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Synthesis and optical properties of multibranched and C_3 symmetrical oligomers with benzene or triphenylamine core and diazines as peripheral groups

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ABSTRACT

We report therein the synthesis and photophysical properties of a new series of two- and tribranched compounds built up from benzene or triphenylamine as central core and electron-withdrawing diazine rings as peripheral group. The arms allowing connection between these two parts are constituted by an ethynylene linker. All these compounds are fluorescent and are of particular interest with generally good quantum yields and good Stokes shifts. Some of them have been tested for two-photon absorption (TPA) properties and had revealed interesting performances.

1. Introduction

Organic materials with extended-π conjugation along their backbone have received high interest owing to their applications in a wide range of electronic and optoelectronic devices.[1] In recent years, a variety of dipolar (donor–bridge–acceptor, D–π–A), quadrupolar (A–π–A, D–π–D, A–π–D–π–A or D–π–A–π–D) and multibranched molecules have been synthesized and investigation of their structure-properties relationships has been achieved. Among them, star-shaped and bent-shaped molecules have highlighted applications in various fields, such as liquid crystals,[2] light-emitting,[3] self-assembling,[4] and octupolar nonlinear optical properties.[5] Another interest of such structures is their potential two-photon absorption (TPA) properties,[6] defined by their cross-sections (δ_{TPA}). These structures could find applications in a large number of new areas, including the fluorescence imaging of biological samples,[7] optical limiting,[8] photodynamic therapy,[9] the three-dimensional optical data storage,[10] and microfabrication.[11] In a general way, the electro-optical properties of the chromophores with such applications increase mainly with the conjugation length, planarity of the π-center and the donor/acceptor strength.[12] Among the factors, which influence the photophysical properties, electron conjugation, and intramolecular charge transfer (ICT) play an important role; therefore by changing the design of compounds it is possible to tune their photophysical and their TPA properties. In this context, a convenient strategy to achieve the desired properties of the chromophores is to optimize the individual fragments of the architecture, such as the core, the π-linkers and the peripheral groups.

In continuation of our work dealing with the synthesis and the study of optical properties of star-shaped conjugated compounds incorporating diazine moieties, we have studied a series of octupolar compounds. These compounds have been built up from an electron-donating or a withdrawing central unit exhibiting a C_3 symmetry. To insure an intramolecular charge transfer (ICT) between the core and the peripheral groups, which must be of different electronic character, the three arms are constituted by an ethynylene linker, allowing either a periphery-to-core or core-to-periphery multidimensional charge transfer. Incorporation of a triple bond as linkage in the backbone has been chosen because it gives a good stability, and leads to coplanar conjugated structures. A planar scaffold is not always observed with aromatic rings as transmitter, because they could generate twisted structures. For compounds of type I (Fig. 1), when the core is constituted by the

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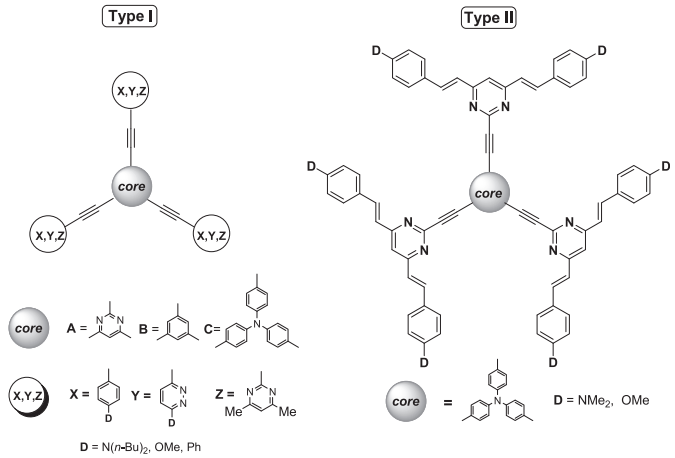


Fig. 1. C_3 symmetrical oligomers incorporating diazine moieties.

pyrimidine ring, known for its π-deficient character, the peripheral groups are phenyl groups *para*-substituted with electron-donors. In contrary, when the central unit is an electron-donating moiety, such as triphenylamine core or benzene ring may behave as moderate donor and acceptor, the peripheral groups are electron-attracting π-deficient diazines (pyridazine or pyrimidine).

Compounds of type I with a triphenylamine core and peripheral strong electron-withdrawing groups as substituents of phenyl rings have been previously reported. Such compounds have highlighted various applications, such as fluorescence,[13] two-photon absorption,[14] Organic Light Emitting Diodes (OLEDs),[15] DNA strainers.[16] Originality of this work is the synthesis of a new series of compounds of type I with incorporation of diazines, known to be good π-deficient moieties.

Dendritic materials alternating double and single bonds have been synthesized and interesting fluorescence properties were obtained.[17] With the aim to modulate the optical properties of these octupolar compounds, structures of type II have been synthesized. In this case, each arm is constituted by a bis(arylvinyl) pyrimidine linked to the triphenylamine central unit through an ethynylene linker (Fig. 1).

The choice of these peripheral π-conjugated chains has been determined by ability of the V-shaped 4,6-bis(arylvinyl)pyrimidine oligomers, previously described, to induce interesting optical properties and to be used as fluorescent sensors.[18]

2. Results and discussion

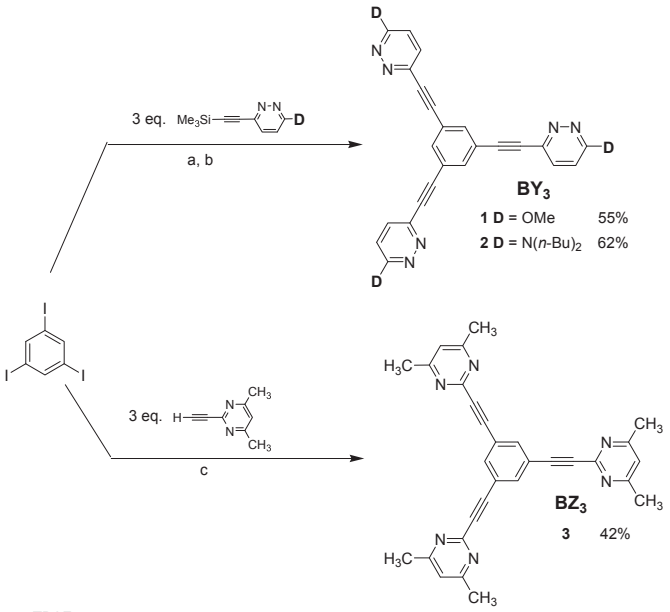
2.1. Synthesis

2.1.1. Compounds of type I

2.1.1.1. Compounds incorporating a pyrimidine core AX_3. The synthesis and optical properties of compounds of type I that we can designate, for example, as AX_3 (i.e., 2,4,6-triphenylpyrimidines) have been previously reported.[19] Using molecular orbital calculations at the DFT 6-31* level theory on these compounds, the energies of their frontier orbitals have been calculated and their geometry fully optimized and established as absolutely planar structures.

2.1.1.2. Compounds incorporating a benzene core BY_3 and BZ_3. The synthetic strategy to access compounds, BY_3 or BZ_3 with a benzene core involves Sonogashira cross-coupling reactions achieved either with 1,3,5-triiodo- or with 1,3,5-triethynyl- benzene as starting materials. This first methodology has been previously used to synthesize compounds of type BX_3 with 4-ethynylaniline.[20] One other way, reaction of 4-substituted arylbenzenes or 4-iodopyridine with 1,3,5-triethynylbenzene has led to various compounds of type I.[21,22]

The synthetic route to the target compounds BY_3 takes advantage of a Sonogashira cross-coupling reaction between the 1,3,5-triiodobenzene and the corresponding 3-methoxy- or 3-di-*n*-butylamino-6-(trimethylsilyl)ethynylpyridazine leading to the three-branched BY_3 compounds **1** and **2** in moderate yields. In this case the desilylation of the ethynyl part has been carried out in situ by reaction with tetrabutylammonium fluoride (TBAF). A similar reaction with the 2-ethynyl-4,6-dimethylpyrimidine gave the BZ_3 compound **3** in 42% yield (Scheme 1).

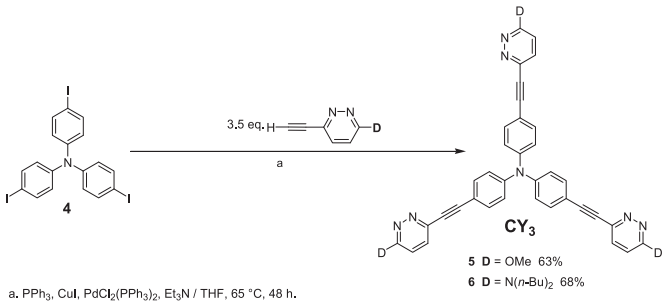


a. TBAF
b. PPh_3, CuI, $Pd_2(dba)_3$, Et_3N / Toluene, 50 °C, 48 h.
c. $PdCl_2(PPh_3)_2$, CuI, Et_3N, 90 °C, 24 h.

Scheme 1. Synthesis of compounds BY_3 and BZ_3.

