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Synthesis, mesomorphism and fluorescence of triphenylene-Bodipy dyads

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ABSTRACT

Four novel triphenylene-Bodipy dyads were synthesized in yields of 32–38% and characterized by MS, NMR, elemental analysis. They exhibit good columnar liquid crystal behaviors at room temperature. The alkyl substitution on the Bodipy unit does not cause the disruption of the mesophase. They possess excellent fluorescence properties with high quantum yields in solution and the weak fluorescence in film. The alkyl substitutions on the Bodipy unit increase the fluorescence intensity and the introduction of triphenylene units reduce the aggregation-caused quenching of orderly stacking of Bodipy units.

In recent years, columnar discotic liquid crystals have been paid considerable attention for their various potential applications including organic field-effect transistors, organic photovoltaic cells, organic light-emitting diodes, gas sensors, etc.[1–4] Lately, the columnar liquid crystals with excellent fluorescence, attracted much research interests due to the broad application in the novel liquid crystalline materials possessing unique properties.[5–10] 4,4-Difluoro-4-borata-3a,4a-diaza-s-indacene (abbreviated as Bodipy) is a class of highly fluorescent dye that are attracting increasing attention based on their intense fluorescence, photochemical stability and energy- and electron-transfer capabilities.[11–16] Investigations have also been carried out to obtain the fluorescent Bodipy liquid crystal. There are two synthetic methods to attain this target up to now. One method was the bridging of a long alkyl chain and a rigid Bodipy unit together (as shown in Fig. 1(a)), which resulted in the nematic liquid crystals in most cases.[17,18] Another method was the bridging of multiple alkyl chains (such as gallic unit with three alkyl chains) onto one Bodipy unit (as shown in Fig. 1(b)).[19–24] However, this kind of liquid crystal using Bodipy unit as columnar core might produce an antinomy between the mesomorphic range and the fluorescence quantum yield, i.e. the increasing alkyl substitution on the Bodipy fluorophore causes the restriction of the rotation of the 8-phenyl ring resulting in an increase in fluorescence intensity, but leads to a disruption of the mesophase.[24] To avoid this antinomy, in theory, if the Bodipy unit is not the only core stacking units for columnar liquid crystal, but is staggered with other columnar core to reduce the aggregation quenching effect (as shown in Fig. 1(c)), the obtained columnar liquid crystal might possess both good mesomorphic property and good fluorescence. However, such Bodipy liquid crystal has not been presented so far.

It is well known that triphenylenes are the popular discotic liquid crystals. They were typical columnar mesophase in most cases because of the strong π–π interactions for the flat, rigid aromatic core structures.[25–29] Indeed, synthetic advances have realized a wide range of symmetrical and asymmetrical substituted triphenylene derivatives possessing various functional groups on the side-chain to be prepared with columnar mesophases based on the strong π–π interactions of triphenylene core.[30–35] Some triphenylene liquid crystal with good fluorescence groups on side-chain also were reported.[34,35] Thus, when the Bodipy unit is introduced onto the side-chain of triphenylene derivatives (as shown in Fig. 1(c)), is this triphenylene-Bodipy dyad possible to have both good columnar phase and excellent fluorescence property? Herein, we wish to report the first synthesis of triphenylene-Bodipy dyads and investigate their mesomorphic properties and fluorescence properties. The results showed that these triphenylene-Bodipy dyads have both good columnar phase and excellent fluorescence property, avoiding successfully the inverse relationship between the mesomorphic range and the fluorescence quantum yield.

