End-Capped, Conjugated (Dimethylamino)naphthyl Nanostructures with Alternating (1-Naphthylethynyl-*p*-phenylethynyl)$_x$ Branches on a 1,3,5-Substituted Benzene Core

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Alternating (1-naphthylethynyl-*p*-phenylethynyl)$_x$ 1,3,5-trisubstituted benzene dendrons were efficiently synthesised by the heterocoupling reaction between (1-naphthylethynyl-*p*-phenyl)$_x$acetylene (x = 1) and 1,3,5-triiodobenzene in the presence of a palladium-copper catalyst system. A longer terminal acetylene chain (x = 2) was obtained from the heterocoupling between 1,3,5-tri(1-ethynyl-5-naphthylethynyl)benzene and the appropriate iodoaryl derivative. The alternating chains, and their dendron structures, show fluorescence emission, with similar wavelengths and quantum yields.

Introduction

The synthesis and characterization of nanometer-sized conjugated molecules of precise length and constitution is of widespread interest due to their inherent synthetic flexibility, which permits the design of molecular architectures with important properties.[1,2] Molecules showing π-extended conjugation, in general, have interesting electronic, magnetic and optical properties.[3] A variety of potential applications, such as artificial photosynthesis,[4] photocatalysis,[5] molecular photovoltaic cells,[6] molecular informatics[7] and optoelectronic devices,[8,9] are beginning to emerge from this new field of research.

Conjugated systems integrated by 1,4-diethynyl or 1,3,5-triethynylphenyl units have been used in the preparation of aromatic oligomers bearing multiple ethynyl groups that exhibit electroluminescence properties,[10] poly(phenylvinylene) with fluorescence properties, as well as dendrimers[11] with a poly(yne) chain.[12] The triple bonds in these systems play the role of a wire while the polyaromatic systems behave as an energy-relay subunit.

Linear 1,4-phenylethynyl conjugated nanostructures show fluorescence radiation emission with excellent quantum yields.[13] Moreover, 1,5-bis(*p*-phenylethynyl)naphthalene also shows excellent quantum yields for the fluorescent emission.[14] Conjugated 1,5-naphthylethynyl nanostructures have also been synthesized with end-capped nitro or dimethylamino groups. The end-capped dimethylamino group on the conjugated chain increases the solubility of the compound.[15]

We report here the synthesis of dendron nanostructures with an alternating 1,5-naphthylethynylphenyl unit and the analysis of the fluorescence properties of the chains.

Results and Discussion

The synthesis of alternating (1-naphthylethynyl-*p*-phenylethynyl)$_x$ chains designed to be the branches of the 1,3,5-substituted benzene dendron structures was carried out by heterocoupling between the appropriate terminal acetylene and the iodoarene, in the presence of a palladium-copper catalyst. Thus, the terminal acetylene *p*-[5-(dimethylamino)naphthyl-1-ethynyl]phenylacetylene (**3**) was obtained by the heterocoupling reaction between 1-(dimethylamino)-5-ethynylnaphthalene (**1**) and 4-(*p*-iodophenyl)-2-methyl-3-butyn-2-ol in the presence of dichlorobis(triphenylphosphane)palladium(II) and cuprous iodide in freshly distilled triethylamine, under a rigorous carbon dioxide atmosphere,[16] to give 4-(4-{[5-(dimethylamino)-1-naphthyl]ethynyl}-1-phenyl)-2-methyl-3-butyn-2-ol (**2**) as a yellow solid in excellent yield (96%; Scheme 1). The homocoupling product 1,4-bis[5-(dimethylamino)-1-naphthyl]buta-1,3-diyne was obtained as a minor product (2%). Compound **2** was treated with a catalytic amount of powdered sodium hydroxide in dry toluene at reflux to obtain the naphthylethynylphenylacetylene **3**, in practically quantitative yield, as a white solid.

The terminal naphthylacetylene homologue **5** was satisfactorily obtained from the heterocoupling reaction between the terminal acetylene **3** and 4-(5-iodo-1-naphthyl)-2-methyl-3-butyn-2-ol, catalysed by the same palladium-copper system in freshly distilled triethylamine, under argon, to yield **4** in good yield (91%),as a pale-brown solid.

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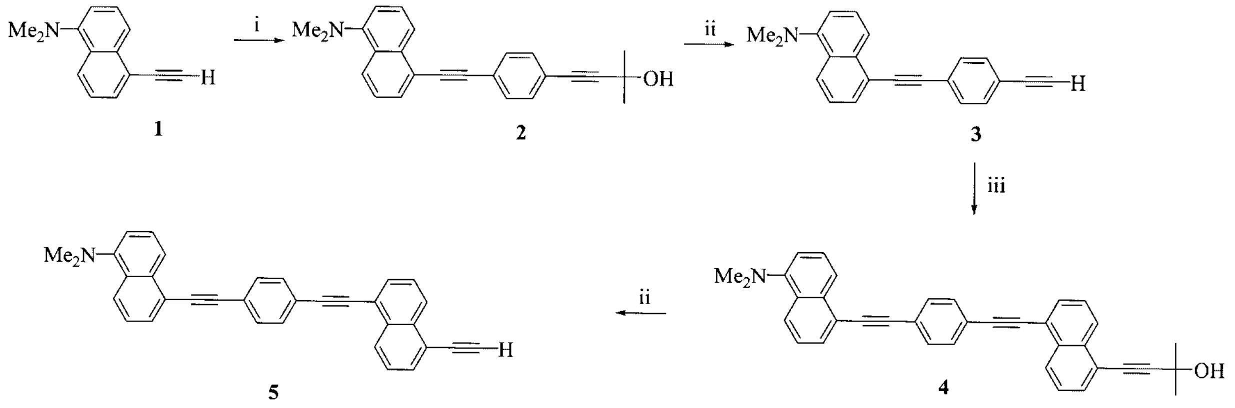


Scheme 1. (i) [$PdCl_2(PPh_3)_2$], Cu_2I_2, NEt_3, 4-(*p*-iodophenyl)-2-methyl-3-butyn-2-ol, CO_2 atmosphere; (ii) NaOH, toluene, reflux; (iii) [$PdCl_2(PPh_3)_2$], Cu_2I_2, NEt_3, 4-(5-iodo-1-naphthyl)-2-methyl-3-butyn-2-ol

Compound **4** was treated with a catalytic amount of powdered sodium hydroxide in dry toluene, at reflux, to give the terminal acetylene **5** as a yellow solid in practically quantitative yield (Scheme 1).

An interesting matter was the structural analysis of the alternating conjugated chain showed in **5**. Recently, we demonstrated that conjugated naphthylethynyl chains connect sequentially through their *anti* rotamers.[15] A structural analysis to determine the relative position of the naphthylethynyl rings along the chain with a *p*-phenylethynyl spacer unit was therefore undertaken. Unfortunately it was not possible to isolate good-quality crystals of compound **5**; however, the picrate derivative (green solid, dichloromethane) gave prismatic crystals suitable for the X-ray diffraction analysis.[17] The molecular structure of the picrate and the X-ray numbering scheme are shown in Figure 1.

