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Novel metallomesogens derived from heterocyclic benzoxazoles

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ABSTRACT

The synthesis, mesomorphic behavior, and optical properties of a new series of transition metal complexes **1a** and **1b** derived from benzoxazoles **2** are reported. The crystal and molecular structure of copper complex of 6-dodecyloxynaphthalene-2-carboxylic acid 4-(6-hexyloxybenzooxazol-2-yl)-3-hydroxyphenyl ester **1a** (n=6; m=12) was determined by means of X-ray structural analysis, and it crystallizes in the triclinic space group P-1. The geometry at copper center is perfectly square-planar, and the overall molecular shape is considered as rod-shape. All precursors **2** with shorter chains (n=0, 1, 4) exhibited nematic, and all others with longer chains (n=6, 7, 8, 10, 12) formed N/SmC phases. In contrast, all copper(II) complexes **1a** and palladium complexes **1b** formed N phase. On the other hand, the temperature range of mesophase in compound **1a** was wider than those in compound **1b**. The difference of the mesomorphic properties in compounds **1a** and **1b** was attributed to the geometry or/and the size of the metal center. The fluorescent properties of these compounds were also examined.

1. Introduction

The incorporation of heterocyclic rings[1] used as core center to generate mesogenic materials has been widely investigated during the past decades. Numerous novel compounds exhibiting unique mesophases were prepared and studied. Among them five- or six-membered rings have been studied mostly due to their varieties in structures and/or known chemistry. Better mesomorphic behavior formed by such structures was often accomplished, which was attributed to their electronic unsaturation and/or more polarizable ability.[2] On the other hand, many heterocyclic molecules[3–7] with a lower symmetry and/or non-planar structure caused by nitrogen, oxygen, sulfur or other heteroatoms incorporated would be easily obtained, leading to practical materials with a lower clearing or/and melting temperature useful in device applications. Benzoxazole derivatives, considered as an important class of heterocyclic compounds, have been studied in a variety of materials research during the past years. Most of the studies were focused on, such as non-linear optics,[8] organic light-emitting diodes,[9] and polymeric materials. However, mesogenic examples derived from benzoxazoles[10] or benzothiazoles[11] were relatively rare. Common phases, for example, nematic, smectic A or/and smectic C phases were often observed, as expected for rod-like molecules.

On the other hand, metal-containing liquid crystals, or so-called metallomesogens,[12–14] have been paid much attention during the past decade. Numerous transition metal complexes with a variety of geometric structures were thus generated, and their mesomorphic properties investigated as well. Many atoms incorporated within a heterocyclic structure, such as nitrogen, oxygen, sulfur or others might provide electron lone pairs for potential coordination site to the transition metals. Depending on the structure of the heterocyclic derivatives, a variety of metal ions, particularly metals with a 3d-orbital were structurally possible in generating this type of metallomesogenic materials. Metal complexes[12–14] with copper(II) and palladium(II) incorporated were all known the most. Cu^{2+} ion is d^9-electronic and paramagnetic, whereas, Pd^{2+} ion is d^8 and diamagnetic configuration. A variety of coordination compounds with tetrahedral (T_d), twisted tetrahedral or square-planar geometry (SP) have been reported and investigated. The difference in electronic configuration or/and coordinative geometry inherent from metal ions often reflected to the formation of the observed mesophases in this type of metallomesogenic materials. A similar compound **5**, benzothiazole was reported,[15] and all free ligands, copper and oxovanadium complexes[15] were found non-mesogenic. A loss of linearity, strong intermolecular dipolar repulsion caused by the presence of lateral hydroxyl group was attributed for the lack of mesomorphic behavior. A palladium complex **1c** with a similar structure has been previously prepared[11] in this group, however, it was in fact non-mesogenic. A transition of crystal-to-isotropic (Cr→I) at 194.6 °C was observed. In this work, as part of our continuing research in metallomesogens[11,16–19] we report the preparation, mesomorphic, and optical studies of a new series of copper(II) and palladium(II) complexes **1a** and **1b** derived from benzoxazole. All copper and palladium complexes exhibit nematic

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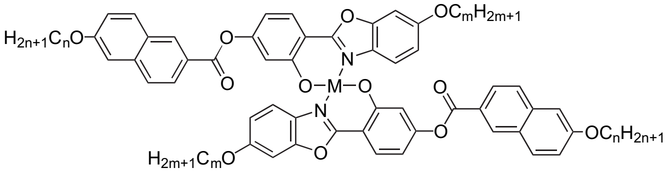
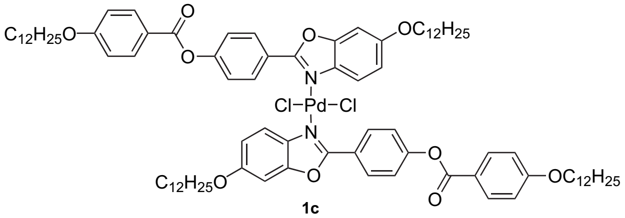
or/and smectic C phases. To our knowledge, this is the first metallomesogens derived from heterocyclic benzoxazoles.

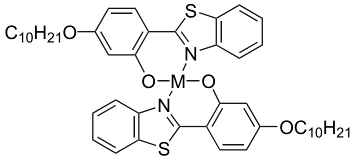


m = 8, 12;
n = 0, 1, 4, 6, 7, 8, 10, 12
1a; M = Cu
1b; M = Pd



1c

$$\mathrm{Cr}\ \underset{174.7\ (16.2)}{\overset{194.6\ (30.8)}{\rightleftharpoons}}\ \mathrm{I}$$



5; M = Cu, VO

2. Results and discussion

2.1. Synthesis and characterization

The synthetic routes[10a] used in this work for benzoxazole derivatives **2** and their copper and palladium complexes **1a** and **1b** were summarized in Scheme 1. The reactions of 2-amino-5-alkylphenols and 6-alkoxylnaphthalene-2-carboxylic acid 4-formyl-3-hydroxyphenyl esters **4** in refluxing absolute ethanol gave 6-alkoxynaphthalene-2-carboxylic acid 4-[(4-alkyl-2-hydroxylphenylimino)-methyl]-3-hydroxyphenyl esters **3**. The final compounds **2**; 6-alkoxynaphthalene-2-carboxylic acid 4-(6-alkylbenzooxazol-2-yl)-3-hydroxyphenyl esters was then obtained by intracyclic reaction of **3** in $CHCl_3$ using lead acetate $Pb(OAc)_4$. The copper(II) and palladium(II) complexes were prepared by the reaction of appropriate benzoxazoles **2** and copper(II) acetate or palladium(II) acetate in refluxing ethanol. ^1H and ^{13}C NMR spectroscopy were used to characterize all intermediates, and the elemental analysis was used to confirm the purity of the metal complexes.

2.2. Single crystal structures of 6-naphthalene-2-carboxylic acid 4-(6-butyloxy benzooxazol-2-yl)-3-hydroxyphenyl ester (2; *n*=0, *m*=4) and copper complex of 6-hexyloxynaphthalene-2-carboxylic acid 4-(6-dodecyloxybenzooxazol-2-yl)-3-hydroxyphenyl ester (1a; *n*=6, *m*=12)

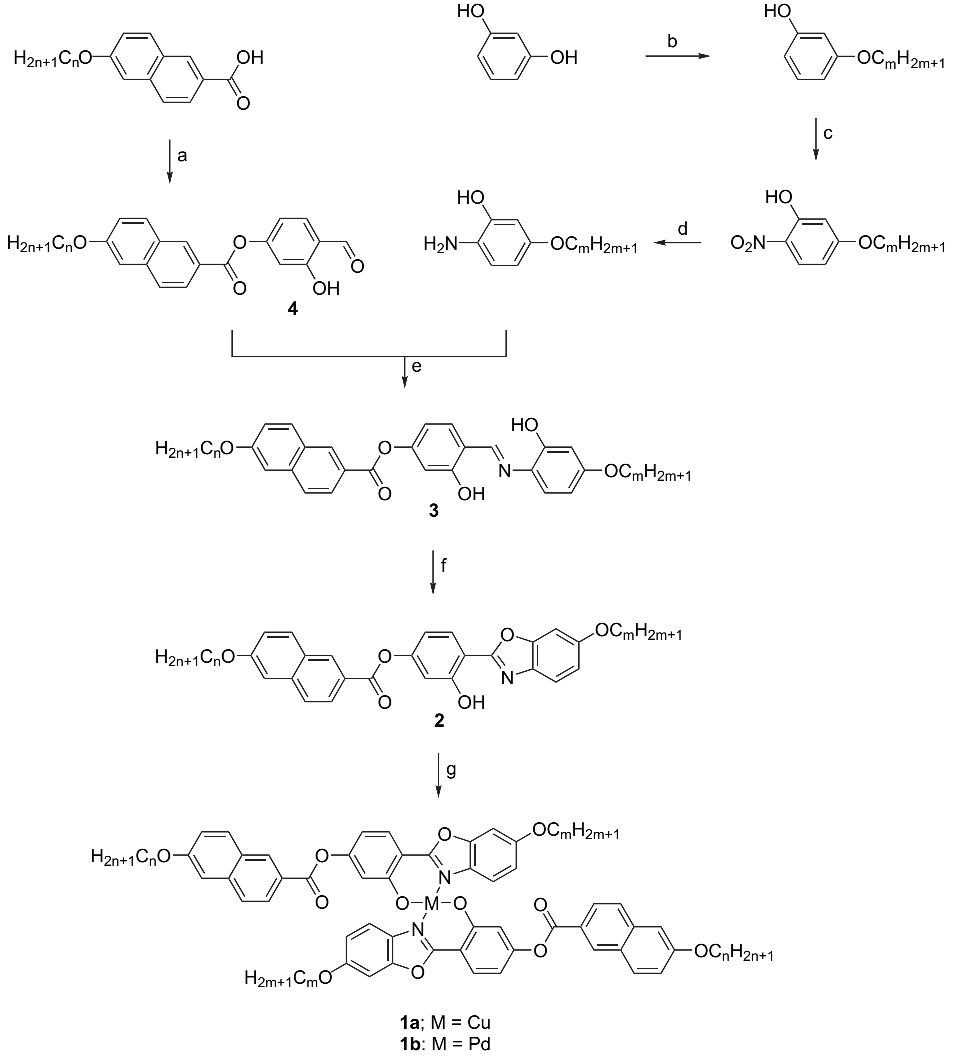
Two single crystals of the non-mesogenic benzoxazole **2** (*n*=0; *m*=4) and mesogenic copper complex **1a** (*n*=6, *m*=12) suitable for crystallographic analysis were obtained by slow vaporization from CH_3Cl at room temperature and their structures resolved. Figure 1 shows the two molecular structures with the atomic numbering schemes. Table 1 lists their crystallographic and structural refinement data for the two molecules. The overall molecular shape of crystal **2** (*n*=0, *m*=4) was considered as a slightly bent structure. The benzoxazole and central phenolic rings were nearly coplanar (dihedral angle<1°), however, they were not coplanar with the naphthalene ring. A dihedral angle of 75.64° was measured. Unsurprisingly, an *intramolecular* H-bond between phenolic O(2)–H2A and N1 atom was observed, and the distance was measured by ca. 1.811 Å. The H-bonding kept the two rings (i.e., benzoxazole and phenolic rings) nearly coplanar, and the coplanar structure was attributed to a preferred better packing both in the solid or/and the liquid crystal state. In the unit cell, all molecules were arranged by antiparallel and head-to-tail arrangements when viewed down *b* axis. The phenolic –OH groups between the neighboring molecules were outwardly pointed each other, therefore, *intermolecular* H-bonding was not possibly formed. The distances measured for all other possible H-bonds were all longer than 3.0 Å. On the other hand, all perpendicular distances between the molecules were measured larger than 4.80 Å, therefore, a π–π interaction was not existent.

