Supplementary Information (SI) for Journal of Materials Chemistry A.

Unveiling barocaloric potential in organometallic-sandwich compounds $[Cp_2M][PF_6]$ (M: Fe^{3+}, Co^{3+})

Supporting Information

Javier García-Ben[a], Ignacio Delgado-Ferreiro[a], Richard J. C. Dixey[b], Socorro Castro García[a], Jorge López-Beceiro[c], Ramon Artiaga[c], Manuel Sánchez Andújar[a], Anthony Phillips[b], Juan Manuel Bermúdez García[a]*, María Antonia Señarís Rodríguez[a]**

a. *University of A Coruna, QUIMOLMAT Group, Dpt. Chemistry, Faculty of Science and Centro Interdisciplinar de Química e Bioloxía (CICA), Zapateira, 15071 A Coruña, Spain.*

b. *School of Physical and Chemical Sciences, Queen Mary University of London, London, E1 4NS UK.*

c. *Universidade da Coruña, Campus Industrial de Ferrol, CITENI-Grupo Proterm, Campus de Esteiro, 15403 Ferrol, Spain.*

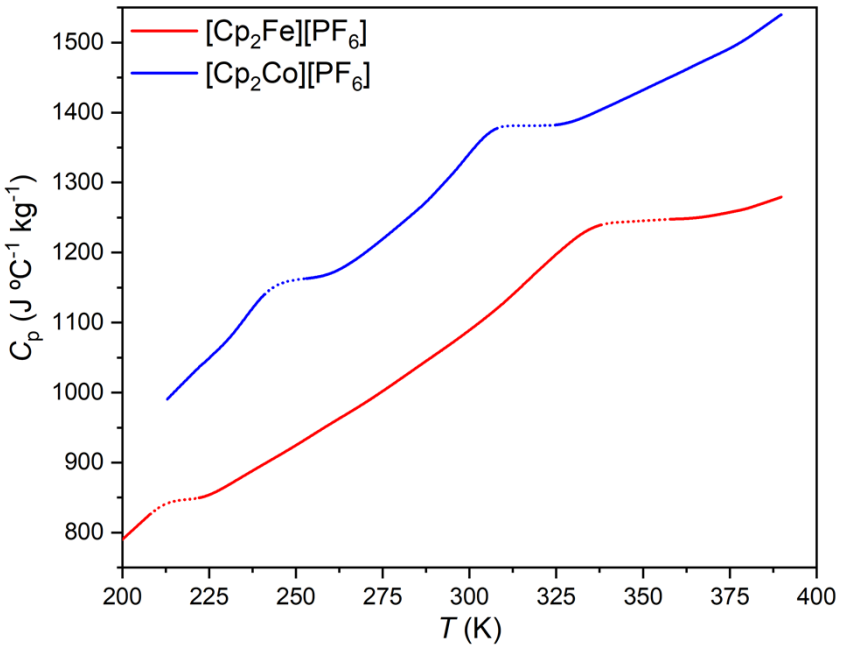

Fig. S1. Heat capacity as function of temperature of compound **1** (red) and compound **2** (blue) between 200 and 400 K. *Note*: the dotted region represents the C_p estimation where phase transitions occur.

