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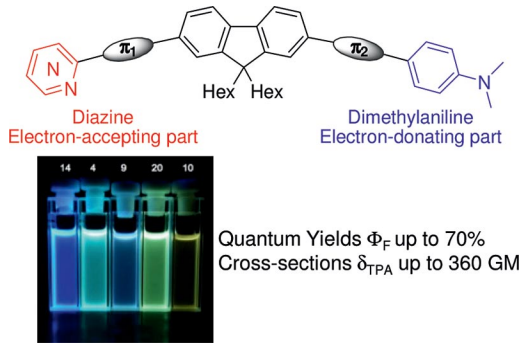
Push–Pull Chromophores



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We report, herein, the synthesis of new push–pull chromophores that incorporate a diazine ring as the electron-withdrawing part and an *N*,*N*-dimethylaniline moiety as the electron-donating part. Both of which are connected to a fluorene core. The length of the conjugated backbone was increased by incorporating ethynyl linkers and triazole rings on the both sides of the fluorene. The optical and two-photon absorption (TPA) properties were investigated, which exhibitied high quantum yields (up to 70%), significant Stokes shifts, and good TPA cross-sections.

Introduction

Over the past two decades, there has been considerable interest in the synthesis and characterization of π-conjugated compounds because of their applications to a wide range of electronic and optoelectronic devices. Indeed, such compounds are used as liquid crystals,[1] components of light-emitting devices (OLEDs) for displays and lighting,[2] field-effect transistors (OFETs),[3] dye-sensitized solar cells,[4] and single molecular electronics.[5] Moreover, organic molecules with large delocalized π-electron systems are relevant to the display of important nonlinear optical (NLO) responses and have applications to photodynamic therapy, confocal microscopy, optical power limiting, and 3D data storage.[6] A crucial factor for exhibiting such properties is the presence and nature of electron-donating and -accepting groups. Push–pull molecules that are constituted of a dissymmetrical conjugated π-electron system that consists of an electron-donor and an electron-withdrawing substituent are one of the typical structures of second- and third-order nonlinear optical chromophores.[7]

Among the diazines, pyrimidine[8] and pyridazine[9] with their highly π-deficient aromatic character are good candidates for incorporation as an electron-withdrawing moiety into push–pull scaffolds that favor intramolecular charge transfer (ICT). Numerous pyrimidine derivatives have been described as highly fluorescent molecules,[10] second-order NLO chromophores,[11] and two-photon absorption (TPA) dyes.[12] Although less numerous, some structures that contain the pyridazine ring exhibit intense fluorescence[13] and NLO properties.[14]

Fluorene is a π-conjugated molecule of choice for incorporation into oligomers and polymers for NLO applications.[15] These fluorene-based compounds are of great interest, as their extended π-electron conjugation leads to high fluorescence efficiency. Another advantage of fluorene is related to the easy substitution at the 9-position by long alkyl chains, which increase its solubility.

Since the discovery of the Cu^{I}-catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC) by Sharpless[16] and Meldal,[17] many examples that incorporate the 1,2,3-triazole ring have been reported. This methodology known as "click chemistry" has been widely used for linking two moieties to lead to more elaborate structures. Otherwise, there are only few examples of the use of this triazole unit as a linker in the conjugation backbone of fluorescent and TPA compounds.[18] Recently, the intramolecular charge transfer in triazole bridge-linked fluorene derivatives has been investigated.[19] At about the same time, we reported the synthesis of push–triazole–pull fluorophores in which the triazole ring allows for better photoluminescence properties, in terms of both quantum yields and Stokes shifts, than a triple bond.[20] These spectral properties are essential for the detection of fluorescent probes.

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The goal of this work is to describe the synthesis of a series of new push–pull chromophores that contain a pyrimidine or pyridazine ring as the electron-attracting part and the *N*,*N*-dimethylaniline moiety as the electron-donating part. Both are connected to the fluorene core by various π-conjugated linkers (see Figure 1). The connection between the fluorene core and the external parts is achieved by the incorporation of ethynyl linkers or 1,2,3-triazole rings on both sides of the fluorene. The syntheses of these structures consist of Suzuki and Sonogashira cross-coupling reactions as well as a CuAAC reaction. Herein, we report the synthesis of a wide range of fluorophores by varying both the length and nature of the conjugated core as well as the electron-withdrawing moiety. The influence of these structural units on the photophysical properties was investigated.

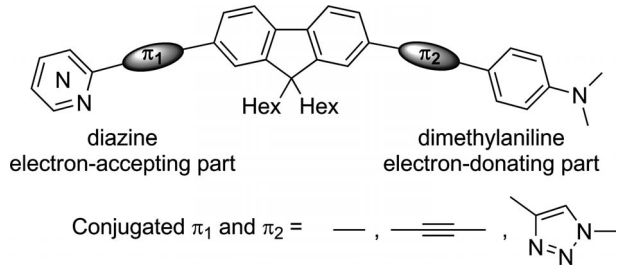


Figure 1. Design of push–pull diazinic fluorophores.

Results and Discussion

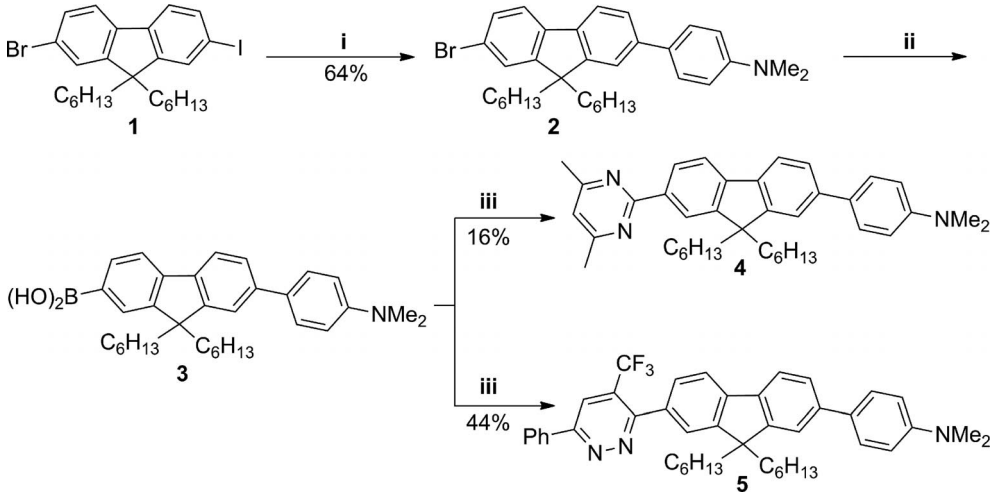
Synthesis

Four types of compounds (i.e., I–IV) were synthesized by starting from 2-bromo-9,9-dihexyl-7-iodo-9*H*-fluorene (**1**).[21] First, compounds of type I were prepared with 9,9-dihexyl-9*H*-fluorene as the central core that was linked by aryl–aryl bonds to a *N*,*N*-dimethylaniline group on one side and a diazine ring on the other side (see Scheme 1). The key steps of this synthetic route involved two successive palladium-catalyzed Suzuki cross-coupling reactions.[22]

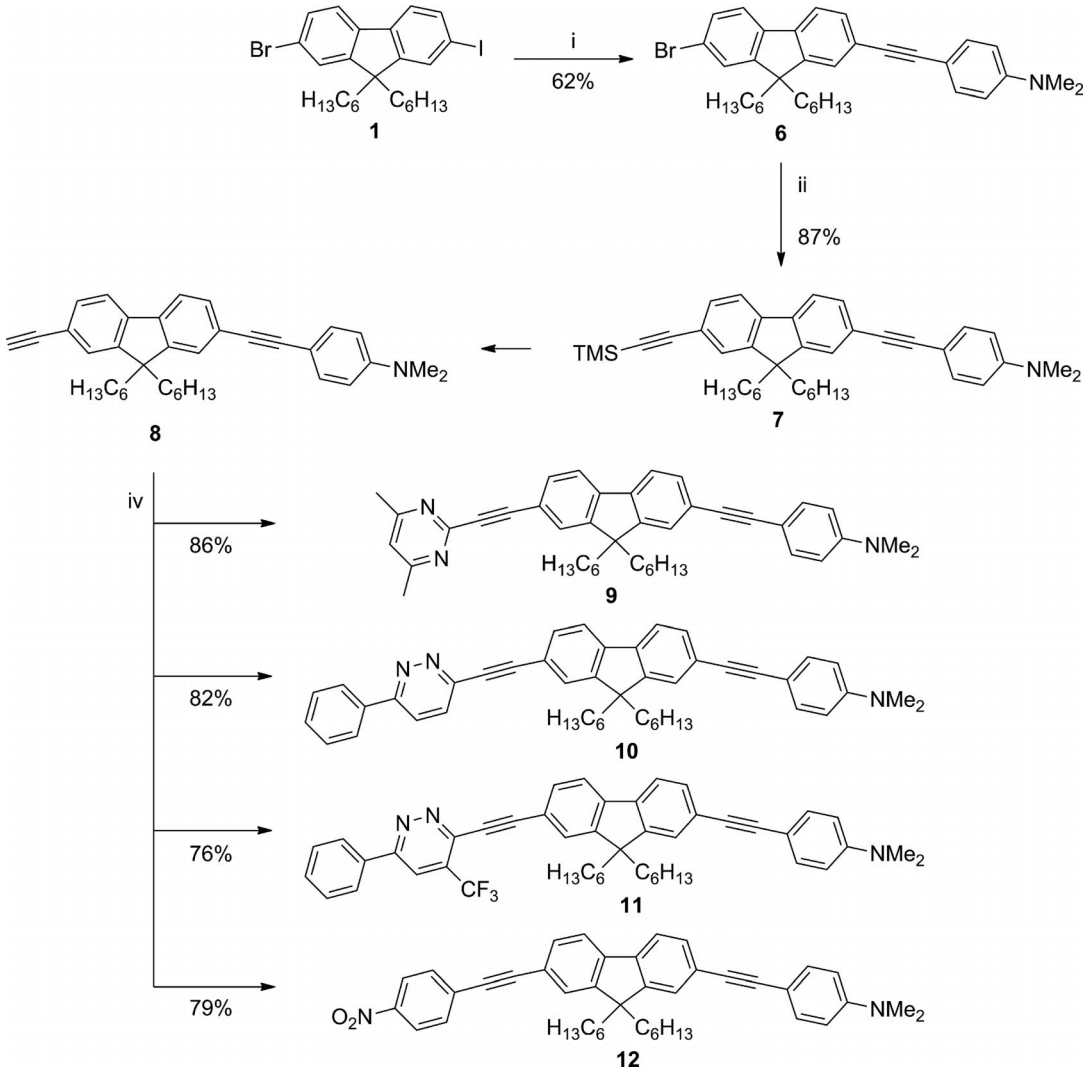
The first step was a Suzuki mono-cross-coupling reaction of 4-(dimethylamino)phenylboronic acid with **1**. The regioselectivity at the iodine atom was sufficient to obtain compound **2** as the main product with a moderate yield (64%). However, in addition to compound **2**, a small amount of 4,4′-(9,9-dihexyl-9*H*-fluorene-2,7-diyl)bis(*N*,*N*-dimethylbenzenamine), which resulted from two simultaneous coupling reactions, was obtained in less than 20% yield. The second step involved the synthesis of boronic acid **3**, which resulted from a halogen–metal exchange followed by treatment with triisopropylborate as an electrophile and a further acidic hydrolysis. Compound **3** was used directly without purification. The last step involved a second Suzuki cross-coupling reaction with compound **3** and a halogenated diazine. Compound **4** was obtained in low yield (16%) in two steps as a result of the reaction with 2-iodo-4,6-dimethylpyrimidine, whereas compound **5** was prepared in 44% yield under the same conditions by using 3-chloro-6-phenyl-4(trifluoromethyl)pyridazine. As reported of Suzuki couplings, a low reactivity is generally observed with chloro derivatives, which can be a result of the strength of the C–Cl bond compared to the C–I bond. Amazingly, the better yield observed for **5** can be explained by the electron-withdrawing trifluoromethyl substituent on the pyridazine ring, which makes the oxidative addition of palladium to a chlorine–carbon bond easier.[23–25]

