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Supporting Information

Sequence effect on self-assembly of discrete amphiphilic copolyoligomers with fluorene-azobenzene semirigid backbones

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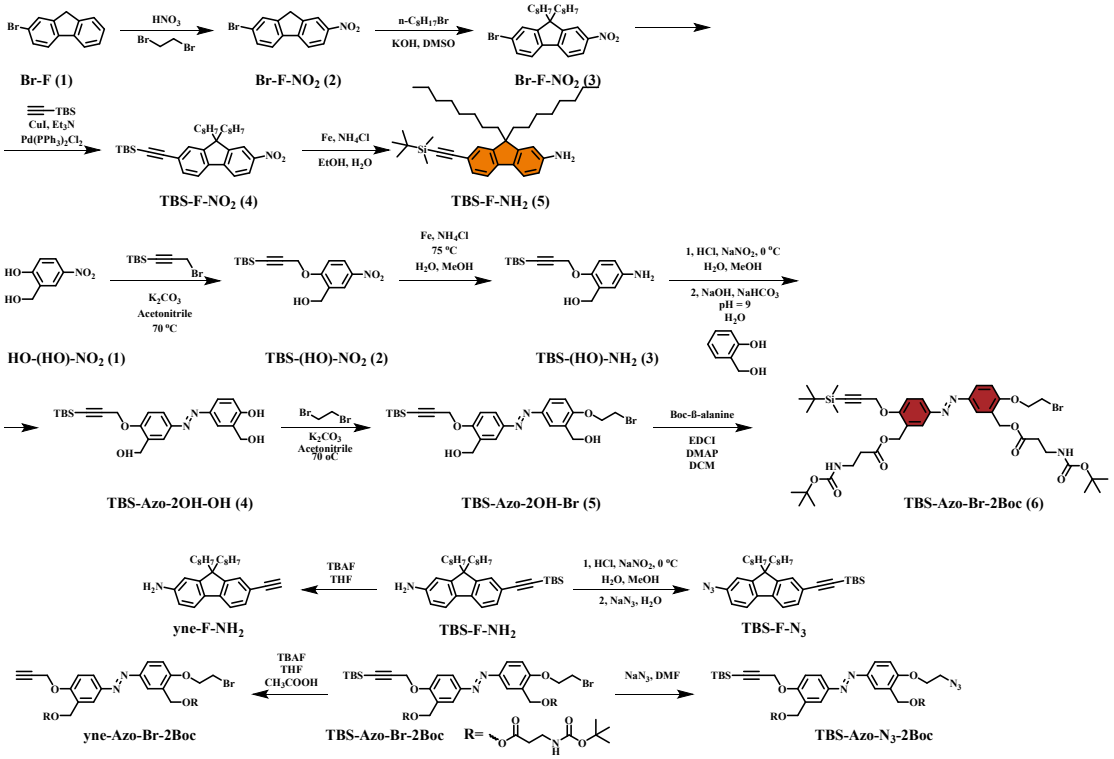
Experimental Procedures

Synthesis

Synthesis of the fluorene monomer TBS-F-NH_2 and azobenzene monomer TBS-Azo-Br-2Boc.



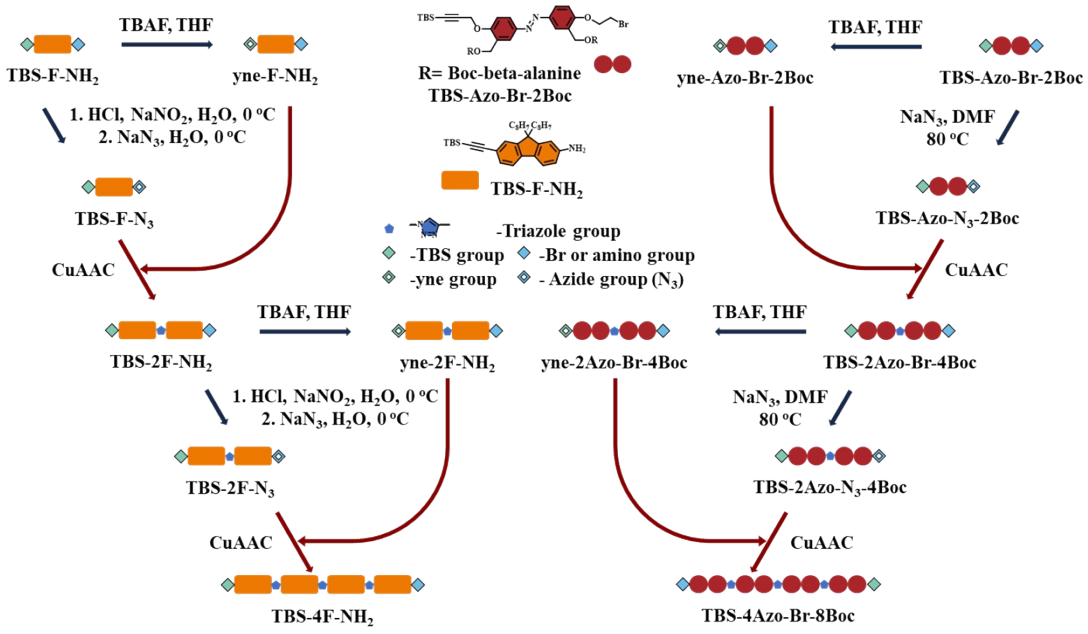
Scheme S1. The synthetic routes of fluorene monomer TBS-F-N_3 and azobenzene monomer TBS-Azo-Br-2Boc.

The synthetic routes of the both monomers of fluorene TBS-F-NH_2 and azobenzene TBS-Azo-Br-2Boc were shown in **Scheme S**1, and synthetic process was conducted according to a previous literature.[S1, S2] TBS-F-N_3 was obtained as a brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (TMS, ppm): 7.60-7.10 (m, 4H, ArH), 6.91-6.66 (m, 2H, ArH), 1.8-1.61 (m, 4H, -C-CH_2-CH_2-), 1.09-0.73 (m, 29H, -CH2-, -Si-$(CH_3)_3$), 0.68-0.54 (m, 6H, -CH_3), 0.34 (d, 4H, -CH_2-), 0.07-0.05 (m, 6H, -Si-CH_3). ^{1}H NMR spectrum and LCMS of TBS-F-N_3 are presented in Figure S1.

