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Electronic Supplementary Information

A muconic acid derivative organic-inorganic metal halide with high-temperature phase transition

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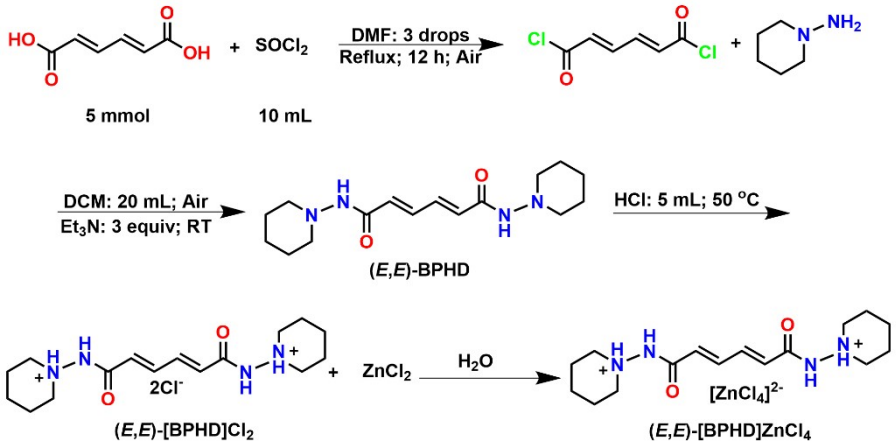

Fig. S1 The preparation procedure of (*E*,*E*)-[BPHD]$ZnCl_4$.

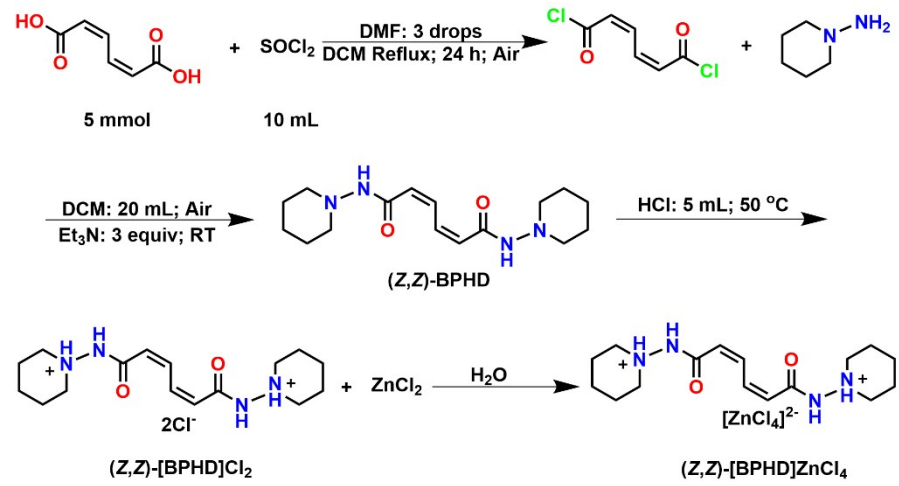

Fig. S2 The preparation procedure of (*Z*,*Z*)-[BPHD]$ZnCl_4$.

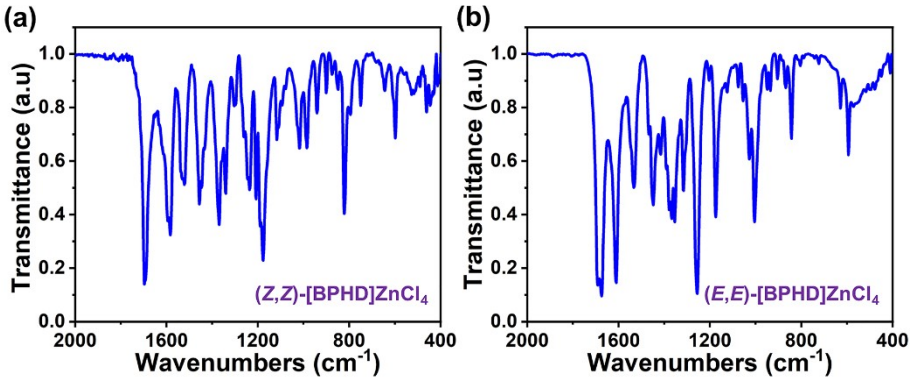

Fig. S3 The Infrared spectrums of (*Z*,*Z*)-[BPHD]$ZnCl_4$ (a) and (*E*,*E*)-[BPHD]$ZnCl_4$ (b) at room temperature.

