Thieno[3,4-*b*]pyrazines and Its Extended Analogs: Important Buildings Blocks for Conjugated Materials

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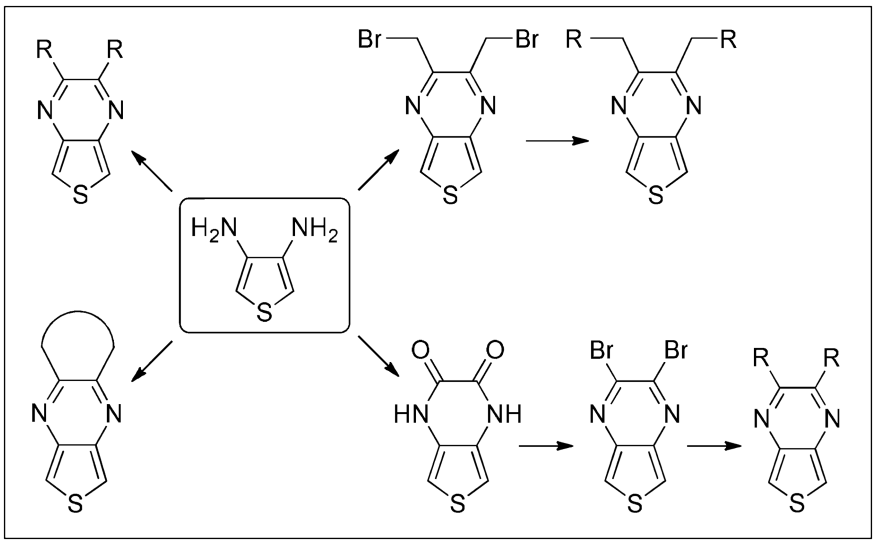

This review describes the synthesis and characterization of thieno[3,4-*b*]pyrazines and its extended fused-ring analogs as important building blocks for the production of low-band gap conjugated materials.

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Contents

1. INTRODUCTION

Fused-ring thiophenes such as the benzo[*b*]thiophenes (**1**), thieno[3,4-*b*]pyrazines (TPs), and thieno[3,4-*b*]thiophenes (**2**) (Chart 1) have been shown to be excellent building blocks for the production of reduced band gap and low-band gap conjugated organic polymers [1–3]. Such conjugated polymers have received considerable fundamental and technological interest due to their combination of electronic and optical properties of typical of inorganic semiconductors with many of the desirable properties of organic plastics, including mechanical flexibility and low production costs. This has resulted in the current growth of the field of organic electronics, with considerable effort focused on the development of technological applications such as electrochromic devices, organic photovoltaics (solar cells), organic light-emitting diodes, and field effect transistors [4,5]. As many desirable properties of conjugated polymers are dependent on the material's band gap, control of this primary characteristic is an important factor in the production of technologically useful

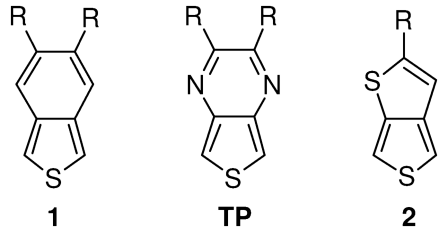


Chart 1. Fused-ring thiophenes commonly applied to low-band gap conjugated polymers.

materials, thus making such fused-ring thiophenes critical to the advancement of this growing field of materials research.

Of the various fused-ring thiophenes used in the development of conjugated polymers, TPs have been a quite popular building block and very successful in producing low-band gap materials. For example, homopolymeric poly(2,3-dialkylthieno[3,4-*b*]pyrazine)s have exhibited band gaps as low as ~0.7 eV [2,3], and the combination of various TP units with other functionalized thiophenes has produced polymeric materials with reported band gaps ranging from 0.36 to 2.1 eV [1–3]. As might be expected, the success of these materials has resulted in the discussion of their synthesis and properties in multiple reviews on low-band gap materials [1–3]. However, although the basic synthesis of TPs has been included in such reviews [1–3], the various electronic, optical, and structural properties of these heterocyclic species have not. In addition, significant advances in the preparation and scope of TPs have been reported in the recent years, making the first such review to focus solely on heterocyclic TPs timely, if not overdue. As such, the following review will strive to collect and organize all the current knowledge of TPs and its extended fused-ring analogs. However, it should be noted that while TPs are also commonly synthesized as the central unit in terthienyl species, such oligothiophenes have been included in previous reviews of thiophene-based materials [1–5], and the scope of the current review will limit itself to the monomeric TPs and their properties.

2. HISTORY

Although their application to organic electronic materials has been limited to the last couple decades, the first report of a TP dates back to 1957 [6]. This report was part of a study by Motoyama and Imoto at Osaka Prefecture University of new ring-forming reactions using the salt of 3,4-diaminothiophene (**4**), which had been obtained by the Sn/HCl reduction of 2,5-dibromo-3,4-dinitrothiophene (**3**) (Scheme 1). It was found that the reaction of this salt with benzil in a mixture of sodium acetate and acidic acid generated the new species 2,3-diphenylthieno[3,4-*b*]pyrazine (**5a**).

Further work on TPs was not reported until 1981 when Binder *et al*. became interested in the potential antibacterial properties of the *N*-oxides of thienopyrazines [7]. Using conditions essentially identical to those previously reported by Motoyama and Imoto, they substituted benzil with 2,3-butadione to generate the analogous 2,3-dimethylthieno[3,4-*b*]pyrazine (**6b**). Further reaction of **6b** with peroxoacids generated both the monoxide and dioxide species, which unfortunately did not exhibit any significant antibacterial activity.

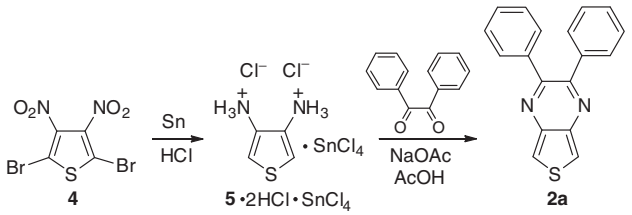
The following year, Outurquin and Paulmier [8] revisited the ring formation reactions of **4**, which they first isolated as the free base by treatment of the initially isolated hexachlorostannate salt with Na_2CO_3. The diamine **4** was then condensed with the corresponding α-dione in ethanol. In addition to **5a** and **6b**, they reported the first synthesis of the unfunctionalized parent **6a** by condensing **4** with glyoxal as well as the first asymmetrical 2-substituted TPs (where substituent = methyl or phenyl) [9]. The methods of Outurquin and Paulmier then remained the standard for the preparation of TPs for the next 20 years. The first application of these fused-ring heterocyclic systems to conjugated materials was not reported until 1992, when Pomerantz *et al*. [10,11] successfully produced the low-band gap polymer poly(2,3-dihexylthieno[3,4-*b*]pyrazine).

