

SUPPORTING INFORMATION

Role of Chain Length on $(C_nH_{2n+1}NH_3)_2PbX_4$ ($n=6, 8, 10, 12, 14, 16$; $X=Br$ and I) 2D Metal Halide Perovskites Physical Properties and Hydrophobicity

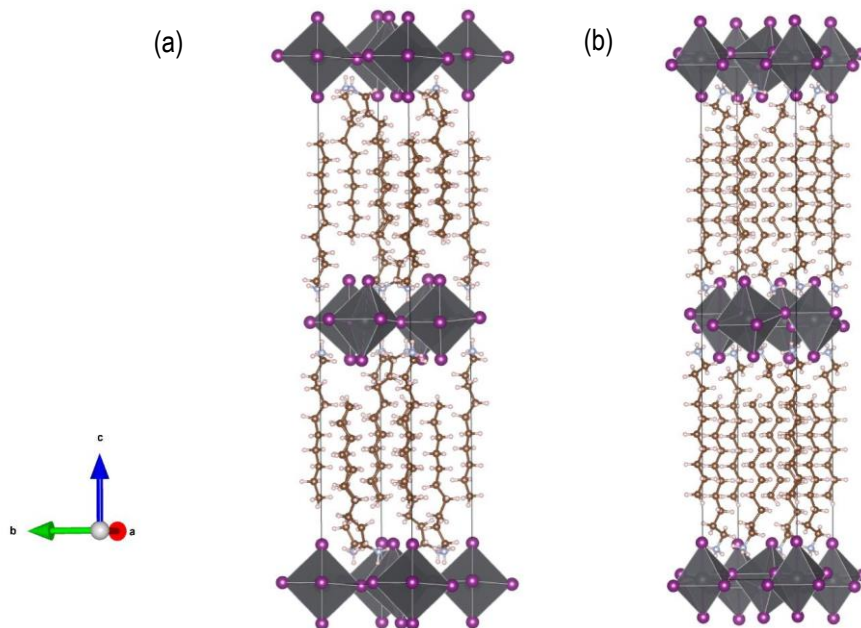


Figure S1. Illustrative crystal structure representation for orthorhombic Phase II (a) and Phase III (b) for $(C_nH_{2n+1}NH_3)_2PbI_4$ sample with $n=10$. Crystal structure data taken from ref. 1.¹

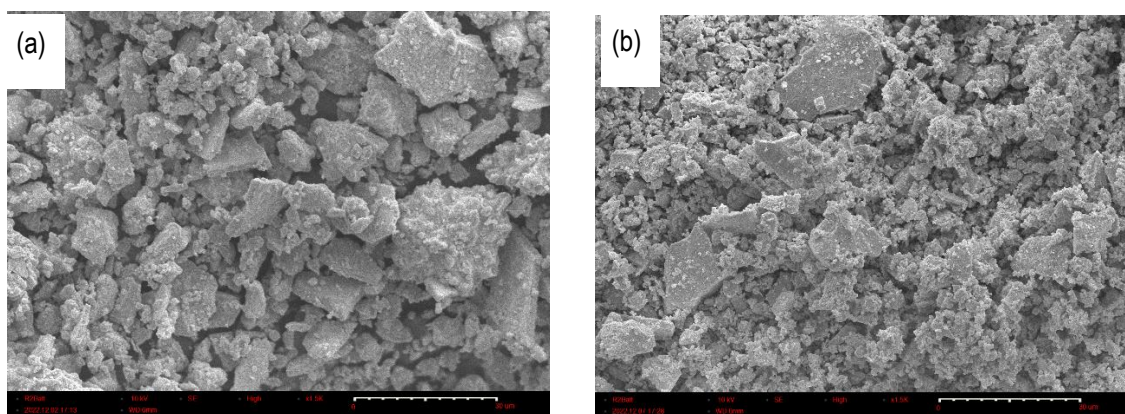


Figure S2. SEM images for $(C_nH_{2n+1}NH_3)_2PbI_4$ samples with $n=6$ (a), and 16 (b).

