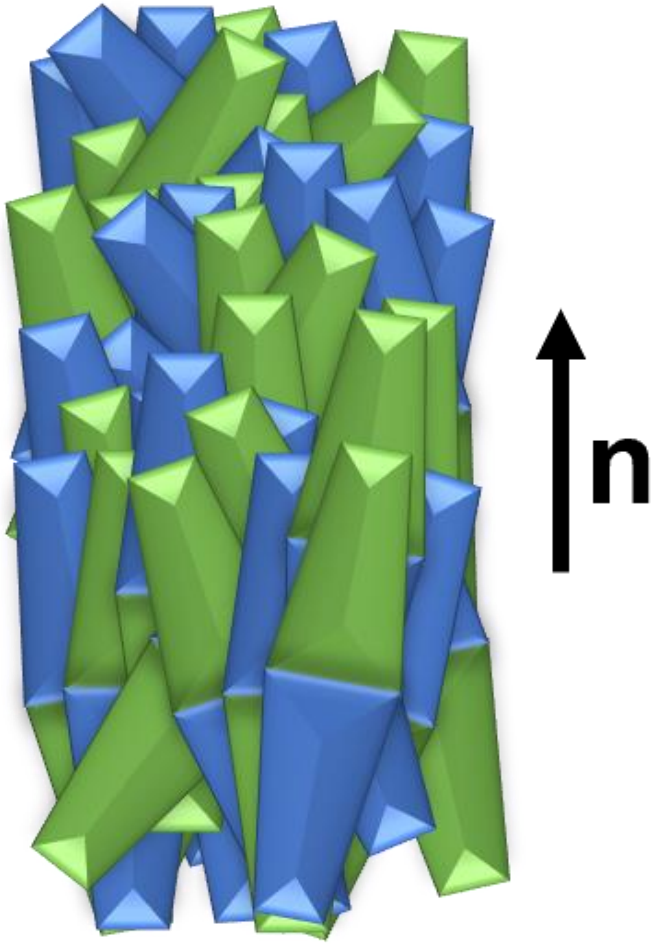
The Influence of Lateral Substituents on the Formation of the Ferroelectric Nematic Phase

Dr Ewan Cruickshank

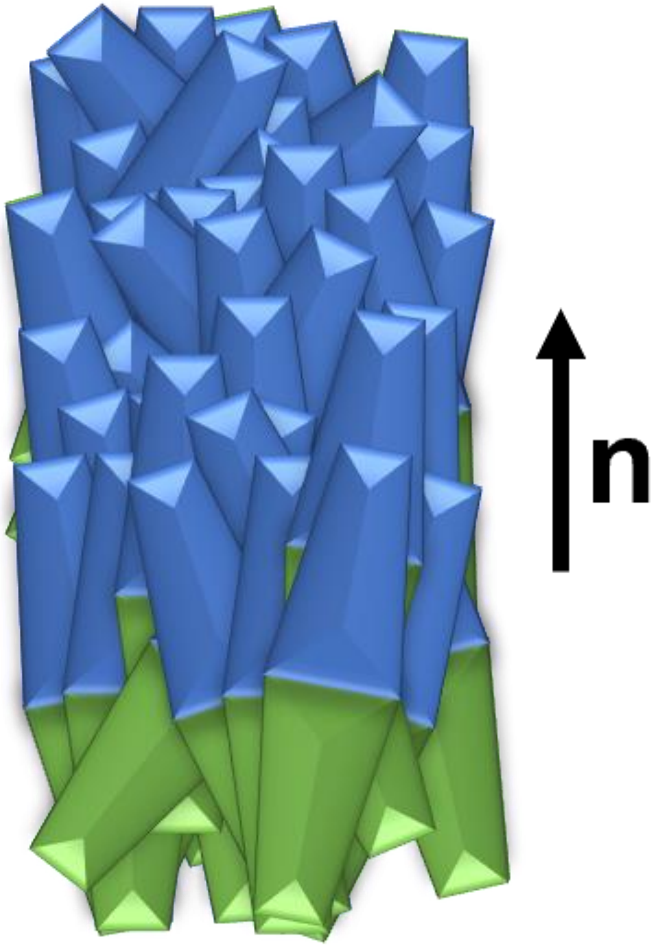
1495 UNIVERSITY OF ABERDEEN

Nematic Phases



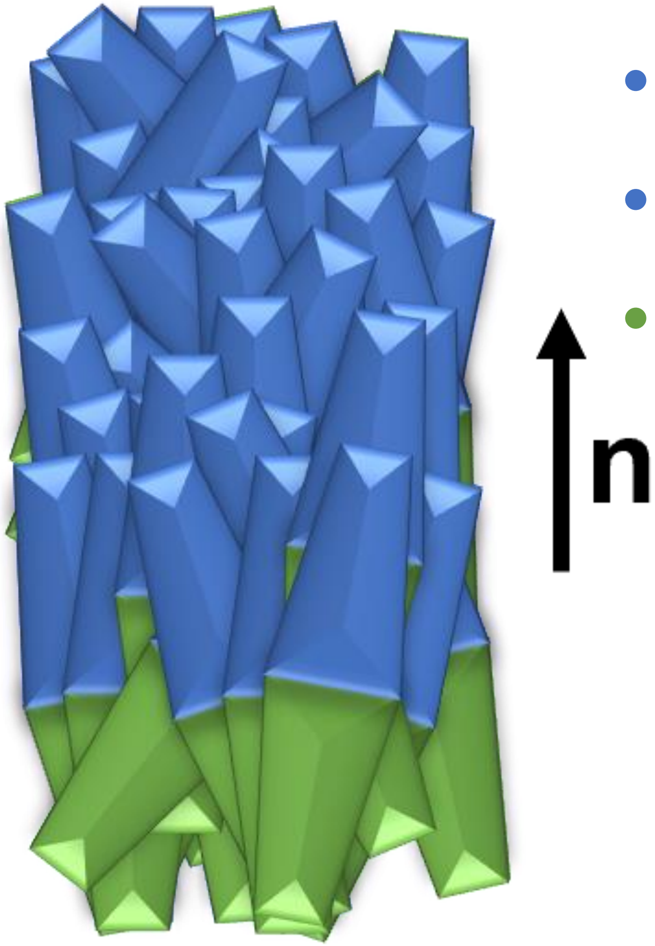
- Molecules align along the director.
- Phase has fluid character.
- **n** = -**n**.
- Phase is non-polar.

Nematic Phases

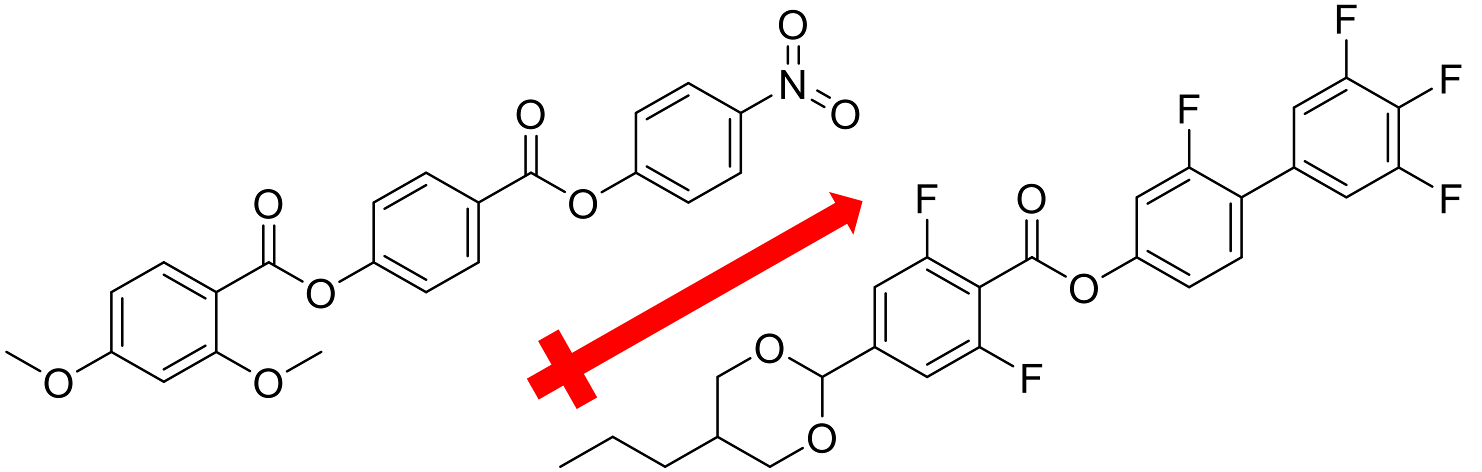


- Molecules align along the director.
- Phase has fluid character.
- **n ≠ -n**.
- Phase is polar.

Nematic Phases



- Spontaneous polarisation is along **n**.
- Easy to align in cells.
- Switching can occur even with a low electric field.

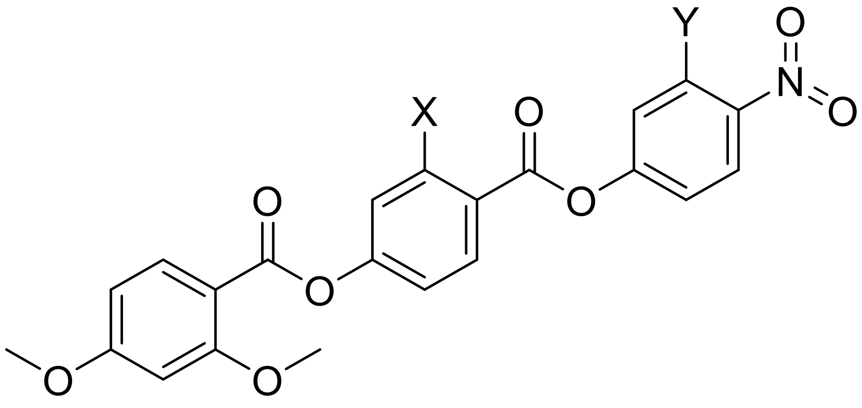


RM734[1]

DIO[2]

1. Mandle, R. J. *et al. Phys. Chem. Chem. Phys.* **19**, 11429–11435 (2017).
2. Nishikawa, H. *et al. Adv. Mater.* **29**, 1702354 (2017).

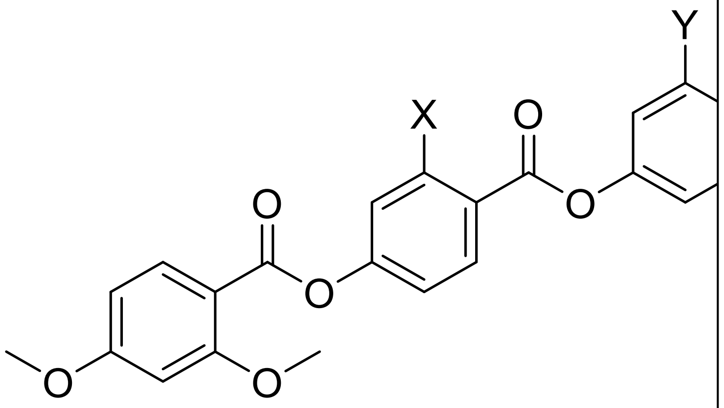
Lateral Fluorination

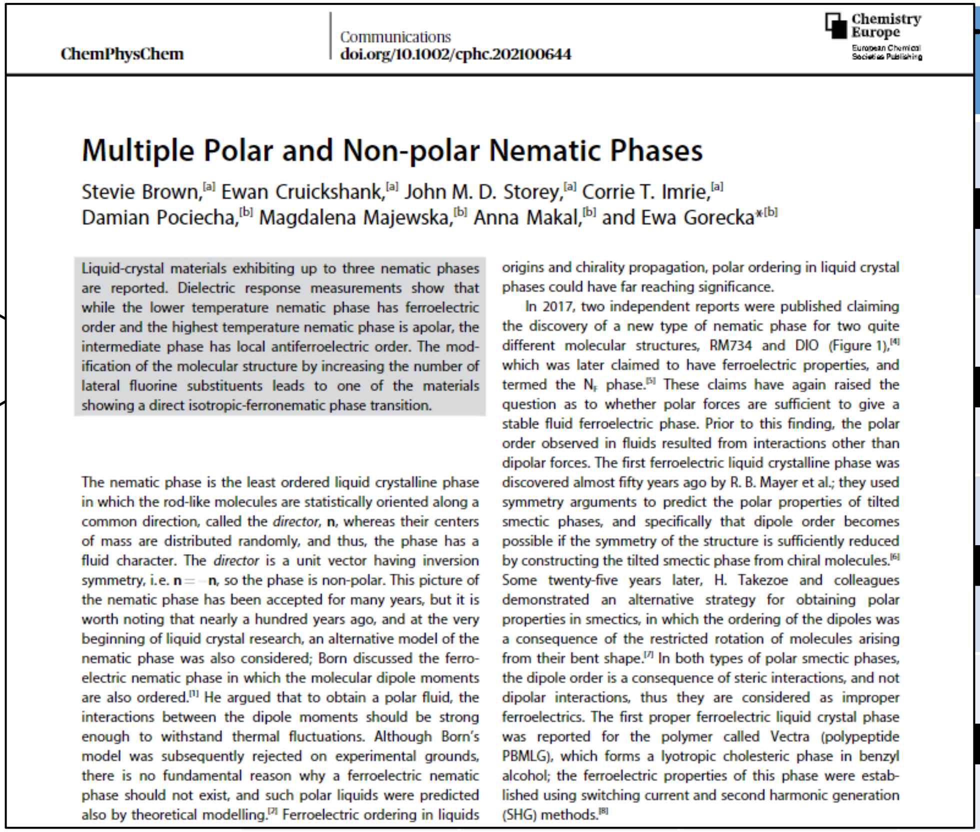


X	Y	m.p.	$T_{N_FN/I}$	T_{NI}	Ref
H	H	139	131	188	1
H	F	165	140	155	1
F	H	161	143	165	3
F	F	151	139		3

1. Mandle, R. J. *et al. Phys. Chem. Chem. Phys.* **19**, 11429–11435 (2017).
3. Brown, S. *et al. ChemPhysChem,* **22**, 2506-2510 (2021)

