A spectroscopic study of the optical properties of a nitrobenzoxadiazole derivative in solution: The role of specific interactions

Claudio Quarti [a], Francesca Villafiorita-Monteoleone [b], Chiara Botta [b], Valentina Daita [c], Dario Perdicchia [c], Paola Del Buttero [c], Mirella Del Zoppo [a,*]

[a] *Politecnico di Milano Dipartimento di Chimica,Materiali e Ing. Chimica CMIC "G. Natta", p.za Leonardo da Vinci 32, 20133 Milano, Italy*
[b] *Istituto per lo Studio delle Macromolecole, CNR, via Bassini 15, 20133 Milano, Italy*
[c] *Università degli Studi di Milano, Dipartimento di Chimica, Via Golgi 19, 20133 Milano, Italy*

Article history:
Received 17 April 2014
In final form 16 July 2014
Available online 24 July 2014

1. Introduction

The modeling of environmental effects on the spectroscopic response of molecular systems is one of the hot topics in theoretical chemistry and various papers [1,2] and reviews [3,4] have been published recently on the subject. In this Letter we consider the optical properties (absorption and emission spectra) of *4-hexylamino-7-nitro-2,1,3-benzoxadiazoles* (NBD) and its solvatochromic behavior. This is a new 4-substituted-NBD derivative compound whose structural formula is reported in Figure 1. Nitrobenzoxadiazoles are used as fluorogenic probes [5–7] and their fluorescence properties depend on the chemical groups used for the functionalization of the NBD skeleton.

The hexylamino functionalization has been envisioned to favor the interaction with an hydrophobic environment such as that present in the inner cavity of a cyclodextrin molecule which will be the topic of a future work where a new host–guest system based on a NBD derivative dye and Cd/CdS quantum dots covered with β-cyclodextrin will be presented with the purpose of obtaining efficient down-converted photoluminescence emission. The electronic structure of benzofurazane derivatives has been studied in the recent past by a variety of computational methods [7,8] and the absorption and emission wavelengths reproduced for the isolated molecule. In this preliminary work our concern is the study of the intermolecular interactions and their effects on the optical properties and is thus focused on the solvatochromic behavior of NBD. The quantum mechanical modeling of environmental effects can be done following two different routes: (i) one can calculate the optical properties of the NBD molecule within the *polarizable continuum model* (PCM). In the PCM model, the solute molecule is embedded into a cavity and the presence of the solvent is mimicked by point charges lying on the cavity surface, whose distribution depends on the reciprocal polarization between the charges themselves and the electron density of the solute [3,9]. In this way, the effects due to the reciprocal polarization between solute and solvent are taken into account. However, within this formalism, specific interactions, such as hydrogen bonds, cannot be described properly. (ii) Otherwise, one can explicitly take into account specific intermolecular interactions using solvent–solute molecular models. An accurate description of the explicit solute–solvent interactions requires complex QM/MM molecular dynamic simulations [1,10,11], in order to properly explore the configurational space of the molecule in solution. However, these methods provide overabundant information and often the chemical detail is lost behind the complexity of the model. For this reason, we have chosen a much simpler approach: we have considered 'ad hoc' molecular systems formed by the NBD molecule and just one solvent molecule, in configurations that allow the formation of a hydrogen

* Corresponding author.
E-mail address: mirella.delzoppo@polimi.it (M. Del Zoppo).

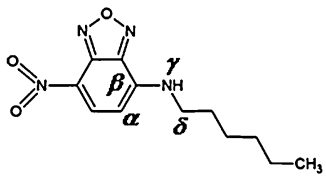

Figure 1. Structural formula of *4-hexylamino-7-nitro-2,1,3-benzoxadiazoles* (NBD).

bond. We do not expect that such simple models are able to quantitatively reproduce the optical properties of the NBD molecule in solution but we await that they are able to get the essential features of the supramolecular interaction effects on the optical properties of the NBD dye in solution.

2. Methods

2.1. Experimental

2.1.1. General experimental procedure

Starting materials and solvents of analytical grade were obtained from commercial sources and used without further purification. All reagents were purchased from Sigma–Aldrich.

