



## Synthesis, Characterization, Catalytic Applications and Optical Sensing Properties of Palladium Complexes Containing Tetradentate Schiff Bases

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In this study, the synthesis, spectroscopic and catalytic properties of PdL<sup>n</sup> (n = 1-6) complexes with tetradentate -ONNO- and -SNNS- type Schiff base ligands L<sup>n</sup>H<sub>2</sub> (n = 1-6) were investigated. The PdL<sup>n</sup> (n = 1-6) complexes were synthesized by the thermal reactions of the Schiff bases and Pd(OAc)<sub>2</sub> in acetonitrile and characterized by elemental analysis, FT-IR, <sup>1</sup>H NMR, UV-visible and TGA/DTG. The spectroscopic studies suggest that all of the ligands are coordinated to the central metal as a tetradentate ligand coordinating *via* the central azomethine nitrogens (C=N) and phenolic oxygen/sulfur atoms. On the palladium-catalyzed Suzuki cross-coupling reactions employing PdL<sup>n</sup> (n = 1-6) complexes toward a various substituted arylbromides and boronic acids were pursued. The conversions were obtained and yields with different arylbromides were calculated and discussed. All the complexes were thermally stable and were not sensitive to air or the moisture. The complexes were easily prepared from low cost precursors that could be used as versatile and catalysts for different C-C coupling reactions (Suzuki-Miyaura reactions). Moreover steady state fluorescence emission and excitation spectra were measured. These studies have been shown that PdL<sup>2</sup> and PdL<sup>3</sup> dyes exhibited high fluorescence intensity and selective and efficient response to cobalt ions over other metal ions in buffered solutions.

**Keywords:** Palladium(II), Schiff bases, Suzuki-Miyaura reaction, -ONNO- and -SNNS- type Schiff bases.

### INTRODUCTION

The design, synthesis and characterization of salicylaldimine complexes are the subject of current interest due to their interesting structural, magnetic, spectral, catalytic and redox properties are used as models for enzymes and several theoretical interests<sup>1-8</sup>. Salen- or Salan-type ligands are easily synthesized and formed complexes with almost all metal ions<sup>9</sup>. Through the years, Schiff bases and transition metal complexes have acted a special role in main group and transition metal coordination chemistry, owing to their great versatility as chelating ligands displaying borderline characteristics between hard and soft Lewis bases<sup>10</sup>. Especially, transition metal complexes of tetradentate Schiff base ligands are good candidates for application in catalysis<sup>11</sup> and as biomimetic enzyme models<sup>12</sup>. Tetradentate Schiff base ligands were prepared by the reaction of diamines with the concerned salicylaldehyde derivative. These reactions are important due to the great number of molecules that can be generated and the well-known ability of these tetradentate ligands to form stable complexes with different metal cations<sup>13</sup>. Metal complexes of Schiff bases derived from substituted

salicylaldehydes and various amines have been widely investigated<sup>14-21</sup>. They played a seminal role in the development of modern coordination chemistry<sup>22</sup>. Symmetric tetradentate Schiff base complexes have been extensively used as macrocycle models<sup>23</sup>.

As a catalyst, palladium has a great importance in pharmaceutical industry. However, it is expensive and toxic for large-scale applications. It is particularly important to reduce both its loss and presence in a product solution. The ability of transition metal catalysts to add or remove hydrogen from organic substrates by either direct or transfer hydrogenation process is a valuable synthesis tool<sup>24</sup>.

Palladium and nickel-catalyzed Suzuki-Miyaura cross-coupling<sup>25-27</sup> is the most significant and efficient strategy for the construction of unsymmetrical biaryl compounds. This cross-coupling methodology allows the use of organic solvents and inorganic bases, tolerates many functional groups, is not affected by steric hindrance of the substrates and is suitable for industrial processes<sup>28</sup>.

The purpose of our study was to find a suitable, strong and easily prepared catalyst valid in a wide range of C-C bond

forming processes. Therefore, the initial step was the selection of a potential catalytic system appropriate to systematic structural and electronic variation. The fact that the sterically hindered Pd(II) metal complexes based on the different molecular structures with -ONNO- and -SNNS- donor sites are thermally stable and not sensitive to oxygen or moisture, as well as their ready economical synthetic access, prompted us to study their activity as catalysts in C-C bond forming reactions.

The usage of metal complexes in the fabrication of electrical and photoelectrical devices such as diodes, transistors, sensors, photodetectors and solar cells is one of the most intriguing recent research topics, deeply involving both chemists and physicists. Knowledge and understanding of electrical and optical properties of inorganic complexes have led to use them in the fabrication of low cost and high efficiency electronic and optical devices. In this study, the synthesis, spectroscopic, catalytic and optical sensing properties of novel PdL<sup>n</sup> (n = 1-6) complexes with tetradentate -ONNO- and -SNNS- type Schiff Bases L<sup>n</sup>H<sub>2</sub> (n = 1-6) were investigated. The synthesized molecules emitted bright fluorescence between 465 and 490 nm when excited with visible light (420 nm) and exhibited significant signal change upon exposure to ionic cobalt in buffered solutions. Spectral response of the synthesized molecules encouraged us to study their emission-based sensing activities.

