



## Triphenylamine substituted dipyrinato metal complexes: Synthesis, optical and electrochemical studies



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### ARTICLE INFO

#### Article history:

Received 3 May 2015

Received in revised form 11 July 2015

Accepted 25 July 2015

Available online 1 August 2015

#### Keywords:

Dipyrins

Triphenylamine dipyrinato complex

Dinuclear metal complex

### ABSTRACT

A series of triphenylamine substituted dipyrinato metal complexes (**1–8**) have been synthesized. The mononuclear type complexes **1–6** have Ni(II), Co(II), Pd(II), In(III), and Zn(II) metal ions in the core. The binuclear type complexes **7** and **8** have Zn(II) metal ion in the center. All the compounds (**1–8**) were characterized by HRMS, NMR, IR, UV–vis absorption, cyclic voltammetry and fluorescence techniques. The presence of large electron rich triphenylamine moiety at dipyrin ligands affected the spectral properties of complexes. Except Co(II) complex, other metal complexes exhibited blue shifted absorption maxima in UV–vis studies. The In(III) and Zn(II) metal complexes **4–6** showed red shifted emission maxima in fluorescence compared to their corresponding phenyl analogues. Complexes **3–8** exhibited good Stokes shifts in the range of 4600 to 7000  $\text{cm}^{-1}$  with reduced quantum yields. Singlet state lifetimes of complexes **3–8** were in the range of 2 to 4 ns; also the decrease in radiative decay constants  $k_r$  and the increase in non-radiative decay constants  $k_{nr}$  were in line with the quantum yield data. CV studies of complexes **1–8** showed anodic shifts in the oxidation potentials, suggesting that *meso*-triphenylamine group has affected the electronic properties of complexes by making them difficult to oxidize.

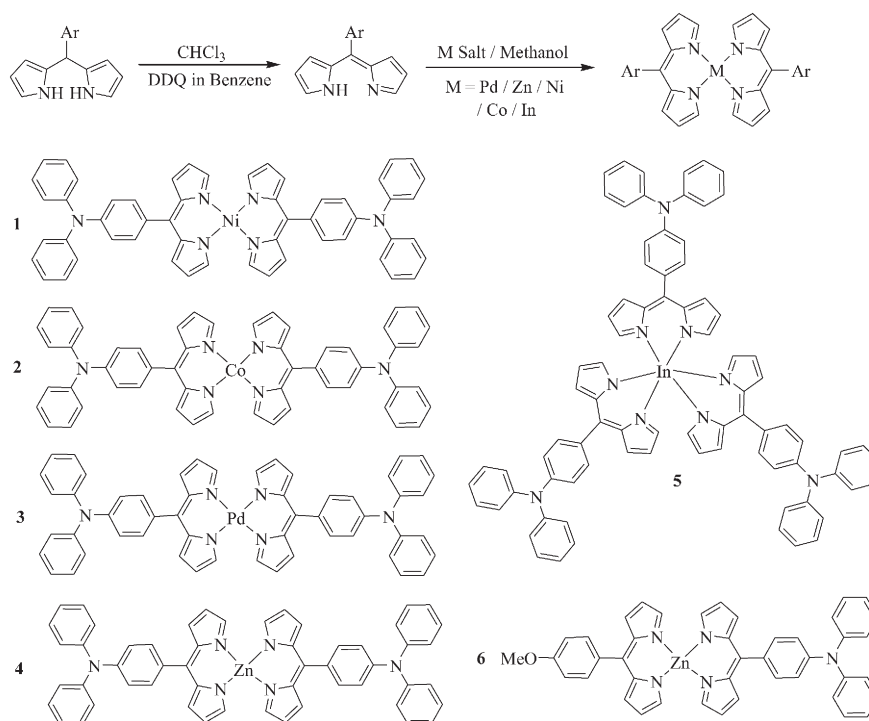
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The chemistry of dipyrans [1] has grown tremendously in last two decades because they have been used as key synthetic precursors for variety of boron based dyes and porphyrin derivatives [2]. The oxidized form of dipyrane is known as dipyrin, it was first reported by Hans Fischer in 1937 [3]. Due to unsaturation the electron density gets delocalized over two pyrrolic rings attached via  $sp^2$  carbon atom in dipyrins. The presence of two coordinating nitrogen atoms in *dipyrin* makes it a good bidentate ligand. The initial efforts to isolate free dipyrins were not so successful; however in the last decade the chemistry of dipyrins has been evolving [4,5]. Dipyrins have been used as ligands to form stable and neutral metal complexes, called metal dipyrinato complexes. Such dipyrinato metal complexes are more stable than free dipyrin ligands. Two kinds of metal–dipyrinato complexes have been reported, first: homoleptic type (contains two similar dipyrin ligands) and second: heteroleptic type (contains two different dipyrin ligands) [6]. A variety of metal complexes has been reported with 3rd row transition metals [7] as well as with 4th and 5th row [8] transition metals. The borondifluoride complexes of dipyrins have found applications in materials and biology due to good photostability and high quantum yields [2]. As compared to dipyrin–borondifluoride

