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Synthesis, mesomorphic behaviour and photo-luminescent property of new mesogens containing 1,3,4-oxadiazole fluorophore

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Synthesis, mesomorphic behaviour and photo-luminescent property of new mesogens containing 1,3,4-oxadiazole fluorophore

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A series of 1,3,4-oxadiazole derivatives, namely cholesteryl 4-(4-(5-(4-(alkoxy)phenyl)-1,3,4-oxadiazol-2-yl) phenylethynyl)benzoate (**Ch-OXD-*n***, $n = 6, 8, 10$) and methyl 4-(4-(5-(4-(alkoxy)phenyl)-1,3,4-oxadiazol-2-yl) phenylethynyl)benzoate (**Me-OXD-*n***, $n = 6, 8, 10$) were synthesised and characterised by means of ^{1}H NMR, ^{13}C NMR, MS and HRMS. The phase behaviours of these two series of compounds have been investigated by polarising microscopic and calorimetric studies. All compounds **Ch-OXD-*n*** exhibited a cholesteric mesophase with wide mesomorphic temperature range, while the compounds **Me-OXD-*n*** displayed nematic and/or smectic A mesophases with relatively narrow temperature ranges. Both **Ch-OXD-*8*** and **Me-OXD-*8*** in chloroform individually exhibited an intense absorption band ($\lambda_{max} = 330$ nm) and a strong blue fluorescence emission ($\lambda_{max} = 404$ nm) with good photoluminescence quantum yields.

Keywords: heterocyclic liquid crystal; spectroscopic property; cholesteric mesophase; synthesis

1. Introduction

The 1,3,4-oxadiazole moiety has been widely used as an important synthon to prepare emissive and/or electron-transporting materials in organic light-emitting devices (OLEDs) due to outstanding advantages such as high photoluminescence quantum yield, good thermal and chemical stabilities, and electron-deficient property [1–3]. The heterocyclic 1,3,4-oxadiazole unit may also be used as a 'mesogenic core' to construct light-emitting liquid crystalline compounds by rational molecule design. Recently, many such liquid crystalline materials have been prepared, including low molecular weight organic monomer, [4–14] dimer [15, 16], oligomer [17–19] and polymer [20–22], and the relationship between the molecular structure and property has been investigated intensively. Although most such mesogens exhibited fluorescent behaviour with high quantum yields, the mesomorphic temperature ranges are usually narrow, which may limit their practical applications. Cholesterol, as another important building block, has been incorporated extensively in the synthesis of various mesogenic compounds, and cholesteric liquid crystals have attracted considerable interest for their unique optical properties, such as thermochromism, selective reflection light and circular dichromism, and advanced applications in non-linear optical devices, full-colour thermal imaging, and organic pigment [23–28]. In addition, cholesteric liquid crystals often exhibit rich mesophases with wide temperature ranges [29, 30].

In taking advantage of the high photoluminescent yields of 1,3,4-oxadiazole derivatives and the unique properties of cholesteric liquid crystals, these two structural motifs are linked by a phenylethyl ester group in order to produce fluorescent liquid crystalline materials with wide mesogenic temperature range in this work. The phenylethyl unit was chosen for linkage because the corresponding tolane-based liquid crystals usually possess low viscosity and high birefringence [31, 32]. Herein we describe the synthesis, mesomorphic and photoluminescent properties of a new class of mesogens comprising a 1,3,4-oxadiazole fluorophore. The synthetic route as well as the reaction conditions for the target compounds is shown in Scheme 1.

2. Results and discussion

2.1 Synthesis

The 1,3,4-oxadiazole-based aryl iodides **2a**–**2c** were obtained by the condensation reaction of the hydrazides **1a**–**1c** with thionyl chloride according to the literature method [33]. The acetylenes **4a**–**4c** were synthesised in good yields from the aryl iodides **2a**–**2c** by Sonogashira coupling with 2-methyl-3-butyn-2-ol followed by protective group elimination [34–36]. The final products **Ch-OXD-*n*** and **Me-OXD-*n*** were prepared in high yields from **4a**–**4c** and cholesteryl 4-iodobenzoate or methyl 4-iodobenzoate by a Pd/Cu^{I}-catalysed coupling reaction [37]. The molecular structures of all the final products were characterised