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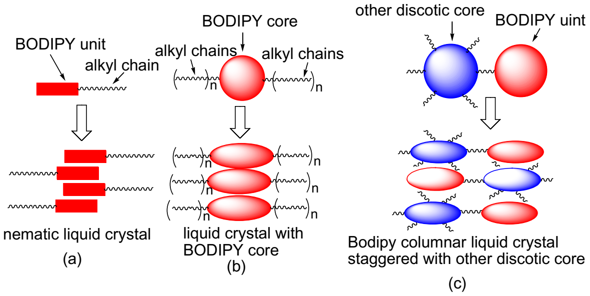
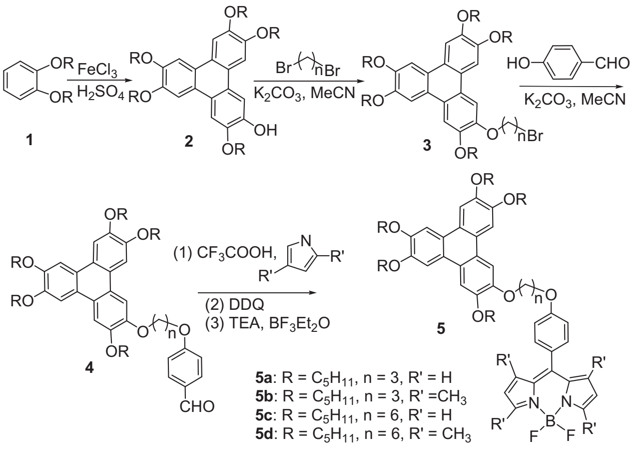


Figure 1. Three kinds of Bodipy liquid crystals. (a) and (b) had been reported, and (c) was not presented.

The synthetic routes were illustrated in Scheme 1. In order to study the influences of alkyl substitution on mesomorphic and fluorescence properties, triphenylene-Bodipy dyads **5a–d** with or without methyl groups on Bodipy were designed. According to the published procedures,[29,36,37] 1,2-bispentyloxybenzene **1** was treated with $FeCl_3$ (5 equiv) to give monohydroxytriphenylene **2**, which was converted to triphenylene derivatives **3a** and **3b** by reacting with excess 1,3-dibromopropane or 1,6-dibromohexane. Further treating **3a** and **3b** with 4-hydroxy benzaldehyde in K_2CO_3/MeCN system afforded triphenylene derivatives **4a** and **4b** in yields of 75% and 78% after column chromatography, respectively. Then, according to the typical procedure for synthesis of Bodipy, the triphenylene-Bodipy dyads **5a–d** were prepared by treating compound **4** with pyrrole (or 2,4-dimethylpyrrole) via sequential condensation, oxidation, and complexation reactions in the moderate yields of 30–40% after columnar chromatography. In their ^{1}H NMR spectra, all obvious peaks were assigned well. The MS, ^{13}C NMR, FT-IR and elemental analysis also supported their structures distinctly.

The mesomorphic properties of triphenylene-Bodipy dyads **5a–d** were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD). Figure 2 and Table 1 showed the DSC traces, phase transfer temperatures and associated enthalpy changes. All dyads **5a–d** displayed typical liquid crystalline melting behavior. Two phase transitions of solid state-mesophase and mesophase-isotropic phase on heating and cooling were observed. Moreover, dyads **5a–d** possessed similar phase transitions temperatures and mesomorphic ranges although they have different substitutions on the Bodipy units. These results were different from the Bodipy liquid crystals with Bodipy units as cores, in which the alkyl substitution on Bodipy caused a disruption of the mesophase.[24] These phenomena could be explained by that the columnar triphenylene units of dyads **5a–d** were similar and the small changes of the structures on Bodipy influenced little on mesophase. Their wide Iso-Col transitions and the wide range of transition enthalpies might be attributed to their big molecular weights and such viscous materials in LC phase, which were usually observed for triphenylene columnar liquid crystals.[38–51] Further observation under POM also suggested the two phase transitions of solid state-mesophase-isotropic phase and the phase transfer temperatures agreed with the peaks of DSC approximately, respectively. They exhibited typical fan-like texture of mesophase (in Fig. 3). These textures were similar to the known textures of triphenylene columnar liquid crystal.[38–51]



Scheme 1. Synthesis of triphenylene-Bodipy dyads **5a–d**.

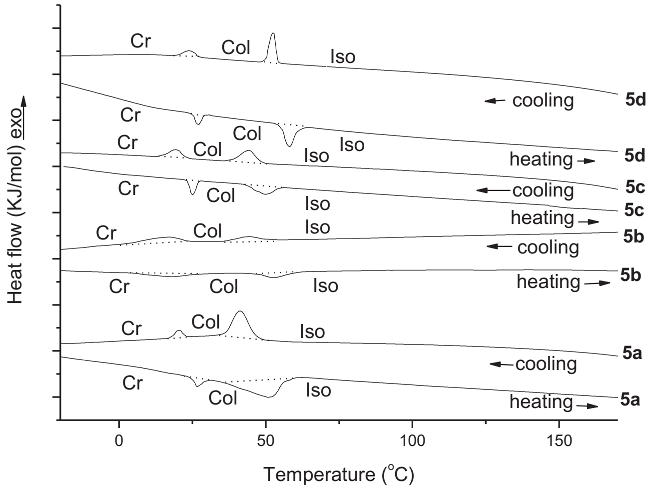


Figure 2. The DSC traces of compounds **5a–d** on heating and cooling (scan rate 10 °C min^{-1}). Cr = crystalline, Col = columnar, Iso = isotropic.

