A EUROPEAN JOURNAL

CHEMPHYSCHEM

OF CHEMICAL PHYSICS AND PHYSICAL CHEMISTRY

Accepted Article

Title: Tetrakis(oxadiazolylphenyl)pyrazines: New St. Andrew's Cross-Shaped Liquid Crystals

Authors: Nico Röder, Tomasz Marszalek, Daniel Limbach, Wojchiech Pisula, and Heiner Detert

To be cited as: *ChemPhysChem* 10.1002/cphc.201800936

Link to VoR: http://dx.doi.org/10.1002/cphc.201800936

A Journal of ChemPubSoc Europe

WILEY-VCH www.chemphyschem.org

10.1002/cphc.201800936

WILEY-VCH

Tetrakis(oxadiazolylphenyl)pyrazines: New St. Andrew's Cross-Shaped Liquid Crystals

Nico Röder,[a] Tomasz Marszalek,[b,c] Daniel Limbach,[a] Wojciech Pisula,*[b,c] and Heiner Detert*[a]

Dedicated to Prof. Gerhard Wenz on the occasion of his retirement

Abstract: π-Conjugated molecules with the shape of St. Andrews cross have been synthesized via fourfold Huisgen reaction. Four 2,5-diaryl-1,3,4-oxadiazol arms are attached to a central pyrazine nucleus. These fluorescent stars, when decorated with a rim of eight alkoxy side chains are discotic liquid crystals. Depending on the substitution pattern, the width of the liquid phase varies within a broad range of 25 °C to 250 °C. In their liquid crystalline phase, the molecules assemble in a typical hexagonal columnar supramolecular arrangement.

Introduction

Thermotropic liquid crystals (LC) are encountered in many areas of everyday life and have revolutionized display technology.[1] This important category of soft matter possesses an additional mesomorphic state between crystalline and liquid phases. Most LC are based on a rigid, rod-shaped nucleus[2] with flexible side chains in the periphery. As early as 1910, Tutin reported the mesomorphous properties of 2,5-di(*p*-methoxyphenyl)pyrazine, the first LC with a pyrazine center.[3] In addition to the mesomorphism of calamitic LCs, Chandrasekhar reported in 1977 that also disc-shaped molecules can form LC phases. [4] Discotic LCs (DLC) are usually composed of a rigid, mostly aromatic core and several aliphatic side chains on the rim.[5] The center is typically a condensed (hetero)aromatic nucleus like (hexaaza)triphenylene,[6] hexabenzocoronene,[7] triazine,[8] triazatruxene, or tistriazolotriazine.[9] Small central rings with three to six conjugated arms are a second successful strategy to DLCs.[10] Tetraphenylpyrazine, first reported in 1845[11] has been explored as building block for electronic materials, e.g. photoconductive materials for electrophotography, as electron-transmitting layers in OLEDs or in high-temperature functional fluids. However, in comparison to the cruciforms with benzene nuclei, only a few mesogens are known.[12]

Materials based on 2,5-diaryl-1,3,4-oxadiazoles have been successfully used as semiconductors in electroluminescent diodes and as non-linear optical materials.[13] Their electron deficient character, high photoluminescence quantum yield, excellent thermal and chemical stability are good prerequisites for application of these compounds as fluorescent sensors for transition metal ions,[14] biologically active agents,[15] as scintillators or emitters in OLEDs.[16] For a long time, 1,3,4-oxadiazoles were not considered to be a building block of liquid crystalline compounds because it was generally accepted that the 134° angle between the substituents on the oxadiazole inhibits the formation of mesophases.[17] In 1989, Chudgar *et al*. published a series of calamitic mesogens with this structural unit.[18] The first DLC with 1,3,4-oxadiazole units was discovered by Park in 2001.[19] The star-shaped mesogen with 1,3,5-triethinylbenzene as the nucleus and three identical 2,5-diphenyloxadiazole branches forms a narrow (10 °C) discotic-nematic phase. Mesomorphism was attributed to result predominantly from *π*-stacking between the arms and less from core-core interactions.

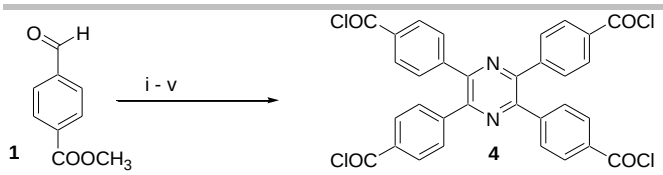
Here we present a novel group of St. Andrew's cross-shaped, symmetrical discotic mesogens, composed of electron deficient heterocycles. Four alkoxyphenyl-oxadiazolyl wing groups are attached to the tetraphenylpyrazine nucleus (TOPP). The central ring is sterically analogous to a 1,2,4,5-tetrasubstituted benzene but with a higher electron affinity. Together with the synthesis of TOPPs, we report the structures of the molecules, their optical properties, the influence of side chain length on thermotropic behavior, and the structures of the mesophases.

Results and Discussions

Structure-property correlations of liquid crystals are often based on variation of the flexible periphery of a rigid core molecule. Retrosynthetic analysis of the TOPPs reveals a *p*-substituted tetraphenylpyrazine as central unit, either with tetrazoles or carboxylic acids. These functional groups are easily converted to 1,3,4-oxadiazoles via Huisgen reaction of activated acid derivatives and tetrazoles.[20] Tetracarboxylic acid **3** is the product of a benzoin condensation[21] of methyl *p*-formylbenzoate **1** and condensation/oxidation in an ammonium acetate melt followed by hydrolysis led directly to the fourfold carboxylic acid **3** (33% over 4 steps, Scheme 1). The fourfold acid chloride **4**, central building block for all TOPPs, was prepared from the thoroughly dried acid and thionyl chloride immediately before reaction with tetrazoles.

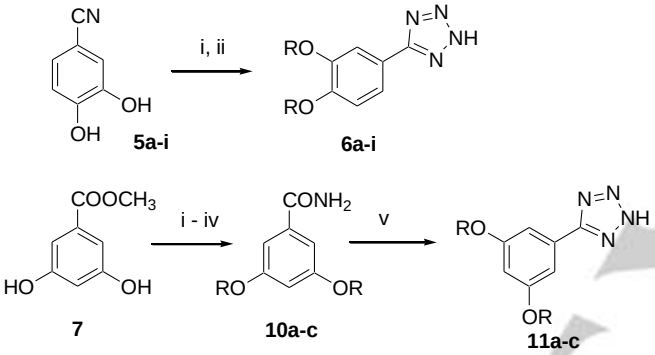
[a] Dr. Nico Röder, Dipl.-Chem. Daniel Limbach, Prof. Heiner Detert
Institute for Organic Chemistry
Johannes Gutenberg University
Duesbergweg 10-14, 55118 Mainz, Germany
E-mail: detert@uni-mainz.de
[b] Dr. Tomasz Marszalek, Prof. Wojciech Pisula
Max Planck Institute for Polymer Research
Ackermannweg 10, 55128 Mainz, Germany
E-mail: pisula@mpip-mainz.mpg.de
[c] Department of Molecular Physics,
Faculty of Chemistry, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland.

