

Supplementary Information

Construction of Smart Temperature-Responsive GPx Mimic Based on the Self-Assembly of Supra-Amphiphiles

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characterization of compound

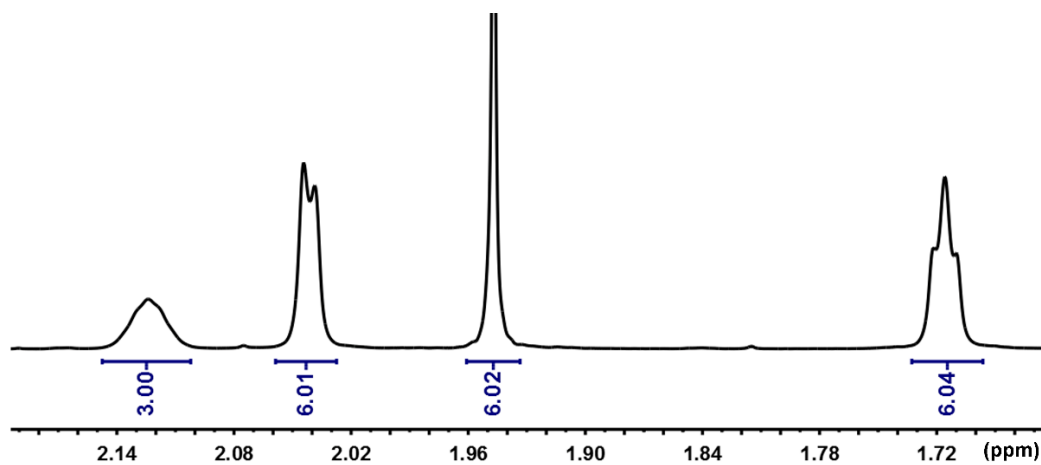


Figure S1. ^1H NMR spectrum of compound 1 in CDCl_3 .

^1H NMR (500 MHz, CDCl_3) δ 2.15-2.10 (3 H, -CH-), 2.05 (6 H, -CH₂-), 1.74-1.70 (6 H, -CH₂-), 1.95 (6 H, -CH₃).

