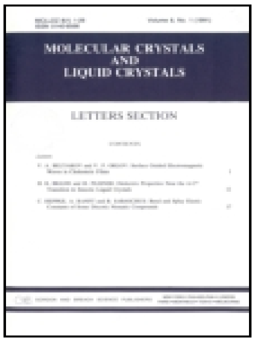

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Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Min-Yan Zheng, Yong-Sheng Wei, Wei Geng & Yuan-Zi Gu (2016) Synthesis of aromatic liquid crystals with asymmetric diester based on rod-like multi-ring system by two-step esterification method, Molecular Crystals and Liquid Crystals, 630:1, 19-27, DOI: 10.1080/15421406.2016.1146862

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1146862

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 630, 19–27
http://dx.doi.org/10.1080/15421406.2016.1146862

Synthesis of aromatic liquid crystals with asymmetric diester based on rod-like multi-ring system by two-step esterification method

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ABSTRACT

A novel method of two-step esterifications was developed to synthesize compounds with asymmetric double ester groups. By using this method, six rod-like double ester compounds were prepared with *p*-hydroxy benzaldehyde, *p*-hydroxy benzoic acid bicyclohexyl carboxylic acid, cyclohexyl benzoic acid and biphenyl carboxylic acid substituted by *n*-propyl and *n*-pentyl as main reactants. The structures and properties of target compounds were confirmed by IR, MS, ^{1}H NMR, elemental analysis, differential scanning calorimetry (DSC) and hot stage polarizing optical microscope (HS-POM). Typical yields of the target molecules were more than 70%. All the molecules have mesophases with the textures of nematic type, indicating a rod-like molecule with a longer rigid skeleton can keep its mesophases. There was no clearing point observed for any of the derivatives before they decomposed so that the temperature ranges of the mesophases could not be determined. The energy differences between frontier molecular orbitals (HOMO-LUMO) (E_g) of the compounds were calculated by cyclic voltammetry (CV). The terminal ring system has an obvious influence on the energy levels and the energy gaps (E_g).

KEYWORDS

Asymmetric diester; esterification; liquid crystal; the frontier molecular orbitals

1. Introduction

Usually, the incorporation of a larger group, such as (2,2,6,6-Tetramethyl-piperidin-1-yl) oxyl (TEMPO) or nitronyl nitroxide radical (NIT), linked with a rod-like liquid crystal core tends to inhibit the formation of a mesophase [1,2]. A common strategy for maintaining mesophase is to increase the linear length of terminal alkyl or alkoxy chains [3–6]. However, the molecules with alkyl or alkoxy (usually more than C_7) would have high viscosity so that the temperature range of their mesophase is narrow or even has no mesophase resulting from their terminal longer alkyl or alkoxy chain (flexible longer linker between rigid parts) were easily tied together [7]. It is found by our previous experience that the long rigid core is able to produce a stable mesophase and even to covert the nematic phase into the smectic phase by increasing the number of its core units (aromatic rings) or the length of a linking group. All of these provide a possibility to prepare molecules with long rigid core and termination by bulky group (such as nitroxyl) which form a liquid crystalline phase, especially a nematic phase. The

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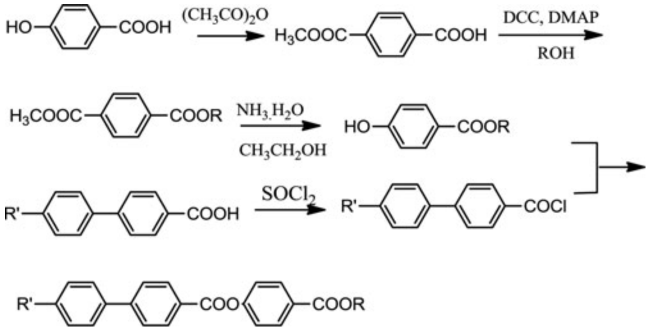
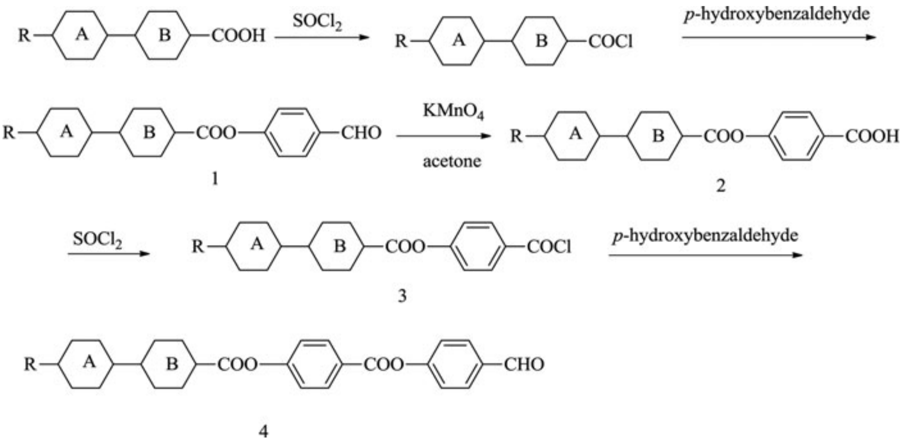


