

Electrochemical Study of the Hydrogen Evolution Reaction using Copper(II) Thiacalix[4]arene-based Catalyst

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Summary: Despite the interesting structure of the generic thiacalix[4]arene containing four coordinating sulfur atoms bridging four phenolic units, there are only a few reported examples of thiacalixarene-based coordination complexes that are used as electrocatalysts. Herein, we report electrocatalytic hydrogen evolution reaction (HER) by a thiacalix[4]arene-based copper(II) complex (I). As expected, two reduction waves were appeared (-0.48 V and -1.30 V vs Ag/AgCl) for Cu²⁺/Cu⁺ and Cu⁺/Cu reduction couples. The HER by proton reduction occurs at -1.03 V with a shift of 0.27 V compared to the second peak potential at -1.30 V. The increase in the number of acetic acid equivalents, from 0 to 17.5 with a frequency of 2.5 eq, was accompanied by an increase in the peak current that reached a maximum value of 183 μA for 15 equivalents of acetic acid.

Keywords: Thiacalix[4]arene, Copper compound, Electrocatalysis, Hydrogen evolution reaction, Cyclic voltammetry.

Introduction

Calix[4]arene (C4A) and its S-containing counterpart thiacalix[4]arene (TC4A) are promising platforms because of the presence of a molecular cavity with four functionalizable sites on both upper and/or lower rims (Fig. 1) [1]. For the preparation of coordination compounds, the functionalisation of C4A with coordinating donor groups is required in most cases. However, four sulfur atoms close to the phenolic units in the generic TC4A made it a powerful coordinating multi-topic ligand. The TC4A forms many transition metal complexes with interesting features and applications [2]. For example, an almost quantitative extraction of Cu(II) ion from both organic and aqueous solution at pH = 7 was reported by Iki *et al.* [3]. It is worth noting that this extraction ability gets lower for other metal ions such as Co²⁺, Ni²⁺ and Zn²⁺. As isolated compounds, Hosseini

and co-workers prepared the first coordination complex based on generic TC4A. The X-ray structure determination showed an attractive tetranuclear copper cluster capped between two TC4As where the four metals are coupled antiferromagnetically [4]. Later, the same group prepared and characterized a series of TC4A-based V(V), W(VI), Mn(II), Ni(II), and Pd(II) complexes [5]. More recently, Fuller *et al.* used the single crystal X-ray diffraction technique to determine the molecular structure of an oxo bridged Fe(III) complex.[6] The prepared complex exhibits an interesting anti-ferromagnetic coupling. To the best of our knowledge, these reported TC4A-based complexes have not been studied for hydrogen evolution reaction (HER) yet.

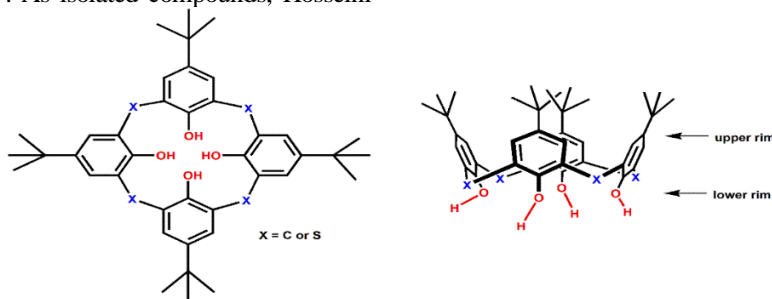


Fig. 1. The chemical structure of C4A (X = C) and TC4A (X = S).

