

## Supporting information

# Rational Self-Assembly of Tricobalt Extended Metal Atom Chains and $[\text{MF}_6]^{2-}$ Building-Blocks into One-Dimensional Coordination Polymers

### Infrared spectroscopy

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### X-ray crystallography

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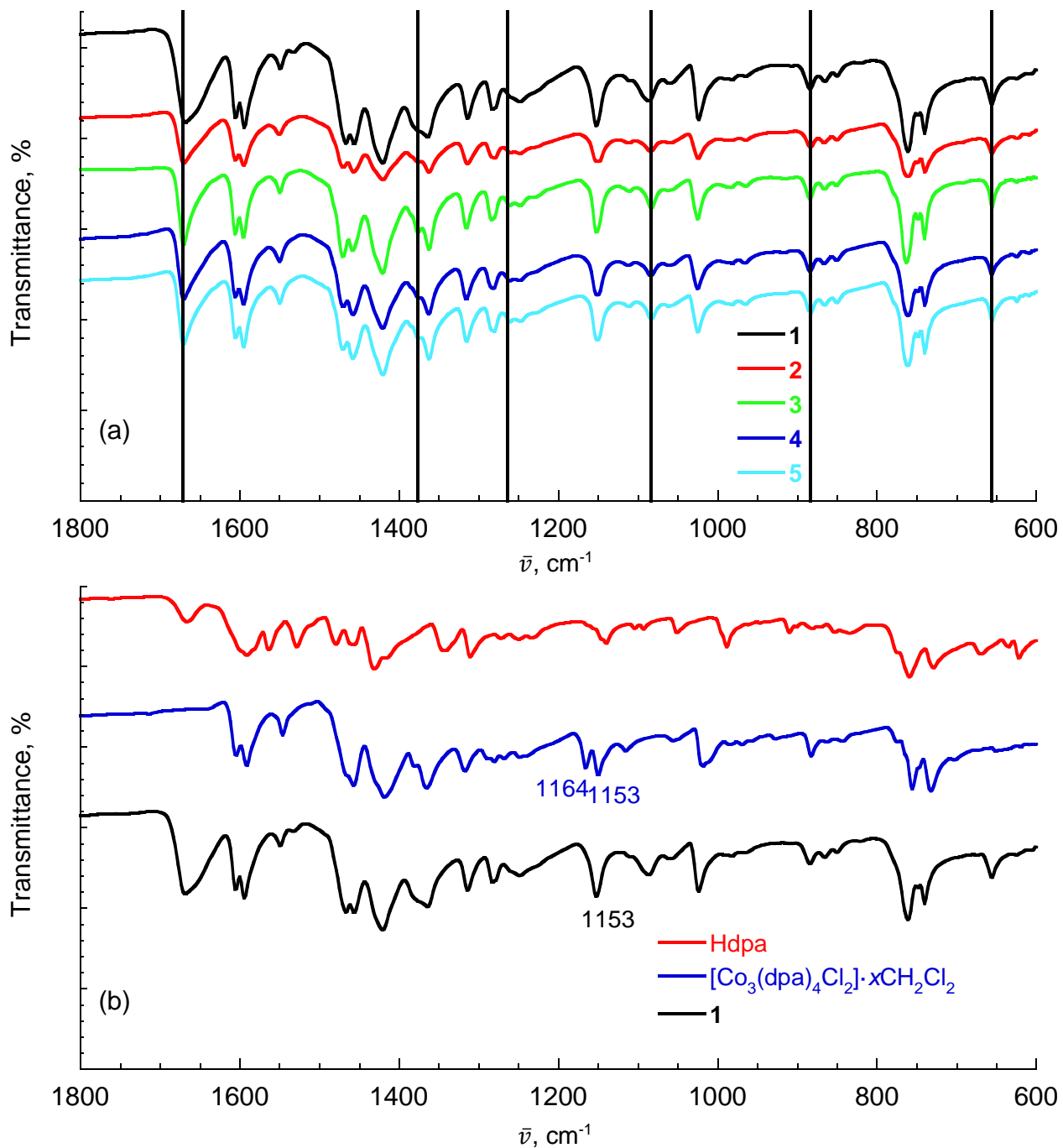
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### TGA and Magnetism

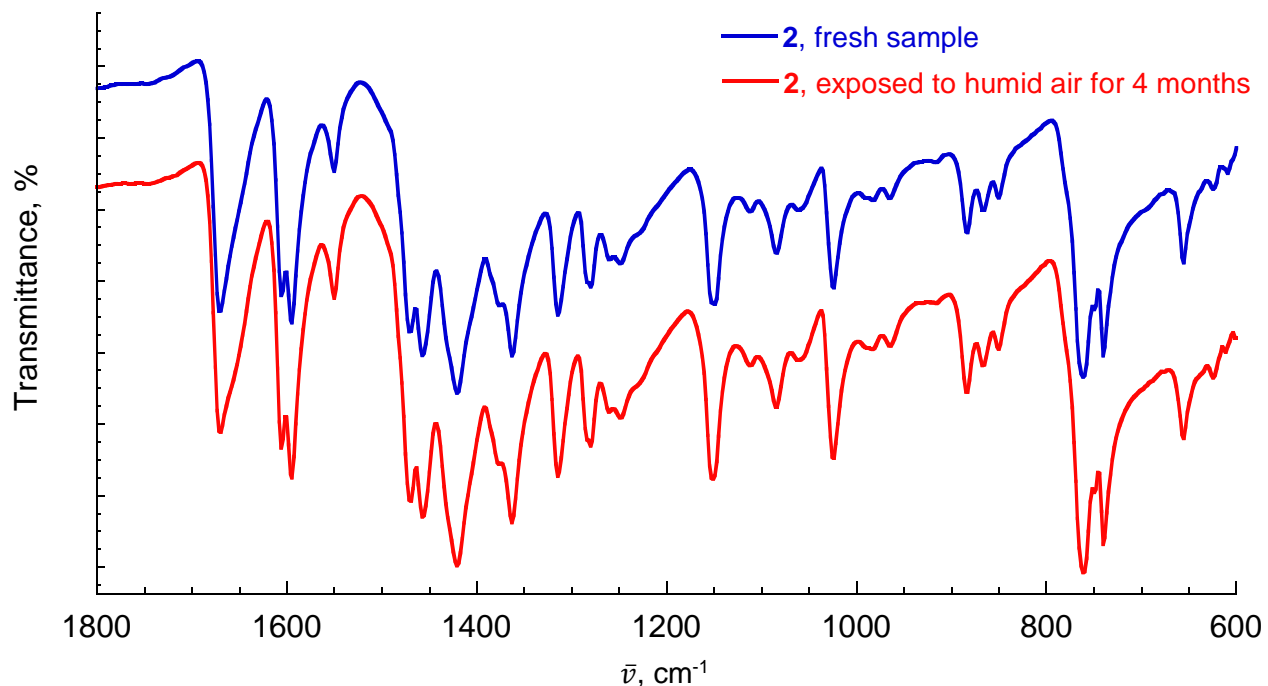
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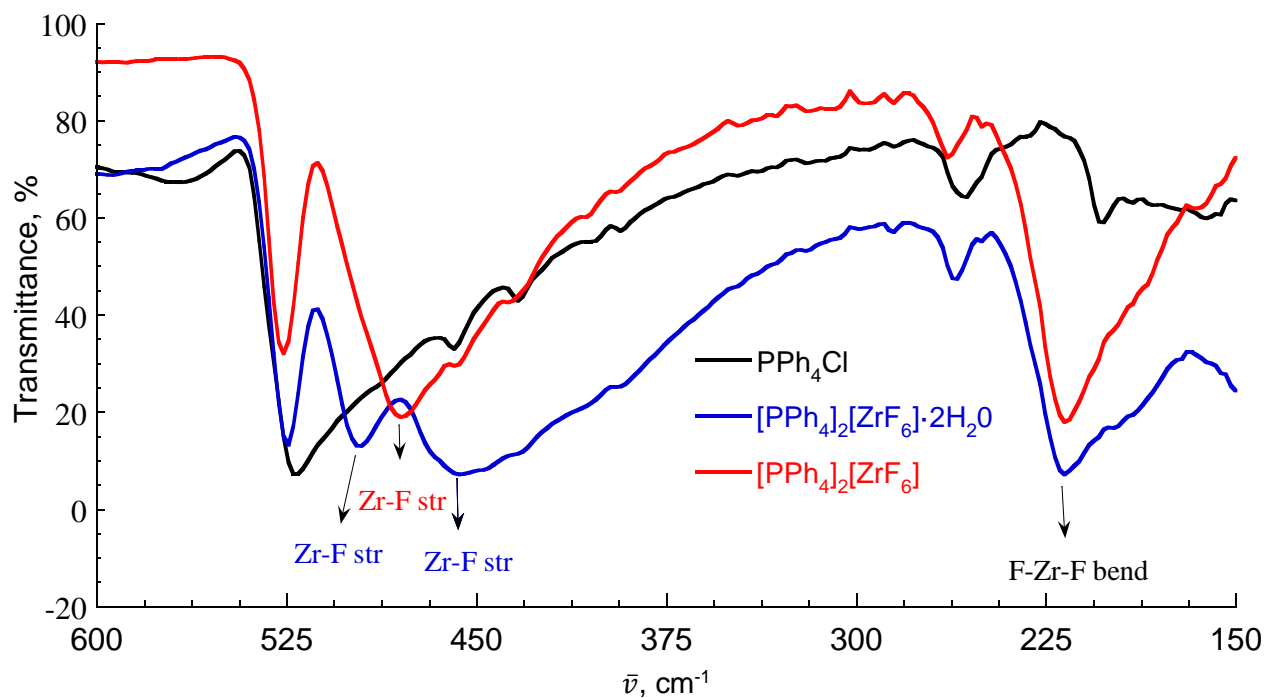
## Infrared spectroscopy



