Information (SI) for the manuscript:

High-temperature spin crossover in a mononuclear six-coordinate cobalt(II) complex

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Experimental Section

Materials. Cobat(II) chloride hexahydrate, potassium tricyanomethanide and the methanol and acetonitrile solvents were purchased from commercial sources and used as received. Tppz was prepared by following a previously reported procedure.[1]

Synthesis. An aqueous solution (5 cm^3) of Ktcm (0.26 g, 2 mmol) was added dropwise to another MeOH:MeCN (1:2 v/v) mixed solvent (15 cm^3) containing $CoCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) and tppz (0.38 g, 1 mmol) under continuous stirring at room temperature for 12 hours. The resulting deep-brown solution was allowed to evaporate in a hood at room temperature. X-ray quality crystals of **1** were grown from this solution after a week. They were collected by filtration and air-dried. Yield ca. 70% (based on tppz). *Anal*. Calc. for $C_{56}H_{32}N_{18}Co$ (**1**): C, 66.21; H, 3.17; N, 24.82%. Found: C, 66.82; H, 3.24; N, 24.97%. IR (KBr, cm^{-1}): 2156 $\nu(C{\equiv}N_{tcm})$ (vs); 1595(m), 1567(sh), 1529(w)) ν(C=N) and ν(C=C). UV-Vis-NIR (solid, nm): 1401, 697, 566, 507, 393, 344 and 264.

Physical techniques. Elemental analysis (C, H, N) of **1** were obtained using a CHNS/O Series II/2400, Perkin Elmer analyser. IR spectra of **1**, Ktcm and tppz were recorded on *Nicolet iS5* spectrometer in the wavelength range 4000-400 cm^{-1} with the samples as KBr pellets. Powder X-ray diffraction (PXRD) measurements were performed on a polycrystalline sample of **1** with a PANalytical *Empyrean* X-ray diffractometer using Cu−Kα radiation (λ = 1.5418Å), in which the X-ray tube was operated at 40 kV and 30 mA ranging from 5 to 80°.

X-ray crystallographic data collection and structure refinement. Crystallographic data of **1** were collected on a Gemini A Ultra diffractometer equipped with Atlas CCD detector and graphite monochromated Mo *K*α radiation (λ = 0.71073 Å) at room temperature. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction[2]. Lorentz, polarization and empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm were applied.[2] The structures were solved by the Direct methods and subsequently completed by the difference Fourier recycling. All the non-

hydrogen atoms were refined anisotropically using full-matrix, least-squares technique. The hydrogen atoms were treated as riding on their parent carbon atoms and assigned isotropic temperature factors equal 1.2 times the value of equivalent temperature factor of the parent atom. SHELXS97 and SHELXL97 programs[3] were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs.

Crystal data for $[Co(tppz)_2](tcm)_2$ (**1**): $C_{56}H_{32}N_{18}Co$, M = 1015.93, triclinic, space group $P(-1)$, a = 8.9397(2), b = 16.2020(4), c = 17.6187(6) Å, α = 78.960(3), β = 87.312(2), γ = 77.093(2)º, V = 2441.38(12) Å^3, Z = 2. Refinement of 676 parameters on 8628 independent reflections out of 22324 measured reflections (R_{int} = 0.0578) led to R_1/wR_2 = 0.0516/0.1340 [$I > 2\sigma(I)$], R_1/wR_2 = 0.0601/0.1416 (all data), $\Delta\rho_{min}$ = -0.601, $\Delta\rho_{max}$ = 1.098 e Å^{-3}.

Magnetic measurements. Variable-temperature magnetic susceptibility measurements on a polycrystalline sample of **1** were carried out on a MPMS2 SQUID magnetometer equipped with a 5.5 T magnet, operating at 0.5 T and 1.9-360 K. Magnetisation versus the magnetic field measurements were done at 2.0 K in the magnetic field range 0-5 T. The magnetic data were corrected for the diamagnetic contribution of the constituent atoms using Pascal's constants and also for the diamagnetism of the sample holder (a small plastic bag).

