A Hydrogen Peroxide-Responsive Supramolecular Pseudopolyrotaxane Driven by Pillararene-Based Molecular Recognition and Metal-Ligand Interaction

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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. **SeP5**[S1] and **G**[S2] were prepared according to published procedures. ^{1}H NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer. The 2D DOSY NMR spectrum was collected on a Bruker Avance DMX 500 using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Isothermal titration calorimetry (ITC) experiment was performed on a VP-ITC micro-calorimeter (Microcal, USA). Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscomeer at 298 K.

2. Synthesis of ***SeP5***, ***SeOP5*** and ***G***

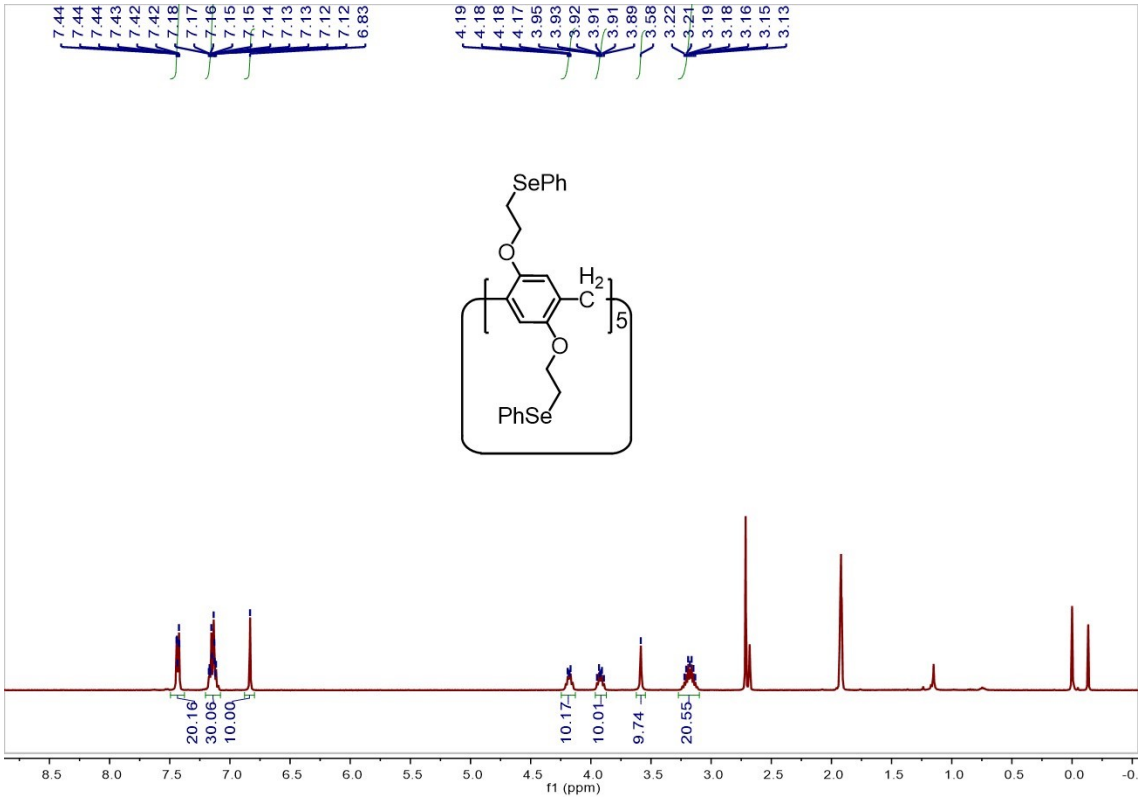


Fig. S1 ^{1}H NMR spectrum (400 MHz, acetone-d_6, 293K) of **SeP5**.[S1]