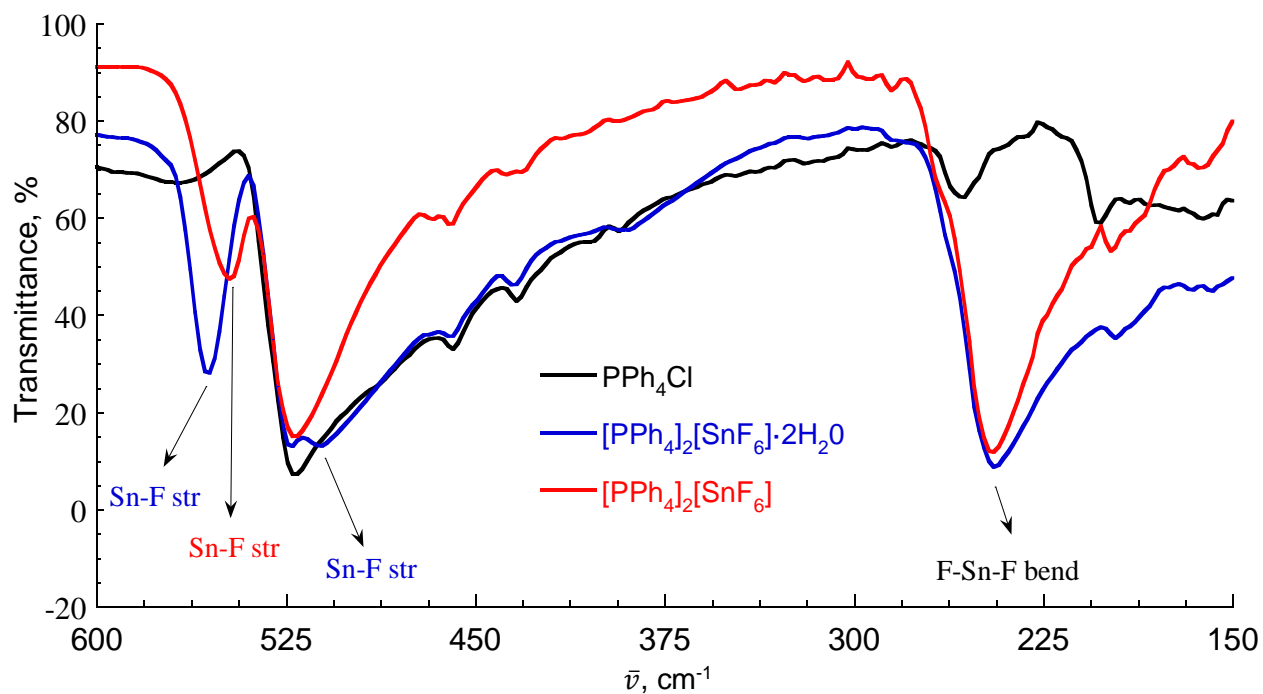
**Figure S1.** FT-IR spectra at room temperature in the 1800-600  $\text{cm}^{-1}$  range of (a)  $[\text{Co}_3(\text{dpa})_4(\text{MF}_6)] \cdot 2\text{DMF}$ , M = Zr (**1**) (black); Sn (**2**) (red); Re (**3**) (light green); Ir (**4**) (dark blue) and Os (**5**) (light blue); the vertical black lines correspond to DMF bands, and (b) Hdpa (red),  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2] \cdot x\text{CH}_2\text{Cl}_2$  (blue) and **1** (black), with some important bands highlighted. The spectra are shifted vertically for clarity.



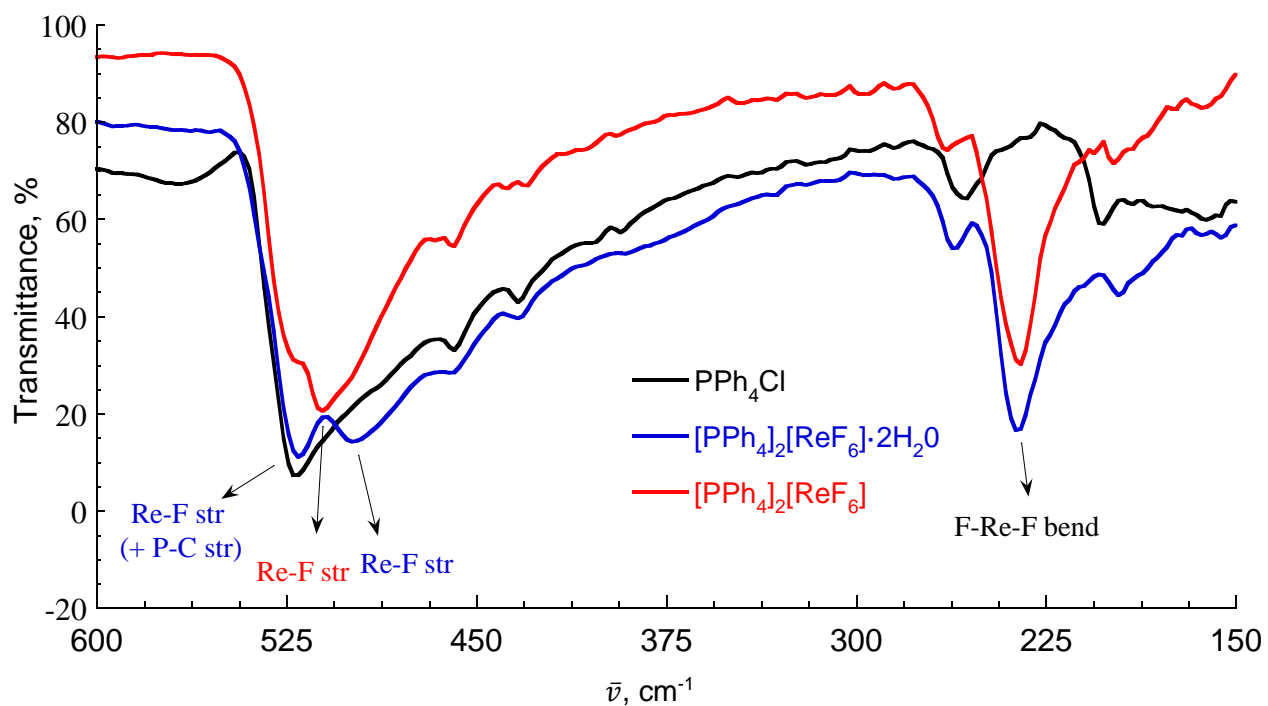
**Figure S2.** FT-IR spectra at room temperature in the 1800-600  $\text{cm}^{-1}$  range of a fresh sample of **2** (blue) and a sample of **2** exposed to humid air for 4 months (red). The spectra are shifted vertically for clarity.



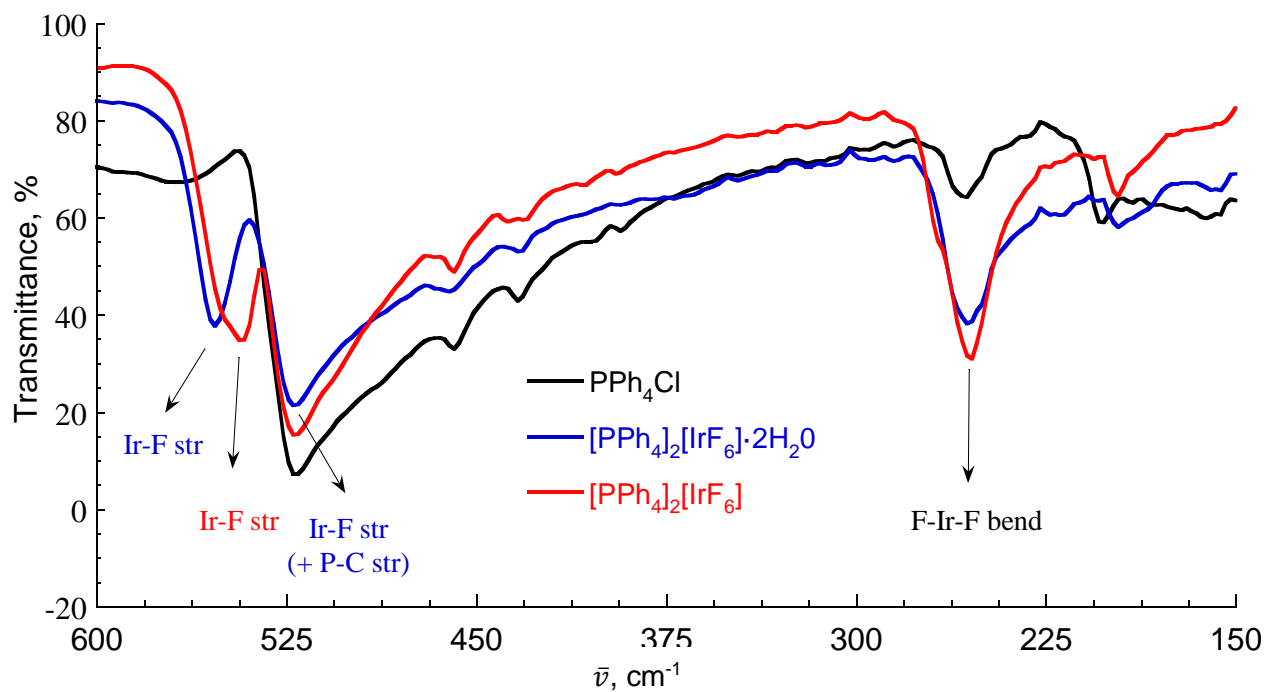
**Figure S3.** FT-IR spectra at room temperature of (l) 2H<sub>2</sub>O (blue), (PPh<sub>4</sub>)<sub>2</sub>[ZrF<sub>6</sub>]·(red) and PPh<sub>4</sub>Cl (black) in the 600-150  $\text{cm}^{-1}$  range.