To increase the length of the conjugated bridge between the 4-(dimethylamino)phenyl donor group and the π-deficient diazine ring, ethynyl spacers were introduced, which led to a second family of compounds of type II (see Scheme 2).

Starting from compound **1**, a regioselective Sonogashira cross-coupling reaction was carried out with 4-ethynyl-*N*,*N*-dimethylaniline to give compound **6** in moderate yield



Scheme 1. Synthesis of the two push–pull fluorophores **4** and **5** of type I. *Reagents and conditions:* (i) 4-(dimethylamino)phenylboronic acid (1 equiv.), $Pd(PPh_3)_4$ (10 mol-%), toluene/aqueous Cs_2CO_3 (2:1 v/v), 90 °C, 24 h; (ii) *n*BuLi (2.5 M solution, 1.3 equiv.), tetrahydrofuran (THF), followed by $B(OiPr)_3$ (3.0 equiv.), –78 °C to room temp., 15 h, then HCl (0.1 N); (iii) 2-iodo-4,6-dimethylpyrimidine (1.0 equiv.) or 3-chloro-6-phenyl-4-(trifluoromethyl)pyridazine (1.0 equiv.), $Pd(PPh_3)_4$ (10 mol-%), carbonate base (2.0 equiv.), toluene, room temp., 20 h.

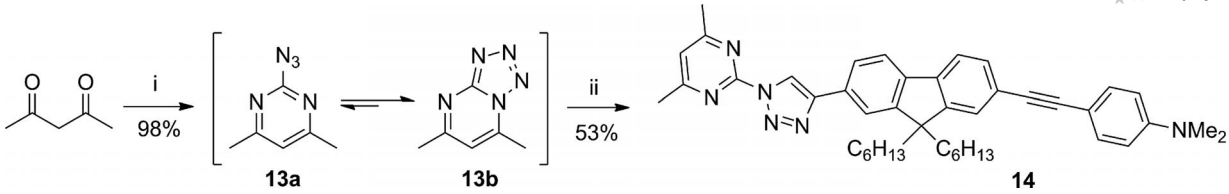


Scheme 2. Synthesis of push–pull fluorophores (i.e., **9**–**12**) of type II. *Reagents and conditions:* (i) 4-ethynyl-*N*,*N*-dimethylaniline (1.0 equiv.), CuI (0.02 equiv.), $Pd(PPh_3)_4$ (0.02 equiv.), iPr$_2$NH/THF (1:1 v/v), room temp., 12 h; (ii) trimethylsilylacetylene (1.5 equiv.), CuI (0.02 equiv.), $Pd(PPh_3)_4$ (0.02 equiv.), iPr$_2$NH/*N*,*N*-dimethylformamide (DMF, 1:1 v/v), 65 °C, 12 h; (iii) KOH (1 M in MeOH), 80 °C, 12 h; (iv) aryl halide (1.0 equiv.), CuI (0.02 equiv.), $Pd(PPh_3)_4$ (0.02 equiv.), iPr$_2$NH/DMF (1:1 v/v), 65 °C, 18 h.

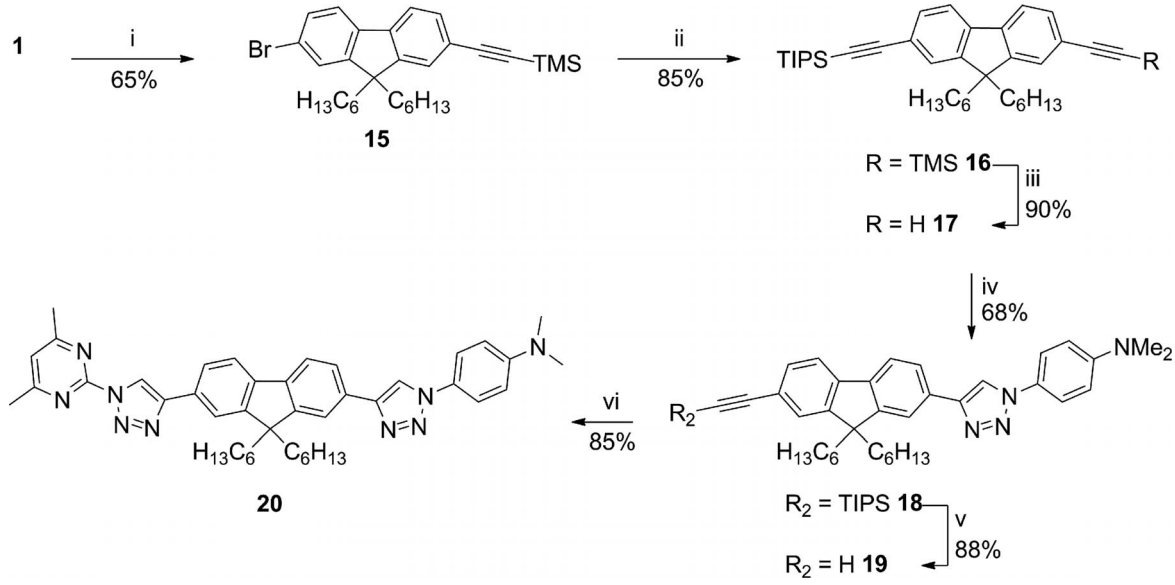
(67%). A second Sonogashira cross-coupling reaction at the remaining bromine atom by treatment with trimethylsilylacetylene followed by trimethylsilyl (TMS) deprotection afforded alkyne **8** in good yield. A final Sonogashira coupling reaction was achieved by using three different halogenated diazine derivatives. Contrary to other palladium-catalyzed cross-coupling reactions, the Sonogashira reaction generally requires an iodine atom even when diazine rings are employed.[25] As previously described, because of the strong electron-withdrawing effect of the trifluoromethyl group, 3-chloro-6-phenyl-4-(trifluoromethyl)pyridazine[26] was used to obtain compound **11** under smooth conditions in good yield. To compare the effect of the diazine rings with that of a *para*-nitrophenyl group, compound **12** was also synthesized.

To evaluate the influence of the linker in compound **9** of type II, either one or two of the ethynyl units were replaced by a triazole ring to give compounds **14** of type III and **20** of type IV. The triazole moiety was introduced through a copper-catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC) between azidopyrimidine **13a** and compound **8**. Previously, the corresponding open-chain azidopyrimidine **13a**, which is in equilibrium with its ring-tautomeric form **13b**, was prepared from pentane-2,4-dione through a cyclodehydration in the presence of 5-aminotetrazole.[27] By this synthetic route, the fluorophore **14** (type III) with only one triazole ring on the diazine side was obtained in moderate yield (53%, see Scheme 3).

Fluorophore **20** with two triazole rings was obtained in six steps by starting from **1** (see Scheme 4). Two successive Sonogashira cross-coupling reactions were performed with trimethylsilylacetylene and then triisopropylsilylacetylene to lead to compounds **15** and **16**, respectively, in good yields. The next step involved a selective deprotection of the trimethylsilyl group by treatment with potassium carbonate to give **17** with an excellent yield (90%). The following step



Scheme 3. Synthesis of push–pull fluorophores **14** of type III. *Reagents and conditions:* (i) $CuCl_2$ (0.1 equiv.), sodium ascorbate (0.1 equiv.) in EtOH and then pentane-2,4-dione (1.0 equiv.), 5-aminotetrazole (1.0 equiv.), room temp. 12 h; (ii) **13** (1.1 equiv.), **8** (1.0 equiv.), sodium ascorbate (0.3 equiv.), $CuSO_4{\cdot}5H_2O$ (0.15 equiv.), H_2O/*t*BuOH (1:1 v/v), 65 °C, 12 h.



