



# Photo-switching and -cyclisation of hydrogen bonded liquid crystals based on resveratrol†‡

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**A series of hydrogen-bonded liquid crystals based on resveratrol and resveratrone is reported and investigated with respect to their photo-switchability (at 405 nm) and photo-cyclisation (at 300 nm).**

Polyphenolic compounds are widespread in natural systems and constitute an important class of phytochemicals.<sup>1</sup> They play a vital role in a number of biochemical processes such as the defence mechanism or coloration of plants as well as in the prevention of UV-light induced damage of tissues. During the past decade phenolic building blocks have regained considerable attention with respect to the design of functional materials,<sup>1c</sup> such as gels,<sup>2</sup> polymers<sup>3</sup> and adhesives.<sup>4</sup>

Due to their hydrogen-bond donating groups polyphenols are also promising supramolecular synthons for the design of supramolecular functional materials, which have a number of advantages compared to conventional materials. They are easy accessible by self-assembly of the pre-tailored building blocks, whereby the reversibility of the non-covalent bond allows for dynamic response to external stimuli, damage (self-healing/-repair) or recycling of the components.<sup>5</sup>

With respect to hydrogen-bonded liquid crystals Kato and Fréchet contributed seminal studies. They investigated self-assembled liquid crystals based on the complementary interaction

between pyridyl derivatives and benzoic acids.<sup>6</sup> In the 1990s, Bruce *et al.* started their systematic work on hydrogen-bonded liquid crystals by combining stilbazole derivatives with various phenolic compounds.<sup>7</sup> Later they reported the first example of halogen-bonded liquid crystals,<sup>8</sup> including trimeric supramolecular mesogens exhibiting halogen- and hydrogen bonding at the same time.<sup>9</sup>

The use of light-responsive entities such as azobenzenes into liquid crystals enables external control over the alignment of mesogens by a non-invasive stimulus and provides a route towards photo-switchable functional materials and photo-controlled self-assembly processes.<sup>10</sup> With respect to the development of responsive supramolecular materials, azopyridine (**Ap**) derivatives have gained considerable attention since they combine the photo-active azobenzene group with the hydrogen/halogen bond-acceptor capability of the pyridyl-group.<sup>11</sup>

In 2016, we started our work on supramolecular liquid crystals by employing a modular approach allowing systematic structure property relationship studies and the fabrication of liquid crystalline assemblies with tailor-made properties.<sup>12</sup> Our initial study reported a series of photo-switchable liquid crystalline assemblies based on azopyridines (**Ap-*n***) and phloroglucinol (**PHG**). Following this approach we systematically investigated the impact of the substitution pattern of the hydrogen-bond donors,<sup>13</sup> the fluorination degree<sup>14</sup> and the impact of the linking group in the hydrogen-bond accepting moiety.<sup>15</sup> Based on these results we were able to stabilize liquid crystalline blue phases (BP I), which usually occur in a temperature range of 1–2 °C, over a temperature range of about 25 °C.<sup>16</sup> In addition, we recently reported the manipulation of the optical properties of photonic crystals by infiltration of the porous materials by hydrogen-bonded liquid crystals.<sup>17</sup>

In the context of our previous studies resveratrol (3,5,4'-trihydroxy-*trans*-stilbene, **Res<sub>01</sub>**), a natural occurring phytoalexin, is a promising hydrogen bond donating moiety.<sup>18</sup>

Therefore, the present study employs our established modular approach to generate resveratrol based hydrogen-bonded liquid crystals and explores their reversible (*trans-cis* isomerisation

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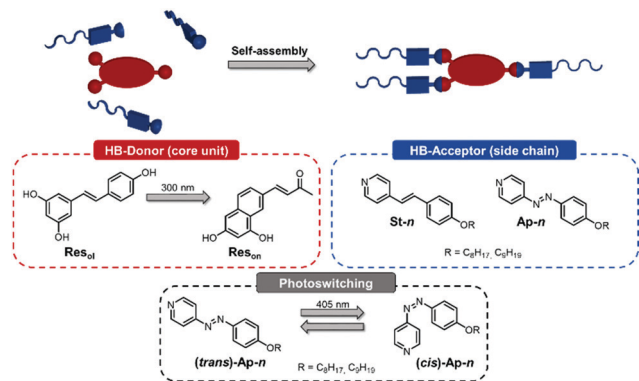
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‡ Electronic supplementary information (ESI) available: Synthetic procedures, IR-, DSC-data and crystal structure analysis. CCDC 1939466 and 1939467. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9cc07721a

