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Synthesis, optical properties and thermal behaviour of 1,3,4-oxadiazole-based twin dimers

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The synthesis, optical properties and thermal behaviour of five new 1,3,4-oxadiazole-based light-emitting twin dimers are described. The synthesised compounds were obtained in good yields following a convergent synthetic approach. The products **8a–8e** display blue fluorescence both in solution and in solid phases. All compounds exhibited dendritic crystalline growth. Furthermore, compound **8b** also exhibited liquid crystal properties. Due their high thermal stabilities thin films of **8a–8e** could be prepared by thermal evaporation technique. The morphology of the film surface was investigated using atomic force microscopy (AFM).

Keywords: 1,3,4-oxadiazole dimers; twin dimers; luminescent materials; OLEDs

1. Introduction

Luminescent organic compounds have attracted significant interest among chemists and physicists due their importance in the development of organic light-emitting diodes (OLEDs), optical devices, lasers and optical sensors (1). In particular, much attention has been given to compounds with twin dimers due to their great importance as models in the study of polymeric materials (2). Some of them have also been reported to exhibit ionic liquid (3) and liquid crystal properties (4). Recently, Araya *et al.* described the use of twin dimers as dopants in display mixtures in order to reduce their rotational viscosity, thus decreasing the time of response without any significant effect on elastic properties (5).

Compounds containing a 1,3,4-oxadiazole moiety have been extensively investigated because of their high quantum yield of luminescence, thermal stability and electron-transport properties (6). In 1989, a 1,3,4-oxadiazole-based compound, 2-biphenyl-4-yl-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), was used for the first time in an OLED composition (7). This compound exhibited higher electron affinity (EA) and ionisation potential (IP) compared to similar compounds reported previously (7). In 2000, another compound, 2,5-dinaphthalen-1-yl-1,3,4-oxadiazole (BND), was found to also exhibit a very similar profile (8). The main problem in the use of small-molecule based compounds, such as PBD and BND, is that generally they do not form stable thin films due to crystallisation during solvent evaporation (6). Bis-1,3,4-oxadiazoles containing aromatic rings or double bonds as the spacer have been

synthesised to increase the stability of thin films (6). Although polymers containing 1,3,4-oxadiazoles have high thermal stability, they are very insoluble in organic solvents and are difficult to purify (9, 10). Therefore, it is clear that luminescent twin dimers containing 1,3,4-oxadiazoles are strong candidates for technological applications, particularly as emitters for optical devices or charge transporters for OLEDs.

