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First Approach to Nitrogen-Containing Fused Aromatic Hydrocarbons as Targets for Organoelectronics Utilizing a New Transformation of *O*-Protected Diaryl Methanols

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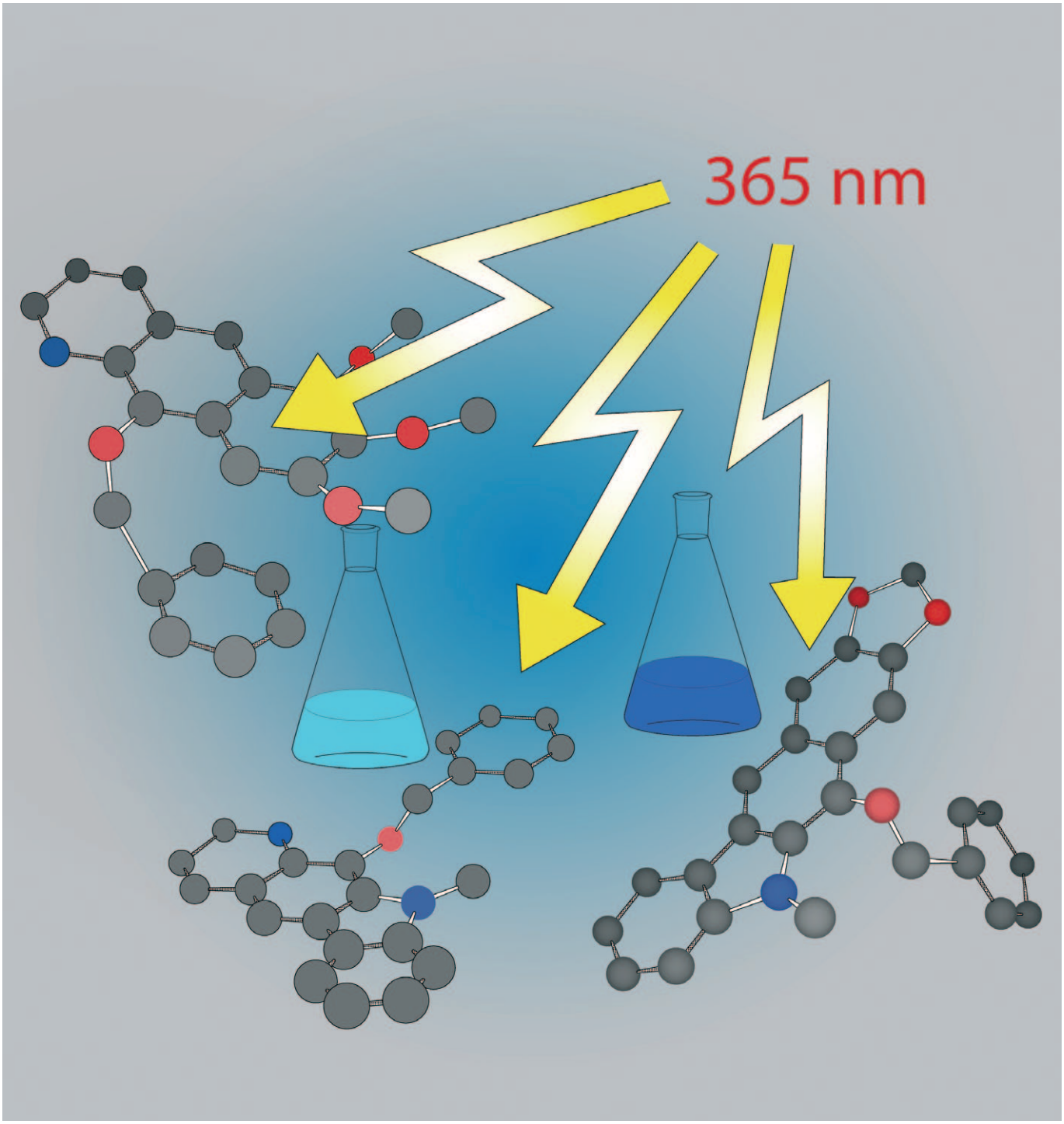
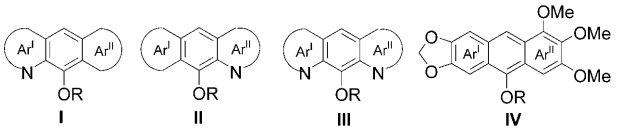


Abstract: A new concise approach for the construction of heteroatom analogues of polycyclic aromatic benzo[*g*]-quinoline, benzo[*b*]carbazole, and pyrido[*b*]carbazole systems via diaryl methanols is described. This transformation involves formation of a central benzene ring fused to two aromatic 5- or 6-membered rings of pyrrole and/or pyridine by using a combination of two aromatic aldehydes, of which at least one contains a ring nitrogen. Analysis of the UV and fluorescent properties, Stokes shifts, quantum yields in solution, and π-stacking interactions in the crystal structures of the new materials was performed. These polycyclic aromatic compounds show potential as small-molecule organoelectronic materials.

Keywords: aromatic substitution · cyclization · energy conversion · fluorescence · synthetic methods

Introduction

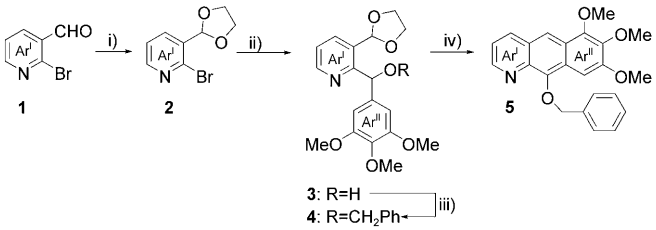
Over the past few years, nitrogen-containing fused aromatic systems have been a subject of interest in several areas, from biologically active substances[1–3] to new materials in organoelectronics.[4–7] For instance, carbazole-containing molecules, such as indolo[3,2-*b*]carbazoles, have been widely used as materials for constructing high-mobility organic field-effect transistors (OFETs),[8] the main logic units in electronic circuits, in which they usually function as either switches or amplifiers. Bisindenocarbazoles[9] were used in construction of organic light-emitting diodes (OLEDs),[10] whereas 2,2′-bispyridyl derivatives found application in luminescent solar concentrators (LSCs). Due to these interesting properties, a number of synthetic approaches to benzocarbazole,[11] benzoquinoline,[5] pyridocarbazole,[6] and other carbazole systems[7] have been described. Progress in the area of small molecules for organic electronic devices has also been recently reviewed.[12,13]



Herein, we demonstrate novel, concise, and low-cost syntheses of three nitrogen-containing systems **I–III**, which have potential applications as materials in organic electronics. These new systems contain nitrogen atoms in their Ar^I and/or Ar^{II} aromatic rings. The present approach to constructing linearly fused poly(hetero)aromatic systems **I–III** is based on the formation of the central six-membered aromatic ring from two existing Ar^I and Ar^{II} rings of independent aromatic aldehydes.[14] For first time we apply our recently discovered reaction, in which the corresponding *O*-benzyl-protected diaryl methanol is transformed directly into electron-rich hexahydroxylated anthracene system **IV** by a multistage mechanism in a one-pot procedure under acidic conditions.[15]

Results and Discussion

In the synthesis of benzoquinoline derivative **5**, as an example of system **I**, key derivative **4** was obtained from *o*-bromoaldehyde **1** (Scheme 1). In contrast to literature reports



Scheme 1. Synthesis of benzoquinoline derivative **5**. Conditions: i) $HOCH_2CH_2OH$/4-$MeC_6H_4SO_3H$ (cat.), benzene, reflux, 4 h, 94 %; ii) *n*-BuLi, −78 °C, 10 min, THF followed by 3,4,5-$C_6H_2(OMe)_3CHO$, −78 → 0 °C, 69 %; iii) NaH, RT, 30 min, THF followed by $C_6H_5CH_2Br$ (1.5 equiv), KI (5 %), 18 h, RT, 83 %; iv) 1 N HCl, MeOH, 5 d, RT, 53 %.