Scheme 4. Synthesis of push–pull fluorophores **20** of type IV. *Reagents and conditions:* (i) trimethylsilylacetylene (1.0 equiv.), CuI (0.02 equiv.), $Pd(PPh_3)_4$ (0.02 equiv.), *i*Pr_2NH/DMF (1:1 v/v), room temp., 12 h; (ii) triisopropylsilylacetylene (1.5 equiv.), CuI (0.02 equiv.), $Pd(PPh_3)_4$ (0.02 equiv.), *i*Pr_2NH/DMF (1:1 v/v), room temp., 12 h; (iii) K_2CO_3 (5.0 equiv.), THF/MeOH, room temp., 16 h; (iv) 4-azido-*N*,*N*-dimethylaniline (1.1 equiv.), sodium ascorbate (0.30 equiv.), $CuSO_4{\cdot}5H_2O$ (0.15 equiv.), H_2O/*t*BuOH (1:1 v/v), 65 °C, 12 h; (v) TBAF (1 M solution, 1.06 equiv.), THF, room temp. 12 h; (vi) **13** (1.1 equiv.), sodium ascorbate (0.3 equiv.), $CuSO_4{\cdot}5H_2O$ (0.15 equiv.), H_2O/*t*BuOH (1:1 v/v), 65 °C.

involved a click reaction of terminal alkyne **17** with the 4-azido-*N*,*N*-dimethylaniline to afford compound **18**. Further deprotection of the triisopropylsilyl (TIPS) group was achieved by using tetra-*n*-butylammonium fluoride (TBAF) to give compound **19**. A second click reaction between compounds **19** and **13** afforded fluorophore **20** of type IV in 85% yield.

UV/Vis and Photoluminescence Spectroscopy

The UV/Vis and photoluminescence spectroscopic data of all the chromophores were recorded in dichloromethane at 25 °C (see Table 1).

All the studied compounds (see Table 1) contain the same 4-(dimethylamino)phenyl moiety as the electron-donating group and differ by the electron-withdrawing aromatic group and the nature of the linkers (optimized geometries of compounds **4** and **5** are shown in Figures 2 and 3). These compounds exhibit absorption maxima (λ_{abs}) in the UV region (358–392 nm) and emission maxima (λ_{em}) in the purple to green region (411–539 nm, see Figures 4 and 5). The comparison between the data for compounds **4** and **5** (type I) reveals similar λ_{abs}, but a lower value for the molar extinction coefficient (ε), an important blueshift for λ_{em}, and a dramatic decrease of the quantum yield (Φ_F) are observed for **5**. These spectroscopic data for **5** could be a consequence of the steric hindrance from the trifluoromethyl group at the position adjacent to the fluorene-pyridazine bond, and, therefore, we speculate that twisting could occur with a loss of conjugation between the two moieties. This

Table 1. Photoluminescence data of chromophores **4**, **5**, **9**–**12**, **14**, and **20** in CH_2Cl_2.

Type	Compd.	λ_{abs} [nm]	ε [$M^{-1}cm^{-1}$]	λ_{em} [nm]	Φ_F[a]	Stokes shift [cm^{-1}]
I	**4**	360	58800	483	0.69	7074
	5	358	39300	423	0.01	4292
II	**9**	372	52094	515	0.64[b]	7464
	10	377	58100	539	0.21	7972
	11	392	74700	500	0.05	5510
	12	391	51900	474	0.01	4478
III	**14**	362	71500	450	0.71	5402
IV	**20**	334	82000	422	0.47[b]	6243

[a] ±10%, harmane (0.1 M in H_2SO_4) was used as reference (Φ_F = 0.58), excitation at 360 nm. [b] Excitation at 300 nm.

hypothesis is supported by the fully optimized geometry of **5**, for which a dihedral angle of 37° was established (see Figure 3), whereas the geometry of **4** reveals a nearly coplanar structure with a dihedral angle of 0.075° between the fluorene core and the pyrimidine ring (see Figure 2). For both compounds, a value of about 35° was determined for the dihedral angle between the central fluorene unit and the benzene ring, which is a result of the steric hindrance from the *ortho* hydrogen atoms.

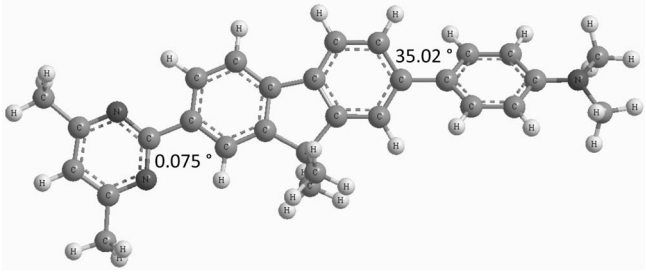


Figure 2. Optimized B3LYP/6-31G* geometry for compound **4**. The printed values correspond to dihedral angles.

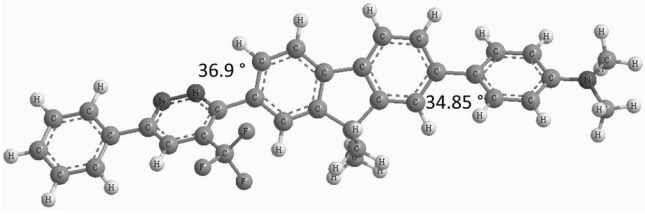


Figure 3. Optimized B3LYP/6-31G* geometry for compound **5**. The printed values correspond to dihedral angles.

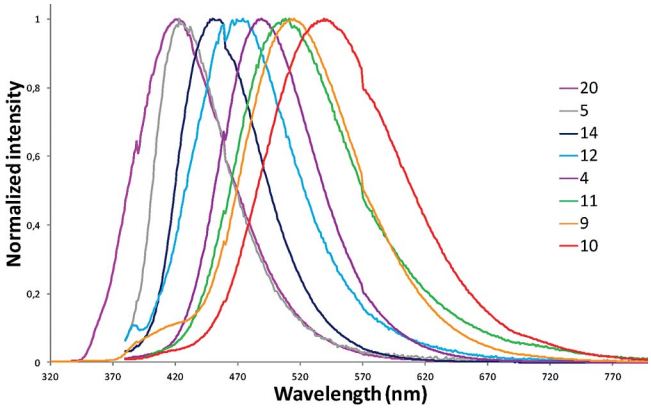


Figure 4. Normalized emission spectra of chromophores **20**, **5**, **14**, **12**, **4**, **11**, **9**, and **10** in CH_2Cl_2.

The comparison between compounds **9**–**12** (type II) demonstrates the influence of the electron-withdrawing aromatic group, as this moiety is linked by a triple bond to the fluorene central unit, which separates the core from the aromatic ring and allows for an absolute planar geometry to force the system into conjugation. The spectral data of compound **12** with a 4-nitrophenyl group could be used as a reference (λ_{abs} = 391 nm, ε = 51900 $M^{-1}cm^{-1}$, λ_{em} = 474 nm, Φ_F = 0.01) to evaluate the influence of the diazine

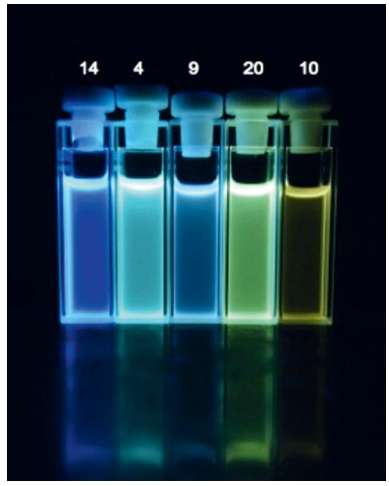


Figure 5. Color of compounds **14**, **4**, **9**, **20**, and **10** in CH_2Cl_2 under UV irradiation (365 nm).

moiety that is present in compounds **9**–**11**. Replacing the 4-nitrophenyl group by the 4,6-(dimethyl)pyrimidine or pyridazine ring caused a redshift of the emission wavelength ($\Delta\lambda$ = 26–65 nm) with an appreciable increase of the quantum yield for compounds **9** and **10**. Incorporating the most electron-attractive trifluoromethylpyridazine moiety rather than the pyridazine ring did not improve the spectroscopic data with the exception of the molecular extinction coefficient (ε) and the decrease of the quantum yield (Φ_F). This result can be explained by the change in the symmetry of the molecule compared to **10**.

The comparison of compounds **4**, **9**, **14**, and **20** that have the 4,6-dimethyl-2-pyrimidinyl and 4-(dimethylamino)-phenyl groups as external substituents allows to evaluate the influence of the linkers. The incorporation of an ethynyl linker instead of a simple bond led to a redshift of the maxima absorption (λ_{abs}) and emission (λ_{em}) with similar values of ε and Φ_F. When a triple bond was replaced by one or two 1,2,3-triazole rings, an increase of the molecular extinction coefficient (ε) was observed in addition to a slight blueshift of the maxima absorption (λ_{abs}) and emission (λ_{em}) as well as high values for the quantum yields.

Two-Photon Absorption Properties

Two-photon absorption cross-sections (δ_{TPA}) were measured by a two-photon-inducted fluorescence technique that used a femtosecond (fs) laser pulse. Because of the laser availability (Ti:sapphire laser), the solutions were excited in the range of 690 to 940 nm. 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 are summarized in Table 2 and Figure 6.

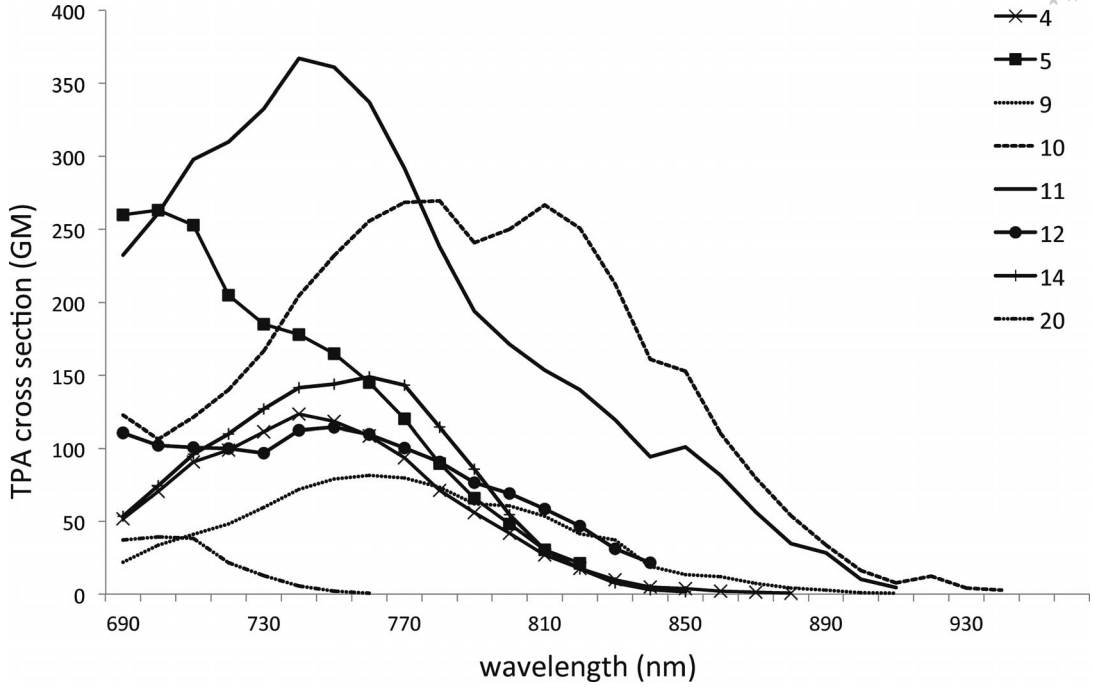


Figure 6. TPA absorption spectra of compounds **4**, **5**, **9**–**12**, **14**, and **20** in CH_2Cl_2.

