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Supplementary Material

Chiral Coordination Polymers of Mandelate and its Derivatives: Tuning Crystal Packing by Modulation of Hydrogen Bonding

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Table S1. Crystallographic parameters compounds **1-3** in this study.

Compound	**[Ni(*R*-man)$_2$(bpb)(H$_2$O)] (1)**	**[Co(*R*-Man)$_2$(dpt)(H$_2$O)] (2)**	**[Co(*S*-Man)$_2$(dptztz)(H$_2$O)] (3)**
Formula	$C_{32}H_{28}N_2NiO_7$	$C_{28}H_{24}CoN_6O_7$	$C_{30}H_{24}CoN_4O_7S_2$
Formula Weight	611.27	615.46	675.58
Temperature (K)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	triclinic
Space Group	$P2_1$	$P2_1$	$P1$
***a* (Å)**	5.7090(11)	5.7030(11)	5.6100(11)
***b* (Å)**	15.069(3)	14.430(3)	8.0200(16)
***c* (Å)**	15.578(3)	15.405(3)	16.030(3)
α (°)	90	90	84.22(3)
β (°)	98.51(3)	98.06(3)	80.45(3)
γ (°)	90	90	88.94(3)
Cell Volume (Å^3)	1325.4(5)	1255.2(4)	707.6(3)
Z	2	2	1
ρ_{calc}g/cm^3	1.532	1.628	1.585
μ/mm^{-1}	0.788	0.748	0.811
F(000)	636.0	634.0	347.0
Crystal size/mm^3	0.06 × 0.04 × 0.02	0.02 × 0.015 × 0.013	0.12 × 0.08 × 0.08
Radiation	Synchrotron (λ = 0.71073)	Synchrotron (λ = 0.71050)	Synchrotron (λ = 0.71073)
Reflections collected	8637	21810	13593
Independent reflections	4815 [R_{int} = 0.0751, R_{sigma} = 0.0895]	6815 [R_{int} = 0.0388, R_{sigma} = 0.0336]	5688 [R_{int} = 0.0207, R_{sigma} = 0.0235]
Data/restraints /parameters	4815/1/384	6815/4/387	5688/6/396
GooF	1.083	1.037	1.139
R_1, wR$_2$ (I > 2σ(I))	R_1 = 0.0839, wR_2 = 0.2298	R_1 = 0.0256, wR_2 = 0.0645	R_1 = 0.0299, wR_2 = 0.0751
R_1, wR_2 (all)	R_1 = 0.0971, wR_2 = 0.2399	R_1 = 0.0257, wR_2 = 0.0646	R_1 = 0.0327, wR_2 = 0.0890
Largest diff. peak/hole/eÅ^{-3}	2.27/−0.64	0.29/−0.59	0.43/−0.79
Flack parameter	0.03(2)	−0.005(4)	0.005(5)

Table S2. Crystallographic parameters compounds **4-6** in this study.

Compound	**[Ni(2,4-difluoro-man)$_2$(bpe)] (4)**	**[Ni((*R*)-ManOMe)$_2$(bpe)] (5)**	**[Co((*R*)-ManOMe)$_2$(bpe)] (6)**
Formula	$C_{28}H_{20}F_4N_2NiO_6$	$C_{30}H_{30}N_2NiO_6$	$C_{30}H_{30}CoN_2O_6$
Formula Weight	615.17	573.27	573.49
Temperature (K)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space Group	*C*2/*c*	*C*2	*C*2
***a* (Å)**	25.335(5)	14.520(3)	14.570(3)
***b* (Å)**	9.938(2)	15.890(3)	15.830(3)
***c* (Å)**	10.850(2)	16.660(3)	16.760(3)
α (°)	90	90	90
β (°)	101.72(3)	114.03(3)	111.49(3)
γ (°)	90	90	90
Cell Volume (Å^3)	2674.8(10)	3510.6(14)	3596.9(14)
Z	4	2	4
ρ_{calc}g/cm^3	1.528	1.085	1.059
μ/mm^{-1}	0.799	0.589	0.512
F(000)	1256.0	1200.0	1196.0
Crystal size/mm^3	0.05 × 0.05 × 0.05	0.15 × 0.12 × 0.02	0.2 × 0.18 × 0.10
Radiation	Synchrotron (λ = 0.710876)	Synchrotron (λ = 0.71073)	Synchrotron (λ = 0.71073)
Reflections collected	23233	47128	48404
Independent reflections	3992 [R_{int} = 0.0895, R_{sigma} = 0.0568]	8279 [R_{int} = 0.0387, R_{sigma} = 0.0225]	8427 [R_{int} = 0.0390, R_{sigma} = 0.0242]
Data/restraints /parameters	3992/129/170	8279/1/305	8427/1/219
GooF	1.038	1.321	1.062
***R*$_1$, wR$_2$ (*I* > 2σ(*I*))**	R_1 = 0.0773, wR_2 = 0.2150	R_1 = 0.0846, wR_2 = 0.2686	R_1 = 0.0876, wR_2 = 0.2498
***R*$_1$, *wR*$_2$ (all)**	R_1 = 0.0900, wR_2 = 0.2327	R_1 = 0.0864, wR_2 = 0.2743	R_1 = 0.0911, wR_2 = 0.2543
Largest diff. peak/hole/eÅ^{-3}	1.40/−1.31	1.41/−0.69	1.83/−1.18
Flack parameter	N/A	0.09(2)	0.20(4)

Table S3. Analysis of the possible coordination geometries using the SHAPE program for the 6-coordinate M(II) centres in compounds **1-3**

Geometry	Symmetry	1 (Ni)	2 (Co)	3 (Ni)	4 (Co)
HP-6	D_{6h}	31.691	32.103	31.898	29.950
PPY-6	C_{5v}	27.135	25.191	24.849	28.569
OC-6	O_h	**0.464**	**0.717**	**0.815**	**0.455**
TPR-6	D_{3h}	14.145	13.292	13.300	15.938
JPPY-6	C_{5v}	30.893	28.867	28.474	31.611

HP-6 = Hexagon; PPY-6 = Pentagonal pyramid; OC-6 = Octahedron; TPR-6 = Trigonal prism; JPPY-6 = Johnson pentagonal pyramid 32. The minima values are indicated in bold.