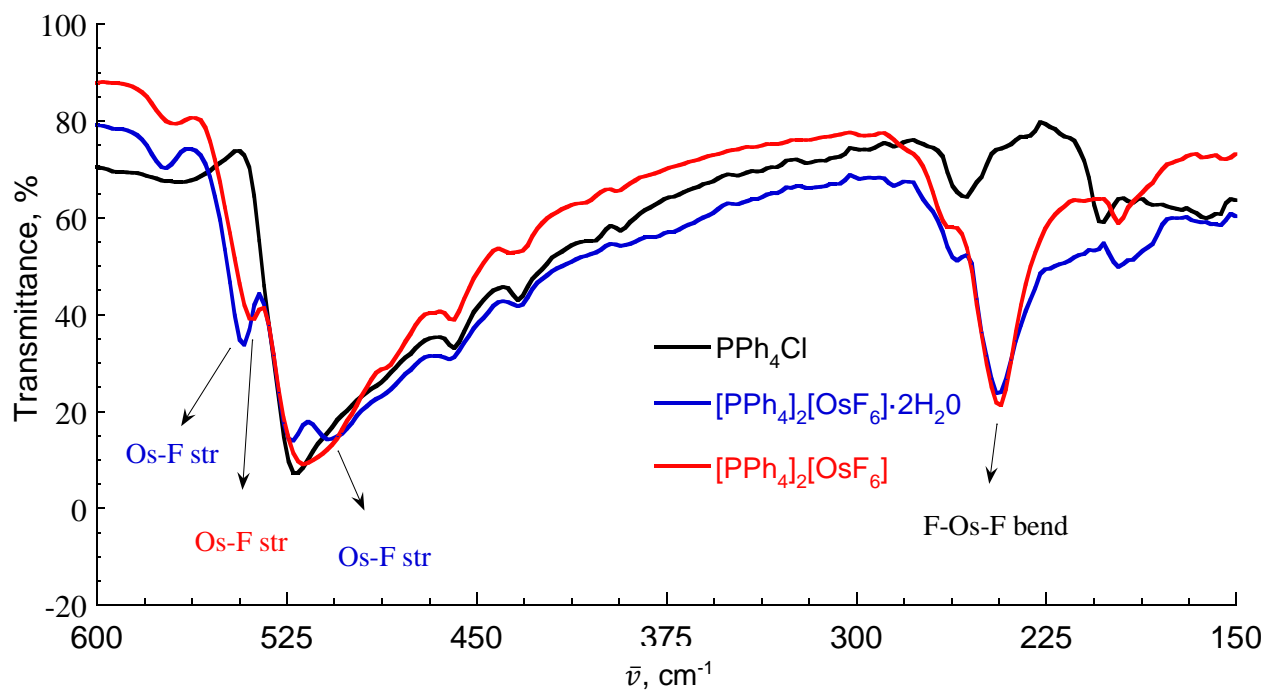
**Figure S4.** FT-IR spectra at room temperature of  $(\text{PPh}_4)_2[\text{SnF}_6] \cdot 2\text{H}_2\text{O}$  (blue),  $(\text{PPh}_4)_2[\text{SnF}_6]$  (red) and  $\text{PPh}_4\text{Cl}$  (black) in the 600-150  $\text{cm}^{-1}$  range.



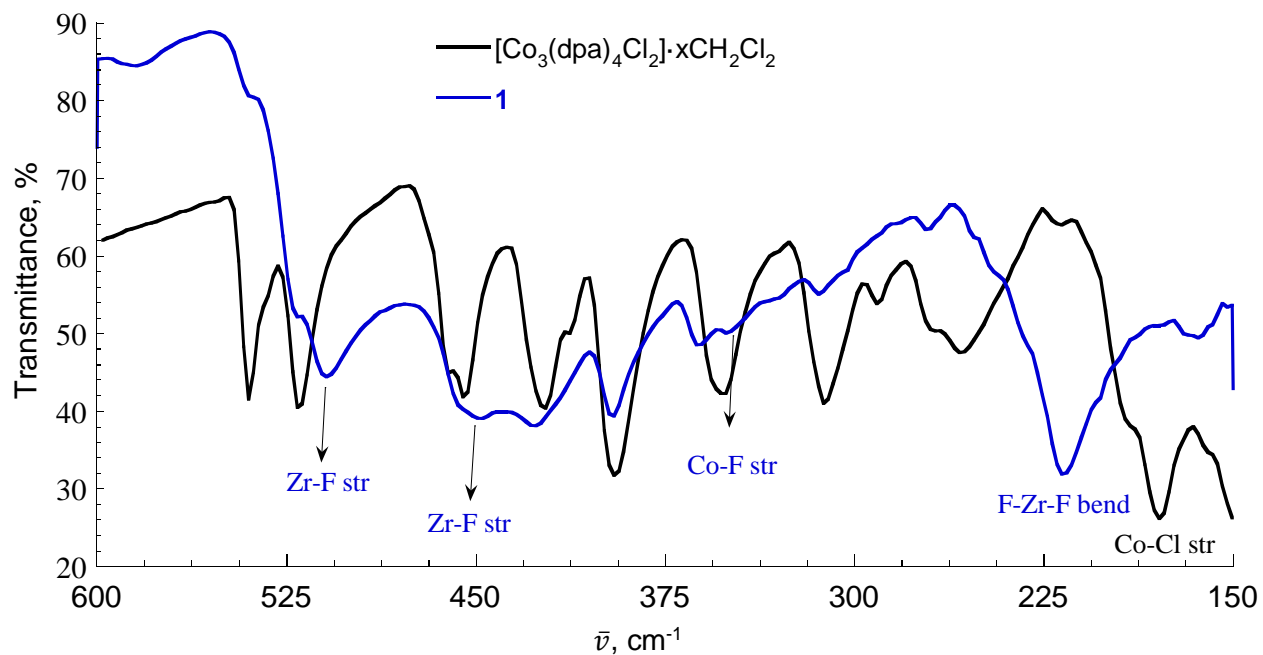
**Figure S5.** FT-IR spectra at room temperature of  $(\text{PPh}_4)_2[\text{ReF}_6] \cdot 2\text{H}_2\text{O}$  (blue),  $(\text{PPh}_4)_2[\text{ReF}_6]$  (red) and  $\text{PPh}_4\text{Cl}$  (black) in the 600-150  $\text{cm}^{-1}$  range.



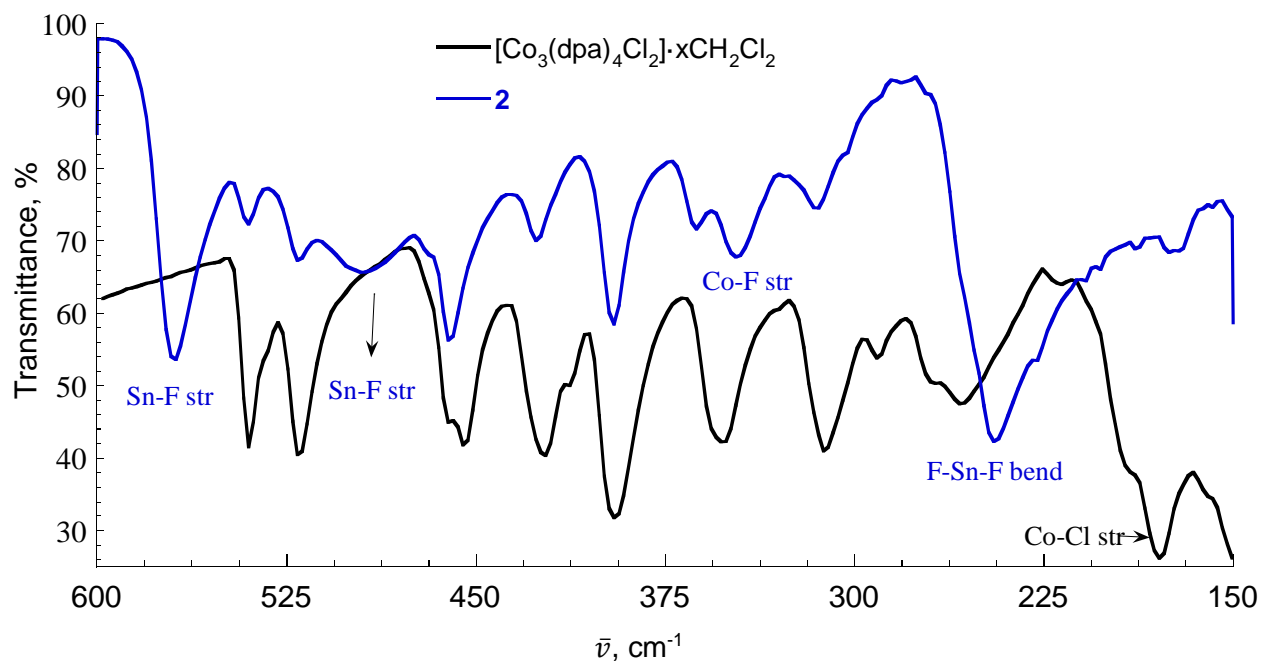
**Figure S6.** FT-IR spectra at room temperature of  $[\text{PPh}_4]_2[\text{IrF}_6] \cdot 2\text{H}_2\text{O}$  (blue),  $[\text{PPh}_4]_2[\text{IrF}_6]$  (red) and  $\text{PPh}_4\text{Cl}$  (black) in the 600-150  $\text{cm}^{-1}$  range.