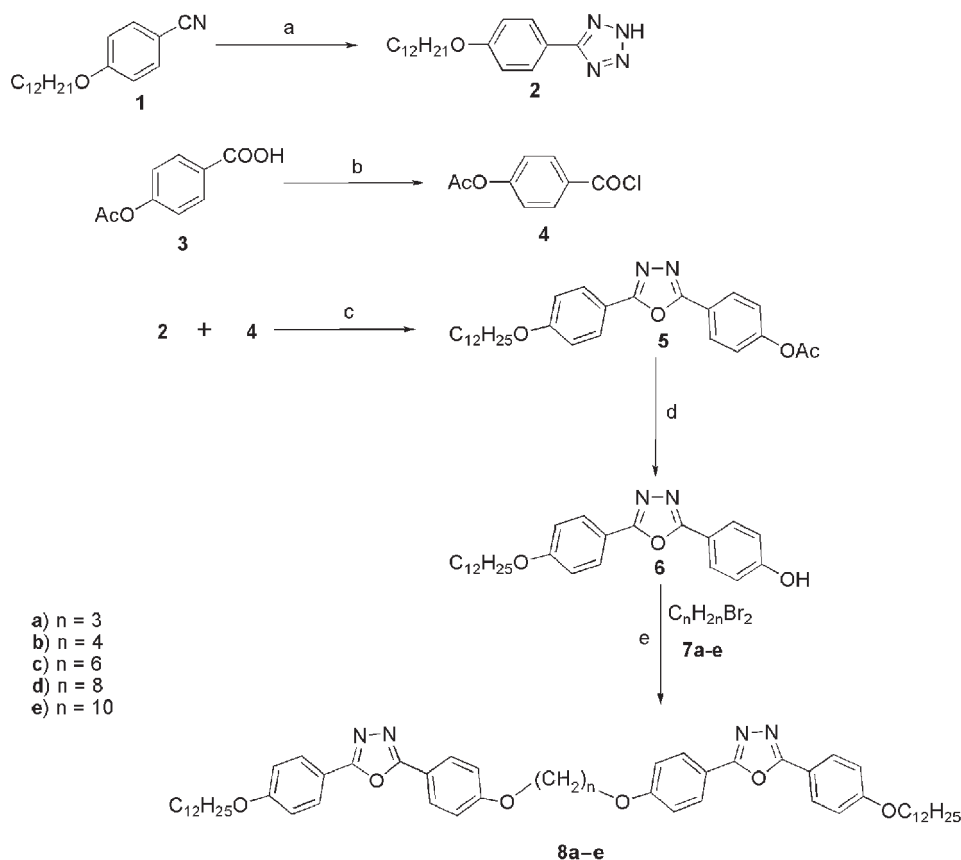
In this paper, we report the synthesis, thermal properties and luminescence studies in solution and solid phase of twin dimers of 1,3,4-oxadiazoles containing an alkyl chain as spacer.

2. Results and discussion

Synthesis

The synthesis of twin dimers **8a–8e** was accomplished following the approach described in Scheme 1. 4-Dodecyloxyphenyltetrazole **2** was synthesised in 84% yield from 4-dodecyloxybenzotrile **1** and sodium azide by 1,3-dipolar cycloaddition. The formation of the 1,3,4-oxadiazole ring was achieved by a Huisgen reaction between tetrazole **2** and freshly prepared acyl chloride **4** in pyridine under reflux. Compound **5** was obtained in 68% yields. Hydrolysis of the acetyl group of **5** yielded compound **6** in 85% yield (6). The reaction of **6** with dibromoalkanes **7a–7e** in butanone under reflux in the presence of K₂CO₃ and a catalytic amount of KI furnished the desired compounds **8a–8e** in good yields (70–81%). Furthermore, we did not observe the formation of monoalkylated products.

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Scheme 1. Synthesis of compounds **8a–8e**. Conditions (yield): (a) NaN_3 , NH_4Cl , DMF, reflux 12 h (84%); (b) SOCl_2 , DCM, reflux 16 h; (c) pyridine, reflux 16 h (68%); (d) KOH , $\text{MeOH}:\text{H}_2\text{O}$, reflux 4 h (85%); (e) K_2CO_3 , $\text{KI}_{(\text{cat})}$, butanone, reflux 12 h (70–81%).

Absorption and fluorescent properties

The UV-vis absorption and fluorescence spectroscopic data in chloroform for final compounds **8a–e** are summarized in Table 3. All synthesized compounds displayed identical absorption and fluorescence spectra (Figure 1). These compounds show maximum absorption peak in 304nm, and maximum emission peak in 357nm. Therefore, the Stokes shift to this series is 53nm. The value of molar absorption to these compounds is around $3\text{--}16 \times 10^{-6} \text{ mol}^{-1} \text{ cm}^{-1}$. The quantum yields of luminescence for these materials are the same as found for the standard compound 2-phenyl-5-(4-diphenyl)-1,3,4-oxadiazole ($\Phi_{\text{PL}} \sim 0.85$). All compounds described in this work exhibited blue emission typical of π -conjugated system. This transition may be attributed to π - π^* fluorescence.