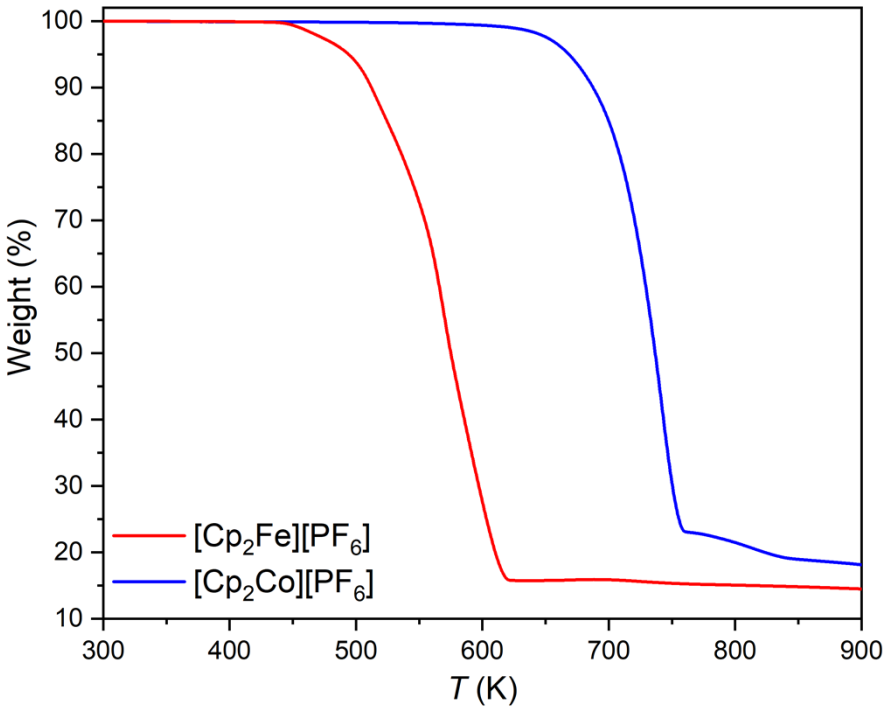

Fig. S2. Thermogravimetric analysis in N_2 atmosphere of compound **1** (red) and compound **2** (blue) between 300 and 900 K.

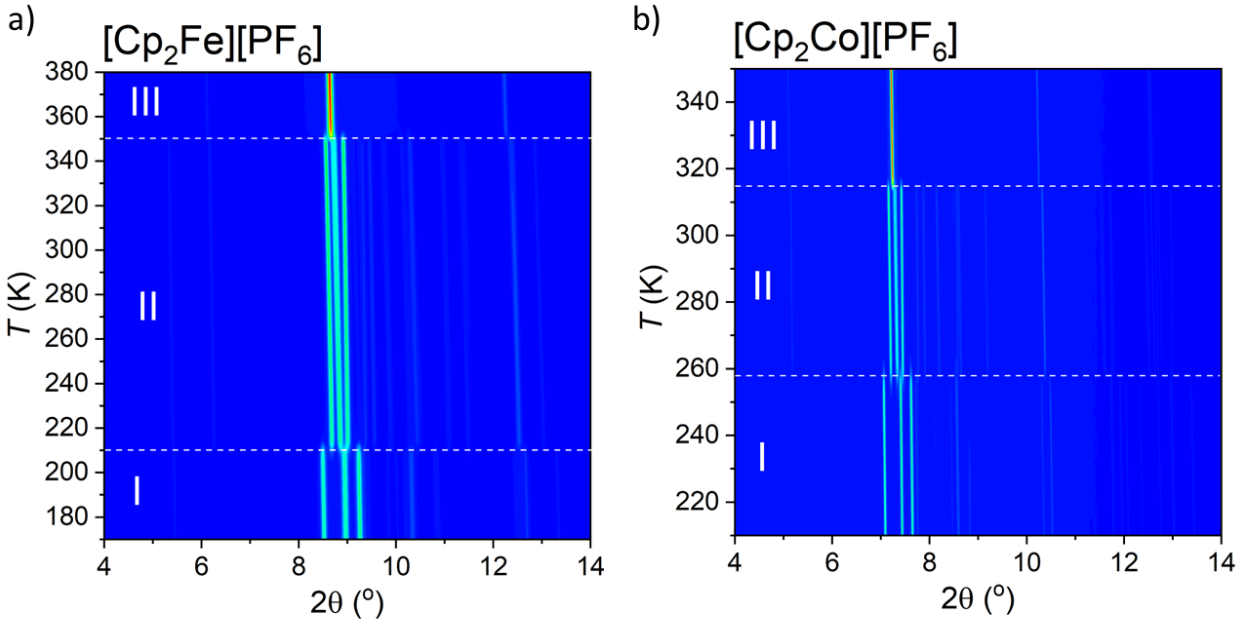

Fig. S3. Evolution comparison of PXRD patterns as a function of temperature of a) **1** and b) **2**.