## EXPERIMENTAL

Reactions were carried out under an oxygen-free nitrogen atmosphere using Schlenk techniques. All glassware was oven-dried at 120 °C. All solvents were dried and degassed using standard techniques and stored under nitrogen until used<sup>29</sup>. Acetonitrile, petroleum ether, dichloromethane, dimethyl formamide and silica gel were purchased from Merck and Pd(OAc)<sub>2</sub> from Aldrich.

**Detection method:** Elemental analyses were performed on a Leco 932 instrument at Technical and Scientific Research Council of Turkey, TUBITAK. UV-visible measurements were carried out using a Shimadzu Model 1800 spectrophotometer. FT-IR spectra were recorded (KBr pellets) on a Varian 1000 FT spectrophotometer. <sup>1</sup>H NMR spectra were recorded in DMSO-*d*<sub>6</sub> on a 500 MHz high performance digital FT-NMR and chemical shifts were referenced to tetramethylsilane (TMS).

Steady state fluorescence emission and excitation spectra were measured using varian cary eclipse spectrofluorometer with a Xenon flash lamp as the light source. The excitation and emission slits were set to 5 or 10 nm and the detector voltage was set to 600 V. Fluorescence lifetimes were measured by time resolved spectrometer of Edinburg instruments of FLS920. The samples were excited by a picosecond pulsed diode laser at the wavelength of 435 nm, at a rate of 10 MHz.

**Metal sensing studies of PdL<sup>n</sup> (n = 1-6):** The pH dependence of the dyes were investigated in acidic (pH = 1), neutral and basic (pH 12) solutions of DMF. The effect of metal ions to the fluorescence intensity of the dyes were investigated by 4 introducing 1 mg L<sup>-1</sup> solutions of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, Hg<sup>+</sup>, Pb<sup>2+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup>, Sn<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> ions in separate solutions of buffered DMF (pH 4.5).

**Syntheses of tetradentate -ONNO- and -SNNS- type Schiff bases ligands:** All of the Schiff-bases ligands N,N'-bis(2-hydroxy-3-methoxy-benzylidene)ethylenediamine (L<sup>1</sup>H<sub>2</sub>); N,N'-bis(2-hydroxyphenol-1-carbaldehyde)-1,3-bis(*p*-aminophenoxy)propane, (L<sup>2</sup>H<sub>2</sub>); N,N-bis(2-hydroxynaphthalin)-1,2-bis(*o*-tiyophenoxy)etane, (L<sup>3</sup>H<sub>2</sub>); N,N-bis(2-hydroxynaphthalin)-1-carbaldehyde)-1,2-bis(*p*-aminophenoxy)ethane, (L<sup>4</sup>H<sub>2</sub>); N,N-bis(2-hydroxynaphthalin)-1-carbaldehyde)-1,4-bis(*p*-aminophenoxy)butane, (L<sup>5</sup>H<sub>2</sub>); N,N-bis(2-aminothiophenol)-1,4-bis(2-carboxaldehydephenoxy)-butane, (L<sup>6</sup>H<sub>2</sub>) were prepared by literature methods<sup>20,30-33</sup>.

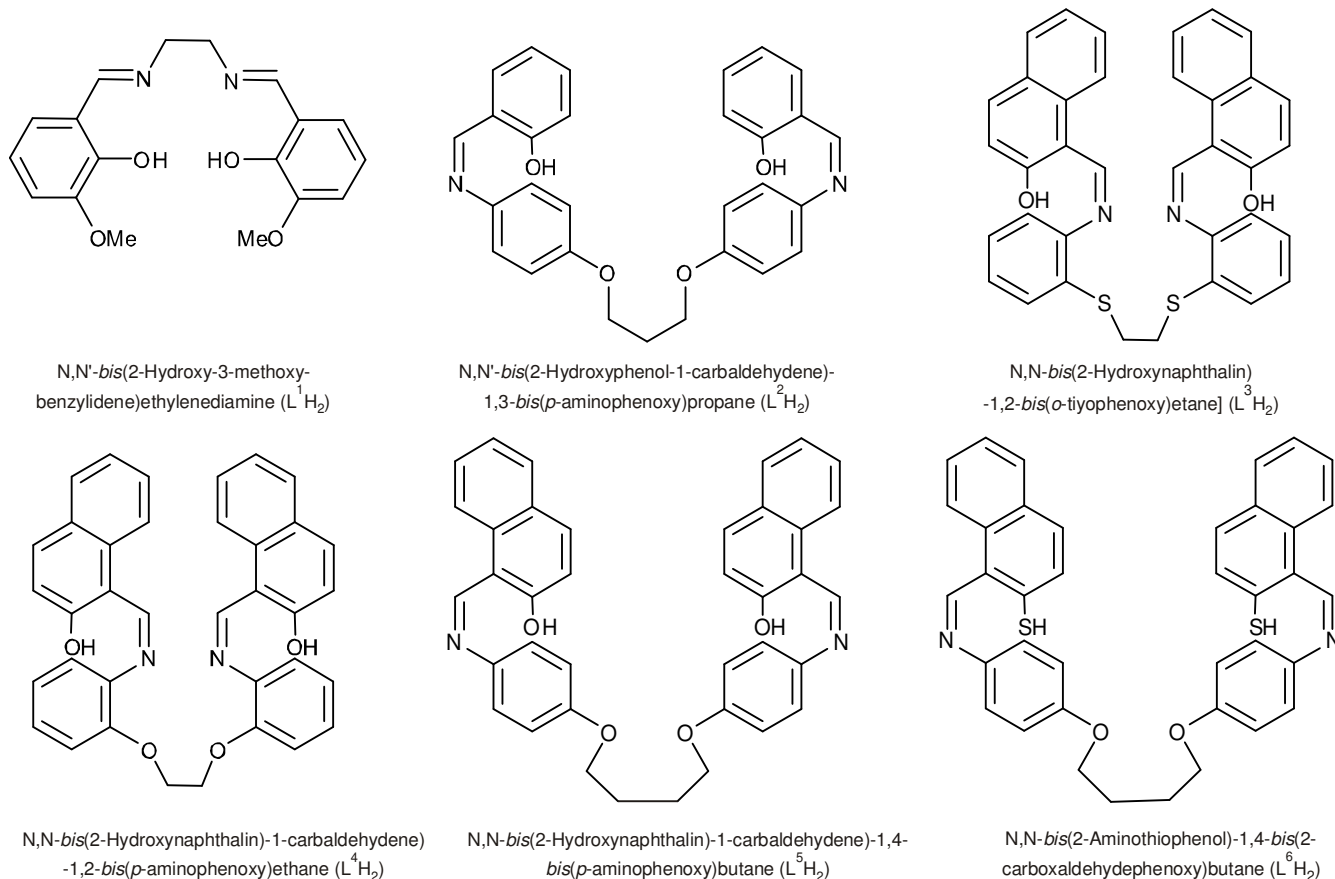
**Syntheses of Pd(L<sup>n</sup>) (n = 1-6) complexes:** The complexes Pd(L<sup>n</sup>) (n = 1-6) were prepared by the thermal reactions of Pd(OAc)<sub>2</sub> with L<sup>n</sup>H<sub>2</sub> (n = 1-6) Schiff-Bases ligands and obtained in 62-73 % yield by similar methods, the following is typical.