Lateral Fluorination





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Multiple Polar and Non-polar Nematic Phases

Stevie Brown,[a] Ewan Cruickshank,[a] John M. D. Storey,[a] Corrie T. Imrie,[a] Damian Pociecha,[b] Magdalena Majewska,[b] Anna Makal,[b] and Ewa Gorecka*[b]

Liquid-crystal materials exhibiting up to three nematic phases are reported. Dielectric response measurements show that while the lower temperature nematic phase has ferroelectric order and the highest temperature nematic phase is apolar, the intermediate phase has local antiferroelectric order. The modification of the molecular structure by increasing the number of lateral fluorine substituents leads to one of the materials showing a direct isotropic-ferronematic phase transition.

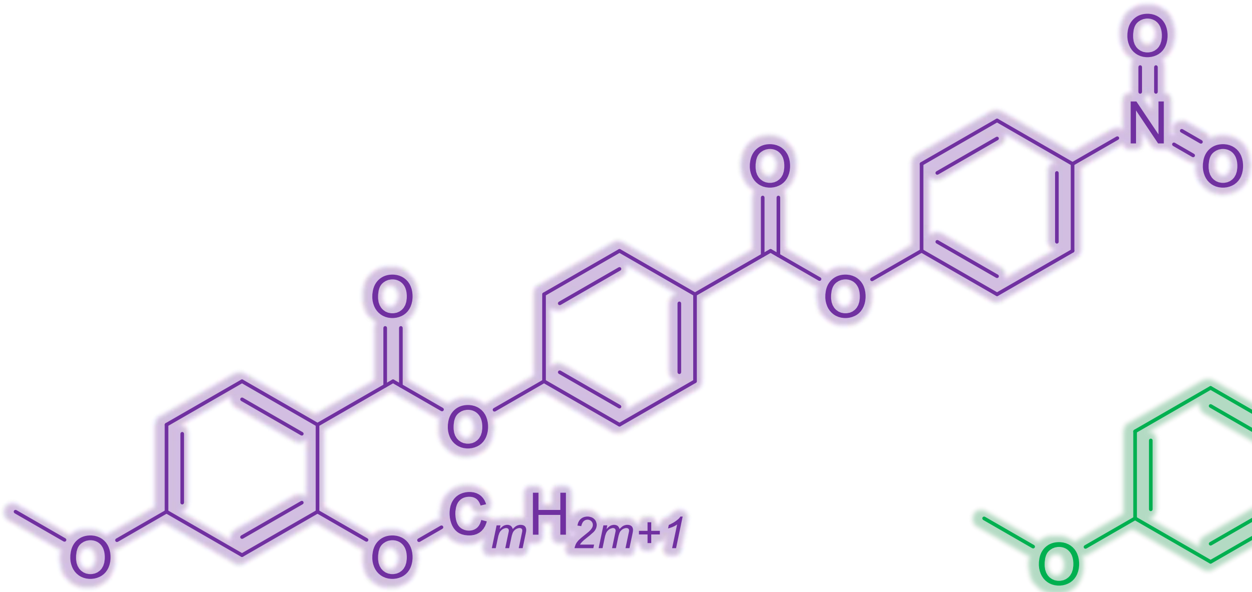
The nematic phase is the least ordered liquid crystalline phase in which the rod-like molecules are statistically oriented along a common direction, called the *director*, **n**, whereas their centers of mass are distributed randomly, and thus, the phase has a fluid character. The *director* is a unit vector having inversion symmetry, i.e. **n** = −**n**, so the phase is non-polar. This picture of the nematic phase has been accepted for many years, but it is worth noting that nearly a hundred years ago, and at the very beginning of liquid crystal research, an alternative model of the nematic phase was also considered; Born discussed the ferroelectric nematic phase in which the molecular dipole moments are also ordered.[1] He argued that to obtain a polar fluid, the interactions between the dipole moments should be strong enough to withstand thermal fluctuations. Although Born's model was subsequently rejected on experimental grounds, there is no fundamental reason why a ferroelectric nematic phase should not exist, and such polar liquids were predicted also by theoretical modelling.[2] Ferroelectric ordering in liquids origins and chirality propagation, polar ordering in liquid crystal phases could have far reaching significance.

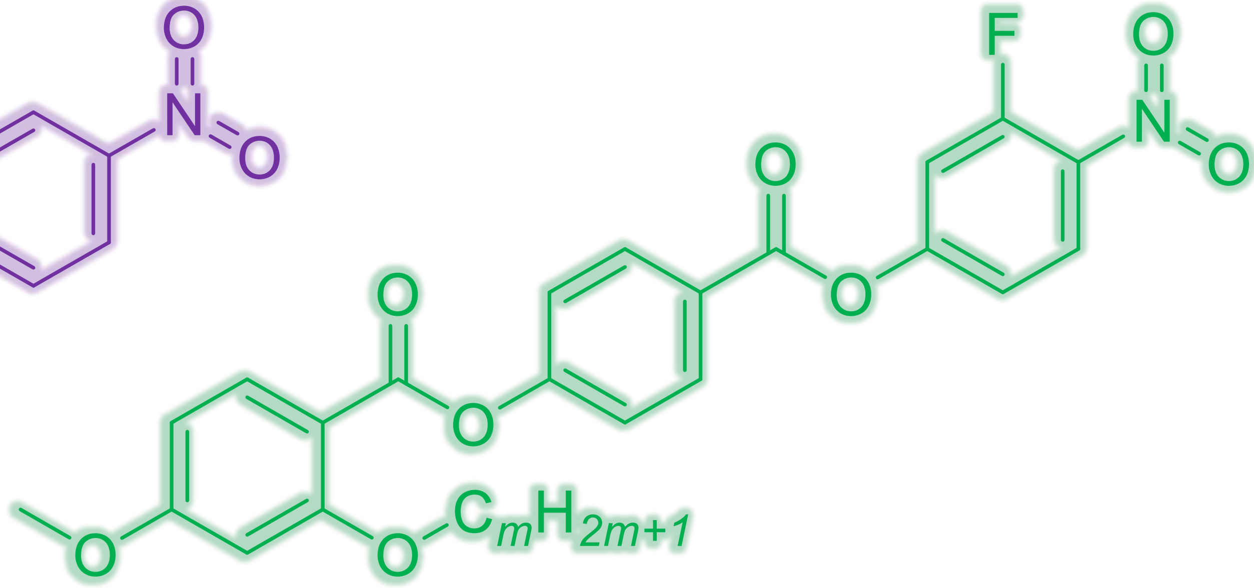
In 2017, two independent reports were published claiming the discovery of a new type of nematic phase for two quite different molecular structures, RM734 and DIO (Figure 1),[4] which was later claimed to have ferroelectric properties, and termed the N_F phase.[5] These claims have again raised the question as to whether polar forces are sufficient to give a stable fluid ferroelectric phase. Prior to this finding, the polar order observed in fluids resulted from interactions other than dipolar forces. The first ferroelectric liquid crystalline phase was discovered almost fifty years ago by R. B. Mayer et al.; they used symmetry arguments to predict the polar properties of tilted smectic phases, and specifically that dipole order becomes possible if the symmetry of the structure is sufficiently reduced by constructing the tilted smectic phase from chiral molecules.[6] Some twenty-five years later, H. Takezoe and colleagues demonstrated an alternative strategy for obtaining polar properties in smectics, in which the ordering of the dipoles was a consequence of the restricted rotation of molecules arising from their bent shape.[7] In both types of polar smectic phases, the dipole order is a consequence of steric interactions, and not dipolar interactions, thus they are considered as improper ferroelectrics. The first proper ferroelectric liquid crystal phase was reported for the polymer called Vectra (polypeptide PBMLG), which forms a lyotropic cholesteric phase in benzyl alcohol; the ferroelectric properties of this phase were established using switching current and second harmonic generation (SHG) methods.[8]

$T_{N_FN/I}$	T_{NI}	Ref
131	188	1
140	155	1
143	165	3
139		3

1. Mandle, R. J. *et al. Phys. Chem. Chem. Phys.* **19**, 11429–11435 (2017).
3. Brown, S. *et al. ChemPhysChem*, **22**, 2506-2510 (2021).

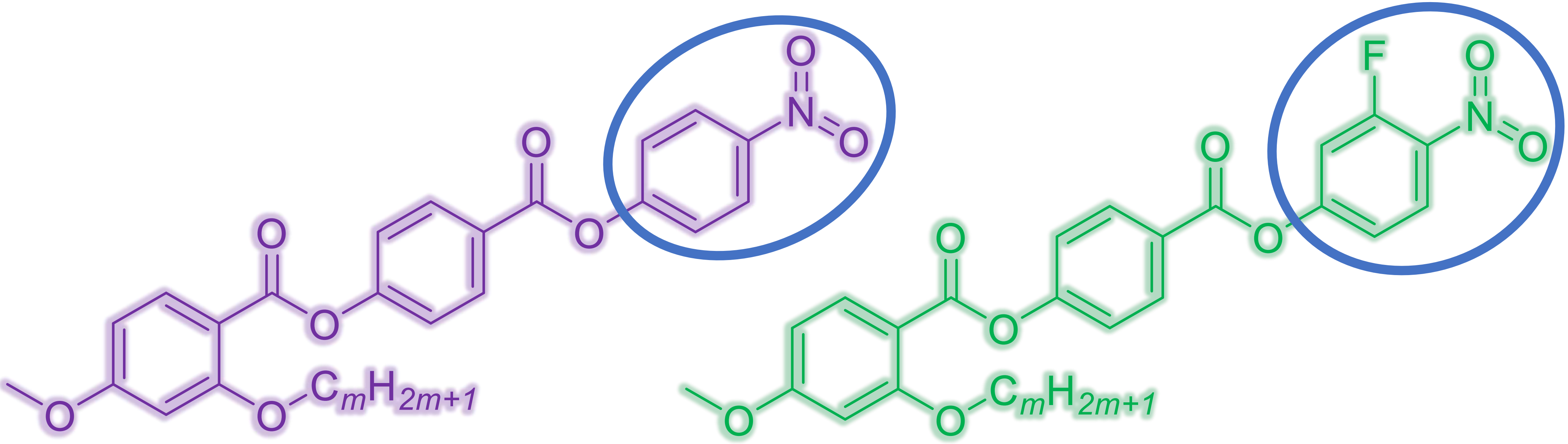
Extension of the Lateral Chain





4. Mandle, R. J. *et al. Chem. - A Euro. J.* **23**, 14554-14562 (2017).
5. Li, J. *et al. Science Advances,* **7**, eabf5047 (2020).

