Electronic Supporting Information for

A Macrocyclic Silver Polycarbene Complex Based on 1,2,4-Triazole Units: Synthesis and Postsynthetic Modification

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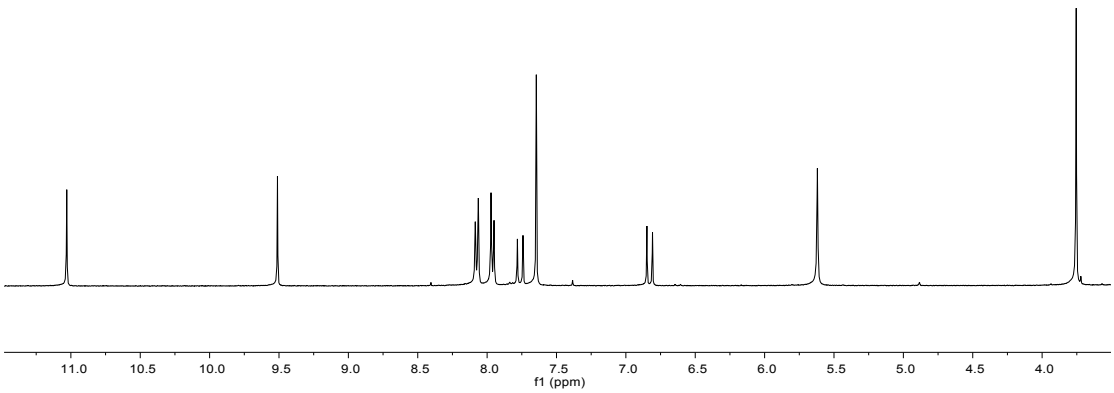


Figure S1. ^{1}H NMR (400 MHz, DMSO-d_6) of H_2-**1**$(BF_4)_2$.

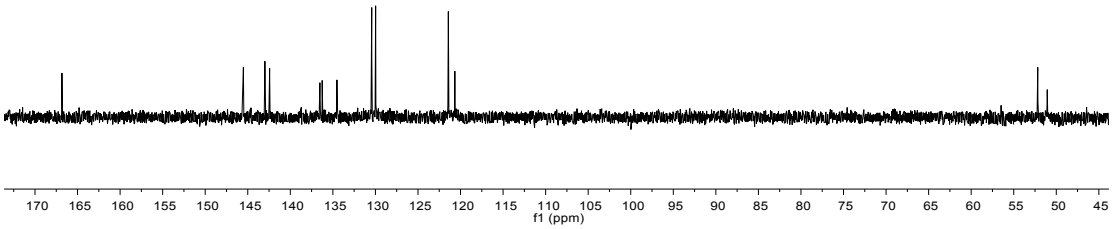


Figure S2. ^{13}C NMR (100 MHz, DMSO-d_6) of H_2-**1**$(BF_4)_2$.

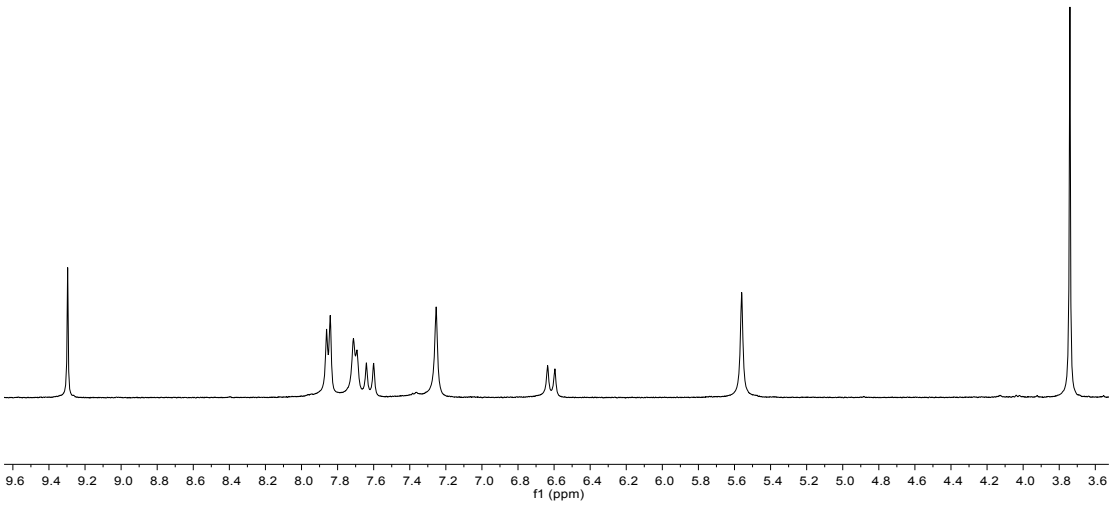


Figure S3. ^{1}H NMR (400 MHz, DMSO-d_6) of $[Ag_2(\mathbf{1})_2](BF_4)_2$.

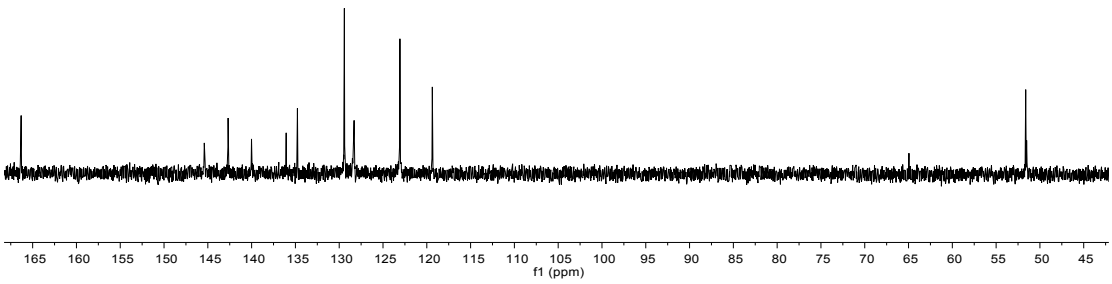


Figure S4. ^{13}C NMR (100 MHz, DMSO-d_6) of $[Ag_2(\mathbf{1})_2](BF_4)_2$.

