

## **Comparative Density Functional Theory Study on Co (III), Ni (II), Zn (II) Organometallic Complexes and their UV-Vis Absorption Spectra in Dichloromethane Solvent**

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### **ABSTRACT**

The structural and electronic energy of Co(III), Ni (II) and Zn (II) complexes, based on phenyl pyrazole (ppz) and acetylacetonate (acac) ligands have been investigated theoretically in details using DFT/B3LYP method. The most stable structure for three metal ions was predicted to be a distorted octahedral, square-planar and tetrahedral for Co(ppz)<sub>2</sub>acac, Ni(ppz)<sub>2</sub> and Zn(ppz)<sub>2</sub>, respectively and the stability ordering of complexes was found to be Zn(ppz)<sub>2</sub> < Ni(ppz)<sub>2</sub> < Co(ppz)<sub>2</sub>acac. The results show that ppz as the most dominant ligand coordinates to all metal ions forming five member-chelating-ring for stabilization complexes. Time-dependent density functional theory (TD-DFT) method included electrostatic influence of the solvent dichloromethane using IEFPCM has been employed to explore the absorption spectra of the complexes. The effect of solvent could contribute the reduction of maximum absorption wavelengths ( $\lambda_{\max}$ ) of the complexes when compared with their gas phase.

*Keywords : organometallic complexes, UV-Vis absorption spectra, time-dependent density functional theory, binding energy*

## INTRODUCTION

In the last decade, organic light emitting diode (OLED) has attracted considerable interest in the fast-growing field of color flat-panel display technology due to its cost effectiveness, energy efficiency and better aesthetics. The development of new materials including advance manufacturing techniques have led to the profitable commercial technology and OLED have already used in small displays in mobile phones, car stereos and digital cameras (Borchardt, 2004). The materials frequently have used in OLED devices are small-molecule organics (Kim *et al.*, 2008), polymer (Burroughes *et al.*, 1990; Remmers *et al.*, 1996) and, recently, organometallic complexes (Hsieh *et al.*, 2011; Baranoff *et al.*, 2011). Iridium (III) cyclometalated complexes along with N-N heteroleptic ligands have considered good candidates to be used for OLED color tuning because of their unique photophysical properties and high phosphorescence quantum yields (Baranoff *et al.*, 2011; Censo *et al.*, 2008; Angelis *et al.*, 2007). Among these N-N heteroleptic ligands, phenyl pyrazol and substituted phenyl pyrazol have been proposed for the synthesis efficient OLED materials (Chi and Chou, 2010; Tamayo *et al.*, 2003).

Theoretical calculations using density functional theory (DFT) methodology have been successfully applied in the study of a large numbers of metal complexes used in OLED materials to evaluate a variety of ground-state properties with an accuracy close to that of experimental electrochemical measurement (Wong *et al.*, 2006; Tamayo *et al.*, 2005; You and Park, 2005). Especially, iridium complexes have gained considerable attention as the most effective materials in OLED to explore their 's electronic structures, spectroscopic properties, optoelectronic properties and nature of lowest excited states because of high thermal stability, short lifetime in excited states and strong spin-orbital couple effect of these complexes (Urinda *et al.*, 2016; Shi *et al.*, 2010; Gu *et al.*, 2008; Avilov *et al.*, 2007).

In this work, a comparative structural and energetic information of organometallic complexes for each metal ions such as Co(III), Ni (II), Zn (II) coordinated with phenyl pyrazole (ppz) and acetylacate (acac) ligands were investigated by quantum chemical calculation using B3LYP hybrid density functional theory (HDFT) method to understand the coordination ability of organic ligands toward transition metal ions. To obtain absorption property in terms of the interaction between the metal and the ligands, TD-DFT included electrostatic influence of the solvent dichloromethane using integral equation formalism of the polarizable continuum model (IEFPCM) was employed to perform the simulated UV-Vis spectra of these organometallic complexes. The main goal in this work is to search the most stable complex structure of each metal ions and to simulate their UV-Vis absorption spectra. In addition, the understanding of the interaction between the metal and these ligands will help future design of novel complexes based on these ligands for many applications in OLEDs.

