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Synthesis of non-symmetrically substituted 1,2,4-oxadiazole derived liquid crystals

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ABSTRACT

Non-symmetrically substituted 1,2,4-oxadiazole derived bent-core liquid crystals have been synthesized by a simple and straightforward synthetic method. All these compounds exhibit enantiotropic nematic phases over exceptionally wide temperature ranges.

1. Introduction

Bent-core or banana-shaped molecules have developed to one of the most important area of research in the field of liquid crystals (LCs) since 1996, when macroscopic polar order (ferroelectricity and antiferroelectricity) and spontaneous achiral symmetry breaking with formation of chiral superstructures were observed for some liquid crystalline phases of these molecules.[1] Very recently the first example of a new ferronematic phase was reported for a special compound derived from the bent 3,5-diphenyl-1,2,4-oxadiazole unit.[2] However, the reported material has a relatively high melting point and the nematic phase is replaced by a smectic phase at lower temperature. In order to confirm these results and to explore the application of such materials in devices it is necessary to improve and optimize this class of compounds by reducing the melting points and removing all undesired smectic LC phases, so that in the ideal case the ferronematic phase is stable down below room temperature. One way to achieve this is to substitute the 3,5-diphenyl-1,2,4-oxadiazole moiety non-symmetrically, as reduced molecular symmetry of bent-cores leads to lower melting temperatures compared to the symmetric counter-parts.[3] However, molecules of this type have been not reported so far. Moreover, such a molecular structure would allow the combination of the LC-forming unit with additional functional units and this provides the possibility to combine these units, for example, with photo-responsive units or fullerenes and to incorporate them into larger structures, such as polymers and dendrimers etc.[4] Therefore, the target was to develop a straightforward route to prepare compound **4** (Scheme 1) as a universal building block for unsymmetrically substituted 1,2,4-oxadiazoles. In this compound one side already represents one leg of the target bent-core mesogen and the phenolic hydroxyl group at the other end provides the possibility to attach different kinds of building blocks by esterification and etherification procedures as shown with the examples reported herein.

The most commonly used routes to construct the 1,2,4-oxadiazole ring are 1,3-dipolar cycloaddition of nitrile oxides to nitriles and cyclization of *O*-acylated amidoximes.[5,6] However, construction of functional materials based on 1,2,4-oxadiazole remains still challenging, because the ring is quite sensitive to nucleophilic attack[7] and the ring oxygen can acts as a good internal leaving group.[6,8] Especially the presence of reactive ester groups in the desired molecules **4**–**8** requires an efficient synthesis under mild conditions. Activation of α-amino acids and their reaction with amidoximes was recently reported by Braga et al. for the one pot-synthesis of α-amino acid derived 1,2,4-oxadiazoles.[9a]

2. Synthesis and characterization

Here we adopted this methodology for the synthesis of liquid crystalline materials. Specifically, we report a simple and straightforward synthetic strategy to accomplish unsymmetrical substituted 1,2,4-oxadiazole derivatives as described in Scheme 1. Accordingly, 4-benzyloxybenzonitrile was treated with hydroxylamine hydrochloride, which yielded the corresponding benzyl-

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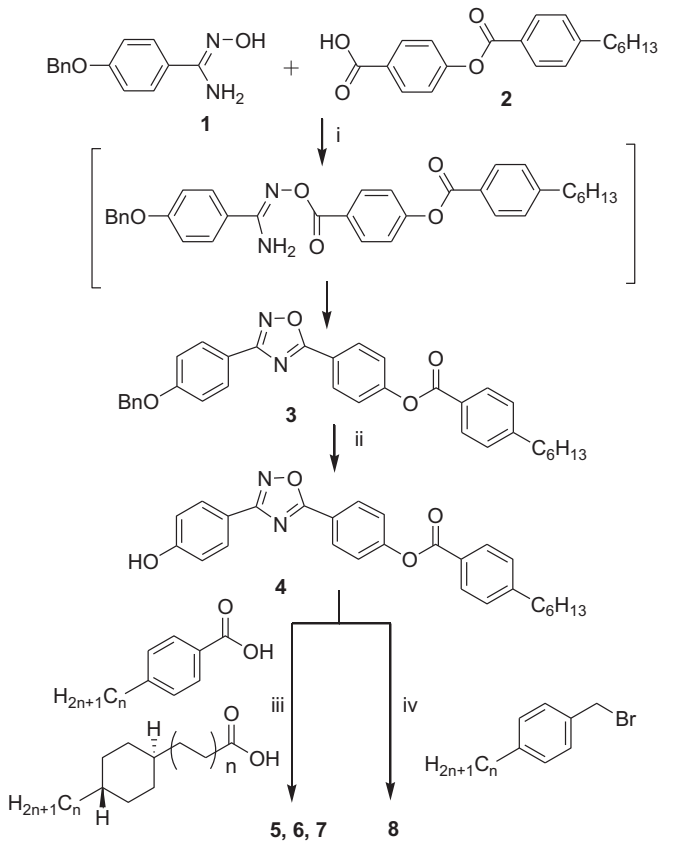