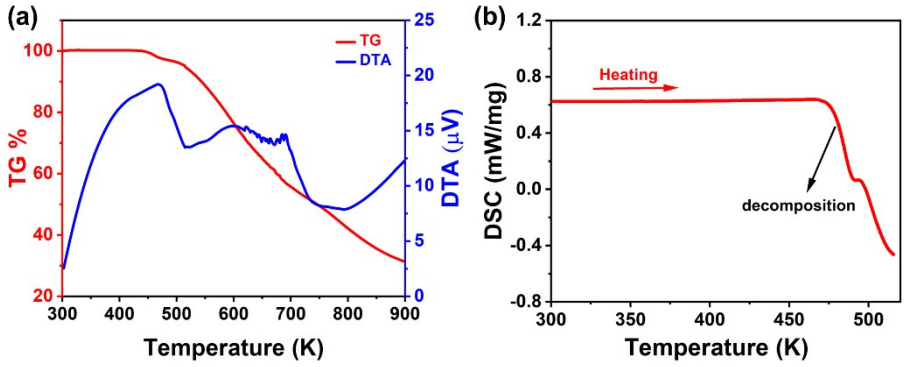

Fig. S4 The TG-DTA (a) and DSC (b) curves of (*Z*,*Z*)-[BPHD]$ZnCl_4$.

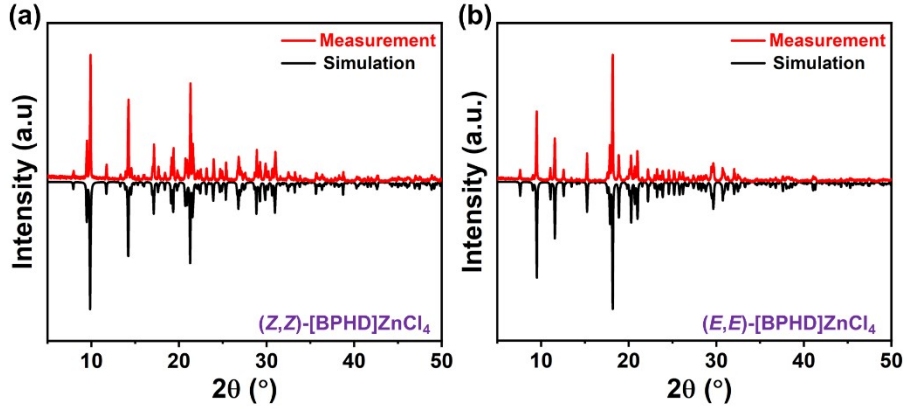

Fig. S5 The PXRD patterns of (*Z*,*Z*)-[BPHD]$ZnCl_4$ (a) and (*E*,*E*)-[BPHD]$ZnCl_4$ (b) at room temperature.

