Supplementary Material

Table S1 Selected bond distances (Å) and angles (°) of **4** and **5**. [a)]

Bond distances			
4'		**5**	
Co1–O3	2.053(7)	Ni1–O6	2.009(2)
Co1–O8	2.088(7)	Ni1–O1	2.064(2)
Co1–O6	2.106(7)	Ni1–O3	2.058(2)
Co1–N1	2.183(8)	Ni1–N2	2.139(2)
Co1–N2	2.238(9)	Ni1–N1	2.186(2)
Co1–O9	2.142(7)	Ni1–O9	2.101(2)
C12–O3	1.263(12)	C6–O1	1.257(3)
C12–O4	1.268(12)	C6–O2	1.266(3)
Fe1–D1 [b)]	1.672(5)	Fe1–D1 [b)]	1.651(1)
Fe1–D2 [b)]	1.647(5)	Fe1–D2 [b)]	1.648(1)
Co2–O4	2.073(7)	Ni2–O5	2.089(2)
Co2–O7	2.042(7)	Ni2–O2	2.000(2)
Co2–O2	2.110(7)	Ni2–O7	2.079(2)
Co2–N3	2.199(8)	Ni2–N4	2.142(2)
Co2–N4	2.259(9)	Ni2–N3	2.160(2)
Co2–O9	2.132(6)	Ni2–O9	2.107(2)
C6–O1	1.254(11)	C12–O4	1.264(3)
C6–O2	1.292(12)	C12–O3	1.263(3)
Fe2–D3 [b)]	1.650(4)	Fe2–D3 [b)]	1.646(1)
Fe2–D4 [b)]	1.651(4)	Fe2–D4 [b)]	1.648(1)
Bond angles			
O1–C6–O2	123.5(9)	O3–C12–O4	125.1(2)
O3–C12–O4	125.9(9)	O1–C6–O2	126.5(2)
O6–Co1–O3	176.2(3)	O6–Ni1–O3	177.25(6)
O6–Co1–O8	84.8(3)	O3–Ni1–O1	84.42(6)
O3–Co1–O8	95.9(3)	O6–Ni1–O1	96.44(6)
O6–Co1–O9	87.5(3)	O3–Ni1–O9	89.65(7)
O3–Co1–O9	88.7(3)	O6–Ni1–O9	87.68(7)
O8–Co1–O9	92.4(3)	O1–Ni1–O9	93.35(6)
O6–Co1–N2	91.9(3)	O3–Ni1–N1	89.66(7)
O3–Co1–N2	87.9(3)	O6–Ni1–N1	89.84(7)
O8–Co1–N2	172.2(3)	O1–Ni1–N1	170.16(6)
O9–Co1–N2	94.5(3)	O9–Ni1–N1	94.48(7)
O6–Co1–N1	92.1(3)	O3–Ni1–N2	90.82(7)
O3–Co1–N1	91.6(3)	O6–Ni1–N2	91.83(7)
O8–Co1–N1	89.8(3)	O1–Ni1–N2	87.55(6)
O9–Co1–N1	177.7(3)	O9–Ni1–N2	179.02(7)
N2–Co1–N1	83.3(3)	N2–Ni1–N1	84.68(7)
O5–C18–O6	124.0(9)	O7–C24–O8	125.0(2)
O7–C24–O8	125.5(9)	O5–C18–O6	126.6(2)
O2–Co2–O7	176.0(6)	O2–Ni2–O7	177.96(6)
O2–Co2–O4	85.1(3)	O7–Ni2–O5	83.24(6)
O7–Co2–O4	98.2(3)	O2–Ni2–O5	96.07(6)
O2–Co2–O9	86.2(3)	O7–Ni2–O9	90.53(7)
O7– Co2–O9	91.4(3)	O2–Ni2–O9	87.57(7)
O4–Co2–O9	92.9(3)	O5–Ni2–O9	92.64(6)
O2–Co2–N3	90.4(3)	O7–Ni2–N4	90.82(7)
O2–Co2–N4	88.1(3)	O7–Ni2–N3	89.25(7)
O4–Co2–N4	169.5(3)	O5–Ni2–N3	169.91(7)
O9–Co2–N4	94.6(3)	O9–Ni2–N3	94.17(7)
O4–Co2–N3	89.0(3)	O5–Ni2–N4	89.06(7)
O7–Co2–N3	91.8(3)	O2–Ni2–N4	91.10(7)

O7–Co2–N4	88.9(3)	O2–Ni2–N3	91.65(7)
O9–Co2–N3	175.9(3)	O9–Ni2–N4	177.95(8)
N3–Co2–N4	83.1(3)	N4–Ni2–N3	84.30(8)
Co1–O9–Co2	113.4(3)	Ni1–O9–Ni2	113.58(8)

a) Standard uncertainties are given in the last significant figure(s) in parenthesis.

b) D1 = centroid of C1 – C5, D2 = centroid of C7 – C11, D3 = centroid of C13 – C17, D4 = centroid of C19 – C23.