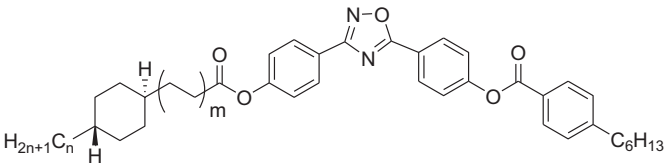
Scheme 1. Synthesis of compounds **3**–**8**; reagent and conditions: (i) DCC, 1,4-dioxane, reflux, 8 h, (75%); (ii) THF/EtOAc (3:7), 10% Pd/C, 100 kPa, 6 h (65%); (iii) DCC, DMAP, CH_2Cl_2, 12 h, (65–71%); (iv) K_2CO_3, butanone, 10 h, (73, 68%).

protected 4-hydroxybenzamidoxime **1**.[10] Activation of the 4-(4-*n*-hexylbenzoyloxy)benzoic acid **2**[11] with *N*,*N*′-dicyclohexylcarbodiimide (DCC) and *O*-acylation of the amidoxime **1** in dry dioxane as a solvent furnished the intermediate *O*-acylamidoxime, which was not isolated and immediately undergoes a cyclodehydration reaction on refluxing for 8 h, delivering the 4-[3-(4-benzyloxyphenyl)-1,2,4-oxadiazol-5-yl]phenyl 4-hexylbenzoate **3**. The peaks at δ=174.76 and 168.68 ppm in the ^{13}C NMR spectrum (see Experimental section) confirms the formation of 1,2,4-oxadiazole ring and the ester group (δ=164.66 ppm) was not affected under these conditions.[9]

Deprotection of **3** was initially tried using numerous procedure reported in literature,[12] but was unsuccessful with all these methods; also the acidolytic deprotection, as reported previously[3c,f] was not possible due to the presence of the ester group in the molecule. Finally we were successful by using a carefully controlled hydrogenation procedure described in the Experimental section to afford the desired compound 4-[3-(4-hydroxyphenyl)-1,2,4-oxadiazol-5-yl]phenyl 4-hexylbenzoate **4** in about 65% yield. It is essential to exactly keep the optimized conditions (*T*, *p*, *t*) given there, as otherwise the oxadiazole ring is cleaved hydrogenolytically. First examples of liquid crystalline target compounds (**5**–**7**) were obtained by *O*-acylation of the phenol **4** with appropriate 4-alkylbenzoic acids, *trans*-4-alkylcyclohexanecarboxylic acids or *trans*-4-alkylcyclohexylpropionic acids using DCC as condensation agent,[13] and compounds **8** were synthesized by Williamson etherification with 1-bromomethyl-4-*n*-alkylbenzenes using K_2CO_3 as base (see Experimental section for details).

The LC phases and transition temperatures of the obtained LC materials are summarized in Tables 1 and 2. It is apparent from these tables that all synthesized compounds display broad regions of LC phases. Particularly, they exhibit broad regions of nematic phases, as indicated by the typical textures observed by polarizing microscopy (crossed polarizers, see Fig. 1).

