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A New Synthesis of Push-Pull Pyrroles, Their Oxidation to Stable 3*H*-Pyrroles and an Unexpected Anellation Reaction

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A new synthesis of push-pull pyrroles of type **5** was developed starting from bis(imidoyl chlorides) **1** and various iminodiacetic acid derivatives **3**. The use of appropriate *N*-trifluoroacetyl residues as protecting/activating group proved to be the method of choice for the straightforward preparation of the 3,4-diarylamino-1*H*-pyrroles **5**. When benzothiazole substructures are present in 2,5-position of heterocycles **5**, a two-electron oxidation leads to 3*H*-pyrroles of type **6** in excellent yields. However, in the case of cyano or ester groups, a further oxidative process immediately led to the new 3*H*-pyrrolo[3,4-*b*]quinoxalines **7** via intramolecular ring anellation.

Introduction

In the course of the last years derivatives of pyrrole have become of major interest due to the fact that this five-membered heterocycle is present in a series of natural products and in addition, pyrrolic compounds feature a wide variety of interesting and useful optical and electronic properties.[1] Especially highly substituted pyrroles have an important function in natural dyes (porphyrins, bile pigments) and were also isolated from maritime organisms. Such derivatives often show a high biological activity and therefore some synthetic strategies were developed for their total syntheses.[2] The blockbuster atorvastatin (Lipocor, Lipitor®) is a representative example in which a high degree of substituents goes hand in hand with strong biological activity. Substituted pyrroles can be synthesised by several cyclization reactions by using a widespread ensemble of building blocks. One procedure to highly substituted pyrroles is similar to the Hinsberg cyclisation: the ring-forming reaction between CC and CNC building blocks to yield symmetrical pyrrols.[3] During the last decade, it was clearly demonstrated that compounds **1** are excellent (and selective) di-electrophiles that can be employed in a wide range as CC building blocks for heterocyclic as well as for carbocyclic compounds.[4] In the course of a cycloacylation–prototropism sequence, a series of new thiophenes which possess interesting spectral properties was synthesized.[4a] Our current goal is to adapt these results in order to integrate these di-electrophiles **1** into the synthesis of tetrasubstituted pyrroles (Figure 1).

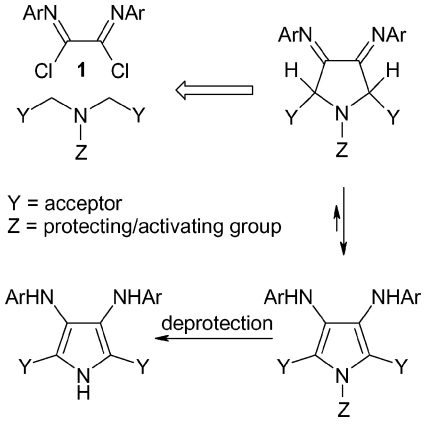

Figure 1. Synthetic entry to push-pull pyrroles.

Results and Discussion

The di-electrophiles **1** are easily accessible from simple starting materials and an optimized protocol consisting of a two-step one-pot reaction was used.[4b] The 4-octyloxyphenyl-substituted bis(imidoyl chloride) **1d** was additionally prepared in order to obtain derivatives with a better solubility in nonpolar solvents (Scheme 2).

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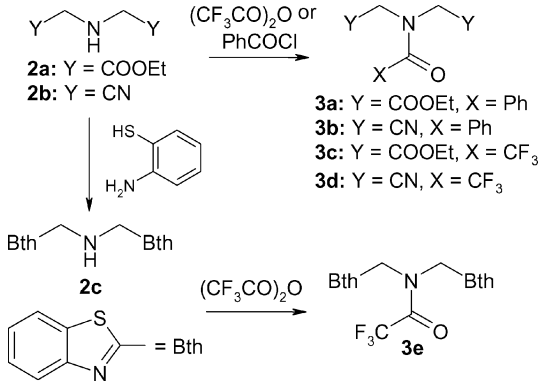
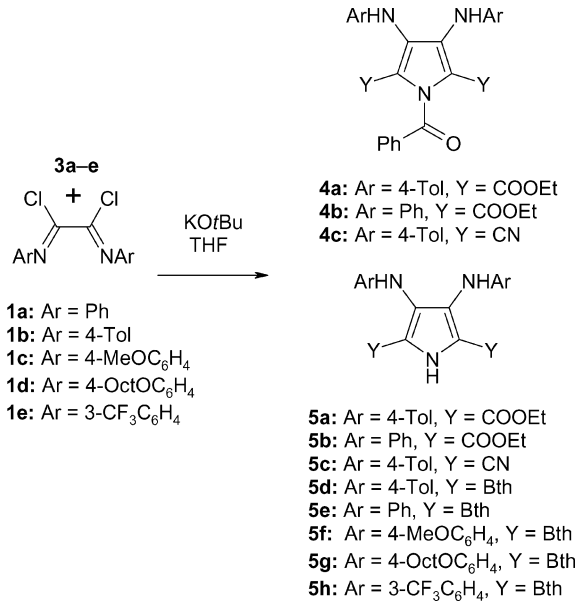
The CNC building blocks diethyl iminodiacetate **2a** and iminodiacetonitrile **2b** which possess electron withdrawing groups, necessary for the Hinsberg-like cyclisation reaction, are commercially available (Scheme 1). In order to prevent undesired acylations at nitrogen atoms and simultaneously, to activate the substrate, the NH in **2a**,**b** must be transformed. Firstly, we introduced the tosyl group for this reason, however, under the cyclisation conditions (THF/KO*t*Bu) only decomposition of the materials was observed. The use of the benzoyl group (derivative **3a**,**b**) was successful and thus, upon cycloacylation, the corresponding pyrroles **4a**–**c** were isolated (see discussion below). The trifluoroacetate group proved to be an additional promising protection/activation group. The corresponding *N*-protected compounds **3c**,**d** were easily prepared by acylation reactions of **2a**,**b** with trifluoroacetic anhydride without any base and were purified by distillation. Interestingly enough, derivatives **3c**,**d** were unknown as of yet (Scheme 1; for their cyclisation see below). A further promising CNC building block was obtained by condensation reaction of **2b** with 2-aminothiophenol. This smooth reaction yielded bis(benzothiazolyl) derivative **2c** (benzothiazole = Bth). The protection of **2c** with trifluoroacetic anhydride allowed the synthesis of trifluoroacetamide **3e** in high yield as colourless crystals.



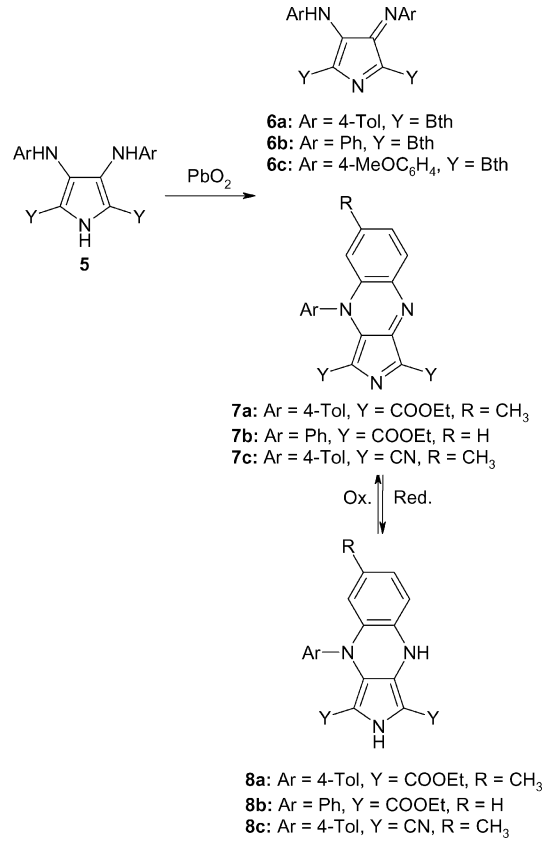
Scheme 1.