Supporting information for this article is given via a link at the end of the document



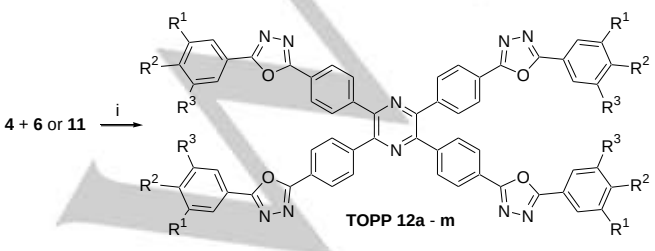
Scheme 1.: 1) KCN, EtOH/H_2O, 63%; ii) CH_3COONH_4, CH_3COOH; iii) I_2, O_2, 140 °C, 53%; iv) KOH, 2-propanol/H_2O; HCl, 99%; iv) $SOCl_2$, toluene.

The most convenient route to 2*H*-tetrazoles is the addition of azide to nitriles, directly[22] or combined with the dehydration of amides (Scheme 2). Alkylation of protocatechunitrile **5** and addition of hydrazoic acid gives the 3,4-disubstituted phenyltetrazoles **6a**-**i** in 60 - 70% yield. The preparation of the 3,5-disubstituted isomers **11a**-**c** succeeded via alkylation of methyl 3,5-dihydroxybenzoate **7**, conversion of the ester **8a**-**c** to primary amide **10a**-c via alkaline hydrolysis, chlorination with thionyl chloride, ammonolysis, and finally dehydration/addition of azide using triazidochlorosilane.[23] This five-step sequence provides the tetrazoles **11a-c** in 25-30% overall yield.



Scheme 2. Reagents and conditions: (i) Br-R, DMF, K_2CO_3, 80 °C, N_2, 42 - 94%; (ii) NaN_3, $(Et)_3N$*HCl, xylene, reflux, 42 - 81%; (iii) KOH/2-propanol, reflux, 80 - 99% (iv) $SOCl_2$, toluene, reflux., 3. NH_3(aq.), 0 °C, 65 - 87%; (v) $SiCl_4$, NaN_3, acetonitrile, reflux, 33 - 76%.

The final reaction of the fourfold acid chloride with four tetrazoles is the convergent thus critical step (Scheme 3). Two procedures were tested; initially, the acid chloride was added carefully to a suspension of tetrazole and collidine in toluene and the mixture was gradually heated to 80 °C to give TOPPs in moderate yields (ca. 40%). The addition of collidine to a stirred suspension of acid chloride and tetrazole in toluene was rewarded with a significant increase in yields, often 70 - 80%. Chromatography on a silica gel column with a head of basic alumina gave the TOPPs without traces of products with three or less arms.



Scheme 3. Synthesis of TOPPs **12a**-**m** (i) collidine, toluene, 80 °C, N_2.

Table 1. Substitution patterns and yields of Tetrakisoxadiazolylphenylpyrazines

TOPP	R^1	R^2	R^3	Yield [%][a]
12a	H	OC_3H_7	H	49
12b	H	OC_3H_7	OC_3H_7	70
12c	H	OC_4H_9	OC_4H_9	73
12d	H	OC_6H_{13}	OC_6H_{13}	81
12e	H	OC_7H_{15}	OC_7H_{15}	24
12f	H	OC_8H_{17}	OC_8H_{17}	36
12g	H	$OC_{10}H_{21}$	$OC_{10}H_{21}$	32
12h	H	$OC_{12}H_{25}$	$OC_{12}H_{25}$	71
12i	H	$OC_{14}H_{29}$	$OC_{14}H_{29}$	72
12j	H	$OC_{16}H_{33}$	$OC_{16}H_{33}$	51
12k	$OC_{10}H_{21}$	H	$OC_{10}H_{21}$	70
12l	$OC_{12}H_{25}$	H	$OC_{12}H_{25}$	37
12m	$OC_{14}H_{29}$	H	$OC_{14}H_{29}$	82

[a] Yields refer to pure product after chromatography.

Molecular Structure

Single crystals of a *p*-propyloxy substituted TOPP (**12a**) were obtained via slow evaporation of a solution in chloroform. According to the single crystal analysis, the twofold *ortho*-disubstitution on the pyrazine results in an anti-orientation of the vicinal, nearly planar (torsion angles < 6°) 2,5-diphenyl-1,3,4-oxadiazole wings.

These are twisted about 42° (at pyrazine-2,5) or 60°(at pyrazine-3,6) out of the plane of the central ring, similar to tetraphenylpyrazine.[24] The molecule adopts a highly three-dimensional, saddle shaped conformation (Figure 1.). The π-π interactions (d = 3.68 Å) of the anti-parallel propoxyphenyl-1,3,4-oxadiazole units connect neighboring molecules.

Figure 1. Molecular structure[25] of tetrakis-(4-propoxyphenyl-1,3,4-oxadiazolylphenyl)pyrazine **12a**.

Thermal Properties

Polarization microscopy, the standard examination method for the observation of mesophases, shows no indication of liquid

crystallinity for propoxy-substituted TOPPs **12a** and **12b**. All other compounds reveal the characteristic textures of discotic LCs in their mesophase. TOPPs with a lateral 3,4-dialkoxy substitution typically display fan-shaped or (pseudo)focal conical textures, whereas mosaic structures have been observed in the case of the 3,5-dialkoxy compounds (see Figure 2. and SI). A comparison of the pyrazine-centered TOPPs with analogues based on benzene as central ring is under investigation.

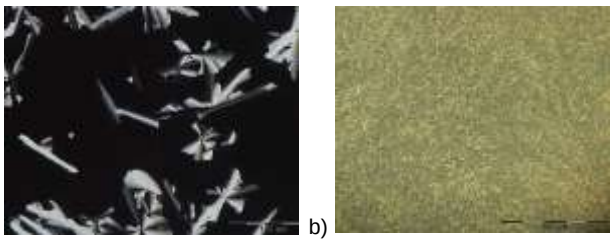


Figure 2. POM-textures (crossed-polarizers) of TOPP **12j** at 175 °C (a) and **12m** at 55 °C (b).

Table 2. Phase transition temperatures and enthalpies of TOPPs.[a]

TOPP	T_m /°C	ΔH_M /kJ mol^{-1}	T_c /°C	ΔH_c /kJ mol^{-1}
12c	103[b]	-	174	5
12d	125	4	196	7
12e	77[c]	2[c]	199	9
12f	74[b]	-	200	9
12g	76[c]	3[c]	196	9
12h	-46	72	202	11
12i	-8	52	196	11
12j	19	84	188	12
12k	91	4	106	1
12l	61	4	85	4
12m	66[a]	-	84	6

[a] T_m: onset melting transition; ΔH_M: melting enthalpy, Tc: onset clearing transition; ΔH_c: clearing transition enthalpy. [b] glass transition; [c] data determined from the first heating curve.

