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Symmetrical dimer liquid crystals derived from benzoxazoles

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ABSTRACT

A series of dimeric twin liquid crystals derived from symmetric heterocyclic benzoxazoles **1a–1f** exhibiting single smectic C phase are reported. All benzoxazoles were prepared by condensation of 2-aminophenols with benzaldehydes and then followed by subsequent intramolecular cyclization. The mesomorphic properties were investigated by DSC and POM, and the structure of the mesophases was confirmed as smectic C phases by powder XRD. The formation of mesophases was attributed to the weak dipole force induced by donor–acceptor interaction (D \rightarrow A). A monolayer conformation was proposed based on the powder XRD data. A value of aspect ratio d/l=0.80-0.92 was calculated from *d*-spacings and the molecular lengths. By contrast, the odd–even effects by a value of entropy changes $\Delta S_{SmC \rightarrow 1}/R=2.00-6.50$ showing odd–even effect for the transition of SmC \rightarrow I phases were also associated in twin system. © 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Liquid crystalline dimers¹ (or also known as twins or bimesogens) have attracted quite extensive attention during the past decades. These dimers were particularly of appealing because of their unique thermal behavior and structural features as model compounds similar to polymeric liquid crystals. Mesogenic dimers can be symmetric or unsymmetric² in structure. The molecular conformations^{1a} and mesomorphic behavior were quite differential from classical (or monomeric) mesogens. On the other hand, their mesomorphic properties were significantly influenced by the spacer length and also the linking group.^{2d,3} This type of molecules is often made by linking either two identical or non-identical moieties through a flexible central spacer. A variety of liquid crystalline dimers made up of two rod-like mesogenic unit as well as disc-like units have been prepared⁷ and studied by using alkylene $(-CH_2-)$,^{3a,4} dioxyalkylene $[-O(CH_2)_nO-]^{1e,5,6}$ or esters $[-COO(CH_2)_nOOC-]^7$ as central spacers. The mesomorphic properties were known to be critically dependent on the length and the parity of the central spacer.⁸ Compared to the conventional rod-like mesogens, the transitional properties produced by such dimeric mesogens are in fact modified to a much larger extent by changes in the length and parity of the alkyl chains. Some twin liquid crystals showed a significant odd–even effect^{3a,5b,9} on mesomorphic behavior with spacer length or/and terminal length. The dimers with an even spacer have generally more parallel orientations than those of other dimers with an odd spacer, thus exhibiting a more stable

mesophase. The difference observed in phase behavior was mostly attributed to the dependence of the average molecular shape and/ or geometry adopted on the parity^{1e,6,10b,10d} of the central spacer when considered in the *all-trans* conformation.

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Most of the mesogenic twins formed smectic or nematic phases. However, some dimeric^{1e,10b,10c,11} twins with a bent-core (BC) or banana-shaped structure exhibited interesting banana phases. The micro-segregations in layer SmA phases have been generated by liquid crystalline dimers¹² possessing an oligo(ethylene glycol) spacer and two terminal alkyl chains. A few novel dimeric compounds^{1c,13} with a chiral and a disulphide-bridged^{1f} cyanobiphenyl spacer all exhibiting a monotropic SmA phase were reported. Known examples including common Schiff bases, stilbenes,^{3c} aromatics, cholesterols,^{1c,14} and tolan moieties were reported.

Three subtypes of proposed structures in smectic layers or phases; for example, monolayer,^{2,5b,14} interdigitated^{1d,10a} or intercalated^{1b,1f,5a,7b,10c,12} conformations were already known depending on their spacing and/or molecular length. Shape effect caused by odd or even carbon number¹⁵ in the spacer group often influence overall molecular conformations, therefore, leading to different phases formed. Benzoxazoles are often considered as fused electron deficient structure (also as acceptor). A weak dipole generated from the donor-acceptor (D-A) interaction might facilitate the formation of mesophase in such heterocyclic compounds. Known examples of mesogenic benzoxazoles¹⁶ were relatively rare. A few heterocyclic benzoxazole derivatives¹⁷ exhibiting smectic or columnar phases were prepared and studied previously in this group. As part of our studies of heterocyclic mesogens, in this paper, we describe the synthesis, characterization, and the mesomorphic properties of a series of calamitic dimeric benzoxazole derivatives with various spacer lengths. A single smectic C phase was observed along the



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series of compounds **1a–1f**. A monolayer conformation in the SmC phase was proposed based on XRD diffraction experiments.

2. Results and discussion

2.1. Synthesis



All benzoxazoles with an odd carbon number (**1a**, **1c**, **1e**, and **1f**; m=3, 5, 7, 11) in spacer length were prepared by procedures summarized in Scheme 1. Most of known benzoxazoles reported in the literatures were prepared by the condensation of 2-aminophenols with benzaldehydes or benzoic acid and then followed by subsequent intramolecular cyclization. All compounds in this work were prepared by this synthetic route. The reactions of bis(4-formy-lphenyl)alkanedioates **3** (m=3, 5, 7, 11) and 2-amino-5-alkoxy-phenols in refluxing absolute ethanol gave compounds **2** (m=3, 5, 7, 11), bis(4-((E)-(4-alkyl-2-hydroxyphenylimino)methyl)phenyl)-alkyldioates with a yield ranged from 69 to 73%. The final



Scheme 1. Reactions and reagents: (a) DMAP (2.1 equiv), stirred in dry THF, rt, 8 h, 48–72%; (b) RBr (1.1 equiv), KHCO₃ (1.5 equiv), refluxing in acetone, 24 h, 60%; (c) HNO₃ (1.2 equiv), NaNO₂ (0.2 equiv), 0°C in CH₂Cl₂, 6 h, 25%; (d) H₂NNH₂ (1.2 equiv), Pd/C (0.1 equiv), refluxed in C₂H₅OH, 24 h, 85%; (e) acetic acid (drops), refluxed in C₂H₅OH, 24 h, 69–73%; (f) Pd(OAc)₄ (1.1 equiv), refluxed in CHCl₃, 2 h, 64–77%.

benzoxazoles **1a**, **1c**, **1e**, **1f** were obtained by reactions of compounds **2** with $Pb(OAc)_4$ in refluxing chloroform and the yields were relatively high in the range 64–77%. In contrast, all other benzoxazoles **1b**, **1d** with an even carbon number (m=4, 6) in spacer length were obtained by procedures summarized in Scheme 2. The final benzoxazoles **1b**, **1d** were obtained by the reactions of compound **4** and adipoyl chloride or suberoyl chloride in dried THF. ¹H and ¹³C NMR spectroscopies were used to identify the intermediates and the final products. All compounds were characterized by elemental analysis.

