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OLIGOMERS CONTAINING ETHYNYLPYRIDAZINE MOIETIES: SYNTHESIS, FLUORESCENCE AND LIQUID CRYSTALLINE PROPERTIES. DIAZINES 50

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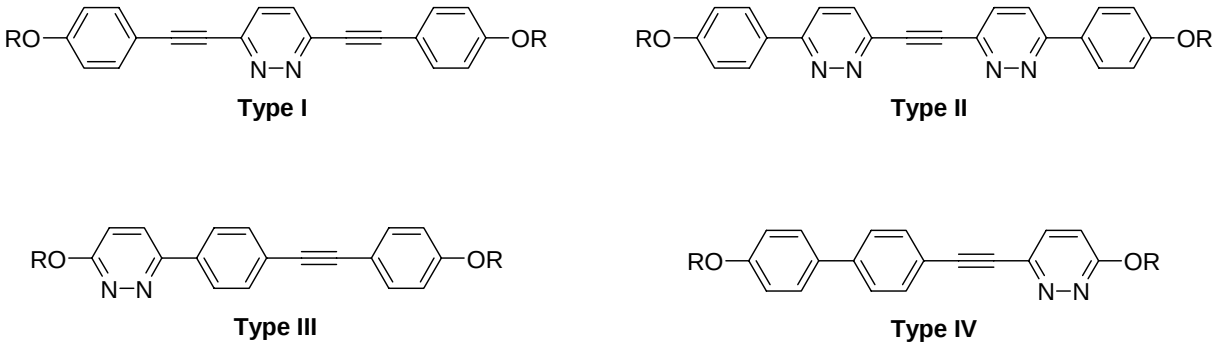
Abstract – Conjugated oligomers with ethynylpyridazine units have been synthetized by Sonogashira and Suzuki cross-coupling reactions. Some of them present interesting liquid crystals properties investigated by differential scanning calorimetry (DSC) and polarized light microscopy. Some of these oligomers are fluorescent.

INTRODUCTION

Linear arylethynyl molecules with extended π-conjugation are of considerable research interest due to their potential applications as molecular wires,[1] liquid crystals,[2] components of organic light emitting devices (OLEDs) for displays and lighting,[3] field effect transistors (FETs)[4] and non-linear optical materials.[5] Incorporation of one π-deficient heterocycle[6] such as pyridine,[7] 1,3,5-triazine,[8] pyrimidine,[9] pyrazine[10] into the backbone of such molecules gives rise to new materials with interesting properties of electron conductivity and transport compared to their phenylene analogues. On an other way, ferroelectric liquid crystal mixtures with high biaxiality were obtained with structures which present an high lateral dipole and a negative dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{//} - \varepsilon_{\perp} < 0$) or with high $\varepsilon_{\perp}$.values. Such material can be achieved by the introduction of lateral, polar groups such as F or CN into the mesogenic molecule. However laterals substituents such as cyano groups lead to a significant increase in the viscosity. Incorporation of 3,6-pyridazinyl moities, whose lone pair electrons, located at the nitrogen atoms, form a

dipole orthogonal to the long axis of the polyarylenes, is also an excellent mean to obtain liquid-crystalline compounds with negative dielectric anisotropy.[11] Ethynyl moities added in the backbone lead to ethynyl aromatic/heteroaromatic systems which are versatile rigid-rod molecules. The main advantage of them compared to their arylenevinylene counterparts is the lack of possible *Z/E* isomerism and their higher stability.[12]

With the aim to synthesize new conjugated structures containing ethynylaromatic/heteroaromatic moieties, we report therein the synthesis of a new family of four types of rod-like oligomers including pyridazine units (Scheme 1):

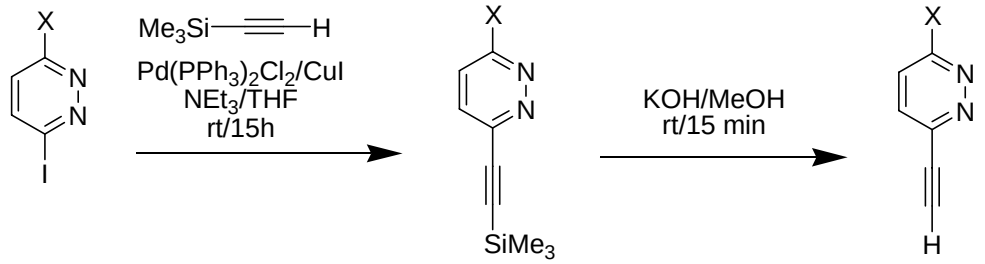


Scheme 1

Such oligomers could present several interesting applications; we report here the liquid crystalline and photophysical properties of some of them. This study is a part of our work dedicated to take advantages of diazines as building blocks for the synthesis of organic molecular materials.[13]

RESULTS AND DISCUSSION

For the synthesis of these alkynylpyridazines, the ethynyl moiety could be introduced using Sonogashira or Negishi reactions with chloro, triflate and iodo derivatives as starting materials.[14] Among these methods, iodopyridazines were the most efficient and convenient starting materials chosen to react with trimethylsilylacetylene under modified Sonogashira conditions ($Pd[PPh_3]_2Cl_2$, CuI, triethylamine in THF).[15] Moreover, due to the π-deficient character of pyridiazine ring, the iodo derivatives can be easily obtained by nucleophilic substitution of a chlorine atom by iodine starting from commercially available chloro derivatives.[16] Using this methodology, monoalkynylpyridazines **4-6** were obtained with moderate to good yields from the corresponding monoiodopyridazine **1-3** (Scheme 2):



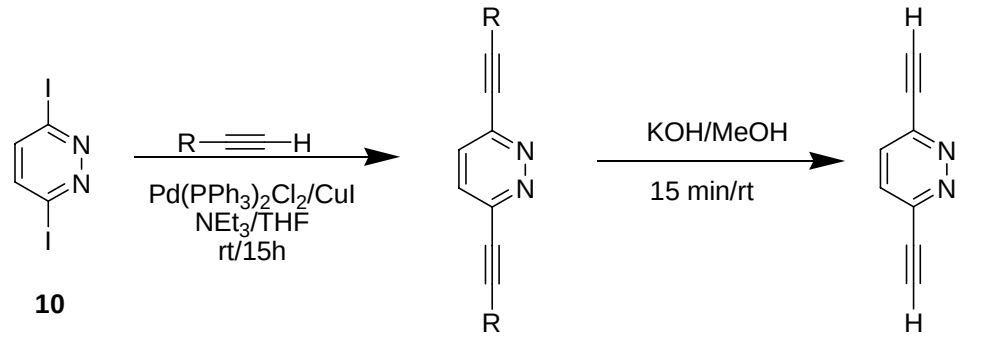
1 X = Ph
2 X = OMe
3 X = NBu_2

4 84%
5 52%
6 86%

7 91%
8 91%
9 93%

Scheme 2

Starting from 3,6-diiodopyridazine **10** and using twice Sonogashira coupling reactions, the dialkynylpyridazines **11-12** were obtained (Scheme 3). In all cases, the deprotection of the trimethylsilyl groups can be easily carried out with potassium hydroxide in methanol [17] leading to the ethynylpyridazines which could be used as building blocks for elaboration of various oligomers.



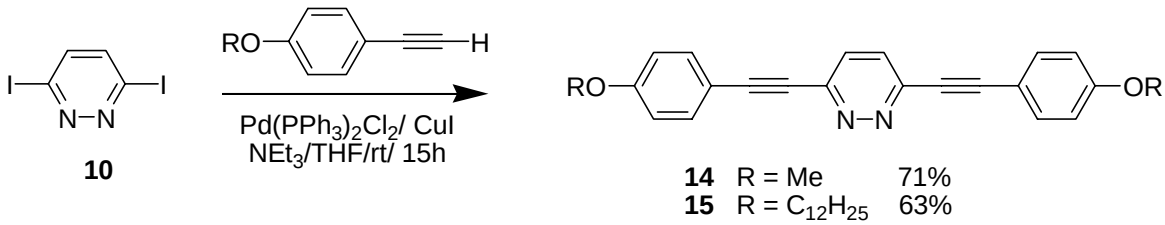
10

11 R = $SiMe_3$ 89%
12 R= C_6H_{13} 59%

13 84%

Scheme 3

The symmetrical oligomers of type I have been achieved by cross-coupling reaction of 4,6-diiodopyridazine **10** with 4-alkoxyphenylacetylene leading to compounds **14-15** (Scheme 4) in moderate yields. It could be noticed that presence of a long terminal alkoxyl chains should induce mesogenic properties for compound **15**.

