Supplementary Information

An octahedral tetrachlorido Fe(II) complex with aminopyrazinium ligands from a serendipitous redox synthesis exhibiting magnetic exchange through non-covalent 3-D architectures

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- 1. Synthesis
- 2. UV-Vis experiments
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- 1. Synthesis

2-Aminopyrazine (1 mmol, 0.095 g) was added to salicylaldehyde (1mmol, 0.122 g) in 1:1 methanol/acetonitrile (20 mL) and stirred for 10 min. Ferric chloride hydrate (2 mmol, 0.541 g) was then added to this solution resulting in a deep purple colour immediately. The solution was filtered after 20 min stirring and small purple rectangular plate-like crystals formed after several days of slow solvent evaporation. The crystals were then washed with acetone. Yield: 35.3 mg, 11.5 %

2-Aminopyrazine (1 mmol, 0.095 g) was added to 3-methoxysalicylaldehyde (1mmol, 0.152 g) in 1:1 methanol/acetonitrile (20 mL) and stirred for 10 min. Ferric chloride hydrate (2 mmol, 0.541 g) was then added to this solution resulting in a deep purple colour immediately. The solution was filtered after 20 min stirring and small purple rectangular plate-like crystals formed after several days of slow solvent evaporation. The crystals were then washed with acetone. Yield: 9.9 mg, 2.5 %

2-Aminopyrazine (1 mmol, 0.095 g) was added to 5-chlorosalicylaldehyde (1mmol, 0.156 g) in 1:1 methanol/acetonitrile (20 mL) and stirred for 10 min. Ferric chloride hydrate (2 mmol, 0.541 g) was then added to this solution resulting in a deep purple colour immediately. The solution was filtered after 20 min stirring and small purple rectangular plate-like crystals formed after several days of slow solvent evaporation. The crystals were then washed with acetone. Yield: 67.4 mg, 17.3 %

2-Aminopyrazine (1 mmol, 0.095 g) was added to propionaldehyde (1mmol, 0.058 g) in 1:1 methanol/acetonitrile (20 mL) and stirred for 10 min. Ferric chloride hydrate (2 mmol, 0.541 g) was then added to this solution resulting in an orange colour. The solution was filtered after 20 min stirring

and small purple rectangular plate-like crystals formed after several days of slow solvent evaporation. The crystals were then washed with acetone. Yield: 61.7 mg, 21.3 %

2-Aminopyrazine (1 mmol, 0.095 g) was added to phenylacetaldehyde (1mmol, 0.120 g) in 1:1 methanol/acetonitrile (20 mL) and stirred for 10 min. Ferric chloride hydrate (2 mmol, 0.541 g) was then added to this solution resulting in an orange colour. The solution was filtered after 20 min stirring and small purple rectangular plate-like crystals formed after several days of slow solvent evaporation. The crystals were then washed with acetone. Yield: 11.5 mg, 3.5 %

2-Aminopyrazine (1 mmol, 0.095 g) was added to benzaldehyde (1mmol, 0.106 g) in 1:1 methanol/acetonitrile (20 mL) and stirred for 10 min. Ferric chloride hydrate (2 mmol, 0.541 g) was then added to this solution resulting in an orange colour. The solution was filtered after 20 min stirring and small purple rectangular plate-like crystals formed after several days of slow solvent evaporation. The crystals were then washed with acetone. Yield: 25.7 mg, 8.9 %

IR (cm⁻¹): 639, 775, 1014, 1207, 1292, 1351, 1417, 1619, 1657, 3050, 3147, 3309

Elemental Calc. (Found): C, 24.65 (23.20), H, 3.10 (3.01), N, 21.56 (20.49)

- Salicylaldehyde + 2-aminopyrazine 12000 0 uL 100 uL 200 uL 10000 300 uL 400 uL 8000 500 uL s (M⁻¹ cm⁻¹) 600 ul 6000 700 uL 800 uL 900 uL 4000 1 mL 2 mL 2000 0 500 200 250 300 350 400 450 550 600 Wavelength (nm) 3-Methoxy salicylaldehyde + 2-aminopyrazine 5-Chloro salicylaldehyde + 2-aminopyrazine 18000 -16000 -0 uL 0 uL 100 uL 100 ul 16000 14000 200 uL 200 uL 300 uL 14000 300 uL 12000 400 uL 400 uL 12000 500 ul 500 uL 10000 ัษ ε (M⁻¹ cm⁻¹) 600 uL 600 uL 10000 700 uL 700 uL R⁻¹ 8000 800 uL 800 ul 8000 900 uL 900 uL 6000 1 mL 6000 1 mL 2 mL 2 mL 4000 4000 2000 2000 0. 0 450 200 250 300 350 400 450 500 550 600 200 250 300 350 400 500 550 Wavelength (nm) Wavelength (nm)
- 2. UV-Vis Experiments