Table S4. Analysis of the possible coordination geometries using the SHAPE program for the 6-coordinate M(II) centres in compounds **1-3**

Geometry	Symmetry	5 (Ni1)	5 (Ni2)	6 (Co1)	6 (Co2)
HP-6	D_{6h}	31.424	31.989	33.553	32.863
PPY-6	C_{5v}	26.746	26.452	24.614	24.525
OC-6	O_h	**0.547**	**0.751**	**1.398**	**1.293**
TPR-6	D_{3h}	14.412	12.797	10.934	11.345
JPPY-6	C_{5v}	30.292	30.200	27.862	27.893

HP-6 = Hexagon; PPY-6 = Pentagonal pyramid; OC-6 = Octahedron; TPR-6 = Trigonal prism; JPPY-6 = Johnson pentagonal pyramid 32. The minima values are indicated in bold.

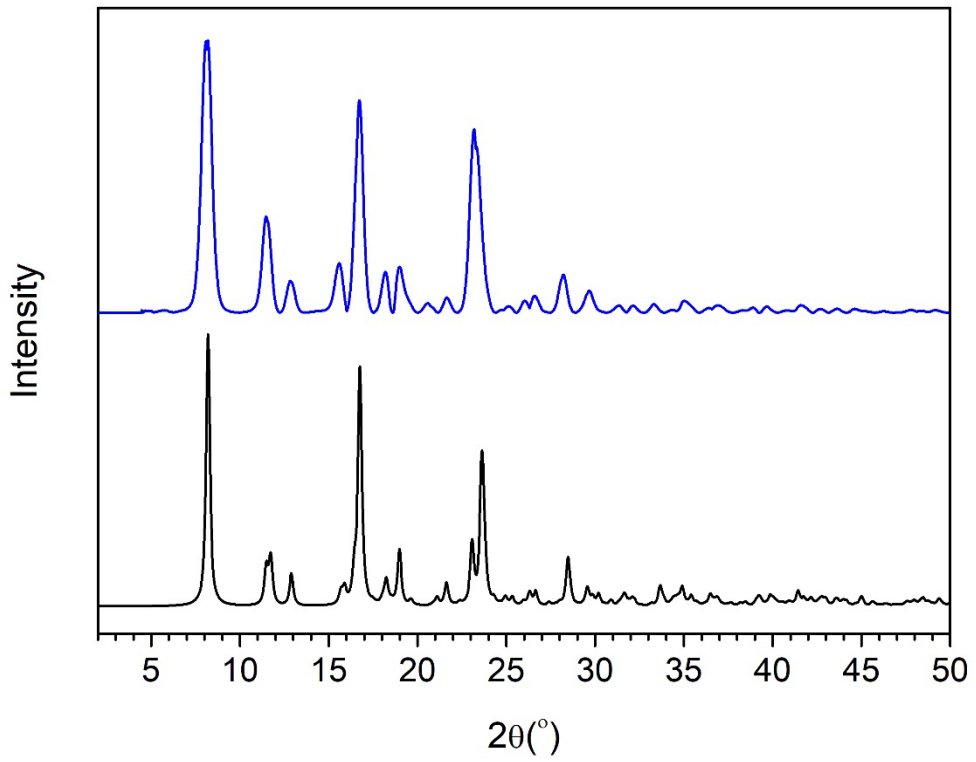

Figure S1. PXRD of [Ni(R-Man)$_2$(bpb)(H$_2$O)] (**1**) (blue) between 2 and 50° 2θ versus the calculated pattern (black).

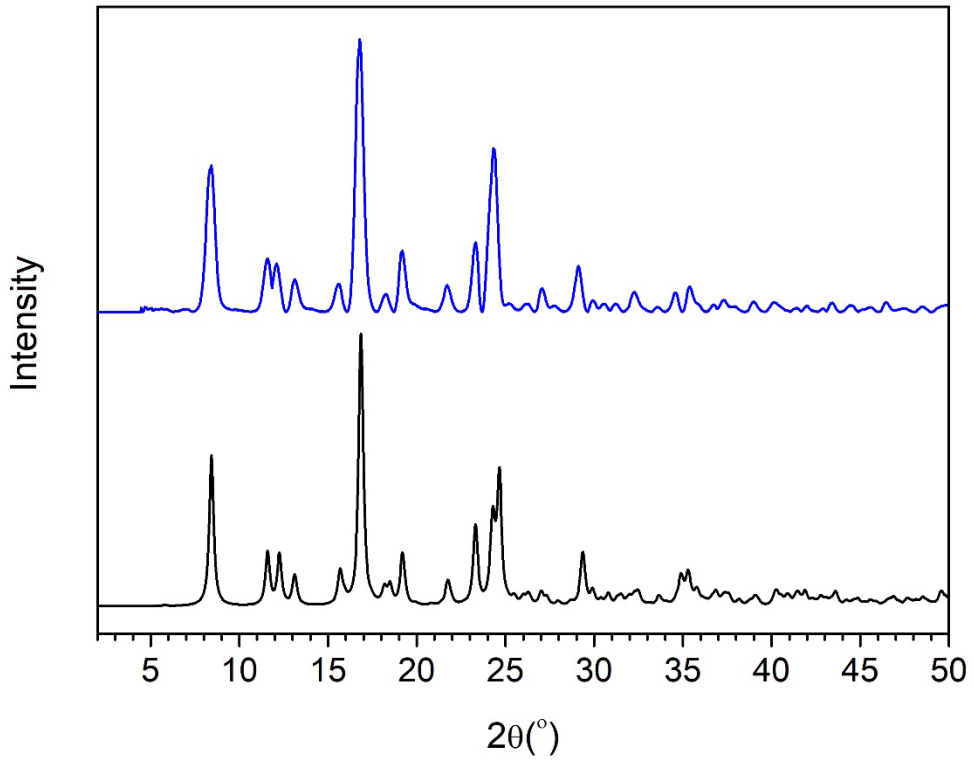

Figure S2. PXRD of [Co(*R*-Man)$_2$(bpt)(H$_2$O)] (**2**) (blue) between 5 and 50° 2θ versus the calculated pattern (black).

