Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

Broadband reflection of polymer-stabilized chiral nematic liquid crystals induced by chiral azobenzene compounds

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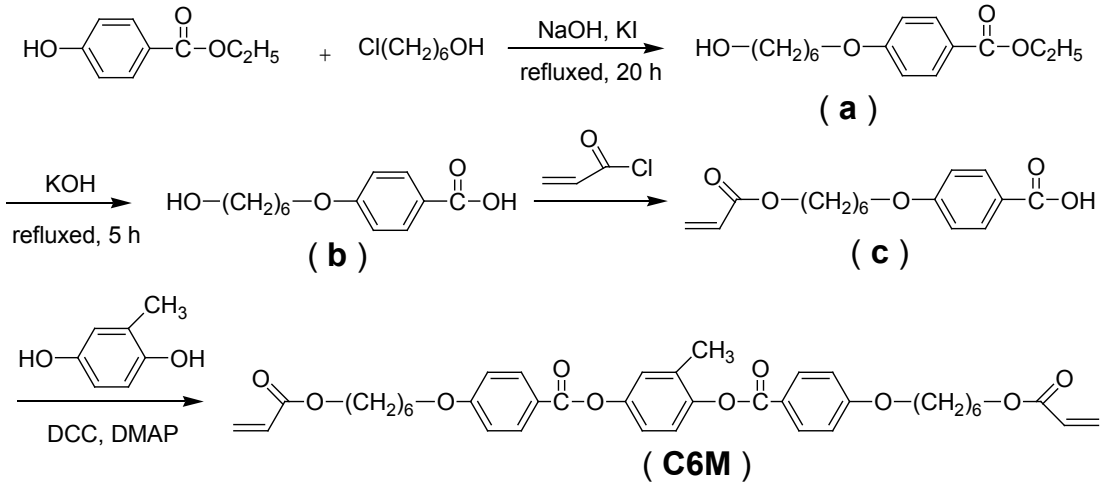
1. Synthesis and properties

1.1 General procedures for the synthesis of C6M.[1]



Scheme 1 The synthetic route to the C6M

The C6M was synthesized following the general procedure as shown in Scheme S1. The structure of the compounds was confirmed by FT-IR and ^{1}H NMR analysis.

1. *4 - (6'-hydroxyhexyloxy) benzoate* (**a**)

Ethylparaben (16.6 g, 0.1 mol), 6-chloro-1-hexanol (16.4 g, 0.12 mol), NaOH (4.0 g, 0.1 mol) and a small amount of KI were added to a stirred solution of Butanone (300 ml). The mixture was stirred at 60 ^{o}C for 20 h, and then cooled to room temperature and filtered to remove the insoluble salts. Next, the mother liquor was evaporated and the residue was washed by 300 ml solution mixed with water and NaOH (0.4 mol/L). After that, the target product was extracted by ether from the solution and then dried in vacuum. At last, a white solid was got. Yield 92%, 24 g.

2. *4 - (6'-hydroxy-hexyloxy) benzoic acid* (**b**)

KOH (15 g, 0.375 mol) and **a** (24 g, 0.9 mol) were added to 300 ml deionized water, and then stirred at 60 ^{o}C for 6 h. Next, the solution was extracted by ether and the water solution was left. After that, 20 ml HCl was added to the water solution and a white precipitation appear, and then the white precipitation was filtered and dried. At last, the precipitation was purified by recrystallization with ethanol twice and got a

white solid. Yield 80%, 17 g. FT-IR (KBr, cm^{-1}): 3400(-OH), 3200-2500(-COOH), 2946, 2868, 1689.