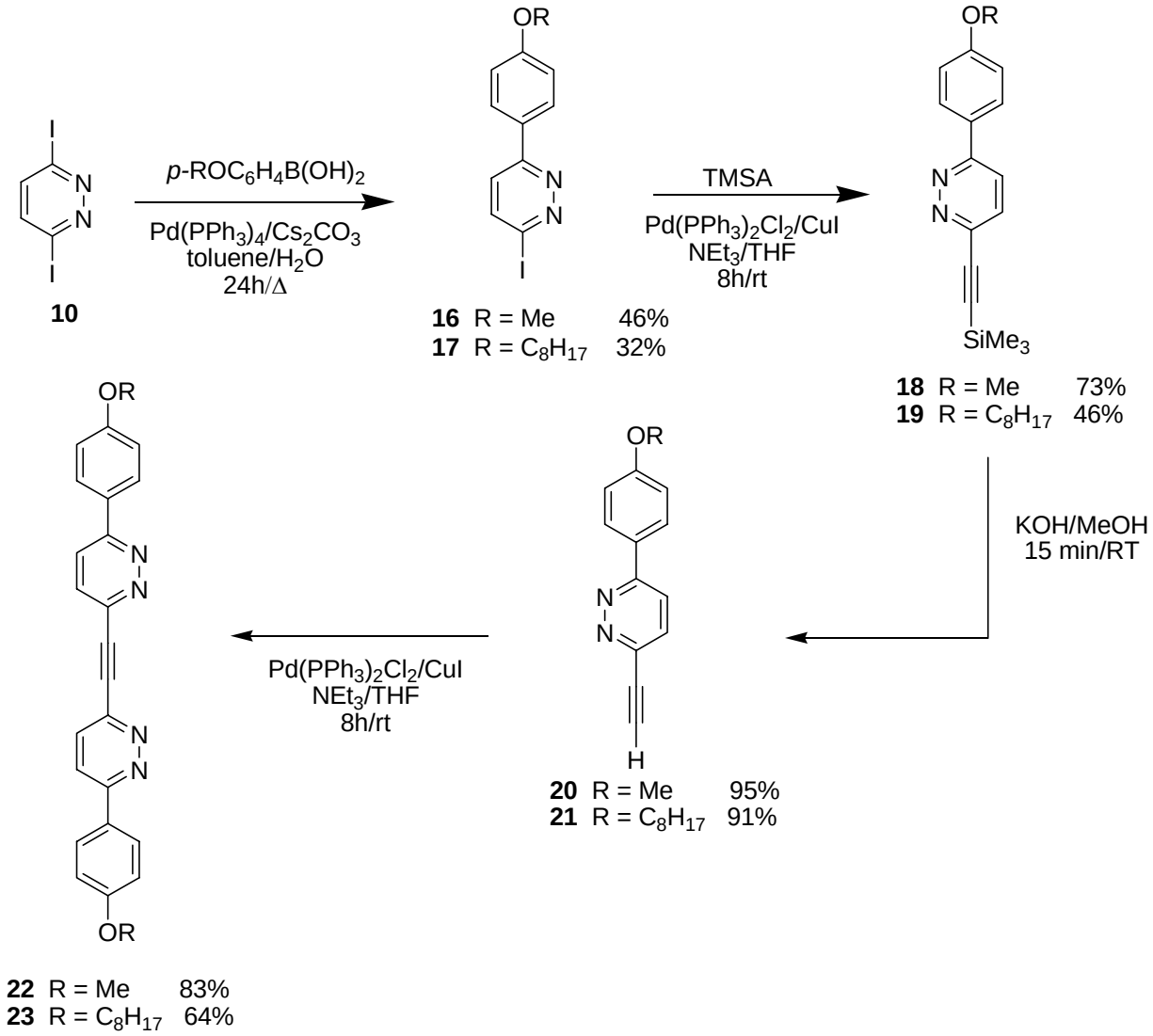


10

14 R = Me 71%
15 R = $C_{12}H_{25}$ 63%

Scheme 4

Symmetrical oligomers of type II are based on a moiety showing the successive sequence pyridazine-ethynyl-pyridazine. The Scheme 5 shows that the synthesis of such oligomers requires a succession of Suzuki and Sonogashira cross-coupling reactions as well as deprotection of terminal alkyne bearing trimethylsilyl groups.



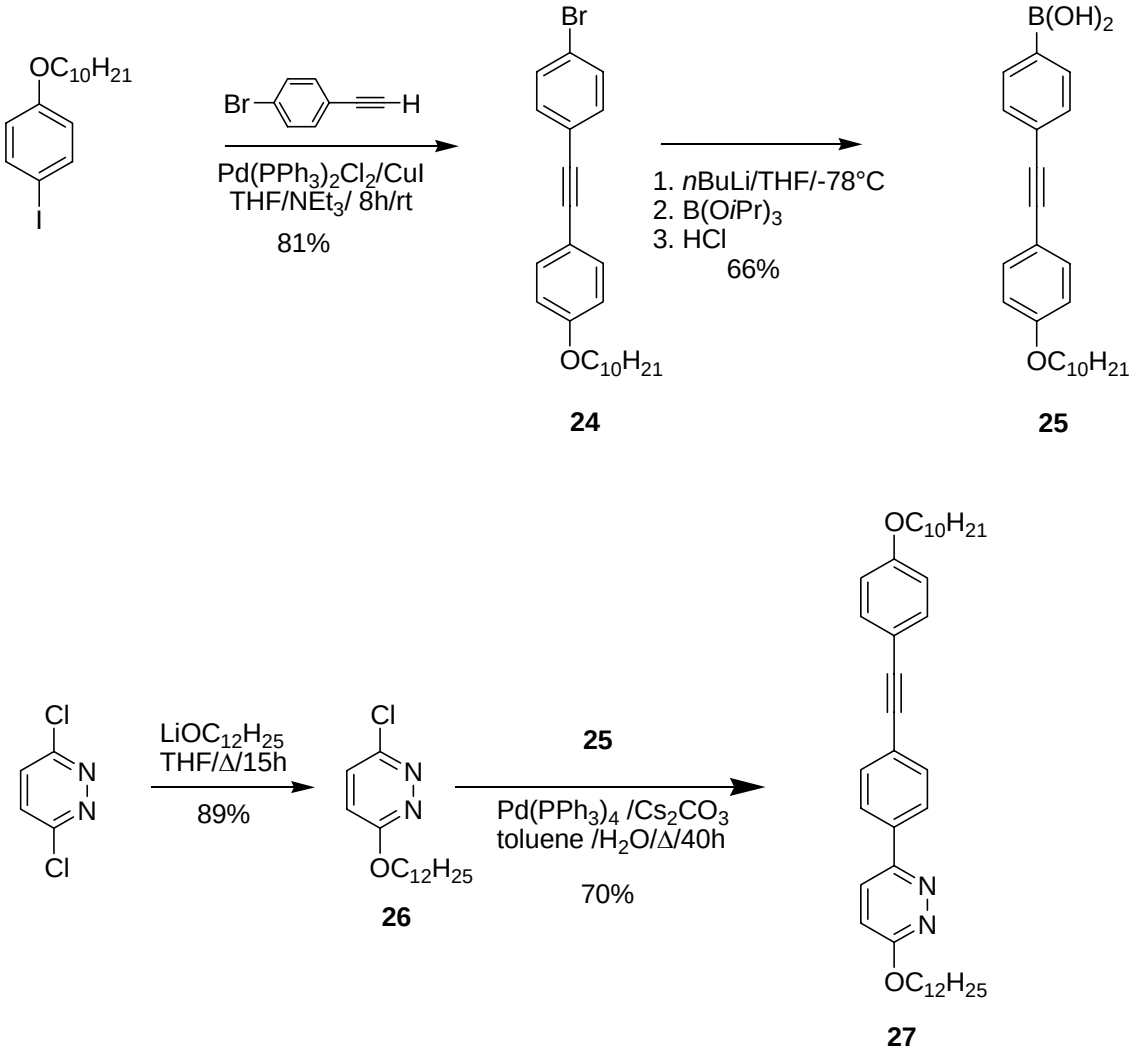
Scheme 5

The first step leads to the iodo derivatives **16** and **17** which are the key intermediates of this synthetic route.

