## Supplementary Materials

## On the Reaction Pathways and Growth Mechanisms of LiNbO<sub>3</sub> Nanocrystals from the Non-Aqueous Solvothermal Alkoxide Route

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**Figure S1.** XRD diffraction patterns of LN nanopowders obtained after a thermal treatment at 230°C of the commercial precursor alone for a period extending from 48h to 72h. After 3 days, the absence of a significant amorphous contribution is attested from the almost flat baseline on the corresponding XRD profile.

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**Figure S2.** TEM image of LN nanoplatelets after dilution with ethanol of the precursor solution giving a molar concentration fixed at 0.077 M. Data treatment of the XRD profile (data not shown) results in a mean nanocrystal of  $S_{012}$  = 77 nm and an anisotropic factor f > 8.0.



**Figure S3.** TEM images of LN nanocrystals at different filling fractions of the Teflon-cup. (Left) 2.5 mL of precursor and 1.9 mL of 1,4-Butanediol for a filling fraction at 19% and (Right) 5 mL of precursor and 3.8 mL of 1,4-Butanediol for a filling fraction at 38%. TEM images are very similar with the mean nanocrystal size S<sub>012</sub> and anisotropic factor estimated at 30 nm and 2.5, respectively, in both cases. Effect of the autogenous pressure is negligible.



**Figure S4.** Influence of the ageing time on a precursor kept under ambient conditions for a composition of the reactive medium corresponding to 5 mL of precursor and 3.8 mL of 1,4-Butanediol. TEM images of LiNbO<sub>3</sub> nanocrystals for a synthesis performed with a freshly new precursor (Left) and after a few openings of the same precursor solution kept under ambient conditions for an ageing time of 1 month (Middle) and 3 months (Right). Note how the size and shape polydispersity is strongly affected in terms of facetization with the appearance of flattened cubic-shape nanocrystals when the precursor solution is not handled under an inert atmosphere.



**Figure S5.** (Left) XRD diffraction patterns of LN nanopowders obtained after a thermal treatment at 230°C for 3 days of the commercial precursor with various co-solvents of increasing chain lengths. The molar ratio of glycol to ethanol is 0.5 in each case. (Right) Closer view at 2 ~ 27.5° of the (012) reflection showing a larger FWHM as long as the glycol chain is increased.



**Figure S6.** Comparison of the TEM images for LiNbO<sub>3</sub> nanocrystals produced at a molar ratio of 0.5 when Butanol (Left) and 1,4- Butanediol (Right) is added to 5 mL of the ethanolic precursor solution. Structure of each co-solvent is indicated in the upper panel and the corresponding optical images illustrate the absence of colloidal stability for the LiNbO<sub>3</sub> nanocrystals prepared with Butanol and dispersed at 0.1 mg/mL in ethanol after a period of 5 days.



**Figure S7.** Comparison of FTIR spectra in the 2500-4000 cm<sup>-1</sup> spectral range for LiNbO<sub>3</sub> nanocrystals obtained with and without 1,4-Butanediol. With the glycol, the higher amount of

hydroxyl groups and aliphatic -CH groups is visible from the large band at 3500 cm<sup>-1</sup> and the two peaks below 3000 cm<sup>-1</sup>, respectively.





**Figure S8.** (Left) XRD diffraction pattern of LN nanocrystals obtained after a thermal treatment at 230°C for 3 days of 5mL of lithium niobium methoxide dissolved in methanol after addition of 4.9 mL of 1,4-Butanediol. (Right) Corresponding TEM image showing a nanocrystal morphology very similar to the one observed in Figure S6.



**Figure S9.** Comparison of the FTIR spectra of water and ethanol with the one of the reaction medium at the end of the 3-day solvothermal treatment does not evidence the characteristic absorption band of water at 1660 cm<sup>-1</sup>.



**Figure S10.** (a) Arrangement of the edge-sharing octahedra surrounding the Nb<sup>5+</sup> (in blue) and the Li+ ions (in Yellow) in the (002) crystalline plane. (b) Partial view of the face-sharing octahedra surrounding Nb<sup>5+</sup> and Li+ along the polar direction whereas a isotropic corner-sharing octahedra arrangement is visible if only Li<sup>+</sup> (or Nb<sup>5+</sup>) ions are considered.