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Fluorophobic Effect Promoting Lamellar Self-Assembly of Donor Acceptor Dyes

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Graphical Abstract



Abstract

To combine liquid crystalline and linear optical properties in the same molecule, the fluorophobic effect was probed for the first time in donor acceptor dyes. Thus, a series of mono-, bi-, and tricyclic donor acceptor dyes with 1H,1H-perfluorinated alkyl chains of different lengths as donor units and nitrile, malononitrile or barbiturate as acceptor units was synthesized in 5 steps and 1.4-6.6 % overall yield. UV/Vis and fluorescence spectroscopy, cyclic voltammetry and DFT calculations revealed that absorption and emission maxima, Stokes shifts and LUMO energies were mainly governed by the chromophore size and acceptor strengths. The perfluorinated chain was electronically almost decoupled from the remaining chromophore and induced only slight changes of the absorption maxima as compared to the alkyl substituted counterparts. However, in contrast to the non-mesomorphic alkyl donor-substituted SmA bilayers

according to differential scanning calorimetry (DSC), polarizing optical microscopy (POM), X-ray diffraction (WAXS, SAXS) studies and electron density profile calculations.

Introduction

The merging of liquid crystalline with dye properties can be achieved either by mixtures of dye guest molecules in liquid crystalline hosts,^[1] or by compounds, that combine both properties on a molecular level. Mixtures of dyes in liquid crystals improved the contrast ratio in displays,^[2] the efficiency and stability of organic solar cells,^[3] allowed tuning of the emission wavelength of lasers ^[4] and were utilized in applications such as windows with an adaptive transmission.^[5] On the other hand liquid crystalline donor acceptor dyes^[6] have been employed as light responsive materials for drug delivery,^[7] components for bulk heterojunction solar cells^[8] and other photovoltaic devices,^[8] emissive dendrimers,^[9] NIR absorbing and fluorescent materials,^[10] photomodulators of dichroism and birefringence,^[11] acido- and photochromic materials,^[12] nematic [60]fullerene supermolecules^[13] and second- or third order nonlinear optical materials.^[14] A huge variety of chromophoric units has been incorporated in liquid crystalline dyes, both discotic mesogens, e.g. perylenes,^[15] pyrrole,^[16] phenazine^[17] and merocyanine derivatives,^[18] as well as calamitic mesogens, e.g. tetrazines,^[19] anthraquinones^[20] and azo derivatives.^[21]

Among these different building blocks for mesomorphic dyes donor acceptor chromophors play a prominent role due to their diverse applications mentioned above. However, donor acceptor chromophors carrying perfluoralkyl donor units rather than alkyl or alkyloxy side chains have only been rarely investigated. This is rather surprising, because the fluorophobic effect and its beneficial influence on liquid crystalline self-assembly is long known and has been extensively studied. As has been recently summarized by Tschierske^[21] for perfluoroalkyl chains, the high polarity and low polarizability of the C-F bond and the *helical* conformation of the perfluorinated chain lead to reduced intermolecular interactions and increased lipophilicity. This results in immiscibility of rigid perfluorinated and flexible aliphatic chains, which preferably adopt a linear *all-trans* conformation. It must be emphasized that the fluorophobic effect originates from contributions of different intra- and intermolecular interactions. The formation of a liquid crystalline mesophase is based upon molecular segments, that exhibit a sufficient immiscibility with respect to each other and therefore lead to nanophase segregation.^[22] When combining perfluorinated with hydrocarbon segments via covalent bonds, ChemPhysChem

the fluorophobic effects leads to immiscibility of these molecular segments due to low polarizability and conformational rigidity (compared to aliphatic counterparts). This immiscibility can drive nanophase segregation resulting in self-ordered mesophase formation. The incompatibility of perfluorinated, aliphatic, aryl and polar segments has been heavily exploited in liquid crystal research.^[23]

