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Synthesis and Properties of Branched Oligo(2-thienyl)- and Oligo(2,2′-bithien-5-yl)-Substituted Pyridine Derivatives

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Dedicated to Professor Goverdhan Mehta on the occasion of his 70th birthday.

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Abstract: Starting from easily accessible precursors we describe the preparation of a series of branched oligo(2-thienyl)- and oligo(2,2′-bithienyl)-substituted pyridine derivatives. With palladium-catalyzed cross-coupling reactions of pyridyl nonaflates/triflates as key steps we synthesized 2,6-di(2-thienyl)pyridines bridged by thiophene or benzene rings. By selective bromination of 2,6-di(2-thienyl)pyridine and 2,4,6-tri(2-thienyl)pyridine and subsequent coupling reactions an access to oligo(2,2′-bithien-5-yl)-substituted pyridine derivatives was gained. The constitution and solid state conformation of 2,6-bis(2,2'-bithien-5-yl)-pyridine was determined by X-ray analysis. This series of new pyridine-thiophene conjugates was systematically investigated by UV/vis spectroscopy. Large Stokes shifts in the neutral and protonated form were observed. The electrochemical oxidation of two typical compounds was studied, however, these oxidations were irreversible forming a polymeric film at the anode. As a selected example, a thiophene-bridged 2,6-di(2-thienyl)pyridine derivative was also investigated by scanning tunneling microscopy showing an interesting self-assembly into a highly ordered monolayer on highly oriented pyrolytic graphite.

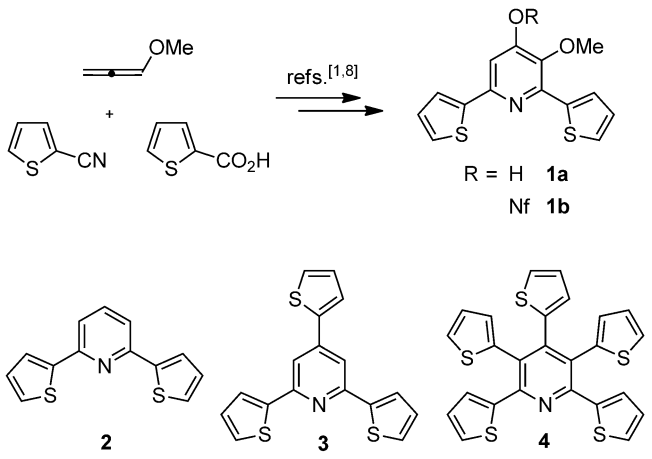
Keywords: electrochemistry; palladium-catalyzed couplings; pyridines; scanning tunneling microscopy; thiophenes; UV/vis spectroscopy

Introduction

Recently we reported that highly functionalized 2-thienyl-substituted pyridine derivatives such as **1**[1] are smoothly available even on a gram scale by our flexible multi-component synthesis of pyridines (Scheme 1).[2] The two differentiated oxygen functionalities of this precursor could be used to introduce additional functional groups or substituents. Nonaflate **1b** is a perfect starting material for palladium-catalyzed coupling reactions allowing the introduction of a third 2-thienyl group at C-4.[3] Alternatively, the nonafloxy (or trifloxy) group can be used for reductive removal of the oxygen functionalities.[4] Playing with these options we prepared precursors **2** and **3** in simple reaction sequences.[1] Since redox and photoactive compounds with sequential thienyl substituents are of high interest as materials for organic electronics,[5–7] we continued our previous studies on the synthesis of per(2-thienyl)-substituted pyridines[1,8] and prepared a series of new extended and branched oligo(2-thienyl)-substituted pyridine derivatives and studied the physical properties of selected examples.

Results and Discussion

Compound **1b** and thiophene-2,5-diboronic acid (**5**) underwent a double Suzuki coupling[9] under standard conditions to efficiently furnish the expected inter-



Scheme 1. 2,6-(2-Thienyl)-substituted pyridine building blocks **1a**, **1b** and products **2**–**4**.

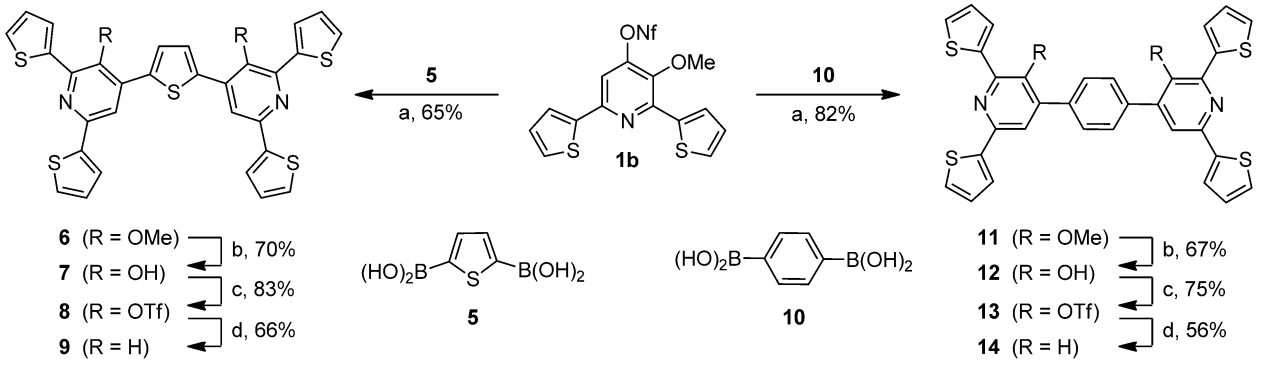
mediate **6** containing seven heterocyclic rings (Scheme 2). Dealkylation of the hetaryl ether moiety with sodium ethanethiolate[10] provided compound **7** which was subsequently converted into bistriflate **8** in very good overall yield. In the final step the trifloxy group was removed using palladium acetate and triethylammonium formate as reducing components.[4] Hence, the first desired oligo(2-thienyl)-substituted pyridine derivative **9** bridged by a 2,5-thiophene unit was easily obtained in a four-step sequence. Analogously, compound **1b** and benzene-1,4-diboronic acid (**10**) furnished the desired 1,4-phenylene-bridged intermediate **11** with good efficacy (Scheme 2). Deprotection to **12** and triflation to **13** were executed as above and the final reductive removal of the trifloxy groups afforded the expected product **14** with two 2,6-(2-thienyl)pyridine moieties in good overall yield.

We next planned to extend the range of our polyheterocyclic compounds by adding more thiophene rings to the already existing thiophene substituents. It is well known that 2-substituted thiophene derivatives undergo a regioselective bromination at C-5, which allows subsequent Stille couplings[11] in this position. Indeed, this turned out to be smoothly applicable to compounds such as **1b** functionalized with a methoxy and a nonafloxy substituent. Bromination with NBS furnished dibromide **15** (Scheme 3) which was directly converted into compound **17** by a three-fold Stille coupling with commercially available 2-tri(*n*-butylstannyl)thiophene (**16**) in good overall yield. Routine removal of the methoxy group *via* intermediates **18** and **19** finally provided the desired 2,6-di(2,2′-bithien-5-yl)-4-(2-thienyl)pyridine (**20**).

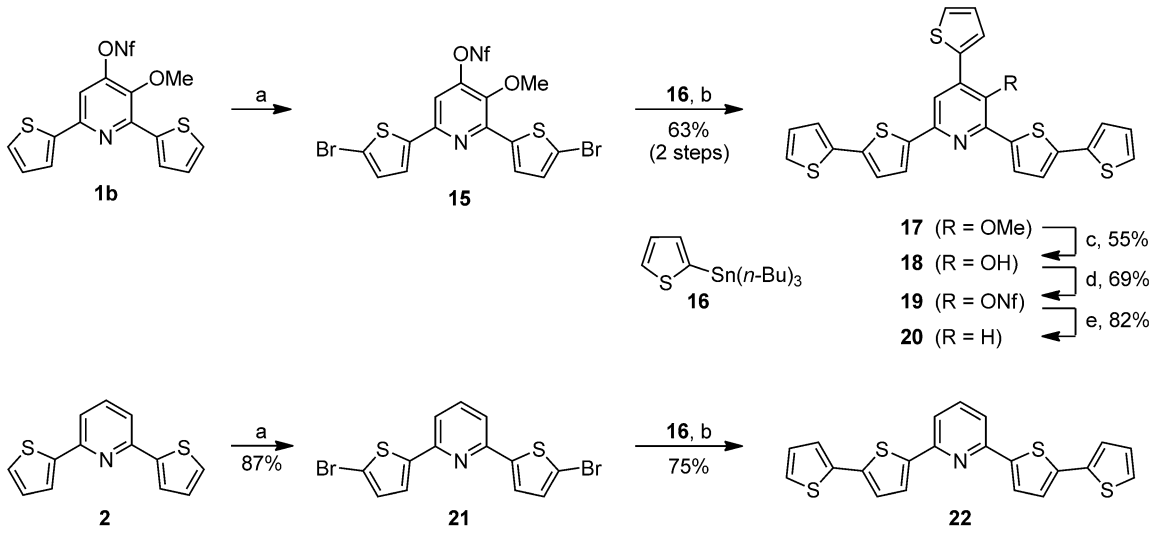
As a further target we envisioned the preparation of a compound very similar to **20** but lacking the 4-(2-thienyl) group at the pyridine core by employing 2,6-di(2-thienyl)pyridine (**2**) as precursor. Its bromination and subsequent substitution occurred without problems furnishing the desired compound **22** in two good-yielding steps. This sequence again demonstrates the high reliability of the bromination/Stille coupling sequence.

