Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information

Cadmium benzylphosphonates – the close relationship between structure and properties

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Structure solution from PXRD

For the structure solution, high-resolution powder patterns were collected. The powder patterns were indexed and the space group was determined using the LSI algorithm based on iterative use of least squares implemented in TOPAS.[1] A Pawley refinement was carried out inclusive of the background, zero-point error, the unit cell parameters and peak-width parameters. The cell volumes are consistent with the volume of one Cd atom, one phosphonate ligand and one water molecule in the asymmetric unit. The structures were solved by simulated annealing routine in the DASH program. For each structure solution, 25 runs a $1x10^9$ moves were calculated. As the starting conformation, the values of the Cambridge Structural Database (CSD)[2] entries TOLWOH, REZZEB, and REZZUR were used for the benzylphosphonate, 3-fluorobenzylphosphonate acid, and 4-fluorobenzylphosphonate, respectively. The starting conformation for 2,3,4,5,6-pentafluorobenzylphosphonate was derived from the conformation of benzylphosphonate by replacing the H-atoms with F-atoms and defining appropriate bond lengths. During simulated annealing, no torsion angles were fixed. The Rietveld refinement was carried out in TOPAS. The background was described by the Chebychev function with 20 parameters. For the Rietveld refinements, restraints have been applied to all bond length and bond angles according to the Mogul statistics. Planar groups were flattened. The Rietveld refinement included unit-cell parameters, background, scale, profile parameters, atomic coordinates and one isotropic displacement parameter for the C, F, O, P and Cd atoms of each molecule. H atoms were included with $B_{iso}(H)=1.2B_{iso}$. For the additional peak shape fitting, peak shape functions PVII and SPVII were used.

