Supporting Information for:

Permanent porosity and role of sulfonate groups in coordination networks constructed from a new polyfunctional phosphonato-sulfonate linker molecule

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Content

1. Phase purity of title compounds

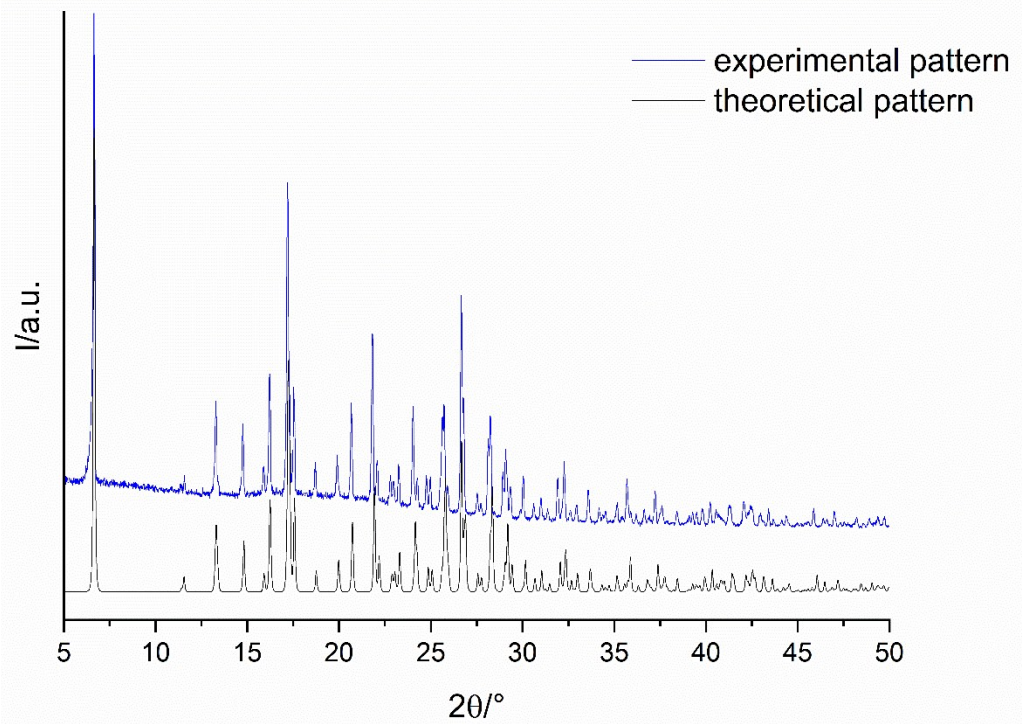

Figure S1: Measured and calculated PXRD pattern of **1** ($[Mg(H_3L)(H_2O)_2]\cdot H_2O$).

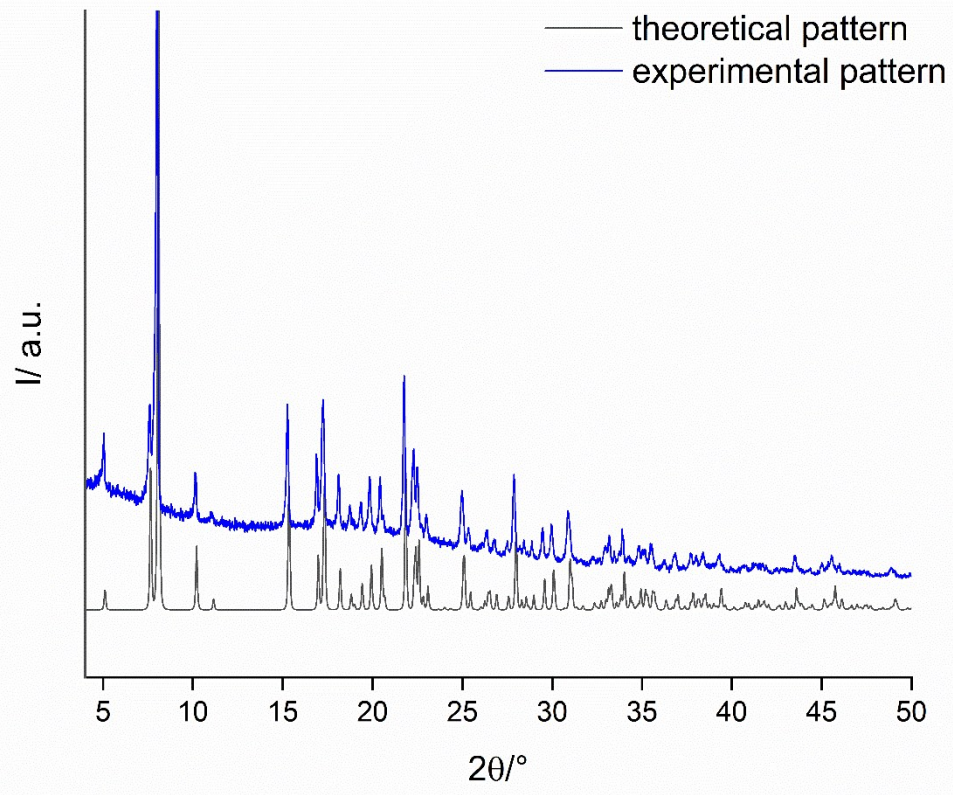

Figure S2: Measured and calculated PXRD pattern of **2** ($[Mg_2(HL)(H_2O)_6]\cdot 2H_2O$).

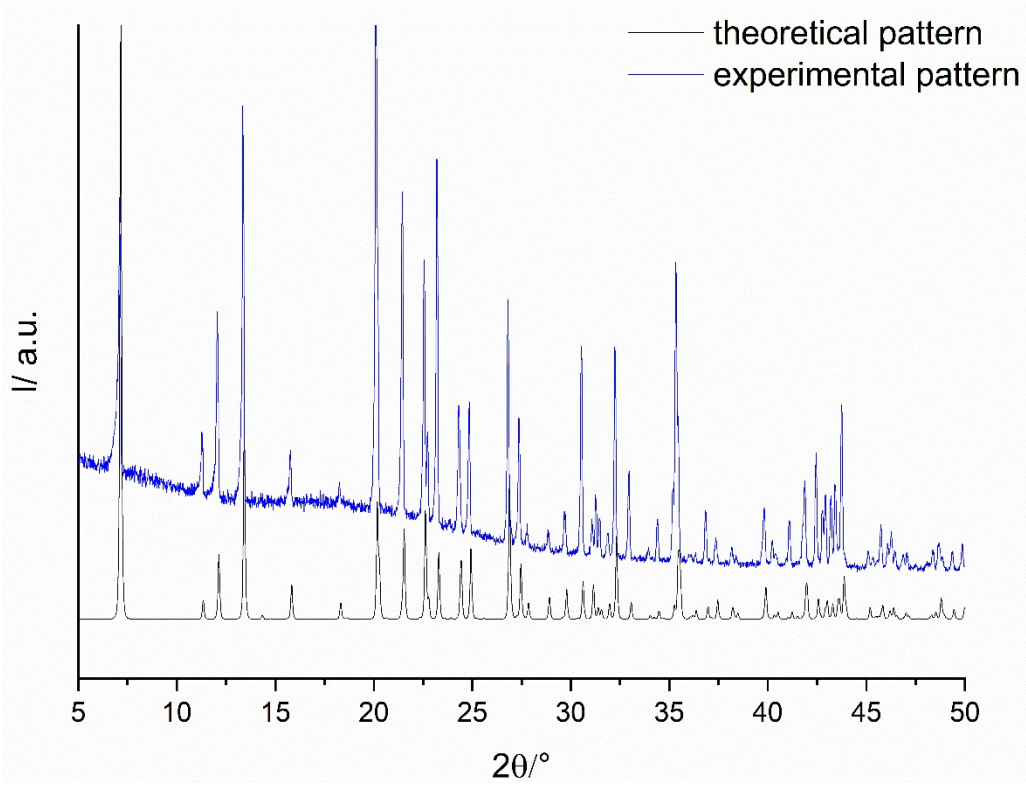

Figure S3: Measured and calculated PXRD pattern of **3** ($[Ba(H_3L)(H_2O)]\cdot H_2O$).

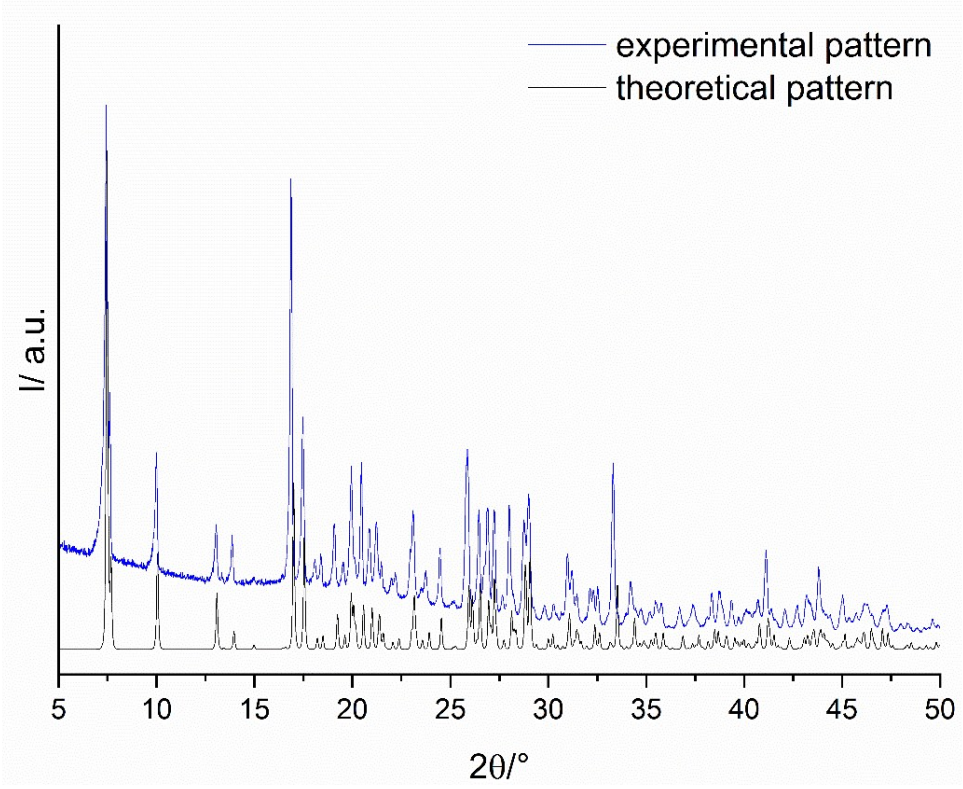

Figure S4: Measured and calculated PXRD pattern of **4** ($Pb_2(HL)\cdot H_2O$).

2. High-Throughput Investigations

To screen for suitable metal ions, a metal screening was carried out in high-throughput reactors with a volume of 250 µl. From this very first high-throughput experiment using H_5L, title compound **3**

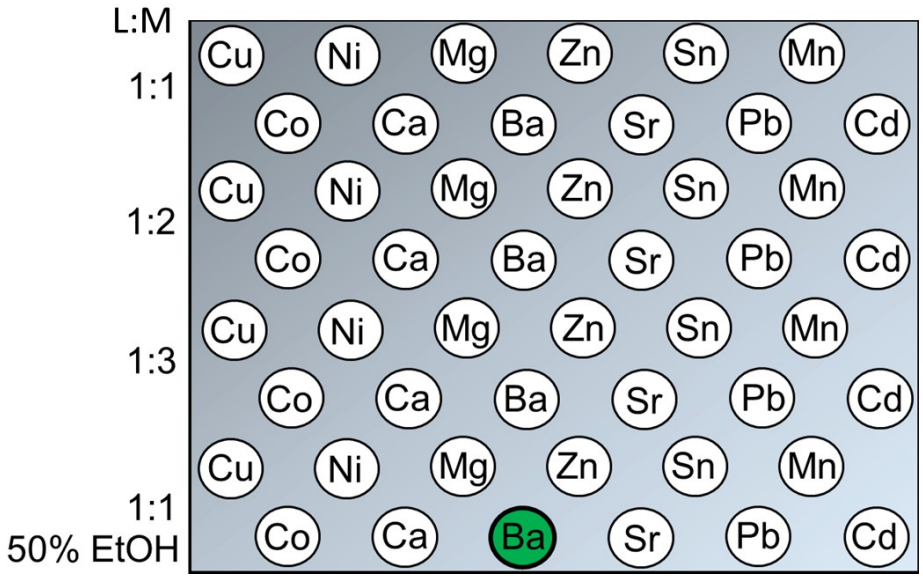

Figure S5: Setup of the first metal screening.

could be isolated.