^{1}H NMR (300 MHz) was taken with a Bruker AMX 300 instrument. Chemical shifts are given as parts per million from tetramethylsilane. Coupling constants (J) values are given in hertz and are quoted to ±0.1 Hz, consistently with NMR machine accuracy.

2.1.2. Synthesis of 4-hexylamino-7-nitro-2,1,3-benzoxadiazoles (NBD)

4-Chloro-7-nitro-2,1,3-benzoxadiazole (400 mg, 2 mmol) was dissolved in methanol (12 mL) and $NaHCO_3$ (505 mg, 6 mmol) was added. After the subsequent addition of hexylamine (0.26 mL, 2 mmol), the solution was stirred for 8 h at room temperature. The reaction mixture was then evaporated to dryness under reduced pressure and the resulting residue chromatographed on silica gel (dichloromethane) to obtain 4-hexylamino-7-nitro-2,1,3-benzoxadiazoles (NBD) in 70% yield (melting point = 105 °C).

^{1}H NMR (300 MHz, DMSO-d_6) δ 0.8 (t, 3H, CH_3), 1.25–1.5 (m, 6H), 1.8 (m, 2H), 3.5 (q, 2H), 6.1 (d, J = 8.7 MHz, 2H), 6.3 (s, NH), 8.5 (d, J = 8.7 MHz, 2H).

2.1.3. Optical characterization

All measurements were performed on solutions of NBD at concentrations of about 10^{-5} M.

Optical absorption measurements were performed using a Perkin-Elmer Lambda-9 spectrometer.

Photoluminescence (PL) spectra were recorded by using a 270 M SPEX spectrometer equipped with a N_2 cooled CCD (charge-coupled device) detector, and by exciting with a Xenon lamp connected to a Gemini monochromator for the wavelength selection. The spectra were corrected for the instrument response.

2.2. Theoretical modeling

The spectroscopic investigation of the optical properties of the NBD dye in solution has been supported by Density Functional Theory (DFT) calculations. The TD-DFT [12–14] theory, generally provides reliable results at a limited computational cost [15,16]. The B3LYP [17] and CAM-B3LYP [18] exchange-correlation (xc) functionals in connection with the 6-31G(d,p) basis set [19] have been used in this work. We have verified that the two methods provide the same physical picture, except for the fact that the B3LYP calculations on some explicit models (interaction 1 and 4 of methanol and interaction 2 and 4 of DMF see later) predict a first singlet excited state of intermolecular charge transfer character (see Supplementary data Table SI1 and SI2). However, it is well known that these charge transfer states are due to a weakness of B3LYP, and in general of all the hybrid xc functionals with low exact exchange fraction [20–22]. On the contrary, the CAM-B3LYP functional is known to perform better in this respect. For this reason in the following, we report only the CAM-B3LYP results (for comparison the B3LYP results can be found in the Supplementary data).

To determine the emission wavelengths, we optimized the geometry of the first dipole allowed exited state.

All calculations are carried out with the GAUSSIAN 09 code [23]. Default converged criteria have been used in optimizations and a maximum step of 5 Bohr for the optimization of the molecular structures in the first singlet excite state S1 has been used.

Table 1
Experimental absorption (λ_{abs}) and emission wavelength (λ_{em}) of the NBD molecule in solution with solvents of increasing polarity. The dielectric relative constant of the solvents (ε) is reported as well.

Solvent	ε	λ_{abs}		λ_{em}	
		(eV)	(nm)	(eV)	(nm)
Ethyl acetate	6.02	2.69	460	2.36	525
Tetrahydrofuran	7.50	2.69	460	2.36	525
Dichloromethane	9.10	2.72	455	2.40	515
Methanol	33.10	2.61	475	2.29	540
Acetonitrile	36.20	2.63	470	2.33	530
Dimethylformamide	38.30	2.58	480	2.31	535

3. Results

3.1. Spectroscopy measurements

The absorption and emission spectra of NBD have been recorded in various solvents of increasing polarity and the absorption and emission maxima wavelengths are listed in Table 1. From Table 1 it is apparent that both the absorption and the emission wavelengths show a non monotonic trend with the polarity of the solvent. This non monotonic modulation of the optical properties of the molecule cannot be explained on the basis of reciprocal polarization effects due to the increase in dielectric constant of the medium. Instead, it is much more reasonable that it is due to specific interactions between the solvent and the dye.

