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Triphenylamine substituted dipyrrinato metal complexes: Synthesis, optical and electrochemical studies



Sudipta Das, Iti Gupta *

Indian Institute of Technology Gandhinagar, VGEC Campus, Chandkheda, Ahmedabad 382424, India

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ABSTRACT

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Keywords: Dipyrrins Triphenylamine dipyrrinato complex Dinuclear metal complex A series of triphenylamine substituted dipyrrinato metal complexes (1–8) have been synthesized. The monouclear 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 dipyrrin 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 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 dipyrranes [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 dipyrrane is known as dipyrrin, it was first reported by Hans Fischer in 1937 [3]. Due to unsaturation the electron density gets delocalized over two pyrrolic rings attached via sp² carbon atom in dipyrrins. The presence of two coordinating nitrogen atoms in dipyrrin makes it a good bidentate ligand. The initial efforts to isolate free dipyrrins were not so successful: however in the last decade the chemistry of dipyrrins has been evolving [4,5]. Dipyrrins have been used as ligands to form stable and neutral metal complexes, called metal dipyrrinato complexes. Such dipyrrinato metal complexes are more stable than free dipyrrin ligands. Two kinds of metal-dipyrrinato complexes have been reported, first: homoleptic type (contains two similar dipyrrin ligands) and second: heteroleptic type (contains two different dipyrrin 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 dipyrrins have found applications in materials and biology due to good photostability and high quantum yields [2]. As compared to dipyrrin-borondifluoride complexes their metal counterparts have been ignored due to lack of fluorescence properties (Ni(II), Cu(II), Co(II) dipyrrinato complexes) or low emission efficiencies (Ga(III), In(III), Pd(II) dipyrrinato complexes). However, coordination chemistry of dipyrrinato 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 dipyrrinato complexes. Recently, alkali metal (Li⁺, Na⁺, K⁺) based dipyrrinato complexes have also been reported [10] and their applications in salt elimination reactions have been tested. Also, the heteroleptic dipyrrinato 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) dipyrrinato 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 bisdipyrrinato 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 dipyrrin 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

^{*} Corresponding author. *E-mail address:* iti@iitgn.ac.in (I. Gupta).



Scheme 1. Synthesis of triphenylamine substituted dipyrrinato metal complexes 1-6.

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

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

purification. Metal salts dissolved in methanol were added to the dipyrrin 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 dipyrrinato complexes **7** and **8** were prepared as per the synthetic procedure shown in Scheme 2. *meta*-benzi and *para*-benzi-bisdipyrranes were prepared as per the literature reported procedure [18]. Tripheynylaminedipyrrane and



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



Fig. 1. ¹H NMR spectrum of Pd(II) complex 3 recorded in CDCl₃.

meta-benzi- and *para*-benzi-bisdipyrranes were oxidized separately in chloroform using DDQ. Then the oxidized dipyrrins were mixed together and zinc acetate dissolved in methanol was added to the mixture. Reaction mixture was allowed to stir at room temperature for several hours. New orange color spot developed on TLC indicated the formation of dinuclear zinc complex. Complexes **7** and **8** were purified by silica gel column chromatography in 20–40% ethyl acetate/pet ether mixture in 10–12% yields.