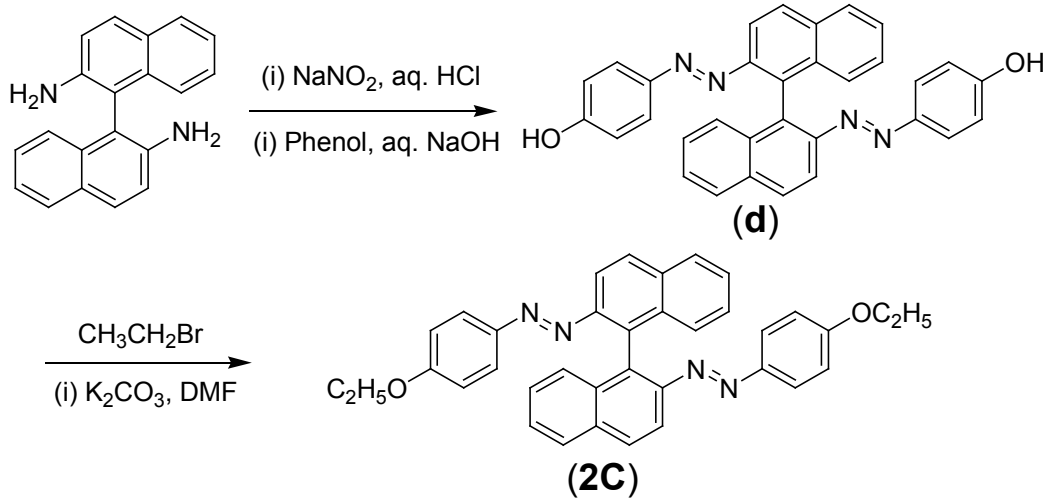
3. *4 - (6'-acryloxy-hexyloxy) benzoic acid* (**c**)

N, N-dimethylaniline (7.27g, 0.06 mol) and **b** (14.3 g, 0.06 mol) were added to 300 ml 1, 4-dioxane solution. Next, the mixture was heated to 60 ^{o}C, and then acryloyl chloride (5.4 g, 0.06 mol) was dropped and stirred for 3h. After that, the solution was poured into 1000 ml water and stirred. And then a precipitation was formed and was filtered. The precipitation was washed by water and purified by recrystallization with isopropanol twice, and then got a white solid. Yield 78%, 13.7g. FT-IR (KBr, cm^{-1}): 3300-2200 (-COOH), 1725, 1685, 1635 (-CH=CH2).

4. *1, 4 - bis (4 - (6'-acryloxy-hexyloxy) benzoyloxy) - 2 - toluene* (**C6M**)

c (3.22 g, 0.011 mol) and N, N-dicyclohexyl carbodiimide (2.48 g, 0.012 mol) were added to 30 ml stirred CH_2Cl_2, and then 80 ml solution of CH_2Cl_2 contained 2-methyl - hydroxy phenol (0.62 g, 0.005 mol) and 4-dimethylaminopyridine (0.14 g, 0.001 mol) was dropped into and stirred for 48 h. Next, the solution was filtered to remove the insoluble salts, then washed by HCl (5%) and aqueous sodium bicarbonate (5%) three times respectively, and then dried with magnesium. After that, the solution was filtered and the residue was purified by silica-gel column chromatography. At last, it was recrystallization with isopropanol twice, and then got white solid. Yield 70.5%, 2.4g. FT-IR (KBr, cm^{-1}): 2942, 2860, 1727, 1635, 1600, 1510, 1170, 760, 650. 1H-NMR (400MHz, $CDCl_3$, δ, ppm): 8.15(4H, t), 7.19-7.06(3H, m), 6.98(4H, q), 6.44(1H, d), 6.38(1H, d), 6.17-6.08(2H, q), 5.84(1H, d), 5.81(1H, d), 4.18(4H, t), 4.06(4H, t), 2.25(3H, s), 1.85(4H, m), 1.73(4H, m), 1.59-1.47(8H, m). MALDI-TOF MS (M+H) calcd for $C_{39}H_{44}O_{10}$: 672.3, found: 672.2.

1.2 General procedures for the synthesis of 2C.[2]



Scheme 2 The synthetic route to the **2C**

1. *4,4'-((1E,1'E)-[1,1'-binaphthalene]-2,2'-diylbis(diazene-2,1-diyl))diphenol* (**d**)

