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Synthesis of Diindolocarbazoles by Cadogan Reaction: Route to Ladder Oligo(*p*-aniline)s

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Symmetric and nonsymmetric diindolocarbazoles were successfully synthesized for the first time by a Cadogan ring closure using *N*-alkyl-2,7-disubstituted carbazole precursors. Cyclization reaction on *N*-alkyl-2,7-di(2′-nitrophenyl) carbazole derivatives is not regioselective and produced a separable mixture of symmetric and nonsymmetric diindolocarbazoles. A carbazole derivative with methyl protective groups at the 1- and 8-positions was therefore used to obtain a symmetric ladder oligo(*p*-aniline) (compound **22**). Optical and electrochemical properties of compound **22** indicate that its neutral semiconducting form is stable in air. This novel class of electroactive ladder oligomers should create new opportunities in micro- and nanoelectronics.

Introduction

A great number of organic semiconducting materials have been developed and tested for the fabrication of organic field-effect transistors (OFET) during the past 20 years.[1] Among all investigated *p*-type materials, regioregular poly(3-alkylthiophene)s,[2] oligothiophenes,[3] oligofluorenes,[4] oligo(2,6-anthrylene)s,[5] and fused aromatic compounds such as pentacene[6] have shown the best performances up to now. In particular, pentacene[6] has received great attention since it shows mobilities up to 5 $cm^2\ V^{-1}\ s^{-1}$ with on−off current ratios of about 10^8. However, pentacene suffers from oxidative instability, insolubility, and sensitivity to visible light, making it unsuitable for practical electronic device applications.[4,7] To address this problem, the design and synthesis of novel organic semiconductors with good stability and processability as well as high charge carrier mobility is desirable.[1,4] Organic synthesis allows a great flexibility at the molecular scale to develop conjugated oligomers having optimized physical and chemical properties for the aimed applications. It could therefore be interesting to develop pentacene-like oligomers that show a similar coplanar structure and favorable packing geometry together with improved stability and processability. From this point of view, synthetic ladder-type π-conjugated molecules could be promising materials for OFET applications. Until now, only few examples of ladder-conjugated oligomers containing fused-ring thiophenes have been reported.[8] Substituted anthradithiophenes with a mixture of syn and anti isomers were also prepared by Laquindanum and co-workers.[9] These compounds show moderate solubility and good solution stability, but no attempt was made to characterize or separate the syn and anti isomers. Sirringhaus and coworkers[10] reported also the synthesis of dibenzothienobisbenzothiophene (DBTBT), but an inseparable mixture of different regioisomers was obtained. Poor FET performances are observed when DBTBT films contain a mixture of different isomers. Their results prove that isomeric purity is of first importance for achieving high charge-transport mobility. Starting from this point, we present here a new class of pentacene-like semiconducting organic materials using ladder electroactive oligo(*p*-aniline) derivatives (see Chart 1).

Interestingly, depending upon the nature of the *R* and *R*′ groups, it may be possible to develop amphiphilic molecules that could lead to well-defined thin films

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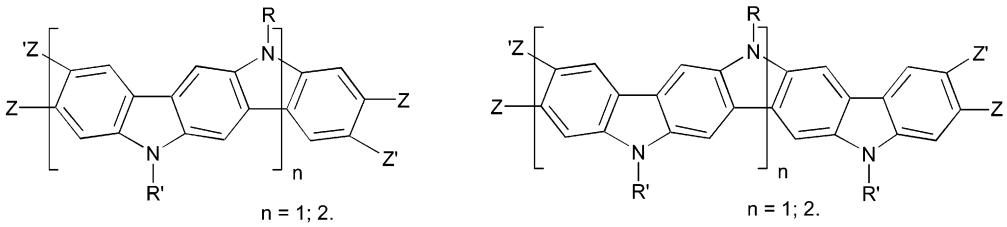
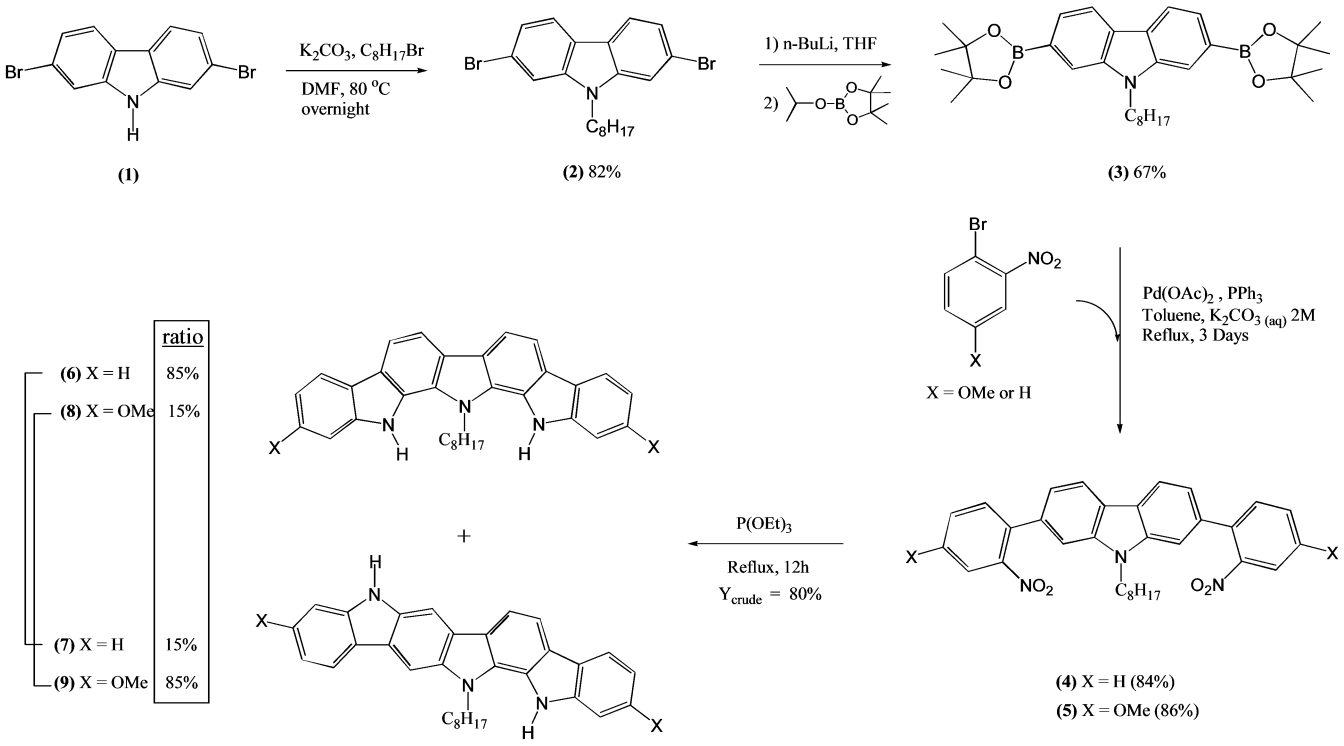
CHART 1. Conjugated Ladder Oligo(*p*-aniline)s