Recently, we investigated the absorption and emission properties of mono-, bi- and tricyclic donor acceptor dyes A-n-Do^H (n = 1, 2, 3) carrying dodecyloxy and piperidyl donor units and keto, malodinitrile and N,N-dimethylbarbiturate acceptor units (Scheme 1).^[24] Experimental and theoretical results revealed the shift of the ground state polarity from the neutral resonance form N favored by dyes with dodecyloxy donor moiety irrespective of the chromophor size to the zwitterionic resonance form Z favored by dyes with a combination of strong piperidyl donor and barbiturate acceptor.^[24] Further studies on related systems were devoted to solvatochromic effects,^[25] dichroism and photostability^[26] as well as solid state properties.^[27] However, despite the presence of long side chains such as dodecyloxy in A-n-Do^H (Do^H = OC₁₂H₂₅) no mesomorphism was detected. Motivated by the promising previous results on mesophase stabilization through the fluorophobic effect, we anticipated that grafting of perfluorinated side chains on the rigidified chromophore A-n-Do^F should not only promote the formation of liquid crystalline phases but should also affect the linear optical properties ultimately leading to unique materials properties. Through systematic variation of donor, acceptor and chromophore unit insight into structure-property relationships as well as scope and limitations of the fluorophobic effect on dye molecules should be obtained. The results towards these goals are reported below.



Scheme 1.

Results and Discussion

Synthesis

Two series of donor acceptor dyes A-n-Do^F were prepared, i.e. malononitriles Mal-n-Do^F and barbiturates **Barb-n-Do^F**. The synthetic route is outlined in Scheme 2 (an overview of all compounds and yields can be found in Scheme S1). The hydroxy function of known vinylogous acids Keto-1-OH and Keto-2-OH^[28] was converted via an Appel reaction to the bromide, which was then substituted by the respective 1H, 1H-perfluorinated donor to give **Keto-1-Do^F** and Keto-2-Do^F. This synthetic approach was not successful for derivative Keto-3-OH with the largest tricyclic chromophore. Therefore, Keto-3-OH was reacted with a 1H,1Hperfluorinated triflate yielding **Keto-3-Do^F** in 15 %. After introduction of the donor group, the synthesis of the acceptor moiety followed our previously established route.^[24] Ketones Keto**n-Do**^F were submitted to a HWE reaction with diethyl cyanomethylphosphonate to give nitriles NC-n-Do^F in 62–84 % yield. Subsequent reduction with DIBAL-H provided aldehydes OHC**n-Do**^F in . These aldehydes **OHC-n-Do**^F were finally treated with either malononitrile or 1,3dimethylbarbituric acid to yield the final products Mal-n-Do^F and Barb-n-Do^F in 25–99 %. It should be emphasized that poor yields below 25 % are mostly observed for dienones Keto-n-Do^F, enals OHC-n-Do^F and some derivatives with exocyclic diene moiety, which are particularly prone to Michael addition, autoxidation and polymerization.



Scheme 2. Synthesis of malononitriles **Mal-n-Do**^F and barbiturates **Barb-n-Do**^F with 1*H*,1*H*-perfluorinated donors. i) For n = 1 and 2: 1. PPh₃, CBr₄, CH₂Cl₂, 76–87 %, 2. KOH, 1*H*,1*H*-perfluoroalcohol, MeCN, 14–60 %; ii) For n = 3: KOH; TfOCH₂Cl₁,F₂₃, THF, 15 %; iii) NaH, (EtO)₂POCH₂CN, DMF, 62–84 %; iv) DIBAL-H, CH₂Cl₂, 14–95 %; v) NEt₃, malononitrile, CH₂Cl₂, 7–96 %; vi) NEt₃, 1,3-dimethylbarbituric acid, CH₂Cl₂, 43–99 %.

Owing to the exocyclic C=C bond, nitriles NC-n-Do^F, malononitriles Mal-n-Do^F, and barbiturates **Barb-n-Do^F** were obtained as E/Z mixtures. An exemplary NOESY spectrum, that was used to assign *E* and *Z* isomers is shown in Figure S1 in the supporting information. The E/Z ratio was determined from the mean integral ratio of the most deshielded proton signals of the conjugated carbon chain (Table S1). All nitriles NC-n-Do^F and malononitriles Mal-n-Do^F showed nearly equimolar E/Z ratios. Barbiturates **Barb-n-Do^F** exhibited an excess of *E* isomer due to the larger acceptor group compared to NC-n-Do^F and Mal-n-Do^F.