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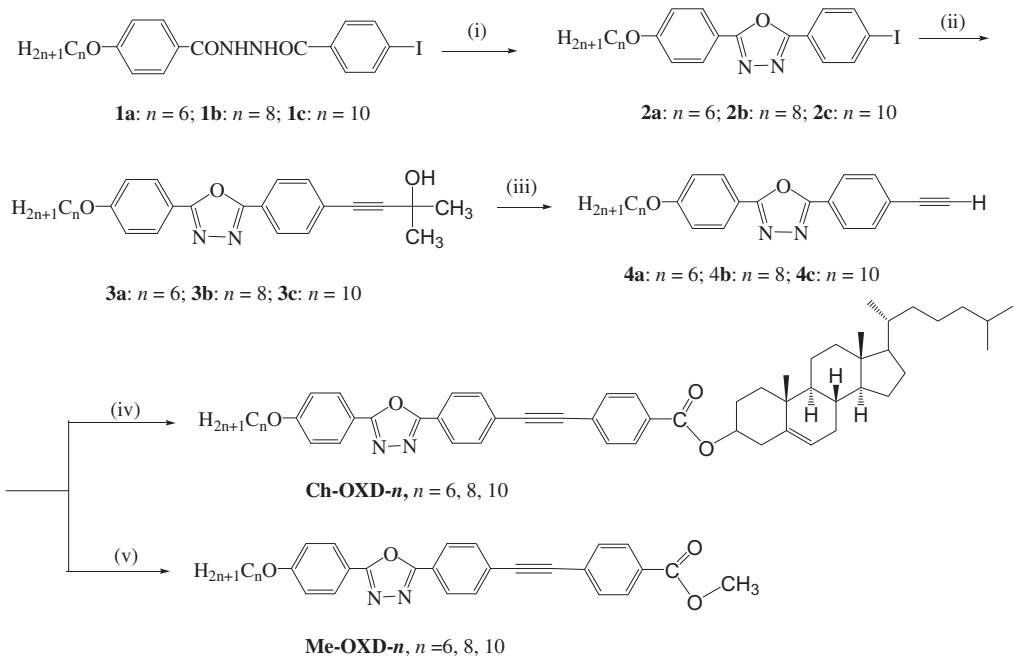

1a: $n = 6$; **1b**: $n = 8$; **1c**: $n = 10$

2a: $n = 6$; **2b**: $n = 8$; **2c**: $n = 10$

3a: $n = 6$; **3b**: $n = 8$; **3c**: $n = 10$

4a: $n = 6$; 4**b**: $n = 8$; **4c**: $n = 10$

Scheme 1. Synthetic route to compounds **Ch-OXD-*n*** and **Me-OXD-*n***. Reagents and conditions: (i) $SOCl_2$; (ii) 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, THF, TEA; (iii) NaOH, toluene; (iv) cholesteryl 4-iodobenzoate, $PdCl_2(PPh_3)_2$, CuI; (v) methyl 4-iodobenzoate, $PdCl_2(PPh_3)_2$, CuI.

by means of ^{1}H NMR ^{13}C NMR, MS and HRMS spectroscopy, and the data are presented in the Experimental details section.

2.2 *Liquid crystalline property*

The thermal behaviours of all of the final products were investigated by polarising optical microscopy (POM) and differential scanning calorimetry (DSC). The endothermic and exothermic peak temperatures obtained in DSC thermograms due to phase transitions were in reasonable agreement with the POM observations. The phase transitions and enthalpy changes for the compounds **Ch-OXD-*n*** and **Me-OXD-*n*** are summarised in Table 1. The cholesteryl benzoates **Ch-OXD-*n*** exhibited only a cholesteric mesophase, which is assigned by the typical oily streaks texture (Figure 1(a)). The observed colour of the textures varies with the change of temperature, which is also the characteristic for the cholesteric phase. It is worthy to note that all of the cholesteryl benzoates **Ch-OXD-*n*** displayed a very wide temperature range during the heating process; however, they all decomposed before the appearance of isotropic liquid, which made it impossible to further investigate the liquid crystalline behaviours upon cooling their isotropic liquid sample. Regarding the methyl benzoates **Me-OXD-*n***, compound **Me-OXD-*6*** exhibited an enantiotropic nematic mesophase with a relatively narrow temperature range. When the terminal alkoxy chain became longer, the analogous compounds **Me-OXD-*8*** and **Me-OXD-*10*** displayed both nematic and smectic A phases enantiotropically, identified respectively through the comparison of the observed textures (Figures 1(b) and 1(c)) with the reference textures collected by Ingo [38]. For the homologous compounds **Me-OXD-*n***, it was found that the stability of the smectic phase increased with the elongation of the terminal alkoxy chains. This

