Mesogens with Aggregation-Induced Emission Formed by Hydrogen Bonding.

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ABSTRACT: In this contribution we combined aromatic thioethers with aggregation-induced emission properties, acting as hydrogen donors with alkoxystilbazoles as hydrogen acceptors yield supramolecular hydogen bonded complexes. These complexes reveal mesogenic behavior as well as photoresponsiveness under UV-light irradiation. Besides that it was found that introduction of a chiral side chain, namely citronellyl, leads to dramatic bathochomic shift of the emission which was not oberseved for linear alkyl chains. The photophysical properties as solid and in the the mesophase were studied as well as liquid crystalline behavior. Here techniques such as differntial scanning calorimetry ansd polarized optical microscopy were used for characterisation

Supramolecular chemistry is an effective tool for the design and synthesis of functional materials such as responsive polymers,[1] gels[2-4] and liquid crystals.[5-7] The employment of self-assembly processes provides a number of advantages such as facile synthesis by simple mixing of pre-tailored building blocks or dynamic response to external stimuli or damages (self-healing/-repair).[1, 8, 9] Thereby, the different intermolecular interactions introduce their specific characteristics (e.g. directionality, selectivity, interactions strength), which opens inexhaustible opportunities to create functional and responsive materials.[10-12]

To this end hydrogen bonds, which play a crucial role in self-assembly processes in nature, are highly promising for the design of supramolecular liquid crystals.[5, 13] Seminal studies by Kato and Fréchet investigated hydrogen-bonded liquid crystals (HB LCs) based on benzoic acid groups and pyridyl derivatives.[14] In 1994, Bruce and coworkers demonstrated that also phenols are suitable hydrogen-bond donors for the formation of supramolecular complexes with liquid-crystalline properties.[15]

Within the past decades, fluorescent LCs are receiving increasing attention, since the combination of the ability to emit light and spontaneously self-assemble into mesoscopic structures within the liquid crystalline phase is crucial for optoelectronic applications, such as anisotropic light-emitting diodes and emissive liquid crystal displays.[16-20] Depending on their alignment in the mesophase (nematic or chiral-nematic) fluorescent LCs may emit linear or circular polarized light. However, a major problem in the development of novel fluorescent liquid crystals is that typically the fluorescence emission is dramatically reduced during the formation of the ordered phase (mesophase or crystalline state).[21, 22] This challenge can be overcame by the use of aggregation-induced emission (AIE) chromophores. These chromophores exhibit a rotor like structure allowing high rotational mobility in organic solvent converting absorbed light into motion, which goes along with a loss in emission. However, upon aggregation intramolecular motion (RIM) or rotation (RIR) is restricted leading to fluorophore or phosphor[23] emission. In general, there are three routes followed to obtain luminescent liquid crystals (LLC). The synthetic approach combines a mesogenic structure with an AIE-active luminophore or modifies the chromophores by attaching alkyl chain to yield LLCs.[21, 24] A second method is to dope a commercially available liquid crystal with AI-emitters and the third, rarely found approach, towards LLCs is based on the self-assembly of pre-tailored molecular building blocks in a supramolecular fashion. Recently, Voskuhl and coworkers reported a novel class of AIE emitters based on aromatic thioethers, which are readily available in high yields and their photophysical properties can easily be manipulated by variation of the substitution pattern and the introduction of different functional groups .[25, 26, 27] Since, the AIE chromophores are available as phenols[27] (see Scheme 1) they are promising hydrogen-bond donors for the development of supramolecular liquid crystals with fluorescent emission. Since 2016, Giese and coworkers employ a modular approach for systematic structure property relationship studies of HB-LCs.[28-31] These studies granted deep insight on the structure-property relationships which govern the

liquid crystalline properties of supramolecular hydrogen-bonded assemblies.

