Chasing Self-Assembly of Thioether-Substituted Flavylium Salts in Solution and Bulk State

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Dedicated to Professor Herbert Mayr on the occasion of his 75th birthday

Two series of flavylium triflates carrying alkoxy side chains in the A-ring (benzo unit of chromylum salt) and thioethers in the B ring (phenyl unit) \( (\text{O}_2\text{-V-Fla-S}) \) as well as thioethers at both A and B ring \( (\text{S}_n\text{-Fla-S}) \) were synthesized in order to understand the effect of thioether functionalization on their self-assembly and electronic properties. Concentration-dependent and diffusion ordered (DOSY) NMR experiments of \( \text{O}_2\text{-V-Fla-S} \) indicate the formation of columnar H-aggregates in solution with antiparallel intracolumnar stacking of the AC unit (chromylium) of the flavylium triflate, in agreement with the solid state structure of \( \text{O}_2\text{-V-Fla-S}_1 \). Thioether substitution on the B ring changes the linear optical properties in solution, whereas it has no effect on the A ring. According to differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction bulk self-assembly of these ionic liquid crystals (ILCs) depends on the total number of side chains, yielding SmA and Lam\(_{\text{col}}\) phases for ILCs with 2–3 chains and Col\(_{\text{im}}\) phases for ILCs with 3–6 chains. Thus, we demonstrated that thioethers are a useful design tool for ILCs with tailored properties.

Introduction

The combination of liquid crystalline materials with dye properties leads to highly attractive hybrid materials with unique self-assembly behavior and physical properties, which are suitable for a broad variety of applications ranging from non-linear optics,[1] photoreponsive and photoalignable materials,[2] di- chroic, chromonic and laser dyes,[3] to electrochromic materials[4] and organic solar cells.[5] For many of these applications, solution processing and proper alignment of the liquid crystalline dyes are critical issues. In most cases, long alkoxy side chains attached to the mesogenic core increase the solubility in organic solvents and promote mesophase formation through van der Waals interactions. Otherwise, there is increasing experimental evidence from comparative studies that the grafting of alkylsulfanyl (thioether) side chains to the aromatic dye cores instead of alkoxy chains can have manifold beneficial effects on the performance of these liquid crystalline materials. For example, it was reported that the replacement of alkoxy by alkylsulfanyl chains in non-mesomorphic benzo[1,2-b:4,5-b’]bis[b]benzothiophenes led to increased melting points, antiperiplanar conformations and tighter packing in the solid state due to S–S interactions.[6] For H-bonded, mesomorphic benzoic acids phase transition temperatures of thioether-substituted derivatives were lower than the alkoxy analogues due to S–S interactions favoring smectic clusters in the nematic phase.[7] Rich polymorphism was observed for asymmetrically end-capped oligothiophenes upon attachment of thioethers.[8] Upon S/O replacement in the side chains of calamitic imidazolium ILCs, a pronounced decrease of the melting temperatures was detected, while clearing transitions remained constant or even increased, resulting in significantly broadened mesophase ranges.[9] For methylimidazolium ILCs the emergence of mesomorphic properties via the sulfur motif was reported.[10] Stabilization of mesophases was also found for columnar palladium complexes with dipicolinic acid-derived pincer ligands[11] and columnar crown ethers carrying thioethers instead of alkoxy side chains.[12] Furthermore, the S/O replacement led to a higher degree of order in columnar mesophases of 6-oxoverdazyl radicals.[13] In calamitic tolane derivatives, the S/O replacement resulted in a strong increase of the birefringence.[14]

Regarding the chromophoric part in liquid crystalline dyes, flavylium salts are very attractive. Flavylium salts, i.e. benzoxanellated 2-phenyloxonium salts belong to a large class of plant dyes (Figure 1).[15] Typical examples are malvin 1 and its aglycon malvidin.[16a] The presence of hydroxy groups in natural flavylium salts enables pH-dependent color shifts. The manifold substitution patterns found in nature lead to a large library of dyes[17] with many applications.[18] Besides their use as food colorants,[19] synthetic flavylium salts have also been employed...
Results and Discussion

Synthesis of Thioether-Substituted Flavylium ILCs

In order to access the two libraries of flavylium ILCs $O_n$-Fla-$S_m$ carrying alkoxy chains on the A ring and alkylsulfanyl chains on the B ring and flavylium ILCs $S_n$-Fla-$S_m$ carrying alkylsulfanyl side chains on both A and B ring, the previously described strategy by Chassaing was employed, where the flavylium core is generated by acid-mediated cyclocondensation of phenols and propargylic ketones.\(^{17,20}\) As shown in Scheme 1, 4-fluorobenzaldehyde $5a$ was treated with dodecanethiol in the presence of Na$_2$CO$_3$ adapting a procedure of Prasad\(^{17}\) yielding $8a$ in 94%. The corresponding aldehydes $8b,c$ with two and three alkylsulfanyl chains were prepared according to Jankowiak\(^{18}\) from known bromides $7b,c$\(^{18}\) by formylation with nBuLi, DMF to give $8b$ in 76% and $8c$ in 82% respectively.