The palladium(II) acetate (0.1124 g, 0.5 mmol) was dissolved in 10 mL of dry acetonitrile in a two necked round bottom flask. At the same time, L<sup>n</sup>H<sub>2</sub> 0.5 mmol (164 mg for L<sup>1</sup>H<sub>2</sub>; 233 mg for L<sup>2</sup>H<sub>2</sub>; 276 mg for L<sup>3</sup>H<sub>2</sub>; 291 mg for L<sup>4</sup>H<sub>2</sub>; 257 mg for L<sup>5</sup>H<sub>2</sub>; 293 mg for L<sup>6</sup>H<sub>2</sub>) was dissolved separately in 10 mL of dry acetonitrile. Then was added ligand solution dropwise into the flask containing the metal solution. The contents were refluxed under argon atmosphere for 24 h. Then, the mixture was washed with a small amount of dichloromethane and then filtered and left to cool to room temperature. The compounds were evaporated in vacuum. The products were recrystallized from dichloromethane/ether.

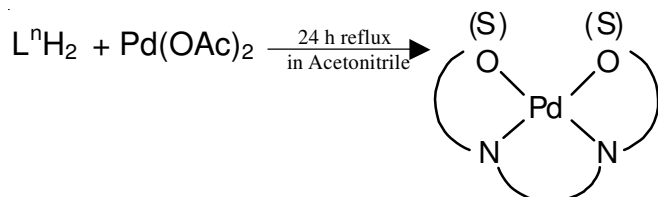
**General procedure for Suzuki-Miyaura coupling reaction:** The catalyst (1.0 mmol % of Pd complexes PdL<sup>n</sup> (n = 1-6)), aryl halides (1 mmol), phenyl boronic acid (1.5 mmol), Cs<sub>2</sub>CO<sub>3</sub> (2 mmol), DMF (3 mL) were all added to a small Schlenk tube and the mixture was heated at 100 °C for 4 h in an oil bath. At the end, the mixture was cooled, filtered and concentrated. The purity of the compounds was checked by NMR and the yields were based on different aryl halides.

## RESULTS AND DISCUSSION

Pd(II) complexes PdL<sup>n</sup> (n = 1-6) were synthesized by the condensation of ligands with palladium acetate. The reaction steps for the synthesis of the ligands and their palladium(II) complexes are given in **Schemes I** and **II**. For the structural characterization of ligands L<sup>n</sup>H<sub>2</sub> (n = 1-6) with their mononuclear Pd(II) complexes elemental analyses, IR spectra, UV-visible spectra and <sup>1</sup>H NMR spectra were used and the corresponding data are given in Tables 1-3. The catalytic activity of PdL<sup>n</sup> (n = 1-6) complexes were tested in the Suzuki-Miyaura coupling reaction. Pd(II) metal complexes were catalyzed Suzuki-Miyaura coupling reaction between phenylboronic acid and different arylbromides affording biphenyls. These spectra of the complexes show that all of the ligands are coordinated to the central metal as a tetradentate ligand coordinating *via* the central azomethine nitrogens (C=N) and phenolic oxygen/sulfur atoms. <sup>1</sup>H NMR data exhibited expected integrals and shifts. C=N/Ar-OH/Ar-SH vibrations have been shifted to lower wave number in the IR spectra of the complexes PdL<sup>n</sup> (n = 1-6), respectively.



