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Solvent effect on the photophysical properties of 4-phenoxy-*N*-methyl-1,8-naphthalimide

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Abstract

The photophysical properties of *N*-methyl-1,8-naphthalimide (NI) and 4-phenoxy-*N*-methyl-1,8-naphthalimide (4-PNI) are studied by steady-state and time-resolved emission measurements. Both absorption and fluorescence spectra are red-shifted when the electron donor phenoxy group (–OPh) is introduced at the C-4 position. Compared to NI, the spectral shift in acetonitrile is 27 and 42 nm for the absorption and fluorescence, respectively. The 4-PNI shows high fluorescence emission in non-polar aprotic solvents that can be ascribed to stabilization of the S_1 state. The emission intensity of the 4-PNI decreases by addition of water to dioxane solution, and the fluorescence quenching occurs by combination of dynamic and static contribution ascribed to specific solute–solvent interaction.

Keywords: Naphthalimide; Solvent effects; Photophysical properties

1. Introduction

Naphthalimides comprise a class of chromophore whose electronic absorption and emission depend on the properties of the surrounding medium. In general, non-substituted 1,8-naphthalimides present low fluorescence quantum yield. These trends have been explained by the fast intersystem crossing from the excited π–π^* singlet state to a close-lying n–π^* triplet state, a mechanism which is particularly efficient in the case of the 1,8-naphthalimide [1]. The photophysical behavior of 1,8-naphthalimide derivatives is a function of C-4 substitution. Substitution of electron-donating groups usually increases the fluorescence emission, particularly when alkoxy-groups at the C-4 position are used. These alkoxy derivatives constitute a very important class of compounds with intensive fluorescence and very good photo-stability. Thus, they have a wide range of applications as organic dyes and luminophores [2], probes for analytical purposes [3], fluorophore for optical chemosensing [4] and liquid crystal displays [2]. Bojinov and Grabchev have used 4-alkoxy-1,8-naphthalimide derivatives as fluorophores for synthetic blue fluorescent polymers [5]. The spectroscopic properties and molecular structure of naphthalimide derivatives have been investigated and described in several publications [6–8].

The ability of 1,8-naphthalimide derivatives to be very sensitive to their surrounding render them as solvatochromic probes where the effects of solvent polarity on the electronic emission and absorption spectra are studied [9].

Since the literature has not yet reported any systematic study of aryl substitution at the C-4 position of 1-8-naphthalimide, its seems to be opportune to detail the photophysics of the 4-phenoxy-*N*-methyl-1,8-naphthalimide (4-PNI) compound, which was synthesized according the Scheme 1. The photophysical properties of 4-PNI in different solvents and in dioxane–water binary mixtures, and the role of probe-solvent interaction, which modulates the intramolecular charge transfer process of 4-PNI is investigated in this contribution.

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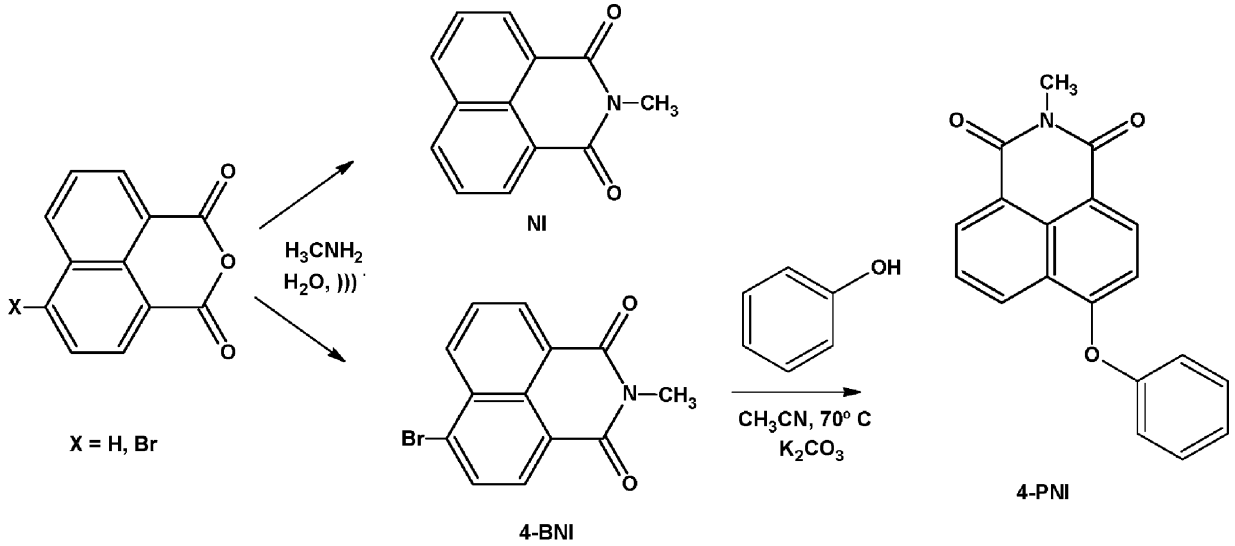

