

### Supporting Information

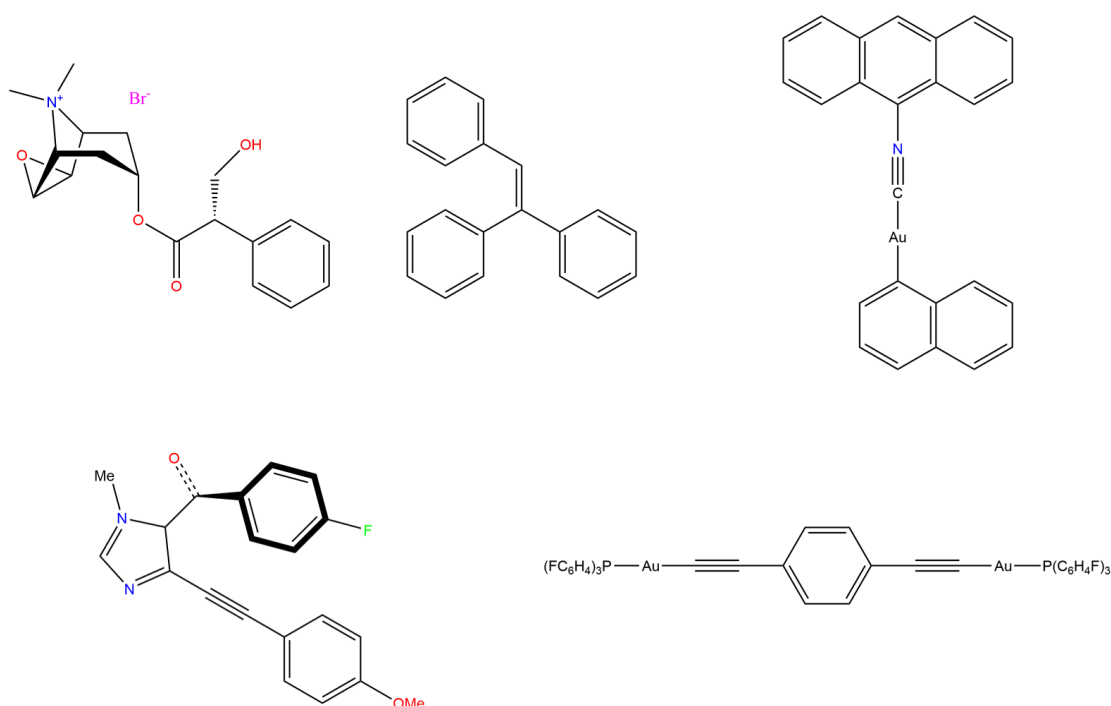
Xingchen Hu <sup>1</sup>, Yuntian Xiao <sup>1</sup>, Luguang Qi <sup>1</sup>, Yunhe Bai <sup>1</sup>, Ying Sun <sup>1</sup>, Yang Ye <sup>1</sup> and Chuang Xie <sup>1,2,3,\*</sup>

<sup>1</sup> School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

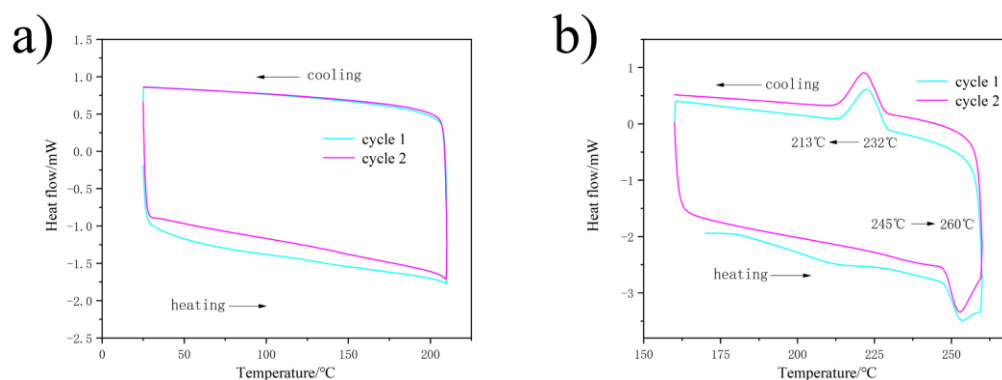
<sup>2</sup> National Engineering Research Center of Industrial Crystallization Technology, Tianjin University, Tianjin 300072, China

