Electronic Supplementary Information

Elemental analyses (Elementar vario MICRO cube Elemental Analyzer, silver boats)
calc. (found) for **1** ($C_{26}H_{20}N_2CoCl_2$, M_r = 490.29): 63.69 (63.71) % C, 5.71 (5.75) % N, 4.11 (4.18) % H; **2** ($C_{26}H_{20}N_2CoBr_2$, M_r = 579.19): 53.92 (53.48) % C, 4.84 (4.88) % N, 3.48 (3.61) % H; **3** ($C_{26}H_{20}N_2CoI_2$, M_r = 673.19): 46.39 (45.98) % C, 4.16 (4.15) % N, 2.99 (3.02) % H.

FT-IR (Nicolet 6700 FT-IR Spectrometer with SmartOrbit™ diamond ATR accessory in the range of 4000–400 cm^{-1})

1: 3075(w), 3055(w), 3026(w), 2997(w), 2951(w), 2910(w), 2827(w), 1614(m), 1597(w), 1581(w), 1567(m), 1549(m), 1506(w), 1486(m), 1434(m), 1404(w), 1393(m), 1375(m), 1319(w), 1306(w), 1281(w), 1266(w), 1232(w), 1200(w), 1177(w), 1160(m), 1106(m), 1078(m), 1028(m), 999(m), 931(w), 910(w), 887(m), 861(m), 843(m), 777(s), 766(m), 738(s), 704(vs), 667(m), 635(m), 612(w), 573(m), 545(m), 523(w), 494(w), 476(w), 456(m), 446(m), 413(w).

2: 3070(w), 3055(w), 3030(w), 2997(w), 2951(w), 2911(w), 2835(w), 1614(m), 1596(w), 1581(w), 1567(m), 1548(m), 1507(w), 1486(m), 1434(m), 1404(w), 1392(m), 1374(m), 1319(w), 1306(w), 1282(w), 1266(w), 1232(w), 1200(w), 1177(w), 1160(m), 1106(m), 1078(m), 1028(m), 998(m), 932(w), 911(w), 888(m), 860(m), 842(m), 777(s), 765(m), 737(s), 704(vs), 667(m), 635(m), 612(w), 573(m), 545(m), 523(w), 493(w), 476(w), 456(m), 446(m), 413(w).

3: 3070(w), 3055(w), 3030(w), 2997(w), 2951(w), 2910(w), 2835(w), 1614(m), 1596(w), 1581(w), 1567(m), 1548(m), 1507(w), 1486(m), 1434(m), 1404(w), 1392(m), 1374(m), 1319(w), 1306(w), 1282(w), 1266(w), 1232(w), 1200(w), 1177(w), 1160(m), 1106(m), 1078(m), 1028(m), 998(m), 932(w), 911(w), 888(m), 860(m), 842(m), 777(s), 765(m), 737(s), 704(vs), 667(m), 635(m), 612(w), 573(m), 545(m), 523(w), 493(w), 476(w), 456(m), 446(m), 413(w).

Single-crystal X-ray structure analyses (Oxford Diffraction Gemini equipped with Atlas S2 CCD detector)
The multi-scan empirical method[1] was used for absorption correction of **1**, while the analytical method[2] was used for absorption corrections of **2** and **3**. The final refinement parameters of **2** are less satisfactory (See Table S1 bellow) as a result of crystal twining of the sample.

[1] Blessing, R. H. *Acta Cryst. A.* **1995**, 51, 33-38.
[2] Clark, R. C., Reid, J. S. *Acta Cryst. A.* **1995**, 51, 887-897.

Table S1 Crystal data and final refinement parameters for **1-3**

		1	**2**	**3**
Empirical formula		$C_{26}H_{20}N_2CoCl_2$	$C_{26}H_{20}N_2CoBr_2$	$C_{26}H_{20}N_2CoI_2$
Formula weight M_r		490.3	579.2	673.2
Temperature [K]		120	120	120
Wavelength [Å]		1.54184	1.54184	1.54184
Crystal system		Monoclinic	Monoclinic	Monoclinic
Space group		$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a [Å]	12.9207(2)	12.9571(4)	12.7126(3)
	b [Å]	22.2792(7)	22.7711(11)	23.7131(7)
	c [Å]	7.8597(4)	7.8738(7)	8.0118(4)
	β [°]	102.627(3)	103.018(4)	98.626(3)
Volume [Å^3]		2207.79(14)	2263.4(2)	2387.88(15)
Z		4	4	4
Density (calculated) [g/cm^3]		1.475	1.699	1.873
Absorption coefficient [mm^{-1}]		8.439	10.196	26.048
Crystal dimensions [mm]		0.44×0.12×0.04	0.26×0.14×0.03	0.53×0.05×0.03
Θ range for data collection [°]		3.51 – 67.07	3.50 – 66.96	3.52 – 66.99
Reflections collected		14675	14673	18588
Independent reflections		3901	3984	4202
R(int)		0.0465	0.0734	0.0477
Completeness to Θ_{max} [%]		0.99	0.99	0.98
Max. and min. transmission		0.379; 1.000	0.256; 0.789	0.058; 0.526
Data / restraints / parameters		3901 / 0 / 280	3984 / 0 / 281	4202 / 0 / 280
Final R indices [$I>2\sigma(I)$]	$R1$	0.0341	0.0588	0.0301
	$wR2$	0.0882	0.1401	0.0779
Final R indices (all data)	$R1$	0.0385	0.0707	0.0408
	$wR2$	0.0920	0.1478	0.0866

