Post-synthetic modifications of iron formate frameworks

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Post-synthetic modifications (PSMs) offers expansive scope for a targeted approach to in-situ tailoring the properties of MOFs. Numerous methods for carrying-out PSMs chemistry have been reported, however the most interesting ones are the ones induced by physical stimuli. Among the most commonly used stimuli are light, temperature and pressure. Owing to the self-contained reaction space, requiring no additional substrates, physically induced PSM can be invaluable for green technologies and for obtaining sophisticated advanced materials on requested sites.[1,2]

To modify the hybrid iron-formate perovskite we have use the hydrostatic pressure generated in diamond anvil cell. Formate α-$DmaFe^{2+}Fe^{3+}For_6$ (Dma = $(CH_3)_2NH_2^+$, For = $HCOO^-$) have been compressed in several pressure transmitting media showing that apart from the pressure range, also the liquid environment of the sample regulates the course of transformations. Three different types of transformations have been observed: classical order-disorder and displacive reversible thermodynamic transitions; reversible chemical reaction; as well as irreversible reaction leading to new mixed valence iron formate. When α-$DmaFe^{2+}Fe^{3+}For_6$ is compressed in Daphne oil or in isopropanol at 1.40 GPa, transforms to a phase γ (of space group $P2_1/n$), different than that obtained at low-temperature (phase β, space group R-3c).[3,4] In glycerol phase α can be compressed to 1.40 GPa, but then reacts to $DmaFe^{2+}For_3$, with all Fe(III) cations reduced. The incubation of phase α in methanol and ethanol at 1.15 GPa yields in mixed-valence framework $Dma_3[Fe^{2+}{}_3Fe^{3+}For_6]_2{\cdot}CO_2$ stable at ambient conditions.

These pressure-induced environment-sensitive modifications have been rationalised by the volume effects in transforming structures, their different chemical composition, voids, ligands and cation oxidation states switching between Fe(II), Fe(III), their high- and low-spin states as well as solubility, molecular size as well as the chemical and physical properties of the pressure transmitting media. This variety of transformations controlled by pressure and the liquid environment broaden the general understanding about the chemistry in extreme conditions, and offer new highly efficient, safe and environment-friendly method for obtaining new materials.

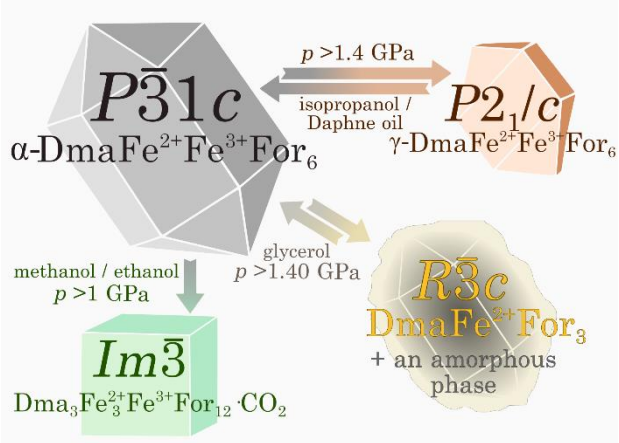

Figure 1. Schematic diagram of phase transformations and reactions of iron formates at various conditions.

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