

Solvation effect and aggregation of semipermanent spiro[indole-phenanthrolineoxazines] in CH₃CN / H₂O binary solvent

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Dedicated to Professor Vladimir Minkin on his 70th birthday

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Abstract

For three 5-alkyloxyspiro[indolephenanthrolineoxazines], the open form possesses a low-polarity semi-quinoidal structure. In acetonitrile-water binary solvent, the merocyanine is stabilized by a specific interaction with a water molecule. At high water content, the hydrated open form gives rise to H-aggregates.

Keywords: Spirooxazines, acetonitrile-water solvent, aggregates

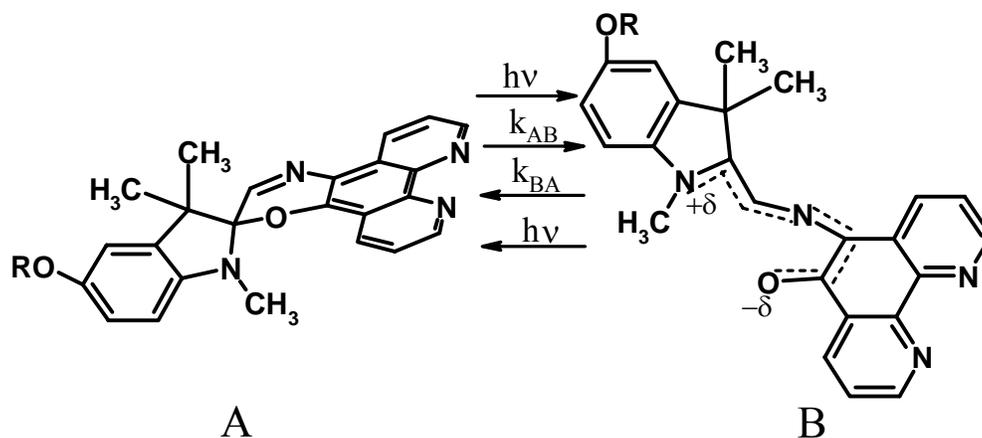
Introduction

Photochromic materials are of considerable interest for their potential applications in variable transmission glasses and photo-switching devices.¹ Among the best known photochromic molecules are spirooxazines which have been extensively investigated because they are expected to exhibit greater photostability than their spiropyran analogs.² Another advantage is their versatility, allowing modulation of their properties by playing with the position and nature of the substituents.³ Among the various spirooxazine compounds available, those containing both a phenanthroline moiety and a long alkyl-chain are promising. The ionophoric properties of phenanthroline enable metal-ion complexation for the future development of light-controlled chemosensors.⁴ The presence of a hydrophobic long-chain substituent is able to promote aggregation leading to a sharp absorption band which could be used for independent erasing or reading in optical memory devices.^{5a-c} Spirooxazine aggregation has received only a limited attention^{6a-b} as association properties have mainly been described for spiropyrans.^{7a-g}

In this paper, we report the first experimental observation of the formation of spirooxazine merocyanine H-aggregates in acetonitrile/water binary solvent.

Results and Discussion

Reversible photochromism and thermal equilibrium. Phenanthroline spirooxazines appear in solution as a mixture of spiro and open forms. The position of their equilibrium is solvent and temperature dependent. However, a significant shift can only be reached by UV or visible irradiation. This photochromic property has been successfully used to investigate the solvation effect on the kinetics of equilibrium relaxation in acetonitrile-water mixtures.⁸



Scheme 1. Photo-thermochromic equilibrium between spiro closed form (A) and open merocyanine B. **1:** R = CH₃; **2:** R = C₉H₁₉; **3:** R = C₁₆H₃₃.

Due to the presence of a thermal equilibrium between the closed and the open forms A and B, the photomerocyanines B are defined as semi-permanent. The solutions always appear to be darkly colored. From NMR and kinetic analysis,⁹ the percentages of open form are given in Table 1.

Table 1. Percentage of the open form at equilibrium in acetonitrile

	1	2	3
% open form B	22.5 ± 1	30 ± 1	31 ± 1

Effect of alkyl chain length on the merocyanine absorption spectra. From UV/visible and NMR measurements accomplished in acetonitrile solution, the molar absorption coefficients (ϵ) (*i.e.* corrected to 100% open form) were determined. Figure 2 shows the regular evolution of the molar absorption coefficients when the alkyl chain is increased from methyl (**1**) to nonyl (**2**) and

hexadecyl (**3**). Note the presence of a shoulder at 570 nm: its intensity is about half of the maximum.

