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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF BIPYRIDINE LIGANDS TOWARDS THE APPLICATION IN DYE-SENSITIZED SOLAR CELLS

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Abstract

An efficient synthetic route was developed to tailor bipyridine ligands basing on the palladium catalyzed Sonogashira cross-coupling of 4-bromo-2,2'-bipyridine. Structures of the modified bipyridines were elucidated by NMR and X-Ray diffraction analyses. It was shown that the introduced alkynes are co-planar with the bipyridine core, revealing an efficient effect of the substituent on the electronic properties of the ligand.

Keywords. DSSC, 2,2'-bipyridine, dye sensitizers, palladium-catalyzed, Sonogashira.

1. INTRODUCTION

Dye sensitizers are known to play an essential role in the function of dye sensitized solar cell (DSSC). Up to now, DSSCs with porphyrin-sensitized and cobalt (II/III)-based redox electrolyte have achieved power conversion efficiencies exceeding 12% under illumination of standard global air mass 1.5 (AM1.5G) [1], but still a long way to meet the energy consumption require. To further enhance the efficiencies of DSSC, much effort was focused on design and synthesis of new sensitizers.

In general, the conversion efficiency of DSSC is proportional to the photon absorption intensity of the dye. Therefore, broadening and red-shifting the absorption band of the sensitizers and/or increasing their absorption intensity is among some effective ways to design ideal dye sensitizers. Various sensitizers have been developed and their performances were investigated during the past decades [2]. The efficiency of DSSC has been found to be strongly governed by substituents of the dyes [3]. Lin et al. [4] have recently reported that incorporated electron-withdrawing groups such as fluorine onto cyanoacrylate can enhance the light-harvesting performance. Replacing an anchoring ligand with a highly conjugated ancillary ligand results in an increasing of extinction coefficients and which in turn increases the photocurrent density of DSSC [5].

Encouraged by these potential modification strategies, we report herein the synthesis and structural characterization of novel π extended bipyridine ligands and their complexation with copper(I). The bipyridine ligand and copper complexes are synthesized by means of Sonogashira cross-coupling [6-8] and ligand exchange reactions [9].

2. EXPERIMENTAL

2.1. Chemicals

Unless otherwise stated, chemical reagents and solvents were purchased from Sigma-Aldrich or Merck and were used as received without further purification. The Sonogashira cross-coupling reaction was carried out under an atmosphere of argon in oven-dried glass wares. Column chromatography was performed with Merck silica gel 60 (0.040-0.063 μm grade).

2.2. Instrumentation

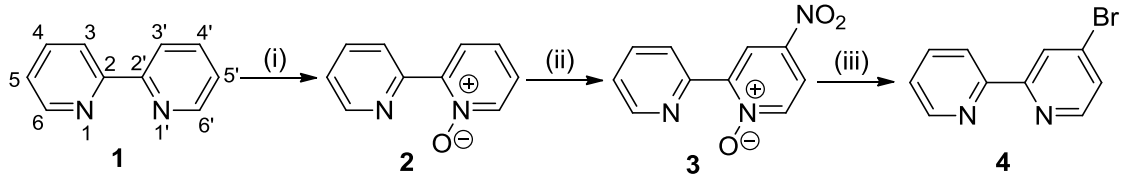
Melting points were measured on a Stuart-Scientific SMP3 apparatus without correction. NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer in $CDCl_3$. The chemical shifts are given in ppm related to tetramethylsilane as internal standard. UV-Vis spectra were recorded on a LIUV 310S Lambda spectrophotometer. LC/MS and ESI analyses were acquired on Controlmicro-GC (Walter) and MAT LCQ mass spectrometers,

respectively. HR-MS spectra were recorded on a LQT Orbitrap XL^{TM} mass spectrometer. X-Ray measurements were performed on an Agilent SuperNova diffractometer at the Department of Chemistry, KU Leuven, Belgium.

2.3. Preparation of ligands and Cu(I) complexes

2.3.1. Synthesis of 4-bromobipyridine

The 4-bromobipyridine was synthesized following the reported procedure [10] (see scheme 1): First, 2,2'-bipyridine was oxidized by *m*-CPBA in $CHCl_3$. The resulting 2,2'-bipyridyl-1-oxide was nitrated with fuming nitric acid in concentrated sulfuric acid, followed by the substitution of the nitro group with a bromine atom under the action of acetyl bromide. The purity and structure of **4** as well as of other intermediates were tested by NMR and LC/MS analyses which are identical with the reported data.