SCHEME 1. Synthesis of the Diortho Symmetric Isomers and Nonsymmetric Isomers



through Langmuir−Blodgett processing or self-assembly procedures. Moreover, the use of organic conjugated molecules, as molecular nanowires or transistors, has recently received much attention.[11] From this point of view, the proposed ladder oligomers, bearing adequate end groups, have the potential to make connections with different nanoelectrodes and to operate as three-way nanoconnectors or molecular transistors.

Results and Discussion

To achieve a general synthesis of this new class of materials, we focused on the Cadogan[12] procedure as the final ring closure reaction on various *N*-alkyl-2,7-diphenylcarbazole precursors. As we recently reported, this reaction was successfully utilized for obtaining a large number of well-defined 2,7-disubstitued carbazole derivatives.[13] Our first approach was based on precursors bearing nitro groups on side phenyl groups such as compounds **4** and **5**. As shown in Scheme 1, these precursors were obtained in three steps from 2,7-dibromocarbazole[14] (compound **1**). N-Alkylation of compound **1** was performed by the action of 1-bromooctane with K_2CO_3 in hot DMF to give compound **2** in an 82% isolated yield after simple crystallization in methanol. On the basis of procedures developed for 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene,[15] compound **2** was then dilithiated by using *n*-butyllithium in THF at a low temperature, followed by a reaction with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, to give the desired compound **3** in satisfactory yields.

Then, a Suzuki coupling reaction was carried out on

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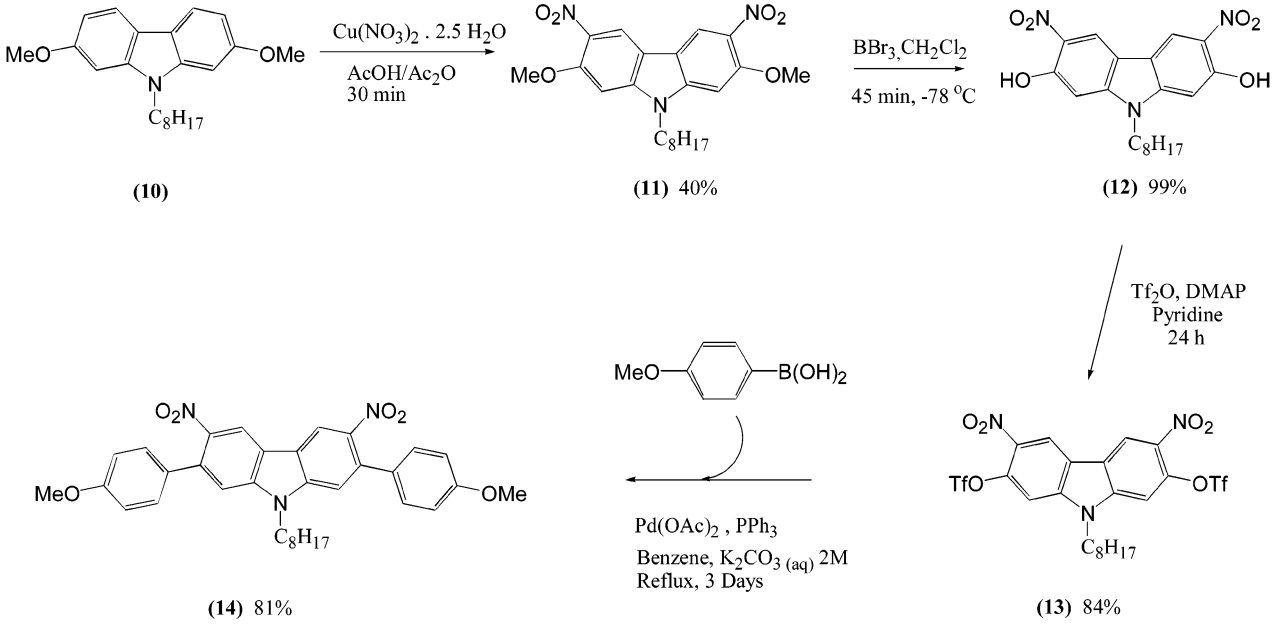
SCHEME 2. Synthesis of *N*-Octyl-3,6-dinitro-2,7-bis(2′-nitrophenyl)carbazole (Compound 14)



compound **3** with 1-bromo-2-nitrobenzene or with 4-bromo-3-nitroanisole using a stable $Pd^{II}(OAc)_2$ complex in combination with 4 equiv of triphenylphosphine ligands to lead to compounds **4** and **5** in good yields. The reductive Cadogan ring closure reaction[12] in hot triethyl phosphite was finally performed on molecules **4** and **5**. As described in Scheme 1, a mixture of two regioisomers was isolated in an 80% yield, but the desired ladder oligo(*p*-aniline) was not formed. Indeed, because of the free rotation between phenyl and carbazole units, ortho and para ring closure reactions are both possible, and consequently three different regioisomers can be produced. In the case of X = H, the crude product contains a mixture with 85% (determined by ^{1}H NMR based on the integration of NH peaks of the crude material) of the diortho symmetric isomer **6** and 15% of the nonsymmetric isomer **7**. The purification of these regioisomers was performed by preparative thin-layer chromatography. Only the major symmetric isomer **6** was isolated in a 35% yield, nonsymmetric isomer **7** being not obtained in a pure form. This result can be explained by the predominant ortho-orienting effect of the nitrogen atom, which prevents the formation of the para-symmetric isomer. The replacement of the hydrogen atoms by methoxy groups produces the same regioisomers but with an inverse ratio. Surprisingly, the nonsymmetric compound **9** was now the major isomer formed (85% determined by ^{1}H NMR based on the integration of NH pics of the crude material). A standard column chromatography technique allowed us to obtain compound **9** in a 40% yield but failed to isolate isomer **8**, which was always contaminated with compound **9**. Only semipreparative HPLC techniques gave a few milligrams of compound **8**.

