Supplementary Information

Photoresponsive Liquid Crystals Based on Halogen Bonding of Azopyridines

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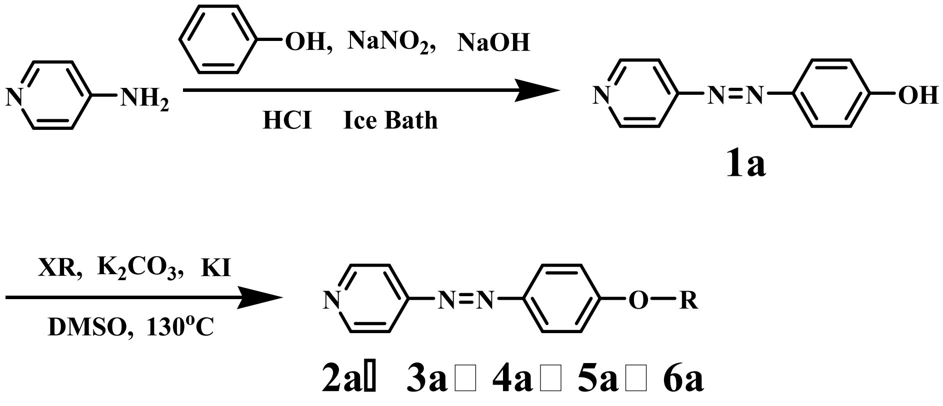
Synthesis of materials

The azopyridyl compounds were synthesized through two steps of chemical reactions, are shown in Figure S1.



2a: R=C_6H_{13}; 3a: R=C_8H_{17}; 4a: R=$C_{10}H_{21}$
5a: R=$C_{12}H_{25}$; 6a: R=$C_{14}H_{25}$; X: Cl or Br

Fig. S1 Synthesis of the azopyridyl compounds with different alkyl chain length.

<Synthesis of 4-(4-hydroxyphenylazo) pyridine (compound 1a)>

A 10 wt% NaOH aqueous solution (20 mL) including sodium nitrate (4.00 g, 58 mmol) and phenol (5.00 g, 53 mmol) were prepared and cooled to 0 °C. Subsequently, it was added dropwise to another aqueous solution with HCl 45 mL (25 mL 11N HCl and 20 mL water) and 4-aminopyridine (6.00 g, 64 mmol). The reaction mixture was stirred under an ice bath (0 °C) for 0.5 h. Then, the pH of the reaction mixture was adjusted to pH=6-7 by addition of a 10 wt% NaOH aqueous solution. A yellow precipitate was collected by filtration. The crude product was washed with water and recrystallized from acetone. After drying over a vacuum for 24 hours, the resulting bright yellow solid was obtained: yield 2.96 g (32.6 %).

<Synthesis of 4-(4-dodecylphenylazo)pyridine (compound 5a)>

1-Chlorododecane (2.05 g, 10 mmol) was dissolved in dimethyl sulfoxide (20 mL), which was added dropwise to a DMSO (20 mL) solution of K_2CO_3 (6.90 g, 5 mmol), KI (0.01g, 0.1mmol) and 4-(4-hydroxyphenylazo)pyridine (2.00 g, 10 mmol) at 130 °C. After 5 hours, the mixture was poured into water (200 mL) and then extracted with ethyl acetate (50 mL×3). A rotary evaporator was used to remove all of the solvent. The crude product was purified by silica gel column chromatography with ethyl acetate as eluent; 2.24 g of the pure product was obtained as an orange powder. The NMR spectrum of compound 2a was recorded in 5 wt% $CDCI_3$ solution, as shown in Figure 1. Yield: 61 %. Mp: 74.2 °C. ^1H NMR ($CDCI_3$) δ 8.77 (2H, d, Ar-H), δ 7.95 (2H, d, Ar-H), δ 7.71 (2H, d, Ar-H), δ 7.03 (2H, d, Ar-H), δ 4.06 (2H, t, -O-CH_2-), δ 1.85 (2H, m, -CH_2-), δ 1.46 (2H, m, -CH_2-), δ 1.27 (16H, m, -C_8H_{16}-), δ 0.90 (3H, t, -CH_3).

