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Carbon Networks Based on 1,5-Naphthalene Units. Synthesis of 1,5-Naphthalene Nanostructures with Extended π-Conjugation

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The synthesis and spectroscopic characterization of nanometer-sized conjugated molecules of 5-X-naphthylethynyl (X= NO_2, NMe_2) units with precise length and constitution have been carried out. A new extended π-conjugated 5-nitronaphthyl family was synthesized by palladium-catalyzed cross-coupling reaction between the protected 5-iodonaphthylethynyl **5a** and 1-ethynyl-5-nitronaphthalene **9**, or the resulting ethynyl compound **11** and the 1-iodo-5-nitronaphthalene **3**. Catalytic oxidative dimerization of the terminal acetylene compounds permits the isolation of the corresponding 1,3-butadiyne derivatives **16**−**18**, with the nitro groups at the ends of the conjugation, in excellent yields. A new family of conjugated 5-nitro-(naphthylethynyl)-[5-(*N*,*N*-dimethylamino)]-naphthalene (**20**−**22**), was also synthesized by palladium-catalyzed cross-coupling reaction between 5-iodo-*N*,*N*-dimethylnaphthalene-1-amine (**19**) with the appropriate terminal acetylene (**9**, **11**, and **13** respectively). Compounds **20**−**22** show a fluorescence emission and also exhibit a charge-transfer absorption in the visible spectrum. X-ray structure of **20** confirms a centrosymmetric dimer association with an interplanar distance of 3.43 Å, and the naphthalene rings adopt an anti conformation around the C≡C triple bond.

Introduction

The synthesis and characterization of nanometer-sized conjugated molecules of precise length and constitution are of widespread interest, which is due to their inherent synthetic flexibility which permits the design of molecular architectures with important properties.[1,2] Molecules showing extended π-conjugation, in general, exhibit high thermal stability and can present electroconductive, magnetic, and optical properties.[3]

In particular, the field of *molecular electronics* involves the search for new materials that favor long-range vectorial electron or energy transfer and/or exhibit nonlinear optical properties.[4−6] A variety of potential applications, such as artificial photosynthesis,[7] photocatalysis,[8] molecular photovoltaic cells,[9] molecular informatics,[10] and optoelectronic devices,[11,12] are beginning to emerge from this new field of research.

Solid-state polymerization of some 1,3-diynes to form crystalline conjugated poly(en-ynes) has attracted much attention by the electronic and optical properties of poly(1,3-diynes).[13]

The naphthalene conjugated system, for example, the 1,4-ethynylnaphthalene unit, has been used in binaphthyl-based oligomers,[14] as a spacer in phenylene or diporphyrin connectors, and applied to studies of intramolecular energy transfer.[15,16] However, the 1,5-di-

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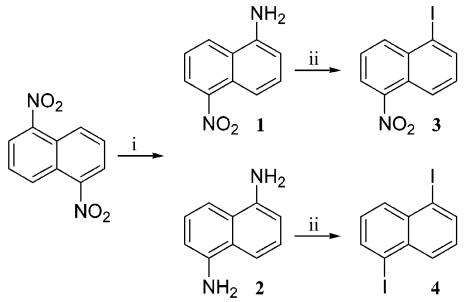
SCHEME 1[a]



[a] Reagents: i, Na_2S, NH_4OH; at 80 °C; ii. $NaNO_2$, H_2SO_4; KI.

ethynylnaphthalene unit has been less used, although it has been integrated into di- and trinuclear alkyne–rhodium(I) complexes.[17]

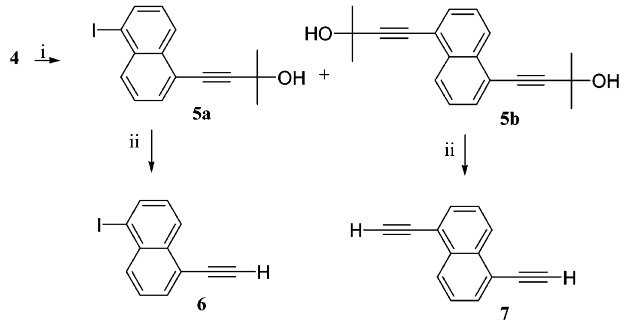
The synthesis and the structure analysis of the novel rigid conjugate nanostructures based on 1,5-diethynylnaphthalene units are now reported.

Discussion

The construction of 1,5-naphthalene conjugated nanostructures has been undertaken from ethynylnaphthalene units. These were prepared by a multistep process from iodonaphthalene derivatives which were prepared starting from 1,5-dinitronaphthalene by reduction with sodium sulfide in a concentrated aqueous ammonia solution, giving 5-nitronaphthalen-1-amine (**1**) and 1,5-diaminonaphthalene (**2**).[18] Compounds **1** and **2** were transformed into 1-iodo-5-nitronaphthalene (**3**) and 1,5-diiodonaphthalene (**4**) through the single or double diazonium salt, respectively, with potassium iodide, Scheme 1.[19,20]

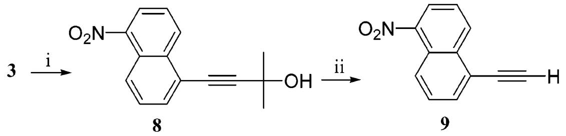
The diiodo compound **4** was transformed into a mixture of 4-(5-iodo-1-naphthyl)-2-methylbut-3-yn-2-ol (**5a**) and 1,5-di-[4-(2-methylbut-3-yn-2-ol)]-naphthalene (**5b**) by cross-coupling with 2-methylbut-3-yn-2-ol, catalyzed by palladium. Both derivatives **5a** and **5b** were individually transformed to the respective acetylenes **6** and **7** by treatment with powdered sodium hydroxide, in toluene at reflux temperature,[21] Scheme 2. However, for compound **5a** was also isolated an insoluble black powder (10%), that by IR and mass spectroscopy shows the naphthylethynyl moiety and proceeds by the nucleophilic substitution of the iodo by the sodium acetylide during the acetone elimination step. This secondary product diminishes under diluted conditions.

SCHEME 2[a]



[a] Reagents: i, 2-methylbut-3-yn-2-ol, $PdCl_2(PPh_3)_2$, Cu_2Cl_2, $HNEt_2$; ii. NaOH, toluene, at reflux temperature.

SCHEME 3[a]



[a] Reagents: i, 2-methylbut-3-yn-2-ol, $PdCl_2(PPh_3)_2$, Cu_2Cl_2, NEt_3; ii. NaOH, toluene, at reflux temperature.

In a similar way, 5-nitronaphthalen-1-amine (**1**) was transformed through the diazonium salt and potassium iodide in the iodo derivative **3**, Scheme 1, which by heterocoupling with 2-methylbut-3-yn-2-ol, catalyzed by palladium, gives the nitroethynyl alcohol **8**, which was transformed into 1-ethynyl-5-nitronaphthalene (**9**) by treatment with powdered sodium hydroxide in refluxing toluene,[21] Scheme 3.

The 1-ethynyl-5-nitronaphthalene and its iodo derivative precursor serve as precursors to nanostructures with an electron-withdrawing nitro group at the end of the conjugated system.

Mononitroaryl Nanostructures: 1-Ethynyl-5-[(5-nitro-1-naphthyl)ethynyl]naphthalene and 1-Ethynyl-5-({5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}-ethynyl)naphthalene (11 and 13). Following the general method discussed in Scheme 2 for the preparation of **5a**,**b**, the cross-coupling reaction, catalyzed by palladium, between compounds **9** and **5a**, yields 2-methyl-4-{5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}but-3-yn-2-ol (**10**) as a yellow solid, in good yield (64%). The treatment of **10** with powdered sodium hydroxide in dry toluene at reflux temperature[21] gives 1-ethynyl-5-[(5-nitro-1-naphthyl)ethynyl]naphthalene (**11**) as a yellow-brown solid in practically quantitative yield.

A DSC analysis of **11** was carried out. The diagram exhibits an endothermic peak corresponding with the melting of the compound at 205.3 °C after which appears a broad exothermic peak of decomposition. In the IR spectrum, the black solid resulting from the thermal treatment shows a band at 2193 cm^{-1} corresponding to C≡C stretching vibration. By ^1H NMR were observed groups of signals corresponding to the decomposition products, but also a group of broad signals in the aromatic region with frequencies related to the monomer, which were assigned to a polymer of **11**.