Thermal behaviour

The transition temperatures, phase assignments and thermal stabilities of the final compounds were investigated by thermal polarising optical microscopy (POM), differential scanning calorimetry (DSC) and

thermogravimetric analysis (TGA); these results are summarised in Table 1. Compounds **8a–8e** exhibit high thermal stability and their decomposition temperatures are between 439 and 450°C.

In order to establish the effects of varying the internal alkoxy chain length on the mesomorphic behaviour, the homologous series **8a–8e** was synthesised. With the exception of **8b**, compounds **8a–8e** did not exhibit mesomorphic behaviour, but their melting transitions (Cr–I) were observed. Although the dimers exhibit dendritic crystalline growth, no liquid crystalline property was observed. The sole exception among them was compound **8b**, which exhibited liquid crystalline behaviour over a short monotropic phase range ($\Delta T = 12^\circ\text{C}$). Figure 2 shows the DSC heating and cooling scans for compound **8b**. A smectic C (SmC) phase was characterised by the nucleation of bâtonnets, which grew upon cooling the sample in the isotropic phase to form both schlieren and broken fan-shaped textures (Figure 3).

The dependence of the melting points on chain length for this series is shown in Figure 4. It can be seen that as the internal chain length is increases, the

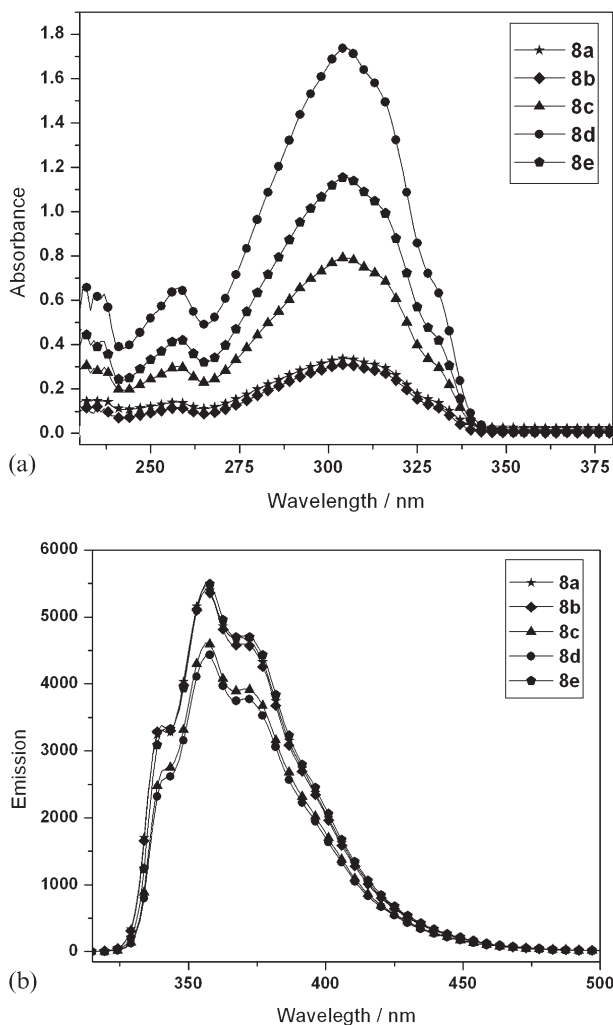


Figure 1. (a) Absorption and (b) fluorescence spectra of compounds **8a–8e** in chloroform solution.

melting points decrease and clearing points increase but, at the same time, the liquid crystalline behaviour disappears. The 2,5-disubstituted 1,3,4-oxadiazoles have a large curvature (II), associated with the bond angle of 134° . Since the number of internal spacer – CH_2 – groups is more than two, they can assume

various conformations, although some of them are not appropriate. In fact, the rigidity of the molecule decreases, leading to the loss of mesomorphism.