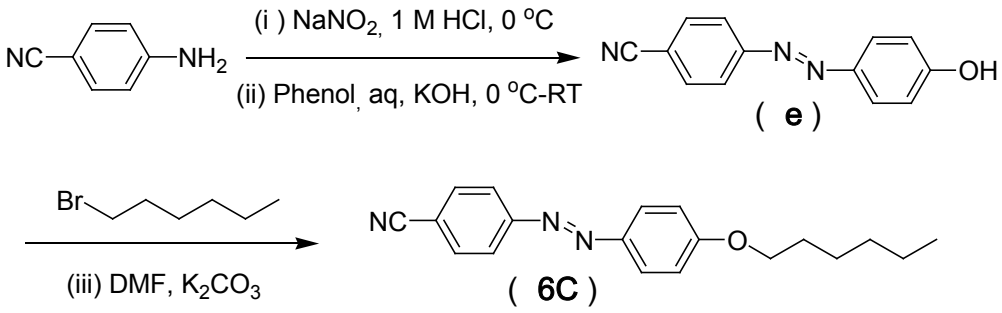
(S)-(-)-1,1'-Binaphthyl-2,2'-diamine (1.00 g, 3.52 mmol) was dissolved in a solution of H_2O (17 mL) and concentrated HCl (2.5 mL). The solution was cooled to 0 ^oC at ice water bath. A solution of sodium nitrite (0.58 g, 8.44 mmol) in H_2O (10 mL) was dropped with stirring. The resulting brown yellow suspension was dropped into the solution of Phenol (0.73, 7.74 mmol) and NaOH (0.90 g, 22.60 mmol) in H_2O (15 mL).The suspension was acidified with aqueous HCl and filtered. The precipitate was washed with H_2O and dried to get the crude **d**, which was purified by chromatography on silica gel to give an orange solid. Yield 80%, 1.4g.

2. *2,2'-bis((E)-(4-ethoxyphenyl)diazenyl)-1,1'-binaphthalene* (**2C**)

The mixture of the intermediate **d** (0.7 g, 1.40 mmol), bromoethane (0.45 g, 4.20 mmol) and potassium carbonate (0.7 g, 4.20 mmol) in DMF (50 mL) was heated to 90 ^oC with stirring for 18 h. The resulting mixture was evaporated to dryness under reduced pressure. The residue was purified by chromatography on silica gel to get orange solid **2C**. Yield 82%, 0.6 g. FT-IR (KBr, cm^{-1}):2977, 2931, 2877, 1597, 1580, 1498, 1473, 1248, 1143, 1040, 840, 821, 748. 1H-NMR (400MHz, $CDCl_3$, δ, ppm): 8.14(2H, d), 8.04(2H, d), 7.97 (4H, d), 7.49-7.42 (4H, d), 7.29 (4H, d), 6.70 (4H, d), 7.93 (4H, m), 1.35 (6H, t). MALDI-TOF MS (M+H) calcd for $C_{36}H_{30}N_4O_2$: 550.2,

found: 550.2.

1.3 General procedures for the synthesis of 6C.[3]



Scheme 3 The synthetic route to the **6C**

1. *4-((4-hydroxyphenyl)diazenyl)benzonitrile* (**e**)

4-aminobenzonitrile (8.4 g, 0.07 mol) was added to stirred solution of hydrochloric acid in 100ml water at 0-5 °C for 30 min. Then dropping another solution mixed with $NaNO_2$ (5.1 g, 0.075 mol) and urea (6 g) in 20 ml water to the reaction solution and stirred for 30min. After that, a solution mixed with phenol (6.6 g, 0.07 mol) and KOH (7.5 g, 0.08 mol) in 100 ml water was dropping into the reaction solution and stirred for 30min. The whole process was kept in ice bath. At last, adjust the PH of the mixture with hydrochloric acid and KOH to 3-5 and filtered, the solid was washed by water and removed the water in vacuum to get a brown solid. Yield 82.5%, 13.1 g. FT-IR (KBr, cm^{-1}): 3318, 2239, 1606, 1586, 1462, 1280, 1217, 1138, 845, 556.