(24 h, toluene, 90 % yield, cat. *p*-TsOH),[16,17] the use of catalytic amounts of *p*-TsOH to protect the aldehyde group in **1** with ethylene glycol in our system gave only trace amounts of **2** after 17 h. The use of 0.5 equivalents of the acidic catalyst was sufficient to complete the reaction within only 4 h in benzene, in very good 92 % yield. A Br/Li exchange reaction with *n*BuLi followed by condensation with 3,4,5-trimethoxybenzaldehyde afforded diaryl methanol **3** in 69 % yield. Further protection of the OH group in **3** with benzyl bromide gave **4** in 83 % yield. An attempt to transform **4** into **5** in methanol (HCl, 15 equiv, 1 N) resulted in deprotection of the 1,3-dioxolane function to give the free aldehyde

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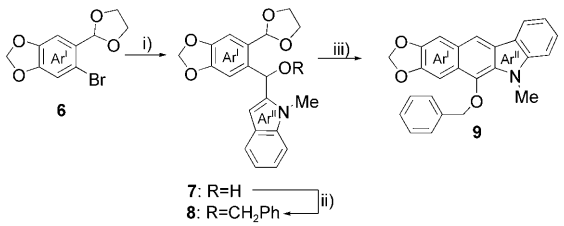
group, and afforded only 5% of desired product **5** after 72 h. When methanol was replaced with acetone, compound **5** was obtained in 27% yield after 72 h, accompanied by substrate **4** (44% yield). Finally, the use of a large excess (30 equiv) of 1 N HCl and extention of the reaction time to 5 d gave **5** in a satisfactory and reproducible yield of 53% (Table 1).

In the approach to nitrogen-containing fused aromatics of type **II** (Scheme 2), we synthesized the unknown 1,3-dioxabenzocarbazole system **9** by starting from diaryl methanol **7**, which was obtained in 66% yield from two independent aromatic aldehydes, that is, protected 6-bromopiperonal **6** and *N*-methylindole-2-carboxaldehyde. After further protection of the OH group in diaryl methanol **7** with benzyl bromide, obtained derivative **8** underwent cyclization to give new system **9** under acidic conditions in methanol, with almost 100% purity (Table 1). Replacing methanol with acetone ensured better solubility of **8** and allowed the reaction time

Table 1. Structures of final products **5**, **9**, **12**, and **13** obtained by acidic transformation of diaryl methanols.

Substrates	Intermediates	Final products
1 R=CHO **2** R=O(CH$_2$)$_2$O — 94%	**3**: R=H (69%) **4**: R=CH$_2$Ph (83%)	**5** (53%)
1 R=CHO **2** R=O(CH$_2$)$_2$O — 94%	**10**: R=H (59%) **11**: R=CH$_2$Ph (99%)	**12** (34%)
R=CHO **6** R=O(CH$_2$)$_2$O — 90%	**7**: R=H (66%) **8**: R=CH$_2$Ph (79%)	**9** (99%)
R=CHO **6** R=O(CH$_2$)$_2$O — 90%	**7**: R=H (66%)	**13** (39%)



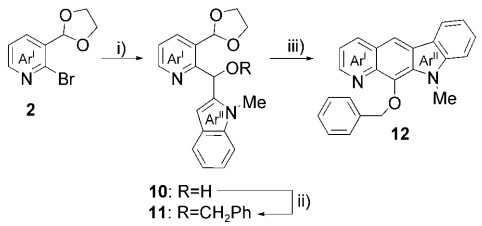
Scheme 2. Synthesis of benzocarbazole derivative **9**. Conditions: i) *n*BuLi, −78 °C, 10 min, THF followed by *N*-methylindole-2-carboxaldehyde, −78→0 °C, 66%; ii) NaH, RT, 30 min, THF followed by $C_6H_5CH_2Br$ (1.5 equiv), KI (5%), 18 h, RT, 79%; iii) 1 N HCl, acetone, 30 min, RT, 99%.

to be shortened from 24 h to 0.5 h. Moreover, the use of other acidic reagents, such as *p*-TsOH, Lewis acids ($ZnCl_2$ or $SnCl_2{\cdot}2H_2O$), or strong acidic ion-exchange resins (Amberlite IR 120, Amberlyst 15), also afforded carbazole **9** in almost quantitative yields (Table 2)

Table 2. Reaction conditions for the quantitative transformation of 1,3-dioxolane **8** into 1,3-dioxabenzocarbazole system **9**.

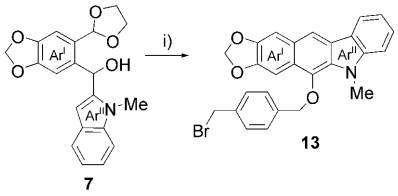
Acid	Solvent	*t* [h]	*T*
1 N HCl	MeOH	24	RT
Amberlite IR 120	acetone	0.5	RT
Amberlyst 15	acetone	2	RT
p-TsOH	acetone	1.5	RT
$ZnCl_2$	acetone	19	RT
$SnCl_2{\cdot}2H_2O$	acetone	24	RT

A combination of two nitrogen-containing aldehydes (protected 2-bromo-3-pyridinecarboxyaldehyde **2** and *N*-methylindole-2-carboxyaldehyde) afforded diaryl methanol **10** in 59% yield. Compound **10** is a key substrate in the synthesis of pyridocarbazole **12** in example system **III** (Scheme 3). An attempt to transform *O*-benzyl-protected derivative **11** into system **12** in the presence of 1 N HCl in methanol or HF in acetone gave the desired product in of 13 and 18% yield, respectively, after 72 h. With HCl, product **12** was accompanied by the starting material, whereas with HF a complex mixture was observed. When methanol was replaced with acetone, compound **12** was afforded in 34% yield after the same reaction time (Table 1).



Scheme 3. Synthesis of pyridocarbazole derivative **12**. Conditions: i) *n*BuLi, −78 °C, 10 min, THF followed by *N*-methylindole-2-carboxaldehyde, −78→0 °C, 59%; ii) NaH, RT, 30 min, THF followed by $C_6H_5CH_2Br$ (1.5 equiv), KI (5%), 18 h, RT, 99%; iii) 1 N HCl, acetone, 3 d, RT, 34%.

Attempted synthesis of the bis(benzocarbazole) system by using two equivalents of **7** and α,α′-dibromo-*p*-xylene unexpectedly afforded **13** in a one-pot reaction catalyzed by trace amounts of HBr that originated from hydrolysis of the dibenzyl substrate (Scheme 4, Table 1). Compound **13** can be used as a benzylating reagent for other diaryl methanols.



Scheme 4. Synthesis of benzocarbazole derivative **13**. Conditions: i) NaH, RT, 30 min, THF followed by α,α′-dibromo-*p*-xylene, 18 h, RT, 39 %.

