Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Crystal Phase Competition by Addition of Second Metal Cation in Solid Solution Metal-Organic Frameworks

C. Castillo-Blas,[a] N. Snejko,[a] V. A. de la Peña-O'Shea,[b] J. Gallardo,[a] E. Guitérrez-Puebla,[a] M. A. Monge,[a] F. Gándara[a].

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Section S1: Structural analyses by single crystal X-ray diffraction

Table S1. Crystal Data and structure refinement for **TMPF-88**; for atomic coordinates, equivalent isotropic displacements parameters, bond length, angles and anisotropic displacement parameters please check the CIF (**CCDC 1429138**)

Identification code	TMPF-88
Formula	$C_{38}H_{23}F_{12}N_6O_{10.46}Zn_3$
Molecular Weight/ g mol^{-1}	1155.12
Temperature/K	296 (2)
Wavelenght/Å	1.54178
Crystal system	Monoclinic
Space group	*C*2/*c*
a/Å	36.4551(9)
b/Å	18.1156(4)
c/Å	14.1588(4)
α/°	90
β/°	93.8165(13)
γ/°	90
V/Å^3	9329.8(4)
Z	8
Dx/ g cm^{-3}	1.645
μ/mm^{-1}	2.789
F (000)	4597.0
GOF F^2	1.082
Final R índices	R_1 = 0.0410
[I>2sigma(I)]	wR_2 = 0.1307
R índices	R_1 = 0.0521
(all data)	wR_2 = 0.1613

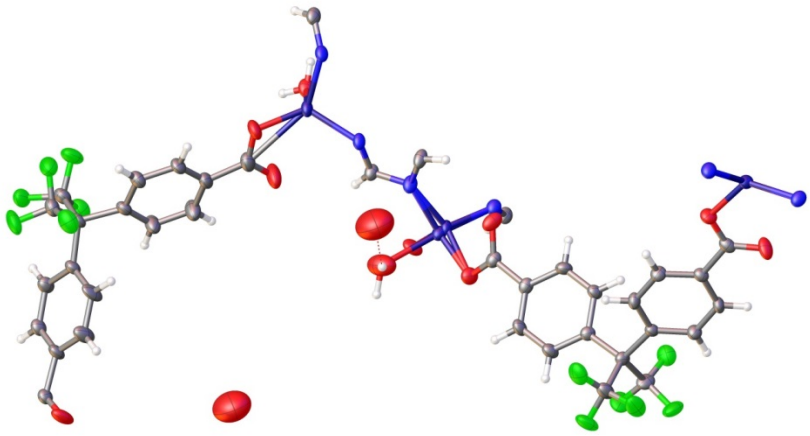

Figure S1. Representation of the asymmetric unit for TMPF-88 material. Atoms: Zn in purple; C in gray; O in red; N in blue; F in green and protons in white. Ellipsoids are displayed at the 50% probability level.

Table S2. Crystal Data and structure refinement for **TMPF-91**; for atomic coordinates, equivalent isotropic displacements parameters, bond length, angles and anisotropic displacement please check the CIF (**CCDC 1429139**)

Identification code	TMPF-91
Formula	$C_{21}H_{13}F_6N_6O_5Zn_2$
Molecular Weight/ g mol^{-1}	674.11
Temperature/K	296 (2)
Wavelenght/Å	1.54178
Crystal system	Monoclinic
Space group	*Cc*
a/Å	10.0888(4)
b/Å	33.8241(11)
c/Å	7.0903(2)
α/°	90
β/°	96.002(2)
γ/°	90
V/Å^3	2406.26(14)
Z	4
Dx/ g cm^{-3}	1.861
μ/mm^{-1}	3.328
F (000)	1340.0
GOF F^2	1.182
Final R índices	R_1 = 0.0410
[I>2sigma(I)]	wR_2 = 0.1137
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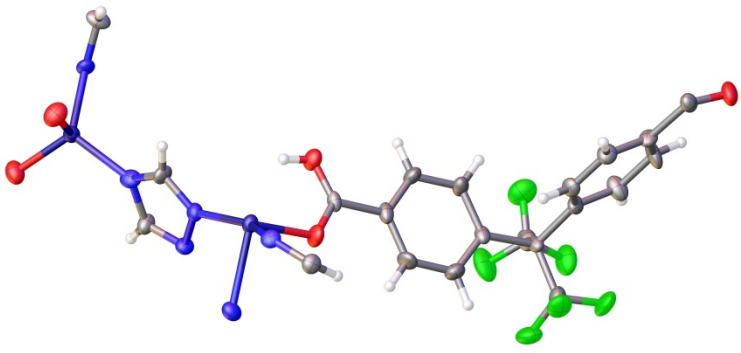

Figure S2. Representation of the Asymmetric unit for TMPF-91 material. Atoms: Zn in purple; C in gray; O in red; N in blue; F in green and protons in white. Ellipsoids are displayed at the 50% probability level.

Table S3. Crystal Data and structure refinement for **TMPF-95**; for atomic coordinates, equivalent isotropic displacements parameters, bond length, angles and anisotropic displacement please check the CIF (**CCDC 1429140**)

Identification codes	TMPF-95
Formula	$C_{72}H_{38}Co_5F_{24}N_6O_{17.48}$
Molecular Weight/ g mol^{-1}	2017.37
Temperature/K	233 (2)
Wavelenght/Å	1.54178
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	14.8692(5)
b/Å	24.8713(8)
c/Å	22.1361(7)
α/°	90
β/°	91.621(2)
γ/°	90
V/Å^3	8183.0(5)
Z	4
Dx/ g cm^{-3}	1.638
μ/mm^{-1}	83887
F (000)	4011.0
GOF F^2	1.013
Final R índices	R_1 = 0.0776
[I>2sigma(I)]	wR_2 = 0.1994
R índices	R_1 = 0.1298
(all data)	wR_2 = 0.2400

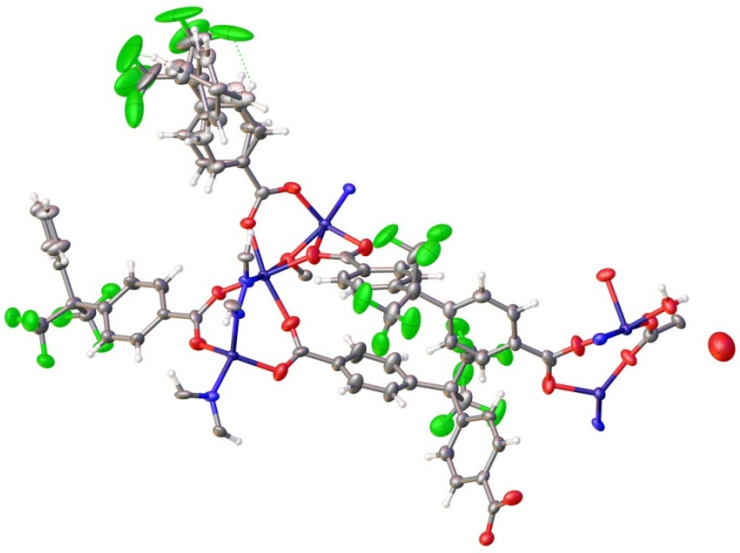

Figure S3. Representation of the asymmetric unit for TMPF-95 material. Atoms: Zn/Co in purple; C in gray; O in red; N in blue; F in green and protons in white. Ellipsoids are displayed at the 50% probability level.

