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Synthesis and characterization of luminescent hockey stick-shaped liquid crystalline compounds

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A general synthetic strategy, based on a convergent approach, allowed us to prepare a series of luminescent unsymmetrical bent-core compounds (2,5-(disubstituted)-1,3,4-oxadiazole derivatives), via the Sonogashira crosscoupling reaction, all possessing a similar hockey stick shape. Their mesophases were characterized using polarizing optical microscopy and differential scanning calorimetry. The observed LC phases possess the classical textures of calamitic liquid crystals. Fluorescence in solution for these compounds exhibits strong blue emission ($\lambda_{max\ em.}$ = 390–460 nm) with good quantum yields (50–85%).

1. Introduction

The design of novel thermotropic liquid crystals as advanced functional materials involves suitable selection of a core fragment, linking group, and terminal functionality. However, anisometric rodlike- or disklike-shaped molecules used to be a fundamental prerequisite for conventional thermotropic liquid crystal formation, because steric packing considerations play an important role in this interesting state of soft matter [1]. More recently, with the discovery of banana-shaped liquid crystals, where bent molecules serve as a core, interest in the incorporation of nonlinear units has gained importance. The study of the mesomorphic properties of these compounds, which has gained considerable importance since the discovery of polar switching in such achiral compounds, and the subsequent detailed analysis of the switching process [2], are mainly driven by their potential for application in display technology [3, 4]. A large number of bent-core or banana-shaped mesogens have been synthesized to examine their novel mesophase structures [5–7]. Most of the compounds reported in the literature are symmetrical around a central phenyl ring and are derived from 1,3-dihydroxybenzene or 2,7-dihydroxynaphthalene [8, 9]. Usually these are five- or six-ring compounds and are substituted with two terminal alkyl/alkoxy chains.

In recent years a wide range of emissive materials has been reported for use in electroluminescent (EL) devices; these vary from low molecular mass molecules to processable polymers [10]. In addition, highly conjugated liquid crystals are desirable as the self-organizing properties of these materials can be exploited to improve device performance and to achieve linearly polarized electroluminescence [11]. For example, Contoret *et al.* [12] have reported polarized electroluminescence from a nematic network, offering a possible substitute for one of the polarizers and the back light of TN-LCDs and STN-LCDs, with a lower power consumption and/or a higher brightness. Among other important aspects are their high charge carrier mobility observed in hexagonal discotic (Col_h), helical (H) and smectic A, B phases and an unidentified smectic X phase [13], and their ability to develop defect-free layers [14].

Functional LCs can be obtained by incorporating new properties into the same molecule, besides its inherent self-organization, such as luminescence. This combination has led to intrinsically luminescent mesogens, which are able to form ordered aggregates with large carrier mobilities for EL devices. In this context, our interest has been focused on luminescent liquid crystals containing the heterocycle 1,3,4-oxadiazole [15, 16]. 1,3,4-Oxadiazole derivatives are well known for their high thermal and hydrolytic stability, resistance to oxidative degradation and electron-accepting properties [17]. They usually exhibit a high photoluminescent quantum yield [18]. The introduction of an oxadiazole ring into a mesogenic core can provide a lateral dipole from oxygen and nitrogen atoms and also a bent rigid core [19].

In this paper, we report the synthesis, mesomorphic behaviour and photophysical properties of several unsymmetrical bent-core compounds based on 2-(4-decyloxyphenyl)-5-(4-phenylethynylaryl)-1,3,4-oxadiazole (figure 1).

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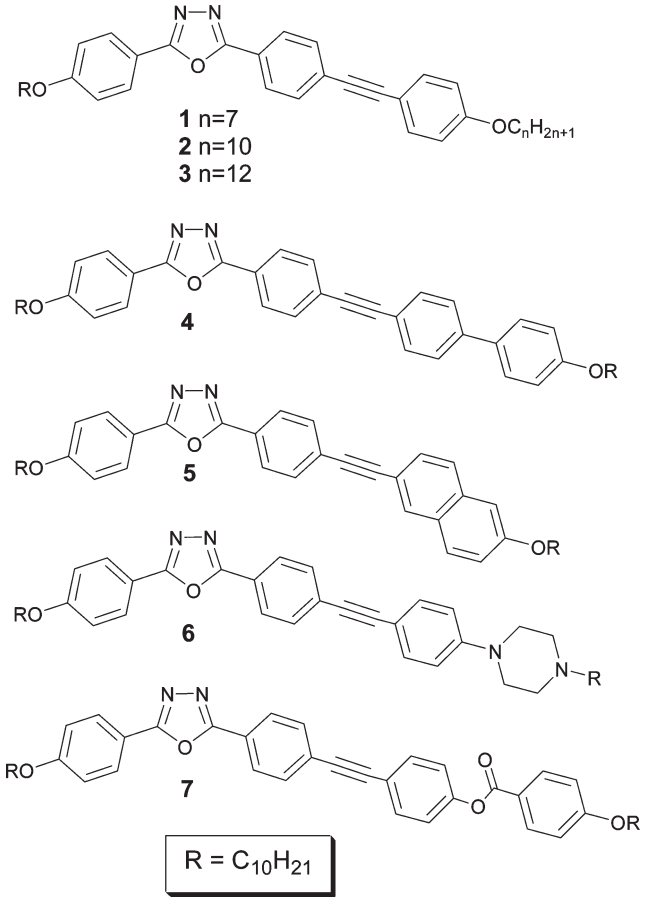


Figure 1. Chemical structures of the final synthesized molecules.

All the compounds were designed with two unsymmetrical arms about a central 1,3,4-oxadiazole ring structure possessing a similar hockey stick shape [20]. In order to contribute to an understanding of the underlying structure–property relationships, different aromatic moieties were used to elongate one of the arms of the hockey stick, such as: phenyl with a different aliphatic long chain (7, 10 and 12 carbon atoms), biphenyl, naphthyl, phenylpiperazine and phenyl benzoate. These aromatic moieties are linked to the mesogenic core through a triple C≡C bond in order to produce a highly π-polarizable and conjugated diarylacetylene moiety.

2. Results and discussion

2.1. *Synthesis*

The initial synthetic route to the final liquid crystalline materials **1**–**7** was carried out according to scheme 1. 1,3,4-Oxadiazole-based aryl bromide **9** was prepared from aryl tetrazole **8** and 4-bromobenzoyl chloride through the Huisgen reaction. The terminal aryl acetylenes **10**–**16** were synthesized from aryl halides by the sequence of alkylation, palladium- catalysed cross-coupling (Sonogashira coupling [21]), with 2-methyl-3-butyn-2-ol followed by protective group elimination. The final step was the Sonogashira coupling between aryl bromide **9** and the terminal aryl acetylenes to afford compounds **1**–**7**.