Spectroscopic measurements. The electronic spectra on a solid sample of **1** was carried out on *Nicolet Evolution 220* and *Nicolet iS50* spectrometers in the ranges 190 – 1100 and 700 – 1500 nm, respectively. X-band EPR spectra of both a powdered sample and a frozen dichloromethane solution of **1** were recorded at different temperatures with a Bruker ER 200 spectrometer equipped with a helium continuous-flow cryostat.

Table S1. Crystal data and structure refinement for $[Co(tppz)_2](tcm)_2$

Empirical formula	$C_{56}H_{32}CoN_{18}$
Formula weight	1015.93
Temperature [K]	293.0(2)
Wavelength [Å]	0.71073
Crystal system	triclinic
Space group	P-1
Unit cell dimensions [Å, °]	a = 8.9397(2)
	b = 16.2020(4)
	c = 17.6187(6) α = 78.960(3) β = 87.312(2) γ = 77.093(2)
Volume [Å ^{3}]	2441.38(12)
Z	2
Density (calculated) [Mg/m^3]	1.387
Absorption coefficient [mm^{-1}]	0.413
F(000)	1046
Crystal size [mm]	0.157 x 0.125 x 0.098
θ range for data collection [°]	3.50 to 25.05
Index ranges	$-10 \leq h \leq 10$ $-19 \leq k \leq 19$ $-20 \leq l \leq 20$
Reflections collected	22324
Independent reflections	8628 (R_{int}=0.0578)
Completeness to 2θ = 25.05° [%]	99.7
Max. and min. transmission	0.736 and 1.000
Data / restraints / parameters	8628 / 0 / 676
Goodness-of-fit on F^2	1.040
Final R indices [I>2σ(I)]	R1 = 0.0516 wR2 = 0.1340
R indices (all data)	R1 = 0.0601 wR2 = 0.1416
Largest diff. peak and hole[e Å $^{-3}$]	1.098 and -0.601

Table S2. Bond lengths [Å] and angles [°] for $[Co(tppz)_2](tcm)_2$

Bond lengths	Experimental	Bond angles	Experimental
Co(1)-N(1)	1.864(2)	N(1)-Co(1)-N(3)	81.69(8)
Co(1)-N(3)	1.977(2)	N(1)-Co(1)-N(5)	81.49(8)
Co(1)-N(5)	1.978(2)	N(1)-Co(1)-N(7)	179.56(8)
Co(1)-N(7)	1.936(2)	N(1)-Co(1)-N(9)	102.17(8)
Co(1)-N(9)	2.1581(19)	N(1)-Co(1)-N(11)	101.03(8)
Co(1)-N(11)	2.1605(19)	N(3)-Co(1)-N(5)	163.15(8)
C(1)-N(1)	1.345(3)	N(3)-Co(1)-N(9)	89.08(8)
C(4)-N(1)	1.344(3)	N(3)-Co(1)-N(11)	93.96(8)
C(2)-N(2)	1.334(3)	N(5)-Co(1)-N(9)	93.54(8)
C(3)-N(2)	1.335(3)	N(5)-Co(1)-N(11)	90.16(7)
C(5)-N(3)	1.363(3)	N(7)-Co(1)-N(3)	98.35(8)
C(9)-N(3)	1.344(3)	N(7)-Co(1)-N(5)	98.47(8)
C(10)-N(4)	1.342(3)	N(7)-Co(1)-N(9)	78.27(8)
C(14)-N(4)	1.331(3)	N(7)-Co(1)-N(11)	78.53(7)
C(20)-N(5)	1.367(3)	N(9)-Co(1)-N(11)	156.80(7)
C(24)-N(5)	1.342(3)	C(1)-N(1)-Co(1)	119.00(16)
C(15)-N(6)	1.342(3)	C(4)-N(1)-Co(1)	119.14(17)
C(19)-N(6)	1.338(4)	C(5)-N(3)-Co(1)	113.85(15)
C(25)-N(7)	1.344(3)	C(9)-N(3)-Co(1)	126.70(17)
C(28)-N(7)	1.344(3)	C(20)-N(5)-Co(1)	114.14(16)
C(26)-N(8)	1.335(3)	C(24)-N(5)-Co(1)	126.60(17)
C(27)-N(8)	1.332(3)	C(25)-N(7)-Co(1)	119.56(16)
C(29)-N(9)	1.346(3)	C(28)-N(7)-Co(1)	119.17(15)
C(33)-N(9)	1.344(3)	C(29)-N(9)-Co(1)	112.60(15)
C(34)-N(10)	1.344(3)	C(33)-N(9)-Co(1)	128.03(16)
C(38)-N(10)	1.339(3)	C(44)-N(11)-Co(1)	112.06(14)
C(44)-N(11)	1.356(3)	C(48)-N(11)-Co(1)	128.86(16)
C(48)-N(11)	1.340(3)	C(4)-N(1)-C(1)	121.9(2)
C(39)-N(12)	1.349(3)	C(2)-N(2)-C(3)	120.5(2)
C(43)-N(12)	1.335(3)	C(9)-N(3)-C(5)	118.8(2)
C(1)-C(2)	1.401(3)	C(14)-N(4)-C(10)	116.8(2)
C(1)-C(5)	1.478(3)	C(24)-N(5)-C(20)	118.8(2)
C(2)-C(10)	1.476(3)	C(19)-N(6)-C(15)	116.7(2)
C(3)-C(4)	1.408(3)	C(28)-N(7)-C(25)	121.3(2)