A new structure **13** was synthesized, increasing **11** by a 5-naphthylethynyl unit. Thus, by cross-coupling between **5a** and **11**, catalyzed by palladium, was isolated 2-methyl-4-[5-({5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}ethynyl)-1-naphthyl]but-3-yn-2-ol (**12**), as a brown solid in moderate yield (50%). The treatment of **12** with sodium hydroxide in refluxing toluene[21] gives

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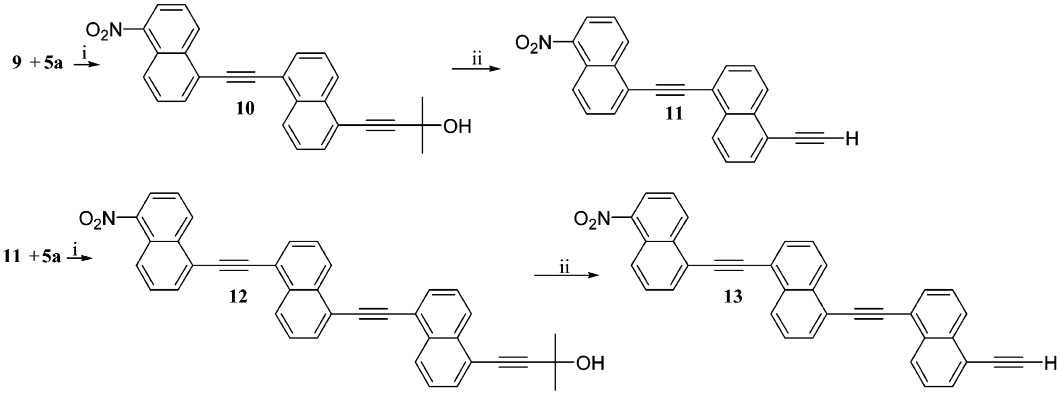
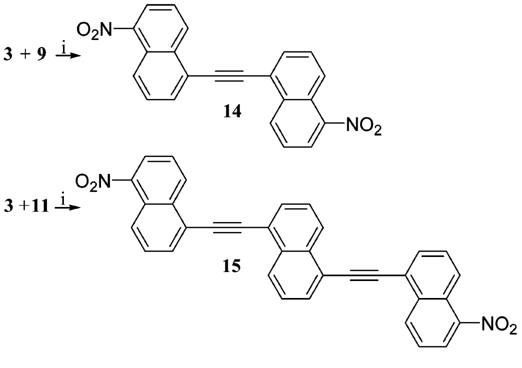
SCHEME 4[a]



[a] Reagents: i. $PdCl_2(PPh_3)_2$, Cu_2Cl_2, NEt_3; ii. NaOH, toluene, at reflux temperature.

SCHEME 5[a]



[a] Reagents: i. $PdCl_2(PPh_3)_2$, Cu_2Cl_2, NEt_3.

1-ethynyl-5-({5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}-ethynyl)naphthalene (**13**), as a dark yellow solid in practically quantitative yield, Scheme 4.

Dinitroaryl Nanostructures: 1-Nitro-5-[(5-nitro-1-naphthyl)ethynyl]naphthalene and 1-Nitro-5-({5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}ethynyl)-naphthalene (14 and 15). The synthesis of an interesting family of compounds, containing symmetrical 5-nitronaphthylethynyl units, has been carried out.

1-Nitro-5-[(5-nitro-1-naphthyl)ethynyl]naphthalene (**14**)-was obtained, by cross-coupling reaction, catalyzed by palladium, between the compounds **3** and **9**, as a yellow solid in good yield (74%), which shows low solubility in common organic solvents.[22] Furthermore, 1-nitro-5-({5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}ethynyl)-naphthalene (**15**), despite the insolubility observed in **14**, was also prepared. Thus, cross-coupling reaction, catalyzed by palladium, between the iodo derivative **3** and 1-ethynyl-5-[(5-nitro-1-naphthyl)ethynyl]naphthalene (**11**), provides **15** as a brown solid in moderate yield (50%), Scheme 5. The compound shows very low solubility in dichloromethane and was isolated in pure form by continuous extraction of the starting reagents.

1,4-Di(5-nitronaphthylethynyl)-1,3-butadiynes 16, 17, and 18: Oxidative Dimerization of the 5-Nitronaphthylethynyl Derivatives 9, 11, and 13. 1-Nitro-5-[4-(5-nitro-1-naphthyl)buta-1,3-diynyl]naphthalene (**16**)[22] and naphthylethynyl homologues **17** and **18** were prepared to explore the solubility of the new compounds and the nitro electron-withdrawing effect on the conjugation and also on the topopolymerization of the 1,3-butadiyne system.[23]

Syntheses of the 1,3-butadiynes (**16**, **17**, and **18**) were carried out by oxidative dimerization of the corresponding 5-nitronaphthylethynyl derivative (**9**, **11**, and **13**, respectively) under adapted Glaser conditions, using copper(I) catalyst in dry pyridine under oxygen atmosphere, at 40 °C, in excellent yields, Scheme 6. Compound **16**, soluble in dichoromethane, was isolated in 98% yield as a pale-brown solid. Compound **17** shows low solubility in dichloromethane and was isolated in 90% yield as a yellow-brown solid. Compound **18** shows very low solubility in dichloromethane and was isolated in 80% yield as a yellow solid.

5-Nitro-(naphthylethynyl)-[5-(*N*,*N*-dimethylamino)]naphthalene Derivatives, 20, 21, and 22. Another family of 5-nitronaphthylethynyl derivatives has been synthesized showing a nitro and a *N*,*N*-dimethylamino groups, with opposite electronic character, at the ends of the conjugated system. The Sonogashira reaction between iodonaphthyl **19** and the appropriate 5-nitronaphthylethynyl derivatives was undertaken. The preparation of 5-iodo-*N*,*N*-dimethylnaphthalene-1-amine **19** was carried out by reduction of 1-iodo-5-nitronaphthalene (**3**)with tin(II) chloride dihydrate,[24] giving 5-iodonaphthalene-1-amine as a pale-brown solid in excellent yield, which was treated with aqueous formaldehyde (37%) and sodium cyanoborohydride in glacial acetic acid,[25] yielding quantitatively **19**, as a brown-red solid, Scheme 7.

The cross-coupling between the iodo derivative **19** and 5-nitronaphthalene **9**, catalyzed by palladium, affords the conjugated compound **20**, as a red-orange solid, in practically quantitative yield; a charge-transfer band appears in the UV−vis spectrum (CH_2Cl_2, in 1×10^{-3} mol L^{-1}), 425 nm (ϵ, 3985), which for lowest concentrations is missing.

N,*N*-Dimethyl-5-({5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}ethynyl)naphthalen-1-amine (**21**) was synthesized by cross-coupling between nitronaphthylethynyl derivative **11** and iodonaphthyl derivative **19**, catalyzed

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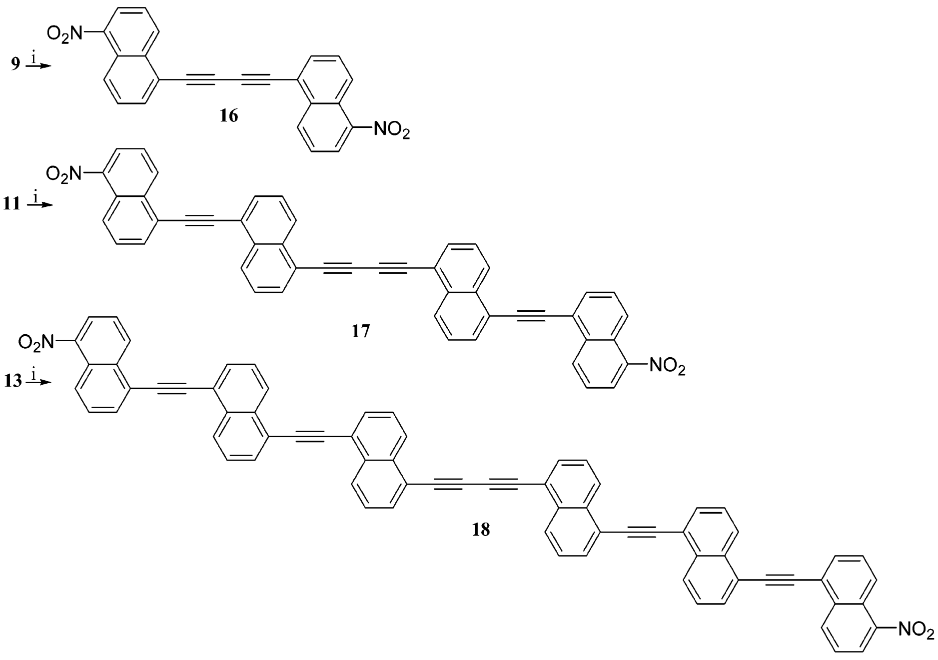
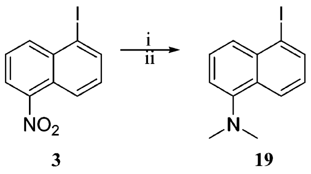
SCHEME 6[a]



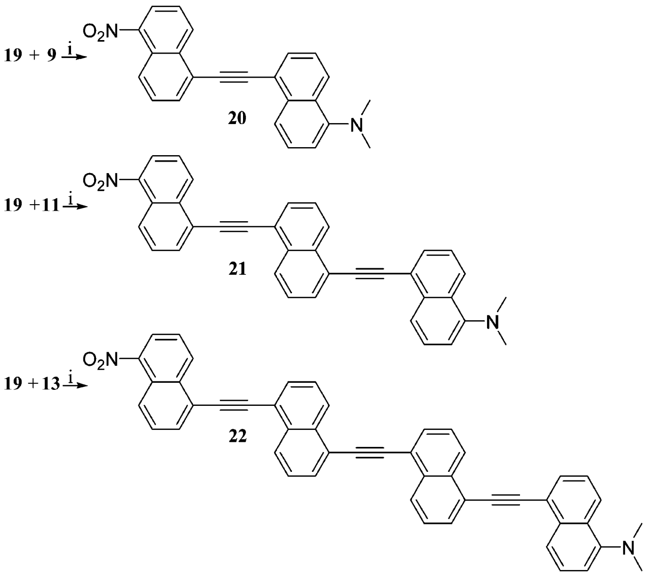
[a] Reagents: i. Cu_2Cl_2, pyridine, oxygen atmosphere.