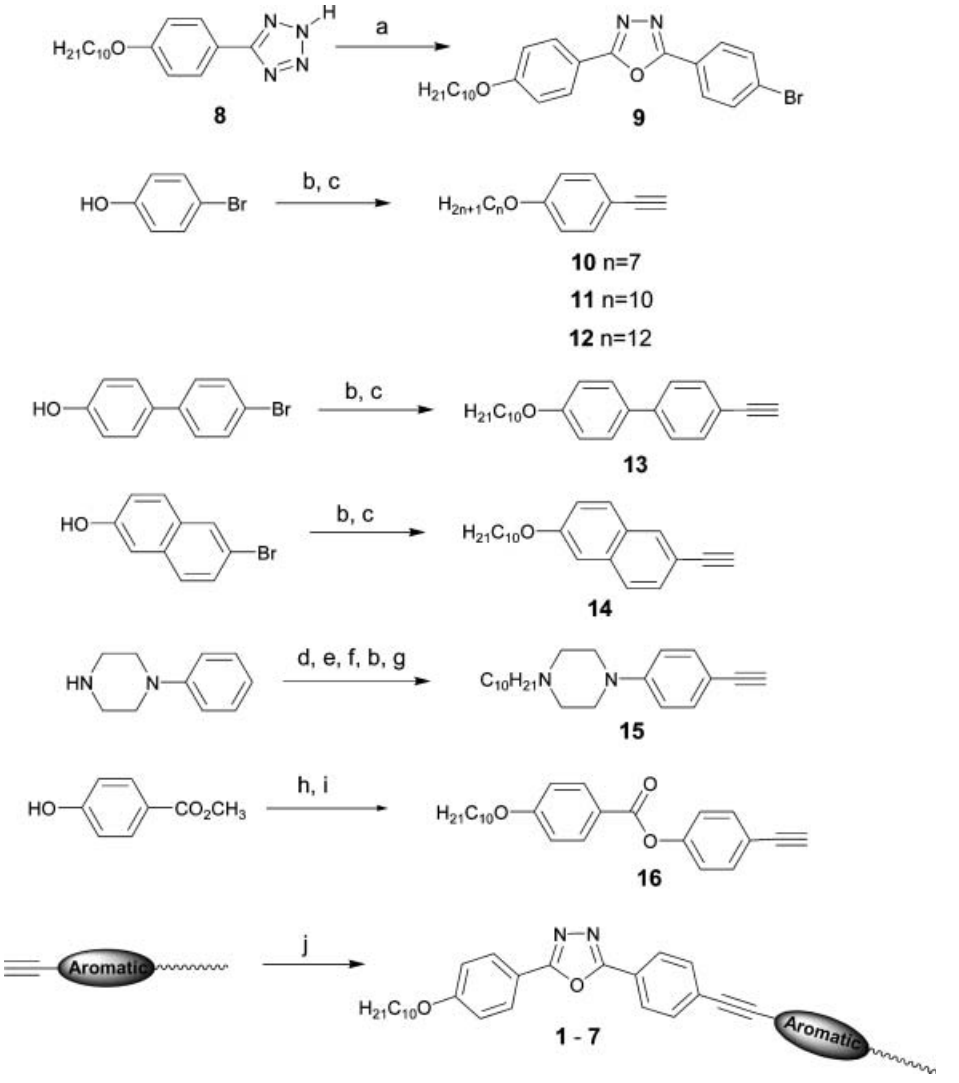
Compounds **1**, **2**, **3**, **5** and **6** were obtained in good and moderate yields; see table 1. However, for compounds **4** and **7** this adopted route only gave traces of the product with a considerable amount of homo-coupling product. The synthesis of these compounds was therefore possible by simply reversing the functionalities according to scheme 2.

2.2. *Mesophases and thermal properties*

The transition temperatures, phase assignments and thermal stabilities of the final compounds were investigated by thermal polarizing optical microscopy (POM), DSC and TGA; the results are given in table 2. All the materials studied exhibited high thermal stability with decomposition temperatures between 390 and 470°C, and showed smectic and nematic phases typical for calamitic liquid crystals.

In order to establish the effects of varying the terminal alkoxy chain length on the mesomorphic behaviour, three homologues (compounds **1**–**3)** were synthesized and their mesomorphic behaviour characterized. The optical observations were performed using clean untreated glass slides. For these compounds it is clear that the SmC phase stability increases with the elongation of the terminal alkyl chain. The first member **1**, having a heptoxy chain, exhibits only an enantiotropic N phase that was identified from the observation of a characteristic schlieren texture. For homologue **2**, with a decyloxy chain, dimorphism was observed, exhibiting an enantiotropic N phase and a monotropic SmC phase, while homologue **3** showed the two enantiotropic phases. The presence of the SmC phase was confirmed from the microscopic observation of the characteristic striated texture immediately after the N–SmC transition, followed by the appearance of a broken fan-shaped texture.

With the addition of a further phenyl ring (compound **4**) there is an increase in the melting point (221.9°C) with short SmC and N ranges. However, the naphthalene unit in compound **5** leads to a lower melting point with more stable SmC and N phases. On cooling, crystallization starts at only 126.8°C. Compound **6** exhibits a trimorphism SmA, SmC and N phases. The presence of the SmA phase was confirmed from the microscopic observations, the phase separates out in the form of *bâtonnets* which coalesce and build up



Scheme 1. Reagents: a. *p*-bromobenzoyl chloride, pyridine; b. 1-bromoalkane, K_2CO_3, butanone; c. 1) 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, TPP, TEA; 2) NaOH, toluene; d. ethyl chloroformate, K_2CO_3, butanone; e. I_2, $NaHCO_3$, CH_2Cl_2/H_2O; f. $NH_2NH_2.H_2O$, KOH, ethylene glycol; g. 1) 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, TEA/THF; 2) NaOH, toluene; h. 1) 1-decylbromide, butanone, K_2CO_3, KI; 2) KOH, $MeOH/H_2O$; 3) HCl conc.; i. DCC, DMAP, 4-ethynylphenol, CH_2Cl_2; j. compound **9**, $PdCl_2(PPh_3)_2$, CuI, TPP, TEA.