2.2. Mesomorphic properties of compounds

The liquid crystalline behavior of compounds 1a-1f was characterized and studied by differential scanning calorimetry and polarized optical microscope. The phase transitions and thermodynamic data are summarized in Table 1. Three derivatives; 1a (m=3; n=6, 8) **1f** (m=11, n=12) exhibited monotropic phases and the mesophase was only obtained during the cooling process. Monotropic behavior was often considered as kinetically unstable and it occurred when aspect ratio of the molecule was not appropriate. All others formed enantiotropic phases regardless of the alkoxy chain length. These compounds all exhibited a layer smectic phase, as expected for the rod-like molecules. For the compounds **1a** (*m*=3; *n*=6, 8, 10, 12, 14, 16) the clearing temperatures were increased with the carbon numbers of the terminal alkyl chains, i.e., $T_{cl}=132.6$ (*n*=6)<142.5 (*n*=12)<145.2 °C (*n*=16), however, the melting temperatures remained at 126.1 (n=10)–129.9 °C (n=16) (Fig. 1). This increase in clearing temperatures was also true for the series of compounds **1c** (*n*=8, 12, 16), i.e., *T*_{cl}=118.7 (*n*=8)<130.6 (n=12)<133.4 °C (n=16). This may probably be attributed to an enhanced dispersive interaction or van der Waals interaction between the terminal alkoxy chains. The phases were identified as smectic C phases, and typical textures described as focal-conic or Schlieren domains (Fig. 2) were easily observed under optical polarized microscope when cooling from isotropic liquid. These textures were not homeotropic, which were often observed in SmA phases. A higher enthalpy (i.e., ΔH =8.65–13.2 and 8.94–10.6 kJ/mol on cooling cycle for compounds 1a and 1c, respectively) for the transition of $SmC \rightarrow I$ phase was obtained. In contrast, both melting temperatures and clearing temperatures have no apparent increasing or decreasing effect on increasing the carbon length of the spacer group with all terminal n=12 considered. However, the temperature range of the mesophase reached to maximum at compound **1b** (m=4, n=12) and then it started to lower to minimum at compound **1f** (*m*=11, *n*=12), i.e., ΔT_{SmC} =19.4 (**1a**, *m*=3)<42.9 (**1b**, *m*=4)>25.7 (**1c**, *m*=5)>21.9 (**1d**, *m*=6)>16.2 (**1e**, m=7)>7.9 °C (**1f**, m=11). On the other hand, the compound **1b** with spacer length m=4 and terminal chain length n=12 has the best aspect ratio in forming the mesophase. In other mesogenic twin systems, most compounds with lower terminal carbon chains often formed nematic phases besides smectic C phase for higher terminal carbon chains. In our system, SmC phase was only observed. This is probably attributed to the weak dipole induced interaction or/and produced by heterocyclic benzoxazoles. Benzoxazole is often considered as an electron deficient fused ring and molecules were tilted in the layer structure in order to reduce the dipole-dipole repulsion. The same mesomorphic behavior was observed in troponoid system.¹⁸

2.3. The odd-even effect

The odd–even effect, quite common in dimeric twins was also observed in this system. For all compounds **1a–1f** with all n=12, the clearing temperatures of compounds **1b** and **1d** were much higher than those of other compounds (**1a**, **1c**, **1e**, **1f**), i.e., $T_{cl}=166.8$



Scheme 2. Reactions and reagents: (a) TEA (1.1 equiv), acetyl chloride, stirred in dry THF, rt, 8 h, 83%; (b) RBr (1.1 equiv), KHCO₃ (1.5 equiv), refluxing in acetone, 24 h, 60%; (c) concd HNO₃ (1.2 equiv), NaNO₂ (0.2 equiv), 0 °C in CH₂Cl₂, 6 h, 25%; (d) H₂NNH₂ (1.2 equiv), Pd/C (0.1 equiv), refluxing in C₂H₅OH, 24 h, 85%; (e) acetic acid (drops), refluxing in C₂H₅OH, 24 h, 78%; (f) Pd(OAc)₄ (1.1 equiv), refluxing in CHCl₃, 2 h, 72%; (g) KOH (1.5 equiv), refluxing in 95% ethanol, 24 h, 93%; (h) DMAP (1.0 equiv), adipoyl chloride or suberoyl chloride (0.50 equiv), refluxing in dry THF, 12 h, 51–72%.

(1b)>147.4 (1d)>142.5 (1a)>133.6 (1c)>122.7 (1e)>105.7 °C (1f). The relationship plot between the melting temperatures, clearing temperatures, and the temperature range for all compounds 1a-1f are shown in Figure 3. When compounds with even carbon spacer and molecules were considered in all-trans conformations, the overall molecules were more likely linear, resulting in a better packing in mesophases. Therefore, their clearing temperatures were often much higher than those of compounds with odd carbon spacer, in which all molecules were considered as more bent-shaped. A ratio of $\Delta S/R$ often used to evaluate the odd–even effect was also calculated in twin systems. The transition entropy ($\Delta S_{N \rightarrow I}/R$), showing the orientational order was generally measured from nematic to isotropic state. However, a SmA phase was not observed, then a value of $\Delta S_{\text{SmC} \rightarrow I}/R$ (R=gas constant in I/mol) was evaluated in our system. This transition entropy ranged from $\Delta S_{\text{SmC} \rightarrow I}/R=2.01$ to 6.5. This entropy change was not correlated with carbon length in spacer group, shown in Figure 4. A value of $\Delta S_{N \rightarrow 1}/R = 0.5 - 2.0$ was observed on other dimeric twins. The value of $\Delta S_{SmC \rightarrow I}/R$ for compounds 1f was particularly large (i.e., ~6.50) due to monotropic transitions.

2.4. Powder X-ray diffraction experiments

The powder X-ray diffraction experiments of four compounds **1a** (m=3, n=12), **1c** (m=5, n=12), **1e** (m=7, n=12), and **1f** (m=11, n=12) were performed to confirm the structure of the smectic C phases. The X-ray diffraction data are summarized in Table 2. As can be seen, they all displayed a similar diffraction pattern with one strong peak and one very weak at lower angle region, and also a very weak and broad diffraction peak at wider angle. These two diffraction pattern was typically characteristic of layer structures

observed for SmC phases. For example, compound **1a** (m=3, n=12) showed two peaks at 45.91 Å and 22.96 Å, shown in Figure 5. Another very broad and very weak peak at 4.44–4.61 Å was also observed, and this peak was assigned to the molten alkoxyl chains. The *d*-spacings of four compounds were all well correlated with the central spacer length.

Two possible structures in such layer mesophases were often proposed in symmetric twins; intercalated and non-intercalated (or monolayer). In intercalated phase the *d*-spacing value was equal to a half of molecular length $d \sim (1/2)L$ whereas *d*-spacing was equal to molecular length d=L in non-intercalated structure. Interdigitated layer structures were not considered in our system. In many mesogenic twin systems, most dimeric molecules exhibiting either SmA or SmC phase will adopt intercalated arrangements. In contrast, the dimeric molecules will form monolayer arrangement when $d/l \sim 1.0$. The molecular length (*L*) in our system was estimated when the most extended conformations were considered. All d/l values of four compounds are given in Table 2 and all values were ranged from d/l=0.80 (**1a**) to 0.92 (**1f**). Therefore, monolayer structure in mesophase was proposed, as shown in Figure 6.

