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# Physico-chemical studies of new luminescent chemosensor for Cu<sup>2+</sup>

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# HIGHLIGHTS

# G R A P H I C A L A B S T R A C T

- The quenching of fluorescence was observed in the presence of copper metal ion.
- ESIPT process plays main role.Competition of intra and
- intermolecular hydrogen bonding in binary solvents.
- ▶ NBO analysis revealed that the  $n(N1) \rightarrow \pi^* O(30)$ -H(31) interaction gives the strongest stabilization to the system.
- PES diagram, MEP and electronic properties studied using Gaussian-03.

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# ABSTRACT

The spectroscopic properties of (E)-2-(2-hydroxybenzylideneamino)-3-phenylpropanoic acid (HBDPPA) has been studied in a series of different solvents. As revealed by absorbance, and emission results, the molecule undergoes fast excited-state intramolecular proton transfer (ESIPT) to yield emission of the corresponding tautomeric species. A large energy barrier for interconversion of the keto-enol rotamers in the ground and excited state have been predicted on the basis of DFT calculations and also supported by HOMO-LUMO energies, PES calculation, NLO and NBO analysis. Hyperpolarizability and octupolar and dipolar components ratio confirmed that HBDPPA can be used as optoelectronic materials. The ground state equilibrium and ESIPT process of HBDPPA are essentially unaffected by the nature of the solvent. Measurements of absorption solvatochromism have been interpreted with Marcus and Reichardt-Dimroth solvent functions to estimate the transition dipoles. Good correlation exists between absorption as well as fluorescence wavenumbers obtained by the multi-component linear regression employing the Taft and Catalan solvent parameters with the experimental values. The prepared Schiff base HBDPPA can be used as a new fluorescent sensor to detect the quantity of Cu<sup>2+</sup> ion in any sample solution depending on the relative intensity change.

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SPECTROCHIMICA ACTA

# Introduction

Schiff bases are used as starting materials in the synthesis of important drugs, such as antibiotics, antiallergic, antiphlogistic, and antitumor substances [1]. On the industrial scale, they have a wide range of applications, such as dyes and pigments [2]. Schiff base complexes have been playing an important role in the devel-

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opment of coordination chemistry related to catalysis and enzymatic reactions [3], magnetism and molecular architectures [4]. Schiff base compounds display interesting photochromic and thermochromic features in the solid state and can be classified in terms of these properties [5]. Photo- and thermochromism arise via H-atom transfer from the hydroxy O atom to the imine N atom [ESIPT] [6]. Such proton-exchanging materials are used for the design of various molecular electronic devices and their investigation during the last few years are in large extent because of their potential applicability in optical communications and many of them show non-linear optic (NLO) behavior [7]. NLO materials have been

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attractive in recent years with respect to their future potential applications in the field of optoelectronic such as optical communication, optical computing, optical switching, and dynamic image processing [8,9]. Literature survey revealed that the DFT has a great accuracy in reproducing the experimental values in geometry, dipole moment, vibrational frequency, etc. [10]. In this paper we report the photophysical studies of *o*-hydroxy Schiff base containing amino acid as component and also its ESIPT process. Density functional theory (DFT) calculation [11] on energy, dipole moment of various species, HOMO, HOMO-1, LUMO and LUMO+1 energies, PES, NLO, NBO and molecular electrostatic potential surface (MEP) studies have been performed to supplement the experimental results.

# Experimental

## Materials and methods

L-Phenylalanine (Sigma–Aldrich Ltd.), salicylaldehyde (S.D. fine) and all other reagents used without further purification.

### Optical measurements and composition analysis

NMR spectrum was recorded for Schiff base on a Bruker 400 MHz. The ultraviolet–visible (UV–Vis) spectra were measured on UV–Vis spectrophotometer (Perkin Elmer, Lambda 35) and corrected for background due to solvent absorption. Photoluminescence (PL) spectra were recorded on a (Perkin Elmer LS55) fluorescence spectrometer. MS spectrum was recorded on a Varian Saturn 2200 GCMS spectrometer.

