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meso-Pyridyl BODIPYs with tunable chemical, optical and electrochemical properties†

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A series of *meso*-pyridyl substituted BODIPY molecules has been synthesized, characterized and their optical and electrochemical properties compared. By utilizing ethanol and dichloromethane during the initial condensation reactions, there is a significant increase in the isolated yields compared to standard protocols. The properties of the highly fluorescent BODIPYs could be tuned by modifying the substituents of the pyridine, leading to pyridyl BODIPY as prospective ligands for future metal complexes. Furthermore, the presented BODIPY derivatives are shown to be applicable for fluorescence pH sensing over selective pH ranges.

Introduction

A large number of pyridine containing metal complexes have been reported, including metal complexes of porphyrins or phthalocyanines with pyridine as an axial substituent.[1–3] For instance, ruthenium phthalocyanines bearing substituted pyridine ligands, have shown to significantly influence the optical and redox properties of the phthalocyanine complex.[4] Cobalt complexes are also known to incorporate pyridine ligands and are useful components for applications such as photocatalytic water-splitting, valence tautomers for magnetoelectronic materials, or as redox mediators in dye sensitized solar cells.[5–7] Chromophore–metal complexes contain additional functionality, including increased absorption and emission features and can be applied for energy or electron transfer applications,[8–11] or for sensing and biological marking.[12,13]

Boron dipyrromethenes (BODIPY) have been and continue to be studied extensively for applications in a multitude of fields.[14–22] Recently, we reported a synthesis for water-soluble cationic BODIPYs, based on a *meso*-pyridyl substituted core.[23] In this study, we present an improved synthesis (up to a sixfold increase in isolated yield) for *meso*-pyridyl BODIPYs. These compounds have interest as prospective ligands for future coordination complexes. For example, a Ru-complex containing the unsubstituted pyridyl BODIPY **1** has been recently reported, which shows the potential for this class of compounds as ligands for coordination chemistry.[24] Several other *meso*-substituted BODIPY derivatives containing pyridines, usually incorporating bipyridine or- terpyridine, have been reported.[25,26] Based on these BODIPY derivatives a variety of metal complexes have been prepared, leading examples include metal centers such as Zn,[27] Cu,[28,29] La,[30] Ru[31] or Pt.[32] The application of BODIPY as the axial substituent of metal complexes has not been widely employed, however, some examples include the axial functionalization of Sb(v)[33] and Sn(iv)[34] porphyrins or Si(iv)[11] phthalocyanines. The linkage is usually made with alkoxide, phenolate or benzoate bridges.

In addition, BODIPY **1** is also known as fluorescent pH sensor,[35] a concept we have extended to additional pH ranges with the described BODIPY derivatives. Several other BODIPY based fluorescent pH sensors have been reported, mainly based on BODIPY bound dimethylaniline, phenol or carboxylic acid groups.[36] In 2007, Harriman *et al.* published a detailed spectroscopic study investigating the processes a *meso*-pyridyl BODIPY undergoes upon protonation or methylation of the pyridine group.[37] The tunability of the redox properties of BODIPY dyes has been elucidated in several studies, and their application in electrochemoluminescence has been described. Such examples show the versatility of the BODIPY chromophore and the many possibilities for fine-tuning their electrochemical potentials.[20,26,38–40] To our knowledge, the substituted pyridyl BODIPYs described here have not been reported.