3. Conclusions

A new series of heterocyclic twin mesogenic benzoxazoles with different spacer lengths was prepared and studied. All the compounds **1a–1f** exhibited liquid crystalline smectic C phase and a strong odd–even effect in the isotropization temperatures. A monolayer structure in this type of dimeric twin liquid crystals was proposed.

Table 1

Phase transitions^a and temperatures of compounds **1a-1f**

1		C.			132.6 (40.9)
1 a ; m=3	п=6	Cr	123.5 ^b	SmC	125.0 ^b
	n_8	Cr			137.5 (44.7)
	<i>n</i> =0	CI	121.7 (31.3)	SmC	131.6 (6.40)
	<i>n</i> =10	Cr	126.1 (46.3)	SmC	139.8 (11.0)
			120.6 (33.5)		137.5 (10.6)
	n=12	Cr	125.9 (55.8)	SmC	142.5 (13.0)
			122.3 (34.9)		141.7 (12.7)
	n-14	Cr	126.5 (63.5)	SmC	144.3 (13.2)
		ei	122.3 (34.9)	enie	143.2 (12.8)
	n_16	Cr	129.9 (49.7)	SmC	145.2 (8.65)
	<i>n</i> =10	CI	117.7 (53.3)		140.2 (8.29)
1h , m 4	n 10	C.	124.4 (43.0)	SmC	166.8 (15.4)
ID, <i>m</i> =4	11=12	CI	122.1 (42.9)	Silic	165.0 (13.7)
1 <i>e</i> rm 5	n 9	C.	110.6 (38.6)	SmC	118.7 (8.94)
IC, <i>m</i> =5	n=o	CI	98.3 (42.5)	SIIIC	117.5 (9.34)
	. 12	C.	116.2 (45.7)		130.6 (10.4)
	n=12	Cr	103.1 (46.0)	SmC	128.8 (10.3)
	n_16	Cr	118.2 (52.5)	SmC	133.4 (10.6)
	<i>n</i> =10	CI	108.7 (54.5)	SIIIC	129.4 (10.4)
1d ; <i>m</i> =6	n=12	Cr	125.4 (23.5)	SmC	147.4 (7.04)
			121.6 (23.8)		143.5 (6.93)
1e ; <i>m</i> =7	n=12	Cr	106.8 (49.1)	SmC	122.7 (16.2)
			105.2 (49.3)		121.4 (16.2)
1f ; <i>m</i> =11	n=12	Cr		00	105.6 (97.6)
			95.2 (77.85)	SmC	103.1 (20.0)

 $^{\rm a}$ m and n are the spacer length and terminal carbon length. Cr=crystal, SmC=smectic C, and I=isotropic phase.

^b Observed by optical microscope.



Figure 1. Bar graphs showing the phase behavior of compounds 1a-1f. All temperatures were taken from cooling process.



Figure 2. The optical textures observed in compounds **1a** (m=4, n=12; top plate) at 139.0 °C, **1b** (m=4, n=12) at 145.0 °C, and **1c** (m=5, n=12; bottom plate) at 120.0 °C.

4. Experimental

4.1. General

¹H and ¹³C NMR spectra were measured on a Bruker DRS-200. DSC thermographs were carried out on a Mettler DSC 822. All phase transitions are determined by a scan rate of 10.0 °C/min. Optical polarized microscope was carried out on Zeiss Axioplan 2 equipped with a hot stage system of Mettler FP90/FP82HT. Elemental analysis for carbon, hydrogen, and nitrogen were conducted at Instrumentation Center, National Taiwan University on a Heraeus CHN-O-Rapid elemental analyzer (Table 3). The powder X-ray diffraction data were collected from the Wiggler-A beam line of the National Synchrotron Radiation Research Center with a wavelength of 1.3305 Å. All compounds of 3-alkoxyphenols, 5-alkoxy-2-



Figure 3. Dependence of melting and clearing temperatures on the number of methylene groups in the spacer of compounds 1a-1f (all with terminal n=12).



Figure 4. The dependence of the entropy change ($\Delta S/R$, unitless) for transition of SmC \rightarrow I phase on the carbon length *m* in spacer chains in compounds **1a–1f** with all terminal *n*=12. R is gas constant in J K⁻¹ mol⁻¹.

nitrophenols, 2-amino-5-aloxyphenols were followed by the literatures. $^{17}\,$

4.2. 3-Dodecyloxyphenol

White solid, yield 60%. ¹H NMR (CDCl₃): δ 0.87 (t, 3H, -CH₃, *J*=6.91 Hz), 1.25–1.43 (m, 18H, -CH₂), 1.72–1.77 (m, 2H, -CH₂), 3.90 (t, 2H, -OCH₂, *J*=6.62 Hz), 6.39–6.40 (m, 2H, Ar–H), 6.46–6.48 (m, 1H, Ar–H), 7.10 (t, 1H, Ar–H, *J*=8.48 Hz). ¹³C NMR (CDCl₃): δ 14.14, 22.71, 26.05, 29.23, 29.37, 29.42, 29.60, 29.63, 29.66, 29.68, 31.94, 68.10, 102.08, 107.10, 107.59, 130.10, 156.68, 160.51.

Table 2 The powder X-ray diffraction data of the compounds 1a, 1c, 1e, and $1f^{\rm a}$

4.3. 5-Dodecyloxy-2-nitrophenol

Yellow solid, yield 25%. ¹H NMR (CDCl₃): δ 0.86 (t, 3H, -CH₃, *J*=6.88 Hz), 1.24–1.44 (m, 18H, -CH₂), 1.75–1.81 (m, 2H, -CH₂), 3.99 (t, 2H, -OCH₂, *J*=6.53 Hz), 6.47–6.49 (m, 2H, Ar–H), 8.00 (d, 1H, Ar– H, *J*=10.1 Hz), 11.02 (s, 1H, Ar–OH). ¹³C NMR (CDCl₃): δ 14.12, 22.69, 25.87, 28.83, 29.27, 29.35, 29.41, 29.52, 29.57, 29.63, 29.64, 29.71, 31.92, 69.15, 101.80, 109.83, 126.91, 127.54, 158.01, 166.74.

4.4. 2-Amino-5-dodecyloxyphenol

White solid, yield 85%. ¹H NMR (CDCl₃): δ 0.86 (t, 3H, -CH₃, *J*=6.91 Hz), 1.24–1.41 (m, 18H, -CH₂), 1.68–1.73 (m, 2H, -CH₂), 3.84 (t, 2H, -OCH₂, *J*=6.61 Hz), 6.32 (d, 1H, Ar-H, *J*=8.58 Hz), 6.41 (s, 1H, Ar-H), 6.75 (d, 1H, Ar-H, *J*=8.57 Hz). ¹³C NMR (CDCl₃): δ 13.94, 22.59, 26.02, 29.25, 29.34, 29.51, 29.53, 29.56, 29.58, 31.85, 68.67, 102.72, 106.75, 120.85, 125.58, 148.06, 154.94.