AFM of thin films

Thin films (130 nm) of compounds **8a–8e** were deposited on glass plates by thermal evaporation. All the films were shown to be homogeneous, as confirmed from AFM images (Figure 5). Measurements of roughness of the surfaces were around 7.00 nm for all the synthesised compounds. The morphology of the films presented the formation of spheres, but no formation of crystallised layers was observed.

3. Conclusion

In summary, we have achieved the synthesis of a series of luminescent 1,3,4-oxadiazole-based twin dimers containing an alkyl chain as the spacer. These compounds displayed blue fluorescence in solution and also in the solid phase. All synthesised compounds presented good thermal stability. Consequently, 130 nm thin films can easily be obtained by thermal evaporation. Studies towards the use of these compounds as emitters for OLEDs are under way.

4. Experimental

Characterisation

All reagents were obtained from commercial sources and used without further purification. Infrared spectra were recorded on a Perkin-Elmer model 283 spectrometer using KBr discs. ^1H NMR spectra were obtained with a Varian Mercury Plus 400 MHz instrument using tetramethylsilane (TMS) as the internal standard. Elemental analyses were performed with a Carlo Erba instrument model E-1110. The melting points, thermal transitions and mesomorphic textures were determined using an Olympus BX50 microscope equipped with a Mettler

Table 1. Transition temperatures ($^\circ\text{C}$) and associated enthalpy values (kJ mol^{-1} , in parentheses) for compounds **8a–8e**.

Compound	Transition	T , heating (ΔH) ^a	T , cooling (ΔH)	$T_{\text{dec}}/^\circ\text{C}$ ^b
8a	Cr–I	219.9 (85.1)	221.6 (–74.4)	442
8b ^c	Cr–I	185.1 (78.5)	—	441
	I–SmC	—	186.2 (–11.6)	
	SmC–Cr'	—	177.3 (–48.3)	
	Cr'–Cr	—	132.8 (–7.36)	
8c	Cr–I	172.1 (79.1)	172.2 (–79.9)	450
8d	Cr–I	167.7 (72.0)	168.0 (–81.8)	449
8e	Cr–I	157.1 (61.9)	155.6 (–63.7)	439

^aDetermined by DSC $10^\circ\text{C min}^{-1}$; ^bBy TGA, onset of decomposition $10^\circ\text{C min}^{-1}$; ^cOptical microscopy shows monotropic smectic C.

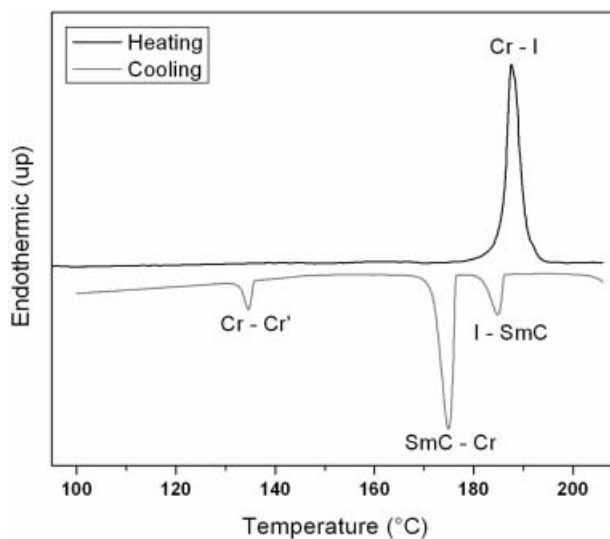


Figure 2. Second heating and cooling DSC trace of **8b**. This liquid crystalline compound exhibited a monotropic thermal range.

Toledo FP-82 hot-stage and a PM-30 exposure control unit. An HP UV-visible model 8453 spectrophotometer was used to record absorption spectra. Fluorescence spectra were recorded on a Hitachi-F-4500. The thin films (~ 130 nm) of compounds **8a–8e** were thermo evaporated ($\sim 10^{-6}$ mbar) over a glass substrate in Auto 306 Vacuum Coating Systems from Edwards Vacuum.

