

The Novel Metalloligand [Fe(bppd)₃] (bppd = 1,3-bis(4-pyridyl)-1,3-propanedionate) for the Crystal Engineering of Heterometallic Coordination Networks with different Silver Salts. Anionic Control of the Structures.

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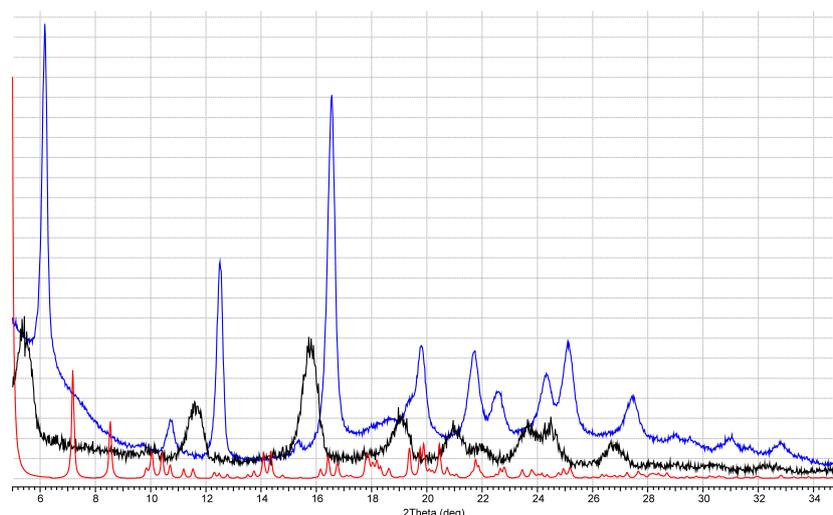


Figure S1. Red: calculated XRPD pattern from the crystal structure of **1a'**; blue: experimental XRPD pattern of **1a**; black: experimental XRPD pattern of **1b**.

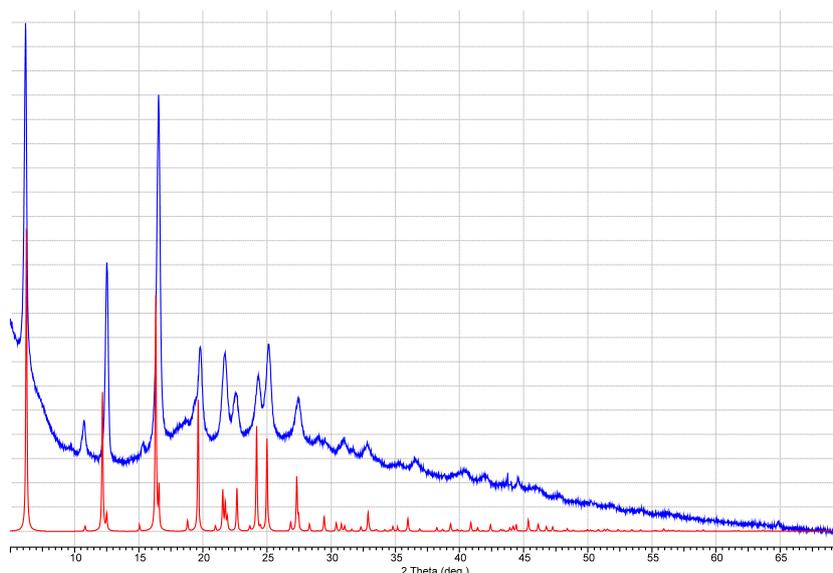


Figure S2. Blue: experimental XRPD pattern of **1a**; red: calculated XRPD pattern from the crystal structure of compound Al(DIPIRF)₃ (DIPIRF = 1-(4-pyridyl)-3-(phenyl)-1,3-propanedionate). Al(DIPIRF)₃ is under investigation in our laboratory and will be published elsewhere (Unit cell parameters: $a = b = 16.333 \text{ \AA}$; $c = 8.465 \text{ \AA}$; $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$; $V = 1956 \text{ \AA}^3$; Space group P-3)

