齊魯工業大學
QILU UNIVERSITY OF TECHNOLOGY

# 本科毕业论文

# 系列3-羟基-2-萘甲酸酯的合成

学院名称　化学与制药工程学院
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# Synthesis of a set of 3-hydroxy-2-naphthoate esters

# 系列 3-羟基-2-萘甲酸酯的合成

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# Contents

# Abstract

Four kinds of new compounds, namely, methyl-3-hydroxy-2-naphthoate, ethyl-3-hydroxy-2-naphthoate, *n*-propyl-3-hydroxy-2-naphthoate and *i*-propyl-3-hydroxy-2-naphthoate, have been generated, which were structurally characterized by UV-Vis spectra, IR spectra and photoluminescent spectra. These compounds reveal a one-dimensional (1D) structure, which will be further extended to a three-dimensional (3D) supramolecular framework via a variety of hydrogen bonds, π···π interactions and C-H···π interactions and so on. The photoluminescent properties of compounds **1-4** were investigated in the solid state at room temperature and meanwhile, in ethanol solution. While the UV-Vis spectra of compounds **1-4** was carried out in ethanol solution.

This paper further studies and analyzes the structures and properties by changing its different substituents.

**Keywords**: methyl-3-hydroxy-2-naphthoate; ethyl-3-hydroxy-2-naphthoate; *n*-propyl-3-hydroxy-2-naphthoate; *i*-propyl-3-hydroxy-2-naphthoate; UV-Vis spectra; IR spectra; photoluminescent spectra

# 摘 要

四种新的复合物，即 3-羟基-2-萘甲酸甲酯，3-羟基-2-萘甲酸乙酯，3-羟基-2-萘甲酸丙酯和 3-羟基-2-萘甲酸异丙酯生成，其结构特征经过紫外-可见光谱，红外光谱，荧光光谱进行了深一步研究与测量。这些化合物显示了一维（1D）结构,并且其通过氢键，π… π相互作用和 C-H… π相互作用等进一步扩展到三维(3D)超分子骨架。化合物 1-4 的光致发光性质是在室温固态状态下和乙醇溶液中分别进行的，而化合物 1-4 的紫外-可见光谱则在乙醇溶液中进行检测。

本文通过改变其不同取代基，对结构和性质等内容进行了进一步研究和分析。

**关键词：**3-羟基-2-萘甲酸甲酯　3-羟基-2-萘甲酸乙酯　3-羟基-2-萘甲酸丙酯　3-羟基-2-萘甲酸异丙酯　荧光光谱　紫外-可见光谱　红外光谱

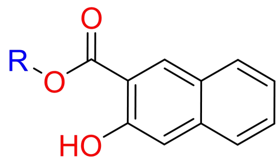
# Chapter 1

## 1.1 Introduction

3-Hydroxy-2-naphthoate is an important intermediate for the synthesis of functional polymers, 3-hydroxy-2-naphthoquinone, and its synthesis technology has been the focus of research in the field of intermediate synthesis and functional materials. Its applications are very extensive, and it is often used as a luminescent reagent for electrochemiluminescence technology, which can effectively improve the sensitivity of electrochemiluminescence. In addition, by using such luminescent reagents, electrochemiluminescence technology can be more widely applied to medicine, biology, pharmacy, clinical, environmental, video, immune, nucleic acid hybridization analysis, industrial analysis and other related fields. With good reagent stability, high luminous efficiency, reaction in the water phase, etc, it can replace some reagents for chemical detection.

Ester is an important class of chemical raw materials, and its use is quite extensive, for example, a fragrance, solvent, plasticizer and organic synthesis intermediate. At the same time, it has important use value in the coating, medicine and other industries. As one of the most basic and important central bridges of liquid crystal compounds, the synthesis of ester groups is of great significance. For a long time in the past, the synthesis of esters mainly used some classic methods, such as acid catalysis, acid chloride method, ester cross-linking method, etc; with the study of various new catalysts and organic reaction mechanisms, some novel synthetic methods have emerged, such as Mitsunobu reaction, Steglich esterification, $Me_3SiCl$ catalysis, etc. The study of these new synthetic methods will help promote the use of simpler, more efficient and gentler methods in the laboratory to produce new organic compounds, and further apply to industrial production and social progress.

## 1.2 Basic Organic Structure of Compounds 1-4



**R**: $-CH_3$ (**1**)
$-CH_2CH_3$ (**2**)
$-CH_2CH_2CH_3$ (**3**)
$-CH(CH_3)_2$ (**4**)

## 1.3 Main Features of methyl-3-hydroxy-2-naphthoate

(1) Density: 1.264 g/cm$^3$

(2) Melting Point: 330.5 °C at 760 mmHg

(3) Flash Point: 142.5 °C

(4) Molecular Weight: 202.206

(5) It is slightly harmful to water. Do not let undiluted or large quantities of products have contact with ground water, waterways or sewage systems. If there is no government permission, do not discharge materials into the surrounding environment.

(6) Stable under normal temperature and pressure, avoiding oxides and alkali contact.

(7) Store in cold, dry conditions, in a ventilated area away from heated and incompatible materials, sealed and preserved.

# Chapter 2 Experiments

## 2.1 Synthesis

### 2.1.1 Synthesis of methyl-3-hydroxy-2-naphthoate (1)

A mixture of 3-hydroxy-2-naphthoic acid (1.88 g, 10 mmol), the dried methanol (10 ml) and 98% $H_2SO_4$ (1 ml) was stirred under 80 °C. TLC was used to monitor the reaction. After finishing the reaction, the reaction mixture was neutralized by saturated $NaHCO_3$. The pale-yellow precipitate was filtered under vacuum and washed by ethanol. Yield (1.56 g, 77.2 %). The samples were recrystallized from ethanol. The pale-yellow needle crystals suitable to single-crystal X-ray diffraction were obtained after 3 days. M.p. 78-80 °C. Elemental analysis calcd (%) for $C_{12}H_{10}O_3$ (202.21): C, 71.28; H, 4.98; found: C, 71.49; H, 4.97. IR (KBr, $cm^{-1}$): 3421(s), 2952(w), 2850(w), 1684(s), 1637(m), 1518(m), 1442(m), 1417(m), 1385(m), 1356(w), 1321(m), 1281(m), 1215(s), 1173(w), 1146(s), 1072(s), 995(m), 955(m), 916(m), 872(w), 787(m), 748(m), 692(w), 623(w), 515(m), 469(w), 418(w).

### 2.1.2 Synthesis of ethyl-3-hydroxy-2-naphthoate (2)

The preparation process of compound **2** was similar to that of **1** except that the dried methanol was replaced by the dried ethanol. Many crystals were obtained from ethanol under room temperature through volatilization of the solvent. The pale-yellow needle crystals suitable to single-crystal X-ray diffraction were obtained. Yield (1.53 g, 70.9 %). M.p. 66-68 °C. Elemental analysis calcd (%) for $C_{13}H_{12}O_3$ (216.24): C, 72.21; H, 5.59; found: C, 72.06; H, 5.58. IR (KBr, $cm^{-1}$): 3552(s), 3473(s), 3415(s), 3236(w), 2993(w), 2964(w), 2931(w), 1776(w), 1680(s), 1641(s), 1618(s), 1572(w), 1520(w), 1462(w), 1425(w), 1383(w), 1321(w), 1284(s), 1215(s), 1169(m), 1141(s), 1074(s), 1014(w), 951(w), 868(w), 791(w), 754(w), 737(w), 702(w), 623(s), 515(m), 478(m).

### 2.1.3 Synthesis of *n*-propyl-3-hydroxy-2-naphthoate (3)

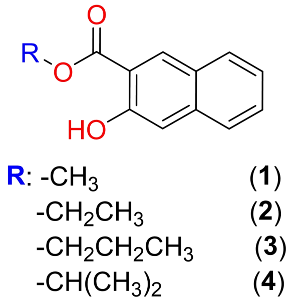
The preparation process of compound **3** was similar to that of **1** except that the dried methanol was replaced by the dried *n*-propanol. Many crystals were obtained from ethanol under room temperature through volatilization of the solvent. The pale-yellow needle crystals suitable to single-crystal X-ray diffraction were obtained. Yield (1.17 g, 50.8 %). M.p. 36-38 °C. Elemental analysis calcd (%) for $C_{14}H_{14}O_3$ (230.26): C, 73.03; H, 6.13; found: C, 73.18; H, 6.14. IR (KBr, $cm^{-1}$): 3552(s), 3473(s), 3415(s), 3238(m), 2964(w), 2933(w), 2875(w), 1942(w), 1867(w), 1817(w), 1770(w), 1682(m), 1641(m), 1618(s), 1516(m), 1464(m), 1423(m), 1327(m), 1286(m), 1215(m), 1173(w), 1146(s), 1070(s), 995(w), 953(m), 906(w), 874(w), 849(w), 787(w), 760(w), 748(w), 623(m), 515(w), 471(w).

### 2.1.4 Synthesis of *i*-propyl-3-hydroxy-2-naphthoate (4)

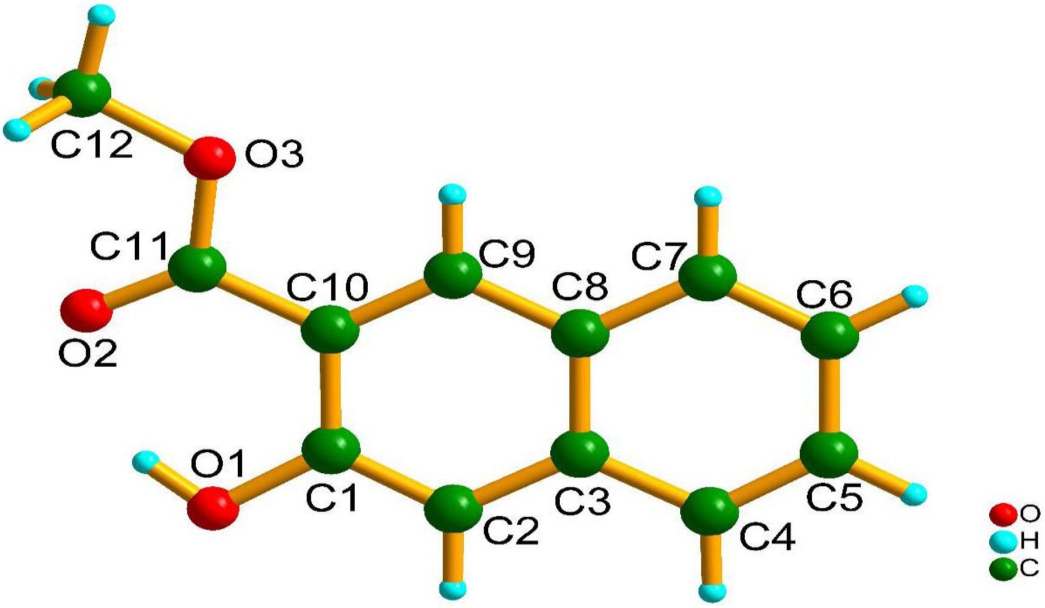
The preparation process of compound **4** was similar to that of **1** except that the dried methanol was replaced by the dried *i*-propanol. Many crystals were obtained from ethanol under room temperature through volatilization of the solvent. The pale-yellow needle crystals suitable to single-crystal X-ray diffraction were obtained. Yield (1.14 g, 49.7 %). M.p. 78-80 °C. Elemental analysis calcd (%) for $C_{14}H_{14}O_3$ (230.26): C, 73.03; H, 6.13; found: C, 73.19; H, 6.12. IR (KBr, $cm^{-1}$): 3464(s), 3419(s), 2978(w), 2941(w), 1795(w), 1770(w), 1680(m), 1637(s), 1618(s), 1556(w), 1508(m), 1464(m), 1385(m), 1311(w), 1215(m), 1176(w), 1147(m), 1103(s), 1068(s), 993(w), 953(w), 908(m), 872(w), 822(w), 789(w), 746(w), 690(w), 623(m), 515(w), 474(w), 445(w), 418(w).

