

## Supporting Information for

### Structure-Directing Role of Phosphonate in the Synthesis of High-Nuclearity Silver(I) Sulfide-Ethynide-Thiolate Clusters

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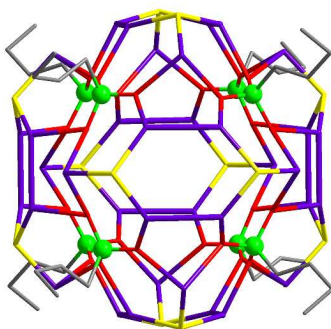
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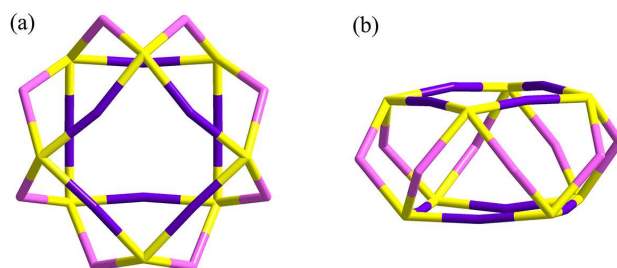
Email: [xieyp@hust.edu.cn](mailto:xieyp@hust.edu.cn) (Y.-P. Xie); [lux@hust.edu.cn](mailto:lux@hust.edu.cn) (X. Lu).

#### X-ray Crystallography.

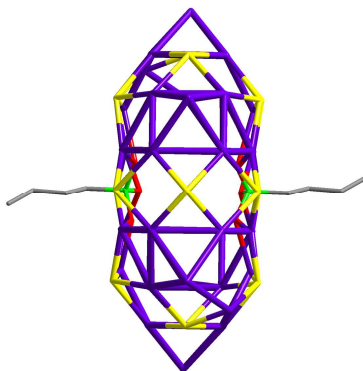
Crystal data were collected on a Bruker D8 Quest diffractometer with Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods with SHELXS-97<sup>S1</sup> and refined by full-matrix least-squares techniques using the SHELXL-97<sup>S2</sup> program within WINGX<sup>S3</sup> and SHELXL-2014 program<sup>S4</sup> within SHELXLE.



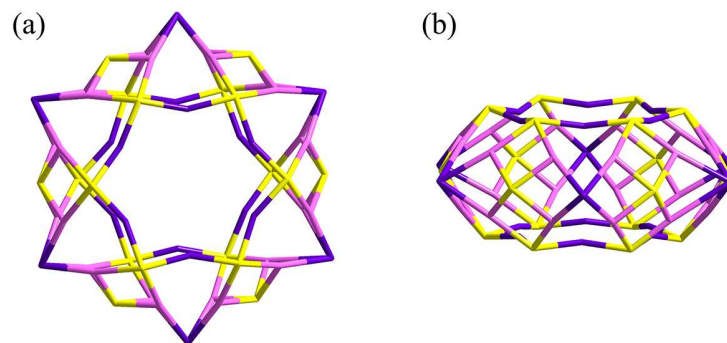
**Figure S1.** The  $[\text{Ag}_{36}(\text{}^4\text{BuC}\equiv\text{C})_{12}(\text{}^4\text{BuS})_{12}(\text{}^4\text{BuPO}_3)_2(\text{}^4\text{BuPO}_3\text{H})_6]^{2+}$  shell structure of **1** with all peripheral  $\text{}^4\text{Bu}$  groups omitted for clarity, and only  $\text{}^4\text{Bu}$  groups from *n*-butylphosphonates are shown. Color code: Ag (shell), violet; S (thiolate), yellow; P, green; O, red; C, gray.



