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Structural Effects on the Electronic Properties of Extended Fused-Ring Thieno[3,4-*b*]pyrazine Analogues

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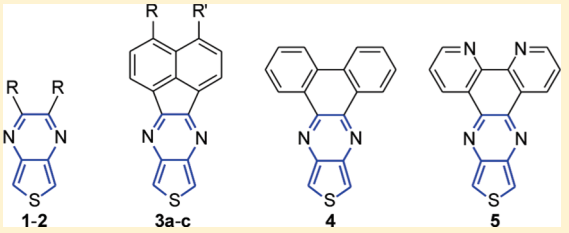
Supporting Information

ABSTRACT: The synthesis and characterization of the extended thieno[3,4-*b*]pyrazine analogues acenaphtho[1,2-*b*]thieno[3,4-*e*]-pyrazine (**3a**), 3,4-dibromoacenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine (**3b**), 3-octylacenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine (**3c**), dibenzo[*f*,*h*]thieno[3,4-*b*]quinoxaline (**4**), and thieno[3′,4′:5,6]pyrazino[2,3-*f*]-[1,10]phenanthroline (**5**) are reported. Comparison of structural, electrochemical, and photophysical properties to those of simple thieno[3,4-*b*]pyrazines are provided in order to provide structure−function relationships within this series of compounds.



The 2,3-disubstituted thieno[3,4-*b*]pyrazines (Chart 1, **1** and **2**) have been shown to be excellent building blocks for the production of low band gap conjugated polymers.[1−9] Poly(2,3-dialkylthieno[3,4-*b*]pyrazine)s have exhibited band gaps as low as ∼0.7 eV,[2−6] and thieno[3,4-*b*]pyrazine-based copolymers have produced band gaps ranging from 0.36 to 2.1 eV.[7−9] Control of the band gap is an important factor in the production of technologically useful materials, and the application of thieno[3,4-*b*]pyrazines has been one of the more successful approaches to this goal.[1]

While the majority of new thieno[3,4-*b*]pyrazines utilize modified functionality at the 2- and 3-positions, a number of extended fused-ring analogues (Chart 1, **3**−**5**) have also been recently applied as potentially improved building blocks.[6c,9b,10−15] Such extended fused-ring analogues have included acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazines[6c,10−12] (**3**), dibenzo[*f*,*h*]thieno[3,4-*b*]quinoxalines[9b,12−16] (**4**), thieno[3′,4′:5,6]pyrazino[2,3-*f*][1,10]phenanthroline[16,17] (**5**), and others.[12b,18] As these studies have focused on the resulting materials, full characterization of the monomeric heterocycles has not been a priority and little effort has been made to correlate the effect of chemical structure on the electronic and optical properties. Collected herein is the complete characterization of compounds **3**−**5**, along with comparison to the simple thieno[3,4-*b*]pyrazines **1** and **2**. The goal is to provide a better understanding of the structure−function relationships in such thieno[3,4-*b*]pyrazines so that they may be better applied to the production of advanced materials.

Synthesis. As with typical 2,3-dialkyl or 2,3-diaryl-thieno[3,4-*b*]pyrazines,[19] compounds **1**−**5** are all produced by the reaction of 3,4-diaminothiophene[20] and an α-dione via a double condensation process (Scheme 1). While the condensation of simple thieno[3,4-*b*]pyrazines can be carried out at room temperature over a period of hours or even minutes at higher temperatures, the generation of the extended fused-ring analogues occurs much more slowly and requires several hours at elevated temperatures. As 3,4-diaminothiophene can be isolated in good yield from the reduction of 2,5-dibromo-3,4-dinitrothiophene[21] and unsubstituted diones such as 1,2-acenaphthenequinone or 9,10-phenanthrenequinone are commercially available, these species are relatively simple to produce for applications to organic materials.

Additional synthesis is required, however, to generate functionalized derivatives, which are important for the generation of processable materials, as well as additional tuning of the corresponding electronic and optical properties.[20] In order to generate the halogenated **3b** as a precursor for families of functionalized acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazines, the production of dione **6** was investigated (Scheme 2). Although previous methods[22] had heated acenaphthenequinone in a bromine slurry to generate **6**, attempts to reproduce these methods revealed that bromination was not sufficiently selective. Attempts to improve selectivity using NBS resulted in no reaction with the applied conditions. Dione **6** was successfully produced from acenaphthene[23] (Scheme 2), but unfortunately both **6** and **3b** exhibited very low solubility, thus severely limiting the application of **3b**.

