

Supporting Information

Construction of $[(\eta^5\text{-C}_5\text{Me}_5)\text{MoS}_3\text{Cu}_3]$ -based Supramolecular Assemblies from the $[(\eta^5\text{-C}_5\text{Me}_5)\text{MoS}_3(\text{CuNCS})_3]^-$ Cluster Anion and Multi-topic Ligands with Different Symmetries

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Synthesis of $[\text{PPh}_4]_2[(\eta^5\text{-C}_5\text{Me}_5)\text{MoS}_3(\text{CuNCS})_3\text{Cl}]\cdot 3\text{CH}_2\text{Cl}_2$

To a stirring solution of 5 mL aniline containing $[\text{PPh}_4][(\eta^5\text{-C}_5\text{Me}_5)\text{MoS}_3(\text{CuNCS})_3]$ (20 mg, 0.02 mmol) was added dropwise of 100 mL CH_2Cl_2 solution containing tpt (80 mg, 0.25 mmol). The solution was vigorously stirred for 72 hours and was concentrated to 20 mL by evaporation. The resulting mixture was centrifuged to remove the white precipitate (un-reacted tpt). Et_2O (10 mL) was diffused into the dark red solution to form black crystals of $[\text{PPh}_4]_2[(\eta^5\text{-C}_5\text{Me}_5)\text{MoS}_3(\text{CuNCS})_3\text{Cl}]\cdot 3\text{CH}_2\text{Cl}_2$ one week later, which were collected and dried in air. Yield 21 mg (63.2%) based on Mo. Anal. Calcd for $\text{C}_{61}\text{H}_{55}\text{ClCu}_3\text{MoN}_3\text{P}_2\text{S}_6$: C 52.09, H 3.94, N 2.99; Found C 51.94, H 3.81, N 2.72. X-ray fluorescence analysis data: Mo : Cu : S : P : Cl = 1.00 : 2.85 : 2.81 : 1.97 : 1.12. IR (KBr disk): 2922 (w), 2900 (w), 2122 (vs), 1628 (w), 1550 (m), 1483 (m), 1436 (s), 1377 (s), 1243 (m), 1108 (s), 996 (w), 968 (m), 801 (w), 723 (m), 689 (m), 528 (m) cm^{-1} . Crystal data: $\text{C}_{64}\text{H}_{61}\text{Cl}_7\text{Cu}_3\text{MoN}_3\text{P}_2\text{S}_6$, fw = 1661.28, monoclinic, space group $P2_1/c$, $a = 12.970(3)$ Å, $b = 29.060(3)$ Å, $c = 28.676(4)$ Å, $\beta = 102.18(3)^\circ$, $V = 6881(2)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.598$ g/cm³, $\mu = 1.635$ mm⁻¹, $F000 = 3336$, $2\theta_{\text{max}}(^\circ) = 50.6$, 35827 reflns. collected, 5384 unique reflns., 4753 observed reflns, 764 variables, $R(I > 2\sigma(I)) = 0.123$, $wR = 0.2448$, GOF = 1.118.

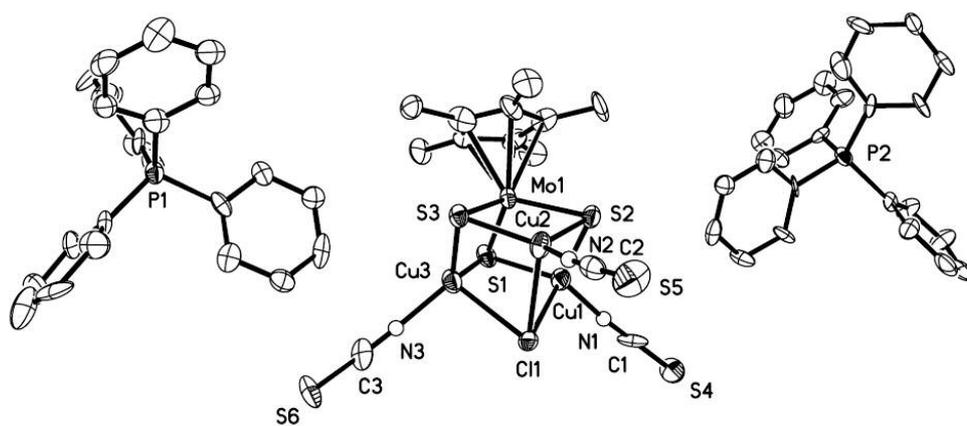


Figure S1. Perspective view of $[\text{PPh}_4]_2[(\eta^5\text{-C}_5\text{Me}_5)\text{MoS}_3(\text{CuNCS})_3\text{Cl}]$ with 50% thermal ellipsoids. All hydrogen atoms were omitted for clarity.

