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## α-Cyanostilbene and fluorene based bolaamphiphiles: synthesis, self-assembly View Article Online AIEE properties with potentials as white-light emissive materials and light-emitting liquid crystal displays

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**Abstract:** Novel bolaamphiphiles containing two  $\alpha$ -cyanostilbene units interconnected with 2,7-substituted-9,9-dialkylated fluorene as the central core and diol unit at each terminal have been synthesized efficiently by palladium catalyzed Suzuki coupling reaction and Knoevenagel condensation reaction as key steps. POM, DSC and XRD investigation reveals that these compounds can organize into single wall triangular honeycomb columnar phases. A unique packing model was established in which the twist  $\pi$ -conjugated backbones stacked alternatively into the walls and were connected through the end diol groups to form triangular honeycomb, the almost perpendicular distributed side alkylchains filled the cells. Such packing was additionally stabilized by the local anti-parallel dipole interactions of  $\alpha$ -cyanostilbene and the H-bonding between CN···H. These compounds showed AIEE effect and emitted yellow luminescence which could be further utilized to generate white light emission by coating on the commercially blue LED lamp. Most interesting light-emitting liquid crystal display (LE-LCD) device could be obtained by dissolution such AIE active distinctive luminogen to commercially available nematic LCs.

## **1** Introduction

Control of the self-assembly of  $\pi$ -conjugated molecules into predictable ordered arrangements is crucial for their application as optoelectrical devices.<sup>1</sup> This can be realized by imprinting information in the molecular components to influence their assembly leading finally to defined complex nanostructures with expected properties.<sup>2</sup> In this sense, study liquid crystal phases formed by  $\pi$ -conjugated rod like molecules are attractive because of their importance for study the basic mechanism of molecular self-assembly, their self-healing properties with formation of defect free and well defined nanostructures as well as their wide applications.<sup>3</sup>

Bolaamphiphiles consisting of a  $\pi$ -conjugated rodlike core, two terminal diol groups, and lipophilic side chains, are able to form various complex nanostructures including a number of polygonal honeycomblike liquid-crystal phases, and various novel lamellar and 3D-ordered mesophases.<sup>4,5,6,7,8,9,10</sup> In the honeycomb structures, the rodlike rigid cores organize into the cylinder frameworks held together by H-bond between the terminal diol groups, the formed cells inside the honeycomb are filled with the side lipophilic chains.<sup>4</sup> Till now, functional groups such as oligophenyl, oligothiophene<sup>11</sup> azobenzene,<sup>12</sup> 2,1,3-benzothiadiazole (BTD)<sup>13</sup> and triazole<sup>14</sup> etc have been introduced into the  $\pi$ -conjugated rodlike core of bolaamphiphiles. The obtained self-assembly principle of such bolaamphiphiles would guide their assembly in a predicted way<sup>15</sup>

and should be very important for their applications as optoelectrical devices.<sup>16,17</sup>

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The fluorene derivatives are famous because of their strongly blue fluorescence emission and highly thermal stability.<sup>18</sup> 9,9-Dialkylfluorene has been used as the  $\pi$ -conjugated link to avoid the dye aggregation and suppress the charge recombination.<sup>19,20,21</sup> Due to the SP<sup>3</sup> hybrid of C-9, the 9,9-dialkyl chains are almost perpendicular to the conjugated backbone, and the central fluorene unit usually twists out of the molecular  $\pi$ -conjugated coplane.<sup>22</sup>

In another side, compounds containing  $\alpha$ -cyanostilbene (CS) motif [-Ar-CHC(CN)-Ar-] belong to one of the  $\pi$ -conjugated substrates that exhibit aggregation-induced emission (AIE) due to restricted molecular rotations and the special supramoleuclar aggregation accompanying with the distinctive electric and geometrical features. Different secondary bonding interactions (different modes of local dipole coupling, C-H··· $\pi$  interaction, C-H···N hydrogen bond,  $\pi$ - $\pi$  stacking) are essential for the molecular packing.<sup>23</sup> Because of their superior emissive characteristics in aggregation state, such CS compounds have found wide applications as optical materials and for sensing biological materials.<sup>24</sup> It should be very interesting to introduce fluorene (F) or cyanostilbene (CS) units into the rigid core of bolaamphiphiles. The question arose, can such CS and F contained bolaamphiphiles self-assemble into novel honeycomb phase? Can the characteristics encoded by CS and F in the molecules be transferred into the self-assembly system? Which photophysical properties would display by such designed bolaamphiphiles? So far to our acknowledgement there is no effort to introduce either fluorene (F) or cyanostilbene (CS) units into the rigid core of bolaamphiphiles. Thus herein novel series of bolaamphiphiles (FT/n)(Scheme 1) containing two CS units interconnected with 4,7-substituted 9,9-dialkylated fluorene as the central core and diol unit at each terminal have been efficiently synthesized by palladium catalyzed Suzuki coupling reaction and Knoevenagel condensation reaction as key steps as shown in Scheme 1. The relationship among molecular structures, the mesogenic properties, photophysical properties and aggregation properties, as well as their potentials as optoelectronic devices were studied.