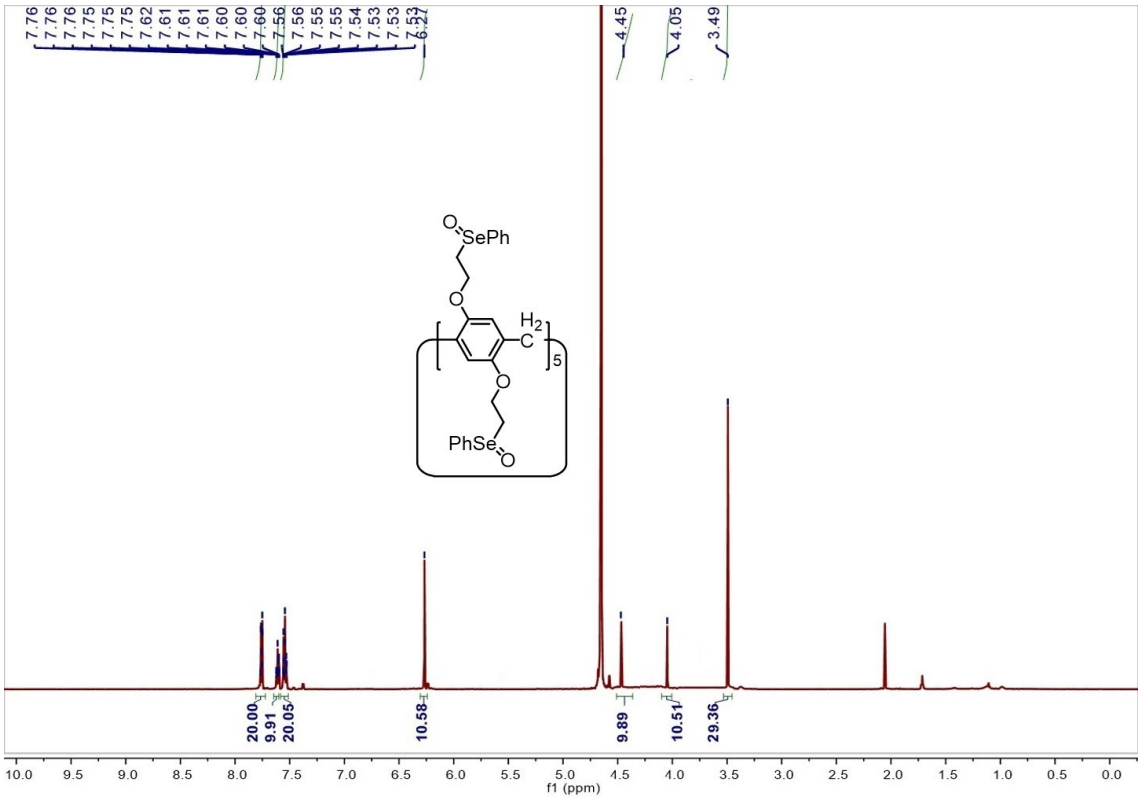


Fig. S2 ^{1}H NMR spectrum (400 MHz, D_2O, 293K) of **SeOP5**.[S1]

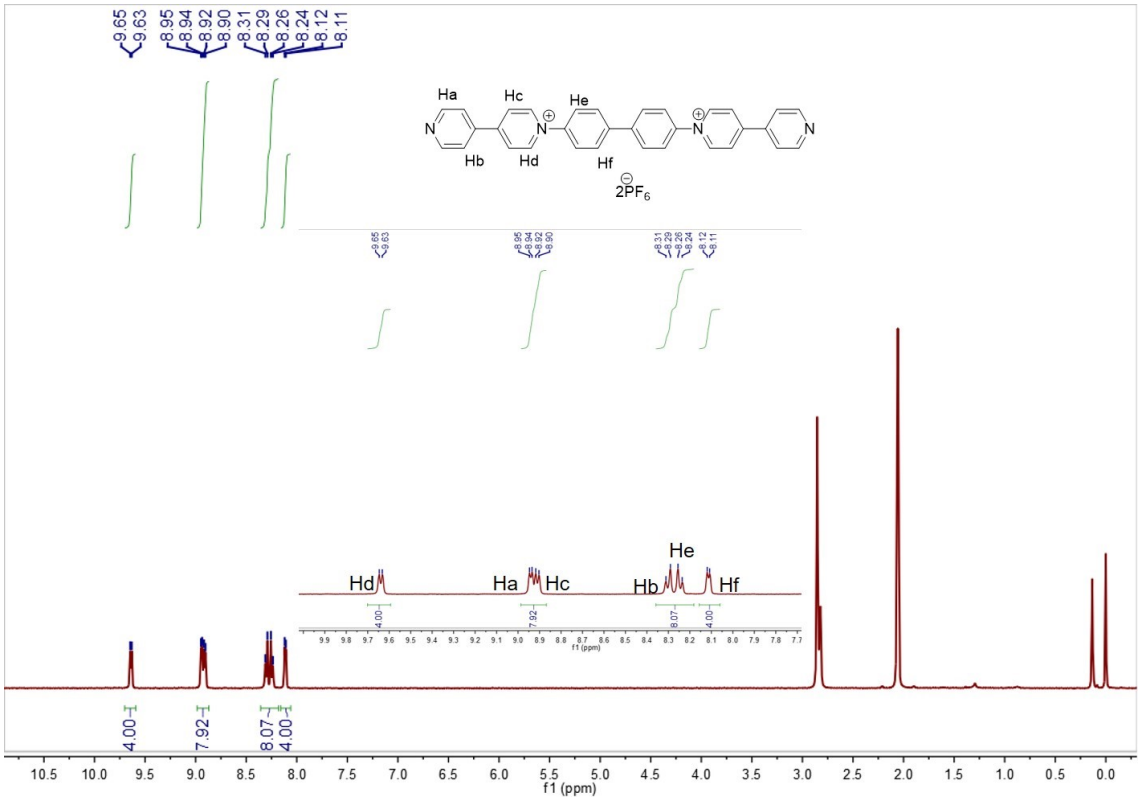


Fig. S3 ^{1}H NMR spectrum (400 MHz, acetone-d_6, 293K) of **G**.[S2]