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† Electronic supplementary information (ESI) available: Additional experimental details for all new compounds and methods. pH dependant fluorescent spectra. ATR-FT IR, ^{1}H and ^{13}C NMR data for new compounds **2–5**, ^{19}F NMR spectra. Crystallographic procedures and data for **2** and **3**. CCDC 935208 and 935207. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj00426k

Results and discussion

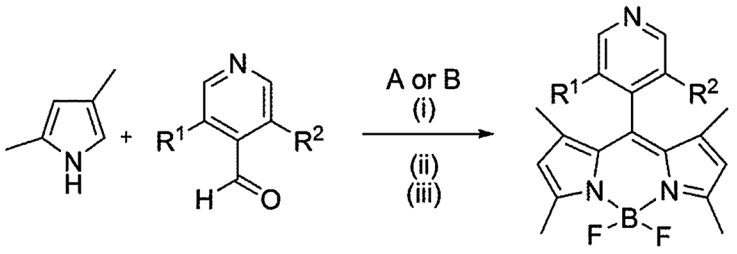
Synthetic aspects

The synthesis of pyridyl BODIPY **1** (1,3,5,7-tetramethyl-8-(4-pyridyl)-4,4′-difluoroboradiaza-indacene) has been described earlier[23,35] and is representative of the standard protocol for the preparation of BODIPY derivatives with substituents on the pyridyl group (in the following denoted as procedure A). It includes the condensation of a pyrrole with a benzaldehyde derivative in dichloromethane in the presence of trifluoroacetic acid. 2,4-Dimethylpyrrole and most of the pyridine-4-carboxaldehydes in this work are commercially available, except 3-methylpyridine-4-carboxaldehyde, which was prepared by the oxidation of 3,4-lutidine with SeO_2, following a published procedure.[41] Condensation is followed by chemical oxidation with chloranil and subsequent complexation with borontrifluoride etherate in the presence of an amine base (*e.g.* diisopropylethylamine (DiPEA)) in a sequential one-pot reaction – Scheme 1. Pyridyl BODIPYs **2**, **4** and **5**, bearing just one substituent on the pyridine, were synthesized, following this general procedure, in typical yields of around 20%. However, we found that procedure A for sterically hindered dichloro-substituted pyridyl BODIPY **3** results in a 3% yield. Earlier, Lindsey and Wagner reported that for the preparation of sterically demanding *meso*-mesityl porphyrins, the use of ethanol as co-solvent dramatically improved yields and afforded high yields of dipyrromethanes.[42] Thus, we used a 1 : 14 (v/v) solvent mixture of ethanol : dichloromethane for the condensation and oxidation steps. To avoid undesirable reactions of borontrifluoride with ethanol, the solvent mixture has to be removed under vacuum after the oxidation step, at which time the crude reaction mixture was re-dissolved in pure dichloromethane for the remaining synthetic procedure, completing a sequential one-pot reaction similar to procedure A. This modified synthetic protocol is denoted as procedure B in Scheme 1, and increases the yield of BODIPY **3** to 20%. The use of ethanol as co-solvent was tested with **1–5**, and was found to increase the isolated yield in all cases. Even though the approach presented here differs from Lindsey and Wagner, we feel that their thorough explanation for the catalytic effects of ethanol addition is relevant to this synthesis and does not warrant further discussion here.[42] The reaction time for the first step of the BODIPY condensation is 3 days, which is long compared to other BODIPY derivatives.[14,15] However, we found this to be necessary to optimize the yield of the isolated product. This can be illustrated by comparing the yield we report for BODIPY **1** (30% following procedure A, 3 days reaction time for the first step) with other studies that have much shorter reaction times (16 h = 13% yield).[43] A rational explanation for the long reaction time is that the basic pyridine starting material can undergo protonation by the trifluoroacetic acid catalyst, reducing the active catalyst concentration and thus extending the reaction time.

NMR spectroscopy of ^{1}H, ^{13}C and ^{19}F has been carried out in order to characterize the synthesized compounds. While the ^{1}H and ^{13}C NMR spectra are unremarkable, ^{19}F NMR spectra showed a distinct influence of the pyridyl substituents. It has been previously described that small changes on the symmetry of the molecule, even in large distance to the ^{19}F core, significantly alter the NMR spectra of BODIPY molecules.[44–46] We found that the symmetrical BODIPY derivatives **1** and **3** show a single quartet, while the derivatives with lowered symmetry (**2** and **4**) show a 14 line spectrum – see Fig. S8 and S9 and the ESI† for further details. This matches exactly the observations reported by Benniston *et al.* in 2008 for unsymmetric *meso*-quinone substituted BODIPY derivatives.[44]

