Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information for: Quantised Molecular Ejection Transition in Liquid Crystal Columns Self-Assembled from Wedge-Shaped Minidendrons

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1 Spacings and average number of molecules per disc n in the $\mathrm{Col_h}$ phase

Table S1: Calculation of average number of molecules $\langle n \rangle$ in a unit cell (disc) of $\mathrm{Col_h}$ phase of 12Li at 70°C

a(Å)	32.1[a]
c(Å)	4.2[b]
Volume of unit cell (10^3 Å^3)	3.74
Volume of 12Li (10^3 Å^3/molecule)	1.24[c]
$\langle n \rangle$	3.0

a: From Fig. 2a. **b**: from Fig. 1d. **c**: Experimental density of 1.02 g/cm^3 for 12Li measured in crystalline state at room temperature[1] was increased by 7% for expansion on melting and extrapolated to 70 °C using thermal expansivity 9.49x10^{-4} + 1.35x10^{-6} T - 0.53x10^{-8} T^2 + 6.28x10^{-11} T^3 K^{-1}, where T is temperature, reported for alkane n-$C_{12}H_{26}$.[3]

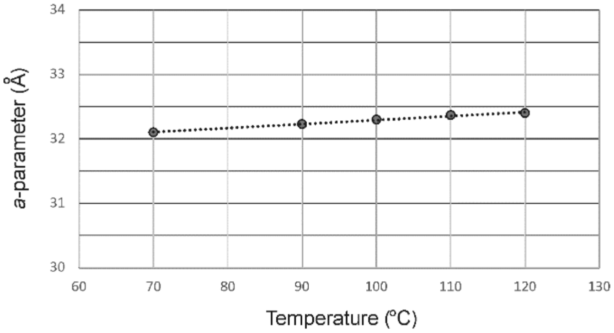

Figure S1: Experimental lattice parameter vs. temperature for the $\mathrm{Col_h}$ phase of 12Li.

Table S2: Lattice parameter and number of molecules of 12Li per disc as a function of temperature.

T(°C)	a(Å)	$\langle n \rangle$
70	32.1	3.0
90	32.23	3.0
100	32.3	3.0
110	32.37	3.0
120	32.4	3.0

Table S3: Lattice parameters and number of molecules of 12Na per disc as a function of temperature.

Phase	T (°C)	a (Å)	b (Å)	c (Å)[a]	V$_{\text{disc}}$ (10^3 Å^3) [b]	V$_{\text{mol}}$ (10^3 Å^3)	$\langle n \rangle$
Col$_\text{r}$	65	39.6[c]	37.8	3.7	4.80	1.19	4.02
	70	39.2[c]	38.2	3.7	4.80	1.20	3.99
	75	39.1[c]	38.6	3.7	4.83	1.21	4.00
Col$_\text{h}$1	80	38.8		3.7	4.82	1.22	3.97
	85	38.8		3.7	4.81	1.22	3.93
	90	38.8		3.7	4.81	1.23	3.91
	95	38.8		3.7	4.82	1.24	3.90
Col$_\text{h}$2	100	35.2		3.9	4.19	1.25	3.36
	105	34.9		3.9	4.11	1.26	3.28

a: measured from fibre X-ray diffraction (Figure S1c). **b**: In calculation of the volume of the 12Na molecule, an experimental density of 1.01 g/cm^3 measured in crystalline state at room temperature is used, corrected by thermal expansion using the formula for alkane n-$C_{12}H_{26}$.[3] **c**: $a/\sqrt{3}$.

2 Calculation of Coulomb Interactions (U_n, J_{mn})

Calculated intra-disk U_n Coulomb interactions (Equation S1), all atoms separated by radii given in Table S4. Radius of O atoms is estimated (Equation S2). O-M-O bond angle minima are 173.456° and 189.356° for configurations of n=4 or n=3 minidendrons per supramolecular disc respectively. O=C-O angle fixed at 120°, see Figure S2(a). Final values (J/mol): U_4 = -479289, U_3 = -479198.

$$U_n = \frac{N_A q^2}{4\pi\epsilon_0 n}\left(\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n(i\neq j)}\frac{1}{|r_{M_i-M_j}|} - \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{2n}\frac{1}{|r_{M_i-O_j}|} + \frac{1}{8}\sum_{i=1}^{2n}\sum_{j=1}^{2n(i\neq j)}\frac{1}{|r_{O_i-O_j}|}\right) \tag{S1}$$

$$R_{O^{\frac{1}{2}}} = \frac{1}{2}\Big(R_{O^0} + \frac{1}{3}(2R_{O^0} + R_{O^{-2}})\Big) \tag{S2}$$