2.1.1.3. Compounds incorporating a triphenylamine core CY_3 and CZ_3. A series of star compounds CY_3 and CZ_3 with C_3-fold symmetry and the triphenylamine as central unit could be synthesized either starting from the tris-(4-iodophenyl)amine **4**,[23,24] which underwent Sonogashira cross-coupling reaction with diazinylethynes (Scheme 2) or starting from the tris-[4-(2-trimethylsilylethynyl) phenyl]amine **9**,[24] which was coupled with iododiazines (Scheme 4). In the first case, coupling reaction of **4** with 6-methoxy- or 6-*n*-dibutylamino-3-ethynylpyridazine[25] afforded compounds **5** and **6** in moderate yields (63–68%).

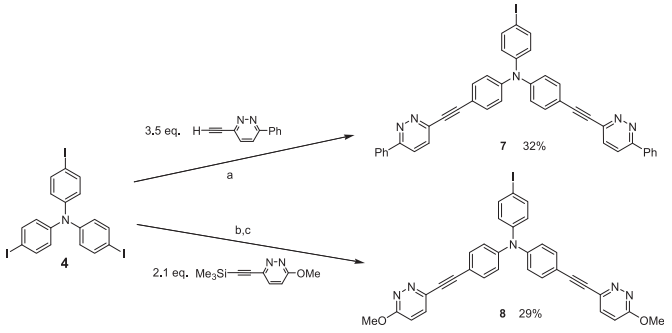
When the reaction was performed under the same conditions with the 3-ethynyl-6-phenylpyridazine, only the dicoupled



a. PPh_3, CuI, $PdCl_2(PPh_3)_2$, Et_3N / THF, 65 °C, 48 h.

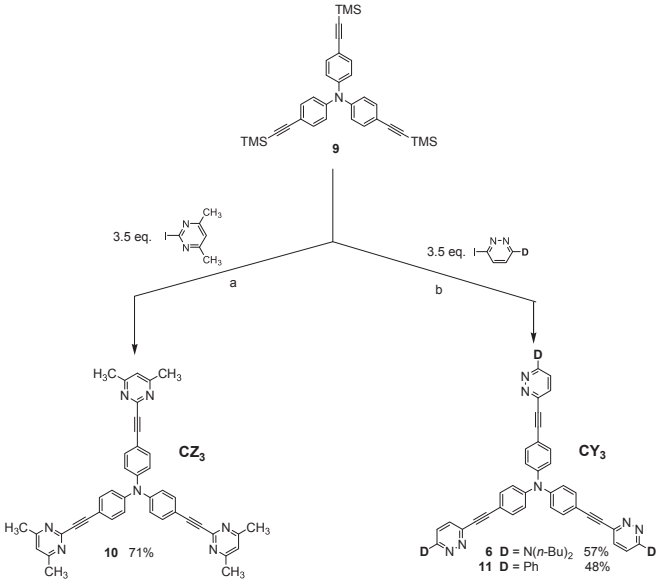
Scheme 2. Synthesis of compounds CY_3 starting from compound **4**.

compound **7** was obtained in 32% yield. On the other hand, when the coupling reaction was achieved between **4** and only two equivalents of 3-ethynyl-6-methoxypyridazine, under modified experimental conditions, the dicoupled compound **8** was obtained in similar low yield (Scheme 3).



a. PPh_3, CuI, $PdCl_2(PPh_3)_2$, Et_3N / THF, 65 °C, 48 h.
b. TBAF; c. PPh_3, CuI, $Pd_2(dba)_3$, Et_3N / Toluene, 50 °C, 48 h.

Scheme 3. Synthesis of two-branched compounds **7** and **8**.

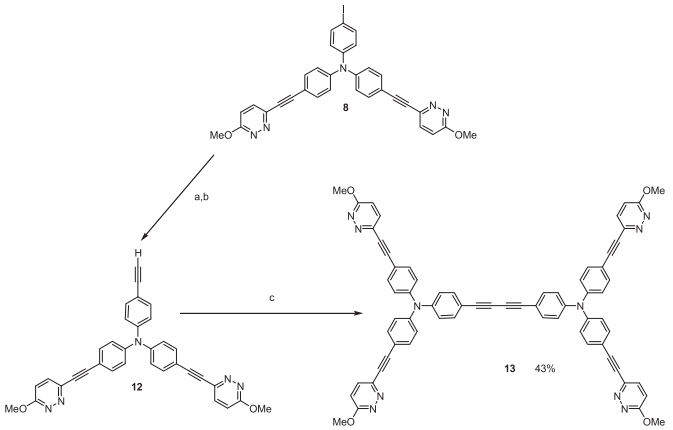


a. TBAF, $Pd(PPh_3)_4$, CuI, Et_3N / Toluene, 50 °C, 24 h.
b. TBAF, PPh_3, CuI, $Pd_2(dba)_3$, Et_3N / Toluene, 50 °C, 24 h.

Scheme 4. Synthesis of compounds CZ_3 and CY_3 starting from compound **9**.

In the second route, the tris-[4-(2-trimethylsilylethynyl)phenyl] amine **9** has been used as starting material. Compound **9** was obtained by a triple coupling of trimethylsilylacetylene (TMSA) with **4**. A one-pot TMS deprotection and subsequent standard Sonogashira coupling reaction with iododiazines afforded the compound **10** with a structure CZ_3 and the compounds **6** and **11** of type CY_3 in moderate yields (Scheme 4).

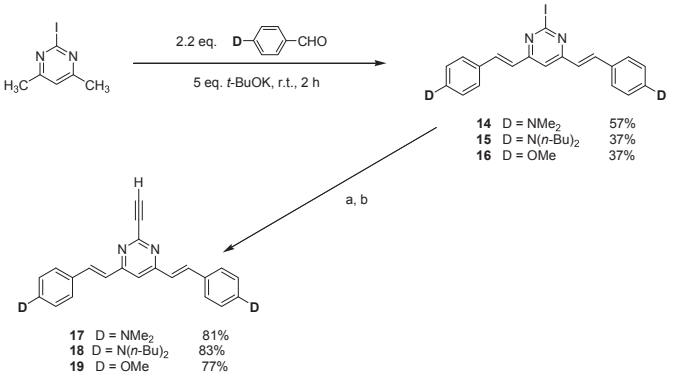
With the aim to access C_3 star-shaped compounds with a triphenylamine core and peripheral groups constituted by a substructure of compound **8**, a new *p*-aminophenylacetylene **12** has been synthesized. The iodo derivative **8** was functionalized with TMSA, a further removal of the TMS group giving **12** in 60% yield. An attempt to perform a Sonogashira coupling between **4** and **12** under standard conditions, previously used, has failed and only compound **13**, resulting from a Glaser's dimerization reaction has been obtained (Scheme 5).



a. 2 eq. TMSA, $PdCl_2(PPh_3)_2$, CuI, Et_3N / Toluene, 60 °C, 48 h.
b. TBAF, THF, r.t., 3h.
c. 0,28 eq. **4**, CuI, $PdCl_2(PPh_3)_2$, Et_3N / Toluene, 60 °C, 48 h.

Scheme 5. Glaser's dimerization leading to the compound **13**.

2.1.2. Compounds of type II. As previously, to access compounds of type II with a triphenylamine as central moiety, two strategic pathways could be considered either starting from the triiodo compound **4** or from the triethynyl derivative **9**. The choice of **4** as starting material seemed to us more appropriate since this compound is easily available. In this case coupling reaction would be achieved between **4** and appropriate substituted 2-ethynylpyrimidines. Synthesis of various 2-iodo-4,6-bis(arylvinyl) pyrimidines **14**–**16** have been performed by solvent free condensation of 2-iodo-4,6-dimethylpyrimidine with corresponding aromatic aldehydes, under the conditions described by Li et al.[26] A further coupling with TMSA and a subsequent desilylation with TBAF afforded the expected 2-ethynyl-4,6-bis(arylvinyl)pyrimidines **17**–**19** in good yields (Scheme 6).

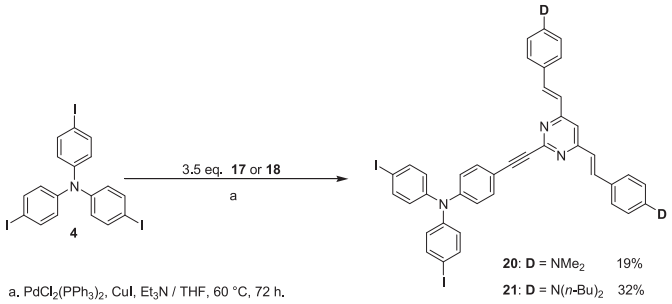


a. 2 eq. TMSA, PPh_3, CuI, $PdCl_2(PPh_3)_2$, Et_3N / THF, 50 °C, 48 h.
b. TBAF, THF, r.t., 3 h.

Scheme 6. Synthesis of 2-ethynyl-4,6-bis(arylvinyl)pyrimidines.

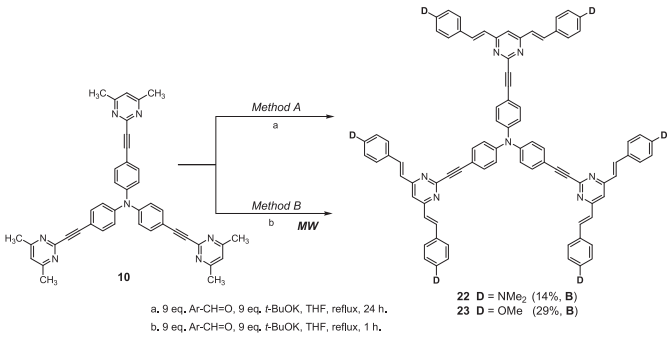
Attempts to obtain tribranched compounds by coupling reaction between **4** and compound **17** or **18** have been performed under classical conditions. Nevertheless, by use of these experimental conditions, only a mono-coupling occurred, leading to compounds **20** and **21** in low yields (Scheme 7).

