# Fine-tuning of a thermosalient phase transition by solid solutions

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## **Electronic Supplementary Information**

#### **Experimental Section:**

All materials, solvents and reagents were used as received from commercial suppliers (Sigma-Aldrich, Fisher Scientific, Alfa Aesar) without further purification.

<u>*Crystal preparation.*</u> 0.1 M solutions of 2,2'-bipyridine (bpy) in CH<sub>2</sub>Cl<sub>2</sub> and acetonitrile (MeCN), and solutions of ZnX<sub>2</sub> (X = Cl or Br) in methanol and DMSO were prepared. No precaution was taken to prevent the absorption of atmospheric water by the hygroscopic zinc(II) salts. Layering of the CH<sub>2</sub>Cl<sub>2</sub> solution of bpy over an equivalent methanol solution of ZnCl<sub>2</sub> and ZnBr<sub>2</sub> in 1:9, 1:4, 3:7 2:3, 1:1. 3:2, 7:3, 4:1 and 9:1 ratio produced needle-shaped single crystals of [Zn(bpy)Br<sub>2x</sub>Cl<sub>2(1-x)</sub>] (**1**<sub>x</sub>). As side product, plate-like crystals of the tris(bpy)zinc complex [Zn(bpy)<sub>3</sub>]X<sub>2</sub> were also obtained (this structure is similar to the structures with CSD codes VADPUM, RUYYIU, NEMPAW and EGOVEB). Needle crystals of **1**<sub>x</sub> were also obtained by mixing the MeCN solution of bpy with an equivalent solution of ZnCl<sub>2</sub> and ZnBr<sub>2</sub> in DMSO with ZnCl<sub>2</sub>-to-ZnBr<sub>2</sub> ratios 1:9, 1:4, 3:7 2:3, 1:1. 3:2, 7:3, 4:1 and 9:1. We note that MeCN/DMSO mixtures produce larger crystals.

<u>Grinding.</u> Mixed phases of  $\mathbf{1}_x$  with Cl/Br ratios of 2:1, 1:1 and 1:2 as well as the pure complexes [Zn(bpy)Br<sub>2</sub>] ( $\mathbf{1}_1$ ) and [Zn(bpy)Cl<sub>2</sub>] ( $\mathbf{1}_0$ ) were prepared by grinding in agate mortar. Due to the high hygroscopicity of the zinc(II) salts and the adsorption of moisture from the air, the grinding experiments would be better regarded as solvent-assisted reaction.

<u>Single crystal X-ray diffraction (XRD)</u>. Single crystal XRD measurements were performed on a Bruker APEX Duo diffractometer equipped with an Oxford Cryosystems Cobra low-temperature system. The diffraction data (Table S1 and S2) were collected with MoKα radiation at varying temperatures. In a typical procedure, the unit cell was first determined at room temperature. If the crystal system was monoclinic, the crystal was heated to 320 K for structure measurement, and if it was triclinic it was cooled to 100 K. After the first measurement the crystal was cooled to 100 K or

heated to 320 K, respectively, for another data collection and structure refinement. For some crystals the variation of the unit cell was also monitored during the heating/cooling. The sample  $1_{0.5}$  was heated to 360 K for approximately 10 minutes before it was cooled to 320 K to facilitate the phase transition. The structures were solved with direct methods and refined against  $|F^2|$  with the Shelxl software.<sup>[1]</sup> In the structure refinement the coordinates and the thermal displacement parameters of chloride and bromide were constrained to be the same. All hydrogen atoms were fixed to the idealized riding positions. For each crystal, the relative halide content was determined by refining the atomic occupancy against the intensity of the diffraction peaks.



Figure S1. Optical photographs of the mixed crystallization products at different halide ratios.

<u>X-ray powder diffraction (XRPD).</u> XRPD patterns of the product obtained by grinding were measured at room temperature on a zero-background silicon plate with a PANalytical Empyrean diffractomer using CuK $\alpha$  radiation. XRPD patterns of the products of crystallization from solution were recorded on a Bruker APEX Duo equipped with an Oxford Cryosystems Cobra cryosystem. Crystals were ground on a glass slide in cryo-oil and mounted on a 200 µm loop. Two 240 seconds images were taken at 320, 290, 260, 230 and 200 K with a detector distance of 15 cm. The powder diffraction patterns from the images were integrated using XRD<sup>2</sup> Eval in the Apex2 program suite.<sup>[2]</sup>



**Figure S2**. The XRPD patterns of solid solutions prepared by grinding. From bottom to top: calculated pattern of EQIPAW ([Zn(bpy)Br<sub>2</sub>] structure refined in *C*2/*c*), grinding with 100% Br, 66% Br, 50% Br, 33% Br, 100% Cl, and calculated pattern of CEFFOI ([Zn(bpy)Cl<sub>2</sub>] structure in *P* 1). The peak at 7.7° in 2 $\theta$  is due to the byproduct, [Zn(bipy)<sub>3</sub>]X<sub>2</sub>.

