Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting materials

$M(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (M=Co, Mn, Zn, Cu) : a new serie of layered metallohosphonate from 6-hydroxy-2-naphthylphosphonic acid precursor

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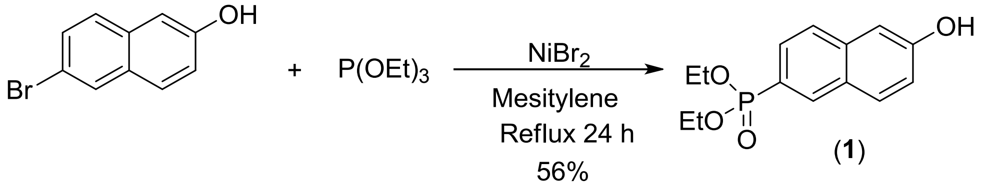
1. Synthesis

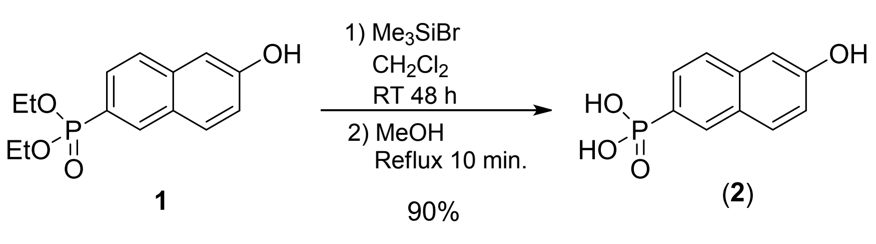
Diethyl 6-hydroxy-2-naphthylphosphonate (**1**)



$NiBr_2$ (1.18 g, 5.38 mmol, 6 mol%), 6-bromo-2-naphtol (20 g, 89.7 mmol, 1.0 eq.) were mixed under nitrogen with mesitylene (25 mL). The solution was heated at 165°C and then triethylphosphite (23.0 mL, 134.5 mmol, 1.5 eq) was added dropwise (warning: an exothermic reaction occurred ; discontinuous dropwise addition is required). At the end of the addition, the reaction was further stirred at 165°C for 24 hours. After cooling, the excess of triethylphosphite and mesitylene were removed by distillation under vacuum (~ 0.1 mbar). The resulting mixture was dissolved in dichloromethane (250 mL) and water (250 mL) was added to remove part of the nickel salt. The solution was stirred at room temperature overnight. The two layers were separated then the organic layer was washed twice with water (2 x 300 mL) and the aqueous layer was extracted with CH_2Cl_2 (2 x 250 mL). The organic layers were combined, dried over $MgSO_4$ and evaporated under reduced pressure to yield yellow oil. The crude product was purified by distillation with Kugelrohr (150°C, 5.10^{-2} mbar) and the oil was diluted with CH_2Cl_2 (150 mL) and extracted four times with NaOH 10 % aqueous solution (4 x 75 mL). The aqueous layer was acidified with HCl 3.7 M and extracted with CH_2Cl_2 (3 x 250 mL). The organic layers were combined, dried over $MgSO_4$ and evaporated under reduced pressure to yield compound **1** (oil, 14.0 g, 56 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.35 (6H, t, ^{3}J= 7.2 Hz, CH_3); 4.09-4.26 (4H, m, CH_2); 7.32-7.34 (2H, m, H_{ar}); 7.64-7.68 (2H, m, H_{ar}); 7.76- (1H, d, ^{3}J= 8.7 Hz, H_{ar}); 8.321 (1H, d, ^{3}J= 15.5 Hz, H_{ar}); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 21.4; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.3 (d, $^{3}J_{PC}$= 6.8 Hz, CH_3); 62.6 (d, $^{2}J_{PC}$= 5.3 Hz, CH_2); 109.6 (CH_{ar}); 119.2 (d, $^{1}J_{CP}$= 191.7 Hz, C_q); 120.0 (CH_{ar}); 126.4 (d, $^{2}J_{CP}$= 10.6 Hz, CH_{ar}); 126.9 (d, $^{3}J_{CP}$= 14.3 Hz, CH_{ar}); 127.4 (C_q); 129.5 (CH_{ar}); 134.0 (d, $^{2}J_{CP}$= 9.8 Hz, CH_{ar}); 137.2 (C_q); 152.8 (C_q); m/z (ESI): (theoretical value M+ : 280.086) 281.20 $[M+H]^+$; 561.25 $[2M+H]^+$; 583.25 $[2M+Na]^+$; IR (cm^{-1}): 1018 (P-O); 1204 (P=O=; 2984 (C-H); 3132 (O-H).

