

Synthesis, spectroscopic properties and DFT calculations of a novel pH sensitive azo dye and its zinc(II) complex

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Abstract

The synthesis and photophysical properties of 5-(diethylamino)-4-[(E)-(4-nitrophenyl)diazenyl]-2-(1,3-benzoxazol-2-yl)phenol (**AB-HBO**) and its zinc complex were examined. The organic molecule acts as a pH sensitive chromophore and as mononegative ligand for zinc(II) ion. Structural features and absorption/emission properties of **AB-HBO** were studied. The solvatochromic blue shift, shown by the ligand in its neutral form, is widely enhanced in its deprotonated form. The color solution ranges from red-orange to violet and blue-green as function of the electronic density deformation. Emissions were recorded on both ligand and zinc complex solutions. DFT calculations have been performed in order to rationalize the absorbance of chromophore and complex.

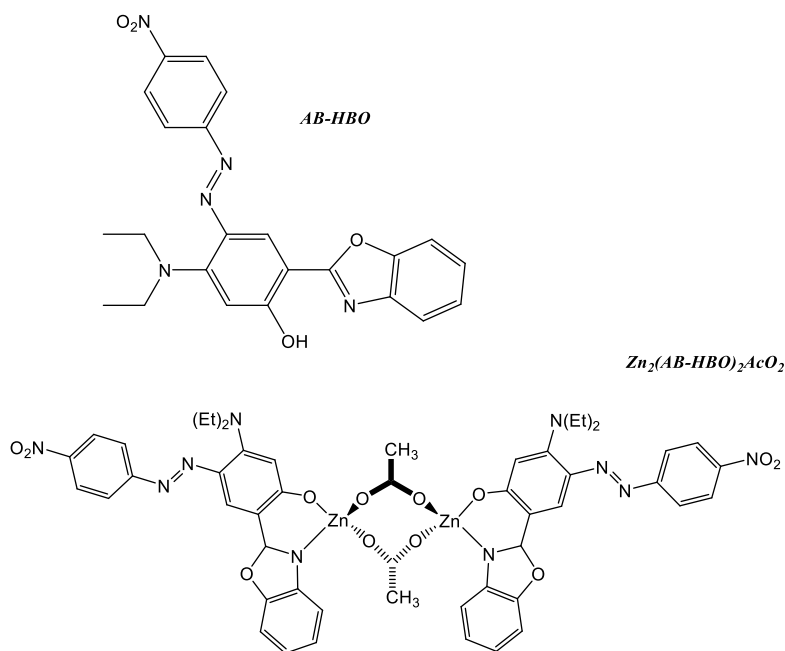
Keywords: *Azo dye, benzoxazole, zinc(II) complex, solvatochromism*

In recent years, the development of organic electronics devices based on high π -conjugated systems, gained an enormous attention because of significant advantages over conventional inorganic crystals. In some cases specifically built push-pull structures produce desirable unique optical properties enjoying widespread applications as photochromic [1], nonlinear optical [2-4], photoluminescent [5-8] or electroluminescent materials [9, 10], photovoltaic polymers [11, 12] chemosensors [13], and organic light-emitting layers in diodes (OLEDs) [14, 15]. In particular, it is well known that aromatic azobenzene compounds with electron withdrawing groups exhibit good tunability of HOMO and LUMO levels[16] and, for this reason they have been employed as industrial dyes. They also potentially provide large

second-order hyperpolarizability associated with fast response time of pair electron rearrangement and show, in some cases, good antimicrobial properties [17]. On the other hand, the presence of a five-membered conjugated heterocycle units within π -conjugated systems can improve several characteristics, from liquid crystal [18] to nonlinear optical (NLO) [19, 20] to emission response [16, 19, 21]. The family of 2-(2'-hydroxyphenyl)benzoxazoles (HBO) comprises fluorescent molecules that present good thermal and photophysical stability due to an excited state intramolecular proton transfer (ESIPT) mechanism and for this reason extensively studied [22, 23] mainly as laser dyes and/or fluorescent probes. The appropriate combination of two conjugated systems can lead to asymmetrical Y or X-shaped charge-transfer chromophores.