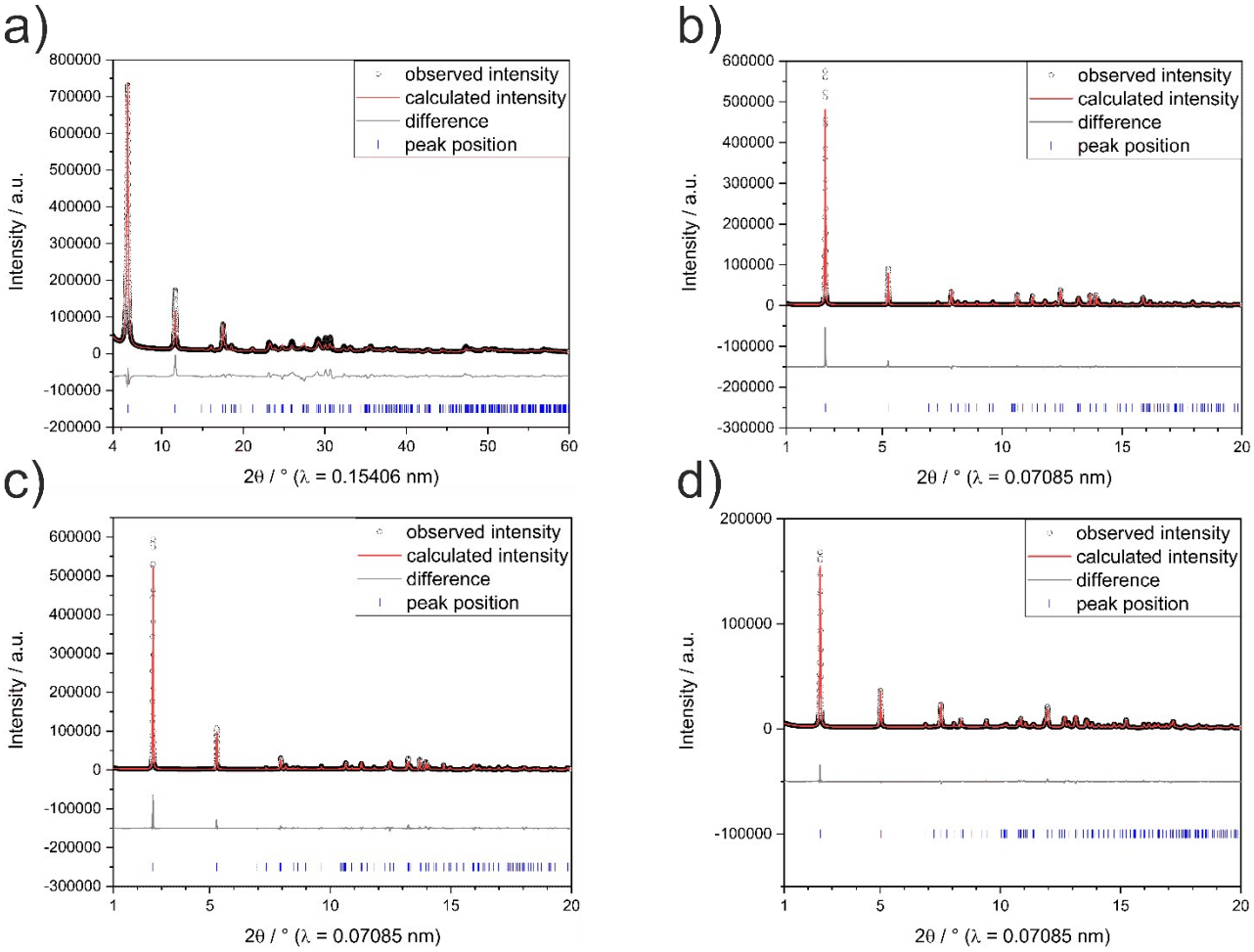


Fig. S1: Rietveld refinement plot for a) cadmiumbenzylphosphonate (1), b) cadmium-3-fluorobenzylphosphonate (2), c) cadmium-4-fluorobenzylphosphonate (3), d) cadmium-2,3,4,5,6-pentafluorobenzylphosphonate (4).

