

## Supporting Information

# Halogenation triggering rules in hybrids for fluorescence and dielectric phase transitions

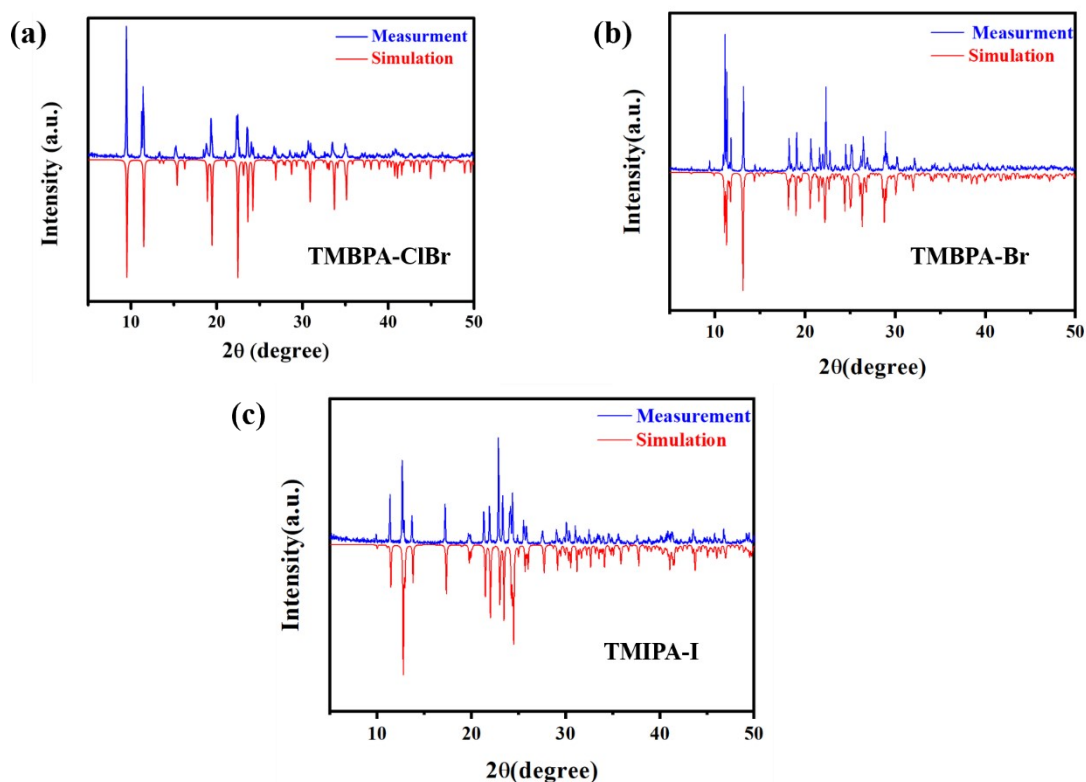
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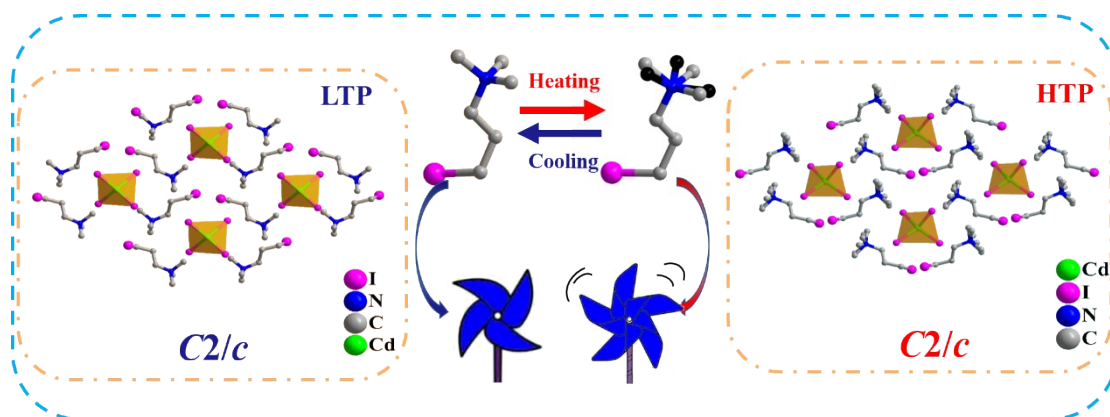