6-hydroxy-2-naphthylphosphonic acid (**2**)

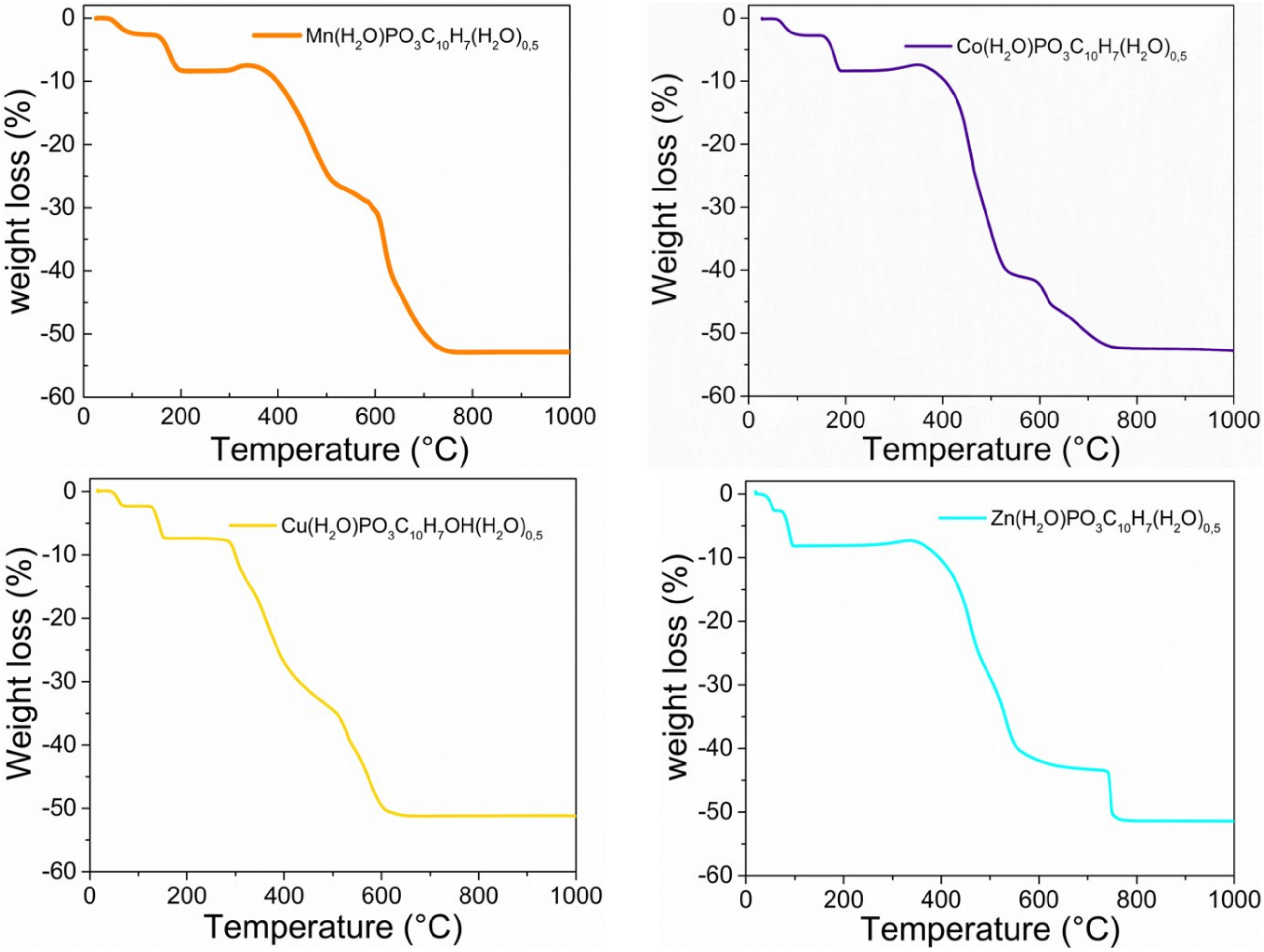


To a solution of **1** (6.0 g, 21.4 mmol, 1.0 eq.) dissolved in anhydrous dichloromethane (75 mL) under nitrogen was added bromotrimethylsilane (11.3 mL, 85.6 mmol, 4.0 eq). The solution was stirred at room temperature overnight. The volatiles were removed under vacuum. The residue was dissolved in methanol (50 mL) and the solution was stirred at reflux 10 minutes. The solution was evaporated under vacuum to yield compound **2** as a grey powder (4.3 g, 90 %).

