



# Electrochemistry and electrochemiluminescence of copper metal cluster



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## ABSTRACT

The electrochemistry and electrochemiluminescence (ECL) of copper metal cluster were studied in this work. The redox behavior observed was originated from the couples of  $\text{Cu}_8^+/\text{Cu}_8^{2+}$ ,  $\text{Cu}_8/\text{Cu}_8^{2+}$ ,  $\text{Cu}_8/\text{Cu}_8^+$  at the cluster metal core. ECL light emissions were observed under both annihilation and tripropylamine co-reactant conditions and only one excited state was involved in this ECL process and this excited state was also at the metal core. Theoretical investigation found that this excitation corresponds to an electron transfer from the metal core to the ligands. And the energy released from excited state was approximate to the LUMO  $\rightarrow$  HOMO gap energy of the cluster.

## 1. Introduction

Metal nanoclusters (NCs, e.g. Au and Ag or intermetallic) as a new class of fluorophores has been used as appealing alternatives to organic dyes and semiconductor quantum dots in biosensing [1,2] and bioimaging and found potential applications in catalysis, medicine, etc. [3–5]. When the size of metal nanoparticle become extremely small ( $< 2$  nm in diameter), significant quantization occurs to the conduction band and the electronic energy levels will be discretized. When the size decrease further to a few metal atoms (usually  $< 10$  or tens atoms), it is comparable to Fermi wavelength and exhibit molecule-like properties, such as a HOMO-LUMO transition of a one-electron nature [1,6]. So adding or removing one metal atom could significantly change the structure and the electronic structure and optical properties of the cluster [7]. These special morphological and electronic properties endorse metal cluster unique fluorescent, chiral, and magnetic properties and allow for the establishment of electronic structure/function relationships for metal clusters [7,8].

Electrochemiluminescence (ECL) is based on light emission from an excited state formed in the course of electron transfer processes between radical cations and anions of a luminophore, electrogenerated at a working electrode. ECL can also be induced by means of co-reactants mechanism where the excited radicals react with highly oxidizing or reducing reactants, such as tripropylamine (TPA) to give enhanced emission intensity. The ECL of  $\text{Au}_{25}$  cluster have been studied by Ding's group and NIR-ECL emissions were observed in both annihilation and co-reactant systems [9,10]. The emission at NIR

ranges (e.g. 893 nm) was attributed to the energy relaxation of the charged  $\text{Au}_{25}$  clusters excited to the ground states [10]. These light emission sources or excited states may be excited  $\text{Au}_{25}^{-*}$ ,  $\text{Au}_{25}^{0*}$  and  $\text{Au}_{25}^{+*}$  depending upon the coreactant used [9]. The wavelength of ECL emissions were in the NIR range but not identical to the photoluminescence (PL) of the cluster due to the self-absorption of Au cluster. The ECL process of quantum dots, such as Si quantum dots [11], CdSe nanocrystal [12], have been reported where the peak value of ECL spectra was red shifted ( $\sim 200$  nm) from the PL, suggesting that surface states play an important role in the ECL emission process. When the quantum dots was passivated (e.g. CdSe/ZnSe), the peak value of ECL spectrum was found to be identical to that in the PL spectrum [13].

Cu nanocluster has been prepared both in organic phase and inorganic phase where the ligands (e.g. proteins, peptide and DNA) were acted as the protective agents [14–16]. As a new class of phosphors, Cu cluster has been used in cellular imaging, temperature sensing and metal ion detecting [17–19]. However, the studies about the electronic structure, energy level, electrochemical behavior or ECL of Cu cluster have not been reported. The PL of nanocluster may originate from transmission between discrete Fermi energy levels, charge transfer from the ligand or ligand-surface metal to the metal cores [2]. So the study on the emission mechanism of cluster, including ECL and PL is of significance to investigate the energy properties of the metal clusters. Here we show the electrochemical behavior and the ECL process of ligand-protected Cu cluster ( $\text{Cu}_8\text{MPP}_4$ , MPP, 2-mercapto-5-n-propylpyrimidine). The ECL has been observed under both annihilation and anode-reactant conditions. Finally the correlation of energy

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released from ECL emissions with the molecular energy level of the cluster has been discussed.