## 2 Results and discussion

## 2.1 Synthesis

Target CS-F bolaamphiphiles FT/n were synthesized by using C-C coupling and Knoevenagel reactions as key steps. Fluorene was converted to 2,7-diiodofluorene 1 by KIO<sub>3</sub>-I<sub>2</sub>, under acid condition,<sup>25</sup> followed by alkylation with 1-bromoalkane afforded 9,9-dialkylated diiodefluorenes 2/n, which were further coupled with (5-formyl thiophene-2-yl) boronic acid under standard Suzuki conditions, leading to the aromatic aldehydes 3/n. The 2-(4-hydroxyphenyl)acetonitrile 4 was etherified with allylbromide to afford 5, the double bond of 5 was then dihydroxylated by co-oxidants OsO<sub>4</sub> and NMMNO. Then the diol groups of 6 was protected with 2,2-dimethoxypropane to produce acetonides 7. Knoevenagel reactions between aromatic aldehydes 3/n with acetonitrile 7, followed by deprotection of the 1,2-O-isopropylideneglycerol units produced target compounds FT/n. FT/n were purified through column chromatography. Details for synthesis procedures are shown in Supporting Information.



Scheme T Synthesis of F1/*n*. *Reagents and conditions*. (*i*)  $I_2$ ,  $H_2SO_4$ ,  $CH_3COOH$ ,  $KIO_3$ ,  $H_2O$ ,  $so^-C$ , I2 II, (*ii*)  $C_nH_{2n+1}Br$ , NaOH, toluene,  $H_2O$ , TBAB, RT, I2 h; (*iii*) (5-formylthiophen-2-yl)boronic acid, Pd(PPh\_3)\_4, K\_2CO\_3, H\_2O, THF, 78 °C, 15 h; (*iv*) K\_2CO\_3, CH\_3CN, allylbromide, reflux, 6 h; (*v*) OsO\_4, N-Methylmorpholine N-oxide (NMMNO, 60% aqueous solution Aldrich),  $H_2O$ , acetone, 50 °C, 5 h; (*vi*) 2,2-dimethoxypropane, pyridinium p-toluene sulfonate, RT, 5 h; (*vii*) ethanol, sodium methoxide, reflux 12 h; (*viii*) 10% HCl, methanol, reflux, 12 h.

## 2.2 Mesomorphic properties

The liquid crystalline characteristics of bolaamphiphiles FT/n were studied by POM, DSC and XRD and the results are summarized in Table 1.

Comp.	n	$T(^{\circ}C) \Delta H(kJ \cdot mol^{-1})$	<i>a</i> (nm)	$n_{\rm cell}$	<i>n</i> <sub>wall</sub>
FT/12	12	Tg 49 $\operatorname{Col}_{hex}\Delta/p6mm$ 143 <sup>b</sup> Iso	4.03	3.56	1.19
		(Iso140 <sup>b</sup> Col <sub>hex</sub> Δ/p6mm 47 Tg)			
FT/14	14	Tg 40 Col <sub>hex</sub> Δ/ <i>p</i> 6 <i>mm</i> 137 [0.8] Iso	3.92	3.17	1.06
		(Iso 131 [0.9] Col <sub>hex</sub> Δ/ <i>p</i> 6 <i>mm</i> 36 Tg)			
FT/16	16	Tg 39 Col <sub>hex</sub> Δ/ <i>p</i> 6 <i>mm</i> 113 [0.2] Iso	3.98	3.08	1.03
		(Iso $110^b \operatorname{Col}_{hex}\Delta/p6mm$ 35 Tg)			

Table 1 Transition temperatures, corresponding enthalpy values and lattice parameters of bolaamphiphiles  $FT/n^{a}$ 

<sup>*a*</sup> measured by DSC (second heating/cooling at 10 K min<sup>-1</sup>); Tg: glass transition temperature;  $Col_{hex}\Delta/p6mm$ : triangular honeycomb hexagonal columnar phase;  $n_{cell}$ : number of molecules in hypothetical 3D unit cell;  $n_{wall}$ : average intercellular wall thickness; calculation means of  $n_{cell}$  and  $n_{wall}$  are displayed in Table S4; <sup>*b*</sup> temperature measured by POM.

