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Photophysical and Electrochemical Properties of Thiophene-Based 2-Arylpyridines

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Dedicated to Professor Gianfranco Scorrano on the occasion of his 72nd birthday

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Two families of thiophene-based 2-arylpyridines, in which aryl is phenyl and 2,4-difluorophenyl, have been developed. The pyridine ring of the new compounds is substituted at the 4-position with π-conjugated electron-rich and electron-poor thiophene-based fragments to tune the optical and energetic properties. The high-yielding synthetic access, which consists of two sequential Suzuki coupling reactions, the first of which is completely regioselective, is of wide applicability and allows access to a large variety of derivatives. The absorption/emission and redox features, as well as the HOMO and LUMO energy levels, have been investigated; the results show that the optical and electronic properties can be tuned over a broad range. The diversity of the characteristics may be effectively exploited by using the thiophene-substituted 2-arylpyridines as ligands in cyclometalated sensitizers for dye-sensitized solar cells and other optoelectronic applications.

Introduction

Pyridine and polypyridine derivatives are widely used as chromophores and nitrogen ligands in a variety of materials science applications, including nonlinear optics (NLO),[1,2] photovoltaics (e.g., dye-sensitized solar cells, DSCs),[3,4] and light emission.[5] One of the strategies for optimizing their properties and increasing their stability involves the insertion of five-membered heteroaromatics into the π-conjugated backbone.[1–3,6] Indeed, highly efficient chromophores and ligands are formed of pyridine rings substituted by thiophene-derived groups, including electron-rich moieties such as 3,4-ethylenedioxythiophene (EDOT). This is a result of the unique properties of the thiophene ring,[7] which is endowed with optimal resonance energy, charge-transport properties, and enhanced stability with respect to more conventional benzenoid groups.

In the field of DSC photosensitizers, which are strategic chromophores that interact with sunlight and promote the formation and collection of charge at device electrodes, the most efficient systems are Ru^{II}–polypyridyl complexes such as the prototypical *cis*-[$Ru(SCN)_2$(2,2′-bipyridyl-4,4′-dicarboxylate)$_2$] (N719).[8] Although these dyes are endowed with unsurpassed efficiency, they suffer from serious limitations, such as a mismatch of the dye-sensitizer absorption and the solar spectrum and a low molar extinction coefficient ε of the metal-to-ligand charge-transfer (MLCT) band, which prevents photocurrent values comparable to those of silicon cells. To partially circumvent these limitations and improve the spectral properties, a large number of thiophene-derived polypyridine complexes have been reported, including those with oligothienyl groups, fused fragments such as thieno[3,2-*b*]thiophene, and EDOT.[9] These Ru^{II} complexes exhibit redshifted MLCT bands with higher ε values. Among other examples, we have recently investigated bi-[10] and quarterpyridine[11] Ru^{II} DSC sensitizers in which the pyridine rings are π-conjugated to EDOT-vinylene substituents. Such substitution enabled us to attain a panchromatic response, enhanced absorptivity extended to the red-NIR portion of the spectrum, and high photo-

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current densities. Similarly, we have recently described pyridine-EDOT heteroarylene-vinylene donor–acceptor low-band-gap polymers for bulk heterojunction organic photovoltaic cells with optimal HOMO, LUMO, and band-gap energies.[12]

Cyclometalated Ir^{III} complexes containing pyridine rings have been widely investigated as nonlinear optical chromophores[13] or as electroluminescent materials in organic light-emitting diodes (OLEDs) owing to their strong photoemissive properties.[5,14] More recently, cyclometalated Ru^{II} and Ir^{II} complexes have emerged as a new generation of thiocyanate-free DSC photosensitizers.[15,16] In these dyes the two thiocyanato ligands of N719 have been replaced by one arylpyridine ligand, thus forming a cyclometalated complex. Thiocyanate-free sensitizers hold great promise for DSC technology, because the incorporation of thiocyanato ligands into Ru^{II} dyes weakens the structure, affording limited chemical and thermal stability and thus hindering long-term outdoor application.[17] Graetzel, Nazeeruddin and co-workers demonstrated for the first time that cyclometalated Ru^{II} complexes containing 2-(2,4-difluorophenyl)-pyridine (**1b**) as a ligand are able to provide power conversion efficiencies comparable to that of N719.[16]

Because of the large variety of thiophene-substituted bipyridine ligands available for DSC complexes with enhanced properties and photovoltaic response, and the pertinence of cyclometalated complexes in important technological fields, we were very surprised to learn that simple 2-phenylpyridine and 2-(2,4-difluorophenyl)pyridine with a thiophene-based substituent at the 4-position of the azine ring (Figure 1) were still completely unknown. Even more amazingly, thiophene-derived 2-phenylpyridines with substitution on the phenyl ring have so far never been reported, with the recent exception of 4-(5-chloro-2-thienyl)-2-(3-hydroxyphenyl)pyridine and its corresponding methyl ether in estrone mimetics studies.[18]

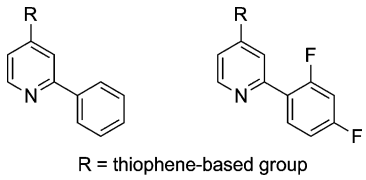


Figure 1. General structure of thiophene-derived 2-phenyl- and 2-(2,4-difluorophenyl)pyridine ligands.

We report herein the synthesis and investigation of the optical and electrochemical properties of a number of representative 2-phenyl- and 2-(2,4-difluorophenyl)pyridines substituted at the 4-position of the azine ring by a π-conjugated thiophene derivative. This unprecedented class of compounds has been prepared through a convenient synthetic route based on a sequence of highly regioselective Suzuki coupling reactions.[19] The new synthetic scheme has wide applicability and can be easily extended to other interesting examples pertaining to this class.

Results and Discussion

Design and Synthesis

The investigated 2-phenylpyridines **2a**–**8a** and 2-(2,4-difluorophenyl)pyridines **2b**–**8b** are listed in Figure 2 along with their pristine derivatives 2-phenylpyridine (**1a**) and 2-(2,4-difluorophenyl)pyridine (**1b**), which we have chosen as reference systems. We decided to base our investigation on the most simple and representative thiophene derivatives: (a) monocyclic thiophene ring (2-arylpyridines **2** and **3**), (b) 2,2′-bithienyl, as a representative example of polycyclic substituents (2-arylpyridines **4**), (c) thieno[3,2-*b*]thiophene, as a representative example of fused thiophene derivatives (2-arylpyridines **5**), and (d) EDOT, as a representative example of electron-rich thiophene derivatives (2-arylpyridines **6**). The presence of the thiophene ring provides the substituent with an electron-rich character, particularly in the presence of alkoxy substituents.[7] We thus also wanted to include in our investigation electron-poor thiophene-based substituents by considering thiophene moieties carrying both a conventional (formyl) and a strong [3-cyano-2-(dicyanomethylene)-4,5,5-trimethyl-2,5-dihydrofuran or Dalton's acceptor][20] electron-withdrawing group, namely 2-arylpyridines **7** and **8**, respectively. The strong electron-withdrawing capacity of the Dalton group has been successfully exploited in several highly efficient NLO chromophores.[21,22] Alkyl chains have been introduced onto the thiophene rings to prevent solubility issues.

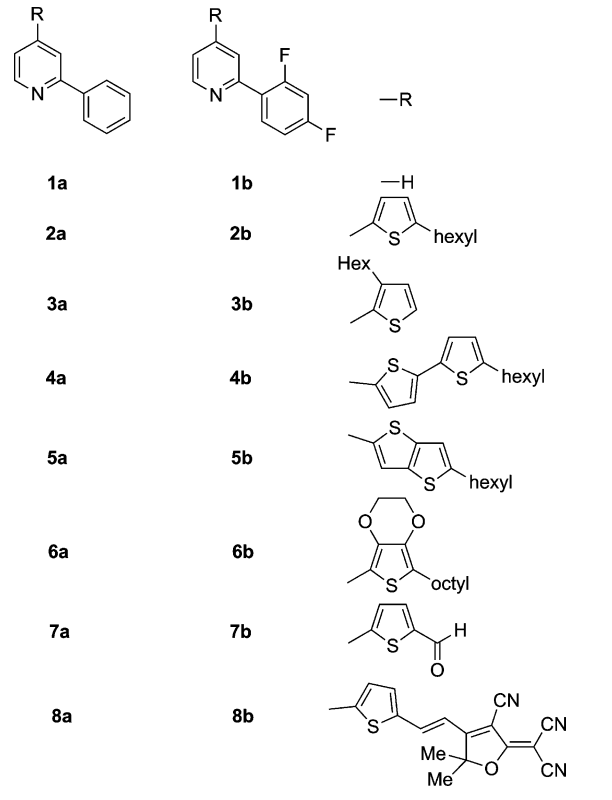
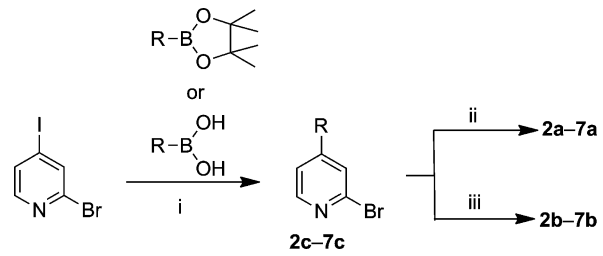


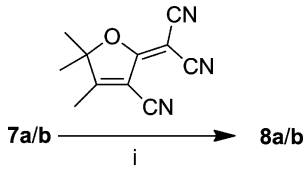
Figure 2. 2-Arylpyridines investigated in this work.

The general synthetic scheme is centered around the regioselective Suzuki cross-coupling reaction of 2-bromo-4-iodopyridine described by Ko and co-workers in the preparation of 2-bromopyridines **2c** and **5c**.[23] We have extended this reaction to other thiophene derivatives, affording the remaining examples of the family of 4-(thiophene-derived)-2-bromopyridines **3c**, **4c**, **6c**, and **7c** (Scheme 1). In all cases, the Suzuki cross-coupling reaction started from the appropriate pinacol boronate ester, with the exception of **7c**, which was prepared by using the commercially available 5-formyl-2-thienylboronic acid. The boronate esters leading to the new 2-bromopyridines were either commercially available (synthesis of **3c** and **4c**) or prepared according to previously reported procedures for other compounds (synthesis of **6c**, starting from the previously unknown 2-octylEDOT).[24]



Scheme 1. Reagents and conditions: (i) $[Pd(PPh_3)_4]$, Na_2CO_3, THF/H_2O, reflux, boronate ester for **3c**, **4c**, and **6c** or boronic acid for **7c**; (ii) 2-phenylboronic acid, $[Pd(PPh_3)_4]$, Na_2CO_3, THF/H_2O, microwaves max. 150 W at 70 °C; (iii) (2,4-difluorophenyl)boronic acid, $[Pd(PPh_3)_4]$, Na_2CO_3, THF/H_2O, reflux or microwaves max. 150 W at 70 °C. Substituents R as in Figure 2.

