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Figure S1. Overall crystal structures of **1** along *b* axis. Red spheres: Ag⁺; green spheres: S; white: C; yellow: O (from the triflate anion, for clarity the rest of the anion is omitted). Carbon atoms of the toluene molecules are in purple color.

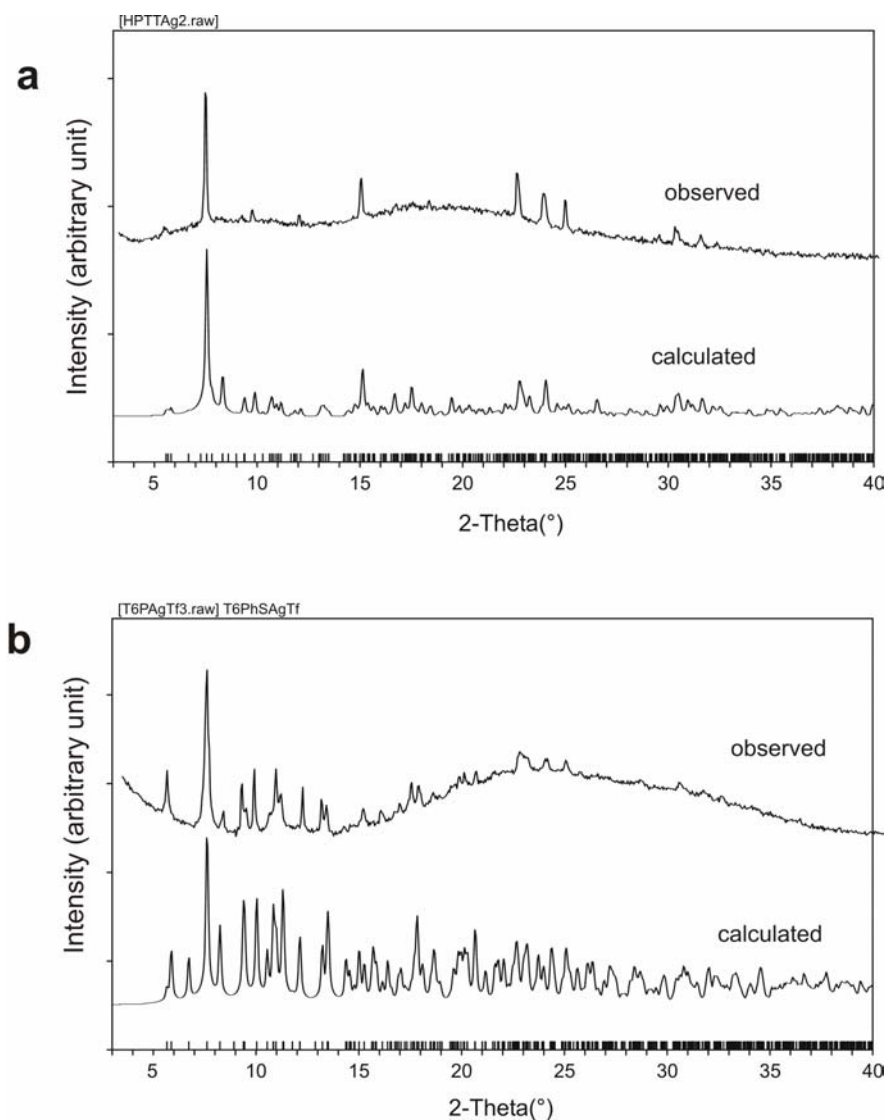


Figure S2. Calculated (from the single crystal structures) and observed X-ray (Cu K α , λ = 1.5418 Å) diffraction patterns of bulk samples of **1** (a) and **2** (b). Samples were pressed onto a glass slide for data collection (in air). No effort was taken to fully grind the crystallites collected from the solutions. The calculation was done using JADE, Materials Data, Inc. For calculating the diffraction pattern of **1**, the preferred orientation for the crystallites was set at 0.4 for the (100) direction [meaning 60% more crystallites of **1** are oriented along the (001) direction when compared to the randomly oriented state].

