Electronic Supplementary Material (ESI) for RSC Advances.

Melting temperatures deduced from molar volumes: A consequence of the combination of enthalpy/entropy compensation with linear cohesive free-energy densities

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Supporting Information (26 pages)

Table S1 Experimental melting temperatures (T_m), melting enthalpies (ΔH_m), melting entropies (ΔS_m) and molar volumes (V_{mol})[a] determined for linear alkanes C_nH_{2n+2} and standard cohesive free energy densities (CFED) computed with eq. 11 and for a reference temperature of 298.15 K.[24]

n	ΔH_m /kJ·mol^{-1}	ΔS_m /J·mol^{-1}·K^{-1}	T_m /K	V_{mol} /cm^3·mol^{-1}	CFED /J·cm^{-3}
1	0.94	10.4	90.7	38.0	-56.7
2	2.86	31.7	90.4	49.4	-133.0
3	3.52	41.2	85.5	75.4	-116.3
4	4.66	34.6	134.9	96.5	-58.5
5	8.40	58.6	143.4	116.2	-78.0
6	13.08	73.5	177.8	131.4	-67.4
7	14.05	77.0	182.6	146.9	-60.6
8	20.74	95.8	216.4	163.4	-48.0
9	21.75	99.0	219.6	179.4	-43.3
10	28.72	117.9	243.5	195.4	-33.0
11	29.04	117.3	247.6	212.1	-28.0
12	36.84	139.7	263.6	228.6	-21.1
13	36.15	135.0	267.8	244.5	-16.8
14	45.07	161.5	279.0	261.7	-11.8
15	43.77	154.6	283.1	277.7	-8.4
16	53.36	183.2	291.3	294.1	-4.2
17	51.13	173.3	295.1	311.1	-1.7
18	61.50	204.0	301.5	327.7	2.1
19	61.07	200.9	304.0	345.1	3.4
20	67.80	219.6	308.8	363.0	6.4
21	63.18	201.4	313.7	360.8	8.7
22	78.50	247.7	316.9	397.8	11.7
23	76.70	239.9	319.7	416.8	12.4
24	81.75	253.9	322.0	433.0	14.0
25	79.391	243.1	326.6	450.5	15.3
26	91.7	278.3	329.5	470.0	18.6
27	89.37	269.3	332.0	488.0	18.6
28	100.08	299.2	334.5	503.2	21.6
29	95.82	284.7	336.6	520.8	21.0
30	106.32	313.9	338.7	538.2	23.7

[a] V_{mol} = MM / ρ where MM is the molecular mass and ρ is the density in the liquid phase.

Table S2 Experimental melting temperatures (T_m), melting enthalpies (ΔH_m), melting entropies (ΔS_m) and molar volumes (V_{mol})[a] determined for linear alkanoic acids $C_nH_{2n+1}COOH$ and standard cohesive free energy densities (CFED) computed with eq. 11 and for a reference temperature of 298.15 K.[24]

n	ΔH_m /kJ·mol^{-1}	ΔS_m /J·mol^{-1}·K^{-1}	T_m /K	V_{mol} /cm^3·mol^{-1}	CFED /J·cm^{-3}
1	12.68	45.0	281.6	37.9	-19.7
2	11.72	40.4	289.8	57.6	-5.9
3	10.66	42.2	252.5	75.0	-25.7
4	11.07	41.3	268.0	92.5	-13.5
5	15.33	64.1	239.2	109.4	-34.6
6	15.06	55.8	270.2	126.1	-12.4
7	15.13	56.9	265.8	142.6	-12.9
8	21.35	73.7	289.7	159.7	-3.9
9	19.82	69.4	285.6	175.4	-5.0
10	27.99	92.0	304.4	193.3	3.0
11	25.98	86.1	301.7	210.6	1.4
12	36.65	115.7	316.9	229.7	9.4
13	33.73	107.1	315.0	245.9	7.3
14	45.10	137.7	327.6	264.9	15.3
15	41.53	127.5	325.7	281.0	12.5
16	54.94	163.5	336.0	300.8	20.6
17	51.34	153.6	334.4	317.2	17.5
18	61.30	178.9	342.8	313.9	25.4
19	57.62	168.9	341.2	372.7	19.5
20	69.20	198.6	348.5	411.9	24.3

[a] V_{mol} = MM / ρ where MM is the molecular mass and ρ is the density in the liquid phase.

Table S3 Experimental melting temperatures (T_m), melting enthalpies (ΔH_m), melting entropies (ΔS_m) and molar volumes (V_{mol})[a] determined for organosilanes and standard cohesive free energy densities (CFED) computed with eq. 11 and for a reference temperature of 200.00 K.[24]

Compd	ΔH_m /kJ·mol^{-1}	ΔS_m /J·mol^{-1}·K^{-1}	T_m /K	V_{mol} /cm^3·mol^{-1}	CFED /J·cm^{-3}
$SiCl_4$	7.60	37.2	204.3	115.6	1.4
$SiC_2H_5Cl_3$	6.96	41.5	167.6	133.4	-10.1
$SiC_2H_6Cl_2$	8.78	44.6	197.1	121.2	-1.1
$SiClC_3H_9$	10.60	45.5	233.2	127.3	11.8
$SiCH_3Cl_3$	8.95	45.8	195.4	118.0	-1.8
SiF_4	9.38	50.3	186.4	64.1	-10.7
$SiCH_4Cl_2$	9.87	54.1	182.6	104.3	-9.0
$SiC_7H_8Cl_2$	12.89	56.1	229.7	162.9	10.2
SiC_8H_{20}	13.39	70.3	190.6	189.3	-3.5

[a] V_{mol} = MM / ρ where MM is the molecular mass and ρ is the density in the liquid phase.

Table S4 Experimental melting temperatures (T_m), melting enthalpies (ΔH_m), melting entropies (ΔS_m) and molar volumes (V_{mol})[a] determined for lanthanide metals and standard cohesive free energy densities (CFED) computed with eq. 11 and for a reference temperature of 1516.31 K.[24]

Compd	ΔH_m /kJ·mol^{-1}	ΔS_m /J·mol^{-1}·K^{-1}	T_m /K	V_{mol} /cm^3·mol^{-1}	CFED /J·cm^{-3}
Ce	5.46	5.1	1071.2	20.7	-109.6
La	6.20	5.2	1191.2	22.6	-74.9
Pm	7.13	5.4	1315.2	20.0	-54.6
Nd	7.14	5.5	1294.2	20.6	-59.6
Pr	6.89	5.7	1204.2	20.8	-85.9
Tb	10.15	6.2	1629.2	19.3	36.4
Gd	10.05	6.3	1586.2	19.9	22.2
Sm	8.62	6.4	1347.2	20.0	-54.1
Dy	11.06	6.6	1685.2	18.8	59.0
Yb	7.66	7.0	1092.2	25.1	-118.7
Eu	9.21	8.4	1095.2	29.0	-122.2
Tm	16.84	9.3	1818.2	18.1	154.3
Ho	17.00	9.7	1747.2	18.8	119.8
Er	19.90	11.0	1802.2	18.4	171.1

[a] $V_{mol} = MM / \rho$ where MM is the molecular mass and ρ is the density in the solid phase.

Table S5 Experimental melting temperatures (T_m), melting enthalpies (ΔH_m), melting entropies (ΔS_m) and molar volumes (V_{mol})[a] determined for transition metals and standard cohesive free energy densities (CFED) computed with eq. 11 and for a reference temperature of 1585.57 K.[24]

Compd	ΔH_m /kJ·mol^{-1}	ΔS_m /J·mol^{-1}·K^{-1}	T_m /K	V_{mol} /cm^3·mol^{-1}	CFED /J·cm^{-3}
Y	11.42	6.4	1795.2	19.9	67.1
Ti	14.15	7.3	1941.2	10.6	244.2
Fe	13.81	7.6	1811.0	7.1	242.4
Sc	14.10	7.8	1814.2	15.0	118.1
Ag	11.28	9.1	1234.9	10.3	-311.8
Pd	16.74	9.2	1828.2	8.9	250.9
Co	16.20	9.2	1768.2	6.6	252.6
Cu	12.93	9.5	1357.8	7.1	-305.9
Cr	21.00	9.6	2180.2	7.3	787.6
V	21.50	9.8	2190.0	8.5	698.9
Zr	21.00	9.9	2128.2	14.0	382.7
Ni	17.48	10.1	1728.2	6.7	215.1
Cd	6.21	10.5	594.2	12.9	-800.9
Zn	7.32	10.6	692.7	9.2	-1029.1
Nb	30.00	10.9	2750.2	10.8	1171.8
Rh	26.59	11.9	2237.2	8.3	934.0
Mo	37.48	12.9	2896.2	9.4	1806.5
Mn	12.91	8.5	1519.2	7.6	-74.1
Tc	33.29	13.7	2430.2	8.5	1357.7
Ru	38.59	14.8	2607.2	8.4	1810.3

[a] $V_{mol} = MM / \rho$ where MM is the molecular mass and ρ is the density in the solid phase.

