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Electronic Supporting Materials

Non-covalent interactions in triglycerides: vaporisation thermodynamics for quantification of dispersion forces

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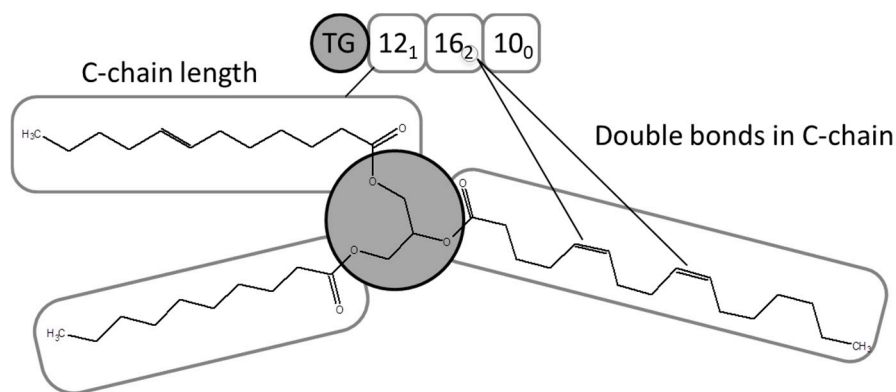


Figure S1. Schematic explanation of the TG abbreviations [1].

The TG molecule depicted in Fig. 1 contains three hydrocarbon side chains with 10, 12, and 16 carbon atoms. The subscripts represent the number of double bonds in a side chain. The C₁₂ side chain in Fig. S1 has one double bond and is thus named 12₁, the C₁₆ chain has two double bonds and is thus named 16₂, and the C₁₀ chain is completely saturated (10₀).

Nomenclature of triglycerides discussed in this paper:

TG 2₀2₀2₀ (triacetin, glycerol triacetate)
 TG 3₀3₀3₀ (tripropionin, glycerol tripropionate)
 TG 4₀4₀4₀ (tributylin, glycerol tributanoate)
 TG 5₀5₀5₀ (tripentanoin, glycerol tripentanoate)
 TG 6₀6₀6₀ (tricapronin, glycerol trihexanoate)
 TG 7₀7₀7₀ (triheptanoin, glycerol triheptanoate)
 TG 8₀8₀8₀ (tricaprylin, glycerol trioctanoate)
 TG 10₀10₀10₀ (tridecanoin, glycerol tridecanoate)
 TG 12₀12₀12₀ (trilaurin, glyceryl tridodecanoate)
 TG 14₀14₀14₀ (trimyristin, glycerol triteradecanoate)
 TG 16₀16₀16₀ (tripalmitin, glycerol trihexadecanoate)
 TG 18₀18₀18₀ (tristearin, glycerol trioctadecanoate)

Vapour pressure measurements. Transpiration method

Absolute vapour pressures of triglycerides were measured using the transpiration method [2; 3]. The main idea of this method is to saturate the gas stream flowing over the sample and to determine the amount of compound transferred by the gas within a given time. Approximately 0.3 to 0.5 g of the sample is mixed with glass beads (diameter 1 mm) and placed in the thermostatted U-shaped saturator. The glass beads are needed to enlarge the contact area between gas and sample. A stream of nitrogen at a well-defined flow rate was passed through the saturator at constant temperature (± 0.1 K), and the transported material was collected in a cold trap. The amount of the condensed substance was determined by weighing with balances (± 0.0002 g). The saturation vapour pressure p_i at each temperature T_i was calculated from the amount of condensate collected within a definite period of time:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i ; \quad V = (n_{N_2} + n_i) \cdot R \cdot T_a / P_a \quad (S1)$$

where V is the volume of the gas phase consisting of the n_{N_2} moles of the carrier gas and n_i mole of gaseous compound under study (with the molar mass M_i) at the atmospheric pressure P_a and the ambient temperature T_a . The volume of the carrier gas V_{N_2} was determined by the digital flow rate sensor from integration with a microcontroller. We used the Honeywell S&C - HAFBLF0200C2AX5 digital flow rate sensor with uncertainty at the level of 2.5 %. The flow rate of the nitrogen stream was also controlled by using a soap bubble flow meter (HP soap film flowmeter (model 0101-0113)) and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The volume of the carrier gas V_{N_2} was readied from the digital flow rate sensor. The amount of the compound under investigation n_i in the carrier gas was estimated at each temperature using the ideal gas law.

