Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

New Types of Cu and Ag Clusters Supported by the Pyrrole-based NNN-Pincer Type Ligand

*Oishi Jana and Ganesan Mani**

Department of Chemistry, Indian Institute of Technology – Kharagpur, Kharagpur, West Bengal,

India 721 302, Fax: +91 3222 282252, E-mail: gmani@chem.iitkgp.ernet.in.

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^{1}H, ^{13}C, ^{19}F NMR, FTIR, and UV spectra

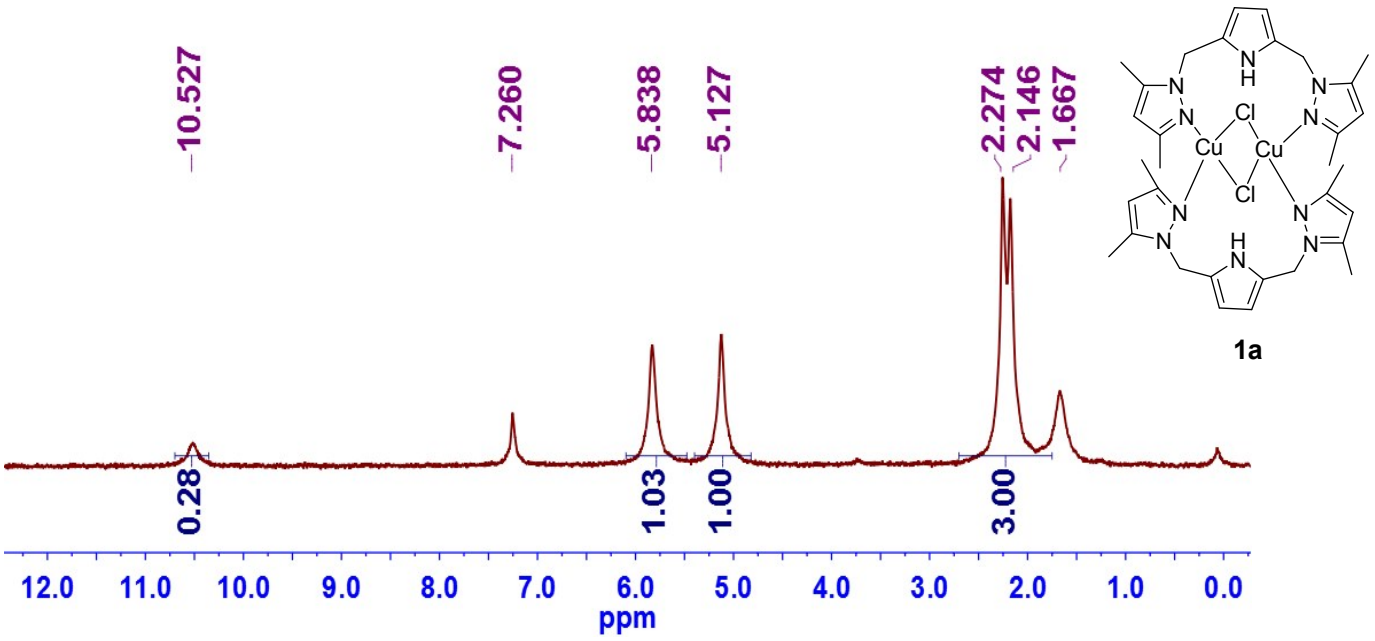

Figure S1. ^{1}H NMR(200 MHz, 25 °C) spectrum of [Cu(μ-Cl)(μ-C_4H_3N-2,5-($CH_2Me_2pz)_2$–*N,N,N*)]$_2$**, 1a** in $CDCl_3$.

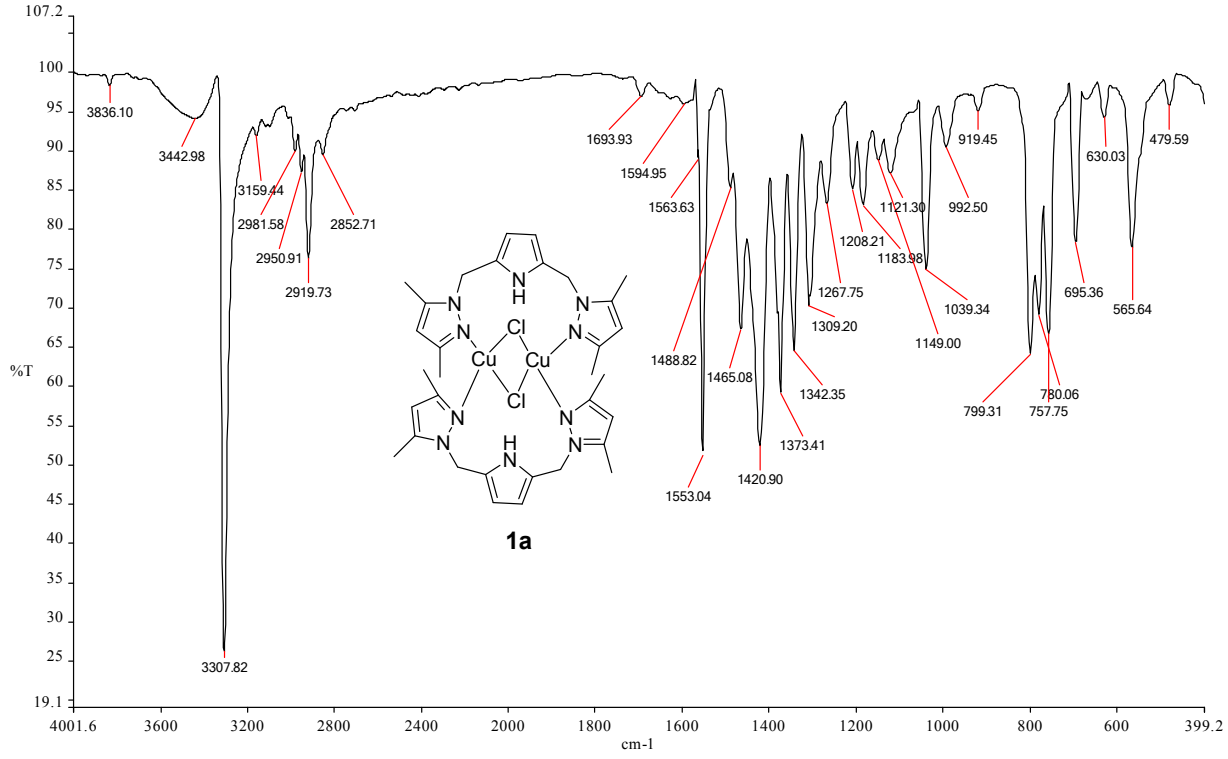

Figure S2. IR spectrum of [Cu(μ-Cl)(μ-C_4H_3N-2,5-($CH_2Me_2pz)_2$–*N,N,N*)]$_2$**, 1a** recorded as KBr disc.

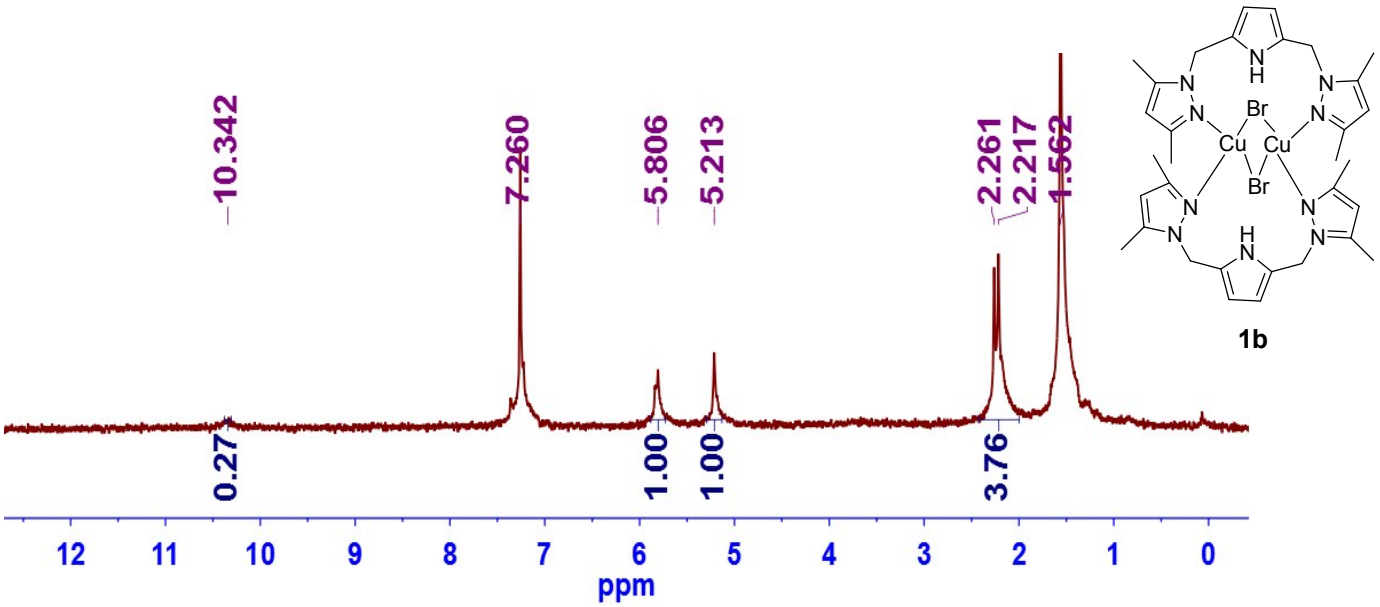

Figure S3. ^{1}H NMR (200 MHz, 25 °C) specturm of [Cu(μ-Br)(μ-C_4H_3N-2,5-$(CH_2Me_2pz)_2$–*N,N,N*], **1b** in $CDCl_3$.