An alternate approach[24] focused on enhancing the solubility of the initial naphthalene in hopes to simplify purification for the subsequent steps. Thus 1-octylnapthalene was produced and then subjected to Friedel−Crafts acylation, forming mixtures of dione **7** and 1,2-bis(4-octylnaphthalene-1-yl)ethane-1,2-dione (**8**). Increasing the yield of **7** proved to be difficult because the

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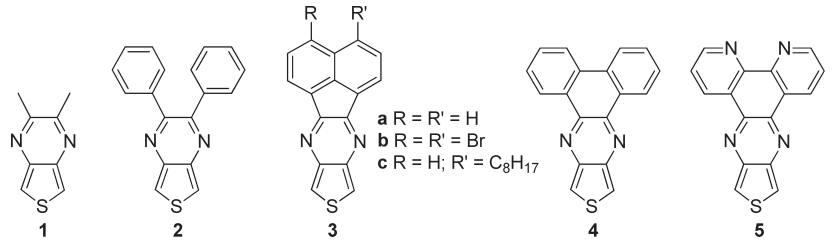
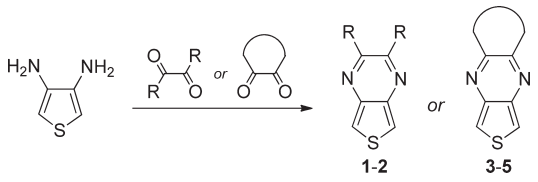
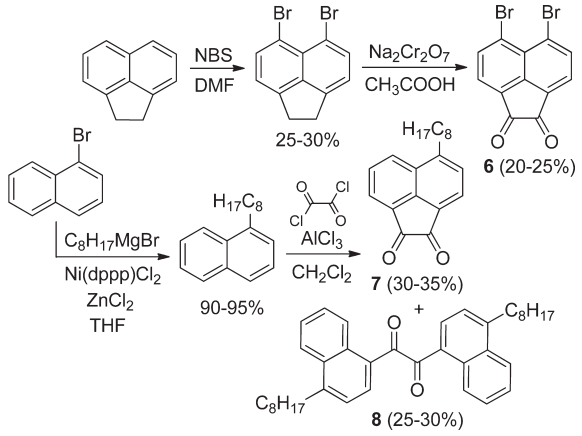
Chart 1. Thieno[3,4-*b*]pyrazines and Extended Fused-Ring Analogues



Scheme 1. Synthesis of Thieno[3,4-*b*]pyrazines and Extended Fused-Ring Analogues



Scheme 2. Synthesis of Fused-Ring Dione Precursors



electrophilic nature of the oxalyl chloride/$AlCl_3$ complex resulted in enhanced reactivity *para* to the octyl substituent, thus allowing the formation of the byproduct **8** even though **7** would appear to be energetically more favorable. Some improvement in yield was accomplished, however, by the slow addition of a dilute 1-octylnapthalene solution to the reaction mixture. The condensation of **7** with 3,4-diaminothiophene successfully allowed the production of the first known alkylacenaptho[1,2-*b*]thieno[3,4-*e*]pyrazine **3c**. However, although **3c** proved to be more soluble then **3a**, it did not result in substantial increases in solubility and more soluble analogues are still needed.

Crystallography. X-ray quality crystals of **3a** were grown by slow evaporation of hexane/ethyl acetate solutions, and selected bond angles are given in Table 1, along with values for **1**, acenaphthylene, thiophene, and pyrazine. The thieno[3,4-*b*]-pyrazine portion of **3a** agrees well with the previous structure of **1**,[19] with minor elongation of several bonds, but no significant differences. Thus as with all previously reported thieno[3,4-*b*] pyrazine structures,[19,20] comparison with the gas phase distances of thiophene and pyrazine[25] shows that the fused thiophene ring is nearly identical to the parent thiophene, while the fused pyrazine shows some bond fixation.[19] Comparison of the acenaptho portion of **3a** with acenaphthylene,[26] however, reveals significant differences. The exterior bonds C(8)−C(9) and C(10)−C(11) of **3a** exhibit shortening, while the interior bonds C(7)−C(12) and C(11)−C(12) show elongation. As a result, the average bond alternation in **3a** is significantly reduced, indicative of enhanced delocalization and conjugation within the extended fused-ring system.

