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# Synthesis of Low Band Gap [1,2,5]-Thiadiazolo[3,4-*g*]quinoxaline and Pyrazino[2,3-*g*]quinoxaline Derivatives by Selective Reduction of Benzo[1,2-*c*;4,5-*c*′]bis[1,2,5]thiadiazole

**Hairong Li,[#] Teck Lip Tam,[#] Yeng Ming Lam, Subodh G. Mhaisalkar, and Andrew C. Grimsdale***

*School of Materials Science and Engineering, Nanyang Technological University,*
*50 Nanyang Avenue, Singapore 639798*

*acgrimsdale@ntu.edu.sg*

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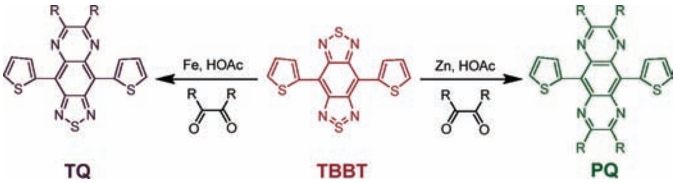
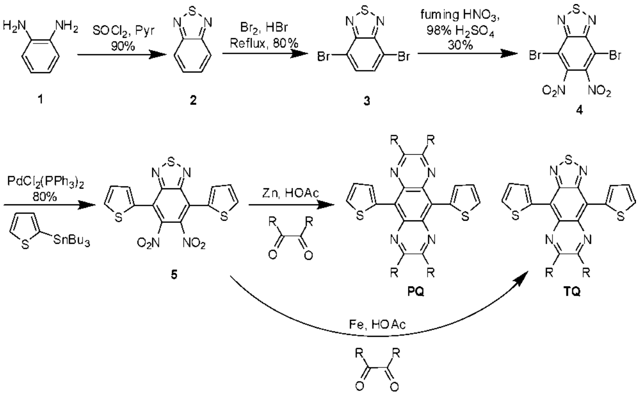
## ABSTRACT



**The reduction of a dithienylbenzobisthiadiazole derivative TBBT can be performed selectively so as to afford either [1,2,5]-thiadiazolo[3,4-*g*]quinoxaline (TQ) or pyrazino[2,3-*g*]quinoxaline (PQ) derivatives. This approach offers a much milder, shorter, and more efficient route to PQ and TQ derivatives than current methods. It is further shown how the optical and electrochemical properties of PQ and TQ can be tuned by choice of appropriate substituents.**

Molecules and polymers based on 1,2,5-thiadiazolo[3,4-*g*]quinoxaline (TQ) and pyrazino[2,3-*g*]quinoxaline (PQ) have received increasing attention since 2005 as n-type materials due to their interesting electronic and photophysical properties.[1] Without exception, their synthesis has been based on the method of Kitamura et al.[2] illustrated in Scheme 1 for 4,9-dithienyl-TQ and 4,8-dithienyl-PQ derivatives. The key intermediate is the dinitrobenzothiadiazole **5**. Reaction of **5** with zinc reduces both the benzothiadiazole ring and the nitro groups to give a tetraamine intermediate that is condensed with 2 equiv of a diketone to give PQ derivatives. By contrast iron does not reduce the ring and so TQ derivatives can be obtained by reduction of **5** under these milder conditions followed by condensation of the resulting diamine with diketones. The main disadvantages of these routes are that the

**Scheme 1.** Current Synthetic Route to Dithienyl-TQ and Dithienyl-PQ Derivatives



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[#] These authors have contributed equally to this work.

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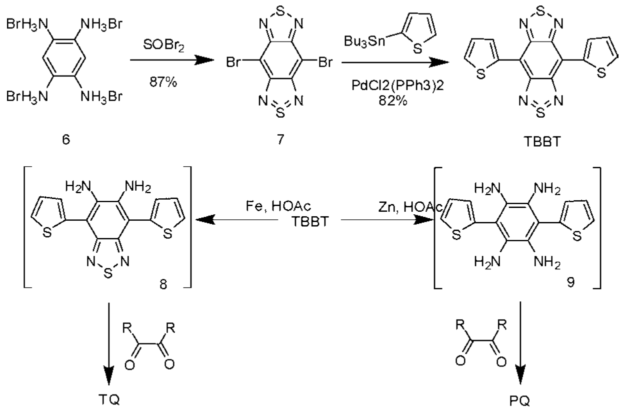
synthesis of **5** requires 4 steps, some using very strong conditions, and proceeds in only low overall yield (17%).