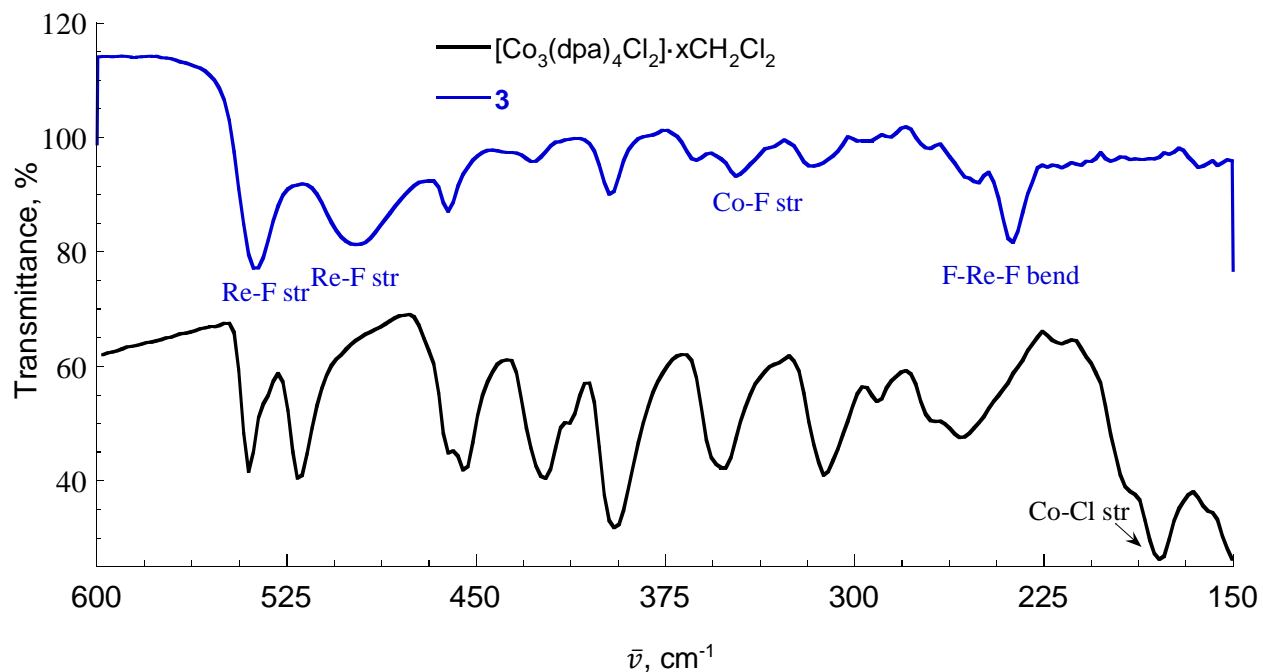
**Figure S7.** FT-IR spectra at room temperature of  $[\text{PPh}_4]_2[\text{OsF}_6] \cdot 2\text{H}_2\text{O}$  (blue),  $[\text{PPh}_4]_2[\text{OsF}_6]$  (red) and  $\text{PPh}_4\text{Cl}$  (black) in the 600-150  $\text{cm}^{-1}$  range.



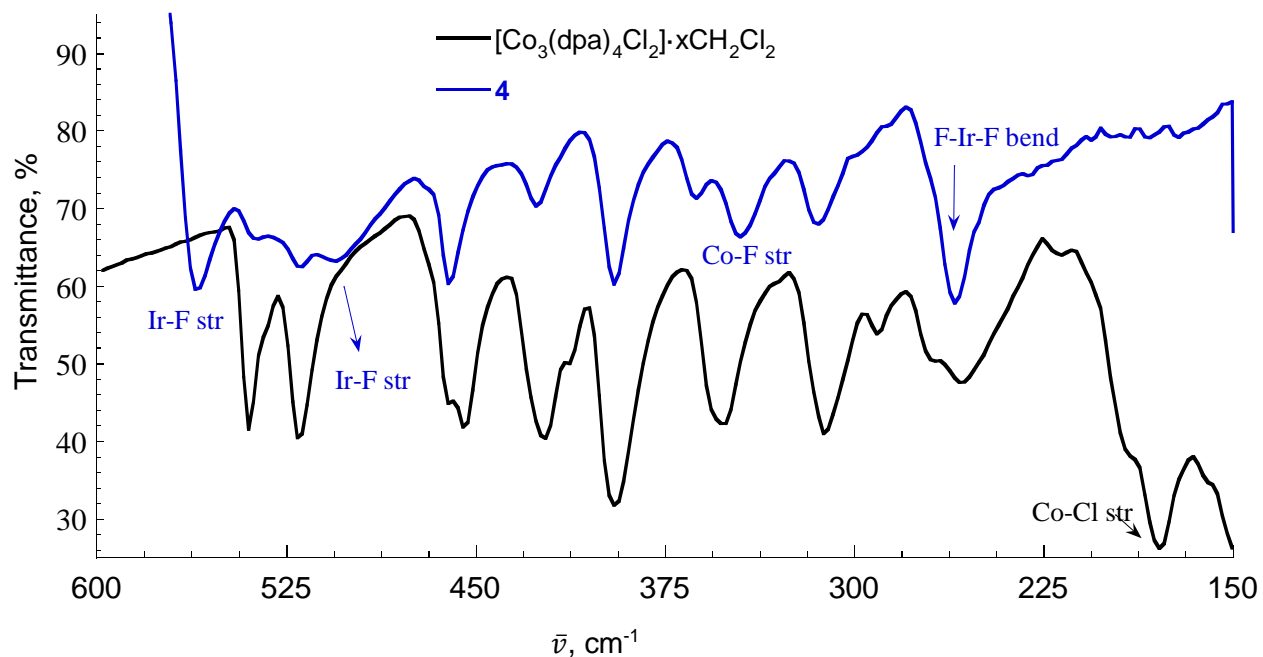
**Figure S8.** FT-IR spectra at room temperature of **1** (blue) and  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2] \cdot x\text{CH}_2\text{Cl}_2$  (black) in the 600-150  $\text{cm}^{-1}$  range.



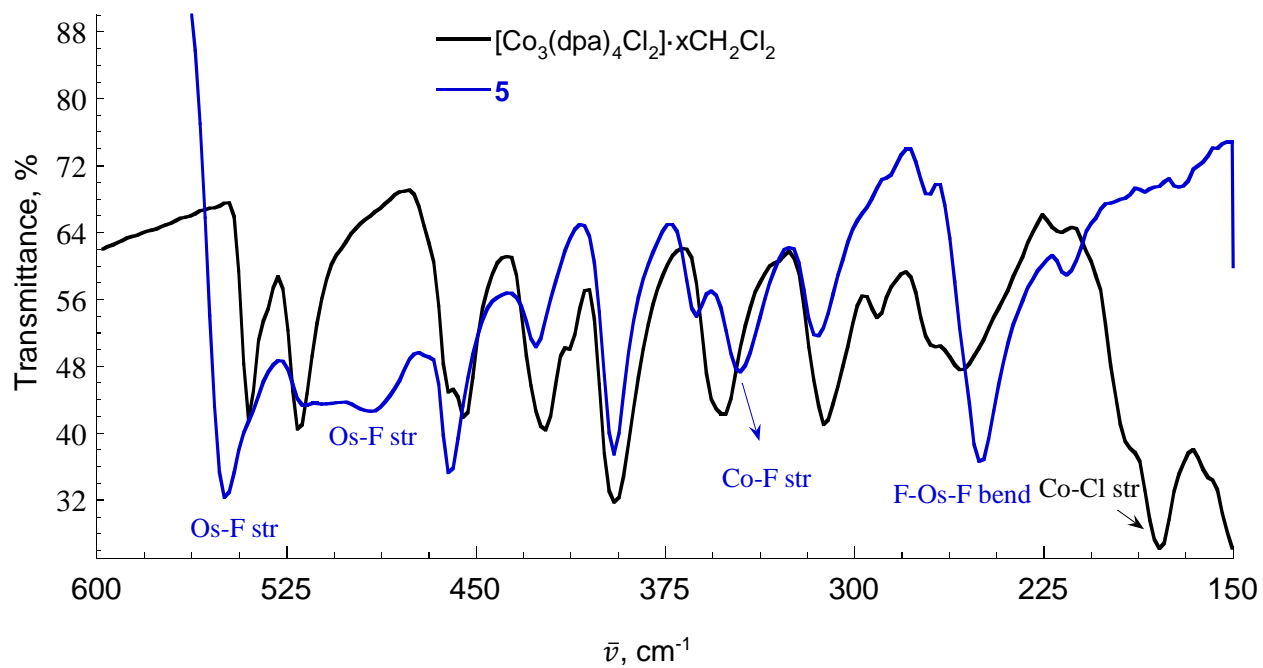
**Figure S9.** FT-IR spectra at room temperature of **2** (blue) and  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2] \cdot x\text{CH}_2\text{Cl}_2$  (black) in the 600-150  $\text{cm}^{-1}$  range.



**Figure S10.** FT-IR spectra at room temperature of **3** (blue) and  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2] \cdot x\text{CH}_2\text{Cl}_2$  (black) in the  $600\text{--}150\text{ cm}^{-1}$  range.



**Figure S11.** FT-IR spectra at room temperature of **4** (blue) and  $[\text{Co}_3(\text{dpa})_4\text{Cl}_2] \cdot x\text{CH}_2\text{Cl}_2$  (black) in the  $600\text{--}150\text{ cm}^{-1}$  range.



**Figure S12.** FT-IR spectra at room temperature of **4** (blue) and [Co<sub>3</sub>(dpa)<sub>4</sub>Cl<sub>2</sub>] $\cdot$ xCH<sub>2</sub>Cl<sub>2</sub> (black) in the 600-150 cm<sup>-1</sup> range.



## X-ray crystallography

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**Table S1.** Bond lengths [Å] for **4**.