<u>Thermal analysis.</u> Hot-stage microscopy experiments were carried out on single crystals whose structure had previously been determined by X-ray diffraction, on a Linkam THMS600-PS stage cooled with liquid nitrogen on a Linkam Imaging station. DSC thermograms were measured on single crystals whose structure had previously been determined by XRD, on a TA DSC Q2000 with a TA refrigerated cooling system. The heating/cooling rate was 10 °C/min.

## Single crystal XRD data

	<b>1</b> <sub>0</sub> (100 K)	<b>1</b> <sub>0.1</sub> (100 K)	<b>1</b> <sub>0.3</sub> (100 K)	<b>1</b> <sub>0.5</sub> (100 K)
Chemical formula	$C_{10}H_8CI_2N_2Zn$	$C_{10}H_8Br_{0.19}CI_{1.81}N_2Zn$	$C_{10}H_8Br_{0.62}CI_{1.38}N_2Zn$	$C_{10}H_8Br_{0.88}CI_{1.12}N_2Zn$
Br occupancy site 1,2	0	0.055(15), 0.130(15)	0.186 (2), 0.433(2)	0.335 (2),0.546(2)
M <sub>r</sub>	292.45	300.71	320.02	331.62
Crystal system, space group	Triclinic, <i>P</i> <sup>1</sup>	Triclinic, P <sup>1</sup>	Triclinic, P <sup>1</sup>	Triclinic, <i>P</i> <sup>1</sup>
Т (К)	100	99	100	99
a, b, c (Å)	7.5299(6) 8.7931(7) 9.0498(7)	7.5668(10) 8.8117(11) 9.0830(11)	7.6518(5) 8.8233(6) 9.1333(6)	7.6883(8) 8.8529(9) 9.1701(9)
α, β, γ (°)	112.8348(19) 94.457(2) 95.707(2)	113.0052(18) 94.6504(19) 95.7870(19)	113.5232(13) 95.1819(15) 95.9954(15)	113.6995(13) 95.3265(14) 95.9991(14)
V (Å <sup>3</sup> )	545.06(7)	549.79(12)	556.37(6)	562.12(10)
Ζ	2	2	2	2
Radiation type	ΜοΚα	ΜοΚα	ΜοΚα	ΜοΚα
μ (mm <sup>-1</sup> )	2.71	3.31	4.73	5.55
Crystal size (mm)	0.20 × 0.08 × 0.06	0.34 × 0.07 × 0.05	0.28 × 0.12 × 0.10	0.29 × 0.17 × 0.15
T <sub>min</sub> , T <sub>max</sub>	0.585, 0.746	0.602, 0.746	0.576, 0.746	0.562, 0.746
No. of reflections (meas, ind. and obs. $[l > 2\sigma(l)]$ )	9415, 3228, 2831	12004, 3324, 3008	7827, 3406, 3098	11998, 3162, 2907
R <sub>int</sub>	0.024	0.019	0.013	0.016
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.732	0.714	0.717	0.696
$R[F^2 > 2\sigma(F^2)], wR(F^2),$ S	0.024, 0.058, 1.04	0.020, 0.048, 1.07	0.018, 0.045, 1.04	0.018, 0.045, 1.07
No. of reflections	3228	3324	3406	3162
No. of parameters	136	138	138	138
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} \ (e \ \text{\AA}^{-3})$	0.54, -0.44	0.48, -0.26	0.52, -0.33	0.47, -0.25

### **Table S1**. Crystallographic parameters of the triclinic form of $[Zn(bpy)Br_{2x}Cl_{2(1-x)}]$ (1<sub>x</sub>) at 100 K

