Supporting Information

Novel lanthanide(III) porphyrin-based metal-organic frameworks: structure, gas adsorption and magnetic properties

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Table S1 Crystal data for **UPJS-10**, **UPJS-11** and **UPJS-12**.

Identification code	UPJS-10	UPJS-11	UPJS-12
Empirical formula	$C_{11}H_6NO_3SPr_{0.25}$	$C_{11}H_6NO_3SEu_{0.10}Sm_{0.15}$	$C_{11}H_6NO_3SCe_{0,25}$
Formula weight	270.96	269.98	267.26
Temperature	120(2) K	120(2) K	250(2) K
Wavelength	0.71073Å	1.54178 Å	0.71073 Å
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space group	P4/mcc	P4/mcc	P4/mcc
Unit cell dimensions	a =15.3898(5) Å	a = 15.3792(5)	a = 15.4360(3)
	b = 15.3898(5) Å	b= 15.3792(5)	b= 15.4360(3)
	c =9.9474(6) Å	c = 9.8583(5)	c = 10.0140(5)
Volume	2356.0(2) $Å^3$	2331.68(19) $Å^3$	2386.04(15) $Å^3$
Z	8	8	8
Density (calculated)	1.528 mg/m^3	1.538 mg/m^3	1.488 mg/m^3
Absorption coefficient	1.276 mm^{-1}	11.1750 mm^{-1}	1.192 mm^{-1}
F(000)	1084	1077	1068
Crystal size	0.348 x 0.178 x 0.164 mm^3	0.664 x 0.248 x 0.162 mm^3	0.216 x 0.134 x 0.118 mm^3
Theta range for data collection	2.960 to 28.122°.	6.435 to 70.232°	2.639 to 27.509°
Index ranges	-20<=h<=20, -20<=k<=20, -13<=l<=13	-18<=h<=16, -15<=k<=18, -12<=l<=8	-16<=h<=20, -19<=k<=16, -13<=l<=7
Reflections collected	51353	8458	5532
Independent reflections	1526 [R(int) = 0.0764]	1182 [R(int) = 0.0710]	1427 [R(int) = 0.0436]
Data completeness	99.5 %	99.3 %	97.1 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2

Data / restraints / parameters	1526 / 6 / 94	1182 / 90 / 93	1427 / 7 / 95
Goodness-of-fit on F2	1.151	1.167	1.148
Final R indices [I>2sigma(I)]	R1 = 0.0721, wR2 = 0.1640	R1 = 0.0773, wR2 = 0.1854	R1 = 0.0552, wR2 = 0.1216
R indices (all data)	R1 = 0.0962, wR2 = 0.1883	R1 = 0.0886, wR2 = 0.1949	R1 = 0.0727, wR2 = 0.1326
Extinction coefficient	n/a	n/a	n/a
Largest diff. peak and hole	2.312 and -2.080 e.Å^{-3}	1.969 and -0.936 e.A^{-3}	1.124 and -1.123 e.A^{-3}
Deposition Number	1998983	2041240	2041241

Table S2 Selected bond lengths [Å] and bond angles [°] for **UPJS-10**.

Bond lengths	[Å]	Bond angles	[°]	Bond angles	[°]
Pr(1A)-O(1)	2.439(6)	O(1)-Pr(1A)-O(1)#1	69.3(4)	O(1)#2-Pr(1A)-O(1)#7	69.3(4)
O(1)-S(1)	1.443(8)	O(1)#2-Pr(1A)-O(1)#4	73.6(2)	O(1)#8-S(1)-O(1)	111.2(6)
S(1)-O(2)	1.428(7)	O(1)#3-Pr(1A)-O(1)#4	87.3(3)	O(2)-S(1)-C(1)	106.1(4)
S(1)-C(1)	1.797(9)	O(1)-Pr(1A)-O(1)#5	156.8(2)		
C(1)-C(2)	1.360(12)	O(1)#1-Pr(1A)-O(1)#5	115.8(4)		
C(2)-C(3)	1.397(9)	O(1)#3-Pr(1A)-O(1)#5	73.6(2)		
C(3)-C(4)	1.368(12)	O(1)#4-Pr(1A)-O(1)#5	69.3(4)		
C(4)-C(5)	1.512(12)	O(1)-Pr(1A)-O(1)#6	73.6(2)		
C(5)-C(9)	1.385(12)	O(1)#1-Pr(1A)-O(1)#6	87.3(3)		
C(5)-C(6)	1.392(12)	O(1)#2-Pr(1A)-O(1)#6	115.8(4)		
C(6)-N(1)	1.382(11)	O(1)#3-Pr(1A)-O(1)#6	69.3(4)		
C(6)-C(7)	1.423(12)	O(1)#4-Pr(1A)-O(1)#6	73.6(2)		
N(1)-C(9)#9	1.380(10)	O(1)#5-Pr(1A)-O(1)#6	127.8(3)		
C(7)-C(8)#9	1.359(13)	O(1)-Pr(1A)-O(1)#7	87.3(3)		
C(9)-C(8)	1.440(12)	O(1)#1-Pr(1A)-O(1)#7	73.6(2)		

Symmetry transformations used to generate equivalent atoms: #1 x,-y,-z+1/2; #2 y,-x,z; #3 y,x,-z+1/2; #4 -x,-y,z; #5 -x,y,-z+1/2; #6 -y,x,z; #7 -y,-x,-z+1/2; #8 x,y,-z; #9 y,-x+1,-z.