3. SYNTHESIS OF THIENO[3,4-*B*]PYRAZINES

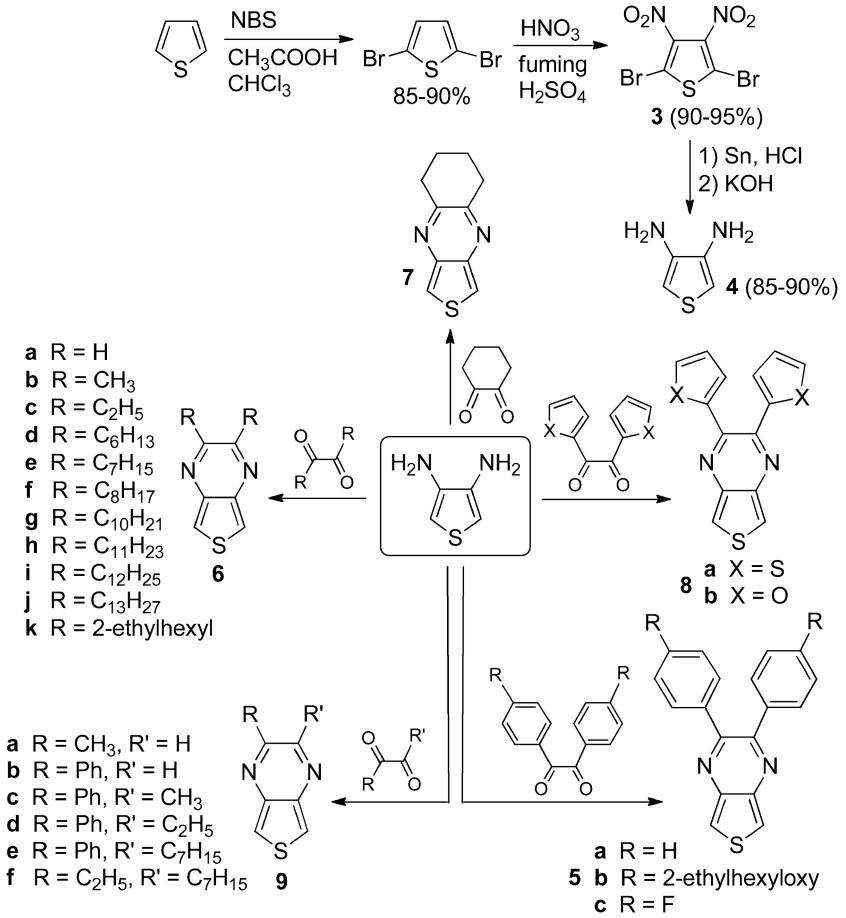
The majority of thieno[3,4-*b*]pyrazines (TPs) are produced using the same general route as published by Outurquin and Paulmier in 1982 [8,9]. As outlined in Scheme 2, TPs can be prepared from thiophene in four steps with high overall yields. This has resulted in the preparation of a wide variety of TPs, from the unfunctionalized parent [9,12], to a number of 2,3-dialkylthieno[3,4-*b*]pyrazines [7,9–16] and 2,3-diarylthieno[3,4-*b*]pyrazines [6,9,12,14,15,17,18], and even several asymmetrically substituted examples [9,13,15].

Although the general route outlined in Scheme 2 has not really changed since the early 1980s, the methods used to generate each of the intermediates have been significantly improved and optimized over the years to result in the modern efficient generation of TPs. The most important of these modifications has been improved methods for the

Scheme 1. Initial synthesis of a thieno[3,4-*b*]pyrazines.



Scheme 2. Conventional synthesis of a thieno[3,4-*b*]pyrazines.



generation of the critical intermediate **3**. Its preparation from the conventional nitration of 2,5-dibromothiophene was first reported by Kreis in 1884 [19], but the most commonly applied methods were later reported by Mozingo *et al*. in 1945 [20]. The use of fuming acids in the methods reported by Mozingo *et al*. and a greater control of the temperature resulted in improved yields for **3**, but still only 30%. Rasmussen and coworkers [12] later found that maximum yields could be increased to 45–50% by extending the reaction time, but the generation of **3** was still a limiting factor for the efficient preparation of TPs.

Rasmussen and Wen [21] returned to study the nitration of 2,5-dibromothiophene in greater detail in 2007. It was found that a complication in the process was the presence of nitrous acid, which can lead to nitrosation of the thiophene, resulting in decomposition via either ring-opening or oxidation of the ring. More critically, it was found that the order and method of acid addition played a large role in the nitration process and by maintaining a large excess of fuming H_2SO_4 in comparison with added HNO_3, the equilibria resulting in nitrosation can be significantly reduced to result in enhanced nitration. Thus, the addition of HNO_3 to sulfuric acid solutions of 2,5-dibromothiophene resulted in consistent yields of 90–95%. In addition, the new methods no longer required the use of fuming HNO_3 and simple purification by recrystallization in MeOH yields **3** as a white solid.

The reduction of **3** to produce the free diamine **4** has also been optimized since the work of Outurquin and Paulmier [8,9], although not as significantly as the improvements to the generation of **3** as discussed earlier. One of the early difficulties was with the purification of the isolated diammonium salt of **4**, which used acetone and ether washes. However, it was found that if the salt was not adequately washed first with ether, acetone would react with an unknown remaining species causing decomposition of the desired product. Rasmussen and coworkers [12] were able to remove this complication by replacing the acetone wash with acetonitrile, which removed the necessary impurities without the unwanted reactivity that resulted in decomposition. Analysis of the resulting purified salt also revealed another interesting complication. Although all previous reports had described this as the hexachlorostannate salt [6–9], elemental analysis of the more highly purified

material did not agree with this assertion. Instead, the data was found to be more consistent with a combination of $SnCl_6^{2-}$ and Cl^- counterions, with an overall composition of $[\mathbf{4}\cdot 2H^+]_x[SnCl_6^{2-}]_{(x-1/2y)}[Cl^-]_y$ [12]. As analysis of multiple samples showed that the exact ratio of counterions was not constant, accurate molar quantities could not be determined from the mass of the stable salt, requiring isolation of the more reactive diamine **4** to determine specific molar quantities.

More recently, Rasmussen and coworkers [22] reported additional modifications to the preparation of **4**, the most significant of which was the grinding of the crystalline **3** before the treatment with Sn and HCl. The smaller particle size of **3** enhances the efficiency of the reduction process and results in higher yields. In addition, it was found that the use of KOH for the neutralization of the resulting salt provided the most efficient isolation of the free diamine **4**. The combination of these effects resulted in an increase in yield to 85–90%.

The final double condensation of **4** with the desired α-dione to generate the final TP has been investigated under multiple conditions, including the effect of acid, temperature, and heating method [6,7,9,12,17]. Representative conditions and corresponding yields of **5a** and **6b** are given in Table 1. As can be seen, the addition of acid is not required and does not seem to have a significant effect on the resulting yield. One particular issue of TPs is their ease of oxidation ($E_{pa} \sim 1.35$ V vs. Ag/Ag^+ for dialkyl TPs [12], see Section 6 for further discussion), resulting in coupling to form oligomeric and polymeric species. As these processes are enhanced at higher temperatures, it is not surprising to observe polymeric byproducts when these condensation processes are carried out at higher temperatures. Rasmussen and coworkers [12] showed that polymerization could be reduced by lowering the temperature, resulting in efficient production of TPs at room temperature. However, as can be seen from Table 1, the diaryl species require increased temperatures to achieve higher yields.

Lindsley and coworkers [17] also investigated the production of diaryl-TPs via microwave-assisted methods. As with the room temperature conditions, these methods produced the TPs without polymerization byproducts. In addition, the methods only required very short reaction times while resulting in yields comparable to the previously reported methods. Although the authors stated that their methods represented the best method for the production of TPs, the only real improvement is in the reduction of reaction time. More importantly, only the more stable diaryl species were investigated, and the efficiency of these methods for the general preparation of TPs is unknown.

One significant limitation of the conventional synthesis shown in Scheme 2 is that the choice of functional groups is dependent on the corresponding dione used. As a consequence, this limits functionality to either alkyl or aryl groups, resulting in a very narrow range of electronic variance within the family of TPs and restricting the extent of possible tuning available in the application of these fused-ring units to the production of low-band gap materials. A solution to this limitation was reported by Rasmussen and coworkers in 2008 [22], with the synthesis of 2,3-dihalothieno[3,4-*b*]pyrazines as shown in Scheme 3.

These methods use thieno[3,4-*b*]pyrazine-2,3(1H,4H)-dione (**10**), which had been previously reported by both Imoto [6] and Paulmier [9], and can be produced through condensation of **4** and with diethyl oxalate. The treatment of **10** with PBr_5 or PCl_5 can then generate the dihaloTPs **11** and **12** in a manner similar to that previously demonstrated for the preparation of 2,3-dihaloquinoxalines [22]. Because of the increased reactivity of TPs in comparison with quinoxalines, modified conditions were required in order to inhibit polymerization of the desired TP products. Most notably was the move from solventless conditions to the use of a high boiling solvent. Further modifications included the addition of base and halide salt to control various equilibria involved and to remove haloacid byproducts generated during the process. Although the dichloro-derivative **12** was also produced, the corresponding yield was very low even under the optimized conditions developed for the production of **11**. It was believed that this is due to a reduced reaction rate in the case of PCl_5, thus resulting in much greater thermal decomposition of **12** during the reaction [22]. The availability of **11** now allowed the production of

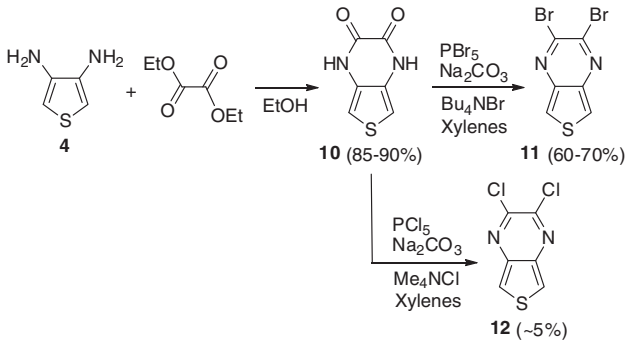
Table 1

Experimental conditions and resulting yields for the production of **5a** and **6b**.