Scheme 1. The synthesis process of compounds with double ester from literature [11].

nematic phase is of great interest because it may be useful as a dopant in the practically used liquid crystal mixtures to improve their order parameter and elastic properties [8]. Based on our previous studies [9], a series of molecules with multi-ring, diester, terminal *n*-propyl or *n*-pentyl and aromatic aldehyde were synthesized by a simple pathway using the ester group as a linking bridge. The target compounds in the paper were important intermediates in designing functional molecules of new types [8]. By comparing these derivatives with similar compounds containing only single ester group, the influences from the length of rigid skeletons of these molecules on their mesophase were also investigated.

Normally, functional group protection is often used to synthesize compounds with asymmetric diester groups [10,11]. More steps are needed in this process, such as protection and deprotection of one or more functional groups, providing a complex process to obtain asymmetric diester compounds (Scheme 1). A better method of one-step oxidation and two-step esterifications to synthesize target compounds was designed by our group several years ago [12] (Scheme 2), which included no group protection and had better yields. To further simplify the synthesis process, a new method involving a two step esterification is described in this paper with fewer reaction steps and no group protection.

In this article, we describe the synthesis, characterization, thermal stability, mesomorphic behavior, electrochemical property of target compounds. Their electrochemical properties were also carried out by cyclic voltammetric method. The energy gaps between their HOMO and LUMO were calculated to assess the influence of molecular structures on their energy gaps.



Scheme 2. The method recorded in literature [12] with the yield about 60%.

Series 1:
a: R = *n*-propyl, A = *trans*-cyclohexyl, B = phenyl;
b: R = *n*-propyl, A = *trans*-cyclohexyl, B = *trans*-cyclohexyl;
c: R = *n*-propyl, A = phenyl, B = phenyl;
Series 2:
d: R = *n*-pentyl, A = *trans*-cyclohexyl, B = phenyl;
e: R = *n*-pentyl, A = *trans*-cyclohexyl, B = *trans*-cyclohexyl;
f: R = *n*-pentyl, A = phenyl, B = phenyl.

2. Experimental

2.1. Materials and characterization

All initial intermediates used in the process were synthesized in our lab. The purities of the intermediates were determined by LC-10A (Shimadzu) instrument with methanol as eluent and flowing rate was 1 mL/min and higher than 99%. Their structures were characterized by IR, GC-MS and ^{1}H NMR methods. Other reagents were from commercial sources and used as received without further purification.

Elemental analyses were conducted by PE-2400 analyzer (Perkin Elmer). UV spectra were determined by Agilent 8453 Spectrometer (Agilent Technologies). IR (KBr) spectra were recorded on a Vertex 70 spectrophotometer (Bruker). Mass spectral data were recorded on a GCMS-QP2010 (Shimadzu) and IE was 70 ev. ^{1}H NMR spectra were obtained on an Avance 500 (Bruker, 500 MHz, solvent $CDCl_3$). Cyclic voltammetric measurements were performed on an Epsilon (BAS) which was run by a General Purpose Electrochemical System software. The conventional three electrodes system was measured against SCE, Platinum wire and glassy carbon severed as reference, counter and working electrodes, respectively.