Syntheses

4-Dodecyloxyphenyltetrazole (**2**).

A mixture of 4-dodecyloxibenzonitrile (10 g, 34 mmol), NaN_3 (3.4 g, 52 mmol) and NH_4Cl (2.8 g, 52 mmol) in DMF (60 ml) was refluxed for 12 h. The reaction contents were then cooled to room temperature and

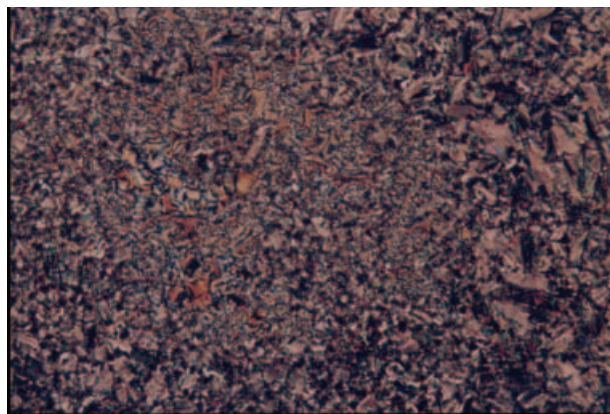


Figure 3. Photomicrograph of schlieren and broken fan-shaped textures of SmC phase exhibited by **8b** at 186.3°C ($33\times$).

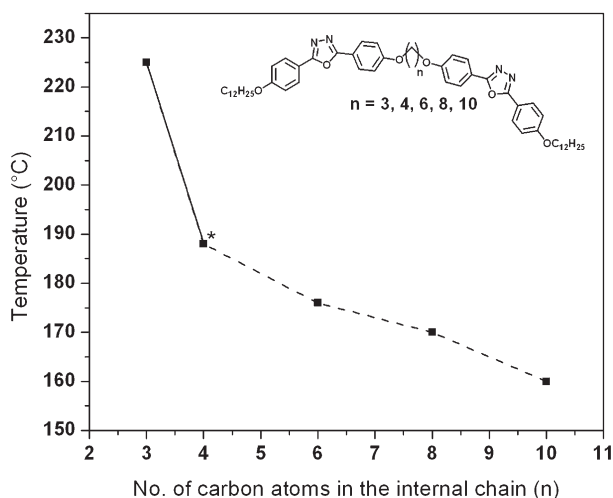


Figure 4. Melting point versus number of carbon atoms in the internal chain (n). (*) Monotropic liquid crystalline compound, **8b**.

poured into cold water. The resulting solution was acidified with 5M HCl. The crude precipitate was filtered off, washed with water and crystallised from EtOH/ H_2O to afford desired product as colourless crystals. Yield 84%, m.p. $153\text{--}154^\circ\text{C}$ [Lit. m.p. $152\text{--}155^\circ\text{C}$ (12)]. The IR and ^1H NMR spectra agreed with the previously reported data (12).

Acetic acid 4-[5-(4-dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl]phenyl ester (**5**).

Freshly prepared 4-acetoxybenzoyl chloride (**13**) (3.00 g, 15 mmol) and (4-dodecyloxyphenyl)tetrazole (5.00 g, 15 mmol) were stirred under reflux in pyridine for 16 h. After cooling, the reaction mixture was poured into cold water. The precipitate was then filtered and crystallised from ethanol to give colourless crystals. Yield 68%, m.p. $103\text{--}104^\circ\text{C}$. IR (KBr, cm^{-1}): 2919, 2849, 1750, 1590, 1552. ^1H NMR (400°MHz , CDCl_3): δ 8.04 (m, 4H), 7.04 (m, 4H), 6.98 (d, $J=9.2$ Hz, 2H), 4.08 (t, $J=6.8$ Hz, 2H), 2.34 (m, 3H), 1.81 (m, 2H), 1.53 (m, 16H), (t, $J=6.8$ Hz, 3H). Elemental analysis: calculated for $\text{C}_{28}\text{H}_{36}\text{N}_2\text{O}_4$, C 72.39, H 7.81, N 6.03; found, C 72.22, H 7.73, N 6.15%.