In this work, insertion of a nitroazobenzene electron-acceptor group in an electron-donor (diethylamino) substituted HBO conjugated skeleton produced a novel two-dimensional multipolar chromophore (***AB-HBO***) with potential NLO response. Hypsochromic UV-visible absorption shifts [24] were recorded on the chromophore depending on the solvent. Moreover, pH-dependent UV-visible measurements gave interesting results, with considerable enhancing of solvatochromism in the deprotonated form. The electronic density was found to move in two different acceptor-donor patterns, leading to different push-pull arrangements in the neutral and deprotonated dye. In both cases, a moderate fluorescence emission was recorded in solution, due to the HBO core, whose ESIPT process is variously influenced by the presence of the azobenzene substituent. Although multipolar chromophores have been often studied as dyes, the presence of a N,O chelating site in the molecule renders it a mononegative ligand, potentially placing it in the widely studied class of chemical detector for metal cations [25]. The ability of ***AB-HBO*** to react with a transition metal was proved with a closed-shell metal as zinc(II). Single-crystal X-ray analysis and ab initio DFT calculations permitted to clarify structural and mechanism aspects. The spectroscopic properties of the complex were compared with the free ligand, achieving information on the changes in the electronic pattern after coordination.

Compound 5-(diethylamino)-4-[(E)-(4-nitrophenyl)diazenyl]-2-(1,3-benzoxazol-2-yl)phenol (***AB-HBO***) and its zinc complex ($Zn_2(AB-HBO)_2(AcO)_2$), see Scheme 1, were prepared according to literature methods [26][20] as detailed in supplementary materials.



Scheme 1. Chromophore and zinc complex formulas

Identification and evaluation of purity degree for *AB-HBO* and $Zn_2(AB-HBO)_2(AcO)_2$ were performed by 1H -NMR in $CDCl_3$. In particular, the presence of the singlet at 1.88 ppm is diagnostic of the acetate bridge hydrogens in the complex. The zinc content, measured as the ZnO percentage from the thermogravimetric analysis (TGA) residue, is consistent with the formula ($\% ZnO_{calc} = 14.6$, $\% ZnO_{exp} = 15.9$). The thermogravimetric pattern also shows a 10.3% weight loss at about 230°C that is consistent with the presence of two acetate bridges (theoretical weight loss 10.6%). Optical observation and DSC-analysis methods evidenced no melting point for the complex with high thermal stability up to 300°C. Absorption/ emission data both for *AB-HBO* and $Zn_2(AB-HBO)_2(AcO)_2$ recorded in solvents with different polarity are reported in Table 1. In all cases, the UV-vis absorption and emission bands of the complex closely match that of the ligand precursor, with a signal centered at about 350 nm and a second broad band recorded after 520 nm, just a little shifted due to metal-perturbed π - π^* ligand-centered transitions. We have observed only a small solvatochromic effect for chromophore and complex, with similar shape and relative intensity of absorption bands. This result can be ascribed on slight changes in the electronic pattern from free ligand to complex, as expected in case of Zn^{2+} that does not typically introduce electron- or energy-transfer mechanisms for the deactivation of the excited state. Contrarily, a remarkable result is the change in absorption pattern in highly alkaline solutions of *AB-HBO* where the phenol group is fully replaced by phenate, with significant consequences on the push-pull characteristics