Section S2: Powder diffraction profile refinement for TMPF-90

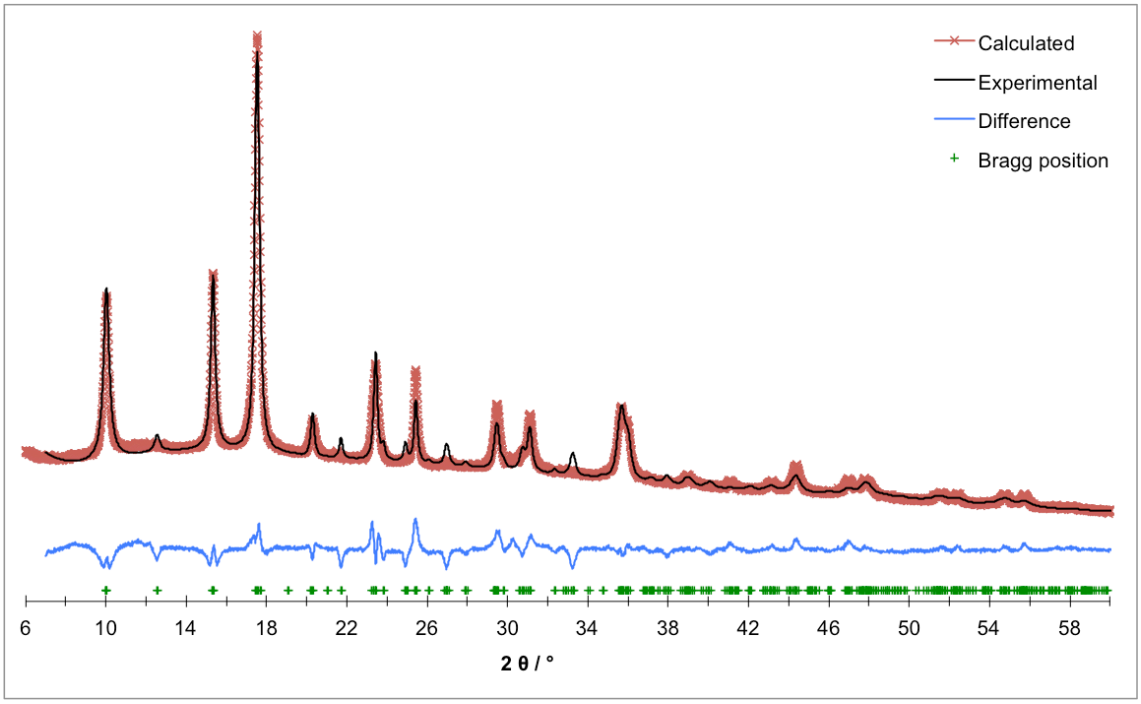

Figure S4. Rietveld refinement plot for TMPF-90, showing calculated (red), refined (black) and difference (blue) patterns. Bragg positions are marked as green crosses.

Section S3: Powder X-ray diffraction

1. PXRD patterns of pure phases

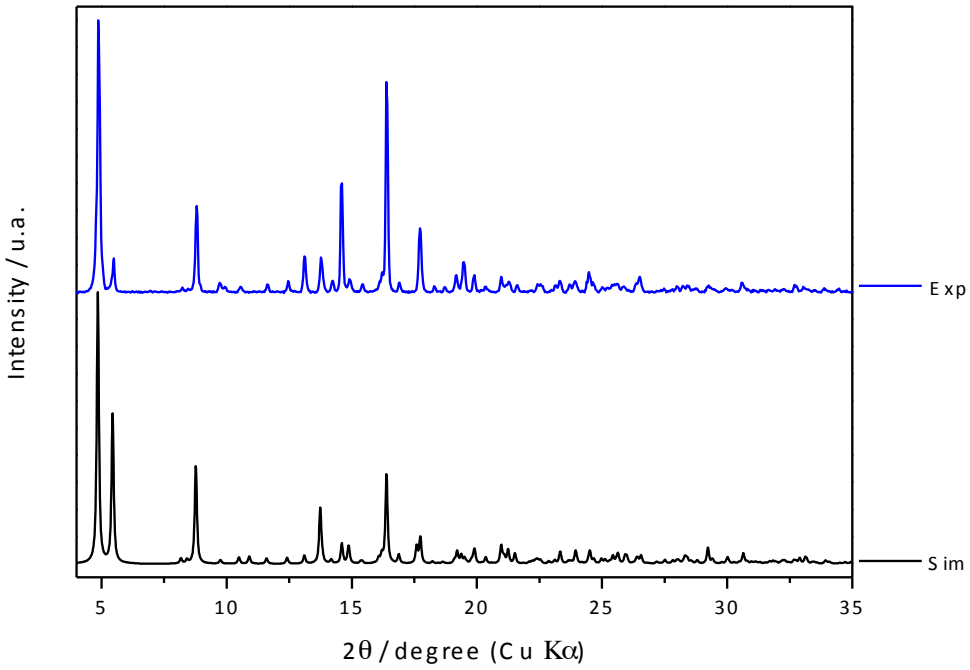

Figure S5. Normalized PXRD patterns of TMPF-88: Simulated (black) and experimental (blue) patterns.

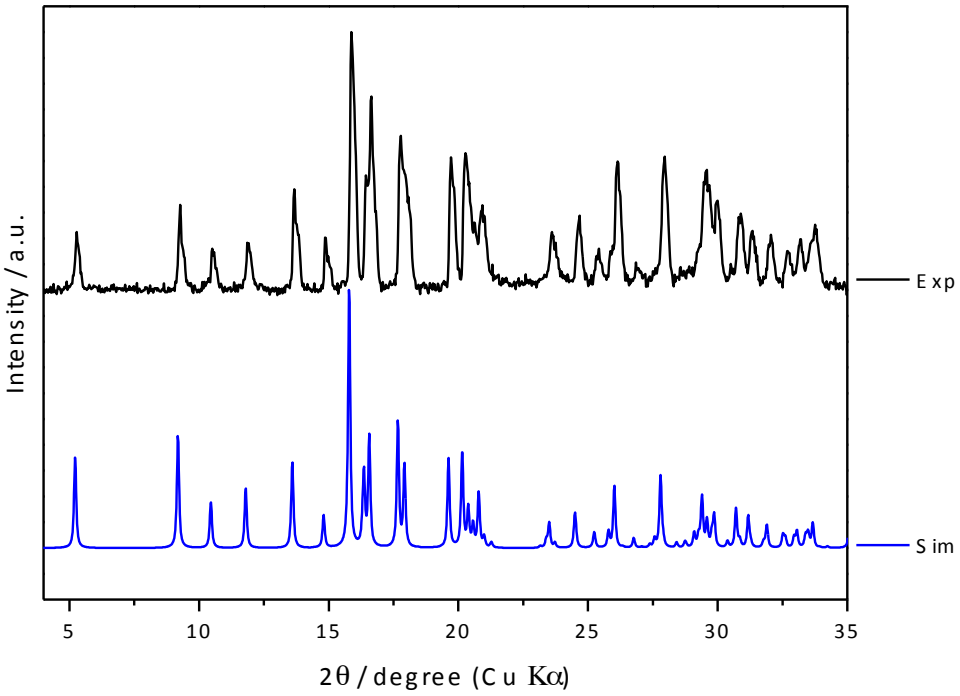

Figure S6. Normalized PXRD patterns of TMPF-91: Simulated (blue) and experimental (black) patterns.

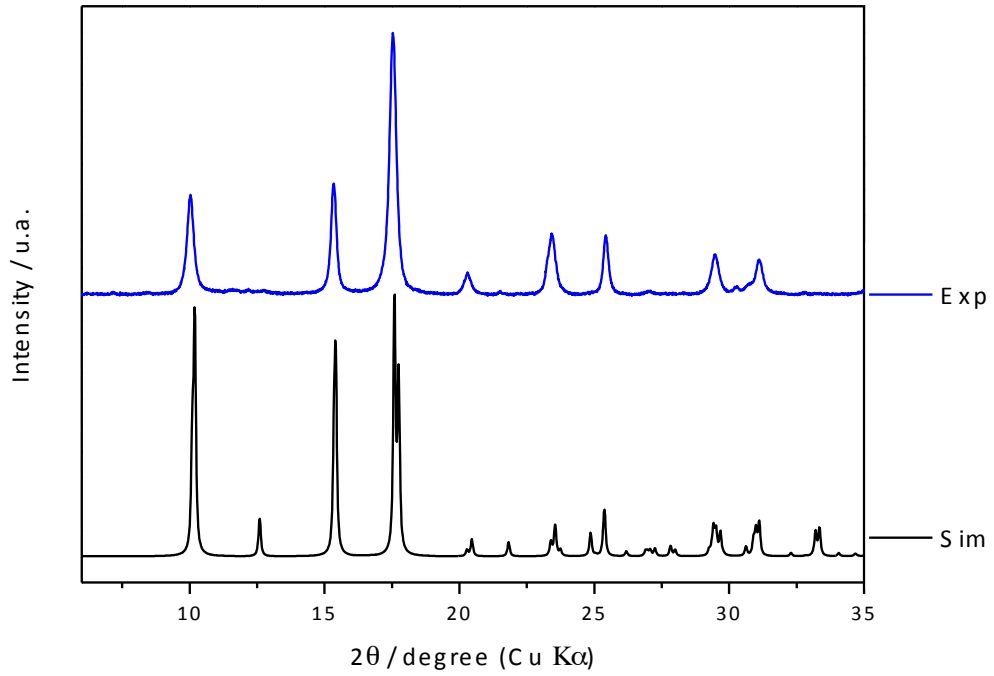

Figure S7. Normalized PXRD patterns of TMPF-91: Simulated (black) and experimental (blue) patterns.

