Supporting Information

Smart Supramolecular Nanofibers and Nanoribbons from Uniform Amphiphilic Azobenzene Oligomers

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Experimental Procedures

Materials

N, N, N′, N″, N″-Pentamethyldiethylenetriamine (PMDETA; 98%; J&K) was dried with 4 Å molecular sieves and distilled under vacuum. Copper(I) bromide (CuBr; chemical pure, Shanghai Chemical Reagent, Shanghai, China) was purified *via* washing with acetic acid, water and ethanol, and then dried in a vacuum. Tetraethylene glycol (TEG; 99.2%, J&K), 3-ethynylaniline (>98%; Aldrich), sodium azide (≥99.5%; Aldrich), tetrabutylammonium fluoride (TBAF; 1.0 mol L−1 in tetrahydrofuran (THF), Energy Chemical), and triethylamine (TEA; analytical reagent) were used as received. Unless otherwise specified, all chemicals were purchased from Shanghai Chemical Reagent Co. Ltd, Shanghai, China.

Characterization

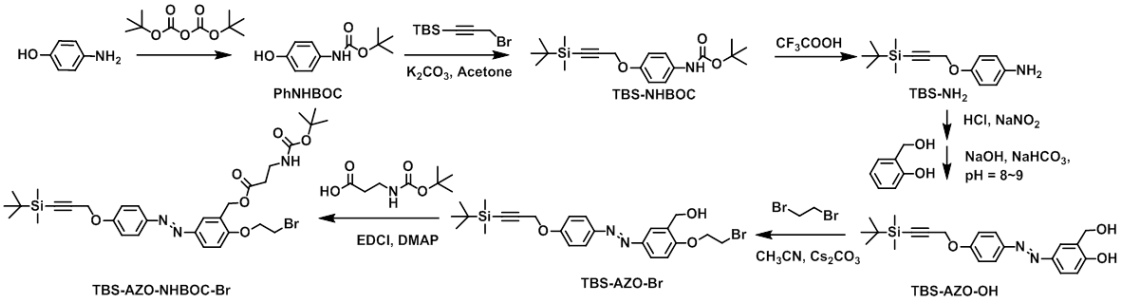
Proton nuclear magnetic resonance (^{1}H NMR) spectra of the samples were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz) using tetramethylsilane (TMS) as the internal standard at room temperature. The number-average molecular weight (M_n) and molecular weight distributions (M_w/M_n) of the samples were determined by a TOSOH HLC-8320 gel permeation chromatography (GPC) equipped with refractive-index and UV detectors, using two TSKgel Super Mutipore HZ-N (3 μm beads size) columns arranged in series with a molecular weight separation ranging from 500 to 190 000 g mol^{-1}, calibrated with polystyrene standard samples. THF was used as the eluent at a flow rate of 0.35 mL/min at 40 °C. In order to purify the crude polymers, an Agilent PL-50 preparative GPC system equipped with a manual injector and a differential refractive index detector was used. The flow rate was maintained at 3 mL/min and THF was used as the eluent. Separations were achieved using a PL gel 10 μm MIXED-D, 300 × 25 mm preparative GPC column held at 40 °C. The dried crude polymer was dissolved in THF at 15-20 mg/mL concentration and filtered through a 0.45 μm PTFE syringe filter prior to injection. Different fractions were collected manually, and the composition of each was determined using the TOSOH HLC-8320 GPC column as described above. Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry was performed by using an UltrafleXtreme MALDI TOF mass spectrometer (Bruker Daltonics) equipped with a 1 kHz smart beam-II laser. The instrument was calibrated, before each measurement, with specific molecular weight PMMA. The matrix compound trans- 2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich, >98%) was prepared at a concentration of 20 mg/mL in $CHCl_3$. The sodium trifluoroacetate prepared in ethanol at a concentration of 10 mg/mL was used as a cationizing agent. All samples were dissolved in THF at a concentration of about 10 mg/mL. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker TENSOR-27 FT-IR spectrometer. Ultraviolet visible (UV-vis) absorption spectra of the samples were determined on a Shimadzu UV-2600 spectrophotometer at room temperature. Transmission electron microscopy (TEM) was recorded on HITACHI HT7700 at a 120 kV accelerating voltage. The surface morphology was measured by atomic force microscope (AFM)

with a tapping mode (Veeco Instruments Inc., Nanoscope IV). The self-assembled polymer solution was dropped onto pre-cleaned silicon wafer and was then left to dry under the ambient conditions. The simulative molecular configuration was calculated with Materials Studio software (MS). Publications of specific relevance to this calculation: Density functional: P91 exchange: Perdew, Physica B 172, 1 (1991). Generation and Use of Delocalized Internal Coordinates in Geometry optimization: Baker Kessi Delley: J. Chem. Phys., 105, 192 (1996); Andzelm Fitzgerald King-Smith: Chem. Phys. Lett., 335, 321 (2001).

Synthesis

1. Synthesis of monomer TBS-AZO-NHBOC-Br

The structure, relative name and synthesis route of TBS-AZO-NHBOC-Br monomer are shown in scheme S1. The synthesis procedure and ^{1}H NMR characterization of each step are provided below.



Scheme S1. Synthetic route towards monomer TBS-AZO-NHBOC-Br.

Synthesis of PhNHBOC

PhNHBOC was prepared followed a reported procedure. 4-aminophenol (32.7g, 300mmol), and 250 mL of dry THF were added to a 500 mL flask, di-tert-butyl dicarbonate (65.4 g, 300 mmol) dissolved in 100 mL of dry THF was added dropwise over 1 hour. The reaction mixture was stirred overnight at room temperature. The solvent was evaporated and the final crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 4/1) to yield as a white solid (59.8 g, 95.4%). ^{1}H NMR (300 MHz, CDCl3) δ 7.17 (d, J = 8.6 Hz, 2H), 6.78 – 6.70 (m, 2H), 6.34 (s, 1H), 5.30 (s, 1H), 1.51 (s, 9H).

Synthesis of TBS-NHBOC

PhNHBOC (52.2g, 250 mmol), TBS-3-bromoprop-1-yne (58.0g, 250 mmol), potassium carbonate (41.4g, 300 mmol), and 600 mL of acetone was added in a 1000 mL round bottom flask. The solution was stirred at 80 °C for 6 h. After cooling to room temperature, the mixture was filtered to remove the solid, and the filtrate was evaporated at reduced pressure. The final crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 8/1) to yield the TBS-NHBOC as a faint yellow liquid (80.4g, 89.1%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (t, *J* = 4.4 Hz, 2H), 6.88 – 6.71 (m, 2H), 6.27 (s, 1H), 4.55 (s, 2H), 1.41 (s, 9H), 0.81 (s, 9H), -0.00 (s, 5H).

Synthesis of TBS-NH_2

TBS-NHBOC (72.2g, 200mmol) was dissolved in 600 mL dry DCM, 300 mL CF_3COOH was added dropwise over 1 hour. The reaction mixture was stirred for 10 hours at room temperature. The DCM layer was extracted twice with 500 mL of 5% Na_2CO_3 water for three times and 500 mL saturated saline water for one time. Organic layer was dried over $MgSO_4$ and the solvent was evaporated at reduced pressure. The final crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 2/1) to yield the TBS-NH_2 as a yellow crystal (50.2g, 96.1%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79 – 6.73 (m, 2H), 6.70 – 6.63 (m, 2H), 4.52 (s, 2H), 4.14 (d, *J* = 77.0 Hz, 2H), 0.80 (d, *J* = 3.0 Hz, 9H), -0.01 (d, *J* = 3.3 Hz, 6H).

Synthesis of TBS-AZO-OH

The preparation of diazonium salt was as follows: To a 500mL beaker, TBS-NH_2 (49.6 g, 190 mmol) was dissolved in 65 mL methanol, then conc. hydrochloric acid (63.3 mL, 760 mmol), 65 mL of deionized water was added under stirring. The resulting mixture was stirred in an ice bath to keep the reaction temperature at 0-5 ºC. Aqueous solution which containing $NaNO_2$ (13.8 g, 200 mmol) and 65 mL deionized water was added dropwise into the mixture. The reaction temperature should be kept at 0-5 ºC during the addition of $NaNO_2$, after which the mixture was stirred for another 60 min, finally the excess $NaNO_2$ was quenched by addition of some urea. Coupling reaction was as follows: a solution of salicyl alcohol (23.5 g, 190 mmol), NaOH (22.8 g, 570 mmol), $NaHCO_3$ (91.2 g, 1086 mmol), 3000 mL deionized water and were prepared into a 4000 mL beaker. The mixture was stirred at 0-5ºC and the diazonium solution was added dropwise into the coupling solution. The final mixture was stirred for another 4 h and then filtered and washed with water for 3 times. The filter cake was dried at 60 ºC for 2 days. The final crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 4/1) to yield TBS-AZO-OH as yellow solid (48.9 g, 65.0%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.64 (m, 4H), 6.98 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 1H), 4.85 (s, 2H), 4.66 (s, 2H), 0.80 (s, 9H), -0.01 (d, *J* = 3.2 Hz, 6H).

Synthesis of TBS-AZO-Br

500 mL round bottom flask was charged with a mixed solution of 100 mL1, 2-dibromoethane and 100 mL acetonitrile and heated up to 60 ºC. TBS-AZO-OH (47.5g, 120mmol) was added in batches to the mixture. TLC was used to track and monitor the reaction process until the end of the reaction. The solvent was evaporated with adding ethanol at 40 ºC at reduced pressure. The final crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3/1) to yield TBS-AZO-OH as yellow solid (51.5g, 85.5%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.81 (m, 4H), 7.03 – 6.96 (m, 2H), 6.85 (d, *J* = 8.7 Hz, 1H), 4.69 (s, 2H), 4.67 (s, 2H), 4.39 – 4.28 (m, 2H), 3.67 – 3.57 (m, 2H), 0.85 – 0.75 (m, 9H), 0.02 – -0.02 (m, 6H).