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All compounds **FT**/*n* display columnar phase (Table 1) as demonstrated by the typical spherulities/DOTC04571C fanlike textures with some dark regions as observed under POM (see Fig. 1). The main  $\pi$ -conjugation route should be vertical to the column long axis because all the LC phases are optically negative. The wide angle scatterings of X-ray diffractions showed diffuse maxima around d = 0.45-0.46 nm (Figs. S2b, S3b and S4 in the Supporting Information), confirming the LC properties of all mesophases.



Fig. 1 The textures of FT/*n* observed under POM: (a)  $\operatorname{Col}_{hex}/p6mm$  phase of FT/12 cooling at 120 °C; (b)  $\operatorname{Col}_{hex}/p6mm$  phase of FT/14 cooling at 110 °C; (c)  $\operatorname{Col}_{hex}/p6mm$  phase of FT/16 cooling at 100 °C. The bottom insets on each texture show the same texture with  $\lambda$ -retarder plate, the indicatrix orientation in the compensator is shown on the top of (a), the columnar phase is optically negative as indicated by the orientation of the blue shifted and yellow shifted fans; this indicates that in the columns the orientation of the intramolecular  $\pi$ -conjugation route, coinciding with the long axis of aromatic cores is generally vertical to the column long axis.

The ratio of the positions of the small angle X-ray spacings is  $1 : 3^{1/2} : 2$  as typical for a two-dimensional p6mm lattice (Figs. 2a, S2a and S3a). The lattice parameters ( $a_{hex}$ ) around 3.9-4.0 nm (see Table 1 and Tables S1-S3) are within the scope of the molecular length (L = 3.9-4.4 nm), this is expected for a triangular honeycomb LC.<sup>11b</sup> For the suggested triangular honeycomb structure, there is about  $n_{cell} = 3.1-3.6$  molecules in each hypothetical 3D unit cell (calculated process see Table S4). Because each unit cell is surrounded by three walls, the thickness of the walls  $(n_{wall} = n_{cell}/3)$  is only about one rodlike core  $(n_{wall} = 1.0)$ . According to the SAXS pattern, the electron density map of triangular cylinder phase has been reconstructed (Fig. 2b), in which purple and blue regions refer to the high electron density areas, green regions are the medium electron density shells, and red areas are the lowest electron density regions, representing H-bond network of terminal glycerol groups, aromatic rigid cores and flexible alkyl chains, respectively. Fig. 2 shows molecular dynamics (MD) annealed model which further confirmed that tight space filling and right lattice parameters are obtained from this arrangement. In order to gain insight into the molecular alignment in honeycomb, we calculated the optimized molecular structure of FT/12 according to density functional theory (DFT) (Gaussian 09W, B3LYP/(6-31G, d)), the optimized molecular structure shows a little twist of the  $\pi$ -conjugated backbone with two cvano groups located at the same side and the sulfurs of the two thiophenes point to another side of the backbone (see Fig. S8). Simultaneously two alkyl chains are arranged almost vertical to the molecular backbones. It should be mentioned that the dihedral angle between the fluorene and CS units could be changeable during the molecular assembly.<sup>22</sup> Taking this conformation in mind, and considering the intermolecular local dipoles as well as C-H···N hydrogen bond interactions, the following packing model was established (Fig. 2c). The honeycomb frames were constructed by walls of antiparallel aligned twisted rodlike aromatic units arranged vertical to the resulting

channel as revealed by the UV investigation (*H*-aggregation, see section 2.3), the planes of the set of the section 2.3), the planes of the set of the section 2.3), the planes of the set of the section 2.3), the planes of the set of the set

Additionally, a weak and diffuse peak centered at 0.85 nm (Figs S2b, S3b and S4) is considered as the assumed distance between the sulfur atoms of every other thiophene unit in packings of alternating antiparallel organization of the molecules.<sup>26</sup>

The C-H···N hydrogen bonds could be confirmed by the FT-IR experiments (Fig. 3). In solid state, the FT-IR spectrum of the representative compound **FT/12** showed three characteristic peaks at 2208cm<sup>-1</sup>, 3200 cm<sup>-1</sup> and 3444 cm<sup>-1</sup>, which could be assigned to C $\equiv$ N stretching vibration of cyano unit, the C-H···N hydrogen bond vibration and O-H stretching vibration of diol respectively. Whereas in LC state, the peaks showed obvious blue-shift (from 2208 to 2164 cm<sup>-1</sup>) and the peak of 3200 cm<sup>-1</sup> became stronger, which indicated that H-bond existed between N atoms of cyano unit and hydrogen of H-C=, and the hydrogen bond between them will be strengthened in the LC state.