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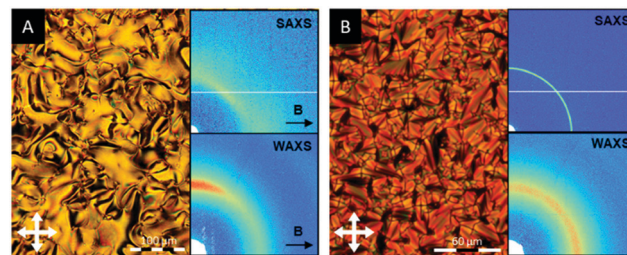


**Scheme 1** Schematic representation of the modular approach towards photo-switchable liquid crystals based on resveratrol and resveratrone as product of the photo-cyclisation by irradiation with UV-light (300 nm). Furthermore, the *trans*-*cis* isomerisation of **Ap-*n*** by irradiation with UV-light (405 nm) is shown.

of azopyridine) and irreversible photo-switchability (photo-induced formation of resveratrone, **Res<sub>on</sub>**) (Scheme 1).

Four hydrogen-bonded assemblies (HBAs) were obtained by mixing acetone solutions of resveratrol with corresponding solutions of stilbazoles or azopyridines in the ratio 1 : 3 (**Res<sub>ol</sub>** : **St-*n***/**Ap-*n***). By irradiation of a solution of resveratrol in methanol with UV light (300 nm), resveratrone was synthesized yielding four additional assemblies by mixing acetone solutions of resveratrone with stilbazoles or azopyridines in the ratio 1 : 2 (resveratrone : **St-*n***/**Ap-*n***). The formation of the HBAs was proven by IR spectroscopy. Taking **Res<sub>ol</sub>(St-8)<sub>3</sub>** as representative example the IR spectra of the assembly shows a significant shift and sharpening of the signal related to the OH-vibration. Comparing the IR-spectra (Fig. S1, ESI†) of resveratrol with the **Res<sub>ol</sub>(St-8)<sub>3</sub>** assembly, a clear shift of the broad OH-band from  $\sim 3200\text{ cm}^{-1}$  to  $\sim 3100\text{ cm}^{-1}$  and the appearance of an additional band at  $\sim 2650\text{ cm}^{-1}$  can be observed, which is indicative for the formation of the hydrogen-bonded assemblies. Analogous shifts can be found for each HBA investigated in the present study.

In addition, the formation of the expected assemblies was proven by single crystal X-ray diffraction (Fig. 1). Slow evaporation

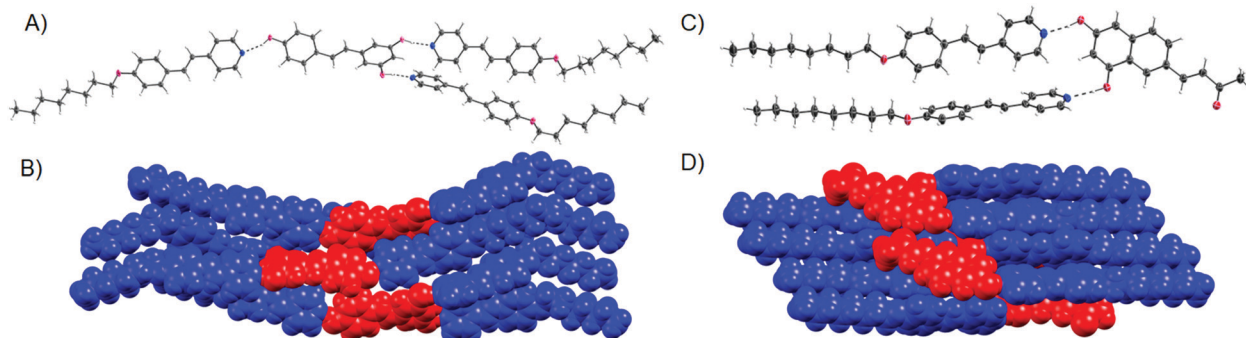


**Fig. 2** Representative POM images of the resveratrol and resveratrone assemblies. (A) Schlieren texture of the nematic phase formed by **Res<sub>ol</sub>(St-9)<sub>3</sub>** at 139 °C and the associated SAXS/WAXS pattern (B) focal-conic texture of the smectic phase of **Res<sub>on</sub>(St-8)<sub>2</sub>** at 120 °C measured with planar boundary conditions under crossed polarizers and the associated SAXS/WAXS pattern.