The single crystal structure of copper complex **1a** (*n*=6, *m*=12) was also resolved. An overall rod-shaped molecule with a length *L* (~41.2 Å) and width *d* (~3.5 Å) was in fact obtained. The geometry at copper center was a perfect square-planar. The two angles of N(1)–Cu–O(1) and N(1)–Cu–O(1A) were of 90.51(8)° and 89.49(8)°, which showed almost an ideal angle of 90° expected for a square-planar geometry. Two benzoxazole and two phenol rings were coplanar, however, they were not coplanar with two naphthalene rings. The dihedral angle of naphthalene (C2–C7) and benzoxazole rings was measured as 13.315°, however, the dihedral angle of naphthalene (C9–C18) and benzene ring (C2–C7) was measured as 73.489°. The closest perpendicular distance between the two naphthalene rings in neighboring molecules is measured ca. 3.682 Å (Fig. 2). Some selected bond distances and angles for compound **1a** are also summarized in Table 2.

2.3. Mesomorphic properties of benzoxazoles 2

The liquid crystalline behavior of benzoxazole derivatives **2** and their copper and palladium complexes **1a** and **1b** was investigated and studied by differential scanning calorimeter (DSC) and polarizing optical microscope. In order to understand the relationship between the structure and the mesomorphic properties in the type of rod-like benzoxazole derivatives, a variety of compounds **2** with carbon chain's length systematically changed on naphthyl ring (*n*=0–12) while another side chain of the benzoxazole ring fixed at *m*=8 or 12 was investigated.

The phase transitions and thermodynamic data of compounds **2** were summarized in Table 3. All compounds **2** formed liquid crystalline phases regardless of the carbon length on the alkoxy side chains, and the formation of mesophases was dependent on the carbon length of terminal chains. Totally five derivatives **2** with a shorter carbon chain (*m*=8, *n*=0, 1; *m*=12; *n*=0, 1, 4) exhibited only nematic (N) phase, however, all other derivatives with a longer carbon length (*m*=12, *n*=6, 7, 8, 10, 12) formed N phase at higher temperature and smectic C (SmC) phases at lower temperature. The mesophase was characterized by optical textures, as shown in Figure 3. This type of mesophase dependence on the carbon length is quite common in rod-like mesogens. Interestingly, compounds **2** with no polar substituent (*n*=0) or a methoxy group (*n*=1) on naphthyl ring were truly mesogenic, which indicated that the terminal 4′-alkoxyl chain (*m*=8, 12) on the benzoxazole ring was crucially required for the formation of mesophases. These two compounds have a relatively short temperature range of mesophase, Δ*T*=6.40 °C (*n*=0; *m*=8)–15.5 °C (*n*=0, *m*=12). The



Scheme 1. Reactions and conditions: (a) 2,4-dihydroxybenzaldehyde (1.0 equiv), DCC (1.2 equiv), DMAP (1.2 equiv) in dried CH_2Cl_2, 24 h, 62%; (b) *n*-alkylbromides (1.1 equiv), $KHCO_3$ (1.3 equiv), KI, refluxed in CH_3COCH_3, 24 h, 35%; (c) $NaNO_2$ (0.1 equiv), HNO_3 (1.2 equiv), in CH_2Cl_2, 6 h, 42%; (d) H_2NNH_2 (1.2 equiv), Pd/C (10%, 0.1 equiv), refluxed in C_2H_5OH, 4 h, 86%; (e) 2-amino-5-alkylphenols (1.0 equiv), CH_3COOH (drops) in absolute C_2H_5OH, 24 h, 88%; (f) $Pb(OAc)_4$ (1.2 equiv), refluxed in $CHCl_3$, 2 h, 70%; (g) $Cu(OAc)_2$ or $Pd(OAc)_2$ (1.0 equiv), refluxed in absolute C_2H_5OH, 24 h, 73–87%.

benzoxazole was relatively considered as a large core, and generally more or longer terminal chains were required to induce the mesophases. The induction of the observed mesophases might be attributed to the better molecular arrangement and the enhanced van der Waals interaction. On the other hand, the single bond of the ester group (–OC=O) on the naphthyl ring might also play an important role in forming the mesophase. The higher flexibility or conformation caused by free rotation of the –OC bond covering a large volume might be considered as a terminal chain at mesogenic temperature. This result was also supported by crystallographic data discussed later. The crystallographic data indicated that all molecules were in fact antiparallel arranged (head-to-tail arrangement) between the neighboring layers, therefore, compounds with no or only methoxy substituent would not drastically alter the overall molecular length.

The mesophase was better improved when a longer chain was attached. The two derivatives (n=1; m=8, 12) with a methoxy group attached have a temperature range, much wider than those of two derivatives without a polar group, i.e., ΔT=106.6 °C (n=1, m=8)–78.7 °C (n=1, m=12)>ΔT=6.40 °C (n=0; m=8)–15.5 °C (n=0, m=12) on heating process. On the other hand, the derivative (n=1, m=8) in this series has the highest isotropic temperature (T_{cl}=207.4 °C), whereas the derivative (n=0, m=8) has the narrowest range (ΔT=6.40 °C) of the nematic mesophase. The clearing temperatures were drastically increased by ca. 85.0 °C (T_{cl}=122.4 °C→207.4 °C; m=8) and 75.6 °C (T_{cl}=107.7 °C→183.3 °C; m=12) when one more methoxy group was substituted. This increase in both clearing temperature and temperature range was probably attributed to the enhanced dipole–dipole interaction. The clearing temperature of all other m=12 derivatives was slightly decreased with carbon length, i.e., T_{cl}=183.3 °C (n=1)>173.7 °C (n=7), 164.6 °C (n=12), and this trend indicated that the dispersive force induced by alkoxy chains played an important role on the formation of the mesophases. The enthalpies for the phase transition of the nematic-to-isotropic were ranged from ΔH=0.30 kJ/mol (n=0, m=8)–1.35 kJ/mol (n=12, m=12) on the heating process. When compounds are substituted with a longer chain (n=6, 7, 8, 10, 12), a second phase, SmC, appeared on the DSC analysis. However, the SmC phase was monotropic and observed for two derivatives with shorter chains (n=6, 7; m=12). However, the SmC phase was enantiotropic and observed at higher temperature for the higher homologues (n=8, 10, 12). The temperature range of the SmC phase was increased with the carbon length, i.e., ΔT=10.9 °C (n=6)>38.2 °C (n=8)>66.0 °C (n=12) on cooling process, however, the temperature range of the N phase was decreased with carbon lengths, i.e., 103.8 °C (n=1)>101.9 °C (n=6)>67.1 °C (n=8)>25.0 °C