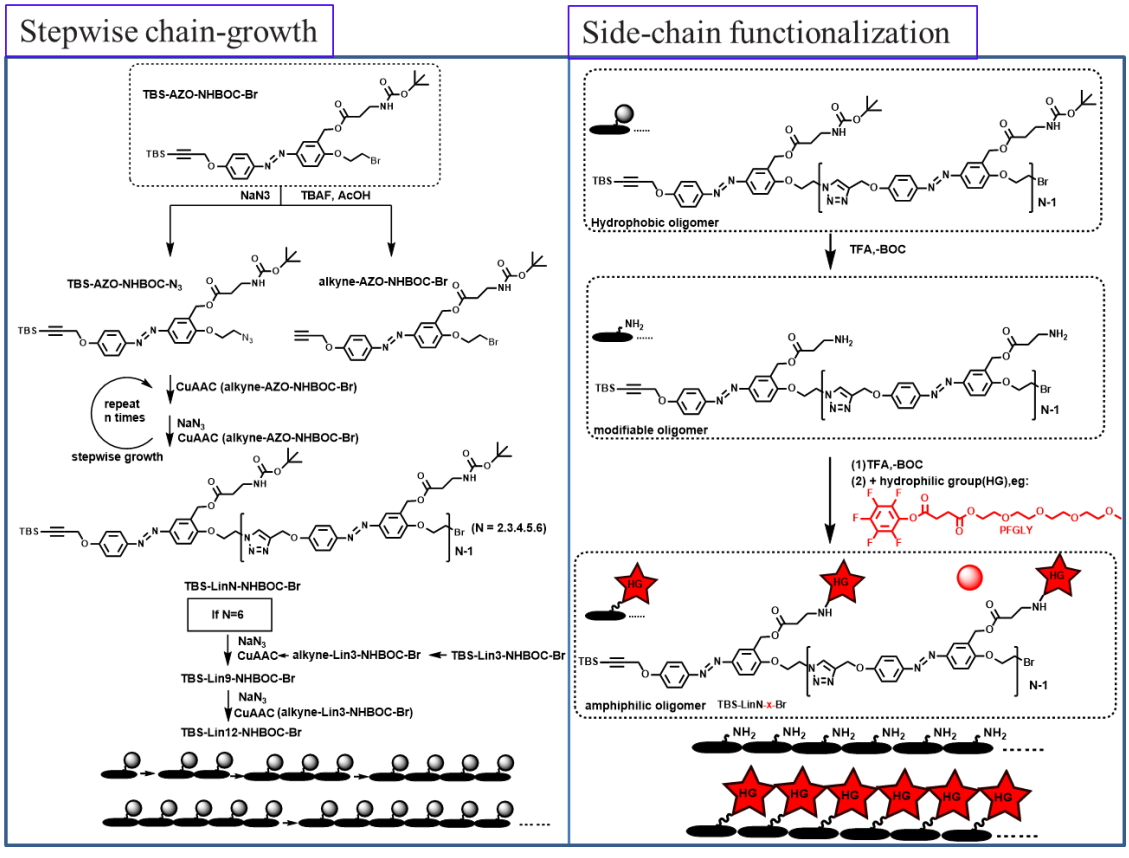
Synthesis of TBS-AZO-NHBOC-Br

TBS-AZO-OH (50.2g, 100mmol), Boc-beta-Ala-OH (18.9g, 100mmol), DMAP (1.22g, 10mmol), 500mL dried DCM was added in a 1000 mL round bottom flask. EDCI (38.2g,

200mmol) dissolved in 200 mL dried DCM was added dropwise over 1 hour. The reaction mixture was stirred overnight at room temperature. The DCM layer was extracted twice with 500 mL distilled water for three times and 500 mL saturated saline water for one time. Organic layer was dried over $MgSO_4$ and the solvent was evaporated at reduced pressure. The final crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 4/1) to yield the TBS-AZO-NHBOC-Br as a yellow crystal (65.5g, 97.3%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (dd, J = 9.6, 2.6 Hz, 4H), 6.99 (d, J = 9.0 Hz, 2H), 6.87 (d, J = 8.6 Hz, 1H), 5.18 (s, 2H), 5.03 (d, J = 32.5 Hz, 1H), 4.67 (s, 2H), 4.31 (t, J = 6.1 Hz, 2H), 3.67 – 3.51 (m, 2H), 3.33 (s, 2H), 2.52 (t, J = 6.0 Hz, 2H), 1.32 (s, 9H), 0.80 (s, 10H), 0.06 –0.03 (m, 6H).

2. Synthesis of hydrophobic oligomer precursors of TBS-LinN-NHBOC-Br (N = 1-6, 9, 12) *via* the stepwise chain-growth approach and amphiphilic oligomers TBS-LinN-x-Br (N = 3, 6, 9, 12) *via* side-chain functionalization

The structure, relative name and synthesis route are shown in scheme S2. The synthesis procedure of each step is provided as below. This part will be divided into two segments: Synthesis of oligomers TBS-LinN-NHBOC-Br via the stepwise chain-growth; (2) Synthesis of amphiphilic oligomers TBS-LinN-x-Br via side-chain functionalization.



Scheme S2. The synthetic routes towards oligomers TBS-LinN-NHBOC-Br (N = 3, 6, 9, 12) *via* the stepwise chain-growth approach and amphiphilic oligomers TBS- LinN-x-Br (N = 3, 6, 9, 12) *via* side-chain functionalization.

Synthesis of TBS-LinN-NHBOC-Br (N = 1-6, 9, 12) *via* the stepwise chain-growth

Synthesis of TBS-AZO-NHBOC-N_3

TBS-AZO-NHBOC-Br (6.73 g, 10mmol), NaN_3 (1.95 g, 30 mmol), and DMSO (50 mL) were added into a 250 mL round-bottom flask with a magnetic stirrer, and the reaction mixture was stirred for 10 h at 40 °C. After cooling to room temperature, 150 mL DCM was added and the DCM layer was extracted twice with 100 mL distilled water for three times and 100 mL saturated saline water for one time. The organic layer obtained was dried with anhydrous MgSO4 overnight, filtered, and evaporated at reduced pressure. The final product was collected and dried for 24 h in a vacuum oven (6.29g, 99.0%).

Synthesis of alkyne-AZO-NHBOC-Br

A solution of tetrabutyl ammonium fluoride (TBAF) in THF (120 mL, 120 mmol) was added to a solution of TBS-AZO-NHBOC-Br (40.38 g, 60 mmol), acetic acid(7.20 g, 120 mmol),1,2-dibromoethane(26.0 mL, 300mmol) in THF (500 mL) and stirred for 10 h at room temperature. The solvent was evaporated and the final crude product was purified by column chromatography. (silica gel, petroleum ether/ethyl acetate = 3/1) The final product was collected and dried for 24 h in a vacuum oven (33.0 g, 98.5%).

Synthesis of TBS- LinN-NHBOC-Br (N = 2-6)

The synthetic routes of TBS- LinN-NHBOC-Br (N = 2-6) via iterative CuAAC coupling reaction are shown in Scheme 2. AZO-NHBOC-Br was used as Chain extension agent in this section. Using TBS- LinN-NHBOC with N = 2 and N = 3 as typical samples, the detailed synthetic procedure is as follows.

Synthesis of TBS- Lin2-NHBOC-Br

A solution of TBS-AZO-NHBOC-N_3 (5.73 g, 9 mmol), AZO-NHBOC-Br (5.03g, 9mmol) in water-free and oxygen-free DCM (250 mL) was added to a 500 mL three-necked flask. The mixture was deoxygenated by bubbling with Ar2 for 0.5 h with stirring at room temperature. Then CuBr (1.29 g, 9 mmol) and PMDETA (2.09 mL, 9 mmol) were charged into the flask under protection of Ar_2. The reaction was allowed to proceed for another period of 1 h at room temperature. The DCM layer was extracted twice with 200 mL of deionized water three times and 200 mL of saturated saline water for one time. The DCM was evaporated at reduced pressure and then purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 1/2) to yield TBS- Lin2-NHBOC-Br as a yellow sticky liquid (10.54 g, 98.0%).

Synthesis of TBS-Lin2-NHBOC-N_3

TBS-Lin2-NHBOC-Br (10.16 g, 8.5mmol), NaN_3 (1.95 g, 25.5 mmol), and DMSO (75 mL) were added into a 250 mL round-bottom flask with a magnetic stirrer, and the reaction mixture was stirred for 10 h at 40 °C. After cooling to room temperature, 150 mL DCM was added and the DCM layer was extracted twice with 100 mL distilled water for three times and 100 mL saturated saline water for one time. The organic layer obtained was dried with anhydrous $MgSO_4$ overnight, filtered, and evaporated at reduced pressure. The final product was collected and dried for 24 h in a vacuum oven (9.65.00g, 98.0%).

Synthesis of TBS- Lin3-NHBOC-Br

A solution of *TBS- Lin2-NHBOC-N_3* (9.27 g, 8 mmol), AZO-NHBOC-Br (4.53g, 8.1mmol) in water-free and oxygen-free DCM (250 mL) was added to a 500 mL three-necked flask. The mixture was deoxygenated by bubbling with Ar_2 for 0.5 h with stirring at room temperature. Then CuBr (1.15 g, 8 mmol) and PMDETA (1.86 mL, 8 mmol) were charged into the flask under protection of Ar_2. The reaction was allowed to proceed for another period of 1 h at room temperature. The DCM layer was extracted twice with 200 mL of deionized water three times and 200 mL of saturated saline water for one time. The DCM was evaporated at reduced pressure and then purified by column chromatography (silica gel, petroleum ether/THF = 1/2) to yield TBS- Lin3-NHBOC-Br as a yellow solid (13.47 g, 98.1%).

Synthesis of TBS- Lin4, 5, 6-NHBOC-Br, TBS- Lin4, 5, 6-NHBOC-N_3 use the same procedure as above

Synthesis of TBS- LinN-NHBOC-Br (n = 9, 12)

Alkyne-Lin3-NHBOC-Br was used as chain extension agent in this section

Synthesis of* alkyne-*Lin3-NHBOC-Br

A solution of tetrabutyl ammonium fluoride (TBAF) in THF (4 mL, 4 mmol) was added to a solution of TBS- Lin3-NHBOC-Br (3.44g, 2mmol), acetic acid (0.24 g, 4 mmol), 1,2-dibromoethane (1.0 mL, 10mmol) in THF (50 mL) and stirred for 10 h at room temperature. The solvent was evaporated and the final crude product was purified by column chromatography. (silica gel, petroleum ether/THF = 2/1) The final product was collected and dried for 24 h in a vacuum oven (3.14g, 97.9%).

Synthesis of TBS-Lin9-NHBOC-Br

TBS-Lin6-NHBOC-N_3 (3.25g, 1mmol), alkyne-Lin3-NHBOC-Br (1.68, 1.05mmol), in water-free and oxygen-free DCM (100 mL) was added to a 100 mL three-necked flask. The mixture was deoxygenated by bubbling with Ar_2 for 0.5 h with stirring at room temperature. Then CuBr (0.29g, 2 mmol) and PMDETA (0.465 mL, 2 mmol) were charged into the flask under protection of Ar_2. The reaction was allowed to proceed for another period of 1 h at room temperature. The DCM layer was extracted twice with 100 mL of deionized water three times and 100 mL of saturated saline water for one time. The DCM was evaporated at reduced pressure and then purified by column chromatography (silica gel, DCM/methanol= 4/1) to yield TBS- Lin9-NHBOC-Br as a yellow solid (4.39 g, 90.5%).

Synthesis of TBS-Lin9-NHBOC-N_3 use the same procedure as synthesis of TBS-Lin2-NHBOC-N_3

Synthesis of TBS-Lin12-NHBOC-Br

TBS-Lin9-NHBOC-N_3 (2.4g, 0.5mmol), alkyne-Lin3-NHBOC-Br (0.82g, 0.51mmol), in water-free and oxygen-free DCM (100 mL) was added to a 100 mL three-necked flask. The mixture was deoxygenated by bubbling with Ar_2 for 0.5 h with stirring at room temperature. Then CuBr (0.29g, 2 mmol) and PMDETA (0.465 mL, 2 mmol) were

charged into the flask under protection of Ar_2. The reaction was allowed to proceed for another period of 1 h at room temperature. The DCM layer was extracted twice with 100 mL of deionized water three times and 100 mL of saturated saline water for one time. The DCM was evaporated at reduced pressure and then purified by column chromatography (silica gel, DCM/methanol= 4/1) to yield TBS-Lin12-NHBOC-Br as a yellow solid (2.87g, 89.5%).

