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Reaction Optimization of Pyrazinoquinoxaline Based Organic Semiconductor with Cruciform Shape

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Introduction

Organic semiconductors have been an active research topic over the past two decades with applications in organic light-emitting diodes (OLEDs), organic solar cells (OSCs), and organic field-effect transistors (OFETs). Organic semiconductors are attractive due to the ability to modify the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy gap via structural modification. Typical organic semiconductors designs are linear; however, cruciform shaped compounds may have an advantage in controlling HOMO-LUMO energy gap.

In past literature, similar pyrazinoquinoxaline based compounds have been synthesized with yields ranging from 20-50%. The inconsistent yield is due to the formation of an unstable air sensitive tetraamine benzene intermediate in the reduction and cyclization step. Resolving this issue is important because the title compound serves as an important platform which can undergo further structural modification to generate compounds with interesting electronic properties. In this work, the title compound PQ-TH is synthesized using two routes in order to establish an optimum reaction condition.

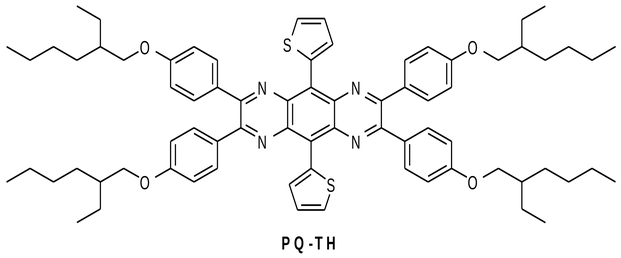
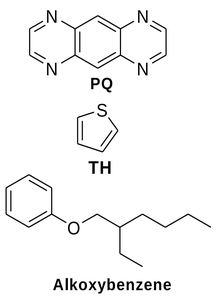


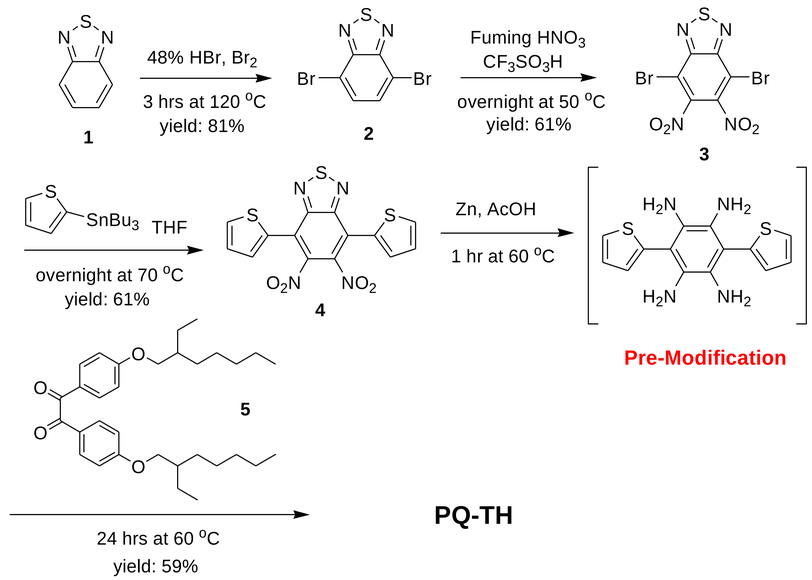
Figure 1. Title compound PQ-TH



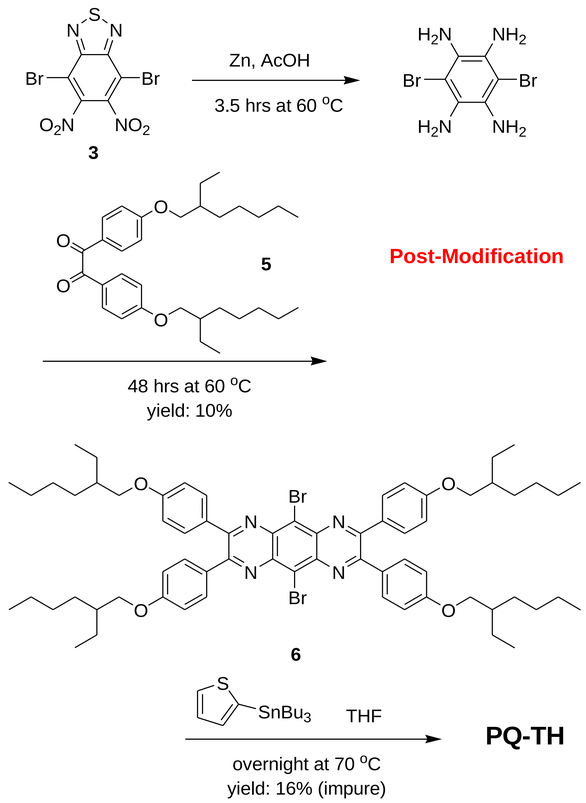
- Pyrazinoquinoxaline (PQ) is acceptor component that influences the LUMO level.
- Thiophene (TH) is the donor component which influences the HOMO level.
- Alkoxybenzene is used to improve solubility and contribute to molecular arrangement in the solid state.

Figure 2. Structural components of PQ-TH

Synthesis



Scheme 1. Synthesis of PQ-TH using the pre-modification route



Scheme 2. Synthesis of PQ-TH using the post-modification route

Results and Discussion

- A yield of 59% was attained using the pre-modification route and 10 % using the post-modification route
- The critical reduction and cyclization step was handled by using a modified glass frit to quickly filter zinc and limit exposure to air and by purging the reaction flask with nitrogen to remove any oxygen.
- Although the post-modification route offers flexibility in structural modification it poses three problems: (1) the electron withdrawing bromine reduces reactivity towards cyclization. (2) There is no color change during the reduction portion to indicate the reaction is finished. (3) Checking the reaction progress via TLC is difficult because of the air sensitive tetraamine benzene intermediate.
- The compounds were characterized using ^{1}H NMR spectroscopy.

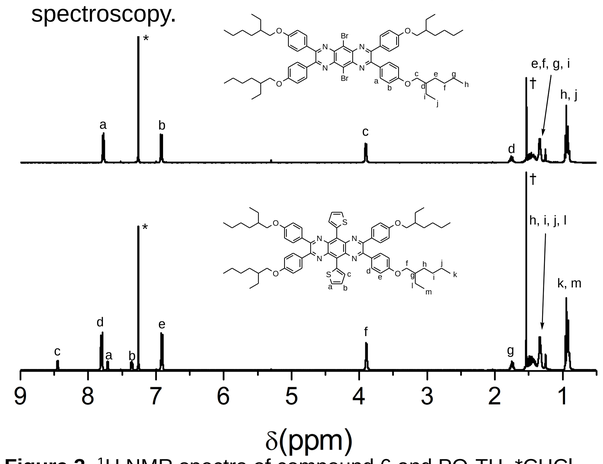


Figure 3. ^{1}H NMR spectra of compound 6 and PQ-TH. *$CHCl_3$ impurity in $CDCl_3$. †H_2O impurity in $CDCl_3$.

Conclusion and Future Work

An optimum reaction condition was established for the pre-modification route; however, an optimum reaction condition for the post-modification route was not established. If the reaction condition for the post-modification route cannot be optimized, stepwise cyclization could be a solution. The establishment of an optimum reaction condition will provide a more efficient and cost-effective synthetic process for structurally modifying this compound in the future.

Acknowledgements

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