To determine the transition temperatures and the enthalpies, all mesomorphous TOPPs were investigated by dynamic differential calorimetry. Unless otherwise specified, the second heating curve was used for data evaluation. Whereas TOPP **12b** with a 3,4-dipropyloxy substitution melts at 204 °C without any sign of mesomorphism, compounds with chain lengths from butyl to hexadecyl display broad LC phases. The clearing points of six out of eight homologous TOPPs **12d** - **i** are around 200 °C, and only the first and last with butyl (**12c**) resp. hexadecyl chains (**12j**) clear at significantly lower temperatures (Table 2). The small range of clearing points indicates very similar core-core interaction within the columns. Contrary to the isotropization, the melting points vary between 125 °C (butyl, **12d**) and -46 °C (dodecyl, **12h**). Since the crystallization of these materials is inhibited due to high viscosity of the LC phase, some compounds solidify as glasses. With a melting point at -46 °C, **12h** displays the broadest mesophase (246 °C) of the investigated TOPPs. The broad range of melting enthalpy is attributed to incomplete crystallization of the highly viscous material.

A change of the 3,4- to a 3,5-disubstitution dramatically affects the width of the mesophase. Clearing temperatures drop by about 100 °C while the melting points raise. The width of the mesophase shrinks to ca 20-25 °C - about 1/10 of the width observed for the 3,4-disubstituted isomers. TGA analysis of TOPPs reveal a high thermal stability, and a significant weight loss was observed only above 418 °C.

Two-dimensional wide-angle X-ray scattering (WAXS) experiments on macroscopically aligned extruded fibers[26] were carried out to determine the intra- and intercolumnar organization of the two isomers **12h** and **12l** in their liquid crystal phases (Figure 2). For 3,4-disubstituted **12h**, the columns arrange in a hexagonal lattice of a_h = 4.45 nm in the mesophase as determined from the equatorial reflections in the pattern of Figure 3a. The intracolumnar π-stacking distance of 0.36 nm between the individual discs is derived from the diffuse wide-angle meridional reflections.[26] The 3,5-disubstituted TOPP **12l** reveals in the mesophase also a hexagonal columnar arrangement, but with a slightly smaller lattice constant of a_h = 3.95 nm. At the same time, the π-stacking distance is increased to 0.38 nm. One possible reason for the denser columnar hexagonal packing is the higher symmetry of **12l** compared to **12h**.[27] The average alkyl chain spacing of 0.44 nm for **12h** and 0.45 nm for **12l** is very similar. Both compounds display diffuse halos in the wide-angle range, caused by the disordered alkyl chains in the periphery of mesogens.

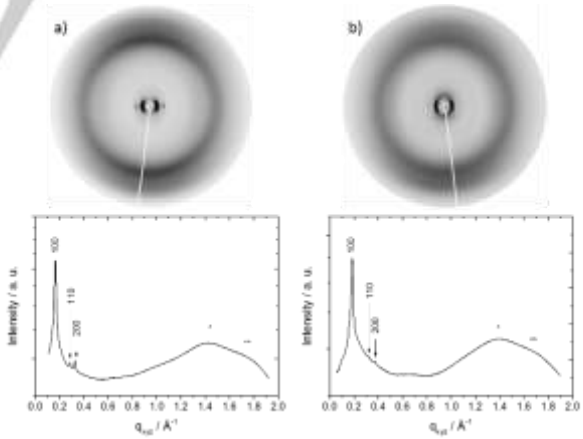


Figure 3. 2DWAXS patterns of a) **12h** and b) **12l** in their mesophases and the corresponding integrations. The fiber samples were placed vertically toward the 2D detector. Peaks are assigned by Miller indices, *: halo, **: π–stacking.

Optical Properties

All TOPPs are yellow and fluorescent, as solids and dissolved in dichloromethane. The optical properties of some TOPPS as representative compounds have been studied by UV-vis and fluorescence spectroscopy in different environments. The results are collected in Table 3.

Generally, photophysical properties of TOPPs are nearly independent from alkyl chain length and substitution pattern. Uniquely, the absorption maximum of TOPP **12a** in cyclohexane peaks at lower energies compared to **12e** with the stronger donor-acceptor character. This is leveled out in the more polar solvent dichloromethane. The long-wavelength absorption maximum of TOPPs with a 3,4-disubstitution peaks at λ_{max} = 362 nm, only 2 nm more bathochromic then the 3,5-isomer, which also show a second, more intense maximum at higher energies, λ_{max} ca. 316 nm. The violet-blue fluorescence (λ^{F}_{max} = 444 - 457 nm) is separated from the long-wavelength absorption maximum by Stokes shifts of ca. $\Delta\tilde{\nu}^{St}$ = 5200 cm^{-1} in cyclohexane, but up to $\Delta\tilde{\nu}^{St}$ = 6100 cm^{-1} in dichloromethane. A weak negative solvatochromism of the absorption of TOPPs has been noted. Fluorescence quantum yields are also depending on the solvent. The highest values of Φ^{F} = 12 - 17% were obtained in toluene. Spin-coated films show very similar optical properties, pristine as well as after annealing.

Table 3. Spectroscopic data of TOPPs in different solvents.

TOPP	solv.	λ_{max} /nm	log ε	λ^{F}_{max} /nm	Φ^{F}	$\Delta\tilde{\nu}^{St}$ /cm^{-1}
	cy	366 (330)	4.54	449	4%	5051
12a	tol	364 (338)	4.85	449		5176
	DCM	356 (328)	4.88	447	5%	5719
	cy	362	4.91	448	7%	5278
12e	tol	363	4.99	451	15%	5400
	DCM	357	4.97	456	7%	6105
	cy	363	4.92	448	6%	5202
12h	tol	364	4.99	452	17%	5300
	DCM	357	4.97	457	7%	6105
	cy	363	4.96	447	12%	5152
12i	tol	363	5.00	455	17%	5570
	DCM	358	5.00	453	9%	5834
	film[a]	334	-	451		7767
	film[b]	334	-	454		7889
	cy	316 (360)	4.95	444	12%	(5255)
12l	tol	318 (360)	4.94	445	12%	(5306)
	DCM	314 (354)	4.96	442	8%	(5153)
	film[a]	318 (366)	-	445		(4850)
	film[b]	318 (366)	-	440		(4621)

cy: cyclohexane; tol: toluene; DCM: dichloromethane [a] pristine spin-coated film; [b] spin-coated film in the liquid crystal phase. Values in brackets: second maximum and corresponding $\Delta\tilde{\nu}^{St}$ The fluorescence quantum yields of TOPPs in highly diluted solution are only moderate, but increase upon aggregation. Figure 4 shows the emission spectrum of **12c** as solution in THF compared to **12c** in poor solvents, THF/water mixtures and heptane. A nearly fourfold fluorescence intensity results from the effect of aggregation induced emission (AIE)[29].