To obtain the formation of the targeted isomer, a new approach, using as precursor a *N*-alkyl-2,7-disubstitued carbazole derivative with nitro groups at the 3- and 6-positions, was developed. As shown in Scheme 2, the 3,6-dinitration of compound **10**[13b] was performed by the action of $Cu(NO_3)_2 \cdot 2.5\ H_2O$ according to a procedure developed by Velasco and co-workers,[16] to give compound **11** in a 40% yield. The deprotection of the methoxy groups into hydroxyl groups was performed[13b] with 1 M boron tribromide at low temperatures to give compound **12**, quantitatively. Then, product **12** was transformed[13b] by the action of DMAP and trifluoromethanesulfonic anhydride in cold pyridine to compound **13** in an 84% yield. The formation of the unclosed trimer **14** was achieved by a Suzuki cross-coupling reaction on compound **13** with commercially available 4-methoxyphenylboronic acid according to a similar procedure to that already described for the formation of compounds **4** and **5**. Several attempts to produce the desired oligomer by the reductive Cadogan ring closure reaction of compound **14** with triethyl phosphite were unsuccessful. However, compound **14** was totally converted to give a multicomponent mixture (more than 10 different products based on thin-layer chromatography).

Following these results, we decided to prepare a new precursor (molecule **21**)**,** with methyl groups at the 1- and 8-positions on the carbazole and nitro groups on the side phenyl groups. The key step of this synthetic methodology is the preparation of a *N*-alkyl-1,8-dimethyl-2,7-disubstituted carbazole. Effectively, as described in Scheme 3, compound **17** was synthesized in two steps from compound **15**.[17] First of all, due to the ortho-orienting effect of the nitrogen atom in the carbazole unit during the halogen/metal permutation,[18] compound **15** reacted regioselectively with 2 equiv of *n*-BuLi to form the corresponding 1,8-dilithiated species, which was then quenched with iodomethane to lead to compound **16**, in a 64% isolated yield. It is important to perform this reaction in a mixture of diethyl ether and THF (5:1) to

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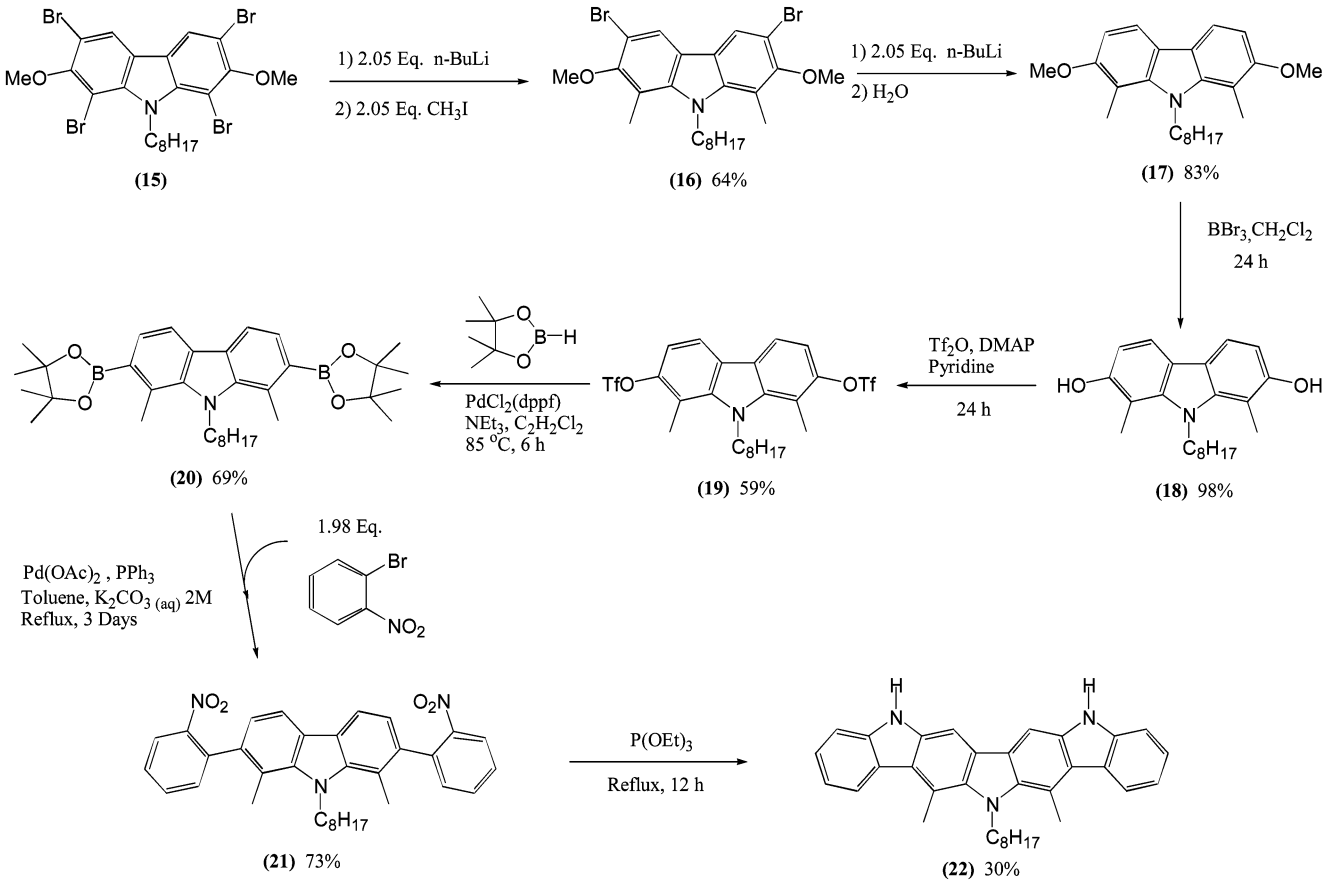
SCHEME 3. Synthesis of 5,8-Dihydro-13,15-dimethyl-14-octyl-diindolo[3,2-*b*:2′,3′-*h*]carbazole (Compound 22)