# Chapter 3 Results and Discussion

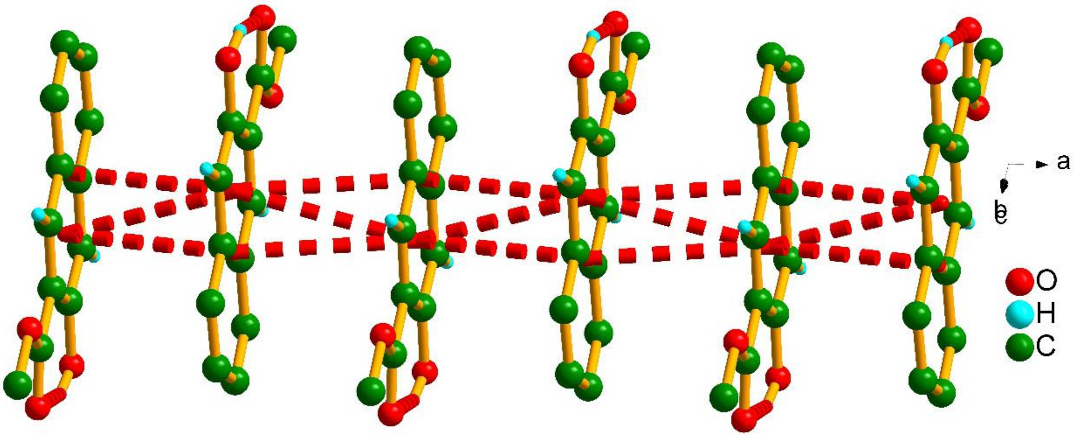
## 3.1 Organic Structures of Compounds 1-4.



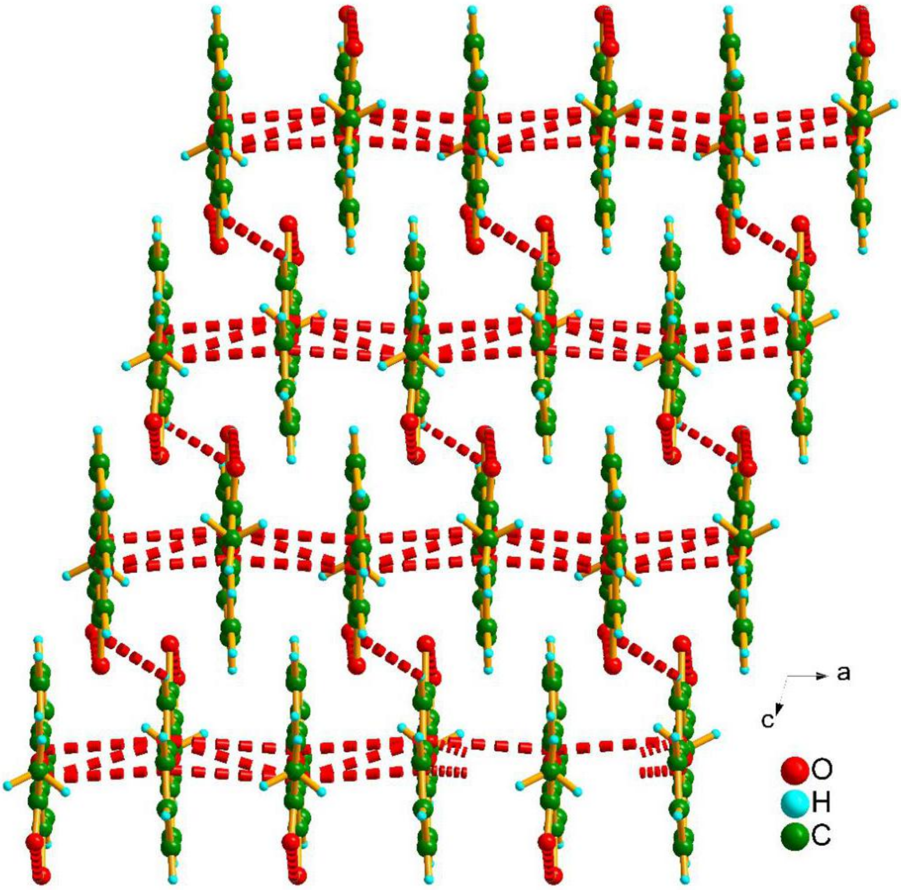
**Scheme 1 The Organic Structure of methyl-3-hydroxy-2-naphthoate**



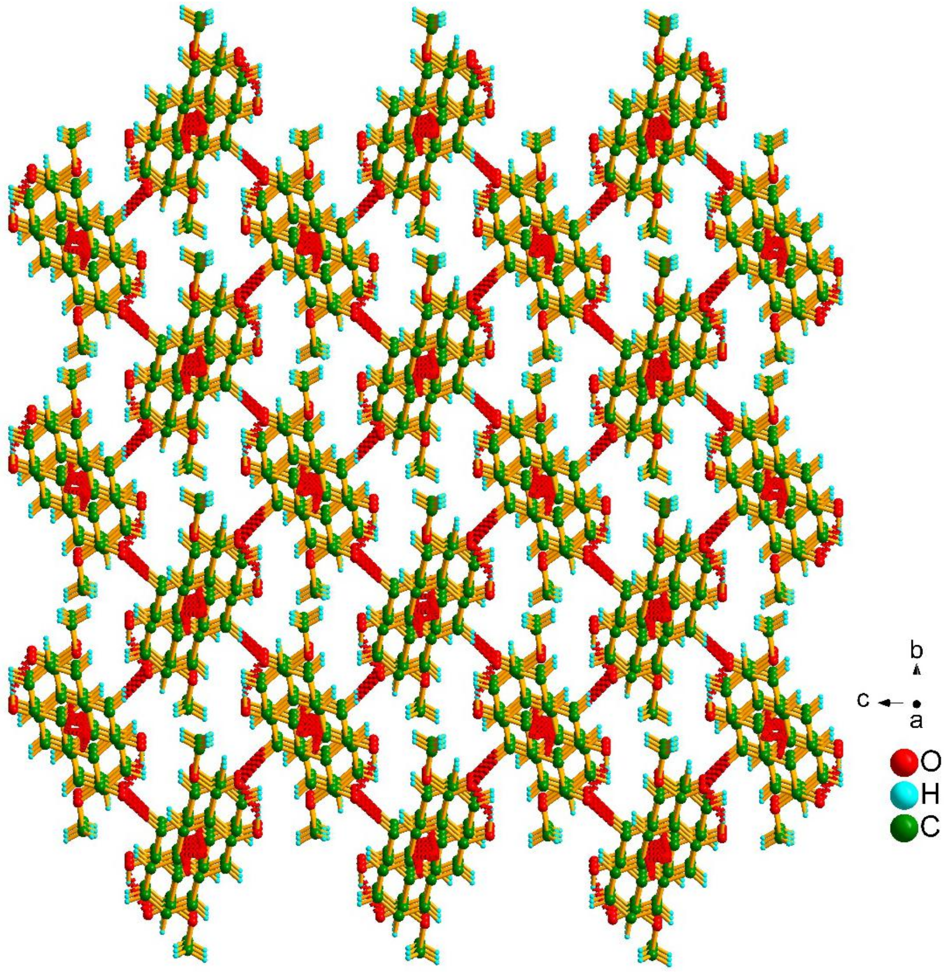
(a)



(b)



(c)



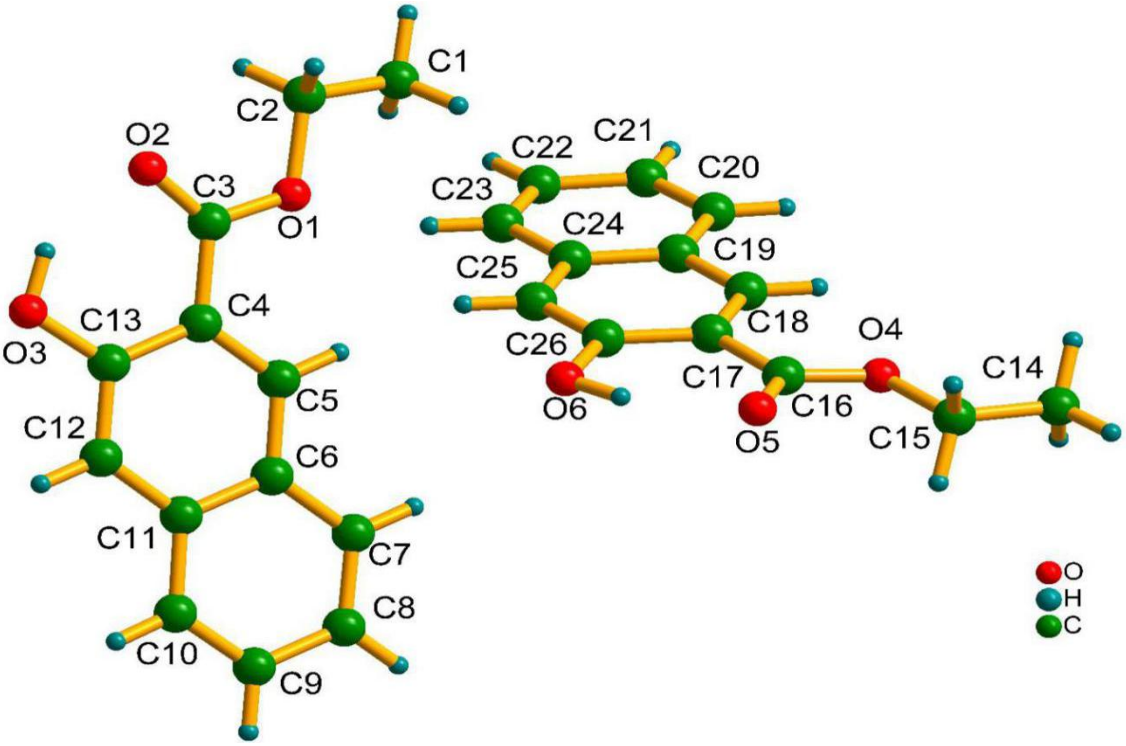
(d)

**Fig. 1**. (a) A perspective view of **1**. (b) A supramolecular 1D chain through the weak hydrogen bonds along the *a* axis. (c) A supramolecular 2D network by hydrogen bonds interactions along the crystallographic *ac* plane in **1**. (d) A stacking diagram of **1** along the *a* axis.