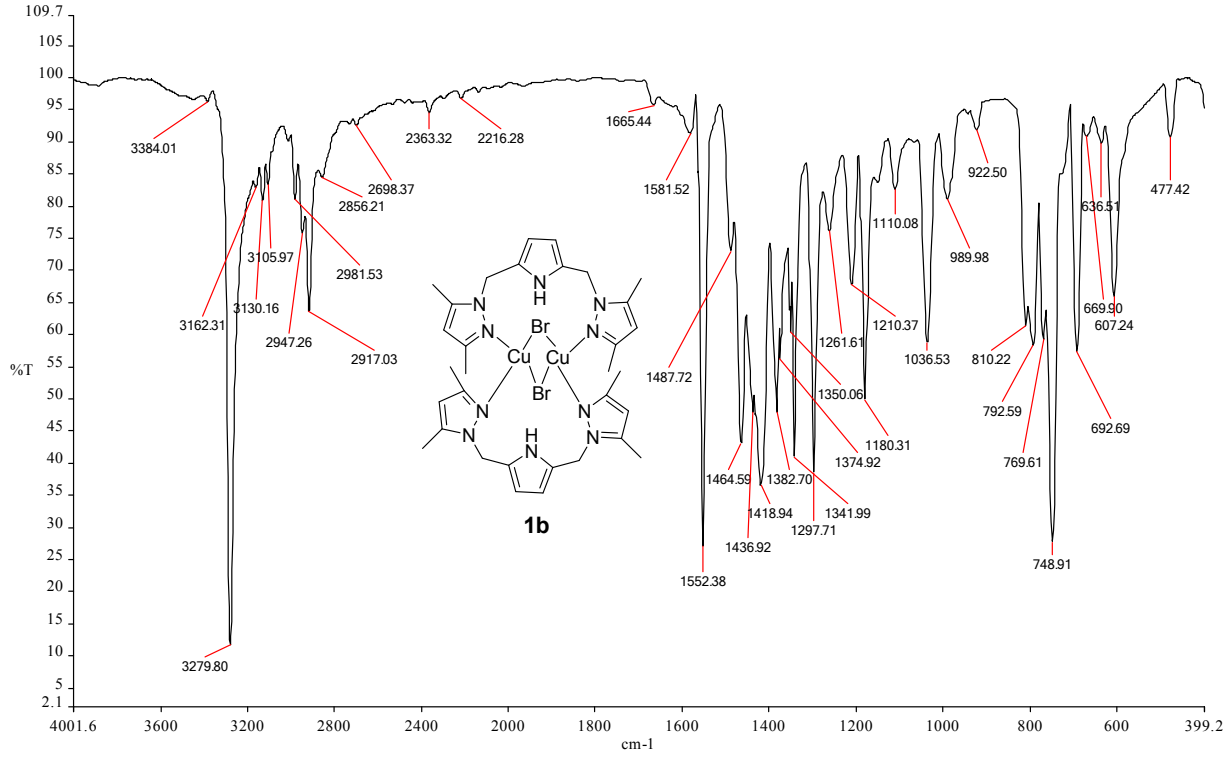

Figure S4. IR spectrum of [Cu(μ-Br)(μ-C_4H_3N-2,5-$(CH_2Me_2pz)_2$–*N,N,N*)]$_2$, **1b** recorded as KBr disc.

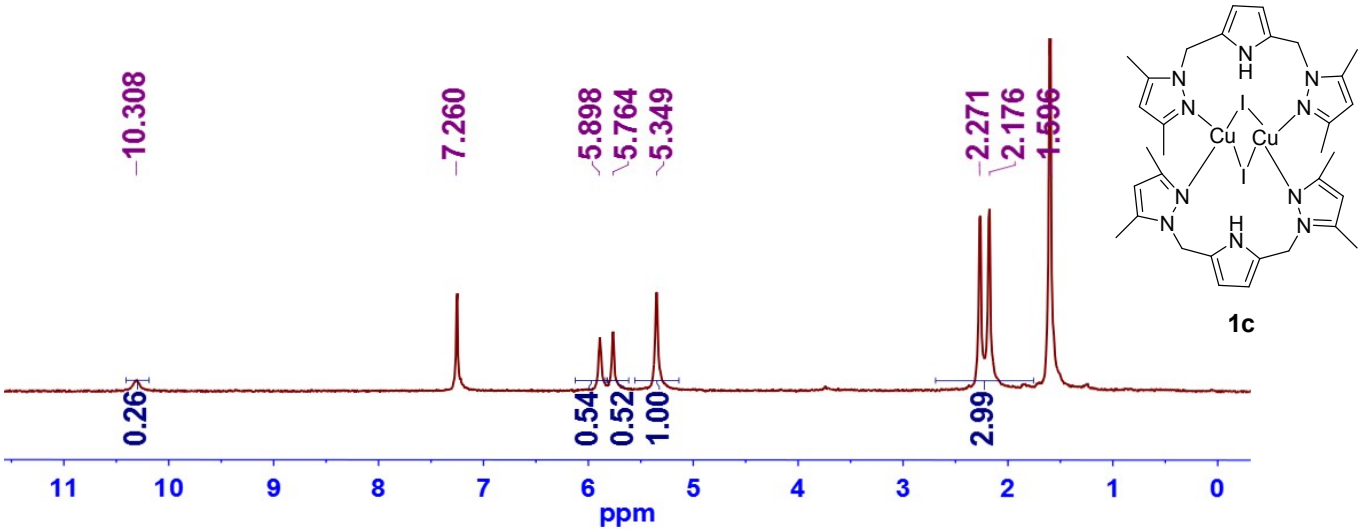

Figure S5. ^{1}H NMR (200 MHz, 25 °C) spectrum of [Cu(μ-I)(μ-C_4H_3N-2,5-$(CH_2Me_2pz)_2$–*N,N,N*)]$_2$, **1c** in $CDCl_3$.

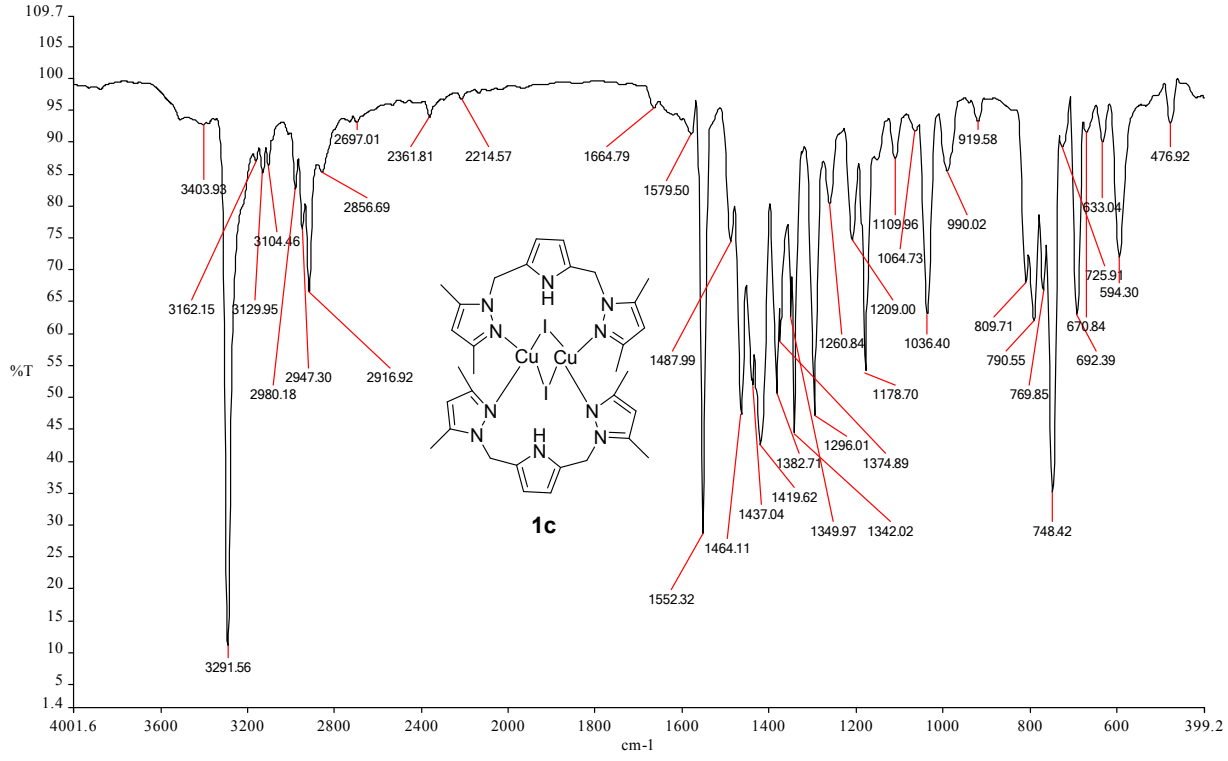

Figure S6. IR spectrum of [Cu(μ-I)(μ-C_4H_3N-2,5-$(CH_2Me_2pz)_2$–*N,N,N*)]$_2$, **1c** recorded as KBr. disc.