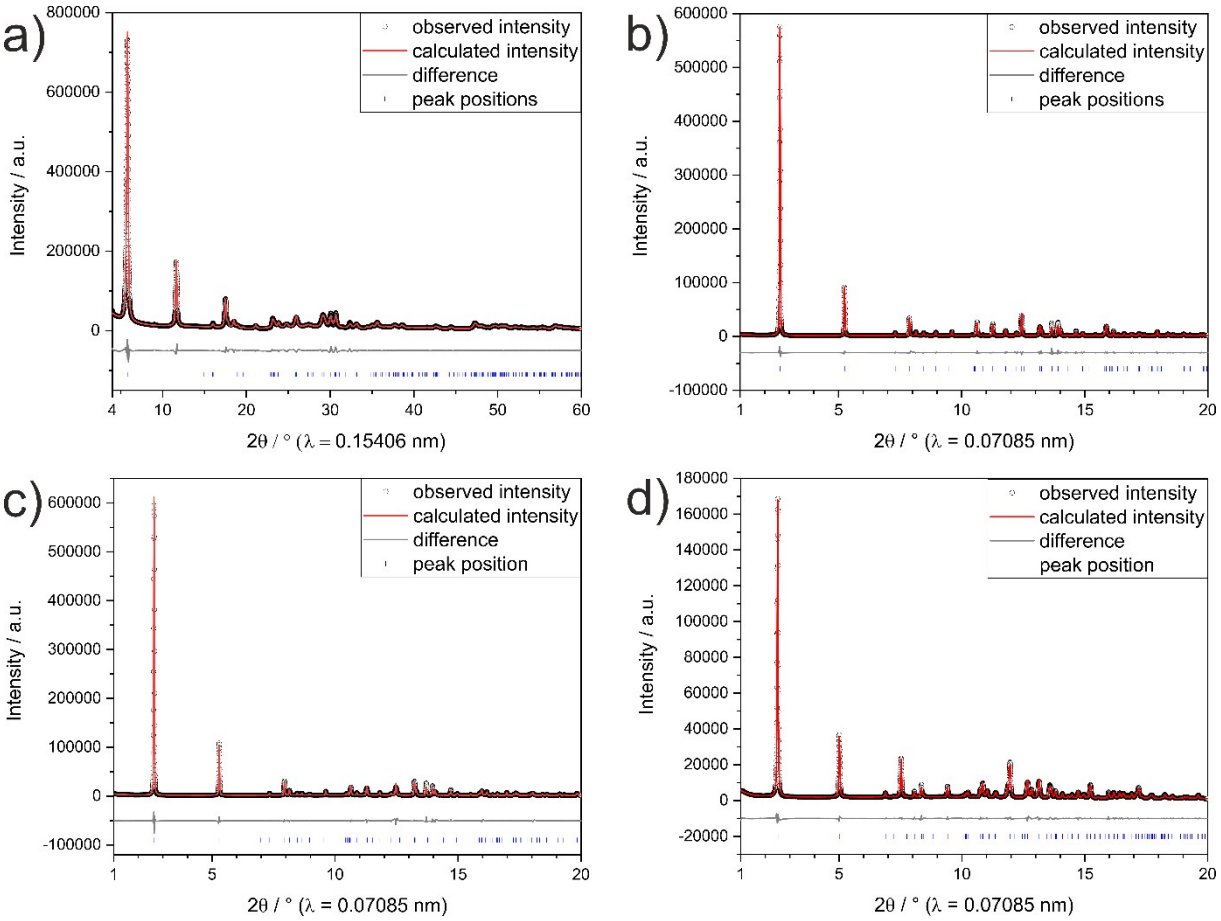


Fig. S2: LeBail fits for a) cadmiumbenzylphosphonate (**1**), b) cadmium-3-fluorobenzylphosphonate (**2**), c) cadmium-4-fluorobenzylphosphonate (**3**), d) cadmium-2,3,4,5,6-pentafluorobenzylphosphonate (**4**).

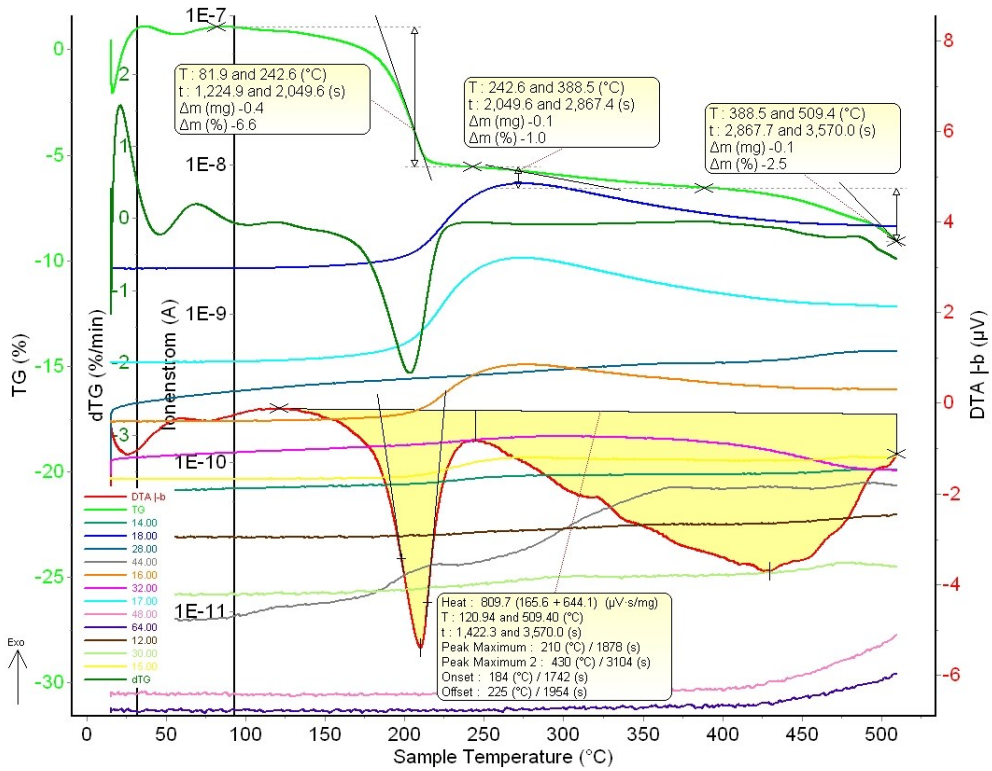


Fig. S3:S DTA/TG measurements for Cd-benzylphosphonate.