Scheme-I: Supposed structures of the ligands



Scheme-II: Preparation of palladium(II) complexes 1-6

TABLE-1  
ELEMENTAL ANALYSIS RESULTS AND  
PHYSICAL PROPERTIES FOR THE COMPLEXES

Complex	Yield (%)	Colour	Elemental analysis (%):		
			Found (calcd.)		
			C	H	N
PdL <sup>1</sup>	62	Light yellow	49.85 (49.96)	4.13 (4.19)	6.43 (6.47)
PdL <sup>2</sup>	65	Light brown	61.08 (61.01)	4.17 (4.24)	4.87 (4.91)
PdL <sup>3</sup>	68	Light yellow	62.58 (62.74)	3.75 (3.80)	4.01 (4.06)
PdL <sup>4</sup>	73	Light orange	65.26 (65.81)	3.82 (3.99)	4.19 (4.26)
PdL <sup>5</sup>	67	Dark orange	78.49 (78.60)	5.33 (5.55)	4.69 (4.82)
PdL <sup>6</sup>	68	Light yellow	63.52 (63.64)	4.13 (4.22)	3.84 (3.91)

### Spectroscopic studies

**<sup>1</sup>H NMR spectra:** The <sup>1</sup>H NMR spectral results obtained for  $L^nH_2$  ( $n = 1-6$ ) ligands and Pd(II) complexes in DMSO-*d*<sub>6</sub>, with their assignments, are given in Table-3. The <sup>1</sup>H NMR spectra of the ligands  $L^nH_2$  ( $n = 1-6$ ) were found to be charac-

teristic. The highly deshielded proton resonance appearing as a singlet in the spectra  $L^nH_2$  ( $n = 1-6$ ) due to the OH/S<sub>H</sub> protons involved in OH/S<sub>H</sub>...N intramolecular H-bonding. The proton signal present in the spectra of the free ligands were found to be absent in the spectra of the complexes PdL<sup>n</sup> ( $n = 1-6$ ). Disappearance of the signals in complexes is due to the formation of chelating from the oxygen or sulfur atoms of the deprotonated Schiff base ligands. All protons of azomethine HC=N and salicylic moieties of these complexes were shifted upfield while the aromatic ring protons exhibited either downfield shift compared with those of the free ligands. Similar magnetic shielding effects were previously observed in the Schiff-base complexes of Pd(II), Zn(II), Co(II) and Cu(II)<sup>33-37</sup> indicates that the  $L^nH_2$  ( $n = 1-6$ ) ligands are coordinated by palladium center through the azomethine nitrogens and phenolic oxygen/thiolic sulfur donor atoms.

**IR spectra:** The main stretching frequencies of the IR spectra of ligands  $L^nH_2$  ( $n = 1-6$ ) and Pd(II) complexes PdL<sup>n</sup> ( $n = 1-6$ ) are given in Table-2. The IR spectra of ligands and their corresponding Pd(II) complexes are found to be very similar to each other. Hence, significant frequencies are selected by comparing the IR spectra of the ligands with those of Pd(II) complexes. The IR of ligands are characterized by the appearance of a band at between 3447-3389 cm<sup>-1</sup> due to the  $\nu(OH/S_{H}\cdots N)$  or  $\nu(OH/S_{H})$  groups<sup>38,30</sup>. In the IR spectra of PdL<sup>n</sup> ( $n = 1-6$ ) complexes, these bands disappeared. These results indicate deprotonation of the phenol and thiol protons of all of the ligands prior to coordination. The free ligands showed strong peaks at 1673-1617 cm<sup>-1</sup>, which are characteristic of

TABLE-2  
CHARACTERISTIC FTIR BANDS (cm<sup>-1</sup>) AND UV-VISIBLE (nm) (A) SPECTRAL DATA  
FOR THE L<sup>1</sup>H<sub>2</sub>, L<sup>2</sup>H<sub>2</sub>, L<sup>3</sup>H<sub>2</sub>, L<sup>4</sup>H<sub>2</sub>, L<sup>5</sup>H<sub>2</sub> AND L<sup>6</sup>H<sub>2</sub> AND 1-6 COMPLEXES