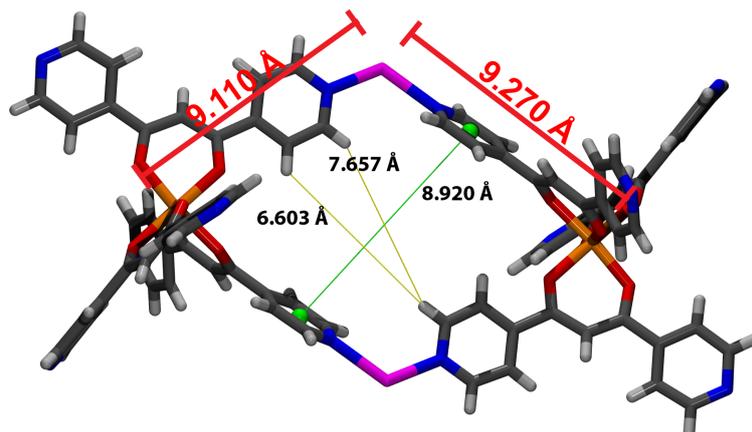


Figure S3. Dimensions of the rhombic cavity where the anions ClO_4^- , BF_4^- , PF_6^- , AsF_6^- and SbF_6^- take place in compounds **2a-e**.

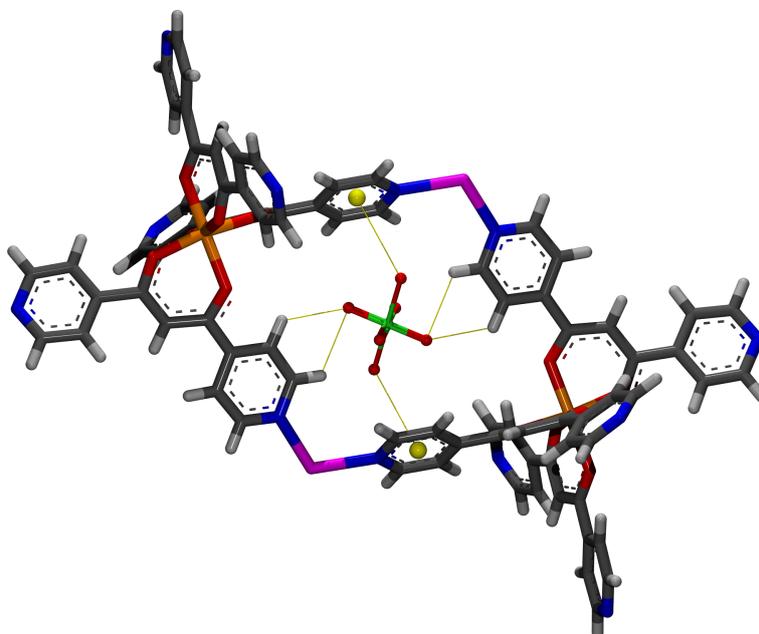


Figure S4. H-bonds and π -anion interactions in compounds **2c**.