Table 1. Thermal properties of all compounds derived from DSC data.

Compound	Phase transitions[a] T(°C)[b]($\triangle H$[kJ mol^{-1}])
Ch-OXD-*6*	Cr_1 115.9 (8.6) Cr_2 231.6 (38.2) Ch 328.3[c] Td
Ch-OXD-*8*	Cr_1 121.6 (4.3) Cr_2 159.1 (13.0) Cr_3 196.2 (26.1) Ch 314.9[c] Td
Ch-OXD-*10*	Cr_1 125.0 (10.3) Cr_2 197.5 (27.5) Ch 324.4[c] Td
Me-OXD-*6*	Cr_1 168.2 (8.0) Cr_2 190.9 (23.5) N 203.5[d] Iso Iso 200.4[d] N 160.9 (−31.0) Cr_3
Me-OXD-*8*	Cr_1 174.5 (18.9) Cr_2 194.3 (39.2) SmA 206.3 (1.2) N 219.4 (0.5) Iso Iso 210.5 (−0.4) N 195.1 (−0.6) SmA 106.4 (−40.6) Cr_2
Me-OXD-*10*	Cr 190.2 (35.3) SmA 205.5 (0.7) N 209.7 (0.4) Iso Iso 207.5[d] N 194.5 (−1.2) SmA 155.0 (−42.1) Cr

Notes: [a] Cr_n = crystal phase (nth); SmA = smectic A phase; N = nematic phase; Ch = cholesteric phase; Iso = isotropic liquid; Td = decomposed temperature. [b] Determined by DSC at a scan rate of 5°C. [c] The sample was decomposed before changing into the isotropic liquid. [d] Transition only detected by optical microscopy.

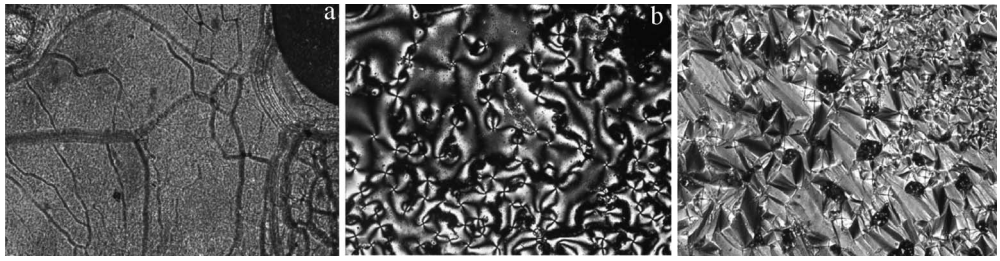

Figure 1. Selected POM images (magnification ×200). (a) Cholesteric phase with oily streaks texture for **Ch-OXD-*6*** at 284.0°C on heating; (b) nematic mesophase with two and four brushes textures for **Me-OXD-*10*** at 198.5°C in cooling cycle; (c) smectic A mesophase with fan-shaped texture for **Me-OXD-*10*** at 190.0°C on cooling (colour version online).

effect of the alkoxy chains on mesomorphic behaviour is common in the calamitic mesogens [39].