3.2. DFT calculations

The ground state geometry of the NBD molecule has been optimized in vacuum. We have optimized the molecular structure of the dye in both *cis* and *trans* configurations with respect to the α, β, γ, and δ atoms of Figure 1 and we have verified that the *cis* configuration is the most stable. The vertical excitation energies have been calculated at the TD-CAM-B3LYP/6-31G(d,p) level. The first excited state is predicted to be dipole allowed, with an oscillator strength of 0.35 and a transition dipole moment, μ, of 2.01 a.u. This excitation essentially corresponds to a transition between the HOMO and LUMO Kohn-Sham orbitals, which are sketched in Figure 2. The predicted excitation energy is 3.58 eV, which largely overestimates the experimental values (2.69 eV in low polarity solvents, e.g. ethyl acetate). The TD-B3LYP calculation predicts an excitation energy of 3.20 eV, in slightly better agreement with experiments but still largely overestimated. However, these results are not completely unexpected since it has already been reported by Jacquemine et al. [24] that the errors obtained for vertical excitation energies by the TD-DFT method are typically of the order of 0.30 eV, with a large variance [15]. Anyway, we will show below that even if the

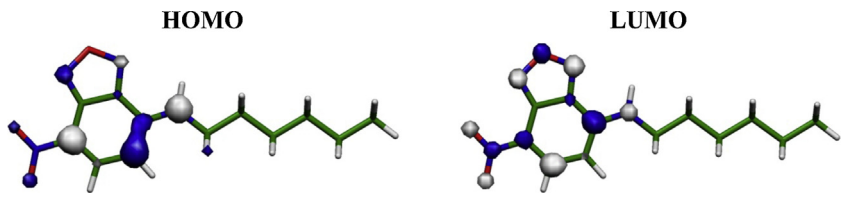

Figure 2. HOMO and LUMO orbitals of the NBD molecule mainly involved in the ground to S1 transition. Calculations carried out at the CAM-B3LYP/6-31G(d,p) level.

absolute value of the excitation energy from the ground to the S1 state is not accurately reproduced, the present method is effective in explaining the solvatochromic behavior of the NBD molecule.

In order to determine the emission energy from the S1 state, we have optimized the molecular structure of the NBD molecule in the S1 state with the TD-DFT method and we find an emission energy of 3.13 eV.

Once the properties of the isolated molecule have been determined, we have studied the properties of the NBD molecule in solution within the framework of the PCM method. The ground state molecular structure of the NBD dye has been optimized again at the CAM-B3LYP/6-31G(d,p) level in PCM, by setting the relative dielectric constant equal to the values reported in Table 1 for the various solvents. Then, we have calculated the vertical excitation energies from the ground to the first dipole allowed excited state at the TD-CAM-B3LYP/6-31G(d,p) level in PCM. The theoretical excitation energies from the ground state to S1 in various solvents are compared with the experimental data in Figure 3. As shown in Figure 3, the PCM calculations do not reproduce the non monotonic solvatochromic behavior of the NBD molecule. Indeed, these calculations predict that the ground to S1 excitation energy red-shifts monotonically with the polarity of the solvent and reaches a plateau for solvents more polar than methanol.

We have investigated also the emission properties of the NBD molecule in PCM. The molecular structure of the dye in the S1 state has been optimized at the TD-CAM-B3LYP/6-31G(d,p) level in PCM. The vertical emission energies (which formally correspond to the energy difference from S1 to the ground state evaluated at the equilibrium geometry of the excited state) computed for the various solvents have been reported in Figure 4 in comparison with experimental data. As for the absorption, the PCM calculations do not reproduce the non monotonic trend in excitation energies and a gradual red-shift of the emission wavelength with solvent polarity is observed. Also in this case, the emission energy reaches a plateau for solvents more polar than methanol.

