SUPPLEMENTARY INFORMATION

Investigation of Cobalt(III)-Triazole Systems as Prototypes for Hypoxia-Activated Drug Delivery

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Materials and Instrument Details

All chemicals for syntheses and analyses were used as received without further purification. The ligands tris(pyridin-2-ylmethyl)amine (TPA), *N,N′*-bis(pyridin-2-ylmethyl)ethylenediamine (py_2en), *N,N′*-dimethyl-*N,N′*-bis(pyridin-2-ylmethyl)ethylenediamine) (py_2enMe_2) and (*E*)-1-phenyl-1*H*-1,2,3-triazole-4-carbaldehyde oxime (HTz) were synthesized, purified and characterized as previously described.[1,2,3] Infrared spectra were recorded on a Varian 600 FTIR equipped with a Pike ATR Miracle accessory (diamond/ZnSe crystal, resolution: 4 cm^{-1}). ^{1}H NMR spectra were recorded at room temperature using a Varian Unity-Plus 500 or 300 MHz spectrometer, in the DMSO-d_6. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hertz (Hz). UV–Vis spectra were collected on a Varian Cary 50 Spectrophotometer using spectroscopic grade solvents. ESI-MS data were collected in a Perkin Elmer SQ-300 mass spectrometer by direct infusion using MeOH (MS grade) as solvent. Microanalyses were performed in a Perkin-Elmer CHN 2400 micro analyzer at Universidade de São Paulo (USP-SP), Brazil. Cyclic voltammetry measurements were performed on a BASi Epsilon Potenciostat–Galvanostat at room temperature, under argon atmosphere (99.999% pure), using 1 x 10^{-3} mol L^{-1} solutions of the complexes with 0.1 mol L^{-1} of $TBAClO_4$ as supporting electrolyte. A standard three-component system was used: a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode for organic media, all acquired from BASi. Ferrocene (Fc^+/Fc) was used as internal reference.[4]

Single Crystal X-ray diffraction

Poor quality single crystals of **2** were obtained from recrystallization in a 2:1 acetonitrile/toluene solution. X-ray diffraction data collection of **2** was performed on an Oxford-Diffraction GEMINI diffractometer using Mo-K_α radiations (λ = 0.71073 Å) at 150 K. Data integration and scaling of the reflections were performed with the *CRYSALIS* suite.[5] Final unit cell parameters were based on the fitting of all reflections positions. Analytical absorption corrections were performed using *CRYSALIS* suite and the space group identification was done with *XPREP*.[6] The structure was solved by direct methods using the *SHELXT* program.[7] The

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[1] Z. Tyeklhr, R.R. Jacobson, N. Wei, N.N. Murthy, J. Zubieta, K.D. Karlin. *J. Am. Chem. Soc.* 1993, **115**, 2611.

[2] C. Hureau, G. Blondin, M.F. Charlot, C. Philouze, M. Nierlich, M. Césario, E. Anxolabéhère-Mallart. *Inorg. Chem.* 2005, **44**, 3669.

[3] D. Gonzaga, M.R. Senger, F.C. Silva, V.F. Ferreira, F.P. Silva-Jr. *Eur. J. Med. Chem.* 2014, **74**, 461.

[4] R. Gagne, C. Koval, G. Licenski. *Inorg. Chem.* 1980, **19**, 2854.

[5] CrysalisPro (2015) Rigaku Oxford Diffraction, CrysAlisPro Software system. Rigaku Corp., Oxford, UK.

positions of all non-hydrogen atoms of $[Co(py_2en)(Tz)]^{2+}$, were unambiguously assigned on consecutive difference Fourier maps. Refinements were performed using *SHELXL* based on F^2 through full-matrix least-squares routine.[8] Hydrogen atoms were located in difference maps and included as fixed contributions according to the riding model [U_{iso}(H) = 1.5 U_{eq}(O) for the water molecules and C–H and N–H = 0.97 Å and U_{iso}(H) = 1.2 U_{eq}(C or N) for methylene groups, aromatic carbon atoms and amide groups].[9] Spread electronic density was observed during the refinements being associated to disordered counter-ions and water and acetonitrile solvent molecules. Perchlorate counter-ions were refined with split atomic positions. Based on elemental analysis and in the electron density maps, a total of 0.6 acetonitrile and 0.8 water molecules could be refined with split atomic positions subject to an occupational disorder. Hydrogen atoms of the water molecules were not modeled. All non-hydrogen atoms of $[Co(py_2en)(Tz)]^{2+}$, were refined with anisotropic atomic displacement parameters whereas all atoms of disordered counter-ions and solvent molecules were refined with isotropic atomic displacement parameters. A summary of the crystal and refinement data is shown in Table S1. CCDC 1486388 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

Computational Details

The geometry optimization calculations of all complexes were performed with the PBE density functional theory method in combination with the def2-TZVP basis set in conjunction with the resolution identity algorithm (RI).[10,11] The stability of the optimized geometries was confirmed by harmonic frequency calculation, since no imaginary frequency was found. All calculations were carried out taking the solvent effects (acetonitrile, ⍰ = 34.688 and n = 1.344) into account using the conductor-like-screening model COSMO.[12] TD-DFT calculations were performed at the PBE0/def2-TZVP/COSMO levels.[13] The vertical excitation with linear response was carried out with 50 states to find all the important transitions and the theoretical spectra were broadened by a Lorentzian function on Chemcraft program.[14] The canonical molecular

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[6] Sheldrick, G. M. *Acta Crystallogr*. 2008, *A64*, 112.

[7] Sheldrick, G. M. *Acta Crystallogr*. 2015, *A71*, 3.

[8] Sheldrick, G. M. *Acta Crystallogr*. 2015, *C71*, 3.

[9] Johnson, C. K. *ORTEP, Crystallographic Computing*, 1971, edited by F. R. Ahmed, pp. 217-219, Copenhagen, Denmark.

[10] C. Adamo, V. Barone. *J. Chem. Phys*. 1999, **110**, 6158.

[11] F.Weigend, R.Ahlrichs. *Phys. Chem. Chem. Phys*. 2005, **7**, 3297.

[12] A. Klamt, G. Schürmann. *J. Chem. Soc., Perkin Trans*. 1993, **2**, 799.

[13] F. Furche, R. Ahlrichs. *J. Chem. Phys.* 2002, **117**, 7433.

orbital surfaces were plot with isocontours of 0.04-0.05 a.u. in the Chemcraft program.[9] All the calculations were carried out in the TURBOMOLE 6.6 package.[15] The electrophilicity index (ω) was calculated as $\omega = \frac{\chi^2}{2\eta}$, where is the global electronegativity and is global hardness and can be calculated as $\chi = \frac{I + A}{2} = -\frac{\epsilon_{HOMO} + \epsilon_{LUMO}}{2}$ and $\eta = I - A = \epsilon_{LUMO} - \epsilon_{HOMO}$.[16] The ionization potential (*I*) is equal to $I = -\epsilon_{HOMO}$ and the electron affinity (*A*) is $A = -\epsilon_{LUMO}$.

Stability and Reactivity Studies

For stability and reactivity experiments, fresh stock solutions of the complexes (1.0 × 10^{-3} mol L^{-1} in HPLC grade DMSO/water 1:9) and ascorbic acid (1.0 × 10^{-2} mol L^{-1} in HPLC grade water) were prepared prior each experiment. Stock 0.05 mol L^{-1} solutions of phosphate buffers were also prepared using distilled water and the pH values were adjusted to 6.2, 7.0 and 7.4 with NaOH 3.0 mol L^{-1}. Aliquots of the complexes and ascorbic acid solutions were diluted in the buffer solutions in order to obtain a final concentration of 1 × 10^{-4} mol L^{-1}. For the experiments under argon and oxygen, the solutions and cuvettes were saturated with the corresponding gas prior each experiment. UV-Visible spectra were collected in a Varian Cary 50 spectrophotometer equipped with a water thermostatted 18 multicell holder. A reaction of complex **3** (1 x 10^{-4} mol L^{-1}) with sodium ascorbate (1:10) in methanol was performed and analyzed by ESI-MS in order to identify the reaction products. After 2 h at 37 °C under argon atmosphere, the reaction solution was diluted in MS-grade methanol (1:10) and analyzed by direct infusion. Then, cysteine was added to the reaction solution analyzed previously. After 15 minutes, a new dilution in MS-grade methanol (1:10) was performed and analyzed by direct infusion.

Synthesis of [Co^{III}(TPA)(Tz)](BF$_4$)$_2$.2H$_2$O (1)

To a solution of $Co(BF_4)_2 \cdot 6H_2O$ (0.17 g, 0.50 mmol) in 20 mL of methanol was added HTz (0.94 mg, 0.5 mmol), followed by 10 mL of a methanol solution of TPA (0.10 g, 0.5 mmol) and triethylamine (70 L, 0.5 mmol). After 30 minutes under magnetic stirring, a small amount of a solid precipitated, which was removed by filtration and discarded. The reaction solution

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[14] http://www.chemcraftprog.com.

[15] TURBOMOLE V6.6 2014, a development of University of Karlsruhe and Forschungszentrum Karlsruhe.

[16] P. K.Chattaraj, U. Sarkar, D. R. Roy. Chem. Rev. 2006, 106, 2065.

was left undisturbed for slow evaporation of the solvent to produce a brown crystalline precipitate (yield: 30%). Elemental analysis calc. for $[Co^{III}(TPA)(Tz)](BF_4)_2.2H_2O$ ($C_{27}H_{29}B_2CoF_8N_8O_3$): C 43.46, H 3.92, N 15.02 %; found: C 43.67, H 3.83, N 15.51 %. IR (ATR, 4000–600 cm^{-1}): 1608 (N=N); 1496, 1441 (C=C); 1313, 1217 (C–N); 1049 (B–F). ^1H NMR (300 MHz, DMSO-d_6) δ ppm: 9.72 (d, *J* 5.1 Hz, 1H), 9.45 (s, 1H), 8.50 (s, 1H), 8.25-8.28 (m, 2H), 8.06-8.20 (m, 5H), 7.76 (d, *J* 7.3 Hz, 4H), 7.62-7.66 (m, 2H), 7.54 (d, *J* 7.3 Hz, 1H), 6.20 (d, *J* 16.9 Hz, 2H), 5.38 (s, 2H), 5.33 (d, *J* 16.9 Hz, 2H). ESI-MS (MeOH): m/z^{2+} = 267.8 for $[Co^{III}(TPA)(Tz)]^{2+}$; m/z^+ = 623.3 for $\{[Co^{III}(TPA)(Tz)](BF_4)\}^+$.