Before starting the vapour pressure measurements, the sample was first pre-conditioned at 310-320 K (within about one hour) in order to remove possible traces of water. The saturator was then kept at 310-320 K (to remove possible traces of volatile compounds). In order to assure the competition of pre-conditioning at the selected temperature, three samples were taken during the sample flashing and weighted. A constant vapour pressure at this temperature indicated that the transpiration experiments could begin.

Thermodynamics of vaporisation

The experimental vapour pressures p_i at different temperatures were fitted with the following equation [2; 3]:

$$R \times \ln(p_i / p_{ref}) = a + \frac{b}{T} + \Delta_1^g C_{p,m}^o \times \ln\left(\frac{T}{T_0}\right) \quad (S2),$$

where $\Delta_1^g C_{p,m}^o$ is the difference of the molar heat capacities of the gas and the liquid phases respectively (see Table 3), a and b are adjustable parameters, $R = 8.31446 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is the molar gas constant, and the reference pressure $p_{ref} = 1 \text{ Pa}$. The temperature T_0 appearing in Eq. (S2) is generally an arbitrarily chosen reference temperature. In this work it was chosen to be $T_0 = 298.15 \text{ K}$. Experimental vapour pressures measured in this work (as well as those from the literature) have been used to obtain the enthalpies of vaporisation using the following equation:

$$\Delta_1^g H_m^o(T) = -b + \Delta_1^g C_{p,m}^o \times T \quad (S3)$$

Experimental vapour pressures temperature dependences were also used to derive the vaporisation entropies at temperatures T by using the following equation:

$$\Delta_1^g S_m^o(T) = \Delta_1^g H_m^o(T) / T + R \times \ln(p_i / p^o) \quad (S4)$$

with $p^o = 0.1 \text{ MPa}$. Coefficients a and b of Eq. (1), $\Delta_1^g H_m^o(T)$ and $\Delta_1^g S_m^o(T)$ values are collected in Table S1. The combined uncertainties of the vaporisation enthalpies include uncertainties from the experimental conditions of transpiration. uncertainties in vapour pressure and uncertainties due to the temperature adjustment to $T = 298.15 \text{ K}$ as described elsewhere [4; 5]. The compilation of the standard molar enthalpies of vaporisation at the reference temperature $T = 298.15 \text{ K}$, calculated according to Eq. (S3) is given in Table 1 (main text).

Table S1

Results of transpiration method for triglycerides measured in this work: absolute vapour pressures p , standard molar vaporisation enthalpies and standard molar vaporisation entropies