*3. Host–guest complexation between **SeP5** and **G***

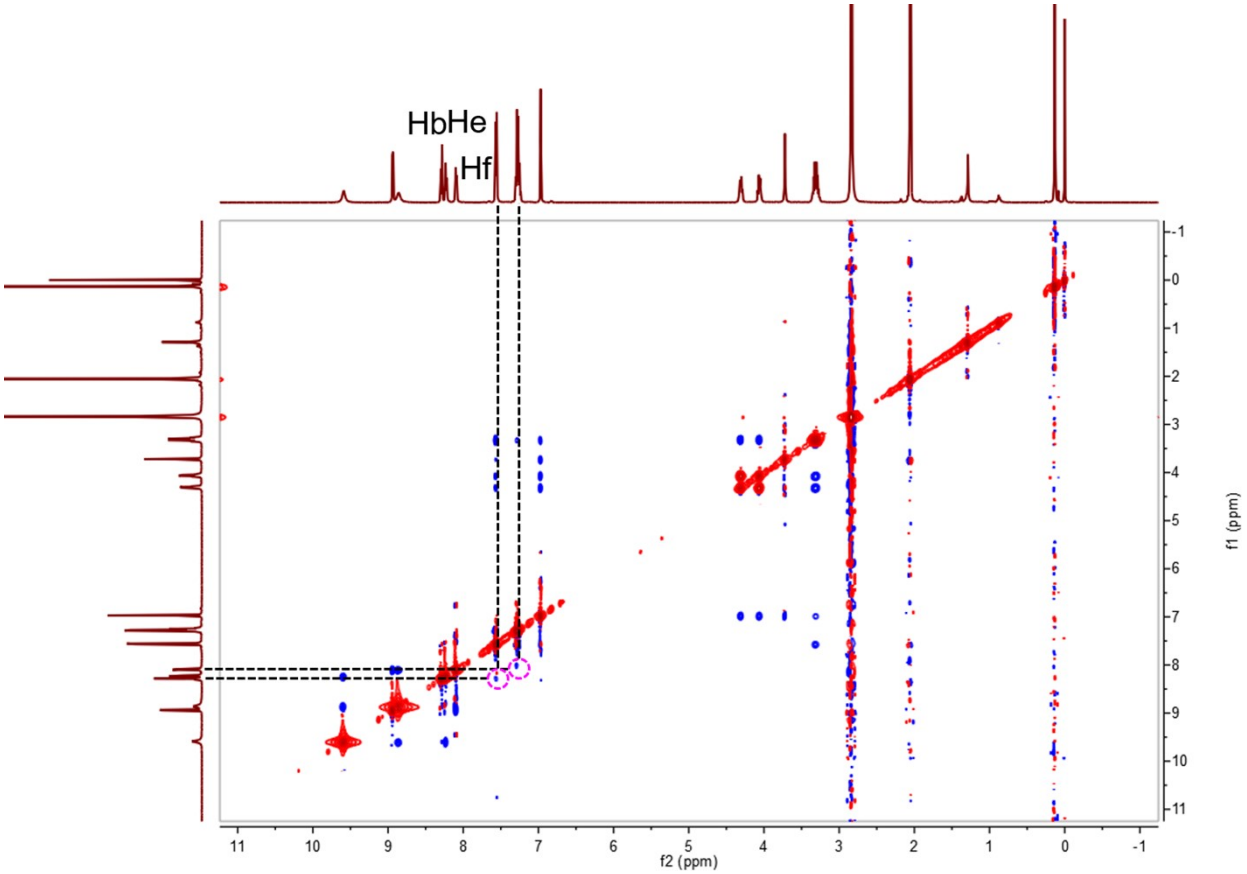


Fig. S4 2D NOESY spectrum (500 MHz, acetone-d_6, 293 K) of **SeP5** (10.0 mM) and **G** (10.0 mM).

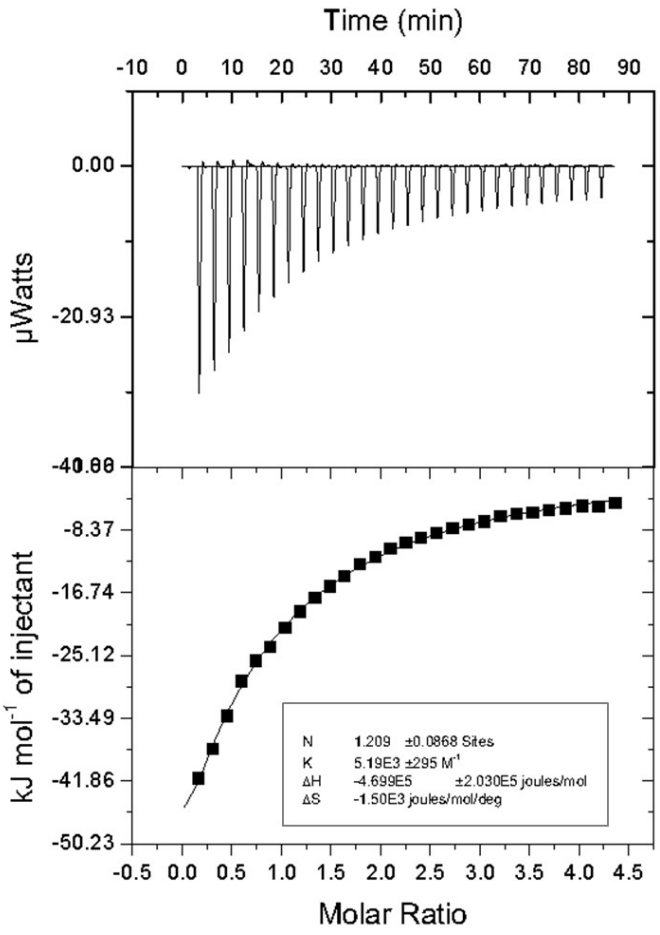


Fig. S5 Microcalorimetric titration of **G** with **SeP5** in acetone at 298 K. (Top) Raw ITC data for 29 sequential injections (10.0 µL per injection) of a **G** solution (2.00 mM) into a **SeP5** solution (0.100 mM). (Bottom) Net reaction heat obtained from the integration of the calorimetric traces.

