

Supplementary Information

Body-centred cubic packing of spheres – The ultimate thermotropic assembly mode for highly divergent dendrons

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Techniques

Chemical analysis and DSC. ¹H-NMR spectra were recorded on a Bruker Advance II DMX 400 spectrometer and ¹³C-NMR spectra were recorded on a Bruker Advance III 500 spectrometer using CDCl₃ as solvent and TMS as internal standard. Chemical shifts are reported as ppm. The purity of products was determined by a combination of techniques including thin-layer chromatography (TLC) on silicagel-coated aluminum plates and elemental analysis system VarioMICRO cube from Elementar Analysensysteme. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer or with a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica,

MA, USA). Thermal transitions of samples were measured on a TA Instruments Q200 and Mettler differential scanning calorimeter (DSC) with 10°C min⁻¹ heating and cooling rates. The samples were dried *in vacuo* at room temperature for 1-2 days prior to the scan, and the DSC cell was flushed with dry nitrogen. First order transition temperatures were reported as the maxima and minima of their endothermic and exothermic peaks, corrected for thermal lag determined from the ascending slope of indium melting endotherm at the appropriate heating rate. Indium was also used to calibrate temperature and heat flow.

X-ray diffraction. Small-angle X-ray diffraction (SAXD) experiments on liquid crystal phases were performed by using both a laboratory X-ray source and synchrotron radiation. The laboratory set-up consisted of a Xenocs microfocus copper source, a Fox3d infinity focussing multilayer mirrors and a collimator containing scatterless Si slits. The detector was a Mar 345 image plate detector, positioned off-centre, 1.3 m from the sample. Primary and scattered beam tubes were evacuated. Synchrotron SAXD experiments were carried out on beamline I22 at Diamond Light Source, UK, using a Pilatus detector bank. In both set-ups the samples were kept in 1 mm X-ray capillaries held in a Linkam hot stage with a bore for the capillary and mica windows to prevent convection. As with the DSC measurements, the samples for X-ray were also dried *in vacuo* at room temperature for 1-2 days prior to the experiment. Immediately on transferring them to the capillaries, the capillaries were evacuated on a vacuum line and sealed. Azimuthally averaged radial scans of scattered intensity were obtained using Fit2d and Fibrefix. 3-D electron density maps were reconstructed as described elsewhere.^{S1} Wide-angle X-ray diffraction was recorded using a Rigaku rotating anode generator with Osmic multilayer mirrors and a Mar 345 image plate detector. A Cryostream N₂ jet was used to control the sample temperature.

Materials

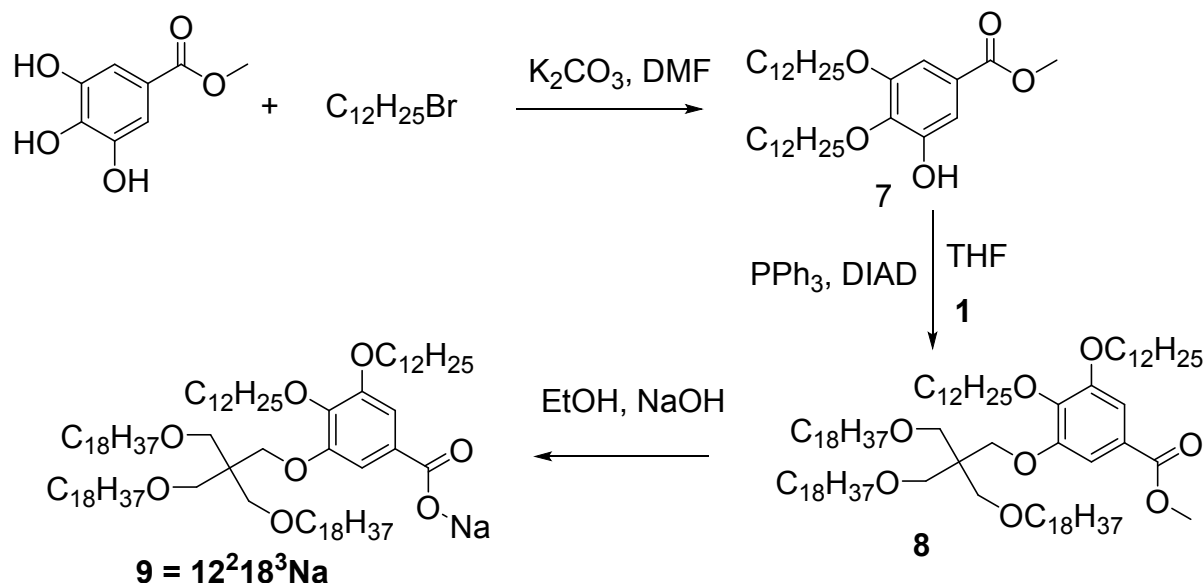
All reagents used were of analytical grade and were purchased from Energy or Aladdin Chemicals. THF was dried by distillation on Na/benzophenone. The other solvents were used without further purification other than drying over molecular sieves.