SCHEME 7[a]



[a] Reagents: i. $SnCl_2{\cdot}2H_2O$, Cu_2Cl_2, NEt_3.

SCHEME 8[a]



[a] Reagents: i. $Cl_2Pd(PPh_3)_2$, Cu_2I_2, NEt_3 (or piperidine for **22**).

by palladium, yielding **21** as an orange solid (60%), Scheme 8; a charge-transfer band appears in the UV–vis spectrum (CH_2Cl_2, in 0.7×10^{-3} mol L^{-1}), 419 nm (ϵ, 5714), which for lowest concentrations is missing.

TABLE 1. Fluorescence Emission: Frequencies and Quantum Yield

compound	λ^{em}	F
20	513.42	6.15×10^{-4}
21	519.01	2.51×10^{-3}
22	542.77	1.2×10^{-2}

In the same way, conjugated compound **22**, a 5-naphthylethynyl homologue of compound **21** and **20**, was prepared. Cross-coupling between the nitronaphthylethynyl derivative **13** and the iodonaphthyl derivative **19**, catalyzed by palladium, gave *N*,*N*-dimethyl-5-{[5-({5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}ethynyl)-1-naphthyl]-ethynyl}naphthalen-1-amine (**22**), as a dark brown solid in low yield (22%), probably due to the low solubility of compound **13**.

5-Nitro-(naphthylethynyl)-[5-(*N*,*N*-dimethylamino)]-naphthalene derivatives (**20**–**22**) in solution exhibit a fluorescence radiation which was analyzed in dichloromethane, Table 1. Remarkably, the quantum yield increases with the separation distance between the nitro and the electron-releasing *N*,*N*-dimethylamino group in dichloromethane; the emission wavelength also increases in **21** and **22** with respect to **20**. Thus, when the nitro and *N*,*N*-dimethylamino groups are separated by one or two 5-naphthylethynyl units (compound **21** or **22**) with respect to **20**, the quantum yield is about 4 or 20 times greater**,** respectively. The quantum yield is very sensitive to protic and polar solvents.[26]

Structural Analysis of the Ethynylnaphthalene Compounds. All the 5-nitronaphthylethynyl structures and intermediates were isolated in pure form and identified unambiguously, in particular by ^1H, ^{13}C NMR (bidimensional $^1H/^{13}C$ and $^1H/^1H$), and IR spectroscopy.

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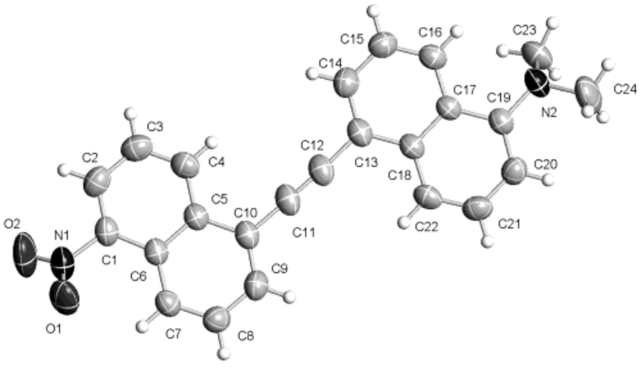

FIGURE 1. The molecule numbering with the thermal ellipsoids at the 50% probability level.

The ^{13}C chemical shifts of a number of the monosubstituted naphthalenes[27] have been reported, and the ^{13}C chemical shifts of 1,5-disubstituted naphthalenes were obtained from the parent compounds used in the synthesis of the naphthylethynyl derivatives.

Moreover, by proton/carbon absorption signals in the spectra, it was assumed that the strong deshielding effect observed on the *peri* protons probably also are influenced by the electron-current anisotropic effect of the triple bond.

By DSC (25 to 300 °C) only a narrow endothermic peak was observed corresponding with the melting of the compounds, and a possible syn conformation disorder phase was not detected. Thus, an anti conjugated conformation in the solid state would be assumed, Schemes 4 and 6.

Compounds **20**, **21**, and **22**, containing nitro and *N*,*N*-dimethylamino groups, in the solid state, show the anti conformation of the naphthalene rings around the acetylene axis, confirmed for **20** by monocrystal X-ray structure analysis.

Crystallographic and Molecular Structure of Compound 20. The crystal X-ray diffraction analysis of **20** has been carried out. The molecular structure, together with its numbering scheme, is shown in Figure 1. Bond distances and angles of compound **20** correlate well with other naphthalene-related structures.[23,28] Some distances in the naphthalene ring show significant deviations due to the stereoelectronic effects of the *N*,*N*-dimethylamino and nitro groups and also to the charge-transfer association between both molecules forming a dimer. Thus, C1−C2, C3−C4, C7−C8, C9−C10, C13−C14, C15−C16, C19−C20, C21−C22 show the shortest distances (1.359(2)−1.377(2) Å) in the naphthalene rings. The electron-releasing effect of the *N*,*N*-dimethylamino group was evidenced by the double bond character of C19−N2 compared with N2−C23 or N2−C24 single bonds of the same group, 1.413(2) vs 1.454(2) or 1.452(2) Å,[29] while the nitro group shows the C1−N1 bond with an important single bond character, 1.469(2) Å.[30] The molecular structure consists of two practically planar conjugated 5-nitronaphthylethynyl-5-(*N*,*N*-dimethylamino)naphthalene molecules which are disposed in a parallel association overlapping the acceptor nitronaphthalene with the donor (*N*,*N*-dimethylamino)naphthalene rings of each molecule of the dimer as a charge-transfer complex, with the nitro and *N*,*N*-dimethylamino substitution at the same extreme. Both molecules in the dimer are related by a symmetry center located in the middle of the plane formed by C11−C12 triple bond [1.196(2) Å] of each molecule. The naphthylethynylnaphthalene hydrocarbon nucleus in compound **20** is nearly planar with C3 at −0.104(2), C15 at 0.143(2), and C16 at 0.116(2) in the maximum deviation from the mean square plane; the nitrogen in the nitro and *N*,*N*-dimethylamino groups are N1 at 0.120(2) and N2 at −0.068(2) Å, respectively. The mean interplanar spacing between the two molecules in the dimer is 3.43 Å, which agrees well with the distances observed in other $\pi-\pi$ naphthalene charge-transfer complexes.[28] The naphthalene rings, around the triple bond, are disposed in an anti conformation.

Figure 2 shows a projection of the structure under the *a*-axis for the molecules of compound **20**. The overlapping between the two molecules related by symmetry center is practically complete, including the nitro and *N*,*N*-dimethylamino groups, and the intermolecular symmetry center coincides with the crystallographic one. The molecular packing in the crystal is governed by van der Waals interaction between the dimer molecules in a herringbone type extended form.

Experimental Section

General. The IR spectra frequencies are given in cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded at 300.13 (or 200.13) and 75.47 MHz, respectively. Chemical shifts are given in δ with TMS as an internal reference, coupling constants J are given in hertz, and the solvent is indicated with each spectrum. The UV−vis spectra frequencies are given in nm and ϵ in L $mol^{-1}.cm^{-1}$. Yields are given after chromatography column separation or solvent extraction.

5-Nitronaphthalen-1-amine (1) and 1,5-Diaminonaphthalene (2).[18] To a suspension of 1,5-dinitronaphthalene (8 g, 0.037 mol) in water (110 mL) was added a solution of ammonium chloride (14 g, 0.263 mol) in concentrated aqueous ammonia (28%). The mixture was stirred and warmed at 80−85 °C, and sodium sulfide (9.5 g, 0.122 mol) was added in three portions each 10 min. The mixture was heated at 85 °C for 4 h (monitored by TLC) and then filtered through a heated Büchner funnel. The solid was extracted twice with dichloromethane (10 mL), dried over anhydrous sodium sulfate, and filtered. After the solvent was removed to afford a residual solid that was purified by silica gel column chromatography, elution with hexane/ethyl acetate (2:1) gave two reduction products, 5-nitronaphthalen-1-amine (**1**) as a brown-red solid, mp 88−90 °C, 3.68 g (54%) yield, and 1,5-diaminonaphthalene (**2**) as a brown solid, mp 186−188°, 2.04 g (34%) yield, which agrees well with a commercial sample.