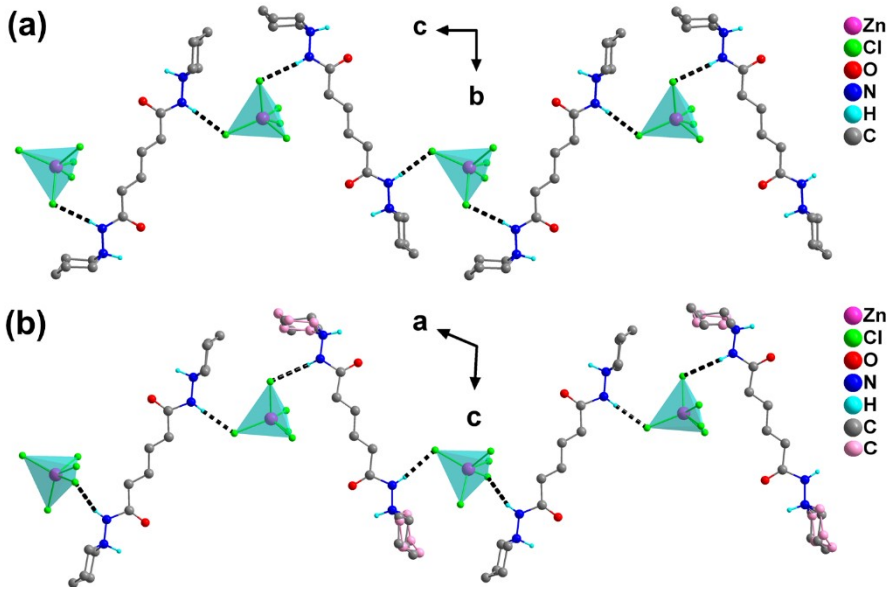

Fig. S6 The zigzag hydrogen-bonded chain of (*E*,*E*)-[BPHD]$ZnCl_4$ in LTP (a) and HTP (b). For clarity, some H atoms are omitted. The black dotted lines represent hydrogen bonds.

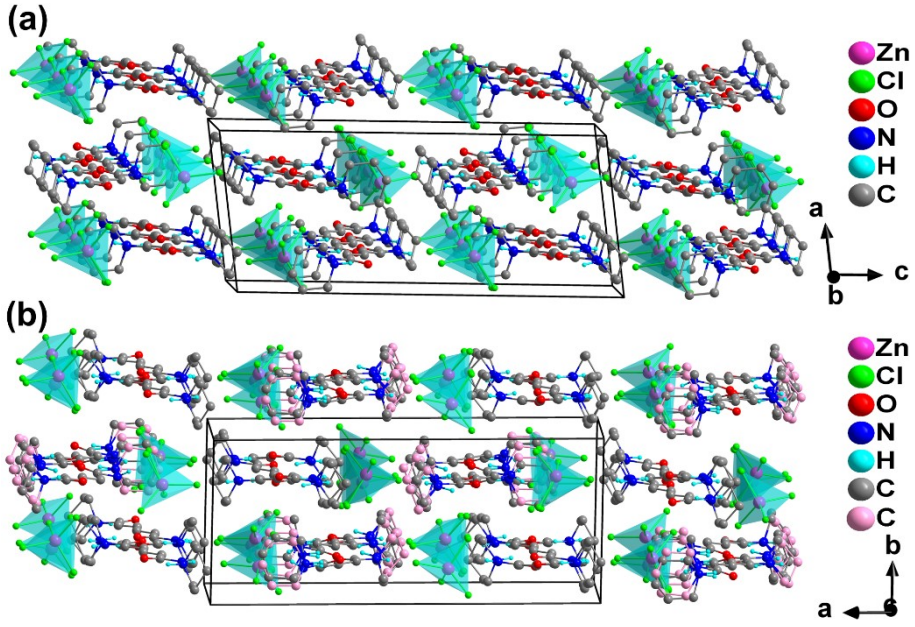

Fig. S7 The packing diagrams of (*E*,*E*)-[BPHD]$ZnCl_4$ at LTP (a) and HTP (b). For clarity, some H atoms are omitted.

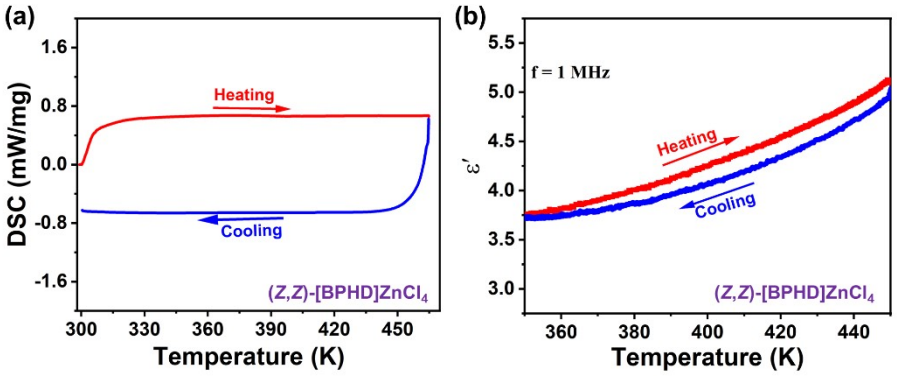

Fig. S8 DSC curves (a) and temperature dependence of the real part of the dielectric constants (ε′) (b) of (*Z*,*Z*)-[BPHD]$ZnCl_4$.

