

## Amphiphilic diselenide-containing supramolecular polymers

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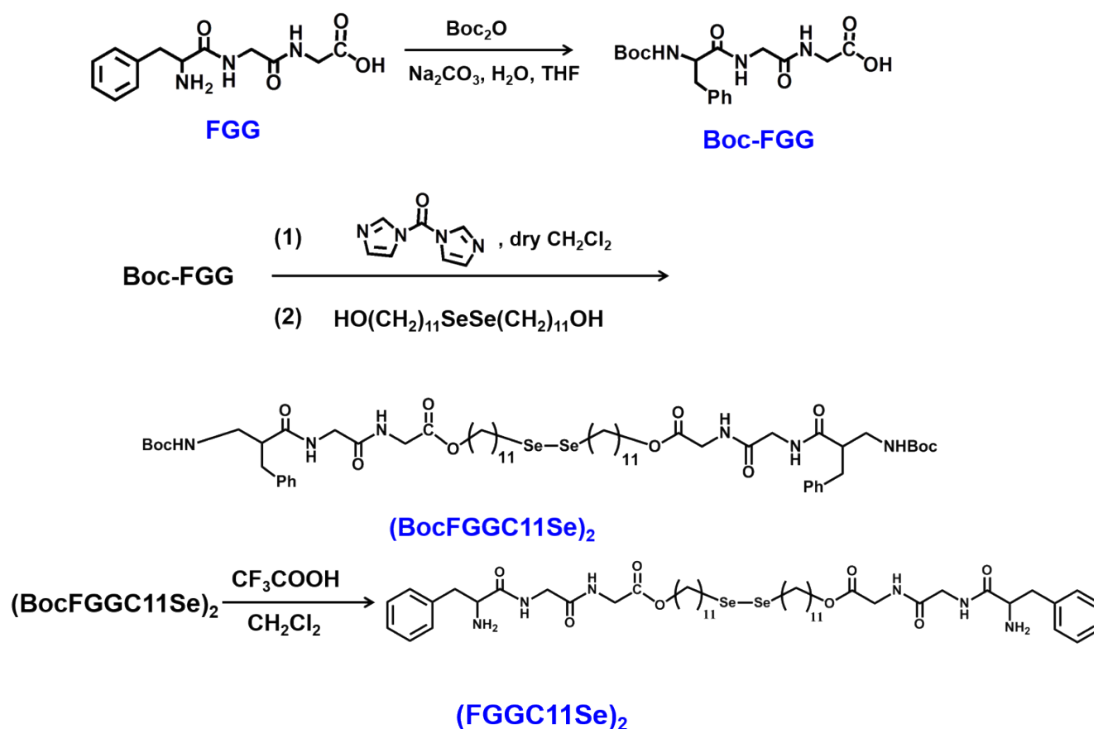
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### 1. Materials and characterization

Boc-FGG and HOC11SeSeC11OH was synthesized using previous methods<sup>1,2</sup>.

**(BocFGGC11Se)<sub>2</sub>**: Boc-FGG (0.401 g (1.05 mmol)) was dissolved into 25mL dry CH<sub>2</sub>Cl<sub>2</sub>, and then 0.207 g (1.28 mmol) N, N'-carbonyldiimidazole was added into the solution. The mixture was stirred for 12 h at room temperature, producing a lot of white precipitate. Then 0.232 g HOC11SeSeC11OH (0.46 mmol) was added into the mixture. The mixture was stirred for 48 h away from light under N<sub>2</sub> atmosphere in room temperature. Then 20 mL NaCl saturated solution (containing about 1 mM HCl) was added into the CH<sub>2</sub>Cl<sub>2</sub> solution. The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×25 mL). The organic phase were combined, dried over MgSO<sub>4</sub>, filtered, and concentrated. The product was finally purified by column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH 40: 1) to give the product (0.519 g, 91.4%) as a yellow solid. <sup>1</sup>H NMR (JOEL JNM-ECA400, 400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ (ppm) = 7.34~7.27 (4H), 7.27~7.17 (6H), 6.95~6.70 (4H), 5.13 (2H), 4.30 (2H), 4.10 (4H), 4.02~3.90 (6H), 3.86 (2H), 3.13 (2H), 3.02~2.87 (6H), 1.72 (4H), 1.60 (4H), 1.37 (18H), 1.35~1.25 (28H).