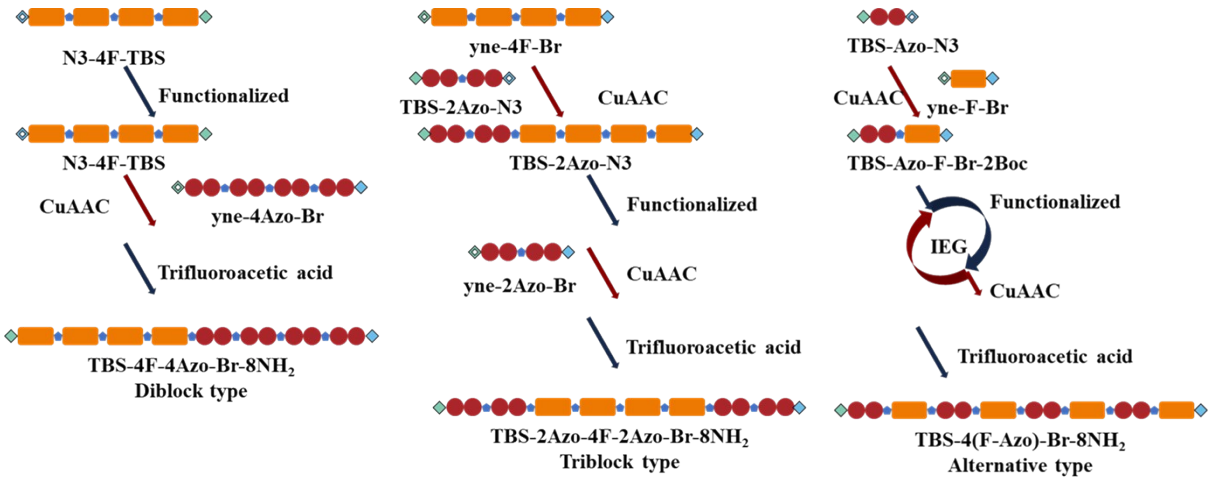
TBS-Azo-Br-2Boc was producted to yield as a yellow solid.^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.90-7.70 (m, 4H, ArH), 7.07 (d, 1H, ArH), 6.87 (d, 1H, ArH), 5.17 (d, 4H, -CH_2-OH), 5.06 (s, 2H, -C-CH_2-O), 4.73 (s, 2H, -CH_2), 4.30 (t, 2H, -CH_2), 3.33 (q, 4H, -CH_2-NH), 2.52 (td, 4H, -COO-CH_2-), 1.32 (s, 18H, -CH_3), 0.79 (s, 9H, -Si-$(CH_3)_3$), 0.08 (s, 6H, -

Si-CH_3). ^{1}H NMR spectrum is presented in Figure S2.

Synthesis of fluorene blocks (TBS-2F-NH_2, TBS-4F-NH_2) and azobenzene blocks (TBS-2Azo-Br-4Boc, TBS-4Azo-Br-8Boc)

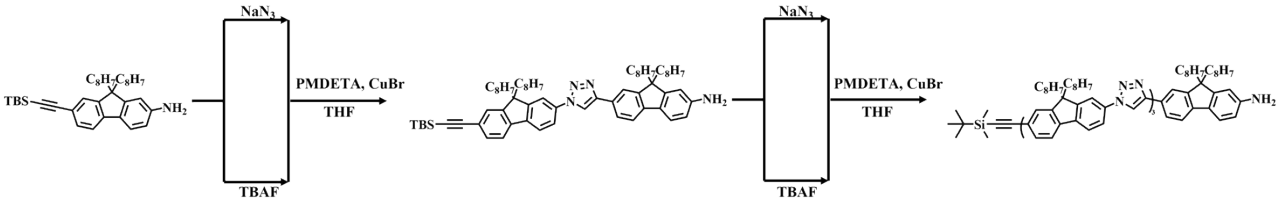


Scheme S2. Schematic diagram of the synthetic routes of fluorene blocks, TBS-2F-NH_2 and TBS-4F-NH_2, and azobenzene blocks, TBS-2Azo-Br-4Boc and TBS-4Azo-Br-8Boc.



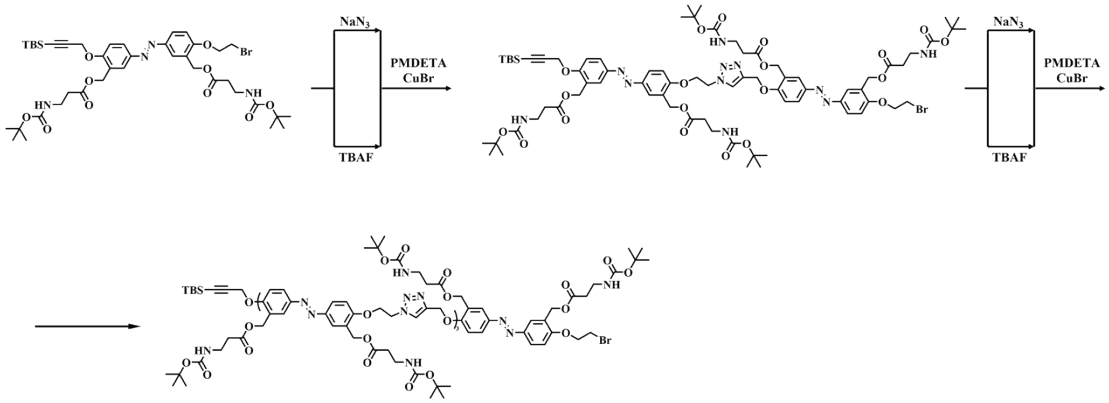
Scheme 3. Schematic diagram of synthetic routes of three sequence isomeric oligomers of 4F-4Azo-8NH_2, 2Azo-4F-2Azo-8NH_2 and 4(F-Azo)-8NH_2

Synthesis of TBS-2F-NH_2 and TBS-4F-NH_2



Scheme S4. The synthetic routes of fluorene blocks TBS-2F-NH_2 and TBS-4F-NH_2

Synthesis of azobenzene blocks TBS-2Azo-Br-4Boc and TBS-4Azo-Br-8Boc



Scheme S5. Synthetic route of TBS-2Azo-Br-4Boc and TBS-4Azo-Br-8Boc.

Synthesis of TBS-2Azo-Br-4Boc and TBS-4Azo-Br-8Boc

^{1}H NMR spectra, MALDI-TOF spectra of TBS-2Azo-Br-4Boc and TBS-4Azo-Br-8Boc are presented in Figures S3(a) and (b), and GPC elution curves of TBS-Azo-Br-2Boc, TBS-2Azo-Br-4Boc and TBS-4Azo-Br-8Boc are presented in Figures S3(c), and IR spectra of TBS-Azo-Br-4Boc, TBS-2Azo-Br-4Boc and TBS-4Azo-Br-4Boc before and after azidation are presented in Figures S3(d).

Additional Results

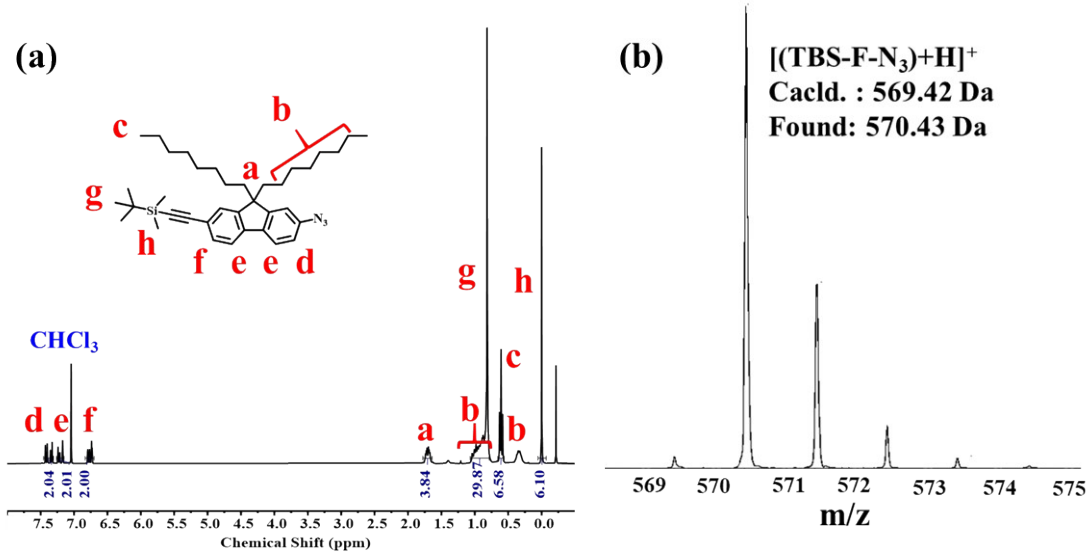


Figure S1. (a) ^{1}H NMR spectrum of TBS-F-N_3 in $CDCl_3$, (b) LCMS of TBS-F-N_3.