To further investigate the influence of the metal cation on the product formation, the following reactions were carried out in high-throughput reactors with a maximum volume of 2 ml. The syntheses highlighted in green led reproducibly to crystalline, phase-pure products, which are presented as title compounds **2** and **4**.

Table S1: High-throughput experiments carried out in autoclaves with a volume of 2 ml. Syntheses highlighted in green represent title compounds (L = ligand).

L:M	M = Metal source	L/µmol	H_2O/µl	EtOH/µl
1:2	$BaCl_2 \cdot 2H_2O$	25	0	1000
1:4	$BaCl_2 \cdot 2H_2O$	25	0	1000
1:6	$BaCl_2 \cdot 2H_2O$	25	0	1000
1:2	$SnCl_2 \cdot 2H_2O$	25	1000	0
1:4	$SnCl_2 \cdot 2H_2O$	25	1000	0
1:6	$SnCl_2 \cdot 2H_2O$	25	1000	0
1:2	$SnCl_2 \cdot 2H_2O$	25	500	500
1:4	$SnCl_2 \cdot 2H_2O$	25	500	500
1:6	$SnCl_2 \cdot 2H_2O$	25	500	500
1:2	$SnCl_2 \cdot 2H_2O$	25	0	1000
1:4	$SnCl_2 \cdot 2H_2O$	25	0	1000
1:6	$SnCl_2 \cdot 2H_2O$	25	0	1000
1:2	$Zn(NO_3)_2 \cdot 2H_2O$	25	1000	0
1:4	$Zn(NO_3)_2 \cdot 2H_2O$	25	1000	0
1:6	$Zn(NO_3)_2 \cdot 2H_2O$	25	1000	0
1:2	$Zn(NO_3)_2 \cdot 2H_2O$	25	500	500
1:4	$Zn(NO_3)_2 \cdot 2H_2O$	25	500	500
1:6	$Zn(NO_3)_2 \cdot 2H_2O$	25	500	500
1:2	$Zn(NO_3)_2 \cdot 2H_2O$	25	0	1000
1:4	$Zn(NO_3)_2 \cdot 2H_2O$	25	0	1000
1:6	$Zn(NO_3)_2 \cdot 2H_2O$	25	0	1000
1:2	$Ni(NO_3)_2 \cdot 6H_2O$	25	1000	0
1:4	$Ni(NO_3)_2 \cdot 6H_2O$	25	1000	0
1:6	$Ni(NO_3)_2 \cdot 6H_2O$	25	1000	0
1:2	$Ni(NO_3)_2 \cdot 6H_2O$	25	500	500
1:4	$Ni(NO_3)_2 \cdot 6H_2O$	25	500	500
1:6	$Ni(NO_3)_2 \cdot 6H_2O$	25	500	500
1:2	$Ni(NO_3)_2 \cdot 6H_2O$	25	0	1000
1:4	$Ni(NO_3)_2 \cdot 6H_2O$	25	0	1000
1:6	$Ni(NO_3)_2 \cdot 6H_2O$	25	0	1000
1:2	$Cd(NO_3)_2 \cdot 4H_2O$	25	1000	0
1:4	$Cd(NO_3)_2 \cdot 4H_2O$	25	1000	0
1:6	$Cd(NO_3)_2 \cdot 4H_2O$	25	1000	0
1:2	$Cd(NO_3)_2 \cdot 4H_2O$	25	500	500
1:4	$Cd(NO_3)_2 \cdot 4H_2O$	25	500	500
1:6	$Cd(NO_3)_2 \cdot 4H_2O$	25	500	500
1:2	$Cd(NO_3)_2 \cdot 4H_2O$	25	0	1000
1:4	$Cd(NO_3)_2 \cdot 4H_2O$	25	0	1000
1:6	$Cd(NO_3)_2 \cdot 4H_2O$	25	0	1000

L:M	M = Metal source	L/µmol	H_2O/µl	EtOH/µl
1:2	$MgCl_2 \cdot 6H_2O$	25	1000	0
1:4	$MgCl_2 \cdot 6H_2O$	25	1000	0
1:6	$MgCl_2 \cdot 6H_2O$	25	1000	0
1:2	$MgCl_2 \cdot 6H_2O$	25	500	500
1:4	$MgCl_2 \cdot 6H_2O$	25	500	500
1:6	$MgCl_2 \cdot 6H_2O$	25	500	500
1:2	$MgCl_2 \cdot 6H_2O$	25	0	1000
1:4	$MgCl_2 \cdot 6H_2O$	25	0	1000
1:6	$MgCl_2 \cdot 6H_2O$	25	0	1000
1:2	$CaCl_2 \cdot 6H_2O$	25	1000	0
1:4	$CaCl_2 \cdot 6H_2O$	25	1000	0
1:6	$CaCl_2 \cdot 6H_2O$	25	1000	0
1:2	$CaCl_2 \cdot 6H_2O$	25	500	500
1:4	$CaCl_2 \cdot 6H_2O$	25	500	500
1:6	$CaCl_2 \cdot 6H_2O$	25	500	500
1:2	$CaCl_2 \cdot 6H_2O$	25	0	1000
1:4	$CaCl_2 \cdot 6H_2O$	25	0	1000
1:6	$CaCl_2 \cdot 6H_2O$	25	0	1000
1:2	$SrCl_2 \cdot 6H_2O$	25	1000	0
1:4	$SrCl_2 \cdot 6H_2O$	25	1000	0
1:6	$SrCl_2 \cdot 6H_2O$	25	1000	0
1:2	$SrCl_2 \cdot 6H_2O$	25	500	500
1:4	$SrCl_2 \cdot 6H_2O$	25	500	500
1:6	$SrCl_2 \cdot 6H_2O$	25	500	500
1:2	$SrCl_2 \cdot 6H_2O$	25	0	1000
1:4	$SrCl_2 \cdot 6H_2O$	25	0	1000
1:6	$SrCl_2 \cdot 6H_2O$	25	0	1000
1:2	$SnSO_4$	25	1000	0
1:4	$SnSO_4$	25	1000	0
1:6	$SnSO_4$	25	1000	0
1:2	$SnSO_4$	25	500	500
1:4	$SnSO_4$	25	500	500
1:6	$SnSO_4$	25	500	500
1:2	$SnSO_4$	25	0	1000
1:4	$SnSO_4$	25	0	1000
1:6	$SnSO_4$	25	0	1000
1:1	$Cu(NO_3)_2 \cdot 3H_2O$	25	1000	0
1:2	$Cu(NO_3)_2 \cdot 3H_2O$	25	1000	0
1:3	$Cu(NO_3)_2 \cdot 3H_2O$	25	1000	0
1:1	$Cu(NO_3)_2 \cdot 3H_2O$	25	500	500
1:2	$Cu(NO_3)_2 \cdot 3H_2O$	25	500	500
1:3	$Cu(NO_3)_2 \cdot 3H_2O$	25	500	500
1:4	$Cu(NO_3)_2 \cdot 3H_2O$	25	500	500
2:1	$Cu(NO_3)_2 \cdot 3H_2O$	25	500	500
3:1	$Cu(NO_3)_2 \cdot 3H_2O$	25	500	500
4:1	$Cu(NO_3)_2 \cdot 3H_2O$	25	500	500
2:4	$Cu(NO_3)_2 \cdot 3H_2O$	25	500	500
4:8	$Cu(NO_3)_2 \cdot 3H_2O$	25	500	500
1:1	$Cu(NO_3)_2 \cdot 3H_2O$	25	0	1000
1:2	$Cu(NO_3)_2 \cdot 3H_2O$	25	0	1000
1:3	$Cu(NO_3)_2 \cdot 3H_2O$	25	0	1000

L:M	M = Metal source	L/µmol	H_2O/µl	EtOH/µl
1:2	$NiCl_2 \cdot 6H_2O$	25	1000	0
1:4	$NiCl_2 \cdot 6H_2O$	25	1000	0
1:6	$NiCl_2 \cdot 6H_2O$	25	1000	0
1:2	$NiCl_2 \cdot 6H_2O$	25	500	500
1:4	$NiCl_2 \cdot 6H_2O$	25	500	500
1:6	$NiCl_2 \cdot 6H_2O$	25	500	500
1:2	$NiCl_2 \cdot 6H_2O$	25	0	1000
1:4	$NiCl_2 \cdot 6H_2O$	25	0	1000
1:6	$NiCl_2 \cdot 6H_2O$	25	0	1000
1:2	$Mn(NO_3)_2 \cdot 4H_2O$	25	1000	0
1:4	$Mn(NO_3)_2 \cdot 4H_2O$	25	1000	0
1:6	$Mn(NO_3)_2 \cdot 4H_2O$	25	1000	0
1:2	$Mn(NO_3)_2 \cdot 4H_2O$	25	500	500
1:4	$Mn(NO_3)_2 \cdot 4H_2O$	25	500	500
1:6	$Mn(NO_3)_2 \cdot 4H_2O$	25	500	500
1:2	$Mn(NO_3)_2 \cdot 4H_2O$	25	0	1000
1:4	$Mn(NO_3)_2 \cdot 4H_2O$	25	0	1000
1:6	$Mn(NO_3)_2 \cdot 4H_2O$	25	0	1000
1:2	$Mg(OAc)_2 \cdot 4H_2O$	25	1000	0
1:4	$Mg(OAc)_2 \cdot 4H_2O$	25	1000	0
1:6	$Mg(OAc)_2 \cdot 4H_2O$	25	1000	0
1:2	$Mg(OAc)_2 \cdot 4H_2O$	25	500	500
1:4	$Mg(OAc)_2 \cdot 4H_2O$	25	500	500
1:6	$Mg(OAc)_2 \cdot 4H_2O$	25	500	500
1:2	$Mg(OAc)_2 \cdot 4H_2O$	25	0	1000
1:4	$Mg(OAc)_2 \cdot 4H_2O$	25	0	1000
1:6	$Mg(OAc)_2 \cdot 4H_2O$	25	0	1000
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1:4	$Fe(OAc)_3 \cdot 3H_2O$	25	1000	0
1:6	$Fe(OAc)_3 \cdot 3H_2O$	25	1000	0
1:2	$Fe(OAc)_3 \cdot 3H_2O$	25	500	500
1:4	$Fe(OAc)_3 \cdot 3H_2O$	25	500	500
1:6	$Fe(OAc)_3 \cdot 3H_2O$	25	500	500
1:2	$Fe(OAc)_3 \cdot 3H_2O$	25	0	1000
1:4	$Fe(OAc)_3 \cdot 3H_2O$	25	0	1000
1:6	$Fe(OAc)_3 \cdot 3H_2O$	25	0	1000
1:2	$Ca(OAc)_2 \cdot 2H_2O$	25	1000	0
1:4	$Ca(OAc)_2 \cdot 2H_2O$	25	1000	0
1:6	$Ca(OAc)_2 \cdot 2H_2O$	25	1000	0
1:2	$Ca(OAc)_2 \cdot 2H_2O$	25	500	500
1:4	$Ca(OAc)_2 \cdot 2H_2O$	25	500	500
1:6	$Ca(OAc)_2 \cdot 2H_2O$	25	500	500
1:2	$Ca(OAc)_2 \cdot 2H_2O$	25	0	1000
1:4	$Ca(OAc)_2 \cdot 2H_2O$	25	0	1000
1:6	$Ca(OAc)_2 \cdot 2H_2O$	25	0	1000