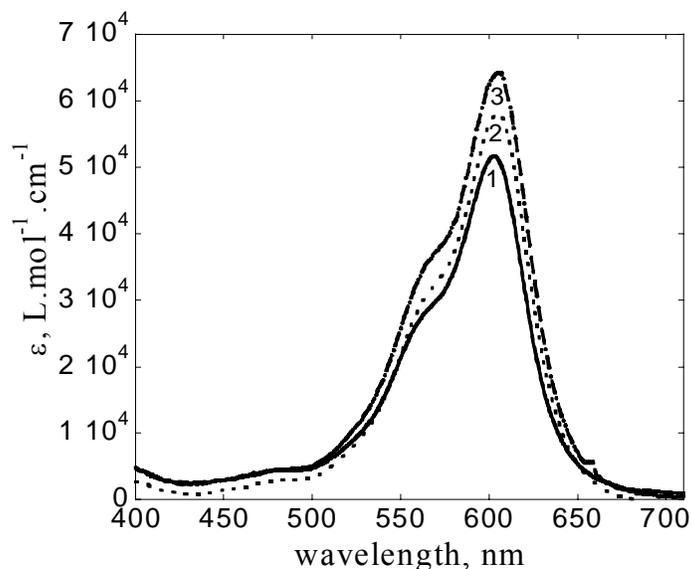


Figure 1. Absorption spectra of compounds **1**, **2** and **3** in acetonitrile. ϵ -values correspond to 100% of the open form.

Solvatochromism. Analysis of the solvatochromism^{7,10a-b} was performed by measuring the wave number ν (cm^{-1}) of the absorption maximum in the visible region.

Table 2. Solvatochromism of the semi-permanent merocyanines (**1**, **2** and **3**) in various solvents: **a**: acetonitrile; **b**: benzene; **e**: ethanol; **h**: heptane; **m**: methanol; **t**: toluene

Solvent	1 λ (nm) / $\nu(\text{cm}^{-1})$	2 $\lambda(\text{nm})$ / $\nu(\text{cm}^{-1})$	3 $\lambda(\text{nm})$ / $\nu(\text{cm}^{-1})$
a	604/16556	604/16556	604/16556
b	596/16779		
e	610/16393	611/16367	611/16367
h		588/17007	588/17007
m	611/16367	608/16447	608/16447
t		601/16639	601/16639

The plot of ν_{max} vs the Kosower empirical parameter of solvent polarity (Z)¹¹ shows a linear dependence. The positive solvatochromism: ($\lambda_{\text{max}} \nearrow$ or $\nu \searrow$ with solvent polarity) indicates that there is no stabilisation of the electronic ground state, which appears to be mainly under a low-polarity semi-quinoidal structure.

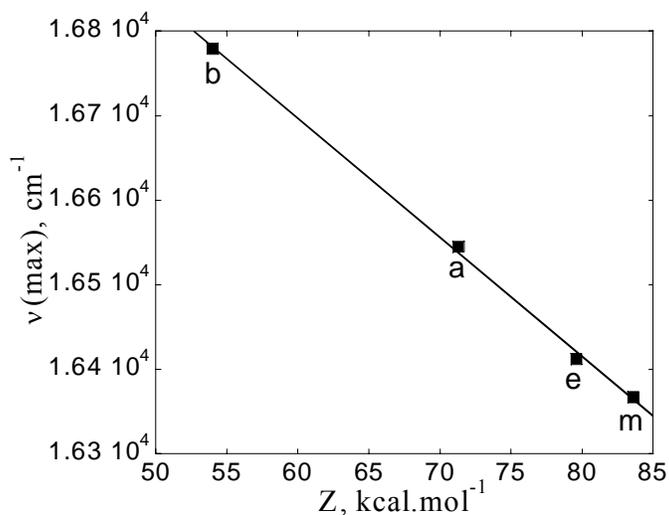


Figure 2. Linear correlation between the wavenumber and the polarity parameter Z of compound **1** in various solvents: **a**: acetonitrile; **b**: benzene; **e**: ethanol; **m**: methanol.

