

# Supporting Information

## Shape-selective Adsorption and Fluorescent Sensing of Aromatics in a Flexible Network of Tetrakis[(4- methylthiophenyl)ethynyl]silane and $\text{AgBF}_4$

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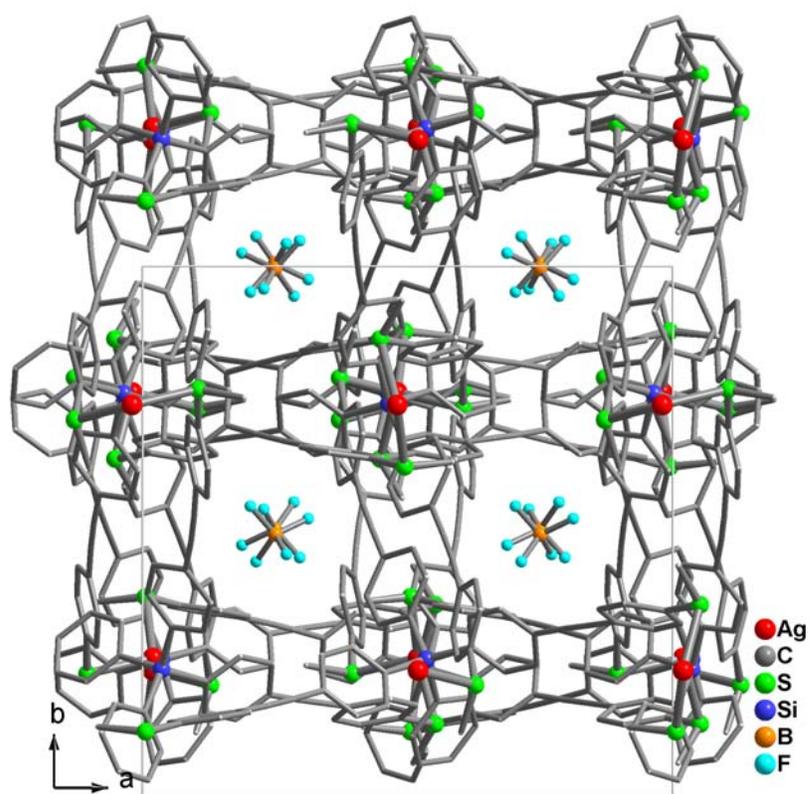
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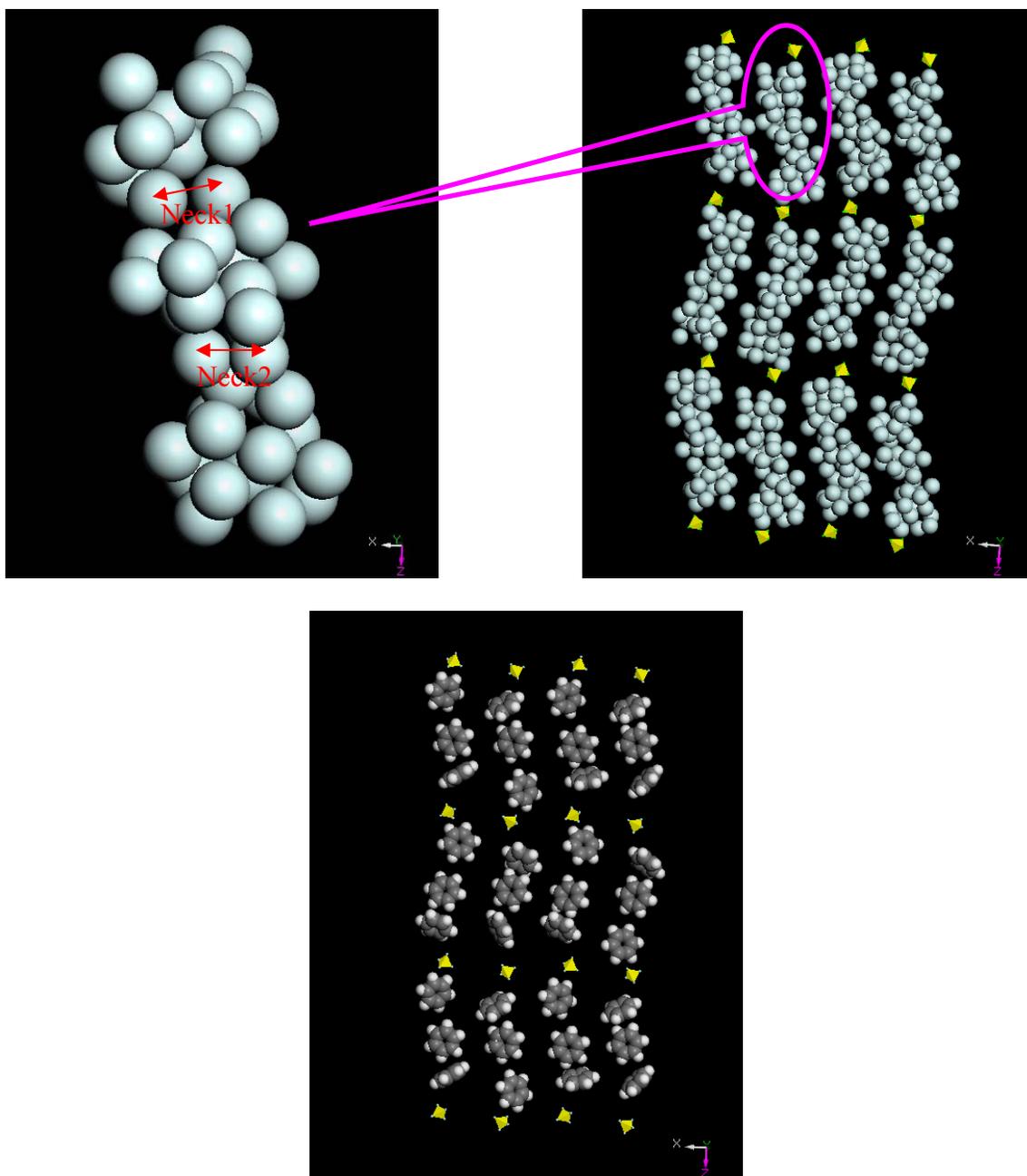
