

SYNTHESIS OF Cu^+ /BIPYRIDYL BASED COMPLEX TOWARDS DYE SENSITIZED SOLAR CELL APPLICATIONS

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Abstract. *This study aims to synthesize the Cu^+ /bipyridyl-based complex using Sonogashira cross coupling. The structure of the ligand and the complex were investigated by nuclear magnetic resonance spectroscopy; by single crystal X-ray diffraction and by UV-VIS absorption spectroscopy. The obtained experimental results were in good agreement with the theoretical calculations. The complex is a potential candidate to be the photo sensitizer in dye-sensitized solar cells.*

Keywords: dye sensitized solar cell, Cu^+ /bipyridine complex.

Classification numbers: 88.40.jr.

I. INTRODUCTION

Solar power is probably one of the most important renewable energy sources today. Solar cell operates according to the photovoltaics effect [1] in which the cell converts directly the solar radiation into a direct current. Three generations of solar cells have been introduced so far in which Si-wafer based cell had a share of around 90% of the total production in 2013 [2]. The first generation, which is Si-wafer based, and the second one, which is amorphous silicon based and copper indium gallium selenide (CIGS) based, are technologically matured and it is hard to reduce the price in fabrication processes. These technologies are also subjected to possible difficulties and environmental impacts after the solar cell life cycle.

The liquid-based dye sensitized solar cell that belongs to the third generation was first reported in Ref. [3, 4], and now becomes alternatives solution to the silicon based technology and its today efficiency is claimed higher than 13% in laboratory and around 10% in module

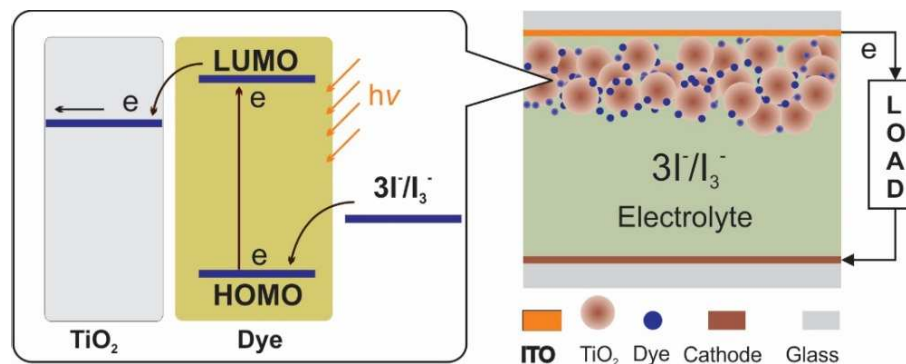


Fig. 1. Structure of a typical DSSC.

scale [5–7]. Numbers of photo-dyes are commercially available and most of which are composed of Ruthenium as for example N3, N719 and Z907 [8]. The Ruthenium based complexes are now dominant in dye-sensitized solar cells (DSSC) research and development (R&D). However, using such expensive and rare earth metal could retain DSSC only at the R&D stage and limit the large-scale production. The current research trends to develop ideal dyes in order to (i) replace expensive and toxic Ruthenium based complexes by low cost, transitional metals, environment friendly or even metalless [9, 10]; (ii) replace the ligand to enhance the radiation adsorption capacity, in particular, in the visible and infrared regions [11, 12]. Replacing Ru^{2+} by alternative and low cost metal ions, such as Mn^+ , is one of the solutions that brought the DSSC to mainstream use. In this work, we tried to replace the rare-earth Ru^{2+} in N3 by Cu^+ using polypyridyl based ligand. The reasons for Cu^+ can be in place of Ru^{2+} are:

- (i) Cu is a multivalence transitional metal. The redox process ($\text{Cu}^+ - e \rightleftharpoons \text{Cu}^{2+}$) is reversible. In addition, its atom radius is close to that of Ruthenium.
- (ii) It is capable of forming stable complex with various ligands.
- (iii) It is able to absorb strongly the solar radiation in wide range of spectrum.
- (iv) The highest occupied molecular orbital (HOMO) of the obtained complex is basically formed from the AOs of Cu^+ .

II. CALCULATION

Models and computational methods

The theory calculation, including the time-dependent density functional theory (TDDFT), generalized gradient approximation (GGA), Perdew,Burke,Ernzerhof (PBE) functional theory; the double zeta polarization (DZP) basis set and the norm-conserving pseudopotentials [13] were used for all atoms. The plane wave cutoff of 150 Ryd for the grid has been chosen for all calculations. The ultra violet – visible (UV-VIS) spectra were calculated by using configuration interaction singles (CIS), in the CIS theory. The absorption energies are the difference between the Hartree–Fock (HF) ground state and CIS excited state energies.