These results urged us to choose another synthetic way, to obtain the expected C_3 compounds of type II. Starting from the CZ_3 compound **10**, it would be possible to carry out condensation under basic conditions with aromatic aldehydes, this methodology having been used with success to access compounds **14**–**16**. Condensation reaction of **10** with 4-dimethylamino- or 4-methoxybenzaldehyde



Scheme 7. Synthesis of compounds **20** and **21** resulting from a mono-coupling reaction.

has been achieved with an excess of aldehyde, and 9 equiv of *t*-BuOK as base, at reflux of THF by a classical thermal heat for 24 h (Method A). Under these conditions only traces of expected compounds **22** and **23** have been observed. When this reaction has been performed with use of microwaves and shorter reaction time (Method B), compounds **22** and **23** were obtained, respectively, in 14% and 29% yields (Scheme 8).



Scheme 8. Synthesis of compounds of type II.

2.2. Linear UV/Vis absorption and single-photon excited fluorescence

In order to determine the influence of the intramolecular charge transfer (ICT) between the core and the peripheral groups, determination and comparison of the spectroscopic properties of various compounds of type I has been achieved. Compounds AX_3 **24**–**26**,[19] with the electron-withdrawing pyrimidine as central unit, bearing on each arm a benzene ring *para*-substituted with a methoxy or a dimethylamino group, present a multidimensional charge transfer from periphery-to-core. In the case of compounds BY_3 and BZ_3, where a benzene ring is the central part, the external diazine moieties Y (pyridazine) or Z (pyrimidine) induce the charge transfer from core-to-periphery. Same kind of ICT is observed with compounds CY_3 and CZ_3 where the central unit is the strong electron releasing triphenylamine (Fig. 2).

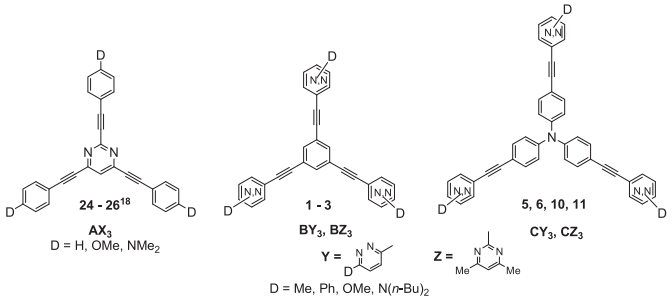


Fig. 2. Compounds of type I.

The UV/Vis and fluorescence spectroscopic data of various oligomers measured in dichloromethane at 25 °C are summarized in Table 1.

Table 1
Photophysical data for octupolar chromophores **1**–**3**, **5**, **6**, **10**, **11**, **24**–**26** in dichloromethane at 25 °C

Type	Compound	D	λ_{abs} [nm]	ε [M^{-1} cm^{-1}]	λ_{em} [nm]	Φ_F[a]	Stokes shift [cm^{-1}]
AX_3	**24**[18]	H	341	38,539	370	0.06	2298
AX_3	**25**[18]	OMe	335	45,073	406	0.48	5220
AX_3	**26**[18]	NMe_2	433	26,155	522	0.24	3938
BY_3	**1**	OMe	286	47,177	460	<0.01	13,226
BY_3	**2**	$N(n\text{-}Bu)_2$	326	24,573	425	<0.01	7145
BZ_3	**3**	—	300	58,573	350	<0.01	4764
CY_3	**5**	OMe	375	64,597	449	0.60	4395
CY_3	**6**	$N(n\text{-}Bu)_2$	380	56,112	450	0.29	4094
CY_3	**11**	Ph	394	52,601	488	0.03	4889
CZ_3	**10**	—	385	56,908	449	0.57	3702

[a] ±10%, harmane (0.1 M in H_2SO_4) was used as reference (Φ_F=0.58).

All the three-branched compounds collected in Table 1 have their absorption wavelengths (λ_{abs}) in the UV region (286–394 nm) and their emission absorption wavelengths (λ_{em}) in the UV or blue region (350–460 nm), an exception was observed for compound AX_3 **26** with D=NMe_2 whose absorption and emission wavelengths are in visible region. Amplitude of the charge transfer has a great influence on the quantum yield, the highest values for Φ_F are observed with the cores A or C, which have a strong electron-withdrawing or donating effect, whereas the lowest values are obtained with the benzene core. It could be noticed that these results are in agreement with the fact that triphenylamine derivatives are well-known as fluorescent materials and exhibit high quantum yields and Stokes shifts when they are included in scaffolds with π-conjugation extension and with strong acceptor groups in periphery. For compounds CY_3 **5**, **6**, **11**, such as for compounds AX_3 **24**–**26**, presence of an electron releasing group on the peripheral rings increases the light-emitting properties. However, in this case and unexpectedly, the methoxy group, which is prone to be less electron-donor than dialkylamino groups is more efficient on the quantum yields. We can notice that compound CZ_3 **10**, with a dimethylpyrimidine as peripheral substituent exhibits a moderate Stokes shift but a great quantum yield.

With the aim to establish the influence of the number of arms, comparison of optical properties of compounds **5**, **7**, **8**, **11**–**13** with a triphenylamine as core and 6-methoxy- or 6-phenylpyridazine as peripheral groups have been studied and are reported in Table 2. All these compounds have similar absorption values in UV (367–394 nm), emission wavelengths in blue region (438–488 nm) and similar Stokes shifts, the main difference is observed for the quantum yields.

Table 2
Photophysical data for multibranched chromophores **5**, **7**, **8**, **11**–**13** in dichloromethane at 25 °C

Compound	λ_{abs} [nm]	ε [M^{-1} cm^{-1}]	λ_{em} [nm]	Φ_F[a]	Stokes shift [cm^{-1}]
5	375	64,597	449	0.60	4395
7	390	29,012	487	0.02	5108
8	375	64,785	455	0.16	4688
11	394	52,601	488	0.03	4889
12	367	27,992	460	0.49	5509
13	386	82,594	438	0.48	3075

[a] ±10%, harmane (0.1 M in H_2SO_4) was used as reference (Φ_F=0.58).

Comparison between the three-branched compounds **5** and **11** and the two-branched analogous iodo derivatives **8** and **7** highlights that compounds **5** and **8**, with a methoxy group on the pyridazine ring, exhibit better quantum yields than their analogous bearing a phenyl group. We can observe that presence of a third arm increases strongly the quantum yields. Comparison of the values for **8** and **12** reveals that replacement of the iodine atom by a triple bond has the effect of large increasing the Φ_F (0.49 vs 0.16). The low quantum yields observed for the compounds **7**–**8** can be explained by the presence of the iodine atom, which can quench the fluorescence. For the dimeric compound **13**, which could be considered as two three-branched moieties, the Φ_F value is close to that observed for **12**. The better quantum yield is obtained for the tripodal C_3 symmetric compound **5**.

Recently synthesis of a series of bis(arylvinyl)pyrimidine oligomers have been reported highlighting interesting photophysical properties (absorption, fluorescence and quantum yields).[18a] Incorporation of such moieties on triphenylamine core through ethynyl linkage leads to compounds of type II. The photophysical properties of the two-branched building blocks **14**–**19**, mono coupled compounds **20**–**21** and three coupled compounds **22**–**23** are collected in Table 3.

Table 3
Photophysical data for multibranched chromophores **14**–**23** in dichloromethane at 25 °C

Compound	D	λ_{abs} [nm]	ε [M^{-1} cm^{-1}]	λ_{em} [nm]	Φ_F[a]	Stokes shift [cm^{-1}]
14	NMe_2	450	46,535	561	0.04	4397
15	$N(n\text{-}Bu)_2$	470	60,651	560	0.08	3419
16	OMe	374	21,387	459	0.01	4951
17	NMe_2	440	43,916	545	0.47	4378
18	$N(n\text{-}Bu)_2$	455	65,407	547	0.52	3696
19	OMe	364	35,244	457	0.02	5590
20	NMe_2	430	24,897	545	0.42	4907
21	$N(n\text{-}Bu)_2$	450	39,625	545	0.52	3874
22	NMe_2	408	77,057	553	0.19	6427
23	OMe	376	134,084	518	0.03	7291

[a] ±10%, harmane (0.1 M in H_2SO_4) was used as reference (Φ_F=0.58).

As previously, we observed that for the iodo derivatives **14**–**16** as well for the ethynyl compounds **17**–**19**, replacement of the methoxy group by a dialkylamino one induces a bathochromic effect for both absorption and emission wavelengths. For the amino derivatives, replacement of the iodine atom in **14**–**15** by an ethynyl group in compounds **17**–**18** resulted in higher quantum yield (0.04–0.08 vs 0.47–0.52) whereas a slightly higher emission was observed for the methoxy derivatives **16** and **19** (0.01 vs 0.02). When a bis(arylvinyl)pyrimidine moiety is incorporated in one arm of the triphenylamine unit leading to compounds **20** and **21**, similar photophysical properties are observed for the both series **17**, **18**, and **20**, **21**. This result seems indicate that such incorporation do not allow an extension of conjugation. When each arm of the three-branched triphenylamine is substituted by a bis(arylvinyl)pyrimidine moiety, a comparison on the one hand between **20** and **22** and one the other hand between **19** and **23**, allows to observe a slight hypsochromic effect for the absorption and emission wavelengths (λ_{abs} and λ_{em}) whereas a dramatic decrease of the quantum yield is noted, with a very low value when the external substituent is a methoxy group **23**.