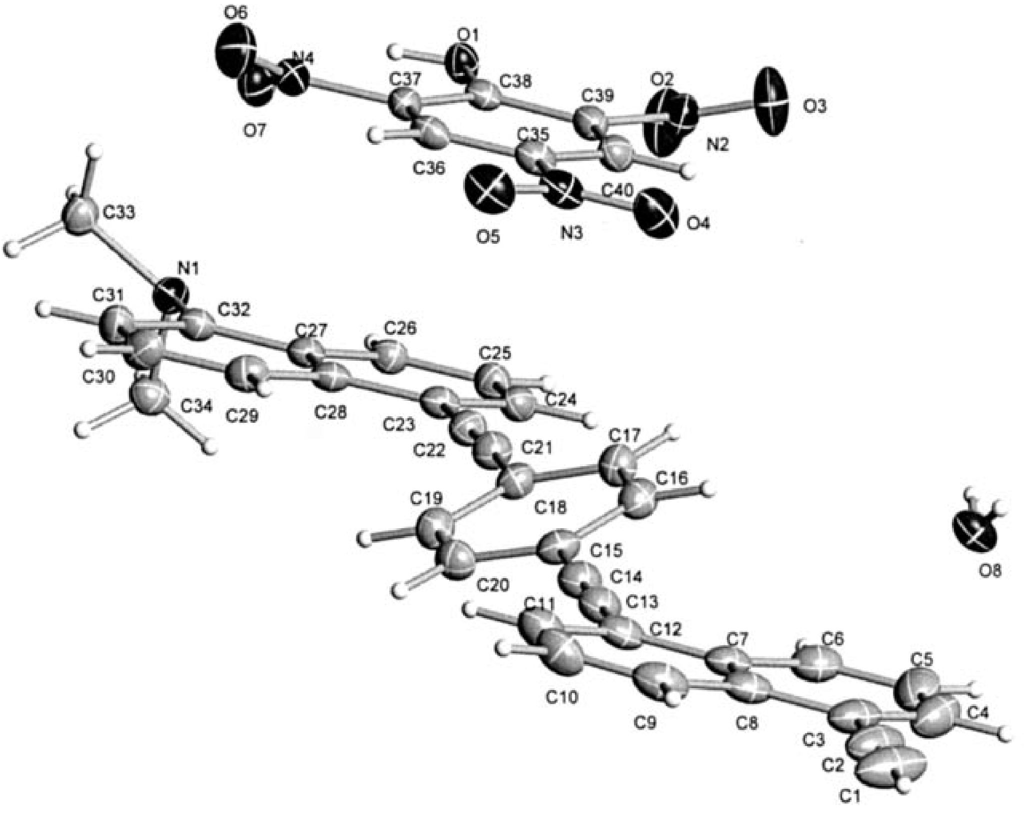


Figure 1. Molecular structure of the picrate complex of **5** (1:1 complex)

The structure of the picrate monohydrate in the solid state confirms that both 1,5-naphthylethynyl rings are present as their *anti* rotamers relative to the acetylene axis (Figure 1). Thus, the molecular structure of the picrate **5** shows the association of one picric acid monohydrate molecule with the 5-(dimethylamino)naphthalene ring. The projection along the *a* axis (Figure 2) shows that the picric acid moiety overlaps the less sterically hindered portion of the 5-(dimethylamino)naphthalene ring; this causes the green colour of the crystals. The projection of the molecule along the *b* axis shows that the two 1,5-naphthalene rings with a *p*-diethynylphenyl spacer unit are not planar (Figure 1). Both naphthalene rings are practically planar and show a deviation angle of 1.5°. However, the benzene ring of the spacer unit, shows with both the 5-(dimethylamino)-naphthalene and the terminal naphthyl ethyne rings, the same deviation angle of 28.6°.

The mean picric acid plane and the associated (dimethylamino)naphthalene plane show a deviation angle of 4.0°; the interplanar contact distance is 3.45 Å, in good agreement with other naphthalene charge-transfer complexes.[18] Furthermore, the picrate complex of **5** has only one picric acid unit linked to the naphthalene ring in the crystal. The 1,2-ethynylene bond lengths show some differences: that linked to the complexed ring [C21−C22: 1.207(3) Å] is slightly longer than C13−C14 [1.199(3) Å]; the terminal acetylene bond length C1−C2 is the shortest [1.192(3)]. The average C−C bond lengths in the benzene spacer ring have the normal value of 1.391(3) Å. The free naphthalene ring shows the typical bond lengths, although the naphthalene distance C23−C24 [1.379(3) Å] is longer than C25−C26, which shows the typical value of 1.363(3) Å.

The terminal acetylene **7** (the phenylethynyl homologue of **5**) was obtained by heterocoupling between the acetylene **5** and 4-(*p*-iodophenyl)-2-methyl-3-butyn-2-ol in triethylamine, in the presence of the palladium-copper system, which gave the propargylic intermediate **6** as a yellow solid in good yield (90%; Scheme 2). The terminal acetylene **6** was then treated with a catalytic amount of powdered sodium hydroxide in dry toluene at reflux to give the terminal acetylene **7** quantitatively as a yellow solid.

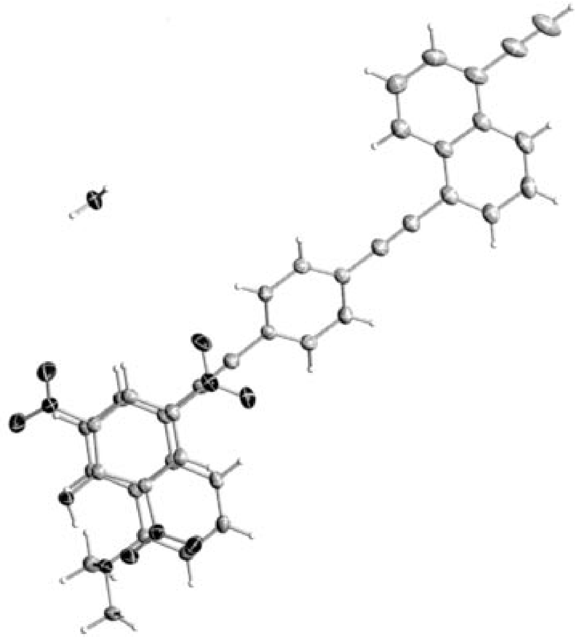
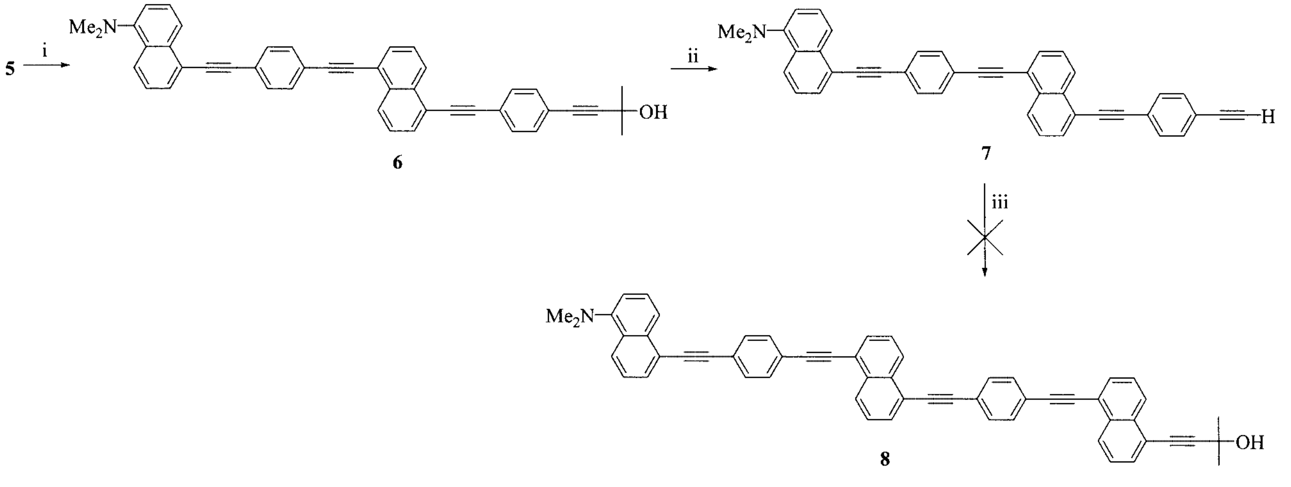