Scheme 1.

2. Experimental details

2.1. Materials

All 1,8-naphthalic anhydrides were purchased from Aldrich. The methylamine 40% aqueous solution (Fluka) was used without further purification. Water used in the experiments was doubly distilled from Millipore-Milli-Q_{plus} system. Other solvents were of spectroscopic grade and were used without further purification.

2.2. Methods

The UV–vis absorption was recorded in a VARIAN-CARY 5 G spectrophotometer and fluorescence spectra were obtained in a HITACHI F-4500. All measurements were carried out at 25 °C. The fluorescence quantum yields (ϕ_f) were calculated relative to the area of the corrected emission spectrum of quinine sulphate in 1N H_2SO_4 ($\phi_f = 0.546$) [10]. Fluorescence decays were measured by a single-photon timing technique using a CD-900 Edinburgh spectrometer operating with a hydrogen-filled nanosecond flash lamp (FWHM = 1.5 ns) at 30 kHz pulse frequency and with an excitation wavelength of 360 nm. The decays were analyzed by a nonlinear least squares iterative routine based on the Marquardt algorithm using Edinburgh software for data analysis.

Solution concentrations in absorption, fluorescence, lifetimes and quantum efficiencies measurements were fixed at 1.0×10^{-5} mol L^{-1}, to avoid aggregation or reabsorption effects.

Melting points were determined by differential scanning calorimetry (DSC) using a Shimadzu TA-50. The samples were kept under a nitrogen flow rate of 20 mL min^{-1} during the measurement. The heating rate was of 10 °C/min. ^1H NMR spectra were recorded on a BRUKER AC-200 in $CDCl_3$ and CD_2Cl_2. Infrared (IR) spectra were recorded on a BOMEM-MB 102-FT-IR spectrometer, employing KBr windows. Capillary GC analyses were performed on a HP-5890 coupled to an MSD-5970 mass selective detector.

2.3. Synthesis and characterization

2.3.1. Synthesis of N-methyl-1,8-naphthalimide (NI)

N-methyl-1,8-naphthalimide was synthesized from 1,8-naphthalic anhydride and methylamine by a sonochemistry route according to a method described recently [11].

2.3.2. Synthesis of 4-bromo-N-methyl-1,8-naphthalimide (4-BNI)

4-Bromo-*N*-methyl-1,8-naphthalimide was obtained from the mixture of 4-bromo-1,8-naphthalic anhydride 98% (1 mmol) with methylamine (10 mmol) in water (25 mL). The solution was sonicated in an ultrasonic cleaner bath (THORNTON, 150 W/25 kHz output) in a 40 mm diameter cylindrical reaction vessel for 2 h. After the reaction, the mixture was poured into diluted HCl, the product was filtered off, washed twice with 25 mL water and dried under vacuum at 60 °C. Yield: 92%; yellow bright crystals; m.p. 182 °C (literature [12] 185–186 °C); FT-IR (KBr, cm^{-1}): 3088, 2947, 1699, 1664, 1592, 1569, 1402, 1286, 1032, 778. ^1H NMR ($CDCl_3$, 200 MHz) δ 3.50 (s, 3H, CH_3), 7.77 (dd, $J = 8.4$ Hz, $J = 7.3$ Hz, 1H, Ar), 7.97 (d, $J = 7.6$ Hz, 1H, Ar), 8.34 (d, $J = 7.6$ Hz, 1H, Ar), 8.49 (dd, $J = 8.4$ Hz, $J = 1.2$ Hz, 1H, Ar), 8.58 (dd, $J = 8.4$ Hz, $J = 1.2$ Hz, 1H, Ar); MS (EI, *m/z*) 289 (M^+, 100); 291 ($M^+ + 2$, 96).