Effect of water on the equilibrium position and relaxation. By adding water to the acetonitrile solution there is no significant wavelength shift ($\lambda_{\max} = 604\text{nm}$). On the contrary, the increase of water content in the acetonitrile/water binary solvent leads to a hyperchromic effect that can be interpreted by a shift of the thermal equilibrium from the closed (A) to the open (B) form. The intensity of the merocyanine band increases more than two-fold going from pure acetonitrile to a 0.87 water molar fraction in the binary mixture. In order to analyse this effect, the equilibrium positions were shifted by visible light irradiation and the relaxation kinetics were recorded (Figure 3).

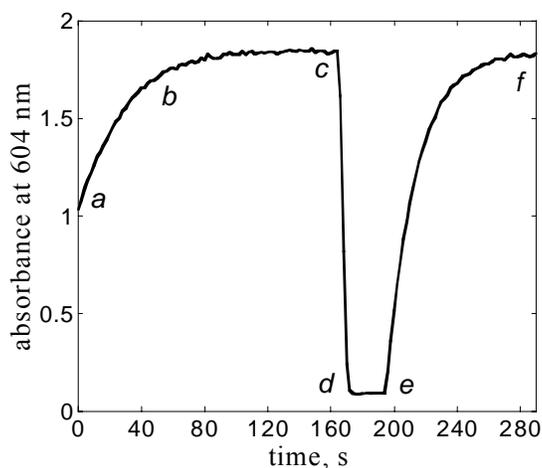


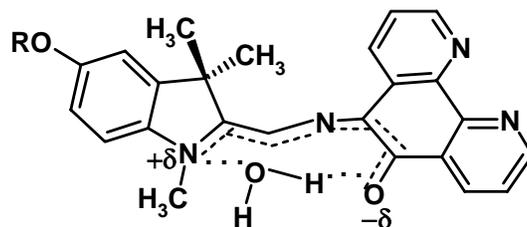
Figure 3. Evolution of the absorbance at 604 nm for the merocyanine **1** immediately after water addition (*a, b, c*), visible light photo-bleaching (*c, d*) and recoloration in the dark (*e, f*). $[\mathbf{1}] = 7.25 \times 10^{-5} \text{ mol.L}^{-1}$; molar fraction of water $x(\text{H}_2\text{O}) = 0.87$.

After water addition to a dry acetonitrile solution of compound **1** (*a*), absorbance increases slowly (*b*) to reach an equilibrium position (*c*). By visible light irradiation of this mixture, there is a significant shift of the equilibrium towards the colorless closed spiro-form (*d*). After switching-off of the irradiation light (*e*), a slow relaxation towards the same equilibrium position (*f*) is observed. By increasing the water molar fraction, it was shown that the absorbance at equilibrium increased while the relaxation time decreased. Quantitative analysis shows that this effect is due to a decrease of the ring-closure rate constant k_{BA} while the ring opening rate constant (k_{AB}) remained unchanged (see experimental section for the details of the calculations).

Table 3. Effect of the water content on the direct (k_{AB}) and the reverse (k_{BA}) individual rate constants of the thermal equilibrium

$x(\text{H}_2\text{O})$	0.07	0.13	0.19	0.24	0.42	0.66	0.81	0.87
Abs _{eq} at 604 nm	1.1	1.195	1.32	1.45	1.64	1.88	2.06	2.13
$k_{\text{obs}}, \text{s}^{-1}$	0.196	0.175	0.156	0.132	0.111	0.095	0.085	0.079
k_{BA}, s^{-1}	0.146	0.125	0.106	0.082	0.071	0.055	0.045	0.039
k_{AB}, s^{-1}	0.05	0.05	0.05	0.05	0.04	0.04	0.04	0.04

The inhibition of the ring-closure reaction could result from specific hydrogen bond formation between the semi-quinoidal merocyanine and a water molecule. When a water molecule is trapped within the space between the indolinic nitrogen atom and phenanthrolic oxygen, spiro-bond formation is hindered. This assumption agrees with X-ray structural analysis of a crystallised merocyanine hydrate.¹²



Scheme 2. Ring-closure water inhibition mechanism.

Solvation states of the open merocyanine and its aggregation. In acetonitrile–water binary mixtures, the merocyanine open-form has been shown to exist in three different solvated states.⁸ Among them, there is a fully hydrated merocyanine of which the concentration exhibits a drastic increase at high water content. Recent computations have permitted the corresponding spectrum to be extracted (spectrum *f* in figure 4). Figure 4 shows that the calculated spectrum of the hydrated form is very similar to the spectrum recorded at the onset of aggregation. Under conditions mentioned above (*i.e.* after addition of water), the association of merocyanines starts with the appearance of a blue-shifted very narrow absorption band ($\lambda_{\text{max}} = 440\text{nm}$). We assume that aggregation begins with the step-by-step association of such hydrated species.