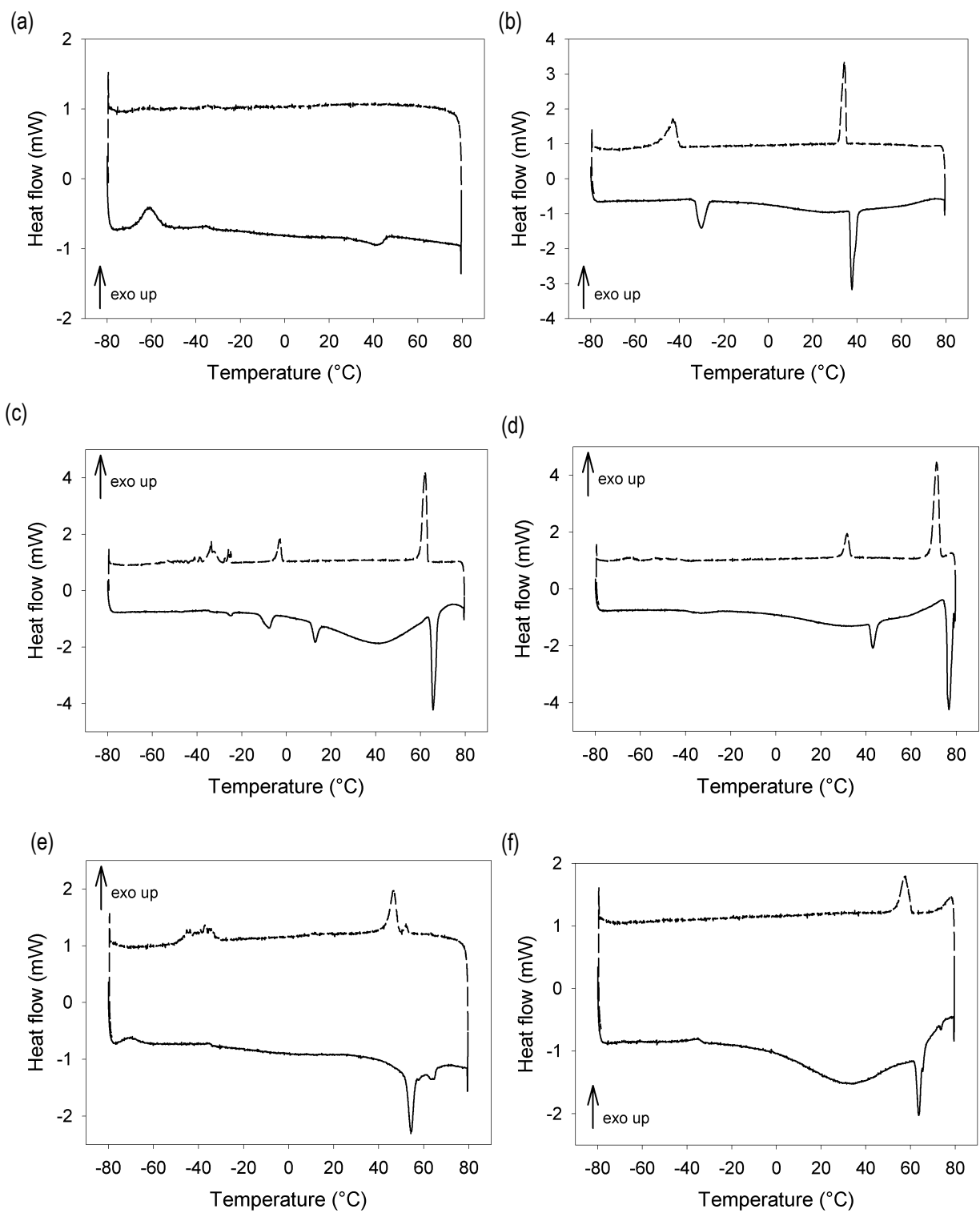


Figure S3. DSC for $(C_nH_{2n+1}NH_3)_2PbI_4$ samples for $n=6$ (a), 8 (b), 10 (c), 12 (d), 14 (e), and 16 (f).

