Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Redox control of GPx catalytic activity through mediating self-assembly of Fmoc-phenyalanine selenide into switchable supramolecular architectures

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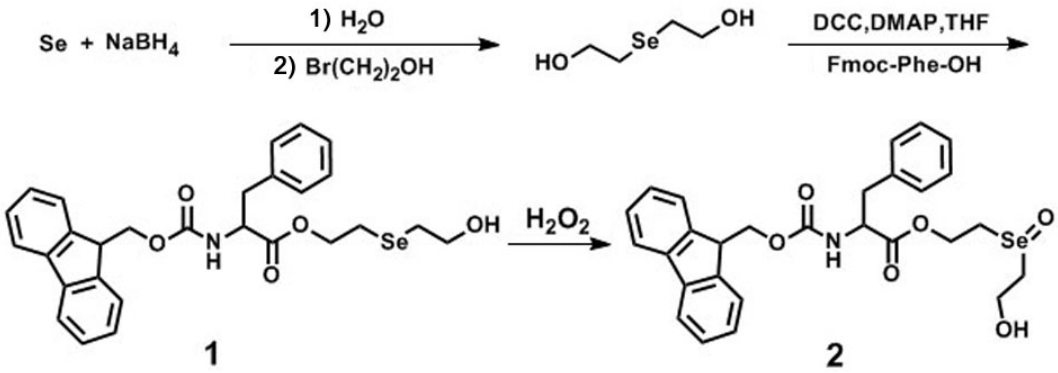
Syntheses and characterizations



Scheme S1. Synthesis route of compounds **1** and **2**

Synthesis and characterization of 2,2'-selenodiethanol: To a round-bottom flask containing selenium powder (789.5 mg, 10 mmol) and $NaBH_4$ (1.894 g, 50 mmol) under a nitrogen atmosphere, 10 mL of H_2O was injected. The suspension was heated until $NaBH_4$ had completely reacted. After the mixture had been cooled down to room temperature, deoxygenized 2-bromoethanol (2.505 g, 20 mmol) was added. The mixture was then stirred over night. The solution was extracted with EtOAc, and the organic layers were dried over anhydrous Na_2SO_4. After filtration, the solvent was removed by vacuum. The resulting crude product was purified by flash chromatography (10:1 EtOAc : petroleum ether) to yield the product as a yellow liquid, total yield 35%. ^{1}H NMR (500 MHz, DMSO-d_6, 25 ℃) δ(ppm): 2.22 (s, 1H), 2.84 (t, 3H), 3.85 (t, 2H).

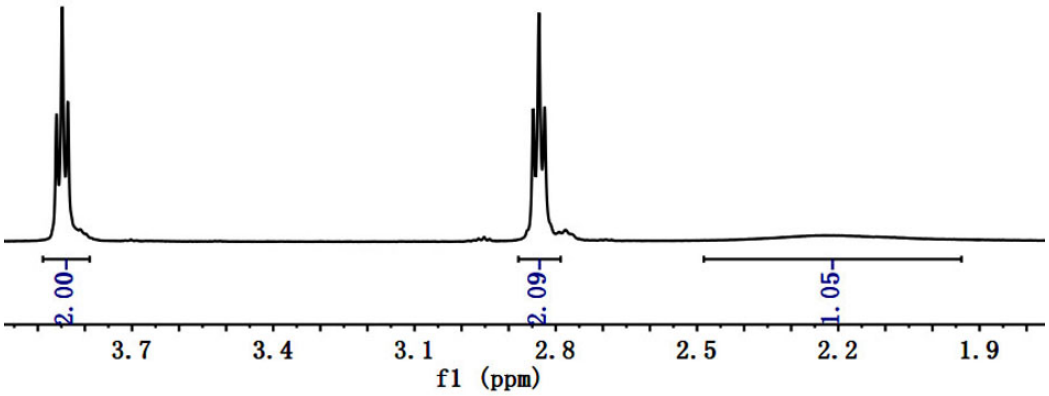


Figure S1. ^{1}H NMR spectrum of 2, 2'-selenodiethanol in $CDCl_3$.