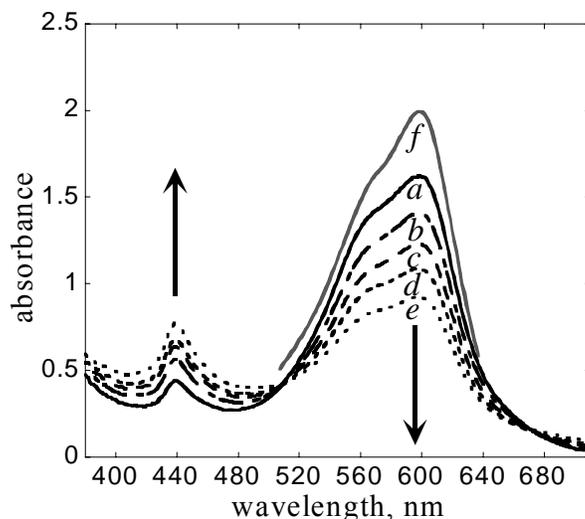


Figure 4. Comparison of the shape of the merocyanine spectra in its hydrated form (**f**) and during aggregation. **a**:20; **b**:30; **c**:40; **d**:50; **e**:70 s. $[1] = 1.72 \times 10^{-4} \text{ mol.L}^{-1}$; $x[\text{H}_2\text{O}] = 0.97$.

Spectral evolution during aggregation and precipitation. The 440nm band in the blue region is the characteristic of the formation of the so-called H- or sandwiched aggregates having an anti-parallel dipole arrangement¹³. This band increases rapidly while the merocyanine maximum decreases. The process lasts less than five minutes exhibiting two isosbestic points lying on both sides of the merocyanine maximum band. The position of the isosbestic points varied from one experiment to another. The first one located in the blue side ranged from 495 to 550 nm while the second situated on the red-side was between 628 and 672nm.

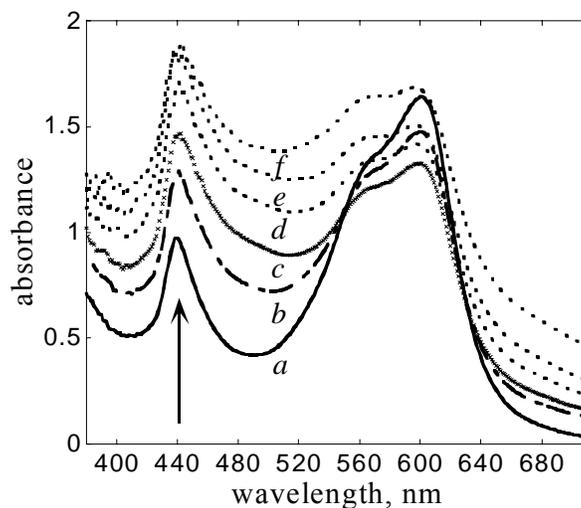


Figure 5. Evolution of the spirooxazine **1** absorption spectrum during aggregation followed by the formation of a light scattering colloidal solution and precipitation.

$[1] = 2.57 \times 10^{-4} \text{ mol.L}^{-1}$, $x(\text{H}_2\text{O}) = 0.96$ (**a**:0; **b**:10; **c**:20; **d**:50; **e**:90; **f**:1020 s after mixing)

Such variations correspond to changes in the spectral shapes recorded. This phenomenon can be attributed to the presence of a meta-stable suspension of colloidal crystals. These spectral changes may also be related to an increase in the size of the aggregates.¹⁴ At the first time, the solution becomes red with an additional maximum at 440 nm. After a while, strong light scattering leads to loss of the isosbestic points with the formation of a suspension that can be stable for several hours. Figure 5 shows the appearance of strong light scattering during the formation of colloidal crystal. Fluff-like heterogeneous particles were formed and then precipitated.¹⁵

Conditions for the observation of aggregation. Aggregation was observed on increasing both the spiroxazine concentration and the water content. Figure 6 shows the concentration domain where H-aggregates are formed. In the "no-aggregation" domain, aggregation did not occur even after several days of observation.

