Electronic Supplementary Information (ESI) for:

Customizing $H_3Sb_3P_2O_{14}$ nanosheet sensors by reversible vapor-phase amine intercalation

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Experimental Section

Nanosheet Synthesis and Spin-coating

$K_3Sb_3P_2O_{14}$ was synthesized from KNO_3 (Merck, for analysis), $NH_4H_2PO_4$ (Acros Organics, >98%) and Sb_2O_3 (Alfa Aesar, 99.6%) as described elsewhere.[1-3]

As reported previously, $K_3Sb_3P_2O_{14}$ was protonated, exfoliated and dried.[1-3] Subsequently, the powder was dissolved in a water-ethanol mixture, ultrasonicated and spin-coated (WS-650MZ-23NPP, Laurell Technology Corporation) as thin films on Si-wafers (1.5 x 1.5 cm, 110 orientation).[1-3] Each wafer was spin-coated twice with 200 µL of the colloidal suspension for 1.5 min (Speed: of 2000 rpm, acceleration: 10000 rpm). Prior to thin film deposition the Si-wafers were cleaned with oxygen plasma for 10 min.

Amine Intercalation

The $H_3Sb_3P_2O_{14}$ nanosheet-based thin films with a thickness of about 160 nm were intercalated with primary amines with an even number of C-atoms ($2 \leq n \leq 12$), over the vapor phase as reported elsewhere.[3] All amines were used as purchased without further dilution or as 3M dilutions in ethanol (ethylamine, Acros Organics, 70% in water; 1-butylamine, Alfa Aesar, 99%; hexylamine, Acros Organics, 99%; *n*-octylamine, Acros Organics, >99%; *n*-decylamine, Acros Organics, 99%, nitrogen flushed; dodecylamine, Aldrich, 98%). All experiments with $n \leq 8$ were performed at room temperature, whereas experiments with $n \geq 10$ were conducted at 80 °C, to evaporate the amine and enhance the intercalation speed. The intercalation process was considered as complete once the films showed a non-changing and uniform color. Subsequently the single step (step one) amine intercalated samples were exposed to a second, different amine (step two). For the gradual fine-tuning of the nanosheets using the two-step intercalation strategy, the samples were taken out of the intercalation chamber after a certain duration (between 1 and 25 min) and left to equilibrate under ambient conditions. After the equilibration step of the co-intercalated samples, they are stable over several months, as verified by out-of-plane X-ray powder diffraction (XRPD) measurements.

For the amine replacement, experiments the samples were kept in the intercalation chamber until a non-changing, uniform color was observed. This indicated that the replacement of the first intercalated amine was completed. All conducted two-step amine exchange experiments are given in Tab. S1.

Tab. S1 Conducted amine intercalation experiments. Intercalation step one is shown vertically while intercalation step two is shown horizontally. A blue X marks the intercalation of a longer amine in the second intercalation step (“upward intercalation”), whereas a green X marks the intercalation of a shorter amine in the second intercalation step (“downward intercalation”).

↑ **First Intercalation Step**

C12			X	X	X	
C10		X	X	X		
C8	X	X	X		X	X
C6	X	X		X	X	X
C4			X	X	X	
C2		X	X	X		
	C2	C4	C6	C8	C10	C12

→ **Second Intercalation Step**

Characterization

Out-of-plane XRPD patterns of all thin films were recorded at room temperature on a D8-Advance (Bruker) diffractometer working in Bragg-Brentano geometry with Ge(111) monochromated Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å). The samples were rotated during the measurement and the scan range was 2 – 80° 2θ (step size: 0.01, time: 2.8 s).

The sample thicknesses and refractive indices (RI) of one- and two-step intercalated thin films were determined with an ellipsometer under ambient conditions (Sopra). Measurements were conducted at three different spots for each sample and the obtained data was fitted using the Cauchy and Lorentz model.

Reflectance measurements were acquired for amine replacement experiments after each intercalation step at two or more spots on two thin films each. After the second intercalation step, the samples were measured at the same spots as after the first step. All measurements were performed at room temperature with a fiber optic spectrometer (Ocean Optics Germany), which was attached to a microscope (Olympus).