The thermal stability of the selected compounds **Ch-OXD-*6***, **Ch-OXD-*8*** and **Me-OXD-*8*** was investigated by thermogravimetric analysis (TGA). The TGA curves of these solid samples recorded at 25–600°C under N_2 atmosphere are depicted in Figure 2, which shows that all of the final products exhibited no weight loss below 320°C, indicating that these organic compounds possess excellent thermal stability. The onset decomposition temperatures (336.3°C for **Ch-OXD-*6***, 326.3°C for **Ch-OXD-*8***, and 351.8°C for **Me-OXD-*8***) revealed that the thermal stability of **Me-OXD-*8*** was slightly better than that of **Ch-OXD-*6*** and **Ch-OXD-*8***, which was also consistent with the POM observations.

2.3 UV-vis absorption and photoluminescence

Usually, the length of the terminal alkoxy chains affected the spectroscopic features of the 1,3,4-oxadiazole derivatives very slightly, [16] so only compounds **Ch-OXD-*8*** and **Me-OXD-*8*** were selected as representative candidates to compare the effect of the terminal cholesteryl and methyl groups on the optical behaviours. The photoluminescence quantum yield, Φ_{PL}, was calculated using the formula [40, 41]

$$\Phi_{PL} \approx \Phi_{std} \times \left(\frac{Abs_{std}}{Abs_{sample}} \times \frac{A_{sample}}{A_{std}} \times \frac{\eta^2_{sample}}{\eta^2_{std}} \right),$$

where Φ_{std} is the photoluminescence quantum yield of the standard quinine sulphate ($\Phi_{std} = 0.546$, 0.1 N sulphuric acid) [42], Abs_{std} and Abs_{sample} are the absorbance of the standard and sample, respectively, A_{sample} and A_{std} are the integrated area of the emission peak of the sample and standard, respectively, and η_{sample} and η_{std} are the refractive indices of the sample and standard solutions.

The UV-vis absorption and photoluminescence spectra under excitation at the absorption maximum for **Ch-OXD-*8*** and **Me-OXD-*8*** in 10^{-6} M chloroform solution are presented in Figure 3. Both **Ch-OXD-*8*** and **Me-OXD-*8*** exhibit an intense broad absorption at ca. 330 nm with high molar absorptivity and a strong blue fluorescence emission (λ_{max} at ca. 404 nm)

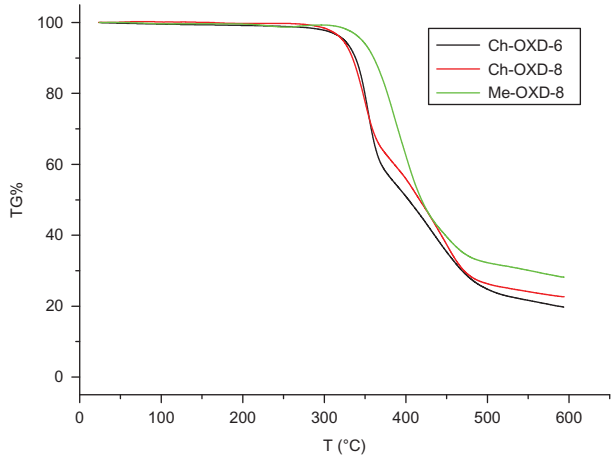

Figure 2. Thermogravimetric analysis of compounds **Ch-OXD-*6***, **Ch-OXD-*8*** and **Me-OXD-*8*** (colour version online).

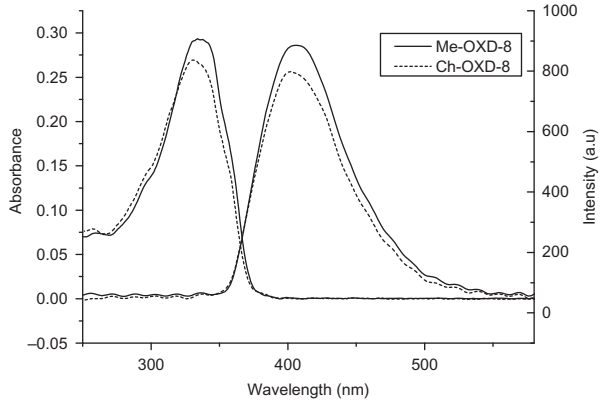

Figure 3. Absorption and photoluminescence spectra of compounds **Ch-OXD-*8*** (solid line) and **Me-OXD-*8*** (dashed line).

with good photoluminescence quantum yields (72% and 75%, respectively). By comparison of the spectroscopic features and the molecular structures of **Ch-OXD-*8*** and **Me-OXD-*8***, we can conclude that the optical properties are mainly determined by the same conjugated core in these compounds, whereas the different terminal cholesteryl and methyl groups have little effect on their optical behaviours.