This synthetic inefficiency in the preparation of compounds **4** and **5**, which had previously been used as intermediates in the synthesis of benzobisthiadiazole (BBT) derivatives, was a major motivation for us to develop our recently reported efficient (87% yield) one-pot synthesis of 4,8-dibromobenzo[1,2-*c*;4,5-*c*′]bis[1,2,5]thiadiazole (**7**).[3] Having developed a short and high yielding route to the dibromo-BBT **7** and its dithienyl adduct (**TBBT**), we were then interested to explore whether reduction of BBT derivatives might offer an effective method for obtaining **PQ** and **TQ** derivatives. As shown in Scheme 2, we now report that reduction of **TBBT** by stirring with a large excess of zinc powder in acetic acid at 80 °C followed by addition of 2 equiv of a diketone affords **PQ** derivatives in only 3 steps from a commercially available tetraaminobenzene. When zinc was replaced by iron powder as the reducing agent under the same reaction conditions, it was found that selective reduction of only one thiadiazole ring in BBT occurred, thus affording a route to **TQ** derivatives by condensation with 1 equiv of the diketone. A smaller excess of reducing agent is required in the synthesis of TQ as compared to PQ derivatives as only one ring is reduced. This selectivity is due to the hypervalent sulfur in one ring in BBT making the reduction of BBT to BT more facile than the reduction of BT.

**Scheme 2.** Novel Synthetic Route to Dithienyl-TQ and Dithienyl-PQ Derivatives



To test the versatility of the reaction procedure and to investigate how the properties of **PQ** and **TQ** molecules could be tuned, we chose to make derivatives with biphenyl (Figure 1, **TQ1** and **PQ1**) and dithienyl (**TQ2** and **PQ2**) substituents. Since **TQ0** and **PQ0**,[2] the reference molecules chosen from the literature for comparison of properties, are not very soluble, longer solubilizing alkyl or alkoxy chains were incorporated.

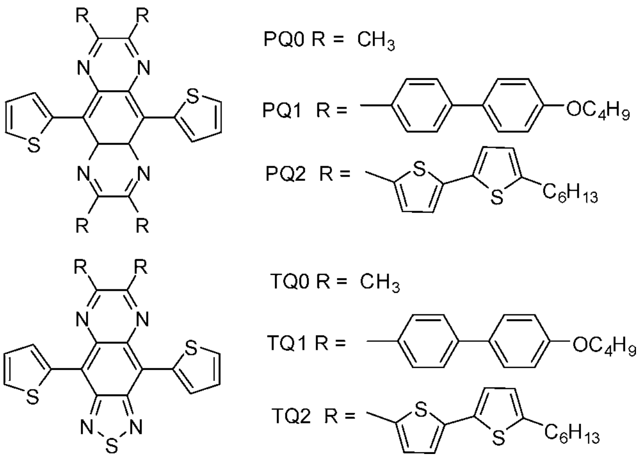


**Figure 1.** Target molecules: **PQ1−2** and **TQ1−2**, and literature models **PQ0** and **TQ0** for comparison.

As shown in Scheme 3, the biphenyl diketone **12** was prepared in good yield by Suzuki coupling of **10** and **11**. The corresponding dithienyl diketone **15** was prepared by Stille coupling of **13** and **14**.

Reduction of **TBBT** with zinc followed by condensation of the resulting crude tetraamine with **12** afforded **PQ1** in 31% yield (22% overall yield). The condensation with **15** was less efficient producing **PQ2** in only 17% yield (12% overall). The condensations of the diketones with the crude diamine from reduction of **TBBT** with iron proceeded in much higher yields with **TQ1** and **TQ2** being obtained in 82% and 65% yield, respectively (58% and 46% overall