2.3.3. Synthesis of 4-phenoxy-N-methyl-1,8-naphthalimide (4-PNI)

A mixture of 4-BNI (1 mmol), phenol (2 mmol) and K_2CO_3 (2 mmol) in acetonitrile (25 mL) was stirred and heated at 70 °C for 6 h. After cooling, the solvent was evaporated and the product was extracted with a 0.5 M solution of cloroform/NaOH to give a bright yellow–green powder. Yield: 89%; m.p. = 181 °C; FT-IR (KBr, cm^{-1}): 3057, 2935, 1694, 1657, 1490, 1399, 1356, 1251, 1204, 776. ^1H NMR (CD_2Cl_2, 200 MHz) δ 3.50

(s, 3H, CH_3), 6.92 (d, $J = 8.2$ Hz, 1H, Ar), 7.20–7.22 (m, 2H, Ar), 7.35–7.32 (m, 1H, Ar), 7.54–7.46 (m, 2H, Ar), 7.80 (dd, $J = 8.2$ Hz, $J = 7.3$ Hz, 1H, Ar), 8.43 (d, $J = 8.2$ Hz, 1H, Ar), 8.63 (dd, $J = 7.3$ Hz, $J = 1.2$ Hz, 1H, Ar), 8.72 (dd, $J = 7.3$ Hz, $J = 1.2$ Hz, 1H, Ar); MS (EI, *m/z*): 303 (M^+, 100), 245, 77, 51.

3. Results and discussion

3.1. Steady-state emission measurements

The fluorescence of 4-PNI (see Fig. 1) depends on the nature of the solvent. Basically its emission spectrum is characterized by a broad band without clear vibrational structure (except for hexane), which seems to be a mirror image of the corresponding absorption band (not shown) as can bee seen from the plot in Fig. 1. As can be seen, the Stokes shift increases with solvent polarity.

In order to highlight the effect of the phenoxy substitution at the C-4 position of the 1,8 naphthalimide, the photophysical characteristics of the NI and 4-PNI compounds were recorded in organic solvents of different polarity. The absorption and fluorescence spectral properties such as absorption (λ_a) and fluorescence (λ_f) maxima, extinction coefficient (ε), Stokes shift ($\nu_a - \nu_f$) and fluorescence quantum yield (ϕ_f) of the compounds, are reported in Table 1. The change in solvent nature produces a small effect on the absorption maximum of 4-PNI, which indicates no evidence for a strong solvent effect in the ground state as found for other 1,8-naphthalimide derivatives [13]. The high extinction coefficients (ε from 11,000 to 13,700) shows that the electronic transition to the first excited state should be of π–π^* character, like the behavior found in 2,3-naphthalimide [14].

The absorption and emission maxima of 4-PNI, when compared to the unsubstituted NI, is red-shifted in ca. 27 and 42 nm (Fig. 2), respectively, thus indicating that the lowest singlet excited state of the 4-PNI compounds has a charge transfer (CT) character. The charge transfer process is possible due to the electron-donating ability of the phenoxy group at C-4 position. The same argument was used to explain the photophysics of 4-methoxy-1,8-naphthalimide [15].