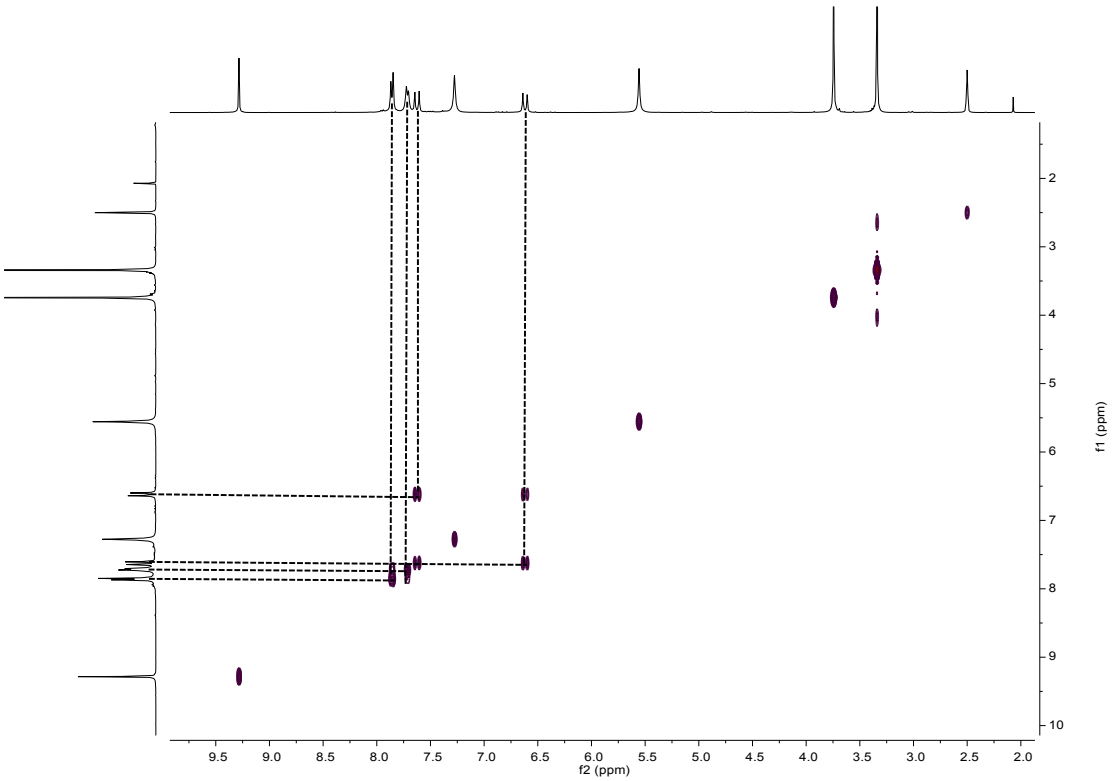


Figure S5. HH-COSY NMR (400 MHz, DMSO-d_6) of $[Ag_2(\mathbf{1})_2](BF_4)_2$.

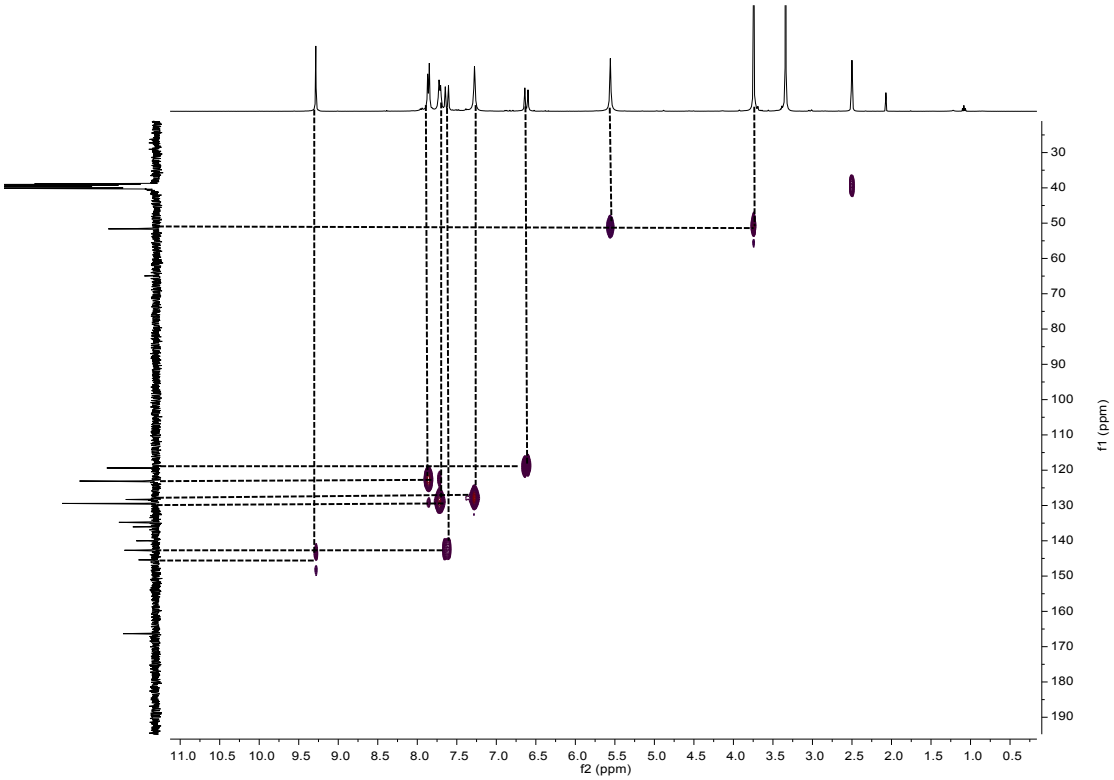


Figure S6. HC-HSQC NMR (400 MHz, DMSO-d_6) of $[Ag_2(\mathbf{1})_2](BF_4)_2$.

