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A new series of rod-like conjugated molecules with a pyrazine or a bipyrazine core. Synthesis and light emitting properties

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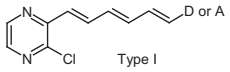
ABSTRACT

In this paper, we describe the synthesis of a wide range of new rod-like conjugated molecules with a pyrazine or a bipyrazine core connected to electron acceptor (A) or donor (D) groups through π-conjugated bridges as transmitters for the internal charge transfer (ICT). The key steps of the synthesis involve metallation and subsequent transmetallation of 2-chloropyrazine derivatives followed by Sonogashira or Negishi cross-coupling reactions. The bipyrazine core was obtained with a Stille cross-coupling reaction between the 2-chloro-6-tributylstannylpyrazine and the 2-chloro-6-iodopyrazine. Functionalization of the 6,6′-dichloro-2,2′-bipyrazine was performed by metallation, transmetallation and cross-coupling reactions. The light emitting properties of the so obtained molecules are then investigated in terms of absorption and emission spectra.

1. Introduction

Organic materials with extended π-extended conjugation along their backbone have received high interest owing to their applications in a wide range of electronic and optoelectronic devices.[1] Among them, rod-like chromophores with a planar and rigid π-conjugated system could be considered as molecular wires for electron and energy transfer[2] and also as materials in organic photo- and electro-luminescent devices. Another interest of such structures is their potential two-photon absorption (TPA) properties,[3] defined by their cross sections (σ_{TPA}), which could find applications in number of new areas, including the fluorescence imaging of biological samples,[4] optical limiting,[5] photodynamic therapy,[6] the three-dimensional optical data storage[7] and microfabrication.[8] The most extensively investigated structural motifs are donor-bridge-acceptor. The structure–property correlations of such chromophores reveal that the cross section σ_{TPA} increases with the donor/acceptor strength, conjugation length and planarity of the π-centre.[2b,c]

Previously, we have reported the synthesis of various linear dipolar D–π-A or quadripolar A–π-A compounds with a pyrazine moiety connected to a donor or and acceptor group through an oligoene chain as a bridge (type I).[9]



Type I

We describe herein the synthesis of various new conjugated compounds with a pyrazine or a bipyrazine core connected to electron acceptor (A) or donor (D) groups through π-conjugated bridges as transmitters for the internal charge transfer (ICT) (Scheme 1). These compounds with such a scaffold belong to dipolar structures with D–π-A systems (type II) or D–π-A–π-A systems (type III) and to quadrupolar structures with D–π-A–π-D system (type IV) where A is a π-deficient heterocycle unit (pyrazine or bipyrazine) (Scheme 1).

Compounds of type III with a D–π-A–π-A system could be compared to compounds of type I or II (D–π-A), allowing to appreciate for compounds of type III the structure–properties relationships due to the presence of a second arm at the C_6 position on the pyrazine ring as well as the nature of the π-conjugated linkers (alkene or alkyne units or polyenic chain). Chromophores of type IV have a centrosymmetric structure with a bipyrazine core and a D–π-A–π-D system, this kind of compounds is generally known to exhibit better two-photon activity (TPA) than the A–π-D–π-A systems.

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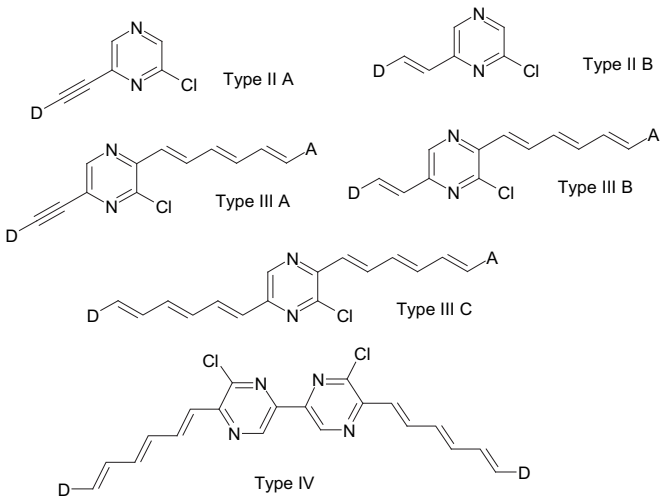


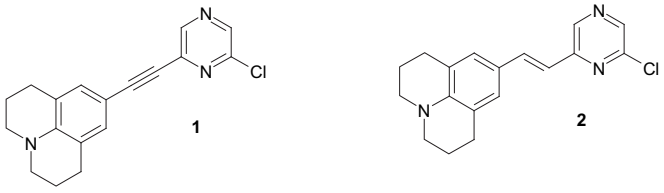
Scheme 1.

2. Results and discussion

2.1. Synthesis

It is well-known that amino groups are efficient electron-donating groups to induce large Stokes shifts in D–π-A systems because of internal charge transfer (ICT) states. Replacing dialkyl amino groups by a cyclic tetrahydroquinoline group would be one way to shift the absorption and emission to longer wavelengths.[10] For this reason we chose to introduce the julolidinyl group because of its high electron-releasing effect.

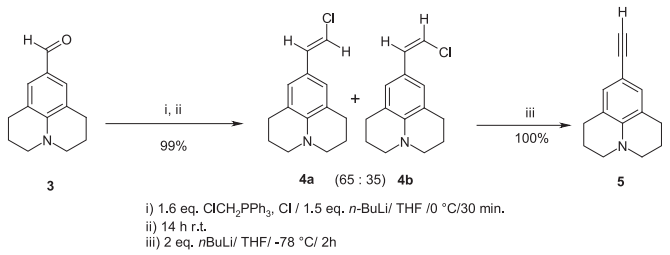
A preliminary synthetic way has been tested to introduce a julolidinylethynyl or a julolidinylvinyl group at the C_6 position of the 2-chloropyrazine (Scheme 2).



Scheme 2.

The 2-chloro-6-julolidinylethynylpyrazine **1** could be obtained either by a Sonogashira cross-coupling reaction between the julolidinylacetylene and the 2-chloro-6-iodopyrazine or by a Neghishi cross-coupling reaction with the organic zinc of the julolidinylacetylene and the 2-chloro-6-iodopyrazine. The two synthetic ways have been tested; the last one has given the better yield and is reported herein.

In a first time it was necessary to synthesize the julolidinylacetylene **5**. This compound was obtained in two steps from the formyljulolidine **3** as starting material, which was prepared by Vilsmeier reaction of julolidine[11] (Scheme 3).



i) 1.6 eq. $ClCH_2PPh_3$, Cl / 1.5 eq. *n*-BuLi/ THF /0 °C/30 min.
ii) 14 h r.t.
iii) 2 eq. *n*BuLi/ THF/ -78 °C/ 2h

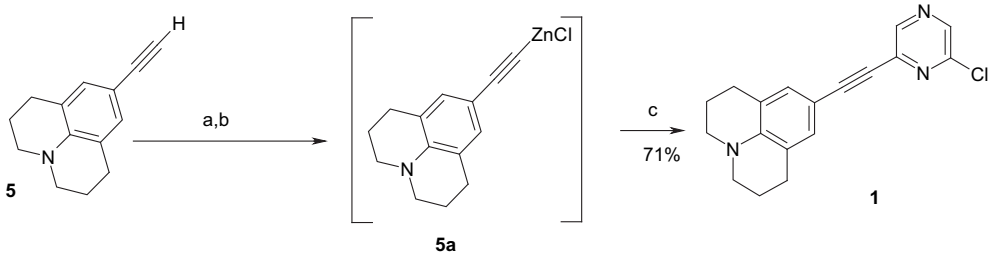
Scheme 3.

The formyljulolidine **3** was reacted with 1.6 equiv of chloromethyltriphenylphosphonium chloride according to the Wittig reaction conditions and with 1.5 equiv of *n*-butyllithium as base, leading to the 1-chloro-2-julolidinylethylenes **4a** and **4b** as a mixture of isomers *Z* and *E* (35:65) with a very good yield (99%). Further dehydrohalogenation carried out with *n*-butyllithium in THF at low temperature gave quantitatively the expected compound **5**.

The pyrazine derivative **1** was synthesized through the organo zinc intermediate **5a**, obtained by deprotonation of **5** with *n*-butyllithium followed by reaction with zinc chloride. The Negishi coupling reaction of **5a** with 2-chloro-6-iodopyrazine afforded **1** in 71% yield (Scheme 4).

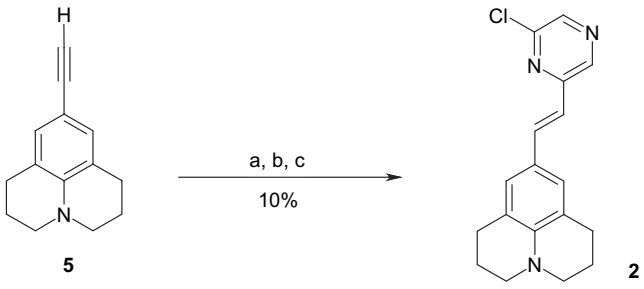
Various attempts have been performed to synthesize compound **2**, the vinylene analogous of **1**. The Stille coupling reactions with stannylpyrazine and 1-chloro-2-julolidinylethylene have failed as well as catalytic reduction of **1** with the Lindlar catalyst. Another way has been tested using the hydrozirconation reaction with the Schwartz's reagent. The acetylenic compound **1** was reacted with 1.1 equiv of Cp_2ZrHCl in THF at room temperature, then a transmetallation of zirconium by zinc was performed by the action of zinc chloride and the Negishi reaction was carried out with 2-chloro-6-iodopyrazine. Under these conditions, the vinylene compound **2** was obtained in low yield (10%) besides the acetylenic compound **1** as major product (16%) (Scheme 5).

In order to appreciate the influence on the optical properties of the length and of the nature of the conjugated chain at the C_6 and C_3 positions of pyrazine ring, we have synthesized three other compounds of type IIIA or IIIB with a D–π-A–π-A system. These compounds were obtained from compounds **1** and **2** using metallation at the C_3 position, induced by the chlorine atom as *ortho*-directing group, followed by transmetallation and cross-coupling reactions (Scheme 6).



a) 1.2 eq. n-BuLi/THF/-78 °C/30 min
b) 3 eq. $ZnCl_2$/THF/-78 °C to r.t.
c) 1 eq. 2-chloro-6-iodopyrazine/ $Pd(PPh_3)_4$/ 5% mol/THF/r.t./4 h

Scheme 4.



a) 1.1 eq Cp_2ZrHCl/THF/ r.t./30 min.
b) 3 eq. $ZnCl_2$/THF/r.t./1 h
c) 1 eq. 2-chloro-6-iodopyrazine/ $Pd(PPh_3)_4$ 5% mol/THF/ r.t./ 5 h

Scheme 5.

Metallation of **1** was performed with LTMP at the C_3 position, a further transmetallation with $ZnCl_2$ gave the organo zinc intermediate **1a**, which reacted with bromopolyenes **6a** or **6b** leading, respectively, to compounds **7** and **8**. For this latter compound **8** an isomerization in all trans configuration was obtained by reaction with iodine at reflux of CH_2Cl_2.[9,12]

The vinyl analogous of compound **8** was obtained in similar conditions leading to compound **9** in 83% yield (Scheme 7).

With the aim to induce an expansion of the conjugation along the chromophores and in order to improve their optical properties, we envisaged to connect a second arm, constituted by an aryl group and a polyenic chain, at the C_6 position of the pyrazine ring of structures of type I affording D–π-A–π-D or D–π-A–π-A systems. Introduction of such substituents requires the presence of a halogen atom or a stannyl group at the C_6 position of pyrazine ring to perform further cross-coupling reactions. The metallation reaction could be the strategic pathway to access to such C_6 substituted pyrazines.