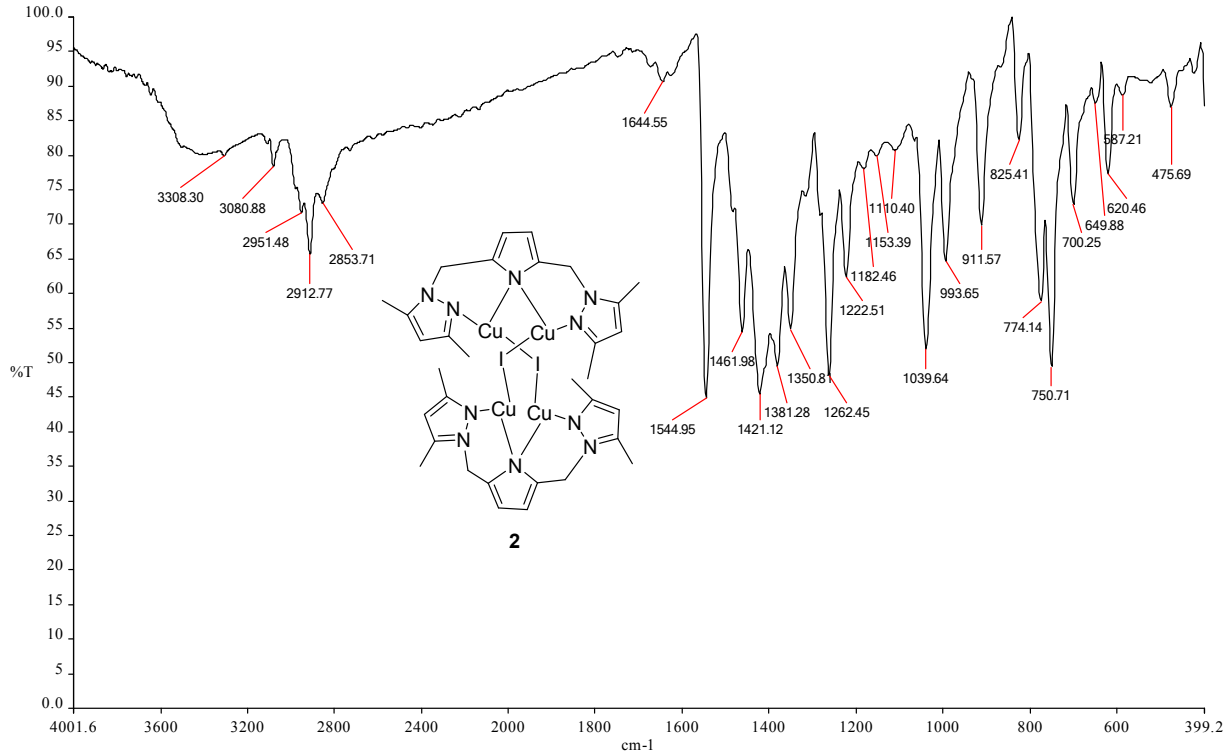

Figure S7. IR spectrum of $[Cu_4(\mu\text{-}I)_2(\mu\text{-}C_4H_2N\text{-}2,5\text{-}(CH_2Me_2pz)_2\text{–}N,N,N)_2]$, **2** recorded as KBr disc. The band around 3500 cm^{-1} is due to the presence of water in KBr used.

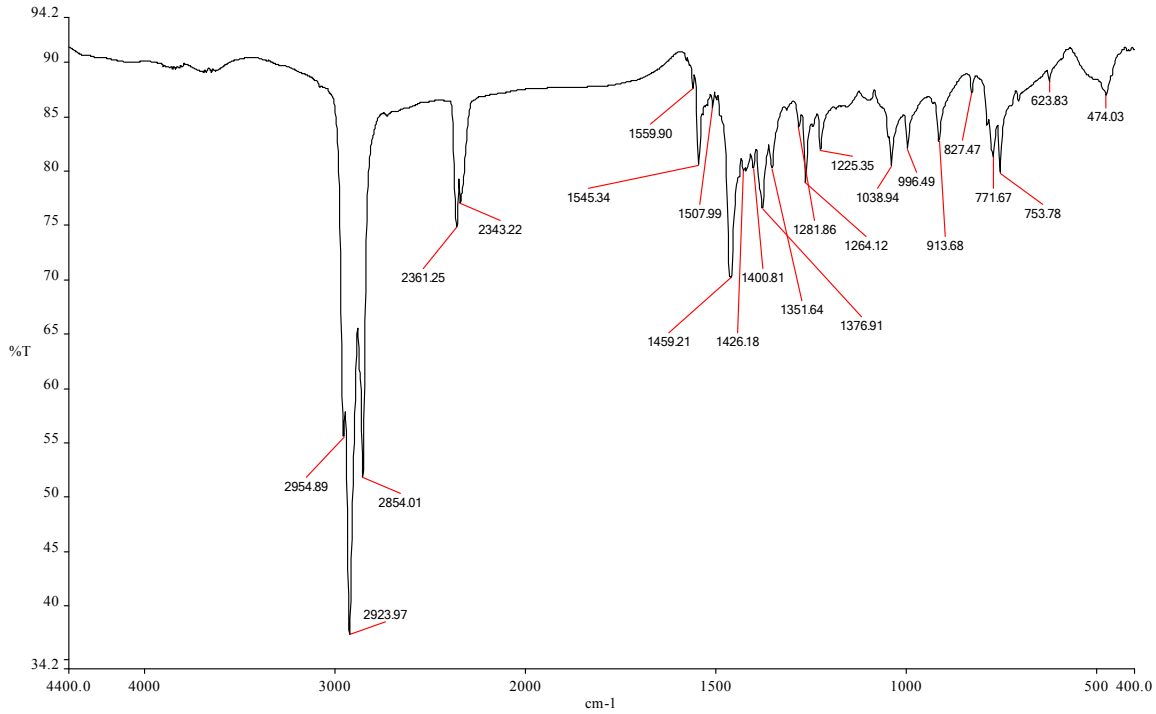

Figure S8. IR spectrum of $[Cu_4(\mu\text{-}I)_2(\mu\text{-}C_4H_2N\text{-}2,5\text{-}(CH_2Me_2pz)_2\text{–}N,N,N)_2]$, **2** recorded as a Nujol mull.

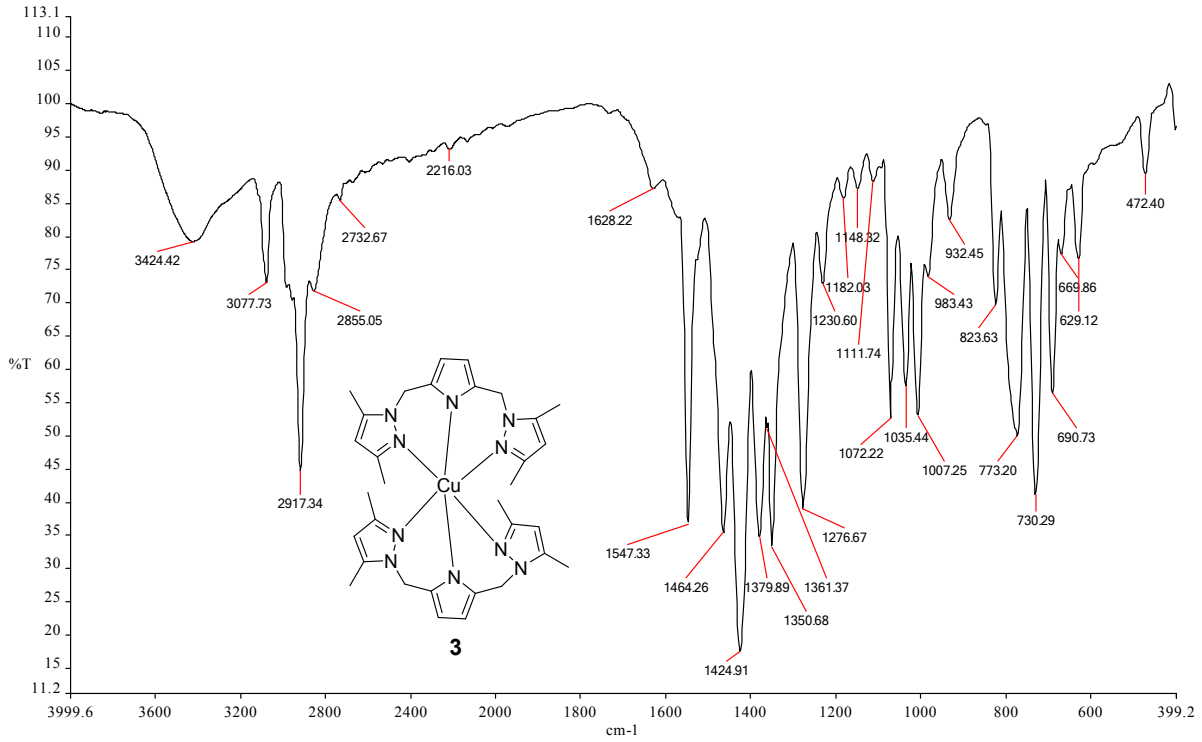

Figure S9. IR spectrum of [Cu{μ-C_4H_2N-2,5-$(CH_2Me_2pz)_2$–*N,N,N*}], **3** recorded as KBr disc. The band around 3400 cm^{-1} is due to the presence of water in KBr used.

