Electronic Supplementary Information

for

Structural, magnetic, redox and theoretical characterization of seven-coordinate first-row transition metal complexes with macrocyclic ligand containing two benzimidazolyl *N*-pendant arms

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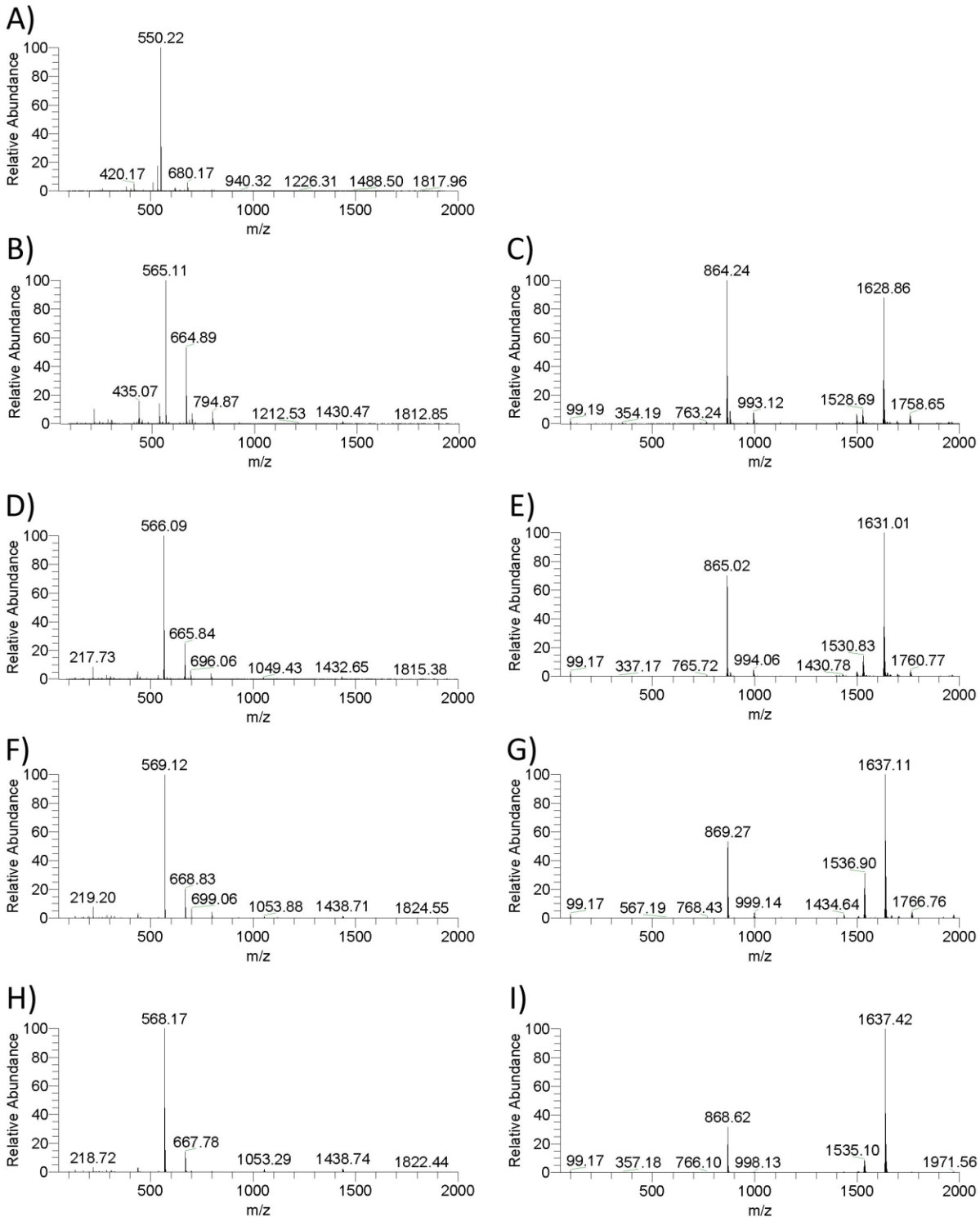

Figure S1 ESI mass spectra of the ligand **L** (A) and studied complexes **1** (B,C), **2** (D,E), **3** (F,G), **4** (H,I) (positive mode: A,B,D,F,H; negative mode: C,E,G,I).