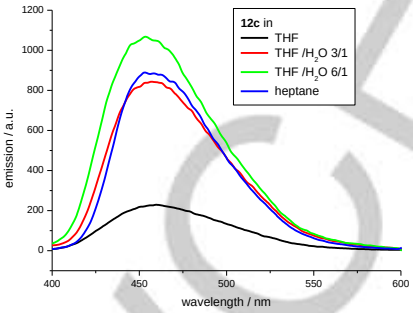


Figure 4. Emission spectra of a solution of **12c** (3*10^{-4} M) in THF solution, as suspension in THF/water mixtures, and heptane

Conclusions

The synthesis and characterization of novel St. Andrews cross-shaped mesogens with central tetraphenylpyrazine nucleus and alkoxyaryl-1,3,4-oxadiazole units as wing groups have been successfully accomplished for the first time. The modular synthesis is based on a fourfold Huisgen reaction as convergent step. Due to the double *ortho*-disubstitution on the pyrazine, the rigid part of TOPPs adopts a saddle-like shape with a height of 9 Å. Nevertheless, even with side chains as short as butyl, these cruciforms are mesomorphous with phase widths up to 246 °C. In the liquid crystalline phases the molecules assemble into characteristic hexagonal columnar structures as confirmed by X-ray scattering analysis on selected compounds. A higher substitution symmetry leads to a tighter columnar packing, but larger intracolumnar distance between individual molecules. Nearly unbiased by the substitution pattern and environment, absorption of the yellow TOPPs peaks around 363 nm and a moderately efficient emission is centered around 450 nm.

Experimental Section

General: Reactions were carried out in dry solvents and under a nitrogen atmosphere or with moisture exclusion. TLC: Polygram SIL G/UV254, Macherey-Nagel. Column chromatography: silica gel 60, Macherey-Nagel. Basic aluminium oxide: Merck. Melting points: Dr. Tottoli apparatus. POM: Olympus BX51 polarization microscope with a heatable sample chamber Linkam TMS94. Images: Olympus DP22. DSC: DSC7 (Perkin Elmer). Heating rate 2nd scan: 10 °C/min. NMR: Bruker AC300; Bruker ARX400; Bruker AMX400; $CDCl_3$ or DMSO-d_6. IR: Jasco FT/IR 4100 Fourier Transform spectrometer, Zn-Se crystal. FD-MS: MAT 90 (Finnigan), HR-MSESI: Q-TOF-ULTIMA 3. Given masses refer to the pure isotopes. UV-Vis spectra: Lambda 16 (Perkin-Elmer). Fluorescence: LSB50 (Perkin-Elmer). Starting materials were prepared according or analogous to literature procedures,[28] details are given in the SI.

Two-dimensional wide-angle X-ray scattering (2D-WAXS): 2D-WAXS measurements were performed using a custom setup consisting of the Siemens Kristalloflex X-ray source (copper anode X-ray tube, operated at

35 kV/20 mA), Osmic confocal MaxFlux optics, two collimating pinholes (1.0 and 0.5 mm Owis, Germany) and an antiscattering pinhole (0.7 mm– Owis, Germany). The patterns were recorded on a MAR345 image plate detector (Marresearch, Germany). The samples were prepared by filament extrusion using a home-built mini-extruder.

General procedure for the synthesis of TOPPs: In a nitrogen atmosphere, **4** (ca. 200 mg) was suspended in 4 mL of thionyl chloride and stirred for 6 hours under reflux and evaporated to dryness. Variant A: The residue was suspended in 5 mL toluene and added dropwise to a solution of 4,4 eq. tetrazole and 1 mL 2,4,6-collidine in 10 mL toluene,. Variant B: The acid chloride **X** and 4,4 eq. of the respective tetrazole were stirred in 10 mL toluene and after 2 h at ambient temperature, 1 mL of 2,4,6-collidine was quickly added. Subsequently (A and B) the mixture was stirred for 16 hours at 80 °C. After complete conversion (TLC), 30 mL 2 M hydrochloric acid was added. The solution was extracted with chloroform, the combined organic layers washed with water and brine and dried over $MgSO_4$. The solvent was evaporated. The crude product was purified on a silica gel column with a top layer of basic Al_2O_3. Toluene followed by toluene/ethyl acetate was used as eluent

2,3,5,6-Tetrakis(4-(5-(4-propoxyphenyl)-1,3,4-oxadiazol-2-yl)phenyl)pyrazine 12a According to general procedure B, 150 mg (0,268 mmol) of 3 and 262,0 mg (1,3 mmol) 5-(4-propoxyphenyl)-2*H*-tetrazole) were used. Column chromatography: toluene/ethyl acetate 2:1; Yield: 157 mg (0,013 mmol, 49 %); m.p. 298 °C; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.15 (d, ^3J = 8.0 Hz, 8H, 3'-H, Ph), 8.06 (d, ^3J = 8.9 Hz, 8H, 2'''-H, Ph), 7.87 (d, ^3J = 8.2 Hz, 8H, 2'-H, Ph), 7.01 (d, ^3J = 8.9 Hz, 8H, 3'''-H, Ph), 4.00 (t, ^3J = 6.5 Hz, 8H, α-OCH_2), 2.26 – 1.67 (m, 8H, β-OCH_2), 1.06 (t, ^3J = 7.4 Hz, 12H, CH_3) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 165.00 (C-5'', Oxa), 163.74 (C-2'', Oxa), 162.24 (C-4''', Ph), 148.07 (C-2, C-3, Pyr), 140.68 (C-1', Ph), 130.73 (C-2', Ph), 128.90 (C-2''', Ph), 127.13 (C-3', Ph), 124.87 (C-4', Ph), 116.08 (C-1''', Ph), 115.16 (C-3''', Ph), 69.90 (α-OCH_2), 22.61 (β-OCH_2), 10.63 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2960, 2926, 2875, 1610, 1585, 1551, 1494, 1471, 1389, 1308, 1254, 1173, 1093, 1064, 1011, 975, 909, 836, 708 cm^{-1}; HR-ESI: calcd. for $C_{72}H_{60}N_{10}O_8$ + H^+: 1193,4668, found: 1193,4671.

2,3,5,6-Tetrakis(4-(5-(3,4-dipropoxyphenyl)-1,3,4-oxadiazol-2-yl)phenyl)pyrazine 12b: According to general procedure B, 150 mg (0.268 mmol) of **3** and 309 mg (1,18 mmol) of **6a** were used. Column chromatography: toluene/ethyl acetate 6:1; Yield: 266 mg (0,186 mmol, 70 %); m.p. 204 °C; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.16 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 8H, Ph), 7.88 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 8H, Ph), 7.73 – 7.56 (m, 8H, Ph), 6.97 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 4H, Ph), 4.15 – 3.90 (m, 16H, α-OCH_2), 1.89 (m, 16H, β-OCH_2), 1.07 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 24H, CH_3) ppm. ^{13}C NMR (75 MHz, 25 °C, $CDCl_3$): δ = 165,12 (Oxa), 163,82 (Oxa), 152.54 (Ph), 149.46 (Ph), 148.05 (Pyr), 140.71 (Ph), 130.74 (Ph), 127.17 (Ph), 124.87 (Ph), 120.69 (Ph), 116.18 (Ph), 113.03 (Ph), 111.83 (Ph), 71.03, 70.69 (α-OCH_2), 22.70, 22.62 (CH_2), 10.64, 10.60 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2965, 2939, 2878, 1607, 1559, 1496, 1470, 1391, 1273, 1219, 1141, 1106, 1010, 978, 853, 720 cm^{-1}. FD-MS: m/z = 1425.0 [M]$^+$.