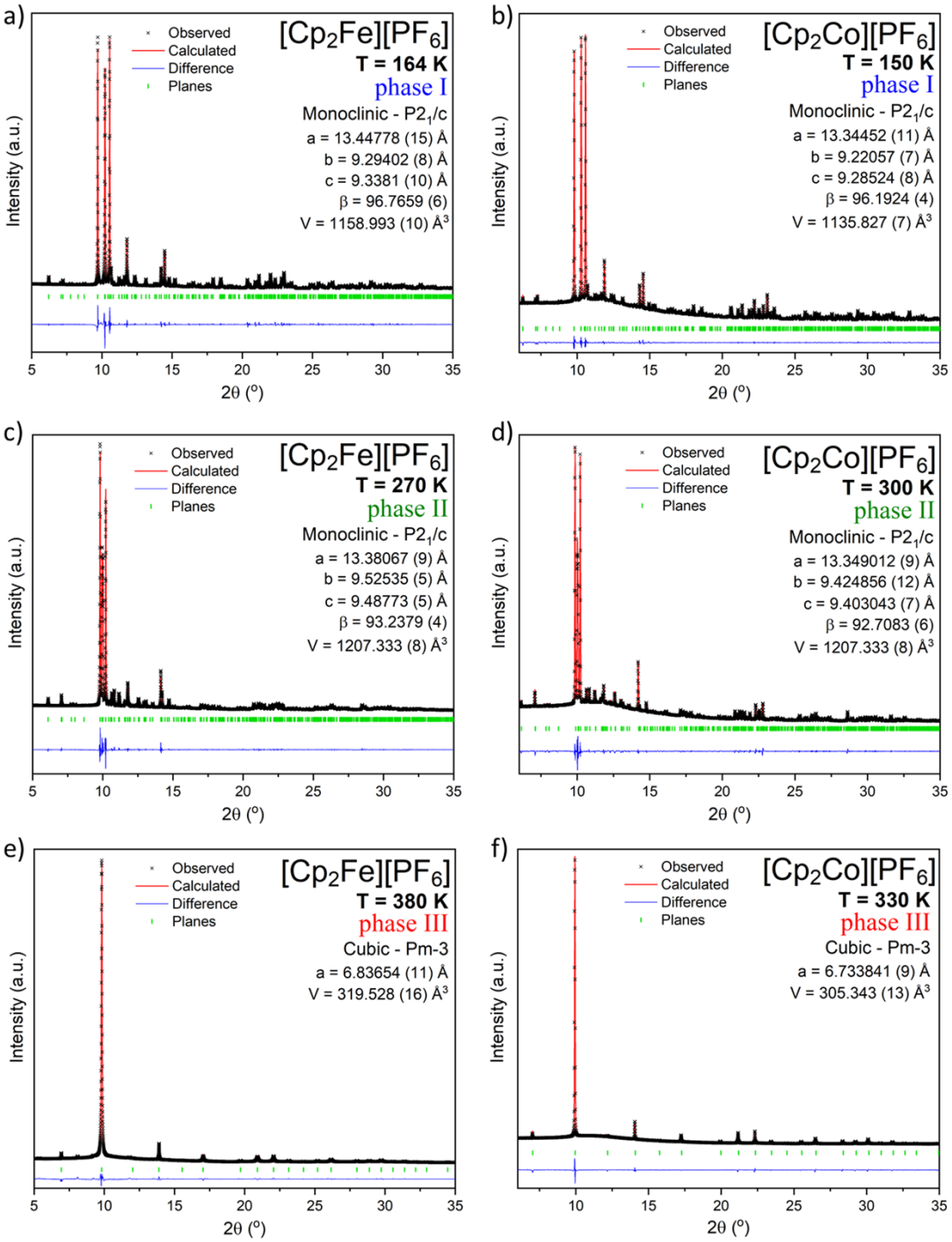

Fig. S4. Le Bail refinements of all the phases of both compounds, a) and b) phase I, c) and d) phase II and e) and f) phase III of compounds **1** and **2**, respectively.