4.5. Bis(4-formylphenyl)glutarate 3 (m=3)

Under nitrogen atmosphere the mixture of 4-hydroxybenzaldehyde (2.00 g, 0.016 mol) and DMAP (2.10 g, 0.017 mol) was dissolved in 25 ml of dry THF. To the solution, a solution of glutaryl chloride (1.38 g, 0.0082 mol) dissolved in 15 ml of dry THF was dropwise added and the solution was stirred for 4 h. The solution was filtered off and the filtrate was concentrated to dryness. The product isolated as white solids were obtained after recrystallization from CH₂Cl₂/MeOH. Yield 72%. ¹H NMR (CDCl₃): δ 2.15–2.22 (m, 2H, –CH₂), 2.76 (t, 4H, –OCOCH₂, *J*=8.47 Hz), 7.26 (d, 4H, Ar–H, *J*=8.63 Hz), 7.90 (d, 4H, Ar–H, *J*=6.74 Hz), 9.97 (s, 2H, –CHO). ¹³C NMR (CDCl₃): δ 19.53, 32.97, 122.17, 131.10, 133.89, 155.02, 170.52, 190.78.

4.6. Bis(4-formylphenyl)heptanedioate 3 (m=5)

White solid, yield 48%. ¹H NMR (CDCl₃): δ 1.25–1.32 (m, 2H, –CH₂), 162–1.69 (m, 4H, –CH₂), 2.47–2.60 (m, 4H, –OCOCH₂), 7.26 (d, 4H, Ar–H, *J*=8.39 Hz), 7.90 (d, 4H, Ar–H, *J*=8.73 Hz), 9.95 (s, 2H, –CHO). ¹³C NMR (CDCl₃): δ 25.79, 29.31, 32.41, 121.38, 129.86, 133.51, 153.82, 171.59, 191.01.

4.7. Bis(4-formylphenyl)tridecanedioate 3 (m = 11)

Yellow solid, yield 60%. ¹H NMR (CDCl₃): *δ* 1.24–1.33 (m, 14H, −CH₂), 1.66–1.77 (m, 4H, −CH₂), 2.48–2.60 (m, 4H, −OCOCH₂), 7.25 (d, 4H, Ar–H, *J*=6.86 Hz), 7.89 (d, 4H, Ar–H, *J*=8.49 Hz), 9.95 (s, 2H, −CHO). ¹³C NMR (CDCl₃): *δ* 25.33, 29.29, 29.41, 29.96, 32.17, 122.03, 130.63, 133.81, 154.20, 170.89, 191.08.

Compounds	Phase	Temp (°C)	d-Spacing (Å)	Miller indices (Å)	Length (Å)	Aspect ratio (d/l)
1a (<i>m</i> =3; <i>n</i> =12)	SmC	126.0	45.91 (45.91)	001	57.68	0.80
			22.93 (22.96)	002		
			4.51	Halo		
1c (m=5; n=12)	SmC	120.0	49.82 (49.82)	001	59.12	0.84
			24.75 (24.91)	002		
			4.48	Halo		
1e (<i>m</i> =7; <i>n</i> =12)	SmC	109.0	56.43 (56.43)	001	62.28	0.91
			28.19 (28.22)	002		
			4.44	Halo		
1f (<i>m</i> =11; <i>n</i> =12)	SmC	105.0	60.83 (60.83)	001	66.11	0.92
			30.19 (30.42)	002		
			4.61	Halo		

^a The molecular length (*l*) was obtained by MM2 model when considered *all-trans* conformation.





4.8. Bis(4-((E)-(4-(dodecyloxy)-2-hydroxyphenylimino)methyl)phenyl)glutarate 2 (m=3, n=12)

Bis(4-formylphenyl)glutarate (0.20 g, 0.00059 mol) was dissolved in 50 ml of warm absolute ethanol and 2-amino-5-



Figure 6. The proposed monolayer arrangements in SmC phase for compounds **1c** (m=5, n=12) with a ratio of d/l (49.82/59.12=0.84)<1.0. The terminal alkoxyl chains might be slightly interdigitated.

hexadecyloxyphenol (0.36 g, 0.0012 mol) dissolved in 50 ml of absolute ethanol with a few drops of glacial acetic acid added was slowly added under nitrogen atmosphere. The solution was refluxed for 8 h. The yellow solids were collected. The product isolated as white solids were obtained after recrystallization from CH₂Cl₂/MeOH. Yield 73%. ¹H NMR (CDCl₃): δ 0.86 (t, 6H, –CH₃, *J*=6.88 Hz), 1.24–1.45 (m, 36H, –CH₂), 1.73–1.78 (m, 4H, –OCH₂CH₂), 2.20–2.23 (m, 2H, –CH₂), 2.76 (t, 4H, –OCOCH₂, *J*=7.22 Hz), 3.94 (t, 4H, –OCH₂, *J*=6.58 Hz), 6.44 (d, 2H, Ar–H, *J*=11.48 Hz), 6.55 (s, 2H, Ar–H), 7.19 (d, 4H, Ar–H, *J*=8.57 Hz), 7.25 (d, 2H, Ar–H, *J*=8.94 Hz), 7.47 (s, 2H, –OH), 7.88 (d, 4H, Ar–H, *J*=8.61 Hz), 8.60 (s, 2H, –NCH). ¹³C NMR (CDCl₃): δ 14.13, 19.90, 22.70, 26.03, 29.21, 29.37, 29.40, 29.58, 29.61, 29.67, 29.70, 31.94, 33.24, 68.31, 100.52, 107.20, 116.20, 122.03, 128.22, 129.50, 134.03, 152.21, 152.63, 153.83, 160.42, 171.03.

4.9. Bis(4-((*E*)-(4-(dodecyloxy)-2-hydroxyphenylimino)methyl)phenyl)heptanedioate 2 (m=5, n=12)

Yellow solid, yield 69%. ¹H NMR (CDCl₃): δ 0.86 (t, 6H, -CH₃, *J*=6.32 Hz), 1.25–1.59 (m, 38H, -CH₂), 1.73–1.91 (m, 8H, -CH₂), 2.62

Table 3	
Elemental analysis data of compounds 1a-1f	

1a ; <i>m</i> =3	<i>n</i> =6	72.20 (71.85)	6.33 (6.45)
	<i>n</i> =8	72.69 (72.84)	7.12 (7.02)
	<i>n</i> =10	73.97 (73.71)	7.58 (7.52)
	<i>n</i> =12	74.65 (74.46)	8.09 (7.95)
	n=14	75.45 (75.13)	8.23 (8.33)
	<i>n</i> =16	76.01 (75.72)	8.69 (8.67)
1b ; <i>m</i> =4	<i>n</i> =12	74.98 (74.64)	8.11 (8.05)
1c ; <i>m</i> =5	n=8	73.54 (73.29)	7.29 (7.28)
	<i>n</i> =12	75.09 (74.80)	7.99 (8.15)
	<i>n</i> =16	76.21 (75.99)	8.86 (8.83)
1d ; <i>m</i> =6	<i>n</i> =12	75.16 (74.97)	8.29 (8.24)
1e ; <i>m</i> =7	<i>n</i> =12	75.64 (75.13)	8.47 (8.33)
1f ; <i>m</i> =11	<i>n</i> =12	75.48 (75.72)	8.59 (8.67)

Calcd value in parentheses.