Table S3 Selected bond lengths [Å] and bond angles [°] for **UPJS-11**.

Bond lengths	[Å]	Bond angles	[°]	Bond angles	[°]
Sm(1)-O(1)#1	2.406(7)	O(1)#1-Sm(1)-O(1)#2	128.0(3)	O(1)#3-Sm(1)-O(1)	116.0(5)
Sm(1)-O(1)#2	2.406(7)	O(1)#1-Sm(1)-O(1)#3	156.5(3)	O(1)#4-Sm(1)-O(1)	128.0(3)
Sm(1)-O(1)#3	2.406(7)	O(1)#2-Sm(1)-O(1)#3	73.7(2)	O(1)#5-Sm(1)-O(1)	156.5(3)
Sm(1)-O(1)#4	2.406(7)	O(1)#1-Sm(1)-O(1)#4	73.7(2)	O(1)#6-Sm(1)-O(1)	73.7(2)
Sm(1)-O(1)#5	2.406(7)	O(1)#2-Sm(1)-O(1)#4	156.5(3)	O(1)#7-Sm(1)-O(1)	86.9(4)
Sm(1)-O(1)#6	2.406(7)	O(1)#3-Sm(1)-O(1)#4	86.9(4)	S(1)-O(1)-Sm(1)	152.9(6)
Sm(1)-O(1)#7	2.406(7)	O(1)#1-Sm(1)-O(1)#5	116.0(5)	O(2)-S(1)-O(1)	112.1(4)
Sm(1)-O(1)	2.406(7)	O(1)#2-Sm(1)-O(1)#5	86.9(4)	O(2)-S(1)-O(1)#8	112.1(4)
C(1)-C(2)	1.353(12)	O(1)#3-Sm(1)-O(1)#5	69.2(5)	O(1)-S(1)-O(1)#8	112.4(8)
C(1)-C(2)#8	1.353(12)	O(1)#4-Sm(1)-O(1)#5	73.7(2)	O(2)-S(1)-C(1)	105.4(5)
C(1)-S(1)	1.812(11)	O(1)#1-Sm(1)-O(1)#6	86.9(4)	O(1)-S(1)-C(1)	107.1(3)
C(2)-C(3)	1.397(12)	O(1)#2-Sm(1)-O(1)#6	116.0(5)	O(1)#8-S(1)-C(1)	107.1(3)
C(3)-C(4)	1.375(12)	O(1)#3-Sm(1)-O(1)#6	73.7(2)		
C(4)-C(5)	1.515(14)	O(1)#4-Sm(1)-O(1)#6	69.2(5)		
C(5)-C(6)	1.389(15)	O(1)#5-Sm(1)-O(1)#6	128.0(3)		
C(5)-C(8)	1.399(15)	O(1)#1-Sm(1)-O(1)#7	73.7(2)		
C(6)-N(1)	1.367(14)	O(1)#2-Sm(1)-O(1)#7	69.2(5)		
C(6)-C(7)	1.429(16)	O(1)#3-Sm(1)-O(1)#7	128.0(3)		
C(7)-C(9)#9	1.350(16)	O(1)#4-Sm(1)-O(1)#7	116.0(5)		
C(8)-N(1)#10	1.384(13)	O(1)#5-Sm(1)-O(1)#7	73.7(2)		
C(8)-C(9)	1.428(15)	O(1)#6-Sm(1)-O(1)#7	156.5(3)		
O(1)-S(1)	1.432(8)	O(1)#1-Sm(1)-O(1)	69.2(5)		
O(2)-S(1)	1.431(8)	O(1)#2-Sm(1)-O(1)	73.7(2)		

Symmetry transformations used to generate equivalent atoms: #1 x,-y,-z+1/2; #2 y,-x,z; #3 -x,-y,z; #4 y,x,-z+1/2; #5 -x,y,-z+1/2; #6 -y,x,z; #7 -y,-x,-z+1/2; #8 x,y,-z; #9 -y+1,x,z; #10 y,-x+1,-z

Table S4 Selected bond lengths [Å] and bond angles [°] for **UPJS-12**.

