# **Supporting Information**

# One-, Two- and Three-dimensional Hierarchical Self-Assembly of Nonamphiphilic Low-Entropy Chains from nanotubes to nanoribbons, porous net-sheet

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# **Materials and Methods**

### 1. 1) Materials

Vinyl acetate (VAc, 99%, Sigma-Aldrich), N-vinylpyrrolidinone (NVP, 97%, Sigma-Aldrich) were passed through a small column of basic alumina for inhibitor removal prior to polymerization. N-isopropylacrylamide (NIPAM, 99%, TCI) was purified by recrystallization from n-hexane/toluene (3/1 v/v). 2,2-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol. Tetrahydrofuran (THF) was distilled to remove the peroxide compounds. N-Bromomethylphthalimide (97%) was purchased from Sigma-Aldrich.  $\alpha$ , $\alpha$ '-Dibromo-o-xylene (97%) was purchased from xiya reagents company. All the other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. (SCRC) and used as received.

2) Methods and Characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on 400 MHz NMR spectrometer. Chemical shifts are reported in ppm versus tetramethylsilane or the residual solvent resonance used as an internal standard.

The assembled structures were imaged using a Hitachi SU-70 Schottky field-emission gun (FEG) Scanning Electron Microscope (SEM) and a JEOL FEG Transmission Electron Microscope (TEM). SEM samples were prepared by casting a 5-10 µL of sample solution on mica and were dried at room temperature. TEM samples were prepared by casting on 300 mesh copper grids covered with carbon film and were dried at room temperature.

**Fluorescence Microscopy** images were recorded under ambient conditions by Olympus BX53. Substances were excited at 405 nm and the emission was collected between 480 nm to 580 nm with 40x magnification. The samples were prepared by directly dropping the corresponding solutions onto slide.

**Atomic Force Microscopy i**mages were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IV operating in the tapping mode regime. cro-fabricated silicon cantilever tips (MPP-11100-10) with a resonance frequency of 299 kHz and a spring constant of 20-80 Nm<sup>-1</sup> were used. The scan rate was varied from

0.5 to 1 Hz. Samples for the imaging were prepared by drop casting the corresponding solutions onto freshly cleaved mica.

Confocal images were captured using a LSM 710 confocal laser scanning microscope system with inverted microscope. Substances were excited at 405 nm and the emission was collected between 480 nm to 580 nm with 60x magnification. The samples were prepared by drop casting the corresponding solution onto a cover slide and dried in room temperature.

Time-correlated Single Photon Counting (TCSPC): Fluorescence decay profiles were recorded using FLSP 920 spectrometer, Edinburgh Instrument. EPLED source of 386 nm was used for excitation.

The absorption spectra were measured by PERKIN LAMBDA 35 UV–Vis spectrometer. The emission spectra were recorded on a SPEX-Fluorolog F112x spectrofluorimeter.

# 2. The Syntheses of chain transfer agents (CTA).

# 1).Synthesis of O-Ethyl S-(Phthalimidylmethyl) Xanthate (CTA 1)

O-Ethyl S-(Phthalimidylmethyl) Xanthate was prepared according to the previous work. A typical procedure was as follows: O-Ethyl xanthic acid potassium salt (1.03 g, 0.0064 mol) was suspended in chloroform (20 ml) in a dry two-necked round-bottomed flask. N-Bromomethylphthalimide (1.00 g, 0.0042 mol) in chloroform (20 ml) was added dropwise with stirring; the solution became paler yellow with the precipitation of white KBr as the reaction proceeded. The solution was stirred at room temperature for 18 h when complete reaction was confirmed by TLC (product  $R_f$  =0.60). Additional chloroform (20 ml) was added prior to washing with deionized water (2 × 50 ml) and brine (1 ×50 ml). The solution was dried over anhydrous MgSO4, filtered and the solvent removed from the filtrate by rotary evaporation to give a pale yellow solid (1.12 g, 95%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$  : 1.46 (3H, CH<sub>3</sub>CH<sub>2</sub>-), 4.68 (2H, CH<sub>3</sub>CH<sub>2</sub>-O), 5.33 (2H, N-CH<sub>2</sub>-S), 7.75 (2H, aromatic H), 7.85 (2H, aromatic H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  : 13.7 (CH<sub>3</sub>CH<sub>2</sub>-), 41.2 (N-CH<sub>2</sub>-S), 70.5 (CH<sub>3</sub>CH<sub>2</sub>-), 123.6 (2×o-Ph, CH), 131.8 (2×Ph, C), 134.4 (2×p-Ph, CH), 166.6 (2×C=O), 210.2 (OCS<sub>2</sub>).



