

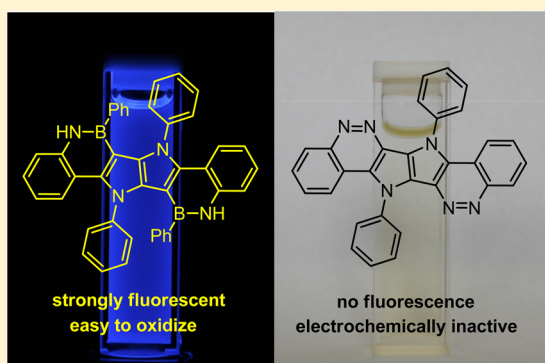
Synthesis and Properties of Ladder-Type BN-Heteroacenes and Diazabenzoindoles Built on a Pyrrolopyrrole Scaffold

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S Supporting Information

ABSTRACT: A simple, three-step synthesis of BN-heteroacenes and diazabenzoindoles based on the pyrrole[3,2-*b*]pyrrole scaffold has been developed. The incorporation of BN units has proven to be effective in modulating the electronic properties and molecular geometries of the π -conjugated backbone, creating a new type of heteroarenes. The unique planar structure and high rigidity of BN-compounds result in very high absorption coefficients and high fluorescence quantum yields, and, at the same time, very small Stokes shifts. A striking difference has been observed for a second type of derivatives: diazabenzoindoles, which remain virtually nonfluorescent, despite having a similar, rigid structure. The former class of heterocycles is characterized by a strong absorption around 400 nm and intense fluorescence observed in the 395–426 nm region, which results in very small Stokes shifts of less than 900 cm^{-1} .



INTRODUCTION

Given that tricoordinate boron represents a novel acceptor moiety for organic optoelectronic applications, the synthesis of polycyclic aromatic compounds with boron embedded in their structures has been a long sought goal.¹ Recent work by Yamaguchi,² Tovar,³ Kawashima,⁴ Liu,⁵ and others⁶ greatly simplified the access to boron-containing, ladder-type, or 2D aromatic hydrocarbons or heterocycles. Among many such π -conjugated systems, BN-embedded heteroacenes (taking advantage of the fact that B–N is isoelectronic with C=C) have recently emerged as interesting fluorescent platforms responding to the fluoride anion,⁷ and as materials exhibiting good charge transport and photoconductivity in optoelectronic applications.⁸ Heteroanalogues of anthracene,^{5b,c} graphene,⁹ and other hydrocarbons^{10,11} as well as compounds possessing a thiophene or furan core^{7a,12} with the BN motif incorporated are known, whereas, to the best of our knowledge, no such heteroacenes based on the pyrrole scaffold have been reported to date except for BN-indole.^{5d}

With respect to ladder-type heterocycles, compounds bearing the thiophene¹³ or preferably the thieno[3,2-*b*]thiophene moiety¹⁴ are favorite topics of research. This trend has been motivated by research applications such as organic semiconductors,¹⁵ organic solar cells,¹⁶ nonlinear optical materials,¹⁷ mechanosensitive membrane probes,¹⁸ open-shell singlet diradicaloids,¹⁹ liquid crystals,²⁰ etc.²¹ Large numbers of structurally interesting heteroacenes, such as dithieno[2,3-*d*:2',3'-*d'*]thieno[3,2-*b*:3',2'-*b'*]dipyrrole,²² dithienothieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophenes,²³ dibenzo-thiopheno[6,5-*b*:6',5'-*f'*]thieno[3,2-*b*]thiophene,²⁴ and benzo-[4',5']thieno[2',3':4,5]thieno[3,2-*b*]indole²⁵ have been synthesized and spectroscopically characterized, including impressive

syntheses of acenes containing up to 10²⁶ and even 21²⁷ fused arene rings.

In spite of the popularity of thiophene-based systems, ladder-type aromatic compounds bearing pyrrole²⁸ or even pyrrole-[3,2-*b*]pyrrole cores have emerged in the past five years as an independent area of research.²⁹ The multicomponent condensation leading directly to pyrrole[3,2-*b*]pyrroles that we developed in 2013³⁰ has the advantage, among many others, of leaving highly electron-rich positions 3 and 6 free, thus offering a unique possibility to quickly assemble large π -architectures, such as 7,14-dihydrobenzo[*g*]benzo[6,7]indolo[3,2-*b*]indoles (BBINs) (Figure 1).³¹

Building on this concept, we recently found, that 2,5-bis(2-nitrophenyl)-substituted tetraarylpyrrolo[3,2-*b*]pyrroles (TAPPs) are convenient starting materials in the synthesis of pyrrole-based ladder-type heteroacenes, such as diindolo[2,3-*b*:2',3'-*f'*]pyrrolo[3,2-*b*]pyrroles (DIPPs)³² and 7,14-dihydroquinolino[3'',4'':4',5']pyrrolo[2',3':4,5]pyrrolo[3,2-*c*]quinolines (QPPQs) (Figure 1).³³ Both DIPPs and QPPQs are easily accessible in a three step synthesis and exhibit very promising properties, including strong absorption in the 350–410 nm region and blue-violet emission. Moreover, DIPPs possess one of the highest HOMOs among all electron-rich heterocycles. Inspired by the lack of a single example of a heterocycle possessing the pyrrolo[3,2-*c*][1,2]azaborinine moiety, we set the goal for ourselves to develop the methodology toward pyrrole[3,2-*b*]pyrrole-based BN-heteroacenes (BNPPs). In order to have an additional electron-deficient model to compare physicochemical properties, we also decided to