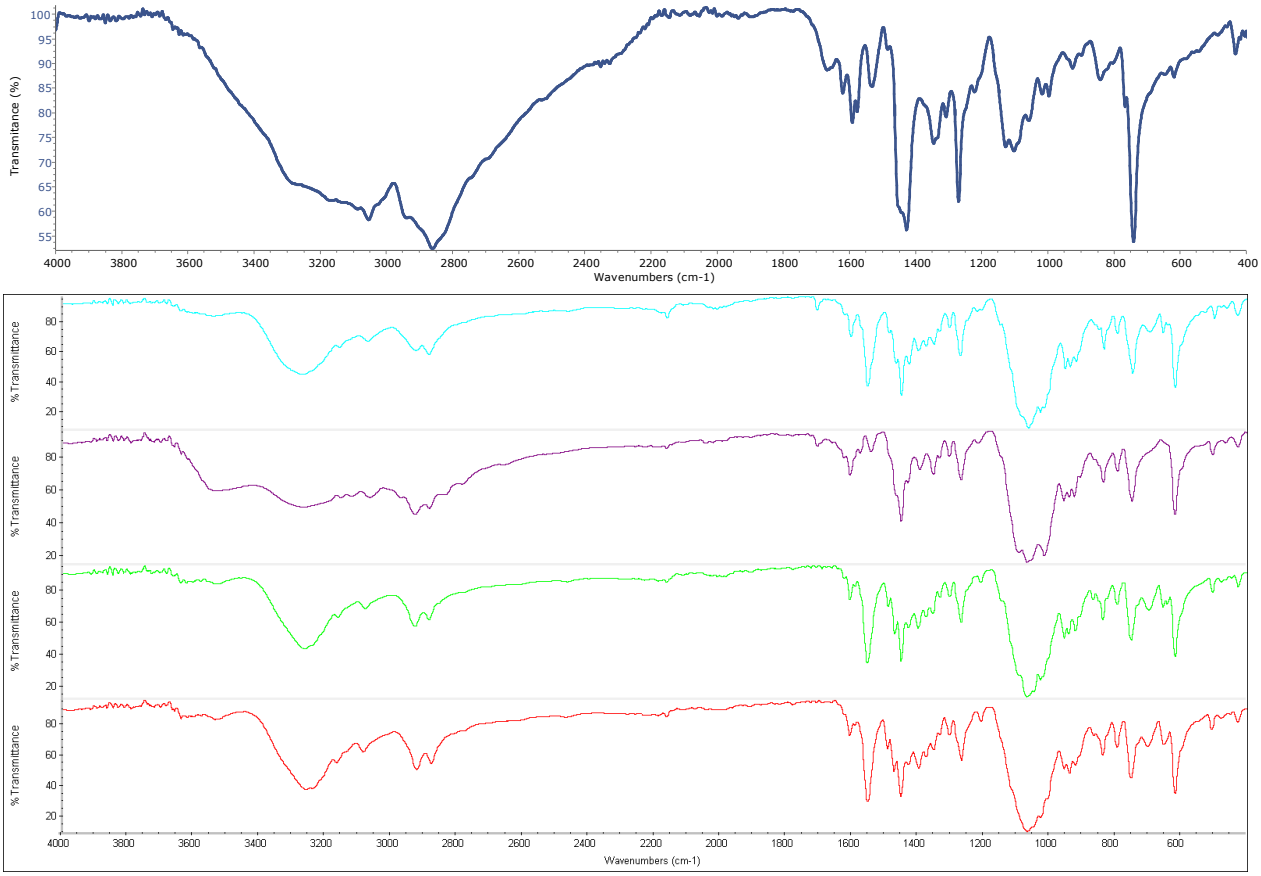

Figure S2 IR spectra of the studied ligand **L** (*dark blue*) and complexes **1** (*light blue*), **2** (*purple*), **3** (*green*) and **4** (*red*).