CTA 1

### 2).Synthesis of S,S-1,2-phenylene-bis(methylene)-0,0-diethyl ester (CTA 2)

A typical procedure was as follows: Ethanol (70 ml) was added to a round bottom flask equipped with a stir bar. Potassium Hydroxide (3.00 g, 0.054 moles) was added and stirred until dissolved. Carbon disulphide (3.02 ml, 0.05 mol) was added dropwise and stirred for 5 h, forming a yellow solution.  $\alpha, \alpha'$ -Dibromo-o-xylene (6.57 g, 0.02 mol) added and the reaction stirred at 50°C for 18 h. The solution was filtered and washed with acetone, then concentrated in vacuo. The residue was purified on a column of silica with 99:1 Hexane:Methanol as the elutant, affording a clear yellow oil. Yield 3.25 g 30%. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$  : 1,45 (3H, CH<sub>3</sub>CH<sub>2</sub>O), 4.48 (2H, S-CH<sub>2</sub>-), 4.68 (2H, CH<sub>3</sub>CH<sub>2</sub>O), 7.28 (4H, aromatic H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  : 13.91 (CH<sub>2</sub>-CH<sub>3</sub>), 40.54 (CH<sub>2</sub>), 70.16 (CH<sub>2</sub>-CH<sub>3</sub>), 127.56 (para CH), 128.72 (meta CH), 129.19 (ortho CH), 214.02 (COS<sub>2</sub>).





# 3 The Syntheses of end-group-functionalized polymers mediated by CTAs

#### 1). Polymerization of vinyl acetate using CTA 1 (PT-PVAc)

CTA 1 (0.26 g, 0.93 mmol), vinyl acetate (10.32 g, 119.97 mmol), AIBN 2,2-Azobis(isobutyronitrile) (0.02 g, 0.12mmol) and THF (11mL) were added to a stoppered vial. The solution was thoroughly degassed with three standard freeze-pump-thaw cycles, and the reaction mixture was then allowed to polymerize at 68 °C for typically 24 h. The yellow solutions were then cooled to room temperature. Poly(vinyl acetate) was then recovered as a yellow sticky solid after precipitation into hexane. The hexane was then decanted and the poly(vinyl acetate) was redissolved in THF, which was then concentrated in vacuo and thoroughly dried under vacuum at 40 °C for 24 h, forming a white crystalline solid. The monomer conversion was 45% as determined by gravimetric calculation.  $M_n$  and  $M_w/M_n$  values were determined by SEC with poly(methyl methacrylate) (PMMA) standards ( $M_{n,SEC}$ =3870 g.mol<sup>-1</sup>,  $M_w/M_n$ =1.88). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$  : 1.30 (3H, CH<sub>3</sub>CH<sub>2</sub>O), 1.70 (2H, -CH<sub>2</sub>-), 2.02 (3H, CH<sub>3</sub>C=O), 3.56 (2H, N-CH<sub>2</sub>-CH<sub>2</sub>), 4.51 (2H, CH<sub>3</sub>CH<sub>2</sub>O), 4.71 (1H, -CHO-CH<sub>2</sub>-), 6.45 (1H, O-CH-S), 7.60 (4H, aromatic H).

2). Hydrolysis of Poly(vinyl acetate) (PT-PVAc) to Poly(vinyl alcohol) (PT-PVA) poly(vinyl acetate) (1.5 g,  $M_{n,SEC}$ =3870 g.mol<sup>-1</sup>,  $M_w/M_n$ =1.88) was dissolved in a methanol (20 mL) and hydrazine hydrate solution (15 mL, 80% in water) in a round-bottom ask. The reaction mixture was stirred at 30 °C for 2 h. The reaction mixture was then dialyzed using distilled water and poly(vinyl alcohol) was recovered as a spongy white solid by freeze-drying the dialysis solution. Deacetylation was determined by1H NMR. 1H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  3.94 (-CHOH-, br, 1H), 1.62 (-CH<sub>2</sub>-, br, 2H).