Received: May 21, 2016

Published: July 18, 2016

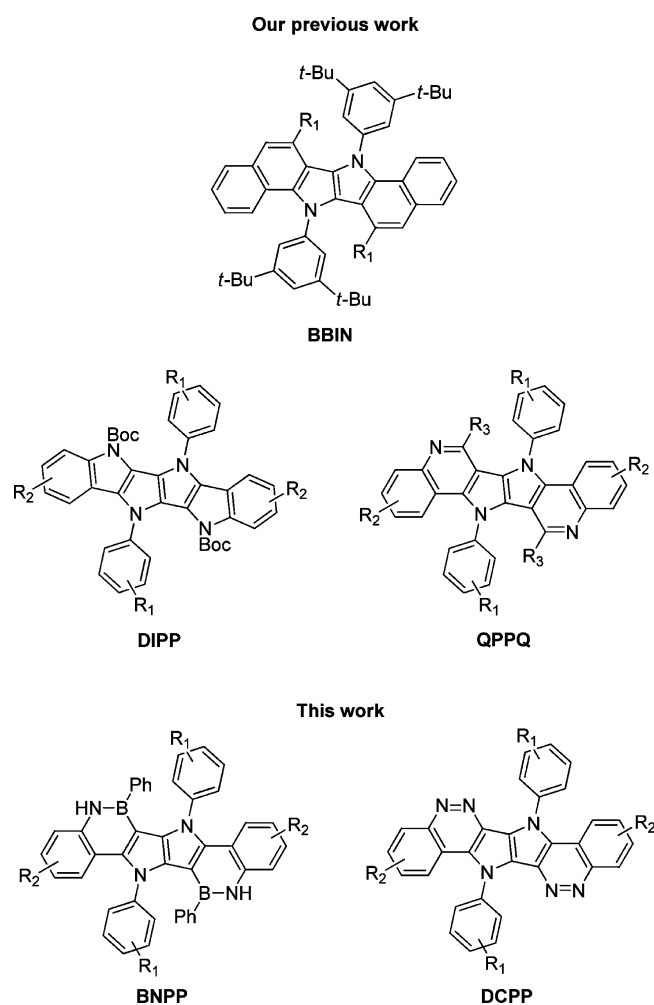


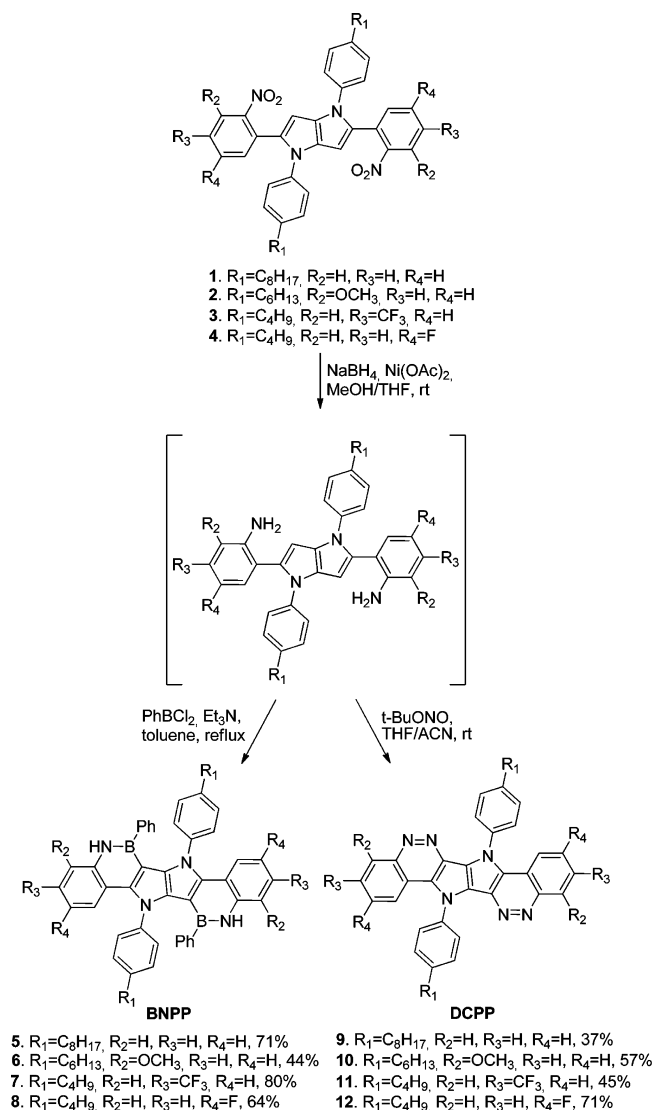
Figure 1. Structures of pyrrole based, ladder-type heteroacenes.

transform TAPPs into the previously unknown ladder-type dicinnolino[3,4-*b*:3'4'-*f*]pyrrolo[3,2-*b*]pyrroles (DCPP) (Figure 1). Structurally related cinnolinoindoles, cinnolinoisindoles, pyrrolotriazines, and indolotriazines, on the other hand, are well-known compounds endowed with a wide range of biological activities.³⁴ Indolo[3,2-*c*]cinnolines exhibit remarkable antiproliferative, antifungal, and antibacterial activity³⁵ and have showed some *in vitro* antileukemic activity.³⁶