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**Fig. 2** (a) SAXS pattern of **FT/16** at T = 100 °C; (b) Reconstructed electron density from the SAXS pattern of (a); (c) The possible self-assembly model of triangular honeycomb phase; the enlarged cylinder wall area is illustrated by a molecular stick model, where the lateral chains are replaced by two methyl groups and the terminal glycerol groups are omitted. The possible intermolecular hydrogen bonding between the N atom of cyano group and the H atom of vinylene (black dotted lines) as well as the local dipoles (purple arrows) have been marked.



Fig. 3 FT-IR spectra of FT/12 in solid and LC states.

## 2.3 Photophysical and electrochemical properties



**Fig. 4** Normalized UV-vis absorption and PL spectra of **FT/12** in THF  $(1.0 \times 10^{-6} \text{ mol } \text{L}^{-1})$  and in thin film state. The excitation wavelength of **FT/12** in THF is 442nm and **FT/12** in thin film state is 434nm.

The UV-vis and fluorescence spectra of representative compound **FT/12** were studied (Fig. 4). The UV-vis spectra of **FT/12** in dilute solution of THF displayed one maximum peak at 442 nm. The UV-vis spectra of **FT/12** in the thin film displayed a little blue-shift at 424 nm. This suggested that an *H*-type parallel  $\pi$ - $\pi$  stacking mode in the solid state was formed.<sup>27</sup> The emission spectra in dilute solution exhibited two maximum emission peaks at 498 nm and 530 nm, respectively and in solid state exhibited maximum peak at 578 nm (Fig. 4), indicating a much larger Stokes shift in the solid state (154 nm) comparing with that in THF solution (88 nm).

The HOMO and LUMO energy levels of **FT/12** in thin films were investigated by cyclic voltammetry (Fig. 5).<sup>28</sup> **FT/12** exhibited one reversible reduction process giving an energy gap  $(E_g^{el})$  of 2.22 eV, which was near to the value induced from absorption in thin film (2.41 eV) (Fig. S7).<sup>29</sup> The electronic features of **FT/12** from DFT calculations (B3LYP/6-31G(d)) (Fig. S8) suggested that the electron densities of HOMO are homogenously distributed over the whole

conjugated core, whereas those of LUMO are also delocalized over the whole conjugated core whereas those of LUMO are also delocalized over the whole conjugated core with control of the conjugated core with diols. The low energy gap (2.22 eV) and LUMO value (-3.96 eV) indicating electron injection property of this molecule.<sup>30</sup>



**Fig. 5** Cyclic voltammogram of **FT/12** on glassy carbon electrode in 0.1 mol/L Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile solution with a scan rate of 50 mV·s<sup>-1</sup>. Reference electrode: SCE.  $E_{\text{HOMO}} = -(E^{\text{ox}} + 4.74 \text{ eV}), E_{\text{LUMO}} = -(E^{\text{red}} + 4.74 \text{ eV}), E_{\text{g}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ .

## 2.4 Aggregation-induced enhanced emission (AIEE)

AIEE characteristics of these compounds in solid states were investigated in a mixture solution of THF/water. As shown in Fig. 6 and Fig. S9, the fluorescence intensity displayed a weakening tendency as the water fraction of the THF/water mixture increased from 0% to 70%. After the water fraction reached 80%, the fluorescence intensity increased with increasing the water fraction up to 90%, which was about 1.4 fold higher than that in the pure THF.



Fig. 6 (a) The fluorescence spectra of FT/12 in THF/H<sub>2</sub>O mixtures with different fractions of H<sub>2</sub>O ( $f_w$ ), excited at  $\lambda = 330$  nm (1 × 10<sup>-5</sup> M); (b) The fluorescence intensity vs  $f_w$ .

## 2.5 White light emission

Bolaamphiphiles **FT**/*n* exhibited yellow emission under 365 nm UV light, which indicated that it was very possible to construct a white light emission device by coating **FT**/*n* film on the commercial blue LED chip.<sup>31</sup> Therefore the yellow fluorophor **FT**/12 was coated on the surface of a commercial blue LED buld. When the LED was switched on, white light can be obtained (see

inset of Fig. 7a). Two bands with maximum at 460 and 540 nm repectively were detected (Fig. 7a). Two bands with maximum at 460 and 540 nm repectively were detected (Fig. 7a). The CIE coordinates were defined to be (0.31, 0.33), which belongs to the white-light domain (Fig. 7b). Thus just by dip-coating bolaamphiphiles FT/n onto the commercial available blue lamp pith, facil and low-cost WLEDs can be achieved.



