Synthesis of Rubrene Derivatives

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Background

- Rubrene is an organic molecule that has long been known for its outstanding semiconductor performance in organic electronic devices.
- Advantages of organic electronic devices include ease of production, low cost and flexibility.
- An application of organic semiconductors is their use in organic photovoltaic devices.
- We are examining the steric and electronic effects of substituted rubrenes on OPV performance.
- In this work, previously known rubrenes 2, 3 and 4 were synthesized as well as unknown rubrene 5.

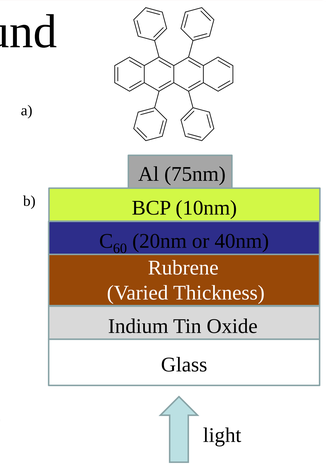


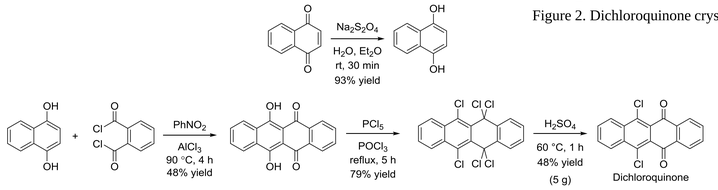
Figure 1. a) Molecular structure of rubrene **1**; b) Diagram of an organic photovoltaic device.

- Braga, D.; Horowitz, G. *Adv. Mater.* **2009**, 21, 1473–1486.
- Saeki, A.; Koizumi, Y.; Zida, T.; Seki, S. *Acc. Chem. Res.* **2012**, 45, 1193–1202.
- Hains, A. W.; Liang, Z.; Woodhouse, M. A.; Gregg, B. A. *Chem. Rev.* **2010**, *110*, 6689–6735.
- Image courtesy of Wade Luhman.

Synthesis of Dichloroquinone

- Our synthesis begins with the formation of dichloroquinone, which is an entry point for the derivation of the outer phenyl rings.
- This synthetic route begins with commercially available starting materials and permits large scale synthesis of the rubrene derivatives.

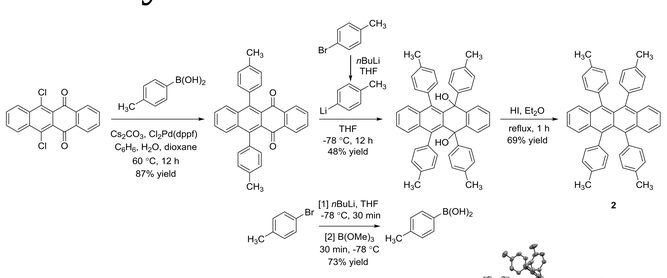
Figure 2. Dichloroquinone crystals.



Scheme 1. The synthetic pathway to the starting dichloroquinone.

- Yagodkin, E.; McGarry, K. A.; Douglas, C. J. *Org. Prep. Proc. Int.* **2011**, *43*, 360–363.
- Balodis, K. A.; Medne, R. S.; Neiland, O. Y.; Kozlova, L. M.; Klyavinya, Z. P.; Mazheika, I. B.; Gaukhman, A. P. *Zh. Org. Khim.* **1985**, *21*, 2423–2427.
- Yagodkin, E.; Xia, Y.; Kalihari, V.; Frisbie, C. D.; Douglas, C. J. *J. Phys. Chem.* C **2009**, *113*, 16544–16548.

Synthesis of Rubrene 2



Scheme 2. The synthesis of rubrene **2**.