3. Conclusions

We report the synthesis and mesomorphism of six new compounds derived from 1,3,4-oxadiazole fluorophore. The compounds **Ch-OXD-*n*** with a terminal cholesteryl segment exhibit a chiral nematic mesophase with very wide temperature range, while the compounds **Me-OXD-*n*** with a terminal methyl group display enantiotropic nematic and smectic A mesophases with relatively narrow temperature ranges. All the target compounds displayed a strong blue fluorescence emission with good quantum yields in chloroform solution. The relationship between the structures and properties was discussed briefly in the context of the terminal groups and the length of alkoxy chains. The results showed that the terminal groups affected the liquid crystalline behaviour greatly, but had little effect on the photoluminescent property.

4. Experimental details

4.1 General

The hydrazides **1a**–**1c** were prepared according to the literature method [33]. All other materials were used as purchased from commercial sources. The solvents used for synthesis were of analytical grade. Crude products were purified by column chromatographic technique using silica gel 60 (Branch of Qingdao Haiyang Chemical Co., Ltd) as a stationary phase. Thin layer chromatography (TLC) was performed on silica gel plates (Merck, silica gel F_{254}).

Solution ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer and the chemical shifts are quoted in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Electrospray ionisation (ESI) mass spectra were recorded on a Finnigan LCQ Advantage spectrometer and high-resolution mass spectra were obtained with a Finnigan MAT 95 mass spectrometer. Melting points were determined with an X-4 melting point apparatus (Beijing Taike Instrument Co. Ltd.), and the thermometer was uncorrected. The liquid crystalline behaviours were investigated by POM (OLYMPUS BX51) equipped with a temperature-controlled hot stage. Thermal analyses of the final products were studied by a NETZSCH DSC 204 differential scanning calorimeter with a heating rate of 5°C/min and pre-calibrated with indium standard. TGA was performed with a Perkin-Elmer TGA-7 with a heating rate of 10°C/min under a stream of flowing N_2. UV/vis spectra were recorded with a Cary 300 spectrophotometer. Steady-state emission spectra were recorded with a VARIAN spectrophotometer.

4.2 Synthesis and characterisation

*4.2.1 General procedure for preparation of **2a–2e***

The mixture of the respective hydrazide **1a–1c** (10 mmol) in 30 ml of thionyl chloride was refluxed for 8 h. Then the excessive thionyl chloride was removed by vacuum distillation. The reaction mixture was slowly poured into cold water in an ice bath, and a solution of dilute sodium hydroxide was added to neutralise the reaction mixture. The precipitate was then collected on a filter, washed with distilled water and further purified by silica gel column chromatography using ethyl acetate/dichloromethane (v/v = 1:15) as an eluent to yield the products **2a–2c**, respectively.

2-(4-Iodophenyl)-5-(4-hexyloxyphenyl)-1,3,4-oxadiazole 2a: Yield, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (d, J = 8.8 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 1.87–1.77 (m, 2H), 1.53–1.43 (m, 2H), 1.41–1.31 (m, 4H), 0.92 (t, J = 6.8 Hz, 3H). ESI-MS: m/z: 449.20 $[M+1]^+$.

2-(4-Iodophenyl)-5-(4-octyloxyphenyl)-1,3,4-oxadiazole 2b: Yield, 81%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 9.2 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 1.87–1.77 (m, 2H), 1.53–1.43 (m, 2H), 1.42–1.25 (m, 8H), 0.92 (t, J = 6.8 Hz, 3H). ESI-MS: m/z: 477.28 $[M+1]^+$.

2-(4-Iodophenyl)-5-(4-decyloxyphenyl)-1,3,4-oxadiazole 2c: Yield, 83%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 9.2 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 1.87–1.77 (m, 2H), 1.56–1.45 (m, 2H), 1.44–1.03 (m, 12H), 0.92 (t, J = 6.8 Hz, 3H). ESI-MS: m/z: 505.35 $[M+1]^+$.

