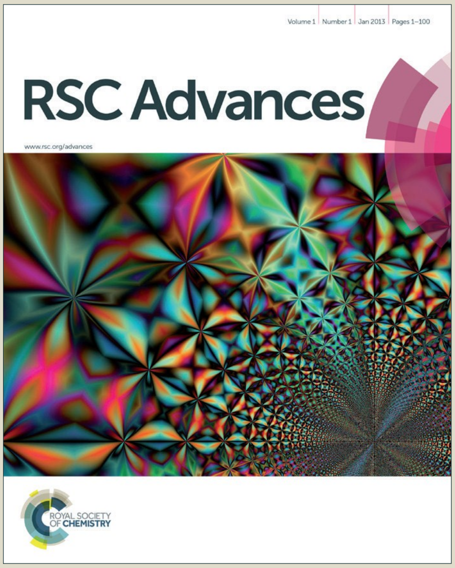
# RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

# Reversible photoresponsive chiral liquid crystal and multistimuli responsive organogels based on a cholesterol-azobenzene dimesogen

Xiaoping Tan,[a] Zhi Li,[a] Meng Xia,[a] Xiaohong Cheng*[a]

[a] Key Laboratory of Medicinal Chemistry for Natural Resources, Chemistry Department,
Yunnan University, Kunming, Yunnan 650091, P. R. China
Fax: (+86) 871 5032905
E-mail: xhcheng@ynu.edu.cn

**Abstract:** An azobenzene based mesogen with a CN group at one end and a cholesterol carbonate attached to the opposite end was synthesized. This compound is a reversible photoresponsive chiral liquid crystal, capable of formation of multistimuli responsive organogels in organic solvents. The liquid crystalline, photo responsive and gelling properties as well as chiral induction and chiral amplification properties were demonstrated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), atomic force microscope (AFM), and affected by UV irradiation. The compound can act as chiral mesogenic dye dopants to induce a high helical-twisting chiral phase in the common nematic phase of 5CB. This compound can show reversible photoresponsive properties in solution, in the liquid crystalline state and in the gel state. The gel formed by this compound in organic solvents can be reversible modified under different environmental stimuli including light, temperature and shear. SEM and AFM reveal that the gelator molecules self-assemble into helical fibers of 58–130 nm in width and tens of micrometers in length and these fibers form three-dimensional networks.

**Keywords:** azobenzene, liquid crystal, photoisomerisation, gellation

---

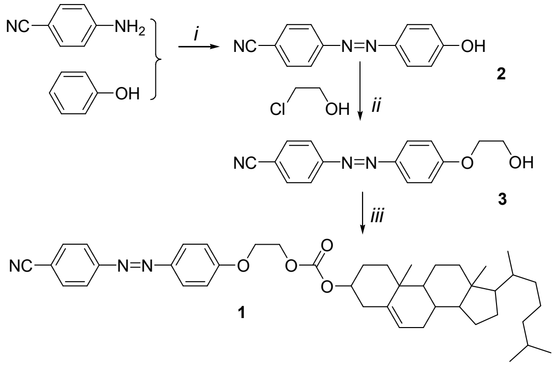
## Introduction

Two important moieties in the supramolecular chemistry of liquid crystals are azobenzene and cholesterol. The azobenzene group is well known for its photoresponsive characteristics[1,2,3,4,5,6,7] and the cholestesteryl unit is special, because of both, its chirality[8,9] and its gelation properties[10,11,12]. It is possible to combine the photoresponsive property of azobenzene with the chiral characteristic and gelation ability of cholesterol to generate new kind of molecular self assembly systems such as LCs and gels with photoresponsive chiral character. Unsymmetrical cholesterol-azobenzene couples were reported mostly as mesogens which could form chiral mesophases including blue phases (BP),[13,14,15,16] chiral nematic (N*)[17,18,19,20], twist grain boundary (TGB)[21] and chiral smectic C (SmC*)[22] phases with photoresponsive character which could be applied for optical switching, in liquid crystal display, holography and data storage [23, 24, 25]. Though the gelation properties of dimesogens were usually not considered, some reports about symmetrical trimesogens incorporating two cholesterol groups as terminal groups at a central azobenzene core unit, were focused on the multiresponsive behaviour combining LC phase formation and gel formation[26,27,28,29] Only recently gelation properties of LC dimesogens combining azobenzene and cholesterol units, have been reported. [30] However, in this case the LC phase characterization was only preliminary and chirality of the formed LC phases was not considered. Herein we report a new unsymmetric cholesterol-azobenzene dimesogen which shows photoresponsive LC, chiral induction, as well as gel formation. In addition, the structure of the dimesogen reported here is different from previous examples[19,20,30] by having a CN group instead of alkyl, acyl or alkoxy chains at the azobenzene moiety. The CN group is known to make a significant difference in LC self-assembly compared to all other substituents, as evidenced by the great success of the cyanobiphenyls (*n*-CB’s) compared to any other biphenyl based LC. [31]