Diethyl *N*-benzoyliminodiacetate **3a** reacted with di-electrophiles of type **1** under mild conditions (THF in the presence of KO*t*Bu at –78 °C) forming pale yellow crystalline products in moderate yields. Elemental analysis and MS data confirmed the presence of 1:1 cyclisation products. Evidence for the symmetric substitution pattern in these novel penta-substituted pyrroles **4a**,**b** (Scheme 2) was provided by single sets of signals in the ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectra, the NH protons of derivative **4a** showed a chemical shift of δ = 6.92 ppm and the protons from the 4-tolyl methyl group at δ = 2.20 ppm. In the ^{13}C NMR spectrum, the signal for the benzoyl group was detected at δ = 169.4 ppm and for the COOEt group of 160.6 ppm. Solutions of compound **4a** are dark yellow ($CHCl_3$: λ_{max} = 390 nm, lg ε = 3.9). *N*-benzoyliminodiacetonitrile **3b** reacted with di-electrophile **1b** under similar mild conditions and the pyrrole **4c** was isolated as yellow crystalline solid in relatively low yield. The *N*-benzoyl group in **4a**–**c** can be removed by heating in ethanol in the presence of catalytic amounts of *p*-toluenesulfonic acid. The corresponding 1*H*-pyrroles **5a**–**c** were isolated as colourless crystals after purification by flash chromatography and recrystallisation.



Scheme 2.

Alternatively, employing the trifluoroacetamides **3c**–**e** as cyclization partners, the 1*H*-pyrroles **5** can be isolated directly after cyclisation reaction with **1**. For example, **3c** reacted with **1** under mild conditions forming a colourless crystalline product in a satisfactory yield. However, elemental analysis and MS data confirmed not only the presence of 1:1 cyclisation products but also an additional release of the trifluoroacetate group. Due to the fact that higher yields were obtained in this procedure, this protocol proved to be the best choice for the synthesis of tetrasubstituted derivatives of type **5** (Scheme 2). Evidence for the symmetric substitution pattern in these novel tetrasubstituted pyrroles **5** (Scheme 2) was provided by single sets of resonances in the ^{1}H and ^{13}C NMR spectra. Taking **5a** as an example, the following key signals were detected: the pyrrole NH proton at δ = 8.91 ppm and the NH protons of the tolylamino group at δ = 6.51 ppm, the C=O of the COOEt group at δ = 160.8 ppm in the ^{13}C NMR spectrum. The pale yellow solution of compound **5a** ($CHCl_3$: λ_{max}: 351 nm, lg ε: 3.8) displayed a yellow fluorescence with a large stokes shift (in $CHCl_3$: λ_{Em} = 550 nm). The cyclisation reaction between trifluoroacetamide **3d** and **1** was accomplished under the same conditions to the 3,4-bis(tolylamino)pyrrole-2,5-dicarbonitrile (**5c**), however, in relatively low yield. While **5c** proved to be stable in the solid state, in solution fast oxidation reaction took place giving a new blue compound (Scheme 3).



Scheme 3.

The cyclisation reaction between **3e** and **1** also led to NH-pyrrols of type **5**. In this manner, the bis(benzothiazolyl)-substituted derivatives **5d**–**h** were isolated as yellow crystals in moderate to good yields. Derivative **5g** was synthesised starting from **3e** and bis(imidoyl chloride) **1d** in order to obtain derivative with a better solubility in nonpolar solvents. The yellow solutions of compound **5d** ($CHCl_3$: λ_{max} = 385 and 405 nm, lg ε = 4.4) display strong blue to yellow fluorescence, whereby the emission wavelength depends on the nature of the solvent (for discussion of the fluorescence properties of pyrroles **5** see below). Further structural details were obtained from a single-crystal X-ray analysis of **5d**. The result of this structure determination showed that **5d** is a monomer in the solid state (Figure 2). The bond lengths and angles were in the expected range for a 1*H*-pyrrole. The bond lengths and the torsion angles between the pyrrole and the benzothiazole rings suggest a conjugation between both heterocycles. The π-systems of the two tolyl rings are nearly perpendicular with respect to the central pyrrole functionality. The lone pairs of N4 and N5 are also oriented perpendicular to the pyrrole and interact with the π-system of the tolyl group. The asymmetric unit of one molecule contains crystal chloroform leading to a slight interaction between N2 and the proton of N1.

All 1*H*-pyrrole solutions of type **5** display fluorescence whereby the emission maxima, Stokes shift and the intensity (quantum yield) depend on the nature of the substituent in the 2-/5-position as well as on the 3,4-arylamino

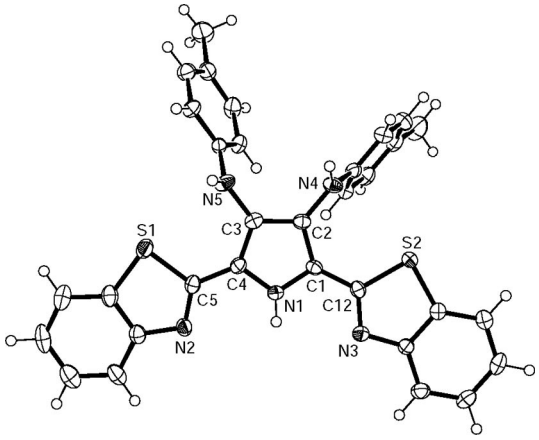


Figure 2. ORTEP plot (50% probability ellipsoids) of the solid-state molecular structure of **5d**, selected bond lengths in Å: S1–C5 1.751(4), S2–C12 1.751(4), N2–C5 1.310(6), N3–C12 1.314(5), N1–C1 1.358(5), N1–C4 1.364(5), C1–C2 1.398(6), C2–C3 1.411(6), C3–C4 1.388(6), N4–C2 1.406(6), N5–C3 1.408(5).

groups. The absorption and fluorescence characteristics of compounds **5** have been investigated in dilute solutions at room temperature. Absorption and fluorescence spectra of selected compounds in toluene are presented in Figure 3. Data of steady state absorption and fluorescence measurements in toluene are summarized in Table 1. Position and intensity of the long wavelength absorption are determined by the substitution at the pyrrol ring in 2,5-position. The bathochromic shift increases in the order Y = CN, COOEt, benzothiazole. The long wavelength absorption edge of all compounds **5** are characterized by a long tail which should be due to flexibility of the arylamino groups in 3- and 4-position. The long wavelength absorption band of the benzothiazolyl-substituted compounds shows two peaks of nearly the same intensity separated by 20 nm and distinct higher absorption coefficients. The fluorescence spectra are broad and with one exception (**5h**) unstructured and have Stokes shifts from 2500 to 7000 cm^{-1}. The fluorescence quantum yields vary from 0.8 to 0.03. The decrease of the quantum yields correlates with the increase of the Stokes shifts. For the 2,5-bis(benzothiazolyl)-3,4-bis(diarylamino)-pyrroles **5** a strong effect of the donor strength of the substituent at the arylamino groups on the fluorescence quantum yield is observed. With increasing donor strength in the order **5h**, **5e**, **5d** and **5f** (see Table 1) the quantum yields decrease (**5g** showing the same spectroscopic characteristics as **5f**).

In order to investigate the excited state deactivation processes and to distinguish between radiative and nonradiative deactivation the fluorescence kinetics of the compounds are measured in toluene. The kinetics show monoexponential decay for all compounds with lifetimes from 1 ns to 3 ns. The values are given in Table 2 together with the calculated radiative and nonradiative rate constants. The data shows that the decrease of the fluorescence quantum yields are as well due to the decrease of the radiative rate constant k_r, as the increase of the nonradiative rate constants k_{nr} with increasing donor strength.

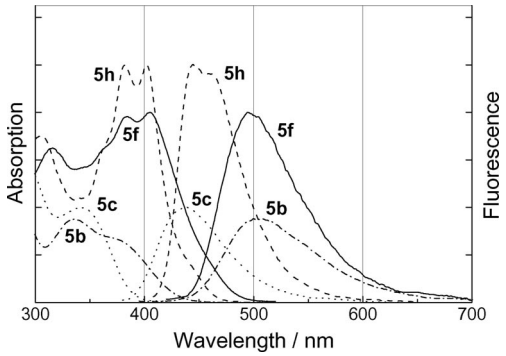


Figure 3. Absorption and fluorescence spectra of selected pyrroles **5** in toluene.

Table 1. Absorption maxima λ_a and coefficients ε, fluorescence maxima λ_f, Stokes shifts $\Delta\nu_{af}$ and fluorescence quantum yields Φ_f in toluene.

	λ_a[a] [nm]	ε[b] (M^{-1} cm^{-1}]	λ_f[a] [nm]	$\Delta\nu_{af}$ [cm^{-1}]	Φ_f
5a	*340*, 381 sh	6300	515	6800	0.12
5b	*335*, 381 sh	7100	505	6400	0.14
5c	342	7900	438	6400	0.04
5h	381, 402	37100	*446*, 462	2450	0.80
5e	385, *404*	31600	462	3100	0.64
5d	384, *407*	22900	478	3650	0.39
5f	386, *407*	25100	498	4500	0.15

[a] Maxima of the long wavelength absorption spectra and of the fluorescence spectra. Values printed in *italics* indicate the major peak. sh: shoulder. [b] Absorption coefficients at the long wavelength absorption maxima in $CHCl_3$.