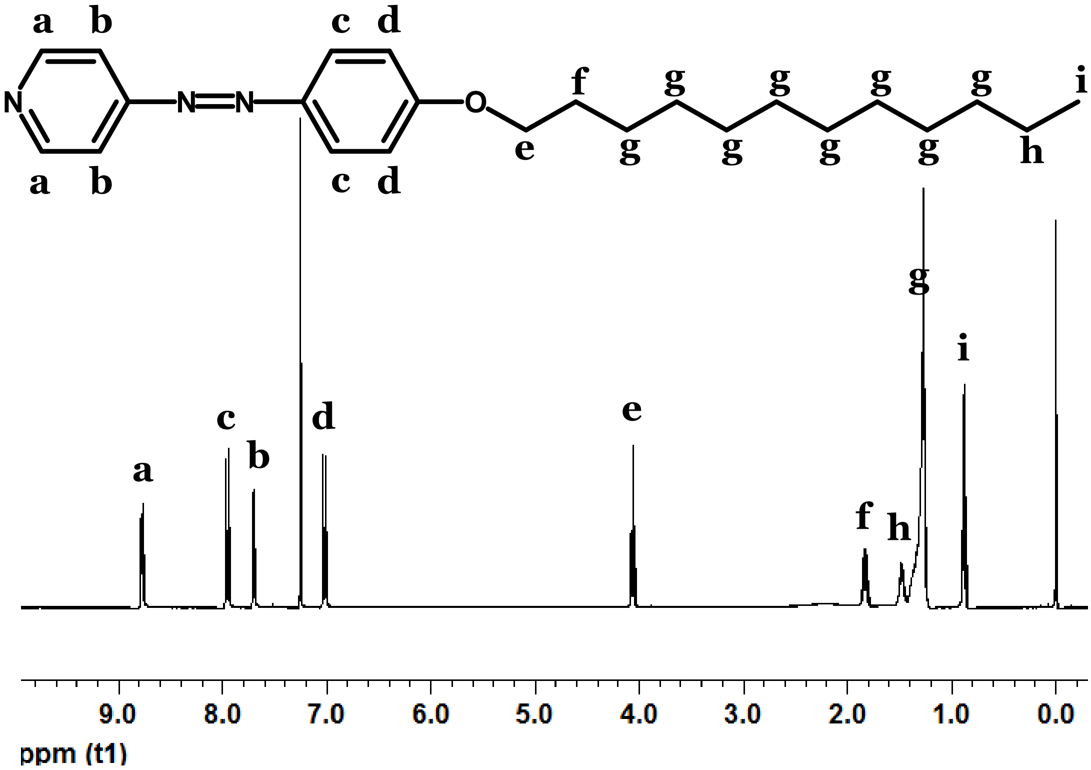


Fig. S2 ^{1}H NMR spectrum of the A12AzPy (compound 5a).

<Synthesis of compound 2a、3a、4a、6a)>

The same procedure as described was used for compound 2a、3a、4a、6a using 1-Bromohexane, 1-Bromooctane, 1-Bromodecane, 1-Bromotetradecane replaced the 1-Chlorododecane, respectively and got orange solid.

<Synthesis of iodine-bonded complexes>

The synthesis of the desired materials according to the literatures.[1] Iodine (0.1269 g, 0.5 mmol) dissolved in hexane (25 cm^3) was added to a solution of azopyridine complexes (0.5 mmol) in chloroform (5 cm^3). The contents were stirred for 2 h at room temperature. The jacinth precipitate was filtered and dried.

< Raman spectra of 12Br >

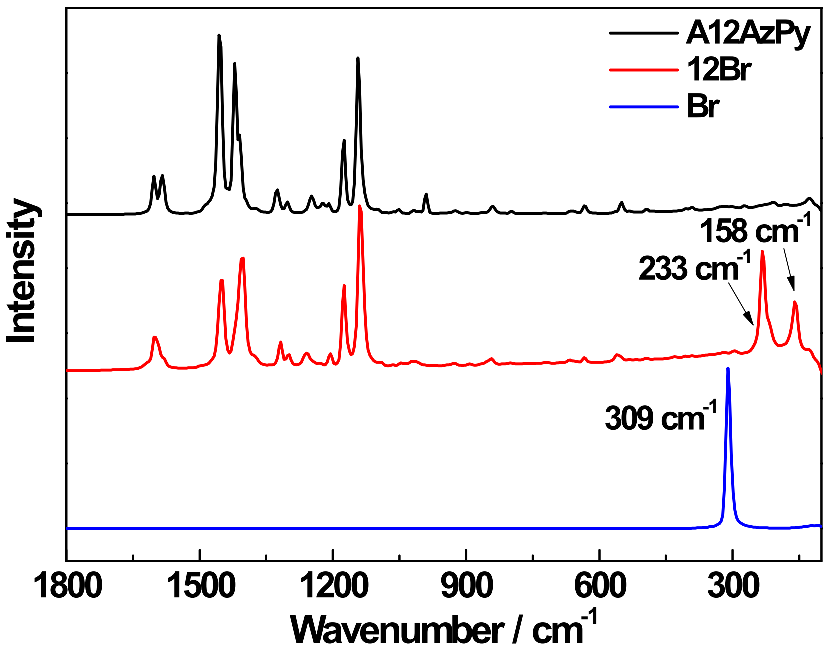


Fig. S3 Raman spectra of Br_2, A12AzPy and 12Br.