### Computational details

Quantum mechanical calculations were used to carry out the optimized geometry, NLO, NBO, PES, HOMO–LUMO and TD–DFT with Guassian-03 program using the Becke3–Lee–Yang–Parr (B3LYP) functional supplemented with the standard 6-31G(d,p) basis set [11,12].

### General procedure for the synthesis of (E)-2-(2hydroxybenzylideneamino)-3-phenyl propanoic acid (HBDPPA)

The Schiff base (HBDPPA) was synthesized according to the procedure reported in literature [13]. A solution of L-phenylalanine (1 mmol) and salicylaldehyde (1.5 mmol) in 20 ml absolute ethanol was refluxed for 2 h. The resulting precipitate was filtered off and purified by column chromatography. Yield: 60 %, m.p: 189 °C. Anal. calcd. for C<sub>16</sub>H<sub>15</sub>NO<sub>3</sub>: C, 71.36; H, 5.61; N, 5.20; O, 17.72. Found: C, 71.34; H, 5.62; N, 5.19; O, 17.74. MS: m/z 269.11, calcd. 269.9. <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>):  $\delta$ 3.27 (d, 2H),  $\delta$ 4.39 (t, 1H),  $\delta$ 5.1 (s, 1H),  $\delta$ 6.85 (d, 1H),  $\delta$ 6.76 (t, 2H),  $\delta$ 7.12 (t, 2H),  $\delta$ 7.21 (m, 2H),  $\delta$ 7.45 (s, 1H),  $\delta$ 11.4 (s, 1H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 38.1, 67.2, 116.1, 121.5, 124.6, 126.1, 127.8, 128.7, 130.6, 132.6, 139.5, 160.9, 161.1, 177.5.

### **Results and discussion**

### Absorption and emission spectra of Schiff base (HBDPPA)

The absorption spectra of Schiff base (Fig. 1) largely depend on the solvent polarity and red shift was observed in hydroxyl solvents. Larger red shift is due to the stabilizing interaction between the hydroxyl group of the alcohol and the Schiff base so that there is greater delocalization of the  $\pi$  electron cloud of the aromatic system, CH=N and N=N bonds. The absorption spectra of HBDPPA in neutral ethanol shows band at 348.5 nm. From the solid state UV–Vis spectrum of Schiff base (HBDPPA) the optical band gap value is found as 2.39 eV [13]. The smaller band gap indicates easy electronic transitions from bulk to vacuum energy level of the compound and has high electrical conductivity as well as fluorescence property. Electronic absorption spectrum has been calculated using TD–DFT based on the B3LYP/6-31G (d,p). The calculated absorption wavelength is displayed in Table 1 which are in comparable with the experimental absorption maximum. Fig. 2 displays the emission spectrum Schiff base in various solvents. With increasing the solvent polarity red shift was observed.

## Schiff base (HBDPPA) as a chemosensor

The changes in the fluorescence properties of HBDPPA caused by different metal ions such as Co<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> were measured in ethanol. The fluorescence of HBDPPA quenched markedly with the gradual addition of Cu<sup>2+</sup> but the fluorescence properties of HBDPPA was slightly influenced by other metal ions (Fig. 3). The fluorescence intensity of HBDPPA was linearly reduced with increase in concentration of Cu<sup>2+</sup>. The quenching in fluorescence intensity of Schiff base HBDPPA by the addition of Cu<sup>2+</sup> cation indicates the complexation of Schiff base (HBDPPA) with Cu<sup>2+</sup>, the Schiff base (HBDPPA) has bidentate sites and forming the expected Cu<sup>2+</sup> complex (Fig. S4) [14]. The possible reason for the fluorescence quenching is the formation of a ground state non-fluorescent complex and the enhancement of spin-orbit coupling [15] for HBDPPA-Cu<sup>2+</sup> is presumed resulting in the fluorescence quenching. According to the obtained results, Schiff base HBDPPA can be used as a new fluorescence sensor to detect the quantity of Cu<sup>2+</sup> ion in any sample solution depending on the relative intensity change.

