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Columnar mesophases and phase behaviors of novel polycatenar mesogens containing bi-1,3,4-oxadiazole

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Abstract—A new series of liquid-crystalline bi-1,3,4-oxadiazole derivatives (2,2′-bis(3,4,5-trialkoxyphenyl)-bi-1,3,4-oxadiazole, BOXD-T*n*, *n*=3, 4, 5, 6, 7, 8, 10, 14) were designed and synthesized. They have been confirmed to give rise to columnar mesophases. The columnar mesophases for BOXD-T*n* (*n*=5, 6, 7, 8, 10) could be supercooled to −20 °C on the cooling runs. A room temperature Col_{ho} phase was obtained for BOXD-T14. All BOXD-T*n* exhibit good fluorescence properties either in cyclohexane or in solid state.

1. Introduction

Organic semiconducting materials with high carrier mobilities are desirable for various electronic applications including light-emitting diodes, solar cells, and field-effect transistors. However, most of the organic compounds known for optoelectronic applications still present some major limitations such as low electron conductivity and/or low luminescence efficiency. 1,3,4-Oxadiazoles derivatives have enjoyed widespread use as electron-transporting/hole blocking (ETHB) materials, emitting layers in electroluminescent diodes or for non-linear optical process, due to the electron-deficient nature of the heterocycle, high photoluminescence quantum yield, and good thermal, and chemical stabilities.[1] Non-mesomorphic 2,5-bis(4-naphthyl)-1,3,4-oxadiazole[2] has been demonstrated as one of the best organic electron conductors, and several oxadiazole-based compounds have been recently used as electron transport materials in organic light-emitting diodes (OLEDs).[3]

Liquid-crystalline materials, which present self-organizing ability, fluidity, and the ease of defect-free orientation with special treatment, have been recently recognized to have great advantages in manipulation of optimized high-efficiency organic electro-optic devices.[4] Materials with columnar mesophases in which molecules self-assemble to columnar structures have attracted increasing attention because the overlapping of π-orbitals results in one-dimensional semiconductors with a better performance than conjugated polymers.[5] Most of the reported mesomorphic 1,3,4-oxadiazole derivatives were generally rod-like molecules[6] exhibiting nematic/smectic phase. For example, 2,5-hexyloxybiphenyl-hexyloxyphenyl-oxadiazole (HOBP-OXD) exhibited smectic phases and high electron mobility (over 10^{-3} $cm^2/V/s$) was found in its high-ordered smectic phase.[6d] In contrast, columnar 1,3,4-oxadiazole derivatives were relatively limited. A star-shaped discotic molecule containing 1,3,5-triethynylbenzene and oxadiazole-based rigid arms was reported to exhibit a discotic nematic phase (N_{Col}).[7] Marder et al. reported that discotic molecules with benzene or triazine cores and three (trialkoxyaryl) oxadiazole arms exhibited columnar mesophases and demonstrated that these materials may find applications in organic electronics.[8] Lai et al. reported that 2,5-bis(3,4,5-trialkoxy phenyl)-1,3,4-oxadiazoles exhibited hexagonal columnar phases (Col_h), while their complexes with metals, Col_r and Col_h.[9]

Our present work aimed at developing new liquid-crystalline 1,3,4-oxadiazole derivatives, e.g., 2,2′-bis(3,4,5-trialkoxyphenyl)-bi-1,3,4-oxadiazole, BOXD-T*n*, *n*=3, 4, 5, 6, 7, 8, 10, 14. They have been confirmed to give rise to columnar mesophases. The columnar mesophases of BOXD-T*n* (n=5, 6, 7, 8, 10) could be supercooled to low temperature (−20 °C) due to their slow crystallization. A room temperature ordered columnar phase was identified for BOXD-T14. All the compounds exhibit good fluorescence properties either in cyclohexane or in bulk.

Keywords: 1,3,4-Oxadiazole; Liquid crystals; Columnar mesophases; Fluorescence.
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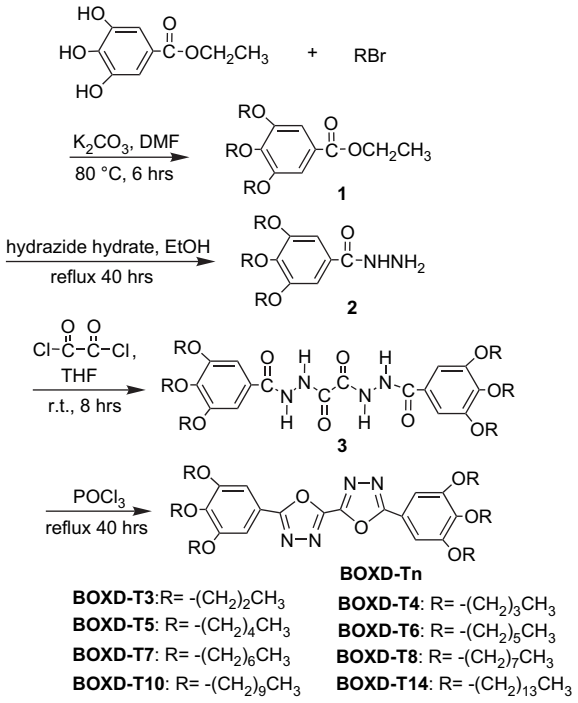
2. Results and discussion