As shown in Fig. S3, the Br-Br stretching peak in molecular bromine was observed at 309 cm^{-1}. However, two Raman bands were observed for 12Br, the stronger situated around 233 cm^{-1} and the weaker at 158 cm^{-1}, indicating the considerable perturbations of the Br-Br stretching mode of the 12Br complexed. Since very few strong bromine complexes have been studied by Raman or infrared technique, the present results should be of interest.[2]

<X-ray photoelectron spectroscopy>

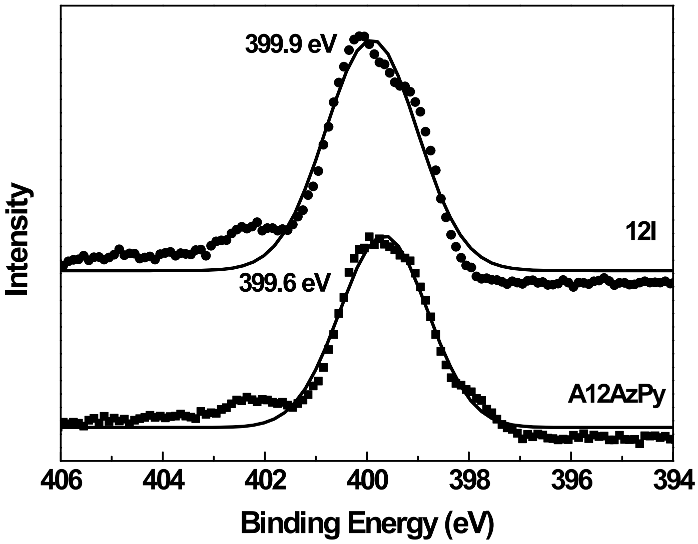


Fig. S4 Comparison of N 1s core-level spectra between one iodine-bonded complex (12I) and one compound A12AzPy.

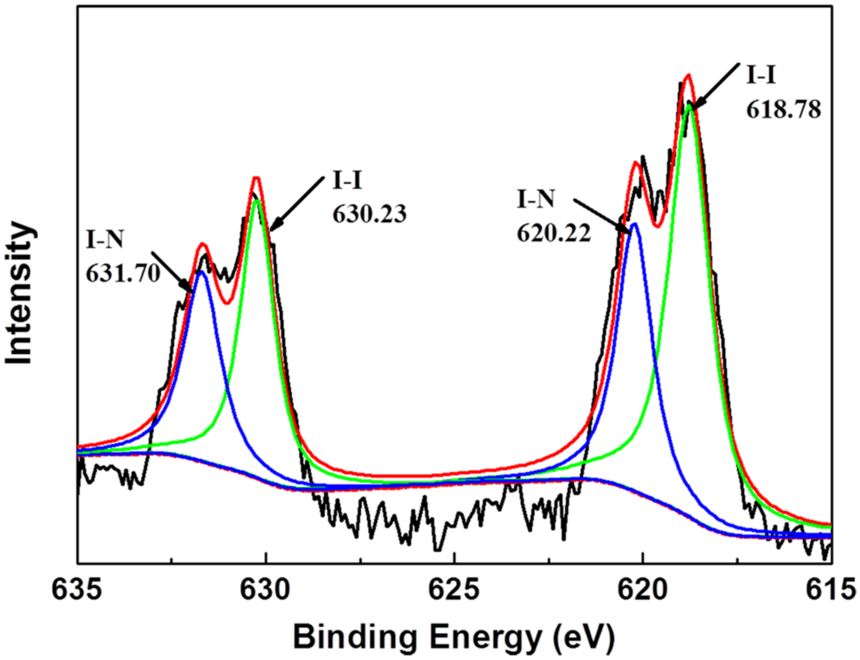


Fig. S5 I 3d core-level spectra of iodine-bonded complex (12I).

It is well-known that X-ray photoelectron spectroscopy (XPS) is one of the most effective methods for investigating halogen-bonded complexes.[3] When the molar ratio of the iodine group to the azopyridyl unit is controlled as 1:1, the binding energy of N 1s shifted from 399.6 eV to 399.9 eV, demonstrating that 12I shows 0.3 eV higher than that of pure A12AzPy. Accordingly, when the nitrogen and iodine atoms are involved in halogen bonds, the electron density of the nitrogen atom would decrease, whereas that of the iodine atom would increase. This leads to the upshift of energy level of N 1s, indicating that XB formed between A12AzPy and I_2. Such an energy-level shift is in agreement with literature values for similar interactions.[4] Fig. S5 shows the I 3d core-level spectra of iodine-bonded complex (12I).

