

<Supporting Information>

Subtle Role of Polyatomic Anions in Molecular Construction. Structures and Properties of AgX Bearing 2,4'-Thiobispyridine ($X^- = NO_3^-$, BF_4^- , ClO_4^- , PF_6^- , $CF_3CO_2^-$, and $CF_3SO_3^-$)

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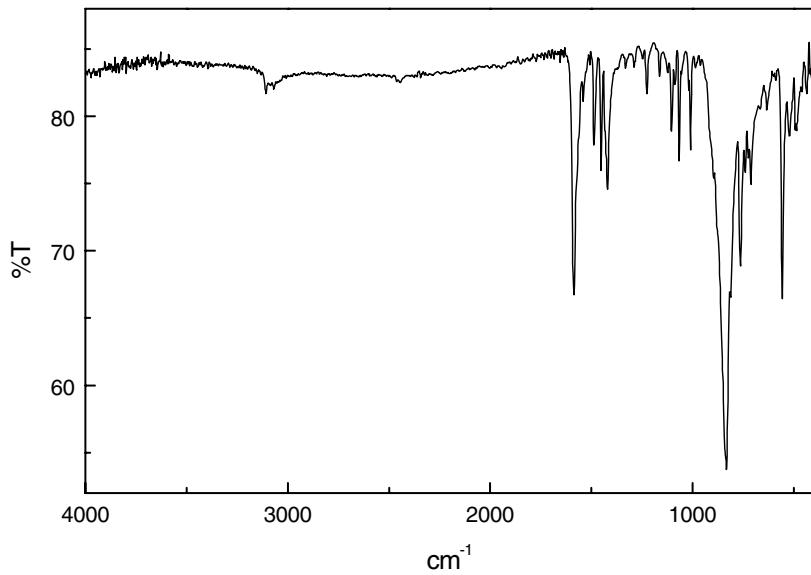


Fig. S1. IR spectrum of $[\text{Ag}_3(2,4'\text{-Py}_2\text{S})_4](\text{PF}_6)_3$ prepared by the anion exchange of $[\text{Ag}_3(2,4'\text{-Py}_2\text{S})_4](\text{BF}_4)_3$ with PF_6^- .

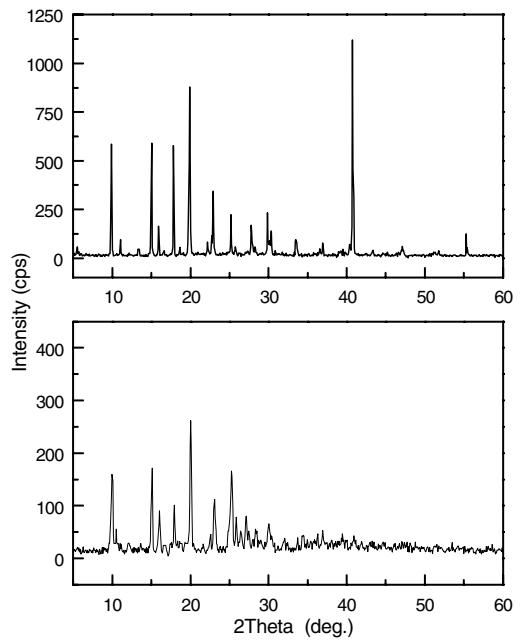


Fig. S2. The X-ray powder diffraction patterns of $[\text{Ag}_3(2,4'\text{-Py}_2\text{S})_4](\text{PF}_6)_3$ prepared by the direct reaction (top) and $[\text{Ag}_3(2,4'\text{-Py}_2\text{S})_4](\text{PF}_6)_3$ prepared by the anion exchange of $[\text{Ag}_3(2,4'\text{-Py}_2\text{S})_4](\text{ClO}_4)_3$ with NaPF_6 (bottom).