Herein, we report a supramolecular approach towards LLCs. In modular approach (see Scheme 1) a series of new HB-LCs with AIE behaviour was obtained. Therefore, the aromatic thioesters developed by Voskuhl et al. were employed as hydrogen bond donors, providing interesting photophysical properties and combined with stilbazole-based hydrogen bond acceptors (St) to induce liquid crystalline behaviour and, in case of St*, chirality. Chiral mesophases are especially important in the context of display,[32] or sensing applications[33], and our aim is to combine chirality with emissive mesogens.
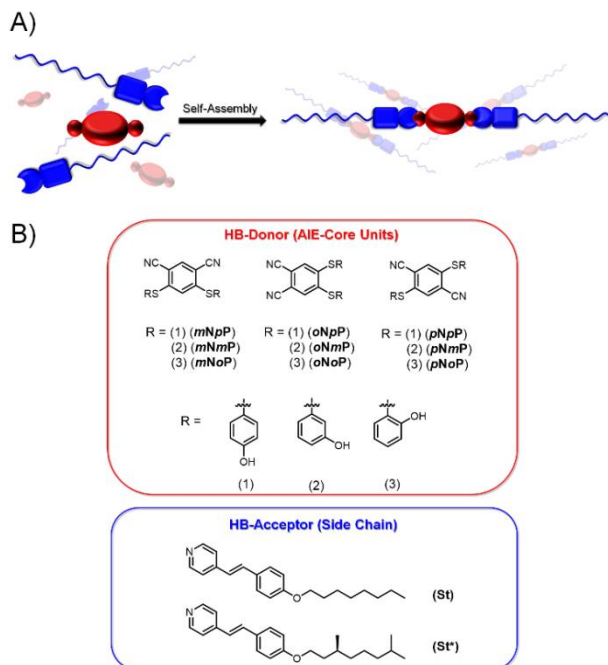

Scheme 1: A) Schematic representation of the supramolecular approach towards AIE-active mesogens by hydrogen-bonding, B) Molecules used in the present study

None of the starting material display any LC behaviour. The hydrogen-bonded assemblies (HBAs) were obtained by mixing of the hydrogen bond donating thioesters and the stilbazoles in the ratio 1:2 in solution. This ratio was chosen since the HB donors feature two free phenolic groups which could interact with the pyridine nitrogen of the stilbazoles. Upon removal of the solvent and thoroughly drying of the HBAs under vacuum, the samples were analysed with respect to their mesomorphic behaviour and their photo-physical properties. It should be noted, that the HBAs based on the pNpP, pNmP and pNoP moieties could not be obtained by this method, due to their extremely low solubility. A co-melting strategy to obtain the HBAs based on pNxP also failed due to decomposition. Therefore, the following discussion focuses on 12 different HBAs. The HBAs were characterized by infrared (IR) spectroscopy, polarized optical microscopy (POM) and differential scanning calorimetry (DSC).

The formation of the hydrogen-bonded assemblies was evident by IR spectroscopy. The biggest changes upon complexation are observed in the OH region. Taking the mNmP-(St)2 assembly as representative example, the IR spectrum (see Figure XX ESI) clearly shows a decrease of the intensity of the IR signal for the OH-group at 3385 cm^{-1} and emerging bands in the region of 2650-2500 cm^{-1}, which is indicative for the formation of the HBAs.[17] In addition, the characteristic hypsochromic shift and intensity decrease of the pyridine bands in the region 3000–3100 cm^{-1} and 1500–1590 cm^{-1} after formation of the HBA was observed.[34] The C–H absorption of the pure stilbazole at 3021 cm^{-1} becomes less intense upon complexation and shifted to 3023 cm^{-1} as a result of a higher positive charge on the pyridyl hydrogens in the complex. A blue shift is also observed for the three bands associated with the pyridine ring breathing vibrations at 1587, 1507, and 1415 cm^{-1}. On the other hand, the pyridyl ring stretching at 994 cm^{-1} is blue shifted compared to the St molecule (987 cm^{-1}), which hints towards a strong hydrogen bond.