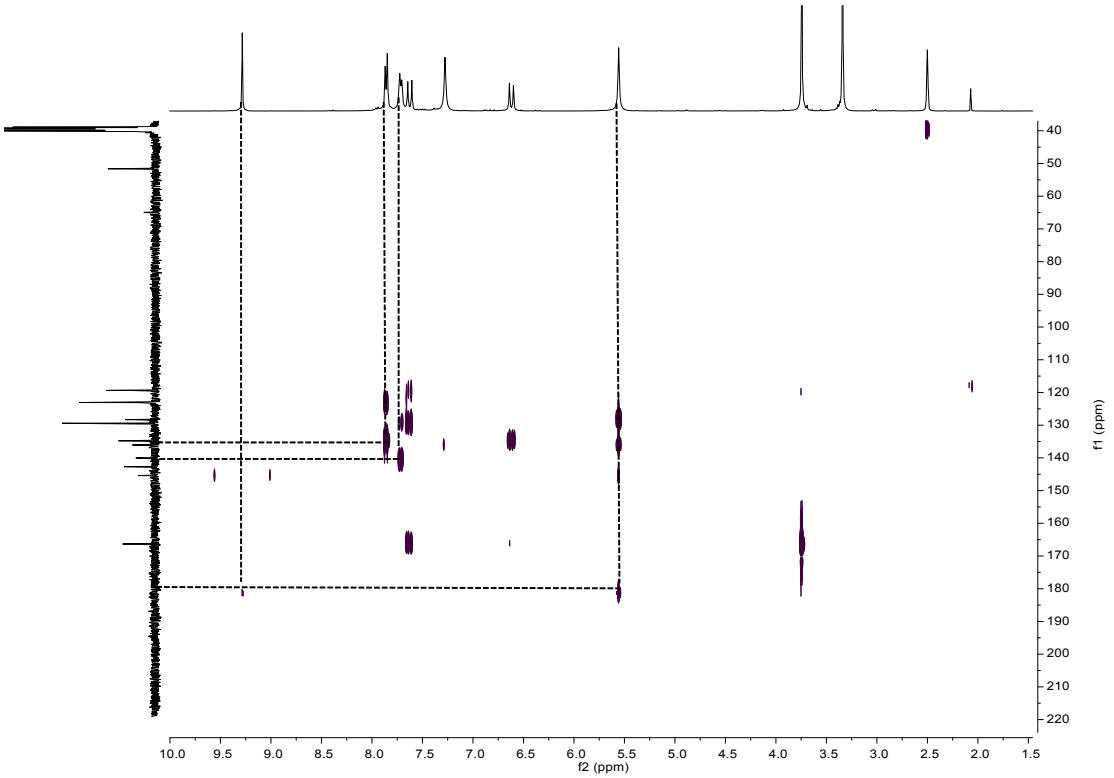


Figure S7. HC-HMBC NMR (400 MHz, DMSO-d_6) of $[Ag_2(\mathbf{1})_2](BF_4)_2$.

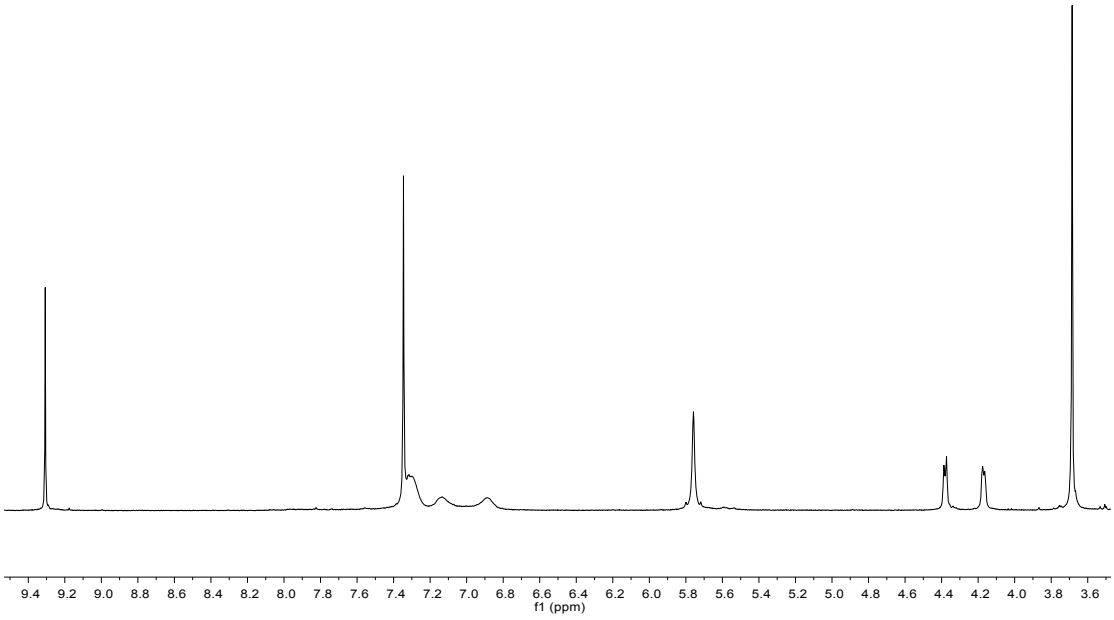


Figure S8. ^{1}H NMR (400 MHz, DMSO-d_6) of $[Ag_2(\mathbf{2})](BF_4)_2$.