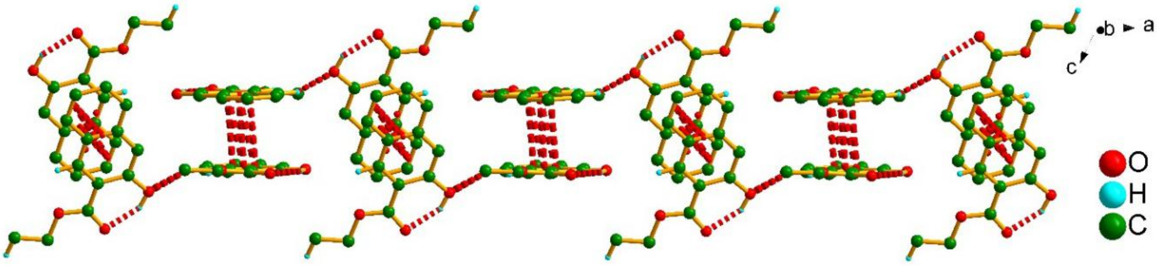
Crystal of compound **1** comprises one naphthalene ring, a hydroxy group, a ester group containing a methyl group. Besides, for 1D (1-dimensional) network, it is observed that a host of units are connected by two weak π···π interactions, namely, Cg(1)···Cg(3) and Cg(1)···Cg(1) along the *a* axis. It is worthy mentioning that the observation of O2-H2 hydrogen bond plays an important role in obtaining the extended 2D (2-dimensional) supramolecular structure. So, according to what mentioned above, generally, thanks to the π···π interactions, the hydrogen bonds and also the significant packing interactions, a 3D supramolecuar structure is finally constructed.

The bond distances of O3-C12, C10-C11, O1-C1 are 1.447, 1.468, 1.355 Å severally, and the bond lengths of two double bonds C6-C7 and C5-C4 are 1.363 and 1.347 Å respectively. Additionally, the weak π···π interactions between Cg(1)···Cg(3) (3.581 Å, 1+x, 1.5-y, 1.5+z) and Cg(1)···Cg(1) (3.652 Å) can be investigated, where the aromatic rings Cg(1) and Cg(3) contain C(1)-C(2)-C(3)-C(8)-C(9)-C(10) and C(1)-C(2)-C(3)-C(4)-C(5)-C(6)-C(7)-C(8)-C(9)-C(10) respectively. Moreover, the presence of O2-H2 hydrogen bond, whose bond distance is 2.570 Å definitely, is founded between the two adjacent units and it is the basis for 1D (1-dimensional) organic chains changed to 2D supramolecular layer along the crystallographic *ac* plane.

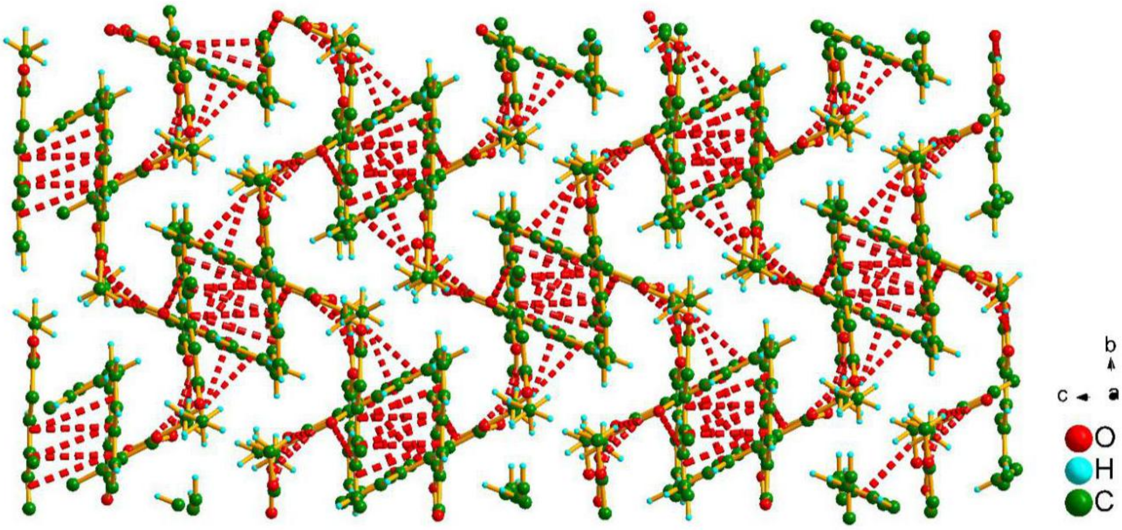
**Scheme 2 The Organic Structure of ethyl-3-hydroxy-2-naphthoate**



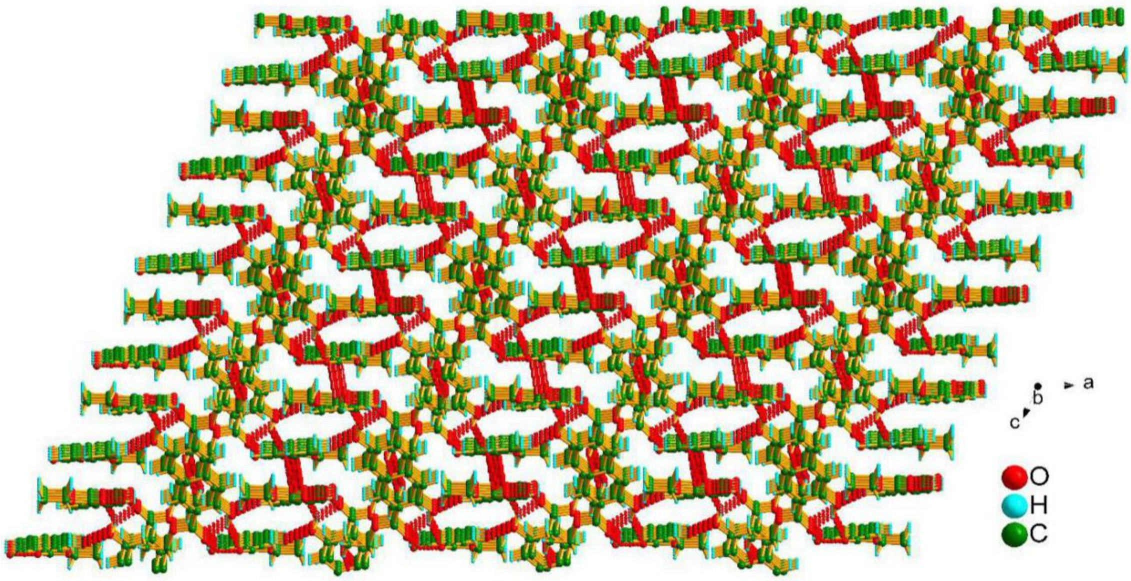
(a)



(b)



(c)

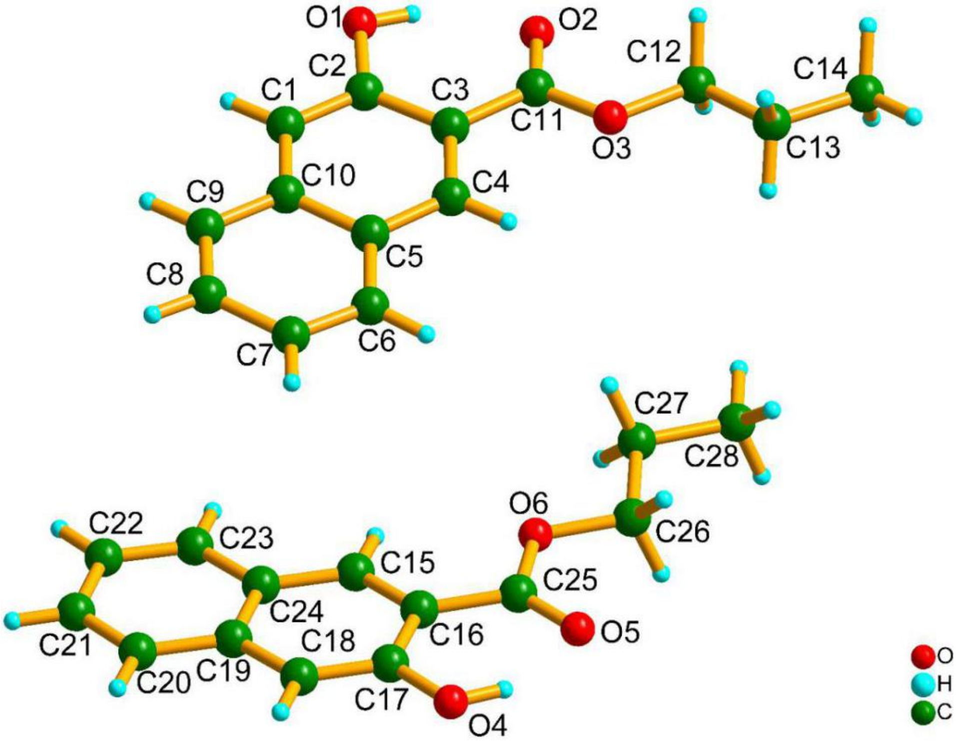


(d)

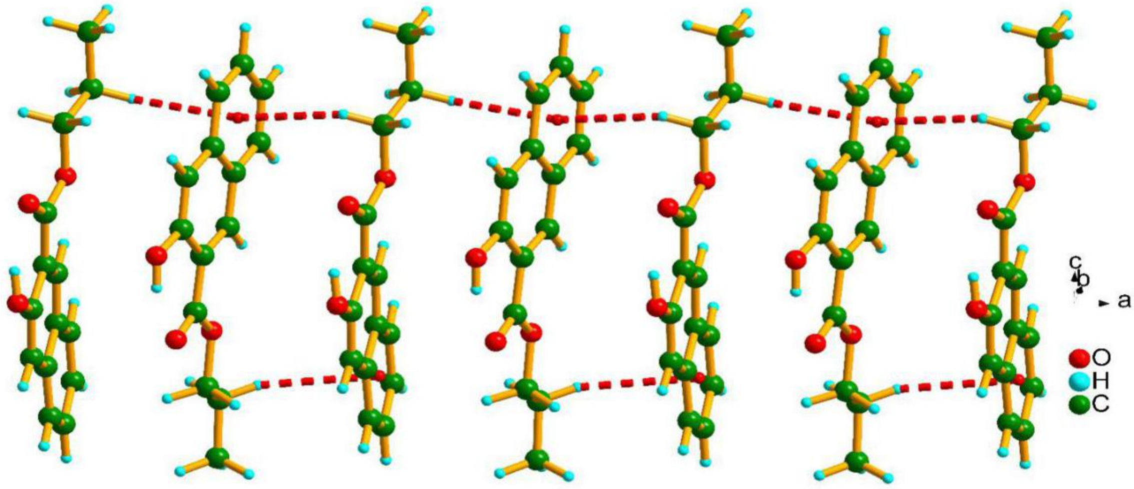
**Fig. 2**. (a) A perspective view of **2**. (b) A supramolecular 1D chain through the weak hydrogen bonds along the *a* axis. (c) A supramolecular 2D network by hydrogen bonds interactions along the crystallographic *bc* plane in **2**. (d) A stacking diagram of **2** along the *b* axis.