complexes their metal counterparts have been ignored due to lack of fluorescence properties (Ni(II), Cu(II), Co(II) dipyrinato complexes) or low emission efficiencies (Ga(III), In(III), Pd(II) dipyrinato complexes). However, coordination chemistry of dipyrinato ligands continues to attract researchers due to their potential applications in photochemistry. Cohen and co-workers [9] have synthesized supramolecular systems such as metal–organic frameworks (MOFs) based on pyridyl and cyanophenyl dipyrinato complexes. Recently, alkali metal ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) based dipyrinato complexes have also been reported [10] and their applications in salt elimination reactions have been tested. Also, the heteroleptic dipyrinato complexes with Rh(II) have been used as sensitizers for DSSCs (Dye Sensitized Solar Cells) [11]. Most of the metal complexes exhibited interesting luminescent and optical properties. Homoleptic Zn(II) and heteroleptic Re(II) dipyrinato complexes have been found to be highly fluorescent with multi-nanosecond lifetime [12,13]. The bulky mesityl group restricted the rotation around the *meso*-carbon single bond thereby enhancing the excited state lifetime. Lindsey and co-workers have reported the synthesis of zinc bis-dipyrinato bridged porphyrin dyads and energy transfer studies of such systems [14]. Extended conjugation across the two pyrrole rings renders promisingly useful optical properties to the dipyrin derivatives. Nishihara and co-workers have used this feature and reported luminescent In(III) and Zn(II) containing heteroleptic complexes with high quantum yields [15,16]. This paper details the synthesis, photophysical and electrochemical properties of six novel triphenylamine

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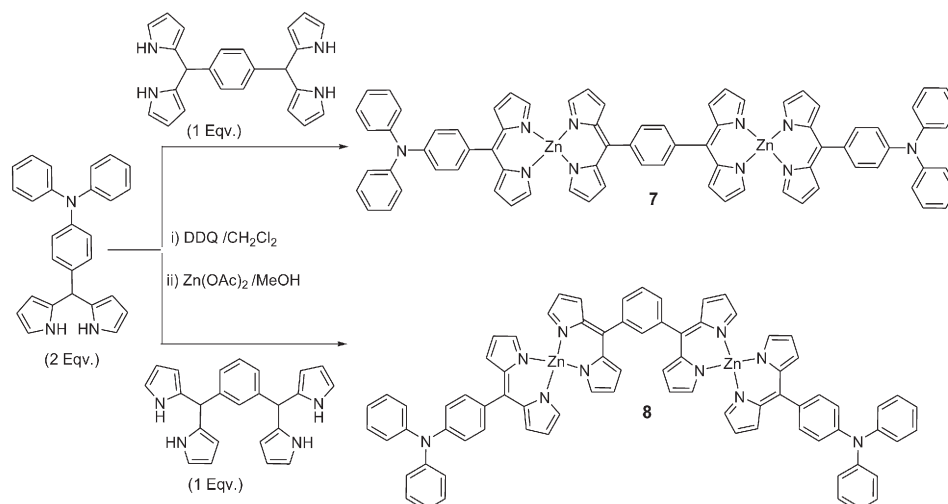


**Scheme 1.** Synthesis of triphenylamine substituted dipyrinato metal complexes **1–6**.

dipyrinato metal complexes having Zn(II), In(III), Pd(II), Ni(II), Co(II) metal ions in the core. Two binuclear zinc complexes based on triphenylamine dipyrinato ligand have also been synthesized and studied. It is anticipated that replacement of *meso*-phenyl groups at dipyrin ligand by bulky and electron rich triphenylamine moiety affects the electronic, photophysical and electrochemical properties of dipyrinato metal complexes.

The triphenylamine aldehyde and corresponding dipyrane were synthesized as per the reported procedure [17]. The triphenylaminodipyrane was oxidized using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) dissolved in benzene and the resulting dipyrin was used immediately to make metal complexes without any

purification. Metal salts dissolved in methanol were added to the dipyrin solution and stirred at room temperature for several hours (Scheme 1). Progress of the reaction was monitored by TLC (thin layer chromatography) and reaction was stopped when new spot developed on TLC plate corresponding to metal complex. Crude metal complexes **1–6** were subjected to silica gel column chromatography and were eluted with 30–50% ethyl acetate/hexane mixture. The pure metal complexes were obtained as reddish maroon color solid in the range of 11–13% yields. Binuclear type zinc dipyrinato complexes **7** and **8** were prepared as per the synthetic procedure shown in Scheme 2. *meta*-benzi and *para*-benzi-bisdipyrans were prepared as per the literature reported procedure [18]. Triphenylaminodipyrane and



**Scheme 2.** Synthesis of binuclear triphenylamine substituted dipyrinato complexes **7** and **8**.

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