Table 2. Results of TPA absorption spectra (λ_{TPA}) and two-photon absorption cross-sections (δ_{TPA}).

	4	**5**	**9**	**10**	**11**	**12**	**14**	**20**
λ_{TPA} [nm][a]	740	700	760	780	740	750	760	700
δ_{TPA} [GM][b]	123	263	82	269	367	114	148	39

[a] Wavelength of maximum TPA cross-section. [b] TPA cross-section ($1\,M = 10^{-50}\,cm^4\,s\,photon^{-1}$).

All the compounds exhibited TPA in the red to the near infrared region. Push–pull structures **4**, **5**, **9**–**12**, **14**, and **20** exhibited TPA cross-sections in CH_2Cl_2 between 39 and 367 GM, which is comparable or higher than that of commercially available TPA dyes. The highest cross-sections were obtained for pyridazine derivatives **5**, **10**, and **11**. When comparing compounds **10** and **11**, the trifluoromethyl group on the pyridazine ring significantly increased the TPA cross-section up to 367 GM. Pyridazine derivatives **10** and **11** exhibited a much higher TPA cross-section than nitro derivative **12**. When comparing compounds **9**, **14**, and **20**, as observed for the fluorescence quantum yield, the replacement of only one triple bond by a triazole unit on the pyrimidine side (i.e., compound **14**) increased the TPA cross-section. When two triazole rings were present on each side of the fluorene (i.e., compound **20**), the TPA cross-section dramatically decreased. Because of the low value of the fluorescence quantum yield for compounds **5** and **12**, the uncertainty of the TPA cross-sections for these compounds is important.

Conclusions

In summary, we have successfully synthesized and characterized a new series of push–pull diazine derivatives that contain fluorene, π-conjugated linkers, and the (dimethylamino)phenyl electron-donating group. The optical properties were studied, and all the molecules displayed absorption wavelengths in the UV region and emitted visible light with significant Stokes shifts. An emission quantum yield up to 0.71 was observed for compound **14**, which contained both an ethynyl group and a triazole ring as linkers. Pyrimidine derivatives exhibited higher quantum yields than pyridazine derivatives. The TPA properties were investigated, and TPA cross-sections were observed up to 367 GM in the red region of the spectrum and were higher for pyridazine derivatives than for pyrimidine compounds. Some molecules such as pyrimidine derivatives **4** and **14** and pyridazine derivative **10** have a combination of a high quantum yield and high TPA cross-section. Current investigations are being carried out in our laboratories to functionalize these structures to obtain water soluble TPA bioimaging dyes.

Experimental Section

General Remarks: All chemicals were purchased from commercial sources and were used without further purification unless otherwise specified. Analytical thin layer chromatography was performed with silica gel plates (Merck® TLC Silica gel 60 F_{254}), and compounds were detected by irradiation with UV light (254 and 365 nm). The 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 (APCI+ or ESI+) were recorded with a LC Waters Acquity that was coupled to a Waters LCT Premier XE instrument. Elemental analyses were performed with a Carlo Erba 1106 apparatus, and the measurement

accuracy is approximately ±0.4% for carbon. Melting points (°C) were measured with a Kofler hot-stage with a precision of 2 °C (±2 °C). The ^{1}H and ^{13}C NMR spectroscopic data were recorded with a Bruker Advance spectrometer that operated at 300 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 ppm, respectively for $CDCl_3$ and 0.00 ppm for $CFCl_3$). The data appear in the order of chemical shift in ppm, number of protons, multiplicity [singlet (s), doublet (d), doublet of doublet (dd), triplet (t), multiplet (m)], and coupling constant J in Hz. For the ^{13}C NMR spectroscopic data, the nature of the carbons (C, CH, CH_2, or CH_3) was determined by recording DEPT and heteronuclear multiple quantum coherence (HMQC) experiments. UV/Vis spectra were recorded with a Varian Can 50 scan spectrophotometer. Fluorescence spectroscopic studies were performed with a Varian Cary Eclipse spectrophotometer. Compounds were excited at their absorption maxima to record the emission spectra, however, different wavelengths were used to determine fluorescence quantum yields in cases where the compounds and standards absorbed significantly. All solutions were measured with optical densities below 0.1. The TPA cross-sections in the range of 790–950 nm were obtained by up-conversion fluorescence using a mode locked with a Ti:sapphire femtosecond laser (Tsunami Spectra-Physics) with a pulse duration of 100 fs and at a repetition rate of 82 MHz. The measurements were carried out at room temperature in dichloromethane (DCM) at a concentration of approximately 5×10^{-6} to 5×10^{-5} M. The excitation beam (5 mm diameter) was focused with a lens (focal length 10 cm) at the middle of the fluorescence cell (10 mm). The fluorescence, which was collected at 90° to the excitation beam, was focused into an optical fiber (diameter 600 μm) that was connected to an Ocean Optics S2000 spectrometer. The incident beam intensity was adjusted to 50 mW to ensure an intensity-squared dependence of the fluorescence over the whole range. The detector integration time was fixed at 1 s. The spectra were compared with the published fluorescein and rhodamine B two-photon absorption spectra.

4-(7-Bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-*N*,*N*-dimethylaniline (2): A mixture of 2-bromo-9,9-dihexyl-7-iodo-9*H*-fluorene (**1**, 250 mg, 0.464 mmol, 1.0 equiv.), 4-(dimethylamino)phenylboronic acid (77 mg, 0.464 mmol, 1.0 equiv.), and $[Pd(PPh_3)_4]$ (53 mg, 0.046 mmol, 10 mol-%) were dissolved in a 2:1 (v/v) solution of toluene (8 mL) and aqueous Cs_2CO_3 (2 M solution, 4 mL). After degassing, the reaction mixture was heated to 90 °C for 24 h and then cooled to room temp. Distilled water (10 mL) was added, and the organic products were extracted with EtOAc (3 × 15 mL). The combined organic layers were dried with $MgSO_4$, filtered, and then evaporated under reduced pressure to give a black solid residue. Purification by flash column chromatography on silica (petroleum ether/toluene, 5:5) gave compound **2** (152 mg, 64%) as a white solid; R_f = 0.30 (petroleum ether/toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.0 Hz, 1 H), 7.60–7.52 (m, 4 H), 7.49–7.43 (m, 3 H), 6.86 (d, J = 9.0 Hz, 2 H), 3.02 (s, 6 H), 2.02–1.91 (m, 4 H), 1.16–1.04 (m, 12 H), 0.77 (t, J = 7.0 Hz, 6 H), 0.69–0.63 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.3 (C_q), 151.1 (C_q), 140.7 (C_q), 140.2 (C_q), 130.0 (CH_{Ar}), 127.9 (CH_{Ar}), 126.1 (CH_{Ar}), 125.3 (CH_{Ar}), 121.0 (CH_{Ar}), 120.7 (CH_{Ar}), 120.0 (CH_{Ar}), 113.0 (CH_{Ar}), 55.5 (C_q), 40.8 (CH_3), 40.5 (CH_2), 31.6 (CH_2), 29.8 (CH_2), 23.8 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. HRMS [TOF MS APCI+ (atmospheric pressure)]: calcd. for $C_{33}H_{43}NBr$ $[M + H]^+$ 532.2579; found 532.2586.

4-[7-(4,6-Dimethylpyrimidin-2-yl)-9,9-dihexyl-9*H*-fluoren-2-yl]-*N*,*N*-dimethylaniline (4): *n*BuLi (2.5 M in cyclohexane, 0.14 mL, 1.3 equiv.) was added to a solution of compound **2** (140 mg, 0.26 mmol, 1.0 equiv.) in THF (3.5 mL) at –78 °C. The resulting solution was stirred at –78 °C for 1 h. Then, triisopropylborate (0.18 mL, 0.78 mmol, 3.0 equiv.) was added, and the solution was warmed to room temp. overnight. HCl (0.1 N solution, 5 mL) was added, and the layers were separated. The aqueous layer was then extracted with EtOAc (3 × 15 mL). The combined organic layers were dried with $MgSO_4$, filtered, and then evaporated under reduced pressure to give the crude product **3** (65 mg). A mixture of crude compound **3** (65 mg, 0.13 mmol, 1.0 equiv.), 2-iodo-4,6-dimethylpyrimidine (30 mg, 0.13 mmol, 1.0 equiv.), and $[Pd(PPh_3)_4]$ (10 mg, 0.009 mmol, 7 mol-%) was dissolved into a 2:1 (v/v) solution of toluene (3.0 mL) and aqueous Na_2CO_3 (2 M solution 1.5 mL). After degassing, the mixture was heated to 90 °C overnight and then cooled to room temp. Distilled water (10 mL) was added, and the organic products were extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried with $MgSO_4$, filtered, and then concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (petroleum ether/CH_2Cl_2, from 90:10 to 50:50) gave compound **4** (12 mg, 16%); m.p. 100–102 °C. R_f = 0.54 (petroleum ether/CH_2Cl_2, 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.47 (dd, J = 1.5, 8.0 Hz, 1 H), 8.42 (s, 1 H), 7.77 (dd, J = 2.5, 8.0 Hz, 2 H), 7.61–7.54 (m, 4 H), 6.92 (s, 1 H), 6.85 (d, J = 8.5 Hz, 1 H), 3.02 (s, 6 H), 2.57 (s, 6 H), 2.12–2.04 (m, 4 H), 1.13–1.04 (m, 12 H), 0.76–0.72 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.8 (C_q), 164.8 (C_q), 152.3 (C_q), 151.3 (C_q), 150.1 (C_q), 143.5 (C_q), 140.6 (C_q), 139.0 (C_q), 136.8 (C_q), 129.9 (C_q), 127.9 (CH_{Ar}), 127.5 (CH_{Ar}), 125.2 (CH_{Ar}), 122.6 (CH_{Ar}), 120.8 (CH_{Ar}), 120.4 (CH_{Ar}), 119.6 (CH_{Ar}), 117.7 (CH_{Ar}), 113.0 (CH_{Ar}), 55.4 (C_q), 40.8 (CH_3), 40.6 (CH_2), 31.7 (CH_2), 29.9 (CH_2), 24.4 (CH_3), 23.9 (CH_2), 22.7 (CH_2), 14.2 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2925, 2854, 1603, 1589, 1526, 1357, 1200, 813, 794 cm^{-1}. HRMS (TOF MS ESI+): calcd. for $C_{39}H_{49}N_3$ $[M + H]^+$ 560.4005; found 560.3984.

