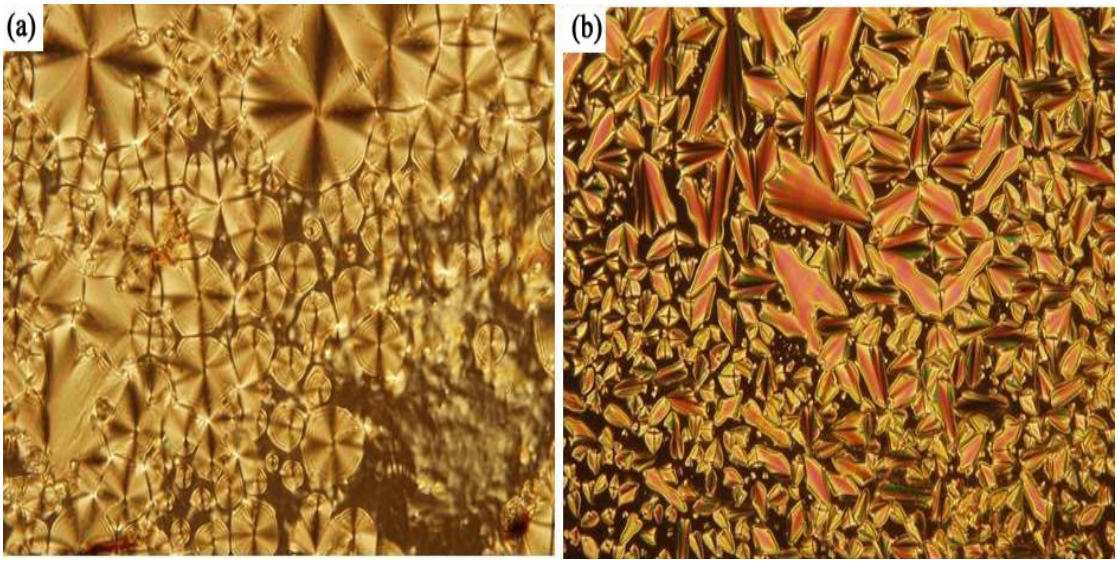


Fig. S5 Representative POM micrograph (× 40) of the textures exhibited by (a) a spherulitic texture with arced striations in crystalline phase of **2a** at 195 ℃; (b) a pseudo-focal-conic texture in liquid crystalline phase of **2a** at 228 ℃.

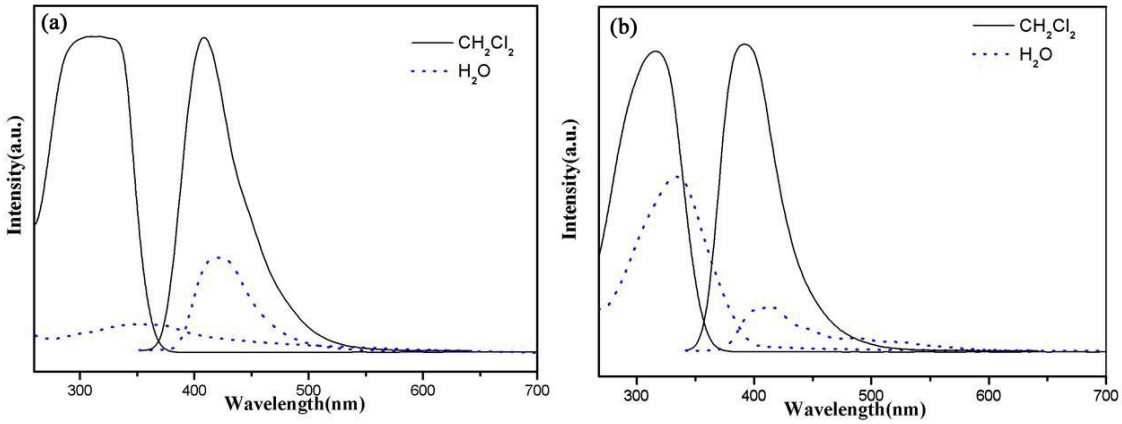


Fig. S6 (a) Absorption and emission spectra of **1b** in dichloromethane and aqueous solution (5×10^{-5} M). (b) Absorption and emission spectra of **2b**.