Extension of the Lateral Chain



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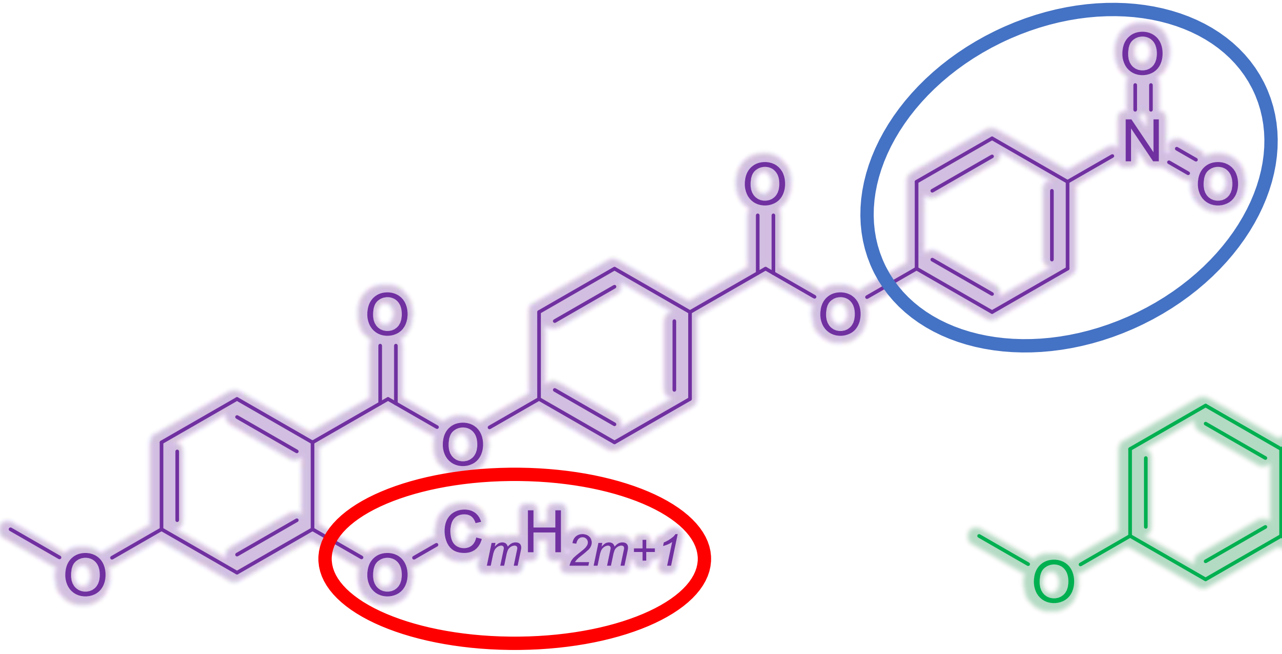
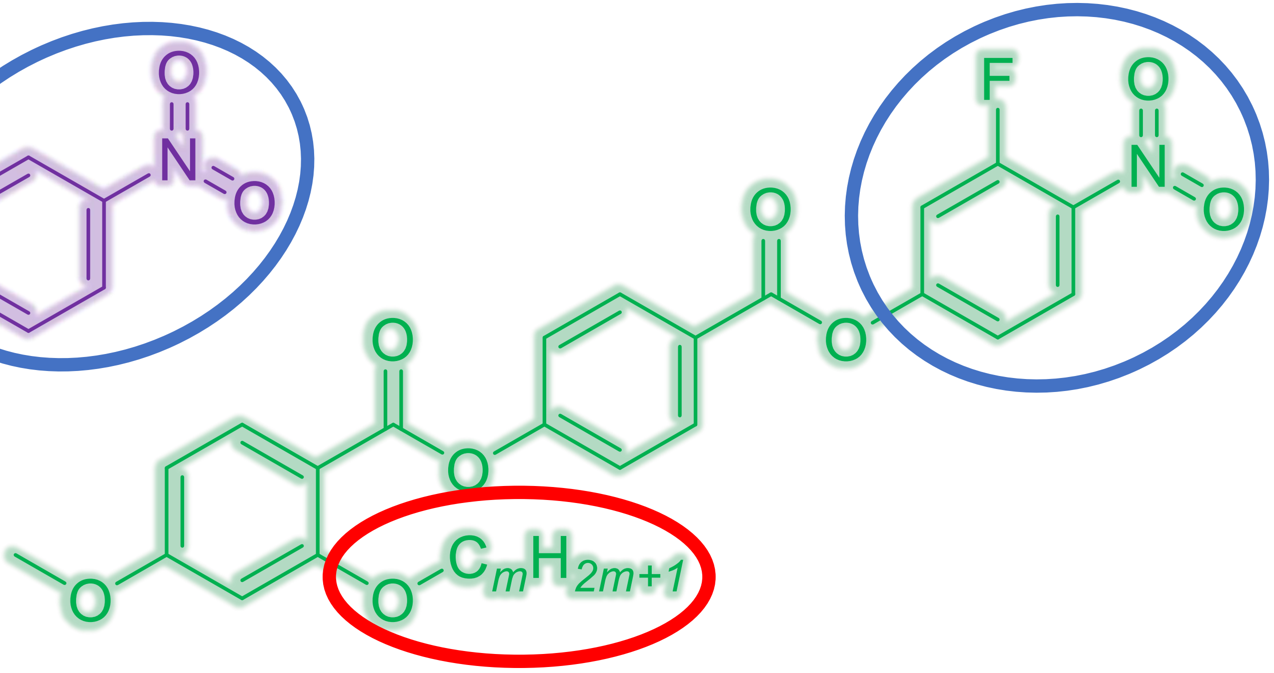


m = 1 - 9



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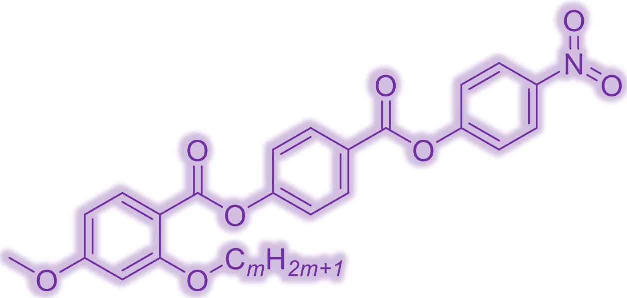
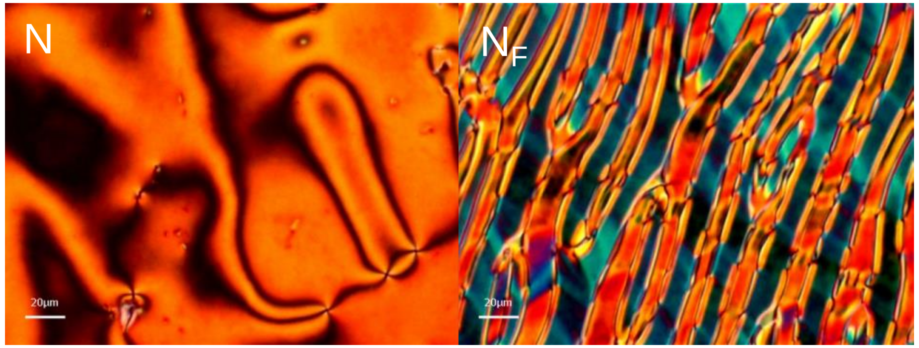
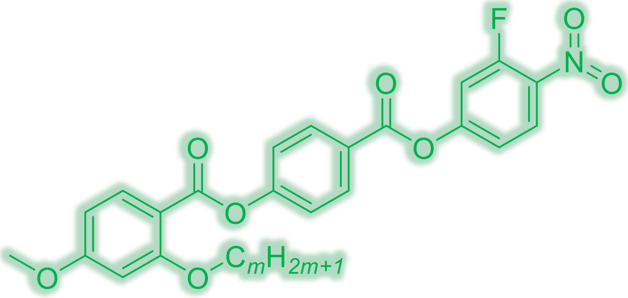
Phase Behaviour