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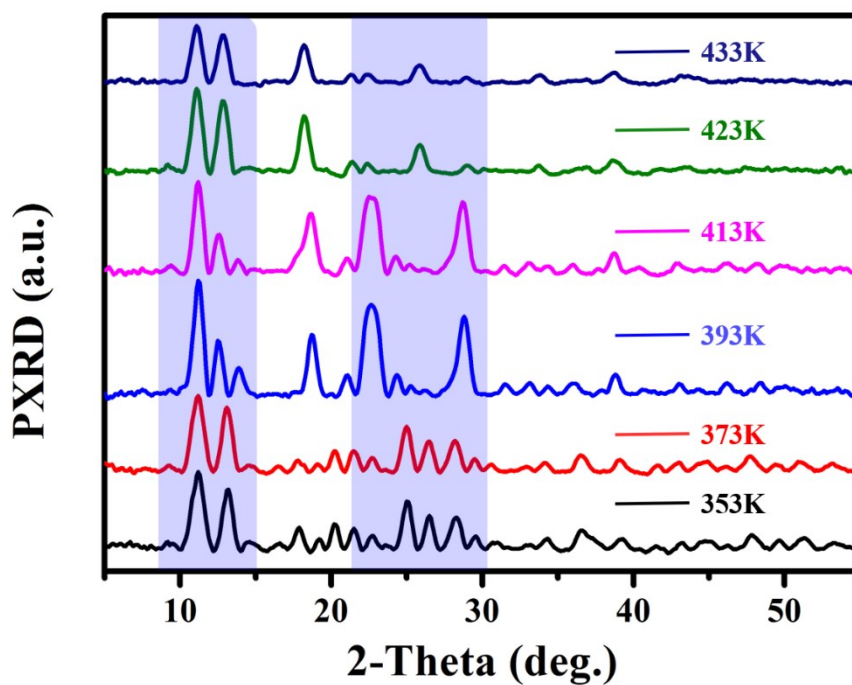
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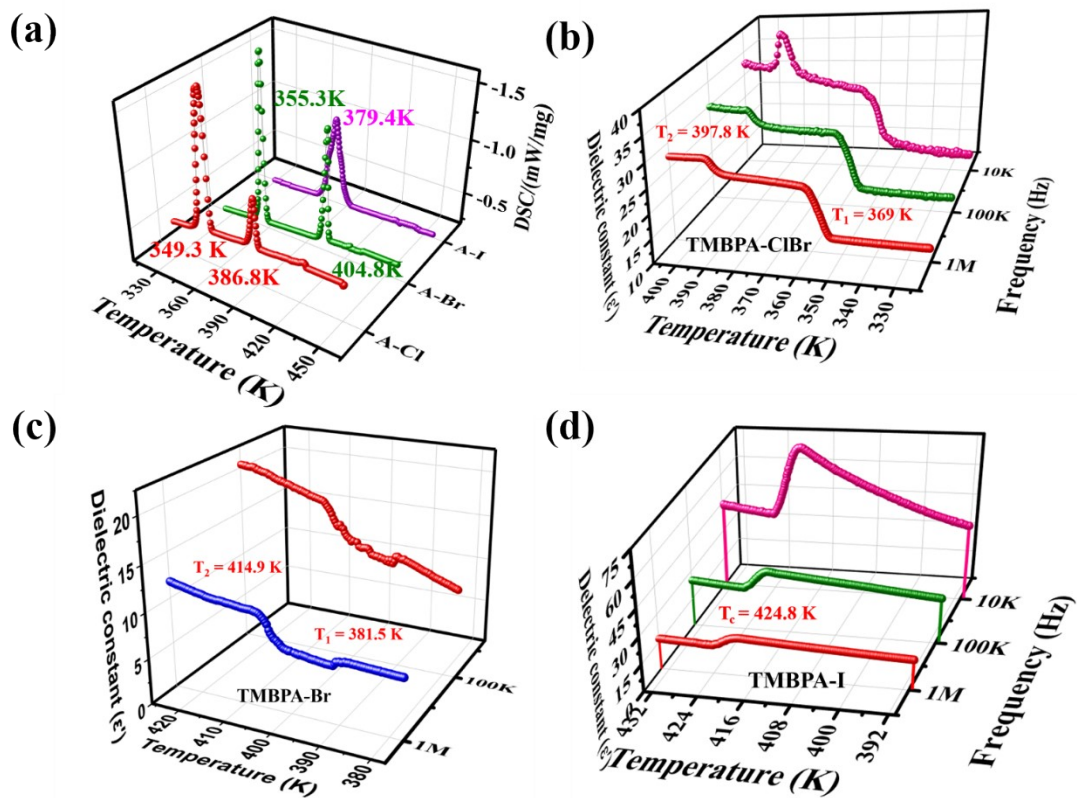
**Figure S1.** PXRD patterns of (a) TMBPA - ClBr, (b) TMBPA - Br, and (c) TMIPA - I at room temperatures.