The mesophase behavior of the dimesogen **1** (see Scheme 1) reported here was carefully studied by POM and DSC. It shows a chiral nematic phase (N*) on heating and a phase transition between N* and a smectic C phase (SmC*) on cooling. This chiral mesogenic dye can be added as dopant to a large amount of a common nematic liquid crystal host to induce mesophase chirality and magnify the photocontrolling effect. The gelation test revealed that this compound could gelate organic solvents. The gels could respond to a number of environmental stimuli including light, temperature and shear forces. SEM studies reveals that the gelator molecules self-assemble into fibers which further order into three-dimensional networks. AFM reveal that the fibers have helical conformations. The photoresponsive character of this compound was proven in solution, in the LC state as well as in the gel state.

## Results and discussion

### *Synthesis*



**Scheme 1** Synthesis of compound **1** *Reagents and conditions*: (*i*) HCl, $NaNO_2$, $H_2O$, 0~5°C, 2 h, 80%; (*ii*) 2-chloroethanol, $K_2CO_3$, KI, DMF, 90°C, 24 h, 87%; (*iii*) toluene, pyridine, cholesteryl chloroformate, 78%.

The dimesogen **1** was synthesized starting with an azo coupling reaction between the diazonium salt of 4-aminobenzonitrile and phenol. The obtained azobenzene **2** was further etherified with 2-chloroethanol yielding **3**. **3** was then condensed with cholesteryl chloroformate gave the final product **1.** The target compound was purified by column chromatography and crystallization from methanol/chloroform (10/1).

### *Liquid crystalline properties*

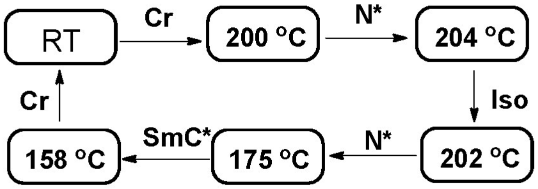
The liquid crystalline properties of compound **1** were studied by polarizing optical microscopy (POM, Optiphot 2, Nikon, in conjunction with a FP 82 HT heating stage, Mettler). The UV irradiation was carried out by a 10 mW/cm$^2$ UV lamp with a 365 nm peak wavelength.

Compound **1** was investigated by POM and DSC, the observed phase behavior is shown in Scheme 2. It forms only the chiral nematic phase (N*) on heating, but a phase transition between the N* phase and a chiral smectic C phase (SmC*) was observed on cooling (Fig. S3). The N* phase was identified by the coexistence of cholesteric schlieren textures and fan-like textures (Fig. 1a). On cooling mainly the fan texture is formed, but applying shear force transforms the texture into a cholesteric oily streaks texture (see Fig. 1b). The N* phase was observed only in a small temperature range (4 K) on heating. During cooling, the N* phase develops at 202 °C, and changes to a smectic C* phase at 175 °C (Fig. 1c).

The light induced phase changes were studied in the following way. On cooling from the isotropic state, the sample was maintained at 168 °C for 5 minutes or longer to reach thermal equilibrium and then exposed at this temperature to UV irradiation at 365 nm with an intensity of 10 mW/cm$^2$ for 10 s, the SmC* phase disappeared gradually and transferred to the N* phase as evidenced by a texture change as shown in Fig. 2b. After 15 s the N* phase was gradually transferred to the isotropic liquid state throughout the whole irradiated area (see Fig. 2c). The phase transitions are due to the fact that the increasing content of non-linear azobenzene *cis* isomers distort the molecular packing. After the exposure, the sample was observed in visible light at the same temperature of 168 °C and the *cis*–*trans* recovery took place, the Isotropic-N* and N*-SmC* phase transitons were observed within 15 s and 30 s respectively (see Fig. 2d, 2e, 2f). So it seems that the *trans*-to-*cis* photo-isomerization effect on the liquid crystalline property of the compound reported here is very strong. The entire photochemical switching process in **1** is schematically represented in Fig. 3.