These compounds were obtained by reaction of one equivalent of 4-substitued phenylboronic acid with the 4,6-diiodopyridazine **10** with moderate yields due to the low stability of the iodo derivatives under standard aqueous Suzuki cross coupling conditions. To improve the global yield, other synthetic routes have been tested to access to compounds **16** and **17** but are kept unsuccessful. Indeed, products **16** and **17** cannot be obtained by halogen exchange using chloro derivatives as starting materials and hydriodic acid since cleavage of the alkoxy groups is observed. The use of bromo derivatives could be an alternative

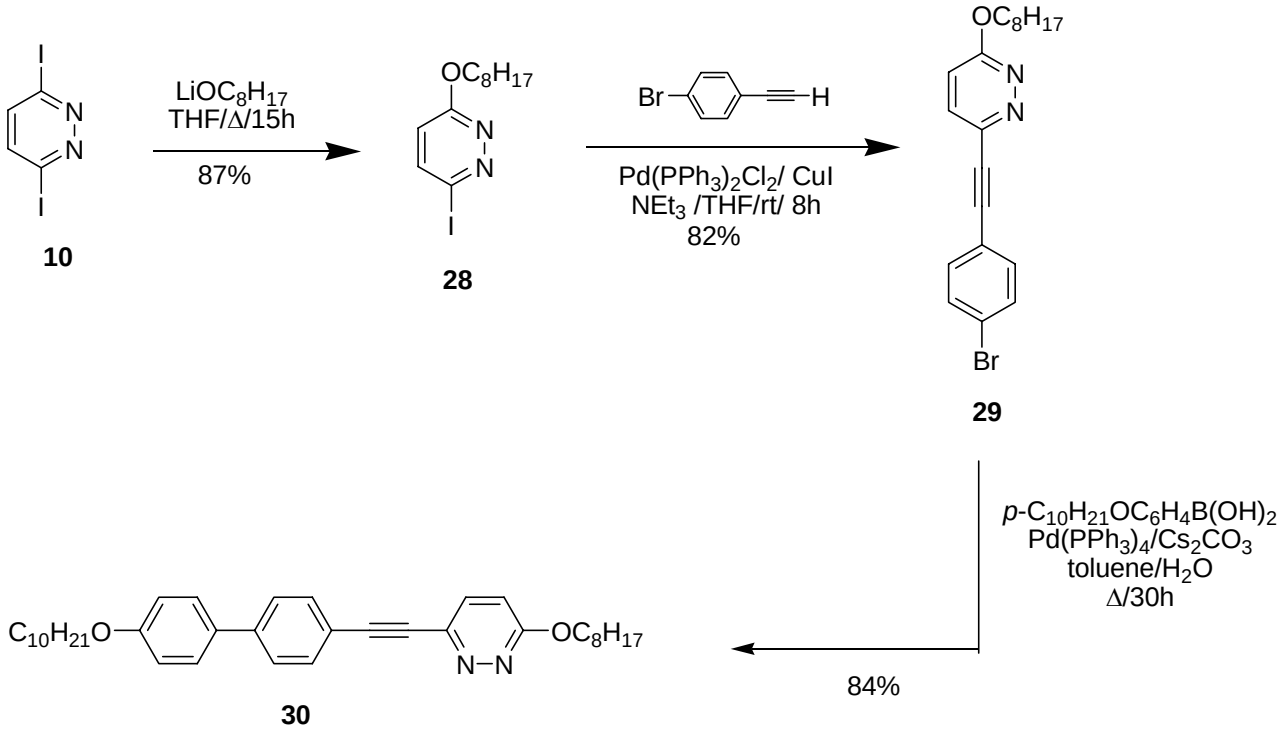
solution, but when they are used to react under cross coupling reaction, only dicoupled products are obtained. In the second step, compounds **16** and **17** were then coupled to trimethylsilylacetylene to afford **18**, **19** in acceptable yields. The deprotection of terminal alkyne by alcoholic potassium hydroxide led to **20** and **21** in good yields. A further Sonogashira cross coupling reaction with compounds **16** and **17** provided the final expected oligomers **22** and **23,** which were obtained in four steps starting from 4,6-diiodopyridazine respectively with a global yield of 26 % and 9 %.

The unsymmetrical oligomer **27** was obtained by a Suzuki cross coupling reaction of 2-alkoxy-6-chloropyridazine **26** with the elaborated phenylboronic acid **25**. This one resulted from a Sonogashira coupling reaction between 1-decyloxy-4-iodobenzene and 4-bromophenylacetylene, leading to bromo derivative **24**. A further halogen-metal exchange followed by reaction with triisopropyl borate as electrophile afforded the expected boronic acid **25**. The intermediate compound **26** resulted from a mono nucleophilic substitution of one chlorine atom of the commercial 4,6-dichloropyridazine with lithium dodecylate (Scheme 6):



Scheme 6

The synthesis of oligomer **30** was carried out in three steps starting from 4,6-diiodopyridazine **10**. The first step was a nucleophilic substitution of an iodine atom by lithium octylate, followed by a Sonogashira cross coupling reaction with 4-bromophenylacetylene affording to bromo derivative **29**. In the last step, a Suzuki coupling reaction of **29** with 4-decyloxyphenylboronic acid provided the oligomer **30** with a global yield of 60 % starting from **10** (Scheme 7):



Scheme 7

To investigate the assumed liquid crystalline properties of the oligomers, their melting behavior was examined by differential scanning calorimetry (DSC) and polarized-light optical microscopy. The oligomer **15** (Type I) showed a liquid crystalline mesophase, identified as smectic by the typical focal conic texture from the melting peak at 133.2 °C (ΔH = 14.75 kJ/mol) to the clearing temperature determinated for 208.2 °C (ΔH = 4.83 kJ/mol) during the heating run, while during the cooling run revealed the clearing peak at 194.8 °C (ΔH = 2.02 kJ/mol) and the crystallisation peak at 114.2 °C (ΔH = 8.92 kJ/mol). Polarization microscopy revealed no liquid crystalline behavior for oligomer **23** (Type II). Compound **27** (Type III) showed liquid crystalline properties with two differents mesophases. The first mesophase consists in a smectic phase between the melting peak at 81.9 °C (ΔH = 10.13 kJ/mol) and the pic corresponding to a smectic/nematic transition observed at 110.0 °C (ΔH = 4.97 kJ/mol) during the heating run (the peaks were observed respectively at 77.5 °C (ΔH = 11.93 kJ/mol) and 103.0 °C (ΔH =

4.29 kJ/mol)). The second mesophase is a nematic phase observed until the clearing peak at 178.0 °C (ΔH = 2.81 kJ/mol) during the heating run (169.3 °C (ΔH = 2.26 kJ/mol) during the cooling run). The transition temperatures and the mesophases for compounds **15**, **27** are summarized in Table 1:

Table 1. Phase transition temperatures (data in parentheses are phase-transition temperature on cooling)

Oligomer	Mesophase
15	C 133.2 (114.2) Sm 208.2 (194.8) I
27	C 81.9 (77.5) Sm 110.0 (103.0) N 178.0 (169.3) I

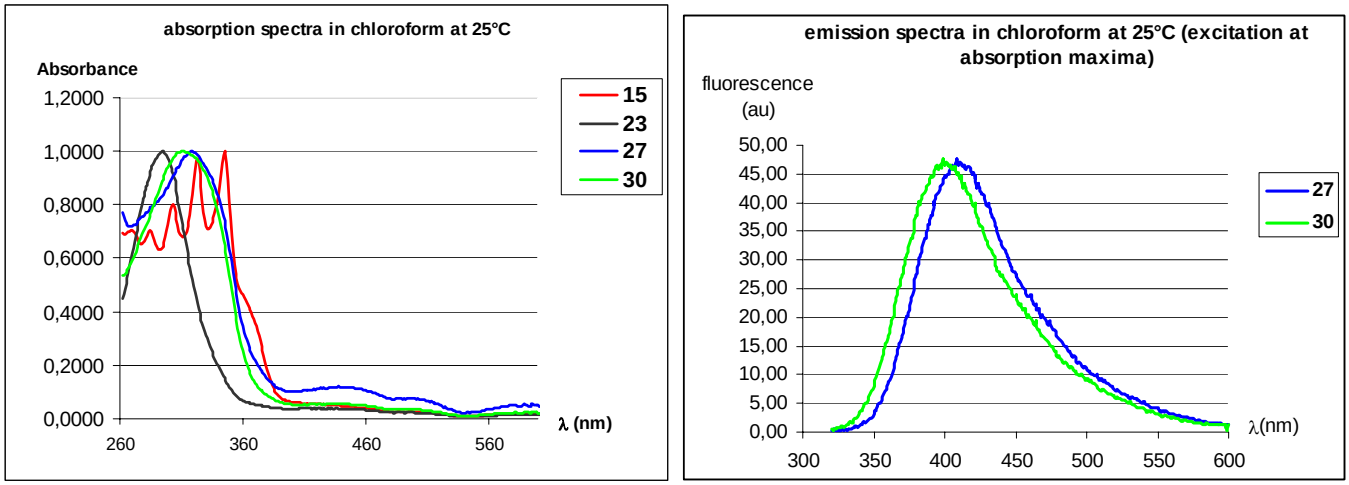


Figure 1

Table 2. Absorption and emission properties

Oligomers	*U.V. Visible*		*Fluorescence*		*Stokes Shift (nm)*
	λ_{abs}max (nm)	ε ($M^{-1}.cm^{-1}$)	λ_{em}max (nm)	ϕ_F	
15	285, 303 323, 345	25997, 29490 35768, 36829	-	-	-
23	294	30013	-	-	-
27	318	24505	422	0.05[a]	104
30	309	25672	413	0.03[a]	104

