

Theoretical study of the solvatochromism of a donor-acceptor bithiophene

Moisés Elías Domínguez · Marcos Caroli Rezende · Sebastián Márquez

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Abstract The solvation and the solvatochromic behavior of the 5-(methylthio)-5'-nitro-2,2'-bithiophene **1** in diethyl ether, dichloromethane, acetonitrile, methanol and formamide was theoretically investigated with an iterative molecular and quantum mechanics (QM/MM) approach. Calculated longest-wavelength solvatochromic absorption band of **1**, obtained as averages of statistically uncorrelated configurations, including the solute and explicit solvent molecules of the first and second solvation layer, were in excellent agreement with the experimental results.

Keywords Polarization effects · QM/MM simulation · Solvation · Solvatochromic shifts

Introduction

Push-pull solvatochromic molecules represent a particularly interesting group of organic dyes that shows outstanding transition energy shifts accompanying a change in the polarity of the medium [1, 2]. Their extreme sensitivity in the UV/Vis-IR region made them convenient probes to evaluate very different chemical environments by means of optical spectroscopy, e.g., pure solvents and solvent mixtures [3–6], micelles [6–9], dendrimers [10] and electrolyte solutions [11, 12].

Despite their wide use, the large number of compounds reported and recent theoretical studies [13–15], solvatochromism remains as a largely unknown phenomenon due to the extremely complex and dynamical solute-solvent interactions that take place in solution.

The theoretical investigation of solvent effects on the spectral behavior of solutions of organic compounds has been a subject of permanent interest, in particular, the use of molecular-mechanics simulation methods coupled with quantum mechanics calculations (QMM/MM) has proved very useful in the study of solvatochromic dyes in polar protic solvents, and of the solute-solvent interactions responsible for their behavior. Examples of such studies include investigations on the behavior of an ortho-betaine [16–18], of pyrimidine nucleobases [19], of p-nitroaniline [20], of a quinolinium betaine dye [21], of phenol blue [22], and of Brooker's merocyanine dye [23, 24].

Among various dyes, bithiophenes constitute a family of compounds that have attracted the interest of various groups because of their exceptional non-linear optical (NLO) properties and their potential application in modern photonic technology [25–28]. Conspicuous members of this family include compounds **1** and **2**, described by Effenberger et al. as exhibiting a positive solvatochromic behavior. Because of its good solubility in a wide range of solvents, and its sensitivity to the medium polarizability, compound **2** was suggested as the basis of a dipolarity-polarisability scale that correlated well with Kamlet-Taft π^* scale [29]. Different groups have tried to reproduce its solvatochromic behavior in various solvents, by employing different theoretical protocols [30–32] (Fig. 1).

The first attempts employed a continuum approach, and a CNDO/S-CI method of calculation [30]. A similar approach with Tomasi PCM model and a B3LYP/6-31G** method of calculations yielded results that *nicely reproduce the experimental trends* [31]. This optimistic view depended on the experimental data that were selected: if the reported

M. E. Domínguez (✉)
Institut für Chemie und Biochemie, Freie Universität Berlin,
Takustrasse 3,
14195 Berlin, Germany
e-mail: moises@zedat.fu-berlin.de

M. E. Domínguez · M. C. Rezende · S. Márquez
Facultad de Química y Biología, Universidad de Santiago,
Av. B.O'Higgins 3363,
Santiago, Chile

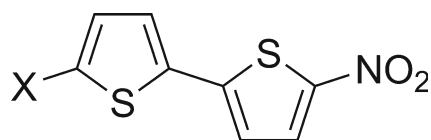


Fig. 1 Donor-acceptor bithiophenes 1 and 2. Conspicuous members of the family of positive solvatochromic dyes

theoretical transition energies are converted to λ_{max} values, the results agreed well in non-polar CCl_4 , but departed considerably from the experimental values in more polar media like dichloromethane (504 nm, exp 537 nm [29]) and dimethylsulfoxide (512 nm, exp 564 nm [29]).

