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Synthesis of Polyarylated Carbazoles: Discovery toward Soluble Phenanthro- and Tetraceno-Fused Carbazole Derivatives

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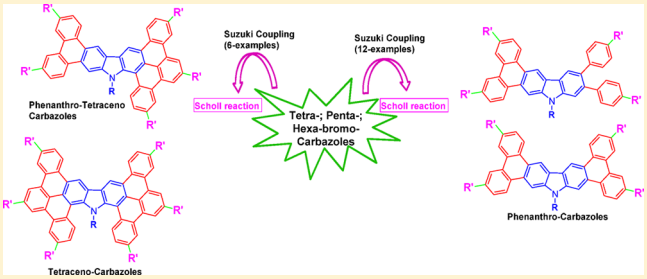
Supporting Information

ABSTRACT: The successful iron chloride-catalyzed Scholl reactions toward a series of polyphenylated carbazole derivatives differing in their *N*-substitution are described. These reactions were found to be compatible over a series of polyaryls possessing fluoro, methoxy, and methyl functional groups, subsequently leading to the synthesis of partially and completely annulated phenanthro- and tetracenocarbazoles in excellent yields. One major consequence of nonsubstitution on carbazolyl-*N* and the unsymmetrical framework of some of the derivatives is the low solubility of the product; thus, a change from *NH*- to *N*-decyl on the carbazole nucleus was carried out. All newly developed derivatives were characterized by spectroscopic techniques, while the chemical structures of fluorophenanthro- and methoxytetracenocarbazoles were confirmed by single-crystal XRD analyses. The present efforts may likely expand the family of growing heteroarenes for future applications as semiconductors and electroluminescent materials.



INTRODUCTION

Highly conjugated polyfused aromatics[1] and heterocyclic compounds[2] have attracted immense attention for their broad applications in electronic devices like organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic solar cells, and other related semiconductor applications. Various features like efficient aggregation, high thermal stabilities, fluorescence color tuning, high quantum yields, and nonlinear optical response were exploited in different electronic and electro-optical applications.[3] In regard to the wide applications, their syntheses suffer from a few potential barriers like poor solubility, lower reactivity of starting materials, and poor yields of the products. To solve the problem of solubility, longer alkyl chains are generally introduced to the aromatic backbone of precursors, yet this may affect the rate of the chemical reaction and thermal stabilities of the final products,[4] not to mention the crystal packing and thus the physical or electric properties originally desired. Moreover, in their synthesis, the reactivity and concentration of a particular reagent and the reaction time of the aromatic coupling reactions are also tricky factors determining the formation of products. For instance, the Scholl reaction frequently employed for oxidative aromatic coupling using concentrated iron chloride is commonly influenced by one of the side reactions called chlorination.[5] Additionally, the use of excessive equivalencies of Lewis acids like $AlCl_3$ and iron chloride can lead to intermolecular polymerizations rather than intramolecular annulations.[6] Thus, to achieve the desired novel polyfused conjugated molecule, a series of optimization studies have to be performed over electrophilic substitution and coupling reactions. Contributors like Clar[7] et al. and Müllen[8] et al. have used many highly fused skeletons, which scale up the core and conjugation in the polyaromatic molecules. Although triazatruxene,[9] indolocarbazoles,[10] and structurally related molecules were synthesized, preparations of highly fused heteroarenes incorporating carbazole were not very successful. In particular, poor yields of the required starting materials such as polybromo derivatives for the preparation of triazatruxene and related heterocyclic compounds restricted their large-scale syntheses and extensive evaluation in electronic devices. Carbazole-based materials, more precisely the compounds with multiple phenyl units aligned around the core, are known to exhibit good solubility and nonaggregating behavior and invoke special interest as nondoped materials in blue light-emitting diodes.[11] One frequent approach for their syntheses employs palladium-catalyzed coupling of heteroaromatic carboxylic acids with alkynes in good yields.[12] Nevertheless, a direct and general route to multiple substitutions at the 1-, 2-, 3-, 6-, 7-, and 8-positions of carbazole is lacking. Additionally, the above-discussed derivatives have *meta*-conjugation[13] at the sides of the carbazole, while *ortho*-substituted derivatives were not implemented for Lewis acid-catalyzed annulations. These results motivated us to study Scholl reactions on carbazole-based polyarylated derivatives and the potential for the aryl groups to be annulated to give polyfused aromatic materials. In the present work, we demonstrate the successful preparation of carbazoles with large number of aryl groups attached at the periphery and their fusion with the carbazole framework for expanded conjugations suitable for further applications. We also

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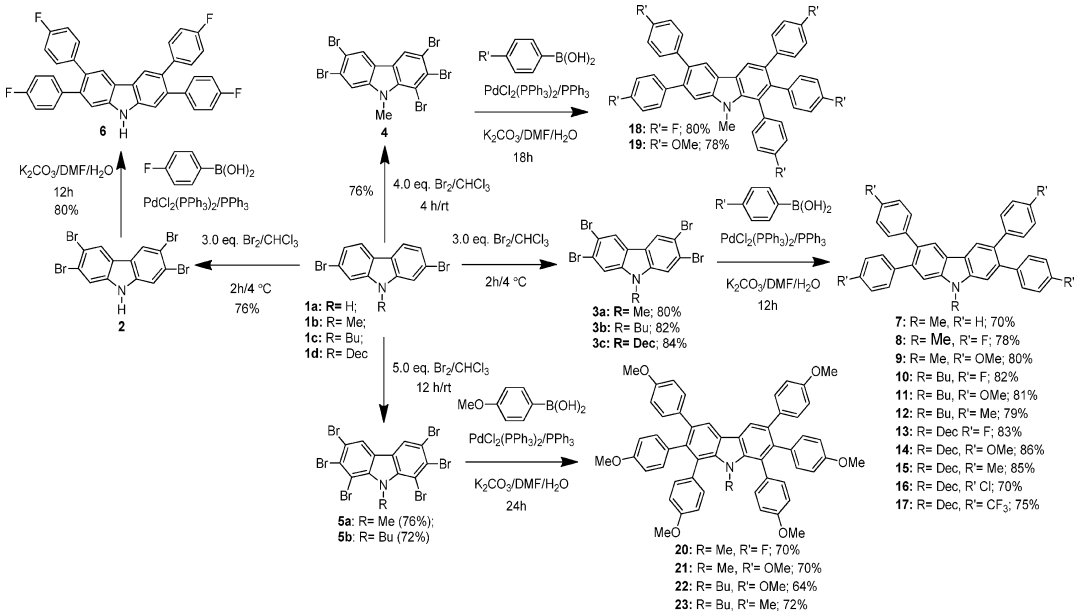
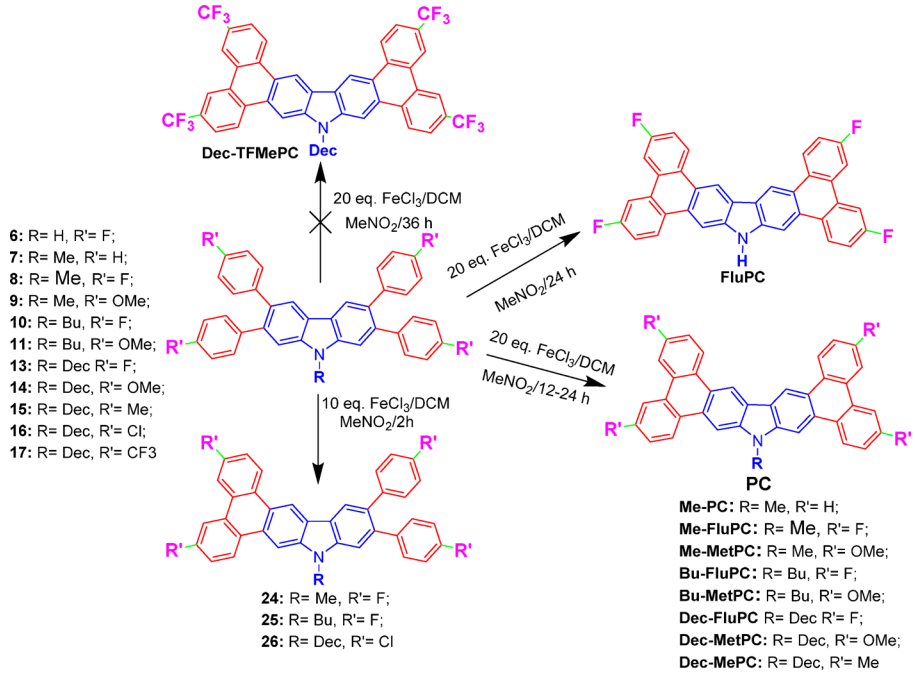
Scheme 1. Synthesis of Polyarylated Carbazoles 6−23



Scheme 2. Synthesis of Diphenanthro[9,10-*b*:9′,10′-*h*]carbazole (PC) Derivatives

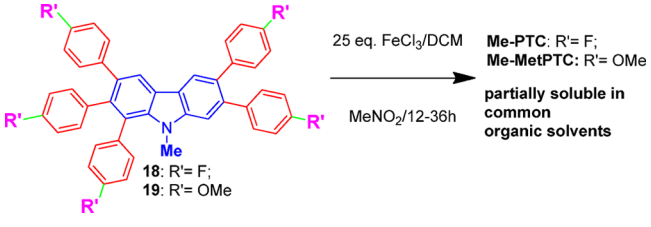


report the electro-optical data for a representative *N*-methyl-substituted derivative, acknowledging the fact that except for the solubility, the optical and electrochemical properties may not be much different by changing the *N*-substitution on carbazole.