$T/$ K ^a	$m/$ mg ^b	$V(\text{N}_2)^c/$ dm ³	$T_a/$ K ^d	Flow/ dm ³ ·h ⁻¹	$p/$ Pa ^e	$u(p)/$ Pa ^f	$\Delta_1^g H_m^o(T)/$ kJ·mol ⁻¹	$\Delta_1^g S_m^o(T)/$ J·K ⁻¹ ·mol ⁻¹
TG202020: $\Delta_1^g H_m^o(298.15 \text{ K}) = (80.2 \pm 0.9) \text{ kJ} \cdot \text{mol}^{-1}$								
$\ln(p_i/p_{ref}) = \frac{346.3}{R} - \frac{106392.2}{RT} - \frac{88}{R} \ln \frac{T}{298.15}; p_{ref} = 1 \text{ Pa}$								
318.1	18.3	99.51	289.0	5.94	2.13	0.06	78.4	157.1
327.5	11.3	26.78	294.8	6.35	4.84	0.13	77.6	154.3
335.9	13.4	15.87	294.8	6.35	9.58	0.26	76.8	151.9
341.4	19.9	14.60	289.0	6.35	15.10	0.40	76.4	150.5
347.9	11.0	5.032	294.4	5.81	24.62	0.64	75.8	148.8
354.9	43.6	11.67	294.4	4.07	41.98	1.07	75.2	147.2
360.9	13.5	2.322	294.8	5.81	65.35	1.66	74.6	145.9
362.9	17.5	2.613	296.6	5.81	75.74	1.92	74.5	145.5
TG808080: $\Delta_1^g H_m^o(298.15 \text{ K}) = (131.9 \pm 1.4) \text{ kJ} \cdot \text{mol}^{-1}$								
$\ln(p_i/p_{ref}) = \frac{500.5}{R} - \frac{185270.7}{RT} - \frac{179}{R} \ln \frac{T}{298.15}; p_{ref} = 1 \text{ Pa}$								
403.2	15.2	383.9	295.9	4.22	0.21	0.01	113.1	171.7
408.2	9.7	161.8	295.9	4.20	0.31	0.01	112.2	169.6
413.2	12.1	134.6	295.9	4.20	0.47	0.02	111.3	167.4
423.2	19.4	100.8	295.9	3.15	1.01	0.03	109.5	163.2
433.2	29.3	77.45	295.9	4.22	1.98	0.05	107.7	158.7
443.2	10.0	13.01	295.9	3.34	4.02	0.11	105.9	154.9
448.2	28.6	27.22	295.9	4.22	5.49	0.16	105.1	152.8
TG100100100: $\Delta_1^g H_m^o(298.15 \text{ K}) = (159.0 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$								
$\ln(p_i/p_{ref}) = \frac{573.1}{R} - \frac{220165.0}{RT} - \frac{205}{R} \ln \frac{T}{298.15}; p_{ref} = 1 \text{ Pa}$								
418.2	5.6	380.0	295.9	4.69	0.065	0.007	134.4	203.1
433.2	9.6	179.3	295.9	4.81	0.237	0.011	131.4	195.6
448.2	18.0	95.59	295.9	4.20	0.835	0.026	128.3	189.1
458.2	24.2	62.93	295.9	4.18	1.705	0.048	126.2	184.3
463.2	36.0	64.39	295.9	4.16	2.479	0.067	125.2	182.2
468.2	32.0	41.48	295.9	4.13	3.420	0.091	124.2	179.8

^a Saturation temperature measured with the standard uncertainty ($u(T) = 0.1 \text{ K}$).

^b Mass of transferred sample condensed at $T = 293 \text{ K}$.

^c Volume of nitrogen ($u(V) = 0.005 \text{ dm}^3$) used to transfer m ($u(m) = 0.0002 \text{ g}$) of the sample. Uncertainties are given as standard uncertainties.

^d T_a is the temperature of the soap bubble meter used for measurement of the gas flow.

^e Vapour pressure at temperature T , calculated from the m and the residual vapour pressure at the condensation temperature calculated by an iteration procedure.

^f Standard uncertainties were calculated with $u(p_i/\text{Pa}) = 0.005 + 0.025(p_i/\text{Pa})$ for pressures below 5 Pa and with $u(p_i/\text{Pa}) = 0.025 + 0.025(p_i/\text{Pa})$ for pressures from 5 to 3000 Pa. The standard uncertainties for T , V , p , m , are standard uncertainties with 0.683 confidence level. Uncertainties of the vaporisation enthalpy are expressed as the expanded uncertainty (0.95 level of confidence, $k = 2$) calculated according to procedure described elsewhere [4; 5]. Uncertainties include uncertainties from the experimental conditions and the fitting equation, vapour pressures, and uncertainties from adjustment of vaporisation enthalpies to the reference temperature $T = 298.15 \text{ K}$.

Quartz Crystal Microbalance (QCM)

Vapour pressures and molar enthalpies of vaporisation of TG10₀10₀10₀ and TG16₀16₀16₀, were measured by using the QCM method [6]. A sample of an IL was placed in an open cavity (Langmuir evaporation) inside of the thermostat block and it was exposed to vacuum (10⁻⁵ Pa) with the whole open surface of the loaded compound (see Fig. S2). The QCM-sensor was mounted directly above the measuring cavity containing the sample. Along the vaporisation into high vacuum, a certain amount of sample was condensed on the quartz crystal surface.