When the ethyl functional group takes place of methyl group of compound **1**, the new crystal of compound **2** could be obtained under the similar reaction conditions. We can obviously see that the bond length of O1-C2 and C13-O3 are 1.457 and 1.358 Å respectively, while the bond distances of C3-C4, C7-C8 as well as C9-C10 are in sequence 1.477, 1.369 and 1.367 Å. In addition, various kinds of π···π interactions between the pyridyl rings Cg(1)···Cg(3) (3.450 Å) and Cg(1)···Cg(1) (3.608 Å) are observed, where the rings Cg(1) and Cg(3) are composed of C(4)-C(5)-C(6)-C(11)-C(12)-C(13) and C(4)-C(5)-C(6)-C(7)-C(8)-C(9)-C(10)-C(11)-C(12)-C(13) respectively. Moreover, apart from these π···π interactions mentioned above, other types are also super significant. Putting it in details, two π···π interactions located at Cg(4)···Cg(5) and three founded at Cg(4)···Cg(6) also play an important role, and their bond distances are 3.687 and 3.496 Å severally, where the Cg(4), Cg(5) and Cg(6) is made up of C(17)-C(18)-C(19)-C(24)-C(25)-C(26), C(19)-C(20)-C(21)-C(22)-C(23)-C(24) and C(17)-C(18)-C(19)-C(20)-C(21)-C(22)- C(23)-C(24)-C(25)-C(26) respectively. At the same time, there still exists the presence of weak hydrogen bond O3-H20 as a bridge for the connection of neighbouring two units, whose bond length is 2.593 Å actually. As revealed in **Fig. 2c**, these 1D chain are extended to a 2D supramolecular network along crystallographic *bc* plane. It is clear that there are four hydrogen bonds lying in O2-H3, O5-H3, 05-H6 and O2-H6 with bonds lengths 1.853, 2.504, 1,798 and 2.586 Å respectively. Thanks to these supramolecular interactions talked above, a steady 3D supramolecular framework and stacking diagram is eventually constructed along the *b* axis.

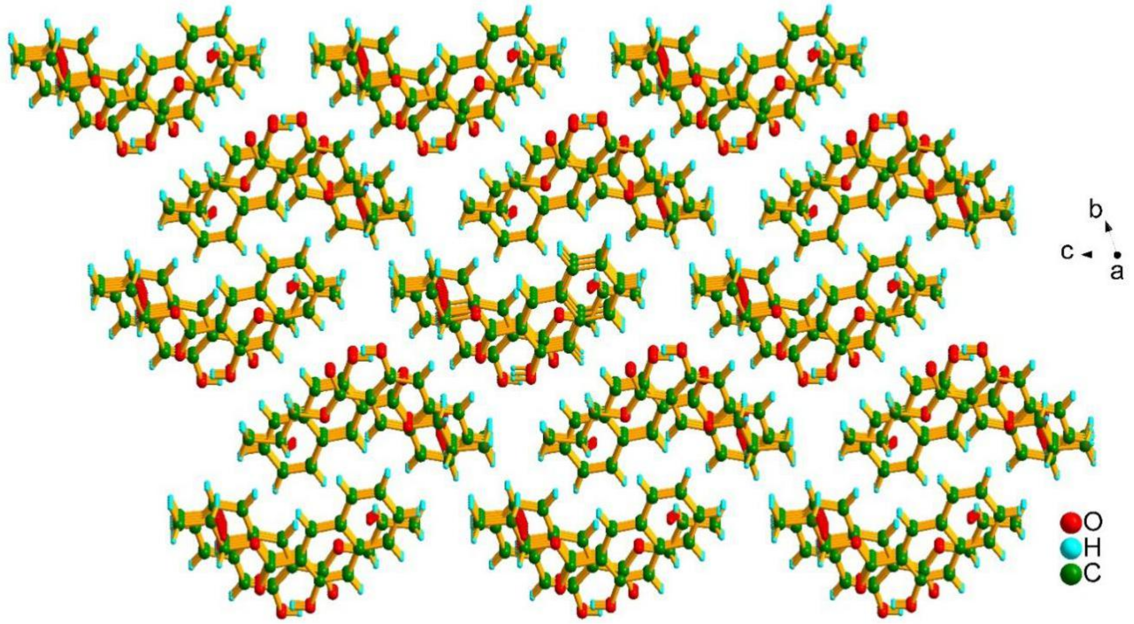
## Scheme 3 The Organic Structure *n*-propyl-3-hydroxy-2-naphthoate



(a)



(b)

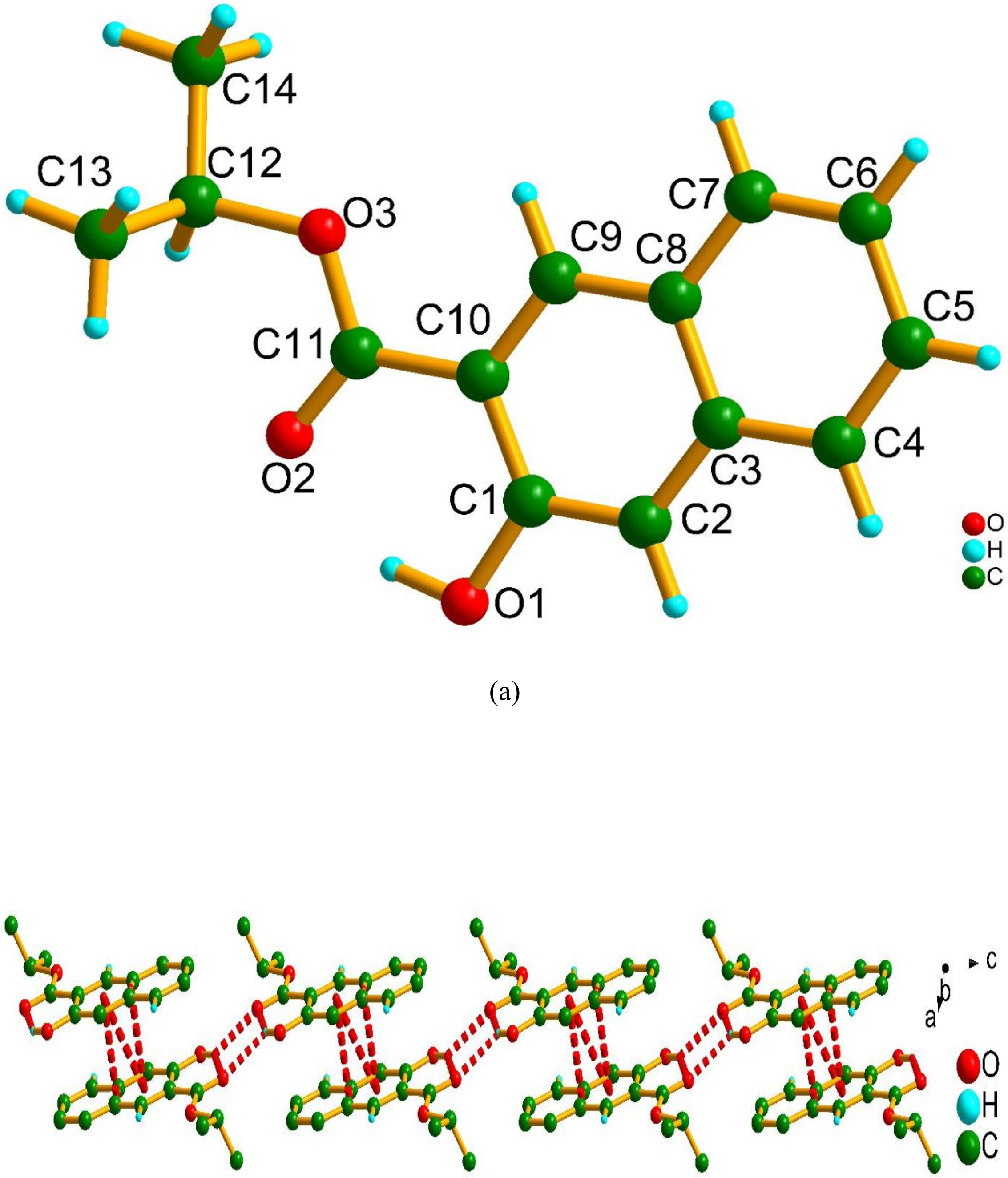


(c)

**Fig. 3**. (a) A perspective view of **3**. (b) A supramolecular 1D chain through the weak hydrogen bonds along the *a* axis. (c) A stacking diagram of **3** along the *a* axis.

