

# Supporting Information

## Three-dimensional Nets from Star-Shaped Hexakis(arylthio)triphenylene Molecules and Silver(I) Salts

*Kunhao Li<sup>a</sup>, Zhengtao Xu<sup>\*b</sup>, Hanhui Xu<sup>a</sup>, Patrick J. Carroll<sup>c</sup> and James C. Fetting<sup>d</sup>*

<sup>a</sup> Department of Chemistry, the George Washington University, 725 21st Street NW,  
Washington, DC 20052.

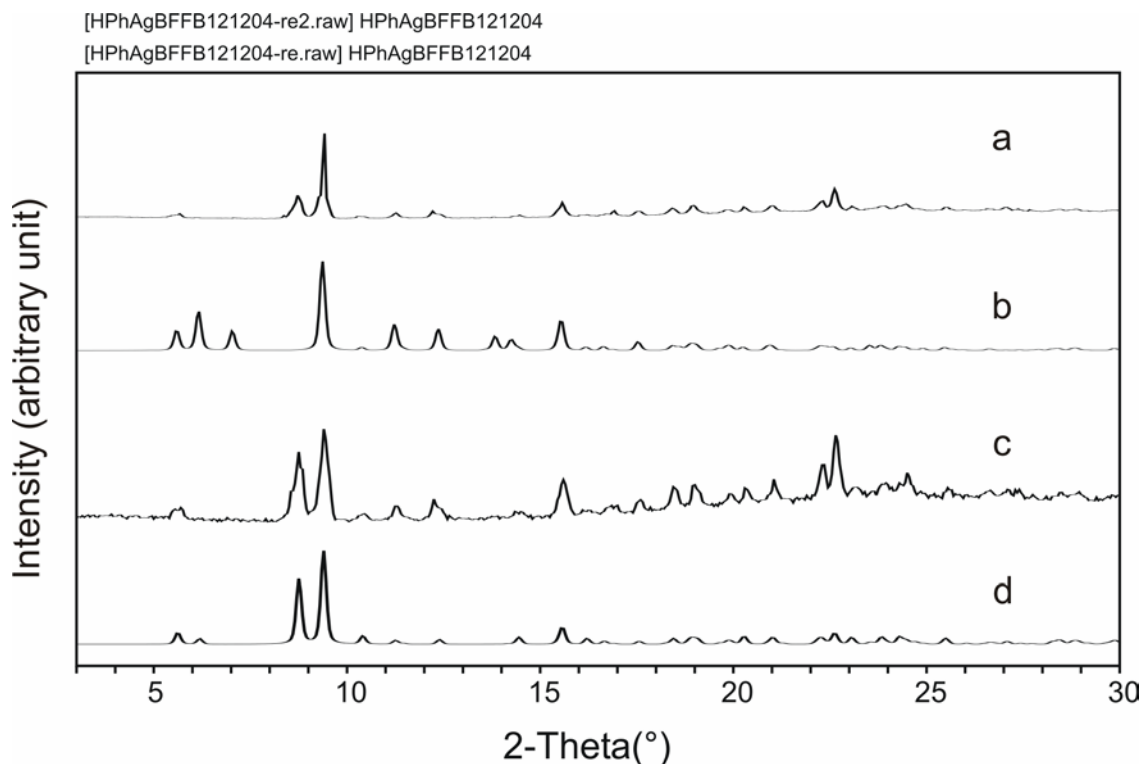
<sup>b</sup> Department of Biology and Chemistry, City University of Hong Kong, 83 Tat Chee  
Avenue, Kowloon, Hong Kong, P. R. China.

<sup>c</sup> P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of  
Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323.

<sup>d</sup> Department of Chemistry and Biochemistry, University of Maryland, College Park, MD  
20742.