A second Suzuki reaction with phenylboronic acid or (2,4-difluorophenyl)boronic acid afforded **2a**–**7a** and **2b**–**7b**, respectively. The 2-phenylpyridine **8a** and 2-(2,4-difluorophenyl)pyridine **8b** with Dalton's acceptor were prepared from aldehydes **7a** and **7b**, respectively, by Knoevenagel condensation with 2-(3-cyano-4,5,5-trimethyl-5*H*-furan-2-ylidene)malononitrile (Scheme 2).[21f]



Scheme 2. Reagents and conditions: (i) Piperidine cat., CH_3CN or EtOH.

The yields of the two sequential Suzuki cross-coupling reactions for the synthesis of 2-bromopyridine intermediates **c** and 2-arylpyridines **a** and **b** are collected in Table 1. The yields are always in excess of 40% and in a few cases surpass 90%, which suggests the wide applicability of the procedure to the rapid and convenient synthesis of 4-substituted-2-arylpyridines.

Table 1. Yields of the Suzuki cross-coupling reactions that yield 2-bromopyridines **2c**–**8c**, 2-phenylpyridines **2a**–7**a**, and 2-(2,4-difluorophenyl)pyridines **2b**–**7b**.

R	Yield [%]		
	c[a]	**a**[b]	**b**[c]
2	[d]	74	66
3	91	44	78
4	94	44	74
5	[d]	82	99
6	58	82	90
7	60	65	87

[a] Scheme 1, step i. [b] Scheme 1, step ii. [c] Scheme 1, step iii. [d] Previously reported in ref.[23]

Optical Characterization

The absorption spectra of 2-phenylpyridines **2a**–**8a** and 2-(2,4-difluorophenyl)pyridines **2b**–**8b**, along with those of the corresponding reference systems **1a** and **1b**, are depicted in Figures 3 and 4, respectively. The main photophysical parameters in CH_2Cl_2 are collected in Table 2. Each of the ligands presents two distinct bands in the UV/Vis region. The high-energy band is in general less intense, with the main exception of the unsubstituted derivatives **1a** and **1b**, for which the opposite behavior is observed. The most apparent features of the absorption spectra are the strong bathochromic shift and increase of molar absorptivity induced by the introduction of π-conjugated thiophene-based substituents onto the six-membered heteroaromatic ring. This results in significantly smaller optical band gaps, the values of which decrease from ca. 4 eV in **1** to nearly 2 eV in **8** (see Table 3). It is therefore evident that the thiophene-derived arylpyridines possess improved optical properties compared with reference systems **1**, which may be particularly useful in the preparation of materials with better light-harvesting characteristics for photovoltaic devices.

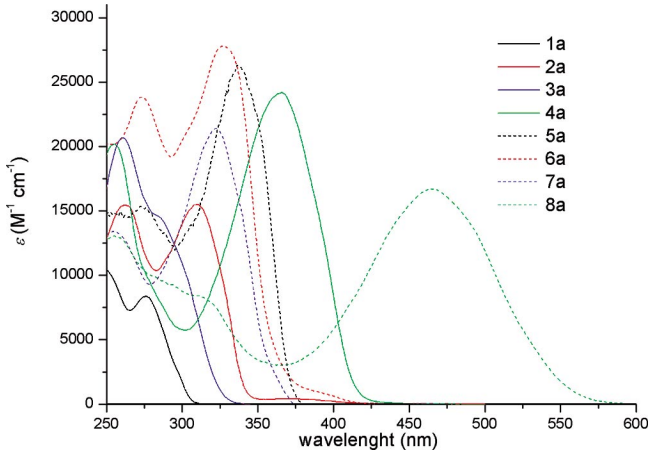


Figure 3. Absorption spectra of 2-phenylpyridines **1a**–**8a** in CH_2Cl_2.

The position of the high-energy band, located at 250–300 nm, is somewhat independent of the substitution pattern and can be attributed to local π–π* transitions involving the arylpyridine core. In contrast, the low-energy transition strongly depends on the presence and nature of

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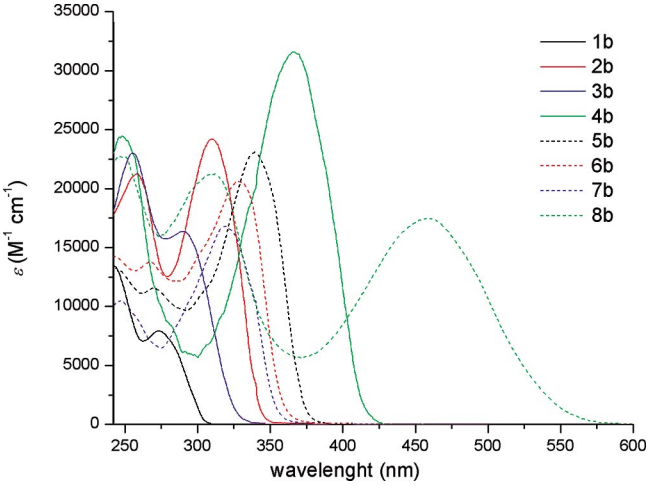

Figure 4. Absorption spectra of 2-(2,4-difluophenyl)phenylpyridines **1b**–**8b** in CH_2Cl_2.

Table 2. Absorption maxima and onset wavelengths of 2-phenylpyridines **1a**–**8a** and 2-(2,4-difluorophenyl)pyridines **1b**–**8b** in CH_2Cl_2.

	λ_{abs}[a] [nm]	ε [$mol^{-1}\,L\,cm^{-1}$]	λ_{onset} [nm]
1a	248 (246)	10500 ± 300	305
	276 (274)	8300 ± 500	
1b	242	13500 ± 200	305
	274	8000 ± 200	
2a	262 (280)	15400 ± 400	420
	310 (310)	15500 ± 400	
2b	258	21200 ± 3000	360
	310	24200 ± 3400	
3a	260 (273)	20700 ± 1500	325
	286 (297)	14000 ± 500	
3b	255	23000 ± 500	325
	290	16400 ± 300	
4a	255 (262)	20200 ± 1500	460
	366 (388)	24200 ± 1700	
4b	248	24600 ± 3200	480
	367	31600 ± 4100	
5a	337 (347)	26300 ± 100	370
5b	340	23100 ± 2200	370
6a	274 (287)	24000 ± 1000	360
	326 (332)	27800 ± 1300	
6b	328	20600 ± 500	360
7a	255 (267)	13400 ± 500	360
	322 (322)	21400 ± 800	
7b	250	10500 ± 1300	365
	320	16800 ± 1600	
8a	461 (487)	16700 ± 2700	550
8b	308	21200 ± 1900	550
	458	17500 ± 1600	

[a] Computed (TDDFT) values for **1a**–**8a** are given in parentheses.

the thienyl substituent and likely corresponds to the intramolecular thiophene-pyridine charge-transfer band. As anticipated, this band is significantly more intense and red-shifted compared with the reference dyes, and its maximum shifts from ca. 270 nm in **1** to ca. 460 nm in **8**. At variance with the pyridine substitution pattern, the addition of the two fluoro substituents on to the phenyl ring does not induce any significant variation in the absorption spectra, although in general the bands of the fluoro-substituted derivatives **b** are more intense than those of their counterparts **a**. We can thus conclude that the optical properties of the arylpyridines **1**–**8** vary over a broad range both in terms of intensity and position of the bands. This is predominantly associated with the presence of thiophene-derived groups with different chemical and electronic features, with the role of the fluoro substituents being much less important. Finally, no or negligible emission was observed upon excitation at the low- or high-energy absorption maxima with the exception of **5a** (emission peak at 400 nm), **5b** (400 nm), and **6b** (388 nm).

Electrochemical Characterization

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV; see the Supporting Information) were performed on 2-phenylpyridines **1a**–**8a** and 2-(2,4-difluorophenyl)pyridines **1b**–**8b** to determine the redox characteristics and frontier molecular orbital energy levels. The measured redox potentials and the HOMO/LUMO and band gap energies are collected in Table 3. When both oxidation and reduction processes were observed, the HOMO and LUMO energies could be electrochemically determined and the corresponding electrochemical band gaps measured. It can be seen that these values match well those derived by optical absorption (optical band gaps). In the remaining cases, in which either the oxidative (HOMO energy) or reductive (LUMO energy) peak was not observable, the missing value was calculated by adding or subtracting the optical band gap (Table 3, values in italics). Typical CV and DPV cathodic curves of **7b** are shown in Figure 5 as an example of the electrochemical characterization. Compound **7b** shows two reversible reductive CV waves at –1.79 and –2.22 V, which correspond to the formation of the radical anion and the dianion, respectively. When the curves are reversible, the LUMO energies can be directly calculated from CV ($E_{1/2}$). In fact, only **7a** and **7b** show reversible features (cathodic processes) with irreversible CV waves generally being observed. In these cases, all the cathodic DPV peaks show a full-width at half-maximum, similar to the peak of the ferrocene/ferrocenium (Fc/Fc^+) couple, which was used as an internal standard, and these DPV peaks were used to determine the LUMO energies.

Oxidation peaks at potentials higher than 1 V vs. Fc/Fc^+ were measured by DPV for the reference compounds **1a** and **1b**, with the latter having a slightly higher oxidation potential due to the presence of the electron-withdrawing fluorine substituents. We could not experimentally observe the reduction processes because of the very low values of the corresponding potential lying close to the electrolyte decomposition limit. This is confirmed by the measured large optical band gaps of ca. 4 eV, which, by starting from the electrochemically measured HOMO levels, predicts LUMO energies of ca. –2 eV, corresponding to potentials of –3 V vs. Fc/Fc^+.

At variance with the pristine derivatives **1**, well-defined reduction processes at potentials of ca. –2.6 to –0.9 V vs.