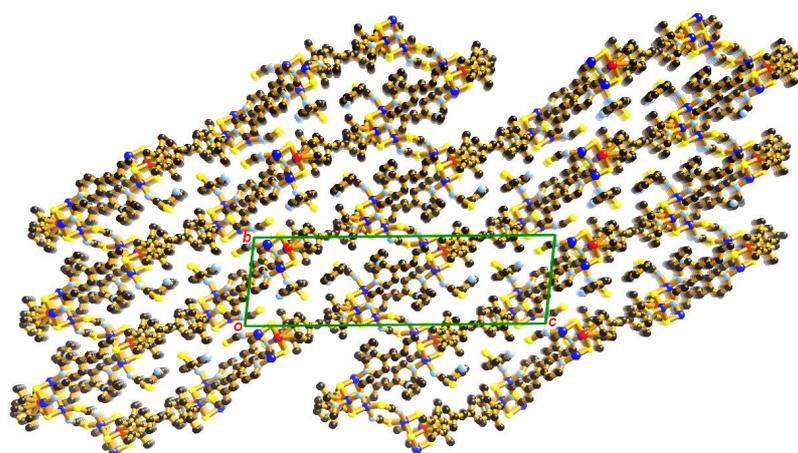


Figure S2. Packing diagram of **2** looking along the *a* axis, displaying 1D channels filled with solvated aniline molecules. All hydrogen atoms were omitted for clarity.

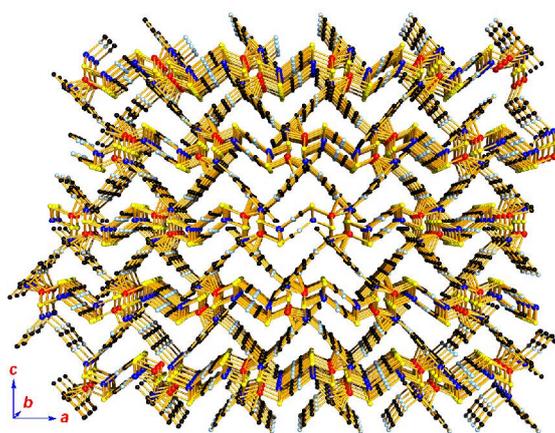


Figure S3. Packing diagram of **3** looking along the *b* axis. All hydrogen atoms omitted for clarity.

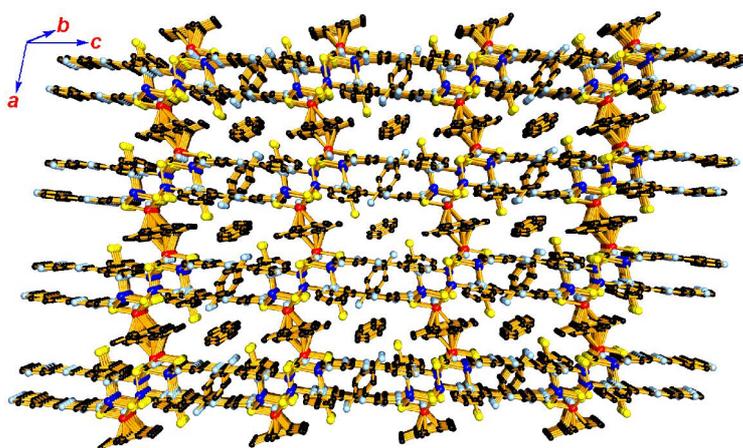


Figure S4. Packing diagrams of **4** looking along the *b* axis. All hydrogen atoms omitted for clarity.

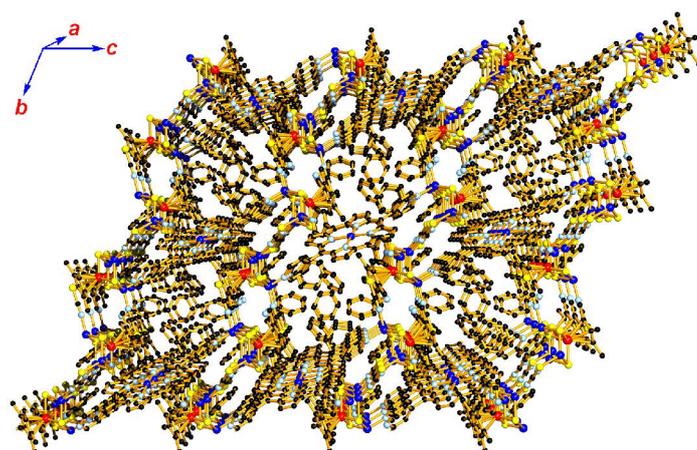


Figure S5. Packing diagrams of **5** looking along the *a* axis. All hydrogen atoms omitted for clarity