**Scheme 2.** Observed phase behavior for **1** by POM[a]

**1**



[a] RT = room temperature; Cr = crystalline; SmC* = smectic C phase; N* = chiral nematic phase; Iso =.isotropic liquid.

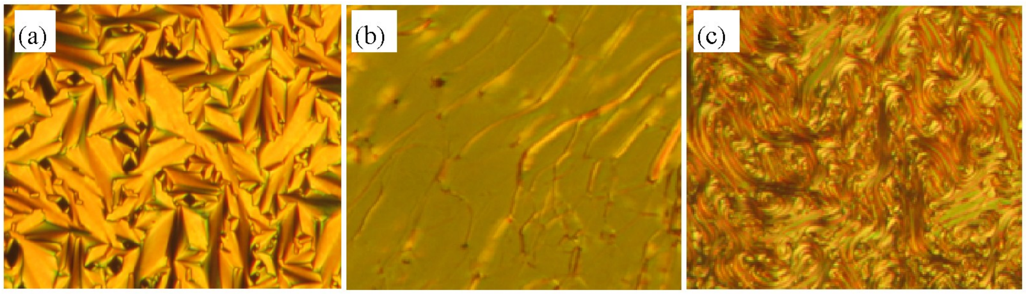


**Fig. 1** POM texture of compound **1** (a) and (b) the N* phase on heating at 200 °C , (c) the SmC* phase on cooling at 175 °C.

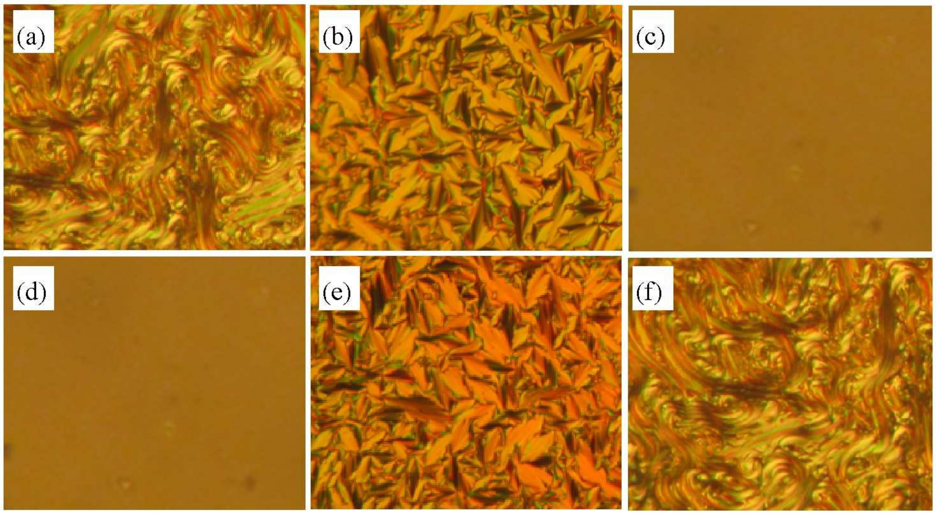


**Fig.** 2 Textural changes as observed by POM at the photoinduced SmC*-N*-Iso transitions and the relaxation Iso-N*-SmC* as observed for compound **1** at 168 °C: (a), before UV irradiation; (b) and (c), after UV irradiation for 10 s, 20 s; (d), before visible light irradiation; (e) and (f), after visible light irradiation for 15 s, 30 s).