RESULTS AND DISCUSSION

Synthesis. The major synthetic plan is displayed in Schemes 2−4, while preparation of the polyphenylated carbazoles is described in Scheme 1. A simple 4-fold substitution on the parent alkylcarbazole by use of excessive bromine in solvents like chloroform and acetic acid has already been reported in the literature.[14] Nevertheless, electrophilic substitution, especially bromination on 2,7-dibromocarbazole,

Scheme 3. Synthesis of Tetraceno[5,6-*ab*]phenanthro[9,10-*h*]carbazole (PTC) Derivatives



has not been attempted so far, except the iodination by using harsh reaction conditions with the reagents I_2/KIO_3 in sulfuric acid.[15] Furthermore, loading of the desired numbers of bromine

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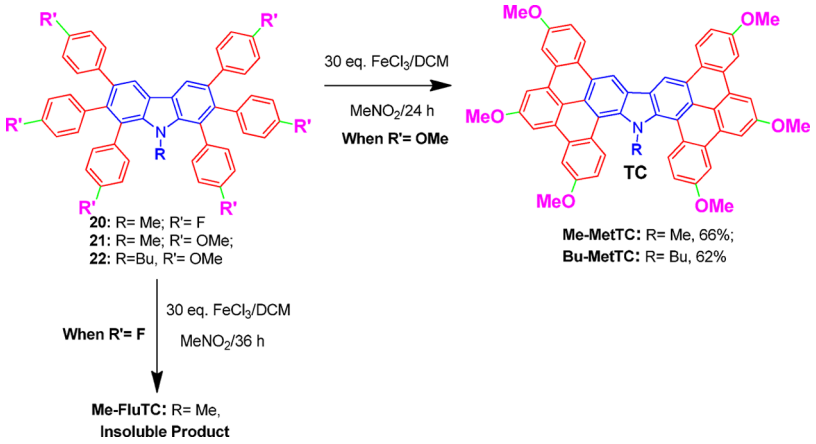
Scheme 4. Synthesis of Tetraceno[5,6-*ab*]benzo[11,12]tetraceno[5,6-*hi*]carbazole (TC) DDerivatives



atoms on a nucleus requires efficient handling and precise control due to the high reactivity and oxidizing nature of bromine.[16] In practice, these derivatives usually exhibit similar R_f values; thus, column-chromatographic separations were difficult. After subsequent optimizations on reaction time, temperature, and bromine concentration, we were able to isolate pure tetra-, penta-, and hexabromocarbazoles **1**−**5** bearing different *N*-alkyl substitutions by scaling up the slight excess of bromine equivalencies (3.0−5.0). A low temperature of 4 °C was maintained to afford tetrasubstituted derivatives **1**−**3** because a rise in temperature could lead to over-bromination.

After sequential brominations, the 18 polyaryls **6**−**23** were targeted via Suzuki coupling on numbers of polybromo substrates using different arylboronic acids (Scheme 1). Initially, bromocarbazoles were applied for C−C coupling using $Pd(PPh_3)_4$ in THF/water mixtures. The reaction with tetrabromo derivatives took longer (36 h) for completion, while penta- and hexabromocarbazoles gave mixtures of arylated products. As a result, an active catalytic system that could affect successful C−C coupling over polybromocarbazoles was needed. Thus, by utilizing the $Pd(PPh_3)_2Cl_2/PPh_3$ with 4.0−6.0 equiv of phenylboronic acids in DMF and water mixtures, excellent yields of polyphenylated carbazoles were obtained (Scheme 1). The enhanced reactivity of this catalyst is considered to be due to in situ generation of active Pd catalyst, $Pd(PPh_3)_4$, during the reaction process. Polyaryls were subjected to iron chloride mediated oxidative coupling by use of 1−5 equiv of catalyst. However, mixtures of non-, partially, and completely annulated products were obtained, which were difficult to be purified by either recrystallization or chromatography. Optimizations of Scholl reactions in terms of Lewis acid concentration, reaction time, etc. were then carried out.

The coupling reactions were eventually optimized by using 10−30 equiv of iron chloride in nitromethane solvent, depending on the number of aryl units present on the substrates. Table 1 lists the reaction time and yields of the final annulated products afforded by oxidative coupling reactions. Electron donors like methoxy not only reduced reaction time but also increased the reaction yield by enhancing reactivity of the particular substrate. Fluoro derivatives required a longer time for the coupling reactions to go to completion due to the weakly deactivating nature of fluorine. The aromatic derivatives carrying halogen atoms are usually reported to undergo oxidative coupling reactions when stronger oxidizing reagents, such as copper triflate, aluminum chloride, or DDQ with trifluoromethanesulfonic acid, are used.[17] The present synthesis was successfully achieved in good yields by use of iron chloride. This is explained by the enhanced electron density of carbazole over arylated hydrocarbons for accelerated oxidative coupling reactions. The presence of four stronger electron-withdrawing groups like trifluoromethyl effectively reduced the electron density on **17**; thus the formation of annulated product was not favored according to the reaction mechanism (Table 1, Entry 11). Similarly, tetraaryl derivatives bearing chlorine atoms (**16**) did not lead to complete fusion. Nevertheless, only partially fused derivative **26** was obtained at a higher concentration of iron chloride. Chlorination is one of the side reactions competing with oxidative coupling to yield mixtures of chlorinated and annulated products. Indeed, the coupling reaction was performed to give fused derivatives as sole products irrespective of the functional groups it carries. Different *N*-alkyl substitutions did not affect the yields of coupling reactions, although an increase in solubility reduced the reaction time (Table 1, entries 6−8). Among tetraaryls, use of the Scholl reaction on **6** having an *N*-H unit produced the

Table 1. Yields and Time for Scholl Reaction Performed on Polyarylated Carbazoles

entry	reactant	product	yield (%)	time (h)
1	**6**	**Flu-PC**	68[a]	24
2	**7**	**Me-PC**	68	12
3	**8**	**Me-FluPC**	52[b]	24
4	**9**	**Me-MetPC**	72	6
5	**10**	**Bu-FluPC**	66	24
6	**11**	**Bu-MetPC**	76	6
7	**13**	**Dec-FluPC**	73	16
8	**14**	**Dec-MetPC**	78	4
9	**15**	**Dec-MePC**	70	10
10	**16**	**26**	85[c]	36
11	**17**	**Dec-TFMePC**	0	36
12	**18**	**Me-FluPTC**	*a*	36
13	**19**	**Me-MetPTC**	*a*	12
14	**20**	**Me-FluTC**	*a*	36
15	**21**	**Me-MetTC**	69	24
16	**22**	**Bu-MetTC**	70	24
17	**7**	**24**	82	2
18	**10**	**25**	84	2

[a]Compounds could not be purified by column chromatography. [b]Compound was purified by vacuum sublimation. [c]Reaction led to partial fusion even at higher equivalence of catalyst.

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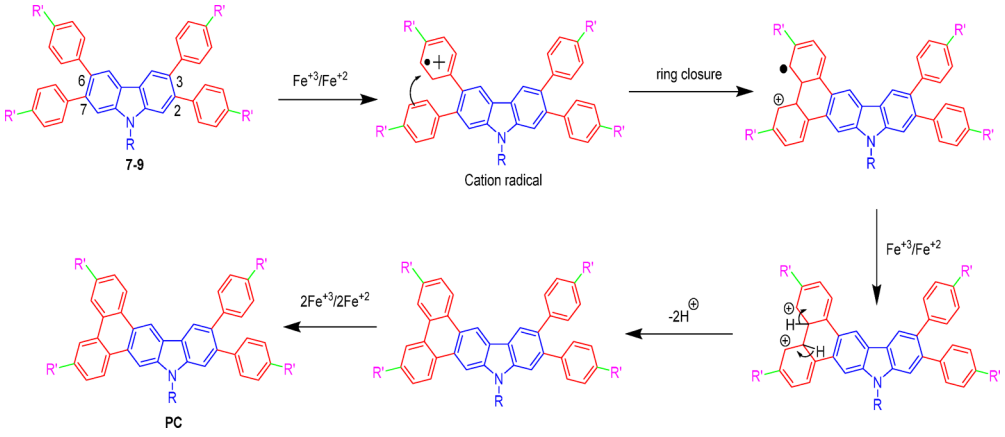
Scheme 5. Suggested Mechanism for the Formation of Phenanthrocarbazoles through the Scholl Reaction



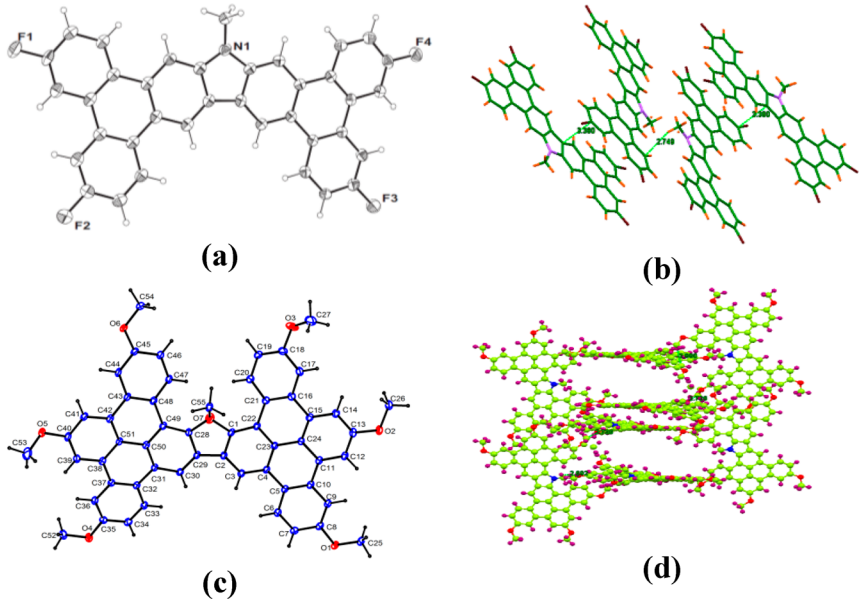


Figure 1. ORTEP plots of the derivatives (a) and (c) **Me-FluPC** (50% thermal ellipsoids) and **Me-MetTC** (45% thermal ellipsoids); (b) $\pi-\pi$ interaction among phenanthrene motifs; (d) van der Waals interactions among −NMe and −OMe groups.

slightly soluble derivative **FluPC** that could not be properly characterized except with the high-resolution MALDI-mass technique. Similarly, an oxidative coupling reaction was performed over pentaarylated derivatives **18** and **19** bearing methoxy and fluoro groups, resulting in unsymmetrical products with poor solubility (MALDI mass recorded, Figures S85 and S86, Supporting Information). These could not be purified by column chromatography or with high vacuum sublimation techniques (Table 1, entries 12 and 13). Interestingly, methoxy-substituted carbazole−tetracene hybrids (**TC**) exhibited good solubility as compared to fluoro substituted hybrids and could be purified through column chromatography using dichloromethane. To complete the experimental studies on annulation reactions, partially fused derivatives **20**−**22** were obtained in excellent yields by increasing the reaction time to 2 h.

The mechanism suggested for the cyclo-dehydrogenation reaction in carbazole derivatives is given in Scheme 5 and Scheme S1 (Supporting Information). According to the mechanistic pathway, loss of one electron from the electron-rich 3,6-substituted phenyls in the derivatives **6**−**17** leads to the formation of cation radicals. Detailed study for the existence of cation radicals in carbazole[18] derivatives and their formation during the annulation reactions to give polyaromatic hydrocarbons[19] is already well-established. These reaction intermediates are effectively stabilized by *N*-alkyl and electron donors on aryls on the carbazole nucleus, thus enhancing the reactivity of polyaryls toward coupling reactions. The cation-radical can undergo successive ring fusion and oxidation reactions to give partially fused derivatives in the presence of Fe^{3+} ions. After consecutive electron loss and ring closures, final phenanthrene derivatives were obtained.