By following the protocol by Chassaing\(^{20}\) the aldehydes $8a-c$ were reacted with ethynyl magnesium bromide in THF to give the secondary propargylic alcohols $9a-c$, which were submitted to IBX oxidation to the ketones $10a-c$ in 46-99% (over 2 steps). In order to obtain the required phenols $11b,c$, bis- and trisdodecyloxysulfanylphenylbromides $7b,c$\(^{18}\) were treated with LiOH in DMSO / H$_2$O (4:1) in the presence of 10 mol% of Cu(acac)$_2$ and 10 mol% of BHMO using the method by Ma\(^{22}\) to yield $11b,c$ in 63% and 31% respectively.

With the desired phenols $11b-g$ including the known bis- or trisalkoxy-substituted phenols $11d-g$ and the propargylic ketones $10a-c$ at hand, the flavylium salts $O_n$-Fla-$S_m$, $S_n$-Fla-$S_m$ were obtained by stirring a solution of the former in EtOAc in the presence of 2-4 equiv. of trifluoromethansulfonic acid for 24 h at room temperature and twofold recrystallization from EtOAc, which provided the mixed flavylium triflates $O_n$-Fla-$S_m$ in

![Figure 1. Flavylium salts found in nature (1)\(^{13}\) as sensitizers for organic solar cells (4)\(^{16}\) and as neuronal mimics (2)\(^{16}\) as well as liquid crystalline flavylium salts $O_n$-Fla-$O_m$\(^{17}\) and new sulfur analogues $O_n$-Fla-$S_m$, $S_n$-Fla-$S_m$.](image-url)

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in more technical applications, such as logical “off-on-off” artificial neuronal mimics 2, 3\(^{16}\) and photosensitizers 4 for Grätzel-type solar cells.\(^{18a-c}\)

We have recently developed flavylium-based\(^{17}\) ionic liquid crystals (ILCs) $O_n$-Fla-$O_m$ ($R = H$, alkyl), which combine the birefringence and self-assembly of thermotropic neutral liquid crystals with the electrostatic interactions and tunability of polarity and solubility characteristic of ionic liquids as well as the absorption and emission characteristics of the flavylium chromophore (Figure 1). As our previous work emphasized the vital role of the substitution pattern on the mesomorphic properties of the flavylium ILCs, we were curious to highlight to what extent grafting of alkylsulfanyl side chains to the flavylium A and B rings (Figure 1) might affect the polymorphism, as well as the optical properties. Kaszynski\(^{19}\) and our group\(^{12}\) reported independently, that the attachment of thioethers to columnar mesogens increased the temperature range and enabled room temperature mesomorphism. These results motivated us to explore both thioether-substituted flavylium salts $O_n$-Fla-$S_m$ carrying thioethers only at the B-ring and flavylium salts $S_n$-Fla-$S_m$ carrying thioethers at both A and B ring. Solution NMR and X-ray diffraction studies were performed to gain insight into their self-assembly. As detailed below in the current manuscript, we report that the position of the thioether, i.e. A vs. B ring has a major impact on the self-assembly in solution and bulk state.

![Scheme 1.](image-url)

Scheme 1. i) NaH, C$_2$H$_5$SH, DMSO, THF, 20 °C, 4 h, 60 °C, 6 h; ii) Na$_2$CO$_3$, C$_6$H$_5$SH, abs. DMSO, 160 °C, 1 d; iii) n-BuLi, abs. THF, 28 °C, 2 h, 2) DMF, 1 h; iv) HCCMgBr, abs. THF, 4 h; v) IBX, EtOAc, 80 °C, 16 h; vi) H$_2$O, H$_2$SO$_4$, CHCl$_3$, MeOH, 16 h; vii) Cu(acac)$_2$ (10 mol%), BHMO (10 mol%), LiOH, H$_2$O, DMSO/H$_2$O (4:1), 120 °C, 6 d; * The alkyloxy derivatives 10d-g were prepared according to literature procedures.\(^{17}\)
NMR Spectroscopic Studies on O₁-V-Fla-S₃

Based on the known propensity of flavylium salts to form dimers and higher aggregates in solution resulting from strong intermolecular H-bonds (in the presence of free OH groups), anion-π, π-π and electrostatic interactions standard 1D ¹H NMR experiments for characterization of flavylium salts O₈-Fla-

Scheme 2. Synthesis of the flavylium salts O₈-Fla-S₃ and S₈-Fla-S₈ from the ketones 10a-c and phenols 11a-g as well as substrate scope.

47–83%, except for compounds O₈-Fla-S₈, O₂-Fla-S₈, which were isolated in lower yields of 19% and 13% respectively (Scheme 2). In general, yields of thioether-substituted flavylium triflates S₈-Fla-S₈ were lower (11 – 32%) as compared to flavylium triflates O₂-Fla-S₈ with mixed alkoxy and thioether chains due to tedious purification requiring multiple recrystallization.