2. *4-(2-(4-(hexyloxy)phenyl)diazenyl)benzonitrile* (**6C**)

1-bromohexane (1.65 g, 0.01 mol), **e** (2.2 g, 0.01 mol) and K_2CO_3 (1.7 g, 0.01 mol) were added to 30 ml N, N-dimethylformamide. The mixture was stirred at 90 °C for 15 h, and then poured into 200 ml water. A precipitation formed and was filtered. Then the precipitation was washed by water and purified by recrystallization with ethanol twice, and then got white solid. Yield 81%, 2.5g. FT-IR (KBr, cm^{-1}): 2938, 2916, 2867, 2220, 1598, 1581, 1497, 1473, 1395, 1248, 1138, 1029, 841, 557. 1H-NMR (300MHz, $CDCl_3$, δ, ppm): 7.97(4H, m), 7.80(2H, d), 7.03(2H, d), 4.07(2H, t), 1.83(2H, t), 1.50(2H, t), 1.42(4H, m), 0.93(3H, t). MALDI-TOF MS (M+H) calcd for $C_{19}H_{21}N_3O$: 307.2, found: 307.2.

2. The absorption property of chiral azobenzene compound 2C

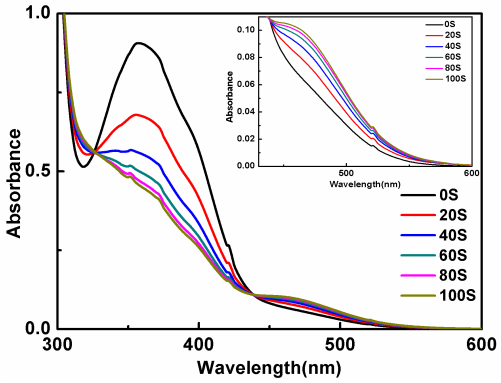


Fig. 1 Change of absorption spectrum of **2C** when irradiated by UV

The absorption properties of the **2C** were determined by the UV-Vis spectroscopy as shown in Fig. 1. The UV-Vis spectroscopy of **2C** was measured in CH_2Cl_2 at 25 ^oC and the corresponding change upon UV light irradiation were studied. It can be found that there was two absorption bands show on the UV spectrum of the pure compound **2C** between 300nm and 500nm region. The one between 300nm and 400nm with the maximum absorption at 360nm is related to π-π* transition of the azo-chromophore while the other one between 400nm and 500nm is related to the n-π* absorption[4]. Owing to photochemical *trans* to *cis* isomerization, the maximum absorption at 360 nm decreases gradually while the 460nm one increases upon UV irradiation, as seen at Fig. 1. After UV irradiation for about 100 s, the photostationary stationary state was reached.

3. The photoresopnsive of 2C doped into liquid crystal

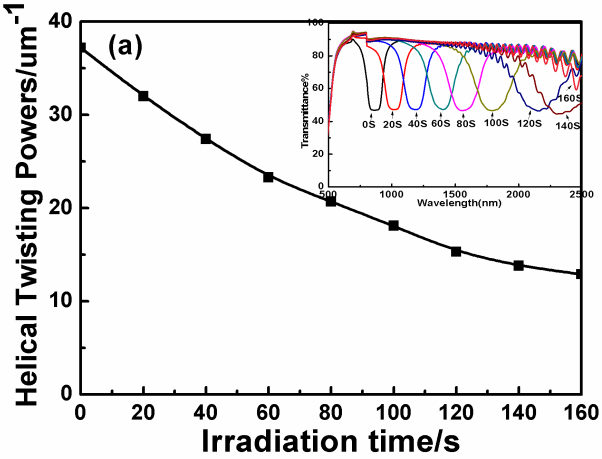


Fig. 2 The HTPs change as the irradiation time increase, the insert is the change of transmittance spectra as the irradiation time increase

The HTPs of the **2C** is determined by the transmittance spectra as shown in Fig. 2.The mixture contains 5% **2C** and 95% SLC-1717. The former studies have indicated that the HTPs can be determined by[5]:

$$\mathrm{HTPs} = \frac{\bar{n}}{\lambda_m \chi_c} \qquad (1)$$

Where $\bar{n}$, λ_m, χ_c are the average refractive index, central reflection wavelength and concentration of the chiral compound. As shown in Fig. 2, it can be found that the reflection wavelengths of the mixture increase with the UV irradiation time increase, which indicates that the HTPs of the mixture decrease with the UV irradiation time increase, as shown in Fig. 2.