Synthesis of $[Co^{III}(py_2en)(Tz)](ClO_4)_2.CH_3CN.2H_2O$ (2)

To a solution of $Co(ClO_4)_2{\cdot}6H_2O$ (0.18 g, 0.50 mmol) in 10 mL of methanol was added HTz (0.94 mg, 0.5 mmol), followed by 5 mL of a methanol solution of py_2en (0.12 g, 0.5 mmol) and triethylamine (70 L, 0.5 mmol). A brown solid was isolated after 30 minutes under magnetic stirring, washed with cold methanol and dried under vaccum (yield: 60 %). After recrystallization in MeCN/toluene 1:1, **1** was obtained as a crystalline solid. Elemental analysis calc. (%) for $[Co^{III}(py_2en)(Tz)](ClO_4)_2.CH_3CN.2H_2O$ ($C_{25}H_{32}Cl_2CoN_9O_{11}$): C 39.28, H 4.22, N 16.49; found: C 38.76, H 3.85, N 16.89. IR (ATR, 4000–600 cm^{-1}): 3141 (N-H); 1600-1400 (C=C;C=N); 1068 (Cl-O); 838-726 (aromatic C-H). ^1H NMR (500 MHz, DMSO-d_6) δ ppm: 9.43 (s, 1H), 8.23 (d, *J* 5.5 Hz, 1H), 8.02-8.12 (m, 5H), 7.71-7.75 (m, 4H), 7.61-7.68 (m, 3H), 7.39-7.42 (m, 1H), 7.31 (d, *J* 6.0 Hz, 1H), 5.33 (dd, *J* 8.2 and 18.7 Hz, 1H), 5.25 (dd, *J* 7.1 and 17.6 Hz, 1H), 4.46 (d, *J* 18.7 Hz, 1H), 4.40 (d, *J* 17.6 Hz, 1H), 2.86-2.92 (m, 2H), 2.66-2.73 (m, 1H), 2.41-2.49 (m, 1H), 2.06 (1H, s). ESI-MS (MeOH): m/z^{2+} = 244.6 for $[Co^{III}(py_2en)(Tz)]^{2+}$; m/z^+ = 587.2 for $\{[Co^{III}(py_2en)(Tz)](ClO_4)\}^+$.

Synthesis of $[Co^{III}(py_2enMe_2)(Tz)](ClO_4)_2.H_2O$ (3)

This complex was prepared by the same procedure described for complex **2,** using the ligand py_2enMe_2 instead of py_2en. A dark brown precipitate was isolated (yield: 56%) and recrystallized in MeCN/toluene to afford a crystalline solid. Elemental analysis calcd (%) for $[Co(py2enMe2)(Tz)](ClO_4)_2.H_2O$, $C_{25}H_{31}Cl_2CoN_8O_{10}$: C 40.94, H 4.26, N 15.28; found: C 41.46, H 4.48, N 15.34. IR (ATR, 4000–600 cm^{-1}): 1600-1400 (C=C;C=N); 1084 (Cl-O); 817-692 (aromatic C-H). ^1H NMR (500 MHz, DMSO-d_6) δ ppm: 9.41 (s, 1H), 8.33 (d, *J* 5.5 Hz, 1H), 8.16 (dt, *J* 1.6 and 7.7 Hz, 1H), 8.11 (dt, *J* 1.6 and 7.7 Hz, 1H), 8.06 (d, *J* 7.7 Hz, 2H), 7.98 (s, 1H), 7.81 (d, *J* 8.2 Hz, 1H), 7.71-7.75 (m, 3H), 7.66-7.69 (m, 2H), 7.61 (d, *J* 5.5 Hz, 1H), 7.41-7.44 (m, 1H), 5.44 (d, *J* 17.0 Hz, 1H), 5.06 (d, *J* 16.5 Hz, 1H), 4.52 (d, *J* 17.0 Hz, 1H), 4.26 (d, *J* 16.5 Hz, 1H), 2.90-3.09 (m, 4H), 2.82 (s, 3H), 2.41 (s, 3H). ESI-MS (MeOH): $m/z^{2+} = 257.8$ for $[Co^{III}(py_2enMe_2)(Tz)]^{2+}$; $m/z^{+} =$ 615.3 for $\{[Co^{III}(py_2enMe_2)(Tz)](ClO_4)\}^{+}$.

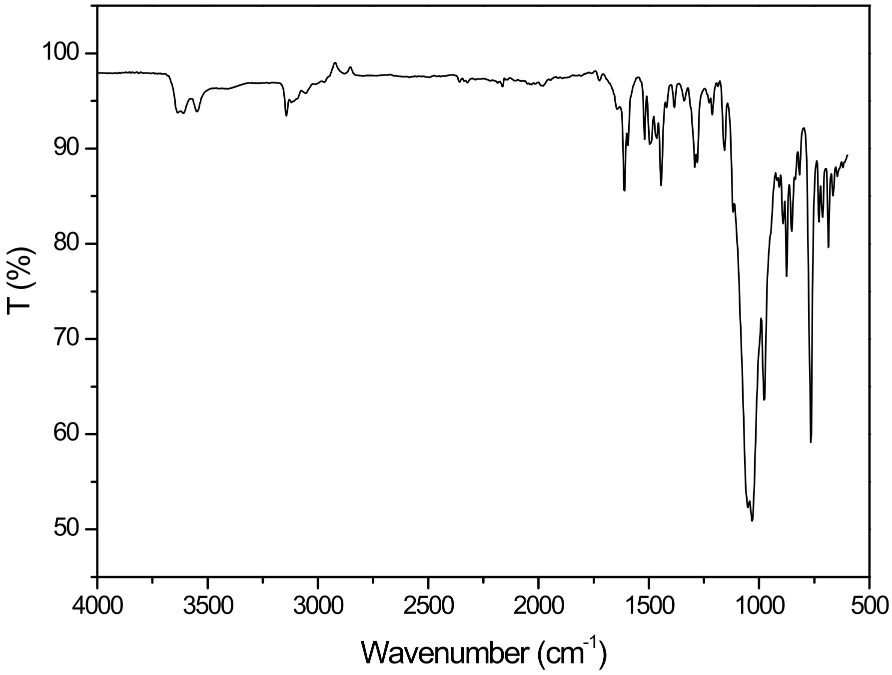


Figure S1. IR (ZnSe/diamond ATR) spectrum of complex **1**.

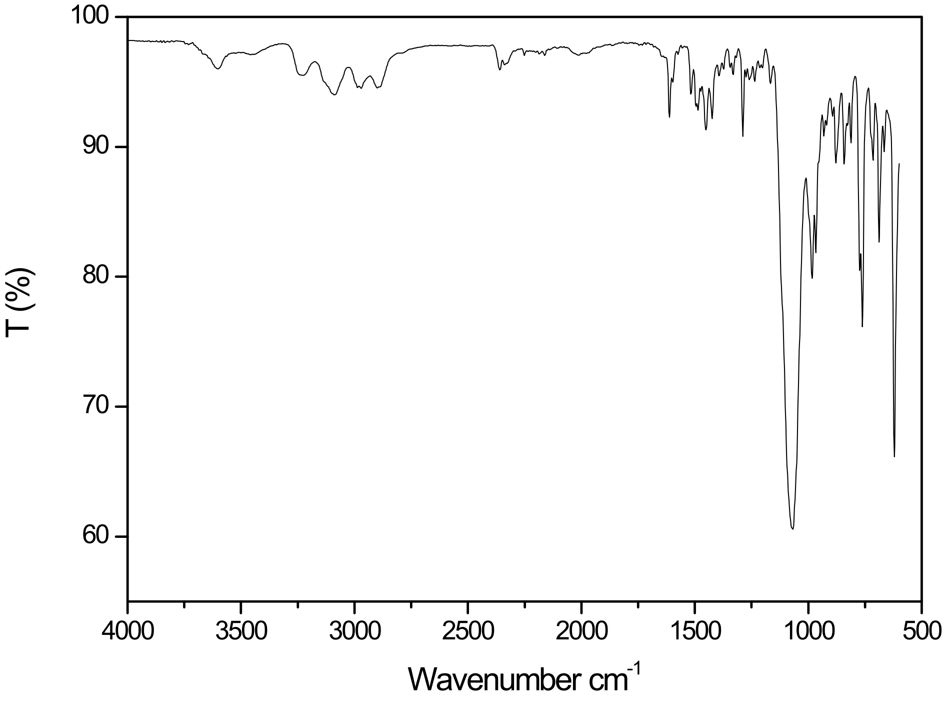


Figure S2. IR (ZnSe/diamond ATR) spectrum of complex **2**.

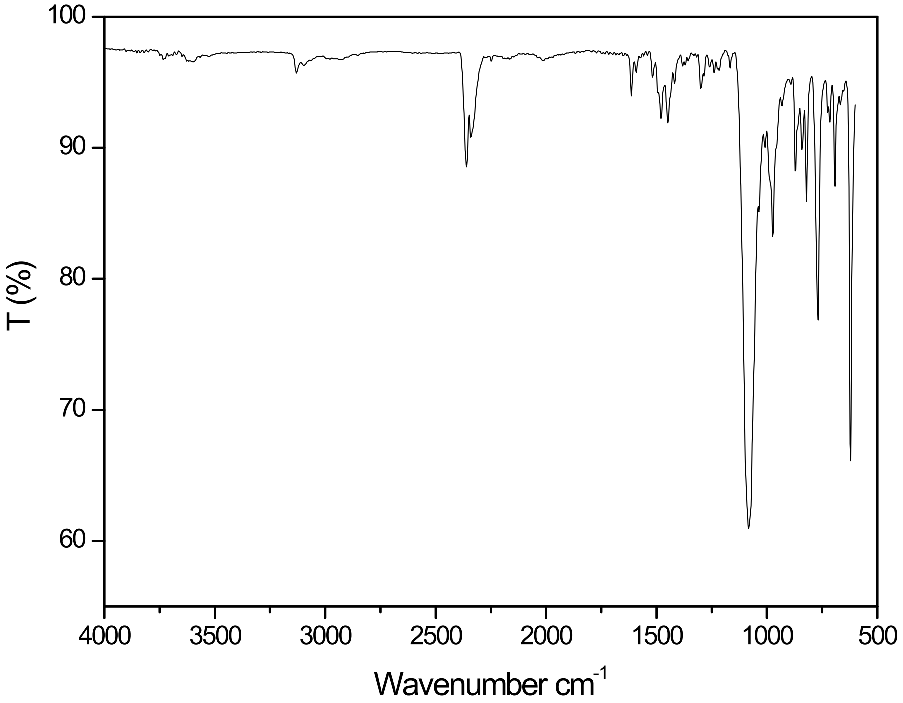


Fig. S3. IR (ZnSe/diamond ATR) spectrum of complex **3**.