Characterization of Compound 1

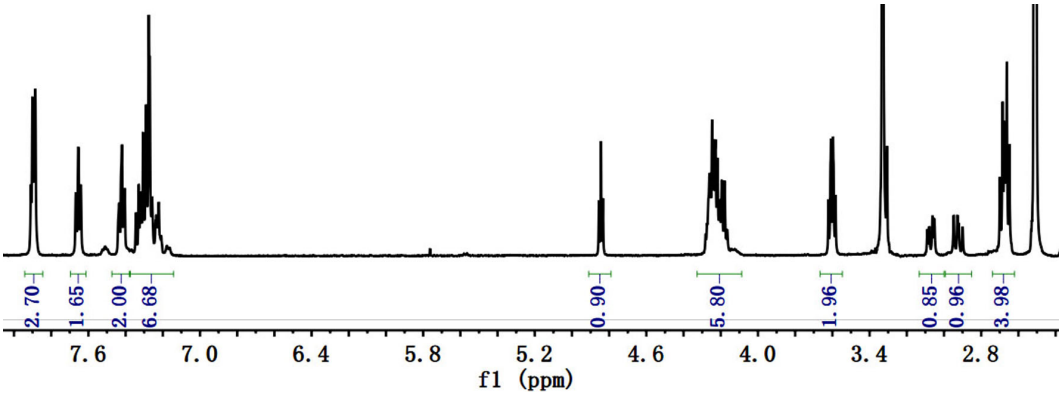


Figure S2. ^{1}H NMR spectrum of compound **1** in DMSO-d_6.

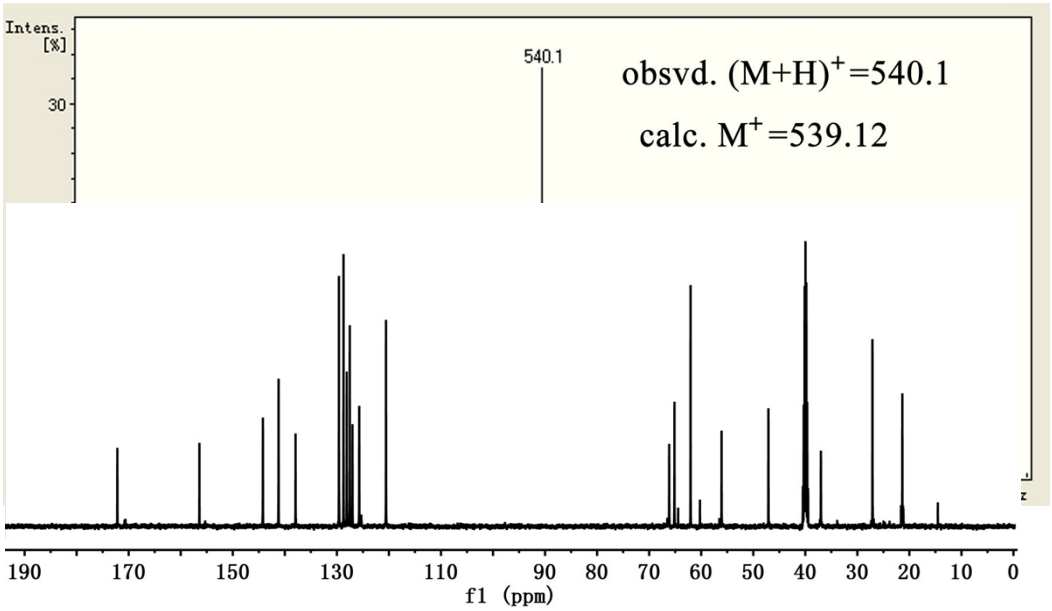


Figure S4. ^{13}C NMR spectrum of compound **1** in DMSO-d_6.

