Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Supporting information for

An unusual plank-shaped nematogen with a graphene nanoribbon core

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General

Spin-coated films of 125 nm thickness with a mean surface roughness of less than 2.0 nm were produced by spinning a solution of 10 mg/mL in chloroform at 1500 rpm for 30 s. The thickness and roughness of the spin-coated films were determined with a Nanosurf Flex AFM, operating in tapping mode under ambient conditions with a scanning rate of 1.0 Hz and 512×512 pixels. Excited state lifetimes were measured at room temperature in air with a DeltaFlex TCSPC system from Horiba using LED excitation at 357 nm and emission collection at 475 nm and 550 nm.

Atomic force microscopy images of the Teflon treated surfaces

The surface micro-grooves are not significantly affected by annealing the film at 260 °C for 30 s.

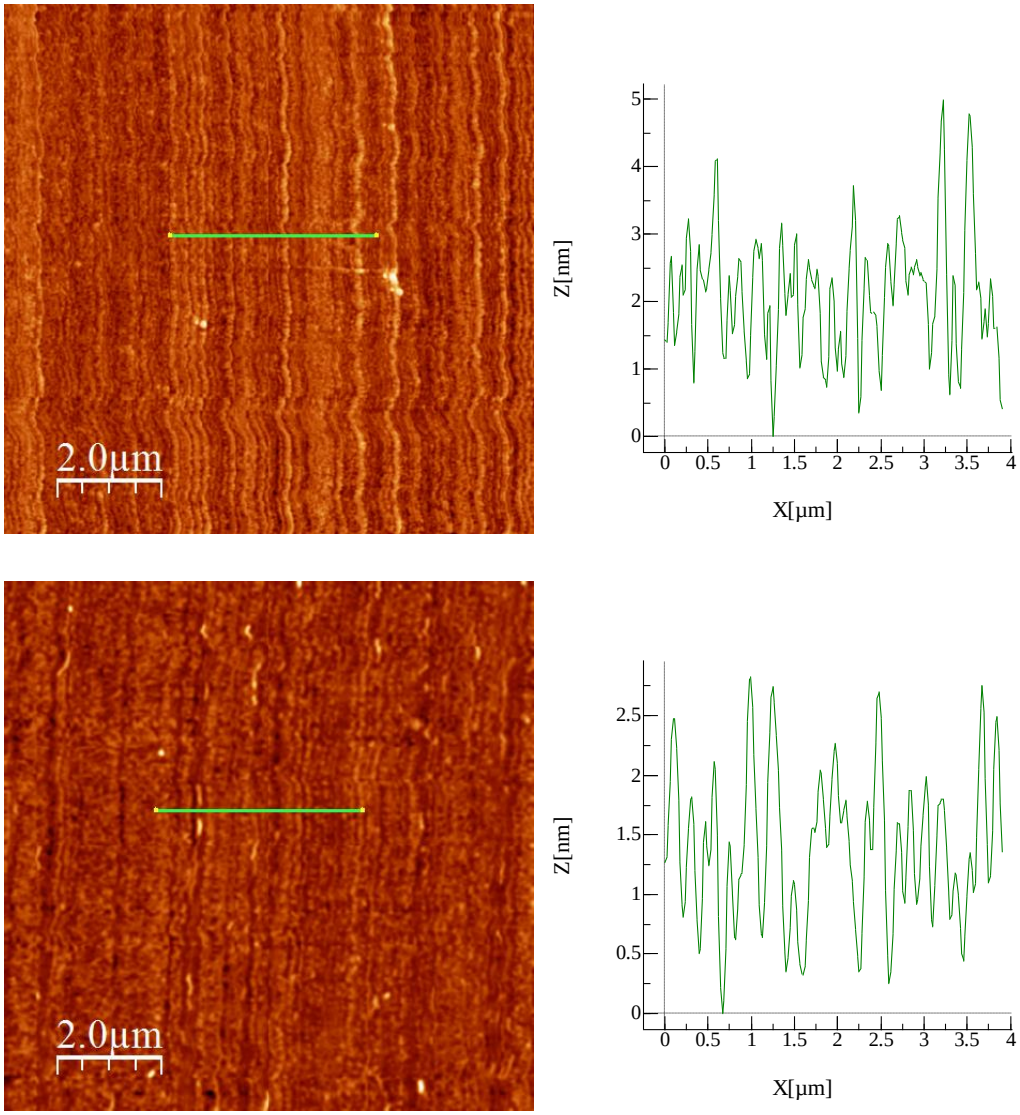
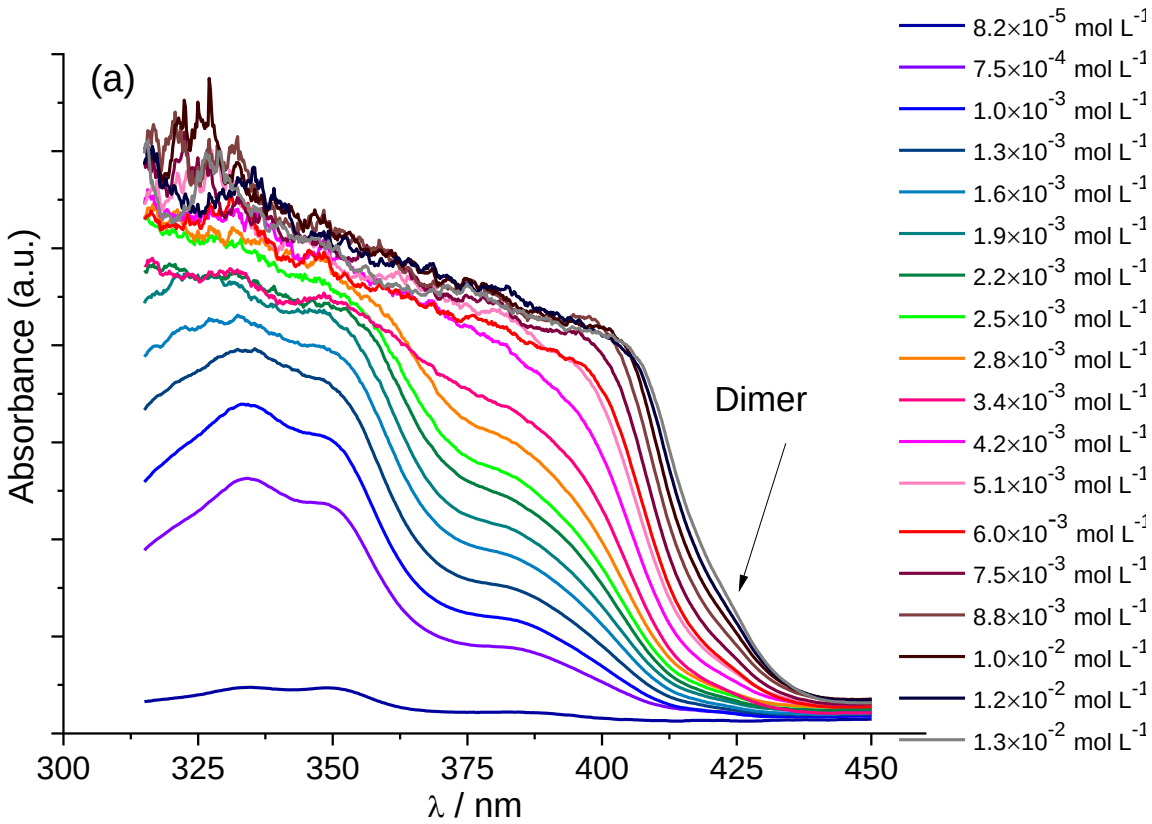