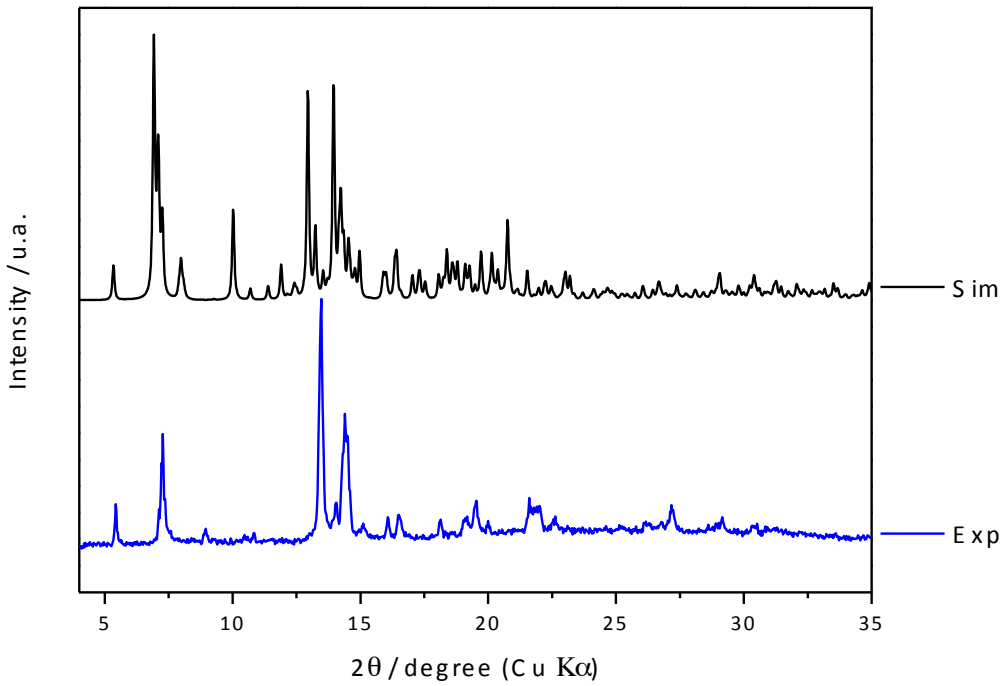

Figure S8. Normalized PXRD patterns of TMPF-95: Simulated (black) and experimental PXRD (blue) patterns.

2. PXRD patterns of synthetic study

a. H_2O:EtOH system

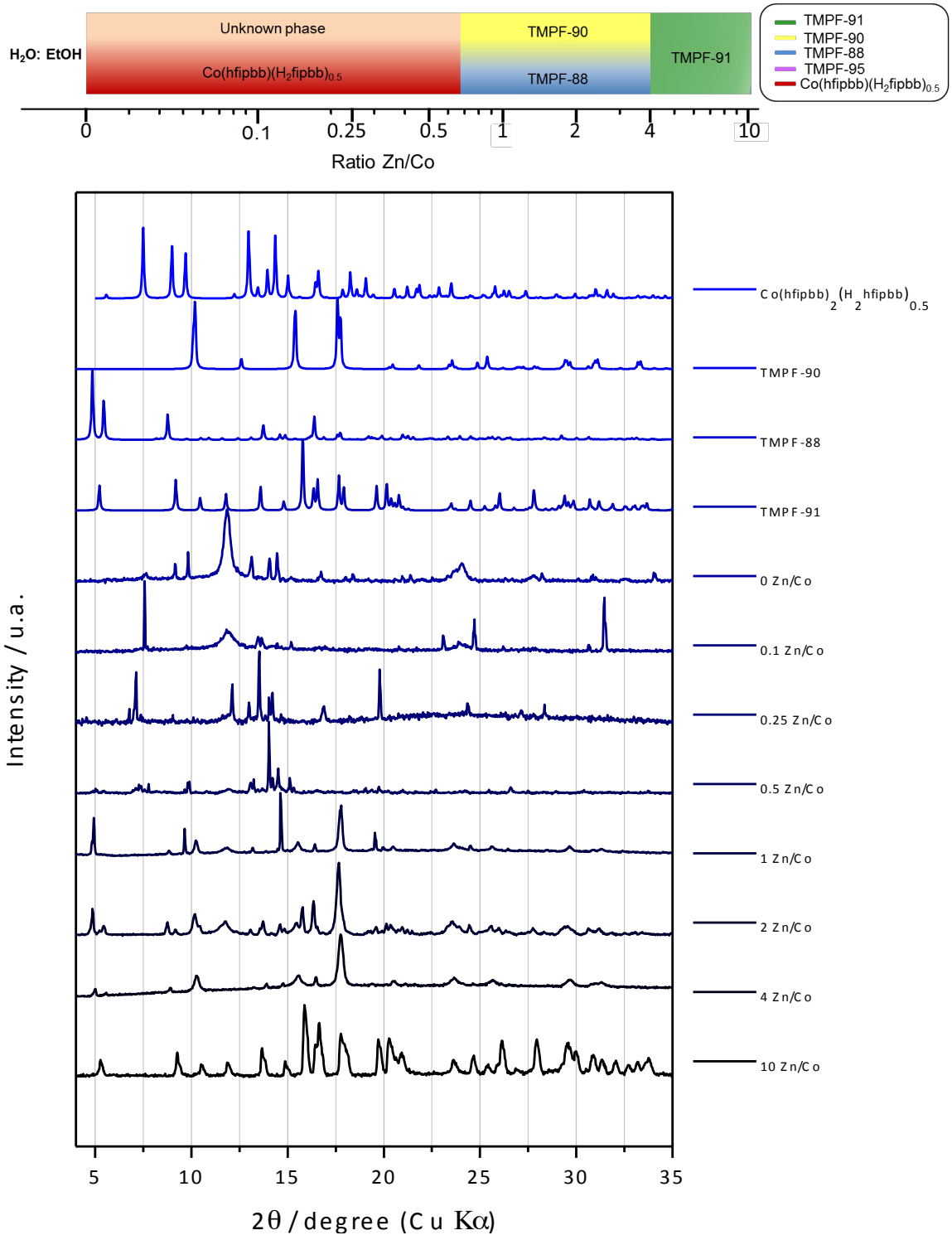

Figure S9. PXRD patterns of samples from synthetic study in water:ethanol (5mL:5mL) system with different Zn/Co ratio. The composition of the initial synthesis mixture is 130 mg, 0.33 mmol of H_2hfipbb; 75 mg, 1.09 mmol of triazole and 0.34 mmol of $M(NO_3)_2$ (M ≡ Co or Zn) in all cases. The simulated PXRD patterns of the phases involved in the synthetic study are shown at the top of the figure, for comparion.

