Supporting Information

Experimental Section

Materials and General Methods

All starting materials were of reagent grade and used as received from the commercial supplier. Fourier transform infrared (FTIR) spectra were recorded with ATR unit in the range 4000–180 cm^{-1} on a Bruker Equinox 55 FT-IR spectrometer. Diffuse reflectance UV/Vis/NIR spectra were recorded in the range 2000–250 nm on a Perkin Elmer λ 750 s spectrometer. Thermogravimetric analysis (TGA) was performed with a TGA Q500 analyzer in the temperature range of 25-900 °C in flowing nitrogen gas at the heating rate of 10 $Kmin^{-1}$. Energy-dispersive X-Ray spectroscopy (EDX) was performed with a Philips XL 30 scanning electron microscope. Argon gas sorption isotherms were measured with a Quantachrome Autosorb-I ASI-CP-8 instrument. Prior to measurements, the samples were heated at 250 ˚C (**1**) and 280 °C (**2**) for 24h in high vacuum to remove the occluded solvent molecules. Argon sorption experiments were performed at 77 K in the range of $1.00\times10^{-5} \leq P/P_0 \leq 1.00$ with argon gas. Temperature-programmed oxidation (TPO) and reduction (TPR) measurements were carried out with BELCAT-B (Bel. Inc. Japan) instrument coupled with a GAM-400 (IPI, Germany) quadrupole mass spectrometer.

Synthesis of Co-MFU-4*l* (1)

Anhydrous cobalt (II) chloride (5.2 g, 40 mmol) was dissolved in DMF (160 mL) and MFU-4*l* (1 g, 0.8 mmol) was added to the solution. The reaction mixture was stirred for 20 h at 140 °C under reflux. The dark-green or dark-blue precipitate was filtered off, washed with DMF, methanol and dichloromethane and dried at 250 °C under vacuum. Yield 0.92 g (94 %).

Synthesis of Co-MFU-4 (2)

Anhydrous cobalt (II) chloride (3.9 g, 30 mmol), anhydrous lithium chloride (2.55 g, 60 mmol) and 1H,5H-benzo(1,2-d:4,5-d')bistriazole (2.4 g, 15 mmol) were dissolved in DMF (240 mL) and the solution was heated in a sealed tube for 48 h at 140 °C. The dark-blue precipitate was filtered off, washed with DMF and methanol and dried at 280 °C under vacuum. Yield 1.9 g (42 %).

Synthesis of [$Co_5Cl_4(Me_2bta)_6$]•2PhBr (3)

The solution of 5,6-dimethylbenzotriazol (1.5 g, 10.2 mmol) and 2,6 dimethylpyridin (1.05 mL, 9.04 mmol) in methanol (20 mL) was added in 1 min to the solution of $CoCl_2$•$6H_2O$ in methanol (25 mL). The red precipitate was filtered off and dried under vacuum. The crude product was refluxed in bromobenzene (500 mL) for 3 h and the solution was evaporated to 250 mL. After 3 days at room temperature, green-blue octahedral crystals of **3** crystallized.

Powder X-ray diffraction measurements and crystal structure determination of 1 and 2

Crystalline samples were ground using an agate mortar and pestle, and were deposited in the hollow well of a sample holder. Diffraction data were collected in the 2θ range of 4-90° with 0.02° steps, with an interval of 6 s per step, using a Seifert XRD 3003 TT diffractometer equipped with Meteor 1D detector.

For the thermal stability characterization, the samples were ground using an agate mortar and pestle and were loaded into a glass capillary. The variable temperature XRPD experiment data were collected in the 2θ range of 4 - 60° with 0.02° steps, with an interval of 1 s per step using a Bruker A8 Advance diffractometer equipped with Lynxeye linear position-sensitive detector, mri TCPU1 oven, transmission geometry. The samples were heated from room temperature to 100, 200, 300, 350, 400, 450 and 500 °C, and once the corresponding temperature was reached, the sample was kept at this temperature for 10 min before starting to measure.

Since Co-MFU4 and Co-MFU4*l* are isostructural with MFU-4 and MFU-4*l* compounds, respectively, a Rietveld refinement process was directly carried out starting from the structural models of their isostructural counterparts. The Rietveld refinement was carried out using the Jana2006 program. Weak geometric restraints on bond distances were used during the refinement process. In both cases hydrogen atoms were placed at idealized positions using the SHELXL program. The experimental details and crystal data for Co-MFU4*l* (**1**) and Co-MFU4 (**2**) are listed in Table 1. The final Rietveld refinement plots for **1** and **2** are presented in Fig. 1 and 2, respectively.

