Supporting Information

Transition between widened blue phases by light irradiation using photo-active bent-core liquid crystal with chiral dopant

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Contents

- 1. Absorption spectra (Figs. S1 and S2)
- 2. Helical pitch as functions of temperature and irradiation time (Figs. S3 and S4)
- 3. Molecular shape (Fig. S5)
- 4. DSC (Fig. S6)

1. Absorption spectra related to trans-cis photo-isomerization of A131

It is not easy to observe absorption spectra using LC cells of A131, since the absorbance is too high in an ultraviolet region. Here we investigated the photo-induced absorption change and relaxation after turning off ultraviolet (UV) light irradiation at 365 nm using a dilute solution of A131. UV/Vis spectrophotometer used was JASCO, V-560. We prepared tetrahydrofuran solution of A131 with the concentration of 0.005 M. As the reported document for the azo-containing bent-core material,¹ the irradiation of 365 nm UV light converts trans azo-containing LC to its cis form, while the irradiation of 436nm blue light takes *cis*-azo-containing LC back to its *trans* form. A131 material shows similar absorption spectra to the other azo-containing bent-core LCs. As shown in Fig. S1, the azo-containing A131 shows large peaks at 260 (cis) and 334 nm (trans) together with a small peak at 440 nm (cis). As the UV (handy UV, the intensity is 10 mW/cm²) irradiation time increases, the absorption at 334 nm decreases quickly while the absorption at 260 nm increases correspondingly; in the meanwhile the broad absorption at 440 nm slightly increases. Trans to cis isomerisation was almost completed within 30 s. In general azo-compounds, upon UV irradiation of around 360 nm (corresponding to the π - π * band of the azo-group) *trans* configuration changes into cis configuration.



Fig. S1. Absorption spectra of THF solution of A131 upon UV light irradiation.

After turning off the UV irradiation, the *cis* configuration thermally relaxed to the *trans* configuration with a very slow rate, as shown in Fig. S2. After UV irradiation for 30 s, *trans* almost changed to *cis*. Under complete dark for 1 h, *cis* only slightly changed to *trans*. But if the sample was kept under room light containing 420 nm (n– π * band), conversion from cis to trans was accelerated. However, even after 40 min under room light, the system did not returned back to the original condition, but in the end (more than 1 h), we obtained the initial state.



Fig. S2. Absorption spectra of THF solution of A131 before and after stopping UV light irradiation.

2. Helical pitch as functions of temperature and irradiation time

Reflection spectra were measured in BPI. Note that no selective reflection peak was observed in BPIII because of the short pitch in the UV region. Figure S3 shows the temperature dependence of the selective reflection peak. With increasing temperature, the selective reflection shifted to shorter wavelength side.



Fig. S3. Temperature dependence of selective reflection.

Next we observed selective reflection as a function of UV exposure time. As shown in Fig. S4, the selective reflection peak shows blue shift, i.e., helical pitch becomes shorter. Finally after 40 min irradiation, the selective reflection peak tends to disappear. This suggests the disorder of the BPI structure.



Fig. S4. (a) Exposure time dependence of the selective reflection peak wavelength. (b) Selective reflection spectra for various UV irradiation times.

3. Molecular shape

Molecular shape of A131 was calculated using Spartan 04. Large change in the molecular shape was predicted by *trans* to *cis* isomerisation.



Fig. S5. Molecular shape of (a) *trans* and (b) *cis* configurations of A131 calculated using Spartan 04.

4. DSC

We measured differential scanning calorimetry (DSC) using ?????. We could clearly observe the Iso-BP transition at least 20 wt% and 27 wt% mixtures, as shown in Fig. S5. The transition anomaly became smaller with increasing the content of chiral molecules and became undetectable in 38 wt% mixture. The similar observation was also reported previously.²



Fig. S6. DSC scan on cooling for 20 wt% and 27 wt% mixtures.

Supporting References

- 1. Y. M. Huang, B.-G. Zhai, F.-F. Zhou., Mol. Cryst. Liq. Cryst., 2009, 510, 34.
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