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Supporting Information

Tetrabutylphosphonium Ions as a New Swelling/Delamination Agent for Layered Compounds

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Figure S1. (a) Optical microscope image and (b) powder XRD pattern of $H_{0.8}[Ti_{1.2}Fe_{0.8}]O_4 \cdot H_2O$ crystals. The crystals after proton exchange maintain the rectangular plate-like shape, and show good transparency under microscope, confirming the high crystallinity. All the reflections in the corresponding XRD pattern can be readily indexed on the basis of the documented body-centered orthorhombic structure with two-layer repetition along the *b*-axis. The cell parameters were refined to be a = 0.37291(7), b = 1.80250(1), c = 0.30017(8) nm, in general agreement with literature values. The lattice dimensions in the *ac* plane are similar to those of parent $K_{0.8}[Ti_{1.2}Fe_{0.8}]O_4$ crystals, a = 0.37783(3), c = 0.29600(3) nm, although the interlayer spacing has increased from 0.78 nm to 0.90 nm on protonation, corresponding to the replacement of K^+ by hydrated H^+.

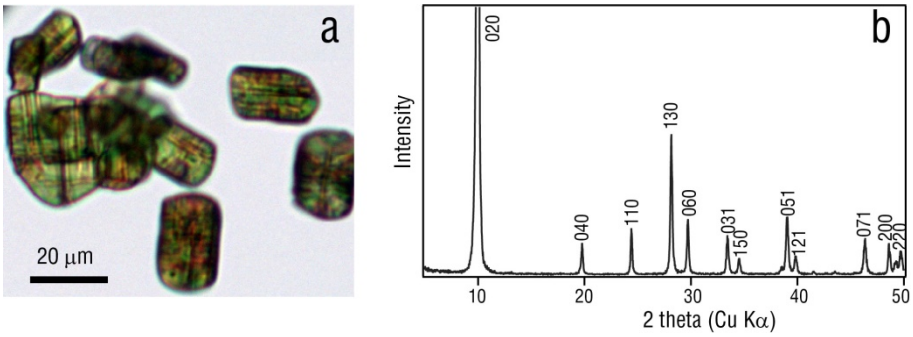

Figure S2. Optical microscope images for the whole series of swollen samples. In the solution at very low concentration, TBPOH/H^+=0.1, the swelling was incomplete with the occasional observation of unswollen crystals. The swollen crystals at the maximum swelling, TBPOH/H^+=0.1, seems fragile, containing fragmented pieces. In concentrated solutions, the swollen crystals exhibit well-difined edges, and the swelling degree or swollen length decreases with increasing concentrations.