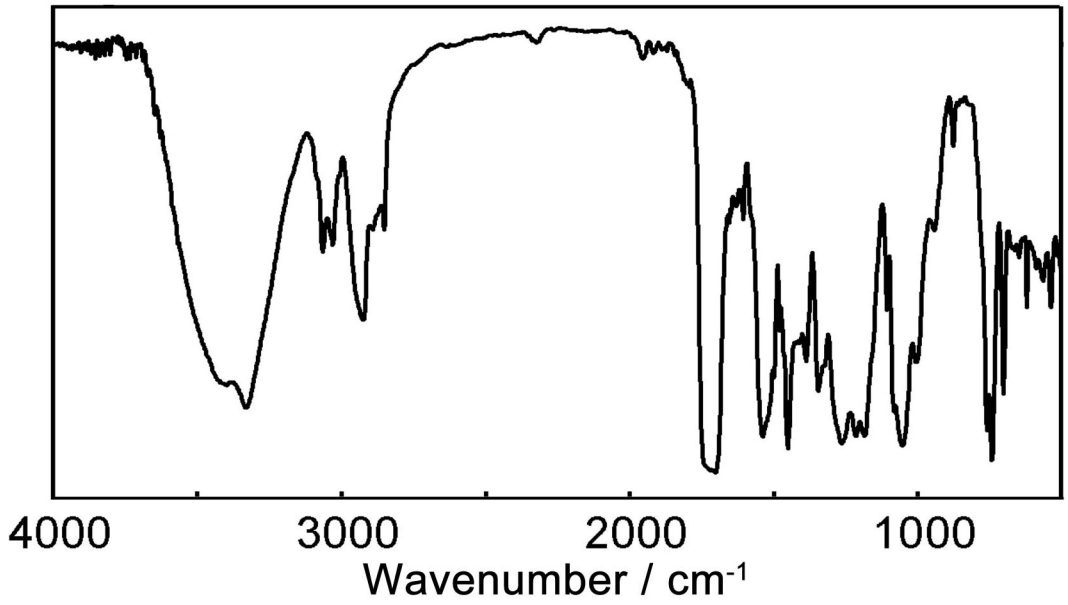


Figure S5. FT-IR spectrum of compound **1**.

Characterization of Compound 2

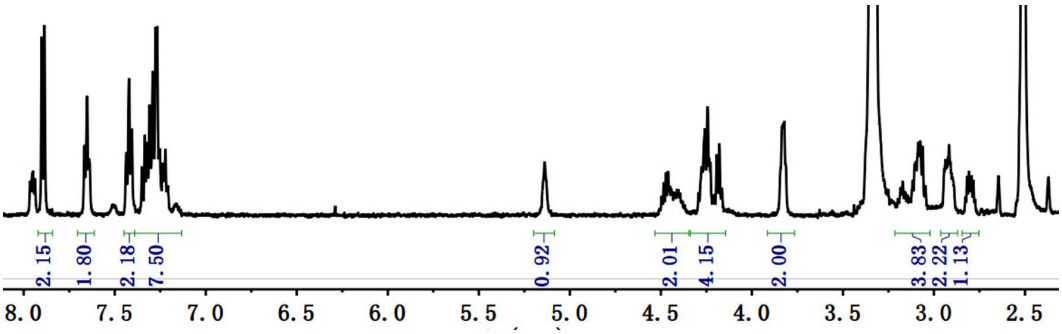


Figure S6. ^{1}H NMR spectrum of compound **2** in DMSO-d_6.

