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χ-Shaped Bis(areno)-1,4-dihydropyrrolo[3,2-*b*]pyrroles Generated by Oxidative Aromatic Coupling

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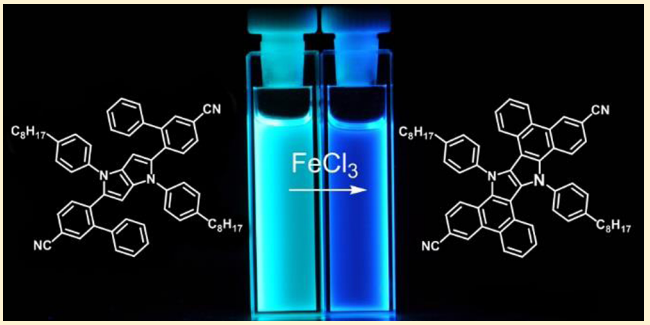
Supporting Information

ABSTRACT: A synthesis of dihydropyrrolo[3,2-*b*]pyrroles fused with two peripheral arenes or heterocyclic units has been realized through the concise route. These nearly planar compounds were prepared starting from assembling the central core via condensation of 2-aryl or 2-heteroarylbenzaldehydes with aromatic amines and diacetyl, followed by double intramolecular oxidative aromatic coupling. This two-step procedure afforded the desired products in overall yields of 5−36%, and it tolerates structural diversity of starting materials. All the final dyes exhibit strong blue fluorescence in solution.



Polycyclic aromatic hydrocarbons (PAHs)[1−5] and their heterocyclic analogues possessing π-expanded structures[6−21] are undergoing a renaissance due to their potential applications in the field of organic electronics, such as organic light emitting diodes (OLEDs),[22,23] organic field effect transistors (OFETs)[24,25] as well as dye-sensitized solar cells.[26] Particular contributions in this ongoing development have ladder-type compounds.[9−19] In contrast to linear heteroacenes, which have been investigated for a long time,[27,28] ladder-type heterocycles became widely studied rather recently.[29−34] A vast majority of known heteroacenes belonging to heteropentalenes family are built on the thieno[3,2-*b*]thiophene, as well as on thieno[3,2-*b*]pyrrole cores.[35−40] In contrast, 1,4-dihydropyrrolo[3,2-*b*]pyrroles (DHPP) are much less investigated.[41,42] Very recently novel methodologies for the synthesis of tetraaryl-pyrrolo[3,2-*b*]pyrroles (TAPP)[43,44] and indolo[3,2-*b*]indoles were discovered.[45,46] Herein we would like to present a straightforward and efficient methodology for the synthesis of χ-shaped π-expanded 1,4-dihydropyrrolo[3,2-*b*]pyrroles together with their photophysical properties.

Oxidative aromatic coupling has a potential to furnish unprecedented polycyclic aromatic compounds.[47] Conditioning that reacting positions possess reasonable electron-density, >100 C−C bonds can be formed at once.[48] We reasoned that intrinsically electron-excessive positions 3 and 6 of 1,4-dihydropyrrolo[3,2-*b*]pyrrole core offer an ideal, electron-rich reacting site. To prove this hypothesis, reaction of commercially available biphenyl-2-carboxaldehyde (**1a**) with 4-*tert*-butylaniline (**2a**) and diacetyl (**3**) in the presence of catalytic amount of TsOH afforded the desired product **4a** in 48% yield (Table 1), which was subjected to intramolecular oxidative aromatic coupling.[49] The use of the classical one-electron oxidant, i.e., iron(III) chloride, smoothly gave π-expanded DHPP **5a** in 75% yield. Its structure was confirmed by X-ray crystallography (Figure 1).

It is noteworthy that the molecular structure of polycyclic ring system of compound **5a** is slightly tilted from planarity at phenathrene moieties, owing to the reasons, which are unclear at the moment (Figure 1).

Once the synthetic protocol was established, we were able to synthesize the library of π-expanded pyrrole[3,2-*b*]pyrroles **5a−g**. To obtain series of 2-aryl and 2-heteroarylbenzaldehydes **1b−f** as well as 3-phenylthiophene-2-carboxaldehyde (**1g**) we employed two methodologies namely Suzuki coupling[50] and direct arylation reaction.[51] Aldehydes **1b**, **1c**, **1f** and **1g** were synthesized via Suzuki coupling utilizing either 2-bromo-4-cyanobenzaldehyde, 2-bromobenzaldehyde with corresponding boronic acid, or 2-formylphenylboronic acid with corresponding bromide. Compound **1g** was obtained from 3-bromothiophene-2-carbaldehyde. Aldehydes **1d** and **1e** were synthesized employing direct arylation protocol utilizing 2-bromobenzaldehyde (see Experimental Section). Having these starting materials, the set of 1,4-dihydropyrrolo[3,2-*b*]pyrroles was obtained in yields up to 48% (Table 1). In different example heterocyclic aldehyde **1g** undergoes the reaction of formation TAPP, however in much lower yield (only 10%) (Scheme 1). These compounds were subsequently transformed into π-expanded DHPPs via oxidative aromatic coupling reaction mediated by iron(III) chloride in nitromethane. We were delighted to find that in all cases oxidation smoothly afforded desired products in yields ranging from 45 to 80%. 4-*tert*-Butylaniline (**2a**) was chosen as the building block imparting reasonable solubility. Bulky *t*-butyl groups should have prevented from π-stacking observed in a large planar aromatic systems, which is responsible for decreasing their solubility. It turned out that in two cases solubility of final product was so