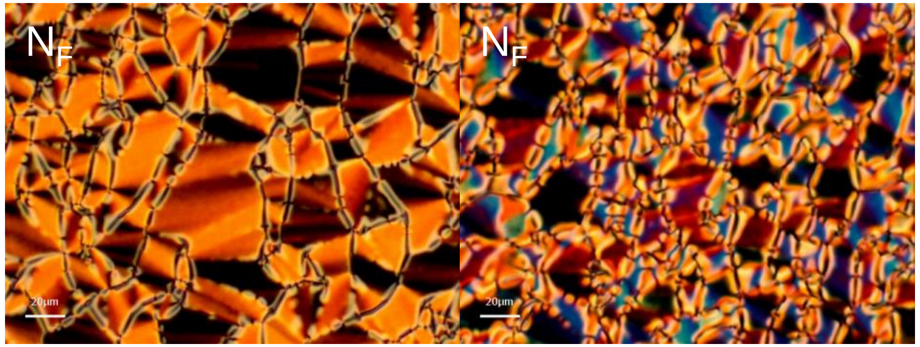
I – N - N_F



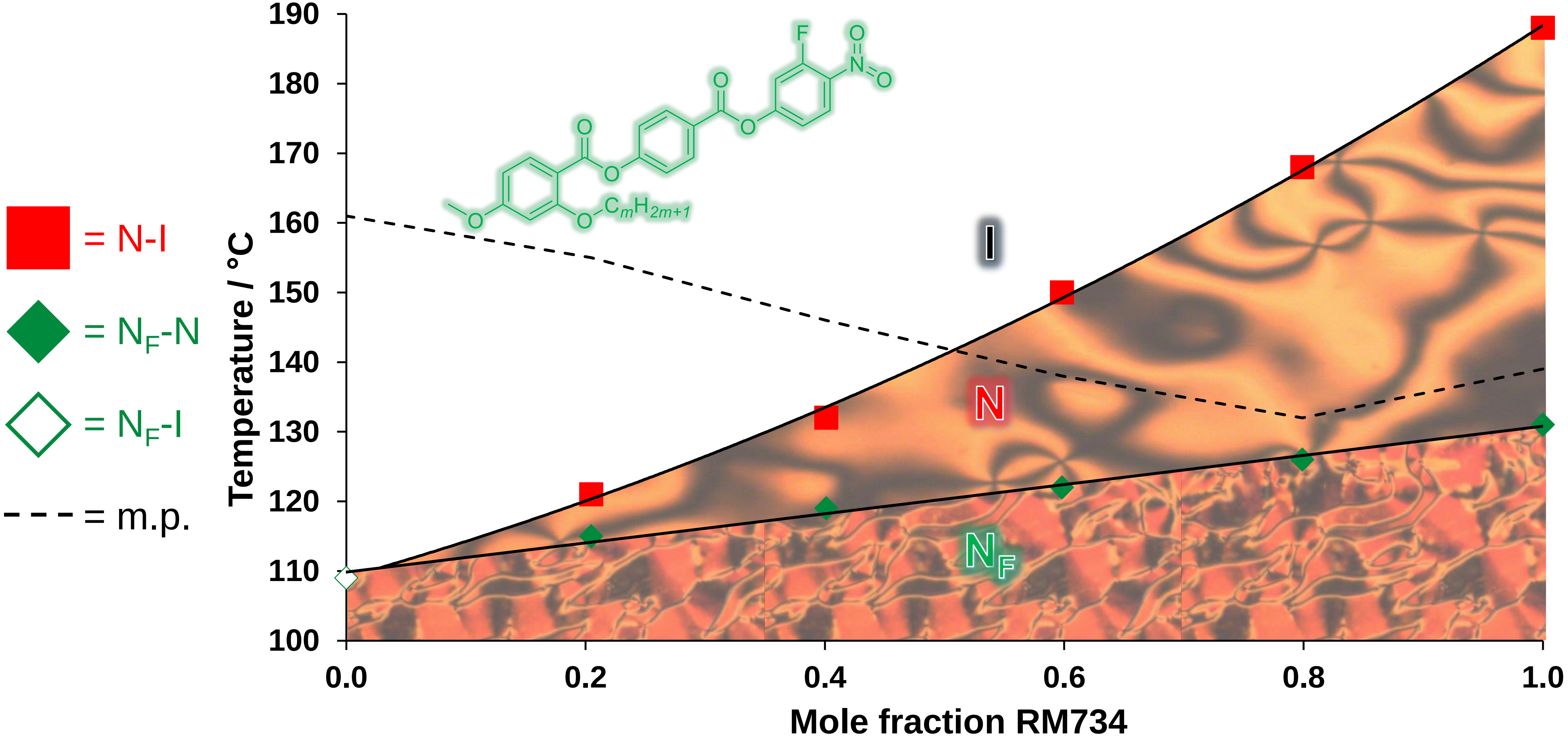


I – N_F

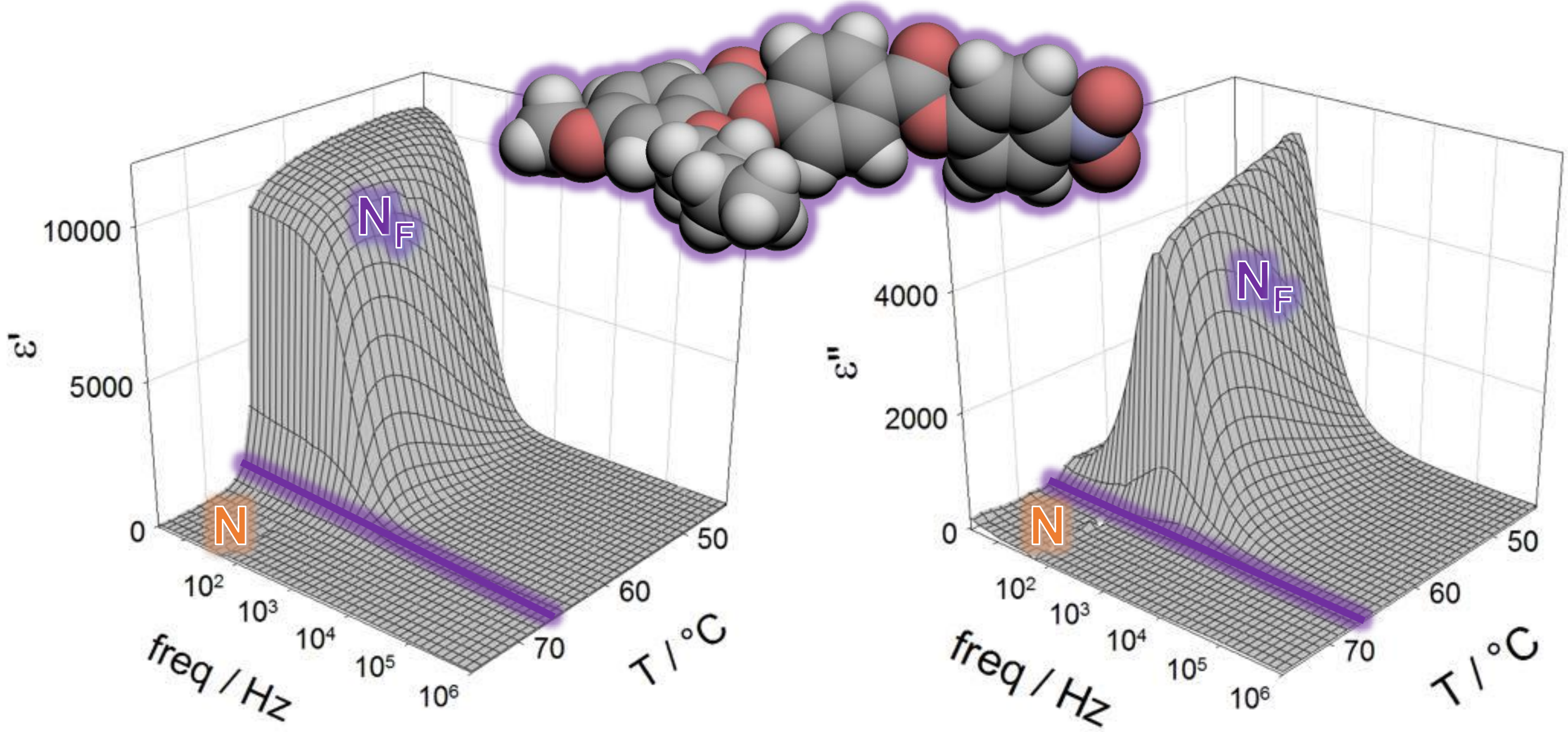




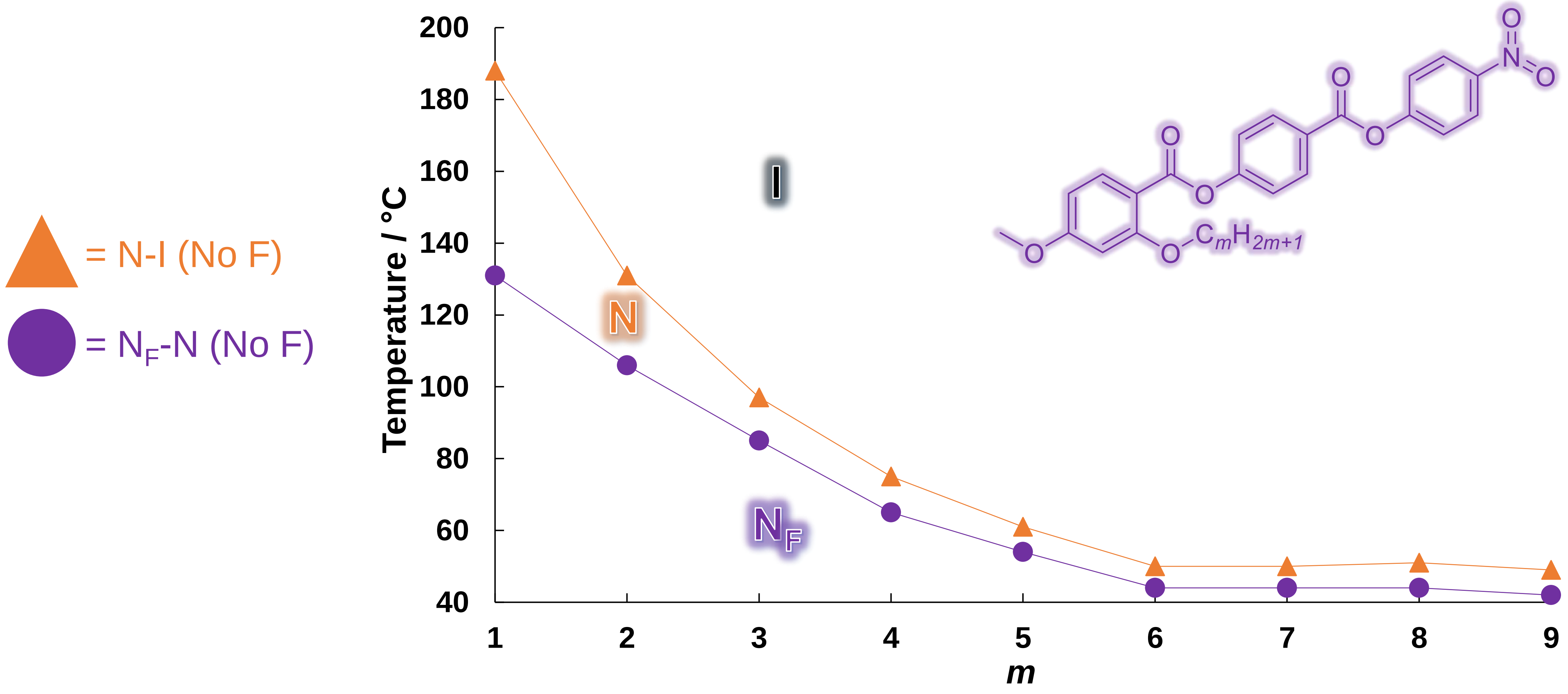
Confirming the N_F Assignments



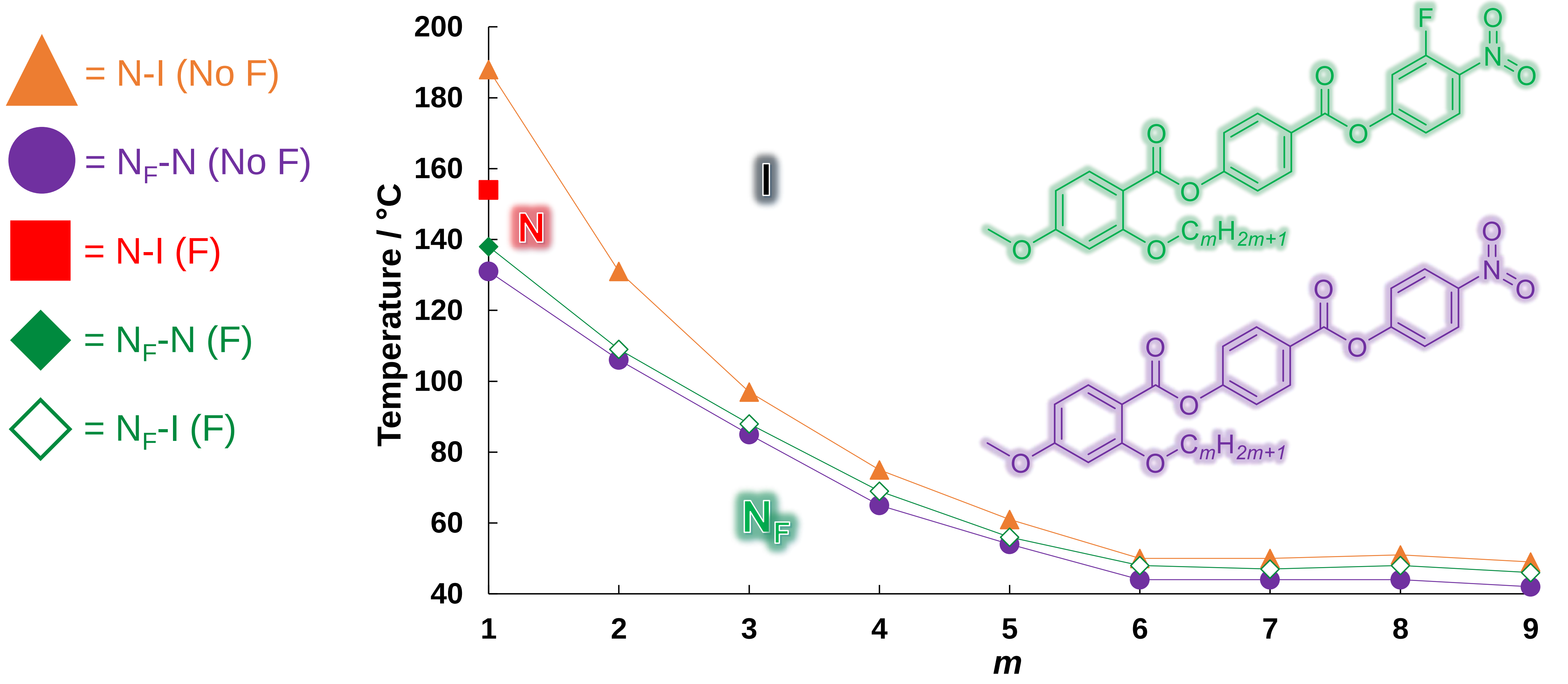
Further Confirming the N_F Assignments



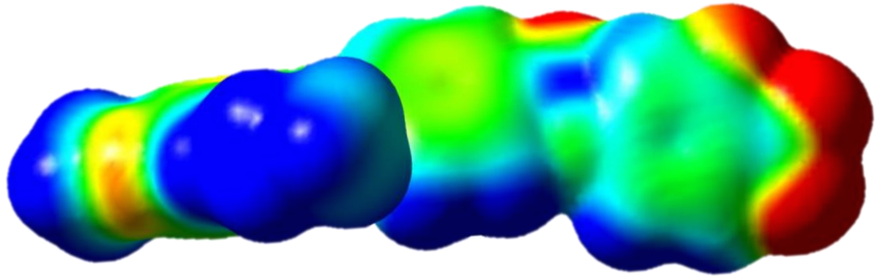
Transition Temperatures



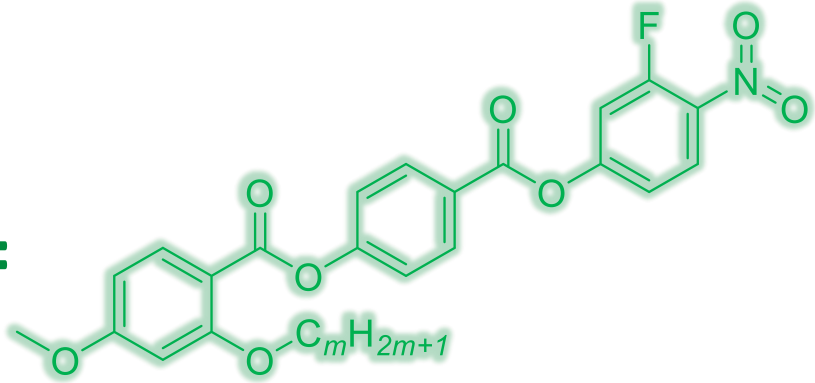
Transition Temperatures

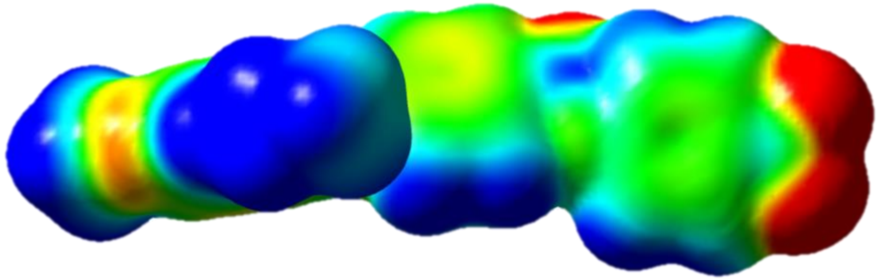


Shape and Dipoles



= 12.201 D =





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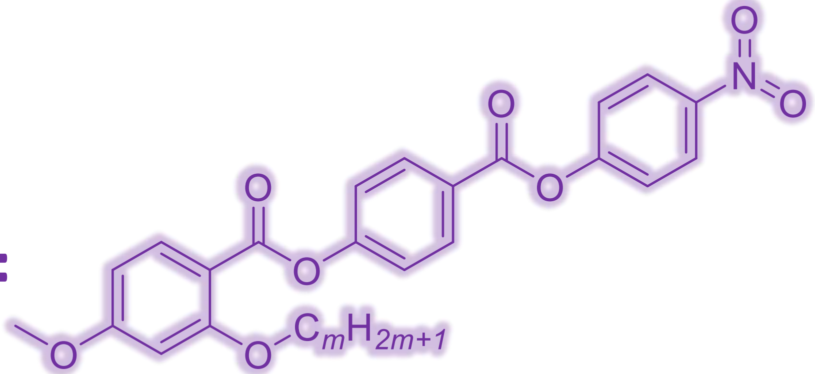
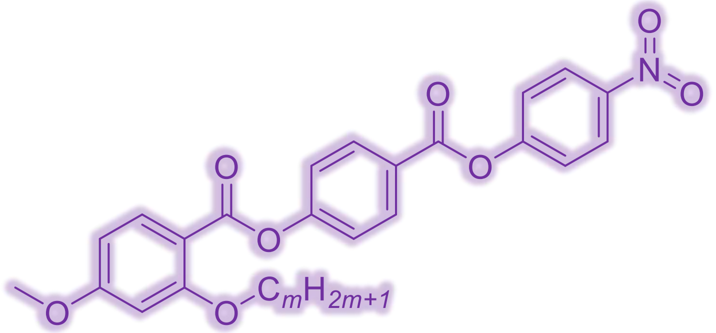


6. Madhusudana, N. V. *Phys. Rev. E.* **104**, 014704 (2021).

Lateral Chains and the N_F Phase



7. Weissflog, W. *et al. Crystal Res. Rech.* **18**, K21-K24 (1983).
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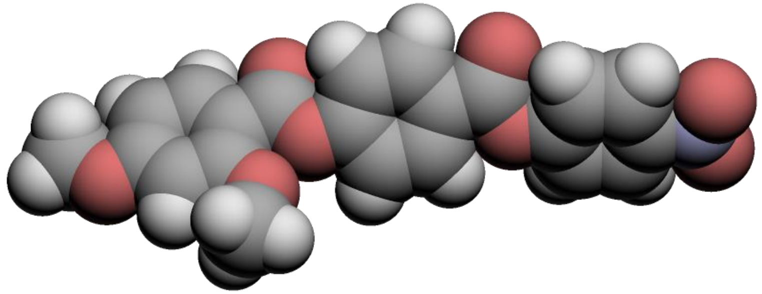

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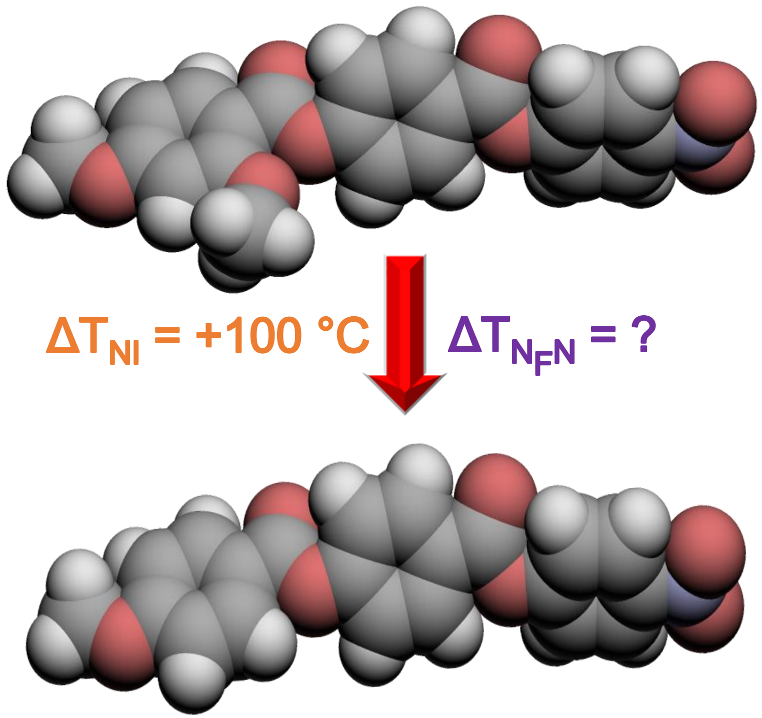

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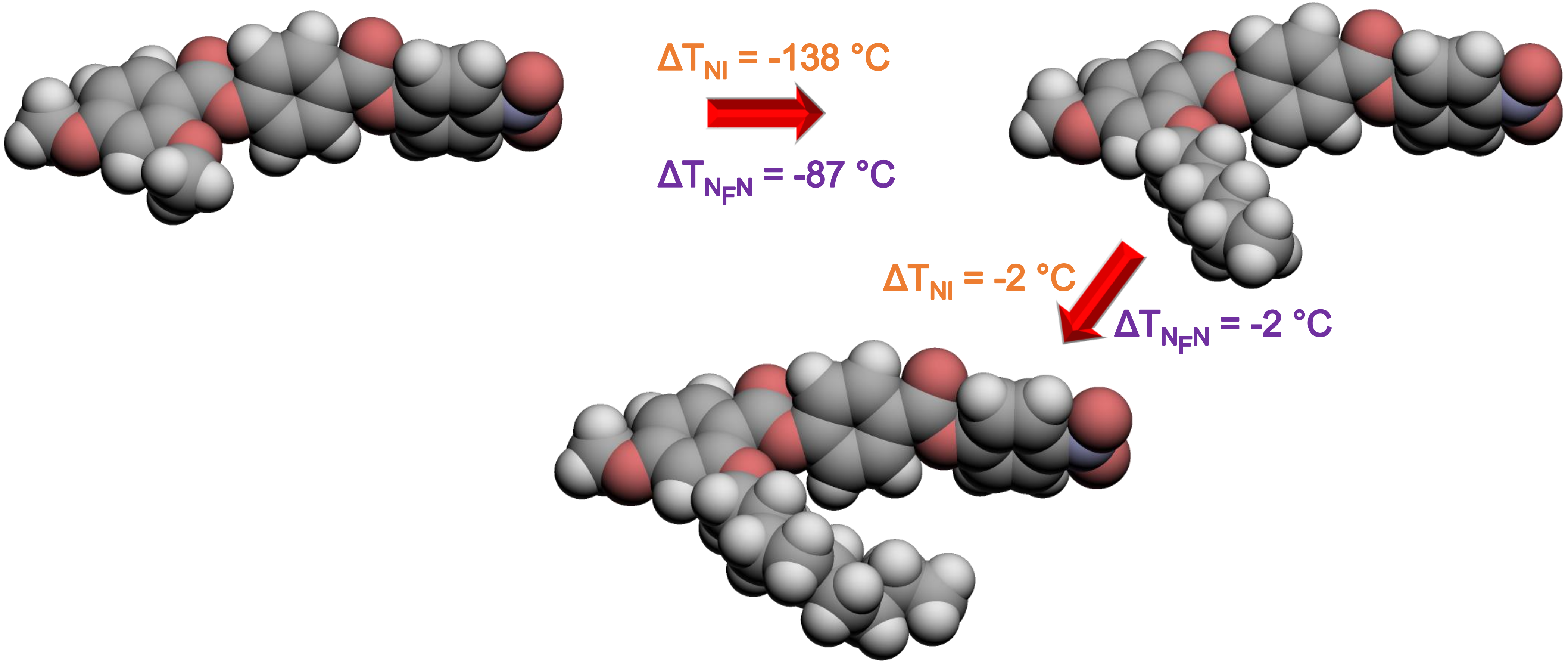

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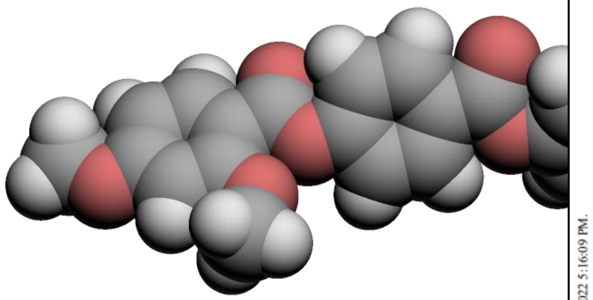

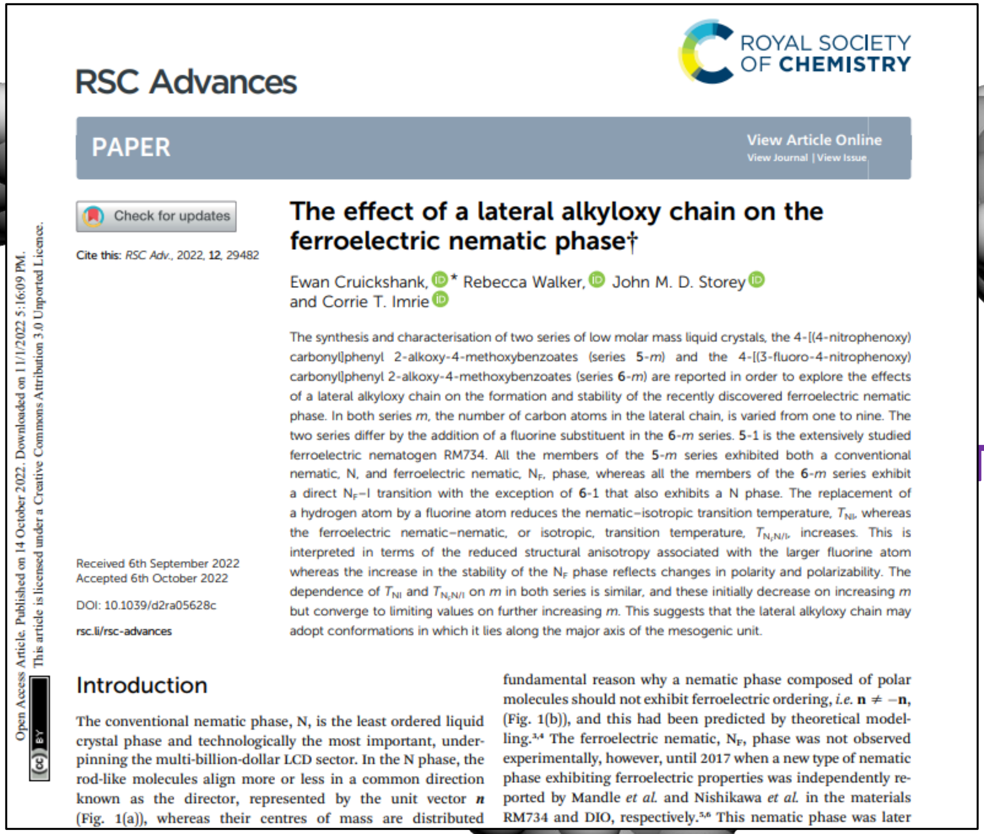

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The effect of a lateral alkyloxy chain on the ferroelectric nematic phase†

Ewan Cruickshank,* Rebecca Walker, John M. D. Storey and Corrie T. Imrie