The C-H vibrations of the alkylamines intercalated in the thin films were analyzed with a LabRAM single grating spectrometer (HORIBA JobinYvon GmbH) for some of the one- and two-step intercalated samples. The measurements were conducted in quasi-backscattering geometry, using the linearly polarized 632.8 nm (red) line of a He/Ne gas laser.

For the co-intercalated samples containing butylamine and hexylamine contact angle measurements were performed to track the change in polarity.

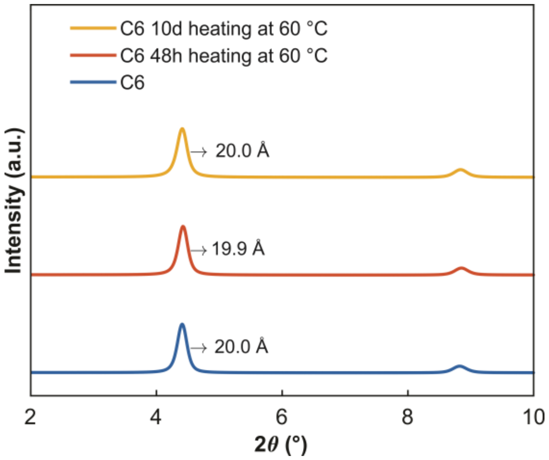

Fig. S1 Comparison of a C6 intercalated sample before heating, after heating for 48 h, and after heating for 10 days at 60 °C.

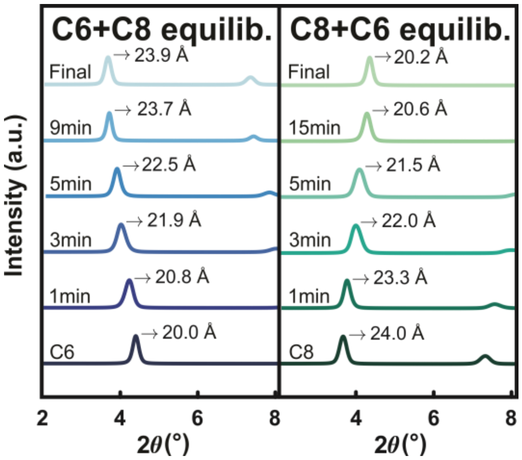

Fig. S2 Modification of primary alkylamine intercalated thin films with other primary alkylamines in a second intercalation step. Out-of-plane XRPD patterns (Cu-$K_{\alpha1}$) at different intercalation times for upward and downward intercalation. Measurements were performed after equilibration under ambient conditions for two weeks. CX+CY corresponds to the amines used during the intercalation process (X = first step, Y = second step).