Fig S1: UV-Vis of salicylaldehyde oxidation at $2x10^{-4}$ M. 0 μ l corresponds to the appropriate salicylaldehyde and 2-aminopyrazine only being present in the cuvette. Then additions of $2x10^{-5}$ M

FeCl3.H $_2$ O in aliquots of 100 μ L over 10 additions, followed by the addition of 1 mL of the same solution to the cuvette.

3. X-ray data analysis.

A suitable crystal was selected and mounted on an Xcalibur, Sapphire3, Gemini diffractometer. The crystal was kept at 149.99(10) K during data collection. Using Olex2¹, the structure was solved with the olex2.solve² structure solution program using Charge Flipping and refined with the ShelXL³ refinement package using Least Squares minimisation.

Empirical formula	$C_8H_{12}Cl_4FeN_6$
Formula weight	389.88
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.1768(5)
b/Å	7.3352(5)
c/Å	7.8852(6)
α/°	115.541(7)
β/°	110.288(7)
γ/°	96.890(6)
Volume/Å ³	333.02(5)
Z	1
$\rho_{calc}g/cm^3$	2.172
µ/mm⁻¹	1.363
F(000)	225.0
Radiation	ΜοΚα (λ = 0.71073)
20 range for data collection/	° 6.384 to 58.958
Index ranges	-6 ≤ h ≤ 9, -9 ≤ k ≤ 7, -9 ≤ l ≤ 10
Reflections collected	2663
Independent reflections	1524 [R _{int} = 0.0235, R _{sigma} = 0.0382]
Data/restraints/parameters	1524/0/88
Goodness-of-fit on F ²	0.823
Final R indexes [I>=2σ (I)]	R ₁ = 0.0323, wR ₂ = 0.1016

Final R indexes [all data] $R_1 = 0.0363$, $wR_2 = 0.1082$ Largest diff. peak/hole / e Å⁻³ 0.64/-0.46



Fig. S2: π - π stacking in **1**. The displaced motif occurs between the complexes in red while the sandwich-type stacking motif occurs between the white and red complexes.



Fig S3: Packing of **1** with halogen bonding in blue and π - π stacking in yellow.

4. Magnetic Measurements

All measurements were carried out on a Quantum Design MPMS[®] SQUID XL-7. The sample was restrained in an eicosane matrix. DC magnetic susceptibility was carried out between 300 and 2 K in an applied field of 1000 *Oe*. AC susceptibility was carried out under 3 *Oe* AC field with various applied DC fields at 2 K. (see Fig S4.).



Fig S4: AC susceptibility for complex **1** at 2 K.

5. Computational details.

Geometries were optimised using density functional theory (DFT) with the ω B97X-D functional¹ and Stuttgart-Bonn TZVP basis set and pseudopotential² (the 6-311G(d) basis set is used for H, C, N and Cl atoms^{3,4}). Gas-phase geometries were optimised with and without symmetry, allowing the C_i symmetry of the molecule to break. Harmonic vibrational frequencies were calculated to confirm the geometries as true minima. Further geometry optimisations including solvent effects were performed using the polarisable continuum solvent (PCM) model⁵⁻⁷ with a dielectric constant, ε , of 78.39. Ligand dissociation energies were calculated by optimising the geometries of the different fragments (see figures S5 and S6, below). All calculations were performed with the Q-Chem software.⁸



Figure S5. Molecular orbitals calculated using DFT at the gas-phase, symmetry broken geometry. SOMO-1 (top left); SOMO (top right); LUMO (bottom left); LUMO+1 (bottom right).



Figure S6. Molecular orbitals calculated using DFT with the optimised geometry within a polarisable continuum solvent (water). SOMO-1 (top left); SOMO (top right); LUMO (bottom left); LUMO+1 (bottom right).

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