[a] sample excited at 299 nm, quantum yield determinated using 2-aminopyridine in H_2SO_4 0,1M : (ϕ_F = 0.60) as standard.[18]

The UV absorption and fluorescence emission spectra in chloroform of **15**, **23**, **27** and **30** are given in Figure 1 and Table 2. The absorption spectrum of compound **15** in chloroform show well-resolved

vibronic structures with four maxima in U. V. (285, 303, 323, 345nm) which infer the rigidity of the core structure. Compounds **15** and **23** do not show any fluorescence properties, it could be explained by a low conjugation into the pyridazine ring. On the other hand, the unsymmetrical compounds **27** and **30** are slightly fluorescent with emission maximum in violet. Their relative fluorescence quantum yields (ϕ_F) are situated between 0.03 and 0.05.

CONCLUSION

In summary, using Sonogashira and Suzuki cross-coupling reactions, we have synthesized various conjugated oligomers with ethynylpyridazine units. Some of them present interesting fluorescent properties and/or liquid crystals properties which are investigated by differential scanning calorimetry (DSC) and polarized light microscopy.

EXPERIMENTAL

Melting points were determined on a Electrothermal 1100 instrument. The ^{1}H and ^{13}C nmr spectra were recorded on a Bruker AC 300 (300 MHz 1H, 75 MHz 13C, 282.5 MHz 19F) instrument. Microanalyses were performed on a Carlo Erba CHNOS 1160 apparatus. The IR spectra were obtained as potassium bromide pellets with a Perkin-Elmer 16 PC FT-IR spectrometer. Mass spectra were recorded on an ATI-Unicam Automass® apparatus. UV-Visible spectra were obtained on a Varian Can 50 scan spectrophotometer. Fluorescence spectroscopic studies were performed in a semi-micro fluorescence cell (Hellma®, 104F-QS, 10 x 4 mm, 1400 µL) with a Varian Cary Eclipse spectrophotometer.

General procedure A for cross coupling reaction under Suzuki conditions: A mixture of halogenoaryl, arylboronic acid, tetrakis(triphenylphosphine)palladium(0) (0.05 equiv. per coupling reaction), cesium carbonate (1 equiv. per coupling reaction), aqueous 2M potassium carbonate (1 equiv. per coupling reaction.) and ethanol (1.5 mL) in degassed toluene (20 mL) was heated to reflux under nitrogen for 30 h. The reaction mixture was cooled, diluted with 20 mL of a mixture of water and EtOAc (1:1) and the organic layer separated. The aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic extracts were dried over magnesium sulfate and evaporated.

General procedure B for cross coupling reaction under Sonogashira conditions: To iodoaryl in 5 mL of THF was added alcyne, 0.5 mL of NEt_3, 3 % mol (per coupling reaction) of CuI and 3 % mol (per coupling reaction) of $Pd(PPh_3)_2Cl_2$. The suspension was stirred at rt for 8h. The reaction mixture was cooled, diluted with 20 mL of a mixture of water and CH_2Cl_2 (1:1) and the organic layer separated. The

aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were dried over magnesium sulfate, filtered and evaporated.

General procedure C for trimethylsilyl groups deprotection: A mixture of arylethynyltrimethylsilane and a solution of potassium hydroxide in MeOH (1M, 10 mL) was stirred at rt for 15 min, Then the solution was neutralized with 1M aqueous HCl and extracted with CH_2Cl_2 (3 x 20 mL) The combined organic extracts were dried over magnesium sulfate, filtered and evaporated.

3-Phenyl-6-(trimethylsilylethynyl)pyridazine (4): Sonogashira cross-coupling reaction of 3-iodo-6-phenylpyridazine (400 mg, 1.42 mmol) with ethynyltrimethylsilane (404 µL, 2.84 mmol) according to the general procedure B gave after purification by column chromatography (silica gel, eluent petroleum ether : EtOAc (90:10)) 300 mg (84 %) of **4** as a beige solid. mp 138 °C. ^{1}H NMR ($CDCl_3$) : δ 0.32 (s, 9H, $Si(Me)_3$), 7.52 (m, 3H, H_{Ph}), 7.62 (d, 1H, J = 8.7 Hz, H_5), 7.82 (d, 1H, J = 8.7 Hz, H_4), 8.09 (m, 2H, HPh) ^{13}C ($CDCl_3$) : δ 0.0, 101.1, 101.2, 123.4, 127.6, 129.5, 130.6, 130.8, 136.1, 146.5, 157.5 IR : 2170, 1540, 1450, 1396, 1277, 1250, 864, 840, 748, 688 cm^{-1} *Anal.* Calcd for $C_{15}H_{16}N_2Si$ (252.11): C, 71.38 H, 6.39 N, 11.10. Found: C, 71.45 H, 6.31 N, 11.00.

3-Methoxy-6-(trimethylsilylethynyl)pyridazine (5): Sonogashira cross-coupling reaction of 3-iodo-6-methoxypyridazine (334 mg, 1.42 mmol) with ethynyltrimethylsilane (404 µL, 2.84 mmol) according to the general procedure B gave after purification by column chromatography (silica gel, eluent CH_2Cl_2) 152 mg (52 %) of **5** as a brown solid. mp 72 °C. ^{1}H NMR ($CDCl_3$) : δ 0.30 (s, 9H, $Si(Me)_3$), 4.16 (s, 3H, OMe), 6.92 (d, 1H, J = 9.0 Hz, H_5), 7.46 (d, 1H, J = 8.7 Hz, H_4) ^{13}C ($CDCl_3$) : δ 0.0, 55.5, 60.8, 100.9, 116.8, 132.8, 143.7, 163.8 IR : 2168, 1591, 1542, 1461, 1406, 1329, 1292, 15252, 1011, 865, 814 cm^{-1} *Anal.* Calcd for $C_{10}H_{14}N_2OSi$ (206.09): C, 58.21 H, 6.84 N, 13.58. Found: C, 57.89 H, 6.61 N, 13.32.

3-Dibutylamino-6-(trimethylsilylethynyl)pyridazine (6): Sonogashira cross-coupling reaction of 3-dibutylamino-6-iodopyridazine (600 mg, 1.8 mmol) with ethynyltrimethylsilane (384 µL, 2.7 mmol) according to the general procedure B gave after purification by column chromatography (silica gel, eluent petroleum ether : EtOAc (8:2)) 469 mg (86 %) of **6** as a colorless oil. ^{1}H NMR ($CDCl_3$) : δ 0.23 (s, 9H, $Si(Me)_3$), 0.92 (t, J = 7.3 Hz, 6H, 2 x Me), 1.36-1.28 (m, 4H, 2 x CH_2), 1.59-1.54 (m, 4H, 2 x CH_2), 3.48 (t, J = 7.7 Hz, 4H, $N(CH_2)_2$), 6.46 (d, J = 9.4 Hz, 1H, H_4), 7.18 (d, J = 9.4 Hz, 1H, H_5) ^{13}C ($CDCl_3$) : δ 0.0, 14.1, 20.4, 29.7, 48.9, 95.8, 102.5, 109.6, 130.3, 137.2, 156.7 IR : 691, 758, 860, 1067, 1290, 1341, 1413,

1465, 1542, 1587, 2227 cm^{-1} *Anal.* Calcd for $C_{17}H_{29}N_3Si$ (303.21): C, 67.27 H, 9.63 N, 13.84. Found: C, 67.23 H, 9.70 N, 13.85.

