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Fluorine in liquid crystal design for display applications

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ABSTRACT

Fluorine is an essential component of most liquid crystalline materials as they are used in LCD devices. The reasons for this are manifold: fluorination limits the coordination ability to cationic impurities and thus improves reliability of the LCD, it provides a custom-tailored molecular dipole moment with the right orientation, and it can stabilize certain conformations and rigidify flexible alkyl chains.

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1. Introduction

After Friedrich Reinitzer's serendipitous, original discovery of the liquid crystalline behaviour of cholesteryl benzoate (**1**) [1], many different varieties of compounds with elongated, rod-like shape were found to exhibit so-called calamitic mesophases [2]. However, the transition from a pure lab curiosity to a useful display technology happened only in 1968 [3]. The first materials used were Schiff bases and azoxybenzenes (**2**, **3**). The final steps towards a technology compatible with mass-production processes were on the one hand the twisted nematic (TN) display mode, and on the other hand the introduction of cyanobiphenyls and related compounds by G. W. Gray, R. Eidenschink, D. Demus and others (Scheme 1) [4]. The first liquid crystal displays (LCDs) were passively addressed, but thus their resolution was limited to small arrays. In order to overcome this limitation, since around 1990 active matrix (AM) LCDs were introduced with essentially unlimited array size. In an AM-LCD, the voltage applied to each pixel is controlled with high accuracy by a thin film transistor (TFT) in combination with a storage capacitor. AM-LCD technology puts much higher demands on the liquid crystal material with regard to reliability. In particular, the voltage holding ratio (VHR) is one of the key reliability parameters of any liquid crystal suitable for AM-LCD [5].

Soon, the VHR of cyano-terminated liquid crystals was found to be intrinsically insufficient for application in AM-LCD technology, and from the early 1990s on only fluorine itself or fluorinated functional groups were used as polar terminal groups in nematic liquid crystals [6] for this application. The reason for the necessity to replace the cyano group by fluorine is the propensity of the cyano group to coordinate to cationic impurities and thus mobilize ions in an applied electric field. The uncontrollable discharge of the pixel-capacitor leads to contrast loss, flicker or image sticking.

Thus, liquid crystals for use in LCDs have become one of the most prominent application areas of fluoroorganic chemistry. In 2013, a total of around 140 km² of LCD area (this corresponds to the area of the city of Frankfurt) has been produced, most of it using fluorinated liquid crystals [7].

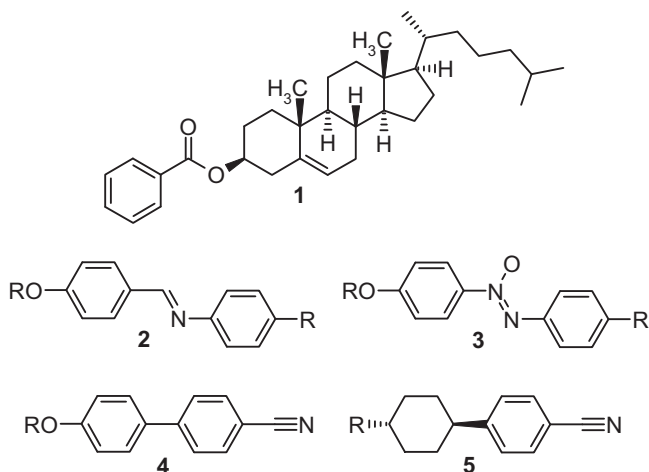
First examples of fluorinated liquid crystals were already synthesized in 1954 in the group of G. W. Gray [8]. In particular, lateral aromatic fluorine substituents [9] were found to often induce a wider nematic mesophase range and soon earned the nickname “nematic fluorine”. Later on, lateral fluorination was used in combination with a polar terminal group as strategy to enhance the molecular dipole moment and the dielectric anisotropy ($\Delta\epsilon$).

2. Fluorinated polar terminal groups

The ability of fluorine itself to induce a high molecular dipole moment and thus a strong dielectric anisotropy ($\Delta\epsilon$) [10] in liquid crystals is quite limited. Therefore, fluorine was soon replaced by a

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Scheme 1. The first generation of liquid crystals. The real break-through for display applications was achieved with materials **4** and **5**.