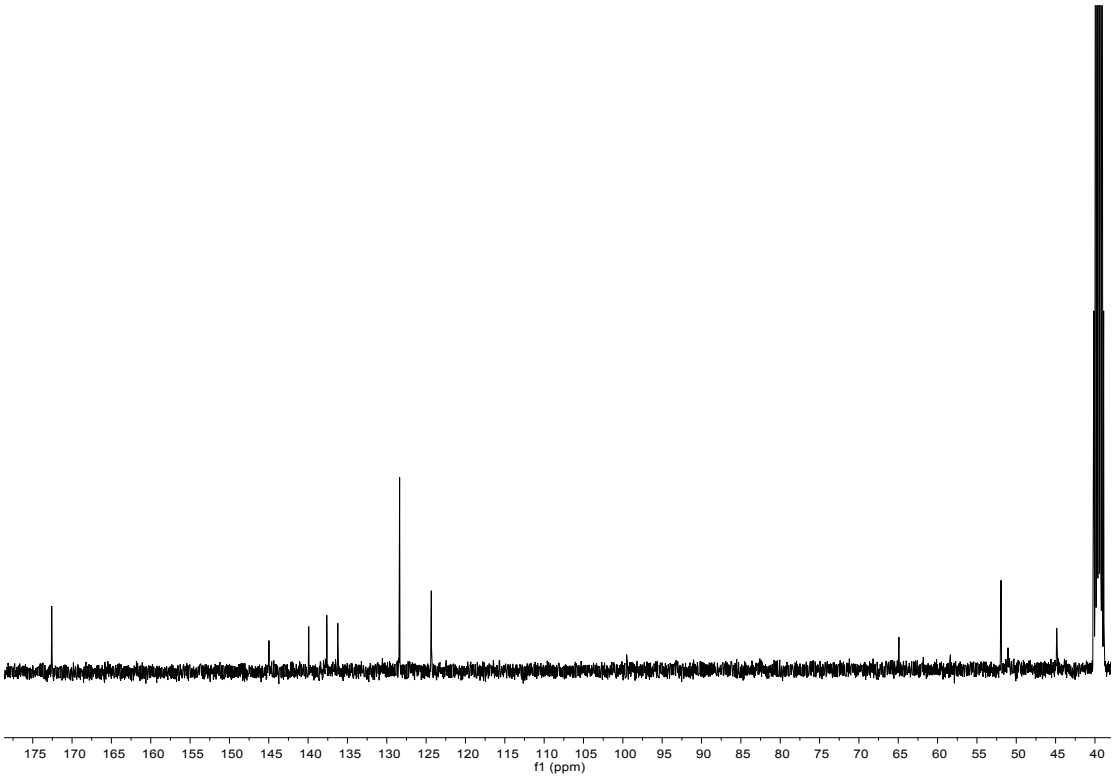


Figure S9. ^{13}C NMR (100 MHz, DMSO-d_6) of $[Ag_2(\mathbf{2})](BF_4)_2$.

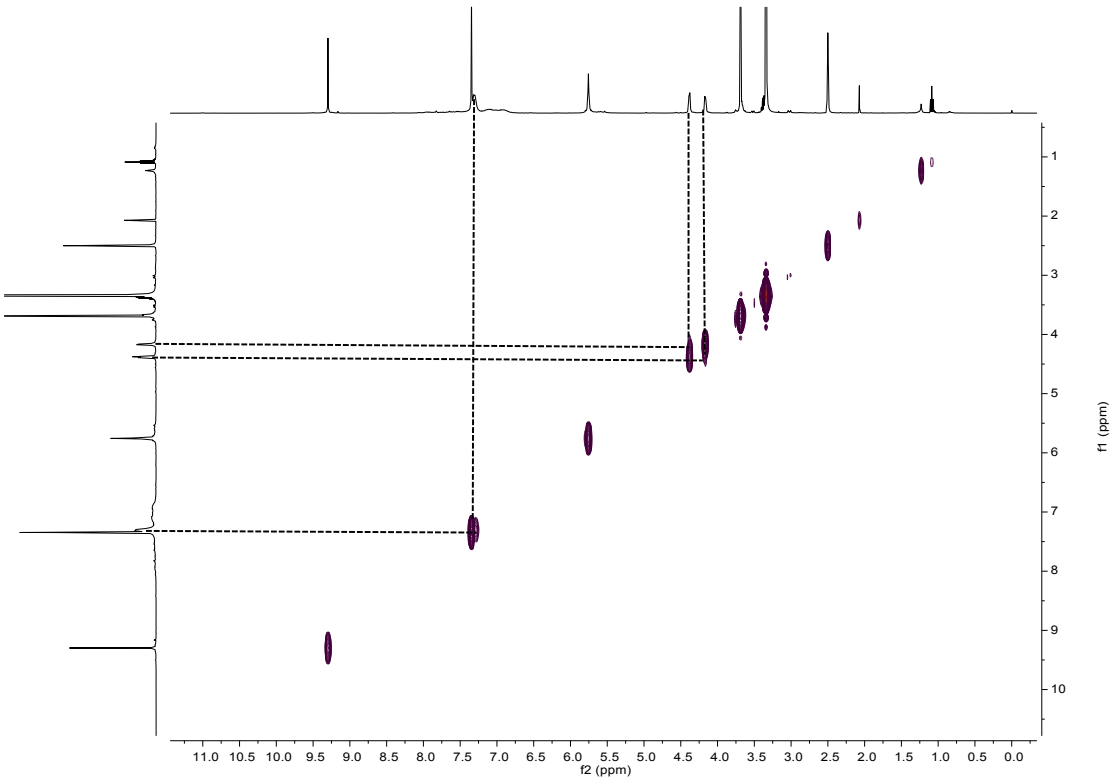


Figure S10. HH-COSY NMR (400 MHz, DMSO-d_6) of $[Ag_2(\mathbf{2})](BF_4)_2$.