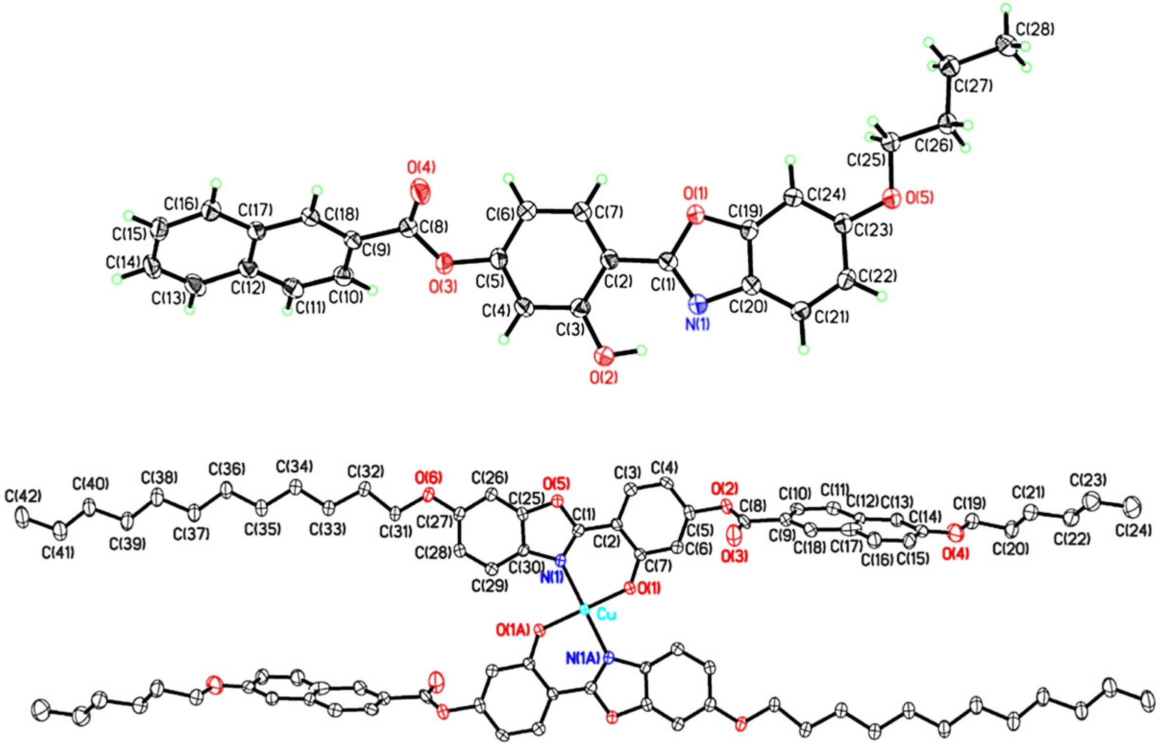


Figure 1. Two ORTEP drawings for compound **2** ($n=0$; $m=4$) and **1a** ($n=6$; $m=12$) with the numbering scheme, and the thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

Table 1
Crystallographic and experimental data for compounds **2** and **1a**

Compound	**2** (n=4, m=0)	**1a** (n=6, m=12)
Empirical formula	$C_{28}H_{23}NO_5$	$C_{84}H_{100}CuN_2O_{12}$
Formula weight	453.47	1393.20
T/K	150(1)	150(1)
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)/c$	P-1
a/Å	7.1202(5)	4.8037(2)
b/Å	16.8522(11)	14.7194(6)
c/Å	18.1847(12)	25.4589(10)
α/°	90.0	91.431(1)
β/°	97.433(2)	91.461(1)
γ/°	90.0	95.785(1)
U/Å^3	2163.7(3)	1789.70(13)
Z	4	1
F(000)	952	743
D_c/Mg/m^3	1.392	1.293
Crystal size/mm^3	0.60×0.33×0.25	0.50×0.10×0.03
Range for data collection/Å	1.65–27.5	0.80–27.5
Reflection collected	21,438	23,880
Data, restraints, parameters	4973/0/311	8210/0/496
Independent reflection	4973[R_{int}=0.0308]	8210[R_{int}=0.0503]
Final $R1$, $wR2$	0.0475, 0.1146	0.0680, 0.1608

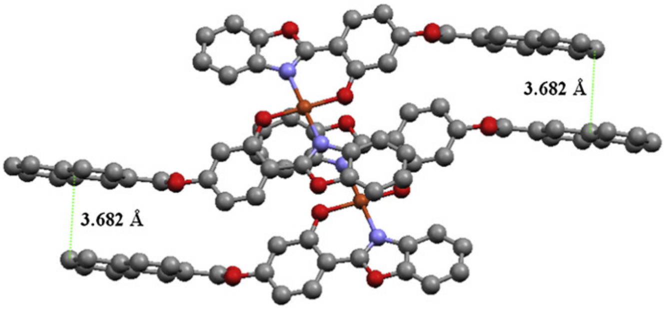


Figure 2. A π–π interaction of 3.682 Å is observed in crystal **1a** (n=6, m=12).

Table 2
Selected bond distances (Å) and angles (°) for **1a**

Cu–O(1)	1.8758(17)
Cu–O(1A)	1.8758(17)
Cu–N(1A)	2.018(2)
Cu–N(1)	2.018(2)
O(1)–Cu–O(1A)	180.00(17)
O(1)–Cu–N(1A)	89.49(8)
O(1A)–Cu–N(1A)	90.51(8)
O(1)–Cu–N(1)	90.51(8)
O(1A)–Cu–N(1)	89.49(8)
N(1A)–Cu–N(1)	180.00(12)

(n=12) on the cooling process. On the other hand, the overall temperature range of mesophases were not quite correlated well with carbon chain length, which were all ranged from ΔT=90.8 °C (n=4)–112.8 °C (n=6). Elongation of overall molecule by increasing the carbon length on the other side of terminal chains led to the formation of more ordered phases, SmC. This is generally attributed to an enhanced dipole–dipole interaction between the terminal chains. The N phase and SmC phase were identified by polarized optical microscope, and under the optical microscope typical Schlieren textures (Fig. 3) for the N and SmC phase was observed upon cooling from the isotropic state. Powder X-ray diffraction experiment for compound **2** (n=12, m=12) was performed to confirm the SmC phase. A diffraction plot at 95.0 °C with three peaks at 31.98 Å, 16.17 Å, and 11.37 Å were observed, which were indexed as 001, 002, and 003 showing a layered structure of SmC phase. The layer spacing of 31.98 Å was much smaller than 48.18 Å, which was the overall molecular length obtained by MM2 molecular calculation, indicating that the molecules were either tilted or interdigitated in the mesophases.

2.4. Mesomorphic properties of compounds 1a and 1b

The phase transitions and thermodynamic data of metal complexes **1a** and **1b** were summarized in Table 4. The melting

Table 3
The phase transitions and the enthalpies[a] of compounds **2**

n	*m*							
Compound **2**								
0	8	Cr			$\xrightleftharpoons[69.9\ (33.4)]{116.0\ (35.3)}$	N	$\xrightleftharpoons[120.4\ (0.29)]{122.4\ (0.30)}$	I
1	8	Cr			$\xrightleftharpoons[52.3\ (8.30)]{100.8\ (20.1)}$	N	$\xrightleftharpoons[205.6\ (0.58)]{207.4\ (0.64)}$	I
0	12	Cr			$\xrightleftharpoons[69.9\ (33.4)]{92.2\ (37.8)}$	N	$\xrightleftharpoons[105.7\ (0.53)]{107.7\ (0.55)}$	I
1	12	Cr			$\xrightleftharpoons[77.9\ (23.1)]{104.6\ (31.6)}$	N	$\xrightleftharpoons[181.7\ (0.52)]{183.3\ (0.57)}$	I
4	12	Cr			$\xrightleftharpoons[89.1\ (49.6)]{119.7\ (51.7)}$	N	$\xrightleftharpoons[179.9\ (0.46)]{182.9\ (0.48)}$	I
6	12	Cr	$\xleftarrow[63.7\ (31.6)]{}$	SmC	$\xrightleftharpoons[74.6\ (0.35)]{96.9\ (40.9)}$	N	$\xrightleftharpoons[176.5\ (0.86)]{178.8\ (0.89)}$	I
7	12	Cr	$\xleftarrow[66.3\ (36.3)]{}$	SmC	$\xrightleftharpoons[88.6\ (0.52)]{97.9\ (39.7)}$	N	$\xrightleftharpoons[171.8\ (1.06)]{173.7\ (1.15)}$	I
8	12	Cr	$\xrightleftharpoons[62.2\ (25.1)]{92.2\ (15.1)}$	SmC	$\xrightleftharpoons[100.4\ (0.55)]{103.8\ (0.47)}$	N	$\xrightleftharpoons[167.5\ (0.94)]{170.3\ (0.95)}$	I
10	12	Cr	$\xrightleftharpoons[64.7\ (26.3)]{86.4\ (26.4)}$	SmC	$\xrightleftharpoons[125.2\ (0.90)]{127.2\ (1.10)}$	N	$\xrightleftharpoons[166.2\ (0.94)]{167.7\ (1.00)}$	I
12	12	Cr	$\xrightleftharpoons[72.0\ (31.1)]{91.9\ (33.7)}$	SmC	$\xrightleftharpoons[138.0\ (1.63)]{139.8\ (1.69)}$	N	$\xrightleftharpoons[163.0\ (1.33)]{164.6\ (1.35)}$	I

[a] *n* represents the carbon numbers in the alkoxy chain. Cr=crystal; SmC=smectic C; N=nematic; I=isotropic phases. The transition temperatures (°C) and enthalpies (in parenthesis, kJ/mol) are determined by DSC.

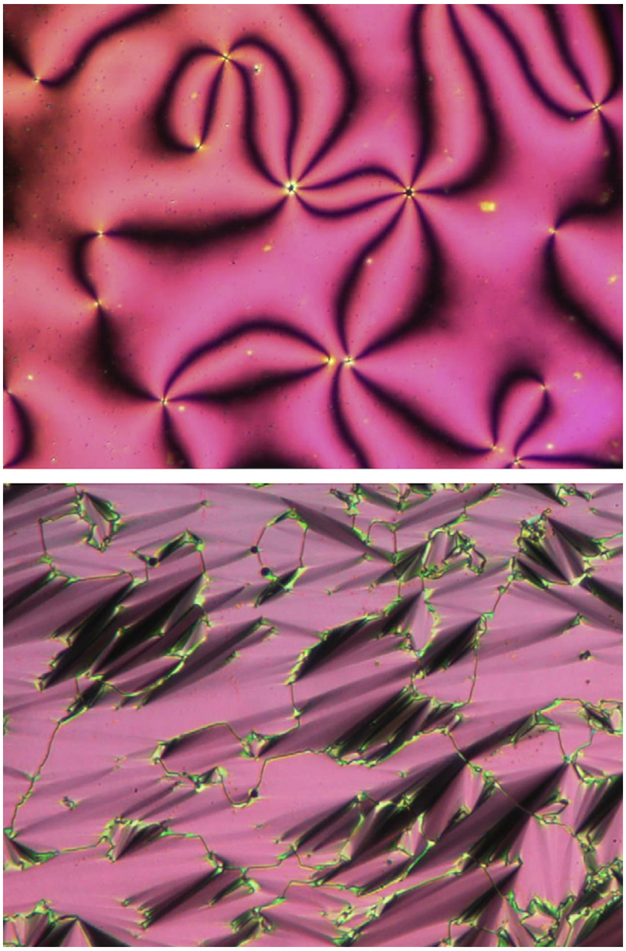


Figure 3. Optical textures observed by compound **2** (*n*=10, *m*=12); N phase at 160 °C (top plate) and SmC phase at 120 °C (bottom plate).