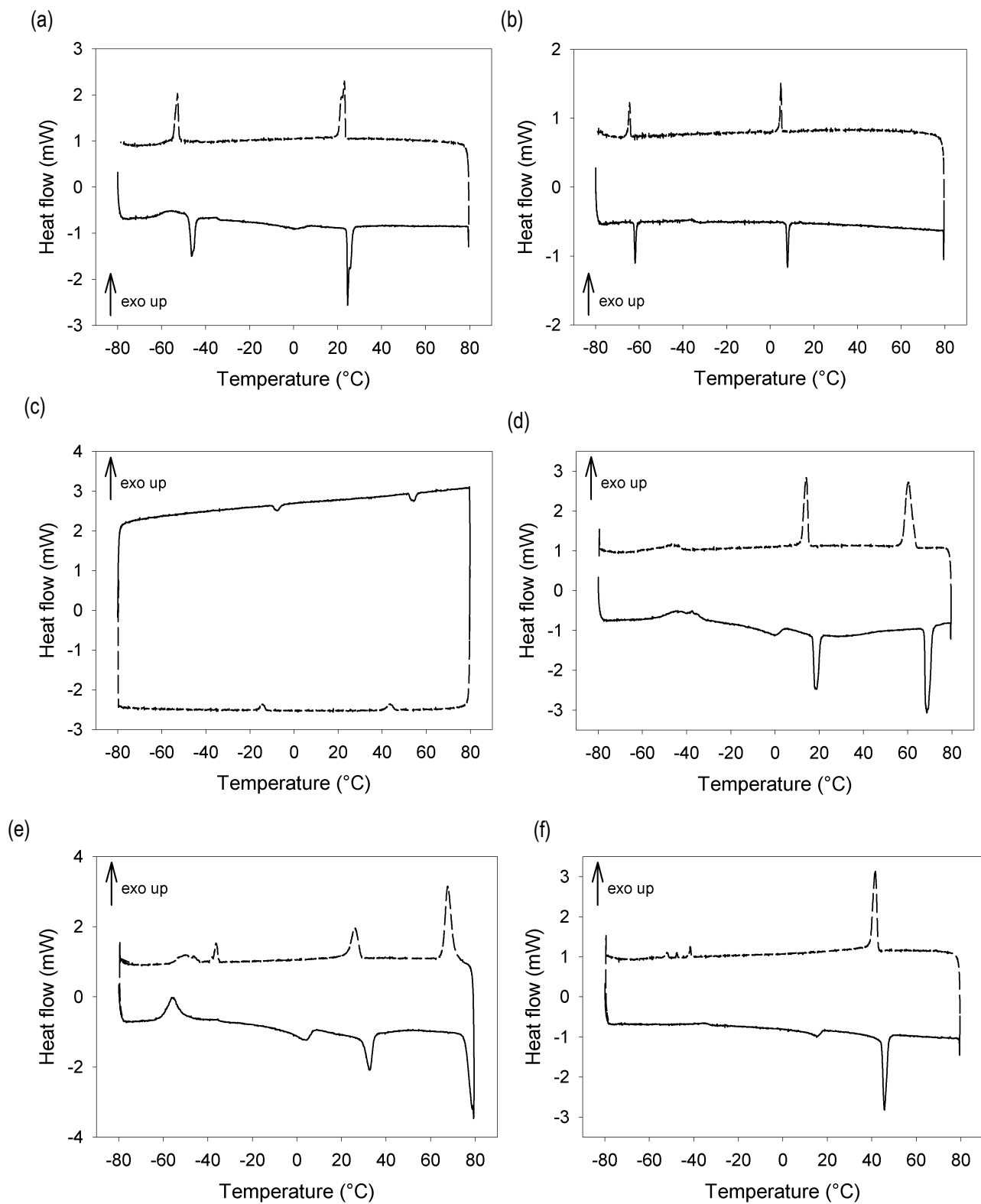


Figure S4. DSC for $(C_nH_{2n+1}NH_3)_2PbBr_4$ samples for $n=6$ (a), 8 (b), 10 (c), 12 (d), 14 (e), and 16 (f).