ensure both the reactivity and the solubility of the starting compound **15**. Similar strategy was used to remove bromine atoms at the 3- and 6-positions. First, *n*-BuLi was used to form the 3,6-dilithiated species, which was then quenched with distilled water to give compound **17** in a good yield. ^{1}H NMR spectrum of compound **17** contains two doublets in the aromatic region with a coupling constant of 8.4 Hz, characteristic of two adjacent aromatic protons. Thereafter, a standard deprotection reaction using BBr_3 in anhydrous dichloromethane was achieved to give the corresponding 2,7-dihydroxy-1,8-dimethylcarbazole **18** in an excellent yield. Compound **18** was treated with DMAP and trifluoromethanesulfonic anhydride in cold pyridine to give compound **19**. Boronic esters can now be easily introduced at the 2,7-positions on compound **19** by Masuda reaction[19] using $PdCl_2(dppf)$[20] as the catalyst. Thus, compound **20** was synthesized in a 69% isolated yield and can be used directly for the Suzuki cross-coupling reaction with commercially available 1-bromo-2-nitrobenzene. A double Suzuki reaction of **20** with 1-bromo-2-nitrobenzene was achieved under standard conditions using air stable $Pd(OAc)_2$ in combination with 4 equiv of triphenylphosphine ligands. After column chromatography, compound **21** was isolated in a 73% yield. Analysis of the ^{1}H NMR spectrum of **21** shows that signals of all protons (with the exception of some aliphatic protons) were doubled. The ^{13}C NMR spectrum was also intriguing, all aromatic and aliphatic carbons being doubled. Restricted rotation around the aryl−aryl bond (between phenyl and carbazole moieties) due to nitro and methyl functions can probably lead to the phenomenon of atropisomerism.[21] However, the double Cadogan ring closure was performed on compound **21** at 160 °C for 24 h, by the use of triethyl phosphite which acted, at the same time, as reagent and solvent. A pale yellow precipitate was formed when the reaction was stopped. The crude product was then purified by column chromatography to give the desired diindolocarbazole (compound **22)** in a 30% isolated yield. The ^{1}H NMR and ^{13}C NMR analyses confirmed the chemical structure of compound **22**. This product, soluble in common organic solvents as THF, CH_2Cl_2, etc., offers the possibility to develop different types of ladder oligo(*p*-aniline) derivatives depending on the nature of the substituents that can react with the free aromatic amine moieties.

Effect of the structure on the optical and electrochemical properties of these isomers was studied by comparing the ortho (compound **6**) and para (compound **22)** symmetric isomers. The optical band gap for compounds **6** and **22** is 3.32 and 2.73 eV, respectively. This is in agreement with structures determined by NMR analyses, where a greater degree of conjugation for oligomer **22** can be expected. Cyclovoltammetric measurements with compounds **6** and **22** were also performed in THF solution

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(with 0.1 M tetrabutylammonium perchlorate). Compound **22** shows a reversible oxidation at 0.70 V versus SCE, while compound **6** shows a nonreversible oxidation at 0.98 V versus SCE. These spectroscopic and electrochemical data indicate that the neutral semiconducting form of both compounds **6** and **22** is stable in air.

Conclusion

In summary, starting from *N*-alkyl-2,7-disubstituted carbazoles, we have developed, for the first time, a general route to new symmetric and nonsymmetric diindolocarbazoles, using the Cadogan ring closure reaction. This reductive reaction realized on *N*-alkyl-2,7-di-(2′-nitrophenyl)carbazole derivatives is not regioselective and produced a separable mixture of symmetric and nonsymmetric diindolocarbazoles. Using a carbazole derivative with methyl groups at the 1- and 8-positions (compound **20**), this reaction occurred regioregularly to offer the symmetric compound **22**. An attractive feature of this synthetic approach is the wide variety of ladder oligo(*p*-aniline)s that can be readily accessible from carbazole **20** by the appropriate choice of aryl groups and substituents. Preliminary studies of the spectroscopic and electrochemical properties of this symmetric diindolocarbazole indicate that this new class of materials could create new opportunities in micro- and nanoelectronics. Utilization of the present compound as an organic semiconductive material in organic field-effect transistors as well as the synthesis of longer oligomers and oligomers with different side chain patterns are currently in progress in our laboratory.

Experimental Procedures

***N*-Octyl-2,7-dibromocarbazole (2).** A 100 mL flame-dried flask was charged with 9.61 g (29.6 mmol) of 2,7-dibromocarbazole 1,[14] 8.18 g (59.2 mmol) of anhydrous K_2CO_3, 7.72 mL (44.4 mmol) of 1-bromooctane, and 60 mL of anhydrous *N*,*N*-dimethylformamide. The resulting mixture was stirred at 80 °C for 12 h under an inert atmosphere. The solution was quenched with 150 mL of distilled water and extracted twice (2 × 100 mL) with $CHCl_3$. The combined organic layers were washed with distilled water (5 × 50 mL) and dried over magnesium sulfate, and the solvent was removed under reduced pressure. Recrystallization from methanol afforded 10.6 g of the title compound as a white solid (82% yield): mp 66−67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, 2H, J = 8.3 Hz), 7.51 (d, 2H, J = 1.6 Hz), 7.33 (dd, 2H, J = 8.3 and 1.6 Hz), 4.16 (t, 2H, J = 7.4 Hz), 1.82 (m, 2H), 1.30 (m, 10H), 0.89 (t, 3H, J = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 122.4, 121.4, 121.2, 119.6, 111.9, 43.3, 31.7, 29.2, 29.1, 28.7, 27.1, 22.6, 14.1; HRMS *m*/*z* calculated for $C_{20}H_{23}NBr_2$ 435.0197, found 435.0201.