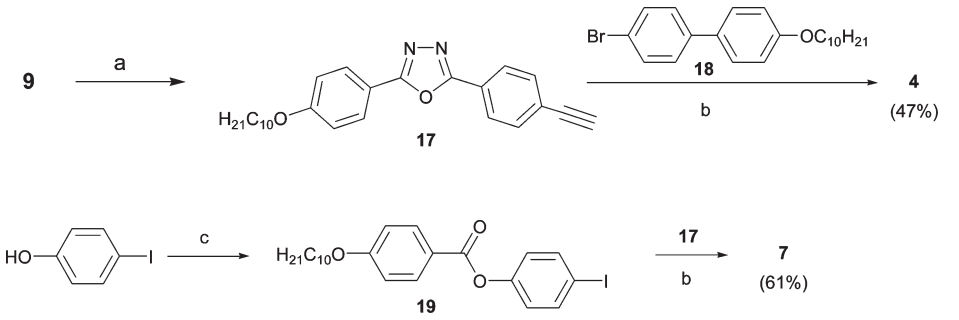
Table 1. Results of the palladium cross-coupling using the route from scheme 1 for compounds **1–7**.

Compound	Yield/%
1	54
2	49
3	56
4	not isolated[a]
5	65
6	55
7	not isolated[a]

[a]Only homocoupling product.

the characteristic focal-conic fan texture. This may be explained by the presence of a piperazine ring in the molecule. This ring is preferentially present in the chair conformation with substituents being arranged in equatorial positions [22]. The polarity and polarizability of the molecule backbone is increased by mutual conjugation between the lone electron pair of the nitrogen and the oxadiazole ring. It is known that these characteristics tend to favour smectic properties [23].

Compound **7** exhibits the most stable liquid crystalline profile, with a melting point of 129.1°C and a wide smectic (an unidentified SmX and SmC) and nematic range. Upon cooling, the schlieren nematic texture



Scheme 2. Reagents: a. 1) 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, TPP, TEA; 2) NaOH, toluene; b. $PdCl_2(PPh_3)_2$, CuI, TPP, TEA/THF; c. 4-decyloxybenzoic acid, DCC, DMAP, CH_2Cl_2.

changes slowly at 188.2°C to schlieren SmC with a clearly visible fingerprint region between the two phases, characterizing a N–SmC transition. From this mesophase at 130.7°C there is a transition to another smectic phase, unidentified SmX, in which the texture change is almost impossible to perceive by optical microscopy, but it is easily established by DSC analysis.

Representative textures obtained by optical microscopy for these compounds are shown in figure 2. All the nematic phases present a schlieren texture

Table 2. Thermal behaviour of compounds **1–7**.

Compound	Transition	T/°C, heating (ΔH/kJ mol^{-1})[a]	T/°C, cooling (ΔH/kJ mol^{-1})[a]	$T_{dec.}$/°C[b]
1	Cr–N	143.4 (35.3)	131.6 (−34.2)	409
	N–I	159.7 (0.26)	158.7 (−0.26)	
2	CrI–CrII	116.1 (7.92)	105.0 (−7.44)	438
	CrII–(SmC)		125.8 (−19.3)	
	(SmC)–N	131.6 (23.1)	128.4 (−0.29)	
	N–I	156.3 (0.67)	152.2 (−0.66)	
3	CrI–CrII	106.4 (3.7)		436
	CrII–CrIII	126.0 (7.0)		
	CrIII–SmC	133.3 (2.3)	121.0 (−11.7)	
	SmC–N	140.1 (broad)	135.9 (−0.35)	
	N–I	153.5 (0.78)	152.9 (−0.73)	
4	CrI–CrII	157.7 (34.1)		475
	CrII–CrIII	180.9 (7.08)		
	Cr–SmC	221.9 (16.9)	214.20 (−14.4)	
	SmC–N	224.6 (broad)	223.4 (−0.02)	
	N–I	235.4 (broad)	232.8 (−0.11)	
5	CrI–CrII	110.5 (16.8)		432
	CrII–CrIII	127.2 (7.51)		
	CrIII–CrIV	141.7 (2.32)		
	CrIV–SmC	150.1 (32.4)	126.8 (−30.1)	
	SmC–N	163.7 (0.11)	160.8 (−0.16)	
	N–I	197.8 (1.04)	194.9 (−1.21)	
6	CrI–CrII	126.2 (9.87)		397
	CrII–SmC	141.1 (0.43)	101.8 (−2.42)	
	SmC–SmA	161.8 (1.67)	159.1 (−3.41)	
	SmA–N	221.9 (broad)	220.6 (−2.11)	
	N–I	231.5 (broad)	230.8 (−0.13)	
7	CrI–CrII	96.65 (18.0)		433
	CrII–SmX	129.1 (33.4)	115.9 (−16.2)	
	SmX–SmC	143.0 (0.81)	130.7 (−3.46)	
	SmC–N	189.3 (1.03)	188.2 (−0.97)	
	N–I	239.3 (1.91)	237.8 (−0.87)	

[a]Determined by optical microscopy and DSC measurements (10°C). [b]Determined by TGA, onset of decomposition in nitrogen (20°C min^{-1}).

