Table SI 1. Comparison of the atomic coordinates of $^{2}_{\infty}[Zn(ccdc)_2] \cdot 4\ H_2O$ (*I* $4_1/a$) with the coordinates of $^{2}_{\infty}[Zn(ccdc)_2] \cdot 0.75\ H_2O$ (*I* 112/*b*, right column). In the left column the coordinates are given together with a set of symmetry equivalent coordinates.

	$^{2}_{\infty}[Zn(ccdc)_2] \cdot 4\ H_2O$ *I* $4_1/a$			$^{2}_{\infty}[Zn(ccdc)_2] \cdot 0.75\ H_2O$ *I* 112/*b* [#]		
	x	y	z	x	y	z
Co1	1/2	3/4	0.44006(2)	**Co1** 1/2	3/4	0.44006(4)
C1	0.6343(2)	0.6169(2)	0.41722(9)	**C1** 0.6346(6)	0.6269(6)	0.4176(2)
C2	0.6368(3)	0.6317(3)	0.47129(9)	**C2** 0.6366(7)	0.6421(6)	0.4716(2)
C3	0.6667(3)	0.7634(3)	0.48235(10)	**C3** 0.6653(7)	0.7772(6)	0.4832(2)
C4	0.6815(3)	0.8308(3)	0.43559(10)	**C4** 0.6785(5)	0.8462(5)	0.4355(2)
C5	0.6624(3)	0.7418(2)	0.39579(10)	**C5** 0.6631(5)	0.7536(5)	0.3956(2)
C6	0.5973(2)	0.4967(2)	0.38834(9)	**C6** 0.6026(6)	0.5028(6)	0.3886(2)
O1	0.6060(2)	0.4979(2)	0.34150(7)	**O1** 0.6201(5)	0.5032(5)	0.3417(2)
O2	0.5600(2)	0.4015(2)	0.41527(6)	**O2** 0.5589(5)	0.4061(4)	0.4156(2)
Zn1	1/2	1/4	3/8	**Zn1** 1/2	1/4	0.37433(4)
O3	0.6291(4)	0.7029(4)	0.2664(1)	**O5*** 0.637(2)	0.714(2)	0.2664(9)
				O6* 0	3/4	0.511(2)
Symmetry equivalent positions 3/4–y, x–1/4, 3/4–z						
Co1'	0	1/4	0.30994	**Co2** 0	1/4	0.30991(4)
C1'	0.1331	0.3843	0.33278	**C7** 0.1456(6)	0.3810(6)	0.3319(2)
C2'	0.1183	0.3868	0.27871	**C8** 0.1285(7)	0.3866(6)	0.2777(2)
C3'	-0.0134	0.4167	0.26765	**C9** -0.0020(7)	0.4196(6)	0.2679(2)
C4'	-0.0808	0.4315	0.31441	**C10** -0.0634(7)	0.4336(6)	0.3153(2)
C5'	0.0082	0.4124	0.35421	**C11** 0.0237(7)	0.4106(7)	0.3552(2)
C6'	0.2533	0.3473	0.36166	**C12** 0.2610(6)	0.3404(6)	0.3604(2)
O1'	0.2521	0.3560	0.40850	**O3** 0.2574(5)	0.3386(5)	0.4075(2)
O2'	0.3485	0.3100	0.33473	**O4** 0.3545(4)	0.3077(4)	0.3324(2)

[#] non-conventional setting of space group *C* 2/*c* (unique axis *c*, cell choice 3 according to International Tables)
* oxygen atoms of solvent water molecules with reduced occupation factor: O5 0.25; O6 0.125

Table SI 2. Comparison of the atomic coordinates of $^{2}_{\infty}$[Zn(ccdc)$_2$] · 4 H_2O (*I* $4_1/a$) with the coordinates of $^{2}_{\infty}$[Cu(ccdc)$_2$] · 1.5 MeOH (*P* 4_1). In the second column a coordinate shift (+1/4, 0, 0) is applied and three sets of symmetry equivalent coordinates are generated, that correspond to the coordinates in $^{2}_{\infty}$[Cu(ccdc)$_2$] · 1.5 MeOH (right column).