RESULTS AND DISCUSSION

The key starting materials in the synthesis of BNPPs and DCPs were previously reported 2,5-bis(2-aminophenyl)-substituted tetraarylpyrrolo[3,2-*b*]pyrroles, obtained by the reduction of appropriate dinitro-compounds 1–4 with NaBH₄/Ni(OAc)₂ (Scheme 1).³³ These amines were used in the final step without any purification, because of their high sensitivity to light and oxygen. We employed 4-*n*-alkylaryl substituents at the nitrogen atoms to secure good solubility of the expected products. The synthesis of new pyrrolopyrrole-based BN-heteroacenes 5–8 was achieved using a well-established protocol involving the reaction of the proper diamine and dichlorophenylborane in boiling toluene in the presence of triethylamine.^{6b} The expected products were isolated by column chromatography in good overall yields (44–80%), in the form of high melting white or off-white solids. It should be pointed out that all BNPPs were perfectly

Scheme 1. Synthesis of BN-Heteroacenes 5–8 (BNPP) and Dicinnolino[3,4-*b*:3'4'-*f*]pyrrolo[3,2-*b*]pyrroles 9–12 (DCPP)



stable as crystals and as a solution in most of organic solvents (toluene, THF, AcOEt for a period of 2 weeks). However, we observed relatively fast decomposition (blackened solution within 30 min at room temperature) in CH₂Cl₂ and CHCl₃. DCPs 9–12 were obtained in moderate overall yields (37–71%) by a modified Sandmeyer reaction via the intramolecular cyclization of diazonium compounds generated from 2,5-bis(2-aminophenyl)-substituted tetraarylpyrrolo[3,2-*b*]pyrroles by treatment with *tert*-butylnitrite.^{34b} All DCPs were sparingly soluble in organic solvents, and they precipitated from the reaction mixture in the form of yellow to orange solids.

Some of the obtained compounds tended to trap molecules of solvent in their crystal lattice. Compound 10, for example, formed a stable 1:1 complex with tetrahydrofuran in the solid state, which was confirmed by NMR. We were able to obtain crystals of 6 suitable for X-ray crystallography by slow diffusion of hexane into a solution of 6 in THF. Compound 6 showed C_{2h} symmetry with an almost perfectly planar pyrrolopyrrole core (178° N–C–C–N torsion angle), and external benzene fused rings were twisted by 8.52° and 10.33° from the plane

determined by the pyrrolo[3,2-*b*]pyrrole scaffold (Figure 2, S1, Table S1). Aryl rings attached both to the nitrogen and to the

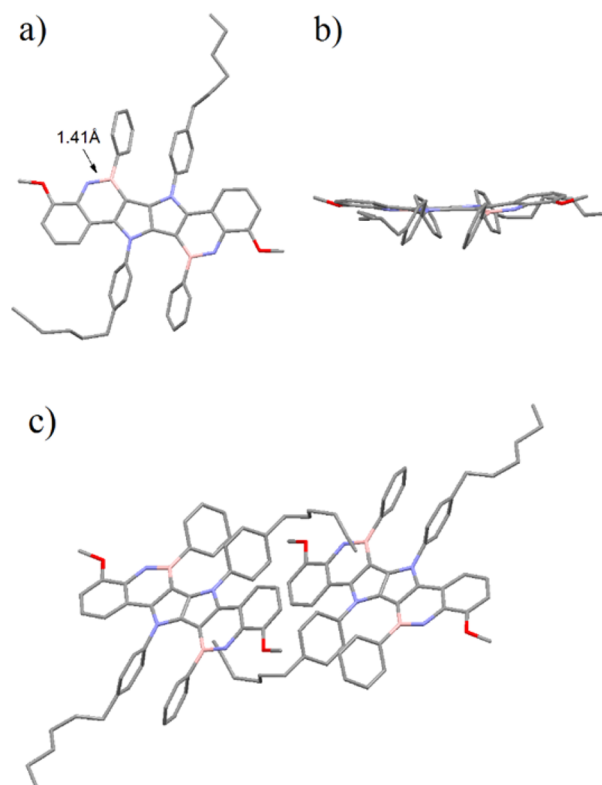


Figure 2. (a) Top view, (b) side view, and (c) packing of **6** in the crystal as determined from X-ray analysis (CCDC 1474772). Hydrogens are omitted for clarity.

boron atoms were twisted by ca. 56° – 60° and 60° , respectively. The lengths of the newly formed B–N bonds were 1.41 Å, within the range of those for other azaborines.^{12c} Compound **6** was the only example among the BNPPs for which a significant downfield shift of ca. 0.8 ppm of NH signal was observed, which is an indication of the strong intramolecular hydrogen bonding between the NH and the OCH₃ present at the flanking benzene ring. The unit cell of the *P*1 triclinc space group contained two molecules of **6**. It seems that the side alkyl chains played a crucial role in such an arrangement of **6** in the crystal lattice, as each alkyl chain interacted with the azaboranaphthopyrrolopyrrole moiety of the neighboring molecule. The distance between the C-2 atom of the alkyl chain of one molecule and the nitrogen atom of the neighboring one was only 3.77 Å.

