Two chiral haloplumbate hybrids with thermochromism luminescence and application as luminescent thermometers

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1. Experimental

1.1. Chemicals and reagents

The reagents and solvents were purchased from commercial sources and used without further purification.

1.2. Physical measurements

Thermogravimetric (TG) experiment was performed with a TA2000/2960 thermogravimetric analyzer from 30 to 800°C at a warming rate of 10 K/min under nitrogen and air atmosphere, and the polycrystalline samples were placed in an aluminum crucible. Powder X-ray diffraction (PXRD) data for the as-prepared was collected using Bruker D8 Advance powder diffractometer operating at 40 kV and 40 mA with Cu K radiation λ = 1.5418 Å at ambient temperature. UV-visible-NIR absorption spectra were taken in the solid state by diffuse reflection method using an integrating sphere of PerkinElmer Lambda 950 spectrometer. Solid state fluorescence spectra were recorded on a Fluorolog Tau-3 Fluorometer for the powdered crystalline sample at selected temperatures. The integration intervals used to calculate the intensities of HE-LE bands and intensity ratios is 350-470 nm for HE bands and 470-820 nm for LE bands, respectively. The temperature sensitivities have been obtained by fitted the linear function in the selected temperature range.

X-ray crystallography. Selected crystals of **1** and **2** at room temperature and 100 K were centered on an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire 3 CCD detector and a graphite monochromated Mo Kα (λ = 0.71073 Å). The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlis.[1] Structures were solved by the direct method and refined by the full-matrix least-squares procedure on F^2 using SHELXL-97 program.[2] The non-Hydrogen atoms were anisotropically refined using the full-matrix least-squares method on F^2.

1.3. Preparations for 1

$[C_6H_{10}(NH_3)_2][PbCl_4]$ (**1**): The hybrid crystals were achieved using the process

below: $PbCl_2$ (0.5 mmol) was dissolved in 3 ml of 10 % HCl and were stirred for 3h, then 0.5 mmol (*R*)-cyclohexane-1,2-diamine was added and stirred another 1h. The solution was filtered, white needle-shape crystals were obtained in solution. The crystal was washed with DMF and acetone and dried in air. The yield is ca. 70% . Anal. Calcd for **1**: C, 15.49; H, 3.46; N, 6.02. Found: C, 15.60; H, 3.55; N, 5.90.

$[C_6H_{10}(NH_3)_2][PbBr_4]$ (**2**): The crystals of 2 were achieved using a similar process to that for 1, and the difference in the preparation process concerns only replacing the reactant $PbBr_2$ with $PbCl_2$ and HBr with HCl. The yield is ca. 70% . Anal. Calcd for **2**: C, 11.20; H, 2.51; N, 4.26. Found: C, 11.52; H, 2.45; N, 4.38.

References:

1. *CrysAlis V1.171*, Oxford Diffraction Ltd., Poland, 2004.
2. G. M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal structure, University of Göttingen, Germany, 1997.

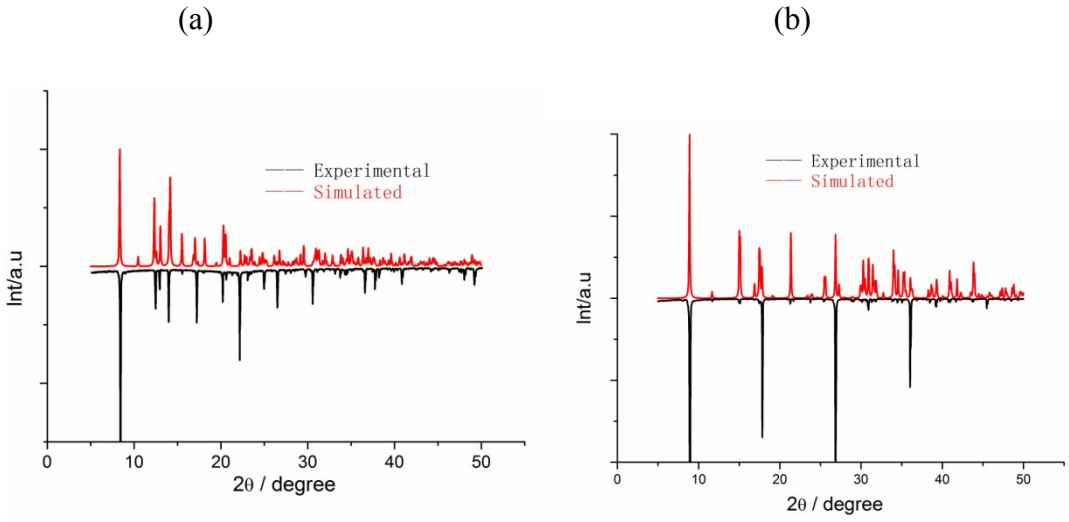

Figure S1 Powder X-ray diffraction patterns for as-prepared sample of (a) **1** and (b) 2 confirming the phase purity of the as-prepared sample (Black lines: experimental patterns; red lines: simulated profiles).