of the chromophore. As it will be discussed below, the neutral chromophore shows a Y-shaped electron transfer path, while the phenate form is characterized by an X-shaped push-pull pattern. In the deprotonated form, a considerable hypsochromic shift occurs depending on solvent polarity (see Table 1), also clearly evidenced in Figure 1. In Figure 2, the absorption spectra of *AB-HBO*, recorded in the same solvent at different pH conditions, are reported. A new peak at ~300nm appears and the intensity of the signals at ~350 nm and ~530 nm changes by increasing the pH, thus revealing that the first and the third transitions are due to the full deprotonated species with significant contribution of the keto resonance form (see Tab. S6 in which the bond length C9-O2 of the deprotonated species is 1.254Å). Fluorescence spectra of the chromophore and the complex recorded in different solvents, such as tetrahydrofuran (THF), ethanol, acetone, and N-methyl-2-pyrrolidone (NMP), show a medium-low intensity peak centered at about 395nm and just 10 nm higher in NMP. As expected, when the equilibrium between protonated and deprotonated form is stuck, i.e. in highly alkaline solutions, ESIPT mechanism is prevented, so the fluorescence intensity recorded on the deprotonated form is in all cases lower. Stokes shift referred to the first absorption peak ranges from 47 to 63nm, while if referred to the second absorption peak, it ranges in a larger range, from 129 to 227nm.

Table 1. Absorption/emission data in various solvents for *AB-HBO* and $Zn_2(AB-HBO)_2(AcO)_2$

<i>Compound</i>	<i>Solvent</i>	$\mu(D)^a$	$\lambda_{abs}(nm)^b$	$\lambda_{abs}(nm)^c$	$\lambda_{em}(nm)$
<i>AB-HBO</i>	THF	1.63	345	524	396
	THF +KOH		347	524	395
	Ethanol	1.69	345	530	395
	Ethanol + KOH		344	562	398
	Acetone	2.88	340	535	391
	Acetone + KOH		344	617	391
	NMP	4.09	344	546	404
	NMP +KOH		349	631	404
$Zn_2(AB-HBO)_2(AcO)_2$	THF	1.63	345	530	401
	Ethanol	1.69	343	531	400
	Acetone	2.88	354	537	405
	NMP	4.09	346	551	409

^{a)} Solvent dipole moment by Handbook of Chemistry and Physics, 59TH Edition, CRC Press, Inc.; ^{b)} Wavelength of UV-VIS absorbance maxima in solution, first maxima ^{c)} Wavelength of UV-VIS absorbance maximum in solution, second maximum

^{d)} Wavelength fluorescence emission maximum in solution irradiated at 350nm.