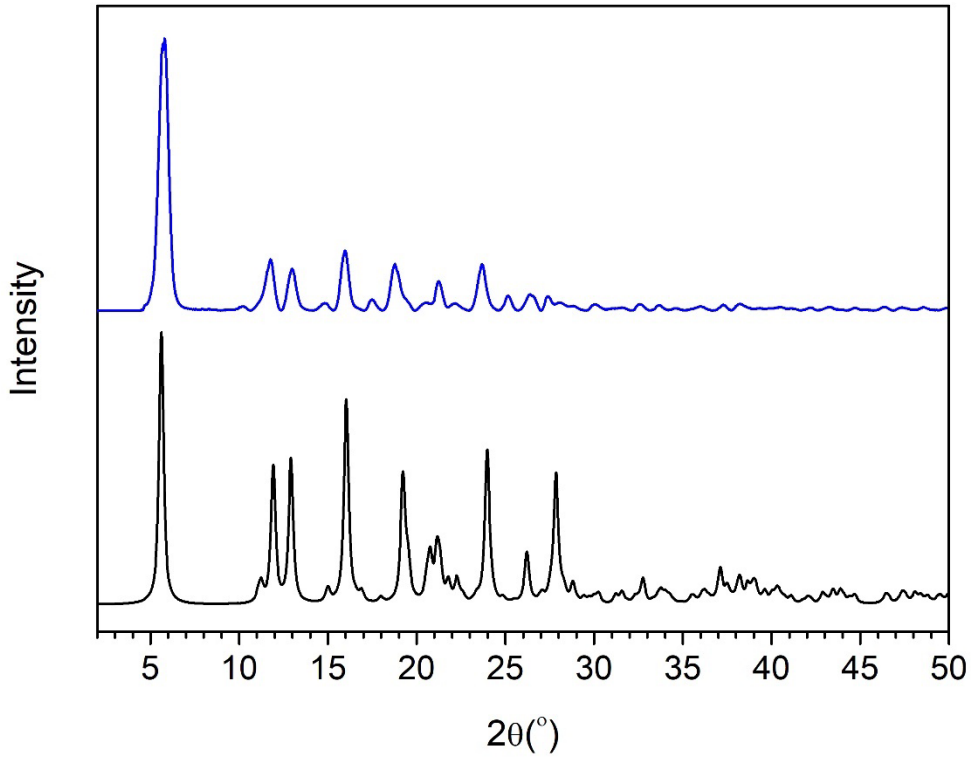

Figure S3. PXRD of [Co(*S*-Man)$_2$(dptztz)(H$_2$O)] (**3**) (blue) between 5 and 50° 2θ versus the calculated pattern (black).

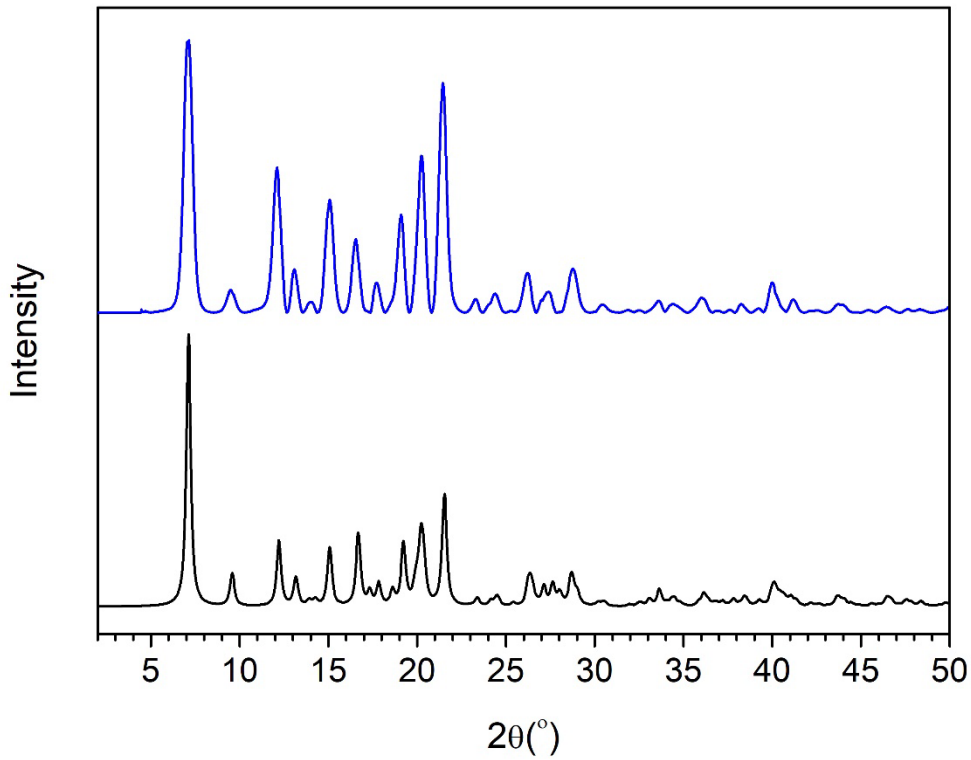

Figure S4. PXRD of [Ni(F$_2$Man)$_2$(bpe)] (**4**) (blue) between 5 and 50° 2θ versus the calculated pattern (black).

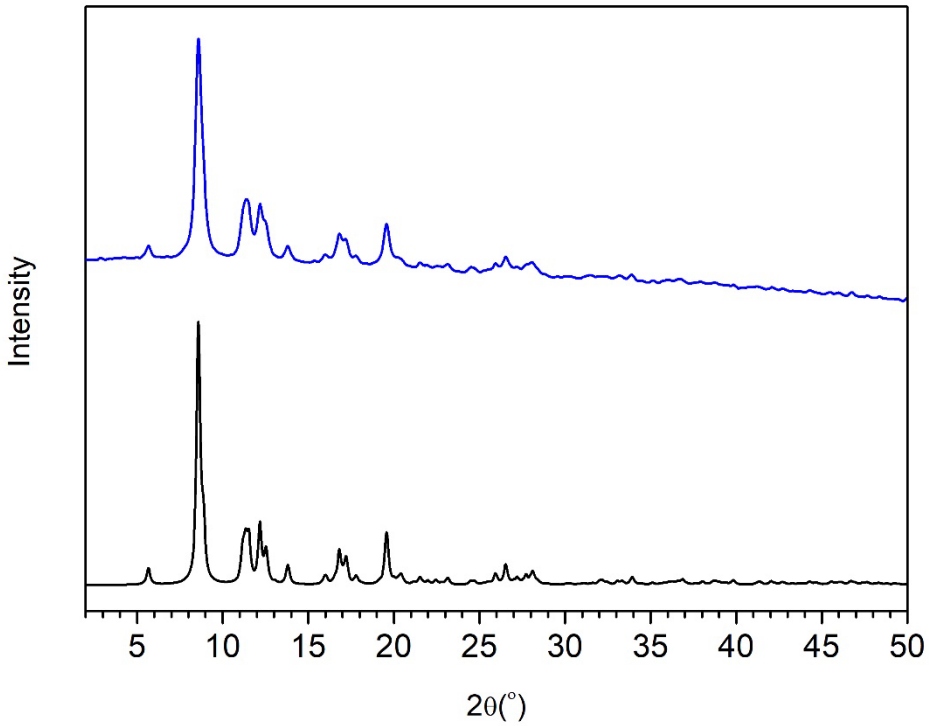

Figure S5. PXRD of [Ni(bpe)(*R*-ManOMe)$_2$] (**5**) (blue) between 5 and 50° 2θ versus the calculated pattern (black).