2.1. Synthesis

Ethyl 3,4,5-trihydroxy benzoate, oxalyl chloride, and 1-bromide alkane were used as received. 3,4,5-Trialkoxy-benzoyl hydrazines **2** were prepared according to the literature.[8] Tetrahydrofuran (THF) was refluxed over sodium under argon and distilled before use. Scheme 1 shows the synthetic route for BOXD-T*n*. Anhydrous K_2CO_3 (30 g) and ethyl 3,4,5-trihydroxy benzoate (5.4 mmol) were added to a deoxygenated mixture of DMF (100 mL) and of 1-bromide alkane (18.1 mmol) under nitrogen. The mixture was heated at 80 °C for 6 h. The reaction mixture was cooled to room temperature, water (500 mL) was added, and the product was extracted with diethyl ether. The extractive solution was washed with water and dried over $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified through a column of silica gel using 2% ethyl acetate in hexane as eluent to afford **1**. A solution of **1** (19.2 mmol) and excess hydrazine monohydrate in ethanol (180 mL) was refluxed for 40 h. Water (100 mL) was added and the resulting precipitate was collected, dried under vacuum, and recrystallized from ethanol/water to give pure **2**. Oxalyl chloride (11.2 mmol) was regularly injected into the THF solution of 3,4,5-trialkoxy-benzoyl hydrazine **2** (23.1 mmol) under vigorous stirring at room temperature for 8 h. The resulted products of oxalyl acid *N*′,*N*′-di(3,4,5-trialkoxylbenzoyl)-hydrazide **3** were purified by recrystallizing from alcohol. The purified **3** was dissolved in phosphorous oxychloride ($POCl_3$) and refluxed for about 40 h. Excess $POCl_3$ was removed through distillation and the residue was slowly added into icewater. After the removal of solvent under reduced pressure, the crude products were further purified through a column of silica gel using 2% ethyl acetate in chloroform as eluent to afford BOXD-T*n*.



Scheme 1. Synthesis of BOXD-T*n*.

2.2. Mesomorphic properties

The phase transition temperatures and transition enthalpies for BOXD-T*n* (*n*=3, 4, 5, 6, 7, 8, 10, 14) are summarized in Table 1. It can be seen that the mesophase behaviors are greatly affected by the length of the terminal chains. BOXD-T3 and BOXD-T4 are non-mesomorphic perhaps due to the shorter terminal alkoxy groups, which cause the higher melting point and thus suppress the LC phase. On the other hand, BOXD-T*n* (*n*=5, 6, 7, 8, 10, 14) with longer alkoxyl terminal groups exhibited columnar phases as confirmed by polarizing microscopy, calorimetry, and X-ray diffraction investigations.

Figures 1 and 2 show the DSC thermograms of BOXD-T*n* (*n*=5, 6, 7, 8, 10, 14) on the first heating and cooling runs at a scanning rate of 10 °C/min. BOXD-T5 exhibited monotropic mesophases, while others with longer terminal chains exhibited enantiotropic mesophases. It should be mentioned that no crystallization was observed for BOXD-T*n* (*n*=5, 6, 7, 8, 10, 14) even when they were cooled to −20 °C at cooling rate of 10 °C/min. On subsequent heating (10 °C/min), the phase transition sequences of BOXD-T*n* (*n*=6, 7, 8, 10, 14) were reversible, while complex thermal behaviors were observed for BOXD-T5 (Fig. 3). Upon heating BOXD-T5 at 10 °C/min, an exothermic process between 56 °C and 74 °C, which was partially overlapped with the endothermic peak centered at 67.8 °C, followed by an endothermic peak centered at 77.1 °C (13.8 kJ/mol) was observed (Fig. 3f). In contrast, this exothermic process shifted to lower temperature, e.g., between 47 °C and 63 °C with the heat of 26.19 kJ/mol at 2 °C/min and the high-temperature endothermic peak centered at 74.7 °C (36.36 kJ/mol), which was assigned to the crystalline–isotropic transition similar to that in its first heating run (Fig. 3g), indicating that crystallization of BOXD-T5 took place during heating the mesophase. The lower the heating rates, the lower the crystallization temperature and the higher the enthalpic changes, suggesting its kinetic-controlled feature of the crystallization. The endothermic peak at 67 °C corresponding to mesophase to isotropic transition

Table 1. Phase transition temperatures (T/°C) and enthalpies (Δ*H*/kJ/mol in brackets) of BOXD-T*n* (*n*=3, 4, 5, 6, 7, 8, 10, 14) on the first heating and cooling runs[a]

Compound	Heating		Cooling	
BOXD-T3	Cr–I	182.3 (38.9)	I–Cr	175.9 (37.8)
BOXD-T4	Cr–I	139.8 (43.9)	I–Cr	122.8 (42.9)
BOXD-T5			Col_r–Col_L	23.2 (0.74)
	Cr–I	76.7 (39.4)	I–Col_L	63.8 (4.23)
BOXD-T6	Cr–Col_L	69.0 (50.8)	Col_L–Col_r	9.0 (0.3)
	Col_L–I	73.2 (3.8)	I–Col_L	70.8 (3.8)
BOXD-T7	Cr–Col_L	67.3 (54.2)		
	Col_L–I	77.7 (4.9)	I–Col_L	76.1 (4.5)
BOXD-T8	Cr–Col_L	67.3 (57.1)		
	Col_L–I	83.5 (4.4)	I–Col_L	81.1 (4.2)
BOXD-T10	Cr1–Cr2	36.4 (5.8)		
	Cr2–Col_L	60.6 (64.9)		
	Col_L–I	83.5 (4.9)	I–Col_L	79.8 (4.8)
BOXD-T14			Col_{II}–Col_{ho}	17.3 (15.2)
			Col_I–Col_{II}	23.1 (5.6)
	Cr–Col_L	68.6 (97.3)	Col_L–Col_I	26.2 (28.9)
	Col_L–I	80.9 (5.4)	I–Col_L	77.7 (5.3)

[a] Scanning rate of 10 °C/min.