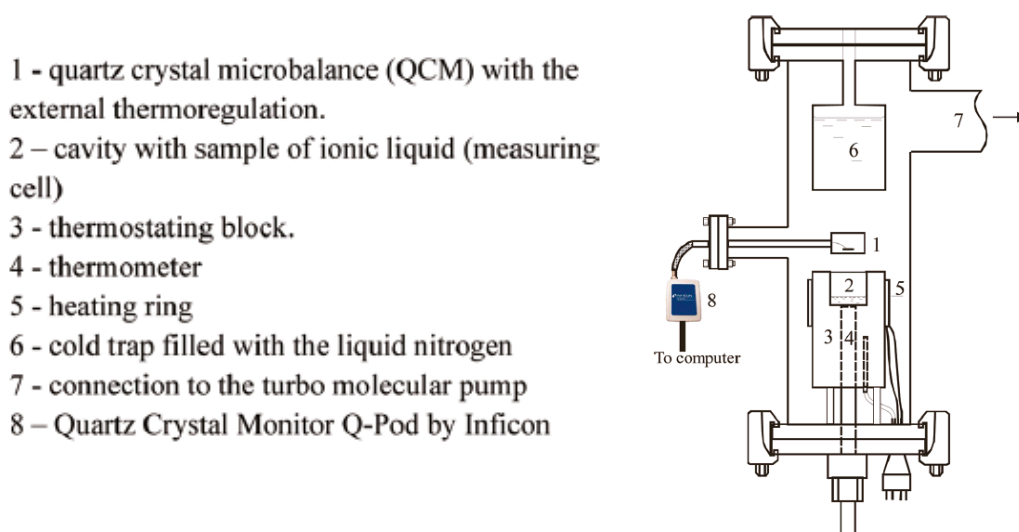


Figure S2. The scheme of the QCM experimental setup from [6].

The change in the vibrational frequency Δf was recorded. It is directly related to the mass deposition Δm on the QCM according to the Sauerbrey equation [7]:

$$\Delta f = -C \times f^2 \times \Delta m \times S_c^{-1} \quad (S5)$$

where f is the fundamental frequency of the crystal (6 MHz in this case) with $\Delta f \ll f$, S_c is the surface of the crystal, and C is a constant. The measured frequency change rates (df/dr) can be used for calculation of absolute vapour pressures p_i according to equation:

$$p_i = K' \frac{df}{dt} \sqrt{\frac{T}{M}} \quad (S6)$$

where the $K' = (9.5 \pm 1.1) \cdot 10^{-6} \text{ Pa} \cdot \text{s} \cdot \text{kg}^{1/2} \cdot \text{Hz}^{-1} \cdot \text{K}^{-1/2} \cdot \text{mol}^{-1/2}$ [8] is the empirical calibration constant including all parameters involved in Eq. (S5), as well as the all apparatus geometry specific parameters. Calibration of the set up was performed with the help of reliable vapour pressure data on very low volatile liquids [C_nPy][NTf₂], [C_nC_nim][NTf₂], and [C_nmim][NTf₂]. The experimental vapour pressures p_i at different temperatures were fitted with Eq. (S2) and the vaporisation enthalpies were derived according to Eq. (S3). A typical experiment was performed in a few consequent series with increasing and decreasing temperature steps. Every series included from 5 to 9 temperature points of mass loss rate determination. Such a procedure allowed for detection of any possible decomposition during frequency loss rate (df/dr) measurements. Reproducibility of results was established in series of randomly performed experimental runs. Uncertainties include uncertainties from the experimental conditions and the fitting equation, vapour pressures, and uncertainties from adjustment of

vaporisation enthalpies to the reference temperature $T = 298.15$ K. Primary experimental results of the QCM studies are provided in Table S2.

Table S2.