Electrochemistry. Electrochemical data of **1**−**5** are given in Table 2, and cyclic voltammograms of **2**−**5** are shown in Figure 1. As previously reported, thieno[3,4-*b*]pyrazines exhibit an irreversible thiophene-based oxidation and a quasireversible pyrazine-based reduction.[19] Typical of thiophene derivatives, the irreversible nature of the oxidation results from the formation and rapid coupling ($\tau < 10^{-5}$ s) of thiophene-based radical cations, thus leading to oligomeric and polymeric products.[27,28] Unlike typical thiophenes, however, thieno[3,4-*b*]pyrazine oxidations occur at much lower potentials and agree well with the oxidation potentials of other analogous fused-ring thiophene systems (1.1−1.5 V).[29] Comparing **1** to its diphenyl analogue **2** shows that the additional conjugation provided by the phenyl groups results in a shift of both oxidation and reduction to lower potentials. The greater effect on the reduction has been shown to be due to the direct placement of the functional groups on the pyrazine ring, which contributes more significantly to the LUMO than the HOMO.[20]

Analogue **3a** can be thought of as thieno[3,4-*b*]pyrazine **2** in which the two phenyl groups have been fused to generate the acenaphthylene group. As expected, this provides greater π-overlap and a greater shift of the redox processes to lower potentials. As the acenaphthylene unit does not exhibit oxidation below 2 V and calculations of the radical cation of **3a** predict the highest spin density at the thiophene α-positions,[10] the oxidation of **3a** is believed to be thiophene-based and analogous to that of thieno[3,4-*b*]pyrazines. The functionalized analogues **3b** and **3c** give shifts consistent with previously reported functional group effects on thieno[3,4-*b*]pyrazines.[20] For **3b**, the electron-withdrawing bromo functionalities result in stabilization of both the HOMO and LUMO, thus lowering the potential for reduction while increasing the potential for oxidation. In contrast, the octyl group of **3c** is weakly electron-donating and causes a slight destabilization of HOMO and LUMO with corresponding shifts in potential. As previously illustrated, the electronic nature of the functional groups affects LUMO levels to a greater extent than HOMO levels.

Analogue **4** can be thought of as thieno[3,4-*b*]pyrazine **2** in which the phenyl groups have been joined via a covalent bond, rather than ring fusion. This results in another planar system with an additional two π-electrons in comparison to **3a**. As a result, **4**

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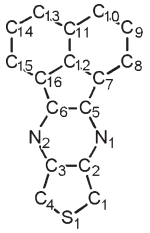
Table 1. Experimental Bond Lengths of Acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine (3a), 2,3-Dimethylthieno[3,4-*b*]pyrazine (1), Acenaphthylene, Thiophene, and Pyrazine



bond	3a	1[a]	acenaphthylene[b]	thiophene[c]	pyrazine[c]
S(1)−C(1)	1.706(2)	1.692(2)		1.714	
C(1)−C(2)	1.377(2)	1.372(3)		1.370	
C(2)−C(3)	1.443(2)	1.427(3)		1.423	1.403
C(2)−N(1)	1.389(2)	1.377(2)			1.339
N(1)−C(5)	1.309(2)	1.307(2)			1.339
C(5)−C(6)	1.473(2)	1.460(3)	1.5024(1)		1.403
C(5)−C(7)	1.473(2)	1.496(3)	1.489(2)		
C(7)−C(8)	1.374(2)		1.3238(2)		
C(7)−C(12)	1.420(2)		1.3505(4)		
C(8)−C(9)	1.416(2)		1.556(2)		
C(9)−C(10)	1.377(2)		1.3866(5)		
C(10)−C(11)	1.420(3)		1.5645(6)		
C(11)−C(12)	1.400(2)		1.198(1)		

[a] Reference 19. [b] Reference 26. [c] Reference 25.

exhibits even further decreases in potentials for oxidation and reduction, providing the lowest potential of oxidation of the series (ca. 1 V). While analogue **5** is isostructural to **4**, the additional nitrogens significantly modify the electronics to stabilize the LUMO of **5**, resulting in a reduction potential of −1.27 V. However, the electron-withdrawing nature of the phenanthroline unit also significantly stabilized the HOMO as well, pushing the potential of oxidation to 1.45 V.