A detailed comparison of three different approaches, the polarized continuum (TD-PCM) model, an explicit solvent model, and a combined discrete/continuum strategy, was applied to the solvatochromic behavior of 2 in five solvents of widely different polarities [32]. The results showed that the TD-PCM model yielded better λ_{max} values than the explicit solvent model, which also employed a TD method of calculation. However, the PCM model was unable to reproduce the positive solvatochromism of 2 in more polar media than dichloromethane. The discrete/continuum strategy, employing explicit solvent molecules and a TD-PCM approach yielded the best results. However, if the reported theoretical transition energies are converted to λ_{max} values, the average deviation between the experimental and theoretical results was a tolerable 27 nm, spanning values that were quite good in non-polar CCl_4 (4 nm), but that increased consistently with the solvent polarity to a large deviation of 47 nm in formamide. The theoretical excitation energies were obtained as averages from 50 snapshots of a 1-ns MD simulation, sampled at regular time intervals but no attempts were made to verify the degree of correlation among these snapshots, which is important statistical information for the validation of the method.

Another limitation of the method originated from the cost of the employed TD-DFT B3LYP/6-3G** method for the calculation of the excitation energies of the supermolecules or clusters formed by solute 2 and some of its solvating molecules. Only the small number of molecules comprising the immediate layer around the NO_2 group were considered, and their number was limited to 13 solvent molecules because of computational costs. This limitation had to be adopted in spite of the observation that increasing the number of solvent molecules in the clusters led to an improvement of the calculated excitation energies [32].

In the present communication we decided to apply a molecular mechanics/quantum mechanics approach capable of overcoming the above limitations to study the solvation and

the spectral behavior of the 5-(methylthio)-5'-nitro-2,2'-bithiophene 1 in a variety of solvents and a wide range of solvents. By the correct reproduction of the solvatochromic trend of 1, a more realistic view of the solvation sphere around this dye and the specific solute-solvent interactions were established.

In this approach, the structure of the polarized molecule in solution was obtained by an iterative procedure, which employed cycles of *ca.* 10^7 Monte-Carlo steps. At the end of each cycle, an averaged distribution of solvent molecules was converted to point charges and the resulting electric field generated new charges on the solute, for a new MC cycle. Termination of the iterative procedure occurred when the solute dipole moment attained a constant value, in an indication of an electrostatic equilibrium with the medium.

A statistical treatment of each MC cycle selected, from all acquired frames, a set of uncorrelated configurations, which were employed for obtaining the distribution functions of solvent molecules around the solute and for the calculation of transition energies involving clusters with a variable number of solvent molecules. The number of uncorrelated frames was larger, and their average statistically more meaningful than other sets of snapshots or frames employed in other dynamics with unknown degrees of correlation. The use of the much less costly semiempirical ZINDO/S method, specifically parameterized for transition energy calculations, allowed the inclusion of a larger number of solvent molecules in each cluster. Solvent distribution functions could be obtained for a given atom of the solute, as a spherical solvent distribution, or for the whole molecule, taking into account its specific geometry, thus yielding more complete pictures of the solute solvating shells.

This QM/MM protocol had been applied successfully before, in the study of the spectra of solvatochromic ortho-betaine in water [16, 17], of pyrimidine in water and CCl_4 [33] and of acrolein in water [34].

Compound 1 was chosen because, unlike its analogue 2, its solvatochromic behavior has not been studied yet. In spite of exhibiting a narrower range of solvatochromic shifts than 1, its behavior is qualitatively the same. It shows positive solvatochromism, like 2, and its CT excitation energy varies, similarly to 2, with the solvent dipolarity-polarizability, correlating with Kamlet-Taft π^* scale [29].

Following the protocol adopted for the study of 2 [32], our choice of solvents included two non-protic non-polar solvents like diethyl ether ($\epsilon=4.34$) and dichloromethane ($\epsilon=8.93$), a non-protic, polar solvent like acetonitrile ($\epsilon=36.64$), a protic, polar solvent like methanol ($\epsilon=32.63$) and a non-protic, highly polar solvent like formamide ($\epsilon=108.94$).