Compound **1**: IR (KBr, cm^{-1}): 3343, 1509, 1322, 770. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, 1H, $J = 11.1$ Hz), 8.07 (d, 1H, $J = 12.9$ Hz), 7.87 (d, 1H, $J = 12.9$ Hz), 7.46 (t, 1H, $J = 12.9$ Hz), 7.41 (t, 1H, $J = 11.1$ Hz), 6.86 (1H, d, $J = 11.1$ Hz), 4.26 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.33, 142.56,

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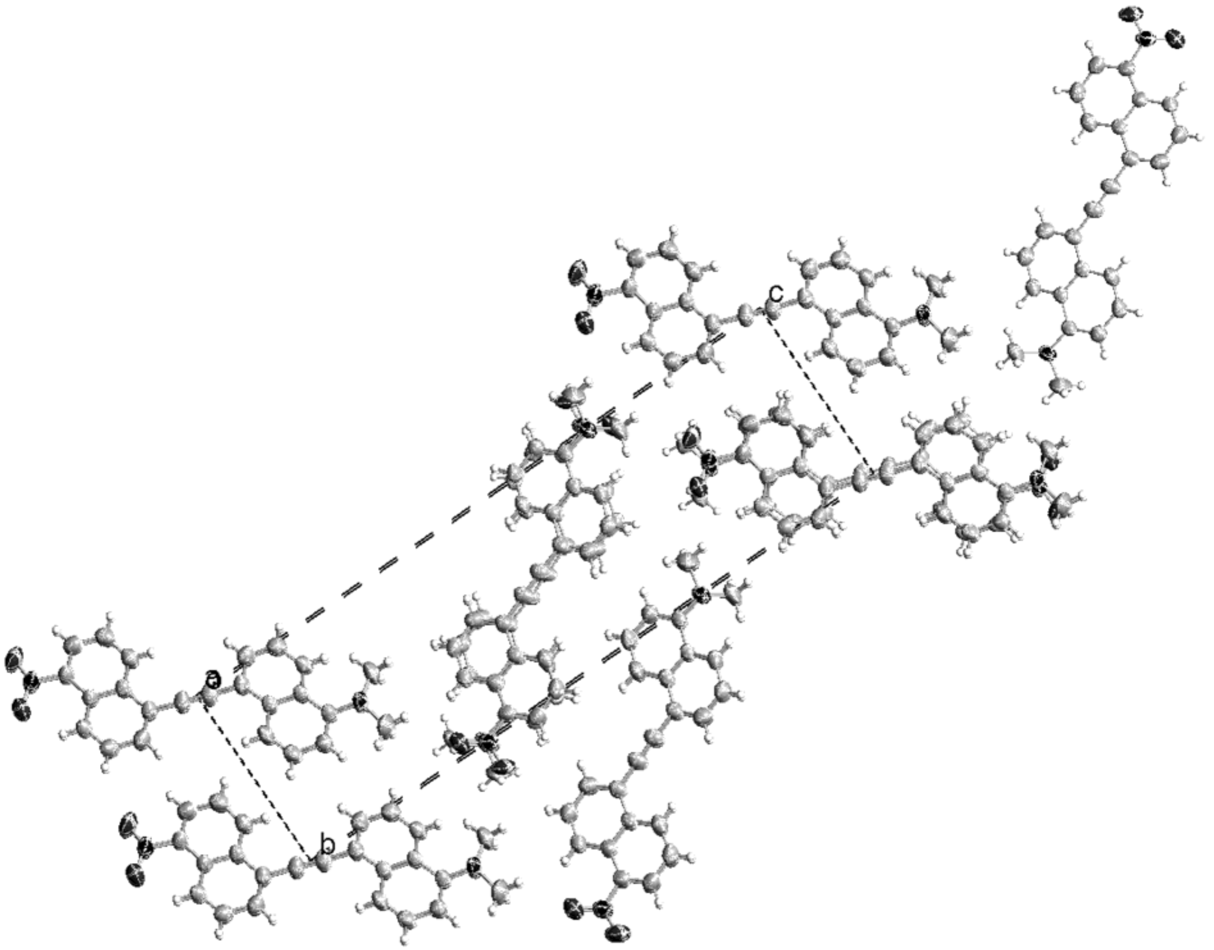

FIGURE 2. View of the molecular packing of the molecules under the *a*-axis projection.

129.97, 127.01, 126.01, 124.39, 123.54, 122.66, 113.31, 111.15. $C_{10}H_8N_2O_2$ (188.06): Anal. Calcd: C 63.83, H 4.28, N 14.89; found: C 63.91, H 4.25, N 14.64.

1,5-Diiodonaphthalene (4). General Procedure for Iodation of Aminoarenes.[19,20] To a solution of sodium nitrite (3 g, 0.044 mol) in concentrated sulfuric acid (25 mL) at 0 °C was added dropwise a solution of 1,5-diaminonaphthalene (**2**) (3 g, 0.019 mol) in glacial acetic acid (25 mL). The mixture was stirred for 15 min and poured onto ice (50 g) and urea (0.25 g), and then a solution of potassium iodide (100 g, 0.6 mol) in water (100 mL) was added and stirred overnight under reduced pressure. The solid was filtered, dried, and extracted with dichloromethane. The combined extracts were refluxed with charcoal and finally purified by silica gel column chromatography, eluting with hexane/dichloromethane (2:1) to give **4** as pale-yellow needles, mp 148−150 °C (lit.[19] mp 147 °C), 5.55 g (77%) yield. IR (KBr, cm^{-1}): 1131, 780. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.13 (d, 4H, $J = 7.6$ Hz), 7.26 (t, 2H, $J = 7.6$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.54 (2C), 134.64 (2C), 133.59 (2C), 128.41 (2C), 99.68 (2C). $C_{10}H_6I_2$ (379.86): Anal. Calcd: C 31.61, H 1.59; found: C 31.48, H 1.65.

4-(5-Iodo-1-naphthyl)-2-methylbut-3-yn-2-ol (5a) and 1,5-Di-[4-(2-methylbut-3-yn-2-ol)]-naphthalene (5b). General Procedure of the Cross-Coupling Reaction. To a solution of aryl iodide **3** (1 g, 2.6 mmol) and 2-methylbut-3-yn-2-ol (241 mg, 2.86 mmol) in freshly distilled diethylamine (or triethylamine) (10 mL), under argon atmosphere and at room temperature, were added dichloro bis(triphenylphosphine)palladium (18 mg, 0.026 mmol) and copper iodide (4.8 mg, 0.003 mmol). The mixture was stirred for 21 h (monitored by TLC), and then the amine was removed under reduced pressure. The crude residue was washed with a saturated aqueous ammonium chloride solution with a little amount of KCN and extracted with dichloromethane. The extracts were dried on 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). Compound **5a** was isolated as a yellow solid, mp 107−108 °C, 470 mg (54%) yield; **5b** was obtained as a yellow solid, mp 124−125 °C, 198 mg (26%) yield.

4-(5-Iodo-1-naphthyl)-2-methylbut-3-yn-2-ol (**5a**): IR (KBr, cm^{-1}): 3323, 2160, 1143, 782. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.31 (d, 1H, $J = 8.8$ Hz), 8.10 (d, 1H, $J = 7.0$ Hz), 8.07 (d, 1H, $J = 8.4$ Hz), 7.68 (d, 1H, $J = 7.2$ Hz), 7.48 (dd, 1H, $J = 7.7$ Hz), 7.24 (t, 1H, $J = 7.8$ Hz), 1,7 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.88, 133.75 (2C), 132.75, 130.98, 127.45, 126.94, 126.67, 120.88, 99.78, 99.33, 79.47, 65.69, 31.52 (2C). $C_{15}H_{13}OI$ (336.00): Anal. Calcd: C 53.59, H 3.90; found: C 53.45, H 3.84.

1,5-Di-[4-(2-methylbut-3-yn-2-ol)]-naphthalene (**5b**): IR (KBr, cm^{-1}): 3335, 2100, 1160, 790. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.26 (d, 2H, $J = 8.2$ Hz), 7.66 (d, 2H, $J = 7.0$ Hz), 7.47 (t, 2H, $J = 8.2$ Hz), 2.32 (s, 2H), 1.73 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.95 (2C), 130.85 (2C), 126.75 (2C), 125.94 (2C), 120.68 (2C), 99.17 (2C), 79.99 (2C), 65.84 (2C), 31.60 (4C). $C_{20}H_{20}O_2$ (292.15): Anal. Calcd: C 82.16, H 6.89; found: C 82.30, H 6.74.

1-Ethynyl-5-iodonaphthalene (6). General Procedure for Arylacetylenes.[21] To a solution of **5a** (88 mg, 0.26 mmol) in anhydrous toluene (30 mL) was added finely powdered sodium hydroxide (7 mg, 0,18 mmol), under argon atmosphere, and the mixture was warmed at the reflux temperature for 1.5 h (monitored by TLC) and then filtered. The solvent was removed at reduced pressure, and the solid residue was purified by silica gel column chromatography, eluting with hexane to give **6** as a pale brown solid, mp 74−75 °C, 49.5 mg (68%) yield. UV−vis (CH_2Cl_2), λ max (nm): 234 (ϵ, 25777), 297s (ϵ, 8399), 307 (ϵ, 11019), 320s (ϵ, 8399). IR (KBr, cm^{-1}): 3271, 2100, 1023, 784. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.39 (d, 1H, $J = 8.2$ Hz), 8.12 (d, 2H, $J = 8.4$ Hz), 7.77 (d, 1H, $J = 7.5$ Hz), 7.50 (dd, 1H, $J = 8.4$ Hz, $J = 7.5$ Hz), 7.25 (dd, 1H, $J = 8.2$ Hz, $J = 8.4$ Hz), 3.48 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 138.19, 134.27, 133.96, 133.55, 132.04, 127.81, 127.15, 126.83, 120.54, 99.78, 82.615, 80.98. $C_{12}H_7I$ (277.96): Anal. Calcd: C 51.83, H 2.54; found: C 51.69, H 2.70.