Table 2. Excited state deactivation: fluorescence quantum yields (Φ_f), lifetimes (τ) and rate constants of radiative (k_f) and radiationless (k_{nr}) deactivation in toluene.

	Φ_f	τ [ns]	k_f[a] [ns^{-1}]	k_{nr}[a] [ns^{-1}]
5a	0.12	2.72	0.044	0.32
5b	0.14	3.24	0.043	0.27
5c	0.04	0.89	0.045	1.08
5h	0.80	2.10	0.38	0.10
5e	0.64	2.39	0.27	0.15
5d	0.39	2.46	0.16	0.25
5f	0.15	2.65	0.057	0.32

[a] $k_f = \Phi_f/\tau$, $k_{nr} = (1 - \Phi_f)/\tau$.

Another interesting property is the solvent dependence of the fluorescence by benzthiazolyl-substituted pyrroles. Whereby only a moderate solvatochromism is observed, an enhanced red shift of the fluorescence spectra is observed in solvents of increasing polarity which indicates a large difference in the dipole moments of the ground (S_o) and excited electronic state S_1. For example, the absorption maximum of **5e** in cyclohexane lies at 399 nm, this maximum is shifted in DMSO to 411 nm. **5e** displays in cyclohexane an emission maximum at λ = 444 nm and a quantum yield of 70%; in toluene: 462 nm, 64%; in $CHCl_3$: 477 nm, 45%; in ethyl acetate: 483 nm, 36%; in acetonitrile: 498 nm, 24%, and in DMSO: 526 nm, 13%. This characteristic solvent dependence can be assumed for a charge-transfer fluorophore where a charge separation in the excited state occurred.

As mentioned above, the pyrroles **5** can easily be oxidised under the formation of blue compounds. Whereas the 2,5-dicyanopyrrole **5c** was oxidised in solution by air within two days, the other pyrroles are relatively stable in solution. However after several days, the colour of the solutions changed to a slightly green. In order to study this behaviour we tested the electrochemical activity of derivatives **5**. The cyclovoltammetric measurements showed that the pyrroles **5** can be oxidized reversibly. Employing square-wave measurements on derivative **5d**, five peaks at 0.991, 1.221, 1.401, 1.616 and at 1.782 V can be ascribed to five different electron transfer steps. The quasi-reversibility of the three first oxidation steps was confirmed by cyclovoltammetric measurements ΔE_1 = 0.067 V, ΔE_2 = 0.094 V and ΔE_3 = 0.119 V. Based on these observations, a suitable oxidation reagent for the pyrroles **5** proved to be lead dioxide. Upon treatment with PbO_2 under mild conditions (dichloromethane, room temp.), the 3*H*-pyrroles of type **6** were isolated in excellent yields. Elemental analysis and MS data confirmed the elimination of two hydrogen atoms. Evidence for the unsymmetrical structure of the 3*H*-pyrroles **6a**–**c** (Scheme 3) was provided by double sets of signals in the ^1H and ^{13}C NMR spectra. In contrast to **4** and **5** the methyl groups of derivative **6a** form two different spin systems in their NMR spectra (^1H NMR: δ = 2.67/2.45 ppm. ^{13}C NMR: 22.8/21.6 ppm). In solution, the 3*H*-pyrroles **6** display a dark turquoise color (**6a**: UV/Vis in $CHCl_3$: λ_{max} = 730 nm, lg ε = 3.7). This broad absorption band with a maximum at about 730 nm originates from a azamerocyanine chromophore. Encouraged by these results, the pyrroles without benzothiazole substructures **5a**–**c** were integrated in the investigations with respect to their oxidative transformation.

Under similar mild conditions, blue products were isolated in very good yields. Somewhat surprisingly, the MS data indicated in this case the loss of four hydrogen atoms. Evidence for the structure of 3*H*-pyrrolo[3,4-*b*]quinoxalines **7** was mainly provided by their ^1H NMR spectra. In addition to the characteristic signals for one 4-tolyl substructure, two "doublets" δ = 8.51, 7.60 ppm and a "singlet" at δ = 7.18 ppm for the aromatic protons were detected. As key signal, a further singlet for an aromatic methyl group at δ = 2.58 ppm clearly underlined that an *ortho*-ring-fusion process took place. A single-crystal X-ray analysis of **7b** confirmed the molecular structure (Figure 4). Compound **7b** is a monomer in the solid state with the bond lengths and angles being in the expected range. Typically, an alternation of bond lengths in the 3*H*-pyrrole core was detected confirming the presence of an azamerocyanine-like chromophore. The C2–C3 bond (1.46 Å) lies in the range for single carbon–carbon bonds in a butadiene system (Figure 4). The π-system of the 4-tolyl ring is nearly perpendicular with respect to the central 3*H*-pyrrolo-quinoxaline functionality. In the UV/Vis spectra, a broad absorption at about 600 nm is originating from the azamerocyanine chromophore

whereas another one at about 380 nm can be ascribed to an enamino-ester subchromophore. A series of other oxidation reagents for the oxidation of **5a**–**c** was tested successfully, however, lead tetraacetate in the presence of potassium carbonate proved to be another suitable system. It must be noted that all attempts to isolate compounds of type **6** which possess ester or cyano groups failed. Even the use of substoichiometric amounts of oxidation reagents led to mixtures consisting of starting material **5** and tricyclic derivatives **7**. On the other hand, when **6a**–**c** were oxidized with lead tetraacetate in the presence of potassium carbonate at 60 °C, only inseparable mixtures of yellow colored/fluorescent compounds were obtained.

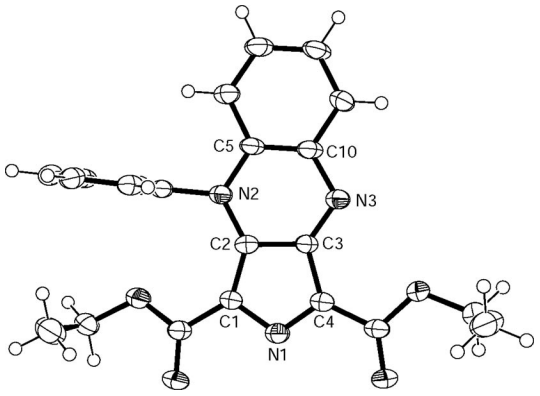


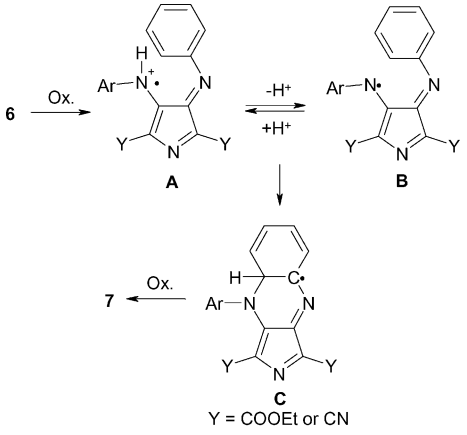
Figure 4. ORTEP plot (50% probability ellipsoids) of the solid state molecular structure of **7b**, selected bond lengths in Å: N1–C1 1.386(3), N1–C4 1.327(3), N2–C2 1.368(3), N3–C3 1.315(3), N2–C5 1.399(3), N3–C10 1.380(3), C1–C2 1.400(3), C2–C3 1.460(3), C3–C4 1.446(3).

The electrochemical activity of 3*H*-pyrrole **6a** can be detected employing square wave measurements which showed two peaks at –0.552 V and 0.724 V. The ring-fused 3*H*-pyrroloquinoxaline **7a** is also electrochemically active and a peak at –0.630 V can be observed. The 3*H*-pyrroles of type **6** can be reduced chemically with sodium dithionite in a water/THF mixture under the formation of the corresponding 1*H*-pyrroles **5**. Under the same conditions, the 3*H*-pyrroloquinoxalines **7** were reduced to yield the 1*H*-pyrroloquinoxalines **8** (Scheme 3). The leuco compound **8a** proved to be stable enough towards air thus allowing its isolation and to obtain the ^{1}H NMR spectroscopic data. The yellow solutions of compounds **8** display a strong yellow fluorescence (**8a**: $CHCl_3$: λ_{max} = 440 nm, λ_{Em} = 550 nm; **8c**: $CHCl_3$: λ_{max} = 422 nm, λ_{Em} = 510 nm). In solution compounds **8** were relatively fast reoxidised by air under the formation of parent compounds **7**.