L:M	M = Metal source	L/µmol	H_2O/µl	EtOH/µl
1:2	$Al(OAc)_2(OH)$	25	1000	0
1:4	$Al(OAc)_2(OH)$	25	1000	0
1:6	$Al(OAc)_2(OH)$	25	1000	0
1:2	$Al(OAc)_2(OH)$	25	500	500
1:4	$Al(OAc)_2(OH)$	25	500	500
1:6	$Al(OAc)_2(OH)$	25	500	500
1:2	$Al(OAc)_2(OH)$	25	0	1000
1:4	$Al(OAc)_2(OH)$	25	0	1000
1:6	$Al(OAc)_2(OH)$	25	0	1000
1:2	$Cr_3(OAc)_7(OH)_2$	25	1000	0
1:4	$Cr_3(OAc)_7(OH)_2$	25	1000	0
1:6	$Cr_3(OAc)_7(OH)_2$	25	1000	0
1:2	$Cr_3(OAc)_7(OH)_2$	25	500	500
1:4	$Cr_3(OAc)_7(OH)_2$	25	500	500
1:6	$Cr_3(OAc)_7(OH)_2$	25	500	500
1:2	$Cr_3(OAc)_7(OH)_2$	25	0	1000
1:4	$Cr_3(OAc)_7(OH)_2$	25	0	1000
1:6	$Cr_3(OAc)_7(OH)_2$	25	0	1000
1:2	$FeCl_3 \cdot 6H_2O$	25	1000	0
1:4	$FeCl_3 \cdot 6H_2O$	25	1000	0
1:6	$FeCl_3 \cdot 6H_2O$	25	1000	0
1:2	$FeCl_3 \cdot 6H_2O$	25	500	500
1:4	$FeCl_3 \cdot 6H_2O$	25	500	500
1:6	$FeCl_3 \cdot 6H_2O$	25	500	500
1:2	$FeCl_3 \cdot 6H_2O$	25	0	1000
1:4	$FeCl_3 \cdot 6H_2O$	25	0	1000
1:6	$FeCl_3 \cdot 6H_2O$	25	0	1000
1:4	$Pb(NO_3)_2$	25	1000	0
1:6	$Pb(NO_3)_2$	25	1000	0
1:8	$Pb(NO_3)_2$	25	1000	0
1:4	$Pb(NO_3)_2$	25	500	500
1:6	$Pb(NO_3)_2$	25	500	500
1:8	$Pb(NO_3)_2$	25	500	500
1:2	$Pb(NO_3)_2$	25	0	1000
1:4	$Pb(NO_3)_2$	25	0	1000
1:6	$Pb(NO_3)_2$	25	0	1000
1:0,5	$Pb(OAc)_2 \cdot 3H_2O$	25	500	500
1:1	$Pb(OAc)_2 \cdot 3H_2O$	25	500	500
1:2	$Pb(OAc)_2 \cdot 3H_2O$	25	500	500
1:4	$Pb(OAc)_2 \cdot 3H_2O$	25	500	500

Table S2: Synthesis optimization of **1** in high-throughput reactors with a maximum volume of 2 ml. Syntheses highlighted in green led to the formation of title compound **1** (L = ligand).

L:M:NaOH	M = Metal source	L/µmol	H_2O/µl	EtOH/µl
1:2:1	$MgCl_2 \cdot 6H_2O$	25	500	500
1:2:2	$MgCl_2 \cdot 6H_2O$	25	500	500
1:2:3	$MgCl_2 \cdot 6H_2O$	25	500	500
1:4:1	$MgCl_2 \cdot 6H_2O$	25	500	500
1:4:2	$MgCl_2 \cdot 6H_2O$	25	500	500
1:4:3	$MgCl_2 \cdot 6H_2O$	25	500	500
1:6:1	$MgCl_2 \cdot 6H_2O$	25	500	500
1:6:2	$MgCl_2 \cdot 6H_2O$	25	500	500
1:6:3	$MgCl_2 \cdot 6H_2O$	25	500	500
2:8:4	$MgCl_2 \cdot 6H_2O$	50	500	500
3:12:6	$MgCl_2 \cdot 6H_2O$	75	500	500

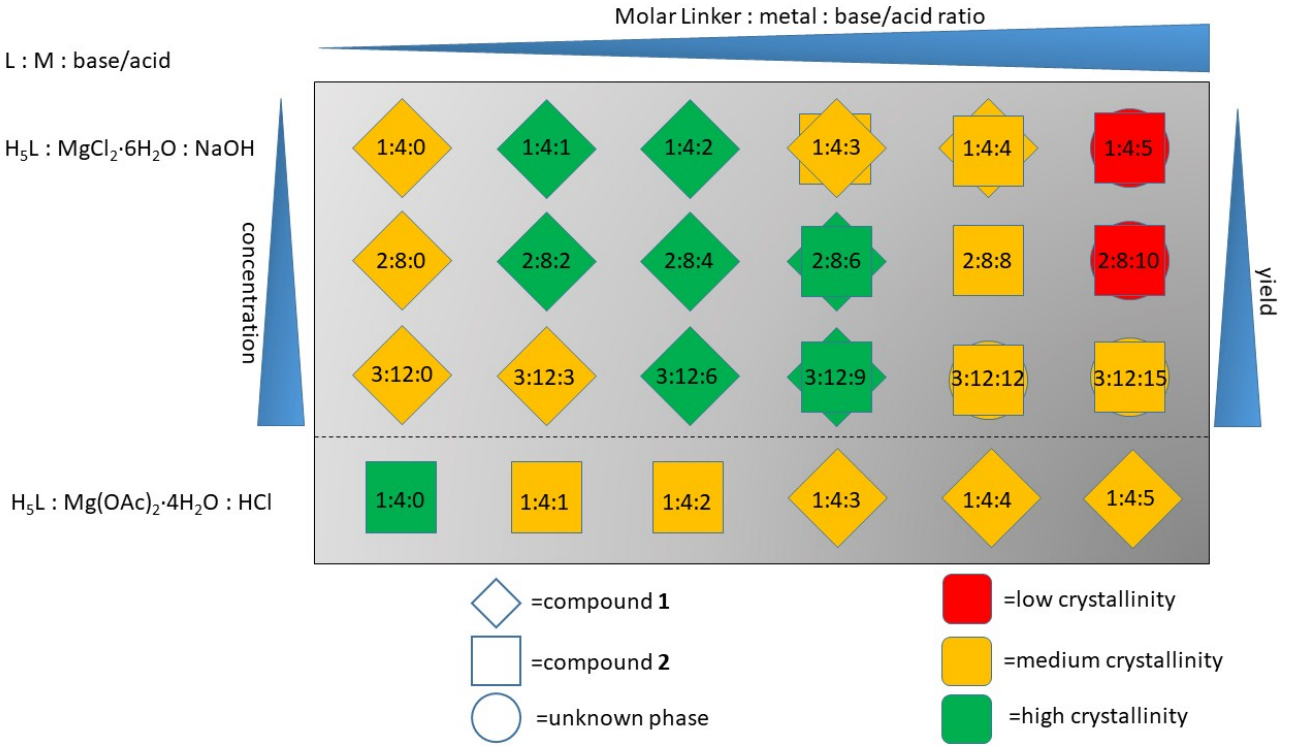


Figure S6: Results of the acid/base-screening for **1** and **2**.

3. Asymmetric units and coordination mode of the title compounds

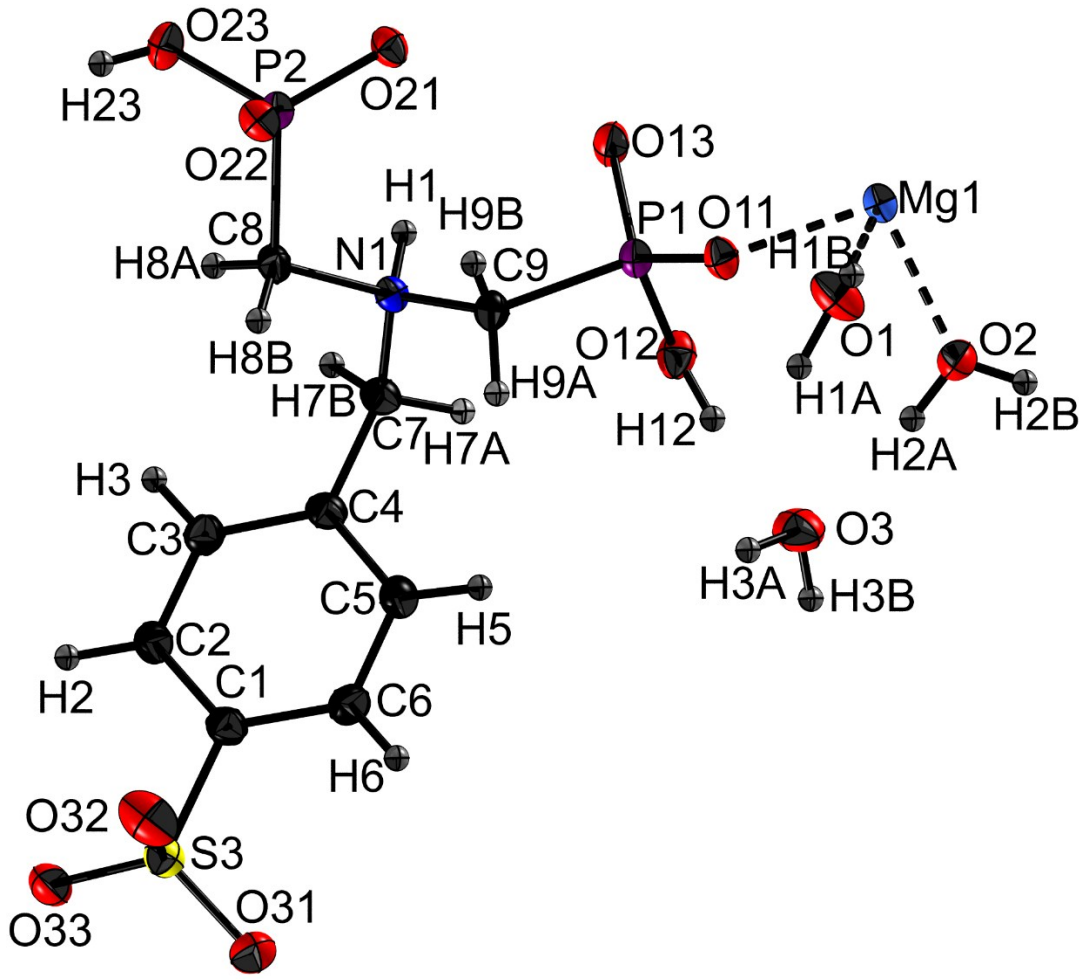


Figure S7: Asymmetric unit of **1** ($[Mg(H_3L)(H_2O)_2] \cdot H_2O$). Ellipsoids drawn at the 50% probability level. Detailed bond lengths are provided in Table S3.