3-Ethynyl-6-phenylpyridazine (7): Trimethylsilyl deprotection reaction of **4** (100 mg, 0.40 mmol) according to the general procedure C (reaction time: 15 min) gave 66 mg (91 %) of **7** as a brown solid. mp 118 °C. ^1H NMR ($CDCl_3$) : δ 3.48 (s, 1H, $H_{2'}$), 7.56-7.53 (m, 3H, H_{Ph}), 7.67 (d, *J* = 9.4 Hz, 1H, H_4), 7.86 (d, *J* = 9.4 Hz, 1H, H_5), 8.13-8.10 (m, 2H, H_{Ph}). ^{13}C ($CDCl_3$) : δ 80.6, 82.4, 123.4, 127.6, 129.5, 130.7, 130.9, 136.0, 145.9, 158.0 IR : 3294, 2118, 1449, 1401, 1115, 1013, 866, 746, 690, 633 cm^{-1} *Anal.* Calcd for $C_{12}H_8N_2$ (180.07) : C, 79.98 H, 4.47 N, 15.55. Found: C, 79.90 H, 4.42 N, 15.48.

3-Ethynyl-6-methoxypyridazine (8): Trimethylsilyl deprotection reaction of **5** (151 mg, 1.12 mmol) according to the general procedure C (reaction time: 15 min) gave after purification by column chromatography (silica gel, eluent CH_2Cl_2) 66 mg (91 %) of **8** as a brown solid. mp <50 °C. ^1H NMR (CDC_{l3}) : δ 3.31 (s, 1H, $H_{2'}$), 4.16 (s, 3H, OMe), 6.94 (d, *J* = 9.4 Hz, 1H, H_4), 7.47(d, *J* = 9.4 Hz, 1H, H_5) ^{13}C ($CDCl_3$) : δ 54.1, 79.2, 95.7, 115.6, 131.5, 141.6, 162.7 IR : 3276, 2115, 1587, 1460, 1406, 1327, 1290, 1099, 1010, 857, 717, 648 cm^{-1} *Anal.* Calcd for $C_7H_6N_2O$ (134.05): C, 62.68 H, 4.51 N, 20.88. Found: C, 62.35 H, 4.74 N, 20.71.

6-Dibutylamino-3-ethynylpyridazine (9): Trimethylsilyl deprotection reaction of **6** (450 mg, 1.48 mmol) according to the general procedure C (reaction time: 15 min) gave 318 mg (93 %) of **9** as a yellow oil. ^1H NMR (CDC_{l3}) : δ 0.90 (t, *J* = 7.3 Hz, 6H, 2 x Me), 1.34-1.27 (m, 4H, 2 x CH_2), 1.57-1.51 (m, 4H, 2 x CH_2), 3.18 (s, 1H, $H_{2'}$), 3.47 (t, *J* = 7.7 Hz, 4H, $N(CH_2)_2$), 6.61 (d, *J* = 9.4 Hz, 1H, H_4), 7.20 (d, *J* = 9.4 Hz, 1H, H_5) ^{13}C ($CDCl_3$) : δ 14.3, 20.5, 30.0, 49.1, 78.8, 81.5, 110.3, 130.9, 136.5, 157.0 IR : 3310, 2958, 2931, 2872, 2110, 1588, 1544, 1487, 1455, 1428, 1373, 1179 cm^{-1} *Anal.* Calcd for $C_{14}H_{21}N_3$ (231.17): C, 72.69 H, 9.15 N, 18.16. Found: C, 72.44 H, 9.02 N, 18.03.

3,6-Bis(trimethylsilanylethynyl)pyridazine (11): Sonogashira cross-coupling reaction of 4,6-diiodopyridazine (250 mg, 0.8 mmol) with Ethynyltrimethylsilane (196 mg, 2.0 mmol) according to the general procedure B gave after purification by column chromatography (silica gel, eluent CH_2Cl_2) 182 mg (94 %) of **11** as a brown solid. mp 124 °C. ^1H NMR ($CDCl_3$) : δ 0.28 (s, 18H, $Si(Me)_3$), 7.50 (s, 2H, $H_{4,5}$) ^{13}C ($CDCl_3$) : δ 0.0, 100.9, 102.8, 129.5, 146.0 IR : 2958, 171, 1528, 1389, 1255, 847, 762 cm^{-1} *Anal.* Calcd for $C_{14}H_{20}N_2Si_2$ (272.12): C, 61.71 H, 7.40 N, 10.28. Found: C, 61.40 H, 7.25 N, 10.25.

3,6-Di(oct-1-ynyl)pyridazine (12): Sonogashira cross-coupling reaction of 4,6-diiodopyridazine (200 mg, 0.6 mmol) with oct-1-yne (165 mg, 1.5 mmol) according to the general procedure B gave after purification by column chromatography (silica gel, eluent CH_2Cl_2) 99 mg (56 %) of **12** as a brown solid. mp < 50 °C. ^{1}H NMR ($CDCl_3$) : δ 0.90 (t, *J* = 6.8 Hz, 6H, Me), 1.68-1.25 (m, 16H, 8 x CH_2), 2.49 (t, *J* = 7.1 Hz, 4H, 2 x CH_2), 7.39 (s, 2H, $H_{4,5}$) ^{13}C ($CDCl_3$) : δ 14.4, 20.0, 22.9, 28.5, 29.0, 31.7, 78.1, 98.0, 129.0, 146.3 IR : 2955, 2931, 2857, 2233, 1528, 1468, 1399, 1283, 872 cm^{-1} *Anal.* Calcd for $C_{20}H_{28}N_2$ (293.23): C, 81.03 H, 9.52 N, 9.45. Found: C, 80.65 H, 9.30 N, 9.08.

3,6-Diethynylpyridazine (13): Trimethylsilyl deprotection reaction of **11** (150 mg, 0.55 mmol) according to the general procedure C (reaction time: 15 min) gave gave after purification by column chromatography (silica gel, eluent CH_2Cl_2) 59 mg (84 %) of **13** as a brown solid. mp 80 °C. ^{1}H NMR ($CDCl_3$) : δ 3.54 (s, 2H, $H_{2'}$), 7.59 (s, 2H, $H_{4,5}$) ^{13}C ($CDCl_3$) : δ 80.0, 84.1, 129.6, 145.8 IR : 3401, 3238, 3161, 2924, 2118, 1528, 1408, 1246, 1107, 849, 760, 714, 525, 481 cm^{-1} *Anal.* Calcd for $C_8H_4N_2$ (128.04): C, 74.99 H, 3.15 N, 21.86. Found: C, 74.85 H, 3.33 N, 21.69.

3,6-Bis-(4-methoxyphenylethynyl)pyridazine (14): Sonogashira cross-coupling reaction of 4,6-diiodopyridazine (298 mg, 0.9 mmol) with 1-ethynyl-4-methoxybenzene (300 mg, 2.27 mmol) according to the general procedure B gave after purification by column chromatography (silica gel, eluent EtOAc : petroleum ether (1:9)) 217 mg (71 %) of **14** as a beige solid. mp 189 °C. ^{1}H NMR ($CDCl_3$) : δ 3.84 (s, 6H, 2 x OMe), 6.91 (d, *J* = 8.7 Hz, 4H, H_{Ph}), 7.56 (s, 2H, $H_{4,5}$), 7.58 (d, *J* = 8.7 Hz, 4H, H_{Ph}). ^{13}C ($CDCl_3$) : δ 55.8, 85.5, 96.3, 113.8, 114.6, 129.0, 134.3, 146.2, 161.1 IR : 2216, 1603, 1531, 1516, 1504, 1396, 1291, 1249, 1161, 1029, 835 cm^{-1} *Anal.* Calcd for $C_{22}H_{16}N_2O_2$ (340.12): C, 77.63 H, 4.74 N, 8.23. Found: C, 77.35 H, 4.89 N, 8.05.

3,6-Bis-(4-dodecyloxyphenylethynyl)-pyridazine (15): Sonogashira cross-coupling reaction of 4,6-diiodopyridazine (298 mg, 0.9 mmol) with 1-dodecyloxy-4-ethynylbenzene (772 mg, 2.70 mmol) according to the general procedure B gave after purification by column chromatography (silica gel, eluent EtOAc : petroleum ether (1:9)) and recrystalisation in ethanol 368 mg (63 %) of **15** as a beige solid. ^{1}H NMR ($CDCl_3$) : δ 0.89 (t, 6H, *J* = 6.8 Hz, 2 x Me), 1.48-1.29 (m, 36H, 18 x CH_2), 1.83-176 (m, 4H, *J* = 6.8 Hz, 2 x $OCH_2C\underline{H_2}$), 3.95 (t, 4H, *J* = 6.8 Hz, 2 x OCH_2), 6.90 (d, *J* = 8.6 Hz, 2H, H_{Ph}), 7.58-7.55 (m, 3H, H_{Ph}) ^{13}C ($CDCl_3$) : δ 14.5, 23.1, 26.1, 26.4, 29.5, 29.8 (2C), 29.9, 30.0 (2C), 32.3, 68.5, 85.5, 96.4, 113.5, 115.1, 128.9, 134.2, 146.2, 160.7 IR : 2921, 2851, 2212, 1604, 1415, 1470, 1404, 1288, 1250,

1162, 830 cm^{-1} *Anal.* Calcd for $C_{44}H_{60}N_2O_2$ (648.47): C, 81.43 H, 9.32 N, 4.32. Found: C, 81.14 H, 9.51 N, 4.01.