2.3. Two-photon absorption (TPA)

Two-photon absorption cross-sections (δ_{TPA}) spectra of the three-branched **5**, **10**, and **12** and the two-branched chromophores **17** and **18**, were determined in the wavelengths range (730–920 nm) by investigating their two-photon induced fluorescence (TPIF) measurements, with a femtosecond (fs) Ti:sapphire laser source. In all cases, the output intensity of two-photon excited fluorescence was linearly dependent on the square of the input laser intensity, thereby confirming the TPA process. The results of some fluorophores having the better quantum yields are summarized in Table 4 and Fig. 3.

Table 4
Photophysical and two-photon absorption data for selected fluorophores **5**, **10**, **12**, **17**, **18**

Compound	λ_{abs} [nm]	ε	λ_{em} [nm]	Φ_F[a]	δ_{max} (GM)	δ_{max}/MW
5	375	64,597	449	0.60	126 (730 nm)	0.19
10	385	56,908	449	0.57	425 (730 nm)	0.67
12	367	27,992	460	0.49	143 (730 nm)	0.27
17	440	43,916	545	0.47	86 (830 nm)	0.22
18	455	65,407	547	0.52	146 (880 nm)	0.26

[a] 10%, harmane (0.1 M in H_2SO_4) was used as reference (Φ_F=0.58).

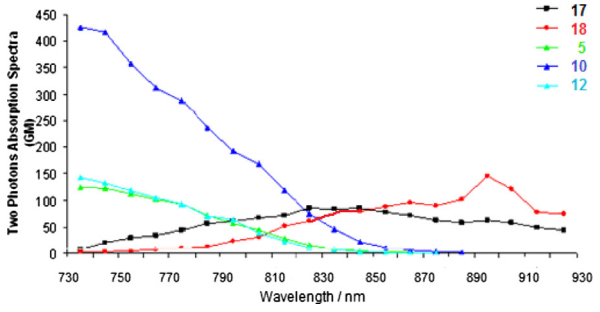


Fig. 3. Two-photon absorption spectra of selected fluorophores **5**, **10**, **12**, **17**, **18** determined by femtosecond TPIF measurements.

The two-branched or V-shaped 2-ethynyl-4,6-bis(arylvinyl)pyrimidines **17**–**18** with significant quantum yields present moderate two-photon absorption cross-sections δ_{max} reaching, respectively, 86 and 146 GM. The TPA performances of the compounds **5**, **10**, and **12** with a triphenylamine as central unit allow to observe that if the two-branched compound **12** and the three-branched compound **5**, bearing both a peripheral 6-methoxypyridazine moiety, have similar δ_{max} around 125–145 GM, replacement of a pyridazine ring with a pyrimidine one increases from one to threefold the cross-sections δ_{max} values, which reaches 425 GM for **10**. This result seems indicate that the nature of the peripheral diazine is more important than the number of branches. It is interesting to note that among the TPA performance the two-photon absorption/molecular weight ratio (δ/MW) is a relevant figure of merit. In this regard, compound **10** with a δ/MW ratio around 0.67 GM g^{-1} mol falls in the range of the very good chromophores reported so far, compared to values of 0.5–1.0 GM g^{-1} mol described for large-sized systems optimized for two-photon absorption.[27]

3. Conclusion

In this paper, we have described the synthesis of novel multipolar fluorophores with benzene or a triphenylamine core and electron-withdrawing diazine rings as peripheral group, these two parts are connected through ethynyl linker to extend the conjugation. Various two- and three-branched compounds have been obtained and their photophysical properties have been determined and compared with those of C_3 symmetrical compounds (AX_3) with

a pyrimidine core. All these compounds are fluorescent and those of C_3 symmetry with a core having a strong character of electron-withdrawing or electron releasing, such as pyrimidine or triphenylamine (AX_3, CY_3, and CZ_3) exhibit the better quantum yields. The TPA performances of some compounds with good quantum yields have been performed, the best result was obtained for the suitable photostable compound **10** (structure CZ_3) with a triphenylamine core and dimethylpyrimidines as peripheral groups. This compound with a moderate molecular weight exhibits an interesting cross-section (425 GM) in the NIR region with a high figure of merit (δ/MW ratio around 0.67 GM g^{-1} mol).

4. Experimental section

4.1. General methods

All chemicals were purchased from commercial sources and were used without further purification unless otherwise specified. Analytical thin layer chromatography was performed on silica gel plates (Merck® TLC Silica gel 60 F_{254}) and compounds were detected by irradiation with UV light (254 and 365 nm). Chromatographic purification of compounds was achieved with silica gel (mesh size 60–80 μm). IR spectra were recorded with a universal attenuated total reflectance (ATR) sampling accessory on a Perkin–Elmer FTIR Spectrum 100 spectrometer. Absorption bands are given in cm^{-1}. HRMS spectra (ESI^+) were recorded on a LC Waters Acquity coupled to a Waters LCT Premier XE instrument. Elemental analyses were performed on a Carlo Erba 1106 apparatus. Measurement accuracy is around ±0.4% on carbon. Melting points (°C) were measured on a Kofler hot-stage with a precision of 2° (±2 °C). The ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance spectrometer operating at 300 MHz and 75 MHz, respectively. The chemical shifts δ are reported in parts per million (ppm) relative to the residual solvent peak (7.26 and 77.16, respectively, for $CDCl_3$, 0.00 for $CFCl_3$). Data appear in the following order: chemical shifts in ppm, number of protons, multiplicity (s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet), coupling constant J in Hertz. Fluorescence spectroscopic studies were performed with a Varian Cary Eclipse spectrophotometer. Compounds were excited at their absorption maxima for recording the emission spectra; however different wavelengths were used to determine fluorescence quantum yields in cases where compounds and standards absorbed significantly. All solutions were measured with optical densities below 0.1. The TPA cross-sections in the range 790–950 nm were obtained by up-conversion fluorescence using a mode locked Ti:sapphire femtosecond laser (Tsunami Spectra-Physics) with pulse duration 100 fs and at a repetition rate of 82 MHz. The measurements were done at room temperature in DCM and at concentration of ca. $5\cdot10^{-6}$ M–10^{-5} M. The excitation beam (5 mm diameter) is focused with a lens (focal length 10 cm) at the middle of the fluorescence cell (10 mm). The fluorescence, collected at 90° to the excitation beam, was focused into an optical fiber (diameter 600 μm) connected to an Ocean Optics S2000 spectrometer. The incident beam intensity was adjusted to 50 mW in order to ensure an intensity-squared dependence of the fluorescence over the whole range. The detector integration time was fixed to 1 s. Comparison of the spectra was performed with the published Fluorescein and Rhodamine B two-photon absorption spectra.

*4.1.1. 1,3,5-Tris-[6-(3-methoxypyridazinyl)ethynyl]benzene (**1**).* To a mixture of 3-methoxy-6-(trimethylsilyl)ethynylpyridazine (0.185 g, 0.766 mmol), 1,3,5-triiodobenzene (0.100 g, 0.219 mmol), $Pd_2(dba)_3$ (0.020 g, 0.021 mmol), CuI (0.004 g, 0.021 mmol), PPh_3 (0.005 g, 0.021 mmol) under nitrogen atmosphere were added dry Et_3N (10 mL) and toluene (10 mL). The reaction mixture was cooled to 0 °C and TBAF (1 M in THF, 1.53 mL) was added dropwise and the reaction mixture was stirred for 10 min. The solution was heated to 50 °C for 48 h. The reaction was cooled, filtered through Celite® and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=2:1) to give the title compound **1** as a brown solid (0.055 g, 55%). Mp: >260 °C. IR (cm^{-1}, neat): 1400, 2952, 2219, 1582, 1538, 1466, 1423, 1403, 1335, 1296, 1166, 1133, 1098, 1010, 965, 873, 841, 759, 673; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 4.19 (s, 9H), 7.00 (d, J=9.3 Hz, 3H), 7.54 (d, J=9.3 Hz, 3H) 7.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 55.3, 87.3, 89.8, 116.8, 123.3, 132.6, 135.6, 143.3, 163.7; MS (TOF MS ESI+); m/z (rel int. %): ($M+H^+$) 475 (100), 516 ($M+H^+$+acetonitrile).