In additional prove for the formation of the HBA is given by single crystal X-ray diffraction. We obtained the crystal structure of mNmP-(St)$_2$ by slow evaporation of a methanol solution. mNmP-(St)$_2$ co-crystallized in the space group C 2/c (Figure 1).
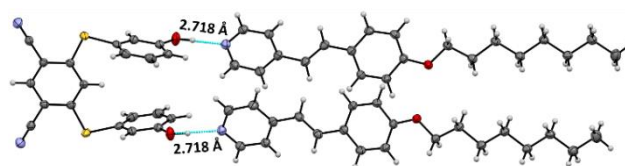
Figure 1: Partial intermolecular landscape of mNmP-(St)$_2$. Blue lines represent short intermolecular contacts below the sum of the van der Waals radii of the respective atoms. Color chart: grey = C, white = H, red = O, purple = N, and yellow = S. Ellipsoids are shown at the 50% probability level.

The molecular structure clearly displays the formation of the HBA with two short hydrogen bonds (O···Npyr distance 2.718 Å) between the phenol moiety of the core unit and the pyridine systems of the two stilbazoles.

In order to quantify the non-covalent interactions occurring in our system and proving that it is truly driven by hydrogen bonding, we analysed the crystal structure of mNmP-(St)$_2$ by employing intermolecular perturbation theory developed by Turner et al.,[35] implemented in the CrystalExplorer software,[36] This methodology was recently applied by our group to quantify the non-covalent interactions in a series of aromatic thioethers featuring AIE and to rationalize their photophysical behaviour.[37] Details on the methodology are given in the ESI.

Notably the dominant interaction in the crystal structure of mNmP-(St)$_2$ is the O···Npyr hydrogen bond (12.7

kcal/mol, Figure ESI XX, Structure Determinant 1), followed by a displaced Core-Side chain interaction (11.5 kcal/mol, Figure ESI XX, Structure Determinant 2).

observed that the complexes mNmP-(Sti)$_2$ and oNmP-(Sti)$_2$ showed either nematic or smectic behavior and appeared in off-white color. Although all building blocks
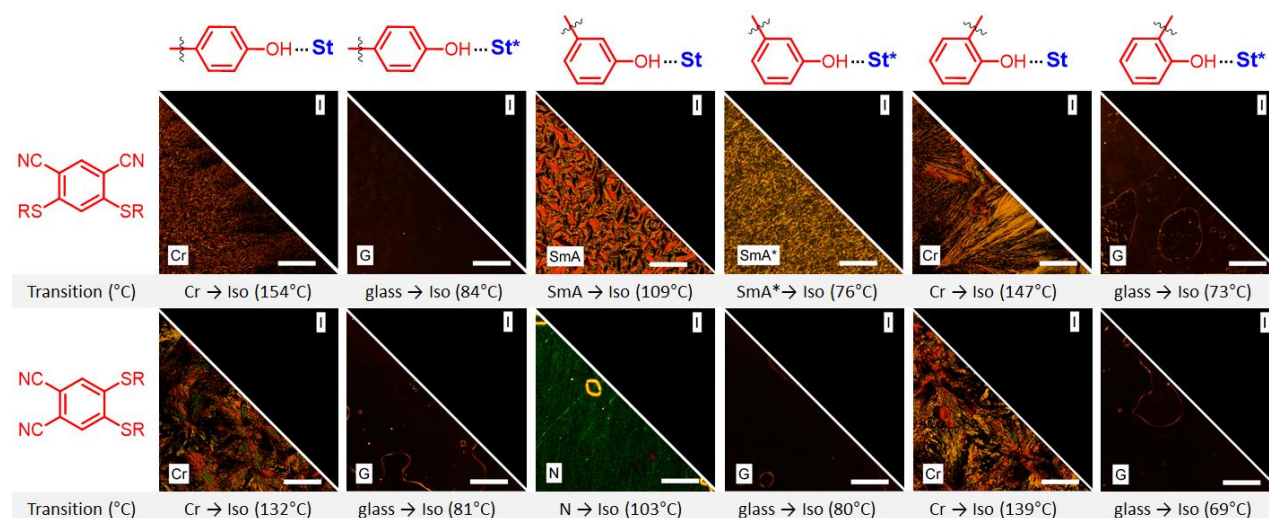
Figure 2: Phase transitions and transition temperatures of the supramolecular assemblies studied in the present work as determined by POM (10 °C/min) under planar anchoring conditions. Polarizers are crossed. Clearing points for monotropic LC → Iso transitions are given. The scale bar represents 100 μm.