***N*-Octyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole (3).** In a 250 mL flame-dried two-necked flask, equipped with a dropping funnel, 8.71 g (19.9 mmol) of **2** was dissolved with 150 mL of freshly distilled THF. The resulting solution was cooled at −78 °C and 16.7 mL (41.8 mmol) of *n*-butyllithium (2.5 M in hexane) was added over 15−20 min under a nitrogen atmosphere. The mixture was stirred at −78 °C for 1.5 h, warmed to 0 °C for 15 min, and cooled again at −78 °C for 15 min. A total of 9.76 mL (47.8 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added rapidly to the solution, and then the resulting mixture was allowed to warm to room temperature and was stirred for 12 h. The mixture was poured into 200 mL of distilled water and then extracted with $CHCl_3$ (3 × 100 mL). The combined organic layers were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by crystallization in methanol or by column chromatography (silica gel, 15% diethyl ether in hexane as eluent) to provide 7.10 g of the title compound as white crystals (67% yield): mp 168−169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, 2H, J = 7.4 Hz), 7.89 (s, 2H), 7.69 (d, 2H, J = 7.4 Hz), 4.39 (t, 2H, J = 7.4 Hz), 1.90 (m, 2H), 1.41 (m, 24H), 1.30 (m, 10H), 0.88 (t, 3H, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 125.09, 124.9, 120.0, 115.3, 83.8, 43.1, 32.0, 29.5, 29.4, 27.3, 25.1, 25.1, 22.8, 14.3; HRMS *m*/*z* calculated for $C_{32}H_{47}NO_4B_2$ 531.3691, found 531.3700.

***N*-Octyl-2,7-bis(2′-nitrophenyl)carbazole (4).** A two-necked 25 mL flask, fitted with a condenser, was charged with 2.00 g (3.77 mmol) of **3**, 1.50 g (7.46 mmol) of 1-bromo-2-nitrobenzene, 9 mL of toluene, and 6 mL of K_2CO_3 2 M. The resulting solution was degassed with a vigorous flow of argon for 30 min, then 68 mg (0.30 mmol) of $Pd(OAc)_2$ and 318 mg (1.21 mmol) of PPh_3 was added under argon, and the mixture was heated under reflux for 48 h. After cooling to room temperature, the mixture was put into 30 mL of distilled water and extracted three times with $CHCl_3$ (3 × 50 mL). The combined organic fractions were dried over magnesium sulfate, and the solvent was removed under reduced pressure to give 2.50 g of the crude material. Crystallization from MeOH afforded 1.65 g of the title product as yellow needles (84% yield): mp 120−121 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.25 (dd, 2H, J = 8.0 and 0.6 Hz), 7.96 (dd, 2H, J = 8.0 and 0.4 Hz), 7.79 (m, 2H), 7.68 (m, 6H), 7.62 (dd, 2H, J = 1.6 and 0.6 Hz), 4.50 (t, 2H, J = 7.2 Hz), 1.90 (m, 2H), 1.30 (m, 10H), 0.81 (t, 3H, J = 6.9 Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 150.4, 141.4, 136.8, 135.6, 132.6 (2C), 128.7, 124.2, 122.5, 121.1, 119.5, 109.1, 43.0, 31.9, 29.5, 29.4, 29.2, 27.2, 22.7, 13.8; HRMS *m*/*z* calculated for $C_{32}H_{31}N_3O_4$ 521.2314, found 521.2310.

***N*-Octyl-2,7-bis(4′-methoxy-2′-nitrophenyl)carbazole (5).** This compound was synthesized according to a similar procedure as the one used for **4** using 2.00 g (3.76 mmol) of **3**, 1.92 g (8.28 mmol) of 1-bromo-2-nitroanisole, 34 mg (0.15 mmol) of $Pd(OAc)_2$, 158 mg (0.60 mmol) of PPh_3, 9 mL of toluene, and 6 mL of K_2CO_3 2 M. After 3 days, the resulting mixture was poured into 50 mL of distilled water and extracted with ethyl acetate (3 × 50 mL). The combined organic fractions were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude material was passed through a short column of silica gel using $CHCl_3$ as eluent to remove catalyst residues. Then, the compound was put in a hot mixture of hexane/ethyl acetate (9:1) and sonicated for 2−3 min. After cooling to 0 °C, the solid was recovered by filtration to provide 1.88 g of the title product as a yellow solid (86% yield): mp 146−147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, 2H, J = 8.0 Hz), 7.49 (d, 2H, J = 8.5 Hz), 7.39 (d, 2H, J = 2.6 Hz), 7.31 (s, 2H), 7.17 (m, 4H), 4.26 (t, 2H, J = 7.1 Hz), 3.93 (s, 6H), 1.86 (m, 2H), 1.30 (m, 10H), 0.85 (t, 3H, J = 6.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 150.1, 141.0, 134.9, 133.1, 129.4, 122.2, 120.7, 119.4, 118.5, 108.9, 108.3, 56.0, 43.2, 31.8, 29.3, 29.1, 28.9, 27.3, 22.6, 14.1; HRMS *m*/*z* calculated for $C_{34}H_{35}N_3O_6$ 581.2526, found: 581.2514.

5,7-Dihydro-6-octyl-diindolo[2,3-*a*:3′,2′-*i*]carbazole (6). A 10 mL flame-dried flask, equipped with a condenser, was charged with 100 mg (0.19 mmol) of **4** and 1.0 mL of triethyl phosphite. The resulting mixture was heated under reflux under nitrogen for 24 h, and then the excess of triethyl phosphite was distilled off under reduced pressure. The ^{1}H NMR spectra of the crude material (80% yield) showed mainly two compounds, **6** and **7**, in a 5:1 ratio. Only compound **6** was isolated on silica gel by preparative thin-layer chromatography (40% ethyl acetate in hexane as eluent) as a pale yellow solid (30 mg, 35% yield): mp 278−280 °C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.67 (s, 2H, NH), 8.18 (d, 2H, J = 7.8 Hz), 8.03 (m, 4H), 7.62 (d, 2H, J = 8.1 Hz), 7.37 (t, 2H, J = 7.5 Hz), 7.23 (t, 2H, J = 7.5 Hz), 5.29 (t, 2H, J = 6.9 Hz), 1.98 (m, 2H),

1.17 (m, 10H), 0.68 (t, 3H, J = 6.9 Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 140.2, 127.2, 126.2, 124.9, 124.5, 123.3, 121.9, 119.7, 119.7, 112.6, 112.2, 111.7, 47.1, 32.1, 31.8, 29.2, 26.2, 22.5, 13.6 (one aromatic carbon missing); HRMS m/z calculated for $C_{32}H_{31}N_3$ 457.2518, found 457.2527.