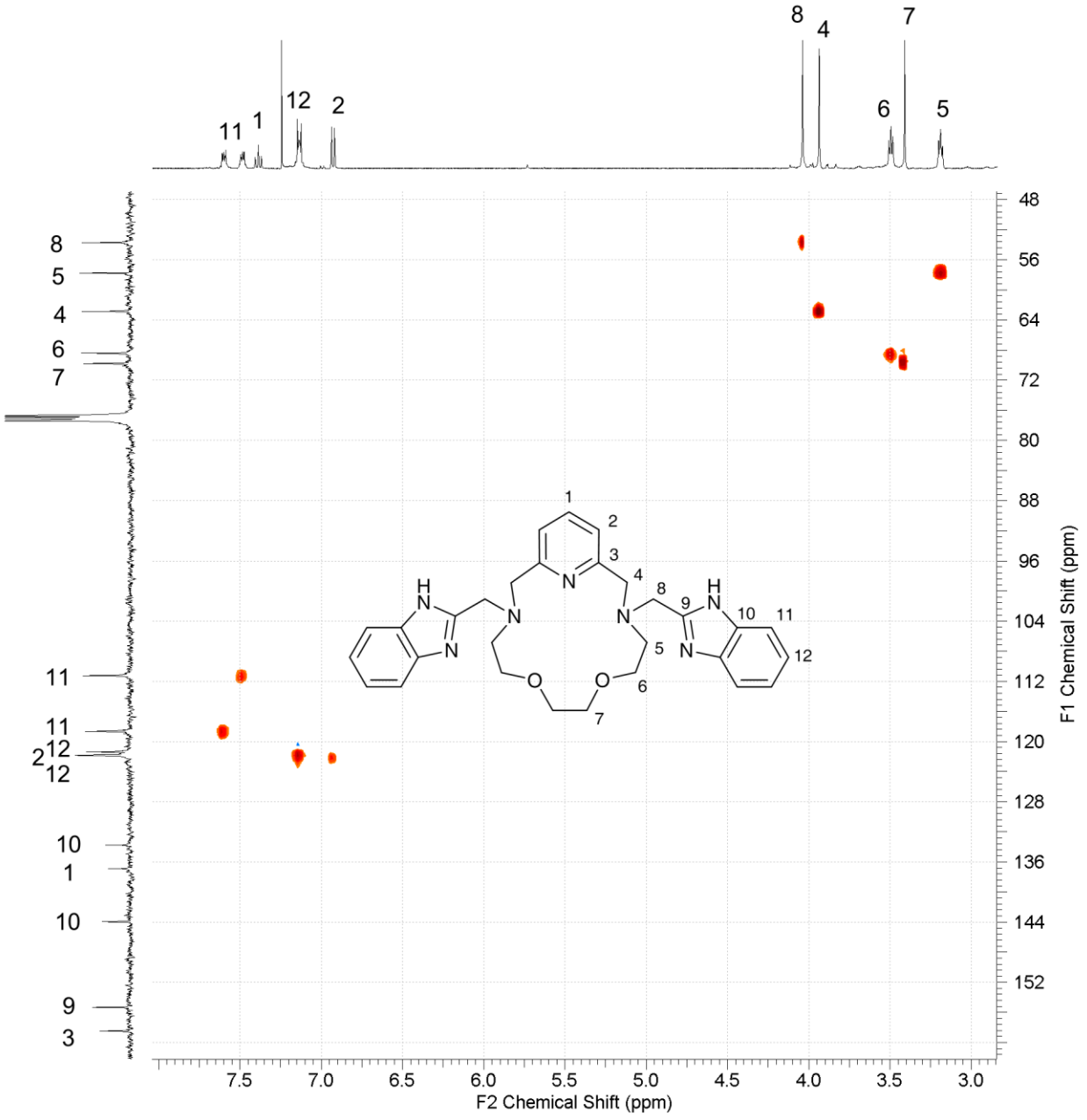

Figure S3 ^{1}H–^{13}C *gs*-HMQC NMR spectrum (400 MHz, $CDCl_3$) of **L** (3,12-bis((1*H*-benzimidazol-2-yl)methyl)-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),14,16-triene) with the residual peak of $CHCl_3$ at 7.27 ppm (^{1}H) and $CDCl_3$ at 77.0 ppm (^{13}C).

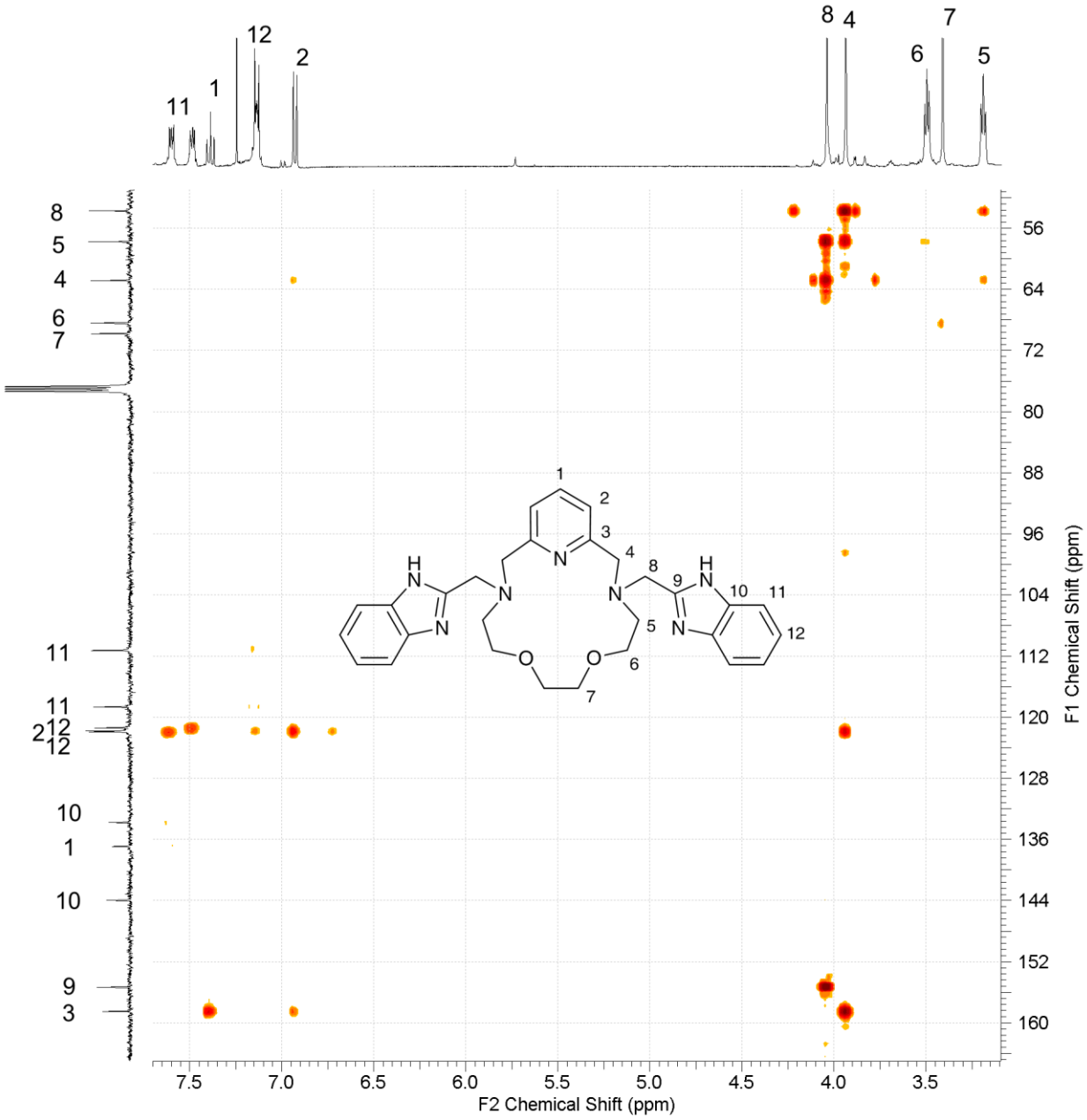

Figure S4 ^{1}H–^{13}C *gs*-HMBC NMR spectrum (400 MHz, $CDCl_3$) of **L** (3,12-bis((1*H*-benzimidazol-2-yl)methyl)-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),14,16-triene) with the residual peak of $CHCl_3$ at 7.27 ppm (^{1}H) and $CDCl_3$ at 77.0 ppm (^{13}C).