Spectroscopy. Representative absorption spectra of **2**−**5** are shown in Figure 2, and photophysical data of **1**−**5** are given Table 3. Previous photophysical studies on 2,3-dialkylthieno[3,4-*b*]pyrazines have shown four electronic transitions. The lowest energy transition at ∼350 nm is a broad charge transfer (CT) band resulting from a transition between a predominately thiophene-localized HOMO and a LUMO of greater pyrazine contribution.[30] A second transition near 300 nm consists of multiple bands of close energetic spacing, which are assigned as various vibrational components of the same $\pi\rightarrow\pi^*$ electronic transition. Two significantly stronger $\pi\rightarrow\pi^*$ transitions are also exhibited at higher energy. The phenyl groups in **2** result in a red shift of the simple $\pi\rightarrow\pi^*$ transitions, which now overlap with the low energy CT transition. This overlap, combined with the rotational freedom of the phenyl groups, results in two broad bands, with the low energy transition centered at 340 nm.

In comparison to **2**, the absorption onset of the fused analogue **3a** is slightly red-shifted, exhibiting a weak and very broad CT transition at 375 nm. The remaining higher energy transitions of **3a** are fairly sharp, presumably due to its rigid structure, and the transition near 320 nm exhibits significant intensity.

Table 2. Electrochemical Data for Extended Thieno[3,4-*b*]pyrazine Analogues[a]

compound	E_{pa} (V)	$E_{1/2}$ (V)	ΔE (mV)	E_{HOMO}[b]	E_{LUMO}[b]
1	1.33	−2.04	90	6.38	3.01
2	1.26	−1.78	75	6.33	3.34
3a	1.18	−1.67	60	6.23	3.38
3b	1.47	−1.25	150	6.52	3.80
3c	1.15	−1.75	90	6.20	3.30
4	0.98	−1.51	90	6.03	3.54
5	1.45	−1.27	110	6.50	3.78

[a] Potentials measured vs Ag/Ag^+ using 0.1 M $TBAPF_6$ in CH_3CN. [b] Determined vs ferrocene (5.1 eV vs vacuum).

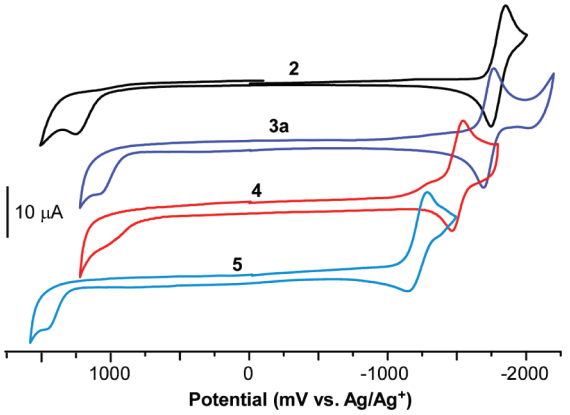


Figure 1. Comparative cyclic voltammograms in CH_3CN.

The strength of this transition in comparison to the rest of the series suggests that this may be due to multiple overlapping transitions. In fact, both **4** and **5** exhibit a great many more absorption bands than either **3a** or **3c**. The addition of the octyl side chain in **3c** has very little effect on the absorption properties, as previously seen for simple thieno-[3,4-*b*]pyrazines.[30]

Consistent with the HOMO and LUMO energies determined electrochemically (Table 2), both **4** and **5** exhibit a significant red-shift in comparison to **3a**. Interestingly, while the CT bands of **4** and **5** are of similar energy with nearly identical absorption onsets, the higher energy $\pi-\pi^*$ transitions of the visible region in **5** are significantly blue-shifted in comparison to **4**. For those transitions below 325 nm, however, we see the opposite trend, with those of **5** red-shifted in comparison to **4**. It should be mentioned that absorption data for **5** in chloroform were previously reported.[17] While only two transitions were reported (368 and 307 nm), they do correlate closely to two of the multiple transitions given here. The corresponding extinction coefficient given for the lower energy transition, however, was nearly twice that given in the current study (25600 vs 13800 M^{-1} cm^{-1}). The cause for this difference is uncertain as it has been previously shown that there are little to no solvent effects on thieno[3,4-*b*]pyrazine absorption spectra.[30] In addition, comparison of the spectra of **5** in both CH_3CN and $CHCl_3$ revealed no significant differences with nearly identical energies and extinction coefficients in both solvents.