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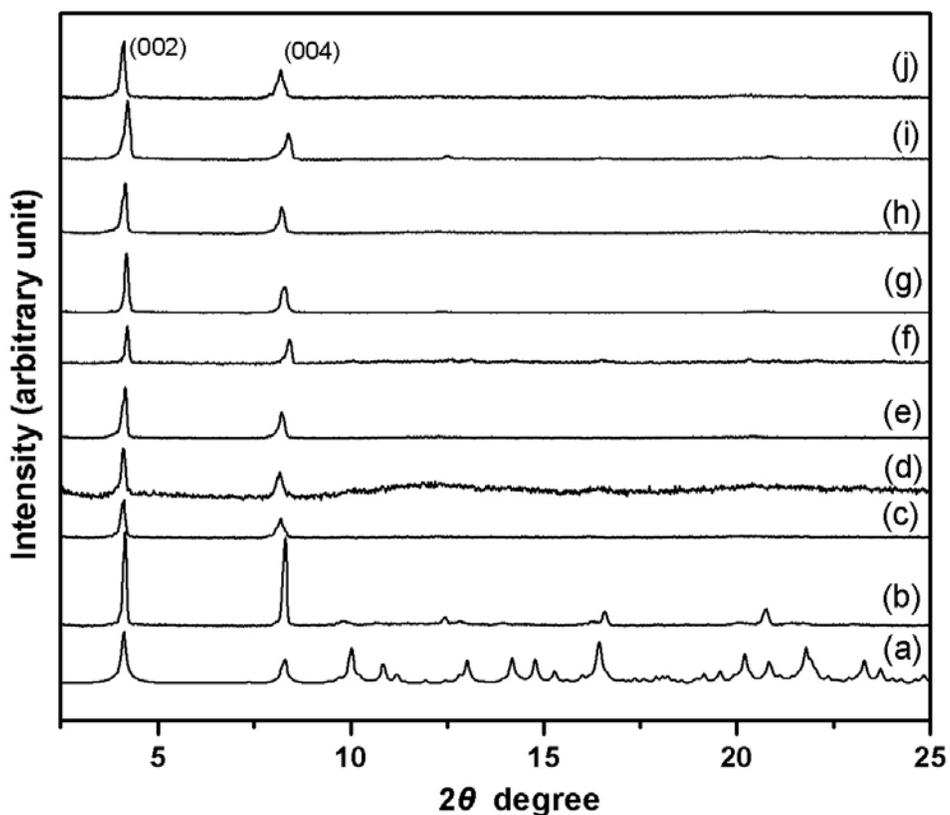
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**Figure S1.** View of the crystal structure of **1** along the *c* axis (solvent molecules are omitted). Red balls: Ag; green balls: S. blue balls: N; sky blue balls: F; orange balls: B.