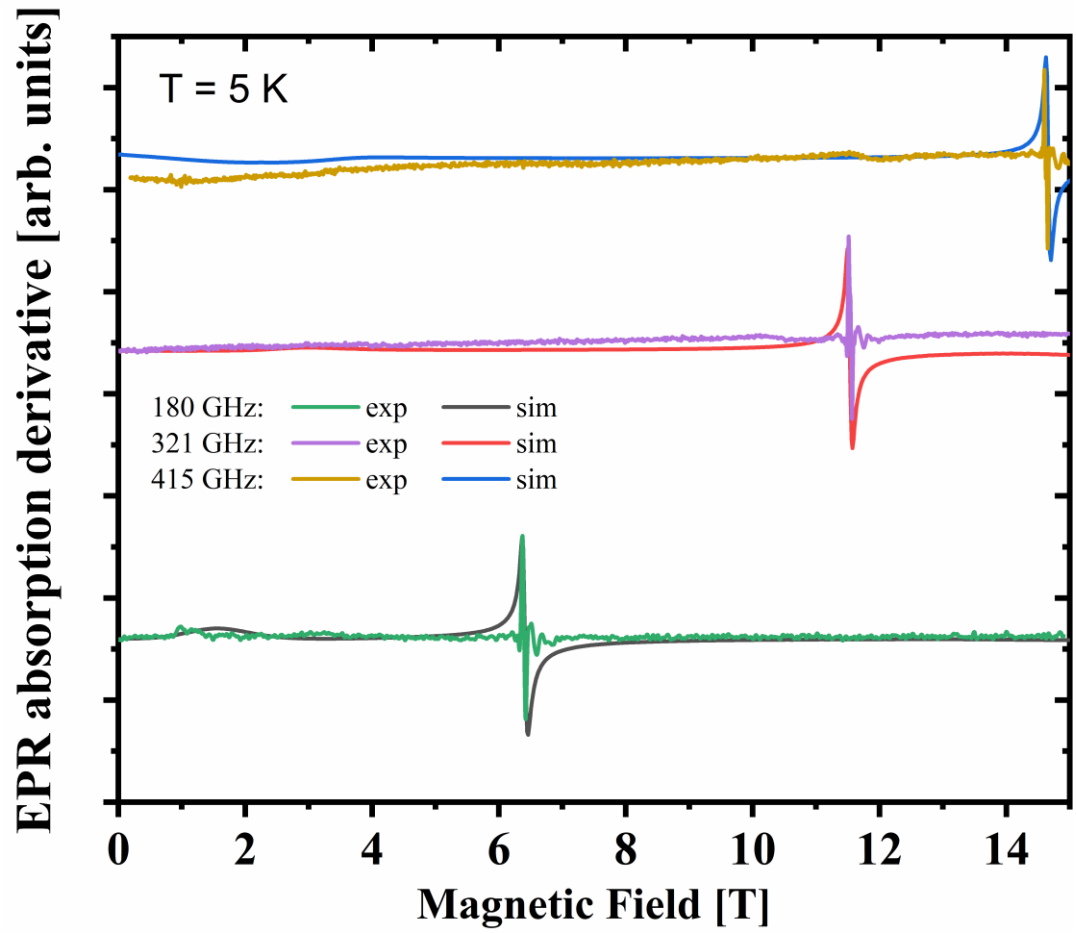

Figure S5 HFEPR measurements of a powder sample of compound **2** at 4 K and 180 GHz, 321 GHz and 415 GHz. At T > 10 K, there was no absorption in any of the tested frequencies (not shown), in agreement with simulated results, which present a significant decrease of the absorption intensity for a small increase in temperature. Relaxation and population of excited states determines the spectra properties at different temperatures. The simulation was performed for a spin S = 2 system using the CASSCF/NEVTP2 calculated *g* values from Table 3, but with D = + 8.2 cm^{-1} and E/D = 0.29. Anisotropic broadening of 50 GHz was included in the simulation in order to fit the experimental data (HStrain in the *y* direction coincident with the higher *g* value.)