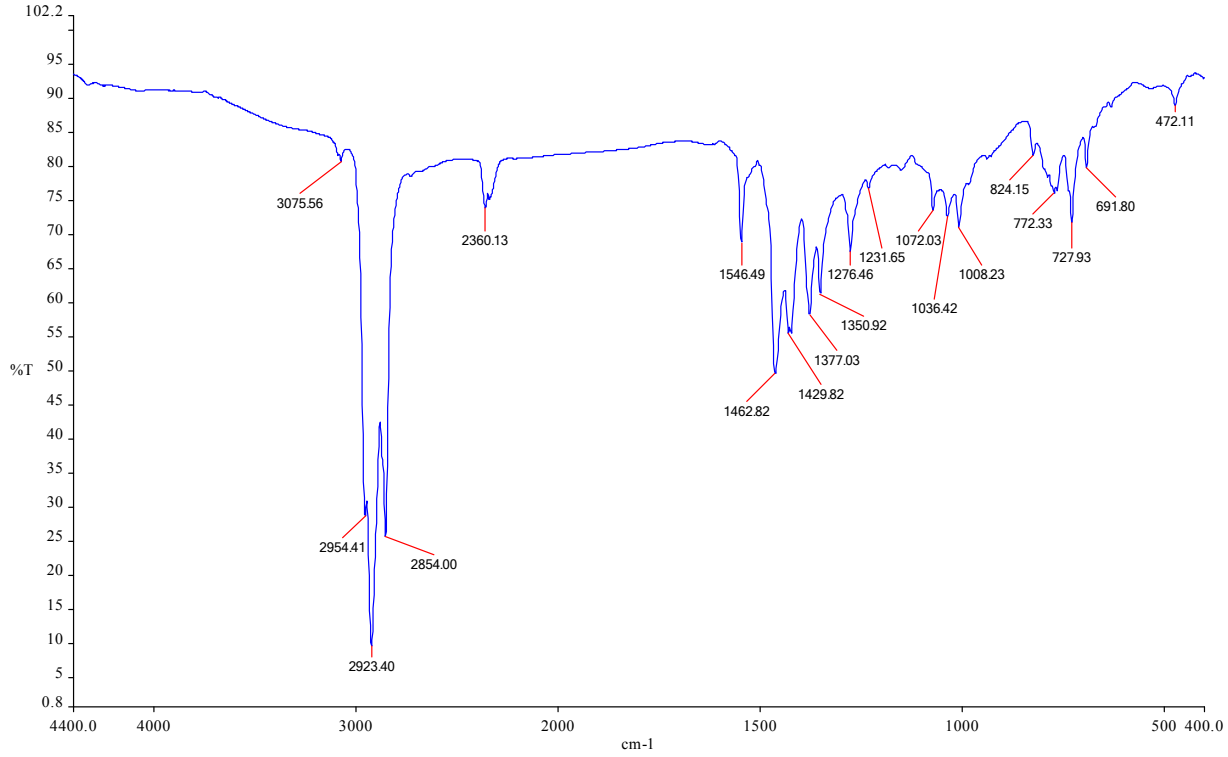

Figure S10. IR spectrum of [Cu{μ-C_4H_2N-2,5-$(CH_2Me_2pz)_2$–*N,N,N*}], **3** recorded as a Nujol mull.

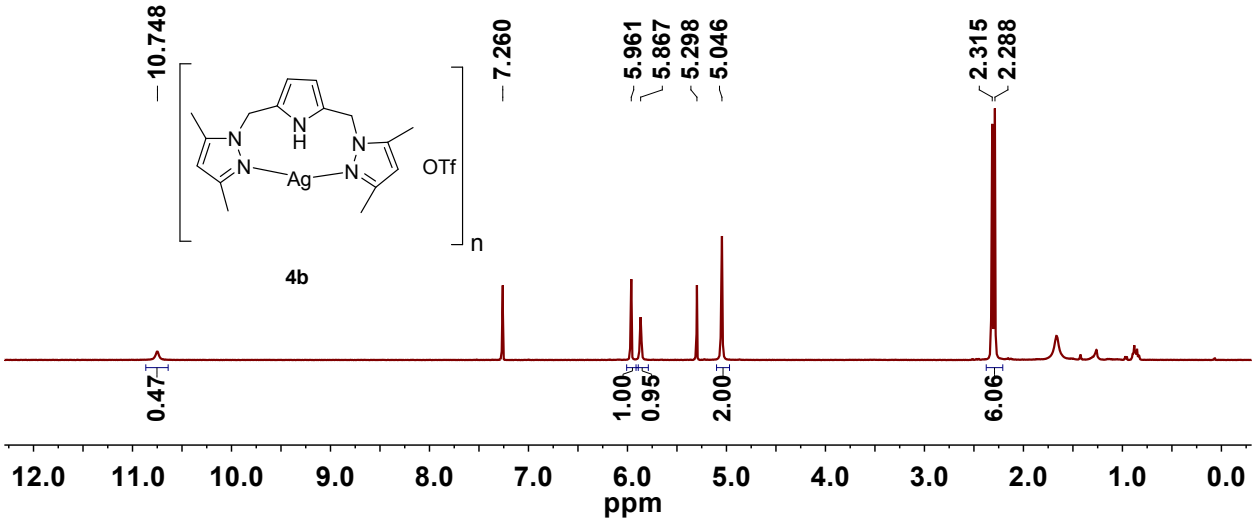

Figure S11. ^{1}H NMR (400 MHz, 25 °C) spectrum of [Ag(μ-C_4H_3N-2,5-($CH_2Me_2pz)_2$–*N,N,N*)(CF_3SO_3)]$_n$, **4a** in $CDCl_3$.

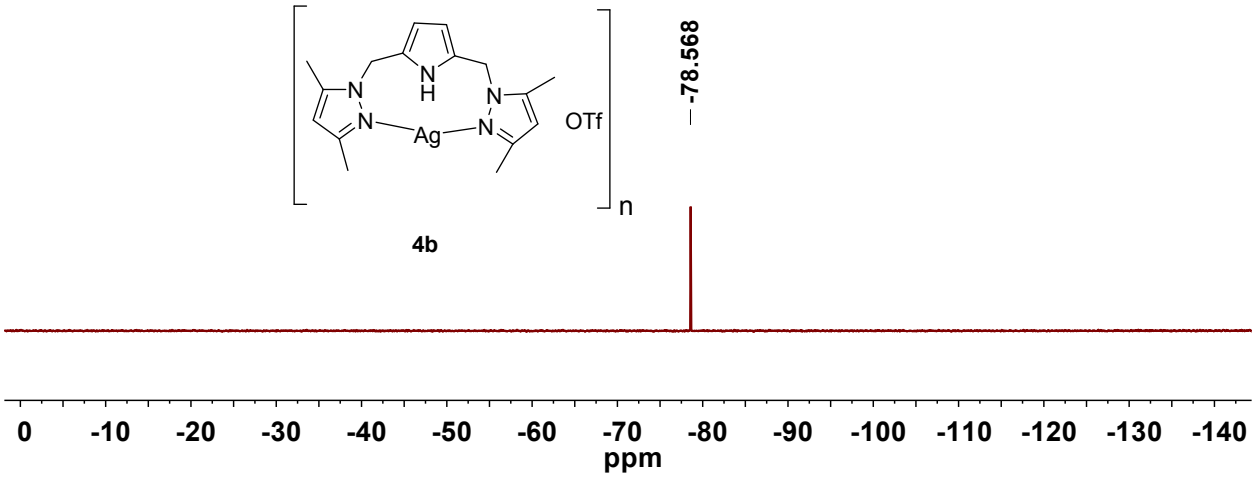

Figure S12. ^{19}F NMR (376.3 MHz, 25 °C) spectrum of [Ag(μ-C_4H_3N-2,5-($CH_2Me_2pz)_2$–*N,N,N*)(CF_3SO_3)]$_n$, **4a** in $CDCl_3$.