Simulation methods

All quantum mechanics calculations were carried out with the Gaussian 03 package [35]. Monte Carlo (MC) simulations in

Table 1 Calculated dipole moments of 1 in all studied solvents, in the gas phase, after initial polarization by the PCM option, and after final convergence

Solvent (ϵ)	Dipole moment μ (Debye)			Number of configurations ^a
	Gas phase	PCM	Converged	
Diethyl ether (4.34)	7.92	9.51	8.67	143
Dichloromethane (8.93)	7.92	10.04	10.36	500
Acetonitrile (36.64)	7.92	10.45	10.89	125
Methanol (32.63)	7.92	10.47	10.87	111
Formamide (108.94)	7.92	10.52	11.37	100

^a Number of configurations with less than 10 % of correlation employed for averaging the solvent distribution in each cycle

diethyl ether, dichloromethane, acetonitrile, methanol and formamide were carried out using the Metropolis sampling in the canonical NVT ensemble at 298 K in cubic boxes ($L=30$ Å) with periodic boundary conditions (PBC). The resulting systems consisted of one molecule of 1 and 156 molecules of diethyl ether ($d=0.713$ g/cm³), 255 dichloromethane ($d=1.33$ g/cm³), 312 acetonitrile ($d=0.777$ g/cm³), 402 methanol ($d=0.792$ g/cm³) and 408 formamide ($d=1.133$ g/cm³) molecules, respectively. The solute-solvent interaction was represented by a Lennard-Jones plus a Coulomb pair-wise potential for each interacting site i (ϵ_i , σ_i and q_i). The LJ parameters were obtained from the literature for diethyl ether [36], dichloromethane [37], acetonitrile [38], methanol [39] and formamide [40].

The LJ parameters for solute 1 were obtained by combining the potentials of methanethiol, of the cyclopentadienyl and the nitro group [41].

The simulations were performed with DICE [42]. An initial thermalization period of $6 \times 10 \times N$ steps was adopted, where N was the number of solvent molecules in the cubic box. This was followed by an averaging stage of $1 \times 10^5 \times N$ steps. To take into account the polarization of the solute by the solvent, an iterative procedure was followed. The structure of dye 1 was optimized with the B3LYP/6-31G** method in the gas phase. It was then initially polarized with the PCM option in the appropriate solvent, with atomic charges obtained with CHELPG [43].

After the Monte Carlo acquisition stage, a set of configurations with less than 10 % of statistical correlation were selected, using the interval of statistical correlation from the auto-correlation function of the energy [44–46].

Employing the ASEC (average solvent electrostatic potential) [47] approach of DICE, 65 % of solvent molecules of each of the uncorrelated configurations were converted to point charges and the resulting electrostatic potentials averaged to polarize the solute and generate a new set of charges for a new MC cycle. Termination of this iterative procedure was indicated by convergence in the values of the calculated dipole moment of the dye.

Minimum distance distribution functions (MDDF) were obtained as an option implemented in DICE [48].

For each uncorrelated configuration selected in an MC cycle, the corresponding longest-wavelength transition

energy of the dye was calculated with the INDO/CIS method [49] applied to the supermolecule formed by the solute and a certain number of solvent molecules. The resulting set of energy values was then averaged to give the calculated transition energy of the dye solvated by that number of solvent molecules.

Results and discussion

Polarization of the dye in each medium

The same protocol was applied to all solvents. The optimized structure of the dye in the gas phase was initially polarized by the B3LYP/6-31G**/PCM method, employing the permittivity value of the corresponding solvent. The resulting structure underwent a first MC cycle from which a number of uncorrelated configurations were selected to yield an average solvent distribution. The solvent molecules were then converted to point charges, generating a first average solvent electrostatic potential (ASEC), which polarized the solute, generating new charges on it and a new dipole moment. These cycles were repeated until the calculated dipole moment of the solute converged to a constant value. In this way, calculations required four iterations for diethyl ether, six for dichloromethane, nine for acetonitrile, eight for methanol and five for formamide.

