

# Polymeric Blatter's Radical via CuAAC and ROMP

Adrian Saal, Christian Friebe, and Ulrich S. Schubert\*

A Blatter radical-containing polymer backbone is synthesized via copper-catalyzed azide-alkyne cycloaddition (CuAAC) and consecutive ring-opening metathesis polymerization. For this, an alkyne-functionalized Blatter radical is synthesized and used for the described CuAAC, yielding a polymerizable derivative of the radical. The resulting polymer is electrochemically investigated in cyclic voltammetry experiments, paving the way for the possible utilization of triazinyl radicals in all-organic polymer batteries. Furthermore, the simple modification of the alkyne bond makes further derivatization easily accessible.

## 1. Introduction

Benzo[1,2,4]triazinyl radicals, also called Blatter radicals, were first described by H. Blatter in 1968.<sup>[1]</sup> This type of radicals stands out for its exceptional stability and interesting electrochemical and magnetic properties.<sup>[2]</sup> Recently, more and more potential applications have been investigated, such as in photodetectors,<sup>[3]</sup> as ligands in coordination chemistry,<sup>[4]</sup> as polymerization mediators,<sup>[5]</sup> and as active units in organic batteries.<sup>[6]</sup> During the last decade, the traditional synthetic routes were drastically improved, making the integration of fused rings,<sup>[2d,7]</sup> planar structures of the radical,<sup>[8]</sup> and several functional groups accessible.<sup>[9]</sup>

In this work, the polymeric Blatter radical **1** is presented. The monomer was synthesized via a new derivative of the 1,2,4-benzotriazinyl radicals, which was functionalized with an alkyne group at the benzene ring in C3-position. This structure can easily be modified under mild conditions using copper-catalyzed azide-alkyne cycloaddition (CuAAC) “click”-reactions, which was done to access the norbornene-containing monomer (**Scheme 1**). Norbornene was chosen for the polymerizable group, as radical polymerizations do not work with radical monomers and

Blatter's radical has been proven to work as a polymerization mediator.<sup>[5]</sup>

## 2. Results and Discussion

### 2.1. Monomer Synthesis

The synthesis of **3** was adapted from Savva et al., who introduced a route to Blatter radicals via Aza-Wittig chemistry.<sup>[10]</sup> In the first step, triisopropyl-silyl (TIPS)-protected acetylene is introduced to the bromo-substituted hydrazide **4** via a Sonogashira cross-coupling reaction (**Scheme 2**).

The reaction is carried out similarly to the common procedure. However, washing with water partly leads to a decomposition of the desired product.<sup>[11]</sup> Furthermore, **5** has to be purified with the help of diol-functionalized silica gel, as hydrazides were found to be in general unstable on unfunctionalized silica.

To avoid the use of mercury compounds for the oxidation to the diazene **6**, as it was described by Savva et al., a straightforward, more gentle method is applied. By using a two-phase mixture of basic, aqueous  $K_3Fe(CN)_6$  as oxidation agent and dichloromethane, the desired product is obtained quantitatively, without further need of purification.<sup>[12]</sup>

To avoid over-oxidation products in the step to the radical, the  $CF_3$ -group was introduced to the C7-position, as non-functionalized radicals easily form benzotriazinones.<sup>[2c]</sup> The preparation of the radical **7** is done as reported by Savva et al.<sup>[10]</sup> In this case, however, the reaction time was adjusted to 45 min using reaction control with HPLC. Furthermore, a screening of different high-boiling solvents was performed to investigate a substitution of diphenylether. The latter is hard to remove from the reaction mixture due to its high boiling point and, furthermore, it elutes very similarly to the product during column chromatography. Nevertheless, all of the tested candidates (benzonitrile, bromobenzene, *N*-methyl-2-pyrrolidone, anisole) led to lower conversions and larger amounts of side products in HPLC and were found to be not suitable (see ESI). It was further tested if the alternative route by Berezin et al., with less harsh reaction conditions and potentially less side products, might be applicable.<sup>[2d]</sup> However, a complex mixture is obtained when trying to arylate **5** with 2-fluoro-1-nitro-4-(trifluoromethyl)benzene. This is attributed to the fact that the utilized base  $K_2CO_3$  is able to cleave the C-Si-bond of the protecting group in alcoholic solvents.<sup>[13]</sup>