4-{9,9-Dihexyl-7-[6-phenyl-4-(trifluoromethyl)pyridazin-3-yl]-9*H*-fluoren-2-yl}-*N*,*N*-dimethylaniline (5): *n*BuLi (2.5 M in cyclohexane, 0.14 mL, 1.3 equiv.) was added to a solution of compound **2** (140 mg, 0.26 mmol, 1.0 equiv.) in THF at –78 °C. The resulting solution was stirred at –78 °C for 1 h. Then, triisopropylborate (0.18 mL, 0.78 mmol, 3.0 equiv.) was added, and the solution was warmed to room temp. overnight. HCl (0.1 N solution, 5 mL) was added, and the layers were separated. The aqueous layer was then extracted with EtOAc (3 × 15 mL). The combined organic layers were dried with $MgSO_4$, filtered, and then evaporated under reduced pressure to give the crude product. A mixture of the crude {7-[4-(dimethylamino)phenyl]-9,9-dihexyl-9*H*-fluoren-2-yl}boronic acid (65 mg, 0.13 mmol, 1.0 equiv.), 3-chloro-6-phenyl-4-(trifluoromethyl)pyridazine (34 mg, 0.13 mmol, 1.0 equiv.), Cs_2CO_3 (42 mg, 0.13 mmol, 1.0 equiv.), K_2CO_3 (2 M solution, 0.1 mL, 1.0 equiv.), and $[Pd(PPh_3)_4]$ (15 mg, 0.013 mmol, 0.1 equiv.) was dissolved in a solution of toluene (10 mL) and ethanol (0.1 mL). After degassing, the mixture was agitated at room temp. for 24 h. Distilled water (20 mL) was added at room temp., and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried with $MgSO_4$, filtered, and then concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (petroleum ether/EtOAc, 95:5) gave compound **5** (39 mg, 44%); m.p. 106–108 °C. R_f = 0.38 (petroleum ether/EtOAc, 5:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24–8.21 (m, 2 H), 8.17 (s, 1 H), 7.85 (d, J = 7.8 Hz, 1 H), 7.80 (d, J = 7.8 Hz, 1 H), 7.68–7.56 (m, 10 H), 6.86 (d, J = 8.7 Hz, 2 H), 3.02 (s, 6 H), 2.07–2.02 (m, 4 H), 1.15–1.06 (m, 12 H), 0.78–0.72 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.2 (C_q), 157.7 (C_q), 152.0 (C_q), 150.9 (C_q), 150.2 (C_q), 143.0 (C_q), 141.0 (C_q), 138.5 (C_q), 135.1

(C_q), 133.8 (C_q), 131.0 (CH_{Ar}), 129.7 (C_q), 129.5 (CH_{Ar}), 128.7 (C_q), 128.4 (CH_{Ar}), 128.3 (C_q), 128.0 (CH_{Ar}), 127.5 (C_q), 127.3 (CH_{Ar}), 125.3 (CH_{Ar}), 123.9 (CH_{Ar}), 120.8 (CH_{Ar}), 120.7 (CH_{Ar}), 120.6 (CH_{Ar}), 119.5 (CH_{Ar}), 113.0 (CH_{Ar}), 55.5 (C_q), 40.8 (CH_3), 40.7 (CH_2), 31.6 (CH_2), 29.8 (CH_2), 23.8 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2927, 1455, 1411, 1343, 1261, 1189, 1135, 1101, 906, 771, 693, 671 cm^{-1}. HRMS (TOF MS ESI+): calcd. for $C_{44}H_{49}N_3F_3$ $[M + H]^+$ 676.3879; found 676.3859.

4-[(7-Bromo-9,9-dihexyl-9*H*-fluoren-2-yl)ethynyl]-*N*,*N*-dimethylaniline (6): A mixture of compound **1** (2.0 g, 3.708 mmol, 1.0 equiv.) and 4-ethynyl-*N*,*N*-dimethylaniline (0.538 g, 3.708 mmol, 1.0 equiv.) was added to a solution of *i*Pr_2NH/THF (1:1 v/v, 20 mL). After degassing, CuI (14 mg, 0.074 mmol, 0.02 equiv.) and $[Pd(PPh_3)_4]$ (85.5 mg, 0.074 mmol, 0.02 equiv.) were introduced to the mixture. The resulting solution was stirred at room temp. for 12 h. Distilled water (20 mL) was added, and the organic products were extracted with EtOAc (3× 15 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica (petroleum ether/CH_2Cl_2, 6:4) gave compound **6** (1.37 g, 67%) as a light yellow solid; m.p. 118–120 °C. R_f = 0.67 (petroleum ether/CH_2Cl_2, 6:4). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.0 Hz, 1 H), 7.50 (d, J = 8.5 Hz, 1 H), 7.48 (d, J = 7.0 Hz, 1 H), 7.42–7.46 (m, 5 H), 6.68 (d, J = 9.0 Hz, 2 H), 3.01 (s, 6 H), 1.90–1.97 (m, 4 H), 1.04–1.15 (m, 12 H), 0.77 (t, J = 7.0 Hz, 6 H), 0.58–0.62 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.0 (C_q), 153.3 (C_q), 150.4 (C_q), 150.2 (C_q), 139.7 (C_q), 139.5 (C_q), 132.8 (CH_{Ar}), 130.5 (CH_{Ar}), 130.1 (CH_{Ar}), 126.2 (CH_{Ar}), 125.6 (CH_{Ar}), 123.0 (C_q), 121.3 (CH_{Ar}), 119.7 (CH_{Ar}), 111.9 (CH_{Ar}), 110.0 (C_q), 91.1 (C_q), 88.3 (C_q), 55.5 (C_q), 40.4 (CH_2), 40.3 (CH_3), 31.6 (CH_3), 29.7 (CH_2), 23.8 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. HRMS (TOF MS APCI+): calcd. for $C_{35}H_{43}NBr$ $[M + H]^+$ 556.2579; found 556.2587.

4-({9,9-Dihexyl-7-[(trimethylsilyl)ethynyl]-9*H*-fluoren-2-yl}ethynyl)-*N*,*N*-dimethylaniline (7): A mixture of compound **6** (1.10 g, 1.976 mmol, 1.0 equiv.) and trimethylsilylacetylene (0.291 g, 2.964 mmol, 1.5 equiv.) was added to a solution of *i*Pr_2NH/THF (1:1 v/v, 10 mL). After degassing, CuI (7.6 mg, 0.040 mmol, 0.02 equiv.) and $[Pd(PPh_3)_4]$ (46.2 mg, 0.040 mmol, 0.02 equiv.) were introduced to the mixture. The resulting solution was stirred at 65 °C for 18 h. Distilled water (5 mL) was added, and the organic products were extracted with Et_2O (3× 10 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica (petroleum ether/toluene, 9:1) gave compound **7** (0.987 g, 87%) as a light yellow solid; m.p. 154–156 °C. R_f = 0.60 (petroleum ether/toluene, 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (m, 2 H), 7.43–7.50 (m, 6 H), 6.72 (d, J = 7.0 Hz, 2 H), 3.0 (s, 6 H), 1.93–1.98 (m, 4 H), 0.98–1.15 (m, 12 H), 0.77 (t, J = 7.1 Hz, 6 H), 0.49–0.64 (m, 4 H), 0.29 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.1 (C_q), 150.0 (C_q), 149.2 (C_q), 140.3 (C_q), 139.0 (C_q), 131.9 (CH_{Ar}), 130.3 (CH_{Ar}), 129.5 (CH_{Ar}), 125.3 (CH_{Ar}), 124.7 (CH_{Ar}), 122.0 (C_q), 120.5 (C_q), 119.0 (CH_{Ar}), 118.8 (CH_{Ar}), 111.0 (CH_{Ar}), 109.1 (C_q), 105.4 (C_q), 93.2 (C_q), 90.2 (C_q), 87.5 (C_q), 54.3 (C_q), 39.6 (CH_2), 39.3 (CH_3), 30.7 (CH_2), 28.9 (CH_2), 22.8 (CH_2), 21.8 (CH_2), 13.2 (CH_3), 0.8 (CH_3 TMS) ppm. HRMS (TOF MS APCI+): calcd. for $C_{40}H_{52}NSi$ $[M + H]^+$ 574.3869; found 574.3869.