of acetone yielded single crystals for **Res<sub>ol</sub>(St-8)<sub>3</sub>** and **Res<sub>on</sub>(St-8)<sub>2</sub>**. **Res<sub>ol</sub>(St-8)<sub>3</sub>** cocrystallized in the space group  $P2_1/n$  and shows short hydrogen bonds between the resveratrol and the three stilbazole units ( $\text{OH} \cdots \text{N}_{\text{py}} = 1.80\text{--}1.87\text{ \AA}$ ) forming an almost linear assembly. **Res<sub>on</sub>(St-8)<sub>2</sub>** crystallized also in the space group  $P\bar{1}$  with two **St-8** units hydrogen-bonded to the resveratrone ( $\text{OH} \cdots \text{N}_{\text{py}} = 1.77\text{--}1.80\text{ \AA}$ ), which is the first successful confirmation of the resveratrone structure by X-ray analysis supporting the findings of Kim and coworkers.<sup>18</sup>

A further, indirect proof of the formation of the HBAs is given by the induction of liquid crystalline behaviour. Neither the individual hydrogen bond donating (**Res<sub>ol</sub>**, **Res<sub>on</sub>**) nor the accepting units (**St-*n***, **Ap-*n***) show LC properties, thus the liquid crystallinity arises from the self-assembly of the molecular building blocks.<sup>19</sup> After formation of the HBAs, however, the samples show the characteristic Schlieren texture of the nematic (in case of the resveratrol based assemblies) or the focal-conic texture of the smectic phase forming out of bâtonnets as proven by polarized optical microscopy. Likewise, small (SAXS) and wide angle (WAXS) X-ray scattering on **Res<sub>on</sub>(St-8)<sub>2</sub>** and **Res<sub>ol</sub>(St-9)<sub>3</sub>** (Fig. 2) show the presence of LC smectic and nematic order. Enantiotropic behaviour can be observed for **St**-HBAs, while the **Ap**-HBAs show monotropic behaviour. The summary of the LC-properties of all assemblies is illustrated in Fig. 3.

In order to understand the differences in the liquid crystalline behaviour between the resveratrol- and the resveratrone-based



**Fig. 1** (A) X-ray structures of the 3 : 1 complex of resveratrol and octylstilbazole **Res<sub>ol</sub>(St-8)<sub>3</sub>** (B) the molecular packing inside the crystal lattice of **Res<sub>ol</sub>(St-8)<sub>3</sub>**, (C) X-ray structures of the 2 : 1 complex of resveratrone and octylstilbazole **Res<sub>on</sub>(St-8)<sub>2</sub>** and (D) the molecular packing inside the crystal lattice of **Res<sub>on</sub>(St-8)<sub>2</sub>**.

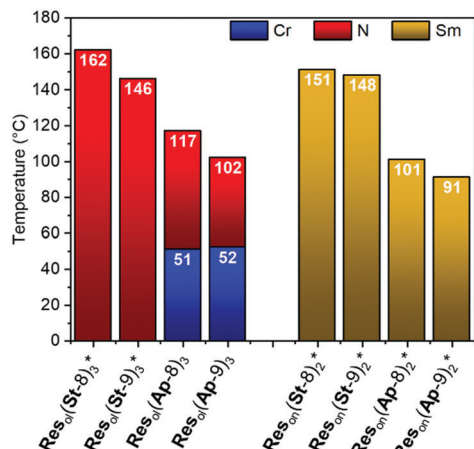


Fig. 3 Summary of the LC-properties of the formed HBAs observed on cooling under POM; clearing points are reported. The \*-marked complexes undergo a transition into a glassy state preserving the liquid crystalline texture.

assemblies, an in-depth packing analysis of the solid state structures supported by computational methods was performed for the Res<sub>ol</sub>(St-8)<sub>3</sub>, and the Res<sub>on</sub>(St-8)<sub>2</sub> assemblies.