*4. H_2O_2-responsiveness of **SeP5** and **G** complex*

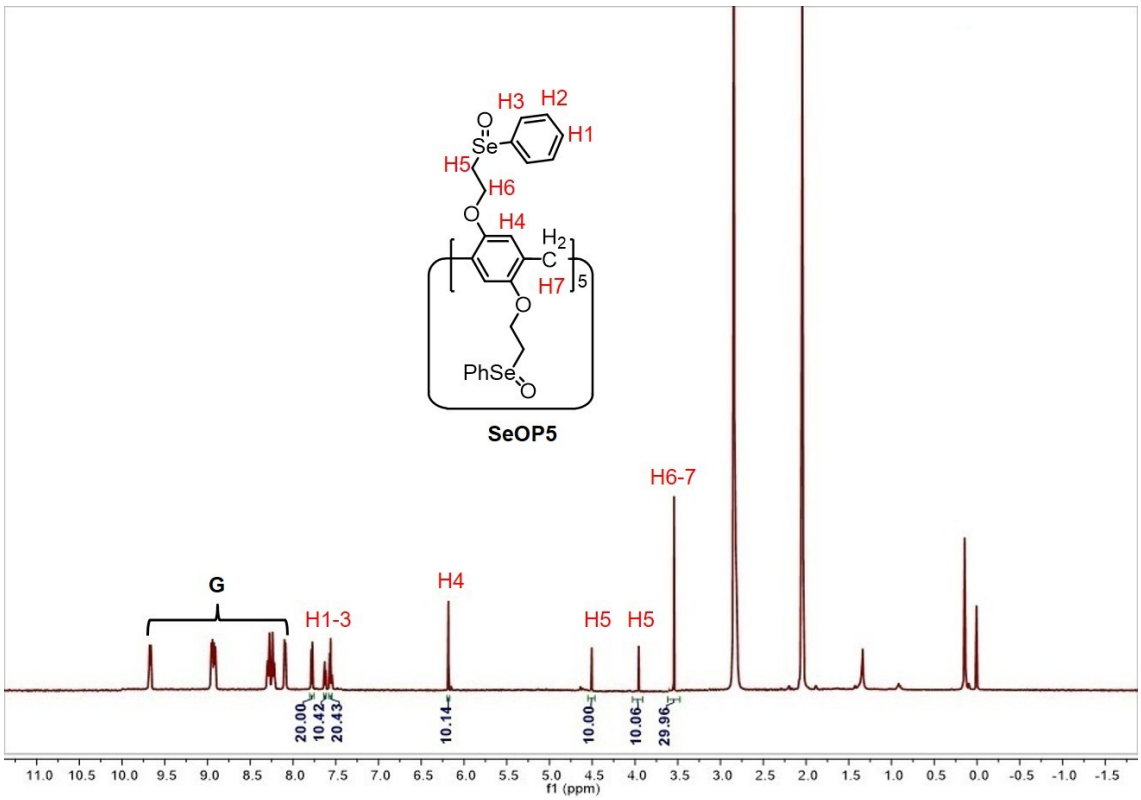


Fig. S6 ^{1}H NMR spectrum (400 MHz, acetone-d_6, 293K) of **SeP5** and **G** complex after adding 30% H_2O_2.