$^{2}_{\infty}$[Zn(ccdc)$_2$] · 4 H_2O *I* $4_1/a$				Coordinate shift (+0.25, 0, 0)			$^{2}_{\infty}$[Cu(ccdc)$_2$] · 1.5 MeOH *P* 4_1			
	x	y	z	x_{trans}	y_{trans}	z_{trans}		x	y	z
C1	0.6343(2)	0.6169(2)	0.41722(9)	0.8843(2)	0.6169(2)	0.41722(9)	**C1**	0.9071(6)	0.6732(6)	0.4974(3)
C2	0.6368(3)	0.6317(3)	0.47129(9)	0.8868(3)	0.6317(3)	0.47129(9)	**C5**	0.8732(6)	0.6998(6)	0.5576(3)
C3	0.6667(3)	0.7634(3)	0.48235(10)	0.9167(3)	0.7634(3)	0.48235(10)	**C4**	0.8959(6)	0.8308(6)	0.5675(3)
C4	0.6815(3)	0.8308(3)	0.43559(10)	0.9315(3)	0.8308(3)	0.43559(10)	**C3**	0.9444(6)	0.8857(6)	0.5150(3)
C5	0.6624(3)	0.7418(2)	0.39579(10)	0.9124(3)	0.7418(2)	0.39579(10)	**C2**	0.9510(6)	0.7888(6)	0.4710(3)
C6	0.5973(2)	0.4967(2)	0.38834(9)	0.8473(2)	0.4967(2)	0.38834(9)	**C6**	0.8823(6)	0.5495(6)	0.4665(3)
Co1	0.5	0.75	0.44006(2)	0.75	0.75	0.44006(2)	**Co1**	0.76942(8)	0.80699(8)	0.50022(3)
O1	0.6060(2)	0.49792(18)	0.34150(7)	0.8560(2)	0.4979(2)	0.34150(7)	**O2**	0.8974(5)	0.5445(4)	0.4121(2)
O2	0.5600(2)	0.40150(16)	0.41527(6)	0.8100(2)	0.4015(2)	0.41527(6)	**O1**	0.8466(4)	0.4612(4)	0.5000(2)
Zn1	0.5	0.25	0.375	0.75	0.25	0.375	**Cu1**	0.77543(7)	0.30990(7)	0.46486(4)
				Symmetry equivalent positions 1.5–x, 1.5–y, z						
C1'				0.6157(2)	0.8830(2)	0.41722(9)	**C7**	0.6427(6)	0.9471(6)	0.4848(3)
C2'				0.6132(3)	0.8683(3)	0.47129(9)	**C11**	0.6592(7)	0.8727(6)	0.4322(3)
C3'				0.5833(3)	0.7366(3)	0.4824(1)	**C10**	0.6244(7)	0.7449(7)	0.4471(3)
C4'				0.5685(3)	0.6692(3)	0.4356(1)	**C9**	0.5862(7)	0.7417(7)	0.5075(3)
C5'				0.5876(3)	0.7582(2)	0.3958(1)	**C8**	0.5982(6)	0.8664(7)	0.5314(3)
C6'				0.6527(2)	1.0033(2)	0.38834(9)	**C12**	0.6767(6)	1.0862(6)	0.4910(3)
O1'				0.6440(2)	1.0021(2)	0.34150(7)	**O3**	0.6671(6)	1.1329(5)	0.5407(2)
O2'				0.6900(2)	1.0985(2)	0.41527(6)	**O4**	0.7083(4)	1.1417(4)	0.4443(2)
				Symmetry equivalent positions y–0.5, 1–x, 0.75–z						
C1''				0.1169(2)	0.1157(2)	0.33278(9)	**C13**	0.1507(6)	0.1877(6)	0.4593(3)
C2''				0.1317(3)	0.1132(3)	0.27871(9)	**C14**	0.1863(6)	0.1769(6)	0.3993(3)
C3''				0.2634(3)	0.0833(3)	0.2677(1)	**C15**	0.3201(6)	0.1568(7)	0.3970(4)
C4''				0.3308(3)	0.0685(3)	0.3144(1)	**C16**	0.3672(6)	0.1555(7)	0.4557(4)
C5''				0.2418(2)	0.0876(3)	0.3542(1)	**C17**	0.2636(6)	0.1767(7)	0.4938(3)
C6''				-0.0033(2)	0.1527(2)	0.36166(9)	**C18**	0.0212(6)	0.2173(6)	0.4809(3)
Co1''				0.25	0.25	0.30994(2)	**Co2**	0.28048(8)	0.32407(9)	0.43726(3)
O1''				-0.0021(2)	0.1440(2)	0.40850(7)	**O5**	-0.0026(4)	0.2102(5)	0.5345(2)
O2''				-0.0985(2)	0.1900(2)	0.33473(6)	**O6**	-0.0583(4)	0.2479(5)	0.4414(2)
				Symmetry equivalent positions 1–y, x–0.5, 0.75–z						
C1'''				0.3831(2)	0.3843(2)	0.33278(9)	**C19**	0.4209(6)	0.4540(6)	0.4283(3)
C2'''				0.3683(3)	0.3868(3)	0.27871(9)	**C23**	0.3498(6)	0.4754(7)	0.4819(3)
C3'''				0.2366(3)	0.4167(3)	0.2677(1)	**C22**	0.2192(6)	0.4985(6)	0.4654(3)
C4'''				0.1692(3)	0.4315(3)	0.3144(1)	**C21**	0.2101(7)	0.4871(6)	0.4018(3)
C5'''				0.2582(2)	0.4124(3)	0.3542(1)	**C20**	0.3347(7)	0.4603(6)	0.3800(3)
C6'''				0.5033(2)	0.3473(2)	0.36166(9)	**C24**	0.5569(6)	0.4131(6)	0.4258(3)
O1'''				0.5021(2)	0.3560(2)	0.40850(7)	**O7**	0.6056(4)	0.3834(4)	0.4743(2)
O2'''				0.5985(2)	0.3400(2)	0.33473(6)	**O8**	0.6088(5)	0.4107(7)	0.3780(2)