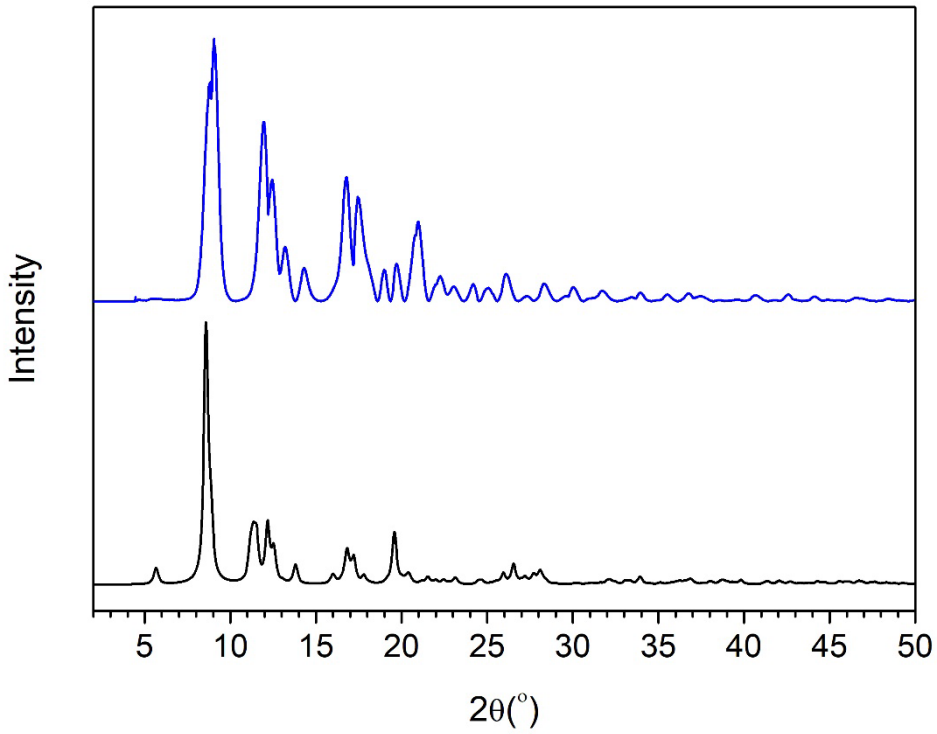

Figure S6. PXRD of [Co(bpee)(*R*-ManOMe)$_2$] (**6**) (blue) between 5 and 50° 2θ versus the calculated pattern (black).

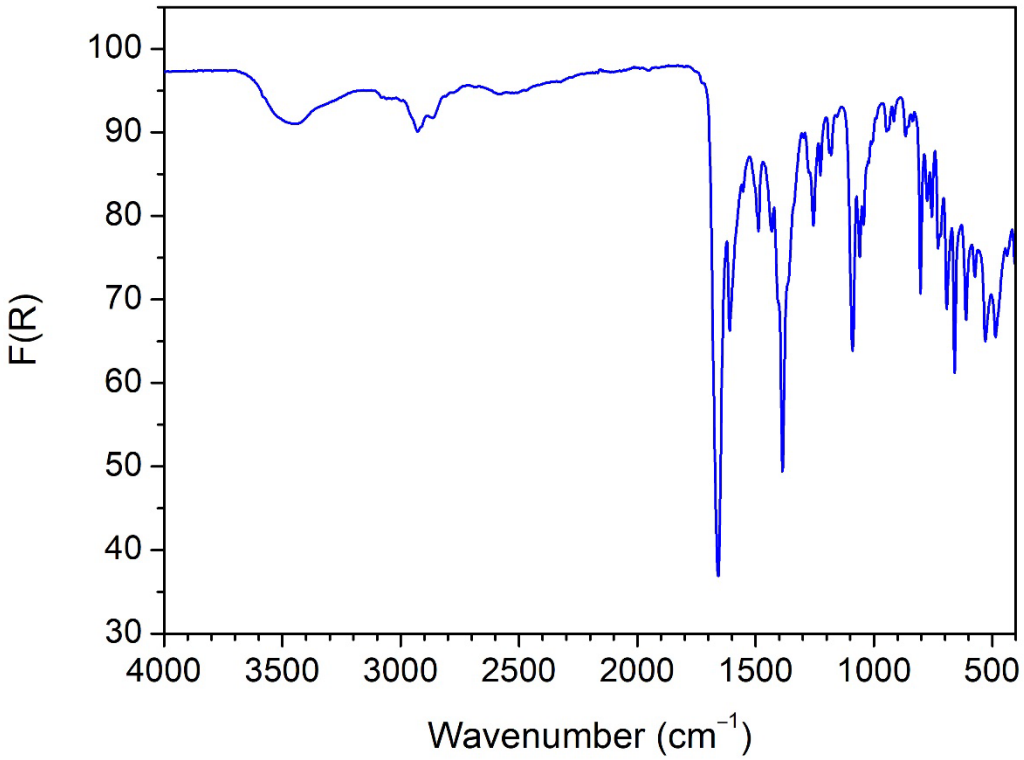

Figure S7. ATR FT-IR spectra of [Ni(*R*-man)$_2$(bpb)(H$_2$O)] (**1**) between 4000 and 400 cm^{-1}.