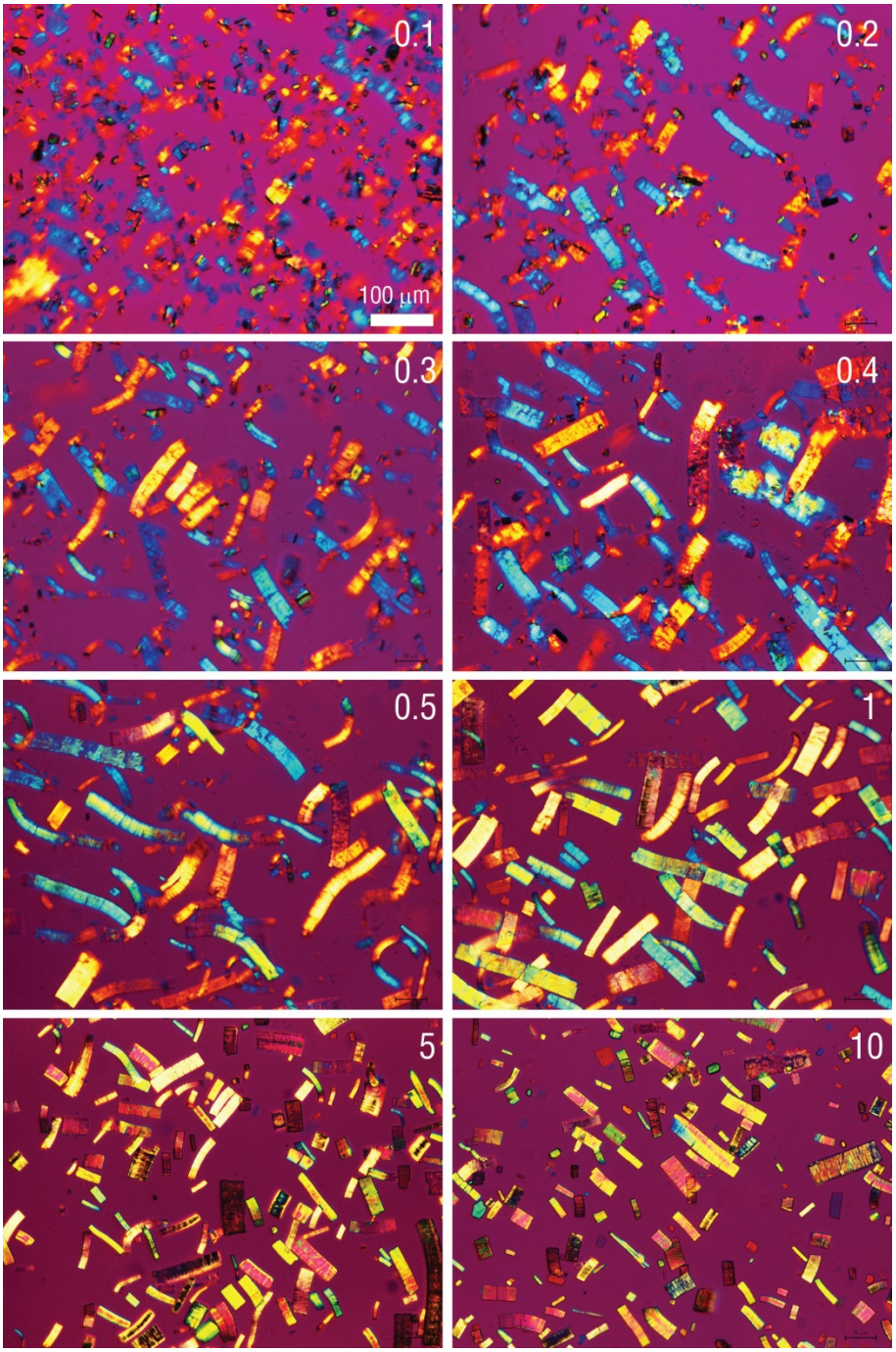

Figure S3. SAXS profiles for TBA-swollen samples. Only a broad, weak 2nd reflection was detected at a concentration of TBAOH/H^+=0.3 because the 1st refection was beyond the measurement range. This 2nd reflection signal was located at 43 nm; therefore, the expanded spacing was roughly determined to be ~86 nm. Upon increasing the concentration, the reflections become sharper and stronger and the 3rd order reflection was detected, which suggests an increased stacking regularity. The reported expanded spacings were 98, 68, and 55 nm for the TBAOH/H^+ = 0.3, 0.5, and 0.7 samples, respectively (*J. Am. Chem. Soc.* DOI: 10.1021/ja501587y), based on the synchrotron SAXS measurements (λ = 0.155 nm). Notably, the swollen spacings from the different sample batches and different measurement techniques deviated slightly with decreasing deviation with increasing concentration, which may reflect an improved stacking regularity or narrowed distribution of expanded spacings in the concentrated solutions. For the TBAOH/H^+ = 0.3 sample, the difference was approximately ten nanometers, 98 nm from the synchrotron measurement and 86 nm from the lab-SAXS measurement. In addition to the intrinsic nature of wide spacing ranges at this concentration, as detailed above, the spacing was deduced from a broad, weak 2nd reflection, which may also account for the differing values.

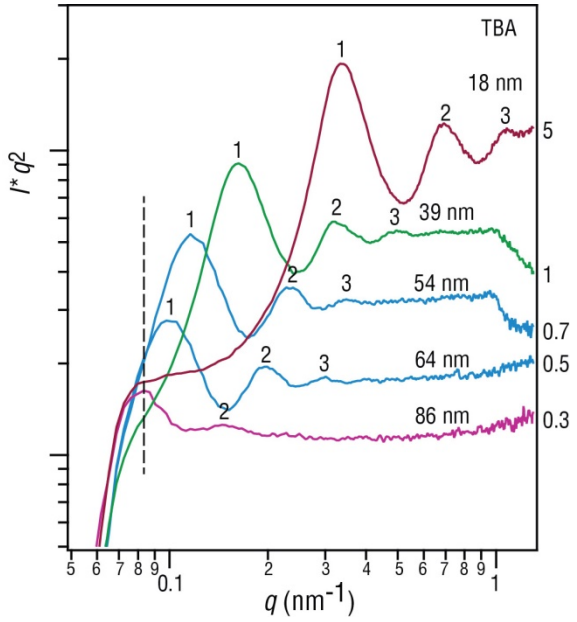
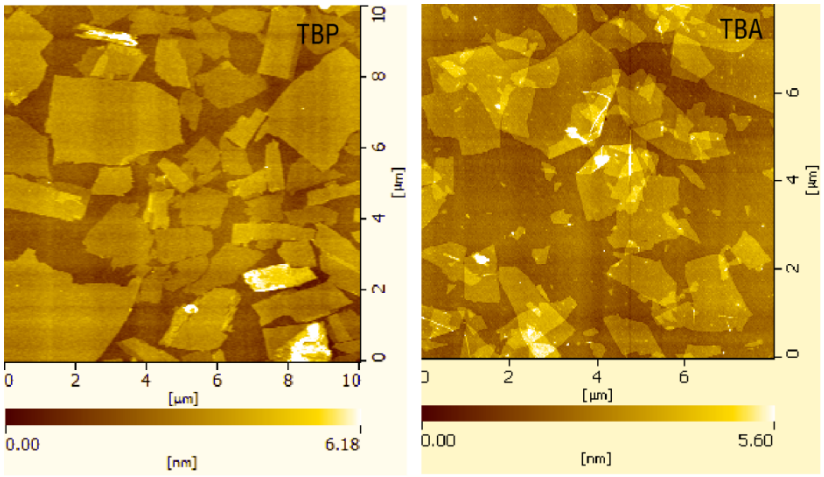
Figure S4. Total delamination can both be achieved employing aqueous solutions of TBPOH and TBAOH. However, the required shaking period is typically shorter for TBPOH, in 1-2 hours compared with several hours for TBAOH. Meantime, the delaminated nanosheets in TBPOH solutions are slightly smaller. Combining the observation of natural fragmentation for TBPOH-swollen crystals, it can be considered that the crystals swollen by TBPOH have more tendency to be fragmented and exfoliated into single-layer nanosheets. The easy exfoliation can be attributed to the ball-like conformation, bulky sizes of TBPOH, and correspondingly relatively weak associations with surrounding H_2O.