### Excited state intramolecular proton transfer (ESIPT) process

The fluorescence spectra of HBDPPA in dioxane contain two emission bands and the emission peak at shorter wavelength at 342.4 nm is assigned to isomer I (Fig. S5) and the small at higher wavelength 367.3 nm reveal that only the isomer II of HBDPPA. However in the case of hydroxyl containing solvent (EtOH), a short wavelength emission band appears for HBDPPA. This result corresponds to the data obtained earlier [16–19] for compounds demonstrating ESIPT and can be explained by the presence of intermolecular hydrogen bonding with solvent molecule leading to the stabilization of solvated isomer IV in which ESIPT is impossible.

For better understanding the ESIPT mechanism in HBDPPA, we have performed DFT calculation of electron density for the keto and enol isomers of the HBDPPA molecule in the ground and the excited states (Table 2) which reveal that excitation of enol isomer (I) leads to an increase in the electron density at N atom and decrease at O atom resulting in ESIPT and formation of the excited keto isomer in excited state. Then, the excited keto isomer emits luminescence and returns to the ground state keto form, which is characterized by a large positive charge at the N atom and negative charge at the O(23) atom. As a result, a reverse process occurs in the ground state of the molecule producing an initial molecule in the form enol form.

# Competition between intramolecular and intermolecular hydrogen bonding

Fluorescence spectra of HBDPPA exhibits two emission peaks at 342.4 and 367.3 nm (cis enol) respectively in pure dioxane. With the addition of water, the emission intensity decreases in enol when water fraction is increased to 20% (v/v), the emission almost



**Table 1** UV–Vis absorption ( $\lambda_{abs}$ ), excitation energy ( $E_{exc}$ ) and oscillator strength (f) for HBDPPA calculated by TD–DFT method.

Parameter	HOMO-LUMO	HOMO-1-LUMO	HOMO-1-LUMO + 1	HOMO-LUMO + 1
$\lambda_{abs}(nm) \ E_{exc}(eV) \ f$	340.95	340.95	282.64	275.91
	3.6365	3.6365	4.3866	4.4937
	0.0023	0.0023	0.0259	0.1090



Fig. 2. Normalized emission spectra of HBDPPA.

vanished. With further increasing water fraction to 40% (v/v), a new emission band at 350.6 nm appeared in addition to the normal emission. This band intensity increased with increasing water fraction and turned to be the main emission when water fraction is high up to 80% (v/v) (Fig. 4). The emission decreases with increasing water fraction in the mixed solvent is due to formation of the intermolecular hydrogen bonding between HBDPPA and water. In

the initial stage, the presence of small amount of water in the dioxane solution must give rise to the solvation of HBDPPA. The intermolecular hydrogen bonding between HBDPPA and water definitely disrupts the ground state intramolecular hydrogen bonding isomers but increases the quantity of species IV, in which ESIPT is inhibited and therefore, the *trans* enol emission decreases with addition of water and finally vanished [20].

F



Fig. 3. Fluorescence spectra of HBDPPA in the presence of various metal ions.

 Table 2

 Electron density of atoms N(3) and O(31) for HBDPPA.

Compound	Atom	Ι	I*	III
HBMBA	N(3) O(30)	$-0.492 \\ -0.588$	-0.545 -0.501	0.441 -0.608

\* corresponds to excited state



Fig. 4. Competition of intra and intermolecular hydrogen bonding of HBMBA in binary solvents.