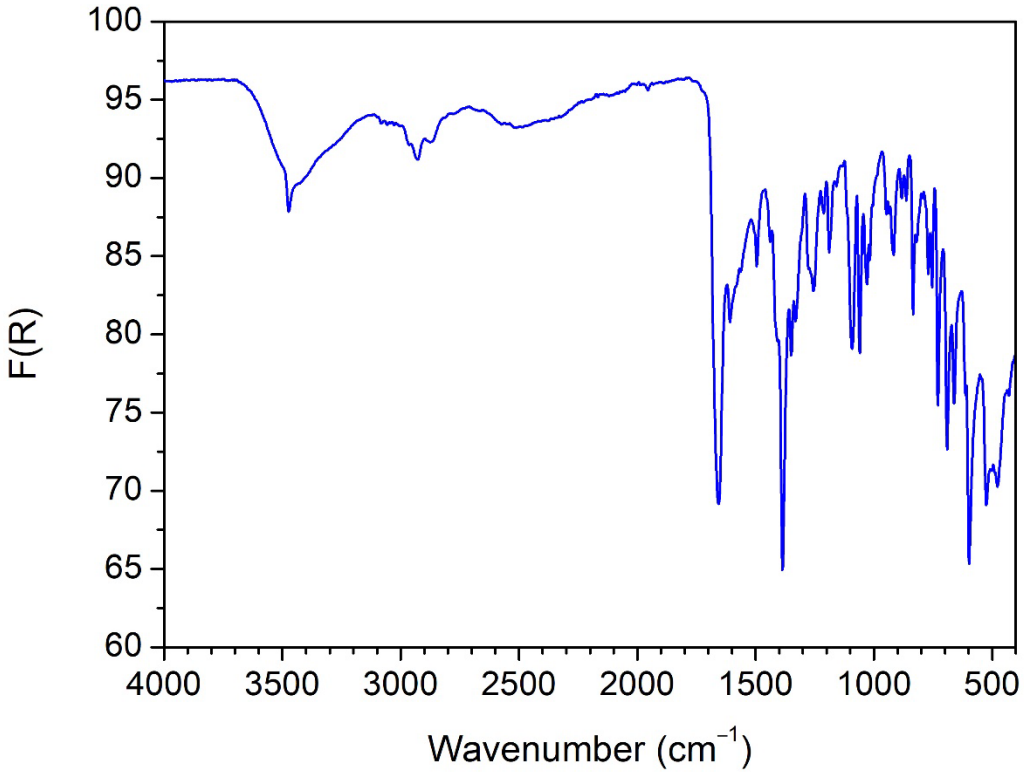

Figure S8. ATR FT-IR spectra of [Co(*R*-Man)$_2$(bpt)(H$_2$O)] (**2**) between 4000 and 400 cm^{-1}.

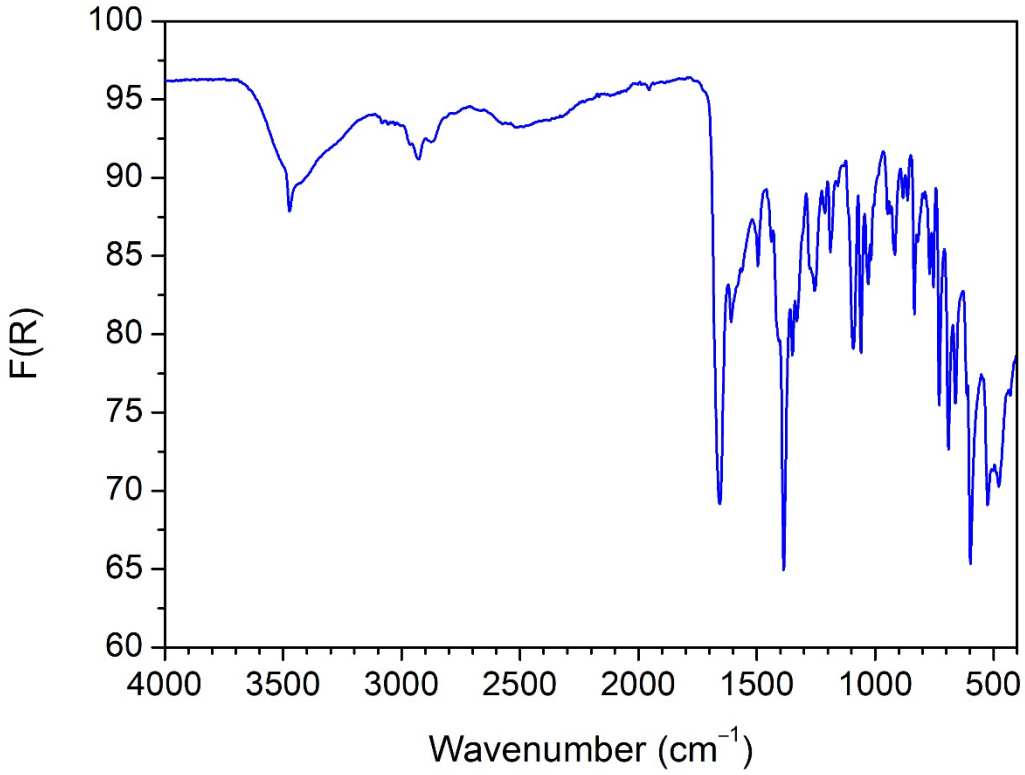

Figure S9. ATR FT-IR spectra of [Co(S-Man)$_2$(dptztz)(H$_2$O)] (**3**) between 4000 and 400 cm^{-1}.

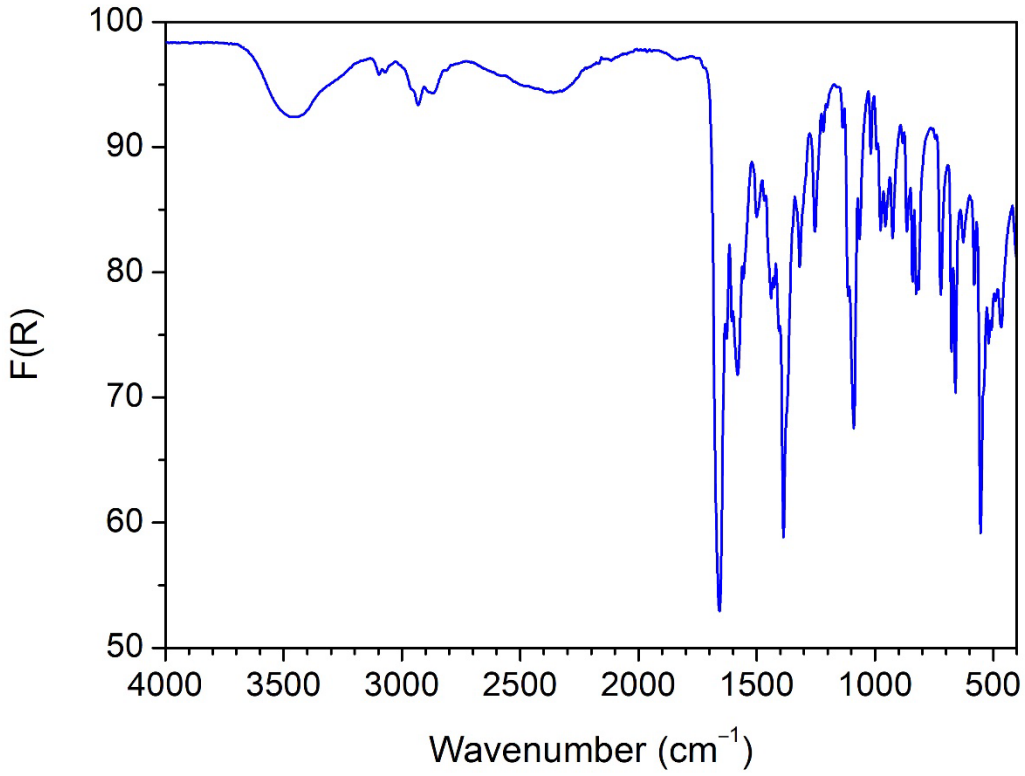

Figure S10. ATR FT-IR spectra of [Ni(F$_2$Man)$_2$(bpe)] (**4**) between 4000 and 400 cm^{-1}.