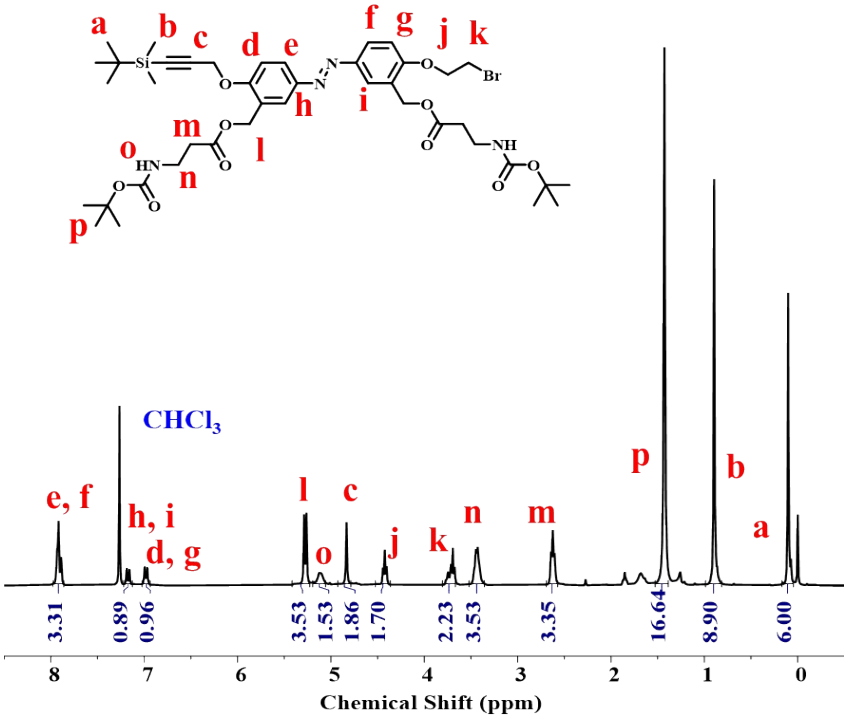


Figure S2. ^{1}H NMR spectrum of TBS-Azo-Br-2Boc in $CDCl_3$.

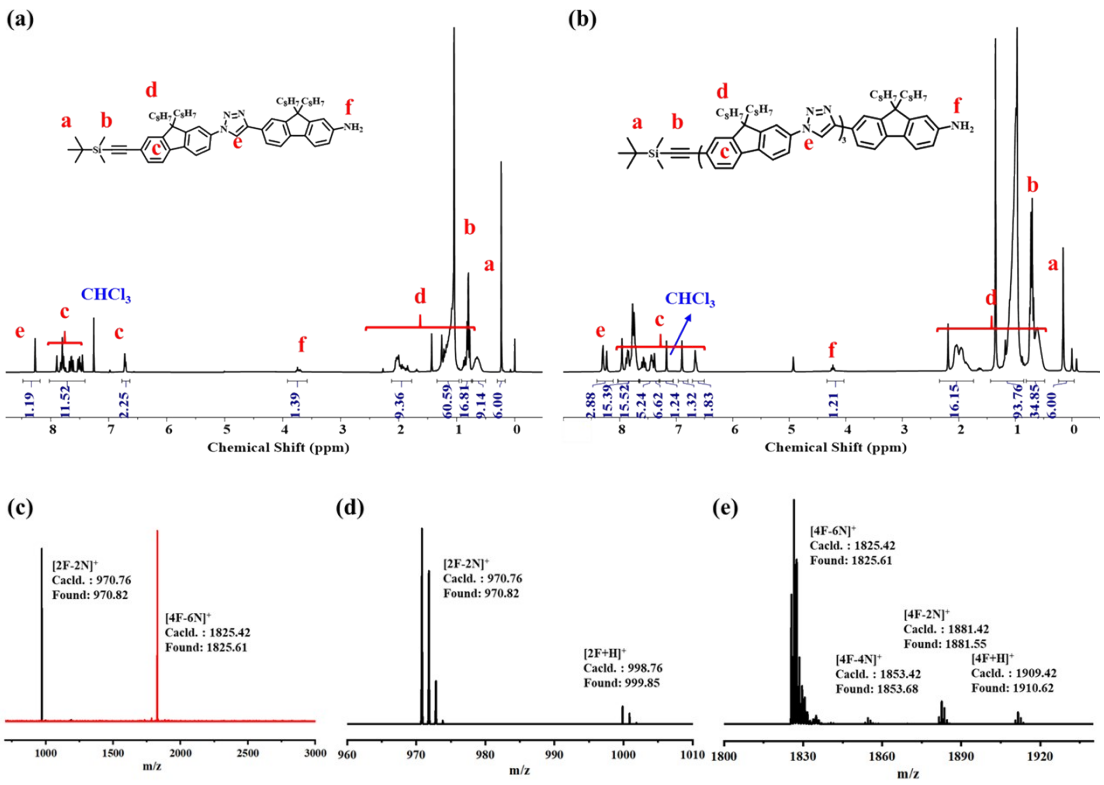


Figure S3. (a) ^{1}H NMR spectra of TBS-2F-NH_2 and TBS-4F-NH_2; (b) MALDI-TOF spectra of TBS-2F-NH_2 and TBS-4F-NH_2; (c) and (d) locally enlarged MALDI-TOF spectra of TBS-2F-NH_2 and TBS-4F-NH_2