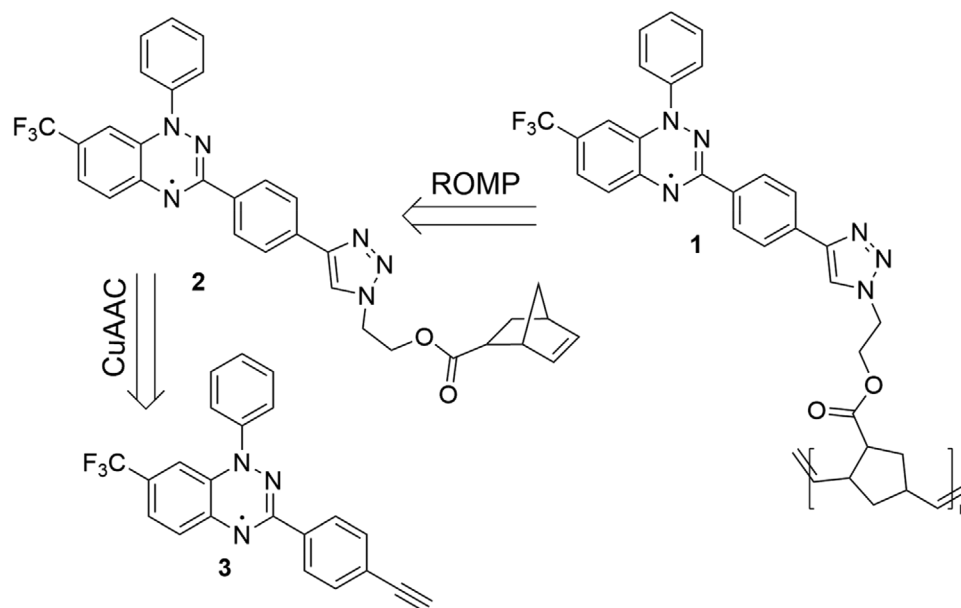
To gain the final product **3** from **7**, the TIPS protective group is removed with tetrabutylammonium fluoride. Similar to radical **7**, the product needs to be purified via column chromatography. Silica that was passivated with  $NEt_3$  revealed the most promising results, compared to diol-functionalized silica and aluminum oxide. The obtained title compound was investigated with EPR

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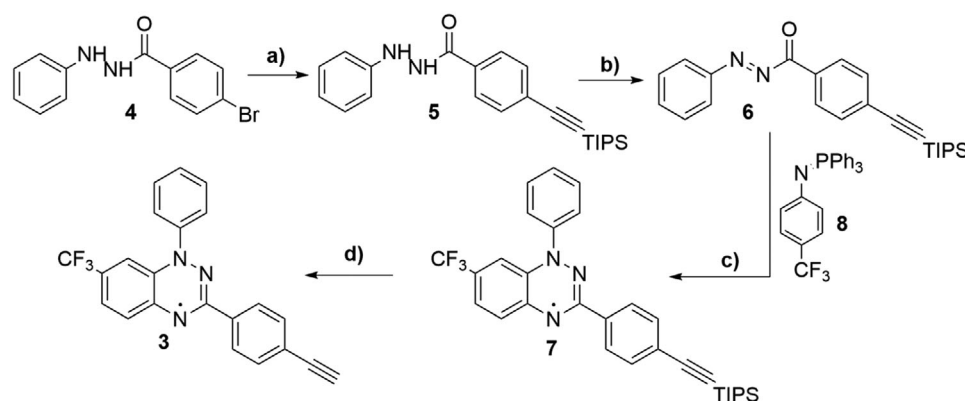
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**Scheme 1.** Schematic representation of the title compound **1**, its monomer **2**, and the alkyne-functionalized Blatter radical precursor **3**, presented in a retrosynthetic approach.