In the hexaphenyl derivatives **20**−**22**, loss of an electron from different aryl arms may occur, yet most likely to occur from 3,6-substituted ones rather than that located on the 2,7- or 1,8-positions. After one ring closure, the side at which ring closure occurred becomes more planar and electron-rich, and thus, the second ring closure can occur at the same side.

Crystal XRD Analysis. Chemical structures of **Me-FluPC** and **Me-MetTC** were confirmed by single-crystal XRD analyses (Figure 1). The phenanthrocarbazole derivative was found to be nearly planar, leading to an efficient stacking among phenanthrene units (distance, ∼3.3 Å). In contrast to **Me-FluPC**, tetracene derivative **Me-MetTC** exhibits a twisted

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geometry, yet polyaromatic segments of two neighboring molecules could achieve π-overlap at a distance of 3.44 Å (Figure 1b,d). Interestingly, steric interaction among benzotetracene units and the −NMe group forced the latter group to bend out of the plane of central carbazole (angle, 29.1°). An intermolecular van der Waals interaction (bonding distance, 2.99 Å) between the methoxy unit attached to C_{45} and the nonplanar −NMe group was established, thus leading to the specific molecular arrangement (Figure 1d).

Optical Properties. Synthesized polyphenylated (**6**−**23**), phenanthrene (**PC**), and methoxy-substituted derivatives (**Met-PC** and **Met-TC**) gave white, yellow, and orange colors, respectively, in their solid states. Selected absorption spectra of **PC** as well as **TC** derivatives recorded in dichloromethane are shown in Figure 2, while relevant photophysical data are

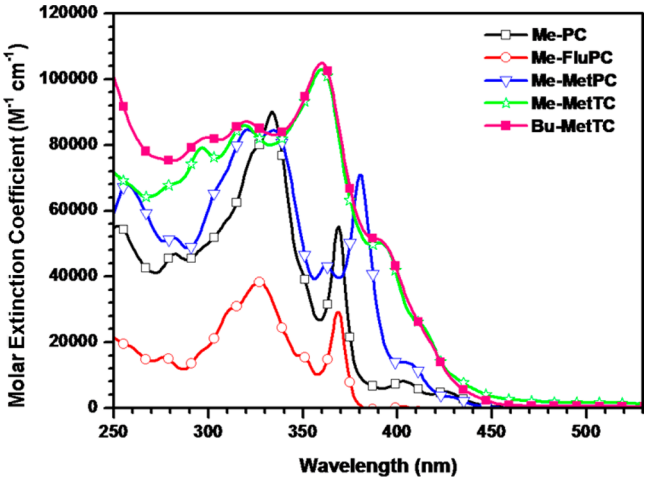

Figure 2. Absorption spectra of carbazole derivatives as recorded in dichloromethane at a concentration of 10^{-5} M.

summarized in Table S2 (Supporting Information). Some substituent effects can be seen that indicate fluoro substitution on phenyl groups leads to shorter wavelength absorption than methoxy substitution (**Me-FluPC** and **Me-MetPC**), whereas methyl or butyl substitution on carbazole nitrogen has little effect on absorption wavelength (**Me-MetTC** and **Bu-MetTC**). The molecular orbital calculation based on optimized geometries of some of the derivatives with Spartan Pro software (Version 1.0.3; Wave function, Inc.) using the semiempirical method at AM1 level was carried out. The energies and detailed Cartesian coordinates are provided in the Supporting Information. The electron density distributions of the frontier orbitals are displayed in Figure 3. In the derivative **PC** series as well as in nonfused derivative **7**, the HOMO orbital has electron distribution over the carbazole and phenyls placed at the 3,6-positions while LUMO has electron distribution over phenyls at the 2,7-positions. In HOMO-1, the electron distribution extended more linearly to phenyls at the 2,7-positions over the molecule. Nonfused derivative **7** displayed two prominent absorption bands at 287 and 323 nm, which may correspond to phenyl-localized (HOMO-1) to LUMO transition and nitrogen-involved (HOMO) to LUMO transitions, respectively.[20] Comparing the derivative **Me-PC** with parent phenylated **7**, fusion of phenyls located at the 2-, 3-, 6-, and 7-positions on carbazole shifts the absorption bands of 287 and 323 nm to longer wavelengths 333 and 369 nm, respectively, presumably due to expansion of conjugation and

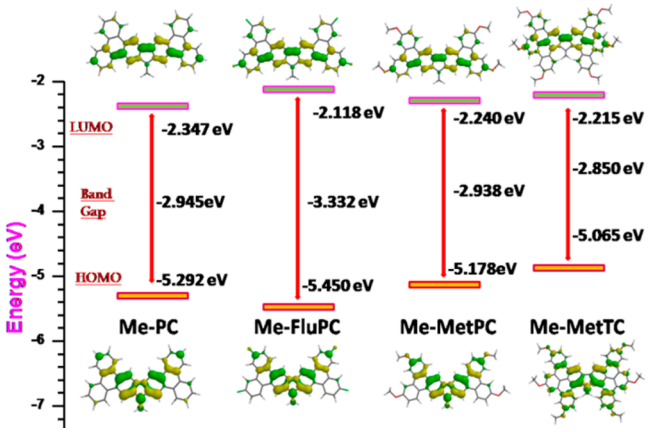

Figure 3. Frontier molecular orbitals and related energies of **PC** and **TC** derivatives: HOMO (bottom), LUMO (top) determined from cyclic voltammetry and UV absorption edge method.

planarization. A new absorption band appears at a shorter wavelength of 252 nm, which was assigned to higher excited-state, phenanthrene-localized $\pi-\pi^*$ transition. The intensities reflect the extent of overlap between the orbitals involved in the transitions. Similarly, for benzotetracene derivative, **Me-MetTC** displayed broadened absorption extended to even longer wavelengths at 295, 322, 360, and 395 nm due to more extensive conjugation in this series.

Phenanthreno and tetraceno derivatives displayed violet-blue, deep blue, and blue-green emission, respectively, in their dilute solutions (Figure S89, Supporting Information). Moreover, the color of emission from nonfused to fused derivatives was shifted from violet-blue to blue-green due to extension of their π-systems. Quantum yields of completely fused compounds were measured with respect to 2-aminopyridine (Φ_F = 60%) as standard to be in the range of 60−75%, suggesting potential application of the designed materials in blue organic light-emitting diodes (Table S2, Supporting Information).

Electrochemical and Thermal Properties. Oxidation potentials of the *N*-methyl-substituted **PC** and **TC** derivatives were measured by cyclic voltammetry using dichloromethane as solvent and 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte (Figure S91a−c, Supporting Information). The carbazole derivatives afforded quasi-reversible single or multiple oxidation waves due to loss of one or more electrons from the carbazole[21] nucleus depending on electron richness and localization of HOMO over the molecules.

Moreover, electron donors like methoxy group on derivatives **PC** and **TC** effectively lowered oxidation potentials as compared to electron-withdrawing fluoro group. Hence the oxidation potential decreases in the order **Me-FluPC** > **Me-PC** > **Me-MetPC** among phenanthrene series. Band gaps of fused derivatives were determined by extrapolation of absorption band edges and E_{LUMO} values were calculated by subtracting the band gap from E_{HOMO} values, as shown in Figure 3. Optical band gap values were reduced from nonfused to completely fused derivatives due to elongation of conjugation (Table **S1**, Supporting Information). Thermal decomposition temperatures of the methyl-substituted derivatives were measured by thermal gravimetric analysis at a heating rate of 10 °C/min with nitrogen as the carrier gas. Based on the 10% weight loss criteria, all derivatives except methoxy-substituted derivative, **Me-MetPC**, were found to have high thermal stability >300 °C,

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presumably owing to highly fused aromatic structures (Figure **S91(d)** and Table **S1**, Supporting Information).

CONCLUSIONS

In conclusion, we have successfully synthesized polyphenylated carbazoles and their annulated analogues bearing different functional groups in good yields. The compounds were completely characterized on the basis of NMR, MALDI mass, and crystal XRD analyses, and their significant electro-optical properties were analyzed. An efficient intermolecular $\pi-\pi$ and van der Waals interaction was observed in the crystal packing of phenanthrene- and tetracene-fused carbazole derivatives. In addition, these compounds displayed deep blue emissions in solution with high quantum yields. Their potentials in organic optoelectronic applications are being explored.

EXPERIMENTAL SECTION

All chemicals were purchased from commercial sources with desired purity. Standard distillation and drying procedures were used for solvents required in spectrophotometric, spectrofluorimetric, and electrochemical analyses. Sonogashira cross-coupling reactions were conducted in N_2 atmosphere. 2,7-Dibromo-9-methyl/butyl/decylcarbazoles were prepared from biphenyl via multistep synthesis reported in literature.[22] Silica gel with 60−230 mesh was used for column chromatographic separations. ^{1}H NMR and ^{13}C NMR spectra were measured in deuterated solvents like chloroform-*d*, DMSO-d_6, and 1,1,2,2-tetrachloroethane-d_2 with tetramethylsilane (TMS) as internal standard. A spectrophotometer and fluorescence spectrophotometer were used to carry out absorption and emission studies with dichloromethane and toluene as solvents. Differential pulse voltammetry (DPV) measurements were performed in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. A three-electrode system with platinum wire as auxiliary electrode, $Ag/AgNO_3$ as reference electrode, and a glassy carbon as working electrode was designed for the operation. Thermal decomposition temperatures of final compounds at 10% weight loss were measured by thermal gravimetric analyzer at a heating rate of 10 °C/min with nitrogen serving as a carrier gas. HOMO/LUMO plots of the derivatives were obtained by using PC Spartan Pro software with semi-empirical methods at the AM1 level.

General Method for the Preparation of 2,3,6,7-Tetrabromocarbazoles 2 and 3a−c. 2,7-Dibromocarbazoles **1a−d** (10.0 mmol) were dissolved in chloroform (200 mL) and stirred at 4 °C. Bromine (1.55 mL, 30.0 mmol) was dissolved in chloroform (60 mL) and added dropwise into the solution kept at 4 °C. While bromine addition was continued for 2 h, progress of the reaction was monitored by thin-layer chromatography. On completion of the reaction, the precipitated product or product retained in solution was treated differently (product precipitated in the case of N-H and N-Me carbazoles, while in the cases of N-Bu and N-Dec the product remained in the solution). Precipitated solid was filtered and dried. The solution was treated with saturated sodium metabisulfite to remove excessive bromine, and solvent was evaporated. Solid product obtained by either of the ways was reprecipitated from dcm/methanol to give the pure product as white solid.