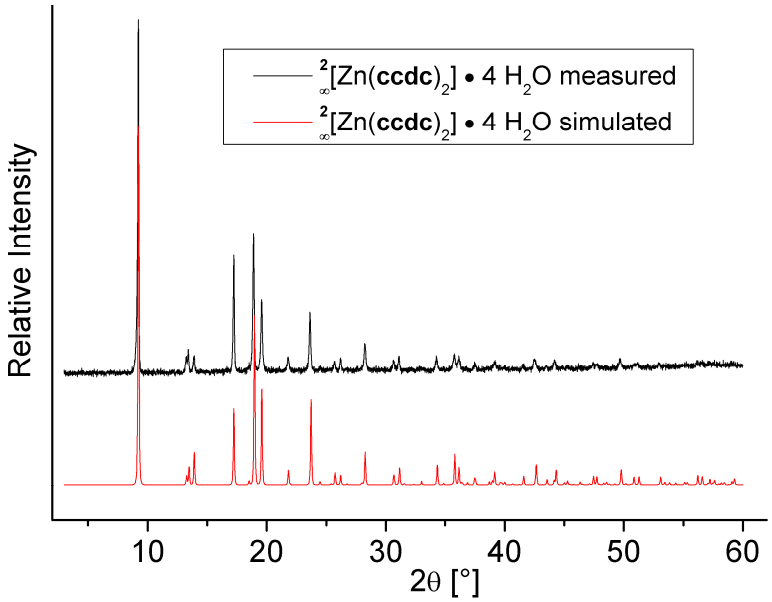

Figure SI 1. X-Ray powder diffraction patterns of $^2_\infty$[Zn(ccdc)$_2$] · 4 H$_2$O (**2** · 4 H$_2$O) at room temperature (λ(Cu-K$_{α1}$) = 154.0598 pm): red - simulated from single crystal data; black - as synthesized material, measured.