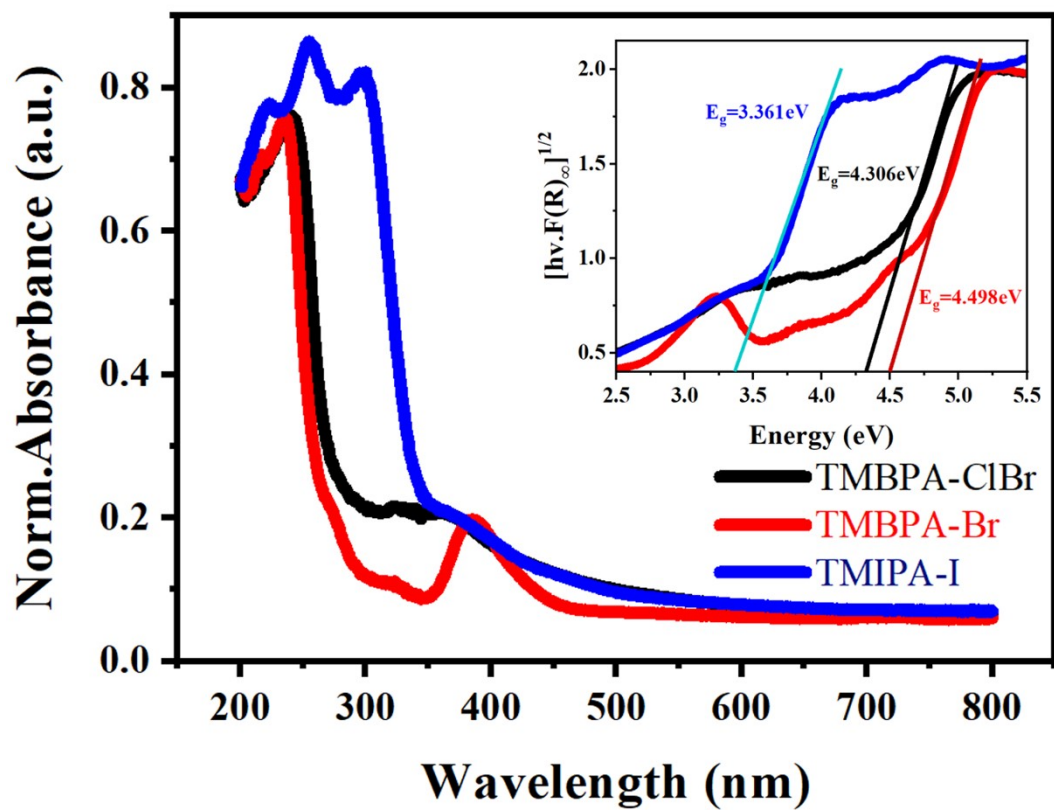
**Figure S2.** The crystal structures (without hydrogen atoms) of TMIPA-I in LTP and HTP.



**Figure S3.** Variable-temperature powder X-ray diffraction (PXRD) patterns of TMBPA-Br measured in the temperature range of 353-433 K.



**Figure S4.** (a) DSC curves of TMBPA - ClBr, TMBPA - Br, and TMBPA - I recorded on cooling. Dielectric constant of (b) TMBPA - ClBr, (c) TMBPA - Br, and (d) TMBPA - I recorded at different frequencies.