Table S4: Atomic radii used in Coulomb calculations.[2]

Element	Radius(Å)	Vdw/Ionic
Na	1.02	Ionic
C	1.70	Vdw
O^0	1.52	Vdw
O^{-2}	1.35	Vdw
$O^{1/2}$	1.49	(Equation S2)

Calculated inter-disk J_{mn} Coulomb interactions (Equation S4), using atomic radii in Table S4 and inter-disk spacing of 3.8 Å . Figure S2(b) depicts 3 different configurations used to produce Figure 5 in the main manuscript, where cations and anions are rotated around an axis perpendicular to their respective centres, see Equation S4. Final calculated minima (J/mol): J_{44} = -11241.2, J_{43} = 1096.3, J_{33} = -10090.2.

$$n^{'} = n_1 + n_2 \tag{S3}$$

$$\begin{aligned} J_{n_1 n_2} = \frac{N_A q^2}{4\pi\epsilon_0 n'}\Bigg(&\frac{1}{2}\sum_{i=1}^{n'}\sum_{j=1}^{n'(i\neq j)}\frac{1}{|r_{M_i-M_j}|} - \frac{1}{2}\sum_{i=1}^{n'}\sum_{j=1}^{2n'}\frac{1}{|r_{M_i-O_j}|} \\ &+ \frac{1}{8}\sum_{i=1}^{2n'}\sum_{j=1}^{2n'(i\neq j)}\frac{1}{|r_{O_i-O_j}|} - n_1 U_{n_1} - n_2 U_{n_2}\Bigg) \end{aligned} \tag{S4}$$

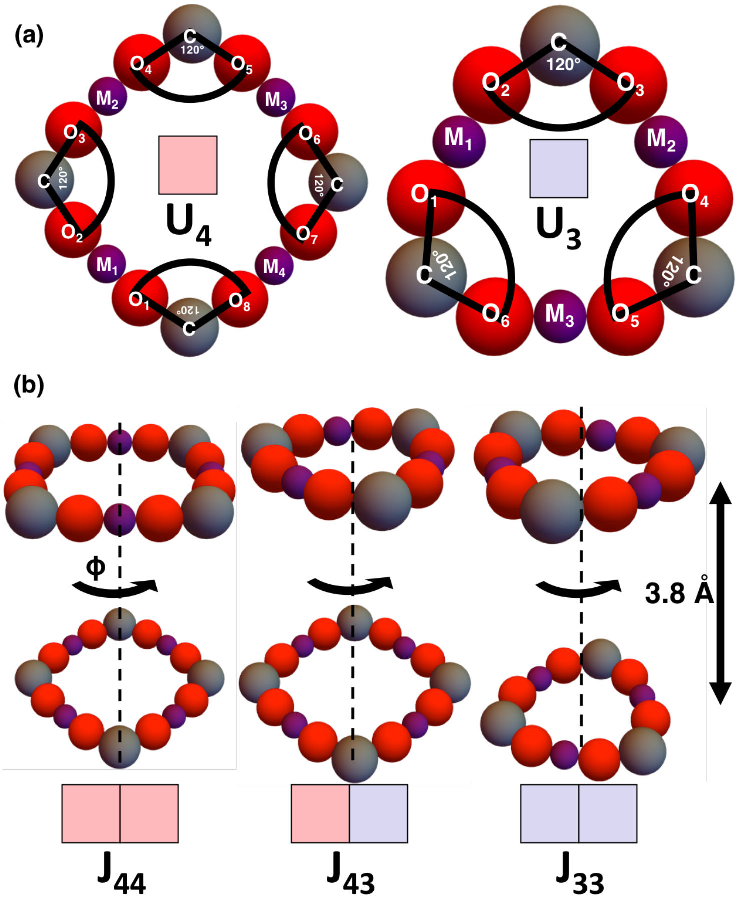

Figure S2: (a) Idealised ring of alternating cations/anions, Carbon-C (gray), Oxygen-O (red), Sodium-Na (purple), O=C-O bond angle drawn explicitly. (b) Schematic of rotating disks with exaggerated inter-disk spacing.