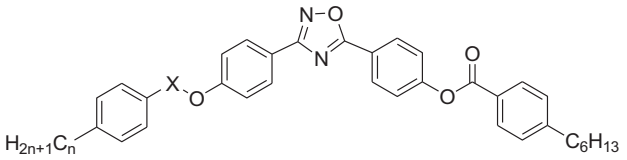
Table 1
Phase transition temperatures (*T*/°C) of compounds (**5a**–**d**) and (**6a**, **b**)[a]



Compd	*m*	*n*	Phase transitions	T_{cr}
5a	0	3	Cr 149 N 305 Iso	85
5b	0	4	Cr 120 N 293 Iso	95
5c	0	5	Cr 129 N 296 Iso	112
5d	0	7	Cr 124 N 283 Iso	98
6a	1	3	Cr 127 N 250 Iso	100
6b	1	5	Cr 123 N 245 Iso	99

[a] Phase transition temperatures were obtained from DSC heating curved (10 K min^{-1}) and confirmed by polarizing microscopy; Abbreviations: Cr=crystalline solid; N=nematic phase; Iso=isotropic liquid; T_{cr}=crystallization temperature on cooling (DSC, 10 K min^{-1}).

Table 2
Phase transition temperatures (*T*/°C) of compounds (**7a**, **b**) and (**8a**, **b**)[a]



Compd	X	*n*	Phase transitions	T_{cr}
7a	CO	4	Cr 146 N 294 Iso	126
7b	CO	5	Cr 154 N 285 Iso	118
8a	CH_2	3	Cr 105 N 241 Iso	89
8b	CH_2	7	Cr 99 N 211 Iso	84

[a] See foot note of Table 1.

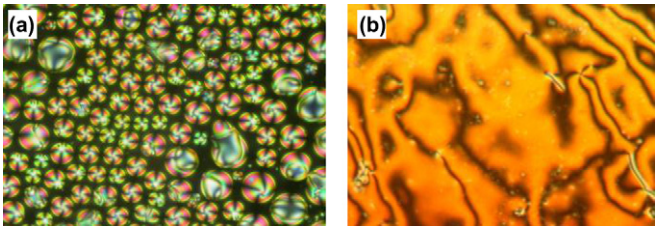


Fig. 1. Microphotograph (crossed polarizers) of representative textures of the nematic phase of compound **5a**: (a) nematic droplets as observed after cooling from the isotropic liquid at 305 °C (dark areas are residues of the isotropic liquid), (b) complete texture after cooling further to *T*=240 °C.

Representative textures of the liquid crystalline phases are shown in Fig. 1 for compound **5a** as example. Typically, nematic droplets occur at the Iso-N transition (Fig. 1a), which coalesce to schlieren textures (Fig. 1b) and also marbled textures on further cooling. This indicates nematic LC phases,[14] which were observed in the whole LC temperature range down to the crystallization temperature (T_{cr}, see Tables 1 and 2) without formation of any additional smectic phase. Also calorimetric investigations are in line with the optical investigations; the transition enthalpies for the transition N-Iso are in the range between 1 and 2 kJ mol^{-1} for all compounds, which is in the typical range as usually observed for these phase transitions of bent-core molecules.

3. Conclusions

Non-symmetric substituted 3,5-diphenyl-1,2,4-oxadiazole based bent-core liquid crystals have been synthesized by a simple and straightforward synthetic strategy. The obtained compounds represent first examples of non-symmetrically substituted 1,2,4-oxadiazole bent-core mesogens and have promising properties. Most compounds exhibit lower melting temperature in comparison to their symmetric counter part and exclusively nematic phase were observed over broad temperature ranges, i.e., undesirable smectic phases were suppressed by appropriate choice of the chain length attached to the used carboxylic acids. The nematic phases of these compounds are presently under more detailed investigation by X-ray diffraction (XRD), electro-optical methods and dielectric spectroscopy to investigate the detailed structure of these nematic phases, to check for ferroelectricity and phase biaxiality, and to explore the application potentials of these new materials.[15]

4. Experimental sections

4.1. General

All the starting materials were obtained from Aldrich Company and used as received. Solvents were purified and dried by standard methods prior to use. The crude samples were purified by column chromatographic technique using silica gel (230–400 mesh) has a stationary phase. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel 60, F_{254}). Investigation of the LC properties was carried out by polarizing microscopy (Optiphot-2, Nikon) on a hot stage (FP 82 HAT, Mettler). Phase transition temperatures were recorded by differential scanning calorimetry (DSC-7, Perkin–Elmer) at 10 K min^{-1} on heating/cooling (T_{cr}).