2,3,5,6-Tetrakis(4-(5-(3,4-dibutyloxyphenyl)-1,3,4-oxadiazol-2-yl)phenyl)pyrazine 12c: According to general procedure B, 100 mg (0.178 mmol) of **3** and 248 mg (0,856 mmol) of **6b** were used. Column chromatography: toluene/ethyl acetate 8:1; Yield: 200 mg (0,130 mmol, 73 %); T_g 103 °C, c.p. 174 °C; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.16 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.88 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.71 – 7.59 (m, 8H, Ph), 6.96 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 4H, , Ph), 4.19 – 3.89 (m, 16H, α-OCH_2), 2.03 – 1.71 (m, 16H, β-OCH_2), 1.59 – 1.44 (m, 16H, CH_2), 1.05 – 0.93 (m, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 165.11 (Oxa), 163.81 (Oxa), 152.54 (Ph), 149.49 (Ph), 148,04 (Pyr), 140.69 (Ph), 130.72 (Ph), 127.16 (Ph), 124.88 (Ph), 120.64 (Ph), 116.19 (Ph), 113.00 (Ph), 111.77 (Ph), 69.29, 68.98 (α-OCH_2), 31.37, 31.27, 19.36 (CH_2), 14.03 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2956, 1606, 1495, 1464, 1388, 1272, 1213, 1139, 1064, 1008, 849, 810, 723, 701 cm^{-1}. FD-MS: m/z = 1537.1 [M]$^+$.

2,3,5,6-Tetrakis(4-(5-(3,4-bis(hexyloxy)phenyl)-1,3,4-oxadiazol-2-yl)-phenyl)pyrazine 12d: According to general procedure B, 100 mg (0.178 mmol) of **3** and 297 mg (0,856 mmol) of **6c** were used. Column chromatography: toluene/ethyl acetate 8:1; Yield: 253 mg (0,144 mmol, 81 %); m.p. 125 °C, c.p. 196 °C; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.16 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.88 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 8H, Ph), 7.74 – 7.56 (m, 8H, Ph), 6.96 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 4H, Ph), 4.24 – 3.97 (m, 16H, α-OCH_2), 1.98 – 1.78 (m, 16H, β-OCH_2), 1.57 – 1.43 (m, 16H, γ-CH_2), 1.43 – 1.20 (m, 32H, CH_2), 1.03 – 0.78 (m, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 165.11 (Oxa), 163.80 (Oxa), 152.51 (Ph), 149.46 (Ph), 148.04 (Pyr), 140.69 (Ph), 130.72 (Ph), 127.16 (Ph), 124.88 (Ph), 120.62 (Ph), 116.16 (Ph), 112.94 (Ph), 111.70 (Ph), 69.55, 69.25 (α-OCH_2), 31.70, 29.28, 29.19, 25.81, 22.74 (CH_2), 14.17 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2931, 2857, 1605, 1495, 1389, 1271, 1138, 1009, 849, 723 cm^{-1}. FD-MS: m/z = 1762.7 [M]$^+$.

2,3,5,6-Tetrakis(4-(5-(3,4-bis(heptyloxy)phenyl)-1,3,4-oxadiazol-2-yl)-phenyl)pyrazine 12e: According to general procedure A, 150 mg (0.268 mmol) of **3** and 297 mg (1,29 mmol) of **6d** were used. Column chromatography: toluene/ethyl acetate 3:1; Yield: 125 mg (0,0625 mmol, 24 %); m.p. 77 °C, c.p. 199 °C; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.16 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.88 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.76 – 7.52 (m, 8H, Ph), 6.96 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 4H, Ph), 4.30 – 3.87 (m, 16H α-OCH_2), 1.95 – 1.76 (m, 16H, β-OCH_2), 1.54 – 1.17 (m, 64H, CH_2), 1.06 – 0.38 (m, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 165.13 (Oxa), 163.81 (Oxa), 152.55 (Ph), 149.49 (Ph), 148.05 (Pyr), 140.71 (Ph), 130.74 (Ph), 127.19 (Ph), 124.88 (Ph), 120.67 (Ph), 116.16 (Ph), 112.98 (Ph), 111.76 (Ph), 69.59, 69.27 (α-OCH_2), 31.95, 29.35, 29.25, 29.22, 26.12, 26.10, 22.76 (CH_2), 14.25 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2926, 1607, 1496, 1468, 1390, 1274, 1216, 1140, 1911, 850, 789, 757 cm^{-1}. HRMS (ESI): calc. for $C_{119}H_{155}N_{10}O_{12}$ [M + H]$^+$: 1917.1854; found 1917.1852.

2,3,5,6-Tetrakis(4-(5-(3,4-bis(octyloxy)phenyl)-1,3,4-oxadiazol-2-yl)-phenyl)pyrazine 12f: According to general procedure A, 150 mg (0.268 mmol) of **3** and 517 mg (1.29 mmol) of **6e** were used. Column chromatography: toluene/ethyl acetate 5:1; Yield: 193 mg (0,097 mmol, 36 %); T_g 74 °C, m.p. 200 °C; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.16 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 8H, Ph), 7.88 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 8H, Ph), 7.69 – 7.62 (m, 8H, Ph), 6.96 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 4H, Ph), 4.32 – 3.85 (m, 16H, α-OCH_2), 1.99 – 1.75 (m, 16H, β-OCH_2), 1.61 – 1.16 (m, 80H, CH_2), 1.18 – 0.44 (m, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 165.10 (Oxa), 163.78 (Oxa), 152.56 (Ph), 149.49 (Ph), 148.02 (Pyr), 140.71 (Ph), 130.73 (Ph), 127.16 (Ph), 124.85 (Ph), 120.66 (Ph), 116.10 (Ph), 112.97 (Ph), 111.75 (Ph), 69.58, 69.27 (α-OCH_2), 31.95, 29.49, 29.40, 29.33, 29.23, 26.16, 26.13, 22.81, 22.79 (CH_2), 14.25 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3062, 2923, 2854, 1607, 1556, 1496, 1467, 1390, 1272, 1220, 1141, 1104, 1010, 850, 810, 723 cm^{-1}. FD-MS: m/z = 1986.5 [M]$^+$.