## Potential energy surface (PES) studies of HBDPPA

The ground-state geometries of the three species, I, II, and III for HBDPPA was optimized using the DFT/6-31G (d,p) method. Complete optimization of all the geometrical parameters gives the ground state energy of each species. The energy of the excited state was calculated using the standard CIS method. Table 3 gives the energies and dipole moment of the species I, II, and III in the ground and the excited state. The potential energy (PE) curves for the interconversion of isomers I and II of HBDPPA in the ground (Fig. 5a) and the excited states (Fig. 5b) reveal that for isolated HBDPPA in the ground state the barrier for interconversion is 5.3

Table	3
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Relative energies an	nd dipole	moment fo	or HBDPPA.
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Rotamer	Ground state		Excited sta	ate
	μ(D)	E(eV)	μ(D)	E(eV)
Ι	5.70	0.10 (0.00)	9.97	4.20 (2.20)
II	4.80	0.14 (0.05)	9.27	4.84 (5.11)

Values in the parentheses corresponds to ethanol.

and 4.6 kcal/mol in ethanol. In the excited state the barrier for HBDPPA in the isolated molecule and in the ethanol medium are 11.0 and 9.5 kcal/mol, respectively. The barriers for interconversion in the excited state are much higher than that in the ground state [21].

### Molecular electrostatic potential

The MEP is related to the electronic density and is a very useful descriptor for determining the sites for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions [22]. To predict reactive sites for electrophilic and nucleophilic attack for the investigated molecule, the MEP at the B3LYP/6-311++G(d,p)optimized geometry was calculated. The negative (red and yellow) regions of the MEP are related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity, as shown in Fig. 6. As can be seen from the figure, this molecule has several possible sites for electrophilic attack. Negative regions in the studied molecule are found around the hydroxyl oxygen O(23) atom. Also, a negative electrostatic potential region is observed around the nitrogen atom N(3). The negative V(r) values are -0.121 a.u. for hydroxyl oxygen atom (23), which is the most negative region, and 0.0546 a.u. for nitrogen atom N(3), which is the least negative region. However, a maximum positive region is localized on the aldehydic C-H bond with a value of +0.0106 a.u., indicating a possible site for nucleophilic attack. According to these calculated results, the MEP map shows that the negative potential sites are on electronegative atoms as well as the positive potential sites are around the hydrogen atoms. These sites give information concerning the region from where the compound can undergo non-covalent interactions.

The MEP is best suited for identifying sites for intra- and intermolecular interactions [23]. When an intramolecular interaction takes place the electrostatic potential of the negative atom becomes less negative and the positive region on the other atom becomes less positive. For the MEP surface in the studied molecule, the weak negative regions associated with the nitrogen atom N(3) and also the weak positive region by the nearby hydrogen atom are indicative of intramolecular (N(3)···H(31)–O(30)) hydrogen bondings.

## Natural bond orbital (NBO) analysis

NBO analysis revealed that the  $n(N(3) \rightarrow *(O(30)-H(31)))$  interactions give the strongest stabilization to the system of the title compound by 36.82 kcal/mol (gas); 40.66 kcal/mol (chloroform) and 46.02 kcal/mol (ethanol) and strengthen the intramolecular  $O(30)-H(31)\cdots N(3)$  hydrogen bond in gas phase. The E(2) value due to the  $n(N(3) \rightarrow *(O(30)-H(31))$  orbital interaction increases with increasing dielectric constant of solvent. This result can be used to explain the enhancement of the  $O-H\cdots N$  hydrogen bond strength with increase of solvent polarity. Thus, it is apparent that  $O-H\cdots N$  interactions significantly influence crystal packing with this molecule.



Fig. 5. PES for the interconversion of the rotamers of HBMBA in the ground and excited state.



Fig. 6. MEP surface diagram of HBDPPA.

### HOMO-LUMO energies of HBDPPA by DFT method

Analysis of the electron density of HOMO and LUMO of HBDPPA can through some light on the ground and excited states proton transfer processes. HOMO of enol form predicts that intramolecular hydrogen bonded (IMHB) ring system (Fig. S9) posses bonding character over hydroxyl oxygen and nitrogen, with a larger electron density over the hydroxyl oxygen. Electron density of HOMO of keto tautomer around IMHB ring shows antibonding character over the hydroxyl oxygen and nitrogen atoms. Again comparison of HOMO of enol form with HOMO of keto form shows much larger electron density on hydroxyl oxygen. In the later case HOMO electron density for both the enol and keto form shows less electron density over the phenyl ring.