1,5-Diethynylnaphthalene (7). Following the general method used for the preparation of **6**, a solution of the compound **5b** (210 mg, 0.72 mmol) in anhydrous toluene (30 mL) was stirred with finely powdered sodium hydroxide (40 mg, 1 mmol), at reflux temperature for 20 h. After filtration, the solvent was removed under reduced pressure giving a residual solid, which was washed with hexane to give **7** as a pale-brown solid, mp 147−150 °C (lit.[31] mp 150 °C), 127 mg (100%) yield. UV−vis (CH_2Cl_2), λ max (nm): 237 (ϵ, 29604), 312 (ϵ, 22858), 327 (ϵ, 19326). IR (KBr, cm^{-1}): 3269, 2100, 792.^{1}H NMR (200 MHz, $CDCl_3$): δ 8.39 (d, 2H, $J = 8.0$ Hz), 7.78 (d, 2H, $J = 7.0$ Hz), 7.52 (t, 2H, $J = 8.0$ Hz), 3.49 (s, 2H).^{13}C NMR (75 MHz, $CDCl_3$): δ 133.22 (2C), 131.81 (2C), 127.33 (2C), 126.11 (2C), 120.26 (2C), 82.43 (2C), 81.45 (2C). $C_{14}H_8$ (176.06): Anal. Calcd: C 95.42, H 4.58; found: C 95.49, H 4.51.

1-Iodo-5-nitronaphthalene (3). Following the general method used for the preparation of **4**, to a solution of sodium nitrite (805 mg, 11.7 mmol) in concentrated sulfuric acid (8 mL), at 0 °C was dropped a solution of **1** (2 g, 10.6 mmol) in glacial acetic acid (15 mL) and stirred for 30 min. Then, the mixture was poured on ice (14 g), urea (0.14 g), potassium iodide (29 g, 0.2 mol), and water (29 mL) and stirred overnight. The solid was filtered, dried, and extracted with dichloromethane. After the solvent was removed and the residual solid was purified by flash chromatography on silica gel, eluting with hexane/ethyl acetate 2:1 gave **3** as a pale-yellow solid, mp 155−156 °C, 2.42 g (76%) yield. IR (KBr, cm^{-1}): 1514, 1322, 1150, 780. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.47 (d, 2H, $J = 8.6$ Hz), 8.24 (d, 1H, $J = 7.6$ Hz), 8.22 (d, 1H, $J = 7.8$ Hz), 7.64 (t, 1H, $J = 8.6$ Hz), 7.38 (dd, 1H, $J = 7.6$ Hz, $J = 8.6$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.11, 139.24, 138.52, 134.69, 129.91, 125.71 (2C), 124.18, 123.71, 99.76. $C_{10}H_6NO_2I$ (298.94): Anal. Calcd: C 40.16, H 2.02, N 4.68; found: C 39.99, H 2.18, N 4.65.

2-Methyl-4-(5-nitro-1-naphthyl)but-3-yn-2-ol (8). Following the general method for the preparation of **5a**, a mixture of dichloro bis(triphenylphosphine)palladium (11.8 mg, 0.017 mmol), copper iodide (0.3 mg, 0.002 mmol), compound **3** (500 mg, 1.67 mmol), 2-methylbut-3-yn-2-ol (169 mg, 2 mmol), and triethylamine (20 mL) was stirred for 13 h. Flash chromatography on silica gel, eluting with hexane/ethyl acetate 2:1 afforded **8** as a red oil, 375 mg (89%) yield. IR (KBr, cm^{-1}): 3375, 2227, 1523, 1343, 1165, 790. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (d, 1H, $J = 8.4$ Hz), 8.26 (d, 1H, $J = 8.7$ Hz), 8.01 (d, 1 H, $J = 7.8$ Hz), 7.55 (d, 1H, $J = 6.9$ Hz), 7.40 (dd, 1H, $J = 8.4$ Hz, $J = 7.8$ Hz), 7.36 (t, 1H, $J = 7.8$ Hz), 3.32 (s, 1H), 1.71 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.71, 133.77, 132.45, 131.45, 128.38, 124.78, 124.71, 124.16, 123.23, 121.31, 100.39, 79.08, 65.71, 31.45 (2C). $C_{15}H_{13}NO_3$ (255.09): Anal. Calcd: C 70.58, H 5.13, N 5.49; found: C 70.62, H 5.22, N 5.35.

1-Ethynyl-5-nitronaphthalene (9). Following the general method used for the preparation of **6**; a mixture of the compound **8** (375 mg, 1.47 mmol), anhydrous toluene (80 mL), and finely powdered sodium hydroxide (41 mg, 1.03 mmol) was stirred for 20 h. Flash chromatography on silica gel, eluting with hexane/ethyl acetate 2:1, gave **9** as a pale-yellow solid, mp 148−150 °C, 258 mg (89%) yield. UV−vis (CH_2Cl_2), λ max (nm): 240 (ϵ, 22021), 255s (ϵ, 19933), 321s (ϵ, 9550), 341 (ϵ, 10857). IR (KBr, cm^{-1}): 2160, 1513, 1345, 1328, 786. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.65 (d, 1H, $J = 8.4$ Hz), 8.50 (d, 1H, $J = 8.7$ Hz), 8.21 (d, 1H, $J = 7.5$ Hz), 7.81 (d, 1H, $J = 7.5$ Hz), 7.61 (dd, 1H, $J = 8.7$ Hz, $J = 7.5$ Hz), 7.59 (t, 1H, $J = 7.5$ Hz), 3.56 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.94, 134.15, 132.49, 132.41, 128.45, 125.07, 124.90, 124.34, 123.99, 120.75, 83.59, 80.67. $C_{12}H_7NO_2$ (197.05): Anal. Calcd: C 73.09, H 3.58, N 7.10; found: C 72.98, H 3.70, N 76.94.

2-Methyl-4-{5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}-but-3-yn-2-ol (10). Following the general method used for the synthesis of **5a**, a mixture of dichloro bis(triphenylphosphine)-palladium (II) 72 mg (0.051 mmol), copper iodide 0.9 mg (0.005 mmol), compound **9** 342 mg (0.51 mmol), compound **5a** 200 mg (0.51 mmol), and triethylamine 30 mL was stirred for 15 h. Flash chromatography on silica gel, eluting with hexane/ethyl acetate 3/1, provided **10** as a yellow solid, mp 176−178 °C, 345 mg (84%) yield. IR (KBr, cm^{-1}): 3545, 2160, 1518, 1329, 1160, 782. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.85 (d, 1H, $J = 8.4$ Hz), 8.55 (d, 1H, $J = 9.0$ Hz), 8.46 (d, 1H, $J = 8.7$ Hz), 8.35 (d, 1H, $J = 8.7$ Hz), 8.26 (d, 1H, $J = 7.2$ Hz), 7.97 (d, 1H, $J = 6.9$ Hz), 7.90 (d, 1H, $J = 6.9$ Hz), 7.73 (d, 1H, $J = 7.5$ Hz), 7.72 (t, 1H, $J = 7.6$ Hz), 7.66 (t, 1H, $J = 8.0$ Hz), 7.59 (t, 1H, $J = 7.8$ Hz), 7.56 (t, 1H, $J = 7.8$ Hz), 1.76 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.07, 134.00, 133.17, 132.94, 132.71, 131.79, 131.34, 131.11, 128.74, 127.50, 126.71, 126.34, 126.12, 125.19, 125.06, 124.40, 123.69, 121.98, 121.07, 120.78, 99.44, 93.68, 91.55, 79.91, 65.91, 31.63 (2C). $C_{27}H_{19}NO_3$ (405.14): Anal. Calcd: C 79.98, H 4.72, N 3.45; found: C 80.09, H 4.58, N 3.62.