## COMPUTATIONAL METHODS

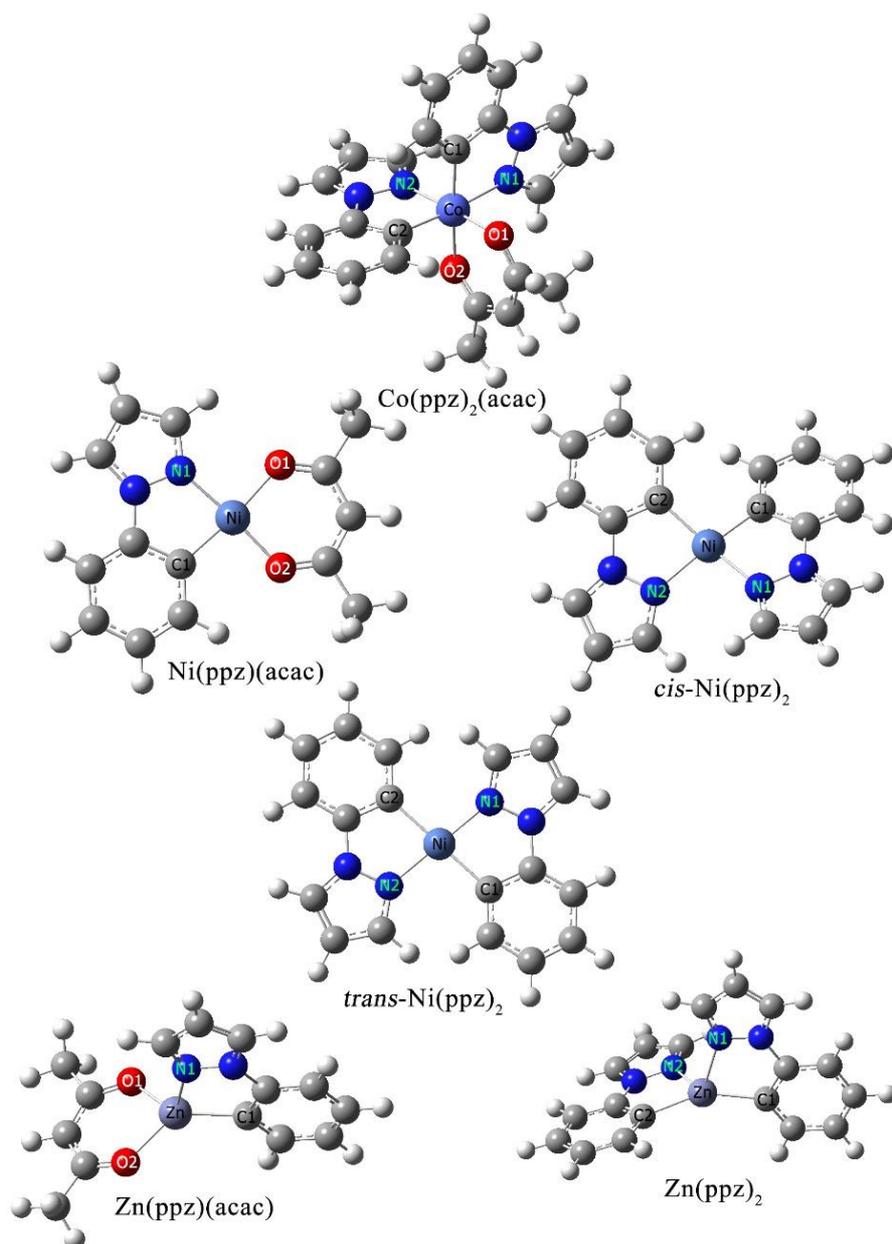
The possible geometries in the singlet ground state ( $S_0$ ) of the each organometallic complex were obtained by complete geometry optimization without any geometrical constraints using the density functional theory with the Beck's three-parameters hybrid exchange functional (Becke, 1993) combined with the Lee, Yang and Parr correlation functional (Lee *et al.*, 1988) as denoted B3LYP. The mixed basis sets, triple  $\zeta$  6-311+G(d,p) for all the constituting atoms of the ligands (ppz, acac) and