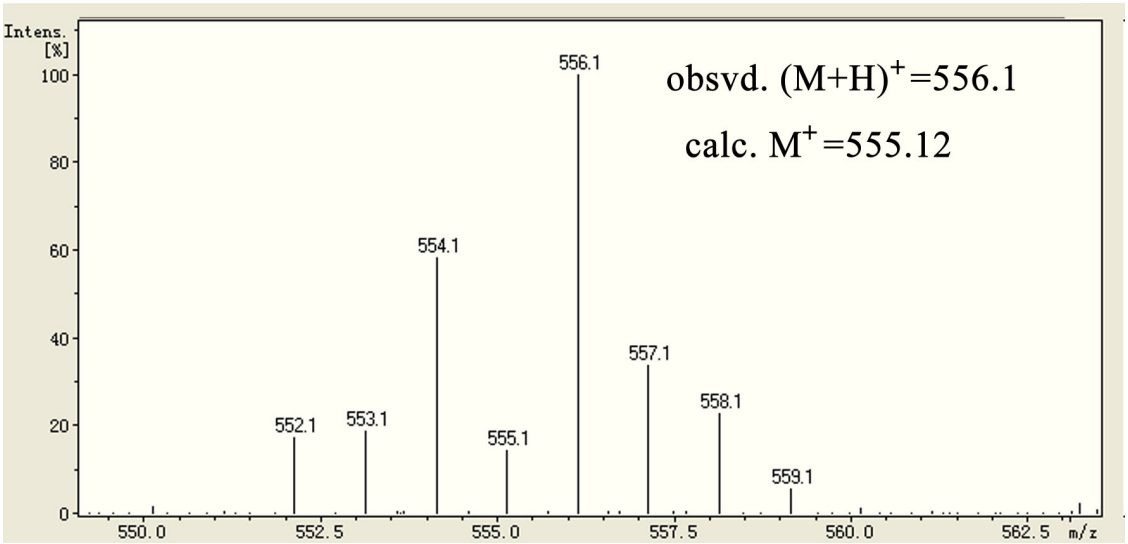


Figure S7. ESI-MS of compound **2.**

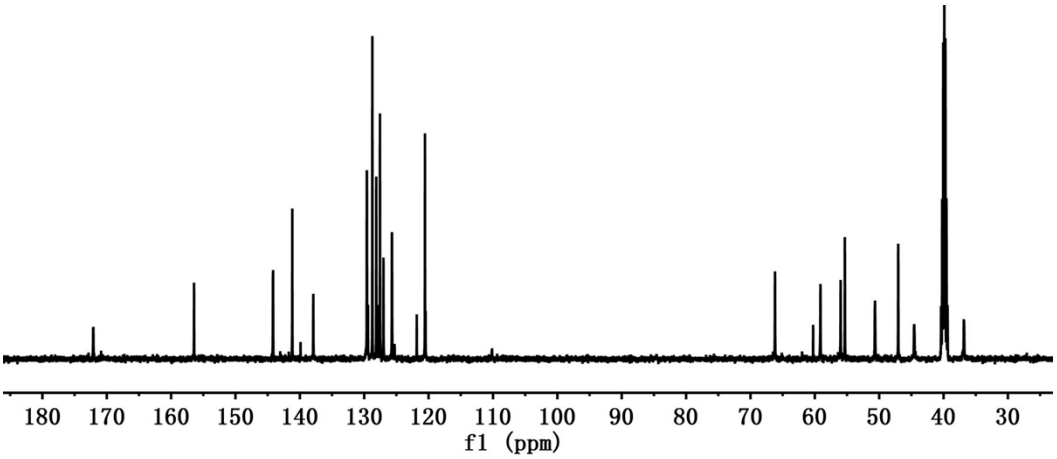


Figure S8. ^{13}C NMR spectrum of compound **2** in DMSO-d_6.