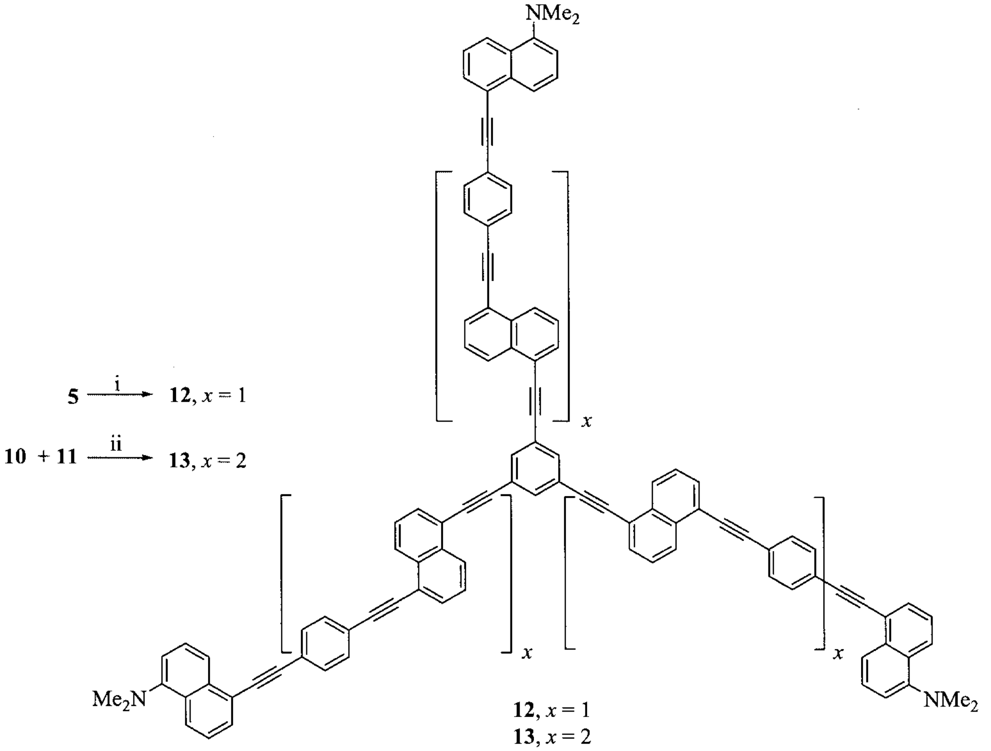
Figure 2. Molecular projection of the picrate complex of **5** along the *a* axis

The synthesis of the dimethylamino end-capped dendron structures such as **12** ($x = 1$) was satisfactorily carried out by heterocoupling between the terminal alternating acetylene **5** and 1,3,5-triiodobenzene,[19] in triethylamine, under an argon atmosphere, in the presence of the palladium-copper catalyst system. Compound **12** was isolated as an orange solid in good yield (80%; Scheme 3).

However, the convergent synthesis of molecular networks frequently means that the heterocoupling between the corresponding haloarene and a large terminal acetylene chain catalysed by the palladium-copper system may become ineffective. Thus, the synthesis of **8** by the heterocoupling of the large terminal acetylene **7** and 4-(5-iodo-1-naphthyl)-2-



Scheme 2. (i) [PdCl$_2$(PPh$_3$)$_2$], Cu$_2$I$_2$, NEt$_3$, 4-(*p*-iodophenyl)-2-methyl-3-butyn-2-ol; (ii) NaOH, toluene, reflux; (iii) [PdCl$_2$(PPh$_3$)$_2$], Cu$_2$I$_2$, NEt$_3$, 4-(5-iodo-1-naphthyl)-2-methyl-3-butyn-2-ol



Scheme 3. (i) [PdCl$_2$(PPh$_3$)$_2$], Cu$_2$I$_2$, NEt$_3$, 1,3,5-triiodobenzene; (ii) [PdCl$_2$(PPh$_3$)$_2$], Cu$_2$I$_2$, NEt$_3$

methyl-3-butyn-2-ol, or the alternative way between **7** and 1,5-diiodonaphthalene, followed by treatment with 1,3,5-tri(ethynyl)benzene, failed under the conditions used for the preparation of **4**; under more drastic conditions in pyridine or quinoline as the base, at reflux, the results were also ineffective. A possible interpretation of this fact could be the difficulty in incorporating the acetylene into the coordination sphere of the palladium complex in a Sonogashira-type mechanism.[20]

A fruitful alternative for the synthesis of dendron **13** consists in the heterocoupling of the shortest terminal acetylene chain with the largest chain of the haloarene, although the terminal acetylene compound has three reactive acetylene groups. Thus, dendron **13** (x = 2) was obtained from the heterocoupling reaction between 1,3,5-tri(1-ethynyl-5-naphthylethynyl)benzene (**10**) and the iodoarene **11**, in the presence of the palladium-copper catalyst system, as a yellow solid in good yield (74%; Scheme 4).