Table 1
Photophysical properties of 4-PNI

Solvents	λ_a (nm)	λ_f (nm)	$\nu_a - \nu_f$ (cm^{-1})	ϕ_f	ε (mol^{-1} L cm^{-1})
Hexane	354	404.8	3545.0	0.53	13573
Dioxane	357	417.2	3972.7	0.92	12052
DMSO	361	442.4	4026.6	0.05	12004
Chloroform	364	423.4	3854.2	0.90	13698
Methanol	361	442.0	5076.4	0.05	11957
Ethanol	361	434.6	4691.2	0.12	11686
Acetonitrile	358	428.2	4579.4	0.29	12897
DMA	360	430.6	4554.4	0.27	11511
Acetone	357	422.8	4359.4	0.44	11303
Octanol	361	426.6	4259.7	0.67	11904
Toluene	357	415.8	3961.2	0.72	13385
Benzene	358	416.4	3917.6	0.70	13323
THF	358	419.0	4066.6	0.85	11946
Ethyl acetate	356	417.6	4143.5	0.82	13273
Ether	356	414.2	3947.0	0.96	13683
n-Pentane	354	405.6	3593.7	0.97	13687
Ethyleglycol	366	447.6	4981.0	0.07	12226
2-Propanol	361	431.2	4509.7	0.35	13043

The Stokes shift for 4-PNI is 3500 cm^{-1} in hexane and increases to 5000 cm^{-1} in MeOH. These results are similar to those found for alkoxy-substituted 1,8-naphthalimides derivatives. In polar solvent the higher Stokes shift is due to major stabilization of S_1 state with contribution of an intramolecular charge transfer effect [16]. Similar effects were observed for 4-methoxy-*N*-methyl-1,8-naphthalimide, which also has an electron-donating moiety [17].

The response of 4-PNI to solvent polarity can be analyzed in terms of the difference in the dipole moments in the ground and excited states. This can be estimated from a Lippert–Mataga plot [18]. The difference between the maximum absorption and emission wavelengths, expressed in wavenumbers ($\nu_a - \nu_f$), is correlated with the solvent polarity parameter (Δf) by the fol-

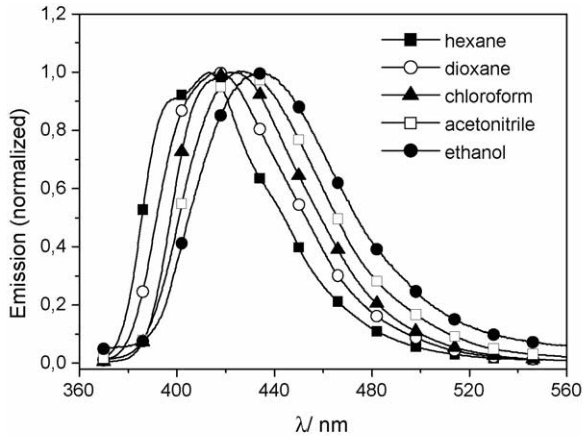

Fig. 1. Normalized fluorescence emission spectra of 4-PNI in different solvents: (■) hexane; (◯) dioxane; (▲) chloroform; (□) acetonitrile; (●) ethanol.

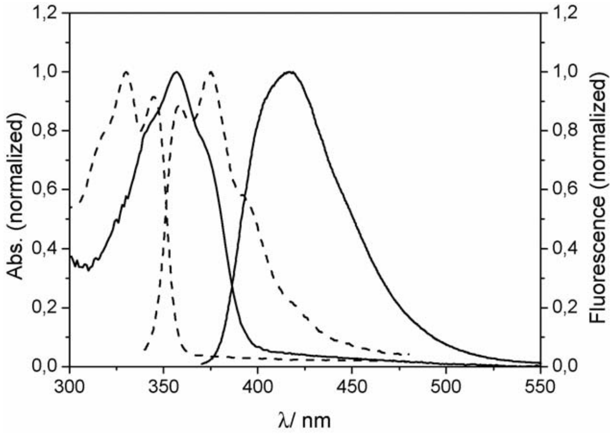

Fig. 2. Normalized absorption and fluorescence spectra of NI and 4-PNI (λ_{ex} = 330–360 nm, respectively) in dioxane 1.0×10^{-5} mol L^{-1}; (- - -) NI and (—) 4-PNI.