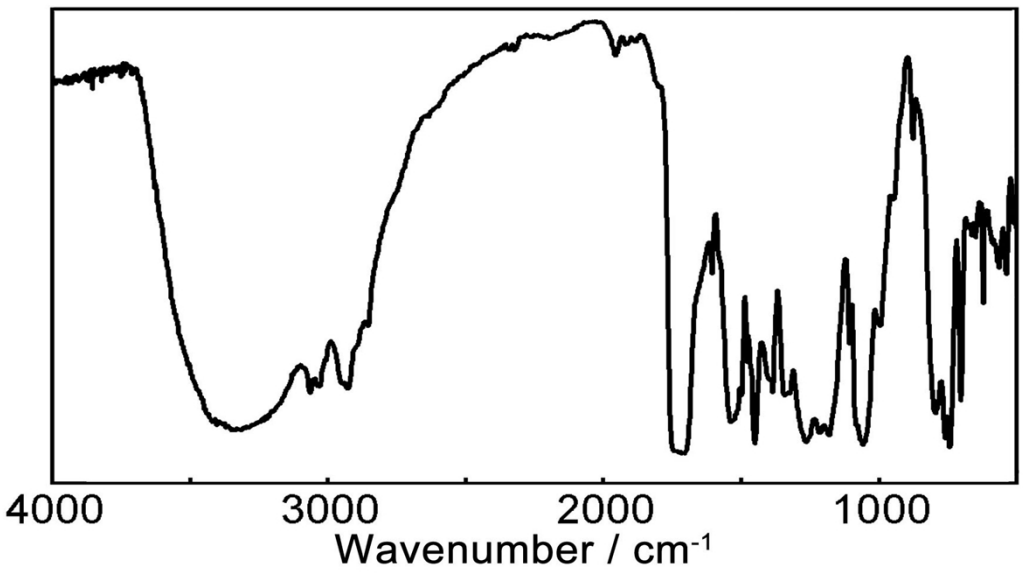


Figure S9. FT-IR spectrum of compound **2**.

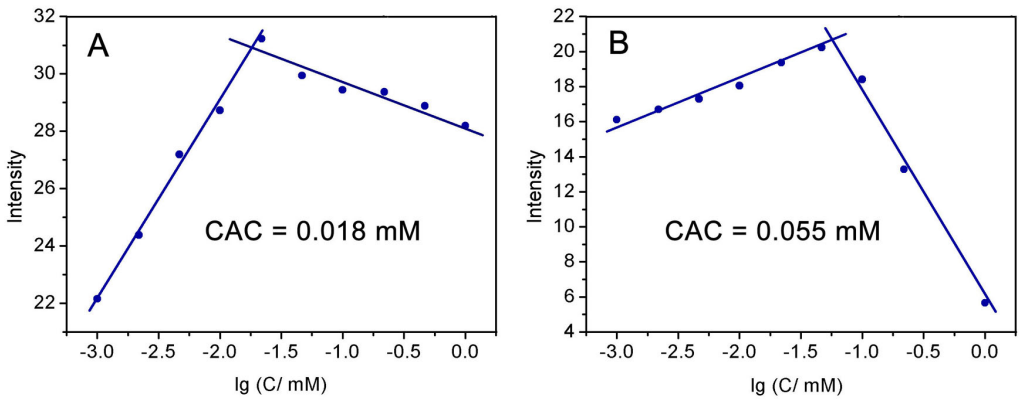


Figure S10. CAC determination of (A) compound **1** and (B) compound **2.**

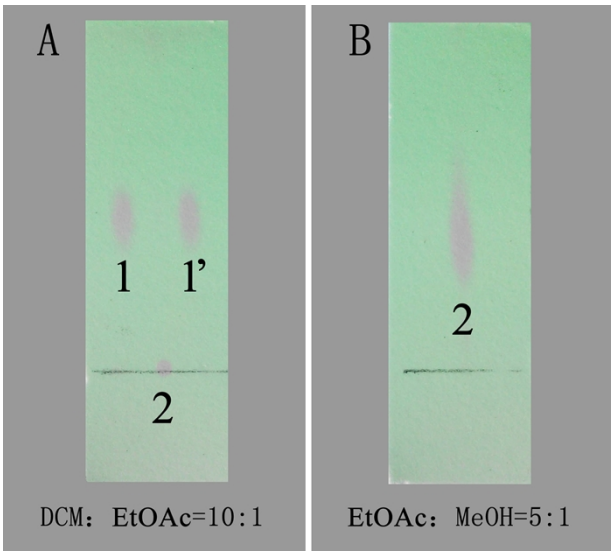


Figure S11. TLC of compound **1** and **2**. (A) After the addition of 2 equiv. of H_2O_2 to the methanol solution of **1**, **2** is obtained. The treatment of **2** with 2 equiv. of GSH produces **1'**, whose Rfs value is the same with that of **1**, implying the reversible conversion between **1** and **2**. (B) The produced **2** can be eluted by polarer developing solvent. No obvious impurity points can be observed in both A and B indicates the conversion is almost quantitative.

