Supplementary Information

Large barocaloric effects in two novel ferroelectric molecular plastic crystals

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1. Computation of the Entropy Curves

The entropy curve across the III to II and II to I phase transitions for HQuin is computed as follows:

$$S(T,p)=\begin{cases} S(T_0,p)+\int_{T_0}^{T}\frac{C_p^{III}}{T}dT & T_0\le T\le T_1(p) \\ S(T_1,p)+\int_{T_1}^{T}\frac{1}{T}\left(C_p+\frac{dQ}{dT}\right)dT & T_1(p)\le T\le T_2(p) \\ S(T_2,p)+\int_{T_2}^{T}\frac{C_p^{II}}{T}dT & T_2(p)\le T\le T_3(p) \\ S(T_3,p)+\int_{T_3}^{T}\frac{1}{T}\left(C_p^{*}+\frac{dQ}{dT}\right)dT & T_3(p)\le T\le T_4(p) \\ S(T_4,p)+\int_{T_4}^{T}\frac{C_p^{I}}{T}dT & T_4(p)\le T \end{cases}$$

Where $C_p=xC_p^{II}+(1-x)C_p^{III}$ and $C_p^{*}=x^{*}C_p^{I}+(1-x^{*})C_p^{II}$; x and x^{*} are the fraction of the sample in the phase II and I respectively, calculated as:

$$x(T,p)=\frac{\int_{T_1}^{T}\frac{1dQ}{TdT}dT}{\int_{T_1}^{T_2}\frac{1dQ}{TdT}dT}$$

where T_1 and T_2 are the starting and finishing temperatures of the transition peak in $\frac{1dQ}{TdT}$.

2. X-Ray diffraction

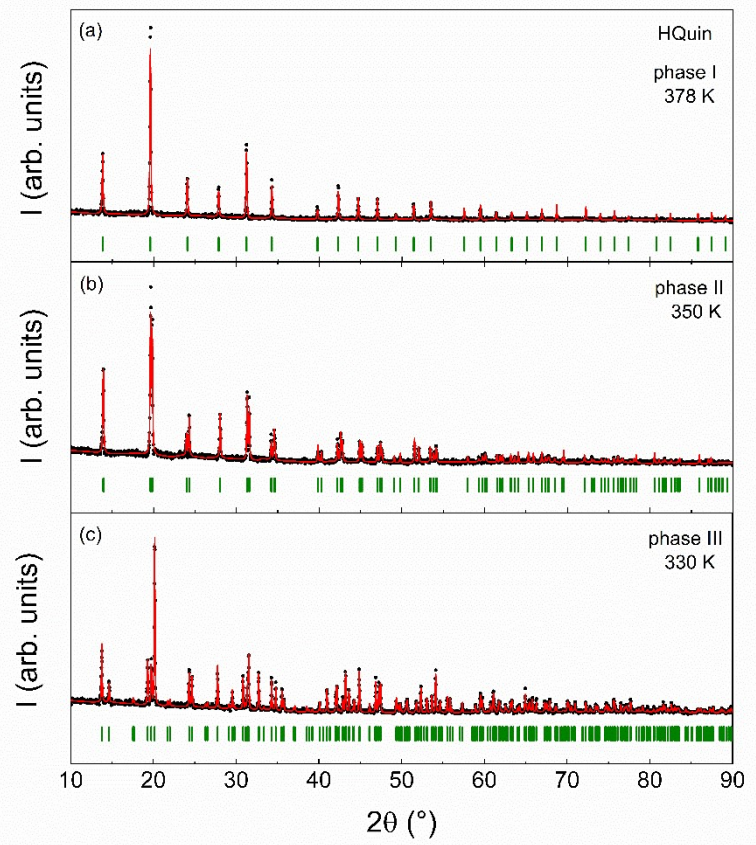

Fig. S1: XRPD patterns recorded at 378 K (phase I, panel a), 350 K (phase II, panel b) and 330 K (phase III, panel c) for HQuin in the interval 2θ = (10, 90)°. Black symbols correspond to experimental data, red lines are calculated patterns via a pattern matching fitting procedure and green lines indicate the position of the Bragg peaks.