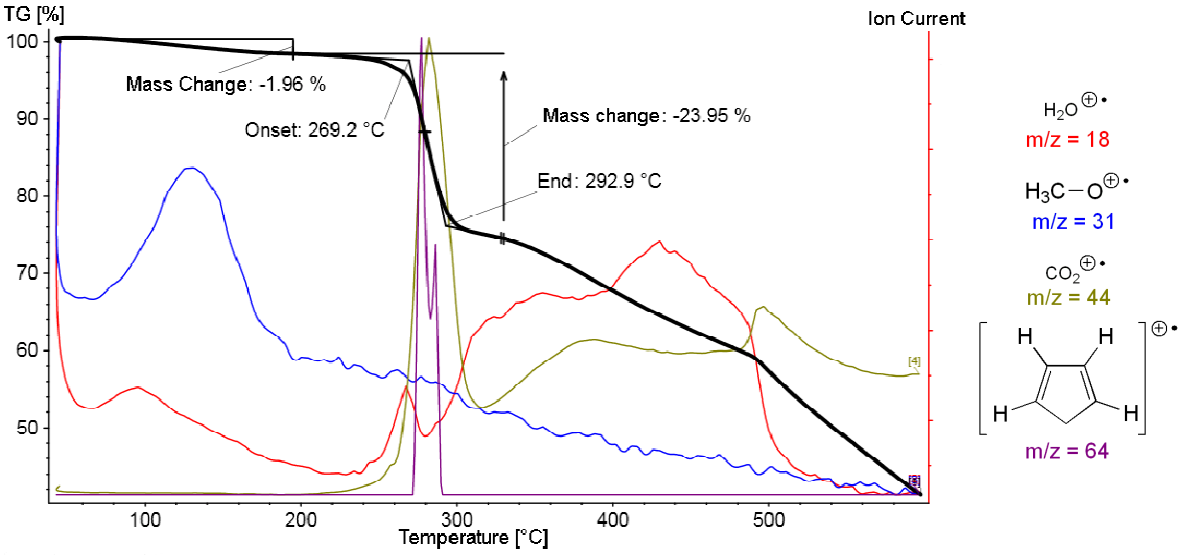

Figure SI 2. TG curve (black) of $^2_\infty$[Zn(ccdc)$_2$] · 4 H$_2$O (**2** · 4 H$_2$O) incl. mass loss steps, onset and offset temperatures and selected m/z-signals from the online TG-MS-coupling (each m/z signal is scaled individually for better visibility; molecule fragments corresponding to m/z depicted right); heating rate 10 K/min, helium atmosphere.