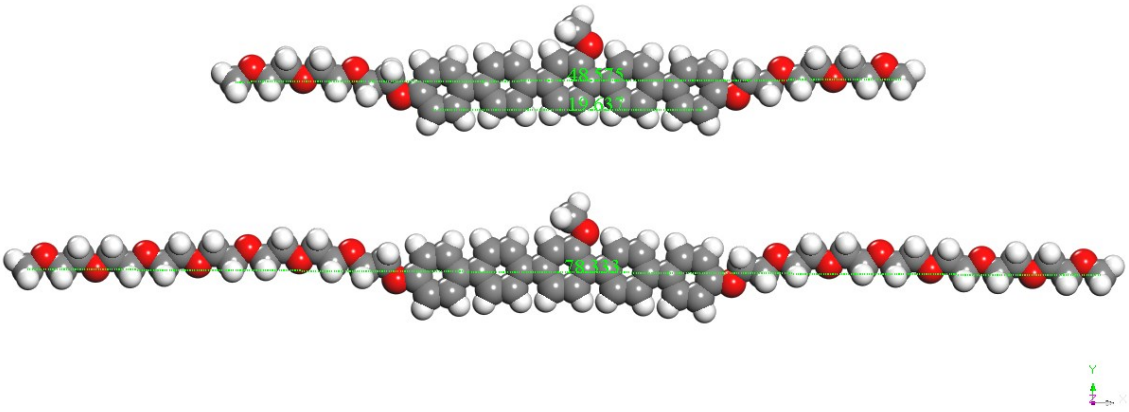


Fig. S7 The length of the rigid cores and the fully stretched molecular lengths of molecules **1a, 1b** by Corey-Pauling-Koltun (CPK) molecular modeling.