Table S6 Experimental melting temperatures (T_m), melting enthalpies (ΔH_m), melting entropies (ΔS_m) and molar volumes (V_{mol})[a] experimentally determined for transition metal oxides and standard cohesive free energy densities (CFED) computed with eq. 11 and for a reference temperature of 1872.41 K.[24]

Compd	ΔH_m /kJ·mol^{-1}	ΔS_m /J·mol^{-1}·K^{-1}	T_m /K	V_{mol} /cm^3·mol^{-1}	CFED /J·cm^{-3}
CuO	11.80	6.9	1719.2	12.6	-83.5
FeO	24.06	14.6	1650.0	12.5	-259.3
TiO	41.80	20.7	2023.2	12.9	241.4
VO2	56.90	25.4	2240.2	18.1	514.8
MnO	54.40	25.8	2112.2	13.1	472.6
TiO_2	66.94	31.6	2116.2	18.9	408.4
NbO	85.00	38.5	2209.2	14.9	868.5
Y_2O_3	105.00	38.7	2711.2	45.1	720.7
NbO_2	92.00	42.3	2174.2	20.9	611.3
Cu_2O	64.80	43.0	1508.2	23.8	-656.3
Nb_2O_5	104.30	58.4	1785.2	57.8	-88.2
Fe_3O_4	138.10	73.8	1870.2	44.8	-3.7

[a] V_{mol} = MM / ρ where MM is the molecular mass and ρ is the density in the solid phase.

Table S7 Entropy-enthalpy correlations fitted for *n*-alkanoic acids $C_nH_{2n+1}COOH$ (n = 1-20).[a]

Function	f / m^{-2}	a	b	c	d
	Unconstrained				
eq. 10	$4(3)\cdot10^{3}$	-	-	-	-
$\Delta S_m = a + b\cdot\Delta H_m$	-	15(1)	$2.69(4)\cdot10^{-3}$	-	-
$\Delta S_m = a + b\cdot\Delta H_m + c\left(\Delta H_m\right)^2$	-	10(2)	$3.1(2)\cdot10^{-3}$	$-5(2)\cdot10^{-9}$	-
$\Delta S_m = a\left(\Delta H_m - b/c - \Delta H_m\right)^d$	-	$3(1)\cdot10^{2}$	$4(2)\cdot10^{3}$	$2.0(8)\cdot10^{5}$	$6.0(10)\cdot10^{-1}$
	Constrained: $\Delta S_m \to 0$ when $\Delta H_m \to 0$				
eq. 10	11.39	-	-	-	-
$\Delta S_m = a + b\cdot\Delta H_m$	-	0	$3.17(6)\cdot10^{-3}$	-	-
$\Delta S_m = a + b\cdot\Delta H_m + c\left(\Delta H_m\right)^2$	-	0	$4.2(2)\cdot10^{-3}$	$-1.3(2)\cdot10^{-8}$	-
$\Delta S_m = a\left(\Delta H_m - b/c - \Delta H_m\right)^d$	-	$2(2)\cdot10^{3}$	0	$9(10)\cdot10^{5}$	$8.1(4)\cdot10^{-1}$

[a] Units used for polynomial fits: a / $J\cdot mol^{-1}\cdot K^{-1}$, b / K^{-1} and c / $J^{-1}\cdot mol\cdot K^{-1}$. Units used for reciprocal Hill fits: a / $J\cdot mol^{-1}\cdot K^{-1}$, b / $J\cdot mol^{-1}$and c / $J\cdot mol^{-1}$.

Table S8 Entropy-enthalpy correlations fitted for organosilanes.[a]

Function	f / m^{-2}	a	b	c	d
	Unconstrained				
eq. 10	124(26)	-	-	-	-
$\Delta S_m = a + b \cdot \Delta H_m$	-	11(8)	3.9(8)·10-3	-	-
$\Delta S_m = a + b \cdot \Delta H_m + c(\Delta H_m)^2$	-	38(45)	-1(9) 10-3	3(4) 10-7	-
$\Delta S_m = a(\Delta H_m - b/c - \Delta H_m)^d$	-	51(7)	6(4) 103	1.4(4) 105	1(5) 10-1
	Constrained: $\Delta S_m \to 0$ when $\Delta H_m \to 0$				
eq. 10	12.35	-	-	-	-
$\Delta S_m = a + b \cdot \Delta H_m$	-	0	5.0(2) 10^{-3}	-	-
$\Delta S_m = a + b \cdot \Delta H_m + c(\Delta H_m)^2$	-	0	6.0(9) 10^{-3}	-9(9) 10^{-8}	-
$\Delta S_m = a(\Delta H_m - b/c - \Delta H_m)^d$	-	50(47)	0	2(2) 10^{4}	5(2) 10^{-1}

[a] Units used for polynomial fits: a / J·mol^{-1}·K^{-1} , b / K^{-1} and c / J^{-1}·mol·K^{-1}. Units used for reciprocal Hill fits: a / J·mol^{-1}·K^{-1} , b / J·mol^{-1}and c / J·mol^{-1}.

Table S9 Entropy-enthalpy correlations fitted for lanthanide metals.[a]

Function	f / m^{-2}	a	b	c	d
	Unconstrained				
eq. 10	13.0(2)	-	-	-	-
$\Delta S_m = a + b \cdot \Delta H_m$	-	3.0(5)	$3.9(4)\cdot10^{-4}$	-	-
$\Delta S_m = a + b \cdot \Delta H_m + c\left(\Delta H_m\right)^2$	-	3(2)	$2.5(32)\cdot10^{-4}$	$5(13)\cdot10^{-9}$	-
$\Delta S_m = a\left(\Delta H_m - b/c - \Delta H_m\right)^d$	-	12(2)	$5(6)\cdot10^{3}$	$4(13)\cdot10^{4}$	$3(7)\cdot10^{-1}$
	Constrained: $\Delta S_m \to 0$ when $\Delta H_m \to 0$				
eq. 10	11.39	-	-	-	-
$\Delta S_m = a + b \cdot \Delta H_m$	-	0	$6.4(3)\cdot10^{-4}$	-	-
$\Delta S_m = a + b \cdot \Delta H_m + c\left(\Delta H_m\right)^2$	-	0	$9.3(7)\cdot10^{-3}$	$-2.1(4)\cdot10^{-8}$	-
$\Delta S_m = a\left(\Delta H_m - b/c - \Delta H_m\right)^d$	-	35(246)	0	$2(10)\cdot10^{5}$	$6(3)\cdot10^{-1}$

[a] Units used for polynomial fits: a / J·mol^{-1}·K^{-1} , b / K^{-1} and c / J^{-1}·mol·K^{-1}. Units used for reciprocal Hill fits: a / J·mol^{-1}·K^{-1} , b / J·mol^{-1}and c / J·mol^{-1}.