Molecular and crystal structure of 9: In the structure of **9** there are two symmetry-independent molecules A and B in the asymmetric unit (Figure 1). The geometric parameters of these two molecules are similar; the bond lengths are the same within 3σ and the bond angles differ by less than 1°. In each symmetry-independent molecule of **9**, the fused carbazole and methylenedioxybenzene rings are practically planar, with the largest deviations from planarity of −0.063(3) and 0.240(4) being for atoms C1A and C1B. Benzyloxy atoms O3A and O3B and methyl atoms C18A and C18B are nearly coplanar with the planes of these rings, whereas benzyloxy atoms C19A and C19B are more coplanar with the planes formed by atoms C20A–C25A and C20B–C25B, respectively. The dihedral angles between the plane of benzene ring and the plane formed by the fused rings are 76.10(7) and 60.57(8)° in A and B, respectively.

The structure of **9** contains both intra- and intermolecular weak hydrogen bonds of type C–H···O. As can be seen in Figure 1, there are three such intramolecular bonds, that is, C18A–H18A···O3A (C18A–H18A = 1.04(2), H18A···O3A = 2.44(2), C18A···O3A = 3.027(3) Å; C18A-H18A-O3A = 115(2)°), C18B–H18F···O3B (C18B–H18F = 0.93(2), H18F···O3B = 2.48(2), C18B···O3B = 2.999(3) Å; C18B-H18F-O3B = 115(2)°), and C25A–H25A···O3A (C25A–H25A = 0.93, H25A···O3A = 2.44, C25A···O3A = 2.762(2) Å; C25A-H25A-O3A = 100°). The two first bonds generate an S(6) graph-set motif[18] and the last bond forms a motif with a graph set of S(5). As mentioned above, there are also two intermolecular C–H···O hydrogen bonds in the crystal structure; the first one is from the C19A benzyloxy atom of the molecule at (*x*, *y*, *z*) via H19A to the O2A 1,3-dioxolane ring atom of the molecule at (1−*x*, −*y*, −*z*) (C19A–H19A = 1.04(2), H19A···O2A = 2.58(2), C19A···O2A = 3.597(3) Å; C19A-H19A-O2A = 168(2)°), which forms the graph-set dimer centered at (0.5,0,0) (motif d in Figure 2a). The second one, that is, the C–H···O intermolecular interaction

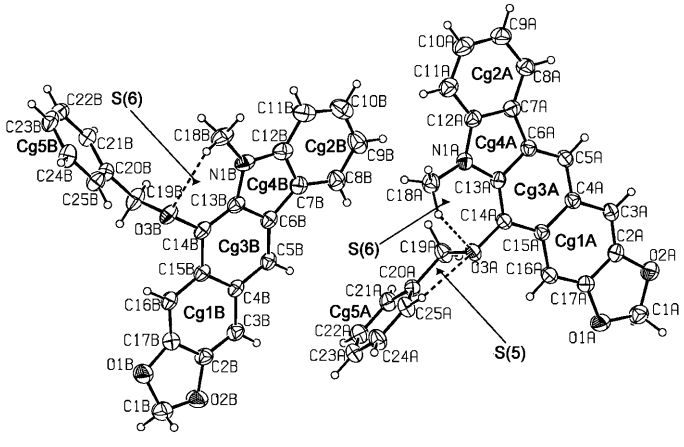


Figure 1. Views of molecules A (right) and B (left) in the crystal structure of **9**, showing the atom numbering schemes. Displacement ellipsoids are drawn at the 30 % probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Cg denotes the centroid of the aromatic rings. The dashed lines depict intramolecular hydrogen bonds that generate the S(5) and S(6) graph-set motifs.

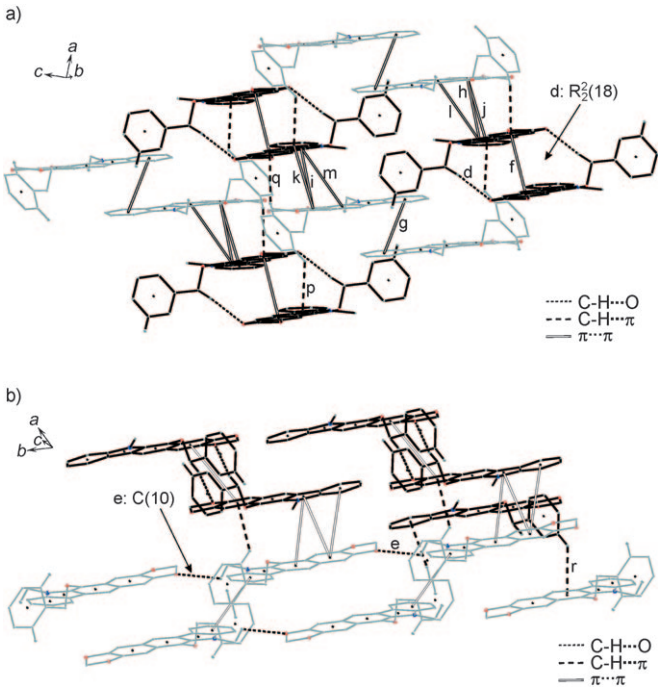


Figure 2. a, b) Parts of the crystal structure of **9** showing the intermolecular C–H···O hydrogen bonds that form the $R_2^2(18)$ graph-set dimers (motif d), and the C(10) chains (motif e). Molecules A and B are depicted by black and grey, respectively. Other interactions: f) Cg1A···Cg1A$^{(i)}$; g) Cg2B···Cg2B$^{(iv)}$; h) Cg4A···Cg1B$^{(iii)}$; i) Cg1B···Cg4A$^{(iii)}$; j) Cg2A···Cg1B$^{(iii)}$; k) Cg1B···Cg2A$^{(iii)}$; l) Cg4A···Cg3B$^{(iii)}$; m) Cg3B···Cg4A$^{(iii)}$; p) C21B–H21B···Cg2A$^{(iv)}$ (C21B–H21B = 0.93, H21B···Cg2A = 2.85, C21B···Cg2A = 3.565(3) Å; C21B-H21B-Cg2A = 135°); q) C25B–H25B···Cg1A$^{(iii)}$ (C25B–H25B = 0.93, H25B···Cg1A = 2.89, C25B···Cg1A = 3.586(3) Å; C25B-H25B-Cg1A = 133°); r) C22A–H22A···Cg3B$^{(v)}$ (C22A–H22A = 0.93, H22A···Cg3B = 2.82, C22A···Cg3B = 3.582(3) Å; C22A-H22A-Cg3B = 140°). Symmetry codes: (i) −*x*, −*y*, −*z*; (iii) 1−*x*, −*y*, 1−*z*; (iv) −*x*, 1−*y*, 1−*z*; (v) −*x*, −*y*, 1−*z*. The centroids of the aromatic rings (Cg; see Figure 1) are denoted by small black spheres. Distances between the ring centroids lie in the range of 3.835(1)–4.435(2) Å and interplanar angles lie in the range of 0.00–7.34°. Hydrogen atoms not involved in the interactions have been omitted for clarity.

between the methyl group (atoms C18B–H18E) of the molecule at (x, y, z) and the 1,3-dioxolane ring (atom O2B) at (x, $1+y$, z) generates a C(10) chain running parallel to the [010] direction (C18B−H18E = 0.96(2), H18E···O2B = 2.59(3), C18B···O2B = 3.094(3) Å; C18B-H18E-O2B = 113(2)°; motif e in Figure 2b).