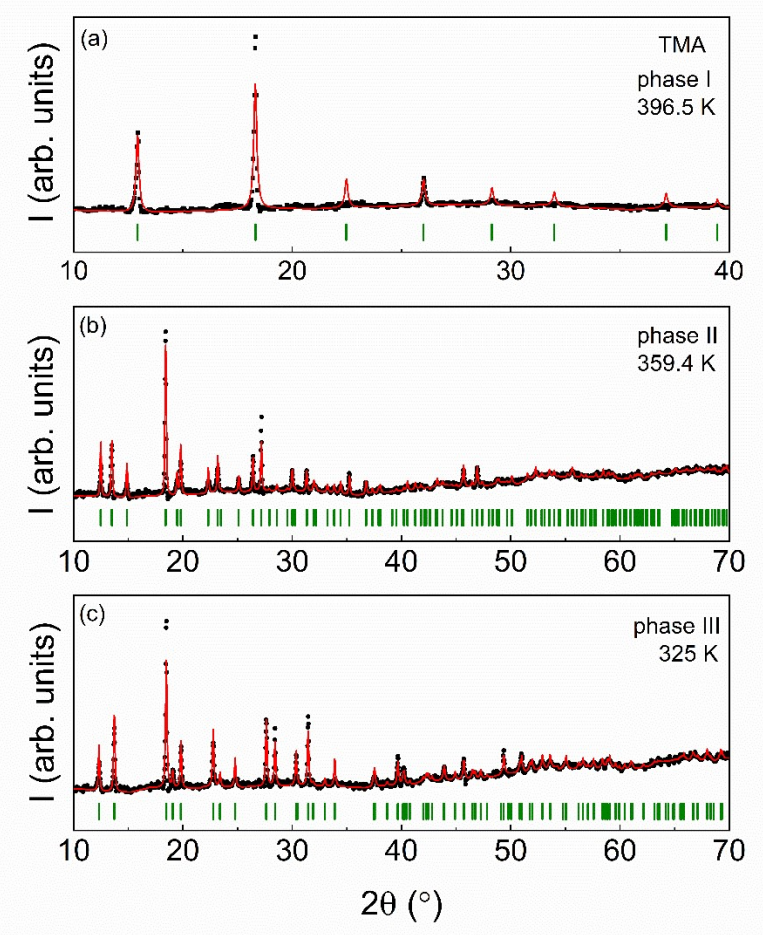

Fig. S2: XRPD patterns recorded at 396.5 K (phase I, panel a), 359.4 K (phase II, panel b) and 325 K (phase III, panel c) for TMA in the interval 2θ = (10, 70)°. Black symbols correspond to experimental data, red lines are calculated patterns via a pattern matching fitting procedure and green lines indicate the position of the Bragg peaks.

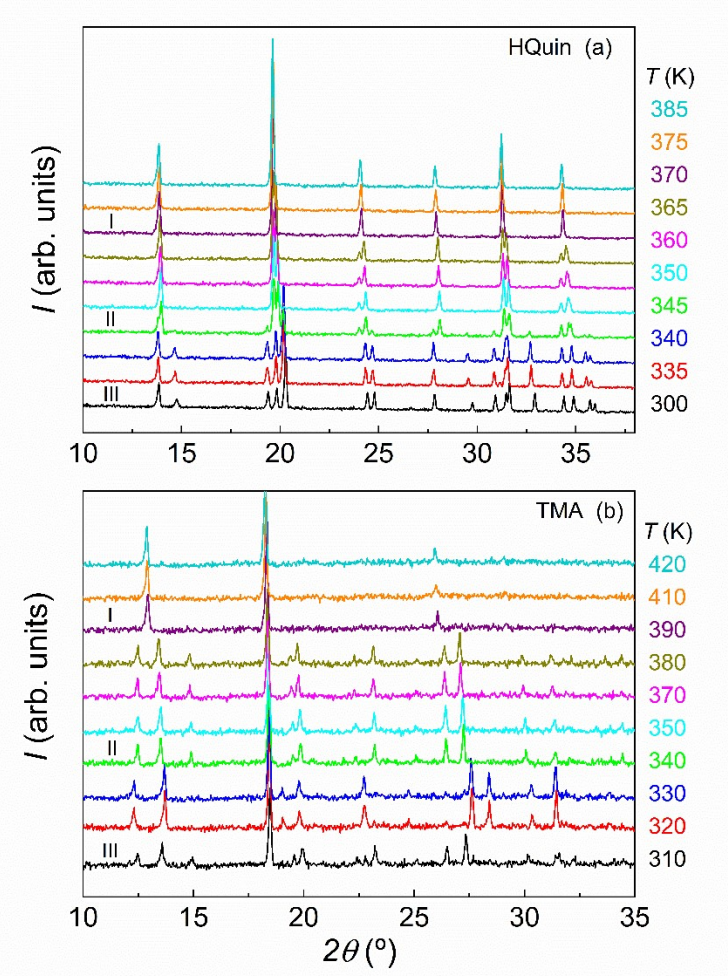

Fig. S3: Temperature evolution of the XRPD patterns trough the I-II and II-III phase transitions for HQUIN (panel a) and TMA (panel b)