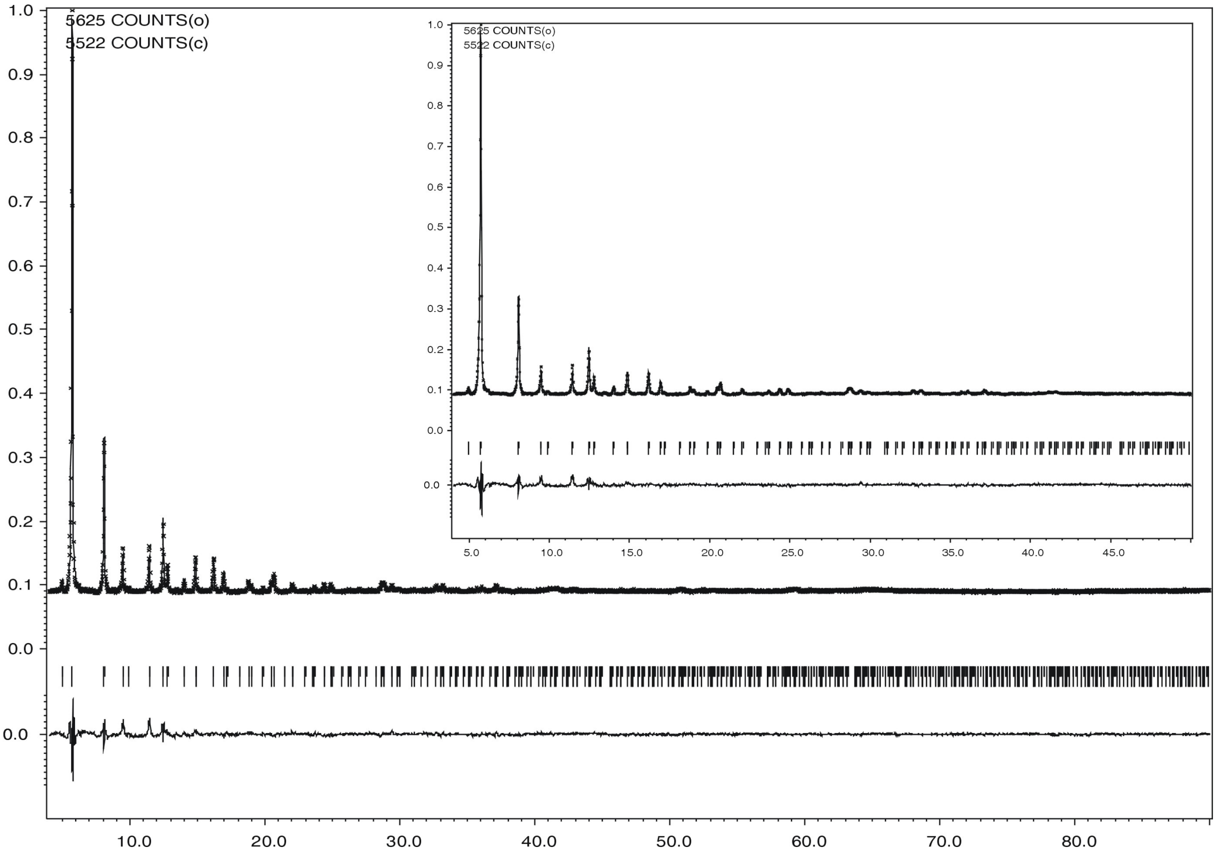

Fig. S1. The Rietveld refinement plots for **Co-MFU4*l***. Dotted and solid lines represent observed and calculated patterns, respectively with peak markers and the difference plot shown at the bottom. For clarity, the insert shows an expanded view in the range 4–50 in 2θ.