Absorption and emission properties

The optical properties of **A-n-Do^F** were investigated via UV/Vis spectroscopy (Table S2). Absorption spectra of barbiturates **Barb-n-OC12^F** displayed broad and unstructured absorption spectra with λ_{max} values at 428 nm, 486 nm and 532 nm, respectively (Figure 1).



Figure 1. UV/Vis absorption spectra of a) barbiturates **Barb-n-OC12^F** and b) malononitriles **Mal-n-OC12^F** in CHCl₃ at room temperature.

In the series of barbiturates **Barb-2-Do**^F with different donor lengths, absorption maxima did not change in CHCl₃ for **Barb-2-OC8**^F (487 nm), **Barb-2-OC10**^F (488 nm), and **Barb-2-OC12**^F (486 nm).

Absorption maxima of **Barb-n-OC12^F** in toluene, THF, CHCl₃ and DMSO were listed in Table S2 and were compared with their aliphatic counterparts **Barb-n-OC12^H**. In comparison, absorption maxima of perfluorinated **Barb-n-OC12^F** were hypsochromically shifted by 4–54 nm compared to **Barb-n-OC12^H** independently on the chromophore size. This hypsochromic shift might be rationalized by a stronger inductive effect of the F atoms as compared to the alkoxy unit. An alternative explanation is the less polar ground state with a larger contribution of the neutral resonance form **N** for perfluorinated **Barb-n-OC12^F**. Further information on the ground state polarity can be derived from ${}^{3}J(H,H)$ coupling constants (Table S3).^[29] The ${}^{3}J(H,H)$ values of **Barb-n-OC12^F** were systematically smaller (0.1–0.3 Hz) than coupling constants of aliphatic **Barb-n-OC12^H**. The smaller ${}^{3}J(H,H)$ constants of

Barb-n-OC12^F indicated a longer C-C bond caused by a weaker donor and therefore confirm an increased contribution of N to S₀ compared to **Barb-n-OC12^H**.

The absorption spectra of malononitriles **Mal-n-OC12^F** are shown in Figure 1. All derivatives displayed a broad and unstructured absorption. An increasing donor length for compounds **Mal-2-OC8^F** (441 nm), **Mal-2-OC10^F** (442 nm) and **Mal-2-OC12^F** (441 nm) did not change the absorption maxima. The absorption maxima of perfluorinated **Mal-n-OC12^F** (Tables S2) displayed a hypsochromic shift of 16–31 nm in comparison with aliphatic analogues **Mal-n-OC12^H**. In analogy to barbiturates, coupling constants ³*J*(*H*,*H*) of perfluorinated **Mal-n-OC12^F** were smaller (0.1–0.2 Hz) as compared to aliphatic **Mal-n-OC12^H** indicating a less polar ground state for **Mal-n-OC12^F**.^[29a] In order to obtain further insight a computational analysis of the ground state geometry for model compounds **Mal-3-Do^F** with an 1*H*,1*H*-perfluorinated **butyloxy** donor was performed. Calculated BLA values showed, that the ground state S₀ of 1*H*,1*H*-perfluorinated **Mal-3-OC4^F** (6.20 pm) had a larger contribution of the neutral resonance form **N** compared to aliphatic **Mal-3-OC2^H** (5.73 pm).

The emission spectra of **Mal-n-OC12^F** and **Barb-n-OC12^F** were recorded in CHCl₃. Malononitriles **Mal-n-OC12^F** displayed emission maxima in the range $\lambda_{max,em} = 453-598$ nm, while the corresponding $\lambda_{max,em}$ values of barbiturates **Barb-n-OC12^F** were between 478 nm and 640 nm (Table S4). In comparison with aliphatic compounds **A-n-Do^H**,^[24] the Stokes shifts of 1*H*,1*H*-perfluorinated dyes **A-n-Do^F** were smaller by 15–38 nm. With increasing chromophor size the emission maxima were bathochromically shifted for each series.