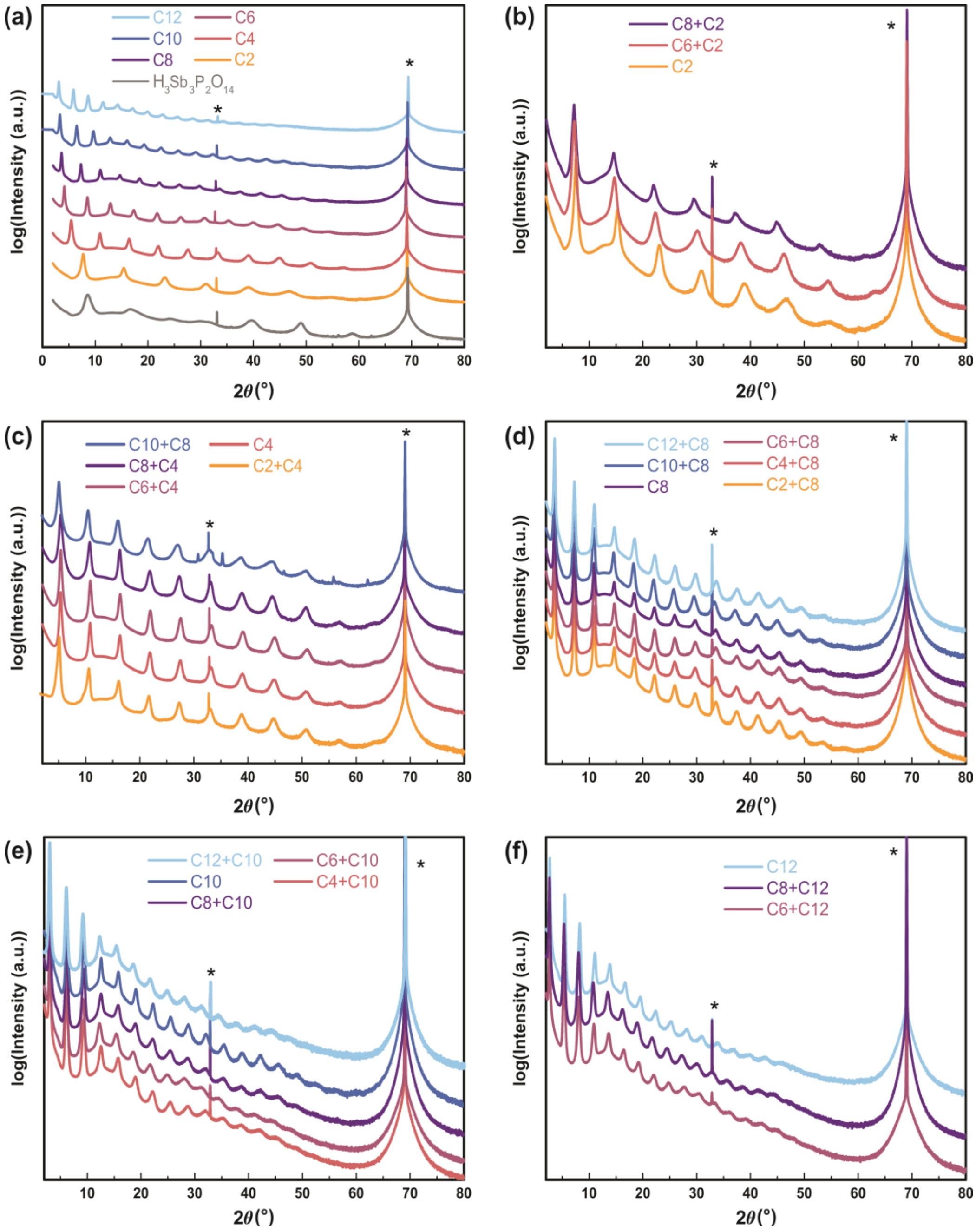

Fig. S3 (a) Out-of-plane XRPD patterns (Cu-$K_{\alpha 1}$) of singly intercalated samples plotted with a logarithmic y-axis for better visibility of the reflections. (b) – (f) Comparison of out-of-plane XRPD patterns of samples after first and second intercalation. CX+CY corresponds to the amines used during the intercalation process (X = first step, Y = second step). The reflections at 32.8 and 69.1° 2θ marked with the asterisks can be assigned to the Si-wafer and were utilized for pattern alignment.