Table S2 Selected geometric parameters [Å, °] for **1-3**

	1 (X = Cl)	**2** (X = Br)	**3** (X = I)
Co1–N1	2.0370(17)	2.036(5)	2.029(3)
Co1–N2	2.0373(17)	2.042(5)	2.031(3)
Co1–X1	2.2112(8)	2.3299(14)	2.5248(8)
Co1–X2	2.2115(7)	2.3315(13)	2.5237(8)
N1–Co1–N2	81.64(7)	81.86(19)	82.13(13)
X1–Co1–X2	119.99(3)	120.77(5)	121.69(3)
N1–Co1–X1	113.59(6)	112.43(15)	111.30(11)
N1–Co1–X2	112.07(6)	112.07(16)	112.24(11)
N2–Co1–X1	109.61(6)	109.33(16)	107.99(11)
N2–Co1–X2	113.67(5)	113.86(15)	114.65(10)

Table S3 Possible π-π interactions [Å, °] for **1-3**

Compound	d(Cg1···Cg1^{i})*	α	β	γ
1	3.935(1)	20	13.4	17.1
2	3.941(3)	20	12.6	16.5
3	4.006(4)	21	18.4	17.1

Symmetry code: (i) x, 0.5 – y, – 0.5 + z

*Cg1 represents the centroid of the aromatic ring containing C5 atom
α denotes the dihedral angle between planes I (plane of the first ring) and J (plane of the second ring);
β denotes the angle between the Cg(I)···Cg(J) vector and normal to plane I;
γ denotes the angle between the Cg(I)···Cg(J) vector and normal to plane J.

Table S4 The shortest C···C contacts [Å] between aromatic C atoms of adjacent complex molecules for **1-3**

	1	**2**	**3**
C(I)···C(J)	d(C···C)	d(C···C)	d(C···C)
C5···C12^{i}	3.488(3)	3.500(8)	3.600(6)
C6···C11^{i}	3.494(3)	3.501(8)	3.558(6)
C5···C11^{i}	3.542(3)	3.553(9)	3.461(6)

Symmetry code: (i) x, 0.5 – y, – 0.5 + z

Table S5 Possible C-H···Cl weak hydrogen bonding interactions [Å, °] for **1**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C18^{ii}-H18^{ii}···Cl1	0.96	2.88	3.554(2)	129
C23^{iii}-H23^{iii}···Cl2	0.96	2.86	3.688(2)	146

Symmetry codes: (ii) 1 – x, – 0.5 + y, 0.5 – z; (iii) 2 – x, – 0.5 + y, 1.5 – z

Table S6 Possible C-H···Br weak hydrogen bonding interactions [Å, °] for **2**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C23^{iv}-H23^{iv}···Br1	0.96	2.96	3.592(7)	124
C23^{iii}-H23^{iii}···Br2	0.96	2.94	3.790(7)	149

Symmetry codes: (iii) 2 – x, – 0.5 + y, 1.5 – z; (iv) 2 – x, – 0.5 + y, 0.5 – z

Table S7 Possible C-H···I weak hydrogen bonding interactions [Å, °] for **3**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C17^{iv}-H17^{iv}···I1	0.96	3.11	4.016(5)	158
C18^{iii}-H18^{iii}···I2	0.96	3.16	3.921(5)	138