We are well aware of the fact that the packing of the molecules in the mesophase cannot directly be correlated with the packing in the solid state. However, the identification and quantification of the non-covalent interactions in the solid state, give useful hints on the liquid crystalline behaviour of our assemblies.

Comparing the overall packing of the two solid state structures already indicated a higher degree of segregation for the Res<sub>on</sub>(St-8)<sub>2</sub> assemblies, which supports the formation of a smectic phase. For the smectic layers we extract a periodicity of 3.86 nm from SAXS. This value is about twice the length of the *c*-axis in its crystalline state and corresponds to the size of an Res<sub>on</sub>(St-8)<sub>2</sub> aggregate along its long direction. A more detailed analysis of the crystal structures was performed by using CrystalExplorer software,<sup>20</sup> which is based on the intermolecular perturbation theory developed by Turner,<sup>21</sup> and seminal work of Gavezzotti.<sup>22</sup> This methodology allowed us recently to rationalize the AIE-behaviour of a series of aromatic thioethers.<sup>23</sup> Details on the methodology are given in the ESI.† A reference molecule in the crystalline packing was defined (as provided by CrystalExplorer) and molecular pairs (= structure determinants) with surrounding molecules were analysed with respect to their intermolecular interactions. In each structure determinant, the interaction energies are calculated and split into the individual contributions of electrostatic, polarization, dispersion and repulsion (Tables S1 and S2, for each individual contribution, ESI.†). The analysis revealed that the packing of Res<sub>ol</sub>(St-8)<sub>3</sub> is mainly driven by three OH...N<sub>py</sub> hydrogen bonds, which dominates the overall interaction budget (Fig. S21, ESI.† structure determinants, 1, 2, and 3). These interactions are dominated by electrostatic, as expected for moderate-to-strong hydrogen bonds. Other, less energetically important contributions involve displaced (structure determinant 4) or T-shaped (structure determinant 6) π...π interactions, which are dominated by dispersion (Fig. S21, ESI.†). Similarly, the most important driving forces of the packing of Res<sub>on</sub>(St-8)<sub>2</sub> are the two electrostatically driven OH...N<sub>py</sub> hydrogen

bonds, which dominates the overall interaction budget (Fig. S22, ESI.† structure determinants, 1 and 2). However, there are important differences between the two structures. The OH...N<sub>py</sub> hydrogen bonds in Res<sub>on</sub>(St-8)<sub>2</sub> are stronger by about 10% compared to these of Res<sub>ol</sub>(St-8)<sub>3</sub>, which can be attributed to the enhanced electron-withdrawing capability of the naphthalene core, compared to the phenyl moiety. This promotes a superior rigidity of the Res<sub>on</sub>(St-8)<sub>2</sub> complex,<sup>24</sup> resulting in a more efficient segregation and the formations of a smectic phase.<sup>6b</sup> Especially the CH<sub>py</sub>...O<sub>carbonyl</sub> interaction of structure determinant 5 in Fig. S22, ESI.† feature important electrostatic contributions which improve the rigidity of the complex and thus might favour the presence of smectic phases.

An interesting feature of the Res<sub>ol</sub>(Ap-8)<sub>3</sub> assemblies is dual photo-activity: the reversible photo-switch due to the *trans-cis* isomerization of the azopyridine ( $\lambda = 405$  nm)<sup>12</sup> and the irreversible photo-cyclization of the resveratrol as reported by Yang *et al.*<sup>18</sup> Therefore, we investigate the photo-activity of the resveratrol and resveratrone-based assemblies by POM. Res<sub>ol</sub>(Ap-8)<sub>3</sub> was brought to its mesophase at 105 °C and irradiated with a commercially available laser pointer ( $\lambda = 405$  nm, 5 mW). Initially the sample shows the characteristic *Schlieren* texture of the nematic phase, which immediately vanished upon irradiation with light ( $\lambda = 405$  nm). After removing the UV irradiation, the *Schlieren* texture recovers within less than a second (see Fig. 4). The extinction of the texture is attributed to a photo-induced phase transition from the mesophase to the isotropic state, due to the large and reversible shape change upon *trans-cis* photoisomerization and the incompatibility of the bent and metastable *cis*-azobenzene configuration with calamitic mesophases.<sup>25,26</sup> Upon removal of the irradiation the mesophase is recovered, due to the thermal relaxation of azopyridines.<sup>27</sup> This photo-induced phase transition is reversible and could be reproduced for at least 20 cycles.