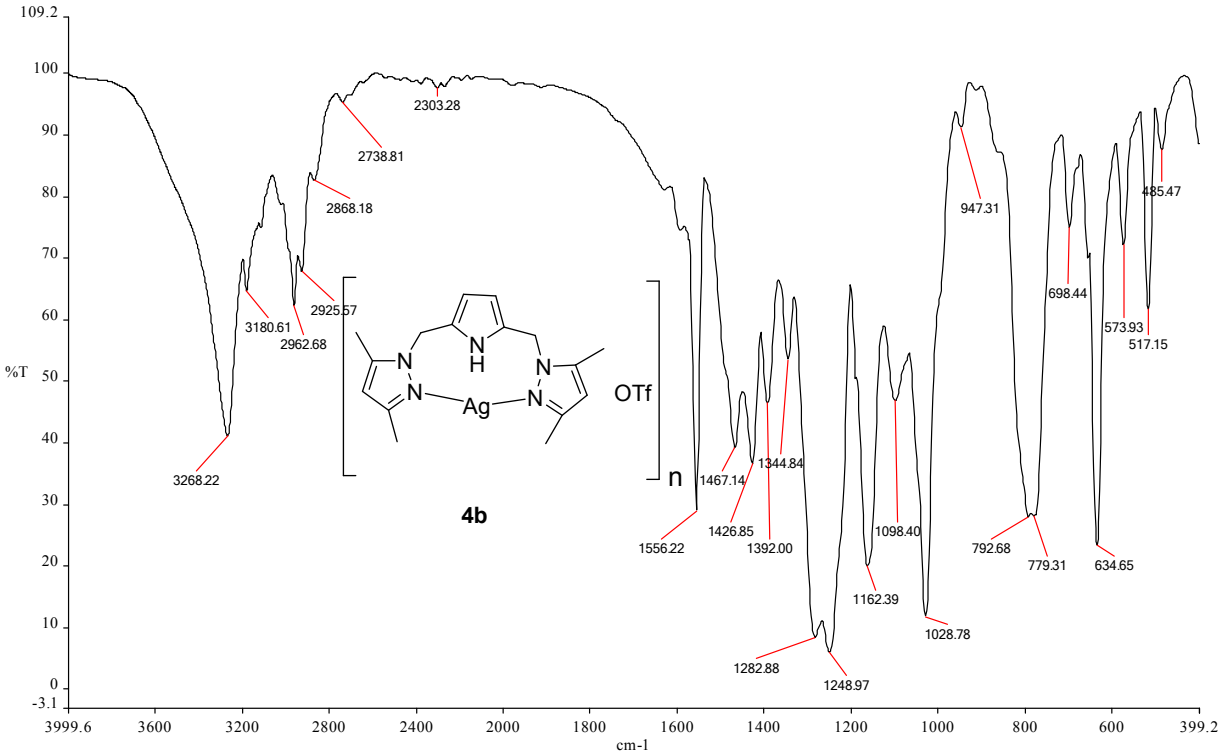

Figure S13. IR spectrum of **[**Ag(μ-C_4H_3N-2,5-$(CH_2Me_2pz)_2$–*N,N,N*)$(CF_3SO_3)]_n$, **4a** recorded as KBr disc.

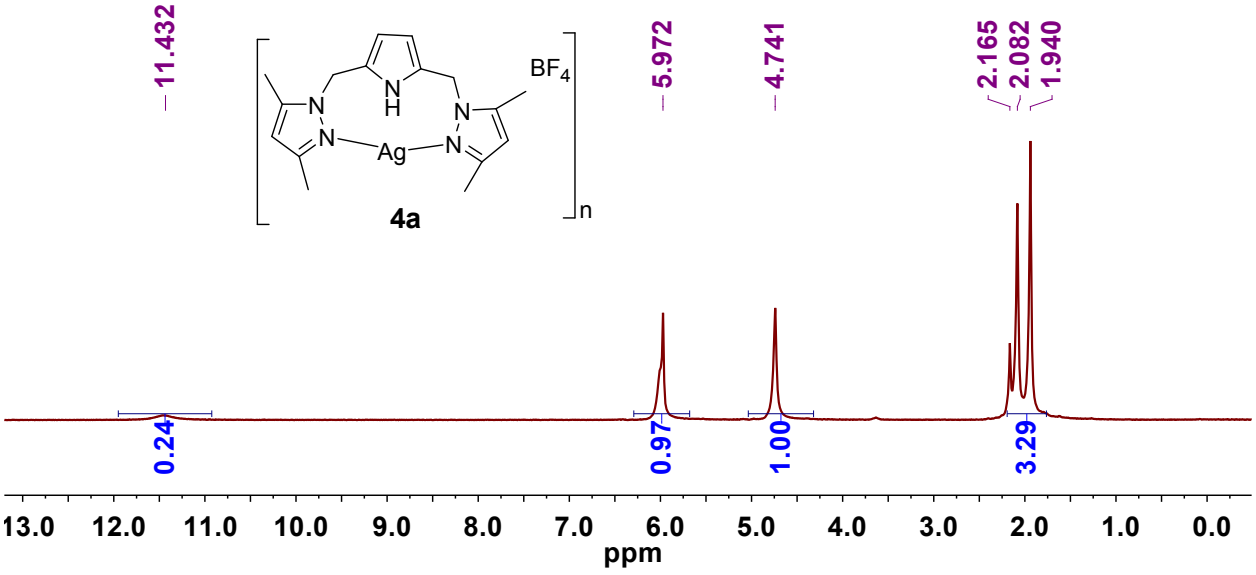

Figure S14. ^{1}H NMR (200 MHz, 25 °C) spectrum of [Ag(μ-C_4H_3N-2,5-$(CH_2Me_2pz)_2$–*N,N,N*)$(BF_4)]_n$, **4b** in CD_3CN.

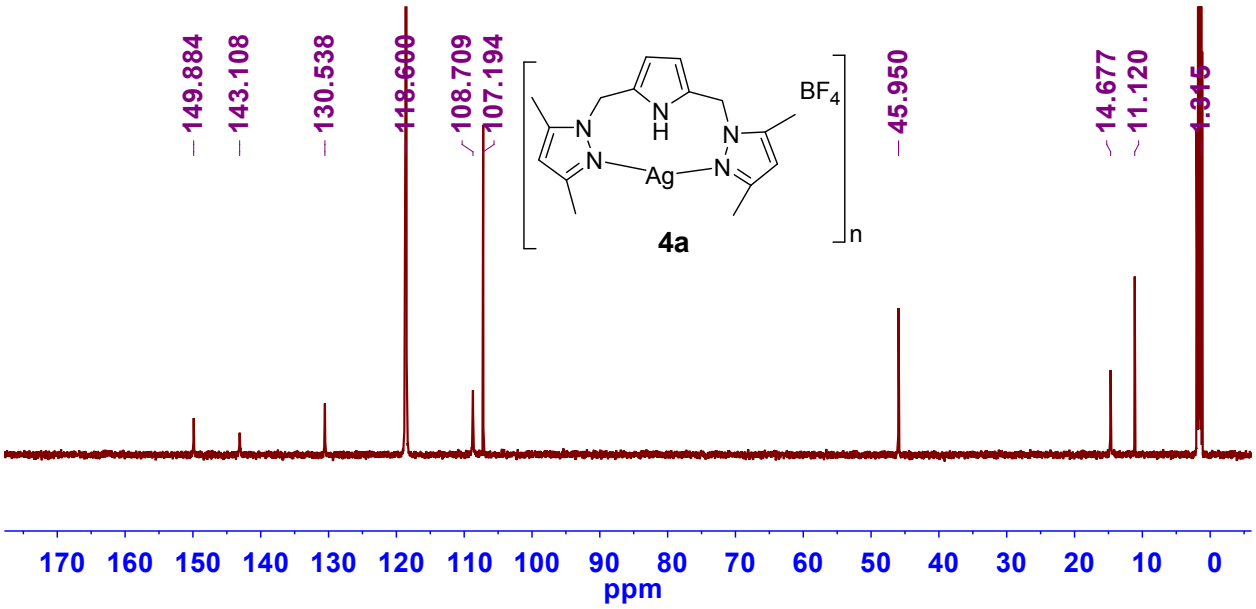

Figure S15. ^{13}C NMR (102.6 MHz, 25 °C) spectrum of $[Ag(\mu\text{-}C_4H_3N\text{-}2,5\text{-}(CH_2Me_2pz)_2\text{–}N,N,N)(BF_4)]_n$, **4b** in CD_3CN.