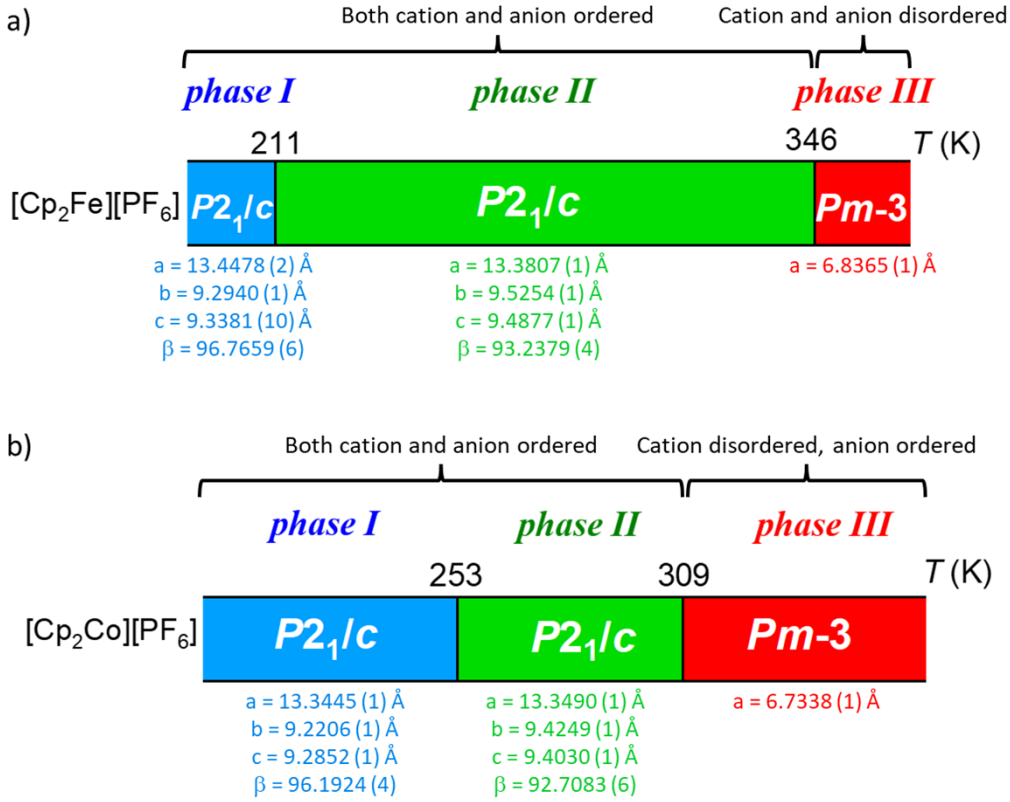

Fig. S5. Structure information of the three phases of a) compound **1** and b) compound **2**.

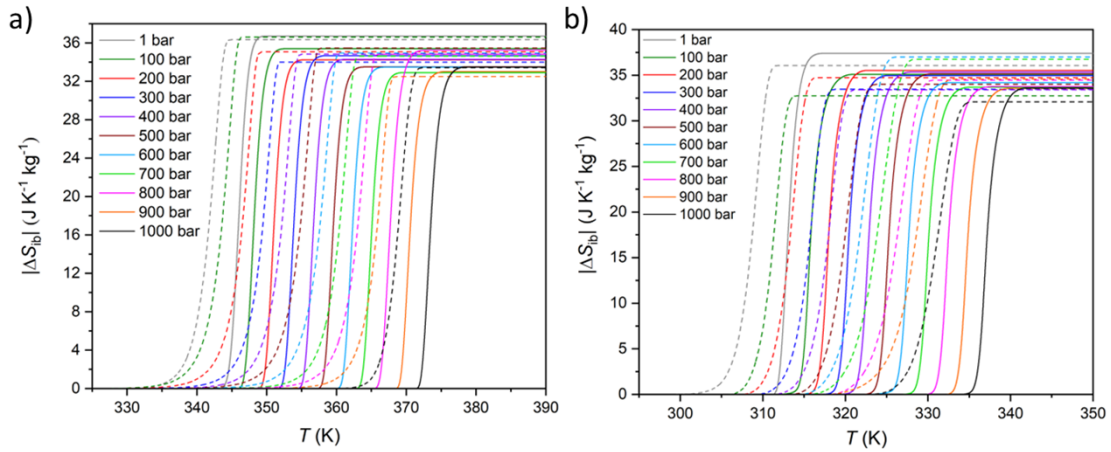

Fig. S6. Isobaric entropy changes of the phase transition II ↔ III for applied pressures from 1 bar to 1000 bar for a) compound **1** and b) compound **2**. *Note*: the solid lines represent the heating curves while the dashed lines represent the cooling curves.

