Supporting Information for

New Hybrid Layered Molybdates Based on $^2/_\infty[Mo_nO_{3n+1}]^{2-}$ Units (n = 7, 9) with Systematic Organic-Inorganic Interfaces

Martine Bujoli-Doeuff, *Rémi Dessapt**, *Philippe Deniard* and *Stéphane Jobic*

Formal equations of formation of the $^{1}/_{\infty}[Mo_3O_{10}]^{2-}$, $^{1}/_{\infty}[Mo_8O_{26}]^{4-}$, and $^{2}/_{\infty}[Mo_7O_{22}]^{2-}$ blocks by acidification of the MoO_4^{2-} anion. The N parameter is defined as the H^+/MoO_4^{2-} molecular ratio.

$$3\ MoO_4^{2-} + 4\ H^+ \rightarrow [Mo_3O_{10}]^{2-} + 2\ H_2O \qquad N = 1.333$$

$$8\ MoO_4^{2-} + 12\ H^+ \rightarrow [Mo_8O_{26}]^{4-} + 6\ H_2O \qquad N = 1.500$$

$$7\ MoO_4^{2-} + 12\ H^+ \rightarrow [Mo_7O_{22}]^{2-} + 6\ H_2O \qquad N = 1.714$$

Figure S1. Representations of the organic-inorganic interfaces in different (A)$[Mo_5O_{16}]$ materials i.e. (a) $(MeH_2N\text{-}(CH_2)_2\text{-}NH_2Me)[Mo_5O_{16}]$, (b) $(H_3N\text{-}(CH_2)_2\text{-}NH_2Me)[Mo_5O_{16}]$, (c) $(H_2pipz)[Mo_5O_{16}]$ and (d) $(H_3N\text{-}(CH_2)_4\text{-}NH_3)[Mo_5O_{16}]$ in a view perpendicular of the normal of the molybdate layers. Color code: Hydrogen (white), carbon (black), nitrogen (green), bridging μ^2-oxygen and terminal oxygen of the $^2/_\infty[Mo_5O_{16}]^{2-}$ layers (purple and red, respectively). The hydrogen bonding networks are displayed as dotted lines. For clarity, the hydrogen atoms of the CH_2 groups of the A^{2+} cations are omitted.

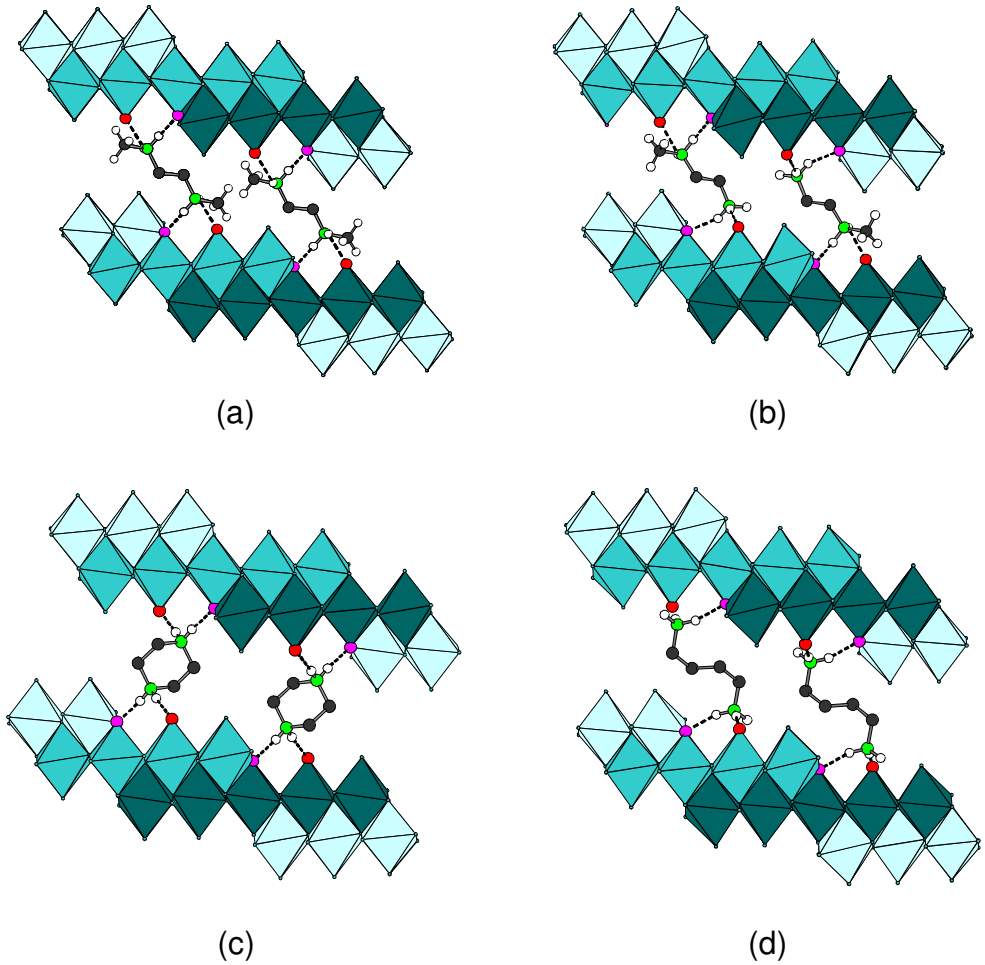

Table S1. Bond Valence Sums[a] for **1**

S_i	**Mo1**	**Mo1**	**Mo2**	**Mo3**	**Mo4**	$\sum S_i$	$V-\sum S_i$
O1			1.68	0.27		1.95	-0.05
O1			1.68				
O2					1.84	1.84	-0.16
O3	1.68				0.33	2.01	0.01
O4			0.40	1.20	0.46	2.07	0.07
O4			0.40				
O5				1.74		1.74	-0.26
O6	0.92			0.42	0.83	2.17	0.17
O7	0.35			1.65		2.00	0.00
O8	0.94	0.39		0.81		2.14	0.14
O8	0.39						
O9			0.93		1.00	1.93	-0.07
O9			0.93				
O10	1.81					1.81	-0.19
O11					1.67	1.67	-0.33
$\sum S_i$	6.09		6.02	6.09	6.13		