5,7-Dihydro-3,9-dimethoxy-6-octyl-diindolo[2,3-*a*:3′,2′-*i*]carbazole (8) and 5,12-Dihydro-3,10-dimethoxy-6-octyl-diindolo[2,3-*a*:2′,3′-*h*]carbazole (9). These compounds were synthesized according to a similar procedure as the one used for **6** using 726 mg (1.40 mmol) of **5** and 5.7 mL of triethyl phosphite. The resulting mixture was heated under reflux under nitrogen for 24 h. After being cooled to room temperature, the mixture was put into hexane containing 4% of acetone at 0 °C. The resulting precipitate was recovered by filtration to provide 533 mg (crude yield = 80%) of a mixture containing mainly molecules **8** and **9** in a 1:5 ratio. The crude product was purified by column chromatography (silica gel, 40% ethyl acetate in hexane as eluent) to provide 290 mg of compound **9** as a pale yellow solid (40% yield). To obtain compound **8**, a small fraction (100 mg) of the crude product was purified by semipreparative HPLC techniques using aqueous acetonitrile (75%) as eluent. Fractions obtained were saturated with brine. The organic layers were dried with anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. **(8):** mp 270 °C dec; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.37 (s, 2H, NH), 7.99 (d, 2H, J = 8.4 Hz), 7.90 (d, 2H, J = 8.2 Hz), 7.84 (d, 2H, J = 8.2 Hz), 7.17 (d, 2H, J = 2.4 Hz), 6.82 (dd, 2H, J = 8.4 Hz), 5.21 (t, 2H, J = 6.6 Hz), 3.88 (s, 6H), 1.75 (m, 2H), 1.18 (m, 3H), 0.99 (m, 7H), 0.64 (t, 3H, J = 7.0 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.9, 141.0, 126.6, 125.3, 121.6, 121.1, 120.3, 117.5, 111.8, 111.7, 108.4, 95.2, 55.4, 46.1, 31.4, 31.2, 28.9, 28.6, 25.6, 22.1, 14.0; HRMS m/z calculated for $C_{34}H_{35}N_3O_2$ 517.2729, found 517.2737. **(9):** mp 250 °C dec; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.18 (s, 1H, NH), 10.90 (s, 1H, NH), 8.19 (s, 1H), 8.07 (m, 2H), 8.01 (d, 1H, J = 8.6 Hz), 7.95 (d, 1H, J = 8.2 Hz), 7.79 (d, 1H, J = 8.2 Hz), 7.16 (d, 1H, J = 2.2 Hz), 6.96 (d, 1H, J = 2.2 Hz), 6.82 (dd, 1H, J = 8.5 and 2.3 Hz), 6.76 (dd, 1H, J = 8.5 and 2.3 Hz), 4.85 (t, 2H, J = 6.7 Hz), 3.88 (s, 3H), 3.85 (s, 3H), 1.84 (m, 2H), 1.21 (m, 10H), 0.73 (t, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.6, 158.0, 142.6, 141.2, 135.7, 135.6, 127.6, 124.7, 122.6, 122.3, 121.6, 121.0, 120.4, 119.7, 117.5, 116.8, 112.1, 110.4, 108.5, 106.8, 99.7, 98.8, 95.1, 94.5, 55.4, 55.4, 44.2, 31.4, 30.3, 30.1, 29.8, 26.3, 22.2, 14.1; HRMS m/z calculated for $C_{34}H_{35}N_3O_2$ 517.2729, found 517.2721.

***N*-Octyl-3,6-dinitro-2,7-dimethoxycarbazole (11).** In a 100 mL flask, 3.64 g (15.6 mmol) of $Cu(NO_3)_2$•2.5 H_2O was dissolved in a mixture of Ac_2O (43.5 mL) and AcOH (21.6 mL) at room temperature, and then 5.00 g (14.7 mmol) of **10**[13b] was added. The mixture was stirred for 30 min at room temperature and then poured into ice water (100 mL), neutralized with 10% NaOH, and extracted with CH_2Cl_2 (3 × 75 mL). The combined organic fractions were washed twice with brine and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude compound was purified by crystallization in $CHCl_3$/diethyl ether to afford 2.55 g of the title product as a green−yellow solid (40% yield): mp 212−214 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (s, 2H), 6.82 (s, 2H), 4.24 (t, 2H, J = 7.1 Hz), 4.05 (s, 6H), 1.87 (m, 2H), 1.32 (m, 10H), 0.86 (t, 3H, J = 6.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 144.8, 134.3, 118.8, 114.9, 93.2, 56.9, 43.7, 31.7, 29.2, 29.0, 28.4, 27.1, 22.5, 14.0; HRMS m/z calculated for $C_{22}H_{27}N_3O_6$ 429.1900, found 429.1905.

***N*-Octyl-3,6-dinitro-2,7-dihydroxycarbazole (12).** A 10 mL flame-dried flask was charged under a nitrogen atmosphere with 100 mg (0.23 mmol) of **11** and 2.3 mL of anhydrous dichloromethane. The solution was cooled to −78 °C, and 1.15 mL (1.16 mmol) of boron tribromide (1 M in dichloromethane) was added to the solution over 15 min. The resulting mixture was stirred under nitrogen atmosphere at −78 °C for 45 min and then quenched slowly (at −78 °C) with 2 mL of HCl 10% (v/v) to destroy the excess of boron tribromide. The resulting mixture was extracted with dichloromethane (3 × 20 mL). The organic layer was washed twice with brine and dried over magnesium sulfate, and the solvent was removed under reduced pressure to provide 93 mg (yield >99%) of the title molecule as a yellow solid: mp 198−200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.19 (s, 2H), 8.75 (s, 2H), 6.93 (s, 2H), 4.13 (t, 2H, J = 7.4 Hz), 1.85 (m, 2H), 1.32 (m, 10H), 0.87 (t, 3H, J = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 148.4, 128.9, 118.0, 116.9, 97.6, 44.1, 31.7, 29.2, 29.1, 28.1, 27.1, 22.5, 14.0; HRMS m/z calculated for $C_{20}H_{23}N_3O_6$ 401.1587, found 401.1590.