Complex	$\nu_{(C=N)}$	$\nu_{(C=O)}$	$\nu_{(C-O)}$	$\nu_{(C-S)}$	UV-visible (nm) (A)
L <sup>1</sup> H <sub>2</sub>	1631 s	3425 m	1252 s	--	$\lambda_1 = 331.0$ (0.562)
Pd(L <sup>1</sup> )	1626 s	--	1247 s	--	$\lambda_1 = 324.5$ (0.363), $\lambda_2 = 344.5$ (0.360), $\lambda_3 = 408.0$ (0.435)
L <sup>2</sup> H <sub>2</sub>	1619 m	3447 m	1247 s	--	$\lambda_1 = 351.5$ (0.431)
Pd(L <sup>2</sup> )	1610 s	--	1242 m	--	$\lambda_1 = 354.5$ (0.302)
L <sup>3</sup> H <sub>2</sub>	1600 m	3389 m	1320 m	--	$\lambda_1 = 318.0$ (0.309); $\lambda_2 = 395.5$ (0.233)
Pd(L <sup>3</sup> )	1559 s	--	1319 w	--	$\lambda_1 = 354.5$ (0.364); $\lambda_2 = 446.0$ (0.197)
L <sup>4</sup> H <sub>2</sub>	1617 s	3418 m	1289 s	--	$\lambda_1 = 325.5$ (0.263); $\lambda_2 = 339.0$ (0.245); $\lambda_3 = 388.5$ (0.337); $\lambda_4 = 443.0$ (0.168); $\lambda_5 = 464.0$ (0.147)
Pd(L <sup>4</sup> )	1613 s	--	1243 m	-	$\lambda_1 = 326.5$ (0.166); $\lambda_2 = 343.5$ (0.202); $\lambda_3 = 424.0$ (0.242)
L <sup>5</sup> H <sub>2</sub>	1618 m	3443 m	1299 w	--	$\lambda_1 = 312.0$ (0.488); $\lambda_2 = 391.5$ (0.288)
Pd(L <sup>5</sup> )	1610 m	--	1236 m	--	$\lambda_1 = 325.0$ (0.879); $\lambda_2 = 425.0$ (0.678)
L <sup>6</sup> H <sub>2</sub> <sup>a</sup>	1673 m, 1592 s	3423 m	1320 m	750 s, 724 w, 687 w	$\lambda_1 = 326.0$ (0.621)
Pd(L <sup>6</sup> )	1615m	--	1315 s	749 m, 680 s	$\lambda_1 = 329.0$ (0.448); $\lambda_2 = 344.5$ (0.605)

<sup>a</sup>Taken from Ref. [32] and [33]

TABLE-3  
<sup>1</sup>H NMR DATA FOR L<sup>1</sup>H<sub>2</sub>, L<sup>2</sup>H<sub>2</sub>, L<sup>3</sup>H<sub>2</sub>, L<sup>4</sup>H<sub>2</sub>, L<sup>5</sup>H<sub>2</sub> AND  
L<sup>6</sup>H<sub>2</sub> AND 1-6 in DMSO-*d*<sub>6</sub> SOLUTION

Comp.	Ar-OH	Ar-SH	Ar-H	HC=N
L <sup>1</sup> H <sub>2</sub>	13.53, s, 2H	--	6.84-6.98, m, 8H	8.54, s, 2H
PdL <sup>1</sup>	--	--	6.47-6.89, m, 8H	8.16, s, 2H
L <sup>2</sup> H <sub>2</sub>	13.24, s, 2H	--	7.34-7.57, m, 8H	8.91, s, 2H
PdL <sup>2</sup>	--	--	7.29-7.55, m, 8H	8.81, s, 2H
L <sup>3</sup> H <sub>2</sub>	12.05, s, 2H	--	7.61-7.42, m, 8H	9.73, s, 2H
PdL <sup>3</sup>	--	--	7.50-7.20, m, 8H	9.31, s, 2H
L <sup>4</sup> H <sub>2</sub> <sup>a</sup>	3.29, s, 2H	--	7.02-8.49, m, 20H	9.63, s, 2H
PdL <sup>4</sup>	--	--	6.98-8.32, m, 20H	9.60, s, 2H
L <sup>5</sup> H <sub>2</sub> <sup>a</sup>	3.27, s, 2H	--	7.00-8.48, m, 20H	9.62, s, 2H
PdL <sup>5</sup>	--	--	6.86-8.41, m, 20H	9.61, s, 2H
L <sup>6</sup> H <sub>2</sub> <sup>b</sup>	--	3.30, s, 2H	7.11-8.00, m, 16H	8.43, s, 2H
PdL <sup>6</sup>	--	--	7.08-7.86, m, 16H	8.40, s, 2H

<sup>a</sup>Taken from Ref. [34], <sup>b</sup>Taken from Ref. [32].

the azomethine  $\nu(C=N)$  group<sup>39</sup>. In case of the complexes, these bands were shifted to the lower frequencies (1626-1559 cm<sup>-1</sup>), indicating that the nitrogen atoms of the azomethine groups are coordinated to the palladium ion as expected<sup>40</sup>.

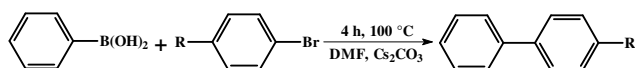
**UV-visible spectra:** Ligands and PdL<sup>n</sup> (n = 1-6) complexes were recorded in the 200-1000 nm range in DMF solutions and the results are given in Table-2. In the electronic spectra of the ligands and their Pd(II) complexes PdL<sup>n</sup> (n = 1-6) the wide range bands seem to be due to both the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  of C=N chromophore or charge-transfer transition arising from  $\pi$  electron interactions between the metal and ligand which involves either a metal-to-ligand or ligand-to metal electron transfer and *d-d* transitions<sup>41,42</sup>. The absorption bands observed within the range of 312-464 nm in DMF are most probably due to the transition of  $\pi \rightarrow \pi^*$  transitions in the benzene ring or  $n \rightarrow \pi^*$  of imine group corresponding to the ligands and their Pd(II) metal complexes<sup>43</sup>. The electronic spectra of PdL<sup>3</sup> and PdL<sup>6</sup> metal complexes in DMF solutions show absorption bands at 354.5 and 344.5 nm are assigned to ligand to metal charge-transfer S  $\rightarrow$  M (LMCT) and <sup>3</sup>A<sub>1g</sub>  $\rightarrow$  <sup>3</sup>T<sub>1g</sub> (*d-d*) transitions, respectively<sup>44,45</sup>.