Compound **22** was crystallized from dichloromethane to obtain a pale yellow crystal suitable for an X-ray analysis (Figure 1). As expected the heterocyclic rings are slightly out of plane with torsion angles between two thiophene rings of −37.4° and −8.5°, respectively. The torsion angles of the inner thiophene rings and the pyridine core are −15.3° and −27.6°. Hence the arrangement in the solid state is surprisingly unsymmetrical. One of the terminal thiophene rings is disordered with respect to a 180° rotation around the carbon-carbon single bond (see Figure S1 in the Supporting Information). In the major orientation (70%) the thiophene sulfur atom S-4 is in a *trans* position to the sulfur atom S-3 of the attached thiophene ring.

We also performed the bromination sequence starting with 2,4,6-tri(2-thienyl)pyridine (**3**) (Scheme 4). Surprisingly, under standard bromination conditions we obtained a tetrabrominated product which turned



Scheme 2. Preparation of bridged oligo(2-thienyl)-substituted pyridine derivatives **9** and **14**. *Reagents and conditions:* a) $Pd(PPh_3)_4$, K_2CO_3, DMF, 70 °C, 24 h; b) NaSEt, DMF, 90 °C, 2 h; c) pyridine, DMAP, Tf_2O, CH_2Cl_2, 0 °C to room temperature, 6–12 h; d) $Pd(OAc)_2$, dppp, Et_3N, HCO_2H, DMF, sealed tube, 90 °C, 2 h.



Scheme 3. Preparation of bis(2,2′-bithien-5-yl)-substituted pyridine derivatives **20** and **22**. *Reagents and conditions:* a) NBS (2.5–3.0 equiv.), DMF, −20 °C to room temperature, 12 h; b) 2 tri(*n*-butylstannyl)thiophene (**16**), $Pd(PPh_3)_4$, DMF, 120 °C, 2 h; c) NaSEt, DMF, sealed tube, 90 °C, 1 h; d) NaH, NfF, THF, room temperature, overnight; e) $Pd(OAc)_2$, dppp, Et_3N, HCO_2H, DMF, sealed tube, 90 °C, 2 h.

out to be compound **23**. Apparently, the more electron-rich character of the tri(2-thienyl)-substituted pyridine core facilitates an electrophilic bromination at C-3 of the pyridine ring. Immediate reaction of compound **23** with stannane **16** resulted in a four-fold Stille coupling leading to compound **24** containing seven thiophene substituents. The overall yield of this sequence with more than 95% per newly formed C–C bond is impressive and underscores the efficacy of palladium-catalyzed coupling processes. Bromination of the central pyridine ring of **3** could be avoided by careful control of the reaction conditions. With 2.5 equivalents of NBS at −20 °C dibromo derivative **25** was isolated in good yield whereas the desired tribromo compound **26** was obtained in 80% yield when four equivalents of the brominating reagent were used. The subsequent Stille couplings of **25** with stannane **16** provided the expected product **20** in good yield. The conversion of tribromo compound **26** into the desired tri(2,2′-bithienyl)-substituted pyridine **28** was achieved either by the Stille protocol (59% yield) or with a Suzuki reaction employing thiophene-2-boronic acid (**27**) which gave a better yield of 76%.

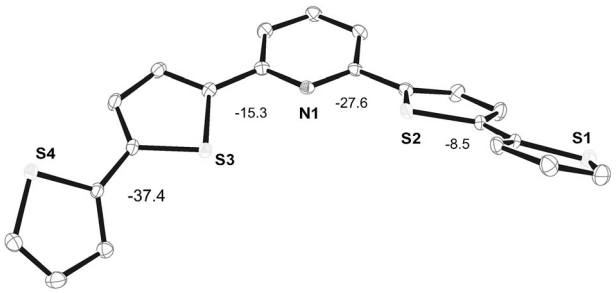


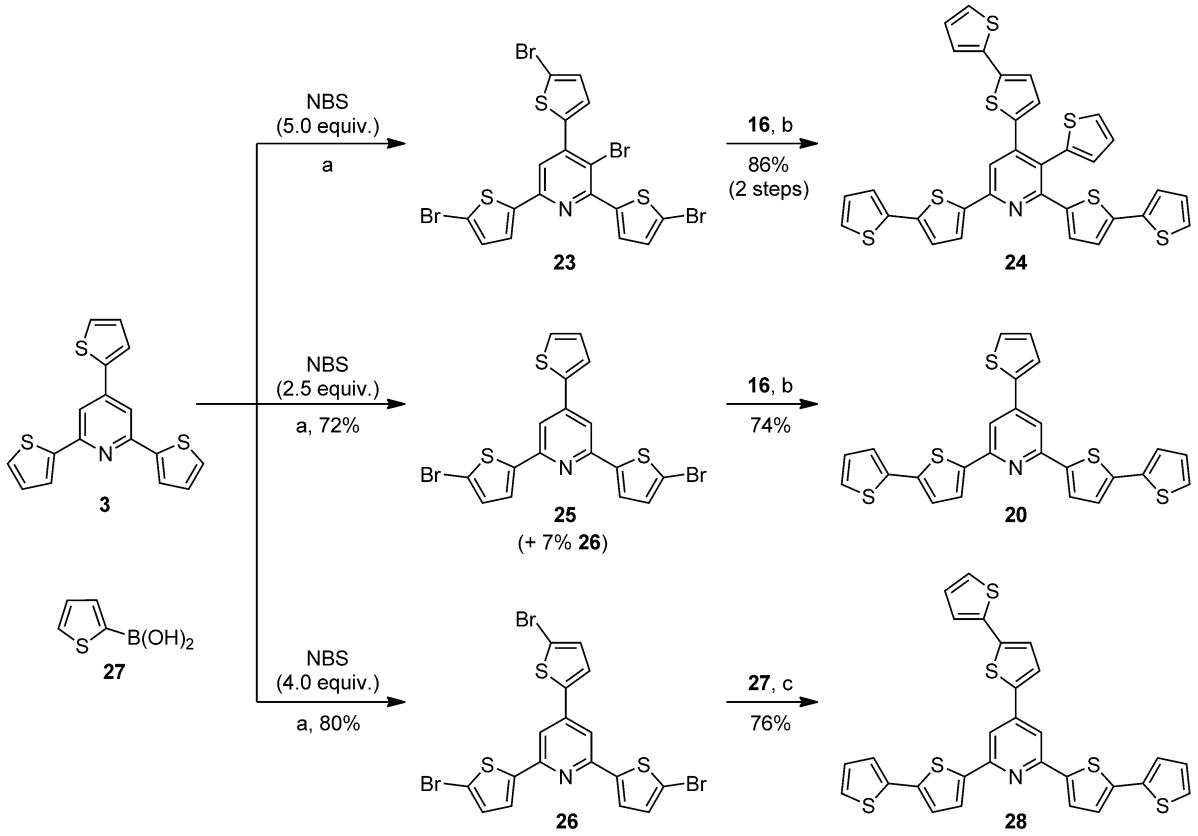
Figure 1. Molecular structure of **22** (ORTEP3 for Windows,[12] 50% probability level), hydrogen atoms omitted for clarity. The numbers represent the torsion angles.

With these straightforward sequences we could prepare a series of novel branched oligo(2-thienyl)-substituted pyridine derivatives employing palladium-catalyzed C–C bond forming steps as the key reaction. The efficacy of these couplings in the presence of a high number of sulfur-containing heterocycles is quite impressive. Selected compounds of our series were studied by physical methods.

Absorption and Fluorescence Spectra

In our earlier reports[1,8] on oligo- and per(thienyl)-substituted pyridine derivatives we already observed remarkable UV/vis and fluorescence spectra with fairly large Stokes shifts and a strong influence exhibited by the protonation of the pyridine nitrogen. As anticipated the newly synthesized bridged oligo(2-thienyl)-substituted pyridines **6**, **9** and **14** as well as the oligo(2,2′-bithien-5-yl)-substituted derivatives **20**, **22**, **24** and **28** also showed similar interesting photophysical properties. Their UV/vis absorption and fluorescence spectra were studied in solution with chloroform and a mixture of chloroform and trifluoroacetic acid (99:1) as solvents. The respective spectra are depicted exemplarily for compound **22** in Figure 2 and for **28** in Figure 3.