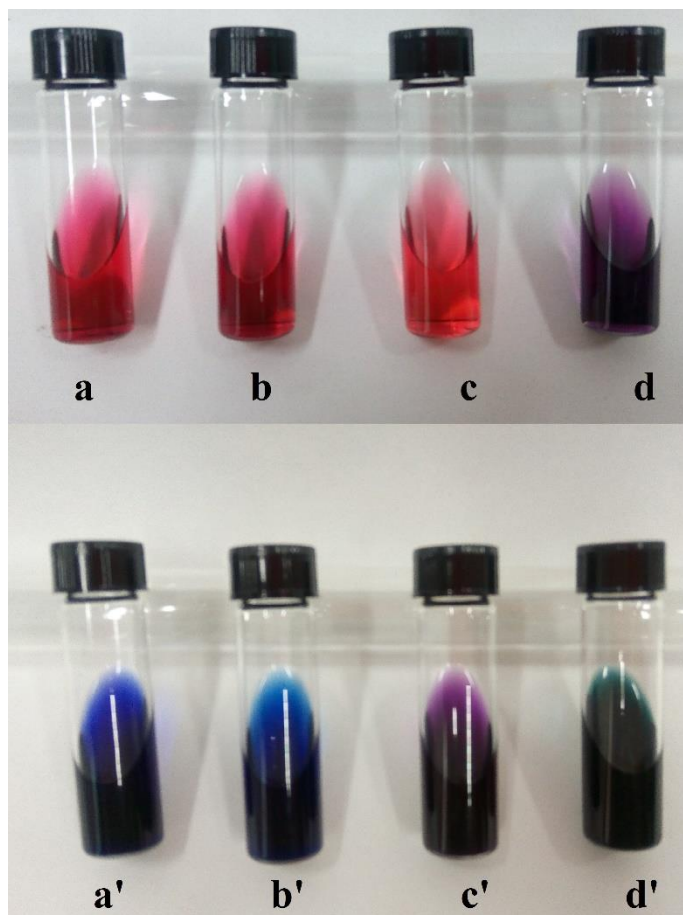


Fig. 1. Color change of solutions of *AB-HBO* in: THF (a); ethanol (b); acetone (c); NMP (d); THF+KOH (a'); ethanol+KOH (b'); acetone+KOH (c'); NMP+KOH (d').

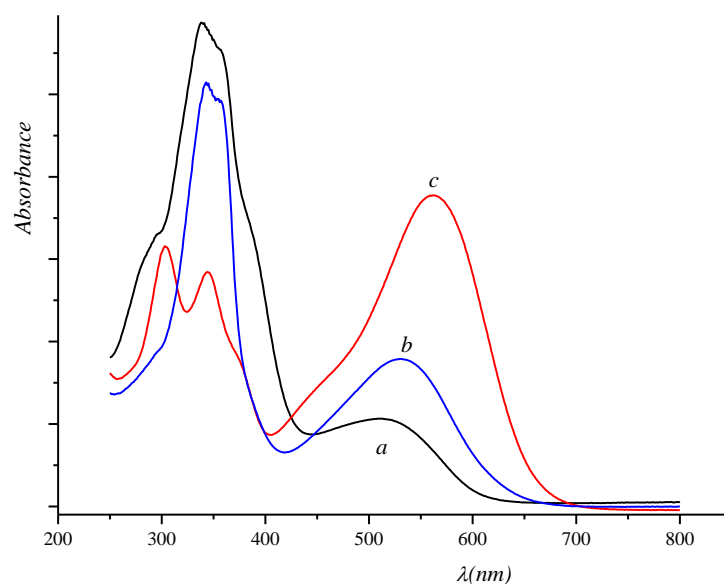


Fig. 2. Comparison of absorption spectra of chromophore *AB-HBO* in ethanol+HCl (a); in ethanol (b); in ethanol+KOH (c).

The X-ray molecular structure of *AB-HBO* is reported in Fig.3. The compound crystallize in the monoclinic P21/c space group with one molecule contained in the independent unit. All bond distances and angles are in the normal range. Crystal data and structural details are reported in the supporting information (Tab. S1).

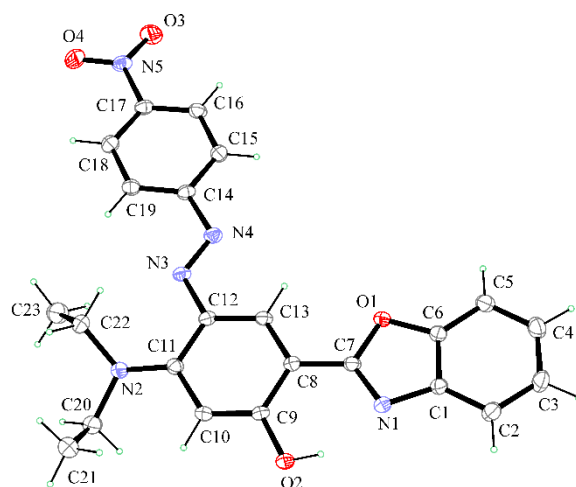


Fig. 3. Ortep view of *AB-HBO* (CRYST_MOL) with thermal ellipsoids drawn at 30% probability level. Selected bond lengths (Å): N2-C11=1.363(2), N3-N4=1.259(2), C7-C8=1.434(3)