*4.2.2 General procedure for the synthesis of compounds **3a-3c***

The respective precursors **2a–2c** (6 mmol, 1 equiv) and 2-methyl-3-butyn-2-ol (12 mmol, 2 equiv) were dissolved in dry THF (60 ml). To the as-formed solution, CuI powder (60 mg) and $Pd(PPh_3)_2Cl_2$ (120 mg)

were added in one portion followed by triethylamine (40 ml). The reaction mixture was stirred under N_2 for 12 h at about 80°C. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure to remove the solvents. The crude product was dissolved in dichloromethane and exacted with aqueous ammonium chloride solution. The organic phase was then washed with brine and dried over anhydrous Na_2SO_4. The crude product was isolated by evaporating the solvent and purified by chromatography on silica gel column using a mixture of dichloromethane and ethyl acetate (15:1 by volume) as eluent.

2-(4-hexyloxyphenyl)-5-[4-(3-hydroxy-3-methylbutynyl)phenyl]-1,3,4-oxadiazole 3a white solid, yield: 97%. m.p. 135–136°C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 8.8$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 4.04 (t, $J = 6.4$ Hz, 2H), 2.18 (s, 1H), 1.87–1.78 (m, 2H), 1.65 (s, 6H), 1.54–1.44 (m, 2H), 1.41–1.31 (m, 4H), 0.92 (t, $J = 6.8$ Hz, 3H). ESI-MS: m/z: 405.38 $[M+1]^+$.

2-(4-octyloxyphenyl)-5-[4-(3-hydroxy-3-methylbutynyl) phenyl]-1,3,4-oxadiazole 3b white solid, yield: 98%; m.p. 101–102°C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 8.8$ Hz, 2H), 7.55 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 8.8$ Hz, 2H), 4.03 (t, $J = 6.4$ Hz, 2H), 2.30(s, 1H), 1.86–1.77 (m, 2H), 1.65 (s, 6H), 1.52–1.43 (m, 2H), 1.41–1.26 (m, 8H), 0.90 (t, $J = 6.8$ Hz, 3H). ESI-MS: m/z: 433.38 $[M+1]^+$.

2-(4-decyloxyphenyl)-5-[4-(3-hydroxy-3-methylbutynyl)phenyl]-1,3,4-oxadiazole 3c white solid, yield: 95%; m.p. 102–104°C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (d, $J = 8.4$ Hz, 2H), 8.06 (d, $J = 8.8$ Hz, 2H), 7.56 (d, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 4.03 (t, $J = 6.4$ Hz, 2H), 2.16 (s, 1H) 1.88–1.77 (m, 2H), 1.65 (s, 6H), 1.53–1.20 (m, 14H), 0.89 (t, $J = 6.8$ Hz, 3H). ESI-MS: m/z: 461.39 $[M+1]^+$.

*4.2.3 General procedure for synthesis of compounds **4a–4c***

The respective compounds **3a–3c** (2.2 g, 5.5 mmol) was dissolved in dry toluene (30 ml). Sodium hydroxide powder (freshly ground from pellets) (30 mmol) was added, and the mixture was stirred for 8 h in an oil bath at 130°C. The reaction mixture was cooled to room temperature, and then filtered through a Celite pad to remove any solids. The filtrate was evaporated in vacuo to yield the crude products, which were chromatographed on a silica gel column using dichloromethane/ethyl acetate 20:1 as eluent.

2(4-hexyloxyphenyl)-5-(4-ethynylphenyl)-1,3,4-oxadiazole 4a white solid, yield: 96%. m.p. 117–118°C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.09 (d, $J = 8.4$ Hz, 2H), 8.06 (d, $J = 8.8$ Hz, 2H), 7.64 (d, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 4.04 (t, $J = 6.4$ Hz, 2H), 3.25 (s, 1H), 1.88–1.76 (m, 2H), 1.54–1.42 (m, 2H), 1.42–1.29 (m, 4H), 0.92 (t, $J = 6.8$ Hz, 3H). ESI-MS: m/z: 347.32 $[M+1]^+$.

