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Photoresponsive Liquid Crystals Based on Halogen Bonding of Azopyridines

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A series of photoresponsive halogen-bonded liquid crystals (LCs) were successfully constructed using molecular halogen and azopyridine compounds, which show interesting properties of photoinduced phase transition upon UV irradiation. In addition, bromine-bonded LCs were first obtained with high mesophase stability.

As the fourth state of matter, liquid crystals (LCs) show characteristics of both the controllable fluidity of an isotropic liquid and the ordered regularity of a crystalline solid, which have greatly influenced our daily life.¹ Azobenzene (AZ) is one of typical and widely studied photochromic molecules, exhibiting reversible *trans/cis* isomerization upon photoirradiation.^{1,2} Combining the photoresponsive properties of AZs with the self-organization feature of LCs, photocontrollable LC actuators have enabled a variety of applications in diverse fields, such as flat panel displays,^{1a} photonics,^{1b} photo-driven devices,^{1c,1d} and more recent nanotechnology.^{1e}

Azopyridine (AzPy) derivatives have the advantage of possessing both the light-activity related to AZs and the capability of self-assembly through pyridyl groups. For example, they can form hydrogen bonds with organic acids,³ ionic bonds with inorganic acids,⁴ organic ligands with metal ions,⁵ and halogen bonds with halide.⁶ AzPy derivatives provide a chance for further functionalization of photoresponsive LCs via differently versatile approaches, such as hydrogen bonding (HB) or halogen bonding (XB), instead of the use of covalent interactions.⁷

A typical halogen bond can be described in general as D...X-Y, where X is the electrophilic halogen atom (Lewis acid, XB donor), D is a donor of electron density (Lewis base, XB acceptor), and Y is a carbon, nitrogen or halogen atom.⁸ The binding nature of XB results in the D...X distances being shorter than the sum of the van der Waals radii of the involved

atoms, and the stronger the XB, the shorter the D...X distance.⁹ Consistent with the rationalization of XB as being an electron donation from D to the anti-bonding X-Y orbital, the formation of XB slightly lengthens the covalent X-Y bond.¹⁰ More importantly, these two noncovalent interactions of XB and HB exhibit a little difference. Firstly, XB is more directional than HB. The angle between the covalent and noncovalent bonds around the halogen atom in D...X-Y is approximately 180°, so that the higher directionality of XB with respect to HB provides a more rigid junction. Secondly, its interaction strength can be tuned by choosing suitable halogen atoms that takes part in the bonding formation without significantly changing the electronic structure of the compound.¹¹ With the exception of these differences, most of the energetic and geometric trends, as well as other features known from spectroscopic and theoretical investigations, have also been found with XB.^{10,12}

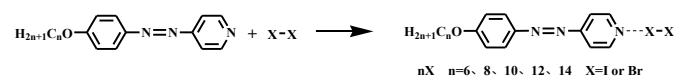


Fig. 1 Possible molecular scheme of halogen complexes of AnAzPy.

In 2004, Bruce *et al.* demonstrated the use of XB as a directing force in realization of LC formation and employed interactions between 4-alkoxystilbazoles and iodopentafluorobenzene.^{13a} Then he reported LCs formed with XB, namely complexes of molecular iodine with alkoxystilbazoles.^{13b} This system had high mesophase stability, which was predicated on an the intermolecular I...I contact. Recently, Priimagi *et al.* demonstrated that the higher directionality of XB provides a more rigid dye-polymer junction, resulting in enhanced surface-relief grating.¹¹ Meanwhile, Marco Saccone *et al.* studied XB donor molecule for assembling photosensitive co-crystals.¹⁴

The above-mentioned features of XB are shown to provide unique possibility in understanding and control of the properties

of soft matter. In the present work, we design a series of supramolecular LC complexes using halogen molecules and AzPy compounds to study the role of both the nature and the strength of XB on the LC formation and photoresponsive property. As shown in Fig. 1, halogen-bonded complexes nX were prepared using halogen molecules and AzPy derivatives having different alkyl chains (AnAzPy). Detailed experiments of synthesis, characterization, measurements and instrumentation are described in the ESI.