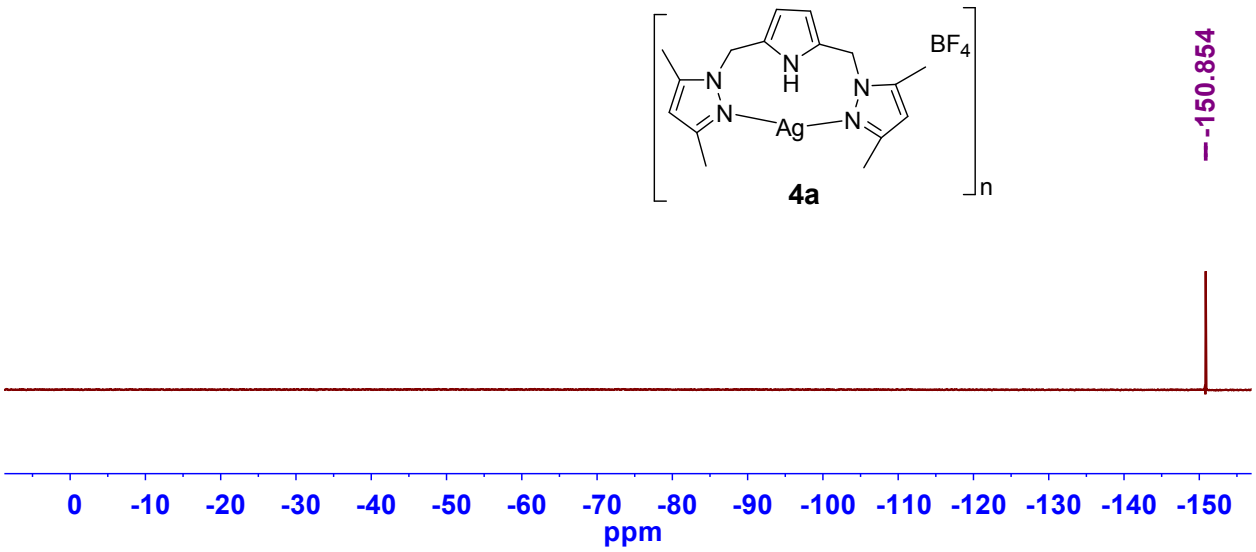

Figure S16. ^{19}F NMR (376.3 MHz, 25 °C) spectrum of $[Ag(\mu\text{-}C_4H_3N\text{-}2,5\text{-}(CH_2Me_2pz)_2\text{–}N,N,N)(BF_4)]_n$, **4b** in CD_3CN.

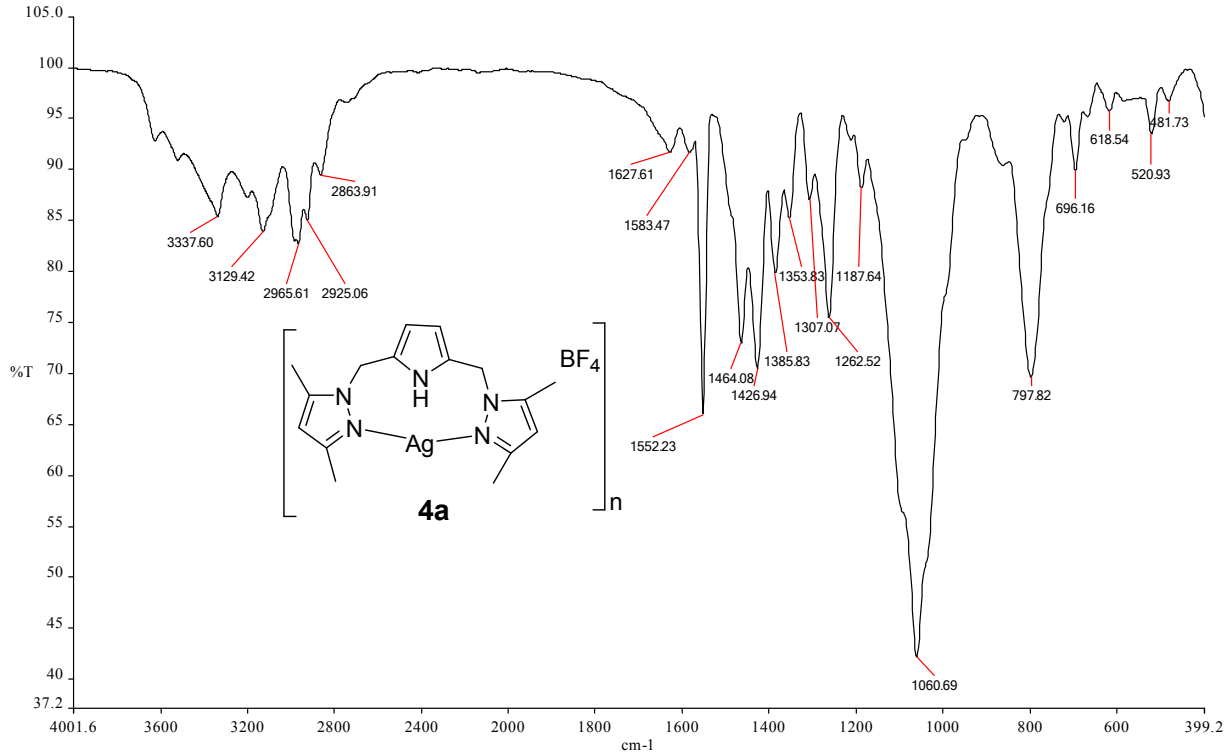

Figure S17. IR spectrum of $[Ag(\mu\text{-}C_4H_3N\text{-}2,5\text{-}(CH_2Me_2pz)_2\text{–}N,N,N)(BF_4)]_n$, **4b** recorded as KBr disc.

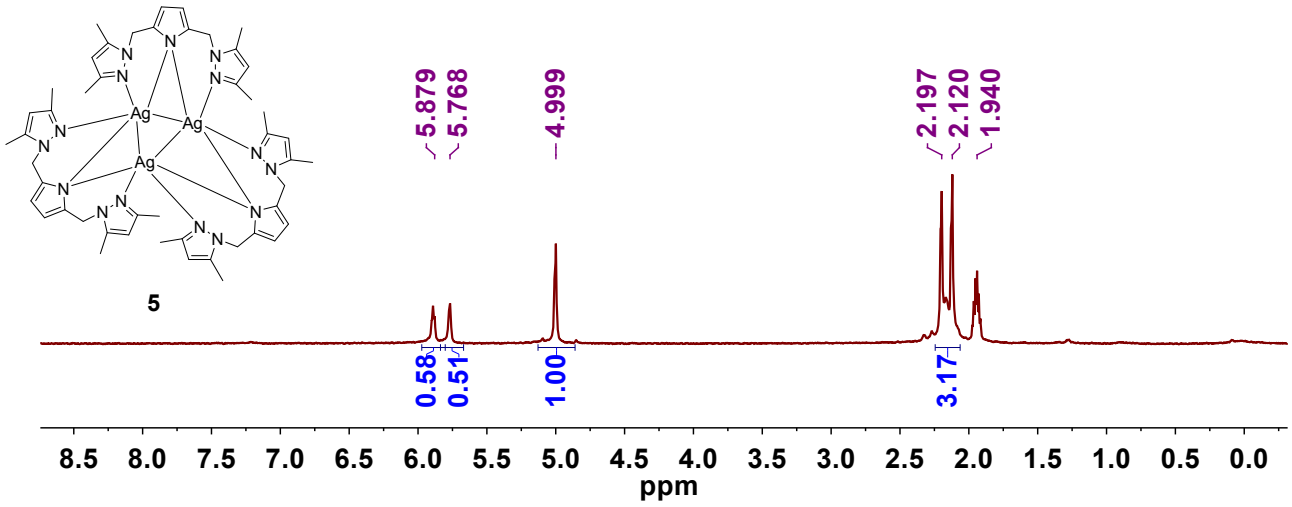

Figure S18. ^{1}H NMR (200 MHz, 25 °C) spectrum of $[Ag\{(\mu\text{-}C_4H_2N\text{-}2,5\text{-}(CH_2Me_2pz)_2)\text{–}N,N,N\}]_3$, **5** in CD_3CN.