The experimental mass loss rates and vapour pressures determined for TG100100100 [1] and TG160160160 with QCM technique

Run	T , K	$10^{10}dm / dt$, kg s ⁻¹	$10^{-6} \times p_i$, Pa
TG100100100: $\Delta_l^g H_m^o(298.15 \text{ K}) = (166.7 \pm 2.6) \text{ kJ} \cdot \text{mol}^{-1}$			
$\ln(p_i/p_{ref}) = \frac{592.7}{R} - \frac{227849.3}{RT} - \frac{205}{R} \ln \frac{T}{298.15}; p_{ref} = 1 \text{ Pa}$			
1	367.81	0.4859	223
	363.18	0.2605	119
	358.38	0.1323	59.9
	353.48	0.06525	29.4
	348.50	0.03108	13.9
	367.80	0.4948	227
2	363.18	0.2637	120
	358.38	0.1322	59.9
	353.48	0.06443	29.0
	348.50	0.03049	13.6
TG160160160: $\Delta_l^g H_m^o(298.15 \text{ K}) = (210.2 \pm 9.2) \text{ kJ} \cdot \text{mol}^{-1}$			
$\ln(p_i/p_{ref}) = \frac{808.7}{R} - \frac{320021.5}{RT} - \frac{369}{R} \ln \frac{T}{298.15}; p_{ref} = 1 \text{ Pa}$			
1	433.19	1.537	339
	427.40	0.8323	182
	422.40	0.4665	102
	417.39	0.2570	56
	412.39	0.1439	31
	407.38	0.08034	17
	402.38	0.04381	10
	397.36	0.02297	5
	392.36	0.01187	2.8
	425.39	0.6421	104
2	419.89	0.3432	55
	414.90	0.1907	31
	409.89	0.1058	17
	404.90	0.05905	9
	399.88	0.03133	5
	394.88	0.01662	2.8
	389.89	0.008619	1.5
	384.87	0.004196	0.81

^aUncertainties are expressed as the expanded uncertainty (0.95 level of confidence, $k = 2$).

Isothermal stepwise TGA method.

We used a Perkin Elmer Pyris 6 TGA to determine $\Delta_l^g H_m^o(298.15 \text{ K})$ from the temperature dependence of the mass loss rate measurements. About 50-70 mg of the sample was placed in a plain platinum crucible inside of the measuring head of the TGA. The sample was step-wise heated and a mass loss from the crucible was recorded at each isothermal step. Isothermal mass loss rate dm/dt was monitored in the temperature range 400-490 K at a nitrogen flow

rate of 140 ml·min⁻¹. According to the results reported in our previous work [9], the optimal conditions for the reliable determination of vaporisation enthalpies of ILs were as follows:

- mass loss dm/dt at each temperature - 0.1-0.8 mg;
- duration of isothermal steps - at least 10 min;
- temperature range - at least 60 K;

Prior to the measurement of vaporisation enthalpy, a careful conditioning of the sample inside the TGA have been performed. A heating ramp of 10 K·min⁻¹ was used, followed by a 4 h static hold period at 383 K, allowing for the slow removal of volatile impurities and traces of water prior to a stepwise isothermal runs. The conditioning was repeated until a reproducible mass loss within two consequent runs was recorded. The detailed experimental procedure has been elaborated in our lab and it was reported elsewhere [9]. Experimental results of the isothermal TGA (ITGA) studies are collected in Table S3.

Table S3

The experimental mass loss rates and vapour pressure determined for TG808080 and TG100100100 with the I-TGA technique [9].