(a) (b)

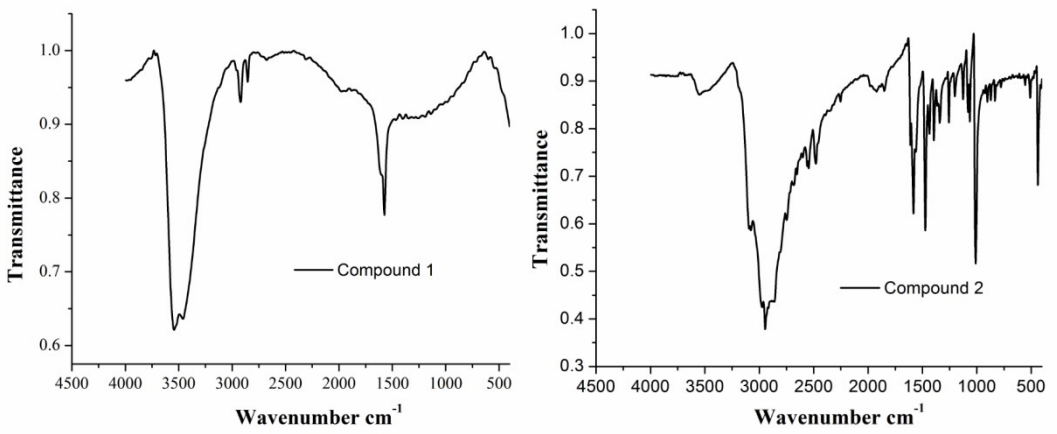

Figure S2 IR spectra of (a) **1** and (b) 2

(a) (b)

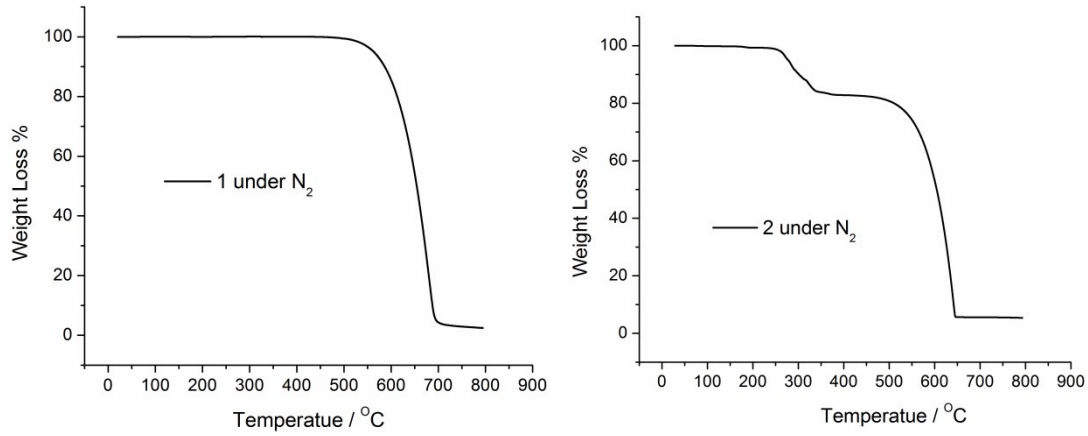

Figure S3 TG plot under N_2 atmosphere for (a) **1** and (b) **2**

(a) (b)