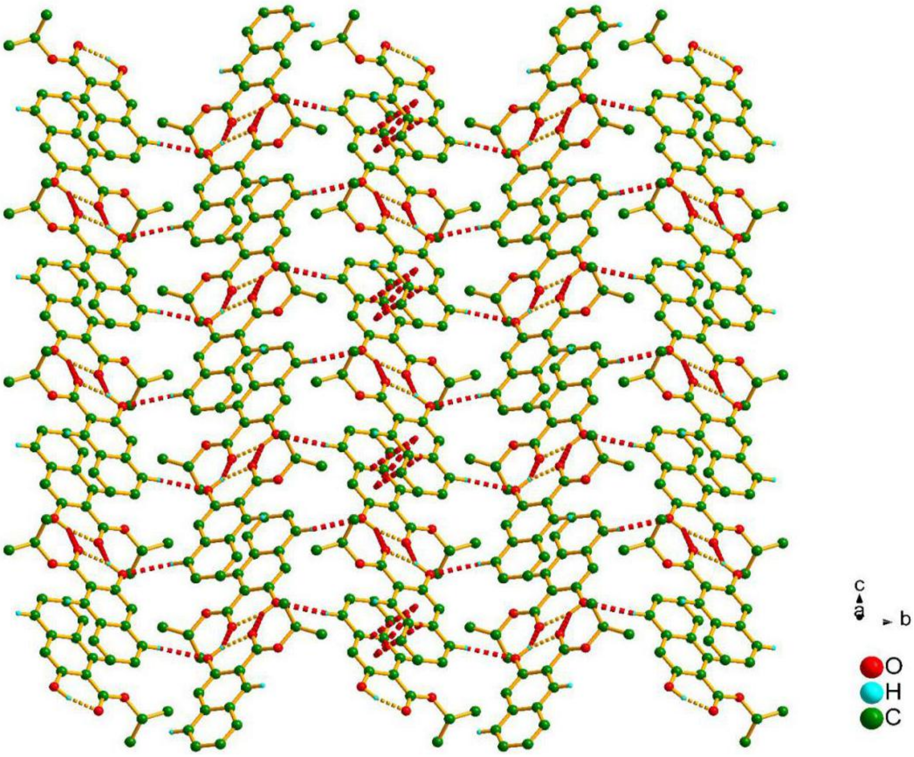
When *n*-propyl functional group substitutes methyl group of compound **1**, a new compound **3** can be got under the similar reaction conditions. As demonstrated in **Fig. 3a**, the bond distances of O3-C12, C1-O2, C6-C7 and C7-C8 are 1.466, 1.364, 1.369 and 1.415 Å respectively. What's more, the presence of three kinds of C-H···π interactions are investigated as well, C13-H12B···Cg(5)$_{(C(19)-C(20)-C(21)-C(22)-C(23)-C(24))}$, C12-H12B···Cg(5) and C27-H27B···Cg(2)$_{(C(5)-C(6)-C(7)-C(8)-C(9)-C(10))}$, where bond distances are 2.696, 2.686 and 2.876 Å relatively. Because of that, a supramolecular 1D chain through the weak hydrogen bonds along the *a* axis is received effectively. Additionally, according to what have mentioned above, a 3D stacking diagram of **3** along the *a* axis is accomplished and further consolidated through these supramolecular interactions.

**Scheme 4 The Organic Structure Synthesis of *i*-propyl-3-hydroxy-2-naphthoate**

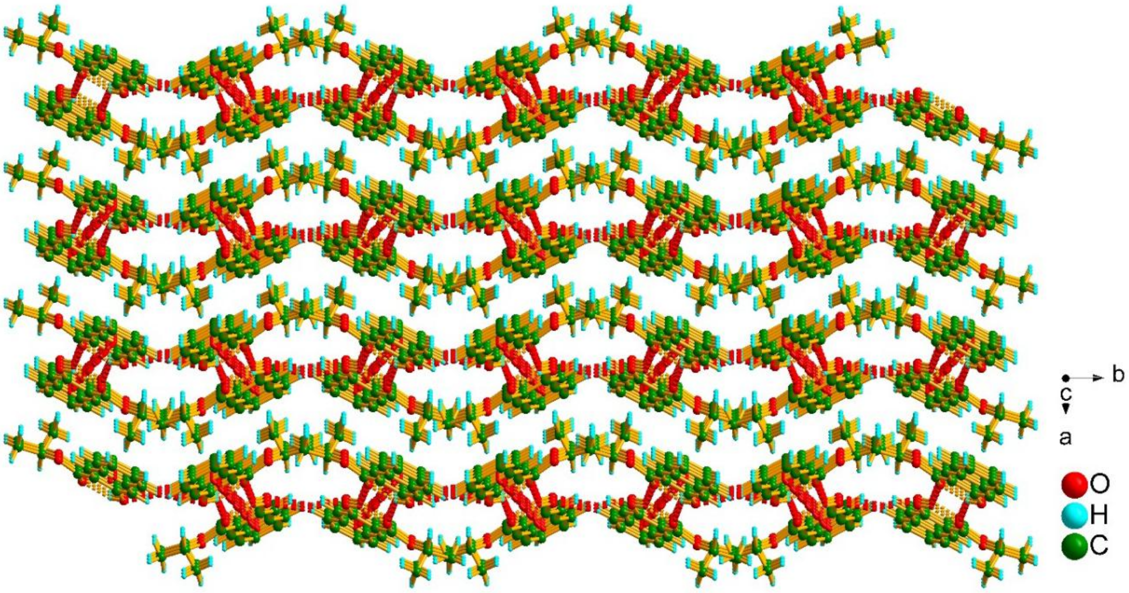


(a)

(b)



(c)



(d)

**Fig. 4**. (a) A perspective view of **4**. (b) A supramolecular 1D chain through the weak hydrogen bonds along the *c* axis. (c) A supramolecular 2D network by hydrogen bonds interactions along the

crystallographic *bc* plane in **4**. (d) A stacking diagram of **4** along the *c* axis.

When *i*-propyl functional group replaces methyl group of compound **1**, a new compound **4** can be generated under the similar reaction conditions. It is found that the bond distances of O3-C12 and O1-C1 are 1.469 and 1.360 Å severally. Besides, the bond lengths of C4-C5 and C5-C6 are 1.364 and 1.412 Å respectively. In an addition, as for 1D (1-dimensional) network, it is under observation that there exists two different types of parallel weak hydrogen bonds along the *c* axis, which lie in O2-H1 with bond length 2.289 and 1.814 Å definitely. Meanwhile, two adjacent basic units are linked by two different π···π interactions, Cg(1)···Cg(1) and Cg(1)···Cg(3) with bond distances 3.431 and 3.545 Å respectively, which Cg(1) = C(1)-C(2)-C(3)-C(8)-C(9)-C(10) and Cg(3) = C(1)-C(2)-C(3)-C(4)-C(5)-C(6)- C(7)-C(8)-C(9)-C(10). Apart from these, based on the hydrogen bonds interactions O1-H4, and its bond distance is 2.577 Å relatively, a 2D (2-dimensional) supramolecular framework is built consequently along the crystallographic *bc* plane. At last, a 3D supramolecular architecture is constructed by a variety of hydrogen bonds, π···π interactions and packing interactions along the *c* axis.

## 3.2 Tables of database

Table 1. Selected bond lengths (Å) and angles (°) for compounds **1-4**

| Bond lengths/bond angles | distances (Å)/angles (°) | bond lengths/bond angles | distances(Å)/angles (°) |
|---|---|---|---|
| **1** | | | |
| O(1)-C(1) | 1.355(4) | O(2)-C(11) | 1.216(4) |
| O(3)-C(11) | 1.330(4) | O(3)-C(12) | 1.447(4) |
| C((1)-C(2) | 1.364(5) | C(1)-C(10) | 1.423(5) |
| C(2)-C(3) | 1.402(5) | C(3)-C(4) | 1.423(5) |
| C(3)-C(8) | 1.414(5) | C(4)-C(5) | 1.347(5) |
| C(5)-C(6) | 1.392(5) | C(6)-C(7) | 1.363(5) |
| C(7)-C(8) | 1.410(5) | C(8)-C(9) | 1.404(5) |
| C(9)-C(10) | 1.372(4) | C(10)-C(11) | 1.468(5) |
| | | | |
| C(11)-O(3)-C(12) | 115.8(3) | O(1)-C(1)-C(2) | 118.4(3) |
| O(1)-C(1)-C(10) | 121.8(3) | C(2)-C(1)-C(10) | 119.8(3) |
| C(1)-C(2)-C(3) | 121.4(3) | C(2)-C(3)-C(4) | 123.1(3) |
| C(2)-C(3)-C(8) | 119.1(3) | C(4)-C(3)-C(8) | 117.7(3) |
| C(3)-C(4)-C(5) | 121.1(3) | C(4)-C(5)-C(6) | 121.3(3) |
| C(5)-C(6)-C(7) | 119.5(3) | C(6)-C(7)-C(8) | 121.1(3) |
| C(3)-C(8)-C(7) | 119.2(3) | C(3)-C(8)-C(9) | 118.8(3) |
| C(7)-C(8)-C(9) | 122.0(3) | C(8)-C(9)-C(10) | 121.6(3) |
| C(1)-C(10)-C(9) | 119.3(3) | C(1)-C(10)-C(11) | 119.0(3) |

| | | | |
|---|---|---|---|
| C(9)-C(10)-C(11) | 121.7(3) | O(2)-C(11)-O(3) | 122.5(3) |
| O(2)-C(11)-C(10) | 124.6(3) | O(3)-C(11)-C(10) | 113.0(3) |

**2**

| | | | |
|---|---|---|---|
| O(1)-C(2) | 1.4565(14) | O(1)-C(3) | 1.3292(16) |
| O(2)-C(3) | 1.2203(15) | O(3)-C(13) | 1.3575(15) |
| C(1)-C(2) | 1.501(2) | C(3)-C(4) | 1.4775(15) |
| C(4)-C(5) | 1.3795(16) | C(4)-C(13) | 1.4305(17) |
| C(5)-C(6) | 1.4067(15) | C(6)-C(7) | 1.4210(17) |
| C(6)-C(11) | 1.4263(19) | C(7)-C(8) | 1.3695(16) |
| C(8)-C(9) | 1.414(2) | C(9)-C(10) | 1.3670(19) |
| C(10)-C(11) | 1.4250(16) | C(11)-C(12) | 1.4094(17) |
| C(12)-C(13) | 1.3770(16) | O(4) -C(15) | 1.4559(14) |
| O(4)-C1(6) | 1.3305(16) | O(5)-C(16) | 1.2233(16) |
| O(6)-C(26) | 1.3607(16) | C(14)-C(15) | 1.505(2) |
| C(16)-C(17) | 1.4761(16) | C(17) -C(18) | 1.3786(17) |
| C(17)-C(26) | 1.4319(18) | C(18)-C(19) | 1.4087(16) |
| C(19)-C(20) | 1.4194(18) | C(19)-C(24) | 1.4284(19) |
| C(20)-C(21) | 1.3686(18) | C(20)-C(21) | 1.3686(18) |
| C(21)-C(22) | 1.415(2) | C(22)-C(23) | 1.366(2) |
| C(23)-C(24) | 1.4249(19) | C(24)-C(25) | 1.4118(19) |
| C(25)-C(26) | 1.3716(19) | | |