Table 1
Phase transfer temperatures (°C) and enthalpy changes (kJ/mol in parentheses) of **5a–d**

Dyads	Phase transition[a]	$T(\Delta H)$ heating Scan	$T(\Delta H)$ cooling scan
5a	Cr-Col	26.4(5.35)	20.4(5.98)
	Col-Iso	50.6(23.28)	41.3(24.61)
5b	Cr-Col	17.9(9.82)	16.6(12.06)
	Col-Iso	52.7(10.33)	43.7(8.24)
5c	Cr-Col	25.1(8.68)	19.4(8.85)
	Col-Iso	50.6(9.86)	44.2(10.01)
5d	Cr-Col	27.1(7.31)	23.8(7.44)
	Col-Iso	58.5(21.69)	52.4(17.85)

[a] Cr = crystalline, Col = columnar, Iso = isotropic.

The XRD data of dyads **5a–d** further confirmed their columnar liquid crystal behaviors as illustrated in Figure 4. Some obvious peaks at small angles and wide angles were observed. Due to compounds **5a–d** possess similar triphenylene columns, their positions of reflection peaks were similar. In small angle, a strong reflection and two weak reflections appeared at $2\theta = 5.03–5.19^\circ$, $8.74–9.02^\circ$ and $10.02–10.42^\circ$, respectively. These degrees indicated the distances of 17.01–17.65 Å, 9.80–10.13 Å, and 8.49–8.78 Å, respectively. These data were in agreement with the ratios of $1:1/\sqrt{3}:1/\sqrt{4}$ approximately for (100), (110) and (200) reflection peaks, suggesting the hexagonal columnar mesophase for compounds **5a–d**. The reflections at about 5° suggested 19.6–20.26 Å for the lattice parameter *a*. The diameters of compounds **5a–d** including both triphenylene units and Bodipy units, neglecting the length of the spacer, were approximately 21 Å based on the CPK model. These values were close to the lattice parameter *a*. The reflections at $2\theta = 16–25^\circ$ (3.56–5.53 Å, broad halo) and

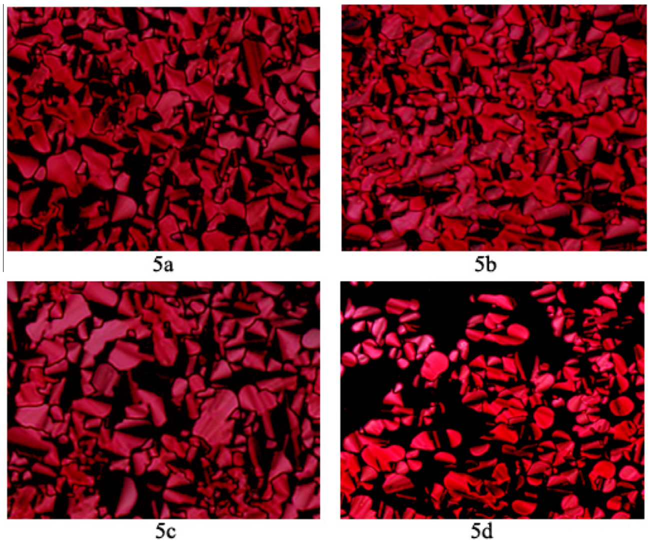

5a 5b
5c 5d

Figure 3. The textures of dyads **5a–d** under POM on cooling at 35 °C (×400).