Bond lengths	[Å]	Bond angles	[°]	Bond angles	[°]
Ce(1A)-O(2)	2.467(4)	O(2)-Ce(1A)-O(2)#1	157.65(16)	O(2)#3-Ce(1A)-O(2)#6	127.24(19)
S(1)-O(1)	1.433(5)	O(2)-Ce(1A)-O(2)#2	73.36(15)	O(2)#4-Ce(1A)-O(2)#6	73.36(15)
S(1)-O(2)	1.435(6)	O(2)#1-Ce(1A)-O(2)#2	127.24(18)	O(2)#5-Ce(1A)-O(2)#6	157.65(16)
S(1)-C(1)	1.783(6)	O(2)-Ce(1A)-O(2)#3	88.1(2)	Ce(1B)#1-Ce(1A)-O(2)#7	122.35(16)
N(1)-C(9)	1.370(8)	O(2)#1-Ce(1A)-O(2)#3	73.36(15)	Ce(1B)-Ce(1A)-O(2)#7	57.65(16)
N(1)-C(6)	1.382(8)	O(2)#2-Ce(1A)-O(2)#3	157.65(16)	O(2)-Ce(1A)-O(2)#7	127.23(18)
C(1)-C(2)	1.349(8)	O(2)-Ce(1A)-O(2)#4	73.36(15)	O(2)#1-Ce(1A)-O(2)#7	73.36(15)
C(2)-C(3)	1.396(7)	O(2)#1-Ce(1A)-O(2)#4	88.1(2)	O(2)#2-Ce(1A)-O(2)#7	69.4(3)
C(3)-C(4)	1.370(8)	O(2)#2-Ce(1A)-O(2)#4	115.3(3)	O(2)#3-Ce(1A)-O(2)#7	115.3(3)
C(4)-C(5)	1.505(8)	O(2)#3-Ce(1A)-O(2)#4	69.4(3)	O(2)#4-Ce(1A)-O(2)#7	157.65(16)
C(5)-C(6)	1.391(9)	O(2)-Ce(1A)-O(2)#5	69.4(3)	O(2)#5-Ce(1A)-O(2)#7	73.36(15)
C(6)-C(7)	1.424(9)	O(2)#1-Ce(1A)-O(2)#5	115.3(3)	O(2)#6-Ce(1A)-O(2)#7	88.1(2)
C(8)-C(9)	1.431(8)	O(2)#3-Ce(1A)-O(2)#5	73.36(15)	O(1)-S(1)-O(2)	112.6(2)
		O(2)#4-Ce(1A)-O(2)#5	127.24(18)	O(2)#8-S(1)-O(2)	111.1(5)
		O(2)-Ce(1A)-O(2)#6	115.3(3)	O(1)-S(1)-C(1)	105.6(3)
		O(2)#1-Ce(1A)-O(2)#6	69.4(3)	O(2)#8-S(1)-C(1)	107.2(2)
		O(2)#2-Ce(1A)-O(2)#6	73.36(15)	O(2)-S(1)-C(1)	107.2(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2; #2 -y+1,x,z; #3 -y+1,-x+1,-z+3/2; #4 y,-x+1,z; #5 x,-y+1,-z+3/2; #6 -x+1,-y+1,z; #7 y,x,-z+3/2; #8 x,y,-z+1; #9 y,-x,-z+1.

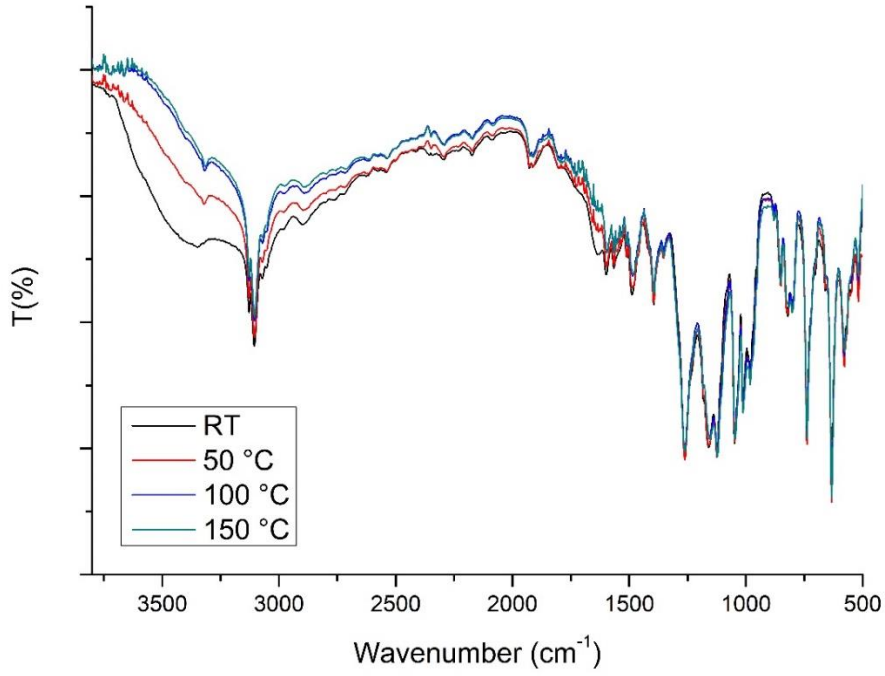

Figure S1 DRIFT mode FT-IR spectrum for **UPJS-10** at different temperature under vacuum.