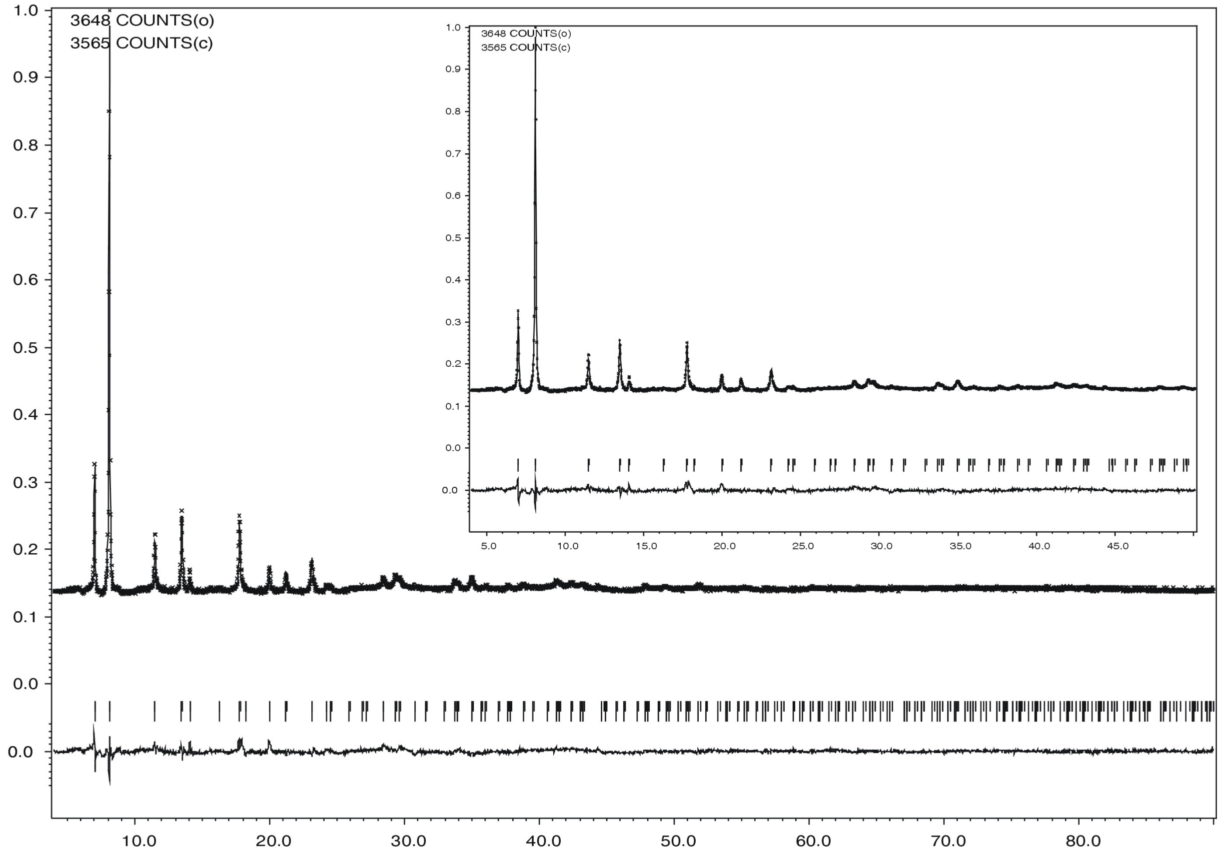

Fig. S2. The Rietveld refinement plots for **Co-MFU4**. Dotted and solid lines represent observed and calculated patterns, respectively with peak markers and the difference plot shown at the bottom. For clarity, the insert shows an expanded view in the range 4–50 in 2θ.

Table 1. Experimental details and crystal data for Co-MFU4*l* (**1**) and Co-MFU4 (**2**)

Compound	**Co-MFU4**	**Co-MFU4*l***
Diffractometer	Seifert XRD 3003 TT	Seifert XRD 3003 TT
X-ray source/wavelength/ Å	Cu, 1.5418	Cu, 1.5418
T/K	293(2)	293(2)
Empirical formula		
Formula	$C_{18}H_6Cl_4Co_5N_{18}$	$C_{36}H_{12}Cl_4Co_4N_{18}O_6Zn$
M_r	910.8	1235.5
Crystal system	cubic	cubic
Space group (no)	$Fd\overline{3}m$ (no. 227)	$Fd\overline{3}m$ (no. 227)
a/Å	21.7309(4)	30.9950(7)
V/Å^3	10262.1(2)	29776.6(7)
Z	8	8
D_c/g cm^{-3}	1.171	0.551
F(000)	3501	4768
2θ Range/°	4-90	4-90
Refls. Obs.	55	86
Number of observation	4300	4300
R_P	1.30	1.38
R_{wp}	1.82	2.25
R_{wobs}	13.97	6.08

Co-MFU4:

Atom	x	y	z	Uiso
Co1	0.25	0.25	0.25	0.014(4)
Co2	0.3411(2)	0.3411(2)	0.3411(2)	0.014(4)
Cl	0.3946(3)	0.3946(3)	0.3946(3)	0.044(10)
N1	0.2863(2)	0.3877(4)	0.2863(2)	0.043(10)
N2	0.25	0.35536(10)	0.25	0.043(10)
C1	0.2741(4)	0.4474(2)	0.2741(4)	0.051(10)
C2	0.2999(6)	0.5	0.2999(6)	0.051(10)
H2	0.3302	0.5	0.3302	0.038

Co1 N2 . . 2.290(2)

Co2 Cl . . 2.014(8)

Co2 N1 . . 1.965(7)

N1 N2 . . 1.319(6)

N1 C1 . . 1.350(10)

C1 C1 . 99_555 1.484(12)

C1 C2 . . 1.391(10)

Co-MFU4*l*:

Atom	x	y	z	Uiso
Co2	0.3185(3)	0.3185(3)	0.181542	0.013(6)
Cl1	0.356(2)	0.356(2)	0.144361	0.05(2)
N1	0.3399(3)	0.2752(2)	0.224812	0.018(10)
C1	0.38267(10)	0.2665(3)	0.233457	0.047(15)
N2	0.3146(6)	0.25	0.25	0.018(10)
C2	0.4215(2)	0.2826(2)	0.217351	0.047(15)
C3	0.4612(2)	0.2669(2)	0.233142	0.047(15)
O1	0.5	0.2834(4)	0.216589	0.04(3)
Zn1	0.25	0.25	0.25	0.04(2)
H1	0.421274	0.303866	0.196134	0.038

Co2 Cl1 . . 2.00(5)

Co2 N1 . . 2.009(9)

N1 C1 . . 1.380(10)

N1 N2 . . 1.355(13)

C1 C2 . . 1.396(7)

N2 Zn1 . . 2.001(19)

C2 C3 . . 1.410(8)

C2 H1 . . 0.930(4)

C3 C3 . 52_555 1.478(6)