Crystallography

In this study, we present the crystal structures of derivatives **2** and **3**[47] and compare them to the crystal structure of **1**.[35] This allows the investigation of the structural influences of the introduction of one or two chloro substituents on the pyridine – Fig. 1 and Table 1. In contrast to **1**, which has two independent molecular structures in the unit cell,[35] compounds **2** and **3** have only one independent molecule in the unit cell. As expected, comparing the bond lengths and angles among these structures allows us to conclude that the molecular structures of compounds **2** and **3** are closely related to the structure of **1**. Any differences of bond lengths and angles, including the dihedral angle of the pyridine plane to the BODIPY core plane are small. The only difference is observed when comparing the angles C2–C3–C6 and C4–C3–C6 respectively. This angle represents the ability of the pyridyl group to bend relative to the BODIPY plane. Compound **1** shows a much larger flexibility, illustrated by structure **1**(B) with the difference of the aforementioned bond angles of 5.8(5)°. The introduction of bulky chloro substituents (one or two) reduces this flexibility and leads to a more linear



	R^1	R^2	procedure A	procedure B
1	H	H	30%	46%
2	Cl	H	26%	34%
3	Cl	Cl	3%	20%
4	F	H	18%	50%
5	Me	H	26%	30%

Scheme 1 Numbering and synthesis of the BODIPY derivatives. (A) Dichloromethane. (B) Ethanol : dichloromethane 1 : 14 (v/v). (i) Trifluoroacetic acid. (ii) Chloranil. (iii) (for B: remove solvent mixture and dissolve in pure dichloromethane) DiPEA, $BF_3 \times Et_2O$.

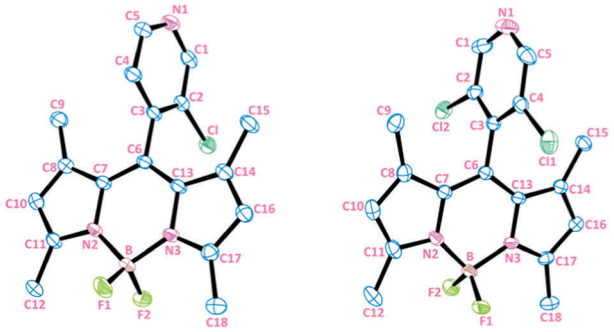


Fig. 1 Crystal structure for compounds **2** (left) and **3** (right). Hydrogen atoms omitted for clarity.

Table 1 Selected bond lengths [Å] and angles [deg] of compounds **1**, **2**, and **3**

Compound	**1**[a]	**2**	**3**
Torsion angle BODIPY plane – pyridine (C4 or C2–C3–C6–C13)	(A): 90.2(4) (B): 98.5(5)	100.5(2)	99.6(2)
Corresponding dihedral angle	(A): 92.0 (B): 98.4	100.3(4)	99.4(3)
Angle C2–C3–C6	(A): 119.3(4) (B): 116.8(4)	121.9(2)	121.9(1)
Angle C4–C3–C6	(A): 121.8(4) (B): 122.6(3)	121.2(2)	122.4(1)
Distance C3–C6	(A): 1.483(5) (B): 1.499(5)	1.493(2)	1.490(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$C2/c$

[a] Data derived from crystal structure in ref. 35.

molecular structure. The difference of the aforementioned bond angles in **2** is 0.7(3)° and 0.5(1)° for **3**. Thus, the pyridine is interlocked between the methyl substituents of the BODIPY plane and the BODIPY plane itself. Despite this finding, the introduction of substituents on the pyridine leads to only minor changes in the rest of the molecular structure, leaving the BODIPY core largely unaffected.