Methyl 4-(benzyloxy)-3,5-dihydroxybenzoate (**2**) was obtained according to ref. S2, methyl 3,4-bis(dodecyloxy)-5-hydroxy-benzoate (**7**) according to ref. ³ and sodium 3,4,5-trialkoxybenzoate (**12** and **13**) according to ref. S4. The procedure used for the preparation of 3-(octadecyloxy)-2,2-bis((octa-decyloxy)methyl)propan-1-ol (**1**) is an improvement on the previous method [S⁵].

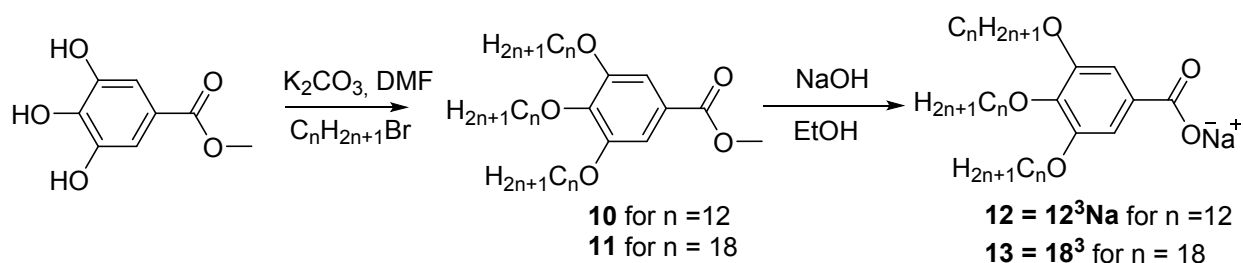
Abbreviations: DCM – dichloromethane; DIAD - diisopropyl azodicarboxylate; DMF – dimethylformamide; EtOAc – ethyl acetate; PE – petroleum ether (fraction 60-90); THF – tetrahydrofuran; TBAB - tetrabutylammonium bromide.

OC(CO)CO.CCCCCCCCCCCCCCCCCCBr>[NaOH].[H2O].TBAB>CCCCCCCCCCCCCCCCOCC(CO)CO.CCCCCCCCCCCCCCCCCCOC **1**
 5h at 80 C
COC(=O)c1cc(O)c(O)cc1.BrCc1ccccc1>[KHCO3].[KI].DMF>COC(=O)c1cc(Oc2ccccc2)c(O)c1.BrCc1ccccc1 **2**
 rt, 20 h
COC(=O)c1cc(Oc2ccccc2)c(O)c1.BrCCCCCCCCCCCCCCCCC>[K2CO3].DMF>COC(=O)c1cc(OC(CO)CO)cc(OC(CO)CO)c1 **3**
 rt, 15 h
COC(=O)c1cc(OC(CO)CO)cc(OC(CO)CO)c1>[H2].[Pd/C].EtOAc>COC(=O)c1cc(OC(CO)CO)cc(OC(CO)CO)c1 **4**
COC(=O)c1cc(OC(CO)CO)cc(OC(CO)CO)c1>[DIAD].[PPh3].THF>COC(=O)c1cc(OC(CO)CO)cc(OC(CO)CO)c1 **5**
COC(=O)c1cc(OC(CO)CO)cc(OC(CO)CO)c1>[NaOH].EtOH>COC(=O)[O-]c1cc(OC(CO)CO)cc(OC(CO)CO)c1 **6 = 18³Na**