(t, 4H, $-\text{OCOCH}_2$, J=7.25 Hz), 3.93 (t, 4H, $-\text{OCH}_2$, J=6.52 Hz), 6.43 (d, 2H, Ar–H, J=11.41 Hz), 6.55 (s, 2H, Ar–H), 7.17 (d, 4H, Ar–H, J=8.53 Hz), 7.25 (d, 2H, Ar–H, J=8.75 Hz), 7.49 (s, 2H, -OH), 7.88 (d, 4H, Ar–H, J=8.57 Hz), 8.58 (s, 2H, -NCH). ¹³C NMR (CDCl₃): δ 14.12, 22.68, 24.42, 26.00, 28.40, 28.51, 29.02, 29.17, 29.34, 29.58, 29.63, 29.67, 31.90, 34.09, 68.25, 100.54, 107.17, 116.37, 122.06, 128.40, 129.58, 133.67, 152.42, 152.84, 153.72, 160.38, 171.63.

4.10. Bis(4-((E)-(4-(dodecyloxy)-2-hydroxyphenylimino)methyl)phenyl)tridecanedioate 2 (m=11, n=12)

Yellow solid, yield 70%. ¹H NMR (CDCl₃): δ 0.86 (t, 6H, -CH₃, *J*=6.39 Hz), 1.25–1.59 (m, 50H, -CH₂), 1.73–1.91 (m, 8H, -CH₂), 2.57 (t, 4H, -OCOCH₂, *J*=7.05 Hz), 3.92 (t, 4H, -OCH₂, *J*=6.34 Hz), 6.44 (d, 2H, Ar-H, *J*=8.80 Hz), 6.55 (s, 2H, Ar-H), 7.16 (d, 4H, Ar-H, *J*=8.25 Hz), 7.25 (d, 2H, Ar-H, *J*=8.80 Hz), 7.47 (s, 2H, -OH), 7.86 (d, 4H, Ar-H, *J*=8.23 Hz), 8.57 (s, 2H, -NCH). ¹³C NMR (CDCl₃): δ 14.11, 22.67, 24.83, 26.20, 28.59, 28.73, 28.92, 29.05, 29.19, 29.36, 29.41, 29.58, 29.64, 31.90, 34.63, 68.22, 100.45, 107.09, 116.20, 122.04, 128.13, 129.45, 133.72, 152.30, 152.82, 153.74, 160.30, 171.95.

4.11. Bis(4-(6-(dodecyloxy)benzo[*d*]oxazol-2-yl)phenyl)-glutarate 1a (*m*=3, *n*=12)

bis(4-((E)-(4-(dodecyloxy)-2-hydroxy-The mixture of phenylimino)methyl)phenyl)glutarate (0.20 g, 0.22 mmol) and lead acetate Pb(OAc)₄ (0.12 g, 0.26 mmol) dissolved in 20 ml of CHCl₃ was refluxed for 2 h. The solution was filtered and the filtrate was extracted with CH₂Cl₂/H₂O. The organic layers were collected and dried (MgSO₄). The product isolated as white solids were obtained after recrystallization from CH₂Cl₂/MeOH. Yield 70%. ¹H NMR (CDCl₃): δ 0.85 (t, 6H, -CH₃, *J*=7.09 Hz), 1.26-1.50 (m, 36H, -CH₂), 1.78-1.84 (m, 4H, -CH₂), 2.21-2.24 (m, 2H, -CH₂), 2.77 (t, 4H, -OCOCH₂, J=7.20 Hz), 4.00 (t, 4H, -OCH₂, J=6.55 Hz), 6.94 (d, 2H, Ar-H, J=8.71 Hz), 7.07 (s, 2H, Ar-H), 7.26 (d, 4H, Ar-H, J=7.31 Hz), 7.60 (d, 2H, Ar-H, J=8.73 Hz), 8.21 (d, 4H, Ar-H, J=8.67 Hz). ¹³C NMR (CDCl₃): § 14.12, 19.88, 22.70, 26.06, 29.23, 29.36, 29.40, 29.58, 29.61, 29.65, 29.67, 31.93, 33.24, 68.91, 96.09, 113.56, 119.91, 122.15, 125.06, 128.57, 135.49, 151.68, 152.73, 157.96, 161.37, 170.95. MS (FAB): calcd for MH⁺ C₅₅H₇₀N₂O₈: 887.2, found: 887.0.

4.12. Bis(4-(6-(hexyloxy)benzo[*d*]oxazol-2-yl)phenyl)-glutarate 1a (*m*=3, *n*=6)

White solid, yield 65%. ¹H NMR (CDCl₃): δ 0.89 (t, 6H, -CH₃, *J*=7.14 Hz), 1.33–1.49 (m, 12H, -CH₂), 1.78–1.83 (m, 4H, -CH₂), 2.20– 2.23 (m, 2H, -CH₂), 2.77 (t, 4H, -OCOCH₂, *J*=7.21 Hz), 4.00 (t, 4H, -OCH₂, *J*=6.54 Hz), 6.93 (d, 2H, Ar–H, *J*=8.72 Hz), 7.07 (s, 2H, Ar–H), 7.25 (d, 4H, Ar–H, *J*=7.56 Hz), 7.59 (d, 2H, Ar–H, *J*=8.72 Hz), 8.20 (d, 4H, Ar–H, *J*=8.66 Hz). ¹³C NMR (CDCl₃): δ 14.05, 19.89, 22.62, 25.74, 29.20, 31.60, 33.24, 68.89, 96.07, 113.49, 119.96, 122.13, 125.18, 128.52, 135.69, 151.70, 152.67, 157.91, 161.37, 170.97. MS (FAB): calcd for MH⁺ C₄₃H₄₆N₂O₈: 718.8, found: 719.0.