All compounds were characterized by Mass, IR, ¹H and ¹³C NMR spectroscopy (ESI). Compounds 1-8 were confirmed by the molecular ion peak in mass spectrometry. Typical HRMS mass analysis showed $[M+1]^+$ peak at 831.3316 for complex **1**. In IR spectra of complexes 1-8 different vibration bands were observed in the range of 654 to 3308 cm⁻¹ corresponding to dipyrrin and triphenylamine groups. Typically, C-H stretching vibrations were observed around 2920 to 3271 cm^{-1} for the dipyrrin and triphenylamine moieties [19]. The ring skeleton C-C stretching and C-H bending vibrations were observed around 1410 to 1709 cm⁻¹. The characteristic C–N stretching vibrations for triphenylamine group were observed between 1328 and 1397 cm^{-1} . The C-H bending (ring) vibrations were observed between 1042 and 1276 cm⁻¹ and out of plane bands were observed around 752 to 976 cm⁻¹. Vibrational bands around 654 to 696 cm⁻¹ were ascribed to ring bending originated from triphenylamine groups [19]. The representative ¹H NMR spectrum of homoleptic palladium complex **3** is shown in Fig. 1. In ¹H NMR of complex 1, eight β -pyrrole protons showed up as two singlets at 6.42 and 6.76 ppm and four α -pyrrole protons showed up as singlet at 7.63 ppm. Twenty eight aromatic protons of triphenylamine appeared as four sets of multiplets between 7.07 and 7.37 ppm. In ¹H NMR of complex **2**, eight β -pyrrole signals were split into three sets and showed up as multiplet at 6.80 and two singlets at 6.48 and 6.19 respectively. Four α -pyrrole proton signals were downfield shifted as compared to complex 1 and appeared as singlet at 8.09 ppm. Twenty eight aromatic protons of triphenylamine appeared as three sets of multiplets between 7.07 and 7.33 ppm. In ¹H NMR of complexes 3 and 4 the signal pattern chemical shift values were similar to complex 1 (ESI). In the case of complex 5 three dipyrrin units were coordinated to indium metal thus six α -pyrrole protons showed up as singlet at 7.87 ppm and twelve β -pyrrole protons appeared as two singlets at 6.99 and 6.59 ppm. The remaining forty two aryl protons showed up as three multiplets at 7.39, 7.23 and 6.99 ppm (the aryl and β -pyrrole proton signals were merged here). In case of heteroleptic complex 6 showed several signals for eighteen aryl protons between 7.41 to 6.98 ppm. The eight β -pyrrole protons showed up as four set of signals between 6.87 and 6.41 ppm, whereas four α -pyrrole protons appeared as two singlets at 7.64 and 7.52 ppm. Three protons of methoxy group appeared as singlet at 3.89 ppm confirming the heteroleptic nature of the complex. The dinuclear zinc complexes 7 and 8 showed doublet for aryl protons of central benzene unit and three set of multiplets for aryl and α -pyrrole protons between 7.31 and 7.11 ppm. The remaining aryl and β -pyrrole protons appeared in between 7.06 and 6.82 ppm in the NMR.

The absorption studies of complexes 1-8 were carried out by UV-vis spectroscopy and solvent dependent molar extinction coefficients in five different solvents were also calculated for all the compounds (Table 1). The comparison of absorption spectra of all the complexes 1-8 is shown in Figs. 2 and 3. The absorption spectra of metal dipyrrinato complexes primarily exhibit the π - π * transition of the dipyrrin ligand [20]. All the complexes 1-8 exhibited intense absorption band in the region of 430–480 nm in toluene, which corresponds to π – π * transitions originated from the dipyrrin ligand. The nickel complex **1** showed single absorption band at 460 nm in dichloromethane (DCM) which was 10 nm blue shifted as compared to the reported diphenyldipyrrinato nickel complex [21]. The cobalt complex 2 showed one major absorption band at 473 nm in DCM (Table 1) which was 10 nm red shifted compared to the corresponding dipyrrin metal complex [22]. Palladium complex 3 showed only one band in DCM at 435 nm (Table 1), whereas the reported dipyrrinato palladium complex exhibited two bands at 400 and 496 nm in the same solvent [23]. The homoleptic zinc complex 4 showed blue shifted absorption band at 426 nm in toluene as compared to the reported diphenyl-dipyrrinato zinc complex [24]. This blue shift

Table 1		
Absorption data of complexes	1-8 in various solvents. Concentration	used was 2×10^{-5} M.

Compound		Solvent					
		Dichloromethane	Chloroform	Ethyl Acetate	Acetonitrile	Toluene	
1	$\lambda_{abs} (\epsilon \times 10^4)$	460 (7.83)	462 (8.10)	480 (7.74)	428 (7.43)	432 (7.73)	
2	$\lambda_{abs} (\epsilon imes 10^4)$	473 (7.83)	475 (7.83)	472 (7.83)	470 (7.83)	476 (7.83)	
3	$\lambda_{abs} (\epsilon \times 10^4)$	435 (10.82)	460 (11.40)	480 (10.07)	432 (8.98)	434 (9.86)	
4	$\lambda_{abs} (\epsilon \times 10^4)$	461 (12.13)	462 (12.17)	425 (10.16)	460 (10.51)	426 (9.93)	
5	$\lambda_{abs} (\epsilon \times 10^4)$	459 (11.64)	462 (11.07)	428 (10.20)	458 (9.27)	435 (8.91)	
6	$\lambda_{abs} (\epsilon \times 10^4)$	481 (12.76)	482 (12.83)	480 (10.87)	479 (10.69)	486 (11.12)	
7	$\lambda_{abs} (\epsilon \times 10^4)$	462 (8.58)	458 (8.39)	427 (6.99)	426 (7.88)	365 (17.86)	
						421 (9.21)	
8	$\lambda_{abs} (\epsilon \times 10^4)$	436 (8.61)	462 (8.52)	425 (7.56)	421 (8.11)	370 (8.71)	
		. ,				428 (9.06)	



Fig. 2. The comparison of absorption spectra of complexes 1, 2, 3 and 5 in toluene.