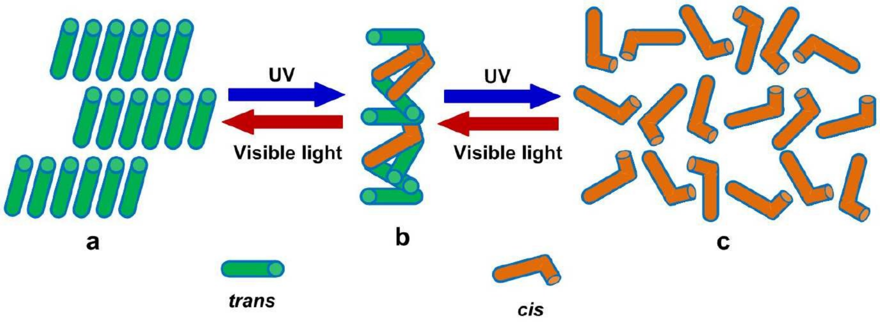


**Fig. 3** Schematic illustration of the photochemical switching process in **1** at LC state: (a) SmC* phase (simplified, shown without helix), (b) N* phase, and (c) Isotropic phase.

In order to identify the chiral induction and chiral amplification effect of **1**, the achiral nematic liquid crystal 5CB (4'-pentyl-4-cyanobiphenyl, N-I transition at 35 °C) was doped with **1** (a mixture of 20% **1** in 5CB). The mixture was put between two thin quartz glass sheets to form a thin film and was placed on a heat stage that can control the sample temperature at a rate of 1 K/ min. A typical fingerprint helical texture was observed at 28 °C, the helical axis of the helical superstructure was perpendicular to the surface normal and the helical pitch was estimated to be 50 μm as shown in Fig. 4a. The sample was exposed to UV irradiation at 365 nm with an intensity of 10 mW/cm$^2$ for 2 s. The helical pitch length of the N* phase was gradually increased and a typical schlieren texture of the achiral N phase was observed (Fig. 4b) under a vertically aligned surface condition. Upon further irradiation with UV light for 5 s, dark spots started to appear in the N phase and developed quickly, and eventually the N-Iso phase transition took place throughout the whole irradiated area. This indicates that the sample transforms to the isotropic liquid phase as evidenced by a texture change as shown in Fig. 4c. It is shown by this experiment that the conversion from the *trans* to the *cis* configuration of the dopant **1** leads to destabilization of the liquid crystalline phase of the mixture. Removal of UV light led to the reverse process of N* domain formation from the isotropic phase within 10 s (see Fig. 4d). So the *trans-cis* photoisomerization allows a reversible switching between N* and Iso at a fixed temperature. This result shows that it is possible to control the phase transitions between a smectic and a chiral N* phase and an achiral isotropic liquid phase by tuning the wavelength of irradiated light, indicating great potentials in the chiral photo-induced molecular switches.[32]

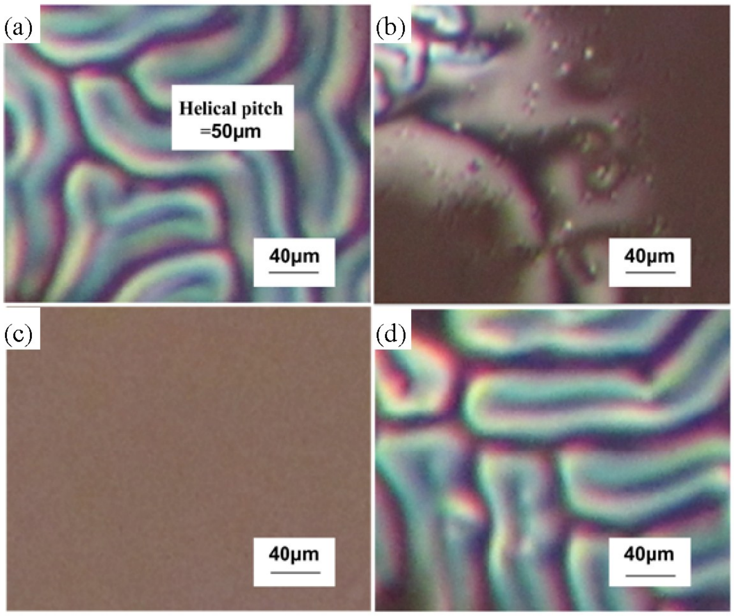


**Fig. 4** POM textures of the mixture of 20% **1** in 5CB on cooling at 26 °C: (a) before UV irradiation; (b) and (c) after UV irradiation for 2 s and 5s respectively; (d) after removal of UV light.