4.13. Bis(4-(6-(octyloxy)benzo[d]oxazol-2-yl)phenyl)glutarate 1a (*m*=3, *n*=8)

White solid, yield 65%. ¹H NMR (CDCl₃): δ 0.87 (t, 6H, -CH₃, *J*=6.87 Hz), 1.28–1.47 (m, 20H, -CH₂), 1.79–1.82 (m, 4H, -CH₂), 2.22–2.23 (m, 2H, -CH₂), 2.77 (t, 4H, -OCOCH₂, *J*=7.20 Hz), 3.99 (t, 4H, -OCH₂, *J*=6.57 Hz), 6.93 (d, 2H, Ar–H, *J*=8.73 Hz), 7.07 (s, 2H, Ar–H), 7.25 (d, 4H, Ar–H, *J*=8.70 Hz), 7.59 (d, 2H, Ar–H, *J*=8.74 Hz), 8.20 (d, 4H, Ar–H, *J*=8.72 Hz). ¹³C NMR (CDCl₃): δ 14.12, 19.89, 22.67, 26.07, 29.24, 29.25, 29.37, 31.83, 33.23, 68.90, 96.06, 113.49, 119.95, 122.13, 125.18, 128.52, 135.68, 151.70, 152.67, 157.91, 161.37, 170.97. MS (FAB): calcd for MH⁺ C₄₇H₅₄N₂O₈: 774.9, found: 775.0.

4.14. Bis(4-(6-(decyloxy)benzo[d]oxazol-2-yl)phenyl)glutarate 1a (m=3, n=10)

White solid, yield 69%. ¹H NMR (CDCl₃): δ 0.86 (t, 6H, -CH₃, *J*=6.76 Hz), 1.26–1.47 (m, 28H, -CH₂), 1.79–1.83 (m, 4H, -CH₂), 2.20–2.25 (m, 2H, -CH₂), 2.77 (t, 4H, -OCOCH₂, *J*=7.17 Hz), 3.99 (t, 4H, -OCH₂, *J*=6.49 Hz), 6.93 (d, 2H, Ar-H, *J*=10.76 Hz), 7.07 (s, 2H, Ar-H), 7.24 (d, 4H, Ar-H, *J*=8.06 Hz), 7.59 (d, 2H, Ar-H, *J*=8.66 Hz), 8.20 (d, 4H, Ar-H, *J*=8.54 Hz). ¹³C NMR (CDCl₃): δ 14.11, 19.90, 22.69, 26.06, 29.24, 29.33, 29.40, 29.57, 29.58, 31.90, 33.24, 68.91, 96.09, 113.50, 119.95, 122.13, 125.18, 128.52, 135.68, 151.72, 152.69, 157.93, 161.38, 170.94. MS (FAB): calcd for MH⁺ C₅₁H₆₂N₂O₈: 831.1, found: 831.0.

4.15. Bis(4-(6-(tetradecyloxy)benzo[d]oxazol-2-yl)phenyl)glutarate 1a (m=3, n=14)

White solid, yield 66%. ¹H NMR (CDCl₃): δ 0.87 (t, 6H, -CH₃, *J*=6.85 Hz), 1.26–1.50 (m, 44H, -CH₂), 1.79–1.82 (m, 4H, -OCH₂CH₂), 2.21–2.24 (m, 2H, -CH₂), 2.76 (t, 4H, -OCOCH₂, *J*=7.18 Hz), 4.00 (t, 4H, -OCH₂, *J*=6.52 Hz), 6.93 (d, 2H, Ar–H, *J*=8.71 Hz), 7.07 (s, 2H, Ar–H), 7.25 (d, 4H, Ar–H, *J*=8.78 Hz), 7.59 (d, 2H, Ar–H, *J*=8.72 Hz), 8.20 (d, 4H, Ar–H, *J*=8.68 Hz). ¹³C NMR (CDCl₃): δ 13.95, 19.98, 22.59, 26.02, 29.24, 29.26, 29.33, 29.51, 29.53, 29.58, 29.60, 29.62, 31.86, 33.30, 69.05, 96.28, 113.51, 119.95, 122.00, 125.26, 128.50, 135.89, 151.77, 152.79, 158.00, 161.39, 170.72. MS (FAB): calcd for MH⁺ C₅₉H₇₈N₂O₈: 943.3, found: 943.0.

4.16. Bis(4-(6-(hexadecyloxy)benzo[*d*]oxazol-2-yl)phenyl)-glutarate 1a (*m*=3, *n*=16)

White solid, yield 77%. ¹H NMR (CDCl₃): δ 0.87 (t, 6H, -CH₃, *J*=6.88 Hz), 1.26–1.49 (m, 52H, -CH₂), 1.80–1.82 (m, 4H, -OCH₂CH₂), 2.22–2.24 (m, 2H, -CH₂), 2.77 (t, 4H, -OCOCH₂, *J*=7.21 Hz), 4.01 (t, 4H, -OCH₂, *J*=6.55 Hz), 6.93 (d, 2H, Ar–H, *J*=8.74 Hz), 7.07 (s, 2H, Ar–H), 7.25 (d, 4H, Ar–H, *J*=8.78 Hz), 7.59 (d, 2H, Ar–H, *J*=8.72 Hz), 8.20 (d, 4H, Ar–H, *J*=8.68 Hz). ¹³C NMR (CDCl₃): δ 13.94, 19.98, 22.59, 26.02, 29.24, 29.27, 29.33, 29.51, 29.53, 29.58, 29.62, 31.86, 33.30, 69.05, 96.28, 113.51, 119.95, 122.00, 125.26, 128.50, 135.89, 151.77, 152.79, 158.00, 161.39, 170.72. MS (FAB): calcd for MH⁺ C_{63H86}N₂O₈: 999.4, found: 999.1.

4.17. Bis(4-(6-(octyloxy)benzo[d]oxazol-2-yl)phenyl)heptanedioate 1c (m=5, n=8)

White solid, yield 64%. ¹H NMR (CDCl₃): δ 0.87 (t, 6H, -CH₃, *J*=6.51 Hz), 1.28–1.57 (m, 22H, -CH₂), 1.79–1.85 (m, 8H, -CH₂), 2.63 (t, 4H, -OCOCH₂, *J*=7.32 Hz), 3.98 (t, 4H, -OCH₂, *J*=6.51 Hz), 6.92 (d, 2H, Ar-H, *J*=8.68 Hz), 7.05 (s, 2H, Ar-H), 7.22 (d, 4H, Ar-H, *J*=8.51 Hz), 7.58 (d, 2H, Ar-H, *J*=8.71 Hz), 8.18 (d, 4H, Ar-H, *J*=8.50 Hz). ¹³C NMR (CDCl₃): δ 14.11, 22.67, 24.47, 26.07, 28.45, 29.25, 29.38, 31.83, 34.12, 68.88, 96.05, 113.46, 119.93, 122.15, 125.04, 128.49, 135.68, 151.68, 152.81, 157.89, 161.41, 171.58. MS (FAB): calcd for MH⁺ C₄₉H₅₈N₂O₈: 803.0, found: 803.0.