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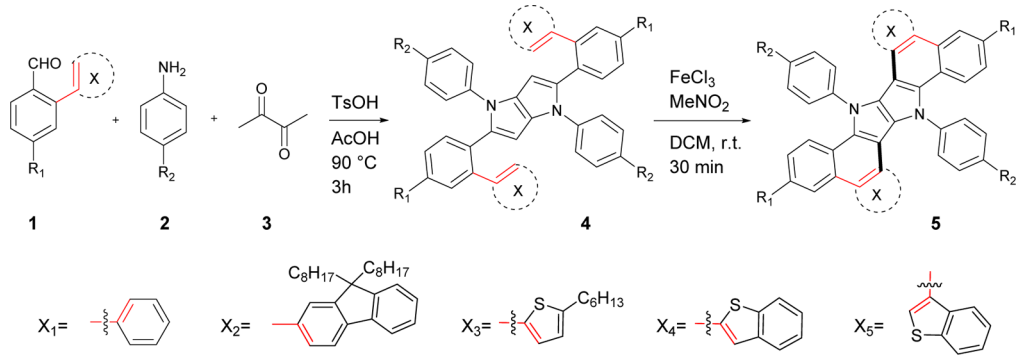
Table 1. General Method for the Synthesis of π-Expanded DHPP 5a–g



aldehyde	R^1	X	amine	R^2	TAPP	yield (%)	π-exp DHPP	yield (%)
1a	H	X_1	**2a**	*t*-butyl	**4a**	48	**5a**	75
1b	CN	X_1	**2b**	*n*-octyl	**4b**	33	**5b**	80
1c	H	X_2	**2a**	*t*-butyl	**4c**	25	**5c**	46
1d	H	X_3	**2a**	*t*-butyl	**4d**	37	**5d**	70
1e	H	X_4	**2a**	*t*-butyl	**4e**	38	**5e**	63
1f	H	X_5	**2b**	*n*-octyl	**4f**	40	**5f**	68

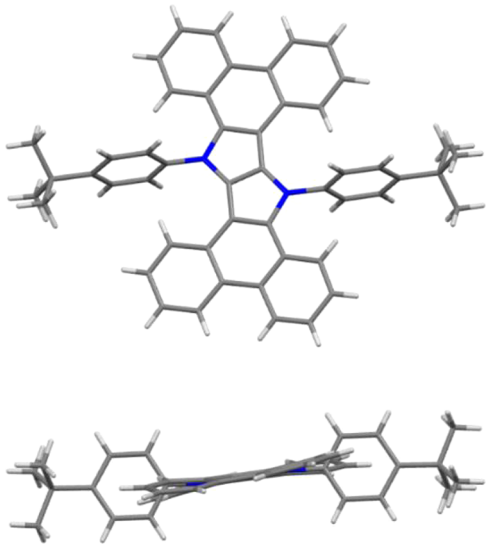
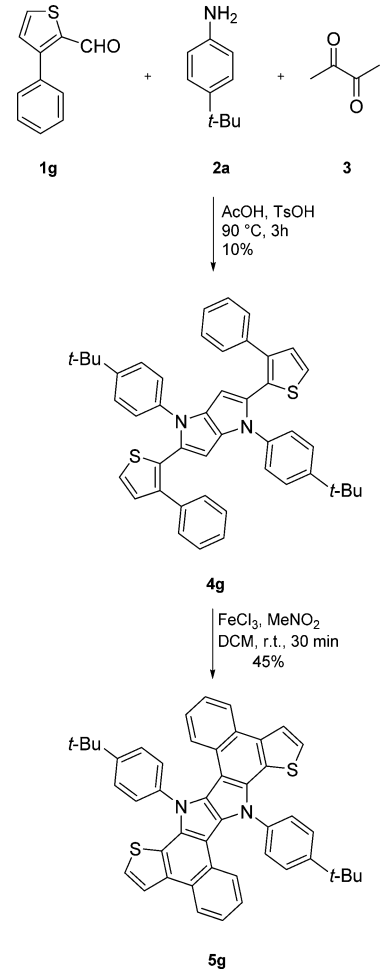


Figure 1. Molecular structure of compound **5a**.

Scheme 1. Synthesis of Compound 5g



low in common organic solvents that decent ^{1}H NMR spectra could not be recorded. Facing such a problem we decided to use 4-*n*-octylaniline (**2b**) instead. Fortunately, synthesis of compounds possessing longer alkyl chain (**5b** and **5f**) entailed appreciable improvement of solubility, and we were able to obtain full set of analyses.

The optical properties of both parent TAPPs and their π-expanded analogues was subsequently investigated (Table 2, Figures 2 and 3). All examined TAPPs possessed absorption bands, which were typically located between 350 and 400 nm, in agreement with data reported earlier.[43,44] All investigated TAPPs have maximum emission in the range from 439 to 524 nm, which corresponds to blue, cyan and green light. Intriguingly, dyes **4e** and **4f** which could be considered as regioisomers, differ significantly regarding their emission spectra (Figure 2). Compound **4e** emits green light (λ_{max} = 524 nm), while **4f** emits blue light (λ_{max} = 439 nm). This is related to the difference in the excited state geometry of both compounds. Smaller steric hindrance in dye **4e** allows for planarization of the molecule in the excited state, which translates to emission at longer wavelength. Generally TAPPs **4a–c** which did not possess sulfur atom in their structure exhibited very high fluorescence quantum yield Φ_{fl} = 80–84%.

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Table 2. Spectroscopic Properties of Synthesized Dyes

cmpd.	λ_{abs} [nm]	λ_{em} [nm]	Stokes shift [cm^{-1}]	ε_{max} [M^{-1} cm^{-1}]	Φ_{fl}[a]
4a	350	452	6400	21 000	0.84
4b	404	482	4000	31 000	0.80
4c	362	481	6800	19 000	0.81
4d	353	471	7100	18 000	0.16
4e	368	524	8100	12 000	0.18
4f	349	439	5900	20 000	0.23
4g	363	481	6800	22 000	0.23
5a	372	428	3500	39 000	0.45
5b	421	440	1000	86 000	0.68
5c	416	460	2300	15 000	0.39
5d	375	430	3400	38 000	0.11
5e	419	436	900	13 000	0.12
5f	393	422	1700	13 000	0.25
5g	404	420	900	39 000	0.62

[a]Determined with quinine sulfate in H_2SO_4 (0.5M) as a standard.