1-Ethynyl-5-[(5-nitro-1-naphthyl)ethynyl]naphthalene (11). Following the general method used for the synthesis of **6**, a mixture of compound **10** (220 mg, 0.54 mmol), anhydrous toluene (40 mL), and finely powdered sodium hydroxide (2 mg, 0.54 mmol) was stirred for 12 h and then filtered. The residual solid was washed with hexane, giving **11** as a yellow-brown solid, mp 205−206 °C (205.3 °C DSC), 186 mg (100%) yield. UV−vis (CH_2Cl_2), λ max (nm): 243 (ϵ, 23134), 336 (ϵ, 8308), 368s (ϵ, 5948). IR (KBr, cm^{-1}): 3263, 2227, 2197, 1521, 1342, 1330, 781. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.88 (d, 1H, $J = 8.7$ Hz), 8.57 (d, 1H, $J = 8.7$ Hz), 8.52 (d, 1H, $J = 8.4$ Hz), 8.45 (d, 1H, $J = 8.7$ Hz), 8.29 (d, 1H, $J = 7.8$ Hz), 8.01 (d, 1H, $J = 7.5$ Hz), 7.94 (d,1H, $J = 6.9$ Hz), 7.83 (d, 1H, $J = 6.9$ Hz), 7.75 (dd, 1H, $J = 8.7$ Hz, $J = 7.5$ Hz), 7.72 (dd, 1H, $J = 8.7$ Hz, $J = 7.8$ Hz), 7.62 (dd, 1H, $J = 6.9$ Hz, $J = 8.7$ Hz), 7.59 (dd, 1H, $J = 6.9$ Hz, $J = 8.4$ Hz), 3.53 (s, 1H, H-20). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.16, 134.10, 133.50, 132.96, 132.75, 131.96, 131.90, 131.44, 128.75, 127.56, 127.32, 126.38, 126.31, 125.29, 125.15, 124.42, 123.79, 122.02, 120.89, 120.54, 93.63, 91.65, 82.67, 81.42. MS (70 eV): 347 (M^+, 100), 317 (34), 300 (47), 287 (17), 149 (18). $C_{24}H_{13}NO_2$ (347.09): Anal. Calcd: C 82.98, H 3.77, N 4.03; found: C 83.12, H 3.60, N 4.20.

2-Methyl-4-[5-({5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}ethynyl)-1-naphthyl]but-3-yn-2-ol (12). Following the general method used for the synthesis of **5a**, a mixture of dichloro bis(triphenylphosphine) palladium (81 mg, 0.115 mmol), copper iodide (2 mg, 0.011 mmol), compound **11** (400 mg, 1.15 mmol), compound **5a** (387 mg, 1.15 mmol), and triethylamine (50 mL) was stirred for 72 h at the reflux temperature. Flash chromatography on silica gel, eluting with hexane/dichloromethane 1:4 gives **12** as a brown solid, mp 249−251 °C, 319 mg (50%) yield.IR (KBr, cm^{-1}): 3500, 2226, 2198, 1518, 1340, 1328, 1164, 781. ^{1}H NMR (300 MHz, NO_2-benzene[d_5], 80 °C): δ 8.04 (d, 1H, $J = 8.7$ Hz), 7.82 (d, 1H, $J = 8.4$ Hz), 7.78 (d, 1H, $J = 9.0$ Hz), 7.75 (d, 1H, $J = 7.8$ Hz), 7.61 (d, 1H, $J = 9$ Hz), 7.57 (d, 1H, $J = 9.6$ Hz), 7.34 (d, 1H, $J = 8.1$ Hz), 7.13 (d, 2H, $J = 6.9$ Hz), 7.09 (d, 2H, $J = 8.1$ Hz), 6.88−6.70 (m, 7H), 0.97 (s, 6H). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.92 (d, 1H, $J = 8.4$ Hz), 8.64 (d, 1H, $J = 8.4$ Hz), 8.59 (d,

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1H, $J = 9.0$ Hz), 8.56 (d, 2H, $J = 9.0$ Hz), 8.37 (d, 1H, $J = 8.4$ Hz), 8.31 (d, 1H, $J = 7.8$ Hz), 8.04 (d, 1H, $J = 6.9$ Hz), 7.98 (d, 2H, $J = 6.6$ Hz), 7.94 (d, 1H, $J = 6.6$ Hz), 7.80−7.56 (m, 7H), 1.76 (s, 6H). ^{13}C NMR (75 MHz, NO_2-benzene[d_5], 80 °C): δ 133.54, 132.69, 132.20, 131.95, 131.76, 131.60, 131.42, 131.31, 127.91, 127.58, 127.41, 127.01, 126.84, 126.66, 126.59, 125.68, 124.50, 122.35, 101.09, 94.18, 93.45, 93.04, 92.29, 79.88, 65.86, 31.76 (2C). Twelve carbons missing as a result of overlap. $C_{39}H_{25}NO_3$ (555.18): Anal. Calcd: C 84.31, H 4.54, N 2.52; found: C 84.18, H 4.48, N 2.71.

1-Ethynyl-5-({5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}ethynyl)naphthalene (13). Following the general method used for the preparation of **6**, a mixture of compound **12** (200 mg, 0.36 mmol), anhydrous toluene (100 mL), and finely powdered sodium hydroxide (14.4 mg, 0.36 mmol) was stirred for 72 h and then filtered. The residual solid was washed with HCl (20%) and hot toluene to give **13** as a dark yellow solid, mp 235−237 °C, 177 mg (100%) yield, which shows low solubility in organic solvents. UV−vis (CH_2Cl_2), λ max (nm): 232 (ϵ, 70409), 301s (ϵ, 8882), 362 (ϵ, 19897). IR (KBr, cm^{-1}): 3260, 2226, 2196, 1521, 1342, 1330, 782. ^{1}H NMR (300 MHz, NO_2-benzene[d_5], 80 °C): δ 8.50 (d, 1H, $J = 8.4$ Hz), 8.28−8.22 (m, 3H), 8.03 (d, 1H, $J = 8.4$ Hz), 7.98 (d, 1H, $J = 8.4$ Hz), 7.79 (d, 1H, $J = 7.5$ Hz), 7.59 (d, 2H, $J = 6.6$ Hz), 7.57 (d, 1H, $J = 6.3$ Hz), 7.54 (d, 1H, $J = 6.9$ Hz), 7.37−7.26 (m, 7H), 3.29 (s, 1H). MS (70 eV): 497 (M$^+$, 100), 467 (6), 450 (10), 449 (14), 448 (22), 224 (21). $C_{36}H_{19}NO_2$ (497.14): Anal. Calcd: C 86.90, H 3.85, N 2.82; found: C 87.15, H 3.69, N 2.95.

1-Nitro-5-[(5-nitro-1-naphthyl)ethynyl]naphthalene (14). Following the general method discussed for **5a**; a mixture of dichloro bis(triphenylphosphine)palladium (36 mg, 0.051 mmol), copper iodide (0.9 mg, 0.005 mmol), compound **9** (100 mg, 0.51 mmol), compound **3** (152 mg, 0.51 mmol), and triethylamine (30 mL) was stirred for 15 h; the solvent was removed to give a brown solid that was washed with hexane, EtOH, and CH_2Cl_2 until the starting compounds were removed, affording **14** as a yellow solid, mp 187.6 °C (DSC), 139 mg (74%) yield, which shows low solubility in organic solvents. UV−vis (CH_2Cl_2), λ max (nm): 232 (ϵ, 65700), 262s (ϵ, 21883), 371 (ϵ, 25746). IR (KBr, cm^{-1}): 1521, 1347, 789.^{1}H NMR (300 MHz, NO_2-benzene[d_5], 90 °C): δ 8.59 (d, 2H, $J = 8.7$ Hz), 8.19 (d, 2H, $J = 8.7$ Hz), 7.94 (d, 2H, $J = 7.5$ Hz), 7.65 (d, 2H, $J = 7.2$ Hz), 7.49−7.37 (m, 4H). MS (70 eV): 368 (M$^+$, 100), 338 (20), 308 (4), 276 (24), 274 (38), 137 (12). $C_{22}H_{12}N_2O_4$ (368.08): Anal. Calcd: C 71.74, H 3.28, N 7.61; found: C 71.52, H 3.31, N 7.84.

1-Nitro-5-({5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}ethynyl)naphthalene (15). Following the method for the synthesis of **5a**, a mixture of dichloro bis(triphenylphosphine)palladium (20 mg, 0.029 mmol), copper iodide (0.6 mg, 0.003 mmol), compound **11** (100 mg, 0.29 mmol), compound **3** (87 mg, 0.51 mmol), and triethylamine (50 mL), was stirred for 24 h at 40 °C. After, the crude was hydrolyzed and extracted with abundant dichloromethane (500 mL). The solvent was removed, and the residual solid was washed with hexane and hot EtOH till the reagents were removed, giving **15** as a brown solid, mp > 295 °C (darken, dec), 75 mg (50%) yield, which shows very low solubility in organic solvents.

UV−vis (CH_2Cl_2), λ max (nm): 231 (ϵ, 98187), 373 (ϵ, 41284). IR (KBr, cm^{-1}): 2198, 1521, 1348, 1328, 781.^{1}H NMR (300 MHz, NO_2-benzene[d_5], 85 °C): δ 8.65, 8.41, 8.20. Fifteen carbons are missing as a result of overlap. MS (70 eV): 518 (M$^+$, 100), 488 (8), 472 (3), 426 (5), 424 (23), 213 (11). $C_{34}H_{18}N_2O_4$ (518.13): Anal. Calcd: C 78.76, H 3.50, N 5.40; found: C 78.89, H 3.34, N 5.67.