2,3,5,6-Tetrakis(4-(5-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)-phenyl)pyrazine 12g: According to general procedure A, 150 mg (0.268 mmol) of **3** and 540 mg (1,18 mmol) of **6f** were used. Column chromatography: toluene/ethyl acetate 3:1; Yield: 188 mg (0.0850 mmol, 32 %); m.p. 76 °C, c.p. 196 °C; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.16 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.88 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.68 – 7.60 (m, 8H, Ph), 6.96 (d, $^3J_{H\text{-}H}$ = 8.9 Hz, 4H, Ph), 4.15 – 3.97 (m, 16H, α-OCH_2), 1.95 – 1.76 (m, 16H, β-OCH_2), 1.55 – 1.15 (m, 112H, CH_2), 1.07 – 0.44 (m, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 165.10 (Oxa), 163.79 (Oxa), 152.51 (Ph), 149.47 (Ph), 148.02 (Pyr), 140.69 (Ph), 130.72 (Ph), 127.15 (Ph), 124.87 (Ph), 120.62 (Ph), 116.16 (Ph), 112.95 (Ph), 111.71 (Ph), 69.56, 69.26 (α-OCH_2), 32.05, 29.85, 29.76, 29.72, 29.56, 29.54, 29.49, 29.33, 29.23, 26.16, 26.13, 22.84 (CH_2), 14.26 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3734, 3628, 2923, 2853, 1734, 1496, 1466, 1274, 1011, 796, 721, 668 cm^{-1}. FD-MS: m/z = 2211.6 [M]$^+$.

2,3,5,6-Tetrakis(4-(5-(3,4-bis(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)-phenyl)pyrazine 12h: According to general procedure B, 150 mg (0.268 mmol) of **3** and 661 mg (1,29 mmol) of **6g** were used. Column chromatography: toluene/ethyl acetate 8:1; Yield: 466 mg (0,191 mmol, 71 %); m.p. -46°C, c.p. 202 °C; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.16 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 8H, Ph), 7.88 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 8H, Ph), 7.73 – 7.62 (m, 8H, Ph), 6.96 (d, $^3J_{H\text{-}H}$ = 8.9 Hz, 4H, Ph), 4.22 – 3.94 (m, 16H, α-OCH_2), 1.94 – 1.79 (m, 16H, β-OCH_2), 1.56 – 1.17 (m, 144H, CH_2), 0.98 – 0.68 (m, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 165.11 (Oxa), 163.79 (Oxa), 152.54 (Ph), 149.49 (Ph), 148.03 (Pyr), 140.70 (Ph), 130.73 (Ph), 127.16 (Ph), 124.87 (Ph), 120.63 (Ph), 116.14 (Ph), 112.96 (Ph), 111.73 (Ph), 69.58, 69.27 (α-OCH_2), 32.07, 29.85, 29.81, 29.77, 29.55, 29.52, 29.49, 29.34, 29.24, 26.17, 26.14, 22.84 (CH_2), 14.27 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2922, 2852, 1734, 1607, 1496, 1466, 1389, 1272, 1216, 1141, 1010, 850, 755, 668 cm^{-1}. FD-MS: m/z = 2435.7 [M]$^+$.

2,3,5,6-Tetrakis(4-(5-(3,4-bis(tetradecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phen-yl)pyrazine 12i: According to general procedure B, 75 mg (0.13 mmol) of **3** and 367 mg (0,642 mmol) of **6h** were used. Column chromatography: toluene/ethyl acetate 8:1; Yield: 251 mg (0,945 mmol, 72 %); m.p. -8 °C, c.p. 196 °C; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.16 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.88 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.73 – 7.58 (m, 8H, Ph), 6.96 (d, $^3J_{H\text{-}H}$ = 9.1 Hz, 4H, Ph), 4.14 – 3.98 (m, 16H, α-OCH_2), 1.91 – 1.78 (m, 16H, β-OCH_2), 1.55 – 1.17 (m, 176H, CH_2), 0.97 – 0.77 (m, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 165.11 (Oxa), 163.80 (Oxa), 152.52 (Ph), 149.49 (Ph), 148.03 (Pyr), 140.69 (Ph), 130.72 (Ph), 127.16 (Ph), 124.89 (Ph), 120.61 (Ph), 116.18 (Ph), 112.95 (Ph), 111.72 (Ph), 69.57, 69.27 (α-OCH_2), 32.08, 32.07, 29.87, 29.83, 29.78, 29.58, 29.56, 29.53, 29.35, 29.25, 26.18, 26.15, 22.85 (CH_2), 14.28 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2918, 2849, 1597, 1557, 1466, 1393, 1285, 1166, 1065, 844, 745, 721, 675 cm^{-1}. HRMS (ESI): calc. for $C_{172}H_{262}N_{10}O_{12}$ [M+2H$^+$]: 1330.0075; found 1330.0099.

2,3,5,6-Tetrakis(4-(5-(3,4-bis(hexadecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)pyrazine 12j: According to general procedure B, 40 mg (0.071 mmol) of **3** and 215 mg (0,343 mmol) of **6i** were used. Column chromatography: toluene/ethyl acetate 12:1; Yield: 105 mg (0.0364 mmol, 51 %); m.p. 19 °C, c.p. 188°C; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.16 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.88 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.77 – 7.51 (m, 8H, Ph), 6.96 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 4H, Ph), 4.22 – 3.93 (m, 16H, α-OCH_2), 2.01 – 1.73 (m, 16H, β-OCH_2), 1.55 – 1.10 (m, 208H, CH_2), 0.97 – 0.64 (m, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 165.11 (Oxa), 163.79 (Oxa), 152.52 (Ph), 149.48 (Ph), 148.02 (Pyr), 140.69 (Ph), 130.72 (Ph), 127.16 (Ph), 124.88 (Ph), 120.61 (Ph), 116.17 (Ph), 112.95 (Ph), 111.72 (Ph), 69.57, 69.27 (α-OCH_2), 32.08, 29.87, 29.82, 29.78, 29.58, 29.52, 29.35, 29.25, 26.18, 26.15, 22.85 (CH_2), 14.28 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2917, 2849, 1607, 1496, 1467, 1389, 1272, 1218, 1141, 1010, 849, 721 cm^{-1}. FD-MS: m/z = 2885.9 [M]$^+$.

2,3,5,6-Tetrakis(4-(5-(3,5-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)pyrazine 12k: According to general procedure B, 50 mg (0.089 mmol) of **3** and 196 mg (0.428 mmol) of **11a** were used. Column chromatography: toluene/ethyl acetate 12:1; Yield: 137 mg (0,0620 mmol, 70 %); T_g 66, c.p. 106 °C; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.17 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.89 (d, ^3J = 8.6 Hz, 8H, Ph), 7.25 (d, $^4J_{H\text{-}H}$ = 2.3 Hz, 8H, Ph), 6.62 (t, $^4J_{H\text{-}H}$ = 2.3 Hz, 4H, Ph), 4.01 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 16H, α-OCH_2), 1.89 – 1.72 (m, 16H, β-OCH_2), 1.53 – 1.18 (m, 114H, CH_2), 0.94 – 0.83 (m, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 165.08 (Oxa), 164.19 (Oxa), 160.89 (Ph), 148.07 (Pyr), 140.87 (Ph), 130.76 (Ph), 127.29 (Ph), 125.19 (Ph), 124.74 (Ph), 105.38 (Ph), 105.29 (Ph), 68.59 (α-OCH_2), 32.04, 29.71, 29.52, 29.46, 29.33, 26.17, 22.83 (CH_2), 14.27 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2922, 2853, 1598, 1547, 1497, 1465, 1441, 1389, 1298, 1165, 1098, 1054, 1011, 907, 850, 730, 679 cm^{-1}. FD-MS: m/z = 2211.7 [M]$^+$.