#### Table S1. Continued

	<b>1</b> <sub>0.7</sub> (100K)	<b>1</b> <sub>0.9</sub> (100 К)	<b>1</b> <sub>1</sub> (100 K)
Chemical formula	$C_{10}H_8Br_{1.37}Cl_{0.64}N_2Zn$	$C_{10}H_8Br_{1.71}Cl_{0.29}N_2Zn$	$C_{10}H_8Br_2N_2Zn$
Br occupancy site 1,2	0.638(4), 0.727(4)	0.815(16), 0.837(16)	1
M <sub>r</sub>	353.14	368.52	381.37
Crystal system, space group	Triclinic, P <sup>1</sup>	Triclinic, P <sup>1</sup>	Triclinic, <i>P</i> <sup>1</sup>
Т (К)	99	100	100
a, b, c (Å)	7.7335(13) 8.9213(15) 9.2304(16)	7.785(4) 8.976(5) 9.255(5)	7.882(6) 9.046(7) 9.355(7)
α, β, γ (°)	114.064(4) 95.245(4) 96.005(4)	114.285(7) 95.568(7) 95.950(8)	114.689(14) 95.786(16) 95.861(15)
<i>V</i> (Å <sup>3</sup> )	571.95(17)	579.4(5)	595.2(8)
Ζ	2	2	2
Radiation type	ΜοΚα	ΜοΚα	ΜοΚα
μ (mm <sup>-1</sup> )	7.03	8.05	8.74
Crystal size (mm)	0.21 × 0.11 × 0.08	0.27 × 0.05 × 0.04	0.40 × 0.14 × 0.12
$T_{\min}, T_{\max}$	0.547, 0.746	0.500, 0.746	0.381, 0.746
No. of reflections (meas., ind. and obs. $[l > 2\sigma(l)]$ )	3448, 3448, 2545	7501, 3114, 2388	6347, 3478, 2301
R <sub>int</sub>	0.063	0.041	0.057
$(\sin \theta / \lambda)_{max} (Å^{-1})$	0.716	0.707	0.726
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.035, 0.081, 0.96	0.063, 0.166, 1.09	0.072, 0.225, 1.05
No. of reflections	3448	3114	3478
No. of parameters	139	139	137
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.32, -1.14	1.42, -1.65	2.03, -1.75

	<b>1</b> <sub>0.5</sub> (320 К)	<b>1</b> <sub>0.7</sub> (320 К)	<b>1<sub>0.9</sub> (320 К)</b>	1 <sub>1</sub> (320 K)
Chemical formula	$C_{10}H_8Br_{0.90}CI_{1.10}N_2Zn$	$C_{10}H_8Br_{1.36}Cl_{0.64}N_2Zn$	$C_{10}H_8Br_{1.77}CI_{0.23}N_2Zn$	$C_{10}H_8Br_2N_2Zn$
Br occupancy	0.450(4)	0.679(3)	0.890(5)	1
Mr	332.48	352.83	370.94	381.37
Crystal system, space group	Monoclinic, C2/c	Monoclinic, C2/c	Monoclinic, C2/c	Monoclinic, C2/c
Т (К)	320	321	320	320
a, b, c (Å)	10.6281(12) 14.7546(16) 7.6742(8)	10.7082(5) 14.7769(7) 7.7285(3)	10.826(3) 14.850(4) 7.813 (2)	10.8238(18) 14.807(2) 7.8103 (12)
β (°)	97.2146(16)	97.3492(14)	97.435(5)	97.425(3)
<i>V</i> (Å <sup>3</sup> )	1193.9(2)	1212.87(9)	1245.6(6)	1241.3(3)
Z	4	4	4	4
Radiation type	ΜοΚα	ΜοΚα	Μο <i>Κ</i> α	ΜοΚα
μ (mm <sup>-1</sup> )	5.28	6.61	7.65	8.39
Crystal size (mm)	0.13 × 0.10 × 0.08	0.21 × 0.11 × 0.08	0.23 × 0.03 × 0.03	0.21 × 0.09 × 0.05
$T_{\min}, T_{\max}$	0.588, 0.746	0.567, 0.746	0.397, 0.746	0.544, 0.746
No. of meas., ind. and obs. $[l > 2\sigma(l)]$ refl.	9629, 1612, 1333	8584, 1863, 1327	9979, 1681, 1143	3978, 1623, 1039
R <sub>int</sub>	0.018	0.021	0.041	0.021
$(\sin \theta / \lambda)_{max} (Å^{-1})$	0.685	0.716	0.685	0.684
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.035, 0.085, 1.17	0.029, 0.073, 1.03	0.031, 0.078, 1.01	0.035, 0.089, 1.03
No. of reflections	1612	1863	1681	1623
No. of parameters	79	79	79	69
$\Delta \rho_{max}$ , $\Delta \rho_{min}$ (e Å <sup>-3</sup> )	0.34, -0.33	0.43, -0.25	0.54, -0.46	0.76, -0.51