Table S2 Selected bond distances (Å) and angles (°) of intramolecular O–H···O hydrogen bonds of **4** and **5**.[a)]

Complex	D–H···A[b)]	D···A	D–H···A
4	O9–H9A···O5	2.528(9)	151
	O9–H9B···O1	2.600(9)	156
5	O9–H1O···O4	2.579(2)	160(3)
	O9–H2O···O8	2.575(2)	166(3)

a) Standard uncertainties are given in the last significant figure(s) in parenthesis.

b) D = donor atom; A = acceptor atom.

Table S3 Selected bond distances (Å) and angles (°) of **7**. [a)]

Bond distances			
Cu1–O1	1.991(2)	Cu1–O4	2.420(1)
Cu1–O2	2.516(2)	Cu1–O3	1.973(2)
Cu1–N1	2.031(2)	Cu1–N2	2.018 (2)
Fe1–D1 [b)]	1.655(1)	Fe2–D2 [b)]	1.643(1)
C6–O1	1.275(3)	C12–O3	1.278(3)
C6–O2	1.254(3)	C12–O4	1.255(3)
Bond angles			
O1–C6–O2	122.5(2)	O3–C12–O4	122.15(18)
O3–Cu1–O1	90.81(6)	O3–Cu1–N2	162.68(7)
O1–Cu1–N2	94.19(8)	O3–Cu1–N1	92.48(6)
O1–Cu1–N1	164.81(7)	N2–Cu1–N1	87.02(8)
O3–Cu1–O4	59.60(6)	O1–Cu1–O4	93.55(5)
N2–Cu1–O4	103.48(7)	N1–Cu1–O4	100.90(6)
N1–Cu1–O2	107.32(6)	O3–Cu1–O2	96.54(5)
N2–Cu1–O2	100.14(6)	O4–Cu1–O2	143.86(5)
O1–Cu1–O2	57.54(6)		

a) Standard uncertainties are given in the last significant figure(s) in parenthesis.

b) D1 = centroid of C1 – C5, D2 = centroid of C7 – C11.

Table S4 Selected bond distances (Å) and angles (°) of **9**. [a)]

Bond distances			
Cu1–O1	1.983(5)	Cu1–N1	2.060(6)
Cu1–N2	2.049(5)	Cu1–N3	2.048(6)
Cu1–O5	2.195(5)	C11–O1	1.243(8)
C11–O2	1.249(9)	C12–O3	1.243(9)
C12–O4	1.250(9)	Fe1–D1	1.657(3)
Fe1–D2	1.655(3)		
Bond angles			
O1–C11–O2	126.1(7)	O3–C12–O4	125.3(6)
O1–Cu1–N3	90.5(2)	O1–Cu1–N2	167.0(2)
N3–Cu1–N2	84.7(2)	O1–Cu1–N1	91.4(2)
N3–Cu1–N1	150.5(2)	N2–Cu1–N1	87.0(2)
O1–Cu1–O5	96.41(19)	N3–Cu1–O5	109.0(2)
N2–Cu1–O5	96.6(2)	N1–Cu1–O5	100.0(2)

a) Standard uncertainties are given in the last significant figure(s) in parenthesis.

b) D1 = centroid of C1 – C5, D2 = centroid of C6 – C10.

Table S5 Selected bond distances (Å) and angles (°) of intermolecular O–H···O hydrogen bonds of **7** and **9**.[a)]

Complex	D–H···A[b)]	D···A	D–H···A
7	O5–H1O···O2	2.829(2)	173(3)
	O5–H2O···O4A	2.822(3)	167(3)
9	O5–H1O···O3A	2.649(7)	142(6)
	O6–H6···O4	2.759(8)	159(4)

a) Standard uncertainties are given in the last significant figure(s) in parenthesis.

b) D = donor atom; A = acceptor atom.