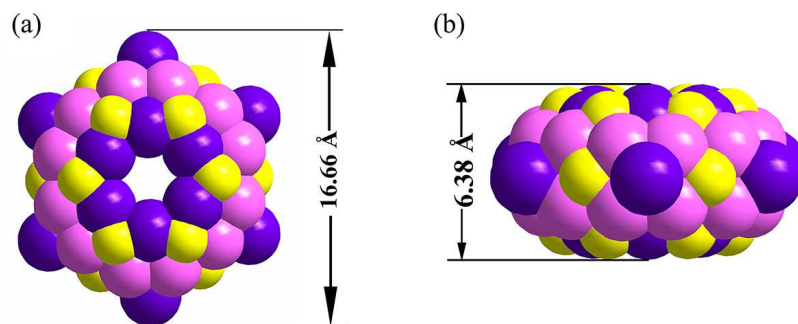
**Figure S2.** (a) Top view of the  $\text{Ag}_{16}\text{S}_8$  shell structure of **2**. (b) Side view of the  $\text{Ag}_{16}\text{S}_8$  shell structure. Color code: Ag (top and bottom layer of  $\text{Ag}_4\text{S}_4$ ), violet; Ag (middle  $\text{Ag}_8$  ring), pink; S (thiolate), yellow.



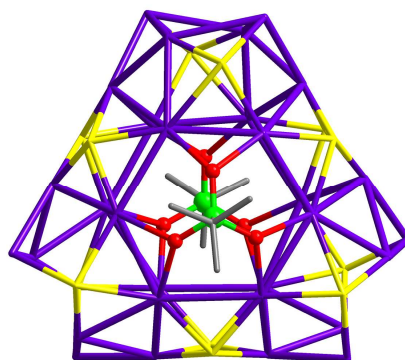
**Figure S3.** Side view of the  $[\text{Ag}_{42}(\text{}^4\text{BuC}\equiv\text{C})_{12}(\text{}^4\text{BuS})_{18}(\text{}^4\text{BuPO}_3)(\text{}^4\text{BuPO}_3\text{H})]^{9+}$  shell structure of **3** with all peripheral  $\text{}^4\text{Bu}$  groups omitted for clarity, and only  $\text{}^4\text{Bu}$  groups from *n*-butylphosphonates are shown. Color code: Ag (shell), violet; S (thiolate), yellow; P, green; O, red; C, gray.



**Figure S4.** (a) Top view of  $\text{Ag}_{42}\text{S}_{18}$  shell arranged with five representative macrocycles parallel  $\text{Ag}_6\text{S}_6\text{-Ag}_{12}\text{-Ag}_6\text{S}_6\text{-Ag}_{12}\text{-Ag}_6\text{S}_6$  of **3**. (b) side view of the  $\text{Ag}_{42}\text{S}_{18}$  shell in **3**. Color code: (layer of  $\text{Ag}_6\text{S}_6$ ), violet; Ag (layer of  $\text{Ag}_{12}$  ring), pink; S (thiolate), yellow.



**Figure S5.** (a) Space-filling view of the  $\text{Ag}_{42}\text{S}_{18}$  shell cluster in **3**. (b) Space-filling view of the  $\text{Ag}_{42}\text{S}_{18}$  shell cluster along the side. Color code: (layer of  $\text{Ag}_6\text{S}_6$ ), violet; Ag (layer of  $\text{Ag}_{12}$  ring), pink; S (thiolate), yellow.



**Figure S6.** The  $[\text{Ag}_{30}(\text{'BuC}\equiv\text{C})_6(\text{'BuS})_{12}(\text{'BuPO}_3)(\text{'BuPO}_3\text{H})(\text{hfac})_6]^{3+}$  shell structure of **4** with all peripheral  $\text{hfac}^-$ ,  $\text{'Bu}$  groups omitted for clarity, and only  $\text{'Bu}$  groups from *tert*-butylphosphonates are shown. Color code: Ag, violet; S, yellow; P, green; O, red; C, gray.