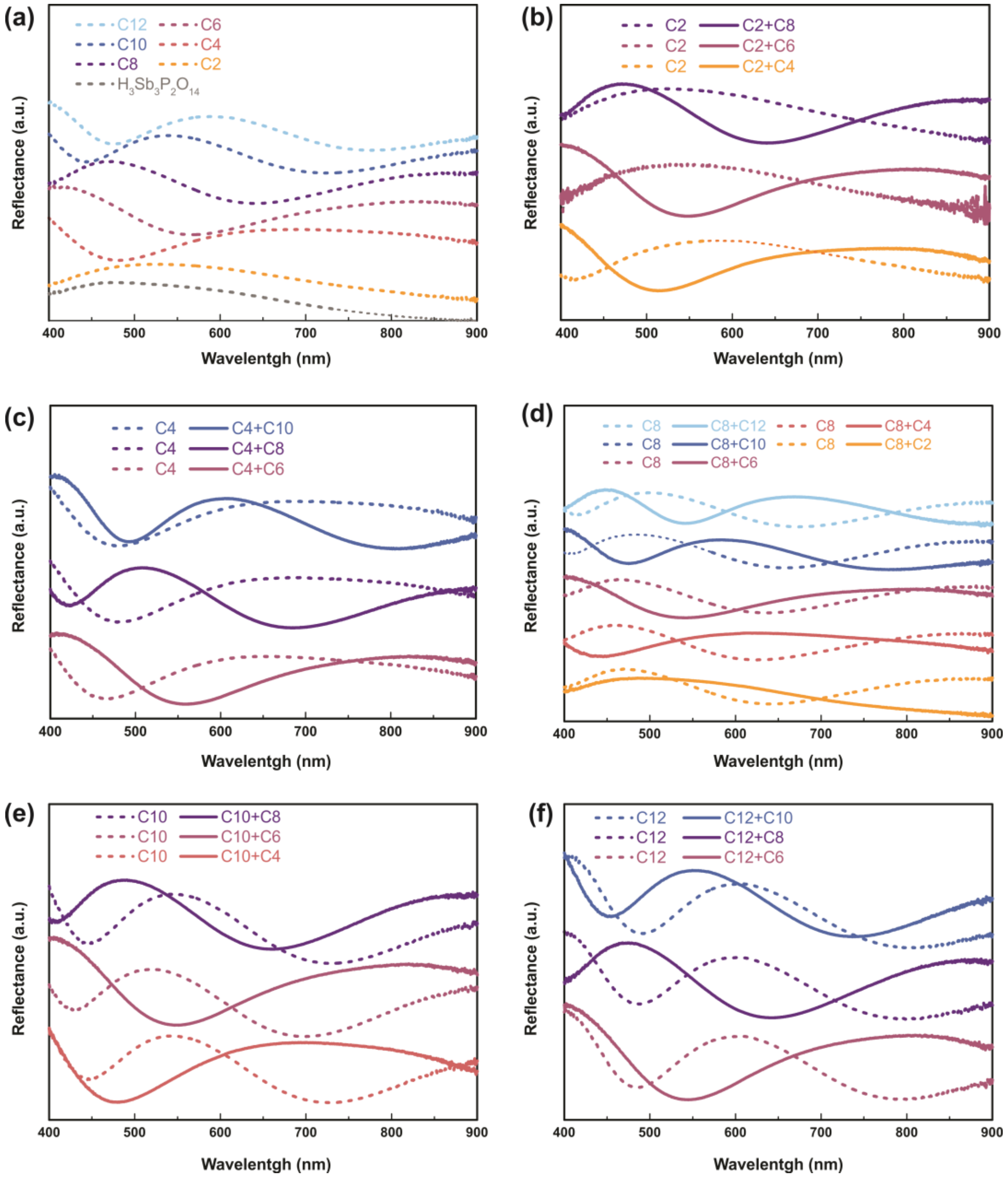

Fig. S4 (a) Reflectance spectra of singly intercalated samples. (b) – (f) Reflectance spectra of samples after the first and second intercalation step (dashed and solid graphs respectively) for all conducted series of experiments.