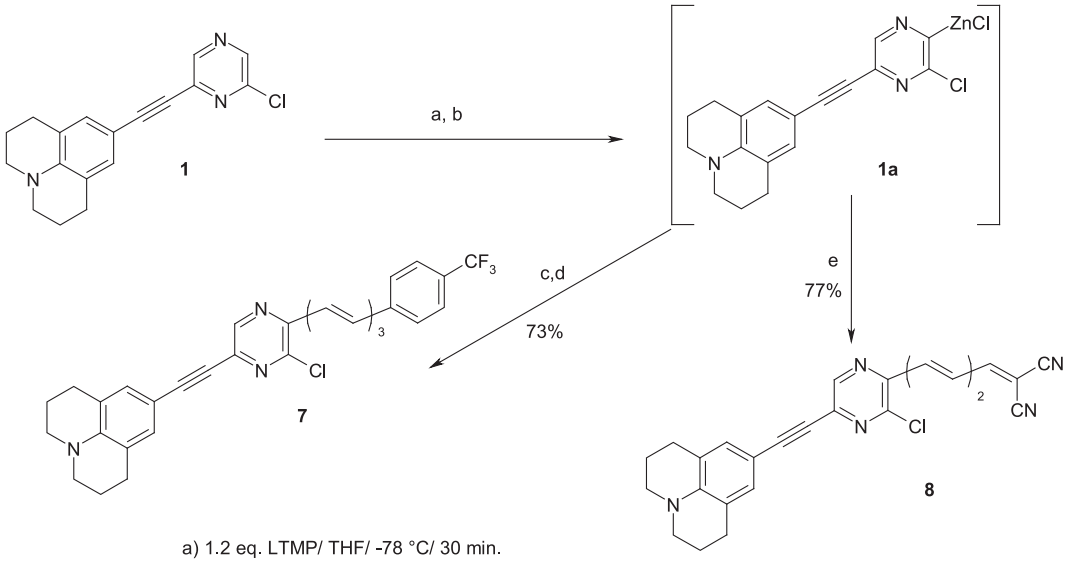
The regioselective functionalization at the C_5 or C_6 position of 2-halogenopyrazines, using this methodology, has been previously described.[13] More recently, the metallation of an acetal derivative, the (2*E*,4*E*)-1,1-diethoxy-5-(3′-chloropyrazin-2′-yl)penta-2,4-diene **10** has been reported.[9] Lithiation of **10**, achieved with 1.3 equiv of LTMP at low temperature and followed by reaction with various electrophiles, has highlighted a complete functionalization of the C_6 position. This regioselectivity has been used to introduce a conjugated bridge at this position, using successively metallation, transmetallation and cross-coupling reactions carried in one step (Scheme 8).

The aldehydes **11** were obtained via a Negishi coupling reaction between the organo zinc **10a** and 1-bromo-6-aryl-hexatrienes as a mixture of isomers (1*E*,3*E*,5*Z*) and (1*E*,3*E*,5*E*).[10] The choice of an organo zinc intermediate has been established because of a better stability than the analogous lithio derivative and of its ability to generate cross-coupling reaction. This latter intermediate results from the regioselective metallation of **10** followed by reaction with zinc chloride. It must be noticed that the yield of compounds **11** depending on the amount of metallating agent, a wide excess of LTMP (4 equiv) was necessary to obtain the compounds **11a** and **11b** in appreciable yields.

A further Knoevenagel condensation was performed with pyrazinylpentadienals **11** and malonitrile under base catalysis involving β-alanine leading to trisubstituted pyrazines **12** in good yields (Scheme 9).

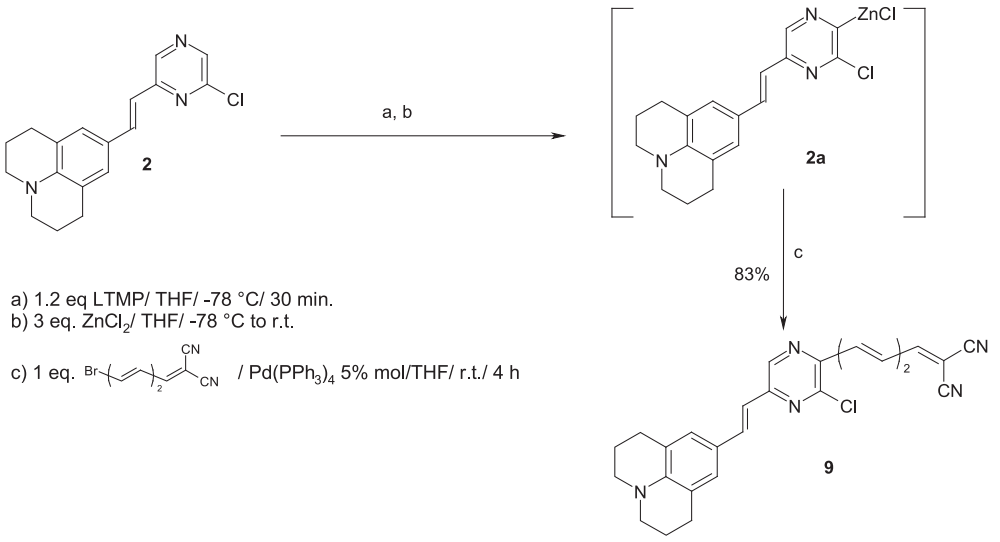
During the condensation reaction of the malonitrile with **11b**, used in mixture of isomers *Z*/*E*, a total isomerization in all trans configuration has been observed leading to compound **12b**. The same configuration all trans was also obtained for **12a**.

Another chromophore of type III was obtained through a Wittig condensation of the pyrazinylpentadienal **11b** with a phosphonium salt and butyllithium as base, leading to **13a** obtained as a mixture of isomers *E*/*Z*. To access to an all trans configuration, which induces a better extended conjugation, an isomerization of chromophore

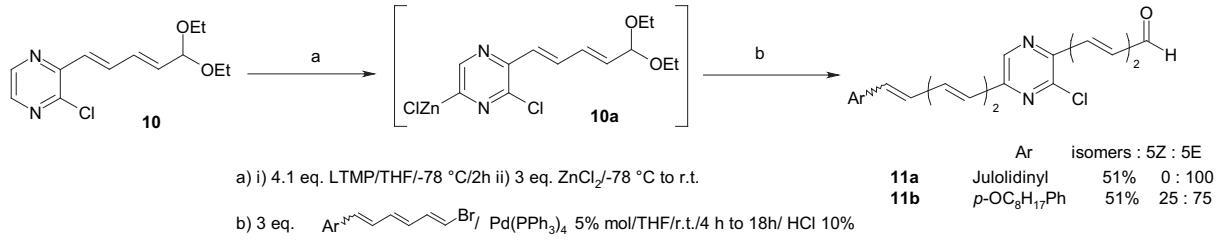


a) 1.2 eq. LTMP/ THF/ -78 °C/ 30 min.
b) 3 eq. $ZnCl_2$/ THF/ -78 °C to r.t.
c) 1 eq. Br–(CH=CH)$_3$–Ph-pCF_3 **6a** / $Pd(PPh_3)_4$ 5% mol/THF/ r.t./ 4 h
d) I_2 10% mol/CH_2Cl_2/Δ/ 4 h
e) 1 eq. Br–(CH=CH)$_2$–C(CN)=CH–CN **6b** /$Pd(PPh_3)_4$ 5% mol/THF/ r.t./5 h

Scheme 6.

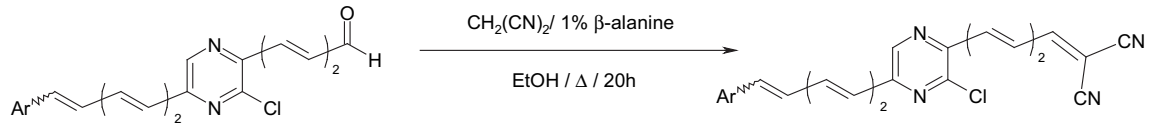


Scheme 7.



	Ar		isomers : 5Z : 5E
11a	Julolidinyl	51%	0 : 100
11b	*p*-$OC_8H_{17}Ph$	51%	25 : 75

Scheme 8.



12a	Ar = Julolidinyl	81%
12b	Ar = *p*-$C_8H_{17}OPh$	79%

Scheme 9.

13a with iodine has been performed leading to **13** in quantitative yield (Scheme 10).

The last series of centrosymmetric chromophores (type IV) belong to D–π-A–π-D system with a bipyrazine core, which could be compared to a bipyridine scaffold, able to induce metal complexation. To access to such structures, an efficient synthetic way could be the functionalization of the bipyrazine core by metallation and subsequent cross-coupling reactions. The 6,6′-dichloro-2,2′-bipyrazine **14** has been chosen as starting material, presence of a chlorine atom on each ring allowing to induce an *ortho*-lithiation of the neighbouring position. Then a further cross-coupling reaction could be performed to obtain the expected structures.

The bipyrazine **14** was synthesized in very good yield with a Stille cross-coupling reaction between the 2-chloro-6-tributylstannylpyrazine and the 2-chloro-6-iodopyrazine (Scheme 11).

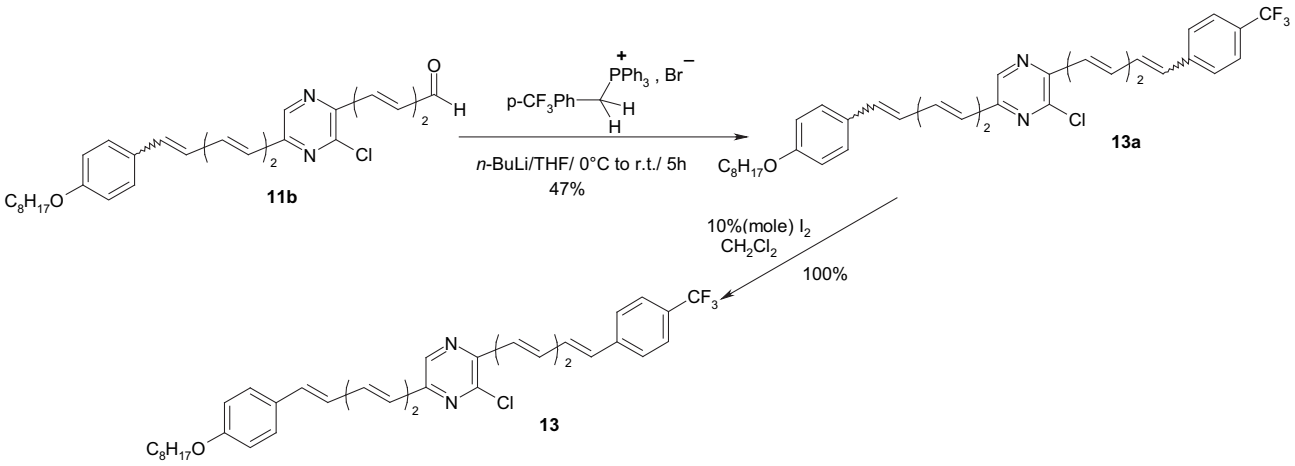
Lithiation of compound **14** was achieved with 2.3 equiv of LTMP at −100 °C in THF with a short time of reaction (5 min) followed by reaction with various electrophiles for a given time *t* leading to the bipyrazine derivatives **15**–**17** (Scheme 12).

The metallation of the two rings occurred at the C_5 position in *para* of the C–C linkage, the use of tributyltin chloride as electrophile afforded compound **16**, which could undergo a further Stille coupling reaction.

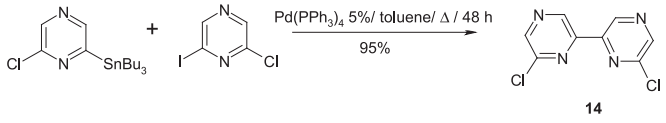
A first compound of type V **18** has been synthesized by two different ways either by a Stille coupling of **16** with 5-bromopentadienal in 37% or by a Negishi reaction of the organo zinc intermediate, resulting of reaction of the dilithio derivative with zinc chloride, which was reacted with 5-bromopentadienal with a better yield (64%) (Scheme 13).

This last synthetic way afforded a compound of type IV with **14** as starting material. The synthesis involved metallation, transmetallation and a Negishi cross-coupling reactions with the 1-bromo-6-julolidinylhexatriene and was achieved in one step, leading to the expected compound **19** in 57% yield (Scheme 14).

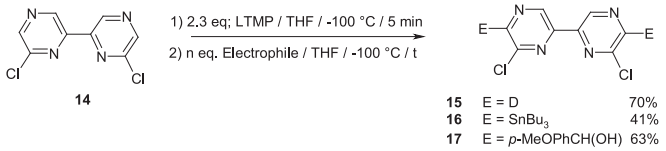
A Wittig reaction carried out with the dialdehyde **18** and an appropriate phosphonium salt using *n*-butyllithium as a base afforded a new chromophore of type IV obtained as a mixture of isomers 5*Z* and 5*E*. Further iodine catalyzed isomerization led to compound **20** in a 74% yield (Scheme 15).



Scheme 10.



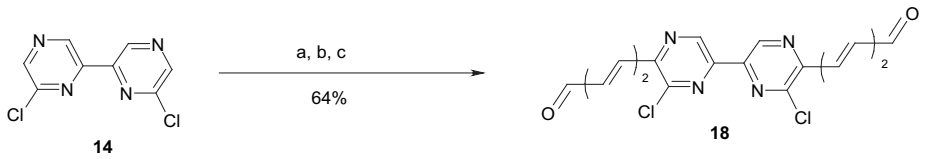
Scheme 11.