All species studied exhibited a single broad emission consistent with that previously reported for **1** and **2**.[30] In comparison to **2**,

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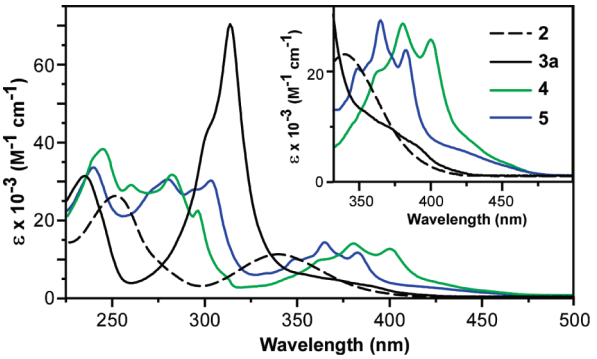

Figure 2. UV−vis spectra of extended thieno[3,4-*b*]pyrazine analogues in CH_3CN.

Table 3. Photophysical Data for Extended Thieno[3,4-*b*]-pyrazine Analogues[a]

compound	λ_{max}^{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{max}^{em} (nm)	Φ_{em}[b]	τ (ns)
1	233	18300	429 (sh)	2.3×10^{-3}	
	292(sh)	7300	468		
	304	11000			
	314	10600			
	350	2400			
2	252	26000	478	3.3×10^{-3}	0.21
	340	10500			
3a	240	31100	479	5.5×10^{-3}	0.42
	303(sh)	42900			
	317	69800			
	375	4300			
3c	241	31000	479	3.5×10^{-3}	0.45
	309(sh)	42700			
	321	69500			
	376	4200			
4	244	37100	519	1.5×10^{-2}	0.62
	281	30600			
	296	21600			
	362(sh)	9200			
	380	13200			
	400	11800			
	426	2400			
5	240	32900	529	1.4×10^{-2}	0.45
	280	30000			
	304	29700			
	348	9600			
	365	13800			
	383	11300			
	418	2500			

[a] All spectra obtained from room temperature CH_3CN solutions using matched, 1 cm quartz cells. (sh) = shoulder. [b] ±0.0005.

the emission of **3a** is essentially identical in energy, although with a slightly enhanced quantum efficiency. The quantum efficiency of the octyl-functionalized **3c** is reduced in comparison to **3a**, most likely due to an increase in high frequency modes as a result of the side chain. The emission maxima of the remaining species **4** and **5** are both significantly red-shifted and exhibit quantum efficiencies essentially twice that of **3a**. As can be seen in Table 3, the emission lifetimes of all fused-ring analogues are at least twice that of **2**, with compound **4** exhibiting the longest lifetime at 0.62 ns.

Conclusion. In conclusion, the synthesis and full characterization of a series of extended thieno[3,4-*b*]pyrazines has been reported. Careful comparison of the structural, electrochemical, and photophysical properties of analogues **3**−**5** with those of previously studied thieno[3,4-*b*]pyrazines provides clear relationships between the chemical structures of these species and their resulting electronic properties. Such increased understanding of such factors should allow the application of specific design criteria when utilizing these building blocks in new conjugated materials. For example, in analogous conjugated polymeric materials, the application of the fused-ring analogues should result in lower band gaps than conventional thieno[3,4-*b*]-pyrazines, with **4** and **5** giving the lowest band gaps. While analogous materials of **4** and **5** should exhibit similar band gaps, materials of **5** should exhibit deeper HOMOs and LUMOs in comparison to those of **4**.