2.2. The synthesis of compounds 1

Take the synthesis of **1a** as an example. **1a** was made with 4-*n*-propyl-(4-*trans*-cyclohexyl benzoyl chloride and *p*-hydroxybenzaldehyde as main reactants according to the literature [8]. **1a** was obtained as a white crystal (0.61, 87%). **1b, 1c, 1d, 1e, 1f** were made with the same method with the yields of 85%, 83%, 86%, 84%, and 82%, respectively.

1**a**, $C_{23}H_{26}O_3$, molecular weight 350.20, white needle, ^{1}H NMR ($CDCl_3$, 500 MHz)δ: 0.91 (t, 3H, J = 7.5 Hz, CH_3), 1.08 (m, 2 H, CH_2), 1.23 (m, 2 H, CH_2), 1.35–2.58 (m, 10 H, the protons of cyclohexane), 7.36 (d, 2 H, J = 8.5 Hz, the protons of aromatic), 7.38 (d, 2 H, J = 9 Hz, the protons of aromatic), 7.97 (d, 2 H, J = 8.5 Hz, the protons of aromatic), 8.11 (d, 2 H, J = 8.5 Hz, the protons of aromatic), 10.03 (s, 1 H, CHO) [12].

2.3. The synthesis of compounds 4

Take the synthesis of **4a** as an example. **2a** was made according to the literature [9]. **2a** was obtained as a white crystal (1.6 g, 88%).

2a, $C_{23}H_{26}O_4$, molecular weight 366.45, white needle, ^{1}H NMR($CDCl_3$, 500 MHz)δ: 0.78 (t, 3 H, J=7.5 Hz, CH_3), 0.97 (m, 2H, CH_2), 1.11 (m, 2H, CH_2), 1.21–2.55 (m, 10H, the H of cyclohexane), 7.30 (d, 2H, J = 8.5 Hz, the protons of aromatic), 7.35 (d, 2H, J = 9 Hz, the protons of aromatic), 7.98 (d, 2H, J = 8.5 Hz, the protons of aromatic), 8.01 (d, 2H, J = 8.5 Hz, the protons of aromatic), 13.00 (s, 1H, COOH).

Table 1. Molecular formula, molecular weight, mass fraction, appearance, yield, m.p. and elementary analysis for target compounds.

							Elementary analysis (calcd.) (%)	
Compd.	Molecular formula	Molecular weight	Mass fraction (LC) (%)	Appearance	Yield (%)	m.p. (°C)	C	H
4a	$C_{30}H_{30}O_5$	470.15	99.2	White crystal	75	155–156	76.36 (76.57)	6.50(6.43)
4b	$C_{30}H_{32}O_5$	476.42	99.1	White crystal	77	144–145	75.41(75.60)	7.72(7.62)
4c	$C_{30}H_{24}O_5$	464.31	99.0	White needle	74	158–159	77.34 (77.57)	5.47(5.21)
4d	$C_{32}H_{34}O_5$	498.22	99.2	White needle	77	137–138	76.90(77.08)	6.79(6.87)
4e	$C_{32}H_{36}O_5$	504.13	99.3	White flake	76	103–104	76.01(76.16)	7.79(7.99)
4f	$C_{32}H_{28}O_5$	492.39	99.2	White flake	70	137–138	78.21(78.03)	5.47(5.73)