the relativistic effective core potentials (ECP) LANL2DZ (Hay and Wadt, 1985) for metals (Co, Ni, Zn), were employed throughout the calculations. All the "inner core electrons" of all metal atoms were replaced and described with a "core" potential while the "valence electrons" (3s, 3p, 3d, 4s orbitals) in the active space were described with a spitting double  $\zeta$  valence basis set without an additional set of polarization functions. The binding energy was obtained as the difference between the total energy of the organometallic complexes and the sum of the total energies of the most stable structures of the isolated moieties. The ZPE energies determined with the zero point vibrational energy (ZPVE) corrections were obtained from the frequency calculations at the same level. All calculations were performed with the Gaussian 03 program software package (Frisch *et al.*, 2006). In order to understand the absorption property, the computed UV-Vis spectra for each metal complexes in solvent dichloromethane simulated from the electronic transitions computed at the IEFPCM/TD-DFT/B3LYP with the same basis set using the GaussSum 2.2 software (O'Boyle *et al.*, 2008).

## RESULTS AND DISCUSSION

### Structure and Energetic Analysis of the Organometallic Complexes

The structures of the organometallic complexes for each metal ion are presented in Figure 1. The energetic analysis of all the organometallic complexes carried out in this study is summarized in Table 1. The calculation predicted one, three and two complexes for  $\text{Co}^{3+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ , respectively as shown in Figure 1. Binding energies,  $\Delta E_{\text{bind}}$ , are defined as the total energy of the organometallic complexes minus the sum of the metal ion and the most stable free ppz and acac ligands. The stability ordering obtained at B3LYP/6-311+G(d,p) combined B3LYP/LANL2DZ level is predicted to be Zn(II) complex < Ni(II) complex < Co(III) complex. Concerning the  $\text{Co}(\text{ppz})_2(\text{acac})$  complex, the nitrogen donor atom of the pyrazole ring and the carbon atom of the phenyl group are able to form one five-membered chelated ring per ligand in binding the  $\text{Co}^{3+}$ . In addition, the two oxygen atoms of acetyl acetate ligand can contribute to coordinate the metal ion center. The stability ordering of Ni(II) complexes establishes that  $\text{Ni}(\text{ppz})(\text{acac}) < \text{trans-Ni}(\text{ppz})_2 < \text{cis-Ni}(\text{ppz})_2$  while it is  $\text{Zn}(\text{ppz})(\text{acac}) < \text{Zn}(\text{ppz})_2$  for Zn (II) complexes. The result may suggest that both ppz ligands play a more dominant role than one ppz and one acac ligand to form two five-membered chelated ring in the stabilization of all metal complexes. In the case of  $\text{Ni}^{2+}$  complexes, *cis*-Ni(ppz)<sub>2</sub> is more stable than *trans*-Ni(ppz)<sub>2</sub> and the  $\Delta E_{\text{bind}}$  difference between those forms is about 7.3 kcal mol<sup>-1</sup> while  $\Delta E_{\text{bind}}$  difference between *cis*-Ni(ppz)<sub>2</sub> and Ni(ppz)(acac) is predicted to be about 13.2 kcal mol<sup>-1</sup>. For the Zn(II) complexes,  $\Delta E_{\text{bind}}$  difference between Zn(ppz)<sub>2</sub> and Zn(ppz)(acac) is about 6.4 kcal mol<sup>-1</sup>. The  $\Delta E_{\text{bind}}(\text{ZPE})$  values for all organometallic complexes corrected for ZPVE are also presented in Table 1. The effect of ZPVE does not modify the stability ordering for all complexes. However, it reduces  $\Delta E_{\text{bind}}$  values of Ni(II) complexes and by contrast, it increases  $\Delta E_{\text{bind}}$  values of Zn(II) complexes and Co(III) complexes.



**Figure 1** Optimized structures of possible Co (III) complexes, Ni (II) complexes and Zn (II) complexes obtained at B3LYP level using 6-311+G(d,p) and LANL2DZ basis sets for both ligands and metal ion, respectively.