The determined extinction coefficients as well as the observed λ_{max} values for the absorption and the fluorescence after excitation at maximum absorption wavelengths are summarized in Table 1.



Scheme 4. Bromination of precursor **3** and subsequent coupling to oligo(2-thienyl)pyridine derivatives **20**, **24** and **28**. *Reagents and conditions:* a) DMF, −20 °C to room temperature, 5–24 h; b) 2-tri(*n*-butylstannyl)thiophene (**16**), $Pd(PPh_3)_4$, DMF, 120 or 90 °C, 2 h; c) thiophene-2-boronic acid (**27**), $Pd(PPh_3)_4$, K_2CO_3, DMF, 80 °C, 3 h.

All studied compounds show a broad absorption ranging from about 260 up to 400 nm with λ_{max} values between 300 and 340 nm for the bridged 2-thienyl-substituted pyridines. Expectedly the increased number of thiophene moieties contained in the 2,2′-bithien-5-yl-substituted pyridines results in λ_{max} values at longer wavelengths as they show the most intensive absorption between 350 and 370 nm. The strongest emission for the bridged 2-thienyl-substituted pyridines **6**, **9** and **14** as well as for compound **22** is observed between 400 and 440 nm. The 2,2′-bithien-5-yl-substituted pyridines **20**, **24** and **28** show respective λ_{max} values again at longer wavelengths between 440 and 467 nm. This results in Stokes shifts between 4700 and 5900 cm^{-1} for the 2,2′-bithien-5-yl-substituted pyridines **20**, **22**, **24**, **28** and the thiophene-bridged compound **9**. For the other bridged 2-thienyl-substituted pyridines significantly higher values of 8200 cm^{-1} for

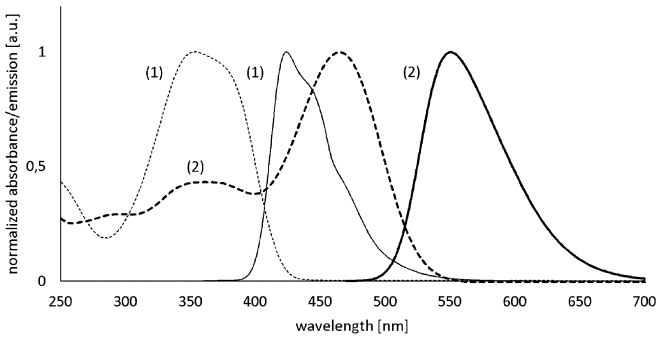


Figure 2. UV (dashed lines) and fluorescence spectra (solid lines) of 2,6-di(2,2′-bithien-5-yl)pyridine **22** in $CHCl_3$ (1) and in $CHCl_3$/TFA (99:1) (2).

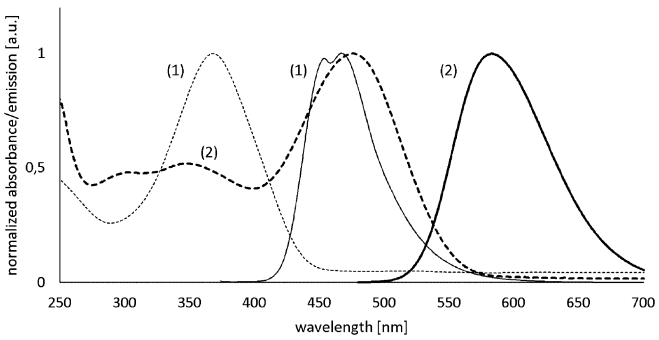
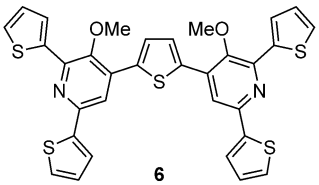
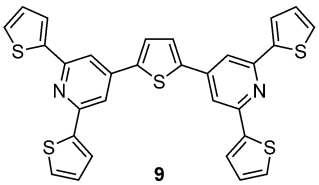
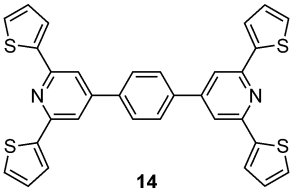
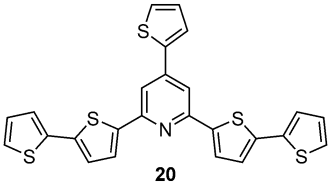
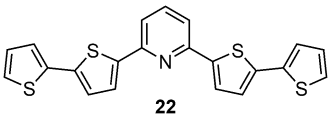
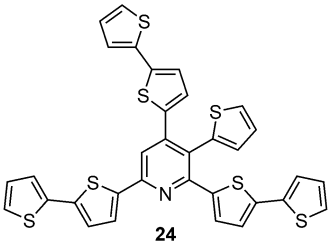
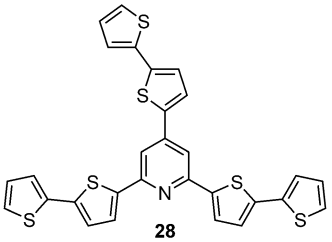


Figure 3. UV (dashed lines) and fluorescence spectra (solid lines) of 2,4,6-tri(2,2′-bithien-5-yl)pyridine **28** in $CHCl_3$ (1) and in $CHCl_3$/TFA (99:1) (2).

Table 1. Absorption and emission data of selected oligo(2-thienyl)-substituted pyridine derivatives.

2-Thienylpyridine	$CHCl_3$			$CHCl_3$/TFA (99:1)		
	Absorption[a] λ_{max} [nm], (log ε)	Emission[b] λ_{max} [nm]	Stokes shift [cm^{-1}]	Absorption[a] λ_{max} [nm], (log ε)	Emission[b] λ_{max} [nm]	Stokes shift [cm^{-1}]
 **6**	299 (4.61), 349 (sh) (4.55)	443	10900	407 (4.69), 298 (sh) (4.44)	530	5700
 **9**	340 (4.69), 303 (sh) (4.63), 266 (sh) (4.54)	417	5400	396 (4.82), 286 (sh) (4.56)	503	5400
 **14**	302 (4.72), 344 (sh) (4.21)	401	8200	340 (4.55), 394 (sh) (4.45)	474	8300
 **20**	349 (4.56), 385 (sh) (4.39)	440, 463 (sh)	5900	352 (4.50), 476 (sh) (4.49)	565	10700 (3300)
 **22**	353 (4.50)	424	4700	465 (4.48), 362 (sh) (4.12), 297 (sh) (3.95)	550	3200
 **24**	368 (4.63)	467, 454 (sh)	5800	476 (4.53), 350 (sh) (4.25), 303 (sh) (4.22)	583	3900
 **28**	367 (4.81)	451, 465 (sh)	5800	468 (4.73), 342 (sh) (4.37)	571	3900

[a] Absorption; recorded at $c = 10^{-5}$ mol·L^{-1} in 1-cm cuvettes.
[b] Emission after excitation at max. absorption wavelength; recorded at $c = 10^{-5}$–10^{-6} mol·L^{-1} in 1-cm cuvettes.

14 and 10900 cm^{-1} for **6** are observed. After protonation of the pyridine moieties with trifluoroacetic acid the absorption and emission λ_{max} values are considerably red-shifted.[13,14] The strongest absorption is observed at about 400 nm for the bridged 2-thienyl-substituted pyridines and in the range of 465 and 475 nm for the 2,2′-bithien-5-yl-substituted pyridines respectively. The emission λ_{max} values are shifted to between

470 and 530 nm for the bridged 2-thienyl-substituted pyridines and range from 550 to 580 nm for the 2,2′-bithien-5-yl-substituted derivatives. The Stokes shifts of the protonated species are also fairly large, ranging from 5400 to 8300 cm^{-1} for the bridged 2-thienyl-substituted pyridines **6**, **9** and **14**, and from 3200 to 3900 cm^{-1} for the 2,2′-bithien-5-yl-substituted pyridines **22**, **24** and **28**. The protonated species of **20** exhibits two λ_{max} values with almost identical intensities (at 352 and 476 nm) in its absorption spectrum and a λ_{max} of 565 nm in the emission spectrum, resulting in Stokes shifts of 10700 and 3300 cm^{-1}, respectively.