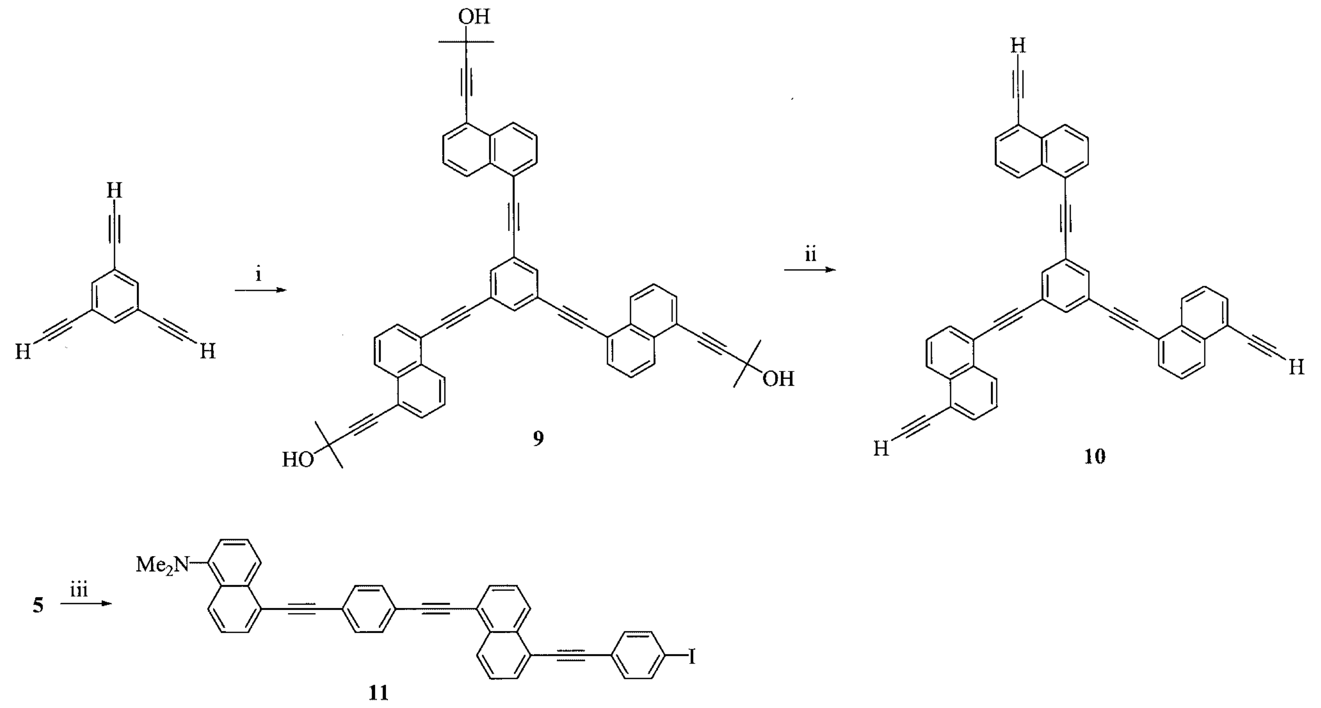
On the basis of the spectroscopic data, the conjugated compounds **5** and **7** display an *anti*-rotamer structure for the naphthalene rings, which, by analogy, can also be proposed for the branches in **12** and **13**.

The terminal triacetylene **10** was obtained from the heterocoupling reaction between 1,3,5-tri(ethynyl)benzene and 4-(5-iodo-1-naphthyl)-2-methyl-3-butyn-2-ol, in the presence of the palladium-copper catalyst system, to give the propargylic intermediate **9**, as a dark-yellow oil, in good yield (83%). This compound was then treated with a catalytic amount of powdered sodium hydroxide in dry toluene at reflux to yield the terminal acetylene **10** quantitatively as a pale-yellow solid. Compound **10** shows very poor solubility in organic solvents (Scheme 4).

The iodoarene **11** was satisfactorily obtained, as a yellow solid in good yield (91%), from the heterocoupling reaction between the acetylene **5** and *p*-diiodobenzene catalysed by the palladium-copper system (Scheme 4).

The UV/Vis absorption and fluorescence-emission spectra of the terminal acetylene units **1**, **3**, **5** and **7** and the dendrons **12** and **13** are summarized in Table 1.

The absorption spectrum of the terminal naphthylacetylene unit **1** shows a λ_{max} at 336 nm with a low ε value. However, **1** shows a fluorescence emission band at λ_{max} = 463 nm with a significant quantum yield (63%). The conjugated phenylethynyl and naphthylethynyl compounds **3** and **5** show a bathochromic effect of the absorption band (λ_{max} = 354 and 364 nm respectively) and a considerable increment of the molar extinction coefficient (ε) with the molecular conjugation. Moreover, compounds **5** and **7** and their related dendron structures **12** and **13** show similar λ_{max} absorption values, although for the terminal phenylacetylene **7** the ε value diminishes with respect to that of **5**. The ε values for the dendron structures **12** and **13** show an expected important increment. The λ_{max} and the quantum yield[21] of the fluorescence emission radiation vary with the conjugated chain size. Thus, by incorporation of a phenylethynyl unit (**1** and **3**) a strong bathochromic effect on the λ_{max} of the emission and a strong decrease in the quantum yield were observed. The same effect, but of more moderate intensity, was observed for all the conjugated compounds with an increase of the conjugated chain size. However, the



Scheme 4. (i) $[PdCl_2(PPh_3)_2]$, Cu_2I_2, NEt_3, 4-(5-iodo-1-naphthyl)-2-methyl-3-butyn-2-ol; (ii) NaOH, toluene, reflux; (iii) $[PdCl_2(PPh_3)_2]$, Cu_2I_2, NEt_3, *p*-diiodobenzene

Table 1. UV/Vis and fluorescence spectra (λ_{exc} = 365 nm) of the terminal acetylenes and dendrons **12** and **13**

Compound	UV/Vis[a](CH_2Cl_2) λ_{max} (nm)	ε ($M^{-1}\cdot cm^{-1}$)	F[b] (CH_2Cl_2) λ_{max} (nm)	Φ_f[c]
1	336	2203	463	0.63
3	354	18300	510	0.32
5	364	69450	526	0.20
7	364	47600	527	0.24
12	366	102900	527	0.18
13	367	210700	530	0.16

[a] At room temperature. [b] At room temperature; concentration:$\cdot 10^{-8}$ M. [c] Fluorescence quantum yield was measured in dichloromethane relative to quinine sulfate in 1 N H_2SO_4.

terminal phenylacetylene **7** shows practically the same λ_{max} of the emission as that of **12** or **13**, although the quantum yield increases slightly.

The dendron structures **12** and **13** and the terminal naphthylacetylene show similar λ_{max} values and quantum-yield parameters for the emission radiation (Table 1).

The large Stokes shift (1587 cm^{-1} for **5**) and the decrease in fluorescence can be explained by intramolecular charge transfer (ICT) or twisted ICT (TICT) interactions due to the presence of the dimethylamino group.[22]

Conclusion

The synthesis of the dendron **12** was carried out by the heterocoupling reaction between **5** and 1,3,5-triiodobenzene in the presence of a palladium-copper catalyst system. The synthesis of the terminal acetylene **8** by the heterocoupling reaction between the large terminal acetylene **7** and 4-(5-iodo-1-naphthyl)-2-methyl-3-butyn-2-ol, or the alternative way between **7** and 1,5-diiodonaphthalene, followed by treatment with 1,3,5-tri(ethynyl)benzene, failed under the same conditions as for the preparation of **4**, and even under more drastic conditions. However, the heterocoupling of the shortest terminal acetylene chain **10** with the largest chain of the haloarene **11** gave the dendron **13** (x = 2) in good yield.