Synthesis of amphiphilic oligomers TBS-LinN-x-Br (N = 3, 6, 9, 12) via side-chain functionalization

TBS-LinN-x-Br was obtained by two main steps. The BOC protecting groups were first removed by trifluoroacetic acid to get the reactive amino groups, then hydrophilic groups were modified in side chain by efficient reaction between pentafluorophenyl ester and amino group. The details were presented as follow.

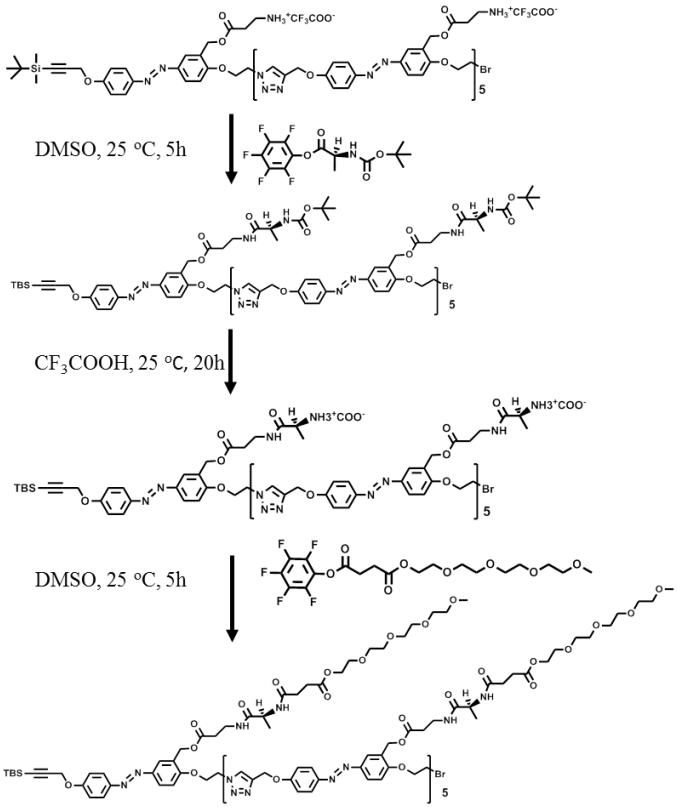
Synthesis of TBS-Lin6-NH_2-Br, TBS-LinN-$NH_3^+CF_3COO^-$-Br

Take the synthesis of TBS-Lin6-$NH_3^+CF_3COO^-$-Br as an example. TBS-Lin6-NHBOC-Br (300mg, 0.091mmol) was dissolved in 1mL of trifluoroacetic acid. After reaction at room temperature for 12 hours, part of trifluoroacetic acid solution was removed by rotary evaporation. The concentrated sample was precipitated in THF solution, and centrifuged to obtain solid powder. The crude product was washed several times with THF to obtain the final product. After drying in the vacuum oven at room temperature, 270 mg product was obtained with a conversion rate of 89.0%. TBS-Lin6-NH_2-Br can be obtained by which the TBS-LinN-$NH_3^+CF_3COO^-$-Br *w*as precipitated in saturated $NaHCO_3$ instead of THF solution, and the subsequent steps were the same as TBS-Lin6-$NH_3^+CF_3COO^-$-Br.

The synthesis of TBS-LinN-x-Br

Take the synthesis of TBS-Lin6-GLY-Br as an example. TBS-Lin6-$NH_3^+CF_3COO^-$-Br 100mg (0.03mmol) was dissolved in 1mL mixture solvent of DMF/DMSO (1:1), then 400 microliters of perfluorophenyl (2,5,8,11-tetraoxatridecan-13-yl) succinate (PFGLY) solution was added. The reaction was stirred gently at room temperature. Track the reaction process with thin layer chromatography (TLC) until finished. The reaction time is about 2 hours. Separation and purification were performed by passing the concentrated crude product through pre-TLC or silica gel (DCM/THF gradient leaching from 4:1 to 1:1). The collected product solution was removed by rotary evaporator and dried under vacuum oven to obtain 115 mg viscoelastic yellow solid with a yield of 86.9%.

The other amphiphilic oligomers, for example the chiral ammonium salts (TBS-Lin6-L-$NH_3^+CF_3COO^-$-Br), and chiral ethylene-glycol hydrophilic side chains (TBS-Lin6-L-GLY-Br) were obtained with the same procedure. The relative synthesis routes are shown in scheme S3.



Scheme S3. Synthetic route towards oligomers TBS-Lin6-L-$NH_3^+CF_3COO^-$-Br and TBS-Lin6-L-GLY-Br with chiral hydrophilic groups.

Self-assembly of the amphiphilic oligomers.

In a typical procedure, the amphiphilic oligomers were first completely dissolved in THF, with an initial concentration of 0.5 mg/mL or 0.1mg/mL. The oligomer solution was then filtered through a PTFE filter with 0.22 μm pore size to remove any dusts to obtain the stock solution. Milli-Q water was then slowly added (0.3 mL/h) to 1.0 mL of the stock solution under gentle shaking at 25°C until the water content reached a predetermined value. After finished, the samples were sealed and stored at 25 °C. The same protocol was followed for all the experiments unless otherwise stated. For the self-assembly of TBS-Lin6-$NH_3^+Cl^-$-Br, because it is insoluble in pure THF, first the TBS-Lin6-NH_2-Br was dissolved in THF, then the water was exchanged with 1mol/L HCl aqueous solution after dropping ultrapure water with 66.7% content.

Additional Results

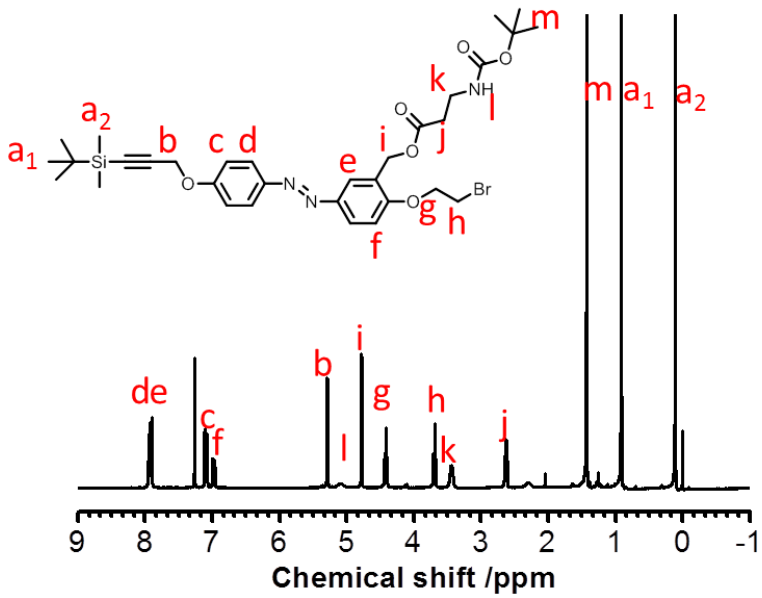


Figure S1. ^{1}H NMR spectrum of TBS-AZO-NHBOC-Br in $CDCl_3$.

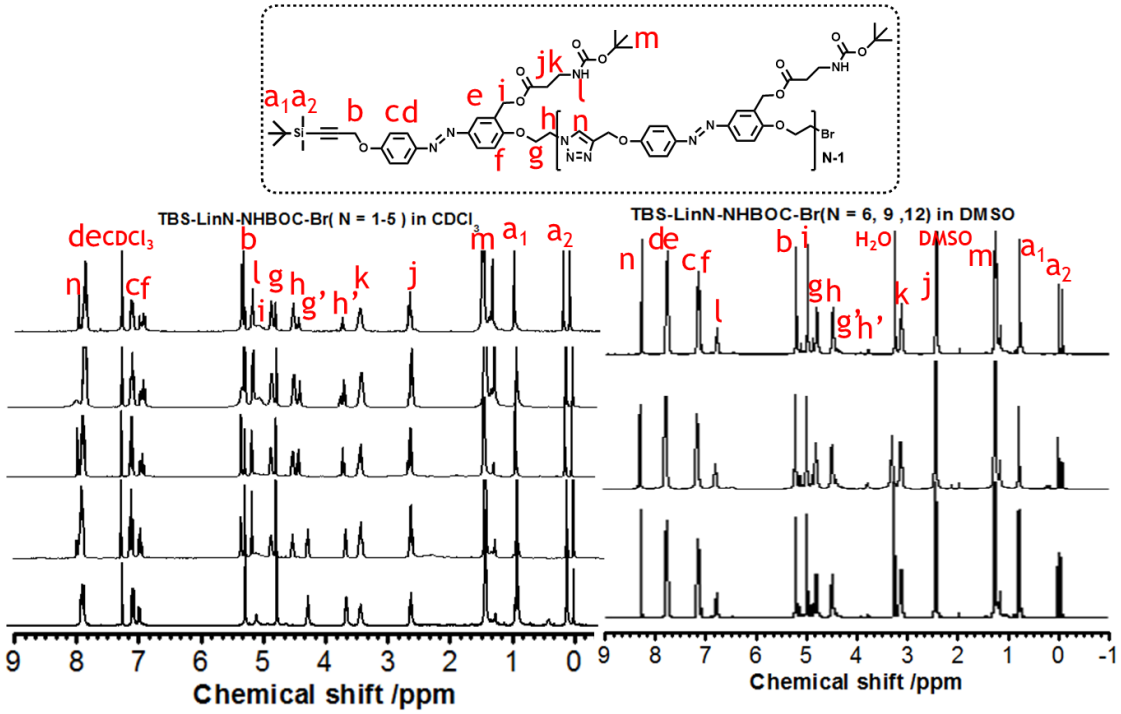


Figure S2. ^{1}H NMR spectra of TBS-LinN-NHBOC-Br in $CDCl_3$ (N = 1-5) and in DMSO (N =6, 9, 12). The chemical shifts and integrals of the typical H atoms of products of each generation (N = 1-6, 9, 12) on the ^{1}H NMR spectra were consistent with the prediction.