4-[5-(4-Dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl]phenol (**6**).

Compound **5** (2.00 g, 4.3 mmol) and KOH (0.33 g, 6.0 mmol) in a mixture of EtOH: H_2O (3:7, 60 ml) were refluxed while stirring for 4 h. The resulting solution was acidified with 5M HCl. The crude precipitate was filtered off, washed with water and crystallised from EtOH to afford the desired product as colourless

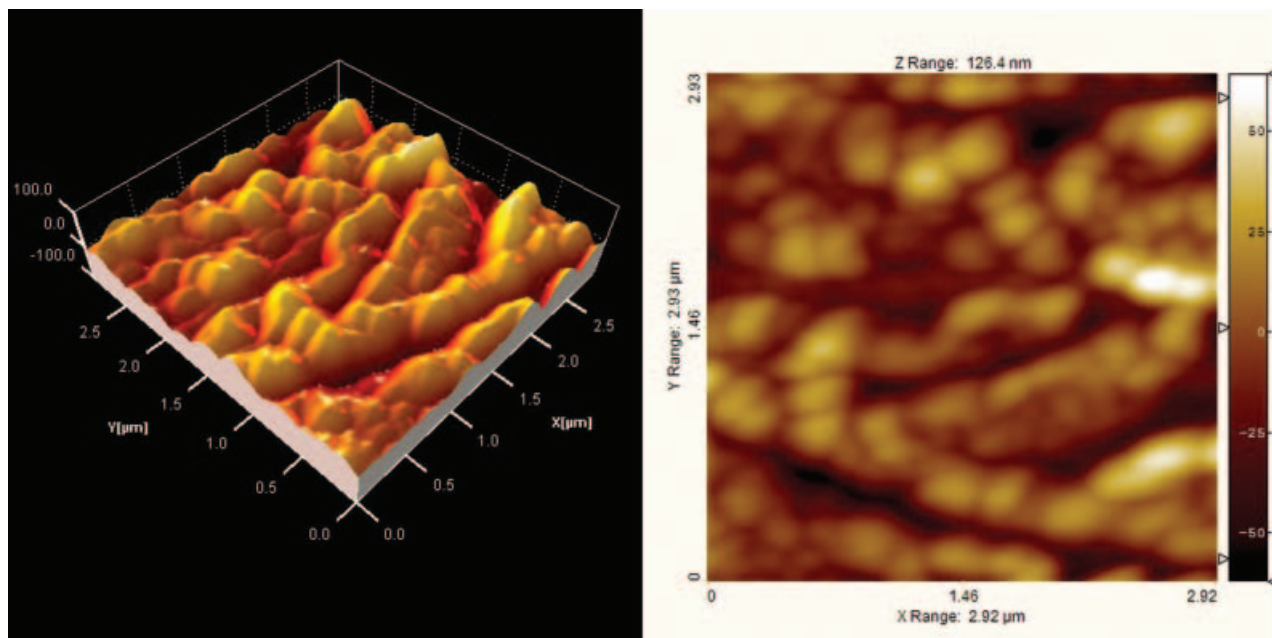


Figure 5. AFM images showing the surface morphology of solid films of compound **8d**.

crystals. Yield 85%, m.p. 146–147°C [Lit. m.p. 145–147°C (*14*)]. The IR and ^1H NMR spectra furnished the same absorptions as reported previously (*14*).

α,ω -Bis{4-[5-(4-dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl]}alkanes (**8a–8e**).