We postulate the following mechanism (Scheme 4) for the unexpected formation of the 3*H*-pyrroloquinoxalines of type **7**. First the "normal" oxidation takes place leading to the intermediar formation of **6** which can also be regarded as an azafulvene and which is isoelectronic to the well known 4*H*-imidazoles.[4e,5] A following oxidation step then formed the radical cation **A** derived from a secondary amine. A relatively strong acidity was predicted for these compounds and consequently, deprotonation may result in the formation of the aminyl radical **B**. Finally, radical **B** is able to intramolecularly substitute the attached aromatic ring to give **C** and finally **7**. However, kinetic studies revealed that cylization reactions of aminyl radical cations are much faster than those of the corresponding neutral radicals.[6] The mechanism in which the key intermediates are aminyl radicals/radical cations is supported by the following experimental facts:

a) Generally, anilines can easily be oxidised and the thus formed amine radical cations tend to deprotonate quickly. Aryl-substituted aminyl radicals are relatively stable and under suitable conditions they undergo aromatic substitution reactions. As an example tetraphenyl hydrazines dissoziates in two diphenyl aminyl radicals, when heated. Subsequently, they react under intramolecular substitution to give derivatives of *N*,*N*′-diphenylphenazine.[7]

b) Other authors also suggest that aminyl cations formed via oxidation processes undergo a final intramolecular cyclization reaction with the attached aromatic ring.[8]



Scheme 4.

Conclusions

Push-pull pyrroles of type **4** and **5** were prepared by a Hinsberg-like cyclisation reaction starting from bis(imidoyl chlorides) **1** and various iminodiacetic acid derivatives **3**. The use of appropriate *N*-trifluoroacetyl residues as protecting/activating groups proved to be the method of choice for the preparation of 1*H*-pyrroles **5**. The pyrroles **5** exhibit a strong solvatofluorescence with large Stockes shifts and quantum yields up to 80%. The oxidation of the 3,4-diarylamino-1*H*-pyrroles **5** was studied. When benzothiazole substructures are present in 2,5-position of heterocycles **5**, a two-electron oxidation leads to 3*H*-pyrroles of type **6** in excellent yields. However, in the case of cyano or ester groups, a further oxidative process immediately led to the new 3*H*-pyrrolo[3,4-*b*]quinoxalines **7** via intramolecular ring anellation.

Experimental Section

General: The reagents described in the following section were purchased from commercial sources and were used directly unless

otherwise stated in the text. All solvents were of reagent grade and were dried according to common practice and were distilled prior to use. Compounds **1a**,**b** were synthesized according to the literature.[4b] Reactions were monitored by TLC, carried out on 0.2 mm Merck silica gel plates (60 F_{254}). The ^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE 250 and 400 spectrometers, shifts are relative to the signals of the solvent. Melting points were measured with a Galen III apparatus (Boëtius system) or with a Kofler-type apparatus and are uncorrected. Electrochemical measurements were carried out in CH_2Cl_2 with a Metrohm 663 VA Stand using platinum electrodes (reterence electrode SCE) and tetrabutylammoniumhexafluorophosphate as conductive salt.

Bis(imidoyl chlorides) 1. General Procedure: To a solution of 0.1 mol of the corresponding aniline in 50 mL of toluene 4.6 mL (6.6 g, 0.052 mol) of oxalyl chloride, dissolved in 50 mL of toluene was added within 10 min. A slurry of the corresponding oxanilide occurred, the mixture was stirred for 20 min at room temp. To the slurry 22.0 g (0.105 mol) of phosphorus pentachloride was added. The mixture was heated under reflux until no further hydrogen chloride is formed. The dark yellow reaction mixture was concentrated in vacuo to dryness and the crude product was recrystallized from *n*-heptane.

***N*,*N*′-Bis(4-methoxyphenyl)oxaldiimidoyl Chloride (1c):** Yellow crystals, yield 12.9 g (74%), m.p. 150 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.29 (d, ^3J = 8 Hz, 4 H,CH-Ar), 6.97 (d, ^3J = 8 Hz, 4 H, CH-Ar), 3.86 (s, 6 H, OCH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 158.8, 138.1, 136.3 (Cl-C=N), 123.8, 114.1, 55.5 (OCH_3) ppm.

***N*,*N*′-Bis(4-octyloxyphenyl)oxaldiimidoyl Chloride (1d):** Yellow crystals, yield 17.0 g (64%), m.p. 93 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.29 (d, ^3J = 8 Hz, 4 H, CH-Ar), 6.96 (d, ^3J = 8 Hz, 4 H, CH-Ar), 4.00 (t, ^3J = 6.5 Hz, 4 H,OCH_2), 1.78 (m, 4 H, CH), 1.38 (m, 20 H, CH), 0.90 (m, 6 H, CH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 158.5, 137.9, 135.9 (C=N), 123.8, 114.6, 68.3 (OCH_2), 31.8, 29.3, 29.2, 26.0, 22.6, 14.0 ppm. MS (EI): *m*/*z* (%) = 536 (4), 534 (10), 532 (15) [M^+], 301 (10), 268 (25), 266 (100) [M/2]$^+$, 154 (30). $C_{30}H_{42}Cl_2N_2O_2$ (533.59): calcd. C 67.53, H 7.93, N 5.29; found C 67.38, H 7.79, N 5.18.

***N*,*N*′-Bis(3-trifluoromethylphenyl)oxaldiimidoyl Chloride (1e):** Pale yellow crystals, yield 16.6 g (82%), m.p. 84–86 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.6–7.5 (m, 4 H, CH-Ar), 7.40 (s, 2 H, CH-Ar), 7.3 (m, 2 H, CH-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.0, 136.6 (C=N), 131.7 (q, J = 32 Hz, C-CF_3), 129.7, 123.5 (q, J = 272 Hz, CF_3), 123.3 (q, J = 4 Hz), 117.5 (q, J = 4 Hz) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –63.2 (s, 6 F, CF_3) ppm.

Bis(2-benzothiazolylmethyl)amine (2c): A modified procedure to ref.[9] was used. In 20 mL of xylene 5.0 g (52 mmol) of iminodiacetonitrile, 13.8 g (110 mmol) of 2-aminothiophenol were heated in the presence of 0.5 mL of quinoline to 150 °C until no further ammonia gas is formed (ca. 1 h). Upon cooling down the product **2c** crystallised from the reaction mixture, the crude product was washed with diethyl ether and after drying it was used without any further purification. Recrystallisation from $CHCl_3$/*n*-heptane yielded **2c** as colourless crystals. 14.7 g (91%), m.p. 134 °C ($CHCl_3$/*n*-heptane) ^1H NMR (250 MHz, $CDCl_3$): δ = 8.1–7.8 (m, 4 H, CH-Ar), 7.5–7.3 (m, 4 H, CH-Ar), 4.41 (s, 4 H, CH_2), 2.78 (s, 1 H, NH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 171.4 (C=N), 153.3, 135.1, 126.0, 125.0, 122.9, 121.8, 50.9 (CH_2) ppm. MS (EI): *m*/*z* (%) = 311 (10) [M^+], 268 (10), 163 (30), 149 (100), 108 (10), 45 (10). $C_{16}H_{13}N_3S_2$ (311.43): calcd. C 61.71, H 4.21, N 13.45, S 20.59; found C 61.74, H 4.23, N 13.39, S 20.85.

***N*-Benzoyliminodiacetonitrile (3b):** The solution of 4.7 g (50 mmol) of iminodiacetonitrile **2b** and 14 mL (10.1 g, 0.1 mol) of triethylamine in 50 mL of pyridine was cooled down to 0 °C. Within 20 min 7.6 mL (9.2 g, 67 mmol) of benzoyl chloride was added. The mixture was stirred for 4 h at room temp. To the formed slurry 100 mL of ice was added, the residue was filtered off, washed with a diluted potassium carbonated solution and water. The crude product was washed with 5 mL of ethanol and was recrystallized from ethanol to yield **3b** as colourless crystals. Yield 9.3 g (93%), m.p. 132 °C (ethanol), 132 °C.[10] ^1H NMR (250 MHz, $CDCl_3$): δ = 7.8–7.5 (m, 5 H, CH-Ph) 4.57 (s, 4 H, CH_2) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 171.3 (C=O), 133.5, 131.6, 129.4, 127.4, 116.5 (CN), 37.6 (CH_2) ppm. MS (EI): *m*/*z* (%) = 199 (100) [M^+], 130 (50), 77 (90). $C_{11}H_9N_3O$ (199.21): calcd. C 66.32, H 4.55, N 21.09; found C 66.52, H 4.71, N 21.01.