Electrochemical properties

The electrochemical behaviour of derivatives **Mal-n-OC12^F** and **Barb-n-OC12^F** (n = 1–3) as well as **Mal-2-OC8^F** and **Barb-2-OC8^F** was investigated by cyclic voltammetry (0.1 M NBu₄PF₆ in CH₂Cl₂). For all compounds, an irreversible oxidation wave hampered the determination of HOMO energies (Figure S2). In the reduction wave, solely derivatives **Mal-3-OC12^F** and **Barb-3-OC12^F** with the largest chromophore showed electrochemically reversible behaviour. The reduction waves of barbiturates **Barb-n-OC12^F** are shown in Figure 2. Compound **Barb-3-OC12^F** with the largest chromophore displayed a reversible reduction, while analogues **Barb-2-OC12^F** and **Barb-1-OC12^F** showed an irreversible reduction.



Figure 2. Cyclic voltammogram of barbiturates **Barb-n-OC12^F** in CH_2Cl_2 at room temperature (concentration: 2 mg mL⁻¹; 0.1 M NBu₄PF₆; scan rate: 50 mV s⁻¹).

For derivatives **Mal-3-OC12^F** and **Barb-3-OC12^F**, LUMO energies were calculated from the half wave potential according to Bazan.^[30] These values are listed in Table 1 and compared with LUMO energies of aliphatic analogues **Mal-3-OC12^H** and **Barb-3-OC12^H** from ref.^[24] Upon comparison of the acceptor moieties, barbiturates **Barb-3-OC12^F** and **Barb-3-OC12^H** showed smaller LUMO energies of 0.15 eV and 0.14 eV in relation to their malononitrile counterparts **Mal-3-OC12^F** and **Mal-3-OC12^H**. A change of donor moieties from 1*H*,1*H*-perfluorinated to aliphatic side chain influenced LUMO energies only by 0.01–0.02 eV indicating that the methylene group which connects the ether unit and the perfluoralkyl chain acts as an electronic stopcock. Therefore, the choice of donor moiety resulted in a negligible change of LUMO energies.

	$E_{1/2}$ / V	LUMO _{CV} / eV		
Mal-3-OC12 ^F	-1.55	-3.55		
Barb-3-OC12 ^F	-1.40	-3.70		
Mal-3-OC12 ^H	-1.53	-3.57		
Barb-3-OC12 ^H	-1.39	-3.71		

Table 1. Half wave potentials $E_{1/2}$ and LUMO energies of A-3-OC12^F and A-3-OC12^H.^[24]

Liquid crystalline properties

Whereas none of the dodecyloxy-substituted chromophors **A-n-C12^H** studied previously^[24] showed any mesomorphic properties, all newly prepared dyes **A-n-Do^F** with perfluorinated tails displayed liquid crystalline behaviour. The mesomorphic properties of **NC-n-Do^F**, **Mal-n-Do^F**

and **Barb-n-Do^F** (n = 1-3) were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD). Phase transition temperatures were determined from onset values of the first cooling cycle due to decomposition issues in some second and third cycles.

For details on the phase behaviour of liquid crystalline dyes A-n-Do^F, see Table S5 and Figure S3 – S7. The DSC curves of nitrile NC-2-OC12^F and barbiturate Barb-2-OC12^F are shown in Figure 3. Upon first heating, NC-2-OC12^F displayed a transition to the isotropic state at 92 °C (Figure 3a). All cooling cycles showed a mesophase between 101 °C and 91 °C. The second and third heating revealed a melting transition of 87 °C and clearing temperatures of 97 °C. Derivative Barb-2-OC12^F showed a clearing transition of 193 °C upon first heating (Figure 3b). In the first cooling cycle, a clearing transition at 157 °C and crystallisation at 68 °C were observed. In the second heating cycle, an endothermal transition at 67 °C and a cold crystallisation at 85 °C as well as a transition to the isotropic phase at 172 °C were seen. Decreasing clearing temperatures of subsequent cooling cycles indicated a thermal decomposition of **Barb-2-OC12^F**. In contrast to Sworakowski and Lakahal, who rationalized decreased isotropization temperatures of azobenzenes and cinnamic acid diacrylates respectively by E-Z photoisomerization,^[31] such scenario could be ruled out in our case. Prolonged isotropization temperatures during XRD experiments resulted in the conversion of the samples into black sticky tars. Similar observations were made upon analyzing a thermally annealed sample by NMR. In summary, nitriles NC-n-OC12^F exhibited a thermally stable, enantiotropic mesophases. Most of malononitriles Mal-n-Do^F and barbiturates Barb-n-Do^F displayed thermal decomposition, as evidenced from decreasing isotropization temperature during repetitive heating/cooling cycles.