## 2. Materials and methods

### 2.1. Chemicals

Copper (II) nitrate trihydrate (99%), sodium borohydride (98%), tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ , 98%), tetra-n-octylammonium bromide (TOAB, 98%) and tripropylamine (TPA, 98%) were obtained from Aladdin Reagent Co. 2-mercapto-5-n-propylpyrimidine (MPP, 98%) were obtained from Alfa Aesar. Trans-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB,  $\geq 99\%$ ) were obtained from Sigma-Aldrich. All chemicals were used as received without further purification. Ultrapure water (18 M $\Omega$  cm) was used in this work.

### 2.2. Synthesis of copper nanoclusters

The synthesis procedure of Cu cluster was adopted from the protocol reported previously [20]. In a typical synthesis procedure, 25 mg of copper (II) nitrate and 136 mg of TOAB were co-dissolved in 25 mL of absolute alcohol, and this solution was stirred at 80 °C for 30 min. This solution was then cooled in ice water. 76.6 mg of MPP was added into this solution with vigorous stirring under an argon stream for 6 h. 5 mL of ethanol dissolved with 47 mg of sodium borohydride was then added into the reaction mixture. The solution was left to react for 7 h. A yellow precipitate was isolated by centrifugation, washed repeatedly with ethanol and vacuum dried.

### 2.3. Characterization

Cu nanocluster dispersed in  $\text{CHCl}_3$  was diluted and then 1  $\mu\text{L}$  of suspension was taken and dropped onto mica substrate. The size of the Cu nanocluster was observed by using MultiMode 8 atomic force microscopy (AFM) with a Nanoscope V controller (Bruker, USA). For imaging with commercially available sharpened  $\text{Si}_3\text{N}_4$  probes (radius of curvature approximately 2 nm, Bruker). All images were collected in ScanAsyst Mode (PeakForce Tapping). UV–vis spectra were recorded with a Thermo Evolution 300 UV–vis spectrophotometer. Photoluminescence spectra were acquired with a Thermo Scientific Lumina spectrophotometer. The electronic structures and surface compositions of the Cu cluster were performed on an ESCLAB MKII (VG Co., United Kingdom). The X-ray photoelectron spectroscopy (XPS) data were collected with monochromatic Al K $\alpha$  radiation. The binding energy scale of the spectra was aligned through the C (1 s) peak at 284.6 eV. Peak fit analysis was done using the program XPS PEAK version 4.0. Matrix-assisted laser-desorption ionization time of flight mass spectrometric (MALDI-TOF MS) studies were performed using a Bruker AutoflexIII Smartbeam MALDI-TOF/TOF-MS (Germany) and Trans-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was used as the matrix.

### 2.4. Electrochemistry and electrochemiluminescence

The glassy carbon (GC) electrode was first polished with alumina slurries (0.05  $\mu\text{m}$ ) and then cleaned electrochemically by potential-recycled in 0.5 M  $\text{H}_2\text{SO}_4$  solution with potential ranged from  $-0.2$  to  $+1.2$  V (vs.  $\text{Ag}/\text{AgCl}$  3 M KCl) until a steady cyclic voltammogram was obtained. After that the GC electrode rinsed with water and dried under argon flow.

Electrochemical and ECL measurements of the Cu nanocluster were carried out in a traditional three-electrode cell filled with high-purity Ar atmosphere during the experimental procedure. The working electrode was a glassy carbon (GC) electrode (3.0 mm diameter), the counter electrode was a platinum foil (0.5 mm diameter), and an  $\text{Ag}/$

$\text{Ag}^+$  electrode was used as the reference electrode. The cell potential was calibrated to NHE using the redox potential of the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) couple (that was taken as 0.47 V vs. NHE). All electrochemical experiments were carried out at room temperature.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) was recorded with a CHI 760C electrochemical workstation (Chenhua Co., Shanghai). The Cu cluster (0.5 mg/mL) was dispersed in  $\text{CH}_2\text{Cl}_2$  and supporting electrolyte was 0.1 M  $\text{Bu}_4\text{NPF}_6$  solutions.