## FT-IR spectra

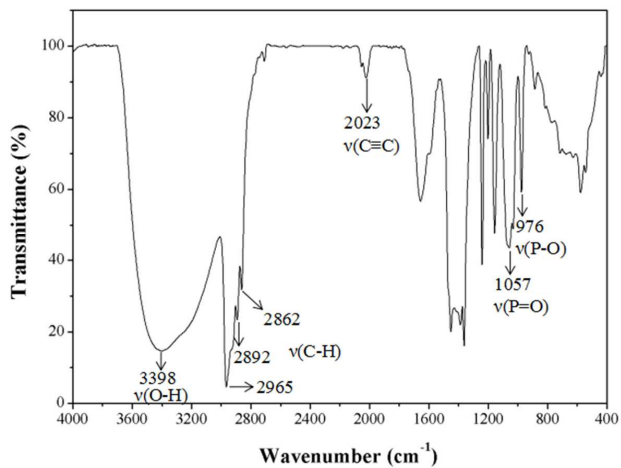


Figure S7. IR spectrum of compound 1

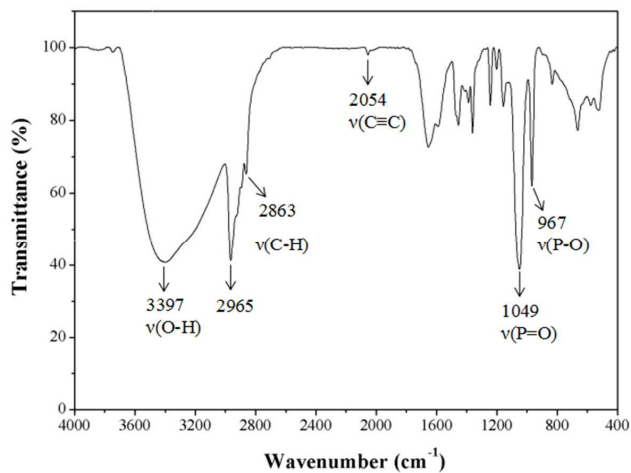


Figure S8. IR spectrum of compound 2

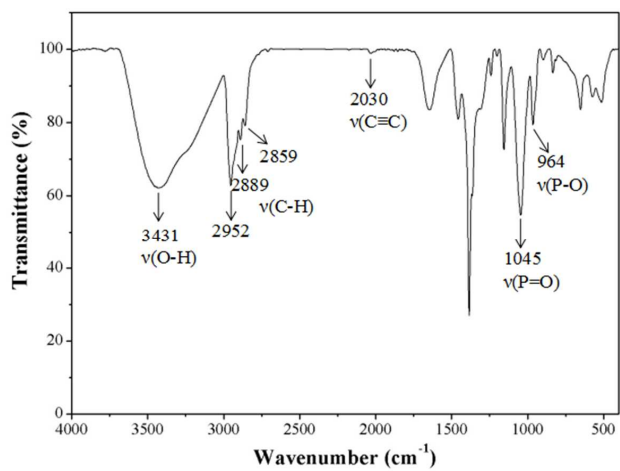
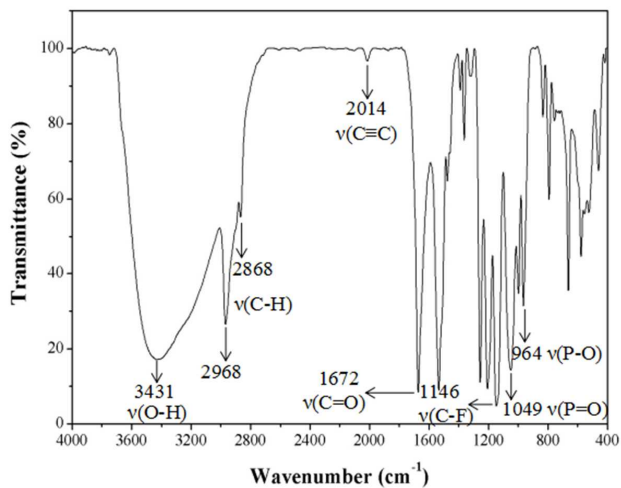


Figure S9. IR spectrum of compound 3



**Figure S10.** IR spectrum of compound **4**

## References

- (S1) Sheldrick, G. M. *SHELX-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, **1997**.
- (S2) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, **1997**.
- (S3) Farrugia, L. J. *WINGX, A Windows Program for Crystal Structure Analysis*; University of Glasgow: Glasgow, UK, **1988**.
- (S4) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.