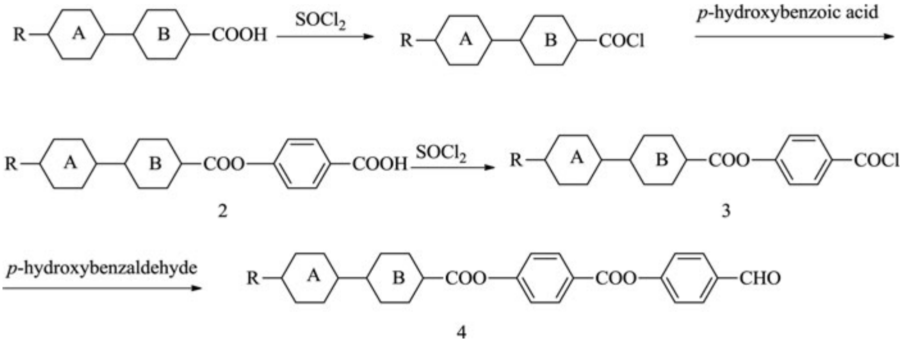
3a was prepared by heating and stirring a mixture of **1a** (3.7 g, 10 mmol), $SOCl_2$ (1.8 g, 15 mmol) and DMF of two to three drops with the method in literature elsewhere [8]. A green solid was obtained and used to next step without further purification. **3a**(3.80 g, 99%), $C_{23}H_{25}ClO_3$, molecular weight 384.90, green solid, ^{1}H NMR($CDCl_3$, 500 MHz)δ: 0.91 (*t*, 3H, J=7.5 Hz, CH_3), 1.25 (m, 2H, CH_2), 1.31 (m, 2H, CH_2), 1.52–2.72 (m, 10H, the H from cyclohexane), 7.45 (d, 2H, J = 8.5 Hz, the protons of aromatic), 7.58 (d, 2H, J = 9 Hz, the protons of aromatic), 8.14 (d, 2H, J = 8.5 Hz, the protons of aromatic), 8.22 (d, 2H, J = 8.5 Hz, the protons of aromatic).

4a was synthesized by dissolving *p*-hydroxybenzaldehyde in CH_2Cl_2 (20 mL) and dropping the mixture into the solution of CH_2Cl_2 (20 mL) and *p*-hydroxybenzaldehyde, then triethylamine of 1.2 mL (10 mmol) was added. The reaction was worked up according to method from the literature [7] to give **4a** as a white crystal (1.8 g, 86%). The **4b, 4c, 4d, 4e, and 4f** were also synthesized by the same way. The synthesis of all target compounds is summarized in Scheme 2 and their structural data are shown in Tables 1 and S1. The spectral data are in accordance with their assigned structures.

3. Results and discussion

3.1. The discussion of method in synthesizing compounds with double ester group

Group protection is a most common method to synthesize asymmetric aromatic diesters. Nowadays, the methods used to synthesize asymmetric aromatic diesters are shown in Scheme 1 and Scheme 2. The total yield of the target products in the process shown in Scheme 1 were about 30%. The pathway involved the protection and de-protection of the hydroxide group so that more reaction steps were needed. The method in Scheme 2 used alkyl substituted carboxylic acids which were esterified with *p*-hydroxybenzaldehyde. Then the esterified products were oxidized by $KMnO_4$ in an acetone solution. The target products with double ester groups were then obtain *via* esterification a second time. There was no any functional group needed to protect, so that the total yield of about 60% can be obtained by the method in Scheme 2. Due to asymmetric diester compounds often used as a moiety of organic material, it is worth to developing a simple route with a higher yield. During the preparation of a series of azo materials [9], through a great deal of attempts, we found that esterification of the hydroxyl in *p*-hydroxy azo benzoic acid can be done at room temperature, while esterification of the carboxyl group of p-hydroxy azo benzoic acid would be carried out at heated condition. Once p-hydroxy azo benzoic acid was substituted by *p*-hydroxy benzoic acid to participate the reaction, if the reaction still work is worth studying. So, the reaction pathway



Scheme 3. A simplified synthetic pathway for two step-esterification of target compounds with yields of more than 70%.

was attempted with *p*-hydroxy benzoic acid as a main reactant, the result showed the reaction process was still work well here. The modified method in Scheme 3 results in greater than 70% yields and fewer reaction steps that previous methods.

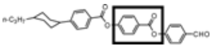
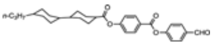
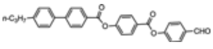
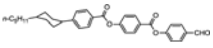
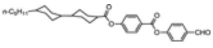
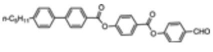
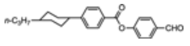
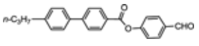
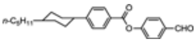
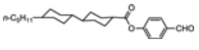
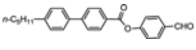
3.2. *The mesophase of target molecules*

The mesophases of target compounds were determined by polarizing microscope. The six compounds showed mesophasic textures of nematic type (on heating process). No smectic and cholesteric phase was observed. No clearing point was found before their decomposition. The POM textures of the six compounds are shown in Figures 1(A)–(F), respectively.