3



Scheme S2. Synthesis of the carboxylate sodium salt **12²18³Na**



Scheme S3. Synthesis of sodium 3,4,5-trialkoxybenzoates **12³Na** and **18³Na**

Synthesis and characterization of compounds

3-(octadecyloxy)-2,2-bis((octa-decyloxy)methyl)propan-1-ol (1) A solution of sodium hydroxide (80 g, 2.0 mol) in water (125 mL) was heated at 80 °C, pentaerythritol (6.3 g, 46 mmol) was added and stirred at this temperature for 30 min. TBAB (6.5 g, 0.020 mol) and then 1-bromooctadecane (66.7 g, 0.20 mol) were added. The mixture was stirred at 80 °C for other 5 hours. The solution was cooled down at 50 °C and CHCl₃ (200 ml) was added. The organic layer was separated, cooled down at r. t., acidulated with HCl 0.1 N until pH = 5, washed with H₂O and dried over MgSO₄ anhydrous. The solvent was removed and the crude product was purified by column chromatography (SiO₂, PE and then PE/EtOAc = 9/1) (R_f = 0.57 for PE/EtOAc = 9/1). The pure product was obtained as a yellow-white solid (10.2 g, 24 % yield).

¹H-NMR (400 MHz, CDCl₃, r.t) δ (ppm): 3.70 (d, 2H, HO-CH₂-, J = 5.6 Hz), 3.43 (s, 6H, -C-(CH₂-O-C₁₈H₃₇)₃), 3.38 (t, 6H, -C-(CH₂-O-CH₂-C₁₇H₃₅)₃, J = 6.5 Hz), 3.18 (t, 1H, -OH, J = 5.9 Hz), 1.53 (m, 6H, (-O-CH₂-CH₂-C₁₆H₃₃)₃), 1.25 (m, 90H, -CH₂-), 0.88 (t, 9H, -CH₃, J = 6.4 Hz).

¹³C-NMR (125 MHz, CDCl₃, r.t.) δ (ppm): 71.8, 71.5, 66.6, 44.7, 31.9, 30.9, 29.3-29.7, 26.2, 22.7, 14.1.

Methyl 4-(benzyloxy)-3,5-bis(octadecyloxy)benzoate (3): To a solution of diol **2** (5.48 g, 20 mmol) and potassium carbonate (6.91 g, 50 mmol) in DMF (100 mL) 1-bromooctadecane (16.67 g, 50 mmol) was added. The mixture was stirred for 20 hours at r.t. The precipitate was filtered. The DMF was distilled off and the crude product was dissolved in EtOAc (30 mL). The organic phase was washed with H₂O and dried over MgSO₄ anhydrous. The solvent was removed and the crude product was purified by column chromatography (SiO₂, DCM/PE = 1/1, R_f = 0.47) to afford a white solid (1.02 g, 7 % yield).

¹H-NMR (400 MHz, CDCl₃, r.t.) δ (ppm): 7.49 (d, 2H, Har, J = 7.44 Hz), 7.37-7.27 (m, 3H, Har), 7.26 (s, 2H, Har), 5.08 (s, 2H, -CH₂-C₆H₅), 4.01 (t, 4H, -O-CH₂-, J = 6.4 Hz), 3.89 (s, 3H, -COO-CH₃), 1.81 (q, 4H, -O-CH₂-CH₂-), 1.47 (q, 4H, -CH₂-), 1.21-1.40 (overlap, 32H, -CH₂-), 0.88 (t, 6 H, -CH₂-CH₃, J = 6.0 Hz).

¹³C-NMR (125 MHz, CDCl₃, r.t.) δ (ppm): 166.8, 152.6, 141.5, 137.6, 128.1, 127.6, 124.9, 107.7, 74.8, 69.1, 52.1, 31.9, 30.9, 29.3-29.6, 26.1, 22.7, 14.1.

Methyl 4-hydroxy-3,5-bis(octadecyloxy)benzoate (4). 10% Pd/C (0.30 g) was added to a solution of compound **3** (2.0 g, 2.6 mmol) in EtOAc (20 mL) and the mixture was stirred under hydrogen for 2 hours. The reaction mixture was filtered and the solvent was evaporated. The product was obtained as a white solid (1.6 g, 90% yield).