The previous results demonstrate that the optical properties of the NBD molecule in solution cannot be rationalized by pure polarization effects but that specific interactions between the dye and solvent molecules must be considered. Thus, in order to explain the solvatochromism of NBD, we have considered possible specific interactions between NBD and one solvent molecule, with the procedure described in Section 1 (point ii). Following this procedure, we have identified (i) two NBD/solvent configurations (here on referred to as 'dimers') for ethyl acetate, (ii) one for tetrahydrofuran (THF), (iii) seven for methanol, (iv) one for acetonitrile and (v) six for dimethylformamide (DMF). The optimized structures of these dimers are reported in Table SI3 of the Supplementary data. The ground state geometry of all these models has been optimized at the DFT level and the computed interaction energies are reported in Table 2.

The optimized structures of all the dimers are reported in Table SI3. For each solvent we found one dimer which is more stable than the others by at least 4 kcal/mol namely, configuration 1 in ethyl acetate, configuration 5 in methanol and configuration 6 in DMF. These configurations are reported in Figure 5. Actually, in the case of DMF two dimers with similar energy are found, namely interaction 1 and interaction 6 (see Table 2). However, the analysis of these two dimers shows that they correspond to the same kind of interaction (see Table SI3) and hence in the following, we neglect configuration 1.

As shown in Figure 5, the most stable interacting dimers are always characterized by the formation of a H-bond between the NH group of the NBD dye and an electronegative atom of the solvent.

We have then calculated the vertical singlet excitation energies of all the interaction models associated to the various solvents, at the TD-CAM-B3LYP/6-31G(d,p) level. The computed ground state to S1 vertical excitation energies are summarized in Table 2. For each

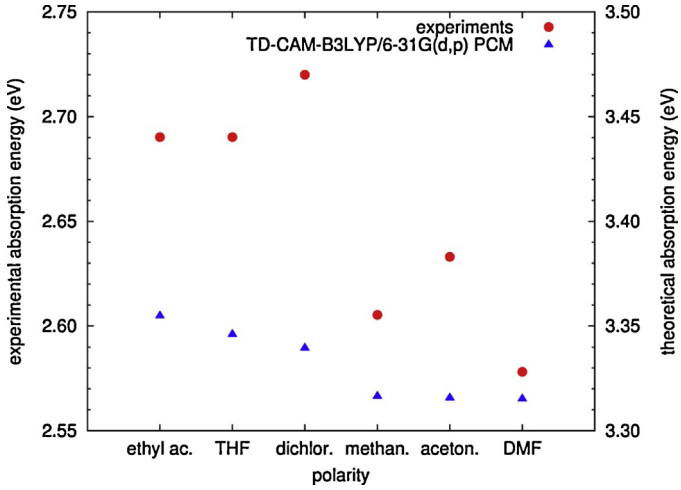

Figure 3. Comparison between experimental and theoretical excitation energies of the NBD molecule in solution. Theoretical data have been obtained within the PCM method. Calculations are carried out at the TD-CAM-B3LYP/6-31G(d,p) level on the optimized CAM-B3LYP/6-31G(d,p) ground state geometry.