Figure S1. AFM images of the Teflon treated surfaces. Top: as rubbed; Bottom: after annealing annealing at 260 °C for 30 s. The left images are cross sections indicated by the green solid line.

Absorption and emission as a function of concentration



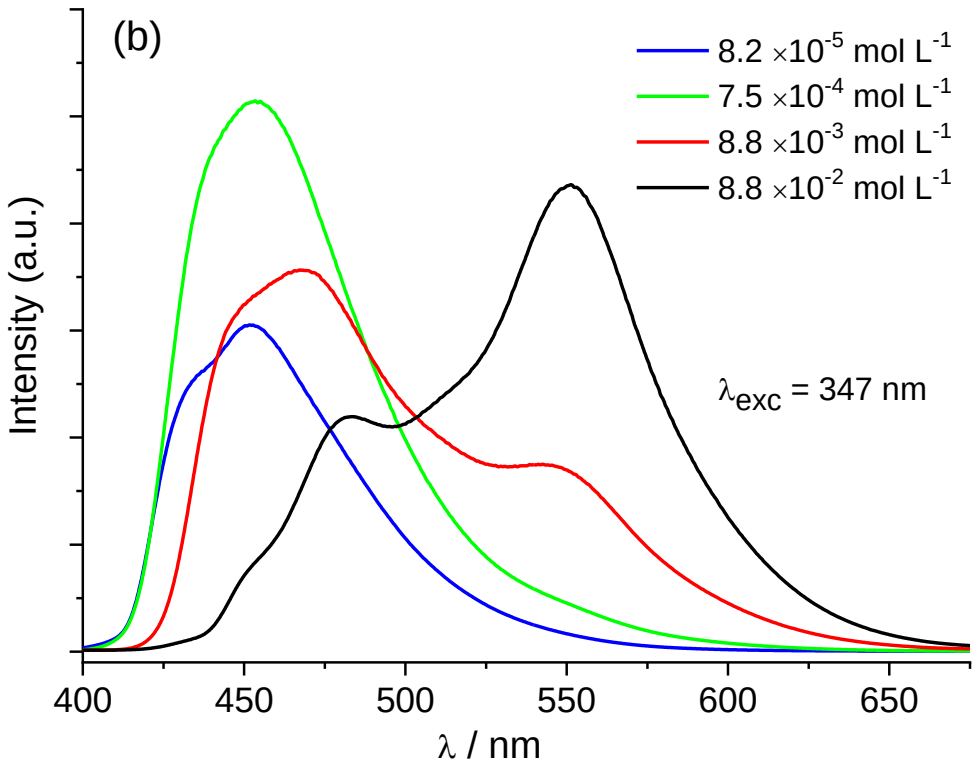


Figure S2. (a) Absorption as a function of concentration in chloroform. For concentrations higher than 5×10^{-3} mol L^{-1} a shoulder around 425 nm is discernible, which is associated to ground state dimers. (b) Fluorescence spectra at various concentrations: 8.2×10^{-5} mol L^{-1} (blue); 7.5×10^{-4} mol L^{-1} (green); 8.8×10^{-3} mol L^{-1} (red) and 8.8×10^{-2} mol L^{-1} (black).

Excited state lifetime measurement

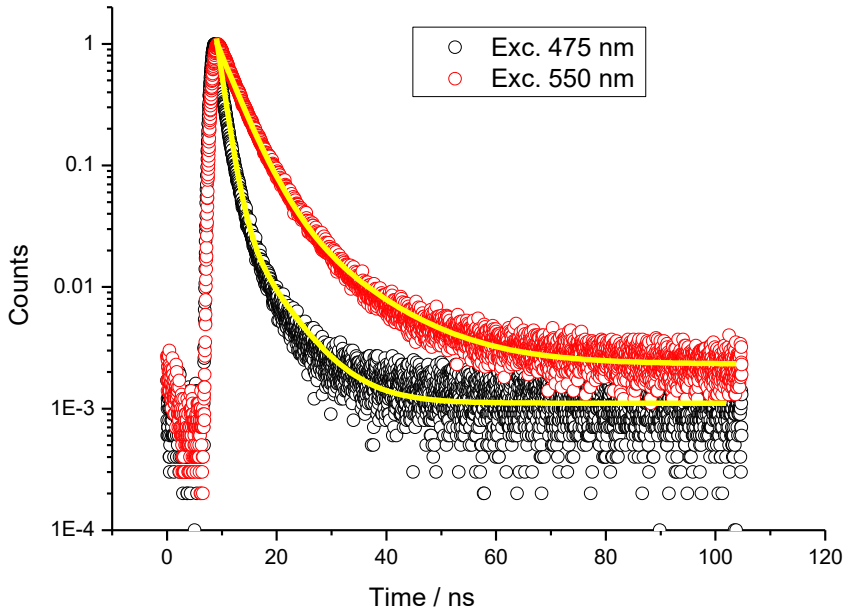


Figure S3. Excited state life time in the nematic glass for different excitation wavelengths – black circles: 475 nm; red circles: 550 nm. Yellow solid lines indicate bi-exponential fitting.

Theoretical Methods

The geometry optimization of **2**-**5** was carried out in vacuum, using the Orca 4.1[1] software package and DFT with the BP86 functional[2,3] and the DEF2-SVP basis set for all atoms.[4-6] Dispersion effects were included using Grimme's D3 correction with Becke-Johnson (BJ) damping.[7-11] The RIJ algorithm was employed to accelerate the evaluation of the functionals using the resolution of identity approximation for the Coulomb part (RIJ). The vibrational frequencies computed on the optimized geometry of **2**-**5** included only small negative frequencies (<30 cm^{-1}). Their analogues with only methyl moieties instead of longer aliphatic carbon chains (**2C-5C**), or without any ester substituents at all (pure polycyclic arenes, **2A-5A**) and their dimers were also optimized, using the same calculation protocol, but their vibrational frequencies were not verified. All the electric properties were obtained using the same calculation protocol under the expectation value formalism, using a more complete DEF2-TZVP basis for all atoms.[4-6] Time-dependent density functional theory (TD-DFT) under Tamn-Dancoff approximation[12] (TDA) was employed to obtain the first 10 singlet excited states. Images of the complex geometries were obtained using the Chemcraft program.[13]

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[13] www.chemcraftprog.com.