**Table 1** Energetic analysis for all organometallic complexes obtained at B3LYP level using 6-311+G(d,p) and LANL2DZ basis sets for both ligands and metal ion, respectively.

Complex	$\Delta E_{\text{bind}}$ (kcal mol <sup>-1</sup> )	$\Delta E_{\text{bind}}$ (ZPE) (kcal mol <sup>-1</sup> )	$\Delta H$ (kcal mol <sup>-1</sup> )	$\Delta G$ (kcal mol <sup>-1</sup> )
Co(ppz) <sub>2</sub> (acac)	-1568.51	-1558.35	-1559.77	-1520.75
Ni(ppz)(acac)	-751.46	-798.23	-799.54	-773.59
<i>cis</i> -Ni(ppz) <sub>2</sub>	-764.67	-812.11	-813.26	-787.12
<i>trans</i> -Ni(ppz) <sub>2</sub>	-757.33	-803.96	-805.79	-777.62
Zn(ppz)(acac)	-635.44	-630.32	-630.80	-609.64
Zn(ppz) <sub>2</sub>	-641.88	-636.68	-636.93	-615.67

**Table 2** Structural parameters for the organometallic complexes of each metal ions (Co<sup>3+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>)<sup>a</sup> (Aton numbering correspond to Figure1).

	Co(ppz) <sub>2</sub> (acac)	Ni(ppz)(acac)	<i>cis</i> - Ni(ppz) <sub>2</sub>	<i>trans</i> - Ni(ppz) <sub>2</sub>	Zn(ppz)(acac)	Zn(ppz) <sub>2</sub>
Bond length (Å)						
M-C1	1.950	1.911	1.920	1.994	2.058	2.080
M-N1	2.043	1.903	1.984	1.925	2.210	2.249
M-C2	1.925	-	1.920	1.994	-	2.080
M-N2	1.947	-	1.984	1.925	-	2.249
M-O1	2.008	1.879	-	-	2.032	-
M-O2	1.932	1.935	-	-	2.031	-
Bond angle (°)						
C1-M-N1	82.45	83.32	83.66	82.39	81.17	79.48
C1-M-O1	173.98	173.62	-	-	131.21	-
C1-M-O2	88.60	92.11	-	-	131.21	-
N1-M-O1	91.76	90.30	-	-	110.88	-
N1-M-O2	89.42	175.43	-	-	110.88	-
O1-M-O2	92.99	94.26	-	-	89.90	-
C2-M-N1	175.21	-	164.32	97.60	-	118.27
C2-M-N2	83.23	-	83.66	82.39	-	79.48
C2-M-C1	94.10	-	98.69	180.00	-	152.00
C2-M-O1	91.58	-	-	-	-	-
N2-M-C1	91.44	-	164.32	97.60	-	118.27
N2-M-N1	93.49	-	98.27	180.00	-	105.97

<sup>a</sup> All organometallic complexes were optimized at B3LYP using 6-311+G(d,p) and LANL2DZ basis sets for ligands (ppz, acac) and metal ions, respectively.