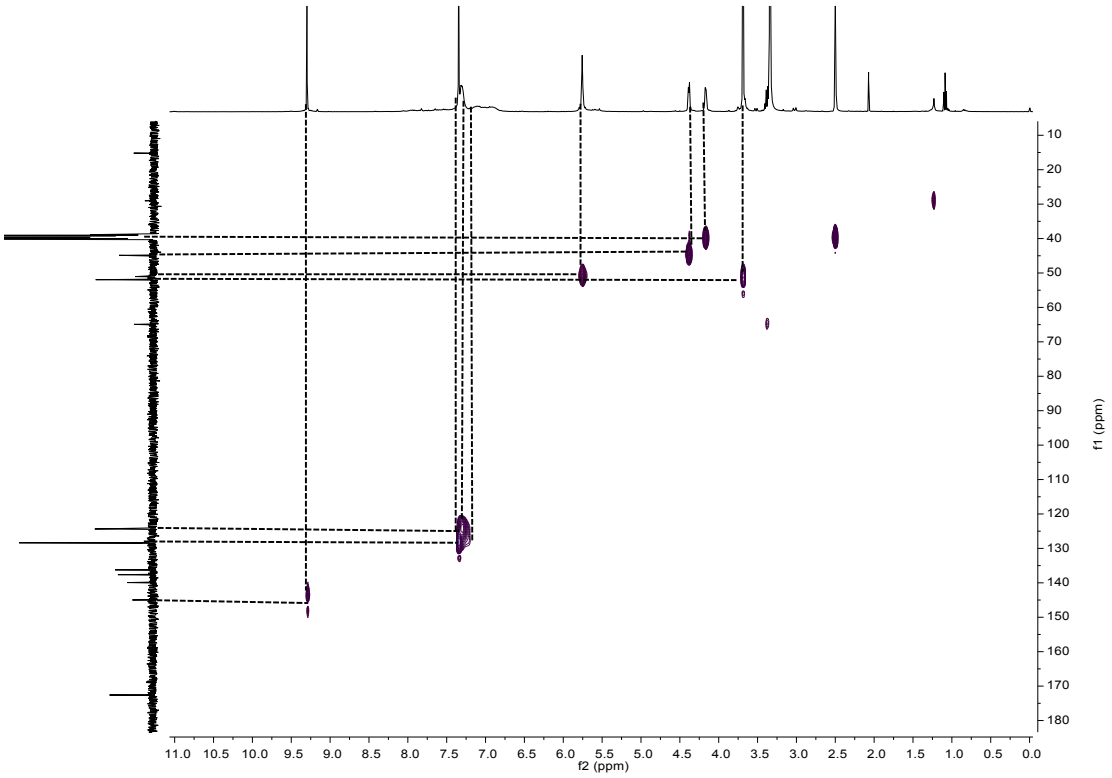


Figure S11. HC-HSQC NMR (400 MHz, DMSO-d_6) of $[Ag_2(\mathbf{2})](BF_4)_2$.

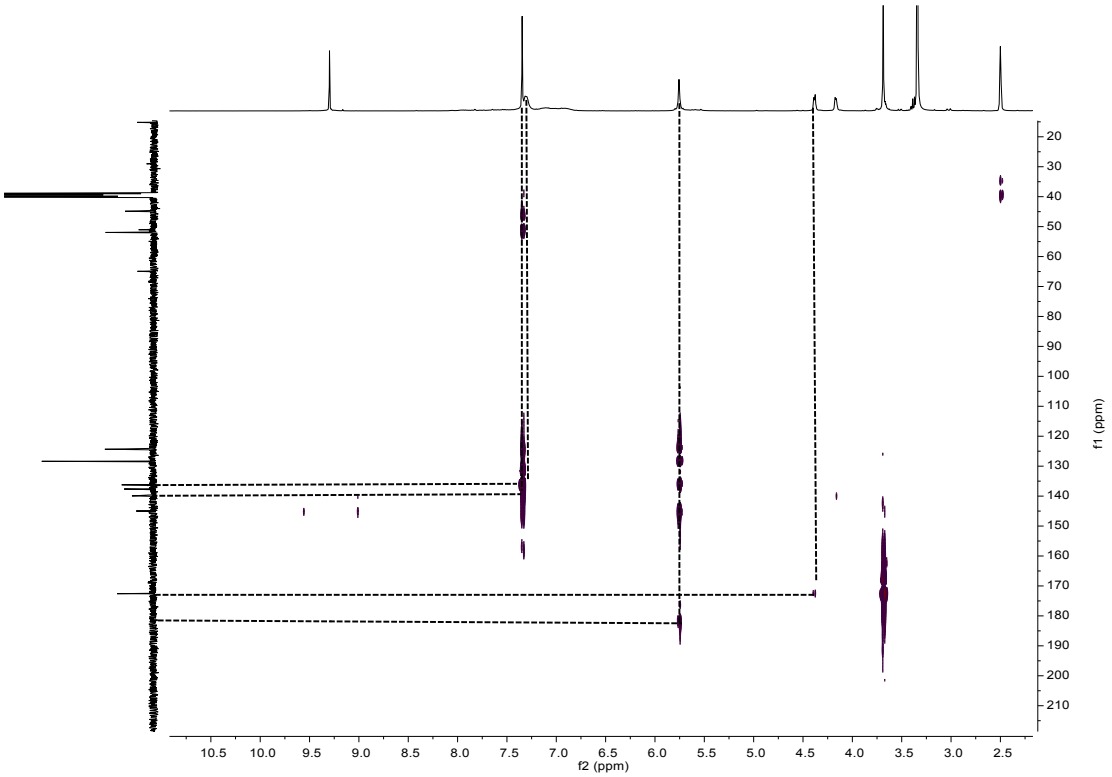


Figure S12. HC-HMBC NMR (400 MHz, DMSO-d_6) of $[Ag_2(\mathbf{2})](BF_4)_2$.

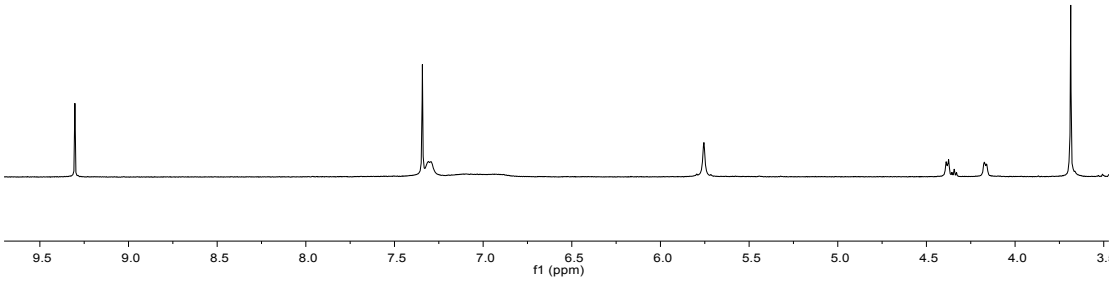


Figure S13. ^{1}H NMR (400 MHz, DMSO-d_6) of $[Ag_2(\mathbf{2})](BF_4)_2$ which obtained directly from the reaction of H_4-$\mathbf{2}(BF_4)_4$ and Ag_2O.