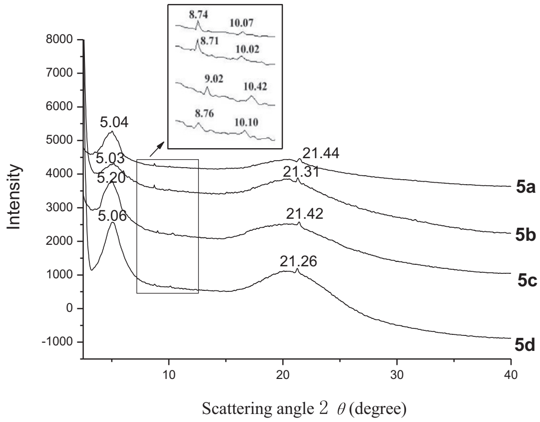


Figure 4. XRD traces of compounds **5a–d** at 35 °C.

$2\theta = 21.26–21.44°$ (4.14–4.18 Å) were assigned to the average distance of the molten alkyl chains and the intracolumnar order, respectively. Thus, based on the above XRD analysis, it was reasonable to propose the schematic representation of the columnar layered molecular arrangement of dyads **5a–d** as shown in Figure 5. However, it should also be noticed that Figure 5 was just the approximation of the most likely molecular stacking due to the broad reflection peaks suggesting a broad diversity of distances among the layers and cylinders. The hexagonal columnar mesophase was composed of triphenylene moiety and Bodipy moiety concurrently. All these XRD data suggested that the dyads **5a–d** possessed hexagonal columnar mesophase and the alkyl substitution on the Bodipy did not cause the disruption of the mesophase.

As dyads **5a–d** possessed similar liquid crystal behaviors regardless of the different structure of Bodipy moiety, it was interesting to study the changes of their fluorescence properties. Their absorption spectra and fluorescence spectra were illustrated in Figures 6 and 7. Due to the triphenylene has no obvious absorption and fluorescence when the wavelength is bigger than 500 nm,[52] their OH-Bodipy precursors **A**[53] and **B**[54] with or without methyl groups, respectively, were used as reference for data comparison. Table 2 displayed the photophysical data collected for dyads **5a–d** and their precursors **A** and **B**. The absorption wavelength and emission wavelengths of **5a–d** were at 503 nm and 520 nm approximately, which were similar with that of the precursors **A** or **B** due to their similar structures of Bodipy units. In Figure 7 and Table 2, both the fluorescence intensity and the fluorescence quantum yield of compounds **5b** and **5d** were far higher than that of compounds **5a** and **5c**, suggesting that the alkyl substitution on the Bodipy increased fluorescence obviously. These phenomena

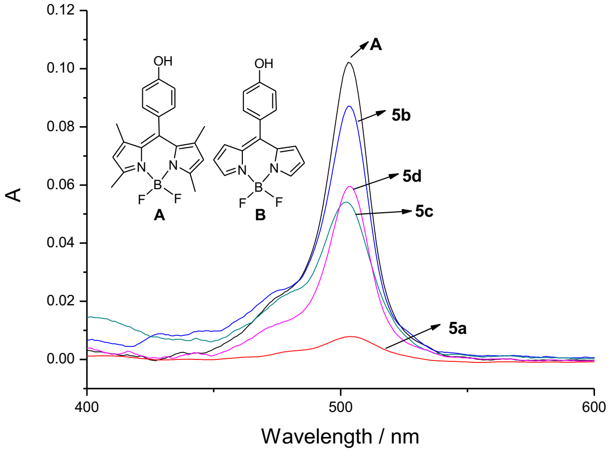


Figure 6. Adsorption spectra of dyads **5a–d** in toluene (10^{-6} M).

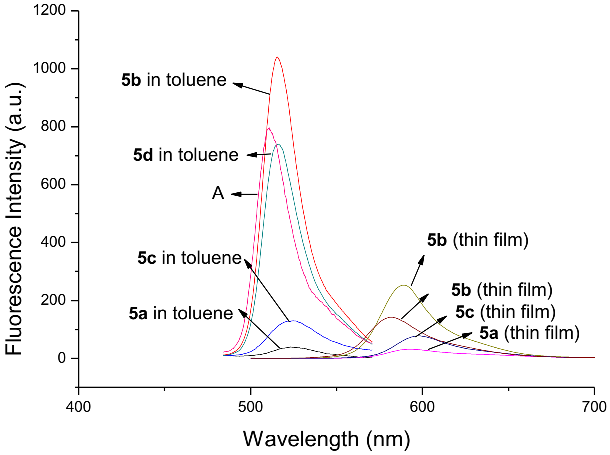


Figure 7. Fluorescence spectra of dyads **5a–d** in toluene (10^{-6} M). All of compounds were excited at 470 nm.

