MS32 Advanced techniques to disclose Structure-Property Relationships

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Understanding photoswitchable ferroelectrics by combined in situ XRD with light and electric field

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Abstract

Ferroelectric switches are of great and continuing interest for a wide range of applications including ultrafast electronics (e.g. ferroelectric capacitors, RAM etc.), solid-state cooling, energy harvesting and solar energy solutions.[1, 2] These materials display spontaneous electrical polarisation that can be reversed by the application of an external stimulus, e.g. electric field.[3] Where the direction of polarisation can be controlled by photoactivation, these materials become desirable for photovoltaic applications. Hybrid pervoskites, e.g. methyl ammonium lead iodide, are a class of photoactive ferroelectric materials that have received particular attention in recent years, and have been successfully applied in new generation solar cell technologies.[4] Despite this, understanding of the key structure-property relationships in these, and related, perovskite-like ferroelectrics remains limited[4] and would benefit significantly from in situ studies with advanced diffraction techniques.

We present the synthesis, crystallisation, dielectric characterisation and in situ crystallographic investigation of the photoactive ferroelectric $(CH_5N_2)[NaFe(CN)_5(NO)].H_2O$ (1), which is designed in analogy with hybrid perovskites. By incorporating the known linkage isomer photoswitch $[Fe(CN)_5(NO)]^{2-}$ into the hybrid material, predicable photoactive behaviour is introduced that could be used to control the electric properties of the system with light. Using an in situ electric field cell[5] at the Small Molecule Single Crystal Diffraction Beamline I19 at Diamond Light Source, UK, we identify a new low-temperature phase on cooling a single crystal of 1 in the presence of a +40 kV cm^{-1} applied field, with associated framework distortions and the $CH_5N_2^+$ cations shifting significantly to align with the field. This result provides unique insight into the structure-property relationships responsible for switching in hybrid organic-inorganic materials. Photoswitching in 1 is also confirmed by photocrystallographic studies, with the crystal illuminated in situ on the diffractometer using 500 nm and 950 nm LED light.

References

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