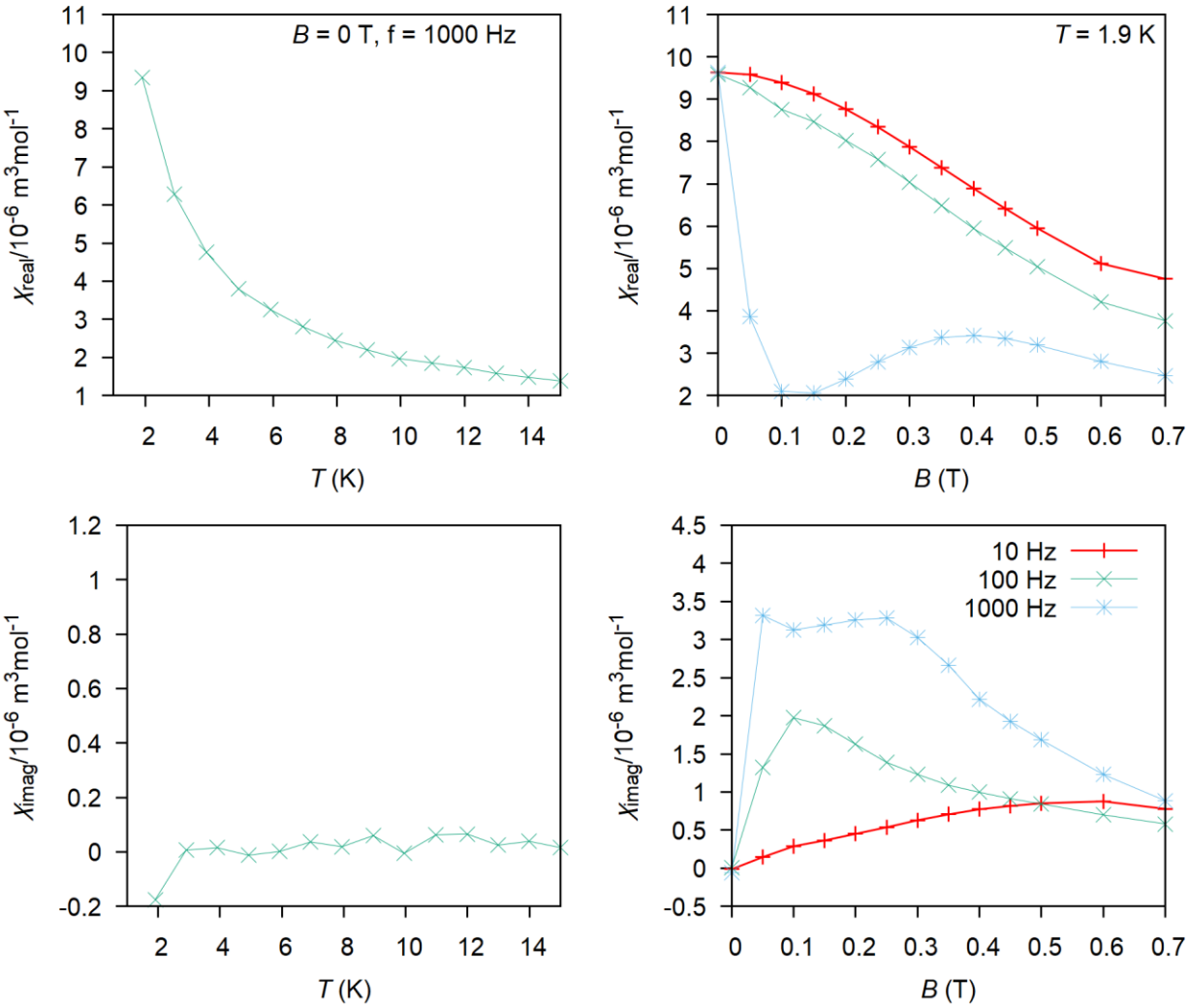

Figure S6 In-phase χ_{real} and out-of-phase χ_{imag} molar susceptibilities for **3** at zero static magnetic field (l*eft*) and in non-zero static field (*right*). Lines serve as guides for the eyes.

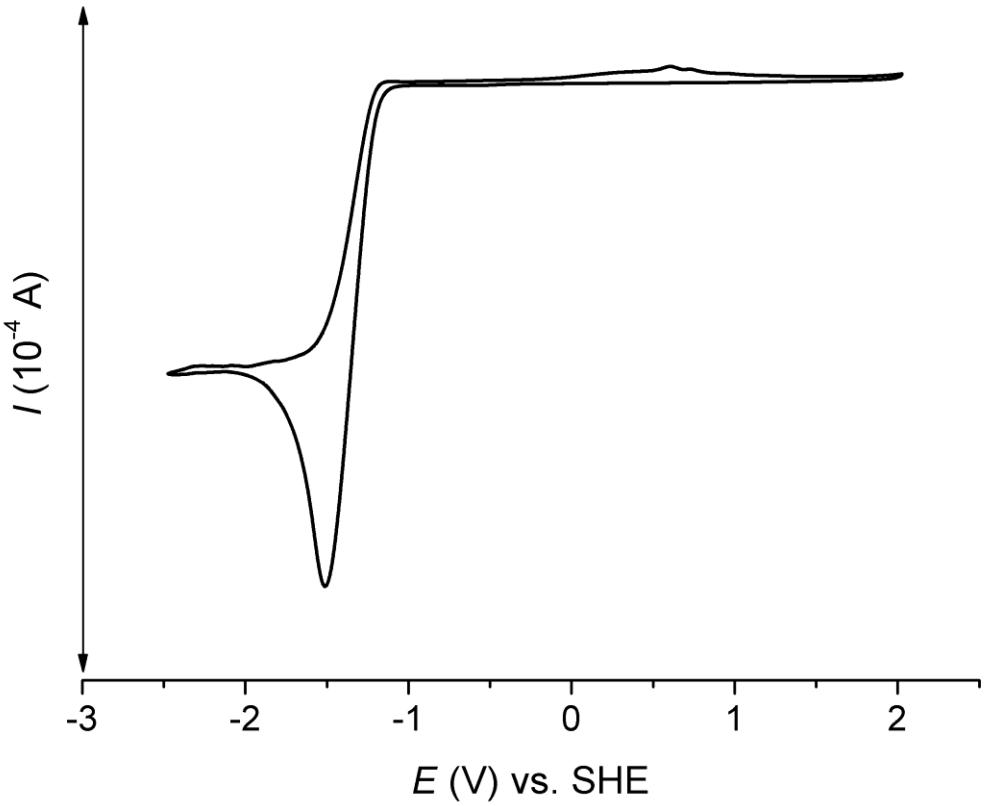

Figure S7 Cyclic voltammogram of **CH_3NO_2** recorded with a glassy carbon electrode at the rate 100 mV/s using 0.1M tetrabutylammonium perchlorate as supporting electrolyte in CH_3CN under argon atmosphere.