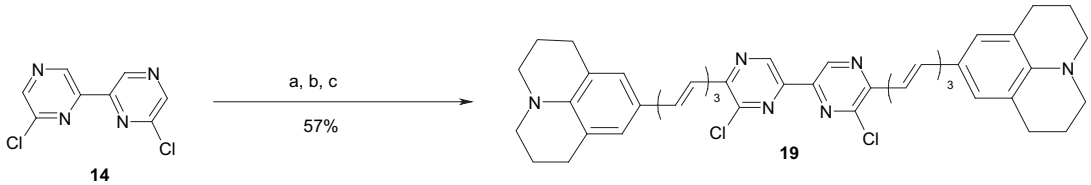
Scheme 12.

2.2. Geometrical and spectral properties

2.2.1. Geometry and electronic properties. Geometry of various conjugated compounds with A–π-D, D–π-A–π-A and D–π-A–π-D systems including a pyrazine or a bipyrazine core has been established using quantum mechanical calculations by DFT methods at the B3LYP level of theory with the 6-31G*[15] set basis. In all cases, the results of the calculations reveal that all molecules adopt an almost rigid planar structure. As a consequence, for compounds **18**–**20** including a bipyrazine core, the zero dihedral angle determined between the two 6-chloropyrazine rings induces a total coplanarity of the central scaffold. For compound **19**, a dihedral angle of 1.9° is determined between the pyrazine and phenyl ring of terminal julolidinyl group, such a geometry allowing a high charge transfer



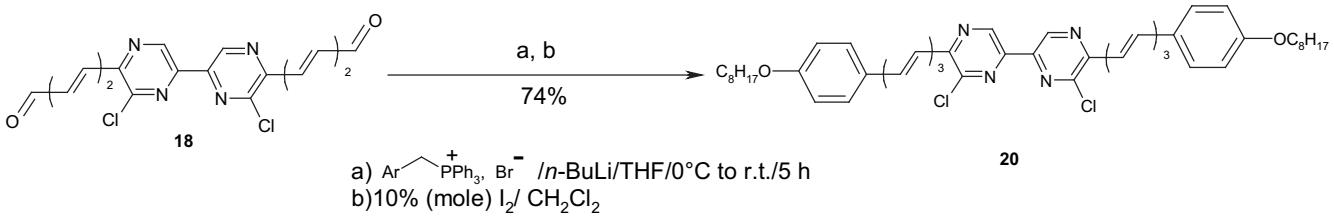
Scheme 13.



Scheme 14.

These two latter syntheses constitute two different routes to access to rod-like compounds belong to D–π-A–π-D system with a central core constituted by a bipyrazine unit A highly π-deficient, linked to electron-releasing groups D with a triene chain of all trans configuration to assure a better internal charge transfer by conjugation.

along this elongated molecule (23.4 Å between the two final nitrogen of the julolidinyl groups) (Fig. 1). It should be noted that such a planar structure has been previously described with conjugated 3,3′-bispyridazine molecules,[14] highlighting that bipyridazine and bipyrazine cores are more than planar than their



Scheme 15.

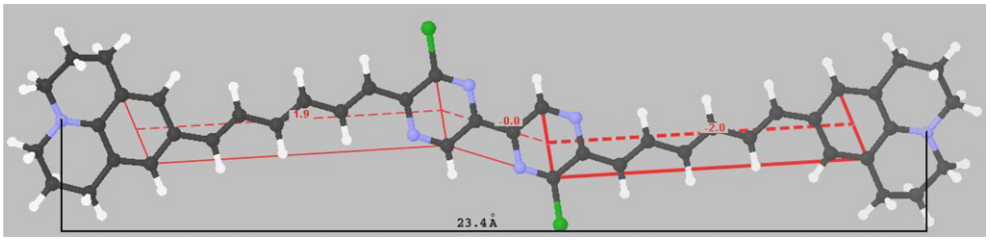


Fig. 1. Optimized B3LYP/6-31G* geometry for **19**, the printed values correspond to dihedral angles and length of the molecule.

3,3′-bipyridine analogous, for which a twisted conformation, with a 34.6° dihedral angle between the pyridine rings, is given in the ground state.

The frontier molecular orbitals calculated by the DFT method for compound **8** (A–π-D) and compound **19** (D–π-A–π-D), which bear the most efficient donating group (i.e., julolidinyl group) are displayed in Fig. 2. As expected for a typical push–pull system, the HOMOs and LUMOs exhibit a specific pattern. The HOMO is mainly localized on the julolidinyl donating group, whereas a reverse pattern is observed for the LUMO, which is mostly localized on the electron-withdrawing part of the molecule (i.e., pyrazine substituted with a dicyanohexatrienyl group) for **8** and the bipyrazine core for **19**.

Solvent polarity induces a significant variation of the emission wavelengths, whereas only a slight change is observed in absorption; a positive solvatochromic shift (i.e., bathochromic shift with increasing polarity) is observed with compounds **1**, **7**, **11b**, **12a** and **20** ($\Delta\lambda$=53–92 nm). This means, for these compounds, that the dipole moment of the molecule is higher in the excited state than in the ground state, indicating the aptitude of transfer charge at the excited state. On the contrary an important negative solvatochromic shift ($\Delta\lambda$=132–142 nm) is observed for compounds **8** and **9** with a dicyanovinylene terminal group and with the centrosymmetric compound **19**.

Comparison of spectroscopic data in CH_2Cl_2 of compounds **1** and **2** (type II) reveals that the nature of the spacer between the julolidinyl group and the pyrazine ring has some influence: as already known replacement of a triple bond by a double one induces a significant red shift (23 nm), a similar behaviour is observed with compounds **8** and **9**. The data of compounds **7** and **8** highlight that compound **8** possessing two electron-attractor groups (cyano groups) directly connected to the polyenic chain has a red shift compared with the values of compound **7**.

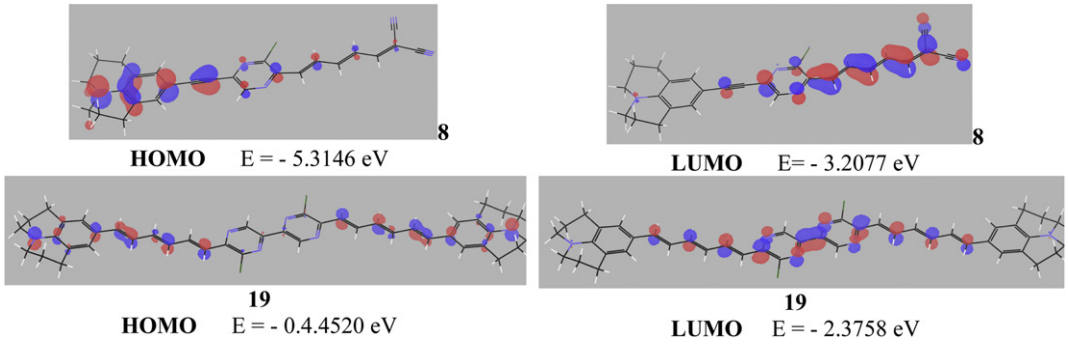


Fig. 2. HOMO and LUMO molecular orbitals for compounds **8** and **19**.

2.2.2. Absorption and fluorescence properties. The UV–vis and fluorescence spectroscopic data of some of the synthesized compounds performed in dichloromethane and toluene at 25 °C are summarized in Table 1. These results could appreciate the influence of the nature of the linkers between the pyrazine or bipyrazine core and those of the substituents together with their electron donor or acceptor character.

All chromophores show an intense absorption band in the near UV–vis region however, it should be noted that for all these compounds the quantum yields are generally low as well in dichloromethane as in a less polar solvent such as toluene, only a slight enhancement of the quantum yield is observed in low-polarity toluene with an exceptional high quantum yield for **1** in toluene.

Comparison of data of compounds **11** and **12** highlights that compounds **11a** and **12a** substituted with a julolidinyl group, known to be a better electron-donor group than alkoxy group, have a higher red shift than **11b** and **12b**.

The compounds **8**, **9** and **12a** belong to type III with a pyrazine core substituted at the C_2 position by a 1,1-dicyanohexatrienyl

Table 1
Optical absorption and emission spectroscopic data for compounds **1**, **2**, **7**–**9**, **11a**,**b**, **12a**,**b**, **13**, **18**–**20**

Solvent	Toluene (ε=2.38)					Dichloromethane (ε=8.93)				
Compound	λ_{abs} nm	ε_{max} (M^{-1} cm^{-1})	λ_{em} nm	ϕ_F[a](%)	Stokes shift (cm^{-1})	λ_{abs} nm	ε_{max} (M^{-1} cm^{-1})	λ_{em} nm	ϕ_F[a](%)	Stokes shift (cm^{-1})
1	415	27,317	501[b]	40	4136	415	27,652	593[b]	0.6	7233
2	—	—	—	—	—	438	30,456	582	3	5649
7	384	33,262	589[b]	6	9064	384	39,898	661[b]	0.5	10,913
8	396	7830	719[c]	<0.1	11,344	396	37,066	573[c]	<0.1	7928
	549	8662			4306	549	33,369			7363
9	403	19,204	744[c]	2	11,373	400	32,845	612[c]	<0.1	8660
	586	32,739				596	46,208			
11a	—	—	—	—	—	530	17,260	661	0.20	3739
11b	470	51,371	568	6	3640	470	54,952	652	3	5902
12a	438	8872	609[b]	0.4	6410	436	11,549	662[b]	0.2	7830
	613	9991				590	8639			
12b	—	—	—	—	—	327	25,790	—	0.0	—
						503	43,210			
13	—	—	—	—	—	347	27,310	—	0.0	—
						465	47,209			
18	—	—	—	—	—	403	46,346	537[a]	0.3	6192
						425	38,390			4907
19	481	21,602	707	0.7	5425	508	88,075	659[b]	0.1	4510
	511	20,739				583	10,584			
	583	10,584								
20	340	3958	567	2	2606	336	16,113	630[b]	5	4329
	494	10,456				490	39,911			

[a] λ_{exc}=360 nm.
[b] λ_{exc}=450 nm.
[c] λ_{exc}=488 nm.

group and at the C_5 position by the julolidinyl group connected through a double, triple or an hexatriene linker. For these compounds, two absorption bands are observed, one between 396 and 436 nm and the other between 549 and 593 nm.

In order to evaluate the influence of the bipyrazine core, a more efficient electron-withdrawing group than pyrazine, the spectroscopic data of the symmetrical chromophores of type IV **18**–**20** are reported. For these compounds, which are prone to be planar, an important red shift is observed for absorption and emission maxima with moderate to low quantum yields.

3. Conclusion

Metallation and transmetallation of 2-chloropyrazine derivatives and bischloropyrazine, followed by Negishi coupling reaction and Wittig condensation allowed synthesis of a wide range of new rod-like conjugated molecules. These compounds have a pyrazine or a bipyrazine core moiety as electron-drawing group, with two arms constituted by all *trans* hexatriene chain as conjugated link substituted by an aromatic bearing electron donating or withdrawing group. The light emitting properties of the so obtained molecules are then investigated in terms of absorption and emission spectra to evaluate the influence of the nature of the core and those of the length and the nature of the conjugated chain with the terminated groups. Incorporation of a double bond or of a hexatriene chain as linker and a bipyrazine as an electron-withdrawing central core increases the spectroscopic data.

4. Experimental section

4.1. General

Melting points were determined on a Reichert-Jung microscope apparatus. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 (300 MHz ^1H, 75 MHz ^{13}C) instrument. $CDCl_3$ was used as a solvent. Microanalyses were performed on a Carlo Erba CHNOS 1160 apparatus. The IR spectra were obtained as potassium bromide pellets with a Perkin–Elmer Paragon 500 spectrometer. Absorption bands are given in cm^{-1}. Mass spectra were recorded with a Jeol JMS-AX500 spectrometer or an ATI Unicam Automass, under electron impact conditions (EI) at 70 eV ionizing potential, fitted (or not) with a GC-mass coupling.

4.2. General procedure for the metallation reaction followed by a Negishi coupling: procedure A

To THF (V mL) under an argon atmosphere and previously cooled at −20 °C were successively added a solution of *n*-butyllithium (1.6 M or 2.5 M, in hexanes, concentration determined with a solution of diphenylacetic acid) and 2,2,6,6-tetramethylpiperidine (TMPH). The reaction mixture was allowed to warm at 0 °C and stirred for 30 min.

To this previously prepared solution of LTMP in THF cooled at θ_1, the appropriate pyrazine derivative dissolved in anhydrous THF was added and the resulting mixture was allowed to react at θ_1 for t_1 min. A solution of zinc dichloride (previously dried under vacuum with a drying gun) in THF (V_1 mL) was then added. The mixture was allowed to warm to room temperature and a solution of the appropriate halogeno derivative and tetrakis (triphenylphosphine) palladium[0] (5 mol %) in THF (V_2 mL) was then added. The reaction mixture was stirred at room temperature for t_2 min. Hydrolysis was carried out with a 20% aqueous solution of EDTA. The reaction mixture was then neutralized with a saturated aqueous solution of sodium hydrogencarbonate and extracted with dichloromethane (3×20 mL). The collected organic layers were dried over magnesium sulfate and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel.