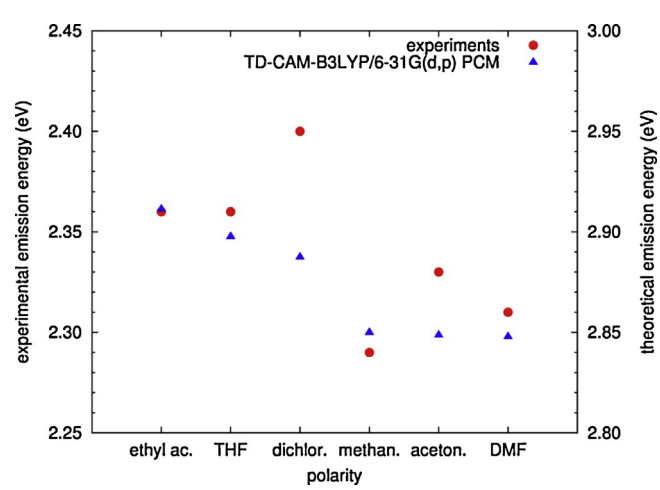

Figure 4. Comparison between experimental and theoretical emission energies of the NBD molecule in solution. Theoretical data have been obtained within the PCM method. Optimization of the molecular structure in S1 has been carried out with TD-CAM-B3LYP/6-31G(d,p).

Table 2
interaction energy and optical absorption properties for the dimers associated to the various solvents. Calculations carried out at the TD-CAM-B3LYP/6-31G(d,p) level on the CAM-B3LYP/6-31G(d,p) optimized structure.

Solvent	Interaction	Interaction energy	Excitation energy		Oscillator strength	Transition dipole moment
		(kcal/mol)	(eV)	(nm)		(a.u.)
Ethyl acetate	1	−10.42	3.46	358	0.3568	2.05
	2	−6.36	3.52	353	0.3588	2.04
Tetrahydrofuran		−14.80	3.45	359	0.3491	2.03
Methanol	1	−7.08	3.55	349	0.4257	2.21
	2	−7.32	3.55	350	0.4243	2.21
	3	−6.37	3.53	351	0.3697	2.04
	4	Converged to the same structure of interaction 3				
	5	−13.52	3.40	365	0.3242	1.97
	6	−6.94	3.53	352	0.3730	2.08
	7	−4.84	3.62	343	0.3536	2.00
Acetonitrile		−8.64	3.45	359	0.3351	1.99
Dimethylformamide	1	−11.61	3.42	362	0.3303	1.98
	2	−5.37	3.54	350	0.4310	2.23
	3	Converged to the same structure of interaction 2				
	4	−7.12	3.51	353	0.3778	2.10
	5	Converged to the same structure of interaction 4				
	6	−13.05	3.43	362	0.3562	2.06

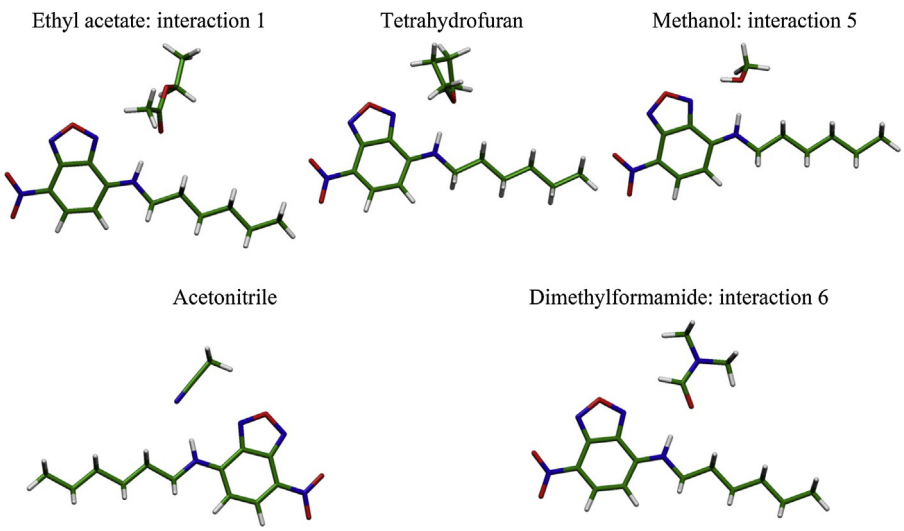

Figure 5. Most stable dimers found for each solvent. Dimer structure optimized at the CAM-B3LYP/6-31G(d,p) level.