[a] Valence sums calculated with the formula $Si = \exp[(R_0 - R_i)/B]$, where S_i is the bond valence of bond i, R_0 is a constant dependent upon the bonded elements, R_i is the bond length of bond i, and B equals 0.37. $\sum S_i$ is the bond valence sum for each atom. V is the predicted valence for a site. $R_0(Mo^{VI}\text{-}O) = 1.907$. Color code: Hydrogen (white), carbon (black), nitrogen (green), molybdenum (turquoise), oxygen (red, pink and blue oxygen of the water molecule).

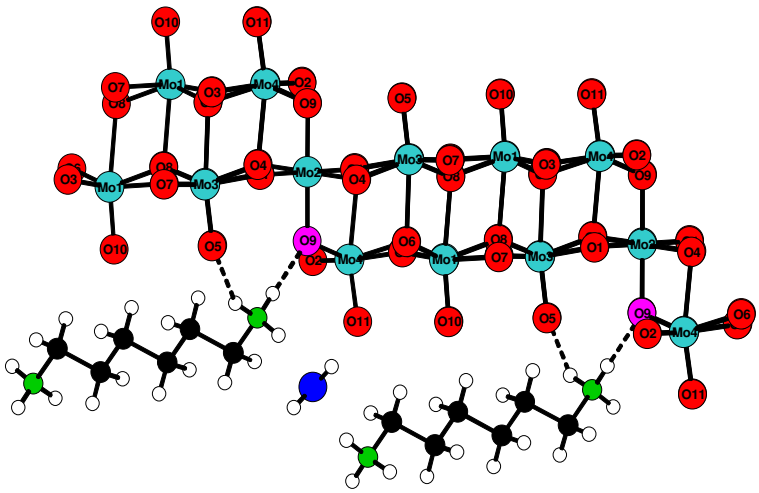

Table S2. Bond Valence Sums for **2**

S_i	Mo1	Mo2	Mo3	Mo4	Mo4	Mo5	$\sum S_i$	$V-\sum S_i$
O1	1.72					0.30	2.02	0.02
O2		0.42	1.19			0.42	2.03	0.03
O2		0.42						
O3	0.34			1.68			2.03	0.03
O4						1.77	1.77	-0.23
O5	0.87			0.93	0.34		2.14	0.14
O5				0.34				
O6		1.70	0.30				2.00	0.00
O6		1.70						
O7		0.96				1.00	1.96	-0.04
O7		0.96						
O8			1.76				1.76	-0.24
O9			1.60	0.37			1.97	-0.03
O10	0.99		0.37			0.78	2.14	0.14
O11	0.39		0.80	0.98			2.17	0.17
O12				1.78			1.78	-0.22
O13						1.74	1.74	-0.26
O14	1.88						1.88	-0.12
$\sum S_i$	6.19	6.16	6.02	6.08		6.00		

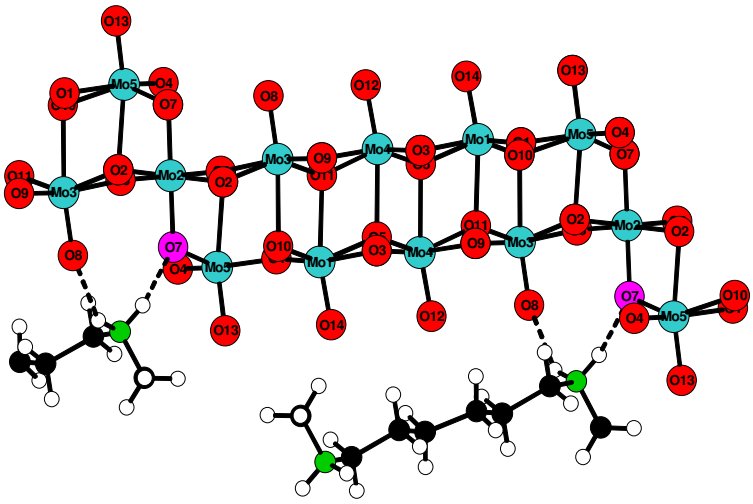

Table S3. Mo_2O stretching vibration frequencies of many $^2/_\infty[Mo_nO_{3n+1}]^{2-}$ containing hybrid compounds.

compound	**νMo_2O (cm^{-1})**
$(MeH_2N–(CH_2)_2–NH_2Me)[Mo_5O_{16}]$	886
$(H_3N–(CH_2)_2–NH_2Me)[Mo_5O_{16}]$	884
$(H_2pipz)[Mo_5O_{16}]$	884
$(H_3N–(CH_2)_4–NH_3)[Mo_5O_{16}]$	885
$(CH_3NH_3)_2[Mo_7O_{22}]$	870
$(Me_2HN–(CH_2)_2–NH_2Me)[Mo_7O_{22}]$	870
$(Me_2HN–(CH_2)_2–NHMe_2)[Mo_7O_{22}]$	868