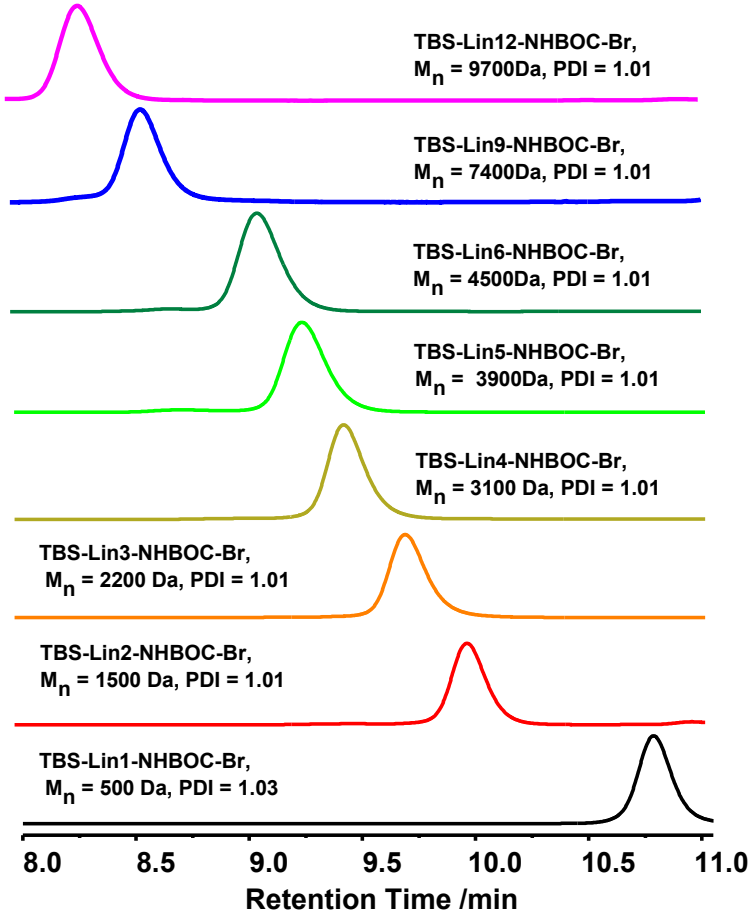


Figure S3. GPC trace of TBS- LinN-NHBOC-Br using THF as the eluent (N = 1–6, 9, 12). From GPC curve, we noticed that all oligomeric products exhibited narrow peaks with polydispersity index (PDI)～1.01.

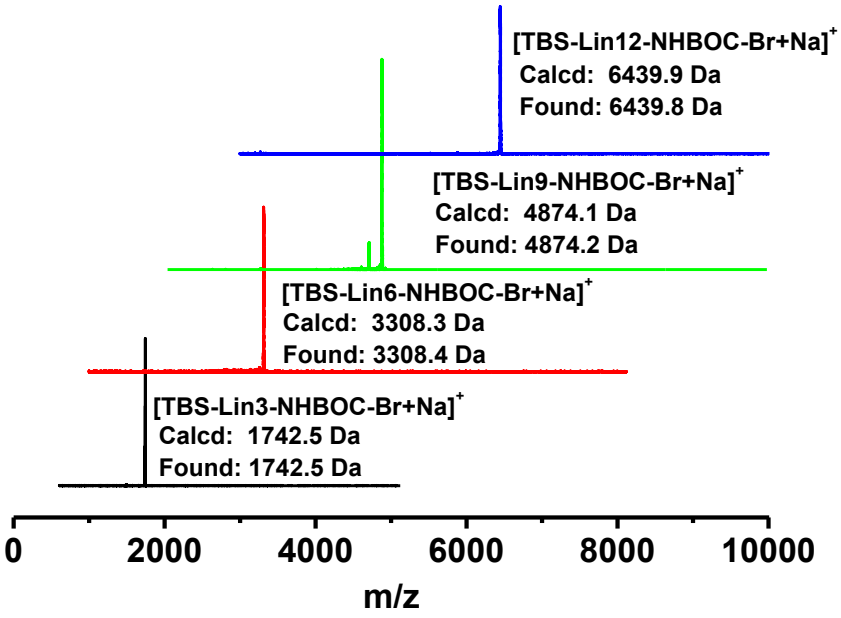


Figure S4. MALDI-TOF mass spectra of TBS- LinN-NHBOC-Br (N = 3, 6, 9, 12). All the measured molecular weight matched well with the calculated values.

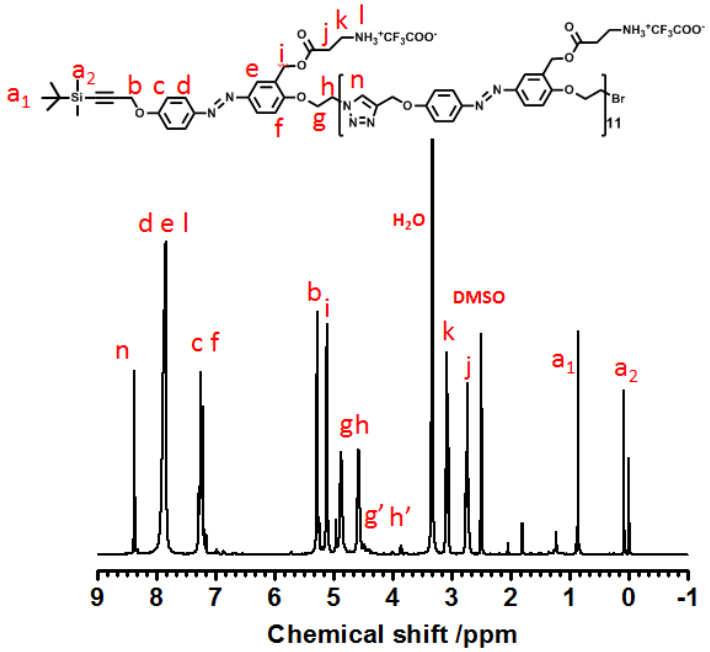


Figure S5. ^{1}H NMR spectrum of TBS-Lin12-$NH_3^+CF_3COO^-$-Br in deuterated DMSO.

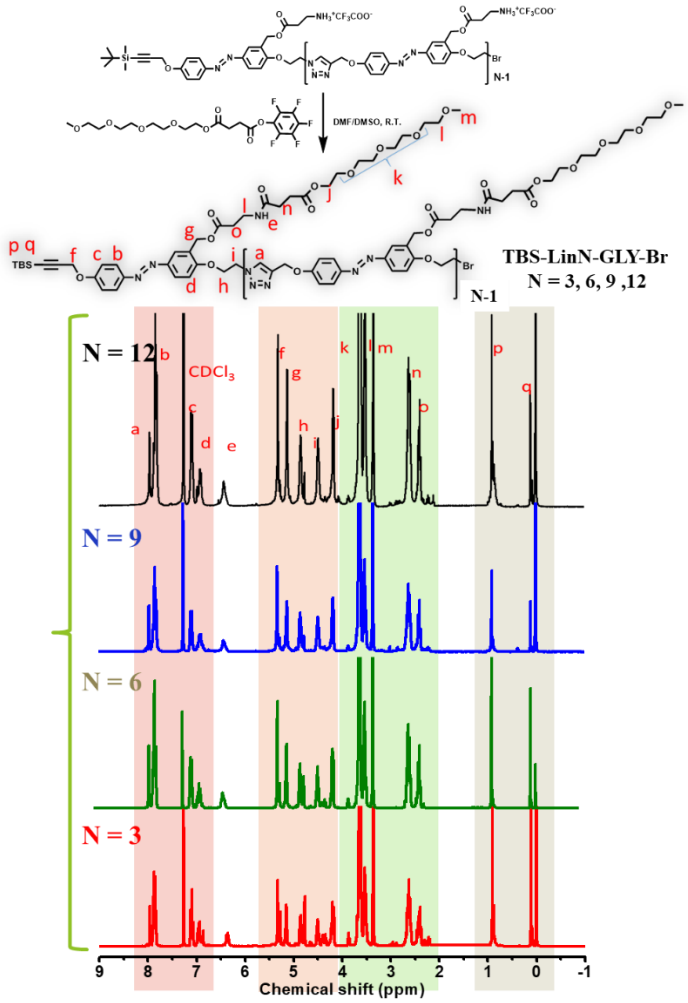


Figure S6. Synthetic routes and ^{1}H NMR spectra of TBS-linN-GLY-Br in $CDCl_3$ (N=3, 6, 9, 12).

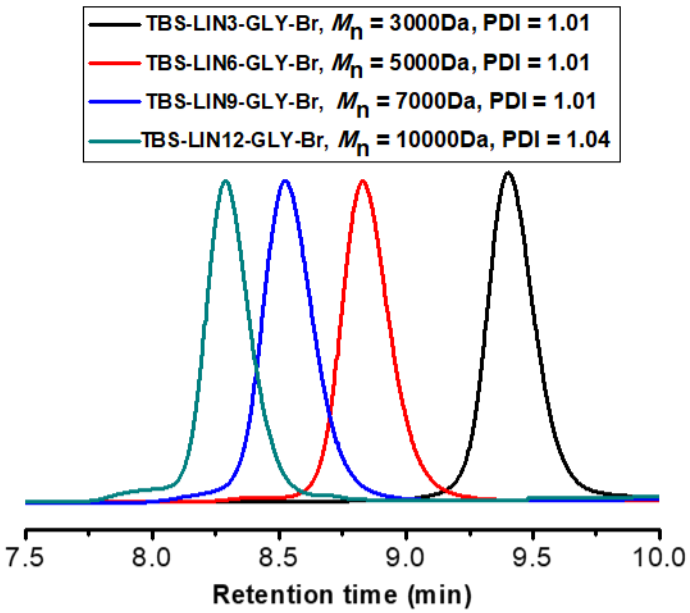


Figure S7. GPC trace of TBS-LinN-GLY-Br (N = 3, 6, 9, 12) using THF as the eluent.

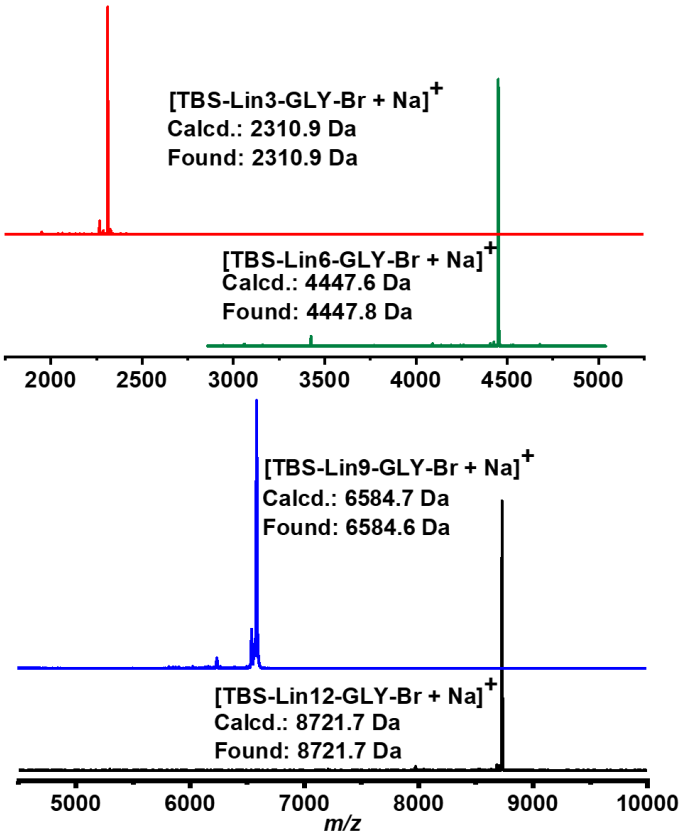


Figure S8. MALDI-TOF mass spectra of TBS-LinN-GLY-Br (N = 3, 6, 9, 12).