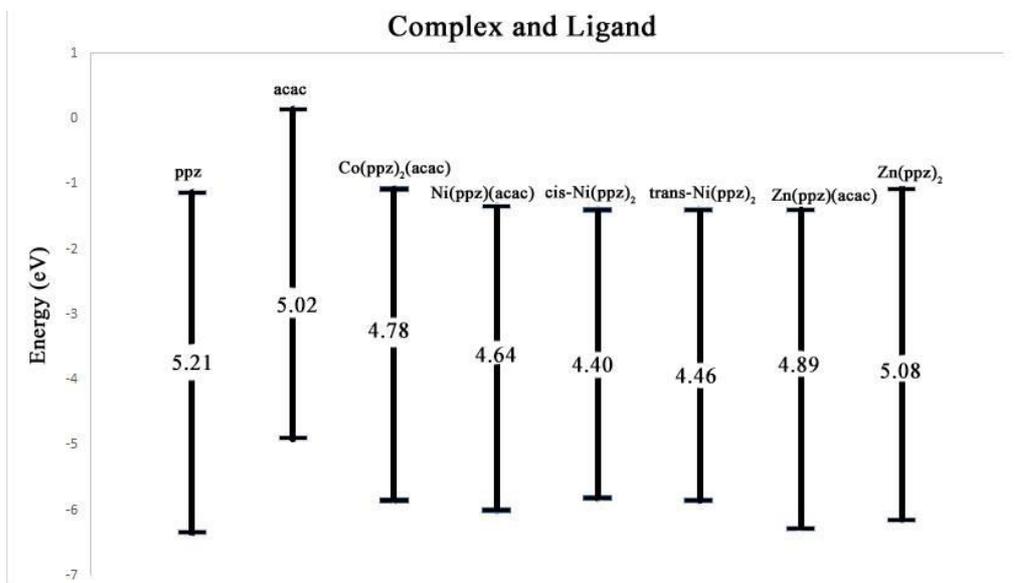
The enthalpy change ( $\Delta H$ ) and free energy change ( $\Delta G$ ) of formation for all organometallic complexes of each metal ion in gas phase were calculated from the frequency calculation at the same level. The  $\Delta H$  of formation for each organometallic complex is denoted as the sum of electronic and thermal enthalpies of the organometallic complex minus the sum of the sum electronic and thermal enthalpies of the metal ion and the most stable free ligands, whereas the  $\Delta G$  of formation for each organometallic complex is defined as the difference of the sum of electronic and thermal free energies for the organometallic complex (product) and the metal ion and the most stable free ligands (reactants). Both the values of  $\Delta H$  and  $\Delta G$  are found to be

negative, which shows that the all complexes are stable and the each complex formation is exothermic process.

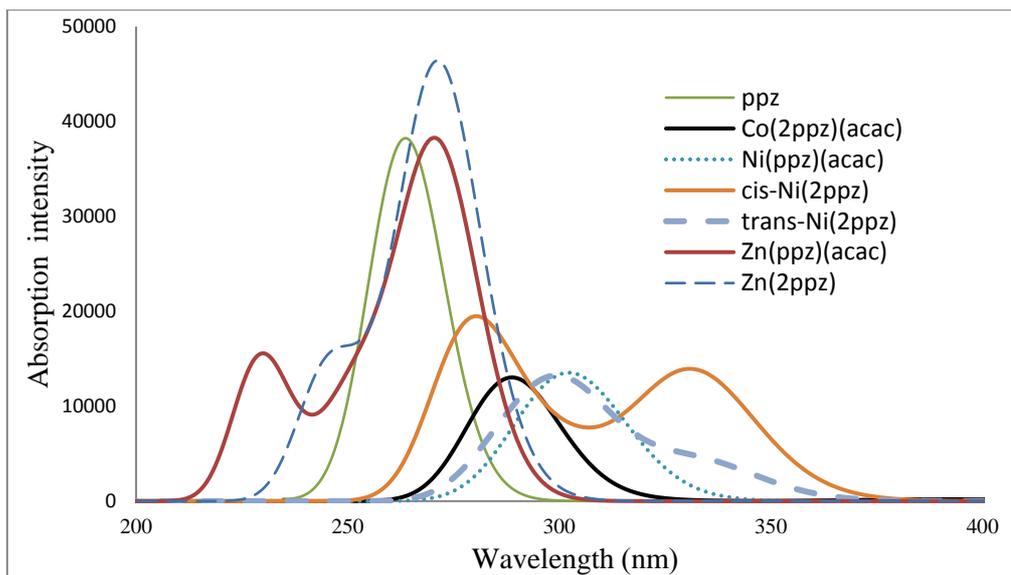
Some relevant geometrical parameters of all metal complexes are presented in Table 2. The geometrical structure of the Co(III) complex is assigned to be a distorted octahedral coordination (Figure 1), which is in a good corresponding to a previous theoretical DFT study on a similar iridium(III) complexes obtained at PBE0/6-31G(d,p) level for all the constituting atoms of the ligands combined with PBE0/LANL2DZ level for Ir (Urinda *et al.*, 2016). The average of bond angles (see Table 2) of the Co(III) complex (89.99°, 175.4°) are close to the standard octahedral structure (90°, 180°). The most stable complex for the Ni<sup>2+</sup> adopts a distorted square planar coordination to the central metal ion, as shown in Figure 1. The average of bond angles (see Table 2) of the Ni(II) complex (89.99°, 174.53°) are close to the standard square planar structure (90°, 180°). This is in a good corresponding to the known preference of Ni<sup>2+</sup> to form four coordinated square planar structure. On the other hand, the most stable complex for Zn<sup>2+</sup> favors a distorted tetrahedral geometry orientation (see Figure 1), which corresponds to a former study on Zn(II) complex with 5-amidopyridine-8-hydroxyquinoline obtained at B3LYP level of DFT and 6-31G(d) basis set for ligand and 3-21G(d) for Zn (Núñez and Vivas, 2008). The average of bond angles of the Zn(II) complex as shown in Table 2 (109.21°) are close to the standard tetrahedral structure (109.5°). Concerning the most stable structures of Ni(II) and Zn(II) complexes, the two M-C distances increase from *cis*-Ni(ppz)<sub>2</sub> to Zn(ppz)<sub>2</sub> in 0.16 Å and the two M-N distances increase from *cis*-Ni(ppz)<sub>2</sub> to Zn(ppz)<sub>2</sub> in 0.27 Å. This indicates that the metal-ligand interaction in *cis*-Ni(ppz)<sub>2</sub> is stronger than in Zn(ppz)<sub>2</sub>, which is in a good corresponding to their stability. Also all bond lengths have a small increase from Ni(ppz)(acac) to Zn(ppz)(acac) in 0.15, 0.30, and 0.10-0.15 Å for M-C, M-N, M-O, respectively, which supports the higher stability on Ni(ppz)(acac) than Zn(ppz)(acac). In addition, the M-C bond lengths are always shorter than the M-N bond lengths for most stable complexes of each metal ions, which reveals the stronger M-C interaction than M-N interaction in complexes.