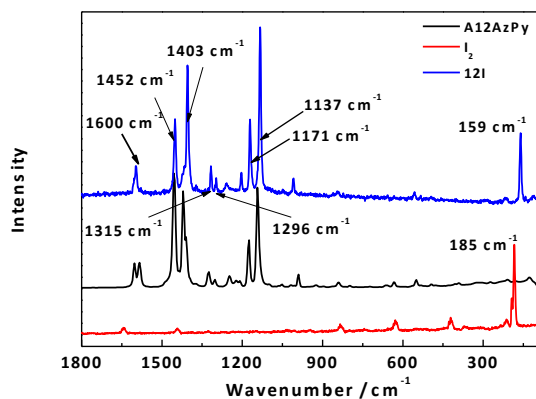


Fig. 2 Raman spectra of I₂, A12AzPy and 12I.

Raman spectroscopy is a powerful way for characterization of XB, as the halogen-stretching frequency is Raman active in both of the complexed and uncomplexed molecules.¹⁵ As shown in Fig. 2, the I-I stretching peak in molecular iodine was observed at 185 cm⁻¹. But this typical peak in the iodine-bonded complex disappeared and a new band at 159 cm⁻¹ appeared, which can be ascribed to higher electron-donating ability of AzPy derivatives. This novel absorption in Raman spectroscopy can be with certainty assigned to the stretching of the donor-halogen charge-transfer bond of the XB interaction.¹⁶ This also suggests that iodine molecules have been interacted with AzPy derivatives, proving the formation of XB via N...I interactions. Meanwhile, the N=N stretching gives rise to a band at 1403 cm⁻¹ and the band at 1600 cm⁻¹ was ascribed to the benzene quadrant stretching. The band at 1452 cm⁻¹ was attributed to an AZ ring vibration. Bands between 1315 and 1296 cm⁻¹ can be ascribed to aromatic ring vibrations, which overlaps with the C-H deformations of aliphatic side-chains.¹⁷ The Raman spectra of Br₂, A12AzPy and 12Br is given in Fig. S3. The formation of XB was further confirmed with X-ray photoelectron spectroscopy (XPS), as shown in Fig. S4 and Fig. S5.

The LC properties of halogen-bonded complexes were measured using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC), which are summarized in Table 1.

As shown in Table 1, the thermal properties of 10I, 12I and 14I are similar, which directly melted to mesophases and then reached the clearing point on heating. All of them showed focal conic fan textures upon POM observation at their LC

temperatures, as shown in Fig. 3a and Fig. S6. These LC textures often appear in smectic LCs. To further identify these mesophases, both the SAXS experiments and LC cells with homeotropic alignment were performed, as shown in Fig. S7 and Fig. S8. However, no LC behaviours were observed for 6I and 8I.

Table 1. Summary of thermal properties of halogen-bonded compounds.

Materials	T / °C	Materials	T / °C	Materials	T / °C
I ₂	C 113.5 I				
A6AzPy	C 56.7 I	6I	----	6Br	C 75.1 SmA 108.8 I
A8AzPy	C 67.9 I	8I	----	8Br	C 100.3 SmA 116.0 I
A10AzPy	C 65.9 I	10I	C 123.6 SmA 135.5 I	10Br	C 100.3 SmA 107.5 I
A12AzPy	C 72.8 I	12I	C 119.6 SmA 135.0 I	12Br	C 70.5 SmA 158.3 I
A14AzPy	C 73.3 I	14I	C 117.2 SmA 133.8 I	14Br	C 94.8 SmA 107.3 I

C: crystal; I: isotropic phase; SmA: smectic A phase.

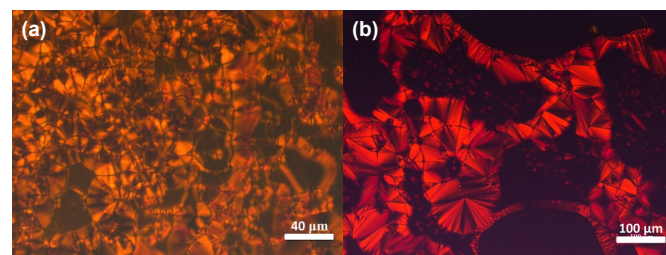


Fig. 3 POM pictures of 12I at 90 °C (a) and 6Br at 93 °C (b) on cooling from the isotropic phase.