4.2. Procedure for the synthesis of compound 3

4-[3-(4-Benzyloxyphenyl)-1,2,4-oxadiazol-5-yl]phenyl 4-hexylbenzoate (**3**). 4-Benzyloxyphenylamidoxime (**1**)[10] (2.0 g, 8.25 mmol, 1 equiv) and 4-(4-*n*-hexylbenzoyloxy)benzoic acid (**2**)[11] (2.9 g, 9.08 mmol, 1 equiv) were dissolved in dry 1,4-dioxane (15 mL) and to the above reaction mixture, a solution of *N*,*N*′-dicyclohexylcarbodiimide (DCC) (1.9 g, 9.08 mmol, 1.1 equiv) in dioxane (10 mL) was added and stirred for a hour at 25 °C. A white precipitate forms in the solution, which was then refluxed for 8 h, after this the solvent was removed under vacuum and the residue was purified by flash chromatography (EtOAc/hexane 3:7). Colourless solid; yield 2.7 g, 2.33 mmol, 75% (after crystallization CH_2Cl_2/EtOH 3:7); phase transitions: Cr 136 °C N 205 °C Iso; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J=8.8 Hz, 2H, Ar), 8.12 (dd, J_1=8.8 Hz, J_2=9.2 Hz, 4H, Ar), 7.44 (m, 5H, Ar), 7.37 (m, 4H, Ar); 7.08 (d, J=8.8 Hz, 2H, Ar), 5.13 (s, 2H, CH_2), 2.72 (t, J=7.2 Hz, 2H, CH_2), 1.68–1.31 (m, 8H, 4× CH_2), 0.87 (t, J=6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.76, 168.68, 164.66, 164.64, 161.13, 154.46, 149.87, 149.68, 136.47, 134.34, 129.63, 129.17, 128.77, 128.71, 128.28, 127.49, 126.55, 126.39, 122.03, 119.64, 115.15, 70.09, 36.10, 36.08, 31.63, 31.05, 28.89, 26.20, 22.55, 14.04; EA, calcd for $C_{34}H_{32}N_2O_4$, 532.63 g/mol: C 76.67, H 6.06, N 5.26, found: C 76.39, H 5.80, N 5.27.

4.3. Procedure for the synthesis of compound 4

4-[3-(4-Hydroxyphenyl)-1,2,4-oxadiazol-5-yl]phenyl 4-hexylbenzoate (**4**). 10% Pd/C (ALDRICH, 100 mg) was added to compound (**3**) (1 g, 4.12 mmol) taken in a mixture of THF/EtOAc (3:7) solution (20 mL) and was hydrogenated at 20 °C for a period of 6 h at 100 kPa in a Parr hydrogenation apparatus. The suspension was filtered through Celite and evaporated, the residue was chromatographed using CH_2Cl_2/EtOAc (9:1) to afford the desired compound. Colourless solid; yield 680 mg, 1.54 mmol, 65%; phase transitions: Cr 155 °C N 192 °C Iso; IR (cm^{-1}): 3345, 2921, 2856, 1741, 1069; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J=8.8 Hz, 2H, Ar), 8.12 (d, J=8.4 Hz, 2H, Ar), 8.06 (d, J=8.4 Hz, 2H, Ar), 7.41 (d, J=8.8 Hz, 2H, Ar), 7.32 (d, J=8.0 Hz, 2H, Ar), 6.94 (d, J=8.8 Hz, 2H, Ar), 2.72 (t, J=7.6 Hz, 2H, CH_2), 1.66–1.24 (m, 8H, 4× CH_2), 0.89 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.66, 168.60, 165.05, 158.35, 154.36, 150.02, 130.41, 129.67, 129.31, 128.81, 126.26, 122.64, 121.97, 119.31, 115.81, 36.12, 31.64, 31.05, 28.89, 22.56, 14.05; EA, calcd for $C_{27}H_{26}N_2O_4$, 442.51 g/mol: C 73.28, H 5.92, N 6.33, found: C 73.12, H 5.74, N 6.25.

4.4. General procedure for the synthesis of compounds 5–7

Compound (**4**) (0.45 mmol), the appropriate carboxylic acid, either *trans*-4-alkylcyclohexanecarboxylic acid or *trans*-4-alkylcyclohexylpropionic acid or 4-alkylbenzoic acid (0.45 mmol, 1 equiv), and 4-dimethylamino pyridine (DMAP) (1 mg, 0.006 mmol) were dissolved in dry CH_2Cl_2 (20 mL) under an argon atmosphere. A solution of *N*,*N*′-dicyclohexylcarbodiimide (DCC) (140 mg, 0.68 mmol, 1.5 equiv) in CH_2Cl_2 (10 mL) was added to above mixture and the mixture was stirred at room temperature for additional 12 h. The precipitate *N*,*N*′-dicyclohexylurea was filtered off and the filtrate was concentrated, the residue was purified by column chromatography on silica gel using CH_2Cl_2/hexane (3/7) as eluent to afford the product as a colourless solid.