The synthesis and characterisation of two series of low molar mass liquid crystals, the 4-[(4-nitrophenoxy)carbonyl]phenyl 2-alkoxy-4-methoxybenzoates (series **5**-*m*) and the 4-[(3-fluoro-4-nitrophenoxy)carbonyl]phenyl 2-alkoxy-4-methoxybenzoates (series **6**-*m*) are reported in order to explore the effects of a lateral alkyloxy chain on the formation and stability of the recently discovered ferroelectric nematic phase. In both series *m*, the number of carbon atoms in the lateral chain, is varied from one to nine. The two series differ by the addition of a fluorine substituent in the **6**-*m* series. **5**-**1** is the extensively studied ferroelectric nematogen RM734. All the members of the **5**-*m* series exhibited both a conventional nematic, N, and ferroelectric nematic, N_F, phase, whereas all the members of the **6**-*m* series exhibit a direct N_F–I transition with the exception of **6**-**1** that also exhibits a N phase. The replacement of a hydrogen atom by a fluorine atom reduces the nematic–isotropic transition temperature, T_{NI}, whereas the ferroelectric nematic–nematic, or isotropic, transition temperature, $T_{N_FN/I}$, increases. This is interpreted in terms of the reduced structural anisotropy associated with the larger fluorine atom whereas the increase in the stability of the N_F phase reflects changes in polarity and polarizability. The dependence of T_{NI} and $T_{N_FN/I}$ on *m* in both series is similar, and these initially decrease on increasing *m* but converge to limiting values on further increasing *m*. This suggests that the lateral alkyloxy chain may adopt conformations in which it lies along the major axis of the mesogenic unit.