<sup>3</sup> State Key Laboratory of Chemical Engineering, Tianjin University, Tianjin 300072, China

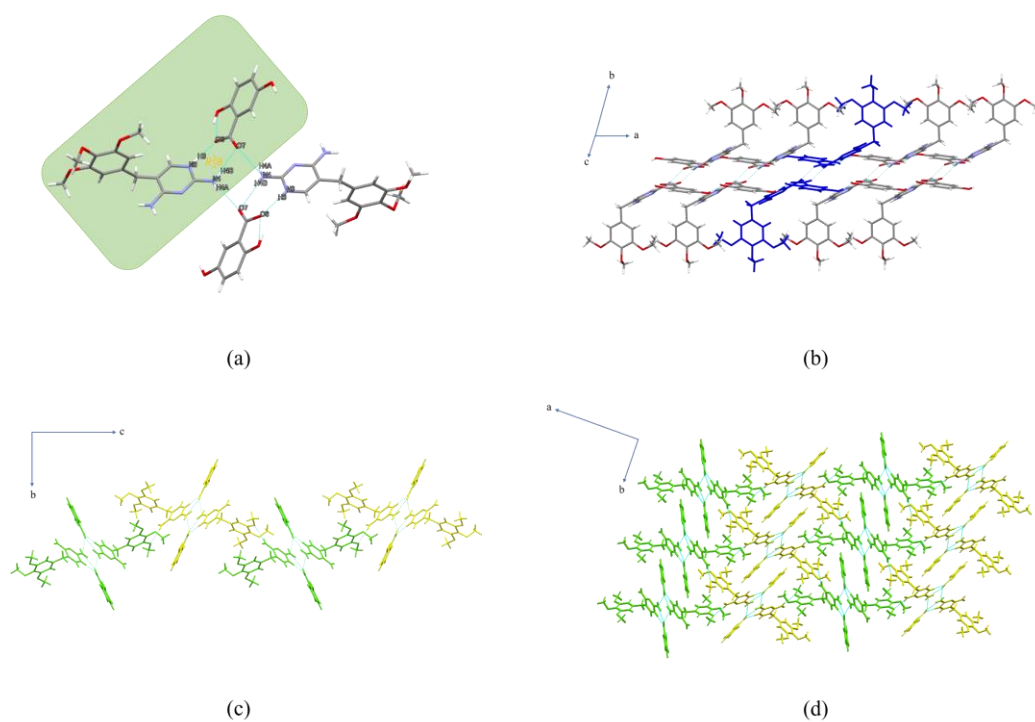
\* Correspondence: acxie@tju.edu.cn



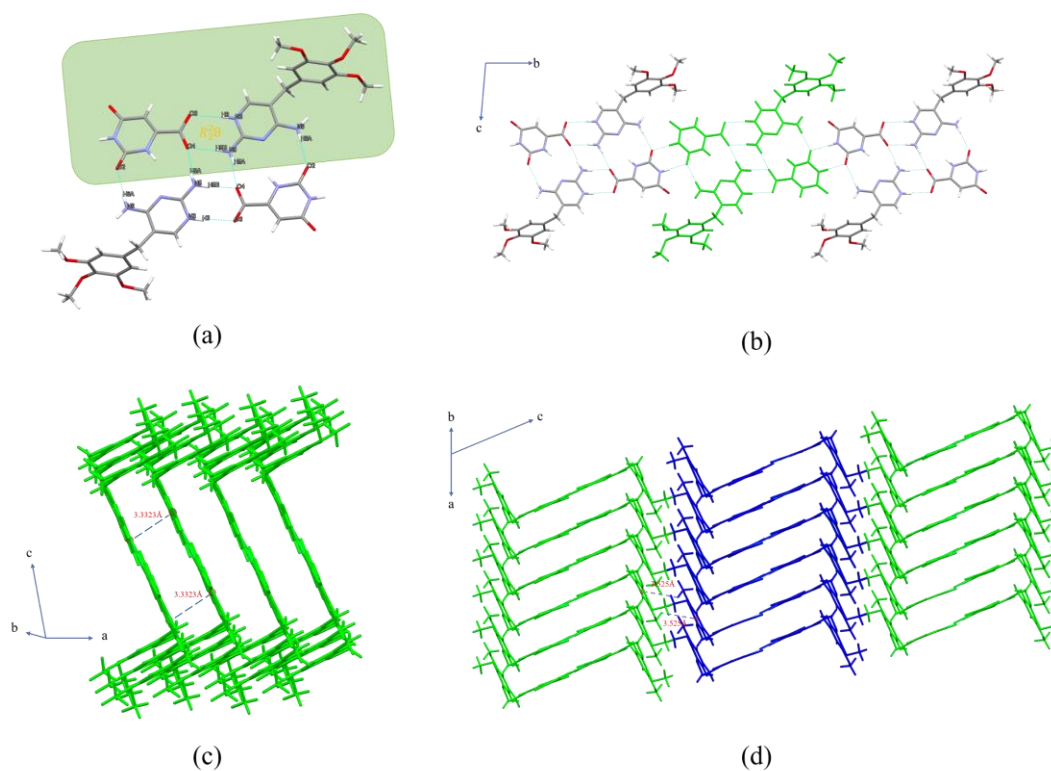
**Figure S1.** Molecular structural formulas of thermosalient crystals