**(FGGC11Se)<sub>2</sub>**: (BocFGGC11Se)<sub>2</sub> 0.373g (0.22 mmol) was stirred in CF<sub>3</sub>COOH–CH<sub>2</sub>Cl<sub>2</sub> (4:1, 5 mL) for 4 h, at room temperature. The solvent was removed *in vacuo*, and then the obtained sticky



solid was dissolved in 1 mL CH<sub>3</sub>OH and precipitated in diethyl ether. The yellow precipitate was washed with diethyl ether. The obtained product (0.125 g) was further purified by HPLC. (Analytical injections were monitored at 214 nm, 254 nm. A SHIMADZU (Prominence LC-20AT) instrument using a semi preparative column (Grace Vydac "Peptide C18", 250 X 10 mM, 10 μm particle size, flow rate 3 mL/min. Gradient: 20-90% CH<sub>3</sub>CN/H<sub>2</sub>O over 30 min.) After dried *in vacuum*, 0.089 g final product was obtained, yielding 71.2%. <sup>1</sup>H NMR (JOEL JNM-ECA600, 600 MHz, CD<sub>3</sub>OD, 25 °C): δ (ppm) = 7.39~7.33 (4H), 7.33~7.27 (6H), 4.16~4.09 (6H), 4.02(2H), 3.96 (4H), 3.83 (2H), 3.25 (2H), 3.06 (2H), 2.90 (4H), 1.73 (4H), 1.64 (4H), 1.44~1.25(28H), as shown in Figure S1. <sup>13</sup>C NMR δ (ppm) = 171.43, 171.27, 170.20, 135.64 130.48, 130.13, 128.86, 66.45, 55.87, 42.99, 41.98, 38.46, 31.96, 30.75, 30.62, 30.59, 30.41, 30.36, 30.18, 29.68, 26.93, as shown in Figure S2. <sup>77</sup>Se NMR δ (ppm) = 301 ppm, as shown in Figure S3. ESI: m/z 513.21 [M+2H]<sup>2+</sup>, 1025.41 [M+H]<sup>+</sup>, as shown in Figure S4.