TP	Solvent	Acid	Temperature	Time	Yield (%)	Reference
5a	AcOH	AcOH/NaOAc	reflux (~118°C)	30 min	75[a]	6
5a	Ethanol	None	reflux (~78.5°C)	15 min	70	9
5a	Ethanol	None	room temperature	3 h	37	15
5a	Methanol	AcOH	60°C (microwave)	5 min	72	17
6b	AcOH	AcOH/NaOAc	reflux (~118°C)	30 min	85.5[a]	7
6b	Ethanol	None	reflux (~78.5°C)	15 min	60	9
6b	Ethanol	None	room temperature	3 h	86	15

[a]As these yields are based on the hexachorostannate salt of **4**, rather than the isolated free base, these entries would be overestimated.

Scheme 3. Synthesis of a 2,3-dihalothieno[3,4-*b*]pyrazines.



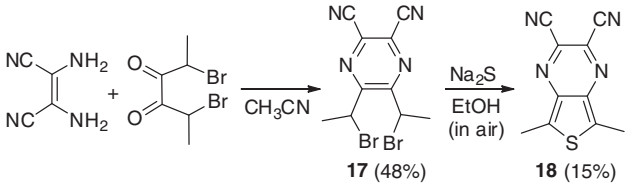
a diverse number of new TPs (Scheme 4), all of which were not previously accessible through the conventional synthesis discussed earlier.

The synthesis of the 5,7-dimethyl analog of **16** was also reported by Mo and coworkers in 2007 [23]. As shown in Scheme 5, this method started with the tetrasubstituted pyrazine **17** and used the formation of the thiophene ring via methods commonly applied to benzothiophenes and thienopyridines. This generated the resulting 2,3-dicyano-5,7-dimethylthieno[3,4-*b*]pyrazine **18** in 15% yield.

Although developing methods for the production of new TPs via the dibromo-TP **11**, Rasmussen and coworkers [22] also reported the production of the bis (bromomethyl) analog **19** via the low temperature condensation of **4** with commercially available 1,4-dibromo-2,3-butanedione (Scheme 6). The preparation of **19** using nearly identical conditions, but at slightly higher temperature (room temperature vs. 0°C), was also reported by Li and coworkers [24]. The higher temperature applied did not seem to affect the resulting yield.

As in the case of **11** earlier, ether functionalities were then efficiently introduced via simple substitution reactions

Scheme 5. Synthesis of 2,3-dicyano-5,7-dimethylthieno[3,4-*b*]pyrazine.

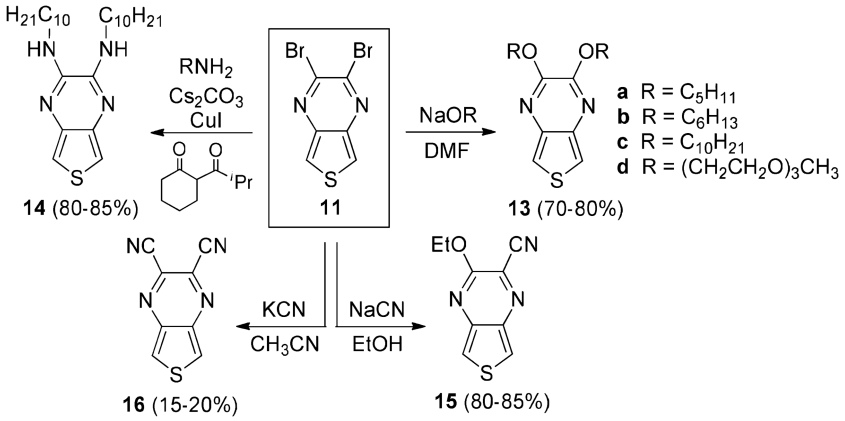


to give the derivatives **20a–d** [22]. The treatment of **19** with hydroxide, however, generated the cyclic dihydrofuran derivative **21**, rather than the dialcohol. Li and coworkers [24] also reported the generation of the phosphoester **22** by reacting **19** with $P(OEt)_3$ at high temperature (135°C) over 3 h. Considering that polymerization is observed when heating TPs at ~78.5°C for 15 min [12], the high yields obtained from these conditions are very surprising. In fact, it should be noted that in our hands, the reproduction of the reported reaction conditions failed to generate **22** and resulted only in polymerization. In contrast, **22** can be readily produced by reacting **19** with $P(OEt)_3$ over a period of 1 day at room temperature [25]. The isolated yields and NMR data of **22** produced via the low temperature route are consistent with that reported by Li and coworkers, which make it unclear if the conditions reported are reflective of the conditions applied.

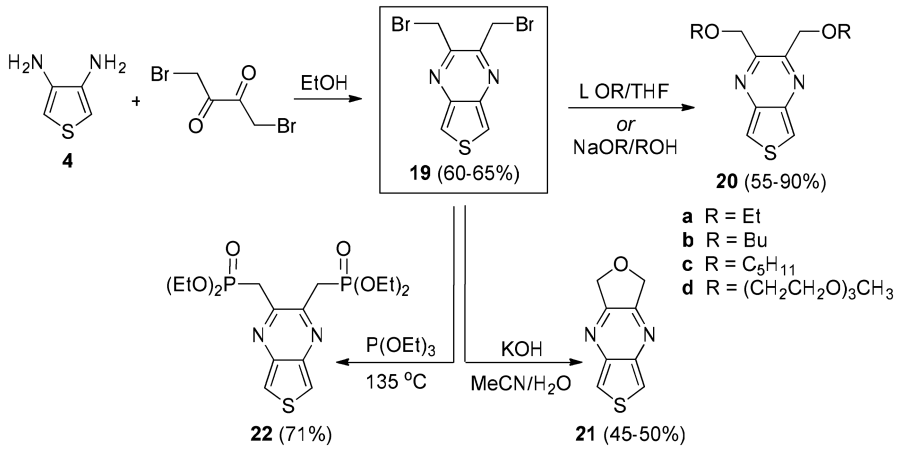
4. THIENO[3,4-*B*]PYRAZINE REACTIVITY

Not surprisingly, TPs share chemical aspects of both thiophenes and pyrazines, combining two aromatic rings with a total of three potentially basic heteroatoms. The earliest investigation of the reactivity of TPs was that of Binder *et al*. in 1981 [7], when the oxidation of the pyrazine nitrogens was studied in order to form the corresponding *N*-oxides. As shown in Scheme 7, treatment of **6b** with 3-chloroperbenzoic acid was reported to

Scheme 4. Synthesis of new 2,3-difunctionalized thieno[3,4-*b*]pyrazines from **11**.



Scheme 6. Synthesis of new 2,3-bis(bromomethyl)thieno[3,4-*b*]pyrazine **19** and related derivatives.



generate the *N*-oxide **23a**, while the stronger conditions of hydrogen peroxide in acetic acid were need to produce the *N*,*N*-dioxide **23b**. In this respect, **6b** followed the established reactivity of other pyrazines. It should be noted that the formation of *S*-oxides and *S,S*-dioxides could also be a possibility via the conditions applied, but no mention of such products is reported, and the reported products are consistent with the measured basicity of the heteroatom lone pairs as discussed below.