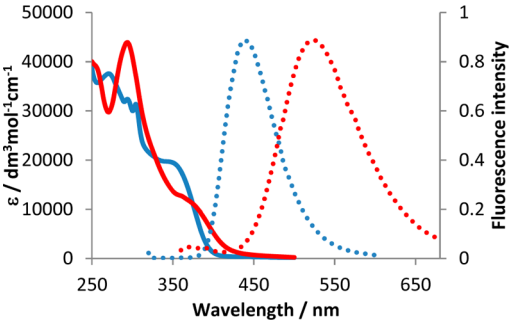

Figure 2. Absorption (solid) and emission (dotted) spectra of compounds **4e** (red line) and **4f** (blue line) measured in dichloromethane.

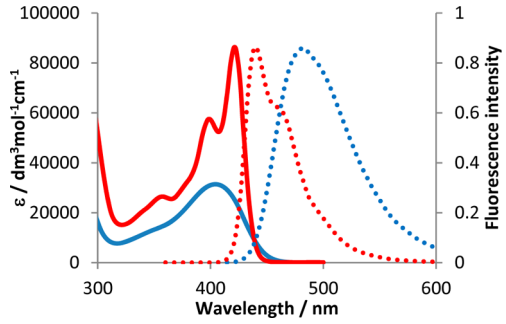

Figure 3. Absorption (solid) and emission (dotted) spectra of compounds **4b** (blue line) and **5b** (red line) measured in dichloromethane.

Dramatic decrease of these values was observed for compounds **4d–g** bearing thiophene moieties (Φ_{fl} = 16–23%).

Extension of the conjugation in π-expanded DHPPs resulted in bathochromic shift of absorption (λ_{max} = 372–421 nm) for all compounds. The angular connectivity between rings is responsible for the fact that this shift is rather moderate. Absorption maxima correspond well with values reported for indolo[3,2-*b*]indoles,[45,46] diindolo[2,3-*b*:2′,3′-*f*]pyrrole[3,2-*b*]-pyrroles,[52] and dithienothieno[2,3-*d*:2′,3′-*d*′]-benzo[1,2-*b*:4,5-*b*′]dithiophenes.[31] Not surprisingly, π-expanded DHPPs display higher values of molar extinction coefficients in the range of 13 000–86 000 M^{-1} cm^{-1}. Distinct difference could be seen by comparison ε values of the dyes **4b** and **5b** which equal 31 000 and 86 000 M^{-1} cm^{-1}, respectively (Figure 3, Table 2). All synthesized π-expanded DHPPs are blue emitters (λ_{max}= 420–460 nm). For dyes **5a–g** hypsochromic shift of the emission (17–88 nm) were observed compared to their parent TAPPs (Table 2). This is very unusual phenomenon since in all known analogous cases, forming C–C bonds and planarization of the molecule caused bathochromic shift of emission.[53,54] Indeed, in some cases the bathochromic shift of fluorescence resulting from closing two aromatic rings via oxidative aromatic coupling was ∼100 nm.[53] The origin of this unexpected phenomenon lies probably in the fact that the dihedral angle between main chromophore and *N*-aryl substituent is close to 90° in compound **5a** (Figure 1), while in various 1,2-diarylindoles it is in the range 67–72°.[55–57] Detailed studies performed by Rettig and co-workers for sterically hindered and unhindered *N*-arylpyrroles clearly shown that absorption for the latter ones (where dihedral angle has to be larger in the ground state) is strongly hypsochromically shifted versus *N*-phenylpyrrole.[58] We think that analogous phenomenon occurs in our case of which results in miniscule bathochromic shift of absorption of **5a–f** versus **4a–f** (Table 2). The same steric hindrance also decreases the possibility for planarization in the excited state, hence emission of **5a–f** is hypsochromically shifted. Fluorescence quantum yields of π-expanded DHPPs decreased significantly in comparison to their parent TAPPs, except for compounds **5g** for which this value increased (Φ_{fl} = 62% compared to **4g** Φ_{fl} = 23%) and **5f** for which Φ_{fl} negligibly increased (Φ_{fl} = 25% compared to **4f** Φ_{fl} = 23%). Different structural features of compounds **4g** and **5g** versus remaining dyes **4a–f** and **5a–f** (i.e., the presence of two thiophene moieties instead of two benzene rings, at peripheral positions) are plausible rationale behind this phenomenon.

Heteroacenes are significant scaffolds in the field of organic electronics.[45,59] It prompted us to undertake an investigation of the electrochemical properties of selected π-expanded DHPP (Table 3, Supporting Information). All investigated compounds

Table 3. Redox Potentials of Selected Compounds[a]

cmpd.	$E^{1/2}_{ox1}$ [V]	$E^{1/2}_{ox2}$ [V]	E_{HOMO} [eV]
5a	0.22	0.84	−5.02
5b	0.50	1.03 (irreversible)	−5.30
5c	0.16	0.76	−4.96
5d	0.24	0.84	−5.04
5f[b]	0.35	0.81	−5.15
5g	0.09	0.67	−4.89

[a]Potentials are given relative to Fc/Fc+. [b]The scan rate ν = 250 mV s^{-1}

relatively easy to oxidize and, with the exception of **5b**, underwent two reversible oxidations. In the latter case the second process was irreversible. The HOMO energy levels were estimated from the first oxidation potentials (Table 3). In principle, they are on similar level ((−4.9)–(−5.3)) as for other heteroacenes bearing dihydropyrrolo[3,2-*b*]pyrrole core,[44–46] slightly higher than the corresponding values for *S*,*N*-heterohexacenes reported by Bäuerle and Würthner,[34] and slightly lower than for diindolo[2,3-*b*:2′,3′-*f*]pyrrolo[3,2-*b*]-pyrroles reported earlier by our group.[52]

Finally, differential scanning calorimetry (DSC) measurement performed for exemplary compound **5b** has proven that this dye is stable up to 270 °C.

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In conclusion, intramolecular oxidative aromatic coupling of electron-rich dihydropyrrolo[3,2-*b*]pyrroles proved to be an efficient strategy for assembling χ-shaped π-expanded systems[60] possessing up to 12 conjugated rings.[61] The approach presented here is general and thus can be used to prepare even larger structures and to install different functional groups on the periphery of such π-expanded dyes. The analysis of the absorption and emission spectra of dihydropyrrolo[3,2-*b*]-pyrroles and π-expanded analogues revealed that planarization of the structures caused rather unusual changes such as hypsochromic shift of emission and decrease in fluorescence quantum yield.