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Hydrogen is the most abundant gas in nature that can be extracted from fossil fuels by reforming. Even though fossil fuel is a renewable natural source, its depletion level and the CO₂ release accompanied with the extraction process have urged the scientist to find alternative production techniques [7]. Therefore, a wide range of coordination compounds was used as catalysts to lower the potential value needed for the HER, e.g. water splitting and proton reduction reactions. One of the very known and powerful pre-catalyst is porphyrin [8]. It is worth mentioning that C4A and TC4A cavitand platforms may be of great interest especially for HER. However, the electrocatalytic activities of a few coordination compounds based on C4A or TC4A encapsulating noble metals such as Pt(II) were studied. For example, Wang and co-workers studied the electrochemical production of hydrogen using an ultrafine Pt nanocluster confined in a calixarene-based {Ni₂₄} coordination cluster [9]. Moreover, Zhang *et al.* studied the HER and oxygen evolution reaction (OER) in the presence of a glassy carbon electrode modified by C4A-functionalized graphene oxide composites [10]. The electrocatalytic activities of C4A molecules patterned by platinum were studied by P. Genorio and co-workers towards hydrogen oxidation and oxygen reduction [11]. Noteworthy, TC4A-based complexes free of noble metals were studied in the reaction of glucose oxidation (GOR) by Liao and co-workers. In this complex, the author suggests that the electrocatalytic reaction is performed in the confined space present in an {Ni₁₈} coordination wheel encapsulated between six TC4A units. More recently, the same research group prepared four other nickel-TC4A encapsulating {Ni₈}, {Ni₂₀}, {Ni₂₄}, or {Ni₃₂} where high electrocatalytic activity toward GOR was highlighted for the {Ni₂₀} species [12].

Herein, we study the electrocatalytic activity of a copper(II) TC4A complex for the HER by proton reduction on a glassy carbon electrode. The choice of TC4A over C4A is based on the fact that the complexes based on S-embedded ligands always showed better electrocatalytic activities [13].

Experimental

Materials

The starting materials used to prepare TC4A ligand and complex (**1**) were purchased from Afaq Sada, where the sources are either Merck or Acros organics (Table-1). Both ligand and complex were prepared according to previously reported protocols [4, 14]. The synthesized compounds were characterized, and all the analytical data were consistent with the literature data.

Electrochemical measurements

Furthermore, the prepared complex (**1**) was characterized by cyclic voltammetry at 25 °C. The solution containing 0.2 M tetrabutylammonium tetrafluoroborate, [NBu₄][BF₄] is introduced in a standard three-compartment cell with the working glassy carbon electrode (surface = 0.07 cm²), the reference Ag/AgCl electrode and platinum wire as the counter electrode. The working electrode is polished before use using emery papers of different grades, then washed with the used solvent and dried. Potentiostat (Autolab PGSTAT 128N) and NOVA 1.10 software are used for recording and processing the electrochemical data.

Results and Discussion

The reaction of the electron-rich TC4A (270 mg, 0.37 mmol) with Cu(OAc)₂ (150 mg, 0.75 mmol) in DMF in the presence of triethylamine produced the compound (**1**, scheme-1), where the analytical data are consistent with the literature [4]. The structure can be described as a tetranuclear species where the copper ions are on the corner of a twisted square sandwiched between two TC4A of cone conformation. The geometry of the metal centre is octahedral with some irregularity in both bond distances and angles. The coordination sphere contains two oxygen and one sulfur atom from each TC4A unit (Fig. 2).

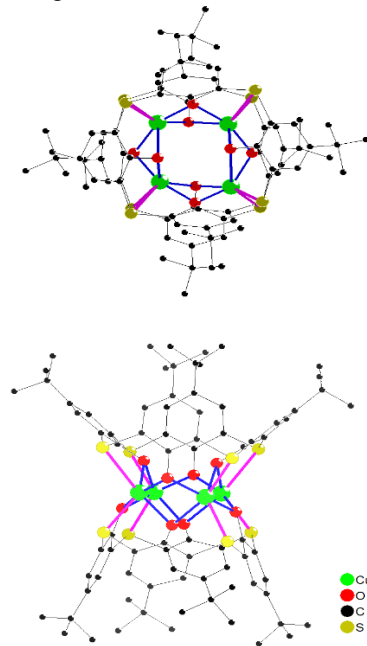
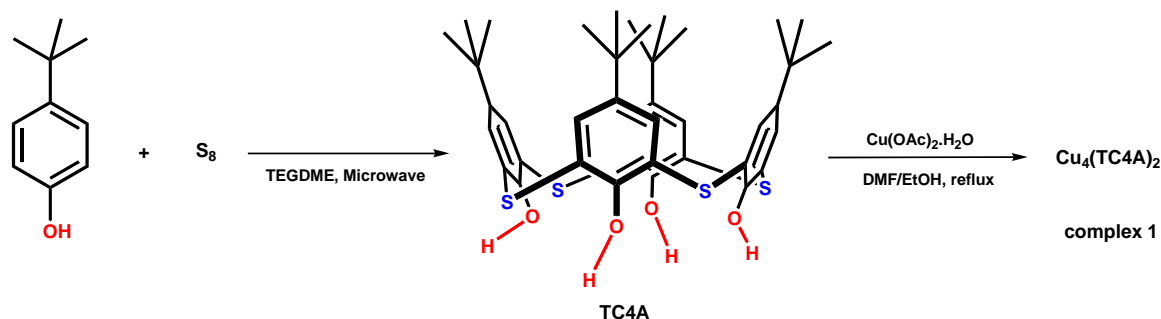