In the molecule a double bond is present at N3-N4 in the E configuration. The clear presence of a double bond at the azo group suggests no relevant conjugation between the azo-phenyl system and the phenol ring. The trigonal planar geometry at N amino atom (sum of bond angles at N2 is near $358.9(2)^\circ$) and a shortening of N2-C11 bond length are compatible with a degree of conjugation of the amine group with the phenol ring. The analysis of benzoxazole bond distances shows no evidence of conjugation between the benzoxazole and the phenol ring systems and is consistent with X-ray data of pushpull molecules containing a 2-phenylbenzoxazole moiety [27]. The molecule assumes an overall planar conformation that is stabilized by the intramolecular hydrogen bond between hydroxy donor group and N acceptor of benzoxazole ($O2-H \cdots N1 = 0.86(3), 1.86(3), 2.641(2) \text{ \AA}, < 150(3)^\circ$). The optimized models obtained by DFT calculations are in good agreement with X-ray analysis, the only difference being a slight rotation of the nitrophenyl group (Fig. S1). The crystal packing is stabilized by normal Van der Waals interactions and weak intermolecular $C_{ar}H \cdots O$ interactions. Rows of π -stacked molecules are formed (Fig. 4 and Fig S2.)

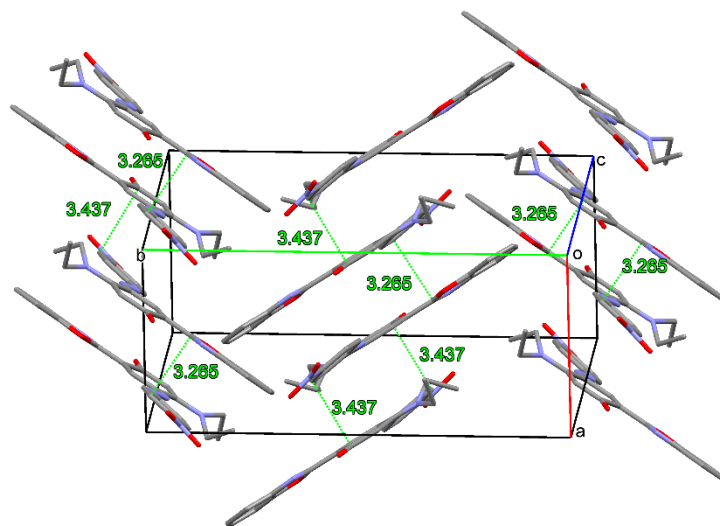


Fig. 4. Crystal packing with $\pi \cdots \pi$ stacking distances drawn as dashed green lines.

To gain information about the electronic structures of the ground and the excited states of the chromophore and its zinc complex, we have carried out a computational analysis at density functional theory (DFT) level. The isolated chromophore with crystalline geometry has been investigated in

solution. The conformational analysis was run using tetrahydrofuran (THF) as solvent. The conformer with the absolute minimum of energy is 3 kcal/mol more stable than the next minimum. For this reason, we have taken into account this conformer only, and studied it in solvents of different polarity. DFT calculations revealed that the solvent polarity has modest effect on the molecular geometry. The results of DFT computations are summarized in Table 2, where the predicted absorption wavelengths and oscillator strengths have been reported, of the two lower energy transitions calculated in various solvent at different polarity for broad band at about 530 nm.

Table 2.

Electronic properties, dipole moments (Debye) of the ground states ($|\mu_g|$) and of the singlet first excited states ($|\mu_{ex}|$) of *AB-HBO* computed at TDDFT level in various solvents.