4-[(7-Ethynyl-9,9-dihexyl-9*H*-fluoren-2-yl)ethynyl]-*N*,*N*-dimethylaniline (8): A solution of potassium hydroxide (1 M in methanol, 30 mL) and **7** (0.650 g, 1.168 mmol) were combined under nitrogen. The mixture was stirred and heated to 80 °C for 12 h. After it was cooled to room temperature, the solution was neutralized with HCl (1 M aqueous solution, 10 mL), and organic products were extracted with CH_2Cl_2 (3× 50 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product (0.653 g). Purification by flash column chromatography on silica (petroleum ether/EtOAc, 9:1) gave compound **8** (0.461 g, 79%) as a light orange solid; m.p. 119–121 °C. R_f = 0.70 (petroleum ether/EtOAc, 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (dd, J = 8.0, 7.5 Hz, 2 H), 7.42–7.50 (m, 6 H), 6.68 (d, J = 9.0 Hz, 2 H), 3.15 (s, 1 H, 1 H), 3.00 (s, 6 H), 1.92–1.98 (m, 4 H), 1.03–1.25 (m, 12 H), 0.76 (t, J = 7.0 Hz, 6 H), 0.57–0.61 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.2 (C_q), 151.1 (C_q), 150.1 (C_q), 141.6 (C_q), 139.8 (C_q), 132.9 (CH_{Ar}), 131.3 (CH_{Ar}), 130.5 (CH_{Ar}), 126.6 (CH_{Ar}), 125.8 (CH_{Ar}), 123.2 (C_q), 120.5 (C_q), 120.1 (CH_{Ar}), 119.9 (CH_{Ar}), 112.1 (CH_{Ar}), 110.3 (C_q), 91.2 (C_q), 88.5 (C_q), 84.9 (C_q), 77.3 (C_q), 55.3 (C_q), 40.5 (CH_2), 23.8 (CH_2), 40.4 (CH_3), 31.7 (CH_2), 29.8 (CH_2), 22.8 (CH_2), 14.1 (CH_3) ppm. HRMS (TOF MS APCI+): calcd. for $C_{37}H_{44}N$ $[M + H]^+$ 502.3474; found 502.3485.

4-({7-[(4,6-Dimethylpyrimidin-2-yl)ethynyl]-9,9-dihexyl-9*H*-fluoren-2-yl}ethynyl)-*N*,*N*-dimethylaniline (9): A mixture of **8** (50 mg, 0.100 mmol, 1.0 equiv.) and 2-iodo-4,6-dimethylpyrimidine (23 mg, 0.1 mmol, 1.0 equiv.) was added to a solution of *i*Pr_2NH/THF (1:1 v/v, 2 mL). After degassing, CuI (0.4 mg, 0.002 mmol, 0.02 equiv.) and $[Pd(PPh_3)_4]$ (2.3 mg, 0.002 mmol, 0.02 equiv.) were introduced to the mixture. The resulting solution was stirred at 65 °C for 18 h. Distilled water (5 mL) was added, and the organic products were extracted with Et_2O (3× 10 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica (petroleum ether/EtOAc, 8:2) gave compound **9** (52 mg, 86%) as a yellow solid; m.p. 84–86 °C. R_f = 0.31 (petroleum ether/EtOAc, 8:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (m, 4 H), 7.43–7.50 (m, 4 H), 6.99 (s, 1 H), 6.67 (d, J = 9.0 Hz, 2 H), 3.00 (s, 6 H), 2.53 (s, 6 H), 1.93–1.98 (m, 4 H), 0.97–1.15 (m, 12 H), 0.76 (t, J = 7.0 Hz, 6 H), 0.54–0.63 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.3 (C_q), 152.8 (C_q), 151.4 (C_q), 160.0 (C_q), 150.2 (C_q), 142.2 (C_q), 139.8 (C_q), 132.9 (CH_{Ar}), 130.7 (CH_{Ar}), 130.5 (CH_{Ar}), 127.5 (CH_{Ar}), 125.7 (CH_{Ar}), 123.4 (C_q), 120.2 (CH_{Ar}), 119.9 (CH_{Ar}), 119.8 (CH_{Ar}), 112.0 (CH_{Ar}), 110.1 (C_q), 91.4 (C_q), 88.48 (C_q), 88.46 (C_q), 88.4 (C_q), 55.3 (C_q), 40.6 (CH_2) 40.3 (CH_3), 31.7 (CH_2), 29.8 (CH_2), 24.1 (CH_3), 23.8 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2925, 2853, 2212, 1600, 1520, 1466, 1363, 1195, 1124, 946, 817, 747, 692, 532 cm^{-1}. HRMS (TOF MS ESI+): calcd. for $C_{43}H_{50}N_3$ $[M + H]^+$ 608.4005; found 608.4006.

4-({9,9-Dihexyl-2-[(6-phenylpyridazin-3-yl)ethynyl]-9*H*-fluoren-7-yl}ethynyl)-*N*,*N*-dimethylaniline (10): A mixture of **8** (50 mg, 0.100 mmol, 1.0 equiv.) and 3-iodo-6-phenylpyridazine (28 mg, 0.1 mmol, 1.0 equiv.) was added to a solution of *i*Pr_2NH/THF (1:1 v/v, 2 mL). After degassing, CuI (0.4 mg, 0.002 mmol, 0.02 equiv.) and $[Pd(PPh_3)_4]$ (2.3 mg, 0.002 mmol, 0.02 equiv.) were introduced to the mixture. The resulting solution was stirred at 65 °C for 18 h. Distilled water (5 mL) was added, and the organic products were extracted with Et_2O (3× 10 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica (petroleum ether/EtOAc, 8:2) gave compound **10** (54 mg, 82%) as a yellow solid; m.p. 109–111 °C. R_f = 0.31 (petroleum ether/EtOAc, 8:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13 (d, J = 9.0 Hz, 2 H), 7.85 (d, J = 9.0 Hz, 1 H), 7.70 (d, J = 9.0 Hz, 1 H), 7.61–7.68 (m, 4 H), 7.48–7.57 (m, 5 H), 7.46 (d, J

= 9.0 Hz, 2 H), 6.68 (d, *J* = 9.0 Hz, 2 H), 3.00 (s, 6 H), 1.97–2.03 (m, 4 H), 1.01–1.17 (m, 12 H), 0.77 (t, *J* = 7.0 Hz, 6 H), 0.57–0.67 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0 (C_q), 151.3 (C_q), 151.2 (C_q), 150.2 (C_q), 146.8 (C_q), 142.3 (C_q), 139.6 (C_q), 136.0 (C_q), 132.9 (CH_{Ar}), 131.4 (CH_{Ar}), 130.6 (CH_{Ar}), 130.4 (CH_{Ar}), 130.4 (CH_{Ar}), 129.2 (CH_{Ar}), 127.3 (CH_{Ar}), 126.7 (CH_{Ar}), 125.7 (CH_{Ar}), 123.5 (C_q), 123.1 (CH_{Ar}), 120.2 (C_q), 120.0 (CH_{Ar}), 119.98 (CH_{Ar}), 112.0 (CH_{Ar}), 110.0 (C_q), 95.6 (C_q), 55.4 (C_q), 91.5 (C_q), 88.4 (C_q), 86.5 (C_q), 40.5 (CH_2), 40.3 (CH_3), 31.7 (CH_2), 29.8 (CH_2), 25.7 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2925, 2854, 2194, 1600, 1521, 1466, 1451, 1400, 1360, 1192, 1110, 818, 747, 691, 572, 529, 412 cm^{-1}. HRMS (TOF MS ESI+): calcd. for $C_{43}H_{51}N_9$ $[M + H]^+$ 656.4005; found 656.3997.

4-[(9,9-Dihexyl-7-{[6-phenyl-4-(trifluoromethyl)pyridazin-3-yl]ethynyl}-9*H*-fluoren-2-yl)ethynyl]-*N*,*N*-dimethylaniline (11): A mixture of **8** (50 mg, 0.1 mmol, 1.0 equiv.) and 3-chloro-6-phenyl-4-(trifluoromethyl)pyridazine (39 mg, 0.1 mmol, 1.0 equiv.) was added to a solution of *i*Pr_2NH/THF (1:1 v/v, 2 mL). After degassing, CuI (0.4 mg, 0.002 mmol, 0.02 equiv.) and $[Pd(PPh_3)_4]$ (2.3 mg, 0.002 mmol, 0.02 equiv.) were introduced to the mixture. The resulting solution was stirred at 65 °C for 18 h. Distilled water was added (5 mL), and the organic products were extracted with Et_2O (3× 10 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica (petroleum ether/EtOAc, 9:1) gave compound **11** (54 mg, 76%) as an orange solid; m.p. 170–172 °C. R_f = 0.51 (petroleum ether/EtOAc, 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16–8.19 (m, 2 H), 8.07 (s, 1 H), 7.65–7.73 (m, 4 H), 7.57–7.63 (m, 3 H), 7.50–7.53 (m, 2 H), 7.46 (d, *J* = 9.0 Hz, 2 H), 6.69 (d, *J* = 9.0 Hz, 2 H), 3.01 (s, 2 H), 1.93–2.03 (m, 4 H), 1.06–1.22 (m, 12 H), 0.77 (t, *J* = 7.0 Hz, 6 H), 0.56–0.67 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.1 (C_q), 151.5 (C_q), 151.3 (CH_{Ar}), 150.2 (C_q), 143.0 (C_q), 142.7 (C_q), 139.5 (C_q), 134.8 (C_q), 132.9 (CH_{Ar}), 131.8 (CH_{Ar}), 131.2 (CH_{Ar}), 131.0 (CF_3), 130.6 (CH_{Ar}), 129.5 (CH_{Ar}), 127.4 (CH_{Ar}), 126.8 (CH_{Ar}), 125.8 (CH_{Ar}), 124.0 (C_q), 123.7 (C_q), 120.3 (CH_{Ar}), 120.1 (CH_{Ar}), 119.5 (C_q), 119.3 (CH_{Ar}), 112.0 (CH_{Ar}), 110.1 (C_q), 101.3 (-C≡C-), 91.6 (-C≡C-), 88.5 (-C≡C-), 83.4 (C_q), 55.4 (C_q), 40.5 (CH_2), 40.4 (2 C, CH_3), 31.7 (CH_3), 29.8 (CH_3), 24.0 (CH_3), 22.7 (CH_2), 14.1 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2925, 2853, 2200, 1599, 1522, 1466, 1450, 1396, 1362, 1265, 1193, 1179, 1140, 947, 912, 890, 815, 784, 689, 528 cm^{-1}. HRMS (TOF MS ESI+): calcd. for $C_{48}H_{49}N_3F_3$ $[M + H]^+$ 724.3879; found 724.3880.