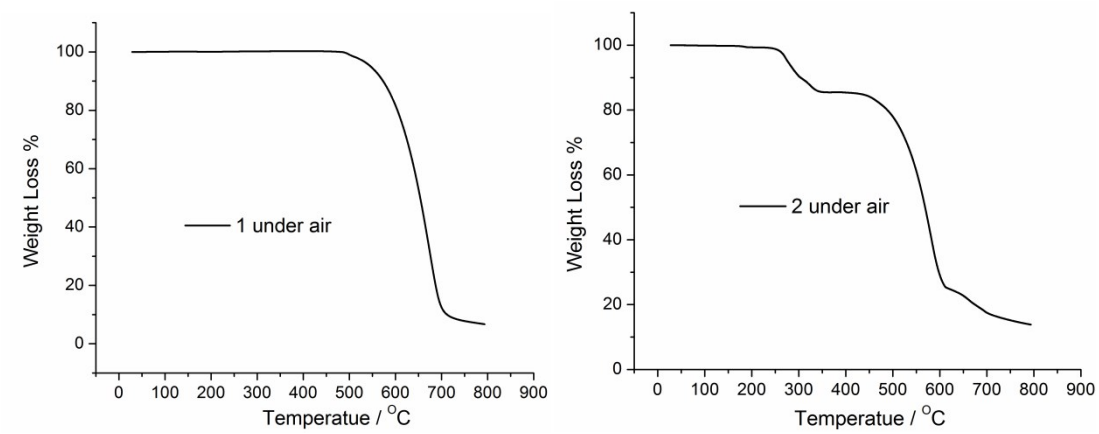

Figure S4 TG plot under air atmosphere for (a) **1** and (b) **2**

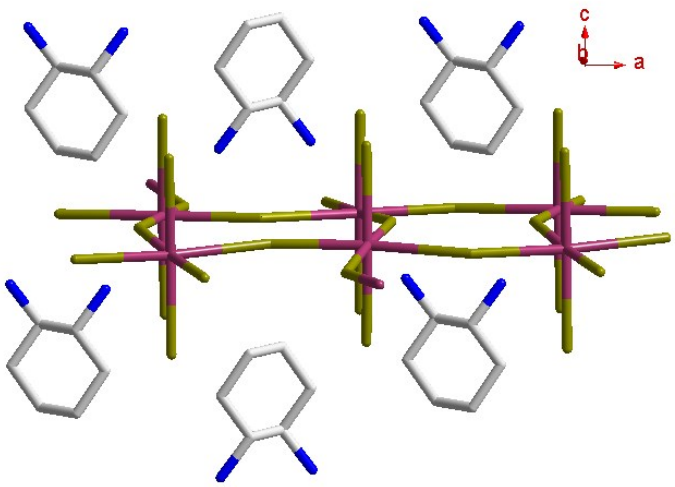

Figure S5 The layer packing structure of **2** along the *b*-axis

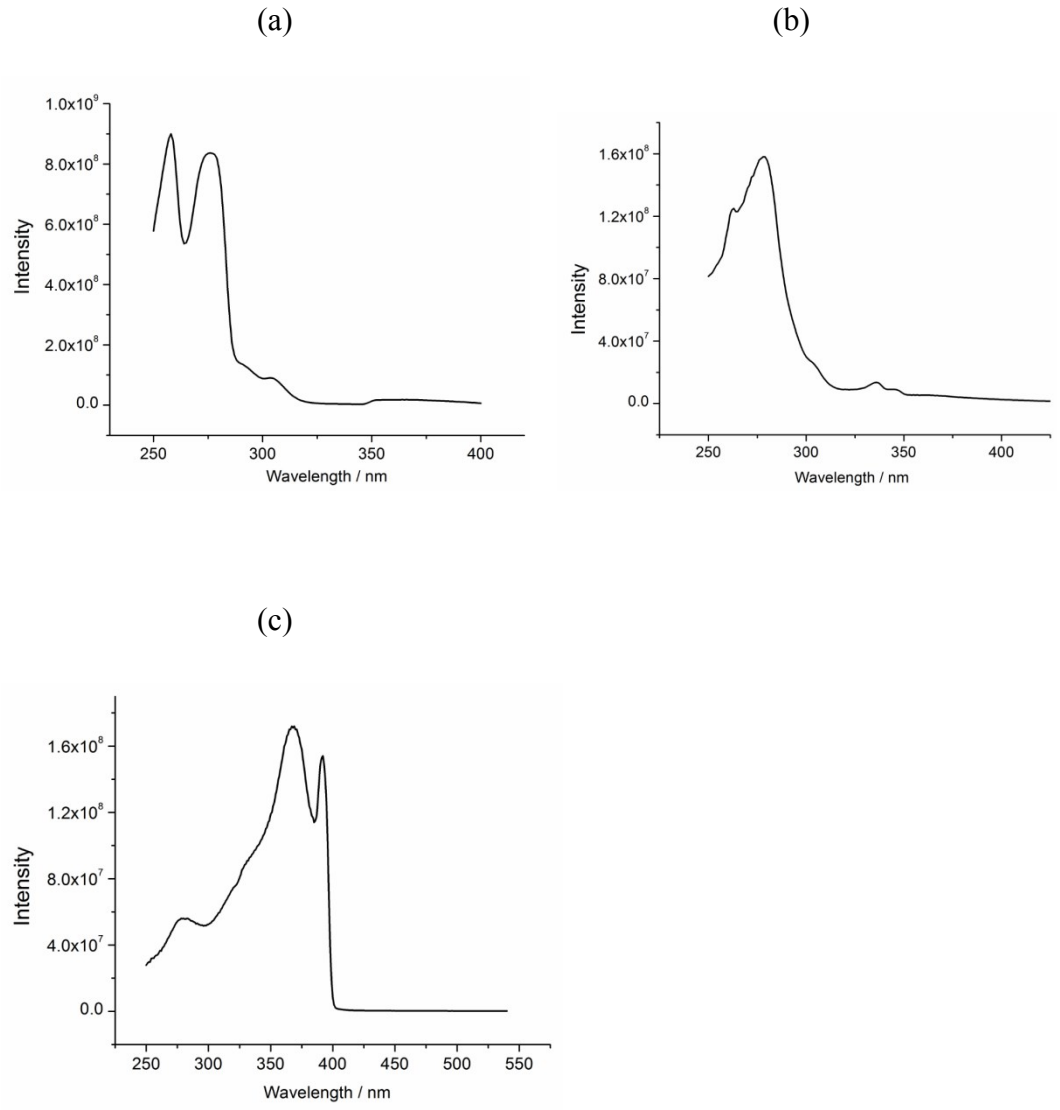

Figure S6 Excitation spectra of 1 at 100 K for monitoring (a) high energy (HE) emission band; (b) low energy (LE) emission band and (c) excitation spectra of 2 at 100 K.

