Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Theoretical insights into inorganic-organic intercalation products of the layered perovskite $HLaNb_2O_7$: perspectives for hybrid proton conductors

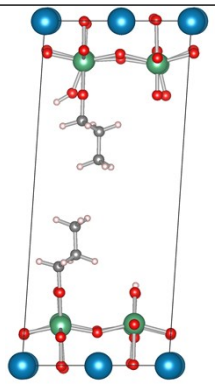
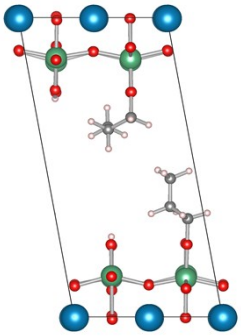
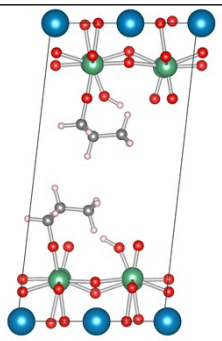
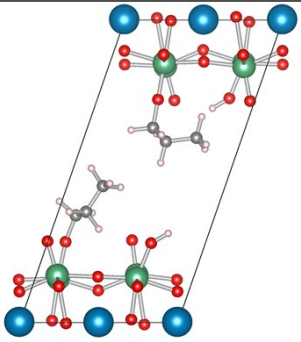
Supporting Information

Computational details

A Monkhorst-Pack shrinking factor [1] of 4 (corresponding to 10 points in the irreducible Brillouin zone for the tetragonal systems here considered and 36 for the triclinic ones) and an *extrafine* numerical integration grid (75 points in the radial part, 974 in the angular one) have been considered for all calculations. All the structures have been optimized considering the default thresholds values of the four convergence criteria, that are maximum and root-mean-square of 0.00045 and 0.00030 a.u. for forces and 0.0018 and 0.0012 a.u. for displacements. Harmonic frequencies have been computed at the Γ point, using an SCF convergence criteria of 10^{-12} Hartree, for the transition state of the proton transfer reaction in the Imi-But-HLN system containing one excess proton. The obtained imaginary frequency well corresponds to the transfer of the proton between the two imidazoles.

[1] Monkhorst, H.; Pack, J. *Phys. Rev. B* **1976**, *13*, 5188-5192.

Table S1. Optimized (B3LYP) lattice parameters (*a*, *b*, *c* in Å and *α*, *β*, *γ* in degrees) and relative energies (ΔE, *kcal/mol*) of different conformations of 2**Pro-HLN$_b$** considering a propyl/HLN ratio of 0.50.

	cell parameters	**E(H)**	**ΔE**
	7.883 7.915 **18.921** 93.74 88.72 89.88	-1262.186089	**13.18**
	7.928 7.871 **16.650** 91.09 79.74 90.01	-1262.192675	**9.05**
	7.929 7.873 **16.154** 96.49 95.39 89.98	-1262.193791	**8.35**
	7.874 7.927 **16.200** 80.60 71.18 89.95	-1262.202064	**3.16**

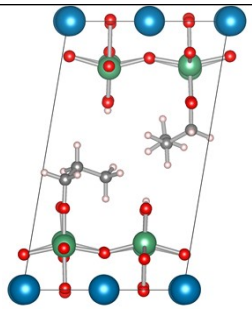
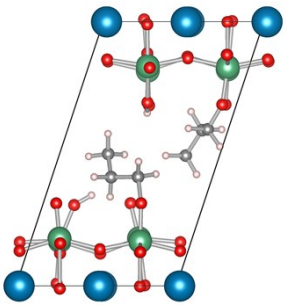
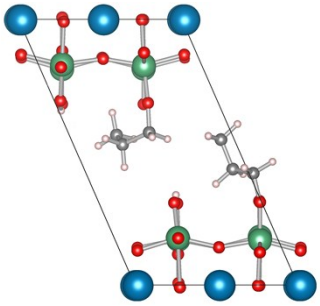
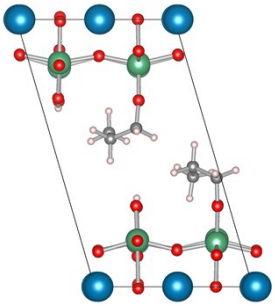
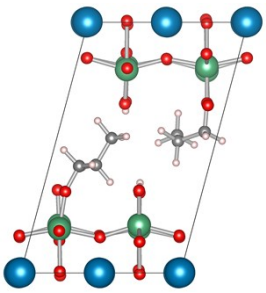
	7.878 7.925 **14.126** 99.12 72.82 89.96	-1262.207095	**0.00**