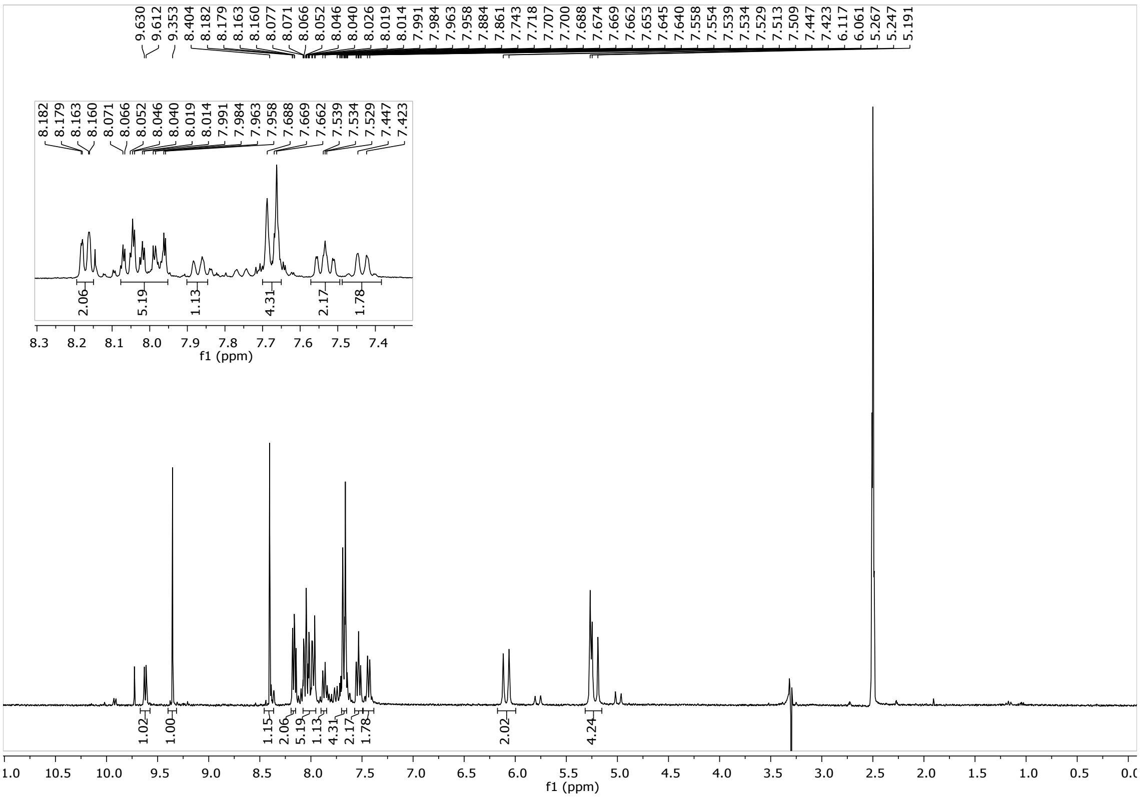


Figure S4. ^{1}H NMR (300 MHz, DMSO-d^6) spectrum of complex **1**.

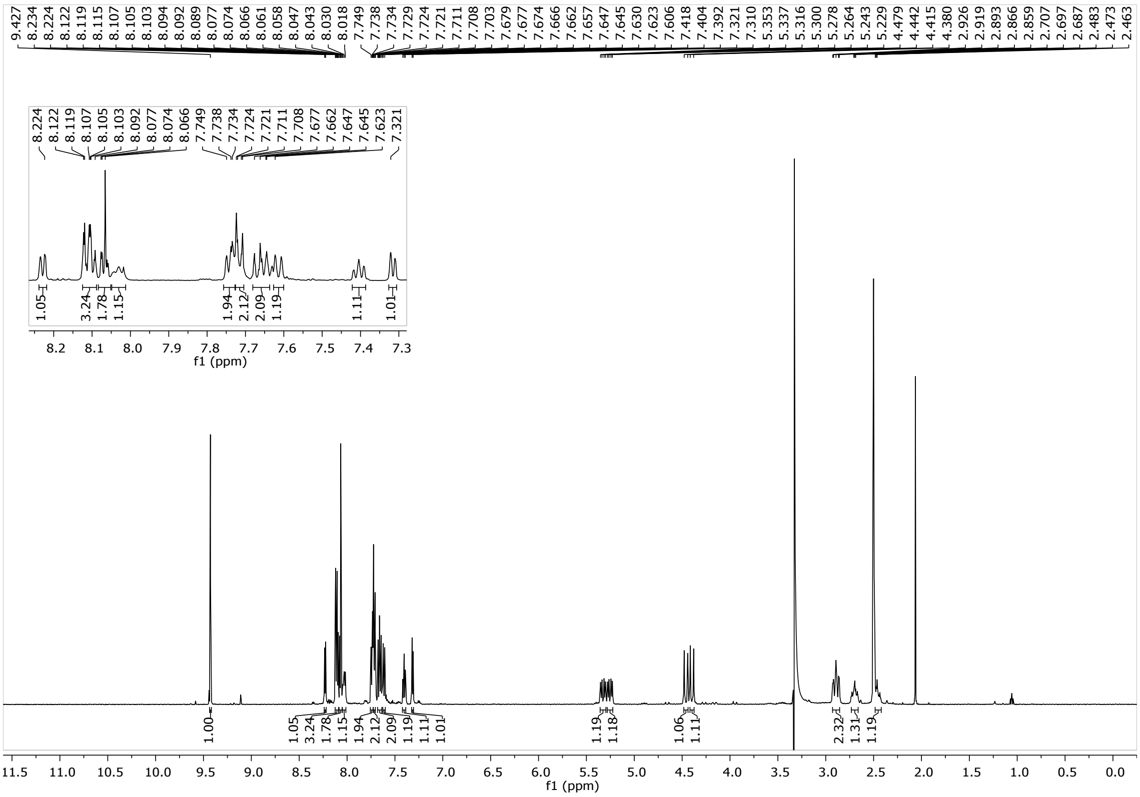


Figure S5. ^{1}H NMR (500 MHz, DMSO-d^6) spectrum of complex **2**.

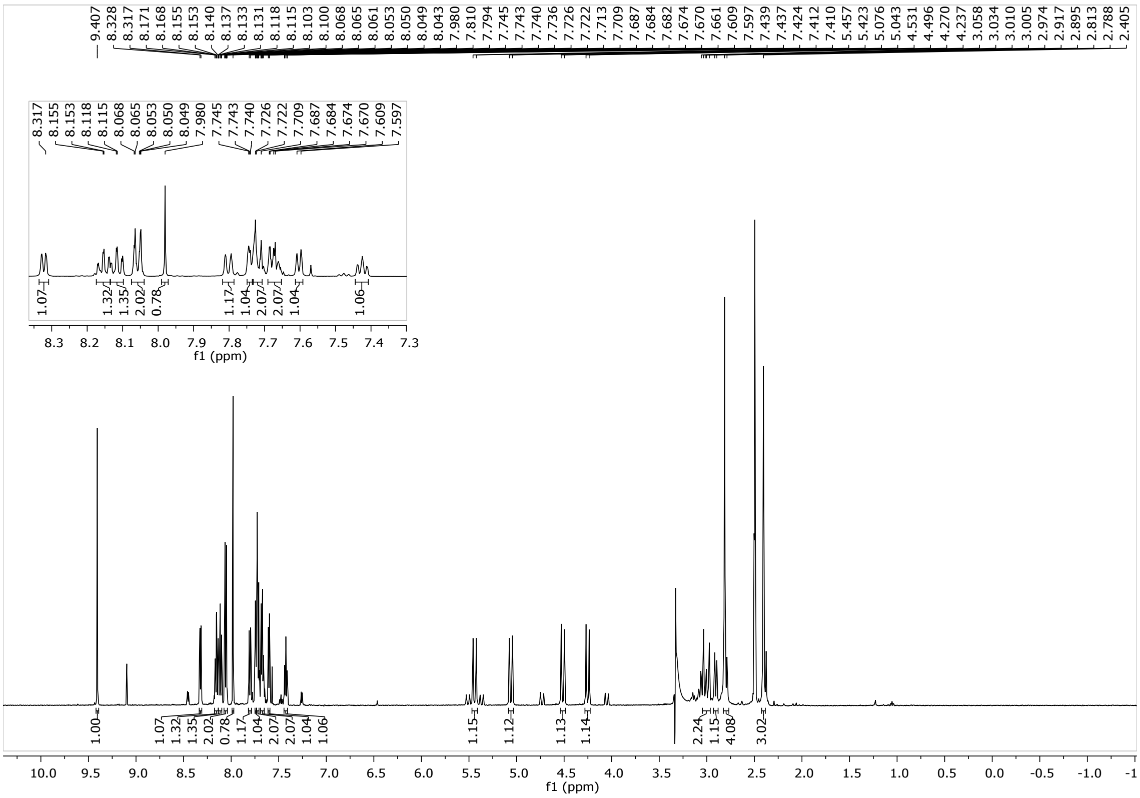


Figure S6. ^{1}H NMR (500 MHz, DMSO-d^6) spectrum of complex **3**.

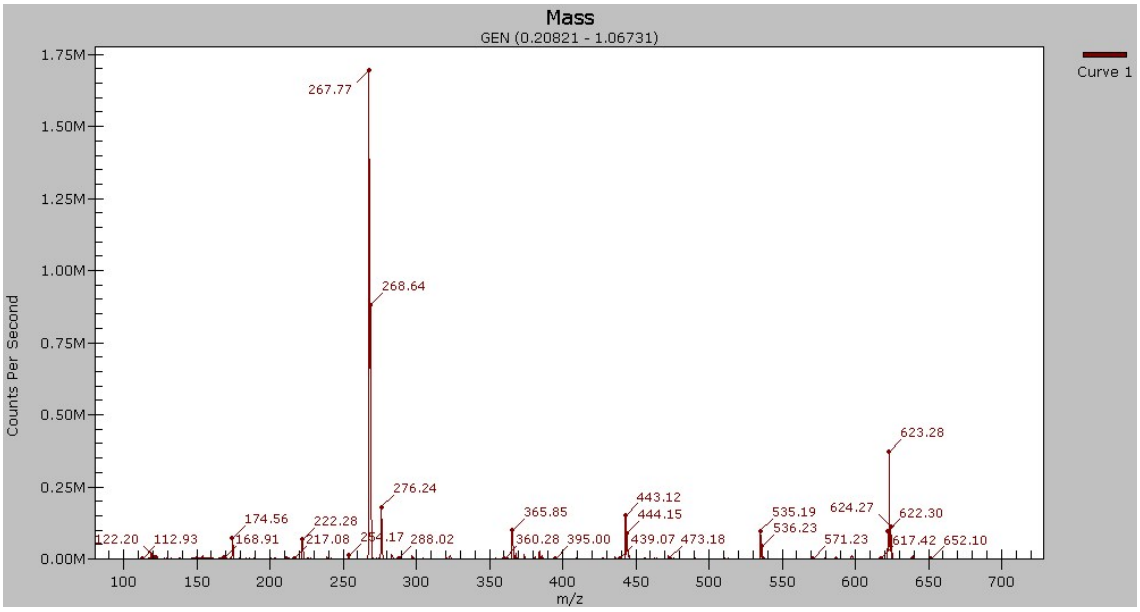


Figure S7. ESI-MS spectrum of complex **1** (MeOH).

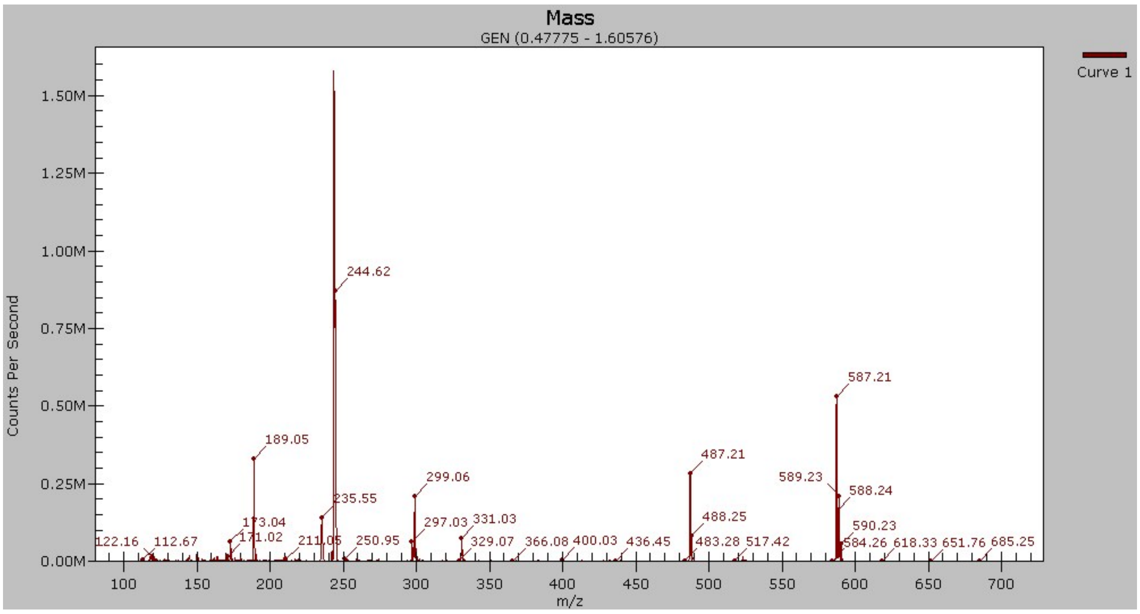


Figure S8. ESI-MS spectrum of complex **2** (MeOH).