could be due to the presence of two large electron rich tri-phenylamine groups in the complex. On the other hand, a heteroleptic zinc complex 6 showed maximum intensity absorption band at 486 nm in toluene (Table 1). This is very close to the reported value (485 nm) of heteroleptic dipyrrinato zinc complex [25]. The binuclear zinc complexes 7 and 8 exhibited two absorption bands in toluene, one band of higher intensity around 380 nm and another band around 427 nm. The absorption pattern of 7 and 8 matched with the reported binuclear zinc dipyrrinato complexes [16,26]. The high energy band was due to vibronic coupling and the lower energy band was assigned to the π - π ^{*} transitions of dipyrrin ligands [16]. The area under the absorption curve is proportional to the number of ligands attached to the metal in the complex. Therefore, higher area under the curve represents higher number of ligands in homoleptic class of complexes. This is indeed the case with the indium complex 5, which exhibited higher area under the absorption curve. The indium ion having +3 oxidation state binds with three dipyrrin ligands; whereas, the other metals in their +2 oxidation state bind with only two dipyrrin ligands. Complex 5 exhibited blue shifted band at 435 nm in toluene as compared to the reported dipyrrinato indium complex, which showed two bands at 444 and 496 nm in non-polar solvent [15,27]. Complexes 2 and 6 did not show much shift in absorption band upon changing the solvents from toluene to ethyl

Fig. 3. The comparison of absorption spectra of Zn(II) complexes 4, 6, 7 and 8 in toluene.

acetate (Table 1). On the other hand complexes **1** and **3–8** showed red shifted absorption band upon changing the solvent from non-polar to polar one (Table 1).

The fluorescence properties of compounds 3-8 in ethyl acetate were investigated both by steady state and time resolved fluorescence techniques. Complexes 1 and 2 containing nickel and cobalt ions respectively were non-fluorescent in nature. Time dependent fluorescence studies were performed in ethyl acetate and single excited state lifetimes were measured. Quantum yields, Stokes shifts and singlet state lifetimes of complexes 3-8 are presented in Table 2. Also, the photographs of dichloromethane (DCM) solutions of 3-8 are shown in Fig. 4. The solutions of complexes 3, 7 and 8 looked brightly luminescent under UV light. The comparison of the normalized emission spectra of 3-8 is shown in Fig. 5 and lifetime decay profiles of **4–6** are shown in Fig. 6. The typical mirror-image relationship was observed for the lowest energy absorption band and emission spectra of all the complexes **3–8**. Complex **3** exhibited one emission band at 625 nm in ethyl acetate, which matched with the corresponding reported complex [24]. The mononuclear zinc complexes 4 and 6 showed about 100 nm red shifted emission bands at 605 and 611 nm respectively (Table 2). The emission maximum for complex 5 with indium center was observed at 560 nm, which was 38 nm red shifted compared to the corresponding compound [27]. Emission bands of binuclear zinc complexes 7 (533 nm) and 8 (503 nm) were 45-75 nm blue shifted compared to the similar binuclear zinc complex [16]. The quantum yields for all compounds 3-8 were not quite high which was ascribed to the non-radiative decay processes involved. Stokes shifts for complexes 3-8 were calculated in ethyl acetate and found to be in the range of 3648 to 7000 cm^{-1} (Table 2). Fluorescence lifetime experiments indicated that complexes **3–6** had first order decay with lifetimes (τ_1) in the nano-second range. The binuclear zinc complexes 7 and 8 showed biexponential decay (Table 2) [16]. The lifetime data for complexes 4-8 was similar to the reported values of their corresponding complexes, except for 3 where the singlet state lifetime was significantly higher than the reported palladium dipyrrinato complex [13]. The nonradiative relaxation from dipyrrin centered excited states primarily takes place depending upon the rotation of the meso-aryl substituents. If rotation of meso-aryl group is hindered then emission gets enhanced. The meso-aryl substituents though, affect the quantum yield and the excited state (S_1) lifetime (τ) ; it does not influence much on the absorption and emission patterns. It is clear from the emission data (Table 2) that the rate of the non-radiative decay process was higher than the radiative process for all the complexes.

Cyclic voltammetry studies of all complexes **1–8** were conducted using BASi epsilon electrochemical workstation. The cyclic voltammetry measurements were carried out in dry DCM at the scan rate of 50 mV/s using 0.1 M tetra-butylammoniumperchlorate (TBAP) as supporting electrolyte. The redox potential data and a comparison of oxidation

Table 2
Emission data and singlet excited state lifetimes of 3–8 in ethyl acetate.