¹H-NMR (400 MHz, CDCl₃, r.t.) δ (ppm): 7.28 (s, 2H, Har), 5.88 (s, 1H, -OH), 4.07 (t, 4H, -O-CH₂-), 3.88 (s, 3H, -COO-CH₃), 1.83 (m, 4H, -O-CH₂-CH₂-), 1.45 (m, 4H, -CH₂-), 1.25 (m, 60H, -CH₂-), 0.88 (t, 6 H, -CH₃, J = 6.4 Hz).

¹³C-NMR (125 MHz, CDCl₃, r.t.) δ (ppm): 167.0, 145.1, 139.8, 120.9, 107.7, 69.5, 52.0, 31.9, 30.9, 29.6-29.7, 29.5-29.6, 29.3, 29.2, 25.9, 22.6, 14.1.

Methyl 3,5-bis(octadecyloxy)-4-(3-(octadecyloxy)-2,2-bis((octadecyloxy)methyl)propoxy)benzoate (5). To compound **4** (0.37 g, 0.50 mmol), pentaerythritol derivative **1** (0.47 g, 0.53 mmol) and PPh₃ (0.14 g, 0.53 mmol) in dry THF (1 mL) was added drop wise DIAD (0.32 mL, 1.62 mmol) under nitrogen at 67 °C. The reaction was refluxed for 4 hours. The solvent was removed and the crude product was dissolved in DCM. The mixture was washed successively with water, NH₄Cl (2 × 50 mL), brine (2 × 20 mL), water and dried over by MgSO₄. The solvent was evaporated under pressure and the product was purified by chromatography (SiO₂, DCM/PE = 1/1, R_f = 0.68) to give a white solid (0.57 g, 38% yield).

LRESIMS: m/z calcd. for [M + Na]⁺ C₁₀₃H₁₉₈NaO₈, 1586.4984, found 1586.4978, error 0.4 ppm.

¹H-NMR (400 MHz, CDCl₃, r.t.) δ (ppm): 7.22 (s, 2H), 4.13 (s, 2H), 3.98 (t, 4H, J = 6.4 Hz), 3.87 (s, 3H), 3.54 (s, 6H), 3.35 (t, 6H, J = 6.5 Hz), 1.81 (m, 4H), 1.48 (m, 10H), 1.25 (m, 90H), 0.88 (t, 15 H, J = 6.4 Hz).

¹³C-NMR (125 MHz, CDCl₃, r.t.) δ (ppm): 167.0, 152.2, 143.0, 124.0, 107.9, 73.1, 71.5, 69.6, 69.1, 52.0, 45.9, 31.9, 30.9, 29.6-29.7, 29.4-29.5, 26.2, 26.1, 22.7, 14.1.

Sodium 3,5-bis(octadecyloxy)-4-(3-(octadecyloxy)-2,2-bis((octadecyloxy)methyl) propoxy)benzoate (6). A mixture of **5** (1.2 g, 0.77 mmol), NaOH (0.18 g, 4.5 mmol) and 90% EtOH (50 ml) was refluxed for 10 hours. After cooling to r.t., the resulting precipitate was filtered off. The compound was purified by recrystallization five times from EtOH (90%) as a white powder (1.1 g, 92 %).

MS: m/z calcd. for $[M + H]^+$ $C_{102}H_{195}O_8Na$, 1572.47, found 1572.48; Anal. Calcd. For $C_{102}H_{195}O_8Na \cdot H_2O$: C 77.02, H 12.48; found: C 76.90, H 12.28.

1H -NMR (400 MHz, $CDCl_3$, r.t.) δ (ppm): 7.11 (s, 2H), 3.98 (s, 4H), 3.81 (t, 4H), 3.54 (s, 6H), 3.35 (t, 6H, $J = 6.5$ Hz), 1.81 (m, 4H), 1.48 (m, 10H), 1.25 (m, 90H), 0.88 (t, 15 H, $J = 6.3$ Hz).

Methyl 3,4-bis(dodecyloxy)-5-(3-(octadecyloxy)-2,2-bis((octadecyloxy)methyl) propoxy)benzoate (8). The method of synthesis is the same as for **5**. The crude product was purified by column chromatography (SiO_2 , DCM/PE = 1/1, $R_f = 0.63$) to give a white solid (0.45 g, 36 % yield).