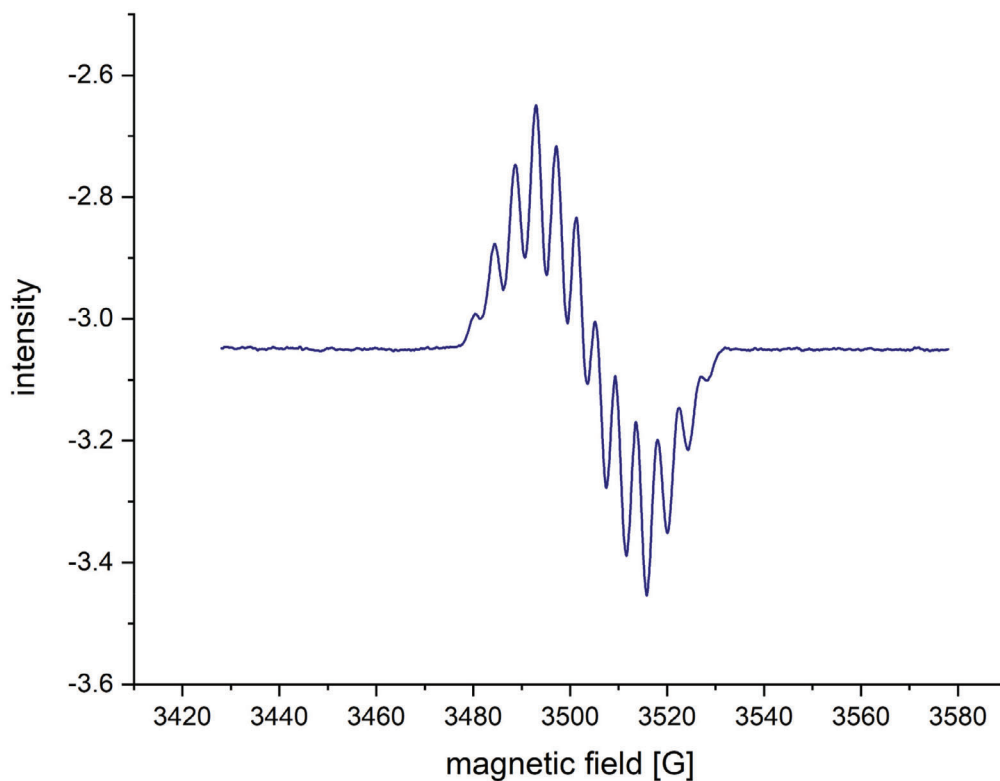
**Scheme 2.** Schematic representation of the reactions to the alkyne-functionalized Blatter radical **3**. a) TIPS-acetylene, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, PPh<sub>3</sub>, CuI, TEA/pyridine, reflux, 2 h, 72%. b) K<sub>3</sub>Fe(CN)<sub>6</sub>, CH<sub>2</sub>Cl<sub>2</sub>/2 M aq. NaOH, r.t., 5 min, 98%. c) Ph<sub>2</sub>O, 200 °C, 45 min, 44%. d) Bu<sub>4</sub>NF, THF, r.t., 10 min, 77%.

spectroscopy (**Figure 1**) and cyclic voltammetry (CV) (**Figure S35**, Supporting Information). The EPR spectrum displays seven signals and a *g*-factor of 2.004, in accordance with other EPR studies of trifluoromethyl-functionalized Blatter radicals.<sup>[2c,14]</sup>

