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Polyhalides as scaffolds for supramolecular, ion-conducting crown ether stacks

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Crown ethers, such as dibenzo-18-crown-6 (DB18C6) are in principle perfect building blocks to be stacked on top of each other for one-dimensional (1D) channel formation. However, in the more than 1000 publications on crown ethers in the solid state, only one case was of channel formation described, but not as main focus of research.[1] We now present a way to systematically induce the stacking of DB18C6 with the help of polyhalides, which play the roles of scaffolds via halogen bonding.[2] These compounds can be considered as "supramolecular straws". Using for example potassium as couter ion for triiodide for example, we obtained a solid which contains three differently filled, parallel channels in the solid state, which are arranged between the polyhalide anions. Exchanging potassium with sodium by immersion of a single crystal into NaOH solution leads to a single-crystal-to-single-crystal transformation into a compound with two channel types. This transition from a system crystallizing initially in the P2-space group to yield a compound in Pccn is only possible under these very special conditions. We will further present how the ion transport through these channels can be quantified and which process is involved in ion exchange. The role of the polyhalide anions, which cannot be replaced by other linear anions, will be emphasized as well.

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