MS: m/z calcd. for $[M + Na]^+$ $C_{91}H_{174}NaO_8$: 1419.39, found 1419.31.

1H -NMR (400 MHz, $CDCl_3$, r.t.) δ (ppm): 7.28 (s, 1H), 7.23 (s, 1H), 3.98 (m, 6H), 3.97 (s, 3H), 3.50 (s, 6H), 3.36 (t, 6H, $J = 6.3$ Hz), 1.8 (m, 4H), 1.49 (m, 10H), 1.25 (m, 84H), 0.88 (t, 15H, $J = 6.3$ Hz).

^{13}C -NMR (125 MHz, $CDCl_3$, r.t.) δ (ppm): 14.1, 22.7, 26.2, 26.1, 29.3-29.6, 30.2, 30.5, 31.0, 31.4, 32.0, 45.4, 52.0, 68.2, 69.0, 69.4, 71.6, 73.4, 107.6, 107.9, 124.7, 142.1, 152.7, 153.0, 166.9.

Sodium 3,4-bis(dodecyloxy)-5-(3-(octadecyloxy)-2,2-bis((octadecyloxy)methyl) propoxy)benzoate (9). The method of synthesis is the same as for **6**.

MS: m/z calcd. for $[M + H]^+$ $C_{90}H_{172}O_8Na$: 1404.34, found: 1405.30; Anal. Calcd. For $C_{90}H_{171}O_8Na \cdot H_2O$: C 76.00, H 12.26; found: C 76.04, H 12.19.

1H -NMR (400 MHz, $CDCl_3$, r.t.) δ (ppm): 7.24 (s, 1H), 7.19 (s, 1H), 3.96 (m, 6H), 3.51 (s, 6H), 3.35 (t, 6H, $J = 6.4$ Hz), 1.73 (m, 4H), 1.27 (m, 84H), 0.90 (t, 15H, $J = 6.2$ Hz).

DSC thermograms

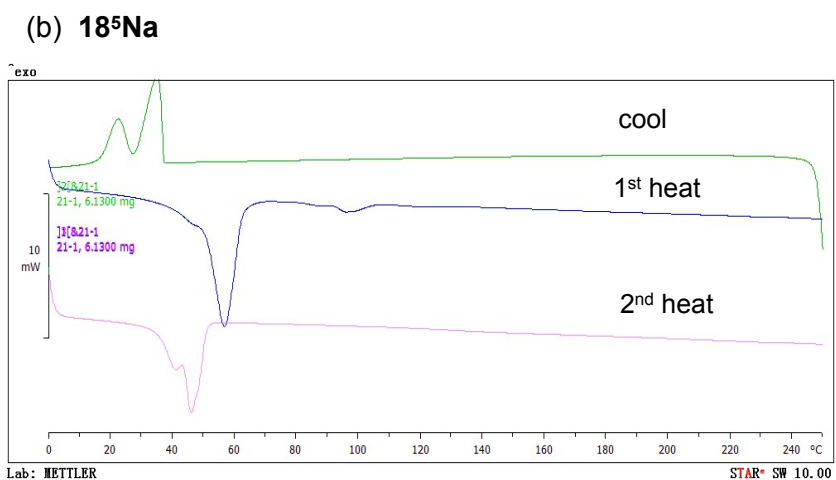
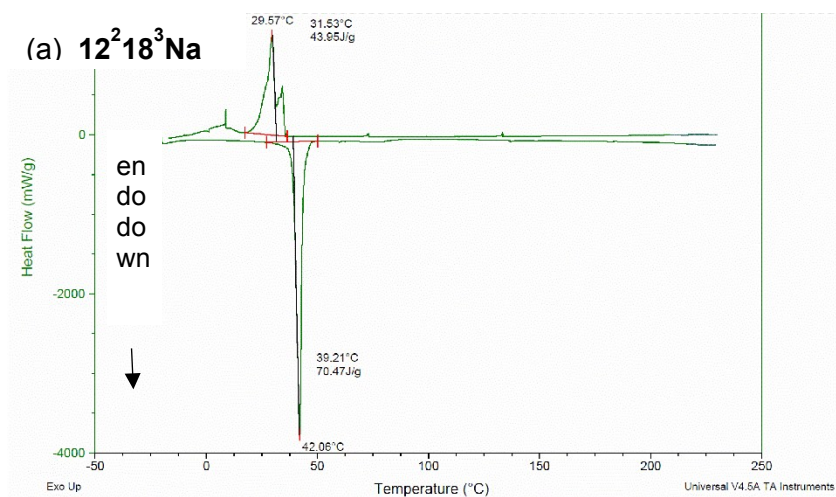


Figure S1. DSC thermograms of (a) $^{12}\text{C}^{18}\text{O}_2$, (b) $^{18}\text{O}_2$. Heating and cooling rates are 10 K min^{-1} .