4.3. General procedure for the metallation reaction followed by quenching with an electrophile: procedure B

The solution of LTMP was prepared as above and cooled at θ_1. The reagent was then added in THF. The reaction mixture was stirred for t_1 min at θ_1. After introduction of the appropriate electrophile, the mixture was stirred for t_2 min at θ_2. Hydrolysis was then carried out at this temperature. When the electrophile was

iodine, a solution of sodium thiosulfate was used to remove the excess of iodine. The resulting mixture was allowed to warm to 0 °C and a saturated aqueous solution of sodium hydrogencarbonate was added in order to obtain a slightly basic medium. THF was partially removed and the residue extracted with dichloromethane (4×20 mL). The collected organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel.

*4.3.1. 1-Chloro-2-(9′-julolidinyl)-ethylene (**4**).* To a solution of chloromethyltriphenylphosphonium chloride (3.98 mmol, 1.6 equiv) in THF (90 mL) at 0 °C under an argon atmosphere, was slowly added *n*-BuLi (1.5 M in hexane, 3.74 mmol, 1.5 equiv). After 30 min stirring at −78 °C, 9-formyljulolidine (2.49 mmol, 1.0 equiv) in THF (20 mL) was slowly added. The reaction mixture was stirred for 10 min at −78 °C and then for 14 h at room temperature. The reaction mixture was quenched with a 10% aqueous solution of $NaHCO_3$ (20 mL). The resulting solution was then extracted with dichloromethane (3×15 mL). The combined organic extracts were washed with saturated brine (10 mL) and dried over $MgSO_4$. After evaporation the crude product was further purified by silica gel column chromatography (pentane/ether: 15/1) to give a mixture of two isomers **4a**/**4b** (65/35). Yield: 0.574 g (99%) as a yellow oil. IR: 3073, 3005, 2937, 2885, 1604, 1505, 1464, 1282, 1073, 1053, 974, 737, 685, 620 cm^{-1}. MS (EI) *m*/*z*: 233–235 ($M^{+\cdot}$, 100%, 34%), 204 (17%), 196 (25%), 168 (24%), 154 (14%), 141 (11%), 115 (13%), 77 (4%). Anal. Calcd for $C_{14}H_{16}ClN$ (233.45): C 71.96, H 6.85, N 6.00; found: C 71.81, H 6.91, N 5.98.

*4.3.2. (1E)-1-Chloro-2-(9′-julolidinyl)-ethylene (**4a**).* ^1H NMR ($CDCl_3$): δ 6.63 (s, 2H, H^{arom}), 6.52 (d, 1H, J_{1-2}=13.7 Hz, H^1), 6.24 (d, 1H, J_{2-1}=13.6 Hz, H^2), 3.05 (t, 4H, $J_{2'-3'}$=5.6 Hz, $H^{2'}$), 2.63 (t, 4H, $J_{4'-3'}$=6.4 Hz, $H^{4'}$), 1.85 (m, 4H, $H^{3'}$). ^{13}C NMR ($CDCl_3$): δ 143.2 ($C^{6'}$), 133.6 (C^1), 125.2 ($C^{8'}$+$C^{10'}$), 122.4 ($C^{9'}$), 121.6 ($C^{5'}$+$C^{7'}$), 113.4 (C^2), 50.2 ($C^{2'}$), 27.9 ($C^{4'}$), 22.2 ($C^{3'}$).

*4.3.3. (1Z)-1-Chloro-2-(9′-julolidinyl)-ethylene (**4b**).* ^1H NMR ($CDCl_3$): δ 7.09 (s, 2H, H^{arom}), 6.28 (d, 1H, J_{2-1}=7.9 Hz, H^2), 5.85 (d, 1H, J_{1-2}=7.9 Hz, H^1), 3.03 (t, 4H, $J_{2'-3'}$=5.6 Hz, $H^{2'}$), 2.63 (t, 4H, $J_{4'-3'}$=6.4 Hz, $H^{4'}$), 1.84 (m, 4H, $H^{3'}$). ^{13}C NMR ($CDCl_3$): δ 143.0 ($C^{6'}$), 129.4 (C^2), 128.5 ($C^{8'}$ and $C^{10'}$), 121.7 ($C^{9'}$), 121.0 ($C^{5'}$ and $C^{7'}$), 112.5 (C^1), 50.2 ($C^{2'}$), 28.0 ($C^{4'}$), 22.2 ($C^{3'}$).

*4.3.4. Julolidinylacetylene (**5**).* To a solution of compound **4** (2.49 mmol, 1.0 equiv) in THF (40 mL) at −78 °C under an argon atmosphere, was slowly added *n*-BuLi (2.5 M in hexane, 4.98 mmol, 2.0 equiv). The reaction mixture was stirred for 2 h at −78 °C. The reaction mixture was quenched with water (20 mL). The resulting solution was then extracted with dichloromethane (3×20 mL). The combined organic extracts were dried over $MgSO_4$. After evaporation the crude product was obtained. Yield: 0.489 g (100%) as a brown solid. Mp=80 °C. IR: 3273, 2927, 2839, 2092, 1604, 1502, 1074, 892 cm^{-1}. MS (EI) *m*/*z*: 197 ($M^{+\cdot}$, 100%), 196 (53%), 198 (14%), 168 (13%), 115 (10%), 166 (7%), 139 (7%). Anal. Calcd for $C_{14}H_{15}N$ (197.28): C 33.71, H 1.87, N 8.74; found: C 33.79, H 1.89, N 8.73.

^1H NMR ($CDCl_3$): δ 6.92 (s, 2H, H^{arom}), 3.16 (t, 4H, $J_{2'-3'}$=5.6 Hz, $H^{2'}$), 2.19 (s, 1H, H^1), 2.69 (t, 4H, $J_{4'-3'}$=6.4 Hz, $H^{4'}$), 1.93 (m, 4H, $H^{3'}$). ^{13}C NMR ($CDCl_3$): δ 143.32 ($C^{6'}$), 131.0 ($C^{8'}$+$C^{10'}$), 121.2 ($C^{5'}$+$C^{7'}$), 107.7 ($C^{9'}$), 85.6 (C^2), 74.4 (C^1), 50.2 ($C^{2'}$), 27.9 ($C^{4'}$), 22.2 ($C^{3'}$).

*4.3.5. 2-Chloro-6-[2″-(9′-julolidinyl)ethynyl]pyrazine (**1**).* To a solution of compound **5** (2.08 mmol, 1.0 equiv) in THF (40 mL) at −78 °C under an argon atmosphere, was slowly added *n*-BuLi (2.5 M in hexane, 2.29 mmol, 1.1 equiv). The reaction mixture was stirred for 0.5 h at −78 °C. A solution of zinc dichloride (4.16 mmol, 2.0 equiv) previously dried under vacuum with a drying gun in THF (20 mL) was then added. The mixture was allowed to warm to room temperature and a solution of 2-chloro-6-iodopyrazine (2.08 mmol, 1.0 equiv) and tetrakis (triphenylphosphine)palladium[0] (5 mol %) in THF (20 mL) was then added. The reaction mixture was stirred at room temperature for 4 h. The reaction mixture was quenched with a 20% aqueous solution of EDTA (20 mL). The resulting solution was neutralized with saturated aqueous solution of sodium hydrogencarbonate and extracted with dichloromethane (3×20 mL). The combined organic extracts were dried over $MgSO_4$. After evaporation the crude product was further purified by silica gel column chromatography (pentane/ether: 80/20). Yield: 1.39 g (71%) as an orange solid. Mp=224 °C. IR: 3037, 2935, 2840, 2612, 2360, 2183, 1600, 1545, 1379, 1312, 1241, 1208, 1184, 1150, 888, 865, 737, 695 cm^{-1}. MS (EI) *m*/*z*: 309–311 ($M^{+\cdot}$, 100%, 34%), 197 (16%), 149 (40%), 105 (43%), 86 (17%), 84 (34%), 77 (27%), 71 (19%), 51 (16%). Anal. Calcd for $C_{18}H_{16}N_3Cl$ (309.45): C 69.80, H 5.17, N 13.57; found: C 69.83, H 5.24, N 13.51.

^1H NMR ($CDCl_3$): δ 8.51 (s, 1H, H^5), 8.36 (s, 1H, H^3), 7.04 (s, 2H, H^{arom}), 3.22 (t, 4H, *J*=5.6 Hz), 2.71 (t, 4H, *J*=6.4 Hz), 1.94 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 148.8 (C^2), 144.9 (C^5), 144.5 (C^{arom}), 141.3 (C^3), 140.8 (C^6), 131.5 ($2C^{arom}$), 121.2 ($2C^{arom}$), 105.9 (C^{arom}), 98.9 ($C^c{\equiv}^c$), 84.0 ($C^c{\equiv}^c$), 50.2 (C^{julo}), 27.8 (C^{julo}), 21.8 (C^{julo}).

*4.3.6. (E)-2-Chloro-6-[2″-(9′-julolidinyl)-ethylenyl]pyrazine (**2**).* To a solution of Cp_2ZrHCl (3.10 mmol, 1.1 equiv) in THF (40 mL) at 20 °C under an argon atmosphere was slowly added a solution of compound **5** (2.82 mmol, 1.0 equiv) in THF (10 mL). The reaction mixture was stirred for 0.5 h at 20 °C. A solution of zinc dichloride (8.47 mmol, 3.0 equiv) previously dried under vacuum with a drying gun in THF (20 mL) was then added. The reaction mixture was stirred for 1 h and a solution of 2-chloro-6-iodopyrazine (2.82 mmol, 1.0 equiv) and tetrakis (triphenylphosphine)palladium [0] (5 mol %) in THF (20 mL) was then added. The reaction mixture was stirred at room temperature for 5 h. The reaction mixture was quenched with a 20% aqueous solution of EDTA (20 mL). The resulting solution was neutralized with saturated aqueous solution of sodium hydrogencarbonate and extracted with dichloromethane (3×20 mL). The combined organic extracts were dried over $MgSO_4$. After evaporation the crude product was further purified by silica gel column chromatography (pentane/ether: 80/20).

Yield: 0.091 g (10%) as an orange solid. Mp=208 °C. IR: 3071, 3035, 2952, 2928, 2840, 1598, 1396, 1315, 1252, 1202, 1135, 1048, 892, 877, 743, 693, 543 cm^{-1}. MS (EI) *m*/*z*: 311–313 ($M^{+\cdot}$, 100%, 37%), 279 (9%), 247 (6%), 218 (6%), 201 (6%), 183 (8%), 167 (16%), 149 (27%), 95 (11%), 85 (9%), 71 (15%), 57 (22%). Anal. Calcd for: $C_{18}H_{18}N_3Cl$ (311.45): C 69.35, H 5.78, N 13.48; found: C 69.59, H 5.51, N 13.32.

^1H NMR ($CDCl_3$): δ 8.40 (s, 1H, H^5), 8.25 (s, 1H, H^3), 7.62 (d, 1H, *J*=16.2 Hz), 7.05 (s, 2H, H^{arom}), 6.79 (d, 1H, *J*=15.8 Hz), 3.22 (t, 4H, *J*=5.6 Hz), 2.76 (t, 4H, *J*=6.4 Hz), 1.97 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 152.9 (C^6), 149.0 (C^2), 144.4 (C^{arom}), 140.8 (C^5), 140.7 (C^3), 137.9 ($C^C{=}^C$), 127.1 ($2C^{arom}$), 122.9 (C^{arom}), 121.4 ($2C^{arom}$), 116.6 ($C^C{=}^C$), 50.2 (C^{julo}), 28.1 (C^{julo}), 22.0 (C^{julo}).