Fig. 2: Structure of Cu₄(TC₄A)₂ (**1**) (Hydrogen and Chlorine atoms are invisible). The side view structure is presented on the left. The top view structure is shown on the right. The Cu-O bond is blue, and the Cu-S bond is purple.



Scheme-1: Preparation method of TC4A and complex (1).

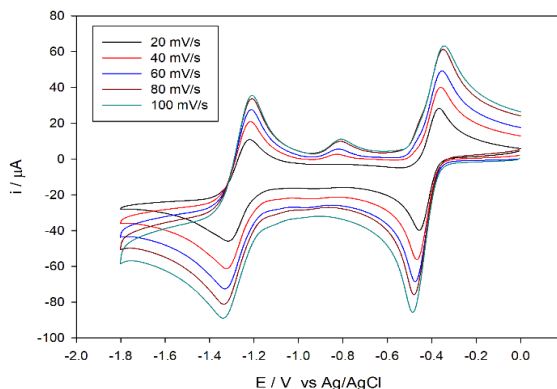


Fig. 3: Cyclic voltammetry of 2.5 mM $\text{Cu}_4(\text{TC}_4\text{A})_2$ (**1**) in DMF solution containing 0.2 M $[\text{NBu}_4][\text{BF}_4]$ at carbon electrode vs Ag/AgCl at different scan rates.

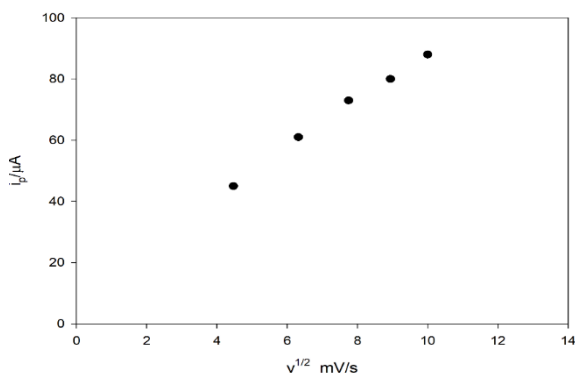


Fig. 4: The root square of the peak potential vs the peak current for 2.5 mM $\text{Cu}_4(\text{TC}_4\text{A})_2$ (**1**) in DMF solution containing 0.2 M $[\text{NBu}_4][\text{BF}_4]$ at carbon electrode vs Ag/AgCl at different scan rates.

Cyclic voltammetry was recorded at glassy carbon vs Ag/AgCl in a dimethylformamide (DMF) solution containing 2.5 mM of complex (**1**) in the presence of 0.2 M tetrabutylammonium

tetrafluoroborate, $[\text{NBu}_4][\text{BF}_4]$. The two reduction peaks for the couples $\text{Cu}^{2+}/\text{Cu}^+$ and Cu^+/Cu were observed at $E_p^{\text{red}} = -0.48$ V and -1.30 V, respectively. Contrarily, the two oxidation waves are retarded because of the resistivity and are observed at -1.22 V and -0.37 V (Fig. 3). In addition, the variation of the voltage vs current was studied at different scan rates. Under the reported work of Dylla *et al.* suggesting that $I_{\text{cap}} = A \cdot C_f \cdot v$ (where A is the surface area exposed to the electrolyte in cm^2 , C_f is the capacitance in Farads, including both double-layer capacitance, and v is the scan rate), the capacitive currents follow a linear dependence on the scan rate between 20-100 mV [15]. In addition, the root square of the scan rate shows a linear dependence on the peak currents indicating a non-absorption process at the electrode (Fig. 4). This is in accordance with the following equation of Randles–Sevcik equation:

$$I_p = - (2.69 \times 10^5) n^{3/2} C_0^{\text{bulk}} D^{1/2} v^{1/2}$$

where C_0^{bulk} is the bulk concentration in mol/cm^3 , D is the diffusion coefficient in $\text{cm}^2 \text{s}^{-1}$, v is the potential scan rate in V s^{-1} and I is the current density in A [16, 17].

The proton reduction reaction using complex (**1**) as an electrocatalyst was studied by cyclic voltammetry. The data were recorded from DMF solution containing 2.5 mM catalyst, 0.2 M $[\text{NBu}_4][\text{BF}_4]$ and the different equivalent of CH_3COOH (2.5 eq. to 17.5 eq.) as a source of the proton. The proton reduction occurs at the second peak potential (-1.30 V) with a shift of about 270 mV and an increase of peak current of about $73 \mu\text{A}$ (from $110 \mu\text{A}$ to $183 \mu\text{A}$) (Fig. 6). The free-catalyst proton reduction under the same conditions occurs at a higher peak potential of -1.85 V (Fig. 5). This result indicates that the presence of a catalyst shifts the potential of about 820 mV and increases the anodic peak current that reaches the saturation at $183 \mu\text{A}$ after adding 15 equivalent of CH_3COOH (Fig. 7). Considering the small size of both H^+ and H_2 and the presence of $\{\text{Cu}_4\}$ clusters near the cavities of the two hollow cavities, let us suggest a proton reduction reaction in the

confined space near the metal ion. These results are promising compared to reported compounds such as the well-known porphyrin or pyridoxal semthiocarbazone derivatives. Zhang *et al.* reported the electrocatalytic hydrogen evolution using the copper(II) meso-tetrakis(pentafluorophenyl)porphyrin in DMF in the presence of acetic acid as source of proton at glassy carbon *versus* Ag/AgNO₃. The hydrogen was produced at a potential of -1.36 V with a shift of 490 mV compared to the catalyst-free solution (Table-2). [18] In addition, Al-Zahrani and co-workers reported the electrocatalytic performance toward hydrogen production of two copper(II) complexes based on pyridoxal semicarbazone and thiosemicarbazone. The hydrogen production, under the same conditions used in the present work, occurred at -1.25 V for S-containing and -1.53 for O-containing copper(II) complexes. [19] Overall, the studied complex (1) produced hydrogen at a potential lower than some reported copper(II) complexes (Table-2). These results are promising and open ways into the use of TC4A derivatives as pre-catalysts for the production of hydrogen.

Table-1: The used chemicals for the synthesis of TC4A and complex (1).

#	Chemical name	Source	Purity	CAS number
1	4-tert-butylphenol	Merck	99 %	98-54-4
2	Sulfur		99.98 %	7704-34-9
3	Tetraethylene glycol dimethyl ether		≥ 99 %	143-24-8
4	Sodium hydroxide		≥ 98 %	1310-73-2
5	Hydrochloric acid, 37 %		≥ 99.8 %	7647-01-0
6	Triethyl amine	Acros Organics	99.7 %	121-44-8
7	Solvent	Acros Organics	Analytical standard	