On the basis of the X-ray structure of the picrate derivative of **5**, and from its spectroscopic data, the alternating conjugated compounds (**5**, **7**, **12** and **13**) display an *anti*-rotamer structure for the naphthalene rings.

The alternating chains and their dendron structures show a fluorescence emission radiation with similar wavelengths and quantum yields. Large Stokes shifts and a decrease in the fluorescence quantum yield were observed for the end-capped dimethylamino alternating conjugated systems; this can be explained by ICT or TICT interactions due to the presence of the NMe_2 group.

Experimental Section

General: Melting points were determined in open capillaries using a Buchi or Reichert hot-stage microscope and are uncorrected. IR spectra of solids were recorded as KBr pellets and IR spectra of oils were recorded as thin films on NaCl plates with a Bruker Vector 22 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Bruker Aspect spectrometer. Chemical shifts are given with respect to TMS as an internal reference and coupling constants, *J*, are given in Hz; the solvent was $CDCl_3$. Mass spectra were recorded on a VG AutoSpec spectrometer at 70 eV and the MALDI-TOF spectra were recorded on a Bruker Reflex III spectrometer. The UV/Vis spectra were recorded on a Hewlett Packard 8453 spectrometer, frequencies are given in nm and absorption coefficients, ε, in $L\cdot mol^{-1}\cdot cm^{-1}$. All fluorescence spectra were recorded at room temperature at a concentration of 10^{-8} M on an SLM Aminco Bowman series 2. The fluorescence quantum yield was determined in dichloromethane on freshly prepared samples (air-equilibrated) with absorbances at the excitation wavelength (365 nm). Quinine sulfate in 1 N H_2SO_4 was employed as a standard ($\Phi_f = 0.55$) to measure the fluorescence quantum yields, which were corrected by taking into account the refractive indices of the solvents used. Yields are given after chromatographic column separation on silica gel 60 (200–400 mesh) using the indicated solvents, or after crystallization.

4-(4-{[5-(Dimethylamino)-1-naphthyl]ethynyl}-1-phenyl)-2-methyl-3-butyn-2-ol (2): A dispersion of **1** (200 mg, 1.03 mmol), 4-(*p*-iodophenyl)-2-methyl-3-butyn-2-ol (295 mg, 1.03 mmol), freshly distilled triethylamine (30 mL), $[PdCl_2(PPh_3)_2]$ (72 mg, 0.10 mmol) and Cu_2I_2 (2 mg, 0.01 mmol) in dry, freshly distilled triethylamine was placed in a Schlenk. Then, dry-ice rods were added and maintained in slow sublimation until a dense white cloud had formed. The carbon dioxide atmosphere was slowly displaced by an external stream of carbon dioxide that had been bubbled through a triethylamine solution. The mixture was stirred at room temperature for 15 h (monitored by TLC). The triethylamine was then removed under reduced pressure. The crude residue was washed with a saturated aqueous ammonium chloride solution containing a small amount of KCN, and extracted with dichloromethane. The extracts were dried over anhydrous sodium sulfate and, after filtration, the solvent was removed to give a brown solid, which was purified by silica gel column chromatography, eluting with hexane/dichloromethane (1:4), to give **2** as a yellow solid. M.p. 100–102 °C, 350 mg (96%) yield. IR (KBr pellet): $\tilde{\nu}$ = 3384, 2925, 2227, 1407, 1151, 839, 784 cm^{-1}. ^{1}H NMR: δ = 1.68 (s, 6 H), 2.91 (s, 6 H), 7.13 (d, *J* = 7.5 Hz, 1 H), 7.46 (d, *J* = 8.4 Hz, 2 H), 7.47 (t, *J* = 7.2 Hz, 1 H), 7.54 (t, *J* = 7.8 Hz, 1 H), 7.61 (d, *J* = 8.4 Hz, 2 H), 7.78 (d, *J* = 6.3 Hz, 1 H), 8.19 (d, *J* = 8.1 Hz, 1 H), 8.31 (d, *J* = 8.4 Hz, 1 H) ppm. ^{13}C NMR: δ = 31.23, 45.15, 65.36, 81.72, 89.76, 93.58, 95.69, 114.50, 120.70, 120.74, 122.48, 123.18, 124.30, 125.17, 126.62, 128.51, 130.35, 131.31, 131.50, 134.46, 151.11 ppm. $C_{25}H_{23}NO$ (353.18): calcd. C 84.95, H 6.56, N 3.96; found C 84.80, H 6.72, N 4.10.

1-(Dimethylamino)-5-[(4-ethynyl-1-phenyl)ethynyl]naphthalene (3). General Procedure: Finely powdered sodium hydroxide (6 mg, 0.14 mmol) was added to a solution of **2** (500 mg, 1.42 mmol) in dry toluene (100 mL), under argon atmosphere; the mixture was heated to reflux temperature for 4 h (monitored by TLC), and then filtered. The solvent was removed under reduced pressure and the solid residue was purified by silica gel column chromatography, eluting with hexane/dichloromethane (1:1), to give **3** as a white solid. M.p. 69–71 °C, 417 mg (100%) yield. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 230 nm (30757 $M^{-1}\cdot cm^{-1}$), 262 (28938), 316 (22582), 354 (18300). IR (KBr pellet): $\tilde{\nu}$ = 3240, 2937, 2103, 1404, 841, 786 cm^{-1}. ^{1}H NMR: δ = 2.95 (s, 6 H), 3.31 (s, 1 H), 7.19 (d, *J* = 7.8 Hz, 1 H), 7.55 (t, *J* = 7.8 Hz, 1 H), 7.60 (d, *J* = 8.1 Hz, 2 H), 7.62 (t, *J* = 7.2 Hz, 1 H), 7.69 (d, *J* = 8.1 Hz, 2 H), 7.87 (d, *J* = 6.9 Hz, 1 H), 8.29 (d, *J* = 8.4 Hz, 1 H), 8.39 (d, *J* = 8.7 Hz, 1 H) ppm. ^{13}C NMR: δ = 45.09, 79.04, 83.28, 90.14, 93.45, 114.53, 120.70 (2 C), 121.74, 123.86, 124.31, 125.27, 126.73, 128.57, 130.44, 131.34, 131.97, 134.47, 151.18 ppm. MS (70 eV): *m*/*z* (%) = 295 (100) $[M^+]$, 294 (15), 278 (7), 265 (2), 252 (12), 147 (3), 125 (6). $C_{22}H_{17}N$ (295.14): calcd. C 89.46, H 5.80, N 4.74; found C 89.54, H 5.95, N 4.39.