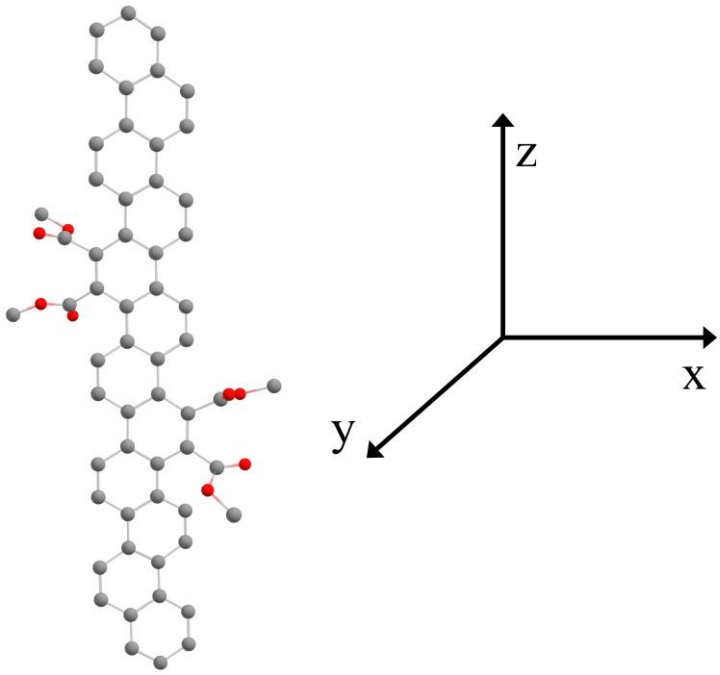

Figure S4. Definition of Cartesian axis used in all calculations: the z axis is along the phenacene ribbon and the y axis is perpendicular to the aromatic plane.

Table S1. Data for the TD-DFT vertical excitations using BP86/def2-TZVP on the optimized ground state geometries. The transition dipoles are in atomic units.

Molecule	Theo. / eV[a]	Exp. / eV[b]	$\lvert\langle I\lvert\mu\rvert F\rangle\rvert^2$	$\lvert\langle I\lvert\mu_x\rvert F\rangle\rvert^2$	$\lvert\langle I\lvert\mu_y\rvert F\rangle\rvert^2$	$\lvert\langle I\lvert\mu_z\rvert F\rangle\rvert^2$	$\lvert\mu_z/\mu_y\rvert$
			Monomers				
2	2.61		2.9474	0.1712	-0.0639	1.7070	26.7136
3	2.55		2.1576	0.0419	0.0463	1.4675	31.6954
4	2.46	2.61	2.3715	-0.1350	0.0009	1.5340	1704.4444
5	2.42		1.5417	0.1021	0.0539	1.2362	22.9350
			Dimers				
2C	2.23		0.8240	0.1611	-0.1545	-0.8798	5.6945
3C	2.19		0.2240	-0.2405	-0.1611	0.3744	2.3240
4C	2.06	2.25	0.0949	-0.1556	-0.0545	0.2602	4.7743
5C	2.06		0.0125	0.0755	-0.0123	-0.0815	6.6260

a. All of the S_1 states could be described simply from a HOMO-LUMO transition. b. From λ_{max} in solid state.