EXPERIMENTAL SECTION

General Remarks. All reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes) were distilled prior to use. DMF was dried over magnesium sulfate and then distilled and stored under argon. Transformations with moisture and oxygen sensitive compounds were performed under a stream of argon. The reaction progress was monitored by means of thin layer chromatography (TLC), which was performed on aluminum foil plates, covered with Silica gel 60 F_{254} or Aluminum oxide 60 F_{254} (neutral). Products purification was done by means of column chromatography with Kieselgel 60 or Aluminum oxide. Occasionally, dry column vacuum chromatography (DCVC) for purification of products obtained was performed using Silica gel Type D 5F. The identity and purity of prepared compounds were proved by ^{1}H NMR and ^{13}C NMR spectrometry as well as by MS-spectrometry (via EI-MS or ESI-MS). For HRMS measurements both quadruple and TOF mass analyzer types were used. NMR spectra were measured on 500 MHz, 600 or 400 MHz instruments with TMS as internal standard. All chemical shifts are given in ppm. All melting points for crystalline products were measured with automated melting point apparatus and were given without correction. The absorbance and fluorescence spectra were measured in dichloromethane.

Linear Optical Measurements. Steady-state fluorescence measurements were performed with dilute solutions (10^{-6} M, optical density <0.1) contained in standard 1 cm quartz cuvettes at room temperature. Compounds were dissolved in dichloromethane unless otherwise noted. Emission spectra were obtained, for each compound, under excitation at λ = 350 nm. Fluorescence quantum yields were measured by using quinine hemisulfate monohydrate in 0.5m sulfuric acid as a standard.

Electrochemistry. The cyclic voltammograms of compounds **5a**–**5d** and **5f**–**5g** were measured at 20 °C, under argon atmosphere, in deoxygenated 0.1 M solutions of tetrabutylammonium hexafluorophosphate in anhydrous dichloromethane. Glassy carbon working electrode, Ag/AgCl reference electrode and auxiliary platinum foil were used, while the scan rate for presented voltammograms was v = 50 mVs^{-1}. All reported values of E [V] are in respect to Fc^+/Fc redox potential. In case of **5b**, the second oxidation process remains irreversible irrespective of the value of v (50–1000 mVs^{-1}). For **5f**, voltammetric curves recorded at v = 50 mVs^{-1}, reveal two anodic peaks located at E_a = 0.39 and 0.88 V, followed by two overlapping cathodic peaks with a visible current maximum at 0.35 V. At higher scan rates, cathodic peaks resolve and both of the values of $E^{1/2}{}_{ox}$ could be determined.

Method A: Suzuki Coupling I. *General Procedure for the Synthesis of **1b**, **1f** and **1g**.* 2-Bromo-4-cyanobenzaldehyde/2-bromobenzaldehyde/3-bromothiophene-2-carbaldehyde (10 mmol), phenylboronic acid/benzo[*b*]thien-3-ylboronic acid (11 mmol), K_2CO_3 (20 mmol), PPh_3 (20% mol), $Pd(OAc)_2$ (10% mol) were placed in a 25 mL Schlenk flask, which was flushed with argon prior to use. Then 16 mL of 1:1 v/v mixture of toluene and water was added, and the resulting mixture was stirred at 80 °C for 16 h. Then 15 mL of water was added, and resulting mixture was stirred for another 15 min. Two phases were separated, water phase was extracted with toluene (3 × 10 mL). Organic phases were combined and dried, solvent was evaporated and crude products were purified by means of flash column chromatography.

Method B: Suzuki Coupling II. *Procedure for the Synthesis of **1c**.* 2-Bromo-9,9-dioctyl-9*H*-fluorene (10 mmol), 2-formylphenylboronic acid (11 mmol), K_2CO_3 (20 mmol), PPh_3 (20% mol), $Pd(OAc)_2$ (10% mol) were placed in a 25 mL Schlenk flask, which was flushed with argon prior to use. Then 16 mL of 1:1 v/v mixture of toluene and water was added, and the resulting mixture was stirred at 80 °C for 16 h. Then 15 mL of water was added, and resulting mixture was stirred for another 15 min. Two phases were separated, water phase was extracted with toluene (3 × 10 mL). Organic phases were combined and dried, solvent was evaporated and crude product was purified by means of flash column chromatography.

Method C: Direct Arylation. *General Procedure for the Synthesis of **1d** and **1e**.* 2-Bromobenzaldehyde (10 mmol), 2-*n*-hexylthiophene/benzothiophene (20 mmol), KOAc (30 mmol), and $PdCl(C_3H_5)$(dppb) (0.1 mmol) were placed in a 25 mL Schlenk flask, which was flushed with argon prior to use. Then 8 mL of dry DMA was added and the resulting mixture was stirred at 150 °C for 20 h. Then 15 mL of water was added and resulting mixture was stirred for another 15 min. Two phases were separated, water phase was extracted with toluene (3 × 10 mL). Organic phases were combined and dried, solvent was evaporated and crude products were purified by means of flash column chromatography.

*5-Cyano-[1,1′-biphenyl]-2-carbaldehyde (**1b**).* White solid. Yield 1.86 g (90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.10 (dd, 1H), 7.79–7.75 (m, 2H), 7.55–7.50 (m, 3H), 7.40–7.35 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.8, 146.2, 136.3, 135.4, 134.5, 130.9, 129.9, 129.1, 128.9, 128.3, 117.7, 116.8. HRMS (EI) calcd for $C_{14}H_9NO$ 207.0684 [M+], found 207.0679.