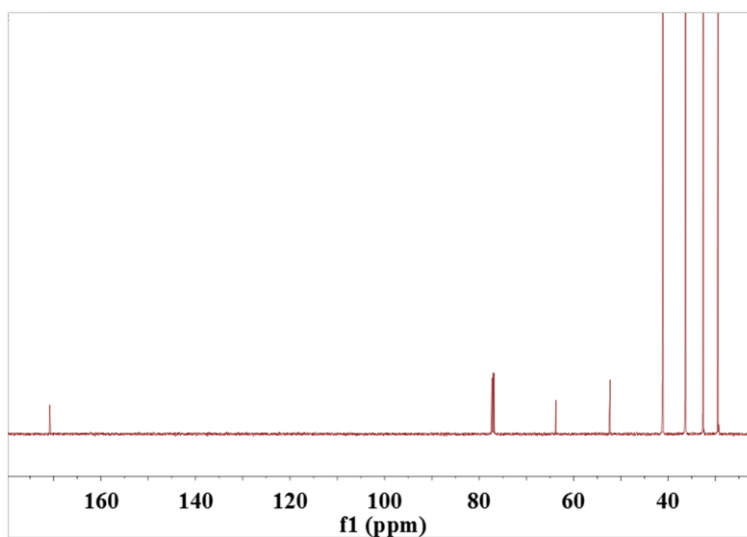


Figure S2. ^{13}C -NMR spectrum of compound 1 in CDCl_3

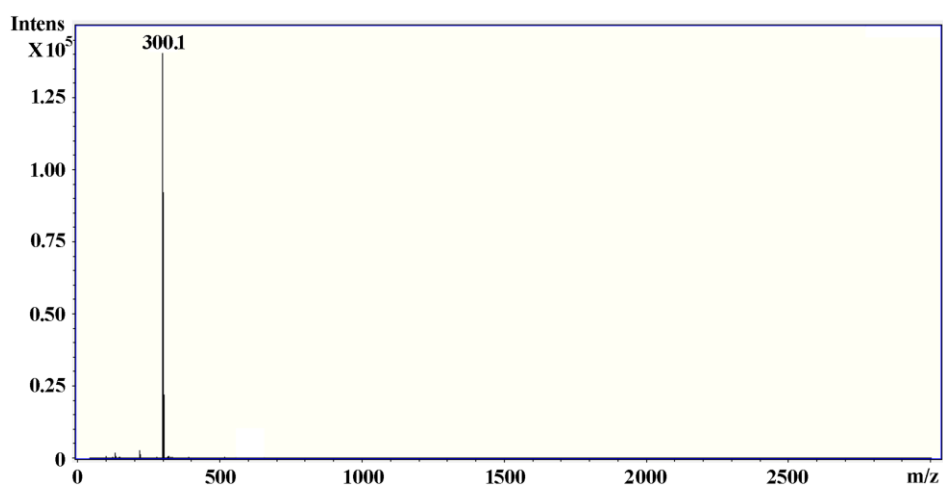


Figure S3. ESI-MS of compound 1

¹H NMR, C-NMR and ESI-MS results demonstrate that compound 1 has been successfully synthesized.

characterization of Ad-PNIPAM

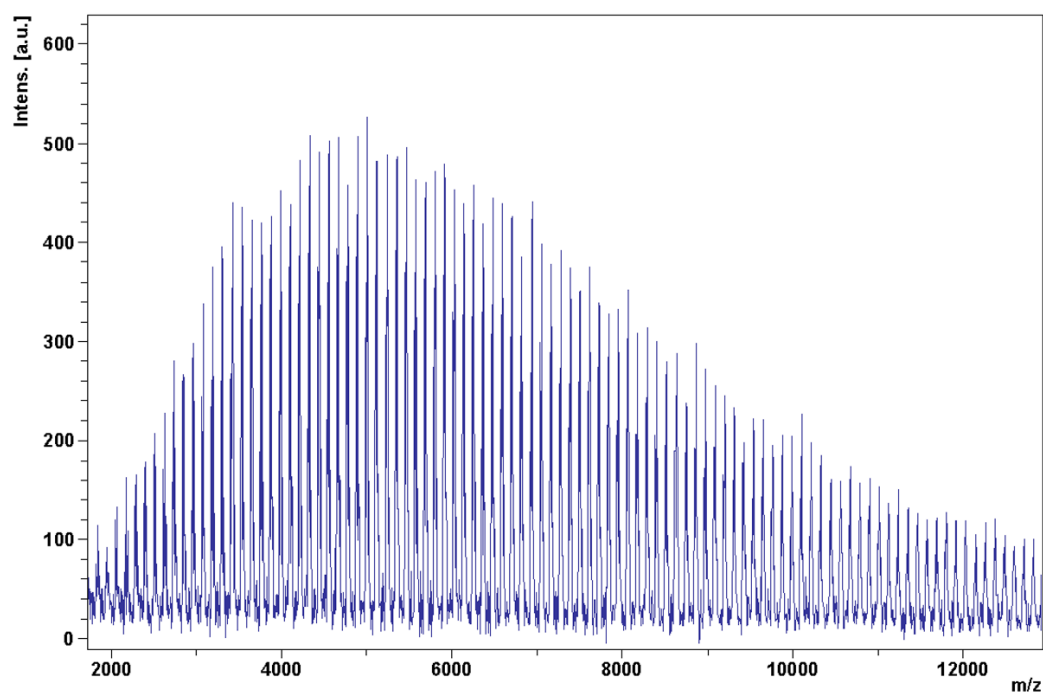


Figure S4. MALDI-TOF of Ad-PNIPAM

^1H NMR (500 MHz, DMSO-d_6) according to calculation based on the Integral area ratio of initiator and NIPAM, the degree of polymerization of Ad-PNIPAM was 65.