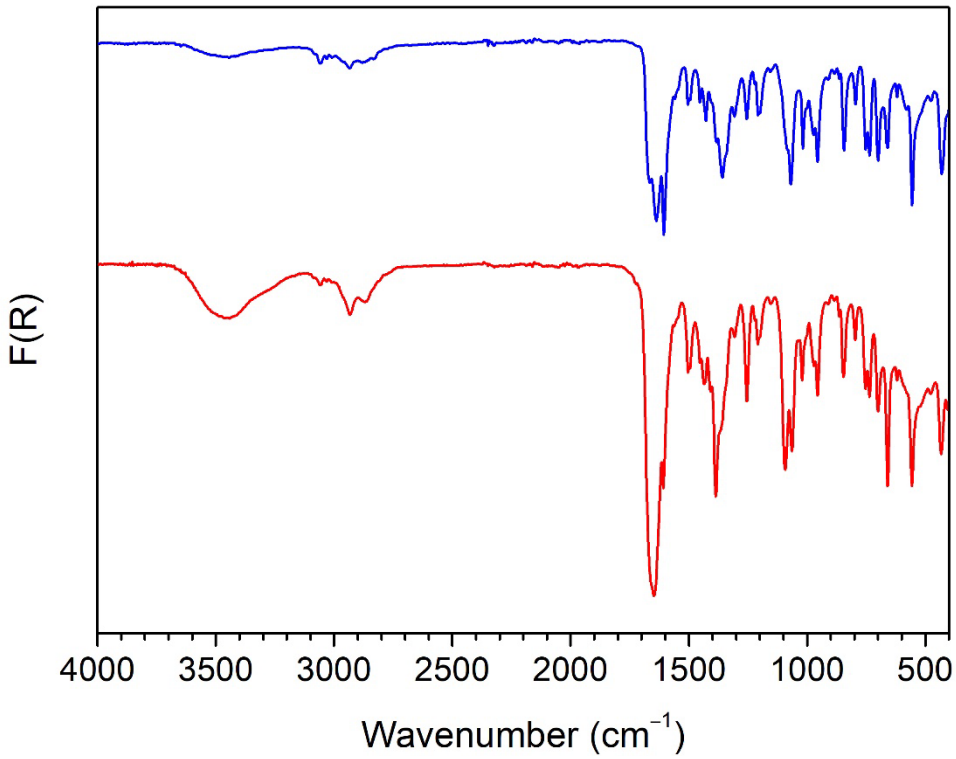

Figure S11. ATR FT-IR spectra of [Ni(bpe)(*R*-ManOMe)$_2$] (**5**) (red) and [Co(bpee)(*R*-ManOMe)$_2$] (**6**) (blue) between 4000 and 400 cm^{-1}.

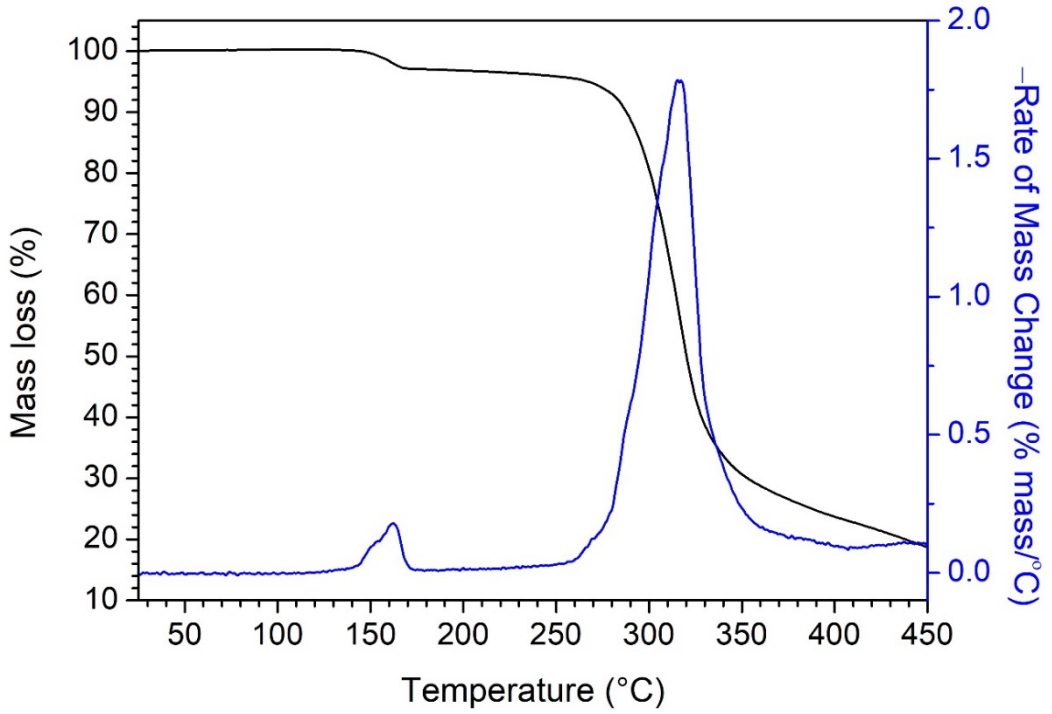

Figure S12. TGA of [Ni(*R*-man)$_2$(bpb)(H$_2$O)] (**1**) between 25 and 400 °C measured under nitrogen gas with a ramp rate of 10 °C/min.