C(15)-C(3)	1.482(3)	C(27)-N(8)-C(26)	120.7(2)
C(20)-C(4)	1.474(3)	C(33)-N(9)-C(29)	119.0(2)
C(6)-C(5)	1.387(3)	C(38)-N(10)-C(34)	116.9(2)
C(6)-C(7)	1.383(3)	C(48)-N(11)-C(44)	118.8(2)
C(8)-C(7)	1.385(4)	C(43)-N(12)-C(39)	116.8(2)
C(8)-C(9)	1.380(4)	N(1)-C(1)-C(2)	118.1(2)
C(10)-C(11)	1.387(4)	N(1)-C(4)-C(3)	117.5(2)
C(11)-C(12)	1.390(4)	N(1)-C(1)-C(5)	111.7(2)
C(13)-C(12)	1.371(4)	N(1)-C(4)-C(20)	112.2(2)
C(14)-C(13)	1.389(4)	N(2)-C(2)-C(1)	119.8(2)
C(15)-C(16)	1.379(4)	N(2)-C(3)-C(4)	119.9(2)
C(17)-C(16)	1.379(4)	N(2)-C(2)-C(10)	117.3(2)
C(18)-C(17)	1.379(5)	N(2)-C(3)-C(15)	116.8(2)
C(18)-C(19)	1.370(4)	N(3)-C(9)-C(8)	122.2(2)
C(21)-C(20)	1.385(3)	N(3)-C(5)-C(1)	112.7(2)
C(21)-C(22)	1.378(4)	N(3)-C(5)-C(6)	121.5(2)
C(23)-C(22)	1.383(4)	N(4)-C(10)-C(2)	116.0(2)
C(24)-C(23)	1.385(4)	N(4)-C(10)-C(11)	123.7(2)
C(25)-C(26)	1.412(3)	N(4)-C(14)-C(13)	123.6(3)
C(29)-C(25)	1.485(3)	N(5)-C(20)-C(4)	112.3(2)
C(26)-C(34)	1.485(3)	N(5)-C(20)-C(21)	121.1(2)
C(28)-C(27)	1.407(3)	N(5)-C(24)-C(23)	122.1(2)
C(39)-C(27)	1.480(3)	N(6)-C(15)-C(3)	115.8(2)
C(44)-C(28)	1.479(3)	N(6)-C(15)-C(16)	123.4(2)
C(30)-C(29)	1.390(3)	N(6)-C(19)-C(18)	123.9(3)
C(31)-C(30)	1.383(4)	N(7)-C(25)-C(26)	117.1(2)
C(31)-C(32)	1.386(4)	N(7)-C(25)-C(29)	114.1(2)
C(33)-C(32)	1.383(4)	N(7)-C(28)-C(27)	117.2(2)
C(35)-C(34)	1.386(4)	N(7)-C(28)-C(44)	114.5(2)
C(35)-C(36)	1.388(4)	N(8)-C(26)-C(25)	118.2(2)
C(36)-C(37)	1.375(4)	N(8)-C(26)-C(34)	117.3(2)
C(38)-C(37)	1.384(4)	N(8)-C(27)-C(28)	118.4(2)
C(39)-C(40)	1.387(4)	N(8)-C(27)-C(39)	117.6(2)
C(41)-C(40)	1.393(4)	N(9)-C(29)-C(25)	113.9(2)
C(42)-C(41)	1.380(4)	N(9)-C(29)-C(30)	121.6(2)
C(42)-C(43)	1.386(4)	N(9)-C(33)-C(32)	122.5(2)
C(44)-C(45)	1.388(3)	N(10)-C(34)-C(26)	114.8(2)
C(46)-C(45)	1.383(3)	N(10)-C(34)-C(35)	123.3(2)
C(47)-C(46)	1.383(4)	N(10)-C(38)-C(37)	123.6(3)