Electrochemistry

The 2,4,6-tris(2,2′-bithienyl)-substituted pyridines **24** and **28** were investigated electrochemically using cyclic voltammetry in chloroform (also see Figures S2 and S3 in the Supporting Information). The compounds were expected to show similar electrochemical behaviour as the previously reported[8] (2-thienyl)-substituted pyridines. Compound **24** is irreversibly oxidized in two steps at 1.335 and 1.571 V *vs.* NHE, whereas derivative **28** shows only one oxidation at 1.290 V *vs.* NHE (Figure 4). Due to the enhanced electron-donating effect of the 2,2′-bithienyl groups the oxidation potentials are slightly shifted towards less positive potentials compared to 2,4,6-tris(2-thienyl)pyridine which was oxidized at 1.36 and 1.86 V.[8] Compound **28** shows the strongest shift to less positive potentials, whereas compound **24** with an additional 3-thiophene moiety is less easily oxidized. This may be due to a higher deviation from planarity due to steric hindrance of the substituents in 2-, 3- and 4-positions of the pyridine core. For both compounds

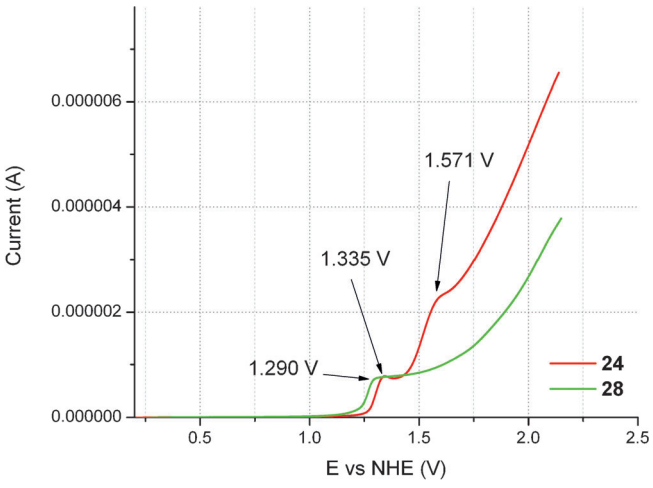


Figure 4. Linear scan voltammograms of **24** and **28** obtained in the range of 0–2.2 V *vs.* NHE on a platinum electrode; sweep rate $\nu = 100\ mV\,s^{-1}$, 0.300 mM and 0.200 mM in 0.1 M Bu_4NPF_6 in chloroform.

we observed immediate film formation at the anode during oxidation as already noticed for compounds previously reported.[8,15] Continuous cycling leads to the disappearance of the oxidation signal (see the Supporting Information), indicating the formation of the new polymeric species, a behaviour well known from related compounds and 1,3,5-(trisaryl)benzenes.[16] These films produced were insoluble in typical solvents such as THF, DMSO, chloroform, acetonitrile, and ethanol.

Scanning Tunneling Microscopy

Due to our continuous interest in multivalent heterocyclic compounds[17] we also studied bispyridyl-substituted thiophene derivative **6** with respect to its ability to form self-assembled monolayers at the interface between the basal plane of highly oriented pyrolytic graphite (HOPG) and 1-phenyloctane.[18] Scanning tunneling microscopy (STM) of a saturated solution of **6** in this solvent reveals molecular self-assembly into two-dimensional crystals with a unit cell size of $A = (4.97 \pm 0.29)\ nm^2$ (Figure 5), which fits to two oppositely oriented molecules per unit cell and interdigitation between the molecules. In our proposed molecular model the bright areas in the STM image correspond to high tunneling current, indicating the positions of the π-systems.[19] The dark lines between the molecules correspond to low tunneling current and designate the gap which is caused by the molecular arrangement. The molecular orbitals were calculated with the DMol3 interface of Accelrys Materials Studio using the local-density approximation method (LDA) and Perdew Wang correlation (PWC).[20] The implemented space-filling models are based on standard van-der-Waals parameters. Our STM measurements show that fully conjugated polyheterocycles with thienyl moieties such as **6** are interesting candidates to achieve highly ordered two-dimensional arrangements on HOPG. The behaviour of these ordered structures and structure-property relationships will be further investigated and compared with related compounds.

Conclusions

In summary, we have continued our earlier studies, searching for new oligo-2-thienylated pyridines as candidates for organic electronic applications.[1,8] Starting with precursors available from our highly flexible three-component reaction[1,2] and using straightforward transformations, we successfully prepared a series of new bridged 2-thienylpyridine conjugates and oligo(2,2′-bithien-5-yl)-substituted pyridines showing interesting photophysical properties. As ex-

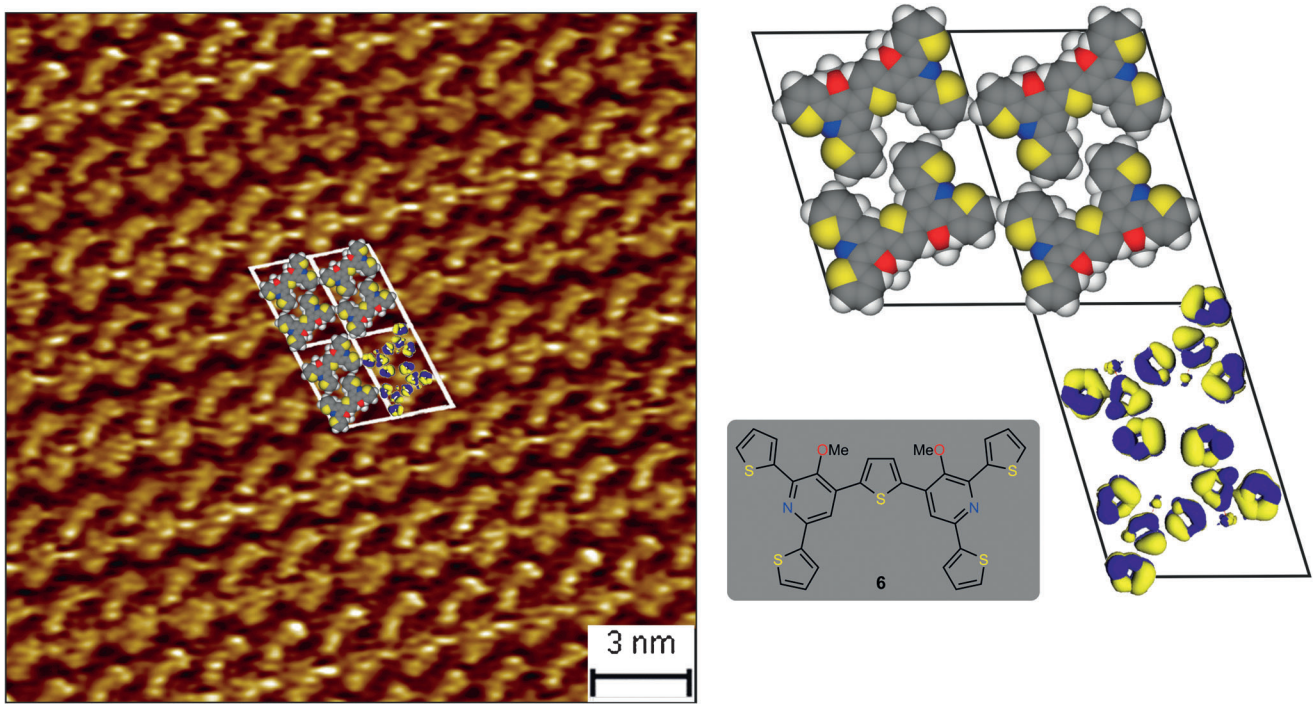


Figure 5. STM current image of compound **6** at the interface between a solution in 1-phenyloctane and the basal plane of HOPG as well as the proposed molecular model in detail. Unit cell size: $a = (2.88 \pm 0.17)$ nm, $b = (1.86 \pm 0.11)$ nm, $\alpha = (75 \pm 3)°$, $A = (4.97 \pm 0.29)$ nm^2. Tunneling parameters were sample bias $U_s = -1.05$ V and tunneling current $I_t = 73$ pA.

pected, the prepared compounds show fluorescence after excitation with UV/vis light. Exemplarily, the oxidation potentials of the (2,2′-bithien-5-yl)-substituted pyridines **24** and **28** were determined by cyclic voltammetry, resulting in irreversible oxidation and the formation of polymeric films. In addition, as revealed by STM, the bridged 2-thienylpyridine conjugate **6** showed a remarkable self-assembly into a highly ordered monolayer on HOPG.