3.3. *The determination of DSC thermograms of compounds 4*

DSC thermograms were recorded at the rate of 10°C/min during heating process. The compounds decompose before clearing to isotropic. The transition temperatures, associated enthalpy values obtained from DSC studies and the ranges of decomposing from thermogravimetric analysis (TG) for the target compounds are summarized in Table 2. The melting temperatures of these series are observed in the range between 104°C and 160°C. The temperature ranges of their decomposing points measured by TG determination are from 216°C to 327°C. Among them, **4f** with terminal *n*-pentyl and two benzene rings is least stable, while

Table 2. The DSC data of compounds 4 and compounds **1**.

Series	Compd.	Structural formula	m.p. (°C)	ΔH_m ($J.g^{-1}$)	d.p. (°C)	ΔH_d ($J.g^{-1}$)	L/W *	Compd.	Structural formula	m.p. (°C)	ΔH ($J.g^{-1}$)	L/W *
1	**4a**		156	54	327	104	5.70	**1a**		100	60	4.11
	4b		144	50	298	109	5.86	**1b**		71	84	3.95
	4c		160	45	245	60	4.98	**1c**		111	64	4.09
2	**4d**		138	73	240	148	6.28	**1d**		93	51	4.62
	4e		104	31	307	25	6.32	**1e**		64	66	4.43
	4f		138	39	216	43	5.05	**1f**		91	47	4.66

* L/W represents the ratios of the molecular length to the its width calculated by Chembio 3D Ultra 12.0.