4-{5-[(4-{[5-(Dimethylamino)-1-naphthyl]ethynyl}-1-phenyl)ethynyl]-1-naphthyl}-2-methyl-3-butyn-2-ol (4). General Procedure for the Cross-Coupling Reaction: Dichlorobis(triphenylphosphane)palladium(II) (48 mg, 0.068 mmol) and cuprous iodide (1.3 mg, 0.007 mmol) were added to a solution of compound **3** (200 mg, 0.68 mmol) and 4-(5-iodo-1-naphthyl)-2-methyl-3-butyn-2-ol (228 mg, 0.68 mmol) in freshly distilled triethylamine (40 mL), under argon atmosphere, at room temperature. The mixture was stirred for 10 h (monitored by TLC), and then the triethylamine was removed under reduced pressure. The crude residue was washed with a saturated aqueous ammonium chloride solution containing a small amount of KCN, and then extracted with dichloromethane. The extracts were dried over anhydrous sodium sulfate and, after filtration, the solvent was removed to give a brown solid, which was purified by silica gel column chromatography, eluting with hexane/ethyl acetate (2:1), to give **4** as a pale-brown solid. M.p. 157–159 °C, 310 mg (91%) yield. IR (KBr pellet): $\tilde{\nu}$ = 3263, 2981, 2220, 1410, 830, 784 cm^{-1}. ^{1}H NMR: δ = 1.75 (s, 6 H), 2.91 (s, 6 H), 7.14 (d, *J* = 6.3 Hz, 1 H), 7.58–7.45 (m, 4 H), 7.67 (s, 4 H), 7.72 (d, *J* = 7.2 Hz, 1 H), 7.77 (d, *J* = 6.9 Hz, 1 H), 7.82 (d, *J* = 6.9 Hz, 1 H), 8.15 (d, *J* = 8.4 Hz, 1 H), 8.29 (d, *J* = 9.0 Hz, 1 H), 8.32 (d, *J* = 8.7 Hz, 1 H), 8.44 (d, *J* = 8.7 Hz, 1 H) ppm. ^{13}C NMR: δ = 31.50, 45.34, 65.75, 80.30, 89.19, 90.17, 93.74, 94.47, 99.23, 114.63, 120.86 (2 C), 121.10 (2 C), 122.96, 123.60, 124.45, 125.34, 126.13 (2 C), 126.79, 126.99 (2 C), 128.71, 130.47, 130.98, 131.60 (3 C), 132.98, 133.10, 134.62, 151.36 ppm. $C_{37}H_{29}NO$ (503.22): calcd. C 88.24, H 5.80, N 2.78; found C 88.01, H 5.64, N 2.91.

1-(Dimethylamino)-5-({4-[(5-ethynyl-1-naphthyl)ethynyl]-1-phenyl}ethynyl)naphthalene (5): Following the general method used for the synthesis of **3**, a mixture of compound **4** (500 mg, 0.99 mmol), dry toluene (150 mL), and finely powdered sodium hydroxide (4 mg, 0.10 mmol) was stirred for 4 h and then filtered. The residual solid was purified by silica gel column chromatography, eluting with hexane/dichloromethane (1:1), to give **5** as a yellow solid. M.p. 125–127 °C, 440 mg (100%) yield. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 237 nm (97512 $M^{-1}\cdot cm^{-1}$), 364 (69450). IR (KBr pellet): $\tilde{\nu}$ = 3296, 2939, 2212, 2109, 1404, 838, 787 cm^{-1}. ^{1}H NMR: δ = 2.92 (s, 6 H), 3.53 (s, 1 H), 7.16 (d, *J* = 7.5 Hz, 1 H), 7.61–7.47 (m, 4 H), 7.68 (s, 4 H), 7.80 (d, *J* = 6.9 Hz, 1 H), 7.83 (d, *J* = 8.1 Hz, 1 H), 7.84 (d, *J* = 7.5 Hz, 1 H), 8.18 (d, *J* = 8.1 Hz, 1 H), 8.31 (d, *J* = 9.0 Hz, 1 H), 8.42 (d, *J* = 8.4 Hz, 1 H), 8.50 (d, *J* = 8.4 Hz, 1 H) ppm. ^{13}C NMR: δ = 45.30, 81.50, 82.43, 89.12, 90.21, 93.76, 94.53, 114.63, 120.28, 120.85, 121.18 (2 C), 122.94, 123.63, 124.43, 125.32, 126.02, 126.31, 126.76, 127.00, 127.47, 128.68, 130.52, 131.08, 131.60 (2 C), 131.79, 132.91, 133.37, 134.62, 151.33 ppm. MS (70 eV): *m*/*z* (%) = 445 (100) $[M^+]$, 428 (3), 402 (5), 222 (12). $C_{34}H_{23}N$ (445.18): calcd. C 91.65, H 5.20, N 3.14; found C 91.70, H 5.44, N 3.02.

4-[4-({5-[(4-{[5-(Dimethylamino)-1-naphthyl]ethynyl}-1-phenyl)ethynyl]-1-naphthyl}ethynyl)-1-phenyl]-2-methyl-3-butyn-2-ol (6): Following the general method used for the synthesis of **4**, a mixture of dichlorobis(triphenylphosphane)palladium(II) (71 mg, 0.10 mmol), cuprous iodide (2 mg, 0.01 mmol), compound **5** (450 mg, 1.01 mmol), 4-(5-iodo-1-naphthyl)-2-methyl-3-butyn-2-ol (289 mg, 1.01 mmol), and freshly distilled triethylamine (40 mL) was stirred for 15 h. Flash chromatography on silica gel, eluting with hexane/ethyl acetate (2:1), gave **6** as a yellow solid. M.p. 221−223 °C, 550 mg (90%) yield. IR (KBr pellet): $\tilde{\nu}$ = 3474, 2931, 2226, 2198, 2126, 1409, 838, 787 cm^{-1}. ^{1}H NMR: δ = 1.65 (s, 6 H), 2.91 (s, 6 H), 7.15 (d, J = 7.7 Hz, 1 H), 7.62−7.43 (m, 8 H), 7.67 (s, 4 H), 7.77 (d, J = 7.3 Hz, 1 H), 7.82 (d, J = 7.3 Hz, 1 H), 7.84 (d, J = 6.9 Hz, 1 H), 8.14 (d, J = 8.1 Hz, 1 H), 8.29 (d, J = 8.5 Hz, 1 H), 8.45 (d, J = 8.1 Hz, 1 H), 8.48 (d, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR: δ = 31.48, 45.37, 65.71, 81.88, 89.08, 89.18, 90.22, 93.76, 94.35, 94.57, 95.77, 114.64, 120.90 (2 C), 121.23 (2 C), 121.129, 122.88, 123.02, 123.10, 123.69, 124.47, 125.39, 126.25 (2 C), 126.81, 127.17, 127.23, 128.65, 130.55, 131.13 (2 C), 131.33, 131.66 (2 C), 131.72, 133.11 (2 C), 134.68, 151.44 ppm. $C_{45}H_{33}NO$ (603.26): calcd. C 89.52, H 5.51, N 2.32; found C 89.34, H 5.75, N 2.49.