Trifluoroacetamides 3c,d. General Procedure: The solution of 50 mmol of diethyl iminodiacetate (**2a**) or iminodiacetonitrile (**2b**) in 50 mL of dry CH_2Cl_2 was cooled down to 0 °C. Within 20 min 7.7 mL (11.6 g, 55 mmol) of trifluoroacetic anhydride was added. The mixture was stirred for 24 h at room temp., the solvent was evaporated in vacuo and after vacuum distillation the product was obtained as colourless oil, in the case of **3d** it solidified upon standing to give a colourless crystalline solid.

Diethyl *N*-(Trifluoroacetyl)iminodiacetate (3c): Colourless oil, yield 12.2 g (86%), bp. 110–112 °C (0.2 mbar), ^1H NMR (250 MHz, $CDCl_3$): δ = 4.25 (m, 8 H, CH_2), 1.28 (m, 6 H, CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 167.6 (COOEt), 167.5 (COOEt), 157.6 (q, ^2J = 40 Hz, $COCF_3$), 115.4 (q, ^1J = 290 Hz, CF_3), 62.1 (OCH_2), 61.8 (OCH_2), 49.3 (q, ^4J = 4 Hz, CH_2), 49.1 (q, ^4J = 1 Hz, CH_2), 13.9 (CH_3) ppm. MS (EI): *m*/*z* (%) = 285 (20) [M^+], 239 (45), 59 (100). $C_{10}H_{14}F_3NO_5$ (285.22): calcd. C 42.11, H 4.95, N 4.91; found C 41.89, H 4.79, N 4.73.

***N*-(Trifluoroacetyl)iminodiacetonitrile (3d):** Colourless crystals, yield 8.5 g (89%), bp. 104–105 °C (0.5 mbar), m.p. 54 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 4.54 (s, 4 H, CH_2CN) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 156.3 (q, ^2J = 40 Hz, $COCF_3$), 115.2 (q, ^1J = 290 Hz, CF_3), 112.8 (CN), 112.5 (CN), 36.1 (q, ^4J = 4 Hz, CH_2), 35.0 (CH_2) ppm. MS (EI): *m*/*z* (%) = 191 (10) [M^+], 122 (100), 69 (40). $C_6H_4F_3N_3O$ (191.11): calcd. C 37.71, H 2.11, N 21.99; found C 37.21, H 1.93, N 21.86.

Preparation of *N*,*N*-Bis(2-benzothiazolylmethyl)trifluoroacetamide (3e): A solution consisting of 15.6 g (50 mmol) of bis(2-benzothiazolylmethyl)amine (**2c**) and 14 mL (10.1 g, 0.1 mol) of triethylamine in 100 mL of dry CH_2Cl_2 was cooled down to 0 °C. Within 20 min 7.7 mL (11.6 g, 55 mmol) of trifluoroacetic anhydride was added. The mixture was stirred for 24 h at room temp. To the mixture 100 mL of water was added and the water layer was extracted to times with CH_2Cl_2. The combined organic layers were washed with water three times, after drying over Na_2SO_4 the solvent was evaporated in vacuo. The crude product was recrystallized from $CHCl_3$/*n*-heptane to yield **3e** as colorless crystals. Yield 22.1 g (92%), m.p. 103 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 8.2–7.8 (m, 4 H, CH-Ar), 7.5–7.4 (m, 4 H, CH-Ar), 5.23 + 5.21 (m, 4 H, CH_2) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 164.3 (C=N), 164.0 (C=N), 157.3 (q, ^2J = 40 Hz, $COCF_3$), 152.9, 152.5, 135.5, 135.1, 126.5, 126.3, 125.8, 125.7, 123.5, 123.3, 121.8, 116.2 (q, ^1J = 290 Hz, CF_3), 49.3 (q, ^4J = 4 Hz, CH_2), 48.4 (CH_2) ppm.

Synthesis of the Pyrroles 4 and 5 by Cycloacylation with 1: The solution of 5 mmol of the corresponding *N*-protected compound **3a**–**e** in 50 mL of dry THF was cooled down to 78 °C and 1.7 g (15 mmol) of *t*BuOK was added. To the solution 5.1 mmol of the corresponding bis(imidoyl chloride) **1** was added. The deep red reaction mixture was stirred at 30 °C for 10–20 min. The mixture was neutralized to pH 7 by addition of HCl/isopropyl alcohol. The

mixture was concentrated in vacuo to dryness. The remaining solid was dissolved in $CHCl_3$ (by **4c**, **5e**, **5h** $CHCl_3$/methanol) and was dried with Na_2SO_4. Upon removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel ($CHCl_3$/*n*-heptane, or $CHCl_3$/methanol) and the crude product was purified by recrystallization from $CHCl_3$/*n*-heptane to yield **4a**–**c** and **5a**–**h**.

Diethyl 1-Benzoyl-3,4-bis(4-tolylamino)pyrrole-2,5-dicarboxylate (4a): Colourless crystals, yield 1.4 g (53%), m.p. 172 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.8–7.5 (m, 5 H, CH-Ph), 6.92 (s, 2 H, NH), 6.84 (d, ^3J = 8 Hz, 4 H, CH-Tol), 6.59 (d, ^3J = 8 Hz, 4 H, CH-Tol), 4.06 (q, ^3J = 7.1 Hz, 4 H, OCH_2), 2.20 (s, 6 H, CH-Tol), 0.97 (t, ^3J = 7.1 Hz, 6 H, CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 169.4 (COPh), 160.6 (COOEt), 139.3, 134.7, 133.8, 130.1, 129.8, 129.0, 128.7, 119.8, 118.2, 116.1, 61.1, 20.6, 13.5 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3372 (NH), 2983 (CH), 2927 (CH), 1743, 1711, 1685, 1512, 1407, 1380, 1336, 1273, 1237, 1219, 1176, 1109, 1020, 807 cm^{-1}. MS (EI): *m*/*z* (%) = 525 (10) $[M]^+$, 329 (90), 105 (100), 77 (50) $[C_6H_5]^+$. $C_{31}H_{31}N_3O_5$ (525.61): calcd. C 70.84, H 5.94, N 7.99; found C 70.68, H 6.06, N 8.16. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 391 (3.9) nm.

Diethyl 1-Benzoyl-3,4-bis(phenylamino)pyrrole-2,5-dicarboxylate (4b): Colourless crystals, yield 1.0 g (40%), m.p. 137–139 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.7–6.9 (m, 15 H, CH), 4.11 (q, ^3J = 7.1 Hz, 4 H, OCH_2) 0.88 (t, ^3J = 7.1 Hz, 6 H, CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 169.1 (COPh), 160.2 (COOEt), 142.3, 139.9, 129.5, 128.8, 126.4, 125.2, 124.9, 122.7, 121.4, 114.4, 61.6, 14.0 ppm. MS (EI): *m*/*z* (%) = 497 (60) $[M^+]$, 301 (100), 105 (80). $C_{29}H_{27}N_3O_5$ (497.56): calcd. C 70.01, H 5.47, N 8.45; found C 69.65, H 5.22, N 8.04.

1-Benzoyl-3,4-bis(4-tolylamino)pyrrole-2,5-dicarbonitrile (4c): Yellow crystals, yield 440 mg (27%), m.p. 153–155 °C. ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 8.19 (s, 2 H, NH), 7.8–7.6 (m, 5 H, CH-Ph), 7.36 (d, ^3J = 8 Hz, 4 H, CH-Tol), 6.89 (d, ^3J = 8 Hz, 4 H, CH-Tol), 2.20 (s, 6 H, CH_3) ppm. ^{13}C NMR (63 MHz, [D$_6$]-DMSO): δ = 165.0 (C=O), 139.2, 137.0, 132.5, 130.5, 130.3, 129.2, 128.9, 117.9, 114.9, 111.3, 96.9, 20.7 ppm. MS (EI): *m*/*z* (%) = 431 (70) $[M^+]$, 327 (40), 155 (40), 105 (100), 91 (80) $[C_7H_7^+]$, 77 (100). $C_{27}H_{11}N_5O$ (431.50): calcd. C 75.16, H 4.31, N 16.23; found C 74.88, H 4.01, N 15.91.