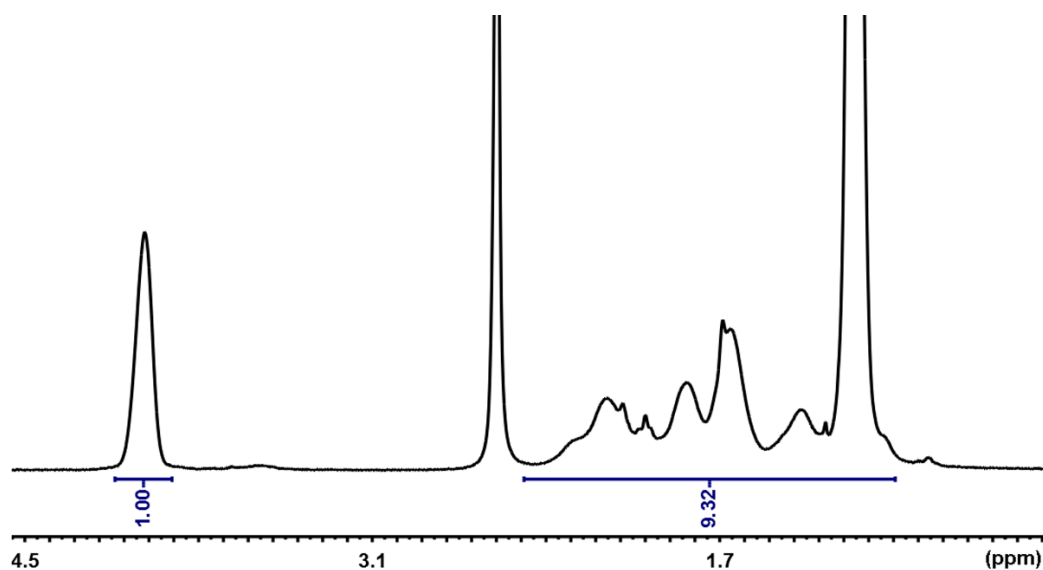


Figure S5. ^1H NMR spectrum of Ad-PNIPAM in DMSO-d_6 .

The number average molecular weight of Ad-PNIPAM is 7948 and PDI is 1.024 based on GPC trace.