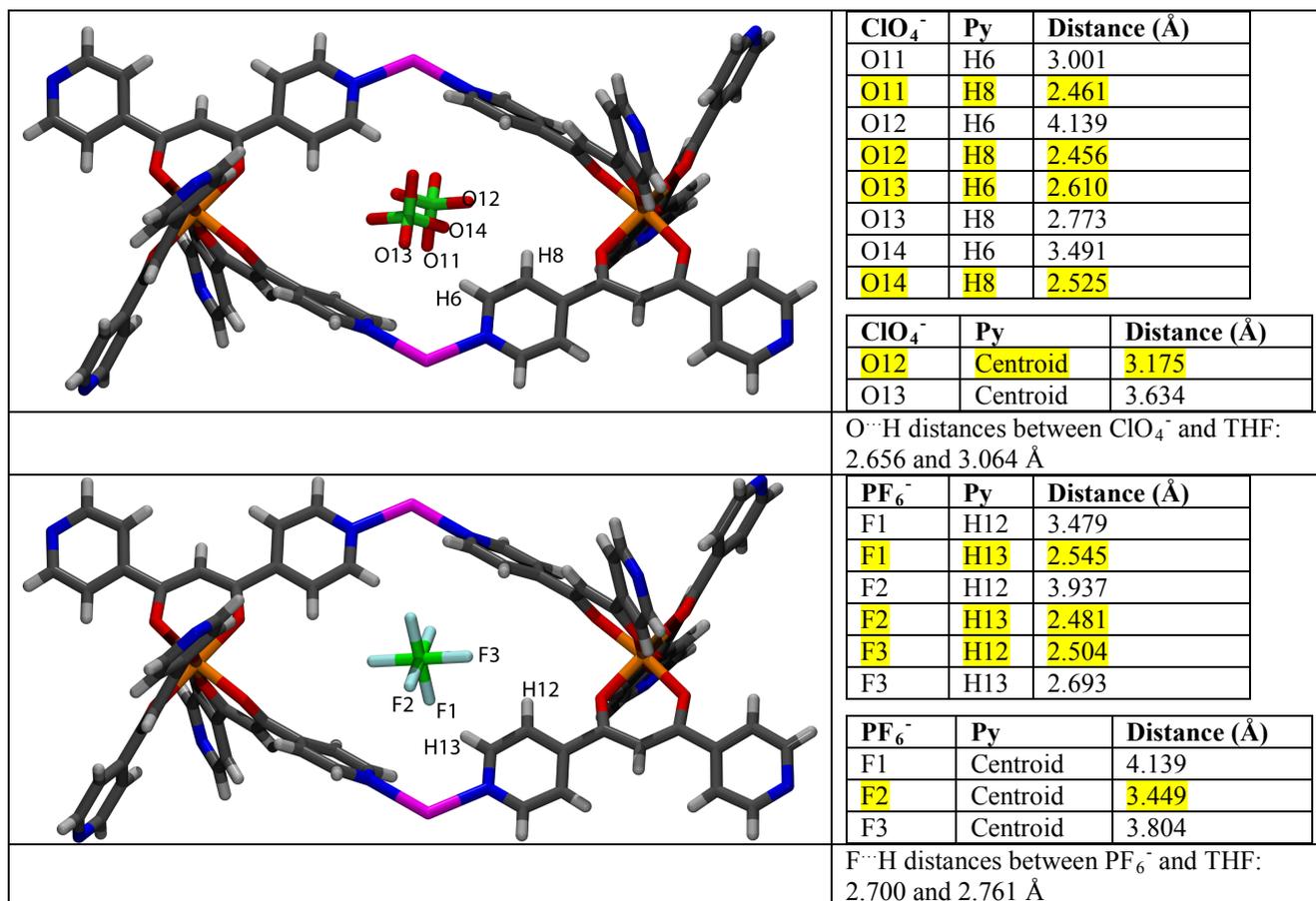


Figure S5. Selected weak interactions in compounds $[\text{Fe}(\text{bppd})_3\text{Ag}]\text{ClO}_4$ (**2b**, top) and $[\text{Fe}(\text{bppd})_3\text{Ag}]\text{PF}_6$ (**2c**, bottom).