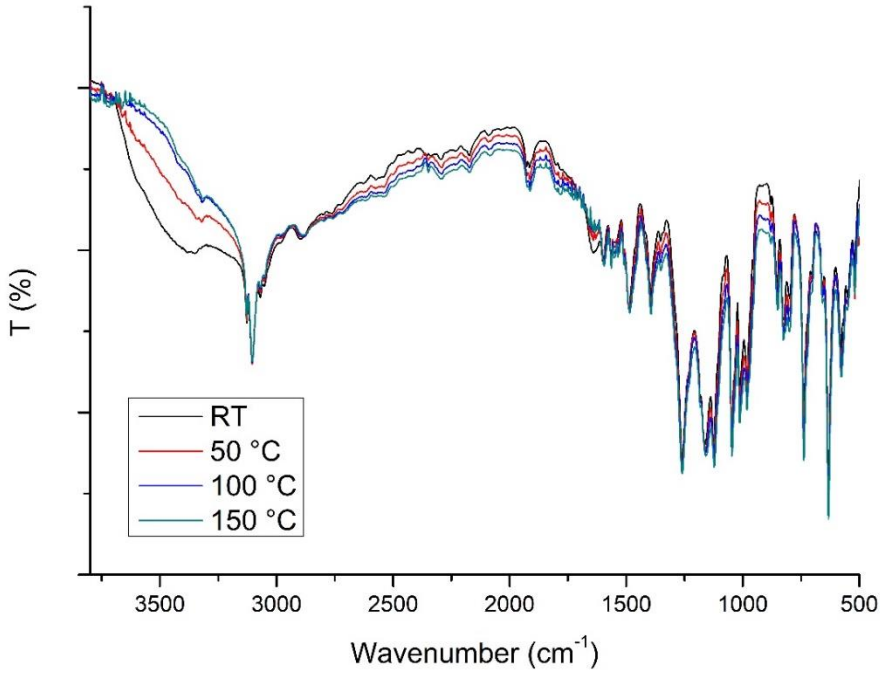

Figure S2 DRIFT mode FT-IR spectrum for **UPJS-12** at different temperature under vacuum.