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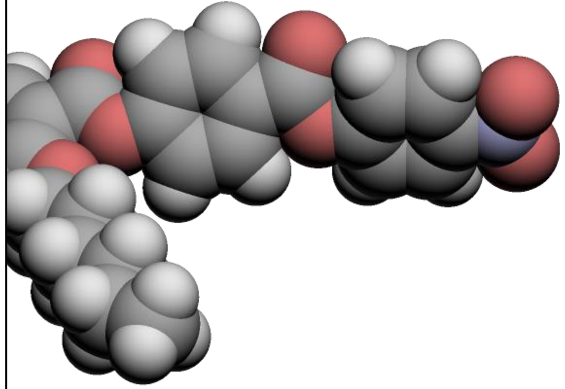
Introduction

The conventional nematic phase, N, is the least ordered liquid crystal phase and technologically the most important, underpinning the multi-billion-dollar LCD sector. In the N phase, the rod-like molecules align more or less in a common direction known as the director, represented by the unit vector ***n*** (Fig. 1(a)), whereas their centres of mass are distributed fundamental reason why a nematic phase composed of polar molecules should not exhibit ferroelectric ordering, *i.e.* **n** ≠ −**n**, (Fig. 1(b)), and this had been predicted by theoretical modelling.[3,4] The ferroelectric nematic, N_F, phase was not observed experimentally, however, until 2017 when a new type of nematic phase exhibiting ferroelectric properties was independently reported by Mandle *et al.* and Nishikawa *et al.* in the materials RM734 and DIO, respectively.[5,6] This nematic phase was later



T_{N_FN} = -2 °C

7. Weissflog, W. *et al. Crystal Res. Rech.* **18**, K21-K24 (1983).
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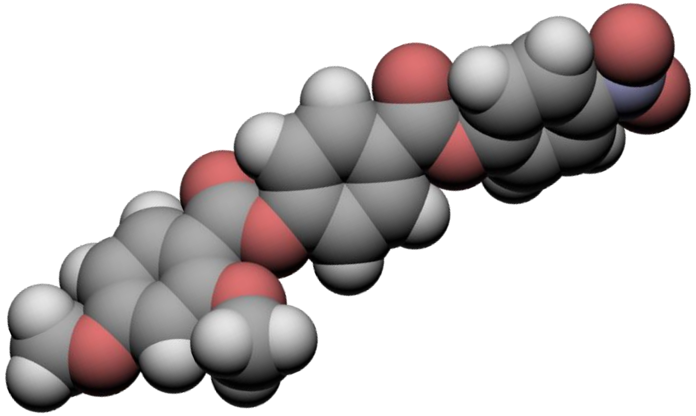
Branched Lateral Chains



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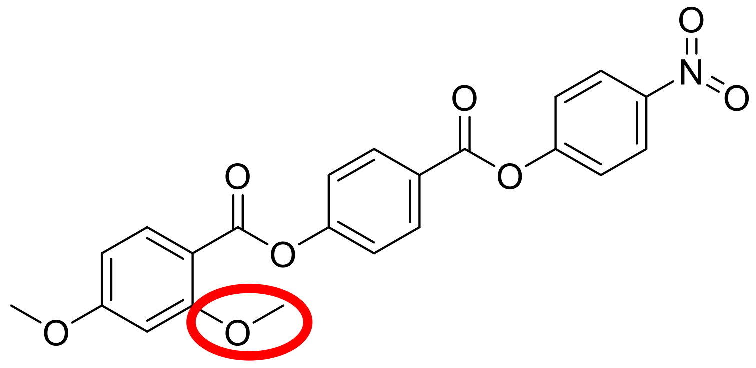

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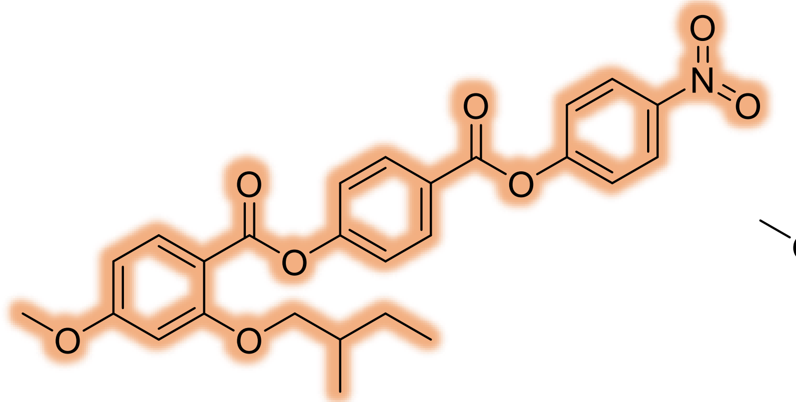

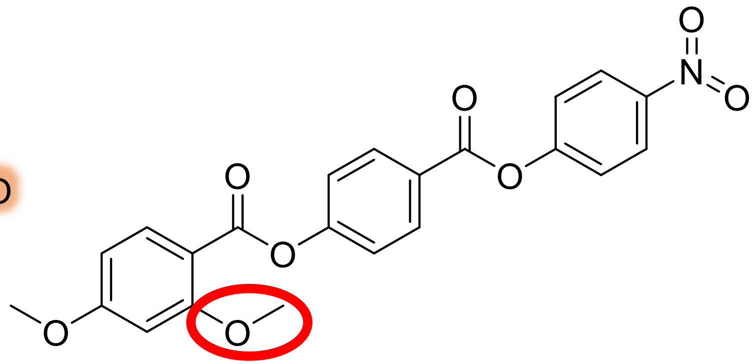

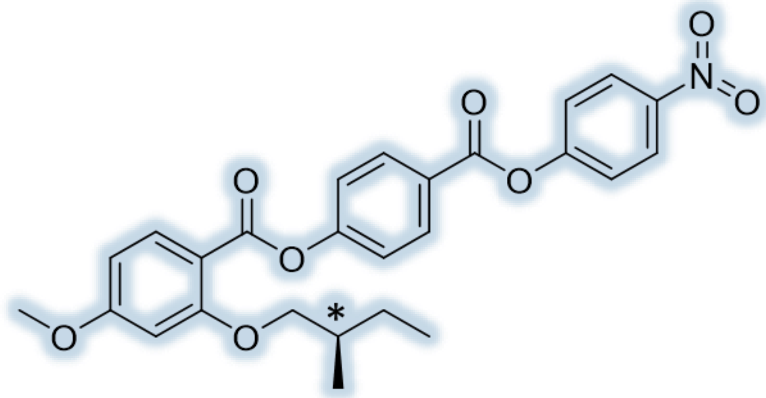

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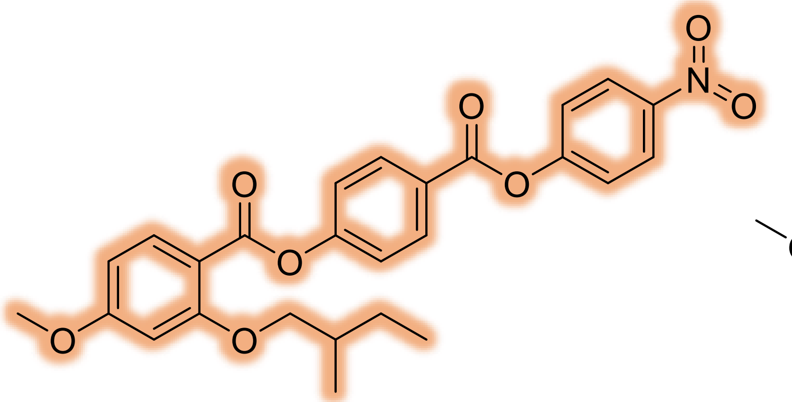