3-Iodo-6-(4-methoxyphenyl)pyridazine (16): Suzuki cross-coupling reaction of 4,6-diiodopyridazine (873 mg, 2.63 mmol) with 4-methoxyphenylboronic acid (400 mg, 2.63 mmol) according to the general procedure A (t = 15 h) gave after purification by column chromatography (silica gel, eluent CH_2Cl_2) 377 mg (46 %) of **16** as an orange solid. mp 208 °C. ^{1}H NMR (DMSO-d_6) : δ 3.86 (s, 3H, OMe), 7.13 (d, J = 9.1 Hz, 2H, H_{Ph}), 7.95 (d, J = 9.0 Hz, 1H, H_4), 8.12 (d, J = 9.1 Hz, 2H, H_{Ph}), 8.18 (d, J = 9.0Hz, 1H, H_5) ^{13}C (DMSO-d_6) : δ 55.7, 114.9, 125.1, 125.4, 127.6, 128.6, 137.8, 157.7, 161.6 IR : 1606, 1505, 1394, 1298, 1250, 1182, 1030, 835, 822, 744, 561 cm^{-1} MS (IE) *m/z:* 312 (M^+, 100), 313 (M^+, 11) *Anal.* Calcd for $C_{11}H_9IN_2O$ (311.98): C, 42.33 H, 2.91 N, 8.98. Found: C, 42.48 H, 2.89 N, 8.87.

3-Iodo-6-(4-octyloxyphenyl)pyridazine (17): Suzuki cross-coupling reaction of 4,6-diiodopyridazine (1.50 g, 4.52 mmol) with 4-octyloxyphenylboronic acid (1.13 g, 4.52 mmol) according to the general procedure A (t = 15 h) gave after purification by column chromatography (silica gel, eluent CH_2Cl_2) and recrystallisation in methylcyclohexane 592 mg (32 %) of **17** as an ivory solid. mp 159 °C. ^{1}H NMR ($CDCl_3$) : δ 0.90 (t, J = 6.8 Hz, 3H, Me), 1.48-1.30 (m, 10H, 5 x CH_2), 1.85-1.80 (m, 2H, CH_2), 4.03 (t, J = 6.4 Hz, 2H, OCH_2), 7.01 (d, J = 8.7 Hz, 2H, H_{Ph}), 7.49 (d, J = 9.0 Hz, 1H, H_4), 7.84 (d, J = 9.0 Hz, 1H, H_5), 8.00 (d, J = 8.7 Hz, 2H, H_{Ph}) ^{13}C ($CDCl_3$) : δ 14.5, 23.1, 26.4, 29.4, 29.6, 29.8, 32.2, 68.6, 115.4, 122.9, 124.7, 127.6, 128.9, 137.6, 158.5, 161.7 IR : 2955, 2921, 2853, 1608, 1394, 1262, 1183, 835, 828 cm^{-1} *Anal.* Calcd for $C_{18}H_{23}IN_2O$ (410.09): C, 52.69 H, 5.65 N, 6.83. Found: C, 52.33 H, 5.41 N, 6.61.

3-(4-Methoxyphenyl)-6-(trimethylsilylethynyl)pyridazine (18): Sonogashira cross-coupling reaction of **16** (155 mg, 0.55 mmol) with ethynyltrimethylsilane (142 µL, 1.0 mmol) according to the general procedure B gave after purification by column chromatography (silica gel, eluent: CH_2Cl_2) 102 mg (73 %) of **18** as a yellow solid. mp 146 °C. ^{1}H NMR ($CDCl_3$) : δ 0.32 (s, 9H, $Si(Me)_3$), 3.88 (s, 3H, OMe), 7.03 (d, J = 8.7 Hz, 2H, H_{Ph}), 7.56 (d, J = 9.0 Hz, 1H, H_4), 7.74 (d, J = 9.0 Hz, 1H, H_5), 8.07 (d, J = 8.7 Hz, 2H, H_{Ph}) ^{13}C ($CDCl_3$) : δ 0.0, 55.8, 100.5, 101.4, 114.8, 122.4, 128.5, 129.0, 130.4, 145.9, 157.0, 161.9 IR: 2167, 1610, 1510, 1397, 1253, 1183, 1034, 867, 829, 761 cm^{-1} *Anal.* Calcd for $C_{16}H_{18}N_2OSi$ (282.12): C, 68.05 H, 6.42 N, 9.92. Found: C, 68.02 H, 6.39 N, 9.93.

3-(4-Octyloxyphenyl)-6-(trimethylsilylethynyl)pyridazine (19): Sonogashira cross-coupling reaction of **17** (355 mg, 0.87 mmol) with ethynyltrimethylsilane (240 µL, 1.73 mmol) according to the general procedure B gave after purification by column chromatography (silica gel, eluent: CH_2Cl_2) 194 mg (59 %) of

19 as a brown solid**.** mp 93 °C. ^{1}H NMR ($CDCl_3$) : δ 0.29 (s, 9H, $Si(Me)_3$), 0.90 (t, *J* = 6.8 Hz, 3H, Me), 1.48-1.30 (m, 10H, 5 x CH_2), 1.84-1.79 (m, 2H, CH_2), 4.01 (t, *J* = 6.4 Hz, 2H, OCH_2), 7.01 (d, *J* = 8.7 Hz, 2H, H_{Ph}), 7.54 (d, *J* = 9.0 Hz, 1H, H_4), 7.73 (d, *J* = 9.0 Hz, 1H, H_5), 8.03 (d, *J* = 8.7 Hz, 2H, H_{Ph}) ^{13}C ($CDCl_3$) : δ 0.0, 14.4, 22.7, 26.1, 29.3 (2C), 29.4, 31.9, 54.7, 99.6, 101.7, 115.2, 122.8, 127.9, 128.8, 130.6, 145.4, 156.8, 161.3 IR : 3428, 2252, 1651, 1249, 1025, 1004, 821, 761 cm^{-1} *Anal.* Calcd for $C_{23}H_{32}N_2OSi$ (380.23): C, 72.58 H, 8.47 N, 7.36. Found: C, 72.41 H, 8.34 N, 7.28.

3-Ethynyl-6-(4-methoxyphenyl)pyridazine (20): Trimethylsilyl deprotection reaction of **18** (80 mg, 0.28 mmol) according to the general procedure C (reaction time: 15 min) gave 57 mg (95 %) of **20** as a brown solid. mp 158 °C. ^{1}H NMR ($CDCl_3$) : δ 3.44 (s, 1H, $H_{2'}$), 3.88 (s, 3H, OMe), 7.04 (d, *J* = 8.7 Hz, 2H, H_{Ph}), 7.60 (d, *J* = 9.0 Hz, 1H, H_4), 7.67 (d, *J* = 9.0 Hz, 1H, H_5), 8.06 (d, *J* = 8.7 Hz, 2H, H_{Ph}) ^{13}C ($CDCl_3$) : δ 55.8, 81.2, 82.1, 114.9, 122.5, 128.4, 129.0, 130.6, 145.3, 157.5, 162.0 IR : 3267, 2115, 1607, 1574, 1510, 1425, 1394, 1274, 1251, 1188, 1032, 829, 663 cm^{-1} *Anal.* Calcd for $C_{13}H_{10}N_2O$ (210.08): C, 74.27 H, 4.79 N, 13.32. Found: C, 74.42 H, 4.46 N, 12.99.