Fortunately, we were able to confirm the structure of O₈-V-Fla-S₈ via single crystal X-ray diffraction, revealing the absence of any S,S interaction in the solid state (for details see Supporting Information, Figure S1). Noteworthy, O₈-V-Fla-S₈ formed columnar stacks with antiparallel orientation of neighboring flavylium ions and resulting in π-π stacking of the pyrylium cores with a distance of 3.50 Å, which is similar to the standard 1D ¹H NMR spectrum of the known alkoxy derivative O₈-V-Fla-Oᵀ.[17]

To get a more detailed insight into the aggregation of O₁-V-Fla-S₈ diffusion ordered NMR spectra (DOSY) were carried out.[25] Here, molecules are spatially labeled by use of field gradients. If they move during a following diffusion time, their position can be decoded by a second gradient. The measured signal is the integral over the whole sample volume, and it is attenuated depending on the diffusion coefficients of the analyte, the diffusion time and the gradient strength and length. The result is a “two-dimensional” NMR spectrum in which ¹H NMR spectrum of the sample is represented in F2 and the components are ordered in F1 with respect to their diffusion coefficients.

The experiments were performed with different concentrations of O₁-V-Fla-S₈ (0.15–35.16 mM). The studies supported the presence of different oligomers in the given concentration range, since the signals of 4-H showed four different diffusion coefficients in the processed DOSY spectrum: 0.15 mM (D = 7.41·10⁻¹⁰ m² s⁻¹), 0.15–1.47 mM (D = 6.46·10⁻¹⁰ m² s⁻¹), 0.29–2.94 mM (D = 5.62·10⁻¹⁰ m² s⁻¹) and 3.67–14.7 mM (D = 4.90·10⁻¹⁰ m² s⁻¹) presumably caused by aggregates with different sizes (Figure S3).

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It should be noted that Freitas reported diffusion and self-association constants of anthocyanins and flavylum/β-cyclo-dextrin inclusion complexes obtained by DOSY,[26] where the diffusion constants decrease with increasing aggregate size due to increasing hydrodynamic diameter. Although the experimentally determined diffusion constants were in a similar order of magnitude, direct comparison with flavylum salt O₁-V-Fla-S₁ is not possible, because the applied solvents (D₂O/DMSO-D₆ vs. CDCl₃) and the investigated flavylum salts differ strongly in their polarity. Nevertheless, the NMR data suggests that the antiparallel columnar packing in the solid state is preserved to some extent in solution.

Mesomorphic Properties of Thioether-Substituted Flavylum ILCs

The mesomorphic properties were studied by optical polarizing microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The results of the DSC measurements are summarized in Table S2. All thioether-substituted flavylum salts O₁-Fla-Sₙ, Sₙ-Fla-Sₙ, and O₁-V-Fla-Sₙ showed no signs of crystallization upon cooling but vitrified in a (metastable) glassy state preserving the mesophase textures. According to our investigations, the thioether-substituted flavylum ILCs could be grouped into two categories: (a) rod-shaped (calamitic) ILCs with up to 2 alkoxy chains on the A ring and only one thioether on the B ring showing lamellar mesophases only, and (b) disk-shaped (discotic) ILCs with 3–6 side chains in total and a minimum of 2 thioethers on the B ring displaying columnar mesophases.

ILCs O₁-V-Fla-Sₙ, and O₂-Fla-Sₙ, belonged to category (a). For example, upon cooling O₁-V-Fla-S₁ from the isotropic phase Bâtonnet textures and large homeotropic areas were visible at 193 °C (Figure 3a), typical of a SmA phase. Upon further cooling, these textures changed into fan-like textures indicating a columnar phase (Figure 3b). Similar behavior was observed for O₂-Fla-S₁ (Figure S14a,b).

On the other hand, members of category (b) behaved differently under the POM. For example, O₁-IV-Fla-Sₙ displayed pseudo-focal conic textures at 147 °C upon cooling (Figure 3c), while O₁-IV-Fla-S₁ showed filament-like textures at 150 °C (Figure 3d). Dendritic growth was detected for O₂-Fla-S₁ at 142 °C (Figure S14c) and fan-like textures with line defects and large homeotropic areas at 140 °C (Figure S14d). Fan-like textures were also observed for O₂-Fla-S₁ at 44 °C (Figure 3e) and O₂-Fla-S₁ at 146 °C (Figure 3f). According to the POM investigations, the fully thioether-substituted flavylum salts also belonged to category (b), showing pseudo-focal conic textures, e.g. for S₃-Fla-S₂ at 72 °C (Figure 3g) and S₂-Fla-S₂ at 22 °C (Figure 3f) with or without line defects and homeotropic regions upon cooling. The violet appearance of the textures is a result of the strong intrinsic color of the flavylum salts. Fan-shaped textures are common for smectic and columnar liquid crystals and further investigation via XRD was necessary to understand the mesomorphic behavior.