By considering LUMO of enol and keto forms, LUMO of the enol tautomer possess high electron density on hydroxyl oxygen. After tautomerization, LUMO of keto-tautomer still shows larger electron density on nitrogen and comparatively smaller density on hydroxyl oxygen .Thus it favors the transfer of a proton from hydroxyl oxygen to imine nitrogen in the excited state (ESIPT). Again our calculation of electron density over the proton transfer co-ordinate in the excited states (i.e., LUMO electron densities) shows that there is a shift of *p*-electron density of HOMO for enol tautomer predicts imine nitrogen has slightly higher bonding character than hydroxyl oxygen. On the other hand, HOMO electron density of keto tautomer shows greater bonding character of

hydroxyl oxygen than imine nitrogen and hence transfer of proton from hydroxyl oxygen to imine nitrogen in the ground state (ESIPT) is quite impossible.

# Hyperpolarizability Vs absorption maximum of HBDPPA by DFT method

To determine the transference region and hence to know the suitability of HBDPPA for microscopic nonlinear optical applications, the absorption maximum was compared with  $\beta$ -components of HBDPPA [24,25]. All the absorption bands are due to  $\pi \rightarrow \pi^*$  transitions. The increased transparency in the visible region might enable the microscopic NLO behavior with non-zero values [26]. The observed red shift in absorption with increasing solvent polarity accompanied with the upward shifts non-zero values in the  $\beta$ -components and hence has rather well microscopic NLO behavior [27]. Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore it was used frequently as a threshold value for comparative purposes. The calculated values of  $\mu_{tot}$ ,  $\alpha_{tot}$  and  $\beta_{tot}$  for the HBDPPA are 6.34 D, 25.4 × 10<sup>-31</sup> and 54.76 × 10<sup>-31</sup> e.s.u which are greater than those of urea. These results indicate that the title compound is a good candidate of NLO material.

#### Octupolar and dipolar components and $\mu\beta_{o}$

The electrostatic first hyperpolarizability ( $\beta$ ) of the *o*-hydroxy Schiff base has been calculated by using Gaussian-03 package [11], it is found that the chromophore show larger  $\mu\beta_0$  value (347.6 × 10<sup>-31</sup> e.s.u), which is attributed to the positive contribution of their conjugation. *o*-hydroxy Schiff base exhibits larger non-linearity and so their absorption is red-shifted. Therefore, the hyperpolarizability is a strong function of the absorption maximum. This *o*-hydroxy Schiff base derivative possess more appropriate ratio of off-diagonal versus diagonal  $\beta$ -tensorial component [r = 1.92] which reflects the non-linearity and the largest  $\mu\beta_0$  values (347.6 × 10<sup>-31</sup> e.s.u).

The  $\beta$ -tensor decomposed in a sum of dipolar  $(J_{=1}^{2D}\beta)$  and octupolar  $(J_{=3}^{2D}\beta)$  tensorial components and the ratio of these two components strongly depends on their '*r*' ratios. The octupolar and dipolar components of the  $\beta$ - tensor has been calculated using the following equations:

$$||_{j=1}{}^{2D}\beta|| = (3/4)[(\beta_{xxx} + \beta_{xyy})^2 + [(\beta_{yyy} + \beta_{yxx})^2]$$
(8)

$$||_{J=3}{}^{2D}\beta|| = (1/4)[(\beta_{xxx} - {}_{3}\beta_{xyy})^2 + [(\beta_{yyy} + \beta_{yxx})^2]$$
(9)



Fig. 7. Correlation of the absorption and fluorescence wave numbers obtained by the multi-component linear regression.