Table S10 Entropy-enthalpy correlations fitted for transition metals.[a]

Function	f / m^{-2}	a	b	c	d
	Unconstrained				
eq. 10	13.2(4)	-	-	-	-
$\Delta S_m = a + b \cdot \Delta H_m$	-	6.6(7)	$1.8(3)\cdot10^{-4}$	-	-
$\Delta S_m = a + b \cdot \Delta H_m + c\left(\Delta H_m\right)^2$	-	10(1)	$2.4(14)\cdot10^{-4}$	$9(3)\cdot10^{-9}$	-
$\Delta S_m = a\left(\Delta H_m - b/c - \Delta H_m\right)^d$	-	11.6(6)	$1.5(2)\cdot10^{4}$	$3.7(5)\cdot10^{4}$	$5(12)\cdot10^{-2}$
	Constrained: $\Delta S_m \to 0$ when $\Delta H_m \to 0$				
eq. 10	11.39	-	-	-	-
$\Delta S_m = a + b \cdot \Delta H_m$	-	0	$4.5(3)\cdot10^{-4}$	-	-
$\Delta S_m = a + b \cdot \Delta H_m + c\left(\Delta H_m\right)^2$	-	0	$7.7(8)\cdot10^{-4}$	$-1.1(3)\cdot10^{-8}$	-
$\Delta S_m = a\left(\Delta H_m - b/c - \Delta H_m\right)^d$	-	29(125)	0	$2(12)\cdot10^{5}$	$5(2)\cdot10^{-1}$

[a] Units used for polynomial fits: a / J·mol^{-1}·K^{-1} , b / K^{-1} and c / J^{-1}·mol·K^{-1}. Units used for reciprocal Hill fits: a / J·mol^{-1}·K^{-1} , b / J·mol^{-1}and c / J·mol^{-1}.

Table S11 Entropy-enthalpy correlations fitted for transition metal oxides.[a]

Function	f / m^{-2}	a	b	c	d
	Unconstrained				
eq. 10	50(16)	-	-	-	-
$\Delta S_m = a + b \cdot \Delta H_m$	-	0.9(42)	$4.8(5)\cdot10^{-4}$	-	-
$\Delta S_m = a + b \cdot \Delta H_m + c\left(\Delta H_m\right)^2$	-	5(7)	$3(2)\cdot10^{-4}$	$10(14)\cdot10^{-10}$	-
$\Delta S_m = a\left(\Delta H_m - b/c - \Delta H_m\right)^d$	-	74(191)	$-5(48)\cdot10^{3}$	$3.7(5)\cdot10^{4}$	$8(5)\cdot10^{-1}$
	Constrained: $\Delta S_m \to 0$ when $\Delta H_m \to 0$				
eq. 10	11.39	-	-	-	-
$\Delta S_m = a + b \cdot \Delta H_m$	-	0	$4.9(2)\cdot10^{-4}$	-	-
$\Delta S_m = a + b \cdot \Delta H_m + c\left(\Delta H_m\right)^2$	-	0	$4.7(9)\cdot10^{-4}$	$2(9)\cdot10^{-8}$	-
$\Delta S_m = a\left(\Delta H_m - b/c - \Delta H_m\right)^d$	-	62(62)	0	$2(2)\cdot10^{5}$	$7(2)\cdot10^{-1}$

[a] Units used for polynomial fits: a / J·mol^{-1}·K^{-1} , b / K^{-1} and c / J^{-1}·mol·K^{-1}. Units used for reciprocal Hill fits: a / J·mol^{-1}·K^{-1} , b / J·mol^{-1}and c / J·mol^{-1}.

Table S12 Experimental melting temperatures (T_m),[a] melting enthalpies (ΔH_m),[a] melting entropies (ΔS_m)[a] and molar volumes (V_{mol})[b] determined for substituted cyanobiphenyls *n*-CB, 12-Me-CB and 12-Me_2-CB (see Fig. 9a for the structures) and standard cohesive free energy densities (CFED) computed with eq. 11 and for a reference temperature of 325.95 K.[17]

Compd	ΔH_m /kJ·mol^{-1}	ΔS_m /J·mol^{-1}·K^{-1}	T_m /K	V_{mol} /cm^3·mol^{-1}	CFED /J·cm^{-3}
12-CB	46.29	130.8	353.9	305.1	12.0
12-Me-CB	50.16	147.2	340.8	316.9	6.9
12-Me-CB	50.27	145.5	345.6	331.6	8.6
5-CB	30.00	93.6	320.7	211.5	-2.3
6-CB	34.81	105.4	330.4	224.4	2.1
7-CB	28.61	88.3	324.2	239.2	-0.7
8-CB	30.71	94.0	326.7	252.4	0.3
9-CB	36.78	109.4	336.2	262.8	4.3
10-CB	39.38	118.3	332.8	277.1	2.9
11-CB	48.83	142.3	343.2	289.9	8.5

[a] Determined by differential scanning calorimetry using a scan rate of 5 deg/min.[17] [b] $V_{mol} = N_{Av} \cdot V_{Connolly} \cdot 10^{-24}$ where N_{Av} is Avogadro number, $V_{Connolly}$ is the Connolly volume in Å^3.[28]

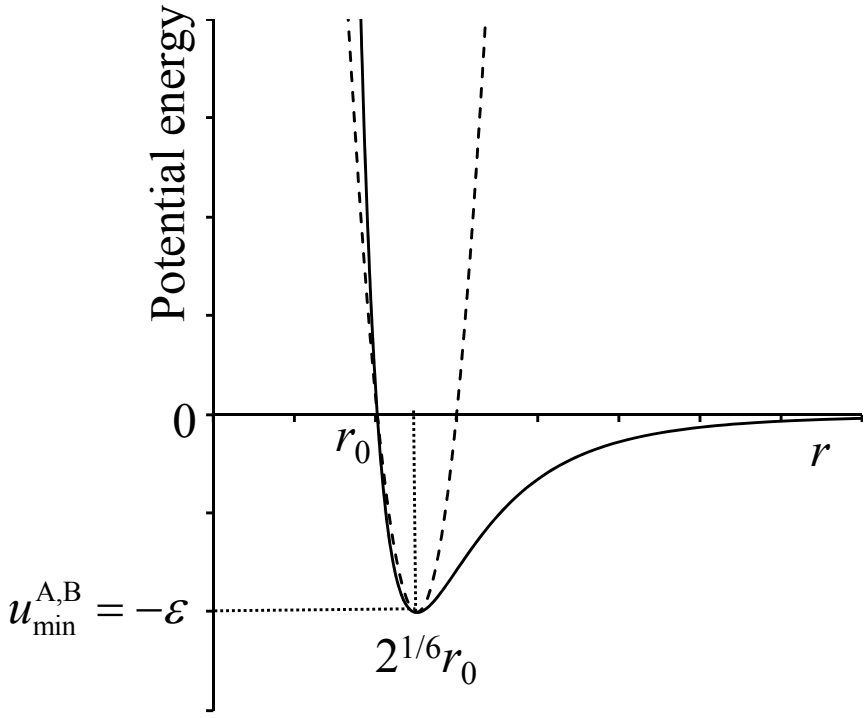

Figure S1 Representation of a *Lennard-Jones* (12,6) potential (full trace) with the interpretation of ε and r_0 parameters, and its harmonic approximation (dashed trace) modelling the intermolecular interactions responsible for the formation of a [AB] complex. Adapted from ref 6d.