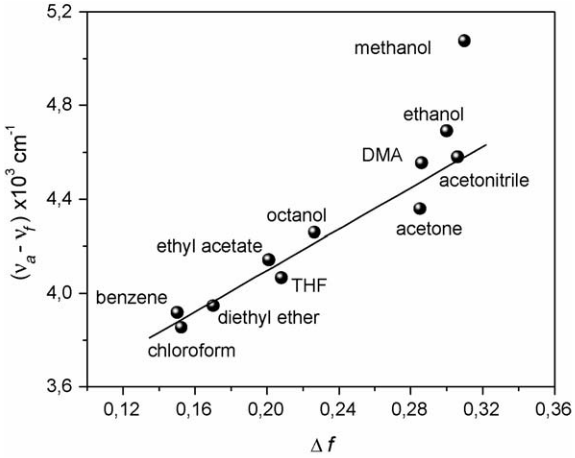

Fig. 3. Plot of the Stokes shift vs. the solvent polarity parameter according to Eq. (1). The line corresponds to the best linear fit ($r = 0.9736$) to the data, excluding the values obtained for ethanol and methanol.

lowing equation:

$$\Delta\nu = (\nu_a - \nu_f) = \frac{2\Delta f}{hca_0^3}\Delta\mu^2 \qquad (1)$$

where $\Delta\mu$ represent the variation between the dipole moments of the excited and ground states, c is the velocity of light, h is Plank's constant, and a_0 is the radius of the Onsager cavity around the fluorophore. The solvent polarity parameter, Δf, is known as the orientation polarizability, which involves ε and n, the solvent dielectric constant and refraction index, respectively. The Onsager radius was estimated from Edward's Method [19] as 3.95 Å, and it is within the range of values found for other naphthalimide derivatives [20]. The change in dipole moment between the ground state and the excited state, estimated from the slope of the plot (Fig. 3) is 5.2 ± 0.2 D.

The addition of water to the dioxane solution of NI and 4-PNI changes the fluorescence emission of both probes, however, in different ways. In the case of NI, addition of 15 mM (30% of water v/v in dioxane) enhances the fluorescence intensity 8-fold (Fig. 4). This enhancement is ascribed to NI's interaction with carbonyl groups [21], which reduces the intersystem crossing from S_1 to T_1 and therefore increases the fluorescence quantum yield. However, with 4-PNI, the emission intensity decreases slightly with addition of small amount of water, and the emission maximum is red-shifted. The fluorescence spectra of 4-PNI in dioxane at various concentrations of water are plotted in Fig. 5. This compound has higher fluorescence intensity in non-polar solvents than in polar and protic solvent.

Several studies have shown that 4-methoxy-*N*-methyl-1,8-naphthalimide (4-MeONI) has no change of its quantum yield (ϕ) and lifetime (τ) in 2% acetic acid solution, but with further acid additions, the fluorescence consecutively decreases and its emission maximum is red-shifted [22]. This indicates that for NI, the effect on the imidic carbonyl is pronounced, and it may promote only a little stabilization of the LUMO orbital. Contrasting with those results, the 4-PNI shows significant changes in its photophysical properties in protic solvent (see Table 1). Nevertheless, it should be recalled that when a phenoxy group substitutes the hydrogen at C-4 naphthalimide position, the emission parameters of the 4-PNI does not change with the first additions of water up to 3 mM in dioxane solution. However, further addition of water at concentrations higher than 3 mM causes a red-shift of the emission maximum and decreases its fluorescence intensity when compared with the emission in pure dioxane (see Fig. 5).

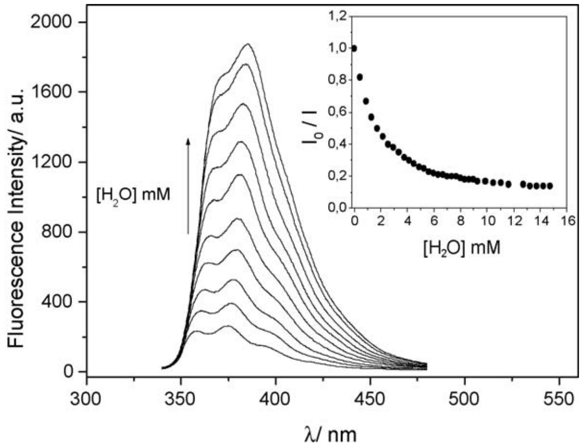

Fig. 4. Fluorescence spectra of NI in dioxane at various concentrations of water. The fluorescence intensity is in order of increasing intensity with addition of water from 0 to 15.0 mM. Inset: Stern–Volmer plot of the data.