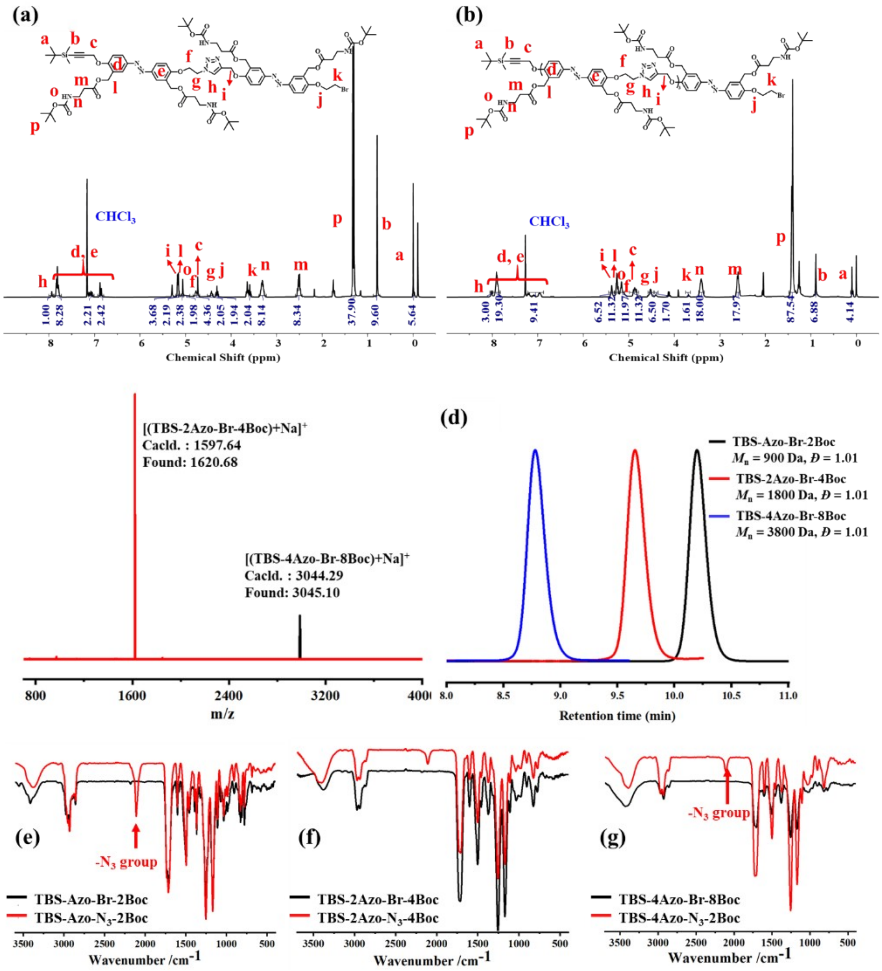


Figure S4. (a) ^{1}H NMR spectra of TBS-2Azo-Br-4Boc and TBS-4Azo-Br-8Boc in $CDCl_3$; (b) MALDI-TOF spectra of TBS-2Azo-Br-4Boc and TBS-4Azo-Br-8Boc; (c) GPC elution curves of TBS-Azo-Br-2Boc, TBS-2Azo-Br-4Boc and TBS-4Azo-Br-8Boc.(d) IR spectra of TBS-Azo-Br-2Boc, TBS-2Azo-Br-4Boc, TBS-4Azo-Br-8Boc before and after azidation.

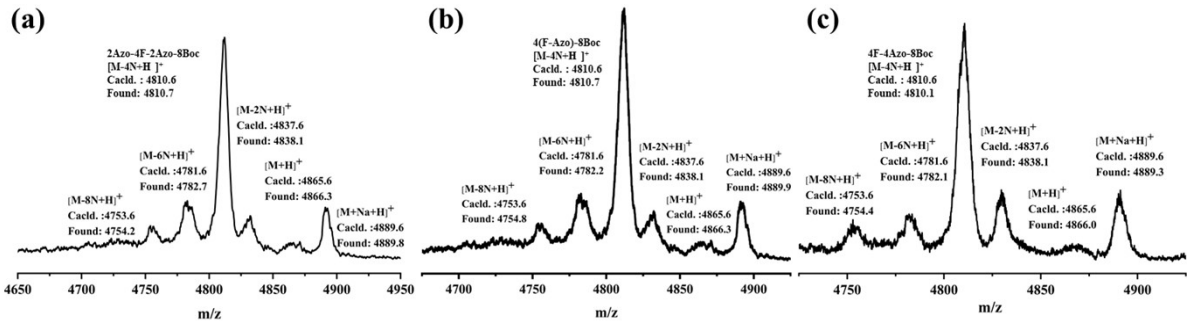


Figure S5. Partially enlarged MALDI-TOF spectra of (a) 2Azo-4F-2Azo-8Boc, (b) 4(F-Azo)-8Boc, (c) 4F-4Azo-8Boc.

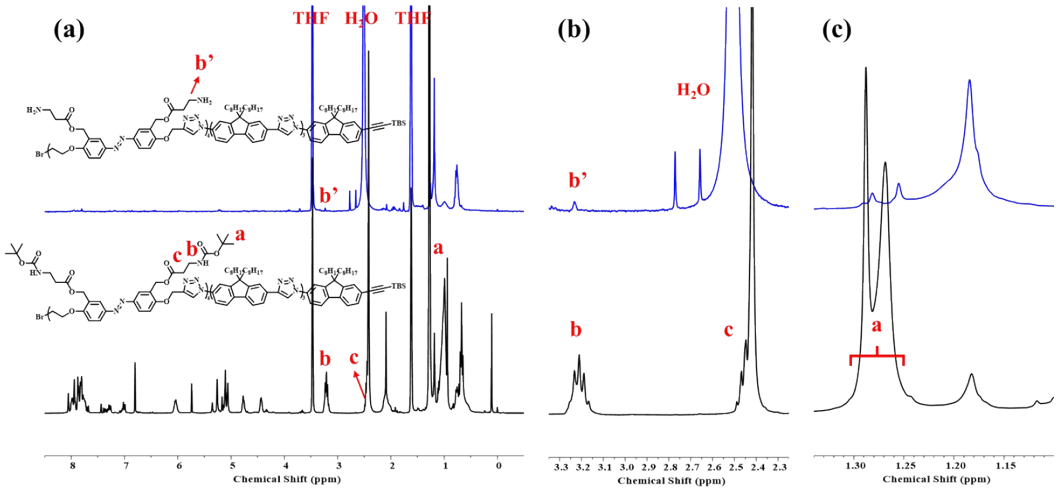


Figure S6. (a) ^{1}H NMR spectra of 4F-4Azo-8Boc and 4F-4Aazo-8NH_2 before and after hydrolysis in THF-d_8 and enlarged spectra in the range of (b) 3.3 ppm -2.3 ppm and (c)1.4 ppm -1.1 ppm.

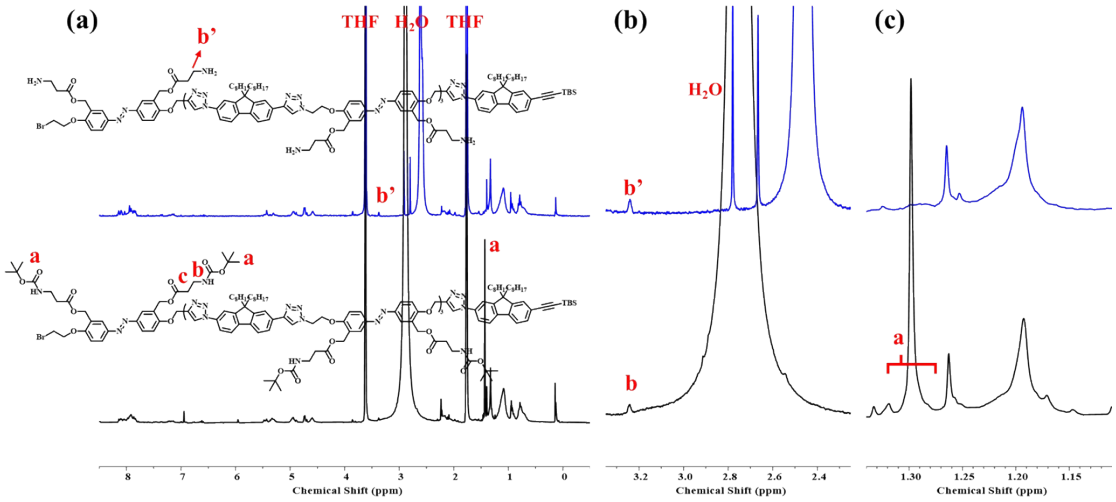


Figure S7. (a) ^{1}H NMR spectra of 4(F-A)-8Boc and 4(F-A)-8NH_2 before and after hydrolysis in THF-d_8 and enlarged spectra in the range of (b) 3.3 ppm -2.3 ppm and (c)1.4 ppm -1.1 ppm.