Mayer bond order calculated as:

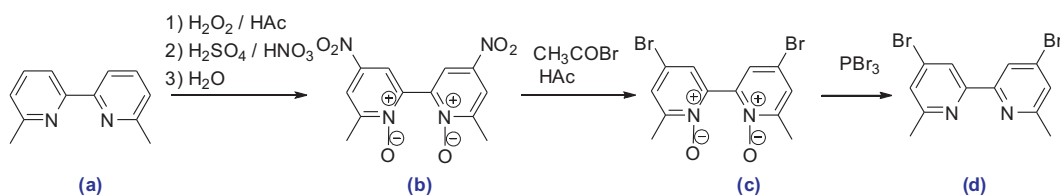
$$B_{AB} = \sum_{a \in A} \sum_{b \in B} [(PS)_{ab}(PS)_{ba} + (P^s S)_{ab}(P^s S)_{ba}]$$

where P and P^s are the total density and spin-density matrices, respectively; S is the overlap integral. By using these tools, the calculation would predict the compatibility of the alternative materials to replace the Ru^{+2} in dye complex.

III. EXPERIMENT

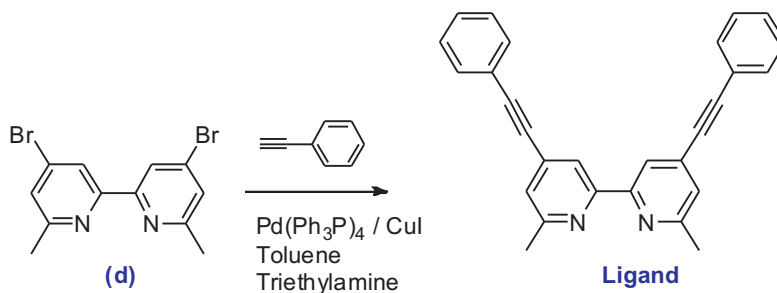
Preparation of intermediates

4,4'-dibromo-6,6'-dimethyl-2,2'-bipyridine (**d**) was prepared via three steps, adapted in [14], from 6,6'-dimethyl-2,2'-bipyridine (**a**). The intermediates (**d**) were obtained in 55% yield as a white solid.



Synthesis of ligand

The alternative ligand was synthesized from the intermediates (**d**) via Sonogashira cross-coupling reaction [15]. 4,4'-Dibromo-6,6'-dimethyl-2,2'-bipyridine (**d**) (0.25 mmol); $Pd(Ph_3P)_4$ tetrakis(triphenylphosphine)palladium (0) (0.025 mmol) catalyst; CuI (0.05 mol); ethynylbenzene (0.3 mmol) were added to a degassed solution of triethylamine (1 ml) and toluene (4 ml) under an argon atmosphere.



The mixture was heated at $100^\circ C$ for 4 h. The product of Sonogashira reaction was purified by silica gel column chromatography. The ligand was obtained in 55% yield as a white solid.

Synthesis of copper (I) complex

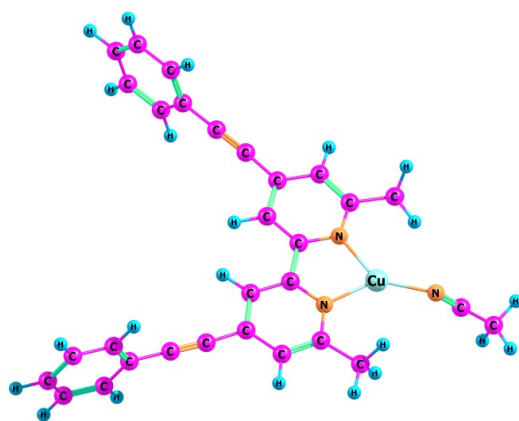
Copper (I) complex with the obtained ligand was prepared via the ligand exchange reaction from tetrakis (acetonitrile) copper (I) hexafluorophosphate $[Cu(CH_3CN)_4][PF_6]$ which is a widely used precursor for the synthesis of other Cu(I) complexes.

$[Cu(CH_3CN)_4][PF_6]$ (18.6 mg, 0.05 mmol) dissolved in CH_3CN (2 ml) was added to a solution of the ligand (0.10 mmol) in $CHCl_3$ (5 ml), and the colorless solution turned red. A red solid precipitated upon addition of ether to the solution. After that the solid was filtered and rinsed with water and ether. The structure of the Cu(I) complex was recorded by single crystal X-ray diffraction.