Also the resveratrone-based assemblies showed reversible, photo-induced phase transition from the smectic to the isotropic state (independent from the HB donor:acceptor ratio; 1:2 or 1:3) when exposed to UV light of  $\lambda = 405$  nm at 60 °C.

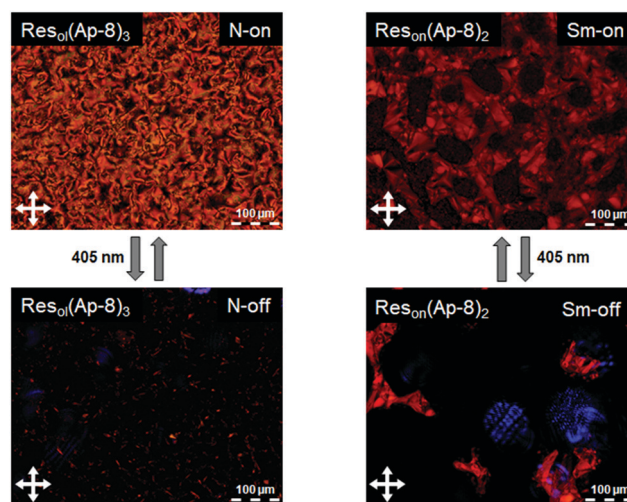


Fig. 4 POM images demonstrating the photo-switchability of Res<sub>ol</sub>(Ap-8)<sub>3</sub> (left) and Res<sub>on</sub>(Ap-8)<sub>2</sub> (right) by 405 nm.

Since resveratrol is known to show photo-cyclization upon irradiation with UV light of  $\lambda = 300$  nm to form resveratrone,<sup>16</sup> we investigated the ability of *in situ* cyclization of the HB-donor moiety in the mesophase. Therefore, the  $\text{Res}_{\text{ol}}(\text{St-8})_3$  was brought into its nematic phase at 105 °C and irradiated with UV light of  $\lambda = 300$  nm for 60 min. However, no significant difference in the POM textures was observed. We attribute the low turnover to the protection of the resveratrol against photo-cyclization by the hydrogen-bonds present in the mesophase.

In order to employ the irreversible switching of the resveratrol in a functional material, we used a recycling approach. Therefore, the reversibly photo-switchable  $\text{Res}_{\text{ol}}(\text{Ap-8})_3$  assembly was separated by column chromatography into its HB donor and acceptor component and the resveratrol was irradiated with UV light of  $\lambda = 300$  nm in methanol to yield resveratrone, which was purified and subsequently transferred to the HBA by mixing with an acetone-solution of Ap-8 in the ratio 1:2 or 1:3. The obtained assemblies showed the same photo-induced phase transition like the resveratrone complexes reported above when exposed to UV of  $\lambda = 300$  nm.

In conclusion, we obtained a series of hydrogen-bonded liquid crystalline assemblies based on resveratrol and resveratrone core units and azopyridine or stilbazole. The resveratrol-based assemblies showed nematic phases, while the resveratrone-based systems formed smectic liquid crystalline phases, which can be explained by the change in the strength of the hydrogen-bonds, the increased rigidity and the increased electronic anisotropy due to the carbonyl-group. In addition, we investigated the photo-switchability of the assemblies with UV-light of  $\lambda = 405$  and 300 nm. Irradiation of the azopyridine assemblies with  $\lambda = 405$  nm led to reversible *cis/trans* isomerisation of the azopyridine-based assemblies and induced phase transitions from the nematic to the isotropic (for the resveratrol-based assemblies). Irradiation of resveratrol recycled from the same samples with  $\lambda = 300$  nm in solution yielded photo-cyclisation of the resveratrol to resveratrone, which showed smectic phases in assemblies with azopyridine, and could reversibly switched *via* irradiation with  $\lambda = 405$  nm. Current studies focus on the *in situ* photo-cyclization combined with segregation of the assemblies in the mesophase.

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## Conflicts of interest

There are no conflicts to declare.

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