Table 3. Electrochemical properties of 2-phenylpyridines **1a**–**8a** and 2-(2,4-difluorophenyl)pyridines **1b**–**8b** in CH_3CN.[a]

	E^{ox} [V]	HOMO[b] [eV]	E^{red} [V]	LUMO[b] [eV]	E_{gap}^{opt}[c] [eV]	E_{gap}^{ec}[d] [eV]
1a	1.02	–6.2	–	*–2.1*	4.1	–
1b	1.10	–6.3	–	*–2.2*	4.1	–
2a	0.37	–5.6	–2.53	–2.7	3.0	2.9
2b	–	*–6.1*	–2.49	–2.7	3.4	–
3a	1.10	–6.3	–2.56	–2.6	3.8	3.7
3b	–	*–6.5*	–2.53	–2.7	3.8	–
4a	0.75	–6.0	–2.30	–2.9	2.7	3.1
4b	0.78	–6.0	–2.25	–3.0	2.6	3.0
5a	–	*–6.2*	–2.39	–2.8	3.4	–
5b	–	*–6.3*	–2.36	–2.9	3.4	–
6a	–	*–6.1*	–2.56	–2.7	3.4	–
6b	–	*–6.0*	–2.59	–2.6	3.4	–
7a	–	*–6.8*	–1.80	–3.4	3.4	–
7b	–	*–6.8*	–1.78	–3.4	3.4	–
8a	1.30	–6.5	–0.88	–4.3	2.3	2.2
8b	1.28	–6.5	–0.89	–4.3	2.3	2.2

[a] All potentials are reported vs. Fc/Fc^+, and the HOMO and LUMO energies are derived from the electrochemical data based on the assumption that the Fc/Fc^+ redox couple is 5.23 eV relative to a vacuum (see ref.[25]). [b] Values in italics were calculated from the optical band gap when the reduction (LUMO) or oxidation (HOMO) process was not observed. [c] Optical band gap (calculated on the low-energy edge of the absorption spectrum, Table 2). [d] Electrochemical band gap, obtained from the difference between the measured reduction and oxidation potentials.

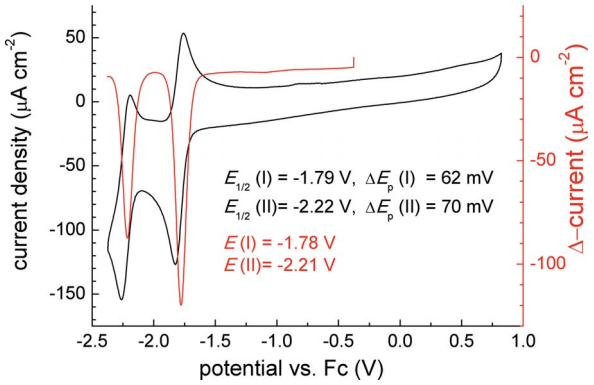

Figure 5. CV (black) and DPV (red) scans of **7b** in CH_3CN with the half-wave potentials ($E_{1/2}$), the peak separation (ΔE_p) for CV, and the peak potential for DPV.

Fc/Fc^+ were observed upon substitution of the pyridine ring by the thiophene-based units in the 2-arypyridines **2**–**8**. This means that the presence of the π-conjugated thiophene substituents shifts the LUMO energies to more negative values compared with the reference systems. The reduction potentials are not apparently affected by the halogen substitution on the phenyl ring (**a** vs. **b**), which suggests that the structures of the LUMO orbitals should be dominated by the contributions of the thiophene atomic orbital. Oxidative DPV waves were often absent either due to the high oxidation potentials of the molecules (matching the electrolyte stability threshold) or to the very poor electrode kinetics of the corresponding anodic reactions. The electrochemically measured HOMO energies were either higher (less negative) or lower (more negative) than those of **1**, with values ranging from –6.5 eV in **8a/b** to –5.6 eV in **2a**. The HOMO values, obtained from the electrochemical LUMO energies and the optical band gaps, were located in the same range as the electrochemical HOMO energies, confirming the reciprocity of the two approaches.

The following more detailed discussion can be made for specific cases. Comparison of the properties of the monocyclic derivatives evidences that **2a** has a higher HOMO value than its isomer **3a**, and thus a smaller electrochemical band gap, as fully confirmed by the optical data. This is likely the consequence of the presence, in the latter, of the alkyl side-chain close to the thiophene–pyridine bond, which hinders to some extent the planarity of the π backbone. As a consequence, the thiophene ring of **3a** raises the HOMO energy less effectively than in **2a**. When replacing the monothienyl substituent in **2** and **3** with dithienyl substituents in **4** the reduction becomes easier (less negative potentials), which corresponds to lower LUMO levels. This confirms that the role of the thiophene substituent is to decrease the LUMO energies and that this effect increases as the number of thiophene rings increases. The HOMO levels of both dyes **4** are –6.0 eV, that is, higher than those of **2b** and dyes **3**. In combination with the lower LUMO energies, this leads to smaller band-gap energies in the dithienyl derivatives **4** compared with the previous examples. Similar conclusions can be drawn for the fused bicyclic derivatives **5**, for which the oxidative events could not be observed even if the optical band gaps predict potentials inside the electrochemical stability window of the electrolyte.

Side-substitution of the conjugated thiophene rings with donor (as in arylpyridines **6**) or acceptor (as in arylpyridines **7** and **8**) groups significantly affects the energies of the molecular orbitals with opposite effects. As expected, the integration of donor alkoxy groups in the EDOT derivatives **6** makes reduction more difficult, leading to the lowest measured cathodic potentials and, accordingly, the highest LUMO energies of the **2**–**8** series. This is in agreement with the larger optical band gaps. HOMO values were not detected, likely due to very poor kinetics of the anodic reactions. In contrast, the presence of electron-withdrawing substituents in **7** and **8** greatly favors the reduction process,

and the reduction potentials are significantly shifted to less negative values. In particular, the inclusion of the very strong Dalton's acceptor[20] decreases by almost 2 V the potential needed for reduction compared with the other derivatives. Consistent with this, the lowest LUMO levels (–4.3 eV) were measured for compounds **8**, to be compared with values of ca. –2 eV for **1**. Although the measured HOMO energies were lowered as well (more difficult anodic oxidation, with potentials higher than 1 V vs. Fc/Fc^+), the strong decrease of the LUMO levels affords very small electrochemical band gaps of ca. 2 eV, in perfect agreement with the UV/Vis analysis. Indeed, such low band gaps are more typical of a highly conjugated framework (oligomers and polymers) rather than a small-molecule system and forecast optimized trade-offs between enhanced light-harvesting abilities and the typical advantages of molecular versus polymeric structures in terms of convenient synthesis, easier purification, and more defined chemical structure. The HOMO, LUMO, and band-gap energies obtained by the optical and electrochemical analyses are summarized schematically in Figure 6.

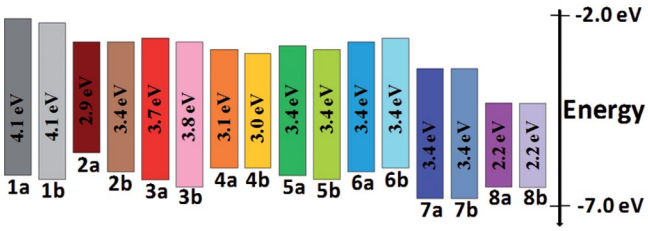

Figure 6. HOMO, LUMO, and band-gap energies obtained by optical and electrochemical investigation.

Table 4. Energies of the lowest-unoccupied (L) and highest-occupied (H) Kohn–Sham orbitals of **1a**–**8a**.

Orbital	Energy [eV]							
	1a	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**	**8a**
H–2	–6.96	–6.81	–6.69	–6.80	–6.38	–6.18	–6.87	–6.88
H–1	–6.79	–6.21	–6.23	–6.22	–6.23	–6.12	–6.53	–6.35
H	–6.17	–5.92	–6.11	–5.41	–5.65	–5.66	–6.30	–6.11
L	–1.19	–1.53	–1.39	–1.83	–1.67	–1.52	–2.36	–3.33
L+1	–0.58	–0.96	–0.91	–1.09	–1.04	–0.87	–1.26	–1.75
L+2	0.13	–0.03	–0.12	–0.61	–0.25	0.01	–0.85	–1.24

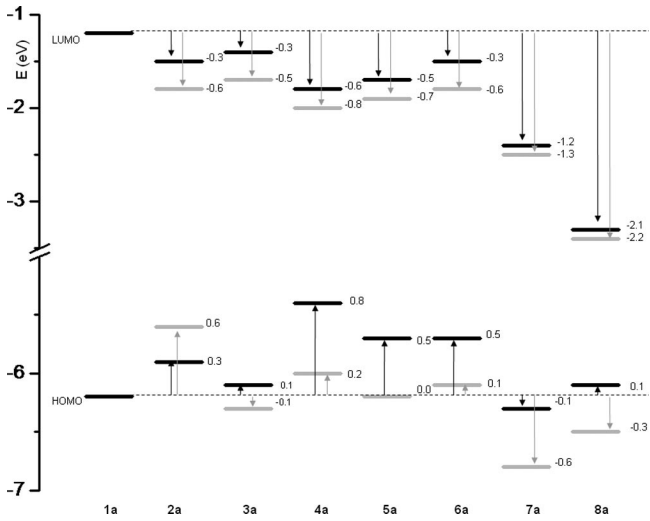

Figure 7. Schematic representation of the relative calculated (black) and experimental (grey) energy levels of 2-phenylpyridines **1a**–**8a**, with compound **1a** set as a reference. To simplify the comparison, the calculated and experimental data for **1a** have been set to the same values.

Computational Investigation

To gain an insight into the structural, electronic, and optical properties of the investigated 2-arylpyridines, we performed density functional theory (DFT) and time-dependent DFT (TDDFT) calculations on their ground and excited states. Because the experimental photophysical and electrochemical investigations have proven that the properties of the compounds are dependent upon the thiophene-based substituent rather than the fluorine substitution on the phenyl ring, we decided to limit the computational study to the 2-phenylpyridines **1a**–**8a**, which we selected as representative examples of the compounds investigated in this work. On the basis of the experimental data, we believe that the conclusions of the calculations can be extended to the series **1b**–**8b** as well.

The main experimental and calculated UV/Vis absorption features of **1a**–**8a** in CH_2Cl_2 are compared in Table 2 and the energies of the frontier molecular orbitals are listed in Table 4. The energy levels are represented schematically in Figure 7. Finally, the isodensity plots of the frontier molecular orbitals are shown in Figure 8.