Experimental Section

General Methods

Reactions were performed under an atmosphere of argon in flame-dried flasks. Solvents and liquid reagents were added by syringe. THF and CH_2Cl_2 were transferred from a MB SPS-800-dry solvent system into the reaction vessels. Dry DMF was purchased from Acros Organics and stored in the presence of molecular sieve under an atmosphere of argon. Et_3N was distilled from CaH_2 and stored over KOH under argon. Pyridine was stored over KOH under argon. All other reagents were purchased from commercial suppliers and used without further purification. Thin layer chromatography (TLC) analyses were performed on TLC plates purchased from Merck (silica gel 60, fluorescence indicator F254, 0.25 mm layer thickness). Products were purified by flash chromatography on silica gel 60 (230–400 mesh, Macherey-Nagel). NMR spectra were recorded with Bruker (AC 500, AVIII 700) and JEOL (Eclipse 500) instruments. Chemical shifts are reported relative to solvent residual peaks or TMS. Integrals are in accordance with assignments, and coupling constants are given in Hz. All ^{13}C NMR spectra are proton-decoupled. ^{13}C NMR signals of Nf-groups [$CF_3(CF_2)_3$] are not given since unambiguous assignment is not possible due to strong splitting by coupling with the ^{19}F nuclei. IR spectra were measured with a Jasco FT/IR-4100 spectrometer. HR-MS analyses were performed with a Varian Ionspec QFT-7 (ESI-FT ICRMS) or an Agilent 6210 (ESI-TOF) instrument. Elemental analyses were carried out with CHN-Analyzer 2400 (Perkin–Elmer), Vario EL or Vario EL III instruments. Melting points were measured with a Reichert apparatus (Thermovar) and are uncorrected. UV/vis spectra were measured with a UV/vis spectrophotometer Scinco S-3150 PDA. Fluorescence spectra were measured with a spectrofluorometer Jasco FP-6500.

X-Ray Crystallography

Single crystals of **22** were obtained by crystallization from a dichloromethane solution. Data were collected using a Bruker AXS SMART diffractometer at 173 K. The structure was solved using direct methods and refined by least squares refinement applying a disorder model for one of the thiophene moieties. Crystal data for **22**: $C_{21}H_{13}NS_4$, $M = 407.56$, monoclinic, $a = 7.330(3)$ Å, $b = 8.228(3)$ Å, $c = 15.279(6)$ Å, $\alpha = 90.00°$, $\beta = 99.262(8)°$, $\gamma = 90.00°$, $V = 909.5(6)$ Å^3, $T = 173(2)$ K, space group $P2_1$, $Z = 2$, MoK_α, 9754 reflections measured, 5444 independent reflections ($R_{int} = 0.0290$). $R_1 = 0.0502$ ($I > 2\sigma(I)$), $wR(F^2) = 0.1146$ (all data). The goodness of fit on F^2 was 1.060. Flack parame-

ter = −0.06(8). CCDC 948665 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.

Electrochemistry

The cyclic voltammetry data were recorded on an Autolab PGSTAT302N potentiostat. Cyclovoltammetric measurements were performed in MeCN containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as conducting salt in a 3-electrode compartment at a scan rate of 100 mV s^{-1}. The working electrode was a platinum disc electrode (ø = 0.2 mm), the counter electrode was a platinum wire electrode, and an Ag/AgCl electrode with 1 M LiCl in ethanol as electrolyte was used as reference electrode. Before all measurements, the electrolyte was purged with nitrogen for 20 min and the reference electrode was calibrated against ferrocene. The potentiostat and all electrodes were purchased from Metrohm.

Scanning Tunneling Microscopy

STM imaging was carried out at room temperature at the interface between freshly cleaved highly oriented pyrolytic graphite (HOPG) substrate and an almost saturated solution in 1-phenyloctane (Aldrich)[21] by employing a home-made set-up at a scan speed between 10 and 50 lines/s. After visualization of the HOPG lattice, a drop of an almost saturated solution was applied to the basal plane of HOPG. The STM images were corrected with respect to the hexagonal HOPG lattice underneath by exploiting SPIP software.[22] In this way, the unit cell of the crystalline adsorbate could be determined with a high degree of precision.

The syntheses of compounds **1b**, **2** and **3** have previously been described.[1]

Typical Procedure 1: 2,5-Bis[3-methoxy-2,6-di(2-thiophenyl)pyridin-4-yl)]thiophene (6)

A mixture of pyridyl nonaflate **1b** (510 mg, 0.89 mmol), $Pd(PPh_3)_4$ (103 mg, 0.09 mmol), K_2CO_3 (92 mg, 0.67 mmol), and thiophene-2,5-diboronic acid (**5**) (115 mg, 0.67 mmol) in DMF (10 mL) was heated at 70 °C for 24 h under an argon atmosphere. The mixture was cooled to room temperature, diluted with brine (10 mL) and extracted with Et_2O (3 × 25 mL). The combined organic phases were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on silica gel (25–50% EtOAc in hexanes) to give **6** as a dark yellow solid; yield: 182 mg (65%); mp 165–170 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.77 (s, 6H, OMe), 7.14 (dd, J = 5.0, 3.6 Hz, 2H, Thio), 7.19 (dd, J = 5.1, 3.8 Hz, 2H, Thio), 7.41 (dd, J = 5.1, 1.0 Hz, 2H, Thio), 7.49 (dd, J = 5.0, 1.0 Hz, 2H, Thio), 7.64 (dd, J = 3.6, 1.0 Hz, 2H, Thio), 7.76, 7.78 (2 s, 2 H each, Py, Thio), 8.11 (dd, J = 3.8, 1.0 Hz, 2H, Thio); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 60.3 (q, OMe), 115.4 (d, Py), 124.6, 127.8, 127.9, 128.1, 128.3, 128.6, 128.7, 136.1, 139.2, 140.9 (7 d, 3 s, Thio), 144.4, 146.3, 147.5, 148.2 (4 s, Py); IR (ATR): ν = 3105–2970 (=C−H, C−H), 1590–1400 (C=C) cm^{-1}; HR-MS: m/z = 627.0308, calcd. for $C_{32}H_{23}N_2O_2S_5$ $[M+H]^+$: 627.0358; anal. calcd. for $C_{32}H_{22}N_2O_2S_5$ (626.8): C 61.31, H 3.54, N 4.47, S 25.58; found: C 61.22, H 3.39, N 4.46, S 25.44.

Typical Procedure 2: 4,4′-(Thiophene-2,5-diyl)bis[2,6-di(2-thiophenyl)pyridin-3-ol] (7)

To a solution of compound **6** (120 mg, 0.19 mmol) in dry DMF (3 mL) was added NaSEt (162 mg, 1.93 mmol) and the resulting mixture was heated in an ACE-sealed tube at 90 °C for 2 h. The mixture was diluted with Et_2O (10 mL), quenched with water (10 mL) and the layers were separated. After cooling to 0 °C the aqueous layer was slowly acidified (litmus paper indication) with 10% aqueous HCl and extracted with EtOAc (3 × 25 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 and the solvent was evaporated under reduced pressure to obtain **7** as a brownish solid which was used without further purification for the next step; yield: 80 mg (70%).

Typical Procedure 3: 4,4′-(Thiophene-2,5-diyl)bis[2,6-di(2-thiophenyl)pyridine-3,4-diyl] Bistriflate (8)

To a solution of crude pyridinol **7** (80 mg, 0.13 mmol) in dry CH_2Cl_2 (5 mL) were added pyridine (0.10 mL, 1.20 mmol) and DMAP (3 mg, 0.03 mmol) at room temperature. After 15 min stirring, the mixture was cooled to 0 °C and Tf_2O (0.20 mL, 1.19 mmol) was added. The temperature was allowed to rise to room temperature and the mixture was stirred for 6 h. The reaction was quenched with water (5 mL) and the product was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (15–25% EtOAc in hexanes) to provide bistriflate **8** as a light yellow solid; yield: 95 mg (83%); mp 210–215 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.16 (dd, J = 5.1, 3.8 Hz, 2H, Thio), 7.19 (dd, J = 5.1, 3.8 Hz, 2H, Thio), 7.50 (dd, J = 5.0, 1.1 Hz, 2H, Thio), 7.58 (dd, J = 5.0, 1.1 Hz, 2H, Thio), 7.65, 7.67 (2 s, 2 H each, Thio, Py), 7.73 (dd, J = 3.8, 1.0 Hz, 2H, Thio), 7.84 (br d, J = 3.8 Hz, 2H, Thio); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 117.7 (d, Py), 126.7, 128.2, 128.5, 129.5, 129.7, 130.2, 130.8, 137.6, 137.7, 138.7 (7 d, 3 s, Thio), 139.5, 142.5, 147.3, 151.9 (4 s, Py), the signal for the CF_3 group was not detected; IR (ATR): ν = 3095–2855 (=C−H, C−H), 1585–1420 (C=C) cm^{-1}; HR-MS: m/z = 862.9033, calcd. for $C_{32}H_{17}F_6N_2O_6S_7$ $[M+H]^+$: 862.9030.