solvent the excitation to S1 is dipole allowed, with an oscillator strength of about 0.36. The analysis of the orbitals demonstrates that the orbitals mainly involved in the ground to S1 transitions are very similar to those found for the molecule in vacuum, which are reported in Figure 2. The coefficients of the orbitals involved in the transition are reported in Table SI4 and the orbitals themselves are shown in Table SI5 of Supplementary data. For each solvent, the vertical excitation energy to the S1 state of the dimers ranges between 3.4 and 3.6 eV, to be compared with the value of 3.58 eV corresponding to the isolated molecule. It is worth noticing that for each solvent the most stable interaction is always that with the smallest excitation energy. Thus, the formation of a H-bond in the specific configuration where a H-bond between the NH group of the dye and an electronegative atom of the solvent is formed, results in a red-shift of the first excited state of the order of 0.15 eV.

In Figure 6, we compare the excitation energy of the most stable interaction model for each solvent (reported in Figure 5) with the experimental UV–vis absorption energy. As shown in Figure 6, our explicit interaction models reproduce very well the solvatochromic behavior of the NBD molecule. We notice that the agreement is only qualitative. In fact, we have already pointed out that the use of such simple models, consisting in the solute and just one solvent molecule, is clearly inadequate to reproduce

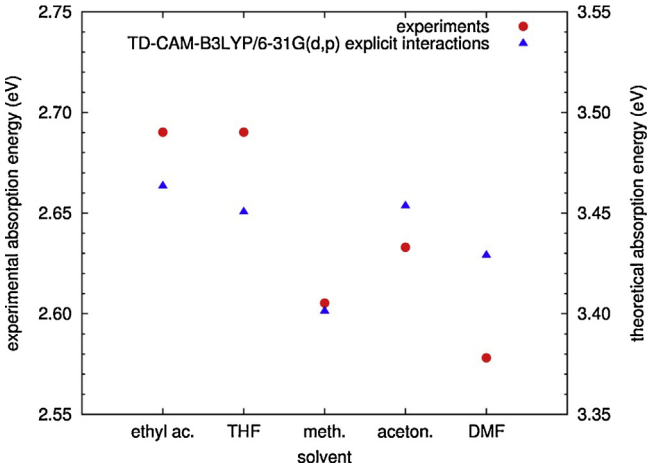

Figure 6. Comparison between experimental and theoretical absorption energies of the NBD molecule. Theoretical absorption energies are evaluated on the most stable dimer associated to each solvent in its electronic ground state geometry. Dimer optimizations and vertical excitation energies have been calculated respectively with the CAM-B3LYP/6-31G(d,p) and the TD-CAM-B3LYP/6-31G(d,p).

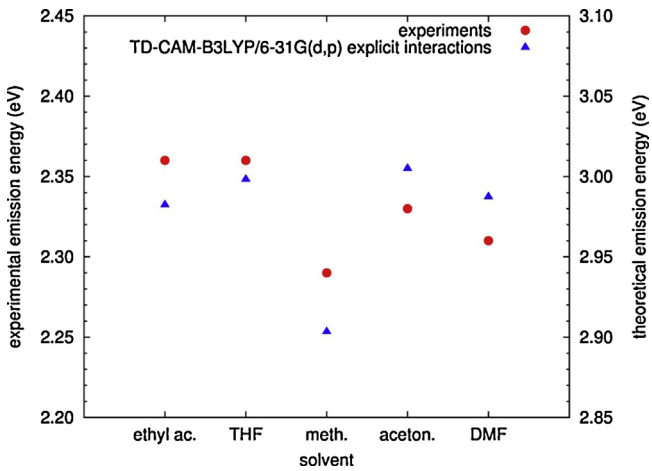

Figure 7. Comparison between experimental and theoretical emission energies of the NBD molecule. Theoretical emission energies are evaluated on the most stable dimer associated to each solvent in its electronic S1 geometry. Dimer optimizations and vertical excitation energies have been calculated at the TD-CAM-B3LYP/6-31G(d,p) level.

the experimental results in a quantitative way. However, our interaction models provide a reasonable overall picture of the role of the intermolecular interactions on the optical properties of the NBD dye. Moreover, they highlight the role of specific solute–solvent interactions, which in the present case involve the formation of a H-bond between the NH group of the NBD molecule and an electronegative atom of the solvent.