Symmetry codes: (iii) 2 – x, – 0.5 + y, 1.5 – z; (iv) 2 – x, – 0.5 + y, 0.5 – z

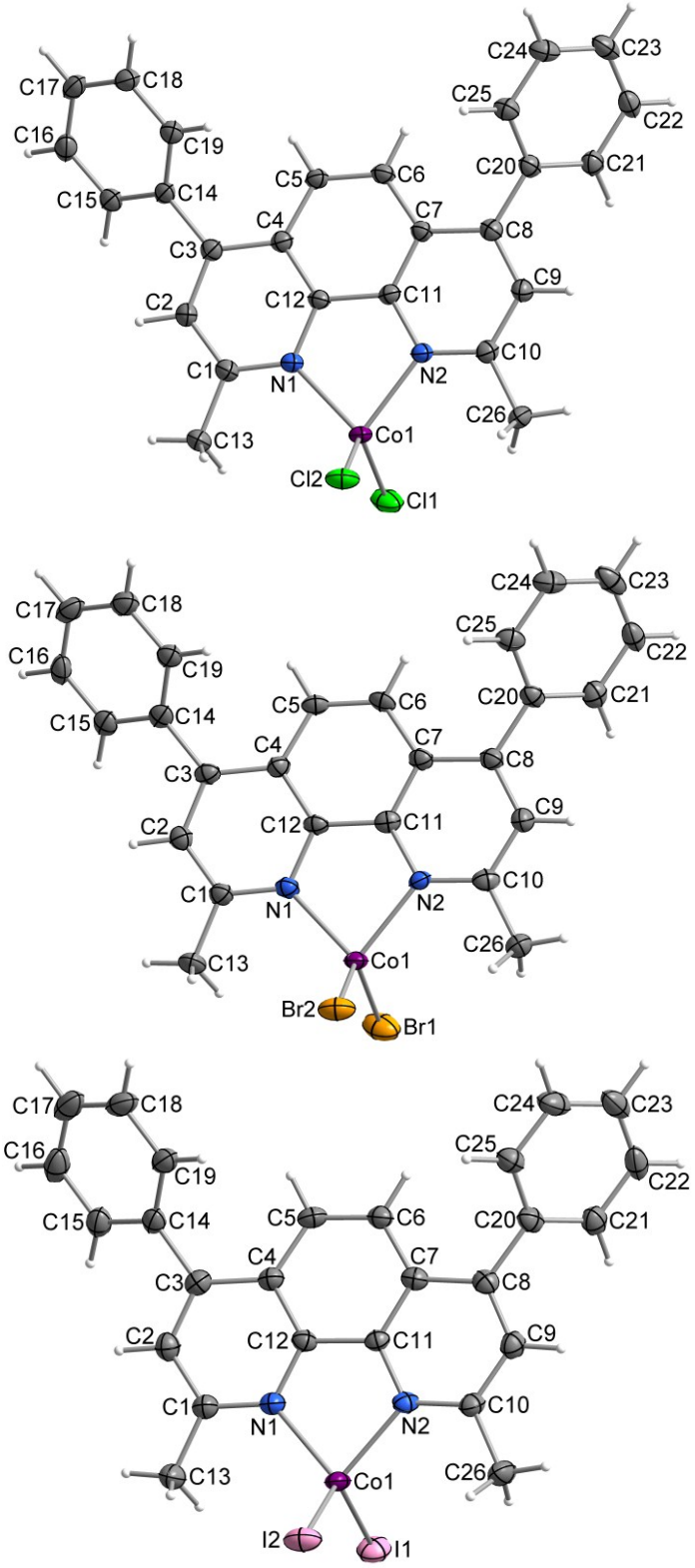

Fig. S1 Thermal ellipsoid plots of **1-3** (from top) showing the atom numbering scheme. The ellipsoids are drawn at 50 % probability level.