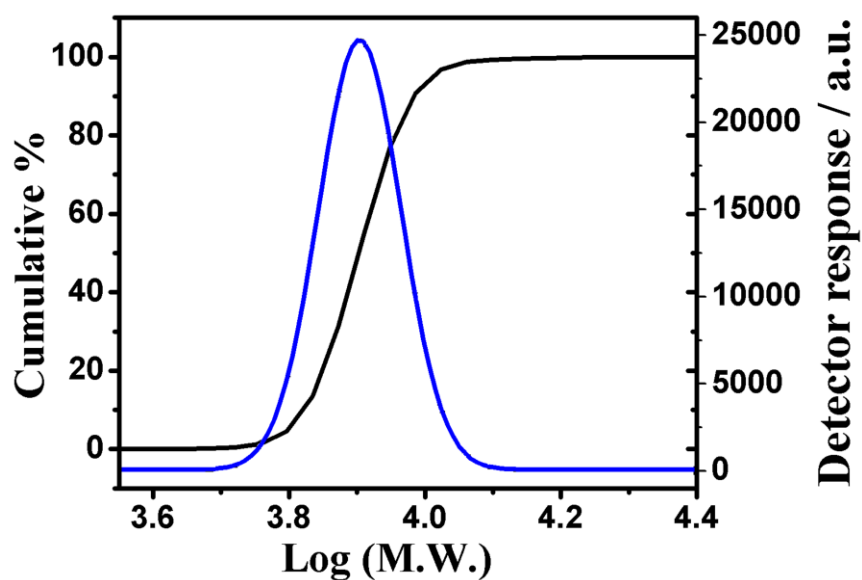


Figure S6. GPC trace for Ad-PNIPAM

characterization of CD-Se

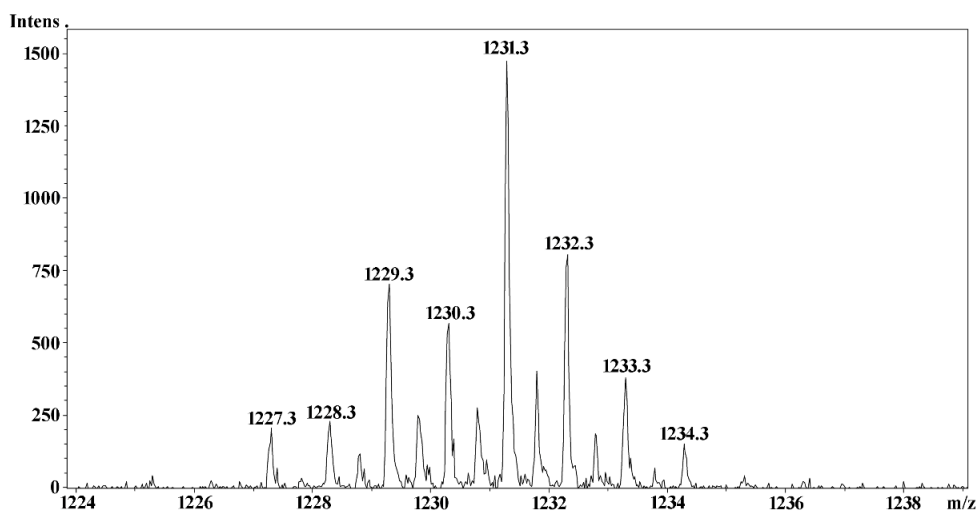


Figure S7. ESI-MS of CD-Se.

The ESI-MS image (Figure S7) shows that we have successfully prepared the CD-Se.

XRD analysis: One drop of sample solution (10^{-4} M) was placed onto a silicon surface at 37 °C. The cryo-dried sample was prepared as follow: the silicon wafer was dipped into sample at 37 °C which was plunged into liquid nitrogen immediately. The redundant water was removed by a freeze-drier. This cryo-dried was used for XRD measurements. The Bragg peak is obtained from the XRD data and the bilayer thickness can be calculated according to the Bragg equation.

characterization of the nanoenzyme

The method of obtaining the cryo-dried samples for SEM and TEM was similar to XRD. From the SEM images in Figure S8, different morphology can be seen at 25 °C and 37 °C. At 25 °C (below the LCST), only host-guest recognition occurred, hardly any vesicular morphology could be observed; while at 37 °C (above the LCST), the complex became amphiphatic and further self-assembled into vesicle.

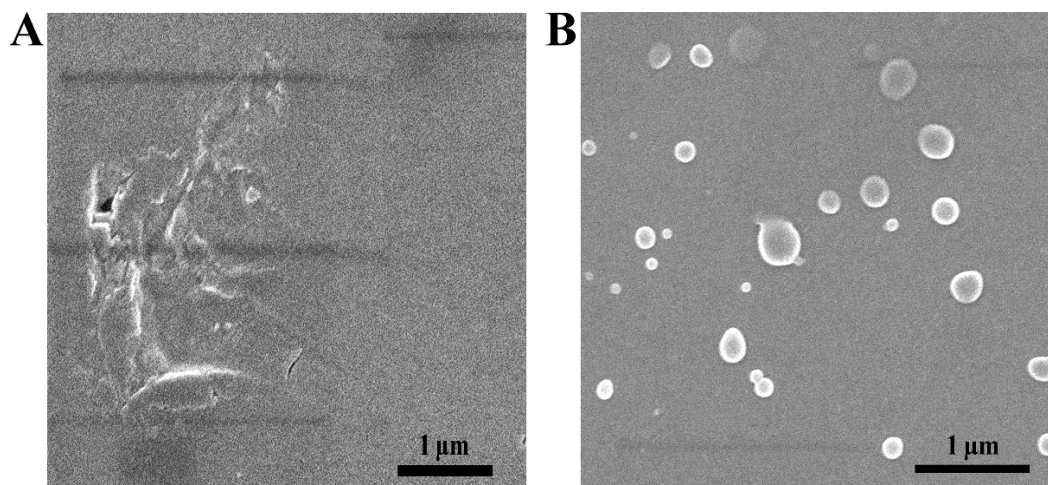


Figure S8. SEM image of the complex. A. at 25 °C; B. at 37 °C, respectively at the concentration of 0.1 mM.