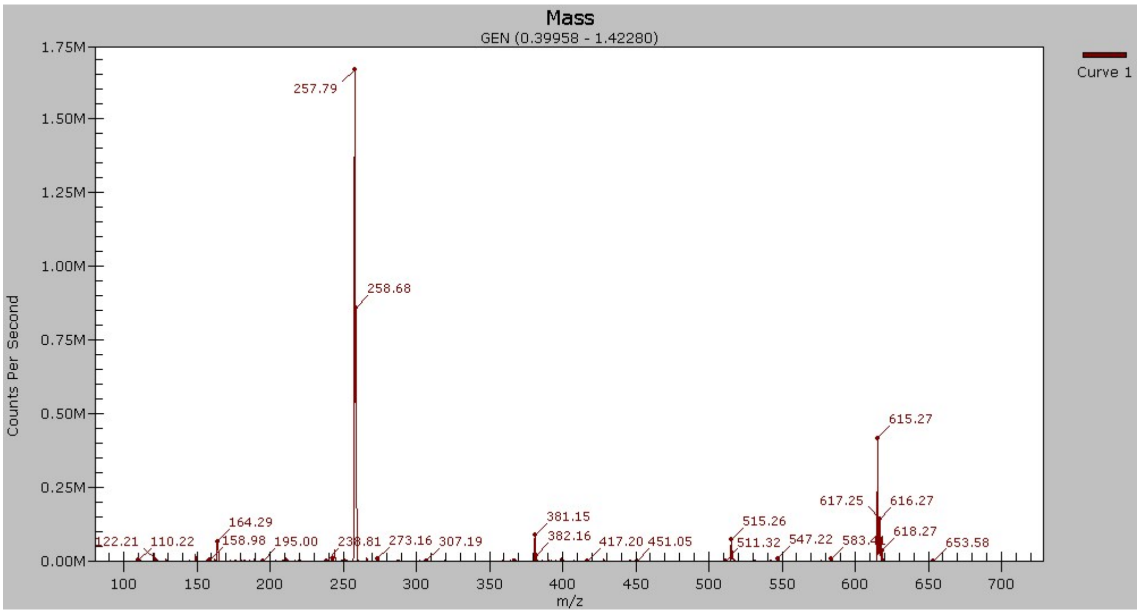


Figure S9. ESI-MS spectrum of complex **3** (MeOH).

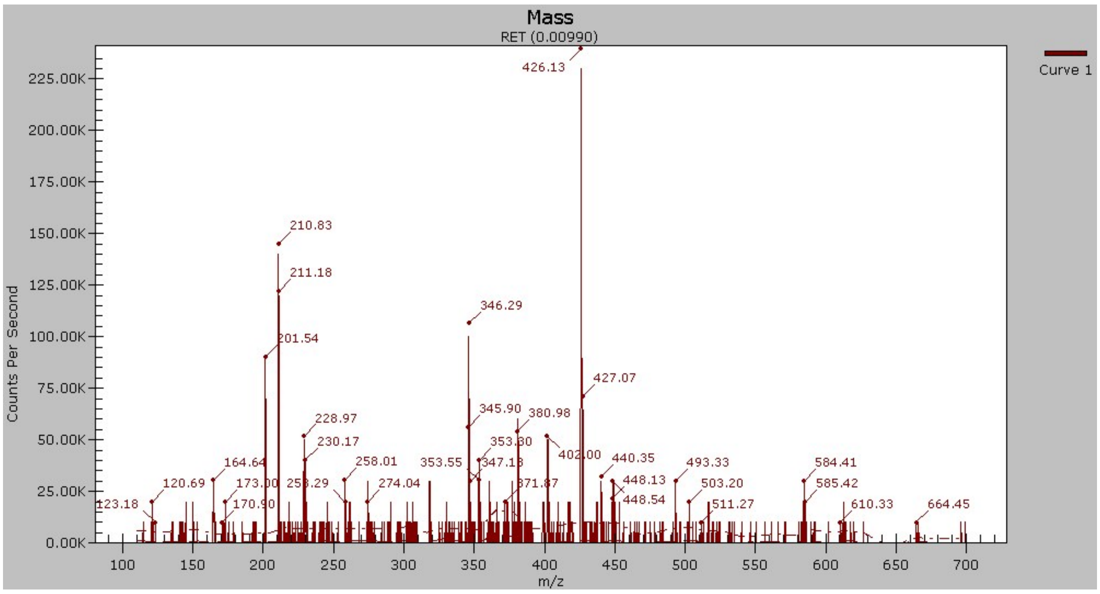


Figure S10. ESI-MS spectrum after reaction of complex **3** with sodium ascorbate (1:10) in MeOH.

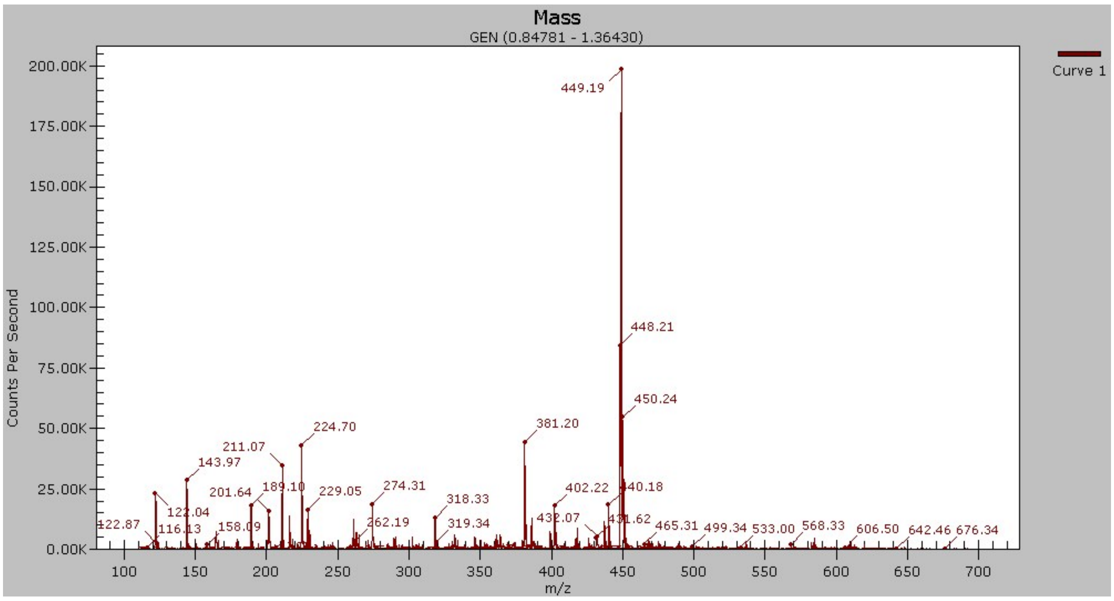


Figure S11. ESI-MS spectrum after reaction of complex **3** with sodium ascorbate (1:10) and cysteine in MeOH, followed by addition of cysteine (1:10).

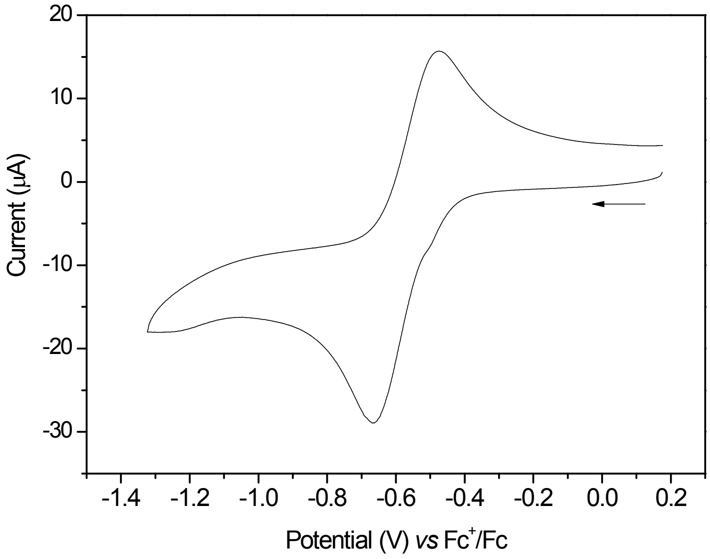


Figure S12. Cyclic voltammogram of complex **1** in acetonitrile (1 x 10^{-3} mol L^{-1}) with 0.1 mol L^{-1} of $TBAClO_4$, at 0.1 V s^{-1}, using glassy carbon, Ag/AgCl(organic, MeCN/$TBAClO_4$ 0.1 mol L^{-1}) and a Pt wire as working, reference and auxiliary electrodes, respectively. Ferrocene was used as internal reference.

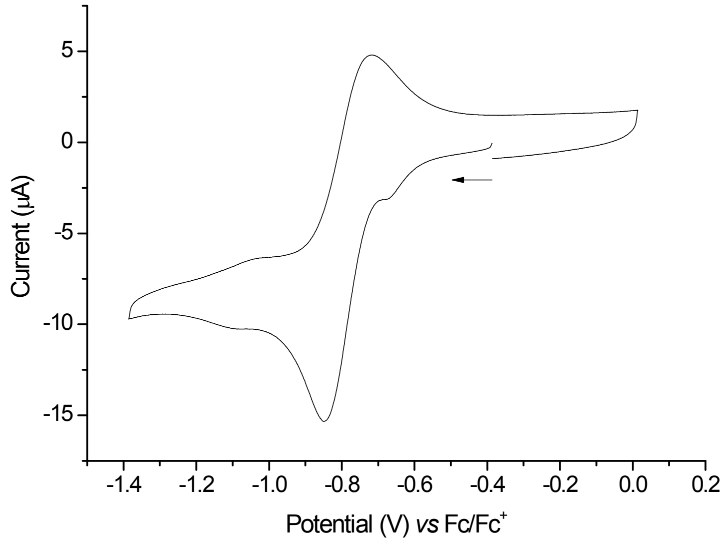


Figure S13. Cyclic voltammogram of complex **2** in acetonitrile (1 x 10^{-3} mol L^{-1}) with 0.1 mol L^{-1} of $TBAClO_4$, at 0.1 V s^{-1}, using glassy carbon, Ag/AgCl(organic, MeCN/$TBAClO_4$ 0.1 mol L^{-1}) and a Pt wire as working, reference and auxiliary electrodes, respectively. Ferrocene was used as internal reference.