b. H_2O system

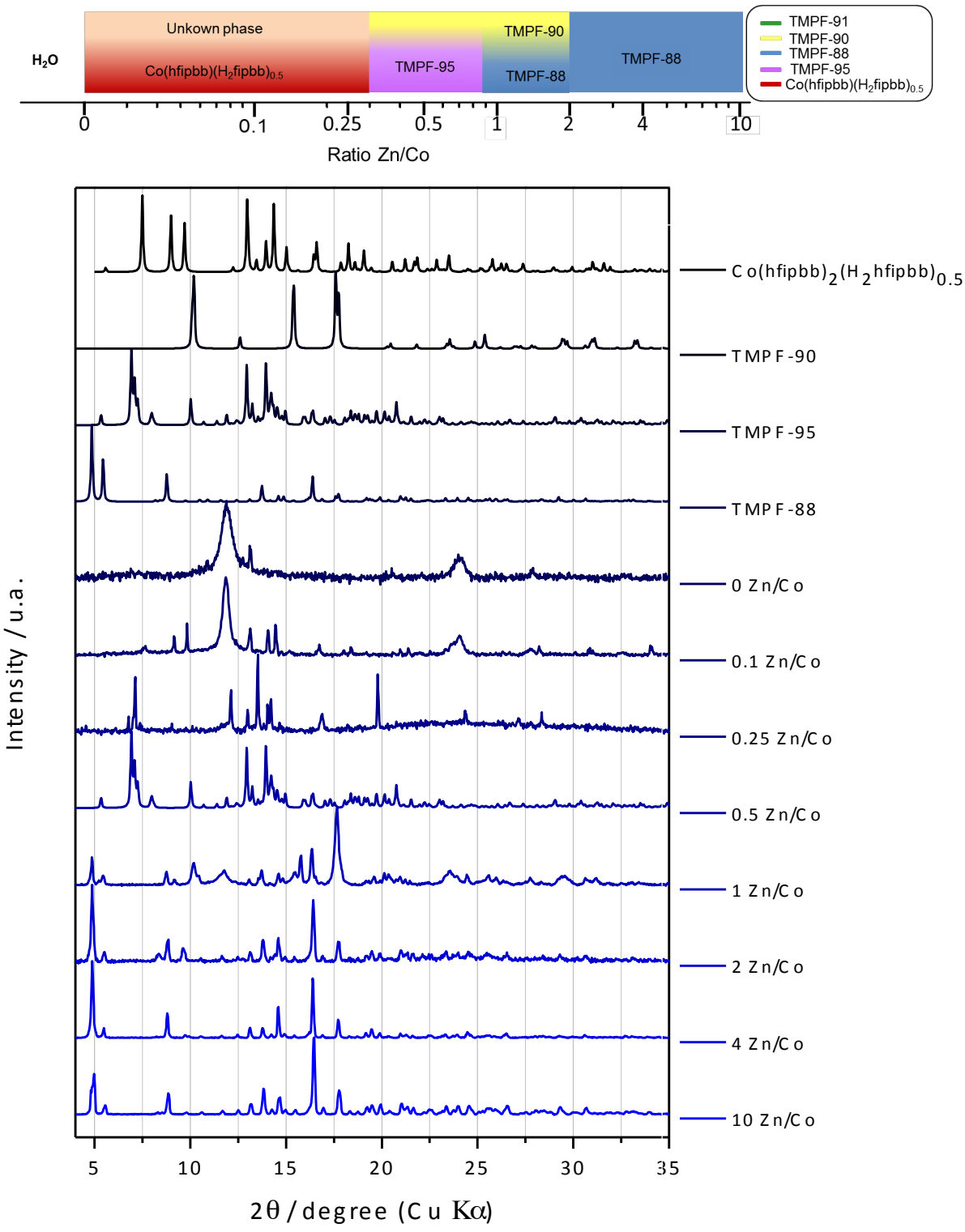

Figure S10. PXRD patterns of samples involved in the synthetic study in water (10 mL) system with different Zn/Co ratio. The composition of the initial synthesis mixture is 130 mg, 0.33 mmol of H_2hfipbb; 75 mg, 1.09 mmol of triazole and 0.34 mmol of $M(NO_3)_2$ (M ≡ Co or Zn) in all cases. The simulated PXRD patterns of the phases involved in the synthetic study are shown in the top of the figure, for comparison.

3. PXRD patterns of kinetic study

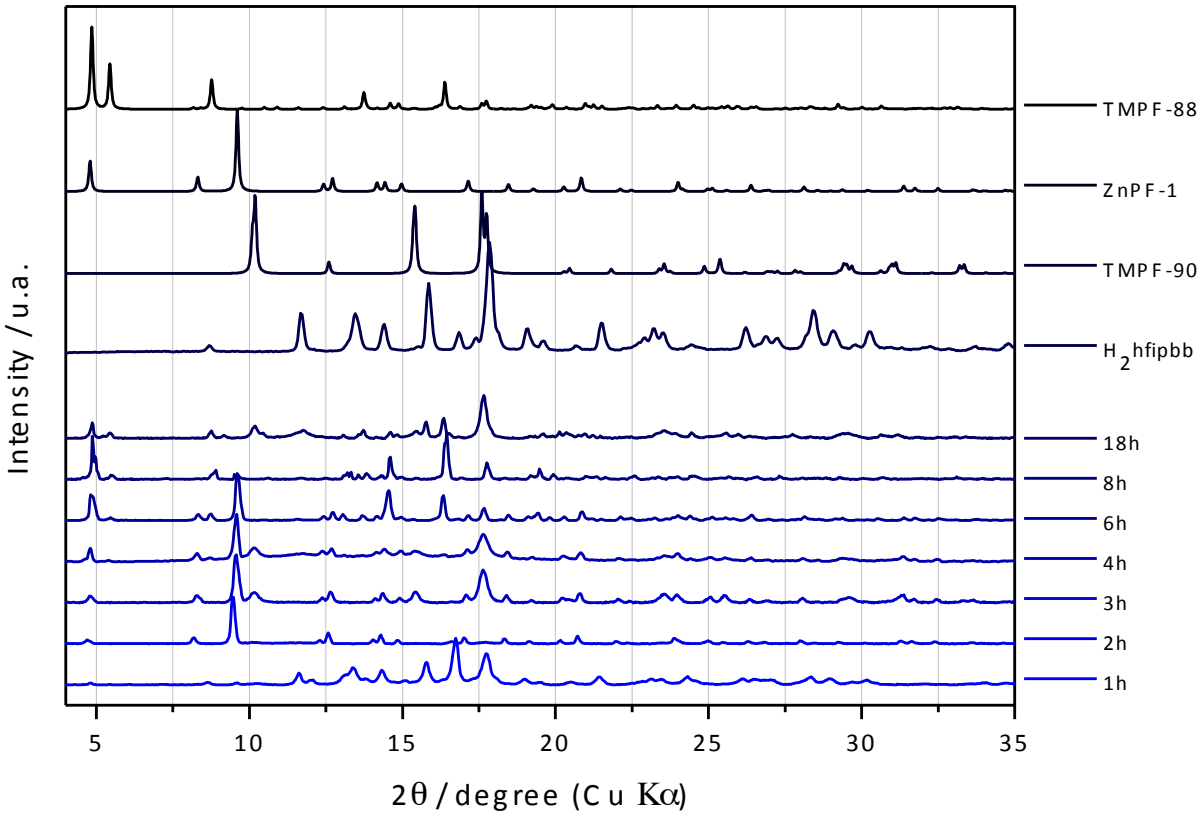

Figure 11X: Plot of the PXRD patterns corresponding to the samples obtained at different reaction times. The composition of the initial synthesis mixture is 130 mg, 0.33 mmol of H_2hfipbb; 75 mg, 1.09 mmol of triazole; 67 mg, 0.23 mmol of $Zn(NO_3)_2$ and 33 mg, 0.11 mmol of $Co(NO_3)_2$ in all cases. The simulated PXRD patterns of the phases involved in the kinetic study are shown in the top of the figure, for comparison.

Section S4: ICP-CHN-EDS analyses

Table S4: CHN analyses, ICP analyses and EDS analyses of all pure phases obtained in Table 1.

Entry	Phase	Formula	CHN Analyses found (calculated)			ICP Analyses		EDS Analyses	
			%C	%H	%N	%Zn	%Co	%Zn	%Co
1	TMPF-91	Zn_2(hfipbb)(triazole)$_2$	38.11 (37.42)	2.37 (1.94)	12.25 (12.47)	17.62	-	13.55	-
2	TMPF-91	$Zn_{1.90}Co_{0.10}$(hfipbb)(triazole)$_2$	36.75 (37.42)	2.15 (1.94)	13.90 (12.47)	16.75	0.87	13.02	0.41
3	TMPF-88	Zn_3(hfipbb)$_2$(triazole)$_2$(H_2O)	39.19 (39.51)	1.89 (2.01)	7.24 (7.27)	16.70	-	10.32	-
4	TMPF-88	$Zn_{2.98}Co_{0.02}$(hfipbb)$_2$(triazole)$_2$(H_2O)	40.95 (39.51)	2.20 (2.01)	6.78 (7.27)	16.86	0.10	13.53	-
5	TMPF-88	$Zn_{2.96}Co_{0.04}$(hfipbb)$_2$(triazole)$_2$(H_2O)	41.11 (39.51)	2.11 (2.01)	6.80 (7.27)	16.76	0.20	12.87	-
6	TMPF-90	$Zn_{2.96}Co_{0.04}$(hfipbb)$_2$(triazole)$_2$(H_2O)	41.20 (39.51)	2.18 (2.01)	6.82 (7.27)	16.75	0.20	13.64	-
7	TMPF-90	$Zn_{0.86}Co_{1.14}$(triazole)$_3$(CH_3CH_2O)	24.12 (23.29)	1.76 (1.67)	36.05 (38.80)	15.19	17.84	8.15	9.15
8	TMPF-90	$Zn_{1.10}Co_{0.90}$(triazole)$_3$(CH_3CH_2O)	24.09 (23.29)	1.81 (1.67)	35.91 (38.80)	19.07	14.06	10.45	8.74
9	TMPF-90	$Zn_{1.21}Co_{0.79}$(triazole)$_3$(CH_3CH_2O)	23.91 (23.29)	1.79 (1.67)	35.95 (38.80)	21.37	12.57	13.84	9.26
10	TMPF-90	Co_2(triazole)$_3$(CH_3CH_2O)	23.80 (23.29)	1.88 (1.67)	37.64 (38.80)	-	-	-	29.13
11	TMPF-95	$Zn_{1.84}Co_{3.16}$(hfipbb)$_4$(triazole)$_2$(H_2O)	42.87 (42.87)	1.94 (1.90)	4.51 (4.17)	5.94	9.20	6.16	9.46

