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Synthesis and Properties of 5,7-Dihydropyrido[3,2-*b*:5,6-*b*′]diindoles

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5,7-Dihydropyrido[3,2-*b*:5,6-*b*′]diindoles were prepared by a highly efficient two-step synthesis that involved a site-selective Suzuki coupling reaction of 2,3,5,6-tetrabromopyridine and a subsequent Pd-catalyzed cyclization that proceeded through a twofold C–N coupling reaction with aromatic and aliphatic amines. With the exception of the parent molecule, which was described in a patent without any characterization data, the 5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindoles are a new chemical entity. Their electrochemical and photochemical properties were investigated. These pyridodiindoles show promising fluorescence properties with good quantum yields and interesting electrochemical behavior. The optical and electronical properties were analyzed and explained by using DFT calculations.

Introduction

Carbolines (pyridoindoles) and their derivatives are used as electronic transport units in host materials.[1] The replacement of a carbazole unit with a carboline moiety improves electron mobility in these materials, and it is assumed that the carbazole ring accelerates the electron-accepting properties because of its electron-deficient ring system.[1a,1b,1e,2] The combination of the carbazole and carboline units promotes the triplet energy, which results in high quantum efficiency. Materials that contain a carboline moiety have been studied for the development of new bipolar host materials. In 2013, Lee et al. synthesized bi- and terphenyl derivatives, which were substituted by carbazole and carboline moieties (through the nitrogen atom). These compounds show a 30% external quantum efficiency and high triplet energy (2.90 eV) in blue phosphorescence organic light-emitting diodes.[1b,2] Kwon et al. prepared new compounds that contained three α-carbolinyl substituents attached to a triphenylamine moiety, which have a longer lifetime than related derivatives with three carbazole moieties.[1a] Recently, Lee et al. showed that related α- and β-carbolines possess a higher quantum efficiency and a higher triplet energy than isomeric γ-carbolines.[1f] The quantum efficiency reached 22.1%.[1c]

On the basis of their optical properties, organic materials that contain acene and heteroacene core structures have found many applications in organic photovoltaic cells,[3] organic light-emitting diodes (OLEDs),[4] and, especially, in organic field-effect transitors (OFETs).[5] In this context, pentacene and its heterocyclic derivatives have received much attention in current research because of their excellent charge mobility. In fact, pentacene-based OFETs show very high charge mobilities in the range of 5–40 $cm^2/(V·s)$.[5b] However, pentacene derivatives are known to be easily oxidized by air,[5c] which results in limitations to their practical applications. The replacement of the heteroatoms in pentacene serves an important role in tuning the electronic properties, solubility, stability, and molecular packing.[5] For example, indolocarbazoles,[6] pentathienoacenes,[7] dibenzothienopyrroles,[8] tetraazapentacenes,[9] N-heteropentacenes,[5] and thiophene–benzene-annulated pentacenes[5,10] provide excellent OFET applications.

Because of the importance of both N-heteropentacenes and carbolines in the field of organic materials, we were interested in the development of a new class of N-heteropentacenes (5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindoles), which combines the indole and δ-carboline core structures. Our approach to 5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindoles involved the Pd-catalyzed twofold C–N coupling of 3,5-dibromo-2,6-bis(2-bromophenyl)pyridine with 2 equiv. of the corresponding amine. The Chida, Nozaki, and Verkade

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groups successfully used this strategy to prepare carbazoles from 2,2′-dihalobiphenyl derivatives and amines (see Figure 1).[11] Very recently, we also applied this method to the synthesis of both 3,9′- and 2,9′-bis(carbazole)s, which are present in many natural alkaloids and organic materials.[12a] We previously reported the synthesis of diindolo[3,2-*b*:4,5-*b*′]-thiophenes and indolo[2,3-*b*]quinoxalines on the basis of the cyclization of *o*-bromophenylboronic acid with tetrabromothiophene and 2,3-dibromoquinoxaline, respectively.[12b,12c] Herein, we report a new and efficient synthesis of 5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindoles by what is, to the best of our knowledge, the first site-selective Suzuki reaction of 2,3,5,6-tetrabromopyridine with *ortho*-(bromophenyl)boronic acid followed by a cyclization that involves a twofold palladium-catalyzed C–N coupling reaction with an amine. The products of this synthetic path exhibit excellent fluorescence properties with good quantum yields. The photophysical and electronic properties were studied in detail experimentally and by using DFT calculations.

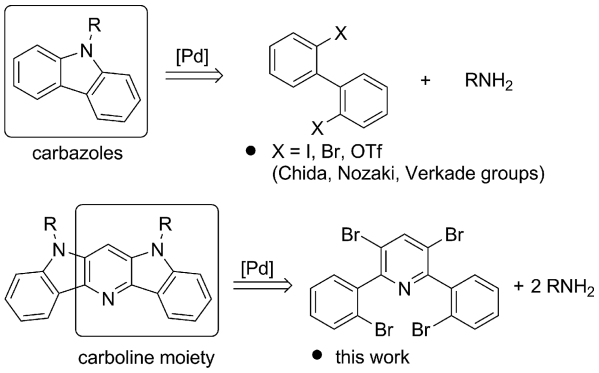

Figure 1. Retrosynthetic analysis of 5,7-dihydropyrido[3,2-*b*:5,6-*b*′]-diindoles (OTf = trifluoromethanesulfonate).

The 5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole core structure is rather new, and only the *N*-hydrogen-substituted parent molecule, 5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole, has been reported so far. This compound was reported in a Korean patent and was prepared by using a different and more complicated synthetic method.[13] However, the compound characterization and details of the synthesis and physical properties were not provided, and, therefore, the patent is of limited use to the chemical community.

Results and Discussion

2,3,5,6-Tetrabromopyridine (**1**) was prepared from 2,6-diaminopyridine according to a procedure by Flowers.[14] The Suzuki–Miyaura reaction of 2,3,5,6-tetrabromopyridine with 2.2 equiv. of *o*-bromophenylboronic acid (**2**) in the presence of 5 mol-% of $Pd(PPh_3)_4$ gave adduct **3** in 80% isolated yield. The reaction proceeded with excellent site selectivity. The Pd-catalyzed cyclization of **3** with amines **4a**–**4t** by using the twofold C–N coupling reaction afforded the desired 5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindoles in good to excellent yields (see Figure 2).

To optimize the reaction, we started with the annulation reaction of adduct **3** with *tert*-butylaniline (**4c**) by using 1,4-dioxane as an internal standard for the ^{1}H NMR analysis (see Table 1). The important parameters to examine included the ligand, the precatalyst, the solvent, and the reaction temperature. The employment of monodentate phosphine ligands such as XPhos [2-(dicyclohexylphosphino)-2′,4′,6′-triisopropylbiphenyl], Xphos·*t*Bu$_2$, SPhos [2-(dicyclohexylphosphino)-2′,6′-dimethoxybiphenyl], DavePhos [2-(dicyclohexylphosphino)-2′-(dimethylamino)biphenyl], RuPhos [2-(dicyclohexylphosphino)-2′,6′-diisopropoxylbiphenyl], PCy_3·HBF_4 (Cy = cyclohexyl), or P(*t*Bu)$_3$·HBF_4 gave **5c** in unsatisfactory yields (see Figure 3 and Table 1). Finally, we realized that the yields significantly improved by using bidentate phosphine ligands such as BINAP [2,2′-bis(diphenylphosphino)-1,1′-binaphthyl], XantPhos [4,5-bis(diphenylphosphino)-9,9-dimethylxanthene], DPEPhos, dppe [1,2-bis(diphenylphosphino)ethane], or dppf (see Figure 3 and Table 1). Our optimization results show that bidentate ligands with bite angles larger than 90° gave the best yields. For example, product **5c** was isolated in up to 90% yield when dppf was employed as the ligand in combination with Pd_2dba_3 (i.e., method A). The use of $Pd(OAc)_2$ as the palladium source resulted in lower yields. Toluene proved to be the best solvent. The success of BINAP, XantPhos, DPEPhos, dppe, and dppf can be explained by their rigid structure and their bidentate character[15] as well as by the influence of diphosphine back-bond-

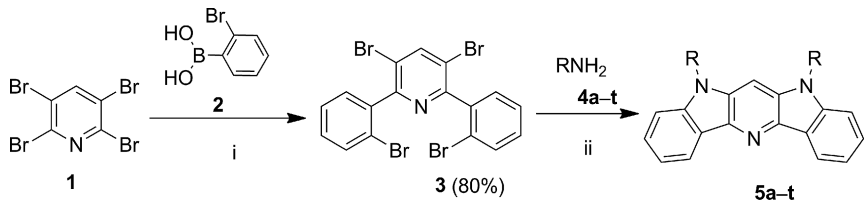

Figure 2. Synthesis of 5,7-disubstituted 5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindoles **5a**–**5t**. Reagents and conditions: (i) **2** (2.2 equiv.), $Pd(PPh_3)_4$ (5 mol-%), NaOH (3 equiv.), tetrahydrofuran (THF), H_2O, 70 °C, 4 h; (ii) **4** (3 equiv.), NaO*t*Bu (6 equiv.), $Pd_2(dba)_3$ (5 mol-%; dba = dibenzylideneacetone), ligand {method A: 10% of 1,1′-bis(diphenylphosphino)ferrocene (dppf); method B: 10% of bis[2-(diphenylphosphino)phenyl] ether (DPEPhos)}, toluene, 100 °C, 7 h.

Table 1. Optimization for the synthesis of **5c**.[a]

Entry	Catalyst	Ligand	Solvent	Time [h]	Temperature [°C]	Yield [%]
1	$Pd_2(dba)_3$	BINAP	toluene	7	100	73
2	$Pd_2(dba)_3$	XantPhos	toluene	7	100	84
3	$Pd_2(dba)_3$	DPEPhos	toluene	7	100	52
4	$Pd_2(dba)_3$	dppe	toluene	7	100	40
5	$Pd_2(dba)_3$	dppf	toluene	7	100	90
6	$Pd_2(dba)_3$	$PCy_3{\cdot}HBF_4$	toluene	7	100	13
7	$Pd_2(dba)_3$	$P(t\text{Bu})_3{\cdot}HBF_4$	toluene	7	100	35
8	$Pd_2(dba)_3$	XPhos	toluene	7	100	31
9	$Pd_2(dba)_3$	XPhos·$t\text{Bu}_2$	toluene	7	100	37
10	$Pd_2(dba)_3$	SPhos	toluene	7	100	12
11	$Pd_2(dba)_3$	DavePhos	toluene	7	100	45
12	$Pd_2(dba)_3$	RuPhos	toluene	7	100	32
13	$Pd(OAc)_2$	dppf	toluene	7	100	34
14	$Pd_2(dba)_3$	dppf	dioxane	7	100	25
15	$Pd_2(dba)_3$	dppf	DMF[b]	7	100	0
16	$Pd_2(dba)_3$	dppf	toluene	7	110	82
17	$Pd_2(dba)_3$	dppf	toluene	7	80	77

[a] Yield calculated by ^{1}H NMR analysis of the crude product by using 1,4-dioxane as an internal standard. [b] DMF = *N*,*N*-dimethylformamide.