It is also worth emphasizing that modification of the molecular structure of the carbazole molecule by replacing one of the C–H and N–H protons by benzyloxy and methyl groups, respectively, results first in transformation of the arrangement of aromatic rings from herringbone in the unsubstituted carbazole (Figure 3a) to a more parallel arrangement in **9** (Figure 3b), followed by elimination of intermolecular interactions of type N–H···π(arene) and appearance of the above-mentioned C–H···O interactions. The arrangement results from a lack of the edge-to-face π···π interactions between the aromatic rings of the planar fused moiety of molecule **9** (moiety 1) and the presence of slipped face-to-face π···π interactions between them (interactions f–m in Figure 2a and b). These interactions connect the planar moieties of 1 into columns in which the two adjacent A molecules (and also two adjacent B molecules) are rotated by 180°, whereas the A and B molecules are rotated by about 110° relative to each other.

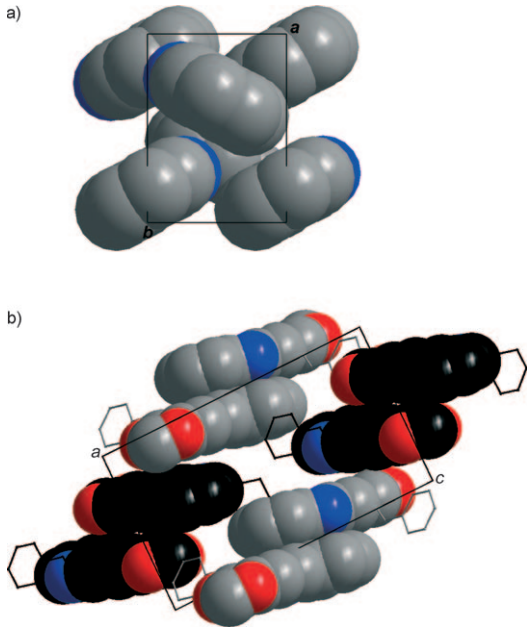


Figure 3. Packing structures of **9** and carbazole in the crystal structures. a) Herringbone packing diagram of carbazole with a space-filling model. b) Columnar stacks of **9** with a space-filling model for planar moiety 1 and a ball-and-stick model for the benzyloxy substitutent. All hydrogen atoms have been omitted for clarity.

Moreover, the benzene rings of sterically demanding benzyloxy substitutents in the structure of **9** are arranged so that they form edge-to-face C–H···π interactions p–r (Figure 2a and b) with the aromatic rings of moieties 1.

Bearing in mind that the materials that give π stacking in the solid state are particularly attractive because they often lead to devices with high charge-carrier mobilities,[19–22] and taking into account the fact that in the crystal structure of **9** the slipped π-stacking is predominant (similarly to the recently synthesized and crystallized tetraphenylbis(indolo-{1,2-a})quinoline,[23] which exhibited field-effect mobilities as high as 1.0 $cm^2 V^{-1} s^{-1}$), we can suppose that this newly synthesized carbazole derivative will turn out to be a promising material for device applications, particularly in the area of organic field-effect transistors (OFETs).

Compounds **5**, **9**, and **12** revealed very interesting photophysical properties and spectacular fluorescence (Figure 4). The absorption spectrum of **5** in chloroform displayed three broad bands with maxima at $\lambda = 237$, 277, and 365 nm

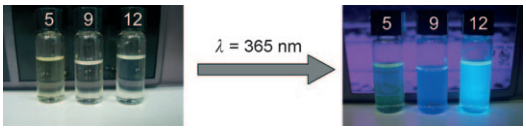


Figure 4. Fluorescence of compounds **5**, **9**, and **12** in solution ($CDCl_3$) before and after UV exposure.

($\varepsilon_{max} = 2.9 \times 10^4 M^{-1} cm^{-1}$, $\lambda = 277$ nm; Figure 5, grey lines). The spectrum of **9** was more structured and displayed many distinct spectral features ($\varepsilon = 4.2 \times 10^4 M^{-1} cm^{-1}$, $\lambda = 279$ nm; Figure 5, black lines). The excitation spectra matched the absorption spectra for both compounds (Figures 6 and 7), which shows that internal conversion from the upper excited singlet states to the lowest ones proceeded with unit quantum efficiency. Compounds **5** and **9** strongly emit greenish ($\lambda_{max.} = 479$ nm) and bluish ($\lambda_{max.} = 410$ nm) fluorescence with quantum yields of 0.24 (**5**) and 0.21 (**9**). In comparison with **5**, compound **12** revealed much more intense green fluorescence at $\lambda_{max} = 453$ nm at the same concentration of 1.5–1.7 × 10^{-4} mol L^{-1} in chloroform (Figure 8).

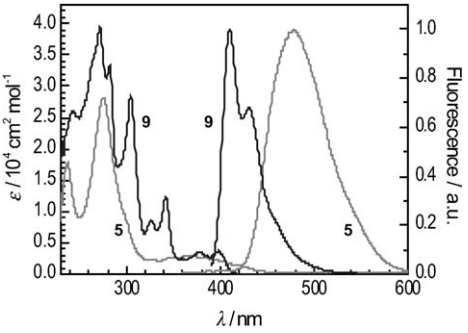


Figure 5. UV/Vis absorption (left) and fluorescence emission spectra (right) of **5** and **9** in chloroform.

The Stokes shift, defined as the difference between the spectral positions of the band maxima of the luminescence

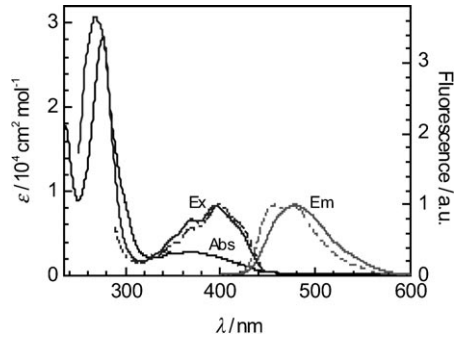


Figure 6. Absorption, fluorescence excitation, and fluorescence emission spectra of **5** in chloroform (solid lines) and toluene (dotted lines).

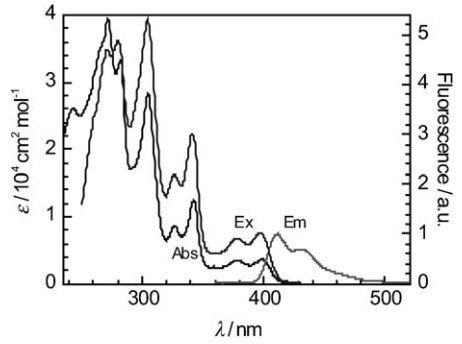


Figure 7. Absorption, fluorescence excitation, and fluorescence emission spectra of **9** in chloroform.

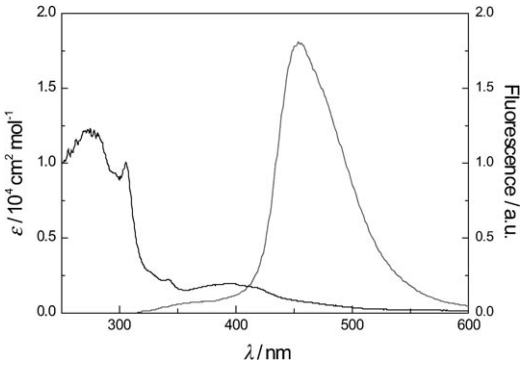


Figure 8. Absorption (left) and fluorescence emission (right) spectra of **12** in chloroform.

and appropriate absorption, is significantly distinct for **5** and **9** (Figures 6 and 7). Generally, 0–0 transitions for nonpolar and stiff molecules have almost the same energy, but in many cases they do not correspond to the maxima positions. The Stokes shift is then larger and increases with solvent polarity if a molecule has a larger dipole moment in the excited state. It also depends upon geometry changes between the ground and fluorescence states. Figure 6 shows that for compound **5**, the large Stokes shift is not due to a specific solute–solvent interaction (amine–protic solvent molecule) but is rather influenced by the above-mentioned factors that change the population of vibronic states in the molecule. The Stokes shift for carbazole derivative **9** amounted to just $\tilde{\nu}=860\,cm^{-1}$, whereas pyridine derivative **5** had an exceptionally high value of $\tilde{\nu}=4500\,cm^{-1}$, which indicates that the ground and fluorescence states might have different geometries. A further contribution to the longer emission wavelength of **5** might result from its higher electric dipole moment in the excited state distorting the local dielectric properties of the solvent. The Stokes shift for **12** also had a high value of $\tilde{\nu}=3435\,cm^{-1}$. Both compounds with high Stokes shifts constitute excellent base materials for further structure optimization towards luminescent solar concentrators,[24] which require large values for both the Stokes shift and quantum yield, and which significantly reduce the costs of photovoltaic power generation by decreasing the required surface area of expensive silicon photovoltaic cells.