without phase transitions that have been previously reported.



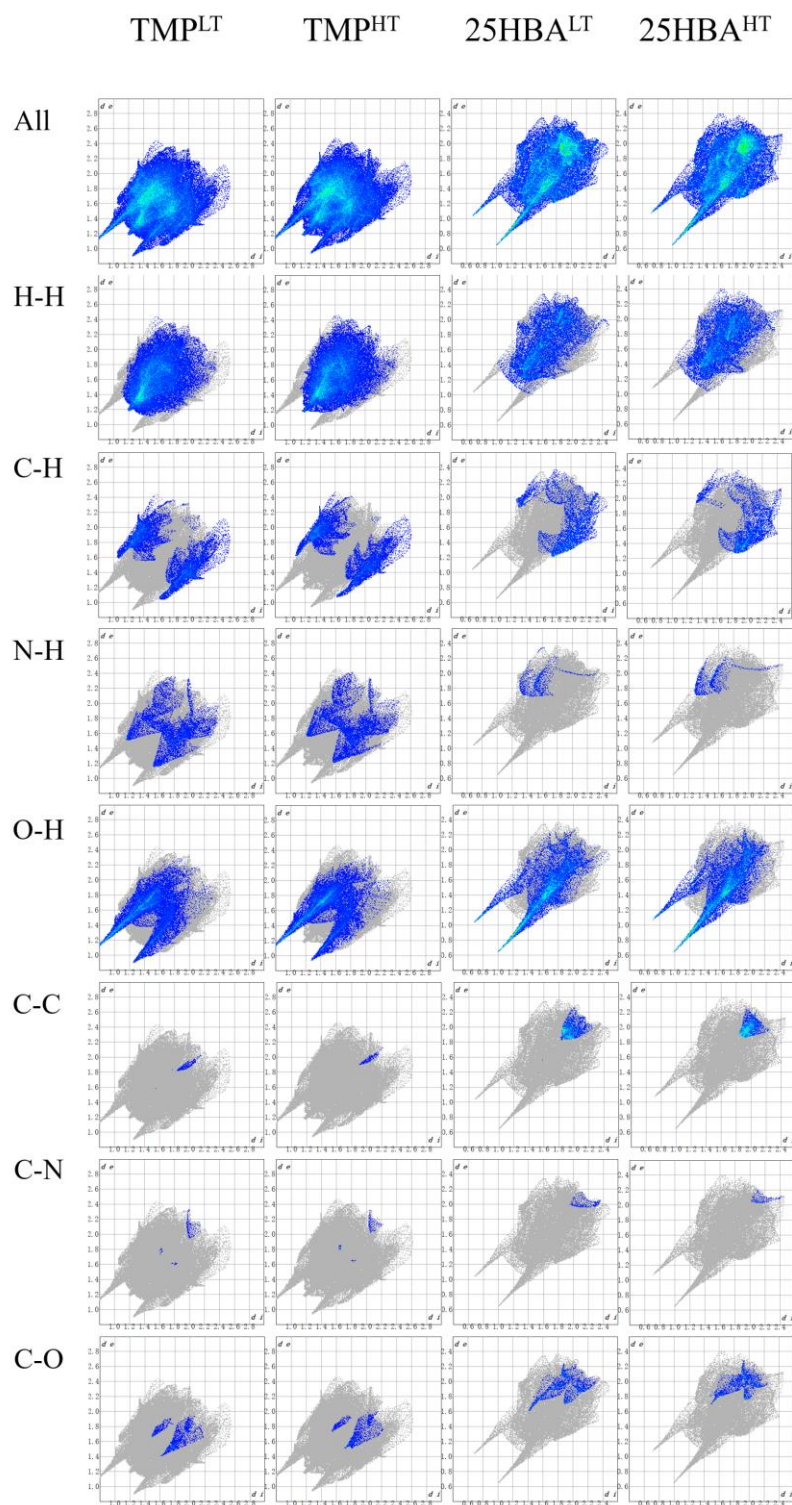
**Figure S2.** a) Differential scanning calorimetry thermograms of two cycles of TMP-25HBA powder. b) Differential scanning calorimetry thermograms of two cycles of TMP-OA powder.