Section S5: N_2 sorption isotherm

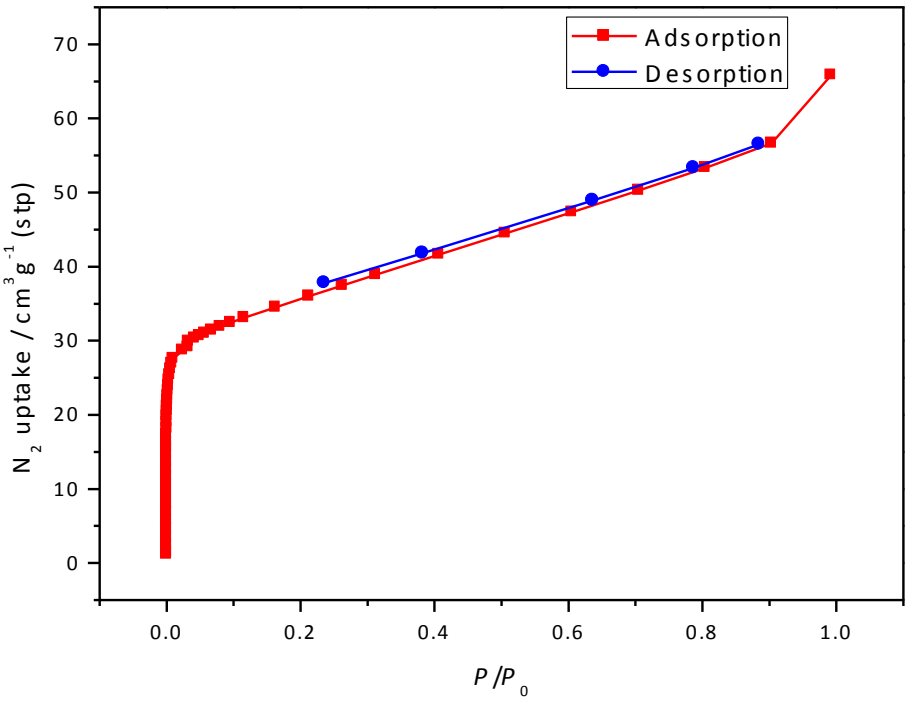

Figure S12. Gas sorption isotherm for TMPF-88 showing adsorption (red) and desorption isotherm (blue) curves.

Section S6: Infrared Spectroscopy

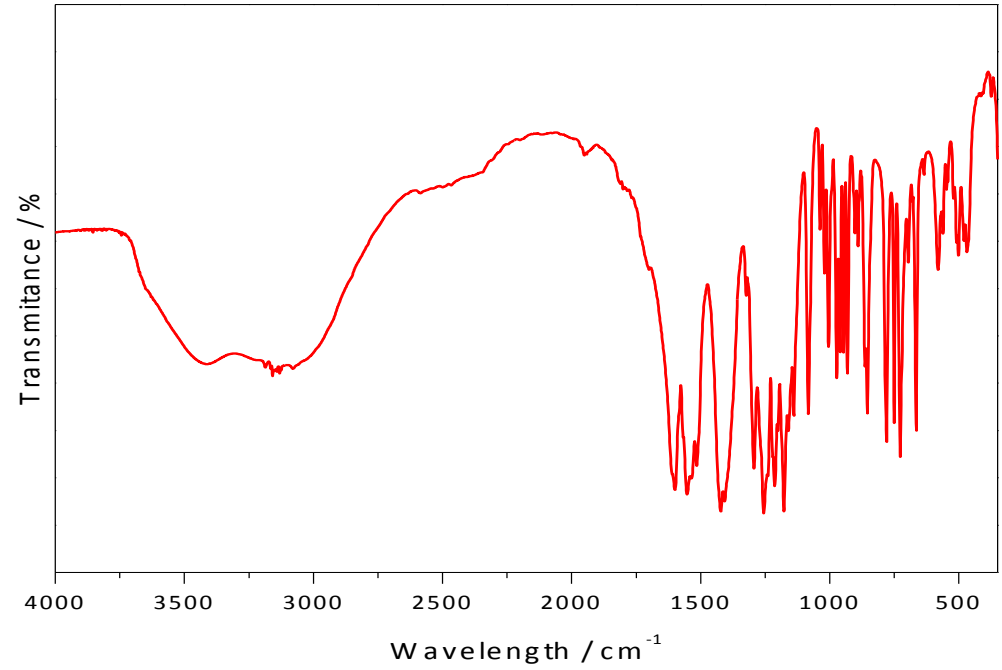

Figure S13. FT-Infrared spectra for TMPF-88 material, in the 4000-450 cm^{-1} range.

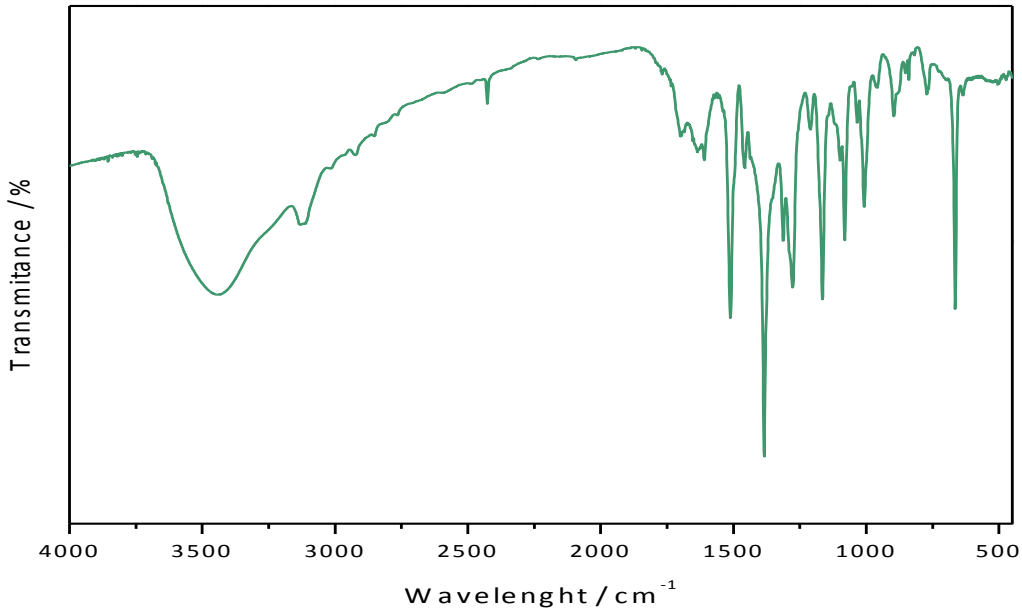

Figure S14. FT-Infrared spectra for TMPF-90 material, in the 4000-450 cm^{-1} range.

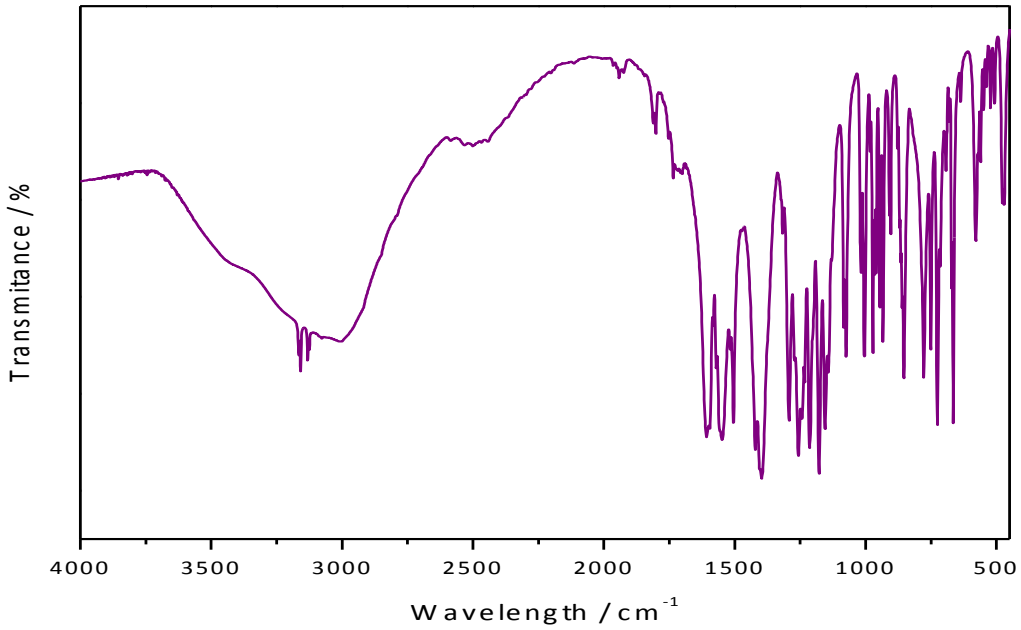

Figure S15. FT-Infrared spectra for TMPF-91 material, in the 4000-450 cm^{-1} range.