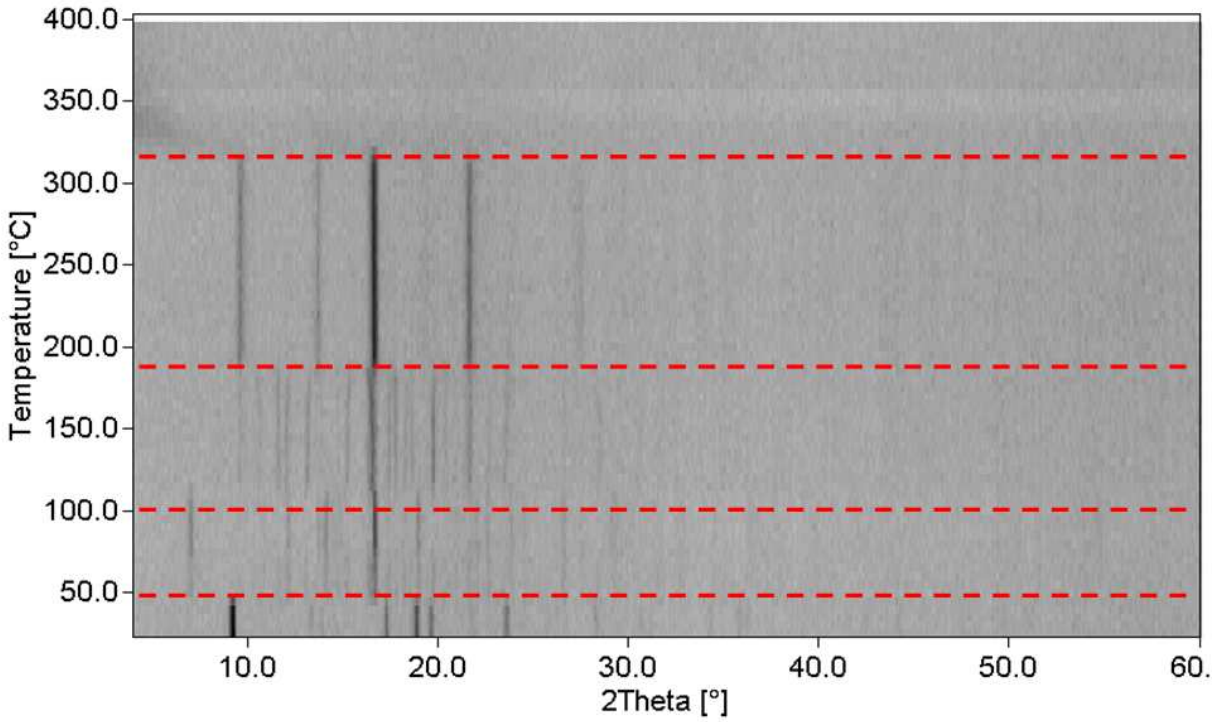

Figure SI 3. Temperature dependent X-Ray powder diffraction pattern of $^{2}_{\infty}[Zn(ccdc)_2] \cdot 4\,H_2O$ (**2** · 4 H_2O) from room temperature to 400 °C; Cu-$K_{\alpha 1}$ radiation (λ = 154.0598 pm).