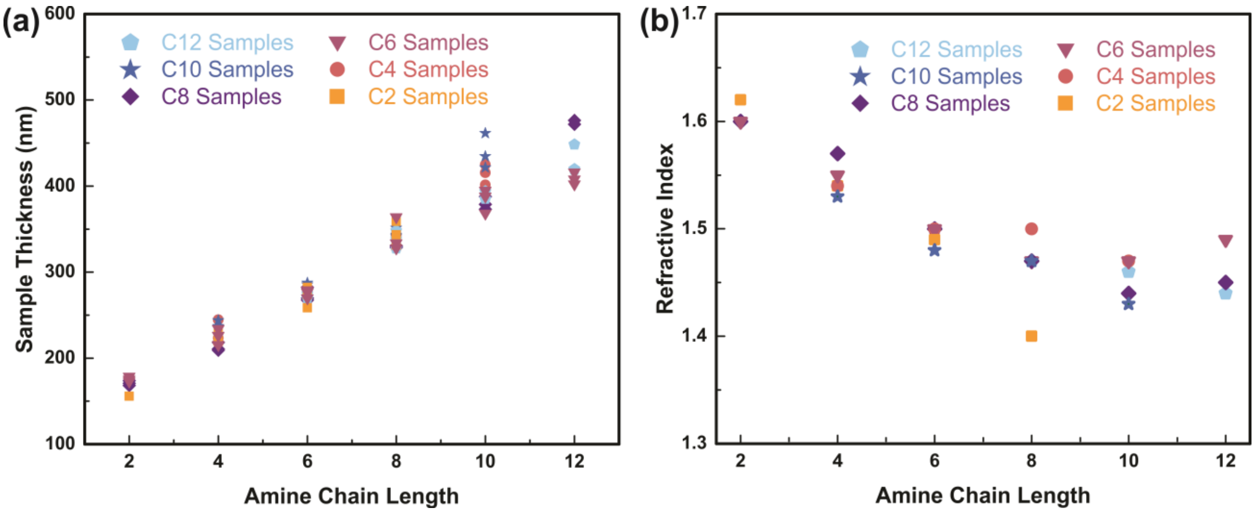

Fig. S5 (a) Sample thickness and (b) refractive indices of all prepared amine replacement samples determined with ellipsometry measurements at ambient conditions.

The C2 intercalated samples show a slightly higher RI than the pristine $H_3Sb_3P_2O_{14}$ thin films (1.61 and 1.59 respectively), which could be assigned to the replacement of the water in between the layers. With increased amine chain length a decrease in the effective RI can be observed, which is due to the fact that the amines have a lower RI than the antimony phosphate nanosheets, and with increasing alkyl chain length the amines' contribution to the effective RI grows. However, the RI of the pure amines increases with increased alkyl chain length. Therefore, the decrease of the RI of the amine intercalated samples is not linear.

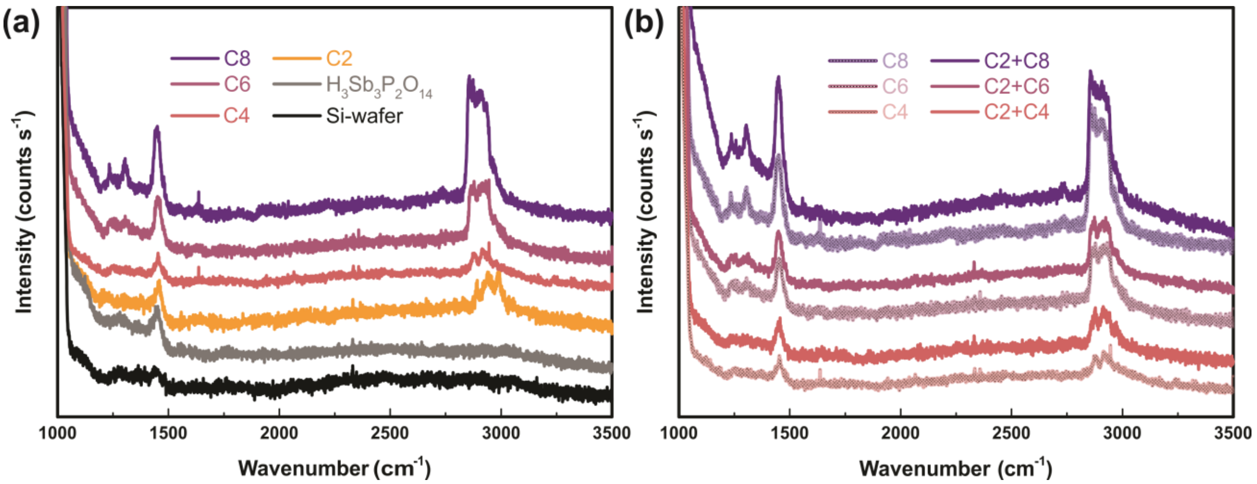

Fig. S6 (a) Raman spectra of singly intercalated samples. (b) Comparison of the Raman spectra of singly and doubly amine intercalated samples for replacement experiments.