Deprotection of Pyrroles 4: A solution of 2 mmol of the corresponding pyrrole **4a**–**c** and 100 mg (0.5 mmol) of *p*-toluenesulfonic acid in 10 mL of ethanol were heated under reflux until no starting material could be detected (TLC, approx. 2 h). The solvent was removed in vacuo, the residue was dissolved in $CHCl_3$, the solution was washed with sodium hydrogen carbonate solution, with water and was then dried with Na_2SO_4. Upon removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel ($CHCl_3$/*n*-heptane) to yield **5a** (yield 0.4 g, 46%), **5b** (0.3 g, 42%), **5c** (0.2 g, 30%).

Diethyl 3,4-Bis(4-tolylamino)pyrrole-2,5-dicarboxylate (5a): Colourless crystals, yield 1.3 g (63%), m.p. 130 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.91 (s, 1 H, NH pyrrole), 6.84 (d, ^3J = 8 Hz, 4 H, CH-Tol), 6.60 (d, ^3J = 8 Hz, 4 H, CH-Tol), 6.41 (s, 2 H, NH), 4.33 (q, ^3J = 7.1 Hz, 4 H, OCH_2), 2.19 (s, 6 H, Tol-CH), 1.32 (t, ^3J = 7.1 Hz, 6 H, CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 160.8 (C=O), 140.8, 129.4, 128.9, 127.5, 117.0, 114.1, 60.8, 20.5, 14.3 ppm. MS (EI): *m*/*z* (%) = 421 (80) $[M^+]$, 375 (20), 330 (30), 329 (100). $C_{24}H_{27}N_3O_4$ (421.50): calcd. C 68.39, H 6.46, N 9.97; found C 68.28, H 6.42, N 9.68. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 34 (3.8), 381 (3.7) nm. CV: E_{OX}^1 = 1.045 V, E_{OX}^2 = 1.421 V.

Diethyl 3,4-Bis(phenylamino)pyrrole-2,5-dicarboxylate (5b): Colourless crystals, yield 1.1 g (57%), m.p. 99.5–100 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.96 (s, 2 H, NH pyrrole), 7.1–7.0 (m, 4 H, CH-Ph), 6.8–6.6 (m, 8 H, CH-Ph, NH), 4.35 (q, ^3J = 7.1 Hz, 4 H, OCH_2), 1.33 (t, ^3J = 7.1 Hz, 6 H, CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 160.8 (C=O), 142.8, 128.3, 126.8, 120.1, 116.9, 114.1, 60.9, 14.3 ppm. MS (EI): *m*/*z* (%) = 393 (90) $[M^+]$, 347 (25), 301 (100), 77 (60). $C_{22}H_{23}N_3O_4$ (393.45): calcd. C 67.16, H 5.89, N 10.68; found C 67.10, H 5.85, N 10.53. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 335 (3.9), 381 (3.7) nm.

3,4-Bis(4-tolylamino)pyrrole-2,5-dicarbonitrile (5c): Colourless crystals, yield 0.6 g (36%), m.p. 187 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.87 (s, 1 H, NH pyrrole), 7.05 (d, ^3J = 8 Hz, 4 H, CH-Tol), 6.71 (d, ^3J = 8 Hz, 4 H, CH-Tol) 5.20 (s, 2 H, NH), 2.28 (s, 6 H, CH-Tol) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 139.5, 131.5, 130.6, 129.9, 117.0, 111.7, 97.7, 20.6 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3330 (NH), 2924 (CH), 2873 (CH), 2209 (CN), 1679, 1612, 1535, 1509, 1187, 1104, 812 cm^{-1}. MS (EI): *m*/*z* (%) = 327 (100) $[M^+]$, 312 (20), 91 (20). $C_{20}H_{17}N_5$ (327.39): calcd. C 73.37, H 5.23, N 21.39; found C 73.03, H 5.01, N 21.11. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 342 (3.8) nm.

2,5-Bis(2-benzothiazolyl)-3,4-bis(4-tolylamino)pyrrole (5d): Yellow crystals, yield 1.8 g (65%), m.p. 255–256 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 12.04 (s, 1 H, NH pyrrole), 8.1–7.9 (m, 4 H, CH-Ar), 7.5–7.3 (m, 4 H, CH-Ar), 7.28 (s, 2 H, NH), 6.81 (d, ^3J = 8 Hz, 4 H, CH-Tol), 6.56 (d, ^3J = 8 Hz, 4 H, CH-Tol), 2.10 (s, 6 H, CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 156.8, 152.6, 144.1, 134.9, 129.7, 126.9, 126.5, 125.1, 124.3, 122.5, 122.3, 114.3, 79.6, 20.6 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3397 (NH), 3371 (NH), 2999, 2916, 1613, 1538, 1511, 1491, 1311, 1241, 1214, 756 cm^{-1}. MS (EI): *m*/*z* (%) = 543 (70) $[M^+]$, 264 (80), 219 (100), 91 (40), 65 (40). $C_{32}H_{25}N_5S_2$ (543.72): calcd. C 70.69, H 4.63, N 12.88, S 11.79; found C 70.41, H 4.32, N 12.63, S 11.97. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 385 (4.4), 405 (4.4) nm. Em: cyclohexane λ_{max} = 452, toluene λ_{max} = 475, $CHCl_3$ λ_{max} = 485, DMSO λ_{max} = 550 nm. CV: E_{RED}^1 = –0.684 V, E_{OX}^1 = 0.991 V, E_{OX}^2 = 1.221 V, E_{OX}^3 = 1.401 V, E_{OX}^4 = 1.616 V, E_{OX}^5 = 1.782 V.

2,5-Bis(2-benzothiazolyl)-3,4-bis(phenylamino)pyrrole (5e): Yellow crystals, yield 1.5 g (59%), m.p. 215–219 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 10.38 (s, 1 H, NH pyrrole), 8.1–7.8 (m, 4 H, CH-Ar), 7.5–7.1 (m, 8 H, CH-Ar), 6.8–6.6 (m, 6 H, CH-Ar) 5.21 (s, 2 H, NH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 156.0, 152.5, 145.3, 134.9, 129.3, 126.4, 125.7, 124.7, 124.3, 122.3, 121.6, 119.7, 114.7 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3441 (NH), 3334 (NH), 3054, 2979, 1673, 1597, 1538, 1494, 1472, 1396, 1313, 1296, 1244, 1206, 1173, 1130, 752, 735 cm^{-1}. MS (EI): *m*/*z* (%) = 515 (100) $[M^+]$, 218 (20), 77 (20). $C_{30}H_{21}N_5S_2$ (515.66): calcd. C 69.88, H 4.10, N 13.58, S 12.44; found C 69.74, H 4.01, N 13.38, S 12.24. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 308 (4.2), 385 (4.5), 404 (4.5) nm. Em: cyclohexane λ_{max} = 444, toluene λ_{max} = 462, $CHCl_3$ λ_{max} = 477, acetonitrile λ_{max} = 498, DMSO λ_{max} = 526 nm.

2,5-Bis(2-benzothiazolyl)-3,4-bis(4-methoxyphenylamino)pyrrole-(5f): Yellow crystals, yield 2.9 g (71%), m.p. 219 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 10.19 (s, 1 H, NH pyrrole), 8.0–7.8 (m, 4 H, CH-Ar), 7.4–7.3 (m, 4 H, CH-Ar), 6.72 (d, ^3J = 8 Hz, 4 H, CH-Ar), 6.61 (d, ^3J = 8 Hz, 4 H, CH-Ar) 5.17 (s, 2 H, NH), 3.74 (s, 6 H, OCH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 156.3, 153.8, 152.5, 138.7, 134.7, 126.5, 126.4, 124.7, 123.5, 122.2, 121.6, 116.7, 114.7, 55.6 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3435 (NH), 3373 (NH), 3316, 3058, 2953, 2833, 1596, 1507, 1461, 1398, 1239, 1134, 886 cm^{-1}. MS (EI): *m*/*z* (%) = 575 (100) $[M]^+$, 560 (10), 452 (10), 436 (20), 272 (30), 218 (40), 122 (30), 108 (20). $C_{32}H_{25}N_5O_2S_2$ (575.72): calcd. C 66.76, H 4.38, N 12.16, S 11.14; found C 66.55, H 4.14, N 12.01,

S 10.87. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 316 (4.3), 386 (4.4), 407 (4.4) nm. Em: cyclohexane λ_{max} = 470, $CHCl_3$ λ_{max} = 525.