<Phase behavior of iodine-bonded complexes>

Fig. S6 The DSC measurements of compounds (a) A10AzPy, (b) 10I, (c) A12AzPy, (d) 12I, (e) A14AzPy, and (f) 14I on heating and cooling recycle and the POM texture of compound 10I, 12I, 14I at 130 °C, 120 °C, 122 °C, respectively.

Fig. S6 shows the DSC thermograms of the raw materials and halogen-bonded complexes. All of the halogen-bonded complexes have two endothermic peaks, which due to crystalline to liquid crystal and to isotropic transitions.

<Small-angle x-ray scattering>

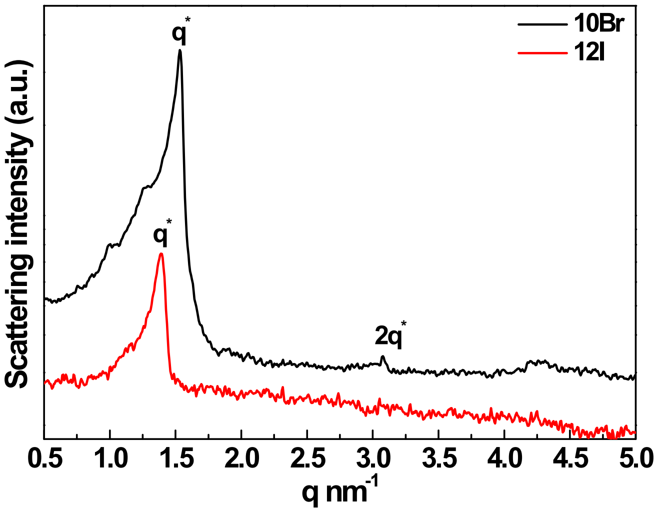


Fig. S7 SAXS patterns of 12I and 10Br after the annealing process with intensity in log scale.

To further study the phase transition and the phase structure of 12I and 10Br, 1D SAXS experiment was subjected to 5 h of annealing at a certain temperature and then cooled to room temperature by liquid nitrogen. As shown in Fig. S7, the peak with q value of 1.39 (q*) was observed for 12I. Combining the POM and DSC, that is suggests the presence of a long-range-ordered lamellar structure. Thus, the structure of 12I could be smectic A. Meanwhile, a first-order sharp peak is centered at q*=1.54 nm^{-1} and a higher-order diffraction peak appear at 2q*=3.07 nm^{-1} for 10Br. The ratio of the scattering vectors of these two peaks was approximately 1:2, indicating a smectic packing of 10Br.[5]

<Polarized optical microscopic>

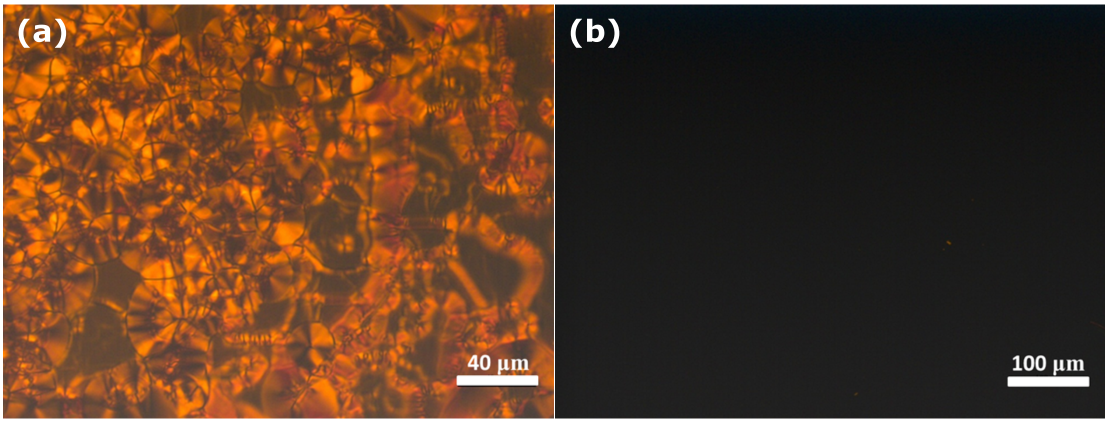


Fig. S8 POM pictures of 12I sample at 90 °C on cooling from the isotropic phase (a) and its LC cell in homeotropic alignment (b).