With a small library of BNPPs and DCPs available, we started a systematic study of their spectroscopic properties. The centrosymmetric nature of previously reported QPPQ,³³ combined with the angular arrangement of the fused rings, allowed us to assume that compounds **5**–**12** could not possess significant bathochromic shifts of absorption, as compared to the starting TAPPs. Photophysical experiments fully confirmed this assumption. All DCPs absorbed in the UV region with single strong bands at 315–322 nm and a weak shoulder at around 370 nm (Table 1, Figures 3, 4). The fluorescence quantum yield (Φ_{fl}) of QPPQs were in the range 2–19%,³³ whereas all DCPs were virtually nonfluorescent ($\Phi_{\text{fl}} < 0.5\%$). This effect was attributed to the presence of diazine rings, leading to the enhancement of nonradiative decay routes and

Table 1. Spectroscopic Properties of Compounds **5**–**12** Measured in Toluene

compd	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	λ_{max} ($\text{M}^{-1}\cdot\text{cm}^{-1}$)	$\lambda_{\text{em}}^{\text{max}}$ (nm)	Stokes shift (cm^{-1})	$\Phi_{\text{fl}}^{\text{a}}$ (%)
5	387	59 100	400	840	70
	368	46 800	417		
6	382	59 500	395	860	62
	363	48 600	413		
7	402	62 500	413	660	78
	382	48 600	434		
8	395	67 400	406	320	64
	375	50 800	426		
9	316	65 500	– ^b	–	–
10	319	59 000	– ^b	–	–
	392	11 500			
11	322	87 100	– ^b	–	–
12	315	74 600	– ^b	–	–

^aFluorescence quantum yield measured with quinine sulfate as a reference. ^bNo measurable fluorescence.

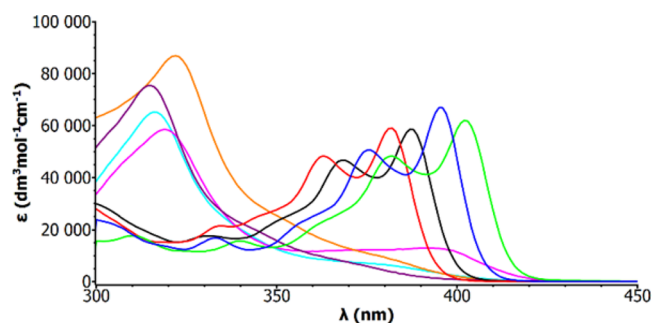


Figure 3. Absorption spectra of **5** (black), **6** (red), **7** (green), **8** (blue), **9** (cyan), **10** (magenta), **11** (orange), and **12** (purple), measured in toluene at concentrations of $(1\text{--}3) \times 10^{-6}$ M.

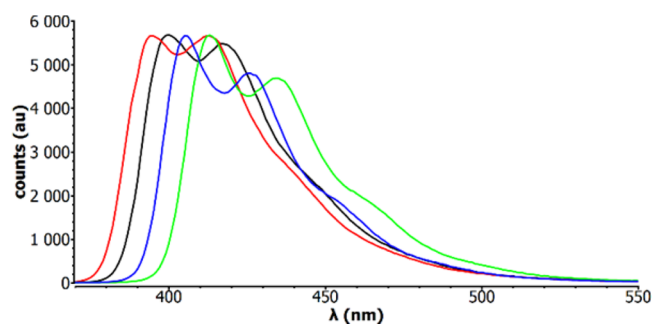


Figure 4. Normalized emission spectra of **5** (black), **6** (red), **7** (green), and **8** (blue), measured in toluene at concentrations of $(1\text{--}3) \times 10^{-6}$ M.

probably to an increase in the intersystem crossing efficiency ($S_1 \rightarrow T_1$).³⁷ The origin of the band recorded at 392 nm for the compound **10** must come from a weak intramolecular charge-transfer process (compound **10** contains the electron-donating methoxy group). On the other hand, the optical properties of BNPPs **5**–**8** should be directly compared to isoelectronic 7,14-dihydrobenzo[*g*]benzo[6,7]indolo[3,2-*b*]indoles (BBINs).^{31b} Absorption bands of new heterocycles **5**–**8** were almost at the same wavelengths as that of their isoelectronic analogs, with two distinct absorption maxima in the 363–402 nm region (Figure 3). In contrast, molar absorption coefficients were an average of three times higher. There was a clear relationship

between the character of the substituent and the value of the extinction coefficients in all the QPPQ,³³ BNPP, and DCPD series. The compounds bearing electron-withdrawing substituents possessed much higher extinction coefficients than their electron-rich analogues. Also, the compounds possessing the electron-withdrawing group (CF₃) as the R₃ substituent in Scheme 1 exhibited well pronounced bathochromic shifts, when compared with other heterocycles in the series. All BNPPs were strongly fluorescent both in solution and in the solid state, with fluorescence quantum yields reaching 78% in toluene (Figure 4). Their fluorescence maxima were observed at the 395–426 nm region, which resulted in very small Stokes shifts of less than 900 cm⁻¹. This result suggests that the geometry of the S₁ excited state is quite similar to that of the S₀ ground state. The strong fluorescence of BNPPs 5–8 stands in stark contrast to the isoelectronic 7,14-dihydrobenzo[*g*]benzo[6,7]indolo[3,2-*b*]indoles,^{31b} which emitted with Φ_f ≈ 20–30%.

The comparison of optical data measured for compound 5 and its previously reported analogue possessing a thiophene core^{12a} revealed that some of the properties of both systems were almost identical. Compound 5 absorbed and emitted at wavelengths that were 4 and 9 nm longer, respectively, and had a 10% higher extinction coefficient than the thiophene analogue. It is worth noting that the pyrrole based system had an almost 3-times higher fluorescence quantum yield.^{12a} Additionally, both compounds emitted strongly in the solid state, which led to the conclusion that the general properties of BNPPs are very similar to the much more studied systems based on thiophene.