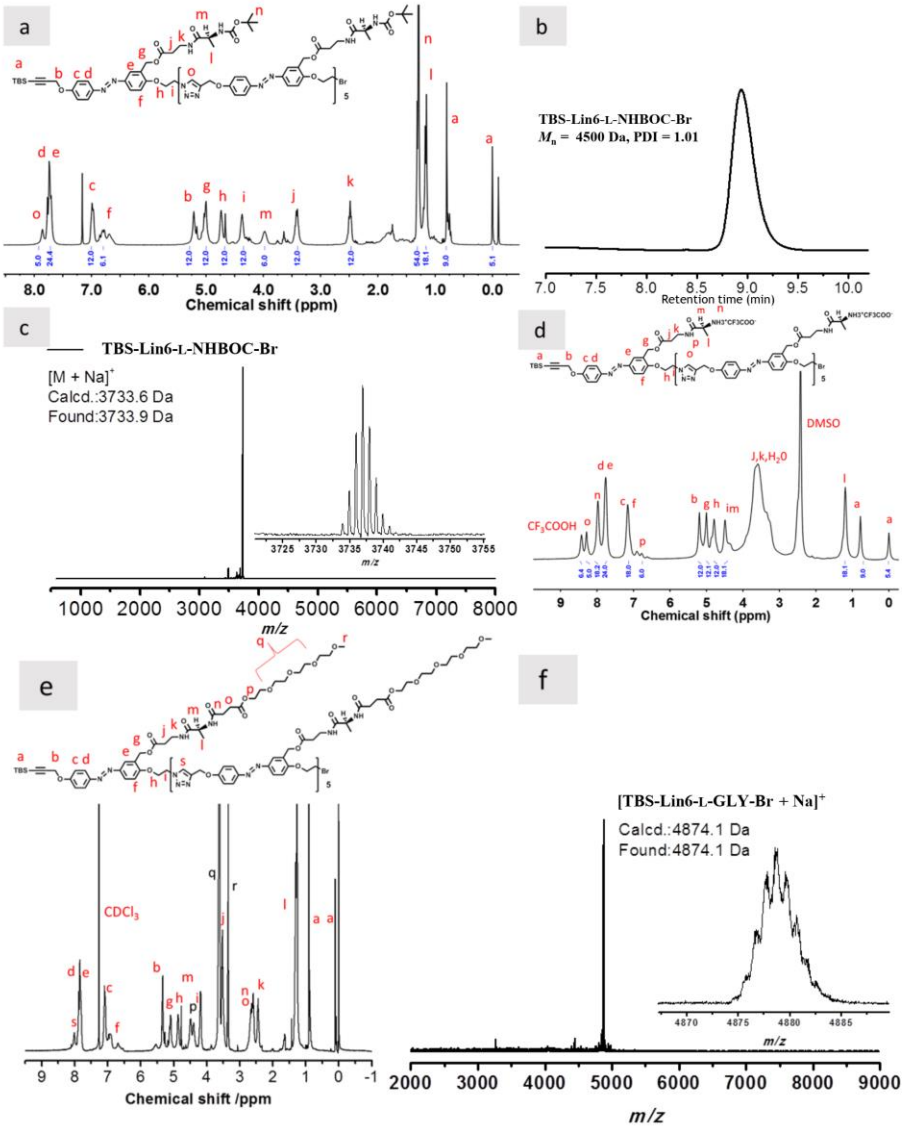


Figure S9. ^{1}H NMR spectra, GPC trace and MALDI-TOF mass spectra of oligomers TBS-Lin6-L-NHBOC-Br (a, b, c), TBS-Lin6-L-$NH_3^+CF_3COO^-$ (d), TBS-Lin6-L-GLY-Br (e, f).

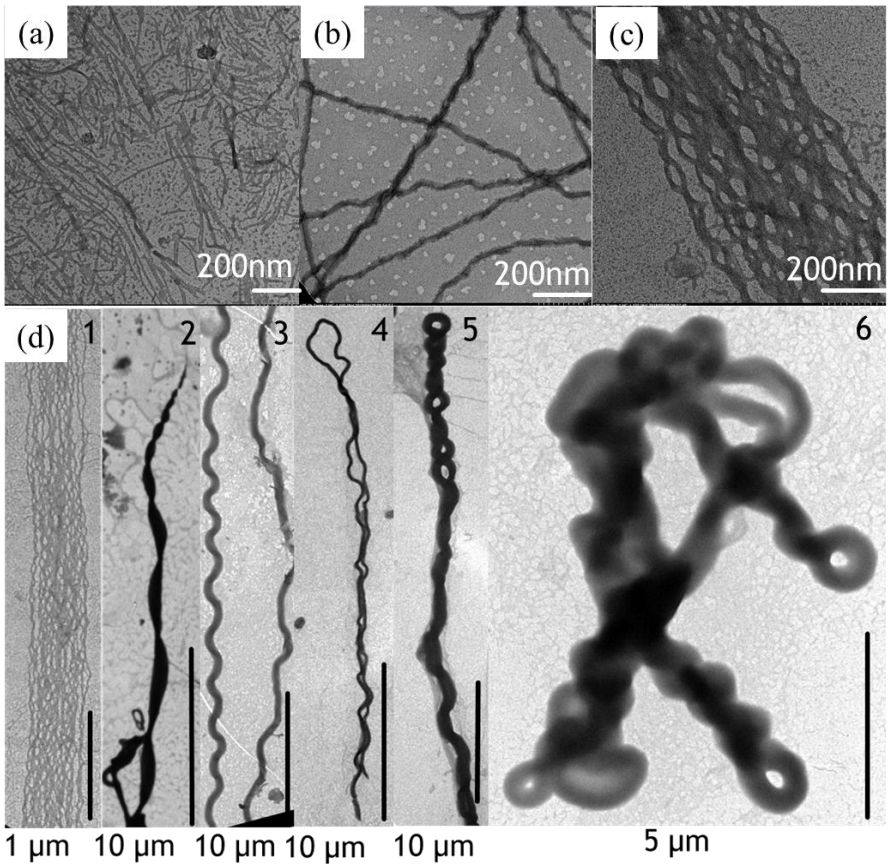


Figure S10. TEM images (stained with phosphotungstic acid) of shape evolution during self-assembly of TBS-Lin6-GLY-Br with different aging time after adding water, (a) 1h, (b) 4 days, (c) and (d1)10 days, (d2-d6) 15days. C_0=0.50mg/mL, THF/water = 1/3.

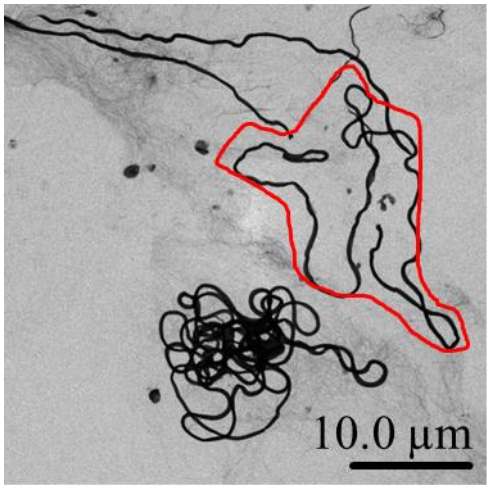


Figure S11. TEM images (stained with phosphotungstic acid) of long fibers of TBS-Lin6-GLY-Br after 15 days aging treatment.

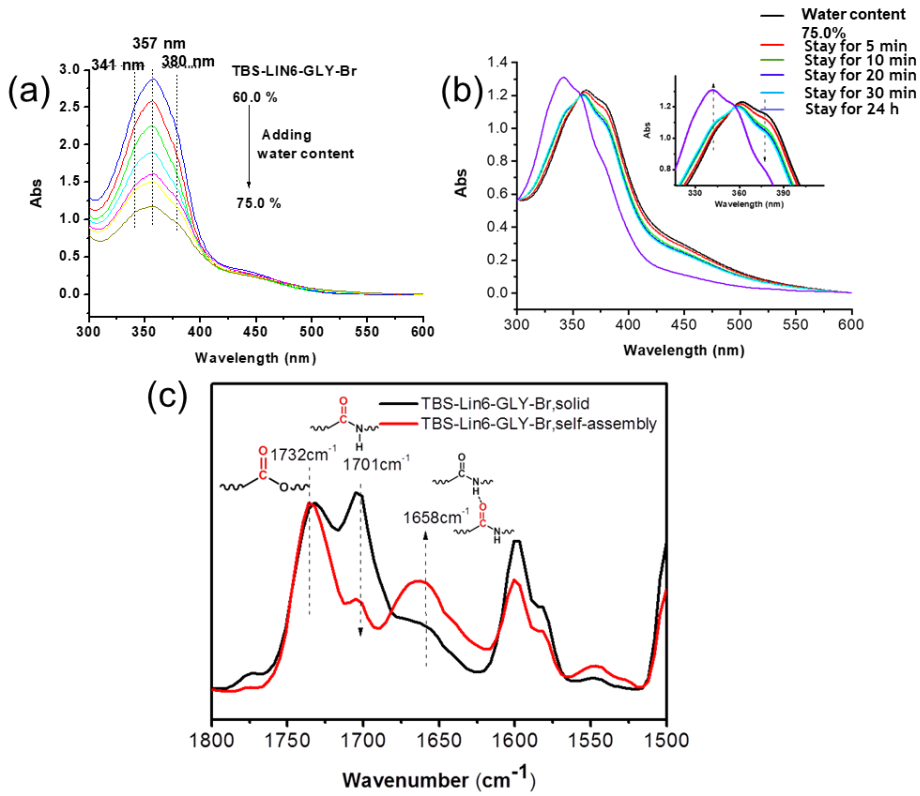


Figure S12. UV−vis absorption spectra of TBS-Lin6-GLY-Br in THF/water solution, C_0 = 0.5mg/mL in THF, (a) during the water adding content from 60.0% to 75.0%. (b) aging for different times after adding water at 75.0% water content. (c) IR spectra of TBS-Lin6-GLY-Br in solid state and freeze-dried sample from self-assembled aggregates.