**Thermal analysis:** Thermal analysis becomes an important tool not only for the study of the thermal stability and the decomposition patterns of complexes but also it provides important information about their structural features and the preferential

ligation of the different groups directly attached to and/or associated with metal ions<sup>46-48</sup>. The thermal analyses of complexes were measured under the N<sub>2</sub> gases, starting from 30 up to 1000 °C at a heating rate of 15 °C/min. TGA/DTG analysis was carried out to know the actual loss of organic moiety present in the complexes. TGA/DTG analysis of PdL<sup>n</sup> complexes (n = 1-6) have not shown a important loss in weight in the temperature range about 30-200 °C. Pd(II) complexes is thermally stable up to 170 °C except for Pd(L<sup>1</sup>), 79.87 °C and its decomposition started at this temperature. The initial decomposition takes places between 160 and 200 °C. Its main and final decompositions take place between 320-750 °C. The final stable solid decomposition products were analyzed to be oxides of general formula PdO/PdS.

**Suzuki cross-coupling reaction:** Palladium and nickel-catalyzed Suzuki-Miyaura cross-coupling<sup>25-27</sup> is the most important and efficient strategy for the construction of unsymmetrical biaryl compounds. Suzuki cross coupling represents a powerful method for C-C bond formation<sup>49</sup>. Recently, the Suzuki reaction of aryl halides catalysed by palladium/tertiary phosphine<sup>50</sup> and palladium/NHC<sup>51,52</sup> systems have been extensively studied due to the economically attractive nature of the starting materials and the production of the less toxic salt by-products *e.g.* NaX (X = Cl, Br and I). This cross-coupling methodology allows the use of organic solvents and inorganic bases, tolerates many functional groups, is not affected by steric hindrance of the substrates and is suitable for industrial processes<sup>28</sup>.

To survey the parameters for the Suzuki reaction, we chose to examine Cs<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> as base and DMF, toluene and isopropyl alcohol as the solvent. It was found that the reactions performed in DMF with Cs<sub>2</sub>CO<sub>3</sub> at 100 °C showed the best performance. Under these conditions, 4-bromoacetophenone and 4-bromotoluene react with phenylboronic acid (**Scheme-III**). In palladium-catalyzed cross-coupling reactions, it is generally accepted that better conversions are assured for aryl halides with electron-withdrawing rather than donating substituent. We started our investigation with the coupling of 4-bromoacetophenone and phenylboronic acid, in the presence of PdL<sup>n</sup> (n = 1-6) metal complexes. It can be seen that the palladium complexes listed in the Table-4 are effective compounds for the coupling of aryl bromides with phenylboronic acid.



**Scheme-III:** Suzuki-Miyaura coupling of different aryl halides with phenylboronic acid

**TABLE-4**  
SUZUKI-MIYAJURA COUPLING OF DIFFERENT ARYL HALIDES WITH PHENYLBORONIC ACID

Entry	R	Product	Yield (%) <sup>(a, b, c)</sup>
PdL <sup>1</sup>	COCH <sub>3</sub>		76
PdL <sup>2</sup>	COCH <sub>3</sub>		73
PdL <sup>3</sup>	COCH <sub>3</sub>		72
PdL <sup>4</sup>	COCH <sub>3</sub>		62
PdL <sup>5</sup>	COCH <sub>3</sub>		63
PdL <sup>6</sup>	COCH <sub>3</sub>		67
PdL <sup>1</sup>	CH <sub>3</sub>		51
PdL <sup>2</sup>	CH <sub>3</sub>		46
PdL <sup>3</sup>	CH <sub>3</sub>		48
PdL <sup>4</sup>	CH <sub>3</sub>		49
PdL <sup>5</sup>	CH <sub>3</sub>		52
PdL <sup>6</sup>	CH <sub>3</sub>		53

<sup>a</sup> Reaction conditions: 1.2 mmol of phenylboronic acid, 2 mmol Cs<sub>2</sub>CO<sub>3</sub>, % 1 mol Pd, 3 mL DMF, <sup>b</sup>Purity of all compounds determined by NMR and the yield calculated on the aryl bromide, <sup>c</sup>Temperature 100°C and time 4h

**Fluorescence based measurements:** The photoluminescence properties were studied at room temperature for 10<sup>-6</sup> M solutions of all compounds in DMF. Excitation and emission slit widths were set at 5 nm. The fluorescence based data are given in Table-5. All of the dyes except PdL<sup>1</sup> exhibited large

emission bands in the range of 400-650 nm. The observed fluorescence is due to intraligand  $\pi \rightarrow \pi^*$  transitions. The maximum excitation wavelengths for the employed dyes were in the visible region of electromagnetic spectrum and were between 420-447 nm. The maximum emission wavelengths were in the range of 465-490 nm. The Stoke's shift values were between 35-60 nm. The high Stoke's shift value allows the emitted fluorescence photons to be easily distinguished from the excitation photons and is of great importance for sensor studies.