***N*-Octyl-3,6-dinitro-2,7-bis(trifluoromethanesulfonyl)-carbazole (13).** A 50 mL flame-dried flask was charged with 1.62 g (4.03 mmol) of compound **12**, 492 mg (4.03 mmol) of 4-(dimethylamino)pyridine, and 20 mL of anhydrous pyridine. The mixture was stirred under inert atmosphere and cooled to 0 °C, and 2.04 mL (12.1 mmol) of trifluoromethanesulfonic anhydride was added dropwise. After 10 min, 5 mL of anhydrous pyridine was added to dissolve the precipitate formed during the addition of anhydride. The solution was stirred at 0 °C for 1 h and at room temperature for 12 h. The excess of anhydride was destroyed by a slow addition of 20 mL of distilled water. The mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic fractions were washed successively with distilled water (5 × 50 mL), aqueous $CuSO_4$ 0.1 M (5 × 50 mL), brine (3 × 50 mL), and again with distilled water (2 × 50 mL). The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, CH_2Cl_2 as eluent) to provide 2.25 g of the title product as an off-white solid (84% yield): mp 158−160 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.07 (s, 2H), 7.49 (s, 2H), 4.41 (t, 2H, J = 7.0 Hz), 1.93 (m, 2H), 1.30 (m, 10H), 0.86 (t, 3H, J = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 141.5, 135.8, 120.8, 120.7, 118.7, 105.6, 45.0, 31.5, 29.1, 28.9, 28.8, 27.2, 22.5, 13.9; HRMS m/z calculated for $C_{22}H_{21}N_3O_{10}F_6S_2$ 665.0572, found 665.0583.

***N*-Octyl-3,6-dinitro-2,7-bis(2′-nitrophenyl)carbazole (14).** This compound was synthesized according to a similar procedure described previously for the synthesis of compound **4** using 1.84 g (2.77 mmol) of **13**, 0.93 g (6.09 mmol) of 4-methoxyphenylboronic acid, 116 mg (0.44 mmol) of PPh_3, 25 mg (0.11 mmol) of $Pd(OAc)_2$, 23 mL of benzene, and 15.4 mL of K_2CO_3 2 M (3 days at reflux; extraction with benzene). The crude product was purified by column chromatography (silica gel, 20% hexane in CH_2Cl_2 as eluent) to afford 1.30 g of the title compound as yellow crystals (81% yield): mp 178−180 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (s, 2H), 7.36 (m, 6H), 7.02 (d, 4H, 8.5), 4.34 (t, 2H, J = 7.2 Hz), 3.89 (s, 6H), 1.89 (m, 2H), 1.28 (m, 10H), 0.85 (t, 3H, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 143.1, 136.2, 130.9, 129.3, 120.8, 118.4, 114.2, 112.0, 55.3, 43.9, 31.6, 29.1, 29.0, 28.8, 27.0, 22.5, 14.0 (one aromatic carbon missing); HRMS m/z calculated for $C_{34}H_{35}N_3O_6$ 581.2526, found 581.2518.

***N*-Octyl-3,6-dibromo-2,7-dimethoxy-1,8-dimethylcarbazole (16).** A 1 L flame-dried flask was charged under an argon atmosphere with 17.0 g (26.0 mmol) of *N*-octyl-1,3,6,8-tetrabromo-2,7-dimethoxycarbazole **(15)**,[17] 520 mL of diethyl ether, and 104 mL of freshly distilled THF. The stirring mixture was cooled to −78 °C, and 21.3 mL (53.2 mmol) of *n*-butyllithium (2.5 M in hexane) was added dropwise to the solution over 15 min. The resulting mixture was stirred for 2 h at this temperature, and then 3.31 mL (53.2 mmol) of iodomethane was added dropwise. The solution was allowed to warm to room temperature and stirred for 2 h. The resulting mixture was quenched with distilled water (200 mL) and extracted with diethyl ether (3 × 100 mL). The combined organic fractions were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, 7% ethyl acetate in hexane as eluent) to afford 8.70 g of the title compound as white crystals (64% yield): mp 120−121 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.17 (2s, 2H), 4.66 (t, 2H, J =

7.7 Hz), 3.82 (s, 6H), 2.72 (2s, 6H), 1.49 (m, 2H), 1.18 (m, 10H), 0.82 (t, 3 H, $J = 7.1$ Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 154.0, 142.6, 122.1, 121.7, 117.3, 109.6, 60.7, 46.5, 31.8, 30.6, 29.3, 29.2, 26.2, 22.7, 13.8, 12.4; HRMS *m*/*z* calculated for $C_{24}H_{31}NO_2Br_2$ 523.0721, found 523.0715.

***N*-Octyl-2,7-dimethoxy-1,8-dimethylcarbazole (17).** This compound was synthesized according to a similar procedure to that one used for compound **16** using 10.8 g (20.5 mmol) of **16**, 205 mL of diethyl ether, 41 mL of THF, and 16.8 mL (42.1 mmol) of *n*-butyllithium (2.5 M in hexane). The resulting mixture was stirred for 1 h at −78 °C, and then 50 mL of distilled water was added (extraction with chloroform). Crystallization from methanol afforded 6.25 g of the title compound as a pale yellow solid or a more pure compound could be obtained by column chromatography (silica gel, 7% ethyl acetate in hexane as eluent) (83% yield): mp 53−54 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 (d, 2H, $J = 8.4$ Hz), 6.87 (d, 2H, $J = 8.4$ Hz), 4.42 (t, 2H, $J = 7.4$ Hz), 3.82 (s, 6H), 2.47 (s, 6H), 1.26 (m, 2H), 1.06 (m, 10H), 0.77 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.3, 143.8, 120.1, 117.5, 109.5, 105.6, 57.0, 46.9, 31.7, 29.8, 29.1, 29.1, 26.2, 22.6, 14.5, 11.9; HRMS *m*/*z* calculated for $C_{24}H_{33}NO_2$ 367.2511, found 367.2502.

***N*-Octyl-2,7-dihydroxy-1,8-dimethylcarbazole (18).** This compound was synthesized according to a similar procedure to that described previously for the synthesis of compound **12** using 6.0 g (16.3 mmol) of **17**, 183 mL of freshly distilled dichloromethane, and 81.6 mL (81.6 mmol) of boron tribromide (1 M in dichloromethane). After stirring at −78 °C for 3 h and at room temperature for 12 h, the mixture was quenched slowly with approximately 200 mL of HCl 10% (v/v). Crystallization from toluene/hexane afforded 5.45 g of the title compound as a slightly green solid (98% yield): mp 189−192 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.05 (s, 2H), 7.51 (d, 2H, $J = 8.2$ Hz), 6.74 (d, 2H, $J = 8.2$ Hz), 4.54 (t, 2H, $J = 7.6$ Hz), 2.54 (s, 6H), 1.37 (m, 2H), 1.20 (m, 10H), 0.81 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 153.5, 143.6, 119.4, 116.4, 109.0, 107.5, 46.7, 31.7, 29.8, 29.3, 29.2, 26.3, 22.6, 13.7, 11.2; HRMS *m*/*z* calculated for $C_{22}H_{29}NO_2$ 339.2198, found 339.2183.