C(47)-C(48)	1.385(4)
C(93)-C(92)	1.401(4)
C(94)-C(92)	1.404(4)
C(95)-C(92)	1.388(5)
C(93)-N(93)	1.156(3)
C(94)-N(94)	1.151(4)
C(95)-N(95)	1.152(5)
C(97)-C(96)	1.409(4)
C(98)-C(96)	1.412(4)
C(99)-C(96)	1.406(4)
C(97)-N(97)	1.150(4)
C(98)-N(98)	1.154(4)
C(99)-N(99)	1.150(4)

N(11)-C(44)-C(28)	113.9(2)
N(11)-C(44)-C(45)	121.6(2)
N(11)-C(48)-C(47)	122.5(2)
N(12)-C(39)-C(27)	114.6(2)
N(12)-C(39)-C(40)	123.4(2)
N(12)-C(43)-C(42)	123.9(2)
C(1)-C(2)-C(10)	123.0(2)
C(2)-C(1)-C(5)	130.2(2)
C(3)-C(4)-C(20)	130.2(2)
C(4)-C(3)-C(15)	123.3(2)
C(6)-C(5)-C(1)	125.6(2)
C(6)-C(7)-C(8)	119.7(2)
C(7)-C(6)-C(5)	118.8(2)
C(9)-C(8)-C(7)	118.9(2)
C(11)-C(10)-C(2)	120.3(2)
C(10)-C(11)-C(12)	118.2(3)
C(12)-C(13)-C(14)	118.9(3)
C(13)-C(12)-C(11)	118.7(3)
C(15)-C(16)-C(17)	118.5(3)
C(16)-C(15)-C(3)	120.8(2)
C(16)-C(17)-C(18)	119.0(3)
C(19)-C(18)-C(17)	118.5(3)
C(21)-C(20)-C(4)	126.4(2)
C(21)-C(22)-C(23)	119.5(2)
C(22)-C(23)-C(24)	118.9(2)
C(22)-C(21)-C(20)	119.3(2)
C(25)-C(26)-C(34)	124.3(2)
C(26)-C(25)-C(29)	128.7(2)
C(27)-C(28)-C(44)	128.2(2)
C(28)-C(27)-C(39)	123.8(2)
C(30)-C(31)-C(32)	119.5(2)
C(30)-C(29)-C(25)	124.3(2)
C(31)-C(30)-C(29)	118.9(2)
C(33)-C(32)-C(31)	118.3(2)
C(34)-C(35)-C(36)	118.4(3)
C(35)-C(34)-C(26)	121.6(2)
C(36)-C(37)-C(38)	118.8(2)
C(37)-C(36)-C(35)	118.9(3)
C(39)-C(40)-C(41)	118.4(2)
C(40)-C(39)-C(27)	121.7(2)
C(41)-C(42)-C(43)	118.7(2)
C(42)-C(41)-C(40)	118.8(2)