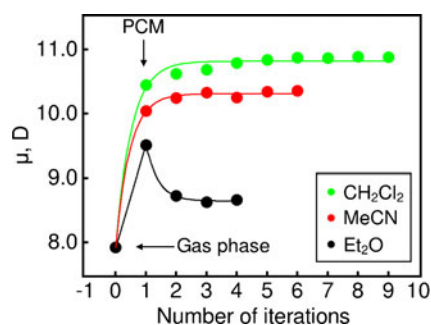


Fig. 2 Variation with the sequential MC iterative process of the calculated dipole moment of dye 1 in diethyl ether, dichloromethane and acetonitrile. Iteration values 0 and 1 correspond to calculations in the gas phase and with the PCM method, respectively

Fig. 3 Distribution of acetonitrile solvent molecules around solute 1 obtained with (a) Radial distribution function (RDF) and (b) Minimum-distance distribution function (MDDF)

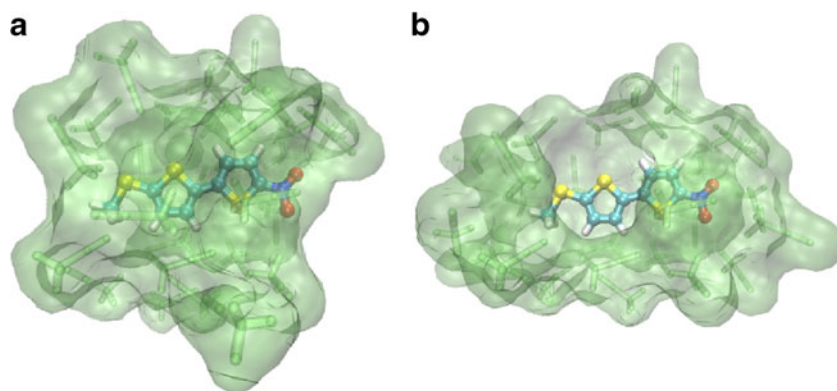


Table 1 illustrates this converging process, with their calculated dipole moments in the gas phase, after the initial polarization by the PCM method, and after final convergence.

The importance of the iterative polarization process is clearly illustrated in Fig. 2, particularly when the solvent was diethyl ether. For dichloromethane, methanol, acetonitrile and formamide, a simple PCM calculation was enough to reach almost complete polarization of 1, with values for the final dipole moments that were 30–40 % larger than those calculated in the gas phase. In diethyl ether, however, the initial polarization by the PCM method yielded an overestimated dipole moment of 9.51 D that was reduced by *ca.* 10 % to the smaller value of 8.67 D by the iterative procedure.

Solvation of dye 1

The final solvent distribution around the solutes could be described with the aid of radial distribution functions (RDF). Spherical radial distribution functions are useful in the description of the environment around a particular atom. When the whole molecule is considered, an RDF around the center of mass of the solute yields a spherical distribution that is suitable for small molecules or for those with a spherical shape, but is not convenient for elongated molecules like 1. A better description of the solvating layers is provided by the minimum-distance distribution function

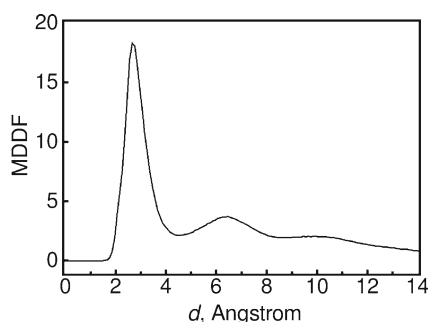


Fig. 4 Minimum-distance distribution functions for 1 in acetonitrile

(MDDF) [48] that yields a homogenous solvent distribution around the nearest atom of the solute. A representation of these two distinct distributions is shown in Fig. 3, for the solvation layer of 1 in acetonitrile. It is seen that the RDF around the center of mass exaggerates the number of solvent molecules in the *polar* regions of the solvating sphere, a deformation that is corrected by the minimum-distance distribution.

The corresponding MDDF of solvent molecules comprising the solvation layers of 1 in acetonitrile is shown in the Fig. 4. The first solvation layer, centered at 2.63 Å from the center of mass of 1, comprised 27 molecules. Addition of a second solvation layer, at 6.35 Å, increased this number to 90 acetonitrile molecules.