Conclusion

We synthesized three nitrogen-containing polycyclic fused aromatic systems of benzo[*g*]quinoline, benzo[*b*]carbazole, and pyrido[*b*]carbazole, which are potential small-molecule organoelectronic materials, by using for the first time a transformation of *O*-protected diaryl methanols. In this new approach to synthesis of linearly fused polycyclic heteroaromatics, a newly formed central benzene ring is fused to two aromatic five- or six-membered rings of pyrrole or pyridine by using a combination of two independent aromatic aldehydes, of which at least one contains a ring nitrogen atom. Easy access to the latter, a one-pot procedure in the final step, and the possibility of further extending this reaction to other heteroaromatic systems constitute undoubted advantages of the new transformation, especially in the context of the need to develop low-cost manufacturing methods in organoelectronic materials chemistry.

Experimental Section

General: The ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded by using a Bruker AV 200 spectrometer. The mass spectra of pure compounds were obtained by using a Finigan Mat 95 spectrometer. Melting points were determined by using Boetius apparatus. UV/Vis absorption spectra were obtained by using a Specord S600 diode array spectrophotometer with 5 cm cuvettes. RT excitation and emission spectra were acquired by using a Perkin–Elmer LS50 luminescence spectrometer. Quantum yields were calculated by using quinine sulfate dihydrate in 0.1 N $HClO_4$ as the standard reference material ($\Phi=0.59$).[25] Column chromatography was performed on Merck silica gel (F_{254} 60, 270–400 mesh). Organic solvents were purified by standard procedures.

2-Bromo-3-(1,3-dioxolan-2-yl)pyridine 1: *p*-TsOH (0.4 g) and ethylene glycol (0.6 mL) were added to a solution of 2-bromo-3-pyridinecarboxaldehyde (1 g, 5.38 mmol) in benzene (50 mL). The resulting mixture was heated at reflux for 4 h with a Dean–Stark trap for the azeotropic removal of water. After evaporation of the solvent, the residue was diluted with ethyl acetate (100 mL) and washed with water (50 mL), $NaHCO_3$ (50 mL), and again with water (50 mL). The organic layer was dried ($MgSO_4$) and then filtered. The solvent was removed under vacuum to leave colorless needles (yield 92%, 1.14 g). M.p. 50–51 °C (lit. 49–50 °C[16,17]); ^1H NMR (C_6D_6, 200 MHz): $\delta=3.35$–3.54 (m, 4H;

OCH_2CH_2O), 5.97 (s, 1H; OCHO), 6.50–6.56 (m, 1H; Py-H), 7.55–7.59 (m, 1H; Py-H), 7.94–7.97 ppm (m, 1H; Py-H); ^{13}C NMR (C_6D_6, 50 MHz): $\delta = 66.03$ (s, OCH_2CH_2O), 102.65 (s, OCHO), 123.38 (s, C_{Py}-H), 135.36 (s, C_{Py}-$CHOCH_2CH_2O$), 136.92 (s, C_{Py}-H), 143.77 (s, C_{Py}-Br), 151.22 ppm (s, C_{Py}-H); MS (CI, isobutane): *m/z*: 230 $[M+1]^+$ (^{79}Br) (100); 232 $[M+1]^+$ (^{81}Br) (98); HRMS (EI, 70 eV): *m/z* calcd for $C_8H_8NBrO_2$: 228.973851; found: 228.973730.

General procedure for the synthesis of diaryl methanols 3, 7, and 10: 1,3-Dioxolane **2** or **6** (1 mmol) was dissolved in dry THF (8 mL) at −78 °C, then *n*BuLi in hexanes (2.3 M, 1.1 mmol) was added. The resulting mixture was stirred for 15 min under argon. The corresponding aldehyde (3,4,5-trimethoxybenzaldehyde or *N*-methylindole-2-carboxaldehyde; 1.2 mmol) in dry THF (3 mL) was added at −78 °C and stirring was continued for 3 h while the temperature was raised from −78 °C to RT. Saturated aqueous NH_4Cl was added and the solvent was evaporated. The residue was diluted with ethyl acetate (50 mL) and washed with water (3×20 mL). The organic layer was dried ($MgSO_4$) and then filtered. The solvent was removed under vacuum to give **3** or **7** as a crude product that was purified by using column chromatography (*n*-hexane/ethyl acetate 2:1).

[3-(1,3-Dioxolan-2-yl)pyridin-2-yl](3,4,4-trimethoxyphenyl) methanol ***3***: Yield: 69 %. M.p.72–74 °C; ^1H NMR (C_6D_6, 200 MHz): $\delta = 3.20$–3.45 (m, 5H; OCH_2CH_2O, OH), 3.35 (s, 6H; *m*-$Ar(OCH_3)_2$), 3.80 (s, 3H; *p*-$ArOCH_3$), 5.78 (s, 1H; OCHO), 6.43 (s, 1H; C*H*OH), 6,76 (s, 2H; *o*-Ar-H), 6.67–6.71 (m, 1H; Py-H), 7.76–7.79 (m, 1H; Py-H), 8.25–8.29 ppm (m, 1H; Py-H); ^{13}C NMR (C_6D_6, 50 MHz): $\delta = 56.47$ (s, *m*-$Ar(OCH_3)_2$), 61.11 (s, *p*-$ArOCH_3$), 65.63 (s, OCH_2CH_2O), 73.25 (s, CHOH), 100.65 (s, OCHO), 106.69 (s, 2×*o*-C_{Ar}-H), 123.18 (s, C_{Py}-H), 131.98 (s, C_{Pyr}-$CHOCH_2CH_2O$), 135.52 (s, C_{Py}-H), 139.77 (s, *p*-C_{Ar}-OCH_3), 148.91 (s, C_{Py}-H), 154 (s, 2x *m*-C_{Ar}-OCH_3), 160.51 ppm (s, C_{Py}-CHOH); MS (CI, isobutane): *m/z*: 348 $[M+1]^+$ (100); 330 $[M+1-H_2O]^+$ (33); 286 $[M+1-H_2O-CH_2CH_2O]^+$ (11); HRMS (EI, 70 eV); *m/z* calcd for $C_{18}H_{21}NO_6$: 347.136887; found: 347.136830.