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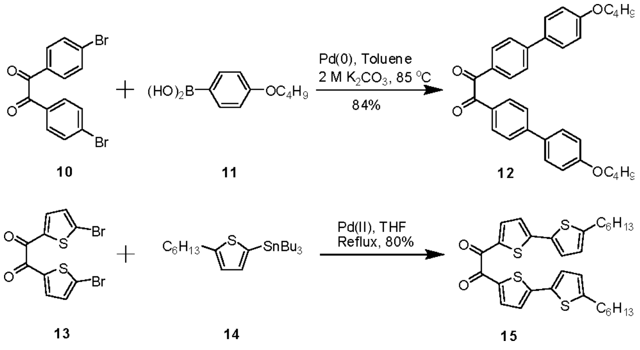
**Scheme 3.** Synthesis of the 1,2-Diketones



yields), thus providing a much shorter and more efficient route to TQ derivatives than those previously reported. This difference in yields may reflect either the greater stability of the less electron-rich diamine intermediate compared to the tetraamine, or the greater efficiency in the reduction. The higher efficiency of the condensations of **12** compared to **15** may reflect the higher electron density of the thienyl molecules making them less susceptible to nucleophilic attack. While the yields from the final step in the synthesis of the **PQ** derivatives are clearly capable of considerable improvement through optimization of the reaction conditions, the overall synthesis is still notably more efficient than the existing route to **PQ** derivatives as **TBBT** can be obtained in much higher yield than **5** (71% cf. 17%) and in 2 fewer steps.

Most work on TQ and PQ derivatives has concentrated on using them to make donor−acceptor copolymers,[1a,b,g−k,m−q] but it is clear that the choice of substituents R on TQ and PQ units can have profound effects on their electronic structures, charge transfer abilities, solubility, and film forming properties.[1c−f,l,2b,4] We have investigated the optical and electrochemical properties of our new molecules **TQ1−2** and **PQ1−2** in order to gain some insight into their structure−property relationships with a view to designing materials with better performance in electronic devices. The absorption maxima, both in solution and as thin films (Figure 2), and the estimated orbital energies for our new molecules are tabulated in Table 1, with the values we measured for **TBBT** and the values from literature for **TQ0** and **PQ0** being given for comparison.

The optical bandgaps were calculated from the onset of absorption in solution (Figure 2) and matched well with the electrochemical bandgaps obtained from CV. The oxidation and reduction processes for all our new compounds appear to be reversible.

It is clear that the bandgaps for both TQ and PQ derivatives are larger than those for TBBT, with those for the TQ derivatives being lower than those for the corresponding PQ derivatives. The bandgaps of our aryl-substituted molecules **TQ1−2** and **PQ1−2** are smaller than those for the alkyl derivatives **TQ0** and **PQ0**, due to the HOMO orbital energies for our derivatives being significantly higher (~0.4 eV) while their LUMO energies are only slightly higher than those for **TQ0** and **PQ0**, though significantly higher than those for **TBBT**. The thienyl-derivatives **TQ2** and **PQ2** had slightly smaller bandgaps than the phenyl-substituted analogues **TQ1** and **PQ1**. This seems to be due predominantly to a decrease in their LUMO energies.

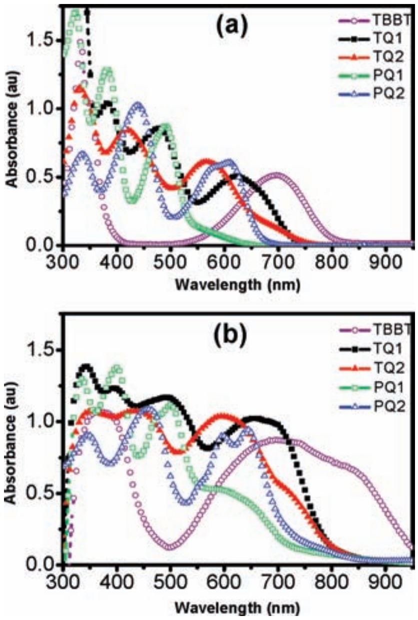


**Figure 2.** Absorption spectra of **TBBT**, **TQ1−2**, and **PQ1−2** in $CHCl_3$ solution (a) and as thin films (b).

Theoretical studies on heterocyclic fused rings as acceptors in donor−acceptor copolymers have predicted that the strength of the acceptor has more effect on the LUMO than HOMO of the polymer, with stronger acceptors lowering the LUMO level more, and the order of electron-withdrawing power is the following: BBT > TQ > PQ.[5] This is consistent with our measurements.

Comparing the absorption spectra for the PQ derivatives shows that while **PQ1** and **PQ2** have similar absorption edges, the thienyl-substituted derivative **PQ2** absorbs much more strongly in solution between 550 and 650 nm than the phenyl analogue **PQ1**. By contrast the thienyl-substituted **TQ2** displays slightly weaker absorption in the red than the phenyl-substituted **TQ1**. What is notable is that all the TQ and PQ derivatives absorb much more strongly in the 400−600 nm range than TBBT.