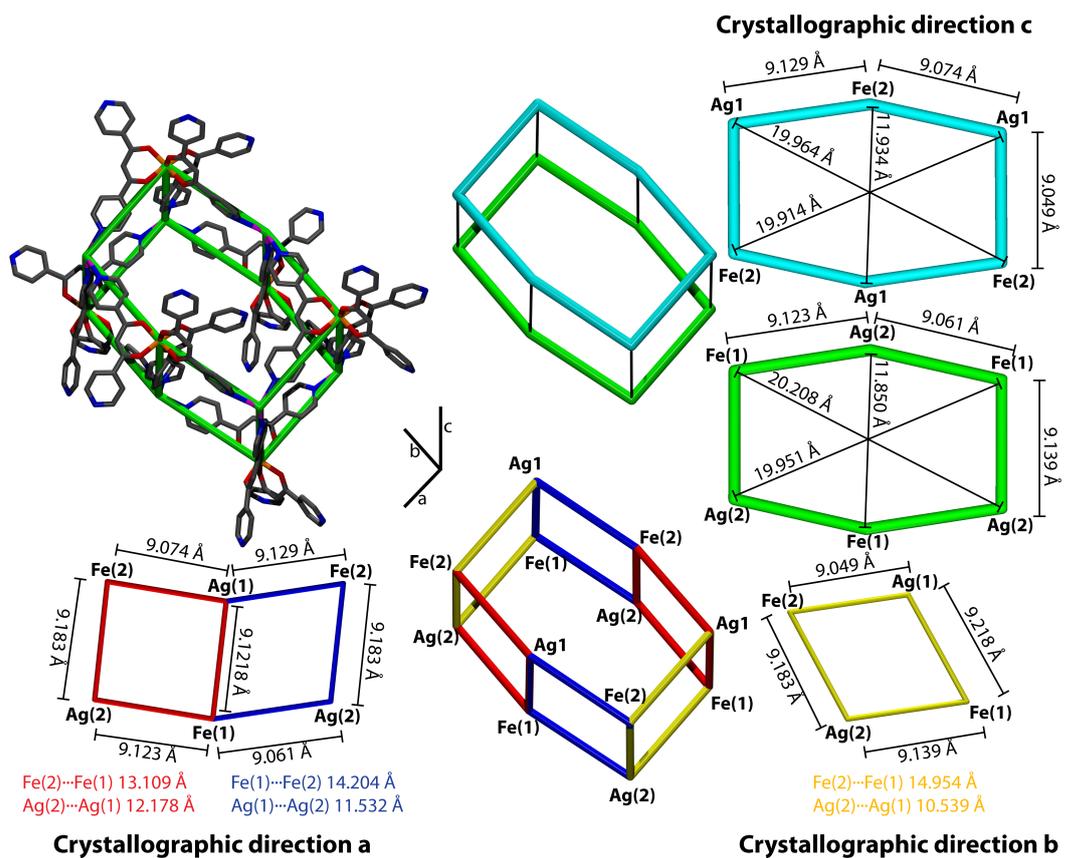


Figure S6. Geometrical details for compound 3a.

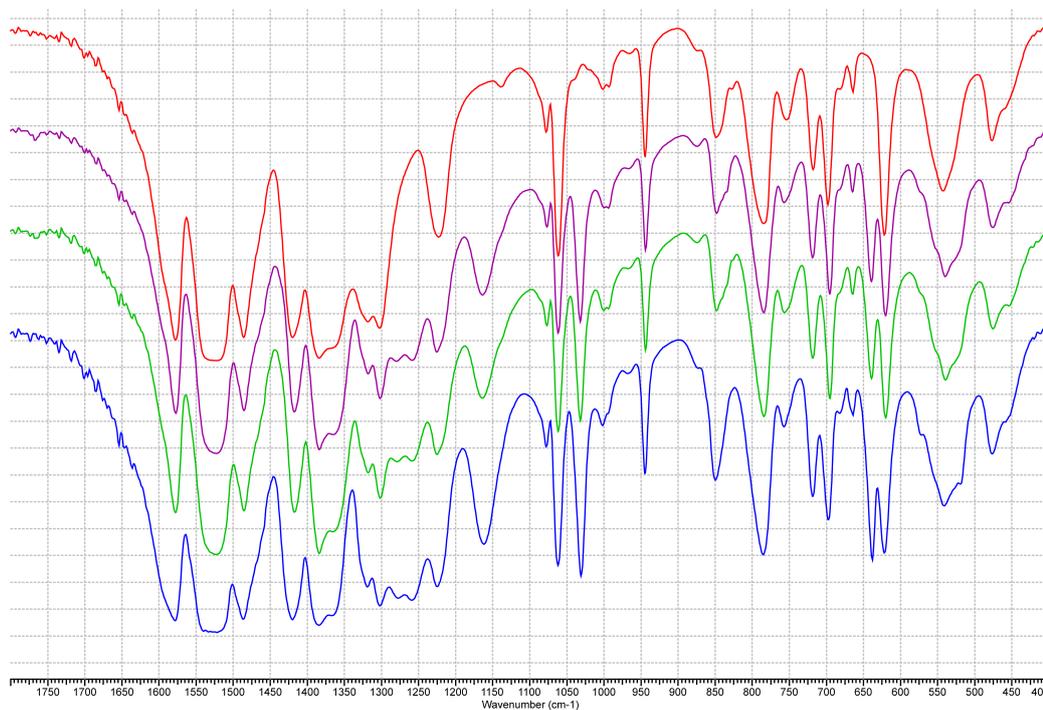


Figure S7. IR spectra of: blue = **3a**; Green = **4y**; Fuchsia = **4x**; Red = **4**.

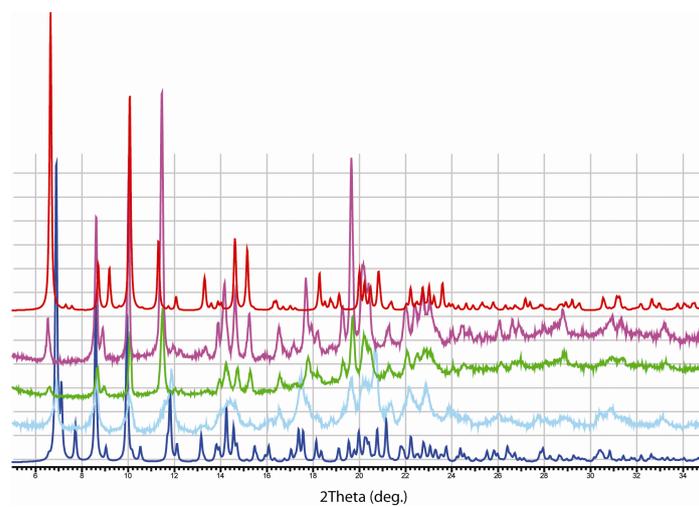


Figure S8. Blue: Calculated XRPD pattern of **3a**; Light blue: experimental XRPD pattern of **3a**; Green: experimental XRPD pattern of **4y**; Fuchsia: experimental XRPD pattern of **4x**; Red: calculated XRPD pattern of **4**.