Dark images were observed with POM (Fig. S8b) and no change occurred when rotating the LC cells, combining the result of Small-angle x-ray scattering, indicating SmA LC phases obtained.

<Synthesis of bromine-bonded complexes>

The synthesis of the desired materials according to the literatures.[1] bromine (0.0799 g, 0.5 mmol) was added to a solution of azopyridine complexes (0.5 mmol) in chloroform (5 cm^3). The contents were stirred for 2 h at room temperature. The jacinth precipitate was filtered and dried.

<Phase behavior of bromine-bonded complexes>

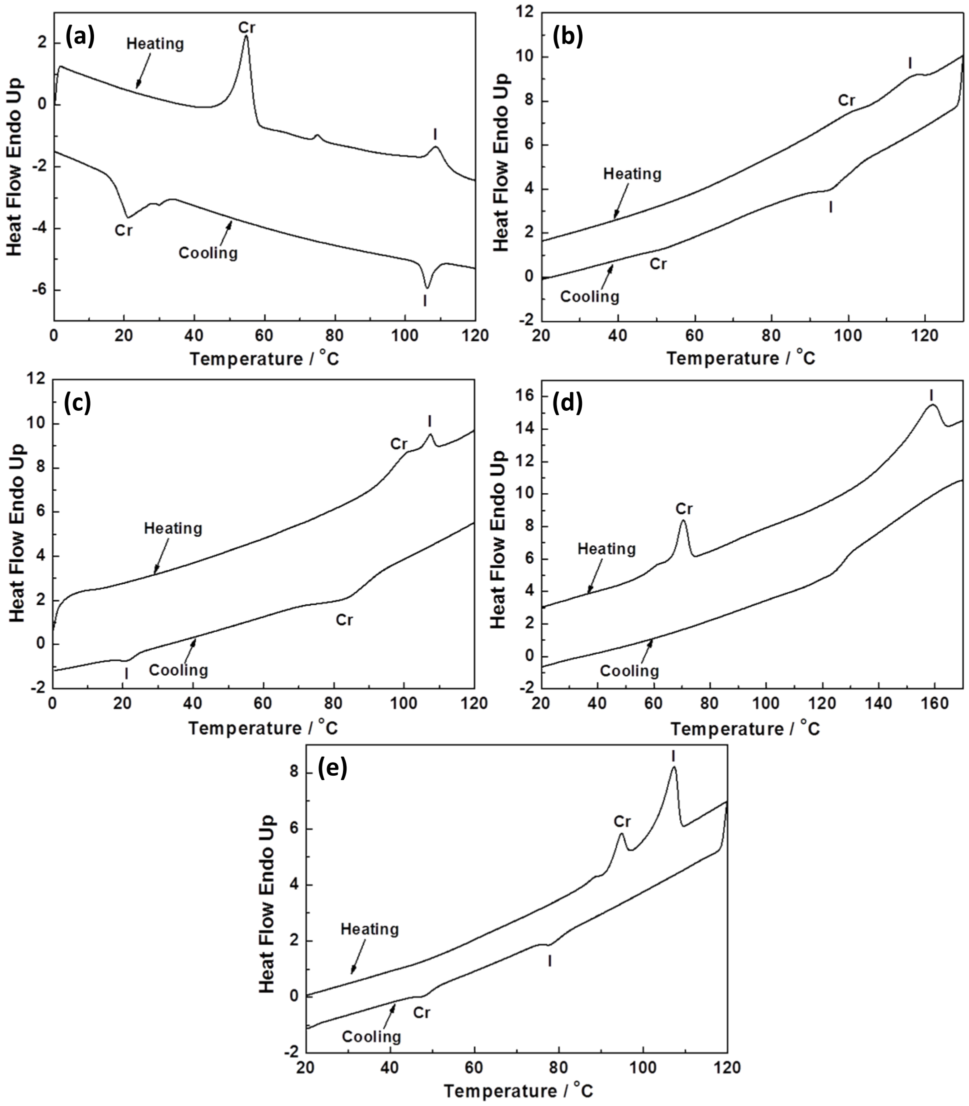


Fig. S9 The DSC measurements of compounds (a) 6Br, (b) 8Br, (c) 10Br, (d) 12Br and (e) 14Br on heating and cooling recycle.