*4.4.1. 4-{3-[4-(trans-4-n-Propylcyclohexylcarbonyloxy)phenyl]-1,2,4-oxadiazol-5-yl}phenyl 4-hexylbenzoate (**5a**).* Colourless solid; yield 70% (after crystallization from CH_2Cl_2/EtOH 2:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J=8.4 Hz, 2H, Ar), 8.19 (d, J=8.8 Hz, 2H, Ar), 8.11 (d, J=8.4 Hz, 2H, Ar), 7.42 (d, J=8.8 Hz, 2H, Ar), 7.33 (d, J=8.0 Hz, 2H, Ar), 7.22 (d, J=8.8 Hz, 2H, Ar), 2.71 (t, J=7.6 Hz, 2H, CH_2), 2.52 (m, 1H, CHCOO), 2.16 (m, 2H, C*H*$_2$CHCOO(cy)), 1.90 (m, 2H, C*H*$_2$CHCOO(cy)), 1.65–0.86 (m, 23H, 1× CH, 8× CH_2, 2× CH_3); EA, calcd for $C_{37}H_{42}N_2O_5$, 594.74 g/mol: C 74.72, H 7.12, N 4.71, found: C 74.47, H 7.04, N 4.70.

*4.4.2. 4-{3-[4-(trans-4-n-Butylcyclohexylcarbonyloxy)phenyl]-1,2,4-oxadiazol-5-yl}phenyl 4-hexylbenzoate (**5b**).* Colourless solid; yield 65% (after crystallization from CH_2Cl_2/EtOH 2:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J=8.8 Hz, 2H, Ar), 8.18 (d, J=8.8 Hz, 2H, Ar), 8.12 (d, J=8.0 Hz, 2H, Ar), 7.42 (d, J=8.8 Hz, 2H, Ar), 7.33 (d, J=8.4 Hz, 2H, Ar), 7.22 (d, J=8.4 Hz, 2H, Ar), 2.72 (t, J=7.6 Hz, 2H, CH_2), 2.53 (m, 1H, CHCOO), 2.17 (m, 2H, C*H*$_2$CHCOO(cy)), 1.90 (m, 2H, C*H*$_2$CHCOO(cy)), 1.65–0.87 (m, 25H, 1× CH, 9× CH_2, 2× CH_3); EA, calcd for $C_{38}H_{44}N_2O_5$, 608.77 g/mol: C 74.97, H 7.29, N 4.60, found: C 74.73, H 7.14, N 4.47.

*4.4.3. 4-{3-[4-(trans-4-n-Pentylcyclohexylcarbonyloxy)phenyl]-1,2,4-oxadiazol-5-yl}phenyl 4-hexylbenzoate (**5c**).* Colourless solid; yield 68% (after crystallization from CH_2Cl_2/EtOH 2:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J=8.4 Hz, 2H, Ar), 8.19 (d, J=8.8 Hz, 2H, Ar), 8.12 (d, J=7.6 Hz, 2H, Ar), 7.42 (d, J=8.4 Hz, 2H, Ar), 7.33 (d, J=8.4 Hz, 2H, Ar), 7.22 (d, J=8.8 Hz, 2H, Ar), 2.72 (t, J=6.8 Hz, 2H, CH_2), 2.49 (m, 1H, CHCOO), 2.15 (m, 2H, C*H*$_2$CHCOO(cy)), 1.89 (m, 2H, C*H*$_2$CHCOO(cy)), 1.65–0.88 (m, 27H, 1× CH, 10× CH_2, 2× CH_3); EA, calcd for $C_{39}H_{46}N_2O_5$, 622.79 g/mol: C 75.21, H 7.44, N 4.50, found: C 75.09, H 7.38, N 4.40.