Other interaction modes are less important (Figure ESI XX). This demonstrates that hydrogen bonding plays the key role in the self-assembly of our complexes, although displaced π···π interactions are also important (see below).

In order to identify interesting combinations of hydrogen bond donors and acceptors with liquid crystalline properties, we initially studied the mesomorphic behavior of the HBAs by POM. The results are summarized in Figure 2.

While the individual building blocks did not show any mesophases, 3 out of 12 HBAs showed monotropic liquid crystalline behavior. For the HBAs based on xNoP and xNpP no liquid crystallinity was observed. This observation demonstrates the impact of the substitution pattern of the aromatic thioethers on the mesomorphic properties of the assemblies. In contrast, the xNmP-based assemblies show liquid crystalline behaviour in a temperature range of about 20° C (determined with a cooling ramp of 10° C/min). Representative POM pictures are collected in Figure 2. For mNmP-(St)$_2$ a SmA phase is observed while oNmP-(St)$_2$, shows the characteristic texture of a N phase. The chiral assembly mNmP-(St*)$_2$ shows the characteristic SmA* texture of a chiral smectic phase.

The aim of the present study is to derive AIE-active mesogens by self-assembly. Therefore, the photo-physical properties of the assemblies and their molecular building blocks were investigated in solution, the solid state and the mesophase.

Since emitters with aggregation-induced emission properties were used for the formation of the hydrogen bonded complexes,[27] we were especially interested in the photo-physical properties of the assemblies. Here we focussed on the complexes which revealed a mesophase. It was

showed blue emission in the solid state (Fig. SX and Fig. 3) and St as well as St* emit also in organic solvents (acetonitrile or chloroform) (Fig. SX), the formed complexes with St reveal no detectable emission in the solid state.
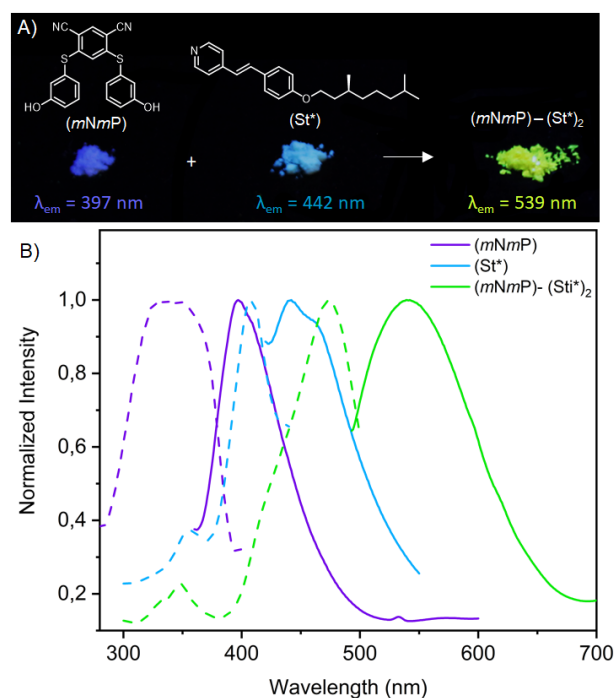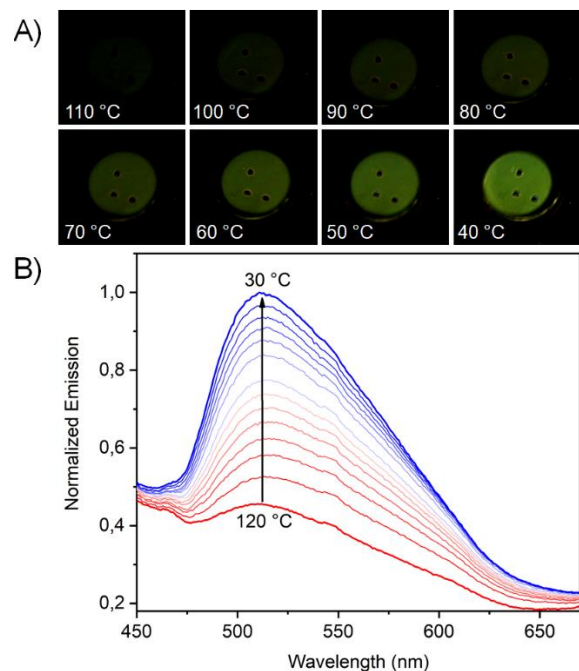