Additional X-ray diffraction data

SAXS diffractograms

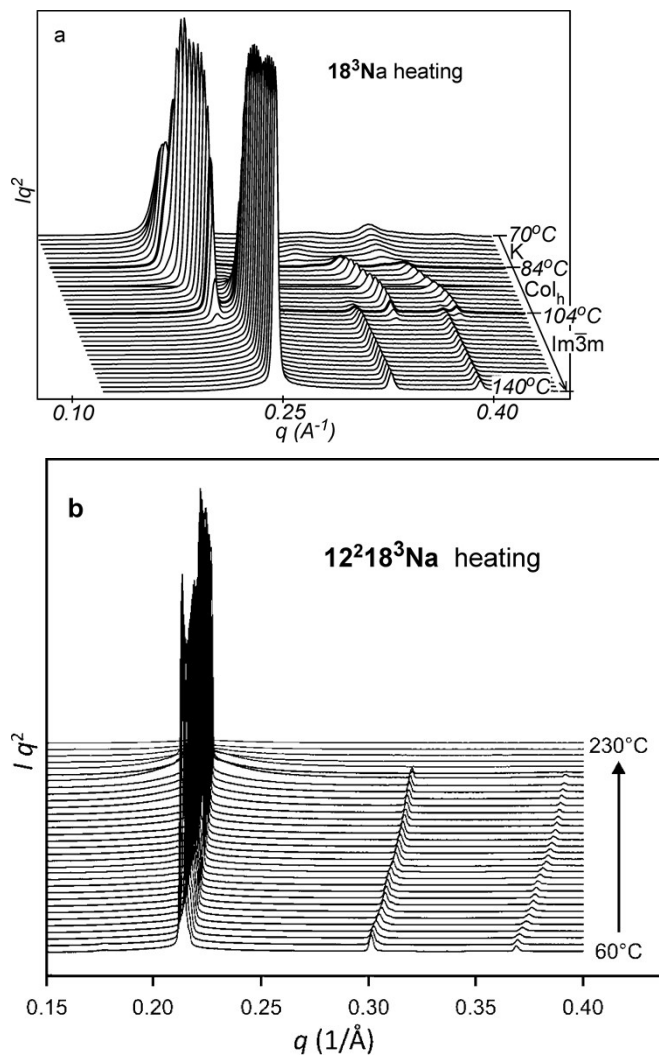


Figure S2. Small-angle X-ray diffractograms recorded during heating of compounds (a) 18^3Na and (b) 12^218^3Na .

Measured spacings, lattice parameter and unit cell volume vs. temperature

As an example we list all measured Bragg spacings from the small-angle X-ray diffractograms as a function of temperature recording on heating and cooling for compound 12^218^3Na on heating and cooling (results from synchrotron experiments).

Table S1. Measured d-spacings of the (110), (200) and (211) diffraction peaks of the BCC phase, lattice parameter a and unit cell volume V , for compound **12²18³Na** on heating.