# 3). Polymerization of N-vinyl-pyrrolidone using CTA 1 (PT-PVP)

CTA 1 (0.22 g, 0.76 mmol), N-vinyl-pyrrolidone (10.74 g, 96.67 mmol), AIBN 2,2-Azobis(isobutyronitrile) (0.02 g, 0.12mmol) and dioxane (12mL) were added to a stoppered vial. The solution was thoroughly degassed with three standard freeze-pumpthaw cycles, and the reaction mixture was then allowed to polymerize at 68 °C for typically 24 h. The yellow solutions were then cooled to room temperature. Poly(N-vinylpyrrolidone) was then recovered as a white sticky solid after precipitation into diethyl ether. The diethyl ether was then decanted and the poly(N-vinyl-pyrrolidone) was redissolved in methanol, which was then concentrated in vacuo and thoroughly dried under vacuum at 40 °C for 24 h, forming a white crystalline solid. The monomer conversion was 52% as determined by gravimetric calculation.  $M_n$  and  $M_w/M_n$  values were determined by SEC with poly(methyl methacrylate) (PMMA) standards ( $M_{n,SEC}$ =4260 g.mol<sup>-1</sup>,  $M_w/M_n$ =1.72). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$  : 3.73 (1H, -CHN-), 3.21 (2H, -NCH<sub>2</sub>CH<sub>2</sub>-), 2.38 (2H, -NCOCH<sub>2</sub>-), 2.23 (2H, -NCH2CH2CH2-), 1.96-1.61 (2H, -CH<sub>2</sub>-), 1.43 (3H, CH<sub>3</sub>CH<sub>2</sub>).

# 4). Polymerization of N-vinyl-pyrrolidone using CTA 1 (PT-PNIPAM)

CTA 1 (0.15 g, 0.35 mmol), N-isopropylacrylamide (3.98 g, 35.19 mmol), AIBN 2,2-Azobis(isobutyronitrile) (0.0092 g, 0.056mmol) and THF (10mL) were added to a stoppered vial. The solution was thoroughly degassed with three standard freeze-pumpthaw cycles, and the reaction mixture was then allowed to polymerize at 68 °C for typically 24 h. The yellow solutions were then cooled to room temperature. Poly(Nisopropylacrylamide) was then recovered as a yellow sticky solid after precipitation into hexane. The hexane was then decanted and the poly(N-isopropylacrylamide) was redissolved in THF, which was then concentrated in vacuo and thoroughly dried under vacuum at 40 °C for 24 h, forming a white solid



1H NMR (400MHz, CDCl3) of PT-PNIPAM

# 5). Polymerization of vinyl acetate using CTA 2 (B-PVAc)

CTA 2 (0.42 g, 1.21 mmol), vinyl acetate (16.54 g, 192.23 mmol), and AIBN 2,2-Azobis(isobutyronitrile) (0.02 g, 0.12mmol) were added to a stoppered vial. The solution was thoroughly degassed with three standard freeze-pump-thaw cycles, and the reaction mixture was then allowed to polymerize at 68 °C for typically 24 h. The solutions were then cooled to room temperature. Poly(vinyl acetate) was then recovered as a yellow sticky solid after precipitation into hexane. The hexane was then decanted and the poly(vinyl acetate) was redissolved in THF, which was then concentrated in vacuo and thoroughly dried under vacuum at 40 °C for 24 h, forming a white crystalline solid. The monomer conversion was 40% as determined by gravimetric calculation.  $M_n$  and  $M_w/M_n$ values were determined by SEC with poly(methyl methacrylate) (PMMA) standards ( $M_{n,SEC}$ =3360 g.mol<sup>-1</sup>,  $M_w/M_n$ =1.52). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$  : 4.61 (-CHO-CH<sub>2</sub>, br, 1H), 1.74 (-CO-CH<sub>3</sub>, br, 3H), 1.53 (-CH<sub>2</sub>-, br, 2H)



Fig S1. The structure of **B-PVAc** 

quantity: 13

maximum size/um 1.10

minimum size/um 0.59

aver	age s	ize/u	n	0.86
No.s	creer	n leng	th	size/um
1	4905	5.09	0.70	
2	4470	).10	0.64	
3	4928	8.80	0.71	
4	6855	5.07	0.98	
5	7517	7.53	1.08	
6	5581	.23	0.80	
7	6251	.76	0.89	
8	7382	2.94	1.06	
9	6399	9.31	0.92	
10	6440	).02	0.92	
11	4112	2.74	0.59	
12	5159	9.15	0.74	
13	7691	.43	1.10	
====	=====	=====		-Statistical Report===============
distri	ibutio	n/um	aver	age size/um quantity frequency
02	.1	0	0.00	0
.24	.3	0	0.00	0
.46	.5	1	0.07	7
.68	.7	4	0.30	8
.8-1	.9	5	0.38	5
1-1.2	21.1	3	0.23	1
1.2-1	1.4	1.3	0	0.000
1.4-1	1.6	1.5	0	0.000
1.6-1	1.8	1.7	0	0.000
1.8-2	21.9	0	0.00	0
*****	*****	*****	*****	*****