**Table S2**. Crystallographic parameters of the monoclinic form of  $[Zn(bpy)Br_{2x}Cl_{2(1-x)}]$  (1<sub>x</sub>) at 320 K

1<sub>0.9</sub> (300 K) 1<sub>0.7</sub> (290 K) 1<sub>0.8</sub> (290 K)  $C_{10}H_8Br_{1.51}CI_{0.49}N_2Zn$ Chemical formula  $C_{10}H_8Br_{1.35}CI_{0.65}N_2Zn$  $C_{10}H_8Br_{1.75}CI_{0.25}N_2Zn$ Br occupancy 0.666(5) 0.759(4) 0.881(4)  $M_{\rm r}$ 352.30 359.69 370.40 Crystal system, Monoclinic, C2/c Monoclinic, C2/c Monoclinic, C2/c space group T (K) 290 290 300 a, b, c (Å) 10.6574 (16), 10.7037 (16), 10.755 (6), 14.801 (2), 14.806 (2), 14.818 (8), 7.7136 (11) 7.7392 (12) 7.775 (4) β (°) 97.568 (9) 97.635 (3) 97.673 (3) V (Å<sup>3</sup>) 1228.2 (12) 1205.9 (3) 1215.6 (3) 4 4 4 Ζ ΜοΚα ΜοΚα Μο Κα Radiation type 6.61 7.07 7.73  $\mu$  (mm<sup>-1</sup>) Crystal size (mm) 0.25 × 0.05 × 0.04 0.22 × 0.04 × 0.04 0.27 × 0.05 × 0.04 0.475, 0.746 0.483, 0.746 0.467, 0.746  $T_{\min}, T_{\max}$ No. of reflections 8568, 1708, 1071 6639, 1655, 1302 15529, 1792, 1247 (meas., ind. and obs.  $[l > 2\sigma(l)])$ 0.051 0.019 0.038 **R**<sub>int</sub>  $(\sin \theta / \lambda)_{max} (Å^{-1})$ 0.697 0.686 0.703  $R[F^2 > 2\sigma(F^2)],$ 0.042, 0.088, 1.03 0.029, 0.074, 1.08 0.031, 0.071, 1.04  $wR(F^2), S$ No. of reflections 1708 1655 1792 No. of parameters 79 79 79  $\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}}$  (e Å<sup>-3</sup>) 0.40, -0.44 0.48, -0.24 0.46, -0.28

**Table S3.** Crystallographic parameters of the monoclinic form of  $[Zn(bpy)Br_{2x}Cl_{2(1-x)}]$  (1<sub>x</sub>) measured at 290/300 K (used for the DSC experiment).

#### Variation cell metrics with Br content



**Figure S3.** Relationship between cell metrics and Br content in the 100 K triclinic structures (the error bars are smaller than the markers.)



**Figure S4.** Relationship between cell metrics and Br content in the 320 K monoclinic structures. (the error bars are smaller than the markers.)



**Figure S5.** Temperature variation of the triclinic angle  $\alpha$  and the *b* and *c* axes in the structure of [Zn(bpy)Br<sub>1.36</sub>Cl<sub>0.64</sub>] (10.7, 68% Br), showing a discontinuity due to the thermosalient phase transition between 240 K and 260 K (the error bars of the temperature axis and the angle  $\alpha$  axis are smaller than the markers.)



Figure S6. DSC trace of the 70% Br sample showing small transition peaks.



**Figure S7.** Variation of the Zn—Cl/Br bond lengths in the triclinic structures of  $[Zn(bpy)Br_{2x}Cl_{2(1-x)}]$  with molar composition (the error bars are smaller than the markers.)



Figure S8. Precession images at 273 (left) and 100 K (right) along the short axis for the monoclinic and triclinic form of  $1_1$  respectively.

- [1] [2]
- Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3-8. Bruker, *APEX2. Bruker AXS Inc., Madison, Wisconsin, USA.* **2012**.