2,5-Bis(2-benzothiazolyl)-3,4-bis(4-octoxyphenylamino)pyrrole 5g: Yellow crystals, yield 1.6 g (42%), m.p. 83–86 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 10.16 (s, 1 H, NH pyrrole), 8.0–7.8 (m, 4 H, CH-Ar), 7.4–7.3 (m, 4 H, CH-Ar), 6.73 (d, ^3J = 8 Hz, 4 H, CH-Ar), 6.59 (d, ^3J = 8 Hz, 4 H, CH-Ar), 5.14 (s, 2 H, NH), 3.86 (t, ^3J = 6.5 Hz, 4 H, OCH_2), 1.80 (m, 4 H CH), 1.4–1.2 (m, 20 H CH), 0.92 (m, 6 H CH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 156.3, 153.3, 152.6, 138.6, 134.7, 126.6, 126.4, 124.6, 123.5, 122.2, 121.6, 116.7, 115.4, 68.6, 31.8, 29.44, 29.41, 29.2, 26.1, 22.6, 14.1 ppm. MS (EI): *m/z* (%) = 772 (40) $[M]^+$, 658 (10), 546 (10), 452 (20), 345 (10), 226 (10), 221 (20), 109 (100). $C_{46}H_{53}N_5O_2S_2$ (772.10): calcd. C 71.56, H 6.92, N 9.07, S 8.31; found C 71.02, H 7.13, N 8.63, S 7.57.

2,5-Bis(2-benzothiazolyl)-3,4-bis(3-trifluoromethylphenylamino)pyrrole 5h: Yellow crystals, yield 1.2 g (38%), m.p. 243 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 10.36 (s, 1 H, N H pyrrole), 8.01 (m, 2 H, CH-Ar), 7.79 (m, 2 H, CHAr), 7.51 (m, 2 H, CH-Ar), 7.35 (m, 2 H, CH-Ar), 7.18 (m, 2 H, CH-Ar), 7.02 (m, 2 H, CH-Ar), 6.81 (m, 2 H, CH-Ar), 6.75 (m, 2 H, CH-Ar), 5.52 (s, 2 H, NH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 155.7, 152.3, 144.9, 134.5, 131.6 (q, ^2J = 32 Hz, CCF_3), 129.6, 126.7, 125.1, 124.1, 124.0 (^1J = 272 Hz, CF_3), 123.8, 122.4, 121.6, 117.8, 116.4 (q, ^3J = 4 Hz), 111.5 (q, ^3J = 4 Hz) ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3419 (NH), 3388 (NH), 3324, 3065, 1616, 1597, 1469, 1334, 1117, 754 cm^{-1}. MS (EI): *m/z* (%) = 651 (10) $[M^+]$, 219 (25), 161 (30), 111 (45), 97 (70), 83 (100), 69 (80), 57 (90). $C_{32}H_{19}F_6N_5S_2$ (651.66): calcd. C 58.98, H 2.94, N 10.75, S 9.84; found C 58.86, H 2.96, N 10.81, S 9.78. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 381 (4.5), 402 (4.6) nm. Em: cyclohexane λ_{max} = 455, toluene λ_{max} = 459, $CHCl_3$ λ_{max} = 466, DMSO λ_{max} = 488 nm.

General Procedure for the Oxidation of Pyrroles of Type 5: To the solution of 2 mmol of the corresponding pyrrole **5** in 50 mL of CH_2Cl_2, 1.4 g (10 mmol) of potassium carbonate and 6.0 g (25 mmol) of lead dioxide was added (alternatively, 2.5–3.5 *g* = 5.6–8.1 mmol of lead tetraacetate can be used for oxidation). The reaction mixture was stirred for 2 h at room temp. When starting material can be detected after this period by TLC, additional 1.2 g (5 mmol) of lead dioxide was added and stirring was continued for 2 h. The reaction mixture was filtered and the residue was washed with CH_2Cl_2, the combined deeply blue organic solutions were washed three times with water and were dried with Na_2SO_4. Upon removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel ($CHCl_3$/methanol) and the crude product was purified by recrystallization from $CHCl_3$/*n*-heptane to yield **6a**–**c** and **7a**–**c** as deeply blue crystals.

2,5-Bis(2-benzothiazolyl)-4-(4-tolylamino)-3-(4-tolylimino)-3*H*-pyrrole (6a): Blue crystals, yield 910 mg (84%), m.p. 290 °C (decomp). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.33 (d, ^3J = 8 Hz, 1 H, CH-Ar), 8.14 (d, ^3J = 8 Hz, 1 H, CH-Ar), 7.92 (d, ^3J = 8 Hz, 1 H, CH-Ar), 7.74 (d, ^3J = 8 Hz, 1 H, CH-Ar), 7.57–7.19 (m, 12 H, CH-Ar), 2.67 (s, 3 H, CH-Tol), 2.45 (s, 3 H, CH-Tol) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 163.5, 162.6, 154.6, 148.0, 145.8, 140.4, 136.3, 136.0, 135.3, 135.0, 132.6, 130.6, 130.0, 128.3, 128.1, 125.7, 125.0, 124.7, 123.6, 123.5, 122.0, 121.3, 121.0, 118.8, 118.5, 116.2, 22.8, 21.6 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3052 (CH), 2918 (CH), 1532, 1511, 1433, 1412, 1163, 1119, 1073, 1008, 922, 746, 725 cm^{-1}. MS (EI): *m/z* (%) = 541 (80) $[M^+]$, 450 (100) $[M - C_7H_7]^+$, 270 (60), 135 (60). $C_{32}H_{23}N_5S_2$ (541.70): calcd. C 70.95, H 4.28, N 12.93, S 11.84; found C 70.55, H 3.99, N 12.46, S 11.23. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 342 (4.8), 369 (4.7), 731 (3.7) nm. CV: $E_{RED}{}^1$ = 0.552 V, $E_{RED}{}^2$ = –0.724 V.

2,5-Bis(2-benzothiazolyl)-4-(phenylamino)-3-(phenylimino)-3*H*-pyrrole (6b): Blue crystals, yield 812 mg (79%), m.p. 305–307 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.63 (d, ^3J = 8 Hz, 1 H, CH-Ar), 8.28 (d, ^3J = 8 Hz, 1 H, CH-Ar), 7.95 (d, ^3J = 8 Hz, 1 H, CH-Ar), 7.79–7.26 (m, 15 H, CH-Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 163.4, 162.6, 154.8, 154.5, 149.6, 138.9, 137.1, 135.9, 135.2, 135.1, 133.8, 133.3, 130.5, 130.4, 129.5, 128.5, 125.9, 125.1, 123.9, 123.7, 122.3, 121.4, 121.0, 118.9, 117.9, 117.0 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3335 (NH), 3054 (CH), 2960 (CH), 2923 (CH), 1534, 1497, 1434, 1398, 1146, 1115, 1070, 1012, 921, 747, 715 cm^{-1}. MS (EI): *m/z* (%) = 513 (30) $[M^+]$, 511 (100), 436 (10), 255 (40), 146 (30), 102 (10). $C_{30}H_{19}N_5S_2$ (513.65): calcd. C 70.15, H 3.37, N 13.03, S 12.48; found C 69.77, H 3.10, N 12.79, S 12.15. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 334 (4.7), 366 (4.6), 746 (3.5) nm.

2,5-Bis(2-benzothiazolyl)-4-(4-methoxyphenylamino)-3-(4-methoxyphenylimino)-3*H*-pyrrole (6c): Blue crystals, yield 993 mg (87%), m.p. 307–308 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.36 (d, ^3J = 8 Hz, 1 H, CH-Ar), 8.23 (d, ^3J = 8 Hz, 1 H, CH-Ar), 7.83–7.16 (m, 14 H, CH-Ar), 6.69 (s, 1 H, NH), 3.96 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 164.4, 163.5, 162.9, 161.3, 154.1, 146.2, 135.2, 134.6, 134.4, 134.1, 133.2, 131.7, 129.4, 125.9, 125.1, 124.8, 123.6, 123.2, 122.0, 121.3, 121.0, 119.3, 119.0, 118.2, 114.8, 97.1, 56.0, 55.7 ppm. MS (EI): *m/z* (%) = 573 (100) $[M^+]$, 571 (70), 466 (40) $[M - C_7H_7O]^+$, 287 (50). $C_{32}H_{23}N_5O_2S_2$ (573.70): calcd. C 67.00, H 4.04, N 12.21, S 11.18; found C 66.68, H 3.76, N 11.88, S 11.07. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 350 (4.8), 372 (4.7), 706 (3.7) nm.