To fully assign the mesophase geometries, XRD studies were performed. All XRD data are summarized in Table 1. First, members of category (a) were examined. For O₁-V-Fla-S₁ (Figure 4a, at 130 °C) a sharp reflection in the small angle region at 31.65 Å and three reflections at 15.89 Å, 9.98 Å and 8.07 Å with smaller intensities were detected. These were assigned as (001), (002), (010) and (003) reflections of a lamellar columnar phase (Lam,col) due to the perpendicular orientation of the (010)
reflection regarding the other small angle reflections (Figure 4a). In the wide-angle section, a broad halo centered around 5.03 Å and an additional peak at 3.99 Å due to the $\pi-\pi$ interactions were detected in the WAXS (Figure 4a). Upon increasing the temperature to 190 °C a distinct sharp reflection in the small angle region (Figure 4b), i.e. the (001) reflection of SmA layers together with a broad halo around 4.91 Å and a small $\pi-\pi$ reflection peak at 3.94 Å were detected in the WAXS section. In a similar fashion, SAXS and WAXS data of O$_2$-Fla-S$_1$ indicated a Lam$_{Col}$ phase at lower temperatures and a SmA phase at higher temperatures. The layer spacing in both compounds is significantly smaller than the molecular length of about 42 Å, derived from the solid-state structure. This is due to a partial interdigitation of the alkyl chains, caused by increased effective cross sections by the anion of the charged ionic core, as previously reported. The calamitic structure of the molecules belonging to category (a) is likely responsible for the formation of lamellar mesophases although a strong tendency for columnar stacking is already evident in the Lam$_{Col}$ phases.

As mentioned above, members of category (b) exhibit different textures compared to category (a) under the POM. A typical diffraction pattern of O$_1$-V-Fla-S$_1$ is shown in Figure 4c. In the small angle regime at 120 °C a sharp intense and 5 weaker reflections were observed, which were indexed as (11)(20)(21)(22)(32) reflections of a Col$_{ro}$ phase. In the wide-angle regime, a broad halo centered around 4.62 Å and a second reflection at around 4.45 Å were detected. Fitting the wide angle regime (Figure 4c, dashed grey traces) revealed the later reflection consisting of the superposition of two reflections at 3.49 Å and 3.43 Å related to the anion distances ($d_{anion}$) and $\pi-\pi$ interactions of the cationic cores ($d_{core}$) respectively. In agreement with our previous report, alkyl chains and the cationic cores tilt out of the columnar plane in the Col$_{ro}$ phase. While the alkyl tilt angle ($\alpha_{alkyl}$) could be directly determined from the azimuthal angle of the halo of an oriented sample, the tilt
Table 1. XRD data of flavylum salts including the tilt angles $\alpha_{\text{alkyl}}$ and $\alpha_{\text{core}}$ for Col$_{\text{ro}}$ phases.

| Compound | Mesophase | Lattice parameters [Å] | $d$ [Å]$^1$ | Miller indices |
|----------|-----------|------------------------|-------------|----------------|
| O$_2$-V-Fla-S$_1$ | SmA at 190 °C | $a = 29.53$ | 4.91 (halo) |
|          | Lam$_{col}$ at 130 °C | $a = 31.65$ | 9.98 (010) |
|          |                         | $a = 15.89$ (15.83) | 8.07 (7.91) |
|          |                         | $a = 5.03$ (halo) | 3.99 (001) |
| O$_2$-Fla-S$_1$ | SmA at 120 °C | $a = 29.33$ | 4.40 (halo) |
|          | Lam$_{col}$ at 90 °C | $a = 30.69$ | 15.42 (15.34) |
|          |                         | $a = 9.98$ (10.23) | 9.99 (10.23) |
|          |                         | $a = 5.03$ (halo) | 9.56 (010) |
| O$_2$-V-Fla-S$_2$ | Col$_{\text{ro}}$ a = 50.3 at 120 °C | $a = 28.37$ | 25.17 (20) |
|          | $p2gg$ Z = 4 | $a = 20.31$ (20.30) | 16.34 (16.25) |
|          | $\alpha_{\text{coli}} = 36^\circ$ | $a = 14.29$ (14.15) | 12.12 (12.05) |
|          | $\alpha_{\text{core}} = (12^\circ)$ | $a = 11.04$ (11.10) | 10.28 (10.29) |
| O$_2$-IV-Fla-S$_2$ | Col$_{\text{ro}}$ a = 51.4 at 100 °C | $a = 28.31$ | 25.71 (20) |
|          | $p2gg$ Z = 4 | $a = 20.46$ (20.49) | 16.21 (16.10) |
|          | $\alpha_{\text{coli}} = 37^\circ$ | $a = 14.29$ (14.15) | 12.12 (12.05) |
|          | $\alpha_{\text{core}} = (13^\circ)$ | $a = 11.04$ (11.10) | 10.28 (10.29) |
| O$_2$-IV-Fla-S$_3$ | Col$_{\text{ro}}$ a = 53.3 at 100 °C | $a = 28.31$ | 25.71 (20) |
|          | $p2gg$ Z = 4 | $a = 20.46$ (20.49) | 16.21 (16.10) |
|          | $\alpha_{\text{coli}} = 37^\circ$ | $a = 14.33$ (14.16) | 12.12 (12.05) |
|          | $\alpha_{\text{core}} = (13^\circ)$ | $a = 11.04$ (11.10) | 10.28 (10.29) |
| O$_2$-Fla-S$_2$ | Col$_{\text{ro}}$ a = 26.6 at 100 °C | $a = 23.03$ | 13.51 (13.30) |
|          | $p6 mm$ | $a = 27.15$ | 15.82 (15.68) |