*Preparation of 2,3,6,7-Tetrabromo-9H-carbazole (**2**).* According to the general procedure, 2,7-dibromo-9*H*-carbazole (**1a**) (3.25 g, 10.0 mmol) and bromine reacted to give the final product as a white amorphous solid. Yield: 3.67 g, 76%. Mp: 227 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (s, 2H), δ 8.09 (s, 1H), δ 8.22 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 115.5, 115.7, 122.5, 122.8, 124.9, 139.4. EIHRMS: calcd for $[C_{12}H_5Br_4N]^+$ 478.7155, found 478.7144.

*Preparation of 2,3,6,7-Tetrabromo-9-methyl-9H-carbazole (**3a**).* According to the general procedure, 2,7-dibromo-9-methyl-9*H*-carbazole (**1b**) (3.39 g, 10.0 mmol) and bromine reacted to give the final product as a white crystalline solid. Yield: 3.97 g, 80%. Mp: 245 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.75 (s, 3H), 7.65 (s, 2H), 8.20 (s, 2H). ^{13}C NMR ($CDCl_3$,100 MHz) δ: 29.5, 113.7, 114.8, 122.0, 122.4, 124.8, 140.9. EIHRMS: calcd for $[C_{13}H_7Br_4N]^+$ 492.7312, found 492.7321.

*Preparation of 2,3,6,7-Tetrabromo-9-butyl-9H-carbazole (**3b**).* According to the general procedure, 2,7-dibromo-9-butyl-9*H*-carbazole (**1c**) (3.81 g, 10.0 mmol) and bromine reacted to give the final product as a white crystalline solid. Yield: 4.42 g, 82%. Mp: 201 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.97 (t, J = 7.5 Hz, 3H), 1.36 (sext, J = 7.5 Hz, 2H), 1.79 (quin, J = 7.5 Hz, 2H), 4.13 (t, J = 7.5 Hz, 2H), 7.63 (s, 2H), 8.17 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.9, 29.4, 30.1, 43.4, 113.8, 114.6, 122.0, 122.2, 124.8, 127.6, 140.3. MALDI-TOF MS: calcd for $[C_{16}H_{13}Br_4N]^+$ 534.7781, found 534.7790.

*Preparation of 2,3,6,7-Tetrabromo-9-decyl-9H-carbazole (**3c**).* According to the general procedure, 2,7-dibromo-9-decyl-9*H*-carbazole (**1d**) (4.65 g, 10.0 mmol) and bromine reacted to give the final product as a white crystalline solid. Yield: 5.23 g, 84%. Mp: 50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89−0.86 (m, 3H), 1.33−1.25 (m, 14H), 1.87−1.80 (m, 2H), 4.15 (t, J = 7.2 Hz, 2H), 7.65 (s, 2H), 8.23 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 22.6, 27.0, 28.6, 29.2, 29.4, 29.5, 31.8, 43.5, 113.7, 114.6, 121.9, 122.2, 124.7, 140.2. EIHRMS: calcd for $[C_{22}H_{25}Br_4N]^+$ 618.8721, found 618.8717.

*Preparation of 1,2,3,6,7-Pentabromo-9-methyl-9H-carbazole (**4**).* 2,7-Dibromo-9-methyl-9*H*-carbazole (**1b**) (3.39 g, 10.0 mmol) was dissolved in chloroform (150 mL) and stirred at room temperature. Bromine (2.06 mL, 40.0 mmol) was dissolved in chloroform (60 mL) and added dropwise into the solution of 2,7-dibromo-9-methyl-9*H*-carbazole. While bromine addition was continued for 4 h, progress of the reaction was monitored by thin-layer chromatography. On completion of the reaction, the precipitated product was filtered. Product was reprecipitated by dcm/methanol to give the pure product as a white amorphous solid. Yield: 4.70 g, 76%. Mp: 236 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.16 (s, J = 7.5 Hz, 3H),7.69 (s, 1H),8.17 (s, 1H), 8.19 s, J = 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 33.2, 107.4, 114.6, 115.6, 115.9, 121.6, 123.1, 123.5, 124.0, 124.5, 127.2, 138.5, 142.1. EIHRMS: calcd for $[C_{13}H_6Br_5N]^+$ 570.6417, found 570.6428.

*Preparation of 1,2,3,6,7,8-Hexabromo-9-methyl-9H-carbazole (**5a**).* 2,7-Dibromo-9-methyl-9*H*-carbazole (**1b**) (3.39 g, 10.0 mmol) was dissolved in chloroform (100 mL) and stirred. Bromine (2.58 mL, 50.0 mmol) was dissolved in chloroform (30 mL) and added dropwise into the carbazole solution at room temperature, and the mixture was further stirred for 12 h. On completion of reaction, the excessive bromine was reduced by saturated sodium metabisulfite solution, and the solvent was removed under vacuum. The product was recrystallized from dcm/methanol to give a white crystalline solid. Yield: 5.0 g, 76%. Mp: 290 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.25 (s, 3H), 8.18 (s, 2H). ^{13}C NMR ($C_2D_2Cl_4$, 100 MHz) δ: 38.1, 109.0, 117.3, 123.2, 124.6, 127.9, 142.5. EI HRMS: calcd for $[C_{13}H_5Br_6N]^+$ 648.5522, found 648.5514.

*Preparation of 1,2,3,6,7,8-Hexabromo-9-butyl-9H-carbazole (**5b**).* 2,7-Dibromo-9-butyl-9*H*-carbazole (**1c**) (1.90 g, 5.0 mmol) was dissolved in chloroform (15 mL). Bromine (1.29 mL, 25.0 mmol) was dissolved in chloroform (15 mL) and added to the carbazole solution at room temperature, and the mixture was further stirred for 12 h. On completion of the reaction, the excessive bromine was reduced by saturated sodium metabisulfite solution, and the solvent was removed under vacuum. The product was reprecipitated from dcm/methanol to give a white fluffy solid. Yield: 2.5 g, 72%. Mp: 220 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.86 (t, J = 7.5 Hz, 3H), 1.19−1.11 (m, 2H), 1.52−1.51 (m, 2H),5.16 (t, J = 8.0 Hz, 2H),8.21 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.7, 19.5, 32.8, 45.3, 109.1, 117.4, 123.2, 125.2, 128.5, 140.5. MALDI-TOF MS: calcd for $[C_{16}H_{11}Br_6N]^+$ 690.5992, found 690.5616.

General Method for Suzuki Coupling for the Formation of Tetraarylated Carbazoles 6−17. Tetrabromocarbazoles **2** and **3a−c** (1.0 mmol) were taken in a mixture of DMF (22.5 mL) and water (2.5 mL). Arylboronic acid (4.5 mmol), potassium carbonate (2.76 g, 20.0 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg), and PPh_3 (25 mg) were added, and the mixture was heated at 110 °C for 12 h under inert atmosphere. On completion of the reaction, the reaction mixture was cooled and poured into water to precipitate the product. The precipitated product

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was filtered, dried, and then purified by column chromatography using dichloromethane/hexane as eluent to afford white solid.

*Preparation of 2,3,6,7-Tetrakis(4-fluorophenyl)-9H-carbazole (**6**).* 2,3,6,7-Tetrabromo-9*H*-carbazole (**2**) (0.48 g, 1.0 mmol), 4-fluorophenylboronic acid (0.63 g, 4.5 mmol), potassium carbonate, $Pd(PPh_3)_2Cl_2$, and PPh_3 were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white solid. Yield: 0.43 g, 80%. Mp: 280 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.01−6.95 (m, 8H), 7.21−7.17 (m, 8H), 7.48 (s, 2H),8.10 (s, 2H), 8.19 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 112.4, 114.7, 114.8, 114.9, 115.0, 122.3, 122.7, 131.6, 131.7, 131.8, 132.2, 138.0, 138.2, 139.7, 160.4, 160.6, 162.8, 163.0. MALDI-TOF MS: calcd for $[C_{36}H_{21}F_4N]^+$ 543.1610, found 543.1624.

*Preparation of 2,3,6,7-Tetraphenyl-9-methyl-9H-carbazole (**7**).* 2,3,6,7-Tetrabromo-9-methyl-9*H*-carbazole (**3a**) (0.50 g, 1.0 mmol), phenylboronic acid (0.54 g, 4.5 mmol), potassium carbonate, $Pd(PPh_3)_2Cl_2$, and PPh_3 were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white solid. Yield: 0.34 g, 70%. Mp: 275 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.93 (s, 3H), 7.30−7.19 (m, 20H),7.46 (s, 2H), 8.16 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.3, 107.1, 110.3, 110.4, 118.9, 120.6, 122.0, 122.1, 122.4, 125.9, 126.3, 127.1, 127.2, 127.6, 127.8, 128.8, 130.3, 130.4, 131.1, 131.8, 132.6, 134.0, 139.1, 139.4, 141.2, 142.1, 142.4, 142.6, 148.6. MALDI-TOF MS: calcd for $[C_{37}H_{27}N]^+$ 485.2144, found 485.2151.

*Preparation of 2,3,6,7-Tetrakis(4-fluorophenyl)-9-methyl-9H-carbazole (**8**).* 2,3,6,7-Tetrabromo-9-methyl-9*H*-carbazole (**3a**) (0.50 g, 1.0 mmol), 4-fluorophenylboronic acid (0.63 g, 4.5 mmol), potassium carbonate, $Pd(PPh_3)_2Cl_2$, and PPh_3 were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white crystalline solid. Yield: 0.43 g, 78%. Mp: 262 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.93 (s, 3H), 7.00−6.92 (m, 8H), 7.23−7.14 (m, 8H), 7.41 (s, 2H), 8.10 (s, 2H). ^{13}C NMR ($CDCl_3$,100 MHz) δ: 29.2, 110.3, 114.7, 114.8, 114.9, 115.0, 122.0, 122.3, 131.5, 131.6, 131.7, 131.8, 138.0, 138.1, 138.2, 138.3, 141.2, 160.3, 160.5, 162.7, 163.0. MALDI-TOF MS: calcd for $[C_{37}H_{23}F_4N]^+$ 557.1767, found 557.1780.