Fluorescence lifetimes were measured by FLS920 which works on the principle of time correlated single photon counting (TCSPC) method in the solvent of dimethyl formamide (DMF). For each measurement an appropriate instrument response function (IRF) was recorded using a colloidal scattering sample (LUDOX solution) with the emission monochromator set to the excitation wavelength of the laser. The fluorescence lifetime is a measure of the time a fluorophore spends in the excited state before returning to the ground state by emitting a photon. The lifetimes of fluorophores can range from picoseconds to hundreds of nanoseconds. Table-5 also shows the measured fluorescence decay times in DMF with relative distributions and chi square values. The quality of the fits was judged from the chi square values ( $\chi^2 = 1.199$ ). The PdL<sup>3</sup> showed single exponential decay indicating that only one fluorescent conformer is present while the PdL<sup>2</sup>, PdL<sup>4</sup>, PdL<sup>5</sup> and PdL<sup>6</sup> exhibited double exponential decay curves. A double exponential decay fits to the following equation:

$$I_{(t)} = B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)}$$

where  $I_{(t)}$  is the time dependent fluorescence intensity,  $B_1$  and  $B_2$  are the amplitudes of the components at time 0,  $t$  is time and  $\tau$  is the fluorescence lifetime. Double exponential decays with two lifetime values indicate in these cases that two different fluorescent conformers could be present. It is clear from the results that the fluorescence characteristics and the lifetime values of the abundant conformer of the dyes are very close to each other and in the range of 4.66-5.42 ns except that of PdL<sup>1</sup>. These lifetime values are longer than some commonly used fluorescent dyes such as fluorescein (4 ns in pH 7.5 phosphate buffer), rhodamine B (1.68 ns in pH 7.8 phosphate buffer), coumarin 6 (2.5 ns in 10 ethanol). The PdL<sup>2</sup> and PdL<sup>3</sup> dyes exhibited higher fluorescence intensity and were tested in terms of metal sensitivity for their probable usage in optical chemical sensor designs.

**pH and metal response:** The PdL<sup>2</sup> and PdL<sup>3</sup> dyes were evaluated in terms of pH and metal sensitivity for probable

**TABLE-5**  
FLUORESCENCE SPECTROSCOPY RELATED DATA: EXCITATION WAVELENGTH ( $\lambda_{ex}$ ), MAXIMUM EMISSION WAVELENGTH, ( $\lambda_{em}$ ), STOKES SHIFT, ( $\Delta\lambda_{ST}$ ), FLUORESCENCE DECAY TIMES OF PdL<sup>a</sup> DYES (10<sup>-6</sup> mol L) in DIMETHYL FORMAMIDE

Dyes	Excitation wavelength, $\lambda_{ex}$ (nm)	Emission wavelength, $\lambda_{em}$ (nm)	Stokes Shift, $\Delta\lambda_{ST}$	Fluorescence Intensity	Fluorescence lifetime, $\tau_{1(ns)}$ (% dist.)	Fluorescence lifetime, $\tau_{2(ns)}$ (% dist.)	Chi square values ( $\chi^2$ )
PdL <sup>1</sup>	-	-	-	-	-	-	-
PdL <sup>2</sup>	430	490	60	2.0×10 <sup>6</sup>	6.26 ± 1.41 × 10 <sup>-2</sup> (2.9 %)	5.42 ± 0.02 (97.1 %)	1.199
PdL <sup>3</sup>	447	490	43	5.0×10 <sup>6</sup>	4.99 ± 0.02 (100 %)	-	1.070
PdL <sup>4</sup>	430	465	35	7.0×10 <sup>4</sup>	0.05 ± 0.01 (19.1 %)	4.84 ± 0.05 (80.9 %)	1.054
PdL <sup>5</sup>	430	475	45	4.0×10 <sup>4</sup>	0.16 ± 0.02 (15.8 %)	4.940 ± 0.004 (84.2 %)	1.076
PdL <sup>6</sup>	420	475	55	3.5×10 <sup>4</sup>	0.28 ± 0.02 (19.0 %)	4.66 ± 0.04 (81.0 %)	1.092

future applications of optical sensor designs. Both of the dyes exhibited maximum excitation and emission wavelengths in the visible region of electromagnetic spectrum, high Stokes shifts and high fluorescence efficiency which are desired characteristics of the dyes employed in sensor designs. The pH dependence of PdL<sup>2</sup> and PdL<sup>3</sup> dyes were investigated in neutral and basic solutions of DMF. Fig. 1 shows the spectral pH dependent response of the dyes. From the figure it can be concluded that both of the dyes exhibited significant pH dependence which showed enhanced fluorescence at basic pH. The pH dependency of the dyes arises from the hydroxyl groups in their structure. The response of the dyes to metal cations was examined in buffered solutions in order to avoid the interfering effect of pH and at a slightly acidic media (pH 4.5). Micro portions of 100 mg L<sup>-1</sup> solutions of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, Hg<sup>+</sup>, Pb<sup>2+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup>, Sn<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> ions were introduced in separate solutions of buffered DMF containing the dye. Fig. 2 concluded that both of the dyes exhibited selective and efficient response to cobalt and mercury ions (1 mg L<sup>-1</sup>) at pH 4.5. Over the employed metal ions by decrease in fluorescence intensity. I<sub>0</sub> and I are the fluorescence intensities when indicator dye was in its unloaded and fully loaded forms, respectively.