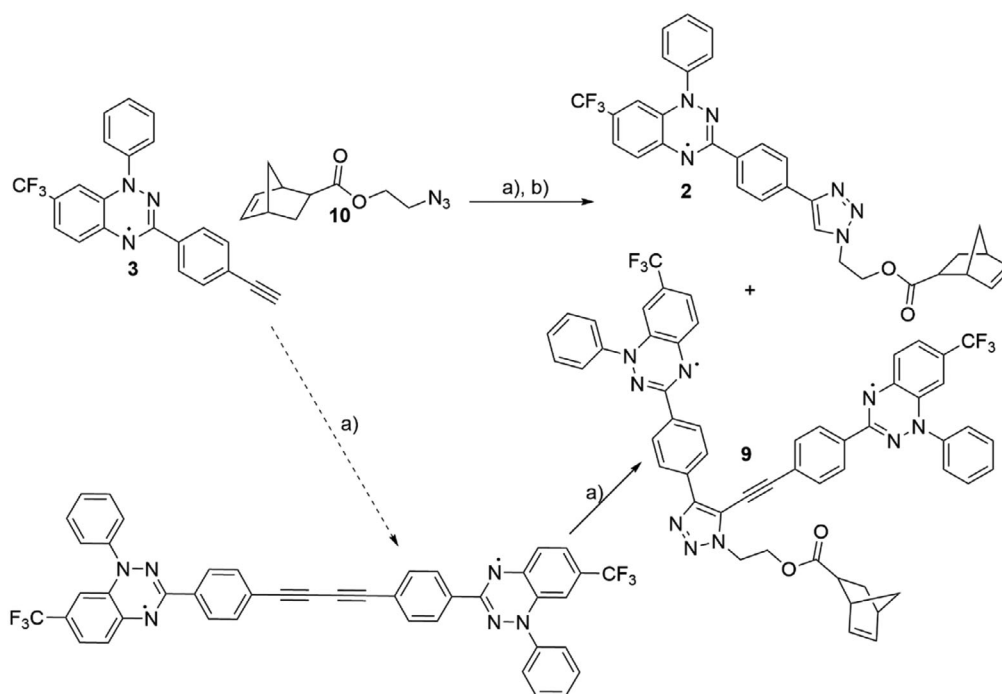
The obtained alkyne-functionalized radical is able to undergo copper-catalyzed cycloaddition reactions with different molecules. In the first experiments, it was coupled to a poly(methacrylate) backbone in a polymer-analogous reaction. The success of the reaction was confirmed by UV-vis spectroscopy of the polymer (**Figure S22**, Supporting Information) and the comparison of UV detector signals in SEC (**Figures S39** and **S40**, Supporting Information). However, no complete conversion of the reaction was observed, as leftover starting material could be isolated from the reaction mixture. Thus, a different approach was chosen. The radical was coupled to an azide-containing norbornene structure **10** to receive a polymerizable radical monomer **2** (**Scheme 3**). This monomer was polymerized

with a Grubbs 3<sup>rd</sup> gen. catalyst in a ring-opening metathesis polymerization (ROMP) to obtain the reported 1,2,4-benzotriazinyl radical polymer **1**. The polymer shows distinct signals in CV measurements, revealing two (quasi)-reversible redox processes ( $E_1 = -0.03$  V and  $E_2 = -1.10$  V vs Fc<sup>+</sup>/Fc) (**Figure 2**). The quasi-reversible behavior of the oxidation reaction at  $-0.03$  V might occur from adsorption processes on the working electrode, as the solubility of the charged species should be decreased in CH<sub>2</sub>Cl<sub>2</sub>. When working with electrode films of insoluble polymer, this issue should be mitigated.