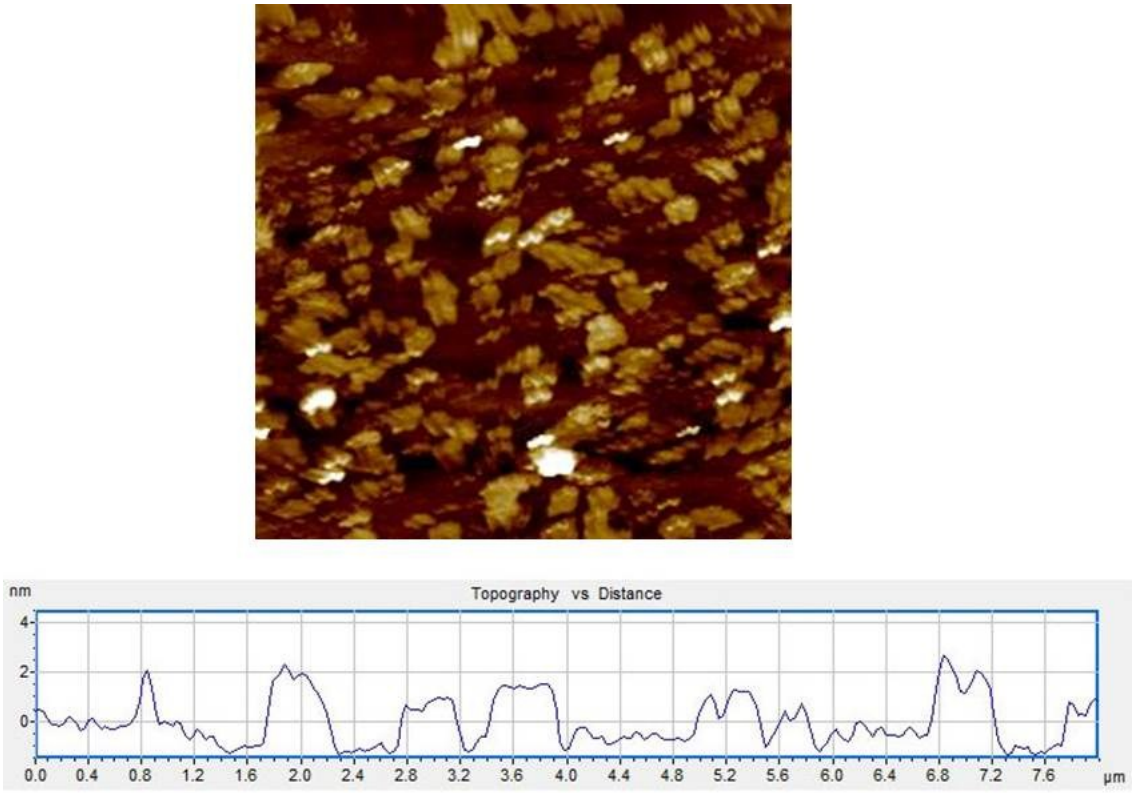


Fig. S8 AFM images of molecule **1a** (0.005 wt% in aqueous solution).

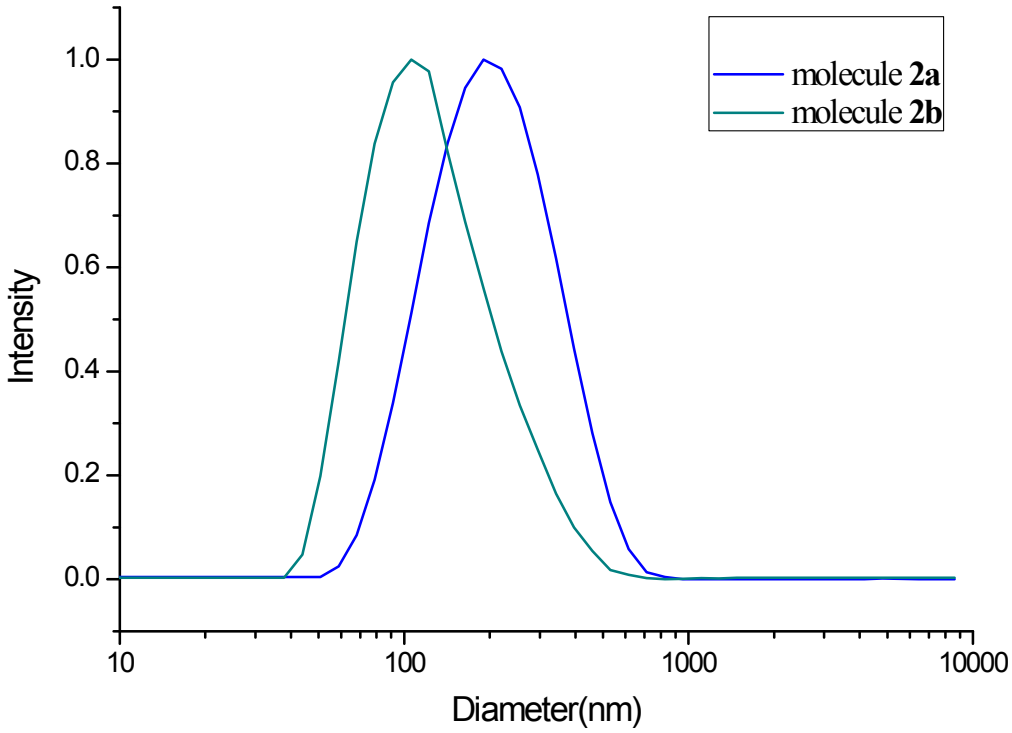


Fig. S9 Size distribution graphs of aqueous solutions of **2a, 2b** (5×10^{-5} M) from DLS measurements.

Table S1 Summary of SAXS data for **1a, 1b** and **2a, 2b** in the bulk state.