*5. H_2O_2-responsiveness of poly-pseudorotaxane **SeP5-G-Ag***

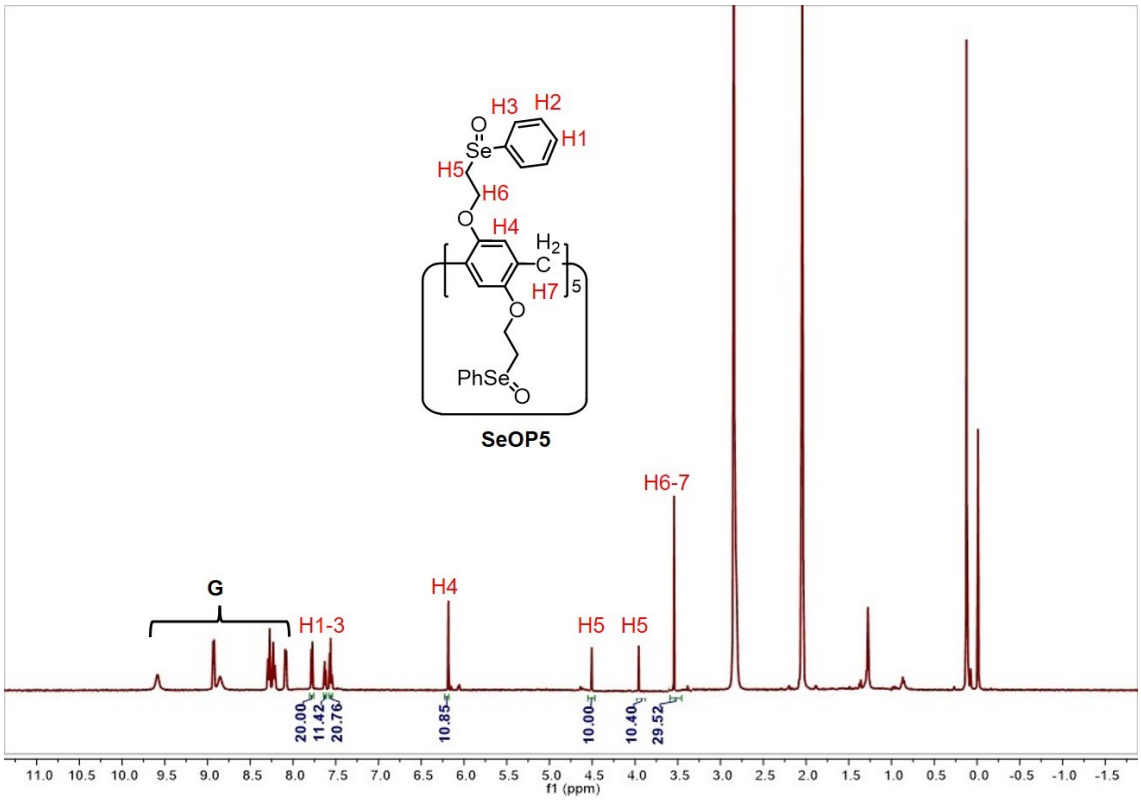
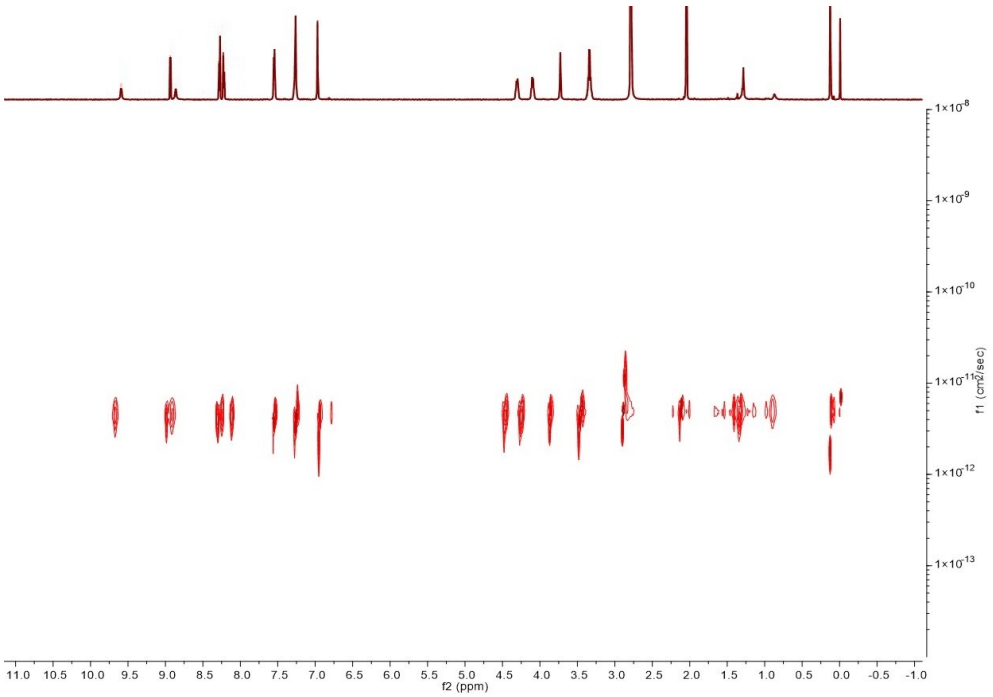
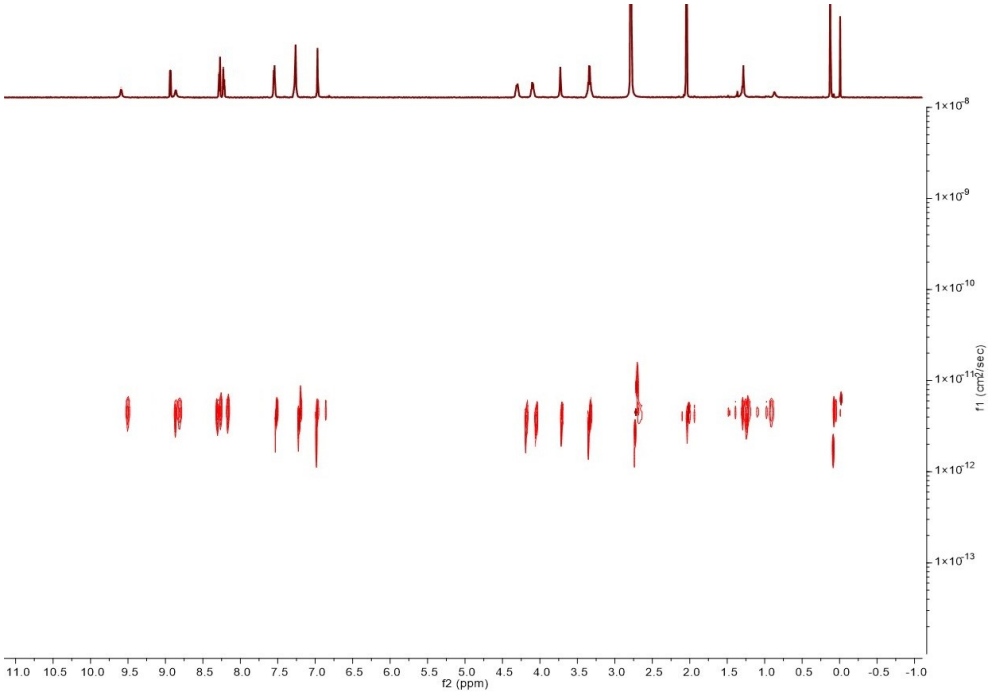


Fig. S7 ^{1}H NMR spectrum (400 MHz, acetone-d_6, 293K) of **SeP5-G-Ag** after adding 30% H_2O_2.