Photophysical properties

The photophysical data for all compounds, recorded in dichloromethane, is summarized in Table 2, while normalized absorption and fluorescence spectra are shown in Fig. 2. The most intense absorption band at around 500 nm undergoes a red-shift upon introduction of electron withdrawing substituents on the pyridine. This shift is 5 nm for one (compounds **2** and **4**) and 10 nm for two substituents (compound **3**). The methyl substituent in compound **5** does not influence the absorption band of the BODIPY. The molar extinction coefficients of all compounds are between 70 000 and 80 000 M^{-1} cm^{-1}. The Stokes shift for these compounds is not significantly altered by incorporation of substituted pyridyl groups and is between 10 and 14 nm for all BODIPYs. The fluorescence quantum yields, however, increase for all of the BODIPYs with a substituted pyridine (**2–5**). While compound **1** has a quantum yield of 0.30, the quantum yields for all other molecules are much higher, between 0.78 (**4**) and approaching unity for BODIPY **3**. Quantum yields of **2–5** were measured relative to BODIPY **1** based on previously published values.[23] A rational explanation for this observation is based on earlier reports, which show that an increase in the rigidity of a BODIPY molecule, especially when blocking the rotation of a *meso*-substituent relative to the BODIPY core, leads to an increase of the fluorescence quantum yield.[48–50] In addition, the fluorescence lifetimes of compounds **1–5** were determined upon excitation of the samples in dichloromethane at 457 nm. These measurements reveal that an increase of the fluorescence lifetime is correlated with the aforementioned increase of the fluorescence quantum yield. Compound **1**, for example, has a fluorescence lifetime of 1.73 ns and a fluorescence quantum yield of 0.30, while compound **3**, with the highest fluorescence quantum yield observed (0.98), shows a much longer fluorescence lifetime of 6.30 ns. These changes of the fluorescence lifetimes corroborate earlier studies investigating the photophysics of sterically hindered BODIPY derivatives in comparison to their sterically unhindered analogues and are a typical consequence for increased rigidity in BODIPY molecules.[48,50] The photophysical investigations support the conclusions obtained by the crystallographic studies, which suggest a more rigid molecular structure for compounds **2–5** compared to compound **1**.

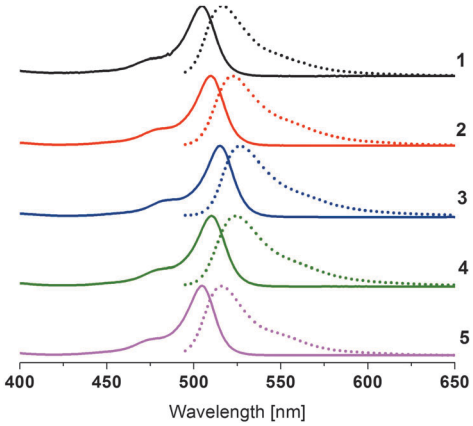


Fig. 2 Normalized absorption (full line) and fluorescence (dotted) spectra of compounds **1–5** recorded in dichloromethane.

Table 2 Overview over the photophysical data of compounds **1–5**. All data was recorded in dichloromethane

Compound	λ_{Abs} [nm]	ε [$\times 10^3$ M^{-1} cm^{-1}]	λ_{Em} [nm]	Φ_F	τ_F [ns]
1[a]	505	76.8	516	0.30	1.73
2	510	83.2	522	0.90	5.56
3	515	73.4	526	0.98	6.30
4	510	75.9	524	0.78	4.66
5	505	75.4	515	0.91	5.33

[a] Data (except Φ_F) derived from ref. 23.