$^1$d refers to the Bragg peak positions, $\pi - \pi'$ indicates the interplanar distances.
angle of the core $\alpha_{\text{core}}$ was determined from the relation of $d_{\text{anion}}$ and $d_{\text{core}}$: $\alpha_{\text{core}} = \cos^{-1}(d_{\text{core}} / d_{\text{anion}})$.[17] For the Col$_{ho}$ phase lattice parameters of $a = 50.3$ Å, $b = 34.3$ Å, $Z = 4$ and tilt angles of $\alpha_{\text{dybl}} = 36^\circ$ and $\alpha_{\text{core}} = 12^\circ$ were calculated. The corresponding isovanillin-derived ILC O$_1$-IV-Fla-S$_2$ possessed similar phases and lattice parameters. For O$_1$-IV-Fla-S$_2$, the unit cell is slightly enlarged, despite the additional thioether side chain. However, the sterically more demanding A ring (as compared to O$_1$-IV-Fla-S$_2$) is compensated by a significant increase in the tilt of the aromatic core of 34°.

For O$_2$-Fla-S$_2$ a high temperature Col$_{ho}$ phase with lattice parameter $a = 30.4$ Å and $Z = 2$ was deduced from the distinct (10) reflection in the SAXS, the broad halo around 4.66 Å and the small $\pi-\pi$ reflection at 3.56 Å. At lower temperatures a Col$_{ho}$ phase was found again. For the higher homologues O$_2$-Fla-S$_3$ and O$_3$-Fla-S$_4$ only Col$_{ho}$ phases with lattice parameters of $a = 26.6$ Å and $a = 25.6$ Å respectively and $Z = 1$ were detected. It should be noted that lattice parameters of the hexagonal columnar mesophase decreased for these three ILCs despite the increased number of side chains. This can be rationalized as follows: In O$_2$-Fla-S$_2$, presumably two molecules form a dimeric dimer whereas the increased B ring substitution in O$_2$-Fla-S$_3$, O$_2$-Fla-S$_4$ suppresses dimer formation. Consequently, when comparing O$_2$-Fla-S$_2$ and O$_3$-Fla-S$_4$, the lattice parameter decreases from $a = 30.4$ Å to $a = 26.6$ Å as the number of molecules in a unit cell decreases from 2 to 1. At the same time, the density decreases from $\rho = 1.31$ g·cm$^{-3}$ to $\rho = 0.99$ g·cm$^{-3}$ presumably due to a decreased space filling of the monomeric dimeric dimer O$_2$-Fla-S$_2$ compared to the dimeric dimer in O$_3$-Fla-S$_4$. Compared to O$_2$-Fla-S$_2$, the additional alkyl chain in O$_2$-Fla-S$_3$ likely results in an increased space filling and thus in a smaller lattice parameter and an increased density of $a = 25.6$ Å and $\rho = 1.13$ g·cm$^{-3}$. Similar behavior was found for the series S$_2$-Fla-S$_2$, S$_2$-Fla-S$_4$, S$_3$-Fla-S$_3$, and S$_3$-Fla-S$_5$ (see Supporting Information, Table S3).

A similar packing behavior was found for fully thioether-substituted ILCs S$_2$-Fla-S$_2$, S$_2$-Fla-S$_4$, S$_3$-Fla-S$_3$, S$_3$-Fla-S$_5$. XRD results of S$_2$-Fla-S$_2$ confirmed a monotropic Col$_{ho}$ phase. The lattice parameter of $a = 31.4$ Å indicated, that two flavylum ions form a dimer. Assuming an anti-parallel stacking of the flavylum cation in the Lam$_{col}$ phase, the increased steric demand of the sulfur atoms should disfavor this packing pattern, leading to reduced intermolecular interactions. As a result, rotation of the mesogens along the short molecular axis is less hindered, which leads to a more disc-like appearance, thus promoting a columnar mesophase. Since 3 side chains are not sufficient to stabilize this phase, the mesogenic building block is a disk-like dimer with 6 side chains in total. According to the XRD data of S$_2$-Fla-S$_2$ and S$_3$-Fla-S$_3$, a Col$_{ho}$ phase containing one flavylum salt per discoid was assigned in both cases (Table 1). The decreased intermolecular interactions of S$_2$-Fla-S$_2$ resulted in the Col$_{ho}$ mesophase rather than a Col$_{ho}$ mesophase as seen in O$_2$-Fla-O$_2$[17] and O$_2$-Fla-S$_2$, requiring stronger interactions to propagate the tilt of the columns. Evidently, molecules belonging to category exhibit columnar mesophases, which can be rationalized by the discotic geometry of derivatives with 2 or 3 thioethers tethered to the B ring.