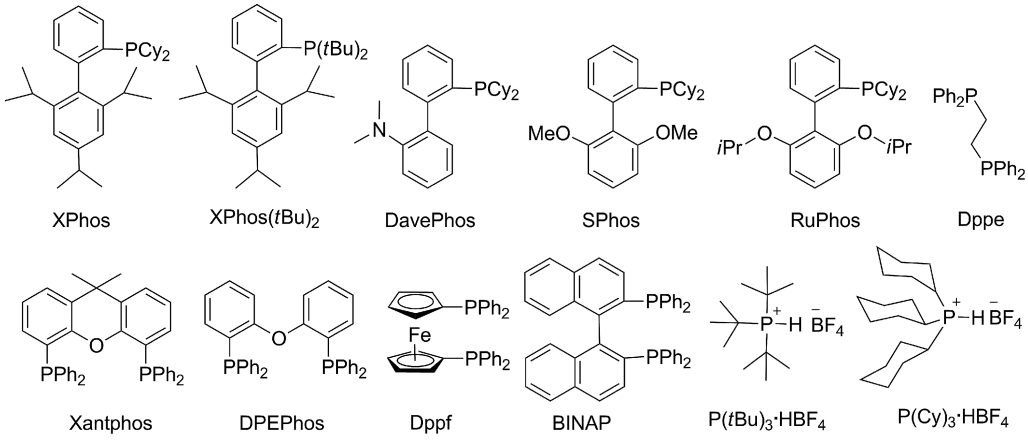

Figure 3. Monodentate and bidentate ligands.

ing.[16] It has been previously reported that the dissociation of one P–Pd bond (arm-off mechanism)[17] leads to an acceleration of the reductive elimination with respect to the β-hydride elimination.

With the optimized conditions (i.e., method A) in hand, we explored the scope of our method. The employment of various aniline derivatives afforded products **5a**–**5h** in good to excellent yields (see Table 2). In general, the yields were higher with electron-rich anilines (more nucleophilic) than with electron-poor ones. 4-(Diethylamino)aniline was an exception to the rule, presumably because of the interaction of the diethylamino group with the catalyst.

However, low yields were obtained when method A was applied to alkylamines. Therefore, further optimization for the synthesis of derivative **5l** was carried out (see Table 3). The best yields of alkyl-substituted products were obtained when DPEPhos was used as the ligand in combination with $Pd_2(dba)_3$ (i.e., method B, see Table 3). Only bidentate ligands catalyzed these reactions, but no correlation between their bite angle and the yields was observed.[17,18] Employ-

Table 2. Synthesis of **5a**–**5t**.

Product **5**	R	Method	Yield [%]
5a	Ph	A	83
5b	4-$t\text{BuC}_6\text{H}_4$	A	84
5c	3,5-$\text{Me}_2\text{C}_6\text{H}_3$	A	85
5d	4-FC_6H_4	A	66
5e	3-$(\text{F}_3\text{C})\text{C}_6\text{H}_4$	A	70
5f	4-$(\text{MeO})\text{C}_6\text{H}_4$	A	93
5g	3,5-$(\text{MeO})_2\text{C}_6\text{H}_3$	A	95
5h	4-$(\text{Et}_2\text{N})\text{C}_6\text{H}_4$	A	69
5i	*n*-C_7H_{15}	B	80
5j	*n*-C_3H_7	B	86
5k	*n*-$\text{C}_{12}\text{H}_{25}$	B	71
5l	allyl	B	84
5m	Bn	B	70
5n	4-$(\text{MeO})\text{C}_6\text{H}_4\text{CH}_2$	B	60
5o	(4-FC_6H_4)CH_2	B	53
5p	3-$(\text{F}_3\text{C})\text{C}_6\text{H}_4\text{CH}_2$	B	52
5q	PhCH_2CH_2	B	75
5r	3,4-$(\text{MeO})_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2$	B	56
5s	$\text{PhCH}_2\text{CH}_2\text{CH}_2$	B	68
5t	cyclohexyl	B	55

Table 3. Optimization for the synthesis of **5l**.[a]

Entry	Catalyst	Ligand	Solvent	Time [h]	Temperature [°C]	Yield [%]
1	$Pd_2(dba)_3$	BINAP	toluene	7	100	11
2	$Pd_2(dba)_3$	XantPhos	toluene	7	100	17
3	$Pd_2(dba)_3$	DPEPhos	toluene	7	100	74
4	$Pd_2(dba)_3$	dppe	toluene	7	100	58
5	$Pd_2(dba)_3$	dppf	toluene	7	100	41
6	$Pd_2(dba)_3$	$PCy_3 \cdot HBF_4$	toluene	7	100	0
7	$Pd_2(dba)_3$	$P(t\text{Bu})_3 \cdot HBF_4$	toluene	7	100	6
8	$Pd_2(dba)_3$	XPhos	toluene	7	100	4
9	$Pd_2(dba)_3$	$XPhos \cdot t\text{Bu}_2$	toluene	7	100	7
10	$Pd_2(dba)_3$	SPhos	toluene	7	100	8
11	$Pd_2(dba)_3$	DavePhos	toluene	7	100	7
12	$Pd_2(dba)_3$	RuPhos	toluene	7	100	5

[a] Yield calculated by ^{1}H NMR analysis of crude product by using 1,4-dioxane as an internal standard.

Table 4. Comparison of bond lengths and bond angles of **5j** on the basis of DFT calculations and X-ray crystal structure analysis.

Bond length	Experimental [Å]	Theoretical [Å]	Bond Angle	Experimental [°]	Theoretical [°]
N-1–C-1	1.335	1.335	N-1–C-1–C-8	124.7	124.3
C-1–C-8	1.427	1.433	N-1–C-1–C-2	128.31	129.08
N-2–C-8	1.387	1.386	N-2–C-2–C-6	128.82	129.37
N-1–C-17	1.339	1.338	N-2–C-7–C-2	109.55	109.30
N-3–C-10	1.380	1.386	C-9–C-8–N-2	130.42	130.12
C-16–C-17	1.444	1.447	C-12–C-10–N-3	108.46	108.85
C-9–C-10	1.387	1.395	N-3–C-11–C-12	128.56	129.30
N-2–C-7	1.392	1.397	N-3–C-11–C-16	109.78	109.31

ment of the $Pd_2(dba)_3$ catalyst allowed for the synthesis of products **5i**–**5t** in good yields (see Table 2).

The structures of **5g** and **5j** were independently confirmed by X-ray crystal structure analyses (see Figures 4 and 5). Moreover, DFT calculations were performed to compare the geometric parameters of the theoretical and experimental structures. The heterocyclic core structure is planar. Some selected calculated bond lengths and bond angles of **5j** (as an example) were compared with those of the crystal structure (see Table 4). A maximum difference of 0.008 Å in bond length was observed between the theoretical and experimental structures, whereas the difference in bond angles reached a maximum of 0.7°. A good correlation was observed between the theoretical and experimental geometric parameters, which illustrates the validity of the computational method applied.

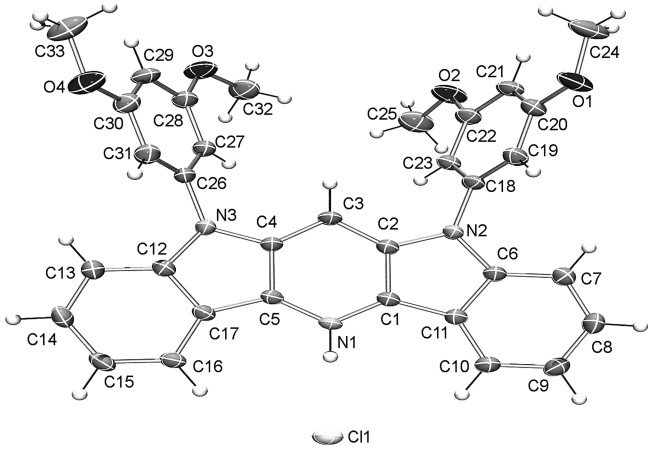

Figure 4. Molecular structure of **5g**.

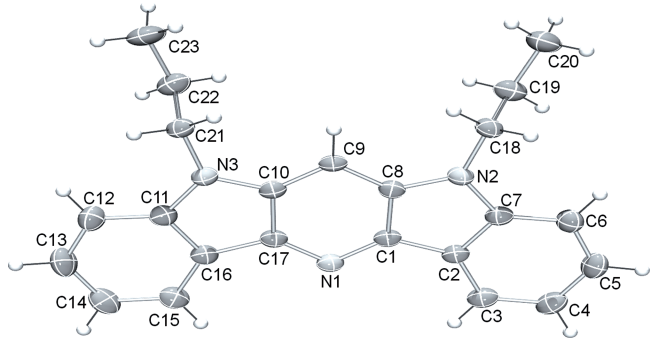

Figure 5. Molecular structure of **5j**.

Electrochemical Properties

The electrochemical properties of some of the δ-carbolines were examined by means of a μAutolab III potentiostat (Ecochemie, Utrecht, The Netherlands) to obtain cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements at three different concentrations (1×10^{-3}, 3×10^{-3}, and 6×10^{-3} mol L^{-1}) in DMF (see Figure 6). These solutions also contained 0.01 mol L^{-1} tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte. All potentials were calibrated with the ferrocene/ferrocenium couple (Fc/Fc^+) as the internal standard. Oxidation and reduction energy levels were determined from the better resolved DPV measurements (see Table 5).