*Preparation of 2,3,6,7-Tetrakis(4-methoxyphenyl)-9-methyl-9H-carbazole (**9**).* 2,3,6,7-Tetrabromo-9-methyl-9*H*-carbazole (**3a**) (0.50 g, 1.0 mmol), 4-methoxyphenylboronic acid (0.68 g, 4.5 mmol), potassium carbonate, $Pd(PPh_3)_2Cl_2$ and PPh_3 were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white powder. Yield: 0.48 g, 80%. Mp: 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.81 (s, 6H), 3.82 (s, 6H), 3.90 (s, 3H), 6.83−6.79 (m, 8H), 7.21−7.15 (m, 8H),7.39 (s, 2H),8.08 (s, 2H). ^{13}C NMR ($CDCl_3$,100 MHz) δ: 29.0, 53.1, 55.3, 110.1, 113.2, 113.3, 114.2, 121.9, 122.0, 128.4, 131.3, 132.0, 135.0, 135.1, 138.3, 140.9, 142.2, 157.8, 158.1. MALDI-TOF MS: calcd for $[C_{41}H_{35}NO_4]^+$ 605.2565, found 605.2577.

*Preparation of 2,3,6,7-Tetrakis(4-fluorophenyl)-9-butyl-9H-carbazole (**10**).* 2,3,6,7-Tetrabromo-9-butyl-9*H*-carbazole (**3b**) (0.54 g, 1.0 mmol), 4-fluorophenylboronic acid (0.63 g, 4.5 mmol), potassium carbonate, $Pd(PPh_3)_2Cl_2$, and PPh_3 were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white crystalline solid. Yield: 0.49 g, 82%. Mp: 220 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.98 (t, J = 7.5 Hz, 3H), 1.51−1.42 (m, 2H), 1.96−1.89 (m, 2H), 4.37 (t, J = 6.9 Hz, 2H), 7.00−6.92 (m, 8H), 7.22−7.15 (m, 8H), 7.40 (s, 2H), 8.10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 20.6, 31.2, 43.1, 110.5, 114.7, 114.8, 114.9, 115.0, 122.1, 122.3, 131.4, 131.7, 138.0, 138.1, 138.3, 140.7, 160.3, 160.5, 162.7, 163.0. MALDI-TOF MS: calcd for $[C_{40}H_{29}F_4N]^+$ 599.2236, found 599.2252.

*Preparation of 2,3,6,7-Tetrakis(4-methoxyphenyl)-9-butyl-9H-carbazole (**11**).* 2,3,6,7-Tetrabromo-9-butyl-9*H*-carbazole (**3b**) (0.54 g, 1.0 mmol), 4-methoxyphenylboronic acid (0.68 g, 4.5 mmol), potassium carbonate, $Pd(PPh_3)_2Cl_2$, and PPh_3 were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white powder. Yield: 0.52 g, 81%. Mp: 145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.97 (t, J = 7.2 Hz, 3H), 1.51−1.43 (m, 2H), 1.95−1.87 (m, 2H), 3.81 (s, 6H), 3.82 (s, 6H), 4.34 (t, J = 6.8 Hz, 2H), 6.84−6.79 (m, 8H), 7.21−7.15 (m, 8H), 7.38 (s, 2H), 8.08 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 20.6, 31.2, 43.0, 55.1, 110.3, 113.3, 121.9, 122.1, 131.2, 131.3, 131.8, 135.0, 135.2, 138.3, 140.5, 157.8, 158.2. MALDI-TOF MS: calcd for $[C_{44}H_{41}NO_4]^+$ 647.3036, found 647.3050.

*Preparation of 2,3,6,7-Tetrakis(4-methylphenyl)-9-butyl-9H-carbazole (**12**).* 2,3,6,7-Tetrabromo-9-butyl-9*H*-carbazole (**3b**) (0.54 g, 1.0 mmol), 4-methylphenylboronic acid (0.61 g, 4.5 mmol), potassium carbonate, $Pd(PPh_3)_2Cl_2$, and PPh_3 were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white powder. Yield: 0.46 g, 79%. Mp: 225 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.96 (t, J = 7.2 Hz, 3H), 1.48−1.42 (m, 2H), 1.94−1.86 (m, 2H), 2.33 (s, 6H), 2.36 (s, 6H), 4.34 (t, J = 6.9 Hz, 2H), 7.10−7.03 (m, 8H), 7.19−7.13 (m, 8H), 7.39 (s, 2H), 8.09 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 20.6, 21.1, 31.2, 43.1, 110.5, 122.1, 122.3, 127.3, 128.0, 128.5, 128.6, 130.1, 130.2, 130.8, 131.7, 132.2, 135.2, 135.8, 138.7, 139.6, 139.9, 140.6. MALDI-TOF MS: calcd for $[C_{44}H_{41}N]^+$ 583.3239, found 583.3229.

*Preparation of 2,3,6,7-tetrakis(4-fluorophenyl)-9-decyl-9H-carbazole (**13**).* 2,3,6,7-Tetrabromo-9-decyl-9*H*-carbazole (**3c**) (0.62 g, 1.0 mmol), 4-fluorophenylboronic acid (0.63 g, 4.5 mmol), potassium carbonate, $Pd(PPh_3)_2Cl_2$, and PPh_3 were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white crystalline solid. Yield: 0.57 g, 83%. Mp: 112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (t, J = 6.8 Hz, 3H), 1.47−1.32 (m, 14H), 1.97−1.90 (m, 2H), 4.36 (t, J = 7.2 Hz, 2H), 7.00−6.92 (m, 8H), 7.22−7.14 (m, 8H), 7.39 (s, 2H), 8.10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 22.6, 27.3, 29.0, 29.3, 29.4, 29.5, 31.9, 43.3, 110.5, 114.7, 114.8, 114.9, 115.0, 122.2, 122.3, 131.4, 131.7, 138.0, 138.1, 138.3, 140.7, 160.3, 160.6, 162.8, 163.0. MALDI-TOF MS: calcd for $[C_{46}H_{41}F_4N]^+$ 683.3175, found 683.3188.

*Preparation of 2,3,6,7-Tetrakis(4-methoxyphenyl)-9-decyl-9H-carbazole (**14**).* 2,3,6,7-Tetrabromo-9-decyl-9*H*-carbazole (**3c**) (0.54 g, 1.0 mmol), 4-methoxyphenylboronic acid (0.68 g, 4.5 mmol), potassium carbonate, $Pd(PPh_3)_2Cl_2$, and PPh_3 were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white powder. Yield: 0.63 g, 86%. Mp: 80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.87 (t, J = 6.8 Hz, 3H), 1.45−1.24 (m, 14H),1.95−1.88 (m, 2H),3.81 (s, 6H), 3.82 (s, 6H),4.32 (t, J = 7.2 Hz, 2H),6.84−6.78 (m, 8H), 7.21−7.14 (m, 8H), 7.37 (s, 2H), 8.07 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 22.6, 27.3, 29.0, 29.3, 29.4, 29.5, 31.9, 43.3, 55.2, 110.3, 113.3, 114.2, 114.5, 122.0, 122.2, 131.3, 131.9, 135.1, 135.3, 138.3, 140.5, 157.8, 158.2. MALDI-TOF MS: calcd for $[C_{50}H_{53}NO_4]^+$ 731.3975, found 731.3933.

*Preparation of 2,3,6,7-Tetrakis(4-methylphenyl)-9-deyl-9H-carbazole (**15**).* 2,3,6,7-Tetrabromo-9-decyl-9*H*-carbazole (**3c**) (0.54 g, 1.0 mmol), 4-methylphenylboronic acid (0.61 g, 4.5 mmol), potassium carbonate, $Pd(PPh_3)_2Cl_2$, and PPh_3 were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white powder. Yield: 0.57 g, 85%. Mp: 75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.87 (t, J = 6.8 Hz, 3H), 1.45−1.24 (m, 14H), 1.95−1.88 (m, 2H), 2.34 (s, 6H), 2.36 (s, 6H), 4.34−4.31 (m, 2H), 7.10−7.04 (m, 8H), 7.19−7.13 (m, 8H), 7.40 (s, 2H), 8.09 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 21.1, 22.6, 27.3, 29.0, 29.3, 29.4, 29.5, 31.9, 43.3, 110.5, 122.1, 122.3, 127.4, 128.5, 128.6, 129.5, 130.1, 130.2, 132.2, 135.2, 135.8, 138.7, 139.6, 139.9, 140.5. MALDI-TOF MS: calcd for $[C_{50}H_{53}N]^+$ 667.4178, found 667.4199.

*Preparation of 2,3,6,7-Tetrakis(4-chlorophenyl)-9-decyl-9H-carbazole (**16**).* 2,3,6,7-Tetrabromo-9-decyl-9*H*-carbazole (**3c**) (0.62 g, 1.0 mmol), 4-chlorophenylboronic acid (0.70 g, 4.5 mmol), potassium carbonate, $Pd(PPh_3)_2Cl_2$, and PPh_3 were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white crystalline solid. Yield: 0.52 g, 70%. Mp: 85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (t, J = 6.8 Hz, 3H), 1.43−1.35 (m, 14H),1.94−1.89 (m, 2H), 4.38−4.33 (m, 2H),7.28−7.13 (m, 16H), 7.39 (s, 2H), 8.09 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 22.6, 27.3 29.0, 29.3, 29.4, 29.5, 31.8, 43.3, 110.6, 122.1, 122.3, 122.4, 128.2, 128.3, 128.8, 128.9, 131.2, 131.4, 131.5, 132.3, 132.8, 137.8, 140.5, 140.7, 140.8. MALDI-TOF MS: calcd for $[C_{46}H_{41}Cl_4N]^+$ 747.1993, found 747.2008.

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*Preparation of 9-Decyl-2,3,6,7-tetrakis(4-(trifluoromethyl)-phenyl)-9H-carbazole (**17**).* 2,3,6,7-Tetrabromo-9-decyl-9*H*-carbazole (**3c**) (0.54 g, 1.0 mmol), 4-(trifluoromethyl)phenylboronic acid (0.85 g, 4.5 mmol), potassium carbonate, $Pd(PPh_3)_2Cl_2$, and PPh_3 were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white powder. Yield: 0.66 g, 75%. Mp: 110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.86 (t, J = 6.4 Hz, 3H), 1.46−1.23 (m, 14H), 1.99−1.91 (m, 2H), 4.40 (t, J = 7.2 Hz, 2H), 7.39−7.33 (m, 8H), 7.46 (s, 2H), 7.57−7.51 (m, 8H), 8.18 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 22.6, 27.3, 29.1, 29.3, 29.4, 29.5, 31.8, 43.5, 111.0, 122.5, 122.9, 125.0, 130.5, 131.2, 137.9, 141.0, 145.4, 145.6. MALDI-TOF MS: calcd for $[C_{50}H_{41}F_{12}N]^+$ 883.3047, found 883.3027.