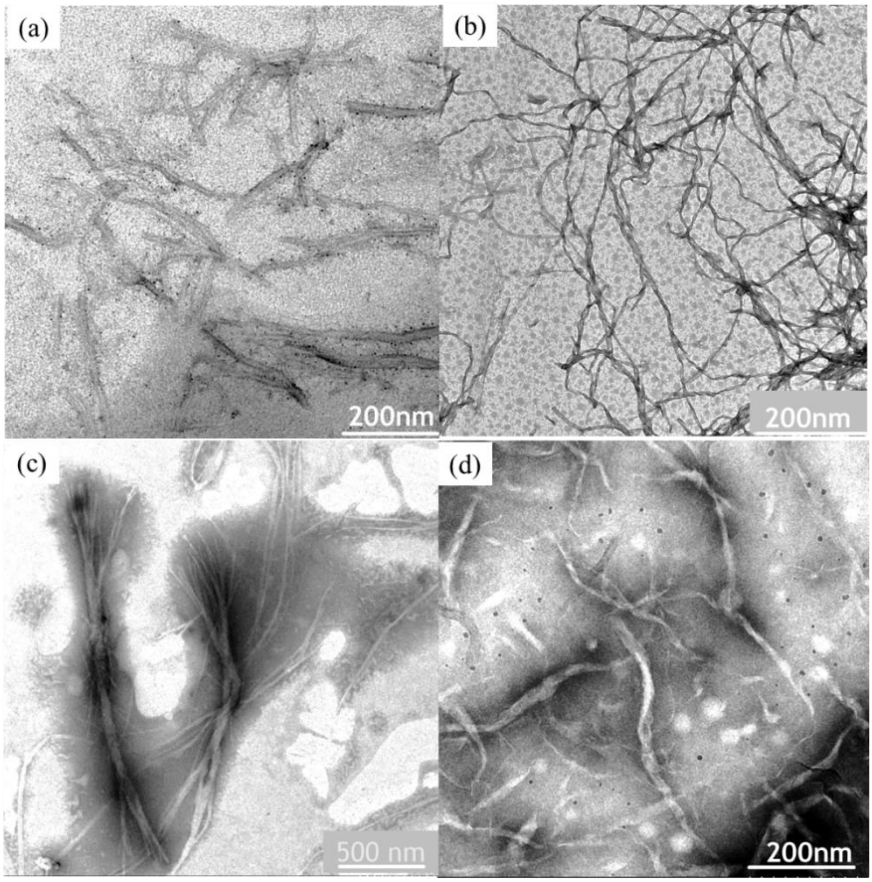


Figure S13. TEM images (stained with phosphotungstic acid) of self-assembled morphologies of TBS-LinN-GLY-Br (N = 3, 6, 9, 12). (a) TBS-Lin3-GLY-Br, (b) TBS-Lin6-GLY-Br, (c) TBS-Lin9-GLY-Br, (d) TBS-Lin12-GLY-Br. C_0 = 0.50mg/mL, THF/water = 1/3.

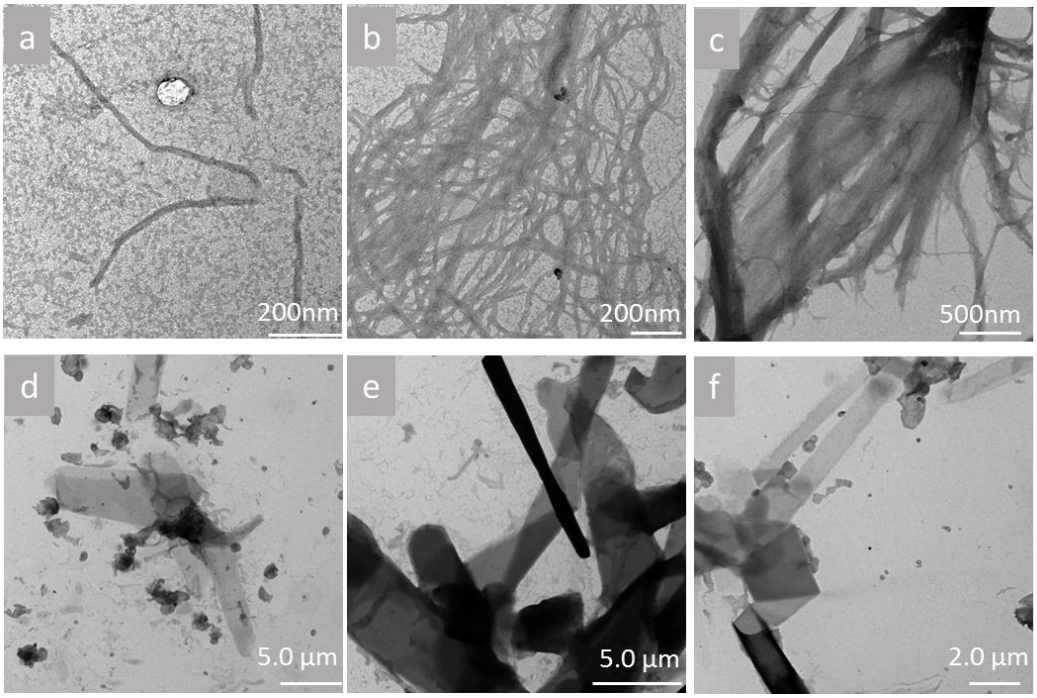


Figure S14. TEM images (stained with phosphotungstic acid) of self-assembled morphologies. C_0=0.1 mg/mL, THF/water = 1/3, (a) TBS-Lin3-GLY-Br, (b) TBS-Lin6-GLY-Br, (c) TBS-Lin9-GLY-Br, (d) TBS-Lin12-GLY-Br, a-d: staying for 1day. (e) c sample staying for 10 days. (f) d sample staying for 10 days.

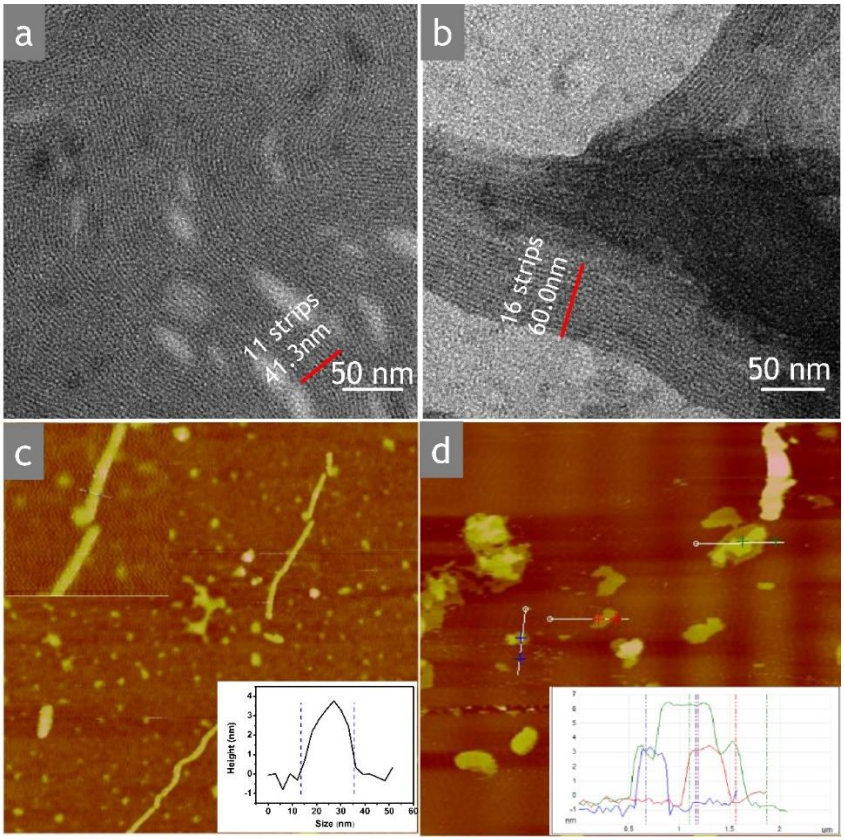


Figure S15. TEM images (stained with phosphotungstic acid) of self-assembled thin fibers with a width of 3.75 nm (a, b). (a) TBS-Lin6-GLY-Br, (b) TBS-Lin9-GLY-Br,

C_0=0.1 mg/mL, THF/water =1/2. AFM images of self-assembled morphologies (c, d). (c) TBS-Lin6-GLY-Br, (d) TBS-Lin9-GLY-Br, C_0 = 0.1 mg/mL, THF/water = 1/3. The TBS-Lin6-GLY-Br fibers and TBS-Lin9-GLY-Br lamellar structures were both 3.75 nm height, which was basically consistent with that of theoretical calculation (4. 2nm) in Figure S16, indicating that the self-assembly of TBS-Lin6-GLY-Br and TBS-Lin9-GLY-Br should be a self-supporting film of a single molecular layer.

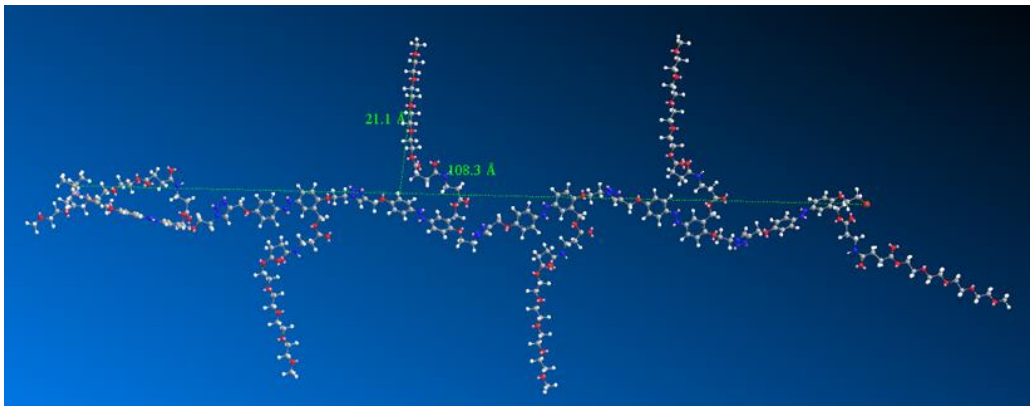
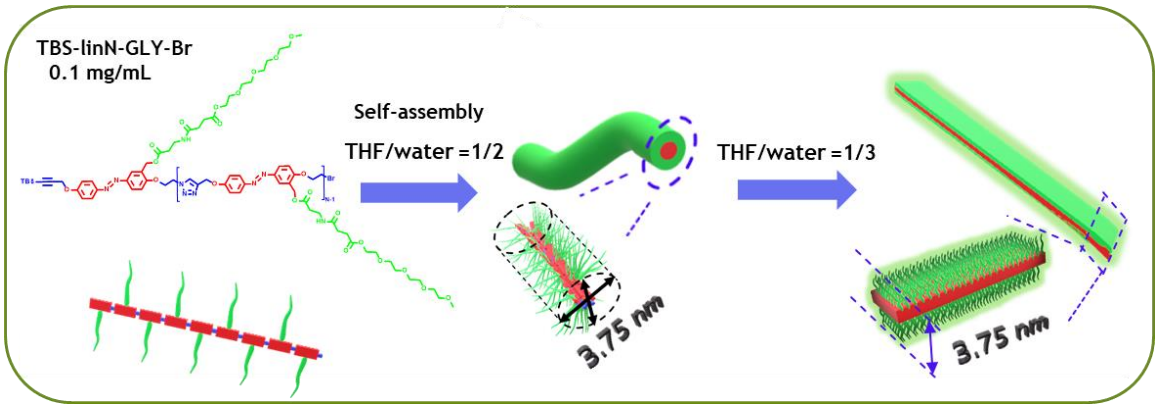


Figure S16. The simulative molecular configuration of TBS-Lin6-GLY-Br calculated with Materials Studio software (MS). The width is 4. 2nm, which is about 2 times of the length of the side chain (21.1Å × 2), and the length is 10.8 nm (108.3 Å).



Scheme S4. Schematic diagram of morphological evolution from thin fibers to lamellar structures during self-assembly of TBS-LinN-GLY-Br (N=6, 9) in THF/water with the initial concentration C_0 = 0.1 mg/mL with the increase of adding water content from THF/water = 1/2 to THF/water = 1/3.

For the fibers, the main-chains of the oligomers were organized in a side-to-side manner along the long axis of the fiber with the main chain of oligomer as the core and the hydrophilic side chain as the shell. When the water content is relatively low at THF/water = 1/2, the degree of aggregation is relatively weak, only a few oligomer molecules was assembled to form the fibers of which the size is about 3.75 nm. With the increase of water content to THF/water = 1/3, the interfacial energy increased, and hence these fibers were accumulated, forming nanoribbons or nanoribbons with the

azobenzene main chain as the core layer and hydrophilic side chain as the corona layer with the thickness of 3.75 nm.