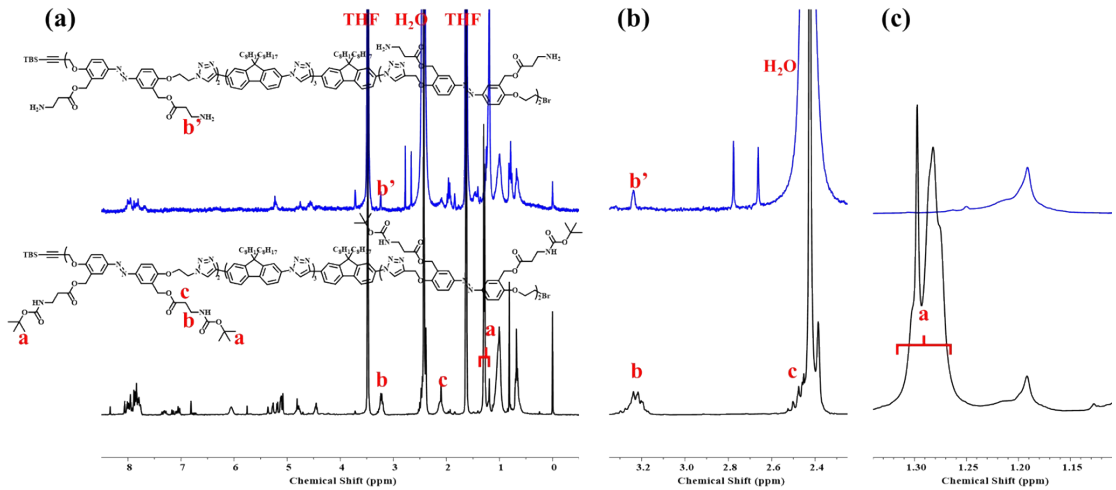


Figure S8. (a) ^{1}H NMR spectra of 2Azo-4F-2Azo-8Boc and 2Azo-4F-2Azo-8NH_2 before and after hydrolysis in THF-d_8 and enlarged spectra in the range of (b) 3.3 ppm -2.3 ppm and (c)1.4 ppm -1.1 ppm.

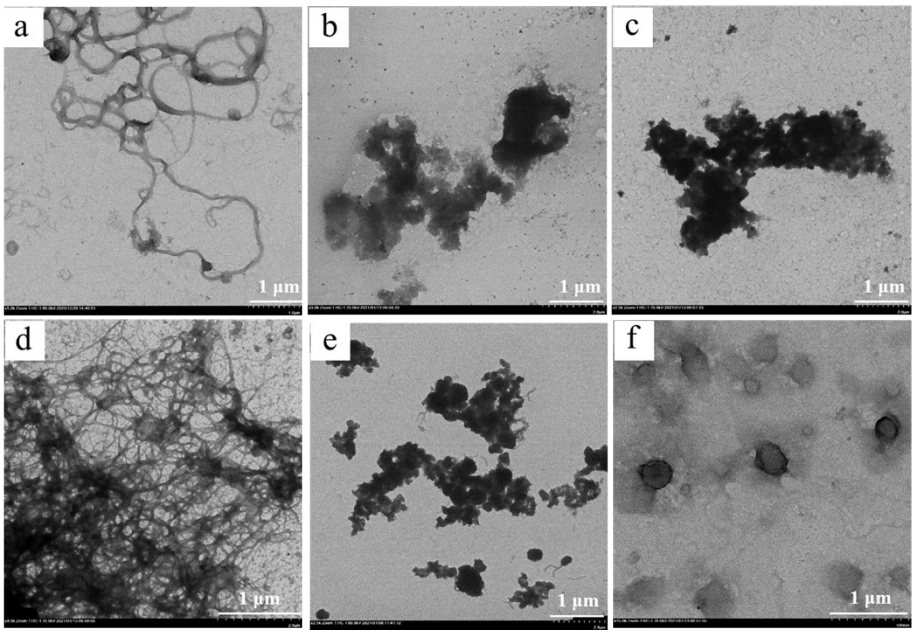


Figure S9. TEM images of assemblies of 4F-4Azo-8NH_2 assembled in THF/water/HCl systems with different volume fraction of THF/water/HCl and the concentration of hydrochloric acid aqueous solution. Assembly conditions: solvent ratio: (a) THF/water/HCl (1.0 M) (v/v/v) = 1:0.5:0.4, (b) THF/water/HCl (1.0 M) (v/v/v) = 1: 1: 0.4, (c) THF/water/HCl(1.0 M) (v/v/v) = 1: 2: 0.4; (d) THF/water/HCl (0.5 M) (v/v/v) = 1: 0.5: 0.4, (e) THF/water/HCl (2.0 M) (v/v/v) = 1:0.5:0.4, (f) THF/water/HCl (4.0 M) (v/v/v) = 1:0.5:0.4. Initial concentration: C_0 = 1.0 mg/mL; drop speed: 0.2 mL/h; temperature: 30 °C; stirring speed: 300 r/min, standing still for 1 h.

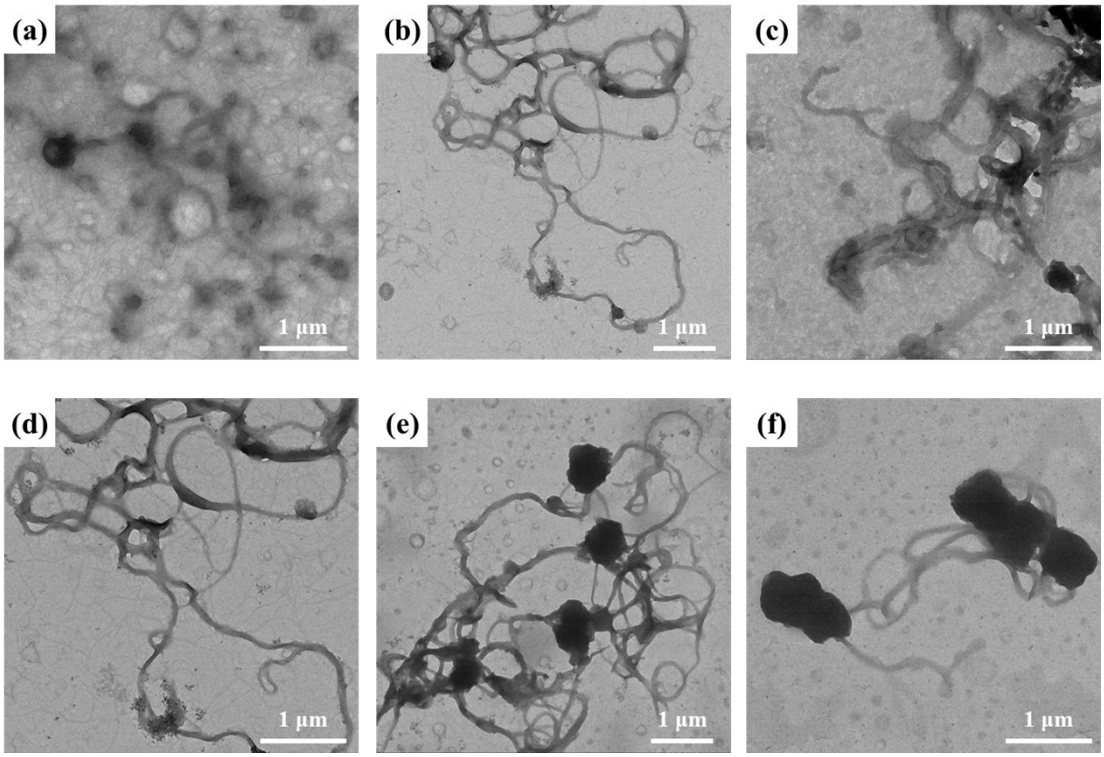


Figure S10. TEM images of the assemblies of 4F-4Azo-8NH_2 in THF/water/HCl (1.0M) at different aging times after completion of assembly. (a) 10 min, (b) 1 h, (c) 2 h, (d) 12 h, (e) 1day, (f) 3 days. Assembly conditions: solvent ratio: THF/water/HCl (1.0M) (v/v/v) = 1/0.5/0.4; initial concentration: C_0 = 1.0 mg/mL; injection speed: 0.2 mL/h; temperature: 30 ^oC; stirring speed: 300 r/min.