3.2. Time-resolved measurements

In order to obtain more information about the excited state dynamics of 4-PNI in different media, the fluorescence decay behavior was studied in several solvents of distinct polarity, and the results obtained are reported in Table 2. The decay profiles of 4-PNI in dioxane and dioxane/water mixtures are plotted in Fig. 6. The fluorescence decay is well described by a single exponential function.

For comparison, the NI system has a fluorescence lifetime less the 1 ns in methanol, but its lifetime increases with water addition to the solvent, suggesting that H-bond interaction with the

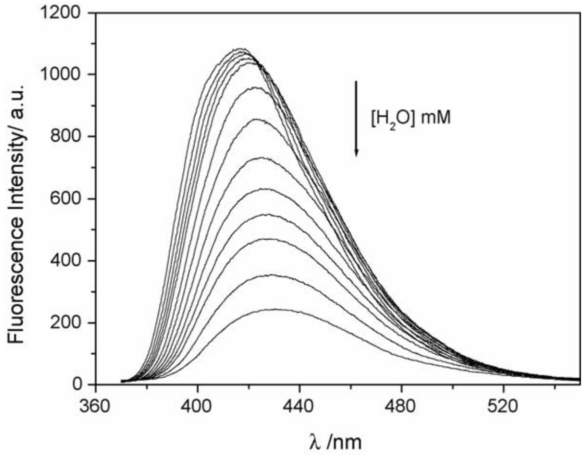

Fig. 5. Water quenching of 4-PNI fluorescence in dioxane with addition of water from 0 to 15.0 mM.

Table 2
Fluorescence lifetimes of NI and 4-PNI in solvents of different polarity

Compounds	Solvents	Lifetimes (ns)
NI	Methanol	0.7
	Methanol:water (20%)	1.1
	Methanol:water (50%)	1.8
	Water	2.1
4-PNI	Dioxane	6.0
	Dioxane/H_2O (3%)	3.5
	Dioxane/H_2O (20%)	2.6
	Chloroform	5.8
	Hexane	4.5

carbonyl group leads to a decrease in the n–π* character of the NI excited state [23a]. The quantum yield of the *N*-methyl-1,8-naphthalimide is 0.005 in hexane, but it reaches a value of 0.22 in ethanol, a polar protic solvent. The weak fluorescence may be due to the lowest singlet state (S_1^*) character, which is a mixing of π–π* and n–π* type states [7,24]. On the other hand, 4-PNI in dioxane has a reduction in lifetime from about 6 to 2.6 ns upon addition of water in the range of 0–20%. This effect is in the opposite direction of that observed with NI in methanol/water solution, and indicates the predominance of the charge transfer effect over the carbonyl–solvent interaction. The push–pull effect of the electron-donating substituent at the C-4 position seems to further increase the stabilization of charge transfer state [23b]. Nevertheless, both polar groups, the phenoxy and the carbonyls, should be solvated by polar protic solvents by H-bond interactions, similar to the behavior found in 1,8-naphthalimide derivatives in different solvents [16] and 4-aminophthalimide in cyclodextrin aqueous solution [25].

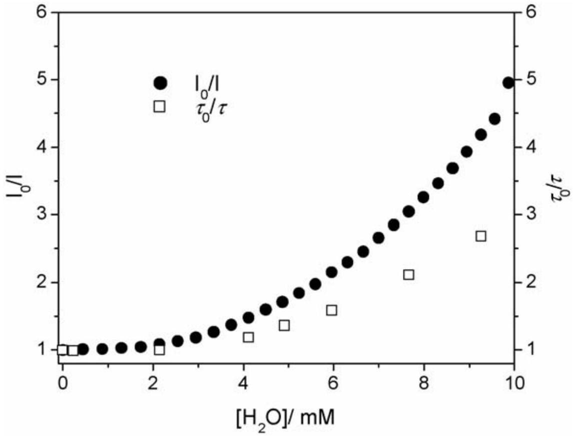

Fig. 7. Stern–Volmer plots of time-resolved (□) and steady-state (●) fluorescence measurements for 4-PNI in dioxane in the absence and the presence of water.