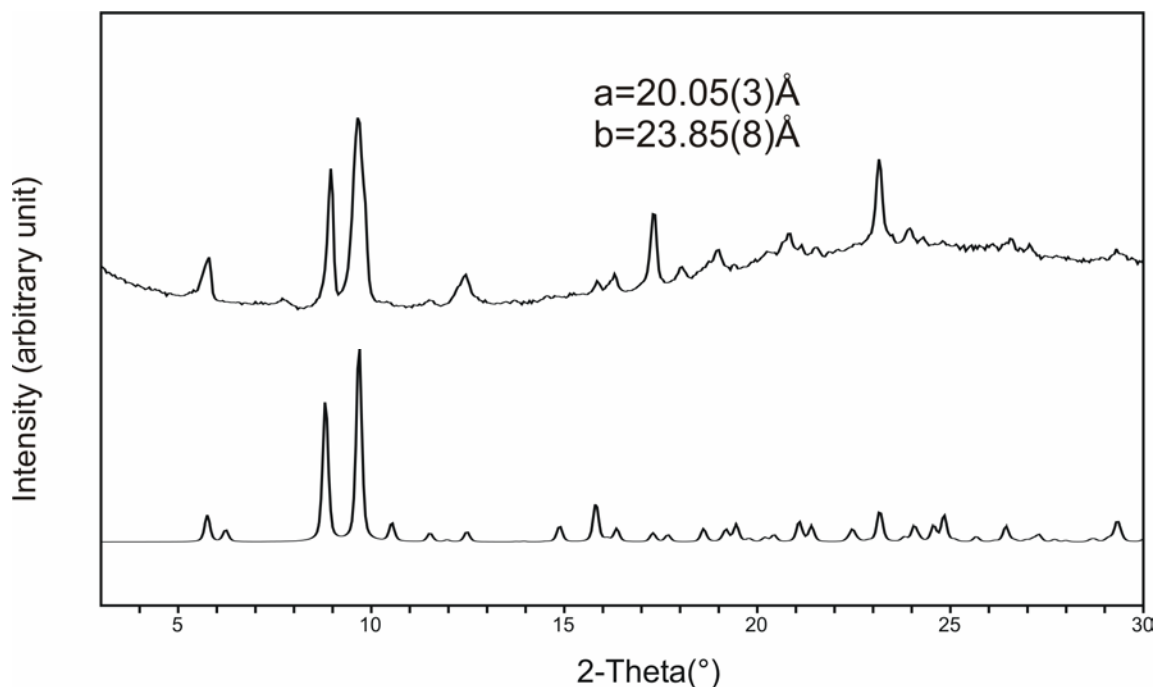
zhengtao@cityu.edu.hk

<sup>\*</sup> Author to whom correspondence should be addressed.

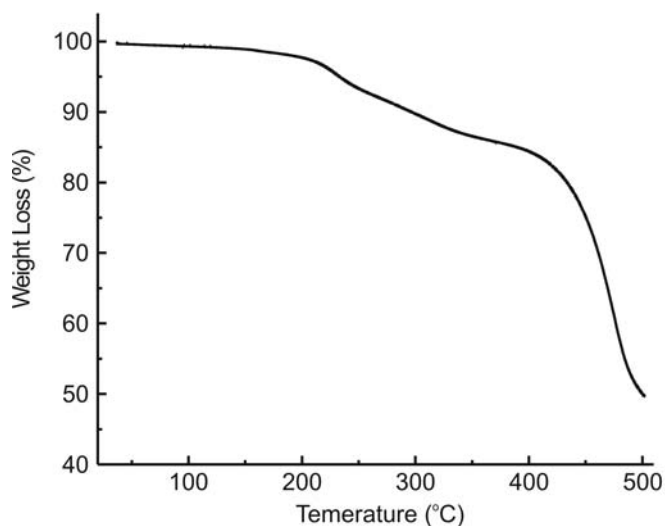


**Figure S1.** X-ray diffraction patterns (Cu K $\alpha$ ,  $\lambda = 1.5418$  Å) for bulk samples of **1a**. a) calculated from the full single crystal structure of **1a**, including the guest molecules of THF and acetone (single crystal data collected at 143 K). The calculation was done using JADE, Materials Data, Inc., with the preferred orientation for the crystallites was set at 0.6 for the (112) direction [meaning 40% more crystallites of **1** are oriented along the (001) direction when compared to the randomly oriented state]. b) observed at room temperature for the as-synthesized crystals with minimal exposure in air. c) calculated from the single crystal structure of **1a** without the guest molecules of THF and acetone [same orientation preference as in a]. d) observed for the same sample exposed to air for two days at room temperature.

**Comments on Figure S1.** Comparison of peak intensity (e.g., that of [200]) among the above four patterns indicated that the as-synthesized sample (a) is more similar to the full crystal structure with the guests (b), whereas over time, the sample loses the guests (c) and becomes more comparable with the crystal structure without the guests.