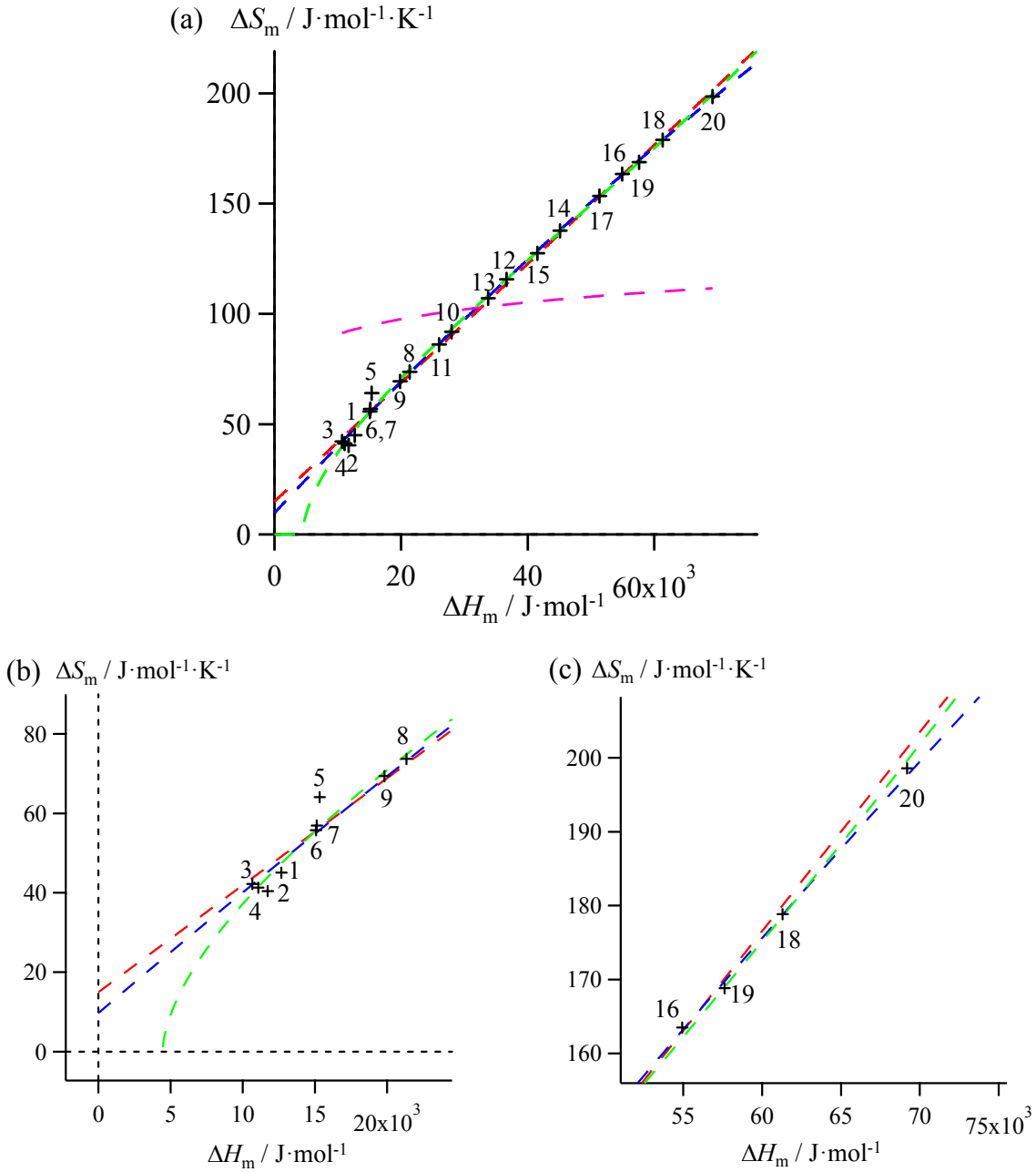

Figure S2 (a) Full representation, (b) low enthalpy inset and (c) high enthalpy inset for plot of melting entropies ΔS_m *versus* melting enthalpies ΔH_m in linear alkanoic acids $C_nH_{2n+1}COOH$ (n = 1-20) and fitted unconstrained correlations using (i) Ford's approach (eq. 10, magenta trace), (ii) a linear H/S function (red trace), (iii) a parabolic H/S function (blue trace) or (iv) a reciprocal Hill plot (green trace).

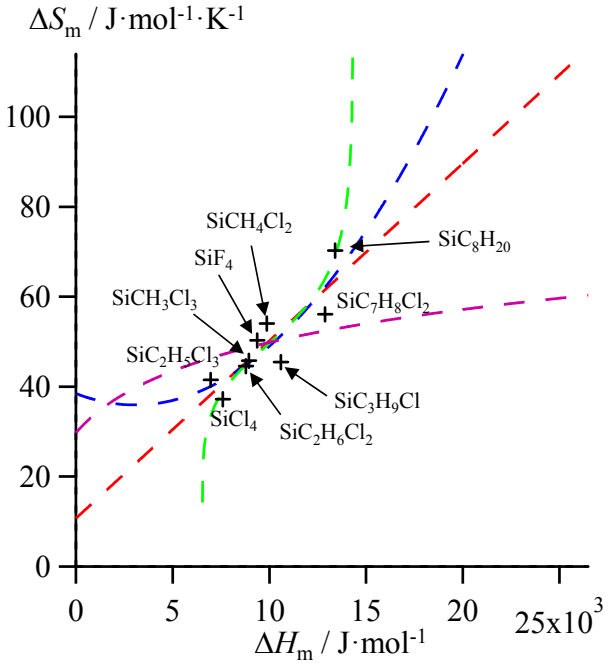

Figure S3 Plot of melting entropies ΔS_m *versus* melting enthalpies ΔH_m in organosilanes and fitted unconstrained correlations using (i) Ford's approach (eq. 10, magenta trace), (ii) a linear *H*/*S* function (red trace), (iii) a parabolic *H*/*S* function (blue trace) or (iv) a reciprocal Hill plot (green trace).

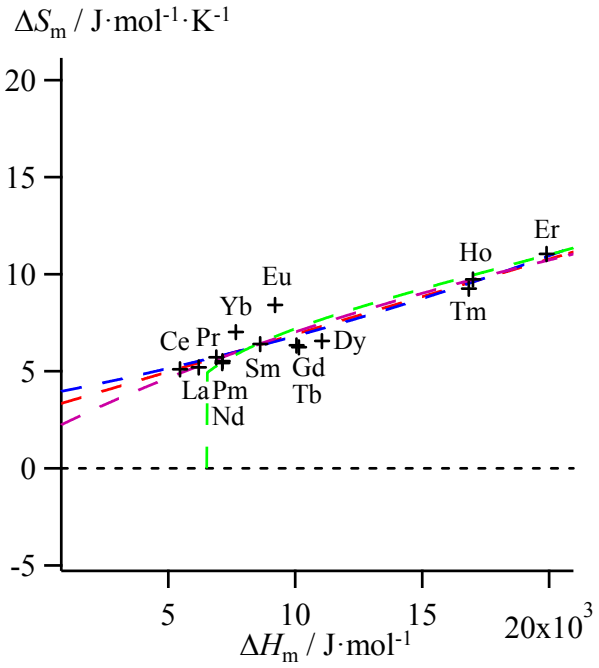

Figure S4 Plot of melting entropies ΔS_m *versus* melting enthalpies ΔH_m in lanthanide metals and fitted unconstrained correlations using (i) Ford's approach (eq. 10, magenta trace), (ii) a linear *H*/*S* function (red trace), (iii) a parabolic *H*/*S* function (blue trace) or (iv) a reciprocal Hill plots (green trace).

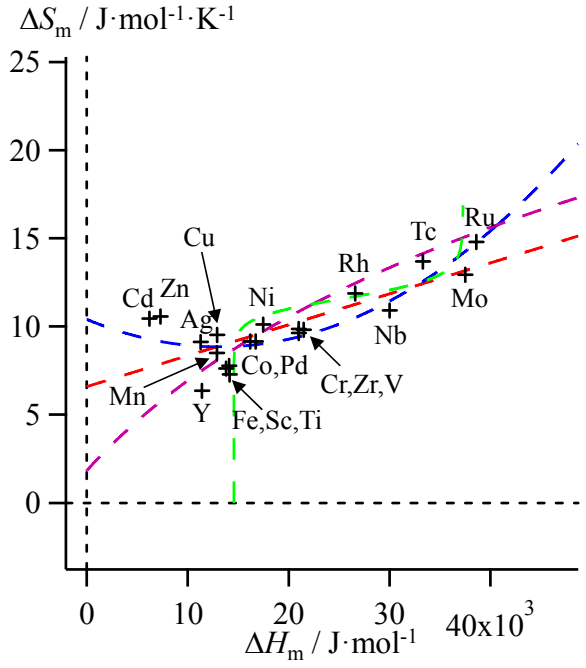

Figure S5 Plot of melting entropies ΔS_m *versus* melting enthalpies ΔH_m in transition metals and fitted unconstrained correlations using (i) Ford's approach (eq. 10, magenta trace), (ii) a linear *H*/*S* function (red trace), (iii) a parabolic *H*/*S* function (blue trace) or (iv) a reciprocal Hill plot (green trace).