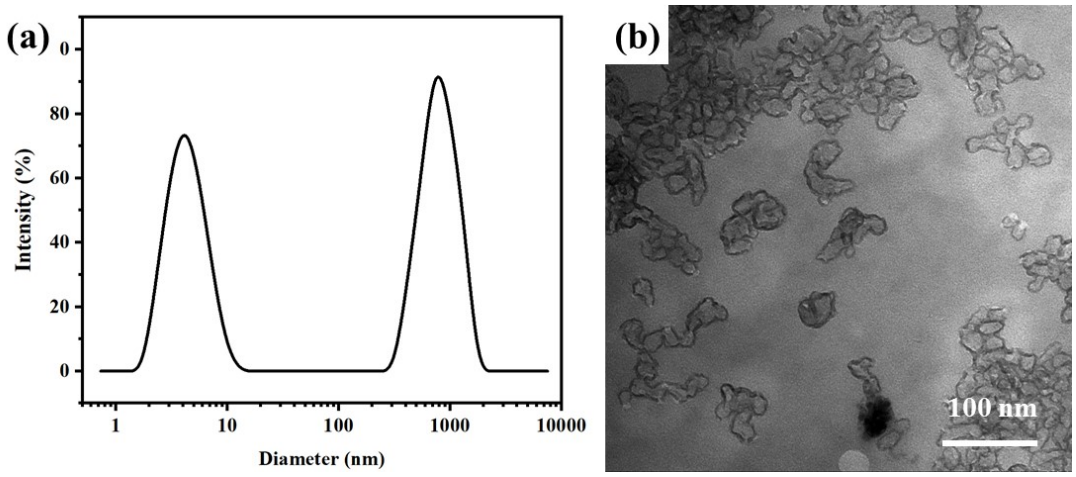


Figure S11. DLS curves of the assemblies of 2Azo-4F-2Azo-8NH_2 (a) and partial enlarged TEM images of smaller vesicles (b). Assembly conditions: solvent ratio: THF/water/HCl $_{(1M)}$ (v/v/v) = 1/0.5/0.4; initial concentration: C_0=1.0 mg/mL; drop speed: 0.2 mL/h; temperature: 30 ^oC; stirring speed: 300 r/min.

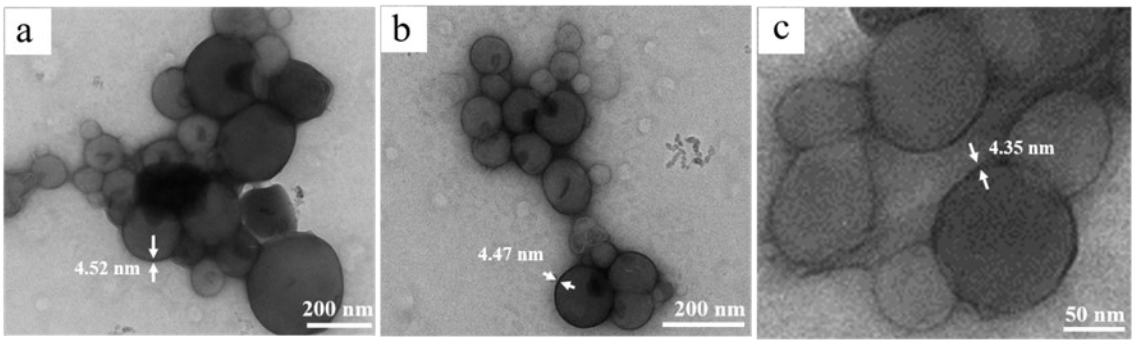


Figure S12. Enlarged TEM image of typical vesicles formed by 2Azo-4F-2Azo-8NH_2. Assembly conditions: solvent ratio: THF/water/HCl (1.0 M) (v/v/v) = 1/0.5/0.4; initial concentration: C_0=1.0 mg/mL; drop speed: 0.2 mL/h; temperature: 30 ^oC; stirring speed: 300 r/min.

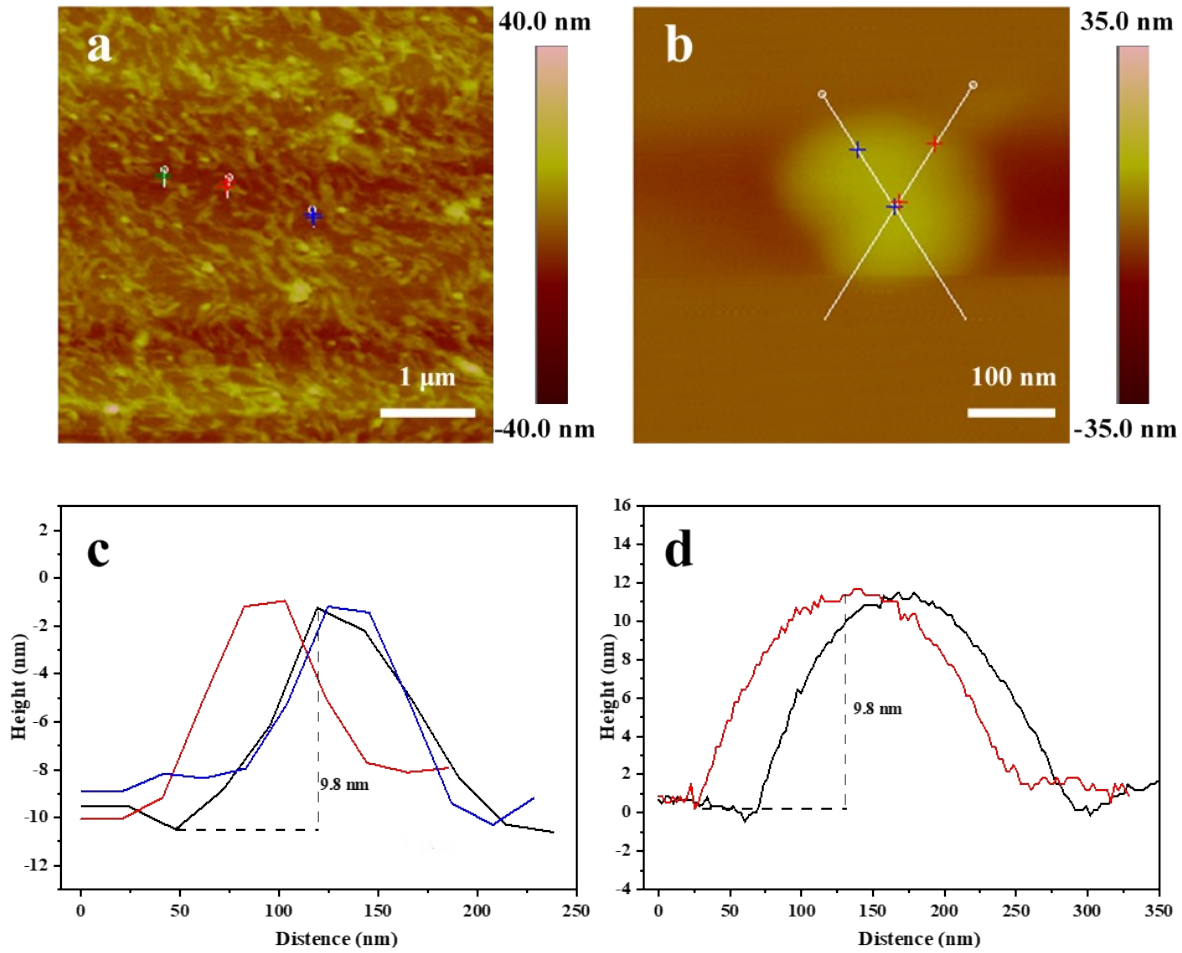


Figure S13. AFM images and height profile of the tiny fibers and vesicles obtained separately by assembly of 4F-4Azo-8NH_2 (a, c) and 2Azo-4F-2Azo-8NH_2 (b, d). Solvent ratio: THF/water/HCl (1.0 M) (v/v/v) = 1/0.5/0.4; initial concentration: C_0 = 1.0 mg/mL; drop speed: 0.2 mL/h; temperature: 30 °C; stirring speed: 300 r/min.

