**Electronic Supplementary Information (ESI)**

# Trivalent acid radical-centered $YLi_4^+$ (Y = $PO_4$, $AsO_4$, $VO_4$) cations: new polynuclear species designed to enrich the superalkali family

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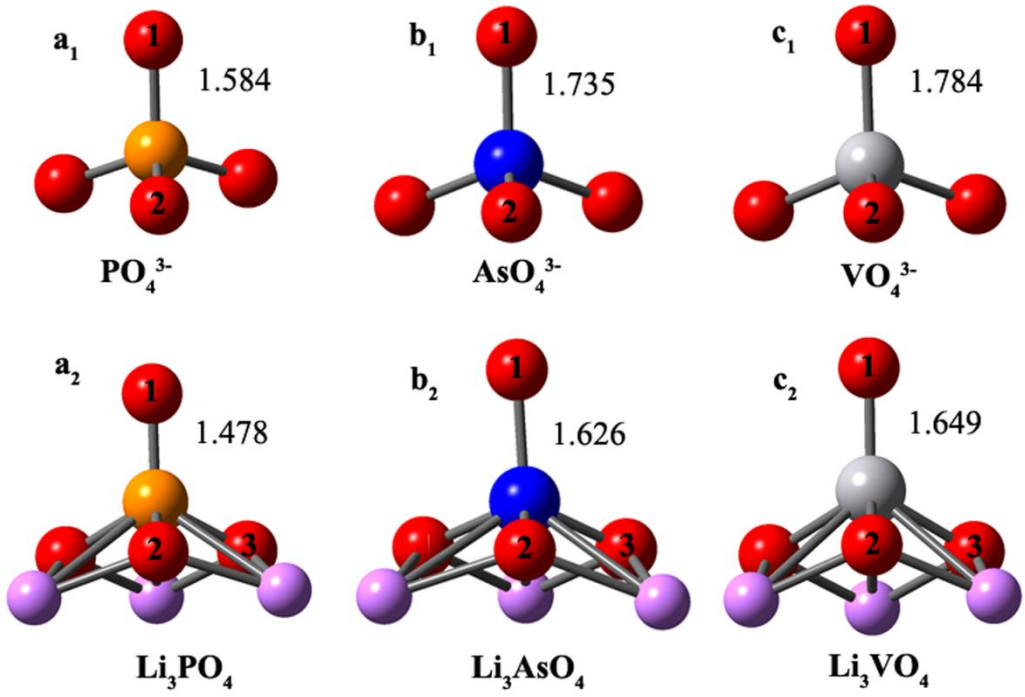


**Figure S1.** Optimized structures of isolated (**a$_1$**) $PO_4^{3-}$ (**b$_1$**) $AsO_4^{3-}$ (**c$_1$**) $VO_4^{3-}$; (**a$_2$**) $Li_3PO_4$ (**b$_2$**) $Li_3AsO_4$ (**c$_2$**) $Li_3VO_4$. Color legend: P, orange-yellow; O, red; Li, purple; As, blue; V, grey.

**Table S1.** The bond length (Å) and the bond angle ( ° ) of (**a**$_1$) $PO_4^{3-}$ (**b**$_1$) $AsO_4^{3-}$ (**c**$_1$) $VO_4^{3-}$; (**a**$_2$) $Li_3PO_4$ (**b**$_2$) $Li_3AsO_4$ (**c**$_2$) $Li_3VO_4$. Nx = P, As, V for **a**, **b** and **c**, respectively.

| structure | Nx-O1 | Nx-O2 | ∠O1NxO2 | ∠O2NxO3 | Nx-Li | O2-Li |
|---|---|---|---|---|---|---|
| **$PO_4^{3-}$** | 1.584 | | 109.5 | | | |
| **$AsO_4^{3-}$** | 1.735 | | 109.5 | | | |
| **$VO_4^{3-}$** | 1.784 | | 109.5 | | | |
| **$Li_3PO_4$** | 1.478 | 1.594 | 115.9 | 102.3 | 2.348 | 1.858 |
| **$Li_3AsO_4$** | 1.626 | 1.749 | 118.9 | 98.6 | 2.447 | 1.884 |
| **$Li_3VO_4$** | 1.649 | 1.788 | 116.9 | 101.1 | 2.403 | 1.885 |