**Fig. 7** (a) PL spectrum of UV-LED lamp with the film containing **FT/12**, inserts show the lamp off and on states respectively; (b) CIE chromaticity coordinates of the coated UV-LED lamp (0.31, 0.33).



2.6 Polarized emission spectra, the dichroic ratio and LE-LCD device

**Fig. 8** Polarized fluorescence spectra of light-emitting LC cell in electric field-off status: a) SLC9023 + 0.5 wt% **FT/16**; b) TEB300 + 0.5 wt% **FT/16**. The dichroic ratio (NF) was calculated from the formula: NF =  $F_{//}/F_{\perp}$ , where  $F_{//}$  and  $F_{\perp}$  are the rubbing direction of the LC cell perpendicular and parallel to the polarization direction of the detector, respectively.



**Fig. 9.** Photograph of the LE-LCD devices with patterned alignment in the electric field-off and field-on status using light-emitting LC mixture. The LC mixture used for a) is SLC9023 + 0.5 wt% **FT/16** and for b) is TEB300 + 0.5 wt% **FT/16**; c) Schematic representation of the structures of the LE-LCD device with patterned alignment in the electric field-off and field-on states using the LC mixture.

Recently it was demonstrated that it is possible to apply AIE-active mesogens to manufacture LE-LCD,<sup>32</sup> which was considered as an excellent alternative to conventional LCDs for enhanced performance. In order to assess the potentials of FT/n in LE-LCD, FT/16 was selected as a representative to blend with commercially available nematic liquid crystals SLC9023 and TEB300 respectively at a concentration of 0.5% w/w (details for sample preparation is shown in SI). The dichroic ratio of polarized emission spectra of the mixture were investigated.<sup>33</sup> The measured dichroic ratios were respectively (Figure 8a and 8b). Such results indicated that the LC mixture of FT/16 and the nematic LCs could be applied for fabrication of the LE-LCDs. Therefore, the LC cell was prepared firstly with patterned ITO glass substrates. Then the monodirectional alignment of LC mixtures were obtained by rubbing the polyimide (PI) aligned layer (details for device fabrication is shown in SI). A UV lamp was applied to irradiate the LC mixture, and a polarizer with the transmission direction parallel to the LC aligned direction was applied to detect the change of PL efficiency. In the electric field-off state, there would be a bright image in the LC-cell under UV illumination. After application of an electric field (1 KHz, 8 v) to the LC cell, only the central region without ITO is still light emissive. The LE-LCD devices manufacture with a mixture of SLC9023 + 0.5 wt% FT/16 and TEB300 + 0.5 wt% FT/16 can display the switching from almost bright to dark yellow/green status observed by naked eyes as shown in Figure 9.

## **3** Conclusion

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Therefore, we have successfully developed a novel series of bolaamphiphilic liquid crystals with triangular honeycomb phase by incorporating 9,9-dialkylated fluorene and cyanostilbene in the aromatic rodlike core, the planes of the fluorenes should parallel to each other and in the plane of the hexagonal lattice, and both chains of one molecule went into the same central lipophilic columns and those of the adjacent molecule filled the space in the other adjacent lipophilic columns. Besides the driving forces usually described for previously reported bolaamphiphiles,<sup>567</sup> the additional interplay among the twist  $\pi$ -conjugated system as well as the antiparallel coupling between the local dipoles in adjacent molecular sheets assisted by multiple C-H···N hydrogen bonds also promoted this specific arrangement in triangular honeycomb LC organization. This approach led to a new type of Bolaamphiphiles consisting of LC molecule with twist  $\pi$ -conjugated and hearly perpendicularly distributed lateral alkyl chains which should be interesting for both the fundamental research and practical applications. Finally such bolaamphiphiles exhibited AIEE property, and the potential application of such bolaamphiphiles as both WLED and LE-LCD devices have been initially demonstrated.

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## **Conflicts of interest**

There are no conflicts to declare. **References** 

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Fluorene and  $\alpha$ -cyanostilbene based bolaamphiphiles could self-assemble into triangular honeycomb phases with unique molecular arrangements, and showed AIEE effect. Their potential application as both WLED and LE-LCD devices have been initially demonstrated.