4.18. Bis(4-(6-(dodecyloxy)benzo[d]oxazol-2-yl)phenyl)heptanedioate 1c (m=5, n=12)

White solid, yield 64%. ¹H NMR (CDCl₃): δ 0.86 (t, 6H, -CH₃, *J*=6.90 Hz), 1.25–1.48 (m, 38H, -CH₂), 1.79–1.86 (m, 8H, -CH₂), 2.63 (t, 4H, -OCOCH₂, *J*=7.38 Hz), 3.98 (t, 4H, -OCH₂, *J*=6.57 Hz), 6.92 (d, 2H, Ar-H, *J*=8.72 Hz), 7.05 (s, 2H, Ar-H), 7.22 (d, 4H, Ar-H, *J*=8.70 Hz), 7.58 (d, 2H, Ar-H, *J*=8.72 Hz), 8.19 (d, 4H, Ar-H, *J*=8.70 Hz). ¹³C NMR (CDCl₃): δ 14.13, 22.70, 24.47, 26.07, 28.45, 29.24, 29.36, 29.41, 29.59, 29.62, 29.65, 29.67, 31.93, 34.13, 68.88, 96.05, 113.47, 119.93, 122.16, 125.04, 128.50, 135.67, 151.68, 152.81, 157.89, 161.41, 171.59. MS (FAB): calcd for MH⁺ C₅₇H₇₄N₂O₈: 915.2, found: 915.1.

4.19. Bis(4-(6-(hexadecyloxy)benzo[d]oxazol-2-yl)phenyl)heptanedioate 1c (m=5, n=16)

White solid, yield 66%. ¹H NMR (CDCl₃): δ 0.87 (t, 6H, -CH₃, *J*=6.73 Hz), 1.26–1.51 (m, 54H, -CH₂), 1.79–1.87 (m, 8H, -CH₂), 2.62 (t, 4H, -OCOCH₂, *J*=7.27 Hz), 4.00 (t, 4H, -OCH₂, *J*=6.48 Hz), 6.93 (d, 2H, Ar-H, *J*=8.67 Hz), 7.06 (s, 2H, Ar-H), 7.23 (d, 4H, Ar-H, *J*=8.90 Hz), 7.58 (d, 2H, Ar-H, *J*=8.69 Hz), 8.19 (d, 4H, Ar-H, *J*=8.56 Hz). ¹³C NMR (CDCl₃): δ 13.94, 22.59, 24.44, 26.03, 28.44, 29.25, 29.26, 29.34, 29.51, 29.53, 29.58, 29.62, 31.86, 34.12, 69.04, 96.27, 113.48, 119.93, 122.02, 125.12, 128.47, 135.89, 151.76, 152.93, 157.97, 161.44, 171.32. MS (FAB): calcd for MH⁺ C₆₅H₉₀N₂O₈: 1027.4, found: 1027.1.

4.20. Bis(4-(6-(dodecyloxy)benzo[d]oxazol-2-yl)phenyl)heptanedioate 1e (m=7, n=12)

White solid, yield 68%. ¹H NMR (CDCl₃): δ 0.85 (t, 6H, -CH₃, *J*=7.03 Hz), 1.23–1.45 (m, 42H, -CH₂), 1.78–1.82 (m, 8H, -CH₂), 2.58 (t, 4H, -OCOCH₂, *J*=7.36 Hz), 3.98 (t, 4H, -OCH₂, *J*=6.42 Hz), 6.92 (d, 2H, Ar-H, *J*=8.20 Hz), 7.03 (s, 2H, Ar-H), 7.22 (d, 4H, Ar-H, *J*=8.33 Hz), 7.59 (d, 2H, Ar-H, *J*=8.59 Hz), 8.20 (d, 4H, Ar-H, *J*=8.21 Hz). ¹³C NMR (CDCl₃): δ 14.46, 23.02, 25.08, 26.38, 29.18, 29.55, 29.70, 29.73, 29.91, 29.94, 30.00, 30.03, 32.26, 34.66, 69.20, 96.38, 113.86, 120.18, 122.53, 125.10, 128.87, 135.68, 151.95, 153.28, 158.25, 161.73, 172.09. MS (FAB): calcd for MH⁺ C₅₉H₇₈N₂O₈: 943.3, found: 942.9.

4.21. Bis(4-(6-(octyloxy)benzo[d]oxazol-2-yl)phenyl)-tridecanedioate 1f (m=11, n=8)

White solid, yield 77%. ¹H NMR (CDCl₃): δ 0.86 (t, 6H, -CH₃, *J*=6.85 Hz), 1.26–1.45 (m, 34H, -CH₂), 1.73–1.80 (m, 8H, -CH₂), 2.656 (t, 4H, -OCOCH₂, *J*=7.50 Hz), 3.97 (t, 4H, -OCH₂, *J*=6.55 Hz), 6.92 (d, 2H, Ar-H, *J*=8.70 Hz), 7.05 (s, 2H, Ar-H), 7.26 (d, 4H, Ar-H, *J*=7.05 Hz), 7.59 (d, 2H, Ar-H, *J*=8.75 Hz), 8.19 (d, 4H, Ar-H, *J*=8.70 Hz). ¹³C NMR (CDCl₃): δ 14.44, 22.99, 25.19, 26.38, 29.40, 29.57, 29.69, 29.72, 29.81, 32.14, 34.73, 69.19, 96.36, 113.86, 120.16, 122.54, 125.04, 128.85, 135.64, 151.93, 153.31, 158.24, 161.74, 172.22. MS (FAB): calcd for MH⁺ C₅₅H₇₀N₂O₈: 887.2, found: 887.0.

4.22. Bis(4-(6-(dodecyloxy)benzo[d]oxazol-2-yl)phenyl)-tridecanedioate 1f (m=11, n=12)

White solid, yield 70%. ¹H NMR (CDCl₃): δ 0.86 (t, 6H, -CH₃, *J*=6.46 Hz), 1.24–1.46 (m, 50H, -CH₂), 1.74–1.81 (m, 8H, -CH₂), 2.57 (t, 4H, -OCOCH₂, *J*=7.47 Hz), 3.98 (t, 4H, -OCH₂, *J*=6.53 Hz), 6.93 (d, 2H, Ar-H, *J*=8.71 Hz), 7.07 (s, 2H, Ar-H), 7.22 (d, 4H, Ar-H, *J*=8.65 Hz), 7.60 (d, 2H, Ar-H, *J*=8.72 Hz), 8.20 (d, 4H, Ar-H, *J*=8.65 Hz). ¹³C NMR (CDCl₃): δ 14.47, 23.03, 25.20, 26.39, 29.41, 29.56, 29.70, 29.74, 29.82, 29.92, 29.94, 29.98, 30.00, 30.04, 32.26, 34.74, 69.21, 96.38, 113.86, 120.18, 122.55, 125.09, 128.86, 135.70, 151.95, 153.32, 158.25, 161.76, 172.24. MS (FAB): calcd for MH⁺ C₆₃H₈₆N₂O₈: 999.4, found: 998.9.