A mixture of compound **6** (1.0 mmol), the appropriate α,ω -dibromoalkane **7a–7e** (0.5 mmol), K_2CO_3 (1.5 mmol) and a catalytic amount of KI were refluxed while stirring in butanone (50 ml) for 18 h. The insoluble inorganic salts were filtered and the organic phase vaporised under reduced pressure. The crude product was crystallised from chloroform to afford the desired compounds.

For 1,3-bis{4-[5-(4-dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl]}propane (**8a**), yield 81%, m.p. 224–225°C. IR (KBr, cm^{-1}): 2919, 2851, 1609, 1496, 1253, 1173. ^1H NMR (400 MHz, CDCl_3): δ 8.06 (m, 8H), 7.03 (m, 8H), 4.17 (m, 4H), 4.05 (t, $J=6.4$ Hz, 4H), 1.83 (m, 2H), 1.27 (m, 40H), 0.86 (t, $J=7.6$ Hz, 6H). Elemental analysis: calculated for $\text{C}_{55}\text{H}_{72}\text{N}_4\text{O}_6$, C 74.63, H 8.20, N 6.33; found, C 74.25, H 8.57, N 6.39%.

For 1,4-bis{4-[5-(4-dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl]}butane (**8b**), yield 75%, m.p. 192–193°C. IR (KBr, cm^{-1}): 2918, 2850, 1610, 1496, 1256, 1172. ^1H NMR (400 MHz, CDCl_3): δ 8.06 (m, 8H), 7.02 (m, 8H), 4.15 (m, 4H), 4.03 (t, $J=6.4$ Hz, 4H), 1.82 (m, 4H), 1.26 (m, 40H), 0.86 (t, $J=7.6$ Hz, 6H). Elemental analysis: calculated for $\text{C}_{56}\text{H}_{74}\text{N}_4\text{O}_6$, C 74.80, H 8.29, N 6.23; found, C 75.04, H 8.10, N 6.30%.

For 1,6-bis{4-[5-(4-dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl]}hexane (**8c**), yield 73%, m.p. 175–176°C. IR (KBr, cm^{-1}): 2918, 2851, 1610, 1496, 1255, 1171. ^1H NMR (400 MHz, CDCl_3): δ 8.06 (m, 8H), 7.04 (m, 8H), 4.04 (m, 8H), 1.82 (m, 8H), 1.26 (m, 40H), 0.86 (t, $J=7.6$ Hz, 6H). Elemental analysis: calculated for $\text{C}_{58}\text{H}_{78}\text{N}_4\text{O}_6$, C 75.13, H 8.48, N 6.04; found, C 75.33, H 8.78, N 6.13%.

For 1,8-bis{4-[5-(4-dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl]}octane (**8d**), yield 70%, m.p. 169–170°C. IR (KBr, cm^{-1}): 2919, 2852, 1610, 1496, 1255, 1173. ^1H NMR (400 MHz, CDCl_3): δ 8.06 (m, 8H), 7.02 (m, 8H), 4.04 (m, 8H), 1.66 (m, 12H), 1.27 (m, 40H), 0.88 (t, $J=7.6$ Hz, 6H). Elemental analysis: calculated for $\text{C}_{60}\text{H}_{82}\text{N}_4\text{O}_6$, C 75.43, H 8.65, N 5.86; found, C 75.51, H 8.42, N 5.88%.

For 1,10-bis{4-[5-(4-dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl]}decane (**8e**), yield 74%, m.p. 160–161°C. IR (KBr, cm^{-1}): 2918, 2850, 1609, 1496, 1253, 1175. ^1H NMR (400 MHz, CDCl_3): δ 8.06 (m, 8H), 7.03 (m, 8H), 4.04 (m, 8H), 1.72 (m, 16H), 1.27 (m, 40H), 0.86 (t, $J=7.6$ Hz, 6H). Elemental analysis: calculated for $\text{C}_{62}\text{H}_{86}\text{N}_4\text{O}_6$, C 75.73, H 8.81, N 5.70; found, C 75.63, H 8.98, N 5.35%.

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