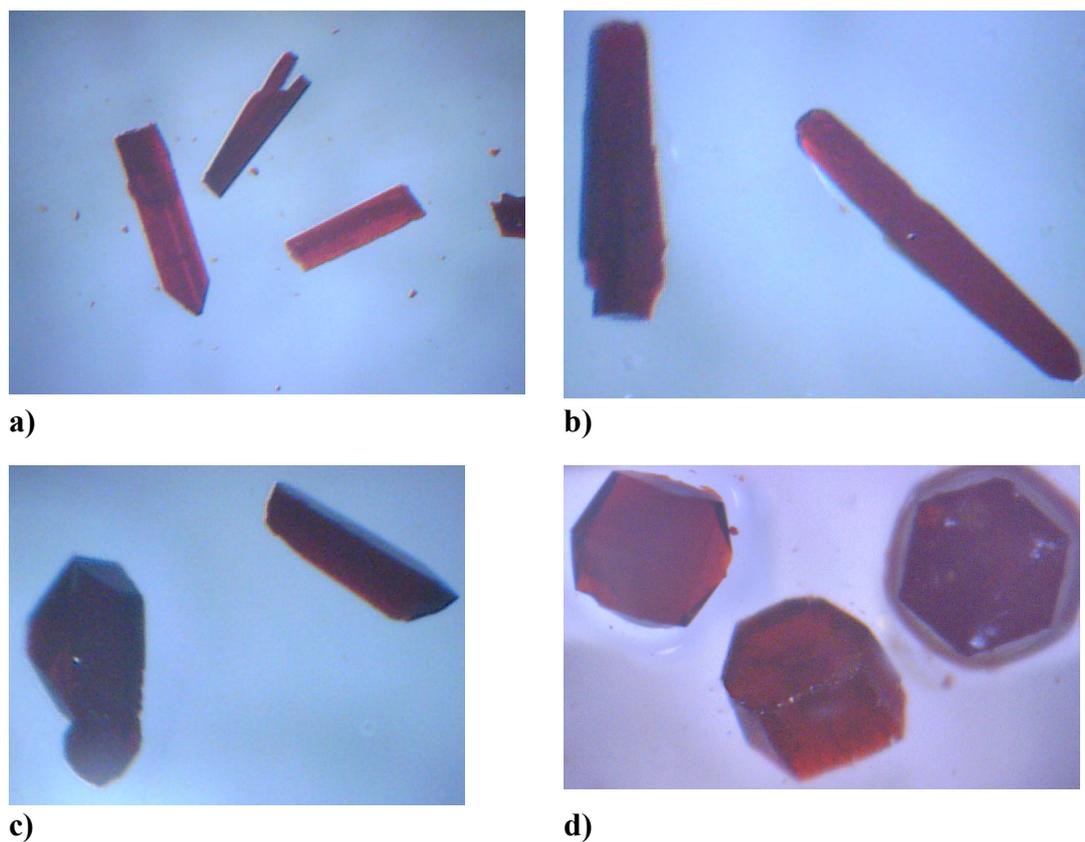


Figure S9. Crystals of: a) $[\text{Fe}^{\text{III}}(\text{bppd})_3\text{Ag}]\text{SbF}_6 \cdot 4\text{THF}$ (**2e**); b) $[\text{Fe}^{\text{III}}_2(\text{bppd})_6\text{Ag}_3](\text{NO}_3)_3$ (**4**); c) $[\text{Fe}_2(\text{bppd})_6\text{Ag}_2](\text{CF}_3\text{SO}_3)_2$ (**3a**); d) $[\text{M}_3(\text{bppd})_9\text{Ag}_5](\text{tosylate})_5$ (**5a**).

Table S1: Cell parameters (single crystals) for compounds **2d**, **2e**.

	System	Space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	U(Å ³)	Temp. K
2d	Monoclinic	C2/c (No.15)	13.15(3)	23.51(5)	17.53(3)	90	98.52(4)	90	536(3)	150
2e	Monoclinic	C2/c (No.15)	13.305(8)	23.98(2)	17.83(1)	90	99.82(1)	90	561(1)	100