C(45)-C(44)-C(28)	124.3(2)
C(46)-C(45)-C(44)	118.9(2)
C(46)-C(47)-C(48)	118.6(2)
C(47)-C(46)-C(45)	119.6(2)
N(93)-C(93)-C(92)	179.3(3)
N(94)-C(94)-C(92)	178.2(3)
N(95)-C(95)-C(92)	178.0(7)
N(97)-C(97)-C(96)	178.9(3)
N(98)-C(98)-C(96)	177.2(3)
N(99)-C(99)-C(96)	177.5(3)
C(93)-C(92)-C(94)	120.2(2)
C(95)-C(92)-C(93)	118.6(3)
C(95)-C(92)-C(94)	121.1(3)
C(97)-C(96)-C(98)	119.1(2)
C(99)-C(96)-C(97)	119.2(3)
C(99)-C(96)-C(98)	121.6(3)

Table S3. Weak C-H···N type interactions for $[Co(tppz)_2](tcm)_2$

C	**N**	**C—H** [Å]	**H•••N** [Å]	**C•••N** [Å]	**C—H•••N** [°]
C(6)	N(4)	0.93	2.57	3.015(4)	110.0
C(9)	N(93)_#1	0.93	2.53	3.273 (4)	137.0
C(11)	N(99)_#2	0.93	2.54	3.283(4)	137.0
C(21)	N(6)	0.93	2.61	3.062(4)	111.0
C(22)	N(98)_#3	0.93	2.60	3.261(4)	129.0
C(24)	N(97)	0.93	2.51	3.242(4)	136.0
C(43)	N(93)_$4	0.93	2.50	3.363(4)	154.0

#1: 1-x,1-y,-z; #2: 1+x,-1+y,z; #3: -x,1-y,1-z; #4: -x,1-y,-z

Table S4. Structural data for examples of cobalt(II) complexes with tppz, terpy and its derivatives.

Compound	Spin state	$T_{X\text{-}ray}$ [K]	Co-$N_{(central)}$ (average; Å)	Co-$N_{(distal)}$ (average; Å)	Σ [°]	θ [°]	ϕ [°]	Ref
$[Co(tppz)_2](tcm)_2$	LS/HS	293	1.90	2.07	81.70	86.35	179.60	this work
$[Co(tppz)_2][PF_6]\cdot CH_3CN$	LS	110	1.88	2.05	85.70	79.84	180.00	4
$[Co(tppz)_2][BArF]_2\cdot C_2Cl_2$	LS	110	1.96	2.07	87.00	90.00	180.00	
$[Co(terpy)_2](ClO_4)_2\cdot 0.5H_2O$	LS/HS	243	2.02	2.14	109.58	90.00	180.00	5
$[Co(terpy)_2][BF_4]_2$	LS HS	30 370	1.92 2.04	2.09 2.15	89.02 119.99	88.68 89.55	178.22 178.37	6
$[Co(C_{16}\text{-terpy})_2](BF_4)_2$	LS/HS	130	1.99	2.13	111.92	86.04	174.01	7
$[Co(C_{14}\text{-terpy})2](BF_4)_2\cdot MeOH$	HS LS	190 10	2.03 1.88	2.15 2.05	119.31 91.63	84.89 85.83	173.68 175.76	8
$[Co(terpyR4)_2](PF_6)_2\cdot 3H_2O$	LS	123	1.86	1.94	75.71	89.16	178.99	9
$[Co(terpyR8)_2](BF_4)_2\cdot 3H_2O$	LS	123	1.87	1.95	65.64	88.87	179.52	
$[Co(tptpy)_2](BF_4)_2\cdot CH_3OH$	$LS_{(75\%)}$/HS	293	1.87	2.00	93.83	83.18	178.53	10
[Co(qptpy)2](BPh4)2·3.5dmf·2H2O	$LS_{(75\%)}$/HS	296	1.92	2.14	88.86	86.86	178.12	
$[Co(4\text{-terpyridone})_2]X_2\cdot nS$ $X=[BF_4]^-$ $S=H_2O$ $X=[BF_4]^-$ and $[SiF_6]^-$ $S=CH_3OH$ $X=[CoNCS_4]^-$ $S=0.5CH_3OH$ $X=I^-$ $S=5H_2O$ $X=[PF_6]^-$	 LS/HS LS/HS LS LS LS HS	 293 293 105 293 293 293	 1.90 1.92 1.91 1.86 1.86 2.03	 2.02 2.09 2.08 1.95 1.95 2.16	 83.40 94.51 90.11 65.28 68.73 122.93	 87.14 89.37 89.58 88.02 88.95 88.60	 178.32 175.73 176.25 179.54 179.23 173.17	11
$[Co(HO\text{-}C6\text{-terpy})_2](BF_4)_2\cdot H_2O$	LS	200	1.91	2.08	91.17	89.75	175.93	12
$[Co(HO\text{-}C12\text{-terpy})_2](BF_4)_2$	LS	279	1.89	2.07	87.87	85.71	177.45	
$[Co(dpzca)_2]$	LS HS	90 298	1.92 2.05	2.20 2.15	76.08 110.04	88.81 89.63	178.11 180.00	13