Figure 3. DSC curves of a) **NC-2-OC12^F** and b) **Barb-2-OC12^F** of first three heating (H) and cooling (C) cycles. Rates 5 K min⁻¹.

The mesophase ranges of nitriles NC-n-OC12^F, dimethyl barbiturates **Barb-n-OC12^F** and malononitriles **Mal-n-OC12^F** (n = 1-3) are shown in Figure 4. For nitriles NC-n-OC12^F (n = 1-3), extension of the chromophore size increased mesophase ranges from NC-1-OC12^F (2 K) over NC-2-OC12^F (10 K) to NC-2-OC12^F (70 K). In an analogous manner, a larger chromophore resulted in increasing phase widths from 12 K for barbiturate **Barb-1-OC12^F** to 89 K for **Barb-2-OC12^F** and 91 K in case of **Barb-3-OC12^F**. Within the series of malononitriles **Mal-n-OC12^F**, an enlargement of the chromophore also increased temperature ranges from 4 K (n = 1) over 44 K (n = 2) to 112 K (n = 3) as well as stability of the mesophase. Comparison of acceptor moieties revealed smaller temperature ranges for nitriles NC-n-OC12^F (2–70 K) compared to barbiturates **Barb-n-OC12^F** (12–91 K) and malononitriles **Mal-n-OC12^F** (4–112 K) with the same chromophore size n. For a specific chromophore size,

clearing temperatures T_{cl} increased in the series nitriles NC-n-OC12^F < barbiturates Barb-n-OC12^F < malononitriles Mal-n-OC12^F.



Figure 4. Mesophase ranges of nitriles NC-n-OC12^F, dimethyl barbiturates Barb-n-OC12^F and malononitriles Mal-n-OC12^F (n = 1-3).

To analyse the clearing points T_{cl} based on intermolecular interactions, dipole moments μ were calculated (for isolated molecules of) **A-3-OC12^F** (Figure 5). The calculated dipole moments μ increased in the series **NC-3-OC12^F** ($\mu = 6.0$ D) < **Barb-3-OC12^F** ($\mu = 7.7$ D) < **Mal-3-OC12^F** ($\mu = 11.8$ D). Within this series, clearing points T_{cl} also increased from 155 °Cover 190 °C to 210 °C. Larger dipole moments increase strength and anisotropy of intermolecular interactions. This increase led to a more stable mesophase with higher clearing temperatures T_{cl} due to enhanced dipolar interactions.^[32]

In addition, due to the fact that E/Z mixtures of the merocyanines were employed in the current study, we surmised that an increasing amount of bent Z isomer should decrease the mesophase stability in a similar fashion as was reported previously by Meier,^[33] Lakehal,^[34] Sworakowski,^[35] Bobrovsky,^[36] and Saïdi-Besbes ^[37] albeit to a smaller extent because the respective double bond is not located in the centre of the merocyanine in contrast to the previously reported stilbenes, azobenzenes and the like. The results in Figure 4 suggest that the amount of *E*-isomer indeed contributes to the mesophase range and stability. This effect is most pronounced in the series of bicyclic merocyanines, where the barbiturate **Barb-2-OC12^F** containing 75 % *E* has a much broader phase width as compared to the nitrile **NC-2-OC12^F** (53 % *E*) and malononitrile **Mal-2-OC12^F** (51 % *E*).