The quantitative determination of the heteroatom basicity was then investigated in 2002 [12]. Spectrometric pH titrations of compounds **6a** and **6b** were performed, and pK_a values determined from these studies are given in Table 2, along with the corresponding values for pyrazine, quinoxaline, and their methyl derivatives. The basicity of **6a** agrees well with pyrazine and quinoxaline, giving a pK_a value of 0.55 for the first protonation. As with quinoxalines, the effect of the fused thiophene ring in TPs has little effect on the basicity. Even in 12 *M* HCl, however, very little of the diprotonated TP **6a** was present at equilibrium, and the pK_a for the second protonation could not be reliably determined. As previously seen for pyrazines and quinxoxalines, the added methyl groups of **6b** provide increased basicity due to the electron-donating effect of the methyl moiety. The pK_a value for the second protonation of **6b** was determined to be −1.29, indicating that TPs are much more basic than simple pyrazines. As pyrazines are well-known ligands for the generation of transition metal complexes, it is not surprising that the formation of transition metal complexes with TPs has also been reported [26,27].

Although the lone pair of the thiophene sulfur is often invoked as a basic position in the literature, it is actually very poorly basic and rarely forms stable *S*-bound Lewis acid complexes [28]. In terms of thiophene protonation, α-protonation of the thiophene ring is actually more favored than protonation of the sulfur heteroatom [29]. As thiophene α-protonation typically promotes substitution and/or polymerization, protonation of the thiophene is not believed to be involved in any of the protonated forms discussed earlier [12].

By far, the most used reactivity of TPs is their ease of electrophilic aromatic substitution, thus allowing efficient access to the corresponding dibromo derivatives as precursors for TP-based conjugated materials (Scheme 8). The electrophilic substitution of thiophene is relatively easy, and it is thus brominated by Br_2 in acetic acid ~10^9 times faster than benzene [29]. For TPs, however, the high

Scheme 7. Reported formation of TP N-oxides.

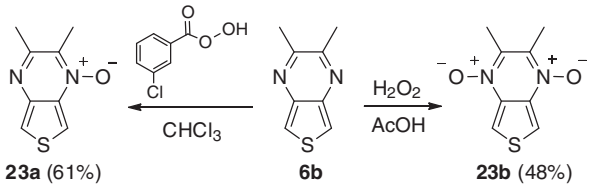
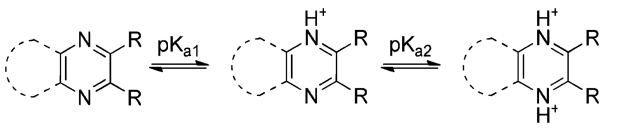


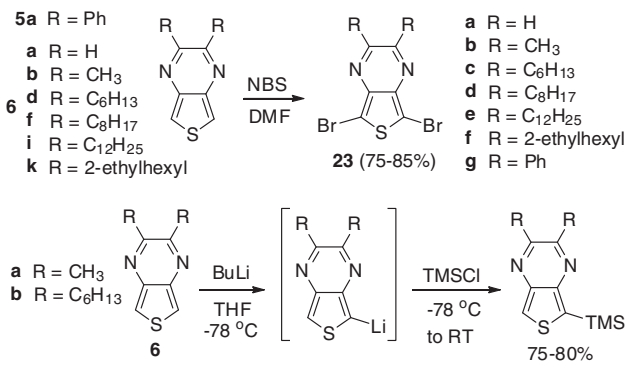
Table 2

pK_a data for pyrazines, quinoxalines, and thieno[3,4-*b*]pyrazines [15].



Compound	pK_{a1}	pK_{a2}
Pyrazine	0.57	−5.51
2-Methylpyrazine	1.41	−4.89
2,3-Dimethylpyrazine	2.24	−4.17
Quinoxaline	0.56	–
2-Methylquinoxaline	0.95	–
Thieno[3,4-*b*]pyrazine (**6a**)	0.55	–
2,3-Dimethylthieno[3,4-*b*]pyrazine (**6b**)	1.66	−1.29

Scheme 8. Bromination and deprotonation of thieno[3,4-b]pyrazines.



oxidizing strength of Br_2 results in competition between TP bromination and oxidation. It is therefore common to use *N*-bromosuccinamide (NBS) as the bromine source, which allows the isolation of the dibromo derivatives in high yield [16,26,29–35]. Under these conditions, bromination of the unfunctionalized parent **6a** is selective to the thiophene ring, with no substitution on the open pyrazine positions [26,30]. As with other typical thiophenes, the resulting TP bromides have also been reported to successfully undergo metal-halogen exchange with organolithium or organomagnesium reagents [31–33].

The deprotonation of TPs by *n*-butyllithium (BuLi) is also selective to the thiophene α-positions and allows efficient generation of lithium TP intermediates [26,31,32]. Such intermediates have allowed access to trimethylsilyl- [31,32], organomagnesium- [26], and trialkylstannyl-TP [31,32] derivatives in good yield. The resulting TP-magnesium and TP-stannyl species can then be used in various aryl–aryl coupling reactions (Stille, Kumada, etc.) for the generation of oligomeric and polymeric species.

5. STRUCTURAL CHARACTERISTICS OF THIENO[3,4-*B*]PYRAZINES

Thieno[3,4-*b*]pyrazines (TPs) are generally crystalline solids, and X-ray quality crystals can be grown by the slow evaporation of TPs in organic solvents. As such, a number of crystal structures have been reported [12,22,23,33], and selected TP bond angles and distances are collected in Table 3, along with the values of thiophene and pyrazine for comparison. Comparing the various TPs with the gas phase distances of thiophene and pyrazine [36] shows that in all cases, the fused thiophene ring is nearly identical to the parent thiophene. In contrast, the fused pyrazine ring shows some bond fixation in comparison with the parent pyrazine. For example, while the delocalized structure of pyrazine results in four equivalent C N bonds, TPs all exhibit elongation of the thiophene-N bonds and shortening of the exterior C N bonds. In fact, the bond lengths of these exterior C N bonds (i.e., N(1)-C(5) = 1.300–1.313 Å) are very close to the 1.28 Å length of localized C N bonds [37]. Other than a slight elongation of the C(2) C(3) bond, substitution at the 5- and 7-positions in **18** and **23c** seems to have little effect on the overall TP structure [23,33]. For **18**, the electron-withdrawing nature of the cyano groups again has little overall effect on the structure other than a slight contraction of the C(5) C(6) pyrazine bond [23].

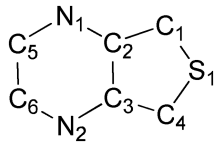
6. OPTICAL AND ELECTRONIC PROPERTIES OF THIENO[3,4-*B*]PYRAZINES

As the primary application of thieno[3,4-*b*]pyrazines (TPs) is as building blocks for the construction of conjugated materials, knowledge of the corresponding optical and electronic properties of these species is quite important. The first investigation of TP electronic properties, however, was a report by Armand *et al*. [13] on the electrochemical properties of **6b** and **9b**, which actually predates their application to conjugated polymers by a year. This study found that in aprotic media, TPs exhibited a one-electron irreversible oxidation and a one-electron reversible reduction. In protic media, the reduction was observed to be a two-electron process, which was assigned to the reduction of pyrazine ring (Scheme 9). The reversibility of this two-electron process was found to be pH dependent, as at lower pH, the reduction product quickly underwent isomerization to the dihydrothiophene. Although the oxidation was believed to be thiophene-based, oxidative coupling to produce oligomers/polymers was not observed, and it was proposed that the nitrogen of the pyrazine ring quenched the electrogenerated radical cation [13].

Rasmussen and coworkers [12] then revisited the electrochemistry of TPs in 2002 with the study of **5a**, **6a**, and a series of dialkyl-TPs. Limiting the electrochemical study to aprotic conditions, the results agreed well with the previous work of Armand *et al*. [13], with the TPs exhibiting a well-defined irreversible thiophene-based oxidation and a quasi-reversible pyrazine-based reduction [12]. As with the previous work, the oxidation was assigned to the formation of a thiophene-based radical cation; but, in contrast, the irreversible nature was assigned to the rapid coupling of the radical cations ($\tau < 10^{-5}$ s for typical thiophenes [38]), resulting in oligomeric and polymeric species [12]. The following year, Kenning and Rasmussen [27] reported the successful electropolymerization of TPs and explained that the previous lack of observed electropolymerization was due to the degradation of the coupled products via overoxidation, not quenching of the radical cation. It should be pointed out that the potential of oxidation for typical dialkyl-TPs is significantly lower than that of thiophene (~1.35 V for TP [12] vs. 1.95 V for thiophene [39]; both potentials vs. Ag/Ag^+). This is counter to the

Table 3

Experimental geometrical parameters of various thieno[3,4-*b*]pyrazines.