Particularly informative is the comparison between methanol and acetonitrile: in Figure 6 we observe that in spite of the increase in the dielectric constant of acetonitrile with respect to methanol, the experimental absorption energy increases. Indeed, our dimer model predicts that the excitation energies of the most stable dimers of methanol and acetonitrile are respectively 3.40 and 3.45 eV (see Table 2) thus reproducing the experimental trend. This is a further indication that, in the theoretical description, the inclusion of specific interactions is mandatory in order to reproduce the experimental data.

Since it is well known that TDDFT results depend heavily on the choice of the basis set and the functional, we tested other possible combinations. First of all, to rule out the effect of the basis set, we repeated the calculations for the CAM-B3LYP functional optimizing the structure of the most stable interaction models for each solvent with the triple-zeta 6-311G** basis set and we calculated the vertical excitation energy with the same basis set. The trend in the excitation energies for the most polar solvent is the same with both 6-31G** and 6-311G** basis set as can be seen in Table SI6 and Figure SI1. Thus, we can state that the basis set has only a minor effect on the predicted excitation energies.

Once the possible effects of the basis set are ruled out, we investigated the effects of different exchange-correlation functionals with the double zeta 6-31G** basis set. As already discussed in Section 2.2 in order to avoid the problem of the presence of fictitious charge-transfer state we excluded all pure functionals and hybrid functionals with a small contribution of the exact HF exchange (e.g. PBE0 that in general provides accurate excitation energies see for example Ref. [8]). The new functionals chosen are BHANDH, M06-2X and M06 HF, the latter being designed specifically to rule out fictitious charge transfer states. Once again the results qualitatively reproduce what already found for the CAM-B3LYP results (see Figures SI2–SI4 and Table SI6).

Given the above discussion on the choice of the functional, we calculated also the emission properties of the NBD molecule only at the TD-CAM-B3LYP/6-31G(d,p) level. Considering only the most stable interaction model of each solvent, we have optimized its structure in the S1 state. The resulting S1 to ground state energy differences in the S1 optimized structure are reported in Figure 7, compared with the experimental emission energy of the NBD dye in the various solvents. Also in this case, we find a very good agreement with the solvatochromic behavior of the NBD molecule. Again, the agreement is not quantitative mainly because of the simplicity of the models but the main features in the emission properties are reproduced satisfactorily well.

4. Conclusions

The experimental and theoretical results presented in this work, investigate the effects of the intermolecular interactions on the optical properties of organic dyes in solution. The *4-hexylamino-7-nitro-2,1,3-benzoxadiazoles* (NBD) molecule has been synthesized and its optical absorption and emission spectra have been measured in solvents of increasing polarity. The spectroscopic measurements have shown that the NBD molecule exhibits a non monotonic shift in solution both in absorption and in emission, which can be hardly associated to dye–solvent relative polarization effects. A thorough theoretical investigation has been carried out at the DFT and TD-DFT levels, by considering the properties of the NBD molecule in (i) the gas phase, (ii) embedded in a polarizable continuum (PCM) and (iii) considering explicit dye–solvent interactions. As expected, calculations with PCM are not able to reproduce the non monotonic solvatochromic behavior of both the absorption and the emission energy of the NBD molecule. On the contrary, molecular models constructed 'ad hoc' in order to take into account specific intermolecular interactions, are able to reproduce the experimental trends in both absorption and emission, demonstrating that the optical properties of the NBD molecule in solution are largely affected by explicit interactions, i.e. H-bonds with the solvent. In addition, our calculations highlight the specificity of the solvent–dye intermolecular interactions. In particular the formation of H-bonds between the NH group of the dye and an electronegative atom of the solvent seems to be favored with respect to other possible interactions.

Acknowledgement

This work has been supported by Fondazione CARIPLO (Project 2010-0528) 'Nanostrutture organiche ed ibride per la conversione dell'energia solare (SOLCO)'.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

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