4. The detail information of the sample 1-4

Table 1 The composition and phase transition temperature of the samples

Sample no.	SLC-1717/Iso-6OBA2/ C6M/651/2C (wt%)	λ_m /nm a	T_{Cr-N*}/°C	T_{N*-I}/°C
4	81.96/2.34/15.00/0.40/0.30	1280	-10	83.7
5	81.87/1.92/15.00/0.40/0.90	1280	-10	82.6

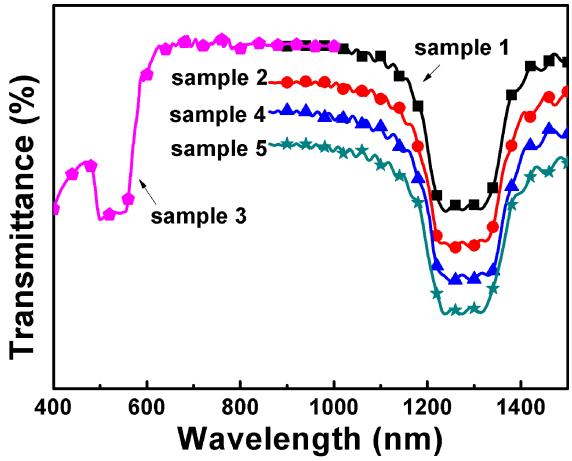


Fig. 3 The transmittance spectra before irradiation of sample1-5.

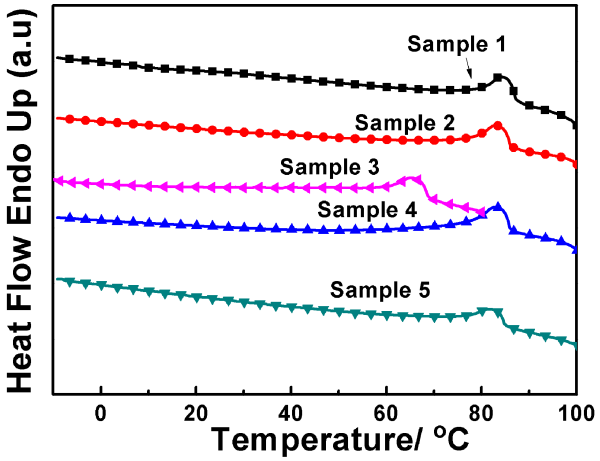


Fig. 4 The DSC of sample 1-5 before irradiated by UV

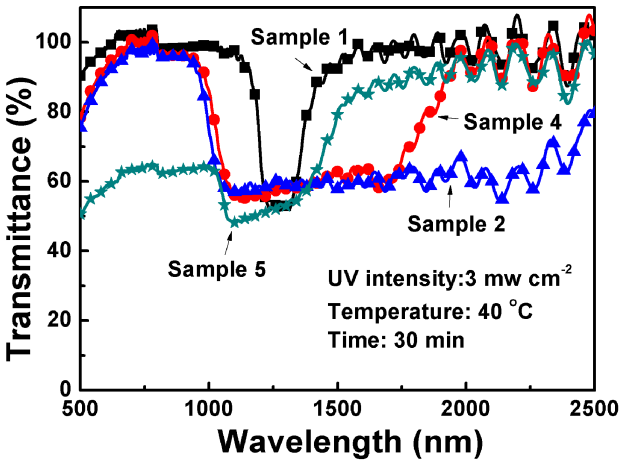


Fig. 5 The transmittance spectra of the samples after irradiated by UV

Fig. 5 is the transmittance spectra of the samples after polymerization. It can be found that the reflection wavelength of the samples can be greatly affected by the concentration of **2C**, which is broadened first and then decrease as the fraction of **2C** increase. And while the fraction of 2C is 0.6%, the reflection wavelength of the sample is the widest, which is about 1400 nm covering 1000-2400 nm. However, with the fraction of **2C** increases to 0.9%, the reflection wavelength of the sample becomes smaller. It can be attributed to strong gradient of UV intensity forms in the cell, which results in that the polymerization rate much faster than the diffusion rate, that is, C6M had polymerized before the diffusion process occurs. So the diffusion of N*-LC is restricted and then prevent the formation of gradient distribution of helix.