*2-(9,9-Dioctyl-9H-fluoren-2-yl)benzaldehyde (**1c**).* White solid. Yield 2.91 g (59%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.05 (dd, *J* 7.8, 1.0 Hz, 1H), 7.78 (d, *J* 7.6 Hz, 1H), 7.76–7.73 (m, 1H), 7.66 (dt, *J* 7.7, 1.4 Hz, 1H), 7.54–7.48 (m, 2H), 7.38–7.31 (m, 5H), 2.03–1.93 (m, 4H), 1.23–1.00 (m, 20H), 0.81 (t, *J* 7.0 Hz, 6H), 0.71–0.62 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4, 151.1, 151.0, 146.5, 141.2, 140.3, 136,3, 134.0, 133.4, 130.9, 129.0, 127.61, 127.58, 127.5, 126.9, 124.7, 123.0, 120.0, 119.6, 55.2, 40.3, 31.7, 30.0, 29.18, 29.16, 23.8, 22.6, 14.0. HRMS (EI) calcd for $C_{36}H_{46}O$ 494.3549 [M+], found 494.3544.

*2-(5-Hexylthiophen-2-yl)benzaldehyde (**1d**).* Yellow oil. Yield 2.07 g (76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.21(s, 1H), 7.98 (dd, *J* 7.7, 1.2 Hz, 1H), 7.58 (dt, *J* 7.3, 1.2 Hz, 1H), 7.52 (dd, *J* 7.8, 1.0 Hz, 1H), 7.46–7.42 (m, 1H), 6.86 (d, *J* 3.5 Hz, 1H), 6.83–6.80 (m, 1H), 2.86 (t, *J* 7.7 Hz, 2H), 1.72 (quint, *J* 7.6 Hz, 2H), 1.45–1.38 (m, 2H), 1.37–1.31 (m, 4H), 0.90 (t, *J* 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3, 148.6, 138.5, 136.0, 134.1, 133.4, 131.0, 129.4, 127.76, 127.74, 124.8, 31.58, 31.53, 30.2, 28.8, 22.5, 14.0. HRMS (EI) calcd for $C_{17}H_{20}OS$ 272.1235 [M$^+$], found 272.1237.

*2-(Benzo[b]thiophen-2-yl)benzaldehyde (**1e**).* Yellow oil. Yield 1.00 g (42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.06–8.03 (m, 1H), 7.89- 7.86 (m, 1H), 7.84–7.81 (m, 1H).

*2-(Benzo[b]thiophen-3-yl)benzaldehyde (**1f**).* Yellow oil. Yield 1.67 g (70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.10 (dd, *J* 7.9, 1.1 Hz, 1H), 7.96–7.93 (m, 1H), 7.69 (dt, *J* 7.5, 1.5 Hz, 1H), 7.58–7.54 (m, 1H), 7.54–7.50 (m, 2H), 7.43–7.35 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.9, 140.0, 139.34, 139.30, 134.9, 133.9, 133.4, 131.3, 128.4, 127.6, 126.4, 124.9, 122.85, 122.69. HRMS (EI) calcd for $C_{15}H_{10}OS$ 238.0452 [M+], found 238.0459.

*3-Phenylthiophene-2-carbaldehyde (**1g**).* Yellow oil. Yield 1.39 g (74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.74 (d, *J* 4.9 Hz, 1H),7.51–7.43 (m, 5H), 7.23 (d, *J* 5.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.2, 151.4, 138.5, 134.05, 133.96, 130.6, 129.6, 128.80, 128.78. HRMS (EI) calcd for $C_{11}H_8OS$ 188.0296 [M+], found 188.0290.

General Procedure for the Synthesis of DHPPs (4a–g). In a 25 mL round-bottom flask equipped with a reflux condenser and magnetic stir bar, 5 mL glacial acetic acid was placed followed by the addition of arylamine (6 mmol), aldehyde (6 mmol) and TsOH (0.6

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mmol). The mixture was stirred at 90 °C for 30 min. After that time butane-2,3-dione (3 mmol) was slowly added via syringe and the resulting mixture was stirred at 90 °C for 3 h. The reaction mixture was then cooled to room temperature. The precipitate of the obtained dye was then filtered off and washed with cooled glacial acetic acid. Recrystallization from AcOEt and drying under vacuum afforded pure product.

*2,5-Di([1,1′-biphenyl]-2-yl)-1,4-bis(4-(tert-butyl)phenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**4a**).* Pale yellow solid. Yield 972 mg (48%). R_f = 0.68 (SiO_2, DCM/hexanes, 1:2). mp 352−354 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62−7.58 (m, 2H), 7.38−7.32 (m, 4H), 7.20−7.17 (m, 2H), 7.11−7.06 (m, 2H), 7.02−6.96 (m, 8H), 6.62 (dd, 4H), 6.50 (dd, 4H), 6.20 (s, 2H), 1.29 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 141.3, 141.0, 136.7, 134.1, 132.7, 131.1, 130.0, 129.3, 128.3, 127.6, 127.4, 127.2, 125.8, 125.0, 122.4, 95.7, 34.3, 31.4. HRMS (EI) calcd for $C_{50}H_{46}N_2$ 674.3661 [M+], found 674.3674. Anal. Calcd for $C_{50}H_{46}N_2$: C, 88.98; H, 6.87; N, 4.15. Found: C, 89.03; H, 6.59; N, 4.07.

*2,5-Bis(5-cyano-[1,1′-biphenyl]-2-yl)-1,4-bis(4-octylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**4b**).* Yellow solid. Yield 828 mg (33%). R_f = 0.42 (SiO_2, DCM/hexanes, 1:1). mp 210−211 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* 8.0 Hz, 2H), 7.61 (dd, *J* 8.0, 1.2 Hz, 2H), 7.46 (d, *J* 0.9 Hz, 2H), 7.16 (dd, *J* 7.4, 7.4 Hz, 2H), 7.05 (dd, *J* 7.7, 7.7 Hz, 4H), 6.84 (dd,4H), 6.61 (dd, 4H), 6.43 (dd, 4H), 6.20 (s, 2H), 2.53 (t, *J* 7.6 Hz, 4H), 1.64−1.54 (m, 4H), 1.40−1.25 (m, 20H), 0.91 (t, *J* 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 139.7, 139.2, 137.0, 136.3, 133.8, 133.2, 131.5, 130.65, 130.63, 128.6, 128.1, 127.9, 126.9, 122.8, 118.9, 111.2, 96.5, 35.3, 31.9, 31.7, 29.5, 29.34, 29.27, 22.7, 14.1. HRMS (EI) calcd for $C_{60}H_{60}N_4$ 836.4818 [M+], found 836.4836. Anal. Calcd for $C_{60}H_{60}N_4$: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.26; H, 7.32; N, 6.46.

