



# Self-assembly of imidazoliums salts based on acridine with silver oxide as coordination polymers: Synthesis, fluorescence and antibacterial activity

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## ABSTRACT

The reaction of iodomethane, n-butane bromide, bromoethane, benzyl bromide and 9-(1-imidazolyl) acridine obtains the corresponding imidazolium salts, which can further react with NH<sub>4</sub>PF<sub>6</sub>, affording **2a–2d**. Then, they were treated with silver oxide in CH<sub>3</sub>CN or DMSO to afford complexes **3a–3d** ({Ag [1-acridinyl-3-methylimidazoly-diene]<sub>2</sub> (PF<sub>6</sub>)} (**3a**), {Ag [1-acridinyl-3-butylimidazoly-diene]<sub>2</sub> (PF<sub>6</sub>) CH<sub>3</sub>CN} (**3b**), {Ag [1-acridinyl-3-ethylimidazolydiene] (PF<sub>6</sub>)}<sub>n</sub> (**3c**), {Ag [1-acridinyl-3-benzylimidazoly-diene] (PF<sub>6</sub>)}<sub>n</sub> (**3d**)). **3a** and **3b** formed mononuclear silver complexes which presented π–π stacking interactions between acriding rings. Amazingly, **3c** and **3d** formed one-dimensional coordination polymers through self-assembly of N1–Ag1–C16 and N1–Ag1–C14 bonds, respectively. Moreover, **3b**, **3c** and **3d** have been found to have efficient anti-bacterial activity against the *Acinetobacter baumannii* and *P. aeruginosa*. In addition, the imidazolium salts and their corresponding silver complexes show a phenomenon of fluorescence quenching.

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## 1. Introduction

Since the first isolation of free N-heterocyclic carbene (NHC) in 1991 [1], NHCs have been developed rapidly in organometallic chemistry [2]. As the NHCs' strong σ-donor, most of which can lead to stable metal-NHCs with strong metal-carbon bonds. Metal-NHCs are more efficient and more excellent stability toward air and moisture in many catalytic reactions compared with phosphine-metal complexes [3,4]. Several strategies which including the reaction metal compounds with free carbene [5], transmetalation reaction [6], the direct reaction of metal precursors with imidazolium salts [6,7] and electrolysis [8] for the synthesis of metal NHC complexes have been described. However, the direct reaction of the metal complex with the free carbene is the most general method, generally obtained by deprotonation of the imidazolium salt, or the transmetalation reaction with silver(I) NHC complexes, which is the favorite for metal NHC complexes.

Up to now, metal-NHCs have revealed their intriguing structural properties and numerous applications in medicine, nanomaterial, catalysis [9]. Additionally, their potential applications in fluorescent switch [10], antibacterial activity [11], anticancer [12] and anti-parasitic therapy [13] have been received increasing attention. Recently, the synthesis of metallollosupermolecular through self-assembly of metal-NHC has also attracted scientists' great interest [14]. Gimeno et al. have reported several imidazolium salts and silver-NHC complexes containing acridine group [6b]. However, metal-NHCs containing acridine group are rarely reported [15].

For the sake of exposing the structure of more metal-NHCs contain acridine. Herein, we report the preparation of the new imidazolium salts and metal-NHC complexes containing the acridine group. The cations of **2a**, **2d**, and **3a** were analogously reported by Gimeno et al. In our works, **3a** and **3b** formed mononuclear silver complexes which shown π–π stacking interactions between acriding rings. To our surprise, **3c** and **3d** formed 1D polymeric chain through self-assembly of N1–Ag1–C16 and N1–Ag1–C14 bonds, respectively. In addition, the optical properties of the imidazolium salts and the silver complexes were researched. More

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importantly, the efficient antibacterial activities against the *Acinetobacter baumannii* and *Pseudomonas aeruginosa* of Ag–NHCs have been studied.

## 2. Result and discussion

### 2.1. Synthesis and characterization of the imidazolium salts

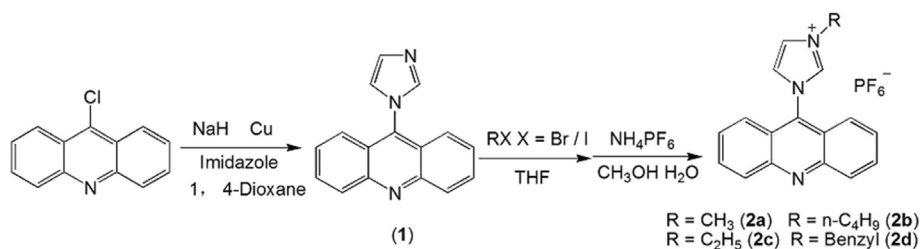
9-(1-imidazolyl) acridine is prepared from imidazole and 9-chloroacridine by NaH as base and powder of copper as catalyst [16]. A high yield is obtained compared to the literature procedure [17]. Compounds (**2a–2d**) were synthesized according to the traditional procedure [15b] (Scheme 1). Additionally, (**2a–2d**) were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectroscopy and elemental analyses. In  $^1\text{H}$  NMR spectrum of **2a–2d**, the chemical shift for the imidazolium, acridine, methylene and methyl protons could be observed (in Supporting Information). The resonances signals (**2a**: 9.75 ppm, **2b**: 9.84 ppm, **2c**: 9.90 ppm, **2d**: 9.93 ppm) corresponding to the NCHN imidazolium proton were found (in Supporting Information), which were confirmed the structures of **2a–2d**.