### *Photoisomerization behavior*

The azobenzene unit of compound **1** in the *trans*-form showed a strong absorbtion band in the UV region (~330 nm) which is attributed to the π-π* transition, and a weakly absorbing band in the visible region (~450 nm) due to the n-π* transition. The *trans*-form is generally more stable than the *cis*-form, but each isomer can be converted into the other by light irradiation. The *trans-cis* transition under UV light irradiation leads to a decrease of the absorption at around 330 nm and an increase at around 450 nm, while the reverse *trans-cis* transition under visible light irradiation leads to an increase of the absorption at around 330 nm and an decrease at around 450 nm. For the compound, under the irradiation of 365 nm UV light of its $CH_2Cl_2$ solution (1 ×

$10^{-5}$ M), the *trans-cis* transition was completely achieved in 120 s (see Fig. 5a). Under visible light, the reverse *trans-cis* transition process was achieved within 240 s (see Fig. 5b).

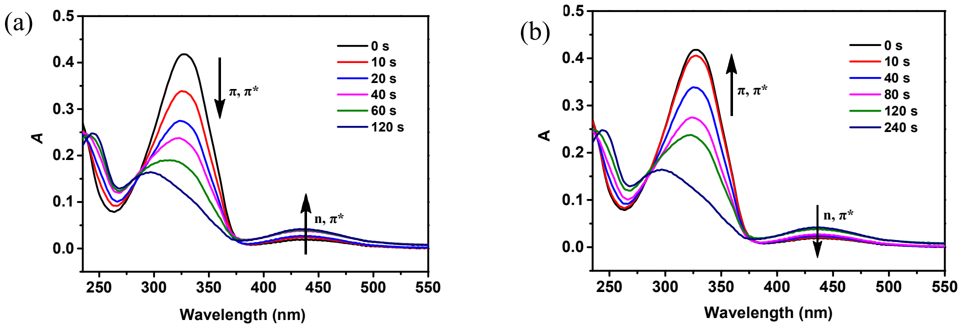


**Fig. 5** Time dependent UV Spectra of **1** in $CH_2Cl_2$ solution ($c = 10^{-5}$ mol $L^{-1}$) (a) *trans*-to-*cis* isomerization under irradiation with 365 nm UV light followed by (b) *cis*-to-*trans* isomerization under irradiation with visible light.

## *Gelation behavior*

**Table 1** Gelation properties of **1** at room temperature[a]

| Solvent | **1** |
|---|---|
| cyclopentanone | TG (1.0) |
| cyclohexanone | TG (1.5) |
| 1-butanol | P |
| toluene | TG (2.0) |
| pyridine | TG (1.0) |
| 1,4-dioxane | G (2.0) |
| cyclohexane | P |
| DMF | G (1.0) |
| DMSO | P |
| n-hexane | I |

[a] G = turbid gel; TG = transparent gel; P = precipitate; I = insoluble; for gels, the minimum gelation concentrations at room temperature are shown in parentheses (mg/mL).