***N*-Octyl-2,7-bis(trifluoromethanesulfonyl)-1,8-dimethylcarbazole (19).** This compound was synthesized according to a similar procedure to that one used for compound **13** using 5.00 g (14.73 mmol) of **18**, 1.80 g (14.73 mmol) of 4-(dimethylamino)pyridine, 45 mL of anhydrous pyridine, and 7.43 mL (44.19 mmol) of trifluoromethanesulfonic anhydride. The crude compound was purified by column chromatography (silica gel, 10% ethyl acetate in hexane as eluent) to provide 5.20 g of the title product as a pale yellow solid 59% yield: mp 70−72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, 2H, $J = 8.5$ Hz), 7.19 (d, 2H, $J = 8.5$ Hz), 4.62 (t, 2H, $J = 7.9$ Hz), 2.75 (s, 6H), 1.51 (m, 2H), 1.17 (m, 10H), 0.84 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 142.6, 123.8, 118.9, 118.6, 115.6, 114.3, 47.0, 31.5, 30.6, 29.0, 29.0, 26.2, 22.5, 14.0, 13.0; HRMS *m*/*z* calculated for $C_{24}H_{27}NO_6F_6S_2$ 603.1184, found 603.1195.

***N*-Octyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,8-dimethylcarbazole (20).** A 25 mL flame-dried two-necked flask equipped with a condenser was charged successively with 1.00 g (1.66 mmol) of **19**, 6.6 mL of freshly distilled 1,2-dichloroethane, 73 mg (0.10 mmol) of $PdCl_2$(dppf), 1.39 mL (9.94 mmol) of freshly distilled triethylamine, and 1.44 mL (9.94 mmol) of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The mixture was stirred under nitrogen at 80 °C for 5 h and then poured in 10 mL of distilled water. The aqueous layer was extracted with $CHCl_3$ (3 × 30 mL). The combined organic layers were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude compound was purified by column chromatography (silica gel, 7% diethyl ether in hexane as eluent) to provide 640 mg of the title product as white crystals (69% yield): mp 168−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, 2H, $J = 7.6$ Hz), 7.65 (d, 2H, $J = 7.8$ Hz), 4.57 (t, 2H, $J = 7.9$ Hz), 2.94 (s, 6H), 1.40 (s, 24H), 1.16 (m, 12H), 0.84 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 129.3, 128.1, 127.7, 117.2, 83.5, 47.3, 31.7, 29.2, 29.1, 29.1, 26.5, 24.9, 22.6, 19.2, 14.0 (the missing peak is due to the carbon linked to the boronic function, which shows no signal in ^{13}C NMR); HRMS *m*/*z* calculated for $C_{34}H_{51}NO_4B_2$ 559.4004, found 559.3996.

***N*-Octyl-2,7-bis(2′-nitrophenyl)-1,8-dimethylcarbazole (21).** This compound was synthesized according to a similar procedure to that one used for compound **4** using 365 mg (0.65 mmol) of **20**, 290 mg (1.44 mmol) of 1-bromo-2-nitrobenzene, 6 mL of toluene, 4.2 mL of K_2CO_3 2 M, 12 mg (0.05 mmol) of $Pd(OAc)_2$, and 53 mg (0.20 mmol) of PPh_3. The crude product was purified by column chromatography (silica gel, 30% diethyl ether in hexane as eluent) to give 260 mg of the title product as yellow solid (73% yield): mp 157−158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (m, 2H), 7.90 (m, 2H), 8.65 (m, 2H), 7.54 (m, 2H), 7.45 (m, 2H), 7.03 (m, 2H), 4.58 (t, 2H, $J = 8.42$), 2.47 (s, 3H), 2.46 (s, 3H), 1.44 (m, 2H), 1.20 (m, 8H), 1.05 (m, 2H), 0.83 (t, 3H, $J = 6.9$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.6, 143.0, 143.0, 137.3, 137.3, 136.3, 136.3, 132.8, 132.7, 132.24, 132.23, 128.11, 128.10, 125.61, 125.60, 124.0, 123.9, 121.5, 121.4, 120.2, 120.0, 117.5, 117.46, 47.3 (2s), 31.6 (2s), 29.8 (2s), 29.1 (2s), 29.0 (2s), 26.4 (2s), 22.6 (2s), 17.3 (2s), 17.2 (2s), 14.0 (2s); HRMS *m*/*z* calculated for $C_{34}H_{35}N_3O_4$ 549.2627, found 549.2638.

5,8-Dihydro-13,15-dimethyl-14-octyl-diindolo[3,2-*b*:2′,3′-*h*]carbazole (22). A 10 mL flame-dried flask, equipped with a condenser, was charged with 115 mg (0.21 mmol) of **21** and 4 mL of triethylposphite. The stirred resulting mixture was heated under reflux under an argon atmosphere for 24 h. The precipitate formed was collected by filtration, washed with hexane, and then purified by column chromatography (silica gel, 30% ethyl acetate in hexane as eluent) to provide 30 mg of the title product as a yellow solid. (yield = 30%): mp 280 °C dec; ^{1}H NMR (400 MHz, THF-d_8) δ 10.12 (s, 2H, NH), 8.26 (d, 2H, $J = 7.8$ Hz), 7.85 (s, 2H), 7.40 (d, 2H, $J = 7.8$ Hz), 7.31 (td, 2H, $J = 7.6$ and 1.0 Hz), 7.12 (td, 2H, $J = 7.5$ and 1.0 Hz), 4.49 (t, 2H, $J = 7.5$ Hz), 3.18 (s, 6H), 1.02 (m, 10H), 0.89 (m, 2H), 0.69 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, THF-d_8) δ 142.9, 142.8, 138.2, 129.3, 125.6, 125.5, 123.6, 123.5, 119.0, 118.4, 111.1, 99.9, 51.8, 32.9, 30.3, 28.0, 27.5, 26.1, 23.6, 17.5, 14.6; HRMS *m*/*z* calculated for $C_{34}H_{35}N_3$ 485.2831, found 485.2816.

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Supporting Information Available: General experimental procedures and ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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