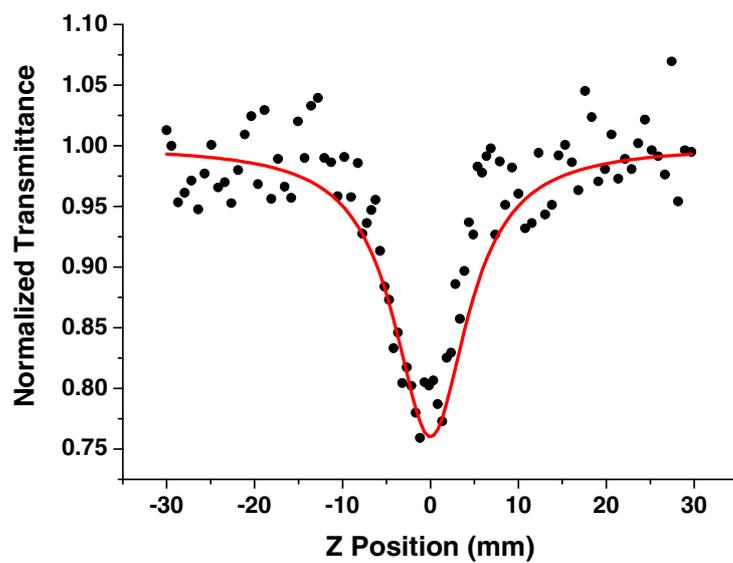


Figure S6. Z-Scan data for the aniline solutions of $3.0 \times 10^{-5} \text{ mol.L}^{-1}$ for **2**. The black solid spheres are experimental data, and the solid curves are the theoretical fit.

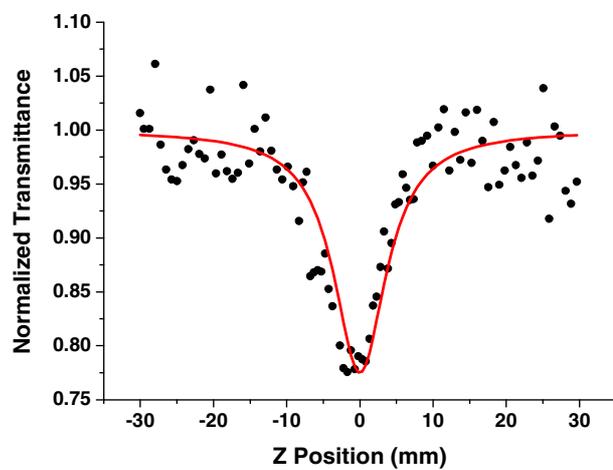


Figure S7. Z-Scan data for the aniline solutions of $3.0 \times 10^{-5} \text{ mol.L}^{-1}$ for **3**. The black solid spheres are experimental data, and the solid curves are the theoretical fit.

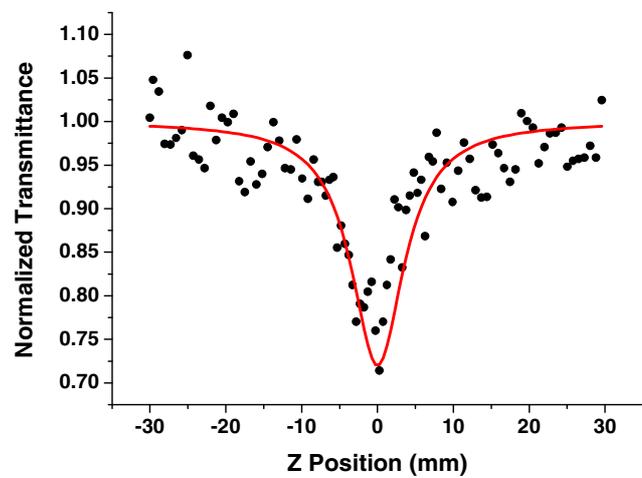


Figure S8. Z-Scan data for the aniline solutions of $1.5 \times 10^{-5} \text{ mol.L}^{-1}$ for **4**. The black solid spheres are experimental data, and the solid curves are the theoretical fit.

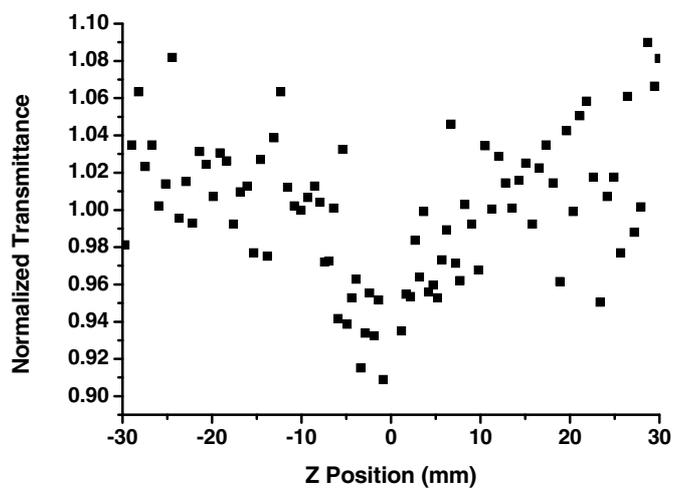


Figure S9. Z-Scan data for the pure aniline solution