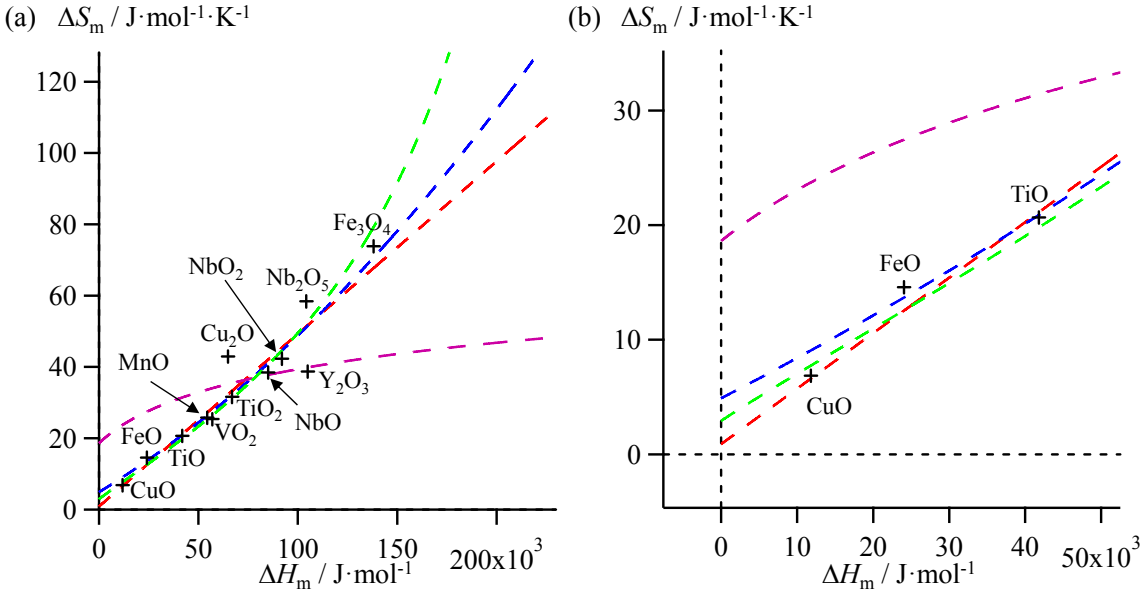

Figure S6 (a) Full representation, (b) low enthalpy inset for plot of melting entropies ΔS_m *versus* melting enthalpies ΔH_m in transition metal oxides and fitted unconstrained correlations using (i) Ford's approach (eq. 10, magenta trace), (ii) a linear *H*/*S* function (red trace), (iii) a parabolic *H*/*S* function (blue trace) or (iv) a reciprocal Hill plot (green trace).

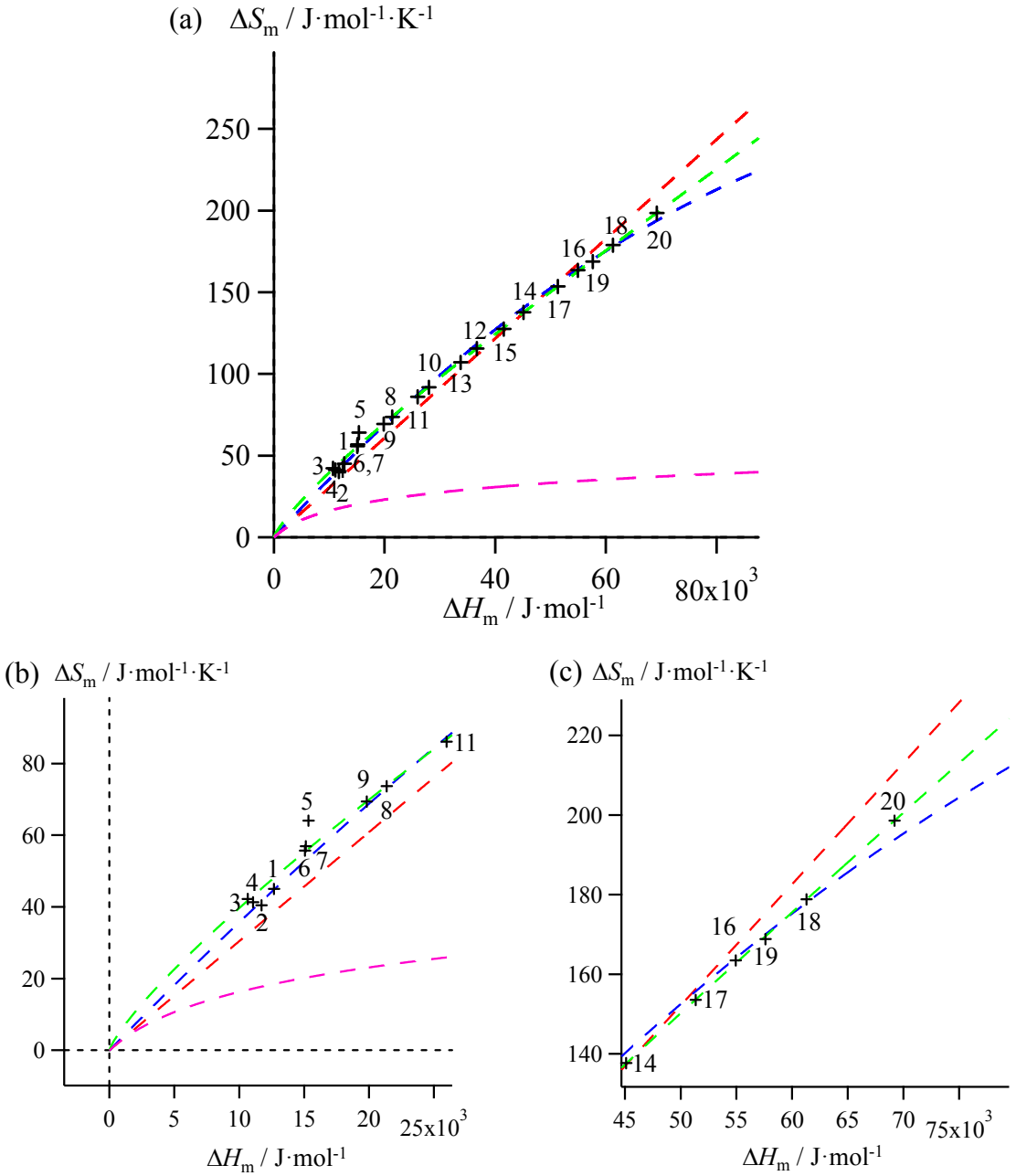

Figure S7 (a) Full representation, (b) low enthalpy inset and (c) high enthalpy inset for plot of melting entropies ΔS_m *versus* melting enthalpies ΔH_m in linear alkanoic acids $C_nH_{2n+1}COOH$ (n = 1-20) and fitted constrained correlations including $\Delta S_m \rightarrow 0$ when $\Delta H_m \rightarrow 0$ and using (i) Ford's approach (eq. 10, magenta trace), (ii) a linear H/S function (red trace), (iii) a parabolic H/S function (blue trace) or (iv) a reciprocal Hill plot (green trace).

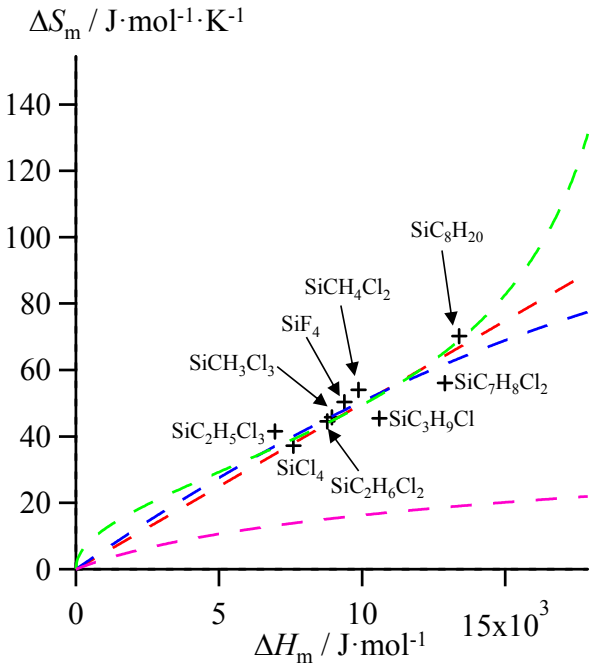

Figure S8 Plot of melting entropies ΔS_m *versus* melting enthalpies ΔH_m in organosilanes and fitted constrained correlations including $\Delta S_m \rightarrow 0$ when $\Delta H_m \rightarrow 0$ and using (i) Ford's approach (eq. 10, magenta trace), (ii) a linear *H*/*S* function (red trace), (iii) a parabolic *H*/*S* function (blue trace) or (iv) a reciprocal Hill plot (green trace).