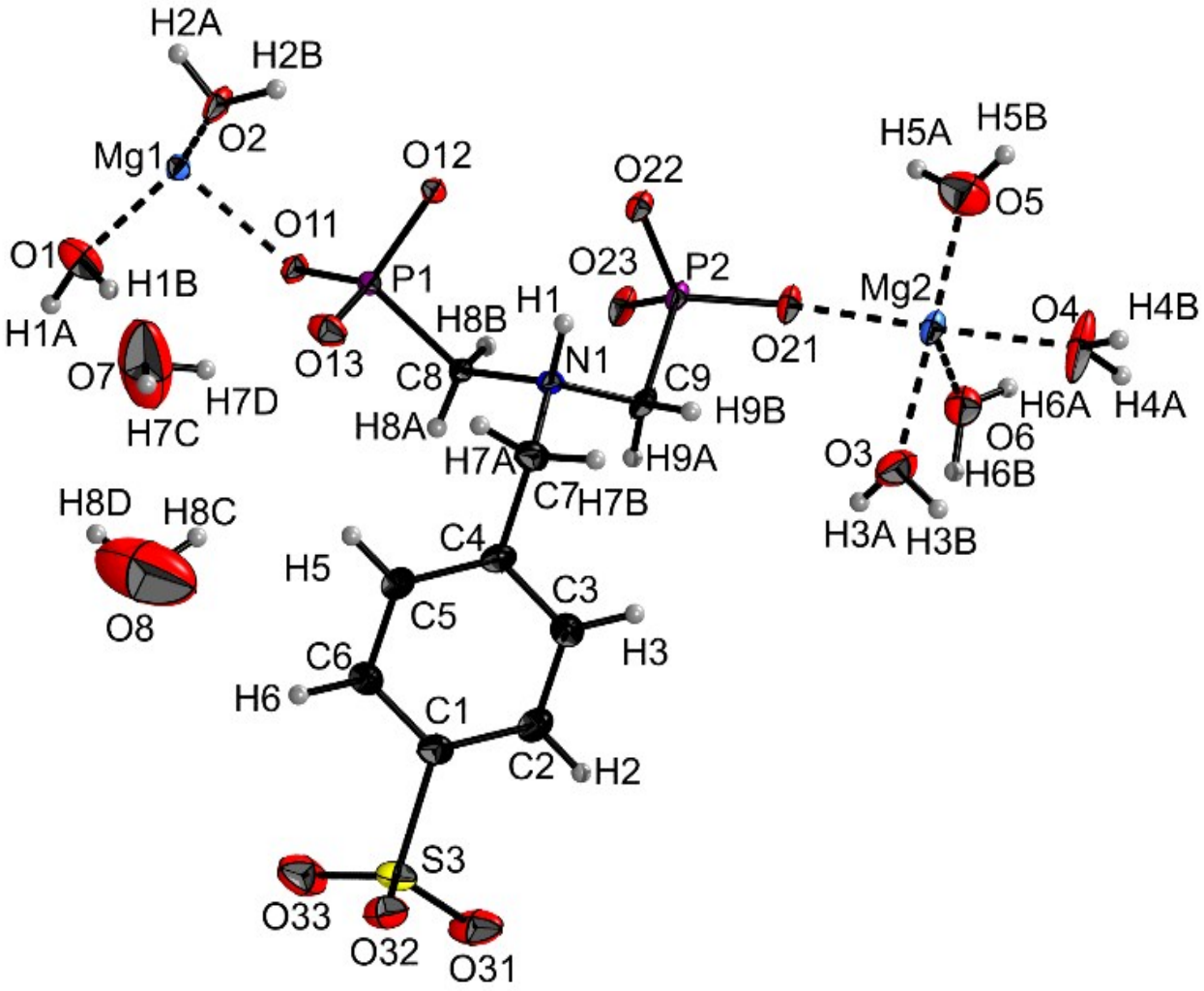


Figure S8: Asymmetric unit of **2** ($[Mg_2(HL)(H_2O)_6] \cdot 2H_2O$). Ellipsoids drawn at the 50% probability level. Detailed bond lengths are provided in Table S5.

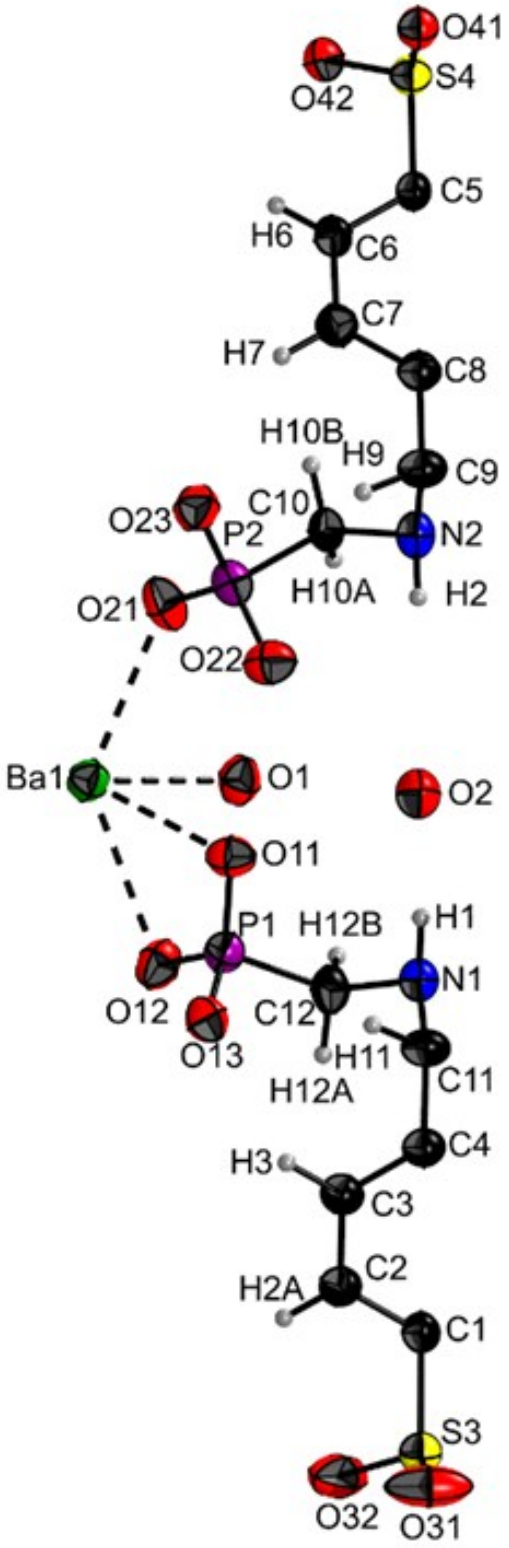
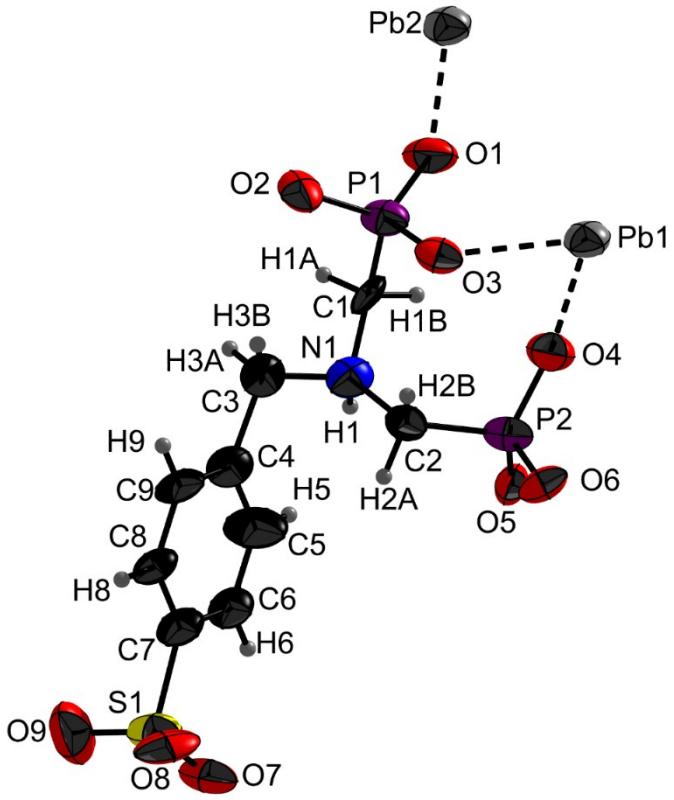


Figure S9: Asymmetric unit of **3** ([Ba(H_3L)(H_2O)]·H_2O). Ellipsoids drawn at the 50% probability level. Detailed bond lengths are provided in Table S7.


Pb2
O1
O2
P1
Pb1
H1A
O3
C1
H1B
H3B
N1
O4
H3A
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C3
H1
P2
H9
C4
C2
O6
C9
H5
H2A
O5
C8
C5
H8
C6
C7
H6
S1
O9
O8
O7

Figure S10: Asymmetric unit of **4** ($Pb_2(HL)\cdot H_2O$). Ellipsoids drawn at the 50%

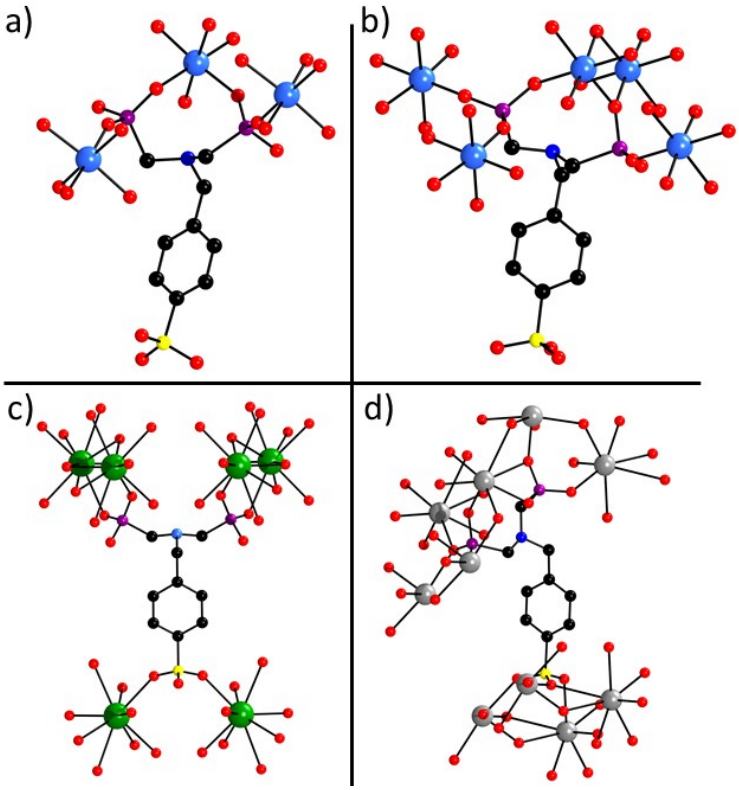

Figure S11: Coordination mode of the linker molecule without polyhedra, a) **1** ($[Mg(H_3L)(H_2O)_2]$ H_2O), b) **2** ($[Mg_2(HL)(H_2O)_6]$ $2H_2O$), c) **3** ($[Ba(H_3L)(H_2O)]\cdot H_2O$), d) **4** ($Pb_2(HL)\cdot H_2O$).

probability level. Detailed bond lengths are provided in Table S9.

4. NMR spectra and elemental analysis of H_5L and title compounds

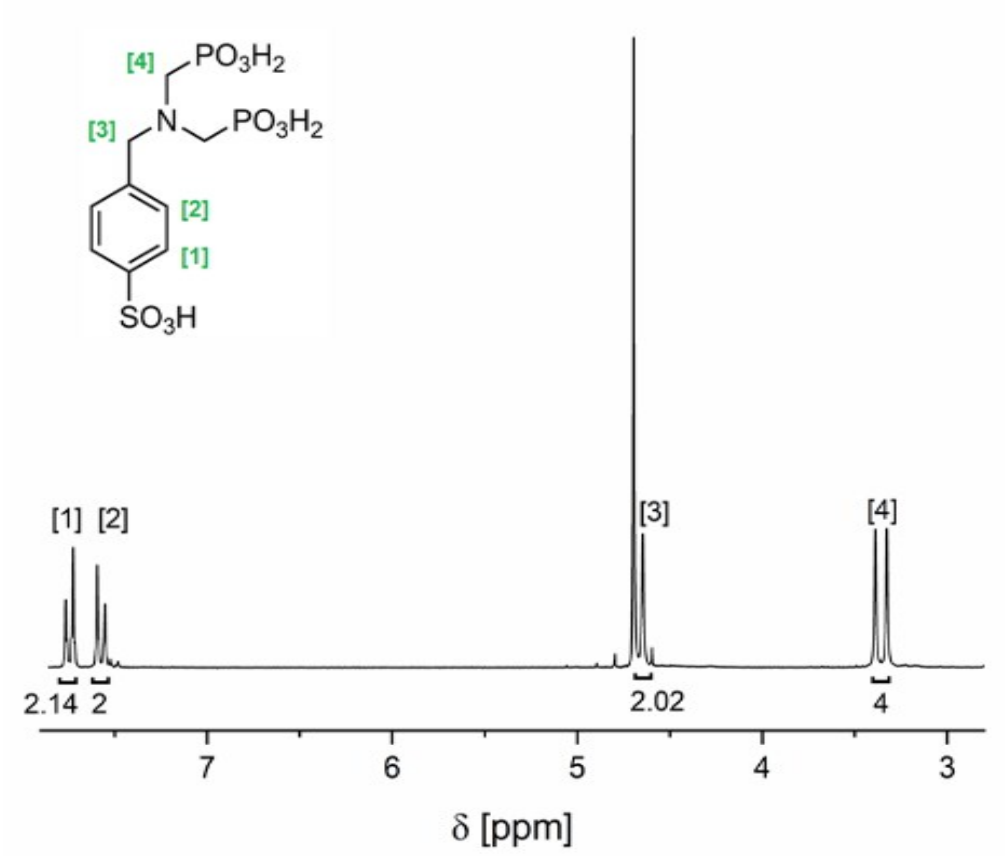

Figure S12: ^{1}H-NMR-spectrum of the linker molecule H_5L.