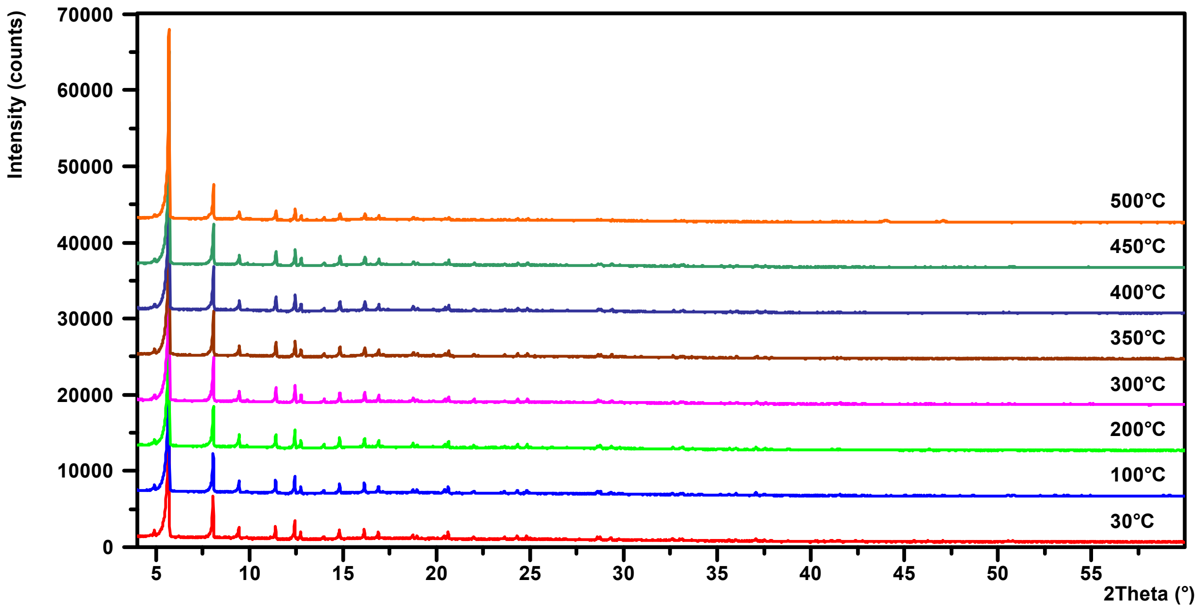

Fig. S3. VT-XRPD measurements of **1**.

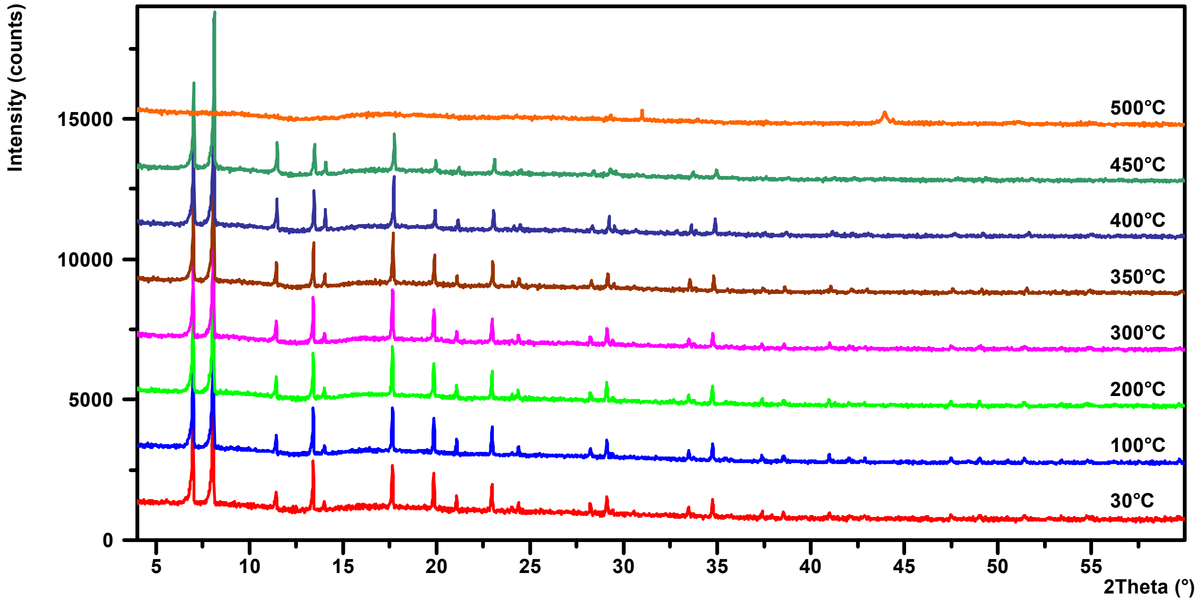

Fig. S4. VT-XRPD measurements of **2**.