**Figure S5.** Ultraviolet-vis absorption spectrum of compounds. Inset: Tauc plot.

**Table S1.** Crystallographic data and structure refinement details of  
TMBPA–ClBr in high and low temperatures.

TMBPA-ClBr	LTP	ITP	HTP
CCDC Code	2220969	2220970	2220971
Formula	C <sub>6</sub> H <sub>15</sub> Br <sub>2</sub> CdCl <sub>2</sub> N	Br <sub>2</sub> C <sub>6</sub> CdCl <sub>2</sub> N	Br <sub>2</sub> C <sub>6</sub> CdCl <sub>2</sub> N
Fw	444.31	429.19	429.19
Temperature	295 K	385.15 K	405.15 K
Crystal Syst	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>Cmcm</i>	<i>Cmcm</i>
<i>a</i> (Å)	11.635(3)	15.411(14)	15.479(5)
<i>b</i> (Å)	7.3428(14)	11.677(9)	11.741(3)
<i>c</i> (Å)	15.379(4)	7.365(7)	7.402(2)
$\alpha$ /°	90	90	90
$\beta$ /°	90	90	90
$\gamma$ /°	90	90	90
<i>V</i> (Å <sup>3</sup> )	1314.0(5)	1325(2)	1345.2(7)
Z	4	4	4
$\mu$ (mm <sup>-1</sup> )	8.108	8.035	7.917
GOF on F <sup>2</sup>	1.052	1.194	1.250
<i>R</i> <sub>1</sub> [[ <i>I</i> > 2σ( <i>I</i> )]	0.0668	0.1080	0.0981
<i>wR</i> <sub>2</sub> (all data)	0.2261	0.2650	0.2398

**Table S2.** Crystallographic data and structure refinement details of  
TMBPA-Br in high and low temperatures.

TMBPA - Br	LTP	ITP
CCDC Code	2220972	2220973
Formula	C <sub>18</sub> H <sub>45</sub> Br <sub>9</sub> Cd <sub>1.5</sub> N <sub>3</sub>	C <sub>12</sub> H <sub>30</sub> Br <sub>6</sub> CdN <sub>2</sub>
Fw	1191.36	794.24
Temperature	288 K	385.15 K
Crystal Syst	Monoclinic	Monoclinic
Space group	<i>P2/c</i>	<i>C2/c</i>
<i>a</i> (Å)	24.015(7)	33.148(18)
<i>b</i> (Å)	9.642(3)	9.669(6)
<i>c</i> (Å)	16.046(4)	15.960(8)
$\alpha$ /°	90	90
$\beta$ /°	91.474(5)	96.244(9)
$\gamma$ /°	90	90
<i>V</i> (Å <sup>3</sup> )	3714.4(18)	5085(5)
<i>Z</i>	4	4
$\mu$ (mm <sup>-1</sup> )	10.560	10.286
GOF on F <sup>2</sup>	1.008	0.989
<i>R</i> <sub>1</sub> [[ <i>I</i> > 2σ( <i>I</i> )]	0.0408	0.0785
<i>wR</i> <sub>2</sub> (all data)	0.1013	0.2746

**Table S3.** Crystallographic data and structure refinement details of  
TMIPA-I in high and low temperatures.

TMIPA - I	LTP	HTP
CCDC Code	2220974	2220975
Formula	C <sub>12</sub> H <sub>30</sub> CdI <sub>6</sub> N <sub>2</sub>	C <sub>12</sub> H <sub>30</sub> CdI <sub>6</sub> N <sub>2</sub>
Fw	1076.18	1076.18
Temperature	223 K	427 K
Crystal Syst	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> (Å)	16.090(2)	16.423(5)
<i>b</i> (Å)	9.3746(12)	9.478(2)
<i>c</i> (Å)	18.4146(19)	18.835(5)
$\alpha$ /°	90	90
$\beta$ /°	106.203(6)	106.070(5)
$\gamma$ /°	90	90
<i>V</i> (Å <sup>3</sup> )	2667.3(6)	2817.3(13)
<i>Z</i>	4	4
$\mu$ (mm <sup>-1</sup> )	7.762	7.348
GOF on F <sup>2</sup>	1.070	1.044
<i>R</i> <sub>1</sub> [[ <i>I</i> > 2σ( <i>I</i> )]	0.0231	0.0484
<i>wR</i> <sub>2</sub> (all data)	0.0484	0.1676