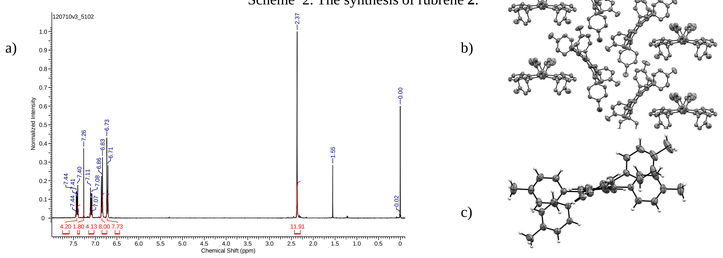
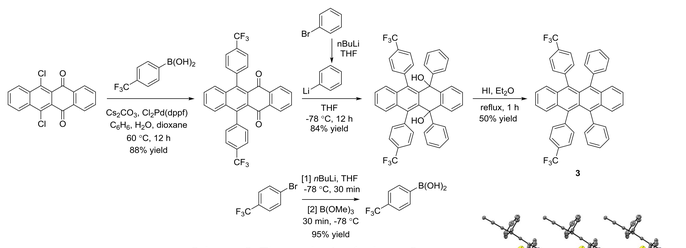


Figure 3. a) ^{1}H NMR spectrum of rubrene **2**; b) Packing structure of rubrene **2**; c) Image of twisted tetracene core.

Synthesis of Rubrene 3



Scheme 3. The synthesis of rubrene **3**.

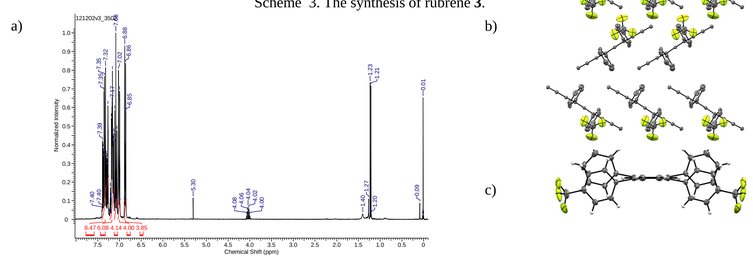
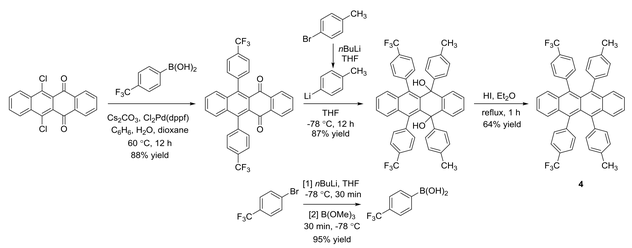


Figure 4. a) ^{1}H NMR spectrum of rubrene **3**; b) Packing structure of rubrene **3**; c) Image of planar tetracene core.

Synthesis of Rubrene 4



Scheme 4. The synthesis of rubrene **4**.

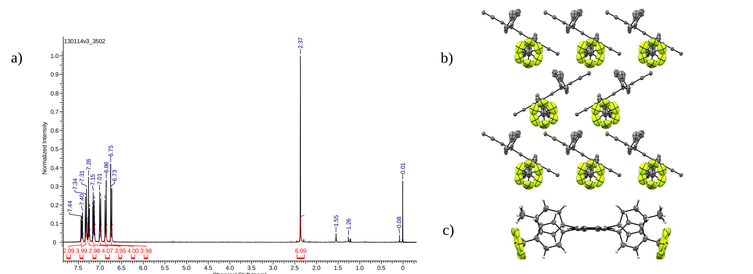


Figure 5. a) ^{1}H NMR spectrum of rubrene **4**; b) Packing structure of rubrene **4**; c) Image of planar tetracene core.