2,3,5,6-Tetrakis(4-(5-(3,5-bis(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)pyrazine TOPP12l: According to general procedure A, 150 mg (0.268 mmol) of **3** and 661 mg (1.29 mmol) of **11a** were used. Column chromatography: toluene/ethyl acetate 10:1; Yield: 236 mg (0,0981 mmol, 37 %); m.p. 61°C, c.p. 85 °C; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.17 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.88 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.25 (d, ^4J = 2.2 Hz, 8H, Ph), 6.62 (t, $^4J_{H\text{-}H}$ = 2.2 Hz, 4H, Ph), 4.01 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 16H, α-OCH_2), 2.10 – 1.70 (m, 16H, β-OCH_2), 1.53 – 1.19 (m, 144H, CH_2), 0.92 – 0.84 (m, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 164.94 (Oxa), 164.05 (Oxa), 160.74 (Ph), 147.93 (Pyr), 140.72 (Ph), 130.62 (Ph), 127.15 (Ph), 125.03 (Ph), 124.59 (Ph), 105.23 (Ph), 105.14 (Ph), 68.45 (α-OCH_2), 31.93, 29.65, 29.58, 29.39, 29.36, 29.19, 26.02, 22.70 (CH_2), 14.14 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2922, 2852, 1734, 1598, 1546, 1441, 1388, 1297, 1166, 1055, 1011, 851, 757, 729, 679 cm^{-1}. FD-MS: m/z = 2435.7 [M]$^+$.

2,3,5,6-Tetrakis(4-(5-(3,5-bis(tetradecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)pyrazine 12m: According to general procedure B, 75 mg (0.13 mmol) of **3** and 367 mg (0,642 mmol) of **11a** were used. Column chromatography: toluene/ethyl acetate 12:1; Yield: 252 mg (0,107 mmol, 82 %); T_g. 66 °C, c.p. 88 °C; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.17 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.88 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 8H, Ph), 7.25 (d, $^4J_{H\text{-}H}$ = 2.2 Hz, 8H, Ph), 6.62 (t, $^4J_{H\text{-}H}$ = 2.3 Hz, 4H, Ph), 4.01 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 16H, α-OCH_2), 1.87 – 1.70 (m, 16H, β-OCH_2), 1.52 – 1.13 (m, 176H, CH_2), 0.96 – 0.67 (m, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 165.08 (Oxa), 164.19 (Oxa), 160.89, (Ph), 148.07 (Pyr), 140.86 (Ph), 130.75 (Ph), 127.29 (Ph), 125.19 (Ph), 124.74 (Ph), 105.37 (Ph), 105.28 (Ph), 68.59 (α-OCH_2), 32.07, 29.84, 29.81, 29.75, 29.72, 29.53, 29.51, 29.34, 26.17, 22.84 (CH_2), 14.27 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2921, 2851, 1597, 1547, 1442, 1388, 1164, 1011, 850, 728, 678 cm^{-1}. FD-MS: m/z = 2260,8 [M]$^+$.

Acknowledgements

T. M. and W. P. acknowledge the Polish National Research Centre under the project code UMO-2015/18/E/ST3/00322; H.D. acknowledges the Deutsche Forschungsgemeinschaft (DFG) for generous financial support, M. Müller (DSC) and Dr. D. Schollmeyer (XRD) for many measurements.

Conflict of interest

The authors declare no conflict of interest.

Keywords: pyrazine • liquid crystals • WAXS • POM • solvatochromism

[1] a) T. Geelhaar, K. Griesar, B. Reckmann, *Angew. Chem.* **2013**, *125*, 8960-8971; *Angew. Chem. Int. Ed.* **2013**, *52*, 8798-8809 b) G. H. Heilmeier, L. A. Zanoni, L. A. Barton, *Proc. IEEE* **1968**, *56*, 1162-1171; c) M. Schadt, W. Helfrich, *Applied Physics Letters* **1971**, *18*, 127-128; d) Laschat, S., Baro, A., Steinke, N., Giesselmann, F., Hagele, C., Scalia, G., Judele, R., Kapatsina, E., Sauer, S., Schreivogel, A., Tosoni, M., *Angew. Chem Int. Ed.* **2007**, *46*, 4832-4887.

[2] a) D. Vorländer, *Ber. dt. chem. Ges.* **1907**, *40*, 1970-1972; b) W. Pisula, K. Muellen in *Handbook of Liquid Crystals* 2nd ed. (Ed.: J. W. Goodby), Wiley-VCH, Weinheim, **2014**, *8*, pp. 627-673; c) T. Wöhrle, I. Wurzbach, J. Kirres, A. Kostidou, N. Kapernaum, J. Litterscheidt, J. C. Haenle, P. Staffeld, A. Baro, F. Giesselmann, S. Laschat, *Chem. Rev.* **2016**, *116*, 1139-1241.

[3] F. Tutin, *J Chem. Soc, Trans* **1910**, *97*, 2495-2524.

[4] S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, *Pramana* **1977**, *9*, 471-480.

[5] a) J. M. Warman, J. Piris, W. Pisula, M. Kastler, D. Wasserfallen, K. Müllen, *J. Am. Chem. Soc*., **2005**, *127*, 14257–1426; b) S. Kumar, *Chem. Soc. Rev.* **2006**, *35*, 83-109.

[6] a) R.J. Bushby, O. R. Lozman, L. A. Mason, N. Taylor, S. Kumar, *Mol. Cryst. Liq. Cryst.* **2004**, *410*, 171-181; b) E. O.Arikainen, N. Boden, R. J. Bushby, O. R. Lozman, J. G. Vinter, A. Wood, *Angew. Chem. Int. Ed.* **2000**, *39*, 2333-2336.

[7] a) C.-y. Liu, A. Fechtenkötter, M. D. Watson, K. Müllen, A. J. Bard, *Chem. Mater.* **2003**,*15*, 124-130; b) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119 - 1122; c) C. Kübel, K. Eckhardt, V. Enkelmann, G. Wegner, K. Müllen, *J. Mater. Chem*. **2000**,*10*, 879-886.

[8] a) D. Goldmann, D. Janietz, C. Schmidt, J. H. Wendorff, *Angew. Chem*. **2000**, *112*, 1922-1925; *Angew. Chem. Int. Ed*. **2000**, *39*, 1851-1854; b) S.J. Lee, J.Y. Chang, *Tetrahedron Lett*. **2003**, *44*, 7493-7497; c) H. Meier, M. Lehmann, H. C. Holst, D. Schwöppe, *Tetrahedron* **2004**, *60*, 6881-6888.