#### 

# DLS measurement report

Size	Intens	ity	Size		Intensity		
d.nm	%		d.nm		%		
0.4	0			68.06		0	
0.4632	0			78.82		0	
0.5365	0			91.28		0	
0.6213	0			105.7		0	
0.7195	0			122.4		0	
0.8332	0			141.8		0	
0.9649	0			164.2		0	
1.117	0			190.1		0	
1.294	0			220.2		0	
1.499	0			255		0	
1.736	0			295.3		0	
2.01	0			342		0	
2.328	0			396.1		0	
2.696	0			458.7		0	
3.122	0			531.2		0	
3.615	0			615.1	12.	6	
4.187	0			712.4	33.	. 4	
4.849	0			825	36.	. 4	
5.615	0			955.4	17.	. 7	
6.503	0			1106		0	
7.531	0			1281		0	
8.721	0			1484		0	
10.1	0			1718		0	
11.7	0			1990		0	
13.54	0			2305		0	
15.69	0			2669		0	
18.17	0			3091		0	
21.04	0			3580		0	
24.36	0			4145		0	
28.21	0			4801		0	
32.67	0			5560		0	
37.84	0			6439		0	
43.82	0			7456		0	
50.75	0			8635		0	
58.77	0		1.0	00E+04		0	
		Pk 1 Avg	Pk 2	Avg	Pk 3 Avg		
Rec #	Z-Avg	(I)	(I)		(I)		DCR

d.nm

d.nm

d.nm d.nm

kcps

862	1468	784	0	0 18.3
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Fig S2. The statistical analysis of FE-SEM images and DLS measurement result of  $2 \times 10^{-3}$  M PT-PVAc solution in THF.



Fig S3. SEM images of aged time-dependent hierarchical self-assembly of 2×10<sup>-5</sup> M THF solution of PT-PVAc. a) freshly prepared, b) aged 12H, c) aged 24H, d) aged 48H.



Fig S4. The phase image with its surface profiles of 8×10<sup>-5</sup> M THF solution of PT-PVAc



Fig S5. a) partial and b) whole <sup>1</sup>H NMR of PT-PVAc in  $CDCI_3$  as a function of concentration.



Fig S6. a) partial and b) whole <sup>1</sup>H NMR of CTA 1 in CDCl<sub>3</sub> as a function of concentration.

# 4. Critical J-aggregate Concentration (CJC) measurement

The self-assembly ability of the PT-PVAc polymers in THF was proved by the fluorescence spectrometry using intrinsic phthalimide as the probe. The fluorescence excitation spectra (emission wavelength is set at 490 nm) of the solution of polymer containing phthalimide were recorded (Fig S7). A red shift of the phthalimide (0,0) band from 340 to 405 nm was observed on increasing the polymer concentration. This change reflects the formation of the supramolecular J-aggregates with increasing the polymer concentration. A plot of the ratio of the intensity of the signal at 405 nm to that at 340 nm( $I_{405}/I_{340}$ ) versus the logarithm of the polymer concentration (Fig S7) results in a CJC value.



Fig S7. Fluorescence excitation spectra of THF solution of PT-PVAc below and above CJC.





Results

			Size (d.n	% Intensity	Width (d.n		
Z-Average (d.nm):	430.8	Peak 1:	481.3	86.3	238.2		
Pdl:	0.736	Peak 2:	72.59	7.0	13.78		
Intercept:	0.927	Peak 3:	5368	6.7	329.6		
Result quality	Refer to qu	uality report					



Fig S8. DLS measurement result of  $2 \times 10^{-3}$  M PT-PVAc solution in THF(top), DLS measurement result of  $2 \times 10^{-3}$  M PT-PVA solution in water(bottom)



Fig S9. Fluorescence images of PT-PVAc solution (a,b,c) and gel (d) in THF, a)  $2.5 \times 10^{-4}$  M, b)  $5.8 \times 10^{-3}$  M, c)  $2.5 \times 10^{-2}$  M, d)  $8.3 \times 10^{-1}$  M.