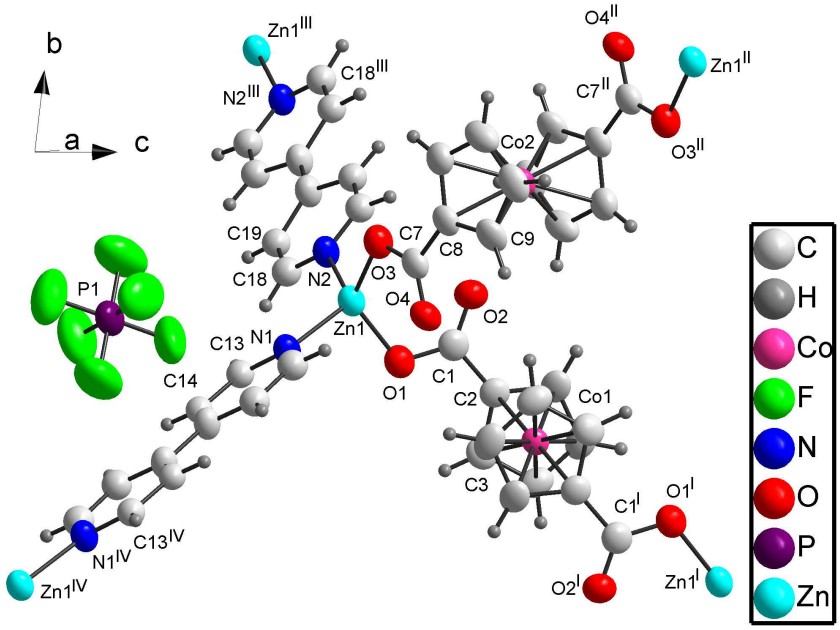

Figure SI 4 Fragment of the crystal structure of $^{3}_{\infty}$[Zn(ccdc)(bipy)]PF_6 (**4**, 50 % ellipsoids, rotational disorder in pyridyl groups not shown)
Symmetry operations I: 1-x, -y, 2-z; II: -x, 1-y, 2-z; III: 2-x, 1-y, 1-z; IV: -x, -y, 1-z
Selected bond lengths and angles:
Zn1-O1 195.5(4); Zn1-O3; 196.0(4); Zn1-N1 208.2(5); Zn1-N2 208.0(4); C1-O1 131.8(6); C1-O2 123.5(7); C7-O3 129.3(6); C7-O4 123.3(6) pm;
O1-Zn1-O3 125.8(2); O1-Zn1-N1 101.4(2); O1-Zn1-N2 102.6(2); N1-Zn1-N2 116.7(2); O3-Zn1-N1 108.2(2); O3-Zn1-N2 102.9(2) °

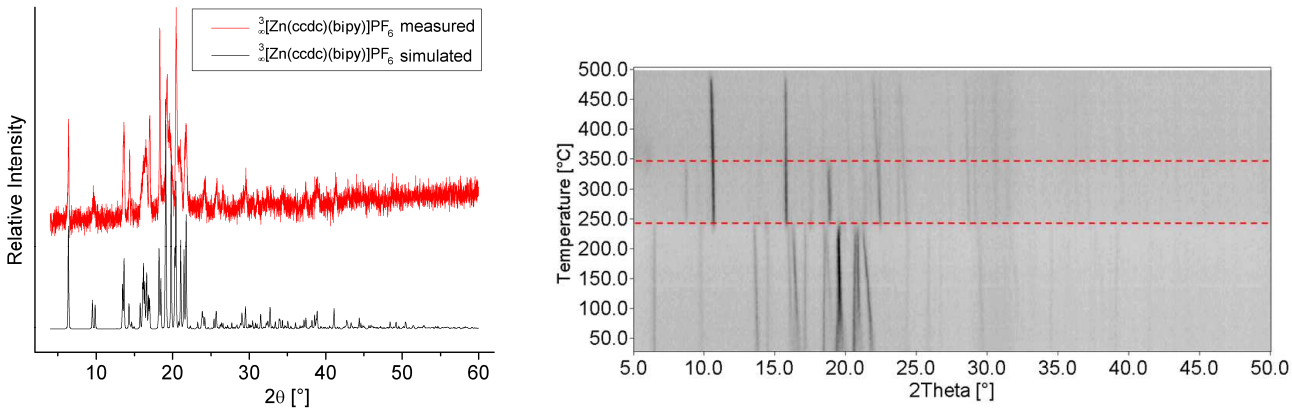

Figure SI 5. X-Ray powder diffraction pattern of $^{3}_{\infty}$[Zn(ccdc)(bipy)]PF_6 (**4**);
left: Simulation based on single crystal data (black) and measured diffraction pattern (red);
right: Temperature dependent diffraction pattern of **4**; λ(Cu-$K_{\alpha 1}$) = 154.0598 pm.