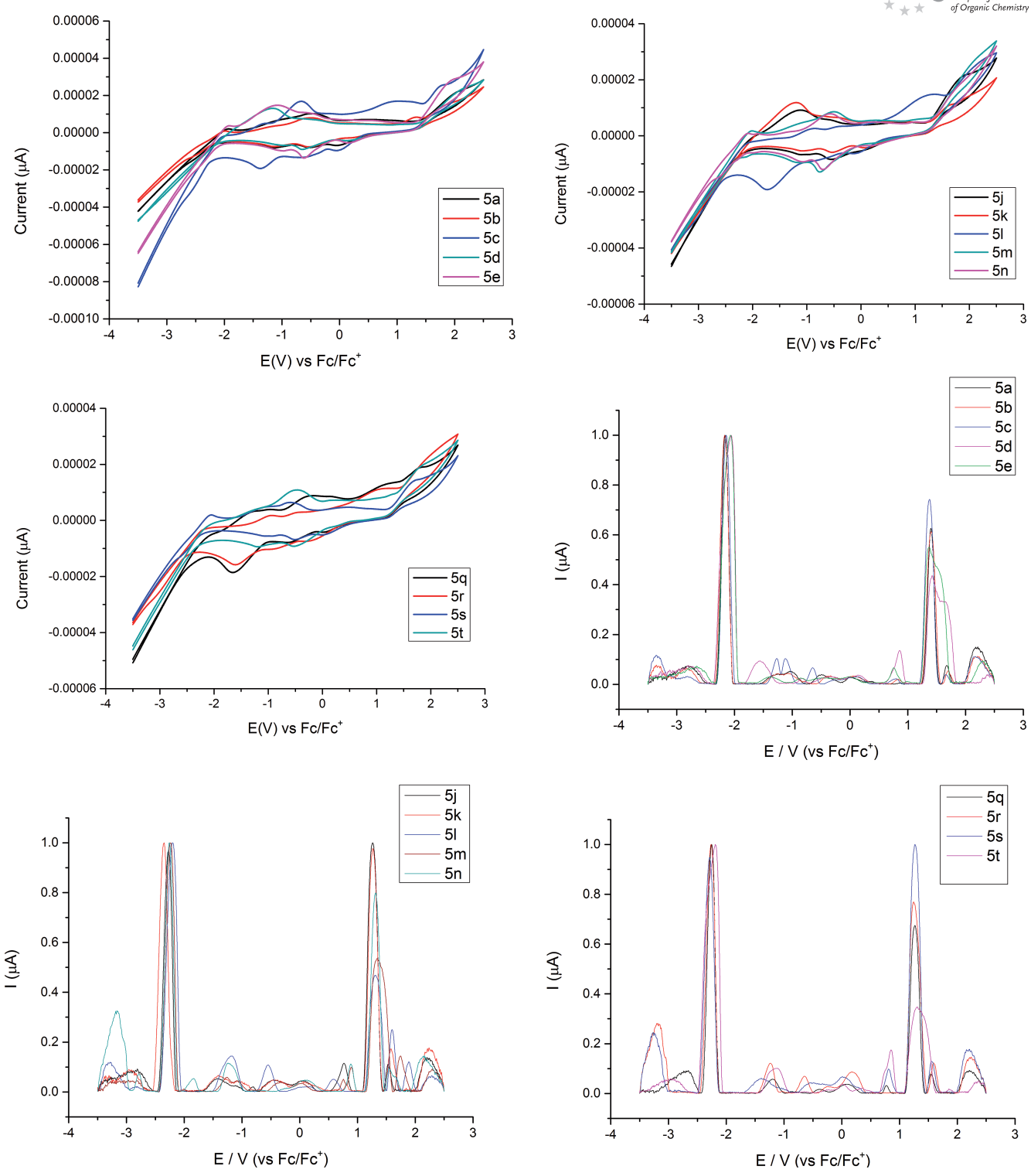

Figure 6. Cyclic voltammograms and differential pulse voltammograms of **5**.

The formal potential of Fc/Fc^+ versus a vacuum was assumed to be –4.8 eV.

Figure 6 depicts voltammograms of **5** with reversible and well-defined redox peaks at around –2.2 V for the formation and reoxidation of the reduced forms of **5**. However, the corresponding redox peaks of the oxidized forms are hardly visible in the cyclic voltammograms because of the overlapping background current. Therefore, the DPV method was employed for the electrochemical investigations, which revealed the redox signals of the oxidized forms of **5** at approximately +1.3 V. The results showed that the band gaps were independent from the structure. It is assumed that the 5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole core plays the key role in the electrochemical properties. Compared to 4,4′-

Table 5. Cyclic voltammetry and differential pulse voltammetry parameters and calculated energy values of **5**.

Compound	$E^{1/2}_{redox}$ [V vs. Fc/Fc$^+$][a]	$E^{1/2}_{ox}$ [V vs. Fc/Fc$^+$][b]	E_{HOMO} [eV][c]	E_{LUMO} [eV][d]	ΔEg [eV][e]	$\Delta Eg_{cal.}$ [eV][f]
5a	–2.167	1.4	–6.250	–2.683	3.567	4.107
5b	–2.171	1.407	–6.207	–2.629	3.578	4.096
5c	–2.143	1.376	–6.176	–2.657	3.519	4.057
5d	–2.056	1.421	–6.221	–2.744	3.477	4.112
5g	–2.07	1.37	–6.170	–2.730	3.440	4.117
5i	–2.268	1.263	–6.063	–2.532	3.531	4.103
5k	–2.35	1.265	–6.065	–2.450	3.615	4.102
5l	–2.197	1.312	–6.112	–2.603	3.509	4.124
5m	–2.003	1.657	–6.457	–2.797	3.660	4.132
5n	–2.256	1.312	–6.112	–2.544	3.568	4.123
5q	–2.254	1.267	–6.067	–2.546	3.521	4.107
5r	–2.264	1.241	–6.041	–2.536	3.505	4.07
5s	–2.299	1.254	–6.054	–2.501	3.553	4.105
5t	–2.191	1.304	–6.104	–2.609	3.495	4.105
CBP	–	–	–5.91	–2.51	3.40	–

[a] $E^{1/2}_{redox} = E_{redox} + (E_{ampli}/2)$. $E_{ampli} = 0.0501$ V. E_{redox} values were determined by DPV in acetonitrile. [b] $E^{1/2}_{ox} = E_{ox} + (E_{ampli}/2)$. E_{ox} values were determined by DPV in acetonitrile; in V vs. Fc/Fc$^+$ in tetrabutylammonium hexafluoroborate ($TBABF_6$, 0.1 M). [c] The HOMO levels were estimated from $E_{HOMO} = -(E^{1/2}_{redox} = +4.8)$ eV. [d] The LUMO levels were estimated from $E_{LUMO} = -(E^{1/2}_{redox} = +4.8)$ eV. [e] Electrochemical band gaps ΔEg were estimated from $\Delta Eg = E_{LUMO} - E_{HOMO}$. [f] The band gaps $\Delta Eg_{cal.}$ were estimated from computational DFT calculations.

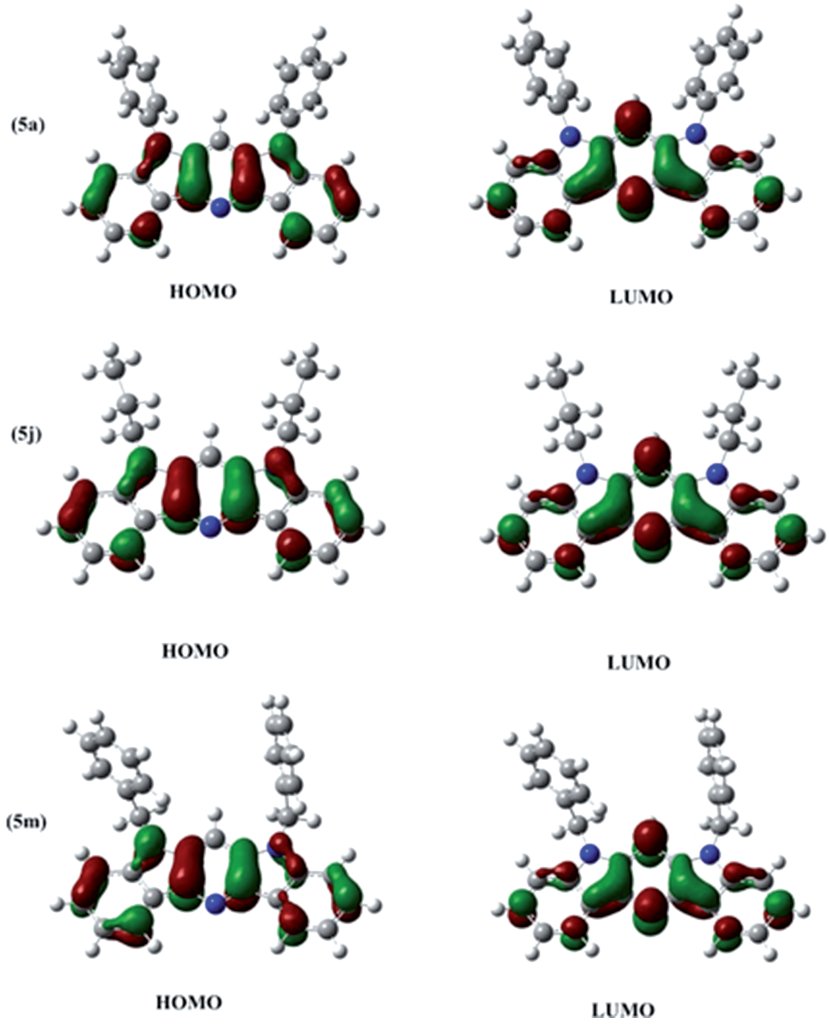

Figure 7. Isodensity plots of HOMO and LUMO orbitals of **5a**, **5j**, and **5m**.

bis(*N*-carbazolyl)-1,1′-biphenyl (CBP), which is commonly used as a host material, **5** has lower HOMO and lower LUMO levels and slightly larger band gaps. Phenyl-substituted derivatives **5a** and **5d** have the lowest HOMO energy levels and band gaps. In contrast, substrates **5r** and **5s**, which are derived from aliphatic amines, have the highest HOMO and highest LUMO level. The smallest band gap was observed in the case of **5d** and **5e**. Phenyl-substituted groups located at the nitrogen position resulted in band gaps smaller than those of derivatives that contained aliphatic substituents. This might be explained by some electronic interaction between the central heterocyclic core and the phenyl substituents. However, it can be anticipated that this interaction is small because of the orthogonal twisting of the aryl groups.

