

# Synthesis of Ditopic Ligands for the Construction of Photoactive Coordination Polymers

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## Abstract

*A form of polymer materials, usually synthesized by the complexation of metal ions with ditopic organic ligands are receiving much attentions these days due to their widespread applications particularly in energy storage and photocatalytic reduction of CO<sub>2</sub>. However, the most efficient photocatalytic systems consist of 2<sup>nd</sup> or 3<sup>rd</sup> row transition metal complexes, usually those of d<sup>6</sup> ruthenium (II) or iridium (III). Although, these complexes are characterized by long-lived metal to ligand charge transfer (MLCT) excited state and have a very negative reduction potential, the design of catalysts based on these rare precious transition metals presents a crucial economic limitation to their widespread usage. Here, we alternatively think of synthesizing complexes which utilize cheaper and, more abundant metals which are comparable with or even surpass in terms of some remarkable features to promotes a bi-metallic and bi-functional coordination polymer which alternatively contain photosensitive and electron accepting site such that the good distribution of the metal centers would be manage by the synthesis of a ditopic polypyridine ligands. Precisely transition metals of the first row series in particular chromium and copper are utilized in this synthesis.*

**Keywords:** ditopic, photocatalytic, polypyridine, MLCT.

## 1. INTRODUCTION

Recent development in the field of energy conversion and storage has necessitated the investigation of the photophysical and photochemical properties of varieties of metal complexes, especially those of Cu(I) phenanthroline [Cu(NN)<sub>2</sub>]<sup>+</sup> owing to the possibility of practical application of these complexes in various field, particularly in the photocatalytic reduction of CO<sub>2</sub>, design of photosensitizers and lots more. Natural photosynthetic machinery gives essential to solar energy conversion that demustrate light. It also helps in transforming sequential electron transfer, accumulating charge to redox center, and several electrons light driven catalysis (Hossain et al, 2014).

Majority of systems developed consist of a combination of separated photosensitizing and catalytic units, while the close association (linking) of these two units are less frequent. The bi-metallic and bi-functional coordination polymers, synthesized by the complexation of metal ions and organic ditopic ligands that are considered as a form of polymer materials which is focus more on electronic properties. This type of polymer has gain significant concern due to several potential elements of energy, information storage, photoluminescent devices and electrochromic displays (Afsar, 2013).

## 2. METHODOLOGY

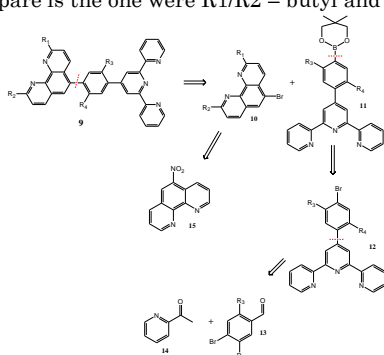
Silica gel 60 was applied to purify chromatography through column chromatography. It is shown<sup>1</sup> H NMR and <sup>13</sup>C NMR spectra were estimated on Avance three 400 Bruker spectrometers; Chemical shifts for <sup>1</sup>H spectra are values from tetramethylsilane in CDCl<sub>3</sub> (δ 0.00 ppm). Chemical shifts for <sup>13</sup>C spectra are values from CDCl<sub>3</sub> (δ 77.16 ppm).

### Materials:

4-bromo-2,5-dimethylbenzaldehyde was prepared using a prescribed procedure. 1,4-dibromo-2,5-dimethylbenzene, nitrophenanthroline, bis(pinacolato)diboron, PdCl<sub>2</sub>(dppf), KOAC, DMF, NH<sub>4</sub>OAc and BuLi were sourced from market suppliers. 4-(4-bromo-2,5-dimethylphenyl)-2,2':6',2''-terpyridine and 4-(4-pinacolatoboron-2,5-dimethylphenyl)-2,2':6',2''-terpyridine were prepared using a prescribed procedure.

## 3. RESULT

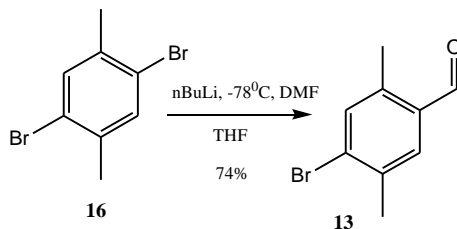
The result revealed as presented in Scheme 2, that the ditopic ligand could be obtained by a Suzuki coupling of a bromo substituted phenanthroline 10 with a boronic terpyridine unit 11. The phenanthroline part could be accessed from commercially available 5-nitrophenanthroline 15 by sequential alkylation, reduction of the nitro followed a diazotization/bromination step. And the terpyridine would be obtained from commercially 4-bromo-2,5-dialkylbenzaldehyde 13 and acetylpyridine 14. The first ligand we started to prepare is the one where R<sub>1</sub>/R<sub>2</sub> = butyl and R<sub>3</sub>/R = methyl.



Scheme 2 : Retrosynthetic analysis of the planned ligand

### Preparation of the starting aldehyde (4-bromo-2,5-dimethylbenzaldehyde)

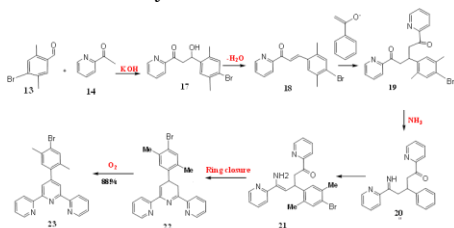
Through a successful metal halogen exchange with nBuLi followed by treatment with DMF, 1,4-dibromo-2,5-dimethylbenzene was transformed to the corresponding aldehyde which serves as the starting material for the subsequent preparation of bromoterpyridine. Detail description of the transformation is given in Scheme 3.