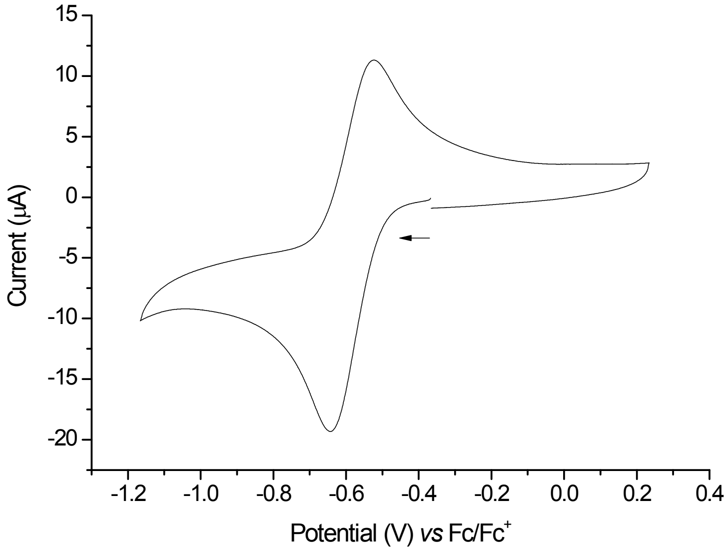


Figure S14. Cyclic voltammogram of complex **3** in acetonitrile (1 x 10^{-3} mol L^{-1}) with 0.1 mol L^{-1} of $TBAClO_4$, at 0.1 V s^{-1}, using glassy carbon, Ag/AgCl(organic, MeCN/$TBAClO_4$ 0.1 mol L^{-1}) and a Pt wire as working, reference and auxiliary electrodes, respectively. Ferrocene was used as internal reference.

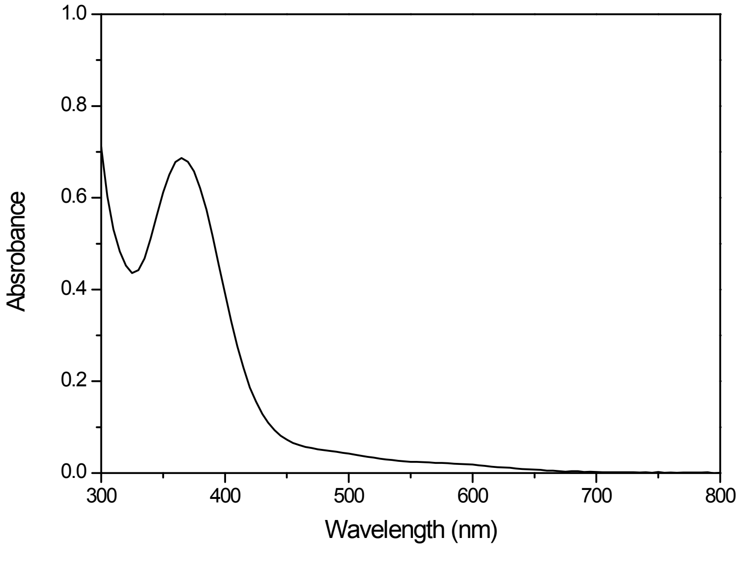


Figure S15. UV–Visible spectrum of complex **1** in acetonitrile (1.3 x 10^{-4} mol.L^{-1}).

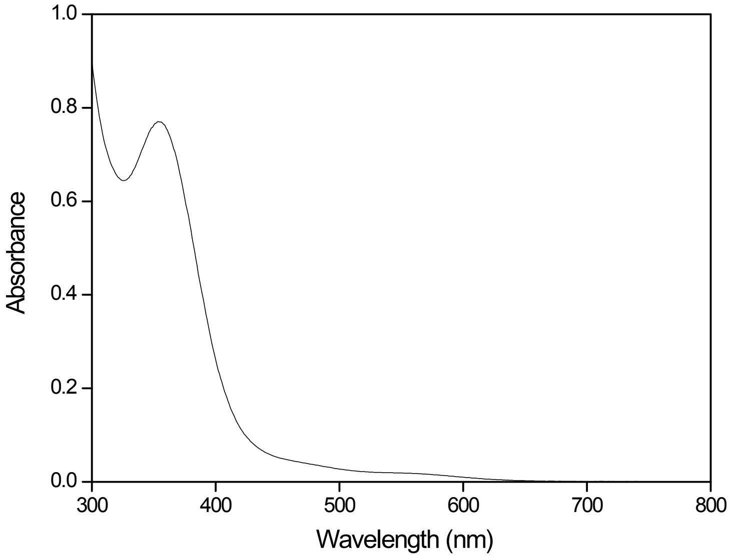


Figure S16. UV-Visible spectrum of complex **2** in acetonitrile (1.2 x 10^{-4} mol L^{-1}).

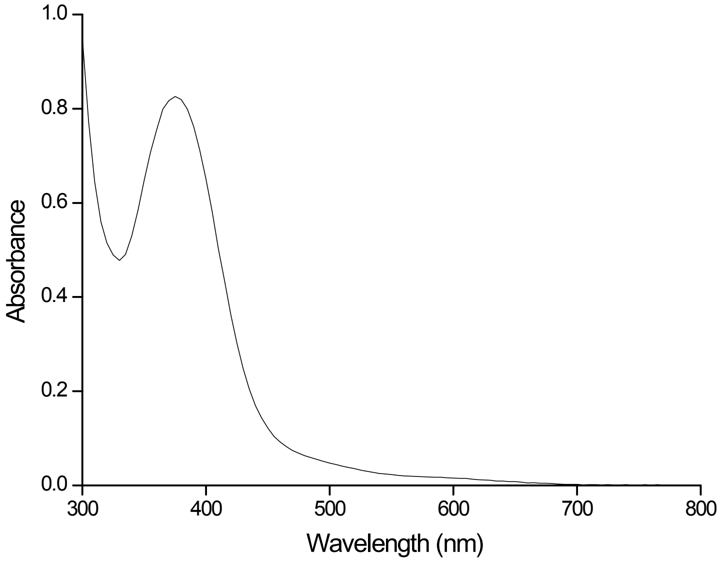


Figure S17. UV-Visible spectrum of complex **3** in acetonitrile (1.3 x 10^{-4} mol L^{-1}).

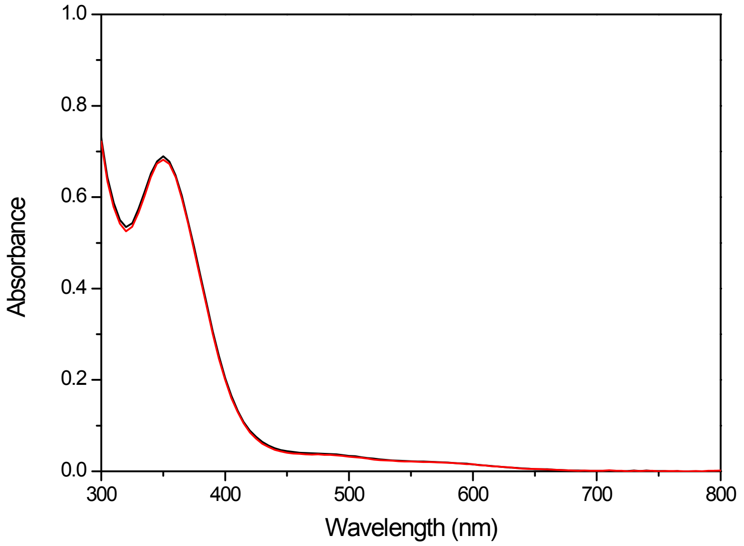


Figure S18. UV–Visible spectra of complex **1** in phosphate buffer / DMSO 1 % at pH 7.0. Spectra measured from freshly prepared solution and after 24 h at 37 ^{o}C.

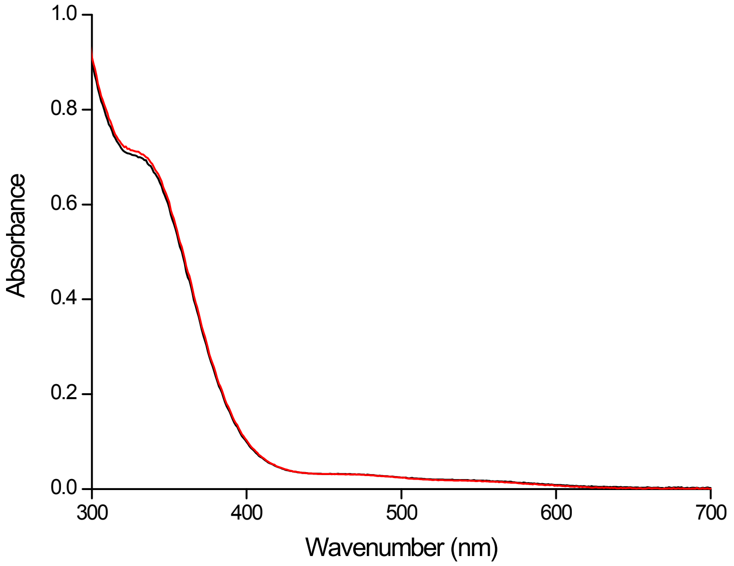


Figure S19. UV–Visible spectra of complex **2** in phosphate buffer / DMSO 1 % at pH 7.0. Spectra measured from freshly prepared solution and after 24 h at 37 ^{o}C.

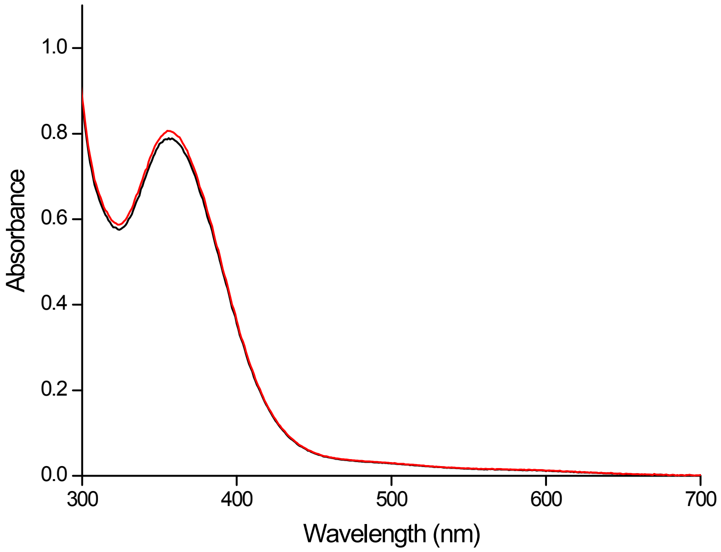


Figure S20. UV–Visible spectra of complex **3** in phosphate buffer / DMSO 1 % at pH 7.0 and 37 °C. Spectra measured from freshly prepared solution and after 24 h at 37 °C.