*4.1.2. 1,3,5-Tris-[6-(3-di-n-butylaminopyridazinyl)ethynyl]benzene (**2**).* According to the procedure described for **1**, a mixture of 3-*n*-dibutylamino-6-(trimethylsilyl)ethynylpyridazine (0.232 g, 0.766 mmol), 1,3,5-triiodobenzene (0.100 g, 0.219 mmol), and TBAF (1 M in THF, 1.53 mL) gave after purification by column chromatography on silica gel (petroleum ether/ethyl acetate=2:1) the title compound **2** as a brown solid (0.104 g, 62%). Mp: 60 °C. IR (cm^{-1}, neat): 2957, 2928, 2871, 2214, 1734, 1701, 1654, 1578, 1540, 1484, 1425, 1371, 1333, 1232, 1171, 1112, 1017, 960, 926, 878, 822, 733, 681; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.95 (t, J=7.4, 18H), 1.24–1.43 (m, 12H), 1.55–1.66 (m, 12H), 3.53 (t, J=7.6, 12H), 6.64 (d, J=9.4 Hz, 3H), 7.29 (d, J=9.4 Hz, 3H), 7.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 14.1, 20.3, 29.6, 48.9, 88.4, 88.8, 109.8, 123.7, 130.5, 134.5, 136.9, 156.7; HRMS: calcd for $C_{48}H_{64}N_9$ $[M+H]^+$ 766.5285; found 766.5295.

*4.1.3. 1,3,5-Tris-[2-(4,6-dimethylpyrimidinylyl)ethynyl]benzene (**3**).* A solution of 1,3,5-triiodobenzene (0.226 g, 0.497 mmol), 2-ethynyl-4,6-dimethylpyrimidine (0.229 g, 1.739 mmol), $Pd(PPh_3)_2Cl_2$ (0.034 g, 0.049 mmol), CuI (0.018 g, 0.097 mmol) in Et_3N (15 mL) was stirred at 90 °C for 24 h under nitrogen atmosphere, the TLC monitoring indicated the consumption of starting materials. The reaction mixture was cooled, filtered through Celite® and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOH was used for the first purification followed by a second one with ethyl acetate as eluent) to afford the title compound **3** as brown solid (0.097 g, 42%). Mp: 230 °C. IR (cm^{-1}, neat): 2962, 2923, 2900, 2172, 1949, 1738, 1587, 1535, 1441, 1346, 1251, 1176, 1036, 956, 943, 845, 788, 761, 704, 634, 619; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.52 (s, 18H), 7.01 (s, 3H), 7.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 24.0, 84.3, 89.4, 119.5, 122.8, 136.6, 152.2, 167.3; HRMS: calcd for $C_{30}H_{25}N_6$ $[M+H]^+$ 469.2141; found 469.2144.

*4.1.4. Tris-(4-iodophenyl)amine(**4**).* A mixture of triphenylamine (1 g, 0.004 mmol), HgO (4.06 g, 0.019 mmol) and I_2 (5.08 g, 0.020 mmol) in EtOH (50 mL) was stirred overnight at room temperature. The solvent was removed, and the product was separated from mercuric salts with boiling toluene. The solution was filtered through the short column of Al_2O_3, and the product was precipitated from hot toluene with MeOH to afford the title compound **4** as white solid (2.33 g, 90%). Mp: 170 °C. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.53 (d, J=8.8 Hz, 6H), 6.81 (d, J=8.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 86.76, 126.12, 138.53, 146.59.[23]

*4.1.5. Tris-[4-(6-methoxypyridazin-3-yl)ethynylphenyl]amine (**5**).* A solution of tris-(4-iodophenyl)amine **4** (0.200 g, 0.321 mmol), 3-ethynyl-6-methoxypyridazine (0.150 g, 1.123 mmol), $Pd(PPh_3)_2Cl_2$ (0.017 g, 0.090 mmol), CuI (0.063 g, 0.090 mmol), PPh_3 (0.047 g, 0.180 mmol) in 30 mL of a mixture of 1/1 THF/Et_3N was stirred at 65 °C for 48 h. The reaction was cooled, filtered through Celite® and evaporated under reduced pressure. The crude product was

purified by column chromatography on silica gel (petroleum ether/ethyl acetate=1:2) to give the title compound **5** as a yellow solid (0.129 g, 63%). Mp: 223 °C. IR (cm^{-1}, neat): 3039, 2949, 2360, 2345, 2218, 1735, 1655, 1594, 1542, 1505, 1462, 1410, 1338, 1318, 1288, 1180, 1153, 1110, 999, 833, 731, 682, 635, 531, 485, 420; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 4.17 (s, 9H), 6.96 (d, J=9.2 Hz, 3H), 7.11 (d, J=8.7 Hz, 6H), 7.51 (d, J=9.2 Hz, 3H), 7.53 (d, J=8.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 55.2, 85.9, 92.0, 116.7, 116.9, 124.2, 132.4, 133.4, 143.8, 147.3, 163.4; HRMS: calcd for $C_{39}H_{28}N_7O_3$ $[M+H]^+$ 642.2254; found 642.2263.

*4.1.6. Tris-[4-(6-N,N-dibutylaminopyridazin-3-yl)ethynylphenyl] amine (**6**).* According to the procedure described for **5**, a mixture of tris-(4-iodophenyl)amine **4** (0.200 g, 0.321 mmol) with the 6-*n*-dibutylamino-3-ethynylpyridazine (0.260 g, 1.123 mmol) gave after purification by column chromatography on silica gel (petroleum ether/ethyl acetate=1:2) the title compound **6** as a dark yellow solid (0.203 g, 68%). Mp: 68 °C. IR (cm^{-1}, neat): 3308, 3660, 3469, 3188, 3040, 2956, 2928, 2870, 2343, 2211, 1596, 1542, 1504, 1424, 1372, 1318, 1288, 1270, 1230, 1168, 1112, 1015, 925, 830, 767, 724, 695, 646, 540, 409; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.95 (t, J=7.3 Hz, 18H), 1.31–1.40 (m, 12H), 1.57–1.63 (m, 12H), 3.52 (t, J=7.6 Hz, 12H), 6.63 (d, J=9.6 Hz, 3H), 7.06 (d, J=8.6 Hz, 6H), 7.27 (d, J=9.4 Hz, 3H), 7.46 (d, J=8.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 14.1, 20.4, 29.7, 48.9, 87.1, 90.5, 109.8, 117.6, 124.1, 130.2, 133.1, 137.5, 146.9, 156.5; HRMS: calcd for $C_{60}H_{73}N_{10}$ $[M+H]^+$ 933.6020; found 933.6021.

*4.1.7. N,N′-Bis-[4-(6-phenylpyridazin-3-yl)ethynylphenyl]-4-iodoaniline (**7**).* According to the procedure described for **5**, a mixture of tris-(4-iodophenyl)amine **4** (0.200 g, 0.321 mmol) with the 3-ethynyl-6-phenylpyridazine (0.202 g, 1.123 mmol) gave after purification by column chromatography on silica gel (petroleum ether/ethyl acetate=2:1) the title compound **7** as a yellow solid (0.0074 g, 32%). Mp: 216 °C. IR (cm^{-1}, neat): 3052, 2921, 2849, 2218, 1597, 1579, 1541, 1450, 1400, 1316, 1287, 1269, 1163, 1113, 1004, 919, 856, 825, 788, 749, 691, 547, 509; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 6.92 (d, J=8.9 Hz, 2H), 7.10 (d, J=8.9 Hz, 4H), 7.52–7.55 (m, 6H), 7.55 (d, J=8.9 Hz, 4H), 7.63 (d, J=8.9 Hz, 2H), 7.67 (d, J=8.9 Hz, 2H), 7.85 (d, J=8.9 Hz, 2H), 8.10–8.14 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 86.3, 88.2, 94.3, 116.3, 123.1, 123.6, 127.3, 127.5, 129.2, 130.0, 130.4, 136.0, 138.9, 146.3, 146.8, 147.7, 157.0; HRMS: calcd for $C_{42}H_{27}IN_5$ $[M+H]^+$ 728.1311; found 728.1313.

*4.1.8. N,N′-Bis-[4-(6-methoxypyridazin-3-yl)ethynylphenyl]-4-iodoaniline (**8**).* According to the procedure described for **1**, a mixture 3-methoxy-6-(trimethylsilyl)ethynylpyridazine (0.097 g, 0.470 mmol), tris-(4-iodophenyl)amine (0.136 g, 0.219 mmol), and TBAF (1 M in THF, 0.94 mL) gave after purification by column chromatography on silica gel (petroleum ether/ethyl acetate=1:2) compound **8** as a yellow solid (0.040 g, 29%). Mp: 64 °C. IR (cm^{-1}, neat): 2942, 2217, 1719, 1596, 1542, 1505, 1483, 1460, 1409, 1339, 1317, 1286, 1178, 1153, 1100, 1061, 1006, 909, 835, 722, 638, 537, 512; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 4.17 (s, 6H), 6.89 (d, J=8.9 Hz, 2H), 6.95 (d, J=9.0 Hz, 2H), 7.06 (d, J=8.7 Hz, 4H), 7.48 (d, J=8.7 Hz, 4H), 7.50 (d, J=9.2 Hz, 2H), 7.60 (d, J=8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 55.2, 85.8, 87.9, 92.2, 116.5, 116.7, 123.6, 127.4, 132.4, 133.4, 138.8, 143.9, 146.4, 147.5, 163.5; HRMS: calcd for $C_{32}H_{23}IN_5O_2$ $[M+H]^+$ 636.0897; found 636.0878.

*4.1.9. Tris-[4-(2-trimethylsilylethynyl)phenyl]amine (**9**).* See Ref. 24.