Besides the effect of acceptor moiety and chromophore, the influence of the donor chain length on mesophase properties was investigated for compounds A-2-Do^F (Figure 5). In case of nitrile NC-2-OC8^F, no crystallisation was observed by DSC and POM upon cooling to -50 °C. With increasing donor chain length, mesophase ranges decreased from > 88 K for NC-2-OC8^F and 40 K for NC-2-OC10^F to 10 K in case of NC-2-OC12^F. In contrast to nitriles NC-2-Do^F, barbiturates **Barb-2-Do^F** and malononitriles **Mal-2-Do^F** exhibited larger mesophase ranges for donor chain elongation. While barbiturate **Barb-2-OC8^F** was non-mesomorphic, **Barb-2-OC10^F** and **Barb-2-OC12^F** exhibited phase ranges of 24 K and 89 K, respectively. In the series of malononitriles, phase ranges increased from **Mal-2-OC8^F** (15 K) over **Mal-2-OC10^F** (21 K) to **Mal-2-OC12^F** (44 K).



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Figure 6. Mesophase ranges of nitriles NC-2-Do^F, dimethyl barbiturates **Barb-2-Do^F** and malononitriles Mal-2-Do^F (n = 1-3).

Under the polarizing optical microscope, nitrile NC-3-OC12^F displayed homeotropic alignment and maltese crosses at 150 °C (Figure 7a). The fan-shaped texture with focal conic defects of malononitrile Mal-2-OC12^F (159 °C) is shown in Figure 7b. All other liquid crystalline derivatives A-n-Do^F displayed analogous textures. The observed textures are characteristic for smectic A phases (SmA).^[38]



Figure 7. POM Textures upon cooling; a) maltese crosses of NC-3-OC12^F at 150 °C; b) fanshaped texture with focal conic defects of Mal-2-OC12^F at 159 °C; cooling rates 5 K min⁻¹.

XRD experiments (SAXS and WAXS) were carried out to study the SmA phases of liquid crystalline dyes **A-n-Do^F** in detail. The WAXS profile and diffraction pattern of **NC-2-OC8^F** and **Mal-3-OC12^F** are shown in Figure 8 and Figure S8. Both compounds displayed a strong SmA fundamental diffraction peak (001), a weak (002) reflection and a diffuse halo in the wide-angle region. These diffraction patterns are typically observed for SmA phases.^[39]



Figure 8. WAXS profile (intensity vs. scattering angle) and diffraction pattern (inlay) of a) NC-2-OC8^F at 29 °C and b) Mal-3-OC12^F at 178 °C.

Compounds **A-n-Do^F** were further investigated by temperature-dependant SAXS measurements in the mesophase. Based on the (001) reflection, layer spacings d_{001} were calculated using Bragg's law through Gaussian fitting of the (001) reflection. For both nitriles **NC-n-Do^F** (Figure 9 a) and malononitriles **Mal-n-OC12^F** as well as barbiturate **Barb-3-OC12^F** (Figure 9 b), d_{001} values decreased with increasing temperature. This negative thermal expansion gives additional proof for the SmA phase.^[40]



Figure 9. Temperature-dependant layer spacings d_{001} of a) nitriles NC-n-Do^F and b) malononitriles Mal-n-OC12^F and barbiturate Barb-3-OC12^F.

The layer spacings d_{001} were extrapolated to the respective clearing temperatures T_{cl} for a better comparability due to the temperature-dependence of d_{001} . The resulting $d(T_{cl})$ values are listed in Table S6 along with the molecular lengths L_{mol} , which were derived from the all-*trans* conformation using Chem3D and MM2 geometry optimization.^[41] Extrapolated layer spacings $d(T_{cl})$ indicated a smectic A phase consisting of semibilayer aggregates (SmA_d) due to $L_{mol} < d(T_{cl}) < 2 L_{mol}$.^[42] This packing model was also reported for other smectic liquid crystals with a terminal perfluorinated carbon chain segment.^[43] In Figure 10, a proposed model of the SmA_d phase with interdigitating perfluorinated chain segments is shown. The calculated layer thickness L_{calc} is in good agreement with experimentally determined $d(T_{cl})$ values (for details, see Table S7–Table S9).