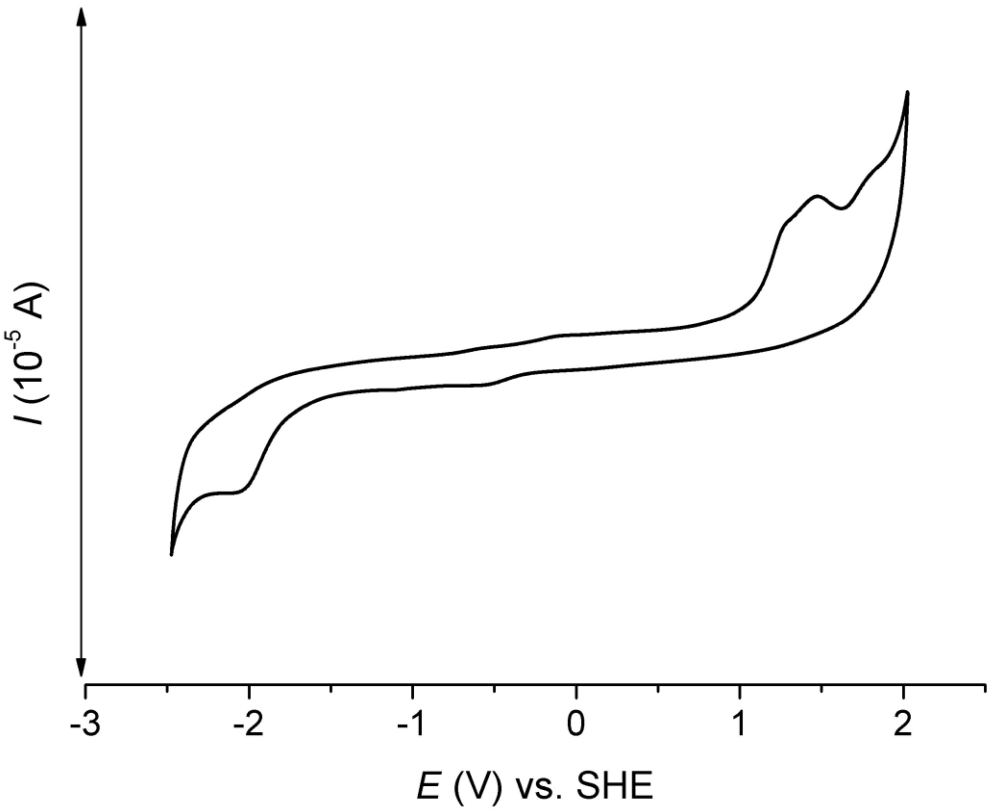

Figure S8 Cyclic voltammogram of **L** recorded with a glassy carbon electrode at the rate 100 mV/s using 0.1M tetrabutylammonium perchlorate as supporting electrolyte in CH_3CN under argon atmosphere.

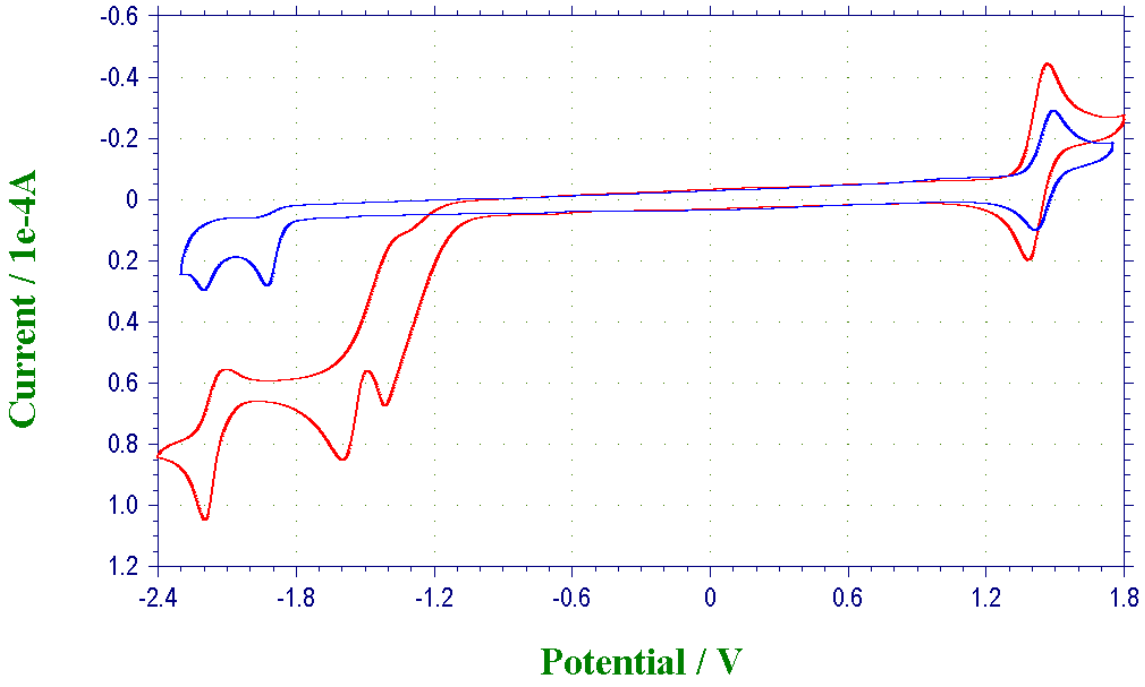

Figure S9 Comparison of cyclic voltammograms of **1** (*red*) and [Mn(**L2**)]$(ClO_4)_2$ (*blue*) recorded with a glassy carbon electrode at the rate 100 mV/s using 0.1M tetrabutylammonium perchlorate as supporting electrolyte in CH_3CN under argon atmosphere.