Density functional theory (DFT) calculations have also been performed to determine the values of the HOMO–LUMO band gaps. A comparison of theoretical and experimental values is provided in Table 5. The calculated band gaps are slightly higher than the experimental values, and the differences between the theoretical and experimental band gaps have previously been discussed by us[19] and others.[20] The energy of the virtual orbitals (LUMO) is not properly captured by DFT methods, which leads to overestimated theoretical band gaps. The results in Table 5 indicate that both theoretical and experimental band gaps are not much affected by structural modifications. The nitrogen substituents of **5a**–**5t** can mainly be categorized as aliphatic, benzylic, and phenyl moieties. No significant differences in the HOMO–LUMO gaps have been observed in these compounds that contain a variety of substituents, which suggests that the HOMO and LUMO are not influenced by the substituents. Towards this end, we analyzed the HOMO and LUMO of **5a**, **5j**, and **5m**, and the orbital diagrams are provided in Figure 7. As expected, the HOMO and LUMO of each compound are spread over the pyridodiindole skeleton only and are not extended to the nitrogen substituents. The highest HOMO–LUMO band gap was calculated for **5m** (4.132 eV), which is consistent with the highest experimental band gap for the same compound (3.66 eV).

Molecular orbitals and isodensity plots of HOMO–2 to LUMO+2 for *N*-phenylpyridodiindole **5a** are shown as a representative example in Figure 8. The HOMO–1 and HOMO–2 are almost equal in energy and lie about 0.13 eV lower in energy relative to the HOMO. The HOMO–1 and HOMO–2 are mainly centered on the pyridodiindole skel-

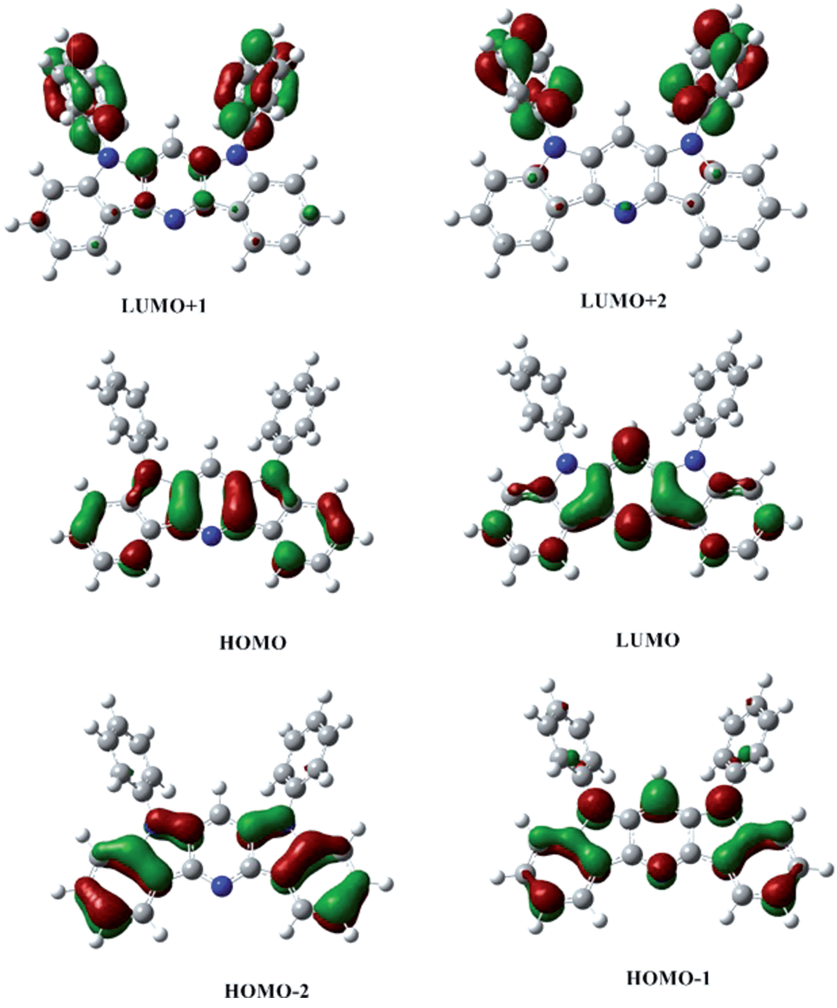

Figure 8. Isodensity plots of HOMO–2 to LUMO+2 of **5a**.

Table 6. Absorption and emission spectroscopic data of **5**.

Compound	λ^{max}_{1abs} [nm]	Log ε λ^{max}_{1abs}	λ^{max}_{2abs} [nm]	Log ε λ^{max}_{2abs}	λ^{max}_{3abs} [nm]	Log ε λ^{max}_{3abs}	λ^{max}_{em} [nm]	Stokes shift [nm]	Φ_{fluo} [%]
5a	290	4.557	310	4.569	379	4.381	402	23	42
5c	291	4.743	311	4.764	380	4.568	403	23	37
5d	288	4.694	310	4.684	378	4.500	402	24	39
5g	290	4.712	311	4.700	379	4.519	402	23	39
5j	291	4.674	311	4.648	382	4.471	407	25	33
5k	291	4.649	312	4.629	382	4.413	407	25	31
5l	288	4.649	310	4.633	380	4.488	404	24	35
5n	289	4.390	311	4.335	381	4.184	404	23	34
5o	288	4.413	310	4.381	379	4.232	402	23	44
5p	288	4.753	310	4.716	380	4.575	402	22	47
5t	292	4.511	312	4.496	383	4.245	407	24	34

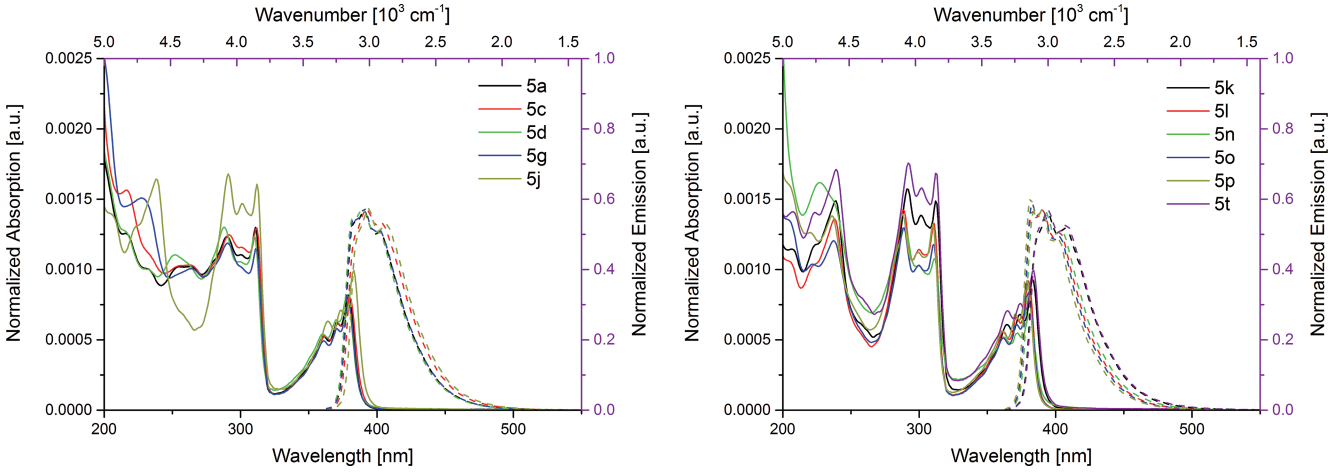

Figure 9. Normalized absorption and emission spectra of **5** measured in acetonitrile. Emission spectra were recorded at an excitation of 360 nm.

eton. The LUMO+1 and LUMO+2 orbitals, on the other hand, have isodensities mostly located on the *N*-phenyl substituents. They are situated approximately 0.36 and 0.66 eV higher in energy, respectively, than the corresponding LUMO.

Absorption and Fluorescence Properties

The optical properties were examined by UV/Vis and fluorescence spectroscopy in acetonitrile, and the data are sumarized in Table 6. The UV/Vis spectra of various derivatives of **5** as the main chromophore are shown in Figure 9. The UV/Vis spectra contain two absorption bands at approximately 290–310 and 380 nm. The substituent located at the nitrogen atom did not have a strong influence. The spectra of compounds **5j**, **5k**, and **5t**, which contain aliphatic subtituents, are slightly redshifted, presumably becaue of the positive inductive effect of the alkyl group. The absorption bands of those compounds that contain electron-withdrawing groups, such as derivative **5d**, are shifted somewhat to shorter wavelengths.

The fluorescence spectra were measured in acetonitrile (excitation at 360 nm) by using a standard quinine hemisulfate salt monohydrate in 0.05 M H_2SO_4, which has a fluorescence yield of 52%.[21] The spectra showed emission bands at approximately 400 nm. The Stokes shifts are in the range of 20 nm. The UV/Vis and fluorescence spectra show a similar pattern, but the quantum yields vary, depending on the type of substituent. Derivatives **5j** and **5k** show the largest Stokes shifts but the lowest quantum yields. Compounds **5o** and **5p**, which contain either a fluoro or trifluoromethyl substituent, showed the highest quantum yields of 44 and 47%, respectively.

Conclusions

We successfully synthesized a new series of N-heteropentacenes (5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindoles) by using a Pd-catalyzed site-selective Suzuki reaction and a twofold C–N coupling annulation. During the optimization of the reaction conditions, the use of bidentate ligands proved to be important. The electrochemical and optical properties of the products were studied in detail. The results of DFT calculations and an experimental study indicate that *N*-phenyl-substituted derivatives have smaller band gaps than the *N*-alkyl-substituted derivatives. The smallest band gaps were observed for compound **5g**. The optical results exhibited very high quantum yields for all derivatives **5a**–**5t** (Φ_{fluo} = 31–47%). The values of the Stokes shifts of **5a**–**5t** are not dependent on the substituents (variation in the range of

only 22–25 nm). In addition to this new and interesting synthesis strategy, the electronic, optical, and electrochemical properties reported herein might be used as an attractive starting point for further applications.