**Figure S3. (a) Tetramer of TMP with 25HBA; (b) 1 D chain formed by tetramers; (c) 2 D plane connected by 1 D chains (green and yellow) (d) 3 D structure arranged between 2 D planes.**



**Figure S4. (a) Tetramer formed between TMP and OA; (b) 1 D chain of Tetramers; (c) The plane connected between the chains; (d) Connection mode of TMP-OA between planes.**



**Figure S5.** 2D fingerprints of different molecules in TMP-25HBA crystals (HT is high temperature, LT is low temperature).

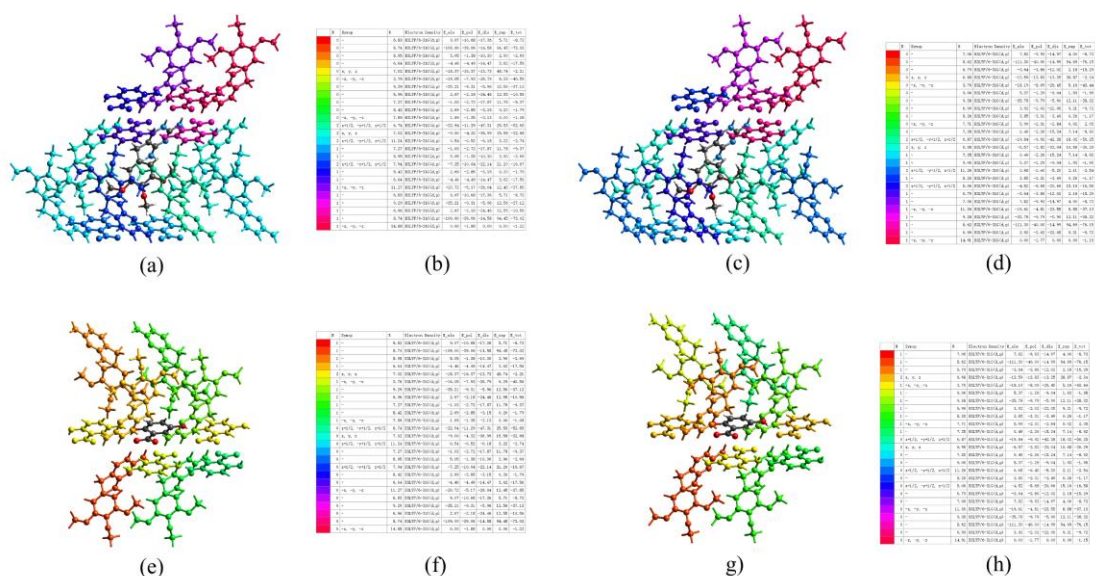