A similar MDDF was obtained for diethyl ether, with a first solvation shell comprising 19 molecules at 2.53 Å, and a second layer at 6.23 Å, increasing this number to 56 solvent molecules.

A different pattern was obtained for the solution of 1 in dichloromethane. The corresponding graph of its MDDF is shown in Fig. 5. The first solvation layer, centered at 2.84 Å and comprising 24 molecules, exhibited a small shoulder at *ca.* 2.5 Å integrating to *ca.* 2.2 molecules. This points to an anisotropic solvent distribution around the molecule, which is confirmed by the radial distribution function of the solvent molecules around the nitro substituent of 1 (insert of

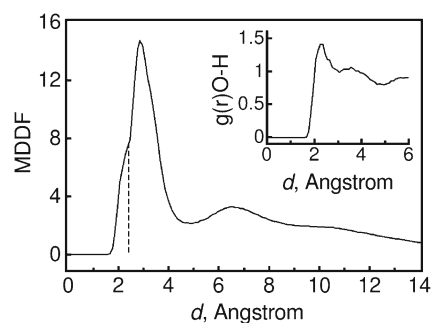


Fig. 5 Minimum-distance distribution function of dichloromethane molecules that solvate 1. The insert shows the radial distribution of CH_2Cl_2 molecules around the nitro substituent of 1, at a variable NO–HC distance from the NO_2 oxygen atom

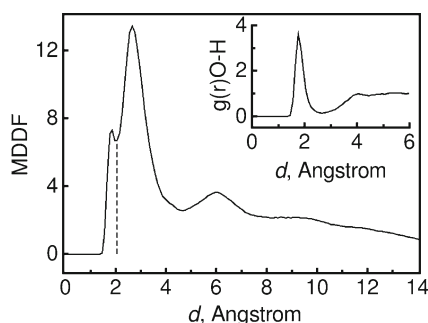


Fig. 6 Minimum-distance distribution function of methanol molecules that solvate 1. The insert shows the radial distribution of methanol molecules around the nitro substituent of 1, at a variable NO–HOMe distance from the NO₂ oxygen atom

Fig. 5). Nearly 2.1 dichloromethane molecules occupy the first spherical layer at 2.4 Å from the NO₂ group.

This is an interesting aspect of the solvation of this dye in pure solvents. Solvent distribution is isotropic in diethyl ether and acetonitrile, but not in dichloromethane, where an incipient hydrogen-bond between the NO₂ substituent and the CH₂Cl₂ molecules is established locally.

An anisotropic distribution of solvent molecules should be expected in more polar, hydrogen-bond donor solvents. Methanol and formamide are particularly interesting systems, because of the possible formation of hydrogen bonds with the oxygen atoms of the NO₂ group. In fact, the first solvation layer of 1 in formamide, as revealed by an MDDF graph (not shown), was not symmetric. As observed for dichloromethane, a shoulder at 2.37 Å integrating for one formamide molecule, pointed to the existence of a hydrogen-bond interaction NO⋯H–NH–CHO between the nitro group and the solvent.

Figure 6, which depicts the MDDF of methanol molecules that solvate 1, is probably the best example of this anisotropic solvation pattern. A particularly well-defined peak centered at 1.79 Å and comprising nearly two methanol molecules is an indication of an anisotropic solvation. This is confirmed by the radial distribution of methanol molecules around one of the NO₂ oxygen atoms, with the

Table 2 Number of solvating molecules and of uncorrelated configurations employed in the QM/MM calculations of the energies of the S₀ → S₁ transition of 1 in all solvents

Solvent	Solvating molecules		Number of averaged configurations
	First layer	First + second layer	
Diethyl ether	19	56	143
Dichloromethane	24	80	500
Acetonitrile	27	90	125
Methanol	26	91	111
Formamide	30	78	100

rather sharp peak shown in the insert of Fig. 6, pointing to a 2-Å hydrogen-bond between the NO₂ oxygen atom and the methanol molecules.

