Electronic Supplementary Information

Assembly of new Mo/Cu/S clusters from [Et₄N][Tp*MoS(S₄)] and Cu(I) salts: syntheses, structures and third-order nonlinear optical properties

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Contents

Figure S4. (a) The supercubic $[MoS_3Cu_3]_4S_4$ core of **7**. All Tp* groups and H atoms were omitted for clearity. Symmetry codes: A: -x, -y + 1/2, z B: x + 1/4, -y + 1/4, -z + 3/4 C: -x + 1/4, y - 1/4, -z + 3/4. (b) A representation of the supercubic cluster core of **7**. Each red sphere represents one $[Tp*MoS_3Cu_3]$ fragment while each yellow sphere represents one μ_3 -S' (S4) atoms......S8



(a)







(c)



(d)



Figure S1. (a) The negative-ion ESI mass spectrum of 2. (b) The negative-ion ESI mass spectrum of 3. (c) The negative-ion ESI mass spectrum of 4. (d) The negative-ion ESI mass spectrum of 5. (e) The negative-ion ESI mass spectrum of 6.





Figure S2. (a) The calculated isotope pattern (top) and the negative-ion ESI mass spectrum (bellow) of the $[Tp*MoS_3 + 2MeCN]^-$ anion of **3**. (b) The calculated isotope pattern (top) and the negative-ion ESI mass spectrum (bellow) of the $[Tp*MoS_3 + 2MeCN]^-$ anion of **4**. (c) The calculated isotope pattern (top) and the negative-ion ESI mass spectrum (bellow) of the $[Tp*MoS_2OCuCN]^-$ anion of **6**.



(a)



Figure S3. (a) View of the cluster anion of **4**. (b) View of the cluster anion of **5**. All hydrogen atoms are omitted for clarity.



Figure S4. (a) The supercubic $[MoS_3Cu_3]_4S_4$ core of **7**. All Tp* groups and H atoms were omitted for clearity. Symmetry codes: A: -x, -y + 1/2, z B: x + 1/4, -y + 1/4, -z + 3/4 C: -x + 1/4, y - 1/4, -z + 3/4. (b) A representation of the supercubic cluster core of **7**. Each red sphere represents one $[Tp*MoS_3Cu_3]$ fragment while each yellow sphere represents one μ_3 -S' (S4) atoms.



Figure S5. (a) The DFWM signal for the DMF solutions of 4×10^{-5} M for **3**. (b) The DFWM signal for the DMF solutions of 4×10^{-5} M for **4**. (c) The DFWM signal for the DMF solutions of 4×10^{-5} M for **5**. (d) The DFWM signal for the DMF solutions of 4×10^{-5} M for **6** with 80 fs and 1.5 mm cell. The black solid squares are experimental data, and the red solid curves are the theoretical fit.