**Table S2.** The NBO charges of the $PO_4Li_4^+$ cations.

| isomer | P | O | | | | Li | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| **P1** | 2.443 | -1.266 | -1.266 | -1.266 | -1.266 | 0.906 | 0.906 | 0.906 | 0.906 |
| **P2** | 2.467 | -1.282 | -1.279 | -1.279 | -1.279 | 0.948 | 0.901 | 0.901 | 0.901 |
| **P3** | 2.417 | -1.179 | -1.269 | -1.269 | -1.331 | 0.907 | 0.906 | 0.912 | 0.906 |
| **P4** | 2.618 | -1.331 | -1.331 | -1.331 | -1.331 | 0.927 | 0.927 | 0.927 | 0.927 |
| **P5** | 2.455 | -1.116 | -1.116 | -1.116 | -1.636 | 0.867 | 0.867 | 0.867 | 0.927 |
| **P6** | 2.495 | -1.214 | -1.073 | -1.073 | -1.661 | 0.966 | 0.831 | 0.831 | 0.899 |
| **P7** | 2.440 | -1.089 | -1.160 | -1.039 | -1.664 | 0.938 | 0.831 | 0.839 | 0.904 |

**Table S3.** The NBO charges of the $AsO_4Li_4^+$ cations.

| isomer | As | O | | | | Li | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| **A1** | 2.476 | -1.279 | -1.279 | -1.279 | -1.279 | 0.909 | 0.909 | 0.909 | 0.909 |
| **A2** | 2.531 | -1.301 | -1.296 | -1.296 | -1.296 | 0.952 | 0.902 | 0.902 | 0.902 |
| **A3** | 2.461 | -1.172 | -1.281 | -1.281 | -1.359 | 0.909 | 0.906 | 0.912 | 0.906 |
| **A4** | 2.487 | -1.205 | -1.205 | -1.365 | -1.375 | 0.903 | 0.903 | 0.958 | 0.898 |
| **A5** | 2.725 | -1.362 | -1.362 | -1.362 | -1.362 | 0.931 | 0.931 | 0.931 | 0.931 |
| **A6** | 1.614 | -1.180 | -1.180 | -0.818 | -0.789 | 0.819 | 0.819 | 0.812 | 0.903 |
| **A7** | 1.625 | -1.306 | -1.301 | -0.725 | -0.789 | 0.858 | 0.839 | 0.883 | 0.916 |
| **A8** | 1.582 | -1.273 | -1.096 | -0.819 | -0.819 | 0.803 | 0.860 | 0.860 | 0.901 |
| **A9** | 1.580 | -1.393 | -1.244 | -0.652 | -0.747 | 0.839 | 0.854 | 0.816 | 0.948 |
| **A10** | 2.514 | -1.239 | -1.069 | -1.069 | -1.660 | 0.965 | 0.838 | 0.838 | 0.899 |
| **A11** | 2.442 | -1.079 | -1.176 | -1.028 | -1.662 | 0.935 | 0.829 | 0.837 | 0.904 |
| **A12** | 1.558 | -1.077 | -1.274 | -0.816 | -0.835 | 0.774 | 0.872 | 0.899 | 0.899 |
| **A13** | 1.560 | -1.087 | -1.274 | -0.810 | -0.806 | 0.904 | 0.809 | 0.809 | 0.894 |

**Table S4.** The NBO charges of the $VO_4Li_4^+$ cations.

| isomer | V | O | | | | Li | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| **V1** | 0.677 | -0.820 | -0.820 | -0.820 | -0.820 | 0.901 | 0.901 | 0.901 | 0.901 |
| **V2** | 0.774 | -0.839 | -0.846 | -0.846 | -0.846 | 0.942 | 0.887 | 0.887 | 0.887 |
| **V3** | 0.678 | -0.552 | -0.840 | -1.036 | -0.840 | 0.902 | 0.901 | 0.893 | 0.893 |
| **V4** | 0.740 | -0.570 | -0.570 | -1.080 | -1.120 | 0.889 | 0.944 | 0.889 | 0.877 |
| **V5** | 0.772 | -0.605 | -1.101 | -0.605 | -1.101 | 0.879 | 0.875 | 0.943 | 0.943 |
| **V6** | 0.810 | -0.651 | -0.651 | -0.651 | -1.393 | 0.869 | 0.869 | 0.869 | 0.929 |
| **V7** | 1.071 | -0.592 | -0.592 | -0.592 | -1.631 | 0.805 | 0.805 | 0.805 | 0.919 |
| **V8** | 1.210 | -0.878 | -0.574 | -0.574 | -1.654 | 0.946 | 0.812 | 0.812 | 0.899 |

**Figure S2.** HOMOs of the $PO_4Li_4^+$ cations.