Run	T, K	$10^{12} dm / dt, kg s^{-1}$	p, Pa^a
TG808080: $\Delta_f^g H_m^o(298.15 K) = (135.0 \pm 4.7) kJ \cdot mol^{-1}$			
$\ln(p_i/p_{ref}) = \frac{507.9}{R} - \frac{188408.3}{RT} - \frac{179}{R} \ln \frac{T}{298.15}; p_{ref} = 1 \text{ bar}$			
1	404.26	226.6	0.226
	410.18	355.1	0.360
	416.09	545.5	0.560
	421.99	849.9	0.885
	427.89	1292	1.36
	433.80	1974	2.11
	439.75	2990	3.25
	445.71	4496	4.95
	451.68	6758	7.53
	398.37	145.9	0.143
	404.24	195.6	0.195
	410.16	374.0	0.379
	416.06	568.2	0.583
	421.96	851.9	0.887
2	427.85	1294	1.37
	433.76	1948	2.09
	439.70	2957	3.21
	445.66	4499	4.95
	451.64	6774	7.55
	398.33	137.5	0.135
	404.20	214.0	0.213
	410.12	353.0	0.357
	416.02	548.6	0.563
	421.92	849.8	0.885
3	427.81	1312	1.39
	433.73	1982	2.12
	439.67	3010	3.27
	445.64	4475	4.92
	451.63	6753	7.53
4	398.33	161.5	0.159

	404.18	222.4	0.222
	410.09	391.0	0.396
	415.99	536.7	0.551
	421.89	774.0	0.806
	427.78	1245	1.31
	433.69	1888	2.02
	439.63	2879	3.12
	445.59	4351	4.79
	451.58	6534	7.28
	402.22	192.3	0.191
	408.12	314.6	0.317
	414.02	477.6	0.489
	419.92	716.6	0.743
	425.80	1105	1.16
5	431.72	1687	1.80
	437.65	2558	2.77
	443.60	3816	4.18
	449.57	5684	6.31
	455.57	8477	9.54
	461.59	12415	14.2
	408.09	279.9	0.282
	413.99	471.1	0.482
	419.89	749.1	0.777
	425.78	1127	1.19
6	431.69	1694	1.81
	437.62	2583	2.79
	443.58	3848	4.22
	449.56	5788	6.43
	455.55	8609	9.69
	461.57	12637	14.4
	408.07	316.1	0.319
	413.98	468.3	0.479
	419.87	737.3	0.765
	425.76	1090	1.15
7	431.67	1651	1.76
	437.60	2543	2.75
	443.56	3834	4.20
	449.53	5762	6.40
	455.52	8525	9.59
	461.54	12365	14.1
	402.15	189.0	0.188
	408.06	326.9	0.330
	413.96	474.9	0.486
	419.86	726.7	0.754
	425.74	1096	1.15
8	431.66	1675	1.79
	437.59	2528	2.73
	443.55	3773	4.13
	449.51	5676	6.30
	455.51	8377	9.43
	461.53	12128	13.8

TG10o10o10o: $\Delta_f^g H_m^o(298.15 \text{ K}) = (169.6 \pm 4.7) \text{ kJ} \cdot \text{mol}^{-1}$

$$\ln(p_i/p_{ref}) = \frac{599.5}{R} - \frac{230762.0}{RT} - \frac{205}{R} \ln \frac{T}{298.15}; p_{ref} = 1 \text{ bar}$$

1	433.93	0.05252	0.344
	439.83	0.08623	0.568
	445.72	0.1388	0.921
	451.66	0.2326	1.55
	457.64	0.3665	2.46
	463.65	0.5896	3.99
	469.68	0.9219	6.28
	475.74	1.417	9.72
	481.73	2.155	14.9
	439.76	0.08927	0.588
2	445.68	0.1481	0.983
	451.63	0.2251	1.50
	457.62	0.3744	2.52
	463.63	0.6004	4.06
	469.66	0.9341	6.36
	475.71	1.443	9.89
	481.70	2.185	15.1
	427.94	0.03171	0.206
	433.83	0.05153	0.337
	439.73	0.08470	0.558
3	445.65	0.1426	0.946
	451.61	0.2240	1.50
	457.60	0.3730	2.51
	463.60	0.5983	4.05
	469.64	0.9251	6.30
	475.69	1.430	9.80
	481.67	2.1745	15.0
	439.71	0.08145	0.537
	445.63	0.1319	0.875
	451.59	0.2214	1.48
4	457.58	0.3582	2.41
	463.57	0.5761	3.90
	469.61	0.8930	6.08
	475.65	1.390	9.53
	481.63	2.110	14.6
	443.68	0.1198	0.793
	449.60	0.1858	1.24
	455.56	0.2947	1.98
	461.55	0.4730	3.19
	467.56	0.7422	5.04
5	473.61	1.152	7.88
	479.64	1.768	12.2
	485.59	2.632	18.2
	491.56	3.886	27.1
	449.57	0.1869	1.25
6	455.54	0.3048	2.04
	461.53	0.4941	3.34
	467.55	0.7677	5.22