mp: 261°C ; ^{1}H NMR (D_2O + K_2CO_3, 400 MHz): δ 6.96 (1H, d, $^4J_{HH}$= 2.2 Hz, H_{ar}); 7.03 (1H, dd, $^4J_{HH}$= 2.4 Hz $^3J_{HH}$= 8.8 Hz, H_{ar}); 7.58-7.66 (2H, m, H_{ar}); 7.76 (1H, d, $^3J_{HH}$= 8.9, H_{ar}); 8.01 (1H, d, $^3J_{HH}$= 13.2, H_{ar}) ; ^{31}P NMR (D_2O + K_2CO_3, 162 MHz): δ 12.8 ; ^{13}C NMR (D_2O + K_2CO_3, 125 MHz): δ 112.5 (CH_{ar}); 125.6 (CH_{ar}); 127.2 (d, $^3J_{PC}$= 12.1 Hz, CH_{ar}); 128.5 (C_q); 130.6 (d, $^3J_{PC}$= 9.1 Hz, CH_{ar}); 132.4 (d, $^3J_{PC}$= 8.3 Hz, CH_{ar}); 132.9 (CH_{ar}); 134.9 (d, $^1J_{PC}$= 170.6 Hz, C_q); 137.2 (C_q); 165.6 (C_q) ; m/z (ESI): (theoretical value 224.024), 222.75 $[M-H]^-$; IR (cm^{-1}): 1005 (P-O); 1104 (P=O); 2730-3023 (O-H).

2. Thermogravimetric analyses (TGA)

a)



b)

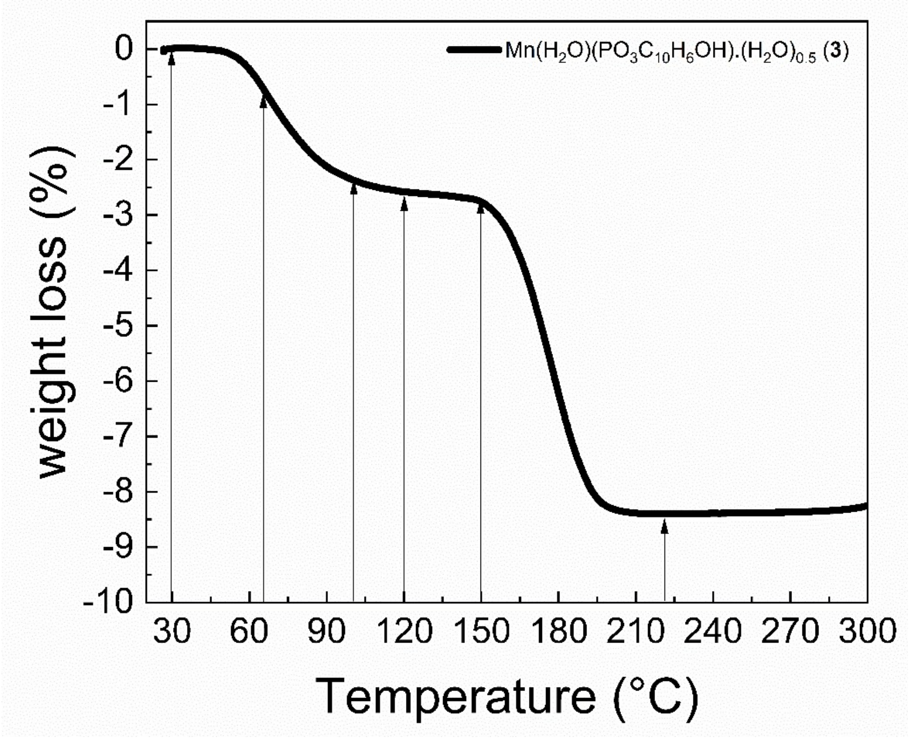


Figure ST1 : a) Thermogravimetric curves obtained under air at the heating rate of 2°C/min of compounds $Mn(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (**3**), $Co(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (**4**), $Cu(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (**5**) and $Zn(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (**6**). b) Inset of the thermogravimetric curves obtained between 27°C and 300°C for compounds $Mn(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (**3**) with the selected temperatures for X-ray powder diffraction study in temperature.