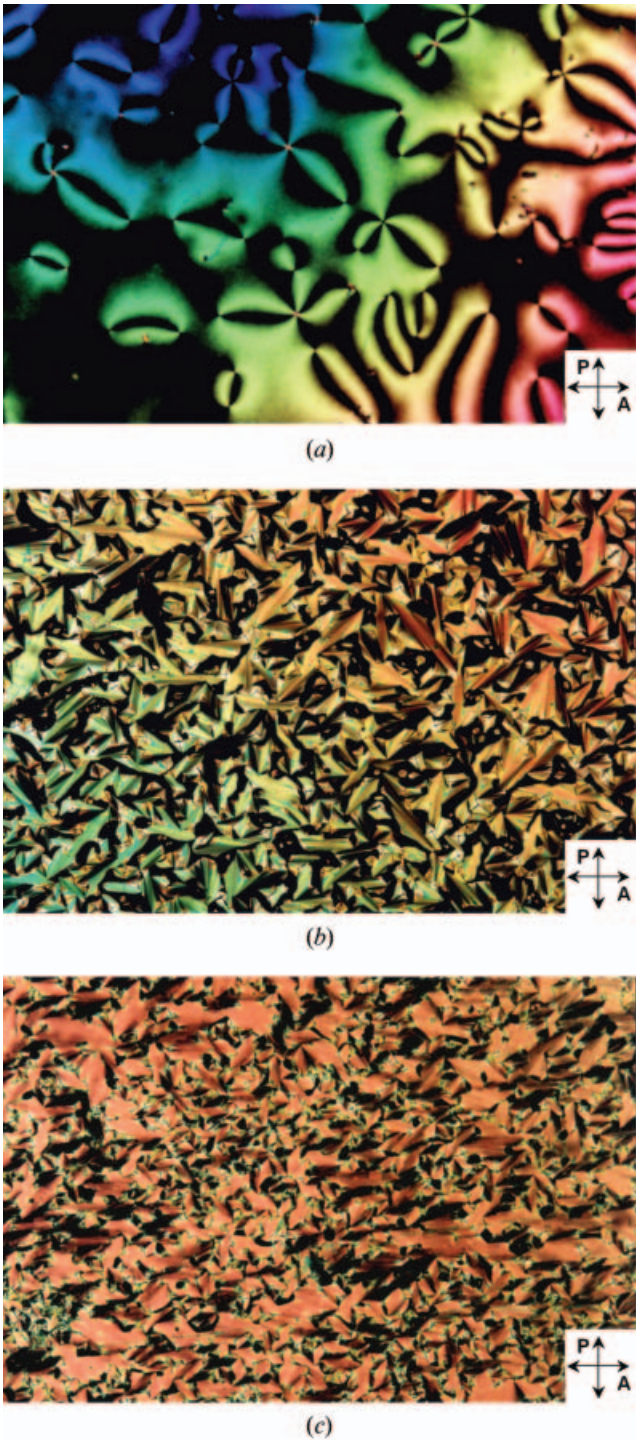


Figure 2. Photomicrographs of (*a*) the N phase schlieren texture at 221.4°C for compound **7** (33x); (*b*) the SmA phase focal-conic texture at 209.1°C for compound **6** (33x); (*c*) the SmC phase broken fan-shaped texture at 149.2°C for compound **6** (33x). Samples were sandwiched between untreated glass slides and viewed through crossed polarizers.

containing two- and four-brush disclinations, excluding the possibility of biaxiality in these phases [24].

2.3. *Fluorescence properties*

The UV-vis absorption and fluorescence spectroscopy data in chloroform solution for final compounds **1**–**7** are summarized in table 3. Similar absorption patterns between 300 and 400 nm are observed with an intense absorption band ($\varepsilon \geqslant 40\,000\ mol^{-1}\ cm^{-1}$) peaking between 330 and 360 nm (figure 3). These compounds displayed blue emission in solution ($\lambda_{max.\ em.} = 390$–$460$ nm) with good photoluminescence quantum yields (50–85%).

Compounds **1**–**3** show maximum absorption peak wavelengths around 340 nm. The highest absorption peak wavelengths for compounds **4**–**6** are red-shifted by a maximum of 14 and a minimum of 7 nm compared with the average for compounds **1**–**3**. On the other hand, compound **7** shows a blue-shift in the spectrum of 7 nm from 340 nm. This could be due to an electronic effect, which lowers the HOMO-LUMO band gap due to the presence of a strong electron-donating substituent like the $-NR_2$ group (compound **6**) or –OR group, together with an elongated conjugation length (**4** and **5**). The opposite occurs in compound **7** (blue-shift), in which the ester linkage breaks the conjugation. This effect is also present in the fluorescence spectra. Compound **6** gave the highest emission peak wavelength with a large Stokes shift (106 nm). This is expected to arise from a push–pull system [25] between a strong electron-donating group ($-NR_2$) and a strong electron–withdrawing group (oxadiazole ring). Nevertheless, this compound showed a lower photoluminescence quantum yield (52.4%). In addition, compounds **4** and **7** gave structured fluorescence spectra with two and three emission peaks, respectively. The luminescence lifetime decay for similar compounds is around 0.7–0.9 ns [16]. Based on this, and on the emission energy and quantum yields the luminescence for compounds **1**–**7** may be attributed to π–π* fluorescence.

3. Conclusions

In summary, a series of π-conjugated bent-core unsymmetric 2,5-(disubstituted)-1,3,4-oxadiazoles was prepared by convergent Sonogashira cross-coupling of building blocks between 2-(bromoarylene)-5-(*n*-decyloxyphenyl)-1,3,4-oxadiazole and the corresponding terminal arylacetylenes. This versatile synthetic route yielded luminescent unsymmetrical bent-core liquid crystalline compounds in high yields. The main advantage of the synthetic pathway is the flexibility to prepare 'tailor-made' building blocks, for example, by simply reversing terminal functionalities. The POM and

Table 3. Summary of photophysical properties of compounds **1–7**, in chloroform solution.

Compound	$\lambda_{abs.\ max}$/ nm (ε)[a]	$\lambda_{em.\ max}$/ nm	Stokes shift/nm	Φ_{PL}[b]
1	341 (4.0×10^4)	395	54	0.804
2	338 (4.0×10^4)	395	57	0.805
3	340 (4.0×10^4)	395	55	0.814
4	353 (5.2×10^4)	389 and 413[c]	36	0.508
5	347 (4.6×10^4)	406	59	0.849
6	354 (5.5×10^4)	460	106	0.524
7	333 (4.3×10^4)	366[c], 388 and 407[c]	55	0.754

[a]Units=$mol^{-1}\,cm^{-1}$. [b]Determined using quinine sulphate as standard (Φ_{PL}=0.546 in 1N H_2SO_4). [c]Shoulder peak.

DSC analysis showed the presence of uniaxial nematic phase with typical schlieren texture in all compounds. Other mesophases observed were smectic C (for all compounds except **1**), smectic A (only for compound **6** with a piperazine unit) and a unidentified smectic X phase (exhibited by compound **7**). Luminescence properties of the final compounds were evaluated. They exhibited strong blue fluorescence from 390 to 460 nm with good quantum yields from 50 to 85%. Efforts to use these compounds for LED designing are currently under way.

4. Experimental

4.1. *General*

Elemental analyses were carried out using a Perkin-Elmer model 2400 instrument. Infrared spectra were recorded on a Perkin-Elmer model 283 spectrometer in KBr discs. ^1H and ^{13}C NMR spectra were obtained with a Bruker AC-200F spectrometer at 200 MHz and 50.4 MHz, respectively, using TMS as the internal standard. The melting points, thermal transitions and mesomorphic textures were determined using an Olympus BX50 microscope equipped with a Mettler Toledo FP-82 heating stage and an exposure control unit PM-30. DSC measurements were carried out using Shimadzu equipment with a DSC-50 module. A Hitachi UV-Vis model 3000 spectrophotometer was used to record absorption spectra. Fluorescence spectra were recorded on a Hitachi-F-4500.