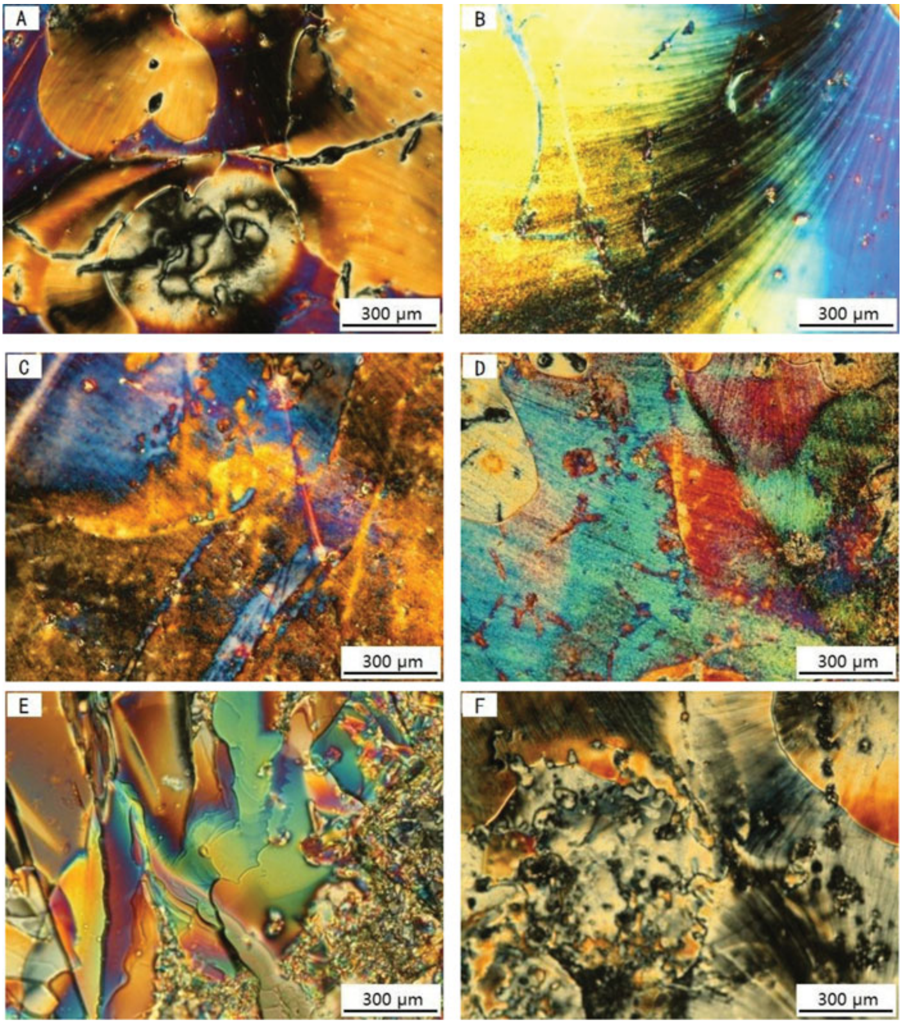


Figure 1. The polarizing optical microscope textures of compounds 4. (A)–(F): The marbled texture of **4a**, **4b**, **4c**, **4d**, **4e**, and **4f** taken at 170°C, 168°C, 184°C, 155°C, 135°C, 165°C, respectively, ×300.

4a with terminal *n*-propyl cyclohexane and one benzene ring is the most stable. The compounds **4c** or **4f** with terminal double benzene rings are the least stable ones in their own series. The transition temperature obtained from DSC analysis is in good agreement with a result observed from POM.

The influence of the benzoyloxy group (marked in black line in **4a**) on thermodynamic property in compounds 4 can be obtained by comparing the melting points between the two kinds of compounds with similar structures (4 and 1). Table 2 tells us that, compounds 1 and compounds 4 have the same trends in m.p. changes. For example, among compounds 1 and 4, the lowest melting points was produced by the compounds with terminal double cyclohexane rings. The influence of the extra benzoyloxy on the melting points can be found by comparing their melting points (between **1a** and **4a**, **1b** and **4b**, **1c** and **4c**, **1d** and **4d**, **1e** and **4e**, **1f**, and **4f**), In comparing **4a**–**4d** to compounds **1a**–**1d**, the melting points are increased in Series 1 by between 49°C and 73°C and the melting points are also increased in Series 2 by 40°C to 47°C.

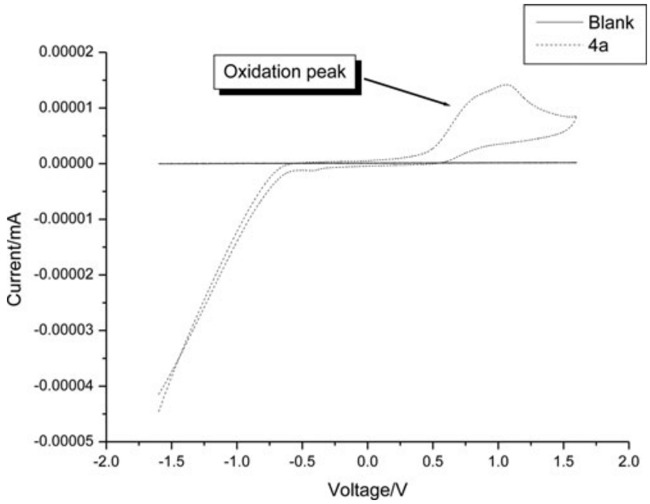


Figure 2. The Cyclic voltammogram of **4a** in dilute THF solution with tetrabutylammonium perchlorate as supporting electrolyte. The dotted line shows CV of blank run under identical condition.

The data in Table 2 also indicates the benzoyloxy has the bigger influence on the melting points of these compounds with terminal *n*-propyl bi-cyclohexane rings, while it has a smaller effect on the melting points of those compounds with terminal *n*-pentyl bi-cyclohexane rings. Comparing with compounds 1, we found the fact that the melting points of compounds 4 are even increasing more in series 1 than those in the series 2 of compounds 4 also suggests the terminal *n*-pentyl has more influence on melting point than the terminal *n*-propyl. In other words, the terminal *n*-pentyl can somehow shield the influence of the one more benzoyloxy in molecules.