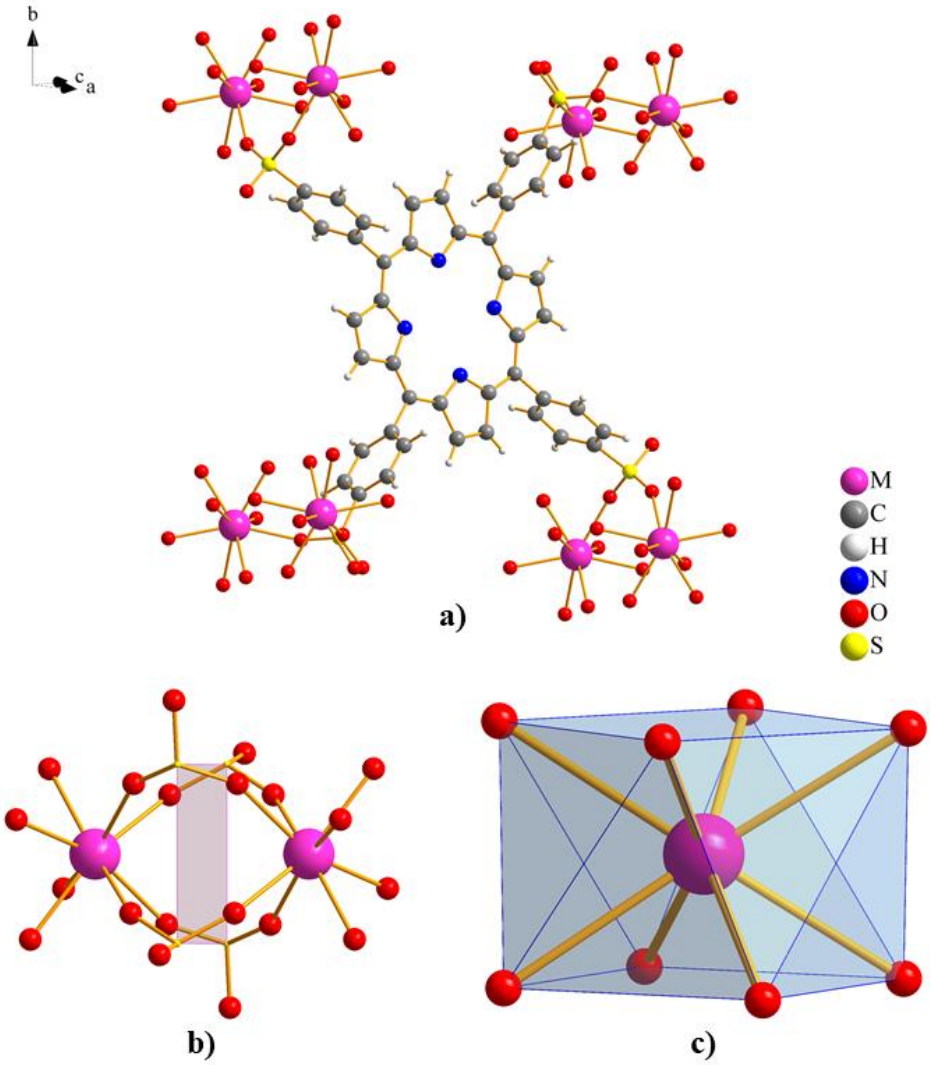

Figure S3 a) The coordination polymer $\{[Eu/Sm(H_2TPPS)]\cdot nH_3O^+\cdot nH_2O\}_n$. b) View of the -M-$(SO_3)_4$-M (M = Eu(III) and Sm(III)) cluster with the representation of an square SBU, c) Deformed square antiprism coordination geometry of M(III).

Table S5 EDS atoms mapping of compound **UPJS-11**.

Processing option: All elements analysed (Normalised). All results in weight%

Spectrum	In stats.	Sm	Eu	Total
Spectrum 2	Yes	59.95	40.05	100.00
Mean		59.95	40.05	100.00
Std. deviation		0.00	0.00	
Max.		59.95	40.05	
Min.		59.95	40.05	

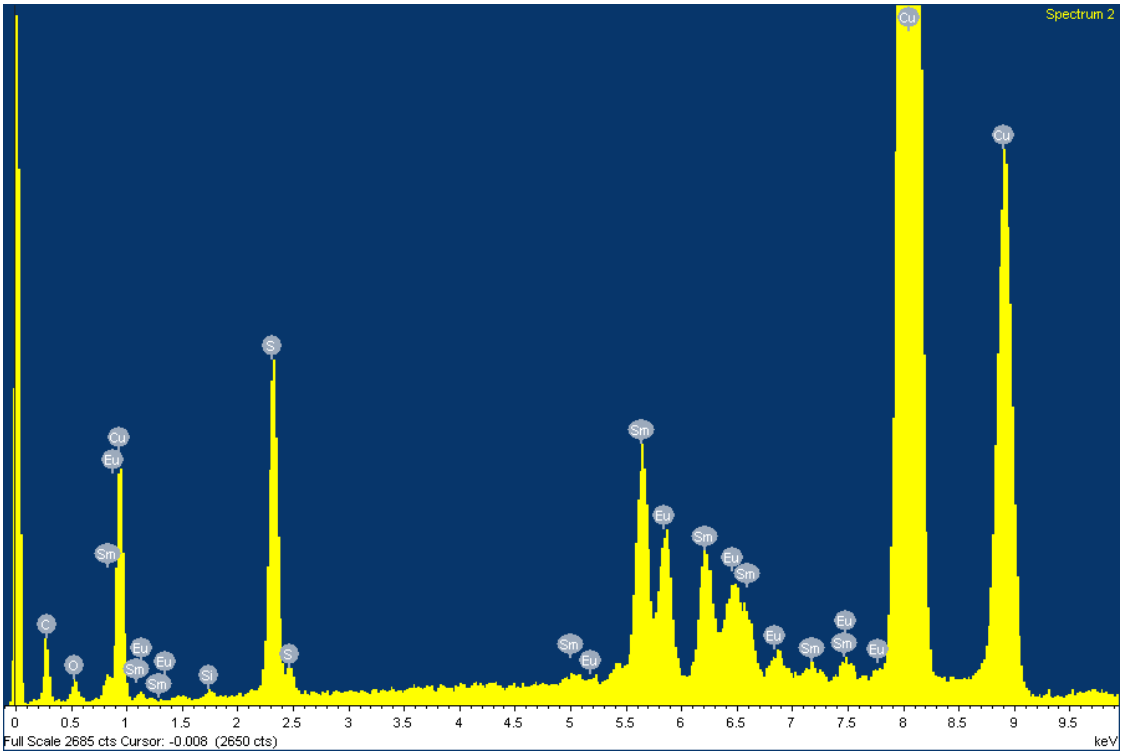

Figure S4 EDS analysis of the compound **UPJS-11**.