Electrochemistry

The electrochemical data for the BODIPY compounds is summarized in Table 3 and visualized in Fig. 3. Each BODIPY shows one reversible reduction potential at around −1.4 V (*vs.* Fc/Fc^+ = 0 V as standard). In addition, the BODIPYs have two oxidation

Table 3 Oxidation and reduction potentials of compounds **1–5** (in V *vs.* Fc/Fc^+ = 0 as internal standard). Data recorded in degassed, dry acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate electrolyte at 200 mV s^{-1}

Compound	E_{red}[a] [V]	E_{ox1}[b] [V]	E_{ox2}[a] [V]
1	−1.46	0.77	0.90
2	−1.40	0.85	0.94
3	−1.35	0.90	0.99
4	−1.39	0.85	0.94
5	−1.47	0.79	0.91

[a] Reversible potential. [b] Irreversible potential.

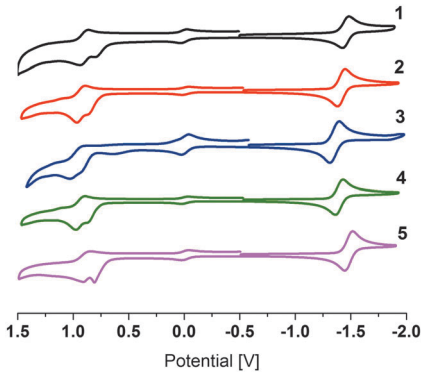


Fig. 3 Cyclic voltammograms of compounds **1–5** recorded in degassed, dry acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate. Electrode setup: glassy carbon working electrode, platinum counter electrode, silver wire as quasi-reference electrode. Ferrocene/ferrocenium (Fc/Fc^+) was used as internal reference and all graphs were referenced for Fc/Fc^+ to be at 0 V. Scan rate 200 mV s^{-1}.

potentials, an irreversible one at around 0.8 V and a reversible one at around 0.9 V. These results are in line with previously published data on a largely similar pyridyl BODIPY derivative, bearing two additional ethyl substituents on the BODIPY core.[37] The authors of the aforementioned study do observe the irreversible oxidation peak in dichloromethane, but not in acetonitrile, which is in contrast to our data. However, since the substitution patterns of the BODIPY derivatives in this report and ref. 37 differ, observations of differential solvent effects are not unexpected. In general, insertion of electron withdrawing groups on the pyridine shifts the potentials toward more positive values. The influence of pyridyl substituents on the BODIPYs redox potentials are moderate (~0.1 V) and consistent with the relative electron withdrawing capabilities of the *meso*-pyridyl group. This is in contrast to direct substitution of the BODIPY core, which has larger effects (~0.7 V).[38]

pH dependent fluorescence

Determining the basicity of the pyridyl group on **1–5** is important for predicting their reactivity with metal centers in future coordination complexes. Additionally, this property allows for these compounds to be considered as tuneable fluorescent pH sensors. It has been previously demonstrated that the fluorescence emission of pyridyl BODIPY **1** can be reversibly quenched by protonation of the pyridine substituent, which is corroborated by our findings.[35,37] A spectroscopic study of the effects that

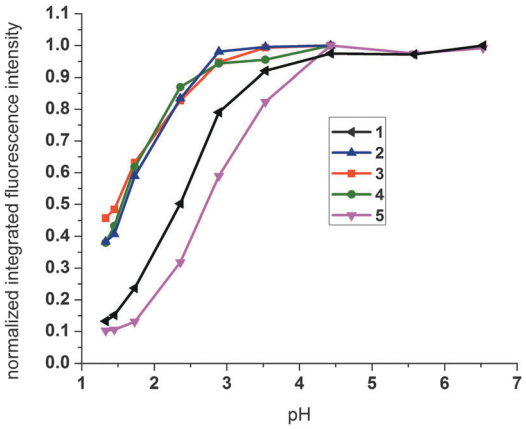


Fig. 4 Plot of the normalized integrated fluorescence intensity of compounds **1–5** *vs.* pH in different buffer solutions (solvent: 25% H_2O–75% methanol; buffer: trifluoroacetic acid/trifluoroacetate or acetic acid/acetate).