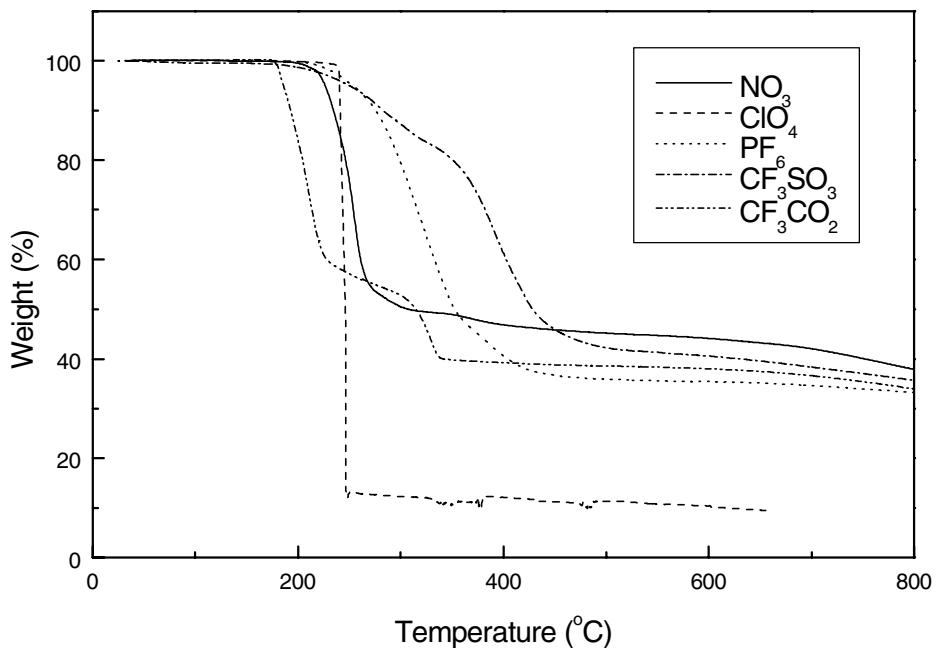


Fig. S3. TGA traces of $[\text{Ag}(2,4'\text{-Py}_2\text{S})(\text{NO}_3)]$, $[\text{Ag}_3(2,4'\text{-Py}_2\text{S})_4](\text{ClO}_4)_3$, $[\text{Ag}_3(2,4'\text{-Py}_2\text{S})_4](\text{PF}_6)_3$, $[\text{Ag}(2,4'\text{-Py}_2\text{S})(\text{CF}_3\text{CO}_2)]$, and $[\text{Ag}_3(2,4'\text{-Py}_2\text{S})_4](\text{CF}_3\text{SO}_3)_3$.

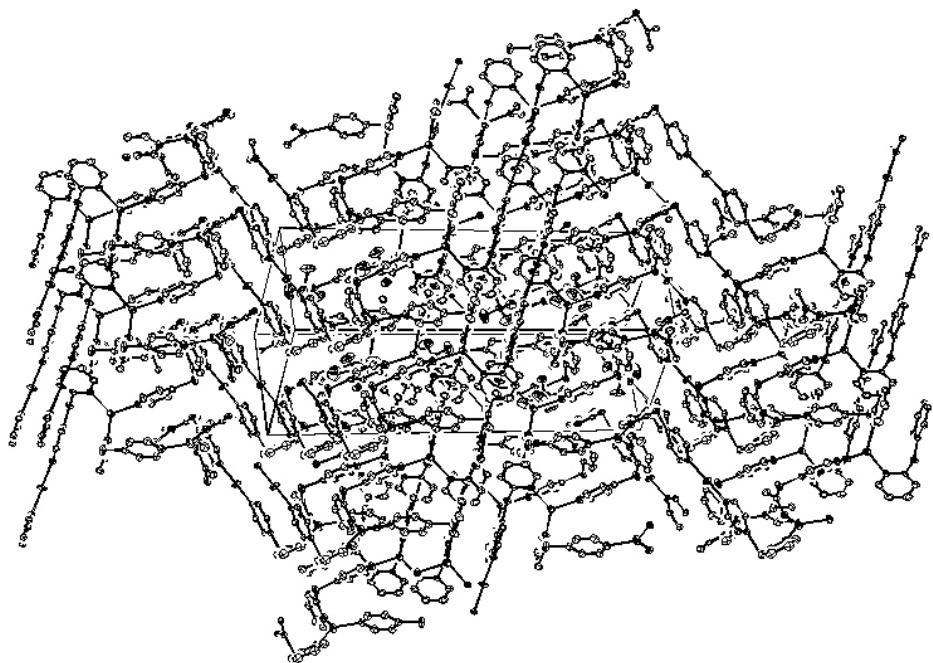


Fig. S4. Packing diagram of $[\text{Ag}_3(2,4'\text{-Py}_2\text{S})_4](\text{ClO}_4)_3$ and $[\text{Ag}_3(2,4'\text{-Py}_2\text{S})_4](\text{PF}_6)_3$.