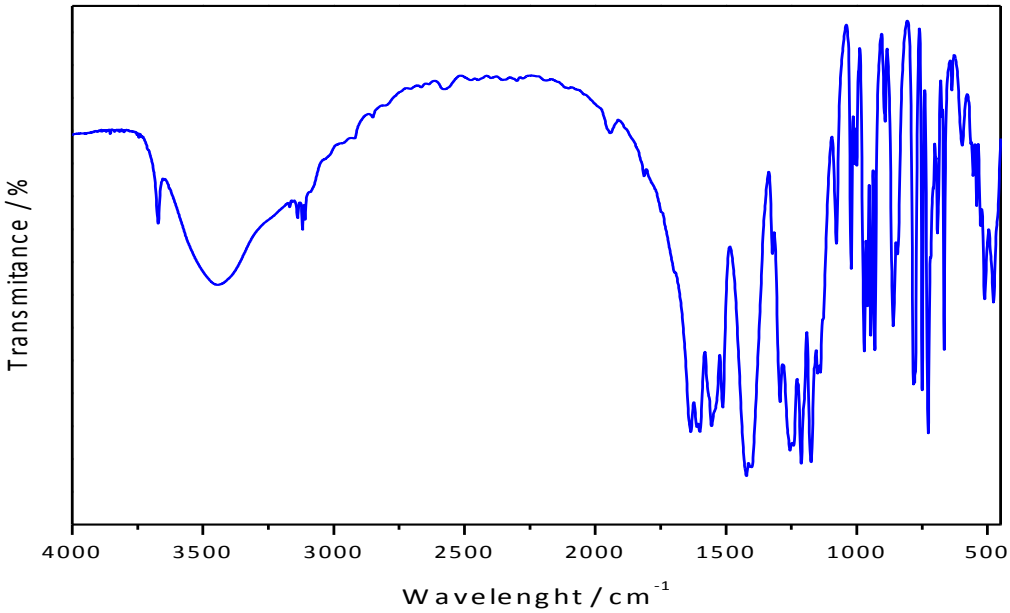

Figure S16. FT-Infrared spectra for TMPF-95 material, in the 4000-450 cm^{-1} range.

Section S7: Thermal Gravimetric analyses

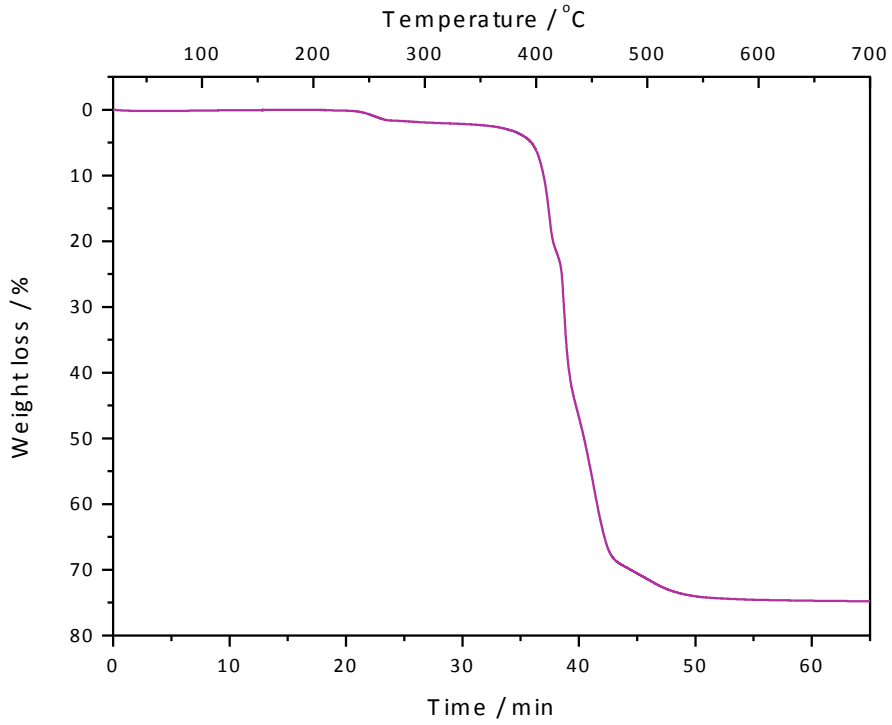

Figure S17 Termogravimetric profile for $Zn_3(hfipbb)_2(triazole)_2(H_2O)$.

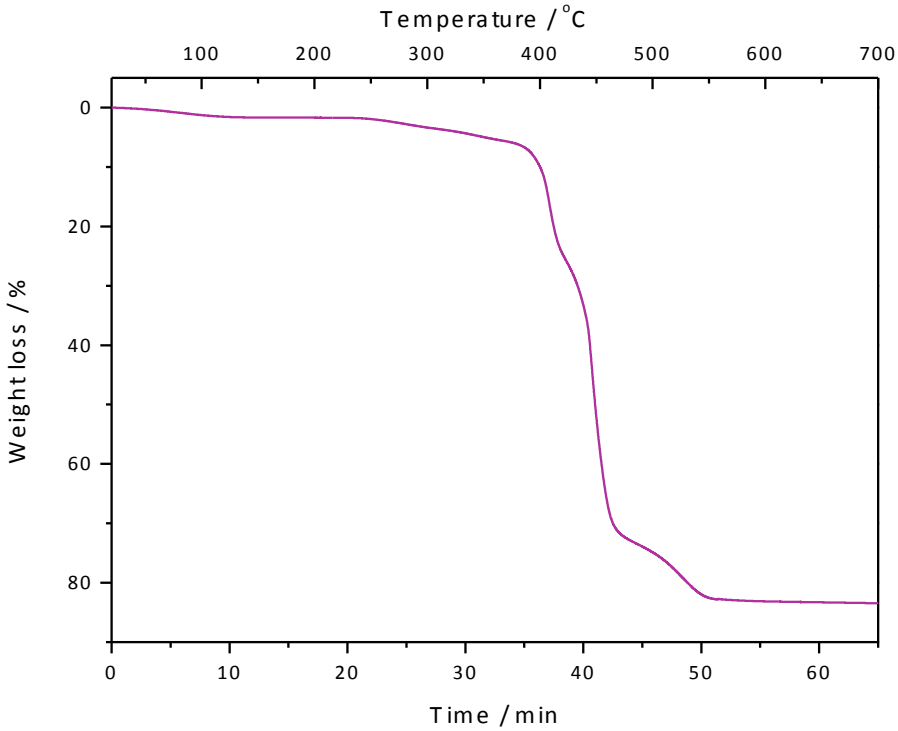

Figure S18. Termogravimetric profile for $Zn_{2.98}Co_{0.02}(hfipbb)_2(triazole)_2(H_2O)$.

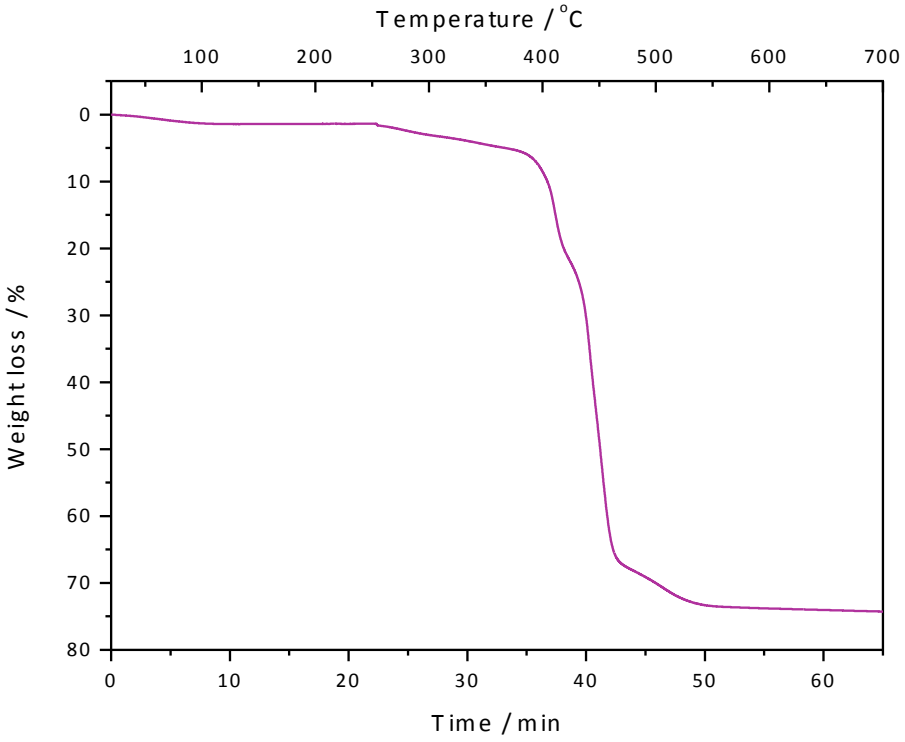

Figure S19. Termogravimetric profile for $Zn_{2.96}Co_{0.04}(hfipbb)_2(triazole)_2(H_2O)$.