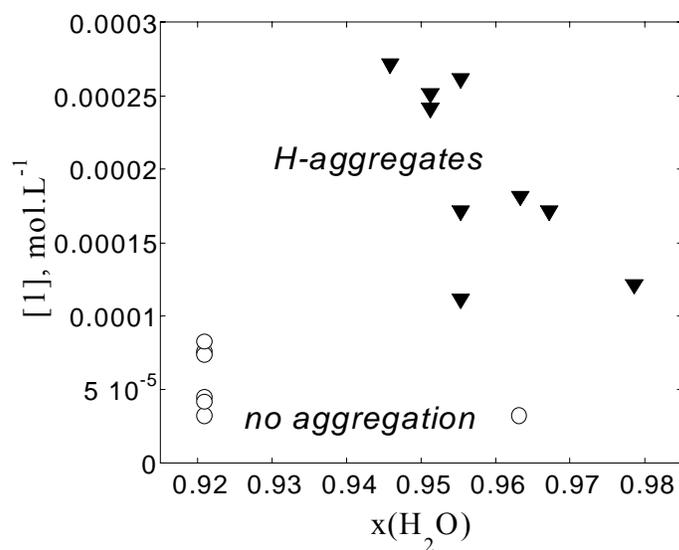


Figure 6. Concentration domain for the observation of meta-stable H-aggregates and their precipitation (\blacktriangledown).

Conclusions

We have shown that the phenanthroloispirooxazines are solvent-sensitive molecules. From the solvatochromic shift analysis, it was shown that the merocyanine open form possesses a semi-quinoidal low-polar character. At sufficiently high water content, there is a bimolecular

hydrogen-bonding interaction between the open form and a water dipole. This interaction inhibits the ring closure process and stabilises the meta-stable open form. At higher water content, the open form exists in a hydrated state which is able to give rise to H-aggregates. This head-to-tail ordering is favored by the semi-quinoidal dipolar character of the merocyanine.

Experimental Section

General Procedures. The absorption spectra and photokinetic data measurements were performed using an Ocean Optics fiber optic diode array spectrophotometer placed in the thermostated block. The NMR analysis technique has been reported earlier.^{8,12} The experimental set up for visible irradiation procedures included a 150 W, IR-filtered halogen lamp with glass-fiber optics.

Typical experimental procedure

In order to obtain the aggregates, to a solution of spirooxazine compound dissolved in neat acetonitrile, a mixture of CH₃CN and H₂O was added. The cuvette was immediately shaken and placed into the cell. After reaching an equilibrium position the solution was irradiated with visible light in order to obtain a photobleached steady state. After switching-off the lamp, relaxation kinetics were recorded. All experiments were accomplished at 25°C.

Products (molecules and solvents). The synthesis of 5-methoxy-1,3,3-trimethylspiro[indole-2,2'-[2H]bipyrido[3,2-*f*][2,3-*h*][1,4]benzoxazine] (**1**), 5-nonyloxy-1,3,3-trimethylspiro[indole-2,2'-[2H]bipyrido[3,2-*f*][2,3-*h*][1,4]benzoxazine] (**2**) and 5-hexadecyloxy-1,3,3-trimethylspiro[indole-2,2'-[2H]bipyrido[3,2-*f*][2,3-*h*][1,4]benzoxazine] (**3**) has been described previously.^{8, 9} Acetonitrile used as a solvent was of the highest spectroscopic grade. Bi-distilled water was used.

Calculations details. Considering the A \rightleftharpoons B equilibrium, the two concentrations [A] and [B] obey two equations: the mass balance equation: [1] [A] + [B] = [A]₀ and the mass action law [2]: $K_{eq} = [B]_{eq}/[A]_{eq} = k_{AB}/k_{BA}$. When it has departed from its equilibrium position the system relaxes with an apparent first order rate constant $k_{obs} = k_{AB} + k_{BA}$. (eq. [3]). By combining eq. [1], [2] and [3], individual rate constants are found: $k_{AB} = k_{obs} [B]/[A]_0$ (eq. [4]) and $k_{BA} = k_{obs}(1 - [B]/[A]_0)$ (eq. [5]). Using Beer's law, eq. [6], $[B] = Abs_{eq}/\epsilon_{B.l}$ allows k_{AB} and k_{BA} to be calculated from Abs_{eq} and k_{obs} .

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