temperatures and clearing temperatures of copper complexes **1a** and palladium complexes **1b** were all higher than their precursor compounds **2**, as expected, which were attributed to the larger molecular size or/and coral rigidity. All copper complexes **1a** except for one derivative (*n*=0, *m*=8) exhibited mesomorphic behavior; the complexes with terminal chains from *n*=4–10 exhibited nematic phase and complex with *n*=12 formed smectic C phase at lower temperature and nematic phase at higher temperature. The complex with the shortest chain (**1a**; *n*=0, *m*=8) was not mesogenic due to the insufficient chain flexibility. The lack of mesomorphic properties in this series of copper complexes was better improved, and their mesophase were induced upon addition of a methoxy group (*n*=1, *m*=8) on the naphthyl ring. In contrast, the complex with *n*=1/*m*=12 was truly mesogenic, which has a temperature range of ΔT=66.9 °C. The clearing temperatures of complexes **1a** were slightly decreased with the carbon chain length, 249.7 °C (*n*=0, *m*=12)>241.6 °C (*n*=7, *m*=12)>220.1 °C (*n*=12, *m*=12). The transition enthalpies of nematic-to-isotropic phases ranged from 0.91 kJ/mol (*n*=1, *m*=8) to 1.05 kJ/mol (*n*=7, *m*=12) were not sensitive to the terminal carbon length. The temperature range of nematic phase was decreased with carbon length, 67.2 °C (*n*=1)>15.5 °C (*n*=8)>9.4 °C (*n*=12) on the heating process. For the complex with *n*=12 a SmC phase was also observed at lower temperature, however, the temperature range of the SmC phase was only 3.80 °C. The phases were identified and confirmed as nematic and smectic C phases by polarized microscope, and typical optical textures, shown in Figure 4, were observed. Palladium compounds **1b** were also prepared and studied in order to understand the influence of incorporated metal on the mesogenic behavior upon formation of the complexes.

Palladium complex **1b** with a terminal chain *n*=1 and *n*=4 exhibited nematic phases, and all other complexes **1b** with *n*=0 and *n*=6 formed crystalline states. A single crystal structure of Pd^{2+} complexes was not possible for a comparison for the relative geometric difference with Cu^{2+} center. However, the palladium complex should have a similar square-planar structure with copper complexes. Palladium complexes **1b** have a higher clearing temperature than copper complex **1a** by ca. 19.5 °C (*n*=4)>14.7 °C (*n*=6)>46.9 °C (*n*=0). An increase in clearing temperature was probably attributed to a stronger intermolecular attraction caused by a larger Pd^{2+} core. The too stronger interaction in the Pd complexes **1b** might also be responsible for the lack of liquid crystallinity for the longer chain derivatives (*n*=6 or higher homologues). On the other hand, the benzoxazole is often considered as an electron deficient heterocycle, therefore, the electronic configuration of the central ions, d^9-Cu and d^8-Pd might be another important factor in determining the mesophase.

2.5. Optical properties

Benzoxazole derivatives have been considered as potential light-emitting materials due to their photophysical and fluorescent properties.[20–22] The luminescent properties observed by such compounds were often affected by substituent and/or conjugation length. The UV–vis absorption and the photoluminescence spectra of the compounds **2** in CH_2Cl_2 solution are shown in Figure 5. The absorption and emission spectra were very similar in shape. The highest absorption peaks of all compounds **2** were found to be insensitive to the carbon length, and they all occurred at ca. 330.5–331.0 nm. On the other hand, a similar trend was also observed in the photoluminescence spectra. The emission peaks were much broader, which occurred at 467.0–470.0 nm for compounds **2**. However, the quantum yields measured in CH_2Cl_2 estimated with

Table 4
The phase transitions and the enthalpies[a] of compounds **1a** and **1b**

n	*m*	
Compound **1a**		
0	8	Cr $\xrightleftharpoons[181.1\ (49.5)]{218.0\ (51.5)}$ I
1	8	Cr $\xrightleftharpoons[173.5\ (20.2)]{201.2\ (33.9)}$ N $\xrightleftharpoons[267.3\ (0.93)]{268.1\ (0.91)}$ I
0	12	Cr $\xrightarrow{170.2\ (45.8)}$ I Cr $\xleftarrow{148.3\ (42.3)}$ N $\xleftarrow{160.8\ (0.68)}$ I
1	12	Cr $\xrightleftharpoons[162.9\ (25.0)]{182.5\ (38.7)}$ N $\xrightleftharpoons[245.6\ (0.56)]{249.7\ (0.84)}$ I
4	12	Cr $\xrightleftharpoons[216.0\ (53.1)]{224.3\ (53.1)}$ N $\xrightleftharpoons[241.0\ (0.64)]{247.0\ (0.58)}$ I
6	12	Cr $\xrightleftharpoons[215.3\ (51.8)]{223.1\ (53.5)}$ N $\xrightleftharpoons[241.7\ (0.74)]{245.6\ (0.68)}$ I
7	12	Cr $\xrightleftharpoons[213.6\ (49.8)]{224.4\ (66.2)}$ N $\xrightleftharpoons[238.2\ (0.94)]{241.6\ (1.05)}$ I
8	12	Cr $\xrightleftharpoons[205.7\ (24.1)]{215.5\ (30.0)}$ N $\xrightleftharpoons[229.7\ (0.74)]{231.0\ (0.62)}$ I
10	12	Cr $\xrightleftharpoons[210.8\ (48.5)]{215.5\ (49.1)}$ N $\xrightleftharpoons[225.3\ (0.71)]{228.1\ (0.74)}$ I
12	12	Cr $\xrightarrow{210.7\ (43.3)}$ N $\xrightleftharpoons[218.4\ (1.00)]{220.1\ (1.02)}$ I Cr $\xleftarrow{203.4\ (36.3)}$ SmC $\xleftarrow{207.2\ (2.26)}$ N
Compound **1b**		
0	12	Cr $\xrightleftharpoons[200.0\ (44.2)]{217.1\ (47.0)}$ I
1	12	Cr $\xrightleftharpoons[212.7\ (8.81)]{248.4\ (39.6)}$ N $\xrightleftharpoons[252.5\ (1.46)]{259.7\ (1.31)}$ I
4	12	Cr $\xrightleftharpoons[244.1\ (42.8)]{260.4\ (51.8)}$ N $\xrightleftharpoons[255.4\ (0.25)]{266.5\ (0.29)}$ I
6	12	Cr $\xrightleftharpoons[254.7\ (39.3)]{260.3\ (55.6)}$ I

[a] *n* represents the carbon numbers in the alkoxy chain. Cr=crystal; N=nematic; SmC=smectic C; I=isotropic phases. The transition temperatures (°C) and enthalpies (in parenthesis, kJ/mol) are determined by DSC.

anthracene as a standard (φ_f=0.27 in hexane) were ranged from 8.5–11.4%.

3. Conclusions

In conclusion, the first series of metallomesogenic materials derived from benzoxazoles exhibiting mesophases was prepared and investigated. Their precursor derivatives **2** were truly mesogenic, and their fluorescent properties were also examined as potential lighting materials. All copper exhibited nematic and/or smectic C phase, however, palladium complexes formed nematic phases. The preparation of metal complexes with other metal ions incorporated is needed in order to understand the effect or the role of metal ion in this type of metallomesogenic materials.

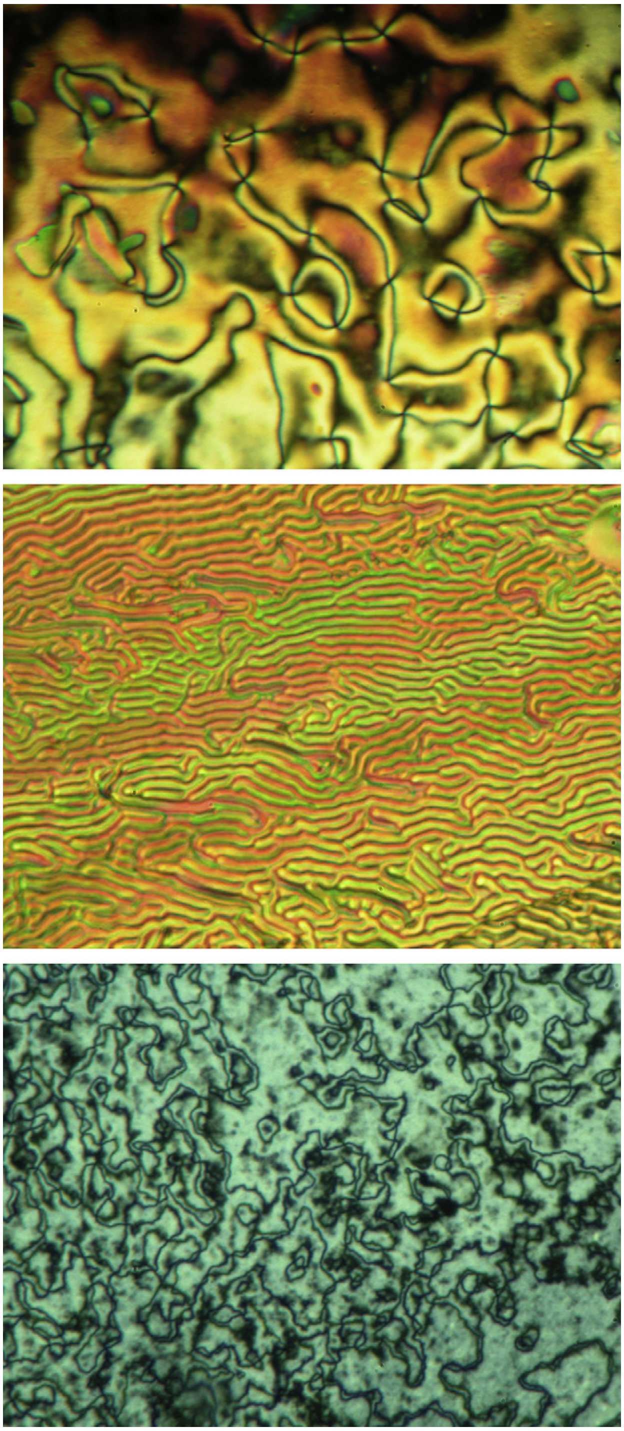


Figure 4. Optical textures observed by **1a** (*n*=12, *m*=12); N phase at 215 °C (top plate); N→SmC transition at 209 °C (central plate), and by **1b** (*n*=4, *m*=12); N phase at 250 °C (bottom plate).