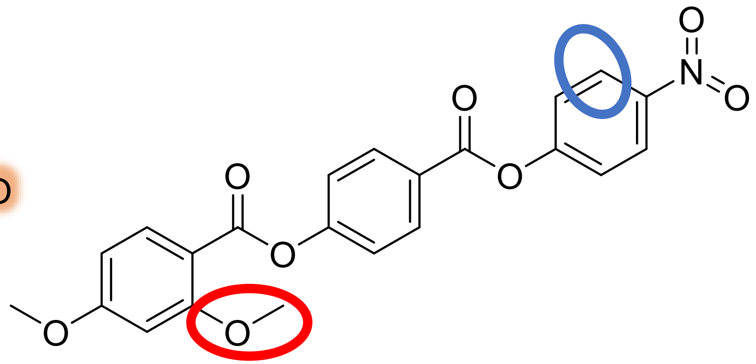

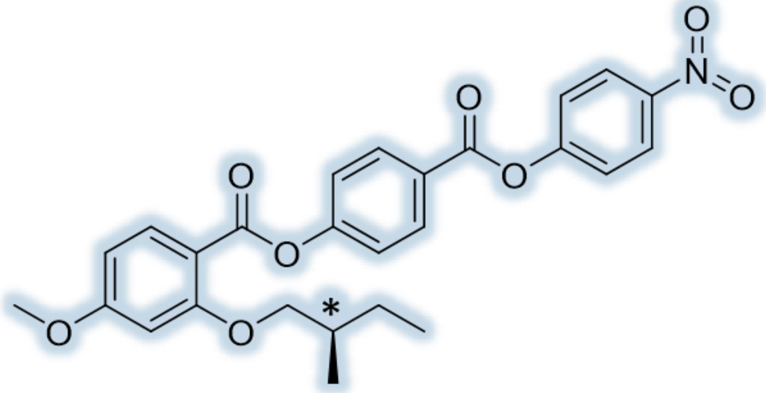

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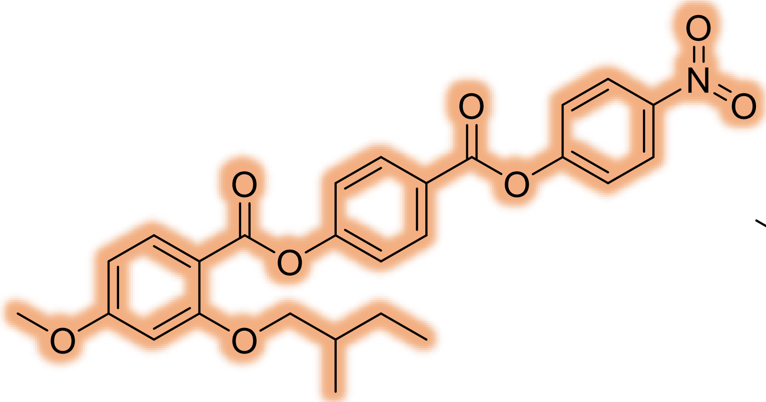
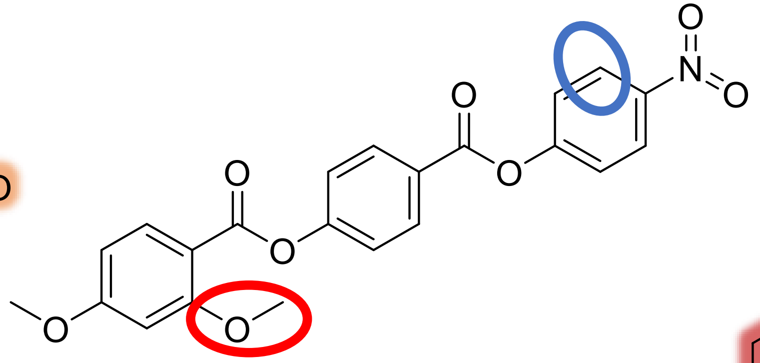
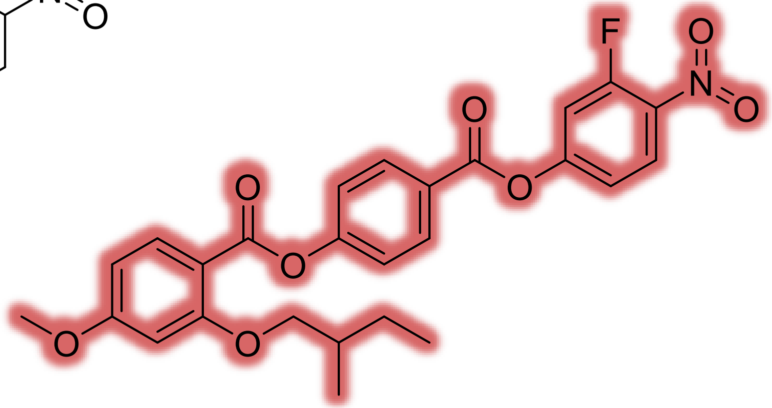
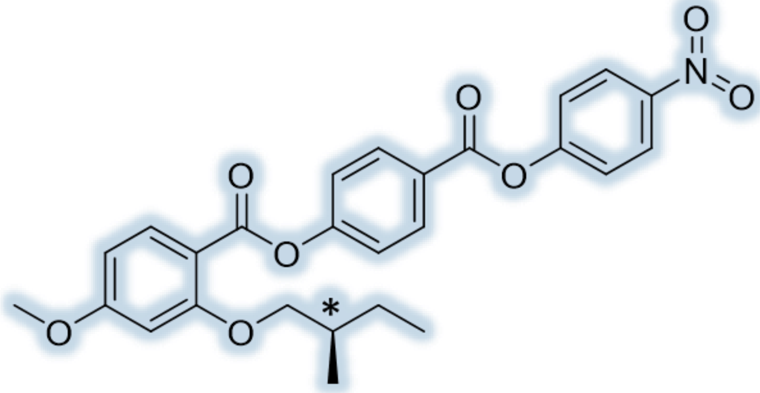
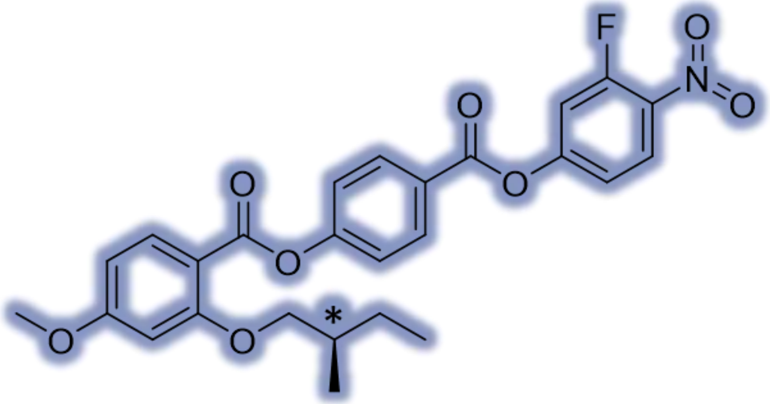


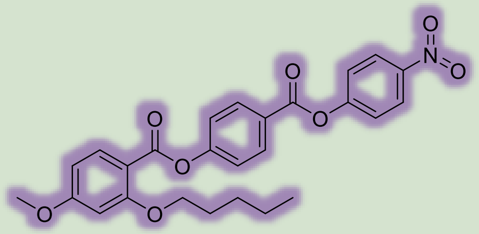
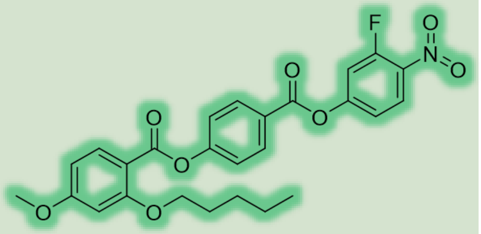
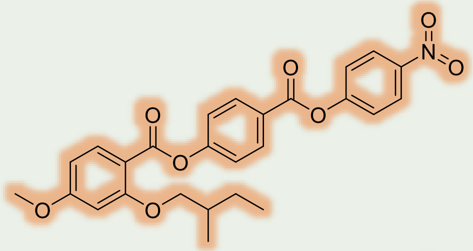
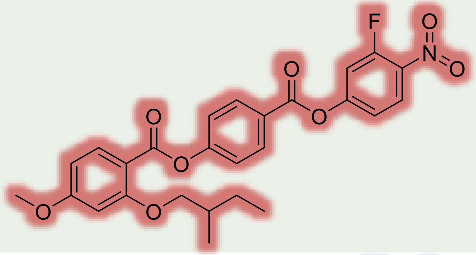
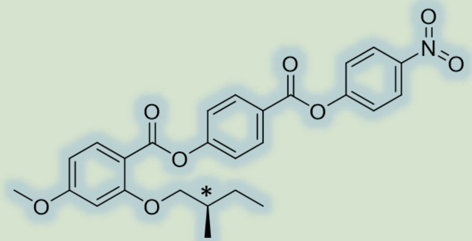
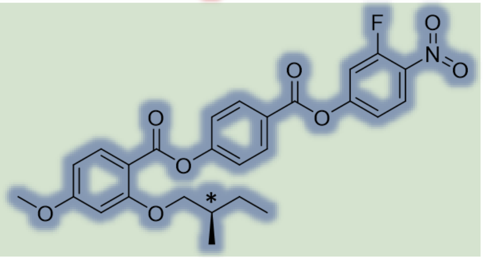






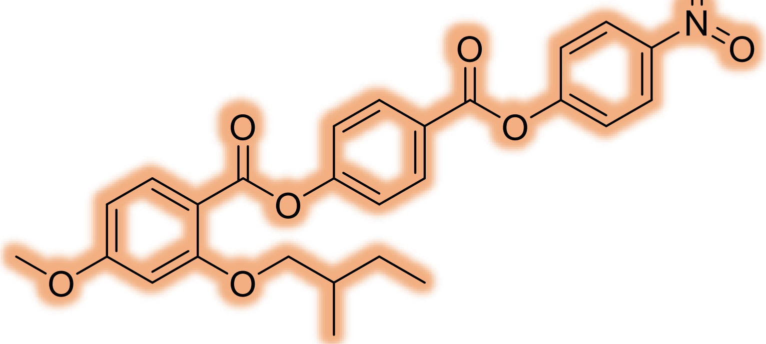


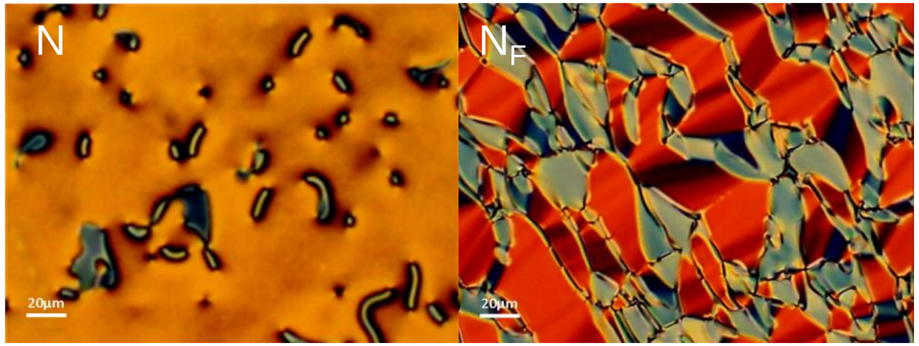
Chiral Ferronematogens

	m.p.	$T_{N_F(*)\text{-}N(*)}$	$T_{N(*)\text{-}I}$		m.p.	$T_{N_F(*)\text{-}I}$
	132	54	61		105	56
	144	54	55		120	56
	140	54	56		111	54