^{1}H-NMR (400 MHz, D_2O, TMS, 300K): δ=7.74 (d, 2H, Ar-*H*), 7.57 (d, 2H, Ar-*H*), 4.64 (s, 2H, Ar-C*H*$_2$-N), 3.35 (d, 4H, N-C*H*$_2$-P) ppm.

Elemental analysis, calculated for $C_9H_{15}O_9NSP_2$:

C=28.61%, H=4.03%, N=3.73%, S=8.55%

found:

C=28.55%, H=4.13%, N=3.61%, S=8.29%

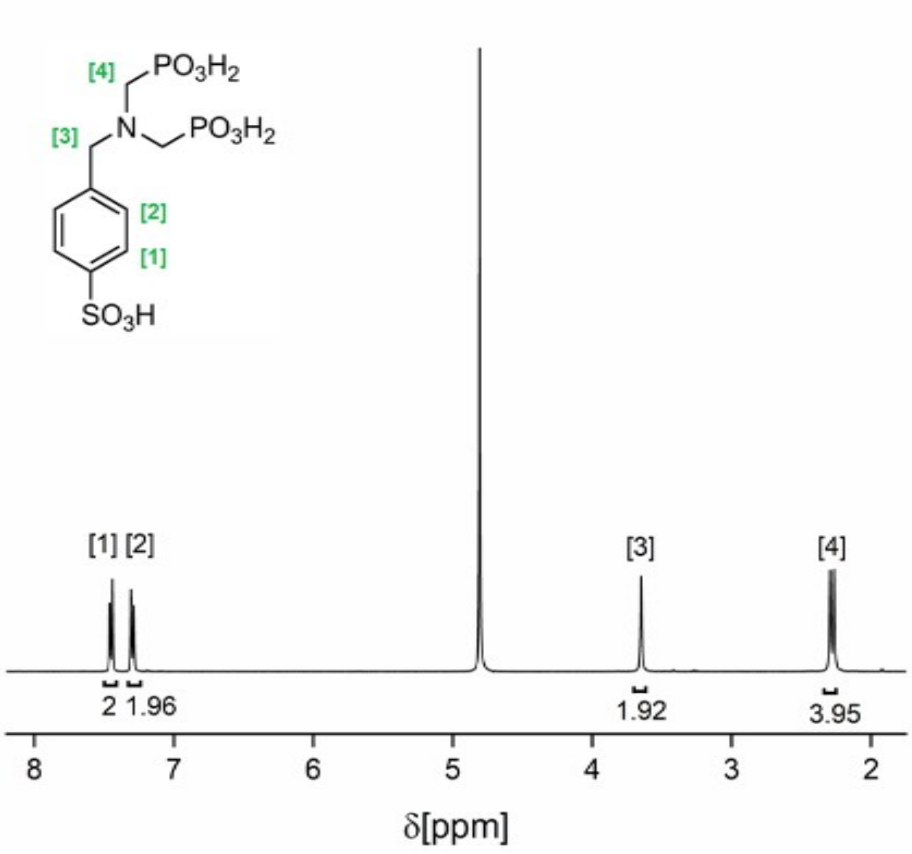

Figure S13: ^{1}H-NMR-spectrum of **1** ([Mg(H_3L)(H_2O)$_2$] · H_2O).

^{1}H-NMR (400 MHz, D_2O/NaOD 10%, TMS, 300K): δ=7.45 (d, 2H, Ar-*H*), 7.3 (d, 2H, Ar-*H*), 3.65 (s, 2H, Ar-C*H*$_2$-N), 2.28 (d, 4H, N-C*H*$_2$-P) ppm.

Elemental analysis, calculated for [Mg($C_9H_{13}O_9NSP_2$)]·3H_2O:

C=23.94%, H=4.24%, N=3.10%, S=7.10%

found:

C=23.94%, H=4.17%, N=3.12%, S=7.71%

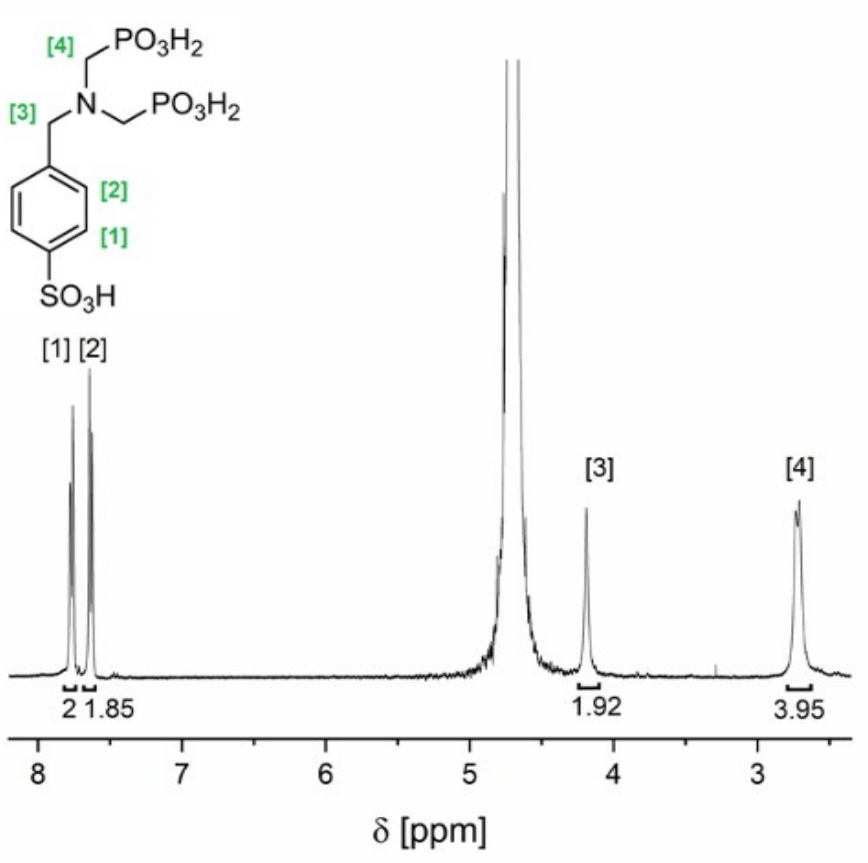

Figure S14: ^{1}H-NMR-spectrum of **2** ([$Mg_2(HL)(H_2O)_6$] · $2H_2O$).

^{1}H-NMR (400 MHz, D_2O/NaOD 10%, TMS, 300K): δ=7.76 (d, 2H, Ar-*H*), 7.63 (d, 2H, Ar-*H*), 4.19 (s, 2H, Ar-C*H*$_2$-N), 2.72 (d, 4H, N-C*H*$_2$-P) ppm.

Elemental analysis, calculated for [$Mg_2(C_9H_{13}O_9NSP_2)$]·$8H_2O$:

C=19.17%, H=4.83%, N=2.48%, S=5.69%

found:

C=17.48%, H=4.90%, N=2.11%, S=4.88%

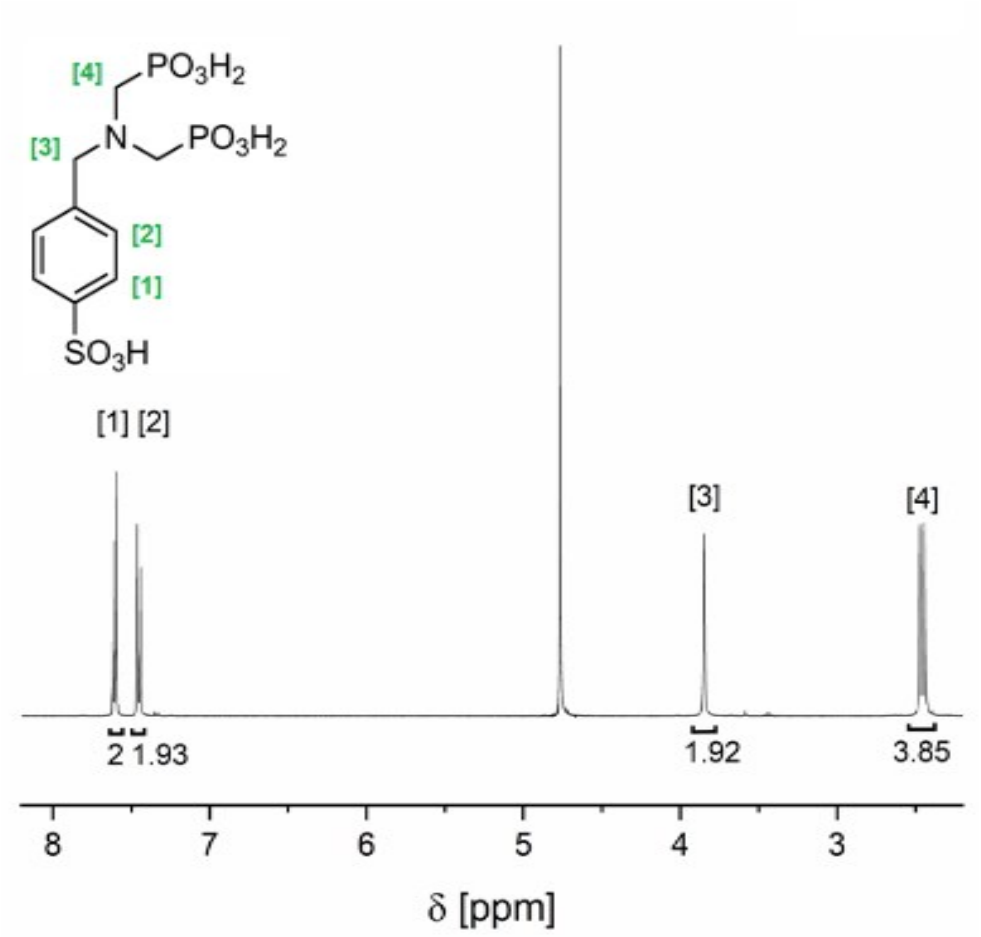

Figure S15: ^{1}H-NMR-spectrum of **3** ([Ba(H_3L)(H_2O)]·H_2O).

^{1}H-NMR (400 MHz, D_2O/NaOD 10%, TMS, 300K): δ=7.61 (d, 2H, Ar-*H*), 7.45 (d, 2H, Ar-*H*), 3.85 (s, 2H, Ar-C*H*$_2$-N), 2.46 (d, 4H, N-C*H*$_2$-P) ppm.