*1,4-Bis(4-(tert-butyl)phenyl)-2,5-bis(2-(9,9-dioctyl-9H-fluoren-2-yl)phenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**4c**).* Yellow solid. Yield 991 mg (25%). R_f = 0.72 (SiO_2, DCM/hexanes, 1:4). mp 175−177 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* 7.6 Hz, 2H), 7.44 (d, *J* 7.3 Hz, 2H), 7.32−7.27 (m, 10H), 7.25−7.19 (m, 4H), 7.03 (dd, 4H), 6.89 (s, 2H), 6.64 (dd, 4H), 6.57 (d, *J* 7.7 Hz, 2H), 6.05 (s, 2H), 1.78−1.68 (m, 4H), 1.62−1.54 (m, 4H), 1.31 (s, 18H), 1.15 (quint, *J* 7.2 Hz, 8H), 1.10−0.86 (m, 36H), 0.79 (t, *J* 7.1 Hz, 12H), 0.72−0.54 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1, 150.3, 147.0, 141.7, 141.0, 140.7, 138.6, 137.4, 134.1, 132.4, 131.9, 130.6, 130.0, 127.4, 127.1, 126.7, 126.6, 126.4, 125.2, 123.3, 123.2, 123.0, 119.4, 118.8, 95.9, 54.6, 39.6, 34.3, 31.8, 31.46, 30.0, 29.3, 29.2, 23.9, 22.6, 14.0. HRMS (ESI-TOF) calcd for $C_{96}H_{118}N_2Na$ 1321.9193 [M+], found 1321.9167. Anal. Calcd for $C_{96}H_{118}N_2$: C, 88.70; H, 9.15; N, 2.15. Found: C, 88.53; H, 9.19; N, 2.13.

*1,4-Bis(4-(tert-butyl)phenyl)-2,5-bis(2-(5-hexylthiophen-2-yl)-phenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**4d**).* Yellow solid. Yield 948 mg (37%). R_f = 0.74 (SiO_2, DCM/hexanes, 1:2). mp 204−205 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60−7.56 (m, 2H), 7.32−7.26 (m, 6H), 7.03 (dd, 4H), 6.70 (dd, 4H), 6.42 (dd, 2H), 6.29 (s, 2H), 6.07 (d, *J* 3.6 Hz, 2H), 2.66 (t, *J* 7.6 Hz, 4H), 1.61 (quint, *J* 7.6 Hz, 4H), 1.40−1.22 (m, 30H), 0.88 (t, *J* 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 145.9, 140.4, 136.6, 135.1, 134.0, 132.3, 131.6, 129.5, 129.3, 127.7, 126.9, 124.99, 124.96, 123.7, 122.6, 95.5, 34.2, 32.0, 31.6, 31.4, 30.1, 28.9, 22.6, 14.1. HRMS (ESI-TOF) calcd for $C_{58}H_{66}N_2S_2Na$ 877.4565 [M+Na$^+$], found 877.4563. Anal. Calcd for $C_{58}H_{66}N_2S_2$: C, 81.45; H, 7.78; N, 3.28, S, 7.50. Found: C, 81.21; H, 7.58; N, 3.14, S, 7.46.

*2,5-Bis(2-(benzo[b]thiophen-2-yl)phenyl)-1,4-bis(4-(tert-butyl)-phenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**4e**).* Yellow solid. Yield 897 mg (38%). R_f = 0.50 (SiO_2, DCM/hexanes, 1:2). mp 329−331 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* 7.9 Hz, 2H), 7.62 (dd, *J* 7.0, 1.4 Hz, 2H), 7.58 (d, *J* 7.8 Hz, 2H), 7.44−7.33 (m, 6H), 7.29−7.25 (m, 2H), 7.25−7.20 (m, 2H), 6.86 (dd, 4H), 6.56 (dd, 4H), 6.48 (s, 2H), 6.29 (s, 2H), 1.25 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 143.6, 140.8, 140.2, 136.5, 134.4, 133.6, 133.0, 131.6, 130.0, 129.8, 128.2, 127.8, 125.1, 123.8, 123.6, 123.4, 122.6, 121.9, 121.7, 96.0, 34.3, 31.3. HRMS (EI) calcd for $C_{54}H_{46}N_2S_2$ 786.3102 [M+], found 786.3100.

*2,5-Bis(2-(benzo[b]thiophen-3-yl)phenyl)-1,4-bis(4-octylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**4f**).* Pale yellow solid. Yield 1.08 g (40%). R_f = 0.68 (SiO_2, DCM/hexanes, 1:4). mp 188−190 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* 8.0 Hz, 2H), 7.67 (dd, *J* 7.0, 1.2 Hz, 2H), 7.42−7.32 (m, 6H), 7.24−7.16 (m, 4H), 7.09 (dd, *J* 7.5, 7.5 Hz, 2H), 6.56−6.50 (m, 6H), 6.46 (AA′XX, 4H), 6.15 (s, 2H), 2.26 (t, *J* 7.7 Hz, 4H), 1.43 (quint, *J* 6.9 Hz, 4H), 1.35−1.23 (m, 20H), 0.90 (t, *J* 6.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 139.0, 138.0, 136.6, 136.0, 134.9, 133.98, 133.97, 131.2, 130.0, 129.4, 127.9, 127.5, 127.2, 123.9, 123.4, 122.44, 122.35, 121.9, 95.8, 35.1, 31.9, 31.1, 29.50, 29.49, 29.3, 22.7, 14.1. HRMS (ESI) calcd for $C_{62}H_{62}N_2S_2Na$ 921.4252 [M + Na]$^+$, found 921.4247. Anal. Calcd for $C_{62}H_{62}N_2S_2$: C, 82.80; H, 6.95; N, 3.12, S, 7.13. Found: C, 82.42; H, 6.96; N, 3.00, S, 6.91.