5. The transmittance spectral of the sample 3.

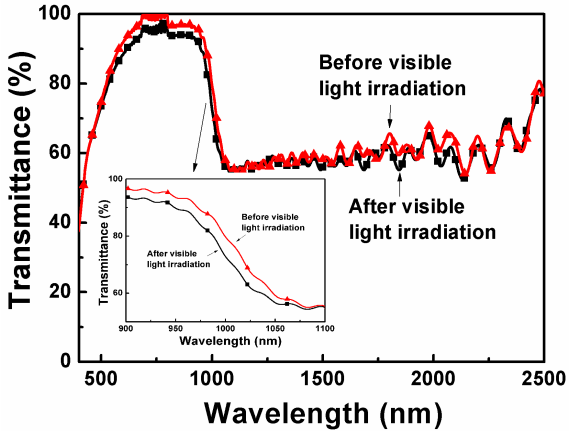


Fig. 6 The transmittance spectral of the sample 3 (before or after visible light irradiation).

Fig. 6 is the transmittance spectral before or after visible light irradiation of the sample 3. It can be found that the one with visible light irradiation is wider than the one without visible light irradiation, which can be seen at the position of 1000 nm. Compare with the location of 2400 nm, which without any change with visible light irradiation, it can be inferred that the 2C have isomerized only at one part of the cell. So the isomerization of 2C can further expand the reflection wavelength of the N*-LC.

6. The absorptivity of the Dye, 6C and 2C.

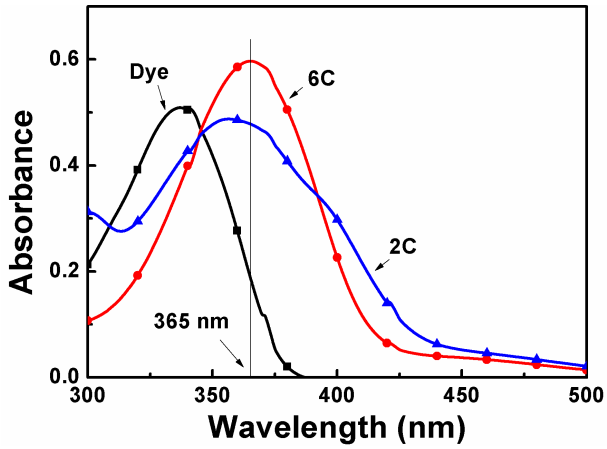


Fig. 7 The absorbance spectra of dye, 6C and 2C dissolve in CH_2Cl_2

Table 2 The concentration, absorbance at 365nm, absorptivity and molar absorptivity of the dye, 6C and 2C dissolved in CH_2Cl_2 at 365 nm

Compound	Concentration g L-1	Absorbance at 365 nm	Absorptivity (L g-1.cm-1)	Molar absorptivity (L mol-1.cm-1)
Dye	0.01	0.19	19.00	8.45*103
6C	0.01	0.60	60.00	1.75*104
2C	0.01	0.48	48.00	2.64*104

Depending on the transmittance spectra of the compounds dissolve in CH_2Cl_2, the absorptivity of the compounds dissolved in CH_2Cl_2 can be calculated as shown in Table 2. It can be calculated by the following formula[6]:

$$E=A/CL \quad (2)$$

$$\varepsilon=ME \quad (3)$$

where A is the absorbance, E is the absorptivity, C is the concentration of the compound, L is the optical path difference, M is the molecular molar mass and ε is the molar absorptivity.

7. The composites of the sample with Dye, 6C and 2C.

Depending on the formula (2), it can be found that the concentration of the compound is inversely proportional to the absorptivity. In order to obtain same absorbance, the concentration of dye and **6C** are determined to 1.52% and 0.48% when the fraction of **2C** is 0.6%, which can be calculated by formula (2) and the detail composites can be seen at Table 3.

Table 3 The composites of the sample doped with **Dye**, **6C** and **2C**.

Sample	SLC-1717/Iso-6OBA2/C6M/651 (wt%)	**Dye** (wt%)	**6C** (wt%)	**2C** (wt%)
5	80.58/2.50/15.00/0.40	1.52		
6	81.59/2.53/15.00/0.40		0.48	
7	81.87/2.13/15.00/0.40			0.60

References

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