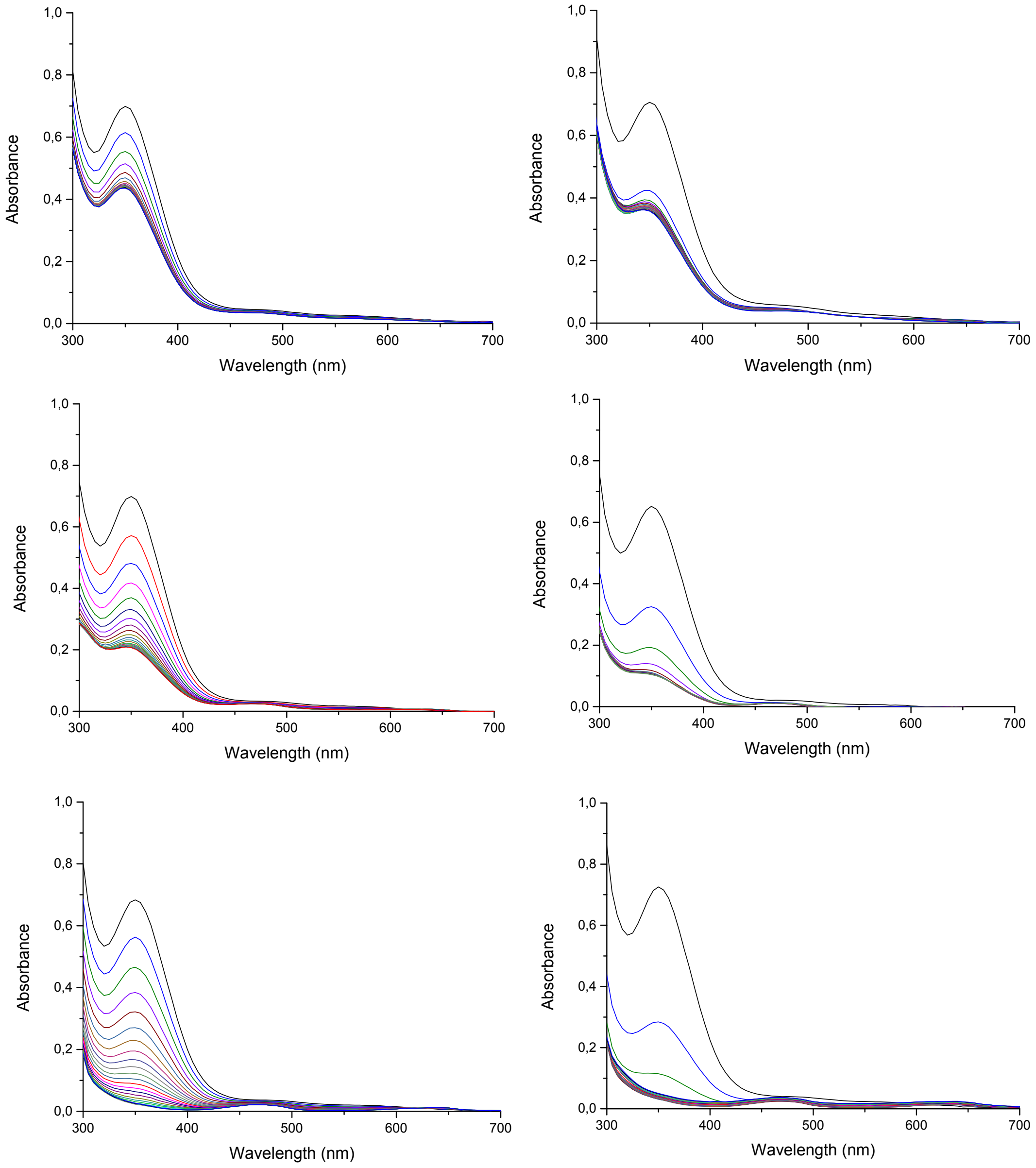


Figure S21. UV-Visible spectra of complex **1** after reaction with ascorbic acid (1:1) in phosphate buffer / DMSO 1 % at pH 7.0, saturated with O_2 (top), air (middle) and argon (bottom), at 25 ^{O}C (left) and 37 ^{o}C (right).

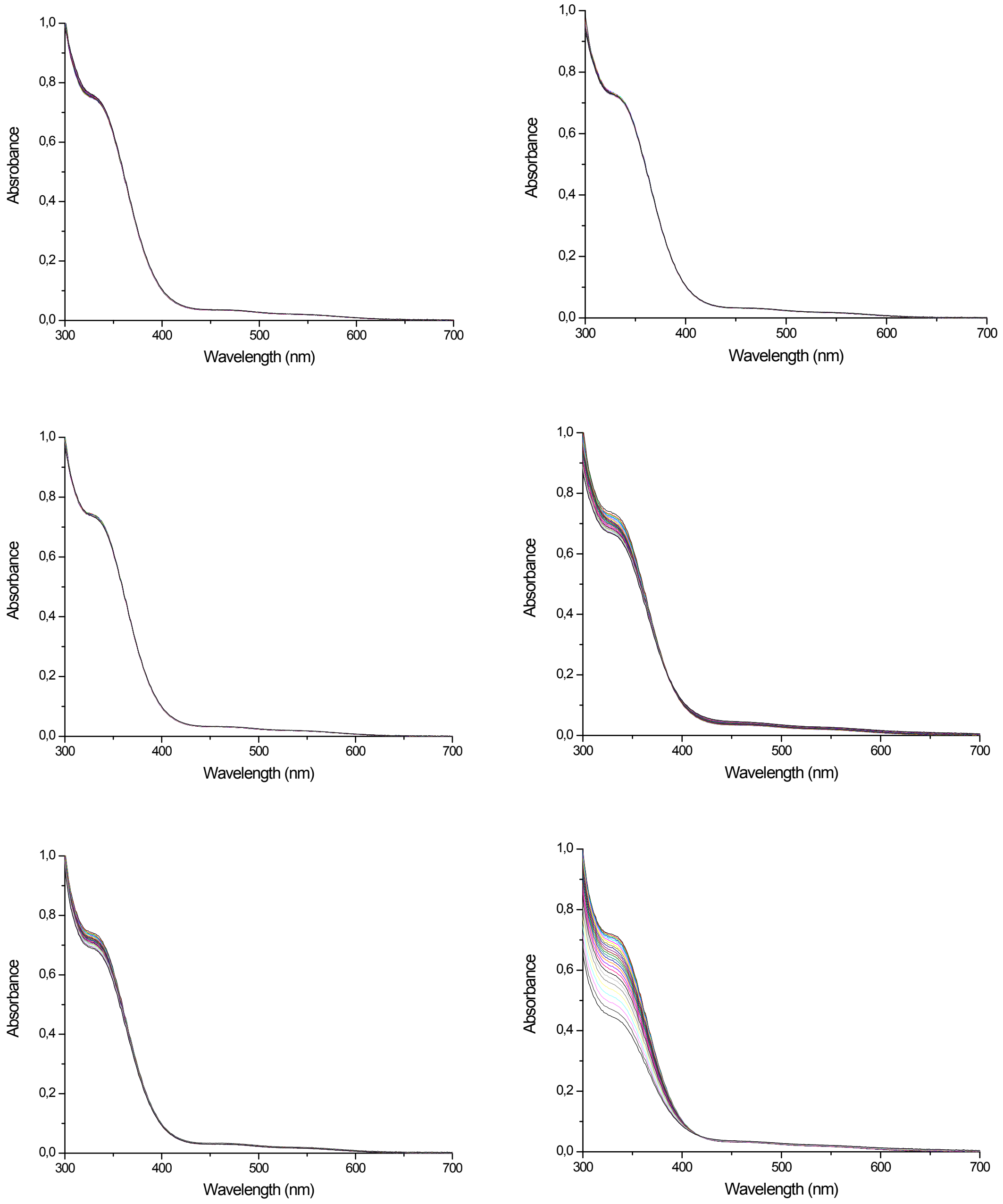


Figure S22. UV-Visible spectra of complex **2** after reaction with ascorbic acid (1:1) in phosphate buffer / DMSO 1 % at pH 7.0, saturated with O_2 (top), air (middle) and argon (bottom), at 25 ^{O}C (left) and 37 ^{o}C (right).

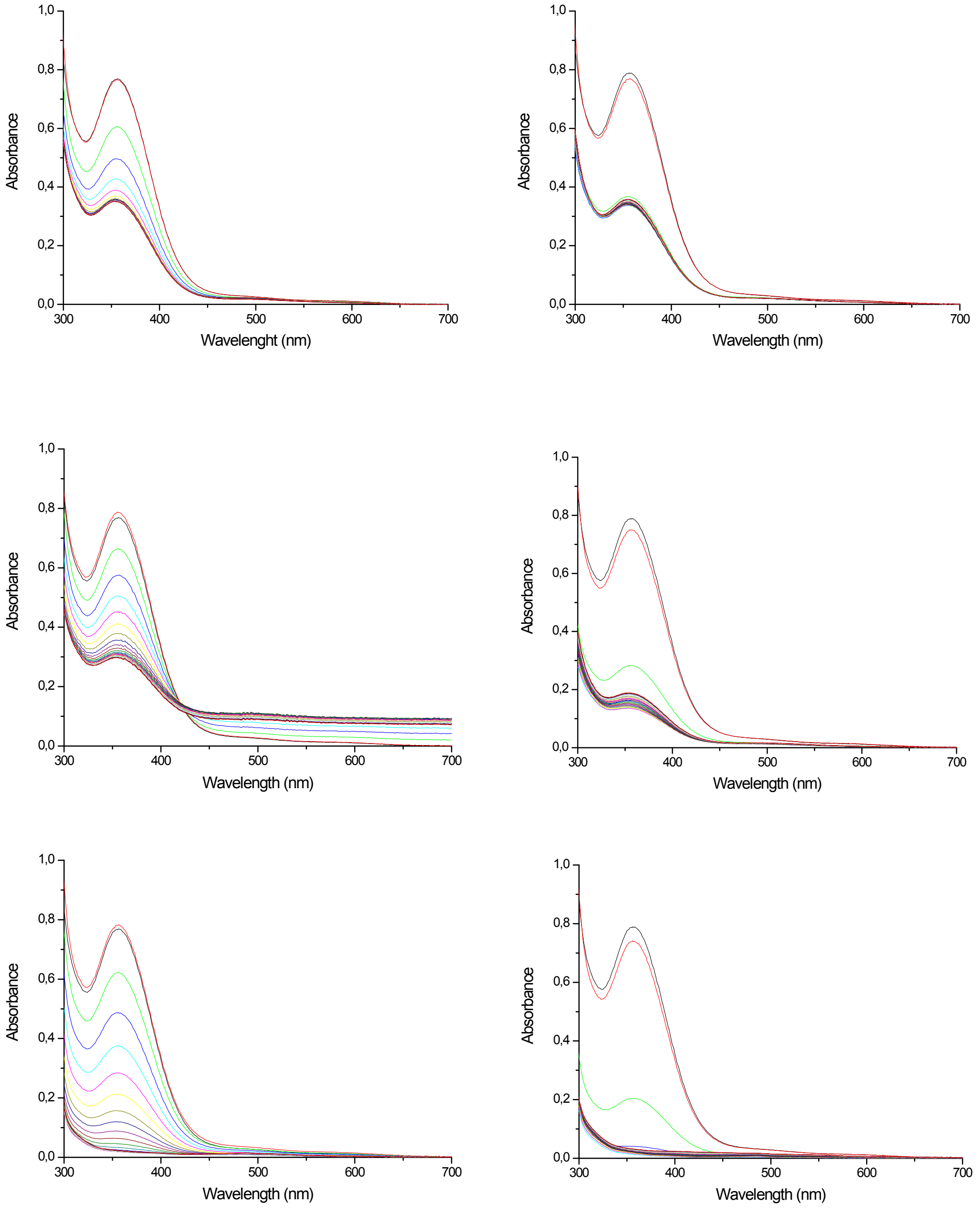


Figure S23. UV-Visible spectra of complex **3** after reaction with ascorbic acid (1:1) in phosphate buffer / DMSO 1 % at pH 7.0, saturated with O_2 (top), air (middle) and argon (bottom), at 25 ^{O}C (left) and 37 ^{o}C (right).