Figure 3: A) Photographs of the solid components as well as the formed complex under UV-light irradiation (λ_{em} = 365 nm), B) Excitation (dotted line) and emission (solid line) spectra of the single components as well as the formed complex in the solid state.

We attributed the quenching of the emission to the packing of the complexes in the solid state, which showed a dense packing involving significant interactions between the alkyl-chains as well as π-π interactions known to decrease the overall emission intensity due to the formation of non-radiative charge transfer complexes. The importance of π-π interactions in the assembly of St-based complexes was explained with theoretical calculations (see above and also ESI). Interestingly upon formation of the complexes (*m*N*m*P)-(St*)$_2$ and (*o*N*m*P)-(St*)$_2$ a drastic color change was observed and bright yellow powders were obtained. Besides that, these obtained complexes showed striking emission in the green to yellow range.

The complex (*m*N*m*P)-(St*)$_2$ shows bright green emission at 539 nm and a SmA* mesophase. The shift in emission can be explained by a combination of a change in the electronic structure due to the hydrogen bonds between the pyridyl units and the phenols as well as decreased π-π contacts due to the introduction of additional methyl groups via the citronellyl side chains hindering dense packing.

A similar behaviour was observed for the complex (*o*N*m*P)-(St*)$_2$ which shows emission of 557 nm in the solid state (Fig. SX). This bathochromic shift (18 nm) compared to the complex (*m*N*m*P)-(St*)$_2$ is in good agreement with the differences in solid state emission of (λ_{em} (*m*N*m*P = 397 nm) and (λ_{em} (*o*N*m*P) = 454 nm) in the solid state showing the direct influence of the used AIE core luminophore on the emission properties in the solid state (Figure 3).

Figure 4: A) Photographs of complex (*m*N*m*P)-(St*)$_2$ at different temperatures under UV light irradiation (λ = 365 nm), B) Normalized emission spectra (*m*N*m*P)-(St*)$_2$ at different temperatures.

Besides investigations of the complexes in the solid state, we also measured temperature dependent emission spectra of (mNmP)-(Sti*)$_2$ which showed the most interesting features, such as a significant bathochromic shift as well as a SmA* phase at 76 °C. To this end we heated the sample to the isotropic state and cooled it slowly to room temperature. Photographs at different temperatures revealed an increase in emission at upon cooling which was attributed to a higher ordered packing going along with a restriction of intramolecular motion (RIM) which is characteristic to emitters with AIE properties. Furthermore we evaluated the increase in emission quantitatively. Temperature dependent emission spectra supported the observations before, that upon cooling an increase in emission was observed supporting our hypothesis that hindered motion enables higher emission, due to the fact that non-radiative pathways, such as vibration and rotation, are less dominant.

To conclude, a novel hydrogen bonded system, based on alkoxystilbazoles and aromatic thioethers, was described. This system showed a drastic bathochromic shift of nearly 100 nm upon complex formation in the case of chiral side chains. This system responds to temperature changes, based on the AIE effect, leading to a fixation of the molecules in the cooled state. Furthermore nematic (oNmP)-(St*), SmA (mNmP)-(St)$_2$ and SmA* (mNmP)-(St*)$_2$ phases were observed and characterized. This unique design enables future applications of this highly flexible system in terms of temperature sensing as well as the recognition of analytes.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Details on the synthesis of the complexes, POM images, DCS measurements, IR spectra, details on the theoretical calculations.

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

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