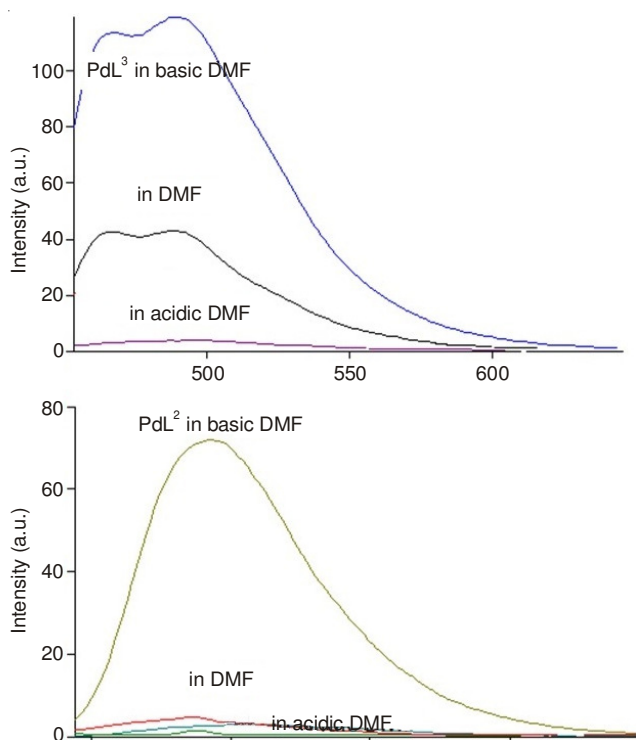


Fig. 1. pH dependent emission based response of PdL<sup>2</sup> and PdL<sup>3</sup> in DMF

## Conclusion

New sterically constrained tetradentate -ONNO- and -SNNS- Schiff-bases ligands and their palladium(II) complexes PdL<sup>n</sup> (n = 1- 6) were synthesized and characterized by elemental analyses, FTIR, UV-visible, <sup>1</sup>H NMR spectra and examined TGA/DTG measurement. The spectroscopic studies suggest that all of the ligands are coordinated to the central metal as a tetradentate ligand coordinating *via* the central azomethine nitrogens (C=N) and phenolic oxygen/sulfur atoms. The Pd(II)

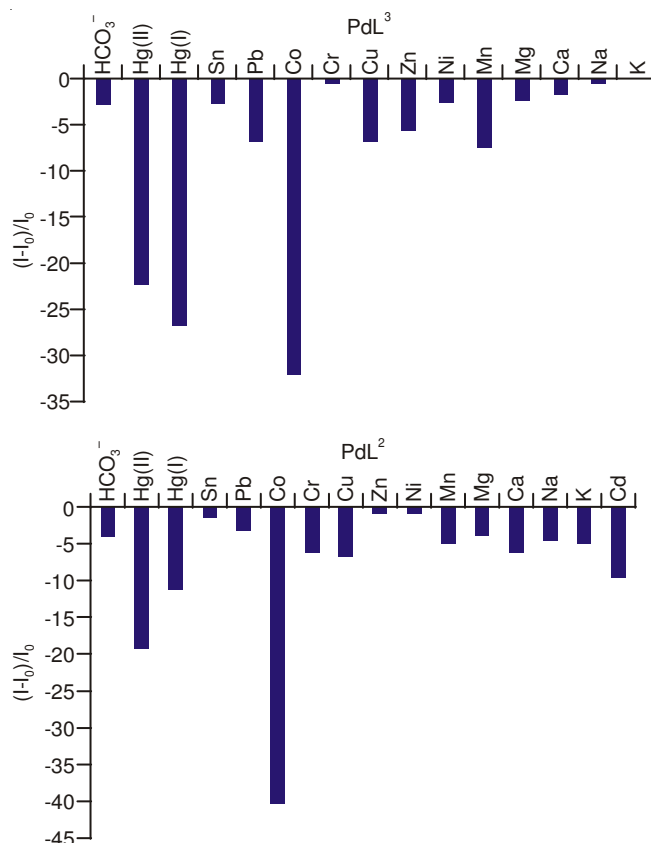


Fig. 2. Metal response of PdL<sup>2</sup> and PdL<sup>3</sup> in DMF (1 mg L<sup>-1</sup>)

metal complexes were found to be active catalysts for the Suzuki-Miyaura crosscoupling of activated different aryl bromides with phenylboronic acid, using DMF as solvent. It can be seen that PdL<sup>n</sup> (n = 1- 6) complexes have a moderate effect for the coupling of aryl bromides with phenylboronic acid.

All of the dyes have promising spectral properties such as visible region excitation and emission wavelengths, high Stokes shifts. PdL<sup>2</sup> and PdL<sup>3</sup> dyes exhibited high fluorescence intensity and selective and efficient response to cobalt and mercury ions over other metal ions in buffered solutions and can be employed as optical chemical sensor agents for further studies. The two dyes are also affected from pH and can be evaluated as pH sensors.

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