Experimental Section

General Methods: Chemicals were purchased from Alfa Aesar and Sigma Aldrich and were used without further purification. The NMR spectroscopic data were recorded with Bruker AV 300 and 250 MHz instruments. IR spectra were recorded with a Perkin–Elmer FTIR 1600 spectrometer [attenuated total reflectance (ATR)]. Mass spectra were obtained with a Hewlett–Packard HPGC–MS 5890/5972 instrument (EI, 70 eV) by using a GC inlet or with an MX-1321 instrument (EI, 70 eV) by using a direct inlet. Column chromatography was performed on silica gel (200 mesh, Merck), and silica gel Merck 60 F254 plates were used for TLC. Commercially available solvents were distilled for column chromatography. All other solvents were purified and dried by standard methods. Crystallographic data were deposited with the CCDC.[22]

General Procedure for the Preparation of 2,3,5,6-Tetrabromopyridine (1): To a solution of pyridine-2,6-diamine (10.9 g, 100 mmol) in glacial acetic acid (200 mL) was added dropwise bromine (11.4 mL, 220 mmol) at 0 °C. The temperature was then increased to room temperature, and the mixture was stirred for 5 h. The reaction mixture was treated with aqueous Na_2SO_3 solution to remove the residual bromine. The solvent was removed in vacuo. Water was added to the mixture, which was neutralized by the addition of NaOH to pH = 8–9. Upon filtration, a brown solid (22 g, 83%) was obtained, which was washed with water and dried in vacuo. To a solution of the 3,5-dibromopyridine-2,6-diamine (10 g, 37.5 mmol) in 48% HBr (30 mL) was added dropwise a saturated aqueous solution of $NaNO_2$ (20.7 g, 300 mmol) at –3 °C. The resulting mixture was stirred at the same temperature for 2 h, and the temperature was then increased to room temperature and maintained at that temperature for an additional 2 h. The pH of the solution was adjusted to 8–9 by the addition of NaOH, and the resulting mixture was extracted with ethyl acetate. The organic layer was collected, dried with $MgSO_4$, filtered, and concentrated in vacuo. The mixture was separated by column chromatography (silica gel; heptanes/dichloromethane, 5:1) to yield 2,3,5,6-tetrabromopyridine (**1**; 3 g, 20%) as white crystals; m.p. 172–174 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (s, 1 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 145.32 (s), 140.60 (s), 123.01 (s) ppm. IR (ATR): $\tilde{\nu}$ = 3084 (m), 3036 (m), 1529 (m), 1502 (s), 1362 (vs), 1352 (vs), 1288 (s), 1277 (s), 1238 (m), 1213 (m), 1149 (vs), 1136 (s), 1016 (vs), 945 (m), 931 (m), 897 (vs), 833 (m), 806 (m), 798 (m), 781 (m), 704 (s), 656 (s), 648 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 395 (100), 314 (42), 235 (26), 154 (13), 75 (42). HRMS (EI): calcd. for $C_5HNBr_3{}^{81}Br$ $[M]^+$ 392.6815, found 392.68185; calcd. for $C_5HNBr_2{}^{81}Br_2$ $[M]^+$ 394.67961, found 394.67983; calcd. for $C_5HNBr^{81}Br_3$ $[M]^+$ 396.67756, found 396.67761.

General Procedure for the Preparation of 3,5-Dibromo-2,6-bis(2-bromophenyl)pyridine (3): 2,3,5,6-tetrabromopyridine (**1**; 1 g, 2.5 mmol), 2-bromophenylboronic acid (**2**; 1.1 g, 5.5 mmol), $Pd(PPh_3)_4$ (73 mg, 63 µmol), and sodium hydroxide (608 mg, 15.2 mmol) were added to a Schlenk flask (500 mL), which was backfilled several times with argon. To the mixture were added THF (70 mL) and distilled water (10 mL), and the flask was then backfilled several times with argon. The reaction mixture was heated at 70 °C for 4 h. The solvent was evaporated in vacuo. The residue was partitioned between water and dichloromethane and then extracted with dichloromethane. The organic layer was dried with $MgSO_4$ and filtered, and the solvent was evaporated in vacuo. The yellow residue was purified by column chromatography (silica gel; heptanes/ethyl acetate, 10:1) to yield 3,5-dibromo-2,6-bis(2-bromophenyl)pyridine (**3**; 1.1 g, 80%) as a white solid; m.p. 174–175 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (s, 1 H), 7.58 (d, *J* = 8.0 Hz, 2 H), 7.37–7.25 (m, 4 H), 7.20 (dd, *J* = 8.4, 7.3 Hz, 2 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 156.75 (s), 143.78 (s), 139.78 (s), 132.75 (s), 130.33 (s), 127.37 (s), 122.50 (s), 120.43 (s) ppm. IR (ATR): $\tilde{\nu}$ = 2922 (m), 2850 (m), 1562 (m), 1529 (m), 1477 (m), 1470 (m), 1441 (m), 1427 (m), 1406 (s), 1348 (m), 1329 (m), 1284 (m), 1275 (w), 1265 (m), 1240 (m), 1194 (m), 1117 (m), 1041 (s), 1024 (s), 1005 (s), 984 (m), 951 (m), 889 (s), 870 (m), 850 (m), 756 (vs), 725 (s), 692 (s), 683 (s), 660 (m), 646 (m), 631 (s), 596 (m), 532 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 547 (21), 468 (73), 227 (100), 193 (10), 113 (13), 75 (11). HRMS (EI): calcd. for $C_{17}H_9NBr_4$ $[M]^+$ 542.74630, found 542.74628; calcd. for $C_{17}H_9NBr_3{}^{81}Br$ $[M]^+$ 544.74425, found 544.74445; calcd. for $C_{17}H_9NBr_2{}^{81}Br_2$ $[M]^+$ 546.74221, found 546.74277; calcd. for $C_{17}H_9NBr^{81}Br_3$ $[M]^+$ 548.74016, found 548.74086; calcd. for $C_{17}H_9N^{81}Br_4$ $[M]^+$ 550.73811, found 550.73897.

General Procedure A for Double C–N Coupling with Aniline Derivatives as Exemplified by the Preparation of 5,7-Diphenyl-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5a): Aniline (0.1 mL, 1.09 mmol) was added to a pressure tube that was charged with **3** (100 mg, 0.18 mmol), $Pd_2(dba)_3$ (8 mg, 9 µmol), dppf (10 mg, 18 µmol), and sodium *tert*-butoxide (105 mg, 1.09 mmol) under argon. The tube was backfilled with argon several times. The mixture was dissolved in anhydrous toluene (10 mL) and then heated at 100 °C for 7 h. After cooling, the reaction mixture was diluted with dichloromethane (20 mL), and the resulting mixture was filtered through a pad of Celite, which was washed with dichloromethane (40 mL). The filtrate was concentrated in vacuo. The crude product was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 10:1:1) to yield **5a** (62 mg, 83%) as a white solid; m.p. 298–300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69 (d, *J* = 7.2 Hz, 2 H), 7.58 (dt, *J* = 8.9, 4.3 Hz, 9 H), 7.50–7.38 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.35, 137.85, 137.31, 134.32, 130.26, 129.08, 127.86, 127.15, 127.09, 126.71, 122.55, 121.08, 120.78, 109.80, 96.93 ppm. IR (ATR): $\tilde{\nu}$ = 3036 (m), 2926 (w), 2852 (w), 1591 (s), 1497 (s), 1479 (m), 1454 (s), 1435 (m), 1404 (s), 1387 (s), 1313 (m), 1242 (s), 1205 (m), 1188 (s), 1178 (s), 1155 (m), 1144 (m), 1103 (m), 1074 (m), 1039 (m), 1028 (m), 1011 (m), 939 (m), 924 (m), 847 (m), 829 (m), 760 (m), 739 (s), 729 (s), 692 (vs), 667 (m), 638 (s), 623 (m), 615 (s), 582 (s), 567 (m), 536 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 409 (100), 332 (8), 204 (14). HRMS (ESI): calcd. for $C_{29}H_{20}N_3$ $[M + H]^+$ 410.16517, found 41016512; calcd. for $C_{29}H_{20}N_3Na$ $[M + Na]^+$ 432.14712, found 432.14744.

5,7-Bis[4-(*tert*-butyl)phenyl]-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5b): Following general procedure A and using compound **3** (100 mg, 0.18 mmol) and 4-(*tert*-butyl)aniline (118 mg, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 8:1:1) to yield **5b** (80 mg, 84%) as a white solid; m.p. 317–319 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 7.5 Hz, 2 H), 7.68–7.59 (m, 5 H), 7.56–7.35 (m, 10 H), 1.42 (s, 18 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 150.65, 142.37, 138.00, 134.61, 134.27, 126.96, 126.72, 126.46, 122.68, 120.65, 120.37, 109.76, 96.77, 34.80, 31.39 ppm. IR (ATR): $\tilde{\nu}$ = 2958 (m), 2902 (w), 2866 (w), 1591 (m), 1518 (m), 1479 (w), 1456 (s), 1408 (m), 1392 (m), 1363 (m), 1350 (w), 1325 (w), 1309 (m), 1290 (w), 1261 (m), 1242 (s), 1207 (m), 1188 (m), 1169 (m), 1153 (m), 1147 (m), 1105 (m), 1036 (m), 1011 (m), 951 (w),

937 (w), 928 (w), 893 (w), 850 (m), 841 (m), 822 (m), 800 (m), 785 (m), 741 (vs), 729 (vs), 706 (m), 660 (m), 640 (m), 625 (m), 592 (w), 561 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 521 (100), 491 (9), 253 (15), 217 (93), 172 (21). HRMS (EI): calcd. for $C_{37}H_{35}N_3$ $[M]^+$ 521.28255, found 521.28186.

5,7-Bis(3,5-dimethylphenyl)-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5c): Following general procedure A and using compound **3** (100 mg, 0.18 mmol) and 3,5-dimethylaniline (175 µL, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 8:1:1) to yield **5c** (72 mg, 85%) as a white solid; m.p. 306–308 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 7.6 Hz, 4 H), 7.48 (s, 2 H), 7.41–7.26 (m, 13 H), 7.11 (s, 8 H), 7.00 (s, 4 H), 2.32 (s, 25 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.23, 139.85, 138.03, 137.20, 134.29, 129.32, 126.73, 124.49, 122.76, 120.70, 120.38, 109.80, 96.90, 21.37 ppm. IR (ATR): $\tilde{\nu}$ = 3045 (w), 2914 (m), 2854 (w), 1589 (s), 1470 (s), 1456 (s), 1435 (m), 1417 (m), 1404 (s), 1387 (m), 1373 (m), 1311 (m), 1298 (m), 1242 (s), 1190 (s), 1153 (m), 1138 (m), 1105 (m), 1011 (m), 916 (m), 864 (m), 843 (s), 785 (m), 741 (vs), 725 (vs), 708 (s), 698 (s), 631 (m), 588 (m), 575 (m), 557 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 465 (100), 233 (12), 79 (7). HRMS (EI): calcd. for $C_{33}H_{27}N_3$ $[M]^+$ 465.21995, found 465.21908.