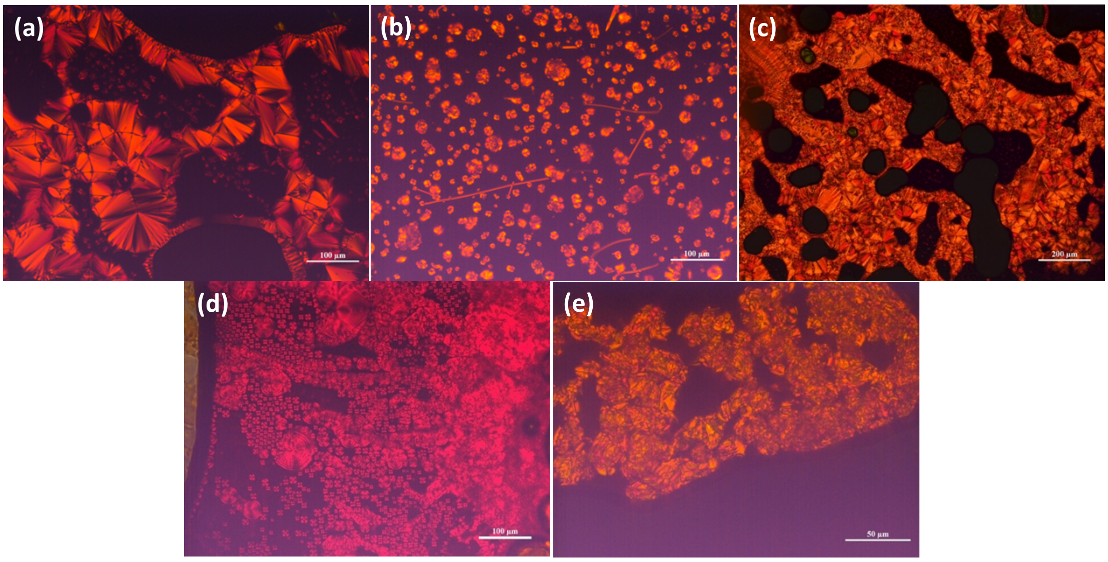


Fig. S10 The POM pictures of (a) 6Br at 93 ^{o}C, (b) 8Br at 109 ^{o}C, (c) 10Br at 105 ^{o}C, (d) 12Br at 145 ^{o}C and (e) 14Br at 106 ^{o}C.

The DSC and POM pictures have indicated that the compounds 6Br, 8Br, 10Br, 12Br and 14Br have the LC behaviours.

