



Synthesis, mesomorphism and fluorescence of triphenylene-Bodipy dyads



Xiaoting Fang^a, Hongyu Guo^a, Jianrong Lin^a, Fafu Yang^{a,b,*}

^a College of Chemistry and Chemical Engineering, Fujian Normal University, Fuzhou 350007, PR China

^b Fujian Key Laboratory of Polymer Materials, Fuzhou 350007, PR China

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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.

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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.

* Corresponding author. Tel./fax: +86 591 83465225.

E-mail address: yangfafu@fjnu.edu.cn (F. Yang).

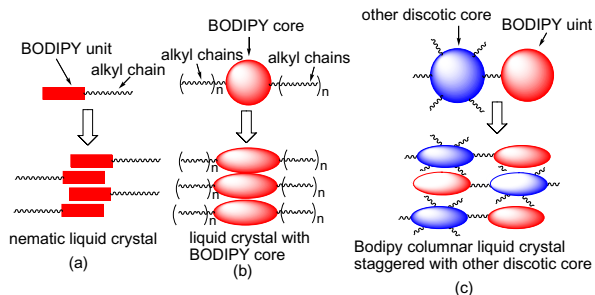
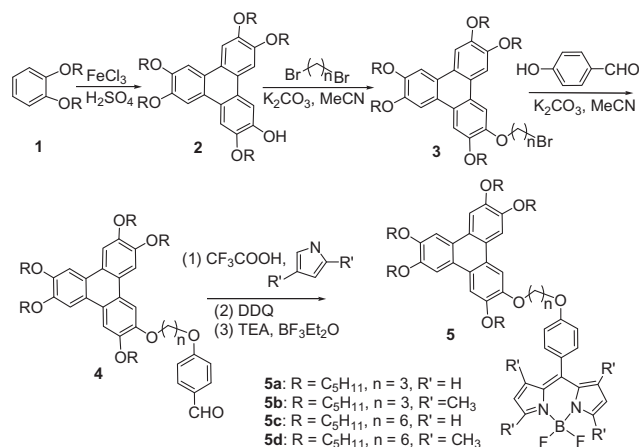


Figure 1. Three kinds of Bodipy liquid crystals. (a) and (b) had been reported, and (c) was not presented.

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-bis(pentyloxy)benzene **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 $\text{K}_2\text{CO}_3/\text{MeCN}$ 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 ^1H 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



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

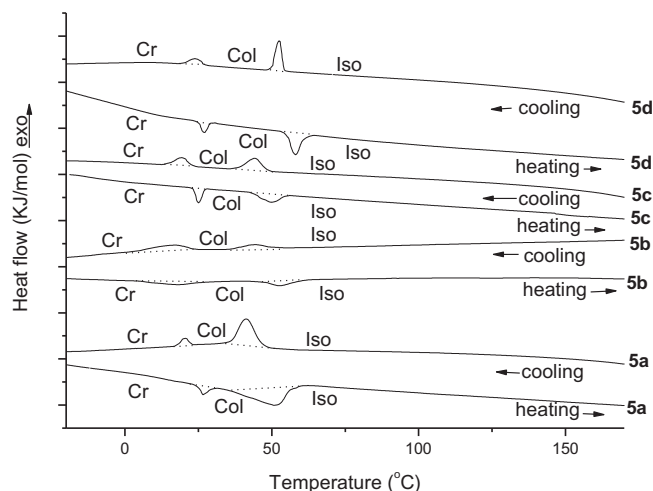


Figure 2. The DSC traces of compounds **5a–d** on heating and cooling (scan rate $10^\circ\text{C min}^{-1}$). Cr = crystalline, Col = columnar, Iso = isotropic.

Table 1

Phase transfer temperatures ($^\circ\text{C}$) 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.

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}

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 $2\theta = 5.03\text{--}5.19^\circ$, $8.74\text{--}9.02^\circ$ and $10.02\text{--}10.42^\circ$, 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 $2\theta = 16\text{--}25^\circ$ (3.56–5.53 Å, broad halo) and

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