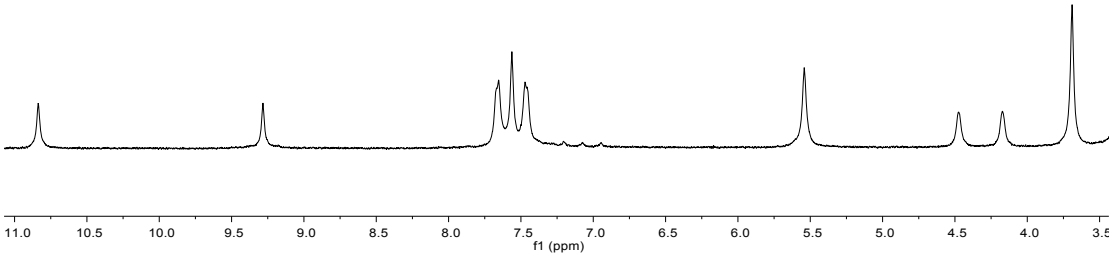


Figure S14. ^{1}H NMR (400 MHz, DMSO-d_6) of H_4-$\mathbf{2}(BF_4)_4$.

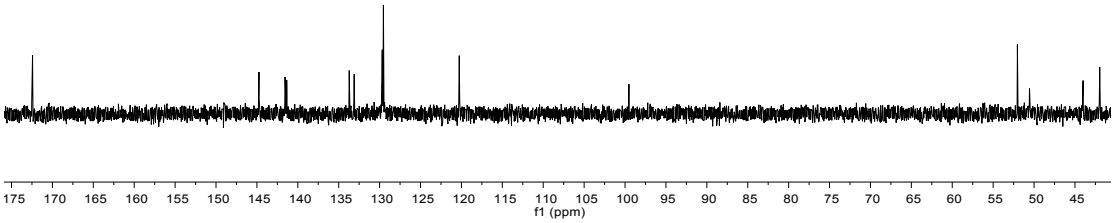


Figure S15. ^{13}C NMR (100 MHz, DMSO-d_6) of H_4-**2**$(BF_4)_4$.

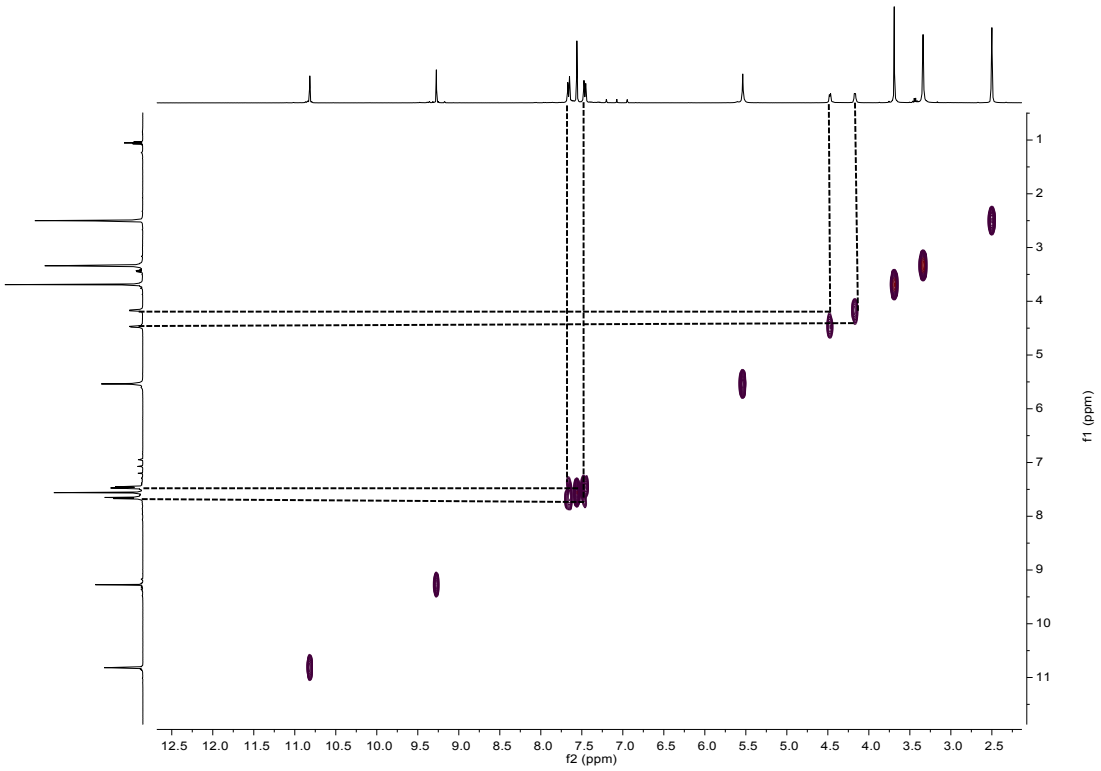


Figure S16. HH-COSY NMR (400 MHz, DMSO-d_6) of H_4-**2**$(BF_4)_4$.