5,7-Bis(4-fluorophenyl)-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5d): Following general procedure A and using compound **3** (100 mg, 0.18 mmol) and 4-fluoroaniline (104 µL, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 8:1:1) to yield **5d** (54 mg, 66%) as a white solid; m.p. 338–340 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 7.3 Hz, 2 H), 7.48–7.28 (m, 9 H), 7.27–7.17 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.03 (d, *J* = 248.1 Hz), 142.62, 138.39, 134.62, 133.36 (d, *J* = 3.1 Hz), 129.20 (d, *J* = 8.6 Hz), 127.24, 122.94, 121.00, 120.96, 117.44 (d, *J* = 22.8 Hz), 109.69, 96.18 ppm. IR (ATR): $\tilde{\nu}$ = 3053 (w), 2918 (w), 2848 (w), 1591 (m), 1506 (vs), 1481 (m), 1456 (s), 1406 (s), 1390 (m), 1311 (s), 1244 (s), 1221 (s), 1192 (s), 1173 (s), 1155 (s), 1113 (m), 1101 (s), 1041 (m), 1011 (m), 935 (m), 889 (m), 835 (s), 812 (s), 800 (m), 744 (vs), 723 (vs), 700 (m), 671 (m), 661 (m), 640 (m), 619 (m), 573 (s), 565 (s), 536 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 445 (100), 222 (10), 95 (8). HRMS (EI): calcd. for $C_{29}H_{17}N_3F_2$ $[M]^+$ 445.13851, found 445.13827.

5,7-Bis[3-(trifluoromethyl)phenyl]-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5e): Following general procedure A and using compound **3** (100 mg, 0.18 mmol) and 3-(trifluoromethyl)aniline (137 µL, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 8:1:1) to yield **5e** (70 mg, 70%) as a white solid; m.p. 268–269 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 7.7 Hz, 2 H), 7.81 (s, 2 H), 7.67 (ddd, *J* = 13.0, 4.7, 1.7 Hz, 6 H), 7.47–7.26 (m, 7 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.78 ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 141.71, 138.69, 137.91, 133.61, 132.80 (q, *J* = 33.2 Hz), 130.85, 129.97, 127.30, 124.35 (q, *J* = 3.6 Hz), 123.65 (q, *J* = 3.9 Hz), 123.53 (q, *J* = 272.7 Hz), 123.01, 121.25, 120.92, 109.38, 96.01 ppm. IR (ATR): $\tilde{\nu}$ = 3061 (w), 2928 (w), 2854 (w), 1591 (m), 1495 (m), 1485 (m), 1460 (s), 1404 (s), 1387 (m), 1354 (m), 1344 (m), 1323 (s), 1309 (s), 1279 (m), 1271 (m), 1244 (s), 1182 (s), 1173 (s), 1155 (s), 1115 (vs), 1097 (s), 1070 (s), 1041 (m), 1012 (m), 1003 (m), 962 (m), 931 (w), 918 (m), 904 (m), 854 (m), 849 (m), 800 (s), 746 (s), 727 (s), 708 (vs), 700 (vs), 669 (m), 661 (s), 646 (m), 609 (w), 582 (m), 538 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 545 (100), 273 (22). HRMS (EI): calcd. for $C_{31}H_{17}N_3$ $[M]^+$ 545.13212, found 545.13199.

5,7-Bis(4-methoxyphenyl)-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5f): Following general procedure A and using compound **3** (100 mg, 0.18 mmol) and *p*-anisidine (135 mg, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 5:1:1) to yield **5f** (80 mg, 93%) as a white solid; m.p. 300–302 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.67–8.58 (m, 1 H), 7.49–7.30 (m, 6 H), 7.14–7.04 (m, 2 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.19, 142.89, 138.11, 134.99, 130.05, 128.70, 126.91, 122.84, 120.81, 120.47, 115.51, 109.78, 96.35, 55.80 ppm. IR (ATR): $\tilde{\nu}$ = 3047 (m), 2951 (m), 2924 (m), 2835 (m), 1614 (w), 1589 (m), 1510 (s), 1477 (m), 1456 (s), 1441 (s), 1408 (s), 1392 (m), 1315 (m), 1298 (m), 1279 (m), 1242 (vs), 1211 (m), 1190 (s), 1180 (s), 1144 (s), 1113 (m), 1103 (s), 1032 (s), 1007 (m), 953 (m), 928 (m), 887 (m), 835 (s), 825 (s), 810 (m), 793 (m), 742 (vs), 733 (s), 727 (s), 671 (m), 660 (m), 642 (m), 619 (m), 584 (s), 575 (s), 542 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 469 (100), 291 (27), 43 (57). HRMS (EI): calcd. for $C_{31}H_{23}O_2N_3$ $[M]^+$ 469.17848, found 469.17813.

5,7-Bis(3,5-dimethoxyphenyl)-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5g):[22] Following general procedure A and using compound **3** (100 mg, 0.18 mmol) and 3,5-dimethoxyaniline (168 mg, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 4:1:1) to yield **5f** (92 mg, 95%) as a white solid; m.p. 230–231 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 6.6 Hz, 2 H), 7.74 (s, 1 H), 7.46 (dd, *J* = 26.3, 6.9 Hz, 6 H), 6.75 (d, *J* = 1.9 Hz, 4 H), 6.57 (s, 2 H), 3.84 (s, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.94, 142.13, 134.11, 127.38, 121.43, 120.89, 110.03, 105.08, 100.05, 55.67 ppm. IR (ATR): $\tilde{\nu}$ = 3066 (w), 2999 (w), 2935 (w), 2841 (w), 1740 (w), 1595 (vs), 1477 (s), 1462 (s), 1446 (m), 1423 (m), 1404 (m), 1346 (m), 1311 (m), 1300 (m), 1292 (s), 1234 (s), 1201 (vs), 1190 (s), 1151 (vs), 1142 (s), 1065 (s), 1055 (m), 827 (s), 741 (s), 733 (s), 708 (m), 690 (s), 579 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 529 (100), 471 (10), 207 (6). HRMS (EI): calcd. for $C_{33}H_{27}O_4N_3$ $[M]^+$ 529.19961, found 529.19898.

5,7-Bis[4-(diethylamino)phenyl]-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5h): Following general procedure A and using compound **3** (100 mg, 0.18 mmol) and N^1,N^1-diethylbenzene-1,4-diamine (182 µL, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptane/dichloromethane/ethyl acetate, 5:1:1) to yield **5h** (70 mg, 69%) as a brown solid; m.p. 290–291 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58–8.49 (m, 2 H), 7.29 (dddd, *J* = 6.7, 6.2, 5.2, 4.4 Hz, 12 H), 6.72 (d, *J* = 9.0 Hz, 4 H), 3.35 (q, *J* = 7.0 Hz, 8 H), 1.15 (t, *J* = 7.1 Hz, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.30, 143.08, 137.58, 135.22, 128.41, 126.38, 124.72, 122.48, 120.44, 119.79, 112.29, 109.75, 96.57, 44.50, 12.67 ppm. IR (ATR): $\tilde{\nu}$ = 3043 (w), 2968 (m), 2929 (m), 2897 (w), 2864 (w), 1732 (w), 1606 (m), 1591 (m), 1520 (vs), 1477 (m), 1460 (s), 1448 (m), 1394 (m), 1373 (m), 1354 (s), 1323 (m), 1309 (s), 1269 (s), 1240 (s), 1192 (s), 1149 (s), 1140 (s), 1119 (m), 1109 (m), 1097 (m), 1074 (m), 1047 (m), 1032 (m), 1007 (m), 930 (m), 922 (m), 885 (m), 841 (m), 823 (m), 812 (s), 793 (m), 785 (m), 750 (vs), 742 (s), 731 (vs), 725 (s), 696 (m), 656 (m), 640 (m), 621 (m), 561 (s), 536 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 551 (100), 507 (15), 463 (13), 268 (7), 69 (20), 44 (59). HRMS (ESI): calcd. for $C_{37}H_{37}N_5$ $[M + H]^+$ 552.31217, found 552.31208; calcd. for $C_{37}H_{37}N_5Na$ $[M + Na]^+$ 574.29412, found 574.2944.

General Procedure B for Double C–N Coupling with Chain Amine Derivatives as Exemplified by the Preparation of 5,7-Diheptyl-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5i): A pressure tube was charged with **3** (100 mg, 0.18 mmol), $Pd_2(dba)_3$ (8 mg, 9 µmol), DPEPhos (10 mg, 18 µmol), and sodium *tert*-butoxide (105 mg,

1.09 mmol) under argon. The tube was backfilled with argon several times and then dissolved in anhydrous toluene (10 mL). *n*-Heptylamine (0.2 mL, 1.09 mmol) was added, and the resulting mixture was heated at 100 °C for 7 h. After cooling, the reaction mixture was diluted with dichloromethane (20 mL), and filtered through a pad of Celite, which was washed with dichloromethane (40 mL). The filtrate was reduced in vacuo. The crude product was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 5:1:1) to yield **5i** (66 mg, 80%) as a white solid; m.p. 162–164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.21 (d, J = 7.6 Hz, 2 H), 8.12 (t, J = 7.3 Hz, 2 H), 8.06–7.60 (m, 15 H), 4.92 (t, J = 6.9 Hz, 4 H), 3.66 (t, J = 6.9 Hz, 4 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 141.13, 138.95, 136.22, 133.59, 128.99, 128.72, 126.80, 126.55, 122.10, 120.83, 119.62, 108.48, 94.63, 44.90, 35.08 ppm. IR (ATR): $\tilde{\nu}$ = 3061 (w), 3020 (w), 2953 (w), 2933 (w), 2877 (w), 2852 (w), 1595 (s), 1466 (s), 1454 (m), 1441 (m), 1410 (m), 1390 (m), 1352 (s), 1319 (s), 1257 (s), 1227 (m), 1203 (m), 1171 (s), 1124 (m), 1111 (m), 1080 (m), 1068 (m), 1012 (m), 827 (m), 742 (vs), 729 (vs), 698 (vs), 687 (s), 648 (m), 594 (m), 579 (m), 563 (m), 544 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 453 (100), 368 (40), 282 (12), 269 (25). HRMS (EI): calcd. for $C_{31}H_{39}N_3$ $[M]^+$ 453.31385, found 453.31353.