3 Chain Free Energy Simulation $F_n(T)$

All atoms lie on the diamond lattice where the first neighbor distance a = 1.54 Å is equal to the C-C bond length in alkanes. The basis vectors are given in Table S5. Starting points of oxygen atoms are (2,-2,0), (1,1,1), (-2,2,0), which sit approximately 2.95 Å from each other. C atoms are confined to a segment thickness of 3.6 Å the closest match available to experimentally determined thickness when restricted to the diamond lattice. H atoms may cross this boundary. Each alkane conformer is formed using alternating sets of basis vectors in Table S5 where immediate back steps are forbidden i.e. a cannot be followed by a'. Conformers are self-avoiding and successive gg' (±60°) torsional angles are disallowed ("pentane interference"). Chains attached at positions 3 and 5 on the benzene ring start at points of a different parity to the central chain attached at 4, hence they can be considered shorter since the position of the first C atom is effectively fixed. Total number of conformers found is 41,376,644 and 69,386,880 for the 90° and 120° geometries, respectively.

Table S5: Diamond lattice vectors

a	(1,1,1)	a'	(-1,-1,-1)
b	(-1,-1,1)	b'	(1,1,-1)
c	(-1,1,-1)	c'	(1,-1,1)
d	(1,-1,-1)	d'	(-1,1,1)

Note: conformers.tar.bz2 containing .dat files are arranged in 3 tab seperated columns. Rows correspond to a unique configuration with 3 entries (3 chains) each with a unique identifier, i.e. 174617474527 corresponds to ac'db'ac'dc'da'bd' as defined in Table S5.

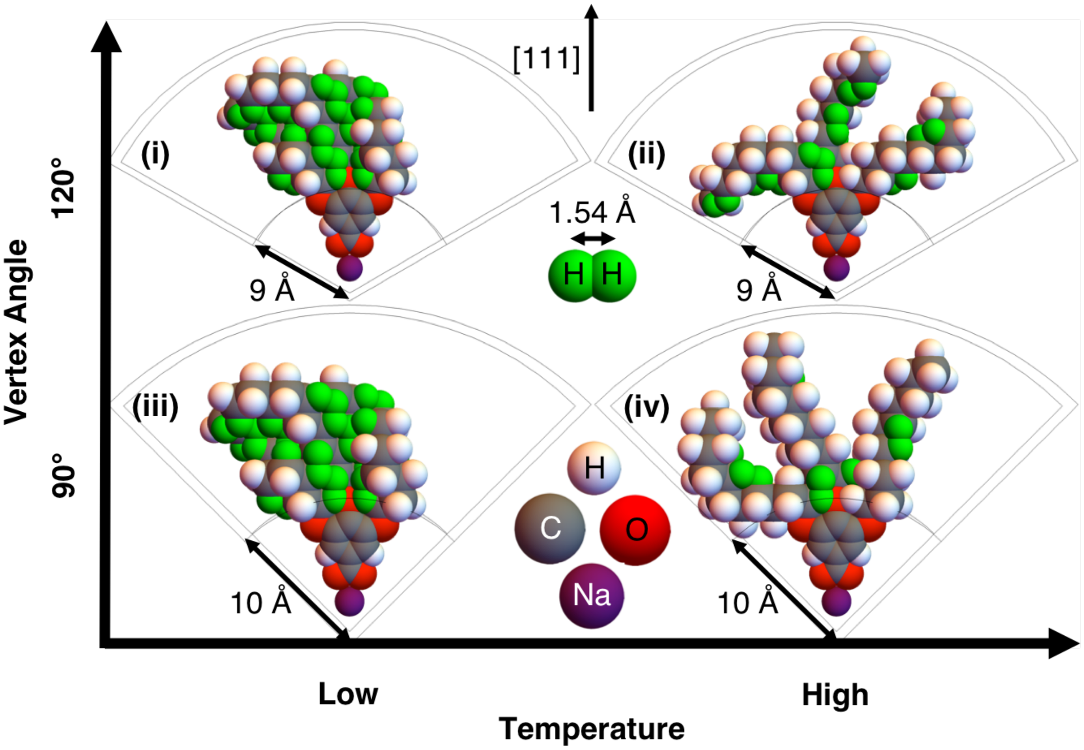

Figure S3: Minidendrons with alkyl chains in confined geometry depicting the effect of vertex angle and temperature on chain conformations. Close contacts (green) show chain crystallization. [111] direction is indicated.

References

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