1-Nitro-5-[4-(5-nitro-1-naphthyl)buta-1,3-diynyl]naphthalene (16) by Homocoupling Reaction of Arylacetylene. General Procedure. To a solution of cuprous chloride (3 mg, 0.015 mmol) in dry pyridine (20 mL), under oxygen atmosphere at 40 °C, was added a solution of arylacetylene **9** (60 mg, 0.3 mmol) in dry pyridine (10 mL), and the mixture was stirred for 5 h. After, solvent was removed to give a residual solid that was washed with ammonium hydroxide till the blue color disappeared, and then it was extracted with dichloromethane. The organic layer was dried on anhydrous magnesium sulfate and after filtration and solvent evaporation was obtained a brown solid, that was purified by silica gel column chromatography, eluting with hexane/dichloromethane 1:1 to give **16** as a pale-brown solid, mp 236−238 °C (dark, dec; DSC), 116 mg (98%) yield. UV−vis (CH_2Cl_2), λ max (nm): 244 (ϵ, 28417), 379 (ϵ, 16327), 290 (ϵ, 10191). IR (KBr, cm^{-1}): 2160, 1521, 1349, 1326, 787. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (d, 2H, $J = 8.1$ Hz), 8.60 (d, 2H, $J = 8.4$ Hz), 8.29 (d, 2H, $J = 7.8$ Hz), 7.97 (d, 2H, $J = 7.2$ Hz), 7.72 (t, 4H, $J = 7.95$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.21 (2C), 134.62 (2C), 133.42 (2C), 132.46 (2C), 128.65 (2C), 125.57 (2C), 125.15 (2C), 124.84 (2C), 124.63 (2C), 120.32 (2C), 80.54 (2C), 79.55 (2C). MS (70 eV): 392 (M$^+$, 100), 362 (12), 346 (3), 334 (6), 316 (9), 300 (19), 298 (34), 288 (24), 287 (33), 149 (19). $C_{24}H_{12}N_2O_4$ (392.08): Anal. Calcd: C 73.47, H 3.08, N 7.14; found: C 73.25, H 3.27, N 7.39.

1-Nitro-5-{[5-(4-{5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}buta-1,3-diynyl)-1-naphthyl]ethynyl}-naphthalene (17). Following the general method used for the synthesis of **16**, a mixture of cuprous chloride (3,2 mg, 0.016 mmol) in dry pyridine (20 mL) and a solution of compound **11** (110 mg, 0.32 mmol) in dry pyridine (10 mL) was stirred for 7 h. After solvent was removed, the residual solid was washed with ammonium hydroxide till the blue color disappeared. The extraction was carried out with abundant dichloromethane (800 mL). The organic layer was dried on anhydrous magnesium sulfate and after filtration and solvent evaporation was obtained a solid, that was washed with hexane, EtOH, and Et_2O till the starting compounds were removed. Compound **17** was isolated as a yellow-brown solid, mp > 158 °C (darken, dec DSC), 100 mg (90%) yield, which shows low solubility in organic solvents. UV−vis (CH_2Cl_2), λ max (nm): 232 (ϵ, 39182), 373 (ϵ, 12784). IR (KBr, cm^{-1}): 2259, 1527, 1363, 784. ^{1}H NMR (300 MHz, NO_2-benzene[d_5], 85 °C): δ 8.39 (d, 2H, $J = 8.4$ Hz), 8.19 (d, 2H, $J = 8.7$ Hz), 7.94 (d, 2H, $J = 7.5$ Hz), 7.65 (d, 2H, $J = 8.1$ Hz), 7.56 (d, 2H, $J = 8.7$ Hz), 7.48−7.26 (m, 14H). MS (MALDI-TOF): 692.2. $C_{48}H_{24}N_2O_4$ (692.17): Anal. Calcd: C 83.23, H 3.49, N 4.04; found: C 83.14, H 3.62, N 4.38.

1-Nitro-5-({5-[(5-{4-[5-({5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}ethynyl)-1-naphthyl]buta-1,3-diynyl}-1-naphthyl)ethynyl]-1-naphthyl}ethynyl)naphthalene (18). Following the general method used for the preparation of **16**, a mixture of cuprous chloride (1,2 mg, 0.006 mmol) in dry pyridine (20 mL) and compound **13** (60 mg, 0.32 mmol) in dry pyridine (20 mL) was stirred for 10 h. After solvent was removed, the residual solid was washed with ammonium hydroxide till the blue color disappeared. The solid was extracted with abundant dichloromethane (800 mL). Compound **18** was obtained as a yellow solid, mp > 250 °C (darken, dec; DSC), 50 mg (80%) yield, which shows very low solubility in organic solvents. UV−vis (CH_2Cl_2), λ max (nm): 236 (ϵ, 205000), 362 (ϵ, 102410). IR (KBr, cm^{-1}): 2258, 1524, 1312, 781. ^{1}H NMR (300 MHz, NO_2-benzene[d_5], 85 °C): δ 8.67 (d, 2H, $J = 8.1$ Hz), 8.46−8.39 (m, 6H), 8.21 (d, 2H, $J = 8.9$ Hz), 8.14 (d, 2H, $J = 8.5$ Hz), 7.98 (d, 2H, $J = 7.7$ Hz), 7.77 (d, 4H, $J = 6.1$ Hz), 7.75 (d, 2H, $J = 5.7$ Hz), 7.72 (d, 2H, $J = 7.3$ Hz), 7.55−7.34 (m, 14H). MS (MALDI-TOF): 992.2. $C_{72}H_{36}N_2O_4$ (992.17): Anal. Calcd: C 87.08, H 3.65, N 2.82; found: C 87.15, H 3.87, N 3.11.

5-Iodo-*N,N*-dimethylnaphthalene-1-amine (19). (a) 5-Iodonaphthalene-1-amine.[18] To a solution of compound **3** (600 mg, 2 mmol) in ethyl acetate (freshly distilled) (30 mL) was added $SnCl_2-2H_2O$ (2.3 g, 0.01 mol), under argon atmosphere. The mixture was stirred for 10 h at the reflux temperature and then poured onto ice (75 g). The pH of the mixture was made basic (9−10) by addition of aqueous sodium hydroxide and finally was extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate, and after filtration, the solvent was removed. The residual brown solid was purified by silica gel column chromatography, eluting with dichloromethane/hexane 2:1 to give 5-iodonaphthalene-1-amine as a pale-brown solid, mp 63−64 °C, 500 mg (93%) yield. IR (KBr, cm^{-1}): 3380, 3209, 1392, 1181, 777. ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.08 (d, 1H, $J = 7.4$ Hz), 7.83 (d, 1H, $J = 8.8$ Hz), 7.57 (d, 1H, $J = 8.6$ Hz), 7.37 (dd, 1H, $J = 8.6$ Hz, $J = 7.4$ Hz), 7.13 (dd, 1H, $J = 7.6$ Hz, $J = 8.8$ Hz), 6.84 (d, 1H, $J = 7.6$ Hz), 4.18 (s, 2H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 142.39, 137.69, 135.10, 127.98, 125.52, 123.99, 123.35, 121.68, 110.66, 100.49. $C_{10}H_8NI$ (268.97): Anal. Calcd: C 44.64, H 3.00, N 5.21; found: C 42.97, H 3.18, N 5.09.

(b) 5-Iodo-*N*,*N*-dimethylnaphthalene-1-amine (19).[19,20] To a solution of compound 5-iodonaphthalene-1-amine (100 mg, 0.37 mmol) and aqueous formaldehyde (37%, 100 mg, 0.37 mmol) in acetonitrile (20 mL) and under argon atmosphere was slowly added sodium cyanoborohydride (70 mg, 1.11 mmol). The mixture was stirred at room temperature, and glacial acetic acid (0.08 mL) was slowly added (for 1 h). The mixture was stirred for 4 h and then washed with two portions of KOH (pH 9−10) and extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate, and after filtration, solvent was removed. The solid residual was purified by silica gel column chromatography, eluting with hexane/dichloromethane (1:1) to give **19** as a brown-red solid, mp 40−42 °C, 100 mg (100%) yield. IR (KBr, cm^{-1}): 1388, 933, 780. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.35 (d, 1H, $J = 8.4$ Hz), 8.13 (d, 1H, $J = 7.2$ Hz), 7.88 (d, 1H, $J = 8.4$ Hz), 7.53 (t, 1H, $J = 7.8$ Hz), 7.21 (dd, 1H, $J = 8.4$ Hz, $J = 7.2$ Hz), 7.17 (d, 1H, $J = 7.2$ Hz), 2.92 (s, 6H).^{13}C NMR (75 MHz, CDCl$_3$): δ 151.15, 137.42, 135.41, 129.59, 127.33, 126.94, 125.87, 125.09, 114.76, 99.87, 45.33 (2C). $C_{12}H_{12}NI$ (297.00): Anal. Calcd: C 48.51, H 4.07, N 4.71; found: C 48.35, H 4.29, N 4.65.