We hypothesize that these results may be explicable in terms of the relative contributions to the electronic structures of these molecules of the quinoid component along the thiophene−benzene−thiophene backbone of the molecule and the cross-conjugation along the arms, as has been observed in other systems.[6] Modeling of the electronic structures of these materials is underway in order to test this.

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**Table 1.** Optical and Electrochemical Properties of **TQ0−2**, **PQ0−2**, and **TBBT**

| | **TBBT** | **TQ0** | **TQ1** | **TQ2** | **PQ0** | **PQ1** | **PQ2** |
|---|---|---|---|---|---|---|---|
| LUMO (−eV) | 3.95 | 3.55 | 3.43 | 3.52 | 3.23 | 3.12 | 3.26 |
| HOMO (−eV) | 5.42 | 5.54 | 5.11 | 5.08 | 5.52 | 5.10 | 5.15 |
| CV $E_g$ (eV) | 1.47 | 1.99 | 1.68 | 1.56 | 2.29 | 1.98 | 1.89 |
| UV $E_g$ (eV) | 1.49 | N/A | 1.70 | 1.65 | N/A | 1.93 | 1.86 |
| $\lambda_{max}$ (nm) in CHCl$_3$ | 699 | 591 | 620 (4.00) | 650 s$^a$ (4.01) | 491 | 543 s$^a$ (3.99) | 607 (4.61) |
| (log $\varepsilon_{max}$) | 350 | 320 | | | 385 | | |
| | 333 | 285 | 477 (4.23) | 567 (4.41) | 294 | 490 (4.78) | 575 (4.58) |
| | | | 383 (4.32) | 418 (4.55) | | 382 (4.90) | 447 (4.84) |
| | | | 323 (4.85) | 331 (4.69) | | 324 (5.03) | 339 (4.65) |
| $\lambda_{max}$ (nm) thin film | 830 s$^a$ | N/A | 695 s$^a$ | 713 s$^a$ | N/A | 555 s$^a$ | 643 |
| | 699 | | 655 | 596 | | 500 | 597 |
| | 385 s$^a$ | | 492 | 437 | | 399 | 459 |
| | 360 | | 394 | 351 | | 335 | 347 |
| | | | 343 | | | | |
| $T_m$ (°C) | N/A | 258 | 242 | 152 | N/A | >300 | 170 |

[a] s: onset of a shoulder or tail down to longer wavelength.

The thin film absorption spectra generally resemble the ones obtained from solution with a red shift of absorption edge and peak broadening observed for all compounds due to aggregation. The most notable changes are that the absorption intensity from 543 nm onward significantly increases for **TQ1** and a shoulder emerges between 550 and 700 nm for **PQ1**. We have not yet succeeded in growing crystals suitable for X-ray diffraction to study the packing of the molecules in the solid state, but comparisons of the melting points suggest that the biphenyl-substituted molecules **PQ1** and **TQ1** pack better in the solid state as they melt at significantly higher temperatures than the thienyl-substituted analogues **PQ2** and **TQ2**. Since biphenyl is known to have higher torsion angle than bithiophene due to stronger repulsion between neighborhood α-protons, there might be a dramatic conformational change in the biphenyl-substituted **TQ1** and **PQ1** between solution and solid state, which could account for the change in the shape of the absorption as the arms become flatter and so have longer effective conjugation. The PQ molecules all possess higher melting points than the corresponding TQ derivatives, but the differences are smaller than those within each class suggesting the arms have a greater effect on the melting points than do the cores.

The new molecules **PQ1−2** and **TQ1−2** are all freely soluble in organic solvents and so it should be relatively straightforward to incorporate them as electron-accepting units into donor−acceptor oligomers and polymers. In view of their relatively low bandgaps we believe such materials should be promising candidates for organic photovoltaic devices, organic transistors, or red or infrared emitting OLEDs.

To sum up, we have demonstrated a new short and relatively efficient synthesis of PQ and TQ derivatives which makes these classes of molecules much more readily available for use as components in new materials for organic electronics applications. We have shown that their optical and electronic properties can be controlled by suitable choice of solubilizing side arms on the heterocyclic cores, thus enabling the potential performance of the final materials to be optimized.

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**Supporting Information Available:** Detailed synthetic procedures and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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