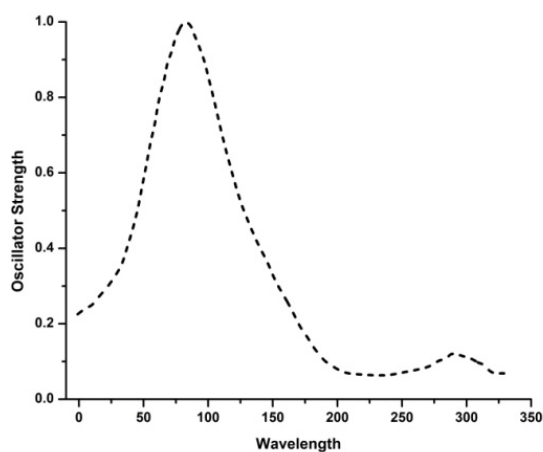
IV. RESULTS AND DISCUSSION

Theoretical calculation

The modification of Cu(I) complex by using new ligands to enhance the photon absorption capacity requires the support of the computational methods. In this work, the structure of $[\text{Cu(L)CH}_3\text{CN}]$ complex was built as Fig. 2 which contains a three-coordinate Cu(I) atom coordinating with a ligand and a molecule of acetonitrile.



(a)



(b)

Fig. 2. The computational UV-VIS spectra of $[\text{Cu(L)CH}_3\text{CN}]^+$.

By employing the models and computational methods above for this structure, the computational UV-VIS spectra of $[\text{Cu(L)CH}_3\text{CN}]^+$ was also obtained. $[\text{Cu(L)CH}_3\text{CN}]^+$ exhibits a dual absorption in the region from 200 to 400 nm in which the spectra are dominated by intensity of oscillator strength in smaller wavelength one.

The structure of ligand

The structure of ligand is confirmed by using Nuclear Magnetic Resonance (NMR) of which the obtained data is listed in Table 1.

Table 1. NMR data of the ligand.

NMR	δ (chemical shift, ppm)
^1H NMR (500 MHz, CDCl_3)	$\delta = 8.35$ (s, 1H); 7.35 (m; 2H); 7.48 (m, 3H); 7.28 (s, 1H); 2.65 (s, 3H).
^{13}C NMR (125 MHz, CDCl_3)	C-aryl: $\delta = 158.2, 155.6, 132.5, 120.6$; CH-aryl: $\delta = 120.6, 132.0, 128.6, 125.0, 120.4$; C-ethynyl: $\delta = 93.3, 87.5$; C-methyl: $\delta = 24.6$.

s = singlet peak; *d* = doublet peak; *m* = multiplet peak. This data evidences the structure as predicted by theoretical calculation.

Structure of copper (I) complex

In our synthetic experiment, the ligand based on a derivative of bipyridine was synthesized by Sonogashira cross-coupling reaction which chemical structure was demonstrated by NMR spectra. The Copper (I) complex with this ligand was also obtained via the ligand exchange reaction from $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{PF}_6]$.