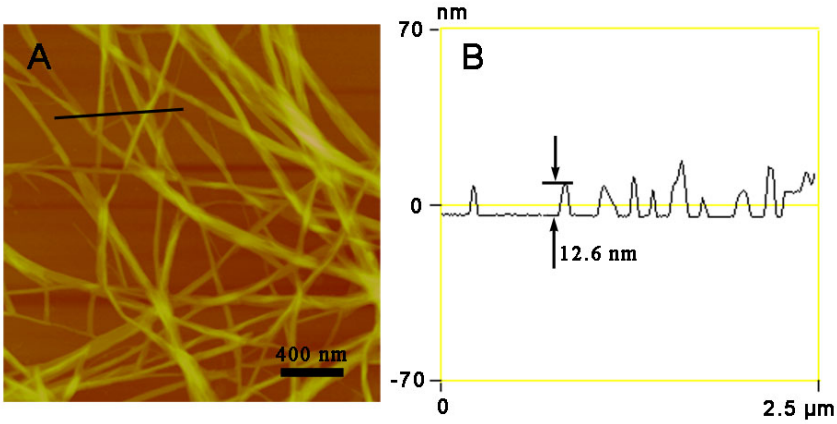


Figure S12. (A) AFM image of the NTs self-assembled from compound **2** in aqueous solution at concentration of 1 mM. (B) Height curve of the NTs from panel A.

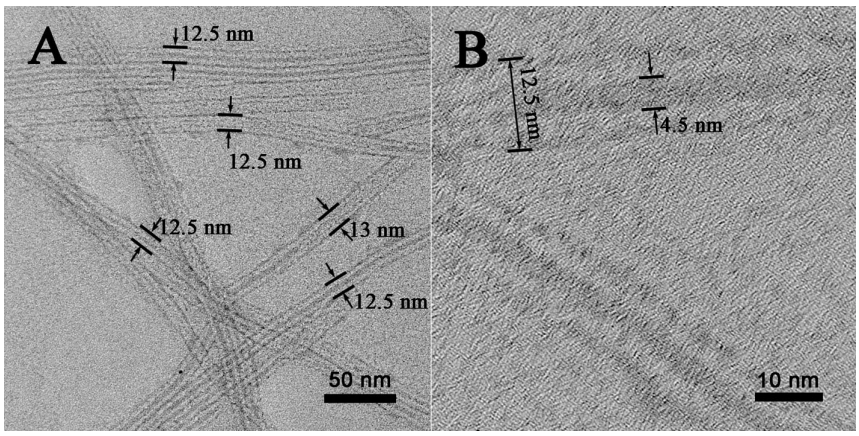


Figure S13. (A) TEM and (B) HR-TEM images of the NTs self-assembled from compound **2** in aqueous solution at concentration of 1 mM.

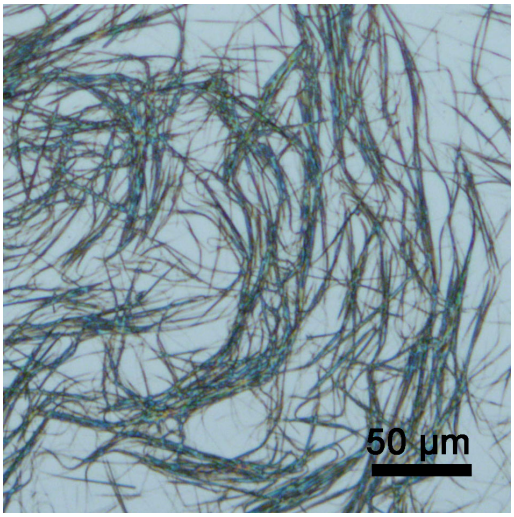


Figure S14. Optical microscopy image of the NTs self-assembled from compound **2** in aqueous solution at concentration of 1 mM.