As can be seen in Table 2, the calculated absorption maxima are in overall excellent agreement with experimental values throughout the investigated series, reproducing well the band-gap modulation exhibited by the various substituents with the calculated (experimental) absorption maxima ranging from 246 to 487 nm (248–461 nm). From Table 4 we note that, although the calculated HOMO values are in reasonable quantitative agreement with experimental values (Table 3), the LUMO energies are substantially less negative. This is somehow expected, considering the larger relaxation energy of the anionic species. The calculated HOMO–LUMO gaps follow the absorption spectral trends and, despite the overestimation of the LUMO, the individual energy levels are consistent with the variations experimentally observed. In particular, by setting the calculated HOMO and LUMO energies for **1a** equal to the corresponding experimental values and by inspecting their variation along the series, we note substantially similar trends, although some discrepancies remain due to the possible participation in the oxidation/reduction processes of significant electron relaxation beyond a simple single particle HOMO–LUMO picture (Figure 7).

The spatial distribution of the HOMOs and LUMOs in the **1a**–**8a** series can be analyzed by inspection of Figure 8. As can be seen, although the HOMOs are mainly localized on the substituted pyridine moiety, **1a** and **7a** being notable exceptions, the LUMOs are slightly more delocalized and,

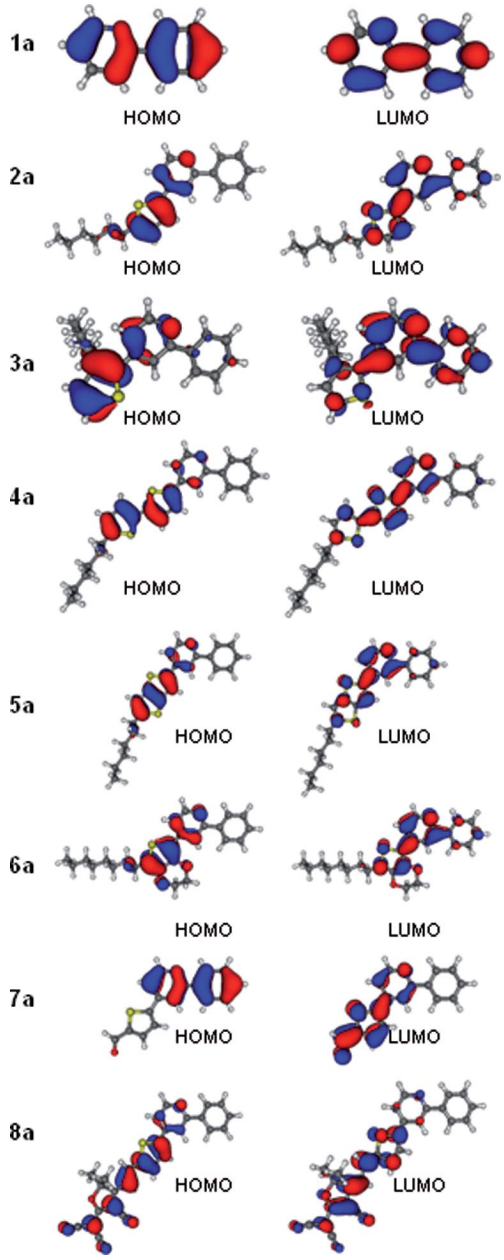

Figure 8. Isodensity plots (isodensity value = 0.035) of the HOMOs and LUMOs of 2-phenylpyridines **1a**–**8a**.

although still mainly localized on the pyridine ring, also show contributions from the phenyl portion of the ligand. Because the lowest excitation energies of all the ligands are essentially of HOMO–LUMO character, the nature of the ensuing excited state can be easily investigated in terms of the corresponding molecular orbitals. In **1a**, the main excitation has a π–π* character, involving no net charge transfer, whereas going from **2a** to **3a** a sizeable charge transfer from the pyridine to the phenyl ring takes place. A variable degree of charge transfer is also observed for **4a**–**6a**, whereas for **7a** the direction of charge transfer is reversed, with a delocalized HOMO electron being excited to a pyridine-localized LUMO due to the presence of an electron-withdrawing group on the thiophene substituent. In **8a**, the significant redshifted absorption spectrum is clearly the result of increased conjugation on the pyridine side, rather than of a charge-transfer process.

Conclusions

Two unprecedented families of 2-arylpyridines substituted by thiophene-based units on the pyridine ring have been investigated by a combination of chemical design and optical and electrochemical analysis. The thienyl substituents include a representative variety of monocyclic, polycyclic, and fused chemical structures with strategically different chemical, redox, and electronic features. By adding appropriate donor and acceptor substituents we were able to further tune the molecular properties and access a significant number of either electron-rich or electron-poor 2-arylpyridines.

The synthetic approach is of wide pertinence and could be conveniently applied to the preparation of other interesting examples by starting from readily available precursors. The optical and electrochemical studies have highlighted the largely tunable, very broad range of optical and energetic properties. Indeed, the absorption and emission bands span from the near-UV to the full visible spectrum, with optical band gaps ranging from nearly 2 to more than 4 eV. Consistent with this, the measured HOMO and LUMO energies vary significantly. The tunable characteristics described might ultimately be converted into enhanced material properties of various metal complexes, making them attractive for photovoltaic and other optoelectronic applications. The investigation of cyclometalated Ru^{II} complexes as DSC sensitizers is underway.

Experimental Section

Synthesis and Optical Characterization: NMR spectra were recorded with a Bruker AMX-500 instrument operating at 500.13 (^{1}H) and 125.77 MHz (^{13}C). ^{13}C multiplicities were assigned on the basis of the results of J-MOD experiments. HRMS data were recorded by using a Bruker Daltonics ICR-FTMS APEX II spectrometer equipped with an electrospray ionization (ESI) source or an Applied Biosystems QSTAR XL hybrid quadrupole time-of-flight mass spectrometer. Flash chromatography was performed with Merck grade 9385 silica gel 230–400 mesh (60 Å). Reactions were performed under nitrogen in oven-dried glassware and monitored by thin-layer chromatography by using UV light (254 and 365 nm) as visualizing agent. Microwave irradiated reactions were performed in a CEM Discover Labmate reactor. All reagents were obtained from commercial suppliers at the highest purity and used without further purification. 2-Phenylpyridine (**1a**), 2-(2,4-difluorophenyl)pyridine (**1b**), and anhydrous solvents were purchased from Sigma–Aldrich and used as received. Extracts were dried with Na_2SO_4 and filtered before removal of the solvent by evaporation. Melting points were measured with an Electrothermal 9100 instrument. Absorption spectra were recorded with a V-570 Jasco spectrophotometer, and emission spectra were recorded with a FP6200 Jasco spectrofluorimeter.

2-Bromo-4-(3-hexylthien-2-yl)pyridine (3c): A mixture of 2-bromo-4-iodopyridine (500 mg, 1.76 mmol), 3-hexylthiophene-2-boronic

Special Section

acid pinacol ester (518 mg, 1.76 mmol; Sigma Aldrich), Na_2CO_3 (299 mg, 2.82 mmol), [$Pd(PPh_3)_4$] (102 mg, 0.088 mmol) in THF (38 mL) and H_2O (23 mL) was heated at reflux for 9 h. After cooling to room temperature, the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The organic layers were combined, dried, and the solvents evaporated to dryness leaving a residue, which was purified by flash chromatography (petroleum ether/CH_2Cl_2, 1:1) to afford the pure product as a yellow viscous oil (518 mg, 1.6 mmol, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.38 (d, J = 5.1 Hz, 1 H), 7.60 (br. s, 1 H), 7.38–7.14 (m, 2 H), 7.02 (d, J = 4.3 Hz, 1 H), 2.70 (t, J = 8.2 Hz, 2 H), 1.62 (m, 2 H), 1.28 (m, 6 H), 0.88 (m, 3 H) ppm. HRMS (ESI): calcd. for $C_{15}H_{19}{}^{79}BrNS$ [M + H]$^+$ 324.0416; found 324.0420; calcd. for $C_{15}H_{19}{}^{81}BrNS$ [M + H]$^+$ 326.0396; found 326.0399.

2-Bromo-4-[5-(5-hexylthien-2-yl)thien-2-yl]pyridine (4c): A mixture of 2-bromo-4-iodopyridine (670 mg, 2.36 mmol), 5′-hexyl-2,2′-bithiophene-5-boronic acid pinacol ester (888 mg, 2.36 mmol; Sigma Aldrich), Na_2CO_3 (375 mg, 3.53 mmol), and [$Pd(PPh_3)_4$] (272 mg, 0.23 mmol) in THF (50 mL) and H_2O (30 mL) was stirred at reflux for 9 h. After cooling to room temp., the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined and dried organic layers left, after evaporation of the solvent under vacuum, a residue, which was purified by flash chromatography (hexane/CH_2Cl_2, 1:1). The pure product **3c** was obtained as a red solid (900 mg, 2.22 mmol, 94%). M.p. 69 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.31 (d, J = 5.2 Hz, 1 H), 7.63 (s, 1 H), 7.40 (d, J = 3.8 Hz, 1 H), 7.37 (d, J = 5.2 Hz, 1 H), 7.10 (d, J = 3.8 Hz, 1 H), 7.07 (d, J = 3.5 Hz, 1 H), 6.72 (d, J = 3.4 Hz, 1 H), 2.81 (t, J = 7.5 Hz, 2 H), 1.69 (quint, J = 7.3 Hz, 2 H), 1.45–1.30 (m, 6 H), 0.89 (t, J = 7.5 Hz, 3 H) ppm. HRMS (ESI): calcd. for $C_{19}H_{21}{}^{79}BrNS_2$ [M + H]$^+$ 406.0299; found 406.0293; calcd. for $C_{19}H_{21}{}^{81}BrNS_2$ [M + H]$^+$ 408.0278; found 408.0275.

3,4-(Ethylenedioxy)-2-octylthiophene: A solution of 3,4-ethylenedioxythiophene (2.0 g, 14.1 mmol) in anhydrous THF (15 mL) was cooled to –78 °C, and *n*-butyllithium (2.5 M in *n*-hexane, 4.5 mL, 11.3 mmol) was added dropwise under nitrogen. The mixture was stirred at 0 °C and for 20 min and then cooled to –78 °C. 1-Bromooctane (2.4 mL, 14 mmol) was then added dropwise. The mixture was stirred at room temp. for 15 h and finally quenched with H_2O (100 mL). The mixture was extracted with Et_2O (3 × 200 mL), and the combined organic layers were treated with aqueous $NaHCO_3$ and, after removal of the solvent, the residue, which was submitted to flash chromatography (petroleum ether/ethyl acetate, 95:5), afforded the pure product as a yellow viscous oil (1.5 g, 5.9 mmol, 42%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.11 (s, 1 H), 4.17 (m, 4 H), 2.62 (t, J = 7.6 Hz, 2 H), 1.59 (quint, J = 7.8 Hz, 2 H), 1.36–1.26 (m, 10 H), 0.88 (t, J = 7.0 Hz, 3 H) ppm.