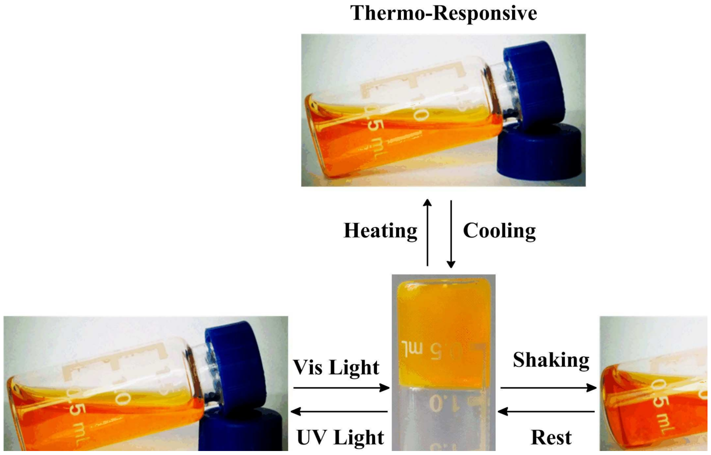


**Fig. 6** Multistimuli responsive organogels formed by compound **1** in DMF (1 mg/ml).

The gelation ability of compound **1** was evaluated in various organic solvents and the results are summarized in Table 1. Compound **1** can gelate in cyclohexanone, cyclopentanone, toluene, pyridine, 1,4-dioxane and DMF, and precipitates in 1-butanol, cyclohexane and DMSO (see Table 1, Fig. 6). Hence, **1** can only form gels in some medium polar organic solvents. Whereas it is insoluble in n-hexane and forms 3D crystals instead of 1D fibrous aggregates in polar solvents[33]. π-π interactions as well as van der Waals forces play an important role for the aggregation of the compound in solvents as exist in many azobenzene-cholesterol based gelators.[26,27,28,29,34,35,36] The organogels exhibit multiple stimuli-responsive behavior upon exposure to a number of environmental stimuli including light, temperature, and shear, etc. Irradiation with UV light, or application of heat or shear resulted in a sol state through disruption of the non-covalent interactions between the molecules, the gel state can be recovered by removal of such stimuli (see Fig. 6). Such multiple stimuli-responsive behaviors could be useful for drug controlled release[37], energy transfer[38], hardeners of solvents and sensors etc.[39]

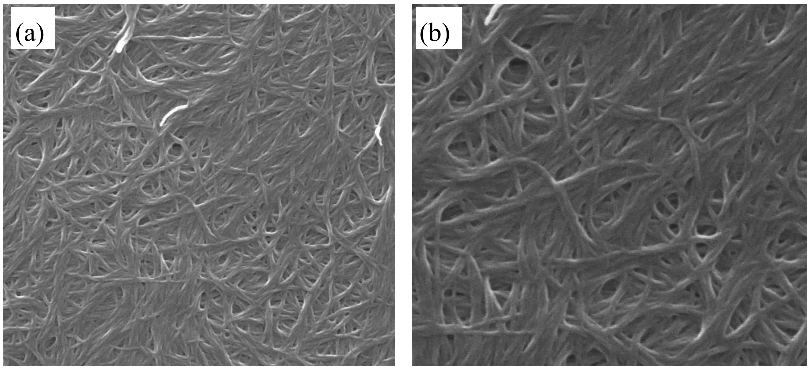


**Fig. 7** SEM images of the gels of the azobenzene compound **1**, (a) scale bar is 3μm and (b) scale bar is 1 μm.

In order to obtain a visual insight into the morphologies of the molecular aggregation mode, the microstructures of the gel were examined with Scanning Electron Microscopy (SEM), as shown in Fig. 7. The xerogel formed by **1** in DMF are fibers of 58–130 nm in width and tens of micrometers in length and these fibers form three-dimensional networks so that the macroscopical flow of the solution stops to induce the formation of a solid-like gel, the three dimensional networks formed from self-assembly of compound **1** into a fibrous structure were responsible for the gelation. Similar fibrous structures were also observed in other azobenzene containing gels.[40,41] Moreover, AFM observation identified that the fibers have helical conformation (see Fig. S2). We also observed the three-dimensional networks for the gel formed by **1** in DMF (1 mg/ml) by POM (Fig. S1). By applying shear force to the gel between two thin ordinary glass plates, the fibrous structure disappears (Fig. S1), and the gel is transformed into a vesicular structure (Fig. S1). These observations imply that without shear **1** tended to aggregate into linear fibers due to π–π interactions but it forms vesicular structures under mechanical stimuli which partly overcome the relatively weak π–π interactions.

## Conclusion

A new unsymmetric azobenzene based dimesogen with a CN group at one end and a cholesterol carbonate fixed via an oxyethylene spacer to the opposite end of the azobenzene unit was synthesized and investigated with respect to its LC and gelation-based self assembly and its photoresponsive behavior. A phase sequence Cr-N*-Iso in the heating processing and N*-SmC*-Cr in the cooling process was observed which is modified by UV-vis light irradiation. Being a chiral mesogenic dye dopant this compound has a very good solubility in a nematic liquid crystal (5CB) host, where it can induce mesophase chirality and magnify the photo-control effect. The gelation test exhibited that the gels formed by this compound in organic solvents have multiple stimuli-responsive behavior upon exposure to a number of environmental stimuli, including temperature, light and shear forces. Such multifunctional materials have potentials in displays, as chiral mesogenic dye dopants, photochemical molecular switches, new versatile low molecular mass gelators and other applications. SEM and AMF reveal that the gelator molecules self-assemble into fibers with helical conformation forming three-dimensional networks.

## Acknowledgment

Thanks are due to Prof C Tschierske (University Halle) for his precious and helpful criticism of this manuscript. This work was supported by the National Natural Science Foundation of China [No. 21364017, No. 21274119], the Yunnan Natural Science Foundation (2013FA007) and the Yunnan Education Department Foundation (ZD2015001).