4.2. *Materials*

All the reagents were obtained from commercial sources and used without further purification. Sonogashira couplings were accomplished under Ar atmosphere. The intermediate 2-(4-bromophenyl)-5-(4-decyloxyphenyl)-1,3,4-oxadiazole (**9**) was obtained from

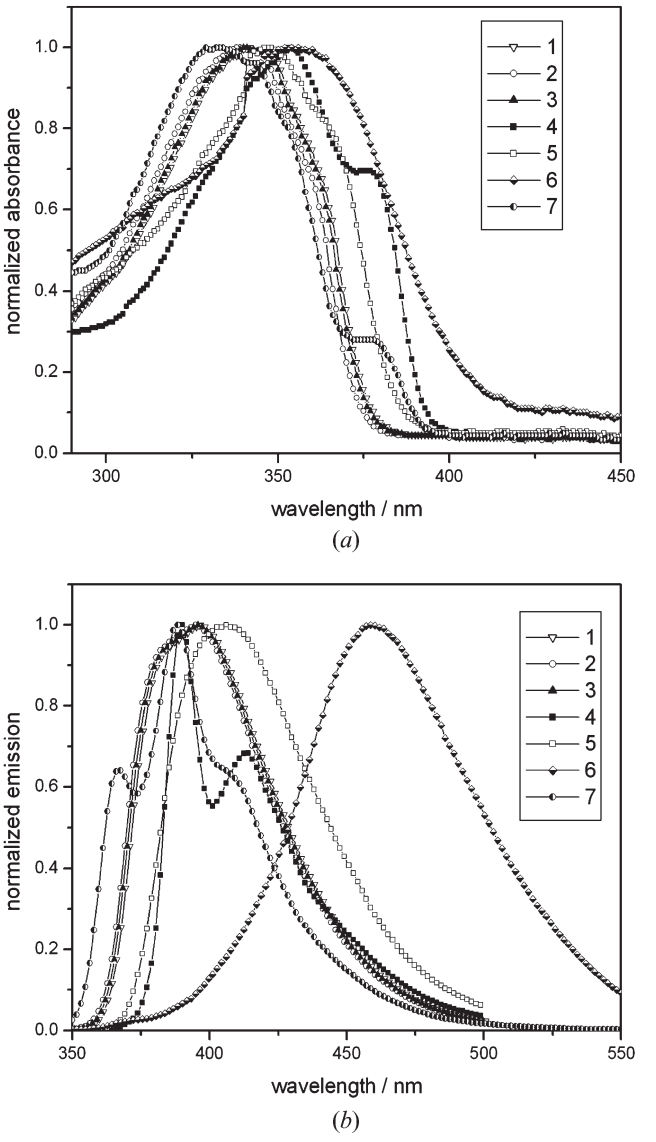


Figure 3. (*a*) Absorption and (*b*) fluorescence spectra of compounds **1–7** in chloroform solution.

5-(4-decyloxyphenyl)tetrazole (**8**) according to a procedure reported previously [16]. The terminal acetylenes 1-alcoxy-4-ethynylbenzene (**10**, **11** and **12**), 4-decyloxy-4′-ethynylbiphenyl (**13**) and 4-ethynylphenyl 4-decyloxybenzoate (**16**) were prepared according to published procedures [26, 27]. The organic solvents were of commercial grade quality except THF (HPLC grade) and all were dried by traditional methods. In general, all the compounds were purified by column chromatography on silica gel (60–120 mesh), and crystallization from analytical grade solvents. The purity of the sample was checked by thin -layer chromatography (Merck Kieselgel 60F254).

4.3. *Synthesis*

4.3.1. 2-Decyloxy-6-ethynylnaphthalene, 14. (a) *Alkylation of 6-bromo-2-naphthol*. A mixture of 6-bromo-2-naphthol (2.5 g, 11.2 mmol), K_2CO_3 (6.2 g, 44.8 mmol), bromodecane (2.72 g, 12.3 mmol) and butanone (60 ml) was stirred under reflux for 20 h. After cooling, the reaction mixture was filtered off and washed with diethyl ether; the filtrate was concentrated and the residue recrystallized from a methanol/ethanol 1/1 mixture; yield 3.7 g (91%), m.p. 57.0–58.5°C. ^{1}H NMR ($CDCl_3$) δ: 7.89 (s, 1H), 7.65–7.45 (m, 3H), 7.18–7.08 (m, 2H), 4.04 (t, 2H), 1.84 (m, 2H), 1.28 (m, 14H), 0.88 (t, 3H). (b) *Coupling with 2-methyl-3-butyn-2-ol*. A mixture of 2-bromo-6-decyloxy-naphthalene (2.0 g, 5.5 mmol), $PdCl_2(PPh_3)_2$ (38.5 mg, 0.055 mmol), CuI (5.2 mg, 0.027 mmol), triphenylphosphine (14.40 mg, 0.055 mmol) and TEA (40 ml) was heated under reflux for 40 min. Pure 2-methyl-3-butyn-2-ol (0.91 ml, 8.25 mmol) was added and the reflux continued for a further 1.5 h. After cooling, the reaction mixture was filtered through a celite pad, washing with 150 ml of THF. The filtrate was evaporated and the residue recrystallized from acetonitrile to give a grey solid; yield 1.87 g (93%), m.p. 72.3–75.0°C. IR (KBr) ν_{max}/cm^{-1}: 3350, 2914, 2850, 1599, 1251, 1171, 857. (c) *Protective group elimination as acetone*. In a 100 ml round-bottomed flask equipped with distillation apparatus, the intermediate 4-(6-decyloxy-naphthalen-2-yl)-2-methyl-but-3-yn-2-ol (1.35 g, 3.68 mmol) was dissolved in toluene (40 ml); NaOH (0.50 g) was then added and the mixture slowly heated, the acetone being distilled off over 7 h. The cooling reaction solution was filtered through a celite pad, washing with toluene; toluene was removed under reduced pressure. Column chromatography of the crude product (eluant hexane) afforded a light yellow solid; yield 0.665 g (59%), m.p. 42.4–46.7°C. IR (KBr) ν_{max}/cm^{-1}: 3298, 2955, 2919, 2850, 1626, 1597, 1469, 1387, 1229, 1021, 860. ^{1}H NMR ($CDCl_3$) δ: 7.94 (s, 1H), 7.66 (t, J=8.2 Hz, 2H), 7.47 (d, J=8.4 Hz, 1H), 7.17–7.08 (m, 2H), 4.06 (t, 2H), 3.09 (s, 1H), 1.82 (m, 2H), 1.28 (m, 14 H), 0.8 (m, 3H). Elemental analysis for $C_{22}H_{28}O$: calcd C 85.66, H 9.15; found C 85.78, H 9.13%.