Images of Rubrenes

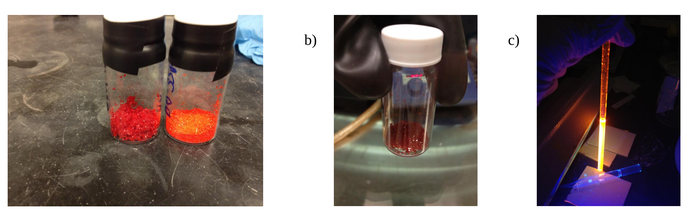
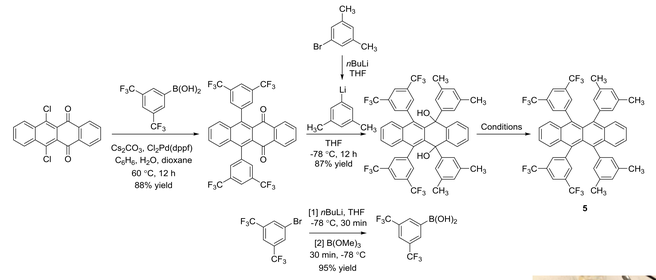


Figure 6. a) Crystals of rubrene **4** (left) next to rubrene **2** (right); b) Crystals of rubrene **3**; c) Yellow fluorescence exhibited by a solution of rubrene **5** under ultraviolent light (365 nm).

Modified Synthesis to Rubrene 5

- Rubrene 5 is a new derivative that was synthesized using a slighly modified scheme.
- The conditions previously employed in the final step were unsuccessful in reducing the diol to the rubrene. This was possibly due to the steric hindrance of the region near the diol.
- In the literature,† $SnCl_2$ is commonly used as a reducing agent for sterically hindered aromatic diols.
- Using the new conditions, the reaction was successful.



Scheme 5. The synthetic pathway to rubrene **5**.

Table 1. Conditions attempted for the last reaction.

Conditions	Outcome
HI, Et_2O, reflux, 30 min	Starting Material
HI, Et_2O, reflux, 2 hr	Starting Material
$SnCl_2$, HCl, THF, rt, 1 hr	Starting Material
$SnCl_2$, HCl, THF, reflux, 2 hr	Rubrene **5**, 91% crude yield

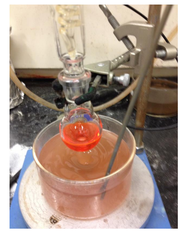


Figure 7. $SnCl_2$ reaction.

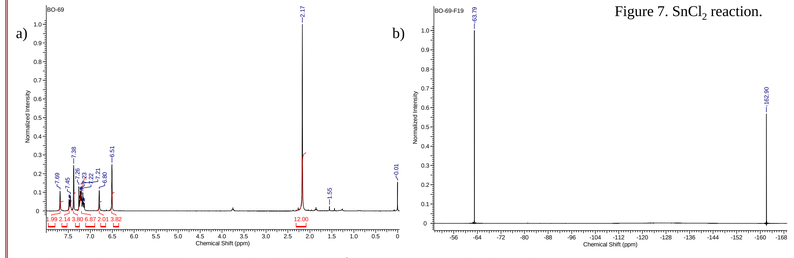


Figure 5. a) ^{1}H NMR spectrum of rubrene **5**; b) ^{19}F NMR spectrum of rubrene **5.**

†Ikeda, H.; Inoue, T.; Kondo, H.; Aromatic Compound and Organic Electroluminescent Device Using Same. U.S. Patent 2007/0106103 A1. May 10, 2007.

Future Work

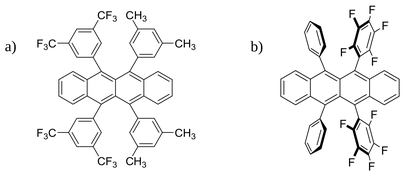


Figure 8. a) Rubrene **5**; b) Molecular structure of future target rubrene **6**.

- The crystal structure of rubrene **5** will be determined.
- Rubrene **6** with one set of rings fluorinated will be synthesised.
- Rubrenes **2**, **3** and **4** will be studied by ultrafast spectroscopy to examine exciton dynamics important in OPVs.

Acknowledgements

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