*1,4-Bis(4-(tert-butyl)phenyl)-2,5-bis(3-phenylthiophen-2-yl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**4g**).* Pale yellow solid. Yield 206 mg (10%). R_f = 0.51 (SiO_2, DCM/hexanes, 1:4). mp 298−300 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* 5.3 Hz, 2H), 7.08−6.99 (m, 10H), 6.97 (d, *J* 5.3 Hz, 2H), 6.79 (dd, 4H), 6.68 (dd, 4H), 6.30 (s, 2H), 1.28 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 139.8, 136.5, 136.4, 130.28, 130.24, 129.3, 127.9, 127.8, 126.9, 126.0, 125.1, 124.6, 123.4, 96.0, 34.3, 31.4. HRMS (EI) calcd for $C_{46}H_{42}N_2S_2$ 686.2789 [M+], found 686.2792.

General Procedure for the Synthesis of π-Expanded DHPPs (5a−g). To a flushed with argon prior to use 50 mL round-bottom flask equipped with magnetic stir bar and septum, 12 mL of dry methylene chloride and 1 mmol of adequate TAPP were placed. To dissolved substrate, 20 mmol of ferric chloride dissolved in 12 mL of dry nitromethane were added via syringe. Reaction was conducted at room temperature for 30 min. Then 15 mL of water was added, and resulting mixture was stirred for another 15 min. Two phases were separated, water phase was extracted with methylene chloride (3 × 10 mL). Organic phases were combined and dried, solvent was evaporated and crude product was purified by means of flash column chromatography.

*9,18-Bis(4-(tert-butyl)phenyl)-9,18-dihydrodibenzo[e,g]dibenzo-[4,5:6,7]indolo[3,2-b]indole (**5a**).* Pale yellow solid. Yield 502 mg (75%). R_f = 0.61 (SiO_2, DCM/hexanes, 1:2). mp >400 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* 7.0 Hz, 2H), 8.63 (d, *J* 8.2 Hz, 2H), 7.76 (s, 8H), 7.60−7.32 (m, 6H), 7.24−7.16 (m, 2H), 6.96 (dd, *J* 7.4, 7.4 Hz, 2H), 6.75 (d, *J* 7.3 Hz, 2H), 1.60 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.4, 141.0, 130.6, 127.2, 127.0, 126.4, 125.8, 123.3, 123.0, 35.2, 31.7. HRMS (EI) calcd for $C_{50}H_{42}N_2$ 670.3348 [M+], found 670.3359. Anal. Calcd for $C_{50}H_{42}N_2$: C, 89,51; H, 6.31; N, 4.18, Found: C, 89.25; H, 6.22; N, 3.99.

*3,12-Difluoro-9,18-bis(4-octylphenyl)-9,18-dihydrodibenzo[e,g]-dibenzo[4,5:6,7]indolo[3,2-b]indole (**5b**).* Greenish solid. Yield 666 mg (80%). R_f = 0.38 (SiO_2, DCM/hexanes, 1:1). mp 308−309 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (s, 2H), 8.58 (d, *J* 8.3 Hz, 2H), 7.69 (d, *J* 7.8 Hz, 4H), 7.58 (d, *J* 7.8 Hz,4H), 7.52 (d, *J* 8.8 Hz, 2H), 7.45 (dd, *J* 7.5, 7.5 Hz, 2H), 7.38 (d, *J* 8.8 Hz, 2H), 7.07 (dd, *J* 7.6, 7.6 Hz, 2H), 6.87 (d, *J* 8.2 Hz, 2H), 2.95 (t, *J* 7.4 Hz, 4H), 1.89 (quint, *J* 7.2 Hz, 4H), 1.60−1.32 (m, 20H), 0.94 (t, *J* 6.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 140.3, 133.0, 131.6, 130.5, 129.2, 128.8, 127.4, 127.3, 127.2, 126.8, 126.6, 126.2, 124.5, 123.1, 122.7, 119.7, 110.1, 107.3, 36.0, 32.0, 31.9, 29.6, 29.40, 29.34, 22.7, 14.1. HRMS (EI+) calcd for $C_{60}H_{56}N_4$ 832.4505 [M+], found 832.4495. Anal. Calcd for $C_{60}H_{56}N_4$: C, 86.50; H, 6.78; N, 6.72. Found: C, 86.23; H, 6.76; N, 6.54.

*7,19-Bis(4-(tert-butyl)phenyl)-1,1,13,13-tetraoctyl-1,7,13,19-tetrahydrobenzo[g]benzo[6,7]fluoreno[3′,2′:4,5]indolo[3,2-b]-fluoreno[3,2-e]indole (**5c**).* Greenish solid. Yield 606 mg (46%). R_f = 0.78 (SiO_2, DCM/hexanes, 1:4). mp 202−203 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84−8.74 (m, 2H), 8.56 (s, 2H), 7.95−7.88 (m, 2H), 7.86 (dd, 4H), 7.81 (dd, 4H), 7.50−7.38 (m, 2H), 7.35−7.27 (m, 8H), 7.21−7.05 (m, 4H), 2.14−1.96 (m, 8H), 1.50 (s, 18H), 1.20−0.96 (m, 40H), 0.77 (t, *J* 7.0 Hz, 12H), 0.70−0.58 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9, 151.4, 146.3, 141.2, 141.1, 140.0, 134.4, 130.6, 130.4, 129.7, 127.2, 127.0, 126.9, 126.7, 126.5, 125.4, 124.7, 123.9, 122.7, 122.0, 121.0, 117.8, 117.0, 109.6, 54.7, 41.0, 35.2, 31.8, 31.5, 30.1, 29.21, 29.19, 23.8, 22.5, 14.01, 13.95. HRMS (ESI-TOF) calcd

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for $C_{96}H_{114}N_2Na$ 1317.8880 $[M + Na]^+$, found 1317.8861. Anal. Calcd for $C_{96}H_{114}N_2$: C, 88.97; H, 8.87; N, 2.16, Found: C, 88.75; H, 8.79; N, 2.16.