5,7-Dipropyl-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5j):[22] Following general procedure B and using compound **3** (100 mg, 0.18 mmol) and *n*-propylamine (90 µL, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 5:1:1) to yield **5j** (54 mg, 86%) as a white solid; m.p. 168–170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.48 (d, J = 7.7 Hz, 2 H), 7.42 (ddd, J = 8.2, 7.1, 1.2 Hz, 2 H), 7.32–7.20 (m, 5 H), 4.09 (t, J = 7.1 Hz, 4 H), 1.90–1.73 (m, 4 H), 0.88 (t, J = 7.4 Hz, 6 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 141.48, 136.73, 133.72, 126.24, 122.31, 120.57, 119.26, 108.50, 94.09, 44.52, 22.09, 11.85 ppm. IR (ATR): $\tilde{\nu}$ = 2958 (m), 2929 (m), 2872 (m), 1593 (m), 1574 (m), 1520 (w), 1464 (s), 1408 (m), 1385 (m), 1365 (m), 1358 (m), 1335 (w), 1315 (s), 1294 (m), 1248 (s), 1225 (m), 1207 (m), 1188 (m), 1151 (m), 1132 (m), 1122 (m), 1111 (m), 1070 (m), 1024 (w), 1011 (m), 984 (w), 968 (m), 957 (w), 935 (m), 922 (m), 893 (m), 847 (w), 837 (m), 823 (s), 741 (s), 721 (vs), 704 (s), 667 (m), 623 (m), 596 (m), 579 (s), 569 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 341 (100), 312 (89), 269 (39), 171 (6), 141 (20). HRMS (EI): calcd. for $C_{23}H_{23}N_3$ $[M]^+$ 341.18865, found 341.18864.

5,7-Didodecyl-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5k): Following general procedure B and using compound **3** (100 mg, 0.18 mmol) and *n*-dodecylamine (203 mg, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 5:1:1) to yield **5k** (77 mg, 71%) as a white solid; m.p. 91–93 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.57 (d, J = 7.5 Hz, 2 H), 7.52 (ddd, J = 8.2, 7.1, 1.2 Hz, 2 H), 7.42–7.29 (m, 5 H), 4.43–4.15 (m, 4 H), 2.05–1.75 (m, 4 H), 1.56–1.07 (m, 36 H), 0.87 (t, J = 6.7 Hz, 6 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 141.42, 136.78, 133.68, 126.28, 122.33, 120.63, 119.28, 108.44, 94.10, 43.06, 31.88, 29.61, 29.59, 29.51, 29.42, 29.31, 28.74, 27.36, 22.66, 14.08 ppm. IR (ATR): $\tilde{\nu}$ = 2918 (s), 2848 (s), 1597 (m), 1466 (s), 1412 (m), 1350 (m), 1321 (s), 1257 (m), 1246 (m), 1209 (m), 1190 (m), 1117 (m), 1076 (w), 1009 (w), 876 (w), 829 (m), 742 (s), 723 (vs) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 593 (100), 438 (45), 270 (16), 44 (21). HRMS (EI): calcd. for $C_{41}H_{59}N_3$ $[M]^+$ 593.47035, found 593.47119.

5,7-Diallyl-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5l): Following general procedure B and using compound **3** (100 mg, 0.18 mmol) and allylamine (82 µL, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 5:1:1) to yield **5l** (52 mg, 84%) as a white solid; m.p. 156–158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (d, J = 7.2 Hz, 2 H), 7.44 (m, 2 H), 7.28 (m, 6 H), 6.02–5.86 (m, 2 H), 5.04 (dd, J = 18.2, 13.7 Hz, 4 H), 4.88–4.75 (m, 4 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 141.45, 133.62, 131.87, 126.46, 120.63, 119.65, 117.03, 108.59, 94.67, 45.31 ppm. IR (ATR): $\tilde{\nu}$ = 3057 (w), 2999 (w), 1616 (w), 1597 (m), 1514 (w), 1464 (s), 1435 (m), 1408 (m), 1385 (m), 1358 (m), 1336 (m), 1317 (s), 1284 (m), 1254 (s), 1223 (m), 1213 (m), 1203 (m), 1184 (m), 1149 (m), 1138 (m), 1126 (m), 1113 (m), 1090 (m), 1068 (m), 1039 (m), 1026 (w), 1011 (m), 997 (m), 933 (s), 916 (m), 901 (m), 839 (m), 825 (s), 783 (w), 766 (w), 741 (s), 721 (vs), 714 (vs), 683 (m), 656 (m), 633 (m), 609 (m), 586 (m), 557 (m), 548 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 337 (100), 296 (70), 255 (28), 127 (16), 43 (37). HRMS (EI): calcd. for $C_{23}H_{19}N_3$ $[M]^+$ 337.15735, found 337.15705.

5,7-Dibenzyl-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5m): Following general procedure B and using compound **3** (100 mg, 0.18 mmol) and benzylamine (120 µL, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 5:1:1) to yield **5m** (56 mg, 70%) as a white solid; m.p. 278–280 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.51 (d, J = 7.6 Hz, 2 H), 7.42–6.94 (m, 18 H), 5.28 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.75, 137.33, 136.56, 133.91, 128.86, 127.61, 126.67, 126.46, 122.58, 120.71, 119.88, 108.79, 95.08, 46.62 ppm. IR (ATR): $\tilde{\nu}$ = 3028 (w), 2922 (w), 2852 (w), 1616 (w), 1597 (m), 1510 (w), 1495 (m), 1483 (w), 1464 (s), 1450 (m), 1441 (m), 1408 (m), 1387 (m), 1350 (m), 1315 (s), 1298 (m), 1277 (w), 1250 (s), 1221 (m), 1211 (m), 1203 (m), 1176 (s), 1155 (m), 1124 (m), 1111 (m), 1078 (m), 1065 (m), 1030 (m), 1011 (m), 1003 (m), 985 (m), 970 (m), 945 (m), 930 (m), 903 (m), 895 (m), 839 (m), 822 (s), 796 (m), 741 (s), 725 (vs), 708 (s), 690 (vs), 665 (s), 634 (m), 623 (s), 615 (s), 604 (m), 582 (s), 563 (s), 555 (s), 532 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 437 (100), 346 (61), 255 (12), 91 (60), 65 (8). HRMS (EI): calcd. for $C_{31}H_{23}N_3$ $[M]^+$ 437.18865, found 437.18850.

5,7-Bis(4-methoxybenzyl)-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5n): Following general procedure B and using compound **3** (100 mg, 0.18 mmol) and 4-methoxybenzylamine (143 µL, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 3:1:1) to yield **5n** (55 mg, 60%) as a white solid; m.p. 217–219 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.53 (d, J = 7.7 Hz, 2 H), 7.44–7.36 (m, 2 H), 7.31–7.21 (m, 6 H), 7.01–6.88 (m, 4 H), 6.76–6.59 (m, 4 H), 5.23 (s, 4 H), 3.64 (s, 6 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 159.02, 141.67, 133.70, 131.97, 128.48, 127.77, 126.67, 120.79, 119.75, 114.17, 108.72, 95.43, 55.18, 46.10 ppm. IR (ATR): $\tilde{\nu}$ = 2955 (w), 2939 (w), 2839 (w), 1608 (m), 1595 (m), 1510 (s), 1464 (s), 1443 (m), 1408 (m), 1389 (m), 1352 (m), 1333 (m), 1321 (m), 1313 (s), 1304 (m), 1282 (m), 1254 (vs), 1244 (vs), 1223 (m), 1205 (m), 1174 (vs), 1157 (m), 1151 (m), 1124 (m), 1111 (m), 1028 (s), 1012 (m), 1001 (m), 924 (m), 843 (m), 829 (s), 816 (s), 756 (m), 748 (s), 741 (s), 727 (vs), 687 (s), 636 (m), 619 (m), 606 (m), 582 (m), 569 (m), 538 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 497 (81), 207 (8), 121 (100), 77 (11). HRMS (EI): calcd. for $C_{33}H_{27}O_2N_3$ $[M]^+$ 497.20978, found 497.20946.

5,7-Bis(4-fluorobenzyl)-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5o): Following general procedure B and using compound **3** (100 mg, 0.18 mmol) and 4-fluorobenzylamine (125 µL, 1.09 mmol) gave the crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 5:1:1) to yield **5o** (46 mg, 53%) as a white solid; m.p. 220–221 °C. ^{1}H NMR

(300 MHz, $CDCl_3$): δ = 8.51 (d, J = 7.6 Hz, 3 H), 7.45–7.37 (m, 3 H), 7.34–7.25 (m, 3 H), 7.25–7.16 (m, 4 H), 7.02–6.74 (m, 14 H), 5.16 (s, 6 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –114.56 (s) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.16 (d, J = 246.3 Hz), 141.54 (s), 137.38 (s), 133.54 (s), 132.13 (d, J = 3.3 Hz), 128.02 (d, J = 8.2 Hz), 126.73 (s), 122.60 (s), 120.71 (s), 119.99 (s), 115.73 (d, J = 21.7 Hz), 108.66 (s), 94.84 (s), 45.84 (s) ppm. IR (ATR): $\tilde{\nu}$ = 3047 (w), 1595 (m), 1506 (s), 1464 (s), 1443 (m), 1406 (m), 1385 (m), 1348 (m), 1317 (s), 1254 (s), 1225 (s), 1215 (s), 1178 (s), 1155 (s), 1124 (m), 1113 (m), 1095 (m), 1063 (m), 1009 (m), 922 (m), 837 (s), 808 (m), 741 (vs), 725 (vs), 700 (m), 692 (m), 665 (m), 638 (m), 621 (m), 613 (m), 596 (m), 579 (m), 567 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%) = 473 (94), 364 (70), 255 (16), 127 (12), 109 (100). HRMS (ESI): calcd. for $C_{31}H_{21}F_2N_3$ $[M + H]^+$ 474.17763, found 474.17793.