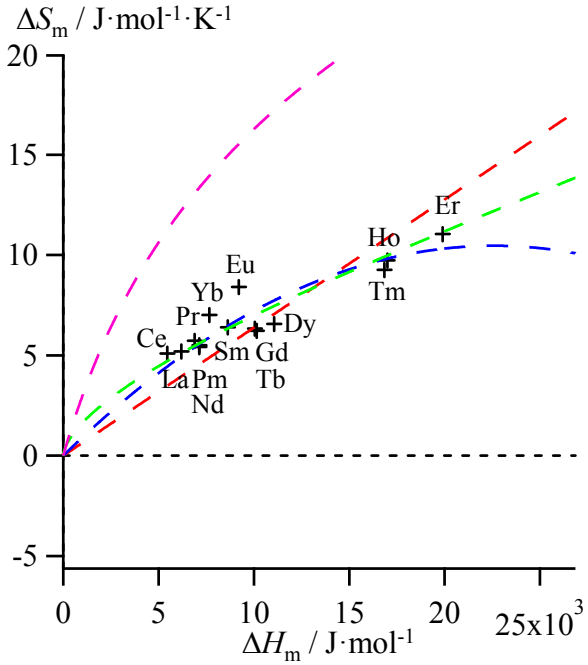

Figure S9 Plot of melting entropies ΔS_m *versus* melting enthalpies ΔH_m in lanthanide metals and fitted constrained correlations including $\Delta S_m \rightarrow 0$ when $\Delta H_m \rightarrow 0$ and using (i) Ford's approach (eq. 10, magenta trace), (ii) a linear *H*/*S* function (red trace), (iii) a parabolic *H*/*S* function (blue trace) or (iv) a reciprocal Hill plot (green trace).

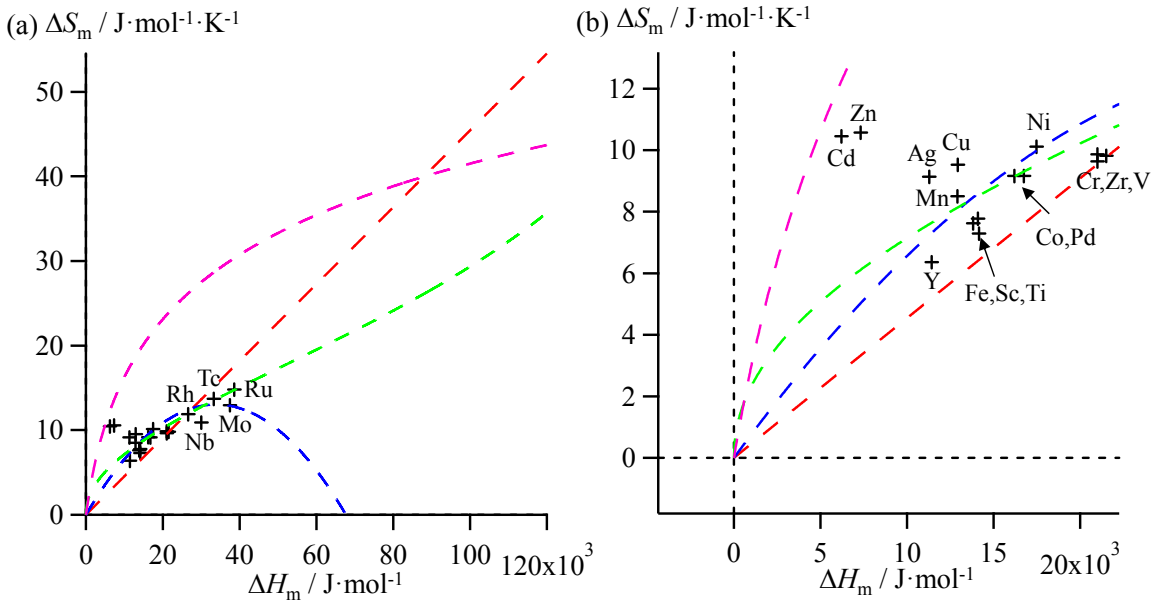

Figure S10 (a) Full representation, (b) low enthalpy inset for of melting entropies ΔS_m *versus* melting enthalpies ΔH_m in transition metals and fitted constrained correlations including $\Delta S_m \rightarrow 0$ when $\Delta H_m \rightarrow 0$ and using (i) Ford's approach (eq. 10, magenta trace), (ii) a linear *H*/*S* function (red trace), (iii) a parabolic *H*/*S* function (blue trace) or (iv) a reciprocal Hill plot (green trace).

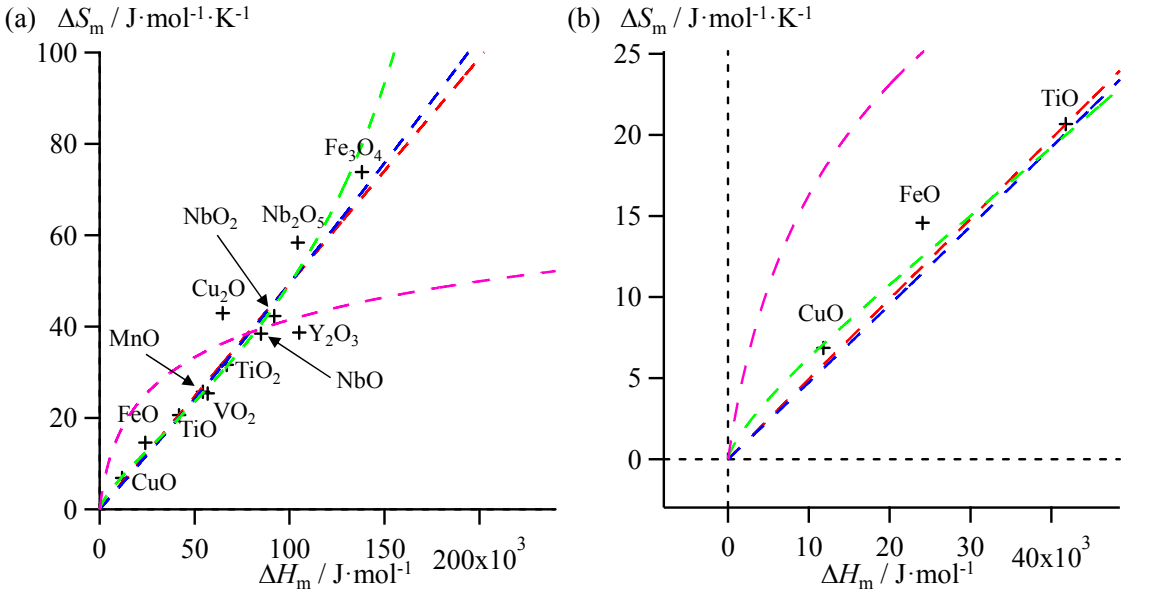

Figure S11 (a) Full representation, (b) low enthalpy inset for plot of melting entropies ΔS_m *versus* melting enthalpies ΔH_m in transition metal oxides and fitted constrained correlations including $\Delta S_m \rightarrow 0$ when $\Delta H_m \rightarrow 0$ and using (i) Ford's approach (eq. 10, magenta trace), (ii) a linear *H*/*S* function (red trace), (iii) a parabolic *H*/*S* function (blue trace) or (iv) a reciprocal Hill plot (green trace).