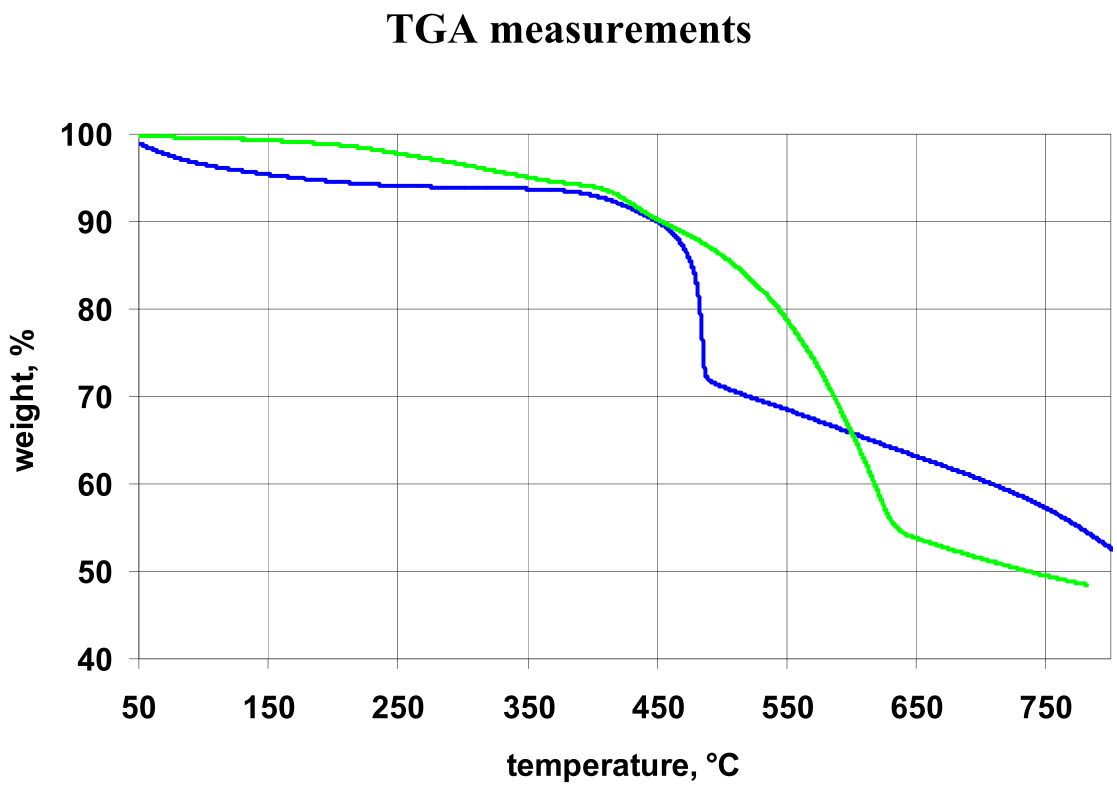

Fig. S5. Temperature-dependent weight-loss of **1** (green) and **2** (blue) under flowing nitrogen gas.

Single crystal structure determination of $[Co_5Cl_4(Me_2bta)_6]$•2PhBr (3)

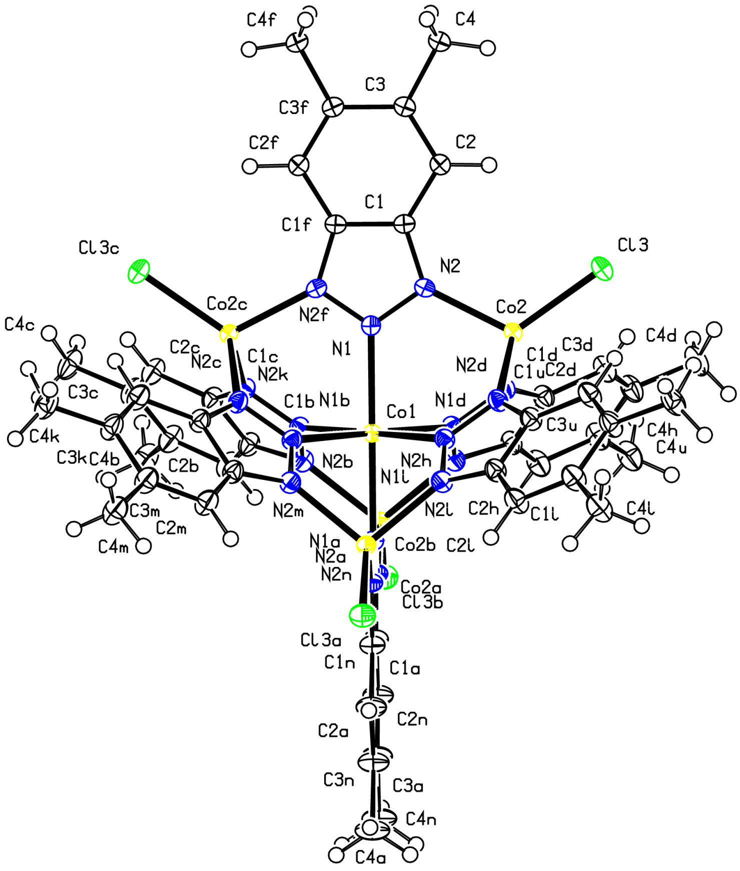

Fig. S6. ORTEP representation of the crystal structure of **3** (50% probability ellipsoids).

Data Collection. A turquoise block-like crystal of **3** with dimensions of 0.08 x 0.07 x 0.07 mm was selected and transferred into a glass capillary which was mounted in a N_2 stream (100(1) K) on a SMART APEX2 fixed-χ goniometer (Bruker). The data collection was carried out at the window of a *IμS* micro-focus sealed tube (50kV, 60 μA; Ag*K*α; *λ* = 0.56087 Å) equipped with a Montel multilayer-optic (Incoatec).