3. X-ray diffraction refinement on powder by Le Bail method

3.1 Sample preparation

X-ray powder diffraction analyses were performed on the four compounds to confirm the homogeneity of each synthesized batch samples. This study was first carried out on the compounds synthetized by hydrothermal route. By this way the X-ray diffraction patterns obtained only presented (0k0) reflections for the compounds (**3**) (**4**) (**6**) and (00l) reflections for the compound (**5**) associated to a strong preferential orientation that exacerbates these specific reflections. To solve this problem intrinsically due to the structure of the materials we decided to reduce the size of the crystals by using a soft chemistry synthesis in round bottom flask applied to the four materials. The use of this method allowed us to synthetize the four compounds as very fine powder and thus to optimize the powder diffraction pattern by decreasing the preferred orientation. The use of this strategy allowed us to obtain the desired pattern matching of the compounds and to confirm their homogeneity.

3.2. X-ray diffraction powder pattern matching of the compounds

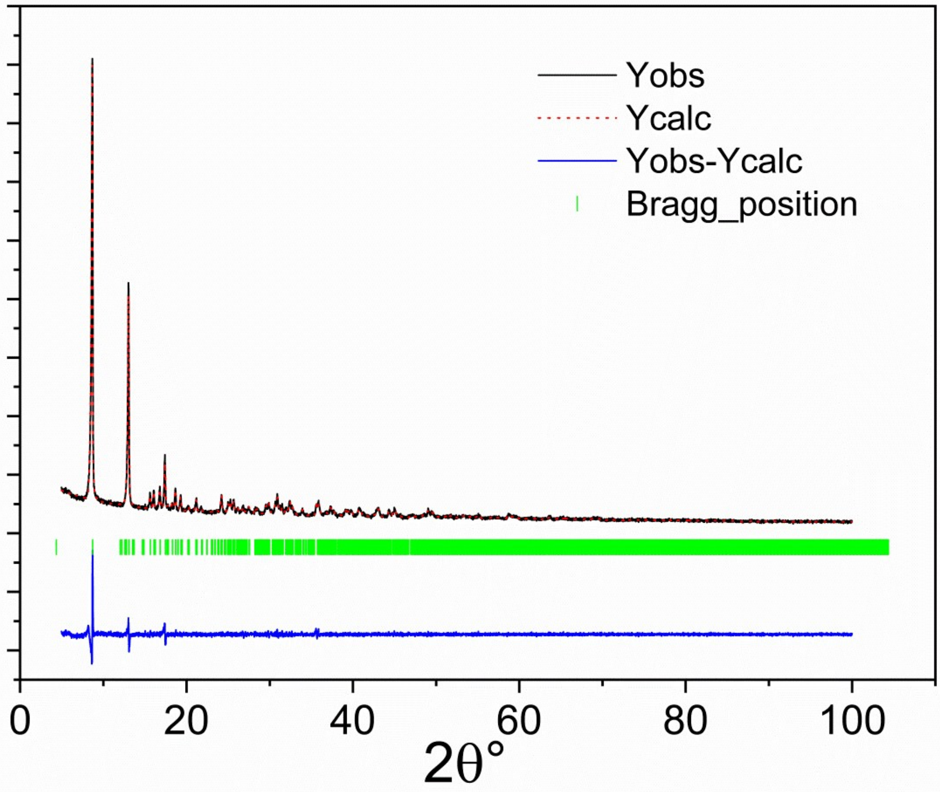


Figure ST2 : Le Bail refinement of $Mn(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (**3**) from X-Ray powder diffraction data on soft chemistry samples synthesized in round bottom flask.