Ir(1)-F(3)	1.919(2)	C(4)-C(5B)	1.46(2)
Ir(1)-F(1)	1.951(3)	C(7A)-C(8A)	1.39(3)
Ir(1)-F(2)	1.965(3)	C(7A)-C(6A)	1.47(2)
Co(1)-N(1)	1.952(3)	C(8A)-C(9A)	1.38(3)
Co(1)-F(1)	2.117(3)	N(2A)-C(1A)	1.394(10)
Co(1)-Co(3)	2.2674(10)	N(2A)-C(6A)	1.400(11)
Co(2)-N(3)	1.963(3)	C(1A)-C(2A)	1.410(12)
Co(2)-F(2)	2.178(3)	C(2A)-C(3A)	1.358(18)
Co(2)-Co(3)	2.2736(10)	C(6A)-N(2A)	1.400(11)
Co(3)-N(2B)	1.909(11)	C(9A)-C(10A)	1.366(17)
Co(3)-N(2A)	1.925(6)	N(2B)-C(1B)	1.341(17)
N(3)-C(10B)	1.34(2)	N(2B)-C(6B)	1.344(18)
N(3)-C(6A)	1.362(10)	C(1B)-N(2B)	1.341(17)
N(3)-C(10A)	1.367(11)	C(1B)-C(2B)	1.39(2)
N(3)-C(6B)	1.377(18)	C(2B)-C(3B)	1.35(3)
N(1)-C(5B)	1.28(2)	C(10B)-C(9B)	1.37(3)
N(1)-C(5A)	1.356(13)	C(6B)-C(7B)	1.31(4)
N(1)-C(1A)	1.379(9)	C(9B)-C(8B)	1.32(4)
N(1)-C(1B)	1.415(14)	C(8B)-C(7B)	1.38(6)
C(4)-C(3A)	1.308(15)	O(1)-C(12)	1.211(18)
C(4)-C(5A)	1.354(14)	C(11)-N(5)	1.59(2)
C(4)-C(3B)	1.41(2)	N(5)-C(12)	1.33(3)

Symmetry transformations used to generate equivalent atoms:

#1  $y, -x+1/2, z$ ; #2  $-y+1/2, x, z$ ; #3  $-x+1/2, -y+1/2, z$ ; #4  $-x+1/2, y, z-1/2$ ; #5  $-x+1/2, y, z+1/2$ ;

#6  $-y+1/2, -x+1/2, z+1/2$ ; #7  $-y+1/2, -x+1/2, z-1/2$ ; #8  $-x+1/2, -y-1/2, z$ ; #9  $y+1/2, x-1/2, -z+5/2$

**Table S2.** Bond lengths [Å] for **5**.

Os1-F(3)	1.917(2)	C(4)-C(5B)	1.44(2)
Os1-F(1)	1.963(3)	C(7A)-C(8A)	1.38(2)
Os1-F(2)	1.975(3)	C(7A)-C(6A)	1.460(19)
Co1-N(1)	1.948(3)	C(8A)-C(9A)	1.373(16)
Co1-F(1)	2.117(3)	N(2A)-C(1A)	1.372(7)
Co1-Co3	2.2699(9)	N(2A)-C(6A)	1.386(8)
Co2-N(3)	1.959(3)	C(1A)-C(2A)	1.406(9)
Co2-F(2)	2.175(3)	C(2A)-C(3A)	1.354(13)
Co2-Co3	2.2793(10)	C(6A)-N(2A)	1.386(8)
Co3-N(2B)	1.910(10)	C(9A)-C(10A)	1.352(12)
Co3-N(2A)	1.916(5)	N(2B)-C(1B)	1.373(15)
N(3)-C(10B)	1.317(17)	N(2B)-C(6B)	1.349(16)
N(3)-C(6A)	1.366(7)	C(1B)-N(2B)	1.373(15)
N(3)-C(10A)	1.371(7)	C(1B)-C(2B)	1.387(18)
N(3)-C(6B)	1.358(15)	C(2B)-C(3B)	1.37(3)
N(1)-C(5B)	1.29(2)	C(10B)-C(9B)	1.39(3)
N(1)-C(5A)	1.346(9)	C(6B)-C(7B)	1.31(4)
N(1)-C(1A)	1.379(6)	C(9B)-C(8B)	1.36(4)
N(1)-C(1B)	1.416(12)	C(8B)-C(7B)	1.40(5)
C(4)-C(3A)	1.341(11)	O(1)-C(12)	1.249(18)
C(4)-C(5A)	1.361(10)	C(11)-N(5)	1.57(2)
C(4)-C(3B)	1.40(2)	N(5)-C(12)	1.35(2)

Symmetry transformations used to generate equivalent atoms:

#1  $y, -x+1/2, z$ ; #2  $-y+1/2, x, z$ ; #3  $-x+1/2, -y+1/2, z$ ; #4  $-x+1/2, y, z-1/2$ ; #5  $-x+1/2, y, z+1/2$ ;

#6  $-y+1/2, -x+1/2, z+1/2$ ; #7  $-y+1/2, -x+1/2, z-1/2$ ; #8  $-x+1/2, -y-1/2, z$ ; #9  $y+1/2, x-1/2, -z+5/2$

**Table S3.** Bond angles [°] for **4**.

F(3)-Ir(1)-F(3)#1	89.995(2)	N(3)#2-Co(2)-Co(3)#4	87.60(7)
F(3)-Ir(1)-F(3)#2	89.996(2)	N(3)#3-Co(2)-Co(3)#4	87.60(7)
F(3)#1-Ir(1)-F(3)#2	178.97(12)	N(3)-Co(2)-Co(3)#4	87.59(7)
F(3)-Ir(1)-F(3)#3	178.97(12)	F(2)-Co(2)-Co(3)#4	180
F(3)#1-Ir(1)-F(3)#3	89.995(2)	N(2B)-Co(3)-N(2B)#1	89.998(3)
F(3)#2-Ir(1)-F(3)#3	89.995(2)	N(2B)-Co(3)-N(2B)#2	90.002(5)
F(3)-Ir(1)-F(1)	89.49(6)	N(2B)#1-Co(3)-N(2B)#2	179.8(5)
F(3)#1-Ir(1)-F(1)	89.48(6)	N(2B)-Co(3)-N(2B)#3	179.8(5)
F(3)#2-Ir(1)-F(1)	89.48(6)	N(2B)#1-Co(3)-N(2B)#3	90.000(6)
F(3)#3-Ir(1)-F(1)	89.48(6)	N(2B)#2-Co(3)-N(2B)#3	90.000(2)
F(3)-Ir(1)-F(2)	90.51(6)	N(2A)-Co(3)-N(2A)#2	89.998(3)
F(3)#1-Ir(1)-F(2)	90.52(6)	N(2A)-Co(3)-N(2A)#1	89.998(4)
F(3)#2-Ir(1)-F(2)	90.52(6)	N(2A)#2-Co(3)-N(2A)#1	179.3(3)
F(3)#3-Ir(1)-F(2)	90.52(6)	N(2A)-Co(3)-N(2A)#3	179.3(3)
F(1)-Ir(1)-F(2)	180	N(2A)#2-Co(3)-N(2A)#3	89.998(4)
N(1)#2-Co(1)-N(1)	89.925(6)	N(2A)#1-Co(3)-N(2A)#3	89.998(3)
N(1)#3-Co(1)-N(1)	175.89(15)	N(2B)-Co(3)-Co(1)	89.9(3)
N(1)#2-Co(1)-N(1)#3	89.926(6)	N(2B)#1-Co(3)-Co(1)	89.9(3)
N(1)#1-Co(1)-N(1)	89.927(6)	N(2B)#2-Co(3)-Co(1)	89.9(3)
N(1)#2-Co(1)-N(1)#1	175.89(15)	N(2B)#3-Co(3)-Co(1)	89.9(3)
N(1)#3-Co(1)-N(1)#1	89.926(6)	N(2A)-Co(3)-Co(1)	89.67(16)
N(1)-Co(1)-F(1)	92.06(7)	N(2A)#2-Co(3)-Co(1)	89.67(16)
N(1)#2-Co(1)-F(1)	92.06(7)	N(2A)#1-Co(3)-Co(1)	89.67(16)
N(1)#3-Co(1)-F(1)	92.06(7)	N(2A)#3-Co(3)-Co(1)	89.67(16)
N(1)#1-Co(1)-F(1)	92.05(7)	N(2B)-Co(3)-Co(2)#5	90.1(3)
N(1)-Co(1)-Co(3)	87.94(7)	N(2B)#1-Co(3)-Co(2)#5	90.1(3)
N(1)#2-Co(1)-Co(3)	87.94(7)	N(2B)#2-Co(3)-Co(2)#5	90.1(3)
N(1)#3-Co(1)-Co(3)	87.94(7)	N(2B)#3-Co(3)-Co(2)#5	90.1(3)
N(1)#1-Co(1)-Co(3)	87.95(7)	N(2A)-Co(3)-Co(2)#5	90.33(16)
F(1)-Co(1)-Co(3)	180	N(2A)#2-Co(3)-Co(2)#5	90.33(16)
N(3)#1-Co(2)-N(3)#2	175.19(14)	N(2A)#1-Co(3)-Co(2)#5	90.33(16)
N(3)#1-Co(2)-N(3)#3	89.899(6)	N(2A)#3-Co(3)-Co(2)#5	90.33(16)
N(3)#2-Co(2)-N(3)#3	89.899(6)	Co(1)-Co(3)-Co(2)#5	180
N(3)#1-Co(2)-N(3)	89.900(6)	Ir(1)-F(1)-Co(1)	180
N(3)#2-Co(2)-N(3)	89.899(6)	C(10B)-N(3)-C(6B)	121.2(11)
N(3)#3-Co(2)-N(3)	175.19(14)	C(6A)-N(3)-C(10A)	115.8(7)
N(3)#1-Co(2)-F(2)	92.40(7)	C(10B)-N(3)-Co(2)	119.3(9)
N(3)#2-Co(2)-F(2)	92.40(7)	C(6B)-N(3)-Co(2)	119.4(7)
N(3)#3-Co(2)-F(2)	92.40(7)	C(6A)-N(3)-Co(2)	122.3(4)
N(3)-Co(2)-F(2)	92.41(7)	C(10A)-N(3)-Co(2)	121.9(5)
N(3)#1-Co(2)-Co(3)#4	87.60(7)	C(5A)-N(1)-C(1A)	116.8(7)
		C(5B)-N(1)-C(1B)	120.7(12)