Typical Procedure 4: 2,5-Bis[2,6-di(2-thiophenyl)-pyridin-4-yl]thiophene (9)

A mixture of bistriflate **8** (70 mg, 0.08 mmol), $Pd(OAc)_2$ (5 mg, 0.02 mmol), dppp (9 mg, 0.02 mmol), Et_3N (0.20 mL, 1.4 mmol) and formic acid (0.05 mL, 1.3 mmol) in dry DMF (3 mL) was placed in an ACE-sealed tube and heated at 90 °C for 2 h. The mixture was diluted with Et_2O (10 mL) and quenched with water (10 mL). The layers were separated and the aqueous phase was extracted with Et_2O (2 × 15 mL). The combined organic layers were washed with brine and dried with Na_2SO_4. The solvent was evaporated and the crude product was subjected to column chromatography on silica gel (5–10% EtOAc in hexanes) to afford compound **9** as a pale yellow solid; yield: 30 mg (66%); mp > 230 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.15 (dd, J = 5.1, 3.8 Hz, 4H, Thio), 7.44 (dd, J = 5.1, 1.0 Hz, 4H, Thio), 7.61 (s, 2H, Thio), 7.68 (s, 4H, Py), 7.73 (dd, J = 3.8, 1.0 Hz, 4H, Thio); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 112.9 (d, Py), 125.2,

126.6, 128.1, 128.2, 142.3, 142.7 (4 d, 2 s, Thio), 144.5, 153.0 (2 s, Py); IR (ATR): $\nu = 3025–2865$ (=C–H, C–H), 1475–1360 (C=C) cm^{-1}; HR-MS: $m/z = 567.0140$, calcd. for $C_{30}H_{19}N_2S_5$ $[M+H]^+$: 567.0146.

1,4-Bis[3-methoxy-2,6-di(2-thiophenyl)pyridin-4-yl]-benzene (11)

According to typical procedure 1, a mixture of nonaflate **1b** (350 mg, 0.61 mmol), benzene 1,4-diboronic acid (**10**) (75 mg, 0.45 mmol), K_2CO_3 (62 mg, 0.45 mmol) and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) in dry DMF (8 mL) upon stirring at 70 °C for 24 h and after purification by column chromatography on silica gel (25–50 % EtOAc in hexanes) provided compound **11** as a pale yellow solid; yield: 157 mg (82%); mp >230 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 3.52$ (s, 6H, OMe), 7.12 (dd, $J = 5.1$, 3.8 Hz, 2H, Thio), 7.18 (dd, $J = 5.1$, 3.8 Hz, 2H, Thio), 7.41 (dd, $J = 5.1$, 1.1 Hz, 2H, Thio), 7.47 (dd, $J = 5.1$, 1.0 Hz, 2H, Thio), 7.56 (s, 2H, Py), 7.61 (dd, $J = 3.8$, 1.0 Hz, 2H, Thio), 7.85 (s, 4H, Ar), 8.15 (dd, $J = 3.8$, 1.1 Hz, 2H, Thio) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): $\delta = 60.2$ (q, OMe), 118.5 (d, Py), 124.5, 127.7, 127.8, 128.1, 128.5, 128.6, 129.2, 136.6, 140.9, 143.1 (7 d, 3 s, Thio, Ar), 144.6, 146.2, 148.1, 148.8 (4 s, Py) ppm. IR (ATR): $\nu = 3105–2930$ (=C–H, C–H), 1585–1455 (C=C) cm^{-1}; HRMS: $m/z = 621.0805$, calcd. for $C_{34}H_{25}N_2O_2S_4$ $[M+H]^+$: 621.0793.

4,4′-(1,4-Phenylene)bis[2,6-di(2-thiophenyl)pyridin-3-ol] (12)

According to typical procedure 2, a mixture of pyridine derivative **11** (150 mg, 0.24 mmol) and NaSEt (203 mg, 2.42 mmol) in DMF (5 mL) was heated in an ACE-sealed tube at 90 °C for 2 h to provide compound **12** as a dark brownish oil which was used without further purification in the next step; yield: 95 mg (67%).

4,4′-(1,4-Phenylene)bis[2,6-di(2-thiophenyl)pyridine-4,3-diyl] Bistriflate (13)

According to typical procedure 3, a mixture of pyridinol derivative **12** (95 mg, 0.16 mmol), pyridine (0.15 mL, 1.9 mmol), DMAP (4 mg, 0.03 mmol) and Tf_2O (0.30 mL, 1.78 mmol) in dry CH_2Cl_2 (10 mL) upon stirring over night at room temperature and after purification by column chromatography on silica gel (10–20% EtOAc in hexanes) provided the corresponding bistriflate **13** as a brown amorphous solid; yield: 103 mg (75%); mp >230 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.15$ (dd, $J = 5.1$, 3.8 Hz, 2H, Thio), 7.19 (dd, $J = 5.1$, 3.8 Hz, 2H, Thio), 7.50 (dd, $J = 5.1$, 1.0 Hz, 2H, Thio), 7.57 (s, 2H, Py), 7.58 (dd, $J = 5.1$, 1.0 Hz, 2H, Thio), 7.71 (dd, $J = 3.8$, 1.0 Hz, 2H, Thio), 7.81 (s, 4H, Ar), 7.85 (br d, $J = 3.6$ Hz, 2H, Thio); ^{13}C NMR ($CDCl_3$, 126 MHz): $\delta =$ 118.7 (d, Py), 126.5, 128.1, 128.4, 129.4, 129.5, 129.9*, 130.0, 136.1, 138.4, 139.6 (7 d, 3 s, Thio, Ar), 142.8, 144.9, 146.9, 151.8 (d, 4 s, Py); a signal for the CF_3 group was not observed; ^{19}F NMR ($CDCl_3$, 470 MHz): $\delta = -74.1$ (s, CF_3); IR (ATR): $\nu = 3105–2990$ (=C–H, C–H), 1550–1425 (C=C) cm^{-1}; HR-MS: $m/z = 856.9491$, calcd. for $C_{34}H_{19}F_6N_2O_6S_6$ $[M+H]^+$: 856.9466.

1,4-Bis[2,6-di(2-thiophenyl)pyridin-4-yl]benzene (14)

According to typical procedure 4, a mixture of the bistriflate **13** (50 mg, 0.06 mmol), $Pd(OAc)_2$ (4 mg, 0.02 mmol), dppp (7 mg, 0.02 mmol), Et_3N (0.20 mL, 1.4 mmol), and formic acid (0.05 mL, 1.3 mmol) in DMF (2 mL) was heated in an ACE-sealed tube at 90 °C for 2 h to afford after purification by column chromatography on silica gel (5–10% EtOAc in hexanes) pyridine derivative **14** as a colorless solid; yield: 19 mg (56%); mp 123–124 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.16$ (dd, $J = 5.0$, 3.6 Hz, 4H, Thio), 7.45 (dd, $J = 5.0$. 1.0 Hz, 4H, Thio), 7.74 (s, 4H, Py), 7.74 (dd, $J = 3.6$, 1.0 Hz, 4H, Thio), 7.87 (s, 4H, Ar); ^{13}C NMR ($CDCl_3$, 126 MHz): $\delta = 114.8$ (d, Py), 124.9, 127.7, 127.9*, 139.2, 144.6 (3 d, 2 s, Thio, Ar), 149.1, 152.7 (2 s, Py), * intensity of the peak corresponds to 2C atoms; IR (ATR): $\nu = 3015–2900$ (=C–H, C–H), 1585–1435 (C=C) cm^{-1}; HR-MS: $m/z = 561.0587$, calcd. for $C_{32}H_{21}N_2S_4$ $[M+H]^+$: 561.0582.

Typical Procedure 5: 2,6-Di([2,2′-bithiophen]-5-yl)-3-methoxy-4-(thiophen-2-yl)pyridine (17)

A solution of *N*-bromosuccinimide (173 mg, 0.97 mmol) in dry DMF (3 mL) was added dropwise under argon to a cooled solution (–20 °C) of nonaflate **1b** (185 mg, 0.32 mmol) in dry DMF (3 mL). The mixture was warmed up to room temperature and stirred overnight. When the starting material was fully consumed (TLC monitoring), 2-tri(*n*-butylstannyl)thiophene (**16**) (588 mg, 0.50 mL, 1.57 mmol) and $Pd(PPh_3)_4$ (56 mg, 0.05 mmol) were added and the resulting mixture was heated at 120 °C for 2 h. The reaction was quenched with water (10 mL) and extracted with Et_2O (2×25 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 and the solvent was evaporated to dryness. The crude product was purified through column chromatography on silica gel (10–25% EtOAc in hexanes) to afford compound **17** as a greenish yellow solid; yield: 104 mg (63%, two steps); mp 120–123 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 3.69$ (s, 3H, OMe), 7.04–7.07 (m, 2H, Thio), 7.16–7.18 (m, 2H, Thio), 7.22–7.26 (m, 3H, Thio), 7.29 (br d, $J = 3.4$ Hz, 1H, Thio), 7.33 (br d, $J = 3.6$ Hz, 1H, Thio), 7.46 (d, $J = 3.9$ Hz, 1H, Thio), 7.51 (br d, $J = 5.1$ Hz, 1H, Thio), 7.64 (s, 1H, Py), 7.70 (br d, $J =$ 3.3 Hz, 1H, Thio), 7.98 (d, $J = 3.9$ Hz, 1H, Thio) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): $\delta = 60.2$ (q, OMe), 115.5 (d, Py), 124.1, 124.2, 124.5, 124.6, 124.7, 124.8, 125.1, 127.6, 128.0*, 128.1, 128.8, 129.3, 136.1, 136.4, 137.6, 137.7, 139.5, 139.7, 140.2 (12 d, 7 s, Thio), 143.0, 146.3, 147.6, 147.8 (4 s, Py), * intensity of the peak corresponds to 2C atoms; IR (ATR): $\nu = 3105–2990$ (=C–H, C–H), 1585–1445 (C=C) cm^{-1}; HR-MS: $m/z = 519.9996$, calcd. for $C_{26}H_{18}NOS_5$ $[M+H]^+$: 519.9986; anal. calcd. for $C_{26}H_{17}NOS_5$ (519.7): C 60.08, H 3.30, N 2.69, S 30.85; found: C 60.22, H 3.10, N 2.59, S 31.11.