Figure S6. (a) and (b) are the energy calculation results of TMP in TMP-25HBA<sup>LT</sup>; (e) and (f) are the energy calculation results of 25HBA in TMP-25HBA<sup>LT</sup>; (c) and (d) are the energy calculation results of TMP in TMP-25HBA<sup>HT</sup>; (g) and (h) are the energy calculation results of 25HBA in TMP-25HBA<sup>HT</sup>;

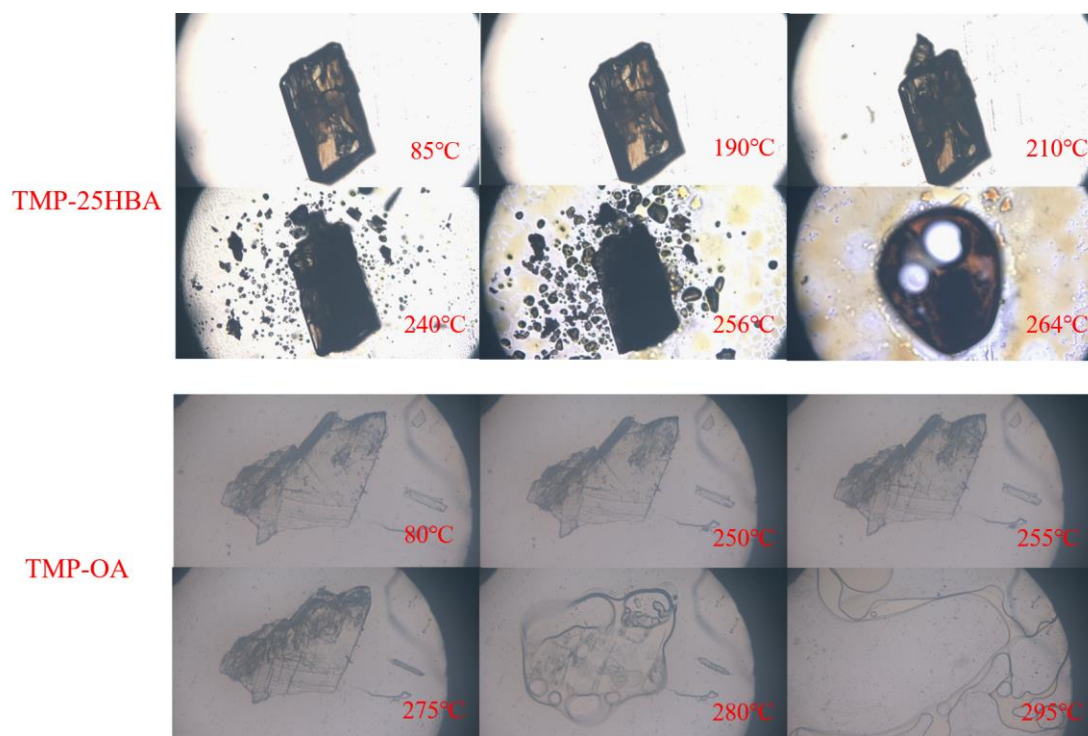


Figure S7. The melting point of the crystal was determined by HSM (To prevent the crystal from jumping out of sight, the crystal was covered with a glass sheet.) and the T(TS)/T(melting) was calculated. T(TS)/T(melting) of TMP-25HBA is 456.15K/513.15K (0.8889). T(TS)/T(melting) of TMP-OA is 533.15K/553.15K (0.9638).