Σ - is the sum of the deviation from 90° of the 12 *cis* angles of the CoN_6 octahedron, θ - the dihedral angle between the least squares planes of the two ligands, ϕ - the $N_{central}$–Co–$N_{central}$ angle, HS/LS –mixture of both states, $T_{X\text{-}ray}$ – temperature of crystal structure measurement, (terpy = 2,2':6',2''-terpyridine, C_{16}-terpy = 4'-hexadecyloxy-2,2':6',2''-terpyridine, C_{14}-terpy = 40-tetradecyloxy-2,2':6',2''-terpyridine, terpyR8 – 4''-octoxy-2,2':6',2''-terpyridine, terpyR4 – 4''-butoxy-2,2':6',2''-terpyridine tptpy = 4′-terphenylterpyridine, qptpy = 4'- quaterphenylterpyridine, dmf = N,N-dimethylformamide, HO–C6-terpy = 4'-(6-hydroxyhexyl)-2,2':6',2''-terpyridine, HO–C12-terpy = 4'-(6-hydroxydodecyl)-2,2':6',2''-terpyridine, Hdpzca = N-(2-pyrazylcarbonyl)-2-pyrazinecarboxamide).

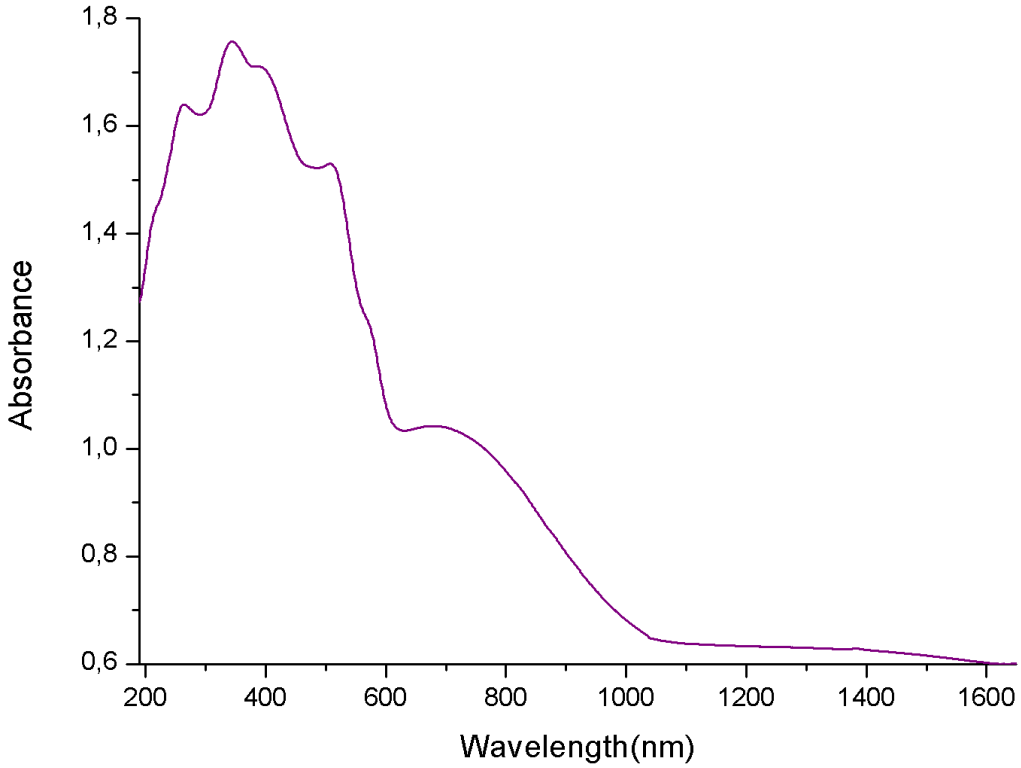