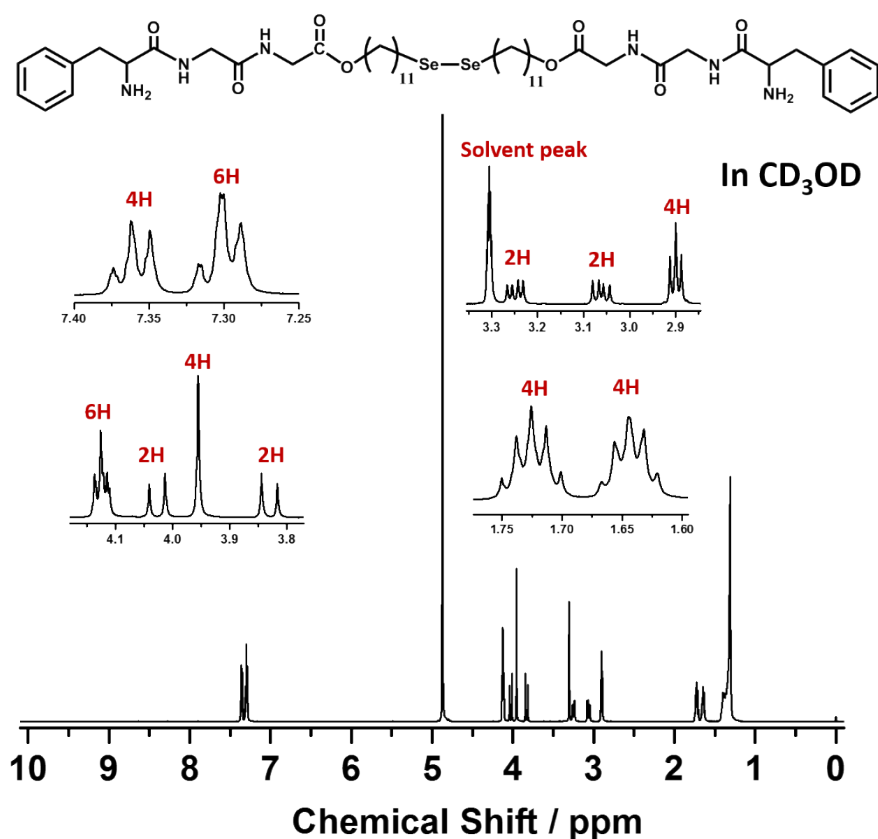


Figure S1 <sup>1</sup>H NMR spectrum of (FGGC11Se)<sub>2</sub>

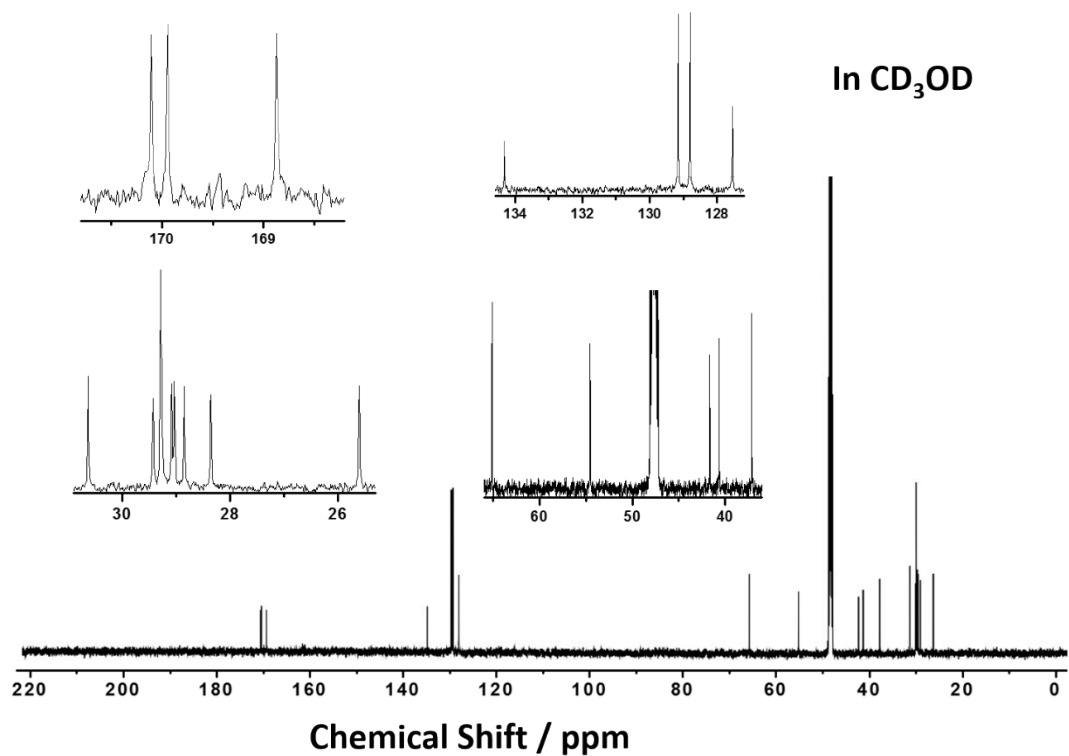


Figure S2 <sup>13</sup>C NMR spectrum of (FGGC11Se)<sub>2</sub>.