*4.1.10. Tris-[4-{2-(4,6-dimethylpyrimidin-2-yl}ethynylphenyl)]amine (**10**).* To a solution of compound **9** (1 g, 1.873 mmol), 2-iodo-4,6-dimethylpyrimidine (1.534 g, 6.550 mmol), $Pd(PPh_3)_4$ (0.211 g, 0.187 mmol) and CuI (0.035 g, 0.187 mmol) in 30 mL of a mixture of 1/1 THF/Et_3N cooled at 0 °C, 11.2 mL of TBAF (1 M in THF, 11.2 mmol) were introduced dropwise under nitrogen atmosphere and the reaction mixture was stirred for 10 min. The solution was heated to 50 °C for 24 h. The reaction was cooled, filtered through Celite® and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=1:4) to give the title compound **10** as a yellow solid (0.850 g, 71%). Mp: >260 °C. IR (cm^{-1}, neat): 2203, 1701, 1653, 1581, 1529, 1503, 1437, 1370, 1343, 1314, 1274, 1220, 1175, 1108, 1028, 958, 847, 830, 785, 773, 730, 627; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.48 (s, 18H), 6.94 (s, 1H), 7.05 (d, J=8.7 Hz, 6H), 7.56 (d, J=8.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 24.1, 87.1, 88.5, 116.5, 119.0, 124.2, 134.2, 147.5, 152.8, 167.2; MS (TOF MS ESI+); m/z (rel int. %): ($M+H^+$) 636 (90).

*4.1.11. Tris-[4-(6-phenylpyridazin-3-yl)ethynylphenyl]amine (**11**).* To a mixture of 3-iodo-6-phenylpyridazine (0.277 g, 0.980 mmol), compound **9** (0.150 g, 0.280 mmol), $Pd_2(dba)_3$ (0.025 g, 0.028 mmol), CuI (0.005 g, 0.028 mmol), PPh_3 (0.007 g, 0.028 mmol) under nitrogen atmosphere were added dry Et_3N (10 mL), and toluene (10 mL). The reaction mixture was cooled to 0 °C and TBAF (1 M in THF, 1.68 mL) was added dropwise and the reaction mixture was stirred for 10 min. The solution was heated to 50 °C for 24 h. The reaction was cooled, filtered through Celite® and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=3:1) to give the title compound **11** as a yellow solid (0.104 g, 48%). Mp: 216 °C. IR (cm^{-1}, neat): 2216, 1773, 1735, 1701, 1648, 1595, 1570, 1535, 1503, 1449, 1400, 1316, 1288, 1268, 1179, 1160, 1108, 1032, 1011, 830, 787, 763, 747, 690; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.15 (d, J=8.4 Hz, 6H), 7.58 (d, J=8.4 Hz, 6H), 7.51–7.54 (m, 9H), 7.68 (d, J=8.7 Hz, 3H), 7.85 (d, J=9.0 Hz, 3H), 8.11 (d, J=6.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 86.5, 94.2, 116.8, 123.1, 124.3, 127.3, 129.2, 130.0, 130.4, 133.7, 136.0, 146.8, 147.5, 157.0; HRMS: calcd for $C_{54}H_{34}N_7$ $[M+H]^+$ 780.2871; found 780.2876.

*4.1.12. 4-Ethynyl-N,N-bis[4-{(6-methoxypyridazin-3-yl)ethynyl}phenyl]aniline (**12**). First step*: In a 50 L two necked round bottom flask, compound **8** (0.410 g, 0.645 mmol), $Pd(PPh_3)_2Cl_2$ (0.013 g, 0.019 mmol, 3%), CuI (0.007 g, 0.038 mmol, 6%), dry toluene (15 mL), and trimethylsilylacetylene (0.17 mL, 1.290 mmol, 2 equiv) were introduced under dry nitrogen atmosphere. Dry Et_3N (15 mL) was added and the mixture was heated at 60 °C for 48 h. The reaction mixture was cooled, filtered through Celite® and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=2:1) to afford the title compound as a brown solid (0.296 g, 76%). Mp: 146 °C. IR (cm^{-1}, neat): 2950, 2218, 2152, 1596, 1543, 1504, 1461, 1409, 1339, 1319, 1286, 1175, 1151, 1104, 1008, 912, 864, 839, 759, 725, 656; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.25 (s, 9H), 4.17 (s, 6H), 6.95 (d, J=9 Hz, 2H), 7.06 (d, J=8.7 Hz, 2H), 7.07 (d, J=8.7 Hz, 4H), 7.40 (d, J=8.7 Hz, 2H), 7.50 (d, J=8.4 Hz, 2H), 7.60 (d, J=8.7 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 0.0, 55.0, 85.7, 92.1, 94.3, 104.7, 116.4, 116.6, 118.5, 123.7, 124.4, 132.2, 133.3, 143.7, 146.4, 147.3, 163.3.

Second step: To a solution of the compound described above (0.170 g, 0.280 mmol) in THF (10 mL) cooled at 0 °C, TBAF (1 M in THF, 0.56 mL) was added dropwise. The reaction mixture was stirred for 10 min at 0 °C and for 3 h at room temperature. Then water (10 mL) was introduced, and the crude mixture was extracted with dichloromethane (2×15 mL). The organic layer was dried with $MgSO_4$, filtered and evaporated. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=2:1) to afford the title compound **12** as a brown solid (0.120 g, 80%). Mp: 146 °C. IR (cm^{-1}, neat): 2922, 2850, 2355, 2218,

2095, 1596, 1539, 1504, 1461, 1410, 1339, 1318, 1288, 1173, 1152, 1106, 1008, 833, 726; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.08 (s, 1H), 4.17 (s, 6H), 6.95 (d, J=9.0 Hz, 2H), 7.06 (d, J=8.7 Hz, 2H), 7.08 (d, J=8.4 Hz, 4H), 7.42 (d, J=8.4 Hz, 2H), 7.48–7.51 (6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 55.1, 83.3, 85.7, 92.0, 116.5, 116.6, 117.4, 123.8, 124.4, 132.3, 133.3, 133.5, 143.7, 146.7, 147.3, 163.3; HRMS: calcd for $C_{34}H_{24}N_5O_2$ $[M+H]^+$ 534.1930; found 534.1926.

*4.1.13. Bis-{[N,N-bis-[4-{2-(6-methoxypyridazin-3-yl)ethynyl}phenyl]-N-(4-ethynylphenyl)} (**13**).* In a 25 mL two necked round bottom flask tris(4-iodophenyl)amine **4** (0.040 g, 0.064 mmol), compound **12** (0.120 g, 0.224 mmol, 3.5 equiv), $Pd(PPh_3)_2Cl_2$ (0.004 g, 0.005 mmol, 9%), CuI (0.002 g, 0.011 mmol, 18%), dry toluene (8 mL), and dry Et_3N (8 mL) were added and the mixture was heated at 60 °C for 48 h. The reaction mixture was cooled, filtered through Celite® and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 1.5:1, first purification; petroleum ether/ethyl acetate 1:1, second purification) to afford the title compound as dark yellow solid (0.029 g, 43%). Mp>260 °C. IR (cm^{-1}, neat): 2213, 1593, 1541, 1500, 1460, 1408, 1335, 1317, 1287, 1171, 1152, 1100, 1006, 832, 725; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 4.17 (s, 12H), 6.95 (d, J=9 Hz, 4H), 7.06 (d, J=8.7 Hz, 4H), 7.10 (d, J=8.7 Hz, 8H), 7.44 (d, J=8.7 Hz, 4H), 7.50 (d, J=9.3 Hz, 4H), 7.52 (d, J=8.7 Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 55.2, 74.3, 81.8, 86.0, 92.1, 116.7, 117.0, 124.1, 124.3, 132.4, 133.5, 134.0, 143.9, 147.3, 163.5; HRMS: calcd for $C_{68}H_{45}N_{10}O_4$ $[M+H]^+$ 1065.3625; found 1065.3610.

*4.1.14. (E,E)-4,6-Bis-(4-dimethylaminostyryl)-2-iodopyrimidine (**14**).* At room temperature, *t*-BuOK (0.479 g, 4.27 mmol) was placed into a dry mortar and milled to very small, then 2-iodo-4,6-dimethylpyrimidine (0.200 g, 0.854 mmol) and 4-dimethyl-aminobenzaldehyde (0.438 g, 1.878 mmol) were added and mixed. The mixture was milled vigorously for about 2 h. The mixture became sticky and then continuously milled for 10 min. After completion (monitored by TLC), the mixture was dispersed in 20 mL methanol. The residual solid was filtered and recrystallized from anhydrous dichloromethane/methanol (10:1) to afford the title compound **14** as a brown solid (0.240 g, 57%). Mp: 153 °C. IR (cm^{-1}, neat): 2896, 2806, 2362, 1602, 1550, 1456, 1442, 1432, 1411, 1364, 1300, 1277, 1250, 1233, 1207, 1188, 1145, 1062, 971, 946, 891, 839, 809, 737, 668, 598, 520; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.9 (s, 12H), 6.78 (d, J=15.6 Hz, 2H), 6.88 (d, J=8.9 Hz, 4H), 7.13 (s, 1H), 7.52 (d, J=8.9 Hz, 4H), 7.78 (d, J=15.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 40.3, 112.0, 113.7, 119.8, 123.4, 129.5, 130.8, 138.5, 151.3, 165.0; HRMS: calcd for $C_{24}H_{26}N_4I$ $[M+H]^+$ 497.1202; found 497.1183.