#### Table 4

Adjusted coefficients  $((v_x)_0, c_a, c_b \text{ and } c_c)$  and correlation coefficients (r) for the multilinear regression analysis of the absorption  $v_{ab}$  and fluorescence  $v_{fl}$  wavenumbers and Stokes shift  $(\Delta v_{ss})$  of HBDPPA with the solvent polarity/polarizability, and the acid and base capacity using the taft  $(\pi^*, \alpha \text{ and } \beta)$  and the Catalan (SPP<sup>N</sup>, SA and SB) scales.

(v <sub>x</sub> )	$(\upsilon_x)_0 \text{ cm}^{-1}$	$(\pi^*)$	Cα	C <sub>β</sub>	r
$\begin{array}{l} \lambda_{ab} \\ \lambda_{fl} \\ \Delta \upsilon_{ss} = \upsilon_{ab} - \upsilon_{fl} \\ (\upsilon_{x}) \end{array}$	$\begin{array}{c} (3.08\pm0.024)\times10^4\\ (2.62\pm0.019)\times10^4\\ (0.32\pm0.005)\times10^4\\ (\upsilon_x)_0\ cm^{-1} \end{array}$	$\begin{array}{l} -(11.81\pm 4.99)\times 10^3\\ -(10.42\pm 4.09)\times 10^3\\ -(1.40\pm 0.95)\times 10^3\\ c_{SPP}^N\end{array}$	$\begin{array}{c} (23.457 \pm 14.92) \times 10^3 \\ (20.72 \pm 12.22) \times 10^3 \\ (2.73 \pm 2.84) \times 10^3 \\ \end{array}$	$\begin{array}{l} -(13.11\pm11.16)\times10^{3}\\ -(11.49\pm9.15)\times10^{3}\\ -(16.28\pm21.29)\times10^{3}\\ c_{SB}\end{array}$	0.78 0.87 0.78 r
$\lambda_{ab}$ $\lambda_{fl}$ $\Delta \upsilon_{ss} = \upsilon_{ab} - \upsilon_{fl}$	$\begin{array}{c} (3.03\pm0.017)\times10^4\\ (2.70\pm0.014)\times10^4\\ (0.33\pm0.034)\times10^4 \end{array}$	$\begin{array}{c} -(17.62\pm 6.15)\times 10^3\\ -(13.79\pm 5.06)\times 10^3\\ -(3.83\pm 1.20)\times 10^3\end{array}$	$\begin{array}{c}(56.24\pm25.77)\times10^{3}\\(43.29\pm20.98)\times10^{3}\\(12.95\pm5.03)\times10^{3}\end{array}$	$\begin{array}{c} -(52.88\pm26.78)\times10^3\\ -(40.69\pm21.80)\times10^3\\ -(12.18\pm5.28)\times10^3\end{array}$	0.85 0.86 0.82



Fig. 8. Stabilization of the resonance structures of the chromophore.

The parameter  $\rho^{2D} [\rho^{2D} = |\frac{||_{r=3}^{2D}\beta||}{||_{r=1}^{2D}\beta||}$  is convenient to compare the relative magnitudes of the octupolar and dipolar components of  $\beta$ . The observed positive  $\rho^{2D}$  values, reveal that the  $\beta$ - tensor components cannot be zero and *o*-hydroxy Schiff base are dipolar components. Since most of the practical applications for second order NLO chromophores based on their dipolar components, this strategy is more appropriate for designing highly efficient NLO chromophores.

### Marcus and Reichardt-Dimroth solvent functions - solvatochromism

Solvent shifts in the absorption and emission of o-hydroxy Schiff base have been measured in different solvents. The emission peaks are observed around 341.5, 365 nm in *n*-hexane (non-polar), 389.8 nm in ethanol (polar protic solvent), 375.6 nm in CH<sub>2</sub>Cl<sub>2</sub> (medium polarity) and 395.4 nm in acetonitrile (a strongly polar aprotic solvent). The peaks shift may be due to the stronger interaction between the solvent and the excited state molecules. The excited state of o-hydroxy Schiff base has been more stabilized in polar solvents than in non-polar solvents. This leads to red shift of emission with increasing solvent polarity. Measurements of absorption solvatochromism have been interpreted with Marcus and Reichardt-Dimroth solvent functions to estimate the transition dipoles in the excited state. The linear correlation (Fig. S10) of absorption energy with Reichardt–Dimroth solvent  $E_{\rm T}$  parameters indicates that the dielectric solute solvent interactions are responsible for the observed solvatochromic shift. Similarly the observed linear correlation (Fig. S11) has been observed between absorption energy and Marcus [28] optical dielectric solvent function  $[(1-D_{op})/(2D_{op}+1)]$  reveal that the transition dipoles are associated with absorption and the direction of excited dipole is opposite to that of the ground state dipole.