3,4-(Ethylenedioxy)-5-octylthiophene-2-boronic Acid Pinacol Ester: A solution of 3,4-ethylenedioxy-2-octylthiophene (430 mg, 1.7 mmol) in anhydrous THF (15 mL) was cooled to –78 °C, and *n*-butyllithium (1.6 M in *n*-hexane, 2.1 mL, 3.4 mmol) was added dropwise under nitrogen. The mixture was stirred at 0 °C for 20 min and then cooled to –78 °C. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.4 mL, 6.8 mmol) was then added dropwise. After stirring at room temp. for 17 h, the reaction mixture was quenched by aqueous NH_4Cl (50 mL) and extracted with Et_2O (3 × 100 mL). The dried combined layers were concentrated to dryness under reduced pressure to afford the pure product as an oil (482 mg, 1.3 mmol, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.27 (m, 2 H), 4.16 (m, 2 H), 2.64 (t, J = 7.7 Hz, 2 H), 1.60 (quint, J = 7.2 Hz, 2 H), 1.36–1.20 (m, 22 H), 0.88 (t, J = 7.0 Hz, 3 H) ppm.

2-Bromo-4-(3,4-ethylenedioxy-5-octylthien-2-yl)pyridine (6c): A mixture of 2-bromo-4-iodopyridine (361 mg, 1.27 mmol), 3,4-(ethylenedioxy)-5-octylthiophene-2-boronic acid pinacol ester (482 mg, 1.27 mmol), Na_2CO_3 (202 mg, 1.91 mmol), and [$Pd(PPh_3)_4$] (73 mg, 0.063 mmol) in THF (25 mL) and H_2O (15 mL) was stirred at reflux for 20 h. After cooling to room temp., the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined and dried organic layers left, after evaporation of the solvent under vacuum, a residue, which was purified by flash chromatography (CH_2Cl_2). The pure product **6c** was obtained as a red oil (300 mg, 0.73 mmol, 58%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.21 (d, J = 5.4 Hz, 1 H), 7.76 (d, J = 1.4 Hz, 1 H), 7.43 (dd, J = 5.3, 1.5 Hz, 1 H), 4.35 (m, 2 H), 4.24 (m, 2 H), 2.66 (t, J = 7.5 Hz, 2 H), 1.61 (quint, J = 7.3 Hz, 2 H), 1.34–1.27 (m, 10 H), 0.88 (t, J = 7.1 Hz, 3 H) ppm. MS (ESI): calcd. for $C_{19}H_{25}{}^{79}BrNO_2S$ [M + H]$^+$ 410; found 410; calcd. for $C_{19}H_{25}{}^{81}BrNO_2S$ [M + H]$^+$ 412.0769; found 412.0890.

2-Bromo-4-(5-formylthien-2-yl)pyridine (7c): A mixture of 2-bromo-4-iodopyridine (213 mg, 0.75 mmol), 5-formyl-2-thienylboronic acid (117 mg, 0.75 mmol; Sigma–Aldrich), Na_2CO_3 (119 mg, 1.12 mmol), [$Pd(PPh_3)_4$] (26 mg, 0.02 mmol) in THF (16 mL) and H_2O (9 mL) was heated at reflux for 20 h. After cooling to room temp., the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, dried, and the solvents evaporated to dryness leaving a residue, which was purified by flash chromatography (ethyl acetate/CH_2Cl_2, 1:9) to afford the pure product (120 mg, 0.45 mmol, 60%) as a yellow solid. M.p. 164 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.95 (s, 1 H), 8.43 (d, J = 5.4 Hz, 1 H), 7.80 (d, J = 4.0 Hz, 1 H), 7.74 (s, J = 1.2 Hz, 1 H), 7.58 (d, J = 4.0 Hz, 1 H), 7.49 (dd, J = 5.2, 1.6 Hz, 1 H) ppm. HRMS (ESI): calcd. for $C_{10}H_7{}^{79}BrNOS$ [M + H]$^+$ 267.9432; found 267.9452; calcd. for $C_{10}H_7{}^{81}BrNOS$ [M + H]$^+$ 269.9411; found 269.9430.

4-(5-Hexylthien-2-yl)-2-phenylpyridine (2a): A mixture of **2c**[23] (230 mg, 0.71 mmol), phenylboronic acid (88 mg, 0.71 mmol), Na_2CO_3 (113 mg, 1.1 mmol), [$Pd(PPh_3)_4$] (50 mg, 0.04 mmol) in THF (15 mL) and H_2O (10 mL) was stirred in a microwave reactor at 70 °C (max. 150 W) for 20 min. After cooling to room temp., the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The organic layers were combined, dried, and the solvents evaporated to dryness leaving a residue, which was purified by flash chromatography (cyclohexane/CH_2Cl_2, 2:8) to afford the pure product as a yellow viscous oil (170 mg, 0.53 mmol, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.63 (d, J = 5.2 Hz, 1 H), 8.01 (d, J = 7.1 Hz, 2 H), 7.84 (d, J = 1.6 Hz, 1 H), 7.51 (t, J = 7.2 Hz, 2 H), 7.44 (t, J = 7.1 Hz, 1 H), 7.39 (d, J = 3.6 Hz, 1 H), 7.38 (dd, J = 5.2, 1.6 Hz, 1 H), 6.82 (d, J = 3.6 Hz, 1 H), 2.85 (t, J = 7.5 Hz, 2 H), 1.71 (quint, J = 7.3 Hz, 2 H), 1.45–1.30 (m, 6 H), 0.92 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.11 (1 C), 150.02 (1 CH), 148.55 (1 C), 142.60 (1 C), 139.36 (1 C), 138.60 (1 C), 129.03 (1 CH), 128.71 (2 CH), 126.98 (2 CH), 125.53 (1 CH), 125.20 (1 CH), 117.98 (1 CH), 116.51 (1 CH), 31.52 (1 C), 31.50 (1 CH_2), 30.35 (1 CH_2), 28.71 (1 CH_2), 22.52 (1 CH_2), 14.02 (1 CH_3) ppm. HRMS (ESI): calcd. for $C_{21}H_{24}NS$ [M + H]$^+$ 322.16240; found 322.16219; calcd. for $C_{21}H_{23}NNaS$ [M + Na]$^+$ 344.14434; found 344.14421.

4-(3-Hexylthien-2-yl)-2-phenylpyridine (3a): A mixture of **3c** (45 mg, 0.14 mmol), phenylboronic acid (17 mg, 0.14 mmol), Na_2CO_3 (22 mg, 0.21 mmol), [$Pd(PPh_3)_4$] (10 mg, 0.008 mmol) in THF (3 mL) and H_2O (2 mL) was stirred under microwave irradiation at 70 °C (max. 150 W) for 20 min. After cooling to room temp., H_2O was added, and the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The solvent was removed from the combined and

dried extracts to leave a residue, which was purified by flash chromatography (cyclohexane/CH_2Cl_2, 2:8) to afford the pure product as a yellow viscous oil (20 mg, 0.062 mmol, 44%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.71 (d, J = 5.0 Hz, 1 H), 8.02 (d, J = 7.4 Hz, 2 H), 7.79 (d, J = 1.6 Hz, 1 H), 7.50 (t, J = 7.3 Hz, 2 H), 7.44 (t, J = 7.1 Hz, 1 H), 7.34 (d, J = 5.2 Hz, 1 H), 7.31 (dd, J = 5.2, 1.3 Hz, 1 H), 7.04 (d, J = 5.1 Hz, 1 H), 2.76 (t, J = 7.8 Hz, 2 H), 1.69–1.63 (m, 2 H), 1.37–1.25 (m, 6 H), 0.86 (t, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.84 (1 C), 149.85 (1 CH), 143.39 (1 C), 140.79 (1 C), 139.30 (1 C), 134.92 (1 C), 130.21 (1 CH), 129.10 (CH), 128.79 (2 CH), 127.05 (2 CH), 125.41 (1 CH), 121.95 (1 CH), 120.51 (1 CH), 31.63 (1 CH_2), 30.95 (1 CH_2), 29.20 (1 CH_2), 28.98 (1 CH_2), 22.59 (1 CH_2), 14.05 (1 CH_3) ppm. HRMS (ESI): calcd. for $C_{21}H_{24}NS$ $[M + H]^+$ 322.16240; found 322.16278; calcd. for $C_{21}H_{23}NNaS$ $[M + Na]^+$ 344.14434; found 344.14500.

4-[5-(5-Hexylthien-2-yl)thien-2-yl]-2-phenylpyridine (4a): A mixture of **4c** (57 mg, 0.14 mmol), phenylboronic acid (17 mg, 0.14 mmol), Na_2CO_3 (22 mg, 0.21 mmol), $[Pd(PPh_3)_4]$ (10 mg, 0.008 mmol) in THF (3 mL) and H_2O (2 mL) was stirred in a microwave reactor at 70 °C (max. 150 W) for 20 min. After cooling to room temp., H_2O was added, and the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The organic layers were combined, dried, and the solvents evaporated to dryness leaving a residue, which was purified by flash chromatography (cyclohexane/CH_2Cl_2, 3:7) to afford the pure product as a yellow viscous oil (25 mg, 0.062 mmol, 44%). M.p. 52 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (d, J = 5.2 Hz, 1 H), 8.03 (d, J = 7.1 Hz, 2 H), 7.86 (d, J = 1.7 Hz, 1 H), 7.50 (t, J = 7.3 Hz, 2 H), 7.46 (d, J = 3.7 Hz, 1 H), 7.44 (t, J = 7.1 Hz, 1 H), 7.39 (dd, J = 5.2, 1.7 Hz, 1 H), 7.13 (d, J = 3.8 Hz, 1 H), 7.07 (d, J = 3.6 Hz, 1 H), 6.72 (d, J = 3.6 Hz, 1 H), 2.81 (t, J = 7.5 Hz, 2 H), 1.70 (quint, J = 7.3 Hz, 2 H), 1.45–1.30 (m, 6 H), 0.93 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.29 (1 C), 150.19 (1 CH), 146.47 (1 C), 141.95 (1 C), 139.80 (1 C), 139.32 (1 C), 139.10 (1 C), 134.11 (1 C), 129.08 (1 CH), 128.72 (2 CH), 126.98 (2 CH), 126.02 (1 CH), 124.97 (1 CH), 124.10 (1 CH), 123.92 (1 CH), 117.88 (1 CH), 116.39 (1 CH), 31.52 (1 CH_2), 31.50 (1 CH_2), 30.18 (1 CH_2), 28.72 (1 CH_2), 22.53 (1 CH_2), 14.01 (1 CH_3) ppm. HRMS (ESI): calcd. for $C_{25}H_{26}NS_2$ $[M + H]^+$ 404.15012; found 404.14979; calcd. for $C_{25}H_{25}NNaS_2$ $[M + Na]^+$ 426.13206; found 426.13203.