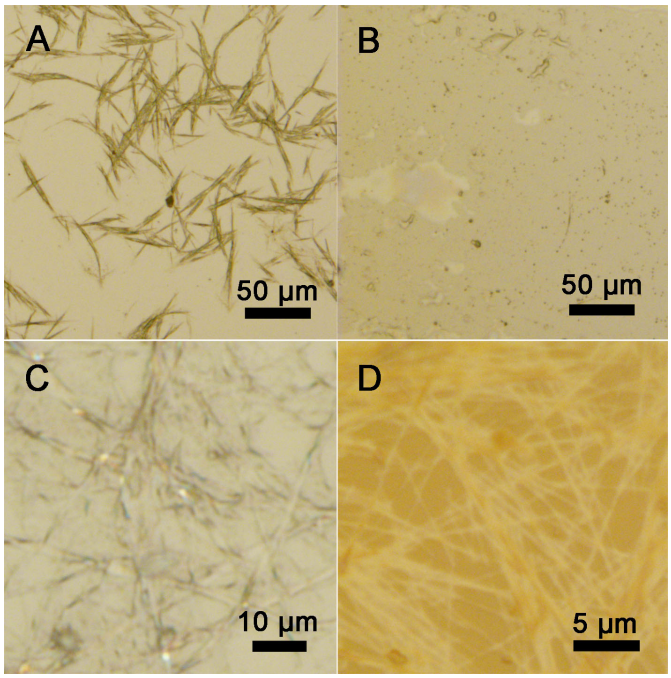


Figure S15. Optical microscopic pictures of the self-assemblies. (A) NTs self-assembled from compound **2** at 1 mM. (B) After addition of 2 equiv. of GSH to the solution of A. (C) After addition of 10 equiv. of H_2O_2 to the solution of B. (D) After addition of 1 equiv. of CUOOH to the solution of B.

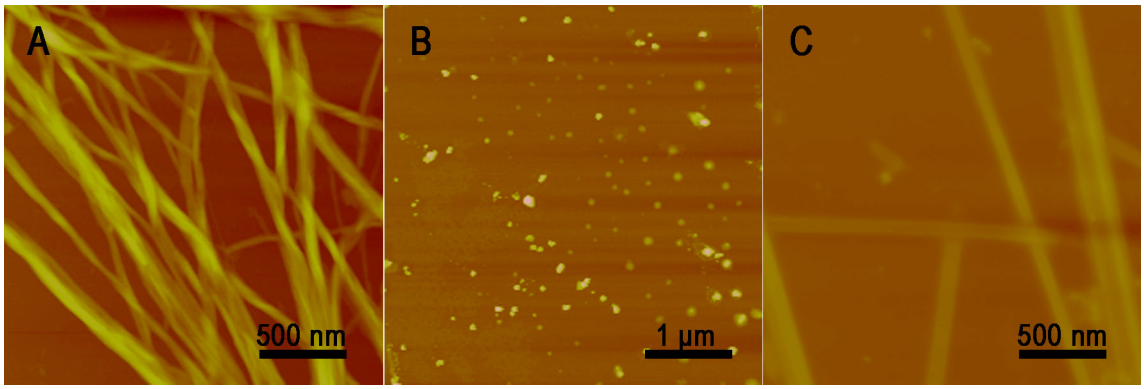


Figure S16. AFM images of the self-assemblies. (A) NTs self-assembled from compound **2** at 1 mM. (B) After addition of 2 equiv. of GSH to the solution of A. (C) After addition of 1 equiv. of CUOOH to the solution of B.

Table S1 The activities for the reduction of ROOH (250μM) by GSH (1.0 mM) in the presence of catalysts at pH 7.0 (50 mM PBS) and 37 ℃.

ROOH	Catalyst[a]	Activity[b] ($\mu M\ min^{-1}\ \mu mol^{-1}$)
CUOOH	NSs	0.00284
	NTs	0.108
H_2O_2	NSs	Not detected
	NTs	0.059

[a] The initial rate of reaction was corrected for the spontaneous oxidation.

[b] The concentration of catalysts was 0.2 mM.