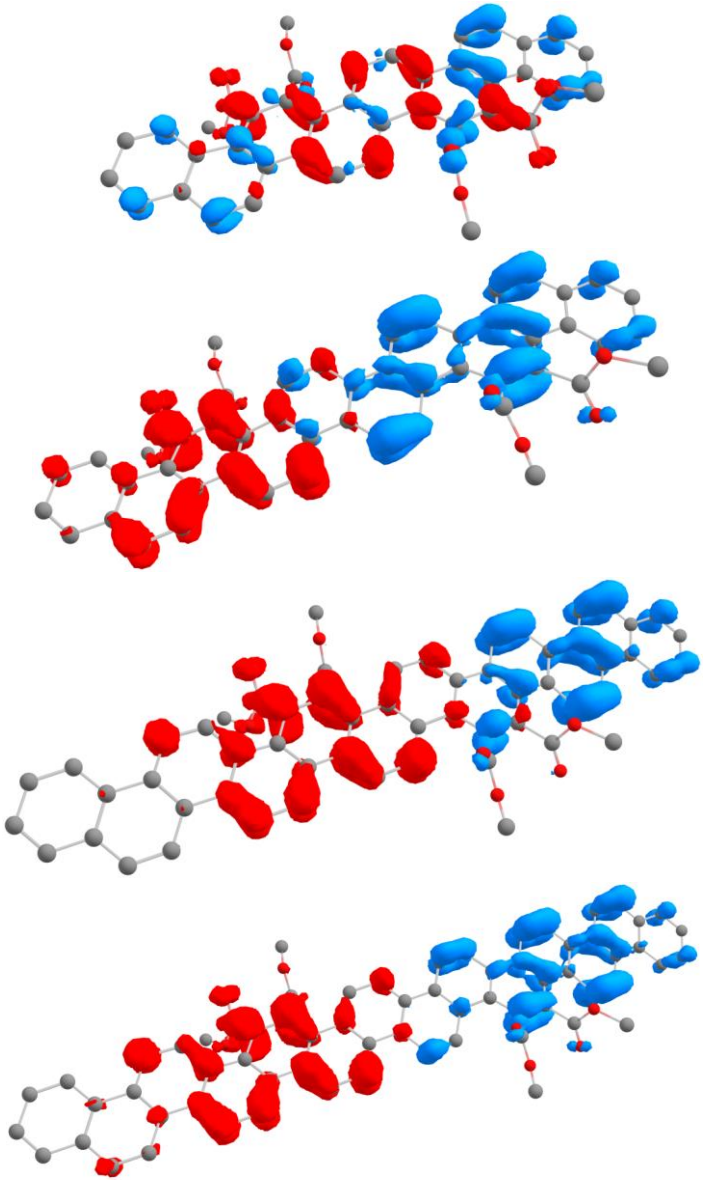

Figure S5. TD-DFT difference densities between ground and first excited states of **2-5** calculated using BP86/def2-TZVP. Hydrogens and aliphatic carbon chains were omitted for clarity. Blue indicates decreased and red indicates increased electronic density.