*4.3.7. (3E,5E)-6-Bromo-1,1-dicyanohexa-1,3,5-triene (**6b**).* A mixture of 5-bromopenta-2,4-dienal (200 mg, 1.24 mmol, 1.00 equiv), malononitrile (82 mg, 1.24 mmol, 1.00 equiv) and β-alanine (1.10 mg, 0.012 mmol, 0.01 equiv) was stirred at 20 °C for 2 h in ethanol (60 L) under an argon atmosphere. The ethanol was removed under vacuum and water was added (20 mL). The resulting solution was then extracted with dichloromethane (3×15 mL) and the combined organic extracts were dried over $MgSO_4$. After evaporation the crude was further purified by silica gel column chromatography (CH_2Cl_2). Yield: 0.197 g (76%) as a brown solid. Mp=211 °C. IR: 3083, 3038, 2924, 2846, 2286, 2228, 1593, 1353, 1327, 1262, 987, 875, 801, 729, 690, 610 cm^{-1}. MS (EI) *m*/*z*: 208–210

($M^{+\cdot}$, 73%), 179 (42%), 175 (40%), 164 (53%), 151 (41%), 141 (53%), 130 (79%), 114 (84%), 109 (75%), 97 (70%), 91 (59%), 83 (73%), 73 (100%), 60 (63%), 57 (91%). Anal. Calcd for $C_8H_5N_2Br$ (208.9): C 45.96, H 2.39, N 13.40; found: C 46.15, H 2.44, N 13.56.

^{1}H NMR ($CDCl_3$): δ 7.56 (d, 1H, J_{2-3}=11.7 Hz, H^2), 7.26 (dd, 1H, J_{4-3}=15.1 and J_{4-5}=11.3 Hz, H^4), 6.90 (dd, 1H, J_{3-4}=15.1 and J_{3-2}=11.7 Hz, H^3), 6.80 (dd, 1H, J_{5-4}=11.3 and J_{5-6}=14.3 Hz, H^5), 6.70 (d, 1H, J_{6-5}=14.3 Hz, H^6). ^{13}C NMR ($CDCl_3$): δ 159.4 (C^2), 144.3 (C^4), 131.4 (C^3), 129.0 (C^5), 121.4 (C^6), 113.5 (C^{CN}), 111.6 (C^{CN}), 85.3 (C^1).

*4.3.8. (1′E,3′E,5′E)-2-chloro-6-[2‴-(9″-julolidinyl)ethynyl]-3-[6′-(p-trifluoromethylphenyl)-hexa-1′,3′,5′-trienyl]pyrazine (**7**).* This compound was obtained according to the general procedure A.

LTMP was prepared from anhydrous THF (50 mL), 2,2,6,6-tetramethylpiperidine (0.27 mL, 1.58 mmol, 1,4 equiv) and *n*-BuLi (0.77 mL, 1.47 mmol, 1.3 equiv, 1.9 M in hexanes) cooled at θ_1=−78 °C and reacted with **1** (1.13 mmol, 1 equiv) in THF (20 mL) for t_1=30 min, $ZnCl_2$ (0.463 g, 3.40 mmol, 3 equiv) in anhydrous THF (20 mL), 1-bromo-6-*p*-trifluoromethylphenylhexa-1,3,5-triene (0.203 g, 0.97 mmol, 1 equiv) and $Pd(PPh_3)_4$ (0.065 g, 0.06 mmol, 5 mol %) in V_2=THF (20 mL) for t_2=5 h. The crude product was recrystallized from ethanol. The isomerization was realized by 10 mol % of iodine in refluxing dichloromethane or toluene during 4 h. A solution of sodium thiosulfate was added and after extraction with dichloromethane (2×15 mL) the combined organic extracts were dried over $MgSO_4$. After evaporation, only isomer all *E* was obtained with good purity. Yield: 0.439 g (73%) as a purple solid. Mp>260 °C. IR: 3026, 2941, 2841, 2186, 1596, 1517, 1444, 1322, 1273, 1164, 1122, 1066, 1002, 890, 866, 809 cm^{-1}. MS (EI) *m*/*z*: 531–533 ($M^{+\cdot}$, 43%, 16%), 505 (14%), 491 (22%), 447 (36%), 358 (25%), 346 (17%), 315 (19%), 281 (36%), 231 (49%), 213 (40%), 178 (41%), 152 (53%), 126 (87%), 117 (55%), 93 (75%), 57 (100%). Anal. Calcd for $C_{31}H_{25}N_3ClF_3$ (531.45): C 70.00, H 4.70, N 7.90; found: C 70.16, H 4.87, N 7.96.

^{1}H NMR ($CDCl_3$): δ 8.46 (s, 1H, H^5), 7.58 (d, 2H, *J*=8.7 Hz, H^{arom}), 7.47 (dd, 1H, $J_{2'-3'}$=10.2 and $J_{2'-1'}$=15.1 Hz, $H^{2'}$), 7.42 (d, 2H, *J*=8.7 Hz, H^{arom}), 7.09 (d, 1H, $J_{1'-2'}$=15.1 Hz, $H^{1'}$), 7.05 (s, 2H, H^{arom}), 7.04–6.90 (m, 2H, $H^{4'}$ and $H^{5'}$), 6.73–6.66 (m, 2H, $H^{3'}$ and $H^{6'}$), 3.25 (t, 4H, *J*=5.6 Hz), 2.75 (t, 4H, *J*=6.4 Hz), 1.95 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 150.0 (C^3), 146.8 (C^{arom}), 146.2 (C^2), 143.7 (C^5), 140.8 (C^{arom}), 140.7 ($C^{6'}$), 137.4 ($C^{4'}$), 137.1 ($C^{2'}$), 134.3 ($C^{5'}$), 133.3 ($C^{3'}$), 131.3 (C^6), 128.7 (C^{arom}), 126.9 (C^{arom}), 126.3 (C^{arom}), 126.1 (C1′), 125.9 (C^{arom}), 123.0 (CF_3), 120.2 (C^{arom}), 105.8 (C^{arom}), 101.7 ($C^c{\equiv}C^c$), 85.0 ($C^c{\equiv}C^c$), 50.2 (C^{julo}), 27.9 (C^{julo}), 21.7 (C^{julo}). ^{19}F NMR ($CDCl_3$): δ −62.9.

*4.3.9. (3E,5E)-1,1-Dicyano-6-[3′-chloro-5′-(julolidinylethynyl)pyrazin-2′-yl]-hexa-1,3,5-triene (**8**).* This compound was obtained according to the general procedure A.

LTMP was prepared from anhydrous THF (50 mL), 2,2,6,6-tetramethylpiperidine (0.23 mL, 1.40 mmol, 1.4 equiv) and *n*-BuLi (0.65 mL, 1.26 mmol, 1.3 equiv, 1.9 M in hexanes) cooled at θ_1=−78 °C and reacted with **1** (0.97 mmol, 1 equiv) in THF (15 mL) for t_1=30 min, $ZnCl_2$ (0.397 g, 2.91 mmol, 3 equiv) in anhydrous THF (15 mL), 6-bromo-1,1-dicyanohexa-1,3,5-triene **6** (0.203 g, 0.97 mmol, 1 equiv) and $Pd(PPh_3)_4$ (0.056 g, 0.05 mmol, 5 mol %) in V_2=THF (20 mL) for t_2=4 h. The crude product was recrystallized from ethanol. Yield: 0.326 g (77%) as a purple solid. Mp>260 °C. IR: 3031, 2934, 2835, 2219, 2179, 1601, 1528, 1312, 1240, 1159, 910, 888, 741, 697 cm^{-1}. MS (EI) *m*/*z*: 437–439 ($M^{+\cdot}$, 15%, 6%), 418 (10%), 392 (44%), 378 (14%), 366 (9%), 349 (46%), 319 (20%), 285 (51%), 264 (28%), 240 (15%), 218 (26%), 208 (30%), 176 (32%), 166 (100%), 148 (62%), 122 (65%), 99 (89%), 84 (100%), 55 (98%). Anal. Calcd for $C_{26}H_{20}N_5Cl$ (437.45): C 71.32, H 4.57, N 16.00; found: C 72.34, H 4.61, N 16.10.

^{1}H NMR ($CDCl_3$): δ 8.50 (s, 1H, $H^{6'}$), 7.65 (dd, 1H, J_{5-4}=11.3 and J_{5-6}=14.7 Hz, H^5), 7.51 (d, 1H, J_{2-3}=11.7, H^2), 7.37 (d, 1H, J_{6-5}=14.7 Hz, H^6),.7.16 (dd, 1H, J_{4-3}=14.7 and J_{4-5}=11.3 Hz, H^4), 7.06 (s, 2H, H^{arom}), 6.96 (dd, 1H, J_{3-4}=14.7 and J_{3-2}=11.3 Hz, H^3), 3.25 (t, 4H, *J*=5.6 Hz), 2.72 (t, 4H, *J*=6.4 Hz), 1.95 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 158.9 (C^2), 148.6 (C^4), 147.9 ($C^{3'}$), 145.3 ($C^{6'}$), 145.0 (C^{arom}), 143.5 ($C^{2'}$), 140.1 ($C^{5'}$), 135.6 (C^6), 134.1 (C^5), 131.9 (C^{arom}), 129.6 (C^3), 121.3 (C^{arom}), 113.8 (C^{CN}), 111.8 (C^{CN}), 105.7 (C^{arom}), 102.1 ($C^c{\equiv}C^c$), 86.0 ($C^c{\equiv}C^c$), 84.3 (C^1), 50.2 (C^{julo}), 27.9 (C^{julo}), 21.7 (C^{julo}).

*4.3.10. (3E,5E)-1,1-Dicyano-6-[3′-chloro-5′-[(E)-2‴-(9″-julolidinyl)-ethylenyl]pyrazin-2′-yl]-hexa-1,3,5-triene (**9**).* This compound was obtained according to the general procedure A.

LTMP was prepared from anhydrous THF (50 mL), 2,2,6,6-tetramethylpiperidine (0.17 mL, 0.98 mmol, 1.4 equiv) and *n*-BuLi (0.47 mL, 0.91 mmol, 1.3 equiv, 1.9 M in hexanes) cooled at θ_1=−78 °C and reacted with **2** (0.70 mmol, 1 equiv) in THF (15 mL) for t_1=30 min, $ZnCl_2$ (0.287 g, 2.10 mmol, 3 equiv) in anhydrous THF (15 mL), 6-bromo-1,1-dicyanohexa-1,3,5-triene **6b** (0.146 g, 0.70 mmol, 1 equiv) and $Pd(PPh_3)_4$ (0.040 g, 0.04 mmol, 5 mol %) in V_2=THF (20 mL) for t_2=4 h. The crude product was recrystallized from ethanol. Yield: 0.254 g (83%) as a blue solid. Mp>260 °C. IR: 3026, 2948, 2841, 2226, 2183, 1593, 1530, 1461, 1310, 1248, 1180, 1143, 1063, 998, 960, 943, 887, 834, 750 cm^{-1}. MS (EI) *m*/*z*: 439–441 ($M^{+\cdot}$, 33%, 10%), 412 (10%), 320 (9%), 264 (8%), 236 (15%), 207 (29%), 196 (13%), 153 (31%), 149 (99%), 121 (34%), 95 (37%), 84 (100%), 55 (47%). Anal. Calcd for $C_{26}H_{22}N_5Cl$ (439.45): C 71.00, H 5.01, N 15.93; found: C 71.07, H 5.12, N 16.02.

^{1}H NMR ($CDCl_3$): δ 8.40 (s, 1H, $H^{6'}$), 7.67 (d, 1H, *J*=15.4 Hz), 7.62 (dd, 1H, J_{5-4}=11.3 and J_{5-6}=14.7 Hz, H^5), 7.52 (d, 1H, J_{2-3}=11.7, H^2), 7.39 (d, 1H, J_{6-5}=14.7 Hz, H^6), 7.16 (dd, 1H, J_{4-3}=14.7 and J_{4-5}=11.3 Hz, H^4), 7.08 (s, 2H, H^{arom}), 6.93 (dd, 1H, J_{3-4}=14.7 and J_{3-2}=11.3 Hz, H^3), 6.81 (d, 1H, *J*=15.4 Hz), 3.25 (t, 4H, *J*=5.6 Hz), 2.76 (t, 4H, *J*=6.4 Hz), 1.97 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 159.2 (C^2), 152.8 ($C^{5'}$), 149.2 (C^4), 148.6 ($C^{3'}$), 145.1 (C^{arom}), 142.8 ($C^{2'}$), 141.7 ($C^{6'}$), 139.5 ($C^c{=}C^c$), 136.6 (C^6), 132.4 (C^5), 128.9 (C^3), 127.7 (C^{arom}), 122.9 (C^{arom}), 121.5 (C^{arom}), 116.5 ($C^c{=}C^c$), 114.0 (C^{CN}), 112.0 (C^{CN}), 83.4 (C^1), 50.3 (C^{julo}), 28.1 (C^{julo}), 21.9 (C^{julo}).

*4.3.11. (2E,4E)-5-[3′-Chloro-5′-[(1″E,3″E,5″E)-6″-(9‴-julolidinyl)-hexa-1″,3″,5″-trienyl]pyrazin-2′-yl]penta-2,4-dienal (**11a**).* This compound was obtained according to the general procedure A.

