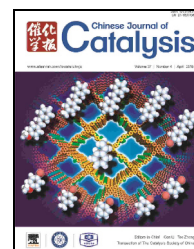


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## Article

# Synthesis of nitrocarbazole compounds and their electrocatalytic oxidation of alcohol



Yinghong Zhu, Jianqing Zhang, Ziyang Chen, Anlun Zhang, Chunan Ma\*

State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, Zhejiang, China

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## ABSTRACT

Three compounds with nitrocarbazole frameworks were synthesized and their electrochemical reversibility as organic electrocatalysts was studied by cyclic voltammetry. The electrochemical reversibility and oxidation-reduction potential of the compounds were greatly affected by their substituents. The oxidation-reduction potential of the compound with an electron-donating group was negative, while that of the compound with an electron-withdrawing group on the carbazole framework was positive. The electrocatalytic oxidation activities of the nitrocarbazole compounds were investigated through cyclic voltammetry and controlled potential electrolysis at room temperature. The electrocatalysts showed excellent selectivity for *p*-methoxybenzyl alcohol, converting it to the corresponding aldehyde through electro-oxidation with just 2.5 mol% of the electrocatalysts presented. The electrocatalysts maintained their excellent electroredox activity following recycling.

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## 1. Introduction

The catalytic oxidation of small organic molecules is an important research area in the field of catalysis. Selective oxidation of alcohols to the corresponding aldehydes and ketones is important in the synthesis of fine chemicals and organic intermediates [1,2]. Many catalysts with high selectivity, stability and low cost have been developed to improve the conversion and selectivity in the oxidation of alcohols to the corresponding aldehydes. For instance, gold-copper bimetallic catalysts [3], and nitrogen-doped carbon nanosphere-supported palladium catalysts [4] have been prepared and used in the catalytic oxidation of benzyl alcohol. Jia et al. [5] reported the selective oxidation of benzyl alcohol to benzaldehyde using alkali-treated ZSM-5 zeolite as a catalyst and H<sub>2</sub>O<sub>2</sub> as an oxidant. Many re-

searchers have also devoted effort to the study of organic catalysts. For example, the organic sulfonate [6], immobilized 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) [7] and Lewis acid-activated TEMPO have been studied as catalysts for the oxidation of alcohol. These approaches are limited by the use of either noble metals or high temperature.

Organic electrocatalysis is recognized as an environmentally compatible methodology because it avoids using toxic and dangerous oxidizing or reducing reagents, and most of the reactions can be carried out under mild conditions [9,10]. However, in direct electro-oxidation synthesis, the working electrode is easily passivated by the formation of a polymer film on the electrode surface, which can sharply decrease current efficiency. Indirect electro-oxidation with an electron transfer mediator is a good way to avoid passivation of the electrode

\* Corresponding author. Tel/Fax: +86-571-88320830; E-mail: [science@zjut.edu.cn](mailto:science@zjut.edu.cn)

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[11,12]. Triarylamines have received extensive attention from researchers as a new type of electro-redox mediator because of their broad range of redox potentials. The oxidation potential of triarylamines can become positive after introduction of an electron-withdrawing group [13–18]. Compared with the triaryamine framework, the carbazole framework has better planarity and the substituents have a greater effect on the redox properties [19]. Carbazole compounds have been widely used as fluorescent materials [20], but have not been employed as an electro-redox mediator in electrocatalytic oxidation, especially carbazole compounds with nitro groups. Based on the intrinsic properties of the carbazole framework and strong electron-withdrawing nature of nitro groups, in this paper, nitrocarbazole compounds were synthesized and used as organic electrocatalysts in the mediated electro-oxidation of alcohols at room temperature.

## 2. Experimental

### 2.1. Preparation of the organic electrocatalysts [21–25]

The route used to synthesize carbazole compounds with different substituents is shown in Scheme 1.

3,6-Dibromo-9H-carbazole (**1**), a solution of *N*-bromosuccinimide (0.21 mol) in DMF (80 mL) was slowly added to a solution of carbazole (0.1 mol) in DMF (20 mL) in an ice bath. After reaction for 30 min, the mixture was poured into ice water (1 L), and the crude product was collected by filtration to give a blue powder. Recrystallization from EtOH/H<sub>2</sub>O afforded blue crystals with a yield of 68%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.14 (d, *J* = 1.9 Hz, 2H), 8.12 (s, 1H), 7.53 (d, *J* = 8.6, 1.9 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H).