protonation/methylation have on a related BODIPY derivative, explaining the fluorescence quenching in detail, was published by Harriman *et al.* in 2007.[37] Since solubility required that these measurements were performed in a 25 : 75 H_2O : MeOH mixture, we refrain from reporting specific pK_a values for these compounds with this method. However, a clear trend for the basicity of compounds **1–5** is demonstrated during pH dependent fluorescence measurements. The basicity of compounds **1–5** is dependent on the functionalization of the pyridyl group of the BODIPY – see Fig. 4 and Fig. S3 (ESI†). The strongest basicity is seen for compound **5**, bearing an electron donating methyl group on the pyridine. This is followed by unsubstituted compound **1**, halogenated compounds **2–4**, with electron withdrawing substituents show much weaker basicity. This trend matches the expectation for such acid–base equilibria,[51] since protonation of the pyridine creates a positive charge that is stabilized in electron rich systems (**1** and **5**) and destabilized in electron poor systems (**2–4**). A similar trend has been shown for the basicity of 3-substituted pyridines.[52] The BODIPY core is identical in **1–5** and acts only as the fluorescence sensor in this experiment. The series of pyridyl BODIPY derivatives **1–5** presented in this study allows for fluorescence pH sensing in acidic media in a pH range between ~1 and ~4. Further experimental details are contained within the ESI.†

Conclusions

In this paper we describe the preparation and characterization of novel pyridyl BODIPYs and demonstrate that the introduction of electron donating and withdrawing groups on the pyridine allow for moderate tuning of the properties of the BODIPY core, while significantly altering the basicity of the pyridine substituent. In addition, we were able to significantly increase the isolated yield of pyridyl BODIPYs by using a solvent mixture (ethanol : dichloromethane, 1 : 14) instead of pure dichloromethane during the initial condensation reactions. A modulated rigidity of the molecular structure leads to an increase of the observed fluorescence quantum yields as well as of the fluorescence lifetimes. We expect these

novel pyridyl BODIPYs to be promising ligands for future metal complexes that incorporate BODIPY functionality (*e.g.* increased absorbance as well as fluorescence features). Additionally, *meso*-pyridyl BODIPY derivatives **1–5** can be applicable as fluorescent pH sensors in a pH range from ~1 to ~4.

Experimental

Materials

Diisopropylethylamine (DiPEA), borontrifluoride etherate, 3-chloro-pyridine-4-carboxaldehyde and 3,4-lutidine were purchased from Alfa Aesar, chloranil from TCI America, 2,4-dimethylpyrrole and selenium dioxide from Sigma-Aldrich, 3-fluoro-pyridine-4-carboxaldehyde and 3,5-dichloro-pyridine-4-carboxaldehyde from Frontier Scientific. All solvents were ACS grade and used as received, unless otherwise noted. Acetonitrile for the electrochemical experiments was dried over CaH_2 and distilled prior to use. Reactions and measurements were carried out under ambient conditions, unless otherwise noted. Deuterated chloroform for NMR experiments was purchased from Cambridge Isotope Laboratories, Inc.