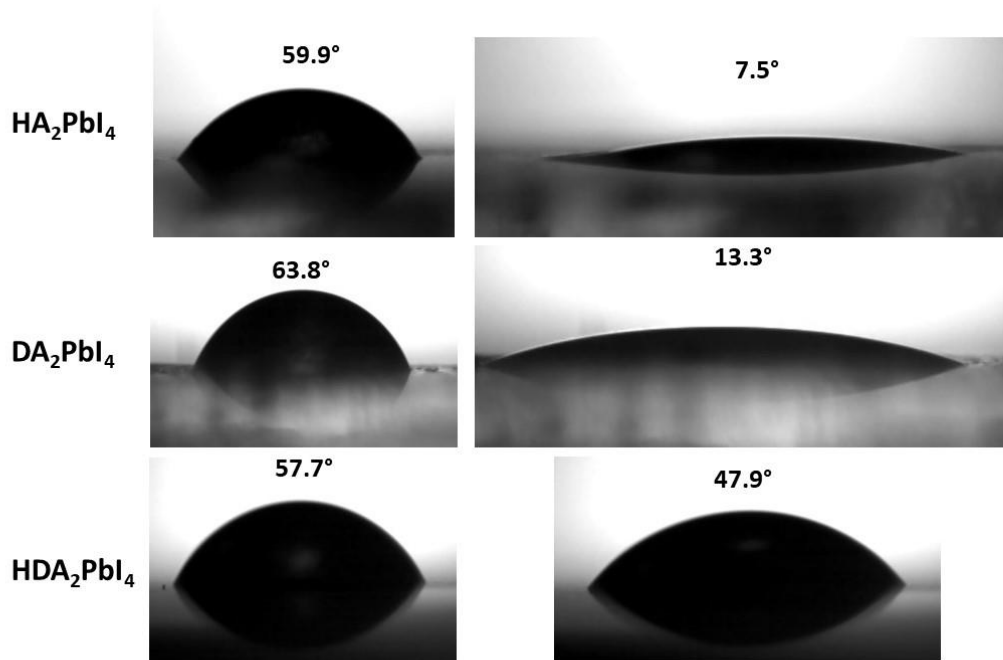


Figure S5. Images of the drop at the beginning and at the end of the contact angle experiment (after 40 second) for the $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{PbI}_4$ sample.

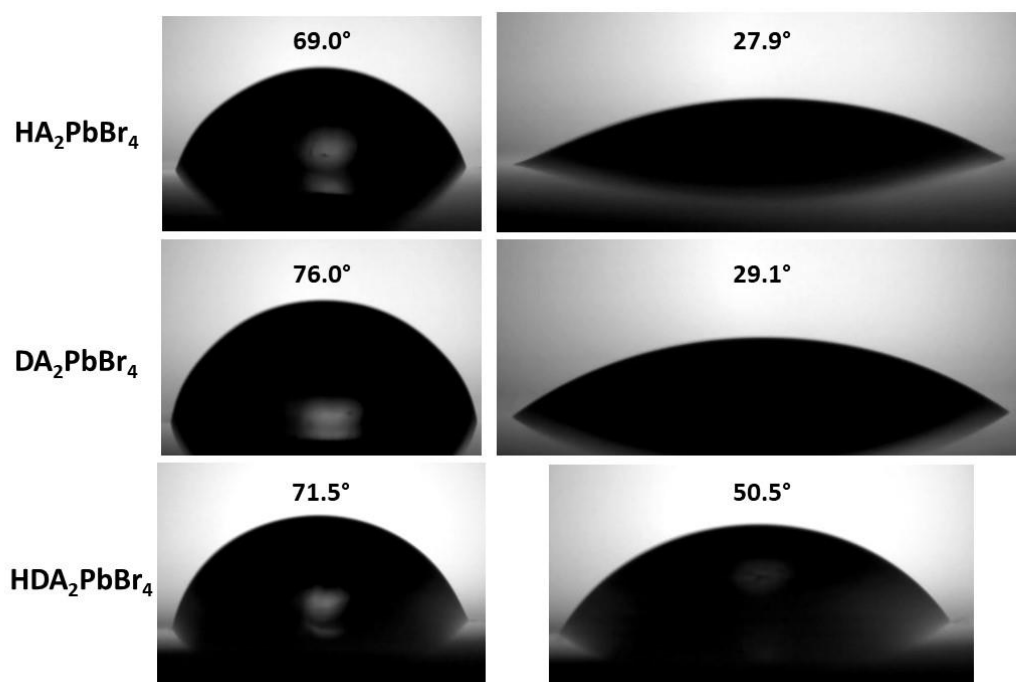


Figure S6. Images of the drop at the beginning and at the end of the contact angle experiment (after 40 second) for the $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{PbBr}_4$ sample.