3,6-Dimethoxycarbazole (**2**), in a 100-mL three-necked flask, a solution of sodium methoxide (0.1 mol) in methanol (15 mL) was stirred at room temperature for 30 min. CuI (0.02 mol), **1** (0.005 mol), and DMF (17 mL) were added and then the mixture was heated under reflux for 8 h under N<sub>2</sub> atmosphere. The solution was filtered while hot to remove CuI and the filtrate was poured into stirred water (1 L). The resulting precipitate was collected by filtration, washed thoroughly with water, and dried to afford a black powder in a yield of 88%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 3.95 (s, 6H, –OCH<sub>3</sub>), 7.00 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 7.53 (s, 2H), 7.79 (s, 1H, –NH).

**3a–3c**, a 100-mL two-necked flask equipped with a reflux condenser was charged with a carbazole compound with a –OCH<sub>3</sub>, H or Br substituent (15.3 mmol), K<sub>2</sub>CO<sub>3</sub> (76.52 mmol), *p*-nitrofluorobenzene (61.4 mmol), and DMF (80 mL). Each reaction mixture was heated under reflux for 12 h, cooled, and then poured into water (500 mL). Each precipitate was filtered, dried, and recrystallized.

**3a**, orange powder, yield 66%. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 8.47 (d, *J* = 8.6 Hz, 2H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.87 (d, 2H), 7.52 (d, *J* = 8.9 Hz, 2H), 7.08 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 6H).

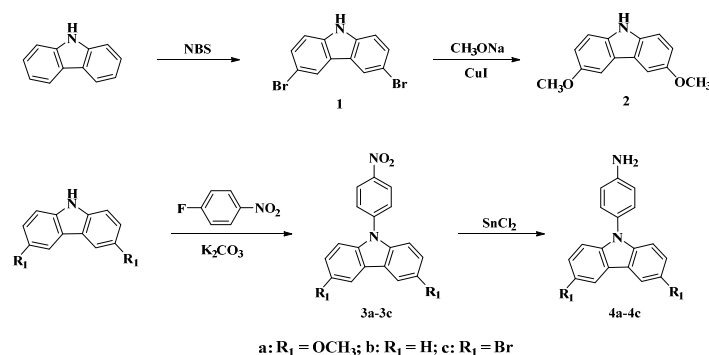
**3b**, bright yellow powder, yield 66%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.48 (d, *J* = 9.0 Hz, 2H), 8.14 (d, *J* = 7.8 Hz, 2H), 7.8 (d, *J* = 9.0 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.46–7.43 (m, 2H), 7.35–7.33 (m, 2H).

**3c**, bright yellow powder, yield 81%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.57–8.47 (m, 2H), 8.23 (d, *J* = 1.9 Hz, 2H), 7.79–7.71 (m, 2H), 7.57 (d, *J* = 8.7, 2.0 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H).

4-(3,6-Dimethoxy-9H-carbazol-9-yl)aniline (**4a**), **3a** (0.41 mmol) was dissolved in ethanol (30 mL), and then SnCl<sub>2</sub>·2H<sub>2</sub>O (2.80 mmol) was added. The reaction mixture was heated under reflux for 15 h and then cooled to room temperature. Subsequently, the reaction mixture was adjusted to basic pH with saturated NaHCO<sub>3</sub>, and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The residue was purified by silica-gel column chromatography to afford an orange powder in a yield of 75%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.57 (d, *J* = 2.4 Hz, 2H), 7.33–7.23 (m, 4H), 7.09–7.01 (m, 2H), 6.90–6.79 (m, 2H), 3.96 (s, 6H), 3.85 (s, 2H).

4-(9H-Carbazol-9-yl)aniline (**4b**), compound **3b** (0.09 mol), 10% Pd/C (0.103 g) and ethanol (20 mL) were added to a 50-mL round-bottom flask equipped with a stirring bar. The reaction mixture was heated under reflux. Hydrazine monohydrate (3 mL) was added slowly to the mixture, and then the solution was stirred under reflux for 10 h. The solution was cooled to room temperature, filtered to remove Pd/C, and then concentrated to afford a light brown viscous liquid in a yield of 80%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.34–7.26 (m, 6H), 6.88–6.87 (m, 2H), 3.83 (s, 2H).

4-(3,6-Dibromo-9H-carbazol-9-yl)aniline (**4c**), compound **4c** was synthesized according the method used to prepare **4a**



Scheme 1. Synthesis of the organic electrocatalysts.

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