4.23. 4-((*E*)-(**4**-(Dodecyloxy)-**2**-hydroxyphenylimino)methyl)phenyl acetate 6

¹H NMR (CDCl₃): δ 0.87 (t, 3H, -CH₃, *J*=6.30 Hz), 1.26–1.42 (m, 18H, -CH₂), 1.69–1.80 (m, 2H, -OCH₂CH₂), 2.31 (s, 3H, -OCOCH₃), 3.93 (t, 2H, -OCH₂, *J*=6.52 Hz), 6.44 (d, 1H, Ar–H, *J*=6.15 Hz), 6.55 (s, 1H, Ar–H), 7.15–7.27 (m, 3H, Ar–H), 7.44 (s, 1H, Ar–OH), 7.86 (d, 2H, Ar–H, *J*=8.58 Hz), 8.56 (s, 1H, -NCH). ¹³C NMR (CDCl₃): δ 14.09, 21.09, 22.65, 26.00, 29.14, 29.31, 29.34, 29.55, 29.60, 31.87, 68.19, 100.42, 107.06, 116.16, 121.99, 128.12, 129.41, 133.83, 152.18, 152.65, 153.74, 160.29, 169.06.

4.24. 4-(6-(Dodecyloxy)benzo[d]oxazol-2-yl)phenyl acetate 5

White solid, yield 72%. ¹H NMR (CDCl₃): δ 0.86 (t, 3H, -CH₃, *J*=6.44 Hz), 1.24–1.44 (m, 18H, -CH₂), 1.76–1.88 (m, 2H, -CH₂), 2.30 (s, 3H, -OCOCH₃), 3.97 (t, 2H, -OCH₂, *J*=6.39 Hz), 6.92 (d, 1H, Ar-H, *J*=8.73 Hz), 6.95 (s, 1H, Ar-H), 7.21 (d, 2H, Ar-H, *J*=8.33 Hz), 7.58 (d, 1H, Ar-H, *J*=8.74 Hz), 8.18 (d, 2H, Ar-H, *J*=8.23 Hz). ¹³C NMR (CDCl₃): δ 14.08, 21.10, 22.65, 26.00, 29.17, 29.31, 29.35, 29.55, 29.61, 31.87, 68.77, 95.94, 113.38, 119.85, 122.10, 124.97, 128.41, 135.57, 151.60, 152.70, 157.81, 160.30, 168.96.

4.25. 4-(6-(Dodecyloxy)benzo[d]oxazol-2-yl)phenol 4

The mixture of 4-(6-(dodecyloxy)benzo[*d*]oxazol-2-yl)phenyl acetate **5** (0.9 g, 0.0021 mol) and KOH (0.18 g, 0.0032 mol) dissolved in 100 ml 95% C₂H₅OH was refluxed for 24 h. The solution was neutralized with dilute aqueous HCl and the white solids were collected. The product isolated as white solid were obtained after recrystallization from CH₂Cl₂/CH₃OH. Yield 93%. ¹H NMR (CDCl₃): δ 0.87 (t, 3H, -CH₃, *J*=6.69 Hz), 1.26–1.50 (m, 18H, -CH₂), 1.77–1.83 (m, 2H, -CH₂), 4.00 (t, 2H, -OCH₂, *J*=6.49 Hz), 6.91–6.96 (m, 3H, Ar–H), 7.07 (s, 1H, Ar–H), 7.56 (d, 1H, Ar–H, *J*=8.67 Hz), 8.06 (d, 2H, Ar–H, *J*=8.35 Hz). ¹³C NMR (CDCl₃): δ 14.38, 23.02, 26.44, 29.66, 29.69, 29.76, 29.93, 29.95, 29.99, 30.01, 32.28, 69.51, 96.83, 113.78, 116.54, 119.64, 119.74, 129.79, 135.54, 151.84, 158.15, 159.66, 163.01.

4.26. Bis(4-(6-(dodecyloxy)benzo[d]oxazol-2-yl)phenyl)butanedioate 1b (m=4, n=12)

The mixture of 4-(6-(dodecyloxy)benzo[d]oxazol-2-yl)phenol 4 (0.15 g, 0.38 mmol) and DMAP (0.046 g, 0.38 mmol) dissolved in 25 ml of dry THF was refluxed for 10 min under nitrogen atmosphere. To the solution, a dilute solution of adipoyl chloride (0.035 g, 0.19 mmol) dissolved in 5.0 ml of dry THF was slowly added. The solution was stirred at room temperature for 4 h. The solution was concentrated under reduce pressure and the product isolated as white solids were obtained after recrystallization from CH₂Cl₂/MeOH. Yield 72%. ¹H NMR (CDCl₃): δ 0.86 (t, 6H, -CH₃, J=6.94 Hz), 1.24-1.47 (m, 36H, -CH₂), 1.79-1.80 (m, 8H, -CH₂), 2.67 (t, 4H, -OCOCH₂, *J*=7.30 Hz), 3.99 (t, 4H, -OCH₂, *J*=6.38 Hz), 6.94 (d, 2H, Ar-H, J=7.93 Hz), 7.07 (s, 2H, Ar-H), 7.24 (d, 4H, Ar-H, J=5.36 Hz), 7.61 (d, 2H, Ar-H, J=8.44 Hz), 8.22 (d, 4H, Ar-H, J=7.88 Hz). ¹³C NMR (CDCl₃): δ 14.48, 23.04, 24.53, 26.40, 29.56, 29.71, 29.74, 29.93, 29.95, 30.01, 30.04, 32.27, 34.33, 69.24, 96.41, 113.97, 120.19, 122.56, 125.14, 128.98, 135.52, 151.95, 153.23, 158.32, 161.72, 171.64. MS (FAB): calcd for MH⁺ C₅₆H₇₂N₂O₈: 901.2, found: 900.9.

4.27. Bis(4-(6-(dodecyloxy)benzo[d]oxazol-2-yl)phenyl)hexanedioate 1d (m=6, n=12)

White solid, yield 51%. ¹H NMR (CDCl₃): δ 0.86 (t, 6H, -CH₃, *J*=7.06 Hz), 1.24–1.46 (m, 40H, -CH₂), 1.79–1.80 (m, 8H, -CH₂), 2.60 (t, 4H, -OCOCH₂, *J*=7.40 Hz), 3.99 (t, 4H, -OCH₂, *J*=6.56 Hz), 6.93 (d, 2H, Ar-H, *J*=8.71 Hz), 7.07 (s, 2H, Ar-H), 7.23 (d, 4H, Ar-H, *J*=9.45 Hz), 7.60 (d, 2H, Ar-H, *J*=8.73 Hz), 8.21 (d, 4H, Ar-H, *J*=8.60 Hz). ¹³C NMR (CDCl₃): δ 14.46, 23.04, 24.97, 26.40, 29.05, 29.57, 29.71, 29.74, 29.93, 29.95, 30.01, 30.04, 32.27, 34.62, 69.25, 96.42, 113.92, 120.18, 122.55, 125.10, 128.92, 135.62, 151.96, 153.31, 158.30, 161.75, 172.04. MS (FAB): calcd for MH⁺ C₅₈H₇₆N₂O₈: 929.2, found: 928.9.

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