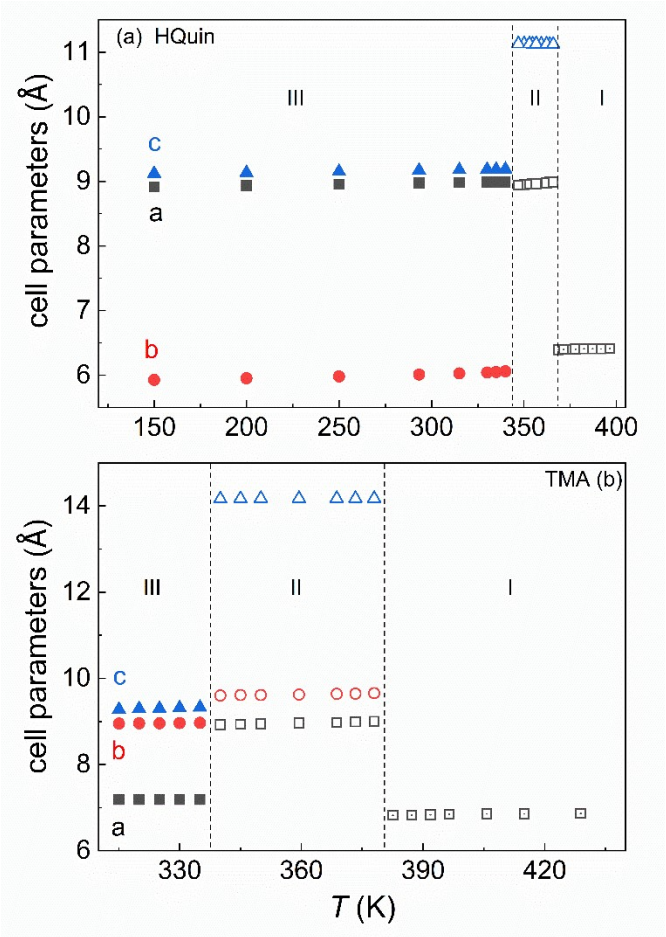

Fig. S4: Normal pressure temperature evolution of the lattice parameters for HQuin (panel a) and TMA (panel b)

3. Heat Capacity

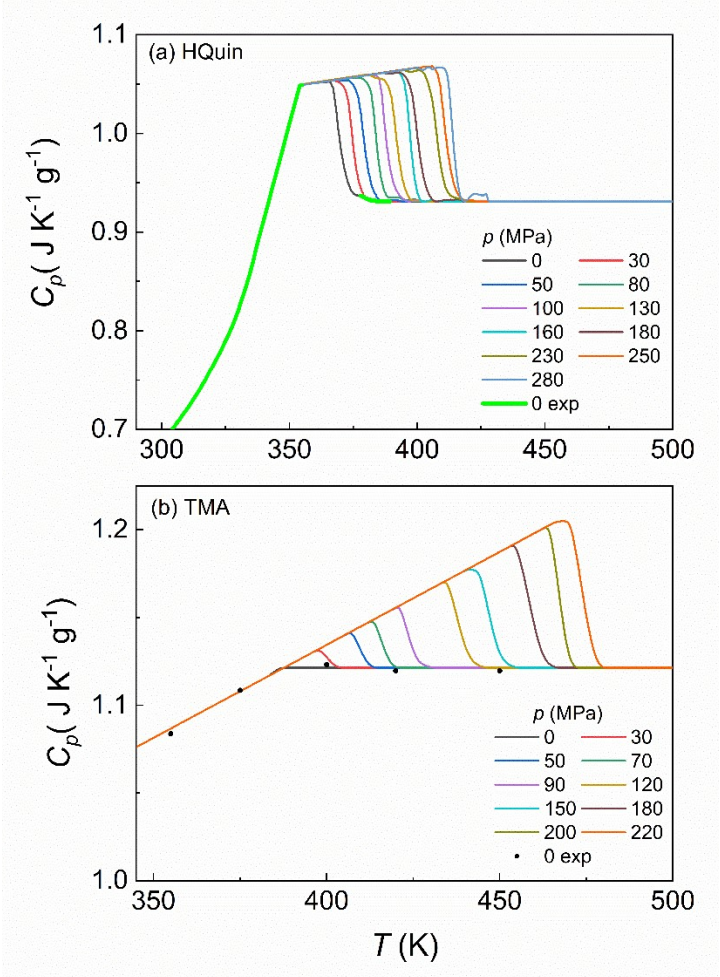

Fig. S5: Pressure-dependent heat capacity constructed from normal pressure modulated DSC experiment for HQuin (panel a) and from isothermal heat-capacity measurements for TMA (panel b)