**Figure S2.** Top: Simulated He filling of a single pore segment (left) and packing of these segments separated by BF<sub>4</sub> ions (right) in **1**. The estimated neck dimensions are 2.3 Å (neck 1) and 2.1 Å (neck 2), respectively, measured from center to center of the two He atoms. Color scheme: BF<sub>4</sub>, yellow tetrahedron; F, green ball; He, light grey ball. Other atoms are omitted for clarify. Bottom: Simulated benzene filling of the pores. Each segment is occupied by three benzene molecules. Color scheme: BF<sub>4</sub>, yellow tetrahedron; F, green ball; C, dark grey; H, white.



**Figure S3.** X-ray diffraction patterns (Cu  $K\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ , 298 K) for powder samples. a): calculated pattern from the single crystal structure (single crystal data collected at 100 K); observed patterns for bulk samples of b) **1** (TMPES $\cdot$ AgBF $_4$  $\cdot$ 3C $_6$ H $_6$ ); c) an apohost (TMPES $\cdot$ AgBF $_4$ ); d) a benzene-filled sample (TMPES $\cdot$ AgBF $_4$  $\cdot$ C $_6$ H $_6$ ); e) a toluene-filled sample (TMPES $\cdot$ AgBF $_4$  $\cdot$ C $_6$ H $_5$ CH $_3$ ); f) a nitrobenzene-filled sample (TMPES $\cdot$ AgBF $_4$  $\cdot$ C $_6$ H $_5$ NO $_2$ ); g) a chlorobenzene-filled sample (TMPES $\cdot$ AgBF $_4$  $\cdot$ C $_6$ H $_5$ Cl); h) an anisole-filled sample (TMPES $\cdot$ AgBF $_4$  $\cdot$ C $_6$ H $_5$ OCH $_3$ ); i) an ethylbenzene-filled sample (TMPES $\cdot$ AgBF $_4$  $\cdot$ C $_6$ H $_5$ C $_2$ H $_5$ ), j) a 1-bromo-4-fluorobenzene-filled sample (TMPES $\cdot$ AgBF $_4$  $\cdot$ FC $_6$ H $_4$ Br).