## References

---

[1] a) G. Zimmerman, L. –Y. Chow, U. –J. Paik, *J. Am. Chem. Soc.*, 1958, **80**, 3528; b) G. S. Kumar and D. C. Neckers, *Chem. Rev.*, 1989, **89**, 1915; c) H. Rau, In Photochemistry and Photophysics, F. J. Rabek ED, CRC Press: Boca Raton, FL, 1990, **2**, 119; d) T. Ikeda, O. Tsutsumi, *Science.*, 1995, **268**, 1873.

---

[2] L. Komitov, C. Ruslim, Y. Matsuzawa, K. Ichimura, *Liq. Cryst*., 2000, **27**, 1011.

[3] L. Komitov, K. Ichimura, A. Strigazzi, *Liq. Cryst*., 2000, **27**, 51.

[4] A. Urbas, V. Tondiglia, L. Natarajan, R. Sutherland, H. Yu, J. -H. Li, T. Bunning, *J. Am. Chem. Soc*., 2004, **126**, 13580.

[5] Y. Zhao and J. He, *Soft Matter*., 2009, **5**, 2686.

[6] L. Zhu, H. Yan, C. Y. Ang, K. T. Nguyen, M. Li, Y. L. Zhao, *Chem.-Eur. J*., 2012, **18**, 13979.

[7] X. W. Chen, L. Wang, C. Y. Li, J. M. Xiao, H. J. Ding, X. Liu, X. G. Zhang, W. L. He and H. Yang, *Chem. Commun*., 2013, **49**, 10097.

[8] B. -T. Heng, G. -Y. Yeap, W. A. K. Mahmood, K. Miyashitab and M. M. Ito, *New J. Chem.,* 2015, **39**, 6864.

[9] E. B. Kyba, K. Koga, L. R. Sousa, M. G. Siegel and D. J. Cram, *J. Am. Chem. Soc*., 1973, **95**, 2691.

[10] S. Shinkai, K. Murata, *J. Mater. Chem*., 1998, **8**, 485.

[11] S, Wang, W. Shen, Y. Feng, H. Tian, *Chem. Commun*., 2006, **14**, 1497.

[12] T. Klawonn, A. Gansäuer, I. Winkler, T. Lauterbach, D. Franke, R. J. M. Nolte, M. C. Feiters, H. Börner, J. Hentschel, K. H. Dötz, *Chem. Commun*., 2007, **19**, 1894.

[13] L. C. Yin, Y. P. Wu, J. G. Gao, J. J. Ma, Z. J. Hu, G. Zhou and Q. J. Zhang, *Soft Matter*., 2015, **11**, 6145.

[14] J. B. Gao, J. Wang, J. Y. Zhang, Y. Shi, X. W. Wang and J. Wei, *J. Mater. Chem. C*., 2014, **2**, 9159.

[15] O. Y. Jin, D. G. Fu, J. Wei, H. Yang and J. B. Guo, *RSC Adv*., 2014, **4**, 28597.

[16] H. -C. Jeong, K. V. Le, M. -J. Gim, S. -T. Hur, S. -W. Choi, F. Araoka, K. Ishikawa and H. Takezoe, *J. Mater. Chem*., 2012, **22**, 4627.

[17] A. Bloon and P. L. K. Hung, *Mol. Cryst. Liq. Cryst*., 1978, **44**, 323.

[18] R. Balamurugan, W. K. Ming, C. –C. Chien and J. H. Liu, *Soft Matter*., 2014, **10**, 8963.

[19] V. A. Mallia and N. Tamaoki, *Chem. Mater*., 2003, **15**, 3237.

[20] Q. Li, L. F. Li, J. Kim, H. -S. Park, and J. Williams, *Chem. Mater*., 2005, **17**, 6018.

[21] M. George , V. A. Mallia , P. K. S. Antharjanam , M. Saminathan and S. Das, *Mol. Crysr. Liq. Crysf*., 2000, **350**, 125.

[22] W. K. Lee, K. N. Kim, M. F. Achardb, and J. L. Jin, *J. Mater. Chem*., 2006, **16**, 2289.

[23] Ikeda, T. *J. Mater. Chem.,* 2003, **13**, 2037.

