Para-Substituted Methoxyphenyl Carbenium: Synthesis, Properties and Applications

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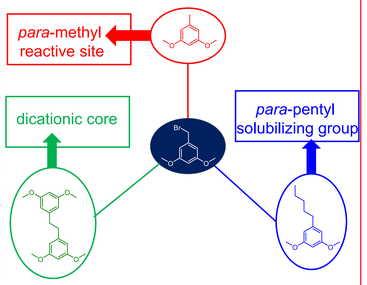
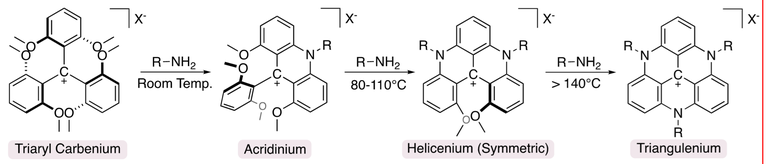
Abstract

We report the synthesis of novel methoxyphenyl carbenium derivatives having different substituents on the *para* position. This enables studying the effect of the more challenging substitution at the *para*-carbons of these molecules on their photophysical and electrochemical properties, as well as their solubilities and the reactivity of the *para*-alkyl substituent. We also report the synthesis of a dicationic molecule with an aliphatic ethylene linker group using the same starting material under different reaction conditions. The latter has an unusual tendency to get oxidized at the ethylene bridge which is promising for various redox applications. Herein, we report the synthesis and properties of these new carbenium molecules.



Stable Carbenium

- **Stable carbocations!**



Scheme 1. Typical synthesis of stable triaryl carbenium ions.

- **Challenges: *para*-position functionalization: *meta*-position is the typical reactive site.**

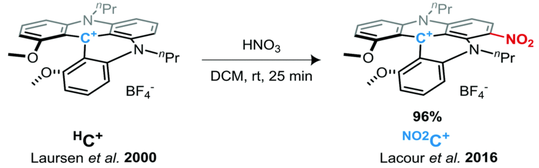


Figure 1. Typical reactive sites illustration.

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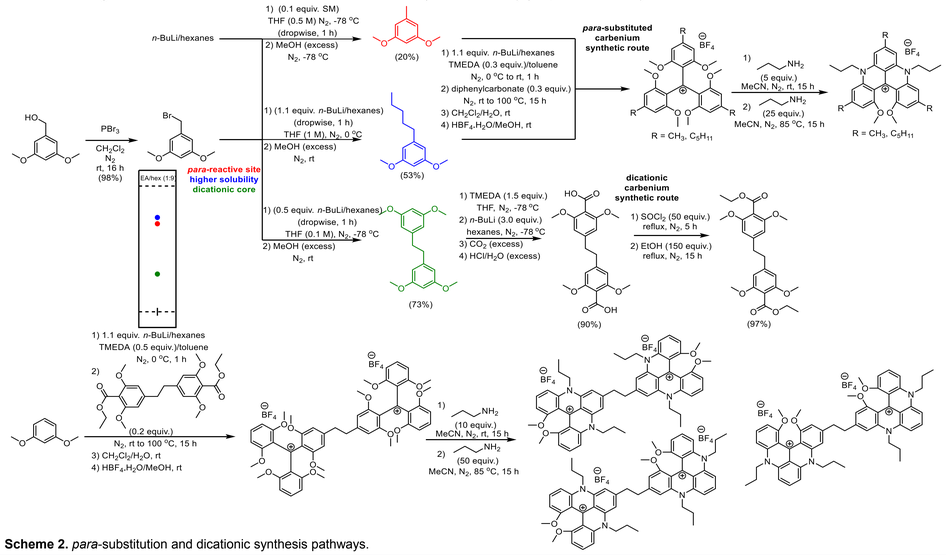
Multiple Targets From Same SM

- Multiple target molecules in fair yields from readily available (3,5-dimethoxyphenyl)methanol (Scheme 2).
- Target molecules confirmed by NMR and HRMS. Selectivity dictated by temperature, concentration, stoichiometry, and order of reagent addition in the *n*-BuLi reaction with 1-(bromomethyl)-3,5-dimethoxybenzene.



Scheme 2. *para*-substitution and dicationic synthesis pathways.

Photophysical Data

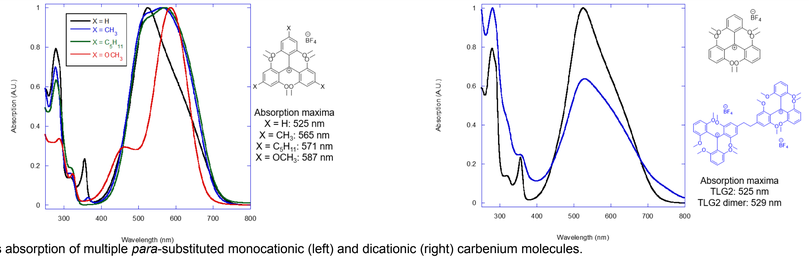


Figure 2. UV-Vis absorption of multiple *para*-substituted monocationic (left) and dicationic (right) carbenium molecules.

Potential Applications

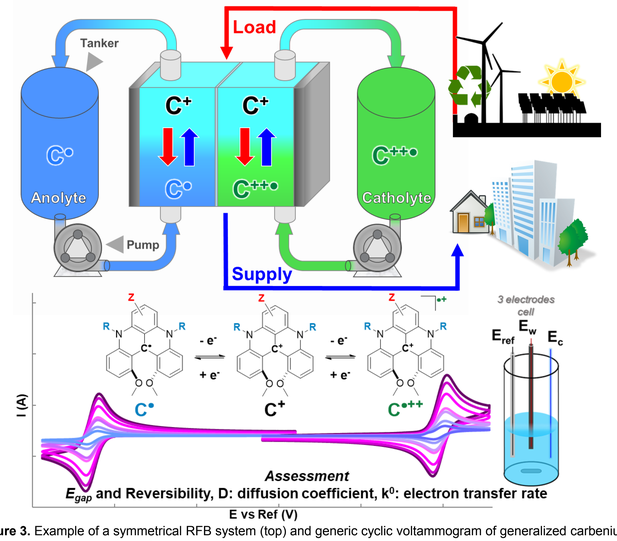


Figure 3. Example of a symmetrical RFB system (top) and generic cyclic voltammogram of generalized carbenium ion complex and a depiction of experimental setup (bottom).

- Moutet, J.; Veleta, J. M.; Gianetti, T. L. *ACS Appl. Energy Mater.* **2021**, *4* (1), 9–14.
- Moutet, J.; El-Assaad, T. H.; Kaur, R.; Mills, D. D.; Gianetti, T. L. *Energy Mater.* **2024** (DOI: 10.20517/energymater.2023.92).

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