The electrochemical behavior of the synthesized compounds was investigated by cyclic voltammetry (CVs). None of the tested compounds 5–8 exhibited any well-developed reduction processes; however, they all displayed one quasi-reversible oxidation wave around 0.07–0.35 V (vs Fc/Fc⁺) (Table 2,

Table 2. Electrochemical Data for BN-Heteroacenes 5–8

compd	E _{ox1} (V) ^a	HOMO (eV) ^b	E _g ^{opt} (eV) ^c	LUMO (eV) ^d
5	0.12	-4.92	3.11	-1.81
6	0.13	-4.93	3.15	-1.78
7	0.35	-5.15	2.99	-2.16
8	0.07	-4.87	3.05	-1.82

^aThe first oxidation potential (vs Fc/Fc⁺). ^bHOMO = -E_{ox1} - 4.8 eV. ^cOptical band gap, estimated from UV-vis absorption edge. ^dLUMO = HOMO + E_g^{opt}.

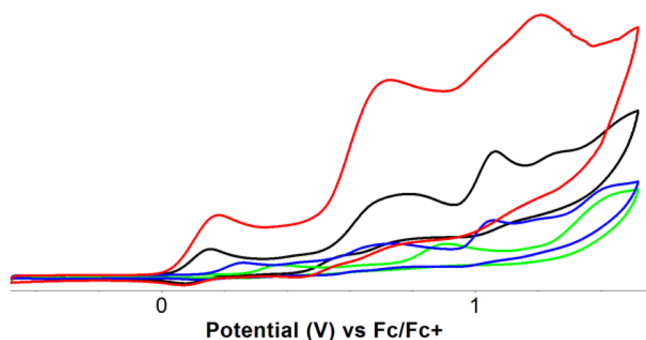
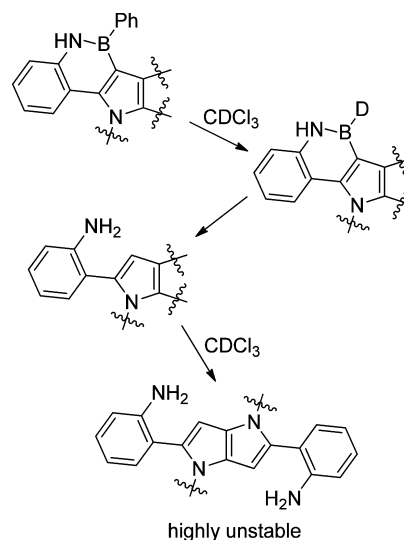


Figure 5. Cyclic voltammograms of 5 (black), 6 (red), 7 (green), and 8 (blue).

Figure 5) and several irreversible oxidation processes at higher potentials. It can be deduced from the shape of the cyclic voltammograms that, at potentials around 0.5 V or higher, complex electrochemical processes take place, probably multiple one-electron oxidations. The first oxidation measured for compounds 5–8 takes place at potentials slightly higher (0.1 V) than those of previously reported DIPP;³² however, the potentials were significantly lower than those measured for the previously reported analogue possessing a thiophene core.^{12a} Consequently, HOMO levels derived from the first oxidation potential (assuming Fc/Fc⁺ at -4.8 eV) are in the range -4.87 to -5.15 eV, whereas LUMO levels, obtained from the absorption edges, are around -1.78 to -2.16 eV. All tested DCPDs were electrochemically inactive in the applied potential window.

We have also tried to elucidate the reason for the instability of the BNPP compounds in chlorinated solvents using ¹H NMR and mass spectrometry techniques. Since significant fragmentation of the molecular ion was observed when electron ionization was employed in the mass spectrometry experiments, we decided to use electrospray as the ionization method. Thus, we dissolved the samples of compounds 5–8 in deuterated chloroform and registered their NMR and mass spectra every 24 h, for a few days. We found that the decomposition process is much slower in the absence of light, at temperatures around 0 °C, and the presence of electron-withdrawing substituents generally increase the stability of BNPP. Nevertheless, all compounds decomposed completely within few days. Their NMR spectra were very complex and not very informative; however, their mass spectra were very easy to analyze, as they contained only two peaks corresponding to [M-75]⁺ and [M-86]⁺ (Figure S2). This led us to the conclusion that the fragmentation process probably includes cleavage of a single phenyl ring which results in the formation of deuterated boron–nitrogen species, which subsequently loses the boron substituent (Scheme 2). Repeating this process and loss of the second phenylboron moiety lead to bis(2-aminophenyl)-substituted tetraarylpyrrolo[3,2-*b*]pyrroles, which were reported to be very unstable.³³

Scheme 2. Possible Decomposition Mechanism Observed in CDCl₃ Solution of Compound 5



CONCLUSIONS

Replacement of the C=C unit with the isoelectronic B–N unit in 7,14-dihydrobenzo[*g*]benzo[6,7]indolo[3,2-*b*]indoles provided a new class of molecules with appealing properties. They emit blue light with high intensity, and they possess fluorescence in the solid state. On the other hand, replacing the C=N bond with the N=N bond in the same ladder-type skeleton leads to a strong decrease in the emission intensity and a drastic decrease in solubility. We have proven that both new heterocycles, i.e., ladder-type BN-heteroacenes and dicinnolino[3,4-*b*:3′4′-*f*]pyrrolo[3,2-*b*]pyrroles can be prepared in a straightforward strategy starting from diacetyl, substituted anilines, 2-nitrobenzaldehydes, and dichlorophenylborane in good overall yields. The dicinnolino[3,4-*b*:3′4′-*f*]pyrrolo[3,2-*b*]pyrroles absorb exclusively UV-irradiation ($\lambda_{\text{max}} \approx 320$ nm) and are virtually nonfluorescent, which is a result of enhancement of nonradiative decay routes caused by the presence of the diazine scaffold. BN-Heteroacenes are electrochemically active, being much more easily oxidized than their thiophene analogues, which highlights their potential in organic electronics.