Table S2. Optimized (B3LYP) lattice parameters (*a*, *b*, *c* in Å and *α*, *β*, *γ* in degrees) and relative energies (ΔE, *kcal/mol*) of different conformations of 2**Pro-HLN$_b$** considering a propyl/HLN ratio of 0.50.

	cell parameters (Å and degrees)	**E(H)**	**ΔE**
	7.852 7.874 **13.669** 96.01 108.24 90.18	-1262.420400	**20.98**
	7.885 7.817 **14.300** 101.60 66.86 90.02	-1262.433424	**12.81**
	7.889 7.825 **13.961** 96.31 73.80 90.02	-1262.431389	**14.08**
	7.828 7.887 **13.297** 104.45 74.09 90.06	-1262.453832	**0.00**

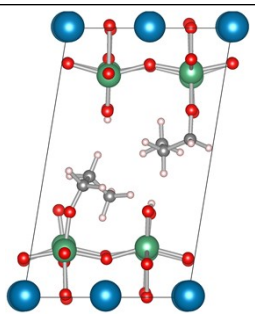
	7.828 7.881 **13.080** 99.30 85.92 90.06	-1262.442516	**7.10**

Table S3. Optimized lattice parameters and some structural details (*a*, *b*, *c* in Å and *α*, *β*, *γ* and other angles in degrees) of propanol - substituted HLN in the bulk model, considering one (**Pro-HLN$_b$**) or two (**2Pro-HLN$_b$**) propanol molecules, obtained with different functionals. Coverage 0.34

		PBE	**SOGGA**	**B3LYP**	**PBE0**	**PBE0-D**
Pro-HLN$_b$	**a**	7.926	7.864	7.924	7.866	7.821
	b	7.863	7.805	7.860	7.808	7.806
	c	12.937	12.328	13.509	13.112	11.327
	α	93.87	93.08	95.76	94.80	92.99
	β	91.69	91.11	91.88	91.64	87.23
	γ	89.97	89.96	89.98	89.98	89.96
	O-C1-C2	109.2	109.0	109.6	109.4	109.7
	Nb-O-C1	170.7	169.3	175.9	174.2	156.2
	Nb-O-C1-C2	-27.7	-21.9	-39.2	-28.5	23.2
2Pro-HLN$_b$	**a**	-	11.802	11.880	11.788	11.768
	b	-	7.806	7.881	7.823	7.791
	c	-	12.606	14.379	14.199	11.957
	α	-	94.15	94.85	94.82	89.90
	β	-	93.69	94.48	94.18	87.69
	γ	-	90.03	90.01	90.00	89.97

Table S4. Experimental and computed (B3LYP/IGLO-III) ^{13}C chemical shifts (*ppm*) of **Pro-HLN** with respect to tetramethylsilane (TMS) absorption, computed for different clusters cut from the periodic structures optimized with different functionals. See figure 2 for carbon labeling.

Pro-HLN

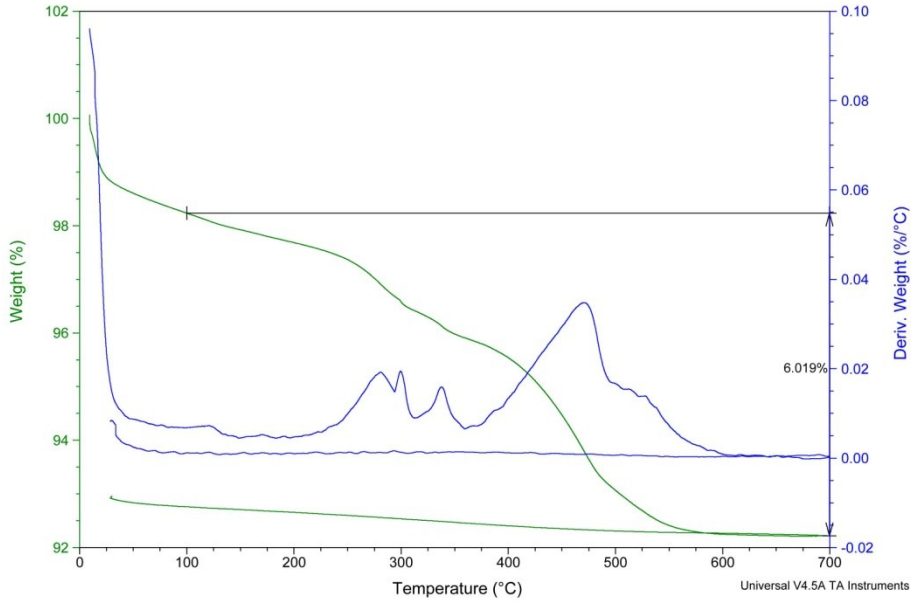
	CLUSTER 1					CLUSTER 2		CLUSTER 3		
PERIODIC STRUCT. / CARBON	**PBE**	**SOGGA**	**B3LYP**	**PBE0**	**PBE0-D**	**SOGGA**	**B3LYP**	**SOGGA**	**B3LYP**	**exp**
C1	94.1	85.6	89.7	89.9	78.3	85.9	83.2	85.8	83.2	**80.9**
C2	37.9	27.6	34.4	35.4	41.7	34.6	32.5	29.2	29.3	**26.0**
C3	21.4	24.4	16.8	18.8	31.2	17.0	13.0	15.0	13.3	**12.2**