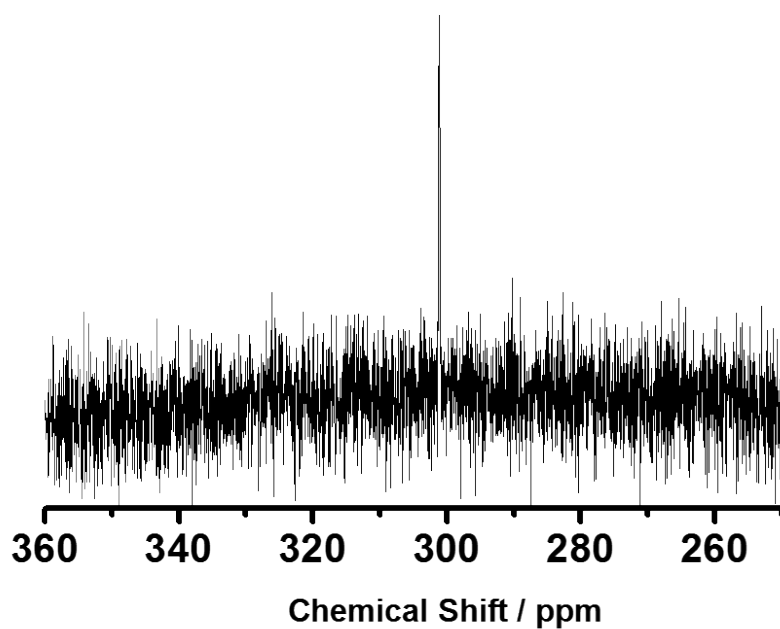
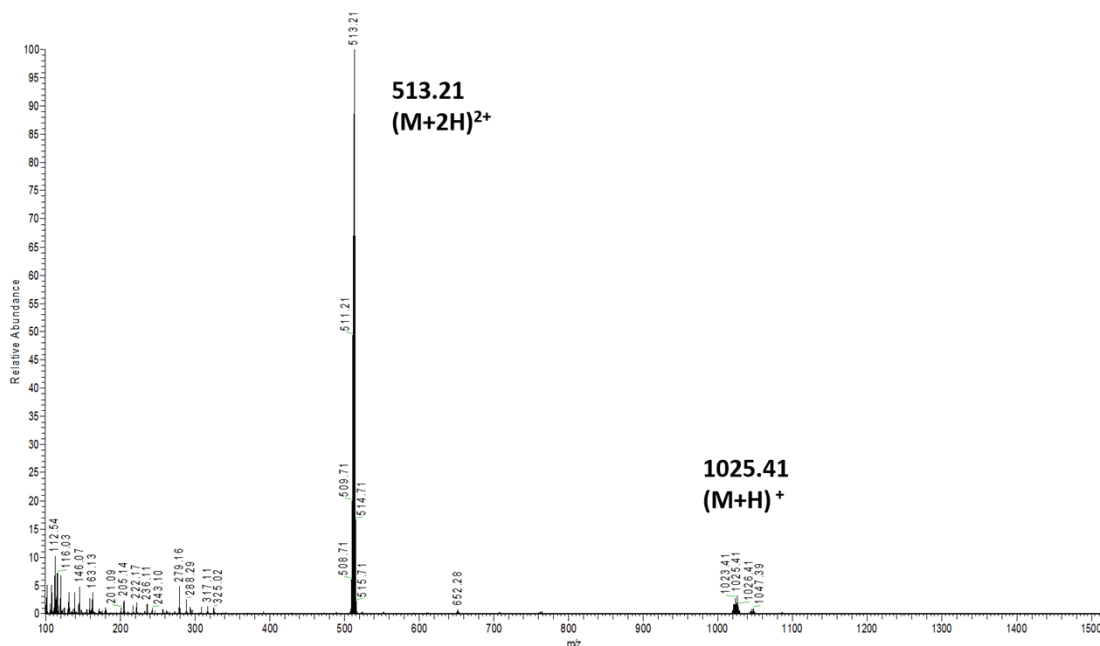


Figure S3 <sup>77</sup>Se NMR spectrum of (FGGC11Se)<sub>2</sub>.



**Figure S4** ESI Mass spectroscopy of (FGGC11Se)<sub>2</sub>

## 2. AFM-based single-molecule force spectroscopy

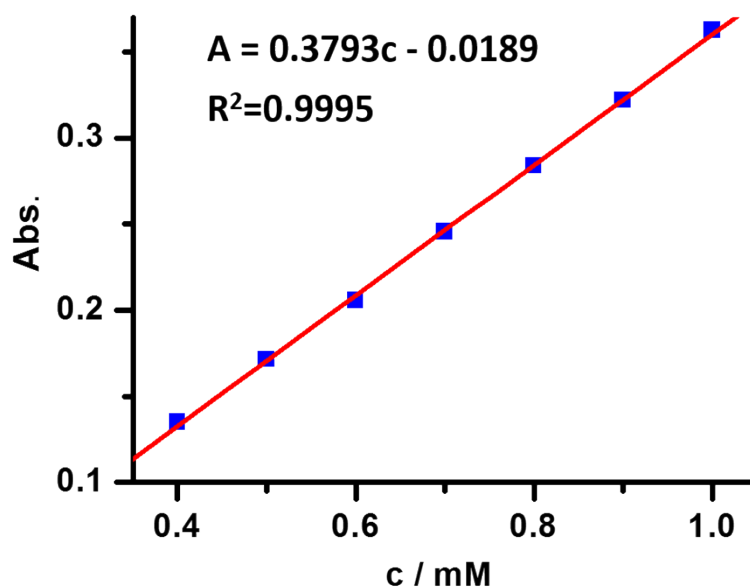
The SMFS experiments were carried out at room temperature utilizing a commercially available molecular force probe 3D (Asylum Research, Santa Barbara, CA) and the commercially available V-shaped Si<sub>3</sub>N<sub>4</sub> AFM cantilevers (Bruker, Santa Barbara, CA) with a sharp tip (radius of curvature 50 nm) at the end of a soft cantilever and a spring constant of 0.010-0.040 N/m. Quartz wafers were treated in hot piranha solution (7:3 v/v 98% H<sub>2</sub>SO<sub>4</sub>: 30% H<sub>2</sub>O<sub>2</sub>) for 1 hour, sonicated in large amounts of deionized water for several times, rinsed with ethanol. After dried in a steam of nitrogen, the fresh quartz wafers were used immediately. (**Caution:** piranha solution is very corrosive and can react violently with organics, so security measures should be taken.) The (FGGC11Se)<sub>2</sub>-CB[8] complex solution (1.0 mM) was dropped onto the quartz wafer and dried in the air, and then the solution was mounted between the AFM tip holder and the quartz wafer.