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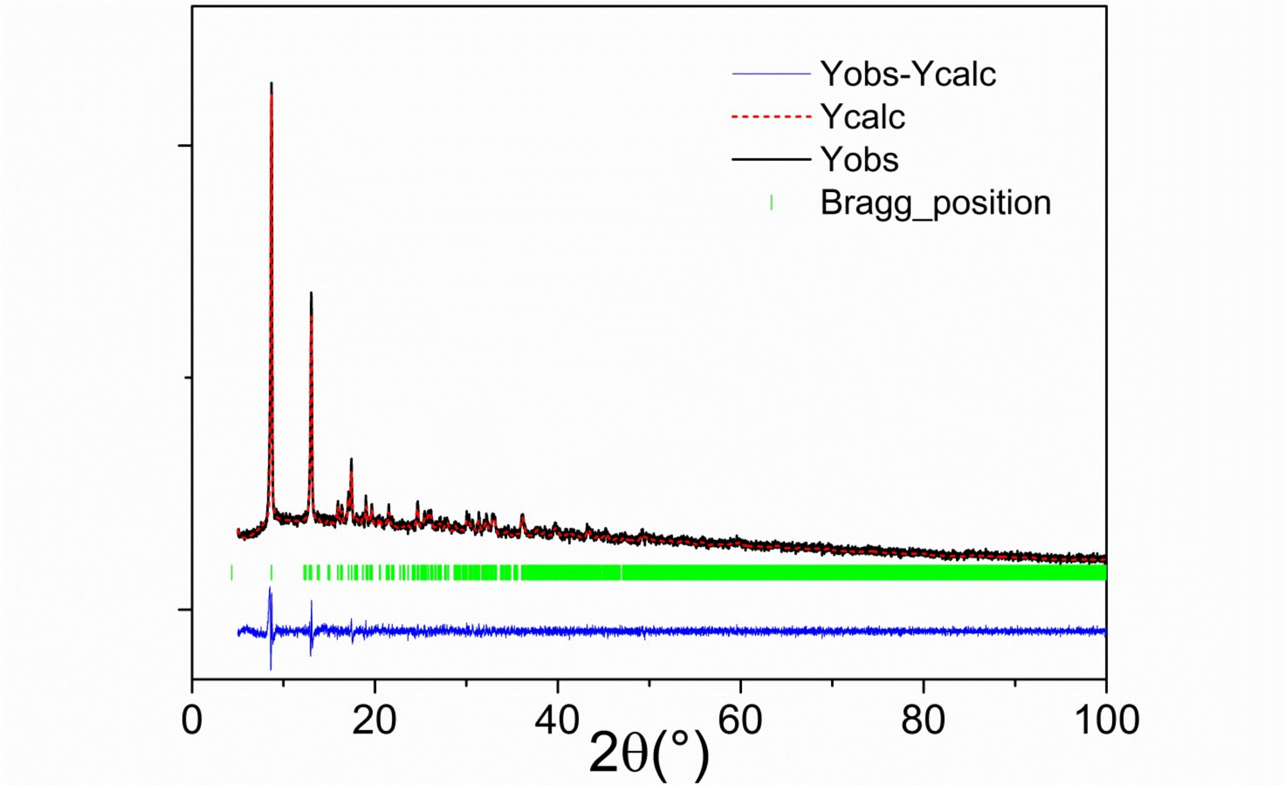

Figure ST3 : Le Bail refinement of Co(H_2O)($PO_3C_{10}H_6OH$).(H_2O)$_{0.5}$ (**4**) from X-Ray powder diffraction data on soft chemistry samples synthesized in round bottom flask.

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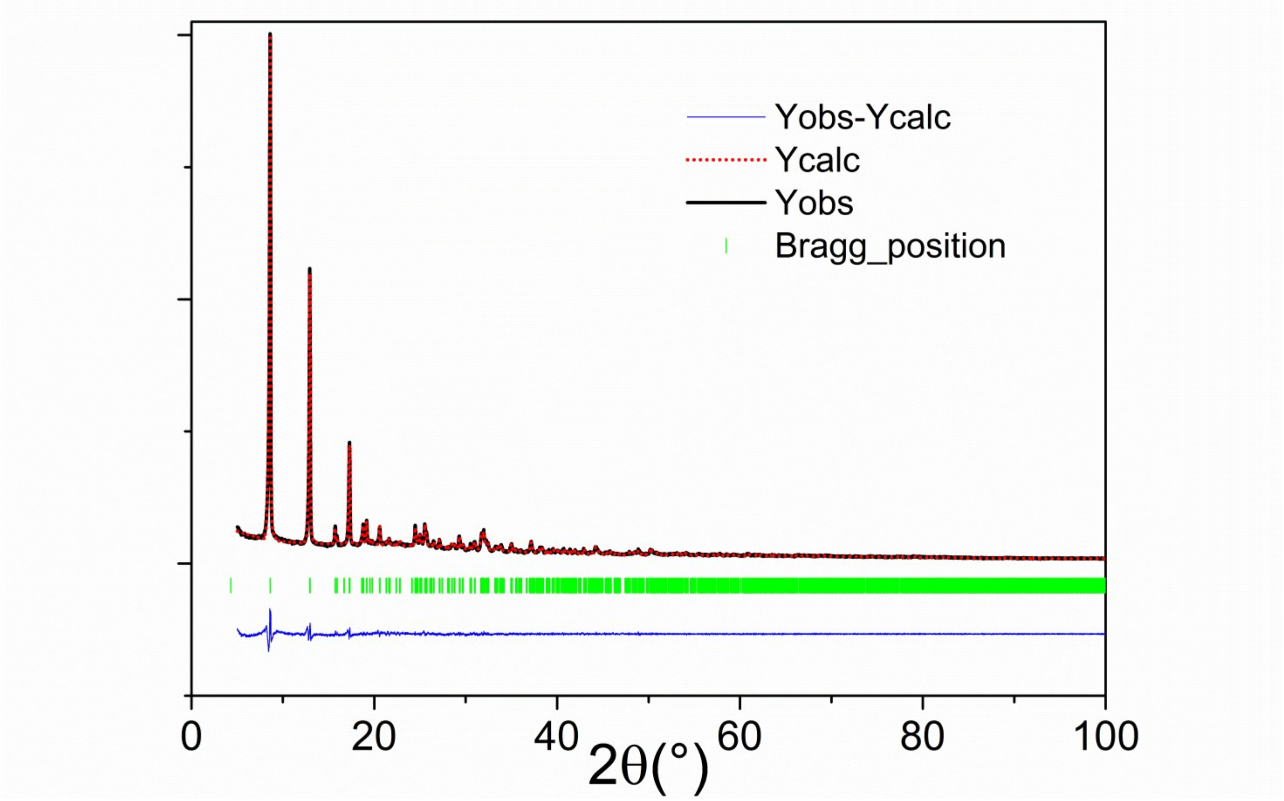