*4.4.4. 4-{3-[4-(trans-4-n-Heptylcyclohexylcarbonyloxy)phenyl]-1,2,4-oxadiazol-5-yl}phenyl 4-hexylbenzoate (**5d**).* Colourless solid; yield 67% (after crystallization from CH_2Cl_2/EtOH 2:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J=8.4 Hz, 2H, Ar), 8.19 (d, J=8.0 Hz, 2H, Ar), 8.12 (d, J=8.4 Hz, 2H, Ar), 7.42 (d, J=8.8 Hz, 2H, Ar), 7.33 (d, J=8.4 Hz, 2H, Ar), 7.22 (d, J=8.8 Hz, 2H, Ar), 2.72 (t, J=7.6 Hz, 2H,

CH_2), 2.50 (m, 1H, CHCOO), 2.16 (m, 2H, CH_2CHCOO(cy)), 1.90 (m, 2H, CH_2CHCOO(cy)), 1.65–0.86 (m, 31H, 1× CH, 12× CH_2, 2× CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.01, 174.14, 168.31, 164.52, 154.54, 153.19, 149.81, 130.33, 129.65, 128.79, 128.75, 126.40, 124.36, 122.66, 122.10, 121.80, 43.85, 37.31, 37.09, 36.25, 32.42, 32.03, 31.78, 31.18, 30.04, 29.47, 29.17, 29.04, 27.01, 22.83, 22.71, 14.24, 14.19; EA, calcd for $C_{41}H_{50}N_2O_5$, 650.85 g/mol: C 75.66, H 7.74, N 4.30, found: C 75.46, H 7.60, N 4.23.

*4.4.5. 4-{3-[4-(trans-4-n-Propylcyclohexylpropanoyloxy)-phenyl]-1,2,4-oxadiazol-5-yl}phenyl 4-hexylbenzoate (**6a**).* Colourless solid; yield 65% (after crystallization from CH_2Cl_2/EtOH 2:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, J=6.8 Hz, 2H, Ar), 8.19 (d, J=6.8 Hz, 2H, Ar), 8.12 (d, J=6.4 Hz, 2H, Ar), 7.42 (d, J=6.8 Hz, 2H, Ar), 7.33 (d, J=6.4 Hz, 2H, Ar), 7.22 (d, J=6.8 Hz, 2H, Ar), 2.71 (t, J=6.0 Hz, 2H, CH_2), 2.60 (m, 2H, CH_2COO), 1.78–0.85 (m, 30H, 2× CH, 11× CH_2, 2× CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.08, 172.17, 168.35, 164.61, 154.57, 153.06, 149.87, 130.34, 129.67, 128.83, 128.76, 126.35, 124.41, 122.67, 122.11, 121.75, 39.67, 37.44, 37.37, 36.09, 33.06, 32.91, 32.20, 32.14, 31.62, 31.04, 28.88, 22.54, 19.98, 14.36, 14.03; EA, calcd for $C_{39}H_{46}N_2O_5$, 622.79 g/mol: C 75.21, H 7.44, N 4.50, found: C 75.08, H 7.32, N 4.43.

*4.4.6. 4-{3-[4-(trans-4-n-Pentylcyclohexylpropanoyloxy)-phenyl]-1,2,4-oxadiazol-5-yl}phenyl 4-hexylbenzoate (**6b**).* Colourless solid; yield 69% (after crystallization from CH_2Cl_2/EtOH 2:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J=6.8 Hz, 2H, Ar), 8.19 (d, J=6.8 Hz, 2H, Ar), 8.12 (d, J=6.4 Hz, 2H, Ar), 7.42 (d, J=6.8 Hz, 2H, Ar), 7.33 (d, J=6.4 Hz, 2H, Ar), 7.23 (d, J=6.8 Hz, 2H, Ar), 2.71 (t, J=6.0 Hz, 2H, CH_2), 2.60 (m, 2H, CH_2COO), 1.80–0.85 (m, 34H, 2× CH, 13× CH_2, 2× CH_3); EA, calcd for $C_{41}H_{50}N_2O_5$, 650.85 g/mol: C 75.66, H 7.74, N 4.30, found: C 75.63, H 7.68, N 4.20.