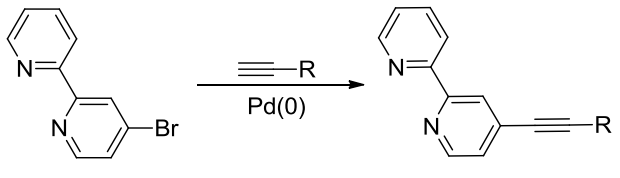


Scheme 1: Preparation of 5-alkynylbipyridine ligands. *Conditions*: (i) *m*-CPBA, $CHCl_3$, 40 ^oC, 24 h; (ii) HNO_3 100%, H_2SO_4, reflux, 6 h; (iii) CH_3COBr/CH_3COOH, rt, 30 min., then PBr_3, 40 ^oC then 100 ^oC for 1 h

4-Nitro-2,2'-bipyridine **3**: **3** was isolated by recrystallization from hot ethanol as yellow needles, mp. 181-183 ^oC, yield 32 %. LC/MS: R_t = 8.78 min., m/z= 217.98 (*positive*), cal. 217.05.

4-Bromo-2,2'-bipyridine **4**: **4** was isolated by SiO_2 column chromatography as a pale yellow solid, mp. 50-51 ^oC, yield 76%. ^1H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.68 (d, *J* = 3.5 Hz, 1 H), 8.62 (d, *J* = 1.0 Hz, 1 H), 8.47 (d, *J* = 5.5 Hz, 1 H), 8.38 (d, *J* = 8.0 Hz, 1 H), 7.82 (dt, *J* = 8.0 and 2.0 Hz, 1 H), 7.47 (dd, *J* = 5.5 and 2.0 Hz, 1 H), 7.33 (dd, *J* = 7.0 and 5.0 Hz, 1 H).

2.3.2. Synthesis of bipyridine ligands by palladium-catalyzed Sonogashira reaction



-R: C_6H_5- (**L1**), 4-MeC_6H_4- (**L2**), Pyridin-3-yl (**L3**), 4-$MeOC_6H_4$- (**L4**), $HO(CH_2)_3$- (**L5**), 4-$CHOC_6H_4$ (**L6**), 6-MeO-napthalen-3-yl (**L7**), 5-Fluorenyl (**L8**), ferrocence (**L9**)

Scheme 2: Preparation of 5-alkynylbipyridine ligands. *Conditions*: terminal alkyne, $Pd(PPh_3)_4$, CuI, *i*-Pr_2NH, deaerated toluene, 50-100 ^oC, 4 h

*General procedure for the synthesis of 4-alkynyl-2,2'-bipyridine **L1÷L9***: Toluene (4.0 ml) was deaerated by exchanging between vacuum and a stream of argon (3 times). To this argon saturated solution were added 4-bromo-2,2'-bipyridine (59 mg, 0.25 mmol), $Pd(PPh_3)_4$ (28.5 mg, 0.025 mmol, 0.1 equiv), CuI (10 mg, 0.050 mmol, 0.2 equiv). The obtained pale yellow mixture was degassed again as described above. To the reaction mixture, a solution of arylacetylene (0.3 mmol, 1.2 equiv) in argon saturated toluene (1.0 ml) was added dropwise in about 30 minutes. The reaction mixture was heated at about 50-100 ^oC for the indicated times. The reaction mixture turned reddish brown when the cross-coupling completed as indicated by TLC (EtOAc:*n*-hexane 1:4, v/v). The reaction mixture was diluted with EtOAc, washed with water (3 times), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was adsorbed on silica gel and purified by SiO_2 column chromatography to furnish the 4-alkynated 2,2'-bipyridine ***L1÷L9***. Besides the desired product, a significant amount of the symmetric diyne resulted from the Glaser homocoupling reaction of the alkyne was separated.

4-(Phenylethynyl)-2,2'-bipyridine **L1**:Starting from **4** and phenylacetylene, **L1** was isolated after 4 h at 50 ^oC as a yellow solid, yield 60 %. ^1H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.70 (d, *J* = 4.5 Hz, 1 H), 8.65 (d, *J* = 5.0 Hz, 1 H), 8.53 (s, 1 H), 8.40 (d, *J* = 8.0 Hz,1 H), 7.82 (dt, *J* = 7.5 Hz and 1.5 Hz, 1 H), 7.58 (m, 2 H), 7.37 (m, 4 H), 7.31 (m,1 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 156.2, 155.5, 149.2, 149.1, 137.0, 132.5, 131.9, 129.1, 128.5, 125.3, 124.0, 123.2, 122.3, 121.2, 93.9 and 87.1 (C≡C).