LTMP was prepared from anhydrous THF (80 mL), 2,2,6,6-tetramethylpiperidine (0.80 mL, 4.70 mmol, 4.2 equiv) and *n*-BuLi (1.84 mL, 4.59 mmol, 4.1 equiv, 2.5 M in hexanes) cooled at θ_1=−78 °C and reacted with **10** (1.12 mmol, 1 equiv) in THF (20 mL) for t_1=15 min, $ZnCl_2$ (0.630 g, 4.59 mmol, 4.1 equiv) in anhydrous THF (20 mL), 1-bromo-6-(9′-julolidinyl)hexa-1,3,5-triene (0.370 g, 1.12 mmol, 1 equiv) and $Pd(PPh_3)_4$ (0.065 g, 0.06 mmol, 5 mol %) in V_2=THF (20 mL) for t_2=18 h. Hydrolysis was carried out with a 10% aqueous solution of HCl (20 mL). The crude product was recrystallized from ethanol. Yield: 0.199 g (51%) as a purple solid. Mp>260 °C. IR: 2939, 2845, 2360, 2337, 1680, 1668, 1574, 1447, 1313, 1206, 1156, 1123, 993, 909 cm^{-1}. MS (EI) *m*/*z*: 443–445 ($M^{+\cdot}$, 25%, 9%), 404 (17%), 362 (26%), 333 (54%), 316 (40%), 278 (40%), 244 (50%), 220 (18%), 208 (21%), 186 (21%), 147 (28%), 127 (45%), 91 (100%), 60 (70%). Anal. Calcd for $C_{27}H_{26}N_3OCl$ (443.45): C 73.06, H 5.86, N 9.47; found: C 73.14, H 5.93, N 9.56.

^{1}H NMR ($CDCl_3$): δ 9.68 (d, 1H, J_{1-2}=7.9 Hz, H^1), 8.36 (s, 1H, $H^{6'}$), 7.63 (dd, 1H, J_{4-3}=11.3 and J_{4-5}=14.7 Hz, H^4), 7.53 (dd, 1H, $J_{2''-3''}$=11.3 and $J_{2''-1''}$=15.1 Hz, $H^{2''}$), 7.40 (d, 1H, J_{5-4}=14.7 Hz, H^5), 7.36 (dd, 1H, J_{3-4}=11.3 and J_{3-2}=15.1 Hz, H^3), 6.91 (s, 2H, H^{arom}), 6.79–6.67 (m, 2H, $H^{4''}$ and $H^{5''}$), 6.61 (d, 1H, $J_{6''5''}$=15.1 Hz, $H^{6''}$), 6.55 (dd, 1H, $J_{3''-4''}$=14.7 and $J_{3''-2''}$=11.3 Hz, $H^{3''}$), 6.48 (d, 1H, $J_{1''-2''}$=14.7 Hz, $H^{1''}$), 6.40 (dd, 1H, J_{2-1}=7.9 and J_{2-3}=15.1 Hz, H^2), 3.19 (t, 4H, *J*=5.6 Hz), 2.74 (t, 4H, *J*=6.4 Hz), 1.95 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 193.9 (C^1), 151.7 ($C^{2'}$), 150.7 (C^3), 148.3 ($C^{3'}$), 143.8 ($C^{5'}$ or C^{arom}), 143.7 ($C^{5'}$ or C^{arom}), 141.7 ($C^{6'}$ or $C^{4''}$), 141.5 ($C^{6'}$ or $C^{4''}$), 139.1

($C^{2''}$), 137.9 ($C^{5''}$), 134.6 (C^2 or C^4), 134.5 (C^2 or C^4), 132.8 (C^5), 129.2 (C3″), 126.4 (C^{arom}), 124.4 (C^{arom}), 124.0 (C6″), 123.7 (C1″), 121.6 (C^{arom}), 50.3 (C^{julo}), 28.1 (C^{julo}), 22.1 (C^{julo}).

*4.3.12. (2E,4E)-5-[3′-Chloro-5′[(1″E,3″E,5″E)-6″-(p-octyloxyphenyl)-hexa-1″,3″,5″-trienyl]pyrazin-2′-yl]penta-2,4-dienal (**11b**).* This compound was obtained according to the general procedure A.

LTMP was prepared from anhydrous THF (40 mL), 2,2,6,6-tetramethylpiperidine (0.58 mL, 3.44 mmol, 4.2 equiv) and *n*-BuLi (2.10 mL, 3.36 mmol, 4.1 equiv, 1.6 M in hexanes) cooled at θ_1=−78 °C and reacted with **10** (0.82 mmol, 1 equiv) in THF (20 mL) for t_1=15 min, $ZnCl_2$ (0.456 g, 3.36 mmol, 4.1 equiv) in anhydrous THF (20 mL), 1-bromo-6-(*p*-octyloxyphenyl)hexa-1,3,5-triene (0.298 g, 0.82 mmol, 1 equiv) and $Pd(PPh_3)_4$ (0.048 g, 0.04 mmol, 5 mol %) in V_2=THF (20 mL) for t_2=4 h. Hydrolysis was carried out with a 10% aqueous solution of HCl (20 mL). After extraction and evaporation the crude product was further purified by silica gel column chromatography (dichloromethane/ethyl acetate: 20/1) to give a mixture of two isomers (75/25). Yield: 0.199 g (51%) as a red solid. Mp=194 °C. IR: 3020, 2927, 2856, 2813, 1674, 1609, 1587, 1396, 1371, 1318, 1301, 1249, 1150, 1113, 812, 795, 725, 641, 615 cm^{-1}. MS (CI, isobutane) *m*/*z*: 477–479 (M+1, 22%, 5%), 476–478 ($M^{+\cdot}$, 35%, 14%), 447 (M−CHO, 14%), 445 (8%), 443 (15%), 441 (M−Cl, 100%), 411 (9%), 363 (6%), 194 (10%), 57 (16%), 55 (13%). Anal. Calcd for $C_{29}H_{33}O_2N_2Cl$ (476.45): C 73.04, H 6.93, N 5.88; found: C 72.91, H 7.12, N 5.87.

^{1}H NMR ($CDCl_3$): δ 9.68 (d, 1H, J_{1-2}=7.9 Hz, H^1), 8.38 (s, 1H, $H^{6'}$), 7.65 (dd, 1H, J_{4-3}=11.3 and J_{4-5}=15.1 Hz, H^4), 7.63 (dd, 1H, $J_{2''-3''}$=11.3 and $J_{2''-1''}$=15.1 Hz, $H^{2''}$), 7.40 (d, 1H, J_{5-4}=14.7 Hz, H^5), 7.34 (dd, 1H, J_{3-4}=11.3 and J_{3-2}=15.1 Hz, H^3), 7.36 (d, 2H, 2H, *J*=8.7 Hz, H^{arom}), 6.86 (d, 2H, 2H, *J*=8.7 Hz, H^{arom}), 6.77 (d, 1H, $J_{6''5''}$=15.1 Hz, $H^{6''}$), 6.75–6.64 (m, 2H, $H^{4''}$ and $H^{5''}$), 6.50 (dd, 1H, $J_{3''-4''}$=14.7 and $J_{3''-2''}$=11.3 Hz, $H^{3''}$), 6.54 (d, 1H, $J_{1''-2''}$=14.7 Hz, $H^{1''}$), 6.40 (dd, 1H, J_{2-1}=7.9 and J_{2-3}=15.1 Hz, H^2), 3.96 (t, 2H, *J*=6.1 Hz), 1.78 (m, 2H), 1.45–1.29 (m, 10H), 0.89 (t, 3H, *J*=6.1 Hz). ^{13}C NMR ($CDCl_3$): δ 193.5 (C^1), 159.5 (C^{arom}), 150.9 ($C^{2'}$), 150.1 (C^3), 147.9 ($C^{3'}$), 143.9 ($C^{5'}$), 141.4 ($C^{6'}$), 139.8 ($C^{4''}$), 138.1 ($C^{2''}$), 135.9 ($C^{5''}$), 134.1 (C^2 or C^4), 133.9 (C^2 or C^4), 132.9 (C^5), 130.8 (C3″), 129.4 (C^{arom}), 128.1 (C^{arom}), 126.3 (C6″), 125.0 (C1″), 114.8 (C^{arom}), 68.1, 0.31.8, 29.3, 29.2, 26.0, 22.6, 14.1.

*4.3.13. (3E,5E)-1,1-Dicyano-6-[3′-chloro-5′-[(1″E,3″E,5″E)-6″-(9‴-julolidinyl)-hexa-1″,3″,5″-trienyl] pyrazin-2′-yl]-hexa-1,3,5-triene (**12a**).* A mixture of aldehyde **11a** (350 mg, 0.79 mmol, 1.00 equiv), malononitrile (63 mg, 0.95 mmol, 1.20 equiv) and β-alanine (0.70 mg, 0.008 mmol, 0.01 equiv) was stirred at 60 °C for 20 h in ethanol (100 mL) under an argon atmosphere. The ethanol was removed under vacuum and water was added (20 mL). The resulting solution was then extracted with dichloromethane (3×15 mL) and the combined organic extracts were dried over $MgSO_4$. After evaporation the crude product was recrystallized from ethanol.

Yield: 0.314 g (81%) as a brown solid. Mp>260 °C. IR: 3440, 2938, 2841, 2222, 2169, 2113, 1583, 1312, 1206, 1181, 1167, 1127, 1063, 996, 893 cm^{-1}. MS (EI) *m*/*z*: 491–493 ($M^{+\cdot}$, 30%, 9%), 446 (11%), 415 (34%), 353 (13%), 334 (11%), 303 (11%), 281 (36%), 250 (35%), 231 (19%), 149 (31%), 156 (59%), 136 (70%), 116 (67%), 84 (78%), 56 (100%). Anal. Calcd for $C_{30}H_{26}N_5Cl$ (491.45): C 73.25, H 5.29, N 14.24; found: C 73.31, H 5.37, N 14.33.

^{1}H NMR ($CDCl_3$): δ 8.37 (s, 1H, $H^{6'}$), 7.61 (dd, 1H, J_{5-4}=11.3 and J_{5-6}=14.7 Hz, H^5), 7.57 (dd, 1H, $J_{2''-3''}$=11.3 and $J_{2''-1''}$=15.1 Hz, $H^{2''}$), 7.53 (d, 1H, J_{2-3}=11.7, H^2), 7.39 (d, 1H, J_{6-5}=14.7 Hz, H^6), 7.16 (dd, 1H, J_{4-3}=14.7 and J_{4-5}=11.3 Hz, H^4), 6.95 (dd, 1H, J_{3-4}=14.7 and J_{3-2}=11.3 Hz, H^3), 6.91 (s, 2H, H^{arom}), 6.75 (d, 1H, $J_{1''-2''}$=15.1 Hz, $H^{1''}$), 6.68 (dd, 1H, $J_{4''-3''}$=14.7 and $J_{4''-5''}$=10.6 Hz, $H^{4''}$), 6.58 (d, 1H, $J_{6''-5''}$=15.1 Hz, $H^{6''}$), 6.51–6.40 (m, 2H, $H^{3''}$ and $H^{5''}$), 3.20 (t, 4H, *J*=5.7 Hz), 2.74 (t, 4H, *J*=6.4 Hz), 1.95 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 159.1 (C^2), 151.9 ($C^{5'}$), 149.0 (C^4), 143.9 (C^{arom}), 143.6 ($C^{3'}$), 143.4 ($C^{2'}$), 141.9 ($C^{6'}$ and $C^{4''}$), 139.6 ($C^{2''}$), 138.2 ($C^{5''}$), 136.3 (C^6), 133.1 (C^5), 129.3 (C^3 or $C^{3''}$), 129.2 (C^3 or $C^{3''}$), 126.4 (C^{arom}), 124.3 (C^{arom}), 124.0 ($C^{6''}$), 123.7 ($C^{1''}$), 121.6 (C^{arom}), 113.9 (C^{CN}), 111.9 (C^{CN}), 83.8 (C^1), 50.3 (C^{julo}), 28.0 (C^{julo}), 22.1 (C^{julo}).

*4.3.14. (3E,5E)-1,1-Dicyano-6[3-chloro-5′-[(1″E,3″E,5″E)-6″-(p-octyloxyphenyl)-hexa-1″,3″,5″-trienyl]pyrazin-2′-yl]-hexa-1,3,5-triene (**12b**).* This compound was obtained according to the same procedure for **12a**.

Aldehyde **11b** (101 mg, 0.21 mmol, 1.00 equiv), malononitrile (14 mg, 0.21 mmol, 1.20 equiv), β-alanine (0.20 mg, 0.002 mmol, 0.01 equiv) ethanol (50 mL).