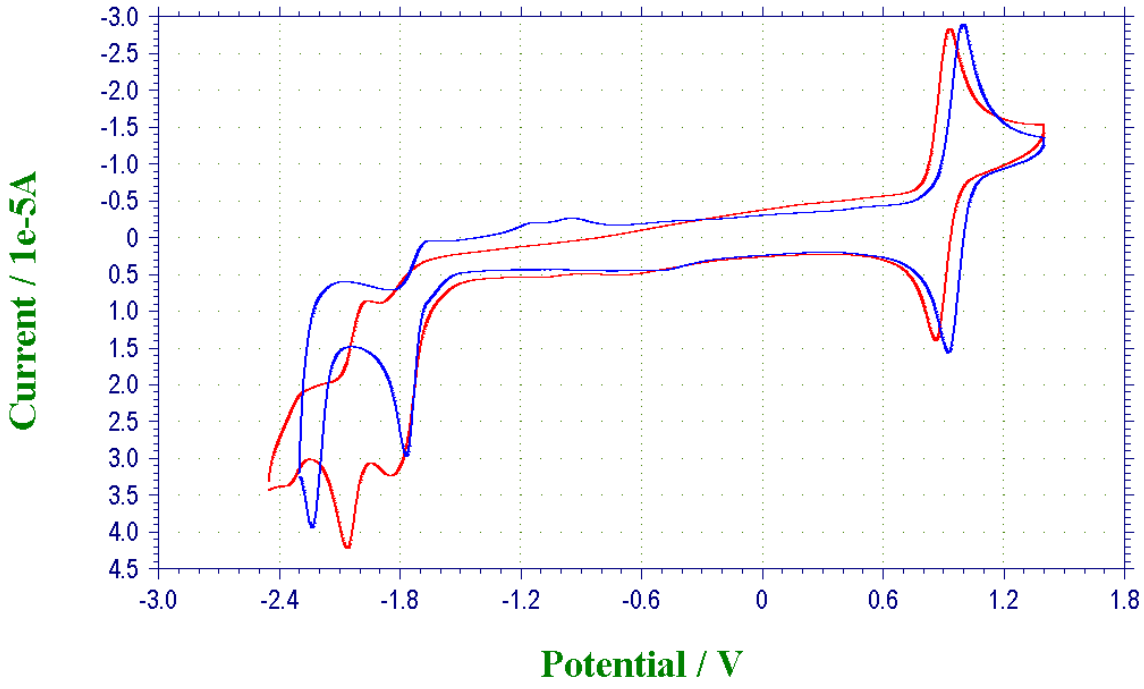

Figure S10 Comparison of cyclic voltammograms of **2** (*red*) and [Fe(**L2**)]$(ClO_4)_2$ (*blue*) recorded with a glassy carbon electrode at the rate 100 mV/s using 0.1M tetrabutylammonium perchlorate as supporting electrolyte in CH_3CN under argon atmosphere.

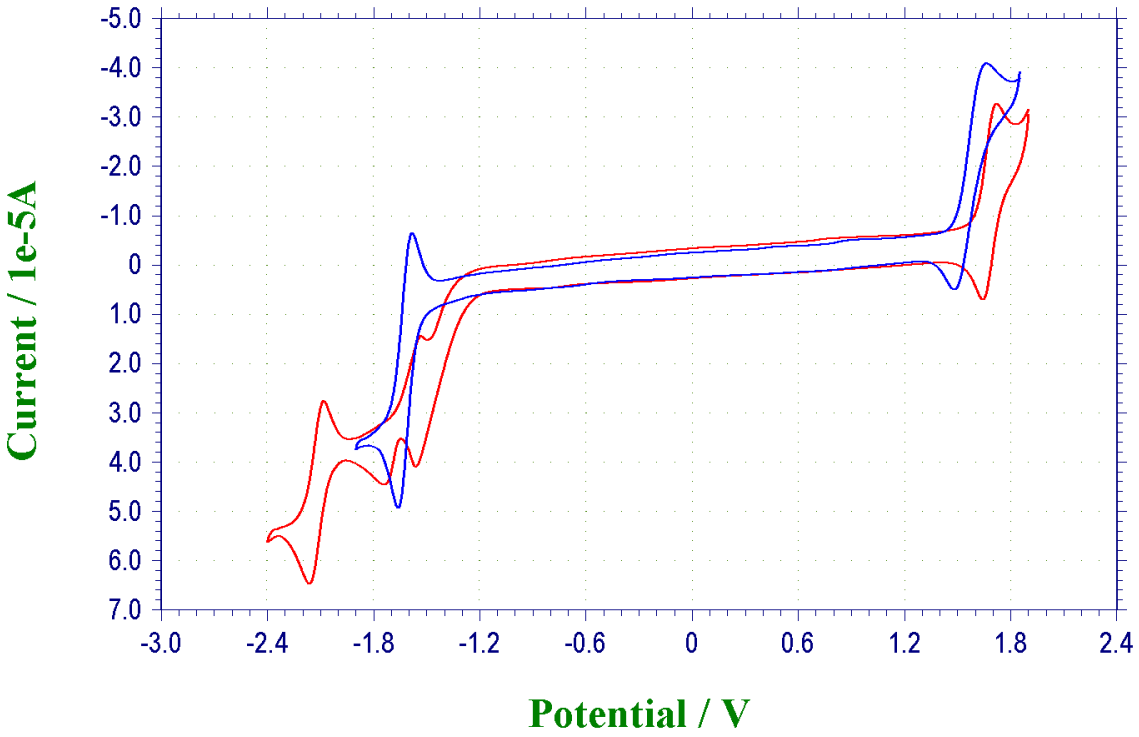

Figure S11 Comparison of cyclic voltammograms of **3** (*red*) and [Co(**L2**)]$(ClO_4)_2$ (*blue*) recorded with a glassy carbon electrode at the rate 100 mV/s using 0.1M tetrabutylammonium perchlorate as supporting electrolyte in CH_3CN under argon atmosphere.