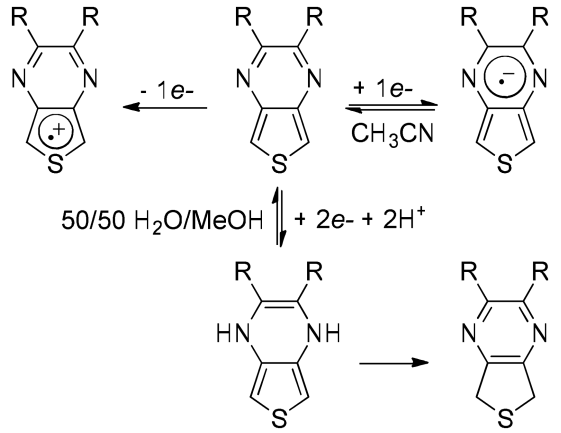
Parameter	**6b**[a]	**6d**[b]	**19**[c]	**18**[d]	**23c**[b]	Thiophene[e]	Pyrazine[e]
S(1) C(1)	1.692(2)	1.684(3)	1.700(6)	1.710(2)	1.708(4)	1.714	
C(1) C(2)	1.372(3)	1.368(5)	1.373(7)	1.384(2)	1.357(6)	1.370	
C(2) C(3)	1.427(3)	1.434(4)	1.434(6)	1.451(2)	1.448(5)	1.423	1.403
C(2) N(1)	1.377(2)	1.372(4)	1.373(6)	1.368(2)	1.365(5)		1.339
N(1) C(5)	1.307(2)	1.300(5)	1.308(5)	1.313(2)	1.313(5)		1.339
C(5) C(6)	1.460(3)	1.463(5)	1.469(6)	1.446(2)	1.469(5)		1.403
C(1) S(1) C(4)	94.25	93.68	93.63	95.99	91.84	92.17	
S(1) C(1) C(2)	110.51	111.63	110.77	108.81	112.33	111.47	
C(1) C(2) C(3)	112.45	111.32	112.03	113.19	111.74	112.45	
N(1) C(2) C(3)	121.35	121.27	121.97	121.75	121.25		122.2
C(2) N(1) C(5)	116.03	116.18	115.72	114.85	116.59		115.6
C(6) C(5) N(1)	122.55	122.75	122.68	123.40	122.12		122.2

[a]Reference 12.
[b]Reference 33.
[c]Reference 22.
[d]Reference 23.
[e]Reference 36.

common misconception that TPs as a whole are electron deficient. Although the pyrazine ring is electron-deficient and thus relatively easy to reduce, the TP thiophene can actually be considered more electron-rich than the parent thiophene and is even slightly easier to oxidize than the very electron-rich 2,4-ethylenedioxythiophene (~1.38 V vs. Ag/Ag^+ [40]).

A broader study was then reported in 2008 investigating the electronic effects of the various electron-donating and -withdrawing groups possible from the TPs produced from **11** and **19** [22]. The redox behavior of all the TPs studied was consistent with the previous two studies, and representative data are combined in Table 4. The overall effect on the potential of oxidation follows normal trends, in which electron-donating groups reduce the potential (as low as 1.13 V) and electron-withdrawing groups increase the potential (as high as 2.13 V). Likewise, the effect on the reduction potentials follows the opposing trend, with electron-withdrawing groups reducing the potential to as low as −0.93 V and electron-donating groups increasing to potential to the extent that the reduction of TPs with strongly donating groups such as alkoxy or alkylamino are no longer within the measurable solvent windows of CH_3CN or CH_2Cl_2.

Scheme 9. Electrochemical processes of thieno[3,4-*b*]pyrazines.



Hammett correlations of both the oxidation and reduction potential variations were also performed and as seen in Figure 1, both plots (oxidation vs. σ_p^+ and the reduction vs. σ_p^-) give linear relationships with respective *R* values of 0.917 and 0.953 [22]. The plot of the potential of oxidation gives $\rho_\pi = 0.340$, which is low in comparison with typical thiophenes ($\rho_\pi = 0.80$ [41]), indicated that functional groups have less effect on the potential of oxidation in the case of the fused-ring TPs. In contrast, the plot of the reduction potentials gives the higher value of $\rho_\pi = 0.463$, indicating a larger effect of the functional group on the reduction in comparison with the corresponding oxidation. As calculations have shown that the pyrazine ring contributes more significantly to the LUMO than the HOMO [42], and the functional groups are bound directly to the pyrazine ring, it is not surprising that a greater effect is seen in the corresponding reduction potentials.

Table 4

Spectral and electrochemical data of various thieno[3,4-*b*]pyrazines in CH_3CN.[a]

	Abs ($S_0 \rightarrow S_1$, CT)		Abs ($S_0 \rightarrow S_2$, $\pi \rightarrow \pi^*$)		Oxidation	Reduction	
TP	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	E_{pa} (V)	$E_{1/2}$ (V)	ΔE (mV)
6a	350[b]	2400[b]	299[b]	10,900[b]	1.55[c]	–	–
6d	349[b]	1900[b]	305[b]	11,200[b]	1.35[c]	−2.01[c]	150[c]
5a	340[b]	10,500[b]	252[b]	26,000[b]	1.26[d]	−1.78[d]	75[d]
11	360	1300	324	8700	1.79	−1.34[e]	–
12	360	900	319	6700	1.69	−1.59[e]	–
19	360	2300	321	9700	1.54	−1.43[e]	–
13a	–	–	303	12,000	1.26	*nwsw*	–
14	–	–	327	18,400	0.52[f], 1.13	*nwsw*	–
15	395	1300	326	14,700	1.51	−1.44	100
16	400	1000	340	6100	2.13	−0.93	100
21	355	2400	318	12,200	1.45	−1.87	100
20b	355	1600	305	8300	1.47	−1.85	125

[a]Unless otherwise noted, all values are from Reference 22; potentials versus Ag/Ag^+.
[b]Reference 42.
[c]Reference 12.
[d]Reference 51.
[e]Irreversible, value corresponds to E_{pc}.
[f]Nitrogen-based oxidation.

The absorption and emission properties of TPs were first reported in 2004 [42]. The initial study was limited to the **5a**, the parent **6a**, and various 2,3-dialkyl-TPs and revealed that with the exception of the diphenylTP **5a**, the absorption spectra of the series exhibit only minor differences. As shown in Figure 2, the parent TP **6a** and its dialkyl analogs exhibit four transitions, of which the lowest energy transition is a broad charge transfer (CT) band centered at ~350 nm [42]. This CT band results from a transition between a predominately thiophene-localized HOMO and a LUMO of greater pyrazine contribution (Fig. 3). The higher energy 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 in the higher-energy region of 200–230 nm. The absorption spectra of TPs are essentially solvent independent, with large changes in solvent polarity resulting in less than 1 nm shifts for the two lowest energy transitions. In contrast, protonation results in significant red shifts of all bands. In addition, the bands initially at ~300 nm significantly increase in intensity, while the lowest energy band becomes much broader with slightly reduced intensity [42].

The parent **6a** and the 2,3-dialkyl-TPs also exhibit a room-temperature singlet emission at approximately 470 nm in CH_3CN (Fig. 2) [42]. Although the excitation spectra show contribution primarily from the transition centered at 350 nm, lesser contributions are also seen from the higher energy transitions. In contrast to the solvent inde-

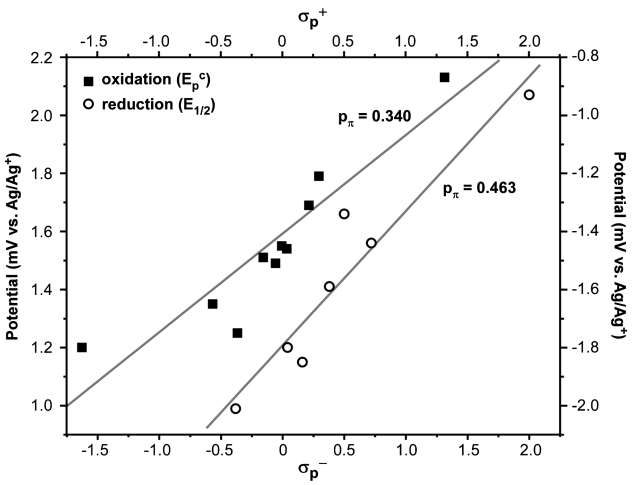


Figure 1. Hammet plot of thieno[3,4-*b*]pyrazines (Reprinted with permission from Ref. 22. Copyright 2008 American Chemical Society).