**Table S4.** The key bond distances (Å) of TMBPA-ClBr at 288 K, 385.15 K and 405.15 K.

Temperature	Bond distances [Å]			
288 K	Cd1-Br2	2.5581(16)	N1-C3	1.463(14)
	Cd1-Cl1	2.6151(13)	N1-C2	1.476(19)
	Cd1-Cl11	2.6151(13)	N1-C24	1.476(19)
	Cd1-Cl12	2.6397(13)	N1-C1	1.512(11)
	Cd1-Cl13	2.6397(13)	N1-C14	1.512(11)
	Br1-C6	1.927(10)	C4-C5	1.507(12)
	N1-C4	1.455(12)	C6-C5	1.500(12)
385.15 K	Br1-C2	1.509(10)	Cd1-Br2	2.524(7)
	Br1-C4	1.466(10)	Cd1-Cl1	2.636(4)
	Br1-C31	1.476(10)	Cd1-Cl12	2.636(4)
	Br1-C3	1.476(10)	Cd1-Cl13	2.636(4)
	C2 - C1	1.565(10)	Cd1-Cl14	2.636(4)
405.15 K	Br1-C1	1.475(10)	C4-C5	1.543(9)
	Br1-C11	1.475(10)	Br2-Cd1	2.538(5)
	Br1-C2	1.467(9)	Cd1-Cl1	2.649(3)
	Br1-C3	1.472(9)	Cd1-Cl12	2.649(3)
	Br1-C31	1.472(9)	Cd1-Cl13	2.649(3)
	Br1-C4	1.898(16)	Cd1-Cl14	2.649(3)
	C1-C11	2.03(3)		



**Table S5.** The key bond distances (Å) of TMBPA-Br at 288 K and 383 K.

Temperature	Bond distances [Å]			
288 K	Cd2-Br10	2.6102(10)	N1-C1	1.509(8)
	Cd2-Br101	2.6102(10)	N1-C3	1.493(9)
	Cd2-Br81	2.5653(10)	N1-C4	1.532(10)
	Cd2-Br8	2.5654(10)	N1-C2	1.493(9)
	Cd1-Br7	2.6193(11)	N2-C10	1.521(9)
	Cd1-Br6	2.6001(11)	N2-C9	1.502(9)
	Cd1-Br5	2.5758(11)	N2-C8	1.514(10)
	Cd1-Br4	2.5728(11)	N2-C7	1.461(11)
	Br2-C12	1.933(8)	C10-C11	1.498(10)
	Br9-C6	1.950(8)	C11-C12	1.519(10)
	Br3-C18	1.927(10)	C16-C17	1.502(11)
	N3-C16	1.520(9)	C4-C5	1.497(11)
	N3-C15	1.498(9)	C6-C5	1.495(11)
	N3-C14	1.480(10)	C17-C18	1.521(12)
	N3-C13	1.506(10)		
383 K	Cd1-Br5	2.624(2)	N1-C5	1.48(3)
	Cd1-Br7	2.601(2)	C1-C10	1.537(9)
	Cd1-Br6	2.580(3)	C1-C3	1.538(19)
	Cd1-Br8	2.576(3)	C10-C12	1.535(9)
	Br4-C12	1.949(10)	Br2-C11	1.844(9)
	N2-C1	1.50(2)	C9-C5	1.559(7)
	N2-C4	1.49(2)	C9-C11	1.560(7)
	N2-C6	1.47(2)	C5-C7	1.596(16)
	N2-C8	1.51(2)	C3-C13	1.537(19)
	N1-C14	1.46(3)	C13-Br3	1.951(10)
	N1-C16	1.44(3)	C7-C15	1.630(15)
N1-C2	1.47(3)	C15-Br1	1.655(15)	

**Table S6.** The key bond distances (Å) of TMIPA-I at 223 K and 427 K.

Temperature	Bond distances [Å]			
223 K	I1-C6	2.161(3)	C4-C5	1.517(4)
	N1-C4	1.509(4)	C5-C6	1.515(5)
	N1-C2	1.498(4)	I3-Cd1	2.7744(3)
	N1-C1	1.502(4)	I2-Cd1	2.7934(4)
	N1C3	1.489(5)		
427 K	Cd1-I3	2.7932(9)	N1-C6	1.503(16)
	Cd1-I31	2.7932(9)	N1-C4	1.513(12)
	Cd1-I2	2.7702(9)	N1-C7	1.496(12)
	Cd1-I21	2.7702(9)	N1-C5	1.502(15)
	I1-C1	2.098(11)	N1-C8	1.500(15)
	N1-C3	1.558(12)	C3-C2	1.468(13)
	N1-C9	1.494(12)	C2-C1	1.517(16)