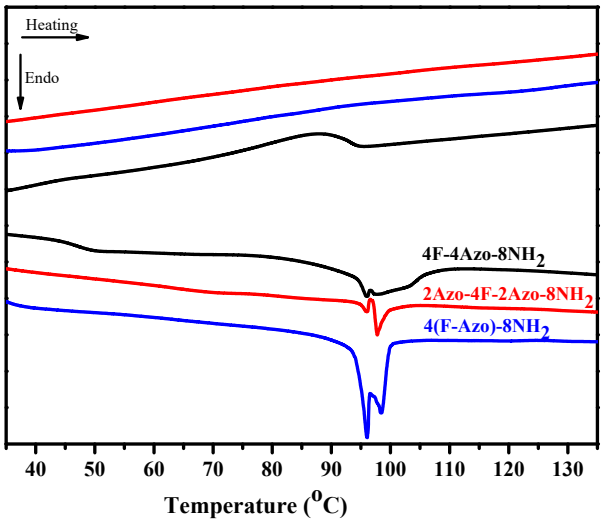


Figure S14. Second DSC heating curves of 4F-4Azo-8NH_2, 2Azo-4F-2Azo-8NH_2 and 4(F-Azo)-8NH_2 with a heating rate of 10 °C/min in N_2.

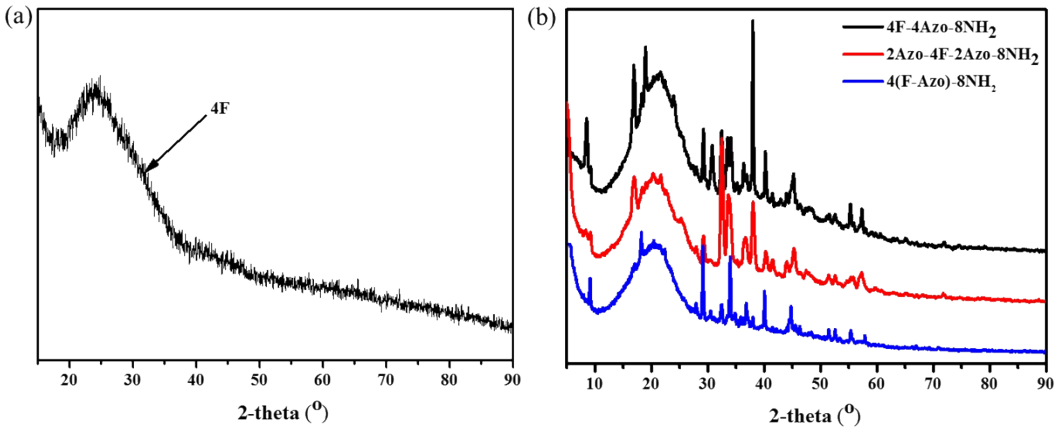


Figure S15. XRD spectra of 4F (a) and oligomers 4F-4Azo-8NH_2, 2Azo-4F-2Azo-8NH_2, 4(F-Azo)-8NH_2 (b).

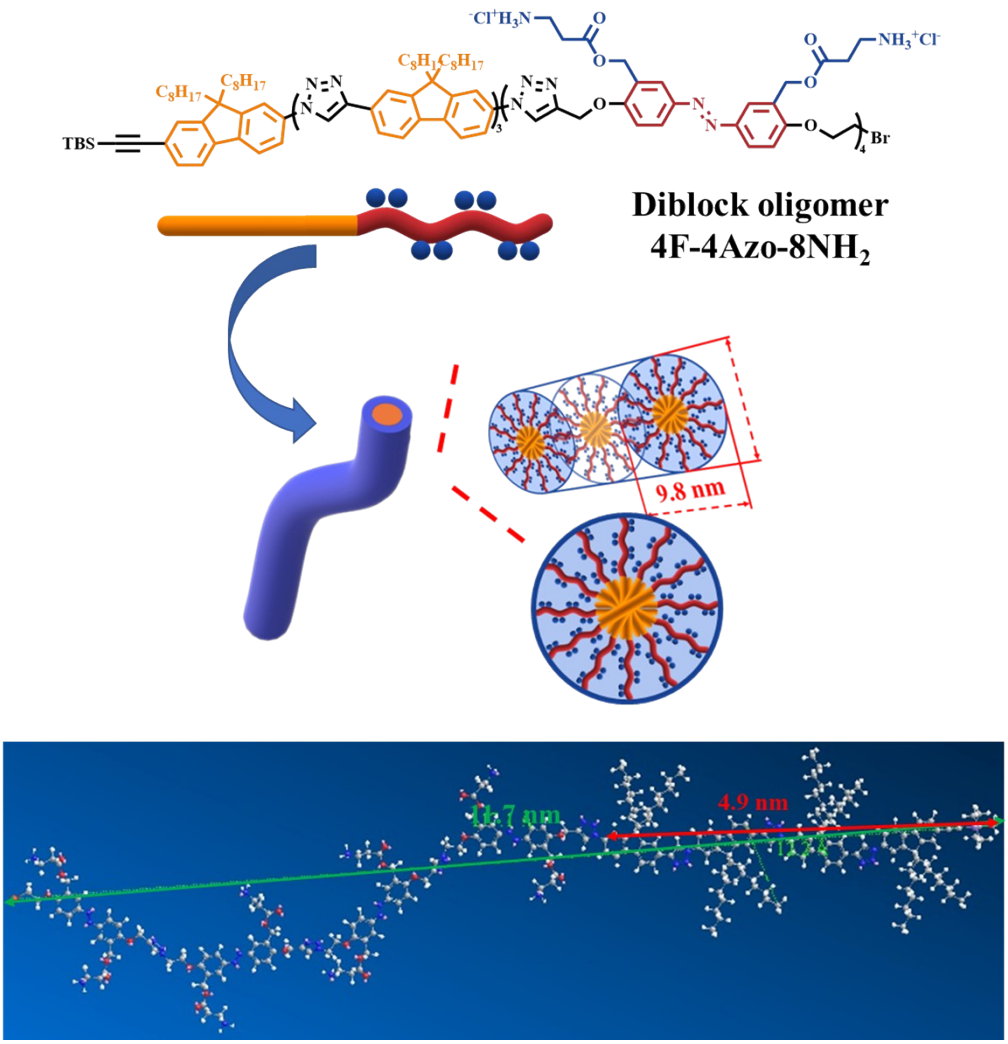


Figure S16. Schematic diagram of molecular stacking of fibers formed by the oligomer 4F-4Azo-8NH_2 during self-assembly in mixed solution THF/water/HCl (Top). The simulative molecular configuration of 4Azo-4F-8NH_2 calculated with Materials Studio software (MS). The molecular length of 4Azo-4F-8NH_2 is 11.7 nm, of which azobenzene block with amino side-chain groups is about 6.8 nm, and fluorene block is 4.9 nm (below).