General Method for Suzuki Coupling To Synthesize Penta- and Hexaarylated Carbazoles 18−23. Penta- or hexabromocarbazole **4** and **5a,b** (1.0 mmol), arylboronic acid (5.5−6.5 mmol), potassium carbonate (25.0−30.0 mmol), $Pd(PPh_3)_2Cl_2$ (53−72 mg), and PPh_3 (38−50 mg) were taken in a mixture of DMF (40.0 mL) and water (10.0 mL). The reaction mixture was heated at 110 °C for 18−24 h under inert atmosphere. On completion of the reaction, the reaction mixture was cooled and poured into water to precipitate the product. Precipitated product was filtered, dried, and then purified by column chromatography using dichloromethane/hexane as eluent to afford white solid.

*Preparation of 1,2,3,6,7-Pentakis(4-fluorophenyl)-9-methyl-9H-carbazole (**18**).* 1,2,3,6,7-Pentabromo-9-methyl-9*H*-carbazole (**4**) (0.57 g, 1.0 mmol), 4-fluorophenyl boronic acid (0.77 g, 5.5 mmol), potassium carbonate (3.45 g, 25.0 mmol), $Pd(PPh_3)_2Cl_2$ (53 mg), and PPh_3 (38 mg) were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white amorphous solid. Yield: 0.52 g, 80%. Mp: 135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.25 (s, 3H), 6.70−6.66 (m, 2H), 6.98−6.79 (m, 10H), 7.20−7.08 (m, 8H), 7.31 (s, 1H), 8.12 (s, 1H), 8.14 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 32.4, 110.4, 110.7, 113.9, 114.1, 114.4, 114.5, 114.6, 114.7, 114.8, 114.9, 115.0, 115.2, 115.5, 115.7, 117.8, 121.1, 122.3, 123.0, 124.3, 128.6, 128.7, 131.5, 131.7, 131.8, 132.8, 133.1, 134.1, 135.8, 138.0, 138.3, 138.9, 142.3, 160.3, 160.6, 160.7, 162.2, 162.8, 163.0, 163.1. MALDI-TOF MS: calcd for $[C_{43}H_{26}F_5N]^+$ 651.1985, found 651.2004.

*Preparation of 1,2,3,6,7-Pentakis(4-methoxyphenyl)-9-methyl-9H-carbazole (**19**).* 1,2,3,6,7-Pentabromo-9-methyl-9*H*-carbazole (**4**) (0.57 g, 1.0 mmol), 4-methoxyphenylboronic acid (0.84 g, 5.5 mmol), potassium carbonate (3.45 g, 25.0 mmol), $Pd(PPh_3)_2Cl_2$ (53 mg), and PPh_3 (38 mg) were taken in a mixture of DMF and water. According to the general procedure, the product was obtained as a white powder. Yield: 0.56 g, 78%. Mp: 105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.22 (s, 3H), 3.68 (s, 3H), 3.77 (s, 3H), 3.80 (s, 3H), 3.81 (s, 3H), 3.82 (s, 3H), 6.53 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H), 6.81−6.77 (m, 8H), 7.19−7.08 (m, 8H), 7.28 (s, 1H), 8.10 (s, 1H), 8.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 32.2, 54.9, 55.1, 110.5, 112.3, 112.7, 112.8, 113.3, 120.6, 121.7, 121.8, 122.7, 125.0, 130.8, 131.2, 131.3, 132.0, 132.6, 132.7, 132.8, 133.3, 135.0, 135.3, 135.6, 138.5, 138.8, 139.0, 142.1, 157.1, 157.5, 157.8, 158.1, 158.3. MALDI-TOF MS: calcd for $[C_{48}H_{41}NO_5]^+$ 711.2985, found 711.3004.

*Preparation of 1,2,3,6,7,8-Hexakis(4-fluorophenyl)-9-methyl-9H-carbazole (**20**).* 1,2,3,6,7,8-Hexabromo-9-methyl-9*H*-carbazole (**5a**) (0.65 g, 1.0 mmol), 4-fluorophenylboronic acid (0.91 g, 6.5 mmol), potassium carbonate (4.14 g, 30.0 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg), and PPh_3 (50 mg) were taken in DMF and water mixtures. According to the general procedure, the product was obtained as a white powder. Yield: 0.57 g, 70%. Mp: 235 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.62 (t, J = 6.8 Hz, 3H), 6.69−6.68 (m, 4H), 6.79−6.76 (m, 4H), 6.89−6.85 (m, 8H), 7.11−7.07 (m, 8H), 8.14 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 36.2, 114.0, 114.2, 114.4, 114.5, 114.6, 114.7, 114.9, 120.8, 122.0, 123.0, 124.7, 128.6, 131.0, 131.6, 131.7, 132.8, 133.0, 133.1, 133.4, 134.1, 134.3, 135.8, 138.4, 138.7, 140.8, 159.8, 160.1, 160.4, 162.2, 162.6, 162.9. MALDI-TOF MS: calcd for $[C_{49}H_{29}F_6N]^+$ 745.2204, found 745.2200.

*Preparation of 1,2,3,6,7,8-Hexakis(4-methoxyphenyl)-9-methyl-9H-carbazole (**21**).* 1,2,3,6,7,8-Hexabromo-9-methyl-9*H*-carbazole (**5a**) (0.65 g, 1.0 mmol), 4-methoxyphenylboronic acid (0.99 g, 6.5 mmol), potassium carbonate (4.14 g, 30.0 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg), and PPh_3 (50 mg) were taken in DMF and water mixtures. According to the general procedure, the product was obtained as a white powder. Yield: 0.57 g, 70%. Mp: 210 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.59 (s, 3H), 3.67 (s, 6H), 3.74 (s, 6H), 3.77 (s, 6H), 6.50 (d, J = 8.8 Hz, 4H), 6.76−6.67 (m, 12H), 7.09−7.02 (m, 8H), 8.10 (s, 2H). ^{13}C NMR ($CDCl_3$,100 MHz) δ: 36.0, 54.9, 55.0, 55.1, 112.3, 112.7, 112.9, 120.3, 123.2, 125.4, 131.3, 132.4, 132.8, 132.9, 133.7, 135.6, 139.0, 141.0, 157.1, 157.5, 157.9. MALDI-TOF MS: calcd for $[C_{55}H_{47}NO_6]^+$ 817.3403, found 817.3423.

*Preparation of 1,2,3,6,7,8-Hexakis(4-methoxyphenyl)-9-butyl-9H-carbazole (**22**).* 1,2,3,6,7,8-Hexabromo-9-butyl-9*H*-carbazole (**5b**) (0.70 g, 1.0 mmol), 4-methoxyphenylboronic acid (0.99 g, 6.5 mmol), potassium carbonate (4.14 g, 30.0 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg), and PPh_3 (50 mg) were taken in DMF and water mixtures. According to the general procedure, the product was obtained as a white powder. Yield: 0.55 g, 64%. Mp: 140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.32−0.28 (m, 2H), 0.44 (t, J = 8.8 Hz, 3H), 0.90−0.86 (m, 2H), 2.92 (t, J = 8.8 Hz, 2H), 3.67 (s, 6H), 3.74 (s, 6H), 3.76 (s, 6H), 6.50−6.48 (m, 4H), 6.76−6.67 (m, 12H), 7.10−7.04 (m, 8H), 8.10 (s, 2H). ^{13}C NMR ($CDCl_3$,100 MHz) δ: 13.7, 19.3, 31.1, 44.3, 54.9, 55.1, 55.2, 112.2, 112.9, 120.3, 124.1, 125.9, 131.1, 131.2, 131.9, 132.3, 132.8, 133.1, 133.9, 135.7, 139.1, 139.9, 157.0, 157.5, 158.0. MALDI-TOF MS: calcd for $[C_{58}H_{53}NO_6]^+$ 859.3873, found 859.3899.

*Preparation of 1,2,3,6,7,8-Hexakis(4-methylphenyl)-9-butyl-9H-carbazole (**23**).* 1,2,3,6,7,8-Hexabromo-9-butyl-9*H*-carbazole (**5b**) (0.70 g, 1.0 mmol), 4-methylyphenylboronic acid (0.88 g, 6.5 mmol), potassium carbonate (4.14 g, 30.0 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg), and PPh_3 (50 mg) were taken in DMF and water mixtures. According to the general procedure, the product was obtained as a white powder. Yield: 0.56 g, 72%. Mp: 180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.24−0.22 (m, 2H), 0.43−0.40 (m, 3H), 0.93−0.85 (m, 2H), 2.15 (s, 6H), 2.24 (s, 6H), 2.91 (s, 6H), 2.89 (t, J = 8.0 Hz, 2H), 6.74−6.69 (m, 8H), 6.98−6.91 (m, 8H), 7.07−7.02 (m, 8H), 8.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.6, 19.1, 21.1, 21.2, 31.2, 44.4, 120.4, 124.0, 126.1, 127.1, 127.3, 127.7, 128.0, 128.1, 128.5, 130.0, 130.2, 130.9, 131.5, 131.7, 134.0, 134.4, 134.8, 135.7, 135.9, 137.6, 139.2, 139.7, 140.3; MALDI-TOF MS: calcd for $[C_{58}H_{53}N]^+$ 763.4178, found 763.4150.

General Method of Scholl Reaction for the Formation of Annulated Carbazoles 24−26, PC, PTC, and TC. Tetra-, penta-, or hexaarylated carbazole **6−23** (1.0 mmol) was taken in anhydrous dichloromethane (30 mL) under inert atmosphere. Iron chloride (10−30 mmol) dissolved in nitromethane (10 mL) was added via syringe, and the mixture was stirred for 2−36 h. The reaction was quenched by adding methanol, and the precipitated solid was filtered and then washed with methanol, hydrochloric acid, and water successively. After drying, the product was purified by column chromatography using dichloromethane depending on its solubility.

*Preparation of 3,6-Difluoro-12,13-bis(4-fluorophenyl)-10-methyl-10H-phenanthro[9,10-b]carbazole (**24**).* According to the general procedure, oxidative coupling on 2,3,6,7-tetrakis(4-fluorophenyl)-9-methyl-9*H*-carbazole (**8**) (0.56 g, 1.0 mmol) using iron chloride (1.62 g, 10.0 mmol) was performed for 2 h. The product was purified by column chromatography using dichloromethane as eluent to give a light yellow solid. Yield: 0.44 g, 80%. Mp: 320 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.00 (s, 3H), 7.02−6.99 (m, 4H), 7.25−7.20 (m, 4H), 7.44−7.38 (m, 3H), 8.12−8.06 (m, 2H), 8.25 (s, 1H), 8.36 (s, 1H), 8.75−8.70 (m, 2H), 9.19 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.4, 101.0, 108.8, 109.0, 109.2, 110.2, 114.7, 114.8, 114.9, 115.0, 115.1, 115.7, 115.9, 116.1, 122.1, 122.2, 122.6, 123.5, 125.2, 125.6 125.7, 127.2, 127.7, 128.0, 129.7, 131.1, 131.6, 131.7, 131.8, 138.1, 138.2, 138.9, 141.6, 142.3, 160.3, 160.7, 160.8, 162.7. MALDI-TOF MS: calcd for $[C_{37}H_{21}F_4N]^+$ 555.1610, found 555.1638.