*[6-(1,3-Dioxolan-2-yl)-1,3-benzodioxol-5-yl](1-methyl-1*H*-indol-2-yl)methanol* ***7***: Yield: 66 %. M.p. 137–139 °C; ^1H NMR (C_6D_6, 200 MHz): $\delta =$ 2.64 (d, $^3J(H,H) = 4.25$ Hz, 1H; OH), 3.18 (s, 3H; CH_3), 3.21–3.53 (m, 4H; OCH_2CH_2O), 5.25 (s, 2H; OCH_2O), 5.89 (s, 1H; OCHO), 6.28 (d, $^3J(H,H) = 4.25$ Hz, 1H; CHOH), 6.65 (s, 1H; Ind-H), 6.99 (s, 1H; Ar-H), 7.02–7.06 (m, 1H; Ind-H), 7.15–7.27 (m, 2H; Ind-H), 7.72 (s, 1H; Ar-H), 7.63–7.68 ppm (m, 1H; Ind-H); ^{13}C NMR (C_6D_6, 50 MHz): $\delta = 30.51$ (s, CH_3), 65.56 (s, OCH_2CH_2O), 67.17 (s, CHOH), 102.03 (s, OCH_2O), 102.55 (s, OCHO), 108.15 (s, C_{Ar}-H), 109.48 (s, C_{Ar}-H), 109.99 (s, C_{Ind}-H), 120.60 (s, C_{Ind}-H), 121.94 (s, C_{Ind}-H), 122.51 (s, C_{Ind}-H), 130.36 (s, *C*-$CHOCH_2CH_2O$), 136.65 (s, *C*-CHOH), 139.34 (s, MeN-C_{Ar}), 141.95 (s, C_{Ar}–NMe), 148.37 (s, OCH_2O-*C*), 149.53 ppm (s, *C*-OCH_2O); MS (CI, isobutane): *m/z*: 354 $[M+1]^+$ (100); 336 $[M+1-H_2O]^+$ (73); 292 $[M+1-H_2O-CH_2CH_2O]^+$ (30); HRMS (EI, 70 eV): Calcd for $C_{20}H_{19}NO_5$ 353.126323; Found 353.126200.

*[3-(1,3-Dioxolan-2-yl)pyridin-2-yl](1-methyl-1*H*-indol-2-yl) methanol* ***10***: Yield: 59 %, yellow oil. ^1H NMR (C_6D_6, 200 MHz): $\delta = 3.08$–3.37 (m, 5H; OCH_2CH_2O, OH), 3.55 (s, 3H; CH_3), 5.74 (s, 1H; OCHO), 5.80 (s, 1H; ArH) 5.89 (s, 1H; C*H*OH), 6.61–6.76 (m, 2H; ArH), 7.04–7.21 (m, 2H; ArH), 7.47–7.52 (m, 1H; ArH), 7.77–7.82 (m, 1H; ArH), 8.24–8.27 ppm (m, 1H; ArH); ^{13}C NMR (C_6D_6, 50 MHz): $\delta = 30.66$ (s, CH_3), 65.47 (s, OCH_2CH_2O), 65.59 (s, OCH_2CH_2O), 66.49 (s, CHOH), 100.62 (s, C_{Ar}-H), 102.12 (s, OCHO), 110.26 (s, C_{Ar}-H), 120.53 (s, C_{Ar}-H), 121.91 (s, C_{Ar}-H), 122.78 (s, C_{Ar}-H), 123.46 (s C_{Ar}-H,), 132.61 (s, *C*-$CHOCH_2CH_2O$), 135.13 (s, C_{Ar}-H), 139.38 (s, MeN-C_{Ar}), 141.91 (s, C_{Ar} -NMe), 148.59 (s, C_{Ar}-H), 158.08 ppm (s, *C*-CHOH); MS (EI, 70 eV): *m/z*: 310 $[M]^+$ (85); 292 $[M-H_2O]^+$ (51); 249 $[M-OCH_2CH_2OH]^+$ (39); HRMS (EI, 70 eV): *m/z* calcd for $C_{18}H_{18}N_2O_3$: 310.131742; found: 310.132160.

General procedure for the synthesis of *O*-benzyl-protected diaryl methanols 4, 8, and 11: A solution of the corresponding diaryl methanol **3** or **7** (1 mmol) in THF (5 mL) was added to a suspension of NaH (1.1 mmol, 60 % in mineral oil) and KI (0.05 mmol) in dry THF (3 mL) at RT. The resulting mixture was stirred for 30 min, then benzyl bromide (1.5 mmol) was added. Stirring was continued for 18 h at the same temperature. After evaporation of the solvent, the residue was diluted with ethyl acetate and washed with water (3×20 mL). The organic layer was dried ($MgSO_4$) and then filtered. The solvent was removed to give the crude product, which was purified by using column chromatography (hexane/acetone 2:1).

2-[(Benzyloxy)(3,4,5-trimethoxyphenyl)methyl]-3-(1,3-dioxolan-2-yl)pyridine ***4***: Yield: 83 %, yellow oil. ^1H NMR (C_6D_6, 200 MHz): $\delta = 3.33$–3.54 (m, 4H; OCH_2CH_2O), 3.44 (s, 6H; *m*-$ArO(CH_3)_2$), 3.82 (s, 3H; *p*-$ArOCH_3$), 4.61 (d, $^2J(H,H) = 11.82$ Hz, $1H_A$; CH_AH_BPh), 4.71 (d, $^2J(H,H) = 11.82$ Hz, $1H_B$; CH_AH_BPh), 6.24 (s, 1H; OCHO), 6.37 (s, 1H; CHOBn), 6.70–6.76 (m, 1H; Pyr-H), 7.07 (s, 2H; *o*-Ar-H), 7.12–7.14 (m, 2H; Ar-H), 7.16 (s, 2H; Ar-H), 7.39–7.46 (m, 1H; Ar-H), 7.86–7.91 (m, 1H; Py-H), 8.48–8.51 ppm (m, 1H; Py-H); ^{13}C NMR (C_6D_6, 125 MHz): $\delta = 56.44$ (s, *m*-$Ar(OCH_3)_2$), 61.09 (s, *p*-$ArOCH_3$), 65.84 (s, OCH_2CH_2O), 65.89 (s, OCH_2CH_2O), 72.18 (s, OCHOH), 83.69 (s, OCH_2Ph), 100.89 (s, OCHO), 106.56 (s, 2×*o*-C_{Ar}-H), 123.34 (s, C_{Py}-H), 128.51 (s, *p*-Ph), 128.97 (s, *m*-Ph), 129.22 (s, *o*-Ph), 133.41 (s, C_{Ar}-$CHOCH_2CH_2O$), 136.24 (s, C_{Ar}-CHOBn), 137.13 (s, *p*-C_{Ar}-OCH_3), 139.73 (s, *ipso*-Ph), 139.73 (s, *ipso*-C_{Ar}), 150.65 (s, C_{Py}-H), 154.76 (s, 2×*m*-C_{Ar}-OCH_3), 159.92 ppm (s, C_{Ar}-CHOBn); MS (CI, isobutane): *m/z*: 438 $[M+1]^+$ (100); 376 $[M+1-HOCH_2CH_2OH]^+$ (12); 286 $[M+1-PhCH_2OH]^+$ (33); HRMS (EI, 70 eV): *m/z* calcd for $C_{25}H_{27}NO_6$: 437.183837; found: 437.184430.