The XRD results revealed the influence of the molecular structure on the mesophase geometry. Whereas calamitic ILCs (type A) such as O$_1$-V-Fla-S$_1$, O$_2$-Fla-S$_1$, consisting of a linear structure formed SmA or Lam$_{col}$ phases, even a slightly bend structure as in O$_1$-IV-Fla-S$_1$ or unsymmetrical compounds such as O$_2$-Fla-S$_1$ with large voids around the thioether side chain in the B ring suppress mesophase formation. On the other hand, with 2 thioethers at the B ring sufficient space filling could be achieved and Col$_{ho}$ phases are favored for ILCs with up to 2 alkoxy chains at the A ring, e.g. O$_2$-Fla-S$_2$. The preference for Col$_{ho}$ was also found, when the A ring carried only one alkoxy chain, as in O$_1$-V-Fla-S$_2$, O$_1$-IV-Fla-S$_2$ and O$_1$-IV-Fla-S$_3$, respectively. In contrast, ILCs with either 3 thioethers at the B ring or $\geq$ 2 thioethers at the A ring displayed Col$_{ho}$ phases. Thus, the increased steric bulk of the thioethers as compared to alkyl chains minimized the free volume and resulted in improved temperature range and stability of the columnar mesophase as evident by comparison of O$_2$-Fla-S$_2$, O$_2$-Fla-S$_3$, S$_2$-Fla-S$_2$ in Figure S5. Members of discotic ILCs (type B) showed Col$_{ho}$ phases mostly when alkyl groups are grafted to the A ring, while Col$_{ho}$ phases were observed for derivatives with thioethers at the B ring.

The results of our DSC measurements and phase assignments were summarized in Figure S5. We want to point out that the investigated flavylum salts often vitrify in a (metastable) glass in agreement with our POM measurements and no crystallization or glass transition was detected in the cooling runs (see Supporting Information, Figure S5–S7 and Table S2). However, most derivatives exhibit a melting transition in the 1st heating cycles indicating a crystalline phase at room temper-

| Table 1. continued |
|---------------------|
| Compound           | Mesophase | Lattice parameters [Å] | $d$ [Å]$^a$ | Miller indices |
|---------------------|-----------|------------------------|-------------|----------------|
| S$_2$-Fla-S$_2$     | Col$_{ho}$ | $a = 27.1$             | 4.62        | (halo)         |
| at 90 °C            | $Z = 1$   |                        | 3.62        | ($\pi-\pi$)    |
| $p6 mm$             |           |                        | 23.48       | (10)           |
|                     |           |                        | 13.70       | (11)           |
| S$_3$-Fla-S$_2$     | Col$_{ho}$ | $a = 26.9$             | 4.51        | (halo)         |
| at 100 °C           | $Z = 1$   |                        | 3.55        | ($\pi-\pi$)    |
| $p6 mm$             |           |                        | 23.49       | (10)           |
|                     |           |                        | 15.36       | (11)           |
|                     |           |                        | 4.40        | (halo)         |
|                     |           |                        | 3.49        | ($\pi-\pi$)    |

[a] Calculated $d$ values are given in parentheses.
temperatures decreased upon increasing the number of alkoxy chains at the A ring melting and clearing temperatures at the B ring. Furthermore, derivatives with melting or clearing points above 150 °C gave no reproducible DSC data indicating thermal decomposition. We therefore decided to investigate transition temperatures from the 1st heating cycles. The results of our DSC measurements and phase assignments were summarized in Figure 5 and allowed us to investigate the influence of substitution patterns on the mesomorphic properties.

Depending on the substitution pattern of the A ring, the following trends were observed. For flavylium salts O$_2$-V-Fla-S$_m$ with one alkoxy chain at the A ring melting and clearing temperatures decreased upon increasing the number of thioethers m at the B ring. Furthermore, the phase type changed from Lam$_{col}$, SmA for O$_2$-V-Fla-S$_1$ to Col$_{ho}$ for O$_2$-V-Fla-S$_2$.

In contrast, in the series of regioisomeric flavylium salts O$_2$-IV-Fla-S$_m$ clearing temperatures increased with larger m. Moreover, grafting of additional thioethers to the B ring induced a Col$_{ho}$ phase in O$_2$-IV-Fla-S$_2$ and increased phase widths and stability in O$_2$-V-Fla-S$_2$.

Flavylium salts O$_2$-Fla-S$_m$ with two alkoxy groups at the A ring displayed higher clearing temperatures respectively, upon increasing m. Within the series phase types changed from Lam$_{col}$, SmA (for O$_2$-Fla-S$_1$) to Col$_{ho}$ for O$_2$-Fla-S$_2$ and SmA$^{B1}$ (for O$_2$-Fla-S$_3$), while simultaneously temperature range and phase stability increased.

On the other hand, flavylium salts O$_2$-Fla-S$_n$ carrying three alkoxy chains at the A ring showed a slight increase of melting transitions but a very pronounced increase of clearing temperatures upon increasing m, resulting in a broad Col$_{ho}$ phase for O$_2$-Fla-S$_3$ in contrast to the non-mesomorphic O$_2$-Fla-S$_1$.

When the A ring carried thioether chains, e.g. in flavylium salts S$_2$-Fla-S$_m$, increased melting and clearing temperatures were observed with larger m. Upon comparison of S$_2$-Fla-S$_3$, with S$_2$-Fla-S$_2$, the two thioethers at both A and B ring in the latter case improved the overall molecular symmetry and thus increased the stability of the Col$_{ho}$ phase. The beneficial effect of molecular symmetry and improved space filling on the mesophase stability is also visible for S$_2$-Fla-S$_3$ with a broad Col$_{ho}$ phase and its non-mesomorphic counterpart S$_2$-Fla-S$_1$.