### Taft and Catalan solvatochromism

Solvent properties mainly affect the photophysical properties of compounds are polarity, H-bond donor capacity and electron donor ability. Different scales for such parameters can be found in the literature, Kamlet and Taft [29] propose the  $\pi^*$ ,  $\alpha$  and  $\beta$  scales, shown as

$$\mathbf{y} = \mathbf{y}_0 + \mathbf{a}_{\alpha} \alpha + \mathbf{b}_{\beta} \beta + \mathbf{c}_{\pi^*} \pi^* \quad (\text{Kamlet} - \text{Taft})$$
(1)

Catalan et al. [30] suggest the SPP<sup>N</sup>, SA and SB scales to described the polarity/polarizability, the acidity and basicity of the solvents as shown as

$$y = y_0 + a_{SA}SA + b_{SB}SB + c_{SPP}SPP \quad (Catalan)$$
(2)

The correlation of the absorption (Fig. 7a) and fluorescence (Fig. 7b) wave numbers obtained by the multi-component linear regression employing the Taft and Catalan solvent parameters with the experimental values given in Table 4. The polarity/polarizability of the solvent coefficient  $[C_{\pi*} \text{ or } C_{\text{SPP}}^{\text{N}}]$  value correlating the solvatochromic shifts with the solvent polarity. The coefficient controlling the basicity of the solvent ( $C_{\beta}$  or  $C_{SB}$ ), has a negative value for o-hydroxy Schiff base. This is interpreted in terms of the stabilization of the resonance structures of the chromophore (Fig. 8). Resonance structure "II" has the positive charge located at the carbon atom and it will be stabilized in acidic solvents. Because these resonance structures is predominant in the S<sub>1</sub> state and the stabilization of the S<sub>1</sub> state with the solvent basicity would be more important than that of the S<sub>0</sub> state. Consequently, the energy gap between the S<sub>1</sub> and S<sub>0</sub> states decreases and the absorption and fluorescence wavelengths shift to longer wavelength with increasing solvent basicity.

### Conclusion

Intermolecular hydrogen bonding of HBDPPA with water giving rise to IV impedes the ESIPT process. ESIPT in o-hydroxy Schiff base confirmed by DFT calculation. PES calculation reveals that the barriers for interconversion in the excited state are much higher than that in the ground state. However, the intermolecular hydrogen bonding with alcohol is not strong enough to compete with the intramolecular hydrogen bonding in HBDPPA. The fluorescence of HBDPPA quenched markedly with the gradual addition of Cu<sup>2+</sup> but the fluorescence properties of HBDPPA was influenced by other metal ions. Therefore Schiff base HBDPPA can be used as a new fluorescence sensor to detect the quantity of Cu<sup>2+</sup> ion in any sample solution depending on the relative intensity change. Molecular orbital coefficient analyses suggest that the electronic spectrum correspond to the  $\pi \rightarrow \pi^*$  electronic transition. The MEP map shows that the negative potential sites are on electronegative atoms while the positive potential sites are around the hydrogen atoms. These sites give information about the region from where the compound can undergo non-covalent interactions. NBO analysis revealed that the n(N1)  $\rightarrow \pi^*$  O(30)–H(31) interaction gives the strongest stabilization to the system. The predicted nonlinear optical (NLO) properties of the title compound are much greater than those of urea.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.06.049.

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