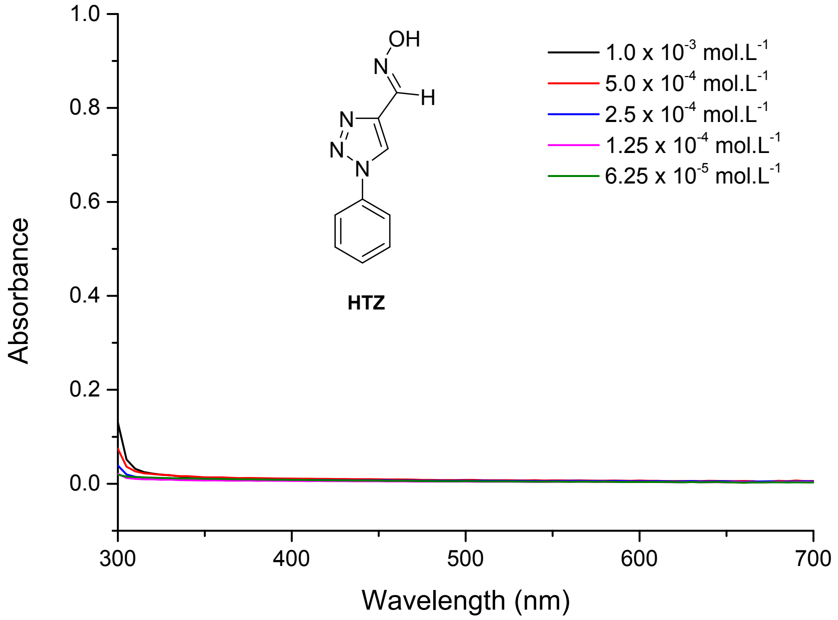


Figure S24. UV–Visible spectra of the ligand **HTz** in phosphate buffer / DMSO 1% at pH 7.0.

Table S1. Crystallographic data for complex **2**.

Empirical formula	C24.20 H26.80 Cl2 Co N8.60 O9.80
Formula weight	724.77
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 16.4893(16) Å b = 14.2294(17) Å c = 13.3861(12) Å β= 110.579(11)°.
Volume	2940.4(6) Å^3
Z	4
Density (calculated)	1.637 Mg/m^3
Absorption coefficient	0.836 mm^{-1}
F(000)	1486
Crystal size	0.65 x 0.12 x 0.08 mm^3
θ range for data collection	2.166 to 26.371°.
Index ranges	-18<=h<=20, -17<=k<=17, -16<=l<=16
Reflections collected	33056
Independent reflections	6021 [R(int) = 0.0713]
Completeness to θ = 25.242°	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6021 / 20 / 411
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0837, wR2 = 0.2074
R indices (all data)	R1 = 0.1087, wR2 = 0.2273
Extinction coefficient	n/a
Largest diff. peak and hole	0.848 and -0.826 e.Å^{-3}

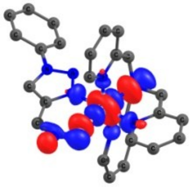
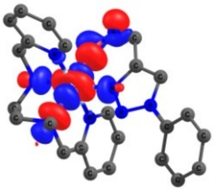
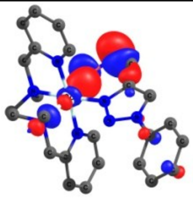
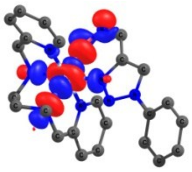
Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8170(3)	1432(4)	1237(4)	33(1)
C(2)	8259(4)	554(4)	871(4)	41(1)
C(3)	7574(4)	-46(5)	621(4)	45(1)
C(4)	6795(4)	231(5)	729(4)	41(1)
C(5)	6740(3)	1129(4)	1082(4)	34(1)
C(6)	5946(3)	1522(4)	1244(5)	39(1)
C(7)	5488(3)	2988(5)	154(4)	42(1)
C(8)	6105(4)	3003(5)	-465(4)	42(1)
C(9)	6956(4)	4452(5)	202(5)	44(2)
C(10)	6748(4)	4846(5)	1124(4)	40(1)
C(11)	6505(4)	5764(5)	1182(5)	52(2)
C(12)	6366(5)	6078(5)	2083(5)	55(2)
C(13)	6453(4)	5448(5)	2899(5)	48(2)
C(14)	6701(4)	4545(5)	2816(4)	39(1)
N(8)	7888(3)	2545(3)	3999(3)	32(1)
C(15)	8636(3)	2861(4)	4075(4)	34(1)
C(16)	8903(3)	3251(4)	3231(4)	30(1)
C(17)	9697(4)	3597(4)	3282(4)	38(1)
C(18)	10164(4)	4396(5)	1893(5)	45(2)
C(19)	10957(4)	4006(6)	2020(5)	54(2)
C(20)	11533(5)	4517(7)	1666(7)	70(2)
C(21)	11276(6)	5395(7)	1191(6)	72(3)
C(22)	10481(6)	5751(6)	1071(6)	65(2)
C(23)	9905(5)	5270(5)	1427(5)	53(2)
N(1)	7424(3)	1721(3)	1334(3)	30(1)
N(2)	5969(3)	2562(4)	1226(3)	35(1)
N(3)	6947(3)	3417(4)	225(3)	35(1)
N(4)	6839(3)	4235(3)	1936(3)	33(1)
N(5)	8358(3)	3356(3)	2211(3)	30(1)
N(6)	8757(3)	3747(3)	1620(3)	34(1)
N(7)	9568(3)	3891(3)	2279(4)	37(1)
O(1)	7214(2)	2545(3)	3064(3)	33(1)
Co(1)	7175(1)	2981(1)	1706(1)	28(1)
Cl(1)	4488(1)	3916(1)	2619(1)	49(1)
O(2)	4980(4)	4294(4)	3637(4)	71(2)
O(3A)	4583(6)	4446(6)	1731(7)	77(2)
O(4A)	4897(4)	3010(5)	2539(6)	48(2)
O(5A)	3620(7)	3783(8)	2423(9)	89(3)
O(3B)	3967(16)	4739(17)	2160(20)	97(7)
O(4B)	4794(18)	3460(20)	2050(20)	114(8)
O(5B)	3693(10)	3409(12)	2777(14)	49(4)
Cl(2A)	1142(2)	1344(3)	1548(3)	45(1)
O(6A)	1710(5)	2004(5)	2281(6)	64(3)
O(7A)	248(3)	1590(8)	1334(10)	76(4)
O(8A)	1310(6)	426(4)	2034(7)	61(3)
O(9A)	1323(7)	1333(8)	570(5)	77(4)
Cl(2B)	818(3)	1180(4)	1275(4)	69(2)
O(6B)	308(7)	433(7)	624(9)	104(4)
O(7B)	248(6)	1790(7)	1582(9)	71(4)
O(8B)	1457(7)	784(10)	2215(8)	138(7)
O(9B)	1215(7)	1722(7)	659(8)	76(3)
N(9)	6292(9)	7083(9)	4605(12)	74(3)
C(24)	6953(15)	7410(16)	4821(18)	109(6)
C(25)	7875(9)	7969(10)	5310(13)	69(3)
OW1	7408(14)	7882(14)	4554(17)	103(6)
OW2	6309(13)	6884(14)	5160(18)	99(6)

Table S3. Selected Bond distances [Å] and angles [°] for **2**.

N(1)-Co(1)	1.942(5)
N(2)-Co(1)	1.955(4)
N(3)-Co(1)	1.983(4)
N(4)-Co(1)	1.926(5)
N(5)-Co(1)	1.904(4)
O(1)-Co(1)	1.899(3)
O(1)-Co(1)-N(5)	93.78(17)
O(1)-Co(1)-N(4)	93.69(17)
N(5)-Co(1)-N(4)	90.02(19)
O(1)-Co(1)-N(1)	90.29(17)
N(5)-Co(1)-N(1)	93.80(18)
N(4)-Co(1)-N(1)	174.30(18)
O(1)-Co(1)-N(2)	84.51(17)
N(5)-Co(1)-N(2)	178.0(2)
N(4)-Co(1)-N(2)	91.1(2)
N(1)-Co(1)-N(2)	85.23(19)
O(1)-Co(1)-N(3)	171.64(17)
N(5)-Co(1)-N(3)	94.41(18)
N(4)-Co(1)-N(3)	84.61(19)
N(1)-Co(1)-N(3)	90.87(18)
N(2)-Co(1)-N(3)	87.34(19)

Table S4. Selected (main) vertical excitation energies and oscillator strengths calculated for compounds 1 – 3 at PBE0/def2-TZVP/COSMO level.

			One-electron excitation components[b]			
Comp.	Wavelength (nm)	*f*[a] (au)	*h*⁺	*e*⁻	Assignments[c]	%
1	319.8	0.134	 HOMO-1	 LUMO	LMCT $\pi_{(oxime)} \rightarrow Co^{3+}(d_z^2)$	55.4
2	315.4	0.075	 HOMO	 LUMO+3	LMCT $\pi_{(oxime)} \rightarrow Co^{3+}(d_z^2)$	40.5
3	323.0	0.122	 HOMO-1	 LUMO	LMCT $\pi_{(oxime)} \rightarrow Co^{3+}(d_z^2)$	49,2

[a] Oscillator strength. [b] Major contributions from one-electron excitations to the transitions, represented as hole-particle excitations ($h^+ \rightarrow e^-$). [c] The assignments were done based on the shape and spatial orientation of the orbitals.

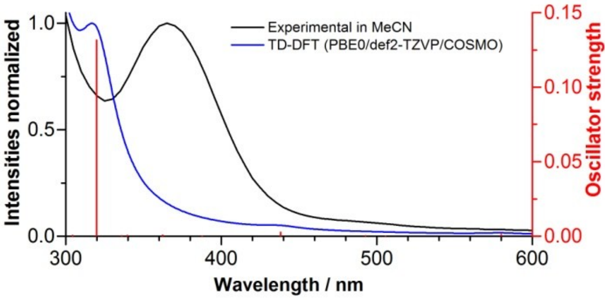


Figure S25. Normalized spectra of complex **1**: experimental in MeCN and TD-DFT at PBE0/def2-TZVP/COSMO level.

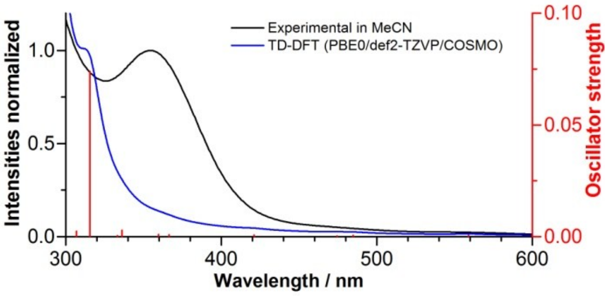


Figure S26. Normalized spectra of complex **2**: experimental in MeCN and TD-DFT at PBE0/def2-TZVP/COSMO level.

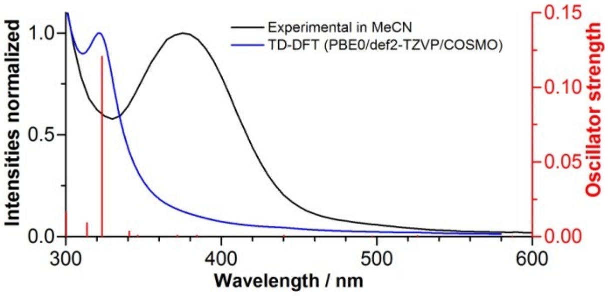


Figure S27. Normalized spectra of complex **3**: experimental in MeCN and TD-DFT at PBE0/def2-TZVP/COSMO level.