Elemental analysis, calculated for [Ba($C_9H_{13}O_9NSP_2$)]·2H_2O:

C=19.70%, H=3.49%, N=2.55%, S=5.85%

found:

C=20.07%, H=3.04%, N=2.44%, S=5.71%

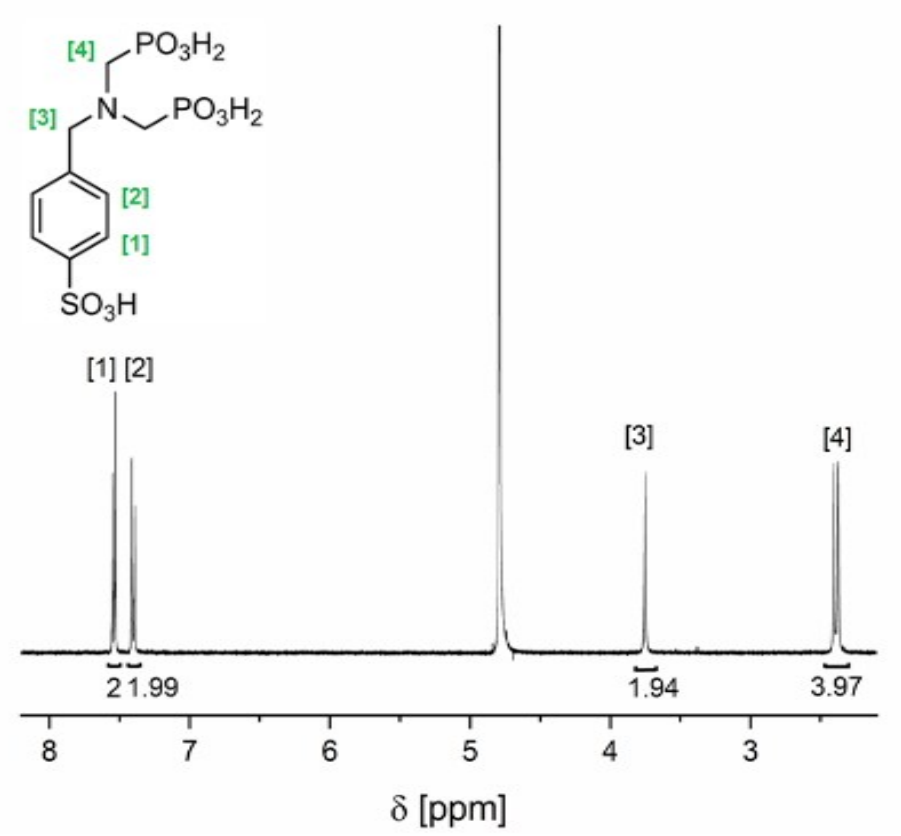

Figure S16: ^{1}H-NMR-spectrum of **4** ($Pb_2(HL)\cdot H_2O$).

^{1}H-NMR (400 MHz, D_2O/NaOD 10%, TMS, 300K): δ=7.54 (d, 2H, Ar-*H*), 7.40 (d, 2H, Ar-*H*), 3.75 (s, 2H, Ar-C*H*$_2$-N), 2.39 (d, 4H, N-C*H*$_2$-P) ppm.

Elemental analysis, calculated for $[Pb_2(C_9H_{13}O_9NSP_2)]\cdot H_2O$:

C=13.45%, H=1.63%, N=1.74%, S=3.99%

found:

C=13.70%, H=1.82%, N=1.80%, S=3.54%

5. Selected bond lengths and hydrogen bonds of the title compounds

Table S3: Selected bond lengths [Å] for **1** ($[Mg(H_3L)(H_2O)_2] \cdot H_2O$).

Atom 1	Atom 2	d [Å]	Atom 1	Atom 2	d [Å]
Mg1	O1	2.099(1)	P1	O11	1.484(1)
	O2	2.068(1)		O12	1.589(1)
	O11	2.026(1)		O13	1.501(1)
	O13	2.102(1)		C9	1.814(2)
	O21	2.061(1)	P2	O21	1.491(1)
	O22	2.071(1)		O22	1.499(1)
				O23	1.569(1)
				C8	1.841(2)
			S3	O31	1.444(2)
				O32	1.466(2)
				O32	1.449(1)
				C1	1.773(2)

Table S4: Hydrogen bonds in **1** ($[Mg(H_3L)(H_2O)_2] \cdot H_2O$).

Donor	Acceptor	D-H [Å]	D···A [Å]	D-H···A [°]
O1	O33	0.89(3)	2.848(2)	170(3)
O2	O3	0.85(3)	2.755(2)	170(3)
O2	O31	0.78(3)	2.728(2)	174(3)
O3	O32	0.88(3)	2.625(2)	171(3)
O12	O3	0.89(3)	2.702(2)	171(3)
N1	O22	0.86(2)	2.747(2)	160(2)

Table S5: Selected bond lengths [Å] for **2** ($[Mg_2(HL)(H_2O)_6] \cdot 2H_2O$)

Atom 1	Atom 2	d [Å]	Atom 1	Atom 2	d [Å]
Mg1	O1	2.095(2)	P1	O11	1.504(2)
	O2	2.047(2)		O12	1.535(2)
	O11	2.071(2)		O13	1.508(2)
	O12	2.121(2)		C8	1.817(3)
	O12	2.118(2)	P2	O21	1.502(2)
	O22	2.102(2)		O22	1.515(2)
Mg2	O3	2.115(2)		O23	1.513(2)
	O4	2.013(2)		C9	1.831(3)
	O5	2.100(3)	S3	O31	1.451(2)
	O6	2.099(2)		O32	1.449(2)
	O21	1.997(2)		O33	1.442(2)
	O23	2.002(2)		C1	1.775(3)

Table S6: Hydrogen bonds in **2** ($[Mg_2(HL)(H_2O)_6]\cdot 2H_2O$).

Donor	Acceptor	D-H [Å]	D···A [Å]	D-H···A [°]
O1	O13	0.96(3)	2.613(3)	161(2)
O2	O23	0.876(17)	2.661(2)	167(3)
O2	O22	0.863(18)	2.746(2)	162(3)
O6	O32	0.87(2)	2.769(3)	167(3)
O4	O32	0.873(19)	2.739(3)	176(4)
O4	O6	0.875(19)	2.862(3)	135(3)
O3	O31	0.82(4)	2.785(3)	173(3)
N1	O11	0.933(31)	3.045(3)	162(2)
O1	O7	0.890(18)	2.789(6)	169(3)
O7	O13	0.85	2.594(5)	158.1

Table S7: Selected bond lengths [Å] for **3** ($[Ba(H_3L)(H_2O)]\cdot H_2O$).

Atom 1	Atom 2	d [Å]	Atom 1	Atom 2	d [Å]
Ba1	O1	2.781(10)	P1	O11	1.487(9)
	O1	2.999(11)		O12	1.487(9)
	O11	2.758(9)		O13	1.551(10)
	O11	3.033(9)		C12	1.827(11)
	O12	2.910(9)	P2	O21	1.482(9)
	O21	2.843(9)		O22	1.485(9)
	O22	2.746(9)		O23	1.554(10)
	O32	2.778(11)		C10	1.813(11)
	O42	2.756(8)	S3	O31	1.439(15)
				O32	1.389(11)
				O32	1.389(11)
				C1	1.778(18)
			S4	O41	1.473(12)
				O42	1.441(8)
				O42	1.441(8)
				C5	1.763(18)

Table S8: Possible hydrogen bonds based on donor-acceptor distances for **3** ($[Ba(H_3L)(H_2O)]\cdot H_2O$).

Donor	Acceptor	D···A [Å]
O23	O12	2.562(14)
O13	O21	2.637(14)
N1	O2	2.74(2)

Table S9: Selected bond lengths [Å] for **4** ($Pb_2(HL)\cdot H_2O$).

Atom 1	Atom 2	d [Å]	Atom 1	Atom 2	d [Å]
Pb1	O1	3.090	P1	O1	1.430
	O2	2.339		O2	1.562
	O3	2.537		O3	1.483
	O4	2.317		C1	1.864
	O5	2.610	P2	O4	1.532
	O8	3.065		O5	1.484
	O9	2.964		O6	1.572
Pb2	O1	2.253		C2	1.764
	O5	2.453	S3	O7	1.394
	O6	2.358		O8	1.399
	O7	2.517		O9	1.384
	O8	2.914		C7	1.790

Table S10: Possible hydrogen bonds based on donor-acceptor distances for **4** ($Pb_2(HL)\cdot H_2O$).

Donor	Acceptor	D···A [Å]
N1	O3	2.591

6. Details on the Hirshfeld surface analysis

In Figure 16, the sections of the crystal structures of **1** and **2** which were used for the generation of the Hirshfeld surfaces are shown. These sections had to be artificially cut off from the rest of the structure, resulting in regions containing no sensible information in terms of Hirshfeld surface analysis. The respective regions are marked

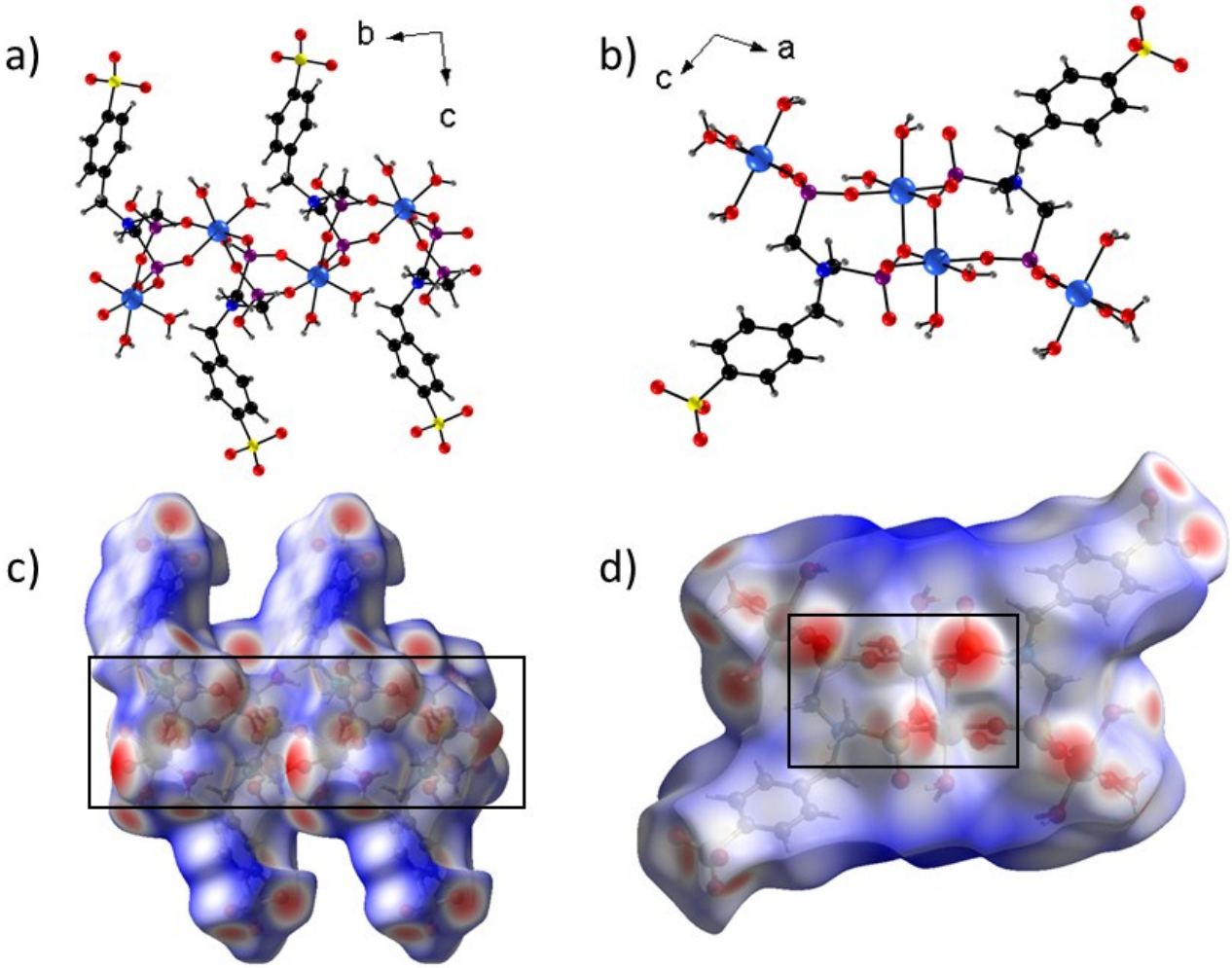

Figure S17: Section of the crystal structures of **1** and **2** which were used for the generation of the Hirshfeld surface, a) Crystal structure of $[Mg(H_3L)(H_2O)_2]$ H_2O (**1**), b) Crystal structure of $[Mg_2(HL)(H_2O)_6]$ $2H_2O$ (**2**),c) Hirshfeld surface of **1**, view along [100], d) Hirshfeld surface of **2**, view along [010].

with a black rectangle.