T (°C)	$d_{(110)}$	$d_{(200)}$	$d_{(211)}$	a (nm)	V (nm ³)
60	2.944	2.083	1.700	4.17	72.26
65	2.937	2.080	1.696	4.16	71.80
70	2.931	2.077	1.694	4.15	71.44
75	2.922	2.070	1.688	4.14	70.74
80	2.909	2.061	1.679	4.12	69.73
85	2.899	2.051	1.675	4.10	69.01
90	2.893	2.042	1.668	4.09	68.28
95	2.887	2.039	1.664	4.08	67.88
100	2.880	2.035	1.662	4.07	67.50
105	2.874	2.033	1.658	4.06	67.13
110	2.868	2.029	1.656	4.06	66.78
115	2.859	2.024	1.650	4.04	66.13
120	2.850	2.014	1.646	4.03	65.43
125	2.838	2.008	1.640	4.02	64.74
130	2.832	2.002	1.636	4.00	64.23
135	2.825	1.999	1.632	4.00	63.84
140	2.820	1.993	1.628	3.99	63.38
145	2.814	1.990	1.624	3.98	63.01
150	2.808	1.985	1.622	3.97	62.63
155	2.801	1.981	1.618	3.96	62.19
160	2.796	1.978	1.614	3.96	61.87
165	2.794	1.975	1.613	3.95	61.66
170	2.790	1.974	1.611	3.95	61.47
175	2.784	1.970	1.608	3.94	61.09
180	2.779	1.967	1.606	3.93	60.81
185	2.776	1.963	1.604	3.93	60.59
190	2.773	1.960	1.602	3.92	60.35
195	2.767	1.958	1.595	3.91	59.85

Table S2. Measured d-spacings of the (110), (200) and (211) diffraction peaks of BCC phase, lattice parameter a and unit cell volume V , of compound **12²18³Na** on cooling.

T (°C)	$d_{(110)}$	$d_{(200)}$	$d_{(211)}$	a (nm)	V (nm ³)
80	2.881	2.047	1.664	4.08	67.99
85	2.881	2.045	1.664	4.08	67.95
90	2.881	2.042	1.663	4.08	67.78
95	2.878	2.039	1.662	4.07	67.57
100	2.876	2.037	1.660	4.07	67.38
105	2.874	2.035	1.656	4.06	67.12
110	2.870	2.033	1.654	4.06	66.86
115	2.868	2.027	1.654	4.05	66.60
120	2.862	2.020	1.650	4.04	66.11
125	2.859	2.014	1.648	4.04	65.72
130	2.856	2.011	1.646	4.03	65.49
135	2.850	2.008	1.644	4.02	65.17
140	2.847	2.007	1.642	4.02	64.99
145	2.843	2.005	1.638	4.01	64.68
150	2.840	2.002	1.636	4.01	64.48
155	2.838	1.999	1.634	4.00	64.21
160	2.834	1.996	1.632	4.00	63.96
165	2.832	1.995	1.628	3.99	63.70
170	2.825	1.993	1.626	3.99	63.41
175	2.823	1.990	1.622	3.98	63.13
180	2.820	1.987	1.620	3.98	62.89
185	2.814	1.981	1.618	3.97	62.48
190	2.810	1.978	1.616	3.96	62.24

Calculation of density and number of molecules per micelle

Table S3. Calculation of densities of $^{12}^{18}\text{Na}$ and ^{18}Na at different temperatures

Temperature T ($^{\circ}\text{C}$)	Expansivity of $n\text{-C}_{16}\text{H}_{37}$ $\alpha \times 10^3$ (deg^{-1}) ^{S6}	at T ($^{\circ}\text{C}$)	Relative volume expansion $(v/v_{20})^b$	density (g cm^{-3}) (based on $\rho_{20} = 0.95 \text{ g cm}^{-3}$ at 20°C) ^{S4}
20	0.897 ^a			
160	1.092 ^a			
200	1.200 ^a			
40	0.911 ^b	60	1.036	0.917
107.5	0.990 ^c	195	1.173	0.810
145	1.060 ^d	270	1.265	0.751

^a) Thermal expansivity α of $\text{C}_{16}\text{H}_{37}$ at stated temperature from ref. S6.

^b) Calculated using average expansivity $\langle\alpha_T\rangle$ in the interval 20°C to T .

Number of molecules per sphere in the BCC phase (μ)

Compound	M (Da)	T ($^{\circ}\text{C}$)	Unit cell volume V (nm^3)	density (ρ) (g.cm^{-3})	μ
^{12}Na	696	220	60.0	0.82	21.3
		258	59.4	0.765	19.8
^{18}Na	948	104	94.9	0.884	26.5
		140	91.3	0.852	24.6
$^{12}^{18}\text{Na}$	1402	60	72.2	0.917	14.2
		195	59.85	0.810	10.4
^{18}Na	1570	60	116.2	0.917	20.4
		270	78.8	0.751	11.4

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