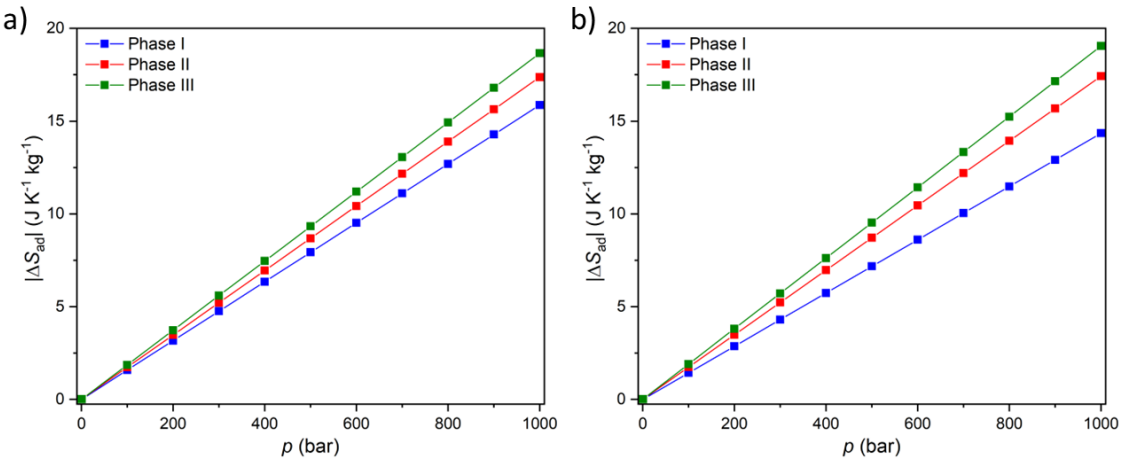

Fig. S7. Entropy caused by volumetric thermal expansion of the II→III transition for a) compound **1** and b) compound **2**.