Comparison of thioether-substituted flavylium salts O$_2$-Fla-S$_m$, S$_2$-Fla-S$_m$ with the corresponding alkoxy-substituted analogues O$_2$-Fla-O$_m$ revealed only a small influence of the thioether/ether replacement on the phase types, but a more pronounced effect on the phase stability. Two extreme cases are O$_2$-Fla-O$_1$, O$_2$-Fla-S$_1$, showing both lamellar phases and O$_2$-Fla-O$_1$, O$_2$-Fla-S$_2$, where the columnar mesomorphism is completely lost in the sulfur case (for further details, see Supporting Information, Figures S12, S13). The number of side chains and substitution pattern determines the overall molecular geometry and thus the phase type (vide infra). With 2–3 side chains at the B ring columnar phases are exclusively formed. Unsymmetrical members with alkoxy chains at the A ring and thioethers at the B ring displayed Col$_{ho}$ phases, while the corresponding ILCs with thioethers at both A and B ring displayed Col$_{ho}$ phases. Thioether/ether replacement decreased the columnar phase stability, presumably due to less efficient packing of the bulkier thioethers and the absence of S–S interactions. However, for symmetrical derivatives S$_2$-Fla-S$_2$, S$_2$-Fla-S$_3$, Col$_{ho}$ phases were much broader and more stable as compared to the O- analogues.

Linear Optical Properties of Thioether-Substituted Flavylium ILCs

All flavylium salts showed bright orange to purple colors in both solid state and solution and were thus investigated via UVVis and fluorescence spectroscopy in CHCl$_3$ solution. The lowest energy absorption bands ($\lambda_{max}$ and $\varepsilon$) are summarized in Table 2 and selected spectra are shown in Figure 6. For example, vanillin-derivative O$_2$-V-Fla-S$_1$ decorated with one alkoxy chain at the A ring and one alkylsulfanyl chain at the B ring displayed three weak absorptions in the UV-range (268 nm, 313 nm, 371 nm) and a strong absorption band in the visible region at 510 nm. Absorption maxima and extinction coefficients changed only marginally when the number of alkoxy chains n in the A ring increased in the series O$_2$-V-Fla-S$_1$, O$_2$-Fla-S$_1$, and O$_2$-Fla-S$_2$ while keeping the B ring pattern constant (Figure 6a). The same trend was observed within the series of O$_2$-Fla-S$_2$ and O$_2$-Fla-S$_3$ (Figure 515). In contrast, when the A ring substitution was kept constant and the number of thioethers at the B ring increased, a distinct change of the absorption properties was detected. Within the series O$_2$-Fla-S$_1$, O$_2$-Fla-S$_2$, O$_2$-Fla-S$_3$, $\varepsilon$ values decreased. A bathochromic shift of 34 cm$^{-1}$ was observed for O$_2$-Fla-S$_2$ as compared to O$_2$-Fla-S$_1$ ($\lambda_{max} = 509$ nm), while O$_2$-Fla-S$_3$ displayed a hypsochromic shift of 89 cm$^{-1}$. The auxochromatic effect

![Figure 5](https://example.com/figure5.png)

Figure 5. (Meso)phases and corresponding temperature ranges of the flavylium salts (temperatures determined from 1st heating cycles, rate = 10 K min$^{-1}$): Cr (crystalline), G (glass), SmA (smectic A), Lam$_{col}$ (lamellocolumnar), Col$_{ho}$ (ordered columnar rectangular), Col$_{ho}$ (ordered columnar hexagonal). $T_m$, $T_c$ determined by slow cooling via POM; monotropic behavior; SmA – Lam$_{col}$ transition determined from 1st cooling cycle.
of the thioethers was even more pronounced for the fully thioether-functionalized compounds S₈-Fla-S₈ resulting in bathochromically shifted absorption bands (552–575 nm) (Figure 6c) compared to the analogues O₈-Fla-S₈.

Albeit most flavylium salts prepared in this work being non-emissive, the three derivatives O₁-V-Fla-S₁, O₁-iV-Fla-S₁ (Figure 6a) and O₂-Fla-S₁ (Figure 6b) exhibited bright emission (λₘₐₓ = 571 nm) upon irradiation in CHCl₃ solution. This is in accordance with the related alkoxy flavylium salts O₁-Fla-O₁, where decoration of the B ring with more than one substituent increased the rotational freedom of the peripheral phenyl ring and thereby partially or fully inhibited emission.[17]