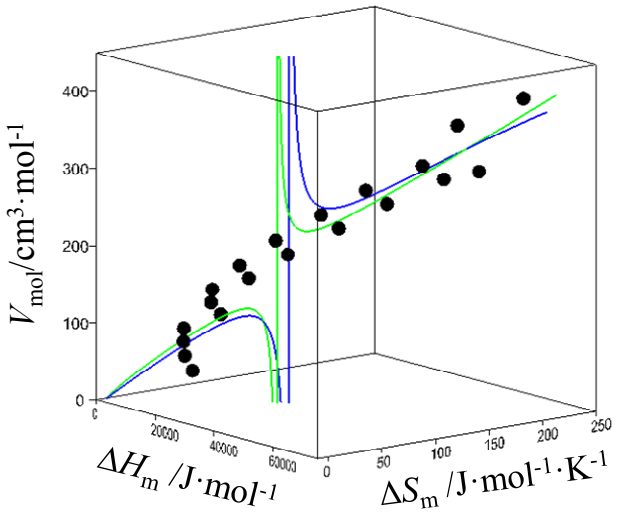

Figure S12 Three-dimensional V_{mol}, ΔH_m, ΔS_m plot for linear alkanoic acids fitted with a parabolic *H*/*S* function (blue trace) or a reciprocal Hill plots (green trace). An asymptotic behaviour is expected to occur when the melting temperature approach the selected reference temperature T^0 = 298.15 K.

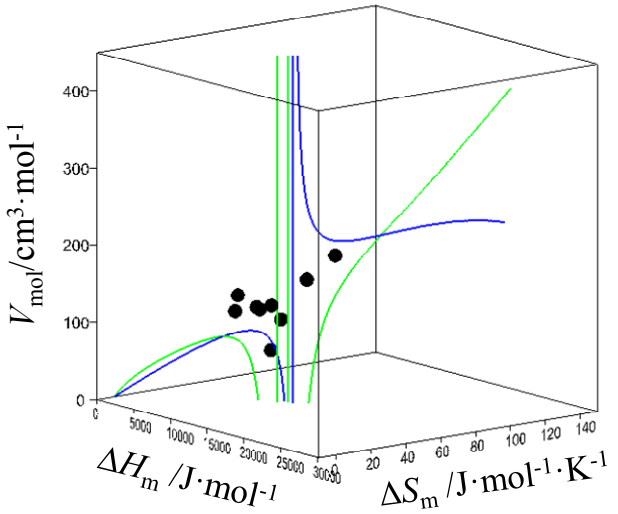

Figure S13 Three-dimensional V_{mol}, ΔH_m, ΔS_m plot for organosilanes fitted with a parabolic *H*/*S* function (blue trace) or a reciprocal Hill plots (green trace). An asymptotic behaviour is expected to occur when the melting temperature approach the selected reference temperature, T^0 = 200.00 K.

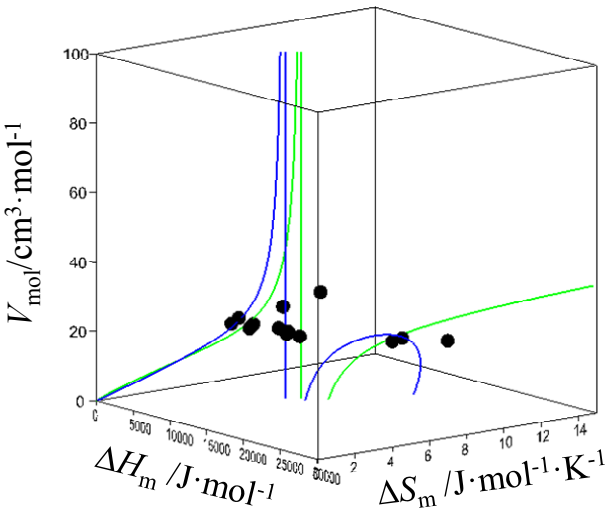

Figure S14 Three-dimensional V_{mol}, ΔH_m, ΔS_m plot for lanthanide metals fitted with a parabolic H/S function (blue trace) or a reciprocal Hill plots (green trace). An asymptotic behaviour is expected to occur when the melting temperature approaches the selected reference temperature T^0 = 1516.31 K.

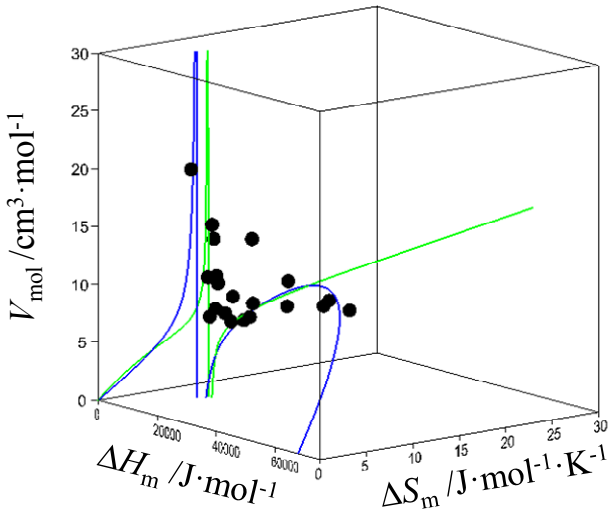

Figure S15 Three-dimensional V_{mol}, ΔH_m, ΔS_m plot for transition metals fitted with a parabolic H/S function (blue trace) or a reciprocal Hill plots (green trace). An asymptotic behaviour is expected to occur when the melting temperature approaches the selected reference temperature T^0 = 1585.57 K.

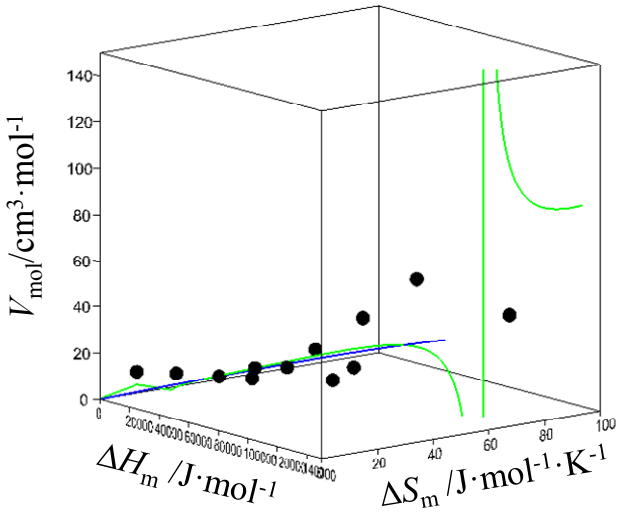

Figure S16 Three-dimensional V_{mol}, ΔH_m, ΔS_m plot for transition metal oxides fitted with a parabolic *H*/*S* function (blue trace) or a reciprocal Hill plots (green trace). An asymptotic behaviour is expected to occur when the melting temperature approaches the selected reference temperature T^0 = 1872.41 K.

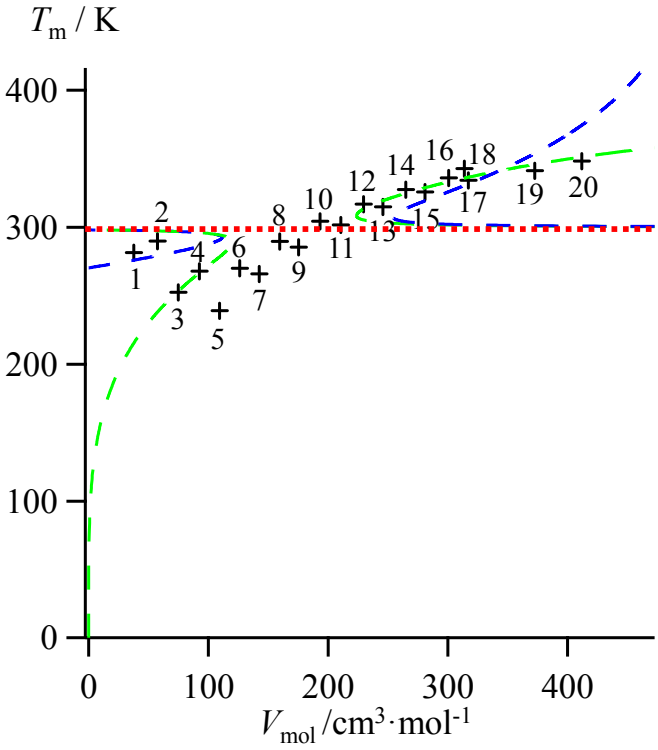

Figure S17 Correlations between molar volumes V_{mol} and melting temperatures T_m for linear alkanoic acids $C_nH_{2n+1}COOH$ (n = 1-20) fitted using a parabolic *H*/*S* function (blue trace) or a reciprocal Hill plots (green trace). The horizontal dotted red trace corresponds to the asymptotical behaviour occurring when the melting temperature approaches the selected reference temperature T^0 = 298.15 K.