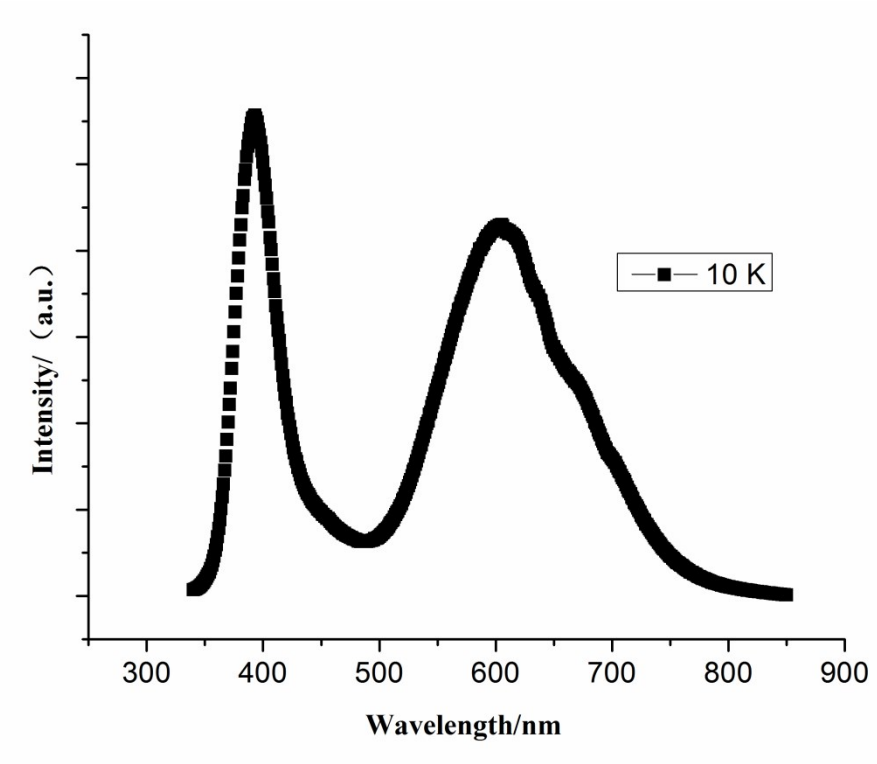

Figure S7 Solid-state emission spectra of **1** at 10 K

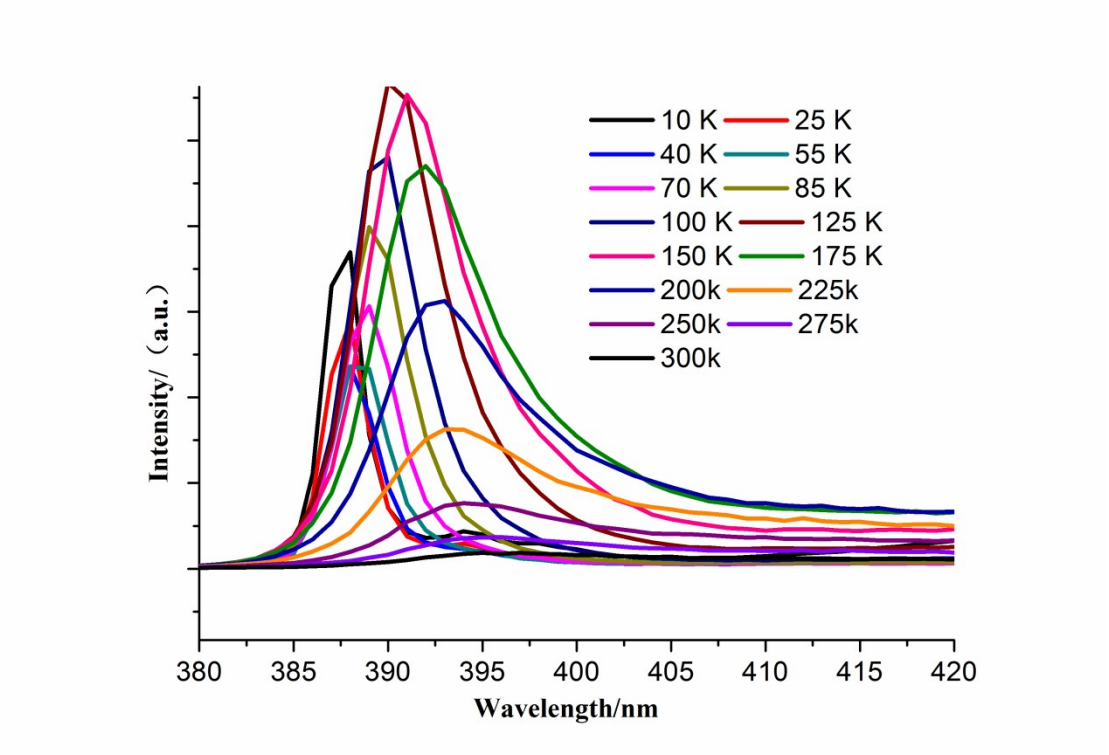

Figure S8 HE emission band of **1** from 10 to 300 K