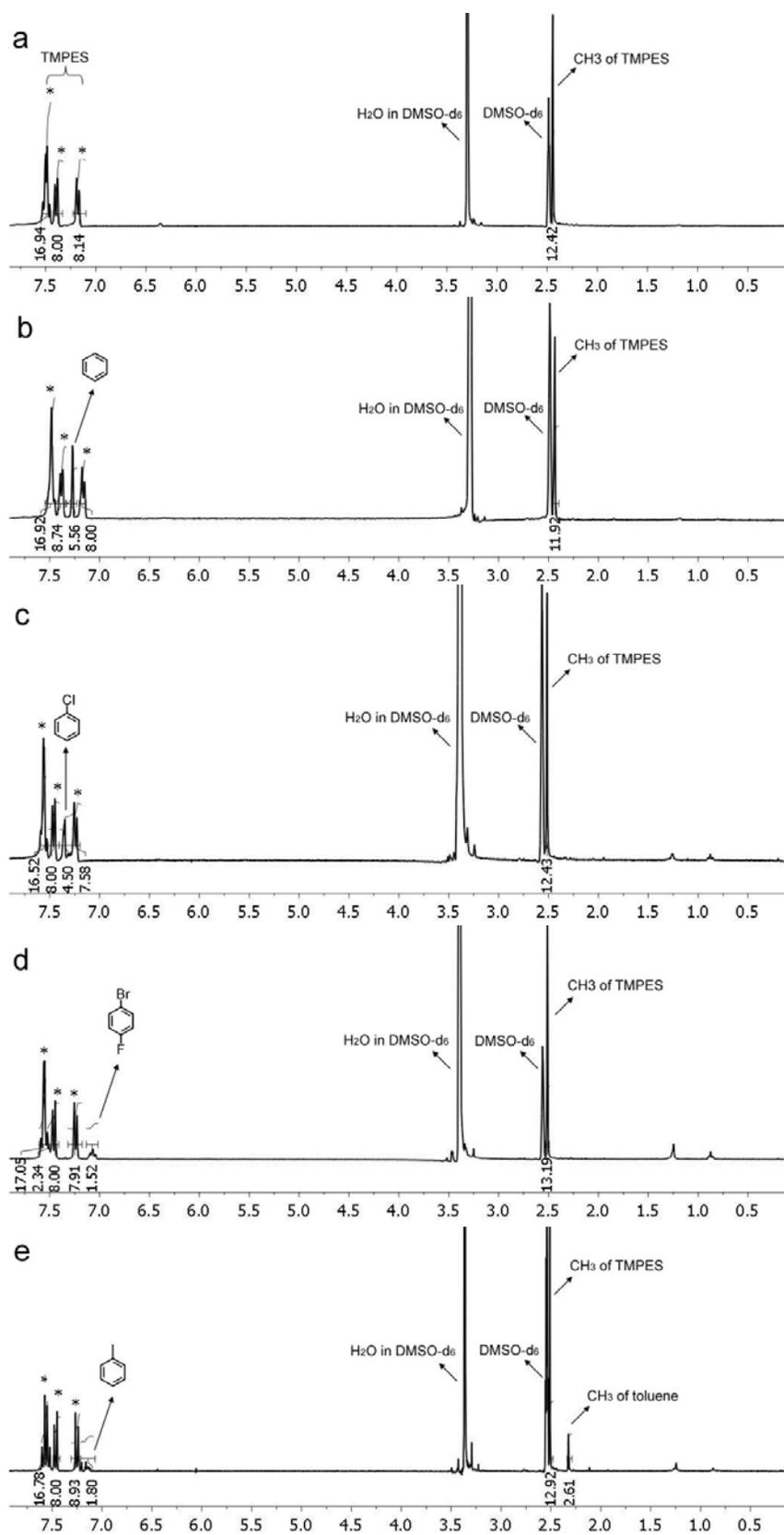
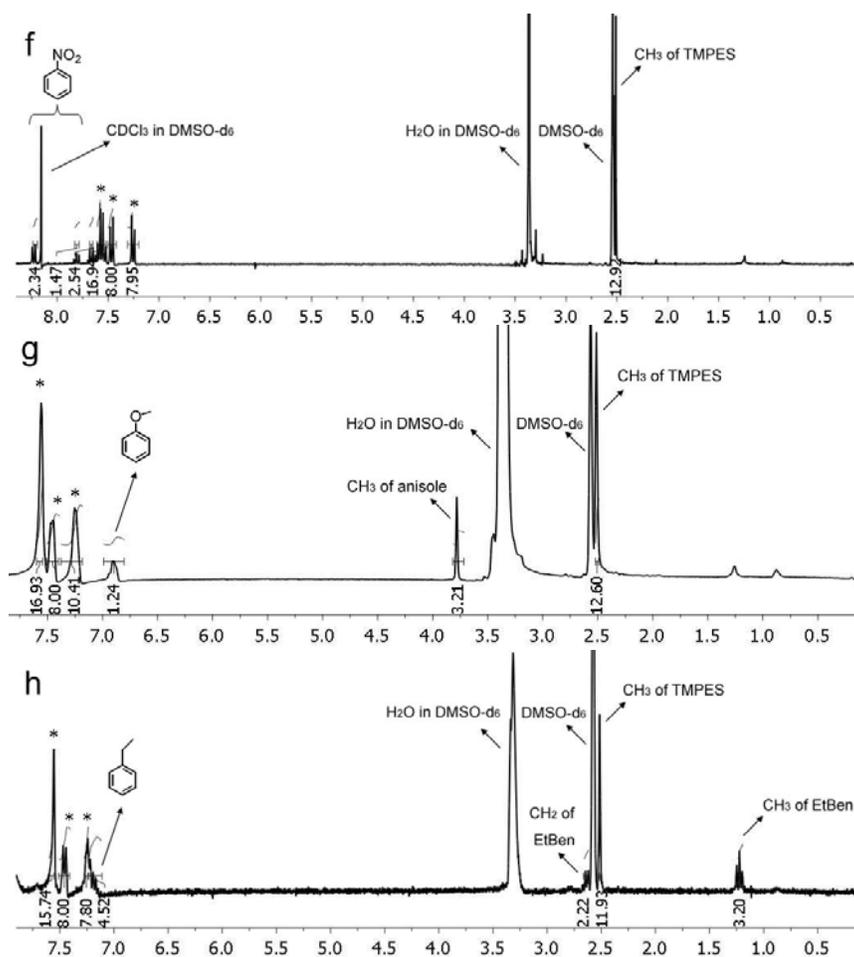
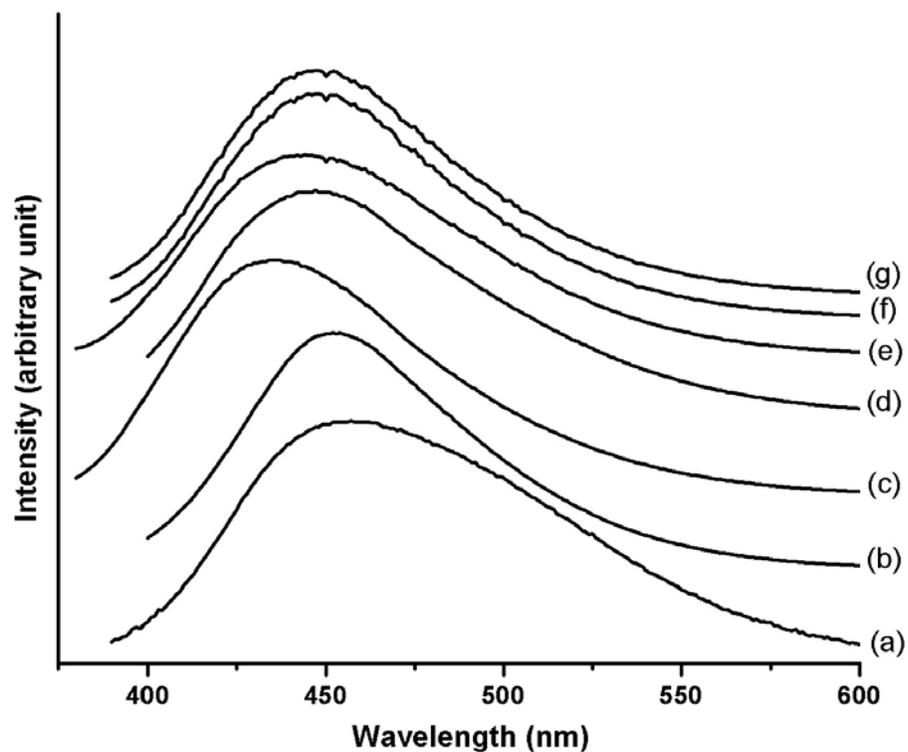