4. Experimental

4.1. General

All chemicals and solvents were reagent grades from Aldrich or Lancaster Co. Solvents used were dried by standard techniques. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AM-300 or Bruker Avance-500. FTIR spectra were performed on Nicolet Magna-IR 550 spectrometer. DSC thermographs were carried out on a Mettler DSC 821 and calibrated with a pure indium sample and all phase transitions are determined by a scan rate of 10.0°/min. Optical polarized microscopy was carried out on an Zeiss AxiaPlan equipped with a hot stage system of Mettler FP90/FP82HT. The UV–vis absorption and fluorescence spectra were obtained using HITACHI F-4500 or JASCO V-530 spectrometer. Elemental analysis for carbon, hydrogen, and nitrogen were conducted on a Heraeus Vario EL-III elemental analyzer at National Taiwan University. The preparation of 3-alkoxyphenols 5-alkoxy-2-nitrophenols and 2-amino-5-alkoxyphenols was followed by literature procedures.

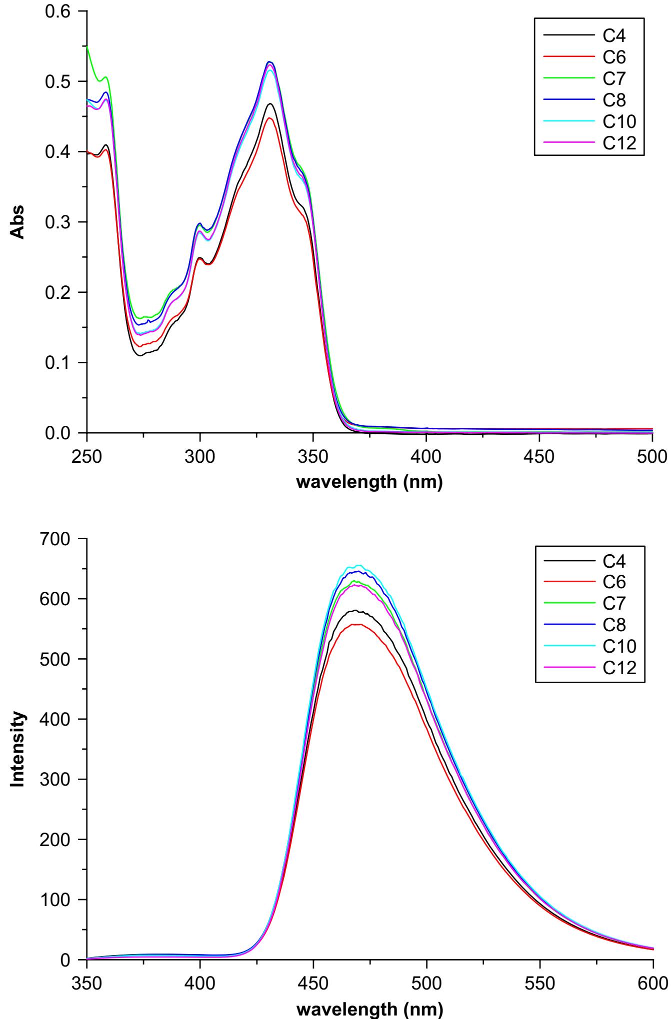


Figure 5. Normalized UV absorption and PL spectra of compounds **2** in CH_2Cl_2.

4.2. 5-Dodecyloxy-2-nitrophenol

Yellow solid, yield 42%. ^1H NMR ($CDCl_3$): δ 0.86 (t, J=6.7 Hz, $-CH_3$, 3H), 1.24–1.38 (m, $-CH_2$, 18H), 1.74–1.82 (m, $-OCH_2CH_2$, 2H), 3.99 (t, J=6.4 Hz, $-OCH_2$, 2H), 6.45–6.51 (m, $-C_6H_3$, 2H), 8.00 (d, J=10.02 Hz, $-C_6H_3$, 1H), 11.03 (s, $-C_6H_3$, 1H). ^{13}C NMR ($CDCl_3$): δ 14.10, 22.66, 28.81, 29.25, 29.26, 29.32, 29.49, 29.54, 29.6, 31.90, 69.12, 101.76, 109.82, 126.89, 127.51, 157.98, 166.72.

4.3. 2-Amino-5-dodecyloxyphenol

White solid, yield 86%. ^1H NMR ($CDCl_3$): δ 0.86 (t, J=6.7 Hz, $-CH_3$, 3H), 1.24–1.38 (m, $-CH_2$, 18H), 1.67–1.71 (m, $-CH_2$, 2H), 3.84 (t, J=6.5 Hz, $-OCH_2$, 2H), 6.42–6.45 (d, J=7.6 Hz, $-C_6H_3$, 2H), 6.74 (d, J=7.6 Hz, $-C_6H_3$, 1H), 11.03 (s, –OH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.10, 23.12, 28.81, 29.25, 29.26, 29.32, 29.49, 29.61, 31.91, 72.28, 102.17, 107.60, 117.23, 125.64, 144.53, 162.17.

4.4. 6-Dodecyloxynaphthalene-2-carboxylic acids

The mixture of 6-hydroxy-2-naphthoic acid (5.0 g, 0.027 mol) and KOH pellets (3.0 g, 0.053 mol) dissolved in 100 ml of ethanol/H_2O (10/1) was gently refluxed for 30 min under nitrogen atmosphere. To this solution was then added 1-bromododecane (13.92 g, 0.056 mol), and the solution was refluxed for 24 h. The solution was neutralized with dilute hydrochloric acid until the pH value reached 6.0. The white solids were collected, and then recrystallized from CH_2Cl_2/CH_3OH. White solid, yield 88%. ^1H NMR ($CDCl_3$): δ 0.85–0.90 (t, J=6.6 Hz, $-CH_3$, 3H), 1.29–1.50 (m, $-CH_2$, 12H), 1.83–1.85 (m, $-CH_2$, 2H), 4.08–4.11 (t, J=6.5 Hz, $-OCH_2$, 2H), 7.14 (s, $-C_{10}H_6$, 1H), 7.18–7.20 (d, J=8.9 Hz, $-C_{10}H_6$, 1H), 7.23 (s, $-C_{10}H_6$, 1H), 7.73–7.75 (d, J=8.6 Hz, $-C_{10}H_6$, 1H), 7.83–7.85 (d, J=8.9 Hz, $-C_{10}H_6$, 1H), 8.04–8.06 (d, J=8.8 Hz, $-C_{10}H_6$, 1H), 8.59 (s, $-C_{10}H_6$, 1H). ^{13}C NMR ($CDCl_3$): δ 13.91, 22.55, 26.05, 29.15, 29.28, 29.35, 31.75, 68.30, 106.72, 119.97, 121.29, 124.16, 126.05, 126.85, 127.85, 130.95, 131.80, 137.75, 159.51.

4.5. 6-Dodecyloxynaphthalene-2-carboxylic acid 4-formyl-3-hydroxyphenyl ester (4, *n*=12)

The mixture of 6-dodecyloxynaphthalene-2-carboxylic acid (2.00 g, 0.006 mol), 4-dimethyl-aminopyridine (DMAP; 0.89 g, 0.007 mol), and 2,4-dihydroxybenzoaldehyde (0.84 g, 0.006 mol) dissolved in 100 ml of dried CH_2Cl_2 was stirred at ice bath temperature for 30 min under nitrogen atmosphere. To the solution was then added *N*,*N*′-dicyclohexyl carbodiimide (DCC; 1.51 g, 0.007 mol) and the solution was stirred at room temperature for 24 h. The solids were filtered off and the filtrate was concentrated to dryness. The product was purified by passage to a short column of silica gel eluting with hexane/CH_2Cl_2 (1:1). White solid, yield 62%. ^1H NMR ($CDCl_3$): δ 0.86–0.90 (t, J=6.7 Hz, $-CH_3$, 3H), 1.27–1.56 (m, $-CH_2$, 18H), 1.83–1.86 (m, $-CH_2$, 2H), 4.08–4.10 (t, J=6.5 Hz, $-OCH_2$, 2H), 6.91 (s, $-C_6H_3$, 1H), 6.93–6.96 (d, J=8.4 Hz, $-C_6H_3$, 1H), 7.15 (s, $-C_{10}H_6$, 1H), 7.20–7.22 (d, J=8.9 Hz, $-C_{10}H_6$, 1H), 7.60–7.62 (d, J=8.4 Hz, $-C_6H_3$, 1H), 7.77–7.79 (d, J=8.6 Hz, $-C_{10}H_6$, 1H), 7.85–7.87 (d, J=8.9 Hz, $-C_{10}H_6$, 1H), 8.08–8.10 (d, J=8.6 Hz, $-C_{10}H_6$, 1H), 8.65 (s, $-C_{10}H_6$, 1H). ^{13}C NMR ($CDCl_3$): δ 14.11, 22.67, 26.10, 29.15, 29.25, 29.37, 31.83, 68.28, 106.48, 110.94, 114.18, 118.68, 120.33, 123.51, 126.00, 127.16, 127.75, 131.04, 132.06, 134.98, 137.86, 157.93, 159.70, 163.25, 164.48, 195.50.