In brief, a polymer chain could absorb onto both the AFM tip and the substrate to form the so-called polymer bridge. With the AFM tip separated from the substrate, the polymer bridge was stretched, resulting into the deflection of the cantilever. The deflection of the cantilever and the extension of the polymer bridge were recorded simultaneously, and finally converted to force–extension curves (in brief, force curves).

## 3. Characterization of adjustment of degree of polymerization by Asymmetric Flow Field Flow Fractionation

The signals of supramolecular polymers were detected by Ultraviolet (UV) detector and Multi-angle Light Scattering (MALS) detectors. The concentration of diselenide-containing supramolecular polymers was measured by UV detector at 270 nm. The molar absorption coefficient of (FGGC11Se)<sub>2</sub>-CB[8] complex at 270 nm was given by the UV absorption-concentration standard curve worked out with UV/vis spectroscopy (Figure S5), and the value is 0.379 L·mmol<sup>-1</sup>·cm<sup>-1</sup> or 147 mL·g<sup>-1</sup>·cm<sup>-1</sup>. The weight average molecular weight and

polydispersity were finally calculated based on the data obtained by MALS.

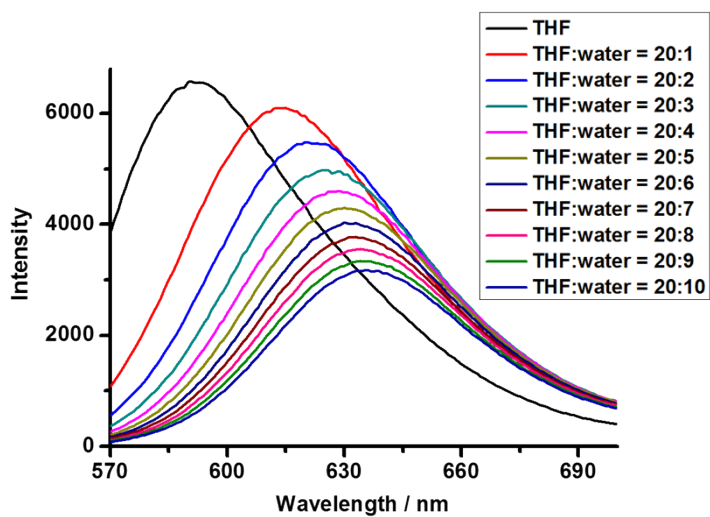


**Figure S5** The UV absorption-concentration standard curve at 270 nm of (FGGC11Se)<sub>2</sub>-CB[8].

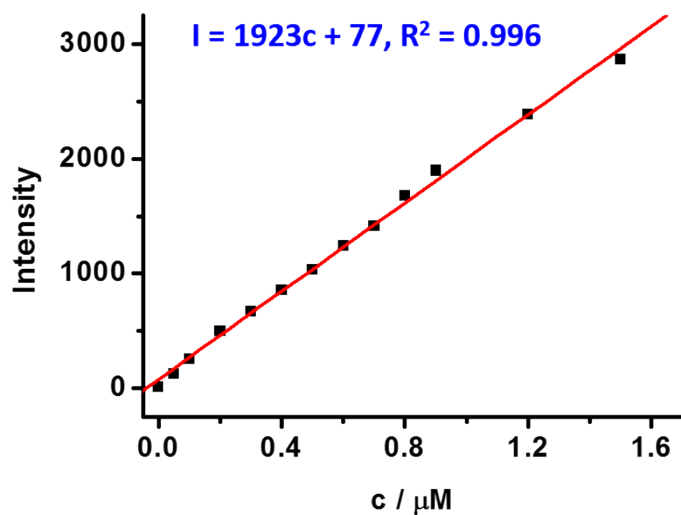
The details of AsF-FFF experimental conditions are set as following: the detector flow was 1 mL/min, cross flow decreased linearly from 1.5 mL/min to 0 mL/min in 15min. The separation membrane was made of polyether sulfone and the carrier was deionized water filtered by a water membrane (0.22 μm)