[9] a) J .Luo, B. Zhao, J. Shao, K.A. Lim, H.S.O. Chan, C. Chi, *J. Mater. Chem*. **2009**, *19*, 8327-8334; b) B. Gómez-Lor, B. Alonso, A. Omenat, J. L. Serrano, *Chem. Commun*. **2006**, 5012-5014; c) T. Rieth, S. Glang, D. Borchmann, H. Detert, *Mol. Cryst. Liq. Cryst.* **2015**, *610*, 89-99; d) R. Cristiano, H. Gallardo, A. J. Bortoluzzi, I. H. Bechtold, C. E. M. Campos, R. L. Longo, *Chem. Commu.* **2008**, 5134-5136.

[10] R. Cristiano, D. M. P. de Oliveira. Santos, H. Gallardo, *Liq. Cryst* **2005**, *32*, 7-14.

[11] A. Laurent, *J. Prakt. Chem*. **1845**, *36*, 1-10.

[12] a) H. Detert, M. Lehmann, H. Meier, *Materials* **2010**, *3*, 3218-3330; b) S. Kumar: *The Chemistry of Discotic Liquid Crystals*, CRC Press, Boca Raton, **2010**; c) S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev*. **2007**, *36*, 1902–1929; d) B. R. Kaafarani, *Chem. Mater*. **2011**, *23*, 378-396.

[13] S. Qu, Q. Lu, S. Wu, L. Wang, X. Liu, *J. Mater. Chem.* **2012**, *22*, 24605-24609.

[14] A.-F. Li, Y.-B. Ruan, Q.-Q. Jiang, W.-B. He, Y.-B. Jiang, *Chem. Eur. J.* **2010**, *16*, 5794-5802.

[15] Bhatia, S.: Gupta, M., *J. Chem. Pharm. Res.* **2011**, *3*, 137-147.

[16] a) V. N. Salimgareeva, R. M. Polevoi, V. A. Ponomareva, N. S. Sannikova, S. V. Kolesov, G. V. Leplyanin, *Russ. J. Appl. Chem.* **2003**, *76*, 1655-1658; b) K. Kotwica, A. S. Kostyuchenko, P. Data, T. Marszalek, L. Skorka, T. Jaroch, S. Kacka, M. Zagorska, R. Nowakowski, A. P. Monkman, A. S. Fisyuk, W. Pisula, A. Pron, *Chem. Europ. J.* **2016**, *22*, 11795-11806.

[17] a) M. Parra, S. Hernandez, J. Alderete, C. Zuniga, *Liq. Cryst.* **2000**, *27*, 995-1000; b) L.-R. Zhu, F. Yao, J. Han, M.-L. Pang, J.-B. Meng, *Liq. Cryst.* **2009**, *36*, 209-213; c) J. Han, X. Chang, B. Cao, Q. Wang, *Soft Mater.* **2009**, *7*, 342-354.

[17] N. K. Chudgar, S. N. Shah, R. A. Vora, *Mol. Cryst. Liq. Cryst. Inc. Nonlinear Op.* **1989**, *172*, 51-56.

[19] a) B. G. Kim, S. Kim, S. Y. Park, *Tetrahedron Lett.* **2001**, *42*, 2697-2699; b) D. D. Prabhu, N. S. S. Kumar, A. P. Sivadas, S. Varghese, S. Das, *J. Phys. Chem. B,* **2012**, *116*, 13071-13080.

[20] R. Huisgen, J. Sauer, H. J. Sturm, J. H. Markgraf, *Chem. Ber*., **1960**, *93*, 2106-2124.

[21] O. Winkelmann, C. Naether, U. Luening, *Org. Biomol. Chem*. **2009**, *7*, 553-556.

[22] a) O. Dimroth, Fester G., *Chem. Ber.* **1910**, *43*, 2219-2223; b) A. Hetzheim, in: *Houben-Weyl*, 4th ed., Vol E8c; E. Schaumann Ed., Thieme, Stuttgart 1954, p. 526.

[23] A.-A. S. El-Ahl, S. S. Elmorsy, A. H. Elbeheery, F. A. Amer, *Tetrahedron Lett.* **1997**, *38*, 1257-1260.

[24] R. Bartnik, R. Faure, K. Gebicki, *Acta Cryst. C*, **1999**, *55*, 1034-1037.

[25] Crystal structure: Mercury 3.3.; CCDC 1826069 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

[26] a) W. Pisula, Ž. Tomović, M. D. Watson, K. Müllen, J. Kussmann, C. Ochsenfeld, T. Metzroth, J. Gauss, *J. Phys. Chem. B*, **2007**, *111*, 7481–7487; b) W. Pisula, M. Kastler, C. Yang, V. Enkelmann, K. Müllen, *Chem. Asian J.* **2007**, *2*, 51-56; c) D. Wu, W. Pisula, V. Enkelmann, X. Feng, K. Müllen, *J. Am. Chem. Soc*. **2009**, *131*, 9620–9621.

[27] X. Feng, W. Pisula, M. Takase, X. Dou, V. Enkelmann, M. Wagner, N. Ding, K. Müllen, *Chem. Mater*. **2008**, *20*, 2872–2874.

[28] a) K. Balakrishnan, A. Datar, R. Oitker, H. Chen, J. Zuo, L. Zang, *J. Am. Chem. Soc.* **2005**, *127*, 10496-10497; b) F. Carta, D. Vullo, A. Maresca, A. Scozzafava, C. T. Supuran, *Bioorg. Med. Chem.* **2013**, *21*, 1564-1569; c) T. Rieth, N. Röder, M. Lehmann, H. Detert, *Chem. Eur. J.* **2018**, *24*, 93-96; d) T. Rieth, T. Marszalek, W. Pisula, H. Detert, *Chem. Eur. J*. **2014**, *20*, 5000-5006; e) S. Glang, T. Rieth, D. Borchmann, I. Fortunati, R. Signorini, H. Detert, *Eur. J. Org. Chem*. **2014**, 3116–3126.

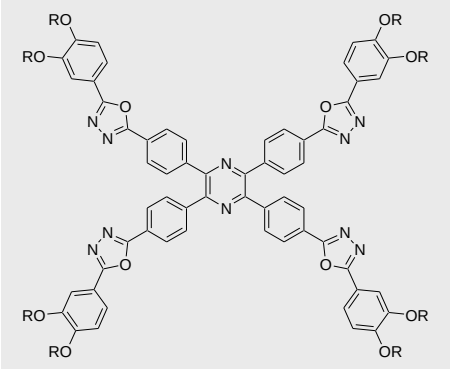
[29] J. Mei, N. L. C. Leung, R.T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Chem. Rev*. **2015**, *115*, 11718−11940.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Tetraphenylpyrazine is the core of a new series of electron deficient fluorophores. Fourfold Huisgen reaction with tetrazoles generates the diaryl-1,3,4-oxadiazole arms with alkoxy chains in the periphery. The saddle-shaped molecules assemble to columns. When alkoxy chains of 4 - 16 carbons are attached, the molecules form broad mesophases up to 246 °C and typically self-assemble in hexagonal columnar superstructures.



Discotic Liquid Crystals

Nico Röder, Tomasz Marszalek, Daniel Limbach, Wojciech Pisula and Heiner Detert**

Page No. – Page No.

Tetrakis(oxadiazolylphenyl)pyrazines:

New St. Andrew's Cross-Shaped

Liquid Crystals