**Table S7.** The key angles (°) of TMBPA-ClBr at 288 K, 385.15 K and

## 405.15 K.

Temperature	angles (°)			
295 K	Br2-Cd1-Cl1	107.03(4)	C4-N1-C14	108.8(7)
	Br2-Cd1-Cl11	107.03(4)	C4-N1-C1	108.8(7)
	Br2-Cd1-Cl12	105.39(4)	C3-N1-C24	119.5(17)
	Br2-Cd1-Cl13	105.39(4)	C3-N1-C2	119.5(17)
	Cl11-Cd1-Cl12	82.38(5)	C3-N1-C14	105.4(8)
	Cl11-Cd1-Cl13	147.54(3)	C3-N1-C1	105.4(8)
	Cl12-Cd1-Cl13	87.59(6)	C24-N1-C2	37(4)
	Cl1-Cd1-Cl12	147.54(3)	C24-N1-C14	39.9(15)
	Cl1-Cd1-Cl11	89.72(6)	C2-N1-C14	76(2)
	Cl1-Cd1-Cl13	82.38(5)	C14-N1-C1	116.4(16)
	Cd1-Cl1-Cd13	97.62(5)	N1-C4-C5	118.4(7)
	C4-N1-C3	112.0(8)	C5-C6-Br1	112.4(7)
	C4-N1-C2	124.6(17)	C6-C5-C4	108.6(9)
	C4-N1-C24	124.6(17)		
385.15 K	C4-Br1-C2	99(4)	Br2-Cd1-Cl14	106.24(6)
	C4-Br1-C3	134(2)	Br2-Cd1-Cl15	106.24(6)
	C4-Br1-C31	134(2)	Cl13-Cd1-Cl14	88.59(15)
	C3-Br1-C2	88.5(11)	Cl13-Cd1-Cl1	147.53(11)
	C31-Br1-C2	88.5(11)	Cl15-Cd1-Cl1	88.59(15)
	C3-Br1-C31	91(5)	Cl14-Cd1-Cl1	82.42(17)
	Br1-C2-C1	146.2(19)	Cl13-Cd1-Cl15	82.42(17)
	C22-C1-C2	152(4)	Cl15-Cd1-Cl14	147.53(11)
	Br2-Cd1-Cl13	106.24(6)	Cd1-Cl1-Cd14	97.58(17)
	Br2-Cd1-Cl1	106.24(6)		
	C1-Br1-Cl11	87.1(18)	C5-C4-Br1	117.9(10)
	C11-Br1-C4	89.9(14)	C42-C5-C4	109.6(16)
	C1-Br1-C4	89.9(14)	Br2-Cd1-Cl1	106.23(4)
	C2-Br1-C1	136.4(9)	Br2-Cd1-Cl13	106.23(4)
C2-Br1-C11	136.4(9)	Br2-Cd1-Cl14	106.23(4)	
C2-Br1-C3	109.0(14)	Br2-Cd1-Cl15	106.23(4)	
405.15 K	C2-Br1-C31	109.0(14)	Cl14-Cd1-Cl13	82.41(13)
	C2-Br1-C4	92.7(11)	Cl13-Cd1-Cl1	88.62(11)
	C3-Br1-C4	75.9(9)	Cl15-Cd1-Cl1	82.41(13)
	C31-Br1-C4	75.9(9)	Cl14-Cd1-Cl1	147.55(9)
	Br1-C1-C1	46.4(9)	Cd15-Cl1-Cd1	97.58(13)

Table S8. The key angles (°) of TMBPA-Br at 288 K and 383 K.