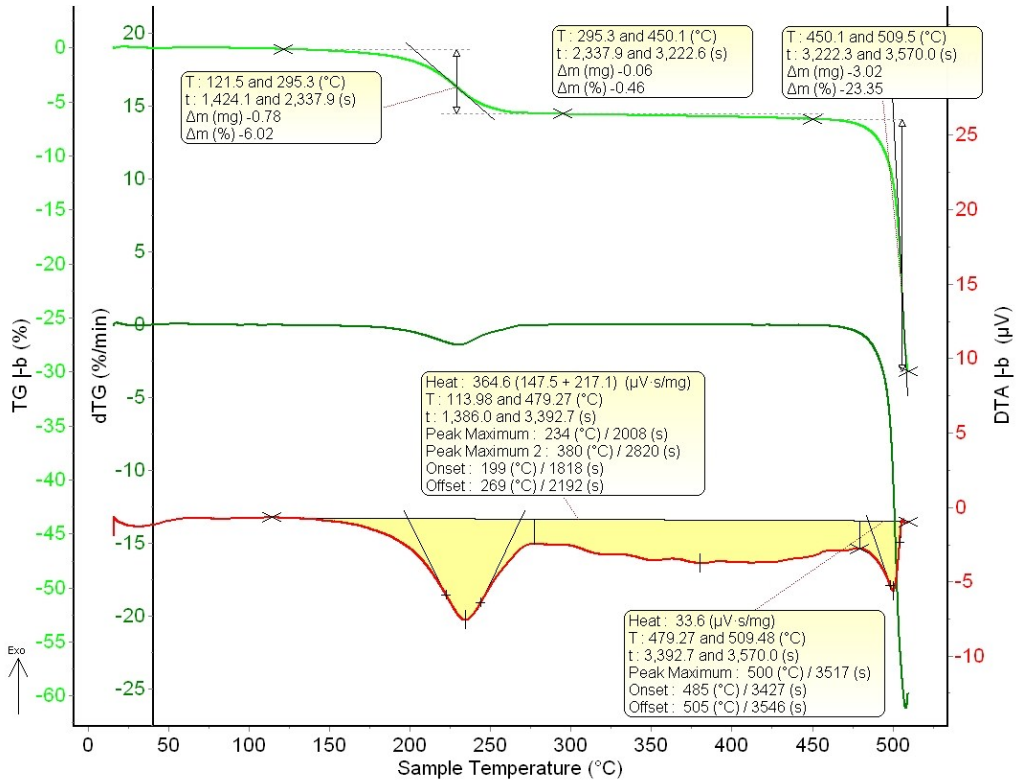


Fig. S4: DTA/TG measurements for Cd-3-fluorobenzylphosphonate.

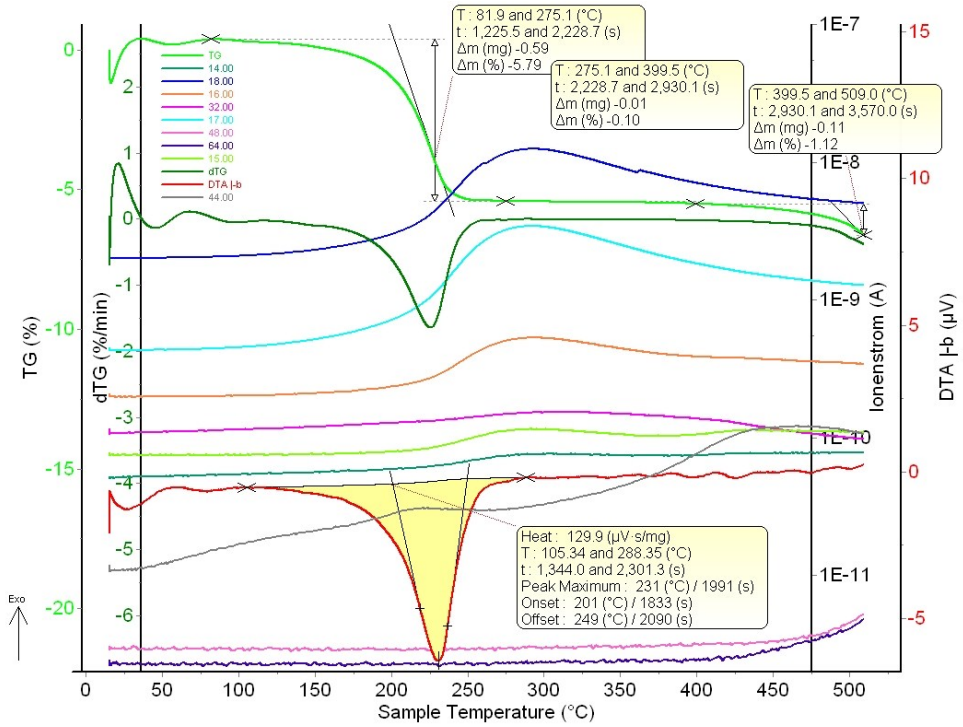


Fig. S5: DTA/TG measurements for Cd-4-fluorobenzylphosphonate.