2,6-Di[(2,2′-bithiophen)-5-yl]-4-(thiophen-2-yl)pyridin-3-ol (18)

According to typical procedure 2, a mixture of pyridine derivative **17** (90 mg, 0.17 mmol) and NaSEt (73 mg, 0.87 mmol) in DMF (3 mL) was heated in an ACE-sealed tube at 90 °C for 1 h to provide compound **18** as a brown oil

which was used as obtained in the next step; yield: 48 mg (55%).

2,6-Di[(2,2′-bithiophen)-5-yl]-4-(thiophen-2-yl)pyridin-3-yl Nonaflate (19)

The crude pyridinol derivative **18** (45 mg, 0.09 mmol) was dissolved in dry THF (5 mL) and NaH (21 mg, 0.89 mmol) was added under an argon atmosphere. Nonafluorobutanesulfonyl fluoride (0.15 mL, 0.83 mmol) was added dropwise. The mixture was stirred overnight at room temperature and then diluted with Et_2O (25 mL) and quenched by slow addition of ice-water. The layers were separated and the aqueous phase was extracted with Et_2O (3×25 mL). The combined organic layers were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on silica gel (5–15% EtOAc in hexanes) to afford nonaflate **19** as a light yellow oil; yield: 49 mg (69%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ=7.05 (dd, J=5.1, 3.6 Hz, 1H, Thio), 7.07 (dd, J=5.0, 3.6 Hz, 1H, Thio), 7.19 (d, J=3.9 Hz, 1H, Thio), 7.20 (dd, J=5.0, 3.6 Hz, 1H, Thio), 7.23 (d, J=3.9 Hz, 1H, Thio), 7.27 (dd, J=5.1, 1.0 Hz, 1H, Thio), 7.29 (dd, J=5.1, 1.0 Hz, 1H, Thio), 7.32 (dd, J=3.6, 2.7 Hz, 1H, Thio), 7.35 (dd, J=3.6, 1.0 Hz, 1H, Thio), 7.52 (s, 1H, Py), 7.52 (br d, J=3.4 Hz, 1H, Thio), 7.55–7.57 (m, 2H, Thio), 7.71 (br d, J=3.9 Hz, 1H, Thio); ^{13}C NMR ($CDCl_3$, 126 MHz): δ=117.8 (d, Py), 124.5, 124.6, 124.7, 124.8, 125.3, 125.4, 127.1, 128.0, 128.1, 128.2, 128.9, 130.1, 130.3, 135.3, 137.1, 137.2, 138.1, 138.3, 138.8, 141.0 (13 d, 7 s, Thio), 141.4, 141.8, 146.9, 151.3 (4 s, Py); ^{19}F NMR ($CDCl_3$, 470 MHz): δ=−80.6 (t, J=9.4 Hz, 3F, CF_3), −110.6, −120.5, −125.7 (3 mc, 2F each, CF_2); IR (ATR): ν=2960–2875 (=C−H, C−H), 1555–1430 (C=C) cm^{-1}; HR-MS: m/z=787.9164, calcd. for $C_{29}H_{15}F_9NO_3S_6$ $[M+H]^+$: 787.9227.

2,6-Di[(2,2′-bithiophen)-5-yl]-4-(thiophen-2-yl)pyridine (20)

Method A: According to typical procedure 4, a mixture of pyridyl nonaflate **19** (40 mg, 0.05 mmol), $Pd(OAc)_2$ (3 mg, 0.01 mmol), dppp (6 mg, 0.01 mmol), Et_3N (0.20 mL, 1.44 mmol), and formic acid (0.05 mL, 1.3 mmol) in DMF (3 mL) was heated in an ACE-sealed tube at 90 °C for 2 h to afford after purification by column chromatography on silica gel (5–10% EtOAc in hexanes) pyridine derivative **20** as a light yellow oil; yield: 20 mg (82%).

Method B: According to typical procedure 5, a mixture of dibromide **25** (25 mg, 0.05 mmol), 2-tri(*n*-butylstannyl)thiophene (**16**) (96 mg, 0.08 mL, 0.26 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol) in DMF (1 mL) upon heating at 90 °C for 2 h and after purification by column chromatography (SiO_2, 5–10% EtOAc in hexanes) provided compound **20** as a light yellow oil; yield: 18 mg (74%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ=7.05 (dd, J=5.1, 3.6 Hz, 2H, Thio), 7.17 (dd, J=5.2, 3.8 Hz, 1H, Thio), 7.20 (d, J=4.0 Hz, 2H, Thio), 7.25–7.26 (m, 2H, Thio), 7.31 (br d, J=3.6 Hz, 2H, Thio), 7.45 (br d, J=5.1 Hz, 1H, Thio), 7.57–7.58 (m, 3H, Thio), 7.62 (s, 2H, Py); ^{13}C NMR ($CDCl_3$, 126 MHz): δ=112.9 (d, Py), 124.3, 124.5, 124.9, 125.6, 125.7, 127.2, 128.0, 128.5, 137.6, 139.9, 141.3, 142.9 (8 d, 4 s, Thio), 143.2, 152.6 (2 s, Py); IR (ATR): ν=3030–2905 (=C−H, C−H), 1550–1435 (C=C) cm^{-1}; HR-MS: m/z=489.9889, calcd. for $C_{25}H_{16}NS_5$ $[M+H]^+$: 489.9881.

2,6-Bis(5-bromothiophen-2-yl)pyridine (21)

A solution of *N*-bromosuccinimide (247 mg, 1.39 mmol) in dry DMF (5 mL) was added dropwise under argon to a cooled solution (−20 °C) of compound **2** (135 mg, 0.56 mmol) in dry DMF (5 mL). The mixture was warmed up to room temperature and stirred for 12 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and quenched with water (10 mL). The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (2×20 mL) and the combined organic layers were washed with brine and dried with Na_2SO_4. The solvent was evaporated and the crude product was purified by chromatography (SiO_2, 25–50% EtOAc in hexanes) to afford compound **21** as a light yellow solid; yield: 196 mg (87%); mp 188–192 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=7.05 (d, J=3.9 Hz, 2H, Thio), 7.32 (d, J=3.9 Hz, 2H, Thio), 7.40 (d, J=7.8 Hz, 2H, Py), 7.67 (t, J=7.8 Hz, 1H, Py); ^{13}C NMR ($CDCl_3$, 126 MHz): δ=114.9, 115.4 (2 d, Py, Thio), 123.9, 130.1, 136.8, 145.3, 150.6 (2 d, 3 s, Py, Thio); IR (ATR): ν=3060–2850 (=C−H, C−H), 1555–1415 (C=C) cm^{-1}; HR-MS: m/z=399.8445, calcd. for $C_{13}H_8Br_2NS_2$ $[M+H]^+$: 399.8459.

Typical Procedure 6; 2,6-Di[(2,2′-bithiophen)-5-yl]-pyridine (22)

A mixture of dibromide **21** (180 mg, 0.45 mmol), 2-tri(*n*-butylstannyl)thiophene (**16**) (0.70 mL, 2.20 mmol) and $Pd(PPh_3)_4$ (51 mg, 0.04 mmol) in dry DMF (5 mL) was heated at 120 °C for 2 h under an argon atmosphere. The reaction was quenched by adding water (10 mL) and the product was extracted with Et_2O (3×25 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 and the solvent was evaporated to dryness. The crude product was purified by column chromatography on silica gel (10–25% EtOAc in hexanes) to afford compound **22** as brown crystals; yield: 138 mg (76%); a sample was recrystallized from CH_2Cl_2 to provide crystals suitable for X-ray structure analysis; mp 145–148 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=7.05 (dd, J=5.1, 3.7 Hz, 2H, Thio), 7.18 (d, J=3.8 Hz, 2H, Thio), 7.25 (dd, J=5.1, 1.0 Hz, 2H, Thio), 7.31 (dd, J=3.6, 1.0 Hz, 2H, Thio), 7.44 (d, J=8.0 Hz, 2H, Py), 7.51 (d, J=3.8 Hz, 2H, Thio), 7.64 (t, J=8.0 Hz, 1H, Py); ^{13}C NMR ($CDCl_3$, 126 MHz): δ=116.5 (d, Py), 124.2, 124.5, 124.8, 125.4, 128.0, 137.2 (6 d, Py, Thio), 137.6, 139.7, 143.4, 151.9 (4 s, Py, Thio); IR (ATR): ν=3100–2925 (=C−H, C−H), 1580–1435 (C=C) cm^{-1}; HR-MS: m/z=408.0017, calcd. for $C_{21}H_{14}NS_4$ $[M+H]^+$: 408.0004.