4-({9,9-Dihexyl-7-[(4-nitrophenyl)ethynyl]-9*H*-fluoren-2-yl}ethynyl)-*N*,*N*-dimethylaniline (12): A mixture of **8** (50 mg, 0.100 mmol, 1.0 equiv.) and *p*-nitroiodobenzene (25 mg, 0.1 mmol, 1.0 equiv.) was added to a solution of *i*Pr_2NH/THF (1:1 v/v, 2 mL). After degassing, CuI (0.4 mg, 0.002 mmol, 0.02 equiv.) and $[Pd(PPh_3)_4]$ (2.3 mg, 0.002 mmol, 0.02 equiv.) were introduced to the mixture. The resulting solution was stirred at 65 °C for 18 h. Distilled water (5 mL) was added, and the organic products were extracted with Et_2O (3× 10 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica (petroleum ether/EtOAc, 9:1) gave compound **12** (49 mg, 79%) as an orange solid; m.p. 91–93 °C. R_f = 0.56 (petroleum ether/EtOAc, 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 9.0 Hz, 2 H), 7.70 (d, *J* = 9.0 Hz, 2 H), 7.64–7.67 (m, 2 H), 7.50–7.56 (m, 4 H), 7.46 (d, *J* = 9.0 Hz, 2 H), 6.69 (d, *J* = 9.0 Hz, 2 H), 3.00 (s, 6 H), 1.97–2.02 (m, 4 H), 0.99–1.17 (m, 12 H), 0.77 (t, *J* = 7.0 Hz, 6 H), 0.56–0.64 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.3 (C_q), 151.2 (C_q), 150.2 (C_q), 146.9 (C_q), 142.1 (C_q), 139.6 (C_q), 134.5 (C_q), 132.9 (CH_{Ar}), 132.3 (CH_{Ar}), 131.2 (CH_{Ar}), 130.6 (CH_{Ar}), 126.2 (CH_{Ar}), 125.7 (CH_{Ar}), 123.8 (CH_{Ar}), 123.5 (C_q), 120.4 (C_q), 120.2 (CH_{Ar}), 120.1 (CH_{Ar}), 111.9 (CH_{Ar}), 110.0 (C_q), 96.2 (C_q), 91.5 (C_q), 88.4 (C_q), 88.0 (C_q), 55.4 (C_q), 40.5 (CH_2), 40.3 (CH_3), 31.7 (CH_2), 29.8 (CH_2), 23.9 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2926, 2847, 2194, 1601, 1520, 1465, 1367, 1337, 1192, 1120, 948, 816, 747, 692 cm^{-1}. HRMS (TOF MS ESI+): calcd. for $C_{43}H_{46}N_2O_2$ $[M + H]^+$ 622.3559; found 622,3574.

2-Azido-4,6-dimethylpyrimidine (13a) and 5,7-Dimethyltetrazolo-[1,5-*a*]pyrimidine (13b): $CuCl_2$ (79 mg, 0.588 mmol, 0.1 equiv.) was dissolved in EtOH (18 mL) to give a green solution, and then sodium ascorbate (104 mg, 0.588 mmol, 0.1 equiv.) was added. The resulting solution was stirred until the solution turned colorless. Then, pentane-2,4-dione (0.6 mL, 5.88 mmol, 1.0 equiv.) and 5-aminotetrazole (500 mg, 5.88 mmol, 1.0 equiv.) were added. The resulting mixture was stirred at room temp. for 12 h under argon. The solution was quenched with a saturated solution of NH_4Cl (20 mL), and the organic product was extracted with EtOAc (5× 40 mL). The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure to give a mixture of compounds **13a** and **13b** (719 mg, 81%) as a white solid that was kept at –20 °C. Data for **13a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 6 H, CH_3), 6.76 (s, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.9 (CH_3), 116.2 (CH_{Ar}), 161.7 (C_q), 169.3 (C_q) ppm. Data for **13b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.77 (s, 3 H, CH_3), 2.96 (s, 3 H, CH_3), 6.92 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.0 (CH_3), 25.5 (CH_3), 112.8 (CH_{Ar}), 144.7 (C_q), 155.1 (C_q), 169.3 (C_q) ppm.

4-({7-[1-(4,6-Dimethylpyrimidin-2-yl)-1*H*-1,2,3-triazol-4-yl]-9,9-dihexyl-9*H*-fluoren-2-yl}ethynyl)-*N*,*N*-dimethylaniline (14): A mixture of product **9** (50 mg, 0.100 mmol, 1.0 equiv.) and 2-azido-4,6-dimethylpyrimidine **13** (16 mg, 0.110 mmol, 1.1 equiv.) was added to a solution of *t*BuOH/H_2O (1:1 v/v, 1 mL). Sodium ascorbate (5.94 mg, 0.03 mmol, 0.3 equiv.) and $CuSO_4 \cdot 5H_2O$ (3.75 mg, 0.015 mmol, 0.15 equiv.) were added to the solution. The resulting mixture was stirred at 65 °C for 12 h. Then, NH_4OH (6 mL) was added at room temp., and the organic products were extracted with EtOAc (3× 15 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica (EtOAc) gave compound **14** (35 mg, 53%) as a pale yellow solid; m.p. 166–168 °C. R_f = 0.80 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.89 (s, 1 H), 7.97 (s, 1 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* = 9.0 Hz, 1 H), 7.51–7.52 (m, 2 H), 7.46 (d, *J* = 9.0 Hz, 2 H), 7.12 (s, 1 H), 6.69 (d, *J* = 9.0 Hz, 2 H), 3.01 (s, 6 H), 2.65 (s, 6 H), 2.00–2.07 (m, 4 H), 1.03–1.33 (m, 12 H), 0.74 (t, *J* = 7.0 Hz, 6 H), 0.59–0.64 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.8 (C_q), 154.1 (C_q), 151.8 (C_q), 151.1 (C_q), 150.1 (C_q), 148.5 (C_q), 141.2 (C_q), 140.3 (C_q), 132.8 (CH_{Ar}), 130.4 (CH_{Ar}), 129.0 (C_q), 125.7 (CH_{Ar}), 125.1 (CH_{Ar}), 122.7 (C_q), 120.4 (CH_{Ar}), 120.3 (CH_{Ar}), 119.9 (CH_{Ar}), 119.8 (CH_{Ar}), 118.6 (CH), 111.9 (CH_{Ar}), 110.1 (C_q), 91.0 (C_q), 88.6 (C_q), 55.5 (C_q), 40.6 (CH_2), 40.3 (CH_3), 31.7 (CH_2), 29.8 (CH_2), 24.2 (CH_3), 23.9 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2925, 2851, 1600, 1524, 1467, 1440, 1412, 1345, 1229, 1199, 1019, 945, 823, 806, 780, 756, 656, 623 cm^{-1}. HRMS (TOF MS ESI+): calcd. for $C_{43}H_{51}N_6$ $[M + H]^+$ 651.4175; found 651.4190.

[(7-Bromo-9,9-dihexyl-9*H*-fluoren-2-yl)ethynyl]trimethylsilane (15): A mixture of 2-bromo-9,9-dihexyl-7-iodo-9*H*-fluorene (**1**, 500 mg, 0.926 mmol, 1.0 equiv.) and trimethylsilylacetylene (0.926 mmol, 1.0 equiv.) was added to a solution of *i*Pr_2NH/THF (1:1 v/v, 4 mL). After degassing, CuI (3.6 mg, 0.019 mmol, 0.02 equiv.) and $[Pd(PPh_3)_4]$ (22.0 mg, 0.019 mmol, 0.02 equiv.) were introduced to

the mixture. The resulting solution was stirred at room temp. for 12 h. Distilled water (10 mL) was added, and the organic products were extracted with EtOAc (3× 15 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica (petroleum ether) gave compound **15** (305 mg, 65%) as a yellow viscous oil; R_f = 0.58 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, J = 7.5 Hz, 1 H), 7.53 (d, J = 9.0 Hz, 1 H), 7.42–7.47 (m, 4 H), 1.90–1.95 (m, 4 H), 1.02–1.26 (m, 12 H), 0.78 (t, J = 7.5 Hz, 6 H), 0.49–0.60 (m, 4 H), 0.29 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.4 (C_q), 152.7 (C_q), 150.4 (C_q), 140.6 (C_q), 139.5 (CH_{Ar}), 131.4 (CH_{Ar}), 130.2 (CH_{Ar}), 126.3 (CH_{Ar}), 121.9 (C_q), 121.7 (C_q), 121.5 (CH_{Ar}), 119.7 (CH_{Ar}), 106.1 (C_q), 94.4 (C_q), 55.6 (C_q), 40.4 (CH_2), 31.7 (CH_2), 29.8 (CH_2), 23.8 (CH_2), 22.8 (CH_2), 0.2 (CH_2) ppm. HRMS (TOF MS APCI+): calcd. for $C_{30}H_{41}SiBr$ $[M + H]^+$ 508.2161; found 508.2179.

({9,9-Dihexyl-7-[(triisopropylsilyl)ethynyl]-9*H*-fluoren-2-yl}ethynyl)trimethylsilane (16): A mixture of **15** (0.280 g, 0.549 mmol, 1.0 equiv.) and triisopropylsilylacetylene (190 μL, 0.824 mmol, 1.5 equiv.) was added to a solution of iPr_2NH/DMF (1:1 v/v, 2 mL). After degassing, CuI (2.1 mg, 0.011 mmol, 0.02 equiv.) and $[Pd(PPh_3)_4]$ (12.7 mg, 0.011 mmol, 0.02 equiv.) were introduced to the mixture. The resulting solution was stirred at room temp. for 12 h. Distilled water (10 mL) was added, and the organic product was extracted with EtOAc (3× 15 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica (pentane) gave compound **16** (0.266 g, 79%) as a white solid; m.p. 144–146 °C. R_f = 0.44 (pentane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59–7.62 (m, 2 H), 7.42–7.49 (m, 4 H), 1.94–1.99 (m, 4 H), 1.19 (s, 18 H), 1.04–1.15 (m, 15 H), 0.79 (t, J = 6.9 Hz, 6 H), 0.56–0.63 (m, 4 H), 0.30 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.1 (C_q), 151.0 (C_q), 141.0 (C_q), 140.8 (C_q), 131.6 (CH_{Ar}), 131.4 (CH_{Ar}), 126.4 (CH_{Ar}), 126.2 (CH_{Ar}), 122.5 (C_q), 121.9 (C_q), 119.9 (CH_{Ar}), 108.2 (C_q), 106.3 (C_q), 94.3 (C_q), 90.7 (C_q), 55.4 (C_q), 40.4 (CH_2), 31.7 (CH_2), 29.8 (CH_2), 23.7 (CH_2), 22.8 (CH_2), 18.9 (CH), 14.2 (CH_3), 11.6 (CH_3), 0.2 (CH_3) ppm. HRMS (TOF MS APCI+): calcd. for $C_{41}H_{63}Si_2$ $[M + H]^+$ 611.4468; found 611.4468.

