

# **Mono- and diradicals derived from dihydrobenzo[e][1,2,4]triazin-4-yl**

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## **Doctoral Dissertation abstract**

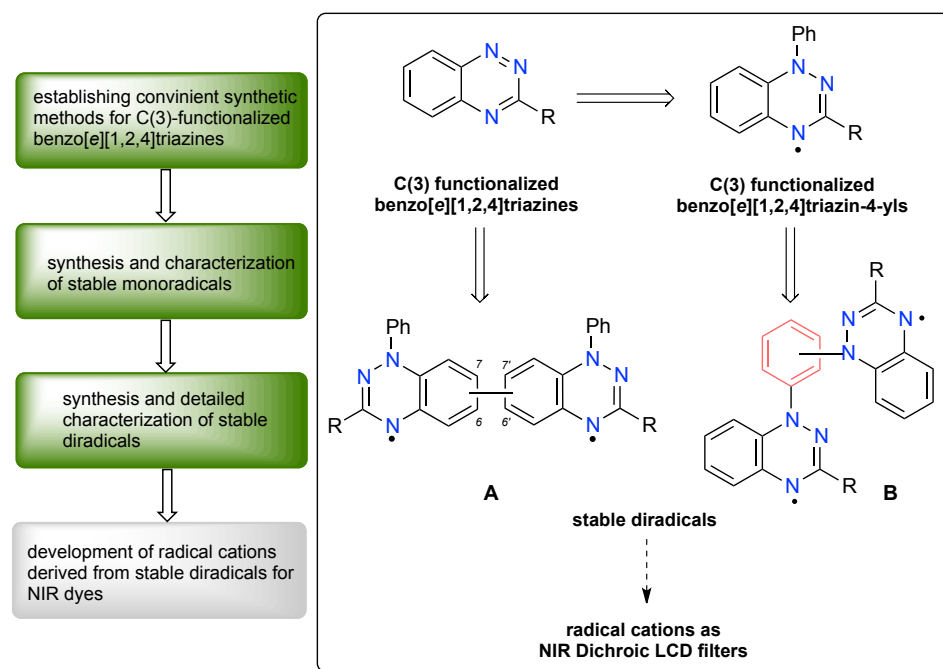
Recent years witness a rapid growth of interest in open-shell organic species for fundamental and applied studies. Such systems exhibit semiconductive properties, which are applicable in areas such as optoelectronic or sensors, and constitute attractive building blocks for magnetic materials employed *e.g.* as spin filters. In this context, stable heterocyclic diradicals based on the benzo[e][1,2,4]triazin-4-yl are of particular interest. Various connections of two paramagnetic units can lead to either a closed-shell Kekulé resonance structure with the preference for a singlet ground state (referred to as diradicaloids) or non-Kekulé molecules, which can exhibit a triplet ground state.

During the last five years, there has been a significant development in the design, characterization and synthesis of diradicals and diradicaloids incorporating the Blatter radical. However many of these derivatives exhibit limited stability and their synthetic access is still cumbersome. Stable diradicals based on the benzo[e][1,2,4]triazin-4-yl are also attractive building blocks for the preparation of paramagnetic liquid crystals and near-infrared dichroic dyes. Therefore, further development of methods allowing for convenient and effective preparation of stable Blatter diradicals as well as understanding of the properties of such species opens up access to a wide range of applications in functional materials and constitutes a significant part of this Doctoral Dissertation.

The presented Dissertation is part of a broad project aimed at developing access to a new class of near-IR dichroic dyes. Stable diradicals incorporating the benzo[e][1,2,4]triazin-4-yl are envisioned to be suitable precursors to radical cations with substituent-tunable absorption in the NIR region, and which are compatible with LC matrix and exhibit high dichroic ratio. This approach is a response for a rapidly growing interest in diradicals as NIR dyes, and overcomes problems *e.g.* low chemical stability and incompatibility with the liquid crystal host which characterizes already investigated systems.