4.6. 6-Dodecyloxynaphthalene-2-carboxylic acid 4-[(4-dodecyloxy-2-hydroxyphenylimino) methyl]-3-hydroxyphenyl ester (3; *n*=12, *m*=12)

To the solution of 6-dodecyloxynaphthalene-2-carboxylic acid 4-formyl-3-hydroxy-phenyl ester (0.35 g, 0.78 mmol) dissolved in 30 ml of hot absolute ethanol with five drops acetic acid added was added dropwise hot ethanolic solution of 2-amino-5-dodecyloxyphenol (0.23 g, 0.78 mmol) under nitrogen atmosphere. The solution was gently refluxed for 24 h. The solution was cooled and the yellow solids were collected by suction. The products isolated as light yellow solids were obtained after recrystallization from THF/CH_3OH. Yield 88%. ^1H NMR ($CDCl_3$): δ 0.87–0.89 (t, J=4.2 Hz, $-CH_3$, 6H), 1.27–1.51 (m, $-CH_2$, 36H), 1.75–1.86 (m, $-CH_2$, 4H), 3.94–3.97 (t, J=6.6 Hz, $-OCH_2$, 2H), 4.10–4.13 (t, J=6.7 Hz, $-OCH_2$, 2H), 6.50–6.51 (d, J=8.4 Hz, $-C_6H_3$, 1H), 6.95 (s, $-C_6H_3$, 1H), 7.10–7.11 (d, J=8.7 Hz, $-C_6H_3$, 1H), 7.20 (s, $-C_{10}H_6$, 1H), 7.21–7.23 (d, J=9.1 Hz, $-C_6H_3$, 1H), 7.42–7.44 (d, J=8.4 Hz, $-C_{10}H_6$, 1H), 7.77–7.79 (d, J=8.6 Hz, $-C_{10}H_6$, 1H), 7.84–7.86 (d, J=9.0 Hz, $-C_{10}H_6$, 1H), 8.11–8.12 (d, J=8.3 Hz, $-C_{10}H_6$, 1H), 8.64 (s, $-C_{10}H_6$, 1H), 8.66 (s, –CHN, 1H). ^{13}C NMR ($CDCl_3$): δ 13.93, 22.58, 26.00, 26.05, 26.16, 29.16, 29.20, 29.25, 29.33, 29.52, 29.56, 29.58, 29.65, 29.96, 30.02, 31.85, 68.34, 68.43, 101.98, 105.56, 106.72, 107.95, 110.54, 118.37, 118.91, 120.14, 120.40, 123.79, 126.04, 127.02, 127.90, 128.05, 130.97, 131.82, 133.11, 136.81, 151.26, 159.22, 160.22, 161.75, 166.98.

4.7. 6-Dodecyloxynaphthalene-2-carboxylic acid 4-(6-dodecyloxybenzooxazol-2-yl)-3-hydroxyphenyl ester (2; *n*=12, *m*=12)

The white solids of 6-dodecyloxynaphthalene-2-carboxylic acid 4-[(4-dodecyloxy-2-hydroxyphenylimino)methyl]-3-hydroxyphenyl ester (0.45 g, 0.622 mmol) was dissolved in 150 ml of hot $CHCl_3$, and the solution was slowly added to lead acetate (0.33 g, 0.746 mmol). The mixture was gently refluxed for 2 h. The solution was filtered off, and concentrated to dryness. The solids were then redissolved in CH_2Cl_2 and then extracted twice with water. The organic layers were collected and dried with anhydrous $MgSO_4$. The product was purified by flash chromatography with hexane/CH_2Cl_2 (1:1). White solids were isolated after recrystallization from CH_2Cl_2/CH_3OH. Yield 70%. ^{1}H NMR ($CDCl_3$): δ 0.86–0.88 (t, $-CH_3$, 6H), 1.25–1.56 (m, $-CH_2$, 36H), 1.82–1.85 (m, $-CH_2$, 4H), 3.99–4.02 (t, $-OCH_2$, 2H), 4.08–4.11 (t, $-OCH_2$, 2H), 6.94 (s, $-C_6H_3$, 1H), 6.95–6.96 (d, J=5 Hz, $-C_{10}H_6$, 1H), 6.97 (s, $-C_6H_3$, 1H), 7.03–7.03 (d, J=2.2 Hz, $-C_6H_3$, 1H), 7.10–7.10 (d, J=2.2 Hz, $-C_6H_3$, 1H), 7.15–7.16 (d, J=2.0 Hz, $-C_6H_3$, 1H), 7.24 (s, $-C_{10}H_6$, 1H), 7.55–7.57 (d, J=8.5 Hz, $-C_{10}H_6$, 1H), 7.77–7.79 (d, J=8.5 Hz, $-C_{10}H_6$, 1H), 7.86–7.87 (d, J=9.0 Hz, $-C_{10}H_6$, 1H), 8.00–8.02 (d, J=8.5 Hz, $-C_{10}H_6$, 1H), 8.12–8.13 (d, J=2.2 Hz, $-C_6H_3$, 1H), 8.68 (s, $-C_{10}H_6$, 1H), 11.59 (s, $-OH$, 1H). ^{13}C NMR ($CDCl_3$): δ 14.11, 22.68, 26.04, 26.08, 29.15, 29.20, 29.35, 29.39, 29.58, 29.60, 29.63, 29.66, 31.92, 68.24, 68.95, 96.19, 106.45, 108.80, 110.75, 113.59, 113.73, 119.15, 120.20, 123.95, 126.08, 127.05, 127.59, 127.77, 131.00, 131.88, 133.46, 137.71, 150.07, 154.71, 158.04, 159.40, 159.54, 161.52, 164.93. Anal. Calcd for $C_{48}H_{63}NO_6$: C, 76.87; H, 8.47; N, 1.87. Found: C, 76.89; H, 8.68; N, 1.68. MS (FAB): calcd for MH^{+} $C_{48}H_{63}NO_6$: 750.0; found: 750.0.

4.8. 6-Methoxynaphthalene-2-carboxylic acid 4-(6-dodecyloxybenzooxazol-2-yl)-3-hydroxyphenyl ester (2; n=1, *m*=12)

White solid, 52%. ^{1}H NMR ($CDCl_3$): δ 0.87–0.89 (t, $-CH_3$, 3H, J=4.5 Hz), 1.26–1.46 (m, $-CH_2$, 18H), 1.79–1.81 (d, $-CC_2$, J=4.7 Hz), 3.90–3.92 (t, $-OCH_3$, 3H, J=6.6 Hz), 3.94–3.96 (d, $-OCH_2$, 2H, J=6.7 Hz), 6.91–6.92 (m, $-C_6H_3$, 2H), 7.03 (s, $-C_6H_3$, 1H), 7.05 (s, $-C_6H_3$, 1H), 7.11 (s, $-C_{10}H_6$, 1H), 7.17–7.19 (d, $-C_6H_3$, 1H, J=8.2 Hz), 7.51–7.53 (d, $-C_6H_3$, 1H, J=8.3 Hz), 7.74–7.76 (d, $-C_{10}H_6$, 1H, J=8.0 Hz), 7.82–7.83 (d, $-C_{10}H_6$, 1H, J=8.5 Hz), 7.93–7.95 (d, $-C_{10}H_6$, 1H, J=8.1 Hz), 8.10–8.11 (d, $-C_{10}H_6$, 1H, J=8.0 Hz), 8.64 (s, $-C_{10}H_6$, 1H), 11.56 (s, $-OH$, 1H). ^{13}C NMR ($CDCl_3$): δ 14.19, 22.75, 26.11, 29.26, 29.43, 29.48, 29.66, 29.68, 29.74, 29.77, 31.98, 55.39, 68.90, 96.08, 105.70, 108.73, 110.69, 113.54, 113.69, 119.10, 119.88, 124.09, 126.13, 127.10, 127.54, 127.86, 131.05, 131.84, 133.39, 137.62, 150.00, 154.68, 158.03, 159.36, 159.92, 161.44, 164.82. Anal. Calcd for $C_{37}H_{41}NO_6$: C, 74.60; H, 6.94; N, 2.35. Found: C, 74.58; H, 6.96; N, 2.12. MS (FAB): calcd for MH^{+} $C_{37}H_{41}NO_6$: 595.7; found: 595.9.

4.9. 6-Butoxynaphthalene-2-carboxylic acid 4-(6-dodecyloxybenzooxazol-2-yl)-3-hydroxyphenyl ester (2; *n*=4, *m*=12)

White solid, 74%. ^{1}H NMR ($CDCl_3$): δ 0.85–0.88 (t, $-CH_3$, 3H, J=4.5 Hz), 0.99–1.02 (t, $-CH_3$, 3H, J=4.9 Hz), 1.27–1.57 (m, $-CH_2$, 20H), 1.82–1.86 (m, $-CH_2$, 4H), 4.00–4.02 (t, $-OCH_2$, 2H, J=6.5 Hz), 4.10–4.12 (t, $-OCH_2$, 2H, J=6.5 Hz), 6.95–6.97 (m, $-C_6H_3$, 2H), 7.03 (s, $-C_6H_3$, 1H), 7.11 (s, $-C_6H_3$, 1H), 7.16 (s, $-C_{10}H_6$, 1H), 7.22–7.23 (d, $-C_6H_3$, 1H, J=6.5 Hz), 7.56–7.58 (d, $-C_{10}H_6$, 1H, J=8.7 Hz), 7.79–7.81 (d, $-C_{10}H_6$, 1H, J=8.5 Hz), 7.86–7.88 (d, $-C_{10}H_6$, 1H, J=9.0 Hz), 8.12–8.14 (d, $-C_{10}H_6$, 1H, J=8.7 Hz), 8.68 (s, $-C_{10}H_6$, 1H), 11.59 (s, $-OH$, 1H). ^{13}C NMR ($CDCl_3$): δ 13.87, 14.13, 19.31, 22.70, 26.06, 27.24, 29.22, 29.36, 29.40, 29.59, 29.61, 29.65, 29.67, 31.22, 31.93, 67.93, 68.97, 96.23, 106.46, 108.83, 110.78, 113.62, 113.76, 119.18, 120.22, 123.99, 126.11, 127.07, 127.62, 127.80, 131.04, 131.91, 133.49, 137.74, 150.09, 154.73, 158.06, 159.42, 159.56, 161.55, 164.95. Anal. Calcd for $C_{40}H_{47}NO_6$: C, 75.33; H, 7.43; N, 2.20. Found: C, 74.96; H, 7.43; N, 1.94. MS (FAB): calcd for MH^{+} $C_{40}H_{47}NO_6$: 637.8; found: 638.0.