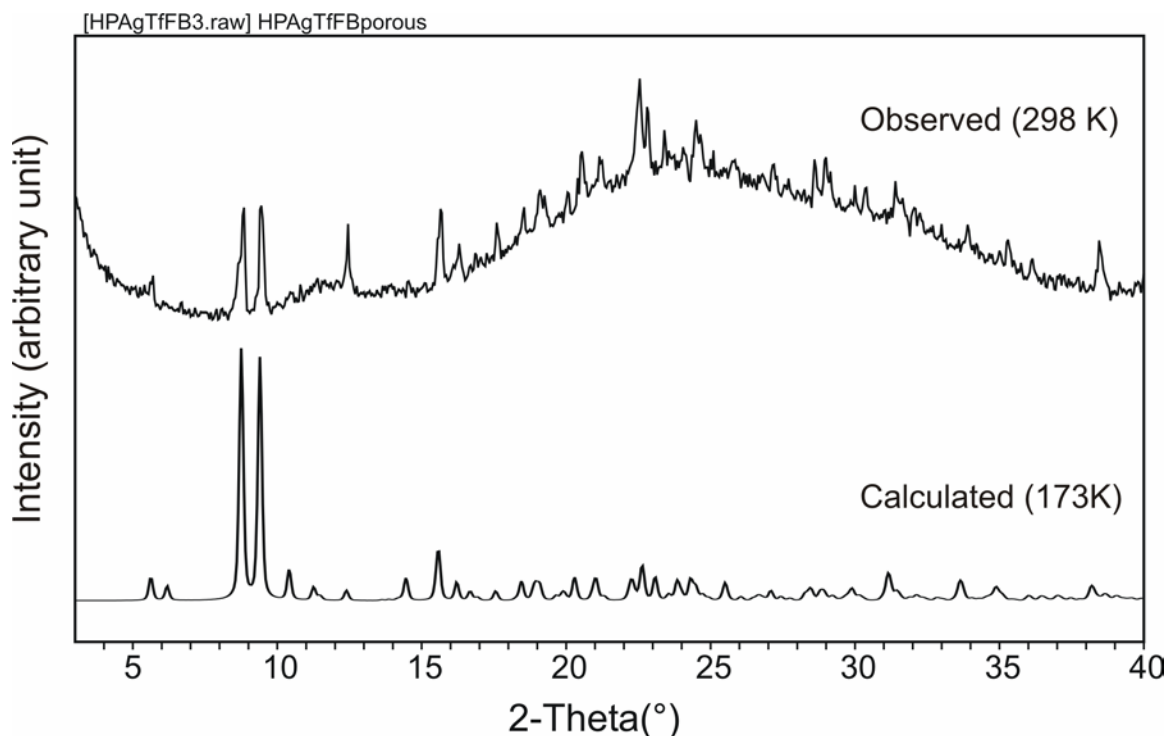


**Figure S2.** X-ray diffraction patterns (Cu  $K\alpha$ ,  $\lambda = 1.5418\text{ \AA}$ ) for the evacuated (heated at  $180\text{ }^{\circ}\text{C}$  for 20 min) sample of **1a**. Bottom: calculated from the single crystal structure of **1a** (single crystal data collected at 143 K). No orientation preference was imposed in the calculation. Top: observed pattern at 298 K.