3-Ethynyl-6-(4-octyloxyphenyl) pyridazine (21): Trimethylsilyl deprotection reaction of **19** (152 mg, 0.40 mmol) according to the general procedure C (reaction time: 15 min) gave 112 mg (91 %) of **21** as a beige solid. mp 117 °C. ^{1}H NMR ($CDCl_3$) : δ 0.90 (t, *J* = 6.8 Hz, 3H, Me), 1.48-1.30 (m, 10H, 5 x CH_2), 1.84-1.79 (m, 2H, CH_2), 3.48 (s, 1H, $H_{2'}$), 4.01 (t, *J* = 6.4 Hz, 2H, OCH_2), 7.03 (d, *J* = 8.7 Hz, 2H, H_{Ph}), 7.58 (d, *J* = 9.0 Hz, 1H, H_4), 7.74 (d, *J* = 9.0 Hz, 1H, H_5), 8.05 (d, *J* = 8.7 Hz, 2H, H_{Ph}) ^{13}C ($CDCl_3$) : δ 14.5, 23.0, 26.4, 29.5, 29.6, 29.7, 32.2, 68.6, 80.3, 82.2, 115.4, 122.6, 128.0, 129.0, 130.6, 145.2, 157.6, 161.6 IR : 3294, 2955, 2920, 2853, 2116, 1609, 1511, 1400, 1255, 1001, 837, 823 cm^{-1} *Anal.* Calcd for $C_{20}H_{24}N_2O$ (308.19): C, 77.89 H, 7.84 N, 9.08. Found: C, 77.74 H, 7.71 N, 9.18.

6,6'-Bis-(4-methoxyphenyl)[3,3']bipyridazinylacetylene (22): Sonogashira cross-coupling reaction of **16** (72 mg, 0.23 mmol) with **20** (72 mg, 0.30 mmol) according to the general procedure B gave after purification by column chromatography (silica gel, eluent CH_2Cl_2) 75 mg (83 %) of **22** as a beige solid. mp 152 °C. ^{1}H NMR ($CDCl_3$) : δ 3.90 (s, 6H, 2 x OMe), 7.06 (d, *J* = 8.7 Hz, 4H, H_{Ph}), 7.53 (d, *J* = 9.0 Hz, 2H, H_4), 7.78 (d, *J* = 9.0 Hz, 2H, H_5), 8.02 (d, *J* = 8.7 Hz, 4H, H_{Ph}) ^{13}C ($CDCl_3$) : δ 54.4, 77.4, 113.5, 121.5, 123.2, 126.5, 127.3, 136.2, 157.0, 160.7 IR : 2961, 2928, 1731, 1608, 1510, 1400, 1299, 1258, 1182, 823 cm^{-1} *Anal.* Calcd for $C_{24}H_{18}N_4O_2$ (394.14): C, 73.08 H, 4.60 N, 14.20. Found: C, 73.39 H, 4.41 N, 13.88.

6,6'-Bis(4-octyloxyphenyl)[3,3']bipyridazinylacetylene (23): Sonogashira cross-coupling reaction of **17** (231 mg, 0.56 mmol) with **21** (115 mg, 0.37 mmol) according to the general procedure E gave after purification by column chromatography (silica gel, eluent CH_2Cl_2) 140 mg (64 %) of **23** as a beige solid. mp 160 °C. ^{1}H NMR ($CDCl_3$) : δ 0.90 (t, *J* = 6.8 Hz, 6H, 2 x Me), 1.48-1.30 (m, 20H, 10 x CH_2), 1.85-1.80 (m, 4H, 2 x CH_2), 4.03 (t, *J* = 6.4 Hz, 4H, 2 x OCH_2), 7.02 (d, *J* = 8.7 Hz, 4H, H_{Ph}), 7.48 (d, *J* = 9.0 Hz, 2H, H_4), 7.84 (d, *J* = 9.0 Hz, 2H, H_5), 8.00 (d, *J* = 8.7 Hz, 4H, H_{Ph}) ^{13}C ($CDCl_3$) : δ 14.5, 23.1, 26.4, 29.6 (2C), 29.7, 32.2, 68.6, 77.4, 115.4, 122.9, 124.6, 127.6, 128.7, 137.6, 158.5, 161.7 IR : 2955, 2922, 2854, 1609, 1394, 1262, 1183, 835, 820 cm^{-1} *Anal.* Calcd for $C_{38}H_{46}N_4O_2$ (590.36): C, 77.25 H, 7.85 N, 9.48. Found: C, 76.97 H, 7.99 N, 9.63.

1-Decyloxy-4-(4-bromophenylethynyl)benzene (24): Sonogashira cross-coupling reaction of 1-decyloxy-4-iodobenzene (1.47 g, 4.08 mmol) with 1-bromo-4-ethynylbenzene (1.05 g, 5.83 mmol) according to the general procedure B gave after purification by column chromatography (silica gel, eluent petroleum ether:EtOAc (9:1)) 1.36 g (81 %) of **24** as a pale yellow solid. mp 82 °C. ^{1}H NMR ($CDCl_3$) : δ 0.90 (t, 3H, *J* = 6.8 Hz, Me), 1.46-1.28 (m, 14H, 7 x CH_2), 1.81-1.68 (m, 2H, *J* = 6.8 Hz, $OCH_2C\underline{H}_2$), 3.98 (t, 2H, *J* = 6.8 Hz, OCH_2), 6.86 (d, 2H, *J* = 9.0 Hz, H_{Ph}), 7.38 (d, 2H, *J* = 9.0 Hz, H_{Ph}), 7.45 (d, 2H, *J* = 9.0 Hz, H_{Ph}), 7.48 (d, 2H, *J* = 9.0 Hz, H_{Ph}) ^{13}C ($CDCl_3$) : δ 14.5, 23.1, 26.4, 29.6 (2C), 29.7, 29.8, 29.9, 30.0, 68.5, 87.3, 91.1, 114.9, 115.0, 122.4, 123.0, 131.9, 133.2, 133.4, 159.8 IR: 2919, 2850, 2216, 1606, 1511, 1287, 1253, 1089, 840, 824 cm^{-1} *Anal.* Calcd for $C_{24}H_{29}BrO$ (412.14): C, 69.73 H, 7.07. Found: C, 63.64 H, 6.96.

4-(4-Decyloxyphenylethynyl) phenylboronic acid (25): To a solution of **24** (1.55 g, 3.78 mmol) in anhydrous THF (100 mL) under nitrogen at –78 °C was added *n*-BuLi (1.6 M in hexanes, 1.2 equiv.) dropwise. The reaction mixture was stirred at –78 °C for 30 min then triisopropyl borate (3 equiv.) was added dropwise, the reaction mixture was stirred again for 30 min at –78 °C and allowed to to warm to 20 °C with stirring overnight. The reaction was quenched with a mixture of THF : HCl : EtOH (8:2:2), neutralized with aqueous saturated $NaHCO_3$, diluted with 50 mL of a mixture of water and Et_2O (1:1) and the organic layer separated. The aqueous layer was extracted with Et_2O (2 x 50 mL). The combined organic extracts were dried over magnesium sulfate and evaporated. If necessary, the product is purified by washing with CH_2Cl_2 to give 944 g (66 %) of **25** as a yelow solid. mp 98 °C. ^{1}H NMR (DMSO-d_6) : δ 0.86 (t, 3H, *J* = 6.8 Hz, Me), 1.41-1.26 (m, 14H, 7 x CH_2), 1.74-1.70 (m, 2H, *J* = 6.8 Hz, $OCH_2C\underline{H}_2$), 4.01 (t, 2H, *J* = 6.8 Hz, OCH_2), 6.98 (d, 2H, *J* = 9.0 Hz, H_{Ph}), 7.50-7.47 (m, 4H, H_{Ph}), 7.81 (d, 2H, *J* = 9.0 Hz, H_{Ph}), 8.18 (s, 2H, H_{Ph}) ^{13}C (DMSO-d_6) : δ 14.1, 22.4, 25.8, 28.9, 29.0, 29.1, 29.2, 29.3, 31.6,

67.9, 88.5, 90.7, 114.3, 115.2, 124.5, 130.4, 133.2, 134.6, 159.4 IR : 3400, 2920, 2850, 2216, 1600, 1404, 1380, 1340, 1286, 1450, 1019, 839, 827 cm^{-1} MS (IC+) *m/z*: 391 ($M-CH_4^+$).