| | | | |
|---|---|---|---|
| C(2)-O(1)-C(3) | 115.89(9) | O(1)-C(2)-C(1) | 106.87(10) |
| O(1) -C(3)-O(2) | 122.93(10) | O(1)-C(3)-C(4) | 113.30(10) |
| O(2)-C(3)-C(4) | 123.77(12) | C(3)-C(4)-C(5) | 120.86(11) |
| C(3)-C(4)-C(13) | 119.66(10) | C(5)-C(4)-C(13) | 119.48(10) |
| C(4)-C(5)-C(6) | 121.78(11) | C(5)-C(6)-C(7) | 121.44(12) |
| C(5)-C(6)-C(11) | 118.45(11) | C(7)-C(6)-C(11) | 120.10(10) |
| C(6)-C(7)-C(8) | 120.22(12) | C(7)-C(8)-C(9) | 120.02(12) |
| C(8)-C(9)-C(10) | 121.02(11) | C(9)-C(10)-C(11) | 120.82(13) |
| C(6)-C(11)-C(10) | 117.82(11) | C(6)-C(11)-C(12) | 119.49(10) |
| C(10)-C(11)-C(12) | 122.69(12) | C(11)-C(12C(13) | 121.16(12) |
| O(3)-C(13)-C(4) | 121.79(10) | O(3)-C(13)-C (12) | 118.56(11) |
| C(4)-C(13)-C(12) | 119.63(11) | C(15)-O(4)-C16) | 115.44(10) |
| O(4)-C(15)-C(14) | 106.33(10) | O(4)-C(16)-O(5) | 122.71(11) |
| O(4)-C(16)-C(17) | 113.63(10) | O(5)-C(16)-C(17) | 123.66(12) |
| C(16)-C(17)-(C18) | 121.09(11) | C(16)-C(17)-C(26) | 119.57(11) |
| C(18)-C(17)-C(26) | 119.33(11) | C(17)-C(18)-C(19) | 121.82(12) |
| C(18)-C(19)-C(20) | 121.78(12) | C(18)-C(19)-C(24) | 118.45(11) |
| C(20)-C(19)-C(24) | 119.76(11) | C(19)-C(20)-C(21) | 120.74(13) |
| C(20)-C(21)-C(22) | 119.73(13) | C(21)-C(22)-C(23) | 120.99(12) |
| C(22)-C(23)-C(24) | 121.00(13) | C(19)-C(24)-C(23) | 117.77(12) |
| C(19)-C(24)-C(25) | 119.27(11) | C(23)-C(24)-C(25) | 122.96(12) |

| | | | |
|---|---|---|---|
| C(24)-C(25)-C(26) | 121.28(12) | O(6 )-C(26)-C(17) | 121.62(11) |
| O(6 )-C(26)-C(25) | 118.54(12) | C(17)-C(26)-C(25) | 119.84(12) |

**3**

| | | | |
|---|---|---|---|
| O(1)-C(2) | 1.364(6) | O(2)-C(11) | 1.219(6) |
| O(3)-C(11) | 1.334(6) | O(3)-C(12) | 1.466(5) |
| C(1)-C(2) | 1.365(6) | C(1)-C(10) | 1.393(6) |
| C(2)-C(3) | 1.435(7) | C(3)-C(4) | 1.367(6) |
| C(3)-C(11) | 1.482(6) | C(4)-C(5) | 1.418(6) |
| C(5)-C(6) | 1.415(6) | C(5)-C(10) | 1.433(7) |
| C(6)-C(7) | 1.369(6) | C(7)-C(8) | 1.415(8) |
| C(8)-C(9) | 1.353(7) | C(9)-C(10) | 1.423(6) |
| C(12)-C(13) | 1.514(7) | C(13)-C(14) | 1.535(6) |
| O(4)-C(17) | 1.358(6) | O(5)-C(25) | 1.219(6) |
| O(6)-C(25) | 1.340(5) | O(6)-C(26) | 1.464(5) |
| C(15)-C(16) | 1.378(7) | C(15)-C(24) | 1.413(6) |
| C(16)-C(17) | 1.425(6) | C(16)-C(25) | 1.483(6) |
| C(17)-C(18) | 1.363(6) | C(18)-C(19) | 1.411(7) |
| C(19)-C(20) | 1.430(6) | C(19)-C(24) | 1.426(6) |
| C(20)-C(21) | 1.361(7) | C(21)-C(22) | 1.411(6) |
| C(22)-C(23) | 1.364(6) | C(23)-C(24) | 1.409(7) |
| C(26)-C(27) | 1.496(6) | C(27)-C(28) | 1.535(6) |

| | | | |
|---|---|---|---|
| C(11)-O(3)-C(12) | 115.4(3) | C(2)-C(1)-C(10) | 121.8(4) |
| O(1)-C(2)-C(1) | 119.0(4) | O(1)-C(2)-C(3) | 121.2(4) |
| C(1)-C(2)-C(3) | 119.8(4) | C(2)-C(3)-C(4) | 118.9(4) |
| C(2)-C(3)-C(11) | 119.1(4) | C(4)-C(3)-C(11) | 122.0(4) |
| C(3)-C(4)-C(5) | 122.5(4) | C(4)-C(5)-C(6) | 123.1(4) |
| C(4)-C(5)-C(10) | 117.2(4) | C(6)-C(5)-C(10) | 119.7(4) |
| C(5)-C(6)-C(7) | 121.0(4) | C(6)-C(7)-C(8) | 119.4(4) |
| C(7)-C(8)-C(9) | 120.9(4) | O(5)-C(25)-O(6) | 123.0(4) |
| C(8)-C(9)-C(10) | 122.0(5) | C(1)-C(10)-C(5) | 119.7(4) |
| C(1)-C(10)-C(9) | 123.3(5) | C(5)-C(10)-C(9) | 117.0(4) |
| O(2)-C(11)-O(3) | 122.9(4) | O(2)-C(11)-C(3) | 123.7(4) |
| O(3)-C(11)-C(3) | 113.4(4) | O(3)-C(12)-C(13) | 106.9(3) |
| C(12)-C(13)-C(14) | 109.6(4) | C(25)-O(6)-C(26) | 115.8(4) |
| C(16)-C(15)-C(24) | 121.9(4) | C(15)-C(16)-C(17) | 119.3(4) |
| C(15)-C(16)-C(25) | 121.0(4) | C(17)-C(16)-C(25) | 119.7(4) |
| O(4)-C(17)-C(16) | 121.1(4) | O(4)-C(17)-C(18) | 118.9(4) |
| C(16)-C(17)-C(18) | 120.1(4) | C(17)-C(18)-C(19) | 121.3(4) |
| C(18)-C(19)-C(20) | 122.0(4) | C(18)-C(19)-C(24) | 119.5(4) |
| C(20)-C(19)-C(24) | 118.5(4) | C(19)-C(20)-C(21) | 120.2(4) |
| C(20)-C(21)-C(22) | 121.3(4) | C(21)-C(22)-C(23) | 119.6(4) |
| C(22)-C(23)-C(24) | 121.3(4) | C(22)-C(23)-C(24) | 121.3(4) |

| | | | |
|---|---|---|---|
| C(22)-C(23)-C(24) | 121.3(4) | C(15)-C(24)-C(19) | 117.9(4) |
| C(15)-C(24)-C(23) | 123.0(4) | C(19)-C(24)-C(23) | 119.1(4) |
| O(5)-C(25)-C(16) | 123.7(4) | O(6)-C(25)-C(16) | 113.3(4) |
| O(6)-C(26)-C(27) | 107.5(4) | C(26)-C(27)-C(28) | 110.4(4) |

**4**

| | | | |
|---|---|---|---|
| O(1)-C(1) | 1.360(2) | O(2)-C(11) | 1.2169(19) |
| O(3)-C(11) | 1.341(2) | O(3)-C(12) | 1.4693(19) |
| C(1)-C(2) | 1.372(2) | C(1)-C(10) | 1.429(2) |
| C(2)-C(3) | 1.410(2) | C(3)-C(4) | 1.423(2) |
| C(3)-C(8) | 1.424(2) | C(4)-C(5) | 1.364(2) |
| C(5)-C(6) | 1.412(3) | C(6)-C(7) | 1.364(2) |
| C(7)-C(8) | 1.420(2) | C(8)-C(9) | 1.409(2) |
| C(9)-C(10) | 1.378(2) | C(10)-C(11) | 1.476(2) |
| C(12)-C(13) | 1.510(2) | C(12)-C(14) | 1.511(2) |

| | | | |
|---|---|---|---|
| C(11)-O(3)-C(12) | 117.11(11) | O(1)-C(1)-C(2) | 117.95(15) |
| O(1)-C(1)-C(10) | 122.54(14) | C(2)-C(1)-C(10) | 119.51(14) |
| C(1)-C(2)-C(3) | 121.72(15) | C(2)-C(3)-C(4) | 122.83(15) |
| C(2)-C(3)-C(8) | 119.01(15) | C(4)-C(3)-C(8) | 118.15(14) |
| C(3)-C(4)-C(5) | 120.53(16) | C(4)-C(5)-C(6) | 121.27(16) |
| C(5)-C(6)-C(7) | 119.79(15) | C(6)-C(7)-C(8) | 120.59(16) |

| | | | |
|---|---|---|---|
| C(3)-C(8)-C(7) | 119.67(14) | C(3)-C(8)-C(9) | 118.49(14) |
| C(7)-C(8)-C(9) | 121.84(15) | C(8)-C(9)-C(10) | 121.90(15) |
| C(1)-C(10)-C(9) | 119.33(14) | C(1)-C(10)-C(11) | 119.89(14) |
| C(9)-C(10)-C(11) | 120.79(14) | O(2)-C(11)-O(3) | 123.04(14) |
| O(2)-C(11)-C(10) | 123.58(15) | O(3)-C(11)-C(10) | 113.37(13) |
| O(3)-C(12)-C(13) | 109.17(13) | O(3)-C(12)-C(14) | 105.15(12) |
| C(13)-C(12)-C(14) | 112.77(14) | | |

Table 2. Hydrogen bond geometries in the crystal structure of compounds **1-4**.

| Compounds | D–H···A$^{a}$ | H···A (Å) | D···A (Å) | D–H···A (°) |
|---|---|---|---|---|
| **1** | O(1)-H(1)···O(2) | 1.87 | 2.614(3) | 146 |
| | C(2)-H(2)···O(2)$^{a}$ | 2.57 | 3.305(4) | 135 |
| | C(9)-H(9)···O(3) | 2.38 | 2.710(4) | 100 |
| **2** | O(3)-H(3)···O(2) | 1.85(2) | 2.6456(13) | 146.1(18) |
| | O(3)-H(3)···O(5)$^{a}$ | 2.505(19) | 3.1941(13) | 134.1(17)' |
| | O(6)-H(6)···O(5) | 1.80(2) | 2.6270(14) | 149(2) |
| | O(6)-H(6)···O(2)$^{b}$ | 2.59(2) | 3.2649(14) | 131.3(18)' |
| | C(5)-H(5)···O(1) | 2.38 | 2.7160(13) | 100 |
| | C(18)-H(18)···O(4) | 2.39 | 2.7241(14) | 100 |
| | C(20)-H(20)···O(3)$^{c}$ | 2.59 | 3.4660(17) | 153 |
| **3** | O(1)-H(1)···O(2) | 1.87 | 2.608(5) | 146 |
| | O(4)-H(4A)···O(5) | 1.87 | 2.619(4) | 147 |
| | C(4)-H(4)···O(3) | 2.41 | 2.746(5) | 100 |
| | C(15)-H(15)···O(6) | 2.38 | 2.725(5) | 101 |
| **4** | O(1)-H(1)···O(2) | 1.81(3) | 2.6519(18) | 146(3) |
| | O(1)-H(1)···O(2)$^{a}$ | 2.29(3) | 2.9569(17) | 127(2)' |
| | C(4)-H(4)···O(1)$^{b}$ | 2.58 | 3.470(2) | 157 |
| | C(9)-H(9)···O(3) | 2.37 | 2.7146(19) | 101 |

Symmetry codes: $^{a}$1-x,-1/2+y,1/2-z for **1**. $^{a}$1-x,-1/2+y,1/2-z; $^{b}$1-x,1/2+y,1/2-z; $^{c}$1+x,y,z for **2**. $^{a}$2-x,1-y,1-z; $^{b}$x,1/2-y,1/2+z for **4**.