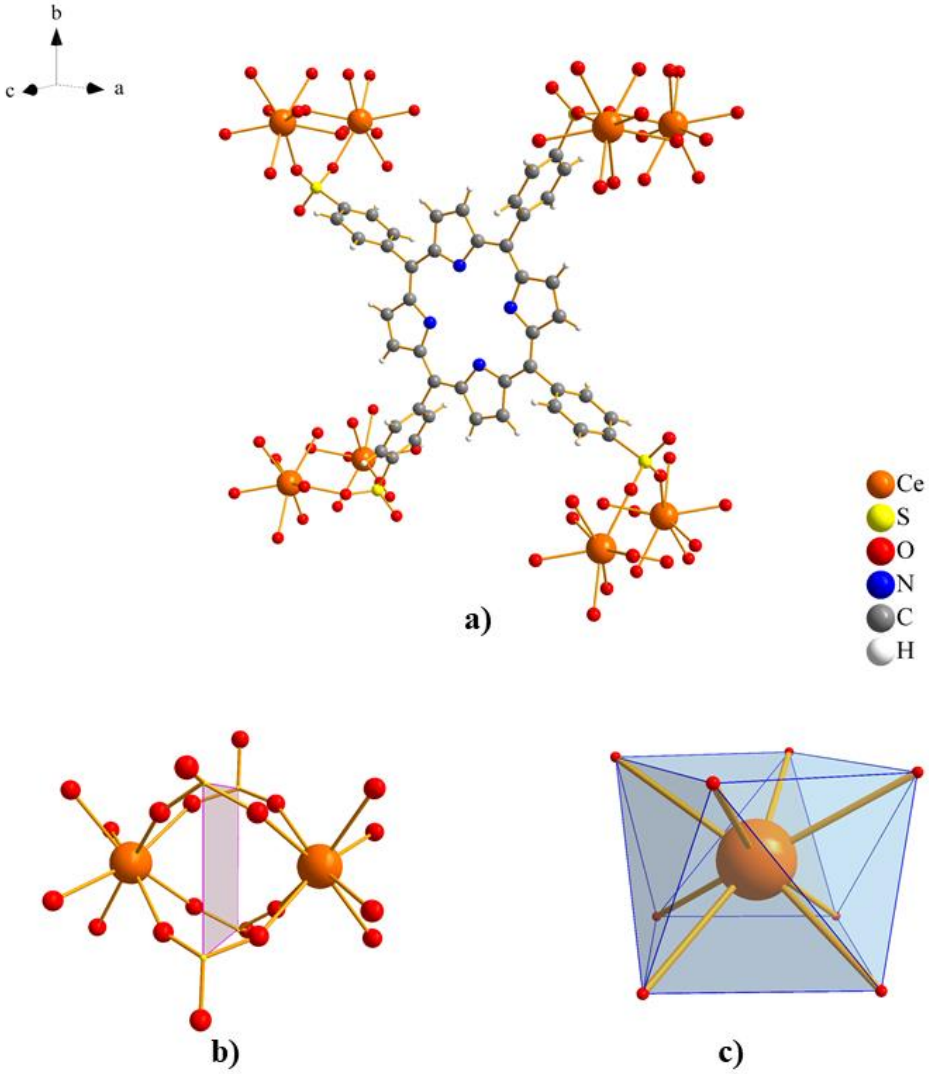

Figure S5 a) The coordination polymer $\{[Ce_4(H_2TPPS)_3]\cdot nH_2O\}_n$. b) View of the Ce-$(SO_3)_4$-Ce cluster with the representation of an square SBU, c) Deformed square antiprism coordination geometry of Ce(III).