### Molecular Orbital Analysis in Ground State

The electron withdrawing abilities of the ligands could be measured by the electronegativity ( $\chi$ ), which can be approximated from the average value of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies as shown in the expression  $\chi = -(E_{\text{HOMO}} + E_{\text{LUMO}})/2$  (Shi *et al.*, 2010). The calculated  $\chi$  values of ppzH (3.74) are higher than of acac (2.38), pointing out that the decreasing of electron withdrawing abilities. Energy gap of both ligands and all organometallic complexes are presented in Figure 2. From Figure 2, ligand ppz has lower HOMO and LUMO energy level than ligand acac and ligand ppz shows a wider HOMO-LUMO energy gap (5.21 eV) than ligand acac (5.02 eV). The formation of all complexes reduce HOMO-LUMO energy gap except Zn(ppz)<sub>2</sub> when compared with both free ligands. Substitution ppz by acac decreases the HOMO and LUMO energies at the same time for Zn(II) complexes but it decreases the HOMO energy and increases slightly LUMO energy at the same time for Ni(II) complexes. As known, the HOMO-LUMO energy gap decreases in the presence of strong electron donating ligand and the HOMO-LUMO energy gap increases in the presence of strong electron withdrawing ligand (Urinda *et al.*, 2016). This situation was found in Zn(II) complex.



**Figure 2** Energy gaps of ligand and organometallic complexes.



**Figure 3** Computed UV-Vis absorption spectra for the ligand and all complexes in dichloromethane. All spectra were simulated from the electronic transitions computed using the IEFPCM/TD-DFT/B3LYP.

**Table 3** The vertical excited singlet states, transition character and oscillator strength and computation absorption energy ( $\lambda_{\max}$ ) of all complexes in dichloromethane media obtained at IEFPCM/TD-DFT/B3LYP using 6-311+G(d,p) and LANL2DZ basis sets for ligands and metal ion, respectively.