Table S5. Average value of Mulliken charges (el) computed at B3LYP level for the atoms belonging to a 2x2 HLN supercell, **Pro-HLN$_b$** and **Imi-HLN$_b$**. Oxygen atoms are divided in two subgroups: the bulk oxygen (labeled O *bulk*) and the surface atoms pointing toward the interlayer spacing (O *interlayer surface*).

	HLN	**Pro-HLN$_b$**	**Imi-HLN$_b$**
H	0.54	0.31	0.30
La	2.46	2.44	2.44
Nb	2.64	2.51	2.51
O *bulk*	-1.27	-1.27	-1.27
O *interlayer surface*	-0.96	-0.72	-0.76
propyl	-	0.37	-
imidazole	-	-	0.80

Figure S1. Thermograms of Pro-HLN and Imi-HLN

Pro-HLN



Imi-HLN

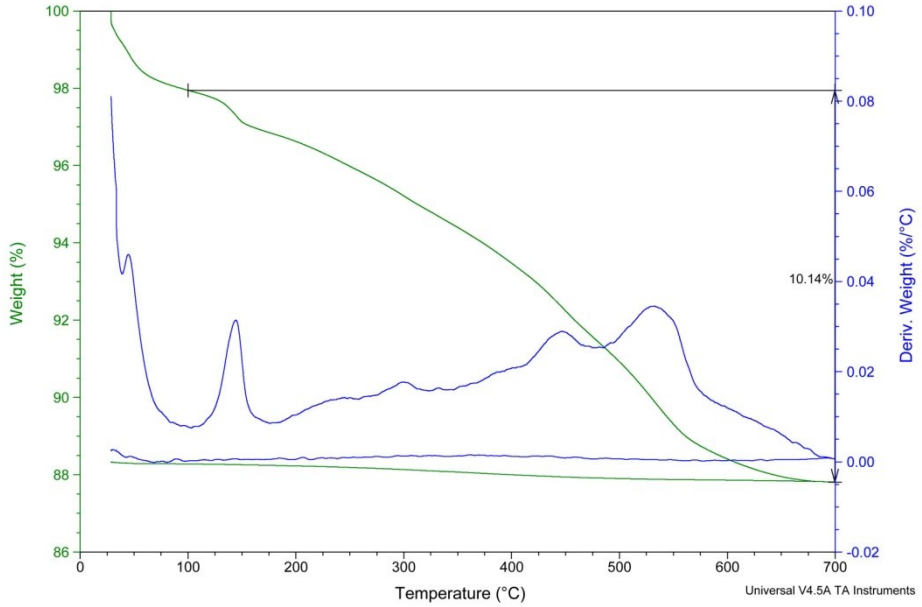


Figure S2. Optimized PBE0-D structure of **Pro-HLN$_b$**

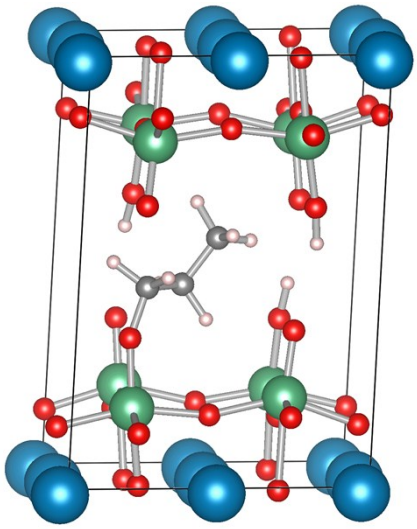


Figure S3. Sketch of the HOCO orbital of **Imi-HLN**$_{b.}$ Isovalue set to 0.02.