4.3.2. 1-Decyl-4-(4-ethynylphenyl)piperazine, 15. (a) *Amine protection*. To a 500 ml three-necked round-bottomed flask *N*-phenylpiperazine (14.5 ml, 94.9 mmol), K_2CO_3 (78.8 g, 519.4 mmol) and butanone (250 ml) were added and the mixture stirred at 0°C. Ethyl chloroformate (37 ml, 379.6 mmol) was added dropwise over 1 h. After addition, the reaction mixture was heated under reflux for a further 1 h, cooled to 0°C and then a 4% methanol solution of NaOH was cautiously added. The suspension was stirred at room temperature overnight and then filtered. The filtrate was concentrated and distilled under vacuum to give 15.44 g (69%) of colourless oil, b.p. 145–150°C (0.2 mm Hg). IR (KBr) ν_{max}/cm^{-1}:2981, 2921, 1700, 1598, 1434, 1230, 761. ^{1}H NMR ($CDCl_3$) δ: 7.25 (t, 2H), 6.87 (t, 3H), 4.16 (q, J=7.1 Hz, 2H), 3.60 (t, J=5.2 Hz, 4H), 3.09 (t, J=5.2 Hz, 4H), 1.28 (t, J=7.1 Hz, 3H). (b) *Iodination*. N-protected piperazine (10.0 g, 42.6 mmol) and $NaHCO_3$ (5.38 g, 64 mmol) in CH_2Cl_2 (160 ml) and water (120 ml) were stirred at 5°C. Iodine (10.2 g, 40.2 mmol) was added over 2 h. The mixture was stirred for a further 2 h at room temperature and sodium thiosulphate added to eliminate excess iodine. The organic phase was concentrated and the residue recrystallized from *n*-hexane; yield 8.28 g (54%) of colourless crystals, m.p. 77.3–77.6°C. ^{1}H NMR ($CDCl_3$) δ: 7.53 (d, J=8.7 Hz, 2H), 6.69 (d, J=8.7 Hz, 2H), 4.16 (q, J=7.1 Hz, 2H), 3.62 (t, J=5.2 Hz, 4H), 3.11 (t, J=5.2 Hz, 4H), 1.28 (t, J=7.1 Hz, 3H). (c) *Amine deprotection*. A mixture of 4-(4-iodophenyl)piperazine-1-carboxylic acid ethyl ester (8.0 g, 22.2 mmol), KOH (32.4 g, 577.0 mmol) and hydrazine monohydrate (5.4 ml, 111.1 mmol) in ethylene glycol was heated under reflux for 2 h. After cooling, the reaction mixture was poured into water (250 ml) and extracted with diethyl ether (5 × 100 ml). The organic solution was dried over $NaSO_4$, evaporated and recrystallized from hexane to give 3.92 g (61%) of a white solid, m.p. 131–133°C. ^{1}H NMR ($CDCl_3$) δ: 7.51 (d, J=8.8 Hz, 2H), 6.65 (d, J=8.8 Hz, 2H), 3.03 (m, 8 H). (d) *Amine alkylation*. A mixture of 1-(4-iodophenyl)piperazine (3.87 g, 13.44 mmol), K_2CO_3 (3.71 g, 26.88 mmol), 1-bromodecane (3.07 ml, 14.78 mmol) in butanone (80 ml) was heated under reflux for 45 h. The cooling mixture was filtered off and the filtrate concentrated to give a solid that was purified by recrystallization from ethanol; yield 4.24 g (73%), m.p. 88.6–89.0°C. ^{1}H NMR ($CDCl_3$) δ: 7.50 (d, J=8.7 Hz, 2H), 6.68 (d, J=8.7 Hz, 2H), 3.18 (t, 4 H), 2.59 (t, 4H), 2.38 (t, 2H), 1.51 (m, 2H), 1,27 (broad, 14 H), 0.86 (t, 3H). (e) *Coupling with 2-methyl-3-butyn-2-ol*. A mixture of 1-decyl-4-(4-iodophenyl) piperazine (2.1 g, 4.9 mmol), $PdCl_2(PPh_3)_2$ (36.3 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol) in THF (8 ml) and TEA (20 ml) was degassed by rapid bubbling of dry argon through it for 20 min. Pure 2-methyl-3-butyn-2-ol (0.8 ml, 7.35 mmol) was added and the mixture stirred at room temperature for 24 h. Another portion of the catalyst was added and the reaction stirred for a further 1 h. The mixture was filtered through a celite pad, washing with THF (250 ml), and the solvents were evaporated. The residue was recrystallized from heptane to give 1.72 g (91%) of white crystals, m.p.

117.0–125.4°C. IR (KBr) ν_{max}/cm^{-1}:3160, 2918, 2849, 2819, 2778, 2222, 1606, 1514, 1465, 1286, 1245, 1171, 824. ^1H NMR ($CDCl_3$) δ: 7.24 (d, J=8.0 Hz, 2H), 6.76 (d, J=8.0 Hz, 2H), 3.24 (m, 4 H), 2.59 (m, 4H), 2.37 (m, 2H), 1.59 (broad, 8H), 1.26 (broad, 14 H), 0.88 (t, 3H). (f) *Protective group elimination as acetone*. The intermediate 4-[4-(4-decylpiperazin-1-yl)phenyl]-2-methyl-3-butyn-2-ol (1.71 g, 4.44 mmol) was dissolved in toluene (50 ml). NaOH (0.5 g) was added and the mixture slowly heated and acetone distilled off over 6 h. Toluene was removed under reduced pressure and the residue recrystallized from acetonitrile to give 1.16 g (80%) of a light yellow crystal, m.p. 69.9°C. IR (KBr) ν_{max}/cm^{-1}:3311, 2929, 2848, 2774, 2096, 1605, 1510, 1247, 1157, 1138, 820. ^1H NMR ($CDCl_3$) δ: 7.37 (d, J=8.7 Hz, 2H), 6.82 (d, J=8.7 Hz, 2H), 3.25 (m, 4 H), 2.97 (s, 1H), 2.59 (m, 4H), 1.59 (broad, 8H), 2.38 (m, 2H), 1.51 (m, 2H), 1.27 (m, 14H), 0.88 (t, 3H). Elemental analysis for $C_{22}H_{34}N_2$: calcd C 80.93, H 10.50, N 8.58; found C 80.98, H 10.47, N 8.33%.