**Table S1. Crystallographic Parameters of TMP-25HBA and TMP-OA.**

Compound	TMP-25HBA	TMP-25HBA	TMP-OA
Empirical formula	C <sub>21</sub> H <sub>24</sub> N <sub>4</sub> O <sub>7</sub>	C <sub>21</sub> H <sub>24</sub> N <sub>4</sub> O <sub>7</sub>	C <sub>19</sub> H <sub>22</sub> N <sub>6</sub> O <sub>7</sub>
Formula weight	444.44	444.44	446.42
Temperature (K)	113.15	463	113.15
Crystal system	monoclinic	monoclinic	Triclinic
Space group	P 2 <sub>1</sub> /n	P 2 <sub>1</sub> /n	P $\bar{1}$
a (Å)	7.0172(3)	6.977(3)	7.0878(6)
b (Å)	28.2186(13)	28.295(9)	7.5969(7)
c (Å)	10.7877(5)	11.103(4)	18.9464(14)
$\alpha$ (°)	90	90	91.152(7)
$\beta$ (°)	103.469(5)	103.232(12)	98.566(7)
$\gamma$ (°)	90	90	103.763(8)
Volume (Å <sup>3</sup> )	2077.38(17)	2133.6(13)	978.19(15)
Z	4	4	2
$P_{\text{calc}}$ (g/cm <sup>3</sup> )	1.421	1.384	1.516
$F(000)$	936	936	468
Reflections collected	26572	19659	14852
Goodness-of-fit on $F^2$	1.041	1.029	1.055
$R_{\text{int}}$	0.0853	0.0578	0.0607
$R_1$ indexes [ $I > 2\sigma(I)$ ]	0.0659	0.0638	0.0757
w $R_2$ indexes [all data]	0.1675	0.1886	0.2146
CCDC	2221421	2244908	2221420

**Table S2. Cell parameters of TMP-25HBA at different temperatures.**

Temperature (°C)	a	b	c	$\alpha$	$\beta$	$\gamma$	V
110	6.987	28.278	11.033	90.00	103.284	90.00	2121.555
130	6.984	28.282	11.054	90.00	103.271	90.00	2125.095
150	6.981	28.287	11.069	90.00	103.258	90.00	2127.555
170	6.979	28.291	11.088	90.00	103.245	90.00	2131.011
190	6.976	28.295	11.103	90.00	103.232	90.00	2133.392
210	6.974	28.299	11.122	90.00	103.219	90.00	2136.846

**Table S3. Cell parameters of TMP-OA at different temperatures.**

Temperature (°C)	a	b	c	$\alpha$	$\beta$	$\gamma$	V
175	7.5481	6.5489	18.9966	89.2995	93.7351	111.6612	870.8040
200	7.5516	6.5390	18.9982	89.2247	93.9695	111.5459	870.4046
225	7.5578	6.5296	19.0061	90.0603	93.4399	111.3246	872.1527
240	7.6024	6.5196	19.0187	89.2675	94.0260	111.0532	877.4877
255	7.7263	6.4637	19.0194	89.7826	93.4981	111.3522	882.9788
265	7.7250	6.4646	19.0156	89.9898	93.5448	110.8484	885.7546

**Movie S1:** Heating of TMP-25HBA starting at 180°C (heating rate 10 K/min).

**Movie S2:** Heating of TM-OA in cycle1 starting at 250°C (heating rate 10 K/min).

**Movie S3:** Cooling of TMP-OA in cycle1 starting at 234°C (cooling rate 10 K/min).

**Movie S4:** Heating of TM-OA in cycle2 starting at 248°C (heating rate 10 K/min).

**Movie S5:** Cooling of TMP-OA in cycle2 starting at 238°C (cooling rate 10 K/min).