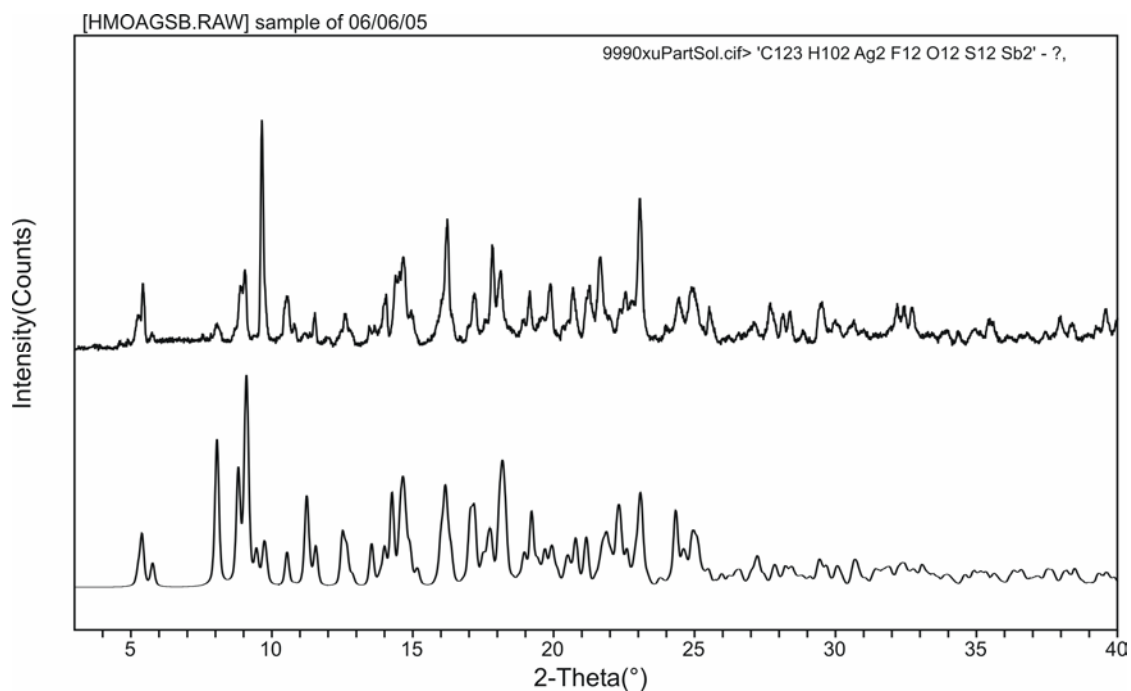


**Figure S3.** Thermograms for a solid sample of **1a** in an argon atmosphere. The heating rate is  $5\text{ }^{\circ}\text{C}/\text{min}$ . The initial loss (up to  $200\text{ }^{\circ}\text{C}$ ) amounts to about 4.0% of the total weight, which is smaller than the solvent loss value (5.7%) calculated from the formula ( $2\text{HPhTT}\cdot 2\text{AgBF}_4\cdot \text{THF}\cdot \text{Acetone}$ ) determined from solution  $^1\text{H}$  NMR. Such a difference suggests that partial loss of the included solvents already occurred at room temperature before being loaded onto the TGA instrument for measurement. Room-temperature loss

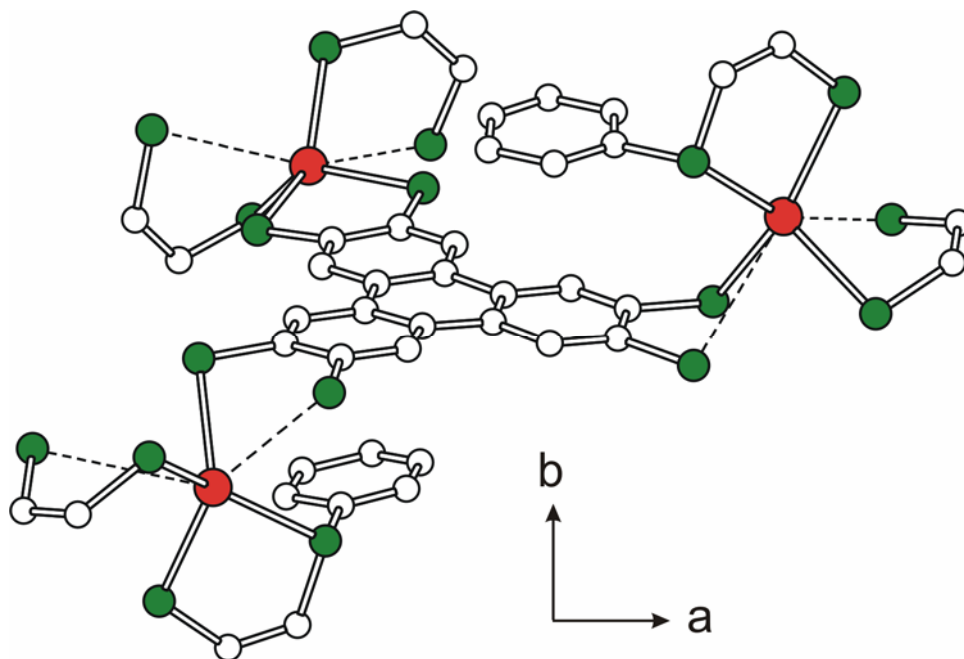
of the solvent molecules is also indicated by the X-ray powder diffraction monitoring of the bulk sample (see Figure S1 above).