<sup>a</sup>. Ref. (Katlenok *et al.*, 2012)

	Excited state	Energy gap (eV)	Transition character	Oscillator strength	$\lambda_{\max}$ (nm) Calc.
ppz	S <sub>1</sub>	4.70	H->L (85%)	0.519	263.60 (255.00) <sup>a</sup>
Co(ppz) <sub>2</sub> (acac)	S <sub>11</sub>	4.32	H-1->L (39%)	0.095	286.85
Zn(ppz)(acac)	S <sub>4</sub>	4.56	H->L+1 (85%)	0.337	271.43
	S <sub>12</sub>	5.42	H->L+2 (24%)	0.124	228.35
Zn(ppz) <sub>2</sub>	S <sub>4</sub>	4.57	H-1->L (60%)	0.332	271.08
Ni(ppz)(acac)	S <sub>8</sub>	4.05	H->L+1 (72%)	0.106	306.41
<i>cis</i> -Ni(ppz) <sub>2</sub>	S <sub>12</sub>	4.44	H-3->L (73%)	0.244	279.06
	S <sub>10</sub>	4.06	H-1->L+1 (47%)	0.057	299.96
<i>trans</i> -Ni(ppz) <sub>2</sub>	S <sub>10</sub>	4.10	H-3->L (86%)	0.145	302.14

### The Simulated UV-Vis Spectra of Organometallic Complexes

To study the absorption spectra, the optimized ground-state geometries of all complexes were performed in gas phase and solvent dichloromethane using IEFPCM/TD-DFT/B3LYP method at the same basis sets for the lowest 12 spin-allowed transitions. The simulated UV absorption spectra of all organometallic complexes in solvent dichloromethane are presented in Figure 3. The convolution of the spectra of Figure 3 were stimulated using the GaussSum 2.2 software, which is very similar to the measure UV spectrum. The vertical excited singlet state, transition energies, transition character, oscillator strength and the corresponding excitation energy absorption wavelength ( $\lambda_{\max}$ ) computed at the B3LYP/6-311+G(d,p) combined B3LYP/LANL2DZ level for all complexes and free ppz ligand in dichloromethane solvent are summarized in Table 3. The Table 3 indicates that for ligand ppz, the excitation energy for the S<sub>1</sub> state is the most significant one. This transition corresponds to the absorption wavelength of 263.6 nm when compared with the previous experimental theory reported as 255 nm (Katlenok *et al.*, 2012). For complexes, S<sub>i</sub> represents the *i*th excited states. From Figure 3, it shows that relative absorption intensities of all complexes: Zn(ppz)<sub>2</sub> > Zn(ppz)(acac) > *cis*-Ni(ppz)<sub>2</sub> > Ni(ppz)(acac) > *trans*-Ni(ppz)<sub>2</sub> > Co(ppz)<sub>2</sub>(acac) while as the maximum absorption wavelengths for all complexes is in order: Ni(ppz)(acac) > *trans*-Ni(ppz)<sub>2</sub> > Co(ppz)<sub>2</sub>(acac) > *cis*-Ni(ppz)<sub>2</sub> > Zn(ppz)<sub>2</sub> > Zn(ppz)(acac). It is noted that the blue-shifting of the absorption maxima vary around 1.5- 9 nm when compared to its gas phase. May be a state specific solvation continuum model could be applied for this issue in a more convenient way.

## CONCLUSION

The comparative study on the organometallic complexes for each metal ion such as Co(III), Ni(II), Zn(II) were analyzed in details. The DFT/B3LYP calculation showed one, three and two structures complexes for  $\text{Co}^{3+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  respectively. The coordination is made by one carbon and one nitrogen in each ppz ligand forming a set five membered ring to play a most important role for the stabilization these complexes. The stability ordering of the most stable structure is found to be Zn(II) complex in a distorted tetrahedral coordination < Ni(II) complex in a distorted square planar coordination < Co(III) complex in a distorted octahedral configuration. Frequency calculations support that the each metal complex formation is a spontaneous exothermic process. In addition, the simulated absorption spectra were performed in dichloromethane solvent by EFPCM/TD-DFT/B3LYP method. The polarizable continuum model of this solvent leads to the reduction of maximum absorption wavelengths of all complexes as compared with their gas phase.

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