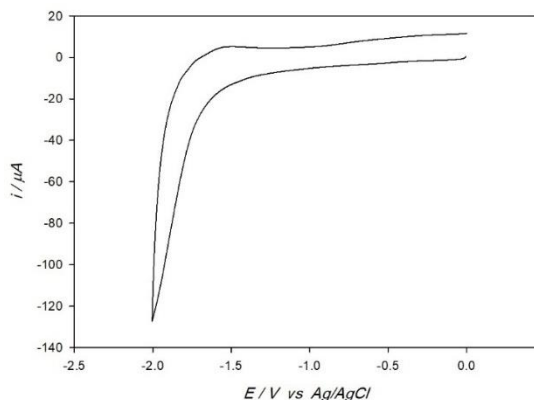


Fig. 5: Cyclic voltammety obtained from the catalyst-free solution of DMF contained 20 mM CH₃COOH and 0.2 M [Bu₄N][BF₄], scan rate 100mVs⁻¹ at glassy carbon electrode under N₂

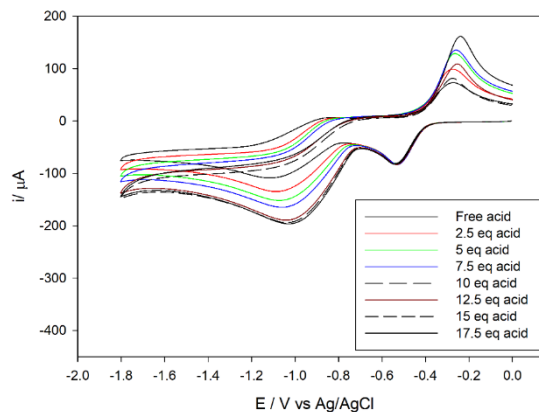


Fig. 6: Cyclic voltammety obtained from the solution of DMF contained 2.5 mM Cu₄(TC₄A)₂ (1), different concentrations of CH₃COOH and 0.2 M [Bu₄N][BF₄], scan rate 100mVs⁻¹ at glassy carbon electrode under N₂.

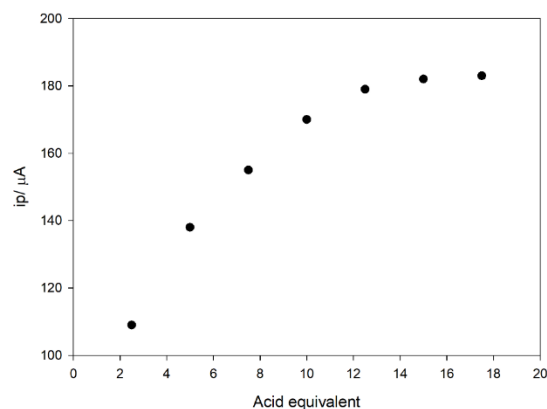


Fig. 7: The number of acetic acid equivalent vs the peak current for the solution of DMF contained 2.5 mM Cu₄(TC₄A)₂ (1), different concentrations of CH₃COOH and 0.2 M [Bu₄N][BF₄], scan rate 100mVs⁻¹ at glassy carbon electrode under N₂.

Table-2: Potential shift of copper catalysts compared to the catalyst-free reaction

#	Complex	Shift / mV more positive values vs. Ag/Ag+ in DMF/DMSO	Ref.
1	[Cu ₄ (TC ₄ A) ₂] (1)	820	This work
2	{Cu(penta fluoro porphyrin)}	490	[18]
3	{Cu(PLSC)}	320	[19]
4	{Cu(PLTSC)}	600	

Conclusion

A divalent copper complex based on the multidentate TC4A ligand has been prepared and characterized by cyclic voltammety. Two reduction

peaks at $E_p^{\text{red}} = -0.48$ V and -1.30 V was observed for the couples $\text{Cu}^{2+}/\text{Cu}^+$ and Cu^+/Cu , respectively. Furthermore, the electrochemical activity of the complex toward proton reduction reaction was evaluated. In the presence of the catalyst, the potential peak shift of about 820 mV compared to the free-catalyst solution and the peak current increase to a maximum of 183 μA for 15 equivalent of CH_3COOH . Based on the small size of H^+/H_2 and the structure of the complex containing an irregular square of metallic cluster sandwiched between two TC4A, we suggest that the proton reduction takes place in a confined space near the metal centers. Our copper(II) complex shows better potential shift compared to analogues reported compounds with ligands such as porphyrin or pyridoxal semicarbazone or thiosemicarbazone.

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