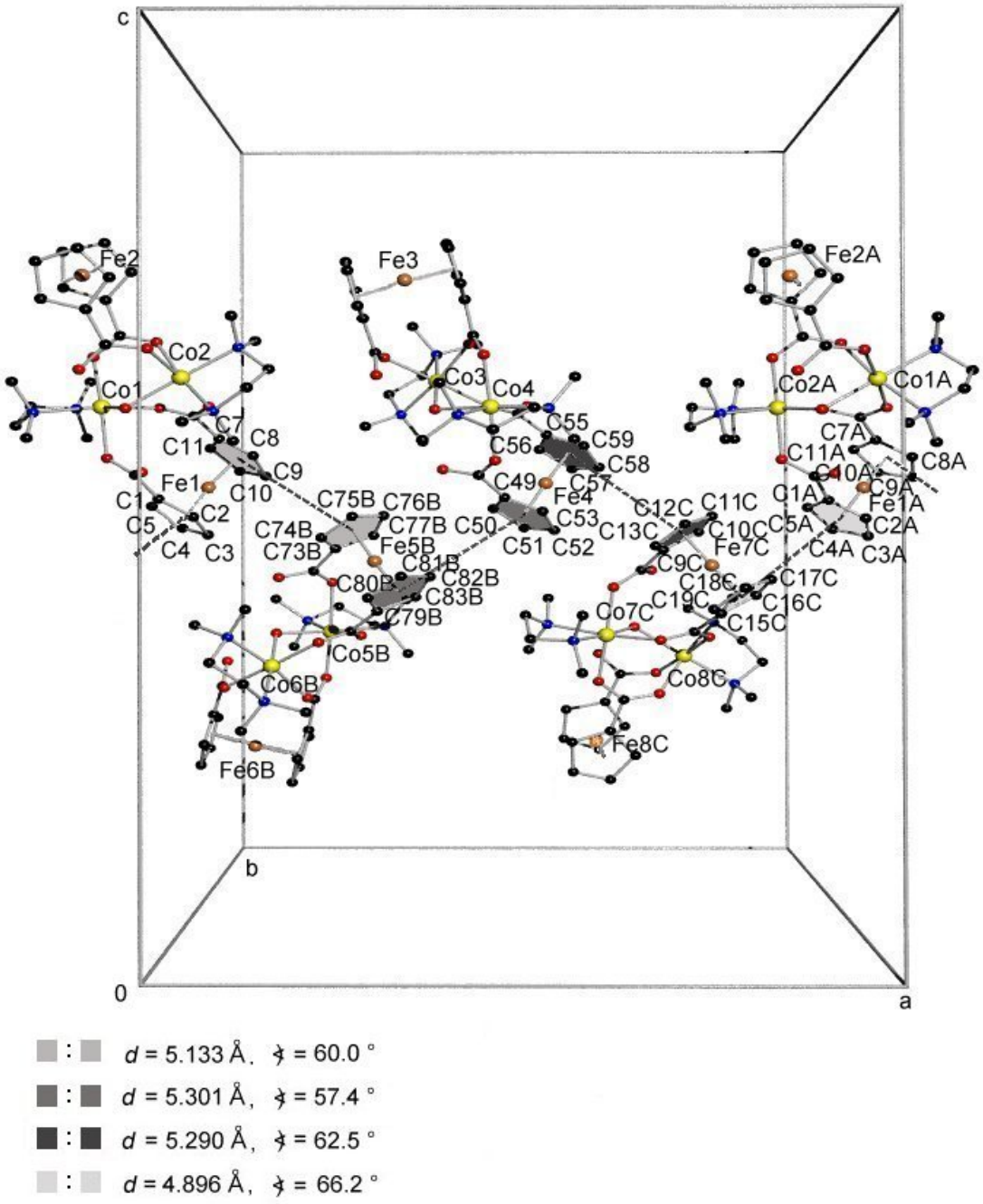

Fig. S1 Graphical representation of the π-π-interactions between discrete molecules of **4** along the crystallographic *a* axis. All hydrogen atoms and the $CHCl_3$ molecules are omitted for clarity. The distance *d* refers to center-to-center distances and angles refer to the inter-planar angles of interacting C_5H_4 units. Label 'A' refers to a symmetry generated molecule of **4'**, label 'B' refers to a symmetry generated molecule of **4'''**, label 'C' refers to a symmetry generated molecule of **4''''**.