1-(Dimethylamino)-5-{[4-({5-[(4-ethynyl-1-phenyl)ethynyl]-1-naphthyl}ethynyl)-1-phenyl]ethynyl}naphthalene (7): Following the general method used for the synthesis of **3**, a mixture of compound **6** (600 mg, 1.0 mmol), dry toluene (150 mL), and finely powdered sodium hydroxide (4 mg, 0.10 mmol) was stirred for 6 h and then filtered. The residual solid was purified by silica gel column chromatography, eluting with hexane/dichloromethane (1:1), to give **7** as a yellow solid. M.p. 180−181 °C, 543 mg (100%) yield. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 245 nm (45498 M^{-1}·cm^{-1}), 271 (27404), 293 (22705), 364 (47600). IR (KBr pellet): $\tilde{\nu}$ = 3301, 2924, 2212, 2107, 1405, 836, 792 cm^{-1}. ^{1}H NMR: δ = 2.91 (s, 6 H), 3.21 (s, 1 H), 7.15 (d, J = 7.2 Hz, 1 H), 7.63−7.45 (m, 8 H), 7.67 (s, 4 H), 7.78 (d, J = 7.2 Hz, 1 H), 7.83 (d, J = 7.5 Hz, 1 H), 7.84 (d, J = 6.9 Hz, 1 H), 8.15 (d, J = 8.7 Hz, 1 H), 8.29 (d, J = 8.1 Hz, 1 H), 8.45 (d, J = 9.3 Hz, 1 H), 8.48 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR: δ = 45.36, 79.06, 83.24, 89.15, 89.28, 90.17, 93.72, 94.15, 94.57, 114.64, 120.88 (2 C), 121.12 (2 C), 121.27, 122.15, 122.98, 123.64, 124.43, 125.36, 126.25 (2 C), 126.81, 127.12, 127.28, 128.76, 130.51, 131.14, 131.52 (2 C), 131.62 (2 C), 132.16, 133.09 (2 C), 134.65, 151.41 ppm. MS (70 eV): *m*/*z* (%) = 545 (100) [M^{+}], 544 (6), 273 (20). $C_{42}H_{27}N$ (545.21): calcd. C 92.45, H 4.99, N 2.57; found C 92.24, H 5.28, N 2.80.

1,3,5-Tris{[5-({4-[(5-{dimethylamino}-1-naphthyl)ethynyl]-1-phenyl}ethynyl)-1-naphthyl]ethynyl}benzene (12): Following the general method used for the synthesis of **4**, a mixture of dichlorobis(triphenylphosphane)palladium(II) (76 mg, 0.11 mmol), cuprous iodide (2 mg, 0.01 mmol), compound **5** (240 mg, 0.54 mmol), 1,3,5-triiodobenzene (80 mg, 0.18 mmol), and freshly distilled triethylamine (40 mL) was stirred for 48 h. Flash chromatography on silica gel, eluting with hexane/dichloromethane (1:2), gave **12** as an orange solid. M.p. 205−208 °C, 203 mg (80%) yield. UV/Vis (CH_2Cl_2)) λ_{max} (ε) = 241 nm (118900 M^{-1}·cm^{-1}), 266 s (60896), 289 s (48390) 366 (102900). IR (KBr pellet): $\tilde{\nu}$ = 2939, 2207, 2131, 1405, 835, 786 cm^{-1}. ^{1}H NMR: δ = 2.92 (s, 18 H), 7.15 (d, J = 6.6 Hz, 3 H), 7.78−7.41 (m, 12 H), 7.68 (s, 12 H), 7.77 (d, J = 7.2 Hz, 3 H), 7.87 (d, J = 6.6 Hz, 3 H), 7.89 (d, J = 6.3 Hz, 3 H), 7.94 (s, 3 H), 8.15 (d, J = 8.1 Hz, 3 H), 8.29 (d, J = 8.7 Hz, 3 H), 8.52 (d, J = 8.1 Hz, 6 H) ppm. ^{13}C NMR: δ = 45.38, 88.80, 89.16, 90.23, 93.04, 93.76, 94.65, 114.65, 120.95, 121.36, 123.01, 123.70 (2 C), 124.30 (2 C), 124.46, 126.27, 126.40, 126.82, 128.58, 128.63, 128.72 (2 C), 130.53, 131.29 (2 C), 131.67 (2 C), 133.11 (2 C), 133.55, 134.86, 151.43 ppm. MS (FAB+): *m*/*z* (%) = 1407.5. $C_{108}H_{69}N_3$ (1407.55): calcd. C 92.08, H 4.94, N 2.98; found C 92.25, H 5.10, N 2.81.

1,3,5-Tris({5-[(4-{[5-({4-[(5-{dimethylamino}-1-naphthyl)ethynyl]-1-phenyl}ethynyl)-1-naphthyl]ethynyl}-1-phenyl)ethynyl]-1-naphthyl}ethynyl)benzene (13): Following the general method used for the synthesis of **4**, a mixture of dichlorobis(triphenylphosphane)palladium(II) (17 mg, 0.024 mmol), cuprous iodide (0.5 mg, 0.002 mmol), compound **10** (50 mg, 0.08 mmol), compound **11** (207 mg, 0.32 mmol), and freshly distilled triethylamine (40 mL) was stirred for 40 h at 65 °C. Flash chromatography on silica gel, eluting with hexane/dichloromethane (1:2), gave **13** as a yellow solid. M.p. 208−209 °C, 128 mg (74%) yield. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 239 nm (209830 M^{-1}·cm^{-1}), 268 s (115630), 293 s (82976), 367 (210700). IR (KBr pellet): $\tilde{\nu}$ = 2226, 2208, 1460, 834, 794 cm^{-1}. ^{1}H NMR: δ = 2.91 (s, 18 H), 7.15 (d, J = 7.7 Hz, 3 H), 7.67 (s, 24 H), 7.78−7.45 (m, 24 H), 7.85 (d, J = 7.2 Hz, 12 H), 8.14 (d, J = 8.4 Hz, 3 H), 8.28 (d, J = 8.7 Hz, 3 H), 8.40 (d, J = 8.4 Hz, 6 H), 8.52 (d, J = 8.7 Hz, 6 H) ppm. ^{13}C NMR: δ = 45.35, 88.97, 90.25 (2 C), 91.73 (2 C), 92.90 (2 C), 93.71 (2 C), 94.74, 114.65, 120.37, 120.87 (2 C), 121.46 (4 C), 122.88 (4 C), 124.44, 125.36, 126.22 (4 C), 126.50 (2 C), 126.81, 127.95 (2 C), 128.76, 131.22 (5 C), 131.66 (4 C), 132.14, 133.03 (2 C), 134.64 (2 C), 139.28, 151.41 ppm. MS (FAB): *m*/*z* (%) = 2157.7 (100) [M^{+}]. $C_{168}H_{99}N_3$ (2157.78): calcd. C 93.43, H 4.62, N 1.95; found C 93.35, H 4.80, N 1.70.