FigureST4 : Le Bail refinement of Cu(H_2O)($PO_3C_{10}H_6OH$).(H_2O)$_{0.5}$ (**5**) from X-Ray powder diffraction data on soft chemistry samples synthesized in round bottom flask.

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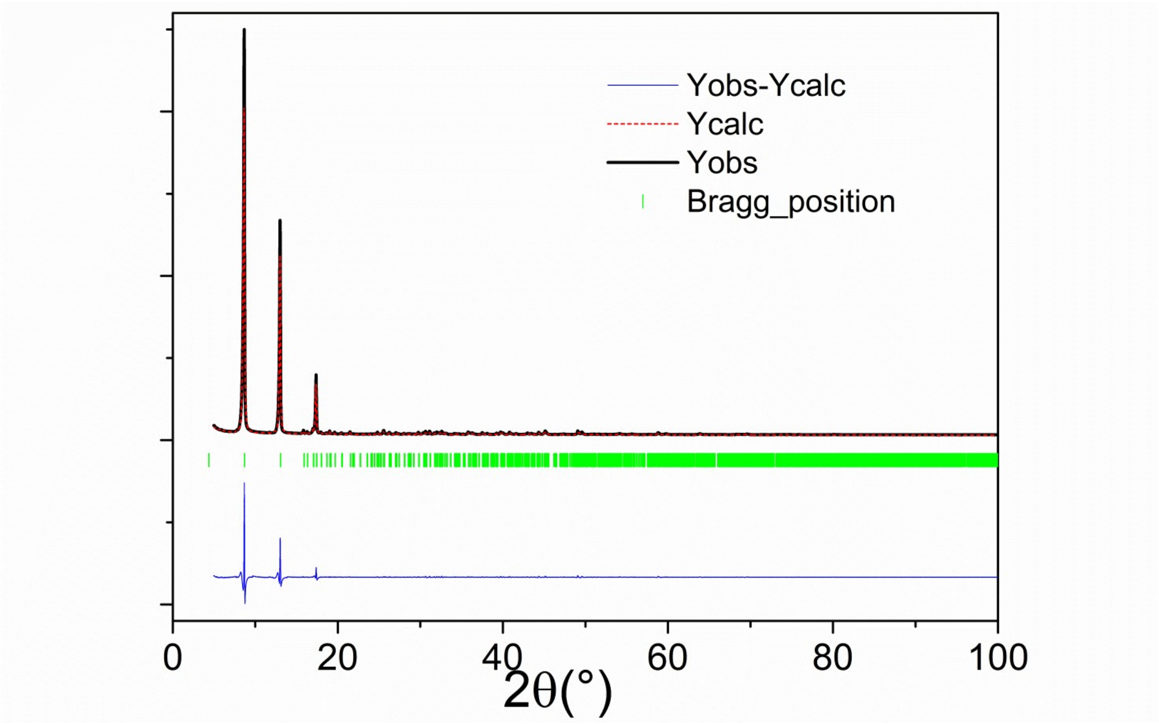


Figure ST5 : Le Bail refinement of Zn(H_2O)($PO_3C_{10}H_6OH$).(H_2O)$_{0.5}$ (**6**) from X-Ray powder diffraction data on soft chemistry samples synthesized in round bottom flask.