*4.1.15. (E,E)-4,6-Bis-(4-n-dibutylaminostyryl)-2-iodopyrimidine (**15**).* At room temperature, *t*-BuOK (0.479 g, 4.27 mmol) was placed into a dry mortar and milled to very small, then 2-iodo-4,6-dimethylpyrimidine (0.200 g, 0.854 mmol) and 4-*n*-dibutyl-aminobenzaldehyde (0.438 g, 1.878 mmol) were added and mixed. The mixture was milled vigorously for about 2 h. The mixture became sticky and then continuously milled for 10 min. After completion (monitored by TLC), the mixture was dispersed in 20 mL methanol. The residual solid was filtered and purified by column chromatography on silica gel (petroleum ether/ethyl acetate=7:1) to afford the title compound **15** as a brown solid (0.210 g, 37%). Mp: 50 °C. IR (cm^{-1}, neat): 2955, 2942, 2868, 2360, 1601, 1551, 1520, 1466, 1431, 1401, 1366, 1276, 1223, 1205, 1181, 1144, 969, 925, 890, 838, 806, 535; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.97 (t, J=7.3 Hz, 12H), 1.31–1.43 (m, 8H), 1.57–1.62 (m, 8H), 3.31 (t, J=7.6 Hz, 8H), 6.62 (d, J=8.9 Hz, 4H), 6.67 (d, J=15.8 Hz, 2H), 7.08 (s, 1H), 7.45 (d, J=8.9 Hz, 4H), 7.73 (d, J=15.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 14.1, 20.4, 29.5, 50.8, 111.4, 113.5, 119.1, 122.4, 129.7, 130.8, 138.5, 149.3, 165.0; $C_{36}H_{49}IN_4$ (664.30): calcd. C 65.05, H 7.43, N 8.43; found C 64.97, H 7.58, N 8.86.

*4.1.16. (E,E)-4,6-Bis-(4-methoxystyryl)-2-iodopyrimidine (**16**).* According to the procedure described for **15**, using 4-methoxybenzaldehyde (0.255 g, 1.878 mmol) gave after purification by column chromatography on silica gel (petroleum ether/ethyl acetate=3:1) the title compound **16** as a yellow solid (0.147 g, 37%). Mp: 168 °C. IR (cm^{-1}, neat): 2930, 2835, 1626, 1603, 1600, 1544, 1477, 1422, 1376, 1303, 1249, 1218, 1175, 1154, 1109, 1027, 969, 891, 822, 769, 595, 537, 521; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.85 (s, 6H), 6.80 (d, J=15.8 Hz, 2H), 6.93 (d, J=8.7 Hz, 4H), 7.15 (s, 1H), 7.55 (d, J=8.7 Hz, 4H), 7.82 (d, J=15.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 55.5, 114.5, 114.7, 122.3, 128.2, 129.5, 138.1, 161.0, 164.8; HRMS: calcd for $C_{22}H_{20}IN_2O_2$ $[M+H]^+$ 471.0570; found 471.0569.

*4.1.17. (E,E)-4,6-Bis-(4-dimethylaminostyryl)-2-ethynylpyrimidine (**17**). First step*: In a two necked round bottom flask, compound **14** (0.200 g, 0.403 mmol), PPh_3 (0.012 g, 0.048 mmol), CuI (0.004 g, 0.024 mmol), $Pd(PPh_3)_2Cl_2$ (0.016 g, 0.024 mmol) were dissolved in dry THF (6.25 mL) under nitrogen atmosphere. Trimethylsilylacetylene (0.11 mL, 0.806 mmol) followed by dry Et_3N (10 mL) were introduced via syringe. The resulting mixture was heated at 50 °C for 48 h and then filtered through Celite® and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=2:1) to give the title product as a brown solid (0.170 g, 90%). Mp>260 °C. IR (cm^{-1}, neat): 1605, 1557, 1525, 1430, 1432, 1354, 1326, 1282, 1249, 1220, 1184, 1160, 1061, 1015, 979, 946, 845, 808, 758, 670, 520; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.32 (s, 9H), 3.03 (s, 12H), 6.71 (d, J=8.7 Hz, 4H), 6.85 (d, J=15.9 Hz, 2H), 7.16 (s, 1H), 7.50 (d, J=8.7 Hz, 4H), 7.80 (d, J=16.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): −0.1, 40.3, 91.8, 103.7, 113.3, 120.8, 123.8, 137.8, 151.3, 152.2, 163.6; MS (ESI); *m*/*z* (rel int. %): (M^+) 467 (100), 391 (30), 247 (28), 178 (18), 157 (40).

Second step: To a solution of the compound described above (0.150 g, 0.321 mmol) in THF (10 mL) cooled at 0 °C, TBAF (1 M in THF, 0.64 mL) was added dropwise. The reaction mixture was stirred for 10 min at 0 °C and for 3 h at room temperature. Then water (10 mL) was introduced, and the crude mixture was extracted with dichloromethane (2×15 mL). The organic layer was dried with $MgSO_4$, filtered and evaporated. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=2:1) to afford the title compound **17** as a brown solid (0.114 g, 90%). Mp: 212 °C. IR (cm^{-1}, neat): 2104, 1603, 1553, 1483, 1431, 1360, 1297, 1229, 1183, 1147, 1061, 970, 945, 883, 835, 807, 724, 671, 639; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.03 (s, 12H), 3.07 (s, 1H), 6.71 (d, J=8.7 Hz, 4H), 6.84 (d, J=15.9 Hz, 2H), 7.14 (s, 1H), 7.51 (d, J=8.7 Hz, 4H), 7.84 (d, J=15.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 40.3, 73.8, 83.1, 112.1, 114.0, 120.6, 123.8, 129.4, 137.9, 151.3, 151.8, 163.7; MS (ESI); *m*/*z* (rel int. %): (M^++H) 395 (100), 316 (10), 264 (24), 196 (6).

*4.1.18. (E,E)-4,6-Bis-(4-n-dibutylaminostyryl)-2-ethynylpyrimidine (**18**). First step*: According to the procedure described for **17**, compound **15** (0.200 g, 0.277 mmol), PPh_3 (0.008 g, 0.033 mmol), CuI (0.003 g, 0.016 mmol), $Pd(PPh_3)_2Cl_2$ (0.011 g, 0.016 mmol) dry THF (6.25 mL), and trimethylsilylacetylene (0.07 mL, 0.554 mmol) gave after purification by column chromatography on silica gel (petroleum ether/ethyl acetate=9:1) the title product as a dark green solid (0.150 g, 86%). Mp<50 °C. IR (cm^{-1}, neat): 3038, 2956, 2932, 2872, 1603, 1560, 1521, 1492, 1460, 1431, 1400, 1353, 1292, 1250, 1222, 1183, 1145, 1110, 1018, 976, 926, 844, 807, 759, 700, 671, 533; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.32 (s, 9H), 0.97 (t, J=7.4 Hz, 12H), 1.38–1.35 (m, 4H), 1.59–1.56 (m, 4H), 3.31 (t, J=7.4 Hz, 4H),

6.62 (d, J=8.6 Hz, 4H), 6.81 (d, J=16 Hz, 2H), 7.14 (s, 1H), 7.46 (d, J=8.7 Hz, 4H), 7.78 (d, J=15.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): −0.1, 14.1, 20.4, 29.6, 50.9, 91.6, 103.7, 111.5, 113.1, 120.2, 122.8, 129.5, 137.8, 149.2, 152.2, 163.7; MS (ESI); m/z (rel int. %): (M^+) 635 (100).

Second step: According to the procedure described for **17**, deprotection of the silylated compound reported above (0.150 g, 0.236 mmol) is achieved with TBAF (1 M in THF, 0.46 mL) and gave after purification by column chromatography on silica gel (petroleum ether/ethyl acetate=7:1) the title compound **18** as a dark green solid (0.128 g, 97%). Mp: 55 °C. IR (cm^{-1}, neat): 3038, 2956, 2932, 2872, 1603, 1560, 1521, 1492, 1460, 1431, 1400, 1353, 1292, 1250, 1222, 1183, 1145, 1110, 1018, 976, 926, 844, 807, 759, 700, 671, 533; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.97 (t, J=7.3 Hz, 12H), 1.33–1.41 (m, 8H), 1.56–1.59 (m, 8H), 3.06 (s, 1H), 3.31 (t, J=7.6 Hz, 8H), 6.62 (d, J=8.7 Hz, 4H), 6.79 (d, J=15.8 Hz, 2H), 7.12 (s, 1H), 7.46 (d, J=8.8 Hz, 4H), 7.81 (d, J=15.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 14.1, 20.4, 29.5, 50.8, 73.6, 83.1, 111.4, 113.8, 119.8, 122.7, 129.5, 137.8, 149.2, 151.6, 163.6; MS (ESI); m/z (rel int. %): (M^++H) 563 (100), 507 (50), 451 (20), 234 (2).