Compound	λ_{ex}^{a} (nm)	λ_{em} (nm)	$\phi_{\rm f}$	Stokes shift (cm ⁻¹)	$\lambda_{ex}^{\ b}$ (nm)	τ_1 (ns)	τ_2 (ns)	k _r (10 ⁹ s ⁻¹) ^c	$_{(10^9 \mathrm{s}^{-1})^{\mathrm{d}}}^{k_{\mathrm{nr}}}$
3	480	625	0.015	4833	445	3.48	-	0.004	0.283
4	458	605	0.013	7000	445	3.90	-	0.003	0.253
5	418	560	0.014	5507	405	1.99	-	0.007	0.495
6	480	611	0.012	4466	445	4.01	-	0.003	0.246
7	432	533	0.022	4657	445	2.71	0.50	0.008	0.361
8	415	503	0.021	3648	405	2.62	0.08	0.008	0.374

^a Excitation wavelength.

^b Laser source excitation wavelength.

^c Data collected at their respective emission maxima.

^d These data fitted to biexponential curve.



Fig. 4. The photographs of 3-8 dissolved in DCM; (a) under ambient light, (b) under UV light. Absorbance was fixed at similar values for all samples.

waves are summarized in Table 3 and Fig. 7 respectively. All the complexes 1-8 showed only reversible or quasi reversible one electron oxidation wave. Also, none of the complex showed any redox wave in negative potential window during electrochemical analysis. All the metal complexes 1-8 have shown ligand centric electrochemistry which is consistent with the literature reports [28,29]. Complex 1 exhibited one reversible oxidation peak at 1.282 V, which was higher than the reported oxidation potentials of bis-dipyrrinato nickel complex (0.80 and 1.09 V) [30]. Complex 2 showed reversible oxidation peak at 1.145 V, whereas the reported ferrocynyldipyrrinato-cobalt complex exhibited oxidation waves at 0.364 V corresponding to Fc/Fc⁺ based oxidations [31]. Same group reported oxidation potential of bis-ferrocenyldipyrrinato palladium complex at 0.349 V, which corresponded to *meso*-ferrocenyl unit in the complex [31]. The palladium complex 3 exhibited guasi-reversible oxidation waves at 1.361 V (Table 3). In the series of all homoleptic type complexes highest oxidation potential was found in the case of palladium complex. On the other hand, lowest value of oxidation potential was found in the case of indium complex 5 at 1.08 V (Table 3). For mononuclear zinc complexes 4 and 6 and binuclear complexes 7 and **8**, only one reversible oxidation wave was observed (Table 3). The corresponding bis-dipyrrinato zinc complex showed two oxidation waves at 0.81 and 0.94 V and no reduction waves were observed for the corresponding oxidation processes [24]. On the other hand the complexes 1-8 described in this report did not show any reduction peaks in the negative potential window. All the complexes 1-8 exhibited higher oxidation potentials than their reported corresponding metal-dipyrrinato complexes, thus making them difficult to oxidize.



Fig. 5. The comparison of normalized emission spectra of 3-6 and 7-8 (inset) in ethyl acetate.

In summary, a series of triphenylamine substituted dipyrrinato metal complexes have been presented. Both homoleptic and heteroleptic type complexes as well as binuclear metal complexes have been synthesized and characterized. The presence of bulky electron rich triphenylamine moiety on the dipyrrinato ligands affected the photophysical properties of the complexes. The absorption maxima were blue shifted for Ni(II), Zn(II), Pd(II), and In(III) dipyrrinato complexes. Except for complex **8**, all the complexes (**3**–**7**) exhibited red shifted emission maxima and reduced quantum yields with respect to their corresponding phenyl substituted metal complexes. Descent Stokes shifts (from 3648 to 7000 cm⁻¹) were observed for complexes **3–8**. The luminescent complexes of zinc and indium have potentials to be used in organic photovoltaics as sensitizers with appropriate functionality.



Fig. 6. Fluorescent lifetime decay profiles of complexes 4, 6 (λ_{ex} = 445 nm) and 5 (λ_{ex} = 405 nm) in ethyl acetate.

Table 3 Electrochemical redox data (V) of complexes **1–8** in DCM, containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV/s scan speed (V vs SCE).

Compound	E_{ox} (V vs SCE)
1	1.282
2	1.145
3	1.361
4	1.286
5	1.088
6	1.17
7	1.268
8	1.209



Fig. 7. Cyclic voltammograms of complexes 1-8 in DCM, containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV/s scan speed (V vs SCE).

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Appendix A. Supplementary material

The experimental section and selected characterization data like ESI-MS, ¹HNMR spectra, fluorescence decay profiles and absorption spectra of reported compounds are available as electronic supplementary material. Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.inoche.2015.07.019.

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