4-(4-Methylphenylethynyl)-2,2'-bipyridine **L2**: Starting from **4** and 4-methylphenylacetylene, **L2** was isolated after 4 h at 50 ^oC as a brownish yellow

solid, yield 64 %. ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.70 (tt, *J* = 5.0 Hz and 1.0 Hz, 1 H), 8.65 (d, *J* = 5.0 Hz, 1 H), 8.52 (s, 1 H), 8.40 (dd, *J* = 8.0 Hz and 0.5 Hz, 1 H), 7.82 (dt, *J* = 7.5 Hz and 1.0 Hz, 1 H), 7.45 (d, *J* = 8 Hz, 2 H, Ar), 7.38 (dd, *J* = 5.0 Hz and 1.0 Hz, 1 H), 7.32 (m, 1 H), 7.19 (d, *J* = 8 Hz, 2 H, Ar), 2.38 (s, 3 H, -C<u>H</u>$_3$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 156.2, 155.6, 149.2, 149.1, 139.5, 137.0, 132.7, 131.8, 129.2, 125.2, 123.9, 123.2, 121.1, 119.2, 94.3 and 86.5 (C≡C), 21.6 (-CH_3).

4-(Pyridine-3-ylethynyl)-2,2'-bipyridine **L3**: Starting from **4** and pyridine-3-ylacetylene (no CuI was used), **L3** was isolated after 4 h at 100 ^{o}C as a white solid, yield 78 %. ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.81 (s, 1 H), 8.71 (s, 2 H), 8.62 (dd, *J* = 5.0 Hz and 1.0 Hz, 1 H), 8.57 (s, 1 H), 8.43 (d, *J* = 7.5 Hz, 1 H), 7.85 (m, 2 H), 7.42 (d, *J* = 8.0 Hz, 1 H), 7.33 (m, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 156.3, 155.3, 152.4, 149.4, 149.3, 149.2, 138.7, 137.0, 131.6, 125.1, 124.0, 123.19, 123.17, 121.2, 119.5, 90.2 (C≡C).

4-(4-Methoxyphenylethynyl)-2,2'-bipyridine **L4**: Starting from **4** and 4-methoxyphenylacetylene, **L4** was isolated after 4 h at 60 ^{o}C as a yellow solid, yield 76 %. ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.70 (d, *J* = 4.0 Hz, 1 H), 8.64 (d, *J* = 5.5 Hz, 1 H), 8.51 (s, 1 H), 8.40 (d, *J* = 8.0 Hz, 1 H), 7.83 (dt, *J* = 8.0 Hz and 2.0 Hz, 1 H), 7.51 (d, *J* = 8.5 Hz, 2 H, Ar), 7.37 (dd, *J* = 5.0 Hz and 1.5 Hz, 1 H), 7.33 (m, 1 H), 6.91 (d, *J* = 8.5 Hz, 2 H, Ar), 3.85 (s, 3 H, -OC<u>H</u>$_3$). ^{13}C NMR of **L4** could not be recorded due to its low solubility in NMR solvents.

4-(5-Hydroxypentyn-1-yl)-2,2'-bipyridine **L5**: Starting from **4** and pent-4-yn-1-ol, **L5** was isolated after 4 h at 100 ^{o}C as a yellow viscous oil, yield 56%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.66 (m, 1 H), 8.58 (dd, *J* = 5.0 Hz and 0.5 Hz, 1 H), 8.36 (m, 2 H), 7.81 (dt, *J* = 7.5 Hz and 1.5 Hz, 1 H), 7.31 (m, 1 H), 7.25 (dd, *J* = 5.0 Hz and 1.5 Hz, 1 H), 3.81 (t, *J* = 6.0 Hz, 2 H, -CH_2-), 2.57 (t, *J* = 6.5 Hz, 2 H, -CH_2-), 1.85 (m, 2 H, -CH_2-). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 156.0, 155.6, 149.1, 149.0, 137.0, 133.1, 125.5, 123.9, 123.4, 121.2, 95.0 and 79.0 (C≡C), 61.3, 31.1 and 16.0 (-CH_2-).