The development of synthetic access to new classes of mono- and diradicals based on the benzo[e][1,2,4]triazin-4-yl and comprehensive analysis of their structure-property relationships

(Figure 1.1.) constitute key steps enabling achieving the ultimate goal and is the main focus of this Doctoral Dissertation. Establishing convenient synthetic methods for a series of C(3)-functionalized benzo[*e*][1,2,4]triazines, gave rise to simple preparation of variety of stable monoradicals incorporating benzo[*e*][1,2,4]triazin-4-yl. Developed synthetic pathways and acquired skills for characterization of such species by spectroscopic and electrochemical methods allowed for understanding structure–property relationships in this class of compounds. These findings constitute a tool for a rational design and preparation of stable diradicals connected either directly (type **A**) or through a  $\pi$ -spacer (type **B**) with properties suitable for application in functional materials (Figure 1.1.). One-electron oxidation of appropriately functionalized diradicals will provide radical cations with substituent-tunable absorption in the NIR region and which are compatible with LC matrix and exhibit high dichroic ratio.



**Figure 1.1.** A graphical representation of the goals and scope of this Dissertation.

The Introduction discusses the properties of heterocyclic stable organic radicals, with a particular emphasis on mono- and diradicals based on the benzo[*e*][1,2,4]triazin-4-yl, as well as the main techniques for studies of magnetic properties. In Section 4.2.2. the general design of high-spin molecules is discussed, which has been used in the rational development of diradicals based on the benzo[*e*][1,2,4]triazin-4-yl unit and exhibiting either the triplet ground state or a thermally populated triplet state. Section 4.2.5. describes the current state-of-the-art in the field of

stable diradicals based on the benzo[*e*][1,2,4]triazin-4-yl reported to date. This part provides an important point of reference for my accomplishments in this area.

The Result and Discussion part of this Dissertation is initially focused on the development of methods for synthesis of C(3)-functionalized benzo[*e*][1,2,4]triazines and benzo[*e*][1,2,4]triazin-4-yls, and understanding of their properties. Section 6.1 provides a brief description of a facile access to a series of structurally diverse C(3)-substituted derivatives of the benzo[*e*][1,2,4]triazine, which are readily available directly from the 3-chloro or 3-iodobenzo[*e*][1,2,4]triazines. In Section 6.2 the synthesis and characterization of a series of C(3)-functionalized derivatives of the Blatter radical obtained by a new synthetic method are described. This method utilizes the cyclization of *N*-substituted guanidines and amidines leading to the formation of the C(3)-amino and C(3)-alkyl benzo[*e*][1,2,4]triazines respectively and followed by addition of phenyllithium to permit the facile access to a series of benzo[*e*][1,2,4]triazin-4-yls. The presented methodology allows to avoid multistep procedures with poorly soluble intermediates. Section 6.3. contains a description of preparation of a series of C(3)-substituted benzo[*e*][1,2,4]triazin-4-yl radicals by addition of PhLi to benzo[*e*][1,2,4]triazines obtained *via* methodology presented in Section 6.1. As a result, convenient access to a series of C(3)-functionalized derivatives of the Blatter radical was developed and the synthetic limitations of these methods were determined. Detailed characterization of the resulting benzo[*e*][1,2,4]triazin-4-yls by spectroscopic (UV-vis, EPR) and electrochemical (Cyclic Voltammetry) methods was performed. A brief description of these accomplishments is located in Sections 6.1. and 6.2. and 6.3, and details are provided in enclosed publications (Chapter 9).

The last two Sections concern with the synthesis, physicochemical and magnetic studies of a series of stable diradicals based on the benzo[*e*][1,2,4]triazin-4-yl. The first contains a detailed description of the synthesis and investigation of a series of regioisomers of di-Blatter diradicals with controlled electronic and magnetic properties connected through the spin rich positions C(6) and C(7) of the benzo[*e*][1,2,4]triazin-4-yl core. The last section of this Dissertation presents two di-Blatter diradicals connected through a spin-coupler at the N(1) position. Access to these derivatives was possible through an effective, one-step addition of dilithio derivatives to the 3-trifluoromethylbenzo[*e*][1,2,4]triazine. These diradicals are the first examples of a potentially broad class of symmetric high-spin molecules with a controlled singlet-triplet gap.