For ECL measurements, GC electrode was coated with 10  $\mu\text{L}$  of Cu nanocluster (1.0 mg/mL dispersed in  $\text{CH}_2\text{Cl}_2$ ) and then dried under atmosphere. ECL detection was carried out with an MPI-AECL detector (Xian Remix Electronics Co. Ltd., China) and the photomultiplier tube was set at 900 V. The ECL spectrum was recorded by using optical filter (from 360 to 650 nm, BPCL CO., Beijing).

### 2.5. Quantum yield measurement of Cu NCs

Quantum yield measurement of Cu cluster was carried out by using quinine sulfate (dissolved in 0.1 M  $\text{H}_2\text{SO}_4$ ) as a reference, following standard protocol. The quantum yield was calculated by using the following equation [21].

$$Q_{\text{Cu NC}} = Q_{\text{ref}} \frac{\text{Grad}_{\text{Cu NC}} n_{\text{Cu NC}}}{\text{Grad}_{\text{ref}} n_{\text{ref}}}$$

where  $Q_{\text{Cu NC}}$  and  $Q_{\text{ref}}$  are the quantum yield of Cu cluster and quinine sulfate, respectively;  $\text{Grad}_{\text{Cu NC}}$  and  $\text{Grad}_{\text{ref}}$  are the slopes of the plot of integrated fluorescence intensity versus absorbance of Cu cluster and quinine sulfate, respectively; and  $n_{\text{Cu NCs}}$  and  $n_{\text{ref}}$  are the refractive indices of Cu cluster and the reference, respectively.

### 2.6. Electrochemiluminescence efficiency

The ECL efficiency,  $\Phi_{\text{ECL}}$ , is defined as the number of photons emitted per faradaic electron passed during the chemiluminescent reaction. ECL efficiency value was calculated by integrating photomultiplier tube responses and the corresponding cyclic voltammogram. Comparing the integrated ECL intensity and the corresponding current value of the Cu cluster/TPA system with those of the reference  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{TPA}$  during experiment [22]. Following equation was used to calculate the ECL efficiency of Cu cluster.

$$\Phi_{\text{Cu}} = \Phi_{\text{ref}} \left( \frac{\int_a^b \text{ECL} dt}{\int_a^b \text{Current} dt} \right)_{\text{Cu}} / \left( \frac{\int_a^b \text{ECL} dt}{\int_a^b \text{Current} dt} \right)_{\text{ref}}$$

where  $\Phi_{\text{ref}}$  is the ECL efficiency of  $[\text{Ru}(\text{bpy})_3]^{2+}$ , taken as 5.0% [23]. ECL is the photomultiplier tube responses, current is the electrochemical current value. Cu is the sample (the Cu cluster/TPA) and ref. is the reference (the  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{TPA}$ ).

For experiment, Cu nanocluster (1.0 mg/mL, dispersed in  $\text{CH}_2\text{Cl}_2$ ) was dropped directly on GC electrode.  $[\text{Ru}(\text{bpy})_3]^{2+}$  (0.1 mM, 5  $\mu\text{L}$ ) was fixed on GC electrode with 5% Nafion solution (DuPont D-520). The concentration of TPA was 5 mM.

### 2.7. Theoretical methods

The geometry of  $\text{Cu}_8\text{MPP}_4$  have been optimized at the density functional theory (DFT) level by using wB97XD hybrid functional [24]. The electronic absorption spectra were calculated and simulated with the time dependent density functional theory (TDDFT) method. In all cases, a LANL2DZ basis set was used for the Cu atoms, and 6-31G (d) basis set was used for other atoms. The solvent effects (chloroform) have been included by using the PCM continuum model [25]. All computations in the present work have been performed by using Gaussian 09 codes [26].

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