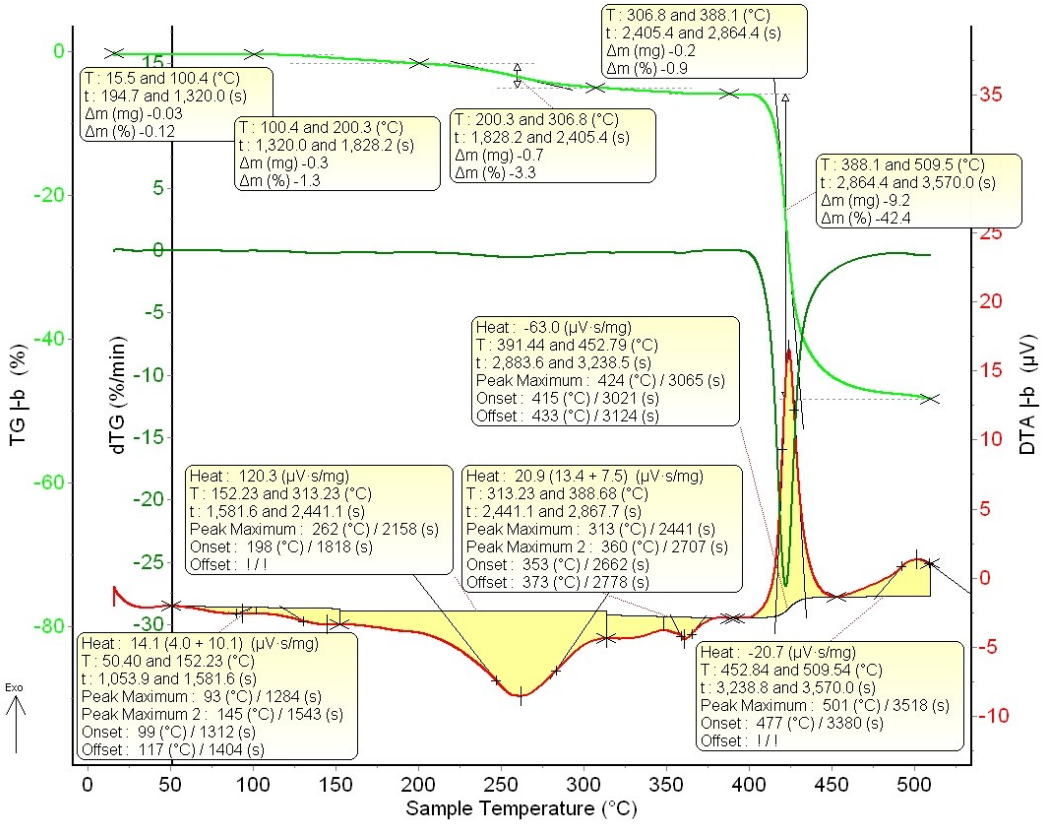
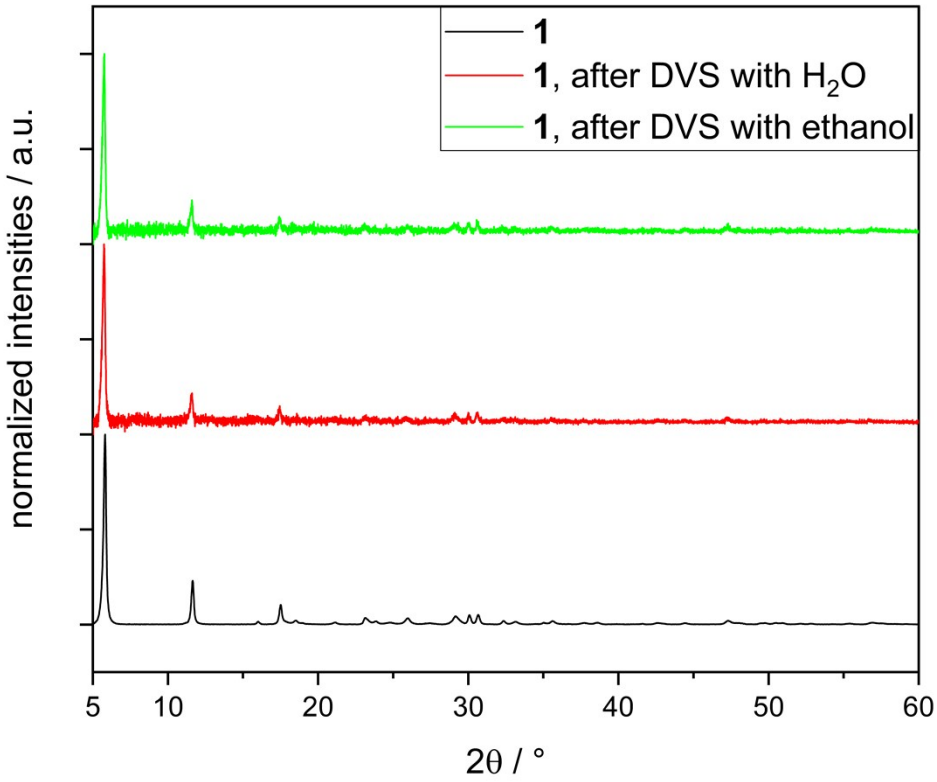