*4.1.19. (E,E)-4,6-Bis-(4-methoxystyryl)-2-ethynylpyrimidine (**19**). First step*: According to the procedure described for **17**, compound **16** (0.200 g, 0.425 mmol), PPh_3 (0.013 g, 0.051 mmol), CuI (0.004 g, 0.025 mmol), $Pd(PPh_3)_2Cl_2$ (0.017 g, 0.016 mmol) dry THF (6.25 mL), and trimethylsilylacetylene (0.12 mL, 0.850 mmol, 2 equiv) gave after purification by column chromatography on silica gel (petroleum ether/ethyl acetate 2:1) the title product as a yellow solid (0.140 g, 77%). Mp: 98 °C. IR (cm^{-1}, neat): 2956, 2835, 2357, 1629, 1604, 1563, 1511, 1463, 1422, 1349, 1303, 1250, 1172, 1153, 1111, 1030, 975, 845, 821, 759, 534; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.33 (s, 9H), 3.85 (s, 6H), 6.96–6.90 (m, 6H), 7.20 (s, 1H), 7.56 (d, J=8.7 Hz, 4H), 7.86 (d, J=16.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): −0.2, 55.5, 92.5, 103.4, 114.1, 114.5, 123.3, 128.5, 137.4, 152.4, 160.9, 163.5; MS (ESI); m/z (rel int. %): (M^+) 441 (100), 379 (12), 279 (18).

Second step: According to the procedure described for **17**, deprotection of the silylated compound reported above (0.150 g, 0.340 mmol) is achieved with TBAF (1 M in THF, 0.68 mL) and gave after purification by column chromatography on silica gel (petroleum ether/ethyl acetate=7:1) the title compound **19** as a yellow solid (0.125 g, conversion 100%). Mp: 235 °C. IR (cm^{-1}, neat): 3270, 2930, 2834, 2117, 1625, 1603, 1564, 1511, 1455, 1436, 1421, 1374, 1346, 1311, 1283, 1249, 1174, 1151, 1110, 1027, 973, 891, 845, 826, 806, 773, 723, 673; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.11 (s, 1H), 3.85 (s, 6H), 6.92 (d, J=16.1 Hz, 2H), 6.93 (d, J=8.7 Hz, 4H), 7.19 (s, 1H), 7.56 (d, J=8.7 Hz, 4H), 7.89 (d, J=16.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 55.5, 74.4, 82.8, 114.5, 114.9, 123.0, 128.5, 129.4, 137.5, 151.8, 160.9, 163.5; MS (TOF MS ESI+); m/z (rel int. %): (M+H^+) 369 (100).

*4.1.20. N,N-Bis-(4-iodophenyl)-4-[4-bis-(E,E)-{4,6-(dimethylaminostyryl)pyrimidin-2-yl}ethynyl]aniline (**20**).* A solution of tris-(4-iodophenyl)amine **4** (0.112 g, 0.181 mmol), compound **17** (0.250 g, 0.633 mmol), $PdCl_2(PPh_3)_2$ (0.021 g, 0.030 mmol), CuI (0.005 g, 0.030 mmol) in a mixture of dry toluene (20 mL), and Et_3N (5 mL) was stirred at 40 °C for 72 h under nitrogen atmosphere. The TLC monitoring indicated no significant evolution of the reaction. The reaction mixture was cooled, filtered through Celite® and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=1.5:1) to give the title compound **20** as a brown solid (0.030 g, 19%). Mp: >260 °C. IR (cm^{-1}, neat): 2918, 2798, 2364, 2210, 1718, 1701, 1685, 1676, 1648, 1604, 1551, 1483, 1432, 1357, 1312, 1285, 1263, 1179, 1148, 1056, 1003, 970, 946, 883, 810, 744, 720, 692; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.03 (s, 12H), 6.71 (d, J=8.9 Hz, 4H), 6.86 (d, J=8.7 Hz, 4H), 6.87 (d, J=15.8 Hz, 2H), 7.00 (d, J=8.5 Hz, 2H), 7.16 (s, 1H), 7.52 (d, J=8.7 Hz, 4H), 7.56–7.59 (6H), 7.83 (d, J=15.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 40.4, 86.2, 87.3, 89.2, 112.2, 112.9, 116.0, 121.0, 122.6, 123.9, 126.9, 129.3, 134.1, 137.7, 138.7, 146.5, 147.6, 151.3, 153.1, 163.7; HRMS: calcd for $C_{44}H_{38}I_2N_5$ $[M+H]^+$ 890.1217; found 890.1224.

*4.1.21. N,N-Bis-(4-iodophenyl)-4-[4-bis-(E,E)-{4,6-(dibutylaminostyryl)pyrimidin-2-yl}ethynyl]aniline (**21**).* A solution of tris-(4-iodophenyl)amine **4** (0.110 g, 0.177 mmol), compound **18** (0.350 g, 0.621 mmol), $PdCl_2(PPh_3)_2$ (0.011 g, 0.016 mmol), CuI (0.006 g, 0.032 mmol) in a mixture of dry THF (15 mL) and Et_3N (5 mL) was stirred at 60 °C for 72 h under nitrogen atmosphere. The TLC monitoring indicated no significant evolution of the reaction. The reaction mixture was cooled, filtered through Celite® and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=6:1 was used for the first purification followed by a second one with petroleum ether/ethyl acetate=7:1) to give the title compound **21** as a dark green solid (0.060 g, 32%). Mp: 63 °C. IR (cm^{-1}, neat): 3038, 2956, 2932, 2872, 1603, 1560, 1521, 1492, 1460, 1431, 1400, 1353, 1292, 1250, 1222, 1183, 1145, 1110, 1018, 976, 926, 844, 807, 759, 700, 671, 533; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.97 (t, J=7.3 Hz, 12H), 1.33–1.41 (m, 8H), 1.56–1.59 (m, 8H), 3.31 (t, J=7.5 Hz, 8H), 6.63 (d, J=8.9 Hz, 4H), 6.83 (d, J=15.3 Hz, 2H), 6.87 (d, J=8.7 Hz, 4H), 7.00 (d, J=8.9 Hz, 2H), 7.13 (s, 1H), 7.47 (d, J=8.9 Hz, 4H), 7.58 (d, J=8.7 Hz, 6H), 7.80 (d, J=15.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 14.1, 20.4, 29.5, 50.8, 85.9, 89.1, 112.4, 112.6, 116.0, 121.0, 122.6, 129.1, 129.5, 134.1, 137.8, 138.7, 146.5, 147.8, 149.2, 153.1, 163.6; HRMS: calcd for $C_{56}H_{62}I_2N_5$ $[M+H]^+$ 1058.3095; found 1058.3124.

*4.1.22. Tris[4-(2-{4,6-bis[4-(dimethylamino)styryl]pyrimidin-2-yl}ethynyl)phenyl]amine (**22**).* A stirred solution of compound **11** (0.100 g, 0.157 mmol), 4-dimethylaminobenzaldehyde (0.211 g, 1.413 mmol), t-BuOK (0.158 g, 1.413 mmol) in THF (30 mL) was heated at 60 °C for 1 h under microwave. The reaction mixture was cooled and evaporated under reduced pressure. Then H_2O was added, and the crude mixture was extracted with DCM (4×10 mL). The organic layer was dried with $MgSO_4$, filtered, and evaporated. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=1:1 was used for the first purification followed by a second one with ethyl acetate) to give the title compound **22** as a brown solid (0.030 g, 14%). Mp: >260 °C. IR (cm^{-1}, neat): 2209, 1617, 1601, 1560, 1556, 1523, 1508, 1500, 1364, 1321, 1273, 1177, 1114, 975, 883, 814; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.03 (s, 36H), 6.72 (d, J=9.2 Hz, 12H), 6.89 (d, J=15.9 Hz, 6H), 7.14 (d, J=8.9 Hz, 6H), 7.16 (s, 3H), 7.53 (d, J=8.9 Hz, 12H), 7.66 (d, J=8.7 Hz, 6H), 7.85 (d, J=16.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 40.4, 86.2, 89.3, 112.2, 112.3, 116.9, 121.0, 124.0, 124.2, 129.4, 134.2, 137.8, 147.5, 151.3, 153.2, 163.7.

*4.1.23. Tris[4-(2-{4,6-bis[4-(methoxy)styryl]pyrimidin-2-yl}ethynyl)phenyl]amine (**23**).* A stirred solution of compound **11** (0.100 g, 0.157 mmol), 4-methoxybenzaldehyde (0.192 g, 1.413 mmol), t-BuOK (0.158 g, 1.413 mmol) in THF (30 mL) was heated at 60 °C for 1 h under microwave. The reaction mixture was cooled and evaporated under reduced pressure. Then H_2O was added, and the crude mixture was extracted with DCM (4×10 mL). The organic layer was dried with $MgSO_4$, filtered, and evaporated. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=1:4 was used for the first purification followed by a second one with DCM to give the title compound **23** as a dark yellow solid (0.060 g, 29%). Mp: 235 °C. IR (cm^{-1}, neat): 2364, 2207, 1634, 1603, 1563, 1554, 1511, 1504, 1456, 1422, 1368, 1317, 1250, 1172, 1104, 1029, 968, 818, 763, 724; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):

3.81 (s, 18H), 6.93 (d, J=8.7 Hz, 12H), 6.96 (d, J=16.2 Hz, 6H), 7.14 (d, J=8.7 Hz, 6H), 7.18 (s, 3H), 7.57 (d, J=8.7 Hz, 12H), 7.66 (d, J=8.7 Hz, 6H), 7.88 (d, J=15.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 55.4, 86.6, 89.2, 113.8, 114.4, 116.7, 123.4, 124.1, 128.6, 129.4, 134.2, 137.2, 147.5, 153.1, 160.8, 163.5.

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