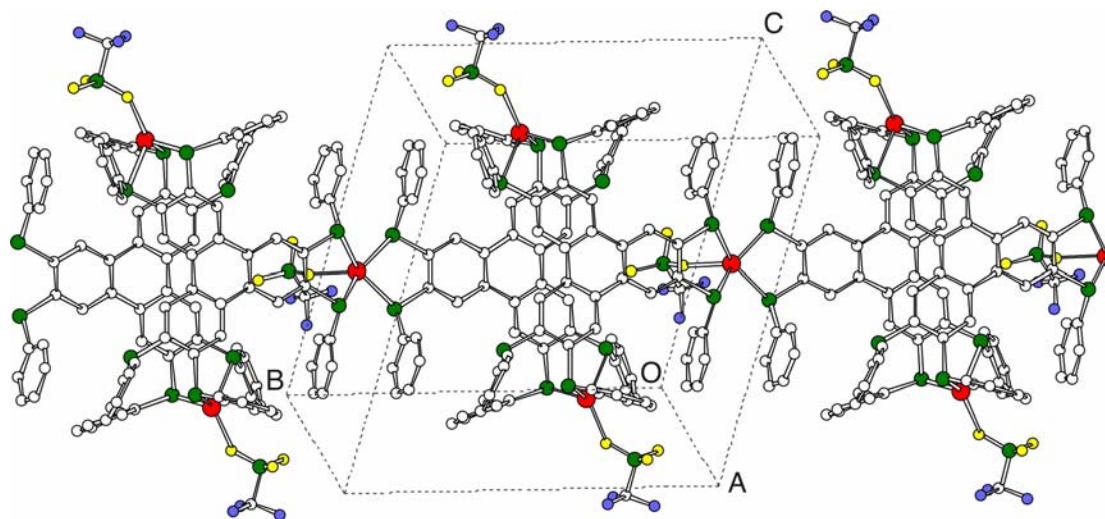


Figure S3. The 1D coordination network in the crystal structure of **2**. Red spheres, Ag; green spheres, S; white, C; yellow, O; purple, F.

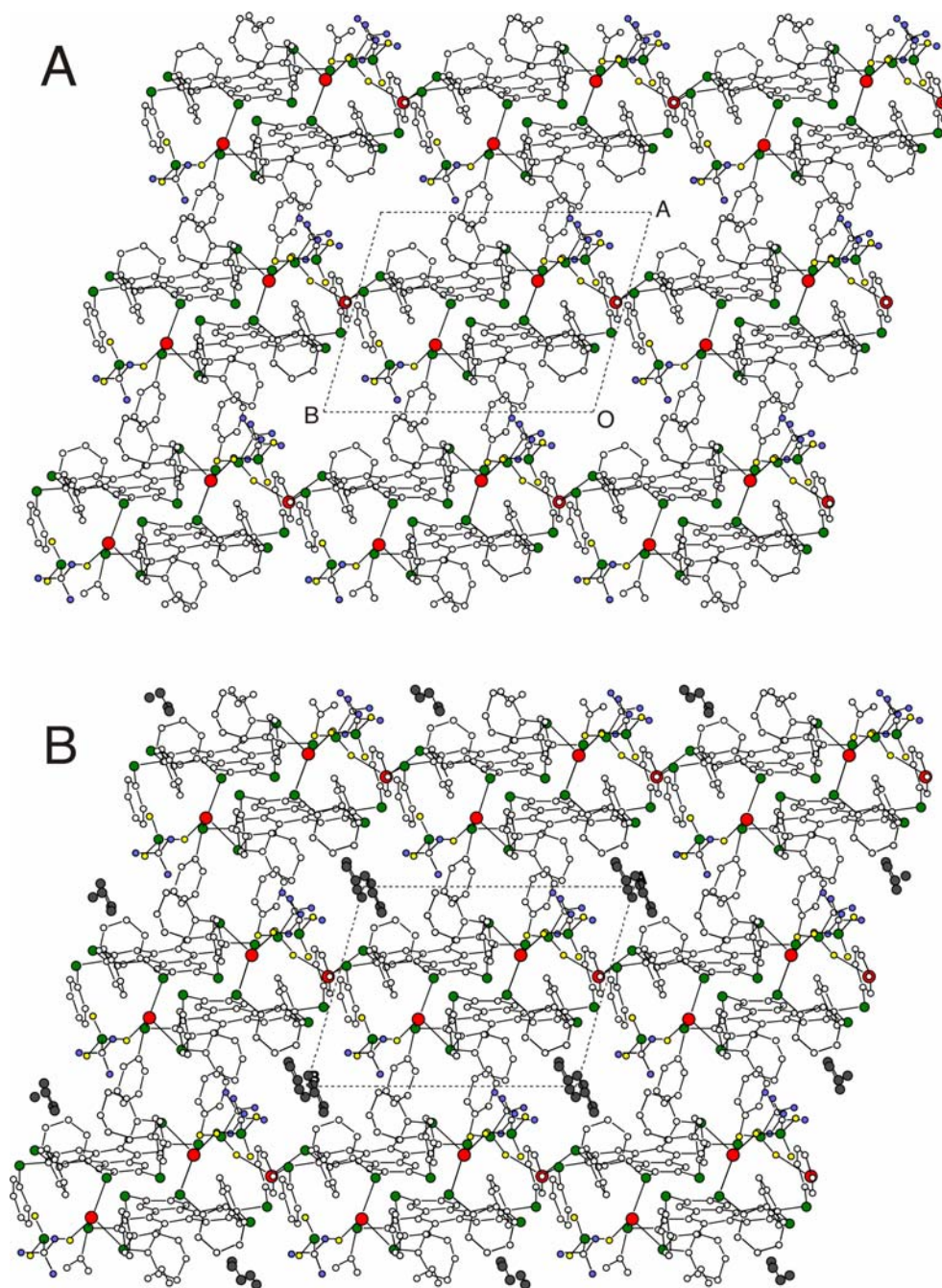


Figure S4. The crystal structure of **2** along *c* axis (showing the channels that contain the tetrahydrofuran molecules). a) without the THF molecules; b) with the THF molecules. Red spheres, Ag; green spheres, S; white, C; yellow, O; purple, F. Carbon atoms of the THF molecules are in grey color.