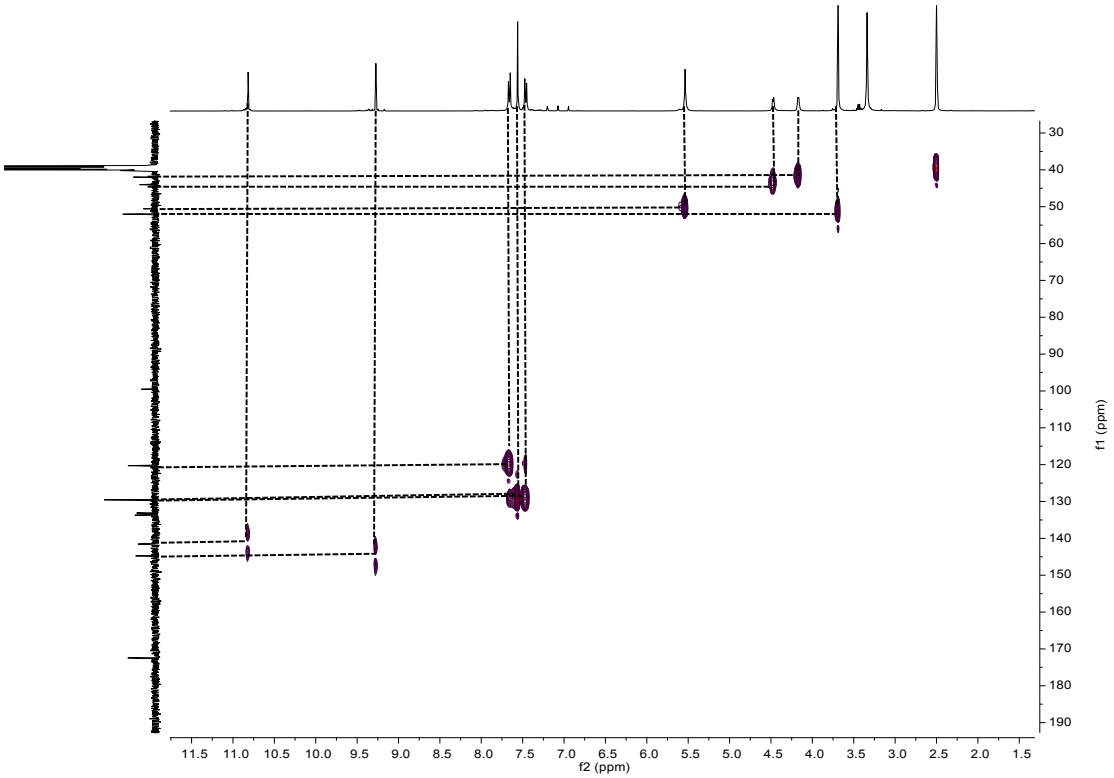


Figure S17. HC-HSQC NMR (400 MHz, DMSO-d_6) of H_4-**2**$(BF_4)_4$.

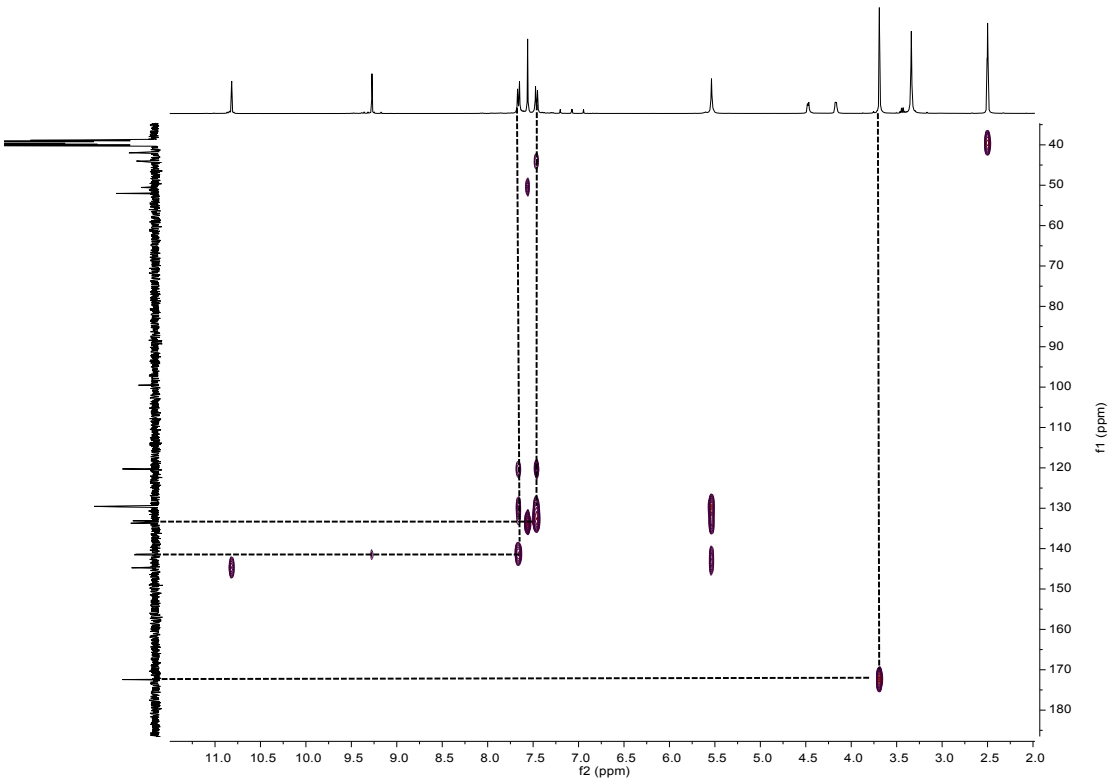
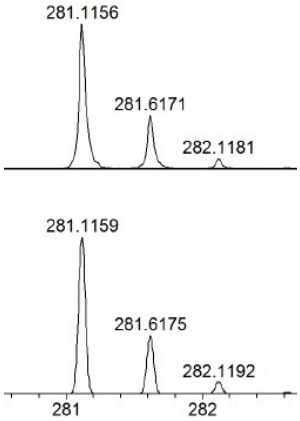
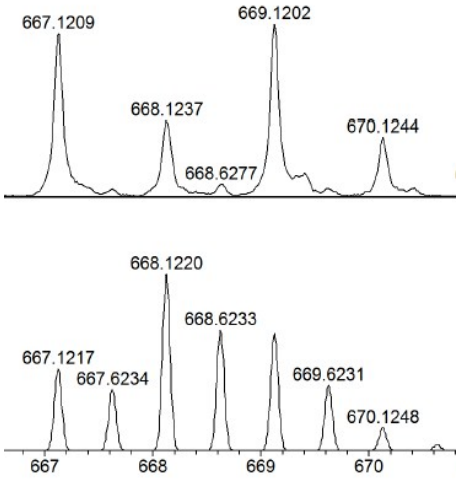


Figure S18. HC-HMBC NMR (400 MHz, DMSO-d_6) of H_4-**2**$(BF_4)_4$.