<Stability of halogen-bonded LCs>

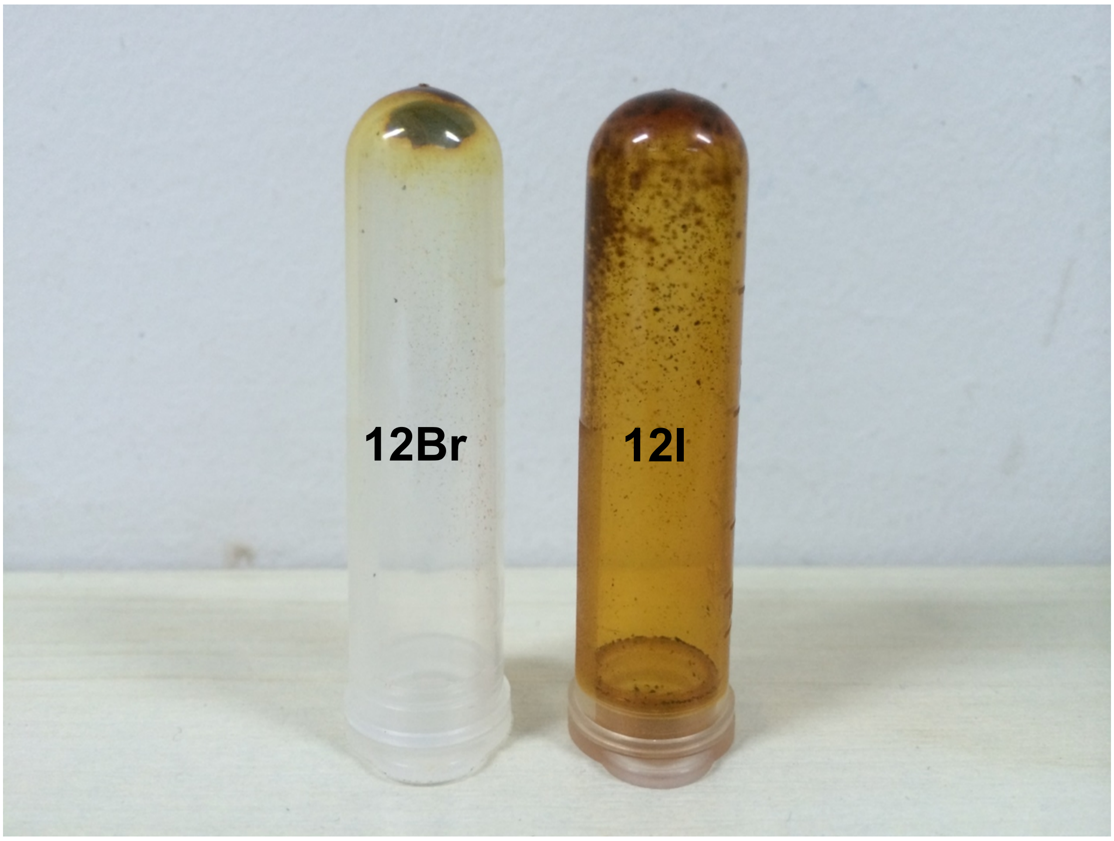


Fig. S11 The picture of the 12Br and 12I after the annealing process at 120 ^{o}C.

From this picture, the centrifuge tube contained 12I was filled with brown after the annealing process at 120 °C for 5 hours. It maybe due to the easy sublimation property of iodine. In this case, the N···Br interaction is more stability than N···I interaction in the present halogen-bonded system.

<UV-vis spectra>

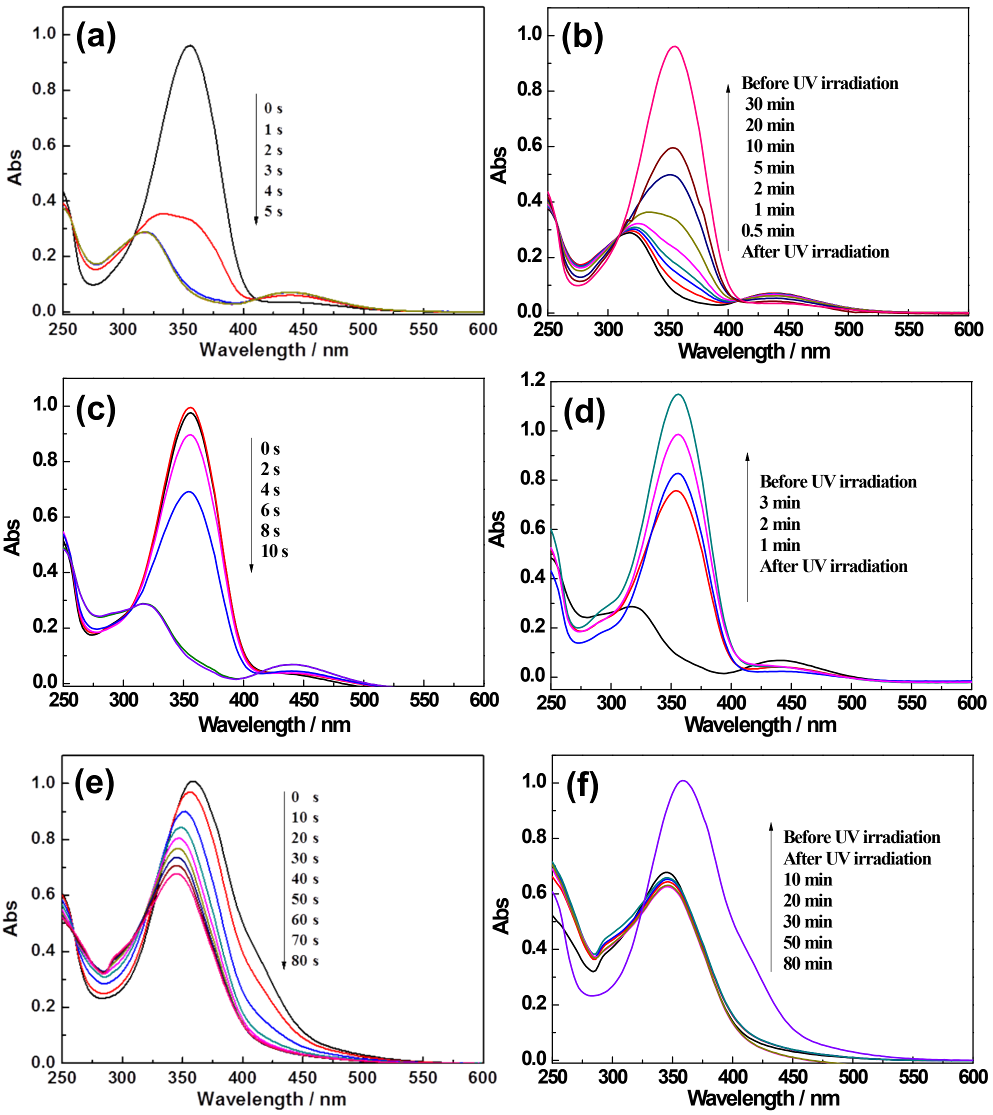


Fig. S12 UV-vis spectra of A12AzPy, 12I and 12Br in THF solution. (a), (c), (e) are A12AzPy, 12I and 12Br upon UV irradiation (at 365 nm); (b), (d), (f) are A12AzPy, 12I and 12Br relaxed in the dark after UV irradiation.