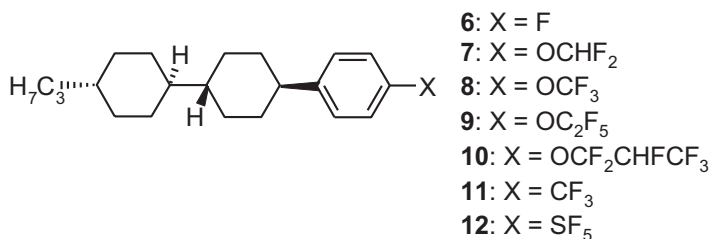
variety of more complex fluorinated terminal groups (Table 1). It strikes the eye that most of these fluorinated groups are rather short. The reason is the tendency of longer perfluorinated groups, such as perfluoroalkyl and perfluoroalkoxy functions (e.g., **9** and **10**), to show poor solubility as well as the occurrence of undesirable smectic mesophases.

An extreme example of this tendency are the partially fluorinated diblock and triblock alkanes, which do not contain any cyclic subunits any more as they are characteristic for liquid crystals, but which still form smectic mesophases (Table 2) [12]. Reasons for this behaviour are the increased conformational rigidity of perfluorocarbons – compared to hydrocarbons – as well as the well-known tendency of hydrocarbon and fluorocarbon molecular segments to phase-segregate on the nanometer scale.

Further enhancement of the dielectric anisotropy of nematic liquid crystals can be achieved by a combination of highly polar terminal groups with extensive lateral fluorination. However, this concept has its limitation, since with each additional fluorine substituents in the series **17–21** the virtual clearing temperature [11] of the material drops by up to 50 K (Table 3).

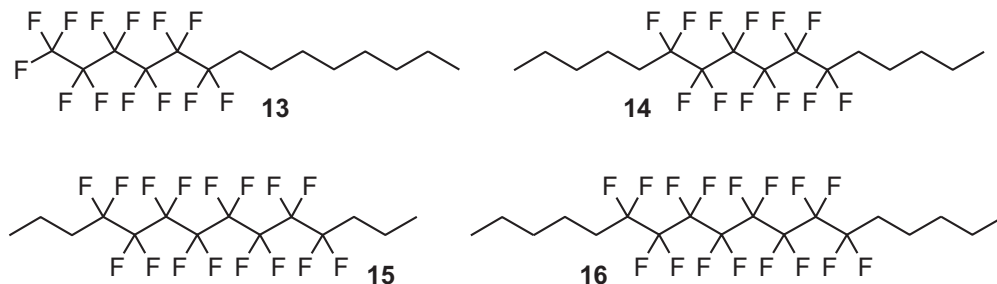
Also, the resulting electrostatic charge distribution often leads to strong attractive interactions between aromatic subunits with

Table 1
Examples of liquid crystals carrying various polar, fluorinated terminal groups [11]. The phase transition temperatures and “virtual” clearing points $T_{\text{NI,virt}}$ are denoted in °C, and the rotational viscosities γ_1 in mPa s.



No.	Mesophases	$T_{\text{NI,virt}}$	$\Delta\epsilon$	Δn	γ_1
6	C 90 N 158.3 I	158.3	3.0	0.094	157
7	C 52 S _B 69 N 173.6 I	163.2	5.2	0.086	–
8	C 39 S _B 70 N 154.7 I	146.2	6.9	0.087	142
9	C 119 S _B 152 N 168.6 I	152.1	6.5	0.088	–
10	C 178 I	157.3	3.9	0.074	–
11	C 133 I	113.2	9.5	0.091	338
12	C 121 I	96.2	11.6	0.093	612

Table 2
Partially fluorinated diblock (**13**) and triblock alkanes (**14–16**) [11]. The phase transition temperatures and $T_{\text{NI,virt}}$ are denoted in °C, and the rotational viscosities γ_1 in mPa s.



No.	Mesophases	$T_{\text{NI,virt}}$	γ_1
13	T_g –42 S _B –8 I	–104.6	–
14	C 28 I	–71.1	35
15	C 5 S ₇ 25 I	–27.8	31
16	C 44 I	–20.2	54

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