Intensity data were collected employing a Bruker APEX II CCD-detector and 0.5° *ω*-scans with a detector-to-sample distance of 50 mm. Two *ω*-scans (118° and 204.5°, 645 images in total) at a detector off-set angle (2*θ*) of 17.5° and 25° employing exposure rates of 60 seconds/frame were recorded (correlated exposures). The unit cell parameters were obtained by full-matrix least-squares refinement of 4491 reflections.

Data Reduction. Compound **3** crystallizes in the cubic space group *Fd-3m* (Int. Tables No. 227) with the cell parameter $a = 23.5130(1)$, $V = 12999.42(10)$ Å^3, $Z = 8$, $F(000) = 5320$. A total of 28354 Bragg reflections were measured ($1.18° < \theta < 23.66°$). The cell refinement and data reduction were performed using the APEX2 software package. The data was analytically corrected for absorption effects employing crystal faces using SADABS [$T_{\mathrm{min}} = 0.95520$, $T_{\mathrm{max}} = 0.96133$]. Solvent molecule contributions have been removed from the intensity data via the SQUEEZE routine as implemented in PLATON. The internal agreement factor was $R_{\mathrm{int}}(F) = 0.066$ yielding 999 unique reflections. The structure was solved by direct methods and refined with standard Fourier techniques. Full-matrix least square refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELX-97 weighting scheme. The non-hydrogen atoms were refined anisotropically, all hydrogen atoms were located in the difference Fourier map and included in the structure factor calculation employing isotropic thermal parameters. The final refinement converged at $R_1 = 0.0425$, $wR_2 = 0.0885$, GooF = 1.056 for all 999 reflections (909 reflections with $I(F_o) > 2\sigma(I)$).

Selected bond lengths:

Atom1	Atom2	Distance [Å]	Atom1	Atom2	Distance [Å]
Co1	N1	2.186(3)	N1	N2_j	1.334(2)
Co1	N1_a	2.186(3)	N2	C1	1.361(3)
Co1	N1_b	2.186(3)	C1	C2	1.410(3)
Co1	N1_d	2.186(3)	C1	C1_j	1.391(2)
Co1	N1_e	2.186(3)	C2	C3	1.375(3)
Co1	N1_h	2.186(3)	C3	C4	1.503(3)
Co2	Cl3	2.2192(5)	C3	C3_j	1.451(2)
Co2	N2	2.0007(15)	C2	H2	0.99(2)
Co2	N2_c	2.0007(15)	C4	H4A	0.98(3)
Co2	N2_e	2.0007(15)	C4	H4B	0.93(3)
N1	N2	1.334(2)	C4	H4B_p	0.93(3)

Selected bond angles:

Atom1	Atom2	Atom3	Angle [°]	Atom1	Atom2	Atom3	Angle [°]
N1	Co1	N1_a	180.00	Co1	N1	N2	124.76(12)
N1	Co1	N1_b	90.00	Co1	N1	N2_j	124.76(12)
N1	Co1	N1_d	90.00	N2	N1	N2_j	110.5(2)
N1	Co1	N1_e	90.00	Co2	N2	N1	118.10(15)
N1	Co1	N1_h	90.00	Co2	N2	C1	134.26(13)
N1_a	Co1	N1_b	90.00	N1	N2	C1	107.65(15)
N1_a	Co1	N1_d	90.00	N2	C1	C2	131.36(16)
N1_a	Co1	N1_e	90.00	N2	C1	C1_j	107.11(18)
N1_a	Co1	N1_h	90.00	C1_j	C1	C2	121.5(2)
N1_b	Co1	N1_d	90.00	C1	C2	C3	117.52(16)
N1_b	Co1	N1_e	90.00	C2	C3	C4	120.60(16)
N1_b	Co1	N1_h	180.00	C2	C3	C3_j	121.0(2)
N1_d	Co1	N1_e	180.00	C3_j	C3	C4	118.45(19)
N1_d	Co1	N1_h	90.00	C1	C2	H2	120.7(19)
N1_e	Co1	N1_h	90.00	C3	C2	H2	121.8(19)
Cl3	Co2	N2	117.59(5)	C3	C4	H4A	110(2)
Cl3	Co2	N2_c	117.59(5)	C3	C4	H4B	112.2(16)
Cl3	Co2	N2_e	117.59(5)	C3	C4	H4B_p	112.2(16)
N2	Co2	N2_c	100.27(6)	H4A	C4	H4B	108(2)
N2	Co2	N2_e	100.27(6)	H4A	C4	H4B_p	108(2)
N2_c	Co2	N2_e	100.27(6)	H4B	C4	H4B_p	106(2)