4-(4-Formylphenylethynyl)-2,2'-bipyridine **L6**: Starting from **4** and 4-ethynylbenzaldehyde, **L6** was isolated after 4 h at 100 ^{o}C as a yellow solid, yield 68%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 10.04 (s, 1 H, CHO), 8.70 (m, 2 H), 8.56 (s, 1 H), 8.42 (d, *J* = 8.0 Hz, 1 H), 7.99 (d, *J* = 8.5 Hz, 2 H), 7.83 (dt, *J* = 7.5 Hz and 1.5 Hz, 1 H), 7.70 (d, *J* = 8.5 Hz, 2 H), 7.41 (dd, *J* = 5.0 Hz and 1,5 Hz, 1 H), 7.34 (m, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 191.3 (CHO), 156.4, 155.4, 149.3, 149.2, 137.0, 136.1, 132.4, 131.6, 129.6, 128.4, 125.2, 124.1, 123.2, 121.2, 92.5 and 90.6 (C≡C). HRMS (ESI, 70 eV): *m/z* (M^+) calcd for $C_{19}H_{12}N_2O$ 284.0950; found 284.1033.

4-(6-Methoxynaphthalen-2-ylethynyl)-2,2'-bipyridine **L7**: Starting from **4** and 6-methoxynaphthalen-2-yl acetylene, **L7** was isolated after 4 h at 100 ^{o}C as a yellow solid, yield 60 %. ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.70 (d, *J* = 4.5 Hz, 1 H), 8.66 (d, *J* = 5.0 Hz, 1 H), 8.56 (s, 1 H), 8.41 (d, *J* = 7.5 Hz, 1 H), 8.01 (s, 1 H), 7.82 (dt, *J* = 8.0 Hz and 2.0 Hz, 1 H), 7.72 (t, *J* = 8.0 Hz, 2 H), 7.55 (dd, *J* = 8.0 Hz and 1.5 Hz, 1 H), 7.40 (dd, *J* = 5.0 Hz and 1.5 Hz, 1 H), 7.33 (m, 1 H), 7.18 (dd, *J* = 8.5 Hz and 2.0 Hz, 1 H), 7.12 (d, *J* = 2.0 Hz, 1 H), 3.92 (s, 3 H, -OCH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 158.7, 156.2, 155.6, 149.2, 149.1, 136.9, 134.6, 132.6, 132.0, 129.5, 128.9, 128.4, 117.1, 127.0, 125.2, 123.9, 123.1, 121.1, 119.6, 105.9, 94.7 and 86.8 (C≡C), 55.3 (-OCH_3).

4-(Fluoren-5-ylethynyl)-2,2'-bipyridine **L8**: Starting from **4** and fluoren-5-ylacetylene, **L8** was isolated after 4 h at 100 ^{o}C as a white solid, yield 52%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.51 (m, 1 H), 8.47 (d, *J* = 5.0 Hz, 1 H), 8.33 (d, *J* = 0.5 Hz, 1 H), 8.25 (d, *J* = 8.0 Hz, 1 H), 7.73 (m, 3 H), 7.58 (d, *J* = 7.5 Hz, 2 H), 7.36 (t, *J* = 7.5 Hz, 2 H), 7.30 (t, *J* = 7.5 Hz, 2 H), 7.21 (m, 2 H), 4.03 (s, 1 H, O<u>H</u>). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 155.8, 155.1, 149.0, 148.8, 146.7, 139.0, 136.9, 131.7, 129.7, 128.5, 125.5, 124.5, 123.9, 123.6, 121.2, 120.1, 94.2 and 80.3 (C≡C), 75.0 (C-OH).

4-(Ferrocencethynyl)-2,2'-bipyridine **L9**: Starting from **4** and ethynylferrocence, **L9** was isolated after 4 h at 100 ^{o}C as a red solid, yield 56 %. ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.71 (d, *J* = 4.0 Hz, 1 H), 8.62 (d, *J* = 5.0 Hz, 1 H), 8.47 (s, 1 H), 8.40 (d, *J* = 8.0 Hz, 1 H), 7.83 (dt, *J* = 8.0 Hz and 1.5 Hz, 1 H), 7.33 (m, 2 H), 4.54 (m, 2 H, ferrocene), 4.30 (m,2 H, ferrocene), 4.25 (s, 4 H, ferrocene). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 156.0, 155.7, 149.2, 149.1, 136.9, 133.1, 124.9, 123.9, 122.8, 121.1, 94.2 and 83.8 (C≡C), 71.8, 70.1, 69.4 and 63.7 (C-ferrocene). HRMS (ESI, 70 eV): *m/z* [M^+] calcd for $C_{22}H_{16}FeN_2$364.0663; found 364.0735.