Table S1 Crystal data and structure refinements for studied complexes **1**–**4**.

Compound	**1**	**2**	**3**	**4**
Formula	$C_{61}H_{75}Cl_4Mn_2N_{17}O_{26}$	$C_{61}H_{75}Cl_4Fe_2N_{17}O_{26}$	$C_{61}H_{75}Cl_4Co_2N_{17}O_{26}$	$C_{61}H_{75}Cl_4Ni_2N_{17}O_{26}$
M_r	1714.06	1715.88	1722.04	1721.60
Temperature (K)	150(2)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P–1	P–1	P–1	P–1
a (Å)	13.8753(4)	13.8335(4)	13.8322(4)	13.8336(4)
b (Å)	14.9584(4)	14.9487(4)	14.9418(4)	14.9837(4)
c (Å)	18.8648(6)	18.7892(5)	18.7191(5)	18.6193(5)
α (°)	77.3590(10)	77.1470(10)	77.1450(10)	76.9370(10)
β (°)	76.2910(10)	76.1020(10)	76.4180(10)	76.3470(10)
γ (°)	86.4830(10)	86.4130(10)	86.2140(10)	86.0280(10)
V, Å^3	3711.50(19)	3677.05(18)	3665.99(18)	3652.76(18)
Z	2	2	2	2
D_{calc}, g cm^{-3}	1.534	1.550	1.560	1.565
μ, mm^{-1}	0.575	0.632	0.691	0.754
F(000)	1772	1776	1780	1784
θ range for data collection (°)	1.669–25.000	1.143–25.000	1.607–25.000	1.153–27.570
Refl. collected	43364	49826	38740	61058
Independent refl.	13083	12969	12915	16876
R(int)[a]	0.0299	0.0191	0.0284	0.0282
Data/restrains/parameters	13083 / 24/ 992	12969/42/992	12915/ 24/992	16876/0/ 994
Completeness to θ (%)	100.0	100.0	100.0	99.8
Goodness-of-fit on F^2	1.045	1.031	1.028	1.021
R_1, wR_2 ($I>2\sigma(I)$[b]	0.0505, 0.1300	0.0535, 0.1487	0.0457, 0.1206	0.0491, 0.1278
R_1, wR_2 (all data)[b]	0.0689, 0.1375	0.0590, 0.1521	0.0607, 0.1273	0.0641, 0.1371
Largest diff. peak and hole / A^{-3}	1.125 and –1.008	1.120 and –1.196	1.034 and –0.892	1.473 and –1.012
CCDC number	1942109	1942110	1942111	1942112

[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$, [b] $R_1 = \Sigma(\left| \left| F_o \right| - \left| F_c \right| \right|) / \Sigma \left| F_o \right|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$

Table S2 Results of continuous shape measures calculations using program Shape 2.1 for compounds **1**–**4**.[a]

CN = 7[b]	HP-7	HPY-7	PBPY-7	COC-7	CTPR-7	JPBPY-7	JETPY-7
1	27.978	22.283	1.653	6.447	4.998	4.625	17.671
2	28.056	22.370	1.482	6.675	5.225	4.202	18.219
3	28.986	22.755	1.208	6.699	5.117	3.806	18.889
4a[c]	29.553	22.661	1.201	6.818	5.114	3.296	20.061
4b[c]	29.760	23.638	1.112	6.559	5.109	3.232	20.354

[a] the listed values correspond to the deviation between the ideal and real coordination polyhedra, the lowest values are in red color.

[b] HP-7 = heptagon, HPY-7 = hexagonal pyramid, PBPY-7 = pentagonal bipyramid, COC-7 = capped octahedron, CTPR-7 = capped trigonal prism.

[c] calculations were performed for two crystallographically independent molecules present in the asymmetric unit of **4**.

Table S3 Parameters of one-component Debye model for **3**.

T/K	χ_S/(10^{-6} m^3mol^{-1})	χ_T/(10^{-6} m^3mol^{-1})	α	τ/(s)
1.9	0.5465	9.3676	0.0360	3.79E-04
2.1	0.4772	8.5063	0.0429	2.95E-04
2.3	0.4723	7.8689	0.0385	2.40E-04
2.5	0.4225	7.2721	0.0410	1.91E-04
2.7	0.3045	6.7651	0.0418	1.50E-04
2.9	0.2364	6.3360	0.0438	1.23E-04
3.1	0.3043	5.9433	0.0284	1.03E-04
3.3	0.4118	5.6110	0.0349	8.89E-05
3.5	0.4167	5.3075	0.0350	7.44E-05
3.7	0.5233	5.0392	0.0077	6.71E-05
3.9	0.3856	4.7989	0.0092	5.59E-05
4.1	0.5628	4.5769	0.0140	5.11E-05
4.3	0.4393	4.3766	0.0068	4.40E-05
4.5	0.6701	4.1932	0.0063	4.05E-05
4.7	0.9442	4.0325	0.0069	4.01E-05
4.9	0.9838	3.8823	0.0072	3.48E-05