Scheme 3: preparation of the starting aldehyde

### Preparation of bromoterpyridine 23

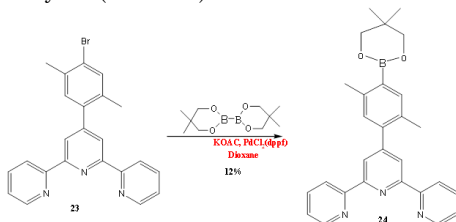
The attempt to prepare bromoterpyridine **23** was successful and was realized in 7 steps (scheme 4), starting from the commercially available acetyl pyridine **14** which was condensed with 4-bromo-2,5-dimethylbenzaldehyde **13** in the presence of  $\text{KOH}$  to provide the corresponding aldol product **17** in a reasonable yield of about 81%. Compound **17** was then dehydrated to give rise to  $\alpha$ - $\beta$  unsaturated product **18** which was then transformed through Michael addition to obtain an intermediate ketone that was utilized in the formation of an imine bearing compound **20** on treatment with ammonia. Subsequent rearrangement of **20** followed by a ring closure resulted in the compound **22** which was finally oxidized by atmospheric oxygen to obtain the bromoterpyridine **23** in 88% overall yield.



Scheme 4: Best route to access bromoterpyridine

### Preparation of the boronic ester

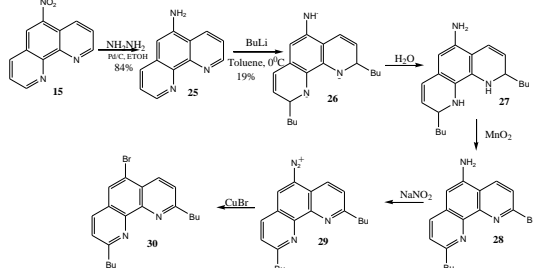
Different palladium catalyst were proposed in order to search for a condition that will give a reasonable borylation yield from the synthesized bromoterpyridine.  $\text{Pd}(\text{dppf})\text{Cl}_2$  was found to be suitable and facilitate the smooth borylation. A Miyaura–Ishiyama borylation reaction between **23** and bis(pinacolato)diboron (molar ratio: 1:1) was carried out in the presence of catalytic  $\text{PdCl}_2(\text{dppf})$  in dioxane to provide boronic ester **24** as a light yellow solid in 12% yield (Scheme 5)



Scheme 5: Palladium catalysis in the borylation of bromoterpyridine

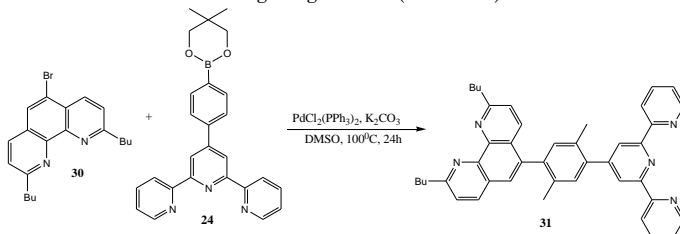
### Preparation of bromophenanthroline

The synthesis of bromophenanthroline **30** was planned in six steps. It begins with the reduction of 5-nitro-1,10-phenanthroline **15** with hydrazine in the presence of Pd/C as catalyst to obtain the corresponding 5-amino-1,10-phenanthroline **25** in 84% yield. It was followed by a deprotonation/nucleophilic addition of the resulting product using BuLi, producing an intermediate ion **26** which upon treatment with water gives rise to **27** in 19% yield. Aminophenanthroline **28** would be obtained as the product of the oxidation of **27** with MnO<sub>2</sub>. This will be followed by the formation of a diazonium salt **29** on reacting compound **28** with NaNO<sub>2</sub>. Finally the transformation of the diazonium salt into the corresponding bromide using CuBr as shown in scheme 6.



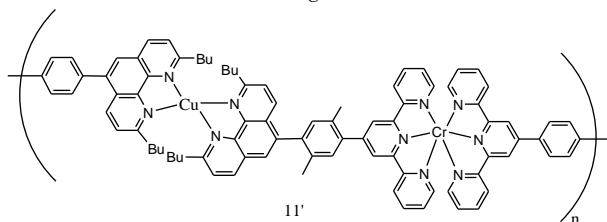
### Formation of the planned ligand

A Suzuki coupling reaction between the bromophenanthroline **30** and the synthesized boronic ester **24** was planned to be conducted according to the method previously described in order to obtain the target ligand **31**. (scheme 7)



### Formation of the coordination polymer

Finally, the planned coordination polymer will be formed from the synthesized bridging ligand **13** by the alternating installation of the two different transition metals (Cu & Cr) along the specific coordination sites of the ligand.



## **5. CONCLUSION**

The stepwise synthesis of the starting aldehyde (4-bromo-2,5-dimethylbenzaldehyde) proceeded well and was obtained in good yield. Likewise the synthesis of bromoterpyridine and boronic ester was equally successful.

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