Figure S4 (continued on next page).



**Figure S4.**  $^1\text{H}$  NMR spectra of (a) an apohost sample ( $\text{TMPES} \cdot \text{AgBF}_4$ ); (b) a benzene-filled sample ( $\text{TMPES} \cdot \text{AgBF}_4 \cdot \text{C}_6\text{H}_6$ ); (c) a chlorobenzene-filled sample ( $\text{TMPES} \cdot \text{AgBF}_4 \cdot \text{C}_6\text{H}_5\text{Cl}$ ); (d) a 1-bromo-4-fluorobenzene-filled sample ( $\text{TMPES} \cdot \text{AgBF}_4 \cdot \text{FC}_6\text{H}_4\text{Br}$ ); (e) a toluene-filled sample ( $\text{TMPES} \cdot \text{AgBF}_4 \cdot \text{C}_6\text{H}_5\text{CH}_3$ ); (f) a nitrobenzene-filled sample ( $\text{TMPES} \cdot \text{AgBF}_4 \cdot \text{C}_6\text{H}_5\text{NO}_2$ ); (g) an anisole-filled sample ( $\text{TMPES} \cdot \text{AgBF}_4 \cdot \text{C}_6\text{H}_5\text{OCH}_3$ ). (h) an ethylbenzene-filled sample ( $\text{TMPES} \cdot \text{AgBF}_4 \cdot \text{C}_6\text{H}_5\text{C}_2\text{H}_5$ ). Peaks with stars are from the TMPES molecule.



**Figure S5.** Room-temperature solid state emission spectra (excitation wavelength  $\lambda_{\text{ex}} = 360$  nm) from: a) an apohost sample (TMPES·AgBF<sub>4</sub>); b) a benzene-filled sample (TMPES·AgBF<sub>4</sub>·C<sub>6</sub>H<sub>6</sub>); c) a toluene-filled sample (TMPES·AgBF<sub>4</sub>·C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>); d) a chlorobenzene-filled sample (TMPES·AgBF<sub>4</sub>·C<sub>6</sub>H<sub>5</sub>Cl); e) an anisole-filled sample (TMPES·AgBF<sub>4</sub>·C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub>); f) an ethylbenzene-filled sample (TMPES·AgBF<sub>4</sub>·C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>H<sub>5</sub>); g) a 1-bromo-4-fluorobenzene-filled sample (TMPES·AgBF<sub>4</sub>·FC<sub>6</sub>H<sub>4</sub>Br).