To evaluate the bonding capability of AzPy derivatives with different halogens, molecular bromine (Br₂) was chosen as one Lewis base to prepare bromine-bonded complexes. Having found iodine complexes, Bruce attempted to prepare a bromine analogue by allowing an alkoxystilbazole with bromopentafluorobenzene and molecular bromine, respectively. Despite several attempts, they had never obtained the bromine-bonded LCs, and it is argued that the strength of halogen bonds decreases as I > Br > Cl (e.g. N...Br interactions tend to be >3 Å in the solid state),^{13,16} Interestingly, we first prepared bromine-bonded LC compounds with molecular bromine, as shown in Table 1, Fig. S9 and Fig. S10. Moreover, the bromine-bonded supramolecular LCs showed high mesophase stability in this system, as shown in Fig. S11. Hence, the results of the present AzPy-halogen system suggest that the N...Br interaction is strong enough to form ordered mesophases.

Then the photoresponsive property of the halogen-bonded samples in their LC phases was carried out upon UV irradiation at 360 nm,¹⁸ which was in-situ observed with POM. As shown in Fig. 4, the initial phase was smectic A at about 120 °C before photoirradiation, where the 12I should be in the *trans* form. Upon UV irradiation, the birefringent LC texture disappeared quickly and only the dark image was obtained, indicating the occurrence of photoinduced phase transition from an LC to isotropic phase (Video S2). Obviously, the phase transition is the result of photoisomerization of AzPy molecules from their *trans* to *cis* form as the bent-shaped *cis* isomers tend to destabilize the ordered LC phase.³ The initial LC texture was recovered after the isotropic sample was irradiated with visible

light for 80 s. Similarly to other AZ-containing LC materials,¹⁻⁴ this photochemical phase transition is brought out by the reversible photoisomerization of AzPy units.^{3,18} In this photoresponsive process, a large change in birefringence can be reversibly induced because of the LC-to-isotropic phase transition, which has potential applications as that of the other photoresponsive LC materials.^{1-4,18} However, compared to iodinated LCs, we have not observed the photochemical phase transition in brominated compounds induced by UV irradiation.

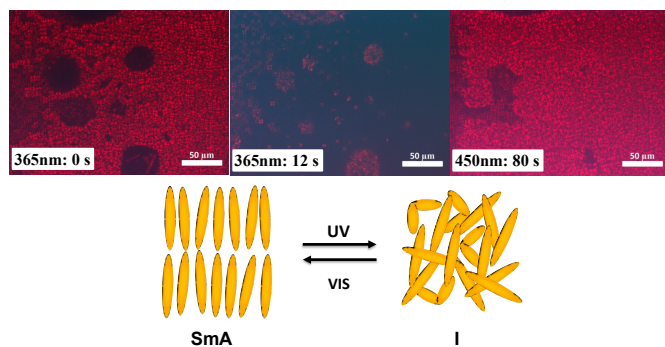


Fig. 4 POM observation of 12I at its LC phase upon UV irradiation. The right picture was obtained after 80 s irradiation of visible light.

In conclusion, supramolecularly halogen-bonded LCs were successfully fabricated using AzPy derivatives with molecular iodine or bromine. The existence of XB interactions was confirmed by XPS, Raman spectroscopy and SAXS results. Meanwhile, the supramolecular LC compounds with bromine were first prepared with high stability, indicating that the N \cdots Br interaction is strong enough to organize into ordered mesophase in this system. The iodine-bonded LCs showed reversibly photoinduced phase transition upon UV irradiation, just like other photoresponsive LC materials containing covalently or hydrogen bonded AZs. However, we have not observed the photochemical phase transition in brominated compounds induced by UV irradiation. This study would provide valuable knowledge of XB interactions for designing and manipulating novel supramolecularly functional materials.

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Electronic Supplementary Information (ESI) available: The molecular structures, synthesis, characterization and photoresponse of compounds. The videos of preparation of halogen-bonded complexes and photoinduced phase transition behaviours of the halogen-bonded complexes. See DOI: 10.1039/c000000x/

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