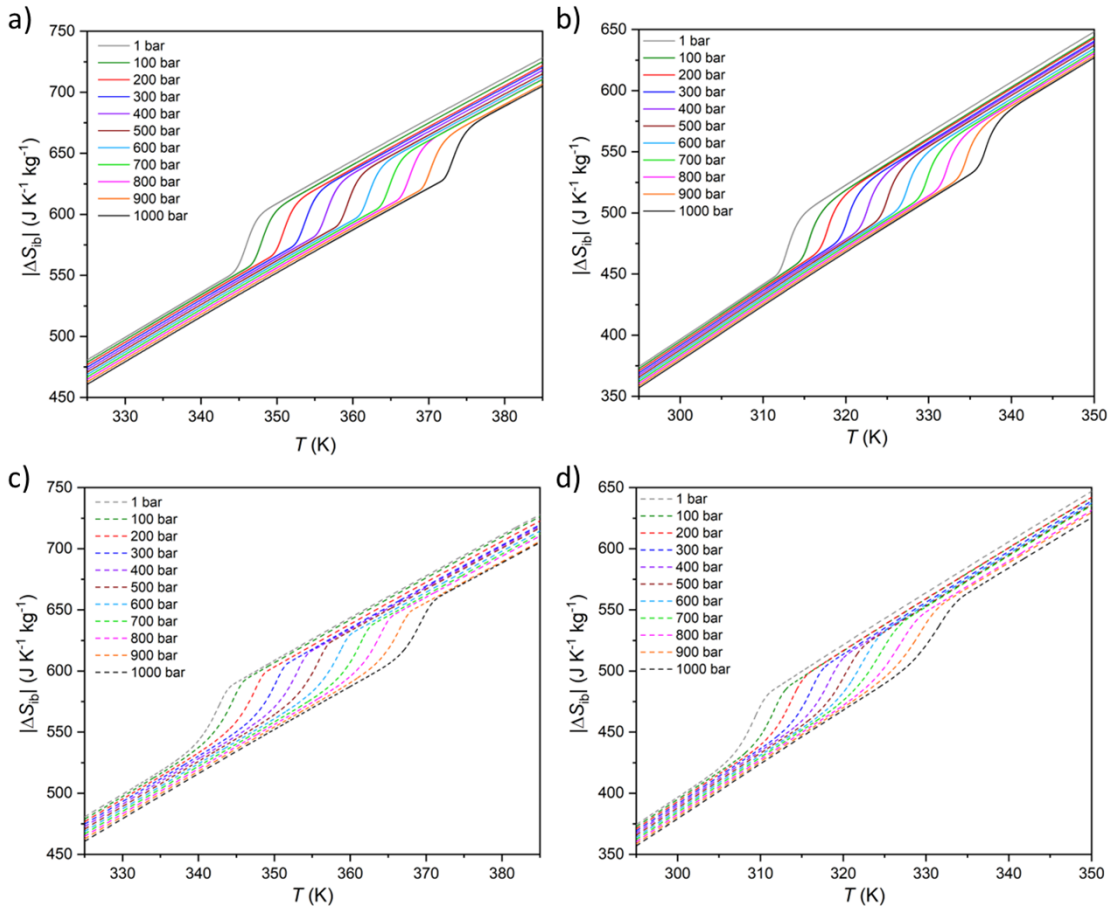

Fig. S8. Thermally driven isobaric changes in entropy of compound **1** a) on heating, b) on cooling and of compound **2** c) on heating and d) on cooling.

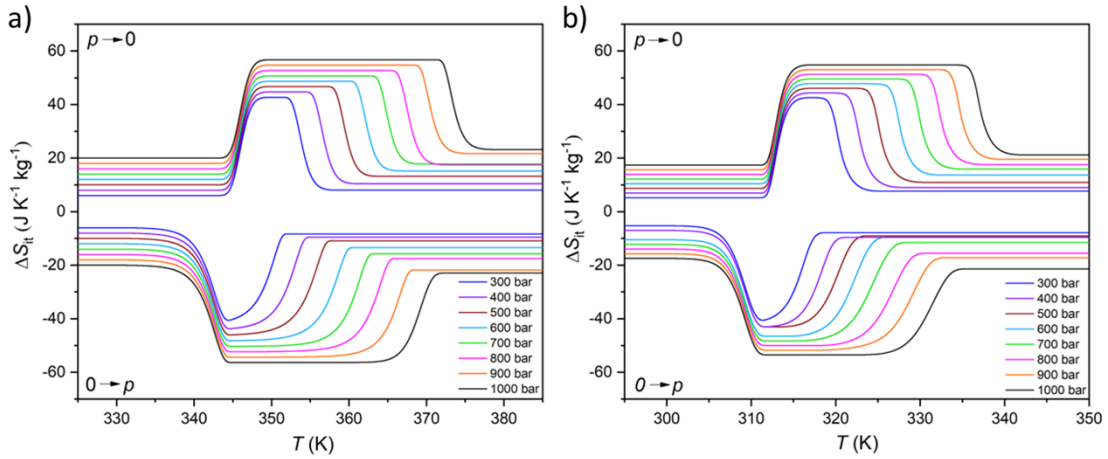

Fig. S9. Irreversible pressure-driven isothermal entropy changes on applying ($0 \rightarrow p$) and removing ($p \rightarrow 0$) pressure of a) compound **1** and b) compound **2**.