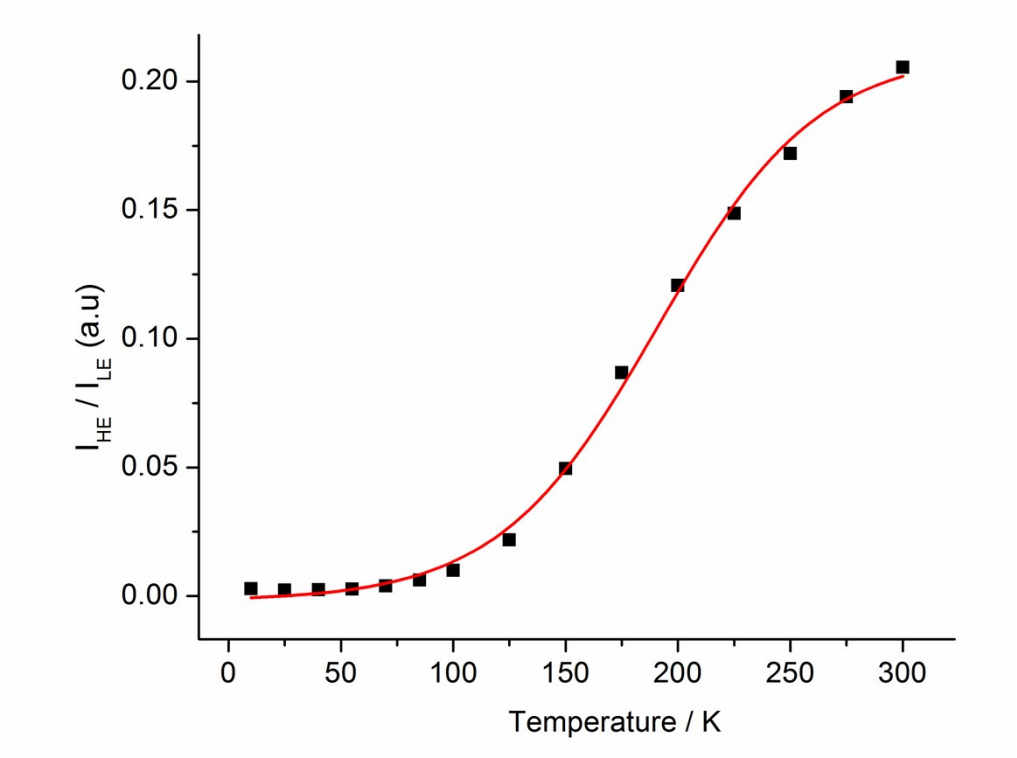

Figure S9 Temperature-dependent emission band intensity ration I_{HE}/I_{LE} and the fitted curve for 2