	473.61	1.201	8.21
	479.63	1.828	12.6
	485.57	2.716	18.8
	491.54	4.008	27.9
	443.60	0.1167	0.773
	449.53	0.1973	1.32
	455.51	0.3006	2.02
	461.51	0.4524	3.05
7	467.54	0.7179	4.88
	473.59	1.140	7.80
	479.62	1.767	12.2
	485.56	2.647	18.3
	491.53	3.895	27.1
	437.68	0.06961	0.458
	449.52	0.1762	1.17
	455.50	0.2753	1.85
	461.50	0.4601	3.11
8	467.53	0.7677	5.22
	473.58	1.183	8.10
	479.61	1.826	12.6
	485.56	2.721	18.8
	491.53	4.026	28.1

^a The expanded uncertainties in the vapour pressures are given at 0.95 confidence level, k=2) and calculated according to equation $U(p_i) = 0.2 p_i$. Experimental vapour pressures of triglycerides determined with the transpiration technique were used for scaling the mass loss rates of TGA results.

Table S4.

Vapour pressures p , standard ($p^0 = 0.1$ MPa) molar vaporisation enthalpies, $\Delta_l^g H_m^0$, and standard ($p^0 = 0.1$ MPa) molar vaporisation entropies, $\Delta_l^g S_m^0$ obtained by the approximation of data collected from SciFinder [10].

T/ K	p_i/Pa	$\Delta_l^g H_m^0(T) / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta_l^g S_m^0(T) / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
TG303030: $\Delta_l^g H_m^0(298.15 \text{ K}) = (94.7 \pm 3.9) \text{ kJ} \cdot \text{mol}^{-1}$			
$\ln(p_i/p_{ref}) = \frac{389.7}{R} - \frac{125975.7}{RT} - \frac{105}{R} \ln \frac{T}{298.15}; p_{ref} = 1 \text{ Pa}$			
403	267	83.7	158.3
405	267	83.5	156.8
449	2666	78.8	145.4
450	2666	78.7	144.8
545	101325	68.8	126.3
TG404040: $\Delta_l^g H_m^0(298.15 \text{ K}) = (102.7 \pm 4.3) \text{ kJ} \cdot \text{mol}^{-1}$			
$\ln(p_i/p_{ref}) = \frac{412.1}{R} - \frac{137926.4}{RT} - \frac{118}{R} \ln \frac{T}{298.15}; p_{ref} = 1 \text{ Pa}$			
394	36	91.4	166.1
398	36	91.0	162.6
401	60	90.6	164.3
403	60	90.4	162.6
463	1999.8	83.3	147.4
578	101325	69.7	120.7
578	101325	69.7	120.7

580	101325	69.4	119.7
583	101325	69.1	118.7
583	101325	69.1	118.7
TG606060: $\Delta_1^g H_m^o(298.15 \text{ K}) = (114.2 \pm 5.6) \text{ kJ} \cdot \text{mol}^{-1}$			
$\ln(p_i/p_{ref}) = \frac{448.6}{R} - \frac{156224.1}{RT} - \frac{141}{R} \ln \frac{T}{298.15}; p_{ref} = 1 \text{ Pa}$			
428	53	95.9	161.3
433	67	95.2	159.0
515	3733	83.6	135.0
517	3733	83.3	133.8
633	101325	67.0	105.9

Table S5

Compilation of data on molar heat capacities $C_{p,m}^o(\text{liq})$ and heat capacity differences $\Delta_1^g C_{p,m}^o$ for the linear aliphatic esters at $T = 298.15 \text{ K}$ (in $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