2.3.3. Synthesis of 4-alkynylated bipyridine-Cu(I) complex

$$[Cu(CH_3CN)_4]PF_6 + 2\mathbf{L} \xrightarrow[CHCl_3]{CH_3CN} [Cu\mathbf{L}_2]PF_6 + 4CH_3CN$$

Scheme 3: Preparation of 5-alkynylbipyridine-Cu(I) complexes. *Conditions*: 5-alkynylbipyridine, $[Cu(CH_3CN)_4][PF_6]$, CH_3CN, RT, 30 min

General procedure for the preparation of 5-alkynylbipyridine-Cu(I) complexes $[Cu(\mathbf{L})_2][PF_6]$*:* $[Cu(CH_3CN)_4][PF_6]$ (18.6 mg, 0.05 mmol, 1.0 equiv) dissolved in degassed CH_3CN (5 ml) was added to a solution of an alkynylated bipyridine **L** (0.10 mmol, 2.0 equiv) in degassed $CHCl_3$ (5 ml). The colorless solution immediately turned red. The solution was stirred under an argon atmosphere for a further 15 min., then concentrated by rotary evaporator to give the corresponding bipyridine-Cu(I) complex.

$[Cu(\mathbf{L1})_2][PF_6]$: deep red solid, ESI-MS (*positive*) m/z 576.8 ($[(Cu(\mathbf{L1})_2]^+$), cal. 575.13. UV-Vis (*solid*): λ_{max} (nm) 605. IR (KBr) υ (cm^{-1}) 3055 (m), 1581 (m), 1531 (m), 1462 (m), 1400 (m).

$[Cu(\mathbf{L6})_2][PF_6]$: brownish red solid. UV-Vis (*solid*): λ_{max} (nm) 650.IR (KBr) υ (cm^{-1}) 3032 (w), 2812 (w), 2723 (w), 1697 (s), C=O, 1597 (m), 1580 (w), 1540 (w), 1458 (w), 1388 (w).

3. RESULTS AND DISCUSSION

3.1. Synthesis and structural characterization of the obtained bipyridine ligands

The Sonogashira reaction of **4** (1.0 equiv) with various terminal alkynes (1.2 equiv) resulted in the selective formation of 4-alkynyl-2,2'-bipyridine **L1÷9** in 52-78 % yields (see scheme 2 and experimental part). The reaction conditions were optimized with regard to catalyst, solvent, base, temperature and time. $Pd(PPh_3)_4$ in toluene in the presence of 3.0 equiv of *i*-Pr_2NH was found to be the most efficient for the current reaction. Other commonly used catalyst systems, such as $Pd(CH_3CN)_2Cl_2$ in THF, $Pd(Ph_3P)_2Cl_2$ in DMF, especially those in amines as co-solvent, such as Et_3N or *i*-Pr_2NH, resulted in the competitive Glaser dimerization of the alkynes [11]. The cross-coupling reactions were carried out at about 50-100 °C in 4 hours under an argon atmosphere.

The structures of the coupling products were established by spectroscopic methods (see experimental part). Looking at the aromatic range of the ^1H and ^{13}C NMR spectra of **L6**, one can find the resonance signals of12 protons as well as of 17 carbons of the molecule, respectively. The singlet at 10.04 ppm is designated to the signal of the proton of the aldehyde group (see figure 1). In the ^{13}C NMR spectra of all compounds, the signals at about 80 and 95 ppm can be safely assigned to the two sp carbons of the ethyne bridge. The geometry of the modified bipyridine **L1÷9**, however, can only be clarified through single-crystal X-ray diffraction analysis. Thus, **L9** yielded X-ray quality crystals grown by slow evaporation of a chloroform solution of the compound. With these crystals, the structure of **L9** can unambiguously be determined by X-ray diffraction analysis as shown in figure 2.