4-(5-Hexylthieno[3,2-*b*]thien-2-yl)-2-phenylpyridine (5a): A mixture of **5c**[23] (45 mg, 0.12 mmol), phenylboronic acid (14 mg, 0.12 mmol), Na_2CO_3 (20 mg, 0.19 mmol), $[Pd(PPh_3)_4]$ (7.0 mg, 0.006 mmol) in THF (3 mL) and H_2O (2 mL) was stirred under microwave irradiation at 70 °C (max. 150 W) for 20 min. After cooling to room temp., H_2O (20 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The extracts were combined, dried, and concentrated under reduced pressure leaving a residue, which was purified by flash chromatography (hexane/ethyl acetate, 8:2) to afford the pure product as a yellow solid (50 mg, 0.012 mmol, 82%). M.p. 215 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (d, J = 5.2 Hz, 1 H), 8.03 (d, J = 7.3 Hz, 2 H), 7.88 (d, J = 0.5 Hz, 1 H), 7.68 (s, 1 H), 7.51 (t, J = 7.2 Hz, 2 H), 7.45 (t, J = 7.3 Hz, 1 H), 7.42 (dd, J = 5.3, 1.5 Hz, 1 H), 6.98 (s, 1 H), 2.91 (t, J = 7.6 Hz, 2 H), 1.73 (quint, J = 7.4 Hz, 2 H), 1.41 (m, 2 H), 1.35–1.25 (m, 4 H), 0.90 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.03 (1 C), 150.72 (1 C), 149.85 (1 CH), 143.20 (1 C), 140.80 (1 C), 139.78 (1 C), 138.91 (1 C), 138.20 (1 C), 129.28 (1 CH), 128.82 (2 CH), 127.05 (2 CH), 118.01 (CH), 116.53 (1 CH), 31.54 (1 CH_2), 31.43 (1 CH_2), 31.28 (1 CH_2), 28.74 (1 CH_2), 22.56 (1 CH_2), 14.08 (1 CH_2), (1 CH_3) ppm. HRMS (ESI): calcd. for $C_{23}H_{24}NS_2$ $[M + H]^+$ 378.13502; found 378.13430; calcd. for $C_{23}H_{23}NNaS_2$ $[M + Na]^+$ 400.11696; found 400.11650.

4-[3,4-(Ethylenedioxy)-5-octylthien-2-yl]-2-phenylpyridine (6a): A mixture of **6c** (60 mg, 0.15 mmol), phenylboronic acid (18 mg, 0.18 mmol), Na_2CO_3 (25 mg, 0.24 mmol), $[Pd(PPh_3)_4]$ (10 mg, 0.008 mmol) in THF (3 mL) and H_2O (2 mL) was stirred in a microwave reactor at 70 °C (max. 150 W) for 20 min. After cooling to room temp., H_2O was added, and the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The organic layers were combined, dried, and the solvents evaporated to dryness leaving a residue, which was purified by flash chromatography (CH_2Cl_2) to afford the pure product as a yellow viscous oil (50 mg, 0.012 mmol, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.58 (d, J = 5.3 Hz, 1 H), 8.01 (d, J = 7.2 Hz, 2 H), 7.98 (d, J = 1.1 Hz, 1 H), 7.50 (dd, J = 5.1, 1.7 Hz, 1 H), 7.48 (t, J = 7.8 Hz, 2 H), 7.42 (t, J = 7.5 Hz, 1 H), 4.35 (m, 2 H), 4.26 (m, 2 H), 2.69 (t, J = 7.7 Hz, 2 H), 1.65 (quint, J = 7.4 Hz, 2 H), 1.40–1.28 (m, 10 H), 0.89 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.70 (1 C), 149.74 (1 CH), 141.43 (1 C), 141.01 (1 C), 139.80 (1 C), 138.18 (1 C), 128.78 (1 CH), 128.63 (2 CH), 126.98 (2 CH), 120.14 (1 CH), 117.88 (1 C), 116.33 (1 C), 110.49 (1 CH), 65.09 (1 CH_2), 64.28 (1 CH_2), 31.85 (1 CH_2), 30.26 (1 CH_2), 29.28 (1 CH_2), 29.21 (1 CH_2), 29.14 (1 CH_2), 25.93 (1 CH_2), 22.65 (1 CH_2), 14.11 (1 CH_3) ppm. HRMS (ESI): calcd. for $C_{25}H_{30}NO_2S$ $[M + H]^+$ 408.19972; found 408.19939; calcd. for $C_{25}H_{29}NNaO_2S$ $[M + Na]^+$ 430.18167; found 430.18132.

4-(5-Formylthien-2-yl)-2-phenylpyridine (7a): A mixture of **7c** (154 mg, 0.57 mmol), phenylboronic acid (71 mg, 0.58 mmol), Na_2CO_3 (77 mg, 0.73 mmol), $[Pd(PPh_3)_4]$ (33 mg, 0.06 mmol) in THF (15 mL) and H_2O (10 mL) was stirred in a microwave reactor at 70 °C (max. 150 W) for 20 min. After cooling to room temp., H_2O (50 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, dried, and the solvents evaporated to dryness leaving a residue, which was purified by flash chromatography (CH_2Cl_2/ethyl acetate, 9:1) to afford the pure product as a yellow solid (100 mg, 0.37 mmol, 65%). M.p. 121 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.96 (s, 1 H), 8.77 (d, J = 5.1 Hz, 1 H), 8.04 (d, J = 7.1 Hz, 2 H), 7.95 (d, J = 1.1 Hz 1 H), 7.81 (d, J = 3.9 Hz, 1 H), 7.64 (d, J = 3.9 Hz, 1 H), 7.54–7.46 (m, 4 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 182.89 (s, CHO), 158.73 (1 C), 150.55 (1 CH), 144.36 (1 C), 141.22 (1 C), 138.67 (1 C), 137.00 (1 CH), 131.89 (1 C), 129.69 (1 CH), 129.04 (2 CH), 127.16 (2 CH), 126.25 (1, CH), 118.88 (1 CH), 117.46 (1 CH) ppm. HRMS (ESI): calcd. for $C_{16}H_{12}NOS$ $[M + H]^+$ 266.06396; found 266.06385; calcd. for $C_{16}H_{11}NNaOS$ $[M + Na]^+$ 288.04590; found 288.04550.

2-(Dicyanomethylene)-3-cyano-5,5-trimethyl-4-{2-[5-(2-phenylpyrid-4-yl)thien-2-yl]ethen-1-yl}-2,5-dihydrofuran (8a): A mixture of **7a** (110 mg, 0.41 mmol), 2-(3-cyano-4,5,5-trimethyl-5*H*-furan-2-ylidene)malononitrile[21f] (125 mg, 0.62 mmol), and three drops of piperidine in CH_3CN (10 mL) was stirred at room temp. for 15 h. After removal of the solvent at reduced pressure, the residue was dissolved in CH_2Cl_2 (5 mL). The precipitate formed after the addition of cyclohexane (40 mL) was collected and taken up with EtOH (10 mL) to afford the product as a red solid (60 mg, 0.13 mmol, 32%). M.p. >250 °C. ^{1}H NMR (500 MHz, [D$_6$]-DMSO): δ = 8.75 (d, J = 5.2 Hz, 1 H), 8.30 (s, 1 H), 8.22 (d, J = 7.3 Hz, 2 H), 8.20–8.16 (m, 2 H), 7.95 (d, J = 4.0 Hz, 1 H), 7.74 (dd, J = 5.1, 1.35 Hz, 1 H), 7.54 (t, J = 7.0 Hz, 2 H), 7.50 (t, J = 7.1 Hz, 1 H), 6.96 (d, J = 16.2 Hz, 1 H), 1.8 (s, 6 H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 177.29 (1 C), 174.79 (1 C), 157.69 (1 C), 151.07 (1 CH), 147.58 (1 C), 141.77 (1 C), 140.97 (1 C), 140.09

(1 CH), 138.61 (1 C), 137.29 (1 CH), 129.94 (1 C), 129.38 (1 CH), 129.24 (1 CH), 127.31 (1 CH), 119.14 (1 CH), 116.63 (1 CH), 115.06 (1 CH), 113.16 (1 C), 112.38 (1 C), 111.28 (1 C), 99.89 (1 C), 99.60 (1 C), 25.76 (2 CH_3) ppm. HRMS (ESI): calcd. for $C_{27}H_{19}N_4OS$ $[M + H]^+$ 447.12796; found 447.12771; calcd. for $C_{26}H_{18}N_4NaOS$ $[M + Na]^+$ 469.10990; found 469.10964.