EXPERIMENTAL SECTION

General Information. All chemicals were used as received unless otherwise noted. Reagent grade solvents (MeCN, CH₂Cl₂, hexane, toluene) were distilled prior to use. All reported NMR spectra were recorded on a 500 MHz spectrometer unless otherwise noted. Chemical shifts (δ ppm) for ¹H and ¹³C NMR were determined with TMS as the internal reference; ¹⁰B spectra were externally referenced to BF₃·Et₂O (0 ppm). *J* values are given in Hz. The solubility of prepared dicinnolino[3,4-*b*:3′4′-*f*]pyrrolo[3,2-*b*]pyrroles was very low; therefore, most of the NMR spectra were measured in CDCl₃ with the addition of a few drops of deuterated trifluoroacetic acid. Consequently, signals that originate from CF₃CO₂D can sometimes be observed in NMR spectra. UV–vis absorption spectra were recorded in toluene. Chromatography was performed on silica (Kieselgel 60, 200–400 mesh). Mass spectra were obtained with an EI ion source and the EBE double focusing geometry mass analyzer or spectrometer equipped with an electrospray ion source with a q-TOF type mass analyzer. The synthesis of compounds 1–4 was described earlier.^{32,33} Cyclic voltammograms of compounds 5–12 (1 mg/mL) were measured at 20 °C, under an argon atmosphere, in deoxygenated 0.1 M solutions of tetrabutylammonium hexafluorophosphate in anhydrous dichloromethane. A glassy carbon working electrode, a Ag/AgCl reference electrode, and auxiliary platinum foil were used, while the scan rate was $v = 50$ mV·s⁻¹. All values of *E* [V] are reported with respect to Fc⁺/Fc redox potential.

Synthesis. *Reduction of 2,5-Bis(2-nitrophenyl)pyrrolo[3,2-*b*]pyrroles.*³³ NaBH₄ (28 mg, 0.75 mmol) was added to the solution of Ni(OAc)₂·4H₂O (62 mg, 0.25 mmol) in MeOH (10 mL), and the resulting dark suspension was stirred at room temperature for 15 min. The solution of 2,5-bis(2-nitrophenyl)pyrrolo[3,2-*b*]pyrrole (0.25 mmol) in THF (10 mL) was added, and the reaction flask was tightly wrapped with aluminum foil to prevent a light-induced decomposition of the product. More NaBH₄ (typically 100–150 mg) was carefully added in several portions, until all starting material was consumed. The reaction mixture was filtered through a pad of Celite, washed with THF, and evaporated to dryness. The dark residue was extracted with AcOEt/water a few times, and the combined organic phases were dried with MgSO₄ and evaporated to dryness. This material was immediately used in the next step without any further purification.

General Procedure for the Synthesis of BN-Heteroacenes (BNPP). 2,5-Bis(2-aminophenyl)pyrrolo[3,2-*b*]pyrrole (crude, ca. 0.25 mmol) was dissolved in dry toluene (10 mL). PhBCl₂ (264 μ L, 2 mmol) and Et₃N (560 μ L, 4 mmol) were added, and the resulting mixture was refluxed under Ar for 24 h. After evaporation with a small amount of silica, the residue was loaded on a column and

chromatographed (silica, dichloromethane/hexanes 1:3). Blue-fluorescent fractions were collected, evaporated, and crystallized from AcOEt/hexanes to afford the desired product of analytical purity.

5,12-Diaza-6,13-dibora-7,14-bis(4-octylphenyl)-6,13-diphenyl-dinaphtho[3,4-*b*:3′4′-*f*]pyrrolo[3,2-*b*]pyrrole (5). White solid, 148 mg, 71%, mp 215–217 °C dec; ¹H NMR (CDCl₃, 500 MHz): δ 7.32 (s, 2H), 7.20–7.00 (m, 18H), 6.82 (AA′BB′, *J* = 8.0 Hz, 4H), 6.74 (d, *J* = 8.5 Hz, 2H), 6.66–6.62 (m, 2H), 2.58 (t, *J* = 7.8 Hz, 4H), 1.74–1.64 (m, 4H), 1.44–1.28 (m, 20H), 0.92 (t, *J* = 7.1 Hz, 6H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 143.2, 143.0, 142.4, 138.7, 138.6, 136.1, 131.2, 129.2, 128.5, 127.2, 126.0, 125.1, 123.2, 119.8, 118.6, 117.7, 105.3, 35.6, 31.9, 30.7, 29.6, 29.4, 22.7, 14.1 ppm. ¹⁰B NMR (CDCl₃, 54 MHz) δ 34.4 ppm. HRMS (EI): *m/z* calculated for C₅₈H₆₂B₂N₄ [M⁺] = 836.5161; found: 836.5175. Elemental analysis calcd (%) for C₅₈H₆₂B₂N₄: C, 83.25, H, 7.47, N, 6.70. Found: C, 83.04, H, 7.30, N, 6.55.