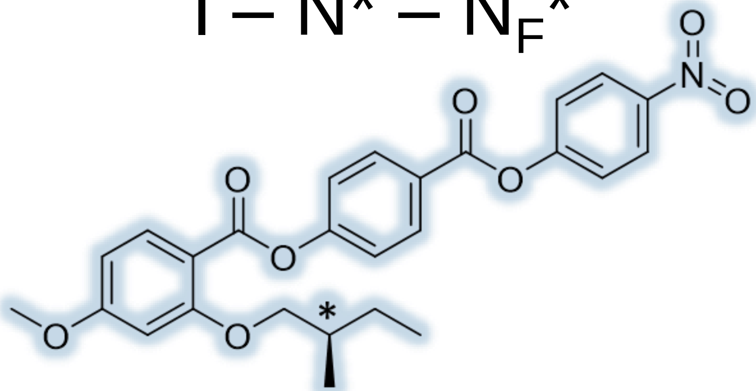
Phase Behaviour

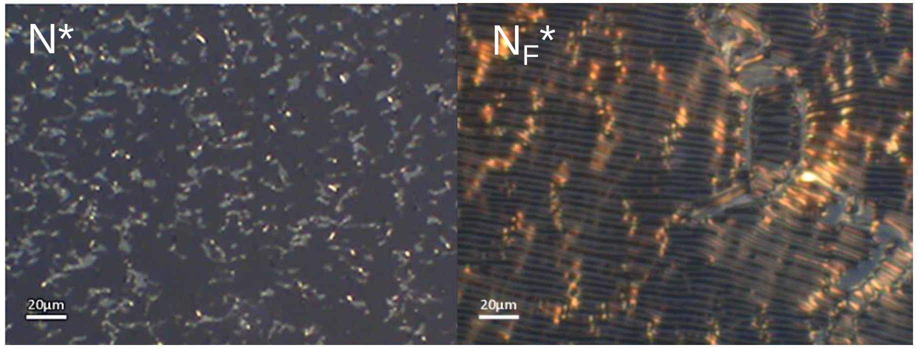
I – N – N_F



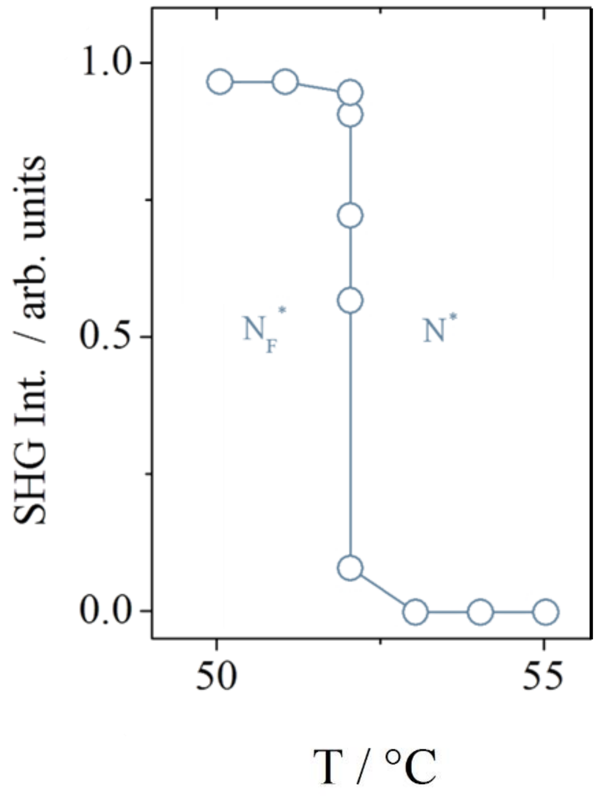


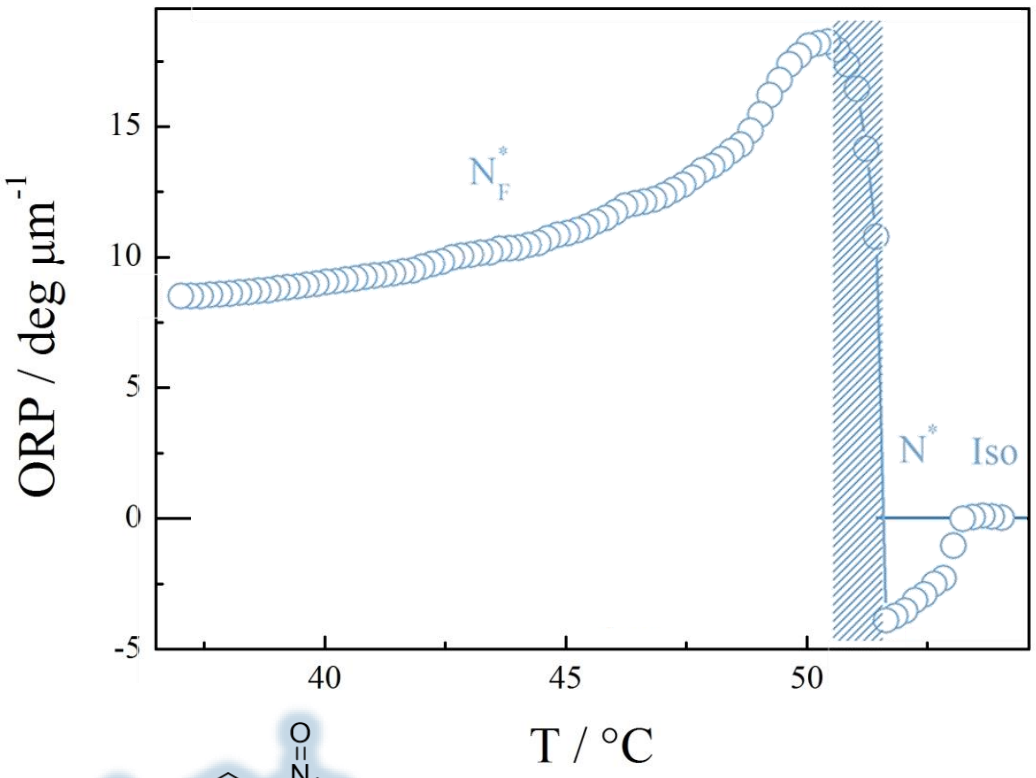
I – N* – N_F*

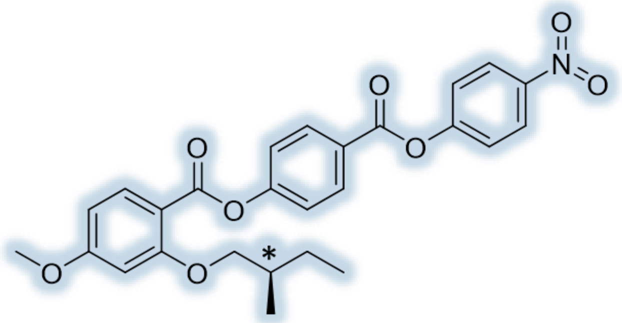




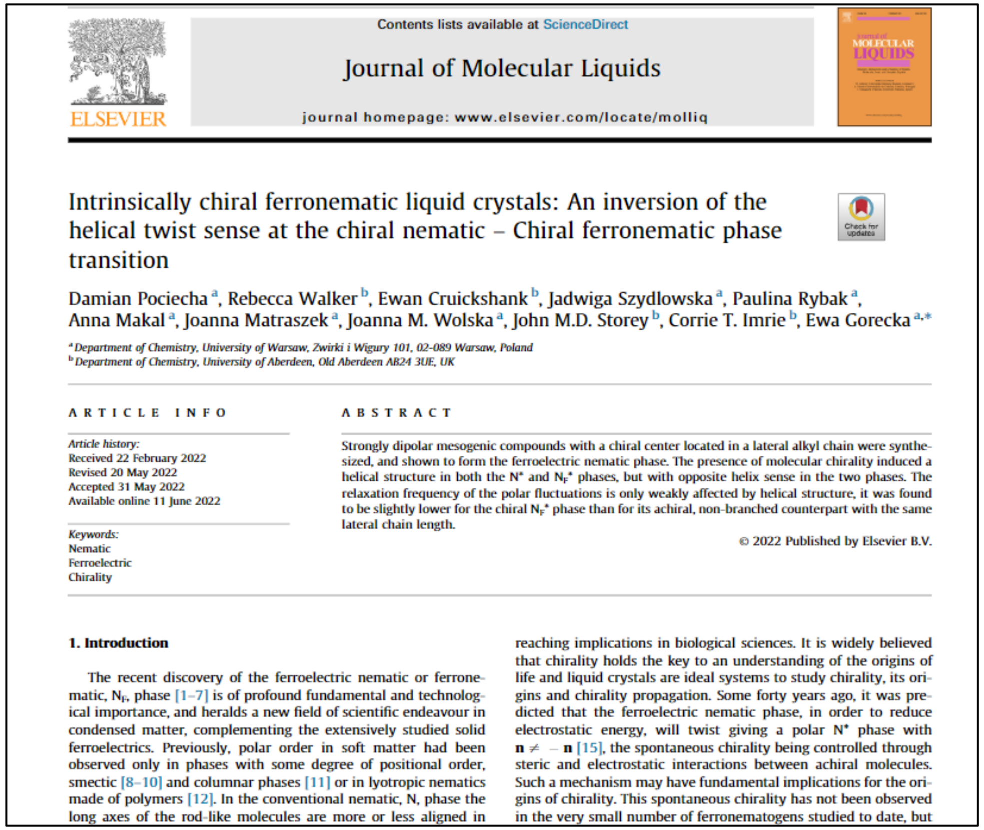
Confirming the N_F* Assignments







Confirming the N_F* Assignments



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Intrinsically chiral ferronematic liquid crystals: An inversion of the helical twist sense at the chiral nematic – Chiral ferronematic phase transition

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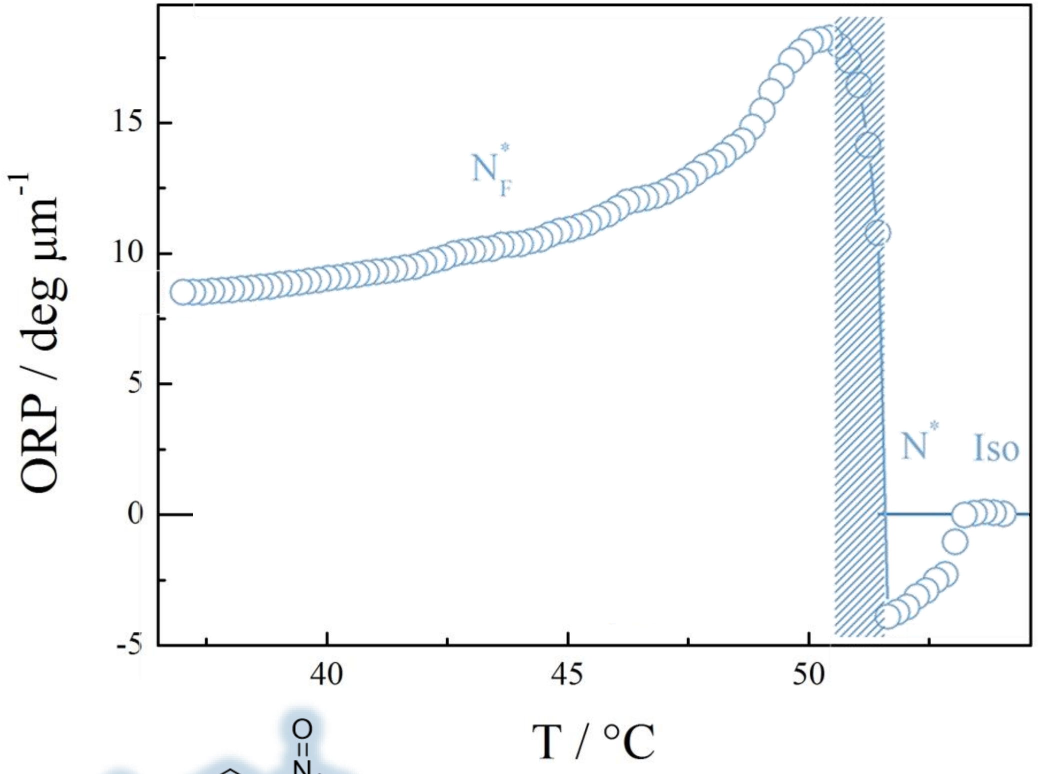
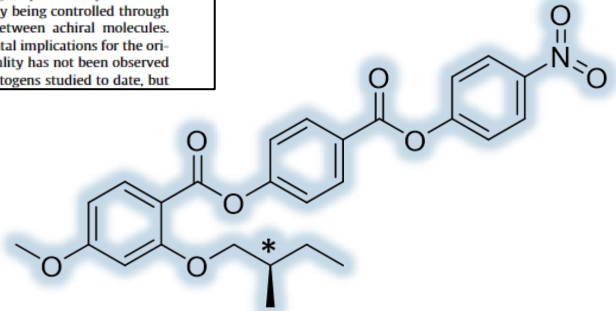
ABSTRACT

Strongly dipolar mesogenic compounds with a chiral center located in a lateral alkyl chain were synthesized, and shown to form the ferroelectric nematic phase. The presence of molecular chirality induced a helical structure in both the N* and N_F* phases, but with opposite helix sense in the two phases. The relaxation frequency of the polar fluctuations is only weakly affected by helical structure, it was found to be slightly lower for the chiral N_F* phase than for its achiral, non-branched counterpart with the same lateral chain length.

1. Introduction

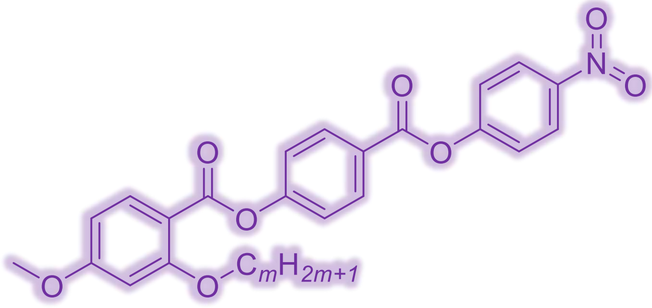
The recent discovery of the ferroelectric nematic or ferronematic, N_F, phase [1–7] is of profound fundamental and technological importance, and heralds a new field of scientific endeavour in condensed matter, complementing the extensively studied solid ferroelectrics. Previously, polar order in soft matter had been observed only in phases with some degree of positional order, smectic [8–10] and columnar phases [11] or in lyotropic nematics made of polymers [12]. In the conventional nematic, N, phase the long axes of the rod-like molecules are more or less aligned in reaching implications in biological sciences. It is widely believed that chirality holds the key to an understanding of the origins of life and liquid crystals are ideal systems to study chirality, its origins and chirality propagation. Some forty years ago, it was predicted that the ferroelectric nematic phase, in order to reduce electrostatic energy, will twist giving a polar N* phase with **n** ≠ − **n** [15], the spontaneous chirality being controlled through steric and electrostatic interactions between achiral molecules. Such a mechanism may have fundamental implications for the origins of chirality. This spontaneous chirality has not been observed in the very small number of ferronematogens studied to date, but

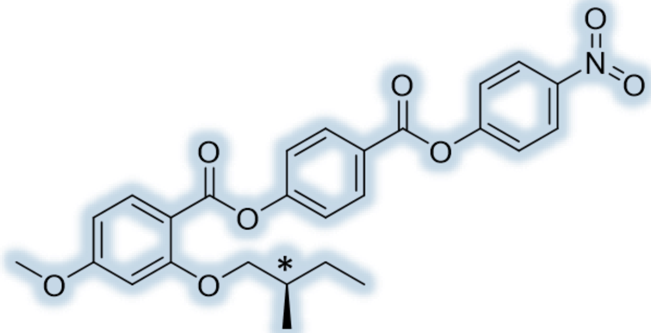


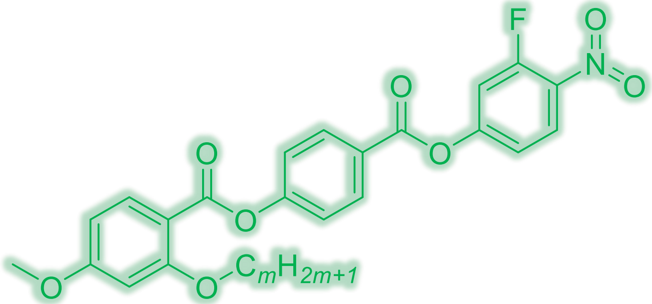


Conclusions

- For all the synthesised materials the NF phase was observed.
- The ability of the NF phase to tolerate bulky lateral substituents can been exploited, for example, in the design of chiral ferroelectric nematogens.
- To date there are now around 200 materials showing the phase.
- However, there is much still to be understood and work in this area has led to the recently reported SmA_F phase.







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