3-Chloro-6-dodecyloxypyridazine (26): To a solution of dodecan-1-ol (2.7 mL, 12.1 mmol) in 20 mL of anhydrous THF under nitrogen at 0 °C was added *n*-BuLi (1.6 M in hexanes, 7.56 mL) dropwise. The reaction mixture was stirred at rt for 30 min then a solution of 3,6-dichloropyridazine (1.5 g, 10.1 mmol) in 10 mL of THF was added dropwise, the reaction mixture was heated to reflux with stirring overnight. The reaction was quenched with a mixture of THF : HCl : EtOH (8:2:2) diluted with 20 mL of a mixture of water and CH_2Cl_2 (1:1) and the organic layer separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were dried over magnesium sulfate and evaporated. The crude product was purified by column chromatography (silica gel, eluent petroleum ether : EtOAc (9:1)) to give 2.68 g (89 %) of **26** as a colorless solid. mp < 50 °C (lit.,[19] mp 53-54 °C) ^{1}H NMR ($CDCl_3$) : δ 0.90 (t, *J* = 6.8 Hz, 3H, Me), 1.49-1.29 (m, 18H, 9 x CH_2), 1.86-1.81 (m, 2H, CH_2), 4.49 (t, *J* = 6.6 Hz, 4H, 2 x OCH_2), 6.98 (d, *J* = 9.0 Hz, 1H, H_5), 7.40 (d, *J* = 9.0 Hz, 1H, H_4) ^{13}C ($CDCl_3$) : δ 14.5, 23.0, 26.3, 29.1, 29.7 (2C), 29.9 (3C), 30.0, 32.3, 63.3, 120.5, 131.0, 151.1, 164.8 IR : 2918, 2852, 1590, 1474, 1438, 1385, 1310, 994, 846, 704 cm^{-1} *Anal.* Calcd for $C_{16}H_{27}ClN_2O$ (298.18) : C, 64.30 H, 9.11 N, 9.37. Found: C, 64.25 H, 9.11 N, 9.35.

3-[4-(4-Decyloxyphenylethynyl)phenyl]-6-dodecyloxypyridazine (27): Suzuki cross-coupling reaction of **26** (359 mg, 1.20 mmol) with **25** (716 mg, 1.89 mmol) according to the general procedure A (t = 40 h) gave after purification by column chromatography (silica gel, eluent heptane : EtOAc (9:1)) 1.28 g (73 %) of **27** as a yellow solid. mp 82 °C. ^{1}H NMR ($CDCl_3$) : δ 0.90 (t, 6H, *J* = 6.8 Hz, 2 x Me), 1.49-1.29 (m, 32H, 16 x CH_2), 1.90-1.79 (m, 4H, 2 x $OCH_2C\underline{H_2}$), 3.99 (t, *J* = 6.8 Hz, 2H, OCH_2), 4.59 (t, *J* = 6.8 Hz, 2H, OCH_2), 6.89 (d, 2H, *J* = 8.4 Hz, H_{Ph}), 7.04 (d, 1H, *J* = 9.2 Hz, H_{Ph}), 7.49 (d, 2H, *J* = 8.4 Hz, H_{Ph}), 7.65 (d, 2H, *J* = 8.4 Hz, H_{Ph}), 7.80 (d, 1H, *J* = 9.2 Hz, H_{Ph}), 8.04 (d, 2H, *J* = 8.4 Hz, H_{Ph}) ^{13}C ($CDCl_3$) : δ 14.5, 23.1, 26.4 (2C), 29.7, 29.8 (2C), 30.0 (2C), 30.1, 32.3, 68.2, 68.5, 88.1, 91.6, 115.0, 115.2, 118.2, 125.1, 126.6, 127.3, 132.3, 133.5, 135.9, 154.6, 159.8, 164.7 IR : 3071, 2918, 2850, 1599, 1447, 1433, 1310, 1286, 1251, 1021, 834 cm^{-1} *Anal.* Calcd for $C_{40}H_{56}N_2O_2$ (596.43): C, 80.49 H, 9.46 N, 4.69. Found: C, 80.86 H, 9.57 N, 4.32.

3-Iodo-6-octyloxypyridazine (28): To a solution of octan-1-ol (0.71 mL, 4.50 mmol) in 20 mL of anhydrous THF under nitrogen at 0 °C was added *n*-BuLi (2.5 M in hexanes, 1.80 mL) dropwise. The reaction mixture was stirred at rt for 30 min then a solution of 3,6-diiodopyridazine (1.20 g, 3.62 mmol)

in 10 mL of THF was added dropwise, the reaction mixture was heated to reflux with stirring overnight. The reaction was quenched with a mixture of THF : HCl : EtOH (8:2:2) diluted with 20 mL of a mixture of water and CH_2Cl_2 (1:1) and the organic layer separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were dried over magnesium sulfate and evaporated. The crude product was purified by column chromatography (silica gel, eluent petroleum ether: EtOAc (9:1)) to give 1.05 g (87 %) of **28** as a beige solid. mp <50 °C. ^{1}H NMR ($CDCl_3$) : δ 0.90 (t, *J* = 6.8 Hz, 3H, Me), 1.48-1.30 (m, 10H, 5 x CH_2), 1.88-1.80 (m, 2H, $OCH_2C\underline{H_2}$), 4.42 (t, *J* = 6.8 Hz, 2H, OCH_2), 6.66 (d, 1H, *J* = 9.2 Hz, H_5), 7.62 (d, 1H, *J* = 9.2 Hz, H_4) ^{13}C ($CDCl_3$) : δ 14.5, 23.0, 26.3, 29.0, 29.6, 29.7, 32.2, 68.3, 117.0, 119.6, 139.6, 165.2 IR : 3075, 2950, 2900, 1620, 1520, 1410, 1310, 1020 cm^{-1} *Anal.* Calcd for $C_{12}H_{19}IN_2O$ (334.05): C, 43.13 H, 5.73 N, 8.38. Found: C, 43.05 H, 5.82 N, 8.34.

3-(4-Bromophenylethynyl)-6-octyloxypyridazine (29): Sonogashira cross-coupling reaction of **28** (303 mg, 0.91 mmol) with 1-bromo-4-ethynylbenzene (1.05 g, 5.83 mmol) according to the general procedure B gave after purification by column chromatography (silica gel, eluent petroleum ether : EtOAc (9:1)) 288 mg (82 %) of **29** as a brown solid. mp 114 °C. ^{1}H NMR ($CDCl_3$) : δ 0.90 (t, *J* = 6.8 Hz, 3H, Me), 1.48-1.30 (m, 10H, 5 x CH_2), 1.88-1.80 (m, 2H, $OCH_2C\underline{H_2}$), 4.54 (t, *J* = 6.8 Hz, 2H, OCH_2), 6.92 (d, 1H, *J* = 9 Hz, H_{Ph}), 7.52-7.43 (m , 5H, H_{Ph}) ^{13}C ($CDCl_3$) : δ 14.5, 23.1, 26.3, 29.2, 29.6, 29.7, 32.2, 68.4, 87.2, 91.2, 117.1, 121.3, 124.0, 132.2, 132.7, 133.7, 143.5, 163.9 IR : 2954, 2920, 2852, 2223, 1488, 1428, 1288, 1006, 832 cm^{-1} Anal. Calcd for $C_{20}H_{23}BrN_2O$ (386.10): C, 62.02 H, 5.99 N, 7.23. Found: C, 61.86 H, 6.24 N, 7.36.

3-(4'-Decyloxybiphenyl-4-ylethynyl)-6-octyloxypyridazine (30): Suzuki cross-coupling reaction of **29** (797 mg, 2.07 mmol) with decyloxyphenylboronic acid (972 mg, 3.50 mmol) according to the general procedure C (t = 40 h) gave after purification by column chromatography (silica gel, eluent heptane : EtOAc (7:3)) 817 mg (73 %) of **30** as a beige solid. mp 160 °C. ^{1}H NMR ($CDCl_3$) : δ 0.90 (t, *J* = 6.8 Hz, 6H, 2 x Me), 1.48-1.23 (m, 24H, 12 x CH_2), 1.82-1.78 (m, 4H, 2 x $OCH_2C\underline{H_2}$), 4.00 (t, *J* = 6.8 Hz, 2H, OCH_2), 4.55 (t, *J* = 6.8 Hz, 2H, OCH_2), 6.92 (d, 1H, *J* = 9 Hz, H_{Ph}), 7.00-6.91 (m, 3H, $H_{Ph} + H_4$), 7.63-7.50 (m, 7H, $H_{Ph} + H_5$) ^{13}C ($CDCl_3$) : δ 14.5, 21.6, 24.9, 25.0 (2C), 27.8, 27.9, 28.2, 28.3, 28.4, 28.6, 28.7, 30.8, 30.9, 66.5, 66.9, 85.2, 91.1, 113.8, 115.6, 118.9, 125.5, 127.0, 131.2, 131.3, 131.4, 140.5, 142.4, 158.1, 162.4 IR : 2952, 2922, 2853, 2223, 1606, 1438, 1289, 1247, 822, 815 cm^{-1} *Anal.* Calcd for $C_{36}H_{48}N_2O_2$ (540.37): C, 79.96 H, 8.95 N, 5.18. Found: C, 80.26 H, 9.18 N, 4.99.

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