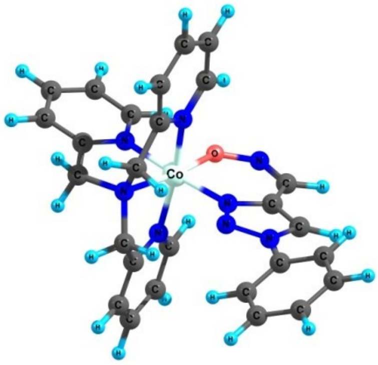


Figure S28. Optimized structure of complex **1** at RI-PBE/def2-TZVP/COSMO level.

Table S5. Xyz coordinates of complex **1**.

Co	7.122441635	2.929847411	14.197182286
N	5.254261220	2.983431622	14.736561234
O	7.373472024	1.061835044	14.583474515
C	8.023485423	2.483850640	16.967948833
N	8.925710048	3.267461027	13.562747673
N	6.729684505	4.788566417	13.499870974
N	7.811991615	4.625912224	16.471926406
N	6.655650075	2.348697994	12.372148114
C	4.728909465	4.236888456	14.759289366
N	8.239808962	4.510803629	17.736485484
N	7.676794805	3.398836379	16.009313271
C	9.152708348	4.565121076	13.233230588

C	11.139902970	2.688230785	12.881422495
H	11.897008122	1.915035921	12.756926904
C	5.683956202	5.345290603	14.407773606
H	6.180451756	5.712074739	15.315717370
H	5.163772500	6.194734724	13.941792718
C	8.029807566	5.521378864	13.528560075
H	8.024959916	6.366430732	12.825526864
H	8.168001250	5.926247227	14.540597205
C	6.330457898	3.337336753	11.514367123
N	7.712636069	0.435447747	15.687932840
C	9.890599416	2.345477637	13.386990122
H	9.635152463	1.321091394	13.656083810
C	4.487337345	1.924537117	15.054933705
H	4.966050597	0.947520828	14.999448209
C	6.181055067	4.702047646	12.104840185
H	5.109628246	4.949204557	12.135723666
H	6.655193312	5.463801313	11.470438775
C	8.489344443	5.676627340	18.527734437
C	6.084354678	3.083843193	10.165311521
H	5.832406652	3.910809818	9.501041173
C	6.730729041	1.078860746	11.922986465
H	7.000820570	0.326051272	12.661755015
C	2.604905226	3.357288925	15.462320675
H	1.562452932	3.505707211	15.745480517
C	8.386186676	3.210877207	18.091909024
H	8.699871461	2.894052784	19.079343443
C	6.482169365	0.756774906	10.594725540
H	6.551965131	-0.283044887	10.277606576
C	3.400106712	4.449525831	15.114524144
H	2.998375900	5.462978138	15.112204737
C	7.706743910	6.818373044	18.336803428
H	6.902474241	6.818774259	17.601935669
C	8.976017349	7.926673400	20.078435707
H	9.166660229	8.810854823	20.688248469
C	7.961162054	7.946516255	19.116659700
H	7.353607124	8.841495814	18.976958022
C	3.156390310	2.076754326	15.429716256
H	2.568666004	1.195663372	15.684383956
C	8.007290504	1.057140611	16.788732451
H	8.277531434	0.421096894	17.631643298
C	9.512164824	5.640949116	19.479279934
H	10.131260742	4.751127198	19.597797573
C	10.379131900	4.964550668	12.708183026
H	10.534041251	6.009643364	12.439596333
C	11.387500420	4.016779063	12.535224122
H	12.354132004	4.312696665	12.126609007
C	6.160372257	1.775583754	9.696764678
H	5.972349445	1.554343053	8.645701506
C	9.746428755	6.774383015	20.258747234
H	10.544339460	6.756384453	21.002068158

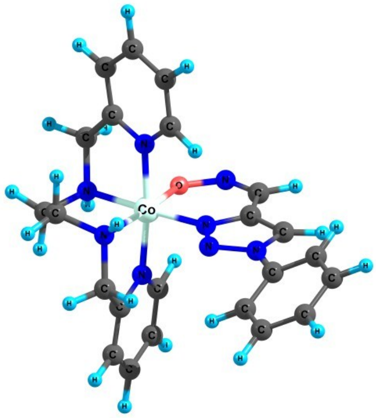


Figure S29. Optimized structure of complex 2 at RI-PBE/def2-TZVP/COSMO level.

Table S6. Xyz coordinates of complex **2**.

C	12.755000237	2.081627636	1.456977049
H	13.543704084	2.807524675	1.644350560
C	13.059638219	0.781757521	1.072866076
H	14.103251886	0.487548133	0.969279965
C	12.017883032	-0.111946413	0.822741607
H	12.225908247	-1.137126683	0.515224662
C	10.703778523	0.329529557	0.959412191
H	9.861013464	-0.332212344	0.759023915
C	10.463257599	1.643639491	1.354291111
C	9.090345843	2.198311992	1.566279807
H	8.369129415	1.784549785	0.847149393
H	8.745605796	1.928596975	2.574665109
C	8.864062701	4.258180972	0.131845418
H	8.427328874	5.255053227	0.276644151
H	8.128990546	3.648749193	-0.412387455
C	10.173115493	4.345332966	-0.626194759
H	10.556096905	3.347915608	-0.876644944
H	10.046410622	4.900644782	-1.567050834
C	11.099082090	6.494430132	0.268992524
H	10.648924058	6.873236048	-0.660423841
H	12.125381996	6.886270052	0.313494283
C	10.339327832	6.973416481	1.469826817
C	9.848126743	8.272939753	1.584287379
H	9.982741096	8.971418676	0.758063909
C	9.191412869	8.653338762	2.752102727
H	8.801505762	9.666032573	2.858820434
C	9.032904544	7.718149121	3.776049007
H	8.519757431	7.968343251	4.703742447
C	9.536598867	6.435450446	3.601325720
H	9.426606270	5.662448995	4.360189792
N	11.059771289	3.498759769	4.931816288
C	12.282333736	3.928133212	5.049507670
C	13.060956841	4.587652929	4.031685958
C	14.345775130	5.110391465	4.091116654
H	15.057678683	5.172766967	4.905430708
C	15.760554113	6.281649738	2.384711012

C	17.000226177	5.906687898	2.910005495
H	17.074259610	5.105763300	3.646290009
C	18.148349316	6.557162833	2.456450388
H	19.120134641	6.269214686	2.859220830
C	18.055763408	7.557617885	1.484698474
H	18.957470042	8.059732852	1.131438845
C	16.807595502	7.914712098	0.965055371
H	16.730155190	8.698659055	0.210684319
C	15.648993660	7.281979240	1.415215349
H	14.670744438	7.569193986	1.031512350
N	11.481915625	2.504427132	1.604519870
N	9.121521474	3.685105625	1.487297032
N	11.184057455	5.008633249	0.246989320
N	10.181640684	6.075052058	2.471723099
N	12.615183611	4.825817949	2.761375826
N	13.526370775	5.450784958	2.041731666
N	14.580236663	5.624979255	2.856684953
O	10.352826884	3.613192258	3.828757205
Co	10.900215529	4.299248367	2.117982314
H	12.118864602	4.755228526	-0.084897371
H	8.406980930	4.041341932	2.128683271
H	12.737532949	3.769959421	6.027368872

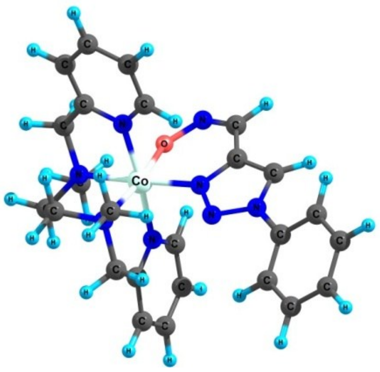


Figure S30. Optimized structure of complex 3 at RI-PBE/def2-TZVP/COSMO level.

Table S7. Xyz coordinates of complex **3**.

C	12.564553050	1.910629862	1.741637335
H	13.385403274	2.581652721	1.985374376
C	12.806706352	0.594312305	1.372410306
H	13.832626635	0.229756256	1.340950002
C	11.726586962	-0.224466303	1.039205492
H	11.885419647	-1.258896852	0.733348800
C	10.439420521	0.302231368	1.100149737
H	9.568219102	-0.302228615	0.847304584
C	10.261915255	1.627002000	1.498431011
C	8.907886412	2.226522892	1.694836802
H	8.188707422	1.861199670	0.946656185
H	8.541726244	1.901649462	2.679863490
C	8.691021299	4.306621620	0.346989128
H	8.383004002	5.351186797	0.487317097

H	7.857991477	3.784560679	-0.148232616
C	9.943244639	4.221869115	-0.482492258
H	10.208453191	3.176575391	-0.688290452
H	9.798477881	4.718906171	-1.454676760
C	11.019847606	6.336544197	0.226771200
H	10.517339716	6.686508697	-0.688291725
H	12.050930968	6.717229552	0.187747146
C	10.374088906	6.907564884	1.452570502
C	9.965295270	8.240022257	1.521842718
H	10.041296776	8.870391348	0.635590394
C	9.476536916	8.742110740	2.724897869
H	9.156138434	9.781827950	2.797253041
C	9.405359728	7.896379313	3.833788065
H	9.035565152	8.246411764	4.796699877
C	9.806938911	6.574453172	3.697992411
H	9.749296239	5.865181429	4.522146476
N	11.058658874	3.312726527	5.006377529
C	12.323534232	3.606300342	5.078646920
C	13.063125001	4.375388646	4.111286102
C	14.314969516	4.962919682	4.223658414
H	15.034836738	4.966493815	5.033344684
C	15.612542126	6.447637580	2.675282295
C	16.886648516	6.083791537	3.119300773
H	17.029896572	5.192877604	3.731560011
C	17.979197714	6.866194267	2.743381269
H	18.977762440	6.588009160	3.082501959
C	17.797864663	7.986772693	1.927740721
H	18.656531678	8.592375542	1.634594413
C	16.516199845	8.331799367	1.487401711
H	16.369550459	9.208985086	0.855984670
C	15.412035342	7.566504213	1.862195983
H	14.407253750	7.840086345	1.541976111
N	11.315115810	2.420750268	1.804919666
N	8.927815789	3.724773681	1.703899463
N	11.096723739	4.842497841	0.241335762
N	10.275075741	6.091056785	2.526816142
N	12.577824641	4.742714341	2.883470119
N	13.430227353	5.525976359	2.253925987
N	14.488234166	5.655659098	3.069395050
O	10.301393430	3.646691231	3.987219208
Co	10.833562348	4.259482955	2.238153326
C	12.335586533	4.432093172	-0.476205370
C	7.828024535	4.174993679	2.601216525
H	12.827460535	3.289781255	5.991806596
H	7.731063308	5.263767331	2.557528400
H	6.882257698	3.723565262	2.264303081
H	8.042862159	3.855927056	3.625922113
H	12.305240550	4.821477393	-1.506162418
H	12.394203199	3.340017328	-0.519890214
H	13.212723016	4.834202715	0.038322766