7. PXRD measurements of the TG residues

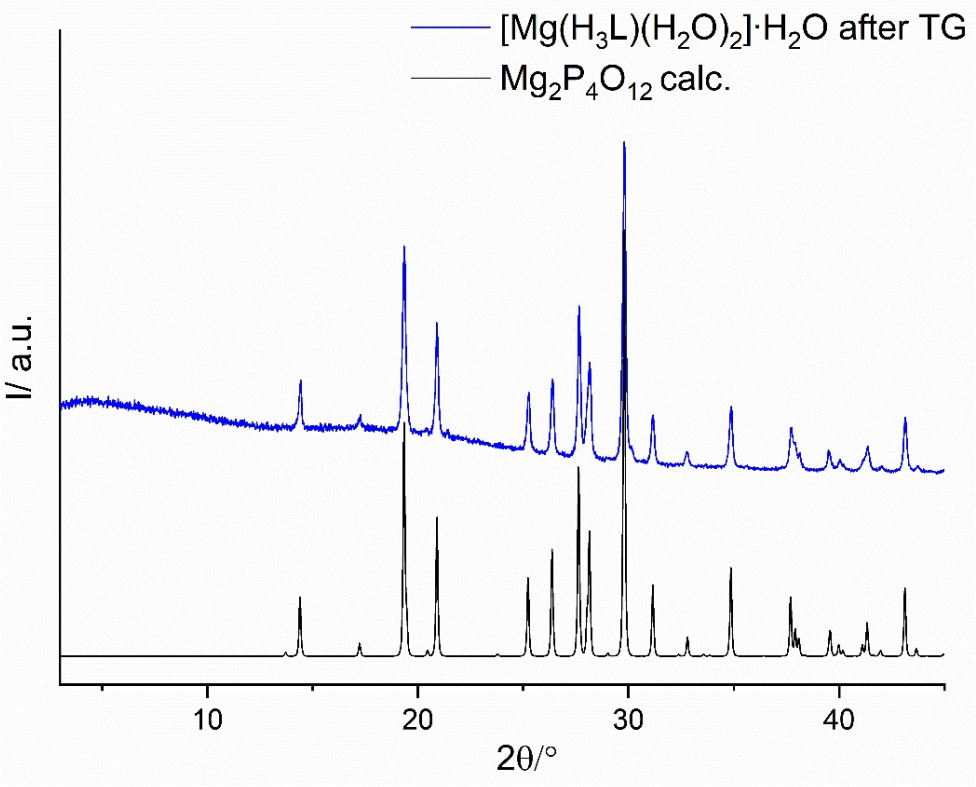

Figure S18: PXRD pattern of **1** after the TG experiment (blue) and calculated PXRD pattern of $Mg_2P_4O_{12}$ (black).

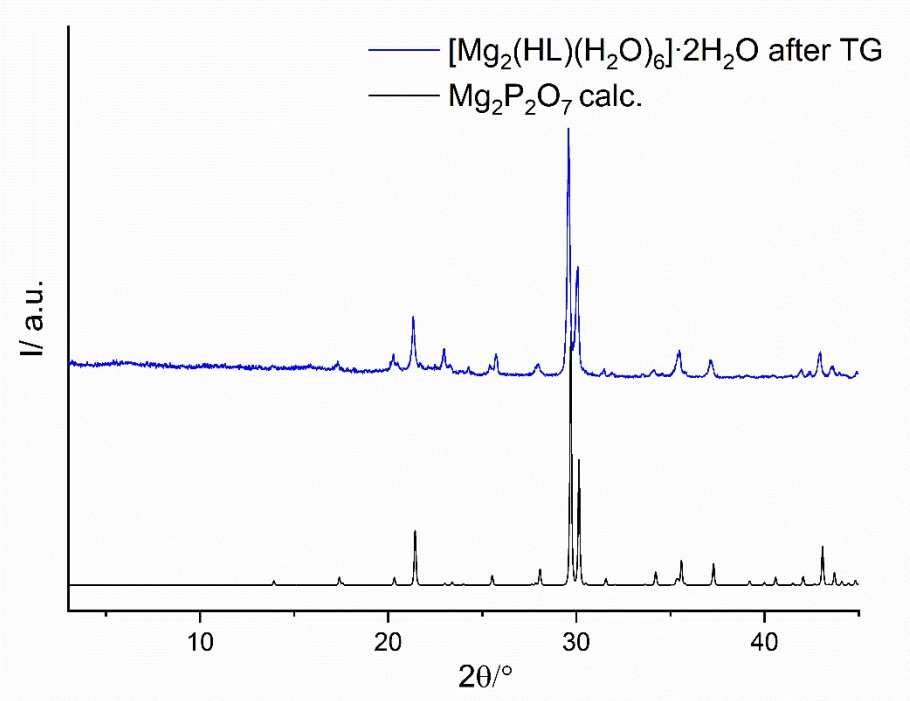

Figure S19: PXRD pattern of **2** after the TG experiment (blue) and calculated PXRD pattern of $Mg_2P_2O_7$ (black).

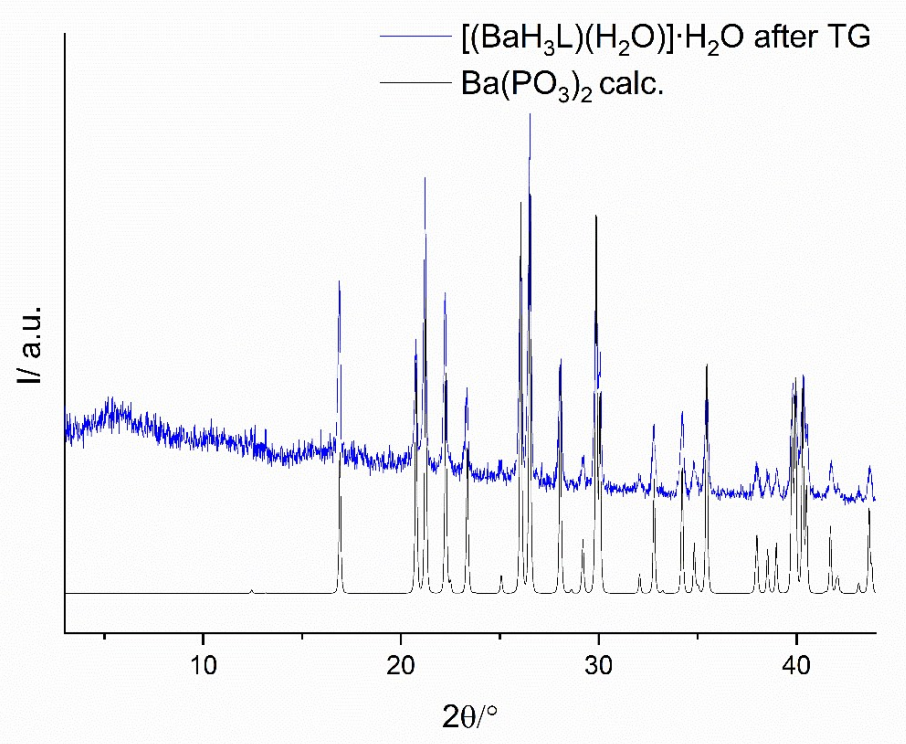

Figure S20: PXRD pattern of **3** after the TG experiment (blue) and calculated PXRD pattern of $Ba(PO_3)_2$ (black).

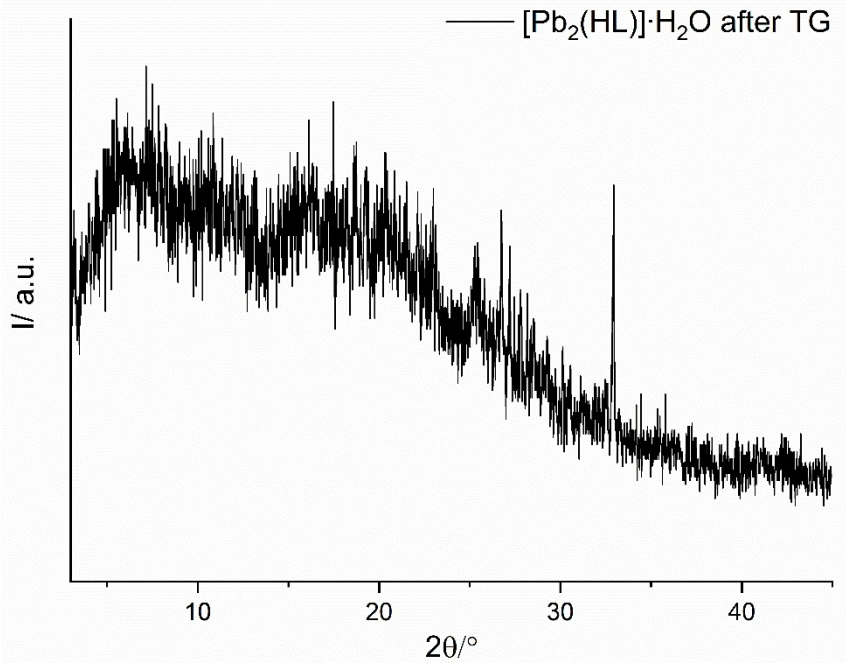

Figure S21: PXRD pattern of **4** after the TG experiment.

8. IR spectroscopy

Table S11: Assignment of the bands occurring in the IR spectra of the title compounds in comparison to the linker molecule.

Vibration $\tilde{\vartheta}$ IR [cm^{-1}]	H_5L	**1**	**2**	**3**	**4**
v (O*H*)	-	3660-3100	3360-3097	3535-3100	3605-3094
δ (O*H*)	-	1658-1645	1678-1618	1653	1630
v (P-O*H*)	3000-2000	3000-2000	-	3000-2000	-
v (*P*=*O*)	1000-1300	1000-1300	1000-1300	1000-1300	-
δ (P-CH_2-R)		1414, 1454	1414, 1454	1413, 1431	1426
v (*S*-*O*)	1000-1300	1000-1300	1000-1300	1000-1300	1000-1300
v (S-*OH*)	3000-2000	-	-	-	-

9. VT PXRD studies

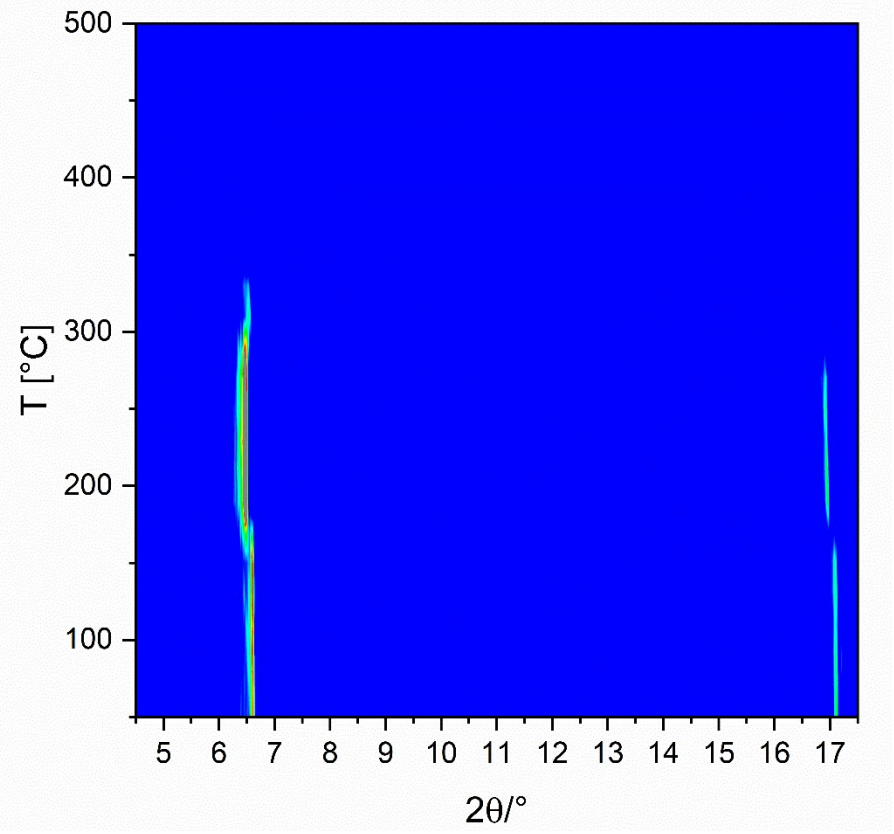

Figure S22: Results of the VT-PXRD study of **1** measured in an open quartz capillary (0.5mm) under atmospheric conditions.