*8,16-Bis(4-(tert-butyl)phenyl)-2,10-dihexyl-8,16-dihydrobenzo[g]-benzo[6,7]thieno[3′,2′:4,5]indolo[3,2-b]thieno[3,2-e]indole (**5d**).* Yellow solid. Yield 596 mg (70%). R_f = 0.71 (SiO_2, DCM/hexanes, 1:2). mp 309−310 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, J 8.2, 0.9 Hz, 2H), 7.79−7.72 (m, 8H), 7.33−7.28 (m, 4H), 7.07 (ddd, J 6.9, 6.9, 1.1 Hz, 2H), 5.47 (s, 2H), 2.67 (t, J 7.5 Hz, 4H), 1.65−1.55 (m, 22H), 1.37−1.28 (m, 12H), 0.90 (t, J 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 144.4, 140.3, 133.6, 130.5, 130.4, 130.1, 128.5, 127.0, 126.9, 124.4, 124.1, 123.8, 122.9, 122.0, 106.8, 35.2, 31.9, 31.7, 31.6, 30.9, 28.7, 22.6, 14.1. HRMS (ES+) calcd for $C_{58}H_{62}N_2S_2Na$ 873.4252 $[M+Na^+]^+$, found 873.4249. Anal. Calcd for $C_{58}H_{62}N_2S_2$: C, 81.83; H, 7.34; N, 3.29, S, 7.53, Found: C, 81.94; H, 7.26; N, 3.09. S, 7.32.

*10,20-Bis(4-(tert-butyl)phenyl)-10,20-dihydrobenzo[g]benzo[4,5]-thieno[3,2-e]benzo[6,7]benzo[4′,5′]thieno[3′,2′:4,5]indolo[3,2-b]-indole (**5e**).* Yellow solid. Yield 493 mg (63%). R_f = 0.48 (SiO_2, DCM/hexanes, 1:2). mp >400 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (dd, J 8.0, 0.5 Hz, 2H), 7.80−7.75 (m, 2H), 7.64 (dd, J 8.4, 6.1 Hz, 4H), 7.53 (dd, 4H), 7.42−7.37 (m, 2H), 7.32 (dd, 4H), 7.13 (ddd, J 8.0, 8.0, 0.9 Hz, 4H), 6.73 (ddd, J 7.9, 7.9, 0.7 Hz, 2H), 1.31 (s, 18H).^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 139.0, 137.6, 137.2, 131.7, 129.2, 128.9, 126.6, 125.6, 125.5, 125.2, 124.3, 124.2, 123.6, 123.3, 122.8, 121.9, 121.5, 106.3, 34.7, 31.4. HRMS (EI) calcd for $C_{54}H_{42}N_2S_2$ 782.2789 [M+], found 782.2824.

*9,19-Bis(4-octylphenyl)-9,19-dihydrobenzo[g]benzo[4,5]thieno-[2,3-e]benzo[6,7]benzo[4′,5′]thieno[2′,3′:4,5]indolo[3,2-b]indole (**5f**).* Pale orange solid. Yield 608 mg (68%). R_f = 0.52 (SiO_2, DCM/hexanes, 1:4). mp 288−289 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (d, J 8.2 Hz, 2H), 8.77 (d, J 8.3 Hz, 2H), 7.80 (dd, 4H), 7.69 (d, J 7.8 Hz, 2H), 7.61 (dd, 5H), 7.50 (dd, J 7.3, 7.3 Hz, 3H), 7.34 (dd, J 7.3, 7.3 Hz, 2H), 7.25−7.20 (m, 4H), 3.00 (t, J 7.5 Hz, 4H), 1.97 (quint, J 7.5 Hz, 4H), 1.63 (quint, J 7.7 Hz, 4H), 1.57−1.48 (m, 4H), 1.47−1.33 (m, 12H), 0.93 (t, J 6.9 Hz, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 139.4, 139.1, 136.7, 131.4, 130.2, 124.4, 123.7, 123.6, 123.5, 122.4, 36.2, 32.4, 32.0, 29,7, 29.5, 29.4, 22.7, 14.1. HRMS (EI+) calcd for $C_{62}H_{58}N_2S_2$ 894.4041 [M+], found 894.4032. Anal. Calcd for $C_{62}H_{58}N_2S_2$: C, 83.18; H, 6.53; N, 3.13, S, 7.16. Found: C, 83.05; H, 6.56; N, 2.96. S, 6.91.

*8,16-Bis(4-(tert-butyl)phenyl)-8,16-dihydrobenzo[e]benzo[4,5]-thieno[3′,2′:6,7]indolo[3,2-b]thieno[3,2-g]indole (**5g**).* Orange solid. Yield 307 mg (45%). R_f = 0.37 (SiO_2, DCM/hexanes, 1:4). mp 350 °C (decomp). ^{1}H NMR (500 MHz, C_5D_5N) δ 8.60 (d, J 8.0 Hz, 2H), 8.21 (d, J 5.3 Hz, 2H), 7.94 (dd, 4H), 7.83 (dd, 4H), 7.54 (dd, J 7.1, 7.1 Hz, 2H), 7.45 (d, J 5.2 Hz, 2H), 7.26 (dd, J 8.1, 8.1 Hz, 2H), 7.22−7.20 (m, 2H), 1.52 (s, 18H). ^{13}C NMR (125 MHz, C_6D_5N) δ 154.6, 138.1, 134.5, 131.7, 130.1, 127.1, 126.6, 126.5, 126.2, 125.5, 124.9, 124.5, 123.9, 123.85, 123.82, 123.1, 123.0, 107.4, 35.3, 31.6. HRMS (EI) calcd for $C_{46}H_{38}N_2S_2$ 682.2476 [M+], found 682.2464.

*X-ray Crystallographic Data for **5a**.* Formula $C_{50}H_{42}N_2$, M_w = 670.86; triclinic, $P\bar{1}$, a = 9.1073(3) Å, b = 9.5689(3) Å, c = 12.2523(4) Å; V = 932.65(5) Å^3, Z = 1; D_x = 1.194 g cm^{-3}; R_1 = 0.0536 ($I > 2\sigma(I)$), wR_2 = 0.1459 (all data), GOF = 1.135.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental, absorption and emission spectra, cyclic voltammograms, and NMR spectra as well as crystallographic data for **5a** (CCDC 1036922) and differential scanning calorimetry data for **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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