Figure S1. UV-Vis diffuse reflectance spectrum of **1** at room temperature.

The reflectance spectrum of the solid complex shows an absorption band at 14 346cm^{-1} attributed to the spin-allowed ligand-field transitions $^2E \rightarrow {}^2T_2$, $^2T_1$ characteristic for the low-spin Co(II) species[14]. The existence of the band at 7 163 cm^{-1} gives definite evidence for the presence of a lower symmetry ligand field component due to the large difference between axial and equatorial Co–N bond lengths in the low-spin state. The higher energy structured band may be assigned to higher energy ligand-field transitions, metal–ligand (MLCT) and ligand-ligand (LLCT) charge transfer transitions.

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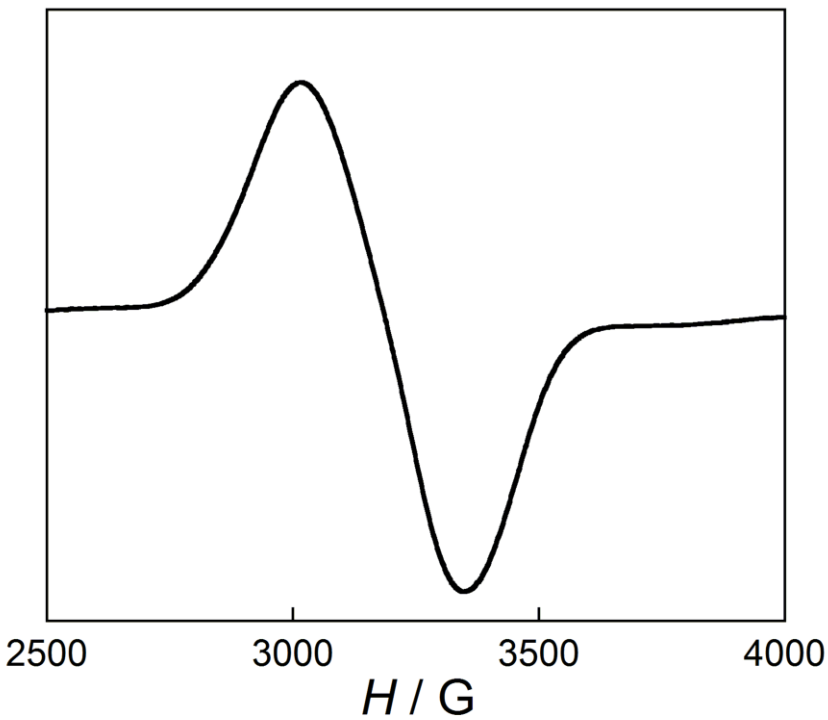

Figure S2. X-band EPR spectrum on a solid sample of **1** at 25 K.

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