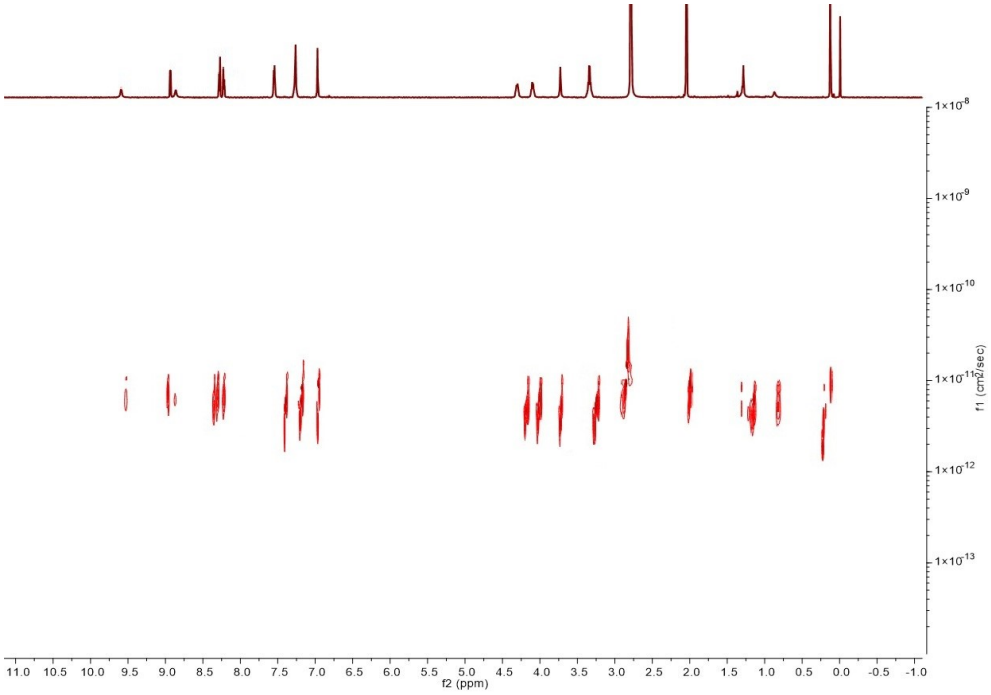
*6. DOSY NMR spectra of **SeP5-G-Ag** at different concentrations*



(a)



(b)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f1 (cm2/sec)
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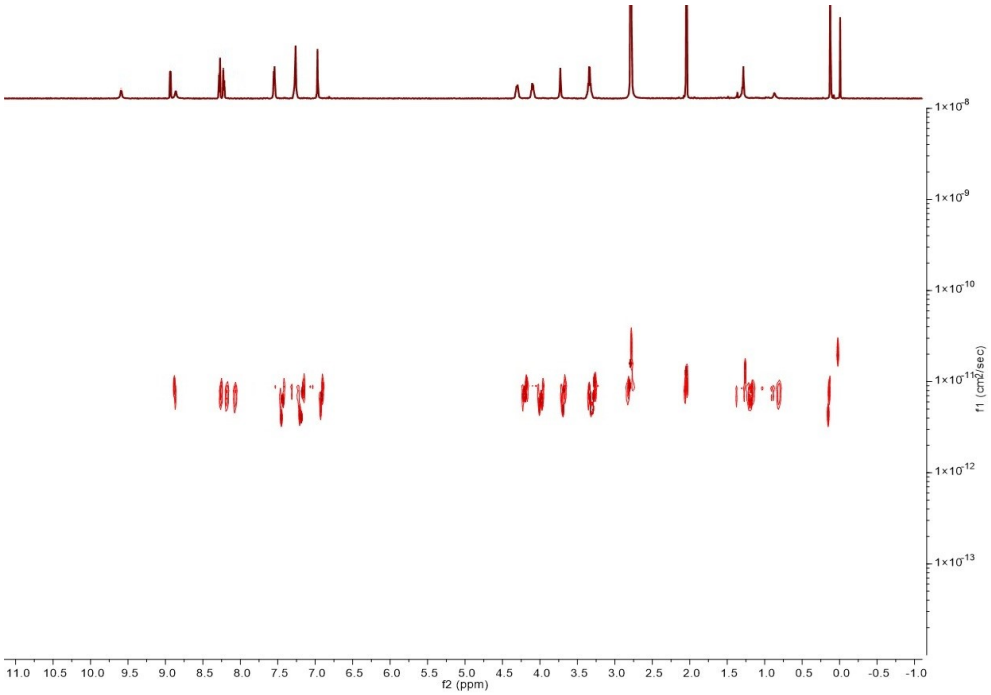
f2 (ppm)