[24] E. Sackman. *J. Am. chem. Soc*., 1971, **93**, 7088.

[25] Y. Wang, Q. Li. *Adv. Mater. ,* 2012, **24,** 1926.

[26] N. Koumura, M. Kudo and N. Tamaoki, *Langmuir*., 2004, **20**, 9897.

[27] L. Green, Y. N. Li, T. White, A. Urbas, T. Bunning and Q. Li, *Org. Biomol. Chem.*, 2009, **7**, 3930.

[28] C. Wang, Q. Chen, F. Sun, D. Q. Zhang, G. X. Zhang, Y. Y. Huang, R. Zhao, and D. B. Zhu, *J. Am. Chem. Soc*., 2010, **132**, 3092.

[29] Y. P. Wu, S. Wu, X. J. Tian, X. Wang, W. X. Wu, G. Zhou and Q. J. Zhang, *Soft Matter*., 2011, **7**, 716.

[30] Y. C. Ren, B. Wang and X. Q. Zhang, *Beilstein. J. Org. Chem*., 2015, **11**, 1089.

[31] D. A. Dunmur, *Liq. Cryst*. 2015, **42**, 678.

[32] D. Y. Kim, S. A. Lee, Y. J. Choi, S. H. Hwang, S. W. Kuo, C. Nah, M. H. Lee, K. U. Jeong, *Chem. Eur. J*., 2014, **20**, 5689.

[33] a) Comprehensive Supramolecular Chemistry (Ed.: J. -M. Lehn), Pergamon Press, Oxford, 1996; b) J. W. Goodby, I. M. Saez, S. J. Cowling, V. Goertz, M. Draper, A. W. Hall, S. Sia, G. Cosquer, S. -E. Lee, E. P. Raynes, *Angew. Chem*., 2008, **120**, 2794; *Angew. Chem. Int. Ed*., 2008, **47**, 2754.

[34] X. Y. Yang, G. X. Zhang, D. Q. Zhang, *J. Mater. Chem*., 2012, **22**, 38.

[35] Y. Ono, K. Nakashima, M. Sano, J. Hojo, S. Shinkai , *J. Mater. Chem*., 2001, **11**, 2412.

[36] a) L. A. Estroff and A. D. Hamilton, *Chem. Rev*., 2004, **104**, 1201; b) N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev*., 2005, **34**, 821.

[37] A. Friggeri, B. L. Feringa and J. van Esch, *J. Controlled Release*, 2004, **97**, 241.

[38] V. K. Praveen, S. J. George, R. Varghese, C. Vijayakumar and A. Ajayaghosh, *J. Am. Chem. Soc*., 2006, **128**, 7542.

[39] R. M. Yang, S. H. Peng and T. C. Hughes, *Soft Matter*., 2014, **10**, 2188.

[40] Y. Takashima, S. Hatanaka, M. Otsubo, M. Nakahata, T. Kakuta, A. Hashidzume, H. Yamaguchi and A. Harada, *Nat. Commun*., 2012, **3**, 1270.

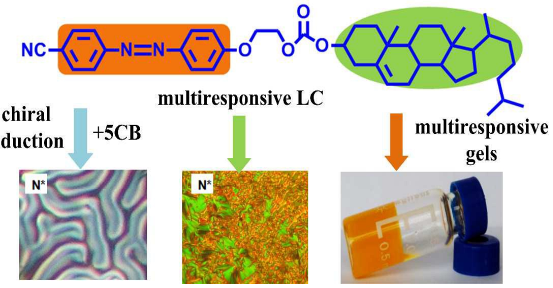
[41] Z. X. Liu, Y. Feng, Z. C. Yan, Y. M. He, C. Y. Liu and Q. H. Fan, *Chem. Mater*., 2012, **24**, 3751.

## Graphical Abstract

# Reversible photoresponsive chiral liquid crystal and multistimuli responsive organogels based on a cholesterol-azobenzene dimesogen

Xiaoping Tan,[a] Zhi Li,[a] Meng Xia,[a] Xiaohong Cheng*[a]

[a] *Key Laboratory of Medicinal Chemistry for Natural Resources, Yunnan University, Kunming 650091, P. R. China*



Cholestrol-azobenzene dimesogens showing chiral induction and chiral amplification effects can self assemble into photoresponsive N* and SmC* phase and multiresponsive gels.