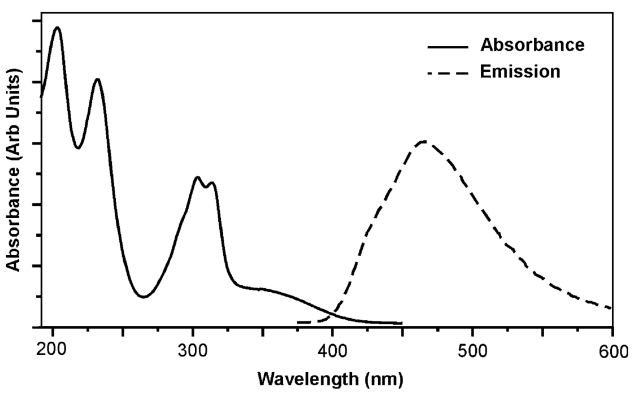


Figure 2. Absorption and emission spectra of **6b**.

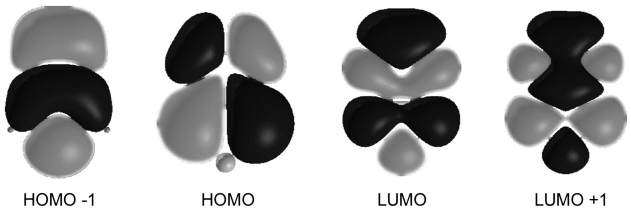


Figure 3. Calculated molecular orbitals of **6a** [38].

pendence of the absorption spectra, the fluorescence exhibit a large solvent dependence, in which the emission red-shifts with increasing solvent polarity, and an overall shift of ~80 nm is seen from the polarity extremes of hexane to water. The quantum yield values for the TP emission are fairly low ($\Phi_F = 1-5 \times 10^{-3}$), but are significantly higher than the quantum yields for either quinoxaline or typical thiophenes [43,44].

A theoretical study of the optical processes of TPs was reported in 2009 by Orti and coworkers [46], in which the electronic transitions were studied using the multiconfigurational second-order perturbation CASPT2 theory with extended atomic natural orbital basis sets. Although this new study was carried out at a higher computational level than the previous ZINDO calculations of Rasmussen and coworkers [42], the results obtained supported the earlier analysis of the optical spectra and the resulting assignments of the electronic transitions. The higher level calculations were able to provide a more detailed interpretation of the highest energy TP transitions [45].

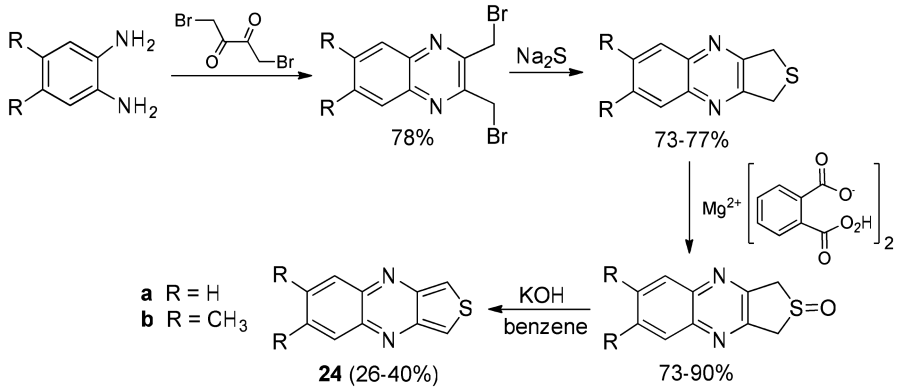
As with the electrochemistry earlier, a broader experimental study was then reported in 2008 to investigate the electronic effects of the various electron-donating and -withdrawing groups possible from the TPs produced from **11** and **19** [22]. Representative data are combined in Table 4, and, for the most part, the additional analogs exhibit similar spectra to the parent and the dialkyl-TPs. However, there are a few notable exceptions. For example, both the diphenylTP **5a** and the alkylamino-functionalized **14** exhibit only two bands, rather than four. In both cases, the two observed bands are considerably more intense than the corresponding bands of the other TPs, and thus these bands may consist of multiple overlapping transitions. Of greater interest, however, is the fact that TPs containing electron-donating groups (**13a–d**, **14**) do not seem to exhibit the CT transition typical of TPs. As electron-withdrawing groups cause the CT transition to red-shift as much as 50 nm, it would be reasonable to postulate that the CT transition in compounds **13a–d** and **14** has blue-shifted and now overlaps with the higher energy transition near 300 nm. However, a red-shift of both the CT transition and the more intense $\pi \rightarrow \pi^*$ transition is observed for compounds **11**, **12**, **15**, **16**, and **19**, while compounds **13a–d** or **14** exhibit no such blue-shift in the transition observed [22].

7. SYNTHESIS OF EXTENDED FUSED THIENO[3,4-*B*]PYRAZINES

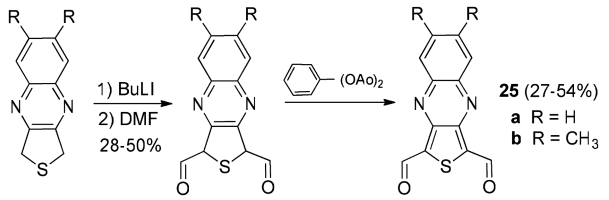
The fused pyrazine ring of thieno[3,4-*b*]pyrazines (TPs) stabilizes the quinoid resonance form of the thiophene backbone in conjugated materials, thus resulting in a significant reduction in band gap [1–3]. As a consequence, more extended fused-ring TP analogs have become of interest as these extended building blocks may provide enhanced properties in comparison with the simple TPs commonly applied. The earliest known extended analog of TPs is thieno[3,4-*b*]quinoxalines (**24**), whose synthesis and attempted isolation were first reported by Roland and Anderson in 1977 [46]. Although the fused-ring products were observed as transient species via trapping experiments, isolation of desired thieno[3,4-*b*]quinoxalines was unsuccessful. Cava and coworkers [47] then revisited this chemistry in 1995 and successfully reported the synthesis and isolation of thieno[3,4-*b*]quinoxalines **24a** and **24b** as shown in Scheme 10.

Unlike the previous TP syntheses, which build the pyrazine ring off of the existing thiophene, routes to the thieno[3,4-*b*]quinoxolines use methods previously successful for

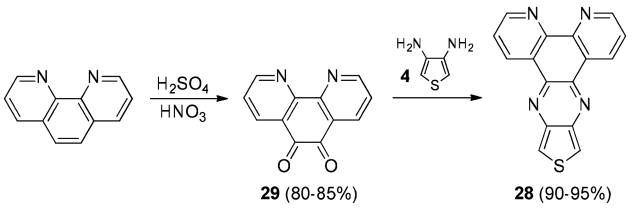
Scheme 10. Synthesis of thieno[3,4-*b*]quinoxolines.



Scheme 11. Synthesis of 1,3-diformylthieno[3,4-*b*]quinoxolines.



Scheme 13. Synthesis of thieno[3′,4′:5,6]pyrazino[2,3-*f*][1,10]phenanthroline.



benzothiophenes and thienopyridines, in which the thiophene is added to the six-membered aromatic precursor. The resulting products **24a** and **24b** were described to be more reactive than TPs and were stable for only several days, provided they were adequately protected from oxygen and light [47]. The more stable formyl derivatives **25** were also prepared (Scheme 11), which were later applied to conjugated materials [48].

The remaining known extended analogs have all been produced via conventional condensation processes in the same manner as the dialkyl- and diaryl-TPs. However, because of the limited solubility of these systems and the efforts required to produce the derivatized diones necessary to produce functionalized derivatives, only a few such extended analogs have been reported. The earliest example of this group was the pyrroloquinoline quinone-derived analog **26** (Scheme 12), reported by Paz and coworkers in 1996 [49]. Although it was stated that **26** was made via the condensation of **4** with dione **27**, no real synthetic details were given, and the report was focused on the applications to various biological inhibitor studies.