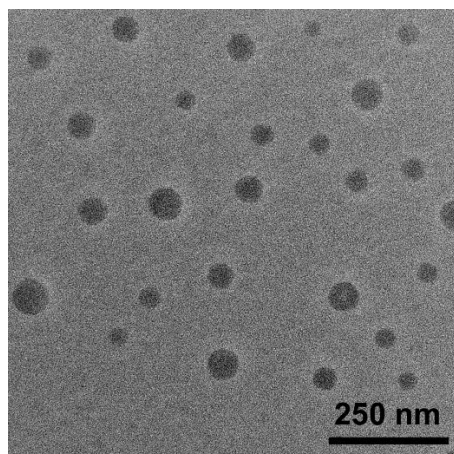


Figure S9. TEM image of the guest molecule Ad-PNIPAM at 37 °C as a contrast at concentration of 0.1 mM.

Activity determination of nanoenzymes

The activities were given assuming that one molecule catalytic center (Se) on the GPx mimic models as one active site of enzyme. The initial rates (v_0) for the reduction of H_2O_2 by GSH at different temperatures were determined by monitoring the UV absorption at 340 nm due to the disappearance of NADPH absorption. (Figure S7). The concrete numerical value of the catalytic activity is $1.24 \mu M \text{ min}^{-1}$ and $19.88 \mu M \text{ min}^{-1}$, respectively.

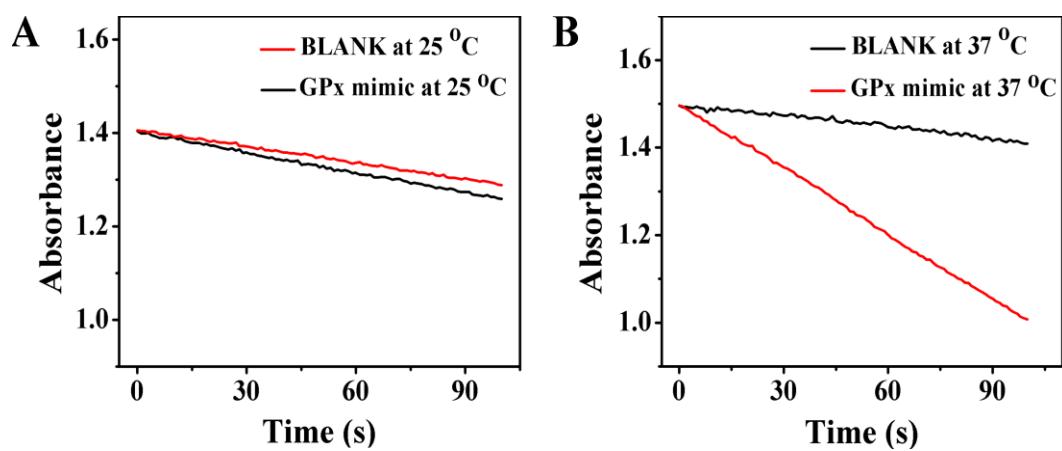


Figure S10. The real-time catalytic plots of absorbance versus time during the catalytic reduction. A. at 25 °C; B. at 37 °C.

Activity determination of nanoenzymes

Catalytic behaviour compared with other systems

Table S1. The initial rates (v_0) and activities for the reduction of hydroperoxides (ROOH) by ArSH in the presence of artificial GPx at pH 7.0 (50 mM, PBS).

number	Abbreviation for the artificial enzyme	ROOH	v_0 ($\mu\text{M min}^{-1}$)
a ¹	Se-enzyme	H ₂ O ₂	0.042
b ²	NTs	H ₂ O ₂	0.059
C ³	SGPxmax	CUOOH	18.75

Notes and references

1. Z. Huang, Q. Luo, S. Guan, J. Gao, Y. Wang, B. Zhang, L. Wang, J. Xu, Z. Dong and J. Liu, *Soft Matter*, 2014, **10**, 9695-9701.
2. J. Li, C. Si, H. Sun, J. Zhu, T. Pan, S. Liu, Z. Dong, J. Xu, Q. Luo and J. Liu, *Chem. Commun.*, 2015, **51**, 9987-9990.
3. Y. Yin, S. Jiao, C. Lang and J. Liu, *RSC Adv.*, 2014, **4**, 25040-25050.