Yield: 0.088 g (79%) as a purple solid. Mp=219 °C. IR: 3015, 2926, 2855, 2226, 1586, 1447, 1369, 1250, 1177, 938, 854, 833, 806, 722, 612 cm^{-1}. MS (EI) *m*/*z*: 524–526 ($M^{+\cdot}$, 34%, 10%), 479 (17%), 448 (24%), 386 (22%), 367 (9%), 336 (11%), 314 (29%), 264 (14%), 182 (31%), 149 (70%), 132 (51%), 121 (48%), 106 (96%), 69 (97%), 56 (100%). Anal. Calcd for $C_{32}H_{33}ON_4Cl$ (524.45): C 73.22, H 6.29, N 10.68; found: C 73.65, H 6.67, N 10.87.

^{1}H NMR ($CDCl_3$): δ 8.39 (s, 1H, $H^{6'}$), 7.63 (dd, 1H, J_{5-4}=11.3 and J_{5-6}=14.7 Hz, H^5), 7.54 (dd, 1H, $J_{2''-3''}$=11.3 and $J_{2''-1''}$=15.1 Hz, $H^{2''}$), 7.51 (d, 1H, J_{2-3}=11.7, H^2), 7.38 (d, 1H, J_{6-5}=14.7 Hz, H^6), 7.37 (d, 2H, H^{arom}), 7.15 (dd, 1H, J_{4-3}=14.7 and J_{4-5}=11.3 Hz, H^4), 6.95 (dd, 1H, J_{3-4}=14.7 and J_{3-2}=11.3 Hz, H^3), 7.87 (d, 2H, H^{arom}), 6.77 (d, 1H, $J_{1''-2''}$=15.1 Hz, $H^{1''}$), 6.76 (dd, 1H, $J_{4''-3''}$=14.7 and $J_{4''-5''}$=10.6 Hz, $H^{4''}$), 6.67 (d, 1H, $J_{6''-5''}$=15.1 Hz, $H^{6''}$), 6.56–6.47 (m, 2H, $H^{3''}$ and $H^{5''}$), 3.97 (t, 2H, *J*=6.4 Hz), 2.74 (t, 4H, *J*=6.4 Hz), 1.78 (m, 2H), 1.45–1.29 (m, 10H), 0.89 (t, 3H, *J*=6.1 Hz). ^{13}C NMR ($CDCl_3$): δ 159.9 (C^{arom}), 159.0 (C^2), 151.5 ($C^{5'}$), 148.7 (C^4), 148.6 ($C^{3'}$), 144.0 ($C^{2'}$), 142.0 ($C^{6'}$), 140.5 ($C^{4''}$), 138.9 ($C^{2''}$), 136.6 (C^6), 136.0 ($C^{5''}$), 133.5 (C^5), 131.1 ($C^{3''}$), 129.7 (C^{arom}), 129.4 (C^3), 128.5 (C^{arom}), 126.6 ($C^{6''}$), 125.3 ($C^{1''}$), 115.1 (C^{arom}), 113.8 (C^{CN}), 111.8 (C^{CN}), 84.1 (C^1), 68.4, 0.32.1, 29.7, 29.6, 26.4, 23.0, 14.5.

*4.3.15. 2-Chloro-6-[(1″E,3″E,5″E)-6″-(p-octyloxyphenyl)-hexa-1″-3″-5″-trienyl]-3-[(1′E,3′E,5′E)-6′-(p-trifluorométhylphenyl)-hexa-1″-3″-5″-trienyl]pyrazine (**13**).* To a solution of phosphonium salt (0.46 mmol, 1.2 equiv) in THF (40 mL) at 0 °C under an argon atmosphere, was slowly added *n*-BuLi (1.6 M in hexane, 0.46 mmol, 1.2 equiv). After 30 min stirring, aldehyde **11** (0.38 mmol, 1.0 equiv) in THF (20 mL) was slowly added. The reaction mixture was stirred for 10 min at 0 °C and 5 h at room temperature. The reaction mixture was quenched with a 10% aqueous solution of $NaHCO_3$ (20 mL). The resulting solution was then extracted with dichloromethane (3×15 mL). The combined organic extracts were washed with saturated brine (10 mL) and dried over $MgSO_4$. After evaporation the crude product was further purified by silica gel column chromatography (pentane/dichloromethane: 35/10) to give a mixture of two isomers (*Z*, *E*). The isomerization was realized by 10 mol % of iodine in refluxing dichloromethane or toluene during 4 h. A solution of sodium thiosulfate was added and after extraction with dichloromethane (2×15 mL) the combined organic extracts were dried over $MgSO_4$. After evaporation, only isomer all *E* was obtained with good purity.

Yield: 0.111 g (47%) as a purple solid. Mp=170 °C. IR: 3019, 2953, 2924, 2867, 2846, 1611, 1584, 1449, 1423, 1391, 1250, 1176, 1124, 915, 868, 853, 724, 616 cm^{-1}. MS (EI) *m*/*z*: 618–620 ($M^{+\cdot}$, 16%, 5%), 540 (9%), 426 (15%), 389 (21%), 285 (29%), 233 (34%), 192 (67%), 172 (71%), 142 (37%), 107 (100%), 92 (99%), 74 (44%), 55 (51%). Anal. Calcd for $C_{37}H_{38}ON_2F_3Cl$ (618.45): C 71.79, H 6.14, N 4.53; found: C 71.46, H 6.12, N 4.49.

^{1}H NMR ($CDCl_3$): δ 8.33 (s, 1H, H^5), 7.55 (d, 2H, H^{arom}), 7.51 (dd, 1H, $J_{2'-3'}$=10.2 and $J_{2'-1'}$=15.1 Hz, $H^{2'}$), 7.46 (d, 2H, H^{arom}), 7.44 (dd, 1H, $J_{2''-3''}$=11.3 and $J_{2''-1''}$=15.1 Hz, $H^{2''}$), 7.33 (d, 2H, H^{arom}), 7.01 (d, 1H, $J_{1'-2'}$=14.7 Hz, $H^{1'}$), 6.95 (dd, 1H, $J_{5'-4'}$=11.3 and $J_{5'-6'}$=15.1 Hz, $H^{5'}$), 6.83 (d, 2H, H^{arom}), 6.77–6.59 (m, 6H, $H^{1''}$, $H^{4''}$, $H^{6''}$, $H^{6'}$, $H^{3'}$, $H^{4'}$), 6.56–6.47 (m, 2H, $H^{5''}$, $H^{3''}$), 3.97 (t, 2H, *J*=6.4 Hz), 3.93 (t, 2H,

J=6.4 Hz), 1.75 (m, 2H), 1.42–1.269 (m, 10H), 0.85 (t, 3H, J=6.4 Hz). ^{13}C NMR ($CDCl_3$): δ 159.7 (C^{arom}), 149.5 (C^6), 147.3 (C^2), 146.1 (C^3), 141.5 (C^5), 140.8 ($C^{10'}$), 139.1 ($C^{4''}$), 137.5 ($C^{2''}$), 136.9 ($C^{4'}$), 136.7 ($C^{2'}$), 135.6 (C^5), 134.6 ($C^{5'}$), 133.4 ($C^{3'}$), 131.4 ($C^{6'}$ and $C^{3''}$), 131.3 ($C^{6'}$ and $C^{3''}$), 129.7 (C^{arom}), 128.4 (C^{arom}), 127.1 (C^{arom}), 127.0 (C^{arom}), 126.8 ($C^{6''}$), 126.3 ($C^{1'}$), 126.0 ($C^{1''}$), 125.8 (C^{arom}), 122.7 (CF_3), 115.1 (C^{arom}), 68.4, 32.2, 29.7, 29.6, 26.4, 23.0, 14.5. ^{19}F NMR ($CDCl_3$): δ −63.0.

*4.3.16. 6,6′-Dichloro-2,2′-bipyrazine (**14**).* A solution of 2-chloro-6-iodopyrazine (466 mg, 1.94 mmol) and 2-chloro-6-tributylstannylpyrazine (782 mg, 1.94 mmol) in anhydrous toluene (100 mL) was degassed and placed under an argon atmosphere. Tetrakis(triphenylphosphine)palladium[0] (112 mg, 5 mol %) was quickly added and the mixture was heated to reflux for 48 h. The mixture was cooled and diluted with diethyl ether (10 mL), filtered on a Celite pad and washed with dichloromethane. The collected organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was further purified by silica gel column chromatography (pentane/ethyl acetate: 70/30). Yield: 0.418 g (95%) as a white solid. Mp=240 °C. IR: 3122, 3057, 2957, 2933, 2868, 1375, 1345, 1199, 1147, 908, 887, 766, 742, 511 cm^{-1}. MS (EI) m/z: 226–228-230 ($M^{+\cdot}$, 95%, 93%, 19%), 201 (22%), 199 (24%), 138 (45%), 108 (24%), 104 (22%), 104 (21%), 89 (45%) 87 (100%), 78 (29%). Anal. Calcd for $C_8H_4N_4Cl_2$ (226.9): C 42.31, H 1.76, N 24.28; found: C 42.14, H 1.78, N 24.59.

^{1}H NMR ($CDCl_3$): δ 9.45 (s, 2H, H^3 and $H^{3'}$), 8.68 (s, 2H, H^5 and $H^{5'}$). ^{13}C NMR ($CDCl_3$): δ 149.0 (C^6 and $C^{6'}$), 147.9 (C^2 and $C^{2'}$), 146.0 (C^5 and $C^{5'}$), 141.3 (C^3 and $C^{3'}$).

*4.3.17. 5,5′-Dideuterio-6,6′-dichloro-2,2′-bipyrazine (**15**).* This compound has been obtained according to general procedure B. LTMP was prepared from TMPH (0.54 mL, 3.20 mmol, 2.4 equiv), n-BuLi (2.12 M in hexanes, 1.44 mL, 3.10 mmol, 2.3 equiv) in THF (40 mL), cooled at −100 °C and treated with 6,6′-dichloro-2,2′-bipyrazine **14** (300 mg, 1.30 mmol, 1.0 equiv) in THF (15 mL) for t_1=5 min. The electrophile was EtOD (0.8 mL, 13.00 mmol, 10.0 equiv) in THF (10 mL) at −100 °C for 30 min. Hydrolysis was carried out with water (20 mL). Eluent for chromatography: dichloromethane. Yield: 0.212 g (70%) as a white solid. Mp=242 °C. IR: 3115, 3065, 1550, 1380, 1149, 1092, 1030, 960, 900, 763, 672, 626 cm^{-1}. MS (EI) m/z: 228–230-232 ($M^{+\cdot}$, 100%, 58%, 10%), 200 (10%), 193 (12%), 141 (29%), 139 (34%), 114 (19%), 88 (39%), 61 (42%). Anal. Calcd for $C_8H_2D_2N_4Cl_2$ (228.9): C 41.94, H 0.87, N 24.46; found: C 41.37, H 1.39, N 24.10.

^{1}H NMR ($CDCl_3$): δ 9.45 (s, 2H, H^3 and $H^{3'}$). ^{13}C NMR ($CDCl_3$): δ 149.0 (C^6 and $C^{6'}$), 147.9 (C^2 and $C^{2'}$), 146.0 (C^5 and $C^{5'}$), 141.3 (C^3 and $C^{3'}$).

*4.3.18. 5,5′-Di(tributylstannyl)-6,6′-dichloro-2,2′-bipyrazine (**16**).* This compound has been obtained according to general procedure B. LTMP was prepared from TMPH (0.38 mL, 2.20 mmol, 2.4 equiv), n-BuLi (1.84 M in hexanes, 1.15 mL, 2.10 mmol, 2.3 equiv) in THF (40 mL), cooled at −100 °C and treated with 6,6′-dichloro-2,2′-bipyrazine **14** (209 mg, 0.90 mmol, 1.0 equiv) in THF (15 mL) for t_1=5 min. The electrophile was Bu_3SnCl (0.63 mL, 2.30 mmol, 2.5 equiv) in THF (10 mL) at −100 °C to −78 °C in 3 h. Hydrolysis was carried out with water (20 mL). Eluent for chromatography: pentane/dichloromethane (9/1). Yield: 0.301 g (41%) as a colourless oil. IR: 2955, 2920, 2852, 1523, 1464, 1240, 1139, 1076, 1037, 781, 694, 638 cm^{-1}. Anal. Calcd for $C_{32}H_{56}N_4Sn_2$ (733.42): C 47.74, H 6.96, N 6.96; found: C 47.62, H 6.88, N 6.85.

^{1}H NMR ($CDCl_3$): δ 9.52 (s, 2H, H^3 and $H^{3'}$), 1.63–1.52 (m, 12H), 1.39–1.23 (m, 24H), 0.87 (t 18H). ^{13}C NMR ($CDCl_3$): δ 173.9 (C^5 and $C^{5'}$), 156.7 (C^6 and $C^{6'}$), 146.6 (C^2 and $C^{2'}$), 141.8 (C^3 and $C^{3'}$), 29.3, 27.6, 14.0, 11.3.