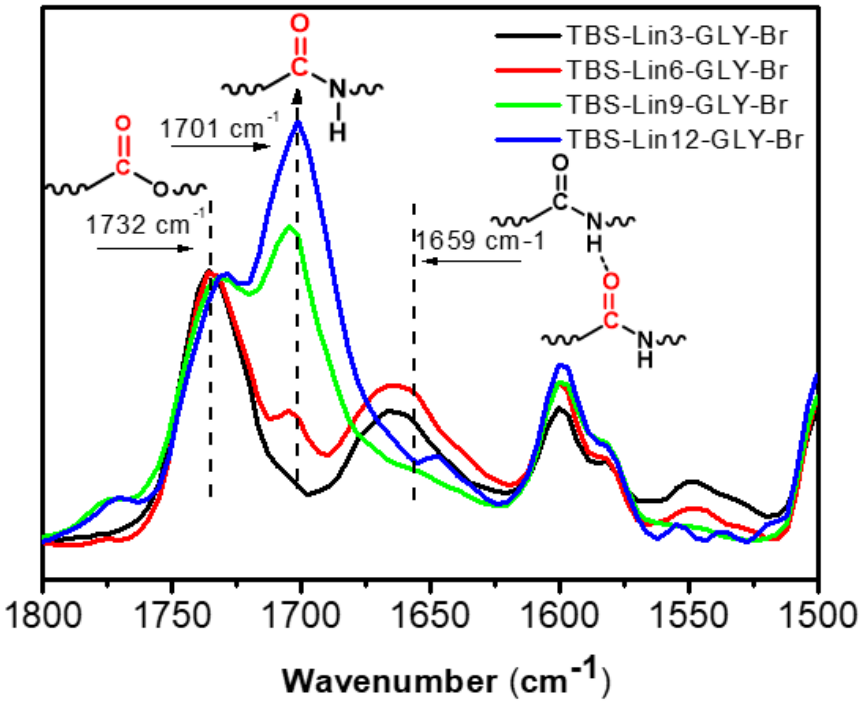


Figure S17. IR spectra of TBS-LinN-GLY-Br (N = 3, 6, 9, 12) freeze-dried sample from self-assembled aggregates. The characteristic peaks at 1701cm^{-1} assigned to the carbonyl stretching bands of non-associated amide increased，while the characteristic peaks at 1659 cm^{-1} assigned to the carbonyl stretching bands of the hydrogen-bonded amide relatively decreased as the molecular weight of oligomers increase, indicating hydrogen bond become weaker as the molecular weight of oligomers increase.

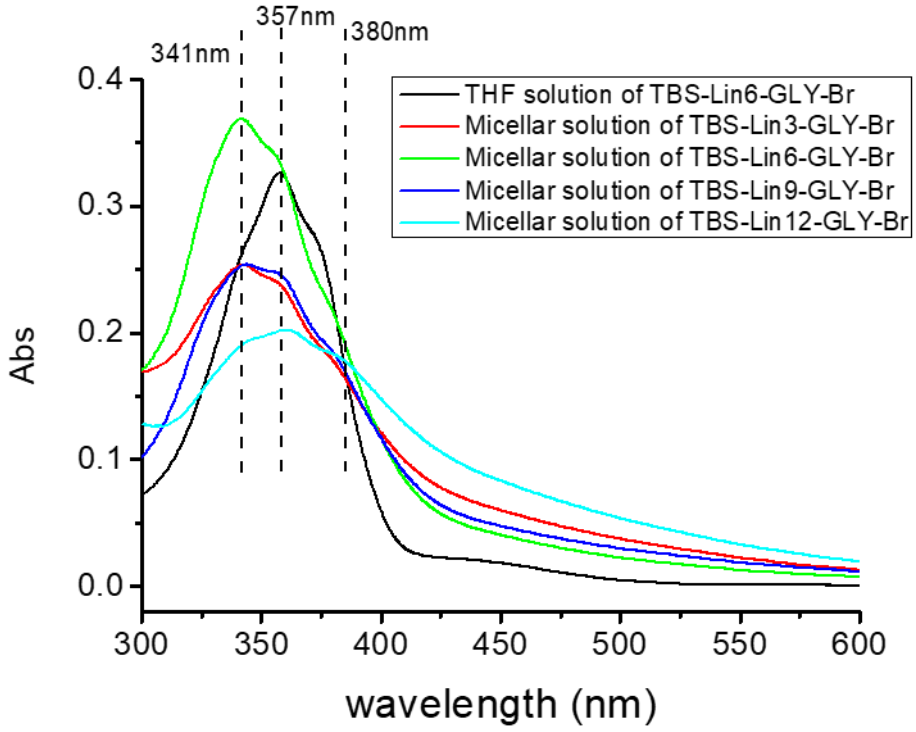


Figure S18. UV−vis absorption spectra of TBS-LinN-GLY-Br (N = 3, 6, 9, 12) micellar solution after dialysis in water (the concentration is 0.033 mg/mL for all) and TBS-Lin6-GLY-Br in THF as contrast (3×10^{-3} mg/mL).

The TBS-Lin6-GLY-Br in aggregates showed an obvious blue shift compared with that in solution state, implying the self-assembly resulted in H-aggregates of oligomers. TBS-Lin3-GLY-Br, TBS-Lin9-GLY-Br also showed distinct H-aggregate but weaker than TBS-Lin6-GLY-Br. The TBS-Lin12-GLY-Br aggregates showed broad absorption around 362nm, including smaller blue-shift of H-aggregation and larger red-shift of J-aggregation. As mention in the main text, face to face arrangement mode of H-aggregates could render azobenzene moieties arrange at higher order in some direction. So, compared with aggregates of the other oligomers, there existed more distorted arrangement of azobenzene moieties in the TBS-Lin12-GLY-Br aggregates. For TBS-Lin3-GLY-Br, H-aggregates enables it to form regular one-dimensional short fibers, but difficult to aggregate tightly into long fibers due to much weaker intermolecular interaction resulted from the smallest molecular weight. For TBS-Lin6-GLY-Br, intermolecular interaction and widely existed H-aggregates led to them form wide range of uniform long fibers. For TBS-Lin9-GLY-Br, of which intermolecular interaction remains increased with the increase of molecule weight, it formed 2D nanosheets and intertwined huge fiber. For TBS-Lin12-GLY-Br, of which longer molecular chain become distorted and tangled, it was difficult to arrange in order, so the irregular 1D aggregates formed during the self-assembly especially at a high initial concentration in THF.

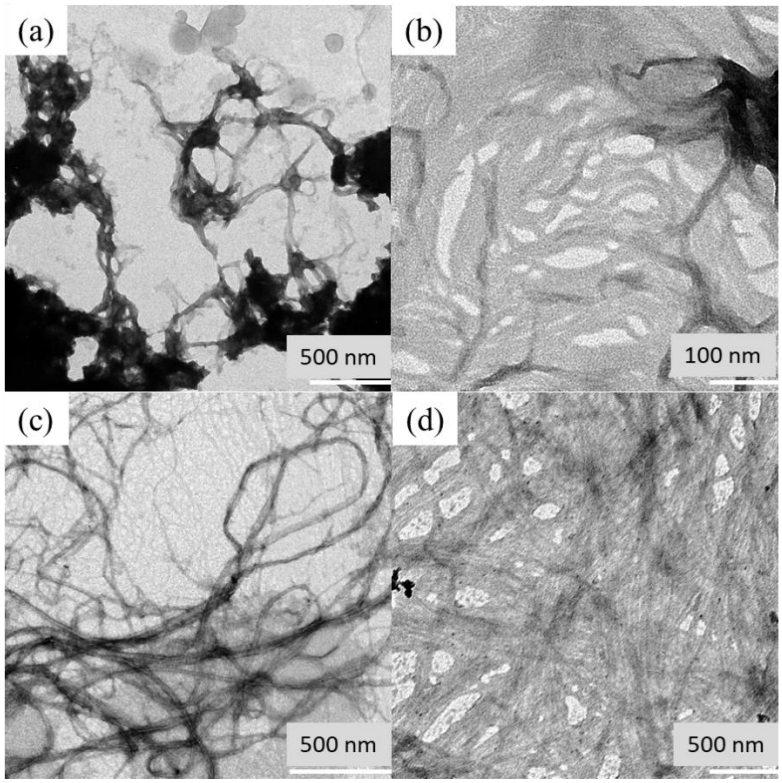


Figure S19. TEM images (stained with phosphotungstic acid) of self-assembled aggregates of TBS-Lin6-x-Br with different hydrophilic side chains: (a, b) TBS-Lin6-NH_2-Br, (c, d) TBS-Lin6-$NH_3^+Cl^-$. C_0 = 0.5 mg/mL, THF/water = 1/3.

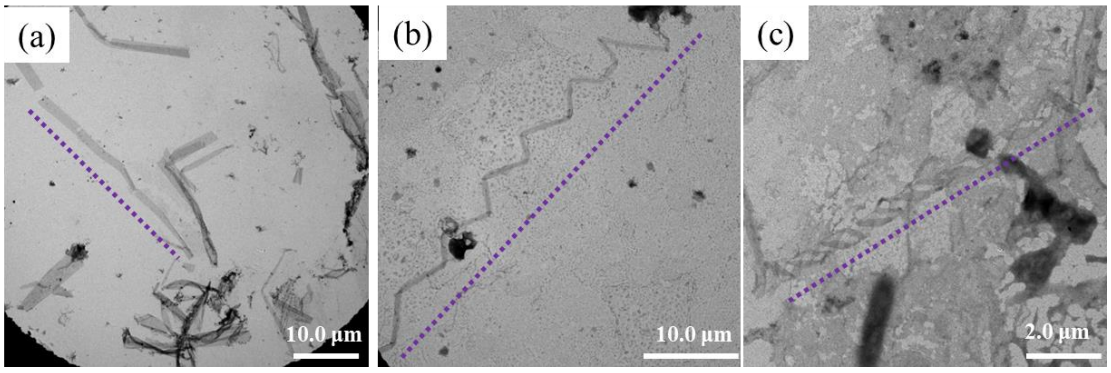


Figure S20. TEM images (stained with phosphotungstic acid) of self-assembled morphologies of TBS-Lin6-L-GLY-Br after being placed at room temperature for different days (a) four days, (b) eight days, (c)12 days. C_0 = 0.5mg/mL, THF/water = 1/3. The purple imaginary line represents the part amplified in Figure 4e.