C(5B)-N(1)-Co(1)	120.7(11)	C(1B)#2-N(2B)-C(6B)#6	122.9(14)
C(5A)-N(1)-Co(1)	122.8(6)	C(1B)#2-N(2B)-Co(3)	118.9(9)
C(1A)-N(1)-Co(1)	119.8(4)	C(6B)#6-N(2B)-Co(3)	118.2(10)
C(1B)-N(1)-Co(1)	117.2(6)	N(2B)#1-C(1B)-C(2B)	126.6(14)
C(3A)-C(4)-C(5A)	118.9(10)	N(2B)#1-C(1B)-N(1)	116.1(12)
C(3B)-C(4)-C(5B)	119.4(16)	C(2B)-C(1B)-N(1)	116.5(13)
C(4)-C(5A)-N(1)	123.1(11)	C(3B)-C(2B)-C(1B)	125.8(18)
C(8A)-C(7A)-C(6A)	117.5(15)	N(3)-C(10B)-C(9B)	123.2(18)
C(9A)-C(8A)-C(7A)	118.3(14)	C(7B)-C(6B)-N(2B)#7	131(2)
Ir(1)-F(2)-Co(2)	180	C(7B)-C(6B)-N(3)	113(2)
C(1A)-N(2A)-C(6A)#6	124.4(7)	N(2A)#7-C(6A)-C(7A)	123.6(11)
C(1A)-N(2A)-Co(3)	117.4(5)	N(2B)#7-C(6B)-N(3)	115.9(14)
C(6A)#6-N(2A)-Co(3)	118.2(6)	C(8B)-C(9B)-C(10B)	116(2)
N(1)-C(1A)-N(2A)	114.6(7)	C(2B)-C(3B)-C(4)	114(2)
N(1)-C(1A)-C(2A)	120.3(8)	N(1)-C(5B)-C(4)	120.5(18)
N(2A)-C(1A)-C(2A)	124.9(8)	C(9B)-C(8B)-C(7B)	119(3)
C(3A)-C(2A)-C(1A)	117.2(10)	C(6B)-C(7B)-C(8B)	127(4)
C(4)-C(3A)-C(2A)	122.9(12)	C(12)-O(1)-O(1)#8	132.3(13)
N(3)-C(6A)-N(2A)#7	113.3(8)	C(12)-N(5)-C(11)	104(2)
N(3)-C(6A)-C(7A)	122.8(11)	C(12)-N(5)-N(5)#9	153.8(13)
C(10A)-C(9A)-C(8A)	121.3(13)	C(11)-N(5)-N(5)#9	76.3(12)
C(9A)-C(10A)-N(3)	123.7(10)	O(1)-C(12)-N(5)	120(2)

Symmetry transformations used to generate equivalent atoms:

#1  $y, -x+1/2, z$ ; #2  $-y+1/2, x, z$ ; #3  $-x+1/2, -y+1/2, z$ ; #4  $-x+1/2, y, z-1/2$ ; #5  $-x+1/2, y, z+1/2$ ;  
 #6  $-y+1/2, -x+1/2, z+1/2$ ; #7  $-y+1/2, -x+1/2, z-1/2$ ; #8  $-x+1/2, -y-1/2, z$ ; #9  $y+1/2, x-1/2, -z+5/2$

**Table S4.** Bond angles [°] for **5**.

F(3)-Os1-F(3)#1	89.993(2)	N(3)#2-Co2-Co3#4	87.48(7)
F(3)-Os1-F(3)#2	89.994(2)	N(3)#3-Co2-Co3#4	87.48(7)
F(3)#1-Os1-F(3)#2	178.81(12)	N(3)-Co2-Co3#4	87.48(7)
F(3)-Os1-F(3)#3	178.82(12)	F(2)-Co2-Co3#4	180
F(3)#1-Os1-F(3)#3	89.994(2)	N(2B)-Co3-N(2B)#1	90.001(3)
F(3)#2-Os1-F(3)#3	89.994(2)	N(2B)-Co3-N(2B)#2	89.999(4)
F(3)-Os1-F(1)	89.41(6)	N(2B)#1-Co3-N(2B)#2	179.8(5)
F(3)#1-Os1-F(1)	89.41(6)	N(2B)-Co3-N(2B)#3	179.8(5)
F(3)#2-Os1-F(1)	89.41(6)	N(2B)#1-Co3-N(2B)#3	90.000(5)
F(3)#3-Os1-F(1)	89.41(6)	N(2B)#2-Co3-N(2B)#3	90.000(2)
F(3)-Os1-F(2)	90.59(6)	N(2A)#1-Co3-N(2A)#2	179.3(2)
F(3)#1-Os1-F(2)	90.59(6)	N(2A)#1-Co3-N(2A)#3	89.998(2)
F(3)#2-Os1-F(2)	90.59(6)	N(2A)#2-Co3-N(2A)#3	89.998(3)
F(3)#3-Os1-F(2)	90.59(6)	N(2A)#1-Co3-N(2A)	89.997(3)
F(1)-Os1-F(2)	180	N(2A)#2-Co3-N(2A)	89.999(2)
N(1)-Co1-N(1)#2	89.918(6)	N(2A)#3-Co3-N(2A)	179.3(2)
N(1)-Co1-N(1)#3	175.67(14)	N(2B)-Co3-Co1	89.9(2)
N(1)#2-Co1-N(1)#3	89.918(6)	N(2B)#1-Co3-Co1	89.9(2)
N(1)-Co1-N(1)#1	89.919(6)	N(2B)#2-Co3-Co1	89.9(2)
N(1)#2-Co1-N(1)#1	175.67(14)	N(2B)#3-Co3-Co1	89.9(2)
N(1)#3-Co1-N(1)#1	89.918(6)	N(2A)#1-Co3-Co1	89.66(12)
N(1)-Co1-F(1)	92.17(7)	N(2A)#2-Co3-Co1	89.66(12)
N(1)#2-Co1-F(1)	92.17(7)	N(2A)#3-Co3-Co1	89.66(12)
N(1)#3-Co1-F(1)	92.17(7)	N(2A)-Co3-Co1	89.66(12)
N(1)#1-Co1-F(1)	92.17(7)	N(2B)-Co3-Co2#5	90.1(2)
N(1)-Co1-Co3	87.83(7)	N(2B)#1-Co3-Co2#5	90.1(2)
N(1)#2-Co1-Co3	87.83(7)	N(2B)#2-Co3-Co2#5	90.1(2)
N(1)#3-Co1-Co3	87.83(7)	N(2B)#3-Co3-Co2#5	90.1(2)
N(1)#1-Co1-Co3	87.83(7)	N(2A)#1-Co3-Co2#5	90.34(12)
F(1)-Co1-Co3	180	N(2A)#2-Co3-Co2#5	90.34(12)
N(3)#1-Co2-N(3)#2	174.96(13)	N(2A)#3-Co3-Co2#5	90.34(12)
N(3)#1-Co2-N(3)#3	89.889(6)	N(2A)-Co3-Co2#5	90.34(12)
N(3)#2-Co2-N(3)#3	89.889(6)	Co1-Co3-Co2#5	180
N(3)#1-Co2-N(3)	89.890(6)	Os1-F(1)-Co1	180
N(3)#2-Co2-N(3)	89.889(6)	C(10B)-N(3)-C(6B)	120.8(10)
N(3)#3-Co2-N(3)	174.97(13)	C(6A)-N(3)-C(10A)	117.4(5)
N(3)#1-Co2-F(2)	92.52(7)	C(10B)-N(3)-Co2	119.0(8)
N(3)#2-Co2-F(2)	92.52(7)	C(6B)-N(3)-Co2	120.1(7)
N(3)#3-Co2-F(2)	92.52(7)	C(6A)-N(3)-Co2	121.3(3)
N(3)-Co2-F(2)	92.52(7)	C(10A)-N(3)-Co2	121.2(4)
N(3)#1-Co2-Co3#4	87.48(7)		