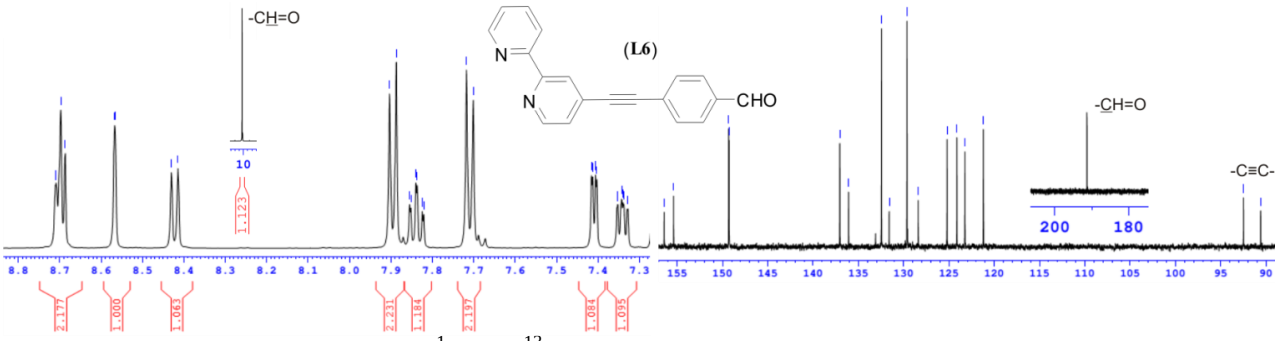


Figure 1: ^1H and ^{13}C NMR spectra of **L6** (*aromatic range*)

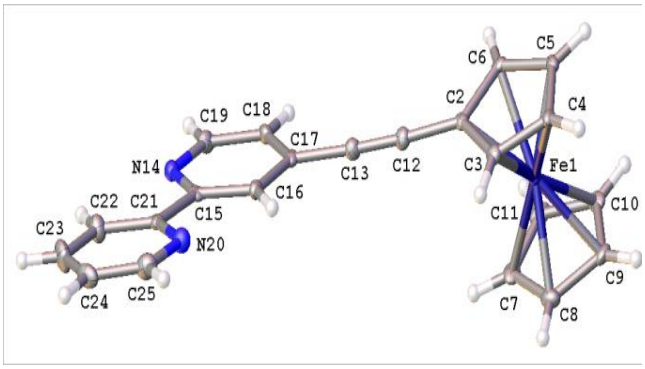


Figure 2: X-Ray crystal structure of **L9**

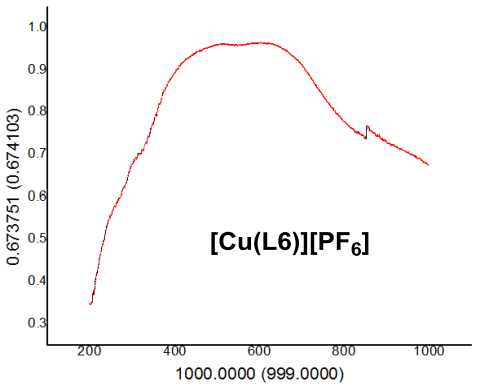


Figure 3: UV-Vis spectrum of $[Cu(\mathbf{L6})_2][PF_6]$

3.2. Synthesis of bipyridine–Cu(I) complexes

The bipyridine–Cu(I) complexes were prepared following reported procedures [9] (see scheme 3).In order to characterize the complex, the solvent was removed and subjected to solid UV analysis (see figure 3). The complex shows very high intensity over the whole visible wavelength range, especially from 400 nm to 800 nm, suggesting that these bipyridine-Cu(I) complexes can be an interesting alternative to Ru(II)-polypyridines for DSSC application as sensitizers.

4. CONCLUSION

We have demonstrated that the palladium catalyzed Sonogashira cross-coupling of 4-bromo-2,2'-bipyridine is a simplified and straightforward synthetic method for alkynylated bipyridines. Based on this strategy, nine novel 4-substituted bipyridines were synthesized whose structures were clarified by spectroscopic analyses. The X-Ray diffraction technique has revealed the planarity of the modified bipyridines which allow fine-tuning of electronic property of the ligand by introducing suitable substituents. Applications of this coupling strategy in the synthesis of modified bipyridines are now underway in our laboratory, and will be reported in due course. In this work, bipyridine-Cu(I) complexes have also been synthesized and studied as sensitizers, with the aim of employing them for DSSCs applications.

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