EXPERIMENTAL SECTION

Materials and Instrumentation. 3,4-Diaminothiophene,[20] 2,3-dimethylthieno[3,4-*b*]pyrazine,[19] and 2,3-diphenylthieno[3,4-*b*]pyrazine,[19] were all prepared as previously reported. THF was distilled from sodium/benzophenone prior to use. Chromatographic separations were performed using standard column methods with silica gel (230−400 mesh). Unless otherwise stated, all other materials were reagent grade and used without further purification, and all reactions were performed under nitrogen atmosphere using oven-dried glassware. Melting points are corrected and were obtained using a heating block with a thermocouple connected to a digital thermometer. Unless otherwise stated, NMR spectra were obtained in $CDCl_3$ on a 400 MHz spectrometer and referenced to the chloroform signal. Electrochemical measurements were performed on an EC Epsilon potentiostat using a Pt disk working electrode and a Pt wire counter electrode. Solutions consisted of 0.1 M $TBAPF_6$ in CH_3CN and were sparged with argon for 20 min prior to data collection and blanketed with argon during the experiment. All potentials are referenced to Ag/Ag^+ reference (0.1 M $AgNO_3$/0.1 M $TBAPF_6$ in CH_3CN; 0.320 V vs SCE).[31] UV−vis spectra were measured on a dual beam scanning spectrophotometer using samples prepared as dilute solutions in 1 cm quartz cuvettes. Emission spectroscopy was performed on a Spex Fluorolog spectrofluorometer utilizing a Hamamatsu R928 photomultiplier tube. All samples were measured as dilute solutions ($<10^{-5}$ M) at room temperature. Quantum yields were determined using secondary methods with 9,10-diphenylanthracene as the reference.[32,33]

5,6-Dibromoacenaphthene. Modified from previously reported procedures.[23,35] Acenaphthene (77.1 g, 0.50 mol) and *N*-bromosuccinimide (222.5 g, 1.25 mol) were combined in DMF (500 mL) and stirred overnight at 30−32 °C. The reaction was then cooled to room temperature, filtered to obtain the crude product, and purified via recrystallization from hexanes (25−30% yield). Mp 169−171 °C (lit.[23] 168−171 °C). ^{1}H NMR: δ 7.78 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 7.6 Hz, 2H), 3.30 (s, 4H). ^{13}C NMR: δ 147.3, 142.16, 136.0, 128.0, 121.1, 114.6, 30.3.

5,6-Dibromo-1,2-acenaphthenequinone (6). Modified from a previously reported procedure.[23] A mixture of 5,6-dibromoacenapthene (3.2 g, 10 mmol) and $Na_2Cr_2O_7$ (17.5 g, 58 mmol) in acetic acid (175 mL) was stirred at 80 °C for 2 h. The solution was then diluted with 500 mL of water and filtered, and the resulting precipitate was washed with 30 mL of boiling aqueous 6% Na_2CO_3. The crude material

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was then dissolved in hot chlorobenzene (500 mL at 50−60 °C), 40% aqueous $NaHSO_3$ (20 mL) was added, and the mixture stirred for 1 h. The precipitate was then collected by filtration, washed first with hot chlorobenzene (2 × 50 mL) and then boiling 10% aqueous HCl (25 mL). The resulting solid was then recrystallized from chlorobenzene to give **6** as yellow crystals (20−25% yield). Mp 326−328 °C (lit.[23] 326−328 °C). ^{1}H NMR: δ 8.25 (d, J = 7.5 Hz, 2 H), 7.92 (d, J = 7.5 Hz, 2 H). ^{1}H NMR data agrees well with previously reported values.[23]

1-Octylnaphthalene. Modified from a previously reported procedure.[24] Octylmagnesium bromide (100 mmol) was added to Ni(dppp)Cl_2 (0.4 g, 1 mol %) and zinc chloride (10.2 g, 75 mmol) in THF (100 mL) and allowed to stir for 30 min. 1-Bromonaphthalene (10.4 mL, 75 mmol) was then slowly added, and the mixture was heated at reflux overnight. Saturated aqueous ammonium chloride (150 mL) was then added, and the solution was extracted with hexanes (3 × 50 mL). The combined organic fractions were then washed with H_2O (100 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated via rotary evaporation. The resulting oil was diluted with hexanes (10 mL) and purified by column chromatography (hexanes) to give a colorless oil (90−95% yield). ^{1}H NMR: δ 8.09 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.52 (m, 2H), 7.43 (dd, J = 8.0 Hz, 6.8 Hz, 1H), 7.36 (d, J = 6.8 Hz, 1H), 3.10 (t, J = 7.2 Hz, 2H), 1.79 (p, J = 7.2 Hz, 2H), 1.48 (m), 1.34 (m), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR: δ 139.3, 134.1, 132.2, 129.0, 126.6, 126.1, 125.8, 125.7, 125.6, 124.2, 33.4, 32.2, 31.1, 30.1, 29.8, 29.6, 22.9, 14.4.