*4.4.7. 4-{3-[4-(4-n-Butylbenzoyloxy)phenyl]-1,2,4-oxadiazol-5-yl} phenyl 4-hexylbenzoate (**7a**).* Colourless solid; yield 68% (after crystallization from CH_2Cl_2/EtOH 2:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J=8.8 Hz, 2H, Ar), 8.25 (d, J=8.8 Hz, 2H, Ar), 8.12 (dd, J_1=8.4 Hz, J_2=8.0 Hz, 4H, Ar), 7.43 (d, J=8.8 Hz, 2H, Ar), 7.38 (d, J=8.8 Hz, 2H, Ar), 7.33 (d, J=1.6 Hz, 2H, Ar), 7.11 (d, J=1.6 Hz, 2H, Ar), 2.72 (t, J=7.2 Hz, 4H, 2× CH_2), 1.64–1.31 (m, 12H, 6× CH_2), 0.96 (m, 6H, 2× CH_3); EA, calcd for $C_{38}H_{38}N_2O_5$, 602.78 g/mol: C 75.72, H 6.35, N 4.65, found: C 75.54, H 6.15, N 4.57.

*4.4.8. 4-{3-[4-(4-n-Pentylbenzoyloxy)phenyl]-1,2,4-oxadiazol-5-yl} phenyl 4-hexylbenzoate (**7b**).* Colourless solid; yield 71% (after crystallization from CH_2Cl_2/EtOH 2:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, J=8.4 Hz, 2H, Ar), 8.25 (d, J=8.8 Hz, 2H, Ar), 8.13 (dd, J_1=8.4 Hz, J_2=8.4 Hz, 4H, Ar), 7.43 (d, J=8.8 Hz, 2H, Ar), 7.38 (d, J=8.8 Hz, 2H, Ar), 7.33 (d, J=2.0 Hz, 2H, Ar), 7.31 (d, J=2.0 Hz, 2H, Ar), 2.72 (t, J=6.8 Hz, 4H, 2× CH_2), 1.66–1.32 (m, 14H, 7× CH_2), 0.96 (m, 6H, 2× CH_3); EA, calcd for $C_{39}H_{40}N_2O_5$, 616.75 g/mol: C 75.95, H 6.54, N 4.54, found: C 75.80, H 6.40, N 4.48.

4.5. General procedure for the synthesis of compounds 8a–b

A mixture of compound (**4**) (0.52 mmol, 1 equiv) and 1-bromomethyl-4-*n*-alkylbenzene (0.52 mmol, 1 equiv) dissolved in dry butanone under argon atmosphere followed by anhydrous K_2CO_3 (1.1 mmol, 2 equiv) and the reaction mixture was refluxed for 10 h. The solvent was evaporated and obtained solid residue poured into water, extracted with CH_2Cl_2, concentrated and purified by column chromatography on silica gel using CH_2Cl_2/hexanes (2/8) as eluent to afford the product as a colourless solid.

*4.5.1. 4-{3-[4-(4-n-Propylbenzyloxy)phenyl]-1,2,4-oxadiazol-5-yl} phenyl 4-hexylbenzoate (**8a**).* Colourless solid; yield 73% (after crystallization from CH_2Cl_2/EtOH 2:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (m, 2H, Ar), 8.12 (m, 4H, Ar), 7.42 (m, 2H, Ar), 7.33 (m, 4H, Ar), 7.20 (m, 2H, Ar), 7.09 (m, 2H, Ar), 5.01 (m, 2H, CH_2), 2.71 (t, J=7.2 Hz, 2H, CH_2), 2.60 (t, J=7.2 Hz, 2H, CH_2), 1.68–0.86 (m, 16H, 5× CH_2, 2× CH_3); EA, calcd for $C_{37}H_{38}N_2O_4$, 574.71 g/mol: C 77.33, H 6.66, N 4.87, found: C 77.06, H 6.43, N 4.61.

*4.5.2. 4-{3-[4-(4-n-Heptylbenzyloxy)phenyl]-1,2,4-oxadiazol-5-yl} phenyl 4-hexylbenzoate (**8b**).* Colourless solid; yield 68% (after crystallization from CH_2Cl_2/EtOH 2:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (m, 2H, Ar), 8.12 (m, 4H, Ar), 7.41 (m, 2H, Ar), 7.35 (m, 4H, Ar), 7.21 (m, 2H, Ar), 7.10 (m, 2H, Ar), 5.09 (m, 2H, CH_2), 2.72 (t, J=7.6 Hz, 2H, CH_2), 2.62 (t, J=7.2 Hz, 2H, CH_2), 1.67–0.85 (m, 24H, 9× CH_2, 2× CH_3); EA, calcd for $C_{41}H_{46}N_2O_4$, 630.81 g/mol: C 78.06, H 7.35, N 4.44, found: C 77.78, H 7.16, N 4.34.

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