4.10. 6-Hexyloxynaphthalene-2-carboxylic acid 4-(6-dodecyloxybenzooxazol-2-yl)-3-hydroxylphenyl ester (2; *n*=6, *m*=12)

White solid, yield 43%. ^{1}H NMR ($CDCl_3$): δ 0.85–0.93 (m, $-CH_3$, 6H), 1.26–1.38 (m, $-CH_2$, 24H), 1.49–1.55 (m, $-CH_2$, 2H), 1.84–1.85 (m, $-OCH_2CH_2-$, 2H), 3.99–4.02 (t, $-OCH_2-$, 2H, J=6.6 Hz), 4.09–4.11 (t, $-OCH$, 2H, J=6.5 Hz), 6.93 (s, $-C_6H_3$, 1H), 6.94–6.96 (d, $-C_6H_3$, 1H, J=6.1 Hz), 6.97 (s, $-C_6H_3$, 1H), 7.03–7.03 (d, $-C_6H_3$, 1H, J=2.2 Hz), 7.11 (s, $-C_6H_3$, 1H), 7.16–7.16 (d, $-C_6H_3$, 1H, J=2.2 Hz), 7.56–7.57 (d, $-C_{10}H_6$, 1H, J=8.7 Hz), 7.78–7.79 (d, $-C_{10}H_6$, 1H, J=8.7 Hz), 7.86–7.88 (d, $-C_{10}H_6$, 1H, J=9.0 Hz), 8.01–8.02 (d, $-C_{10}H_6$, 1H, J=8.6 Hz), 8.10–8.11 (d, $-C_{10}H_6$, 1H, J=8.6 Hz), 8.78 (s, $-C_{10}H_6$, 1H), 11.59 (s, $-OH$, 1H). ^{13}C NMR ($CDCl_3$): δ 14.05, 14.13, 22.62, 22.70, 25.78, 26.06, 29.14, 29.22, 29.36, 29.41, 29.59, 29.61, 29.65, 29.67, 31.60, 31.93, 68.26, 68.97, 96.22, 106.47, 108.83, 110.77, 113.61, 113.75, 119.18, 120.22, 123.98, 126.10, 127.07, 127.61, 127.80, 131.03, 131.90, 133.49, 137.74, 150.09, 154.73, 158.06, 159.42, 159.56, 161.54, 164.95. Anal. Calcd for $C_{42}H_{51}NO_6$: C, 75.76; H, 7.72; N, 2.10. Found: C, 75.63; H, 7.90; N, 1.92. MS (FAB): calcd for MH^{+} $C_{42}H_{51}NO_6$: 665.9; found: 666.0.

4.11. 6-Heptyloxynaphthalene-2-carboxylic acid 4-(6-dodecyloxybenzooxazol-2-yl)-3-hydroxylphenyl ester (2; *n*=7, *m*=12)

White solids, yield 64%. ^{1}H NMR ($CDCl_3$): δ 0.85–0.91 (m, $-CH_3$, 6H), 1.26–1.37 (m, $-CH_2$, 26H), 1.48–1.55 (m, $-CH_2$, 2H), 1.84–1.86 (m, $-CH_2$, 2H), 3.99–4.02 (t, $-OCH_2$, 2H, J=6.5 Hz), 4.08–4.11 (t, $-OCH_2$, 2H, J=6.6 Hz), 6.94–6.94 (d, $-C_6H_3$, 1H, J=2.2 Hz), 6.97–6.97 (d, $-C_6H_3$, 1H, J=2.3 Hz), 7.03 (s, $-C_6H_3$, 1H), 7.11 (s, $-C_6H_3$, 1H), 7.16 (s, $-C_6H_3$, 1H), 7.22–7.23 (d, $-C_6H_3$, 1H, J=6.5 Hz), 7.56–7.57 (d, $-C_{10}H_6$, 1H, J=8.7 Hz), 7.78–7.79 (d, $-C_6H_3$, 1H, J=8.7 Hz), 8.01–8.02 (d, $-C_{10}H_6$, 1H, J=8.6 Hz), 8.10–8.11 (d, $-C_{10}H_6$, 1H, J=8.6 Hz), 8.68 (s, $-C_{10}H_6$, 1H), 11.59 (s, $-OH$, 1H). ^{13}C NMR ($CDCl_3$): δ 14.10, 14.13, 22.63, 22.70, 26.07, 29.08, 29.18, 29.22, 29.36, 29.41, 29.59, 29.61, 29.65, 29.67, 31.80, 31.93, 68.26, 68.97, 96.22, 106.47, 108.83, 110.77, 113.61, 113.76, 119.18, 120.22, 123.98, 126.10, 127.07, 127.61, 127.80, 131.03, 131.90, 133.49, 137.73, 150.09, 154.73, 158.06, 159.42, 159.56, 161.54, 167.95. Anal. Calcd for $C_{43}H_{53}NO_6$: C, 75.96; H, 7.86; N, 2.06. Found: C, 75.67; H, 7.97; N, 1.85. MS (FAB): calcd for MH^{+} $C_{43}H_{53}NO_6$: 679.9; found: 680.0.

4.12. 6-Heptyloxynaphthalene-2-carboxylic acid 4-(6-dodecyloxybenzooxazol-2-yl)-3-hydroxylphenyl ester (2; *n*=8, *m*=12)

White solid, yield 58%. ^{1}H NMR ($CDCl_3$): δ 0.87–1.26 (m, $-CH_3$, 6H), 1.26–1.49 (m, $-CH_2$, 28H), 1.81–1.84 (m, $-CH_2$, 4H), 3.96–3.99 (d, $-OCH_2$, 2H, J=6.5 Hz), 4.05–4.07 (d, $-OCH_2$, 2H, J=6.5 Hz), 6.91–6.94 (m, $-C_6H_3$, 2H), 7.03 (s, $-C_6H_3$, 1H), 7.07 (s, $-C_6H_3$, 1H), 7.12 (s, $-C_{10}H_6$, 1H), 7.19–7.20 (d, $-C_6H_3$, 1H, J=8.6 Hz), 7.53–7.54 (d, $-C_{10}H_6$, 1H, J=8.8 Hz), 7.75–7.76 (d, $-C_6H_3$, 1H, J=8.7 Hz), 7.83–7.85 (d, $-C_{10}H_6$, 1H, J=9.0 Hz), 7.96–7.97 (d, $-C_{10}H_6$, 1H, J=8.6 Hz), 8.10–8.11 (d, $-C_{10}H_6$, 1H, J=8.7 Hz), 8.65 (s, $-C_{10}H_6$, 1H), 11.57 (s, $-OH$, 1H). ^{13}C NMR ($CDCl_3$): δ 14.17, 22.71, 22.74, 26.10, 26.14, 29.20, 29.25, 29.31, 29.41, 29.43, 29.46, 29.64, 29.67, 29.70, 29.72, 31.88, 31.97, 68.23, 68.91, 96.12, 106.40, 108.75, 110.72, 113.57, 113.71, 119.13, 120.18, 123.94, 126.08, 127.05, 127.56, 127.76, 131.00, 131.87, 133.42, 137.71, 150.03, 154.70, 158.03, 159.38, 159.53, 161.48, 164.89. Anal. Calcd for $C_{44}H_{55}NO_6$: C, 76.38; H, 7.72; N, 2.02. Found: C, 76.59; H, 8.07; N, 2.71. MS (FAB): calcd for MH^{+} $C_{44}H_{55}NO_6$: 693.9; found: 694.0.

4.13. 6-Decyloxynaphthalene-2-carboxylic acid 4-(6-dodecyloxybenzooxazol-2-yl)-3-hydroxylphenyl ester (2; *n*=10, *m*=12)

White solid, yield 70%. ^{1}H NMR ($CDCl_3$): δ 0.85–0.88 (m, $-CH_3$, 6H), 1.26–1.38 (m, $-CH_2$, 30H), 1.48–1.54 (m, $-CH_2$, 2H), 1.84–1.86

(d, –CH_2, 2H, *J*=4.0 Hz), 3.99–4.02 (t, –OCH_2, 2H, *J*=6.5 Hz), 4.08–4.11 (t, –OCH_2, 2H, *J*=6.5 Hz), 6.92–6.92 (d, –C_6H_3, 1H, *J*=2.2 Hz), 6.93–6.93 (d, –C_6H_3, 1H, *J*=2.3 Hz), 6.94 (s, –C_6H_3, 1H), 7.03 (s, –C_6H_3, 1H), 7.11 (s, –$C_{10}H_6$, 1H), 7.16–7.16 (d, –C_6H_3, 1H, *J*=2.2 Hz), 7.56–7.57 (d, –$C_{10}H_6$, 1H, *J*=8.7 Hz), 7.78–7.79 (d, –C_6H_3, *J*=8.7 Hz), 7.86–7.88 (d, –$C_{10}H_6$, 1H, *J*=9.0 Hz), 8.01–8.03 (d, –$C_{10}H_6$, 1H, *J*=8.6 Hz), 8.10–8.11 (d, –$C_{10}H_6$, 1H, *J*=8.5 Hz), 8.68 (s, –$C_{10}H_6$, 1H), 11.59 (s, –OH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.67, 26.05, 26.09, 29.17, 29.22, 29.31, 29.34, 29.39, 29.57, 29.63, 29.65, 31.89, 31.91, 68.27, 69.00, 96.27, 106.53, 108.82, 110.76, 113.59, 113.76, 119.17, 120.19, 124.02, 126.09, 127.06, 127.60, 127.82, 131.01, 131.88, 133.53, 137.74, 150.11, 154.77, 158.09, 159.44, 159.57, 161.57, 164.91. Anal. Calcd for $C_{46}H_{59}NO_6$: C, 76.53; H, 8.24; N, 1.94. Found: C, 76.22; H, 8.41; N, 1.76. MS (FAB): calcd for MH^+ $C_{46}H_{59}NO_6$: 722.0; found: 722.0.