Diethyl 6-Methyl-4-(4-tolylamino)-3*H*-pyrrolo[3,4-*b*]quinoxaline-1,3-dicarboxylate (7a): Blue crystals, yield 628 mg (75%), m.p. 229 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.51 (d, ^3J = 8 Hz, 1 H, CH-Ar), 7.60 (dd, ^3J = 8, ^4J = 2 Hz, 1 H, CH-Ar), 7.49 (d, ^3J = 8 Hz, 2 H, CH-Tol), 7.34 (d, ^3J = 8 Hz, 2 H, CH-Tol), 7.18 (m, 1 H, CH-Ar), 4.57 (q, ^3J = 7.1 Hz, 2 H, OCH_2), 4.04 (q, ^3J = 7.1 Hz, 2 H, OCH_2), 2.58 (s, 3 H, CH-Ar), 2.53 (s, 3 H, CH-Ar), 1.51 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.21 (t, ^3J = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 162.53, 162.47, 147.9, 146.1, 140.8, 137.0, 136.1, 132.8, 130.4, 129.63, 129.59 129.2, 127.0, 122.1, 116.1, 115.4, 60.9, 60.6, 22.8, 21.5, 14.5, 14.3 ppm. MS (EI): *m/z* (%) = 417 (50) $[M^+]$, 299 (95), 273 (100), 271 (90), 91 (100). MS (micro-ESI) *m/z* (%) = 456 (10) $[M + K^+]$, 440 (100) $[M + Na^+]$. HRMS: calcd. for $C_{24}H_{23}N_3NaO_4$: 440.159; found 440.156. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 292 (4.7), 378 (4.2), 594 (3.6) nm. CV: $E_{RED}{}^1$ = 0.630 V.

Diethyl 4-(Phenylamino)-3*H*-pyrrolo[3,4-*b*]quinoxaline-1,3-dicarboxylate (7b): Blue crystals, yield 560 mg (72%), m.p. 227 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.65 (m, 1 H, CH-Ar), 7.8–7.7 (m, 5 H, CH-Ar), 7.5–7.4 (m, 3 H, CH-Ar), 4.58 (q, ^3J = 7.1 Hz, 2 H, OCH_2), 4.04 (q, ^3J = 7.1 Hz, 2 H, OCH_2), 1.51 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.21 (t, ^3J = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 162.36, 162.32, 148.9, 138.6, 137.9, 134.0, 133.2, 130.7, 130.2, 129.9, 129.2, 127.3, 126.9, 121.9, 117.2, 115.3, 61.1, 60.6, 14.5, 14.3 ppm. MS (EI): *m/z* (%) = 389 (75) $[M^+]$, 270 (100), 245 (95), 244 (90). MS (micro-ESI) *m/z* (%) = 428 (10) $[M + K^+]$, 412 (100) $[M + Na^+]$. HRMS: calcd. for $C_{22}H_{19}N_3NaO_4$: 412.127; found 412.128. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 288 (4.6), 357 (4.0), 600 (3.5) nm.

6-Methyl-4-(4-tolylamino)-3*H*-pyrrolo[3,4-*b*]quinoxaline-1,3-dicarbonitrile (7c): Blue crystals, yield 440 mg (68%), m.p. 291–293 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.46 (d, ^3J = 8 Hz, 1 H, CH-Ar), 7.74 (dd, ^3J = 8, 1 H, ^4J = 2 Hz, CH-Ar), 7.62 (d, ^3J = 8 Hz,

2 H, CH-Tol), 7.42 (d, ^3J = 8 Hz, 2 H, CH-Tol), 7.29 (s, 1 H, CH-Ar), 2.62 (s, 6 H, CH-Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 148.6, 143.1, 140.1, 137.8, 132.5, 132.4, 131.4, 130.9, 129.7, 127.0, 126.8, 115.7, 114.8, 114.1, 113.7, 97.5, 23.1, 21.6 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 2922 (CH), 2852 (CH), 2215 (CN), 1557, 1509, 1391, 1358, 1152, 1108, 1025, 825, 754 cm^{-1}. MS (EI): *m*/*z* (%) = 323 (100) [M$^+$], 308 (10), 91 (10). MS (micro-ESI) *m*/*z* (%) = 363 (10) [M + K$^+$], 346 (100) [M + Na$^+$], 324 (40) [M + H$^+$]. HRMS: calcd. for $C_{20}H_{14}N_5$: 324.126; found 324.125. UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 282 (4.5), 378 (4.1), 500 (3.4) nm.

Reduction of *3H*-Pyrroles 6 and 3*H*-Pyrrolo[3,4-*b*]quinoxalines 7: To the solution of 1 mmol of the corresponding 3*H*-pyrrole **6** or **7** in 20 mL of THF, 1.1 g (12 mmol) of sodium dithionite dissolved in 20 mL of water was added. The reaction mixture was stirred for one hour at room temp. and then the yellow organic layer was separated. The aqueous layer was extracted with $CHCl_3$ and the combined organic layers were dried with Na_2SO_4. Upon removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel ($CHCl_3$/*n*-heptane) to yield **5** and **8a**–**c**. The compounds of type **8** quickly reoxidize in the presence of air.

Diethyl 6-Methyl-4-(4-tolylamino)-1*H*-pyrrolo[3,4-*b*]quinoxaline-1,3-dicarboxylate (8a): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.8–7.7 (m, 4 H, CH-Ar), 7.6–7.5 (m, 3 H, CH-Ar), 6.9 (s, 1 H, CH-Ar), 4.36 (q, ^3J = 7.1 Hz, 2 H, OCH_2), 3.89 (q, ^3J = 7.1 Hz, 2 H, OCH_2), 2.58 (s, 3 H, CH-Ar), 2.53 (s, 3 H, CH-Ar), 1.39 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.04 (t, ^3J = 7.1 Hz, 3 H, CH_3) ppm.

Crystal Structure Determination for 5d and 7b: The intensity data for the compound was collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[11] The structure was solved by direct methods (SHELXS)[12] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[13] All hydrogen atoms were included at calculated positions with fixed thermal parameters. For the amine groups of **5d** the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non hydrogen atoms were refined anisotropically.[13] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

CCDC-719950 (for **5d**) and CCDC-719951 (for **7b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 5d: $C_{32}H_{25}N_5S_2$, $CHCl_3$, *Mr* = 663.06 g mol^{-1}, yellow prism, size 0.04 × 0.04 × 0.04 mm^3, monoclinic, space group $P2_1/n$, *a* = 16.4899(9), *b* = 10.7066(5), *c* = 17.3076(9) Å, β = 93.071(3)°, *V* = 3051.3(3) Å^3, *T* = –90 °C, *Z* = 4, $\rho_{calcd.}$ = 1.443 g cm^{-3}, μ (Mo-K_α) = 4.71 cm^{-1}, *F*(000) = 1368, 19174 reflections in *h*(–17/21), *k*(–13/13), *l*(–21/22), measured in the range 1.75° ≤ Θ ≤ 27.42°, completeness Θ_{max} = 98.8%, 6867 independent reflections, R_{int} = 0.0659, 4299 reflections with $F_o > 4\sigma(F_o)$, 400 parameters, 0 restraints, $R_{1,obsd.}$ = 0.0795, $wR^2_{obsd.}$ = 0.1884, $R_{1,all}$ = 0.1344, $wR_{2,all}$ = 0.2210, GOOF = 1.033, largest difference peak and hole: 2.235/–1.325 e Å^{-3}.

Crystal Data for 7b: $C_{22}H_{19}N_3O_4$, *Mr* = 389.40 g mol^{-1}, purple prism, size 0.05 × 0.05 × 0.05 mm^3, monoclinic, space group $P2_1/n$, *a* = 12.0835(12), *b* = 10.9753(10), *c* = 14.0578(11) Å, β = 100.090(6)°, *V* = 1835.5(3) Å^3, *T* = 90 °C, *Z* = 4, $\rho_{calcd.}$ = 1.409 g cm^{-3}, μ (Mo-K_α) = 0.99 cm^{-1}, *F*(000) = 816, 11529 reflections in *h*(–14/15), *k*(–14/13), *l*(–18/18), measured in the range 2.05° ≤ Θ ≤ 27.44°, completeness Θ_{max} = 99.5%, 4158 independent reflections, R_{int} = 0.0843, 2319 reflections with $F_o > 4\sigma(F_o)$, 264 parameters, 0 restraints, $R_{1,obsd.}$ = 0.0589, $wR^2_{obsd.}$ = 0.1332, $R_{1,all}$ = 0.1262, $wR_{2,all}$ = 0.1637, GOOF = 1.021, largest difference peak and hole: 0.484/–0.297 e Å^{-3}.

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