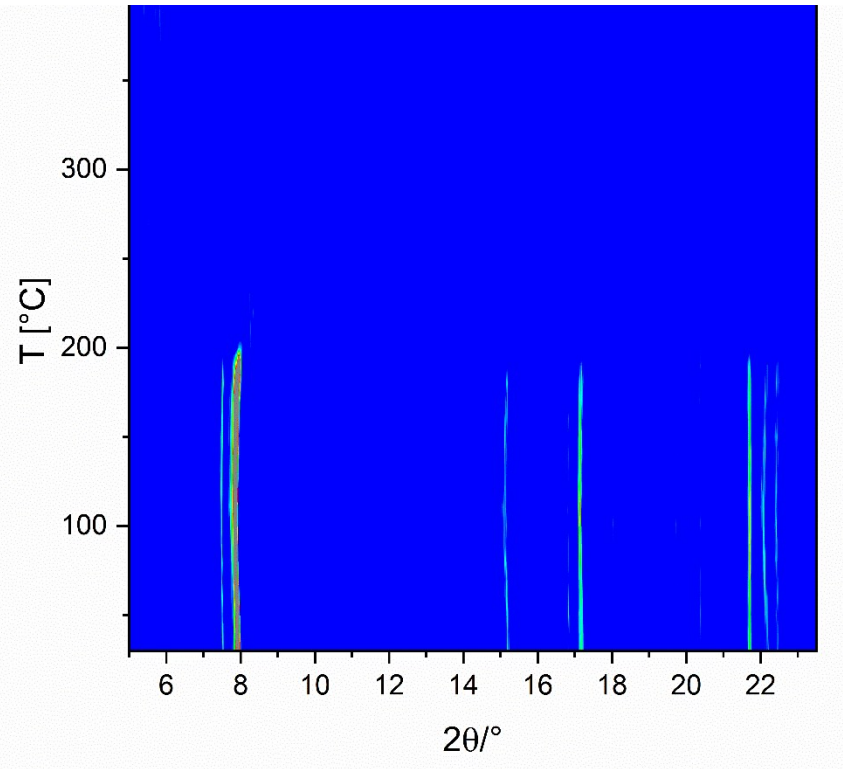

Figure S23: Results of the VT-PXRD study of **2** measured in an open quartz capillary (0.5mm) under atmospheric conditions.

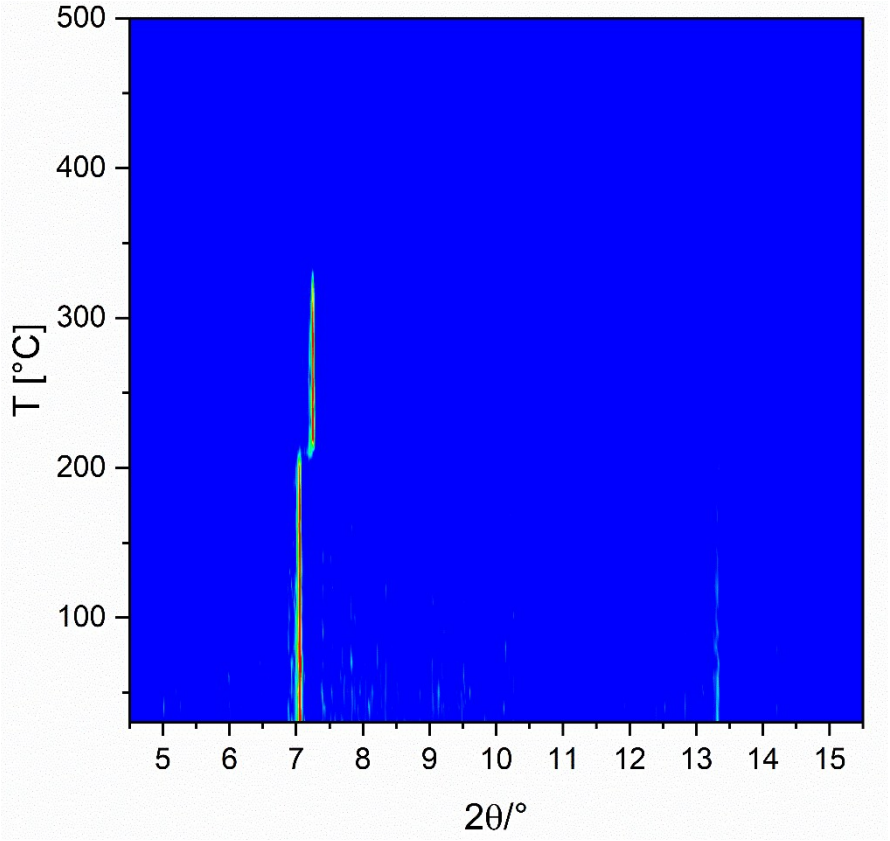

Figure S24: Results of the VT-PXRD study of **3** measured in an open quartz capillary (0.5mm) under atmospheric conditions.

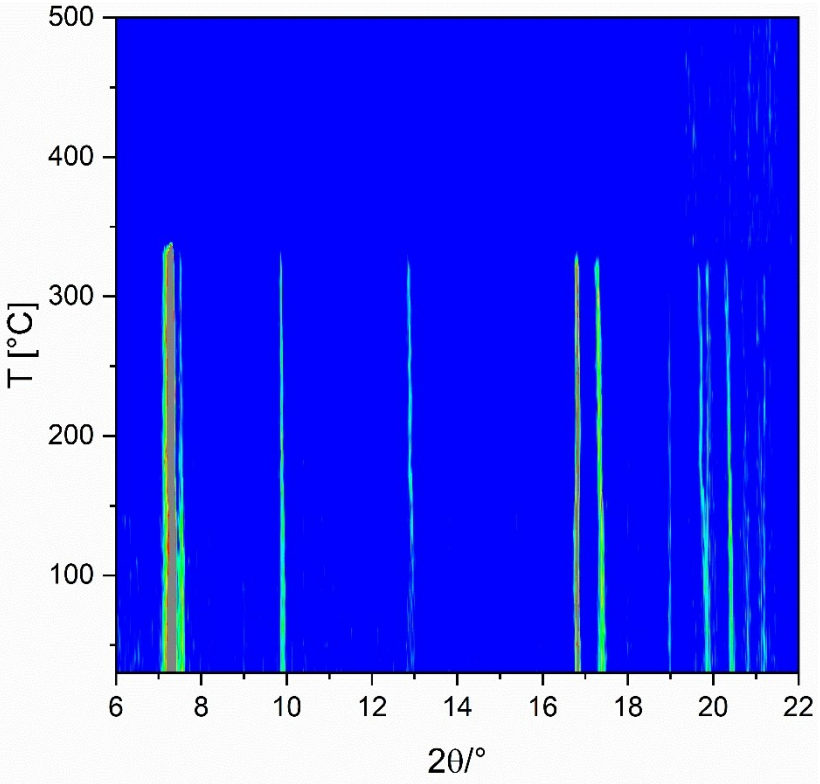

Figure S25: Results of the VT-PXRD study of **4** measured in an open quartz capillary (0.5mm) under atmospheric conditions.

10. Table of literature compounds containing linker molecules of similar geometry

Table S12: Overview of compounds containing {[bis(phosphonomethyl)amino]methyl}benzene derivatives as linker molecules. **X** equals the respective substituent in *para*-position.

X=	Compound	Structure dimensionality	Space group
H			
	$Co(H_2L)(H_2O)$[1]	1D	C*c*
	$[Ln(H_3L)(C_2O_4)]\cdot 2H_2O$ (Ln=La-Dy, Er and Y)[2]	2D	*C*2/*c*
	$[Pb_5(H_2L)_2(HL)_2]\cdot 2H_2O$[3]	2D	*P*bca
	$[Pb_3(H_2L)_2Cl(H_2O)_3Cl]\cdot 2H_2O$[3]	2D	*I*2/*a*
	$(NH_4)_3[Co_2(HL)_2(HCOO)(H_2O)_2]$[5]	1D	*C*2/*c*
	$[Co(H_2L)(H_2O)_2]\cdot 2H_2O$[5]	1D	$P2_1/c$
	$[Co(H_2L)(H_2O)_2]\cdot H_2O$[5]	1D	$P2_1/c$
	$[Pb_3L(H_2L)]\cdot 1.5H_2O$[4]	2D	$P2_1/c$
	$[Pb_3(HL)_2]\cdot 2H_3BTC\cdot 2H_2O$[4]	2D	$P\bar{1}$
	$Mn(H_2L)$[6]	2D	$P2_1/n$
	$Mn(H_3L)_2$[6]	1D	*C*2/*c*
	$Ln(H_2L)(H_3L)$ (Ln=La, Pr, Nd, Sm, Eu, Gd)[7]	1D	$P\bar{1}$

	$Ln(H_2L)(H_3L)$ (Ln=Gd, Tb)[7]	1D	$P2_12_12_1$
	$ZrF(HL)$[8]	2D	*P*bca
	$Cd(H_3L)_2$[9]	1D	*C*2/*c*
	$[Zr(HPO_4)(L)_{0.5}]\cdot 2H_2O$[10]	2D	n/a
CH_3			
	$[Mn_2(H_2L)_2(H_2O)]$[6]	2D	*I*2/*a*
	$Cd(H_3L)_2$[9]	1D	*C*2/*c*
F			
	$[Co_3(HL)_2(H_2O)_4]\cdot 2H_2O$[11]	2D	$P2_1/c$
	$[Cu(H_2L)(H_2O)]$[11]	2D	$P2_1/c$
	$[Fe_3(L)_2(H_2O)_3OH]\cdot 2H_2O$[11]	2D	*I*2/*a*
	$[Cu_2(L)(4,4'\text{-bipy})_{1.5}]\cdot 5H_2O$[11]	3D	$P2_1/c$
	$Co(H_2L)(4,4'\text{-bipy})_{0.5}$[11]	3D	$P\bar{1}$
	$Ni(H_2L)(4,4'\text{-bipy})_{0.5}$[11]	3D	*C*2/*m*
	$[Ni_3(HL)_2(H_2O)_{10}]\cdot 4H_2O$[15]	1D	$P2_1/c$
COOH			
	$[Sn_2(HL)(H_2O)_2]$[12]	2D	*C*2/*c*
	$[Pb_2Cl(H_2L)]$[12]	3D	C*c*
	$[Zn(H_3L)]\cdot 2H_2O$[17]	1D	*P*ba2
	$[Pb(H_3L)(H_2O)_2]$[17]	2D	$P\bar{1}$
	$Fe_2(HL)(H_2O)$[13]	2D	$P2_1/c$
	$Fe(H_4L)_2$[13]	2D	$P2_1/c$
	$Zn(H_3L)$[13]	1D	*P*ccn
	$Zn_2(HL)$[13]	2D	$P2_1/c$
	$Ca(H_3L)(H_2O)$[18]	2D	$P\bar{1}$
	$Sr(H_3L)(H_2O)_2$[18]	2D	$P\bar{1}$
	$Ba(H_3L)(H_2O)$[18]	2D	$P\bar{1}$
	$Ni_3(H_2L)_2(4,4'\text{-bipy})(H_2O)_4$[19]	3D	*C*2/*c*
	$[Co_2(HL)]\cdot H_2O$[14]	2D	$P2_1/a$
	$[Cd_3(H_2O)_3((H_2L)_2]\cdot 11H_2O$[16]	2D	$P\bar{1}$
	$[La(H_4L)(H_3L)(H_2O)]\cdot 2H_2O$[20]	2D	$P\bar{1}$
	$Er(H_3L)(H_4L)$[20]	1D	$P\bar{1}$

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