*Preparation of 3,6-Difluoro-12,13-bis(4-fluorophenyl)-10-butyl-10H-phenanthro[9,10-b]carbazole (**25**).* According to the general procedure, oxidative coupling on 2,3,6,7-tetrakis(4-fluorophenyl)-9-butyl-9*H*-carbazole (**10**) (0.60 g, 1.0 mmol) using iron chloride (1.62 g, 10.0 mmol) was performed for 2 h. The product was purified by

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column chromatography using dichloromethane as eluent to give a light yellow solid. Yield: 0.51 g, 86%. Mp: 270 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.30 (t, J = 7.2 Hz, 3H), 2.85−2.75 (m, 2H), 3.27 (t, J = 6.8 Hz, 2H), 5.74−5.71 (m, 2H), 8.31−8.26 (m, 4H), 8.54−8.39 (m, 4H), 8.73−8.68 (m, 3H), 9.40−9.35 (m, 2H), 9.55 (s, 1H), 9.65 (s, 1H), 9.99−9.95 (m, 2H), 10.5 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 20.7, 31.1, 43.1, 101.1, 108.7, 108.9, 109.1, 110.3, 114.6, 114.8, 114.9, 115.0, 115.1, 115.6, 115.8, 116.0, 122.0, 122.1, 122.6, 123.4, 125.0, 125.1, 125.6, 125.7, 127.2, 127.7, 127.8, 129.5, 131.0, 131.4, 131.7, 131.8, 138.1, 138.3, 138.7, 140.9, 141.7, 160.2, 160.6, 163.1. MALDI-TOF MS: calcd for $[C_{40}H_{27}F_4N]^+$ 597.2080, found 597.2079.

*Preparation of 3,6-Dichloro-12,13-bis(4-chlorophenyl)-10-decyl-10H-phenanthro[9,10-b]carbazole (**26**).* According to the general procedure, oxidative coupling on 2,3,6,7-tetrakis(4-clorophenyl)-9-decyl-9*H*-carbazole (**16**) (0.68 g, 1.0 mmol) using iron chloride (1.62 g, 10.0 mmol) was performed for 2 h. The product was purified by column chromatography using dichloromethane as eluent to give a light yellow solid. Yield: 0.53 g, 78%. Mp: 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.85 (t, J = 6.6 Hz, 3H), 1.48−1.22 (m, 14H), 1.99−1.92 (m, 2H), 4.35 (t, J = 7.1 Hz, 2H), 7.30−7.19 (m, 7H), 7.36 (s, 1H), 7.59−7.53 (m, 2H), 8.19 (s, 1H), 8.23 (s, 1H), 8.36−8.34 (m, 2H), 8.55−8.49 (m, 2H), 9.04−8.34 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 22.6, 27.3, 28.7, 29.3, 29.6, 31.8, 43.1, 100.7, 100.9, 110.3, 114.3, 114.4, 121.8, 122.2, 122.6, 122.7, 122.9, 123.4, 124.2, 124.6, 127.4, 127.6, 128.3, 128.5, 128.8, 129.3, 129.8, 131.0, 131.5, 132.0, 132.4, 132.9, 138.4, 140.4, 140.6, 140.8, 140.9, 141.7. MALDI-TOF MS: calcd for $[C_{46}H_{39}Cl_4N]^+$ 745.1837, found 745.1812.

*Preparation of 3,6,14,17-Tetrafluoro-10H-diphenanthro[9,10-b:9′,10′-h]carbazole (**FluPC**).* According to the general procedure, oxidative coupling on 2,3,6,7-tetrakis(4-fluorophenyl)-9-9*H*-carbazole (**6**) (0.54 g, 1.0 mmol) using iron chloride (3.24 g, 20.0 mmol) was performed for 12 h. The product was slightly soluble in common organic solvents and, thus, could not be purified by column chromatography. Additionally, purification by vacuum sublimation could not give satisfactory purity. MALDI-TOF MS: calcd for $[C_{36}H_{17}F_4N]^+$ 539.1297, found 539.1311.

*Preparation of 10-Methyl-10H-diphenanthro[9,10-b:9′,10′-h]-carbazole (**Me-PC**).* According to the general procedure, oxidative coupling on 2,3,6,7-tetraphenyl-9-methyl-9*H*-carbazole (**7**) (0.49 g, 1.0 mmol) using iron chloride (3.24 g, 20.0 mmol) was performed for 12 h. The product was purified by column chromatography using dichloromethane as eluent to give a light yellow solid. Yield: 0.35 g, 72%. Mp: 340 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.97 (s, 3H), 7.72−7.61 (m, 8H), 8.37 (s, 2H), 8.67−8.63 (m, 4H), 8.74−8.72 (m, 2H), 8.41 (d, J = 8.0 Hz, 2H), 9.38 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 29.3, 100.9, 115.1, 123.1, 123.3, 123.5, 123.7, 126.1, 127.1, 127.3, 128.7, 129.5, 130.0, 130.3, 130.9, 142.7. MALDI-TOF MS: calcd for $[C_{37}H_{23}N]^+$ 481.1830, found 481.1844.

*Preparation of 3,6,14,17-Tetrafluoro-10-methyl-10H-diphenanthro[9,10-b:9′,10′-h]carbazole (**Me-FluPC**).* According to the general procedure, oxidative coupling on 2,3,6,7-tetrakis(4-fluorophenyl)-9-methyl-9*H*-carbazole (**8**) (0.56 g, 1.0 mmol) using iron chloride (3.24 g, 20.0 mmol) was performed for 24 h. The compound was not properly soluble in common organic solvents. As a result, it was purified by vacuum sublimation at 390−400 °C at 10^{-5} Torr to give a yellow solid. Yield: 0.28 g, 50%. Mp: 360 °C. ^{1}H NMR (400 MHz, DMSO-*d*) δ: 4.21 (s, 3H), 7.69−7.59 (m, 4H), 8.59−8.55 (m, 4H), 8.77 (s, 2H), 9.11−9.02 (m, 4H), 9.81 (s, 2H). Because of solubility problems we were not able to record a ^{13}C NMR spectrum for this compound. MALDI-TOF MS: calcd for $[C_{37}H_{19}F_4N]^+$ 553.1454, found 553.1467.

*Preparation of 3,6,14,17-Tetramethoxy-10-methyl-10H-diphenanthro[9,10-b:9′,10′-h]carbazole (**Me-MetPC**).* According to the general procedure, oxidative coupling on 2,3,6,7-tetrakis(4-methoxyphenyl)-9-methyl-9*H*-carbazole (**9**) (0.61 g, 1.0 mmol) using iron chloride (3.24 g, 20.0 mmol) was performed for 6 h. The product was purified by column chromatography using dichloromethane as eluent to give an orange-yellow solid. Yield: 0.45 g, 74%. Mp: 325 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.49 (s, 3H), 3.95 (s, 6H), 3.98 (s, 6H), 7.13 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.8 Hz, 2H), 7.77 (s, 6H), 8.36−8.33 (m, 2H), 8.48 (s, 2H), 8.79 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 29.1, 55.3, 55.4, 106.0, 106.3, 113.8, 114.3, 115.1, 115.3, 115.4, 120.6, 124.6, 125.0, 128.1, 128.5, 129.4, 130.8, 132.2, 141.7, 157.9, 158.4. MALDI-TOF MS: calcd for $[C_{41}H_{31}NO_4]^+$ 601.2252, found 601.2267.

*Preparation of 3,6,14,17-Tetrafluoro-10-butyl-10H-diphenanthro[9,10-b:9′,10′-h]carbazole (**Bu-FluPC**).* According to the general procedure, oxidative coupling on 2,3,6,7-tetrakis(4-fluorophenyl)-9-butyl-9*H*-carbazole (**10**) (0.60 g, 1.0 mmol) using iron chloride (3.24 g, 20.0 mmol) was performed for 24 h. The compound was purified by recrystallization from benzene to give yellow solid. Yield: 0.52 g, 88%. Mp: 340 °C. ^{1}H NMR (400 MHz, DMSO-*d*) δ: 0.96 (t, J = 7.2 Hz, 3H), 1.54−1.45 (m, 2H), 2.01−1.93 (m, 2H), 4.82 (t, J = 6.8 Hz, 2H), 7.72−7.62 (m, 4H), 8.63−8.59 (m, 4H), 8.84 (s, 2H), 9.10−9.06 (m, 2H), 9.18−9.14 (m, 2H), 9.89 (s, 2H). ^{1}H NMR (100 MHz, DMSO-*d*) δ: 14.3, 20.3, 31.1, 42.7, 102.6, 110.0, 110.3, 116.4, 116.7, 122.0, 123.9, 126.3, 127.7, 128.2, 128.7, 129.8, 131.3, 142.5, 160.4, 162.8, 163.4. MALDI-TOF MS: calcd for $[C_{40}H_{25}F_4N]^+$ 595.1923, found 595.1939.

*Preparation of 3,6,14,17-Tetramethoxy-10-butyl-10H-diphenanthro[9,10-b:9′,10′-h]carbazole (**Bu-MetPC**).* According to the general procedure, oxidative coupling on 2,3,6,7-tetrakis(4-methoxyphenyl)-9-butyl-9*H*-carbazole (**11**) (0.61 g, 1.0 mmol) using iron chloride (3.24 g, 20.0 mmol) was performed for 6 h. The product was purified by column chromatography using dichloromethane as eluent to give an orange-yellow solid. Yield: 0.58 g, 89%. Mp: 285 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02 (t, J = 7.2 Hz, 3H), 1.52−1.48 (m, 2H), 2.02−1.98 (m, 2H), 4.03 (s, 12H), 4.37 (t, J = 6.9 Hz, 2H), 7.30−7.26 (m, 4H), 7.92 (s, 4H), 8.19 (s, 2H), 8.57 (d, J = 8.8 Hz, 2H), 8.69 (d, J = 8.8 Hz, 2H), 9.15 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 20.8, 30.9, 43.1, 55.5, 100.3, 106.3, 114.3, 115.4, 115.6, 122.2, 123.2, 124.7, 124.8, 125.1, 125.4, 128.5, 129.6, 131.1, 141.7, 158.0, 158.7. MALDI-TOF MS: calcd for $[C_{44}H_{37}NO_4]^+$ 643.2723, found 643.2737.