C(5A)-N(1)-C(1A)	118.3(5)	C(6B)#6-N(2B)-C(1B)#2	123.7(11)
C(5B)-N(1)-C(1B)	118.9(10)	C(6B)#6-N(2B)-Co3	118.0(9)
C(5B)-N(1)-Co1	121.2(9)	C(1B)#2-N(2B)-Co3	118.4(7)
C(5A)-N(1)-Co1	121.9(4)	N(2B)#1-C(1B)-C(2B)	126.1(11)
C(1A)-N(1)-Co1	119.3(3)	N(2B)#1-C(1B)-N(1)	114.8(9)
C(1B)-N(1)-Co1	118.3(5)	C(2B)-C(1B)-N(1)	118.7(11)
C(3A)-C(4)-C(5A)	118.4(7)	C(3B)-C(2B)-C(1B)	123.6(15)
C(3B)-C(4)-C(5B)	120.2(13)	N(3)-C(10B)-C(9B)	123.3(16)
N(1)-C(5A)-C(4)	122.8(7)	C(7B)-C(6B)-N(2B)#7	126(2)
C(8A)-C(7A)-C(6A)	119.4(14)	C(7B)-C(6B)-N(3)	118(2)
C(9A)-C(8A)-C(7A)	118.3(11)	N(2B)#7-C(6B)-N(3)	116.3(12)
Os1-F(2)-Co2	180	C(8B)-C(9B)-C(10B)	114.7(19)
C(1A)-N(2A)-C(6A)#6	124.3(5)	C(2B)-C(3B)-C(4)	114.2(17)
C(1A)-N(2A)-Co3	118.0(4)	N(1)-C(5B)-C(4)	120.7(15)
C(6A)#6-N(2A)-Co3	117.7(4)	C(9B)-C(8B)-C(7B)	120(3)
N(2A)-C(1A)-N(1)	115.3(5)	C(6B)-C(7B)-C(8B)	123(4)
N(2A)-C(1A)-C(2A)	125.1(5)	C(12)-O(1)-O(1)#8	130.5(12)
N(1)-C(1A)-C(2A)	119.3(5)	N(5)-C(11)-N(5)#9	50.6(11)
C(3A)-C(2A)-C(1A)	118.6(7)	C(12)-N(5)-N(5)#9	153.4(13)
C(4)-C(3A)-C(2A)	122.0(8)	C(12)-N(5)-C(11)	103(2)
N(3)-C(6A)-N(2A)#7	114.5(6)	N(5)#9-N(5)-C(11)	75.4(13)
N(3)-C(6A)-C(7A)	120.0(10)	C(12)-N(5)-C(11)#9	128.3(16)
N(2A)#7-C(6A)-C(7A)	125.4(10)	N(5)#9-N(5)-C(11)#9	54.0(16)
C(10A)-C(9A)-C(8A)	121.1(8)	C(11)-N(5)-C(11)#9	127.4(14)
C(9A)-C(10A)-N(3)	123.5(7)	O(1)-C(12)-N(5)	120(2)

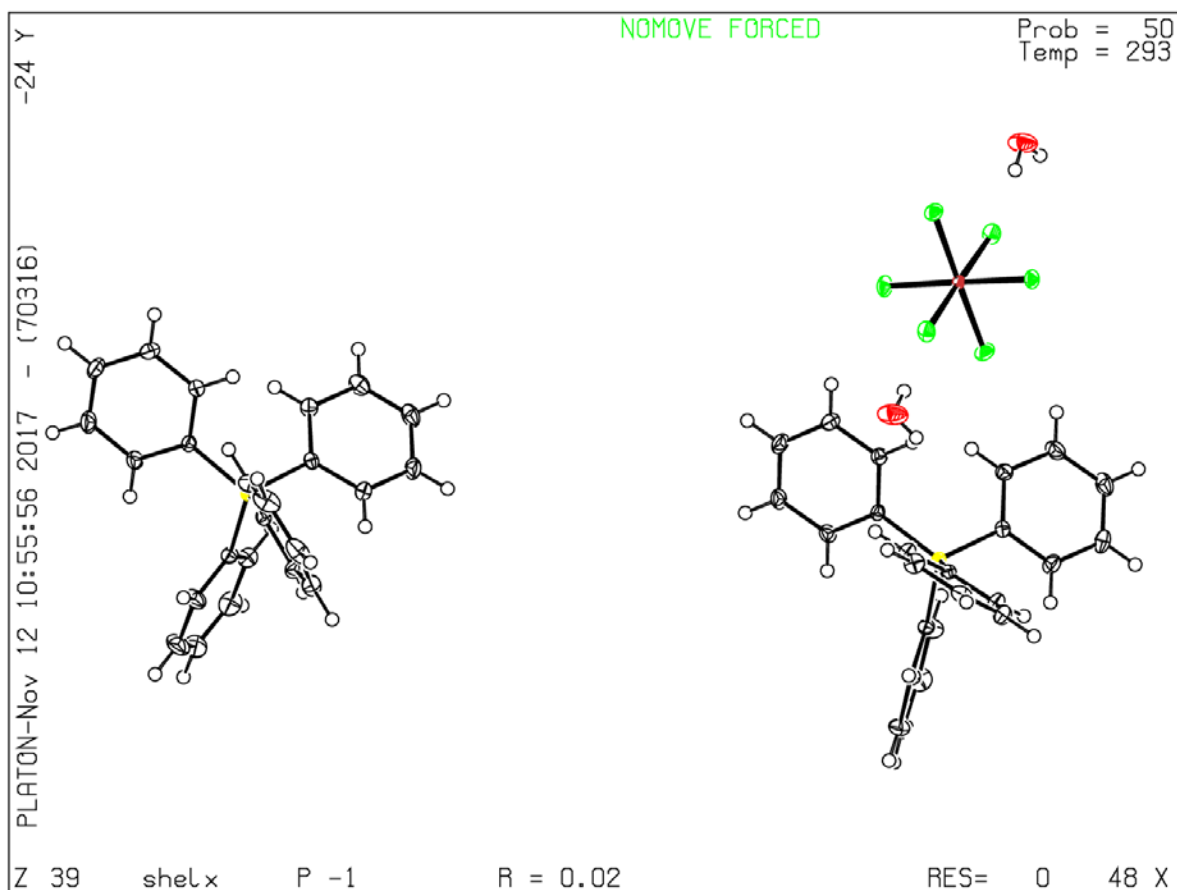
Symmetry transformations used to generate equivalent atoms:

#1 y, -x+1/2, z; #2 -y+1/2, x, z; #3 -x+1/2, -y+1/2, z; #4 -x+1/2, y, z-1/2; #5 -x+1/2, y, z+1/2;

#6 -y+1/2, -x+1/2, z+1/2; #7 -y+1/2, -x+1/2, z-1/2; #8 -x+1/2, -y-1/2, z; #9 y+1/2, x-1/2, -z+5/2



**Figure S13.** Arrangement of the DMF molecules at (right) half-occupancy and (left) full occupancy.



**Figure S14.** Platon thermal ellipsoid plot of  $(\text{PPh}_4)_2[\text{SnF}_6] \cdot 2\text{H}_2\text{O}$ .

**Table S5.** Crystal data and structure refinement for (PPh<sub>4</sub>)<sub>2</sub>[SnF<sub>6</sub>]·2H<sub>2</sub>O.

Empirical formula	C <sub>48</sub> H <sub>44</sub> F <sub>6</sub> O <sub>2</sub> P <sub>2</sub> Sn
Formula weight	947.46
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	<i>a</i> = 10.0145(5) Å <i>b</i> = 11.0176(5) Å <i>c</i> = 21.0953(11) Å <i>α</i> = 75.803(2)° <i>β</i> = 77.900(2)° <i>γ</i> = 71.137(2)°
Volume	2113.64(18) Å <sup>3</sup>
<i>Z</i>	2
Density (calculated)	1.489 g/cm <sup>3</sup>
Absorption coefficient	0.746 mm <sup>-1</sup>
<i>F</i> (000)	964
Crystal size	0.350 x 0.300 x 0.300 mm <sup>3</sup>
Theta range for data collection	1.006 to 30.094°
Index ranges	-13 ≤ <i>h</i> ≤ 14, -15 ≤ <i>k</i> ≤ 15, -29 ≤ <i>l</i> ≤ 29
Reflections collected	46234
Independent reflections	12370 [ <i>R</i> (int) = 0.0235]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	12370 / 0 / 548
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.035
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0207, <i>wR</i> <sub>2</sub> = 0.0507
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0226, <i>wR</i> <sub>2</sub> = 0.0521
Extinction coefficient	n/a
Largest diff. peak and hole	0.469 and -0.468 e.Å <sup>-3</sup>

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ ,  $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$ , where  $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$ .



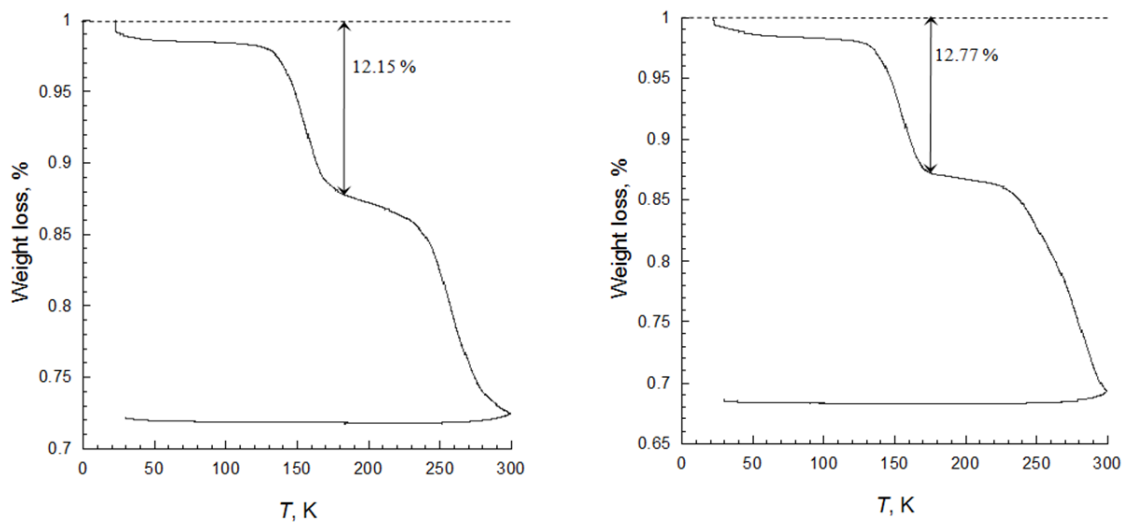
**Table S6.** Bond lengths [Å] for (PPh<sub>4</sub>)<sub>2</sub>[SnF<sub>6</sub>]·2H<sub>2</sub>O.