4. Thermal Conductivity

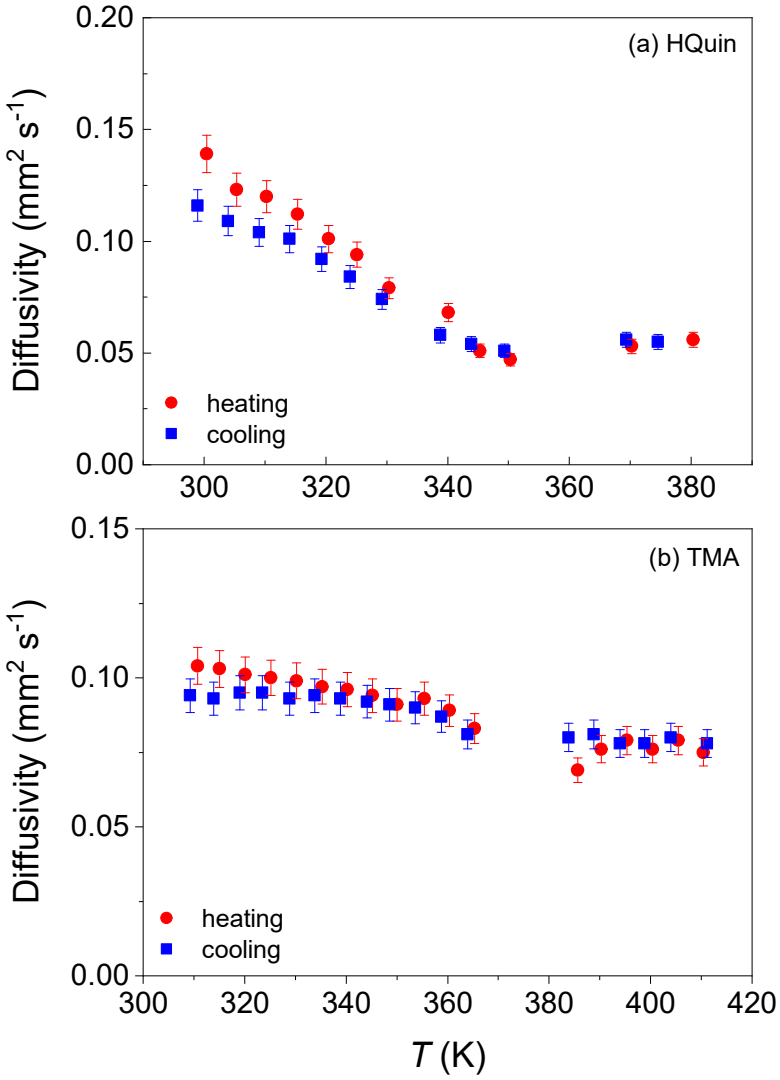

Fig. S6: *Thermal diffusivity as a function of temperature for HQuin (panel a) and TMA (panel b). Error bars indicate a ±6% error on the absolute values.*

5. Comparison to other barocaloric materials

Table 1: Transition temperature T_t, reversible entropy change and reversible temperature change under pressure changes Δp, hysteresis and thermal conductivity for different barocaloric materials (data in brackets indicates irreversible processes).

Material	T_t (K)	Δp (MPa)	ΔS_{rev} (J kg^{-1} K^{-1})	ΔT_{rev} (K)	ΔT_{hyst} (K)	κ (W m^{-1} K^{-1})	Ref.
Ferroelectric plastic crystals							
TMA	384	90	81	21	0	0.12-0.14	this work
HQuin (III-II)	344	100	60	6	3	0.11-0.17	this work
HQuin (II-I)	367	100	26	8	0	0.11	this work
Plastic crystals							
$(CH_3)C(CH_2OH)_3$	354	150	252	4	12	0.23-0.36	[1,2]
$(CH_3)_2C(CH_2OH)_2$	315	190	165	6	24	0.11-0.37	[2,3]
$(CH_3)_3C(CH_2OH)$	232	260	320	16	40	-	[1]
$C_{10}H_{15}Br$	250	100	136	19	8	-	[4]
$C_{10}H_{15}Cl$	312	100	159	21	11	-	[4]
1-Adamantanol	359	160	175	11	15	-	[5]
2-Adamantanol	389	130	65	6	1	-	[5]
$C_{11}H_{18}O$	368	80	300	7	11	-	[5]
ortho-carborane	277	60	80	-	8	-	[6]
para-carborane	308	60	97	-	11	-	[6]
meta-carborane	286	60	71	-	9	-	[6]
C_{60}	256	100	31	10	3	0.4	[7,8]
Inorganic materials							
NH_4I	275	40	71	34	25	0.7	[9,10]
KPF_6	298	80	144	-	-	-	[11]
NH_4SCN	362	100	(128)	(30)	25	-	[12]
Spin-crossover materials							
$Fe_3(bntrz)_6(tcnset)_6$	318	100	95	22	2	-	[13]
Hybrid perovskites							
$(C_{10}H_{21}NH_3)_2MnCl_4$	312	100	250	12	9	0.36	[14,15]
Polymers							
Acetoxy Silicone Rubber	250	170	182	21	14	-	[16]

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