Fig S10. The time-resolved emission spectra of 0.025 M solution of PT-PVAc in THF (  $\lambda ex=386 \text{ nm}$ )



Fig S11. The time-resolved fluorescence anisotropy of 0.025 M solution of PT-PVAc in THF



Fig S12. a,b) SEM images c,d,e) AFM images f) TEM images of vesicles formed from PT-PNIPAM in water. a)  $4 \times 10^{-4}$  M, b)  $8 \times 10^{-4}$  M, c) the height images of  $4 \times 10^{-5}$  M, d) the 3D images of  $4 \times 10^{-5}$  M, e) the magnified height images of  $4 \times 10^{-5}$  M, the ratio of height to diameter is 8, f)  $1 \times 10^{-5}$  M.



Fig S13. SEM images (a-e) of concentration-dependent hierarchical self-assembly of PT-PNIPAM in water as a function of concentration. a)  $2 \times 10^{-5}$  M, b)  $4 \times 10^{-5}$  M, c)  $1 \times 10^{-4}$  M, d)  $1 \times 10^{-3}$  M, e)  $1 \times 10^{-2}$  M.



Fig S14. a, b) SEM images c) AFM images d) TEM images of vesicles made from **PT**-**PVP** in water. a)  $4 \times 10^{-5}$  M, b)  $8 \times 10^{-5}$  M, c) the height images of  $4 \times 10^{-5}$  M, d)  $4 \times 10^{-5}$  M.



wavelength (nm)

Fig S15. A) SEM image B) TEM image of vesicles made from  $4 \times 10^{-4}$  M solution of B-PVAc in THF. C) Fluorescence emission spectra of B-PVAc in THF, a)  $1 \times 10^{-5}$  M, b)  $1 \times 10^{-4}$  M, c)  $2 \times 10^{-3}$  M, d)  $2 \times 10^{-2}$  M, e)  $8 \times 10^{-2}$  M. It should noted that, upon increasing concentration, the maximum emission peak red-shifts from 350 nm to 395 nm, at last to 410 nm. ( $\lambda$ ex=320 nm)

# 5. Fluorescence imaging studies in vitro.

For cell imaging in vitro, CT1 cells were seeded and grown in Lab-Tek chambered coverglass wells (4 well, Nalge Nunc Int. Rochester, NY, USA) at a density of 3000 cells

per mL medium (DMEM, Hyclone, Utah, USA) containing 10% fetal bovine serum (FBS, Sijiqing Company Ltd., Hangzhou, China) for 36 h at 37 °C in 5% CO<sub>2</sub> before the cellular uptake study. The coverglass wells were washed with PBS (×2) and incubated in PT-PVA solution (0.07% wt) with DMEM (40%, v/v) for 2 h at 37°C. Afterwards, the cells were washed with PBS (×3), and the imaging experiments were performed with a **LSM 710 confocal laser scanning microscope (Carl Zeiss, Jena, Germany)** using a 40×/1.3 Oil DIC Plan NeoFluar objective. Polymer loaded cells at 405 nm (blue channel) was carried out with a diode laser, and emission was collected using a META detector between 480 and 580 nm. All images were acquired with ZEN 2009 software (Carl Zeiss Microimaging).



6. Calculation of size of PT-PVAc and corresponding bilayer using Chem 3D.

Fig S16. Calculation of size of PT-PVAc and corresponding bilayer using Chem 3D.

Caculation																	
Minimize ene	rgy																
Pi System:	10	9	6	1	2	3	5	4	7	11							
Warning: Sor	ne pa	rame	ters	are	gues	sed	(Qua	lity =	: 1).								
Iteration 10	0964:	Minii	miza	tion	term	ninate	ed no	orma	lly b	ecau	se	the	grad	ient	norn	n is	less
than the mini	mum g	gradi	ent r	norm	ו												
Stretch:				3.70	)65												
Bend:				17.8	8612												
Stretch-Be	nd:			1.0	346												
Torsion:			-	2.99	915												
Non-1,4 VI	DW:			-13.	3426	i											
1,4 VDW:				39.	7798												

Dipole/Dipole:2.6258Total Energy:48.6737 kcal/molCalculation completed



Fig S17. a) FE-SEM images of single 0.02 M THF solution of CTA 1





Fig S18 FE-SEM images of  $8{\times}10^{\text{-5}}$  M PT-PVAc in THF A), PT-PVAc in DMSO B)

 $8{\times}10^{\text{-5}}~M$  PT-PVP in water C), PT-PVP in ethanol D)