5,12-Diaza-6,13-dibora-4,11-dimethoxy-7,14-bis(4-hexylphenyl)-6,13-diphenyl-dinaphtho[3,4-*b*:3′4′-*f*]pyrrolo[3,2-*b*]pyrrole (6). White solid, 93 mg, 44%, mp 254–256 °C dec; ¹H NMR (CDCl₃, 500 MHz): δ 8.16 (s, 2H), 7.20–7.17 (m, 6H), 7.16, 6.81 (AA′BB′, *J* = 8.0 Hz, 8H), 7.03 (t, *J* = 7.4 Hz, 4H), 6.67 (d, *J* = 7.9 Hz, 2H), 6.56 (t, *J* = 8.2 Hz, 2H), 6.35 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 6H), 2.58 (t, *J* = 7.7 Hz, 4H), 1.73–1.65 (m, 4H), 1.44–1.38 (m, 12H), 0.96 (t, *J* = 6.9 Hz, 6H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 147.9, 143.6, 142.9, 142.6, 138.7, 136.1, 131.4, 129.3, 129.1, 128.6, 127.1, 125.8, 118.7, 117.9, 115.6, 105.8, 105.0, 55.6, 35.6, 31.8, 30.6, 29.1, 22.7, 14.2 ppm. ¹⁰B NMR (CDCl₃, 54 MHz) δ 34.3 ppm. HRMS (ESI): *m/z* calculated for C₅₆H₅₉B₂N₄O₂ [M + H⁺] = 841.4824; found: 841.4838. Elemental analysis calcd (%) for C₅₆H₅₈B₂N₄O₂: C, 80.00, H, 6.95, N, 6.66. Found: C, 79.91, H, 6.78, N, 6.65.

5,12-Diaza-6,13-dibora-7,14-bis(4-butylphenyl)-6,13-diphenyl-3,10-bis(trifluoromethyl)-dinaphtho[3,4-*b*:3′4′-*f*]pyrrolo[3,2-*b*]pyrrole (7). Pale-green solid, 173 mg, 80%, mp 278–279 °C dec; ¹H NMR (CDCl₃, 500 MHz): δ 7.43 (d, *J* = 9.6 Hz, 4H), 7.22–7.18 (m, 2H), 7.17–7.13 (m, 8H), 7.08–7.03 (m, 4H), 6.89–6.82 (m, 8H), 2.60 (t, *J* = 7.8 Hz, 4H), 1.72–1.65 (m, 4H), 1.50–1.43 (m, 4H), 1.04 (t, *J* = 7.4 Hz, 6H) ppm. ¹³C NMR (THF-*d*₆, 125 MHz): δ 143.3, 141.7, 139.0, 138.5, 136.9, 131.1, 129.4, 128.4, 126.9, 125.8, 125.7 (q, *J* = 33 Hz), 124.6 (q, *J* = 270 Hz), 123.2, 119.9, 115.6 (q, *J* = 4 Hz), 115.0 (q, *J* = 4 Hz), 35.2, 32.8, 22.4, 13.4 ppm. ¹⁰B NMR (CDCl₃, 54 MHz) δ 35.6 ppm. HRMS (EI): *m/z* calculated for C₅₂H₄₄B₂N₄F₆ [M⁺] = 860.3656; found: 860.3678.

5,12-Diaza-6,13-dibora-2,7-difluoro-7,14-bis(4-butylphenyl)-6,13-diphenyl-dinaphtho[3,4-*b*:3′4′-*f*]pyrrolo[3,2-*b*]pyrrole (8). White solid, 121 mg, 64%, mp 282–284 °C dec; ¹H NMR (CDCl₃, 500 MHz): δ 7.30 (s, 2H), 7.20–7.15 (m, 10H), 7.09–7.02 (m, 6H), 6.88–6.84 (m, 6H), 6.32 (dd, *J* = 12.5, 2.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 4H), 1.72–1.65 (m, 4H), 1.48–1.40 (m, 4H), 1.01 (t, *J* = 7.4 Hz, 6H) ppm. ¹³C NMR (THF-*d*₆, 125 MHz): δ 156.1 (d, *J* = 234 Hz), 143.1, 141.78, 141.76, 138.5, 136.4, 136.0, 131.2, 129.4, 128.5, 126.8, 125.5, 119.6 (d, *J* = 9 Hz), 117.8 (d, *J* = 9 Hz), 112.1 (d, *J* = 24 Hz), 107.8 (d, *J* = 24 Hz), 35.2, 32.9, 22.1, 13.4 ppm. ¹⁰B NMR (CDCl₃, 54 MHz) δ 33.8 ppm. HRMS (EI): *m/z* calculated for C₅₀H₄₄B₂F₂N₄ [M⁺] = 760.3720; found: 760.3738. Elemental analysis calcd (%) for C₅₀H₄₄B₂F₂N₄: C, 78.96, H, 5.83, N, 7.37. Found: C, 78.78, H, 5.80, N, 7.37.

General Procedure for the Synthesis of Dicinnolino[3,4-*b*:3′4′-*f*]pyrrolo[3,2-*b*]pyrroles (DCPP). 2,5-Bis(2-aminophenyl)pyrrolo[3,2-*b*]pyrrole (crude, ca. 0.25 mmol) was dissolved in the mixture of THF (5 mL) and acetonitrile (1 mL). *tert*-Butylnitrite (238 μ L, 2 mmol) was slowly added, and the reaction mixture was stirred at room temperature for 24 h. The resulting orange precipitate was filtered off, washed with acetonitrile, and dried under high vacuum at 60 °C to afford the desired product of analytical purity. If necessary, a second crop of the product can be obtained by evaporation of supernatant and crystallization from pure acetonitrile.

