Electronic Supplementary Data

Synthesis and structural characterization of bis(μ₂-aqua)tetrakis(aqua)dilithium(I) bis(4-nitrobenzoate)

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Fig. S1 – UV-Visible spectra of [(H₂O)₂Li₂(μ-H₂O)₂](4-nba)₂ (1) and [Na(4-nba)(H₂O)₃]ₙ (2).

Fig. S2 – Fluorescence spectra of 4-nbaH, [(H₂O)₂Li₂(μ-H₂O)₂](4-nba)₂ (1) and [Na(4-nba)(H₂O)₃]ₙ (2).
Fig. S3 - $^1$H NMR ($D_2$O) δ (in ppm) of [(H$_2$O)$_2$Li$_2$($H_2$O)$_2$]$_3$(4-nba)$_2$ (1): 8.05 (d, $J = 8.8$ Hz, Ha), 8.31 (d, $J = 9.2$ Hz, Hb) (top); $^1$H NMR ($D_2$O) δ (in ppm) of [Na(4-nba)(H$_2$O)$_3$]$_n$ (2): 8.03 (d, $J = 8.8$ Hz, H$_a$), 8.29 (d, $J = 8.8$ Hz, H$_b$) (bottom)
Fig. S4 – Infrared spectra of [(H$_2$O)$_4$Li$_2$(µ-H$_2$O)$_2$](4-nba)$_2$ (1) and [Na(4-nba)(H$_2$O)$_3$]$_n$ (2).

Fig. S5 – X-ray powder pattern of [(H$_2$O)$_4$Li$_2$(µ-H$_2$O)$_2$](4-nba)$_2$ (1) and [Na(4-nba)(H$_2$O)$_3$]$_n$ (2).
Fig. S6 – IR spectra of \( [(\text{H}_2\text{O})_2\text{Li}_2(\mu-\text{H}_2\text{O})_2](\text{4-nba})_2 \) (1) and (1) after heating at 130 °C (top); IR spectra of \( [\text{Na}(\text{4-nba})(\text{H}_2\text{O})_3] \) (2) and (2) after heating at 130 °C (bottom).

Fig. S7 – H-bonding situation around the 4-nba anion showing its linking to three symmetry related \( [(\text{H}_2\text{O})_2\text{Li}_2(\mu-\text{H}_2\text{O})_2]^2^+ \) units with the aid of five O-H···O interactions and a 4-nba anion via a C-H···O interaction.

Fig. S8 – H-bonding situation around the dimeric \( [(\text{H}_2\text{O})_2\text{Li}_2(\mu-\text{H}_2\text{O})_2]^2^+ \) dication showing its linking to eight different 4-nba anions and two symmetry related cations.
Fig. S9 – A portion of the supramolecular chain of \([\{\text{H}_2\text{O}\}_4\text{Li}_2(\mu-\text{H}_2\text{O})_2\}]^{2+}\) cations in I extending along \(b\) axis.

Fig. S10 – The crystal structure of \([\text{Na}(4\text{-nba})(\text{H}_2\text{O})_3]_n\) (2) showing the two unique Na(I) cations, two crystallographically independent 4-nba anions and six water molecules.

Fig. S11 – A view of the unique symmetric bridging bidentate ligand, binding the unique Na ions via the nitro oxygen atoms O3 and O4. Note that this bridging leads to isolated dimeric units. For clarity the terminal and bridging water ligands (O21 to O26) and the unique free 4-nba anion (O13, O14) are not shown.