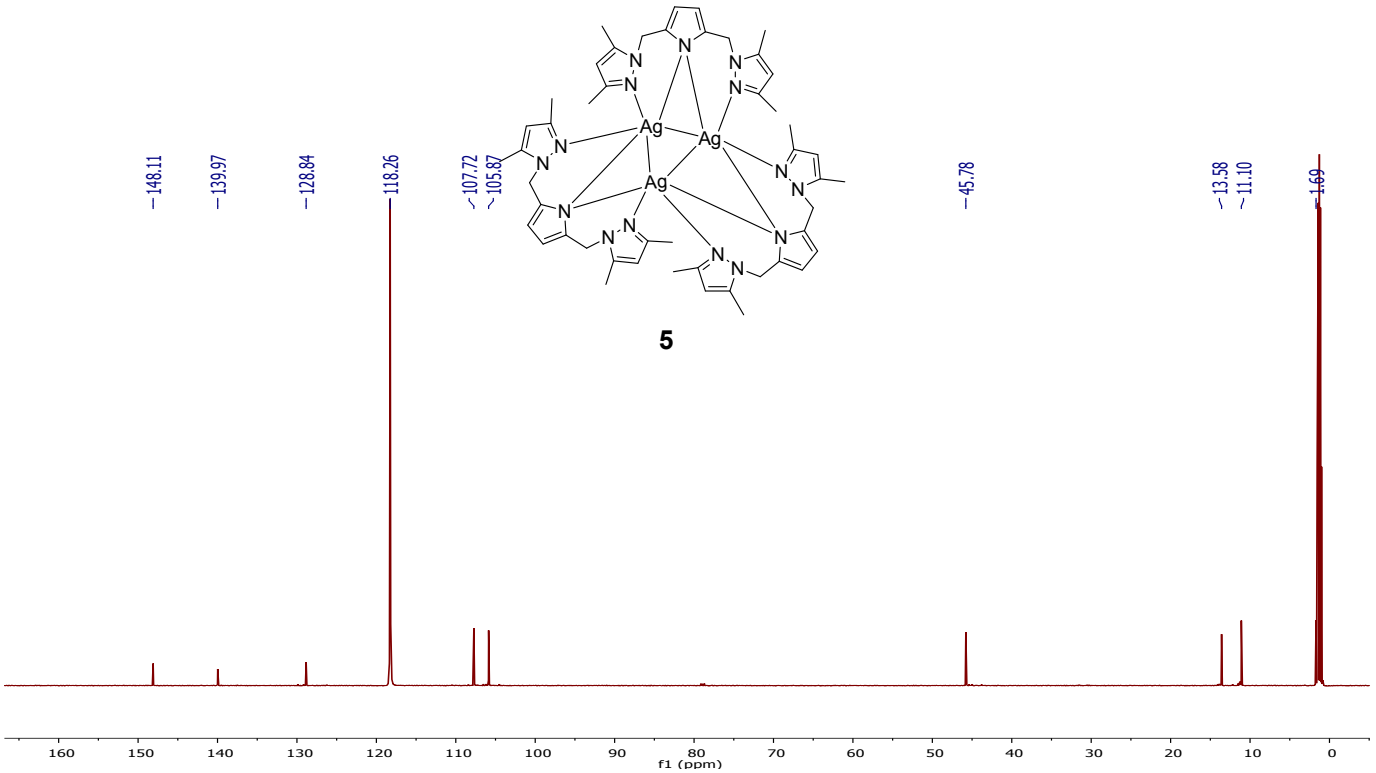

Figure S19. ^{13}C NMR (153.9 MHz, 25 °C) spectrum of [Ag{(μ-C_4H_2N-2,5-$(CH_2Me_2pz)_2$)–*N,N,N* }]$_3$, **5** in CD_3CN.

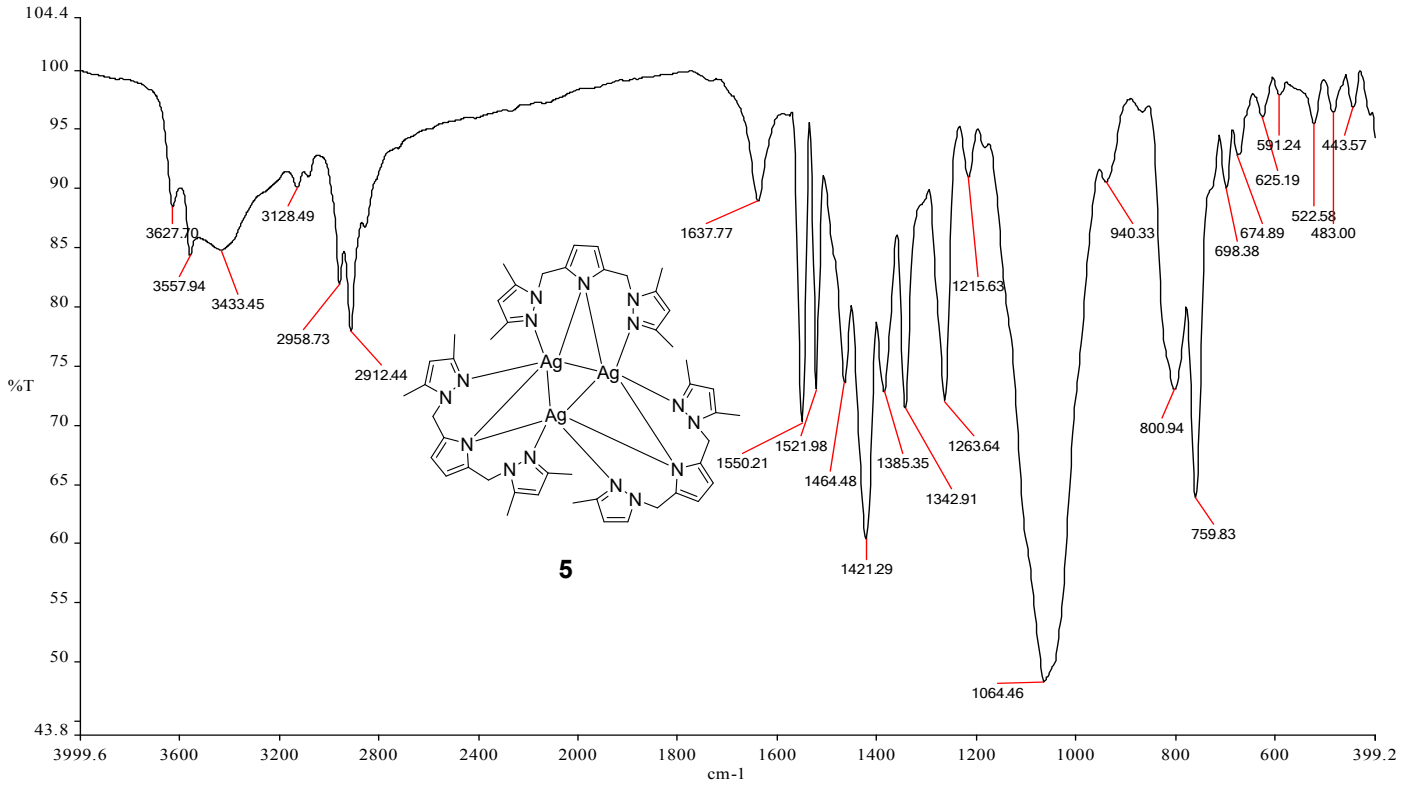

Figure S20. IR spectrum of [Ag{(μ-C_4H_2N-2,5-($CH_2Me_2pz)_2$)–*N,N,N*}]$_3$, **5** recorded as KBr disc. The band around 3400 cm^{-1} is due to the presence of water in KBr used.

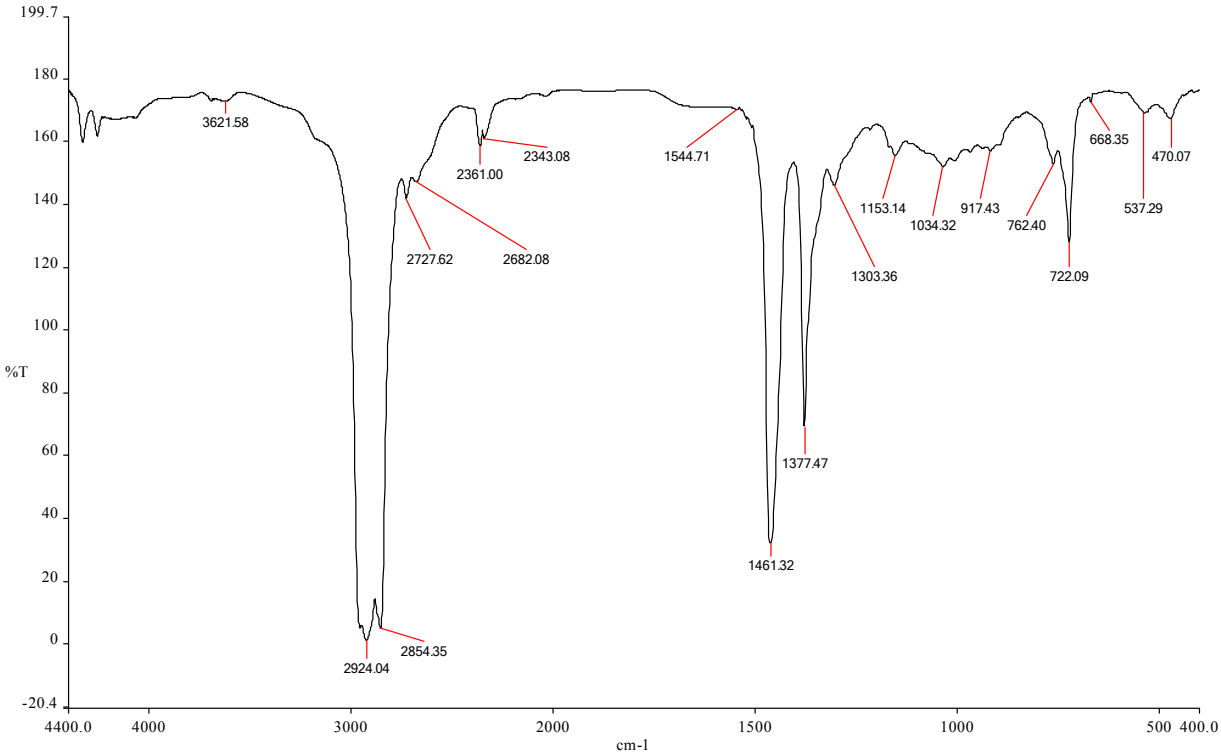

Figure S21. IR spectrum of [Ag{(μ-C_4H_2N-2,5-($CH_2Me_2pz)_2$)–*N,N,N*}]$_3$, **5** recorded as a Nujol mull.