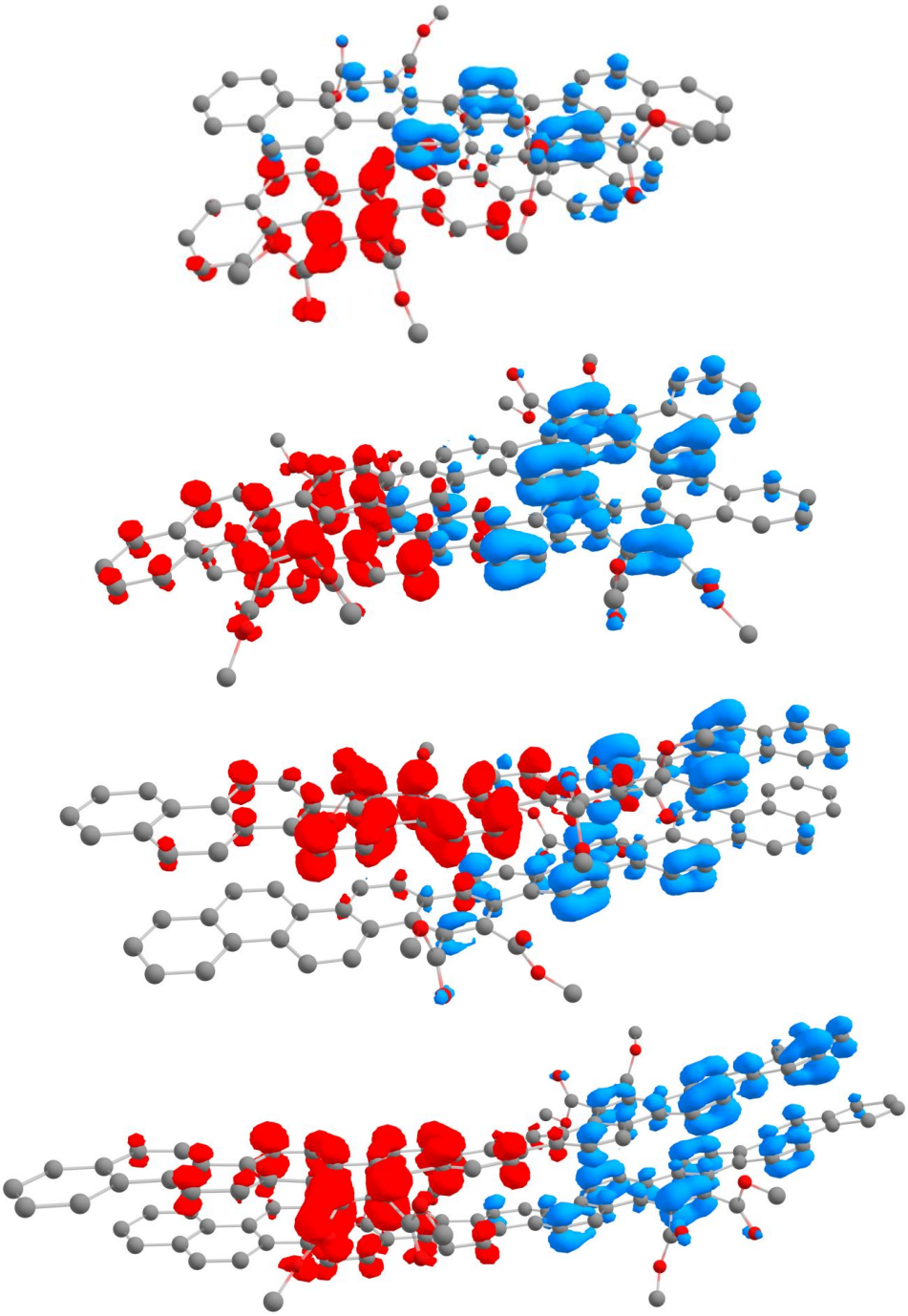

Figure S6. TD-DFT difference densities between ground and first excited states of the dimers of **2C-5C** calculated using BP86/def2-TZVP. Hydrogens were omitted for clarity. Blue indicates decreased and red indicates increased electronic density.

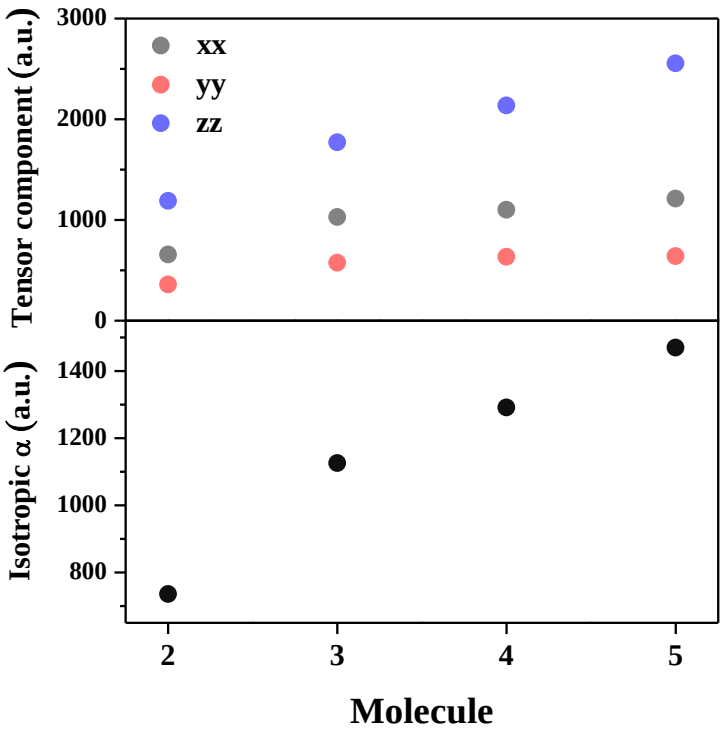

Figure S7. Calculated isotropic polarizability and its tensor components (in atomic units) for **2-5** at the BP86/def2-TVZP theory level.

Table S2. Calculated isotropic polarizability and its tensor components (in atomic units) for **2**-**5** and their methyl ester and unsubstituted analogues, at the BP86/def2-TVZP theory level. Compounds **6-7** are similar to **5**, but extending the phenacene ribbon by one (**6**) or two (**7**) benzo (i.e. C4H2) unit(s) on each end.