Figure 10. Proposed semibilayer SmA_d phase of nitriles NC-n-Do^F.

 $L_{\text{calc}, E/Z}$ values, which take the E/Z ratio from the ¹H NMR into account, were calculated from layer thickness $L_{calc,E}$ and $L_{calc,Z}$ of the respective E and Z isomer (Table S8). Experimentally determined $d(T_{cl})$ values are displayed along with $L_{calc, E/Z}$ in Figure 11. For nitriles NC-n-Do^F, calculated $L_{\text{calc}, E/Z}$ were smaller by 0.9–5.3 Å compared to $d(T_{\text{cl}})$ (Figure 11a). This can be explained by an incomplete interdigitation of perfluorinated segments. In contrast to nitriles NC-n-Do^F, L_{calc,E/Z} values of barbiturate Barb-3-OC12^F and malononitriles Mal-n-OC12^F shown in Figure 11b were larger than $d(T_{cl})$. The smaller $d(T_{cl})$ values of Mal-n-OC12^F and Barb-3-OC12^F are probably due to interdigitation of both perfluorinated segments and polar acceptor moieties (shown in Figure S9). Layer thicknesses $L_{\text{fi}, E/Z}$ with fully interdigitated perfluorinated and acceptor groups were only by 0.3–1.3 Å larger as compared to experimental $d(T_{\rm cl})$ values. This small deviation may be rationalized by a thermal molecular fluctuation within the smectic layers close to clearing temperatures $T_{cl} = 155-210$ °C.^[40] In this case, a time-dependant, random molecular tilt reduces the smectic layer thickness as observed in Figure 11b. It should be emphasized that mesophase ranges are also depended on matching lengths of core and chain.^[48] However, in our case no clear trend could be deduced (Table S7 - S9).



Figure 11. Experimentally determined layer thickness $d(T_{cl})$, calculated layer spacing $L_{calc, E/Z}$ with interdigitating perfluorinated groups and layer spacing $L_{fi, E/Z}$ with full interdigitation of both perfluorinated donor moieties and polar acceptor groups.

Electron density profile $\rho(z)$

The diffraction pattern of an X-ray measurement origins from a Fourier transformation of the electron density distribution along the layers of a smectic phase.^[44] This means, one can extract the electron density from the diffraction profile. The deviation $\rho(z)$ from the mean electron density can be calculated by a discrete cosine transformation according to equation (3).^[44] In this calculation, each (00*l*) reflection contributes with a coefficient a_l . The square of the absolute values $|a_l|^2$ can be obtained after correction of the Lorentz factor.^[45]

$$\rho(z) = \sum_{l=1}^{m} a_l \cos\left(l \ 2\pi \ z \ d_{001}^{-1}\right)$$
(3)

For nitriles NC-2-OC8^F, NC-2-OC10^F, and NC-2-OC14^F as well as malononitriles Mal-2-OC12^F and Mal-3-OC12^F, first and second order diffraction reflexes were observed in

the SAXS diffraction profile. In this case, the cosine transformation simplifies to equation (4) with two cosine terms.

$$\rho(z) = a_1 \cos\left(2\pi z \, d_{001}^{-1}\right) + a_2 \cos\left(4\pi z \, d_{001}^{-1}\right) \tag{4}$$

The d_{001} and d_{002} values of **A-n-Do^F** as well as corresponding coefficients a_1 and a_2 are listed in Table 2. Owing to the square of the absolute values $|a_l|^2$, all combinations of coefficients $\pm a_l$ have to be examined with regard to plausibility.^[45]

Table 2. Experimentally determined d_{001} and d_{002} values of nitriles **NC-n-Do^F** and malononitriles **Mal-n-OC12^F** at temperatures *T* and the corresponding coefficients a_1 and a_2 .