2-(4-octyloxyphenyl)-5-(4-ethynylphenyl)-1,3,4-oxadiazole 4b white solid, yield: 95%. m.p. 110–111°C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.08 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 9.2$ Hz, 2H), 7.64 (d, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 9.2$ Hz, 2H), 4.03 (t, $J = 6.4$ Hz, 2H), 3.25 (s, 1H), 1.88–1.76 (m, 2H), 1.53–1.43 (m, 2H), 1.41–1.23 (m, 8H), 0.90 (t, $J = 6.8$ Hz, 3H). ESI-MS: m/z: 375.27 $[M+1]^+$.

2-(4-decyloxyphenyl)-5-(4-ethynylphenyl)-1,3,4-oxadiazole 4c white solid, yield: 92%. m.p. 105–106°C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.09 (d, $J = 8.0$ Hz, 2H), 8.06 (d, $J = 8.8$ Hz, 2H), 7.64 (d, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 4.04 (t, $J = 6.4$ Hz, 2H), 3.25 (s, 1H), 1.88–1.76 (m, 2H), 1.52–1.43 (m, 2H), 1.40–1.19 (m, 12H), 0.89 (t, $J = 6.4$ Hz, 3H). ESI-MS: m/z: 403.30 $[M+1]^+$.

4.2.4 General procedures for synthesis of **Ch-OXD-*n*** *and* **Me-OXD-*n***

These final products were synthesised in the same manner as described above in the preparation of the intermediate compound **3a–3c**.

Cholesteryl 4-(4-(5-(4-(hexyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenylethynyl)benzoate Ch-OXD-*6* white solid, yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.13 (d, $J = 8.0$ Hz, 2H), 8.07 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 7.03 (d, $J = 8.4$ Hz), 5.46–5.40 (m, 1H), 4.94–4.80 (m, 1H), 4.04 (t, $J = 6.4$ Hz, 2H), 2.47 (d, $J = 7.6$ Hz, 2H), 2.09–0.82 (m, 48H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 165.3, 164.8, 163.5, 162.1, 139.5, 132.3, 131.6, 130.6, 129.6, 128.7, 127.1, 126.7, 125.9, 123.9, 122.9, 115.9, 115.0, 91.4, 91.3, 74.9, 68.3, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 31.9, 31.8, 31.6, 29.1, 28.2, 28.0, 27.9, 25.7, 24.3, 23.9, 22.9, 22.7, 22.6, 21.0, 19.4, 18.7, 14.1, 11.9. ESI-MS: m/z: 835.57 $[M+H]^+$. HRMS $[M+H]^+$ Calcd for $C_{56}H_{69}N_2O_4$: 835.5408; Found: 835.5404.

Cholesteryl 4-(4-(5-(4-(octyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenylethynyl)benzoate Ch-OXD-*8* white solid, yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.13

(d, $J = 8.4$ Hz, 2H), 8.07 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.4$ Hz, 2H), 5.48–5.38 (m, 1H), 4.93–4.80 (m, 1H), 4.04 (t, $J = 6.4$ Hz, 2H), 2.47 (d, $J = 8.4$ Hz, 2H), 2.11–0.87 (m, 52H), 0.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 165.3, 164.8, 163.6, 162.1, 139.5, 132.3, 131.6, 130.6, 129.6, 128.7, 127.1, 126.7, 125.9, 123.9, 122.9, 115.9, 115.0, 91.4, 91.3, 74.9, 68.3, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 32.0. 31.9, 31.8, 29.4, 29.3, 29.1, 28.3, 28.0, 27.9, 26.0, 24.3, 23.8, 22.9, 22.7, 22.6, 21.1, 19.4, 18.7, 14.1, 11.9. ESI-MS: m/z: 863.43 $[M+1]^+$. HRMS $[M+1]^+$ Calcd for $C_{58}H_{73}N_2O_4$: 863.5721; Found: 863.5718.