Intermolecular P---P distances	$Mn(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (**3**)	$Co(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (**4**)	$Cu(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (**5**)
Along the a direction	7.467 Å	7.334 Å	5.660 Å
Along the c direction	8.076 Å	7.440 Å	4.752 Å

Tableau ST1 : Intermolecular P---P distances obtained from the single crystal study performed on $Mn(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (3), $Co(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (4), $Cu(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (5) and $Zn(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (6).

$Mn(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$	Intercolumnar distances d(C---H-C) between two naphthalene moieties			
	C21···H1-C17	3.236 Å	C21···H1-C17	3.144 Å
	C13···H1-C17	3.286 Å	C13···H1-C17	3.157 Å
	C8···H1-C20	3.293 Å	C12···H1-C21	3.102 Å
	C15···H1-C20	3.242 Å	C5···H1-C21	3.080 Å

Tableau ST2 : C···H-C bond distances between two naphthalene moieties tilted with an angle of 31.6 ° in compound (3).

$Co(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$	Intercolumnar C---H-C bonds between two tilted naphthalene moieties with an angle of 31.6 °			
	C21-H1---C12	3.011	C21-H1---C13	3.248
	C21-H1---C25	3.029	C21-H1---C20	3.276
	C14-H1---C21	3.150	C13-H1---C4	2.954
	C14-H1---C8	3.200	C13-H1---C15	2.982
	C13-H1---C16	3.295	C13-H1---C21	3.270

Tableau ST3 : $Co(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ intercolumnar C---H-C bonds between two tilted naphthalene moieties with an angle of 31.6 °

$Cu(H_2O)(PO_3C_{10}H_6OH).(H_2$	Interlayer O---H-O bonds between free water molecule and hydroxyl groups			
	O29-H2---O11	2.773	O29-H2---O2	2.358

$O)_{0.5}$	O11-H2---O29	3.249	O29-H1---O2	2.403
	O11-H2---O29	2.742	O2-H1---O29	2.396
	O2-H1---O29	3.212	O2-H1---O11	2.551
	O11-H2---O2	2.551		

Tableau ST4 : $Cu(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ interlayer O---H-O bonds between free water molecule and hydroxyl groups

$Mn(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$	Hydrogen bond distances d(O···H-O) between free water molecules and hydroxyl groups			
	O11-H1···O9	2.858 Å	O11-H1···O9	2.091 Å
	O11-H2···O10	2.923 Å	O10-H1···O11	2.149 Å
	O11-H2···O10	3.249 Å	O11-H2···O9	2.743 Å
	O9-H1···O10	1.616 Å	O10-H1···O9	3.047 Å

Tableau ST5 : Hydrogen bond distances between–OH groups and H_2O molecules present at the interface of 2 organic layers in compound (3).