Table S1 – Value of the bandgaps in eV for the two series of samples

<i>n</i> value	Bandgap (C_nH_{2n+1}NH₃)₂PbI₄)	Bandgap (C_nH_{2n+1}NH₃)₂PbBr₄)
6	2.258	2.919
8	2.229	2.926
10	2.237	2.981
12	2.322	3.005
14	2.349	3.011
16	2.379	3.0230

Table S2 – Emission peak values in eV for two series of samples

<i>n</i> value	Emission peak max (C_nH_{2n+1}NH₃)₂PbI₄)	Emission peak max (C_nH_{2n+1}NH₃)₂PbBr₄)
6	2.384	3.077
8	2.389	3.061
10	2.394	3.139
12	2.490	3.139
14	2.505	3.123
16	2.505	3.123

Experimental

Sample Preparation and X-ray Diffraction

Samples of general formula $(C_nH_{2n+1}NH_3)_2PbBr_4$ and $(C_nH_{2n+1}NH_3)_2PbI_4$ (1 g) were prepared by dissolving lead acetate in an excess of HBr or HI aqueous solutions (Aldrich). After reaching 90°C, under nitrogen flux, the different amines $C_nH_{2n+1}NH_2$ with $n=6, 8, 10, 12, 14, 16$ have been added to the reaction mixture. The solution was then left to cool down to room temperature and the samples have been recovered by filtration. The crystal structure of the samples has been characterized by room temperature Cu-radiation XRD acquired with a Bruker D8 diffractometer.

UV-Vis and PL Spectroscopy Measurements

DRS spectra were acquired in the wavelength range 300- 800 nm directly on the powders by using a Jasco V-750 spectrophotometer, equipped with an integrating sphere (Jasco ISV-922). The photoluminescence (PL) measurements were recorded by means of a Fluorolog®-3 spectrofluorometer (HORIBA Jobin-Yvon), equipped with a 450 W xenon lamp as exciting source and double grating excitation and emission monochromators. All the optical measurements were performed at room temperature on powder dispersed samples as obtained from the synthesis without any size sorting treatment. The PL emission spectra were recorded by using an excitation wavelength of 350 nm for Bromide containing samples and at 400 nm for Iodide containing ones.

Micro-Raman Measurements

Micro-Raman measurements were performed at room temperature using an automated and integrated confocal spectrometer, XploRA Plus HORIBA Scientific, equipped with an Olympus microscope BX43. The 638 nm laser light was used as excitation. Neutral filters with different optical density allow to set the incident laser power. The spectrometer is equipped with a motorized xy stage on which the investigated samples are positioned. Spectral resolution is about 1 cm^{-1} . An Open Electrode CCD camera, with a multistage Peltier air-cooling system, is used as detector. All the reported spectra have been obtained as the average over a set of 30 spectra resulting from a linear scanning for each sample covering a length of about 100 microns.

Contact Angle Measurements

Contact angle was determined using a DMe-211 Plus Contact Angle Meter (Kyowa Interface Science Co Ltd., Saitama, Japan) according to the $\theta/2$ method. For the measurements, perovskites in the form of thin films have been prepared on quartz substrate through spin-coating method. For the test, a drop (10 μl) of water was deposited on the surface of the samples and the contact angle was calculated over time at 1 second intervals up to 40 seconds using FAMAS Dropmaster Software. The experiments were run 10 times for each sample.

Differential scanning calorimetry (DSC) measurements

Differential scanning calorimetry (DSC) was performed by a Q2000 apparatus (TA Instruments, New Castle, DE, USA) interfaced with a TA5000 data station by heating about 3 mg of powder in an open aluminium crucible from $-80\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$ and then cooling down to $-80\text{ }^{\circ}\text{C}$ (heating and cooling rate = 5 K min^{-1}) under nitrogen flux (50 mL min^{-1}). Three independent measurements were taken on each sample. The temperature accuracy of the instrument is $\pm 0.1\text{ }^{\circ}\text{C}$, the precision is $\pm 0.01\text{ }^{\circ}\text{C}$, and the calorimetric reproducibility is $\pm 0.05\%$. DSC data were analyzed by the Universal Analysis software by TA Instruments.

References

1 A. Lemmerer and D. G. Billing, *Dalton Trans.*, 2012, **41**, 1146–1157.