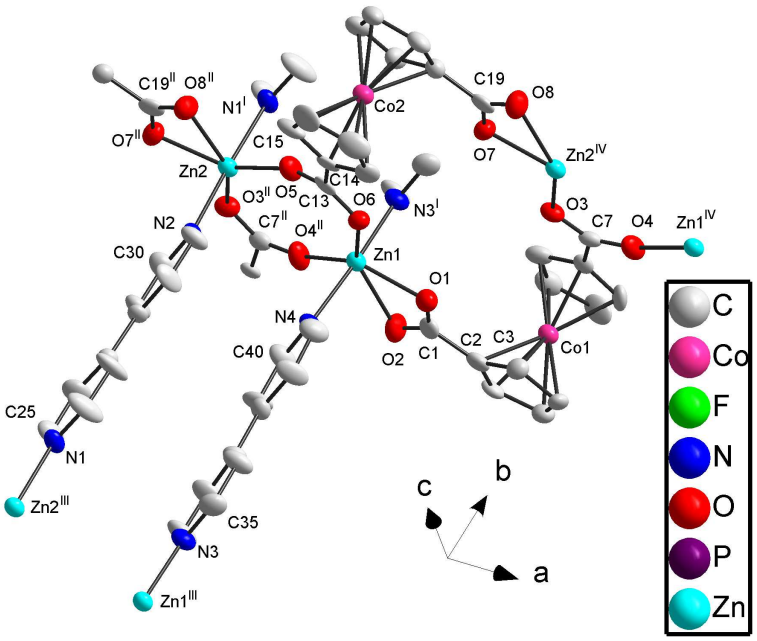

Figure SI 6. Fragment of the crystal structure of $^{2}_{\infty}$[Zn(ccdc)(bipy)]PF_6 (**5**, 50 % ellipsoids); Symmetry operations I: x, 1+y, z; II: -0,5+x, 1,5-y, z; III: x, -1+y, z; IV: 0,5+x, 1,5-y, z

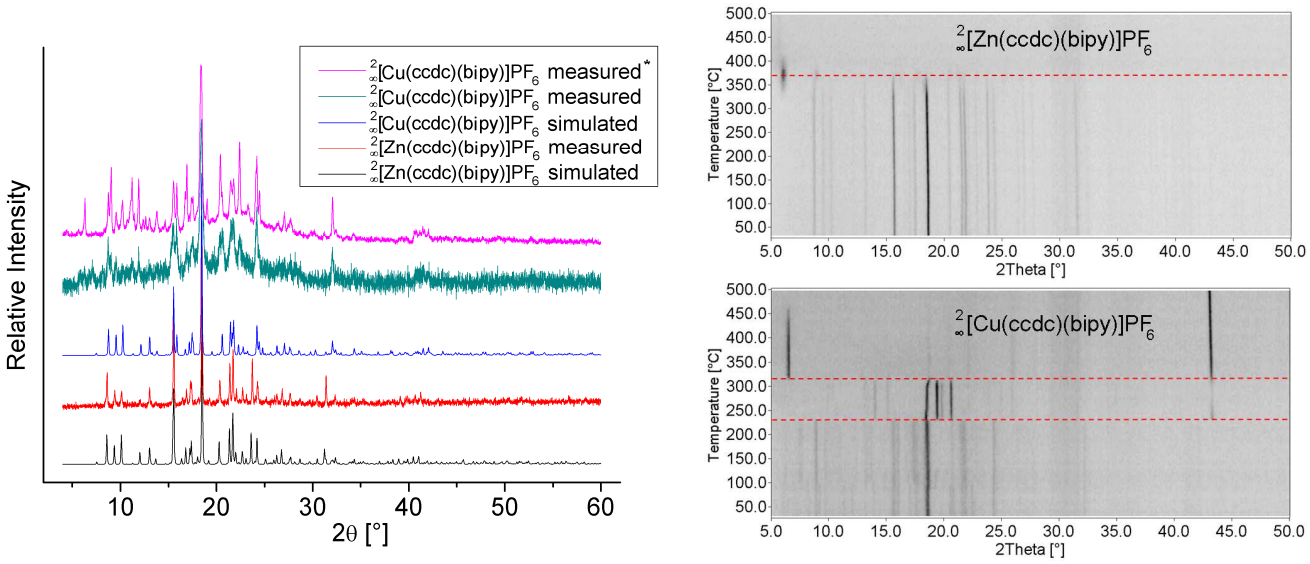

Figure SI 7. X-Ray powder diffraction pattern of $^{2}_{\infty}$[Zn(ccdc)(bipy)]PF_6 (**5**) and $^{2}_{\infty}$[Cu(ccdc)(bipy)]PF_6 (**6**)
left: Simulation based on single crystal data (black for **5** and blue for **6**) and measured diffraction patterns (red for **5**); the pink diffraction pattern (*) belongs to a sample of **6** synthesized in presence of additional KPF_6.
right: Temperature dependent diffraction patterns of **5** and **6**; λ(Cu-$K_{\alpha1}$) = 154.0598 pm.