[(7-Ethynyl-9,9-dihexyl-9*H*-fluoren-2-yl)ethynyl]triisopropylsilane (17): A solution of **16** (240 g, 0.392 mmol, 1.0 equiv.) and K_2CO_3 (272 mg, 1.960 mmol, 5.0 equiv.) were added to a solution of THF (8 mL) and MeOH (8 mL) under argon. The mixture was stirred at room temp. for 16 h. K_2CO_3 was removed by filtration, and the filter cake was washed with CH_2Cl_2. The solvents were evaporated under reduce pressure to give the crude product. Purification by flash column chromatography on silica (petroleum ether) gave compound **17** (170 mg, 80%) as a yellow oil; R_f = 0.30 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (m, 2 H), 7.46–7.49 (m, 2 H), 7.45 (s, 1 H), 7.39 (s, 1 H), 3.15 (s, 1 H), 1.91–1.97 (m, 4 H), 1.17 (s, 18 H), 0.97–1.12 (m, 15 H), 0.77 (t, J = 7.0 Hz, 6 H), 0.56–0.60 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.1 (C_q), 151.06 (C_q), 141.2 (C_q), 140.6 (C_q), 131.5 (CH_{Ar}), 131.3 (CH_{Ar}), 126.6 (CH_{Ar}), 126.2 (CH_{Ar}), 122.5 (C_q), 121.8 (C_q), 120.0 (CH_{Ar}), 119.9 (CH_{Ar}), 108.1 (C_q), 90.8 (C_q), 84.7 (C_q), 77.4 (C_q), 55.3 (C_q), 40.3 (CH_2), 31.0 (CH_2), 29.7 (CH_2), 23.7 (CH_2), 22.7 (CH_2), 18.8 (CH), 14.1 (CH_3), 11.5 (CH_3) ppm. HRMS (TOF MS APCI+): calcd. for $C_{38}H_{55}Si$ $[M + H]^+$ 539.4073; found 539.4065.

4-(4-{9,9-Dihexyl-7-[(triisopropylsilyl)ethynyl]-9*H*-fluoren-2-yl}-1*H*-1,2,3-triazol-1-yl)-*N*,*N*-dimethylaniline (18): [(7-Ethynyl-9,9-dihexyl-9*H*-fluoren-2-yl)ethynyl]triisopropylsilane (**17**, 208 mg, 0.39 mmol, 1.0 equiv.) and 4-azido-*N*,*N*-dimethylaniline (70 mg, 0.43 mmol, 1.1 equiv.) were introduced to a mixture of *t*BuOH/H_2O (1:1 v/v, 3 mL). Sodium ascorbate (23 mg, 0.12 mmol, 0.3 equiv.) and $CuSO_4$·5H_2O (15 mg, 0.06 mmol, 0.15 equiv.) were added, and the resulting mixture was stirred at 65 °C for 12 h. Then, NH_4OH was added (6 mL), and the organic products were extracted with EtOAc (3× 10 mL). The combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica (petroleum ether/EtOAc, 9:1) gave compound **18** (186 mg, 68%); R_f = 0.23 (petroleum ether/EtOAc, 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.98 (s, 1 H), 7.81 (dd, J = 1.0, 8.0 Hz, 1 H), 7.72 (d, J = 8.0 Hz, 1 H), 7.63–7.59 (m, 3 H), 7.48 (dd, J = 1.0, 8.0 Hz, 1 H), 7.43 (br. s, 1 H), 6.77 (d, J = 9 Hz); 3.01 (s, 6 H), 2.06–1.99 (m, 4 H), 1.18 (s, 18 H), 1.14–0.90 (m, 15 H), 0.75 (t, J = 7.0 Hz, 6 H), 0.63–0.66 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.0 (C_q), 151.0 (C_q), 150.7 (C_q), 148.5 (C_q), 141.2 (C_q), 140.7 (C_q), 131.5 (CH_{Ar}), 129.9 (C_q), 126.9 (C_q), 126.2 (CH_{Ar}), 124.8 (CH_{Ar}), 122.1 (CH_{Ar}), 122.0 (C_q), 121.5 (CH_{Ar}), 120.2 (CH_{Ar}), 119.6 (CH_{Ar}), 118.0 (CH), 112.4 (CH_{Ar}), 108.3 (C_q), 90.5 (C_q), 55.5 (C_q), 40.6 (CH_3), 40.5 (CH_2), 31.6 (CH_2), 29.8 (CH_2), 23.8 (CH_2), 22.7 (CH_2), 18.9 (CH), 14.1 (CH_3), 11.6 (CH_3) ppm. HRMS (TOF MS ESI+): calcd. for $C_{46}H_{65}N_4Si$ $[M + H]^+$ 701.4979; found 701.4968.

4-[4-(7-Ethynyl-9,9-dihexyl-9*H*-fluoren-2-yl)-1*H*-1,2,3-triazol-1-yl]-*N*,*N*-dimethylaniline (19): 4-(4-{9,9-dihexyl-7-[(triisopropylsilyl)ethynyl]-9*H*-fluoren-2-yl}-1*H*-1,2,3-triazol-1-yl)-*N*,*N*-dimethylaniline (**18**, 186 mg, 0.27 mmol, 1.0 equiv.) and tetra-*n*-butylammonium fluoride (1 M in THF, 0.45 mL, 0.45 mmol, 1.06 equiv.) were introduced to THF (27 mL) under argon. After 12 h of stirring at room temp., the solvent was evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica (petroleum ether/EtOAc, 6:4) gave compound **19** (129 mg, 88%); R_f = 0.60 (petroleum ether/EtOAc, 6:4). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.97 (s, 1 H), 7.83 (d, J = 8.0 Hz, 1 H), 7.74 (d, J = 8.0 Hz, 1 H), 7.64 (dd, J = 9.0, 8.5 Hz, 3 H), 7.48–7.51 (m, 2 H), 6.80 (d, J = 9.0 Hz, 2 H), 3.16 (s, 1 H), 3.04 (s, 6 H), 2.10–1.93 (m, 4 H), 1.13–0.97 (m, 12 H), 0.75 (t, J = 7.0 Hz, 6 H), 0.68–0.54 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.0 (C_q), 151.1 (C_q), 150.8 (C_q), 148.4 (C_q), 141.7 (C_q), 140.5 (C_q), 131.3 (CH_{Ar}), 130.1 (C_q), 126.9 (C_q), 126.6 (CH_{Ar}), 124.8 (CH_{Ar}), 122.6 (CH_{Ar}), 122.2 (CH_{Ar}), 120.4 (C_q), 120.2 (CH_{Ar}), 119.8 (CH_{Ar}), 118.0 (CH), 112.5 (CH_{Ar}), 84.9 (C_q), 77.4 (C_q), 55.5 (C_q), 40.64 (CH_3), 40.56 (CH_2), 31.7 (CH_2), 29.8 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. HRMS (TOF MS ESI+): calcd. for $C_{37}H_{45}N_4$ $[M + H]^+$ 545.3644; found 545.3660.

4-(4-{7-[1-(4,6-Dimethylpyrimidin-2-yl)-1*H*-1,2,3-triazol-4-yl]-9,9-dihexyl-9*H*-fluoren-2-yl}-1*H*-1,2,3-triazol-1-yl)-*N*,*N*-dimethylaniline (20): A mixture of 4-[4-(7-ethynyl-9,9-dihexyl-9*H*-fluoren-2-yl)-1*H*-1,2,3-triazol-1-yl]-*N*,*N*-dimethylaniline (**19**, 129 mg, 0.237 mmol, 1.0 equiv.) and 2-azido-4,6-dimethylpyrimidine (**13**, 44.7 mg, 0.300 mmol, 1.1 equiv.) was added to a solution of *t*BuOH/H_2O (1:1 v/v, 1 mL). Sodium ascorbate (14.1 mg, 0.07 mmol, 0.30 equiv.) and $CuSO_4$·5 H_2O (9.0 mg, 0.036 mmol, 0.15 equiv.) were added to the solution. The resulting mixture was stirred at 65 °C for 3 d. Then, NH_4OH was added (6 mL), and the organic products were extracted with EtOAc (3× 15 mL). The combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure to give a yellow residue. Purification by flash column chromatography on silica (petroleum ether/EtOAc, 5:5) gave compound **20** (138 mg, 85%) as a pale yellow solid; m.p. 235–237 °C. R_f = 0.4 (petroleum ether/EtOAc, 5:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.87 (s, 1 H), 8.15 (s, 1 H), 7.99 (s, 1 H), 7.90 (d, J = 8.0 Hz, 1 H),

7.77 (d, J = 9.0 Hz, 1 H), 7.75–7.72 (m, 2 H), 7.69 (d, J = 9.0 Hz, 2 H), 7.08 (s, 1 H), 6.77 (d, J = 9.0 Hz, 2 H), 3.00 (s, 6 H), 2.61 (s, 6 H), 2.12–2.06 (m, 4 H), 1.11–0.99 (m, 12 H), 0.73–0.66 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.8 (C_q), 154.1 (C_q), 151.9 (C_q), 151.8 (C_q), 150.6 (C_q), 148.5 (C_q), 141.3 (C_q), 140.8 (C_q), 129.6 (C_q), 129.0 (C_q), 126.8 (C_q), 125.1 (CH_{Ar}), 124.7 (CH_{Ar}), 122.0 (CH_{Ar}), 120.4 (CH_{Ar}), 120.3 (C_q), 120.2 (CH_{Ar}), 119.8 (CH_{Ar}), 118.5 (CH_{Ar}), 117.9 (CH_{Ar}), 112.4 (CH_{Ar}), 55.6 (C_q), 40.6 (CH_3), 40.5 (CH_2), 31.6 (CH_2), 29.8 (CH_2), 24.1 (CH_3), 23.9 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2955, 2927, 2855, 1602, 1529, 1439, 1348, 1232, 1023, 817 cm^{-1}. HRMS (TOF MS ESI+): calcd. for $C_{43}H_{51}N_9$ $[M + H]^+$ 694.4346; found 694.4338.

Supporting Information (see footnote on the first page of this article): Characterization data, ^{1}H and ^{13}C NMR spectra, UV/Vis absorption, excitation spectra.

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