Molecule	Crystalline phase						Liquid crystalline phase				
	HPL		Col_o				Col_o				*N*
	a(nm)	*c*(nm)	*a*(nm)	*b*(nm)	γ(°)	*n*	*a*(nm)	*b*(nm)	γ(°)	*n*	
1a		—	2.7	2.3	66	~3		—			√
1b		—	3.2	2.5	62	~3		—			√
2a	3.8	6.0		—			3.6	2.7	60	~4	—
2b	6.4	8.1		—			3.9	3.2	65	~4	—

a, b, c, lattice constant (nm); γ , characteristic angle; n, the average number of molecules per crosssectional slice of the column, n = abc sin γ ρ N_A / M_W (c = 0.5 according to WAXS; M_W, molecular weight; N_A, Avogadro's number. ρ Molecular density); the lattice plane spacing, $d = \frac{2\pi}{q_{hkl}}$. The cell parameters of the hexagonal perforated lamellar lattice (a, c) , were calculated according to the following equation: $\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$. The cell parameters of the oblique columnar lattice (a, b) , were calculated according to the following equation: $\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$ (where h, k, and l are the Miller indices).

Table S2 Small-angle X-ray diffraction data of the oblique columnar structure for molecule **1a** (measured at 75℃, λ = 0.154 nm)

q_{obsd}	q_{calcd}	h	k	l
2.565	**2.563**	**1**	**0**	**0**
2.969	**2.976**	**0**	**1**	**0**
3.054	**3.047**	**1**	**1**	**0**

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections.

Table S3 Small-angle X-ray diffraction data of the oblique columnar structure for molecule **1b** (measured at 25℃, λ = 0.154 nm)

q_{obsd}	q_{calcd}	h	k	l
2.166	**2.164**	**1**	**0**	**0**
2.797	**2.791**	**0**	**1**	**0**
3.923	**3.629**	**2**	**1**	**0**

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections.

Table S4 Small-angle X-ray diffraction data of the hexagonal perforated lamellar structure for molecule **2a** (measured at 160℃, λ = 0.154 nm)

q_{obsd}	q_{calcd}	h	k	l
1.908	**1.908**	**1**	**0**	**0**
2.083	**2.079**	**0**	**0**	**2**
3.910	**3.915**	**1**	**1**	**2**
3.961	**3.958**	**0**	**2**	**1**

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections.

Table S5 Small-angle X-ray diffraction data of the oblique columnar structure for molecule **2a** (measured at 225℃, λ = 0.154 nm)

q_{obsd}	q_{calcd}	h	k	l
2.028	**2.036**	**1**	**0**	**0**
2.713	**2.719**	**0**	**1**	**0**
4.057	**4.057**	**2**	**0**	**0**

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections.

Table S6 Small-angle X-ray diffraction data of the hexagonal perforated lamellar structure for molecule **2b** (measured at 80℃ , λ = 0.154 nm)

q_{obsd}	q_{calcd}	h	k	l
1.370	**1.367**	**1**	**0**	**1**
1.545	**1.552**	**0**	**0**	**2**
3.093	**3.090**	**2**	**1**	**1**
3.485	**3.488**	**3**	**0**	**1**

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections.

Table S7 Small-angle X-ray diffraction data of the oblique columnar structure for molecule **2b** (measured at 120℃, λ = 0.154 nm)

q_{obsd}	q_{calcd}	h	k	l
1.782	**1.780**	**1**	**0**	**0**
2.140	**2.136**	**0**	**1**	**0**
4.279	**4.285**	**2**	**1**	**1**

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections.

References for Electronic Supplementary Information

[1]. D. W. Lee, T. Kim, M. Lee, *Chem. Commun.* 2011*, **47, 8259.***

[2]. Z. Wang, K. Zhong, Y. Liang, T. Chen, B. Yin and L. Y. Jin, *J Polym Sci Part A:*

Polym Chem, 2015, **53**, 85.