Molecule	xx	yy	zz	Isotropic α
		Complete molecules		
2	656.26	359.42	1189.98	735.22
3	1029.29	576.67	1770.62	1125.52
4	1102.71	633.90	2136.97	1291.19
5	1212.18	639.93	2555.86	1469.32
		Methyl ester analogues		
2C	537.94	363.00	1144.87	681.94
3C	668.46	387.72	1496.32	850.83
4C	769.61	386.82	1915.73	1024.05
5C	818.01	452.21	2331.74	1200.65
6C	1051.17	569.73	2496.14	1372.35
7C	1116.09	736.35	2751.34	1534.59
		Unsubstituted arene analogues		
2A	401.79	179.37	1028.37	536.51
3A	480.18	231.78	1393.40	701.79
4A	582.03	259.51	1779.69	873.75
5A	658.21	340.74	2150.19	1049.71
6A	667.69	297.79	2183.43	1049.63
7A	749.78	470.17	2464.68	1228.21

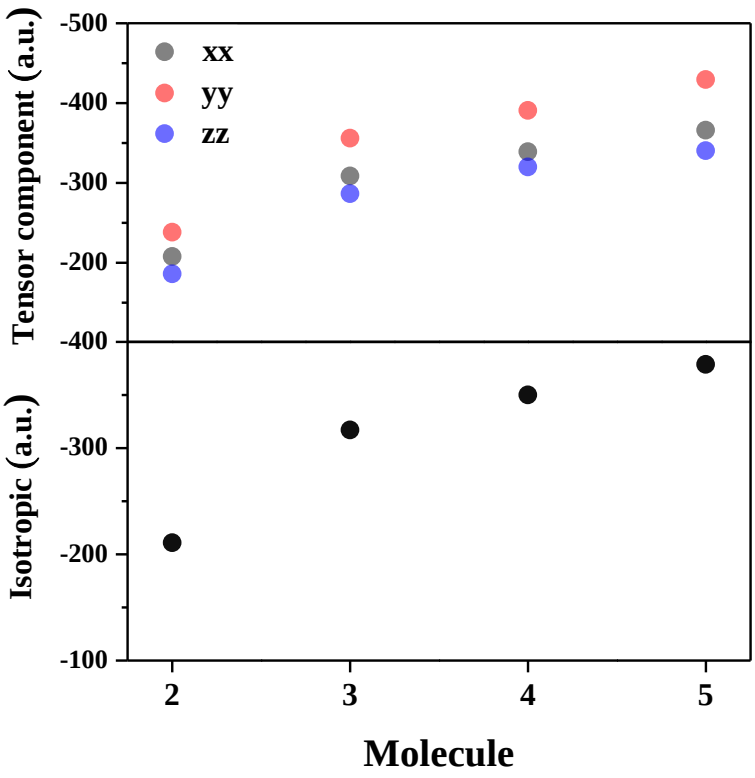

Figure S8. Calculated isotropic quadrupole and its tensor components (in atomic units) for **2-5** at the BP86/def2-TVZP theory level.

Table S3. Calculated isotropic quadrupole and its tensor components (in atomic units) for **2**-**5** at the BP86/def2-TVZP theory level.

Molecule	xx	yy	zz	Isotropic
2	-207,93596	-238,33819	-186,20976	-210,82797
3	-308,62054	-355,99027	-286,54043	-317,05041
4	-339,10475	-391,11776	-320,10496	-350,10916
5	-366,1853	-429,42377	-340,33269	-378,64726

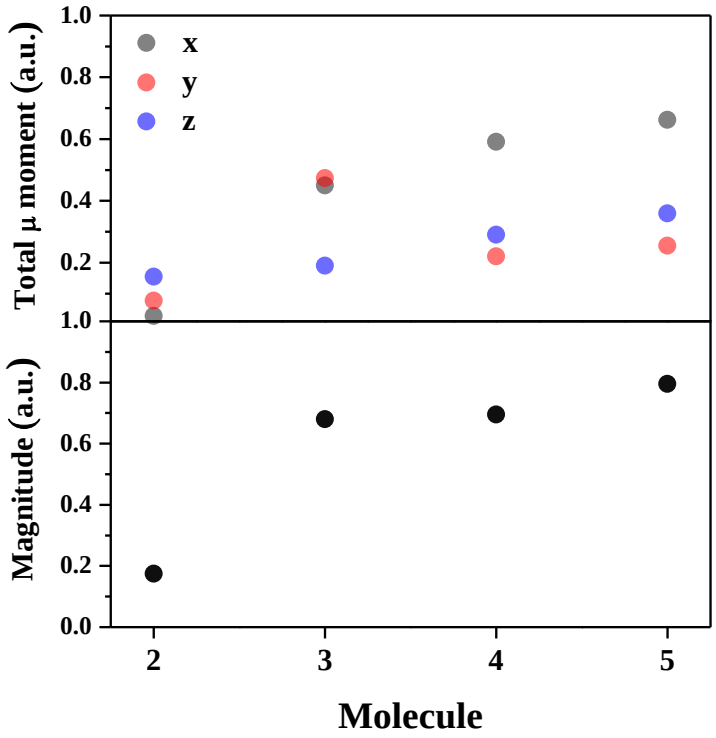

Figure S9. Calculated isotropic polarizability and tensor components for **2-5** at the BP86/def2-TVZP theory level.