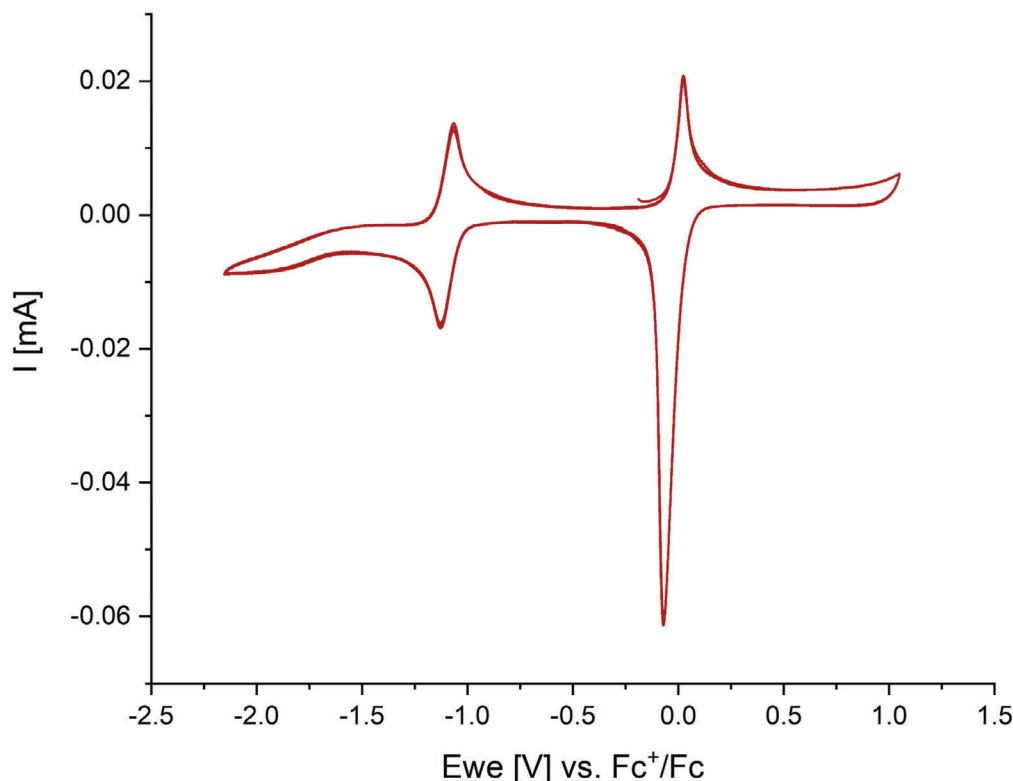
When CuBr was used in the cycloaddition reaction of **3** and **10**, a side product (**9**) was isolated (**Scheme 3**). The side product is an adduct of a Glaser-type oxidative coupling between the alkyne bonds of two molecules **3** and a further CuAAC at one of the internal triple bonds. The intermediate product is most likely produced due to partial oxidation of the Cu(I) to Cu(II) prior to the reaction. This side reaction is prevented by utilizing a Cu(II) salt



**Figure 1.** EPR spectrum of **3**. Measured in a 1 mm solution in deoxygenated  $\text{CH}_2\text{Cl}_2$ .



**Scheme 3.** Schematic representation of the CuAAC of **3**. a)  $\text{CuBr}$ , PMDETA, DMF, Ar, r.t., overnight, 53% of **2**, 20% of **9**. b)  $\text{Cu(II)SO}_4 \cdot 5\text{H}_2\text{O}$ , sodium ascorbate, THF/ $\text{H}_2\text{O}$  5:1, Ar, 60 °C, overnight, 76% of **2**, 0% of **9**.



**Figure 2.** Cyclic voltammetry of **1** (2 mM solution of **1** in 0.1 M  $\text{Bu}_4\text{NClO}_4$  in  $\text{CH}_2\text{Cl}_2$ , vs  $\text{Fc}^+/\text{Fc}$ , scan rate  $125 \text{ mV s}^{-1}$ ).

and an excess of sodium ascorbate as an in situ reducing agent. Under these reaction conditions, the radical is partially reduced to the leuco-form but can easily be reconverted to the radical by oxidation in air in the presence of alkali.

### 3. Conclusion

In summary, an electrochemically active polymer was synthesized with the help of an alkyne-functionalized Blatter radical as a building block. A norbornene group was introduced to the 1,2,4-triazinyl radical via a CuAAC and furthermore polymerized to yield the title substance. Due to the stability of this class of radicals, the promising results in CV experiments, and the amphoteric nature of the radical, the described polymer might be applicable as an active material in organic thin-film batteries, where it could act as both anode and cathode material. For this, further optimization is necessary, for example cross-linking and the construction of proper electrodes. In our opinion, the CuAAC “click” reaction is, in particular, promising for further functionalization of the radical as it is a straightforward and mild reaction, applicable to a broad spectrum of substances. These results hint towards versatile synthetic possibilities of the alkyne-functionalized Blatter radical and open pathways to new derivatives of this radical class.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Keywords

alkyne-functionalized triazinyl radicals, Blatter radicals, copper-catalyzed azide-alkyne cycloaddition, electrochemical investigations, polymer batteries

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