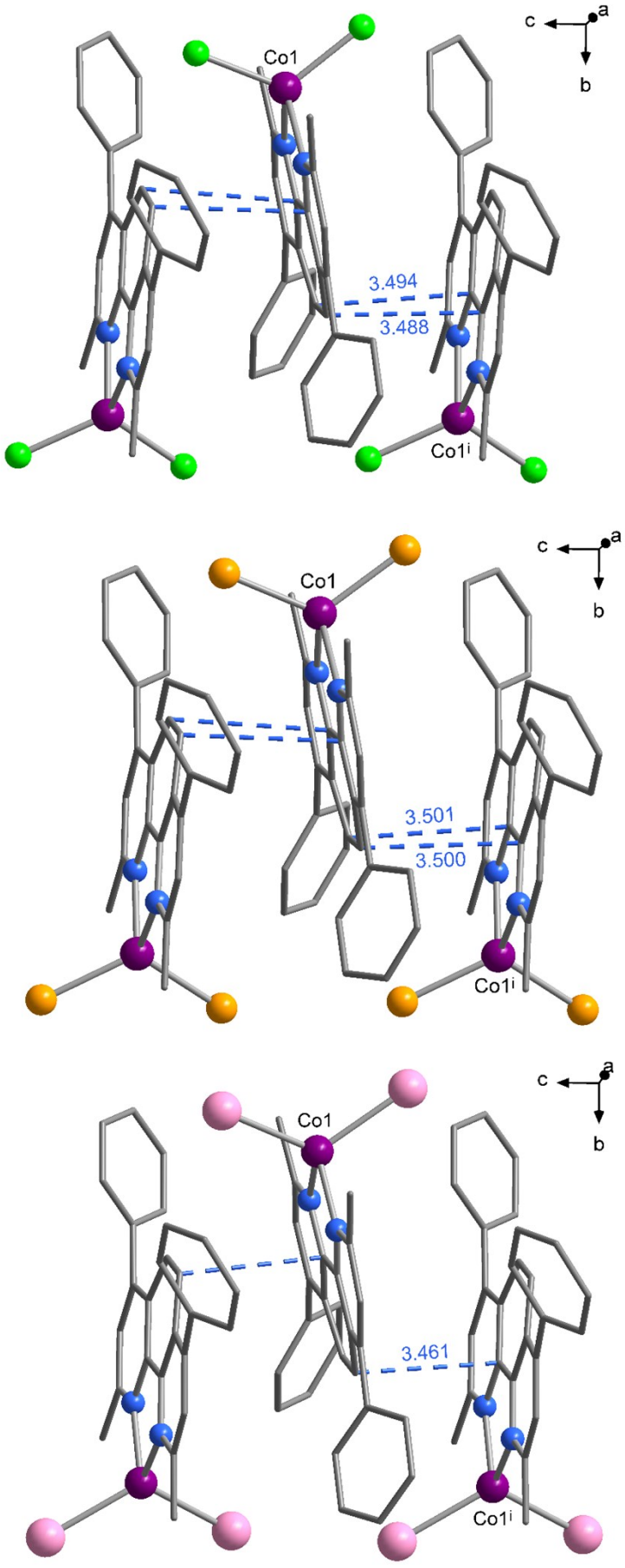

Fig. S2 The shortest C···C contacts [Å] between carbon atoms of adjacent complex molecules present in the crystal structures of **1-3** (from top). Hydrogen atoms are omitted for clarity.

AC magnetic data

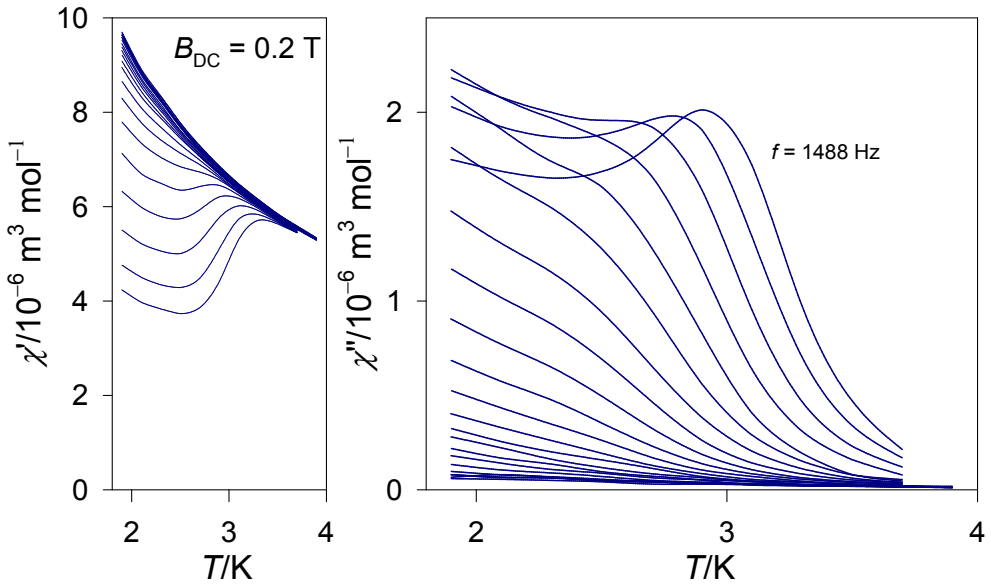

Fig. S3 Temperature dependence of the AC susceptibility components for **1**.

Table S8 Fitted parameters of the Debye model for **1** at B_{DC} = 0.2 T

T/K	$R(\chi')$/%	$R(\chi'')$/%	χ_S	χ_{T1}	α_1	τ_1 /10^{-3} s
1.9	0.57	3.7	2.27(10)	9.66(2)	0.32(1)	0.323(11)
2.1	0.46	3.3	2.22(7)	8.87(1)	0.29(1)	0.305(8)
2.3	0.50	3.2	2.28(7)	8.27(1)	0.25(1)	0.289(7)
2.5	0.51	3.0	2.14(7)	7.70(1)	0.22(1)	0.236(6)
2.7	0.57	3.6	1.99(9)	7.21(1)	0.18(1)	0.169(6)
2.9	0.63	4.0	1.77(15)	6.79(1)	0.13(1)	0.0996(50)
3.1	0.75	4.7	1.50	6.38(1)	0.09(1)	0.0480(10)