1,3,5-Tris{1-(3-hydroxy-3-methyl-1-butyn)-5-naphthylethynyl}benzene (9): Following the general method used for the synthesis of **4**, a mixture of dichlorobis(triphenylphosphane)palladium(II) (141 mg, 0.20 mmol), cuprous iodide (3.8 mg, 0.02 mmol), 1,3,5-triethynylbenzene (190 mg, 0.67 mmol), 4-(5-iodo-1-naphthyl)-2-methyl-3-butyn-2-ol (1.3 g, 12.06 mmol), and freshly distilled triethylamine (40 mL) was stirred for 48 h. Flash chromatography on silica gel, eluting with hexane/ethyl acetate (1:1), gave **9** as a dark amber oil, 431 mg (83%) yield. IR (film): $\tilde{\nu}$ = 3387, 1400, 956, 786 cm^{-1}. ^{1}H NMR: δ = 1.77 (s, 18 H), 7.43 (dd, J = 8.2, J = 7.0 Hz, 6 H), 7.64 (d, J = 7.0 Hz, 3 H), 7.70 (d, J = 7.0 Hz, 3 H), 7.79 (s, 3 H), 8.22 (d, J = 8.2 Hz, 3 H), 8.34 (d, J = 8.2 Hz, 3 H) ppm. ^{13}C NMR: δ = 31.48, 65.67, 79.95, 88.74, 92.92, 99.24, 120.65, 120.75, 124.09, 125.89, 125.99, 126.66, 127.07, 130.88, 131.03, 132.82, 132.95, 134.03 ppm. $C_{57}H_{42}O_3$ (774.31): calcd. C 88.34, H 5.46; found C 88.56, H 5.70.

1,3,5-Tris{1-ethynyl-5-naphthyethynyl}benzene (10): Following the general method used for the synthesis of **3**, a mixture of **9** (150 mg, 0.19 mmol), dry toluene (40 mL), and finely powdered sodium hydroxide (1 mg, 0.02 mmol) was stirred for 20 h and then filtered. The residual solid was purified by silica gel column chromatography, eluting with hexane/dichloromethane (2:1), to give **10** as a pale-yellow solid. M.p. > 300 °C (dark, dec.), 112 mg (100%) yield, which shows very poor solubility in organic solvents. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 238 nm (190160 M^{-1}·cm^{-1}), 284 (30536), 340 (1145708), 356 (112110). IR (KBr pellet): $\tilde{\nu}$ = 3288, 2210, 2102, 967, 779 cm^{-1}. ^{1}H NMR (55 °C): δ = 3.50 (s, 3 H), 7.58 (dd, J = 8.1, J = 7.2 Hz, 6 H), 7.82 (d, J = 7.2 Hz, 3 H), 7.86 (d, J = 6.9 Hz, 3 H), 7.91 (s, 3 H), 8.43 (d, J = 8.1 Hz, 3 H), 8.50 (d, J = 7.8 Hz, 3 H) ppm. ^{13}C NMR (55 °C): δ = 81.62, 82.43, 88.87, 93.11, 120.63, 121.06, 124.52, 126.20, 126.34, 127.42, 127.49, 131.40, 131.96 (3 C), 134.32 ppm. MS (MALDI-TOF): *m*/*z* (%) = 600.0. $C_{48}H_{24}$ (600.19): calcd. C 95.97, H 4.03; found C 96.08, H 4.32.

1-(Dimethylamino)-5-{[4-({5-[(4-iodo-1-phenyl)ethynyl]-1-naphthyl}ethynyl)-1-phenyl]ethynyl}naphthalene (11): Following the general method used for the synthesis of **4**, a mixture of dichlorobis(triphenylphosphane)palladium(II) (16 mg, 0.023 mmol), cuprous iodide (0.4 mg, 0.002 mmol), compound **5** (100 mg, 0.23 mmol), 1,4-diiodobenzene (303 mg, 0.92 mmol), and freshly distilled triethylamine (100 mL) was stirred for 15 h. Flash chromatography on silica gel, eluting with hexane/dichloromethane (1:1), gave **11** as a yellow solid. M.p. 203−204 °C, 135 mg (91%) yield. IR (KBr pellet): $\tilde{\nu}$ = 2924, 1405, 962, 837, 788 cm^{-1}. ^{1}H NMR: δ = 2.91 (s, 6 H), 7.15 (d, J = 7.3 Hz, 1 H), 7.38 (d, J = 8.5 Hz, 2 H), 7.85−7.46

(m, 9 H), 7.83 (s, 4 H), 8.14 (d, $J = 8.1$ Hz, 1 H), 8.29 (d, $J = 8.5$ Hz, 1 H), 8.43 (d, $J = 8.1$ Hz, 1 H), 8.48 (d, $J = 8.1$ Hz, 1 H) ppm. ^{13}C NMR: $\delta = 45.35$, 88.74, 89.13, 90.19, 93.37, 94.37, 94.57, 114.04, 114.65, 120.87 (2 C), 121.09 (2 C), 121.29, 122.99, 123.68, 124.44, 125.36, 126.25, 126.78, 127.09, 127.25, 128.76, 130.52, 131.10 (2 C), 131.63 (2 C), 133.11, 134.64 (2 C), 137.66, 139.27, 151.41 ppm. MS (70 eV): m/z (%) = 647 (100) [M$^+$], 520 (10), 323 (24). $C_{40}H_{26}IN$ (647.11): calcd. C 74.19, H 4.05, N 2.16; found C 73.98, H 4.28, N 1.99.

X-ray Diffraction Analysis of the Picrate Derivative of Compound 5: A crystal of 0.12 × 0.04 × 0.02 mm was selected for data collection in a rotatory anode MAC SCIENCE, SMART 6000 CCD diffractometer, using graphite-monochromated Cu-K_α radiation in the ω-2θ scan mode. The lattice parameters were refined on the setting angles of 56 reflections in the range $5 \leq \theta \leq 32°$. The intensities of 10577 reflections were measured; 5448 were considered as observed [$I > 2\sigma(I)$], in the range $2 \leq \theta \leq 70°$. Lorentz and polarization corrections but not absorption corrections were applied. The structure was solved by direct methods.[23] The refinement was carried out by least-squares methods.[24] All non-H atoms were refined anisotropically. H atoms were located by the electron density map analysis and refined with their isotropic temperature factors constant. The final R values together with other experimental and crystallographic data are given in Table 2. Geometrical calculations were performed.[25]

Table 2. Crystal data and structure refinement for the picrate derivative of compound **5**

Empirical formula	$C_{40}H_{28}N_4O_8$
Molecular mass	698.66
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	$a = 6.9711(1)$ Å; $\alpha = 79.493(1)°$ $b = 10.6154(2)$ Å; $\beta = 86.028(1)°$ $c = 22.8205(3)$ Å; $\gamma = 79.493(1)°$
Volume	1631.45(4) Å^3
Z, calculated density	2, 1.410 Mg/m^3
Absorption coefficient	0.541 mm^{-1}
F(000)	720
Crystal size (mm)	0.12 × 0.04 × 0.02
Theta range for data collection	1.97 to 70.38°
Index ranges	$-7 \leq h \leq 8$, $-12 \leq k \leq 12$, $-25 \leq l \leq 25$
Reflections collected/independent	10577/5448 [R(int) = 0.0308]
Completeness to theta = 70.38°	87.4%
Absorption correction	SADABS ver. 2.03
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5448/0/479
Goodness-of-fit on F^2	1.038
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0468$, $wR2 = 0.1309$
R indices (all data)	$R1 = 0.0604$, $wR2 = 0.1419$
Largest diff. peak and hole	0.688 and −0.569 e·A^{-3}

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