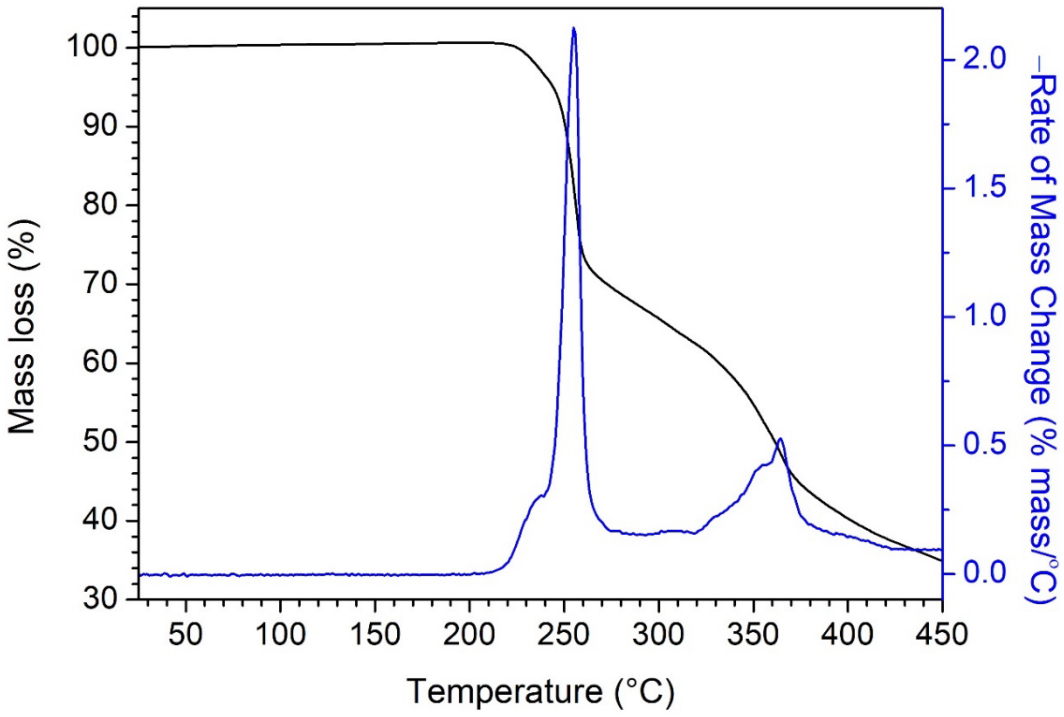

Figure S13. TGA of [Co(*R*-Man)$_2$(bpt)(H$_2$O)] (**2**) between 25 and 400 °C measured under nitrogen gas with a ramp rate of 10 °C/min.

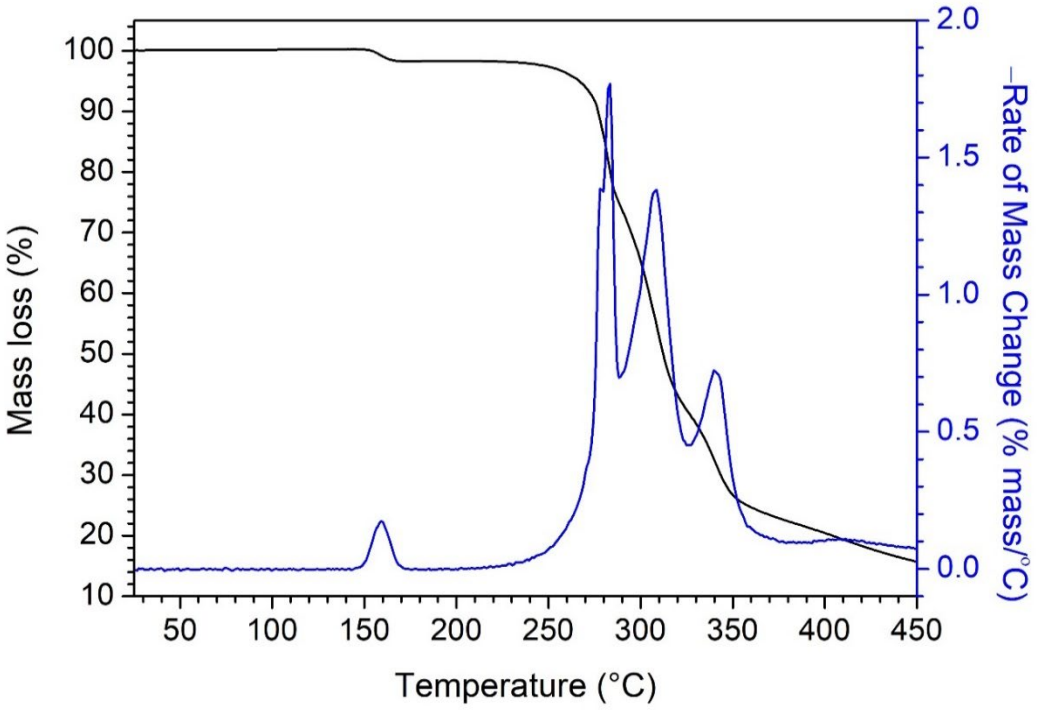

Figure S14. TGA of [Co(*S*-Man)$_2$(dptztz)(H$_2$O)] (**3**) between 25 and 400 °C measured under nitrogen gas with a ramp rate of 10 °C/min.