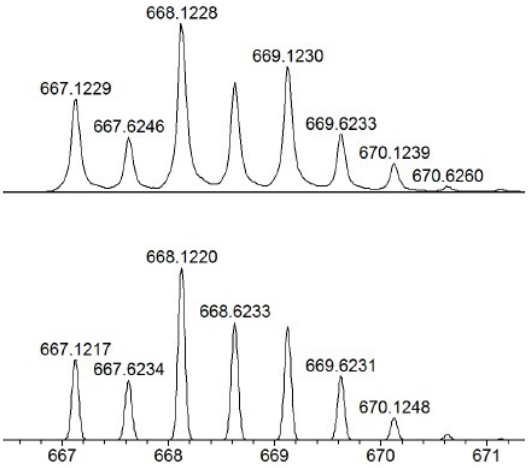
ESI-MS (positive ions) for $\{[H_2\text{-}\mathbf{1}]\}^{2+}$: Top (tested) and bottom (Calcd).

Figure S19. ESI-MS spectra of H_2-**1**$(BF_4)_2$.



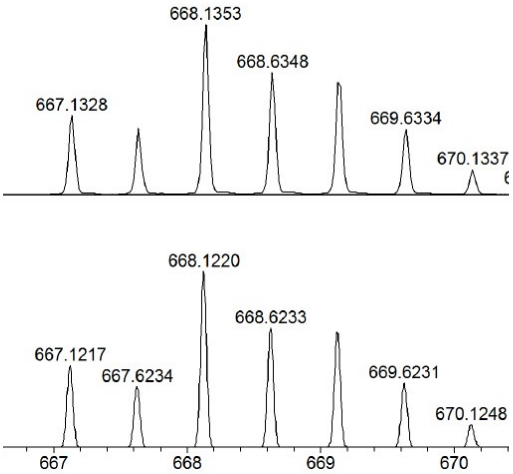
ESI-MS (positive ions) for $\{[Ag_2(\mathbf{1})_2]\}^{2+}$: Top (measured) and bottom (Calcd.).

Figure S20. ESI-MS spectra of $[Ag_2(\mathbf{1})_2](BF_4)_2$.



ESI-MS (positive ions) for $\{[Ag_2(\mathbf{2})]\}^{2+}$: Top (measured) and bottom (Calcd.).

Figure S21. ESI-MS spectra of $[Ag_2(\mathbf{2})](BF_4)_2$.



ESI-MS (positive ions) for $\{[Ag_2(\mathbf{2})]\}^{2+}$: Top (measured) and bottom (Calcd.).

Figure S22. ESI-MS spectra of $[Ag_2(\mathbf{2})](BF_4)_2$ which obtained directly from the reaction of H_4-$\mathbf{2}(BF_4)_4$ and Ag_2O.

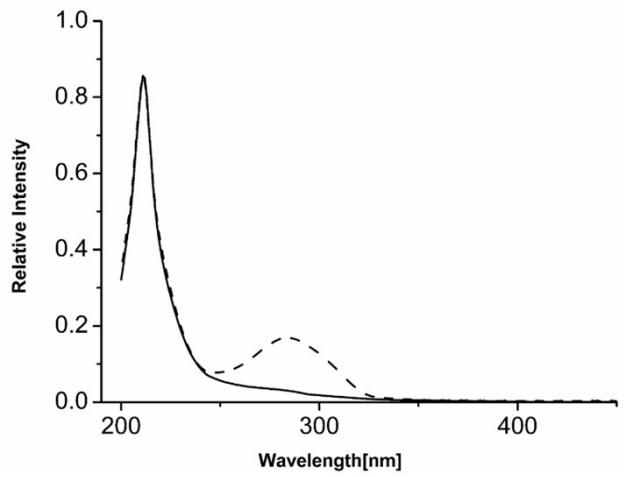


Fig. S23 UV−vis spectra of $[Ag_2(\mathbf{1})_2](BF_4)_2$ (5 μM) in CH_3CN before $[Ag_2(\mathbf{1})_2](BF_4)_2$ (dash line) and after $[Ag_2(\mathbf{2})](BF_4)_2$ (soild line) photoreaction

Table S1. Crystal data of complex $[Ag_2(\mathbf{1})_2](BF_4)_2$.

Empirical formula	$C_{68}H_{64}Ag_2B_2Cl_8F_8N_{12}O_8$
Formula weight	1850.27
Temperature/K	296(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.0041(14)
b/Å	10.5386(16)
c/Å	20.971(3)
α/°	94.863(2)
β/°	93.285(2)
γ/°	106.354(2)
Volume/Å^3	1895.7(5)
Z	1
ρ_{calc}g/cm^3	1.621
μ/mm^{-1}	0.880
F(000)	932.0
Crystal size/mm^3	0.130 × 0.120 × 0.120
Radiation	MoK_α (λ = 0.71073)
2θ range for data collection/°	3.912 to 50.018
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -24 ≤ l ≤ 24
Reflections collected	32149
Independent reflections	6594 [R_{int} = 0.0332, R_{sigma} = 0.0265]
Data/restraints/parameters	6594/0/489
Goodness-of-fit on F^2	1.047
Final R indexes [I⩾2σ (I)]	R_1 = 0.0364, wR_2 = 0.0939
Final R indexes [all data]	R_1 = 0.0426, wR_2 = 0.0982
Largest diff. peak/hole / e Å^{-3}	1.97/-0.54