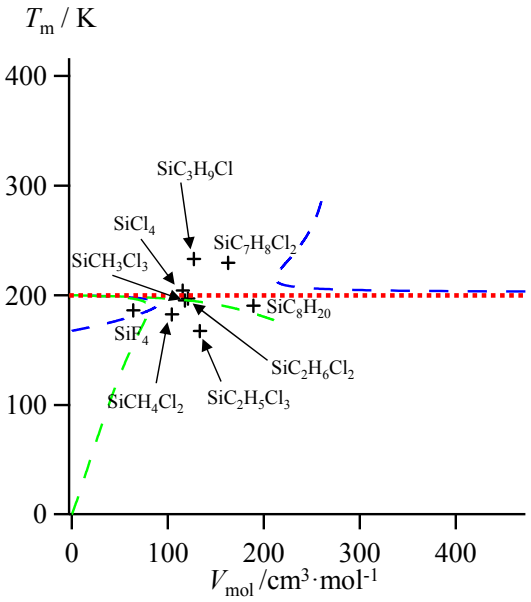

Figure S18 Correlations between molar volumes V_{mol} and melting temperatures T_m for organosilanes fitted using a parabolic *H*/*S* function (blue trace) or a reciprocal Hill plots (green trace). The horizontal dotted red trace corresponds to the asymptotical behaviour occurring when the melting temperature approaches the selected reference temperature $T^0 = 200.00$ K.

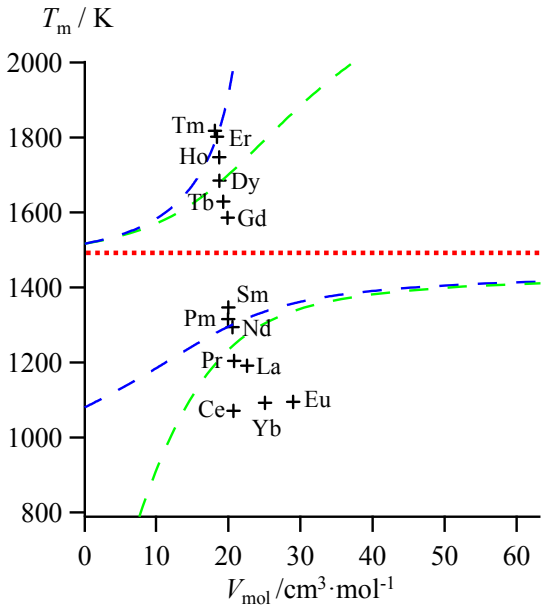

Figure S19 Correlations between molar volumes V_{mol} and melting temperatures T_m for lanthanide metals fitted using a parabolic *H*/*S* function (blue trace) or a reciprocal Hill plots (green trace). The horizontal dotted red trace corresponds to the asymptotical behaviour occurring when the melting temperature approaches the selected reference temperature $T^0 = 1516.31$ K.

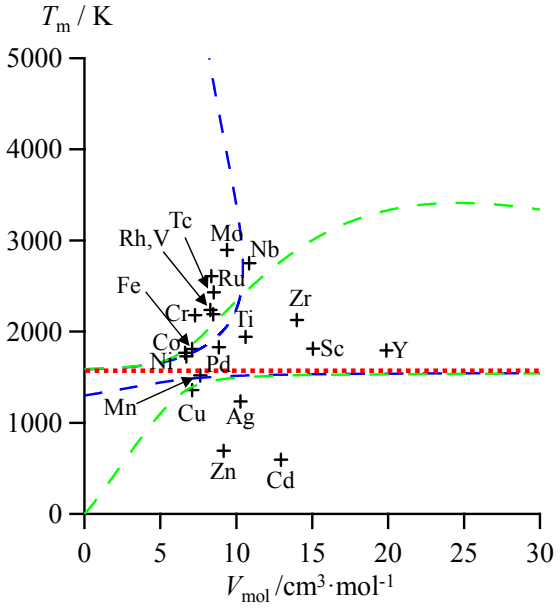

Figure S20 Correlations between molar volumes V_{mol} and melting temperatures T_m for transition metals fitted using a parabolic H/S function (blue trace) or a reciprocal Hill plots (green trace). The horizontal dotted red trace corresponds to the asymptotical behaviour occurring when the melting temperature approaches the selected reference temperature $T^0 = 1585.57$ K.

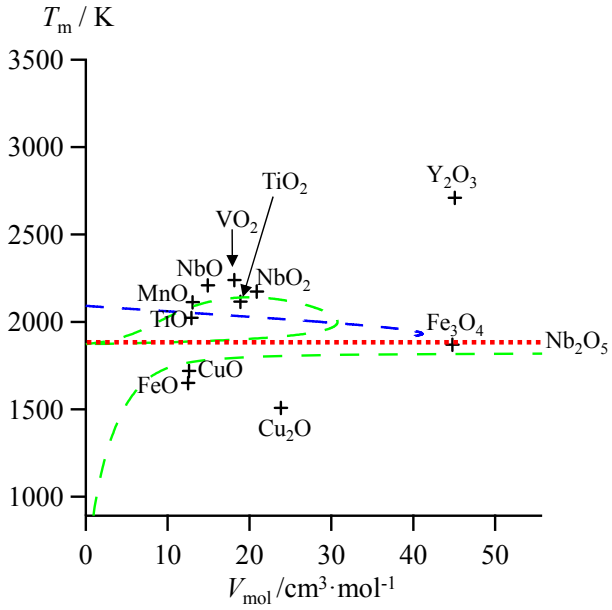

Figure S21 Correlations between molar volumes V_{mol} and melting temperatures T_m for transition metal oxides fitted using a parabolic H/S function (blue trace) or a reciprocal Hill plots (green trace). The horizontal dotted red trace corresponds to the asymptotical behaviour occurring when the melting temperature approaches the selected reference temperature $T^0 = 1872.41$ K.

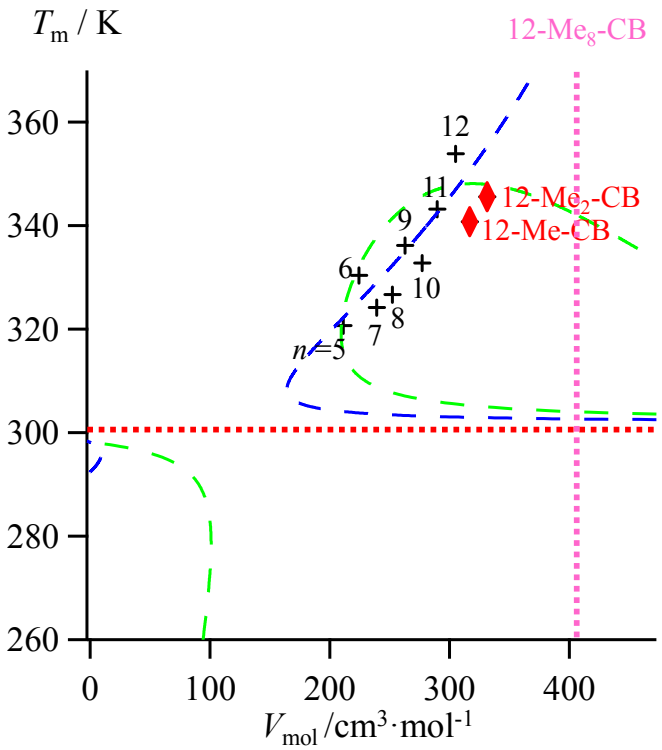

Figure S22 Correlations between molar volumes V_{mol} and melting temperatures T_m for substituted lipophilic cyanobiphenyls fitted using a parabolic *H*/*S* function (blue trace) or a reciprocal Hill plots (green trace). The horizontal dotted red trace corresponds to the asymptotical behaviour occurring when the melting temperature approaches the selected reference temperature T^0 = 298.15 K. The vertical dotted magenta trace shows the predictions obtained for the permethylated cyanobiphenyl 12-Me$_8$-CB.