5-Octylacenaphthylene-1,2-dione (7). Modified from a previously reported procedure.[24] Oxalyl chloride (6.47 g, 50 mmol) was added to a stirred suspension of $AlCl_3$ (13.3 g, 100 mmol) in 300 mL of CH_2Cl_2 at −5 °C. 1-Octylnaphthalene (12.02 g, 50 mmol) in 100 mL of CH_2Cl_2 was then added dropwise, and the mixture was allowed to stir for an additional 5 h (below 0 °C). The reaction mixture was then poured over ice (200 g) and allowed to warm to room temperature. The resulting layers were separated. The organic layer was isolated, washed with a saturated Na_2CO_3 solution (1 × 100 mL), followed by a water wash (1 × 100 mL), and then dried with anhydrous $MgSO_4$. The mixture was filtered, concentrated via rotary evaporation, and purified by column chromatography (10% EtOAc in hexanes) to yield a yellow solid (3.74 g, 30%). Mp 131−132 °C. ^{1}H NMR: δ 8.33 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 6.8 Hz, 1H), 7.98 (d, J = 7.2 Hz, 1H), 7.80 (dd, J = 8.0 Hz, 6.8 Hz, 1H), 7.62 (d, J = 7.2 Hz, 1H), 3.16 (t, J = 7.2 Hz, 2H) 1.78 (p, J = 7.2 Hz, 2H), 1.44 (m, 2H), 1.25 (m, 8H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C NMR: δ 189.1, 187.9, 147.8, 146.4, 130.1, 129.9, 129.1, 128.1, 127.2, 126.8, 122.4, 121.7, 33.3, 32.0, 30.8, 29.9, 29.6, 29.4, 22.8, 14.3. HRMS: m/z 317.1513 $[M + Na]^+$ (calcd for $C_{20}H_{22}NaO_2$ 317.1518).

General Procedure for the Preparation of Acenaphtho[1,2-*b*]thieno[5,4-*e*]pyrazines 3a−c. Modified from previously reported procedures.[6c,10] 3,4-Diaminothiophene (0.51 g, 5.0 mmol) was dissolved in 50 mL of absolute ethanol. 1,2-Acenaphthenequinone, or its derivative **6** or **7** (5.0 mmol), was then added, and the solution was heated at reflux for 3 h. The mixture was then cooled to room temperature, diluted with 100 mL of water, and extracted with dichloromethane. The combined organic layers were dried with anhydrous Na_2SO_4, and the solvent was removed by rotary evaporation. The resulting solid product was then purified by recrystallization or column chromatography.

Acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine (3a). The crude product was dissolved in CH_2Cl_2, run through a 5 cm silica plug, and concentrated to give a yellow solid. Recrystallization from methanol gave **3a** as yellow needles (55−60% yield). Mp ∼150 °C (dec); ^{1}H NMR: δ 8.25 (dd, J = 7.2, 0.4 Hz, 2H), 8.03 (dd, J = 8.4, 0.4 Hz) 2H), 7.98 (s, 2H), 7.77 (dd, J = 8.4, 7.2 Hz, 2H). ^{13}C NMR: δ 154.5, 142.1, 138.5, 131.7, 130.4, 129.3, 128.9, 121.1, 117.8. NMR spectral data agrees well with previously reported values.[10]

3,4-Dibromoacenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine (3b). Recrystallization of the crude product in dichloromethane gave **3b** as yellow needles (15−20% yield). Mp ∼130 °C (dec). ^{1}H NMR: δ 8.21 (d, J = 7.6 Hz, 2H), 8.11 (d, J = 7.6 Hz, 2H), 8.04 (s, 2H). ^{13}C NMR spectrum not obtained due to poor solubility. Anal. Calcd for $C_{16}H_6Br_2N_2S$: C, 45.96; H, 1.45; N, 6.70. Found: C, 46.22; H, 1.31; N, 6.69.