#	Transition type	GAS		CHCl ₃		THF		Acetone		EtOH		MeOH	
		λ (nm)	f	λ (nm)	f	λ (nm)	f	λ (nm)	f	λ (nm)	f	λ (nm)	f
1	HOMO→LUMO	527.4	0.13	547.1	0.37	549.8	0.40	553.2	0.42	554.7	0.35	554.7	0.33
2	HOMO→LUMO	484.9	0.31	528.6	0.21	531.0	0.18	533.8	0.15	538.1	0.21	538.3	0.22
3	HOMO-1→LUMO	-	-	-	-	-	-	-	-	405.5	0.47	-	-
4	HOMO-4→LUMO	-	-	-	-	-	-	-	-	326.7	0.36	-	-
5	HOMO→LUMO+2	-	-	-	-	-	-	-	-	325.3	0.52	-	-
	HOMO-4→LUMO	-	-	-	-	-	-	-	-				
$ \mu_g $		6.2		7.7		7.9		-		8.0		-	
$ \mu_{ex} $		9.3		16.1		17.3		-		17.7		-	
$ \mu_{ex}-\mu_g $		3.0		8.5		9.5		-		9.8		-	

According to the experimental data, these calculations show a modest shift (~10 nm) by increasing the solvent polarity, confirming the scarce solvatochromic effect shown by UV/Vis spectra, and suggesting the weak push-pull character of the chromophore in its phenolic form. However, the intense lower energy transition is HOMO→LUMO, where the charge transfer (Fig.5) occurs among the nitrophenyl, as acceptor, and two donors, the amine group and, unexpectedly, the benzoxazole ring. The weak push-pull character is also confirmed by the analysis of the values of dipole moments that shows a slight variation (~1 D) as increasing the solvent dielectric constant, from chloroform to ethanol, as reported in table S7.

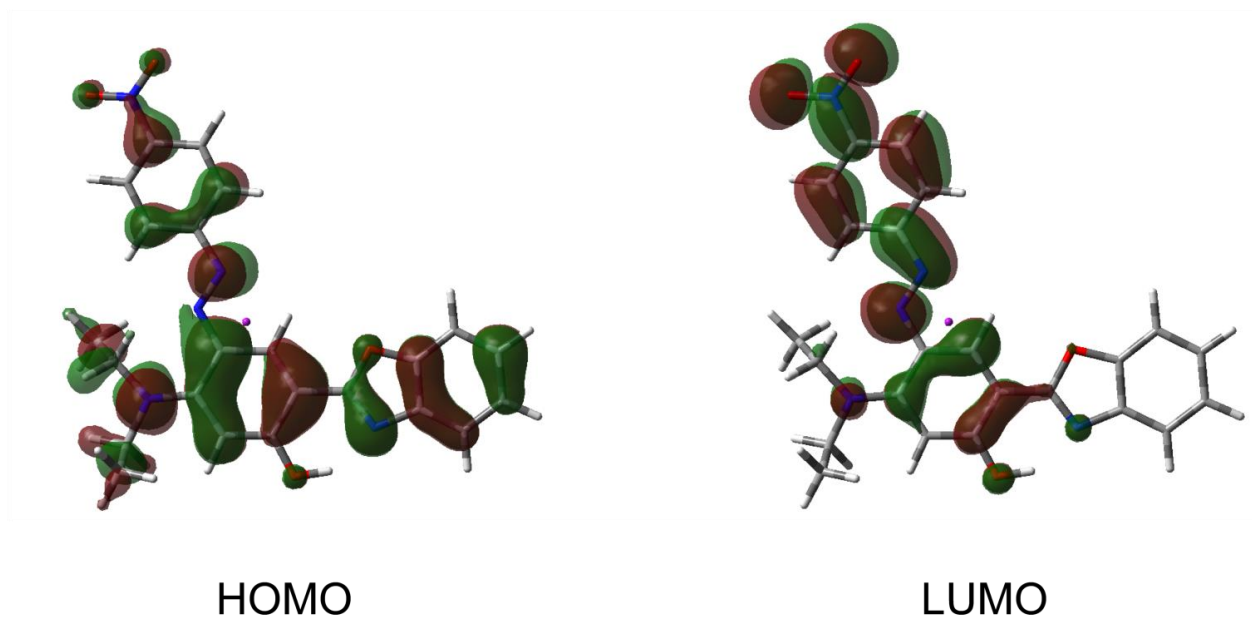


Fig. 5. Isodensity surface plots of frontier orbitals predicted by PCM(THF)M06/6-31+G** computations.