2-(2,4-Difluorophenyl)-4-(5-hexylthien-2-yl)pyridine (2b): A solution of **2c**[23] (329 mg, 1.02 mmol), (2,4-difluorophenyl)boronic acid (161 mg, 1.02 mmol), Na_2CO_3 (256 mg, 2.41 mmol), and $[Pd(PPh_3)_4]$ (35 mg, 0.03 mmol) in THF (5 mL) and H_2O (3 mL) was heated at reflux for 24 h. After cooling to room temp., the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The organic layers were combined, dried, and the solvents evaporated to dryness leaving a residue, which was purified by flash chromatography (hexane/AcOEt, 9:1) to afford the pure product as a yellow viscous oil (200 mg, 0.56 mmol, 66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.63 (d, J = 5.2 Hz, 1 H), 8.00 (td, J = 8.8, 6.7 Hz, 1 H), 7.87 (br. s, 1 H), 7.40–7.35 (m, 2 H), 7.01 (ddd, J = 9.0, 8.7, 2.5 Hz, 1 H), 6.93 (ddd, J = 11.3, 8.8, 2.5 Hz, 1 H), 6.81 (d, J = 2.8 Hz, 1 H), 2.84 (t, J = 7.6 Hz, 2 H), 1.70 (quint, J = 7.7 Hz, 2 H), 1.45–1.35 (m, 2 H), 1.35–1.30 (m, 4 H), 0.90 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.22 (dd, J_{CF} = 251.1, 12.1 Hz, 1 CF), 160.57 (dd, J_{CF} = 251.1, 11.9 Hz, 1 CF), 153.09 (d, J_{CF} = 2.2 Hz, 1 C), 150.11 (1 CH), 148.74 (1 C), 142.34 (1 C), 138.28 (1 C), 132.15 (d, J_{CF} = 9.6 Hz, CH), 125.56 (1 CH), 125.39 (1 CH), 123.78 (dd, J_{CF} = 11.7, 3.6 Hz, 1 C), 119.95 (d, J_{CF} = 9.1 Hz, 1 CH), 118.23 (1 CH), 111.84 (dd, J_{CF} = 20.9, 3.5 Hz, 1 CH), 104.36 (t, J_{CF} = 26.4 Hz, 1 CH), 31.52 (1 CH_2), 31.50 (1 CH_2), 30.34 (1 CH_2), 28.73 (1 CH_2), 22.54 (1 CH_2), 14.04 (1 CH_3) ppm. HRMS (ESI): calcd. for $C_{21}H_{22}F_2NS$ $[M + H]^+$ 358.14410; found 358.14322; calcd. for $C_{21}H_{21}F_2NNaS$ $[M + Na]^+$ 380.12605; found 380.12548.

2-(2,4-Difluorophenyl)-4-(3-hexylthien-2-yl)pyridine (3b): A solution of **3c** (500 mg, 1.54 mmol), (2,4-difluorophenyl)boronic acid (244 mg, 1.54 mmol), Na_2CO_3 (245 mg, 2.31 mmol), $[Pd(PPh_3)_4]$ (53 mg, 0.05 mmol) in THF (32 mL) and H_2O (19 mL) was heated at reflux for 9 h. After cooling to room temp., the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The organic layers were combined, dried, and the solvents evaporated to dryness leaving a residue, which was purified by flash chromatography (petroleum ether/CH_2Cl_2, 1:1) to afford the pure product as a yellow viscous oil (430 mg, 1.2 mmol, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.71 (d, J = 5.1 Hz, 1 H), 8.04 (td, J = 6.7, 8.9 Hz, 1 H), 7.83 (m, 1 H), 7.34 (d, J = 5.3 Hz, 1 H), 7.32 (dd, J = 5.1, 1.7 Hz, 1 H), 7.03–6.99 (m, 2 H), 6.93 (ddd, J = 9.5, 8.8, 2.5 Hz, 1 H), 2.75 (t, J = 7.8 Hz, 2 H), 1.65 (q, J = 7.3 Hz, 2 H), 1.34 (m, 2 H), 1.37–1.26 (m, 4 H), 0.86 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.33 (dd, J_{CF} = 249.6, 11.9 Hz, 1 CF), 160.68 (dd, J_{CF} = 251.0, 11.5 Hz, 1 CF), 152.77 (1 C), 149.89 (1 CH), 143.17 (1 C), 141.05 (1 C), 134.61 (1 C), 132.20 (dd, J_{CF} = 4.4, 9.6 Hz, CH), 130.30 (1 CH), 125.52 (1 CH), 123.90 (d, J_{CF} = 9.4 Hz, 1 C), 123.69 (d, J_{CF} = 11.2 Hz, 1 CH), 122.21 (1 CH), 111.91 (dd, J_{CF} = 21.0, 3.5 Hz, 1 CH), 104.40 (t, J_{CF} = 27.5 Hz, 1 CH), 31.58 (1 CH_2), 30.87 (1 CH_2), 29.10 (1 CH_2), 28.93 (1 CH_2), 22.53 (1 CH_2), 13.99 (1 CH_3) ppm. HRMS (ESI): calcd. for $C_{21}H_{22}F_2NS$ $[M + H]^+$ 358.14410; found 358.14323; calcd. for $C_{21}H_{21}F_2NNaS$ $[M + Na]^+$ 380.12605; found 380.12539.

2-(2,4-Difluorophenyl)-4-[5-(5-hexylthien-2-yl)thien-2-yl]pyridine (4b): A solution of **4c** (300 mg, 0.74 mmol), (2,4-difluorophenyl)-boronic acid (140 mg, 0.89 mmol), Na_2CO_3 (118 mg, 1.1 mmol), and $[Pd(PPh_3)_4]$ (26 mg, 0.022 mmol) in THF (5 mL) and H_2O (3 mL) was stirred at reflux for 16 h. After cooling to room temp., the reaction mixture was extracted with AcOEt (3 × 100 mL). The organic layers were combined, dried, and the solvent was evaporated to dryness. The pure product **4b** was obtained by silica gel chromatography (petroleum ether/AcOEt, 8:2) as a yellow solid (270 mg, 0.55 mmol, 75%). M.p. 54 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.65 (d, J = 5.4 Hz, 1 H), 8.02 (td, J = 8.8, 6.7 Hz, 1 H), 7.88 (br. s, 1 H), 7.42 (d, J = 3.8 Hz, 1 H), 7.38 (dd, J = 5.2, 1.7 Hz, 1 H), 7.10 (d, J = 3.8 Hz, 1 H), 7.07 (d, J = 3.5 Hz, 1 H), 7.01 (ddd, J = 9.6, 8.6, 2.5 Hz, 1 H), 6.94 (ddd, J = 11.2, 8.8, 2.5 Hz, 1 H), 6.70 (d, J = 3.6 Hz, 1 H), 2.80 (t, J = 7.5 Hz, 2 H), 1.69 (quint, J = 7.6 Hz, 2 H), 1.43–1.37 (m, 2 H), 1.37–1.28 (m, 4 H), 0.90 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (126 Hz, $CDCl_3$): δ = 163.30 (dd, J_{CF} = 251.1, 12.0 Hz, 1 CF), 160.62 (dd, J_{CF} = 251.1, 11.7 Hz, 1 CF), 153.21 (d, J_{CF} = 2.4 Hz, 1 C), 150.19 (1 CH), 146.53 (1 C), 141.78 (1 C), 140.04 (1 C), 138.71 (1 C), 134.05 (1 C), 132.17 (dd, J_{CF} = 9.6, 4.3 Hz, 1 CH), 126.25 (1 CH), 124.98 (CH), 124.16 (1 CH), 123.93 (1 CH), 123.66 (dd, J_{CF} = 11.6, 3.6 Hz, 1 C), 119.87 (d, J_{CF} = 9.2 Hz, 1 CH), 118.15 (1 CH), 111.86 (dd, J_{CF} = 20.9, 3.5 Hz, 1 CH), 104.38 (t, J_{CF} = 26.0 Hz, 1 CH), 31.53 (1 CH_2), 31.50 (1 CH_2), 30.18 (1 CH_2), 28.73 (1 CH_2), 22.54 (1 CH_2), 14.02 (1 CH_3) ppm. HRMS (ESI): calcd. for $C_{25}H_{24}F_2NS_2$ $[M + H]^+$ 440.13182; found 440.13086; calcd. for $C_{25}H_{23}F_2NNaS_2$ $[M + Na]^+$ 462.11377; found 462.11294.

2-(2,4-Difluorophenyl)-4-(5-hexylthieno[3,2-*b*]thien-2-yl)pyridine (5b): A solution of **5c**[23] (45 mg, 0.12 mmol), (2,4-difluorophenyl)-boronic acid (19 mg, 0.12 mmol), Na_2CO_3 (20 mg, 0.19 mmol), and $[Pd(PPh_3)_4]$ (7 mg, 0.006 mmol) in THF (3 mL) and H_2O (2 mL) was stirred in a microwave reactor at 70 °C (max. 150 W) for 20 min. After cooling to room temp., THF was evaporated under reduced pressure, and H_2O (20 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, dried, and the solvents evaporated to dryness leaving a residue, which was purified by flash chromatography (hexane/ethyl acetate, 8:2) to afford the pure product as a yellow solid (52 mg, 0.12 mmol, 99%). M.p. 71 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (d, J = 5.2 Hz, 1 H), 8.03 (td, J = 6.7, 8.9 Hz, 1 H), 7.92 (m, 1 H), 7.65 (s, 1 H), 7.41 (dd, J = 5.1, J = 1.7 Hz, 1 H), 7.02 (ddd, J = 10.3, 8.0, 1.9 Hz, 1 H), 6.97 (s, 1 H), 6.94 (ddd, J = 11.3, 8.8, 2.5 Hz, 1 H), 2.89 (t, J = 7.5 Hz, 2 H), 1.73 (quint, J = 7.3 Hz, 2 H), 1. 39 (m, 2 H), 1.32 (m, 4 H), 0.90 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.28 (dd, J_{CF} = 249.6, 12.0 Hz, 1 CF), 160.59 (dd, J_{CF} = 251.0, 11.9 Hz, 1 CF), 153.17 (d, J = 2.1 Hz, 1 C), 150.66 (1 C), 150.20 (1 CH), 142.72 (1 C), 140.64 (1 C), 139.78 (1 C), 138.18 (1 C), 132.17 (dd, J_{CF} = 4.4, 9.6 Hz, 1 CH), 123.62 (dd, J_{CF} = 11.5, 3.9 Hz, 1 C), 119.95 (d, J_{CF} = 9.4 Hz, 1 C), 118.27 (1 CH), 118.01 (1 CH), 116.48 (1 CH), 111.92 (dd, J_{CF} = 20.9, 3.3 Hz, 1 CH), 104.42 (t, J_{CF} = 26.1 Hz, 1 CH), 31.54 (1 CH_2), 31.43 (1 CH_2), 31.26 (1 CH_2), 28.73 (1 CH_2), 22.56 (1 CH_2), 14.07 (1 CH_3) ppm. HRMS (ESI): calcd. for $C_{23}H_{22}F_2NS_2$ $[M + H]^+$ 414.11617; found 414.11570; calcd. for $C_{23}H_{21}F_2NNaS_2$ $[M + Na]^+$ 436.09812; found 436.09460.