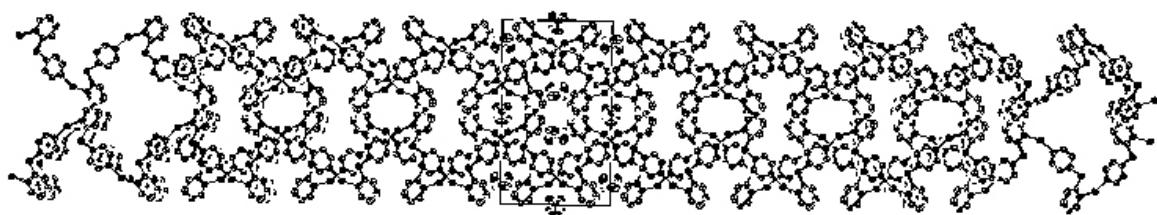


Fig. S5. Packing diagram of $[\text{Ag}(2,4'\text{-Py}_2\text{S})(\text{NO}_3)]$.

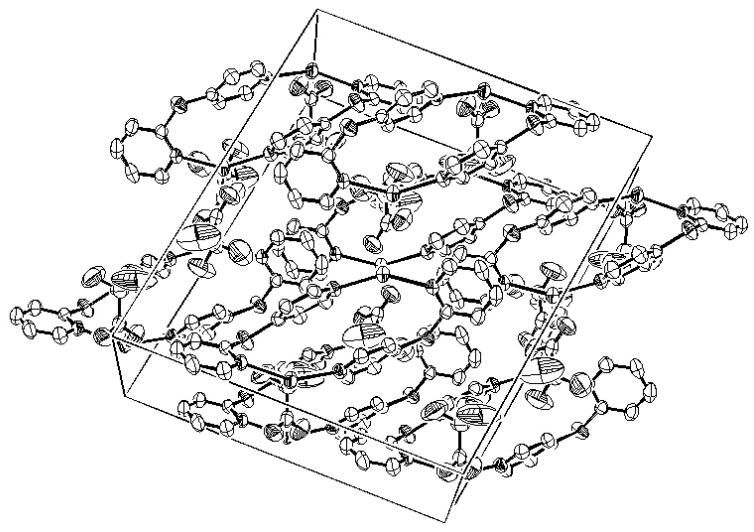


Fig. S6. Packing diagram of $[\text{Ag}(2,4'\text{-Py}_2\text{S})(\text{CF}_3\text{CO}_2)]$.

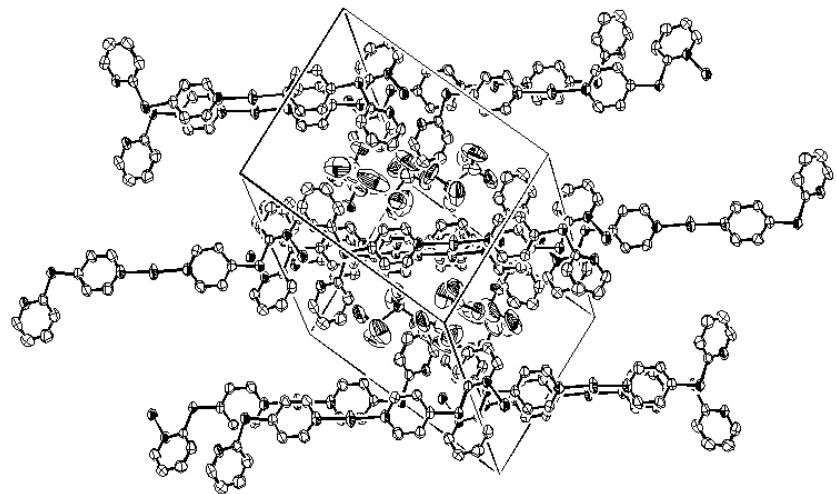


Fig. S7. Packing diagram of $[\text{Ag}_3(2,4'\text{-Py}_2\text{S})_4](\text{CF}_3\text{SO}_3)_3$.