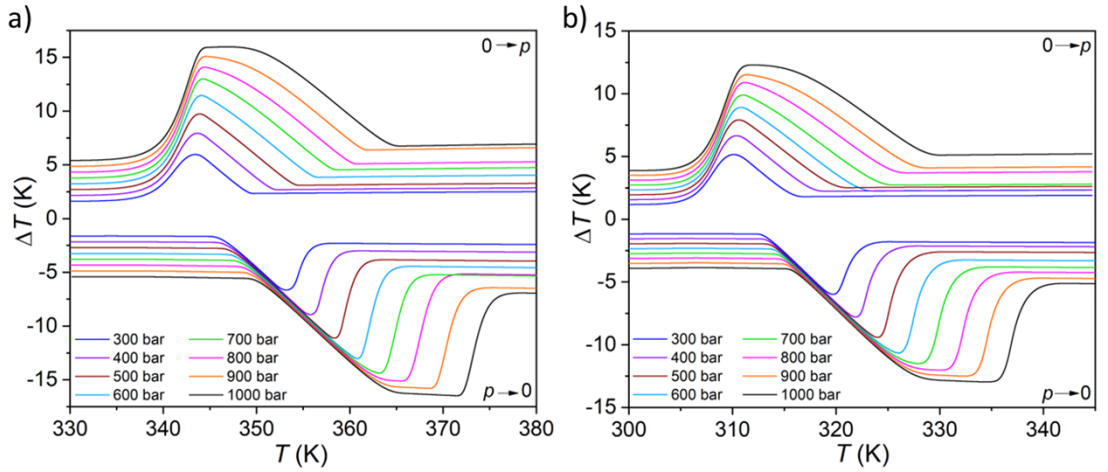

Fig. S10. Irreversible adiabatic temperature changes on applying ($0 \rightarrow p$) and removing ($p \rightarrow 0$) pressure for a) compound **1** and b) compound **2**.

Table S1. Barocaloric parameters of reported barocaloric materials, some represented in Figure 9.