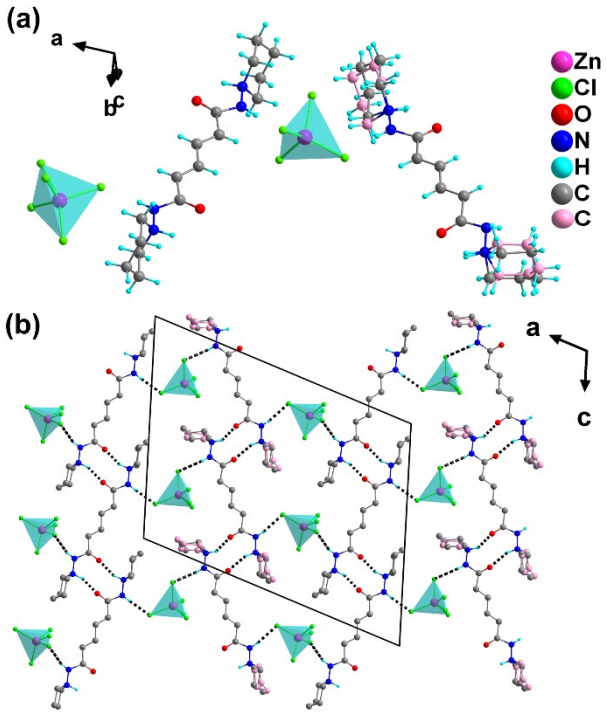

Fig. S9 The asymmetric unit (a) and packing diagrams along *b*-axis (b) of (*E*,*E*)-[BPHD]$ZnCl_4$ at 458 K. For clarity, the C-H bonds in (b) are omitted. The black dotted lines represent hydrogen bonds.

Table S1. The T_c of some typical OIMH phase transition materials including the Zn-based ones.

Compounds	T_c	**References**
$[(CH_3)_3N(CH_2)_2Cl]_2ZnCl_4$	333 K	1
$[(CH_3)_3NCH_2Cl]_2ZnCl_4$	258 K and 337 K	2
$[CH_3CH_2NH_3]_2ZnCl_4$	231 K, 234 K, 237 K, 247 K and 312 K	3
$[(CH_2)_4N(CH_2)_5]_2ZnBr_4$	380 K	4
$[(CH_3)_3NCH_2Br]_2ZnBr_4$	387 K	5
$[NH_3(CH_2)_6NH_3]ZnBr_4$	370 K and 430 K	6
$[(CH_3)_3CN(CH_3)_2CH_2F]_2ZnBr_4$	235 K and 262 K	7
$[4\text{-}(CH_3O)(C_6H_4)CH_2NH_3]_2ZnI_4$	359.55 K	8
$[CH_3N(CH_2CH_2)_3NCH_3]ZnI_4$	296.8 K	9
$[4\text{-}F\text{-}(C_6H_4)(CH_2)_2NH_3]_2CuCl_4$	348 K and 393 K	10
$[(CH_2CF_2CH_2CH_2)NH_2]CuCl_4$	380 K	11
$[(CH_3)_3NCH_2Cl]MnCl_3$	406 K	12
$[(CH_2)_4NH_2]MnBr_3$	219 K	13
$[NH_3CH_2CH_2F]_3BiCl_6$	361.5 K	14
$[CH_3CH_2NH_3]_2BiBr_5$	120 K and 160 K	15
$[(CH_2)_4NH_2]_2SbCl_5$	236 K, 248 K and 255 K	16
$[2\text{-}(H_3NCH_2)(C_5H_4NH)]SbI_5$	360 K and 390 K	17
$[CH_3CH_2NH_3]_4Pb_3Cl_{10}$	415 K	18
$[ICH_2N(CH_3)_3]PbI_3$	312 K	19
$[I(CH_2)_3NH_2CH_3]_2PbI_4$	390 K	20
$[(CH_2CH_2)CF_2(CH_2CH_2)NH_2]_2PbI_4$	428.5 K	21
$[Br(CH_2)_3NH_3]_2SnCl_6$	284.24 K	22
$[Br(CH_2)_3NH_3]_2SnBr_6$	301.89 K	22
$[(CH_2)_4NHCH_3]_2SnBr_6$	352 K	23
$[CH_3PH_3]SnI_3$	298 K	24
$[(CH_3)_3NCH_2Cl]CdCl_3$	400 K	25
$[(CH_2)_4NHCH_3]CdCl_3$	254 K	26
$[(CH_2)_3NH_2]CdBr_3$	197 K, 231 K and 437 K	27
$[(CH_2CH{=}CHCH_2)NH_2]CdCl_3$	316 K	28
(*E*,*E*)-$[BPHD]ZnCl_4$	449.4 K	this work