3-Octylacenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine (3c). The crude product was purified by column chromatography (1:1 CH_2Cl_2/hexanes) to yield **3c** as a yellow solid (20−25% yield). Mp 114.5−115.7 °C (lit.[6c] 114.5−115.7 °C). ^{1}H NMR: δ 8.30 (d, J = 6.8 Hz, 1H), 8.24 (d, J = 7.2 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.82 (dd, J = 6.8, 7.2 Hz, 1H), 7.63 (d, J = 7.2 Hz, 1H) 3.19 (t, J = 7.6 Hz, 2H), 1.83 (p, J = 7.6 Hz, 2H), 1.47 (m, 2H) 1.31 (m, 8H), 0.83 (t, J = 7.2 Hz, 3H). ^{13}C NMR: 154.7, 154.4, 143.6, 142.1, 142.0, 138.0, 132.0, 129.6, 129.5, 128.4, 128.3, 126.4, 121.2, 120.7, 117.6, 117.3, 32.8, 32.1, 31.6, 30.0, 29.7, 29.5, 22.9. NMR spectral data agrees well with previously reported values.[6c]

Dibenzo[*f*,*h*]thieno[3,4-*b*]quinoxaline (4). Compound **4** was prepared and purified as for **3a** above, subsituting 9,10-phenanthrenequinone for 1,2-acenaphthenequinone (65−70% yield). Mp: ∼125 °C (dec). ^{1}H NMR: δ 9.20 (dd J = 7.2, 1.6 Hz, 2H), 8.44 (dd, J = 7.2, 0.8 Hz, 2H), 8.20 (s, 1H), 7.72 (dt, J = 7.2, 1.6, 2H), 7.66 (dt, J = 7.2, 0.8 Hz, 2 H). ^{1}H NMR spectral data agrees with previously reported values.[12]

1,10-Phenanthroline-5,6-dione (9). Modified from previously reported procedures.[34] 1,10-Phenanthroline (2.0 g, 11.1 mmol) and KBr (3.0 g, 25.2 mmol) were slowly added to concentrated H_2SO_4 (20 mL) cooled in an ice-bath, maintaining a temperature below 5 °C. Concentrated HNO_3 (10 mL) was then added dropwise to give a red solution. The mixture was stirred for 1 h and then heated to 80 °C for an additional h. The solution was allowed to cool, poured over 100 g of ice, and then carefully adjusted to pH 7 using Na_2CO_3. The neutralized solution was extracted with dichloromethane, and the combined organic layers were dried with anhydrous $MgSO_4$ and concentrated by rotary evaporation. The resulting solid was redissolved in CH_2Cl_2, run through a 5 cm silica plug, and concentrated to give an orange solid (80−85% yield). Mp 275−277 °C (lit.[26] 271−272 °C). ^{1}H NMR: δ 9.12 (d, J = 4.8 Hz, 2H), 8.50 (d, J = 8.0 Hz, 2H), 7.59 (dd, J = 8.0, 4.8 Hz, 2H). ^{13}C NMR: δ 178.9, 156.3, 153.2, 137.5, 128.3, 125.8.

Thieno[3′,4′:5,6]pyrazino[2,3-*f*][1,10]phenanthroline (5). 3,4-Diaminothiophene (0.34 g, 3.0 mmol) was dissolved in 100 mL of absolute ethanol. 1,10-Phenanthroline-5,6-dione (0.52 g, 2.4 mmol) was then added, and the solution was heated at reflux for 1 h. The mixture was then cooled to room temperature and filtered, and the isolated solid was washed with cold ethanol. The filtrate was then diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried with anhydrous Na_2SO_4, and the solvent was removed by rotary evaporation. The resulting solid was then dissolved in CH_2Cl_2, run through a 5 cm silica plug, and concentrated to give **5** as an orange solid (90−95% yield). Mp ∼140 °C (dec). ^{1}H NMR: δ 9.46 (dd J = 8.0, 2.0 Hz, 2H), 9.20 (dd, J = 4.4, 2.0 Hz, 2H), 8.29 (s, 1H), 7.72 (dd, J = 8.0, 4.4 Hz, 2H). ^{1}H NMR data agrees with previously reported values.[17] ^{1}H NMR (d_6-DMSO): δ 9.29 (dd J = 8.0, 2.0 Hz, 2H), 9.08 (dd, J = 4.4, 2.0 Hz, 2H), 8.65 (s, 1H), 7.80 (dd, J = 8.0, 4.4 Hz, 2H). ^{13}C NMR (d_6-DMSO): δ 152.9, 149.0, 142.4, 141.6, 133.7, 128.3, 125.2, 119.3. HRMS: m/z 311.0358 $[M + Na]^+$ (calcd for $C_{16}H_8N_4NaS$ 311.0362).

■ ASSOCIATED CONTENT

Supporting Information. NMR spectra for **3**−**7** and crystallographic data for **3a** including CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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