Supporting Information



Figure S1. View of a stacking of fundamental building blocks. Dashed lines (*a-a'*, *b-b'*) display conventional direction of this fragment to derive intersections of the secondary building.



Figure S2a. Cyclic window-like intersection of fundamental building blocks in a frame *b-a*'.



Figure S2b. Cyclic window-like intersection of fundamental building blocks in a frame a'-b'.



Figure S2c. Cyclic window-like intersection of fundamental building blocks in a frame b'-a.



Figure S3. Measured UV-Vis diffuse electron spectra for K5Ta8BP4O34 with the onset of absorption edges labelled



Figure S4. FTIR spectrum of K₅Ta₈BP₄O₃₄



Figure S5. Thermogravimetric analysis of K5Ta8BP4O34



Figure S6. Le Bail profile matching of residual phases after thermogravimetric analysis (Y_{obs} is a blue crosses, Y_{calc} is a red line, Y_{obs} - Y_{calc} is black line, Bragg positions are marked with dark blue vertical ticks).



Figure S7. Rietveld refinement plot of as-synthesized $K_5Ta_8BP_4O_{34}$ (Y_{obs} is a blue crosses, Y_{calc} is a red line, Y_{obs} - Y_{calc} is black line, Bragg positions are marked with dark blue vertical ticks).