*Preparation of 3,6,14,17-Tetrafluoro-10-decyl-10H-diphenanthro[9,10-b:9′,10′-h]carbazole (**Dec-FluPC**).* According to the general procedure, oxidative coupling on 2,3,6,7-tetrakis(4-fluorophenyl)-9-decyl-9*H*-carbazole (**13**) (0.68 g, 1.0 mmol) using iron chloride (3.24 g, 20.0 mmol) was performed for 16 h. The product was purified by recrystallization from dichloromethane/hexane to give a yellow solid. Yield: 0.55 g, 81%. Mp: 204 °C. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ: 0.83 (t, J = 6.4 Hz, 3H), 1.57−1.21 (m, 14H), 2.10−2.03 (m, 2H), 4.51 (t, J = 6.8 Hz, 2H), 7.45 (t, J = 7.2 Hz, 4H), 8.08 (t, J = 8.8 Hz, 4H), 8.30 (s, 2H), 8.67 (d, J = 7.6 Hz, 2H), 8.79 (d, J = 8.0 Hz, 2H), 9.24 (s, 2H). ^{13}C NMR could not recorded because of solubility problems. MALDI-TOF MS: calcd for $[C_{46}H_{37}F_4N]^+$ 679.2862, found 679.2877.

*Preparation of 3,6,14,17-Tetramethoxy-10-decyl-10H-diphenanthro[9,10-b:9′,10′-h]carbazole (**Dec-MetPC**).* According to the general procedure, oxidative coupling on 2,3,6,7-tetrakis(4-methoxyphenyl)-9-decyl-9*H*-carbazole (**14**) (0.73 g, 1.0 mmol) using iron chloride (3.24 g, 20.0 mmol) was performed for 4 h. The product was purified by column chromatography using dichloromethane as eluent to give an orange-yellow solid. Yield: 0.66 g, 90%. Mp: 180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.83 (t, J = 6.8 Hz, 3H), 1.49−1.21 (m, 14H), 1.95 (t, J = 6.8 Hz, 2H), 4.00 (s, 6H), 4.02 (s, 6H),4.26−4.22 (m, 2H), 7.27−7.22 (m, 4H), 7.88 (s, 4H), 8.08 (s, 2H), 8.50 (d, J = 8.4 Hz, 2H), 8.63 (d, J = 8.8 Hz, 2H), 9.05 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 22.6, 27.2, 29.3, 29.6, 31.9, 41.2, 55.2, 99.4, 105.7, 113.5, 114.8, 115.0, 121.5, 122.7, 124.3, 124.5, 124.7, 125.2, 127.8, 129.2, 130.7, 140.9, 157.4, 158.1. MALDI-TOF MS: calcd for $[C_{50}H_{49}NO_4]^+$ 727.3662, found 727.3682.

*Preparation of 3,6,14,17-Tetramethyl-10-decyl-10H-diphenanthro[9,10-b:9′,10′-h]carbazole (**Me-MePC**).* According to the general procedure, oxidative coupling on 2,3,6,7-tetrakis(4-methylphenyl)-9-decyl-9*H*-carbazole (**15**) (0.67 g, 1.0 mmol) using iron chloride (3.24 g, 20.0 mmol) was performed for 10 h. The product was purified by column chromatography using dichloromethane as eluent to give a yellow solid. Yield: 0.54 g, 81%. Mp: 189

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J. Org. Chem. 2015, 80, 5066−5076

°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.84 (t, J = 6.4 Hz, 3H), 1.49−1.22 (m, 14H), 1.95 (t, J = 7.2 Hz, 2H), 2.63 (s, 6H), 2.66 (s, 6H), 4.31−4.27 (m, 2H), 7.50−7.44 (m, 4H), 8.22 (s, 2H), 8.39 (d, J = 4.8 Hz, 4H), 8.52 (d, J = 8.4 Hz, 2H), 8.66 (d, J = 8.4 Hz, 2H), 9.22 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 21.8, 22.7, 27.2, 28.4, 29.3, 29.6, 29.7, 31.9, 42.5, 100.1, 114.2, 122.3, 122.9, 123.1, 123.2, 128.0, 128.1, 128.3, 128.7, 129.7, 134.9, 136.1, 141.4. MALDI-TOF MS: calcd for $[C_{50}H_{49}N]^+$ 663.3865, found 663.3882.

*Attempted Synthesis of 10-Decyl-3,6,14,17-tetrakis-(trifluoromethyl)-10H-diphenanthro[9,10-b:9′,10′-h]carbazole (**Me-TfMePC**).* According to the general procedure, oxidative coupling on 9-decyl-2,3,6,7-tetrakis(4-(trifluoromethyl)phenyl)-9*H*-carbazole (**17**) (0.88 g, 1.0 mmol) using iron chloride (3.24 g, 20.0 mmol) was performed for 36 h. Starting material was recovered.

*Preparation of 3,6,9,16,19-Pentafluoro-23-methyl-23H-benzo-[11,12]tetraceno[5,6-ab]phenanthro[9,10-h]carbazole (**Me-FluPTC**).* According to the general procedure, oxidative coupling on 1,2,3,6,7-penta(4-fluorophenyl)-9-methyl-9*H*-carbazole (**18**) (0.65 g, 1.0 mmol) using iron chloride (4.05 g, 25.0 mmol) was performed for 36 h. The product was insoluble in common organic solvents and thus could not be purified by column chromatography. Additionally, purification by vacuum sublimation could not give satisfactory purity. MALDI-TOF MS: calcd for $[C_{43}H_{20}F_5N]^+$ 645.1516, found 645.1540.

*Preparation of 3,6,9,16,19-Pentamethoxy-23-methyl-23H-benzo-[11,12]tetraceno[5,6-ab]phenanthro[9,10-h]carbazole (**Me-MetPTC**).* According to the general procedure, oxidative coupling on 1,2,3,6,7-penta(4-methoxyphenyl)-9-methyl-9*H*-carbazole (**19**) (0.71 g, 1.0 mmol) using iron chloride (4.05 g, 25.0 mmol) was performed for 12 h. The product was insoluble in common organic solvents and thus could not be purified by column chromatography. Additionally, purification by vacuum sublimation could not give satisfactory purity. MALDI-TOF MS: calcd for $[C_{48}H_{35}NO_5]^+$ 705.2515, found 705.2543.

*Preparation of 3,6,9,16,19,22-Hexafluoro-25-methyl-25H-benzo-[11,12]tetraceno [5,6-ab]benzo[11,12]tetraceno[5,6-hi]carbazole (**Me-FluTC**).* According to the general procedure, oxidative coupling on 1,2,3,6,7,8-hexakis(4-fluorophenyl)-9-methyl-9*H*-carbazole (**20**) (0.82 g, 1.0 mmol) using iron chloride (4.86g, 30.0 mmol) was performed for 36 h. The product was insoluble in common organic solvents and thus could not be purified by column chromatography. Additionally, purification by vacuum sublimation could not give satisfactory purity.

*Preparation of 3,6,9,16,19,22-Hexamethoxy-25-methyl-25H-benzo[11,12]tetraceno [5,6-ab]benzo[11,12]tetraceno[5,6-hi]-carbazole (**Me-MetTC**).* According to the general procedure, oxidative coupling on 1,2,3,6,7,8-hexakis(4-methoxyphenyl)-9-methyl-9*H*-carbazole (**21**) (0.82 g, 1.0 mmol) using iron chloride (4.86 g, 30.0 mmol) was performed for 24 h. The product was purified by column chromatography using dichloromethane as eluent to give orange solid. Yield: 0.53 g, 66%. Mp: 270 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.88 (s, 3H), 3.97 (s, 6H), 3.99 (s, 6H), 4.09 (s, 6H), 7.08−7.02 (m, 4H), 7.85 (d, J = 12.0 Hz, 4H), 8.06 (s, 4H), 8.31 (d, J = 7.2 Hz, 2H), 8.63 (s, 2H), 8.78 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 40.9, 55.3, 55.6, 105.9, 106.1, 106.3, 107.2, 111.6, 114.4, 115.5, 115.6, 120.3, 122.6, 122.9, 123.6, 124.8, 125.0, 126.9, 129.8, 129.9, 130.8, 131.2, 144.8, 157.4, 158.0, 158.1. MALDI-TOF MS: calcd for $[C_{55}H_{39}NO_6]^+$ 809.2777, found 809.2794.

*Preparation of 25-Butyl-3,6,9,16,19,22-hexamethoxy-25H-benzo[11,12]tetraceno[5,6-ab]benzo[11,12]tetraceno[5,6-hi]-carbazole (**Bu-MetTC**).* According to the general procedure, oxidative coupling on 1,2,3,6,7,8-hexakis(4-methoxyphenyl)-9-butyl-9*H*-carbazole (**22**) (0.86 g, 1.0 mmol) using iron chloride (4.86g, 30.0 mmol) was performed for 24 h. The product was purified by column chromatography using dichloromethane as eluent to give orange solid. Yield: 0.53 g, 62%. Mp: 210 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: −0.26 to −0.27 (m, 3H), −0.13 to −0.22 (m, 2H), 3.96 (t, J = 7.2 Hz, 2H), 4.05 (s, 6H), 4.06 (s, 6H), 4.11−4.09 (m, 2H), 4.14 (s, 6H), 7.15 (d, J = 9.2 Hz, 2H), 7.22 (d, J = 2.0 Hz, 2H), 8.00−7.93 (m, 4H), 8.18 (d, J = 9.6 Hz, 4H), 8.55 (d, J = 8.8 Hz, 2H), 8.91 (s, 2H), 9.06 (d, J = 8.8 Hz, 2H). ^{13}C NMR (DMSO-*d*, 100 MHz) δ: 12.9, 19.0, 28.3, 50.2, 56.0, 56.3, 106.9, 107.3, 108.0, 108.9, 113.6, 116.0, 116.3, 117.2, 120.0, 122.4, 122.6, 124.2, 125.0, 126.1, 128.6, 129.8, 130.2, 131.2, 131.5, 142.4, 158.5, 159.0. MALDI-TOF MS: calcd for $[C_{58}H_{45}NO_6]^+$ 851.3247, found 851.3267.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete spectroscopic characterization including X-ray data (CIF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00423.

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Notes

The authors declare no competing financial interest.

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