Fig. S6: DTA/TG measurements for Cd-2,3,4,5,6-pentafluorobenzylphosphonate.



1 before DVS measurements (black) and after the DVS measurements with water (red) and ethanol (green).

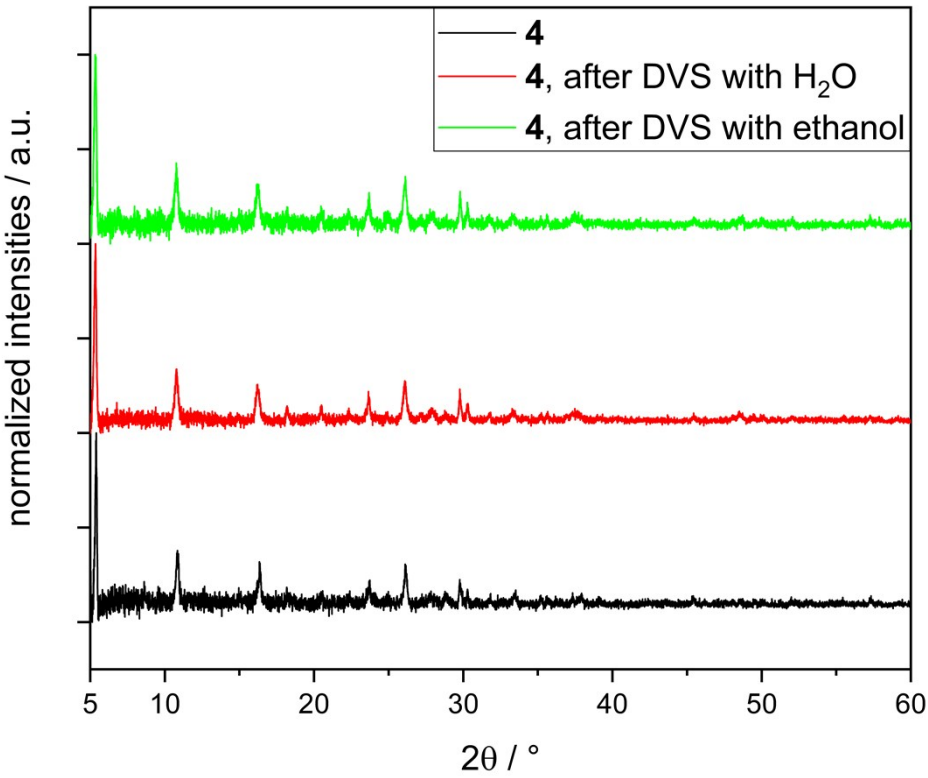


Fig. S8: PXRD patterns for Cd-2,3,4,5,6-pentafluorobenzylphosphonate 4 before DVS measurements (black) and after the DVS measurements with water (red) and ethanol (green).

1. A. Coelho, *J. Appl. Crystallogr.*, 2003, **36**, 86-95.
2. C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallographica Section B*, 2016, **72**, 171-179.