3.4. Electrochemical analysis

The energy levels and energy gaps of the compounds 4 and 1 were measured out by cyclic voltammetric method with three electrodes system (SCE, platinum wire and glassy carbon serves as reference, counter and working electrodes, respectively, concentration is 4×10^{-3} mol/L with THF as solvent and tetrabutyl ammonium perchlorate as supporting electrolyte). The E_{HOMO}, E_{LUMO} and the corresponding band gap (E_g) were calculated by following equations:

$$E_{\mathrm{HOMO}} = -e\,(E_{\mathrm{onset}}{}^{\mathrm{ox}} + 4.4)\ (\mathrm{eV})\,;$$

$$E_{\mathrm{LUMO}} = -e\left(E_{\mathrm{onset}}{}^{\mathrm{red}} + 4.4\right)\ (\mathrm{eV})\,;$$

$E_g = -\mathrm{e}\Delta\Phi$, $\Delta\Phi = \Phi_p - \Phi_n$ [13]. where e is elementary charge, Φ_p is the onset oxidation potential, Φ_n is the onset reduction potential and E_g is the E_{gap} presumably. The typical voltammogram of **4a** is shown in Fig. 2. A obvious oxidation peak can be observed in the CV curve of **4a** (Fig. 2). All these compounds (4 and 1) each has an oxidation peak, but no reduction peak is observed. In the CV curve, E_{ox} is the potential value of the intersection point between the electric current datum line and the tangent line of the starting point of the oxidation peak. The E_{HOMO}, E_{LUMO}, and E_g of every compound were summarized in Table 3.

Table 3. Redox potentials, E_{HOMO}, E_{LUMO} and energy gaps of target compounds.

Series	Compd.	E_{ox} (Φ_p) (eV)	λ_{max}(λ_{onset}) (nm)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	Compd.	E_{ox} (Φ_p) (eV)	λ_{max}(λ_{onset}) (nm)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
1	**4a**	0.40	257(297)	−4.80	−0.63	4.17	**1a**	0.46	257(294)	−4.86	−0.65	4.21
	4b	0.37	257(295)	−4.77	−0.57	4.20	**1b**	0.41	259(292)	−4.81	−0.56	4.25
	4c	0.55	286(330)	−4.95	−1.20	3.75	**1c**	0.49	289(325)	−4.89	−1.07	3.82
2	**4d**	0.49	256(293)	−4.89	−0.66	4.23	**1d**	0.40	257(295)	−4.80	−0.60	4.20
	4e	0.40	255(297)	−4.80	−0.63	4.17	**1e**	0.34	257(300)	−4.74	−0.61	4.13
	4f	0.51	287(327)	−4.91	−1.12	3.79	**1f**	0.45	290(335)	−4.85	−1.15	3.70

[a] Optical band gaps were calculated from onset absorption wavelengths using equation, $E_g = 1240/\lambda_{onset}$ [14].

The data of the E_{HOMO}, E_{LUMO}, and the E_g of each compound were different from each other and has obvious change rules. These energy levels have a relationship with their terminal ring structures. Compared with compounds 1, having a terminal benzene ring impacts $\boldsymbol{E_g}$, but having an extra benzoyloxy group has little effect on E_g.

In Table 3, we have found that the only structural difference that yielded a change in electrochemical properties was the inclusion of additional terminal benzene rings. So **1c**, **1f**, **4c**, and **4f** have the narrowest E_g in their own series, respectively. Their E_{ox} are higher, their E_{HOMO}, E_{LUMO}, and E_g are lower. The result is in good agreement that compounds composed with longer conjugate system (double benzene rings) have lower energy gaps between their frontier molecular orbitals (HOMO and LUMO). The terminal *n*-propyl and *n*-pentyl show no obvious effect on E_{ox}, E_{HOMO}, E_{LUMO}, and E_g.

4. Conclusion

A new method was developed to synthesize compounds of asymmetric double ester group with yields of more than 70% and without functional group protection. With other methods for making similar compounds, more reaction steps were required with the total yield about 60% [12] or less than 30% [9].

By comparing compounds 4 and 1, the influences of an additional ester group, terminal ring system and alkyl chain on the thermodynamic property of those compounds could be determined.

The result in this paper tell us when the linear length of the molecule were increased by a rigid skeleton of multi-ring system and multi-ester groups, it would be easier to maintain its mesophase than those compound only with longer alkyl or alkoxy chain. It is because that the longer rigid skeleton would increase the sequence of molecules in a longer rod-like molecule in order to keep their mesophase. The CV illustrate that the terminal ring system have an obvious influence on the energy levels (HOMO, LUMO, and E_g) of target molecules.

Acknowledgments

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 21102121), the Natural Science Foundation of Shaanxi Province (No. 2014JM2-2014).

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