#### **4. Fluorescence intensity–NR concentration standard curve and loading of NR**

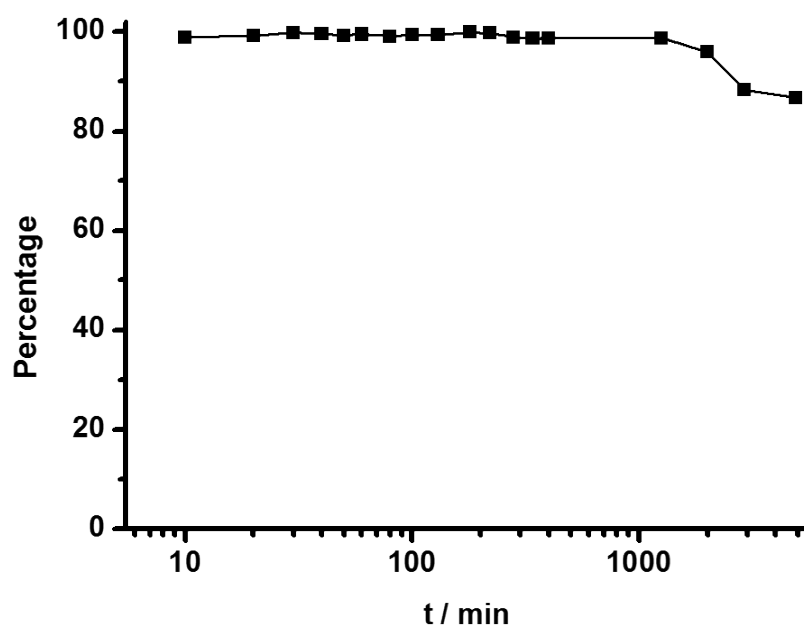
The loading of NR is done as following procedures: 10 μL NR solution (10 μmol·L<sup>-1</sup> in THF) was dispersed into 2 mL (FGGC11Se)<sub>2</sub>-CB[8] or (FGGC11Se)<sub>2</sub> solution and then the mixed solution was sonicated for two minutes to vapor most of THF. After set in dark for 12 hours, the solution was centrifuged for 5 min with 4500 r·min<sup>-1</sup>, and then, the supernatant was used for fluorescence measurement. The fluorescence wavelength of Nile Red (NR) in the solution with different volume ratio of THF: water was measured, as shown in Figure S6. In the V<sub>THF</sub>: V<sub>water</sub> = 4:1 solution, the fluorescence peak is at 630 nm, the same with that of NR in 0.2 mM (FGGC11Se)<sub>2</sub>-CB[8] complex solution. Then the fluorescence intensity–NR concentration standard curve was worked out in In the V<sub>THF</sub>: V<sub>water</sub> = 4:1 solution, as shown in Figure S7.



**Figure S6** Fluorescence spectra of NR in the solution with different volume ratio of THF: water.



**Figure S7** Fluorescence intensity-NR concentration standard curve In the  $V_{\text{THF}}: V_{\text{water}} = 4:1$  solution.



**Figure S8** NR can be retained in the aggregates of the amphiphilic diselenide-containing supramolecular polymers for a relatively long time.

**6. Reference:**

- (1) N. Ma, Y. Li, H. Xu, Z. Wang, and X. Zhang, *J. Am. Chem. Soc.* 2010, **132**, 442.
- (2) X. Tan, L. Yang, Y. Liu, Z. Huang, H. Yang, Z. Wang, and X. Zhang, *Polym. Chem.* 2013, **4**, 5378.