Number	Material	T_t (K)	p (bar)	dT/dp (K kbar^{-1})	ΔS_{rev} (J K^{-1} kg^{-1})	ΔT_{rev} (K)	Reference
Organometallic-Sandwich Plastic Crystals							
1	$[Cp_2Fe][PF_6]$	347	1000	27.6	56.7	15.9	This work
2	$[Cp_2Co][PF_6]$	312	1000	24	54.8	12.0	This work
Hybrid Organic-Inorganic Plastic Crystals							
3	Quinuclidinium perrhenate	344	1000	13.8	26	8	[1]
4	$[Me_4N][FeCl_4]$	384	900	40.0	81	21	[1]
5	$[(CH_3)_3(ClCH_2)N][FeCl_4]$	326	800	19.7	123	-	[2]
6	$[(CH_3)_3S][FeCl_4]$	315	1000	19.9	125	-	[2]
7	$[DBA][BF_4]$	269	1000	28.9	254	17	[3]
Organic Plastic Crystals							
8	C_{60}	257	1000	17	32	9.7	[4]
9	$(CH_3)_2C(CH_2OH)_2$	314	2500	11.3	416	8.2	[5]
10	$(CH_3)_3C(CH_2OH)$	354	2400	8.6	498	22.6	[6]
11	$(CH_3)C(CH_2OH)_3$	232	3300	17	340	9.9	[6]
12	$C_{10}H_{15}Cl$	254	1000	27.4	153	16.1	[7]
13	$C_{10}H_{15}Br$	316	1000	35.5	134	19.6	[7]
14	1-Adamantanol	361	1600	17.9	175	11	[8]
15	2-Adamantanol	326	1850	21	100	8	[8]
16	2-Methyl-2-adamantanol	375	800	24.1	300	7	[8]
17	*o*-carborane	277	600	30	79	14**	[9]
18	*m*-carborane	286	600	34	71	-	[9]
19	*p*-carborane	308	600	31	97	-	[9]
Ammonium Salts							
20	$(NH_4)_2SnF_6$	110	1000	-15.7	-61*	-11**	[10]
21	NH_4HSO_4	160	1000	-12.3	-60*	-10**	[11]
22	NH_4I	268	800	81	71	34**	[12]
23	FAI	345	1000	9.7	49.9	24**	[13]
Hybrid Organic-Inorganic Perovskites (HOIPs)							
24	$[Pr_4N][Mn(dca)_3]$	330	70	23.1	30.5	4.1**	[14]
25	$[Pr_4N][Cd(dca)_3]$	385	70	38.2	11.5	-	[15]
26	$[(CH_3)_4N][Mn(N_3)_3]$	305	1100	12	70	-	[16]
27	$[C_{10}H_{21}NH_3]_2[MnCl_4]$	312	1000	25	241	12	[17]
28	$[C_9H_{19}NH_3]_2[MnCl_4]$	294	1000	17.2	212	10	[18]
29	$[C_9H_{19}NH_3]_2[CuBr_4]$	305	150	26.7	75	2.3	[19]
30	$[CH_3NH_3][PbI_3]$	240	1000	6.4	28.2	4.4	[20]
Polymers							
31	Acetoxy Silicone Rubber	250	1730	27	182*	21	[21]
32	Vulcanized Natural Rubber	303	1730	6.07	17*	10.5	[22]
Spin-Crossover Materials (SCO)							
33	$[Fe(hyptrz)_3]A_2{\cdot}H_2O$	273	900	33.2	56*	10	[23]
34	$Fe[HB(tz)_3]_2$	332	120	21.5	89	1.7	[24]
35	$[FeL_2][BF_4]_2$	257	430	15	68*	4	[25]
36	$Fe_3(bntrz)_6(tcnset)_6$	318	1200	25.6	100	22	[26]
37	$[Fe(pzt)_6](PF_6)_2$	74	1000	29	46*	27	[27]
Metal Alloys							
38	$MnNiSi_{0.59}FeCoGe_{0.41}$	247	2300	7.5	24	1.8	[28]
39	$Ni_{50}Mn_{31.5}Ti_{18.5}$	249	3800	0.26	35*	12***	[29]
40	$LaFe_{11.33}C_{o0.47}Si_{1.2}$	250	2000	9.4	8.7*	-	[30]
41	$Gd_2Si_5Ge_5$	260	2000	3.5	6.2*	-	[31]
42	Mn_3NiN	262	2800	1.4	35*	3.4***	[32]
43	$Ni_{44.6}Co_{5.5}Mn_{35.5}In_{14.4}$	272	6000	4.4	15.6*	6***	[33]
44	$Ni_{0.95}Fe_{0.05}S$	274	1000	7.5	39.6*	8***	[34]
45	$Ni_{2.00}Mn_{1.32}In_{0.68}$	275	2500	1.88	4	3***	[35]
46	$Co_{50}Fe_{2.5}V_{31.5}Ga_{16}$	277	5000	2.5	31	6	[36]
47	$MnNiSi_{0.60}FeCoGe_{0.40}$	280	2300	7.3	47	4	[28]
48	$MnCoGeB_{0.03}$	286	2600	10	30	15***	[37]
49	Mn_3GaN	290	930	6.5	21.6*	1.3**	[38]
50	$Ni_{35.5}Co_{14.5}Mn_{35}Ti_{15}$	291	1000	5	8.5	4.2***	[39]
51	$N_{i49.26}Mn_{36.08}In_{14.66}$	293	2500	1.8	10*	9.4***	[40]
52	$Ni_{0.875}Fe_{0.125}S$	294	1000	7.5	49.5*	-	[34]
53	$Ni_{0.85}Fe_{0.15}S$	303	1000	7.5	52.8*	-	[34]
54	$Ni_{1.99}Mn_{1.34}In_{0.67}$	306	2000	1.37	4	-	[35]
55	$MnCoGe_{0.99}In_{0.01}$	310	3000	7.7	52*	2.1***	[41]
56	$Fe_{49}Rh_{51}$	310	2500	6	12	5	[42]
57	$MnNiSi_{0.61}FeCoGe_{0.39}$	311	2300	7	44	6	[28]
58	$Ni_{58.3}Mn_{17.1}Ga_{24.6}$	318	10500	0.4	13.6*	-	[43]
59	$Ni_{0.825}Fe_{0.175}S$	318	1000	7.5	46.8*	-	[34]
60	$Ni_{42.3}Co_{7.9}Mn_{38.8}Sn_{11.0}$	327	6200	4.7	15	10***	[44]
61	$Ni_{1.99}Mn_{1.37}In_{0.64}$	329	2500	19.5	6	3.8***	[35]
62	$Ni_{2.05}Mn_{1.30}In_{0.65}$	330	2500	1.65	5	3.8***	[35]
63	$MnNiSi_{0.62}FeCoGe_{0.38}$	338	2700	7.5	57*	-	[28]
64	$Ni_{2.02}Mn_{1.36}In_{0.62}$	346	2500	1.83	10	4***	[35]

Note: * = Isobaric entropy change; ** = Adiabatic temperature change was calculated by indirect method ($\Delta T_{rev} = \Delta S * T_t / C_p$); *** = Irreversible adiabatic temperature change

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