4.3.3. 2-(4-Decyloxyphenyl)-5-[4-(4-heptyloxyphenyl-ethynyl)phenyl]-1,3,4-oxadiazole, 1. A mixture of 0.5 g (1.09 mmol) of 2-(4-bromophenyl)-5-(4-decyloxyphenyl)-1,3,4-oxadiazole (**9**), $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol), CuI (9.5 mg, 0.05 mmol) and triphenylphosphine (26.2 mg, 0.1 mmol) in TEA (25 ml) was stirred under reflux for 45 min. 1-Heptyloxy-4-ethynylbenzene (**10**) (0.235 g, 1.09 mmol) dissolved in 5 ml of TEA was then added dropwise. The reaction mixture was heated under reflux for a further 2.5 h, cooled at room temperature and filtered, washing with THF (80 ml). The solvents were evaporated and the crude product was recrystallized from ethanol to give the product (0.348 g, 54 %). IR (KBr) ν_{max}/cm^{-1}: 2921, 2849, 2211, 1603, 1511, 1497, 1468, 1247, 839, 830. ^1H NMR ($CDCl_3$) δ: 8.07 (t, 4H, J=7.3 Hz), 7.63 (d, 2H, J=8.0 Hz), 7.47 (d, 2H, J=8.3 Hz), 7.01 (d, 2H, J=8.3 Hz), 6.88 (d, 2H, J=8.1 Hz), 4.0 (m, 4H), 1.78 (m, 4H), 1.27 (broad, 22H), 0.89 (t, 6H). ^{13}C NMR ($CDCl_3$) δ: 164.62, 163.67, 161.98, 159.57, 133.16, 131.87, 128.64, 126.96, 126.59, 122.95, 115.96, 114.93, 114.56, 114.42, 92.57, 87.37, 68.24, 68.06, 31.86, 31.73, 29.52, 29.31, 29.11, 25.95, 22.63, 22.58, 14.07. Elemental analysis for $C_{39}H_{48}N_2O_3$: calcd C 79.02, H 8.16, N 4.73; found C 79.13, H 8.14, N 4.64%.

4.3.4. 2-(4-Decyloxyphenyl)-5-[4-(4-decyloxyphenyl-ethynyl)phenyl]-1,3,4-oxadiazole, 2. This compound was synthesized as described for compound **1**, using 1-decyloxy-4-ethynylbenzene (**11**); yield 49%. IR (KBr) ν_{max}/cm^{-1}: 2920, 2848, 2209, 1606, 1503, 1464, 1247, 836. ^1H NMR ($CDCl_3$) δ: 8.08 (d, 2H, J=8.2 Hz), 8.05 (d, 2H, J=8.6 Hz), 7.63 (d, 2H, J=8.3 Hz), 7.47 (d, 2H, J=8.6 Hz), 7.01 (d, 2H, J=8.7 Hz), 6.87 (d, 2H, J=8.7 Hz), 4.0 (m, 4H), 1.78 (m, 4H), 1.27 (broad, 28H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$) δ: 162.67, 160.28, 133.87, 132.60, 129.33, 127.67, 127.31, 123.71, 116.72, 115.27, 93.28, 88.10, 68.95, 68.77, 32.57, 30.23, 29.83, 26.67, 23.35, 14.79. Elemental analysis for $C_{42}H_{54}N_2O_3$: calcd C 79.46, H 8.57, N 4.41; found C 79.24, H 8.36, N 4.30%.

4.3.5. 2-(4-Decyloxyphenyl)-5-[4-(4-dodecyloxyphenyl-ethynyl)phenyl]-1,3,4-oxadiazole, 3. This compound was synthesized as described for compound **1**, using 1-dodecyloxy-4-ethynylbenzene (**12**); yield 56%. IR (KBr) ν_{max}/cm^{-1}: 2919, 2850, 1605, 1511, 1497, 1253, 811. ^1H NMR ($CDCl_3$) δ: 8.08 (m, 4H), 7.64 (d, 2H, J=7.7 Hz), 7.48 (d, 2H, J=7.7 Hz), 7.02 (d, 2H, J=8.0 Hz), 6.88 (d, 2H, J=8.0 Hz), 4.0 (m, 4H), 1.79 (m, 4H), 1.27 (broad, 32H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$) δ: 164.65, 163.72, 162.03, 159.60, 133.19, 131.90, 128.69, 127.00, 126.63, 122.99, 116.00, 114.97, 114.59, 92.60, 87.39, 68.27, 68.11, 31.88, 29.56, 29.34, 25.98, 22.67, 14.10. Elemental analysis for $C_{44}H_{58}N_2O_3$: calcd C 79.72, H 8.82, N 4.23; found C 79.70, H 9.09, N 4.07%.

4.3.6. 2-[4-(6-Decyloxy-naphthalen-2-ylethynyl)-phenyl]-5-(4-decyloxy-phenyl)-1,3,4-oxadiazole, 5. This compound was synthesized as described for compound **1**, using 2-decyloxy-6-ethynylnaphthalene (**14**), with a little modification in the work-up. The product was insoluble in TEA, so the reaction mixture was filtered and washed with TEA (50 ml). The white solid residue was purified by column chromatography (silica gel, chloroform), and twice recrystallized from ethanol affording the pure product; yield: 65%. IR (KBr) ν_{max}/cm^{-1}: 2919, 2850, 1612, 1497, 1470, 1256, 842. ^1H NMR ($CDCl_3$) δ: 8.07 (m, 5H), 7.70 (m, 4H), 7.54 (d, 2H, J=8.6 Hz), 7.19–7.00 (m, 4H), 4.06 (m, 4H), 1.83 (m, 4H), 1.28 (broad, 28H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$) δ: 164.69, 163.72, 162.05, 158.11, 134.45, 132.06, 131.62, 129.33, 128.72, 128.35, 126.87, 126.68, 123.26, 119.86, 117.37, 116.04, 115.00, 106.61, 93.07, 88.32, 68.29, 68.14, 31.86, 29.55, 29.31, 29.18, 26.08, 25.99, 22.66, 14.08. Elemental analysis for $C_{46}H_{56}N_2O_3$: calcd C 80.66, H 8.24, N 4.09; found C 80.11, H 8.79, N 4.07%.

4.3.7. 1-Decyl-4-(4-{4-[5-(4-decyloxyphenyl)-1,3,4-oxadiazol-2-yl]phenylethynyl}phenyl)piperazine, 6. This compound was synthesized as described for compound **1**, using 1-decyl-4-(4-ethynylphenyl)piperazine (**15**), with similar work-up as described for compound **5**; yield 55% of a light yellow powder. IR (KBr) ν_{max}/cm^{-1}: 2921, 2849, 2209, 1602, 1515, 1496, 1468, 1244, 840, 818. ^1H

NMR ($CDCl_3$) δ: 8.09–8.04 (m, 4H), 7.62 (d, 2H, J=8.8 Hz), 7.44 (d, 2H, J=8.8 Hz), 7.01 (d, 2H, J=9.2 Hz), 6.87 (d, 2H, J=8.8 Hz), 4.03 (m, 2H), 3.28 (t, J=5.2 Hz), 2.59 (t, J=5.2 Hz), 2.37 (m, 2H), 1.27 (broad, 28H), 0.88 (m, 6H). ^{13}C NMR ($CDCl_3$, ppm) δ: 165.32, 164.47, 162.71, 151.86, 133.52, 132.49, 129.37, 127.97, 127.31, 123.49, 116.76, 115.55, 113.02, 112.17, 93.98, 88.02, 68.98, 59.47, 53.53, 48.73, 32.56, 30.25, 29.99, 29.81, 28.26, 27.53, 26.68, 23.34, 14.77. Elemental analysis for $C_{46}H_{62}N_4O_2$: calcd C 78.59, H 8.89, N 7.97; found C 78.55, H 9.18, N 7.95%.