Table S2. Crystal data and structure refinements for (*Z*,*Z*)-[BPHD]$ZnCl_4$ at 293 K and (*E*,*E*)-[BPHD]$ZnCl_4$ at 293 K and 458 K.

	(*Z*,*Z*)-[BPHD]$ZnCl_4$	**(*E*,*E*)-[BPHD]$ZnCl_4$**	
Temperature	**293 K**	**293 K**	**458 K**
Weight	515.59	515.59	515.59
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	12.5308(2)	9.8459(1)	25.3180(14)
b/Å	15.1230(2)	10.1619(1)	9.9961(5)
c/Å	13.3651(2)	23.4264(3)	20.3268(1)
α/°	90	90	90
β/°	117.152(2)	97.414(1)	109.869(6)
γ/°	90	90	90
Volume/Å^3	2253.6(1)	2324.3(1)	4838.1(5)
Z	4	4	8
R1 [I>2σ(I)]	0.0274	0.0641	0.1440
wR2 [I>2σ(I)]	0.0713	0.1433	0.2837
GOF	1.044	1.081	1.084

Table S3. Selected bond lengths/Å and bond angles/° for compound (*Z*,*Z*)-[BPHD]$ZnCl_4$ at 293 K.

Temperature	**Bond lengths**		**Bond angles**	
293 K	Zn1—Cl1	2.313(5)	Cl1—Zn1—Cl2	106.22(2)
	Zn1—Cl2	2.250(5)	Cl1—Zn1—Cl3	109.31(2)
	Zn1—Cl3	2.270(5)	Cl1—Zn1—Cl4	104.13(2)
	Zn1—Cl4	2.279(5)	Cl2—Zn1—Cl3	111.35(2)
			Cl2—Zn1—Cl4	114.57(2)
			Cl3—Zn1—Cl4	110.80(2)

Table S4. Selected bond lengths/Å and bond angles/° of hydrogen bonding for (*Z*,*Z*)-[BPHD]$ZnCl_4$ at 293 K.

D—H···A	**D—H**	**H···A**	**D···A**	**D—H···A**
N1—H1···Cl1	0.88	2.37	3.214(2)	160
N2—H2···Cl3^{i}	0.79	2.47	3.254(2)	178
N3—H3···Cl4	0.92	2.29	3.143(2)	155
N4—H4···Cl1^{ii}	1.04	2.34	3.297(2)	154

Symmetry codes: $^{(i)}$ 1-x, 1-y, 1-z; $^{(ii)}$ x, 3/2-y, 1/2+z.

Table S5. Selected bond lengths/Å and bond angles/° for compound (*E*,*E*)-[BPHD]$ZnCl_4$ at 293 K.