Temperature	angles (°)			
288 K	Br10-Cd2-Br101	106.48(5)	C3-N1-C4	113.0(6)
	Br81-Cd2-Br101	109.95(3)	C2-N1-C1	108.7(6)
	Br8-Cd2-Br10	109.95(3)	C2-N1-C3	109.3(6)
	Br8-Cd2-Br101	103.01(4)	C2-N1-C4	105.8(6)
	Br81-Cd2-Br10	103.01(4)	C9-N2-C10	111.0(6)
	Br81-Cd2-Br8	123.52(5)	C9-N2-C8	108.4(6)
	Br6-Cd1-Br7	106.76(4)	C8-N2-C10	107.6(6)
	Br5-Cd1-Br7	107.71(4)	C7-N2-C10	111.5(6)
	Br5-Cd1-Br6	109.90(4)	C7-N2-C9	109.3(7)
	Br4-Cd1-Br7	105.66(4)	C7-N2-C8	109.0(7)
	Br4-Cd1-Br6	110.06(4)	C11-C10-N2	116.2(6)
	Br4-Cd1-Br5	116.23(4)	C10-C11-C12	108.6(6)
	C15-N3-C16	110.3(6)	C17-C16-N3	115.5(7)
	C15-N3-C13	108.6(6)	C5-C4-N1	115.9(7)
	C14-N3-C16	112.2(6)	C11-C12-Br2	112.3(5)
	C14-N3-C15	110.1(6)	C5-C6-Br9	114.3(6)
	C14-N3-C13	107.9(6)	C6-C5-C4	112.9(7)
	C13-N3-C16	107.5(6)	C16-C17-C18	114.2(8)
	C1-N1-C4	110.5(6)	C17-C18-Br3	112.3(7)
	C3-N1-C1	109.3(6)		
383 K	Br7-Cd1-Br5	106.33(9)	C16-N1-C2	109(2)
	Br6-Cd1-Br5	106.21(9)	C16-N1-C5	112(2)
	Br6-Cd1-Br7	108.13(9)	C2-N1-C5	98(2)
	Br8-Cd1-Br5	104.30(10)	N2-C1-C10	115.9(17)
	Br8-Cd1-Br7	109.78(10)	N2-C1-C	119(7)
	Br8-Cd1-Br6	121.08(11)	C12-C10-C1	112.0(19)
	C1-N2-C8	109.2(15)	C10-C12-Br4	110.6(14)
	C4-N2-C1	113.7(15)	C5-C9-C11	84(4)
	C4-N2-C8	110.2(16)	N1-C5-C9	117(3)
	C6-N2-C1	108.3(15)	N1-C5-C7	110(2)
	C6-N2-C4	110.0(15)	C9-C11-Br2	111(5)
	C6-N2-C8	105.1(15)	C13-C3-C1	132(10)
	C14-N1-C2	110(2)	C3-C13-Br3	103(10)
	C14-N1-C5	112(2)	C5-C7-C15	105.8(19)
	C16-N1-C14	115(2)	C7-C15-Br1	116.0(18)

**Table S9. The key angles (°) of TMIPA-I at 223 K and 427 K.**

Temperature	angles (°)			
223 K	C2-N1-C4	108.4(2)	C5-C6-I1	113.7(2)
	C2-N1-C1	107.7(3)	I3-Cd1-I31	112.378(17)
	C1-N1-C4	111.4(3)	I3-Cd1-I21	107.748(11)
	C3-N1-C4	110.4(3)	I31-Cd1-I21	109.370(10)
	C3-N1-C2	108.5(3)	I3-Cd1-I2	109.370(10)
	C3-N1-C1	110.4(3)	I31-Cd1-I2	107.748(11)
	N1-C4-C5	115.6(3)	I21-Cd1-I2	110.230(17)
	C6-C5-C4	111.7(3)		
427 K	I3-Cd1-I31	110.62(4)	C4-N1-C3	110.9(11)
	I2-Cd1-I3	107.87(3)	C7-N1-C3	111.0(10)
	I21-Cd1-I31	107.87(3)	C7-N1-C5	97(2)
	I2-Cd1-I31	108.42(3)	C7-N1-C8	87(2)
	I21-Cd1-I3	108.42(3)	C5-N1-C3	112.6(19)
	I2-Cd1-I21	113.65(5)	C8-N1-C3	109(2)
	C9-N1-C3	103.8(10)	C8-N1-C5	133(3)
	C9-N1-C6	135(4)	C2-C3-N1	117.6(8)
	C9-N1-C4	96.0(17)	C3-C2-C1	112.9(10)
	C6-N1-C3	109(3)	C2-C1-I1	116.3(8)
	C6-N1-C4	100(4)		