4.14. Naphthalene-2-carboxylic acid 4-(6-butyloxybenzooxazol-2-yl)-3-hydroxylphenyl ester (2; *n*=0, *m*=4)

White solid, yield 65%. ^1H NMR ($CDCl_3$): δ 0.98–1.01 (t, –CH_3, 3H, *J*=4.9 Hz), 1.50–1.54 (m, –CH_2, 2H), 1.77–1.83 (t, –CH_2, 2H, *J*=7.5 Hz), 3.98–4.01 (d, –OCH_2, 2H, *J*=6.5 Hz), 6.93–6.96 (m, –C_6H_3, 2H), 7.05 (s, –C_6H_3, 1H), 7.08 (s, –C_6H_3, 1H), 7.54–7.55 (d, –$C_{10}H_7$, 2H, *J*=4.4 Hz), 7.88–7.90 (d, –C_6H_3, 1H, *J*=8.2 Hz), 7.91–7.93 (d, –$C_{10}H_7$, 1H, *J*=8.6 Hz), 7.97–8.00 (t, –$C_{10}H_7$, 2H, *J*=7.7 Hz), 8.15–8.17 (d, –$C_{10}H_7$, 1H, *J*=8.5 Hz), 8.76 (s, –$C_{10}H_7$, 1H), 11.60 (s, –OH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.10, 19.29, 31.27, 68.60, 96.14, 108.91, 110.72, 113.53, 113.74, 119.7, 125.42, 126.40, 126.92, 127.64, 127.86, 128.48, 128.77, 128.83, 130.92, 132.12, 132.48, 133.42, 135.90, 150.48, 154.58, 158.06, 159.40, 161.45, 164.79.

4.15. Naphthalene-2-carboxylic acid 4-(6-dodecyloxybenzooxazol-2-yl)-3-hydroxyphenyl ester (2; *n*=0, *m*=12)

White solids, yield 56%. ^1H NMR ($CDCl_3$): δ 0.87–0.89 (t, –CH_3, 3H, *J*=4.5 Hz), 1.34–1.50 (m, –CH_2, 18H), 1.78–1.84 (m, –CH_2, 2H), 3.97–3.99 (d, –OCH_2, 2H, *J*=6.5 Hz), 6.93–6.95 (m, –C_6H_3, 2H), 7.05 (s, –C_6H_3, 1H), 7.08 (s, –C_6H_3, 1H), 7.53–7.55 (d, –C_6H_3, 2H, *J*=8.9 Hz), 7.60–7.61 (d, –$C_{10}H_7$, 1H, *J*=8.6 Hz), 7.88–7.89 (d, –$C_{10}H_7$, 1H, *J*=8.1 Hz), 7.91–7.92 (d, –$C_{10}H_7$, 1H, *J*=8.6 Hz), 7.98–7.99 (t, –$C_{10}H_7$, 2H, *J*=4.2 Hz), 8.15–8.16 (d, –$C_{10}H_7$, 1H, *J*=8.7 Hz), 8.76 (s, –$C_{10}H_7$, 1H), 11.60 (s, –OH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.18, 22.75, 26.10, 29.25, 29.42, 29.47, 29.65, 29.67, 29.73, 29.76, 31.98, 68.93, 96.13, 108.89, 110.71, 113.52, 113.74, 119.16, 125.42, 126.41, 126.91, 127.62, 127.86, 128.48, 128.76, 129.53, 132.11, 132.49, 133.41, 135.90, 150.04, 154.58, 159.40, 161.44, 164.77. Anal. Calcd for $C_{36}H_{39}NO_6$: C, 76.43; H, 6.95; N, 2.48. Found: C, 76.93; H, 7.26; N, 2.18. MS (FAB): calcd for MH^+ $C_{36}H_{39}NO_5$: 565.7; found: 565.9.

4.16. 6-Methoxynaphthalene-2-carboxylic acid 4-(6-octyloxybenzooxazol-2-yl)-3-hydroxyphenyl ester (2; *n*=1, *m*=8)

White solids, yield 46%. ^1H NMR ($CDCl_3$): δ 0.88–0.90 (t, –CH_3, 3H, *J*=4.2 Hz), 1.28–1.46 (m, –CH_2, 10H), 1.78–1.83 (m, –CH_2, 2H), 3.91–4.00 (m, –OCH_2 & –OCH_3, 5H), 6.91 (s, –C_6H_3, 1H), 6.93–6.95 (d, –C_6H_3, 1H, *J*=6.1 Hz), 6.95 (s, –C_6H_3, 1H), 7.03–7.06 (d, –C_6H_3, 1H, *J*=6.5 Hz), 7.13 (s, –$C_{10}H_6$, 1H), 7.18–7.20 (d, –C_6H_3, 1H, *J*=8.8 Hz), 7.52–7.53 (d, –$C_{10}H_6$, 1H, *J*=8.7 Hz), 7.75–7.77 (d, –$C_{10}H_6$, 1H, *J*=8.6 Hz), 7.82–7.84 (d, –$C_{10}H_6$, 1H, *J*=8.9 Hz), 7.94–7.96 (d, –$C_{10}H_6$, 1H, *J*=8.5 Hz), 8.10–8.12 (d, –$C_{10}H_6$, 1H, *J*=8.6 Hz), 8.65 (s, –$C_{10}H_6$, 1H), 11.57 (s, –OH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.16, 22.71, 26.10, 29.25, 29.29, 29.42, 31.86, 68.92, 96.11, 108.76, 110.71, 113.57, 113.71, 114.14, 119.12, 124.09, 126.05, 126.14, 127.57, 127.86, 131.86, 132.01, 133.40, 134.98, 150.14, 154.68, 159.36, 161.45, 164.86. Anal. Calcd for $C_{33}H_{33}NO_6$: C, 73.45; H, 6.16; N, 2.60. Found: C, 73.55; H, 6.18; N, 2.67. MS (FAB): calcd for MH^+ $C_{33}H_{33}NO_6$: 539.6; found: 540.0.

4.17. Naphthalene-2-carboxylic acid 4-(6-octyloxybenzooxazol-2-yl)-3-hydroxyphenyl ester (2; *n*=0, *m*=8)

White solids, yield 72%. ^1H NMR ($CDCl_3$): δ 0.88–0.90 (t, –CH_3, 3H, *J*=4.5 Hz), 1.25–1.49 (m, –CH_2, 10H), 1.79–1.84 (m, –CH_2, 2H), 3.98–4.00 (d, –OCH_2, 2H, *J*=6.5 Hz), 6.93–6.96 (m, –C_6H_3, 2H), 7.04 (s, –C_6H_3, 1H), 7.09 (s, –C_6H_3, 1H), 7.54–7.56 (d, –$C_{10}H_7$, 2H, *J*=4.4 Hz), 7.61–7.62 (d, –C_6H_3, 1H, *J*=8.5 Hz), 7.88–7.90 (d, –C_6H_3, 1H, *J*=8.2 Hz), 7.92–7.93 (d, –$C_{10}H_7$, 1H, *J*=8.6 Hz), 7.97–8.01 (t, –$C_{10}H_7$, 2H, *J*=8.2 Hz), 8.16–8.17 (d, –$C_{10}H$, 1H, *J*=8.4 Hz), 8.77 (s, –$C_{10}H_7$, 1H), 11.60 (s, –OH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.15, 22.70, 26.09, 29.24, 29.29, 31.86, 68.94, 96.15, 108.92, 110.73, 113.53, 113.76, 114.59, 119.18, 125.43, 126.41, 126.92, 127.64, 127.86, 128.49, 128.77, 129.54, 132.13, 132.49, 133.42, 135.91, 150.06, 154.58, 159.40, 161.45, 164.80. Anal. Calcd for $C_{32}H_{31}NO_5$: C, 75.42; H, 6.13; N, 2.75. Found: C, 75.11; H, 5.87; N, 2.64. MS (FAB): calcd for MH^+ $C_{32}H_{31}NO_5$: 509.6; found: 509.9.

4.18. Copper complex of 6-dodecyloxynaphthalene-2-carboxylic acid 4-(6-dodecyloxybenzooxazol-2-yl)-3-hydroxyphenyl ester (1a; *n*=12, *m*=12)

The mixture of 6-dodecyloxy-naphthalene-2-carboxylic acid 4-(6-dodecyloxybenzooxazol-2-yl)-3-hydroxyphenyl ester (0.10 g, 0.138 mmol) and copper(II) acetate (0.014 g, 0.0693 mmol) was refluxed in 50 ml of ethanol for 24 h. The solids were collected. The product isolated as brown solids was obtained after recrystallization from THF/CH_3OH. Yield 87%. Anal. Calcd for $C_{96}H_{124}N_2O_{12}Cu$: C, 73.84; H, 8.00; N, 1.79. Found: C, 73.90; H, 8.04; N, 1.70.

4.19. Palladium complex of 6-dodecyloxynaphthalene-2-carboxylic acid 4-(6-dodecyloxybenzooxazol-2-yl)-3-hydroxyphenyl ester (1b; *n*=12, *m*=12)

The synthetic procedures were similar to copper complex as described above except palladium(II) acetate was used. Yellow to light orange solids, yield 73%. Anal. Calcd for $C_{96}H_{124}N_2O_{12}Pd$: C, 71.86; H, 7.79; N, 1.75. Found: C, 71.78; H, 7.82; N, 1.52.

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