The yellow crystal of **2b** was grown by slow diffusion of Et<sub>2</sub>O into CH<sub>3</sub>CN solution at room temperature, which had been confirmed by X-ray diffraction. The solid-state molecular structure is depicted in Fig. 1. In molecular structure of **2b**, the imidazole ring and its adjacent acridine ring form a dihedral angle of 64.93°. C14–H14 ... N1 hydrogen bond links the two cations into dimeric unit. In

addition, an interesting phenomenon in the packing diagrams of **2b** is that aromatic  $\pi$ – $\pi$  stacking interactions are observed [18]. Two types of  $\pi$ – $\pi$  interactions for face to face and edge to face are observed in Fig. 2 (center to center and edge to center distances: 3.5753 Å and 3.6167 Å, respectively), which lead to the formation of 2-D supramolecular layer (Fig. 2).

### 2.2. Synthesis and characterization of the complexes

Complexes (**2a–2d**) were treated with silver oxide (Ag<sub>2</sub>O, 0.6 mol equivalent) in CH<sub>3</sub>CN or DMSO to afford complexes (**3a–3d**) (Scheme 2), respectively. Moreover, (**3a–3d**) were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectroscopy and elemental analyses. In the  $^1\text{H}$  NMR spectrum of complexes **3a–3d**, the signals for NCHN imidazolium proton has been disappeared, which have confirmed the formation of the silver-NHCs. Additionally, in the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra an interesting phenomenon was found that the chemical shifts of the methyl for **3a** and methylene for **3b** moved toward high magnetic field compared to their precursors, this can be attributed to the shielding effect of acridine. As is known to us, many influencing factors can result in the difference of metal complexes structures, but ligand and solvent are generally regarded as the primary factors [19]. Complexes **3a–3d** were obtained in two different kinds of structural types, which could be ascribed to the reason that nitrogen atom of acetonitrile coordinated to metal atom of metal NHCs.



Scheme 1. Synthesis of the imidazolium salts.

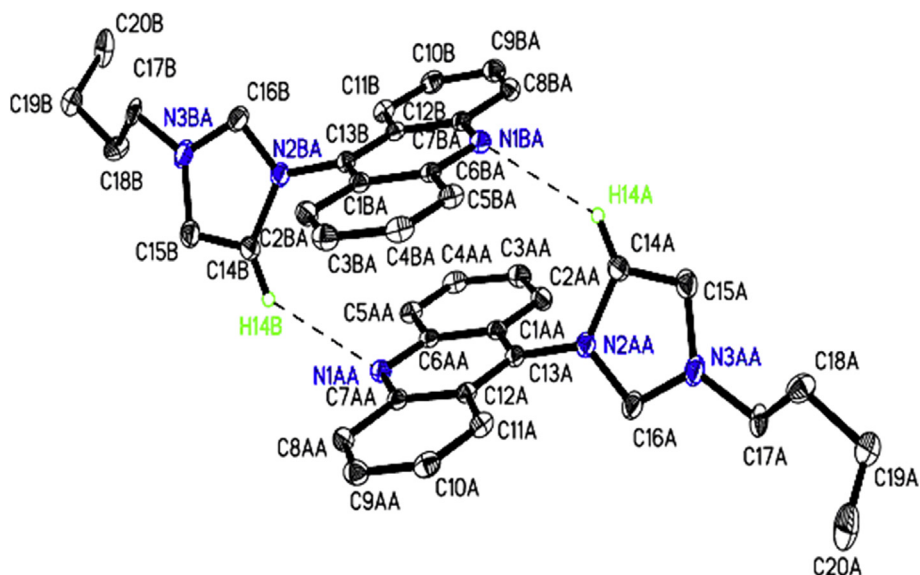


Fig. 1. ORTEP diagram of **2b** with 50% probability ellipsoids. Most hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): N1AA–C6AA 1.3518, C1AA–N2AA 1.1360, C14A–H14A 0.9500, and C16A–N3AA–C17A 119.45.

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