In the range of high wavelengths, two coupled transitions at 325 and 326 nm and one at 405 nm are predicted for the chromophore *AB-HBO*. The experimental UV/Vis spectra record a double peak band at 345-355 nm and a change of slope at about 380 nm, which matches with the estimated transitions. The electronic density variations between the fundamental and excited states is displayed in Fig.6 where the most intense contribute is provided from the coupled transition at 325 and 326. Hereby the weak push-pull character of the chromophores is confirmed with the shift of the electronic density from benzoxazole ring to nitrophenyl group.

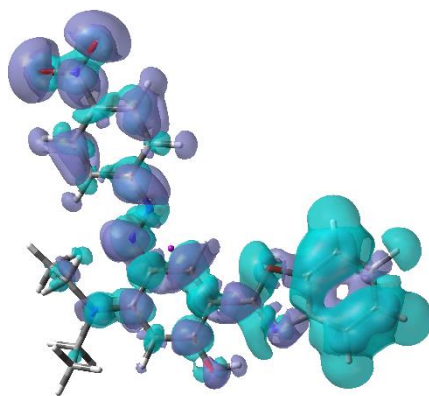


Fig. 6. Increasing (purple) and decreasing (light blu) electronic density change between the fundamental and the excited state for *AB-HBO*.

Conformational analysis carried out for the deprotonated form of *AB-HBO* in ethanol shows the presence of two isoenergetic conformers, which differ in the torsion angle between the benzoxazole and phenyl planes (Fig. S3). The results of TDDFT computations are summarized in Table S3, where the predicted absorption wavelengths and oscillator strengths have been reported. The most intense transition with HOMO-LUMO character is at ~560 nm and it is identified as a charge transfer from the benzoxazole ring and phenate to the nitrophenyl, whereas the electronic density variation between the amino group and nitrophenyl is less appreciable. The transitions distinctive of the deprotonated form are centered at about 300 nm and 350 nm in the experimental spectra and predicted at 303 nm and 330 nm, respectively. For the higher energy transition, the electronic density moves from the amino and deprotonated hydroxyl group to benzoxazole and nitrophenyl moiety, both acceptor groups. Even though the second transition is isoenergetic with that of neutral form of *AB-HBO*, it is characterized by shift of electronic density in the opposite direction, in detail the charge moves from nitrophenyl to benzoxazole group.

The configuration study on zinc complex led to the identification of two isomers (Fig.S4) differing in the dihedral angle between Zn and nitrogen of the benzoxazole substituents (2.6° for isomer I and 119.5° for isomer II) and having an energy difference of 3 kcal/mol. Other conformers are not populated at room temperature. The singlet excited states of the two isomers are investigated via TDDFT method and the calculated transitions are in good agreement with experimental data, as shown in Fig S5. The charge transfer character of the computed transitions of the complex closely matches with the ligand precursor. Notably, both the spectra of the deprotonated form of *AB-HBO* and the complex $Zn_2(AB-HBO)_2(AcO)_2$ show a shoulder in the range of 450-500 nm. In this transition, the electron density variation is between the phenate group and the nitrophenyl group for both the species, furthermore the complex shows the low electronic contribute of the metal. In conclusion, DFT calculations have pointed out the donor feature of the benzoxazole ring and the amine group in *AB-HBO*, quite similarly to $Zn_2(AB-HBO)_2(AcO)_2$, with charge transfer towards the nitrophenyl. In the deprotonated form, the different push-pull arrangement leading to an increase of solvatochromism was connected to the electronic density moving from the amino and deprotonated hydroxyl group to benzoxazole and nitrophenyl moiety.

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Appendix A.

Supporting information to this article can be found online at ****

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