Methods and instrumentation

NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrometer. Values are given in ppm, relative to the solvent signal of $CDCl_3$ (7.26 ppm for ^{1}H NMR (measured at 400 MHz) and 77.16 ppm for ^{13}C NMR (measured at 100 MHz)). ^{19}F NMR spectra were recorded at 376 MHz, values are given in ppm relative to hexafluorobenzene as external reference (−162.23 ppm). Absorption spectra were recorded on an Agilent 8453 Diode Array Spectrophotometer, fluorescence spectra on a QuantaMaster™ 40 spectrofluorometer (Photon Technology International, PTI). Fluorescence quantum yields of new compounds were recorded relative to BODIPY **1** with a reported fluorescence quantum yield of 0.30.[23] Fluorescence lifetimes were measured on a Horiba Jobin Yvon Fluorolog 3 spectrofluorometer. Samples were excited by a Jobin Yvon NanoLED 460 with an excitation maximum at 457 nm, emission for time-correlated single photon counting (TCSPC) was detected at 530 nm for all samples. ATR/FT-IR (Attenuated Total Reflectance/Fourier Transformed Infrared) spectra were measured on a Bruker Vertex 80V FT-IR spectrometer equipped with a Platinum ATR accessory. pH measurements were performed utilizing a Fisher Scientific accumet pH meter. Electrochemical measurements were performed on a BioLogic SP-200 potentiostat/galvanostat using a glassy carbon working electrode, a platinum counter electrode and a silver wire as quasi-reference electrode. All measurements were carried out in degassed, dry acetonitrile with a 0.1 M tetrabutylammonium hexafluorophosphate electrolyte. Fc/Fc^+ was used as internal reference and all graphs were referenced for Fc/Fc^+ to be at 0 V. High resolution exact mass spectrometry measurements-ESI (HRMS-ESI) were carried out on an Agilent Technologies (Santa Clara, California) 6210 LC-TOF mass spectrometer. Samples were diluted in methanol and analyzed *via* a 1 μL min^{-1} flow injection at 300 μL min^{-1} in a water : methanol mixture (75 : 25 v/v) with 0.1% formic acid. The mass spectrometer was operated in positive-ion mode with a capillary voltage of 4 kV, the fragmentor and skimmer voltages were 180–210 V and 60 V, respectively. Crystal structures were measured on an Agilent Gemini Ultra diffractometer with Cu Kα radiation (λ = 1.54184 Å) at 100(1) K. Crystal structures were solved by direct methods (SHELXS-97) and expanded using difference Fourier techniques. The structures were refined with SHELXL-97 using full-matrix least-squares calculations. CCDC reference numbers: **2** – 935208, **3** – 935207.

General synthetic procedure B

Procedure A is similar to our previously published synthetic protocol[23] and can be found in detail in the ESI,† as well as purification methods and the characterization of all new compounds. The optimized general procedure B for compounds **1–5** is as follows (one equivalent is typically 5.36 mmol):

Two equivalents 2,4-dimethylpyrrole (approx. 1.1 g) and one equivalent of the pyridine-4-carboxaldehyde derivative were dissolved in a deoxygenated 1 : 14 (v/v) mixture of ethanol (200 proof) and dichloromethane. Several drops of trifluoroacetic acid were added and the reaction mixture was stirred for 3 days under N_2 atmosphere. Following this, one equivalent of chloranil was added and the mixture was stirred for additional 2 hours. Next, the solvent was removed under high vacuum und the remaining crude solids were dissolved in dichloromethane. Subsequent addition of DiPEA and borontrifluoride followed by stirring for 30 min and 3 hours, respectively, completed the synthesis. Workup is identical to procedure A and all compounds show identical properties after purification – see ESI.†

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47 Crystallographic data for **2**: a = 7.3678(1) Å, b = 22.1323(3) Å, c = 10.9276(2) Å, $\alpha = \gamma = 90^\circ$, β = 109.642(2)°, V = 1678.24(4) Å^3, Z = 4, D_x = 1.423 Mg m^{-3}, crystal dimensions: 0.35 × 0.17 × 0.04 mm^3. The total number of reflections collected was 34 862, of which 2981 were independent (R_{int} = 0.0383). For $I > 2\sigma(I)$ the final R_1 value was 0.0352 and wR_2 was 0.0918. Crystallographic data for **3**: a = 20.3327(3) Å, b = 7.2956(1) Å, c = 26.1828(5) Å, $\alpha = \gamma = 90^\circ$, β = 114.731(2)°, V = 3527.7(1) Å^3, Z = 8, D_x = 1.484 Mg m^{-3}, crystal dimensions: 0.24 × 0.21 × 0.09 mm^3. The total number of reflections collected was 30 627, of which 3146 were independent (R_{int} = 0.0267). For $I > 2\sigma(I)$ the final R_1 value was 0.0250 and wR_2 was 0.0660.
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