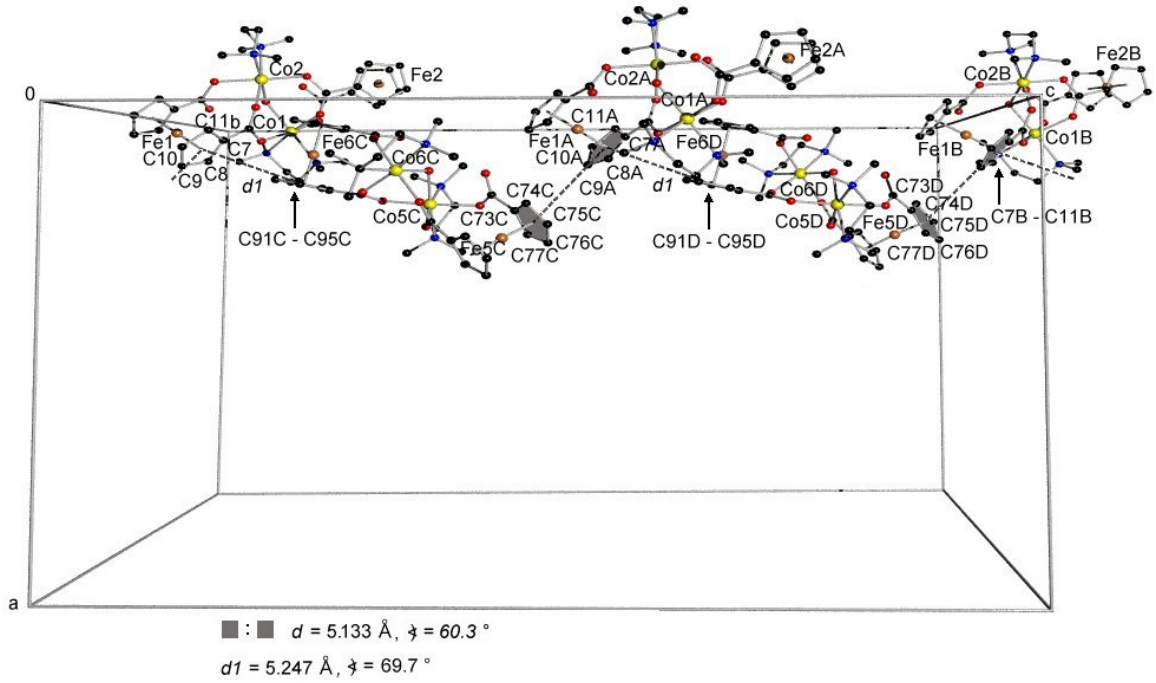

Fig. S2 Graphical representation of the π-π-interactions between discrete molecules of **4** along the crystallographic *c* axis. All hydrogen atoms and the $CHCl_3$ molecules are omitted for clarity. The distance *d* refers to center-to-center distances and angles refer to the inter-planar angles of interacting C_5H_4 units. Label 'A' and 'B' refer to a first and second symmetry generated molecule of **4'**, respectively, whereas label 'C' and 'D' refer to a first and second symmetry generated molecule of **4'''**, respectively.