C(1)-C(2)	1.3941(16)	C(26)-C(27)	1.3871(16)
C(1)-C(6)	1.4031(16)	C(27)-C(28)	1.3949(18)
C(1)-P(1)	1.7940(12)	C(28)-C(29)	1.3882(18)
C(2)-C(3)	1.3931(19)	C(29)-C(30)	1.3921(17)
C(3)-C(4)	1.381(2)	C(31)-C(32)	1.3900(16)
C(4)-C(5)	1.387(2)	C(31)-C(36)	1.3996(18)
C(5)-C(6)	1.3823(18)	C(31)-P(2)	1.7958(11)
C(7)-C(12)	1.4000(16)	C(32)-C(33)	1.3967(17)
C(7)-C(8)	1.4029(16)	C(33)-C(34)	1.378(2)
C(7)-P(1)	1.7910(11)	C(34)-C(35)	1.390(2)
C(8)-C(9)	1.3899(17)	C(35)-C(36)	1.3873(19)
C(9)-C(10)	1.3886(19)	C(37)-C(38)	1.3951(15)
C(10)-C(11)	1.389(2)	C(37)-C(42)	1.4023(16)
C(11)-C(12)	1.3910(17)	C(37)-P(2)	1.7930(11)
C(13)-C(14)	1.3958(17)	C(38)-C(39)	1.3902(16)
C(13)-C(18)	1.3978(17)	C(39)-C(40)	1.3847(19)
C(13)-P(1)	1.7940(11)	C(40)-C(41)	1.3912(19)
C(14)-C(15)	1.3916(18)	C(41)-C(42)	1.3862(17)
C(15)-C(16)	1.384(2)	C(43)-C(48)	1.3986(16)
C(16)-C(17)	1.388(2)	C(43)-C(44)	1.3995(16)
C(17)-C(18)	1.3918(18)	C(43)-P(2)	1.8012(12)
C(19)-C(20)	1.3951(16)	C(44)-C(45)	1.3936(17)
C(19)-C(24)	1.3993(16)	C(45)-C(46)	1.3861(18)
C(19)-P(1)	1.7957(11)	C(46)-C(47)	1.3915(18)
C(20)-C(21)	1.3952(17)	C(47)-C(48)	1.3825(18)
C(21)-C(22)	1.3841(19)	F(2)-Sn(1)	1.9846(7)
C(22)-C(23)	1.3884(19)	F(3)-Sn(1)	1.9528(7)
C(23)-C(24)	1.3859(17)	F(4)-Sn(1)	1.9590(7)
C(25)-C(30)	1.3965(16)	F(5)-Sn(1)	1.9761(7)
C(25)-C(26)	1.4045(15)	F(6)-Sn(1)	1.9540(7)
C(25)-P(2)	1.7920(11)	F(7)-Sn(1)	1.9505(7)

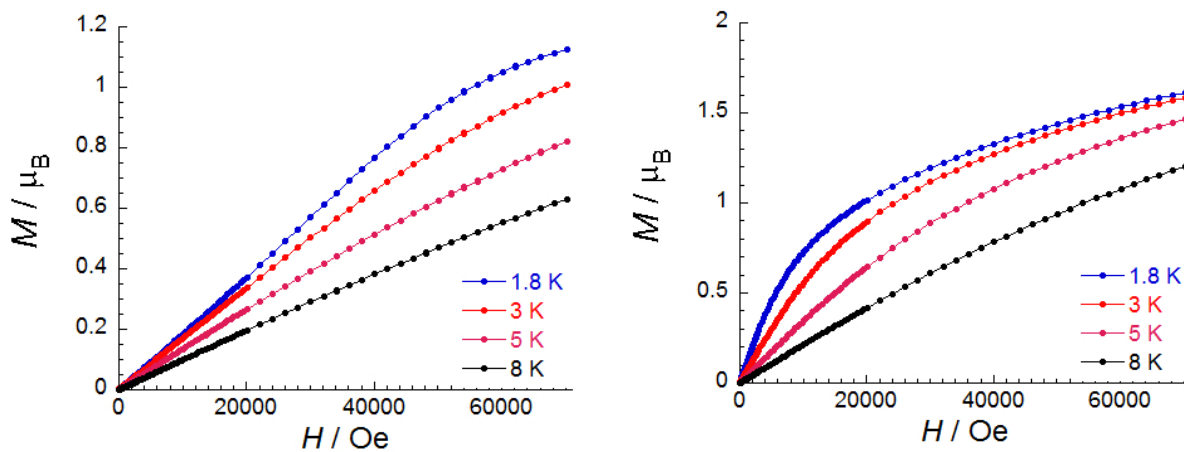
**Table S7.** Bond angles [°] for (PPh<sub>4</sub>)<sub>2</sub>[SnF<sub>6</sub>]·2H<sub>2</sub>O.

C(2)-C(1)-C(6)	119.76(11)	C(24)-C(23)-C(22)	119.97(12)	C(46)-C(45)-C(44)	120.23(11)
C(2)-C(1)-P(1)	121.18(9)	C(23)-C(24)-C(19)	119.98(12)	C(45)-C(46)-C(47)	120.00(11)
C(6)-C(1)-P(1)	118.89(9)	C(30)-C(25)-C(26)	120.31(10)	C(48)-C(47)-C(46)	120.17(11)
C(3)-C(2)-C(1)	119.50(12)	C(30)-C(25)-P(2)	119.77(8)	C(47)-C(48)-C(43)	120.36(11)
C(4)-C(3)-C(2)	120.54(13)	C(26)-C(25)-P(2)	119.80(9)	C(46)-C(45)-C(44)	120.23(11)
C(3)-C(4)-C(5)	119.97(12)	C(27)-C(26)-C(25)	119.37(11)	C(45)-C(46)-C(47)	120.00(11)
C(6)-C(5)-C(4)	120.39(12)	C(26)-C(27)-C(28)	120.02(11)	C(7)-P(1)-C(19)	110.90(5)
C(5)-C(6)-C(1)	119.82(12)	C(29)-C(28)-C(27)	120.77(11)	C(1)-P(1)-C(19)	109.23(5)
C(12)-C(7)-C(8)	120.13(10)	C(28)-C(29)-C(30)	119.61(11)	C(13)-P(1)-C(19)	107.97(5)
C(12)-C(7)-P(1)	120.04(9)	C(29)-C(30)-C(25)	119.89(11)	C(25)-P(2)-C(37)	111.43(5)
C(8)-C(7)-P(1)	119.79(9)	C(32)-C(31)-C(36)	120.32(11)	C(25)-P(2)-C(31)	110.02(5)
C(9)-C(8)-C(7)	119.51(11)	C(32)-C(31)-P(2)	121.49(9)	C(37)-P(2)-C(31)	106.45(5)
C(10)-C(9)-C(8)	119.98(12)	C(36)-C(31)-P(2)	118.17(9)	C(25)-P(2)-C(43)	107.88(5)
C(9)-C(10)-C(11)	120.85(12)	C(31)-C(32)-C(33)	119.23(12)	C(37)-P(2)-C(43)	111.68(5)
C(10)-C(11)-C(12)	119.69(12)	C(34)-C(33)-C(32)	120.29(13)	C(31)-P(2)-C(43)	109.37(5)
C(11)-C(12)-C(7)	119.81(11)	C(33)-C(34)-C(35)	120.68(12)	F(7)-Sn(1)-F(3)	90.39(3)
C(14)-C(13)-C(18)	120.23(11)	C(36)-C(35)-C(34)	119.61(13)	F(7)-Sn(1)-F(6)	90.40(3)
C(14)-C(13)-P(1)	120.09(9)	C(35)-C(36)-C(31)	119.85(13)	F(3)-Sn(1)-F(6)	179.07(3)
C(18)-C(13)-P(1)	119.59(9)	C(38)-C(37)-C(42)	119.80(11)	F(7)-Sn(1)-F(4)	178.59(3)
C(15)-C(14)-C(13)	119.50(13)	C(38)-C(37)-P(2)	121.87(9)	F(3)-Sn(1)-F(4)	89.71(3)
C(16)-C(15)-C(14)	119.99(13)	C(42)-C(37)-P(2)	118.33(9)	F(6)-Sn(1)-F(4)	89.51(3)
C(15)-C(16)-C(17)	120.91(12)	C(39)-C(38)-C(37)	119.48(11)	F(7)-Sn(1)-F(5)	91.11(3)
C(16)-C(17)-C(18)	119.51(13)	C(40)-C(39)-C(38)	120.77(12)	F(3)-Sn(1)-F(5)	90.10(3)
C(17)-C(18)-C(13)	119.84(12)	C(39)-C(40)-C(41)	119.82(11)	F(6)-Sn(1)-F(5)	89.40(3)
C(20)-C(19)-C(24)	120.01(11)	C(42)-C(41)-C(40)	120.16(12)	F(4)-Sn(1)-F(5)	90.30(3)
C(20)-C(19)-P(1)	121.60(9)	C(41)-C(42)-C(37)	119.94(11)	F(7)-Sn(1)-F(2)	89.55(3)
C(24)-C(19)-P(1)	118.35(9)	C(48)-C(43)-C(44)	119.35(11)	F(3)-Sn(1)-F(2)	89.16(3)
C(19)-C(20)-C(21)	119.38(11)	C(48)-C(43)-P(2)	120.20(9)	F(6)-Sn(1)-F(2)	91.33(3)
C(22)-C(21)-C(20)	120.34(12)	C(44)-C(43)-P(2)	120.42(9)	F(4)-Sn(1)-F(2)	89.04(3)
C(21)-C(22)-C(23)	120.32(11)	C(45)-C(44)-C(43)	119.89(11)	F(5)-Sn(1)-F(2)	179.01(3)

## TGA and Magnetism



**Figure S15.** Thermogravimetric analysis of **4** (left) and **5** (right) with the specified mass attributed to solvent loss (1 K/min).



**Figure S16.** Field dependence of magnetization for **4** (left) and **5** (right) below 8 K.