UV/vis/NIR Spectroscopy

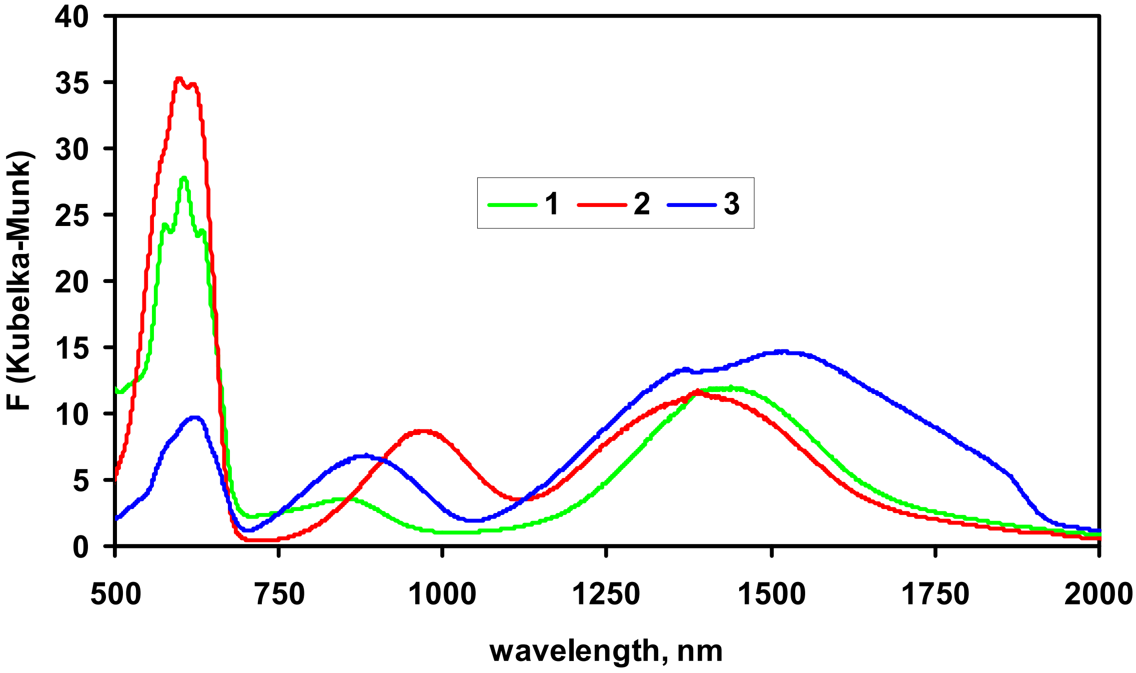

Fig. S7. UV/vis/NIR spectra of compounds **1-3**.

FTIR Spectroscopy

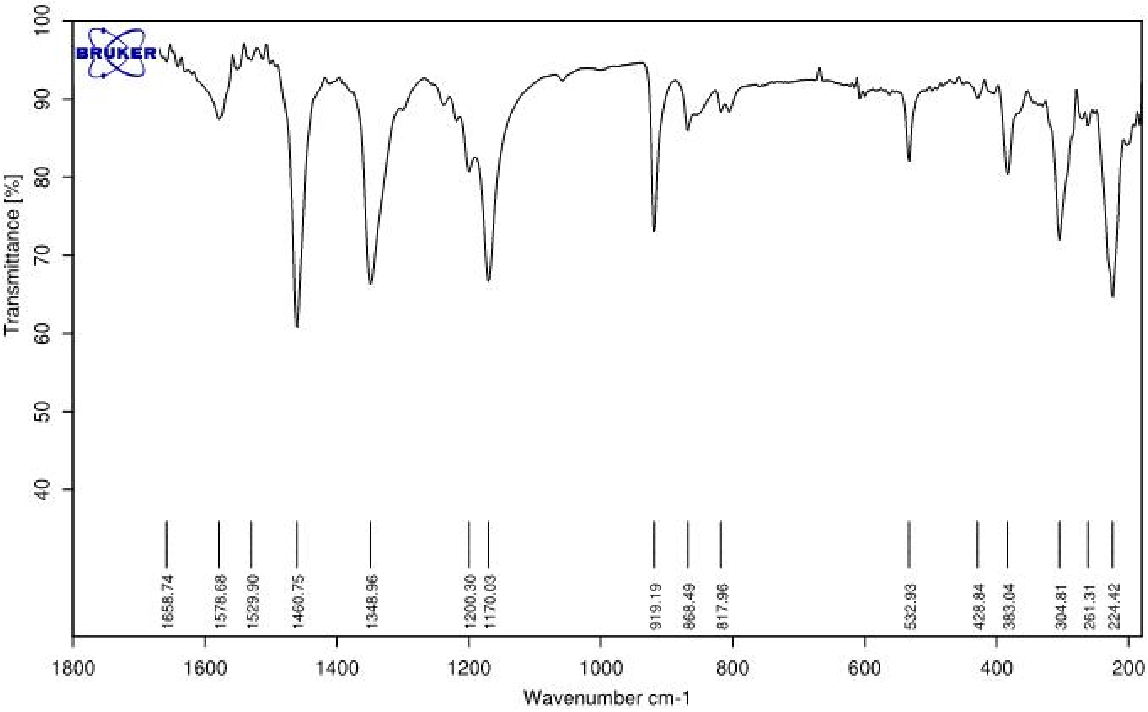

Fig. S8. FTIR spectra of **1**.