5,7-Bis[3-(trifluoromethyl)benzyl]-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5p): Following general procedure B and using compound **3** (100 mg, 0.18 mmol) and 3-(trifluoromethyl)benzylamine (157 μL, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 5:1:1) to yield **5p** (54 mg, 52%) as a white solid; m.p. 229–231 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.53 (d, J = 7.6 Hz, 2 H), 7.52–7.28 (m, 9 H), 7.18 (t, J = 6.9 Hz, 3 H), 6.96 (d, J = 8.7 Hz, 3 H), 5.24 (s, 4 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.70 (s) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.50 (s), 137.49 (s), 133.54 (s), 131.24 (q, J = 32.5 Hz), 129.46 (s), 129.42 (s), 126.95 (s), 124.55 (q, J = 3.4 Hz), 123.81 (q, J = 272.5 Hz), 123.12 (q, J = 3.7 Hz), 122.63 (s), 120.81 (s), 120.28 (s), 108.59 (s), 94.52 (s), 46.11 (s) ppm. IR (ATR): $\tilde{\nu}$ = 3047 (w), 2926 (w), 1595 (m), 1466 (m), 1443 (m), 1410 (m), 1327 (vs), 1315 (vs), 1254 (s), 1223 (m), 1182 (s), 1167 (s), 1111 (vs), 1097 (vs), 1070 (vs), 1007 (m), 968 (m), 949 (m), 937 (m), 930 (m), 916 (m), 881 (m), 862 (m), 823 (m), 804 (m), 789 (s), 744 (vs), 733 (s), 714 (m), 696 (vs), 661 (s), 634 (m), 615 (m), 602 (m), 582 (m), 565 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%) = 573 (100), 414 (42), 255 (30), 159 (10). HRMS (EI): calcd. for $C_{33}H_{21}N_3F_6$ $[M]^+$ 573.16342, found 573.16519.

5,7-Diphenethyl-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5q): Following general procedure B and using compound **3** (100 mg, 0.18 mmol) and phenylethylamine (138 μL, 1.09 mmol) gave the crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 5:1:1) to yield **5q** (64 mg, 75%) as a white solid; m.p. 124–126 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.47 (d, J = 7.6 Hz, 2 H), 7.38 (t, J = 7.3 Hz, 2 H), 7.30–6.79 (m, 16 H), 4.19 (t, J = 6.9 Hz, 4 H), 2.93 (t, J = 6.9 Hz, 4 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 141.00, 138.83, 133.46, 128.87, 128.59, 126.68, 126.43, 120.70, 119.50, 108.35, 94.50, 44.77, 34.96 ppm. IR (ATR): $\tilde{\nu}$ = 2951 (m), 2928 (m), 2874 (m), 2856 (m), 2845 (m), 1591 (s), 1481 (m), 1470 (s), 1464 (s), 1412 (m), 1387 (m), 1371 (m), 1354 (m), 1319 (s), 1250 (s), 1230 (s), 1215 (m), 1201 (m), 1186 (m), 1174 (m), 1144 (s), 1124 (m), 1113 (s), 1070 (m), 1024 (w), 1011 (m), 903 (m), 847 (m), 744 (s), 725 (vs), 706 (s), 696 (m), 673 (m), 596 (m), 577 (m), 565 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%) = 465 (35), 374 (100), 282 (42). HRMS (EI): calcd. for $C_{33}H_{27}N_3$ $[M]^+$ 465.21995; found 465.21945.

5,7-Bis(3,4-dimethoxyphenethyl)-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5r): Following general procedure B and using compound **3** (100 mg, 0.18 mmol) and (3,4-dimethoxyphenyl)ethylamine (185 μL, 1.09 mmol) gave the crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 3:1:1) to yield **5r** (60 mg, 56%) as a white solid; m.p. 164–165 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.45 (s, 2 H), 7.42–7.34 (m, 2 H), 7.28–7.16 (m, 4 H), 6.72–6.50 (m, 5 H), 6.19 (s, 2 H), 4.29 (d, J = 6.4 Hz, 4 H), 3.60 (s, 6 H), 3.39 (s, 6 H), 2.92 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.94, 147.90, 141.20, 133.51, 131.47, 126.39, 120.71, 120.56, 119.55, 112.48, 111.26, 108.52, 94.37, 55.78, 55.67, 45.07, 34.52 ppm. IR (ATR): $\tilde{\nu}$ = 2955 (w), 2937 (w), 2916 (w), 2833 (w), 1597 (m), 1516 (s), 1464 (m), 1454 (m), 1441 (w), 1435 (w), 1414 (m), 1387 (w), 1354 (m), 1327 (m), 1317 (m), 1261 (vs), 1236 (s), 1228 (s), 1211 (m), 1198 (m), 1190 (m), 1157 (s), 1136 (s), 1122 (m), 1041 (w), 1030 (m), 1018 (s), 860 (m), 808 (m), 764 (m), 742 (vs), 727 (vs), 683 (m), 644 (m), 557 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%) = 585 (45), 434 (100), 284 (27). HRMS (ESI): calcd. for $C_{37}H_{35}N_3O_4$ $[M + H]^+$ 586.26276, found 586.2700.

5,7-Bis(3-phenylpropyl)-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5s): Following general procedure B and using compound **3** (100 mg, 0.18 mmol) and 3-phenylpropylamine (156 μL, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 5:1:1) to yield **5s** (61 mg, 68%) as a white solid; m.p. 194–196 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.46 (d, J = 7.6 Hz, 2 H), 7.39 (ddd, J = 8.3, 7.3, 1.2 Hz, 2 H), 7.28–6.97 (m, 16 H), 4.05 (t, J = 7.3 Hz, 4 H), 2.58 (t, J = 7.5 Hz, 4 H), 2.19–1.99 (m, 4 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 141.30, 140.90, 136.80, 133.47, 128.54, 128.39, 126.34, 126.22, 122.38, 120.61, 119.41, 108.45, 93.98, 42.10, 33.11, 29.72 ppm. IR (ATR): $\tilde{\nu}$ = 3024 (w), 2924 (w), 1593 (s), 1497 (m), 1464 (s), 1452 (s), 1435 (m), 1408 (m), 1387 (m), 1356 (m), 1315 (s), 1250 (s), 1227 (m), 1207 (m), 1194 (m), 1174 (m), 1163 (m), 1149 (m), 1124 (m), 1111 (m), 1088 (m), 1070 (m), 1028 (m), 1016 (m), 1009 (m), 928 (w), 831 (m), 768 (m), 742 (vs), 729 (vs), 694 (vs), 615 (m), 584 (m), 575 (m), 557 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%) = 493 (100), 388 (48), 269 (18), 69 (23), 44 (38). HRMS (ESI): calcd. for $C_{35}H_{31}N_3$ $[M + H]^+$ 494.25907, found 494.25922; calcd. for $C_{35}H_{31}N_3Na$ $[M + Na]^+$ 516.24102, found 516.2405.

5,7-Dicyclohexyl-5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindole (5t): Following general procedure B and using compound **3** (100 mg, 0.18 mmol) and cyclohexylamine (127 μL, 1.09 mmol) gave a crude product, which was purified by flash chromatography (silica gel; heptanes/dichloromethane/ethyl acetate, 5:1:1) to yield **5t** (42 mg, 55%) as a white solid; m.p. 277–279 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, J = 7.7 Hz, 2 H), 7.58 (s, 2 H), 7.47–7.36 (m, 4 H), 7.23 (ddd, J = 7.9, 6.0, 2.1 Hz, 2 H), 5.19–5.03 (m, 2 H), 2.42–1.63 (m, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.81, 137.05, 132.62, 126.12, 122.85, 120.83, 119.21, 109.65, 96.35, 55.93, 28.96, 25.48 ppm. IR (ATR): $\tilde{\nu}$ = 2928 (m), 2854 (m), 1591 (m), 1485 (m), 1454 (m), 1416 (m), 1404 (m), 1377 (m), 1344 (m), 1327 (m), 1304 (m), 1250 (m), 1225 (s), 1188 (s), 1155 (m), 1142 (m), 1126 (m), 1117 (m), 1072 (m), 1057 (m), 1028 (m), 1012 (m), 968 (m), 893 (m), 837 (m), 742 (s), 729 (vs), 700 (m), 658 (m), 594 (m), 577 (s), 532 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%) = 421 (100), 256 (31), 55 (22). HRMS (EI): calcd. for $C_{29}H_{31}N_3$ $[M]^+$ 421.25125, found 421.25089.

Computational Methods: All calculations were carried out by using Gaussian 09, Revision C.01.[23] The geometry of the 5,7-dihydropyrido[3,2-*b*:5,6-*b*′]diindoles was optimized without any symmetry constraints at the B3LYP/6-31G* level of theory.[24] The optimized geometry of each was confirmed as minima by frequency calculations at the same level (zero imaginary frequency). The B3LYP method consists of the three hybrid exchange functional of Becke[25] combined with the correlation function of Lee, Yang, and Parr (LYP),[26] and it provides a nice balance between cost and accuracy. The B3LYP/6-31G* level of theory was applied to the

study of the geometric and electronic properties of neutral[19] and charged systems,[27] which includes simple molecular to large polymeric structures.[28] The molecular orbitals were also simulated at the B3LYP/6-31G* level of theory.

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization of new compounds, and copies of the ^{1}H and ^{13}C NMR spectra.

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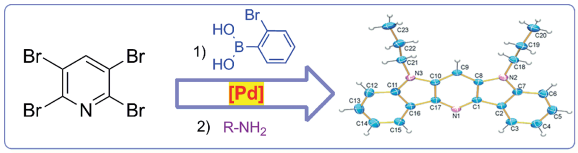

5,7-Dihydropyrido[3,2-*b*:5,6-*b*′]diindoles were prepared by a highly efficient two-step synthesis that involved a site-selective Suzuki coupling reaction of 2,3,5,6-tetrabromopyridine and a subsequent Pd-catalyzed cyclization that proceeded through a twofold C–N coupling reaction with aromatic and aliphatic amines. R = *n*-C_3H_7.

Keywords: Nitrogen heterocycles / Cross-coupling / Cyclization / Electrochemistry / UV/Vis spectroscopy / Fluorescence spectroscopy