Solvatochromism of 1

Validation of the solvation patterns of the dye in the five studied solvents was obtained by comparing the estimated solvatochromic bands derived from these simulations with experimental data.

The experimental λ_{max} values for the charge-transfer band of dye 1 were obtained from the corresponding excitation energies λ_{max}, according to λ_{max} (nm)=10⁶ / ν_{max}(cm⁻¹). These excitation energies are reported to correlate linearly with Kamlet-Taft π* parameter, according to Eq. 1

$$\nu_{\max} = 25420 - 2200 \pi^*, \quad (1)$$

where π* = 0.27 (diethyl ether), 0.82 (dichloromethane), 0.75 (acetonitrile), methanol (0.60) and 1.12 (formamide) [29].

For the calculation of the λ_{max} value corresponding to the S₀ → S₁ transition in a given solvent, λ_{max} values were calculated for all uncorrelated configurations, after convergence was achieved, and the obtained values averaged over all configurations. These calculations were performed on supermolecules which included the solute and all solvent molecules comprising one or two solvation layers, as determined by the MDDF plots in each solvent. The number of solvent molecules in the solvation layers, and the number of uncorrelated configurations that were averaged to yield the calculated λ_{max} values are given in Tables 1 and 2.

A more detailed picture of the distribution of calculated λ_{max} values of all uncorrelated configurations may be obtained from histograms, like those depicted in Fig. 7. It reproduces the distribution of the calculated λ_{max} values for all configurations in diethyl ether, acetonitrile and formamide, when solvent molecules from the two solvation layers

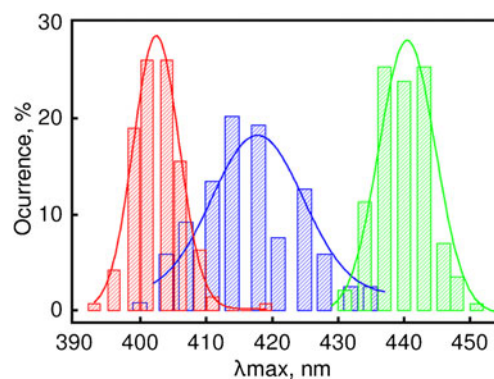


Fig. 7 Distribution of the calculated λ_{max} values in diethyl ether (red), acetonitrile (blue) and formamide (green) for all statistically uncorrelated configurations of 1. Calculations were performed with clusters that incorporated the two solvation layers of the solutes, with the number of solvent molecules given in Table 2

Table 3 Theoretical and experimental λ_{\max} values for the longest-wavelength band of **1** in various media

Solvating environment	Solvent				
	(C ₂ H ₅) ₂ O	CH ₂ Cl ₂	CH ₃ CN	CH ₃ OH	CHONH ₂
Gas-phase INDO/CIS	396	398	400	400	400
Gas-phase TD-DFT ^a	430	430	431	431	431
PCM TD-DFT ^a	477	477	478	477	478
INDO/CIS with explicit solvent molecules ^b	399	414	406	409	423
INDO/CIS with explicit solvent molecules ^c	401	417	419	416	437
Experimental value ^d	403	423	421	415	436

^a With the B3LYP/6-31G** method, ^b Of the first solvation layer; ^c of the first and second solvation layers; ^d values from reference [29]

were incorporated into the calculations. Similar histograms were obtained for the dichloromethane and methanol solutions.

Figure 7 adequately reproduces the positive solvatochromic behavior of dye **1** in the studied solvents.

In Table 3 the experimental λ_{\max} values are compared with theoretical values employing different methods of calculation. They include a gas-phase calculation, employing the semi-empirical INDO/CIS method, and two time-dependent density-functional theory (TD-DFT // B3LYP/6-31G**) calculations, in the gas-phase and assuming some correction for the solvent, employing a continuum (PCM) method. These theoretical values are compared with two results from the present QM/MM protocol, which explicitly took into account the solvent molecules that comprised one or two solvation layers of the solute.