The slightly lower quantum yields of O₁-V-Fla-S₁, O₁-iV-Fla-S₁ and O₂-Fla-S₁ compared to their alkoxy analogues[17] might be due to the decreased contribution of the flat Lewis structure with C–C double bond between A and C ring, resulting from the smaller electron-donating +M effect and less efficient orbital interaction of the larger thioethers as compared to the alkoxy chains.[17] It should be noted, that no evidence for side chains intercalating between the π-systems, as recently reported by Douce for luminescent naphthalene imidazolium ILCs,[27] could be found in our case. Additionally, the heavy atom effect[18] of the sulfur might be responsible for the experimental results. The unfavourable influence of sulfur-containing side chains on the luminescence was even more pronounced, when both A and B rings carried thioethers. For example, compound S₂-Fla-S₁ (λₘₐₓ = 602 nm, Figure 10c) was the only emitting compound of the series Sₙ-Fla-Sₙ with a very low quantum yield < 0.01. The rate of nonradiative relaxation usually increases with decreasing energy difference between S₁ and S₀ simply owing an improved overlap of higher vibrationally excited states in S₀ and the zeroth vibrational state in S₁ facilitating vibrational decay. This effect is commonly referred to as energy gap law[29] and might, in addition to the even more pronounced heavy atom effect, be responsible for the (almost) non-emissive behavior of the series Sₙ-Fla-Sₙ.

| Compound | λₘₐₓ (ε) [nm (10⁴ L mol⁻¹ cm⁻¹)] [a] | λₘₐₓ (Φ) [nm (a.u.)] [b] |
|----------|--------------------------------------|-----------------------|
| O₁-Fla-S₁ | 510 (6.0) | 571 (0.84) |
| O₁-V-Fla-S₁ | 518 (5.0) | - |
| O₁-iV-Fla-S₁ | 509 (4.9) | 571 (-) |
| O₂-Fla-S₁ | 487 (2.8) | - |
| O₂-V-Fla-S₁ | 510 (6.5) | 571 (0.86) |
| O₂-iV-Fla-S₁ | 518 (5.3) | - |
| S₁-Fla-S₁ | 487 (3.0) | - |
| S₁-V-Fla-S₁ | 513 (5.8) | - |
| S₁-iV-Fla-S₁ | 488 (2.8) | - |
| S₂-Fla-S₁ | 571 (4.6) | 602 (<0.01) |
| S₂-V-Fla-S₁ | 552 (9.8) | - |
| S₂-iV-Fla-S₁ | 567 (5.0) | - |
| S₈-Fla-S₈ | 575 (6.7) | - |

[a] measured in CHCl₃ (c = 2·10⁻³ molL⁻¹), ε determined from 5 different concentrations; [b] measured in degassed CHCl₃ (c = 2·10⁻³ molL⁻¹), λₘₐₓ = 510 nm, Φ measured with a calibrated integration sphere.

Figure 6. Absorption (solid lines) and, if applicable, emission (dashed lines) spectra of a) the series O₁-Fla-S₁, b) the series O₂-Fla-S₂ and c) the series S₂-Fla-S₂ recorded in CHCl₃ (c = 2·10⁻³ mol L⁻¹, λₘₐₓ = 510 nm).
Conclusions

In this work we have probed the self-assembly of ILCs based on flavylium salts with alkoxy side chains on the A ring and thioethers on the B ring (Oₙ-Fla-Sₘ series), as well as thioethers on both A and B ring (Sₘ-Fla-Sₘ series) and compared them with the corresponding known O-analogues Oₙ-Fla-Oₙ⁻. Among the studied flavylium salts only O₂-ν-Fla-S₁ and Oₙ-IV-Fla-S₁ and O₂-IV-Fla-S₁ with one thioether in the B ring displayed a bright green emission with high quantum yields (Φ = 84%), while S₂-Fla-S₁ showed only a weak yellow emission (Φ < 1%). All other derivatives seem to favor conformations with a high degree of rotational freedom and thus a strong tendency for thermal deactivation. Presumably, formation of H-aggregates also contributes to fluorescence quenching.

In the bulk state, POM, DSC and XRD provided insight into the liquid crystalline self-assembly. In the Oₙ-Fla-Sₘ series the presence of thioether in the B ring led to lower clearing points except for O₂-IV-Fla-S₁, which has a higher clearing temperature as compared to the O-analogues O₂-IV-Fla-O₁.

For mixed O/S-substituted ILCs, the mesophase type changed upon increasing the number of thioethers on the B ring from SmA, LamCol for calamitic ILCs carrying one thioether at the B ring and 1–2 alkoxy chains at the A ring, via Col, to Discotic ILCs carrying 2–3 thioethers at the B ring and 1–2 alkoxy chains at the A ring to Col for discotic ILCs carrying up to 3 thioethers at both A and B rings. The replacement of O by S in the side chain resulted in most cases in decreased mesophase stability and temperature range without affecting the phase type, in particular for ILCs carrying alkoxy chains at the A ring and thioethers at the B ring. However, for fully thioether-substituted derivatives S₁-Fla-S₁, S₂-Fla-S₁, S₃-Fla-S₁, a significant stabilization of the Colₙ phase was observed. Moreover, for S₂-Fla-S₁ the bulkiness of the thioethers induced a switch of the phase type from LamCol / SmA found for the alkoxy analogues O₂-Fla-S₁, O₂-Fla-O₁ to Colₙ.

Thus, the attachment of thioethers rather than alkoxy side chains to flavylium ILCs strongly favors columnar aggregates both in solution as well as in the bulk state. Future work must demonstrate whether this O/S replacement-induced change of mesophase type can be applied to other classes of ILCs as well.

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Conflict of Interest

There are no conflicts to declare.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

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