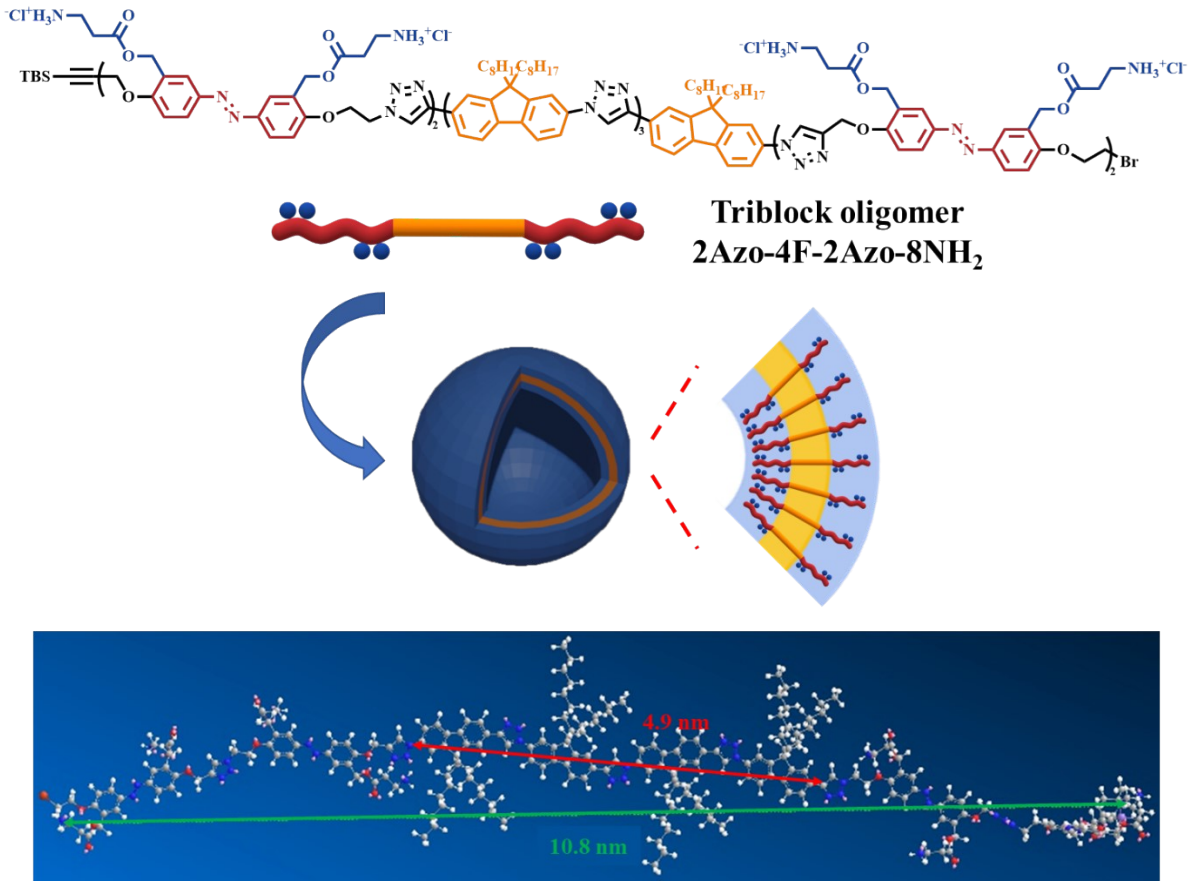


Figure S17. Schematic diagram of molecular stacking of vesicles formed by the oligomer 2Azo-4F-2Azo-8NH_2 during self-assembly in mixed solution THF/water/HCl (Top). The simulative molecular configuration of 2Azo-4F-2Azo-8NH_2 (b) calculated with Materials Studio software (MS). The molecular length of 2Azo-4F-2Azo-8NH_2 is 10.8 nm, of which two azobenzene blocks with amino side-chain groups is 2.95 nm respectively, and fluorene block is 4.9 nm (below).

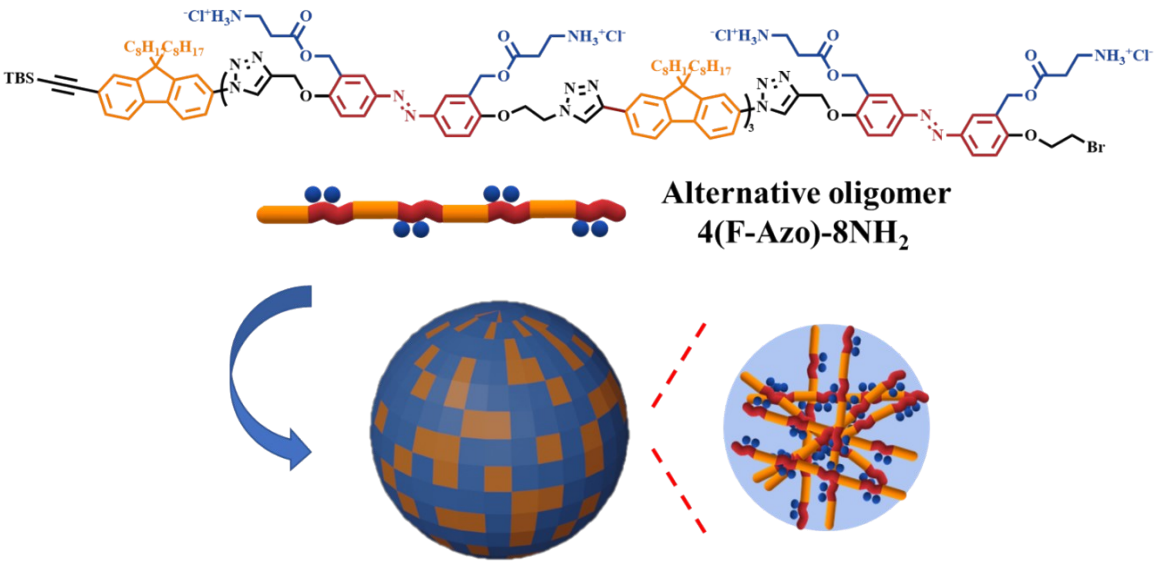


Figure S18. Schematic diagram of molecular stacking of micellar complex formed by the oligomer 4(F-Azo)-8NH_2 during self-assembly in mixed solution THF/water/HCl

References

[S1] Min Liu, Xianheng Shi, Lishan Li, Jiandong Zhang, Zhihao Huang, Wei Zhang,Nianchen Zhou,* Zhengbiao Zhang,* and Xiulin Zhu, Synthesis of Discrete Conjugated Fluorene-Azo Oligomers for the Investigation of Azobenzene Position-Dependent Physical Properties and Photoresponsive Behavior, *Macromol. Chem. Phys.,* **2021**, 2100092.

[S2] An Hu, Xianheng Shi, Lishan Li,* Wei Zhang, Zhengbiao Zhang,* Nianchen Zhou,*and Xiulin Zhu, A Consequence of Dispersity on the Self-Assembly of Amphiphilic Homopolymers Containing Main-Chain Azobenzene, *Macromol. Chem. Phys.,* **2021**, 2100202.