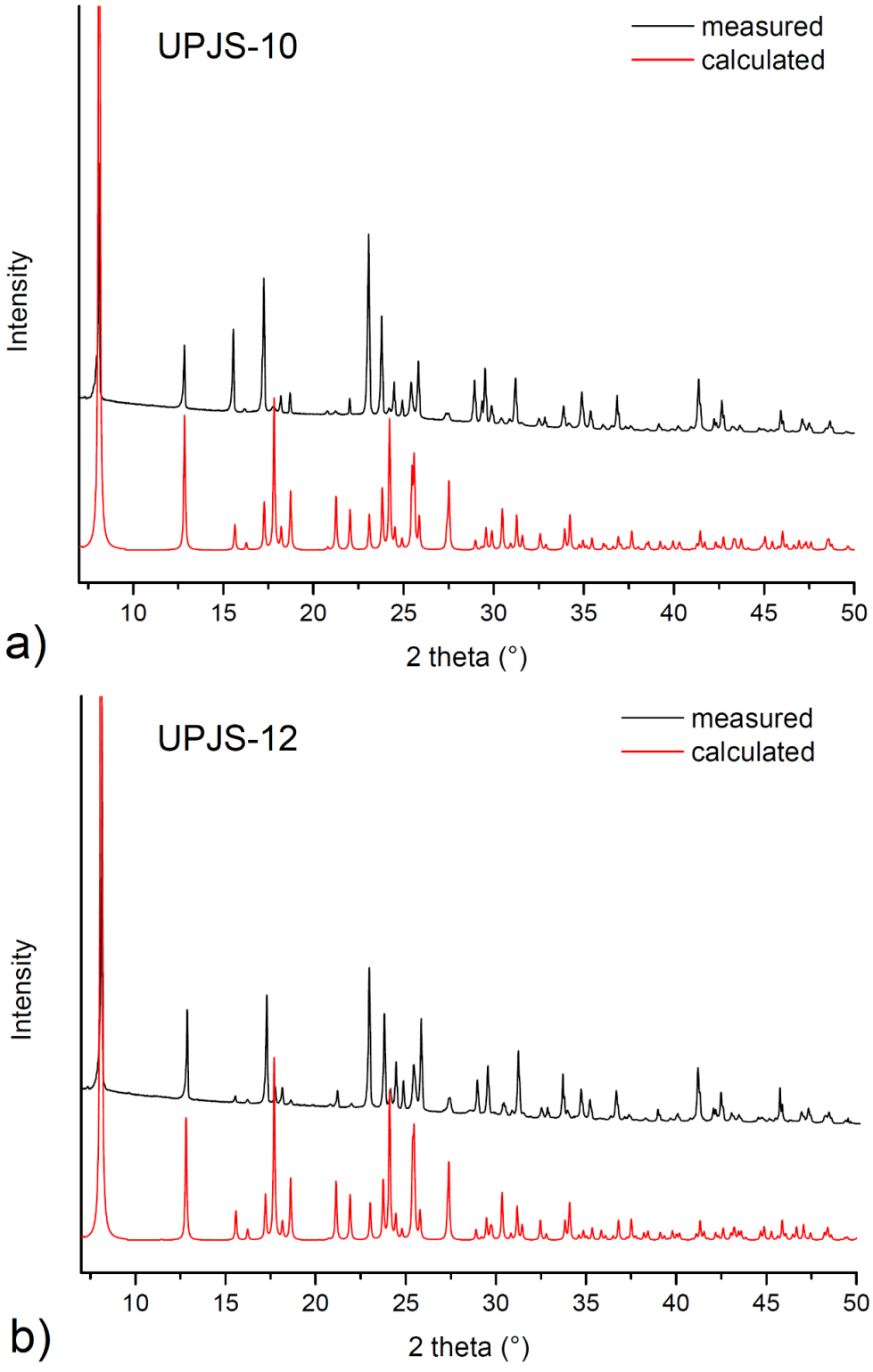

Figure S6 Comparison of PXRD patterns of as synthesized samples (black line) and the calculated patterns from single X-ray diffraction data (red line) for a) **UPJS-10** and b) **UPJS-12.**

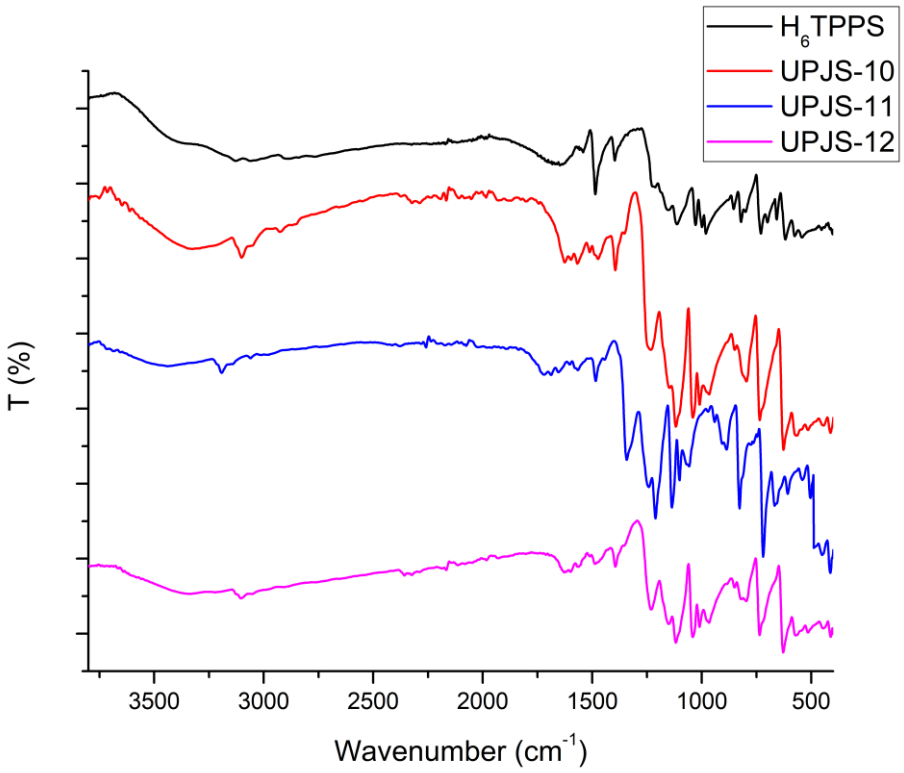

Figure S7 FT-IR spectrum of the H_6TPPS ligand and complexes **UPJS-10**, **UPJS-11** and **UPJS-12**.