Ester	$C_{p,m}^o(\text{liq})$ [11]	$\Delta_1^g C_{p,m}^o$ ^a
Methyl propanoate	172.0	-40
Methyl butyrate	198.1	-47
Methyl pentanoate	229.0	-53
Methyl hexanoate	245.3	-70
Methyl heptanoate	285.0	-75
Methyl octanoate	316.2	-77
Methyl nonanoate	346.1	-78
Methyl decanoate	375.3	-85
Methyl undecanoate	407.1	-90
Methyl dodecanoate	436.9	-100
Methyl tridecanoate	467.9	-105
Methyl tetradecanoate	499.0	-112
Methyl pentadecanoate	524.7	-115
Methyl hexadecanoate	561.9	-120
Methyl heptadecanoate	592.2	-125
Methyl octadecanoate	620.3	-130
Methyl nonadecanoate	681.6	-135
Methyl eicosanoate	719.7	-145

^a Values recommended for the temperature adjustment of vaporisation enthalpies of aliphatic esters.

Table S6

The chain length dependence of the molar heat capacities $C_{p,m}^o(\text{liq})$ for the linear aliphatic esters at $T = 298.15 \text{ K}$ (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

Ester	N_C ^a	$C_{p,m}^o(\text{liq})_{\text{exp}}$ [11]	$C_{p,m}^o(\text{liq})_{\text{calc}}$ ^b	Δ ^c
Methyl propanoate	3	172.0	159	13
Methyl butyrate	4	198.1	191	7
Methyl pentanoate	5	229.0	222	7
Methyl hexanoate	6	245.3	254	-8
Methyl heptanoate	7	285.0	285	0
Methyl octanoate	8	316.2	317	-1
Methyl nonanoate	9	346.1	348	-2
Methyl decanoate	10	375.3	380	-4
Methyl undecanoate	11	407.1	411	-4
Methyl dodecanoate	12	436.9	443	-6
Methyl tridecanoate	13	467.9	474	-6
Methyl tetradecanoate	14	499.0	506	-7
Methyl pentadecanoate	15	524.7	537	-13
Methyl hexadecanoate	16	561.9	569	-7
Methyl heptadecanoate	17	592.2	600	-8
Methyl octadecanoate	18	620.3	632	-11
Methyl nonadecanoate	19	681.6	663	18
Methyl eicosanoate	20	719.7	695	25

^a Number of C-atoms in the alkyl chain.

^b Calculated using correlation:

$C_{p,m}^o(\text{liq}) = 31.5 \times N_C + 64.7$ (with $R^2 = 0.996$), derived from data given in this table.

^c Difference between column 3 and 4.

Table S7

Comparison of experimental and additive enthalpies of vaporisation, $\Delta_l^g H_m^o(298.15 \text{ K})$, for triglycerides with the linear saturated alkyl chains (in kJ mol^{-1})

	$\Delta_l^g H_m^o(298.15 \text{ K})_{\text{exp}}^a$	$\Delta_l^g H_m^o(298.15 \text{ K})_{\text{calc}}^b$	Δ^c
TG 303030	90.4±0.5	91.1	-0.7
TG 404040	97.5±0.6	101.6	-4.1
TG 505050	105.0±0.7	115.9	-10.9
TG 606060	114.9±3.6	130.2	-15.3
TG 707070	127.0±2.1	144.4	-17.4
TG 808080	134.1±1.2	158.7	-24.6
TG 100100100	160.1±0.9	187.3	-27.2
TG 120120120	174.9±3.0	215.8	-40.9
TG 140140140	194.2±2.9	244.4	-50.2
TG 160160160	211.0±2.1	273.0	-62.0
TG 180180180	232.1±3.0	301.5	-69.4

^a Values evaluated and recommended (given in bold) in Table 1 (main text). Uncertainty of the vaporisation enthalpy is expressed as the expanded uncertainty (0.95 level of confidence, $k = 2$).

^b Calculated using group-additivity (GA) with increments collected in Table 7 (main text).

^c Difference between column 2 and 3, assigned as dispersion interactions in triglycerides (see Section 3.6).

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