***N*,*N*-Dimethyl-5-[(5-nitro-1-naphthyl)ethynyl]naphthalen-1-amine (20).** Following the general method used for the preparation of **5a**, a mixture of dichloro bis(triphenylphosphine)palladium (36 mg, 0.051 mmol), copper iodide (1 mg, 0.005 mmol), compound **9** (100 mg, 0.51 mmol), compound **19** (150 mg, 0.51 mmol), and triethylamine (40 mL) was stirred for 20 h. Flash chromatography on silica gel, eluting with hexane/dichloromethane 3:1, provides **20** as a red-orange solid, mp 137.5 °C (DSC), 181 mg (97%) yield. UV−vis (CH$_2$Cl$_2$), λ max (nm): 238 (ϵ, 50072), 262s (ϵ, 17711), 328 (ϵ, 13817), 371 (ϵ, 13059). IR (KBr, cm^{-1}): 2200, 1518, 1341, 1325, 1414, 779. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.90 (d, 1H, $J = 8.1$ Hz), 8.55 (d, 1H, $J = 8.7$ Hz), 8.34 (d, 1H, $J = 8.4$ Hz), 8.27 (d, 1H, $J = 7.2$ Hz), 8.19 (d, 1H, $J = 8.4$ Hz), 7.99 (d, 1H, $J = 7.2$ Hz), 7.87 (d, 1H, $J = 6.9$ Hz), 7.72 (t, 1H, $J = 8.4$ Hz), 7.67 (t, 1H, $J = 7.8$ Hz), 7.55 (t, 1H, $J = 8.0$ Hz), 7.52 (t, 1H, $J = 7.8$ Hz), 7.17 (d, 1H, $J = 7.5$ Hz), 2.93 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 151.53, 147.07, 134.61, 134.10, 132.84, 131.69, 130.82, 128.80, 128.76, 127.07, 125.77, 125.23, 124.99, 124.47, 124.35, 123.43, 122.33, 120.70, 120.57, 114.77, 94.55, 90.96, 45.22 (2C). MS (70 eV): 366 (M$^+$, 100), 336 (9), 304 (19), 292 (4), 276 (24), 138 (20). $C_{24}H_{18}N_2O_2$ (366.14): Anal. Calcd: C 78.67, H 4.95, N 7.65; found: C 78.82, H 5.12, N 7.49.

Crystal Structure of Compound 20. Crystals of composition $C_{48}H_{36}N_4O_4$ (dimer of compound **20**) were grown from a dichloromethane solution as orange prisms.[32] A prismatic crystal of 0.20 × 0.15 × 0.10 mm was selected for X-ray analysis using a rotary anode diffractometer, with graphite-monochromated Cu Kα radiation.

Sixty reflections up to $2\theta = 70°$ were measured for the refinement of the lattice constants. The crystals are monoclinic and belong to the space group $P2_1/c$. Accurate cell constants were $a = 7.8944(1)$, $b = 8.2364(1)$, $c = 28.0376(4)$ Å, $\beta = 92.790(1)°$, $V = 1820.88(4)$ Å^3, Z = two dimer molecules (or four molecules of **20**). $D_c = 1.337(2)$ mg m^{-3}, $M = 732.326$, $F(000) = 768$, $\mu = 0.686(1)$ mm^{-1}, at 296 K. Intensities were collected in $\omega - 2\theta$ scan mode using Cu Kα ($\lambda = 1.54180$ Å) radiation with a graphite monochromator ($-9 < h < 9$; $0 < k < 10$; $0 < l < 33$) up to $\theta = 76°$. Two reference reflections after every 90 min showed negligible variation. From 3312 reflections measured, the structure was solved by direct methods[33] and difference Fourier techniques; no absorption correction was applied. After preliminary adjustment of the heavy atoms, H-atoms were positioned from difference Fourier maps and then the coordinates refined. Thereafter, several cycles of full-matrix least-squares calculations were carried out for heavy atoms, with anisotropic thermal parameters and the hydrogens atoms included as fixed contributors.[34] The refinement converged at $R = 0.0348$ and $R_w = 0.0975$ for $I > 2\sigma$ and $R = 0.0476$ and $R_w = 0.1045$ for all data. A weighting scheme to prevent trends in $w\Delta^2F$ vs $\langle F_o \rangle$ and vs $<\sin\theta/\lambda>$ was applied. Largest differences of peak and hole were 0.104 and −0.115 e Å^{-3}. The atomic scattering factors and the anomalous dispersion correction were taken from the International Tables for X-ray Crystallography.[35]

***N*,*N*-Dimethyl-5-({5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}ethynyl)naphthalen-1-amine (21).** Following the general method used for the preparation of **5a**, a mixture of dichloro bis(triphenylphosphine)palladium (24 mg, 0.034 mmol), copper iodide (1 mg, 0.003 mmol), compound **11** (118 mg, 0.34 mmol), compound **19** (100 mg, 0.34 mmol), and triethylamine (30 mL) was stirred for 40 h. Flash chromatography on silica gel, eluting with hexane/dichloromethane (1:1), gave compound **21** as an orange-yellow solid, mp 195−198 °C, 105 mg (60%) yield. UV−vis (CH$_2$Cl$_2$), λ max (nm): 232 (ϵ, 33997), 372 (ϵ, 30377). IR (KBr, cm^{-1}): 2202, 1522, 1342, 1329, 1419, 797. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.92 (d, 1H, $J = 8.7$ Hz), 8.65 (d, 1H, $J = 8.7$ Hz), 8.58 (d, 1H, $J = 9.0$ Hz), 8.54 (d, 1H, $J = 8.7$ Hz), 8.32 (d, 1H, $J = 8.7$ Hz), 8.30 (d, 1H, $J = 8.4$ Hz), 8.26 (d, 1H, $J = 8.1$ Hz), 8.03 (d, 1H, $J = 7.2$ Hz), 7.97 (d, 2H, $J = 6.9$ Hz), 7.89 (d, 1H, $J = 7.2$ Hz), 7.77 (dd, 1H, $J = 8.7$ Hz, $J = 7.2$ Hz), 7.71 (t, 1H, $J = 7.8$ Hz), 7.67 (dd, 2H, $J = 8.4$ Hz, $J = 7.2$ Hz), 7.56 (t, 1H, $J = 8.4$ Hz), 7.52 (dd, 1H, $J = 8.7$ Hz, $J = 7.2$ Hz), 7.17 (d, 1H, $J = 6.6$ Hz), 2.93 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 151.48, 147.15, 134.68, 134.09, 133.23, 133.15, 132.80, 131.88, 131.44, 131.20, 130.67, 128.78, 127.88 (2C), 126.92, 126.75, 126.57, 126.27, 125.44, 125.26, 125.13, 124.52, 124.43, 123.72, 122.06, 122.00, 121.03, 120.94, 120.86, 114.70, 93.78, 93.66, 91.73, 91.60, 45.37 (2C). MS (70 eV): 516 (M$^+$, 100), 486 (6), 470 (4), 424 (8), 212 (12). $C_{36}H_{24}N_2O_2$ (516.18): Anal. Calcd: C 83.70, H 4.68, N 5.42; found: C 83.79, H 4.44, N 5.71.

***N*,*N*-Dimethyl-5-{[5-({5-[(5-nitro-1-naphthyl)ethynyl]-1-naphthyl}ethynyl)-1-naphthyl]ethynyl}naphthalen-1-amine (22).** Following the general method used for the preparation of **5a**, a mixture of dichloro bis(triphenylphosphine)palladium (30 mg, 0.042 mmol), copper iodide 0.8 mg, 0.004 mmol), compound **13** (100 mg, 0.21 mmol), compound **19** (62 mg, 0.51 mmol), and piperidine (50 mL) was warmed at reflux temperature for 4 days. The crude residue after hydrolysis was extracted with abundant dichloromethane (800 mL). Compound **22** was obtained as a dark brown solid, mp > 298 °C (dark, dec), 30 mg (22%) yield, which shows very low

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[32] The crystallographic data of compound **20** (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 186048. A copy of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk).

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solubility in organic solvents. UV−vis (CH_2Cl_2), λ max (nm): 231 (ϵ, 13677), 298 (ϵ, 4650), 318 (ϵ, 4877), 340 (ϵ, 5451), 372 (ϵ, 6109). IR (KBr, cm^{-1}): 2166, 1524, 1344, 1443, 788. ^{1}H NMR (300 MHz, NO_2-benzene[d_5], 85 °C): δ 8.66 (d, 1H, J = 7.8 Hz), 8.48 (d, 1H, J = 8.4 Hz), 8.45 (d, 1H, J = 7.8 Hz), 8.41 (d, 1H, J = 9.0 Hz), 8.21−7.65 (m, 11H), 7.56−711 (m, 8H), 6.89 (d, 1H, J = 7.5 Hz), 2.93 (s, 6H). MS (70 eV): 666 (M^+, 17). MS (MALDI-TOF): 666.0. $C_{48}H_{30}N_2O_2$ (666.23): Anal. Calcd: C 86.46, H 4.54, N 4.20; found: C 86.57, H 4.40, N 4.47.

Supporting Information Available: The structural assignments and spectral data (^{1}H, ^{13}C and bidimensional ^{1}H/^{13}C and ^{1}H/^{1}H) of compounds **3**, **9**, **11**, **19**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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