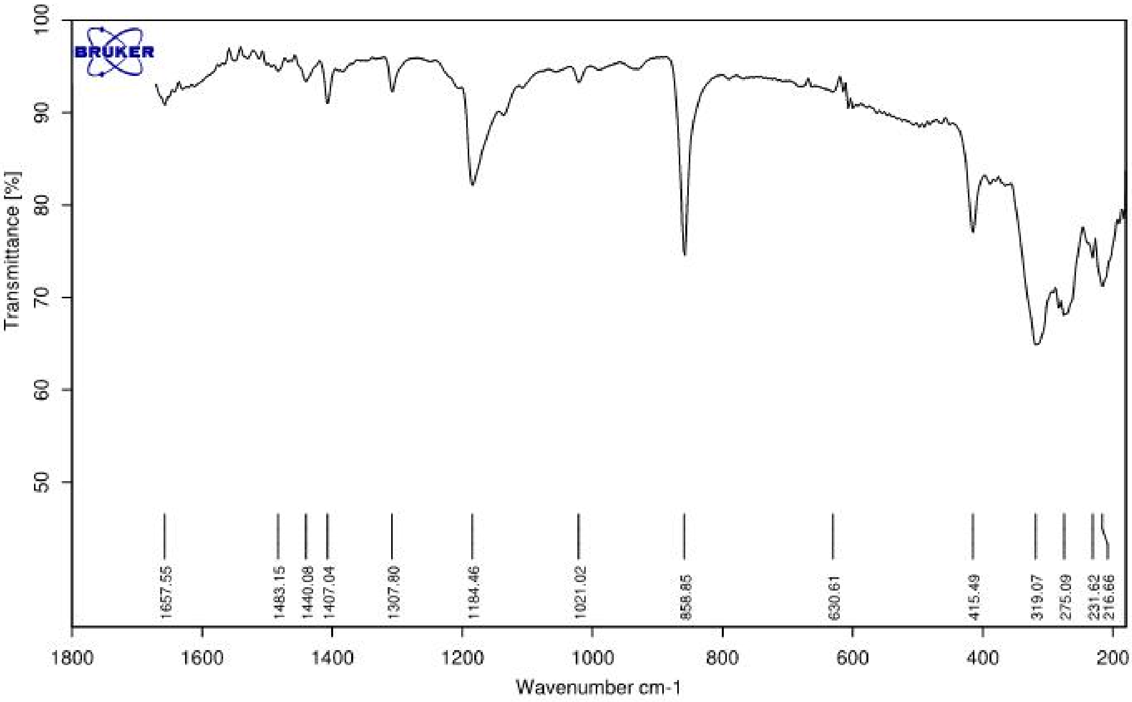

Fig. S9. FTIR spectra of **2**.

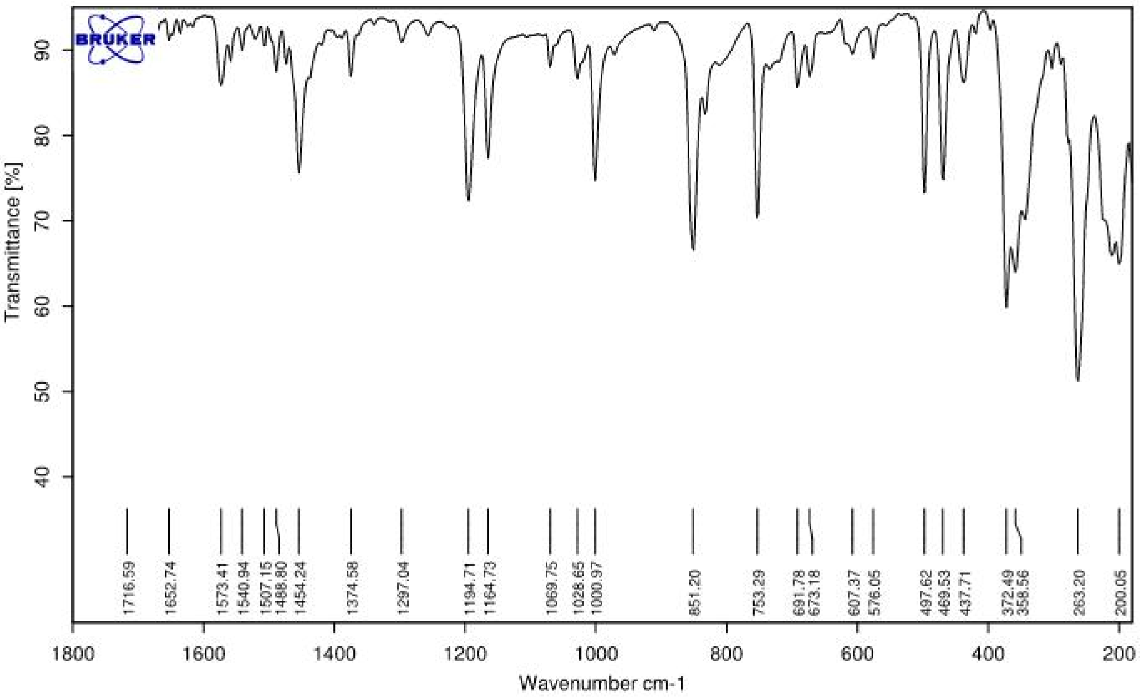

Fig. S10. FTIR spectra of **3**.