Čík *et al*. [50] then reported the somewhat more straightforward analog thieno-[3′,4′:5,6]pyrazino[2,3-*f*][1,10]-phenanthroline (**28**) in 2001. Although the authors reported the characterization and application of **28**, its synthetic details were not included and the reader directed to the proceedings of a 1995 symposium in the Czech Republic. However, it can be reasonably assumed that it was obtained from the simple condensation of the known dione **29** with either **4** or its salt. More recently, Rasmussen *et al*. [51] reported the full synthetic details using exactly those methods as shown in Scheme 13.

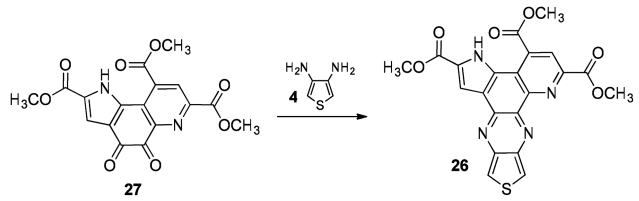
Although 1,10-phenanthroline-5,6-dione **29** is commercially available, it can be easily produced via the simple oxidation of 1,10-phenanthroline in high yield. Condensation of **29** with **4** in ethanol at reflux for 1 h then allows the production of **28** in yields of ∼95% [51]. It should be pointed out that while the condensation to produce simple dialkyl-TPs can readily occur at room temperatures, the production of such extended analogs all require heating at elevated temperatures to achieve effective yields. As might be expected, **28** is an effective chelating ligand, and Ji and coworkers [52,53] have reported its transition metal complexes.

Perhaps, the most studied of these extended analogs is acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine (**30a**) and its derivatives. The parent monomeric **30a** was first reported by Rasmussen and coworkers in 2008 as shown in Scheme 14 [54]. This initial report gave yields of 55–60% when heated at reflux for 3 h. Bao and coworkers [55] later reported modified conditions in which the HCl salt of **4** was used rather than the free base, and heating was continued for 2 days. These conditions increased the yield of **30a** to 70%. In the same report, they also reported the bromination of **30a** to give **31**. As with the previous bromination of TPs, bromination was selective to the thiophene ring.

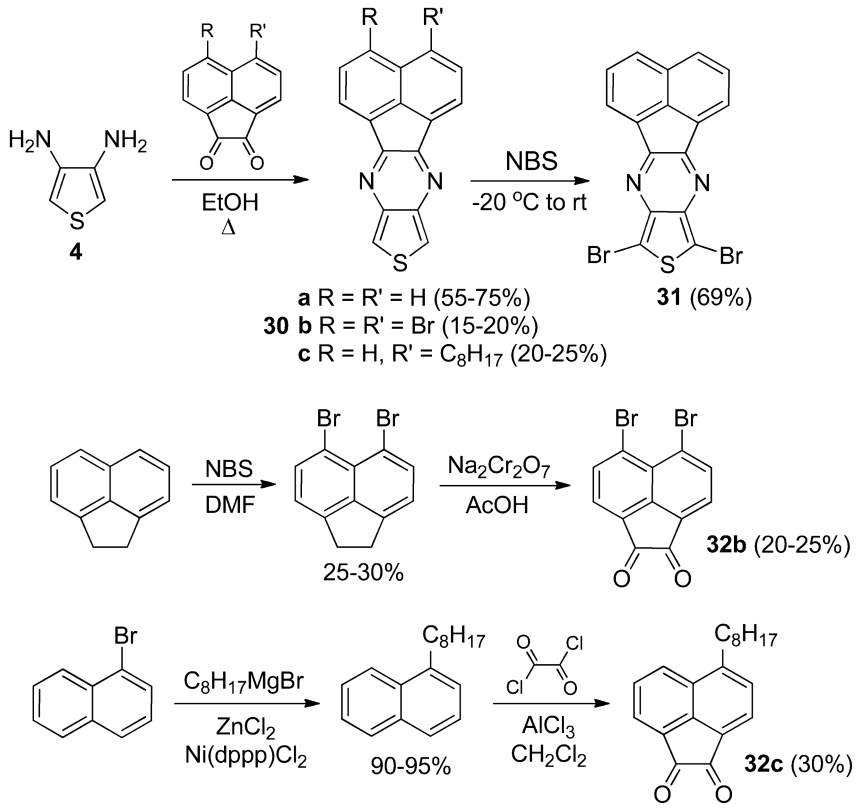
In an attempt to produce derivatives with increased solubility, Rasmussen and coworkers [51,56] reported the synthesis of **30b** and **30c**. Initially, hoping to produce a family of derivatives in a manner similar to their earlier work in TPs, the synthesis of dione **32b** was applied to the generation of the dibromo species **30b**. Unfortunately, **30b** had such low solubility that it could not be effectively used to generate further derivatives [51]. Dione **32c** had been initially reported by Vanderzande and coworkers in 2008 [57], and Rasmusssen and coworkers then applied this to the generation of **30c** in 2009 [56]. Unfortunately, the inclusion of the single alkyl side chain did not sufficiently enhance the solubility in comparison with **30a**. Rasmussen and coworkers [51] included a more detailed preparation of both **32c** and **30c** in a recent report.

Bao and coworkers [55] also reported dibenzo[*f*,*h*]thieno [3,4-*b*]quinoxaline (**33**), an isostructural analog to **28**. As shown in Scheme 15, nearly identical conditions for the generation of **30a** were applied, although with more limited yields. Contrary to the results discussed earlier for **30a**, Rasmussen and coworkers [51] found significantly higher yields when using the free base **4** and only heating for 3 h. The selective bromination of **33** to generate **34**

Scheme 12. Synthesis of thieno[3,4-*b*]pyrazine analog of pyrroloquinoline quinone-triester.



Scheme 14. Synthesis of acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazines.

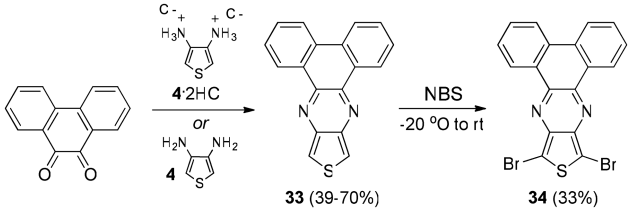


was also reported by Bao and coworkers [55] using identical methods to the generation of **31**.

An unusual, but quite interesting, extended TP analog was the iptycene derivative **36**, reported by Swager and coworkers in 2008 [58]. As shown in Scheme 16, the required dione precursor **35** was prepared from anthracene in three steps in high yields. The TP analog **36** was then synthesized using a modification of the methods of Imoto [6]. The dibromo derivative **37** was then successfully produced in high yield via standard conditions for the bromination of TPs as discussed above [58].

Last, some fused porphyrin-TP derivatives were reported in 1997 from the Crossley group [59]. As shown in Scheme 17, these were prepared by the condensation of **4** with porphyrin diones **38** and **39** in chloroform at reflux for 2 h. Porphyrin **40** could be produced in yields of 76% when using an excess of **4** (2 equiv). The doubly TP-functionalized **42** could be produced in yields as high as 80% when 2.8 equiv of **4** were used. In contrast, the highest yields of **41** were achieved when only 0.7 equiv of **4** were used.