*2-[(Benzyloxy)[6-(1,3-dioxolan-2-yl)-1,3-benzodioxol-5-yl]methyl]-1-methyl-1*H*-indole* ***8***: Yield: 77 %, yellow oil. ^1H NMR (C_6D_6, 200 MHz): $\delta = 3.31$ (s, 3H; CH_3), 3.19–3.55 (m, 4H; OCH_2CH_2O), 4.45 (d, $^3J(H,H) =$ 11.47 Hz, 1H; OCH_2Ph), 4.61 (d, $^3J(H,H) = 11.47$ Hz, 1H; OCH_2Ph), 5.32 (s, 2H; OCH_2O), 6.02 (s, 1H; OCHO), 6.15 (s, CH, CHOBn), 6.65 (s, 1H; ArH), 6.38 (s, 1H; ArH), 7.04–7.09 (m, 1H; ArH), 7.12 (s, 1H; ArH), 7.19–7.31 (m, 4H; ArH), 7.37 (s, 1H; ArH), 7.51 (s, 1H; ArH), 7.57–7.87 ppm (m, 1H; ArH); ^{13}C NMR (C_6D_6, 50 MHz): $\delta = 31.75$ (s, CH_3), 64.36 (s, OCH_2CH_2O), 77.34 (s, CHOBn), 98.21 (s, OCH_2Ph), 101.62 (s, OCH_2O), 105.28 (s, OCHO), 109.30 (s, C_{Ar}-H), 115.14 (s, C_{Ar}-H), 120.00 (s, C_{Ar}-H), 120.53 (s, C_{Ar}-H), 121.49 (s, C_{Ar}-H), 124.32 (s, C_{Ar}-H), 125.44 (s, C_{Ar}-H), 126.90 (s, *p*-Ph), 127.15 (s, *m*-Ph), 127.70 (s, *o*-Ph), 129.49 (s, *C*-$CHOCH_2CH_2O$), 138.39 (s, *ipso*-Ph), 138.57 (s, *ipso*-C_{Ar}), 144.87 (s, C_{Ar}-NMe), 147.14 (s, OCH_2O-*C*), 149.01 (s, *C*-OCH_2O), 152.90 ppm (s, C_{Ar}-CHOBn); MS (CI, isobutane): *m/z*: 444 $[M+1]^+$ (56); 336 $[M+1-PhCH_2OH]^+$ (100); HR MS (EI, 70 eV): *m/z* calcd for $C_{27}H_{25}NO_5$: 443.173273; found: 443.173720.

*2-[Benzyloxy-(3-[1,3]dioxolan-2-yl-pyridin-2-yl)-methyl]-1-methyl-1*H*-indole* ***11***: Yield: 99 %, yellow oil. ^1H NMR (C_6D_6, 200 MHz): $\delta = 3.39$ (s, 3H; CH_3), 3.21–3.54 (m, 4H; OCH_2CH_2O), 4.46 (d, $^3J(H,H) = 11.06$ Hz, $1H_A$; OCH_AH_BPh), 4.66 (d, $^3J(H,H) = 11.06$ Hz, $1H_B$; OCH_AH_BPh), 6.35 (s, 1H; OCHO), 6.47 (s, CH, CHOBn), 6.54 (s, 1H; ArH), 6.78–6.84 (m, 1H; ArH), 7.06–7.22 (m, 5H; ArH), 7.32–7.36 (m, 2H; ArH), 7.55–7.59 (m, 1H; ArH), 7.99–8.03 (m, 1H; ArH), 8.42–8.45 ppm (m, 1H; ArH); ^{13}C NMR (C_6D_6, 50 MHz): $\delta = 31.05$ (s, CH_3), 65.83 (s, OCH_2CH_2O), 65.90 (s, OCH_2CH_2O), 72.43 (s, CHOBn), 80.18 (s, OCH_2Ph), 100.43 (s, C_{Ar}-H), 104.47 (s, OCHO), 110.20 (s, C_{Ar}-H), 120.47 (s, C_{Ar}-H), 122.03 (s, C_{Ar}-H), 122.81 (s, C_{Ar}-H), 123.93 (s, C_{Ar}-H), 129.49 (s, C_{PhH}), 134.65 (s, *C*-$CHOCH_2CH_2O$), 136.78 (s, C_{Ar}-H), 138.64 (s, *ipso*-C_{Ar}), 138.19 (s, MeN-C_{Ar}), 139.65 (s, C_{Ar}-NMe), 147.14 (s, OCH_2O-*C*), 150.43 (s, $C_{Ar}H$), 158.01 ppm (s, C_{Ar}-CHOBn); MS (EI, 70 eV): *m/z*: 400 $[M]^+$ (30); 292 $[M-PhCH_2OH]^+$ (100); HRMS (EI, 70 eV): *m/z* calcd for $C_{25}H_{24}N_2O_3$: 400.182715; found: 400.17910.

10-(Benzyloxy)-6,7,8-trimethoxybenzo[*g*]quinoline 5: Diaryl methanol **4** (0.244 g, 0563 mmol) was dissolved in acetone (30 mL), then aqueous HCl (1 N, 17 mL) was added. The mixture was stirred at ambient temperature for 5 d, then extracted with ethyl acetate (50 mL) before the organic layer was washed with water (20 mL), aqueous $NaHCO_3$ (20 mL), and again with water (20 mL), then dried ($MgSO_4$). The solvent was removed and the product was purified by using column chromatography (petroleum ether/acetone 2:1) to give the pure product (yield 53 %, 0.113 g). ^1H NMR (C_6D_6, 200 MHz): $\delta = 3.86$ (s, 3H; OCH_3), 4.02 (s, 3H; OCH_3), 4.13 (s, 3H; OCH_3), 5.63 (s, 2H; OCH_2Ph), 7.31–7.39 (m, 5H; Ph), 7.57–7.61 (m, 2H; Ar-H), 8.28–8.34 (m, 2H; Ar-H), 8.98–9.01 ppm (m, 2H; Ar-H); ^{13}C NMR (C_6D_6, 50 MHz): $\delta = 55.64$ (s, OCH_3), 61.13 (s, OCH_3), 61.34 (s, OCH_3), 77.53 (s, OCH_2Ph), 96.42 (s, C_{Ar}-H), 115.68 (s, C_{Ar}-H), 119.72 (s, C_{Ar}-H), 125.09 (s, C_{Ar}-OMe), 125.36 (s, C_{Ar}-OMe), 125.80 (s,

C_{Ar}-OMe), 127.91 (s, *p*-Ph), 128.35 (s, 2×*o*-Ph), 128.60 (s, 2×*m*-Ph), 136.90 (s, C_{Ar}-H), 137.55 (s, *ipso*-Ph), 138.20 (s, C), 141.08 (s, C), 146.72 (s, C), 149.57 (s, C), 149.88 (s, C-H), 153.27 ppm (s, *C*-OCH_2Ph); MS (CI, isobutane): *m/z*: 376 $[M+1]^+$ (100); HRMS (EI, 70 eV): *m/z* calcd for $C_{23}H_{19}NO_4$: 375.147058; found: 375.145820.

