2D Framework Materials for Energy Applications and Molecular Separations

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Abstract

Framework materials like metal-organic frameworks or covalent organic frameworks (COFs) are porous, crystalline materials constructed from molecular building blocks. In COFs, the building blocks are connected via covalent bonds, forming robust networks. If they are flat, highly symmetric molecules, two dimensional frameworks can be constructed, which are stacked in the third dimension by weak interactions for instance hydrogen bonds or π-π interactions.[1] By functionalization of the framework backbone with aliphatic side chains the stacking is weakened and their surface properties drastically change, making them hydrophobic. This can be leveraged for instance in pyrene-based COFs, which can be exfoliated from organic solvents into nanosheets with average thicknesses below 1.5 nm, which were integrated into separator membranes for lithium-ion batteries.[2] This concept was transferred to electrocatalytically active metalloporphyrin COFs and the inclusion of side chains improved their stability in alkaline media, increasing their robustness during the oxygen evolution reaction and lowering the overpotential compared to non-functionalized analogues.[3] Furthermore, the stacking-offset between adjacent layers in metalloporphyrin COFs can be adjusted by the type of attached side chain, as well as the degree of metalation. Stacking-offsets can also be leveraged for molecular separations. Introduction of alkyne bridges into a pyrene-based 2D COF induced a shift between neighbouring layers, which created electron-rich pockets. These pockets are used for static bromine adsorption from the gas phase, as well as for the selective uptake of Br_2 from mixed Br_2/I_2 solutions.[4] Hydrophobization of the framework backbone can not only be achieved by installation of aliphatic side chains, but also by substituting aromatic linkers with saturated molecules. With this strategy, a cyclohexane-bridged COF was prepared, which has an increased affinity towards the adsorption of saturated hydrocarbons, showing high adsorption selectivity towards ethane over ethylene.[5]

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