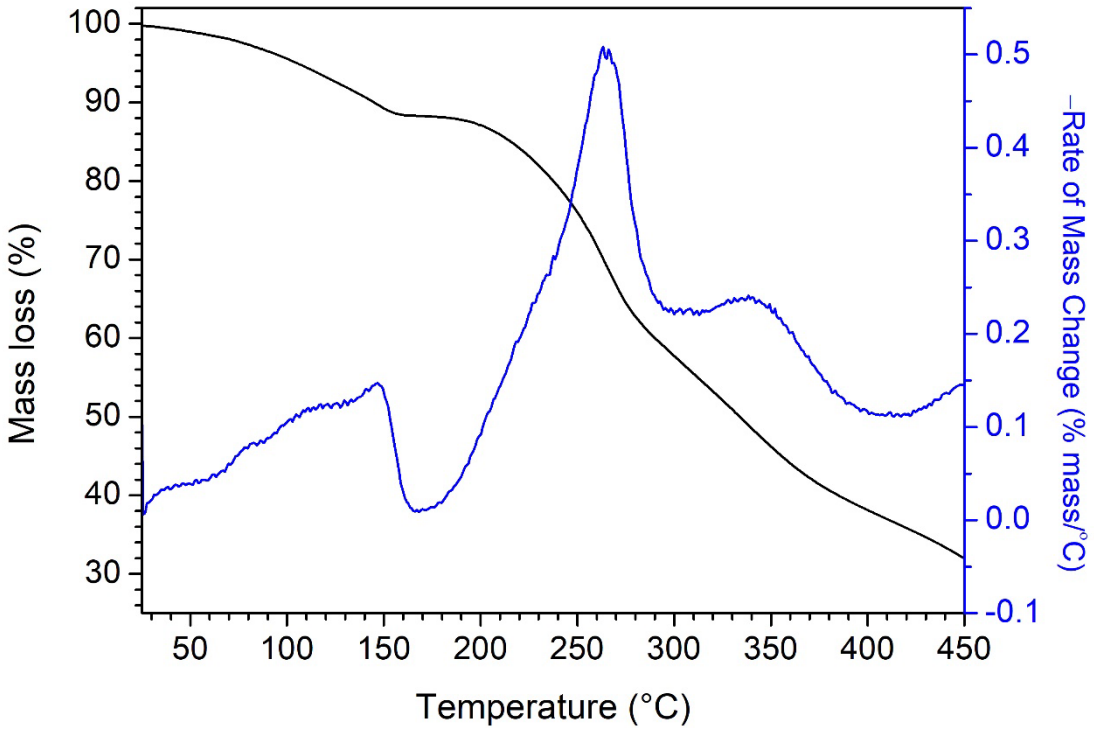

Figure S15. TGA of [Ni(F$_2$Man)$_2$(bpe)] (**4**) between 25 and 400 °C measured under nitrogen gas with a ramp rate of 10 °C/min.

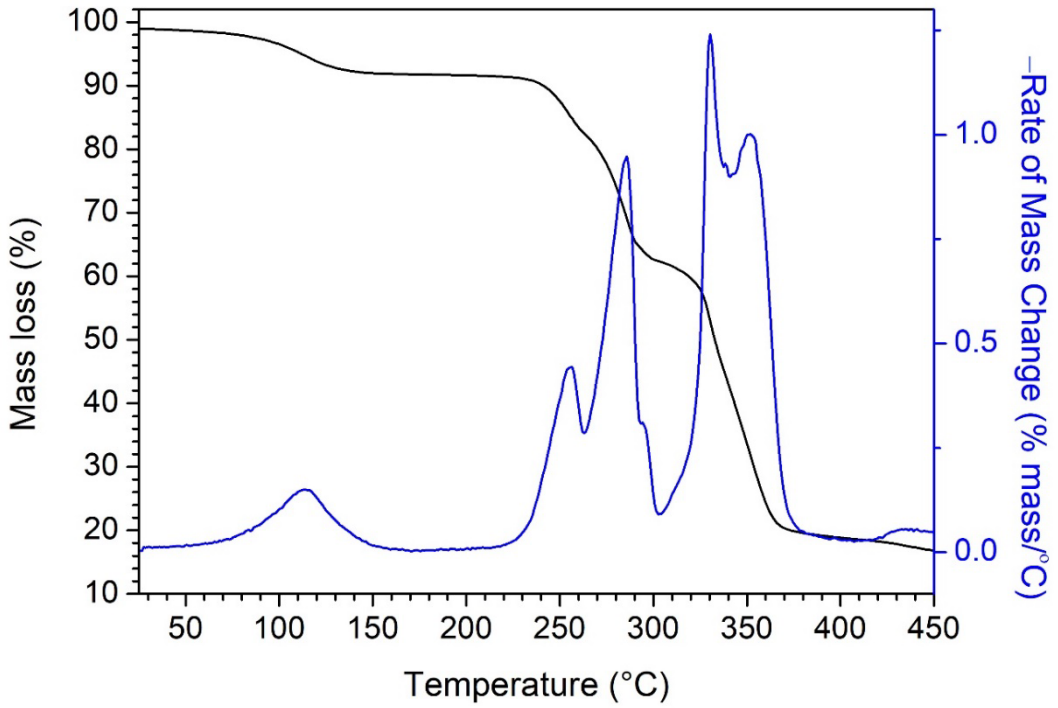

Figure S16. TGA of [Ni(bpe)(*R*-ManOMe)$_2$] (**5**) between 25 and 400 °C measured under nitrogen gas with a ramp rate of 10 °C/min.

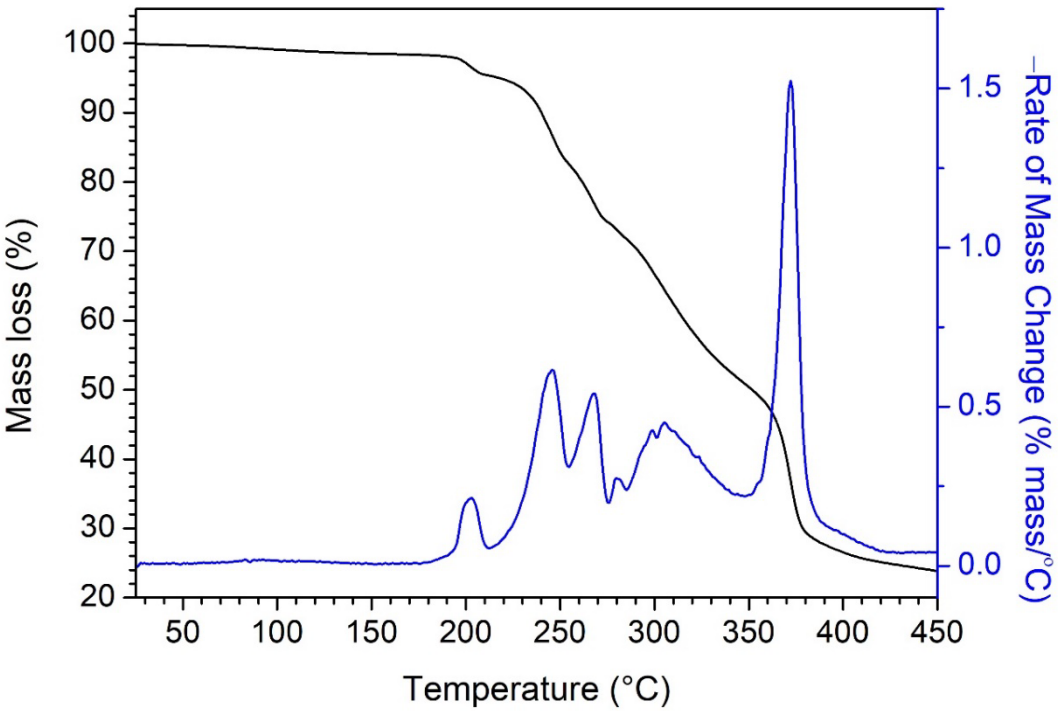

Figure S17. TGA of [Co(bpee)(*R*-ManOMe)$_2$] (**6**) between 25 and 400 °C measured under nitrogen gas with a ramp rate of 10 °C/min.