(c)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f1 (cm2/sec)
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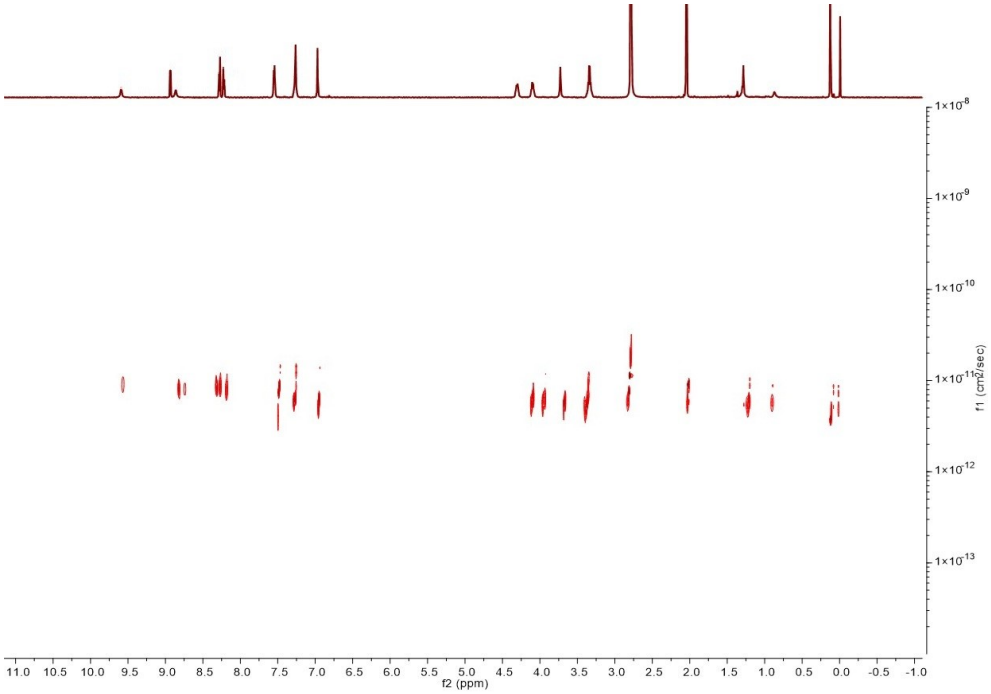
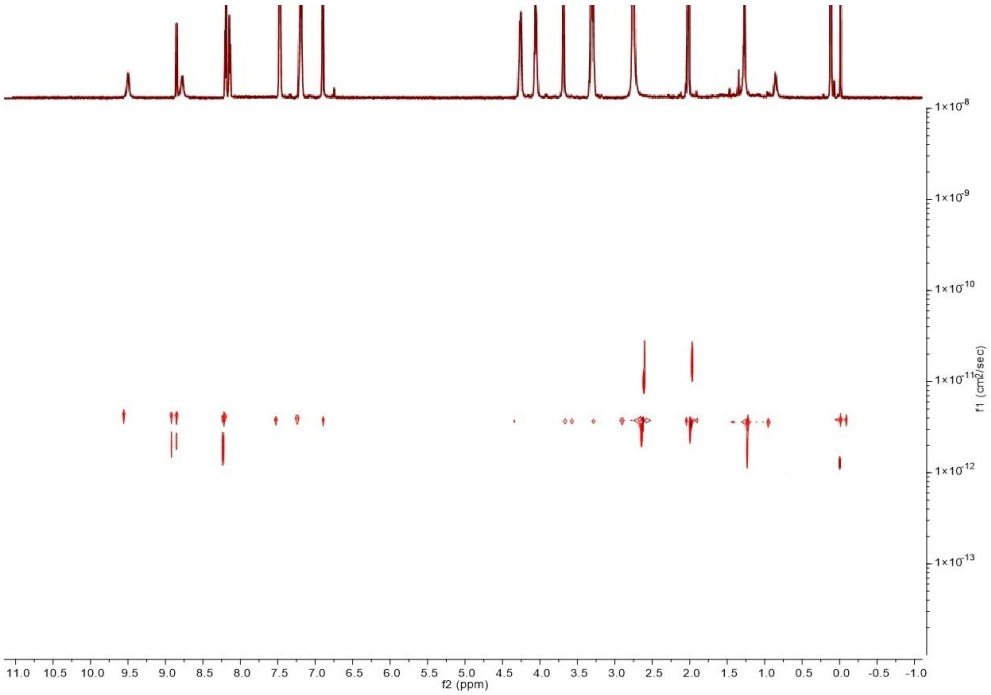
f2 (ppm)

(d)



(e)



(f)

Fig. S8 DOSY NMR spectra of **SeP5-G-Ag** (500 MHz, acetone-d_6, 298 K) at different concentrations: (a) 100.0 mM; (b) 75.0 mM; (c) 50.0 mM; (d) 25.0 mM; (e) 12.50 mM; (f) 6.0 mM.