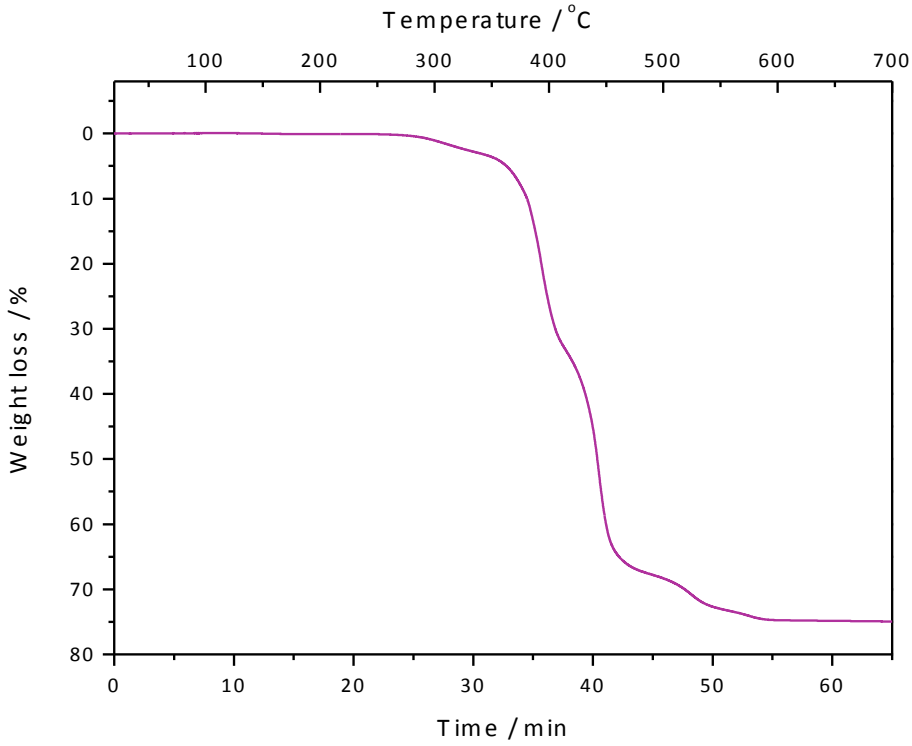

Figure S20. Thermogravimetric profile for $Zn_2(hfipbb)(triazole)_2$

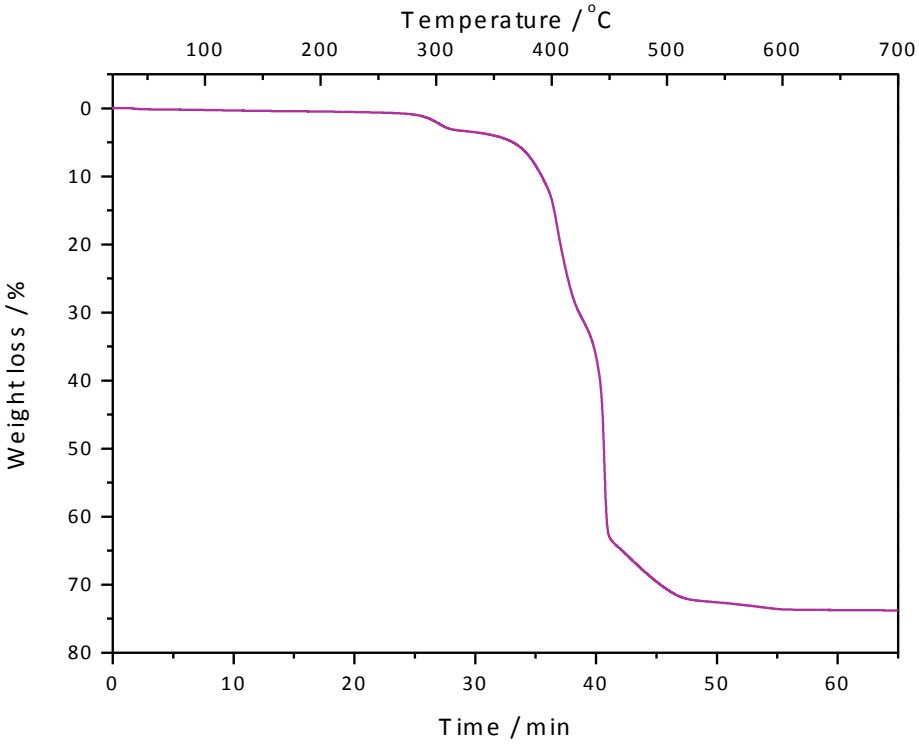

Figure S21. Thermogravimetric profile for $Zn_{1.90}Co_{0.10}$(hfipbb)(triazole)$_2$

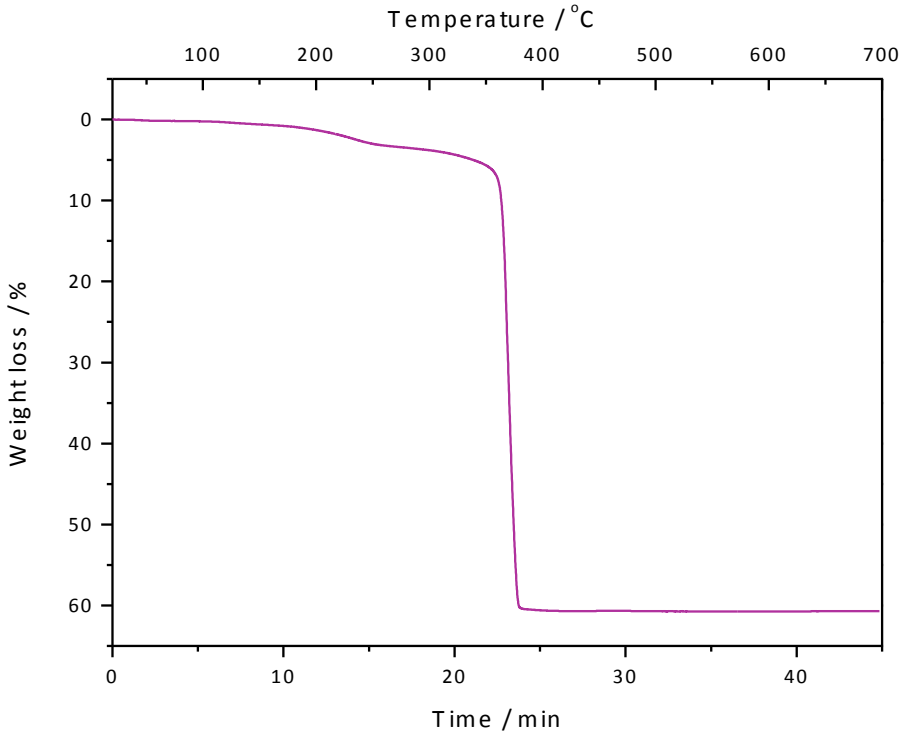

Figure S22. Thermogravimetric profile for $Zn_{1.14}Co_{0.88}$(triazole)$_3$(CH_3CH_2O)