Fig. S12 shows the UV-vis absorption spectra of the A12AzPy, 12I and 12Br in THF solution. The maximum absorption peaks of the A12AzPy, 12I and 12Br in THF solution appeared at 356 nm, 356 nm and 359 nm, respectively. The absorbance peaks of A12AzPy and 12I at 450 nm increased and at 356 nm decreased upon UV irradiation. However, different photoresponsive behavior was obtained in 12Br, in which 12Br only showed a decrease in absorbance at 359 nm but not showed a decrease in absorbance at 450 nm. Meanwhile, the A12AzPy and 12I existed a back *cis-trans* isomerization by keeping them in the dark at room temperature, as shown in Fig. S12 (b) and (d). In contrast, the 12Br was hardly recovered to its initial state (Fig. S12 (f)).

< Stoichiometry >

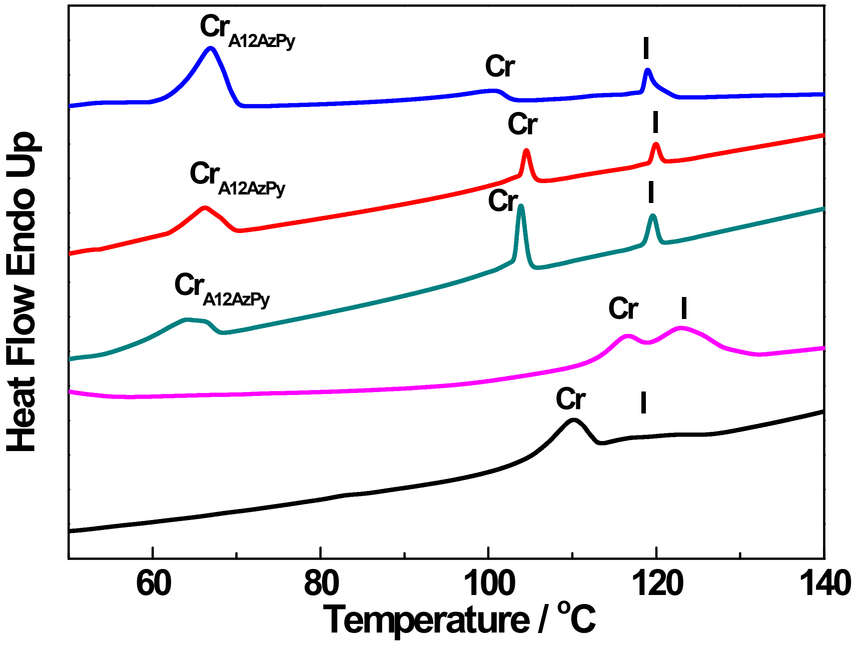


Fig. S13 The DSC curves of complexes with different molecular ratios on heating. The ratios of I_2 to A12AzPy are 1:0.5 (a), 1:1 (b), 1:1.5 (c), 1:2 (d) and 1:2.5 (e), respectively.

To make sure the stoichiometry of the complexes, we studied the different molecular ratios of complexation between I_2 and A12AzPy, as shown in Fig. S13. When the molecular ratios are 1:0.5 and 1:1, there are two endothermic peaks, which due to crystalline to liquid crystal and to isotropic transitions. When the molecular ratios are 1:1.5, 1:2 and 1:2.5, the melt point of raw material (A12AzPy) appeared, indicating the A12AzPy is excessive. According to Bruce et al,[1] the molecular ratio of I_2 to A12AzPy should be 1:1.

Measurements

^{1}H-NMR spectra of the compounds were recorded on a Bruker Avance III 400. Differential scanning calorimetry (DSC) examination was carried out on a Perkin-Elmer Pyris 6 calorimeter with a heating and a cooling rate of 10 ^{o}C/min under a dry nitrogen purge. Polarized optical microscope (POM) observations were performed with Zeiss Axio Scope A1 Microscope equipped with a hot stage. XPS photoelectron spectroscopies were made with an Axis Ultra (Kratos Analytical Ltd). Raman spectroscopies were taken on Jobin Yvon Laboratory HR800.

Supporting Video S1. Preparation of iodine-bonded complexes.

Supporting Video S2. Photoinduced phase transition behaviours of the iodine-bonded complexes.

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