2,4,6-Tri[(2,2′-bithiophen)-5-yl]-3-(thiophen-2-yl)-pyridine (24)

A solution of *N*-bromosuccinimide (205 mg, 1.15 mmol) in dry DMF (3 mL) was added dropwise to a cooled solution (−20 °C) of compound **3** (75 mg, 0.23 mmol) in dry DMF (3 mL). The mixture was warmed up to room temperature and stirred for 24 h. After full consumption of the starting material (TLC monitoring), 2-tri(*n*-butylstannyl)thiophene (**16**) (470 mg, 0.40 mL, 1.26 mmol) was injected slowly and $Pd(PPh_3)_4$ (53 mg, 0.05 mmol) was added and the resulting

mixture was heated at 120 °C for 2 h. The mixture was diluted with Et_2O (10 mL) and quenched with water (10 mL). The layers were separated and the aqueous phase was extracted with Et_2O (2×25 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (5–20% EtOAc in hexanes) to give compound **24** as a greenish yellow solid; yield: 130 mg (86%, two steps); mp 118–122 °C. ^{1}H NMR (C_6D_6, 500 MHz): δ = 6.55 (d, J = 4.0 Hz, 1 H, Thio), 6.59–6.61 (m, 2 H, Thio), 6.65 (dd, J = 5.1, 3.6 Hz, 1 H, Thio), 6.67–6.69 (m, 3 H, Thio), 6.73 (dd, J = 5.1, 1.1 Hz, 1 H, Thio), 6.76–6.80 (m, 4 H, Thio), 6.95 (dd, J = 3.6, 1.0 Hz, 1 H, Thio), 7.01–7.03 (m, 2 H, Thio), 7.06 (d, J = 3.9 Hz, 1 H, Thio), 7.07–7.08 (m, 1 H, Thio), 7.26 (d, J = 3.8 Hz, 1 H, Thio), 7.47 (s, 1 H, Py); ^{13}C NMR (C_6D_6, 126 MHz): δ = 115.7 (d, Py), 121.5, 123.7, 124.2, 124.3, 124.55, 124.56, 124.58, 124.7, 124.8, 124.9, 126.2, 127.71, 127.73, 127.9, 128.1, 128.2, 129.30, 129.32, 130.2, 136.9, 137.5, 137.6, 138.3, 138.8, 140.1, 140.6*, 143.0 (17 d, 10 s, Thio), 143.7, 144.6, 151.7, 152.4 (4 s, Py), *intensity of the peak corresponds to 2 C atoms; IR (ATR): ν = 3070–2865 (=C–H, C–H), 1615–1470 (C=C) cm^{-1}; HR-MS: m/z = 653.9696, calcd. for $C_{33}H_{20}NS_7$ $[M+H]^+$: 653.9635.

2,6-Bis(5-bromothiophen-2-yl)-4-(thiophen-2-yl)-pyridine (25)

A solution of *N*-bromosuccinimide (45 mg, 0.25 mmol) in dry DMF (0.5 mL) was added dropwise under argon to a cooled solution (−20 °C) of compound **3** (33 mg, 0.10 mmol) in dry DMF (0.5 mL). The mixture was warmed up to room temperature and stirred for 6 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and quenched with water (5 mL). The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (2×10 mL), the combined organic layers were washed with brine and dried with Na_2SO_4. The solvent was evaporated and the crude product was purified by chromatography on silica gel (10% EtOAc in hexanes) to afford dibromo compound **25** (yield: 35 mg, 72%) and tribromo compound **26** (yield: 4 mg, 7%), both as colorless solids.

Data of **25**: mp 235–240 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.08 (d, J = 3.9 Hz, 2 H, Thio), 7.17 (dd, J = 5.1, 3.7 Hz, 1 H, Thio), 7.39 (d, J = 3.9 Hz, 2 H, Thio), 7.45 (dd, J = 5.1, 1.1 Hz, 1 H, Thio), 7.55 (dd, J = 3.7, 1.1 Hz, 1 H, Thio), 7.57 (s, 2 H, Py); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 112.7, 115.9, 124.9, 125.7, 127.5, 128.5 (6 d, Py, Thio), 130.9, 141.0, 143.3 (3 s, Thio,), 145.9, 152.0 (2 s, Py); IR (ATR): ν = 2960–2870 (=C–H, C–H), 1520–1355 (C=C) cm^{-1}; HR-MS: m/z = 483.8333, calcd. for $C_{17}H_{10}Br_2NS_3$ $[M+H]^+$: 483.8337.

2,4,6-Tris(5-bromothiophen-2-yl)pyridine (26)

A solution of *N*-bromosuccinimide (88 mg, 0.49 mmol) in dry DMF (1 mL) was added dropwise under argon to a cooled solution (−20 °C) of compound **3** (40 mg, 0.12 mmol) in dry DMF (1 mL). The mixture was warmed up to room temperature and stirred for 5 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and quenched with water (5 mL). The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (2×10 mL), the combined organic layers were washed with brine and dried with Na_2SO_4. The solvent was evaporated and the crude product was purified by column chromatography on silica gel (10% EtOAc in hexanes) to afford tribromo compound **26** as a colorless solid; yield: 54 mg (80%); mp 145–148 °C. ^{1}H NMR ($CDCl_3$, 700 MHz): δ = 7.06 (d, J = 4.2 Hz, 2 H, Thio), 7.11 (d, J = 4.2 Hz, 1 H, Thio), 7.28 (d, J = 4.2 Hz, 1 H, Thio), 7.34 (d, J = 4.2 Hz, 2 H, Thio), 7.41 (s, 2 H, Py); ^{13}C NMR ($CDCl_3$, 176 MHz): δ = 112.0, 114.6, 116.0 (3 d, Thio, Py), 124.8, 125.8 (2 d, Thio), 130.9, 131.3 (2 s, Thio), 142.2, 145.6, 152.0 (3 s, Py, Thio), only 10 C atoms with different chemical shifts could be detected; IR (ATR): ν = 2960–2865 (=C–H), 1465–1360 (C=C) cm^{-1}; HR-MS: m/z = 559.7457, calcd. for $C_{17}H_9Br_3NS_3$ $[M+H]^+$: 559.7442.

2,4,6-Tri[(2,2′-bithiophen)-5-yl]pyridine (28)

According to typical procedure 1, a mixture of tribromide **26** (25 mg, 0.044 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), K_2CO_3 (31 mg, 0.22 mmol), and thiophene-2-boronic acid (**27**) (29 mg, 0.22 mmol) in DMF (1.1 mL) was heated at 80 °C for 3 h under an argon atmosphere. The mixture was cooled to room temperature, diluted with brine (10 mL) and extracted with Et_2O (3×20 mL). The combined organic phases were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on silica gel (5–10% EtOAc in hexanes) to give **28** as a light yellow solid; yield: 19 mg (76%); mp 240–244 °C. ^{1}H NMR ($CDCl_3$, 700 MHz): δ = 7.04–7.08 (m, 3 H, Thio), 7.21 (d, J = 3.5 Hz, 2 H, Thio), 7.22 (d, J = 3.5 Hz, 1 H, Thio), 7.25–7.27 (m, 2 H, Thio), 7.28 (dd, J = 3.5, 1.4 Hz, 1 H, Thio), 7.29 (dd, J = 5.6, 1.4 Hz, 1 H, Thio), 7.32 (dd, J = 3.5, 1.4 Hz, 2 H, Thio), 7.50 (d, J = 3.5 Hz, 1 H, Thio), 7.59 (d, J = 3.5 Hz, 2 H, Thio), 7.60 (s, 2 H, Py); ^{13}C NMR ($CDCl_3$, 176 MHz): δ = 112.4, 124.2, 124.4, 124.5, 124.7, 124.8, 125.3, 125.6, 126.2, 127.9, 128.0 (11 d, Thio, Py), 136.8, 137.5, 139.2, 139.5, 139.9, 142.4, 143.0, 152.5 (8 s, Thio, Py); IR (ATR): ν = 2960–2865 (=C–H), 1465–1360 (C=C) cm^{-1}; HR-MS: m/z = 571.9773, calcd. for $C_{29}H_{18}NS_6$ $[M+H]^+$: 571.9758.

Supporting Information

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of all new compounds; UV/vis and emission spectra of **6**, **9**, **14**, **20**, **22**, **24** and **28**; cyclic voltammogramms of **24** and **28** are given in the Supporting Information.

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