	$T / ^{\circ}\mathrm{C}$	d_{001} / Å	d_{002} / Å	a_1	a ₂
NC-2-OC8	29	30.7	15.4	1.00	0.35
NC-2-OC10	45	41.2	20.5	1.00	0.66
NC-3-OC12	107	44.9	22.5	1.00	0.51
Mal-2-OC12	133	39.8	20.0	1.00	0.53
Mal-3-OC12	178	43.6	21.9	1.00	0.58

An overview on the electron densities $\rho(z)$ for all compounds **A-n-Do** is given in Figure S10. A typical electron profile is shown in Figure 12 along with a model of the SmA_d phase with both interdigitating perfluorinated segments and polar acceptor moieties. The electron density profile $\rho(z)$ showed good agreement with the proposed SmA_d phase. In the region of interdigitating perfluorinated chains, $\rho(z)$ displayed an intense maximum. Such a high electron density in perfluorinated segments compared to aliphatic regions has been previously reported by Marczuk for partially fluorinated alkanes.^[46] Along the aliphatic chromophore, $\rho(z)$ showed a global minimum. For the adjacent acceptor groups, a local maximum was observed due to an antiparallel overlap of these polar moieties. Such layered packing is in good agreement with previous work by Ungar, Percec ^[44 d)] and Pociecha ^[47] on polyphilic fluorinated smectic liquid crystals based on 4-alkoxybenzoates.



Figure 12. Electron density profile $\rho(z)$ and proposed structure model of a SmA_d phase with both interdigitating perfluorinated segments and polar acceptors.

Conclusion

To obtain liquid crystalline donor acceptor dyes, the fluorophobic effect was probed for the first time on this class of chromophores. For this purpose, a series of compounds **A-n-Do^F** was prepared where a 1H, 1H-perfluoroalkyl donor was grafted onto a mono-, bi- or tricyclic chromophore unit. These chromophores were equipped with nitrile, malononitrile or barbiturate acceptor, respectively. The synthesis provided **A-n-Do^F** in 4 steps in 2–6 % overall yield, starting from vinylogous acids **Keto-n-OH**. Investigation of the UV/Vis spectra in solution revealed a bathochromic shift of the absorption maxima with increasing chromophore size n and a hypsochromic shift upon replacement of the barbiturate by the weaker acceptor malononitrile. Fluorescence spectra showed a similar trend with smaller Stokes shifts as compared to the aliphatic counterparts. The results revealed that the single methylene unit between the ether oxygen and the perfluoralkyl chain in the donor moiety is sufficient to achieve almost complete electronic decoupling of the perfluorinated tail and the chromophore moiety. This was further supported by the LUMO energies of the perfluorinated dyes **A-n-Do^F** and their alkyl-substituted counterparts **A-n-Do^H**, which showed very similar values according to the cyclic voltammetry experiments.

In strong contrast to the minor influence of the perfluorinated chains on the optical and electronic properties in solution, the fluorophobic effect strongly promoted liquid crystalline self-assembly of the donor acceptor dyes **A-n-Do**^F. Except for the bicyclic barbiturate with OCH₂C₇F₁₅ chain **Barb-2-OC8**^F all other members of the series **A-n-Do**^F displayed enantiotropic smectic A mesophases. Mesophase widths and stability increased with increasing

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dipole moments, chromophore size and chain lengths. From the X-ray diffraction data, the electron density profile was calculated, which supported the proposed partially interdigitated bilayer packing in the SmA_d phase.

In conclusion, we have shown for rigidified donor acceptor dyes that the fluorophobic effect strongly promotes lamellar self-assembly without compromising the absorption and emission properties of these dyes. The linear optical properties are mostly governed by the size of the chromophore subunit and the strengths of the acceptor moiety, i.e. the overall molecular dipole moment. Future work must demonstrate, whether grafting of perfluoroalkyl chains to other chromophore classes also leads to novel self-assembled materials.



Figure 13 Influence of the acceptor-dependant dipole moment, chromophore size and donor length on mesophase ranges, clearing temperatures and absorption maxima.

Experimental Section

Detailed information on synthetical methods and measurements are given in the electronic supporting information.

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