The Stern–Volmer plots of the stationary and time-resolved fluorescence data upon addition of water to dioxane solution show an upward curvature in both sets of data (see Fig. 7). This suggests that the 4-PNI is quenched in both dynamic and static ways. Initial addition of water in dioxane has only a small change in lifetime, similar to what has been shown by stationary measurements. However, above 3 mM of water in dioxane, the nonlinear quenching process is dominant. Note that the increase of the water concentration up to 20% gives a lifetime of 2.6 ns for 4-PNI, a value that is approaching to the lifetime of NI in water of 2 ns (see values in Table 2). The nonlinear behavior of the lifetime ratio of 4-PNI with the amount of water added to dioxane may be a combination of nonradiative deactivation rate of the excited state by protic solvent shell, which is supported by the shift of the emission spectra (see Fig. 5), and dynamic quenching by free water molecules in solution.

Although the static and dynamic quenching contribution are nonlinear with water concentration in dioxane, their ratio gives rise to a linear behavior as can be seen from the plot given in Fig. 8. The apparent static quenching constant K_a calculated from the slope of the linear plot gives a value of 60 M^{-1}.

This static constant K_a can be ascribed to a specific water solvation of 4-PNI by H-bond with the phenoxy and carbonyl groups. If the probe-water association equilibrium is written as

$$\text{4-PNI}+H_2O\overset{K_a}{\rightleftharpoons}\text{4-PNI}\cdots H_2O$$

then the value of K_a at 298 K provides a change in enthalpy (discounting the entropy change due to bimolecular association) of about −11.9 KJ/mol. This value found is within the range

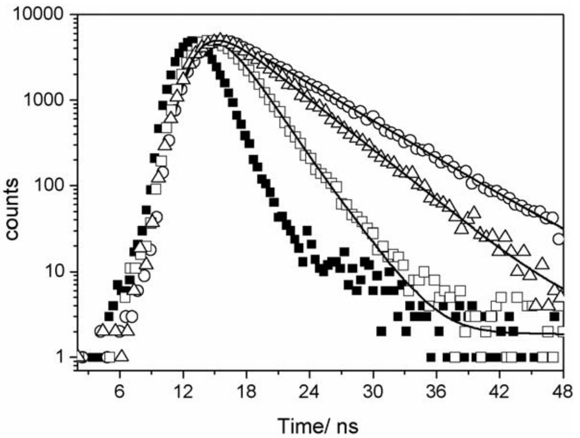

Fig. 6. Decays of 4-PNI in dioxane (○) and water additions: (△) 10%; (□) 20%; (■) irf.

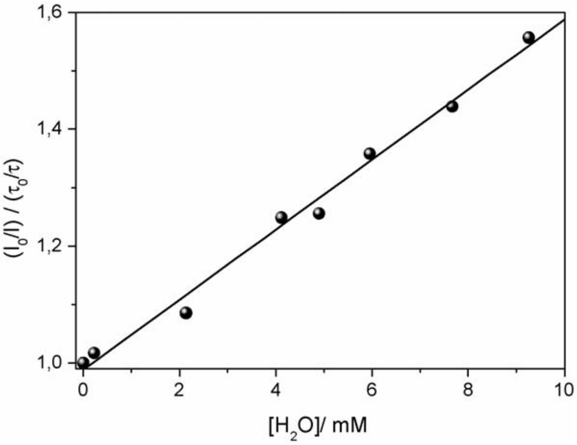

Fig. 8. Ratio between the relative intensity and lifetime as a function of water concentration.

expected for a moderately strong H-bond, and it gives support to the assumed quenching mechanism.

4. Conclusion

The phenoxy group at the C-4 position in NI leads to an increase in the emission character of this derivative as compared to unsubstituted NI. The effect may be ascribed mainly to the lowering of the singlet excited state and change in the relative energy of the π–π^* and n–π^* states with respect to the triplet energy of the same manifold. The Stern-Volmer plots of relative intensity and the relative lifetime upon addition of water to dioxane solution of 4-PNI are both nonlinear function of the added co-solvent. Water is an active static and dynamic quencher species. The static quenching constant is interpreted as a probe–water association constant, and the calculated enthalpy change associated to the process is within the range expected for H-bonding between 4-PNI and water in dioxane solution.

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