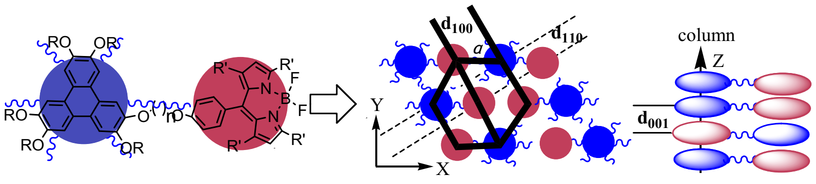


Figure 5. The proposed schematic representation of the columnar layered molecular arrangements of dyads **5a–d**.

Table 2
Absorption and fluorescence data for the dyads **5a–d** in toluene at 298 K

Dyads	λ_{max}/nm (log ε)	λ_{em}/nm	Φ_F (τ_F/ns) in toluene	λ_{em}/nm in thin film	Φ_F in thin film
5a	503(4.40)	523	0.29(2.6)	582	0.02
5b	504(4.97)	516	0.97(4.7)	589	0.05
5c	503(4.76)	525	0.38(3.0)	597	0.03
5d	503(4.89)	516	0.95(4.6)	594	0.04
A[a]	503(4.99)	514	0.94(4.3)	No	0
B[b]	501(/)	518	0.08(/)	No	0

[a] The data of compound **A** were cited in Ref. 53.
[b] The data of compound **B** were cited in Ref. 54.

were similar with the literature report,[24] which could be attributed to additional rotation restriction of the alkyl groups on Bodipy units.

On the other hand, the fluorescence intensity of dyads **5b** and **5d** were almost same or strong comparing with their precursors **A**, indicating no electronic or energy transfer between triphenylene and Bodipy. The quantum yields of **5b** and **5d** were as high as the precursor **A** and were more excellent than the other Bodipy liquid crystals (their values of $\Phi_F < 0.7$ in most cases).[19–24] The quantum yields of dyads **5a** and **5c** were also far higher than that of their precursor **B**. Moreover, photoluminescence properties of dyads **5a–d** as thin film were measured. Their emission spectra were shown in Figure 7 and the quantum yields listed in Table 2. The peaks were obviously red-shifted and boardening indicating the existence of aggregation-caused quenching. However, in contrast to their precursors **A** and **B** which showed no solid fluorescence due to the strong aggregation-caused quenching, dyads **5a–d** exhibited corresponding solid fluorescence although the quantum yields were low (0.02–0.05). The reinforced fluorescence in solution and solid state of dyads **5a–d** could be attributed to the additional aggregation restriction of the triphenylene groups for Bodipy units resulting in the decreases of the aggregation-caused quenching. The low quantum yield in film might indicate that triphenylene units and Bodipy units stacked randomly in film. Some alternate stacking of triphenylene units and Bodipy units was favorable for fluorescence but the other stacking of Bodipy units only resulted in aggregation-caused quenching. All these data suggested that the fluorescence properties of dyads **5a–d** were more excellent than that of precursors **A** and **B**, respectively. The triphenylene unit was favorable not only for producing columnar liquid crystal but also for reinforcing fluorescence. Combing both the mesomorphic and photophysical studies of dyads **5a–d**, it could be concluded that dyads **5a–d** possessed both good columnar liquid crystal and fluorescence properties. These results made important progress in comparison with the literature that the antinomy existed for the relationship of the mesomorphic property and the fluorescence property.[24]

In conclusion, four novel triphenylene-Bodipy dyads **5a–d** were designed and synthesized in yields of 32–38%. They exhibited both good liquid crystal properties and excellent fluorescence properties with high quantum yields in solution. These researches avoided successfully the previous antinomy for the relationship of the mesomorphic range and the fluorescence quantum yield, and confirmed that the stagger stacking of Bodipy moiety with triphenylene moiety maintained both columnar mesomorphic property and good fluorescence as expected. This paper provides a new idea on design and synthesis of novel Bodipy liquid crystal with good fluorescence.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.09.082.

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