Temperature	Bond lengths		Bond angles	
293 K	Zn1—Cl1	2.252(1)	Cl1—Zn1—Cl2	111.78(6)
	Zn1—Cl2	2.290(1)	Cl1—Zn1—Cl3	104.14(6)
	Zn1—Cl3	2.307(2)	Cl1—Zn1—Cl4A	117.35(2)
	Zn1—Cl4A	2.273(7)	Cl1—Zn1—Cl4B	104.03(4)
	Zn1—Cl4B	2.240(4)	Cl4A—Zn1—Cl2	114.17(2)
			Cl4B—Zn1—Cl3	120.88(6)
			Cl4B—Zn1—Cl2	107.74(2)
			Cl4A—Zn1—Cl3	99.26(2)
			Cl3—Zn1—Cl2	108.16(6)

Table S6. Selected bond lengths/Å and bond angles/° of hydrogen bonding (*E*,*E*)-[BPHD]$ZnCl_4$ at 293 K.

D—H…A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.98	1.99	2.914(4)	156
N2—H2···Cl2	0.86	2.31	3.166(3)	173
N3—H3···Cl3^{iii}	0.86	2.45	3.307(3)	175
N4—H4···O1^{ii}	0.98	1.86	2.732(4)	146

Symmetry codes: $^{(i)}$ x, -1+y, z; $^{(ii)}$ x, 1+y, z;$^{(iii)}$ x, 1/2-y, -1/2+z.

Table S7. Selected bond lengths/Å and bond angles/° for compound (*E*,*E*)-[BPHD]$ZnCl_4$ at 458 K.

Temperature	Bond lengths		Bond angles	
458 K	Zn1—Cl1	2.252(4)	Cl1—Zn1—Cl2	109.60(2)
	Zn1—Cl2	2.275(5)	Cl2—Zn1—Cl3	105.21(2)
	Zn1—Cl3	2.236(5)	Cl3—Zn1—Cl4A	99.12(3)
	Zn1—Cl4A	2.264(5)	Cl3—Zn1—Cl4B	112.07(3)
	Zn1—Cl4B	2.254(6)	Cl3—Zn1—Cl1	112.10(2)
	Zn2—Cl5	2.256(5)	Cl4A—Zn1—Cl1	101.82(2)
	Zn2—Cl6	2.287(3)	Cl4B—Zn1—Cl1	112.06(3)
	Zn2—Cl7	2.247(5)	Cl4A—Zn1—Cl2	128.47(2)
	Zn2—Cl8A	2.246(10)	Cl4B—Zn1—Cl2	105.31(3)
	Zn2—Cl8B	2.253(9)	Cl6—Zn2—Cl5	109.79(2))
			Cl6—Zn2—Cl7	110.63(2)
			Cl6—Zn2—Cl8A	104.82(3)
			Cl5—Zn2—Cl7	105.13(2)
			Cl5—Zn2—Cl8A	125.83(4)
			Cl5—Zn2—Cl8B	95.25(4)
			Cl6—Zn2—Cl8B	113.66(3)
			Cl7—Zn2—Cl8B	120.45(4)
			Cl7—Zn2—Cl8A	99.87(4)

Table S8. Selected bond lengths/Å and bond angles/° of hydrogen bonding (*E*,*E*)-[BPHD]$ZnCl_4$ at 458 K.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{ii}	0.98	1.94	2.868(11)	158
N2—H1B···Cl4B	0.86	2.48	3.229(14)	146
N3—H3···Cl6	0.86	2.23	3.086(9)	178
N4—H4···O1^{i}	0.98	1.94	2.868(11)	158
N5—H5A···O4^{i}	0.98	1.84	2.678(11)	142
N5—H5B···O4^{ii}	0.98	1.81	2.678(11)	147
N6—H6···Cl5^{iii}	0.86	2.71	3.310(9)	127
N7—H7···Cl1	0.86	2.35	3.207(9)	171
N8—H8A···O3^{ii}	0.98	2.11	3.006(12)	152
N8—H8B···O3^{ii}	0.98	2.12	3.006(12)	149

Symmetry codes: $^{(i)}$ x, 3/2-y, 1/2+z; $^{(ii)}$ x, 3/2-y, -1/2+z; $^{(iii)}$ -1+x, 3/2-y, -1/2+z.

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