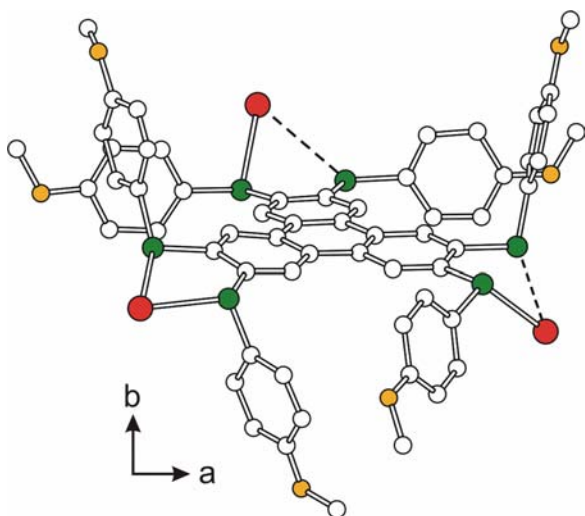
**Figure S4.** X-ray diffraction patterns (Cu K $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ) for a bulk sample of **1b**. Bottom: calculated from the single crystal structure of **1b** (single crystal data collected at 143 K). Top: observed for a sample (exposed in air for overnight) at 298 K. The relatively strong background was probably due to the small amount of sample used in the data collection.



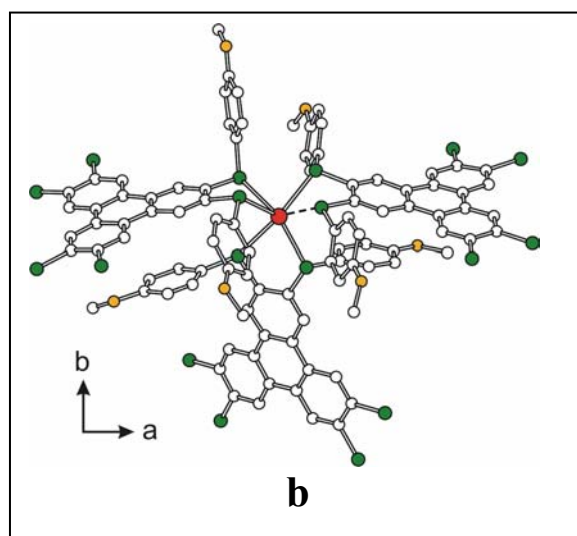
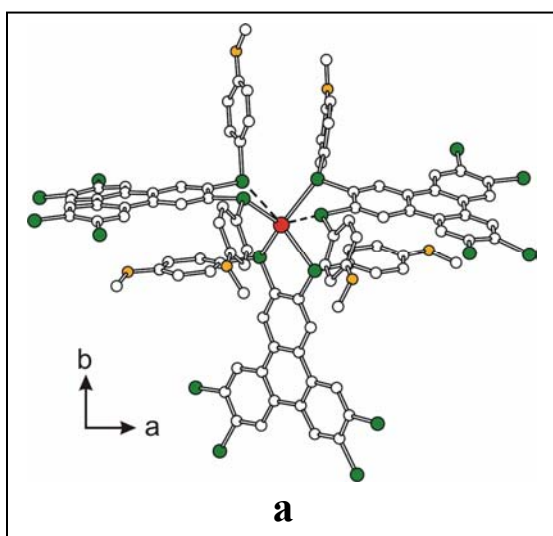
**Figure S5.** X-ray diffraction patterns (Cu K $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ) for the evacuated (heated at  $180 \text{ }^{\circ}\text{C}$  for 20 min) sample of **2**. Bottom: calculated from the single crystal structure of **2** (single crystal data collected at 143 K). Top: observed pattern at 298 K.



**Figure S6.** The triphenylene core of an HPhTT molecule and its interactions with Ag(I) ions and the phenyl groups from neighboring HPhTT molecules in the crystal structure of **1a**. Red spheres: Ag(I); green spheres: S; white spheres: C. Dotted lines indicate C-C contacts shorter than 3.4 Å.



**Figure S7.** Conformation of the other crystallographically unique HMOPhTT molecule and the associated  $\text{Ag}^+$  ions in the crystal structure of **2**. Red sphere:  $\text{Ag}^+$ ; green sphere: S; yellow spheres: O; white sphere: C.



**Figure S8.** Coordination environments around Ag1 (a) and Ag2 (b) in the crystal structure of **2**. Red sphere:  $\text{Ag}^+$ ; green sphere: S; yellow spheres: O; white sphere: C.