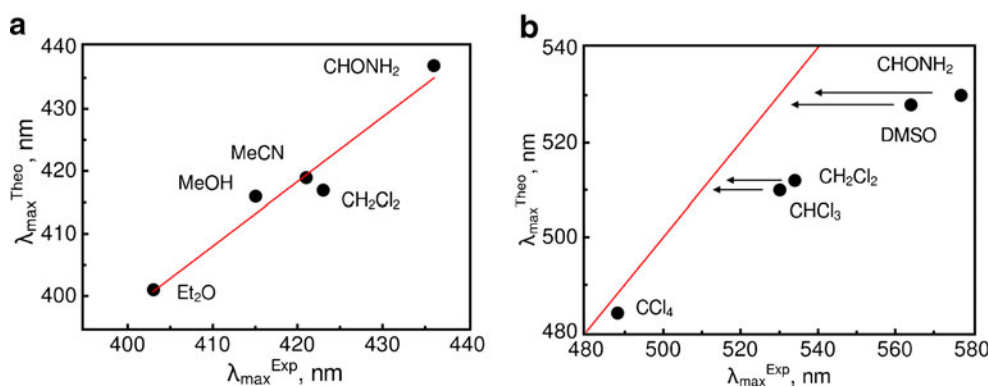
As can be seen in the table, gas-phase calculations employing the semi-empirical INDO/CIS method yielded λ_{\max} values were smaller than the ones obtained with the TD-DFT method. This situation is reversed in a polar media like formamide, where the DFT-DFT method yields a better result than the INDO/CIS.

A second observation from Table 3 is the failure of the PCM TD-DFT approach to yield reasonable λ_{\max} values in all solvents. As observed by Meng and Ma [32] for the simulations of the analogue **2** in the same

media, the PCM approach is unable, even qualitatively, to reproduce the positive solvatochromism of these dyes, yielding λ_{\max} values that are essentially independent of the solvent.

The iterative QM/MM results proved superior in comparison with the preceding methods. Explicit calculations incorporating solvent molecules of one solvation layer represented a great improvement over gas-phase or continuum calculations. In addition, they adequately reproduced the solvatochromic behavior of the dyes in the various solvents. When solvent molecules of a second solvation layer were included in the calculations, there was an excellent agreement between theoretical results and experimental data for the whole range of solvent polarities. This is clearly illustrated in Fig. 8, where the theoretical λ_{\max} values reported for **2** [32] and those calculated for **1** in the present work are compared with straight lines that correspond to the ideal reproduction of the experimental values. Unlike the results of the combined discrete/continuum strategy employed for compound **3**, where deviations between calculated and experimental λ_{\max} values increased consistently with the medium polarity, attaining a not negligible deviation of 8 % in formamide (Fig. 8b), the results of the present approach in the same media showed deviations not larger than 1.5 %, irrespective of the medium polarity (Fig. 8a).

Fig. 8 Correlations between the calculated and the experimental longest-wavelength λ_{\max} values of **1** and **2** in five solvents of different polarity. The straight lines correspond to the ideal reproduction of the experimental values. Data for (a) from this work, data for (b) from reference [32]



Conclusions

In the present communication, a sequential QM/MM methodology was employed to study the solvation and the spectral behavior of a solvatochromic bithiophene in five protic or non-protic solvents (diethyl ether, dichloromethane, acetonitrile, methanol and formamide), with a wide range of solvent polarities.

An interesting result of the present study was the detailed description of the cybotactic region surrounding bithiophene 1 in all solvents, as obtained from the analysis of the minimum-distance distribution function (MDDF) of its solvating molecules. Even in a pure solvent, solvating molecules may concentrate in a particular region, surrounding an atom or part of a molecule, in an anisotropic distribution. Such description is impossible to achieve by continuum models or by the traditional spherical radial distribution function (RDF) analysis.

The sequential QM/MM methodology was capable of reproducing the positive solvatochromic behavior of dye 1 in the wide range of employed solvents. The results showed the importance of incorporating a large number of explicit solvent molecules to calculate λ_{\max} values that are closer to the experimental values. The excellent agreement between the experimental data and the theoretical results validated the protocol, with calculated λ_{\max} values that deviated on the average only 2–3 nm from the experimental values.

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