Table 3. π···π and C–H···π geometries in the crystal structure of compounds **1-4**

| Compounds | Cg···Cg | π···π (Å) | C–H···Cg | C–H···π (Å) |
|---|---|---|---|---|
| **1** | Cg(1)···Cg(1)$^a$ | 3.6518(19) | | |
| | Cg(1)···Cg(1)$^b$ | 3.6885(19) | | |
| | Cg(1)···Cg(3)$^a$ | 3.5815(18) | | |
| | Cg(1)···Cg(3)$^b$ | 3.6316(19) | | |
| | Cg(3)···Cg(1)$^a$ | 3.5814(18) | | |
| | Cg(3)···Cg(1)$^b$ | 3.6317(19) | | |
| **2** | Cg(1)···Cg(1)$^a$ | 3.6083(6) | C(1)-H(1A)···Cg(2)$^c$ | 3.7767(14) |
| | Cg(1)···Cg(2)$^a$ | 3.7135(6) | C(1)-H(1A)···Cg(3)$^c$ | 3.4576(13) |
| | Cg(1)···Cg(3)$^a$ | 3.4503(6) | | |
| | Cg(2)···Cg(1)$^a$ | 3.7135(6) | | |
| | Cg(3)···Cg(1)$^a$ | 3.4502(6) | | |
| | Cg(3)···Cg(3)$^a$ | 3.7116(5) | | |
| | Cg(4)···Cg(4)$^b$ | 3.7257(6) | | |
| | Cg(4)···Cg(5)$^b$ | 3.6867(6) | | |
| | Cg(4)···Cg(6)$^b$ | 3.4957(6) | | |
| | Cg(5)···Cg(4)$^b$ | 3.6866(6) | | |
| | Cg(6)···Cg(4)$^b$ | 3.4957(6 | | |
| | Cg(6)···Cg(6) | 3.6813(5) | | |
| **3** | | | C(12)-H(12B)···Cg(5)$^a$ | 3.510(5) |

| | | | | |
|---|---|---|---|---|
| | | | C(13)-H(13B)···Cg(5)$^{b}$ | 3.583(5) |
| | | | C(27)-H(27B)···Cg(2)$^{a}$ | 3.766(5) |
| **4** | Cg(1)···Cg(1)$^{a}$ | 3.5449(10) | | |
| | Cg(1)···Cg(2)$^{a}$ | 3.7392(10) | | |
| | Cg(1)···Cg(3)$^{a}$ | 3.4307(9) | | |
| | Cg(2)···Cg(1)$^{a}$ | 3.7392(10) | | |
| | Cg(3)···Cg(1)$^{a}$ | 3.4307(9) | | |
| | Cg(3)···Cg(3)$^{a}$ | 3.7361(8) | | |

Symmetry codes: $^{a}$1-x,-y,1-z; $^{b}$2-x,-y,1-z for **1**. $^{a}$1-x,1-y,1-z; $^{b}$ 2-x,1-y,1-z; $^{c}$1-x,-1/2+y,1/2-z for **2**. $^{a}$1-x,1-y,1-z; $^{b}$2-x,1-y,1-z for **3**. $^{a}$2-x,1-y,2-z for **4**.

Cg(1) = C(1)-C(2)-C(3)-C(8)-C(9)-C(10);

Cg(3) = C(1)-C(2)-C(3)-C(4)-C(5)-C(6)-C(7)-C(8)-C(9)-C(10) for **1**.

Cg(1) = C(4)-C(5)-C(6)-C(11)-C(12)-C(13);

Cg(2) = C(6)-C(7)-C(8)-C(9)-C(10)-C(11);

Cg(3) = C(4)-C(5)-C(6)-C(7)-C(8)-C(9)-C(10-C(11-C(12)-C(13);

Cg(4) = C(17)-C(18)-C(19)-C(24)-C(25)-C(26);

Cg(5)= C(19)-C(20)-C(21)-C(22)-C(23)-C(24);

Cg(6)= C(17)-C(18)-C(19)-C(20)-C(21)-C(22)-C(23)-C(24)-C(25)-C(26) for **2**.

Cg(2)= C(5)-C(6)-C(7)-C(8)-C(9)-C(10);

Cg(5) = C(19)-C(20)-C(21)-C(22)-C(23)-C(24)for **3**.

Cg(1) = C(1)-C(2)-C(3)-C(8)-C(9)-C(10);

Cg(2) = C(3)-C(4)-C(5)-C(6)-C(7)-C(8);

Cg(3) = C(1)-C(2)-C(3)-C(4)-C(5)-C(6)-C(7)-C(8)-C(9)-C(10) for **4**.

### 3.3 The UV-Vis spectra

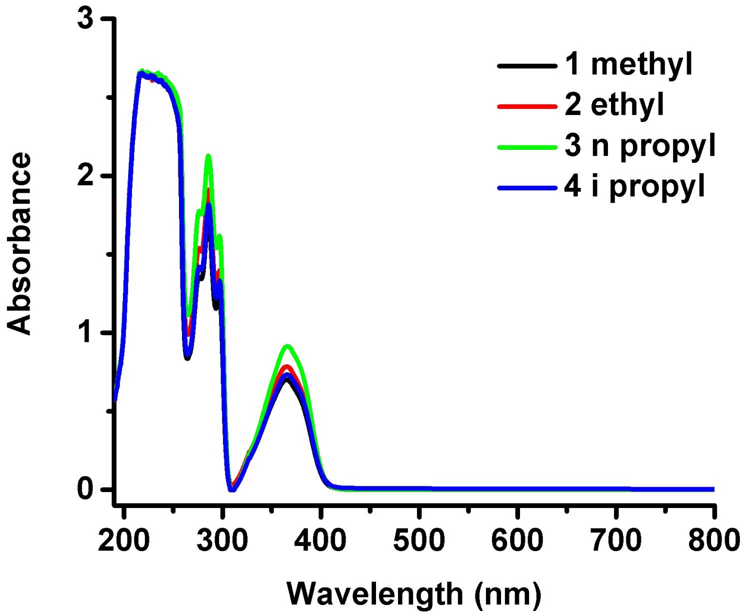
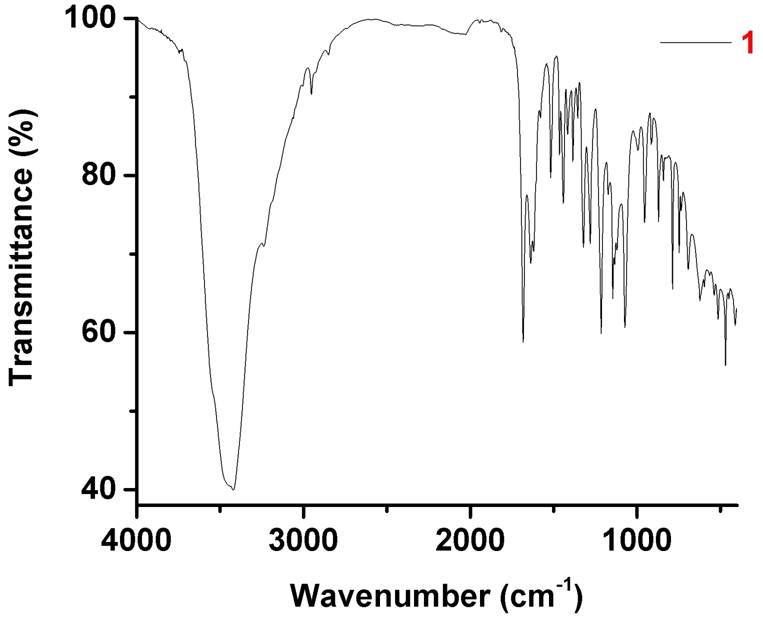


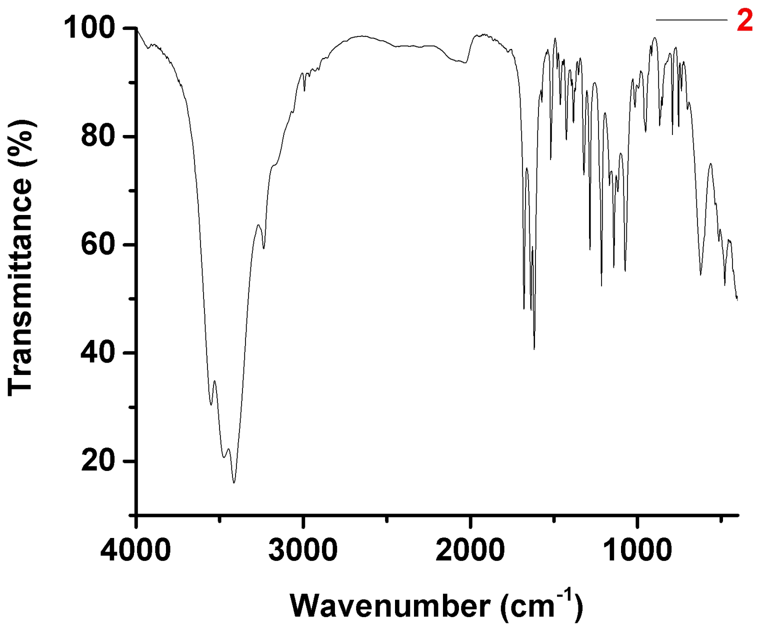
**Fig. 5** The UV-Vis spectra of compounds 1-4 in ethanol solution ($1\times10^{-5}$ M).

To further examine the properties of compounds **1-4**, the UV-Vis absorption analyses of these target compounds was carried out under the ethanol solution, which is illustrated in **Fig**. **5**. Clearly, it is seen that compounds **1-4** have almost similar absorption characteristics despite of some small differences owing to the various kinds of functional groups. Besides, the absorption maxima appears at around 290 nm definitely, and it can be assigned to the π-π* transition of conjugate backbond.