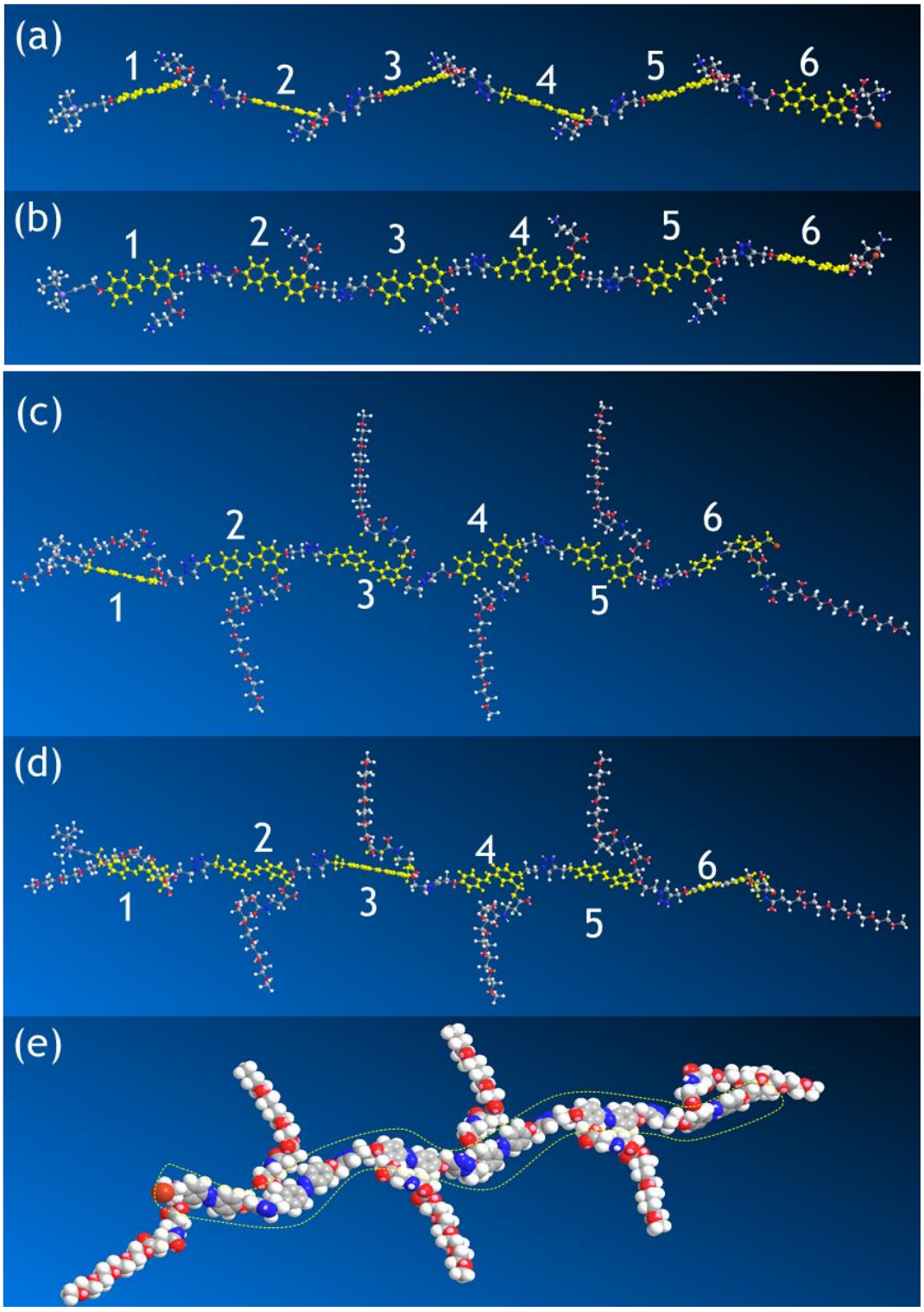


Figure S21. Front view and vertical view conformation of (a, b) TBS-Lin6-NH_2-Br, (c, d) TBS-Lin6-GLY-Br using ball-and-stick model; (e) Conformation of TBS-Lin6-GLY-Br using space filling model calculated with Materials Studio software (MS). In (a), the azobenzenes from No.1 to No.5 are all perpendicular to the plane of the paper, in (b) the azobenzenes from No.1 to No.5 are all parallel to the plane of paper. That is to say, the normal lines of azobenzenes from No.1 to No.5 are coplanar, so the TBS-Lin6-NH_2-Br take 'wave' conformation. For (c), except No.1, all the other azobenzenes are not

perpendicular to the plane of paper; from (d), azobenzenes 3, 6 are perpendicular to the plane of paper, while the others are not. So, the normal lines of these azobenzenes are not coplanar, and hence TBS-Lin6-GLY-Br takes twist or helix conformation. From (e) we can see clearly the twist or helix conformation of the main chain.

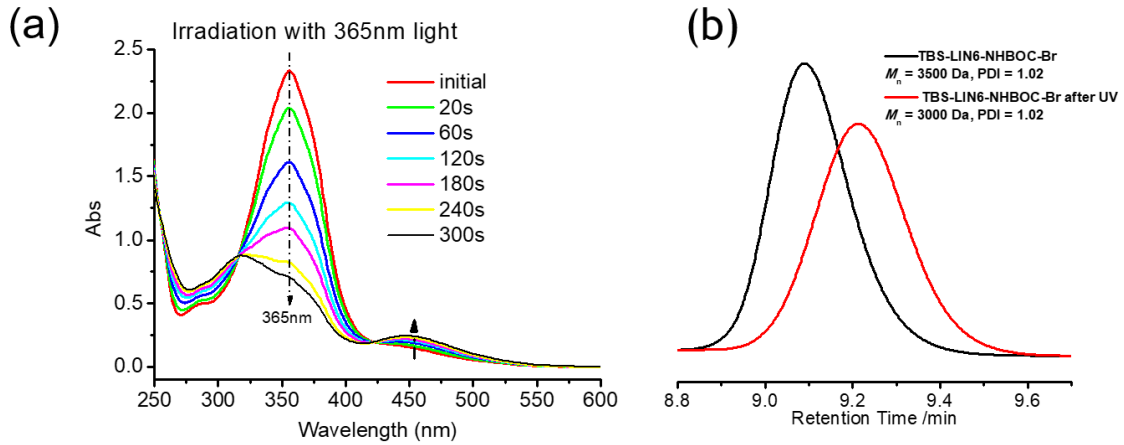


Figure S22. (a) UV-vis absorption changes of TBS-Lin6-NHBOC-Br in THF under 365 nm UV light irradiation (0.5 mW/cm^2) at different time interval at room temperature. The concentration of solution is 0.03 mg/mL. (b) GPC curves of TBS-Lin6-NHBOC-Br before light irradiation (black), and after light irradiation with 365 nm (0.5 mW/cm^2) at room temperature for 300 s (red), using DMF as eluent.

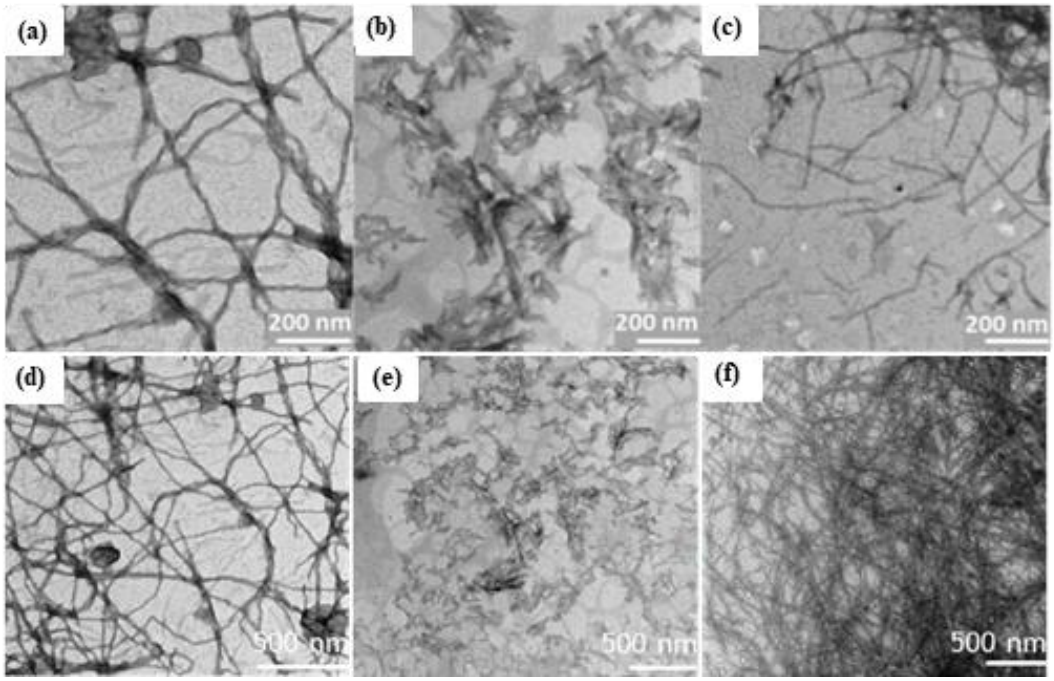


Figure S23. TEM images of TBS-Lin6-GLY-Br self-assemblies (a, d) in THF/water (V = 1/3), (b, e) morphologic change after 365 nm light irradiation and (c, f) morphologic recovery by 435 nm visible light irradiation, standing still for 1day, C_0 = 0.5 mg/mL.

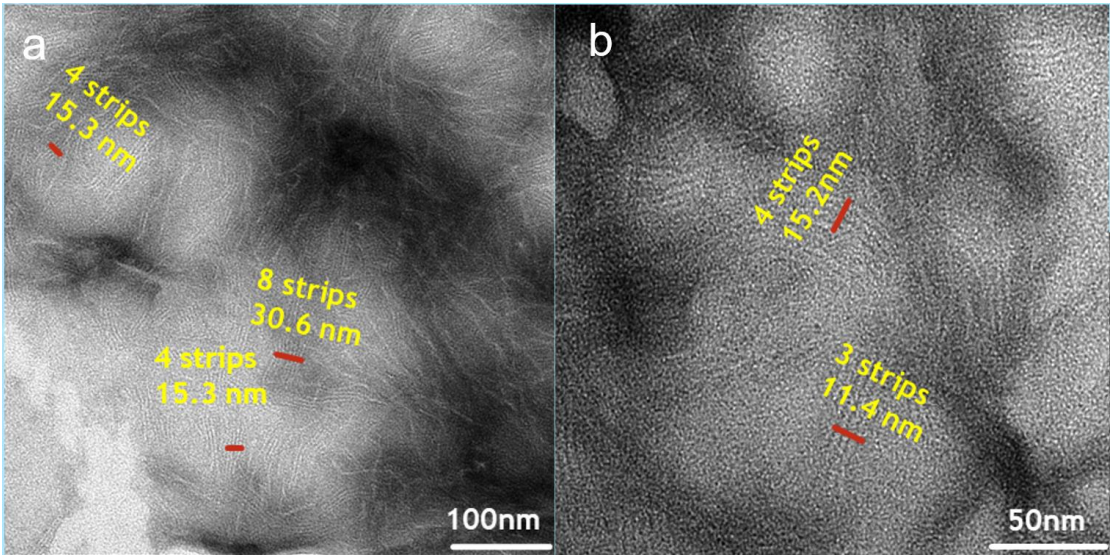


Figure S24. TEM images (stained with phosphotungstic acid) of gradual regenerating TBS-Lin6-GLY-Br nanofibers after visible light irradiation for 5 min at different scale. The diameter of the fiber is about 3.8nm.