2-(2,4-Difluorophenyl)-4-(3,4-ethylenedioxy-5-octylthien-2-yl)-pyridine (6b): A solution of **6c** (82 mg, 0.20 mmol), (2,4-difluorophenyl)boronic acid (32 mg, 0.20 mmol), Na_2CO_3 (34 mg, 0.32 mmol), and $[Pd(PPh_3)_4]$ (11 mg, 0.010 mmol) in THF (3 mL) and H_2O (2 mL) was stirred under microwave irradiation at 70 °C (max. 150 W) for 20 min. After cooling to room temp., THF was evaporated under reduced pressure, and H_2O (20 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 50 mL). The extracts were combined and dried, and, after evaporation of the solvent under reduced pressure, the residue was submitted to flash chromatography (CH_2Cl_2/hexane, 8:2) to afford the pure product as a white solid (80 mg, 0.18 mmol, 90%). M.p. 49 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.58 (d, J = 5.1 Hz, 1 H), 7.97 (s, 1 H),

7.96 (td, J = 6.7, 8.8 Hz, 1 H), 7.51 (dd, J = 5.1, 1.7 Hz, 1 H), 6.99 (ddd, J = 11.0, 8.5, 2.0 Hz, 1 H), 6.92 (ddd, J = 11.3, 8.8, 2.5 Hz, 1 H), 4.34 (m, 2 H), 4.25 (m, 2 H), 2.67 (t, J = 7.5 Hz, 2 H), 1.63 (quint, J = 7.3 Hz, 2 H), 1.39–1.27 (m, 10 H), 0.88 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.06 (dd, J_{CF} = 249.0, 11.7 Hz, 1 CF), 160.52 (dd, J_{CF} = 251.0, 11.9 Hz, 1 CF), 152.72 (d, J = 2.1 Hz, 1 C), 149.77 (1 CH), 141.25 (1 C), 141.16 (1 C), 138.18 (1 C), 132.12 (dd, J_{CF} = 4.5, 9.6 Hz, 1 CH), 124.28 (dd, J_{CF} = 11.5, 4.0 Hz, 1 C), 120.43 (1, CH), 119.79 (d, J_{CF} = 8.5 Hz, 1 C), 118.12 (1 CH), 111.70 (dd, J_{CF} = 20.9, 3.6 Hz, 1 CH), 104.30 (t, J_{CF} = 26.0 Hz, 1 CH), 65.07 (1 CH_2), 64.26 (1 CH_2), 31.84 (1 CH_2), 30.24 (1 CH_2), 29.27 (1 CH_2), 29.20 (1 CH_2), 29.12 (1 CH_2), 22.64 (1 CH_2), 14.08 (1 CH_3) ppm. HRMS (ESI): calcd. for $C_{25}H_{28}F_2NO_2S$ [M + H]$^+$ 444.18088; found 444.17995; calcd. for $C_{25}H_{27}F_2NNaO_2S$ [M + Na]$^+$ 466.16283; found 466.16243.

2-(2,4-Difluorophenyl)-4-(5-formylthien-2-yl)pyridine (7b): A solution of **7c** (120 mg, 0.45 mmol), 2,4-difluorophenylboronic acid (71 mg, 0.44 mmol), Na_2CO_3 (70 mg, 0.66 mmol), [$Pd(PPh_3)_4$] (16 mg, 0.013 mmol) in THF (9 mL) and H_2O (6 mL) was heated at reflux for 9 h. After cooling to room temp., H_2O was added, and the mixture was extracted with CH_2Cl_2 (2 × 25 mL). The organic layers were combined, dried, and the solvents evaporated to dryness leaving a residue, which was purified by flash chromatography (ethyl acetate/CH_2Cl_2, 1:9) to afford the product (115 mg, 0.38 mmol, 87%) as a yellow solid. M.p. 140 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.0 (s, 1 H), 8.75 (d, J = 5.1 Hz, 1 H), 8.05 (td, J = 6.6, 8.8 Hz, 1 H), 7.99 (m, 1 H), 7.79 (d, J = 3.9 Hz, 1 H), 7.61 (d, J = 3.9 Hz, 1 H), 7.48 (dd, J = 5.1, 1.7 Hz, 1 H), 7.03 (ddd, J = 9.5, 8.0, 2.0 Hz 1 H), 6.95 (ddd, J = 11.2, 8.8, 2.5 Hz, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 182.69 (CHO), 163.49 (dd, J_{CF} = 250.5, 12.0 Hz, 1 CF), 160.68 (dd, J_{CF} = 251.4, 12.0 Hz, 1 CF), 153.65 (d, J_{CF} = 2.1 Hz, 1 C), 150.61 (1 CH) 150.20 (1 C), 144.32 (1 C), 140.72 (1 C), 136.77 (1 CH), 132.20 (dd, J_{CF} = 4.3, 9.7 Hz, 1 CH), 125.92 (1 CH), 123.12 (dd, J_{CF} = 11.4, 3.9 Hz, 1 C), 120.76 (d, J_{CF} = 9.8 Hz, 1 CH), 119.02 (1 CH), 112.06 (dd, J_{CF} = 21.0, 3.4 Hz, 1 CH), 104.49 (t, J_{CF} = 26.3 Hz, 1 CH) ppm. HRMS (ESI): calcd. for $C_{16}H_{10}F_2NOS$ [M + H]$^+$ 302.04457; found 302.04436; calcd. for $C_{16}H_9F_2NNaOS$ [M + Na]$^+$ 324.02651; found 324.02646.

3-Cyano-2-(dicyanomethylene)-4-(2-{5-[2-(2,4-difluorophenyl)pyrid-4-yl]thien-2-yl}ethen-1-yl)-5,5-trimethyl-2,5-dihydrofuran (8b): A mixture of **7b** (280 mg, 0.93 mmol), 2-(3-cyano-4,5,5-trimethyl-5*H*-furan-2-ylidene)malononitrile[21f] (281 mg, 1.39 mmol), and three drops of piperidine in EtOH (20 mL) was stirred at room temp. for 15 h. After removing the solvent at reduced pressure, the residue was dissolved in CH_2Cl_2 (5 mL). The precipitate formed after the addition of cyclohexane (40 mL) was collected and taken up with EtOH (10 mL) to afford the product as a red solid (220 mg, 0.46 mmol, 49%). M.p. >250 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.78 (d, J = 5.1 Hz, 1 H), 8.07 (td, J = 8.9, 6.7 Hz, 1 H), 7.99 (m, 1 H), 7.83 (d, J = 16.0 Hz, 1 H), 7.62 (d, J = 4.0 Hz, 1 H), 7.52 (d, J = 4.0 Hz, 1 H), 7.47 (dd, J = 5.2, 1.7 Hz, 1 H), 7.05 (ddd, J = 9.2, 7.9, 1.8 Hz, 1 H), 6.97 (ddd, J = 11.2, 8.7, 2.5 Hz, 1 H), 6.78 (d, J = 16.0 Hz, 1 H), 1.79 (s, 6 H) ppm. ^{1}H NMR (500 MHz, [D_6]-DMSO, T = 100 °C): δ = 8.78 (d, J = 5.1 Hz, 1 H), 8.15–8.00 (m, 3 H), 7.94 (d, J = 4.0 Hz, 1 H), 7.88 (d, J = 4 Hz, 1 H), 7.73 (dd, J = 5.2, 1.7 Hz, 1 H), 7.30 (ddd, J = 8.2, 6.3, 1.8 Hz, 1 H), 7.22 (ddd, J = 8.7, 6.2, 2.5 Hz, 1 H), 6.98 (d, J = 16.0 Hz, 1 H), 1.83 (s, 6 H) ppm. ^{13}C NMR (125 MHz, [D_6]DMSO, T = 100 °C): δ = 176.89 (1 CN), 174.94 (2 CN), 163.34 (dd, J_{CF} = 250.5, 12.0 Hz, 1 CF), 160.69 (J_{CF} = 251.4, 12.0 Hz, 1 CF), 153.74 (1 C), 151.15 (d, J_{CF} = 2.1 Hz, 1 C), 147.13 (1 C), 141.94 (1 C), 140.91 (1 C), 139.58 (1 CH), 136.36 (1 CH), 132.83 (dd, J_{CF} = 4.3, 9.7 Hz, 1 CH), 129.02 (CH), 120.29 (dd, J_{CF} = 11.4, 3.9 Hz, 1 C), 119.43 (1 CH), 115.44 (1 CH), 112.72 (1 C), 112.40 (dd, J_{CF} = 21.0, 3.4 Hz, CH), 111.98 (1 C), 111.04 (1 C), 104.93 (t, J_{CF} = 26.3 Hz, 1 CH), 99.72 (1 C), 99.42 (1 C), 25.82 (1 CH_3) ppm. HRMS (ESI): calcd. for $C_{27}H_{17}F_2N_4OS$ [M + H]$^+$ 483.10911; found 483.10982; calcd. for $C_{27}H_{16}F_2N_4NaOS$ [M + Na]$^+$ 505.09106; found 505.09004.

Electrochemical Characterization: Samples submitted to electrochemical characterization were dissolved (10^{-4} M) in a 0.1 M solution of tetrabutylammonium perchlorate (Fluka, electrochemical grade, ≥99.0%) in anhydrous acetonitrile (Aldrich, 99.8%) as the supporting electrolyte. Differential pulsed voltammetry (DPV) and cyclic voltammetry (CV) were carried out at a scan rate of 20 and 50 mV s^{-1}, respectively, by using a PARSTA2273 potentiostat in a single-chamber three-electrode electrochemical cell in a glovebox filled with argon ([O_2] ≤ 1 ppm). The working, counter, and pseudo-reference electrodes were an Au pin, a Pt flag, and an Ag/AgCl wire, respectively. The working electrode discs were well polished with a 0.1 μm alumina suspension, sonicated for 15 min in deionized water, and washed with 2-propanol before use. The Ag/AgCl pseudo-reference electrode was calibrated by adding ferrocene (0.1 mM) to the test solution.

Computational Investigations: All the calculations were performed by using the GAUSSIAN 03 program package.[26] We optimized the molecular structures of **1a**–**8a** in vacuo by using the B3LYP exchange-correlation functional[27] and a 3-21G* basis set.[28] TDDFT calculations of the lowest singlet–singlet excitations were performed for all the considered compounds by using the B3LYP xc functional, the 6-31G* basis set,[29] and the CH_2Cl_2 solution effects were included by using the PCM nonequilibrium version[30] as implemented in G03.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of compounds **2a**–**8a** and **2b**–**8b** and DPV scans of compounds **1a**–**8a** and **1b**–**8b**.

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