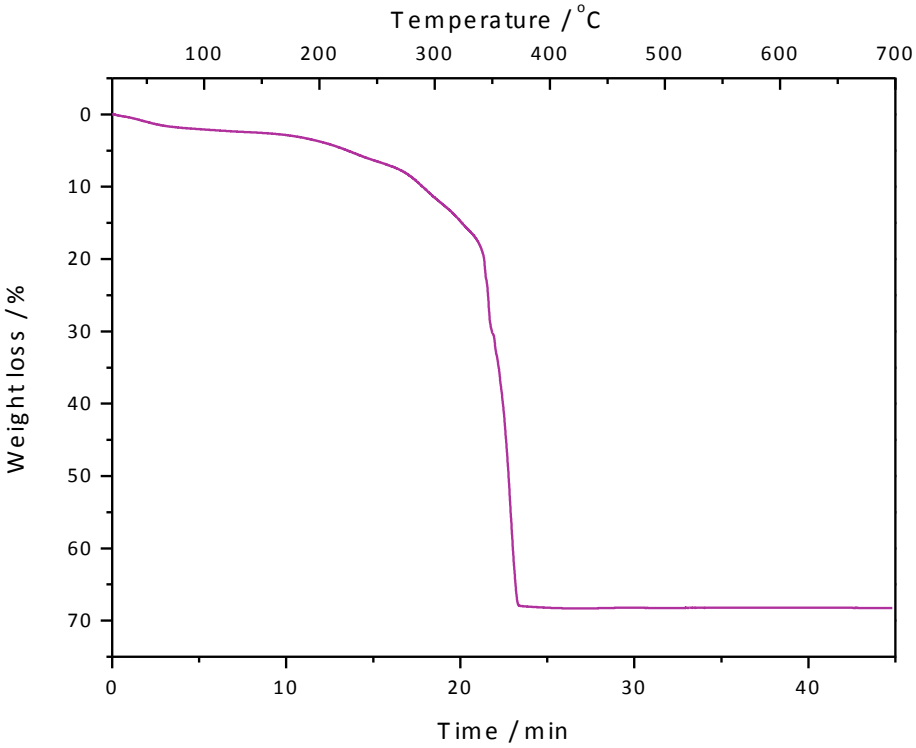

Figure S23. Thermogravimetric profile for $Zn_{1.10}Co_{0.90}(triazole)_3(CH_3CH_2O)$

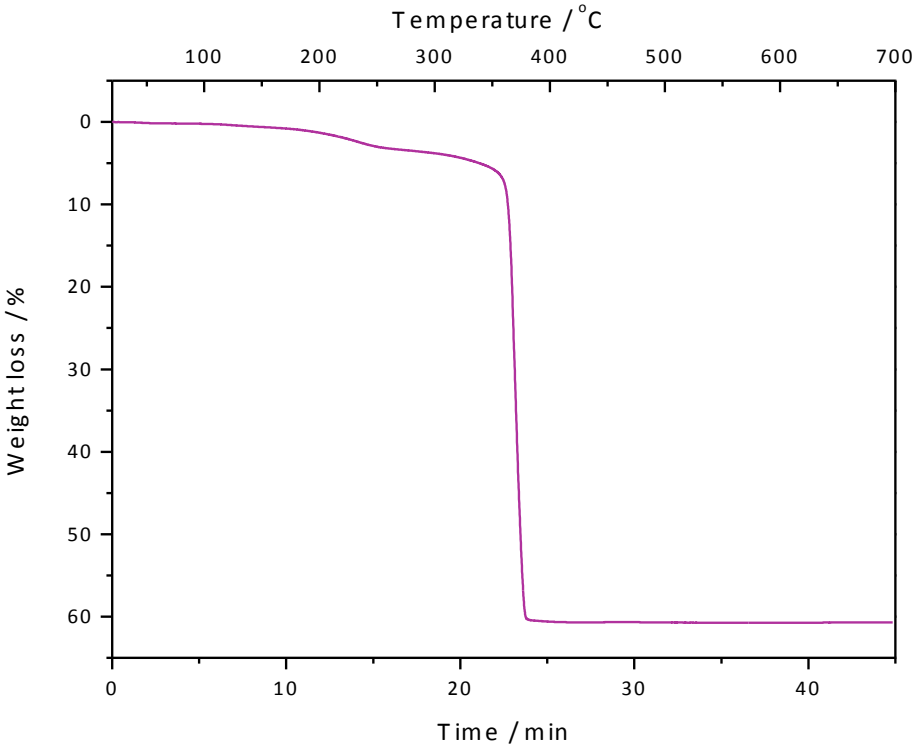

Figure S24. Thermogravimetric profile for $Zn_{1.21}Co_{0.79}(triazole)_3(CH_3CH_2O)$

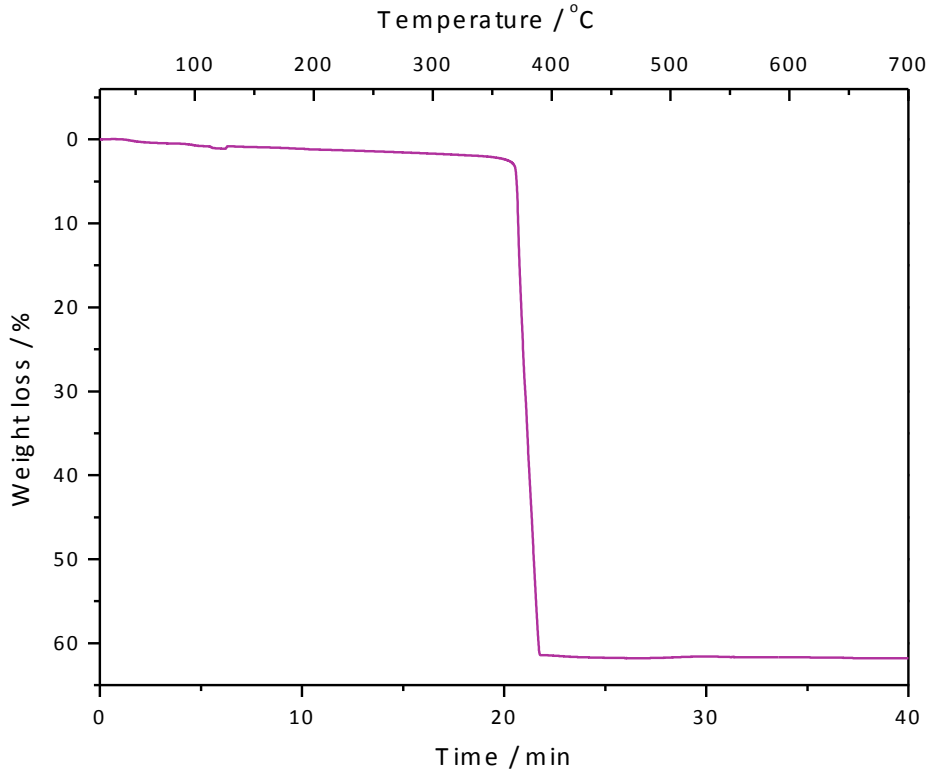

Figure S25. Thermogravimetric profile for $Co_2(triazole)_3(CH_3CH_2O)$

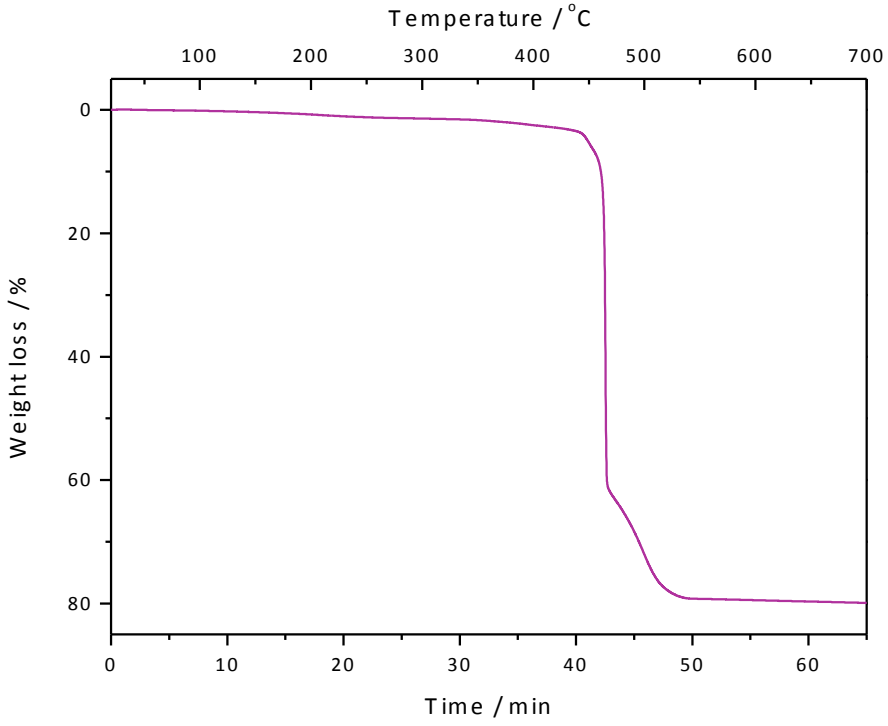

Figure S26. Thermogravimetric profile for $Zn_{1.84}Co_{3.16}(hfipbb)_4(triazole)_2(H_2O)$