The results of the singly intercalated samples are given in Fig. S5a along with the ones of the pristine Si-wafer and an $H_3Sb_3P_2O_{14}$ thin film as references. Comparing the amine containing samples with the reference, it can be observed that all measurements show a pronounced peak at about 1400 cm^{-1}. Furthermore, the amine intercalated samples exhibit peaks at about 1200, 1300 (both νC-C or δC-H), 2900 and 3000 cm^{-1} (νCH_2 and νCH_3), which are not present in the reference. It can be stated that the peak positions at around 2900 cm^{-1} are shifted to slightly smaller wavenumbers with increasing chain length. This might be due to the fact that the CH_3 stretching vibration appears at higher wavenumbers then the CH_2 stretching vibration and the longer the amine gets the smaller the impact of the CH_3 vibration is. Apart from that, the intensity of these peaks increases for longer amines. Regarding the peaks at around 1200 cm^{-1} it can be observed that they increase with the chain length. A comparison of the Raman spectra of singly (light graphs) and the corresponding doubly (solid graphs) intercalated samples (Fig. S5b) shows that they are in good agreement regarding the shape and the position of the peaks (at about 1200, 1300, 2900 and 3000 cm^{-1}), which confirms the replacement of the first intercalated amine.

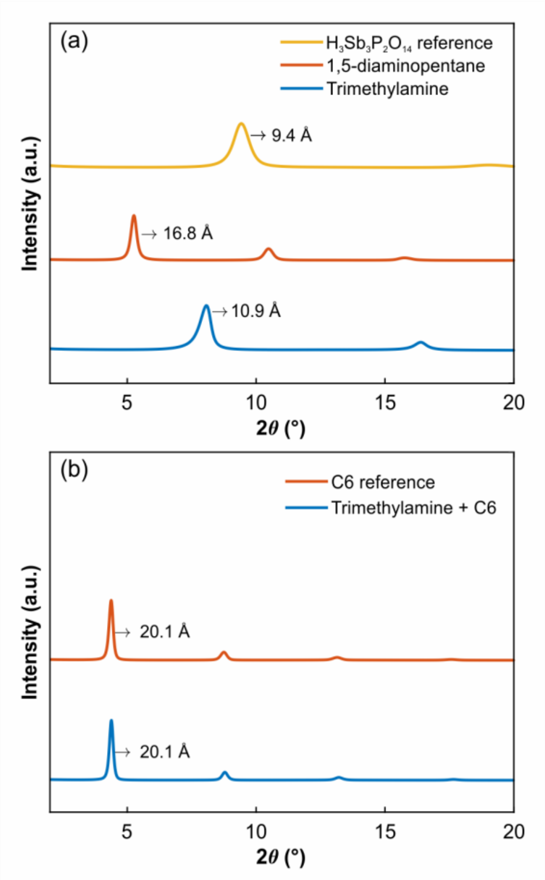

Fig. S7 Out-of-plane XRPD patterns (Cu-K$_{\alpha 1}$) of (a) the pristine sample (yellow) along with singly intercalated samples (red: 1,5-diaminopentane; blue: trimethylamine) and (b) the sample in which trimethylamine was exchanged for C6 (blue) along with a C6 singly intercalated sample as reference (red).

The out-of-plane XRPD patterns in Fig. S7a indicate that trimethylamine and 1,5-diaminopentane, which are both produced through the microbial spoilage of fish and meat, can be intercalated into the thin films in the same manner as the primary alkylamines. The out-of-plane XRPD pattern of the sample where trimethylamine was exchanged with C6 is given in Fig. S7b.

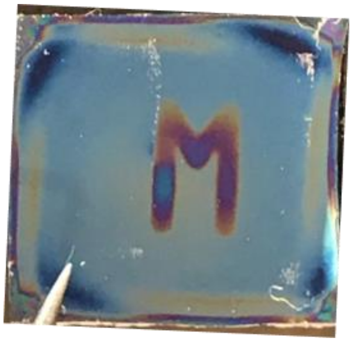

Fig. S8 Photograph of an $H_3Sb_3P_2O_{14}$ thin film intercalated with C10 using a mask.

References

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2. P. Ganter, L. M. Schoop and B. V. Lotsch, *Adv. Mater.*, 2017, **29**, 1604884.
3. P. Ganter, L. M. Schoop, M. Däntl and B. V. Lotsch, *Chemistry of Materials*, 2018.