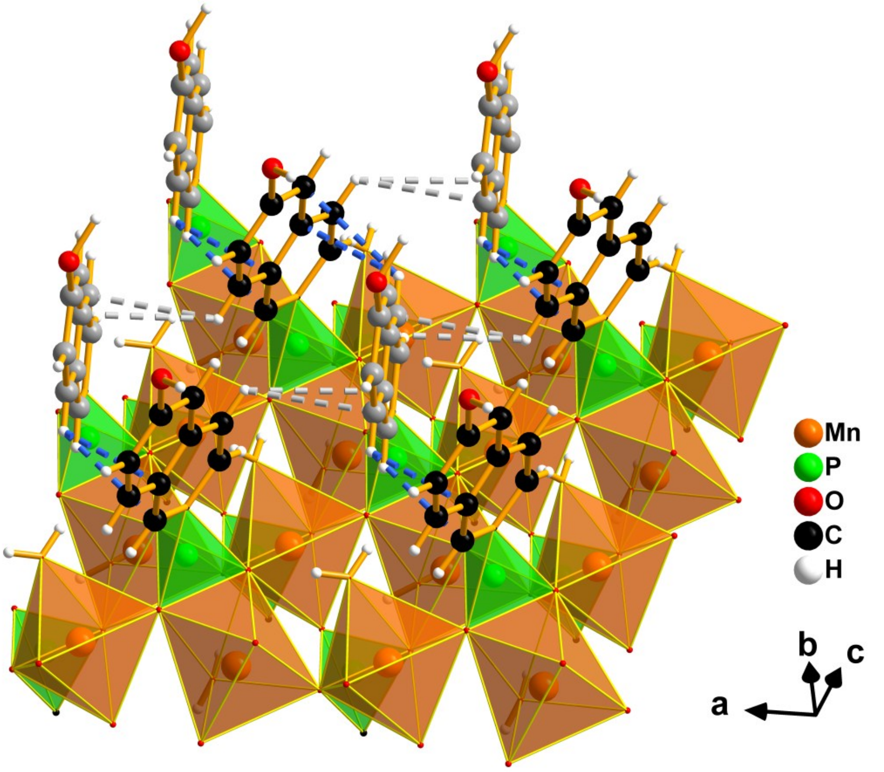


Figure ST6 : C···H–C hydrogen bonds between two neighboring rings of $Mn(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (3).

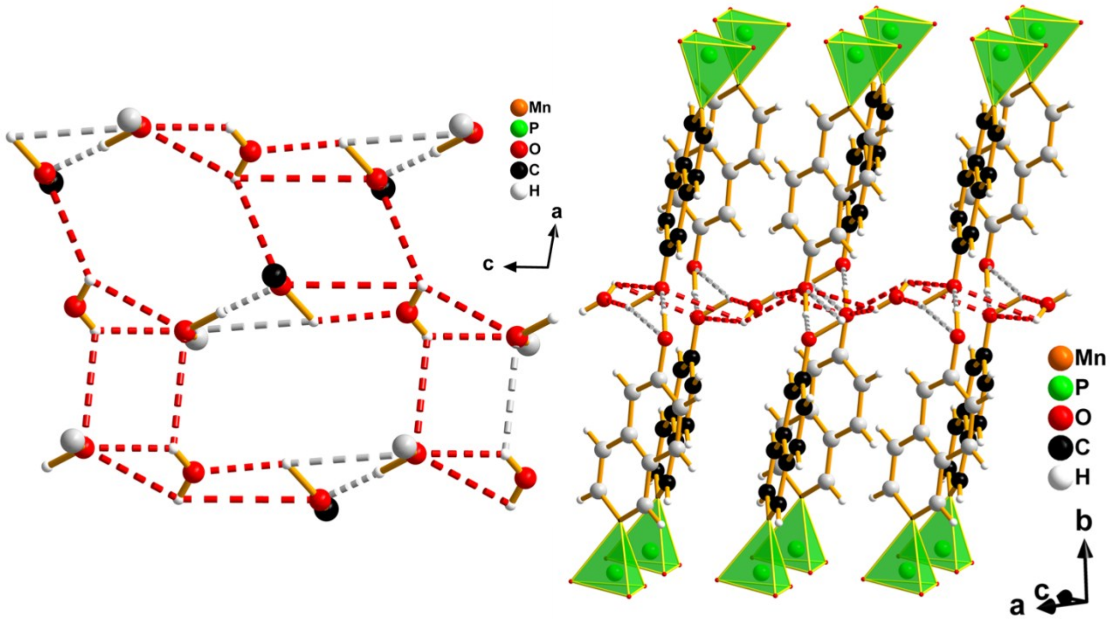
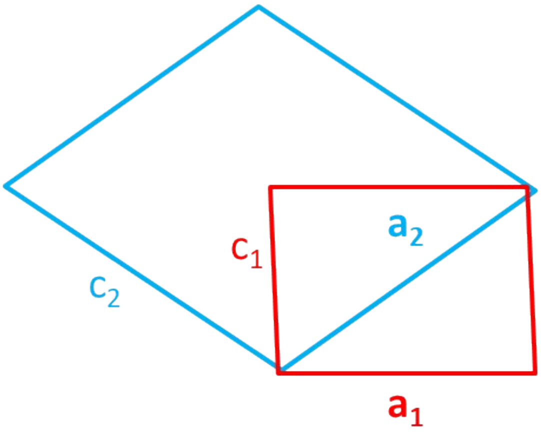


Figure ST7 : O···H–O hydrogen bonds network between the free water molecules and the hydroxyl groups present at the interface of two organic layers of $Mn(H_2O)(PO_3C_{10}H_6OH).(H_2O)_{0.5}$ (3). In grey: hydrogen bonds between –OH groups and H_2O molecules; in red hydrogen



$$\begin{pmatrix} a_2 \\ b_2 \\ c_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} a_1 \\ b_1 \\ c_1 \end{pmatrix}$$

Figure ST8 : Schema and transfer matrix allowing passing from the monoclinic cell 1 to the monoclinic cell 2