*4.3.19. 5,5′-Bis(p-methoxyphenylhydroxymethyl)-6,6′-dichloro-2,2′-bipyrazine (**17**).* This compound has been obtained according to general procedure B. LTMP was prepared from TMPH (0.56 mL, 3.3 mmol, 2.4 equiv), n-BuLi (2.0 M in hexanes, 1.6 mL, 3.2 mmol, 2.3 equiv) in THF (40 mL), cooled at −100 °C and treated with 6,6′-dichloro-2,2′-bipyrazine **14** (310 mg, 1.4 mmol, 1.0 equiv) in THF (20 mL) for t_1=5 min. The electrophile was 4-methoxybenzaldehyde (0.56 g, 4.1 mmol, 3.0 equiv) in THF (20 mL) at −100 °C to −78 °C in 2 h. Hydrolysis was carried out with water (20 mL). Eluent for chromatography: ethyl acetate/dichloromethane (1/10). Yield: 0.430 g (63%) mixture of diastereomer as a yellow solid. Mp=242 °C. IR: 3476, 3076, 3009, 2955, 2897, 2837, 1609, 1584, 1387, 1251, 1039, 930, 869, 794, 757, 579 cm^{-1}. MS (EI) m/z: 498–500–502 ($M^{+\cdot}$, 14%), 465 (11%), 433 (16%), 380 (16%), 367 (20%), 344 (23%), 321 (21%), 290 (31%), 275 (45%), 219 (30%), 191 (38%), 177 (73%), 152 (38%), 139 (66%), 96 (66%), 73 (100%). Anal. Calcd for $C_{24}H_{20}O_4Cl_2N_4$ (498.9): C 57.73, H 4.01, N 11.22; found: C 57.48, H 3.95, N 11.25.

^{1}H NMR ($CDCl_3$): δ 9.45 (s, 2H, H^3 and $H^{3'}$), 7.29 (d, 2H, J=8.7 Hz, H^{arom}), 6.87 (d, 2H, J=8.7 Hz, H^{arom}), 6.05 (d, 2H, J=7.9 Hz), 4.58 (d, 2H, J=7.9 Hz, OH), 3.79 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 160.0 (C^{arom}), 156.0 (C^5 and $C^{5'}$), 146.9 (C^2 and $C^{2'}$ or C^6 and $C^{6'}$), 146.8 (C^2 and $C^{2'}$ or C^6 and $C^{6'}$), 139.8 (C^3 and $C^{3'}$), 132.5 (C^{arom}), 129.2 (C^{arom}), 114.5 (C^{arom}), 72.2 (C^{OH}), 55.6 (CH_3).

*4.3.20. (2″E,4″E)-Bis[6-chloro-5-(penta-2″,4″-dienal)]-2,2′-bipyrazine (**18**).* This compound was obtained according to the general procedure A. LTMP was prepared from anhydrous THF (80 mL), 2,2,6,6-tetramethylpiperidine (0.54 mL, 3.17 mmol, 2.4 equiv) and n-BuLi (1.60 mL, 3.04 mmol, 2.3 equiv 1.91 M in hexanes) cooled at θ_1=−100 °C and reacted with 6,6′-dichloro-2,2′-bipyrazine **14** (1.32 mmol, 1 equiv) in THF (20 mL) for t_1=5 min, $ZnCl_2$ (0.722 g, 5.28 mmol, 4.0 equiv) in anhydrous THF (20 mL), 5-bromo-penta-2,4-dienal (0.427 g, 2.64 mmol, 2.0 equiv) and $Pd(PPh_3)_4$ (0.152 g, 0.13 mmol, 10 mol %) in V_2=THF (30 mL) for t_2=5 h. The crude product was recrystallized from dichloromethane. Yield: 0.328 g (64%) as a yellow solid. Mp>260 °C. IR: 3054, 2970, 2846, 1680, 1619, 1490, 1423, 1300, 1150, 1099, 1065, 1019, 996, 878, 802, 748, 693, 524 cm^{-1}. MS (EI) m/z: 386–388-390 ($M^{+\cdot}$, 14%, 5%), 346 (9%), 314 (17%), 291 (20%), 281 (27%), 221 (17%), 213 (22%), 197 (23%), 189 (24%), 163 (29%), 142 (19%), 129 (40%), 107 (96%), 106 (100%), 91 (62%), 79 (74%), 57 (71%). Anal. Calcd for $C_{18}H_{12}O_2N_4Cl_2$ (386.9): C 55.83, H 3.10, N 14.47; found: C 56.01, H 3.21, N 14.68.

^{1}H NMR ($CDCl_3$): δ 9.73 (d, 2H, $J_{1''-2''}$=7.5 Hz, $H^{1''}$), 9.45 (s, 2H, H^3 and $H^{3'}$), 7.84 (dd, 2H, $J_{4''-3''}$=11.3 and $J_{4''-3''}$=11.3 Hz, $H^{4''}$), 7.45 (d, 2H, $J_{5''-4''}$=15.1 Hz, $H^{5''}$), 7.39 (dd, 2H, $J_{3''-4''}$=11.3 and $J_{3''-2''}$=15.1 Hz, $H^{3''}$), 6.48 (dd, 2H, $J_{2''-1''}$=7.5 and $J_{2''-3''}$=15.1 Hz, $H^{2''}$). ^{13}C NMR ($CDCl_3$): δ 193.7 ($C^{1''}$), 149.5 ($C^{3''}$), 148.5 ($C^5$and $C^{5'}$), 147.8 (C^6 and $C^{6'}$), 146.7 (C^2 and $C^{2'}$),141.7 (C^3 and $C^{3'}$), 136.0 ($C^{2''}$), 135.5 ($C^{4''}$), 133.3 ($C^{5''}$).

*4.3.21. 6,6′-Dichloro-5,5′-bis[6″-(9‴-julolidinyl)-(1″E,3″E,5″E)-hexa-1″,3″,5″-trienyl]-2,2′-bipyrazine (**19**).* This compound was obtained according to the general procedure A. LTMP was prepared from anhydrous THF (80 mL), 2,2,6,6-tetramethylpiperidine (0.45 mL, 2.64 mmol, 2.4 equiv) and n-BuLi (1.30 mL, 2.53 mmol, 2.3 equiv, 1.94 M in hexanes) cooled at θ_1=−100 °C and reacted with 6,6′-dichloro-2,2′-bipyrazine **14** (1.10 mmol, 1 equiv) in THF (20 mL) for t_1=5 min, $ZnCl_2$ (0.722 g, 4.40 mmol, 4.0 equiv) in anhydrous THF (20 mL), 1-bromo-6-julolidinylhexa-1,3,5-triene (0.727 g, 2.20 mmol, 2.0 equiv) and $Pd(PPh_3)_4$ (0.127 g, 0.11 mmol, 10 mol %) in V_2=THF (30 mL) for t_2=5 h. The crude product was recrystallized from dichloromethane.

Yield: 0.451 g (57%) as a purple solid. Mp>260 °C. IR: 3020, 2938, 2841, 1568, 1311, 1237, 1203, 1135, 1061, 998, 845 cm^{-1}. MS (EI) m/z: 724–726-728 ($M^{+\cdot}$, 18%, 6%), 476 (40%), 444 (15%), 372 (21%), 281 (27%), 163 (15%), 129 (35%), 106 (66%), 83 (43%), 57 (100%). Anal. Calcd for $C_{44}H_{42}N_6Cl_2$ (724.9): C 72.83, H 5.79, N 11.59; found: C 72.97, H 5.85, N 11.65.

^{1}H NMR ($CDCl_3$): δ 9.27 (s, 2H, H^3), 7.73 (dd, 2H, $J_{2''-3''}$=11.3 and $J_{2''-1''}$=15.1 Hz, $H^{2''}$), 6.91 (s, 4H, $H^{8'''}$ and $H^{10'''}$), 6.83 (d, 2H, $J_{1''-2''}$=15.1 Hz, $H^{1''}$), 6.69 (dd, 2H, $J_{4''-5''}$=10.6 and $J_{4''-3''}$=14.3 Hz, $H^{4''}$), 6.60 (d, 2H, $J_{6''-5''}$=15.1 Hz, $H^{6''}$), 6.52 (dd, 2H, $J_{5''-4''}$=10.6 and $J_{5''-6''}$=15.1 Hz, $H^{5''}$), 6.47 (dd, 2H, $J_{3''-2''}$=11.3 and $J_{3''-4''}$=14.3 Hz, $H^{3''}$), 3.17 (t, 8H, J=5.7 Hz), 2.73 (t, 8H, J=6.4 Hz), 1.98 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 150.3 ($C^5$and $C^{5'}$), 146.5 (C^6 and $C^{6'}$), 144.1 (C^2 and $C^{2'}$), 142.4 (C^3 and $C^{3'}$), 144.1 ($C^{6''}$), 141.4 ($C^{4''}$), 140.6 ($C^{2''}$), 138.1 ($C^{5''}$), 130.1 ($C^{3''}$), 126.7 ($C^{8'''}$ and $C^{10'''}$), 124.3 ($C^{9'''}$), 123.0 ($C^{6''}$), 122.1 ($C^{1''}$), 122.0 ($C^{5'''}$ and $C^{7'''}$), 50.3 ($C^{2'''}$), 28.0 ($C^{4'''}$), 22.2 ($C^{3'''}$).

*4.3.22. (1″E,3″E,5″E)-6,6′-Dichloro-5,5′-bis[6″-(p-n-octyloxyphenyl)-hexa-1″,3″,5″-trienyl]-2,2′-bipyrazine (**20**).* This compound was obtained according to the same procedure as for **13**. Phosphonium salt (2.17 mmol, 2.4 equiv), THF (100 mL), *n*-BuLi (2.4 M in hexane, 2.17 mmol, 2.4 equiv), dialdehyde **18** (0.90 mmol, 1.0 equiv), THF (20 mL), 16 h at room temperature. The crude product was further purified by recrytallization from dichloromethane. The isomerization was realized by 10 mol % of iodine in refluxing dichloromethane.

Yield: 0.530 g (74%) as a red solid. Mp=255 °C. IR: 3295, 3003, 2953, 2921, 2858, 1585, 1476, 1414, 1304, 1264, 1242, 996, 860, 837, 799, 742, 619 cm^{-1}. MS (EI) *m*/*z*: 790–792-794 ($M^{+\cdot}$, 4%), 548 (4%), 475 (6%), 402 (5%), 376 (9%), 328 (6%), 285 (7%), 279 (11%), 224 (21%), 175 (20%), 130 (77%), 106 (100%), 72 (56%). Anal. Calcd for $C_{48}H_{56}O_2N_4Cl_2$ (790.9): C 73.83, H 7.08, N 7.08; found: C 73.94, H 7.15, N 7.11.

^{1}H NMR ($CDCl_3$): δ 9.32 (s, 2H, H^3), 7.73 (dd, 2H, $J_{2''-3''}$=11.3 and $J_{2''-1''}$=15.1 Hz, $H^{2''}$), 7.38 (d, 4H, J=8.7 Hz, H^{arom}), 7.02 (d, 2H, $J_{1''-2''}$=14.7 Hz, $H^{1''}$), 6.88 (d, 4H, J=8.7 Hz, H^{arom}), 6.87 (d, 2H, $J_{6''-5''}$=15.1 Hz, $H^{6''}$), 6.75 (dd, 2H, $J_{4''-5''}$=11.3 and $J_{4''-3''}$=15.1 Hz, $H^{4''}$), 6.69 (dd, 2H, $J_{5''-4''}$=10.9 and $J_{5''-6''}$=15.1 Hz, $H^{5''}$), 6.59 (dd, 2H, $J_{3''-2''}$=11.3 and $J_{3''-4''}$=14.7 Hz, $H^{3''}$), 3.97 (t, 4H, J=6.1 Hz), 1.78 (m, 4H). 1.45–1.29 (m, 20H), 0.89 (t, 6H, J=6.4 Hz). ^{13}C NMR ($CDCl_3$): δ 159.8 (C^{arom}), 150.2 ($C^5$and $C^{5'}$), 146.4 (C^6 and $C^{6'}$), 144.2 (C^2 and $C^{2'}$), 142.5 (C^3 and $C^{3'}$), 140.4 ($C^{4''}$), 139.9 ($C^{2''}$), 136.2 ($C^{5''}$), 131.6 ($C^{3''}$), 129.8 (C^{arom}), 128.5 (C^{arom}), 126.8 ($C^{6''}$), 124.0 ($C^{1''}$), 115.1 (C^{arom}), 68.5, 32.2, 29.7, 29.6, 26.4, 23.0,14.5.

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