7. The host–guest control experiment

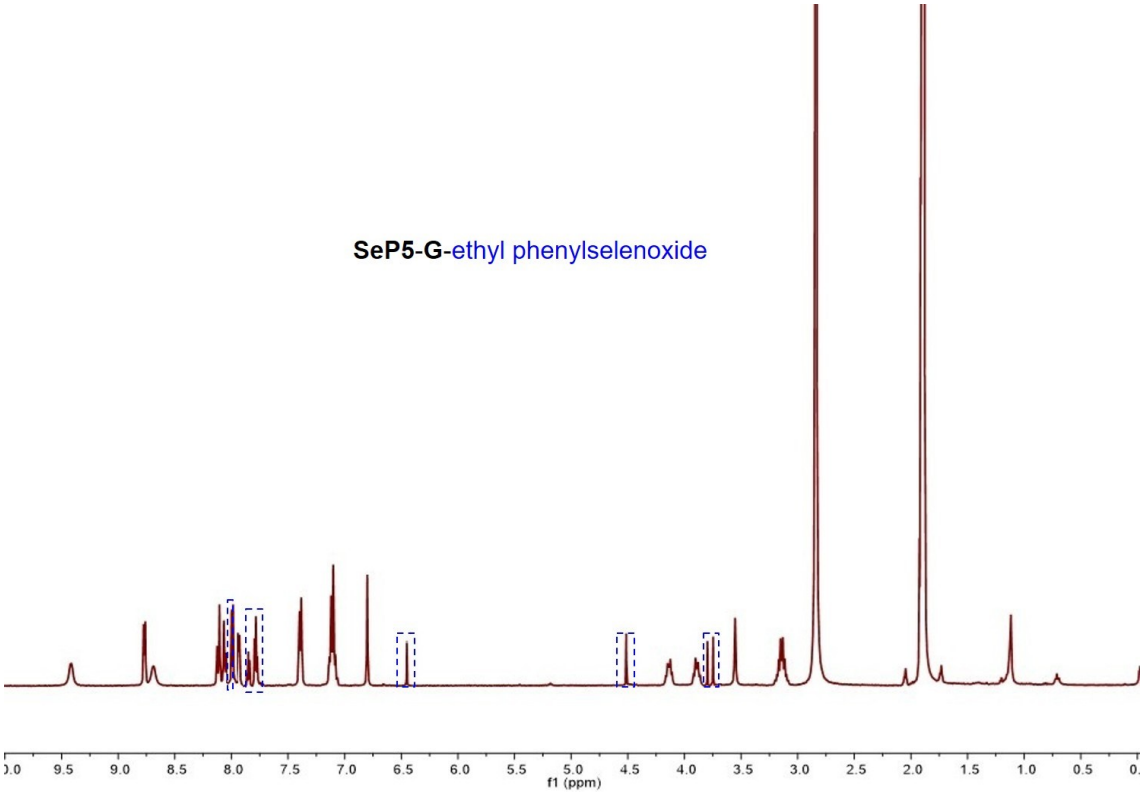


Fig. S9 ^{1}H NMR spectrum (400 MHz, acetone-d_6, 293K) of **SeP5-G** after adding 10 equiv. ethyl phenylselenoxide.

*8. H_2O_2-responsiveness of **G-Ag***

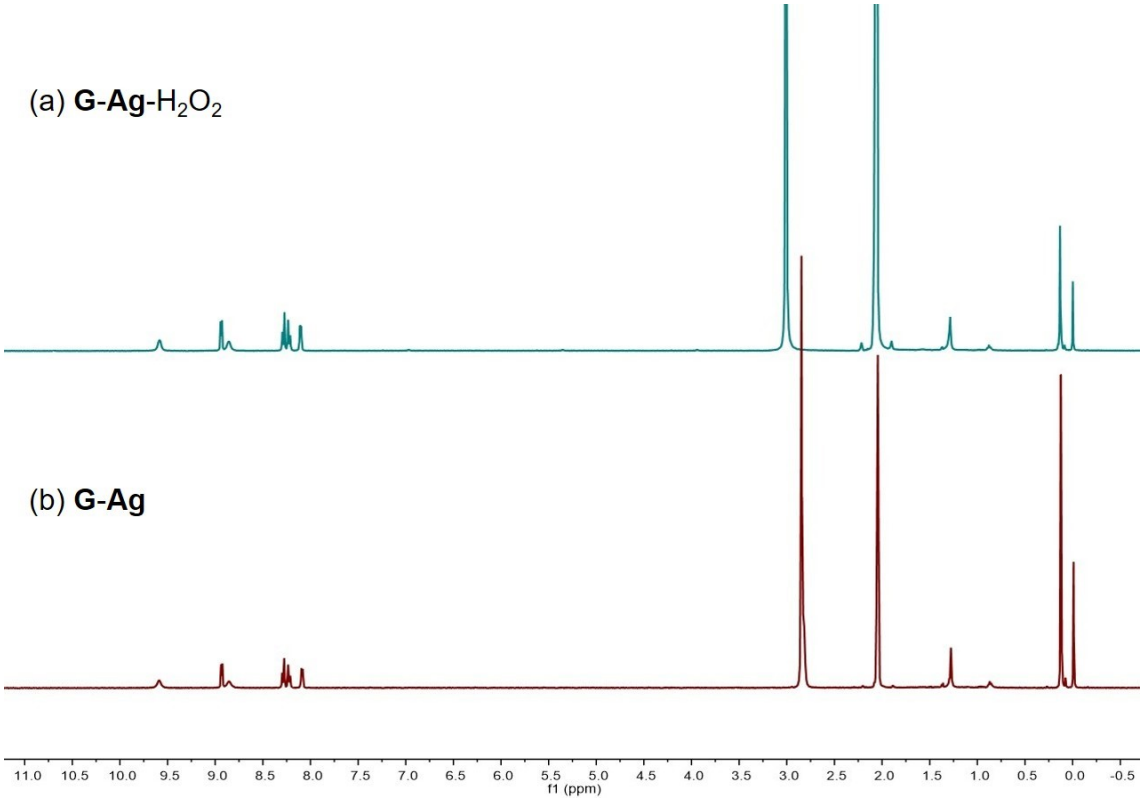


Fig. S10 ^{1}H NMR spectrum (400 MHz, acetone-d_6, 293K) of **G-Ag** (bottom) after adding 30% H_2O_2 (top).

References

S1. Y. Zhou, K. Jie and F. Huang, *Chem. Commun.*, 2017, **53**, 8364.

S2 S. K. Samanta, K. G. Bray and L. Isaacs, *Chem. Commun.*, 2017, **53**, 2756.