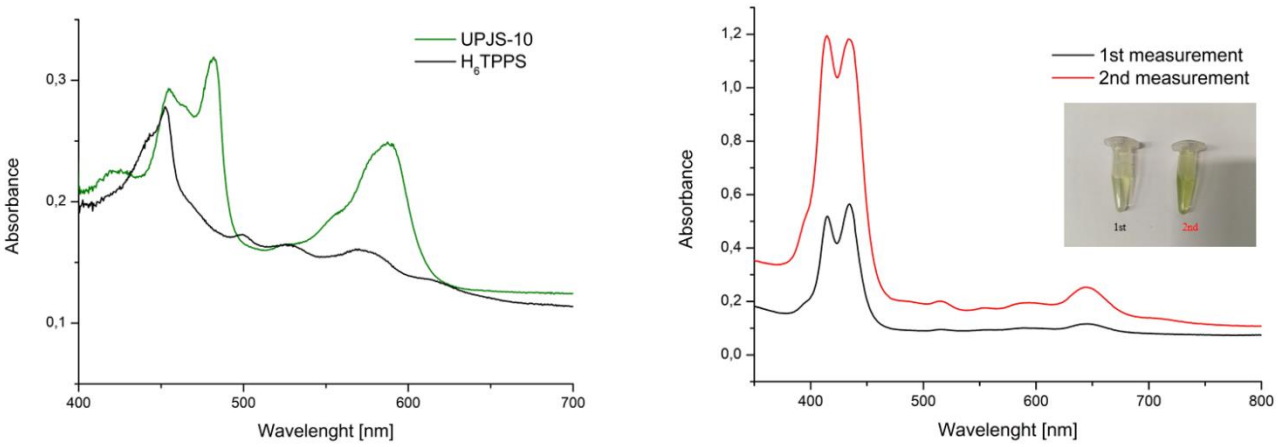

Figure S8 UV-VIS spectrum of: a) solid state of **UPJS-10** and H_6TPPS, b) solution state spectrum of **UPJS-10** for $^1O_2$ measurements. (Photo was taken by author N. Király, the image is free domain.)

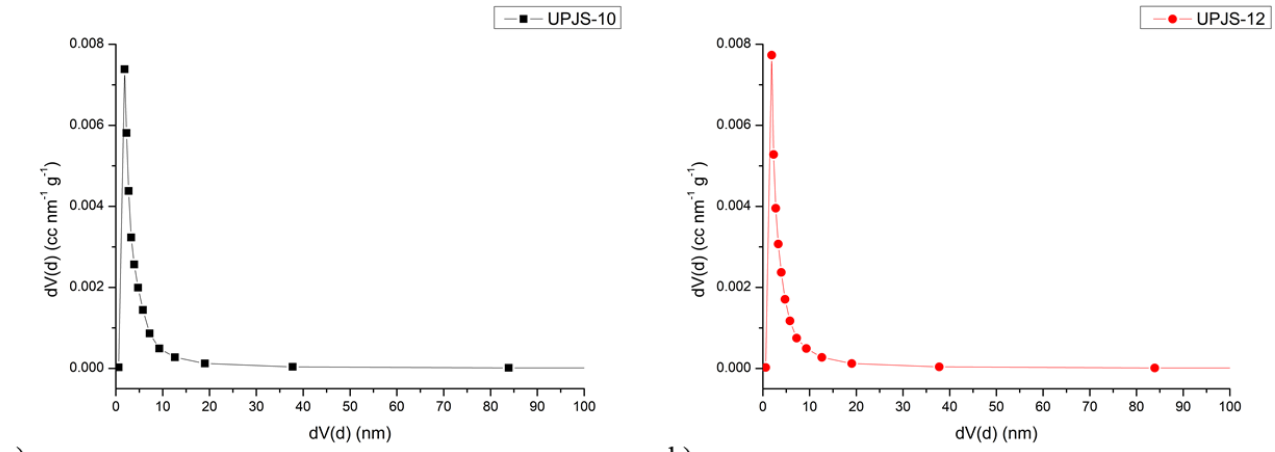

Figure S9 Pore size distribution DFT Calc. Model: Ar at 87K zeolites/silica (spher./cylindr. Pores, NLDFT equi.) for a) **UPJS-10** and b) **UPJS-12**.