X-ray structures

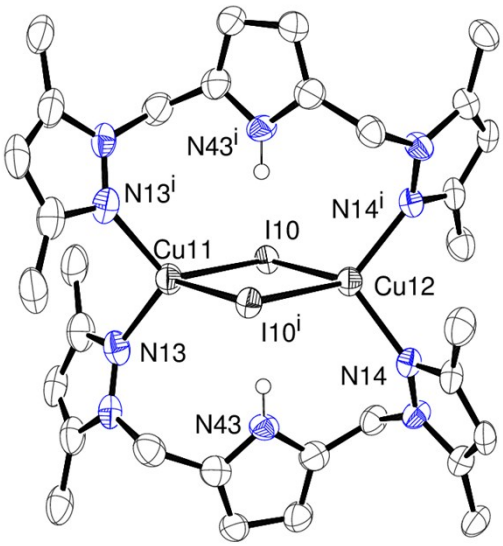

Figure S22. ORTEP diagram of complex **1c** with 50% probability ellipsoids; most H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N13–Cu11 2.051(11), N14–Cu12 2.027(10), Cu11–I10 2.7063(17), Cu12–I10 2.7205(17); Cu12–I10–Cu11 85.29(6), N13'–Cu11–N13 109.5(6), I10'–Cu12–I10 94.39(7), N13–Cu11–I10 102.0(3). Symmetry transformations used to generate equivalent atoms: (i) 1–y,1–x, 3/2–z; (ii) –y, –x, 3/2–z.

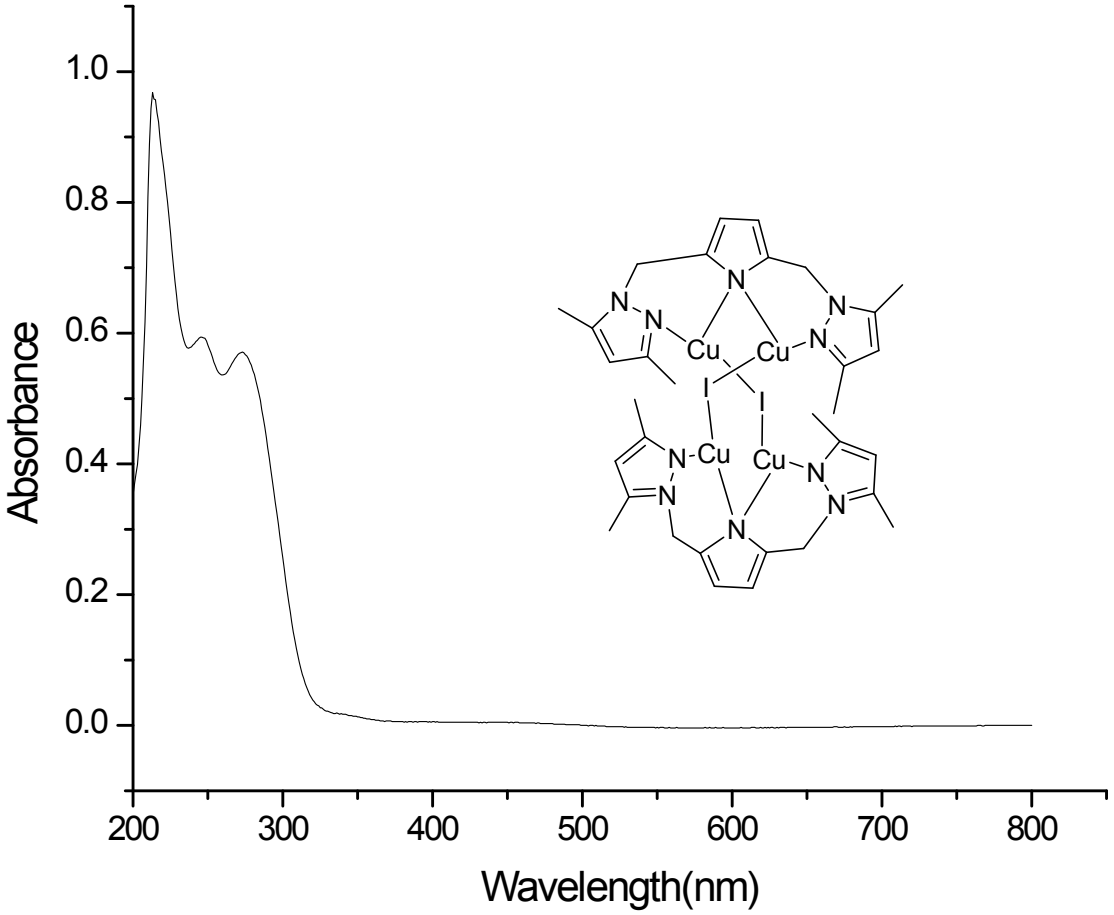

Figure S23. UV-vis spectrum of the tetranuclear copper(I) complex $[Cu_4(\mu\text{-}I)_2(\mu\text{-}C_4H_2N\text{-}2,5\text{-}(CH_2Me_2pz)_2\text{-}N,N,N)_2]$ **2** with concentration of 10^{-5} M solution in CH_3CN. 0.0003 g of this complex dissolved in 25 mL of CH_3CN and then UV recorded within 1 hr. The color of the solution appeared almost colorless.

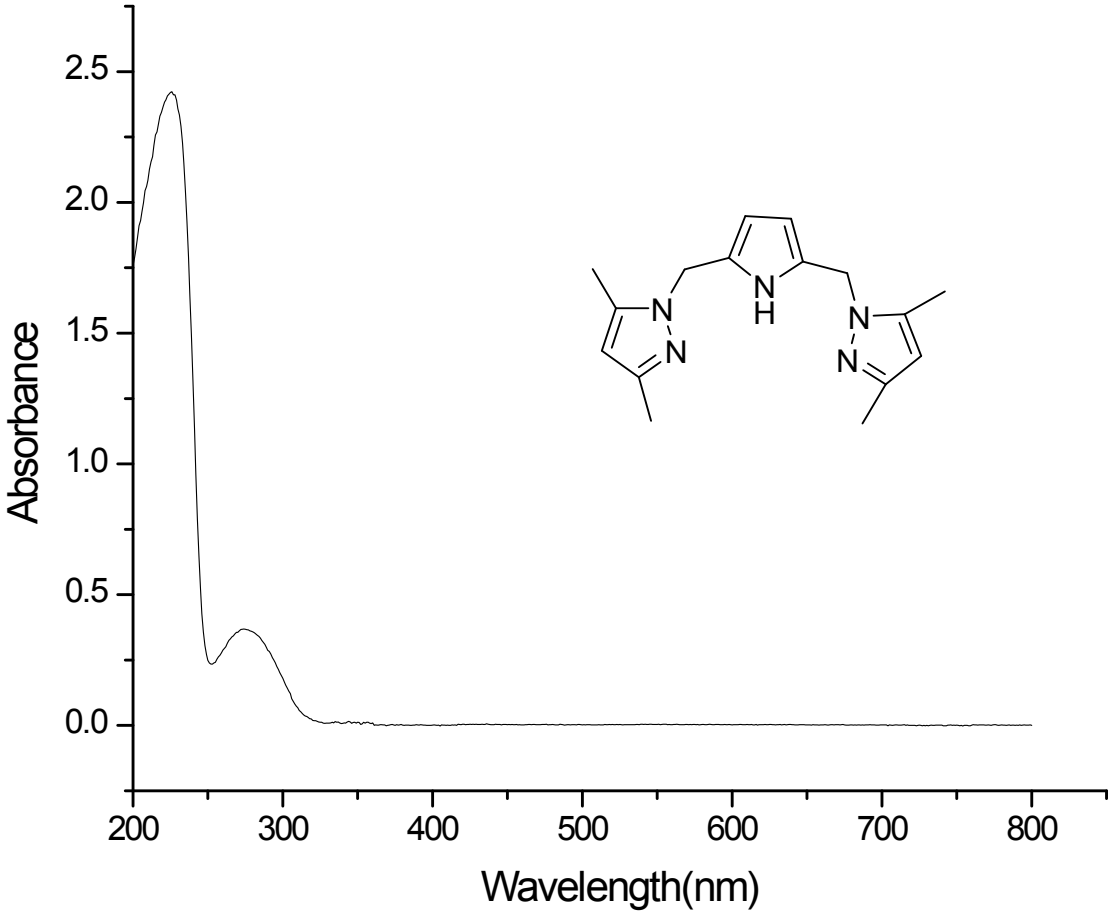

Figure S24. UV-vis spectrum of the NNN pincer ligand, 2,5-Bis(3,5-dimethylpyrazolylmethyl)pyrrole **LH**, with concentration of 10^{-4} M solution in CH_3CN.