4.3.8. 2-(4-Decyloxyphenyl)-5-(4-ethynylphenyl)-1,3,4-oxadiazole, 17. (a) *Coupling with 2-methyl-3-butyn-2-ol*. A mixture of compound **9** (2.63 g, 5.76 mmol), $PdCl_2(PPh_3)_2$ (42.0 mg, 0.06 mmol), CuI (5.7 mg, 0.03 mmol) and TPP (15.7 mg, 0.06 mmol) in TEA (50 ml) was kept at 60°C for 40 min. Pure 2-methyl-3-butyn-2-ol (0.95 ml, 8.64 mmol) was added and the mixture stirred under reflux for 4 h. After cooling, the mixture was filtered through a celite pad washing with THF (150 ml). The solvents were evaporated to give a yellow powder; yield 2.21 g (84%), m.p. 126.7°C. IR (KBr) ν_{max}/cm^{-1}: 3369, 2923, 2852, 1612, 1495, 1258, 1170, 843. (b) *Protective group elimination as acetone*. The intermediate alkynol (2 g, 4.35 mmol) was dissolved in 40 ml of toluene. NaOH (0.5 g) was added and the mixture was slowly heated and acetone distilled off over 4 h. Toluene was removed under reduced pressure and the residue recrystallized from heptane to give 1.2 g (69%) of a pale yellow powder, m.p. 109.7°C. IR (KBr) ν_{max}/cm^{-1}:3273, 2956, 2918, 2850, 1610, 1496, 1478, 1260, 1177, 841. ^{1}H NMR ($CDCl_3$) δ: 8.06 (m, 4 H), 7.63 (d, J=8.2 Hz, 2H), 7.01 (d, J=8.7 Hz, 2H), 4.03 (t, 2H), 3.24 (s, 1H), 1.82 (m, 2H), 1.28 (broad, 14H), 0.88 (t, 3H). ^{13}C NMR ($CDCl_3$) δ: 165.5, 164.2, 162.8, 133.4, 129.4, 127.3, 126.0, 124.8, 116.6, 115.7, 83.4, 80.6, 69.0, 32.6, 30.2, 30.0, 29.8, 26.7, 23.4, 14.8.

4.3.9. 4-Iodophenyl 4′-decyloxybenzoate, 19. 4-Decyloxy benzoic acid [20] (1.26 g, 4.55 mmol) and 4-iodophenol (1.09 g, 1.26 mmol) were suspended in CH_2Cl_2 (25 ml) under Ar atmosphere. After addition of DCC (0.94 g, 4.55 mmol) and DMAP (0.049 g, 0.45 mmol) the mixture was stirred for 24 h. The resulting white precipitate was filtered off and washed with CH_2Cl_2 (100 ml). The solvent was evaporated and the white solid recrystallized from ethanol to give 1.51 g (70%) of product, m.p. 86.9°C SmA, 87.8°C I. IR (KBr) ν_{max}/cm^{-1}: 2946, 2918, 2851, 1724, 1606, 1510, 1283, 1265, 1206, 1169, 1053, 847, 758. ^{1}H NMR ($CDCl_3$) δ: 8.11 (d, J=8.7 Hz, 2H), 7.72 (d, J=8.4 Hz, 2H), 6.97 (m, 4H), 4.03 (t, 2H), 1.82 (m, 2H), 1.28 (broad, 14H), 0.88 (t, 3H).

4.3.10. 2-[4-(4′-Decyloxybiphenyl-4-yl-ethynyl)phenyl]-5-(4-decyloxyphenyl)-1,3,4-oxadiazole, 4. Aryl bromide **18** (0.14 g, 0.36 mmol), $PdCl_2(PPh_3)_2$ (25.5 mg, 0.036 mmol), CuI (3.4 mg, 0.018 mmol) and TPP (10.0 mg, 0.036 mmol) in TEA (30 ml) were kept at 60°C for 40 min. Compound **18** (0.146 g, 0.36 mmol), dissolved in 10 ml of THF, was then added dropwise. The reaction mixture was heated under reflux for a further 24 h and left to cool to room temperature. The precipitate was filtered, washing with TEA (50 ml). The solid residue was purified by column chromatography (silica gel, chloroform), and twice recrystallized from ethanol affording the pure product; yield 0.122 g (47%). IR (KBr) ν_{max}/cm^{-1}: 2919, 2849, 1609, 1494, 1474, 1303, 1258, 1175, 1013, 840. ^{1}H NMR ($CDCl_3$) δ: 8.11–8.06 (m, 6H), 7.68 (m, 4H), 7.50 (m, 2H), 7.02 (m, 4H), 4.03 (m, 4H), 1.80 (m, 4H), 1.27 (broad, 28H), 0.87 (t, 6H). Elemental analysis for $C_{48}H_{58}N_2O_3$: calcd C 81.09, H 8.22, N 3.94; found C 81.04, H 8.29, N 3.87%.

4.3.11. 4-Decyloxybenzoic acid 4-{4-[5-(4-decyloxyphenyl)-1,3,4-oxadiazol-2-yl]phenylethynyl}phenyl ester, 7. This compound was obtained by coupling between arylacetylene **17** and 4-iodophenyl 4′-decyloxybenzoate **19** using the same procedure as described for compound **4**; yield 61%. IR (KBr) ν_{max}/cm^{-1}: 2954, 2918, 2850, 1724, 1609, 1497, 1252, 841. ^{1}H NMR ($CDCl_3$) δ: 8.08 (m, 6H), 7.69 – 7.60 (m, 4H), 7.25 (d, 2H, J=8.8 Hz), 7.01 (m, 4H), 4.05 (m, 4H), 1.81 (m, 4H), 1.28 (broad, 28H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$, ppm) δ: 165.1, 164.8, 164.0, 163.9, 151.5, 133.6, 132.7, 129.1, 128.8, 127.1, 123.8, 122.8, 121.9, 116.3, 116.2, 115.7, 113.9, 91.8, 88.9, 68.6, 68.5, 32.1, 29.8, 29.6, 29.5, 29.3, 26.2, 22.9, 14.3. Elemental analysis for $C_{49}H_{58}N_2O_5$: calcd C 77.95, H 7.74, N 3.71; found C 77.48, H 7.56, N 3.73%.

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