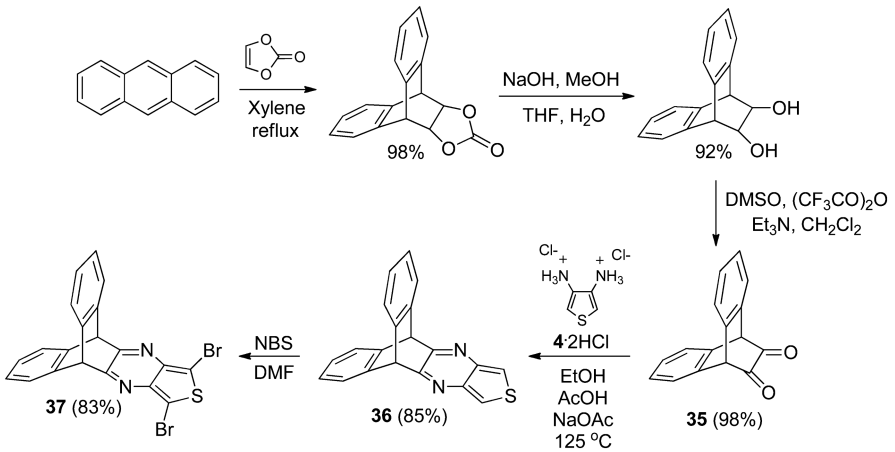
Scheme 15. Synthesis of dibenzo[*f*,*h*]thieno[3,4-*b*]quinoxaline.



8. PROPERTIES OF EXTENDED FUSED THIENO[3,4-*B*]PYRAZINES

The properties of the extended fused-ring analogs have been studied to a much lesser degree than TPs. Although a number of X-ray structures have been reported for functionalized TPs, the only extended analog that has been studied crystallographically is **30a** [51]. The reported bond lengths are given in Table 5, along with TP **6b** and acenaphthylene [60] for reference. Comparison with **6b** shows that the TP portion of **30a** exhibits nearly identical structural characteristics as with all previously reported TP structures [12,22,23,33]. Comparison of the acenaptho portion of **30a** with acenaphthylene, however, reveals significant differences. Shortening is observed in the exterior bonds C(8)–C(9) and C(10)–C(11) of ATP, while the interior bonds C(7)–C(12) and C(11)–C(12) show significant elongation. These differences result in a significant

Scheme 16. Synthesis of 5,10-dihydro-5,10[1′,2′]benzenobenzo[*g*]thieno[3,4-*b*]quinoxaline.



reduction of average bond alternation in **30a**, indicative of enhanced delocalization, and conjugation within the extended fused-ring system.

The electronic and optical properties of several extended fused TP analogs have been recently characterized [51], and the absorption and electrochemical data is collected in Table 6. For the most part, all the extended analogs undergo both oxidation and reduction at lower potentials than simple dialkyl- or diaryl-TPs, which is consistent with the increased delocalization of the π-electrons within these larger conjugated systems [51]. As previously discussed for the TPs in Section 6 earlier, the use of electron-withdrawing or electron-donating groups will result in modulation of the HOMO and LUMO energies, with functionalities having a greater effect on the LUMO than the HOMO [22]. Thus, extended analogs with strong electron-withdrawing groups exhibit the lowest potentials for reduction, but undergo oxidation at higher potentials than typical TPs [51].

Comparing the absorption properties of the extended analogs to dialky- and diaryl-TPs reveals similar characteristics,

Scheme 17. Synthesis of fused porphyrin-TP derivatives.

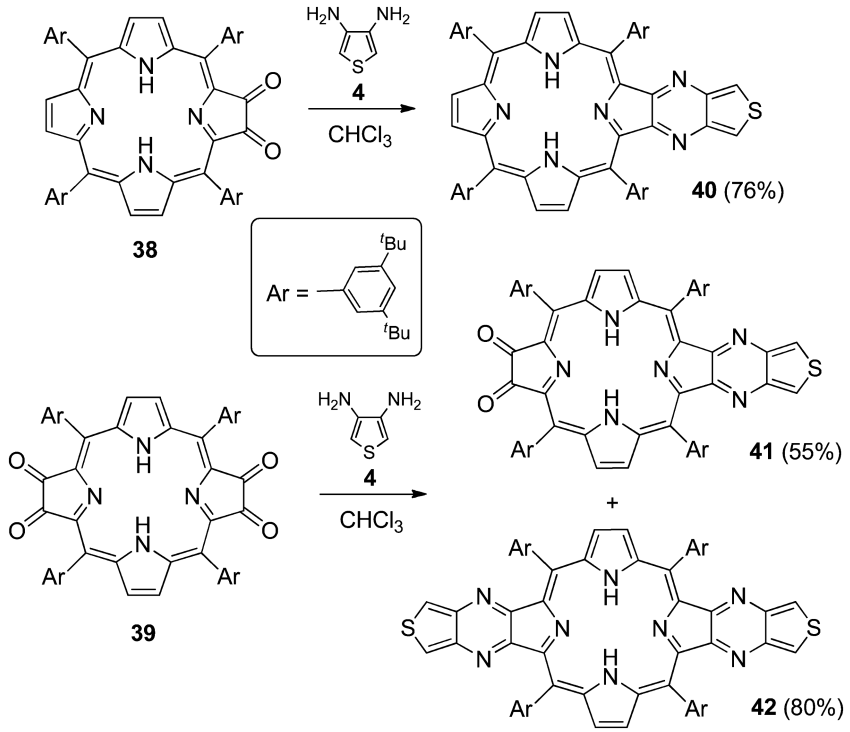
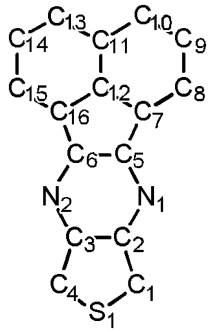


Table 5

Experimental bond lengths of acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine (**30a**), 2,3-dimethylthieno[3,4-*b*]pyrazine (**6b**), and acenaphthylene.



Bond	**30a**[a]	**6b**[b]	Acenaphthylene[c]
S(1) C(1)	1.706(2)	1.692(2)	
C(1) C(2)	1.377(2)	1.372(3)	
C(2) C(3)	1.443(2)	1.427(3)	
C(2) N(1)	1.389(2)	1.377(2)	
N(1) C(5)	1.309(2)	1.307(2)	
C(5) C(6)	1.473(2)	1.460(3)	1.5024(1)
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 51.
[b]Reference 12.
[c]Reference 60.

but with red-shifts as expected for larger conjugated systems, and all systems studied exhibit the same low-energy CT transition typical of TPs [51]. In contrast to the normal higher energy transitions, however, the acenaphtho[1,2-*b*]thieno[3,4-*e*] pyrazines exhibit a somewhat sharp, but very intense transition near 320 nm. The strength of this transition in comparison with typical TPs or the rest of the studied extended analogs suggests that this may be due to multiple overlapping transitions. The remaining analogs **28** and **33** exhibit a great many more absorption bands than either the acenaphtho[1,2-*b*]thieno[3,4-*e*] pyrazines or typical TPs and are significantly red-shifted, consistent with the HOMO and LUMO energies determined from the electrochemistry [51]. In addition to the two transitions given in Table 6 for thieno[3,4-*b*]-quinoxaline **24b**, a third lower energy transition was reported at 469 nm [47]. However, the energy of this transition is inconsistent with the rest of the extended TP analogs and is likely due to some small amount of oligomeric species.

9. CONCLUSIONS

For materials chemists to design and produce improved electronic materials, it is critically important to understand the various structure-function relationships involved. Understanding such structure-function relationships in the polymeric products can really only be accomplished by fully determining the analogous relationships in the monomeric precursors, which more often than not are either ignored or overlooked. In this current review, we have tried to provide a good overview of the breadth of reported knowledge on one of the more commonly used building blocks for the construction of low-band gap conjugated materials. In addition, the collected works discussed illustrates the wide variety of TPs now known and provides materials chemists with the proper knowledge to be able to apply the correct TP monomer to best achieve the desired optical or electronic properties in their resulting materials.

Table 6

Spectral and electrochemical data of extended thieno[3,4-*b*]pyrazine analogs in CH_3CN.[a]

	Abs ($S_0 \rightarrow S_1$, CT)		Abs ($S_0 \rightarrow S_2$, $\pi \rightarrow \pi^*$)		Oxidation	Reduction	
TP	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	E_{pa} (V)	$E_{1/2}$ (V)	ΔE (mV)
24b	371[b]	*nr*	251[b]	*nr*			
30a	375	4300	317	69,800	1.18	−1.67	60
30c	376	4200	321	69,500	1.15	−1.75	90
33	426	2400	400	11,800	0.98	−1.51	90
28	418	2500	383	11,300	1.45	−1.27	110

[a]Unless otherwise noted, all values are from Reference 51; *nr* = not reported.
[b]In EtOH, Reference 47.

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