Cholesteryl 4-(4-(5-(4-(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenylethynyl)benzoate Ch-OXD-*10* white solid, yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.13 (d, $J = 8.4$ Hz, 2H), 8.07 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.61 (t, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 5.46–5.40 (m, 1H), 4.93–4.82 (m, 1H), 4.04 (t, $J = 6.4$ Hz, 2H), 2.47 (d, $J = 7.2$ Hz, 2H), 2.08–0.80 (m, 56H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 164.3, 163.7, 162.5, 161.0, 138.5, 131.2, 130.5, 129.6, 128.5, 127.7, 126.1, 125.7, 124.9, 122.8, 121.9, 114.9, 113.9, 90.4, 90.2, 73.9, 67.3, 55.6, 55.1, 49.0, 41.3, 38.7, 38.5, 37.2, 36.0, 35.6, 35.1, 34.8, 30.9, 30.8, 28.5, 28.4, 28.3, 28.1, 27.2, 27.0, 26.8, 25.0, 23.3, 22.8, 21.8, 21.7, 21.6, 20.0, 18.3, 17.7, 13.1, 10.8. ESI-MS: m/z: 891.53 $[M+1]^+$. HRMS $[M+1]^+$ Calcd for $C_{60}H_{77}N_2O_4$: 891.6034; Found: 891.6016.

Methyl 4-(4-(5-(4-(hexyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenylethynyl)benzoate Me-OXD-*6* white solid; yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.13 (d, $J = 8.4$ Hz, 2H), 8.07 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.62 (t, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 4.04 (t, $J = 6.8$ Hz, 2H), 3.94 (s, 3H), 1.88–1.75 (m, 2H), 1.55–1.43 (m, 2H), 1.42–1.30 (m, 4H), 0.92 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 165.4, 163.7, 162.5, 161.0, 131.2, 130.6, 128.8, 128.5, 127.7, 126.3, 125.7, 124.8, 122.8, 114.8, 113.9, 90.4, 90.2, 67.2, 51.3, 30.5, 28.0, 24.6, 21.6, 13.0. ESI-MS: m/z: 481.36 $[M+1]^+$. HRMS $[M+1]^+$ Calcd for $C_{30}H_{28}N_2O_4$: 481.2122; Found: 481.2139.

Methyl 4-(4-(5-(4-(octyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenylethynyl)benzoate Me-OXD-*8* white solid, yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.12 (d, $J = 8.4$ Hz, 2H), 8.06 (d, $J = 8.0$ Hz, 2H), 8.05 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.62 (t, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 8.4$ Hz, 2H), 4.03 (t, $J = 6.4$ Hz, 2H), 3.94 (s, 3H), 1.87–1.77 (m, 2H), 1.54–1.42 (m, 2H), 1.42–1.26 (m, 8H), 0.90 (t, $J = 6.4$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 166.5, 164.8, 163.6, 162.1, 132.3, 131.6, 129.9, 129.6, 128.7, 127.4, 126.7, 125.9, 123.9, 116.0, 115.0, 91.4, 91.3, 68.3, 52.3, 31.8, 29.4, 29.2, 29.1, 26.0, 2.7, 14.1. ESI-MS: m/z: 509.38 $[M+1]^+$. HRMS $[M+1]^+$ Calcd for $C_{32}H_{32}N_2O_4$: 509.2435; Found: 509.2447.

Methyl 4-(4-(5-(4-(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenylethynyl)benzoate Me-OXD-*10* white solid, yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.13 (d, $J = 8.4$ Hz, 2H), 8.07 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.62 (t, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 4.04 (t, $J = 6.4$ Hz, 2H), 3.94 (s, 3H), 1.87–1.77 (m, 2H), 1.53–1.43 (m, 2H), 1.42–1.21 (m, 12H), 0.89 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 166.5, 164.8, 163.6, 162.1, 132.3, 131.6, 129.9, 129.6, 128.7, 127.4, 126.7, 125.9, 123.9 115.9, 115.0, 91.4, 91.3, 68.3, 52.3, 31.9, 29.6, 29.4, 29.3, 29.1, 26.0, 22.7, 14.2. ESI-MS: m/z: 537.49 $[M+1]^+$. HRMS $[M+1]^+$ Calcd for $C_{32}H_{32}N_2O_4$: 537.2748; Found: 537.2758.

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