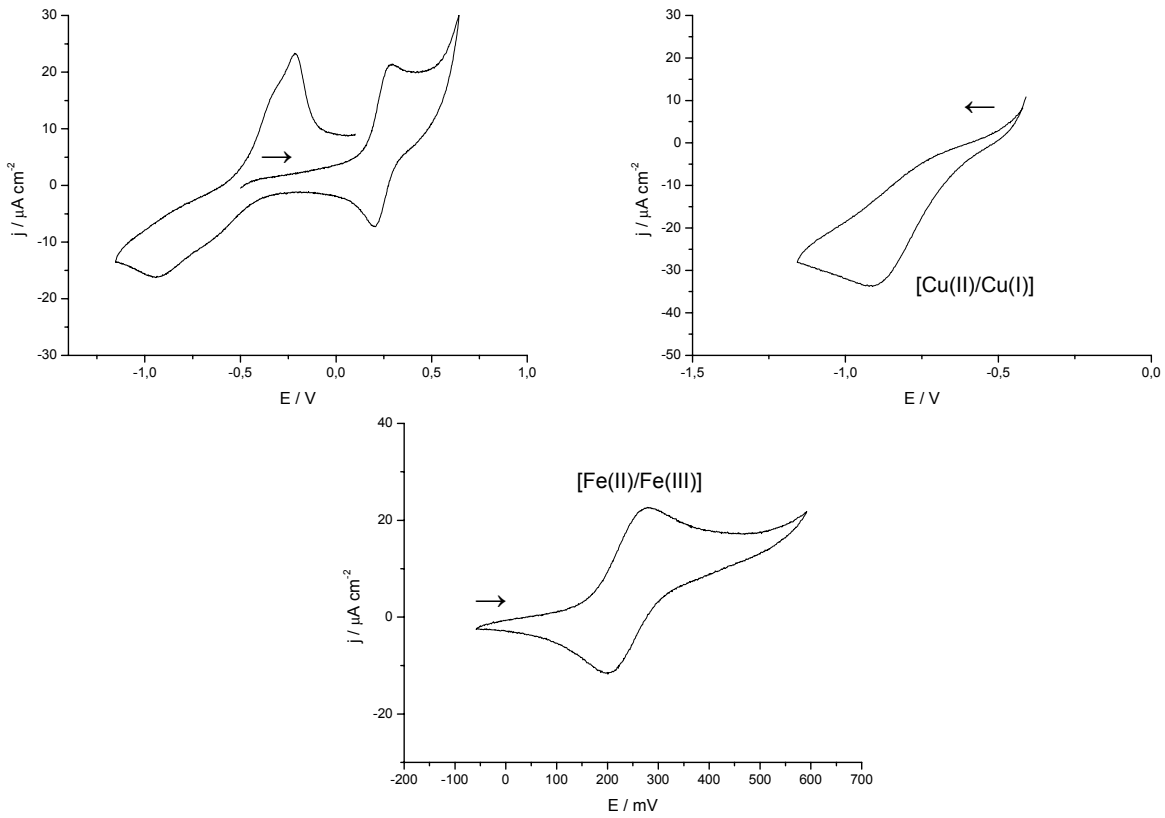

Fig. S3 Cyclic voltammogram of **7** (complete: top left; [Cu(II)/Cu(I)]: top right: [Fe(II)/ Fe(III)]: bottom) ($1 \cdot 10^{-3}$ M solution in methanol at 25 °C with [^{n}Bu$_4$N]PF$_6$ (0.1 M) as supporting electrolyte, scan rate = 0.10 V s^{-1}). All potentials are referenced to the [FcH/FcH^{+}] redox couple (FcH = (η^5-C$_5$H$_5$)$_2$Fe) with E_0 = 0.00 V).[26]

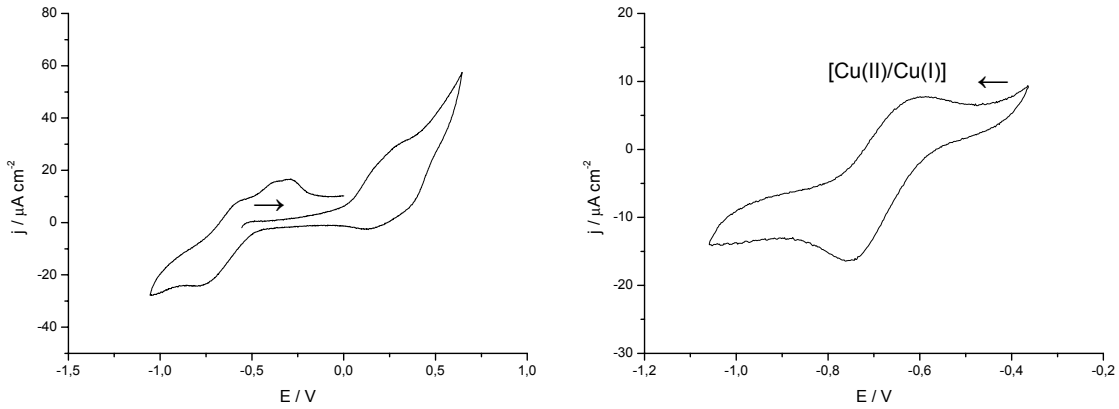

Fig. S4 Cyclic voltammogram of **9** (complete: left; [Cu(II)/Cu(I)] reduction: right) ($1 \cdot 10^{-3}$ M solution in methanol at 25 °C with [*n*-Bu_4N]PF_6 (0.1 M) as supporting electrolyte, scan rate = 0.10 V s^{-1}). All potentials are referenced to the [FcH/FcH^+] redox couple (FcH = (η^5-$C_5H_5)_2Fe$) with E_0 = 0.00 V).[26]