Table S4. Calculated total dipole moment (in atomic units) and its magnitude for **2**-**5** at BP86/def2-TVZP theory level.

Molecule	μ_x	μ_y	μ_z	Magnitude
2	0.02718	0.07705	0.15424	0.17454
3	0.44996	0.4736	0.18979	0.68028
4	0.59137	0.21987	0.29075	0.69469
5	0.66273	0.25474	0.3593	0.79574

Differential scanning calorimetry of compound 3

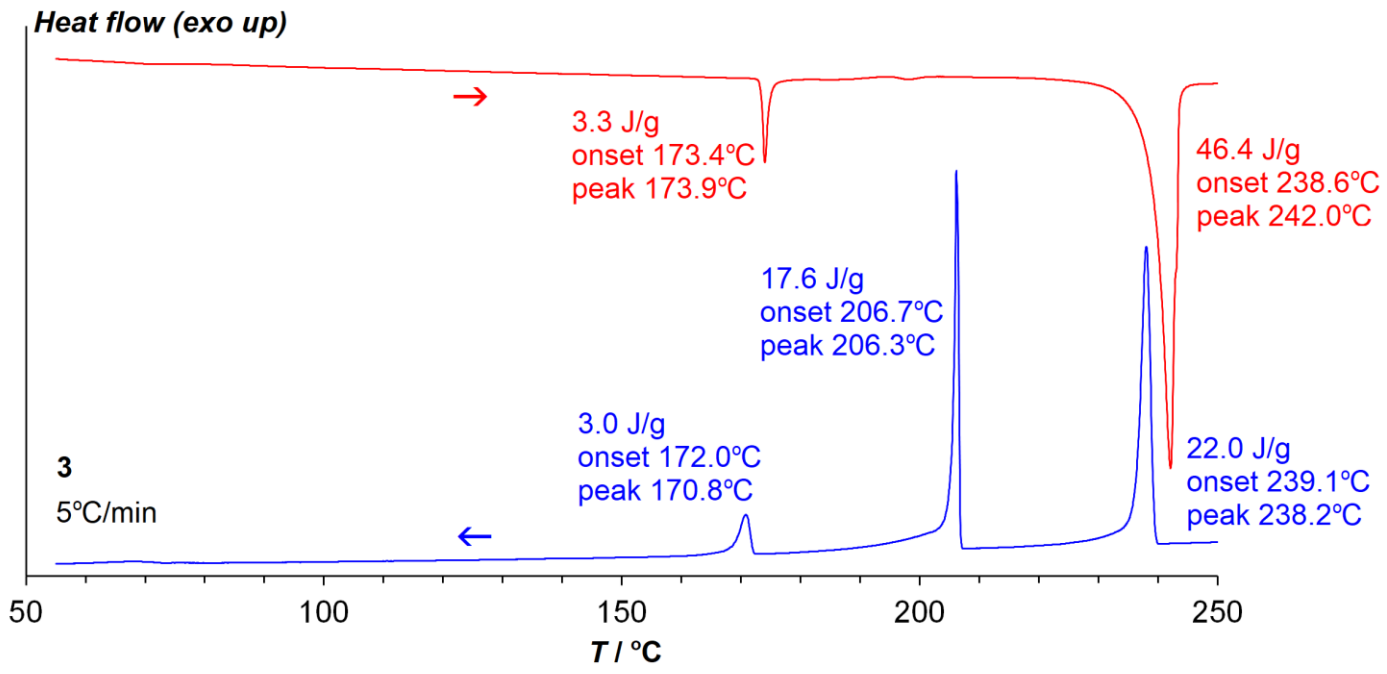

Figure S10. DSC traces for homologue **3** (that melts at a similar temperature but contrary to **4** shows no nematic phase) on cooling from the isotropic liquid (blue) and subsequent reheating (red), with transition enthalpies and temperatures.