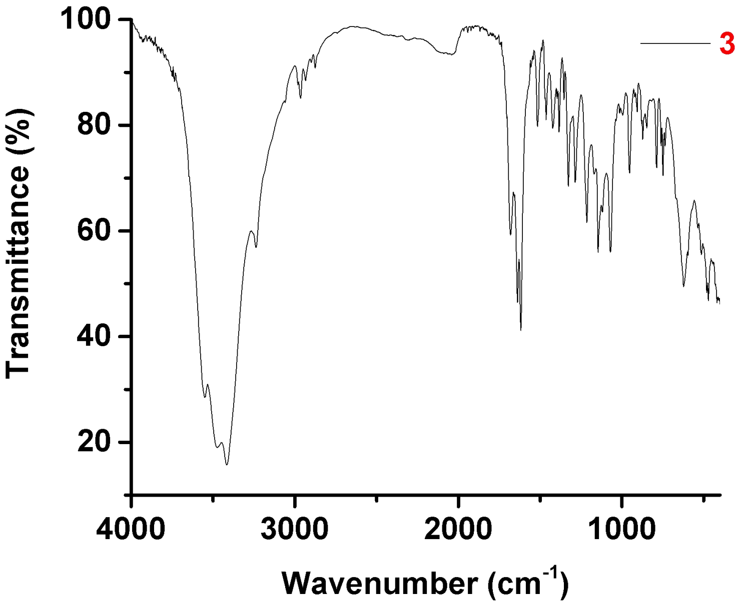
## 3.4 IR spectra



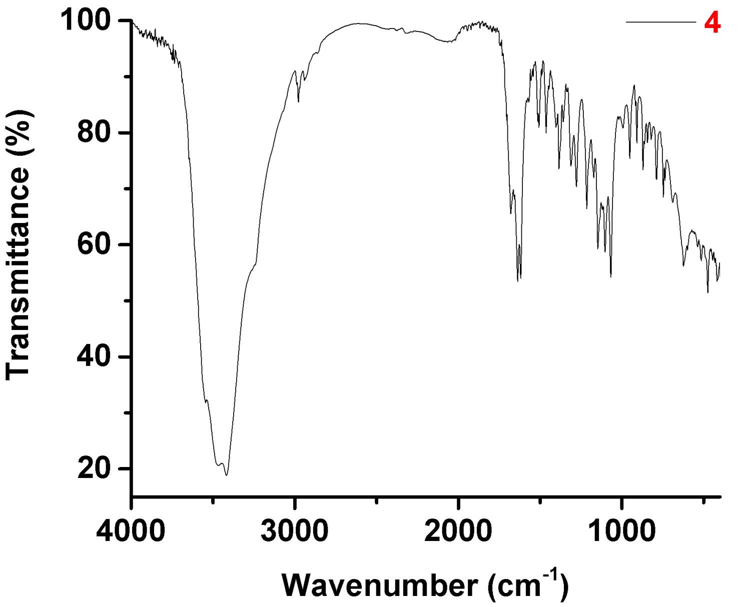
(a)



(b)



(c)



(d)

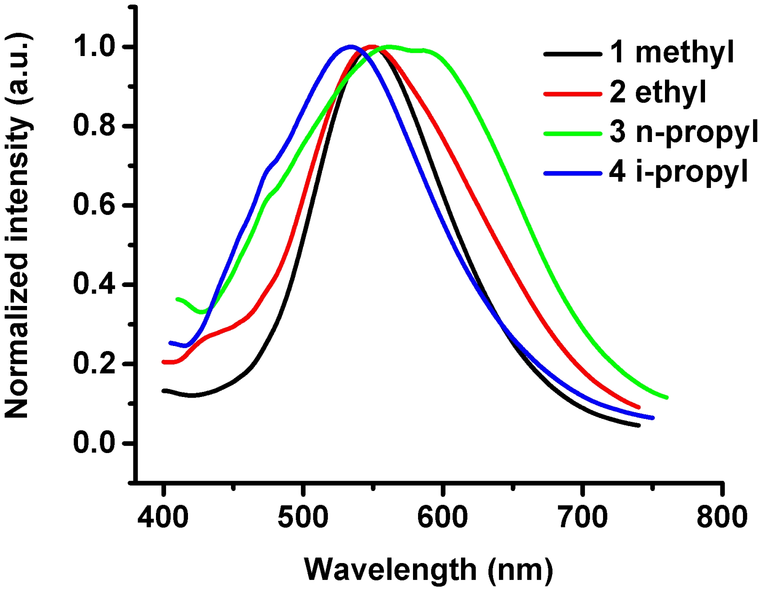
**Fig. 6**. IR spectra of compounds **1-4**.

As shown in **Fig. 6a,** in the compound **1**, the strong absorption peak at 3421 $cm^{-1}$ is observed, which can be ascribed to $\nu_{OH}$ stretching vibration. Besides, the strong absorption peak of 1684cm$^{-1}$ obviously indicates the existence of stretching vibration of $\nu_{c=o}$, and the weak peak located in 2850 cm$^{-1}$ demonstrates the stretching vibration of $\nu_{CH3}$, respectively. Moreover, there are several bonds founded in the range of 1637-1417cm$^{-1}$, revealing the attribution of $\nu_{c=c}$ stretching vibration of aromatic skeleton.

As shown in **Fig. 6b,** in compound **2**, several bonds are found in range of 1618-1425 cm$^{-1}$, which can be ascribed to two $\nu_{c=c}$ stretching vibrations of aromatic skeleton. Besides, the weak peak of around 2930 cm$^{-1}$ usually can be attributed to the blending vibration of ethyl group. In addition, compared with compound **1**, the shifted values in compound **2** are comparable, suggesting that the coordination modes of the derivative of a benzene ring are similar, respectively.

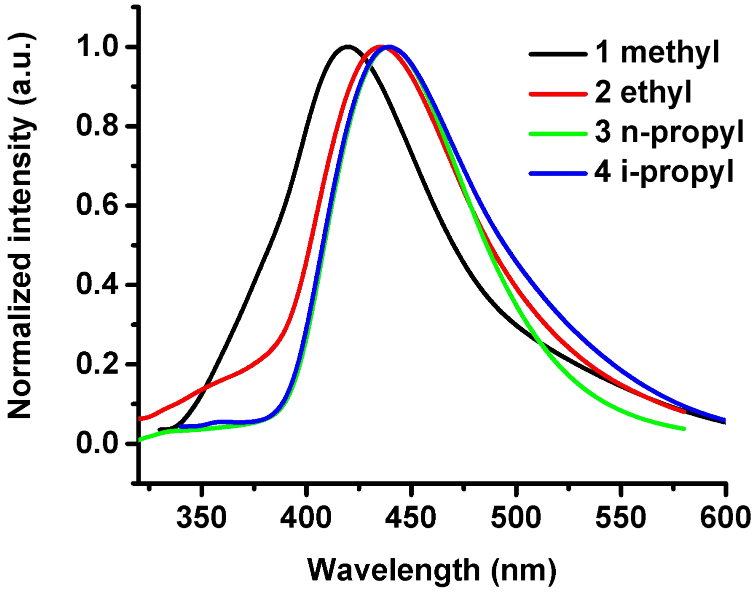
As revealed in **Fig. 6c** and **Fig. 6d,** the characteristic peaks of compound **3** and **4** are basically analogical to those compounds **1** and **2**. However, there still exists a medium band which is located at 1423 and 1464 cm$^{-1}$ respectively can be assigned to the stretching vibration of propyl group and *i*-propyl group separately.

### 3.5 The photoluminescent spectra

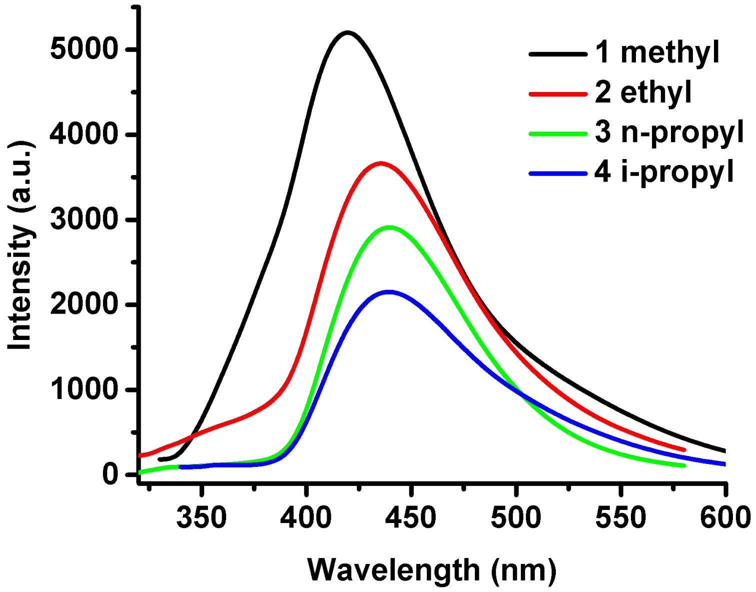


(a)

**Fig. 7** The solid-state photoluminescent spectra of compounds **1-4** at room temperature.



(b)



(c)

**Fig. 8** The photoluminescent spectra of compounds 1-4 at room temperature in ethanol solution.

As illustrated in **Fig. 7**, the solid-state luminescence properties of compounds **1-4** have been observed at room temperature. It is shown clearly that these four maximal peaks are extremely close, locating at around 550 nm for methyl and ethyl functional groups, 560 nm for *n*-propyl functional group and 530 nm for *i*-propyl functional group, respectively. In order to further know more about the luminescent profiles of compounds **1-4**, more attention have been paid to the deep studies of photoluminescent behaviors due to these four different groups in ethanol solution at room temperature. By the comparison of intensity and normalized intensity, some big differences are obviously investigated in **Fig. 8**. Specifically, according to the highest emission peaks demonstrated above, apart from the methyl group with its emission maxima at about 420 nm, the three remaining groups are at nearly 440 nm, respectively. However, by contrast with the normalized intensity, we find that the intensity of these compounds follow the order: **1**＞**2**＞**3**＞**4** with the similar wavelengths severally.

# Conclusion

The experiments show that during the esterification process, the temperature directly affects the yields of the products. When the temperature is too low, the reaction is incomplete, and meanwhile, the reaction time would increases. In addition, the purity of these compounds will increase with increasing temperature, and the product purities are able to reach the peak when the reaction temperatures reach the boiling points of the system.

What's more, using sulfuric acid as a catalyst for the synthesis of compounds **1-4** is better. In the process of the reaction, if the amount of concentrated sulfuric acid is too small, the reaction proceeds incompletely, and the reaction would be carried out for a long time, resulting in a low product content. However, if the amount of concentrated sulfuric acid is too large, the product efficiency could not be significantly improved, and at the same time, a host of acidic waste water, waste of drugs would be produced and requires subsequent treatment, which is certainly contrary to the concept of green chemistry.

All in all, the compounds **1-4** prepared by our group have got good structural characteristics and exhibit good performance. In the preparation process, the esterification process can be tested to find the optimal reaction conditions and gradually industrialized. It is believed that there still exists room for further improvement.

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