7,14-Bis(4-octylphenyl)dicinnolino[3,4-*b*:3′4′-*f*]pyrrolo[3,2-*b*]pyrroles (9). Orange solid, 64 mg, 37%, mp 178–179 °C. ¹H NMR (CDCl₃, 500 MHz): δ 8.68–8.63 (m, 2H), 8.20 (t, *J* = 7.8 Hz, 2H), 7.95 (t, *J* = 7.7 Hz, 2H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.75, 7.69 (AA′BB′, *J*

= 8.0 Hz, 8H), 2.93 (t, $J = 7.9$ Hz, 4H), 1.88–1.81 (m, 4H), 1.55–1.31 (m, 20H), 0.92 (t, $J = 7.1$ Hz, 6H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ 148.5, 137.9, 134.8, 133.4, 133.1, 132.3, 131.3, 130.6, 130.4, 126.1, 121.8, 121.1, 117.6, 35.8, 31.8, 31.0, 29.4, 29.3, 29.2, 22.6, 13.9 ppm. HRMS (EI): m/z calculated for $\text{C}_{46}\text{H}_{51}\text{N}_6$ [$\text{M} + \text{H}^+$] = 687.4175; found: 687.4177.

4,11-Dimethoxy-7,14-bis(4-hexylphenyl)dicinnolino[3,4-b:3'4'-f]-pyrrolo[3,2-b]pyrroles (10). Orange solid, 98 mg, 57%, mp 270–271 °C dec; ^1H NMR of **10**·THF (CDCl_3 , 500 MHz): δ 7.83 (dd, $J = 8.1$, 8.4 Hz, 2H), 7.76, 7.65 (AA'BB', $J = 8.3$ Hz, 8H), 7.45 (d, $J = 7.9$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 4.24 (s, 6H), 3.94–3.90 (m, 4H, THF), 2.93 (t, $J = 7.9$ Hz, 4H), 2.00–1.96 (m, 4H, THF), 1.87–1.80 (m, 4H), 1.54–1.48 (m, 4H), 1.45–1.39 (m, 8H), 0.96 (t, $J = 7.1$ Hz, 6H) ppm. ^{13}C NMR of **10**·THF (CDCl_3 , 125 MHz): δ 150.0, 148.1, 134.2, 132.9, 132.4, 131.0, 130.82, 130.80, 129.9, 126.4, 118.6, 113.0, 111.7, 68.0 (THF), 57.4, 35.8, 31.6, 30.9, 29.1, 25.4 (THF), 22.6, 14.0 ppm. HRMS (EI): m/z calculated for $\text{C}_{44}\text{H}_{47}\text{N}_6\text{O}_2$ [$\text{M} + \text{H}^+$] = 691.3760; found: 691.3755.

7,14-Bis(4-butylphenyl)-3,10-bis(trifluoromethyl)dicinnolino[3,4-b:3'4'-f]pyrrolo[3,2-b]pyrroles (11). Yellow solid, 80 mg, 45%, mp 319–320 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 8.90 (s, 2H), 7.81, 7.58 (AA'BB', $J = 8.3$ Hz, 8H), 7.78 (d, $J = 7.3$ Hz, 2H), 7.72 (dd, $J = 9.0$, 1.5 Hz, 2H), 2.88 (t, $J = 7.8$ Hz, 4H), 1.87–1.80 (m, 4H), 1.58–1.49 (m, 4H), 1.06 (t, $J = 7.3$ Hz, 6H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ 145.4, 144.9, 135.3, 132.9, 130.4, 129.7 (q, $J = 33$ Hz), 128.7 (q, $J = 5$ Hz), 127.3, 127.2, 125.3 (q, $J = 5$ Hz), 123.5 (q, $J = 271$ Hz), 122.1, 117.2, 35.6, 33.4, 22.6, 14.0 ppm. HRMS (EI): m/z calculated for $\text{C}_{40}\text{H}_{33}\text{N}_6\text{F}_6$ [$\text{M} + \text{H}^+$] = 711.2671; found: 711.2666. Elemental analysis calcd (%) for $\text{C}_{40}\text{H}_{33}\text{N}_6\text{F}_6$: C, 67.60, H, 4.54, N, 11.82. Found: C, 67.31, H, 4.50, N, 11.57.

7,14-Bis(4-butylphenyl)-2,9-difluorodicinnolino[3,4-b:3'4'-f]-pyrrolo[3,2-b]pyrroles (12). Orange solid, 108 mg, 71%, mp 253–255 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 8.78 (dd, $J = 9.6$, 4.5 Hz, 2H), 7.97–7.92 (m, 2H), 7.73, 7.71 (AA'BB', $J = 8.6$ Hz, 8H), 7.37 (dd, $J = 8.4$, 2.5 Hz, 2H), 2.95 (t, $J = 7.8$ Hz, 4H), 1.87–1.80 (m, 4H), 1.57–1.48 (m, 4H), 1.05 (t, $J = 7.3$ Hz, 6H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ 163.5 (d, $J = 264$ Hz), 148.8, 135.4, 132.5 (d, $J = 6$ Hz), 131.7, 131.5, 130.5, 129.7, 126.1, 125.8, 125.6, 125.1 (d, $J = 10$ Hz), 119.4 (d, $J = 11$ Hz), 106.3 (d, $J = 26$ Hz), 35.5, 33.1, 22.3, 13.7 ppm. HRMS (EI): m/z calculated for $\text{C}_{38}\text{H}_{33}\text{N}_6\text{F}_2$ [$\text{M} + \text{H}^+$] = 611.2735; found: 611.2733.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01209.

^1H , ^{13}C , and ^{10}B NMR spectra of new compounds, crystallographic data, mass spectra of decomposed sample of **5**, photographic image of powdered compound **5–8** (PDF)

Crystallographic data for **6** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank the National Science Centre, Poland (Grant MAESTRO-2012/06/A/ST5/00216) for financial support.

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