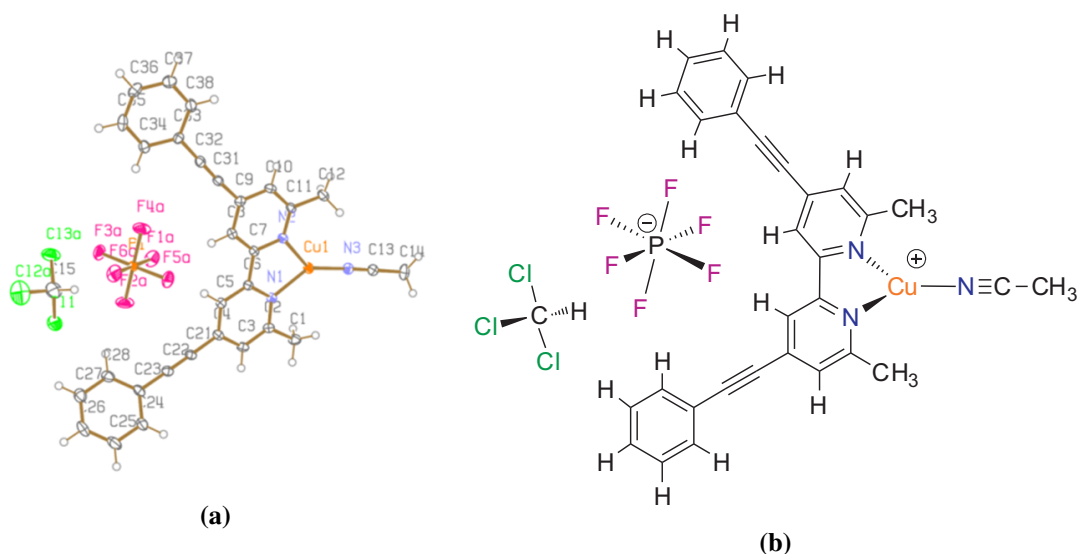


Fig. 3. a) Single crystal X-ray diffraction of $[\text{Cu}(\text{L})\text{CH}_3\text{CN}]^+$ and b) the illustrative formula.

Single crystal X-ray Diffraction is a non-destructive analytical technique that provides detailed information about crystal structures and atomic spacing. As the result in Fig. 3, Copper (I)

complex with the ligand crystallized in the asymmetric unit which contains a molecule of the ligand and a molecule of acetonitrile coordinating the copper (I) atom through their nitrogen atoms (CuN₃). Interestingly, the copper (I) cation in this complex has trigonal planar geometry which is more uncommon than the tetrahedral geometry of the other copper (I) complexes, for example [Cu(CH₃CN)₄][PF₆] precursor. However, the electrochemical behavior of the other similar three-coordinate CuN₃ complexes has been confirmed. As the result, the Cu(II)/Cu(I) redox couple corresponding with the CuN₃ complex exhibits a fully reversible with a positive redox potential which is a necessary requirement for dye-sensitizer [16].

Experimental absorption spectra

The UV-VIS absorption spectra of [Cu(L)CH₃CN][PF₆] was recorded in acetonitrile solutions at room temperature, as shown in Fig. 4. This synthetic complex exhibits characteristics that are well matched with those obtained by the theoretical calculation. The spectra compose dual absorption in the certain range and the smaller intense absorption of the longer wavelength one. Especially, the experimental absorption spectra of [Cu(L)CH₃CN][PF₆] is dominated by an intense absorption band in the visible light range (from 350 nm to 550 nm).

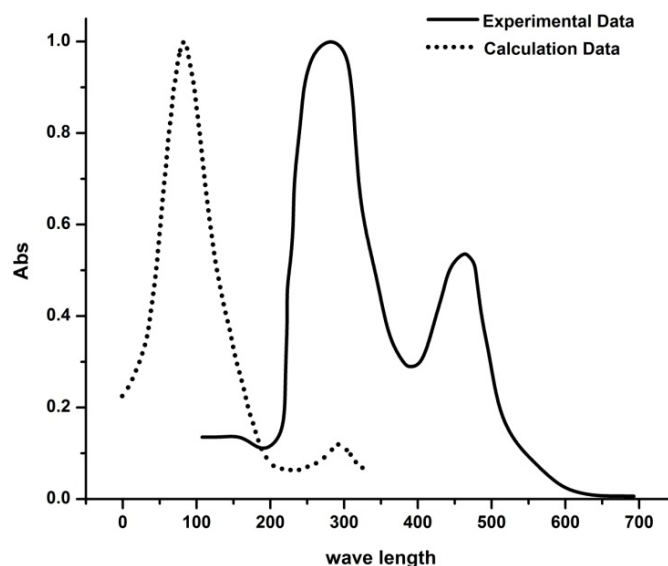


Fig. 4. The UV-VIS absorption spectra of [Cu(L)CH₃CN][PF₆].

Thus, the current synthetic copper (I) complex shows bathochromic shift in comparison with the computational UV-VIS spectra. This result can be explained by the presence of the solvent in the media from which the spectra data was recorded (the theoretical calculation was conducted without any solvent). Although the acetonitrile solvent (used in UV-VIS spectra examination) shift the absorption bands but the similar spectra shape was obtained. It is noted that the acetonitrile is also employed in the triiodide/iodide electrolyte of the DSSC that we are developing.

V. CONCLUSION

This study developed an alternative dye for the replacement of Ruthenium based complexes which are dominant as the photosensitizer in dye sensitized solar cell. Cu^+ was chosen as the central ion because its transitional multivalence allows the reversible redox reaction as well as it is possible to form chemically stable complex. The ligand, bipyridine derivative, was prepared by the Sonogashira cross coupling that was employed for the complex synthesis. The data given by the theoretical calculation as well as the experimental results revealed that $[\text{Cu}(\text{L})\text{CH}_3\text{CN}]^+$ is potential to be the photosensitizer in DSSC.

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