5-(Benzyloxy)-6-methyl-6*H*-[1,3]benzodioxolo[3,2-*b*]carbazole 9: Diaryl methanol **8** (0.062 g, 0.140 mmol) was dissolved in acetone (4 mL) and then aqueous HCl (1 N, 2 mL) was added. The mixture was stirred at ambient temperature for 0.5 h, then extracted with ethyl acetate (20 mL) before the organic layer was washed with water (5 mL), aqueous $NaHCO_3$ (5 mL), and again with water (5 mL), and then dried ($MgSO_4$). The solvent was removed to give the pure product (yield 98%, 0.052 g). M.p. 154–155 °C; ^{1}H NMR (C_6D_6, 200 MHz): δ = 3.59 (s, 3H; CH_3), 4.80 (s, 2H; OCH_2Ph), 5.39 (s, 2H; OCH_2O), 6.99–7.03 (m, 2H; Ar-H), 7.13–7.22 (m, 4H; Ar-H), 7.24–7.43 (m, 3H; Ar-H), 8.08–8.11 (m, 2H; Ar-H), 7.83 ppm (s, 1H; Ar-H); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 4.10 (s, 3H; CH_3), 5.14 (s, 2H; OCH_2Ph), 6.05 (s, 2H; OCH_2O), 7.24–7.35 (m, 4H; Ar-H), 7.44–7.62 (m, 7H; Ar-H), 8.11–8.18 ppm (m, 2H; Ar-H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 31.32 (s, *C*H_3), 76.67 (s, O*C*H_2Ph), 96.94 (s, O*C*H_2O), 96.93 (s, C_{Ar}-H), 100.87 (s, C_{Ar}-H), 104.00 (s, C_{Ar}-H), 108.20 (s, C_{Ar}-H),113.83 (s, C_{Ar}-H), 118.90 (s, C_{Ar}-H), 120.32 (s, C_{Ar}-H), 122.97 (s, C), 124.01 (s, C), 125.74 (s, C), 125.74 (s, C), 126.71 (s, C_{Ar}-H), 127.59 (s, 2×*o*-Ph), 128.14 (s, *p*-C_6H_5), 128.67 (s, 2×*m*-C_6H_4), 131.34 (s, *ipso*-Ph), 137.08 (s, C), 137.17 (s, C), 143.61 (s, C), 145.76 (s, C), 147.62 ppm (s, C); MS (CI, isobutane): *m/z*: 382 $[M+1]^+$ (100); 192 $[M+1-CH_2Ph]^+$ (58); HRMS (EI, 70 eV): *m/z* calcd for $C_{25}H_{19}NO_3$: 381.136493; found: 381.136260.

11-Benzyloxy-10-methyl-10*H*-pyrido[2,3-*b*]carbazole 12: Diaryl methanol **11** (0.062 g, 0.140 mmol) was dissolved in acetone (3 mL), then aqueous HCl (1 N, 1.5 mL) was added. The mixture was stirred at ambient temperature for 3 d, then extracted with ethyl acetate (20 mL) before the organic layer was washed with water (5 mL), aqueous $NaHCO_3$ (5 mL), and again with water (5 mL), and then dried ($MgSO_4$). The solvent was removed and the product was purified by using column chromatography (petroleum ether/acetone 2:1) to give pure **12** (yield 34%, 0.01 g). ^{1}H NMR (C_6D_6, 200 MHz): δ = 3.62 (s, 3H; CH_3), 5.69 (s, 2H; OCH_2Ph), 6.89–6.95 (m, 2H; ArH), 7.13–7.25 (m, 4H; ArH), 7.36–7.43 (m, 1H; ArH), 7.61–7.65 (m, 2H; ArH), 7.91–7.96 (m, 1H; ArH), 8.03 (s, 1H; ArH), 8.05–8.09 (m, 1H; ArH), 8.90–8.94 ppm (m, 1H; ArH); ^{13}C NMR (C_6D_6, 50 MHz): δ = 32.07 (s, CH_3), 78.13 (s, O*C*H_2Ph), 102.36 (s, C_{Ar}-H), 109.44 (s, C_{Ar}-H), 114.32 (s, C_{Ar}-H), 118.92 (s, C_{Ar}-H), 120.15 (s, C_{Ar}-H), 121.84 (s, C_{Ar}-H), 123.64 (s, C_{Ar}-H), 135.42 (s, C), 137.05 (s, C_{Ar}-H), 139.43 (s, C_{Ar}-NMe), 145.46 (s, C), 149.30 (s, C_{Ar}H), 155.75 (s, C), 161.26 ppm (s, *C*); MS (EI, 70 eV): *m/z*: 338 $[M]^+$ (30); 247 $[M-CH_2Ph]^+$ (100); HRMS (EI, 70 eV): *m/z* calcd for $C_{23}H_{18}N_2O$: 338.141913; found: 338.140810.

5-[(4-Bromomethyl)benzyloxy]-6-methyl-6*H*-[1,3]benzodioxolo[3,2-*b*]carbazole 13: A solution of diaryl methanol **7** (0.666 g, 1.894 mmol) in THF (7 mL) was added to a suspension of NaH (0.1 g, 4.168 mmol; 60% in mineral oil) in dry THF (8 mL) at RT. The resulting mixture was stirred for 30 min, then α,α′-dibromo-*p*-xylene (0.499 g, 1.894 mmol) was added and stirring was continued for 18 h at the same temperature. After evaporation of the solvent, the residue was diluted with ethyl acetate and washed with water (3×20 mL). The organic layer was dried ($MgSO_4$) and then filtered. The solvent was removed to give the crude product, which was purified by using column chromatography (petroleum oil/acetone 2:1) to give **13** as a dark solid (yield 39%, 0.148 g). ^{1}H NMR (C_6D_6, 200 MHz): δ = 3.56 (s, 3H; N-CH_3), 4.01 (s, 2H; CH_2Br), 4.72 (s, 2H; OCH_2Ph), 5.38 (s, 2H; OCH_2O), 6.82 (s, 1H; Ar-H), 7.01–7.44 (m, 5H; ArH), 7.81 (s, 1H; Ar-H), 8.10–8.12 ppm (m, 2H; Ar-H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 31.73 (s, CH_3), 76.76 (s, OCH_2Ph), 98.05 (s, OCH_2O), 101.67 (s, $C_{Ar}H$), 105.30 (s, $C_{Ar}H$), 109.31 (s, $C_{Ar}H$), 115.21 (s, $C_{Ar}H$), 120.07 (s, $C_{Ar}H$), 121.51 (s, $C_{Ar}H$); 124.29 (s, $C_{Ar}H$), 125.33 (s, $C_{Ar}H$), 127.13 (s, $C_{Ar}H$), 130.18 (s, C), 132.49 (s, C), 138.50 (s, $C_{Ar}H$), 144.84 (s, C), 147.16 (s, C); 149.04 ppm (s, C_{Ar}); MS (CI, isobutane): *m/z*: 474 $[M(Br^{79})+1]^+$ (5); 476 $[M(Br^{81})+1]^+$ (4); 396 $[M+1-Br]^+$ (10); 306 $[M+1-BrCH_2Ph]^+$ (30); 292 $[M+1-BrCH_2PhCH_2]^+$ (100); HRMS (EI, 70 eV): *m/z* calcd for $C_{26}H_{20}NO_3Br$: 473.062666; found: 473.062320.

Crystallographic data for 9: $C_{25}H_{19}NO_3$; M_r = 418.43; triclinic; $P\bar{1}$; *a* = 11.2834(7), *b* = 11.5421(7), *c* = 17.5873(11) Å; α = 71.108(5), β = 79.767(5), γ = 60.877(6)°; *V* = 1892.6(2) Å^3; *Z* = 4; ρ_{calcd} = 1.339 g cm^{-3}; *F*(000) = 800; crystal size 0.33×0.25×0.12 mm. Diffraction data were collected at 290(2) K by using an Xcalibur 3 diffractometer equipped with a CCD detector ($Mo_{K\alpha}$ radiation, θ range 2.38–25.19°). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with SHELX-97.[26] Carbon, nitrogen, and oxygen atoms were refined anisotropically, all aromatic hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms with C–H distances of 0.93 Å and with U_{iso} values of 1.2U_{eq}(C); all other H atoms were located in difference maps and refined isotropically to give C–H distances in the range 0.92(2)–1.06(2) Å. *R* = 0.040, *wR* = 0.1040, *S* = 1.09 for 4352 unique reflections with $I > 2\sigma(I)$ and 566 parameters.

CCDC-688739 (**9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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