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Waterchromism of protonated photomerocyanine dye

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Abstract

The red protonated photomerocyanine (PMCH) of spirooxazine (SPO) experiences a stepwise color modulation from red to purple and ultimately blue upon gradual addition of water. Both UV–vis absorption spectra and thermal bleaching kinetics indicate that the blue solution differs from the open form of SPO, i.e., photomerocyanine (PMC), and computer assisted simulations show that the blue solution is a complex composed of one PMCH and two water molecules, which are connected through hydrogen bonds. Thus, water has a characteristic effect on PMCH, and this phenomenon is proposed as waterchromism.

Keywords: Waterchromism; Photomerocyanine; Color modulation; Absorption spectra; Thermal bleaching kinetics

1. Introduction

Spirooxazines (SPO) are well known for their interesting photochromic behavior. Upon UV irradiation, SPO transforms to its open form, i.e., photomerocyanine (PMC), which reverts to SPO after thermal treatment or under visible light irradiation. Such bi-stability of SPO is considered to be potentially useful in ophthalmic lenses, authentication systems, optical switches, optical information storages, reversible holographic recording, nonlinear optical devices, etc. [1–6], and the related photochemical process has been well elucidated [7–11]. It is known that in solution a proton can make the colorless SPO turn red as a result of the formation of a protonated photomerocyanine dye (PMCH). The photochromism of an SPO compound, SPOI, and its protonated processes are presented in Scheme 1 [12–14]. In this presentation, we show that aqueous PMCH solution of acetonitrile can experience stepwise color modulation depending on the content of water. Such water-induced chromism can be termed as ‘waterchromism’, which is attributed to the formation of a complex composed of one PMCH and two water molecules.

2. Experimental

2.1. Materials and instruments

The synthesis of SPO compounds is described in Section 2.2. Acetonitrile and CF_3COOH were of spectroscopic quality, while aniline and pyridine were of analytical grade. The aqueous HCl ($13\ \mathrm{mol\,L^{-1}}$) was of analytical grade as well, and was diluted to $0.1\ \mathrm{mol\,L^{-1}}$ by acetonitrile before use. Ultrapure water was produced using a Milli-Q apparatus with a resistibility of $18.2\ \mathrm{M\Omega\,cm}$ (Millipore).

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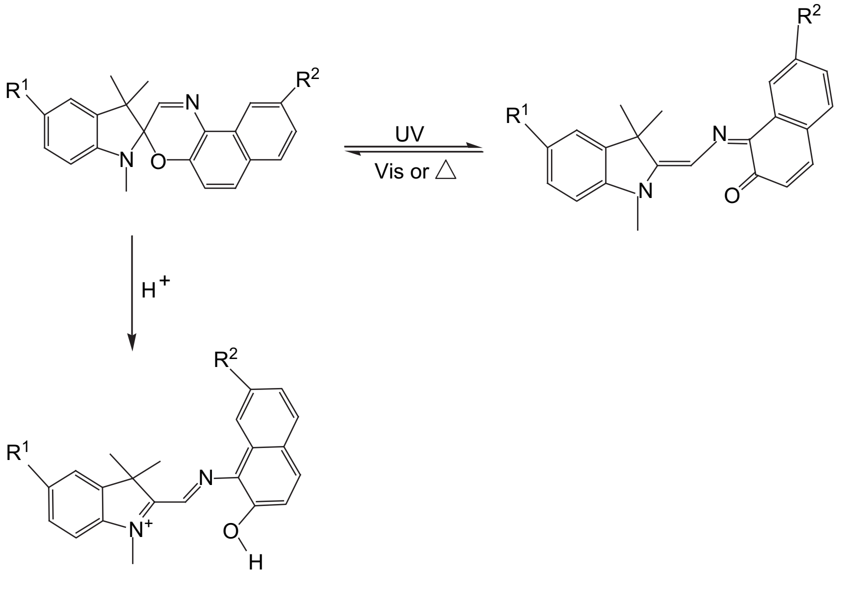


SPOI: R^1=CH_3O-, R^2=3-(3, 5-di-t-butyl-4-hydroxyphenyl) propanoyloxy-;

Scheme 1. Photochromism of SPOI and the formation of protonated photomerocyanine from SPOI.

The UV–vis absorption spectra were measured using a Shimadzu UV-1601 PC double-beam spectrophotometer. The ^{1}H NMR spectra were measured with a Bruker Avance 600 spectrometer. MALDI-TOF mass spectra were measured using a BIFLEXIII mass spectrograph.

2.2. Synthesis and characterization

SPOI: The synthesis of the SPOI can be summarized as follows: firstly, 1,3,3-trimethyl-5-methoxy-α-methyleneindoline is condensed with 2,7-dihydroxy-1-nitrosonaphthalene to give the precursor spirooxazine (Scheme 2, compound **III**). The synthesis of the antioxidant (2,6-di-*t*-butyl-4-hydroxylphenylpropionic acid, compound **IV**) was the adduct of 2, 6-di-*t*-butyl phenol and methyl acrylate in the presence of a strong base, namely sodium methoxide (Scheme 3). Finally, compound **IV** was connected to compound **III** through esterification, and SPOI was obtained as a result (Scheme 4).

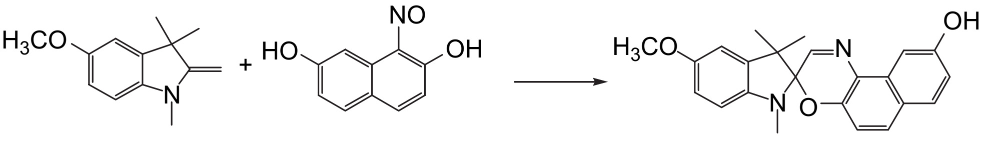
^{1}H NMR (600 MHZ, CD_3CN, 298 K) δ 1.30 (s, 3H), 1.34 (s, 3H), 1.44 (s, 18H), 2.68 (s, 3H), 2.94 (t, $J = 3$ Hz, 2H), 3.00 (t, $J = 3$ Hz, 2H), 3.77 (s, 3H), 5.37 (s, 1H), 6.55 (d, $J = 8.4$ Hz, 1H), 6.76 (d, $J = 8.4$ Hz, 1H), 6.80 (s, 1H), 7.00 (d, $J = 8.4$ Hz, 1H), 7.07 (d, $J = 8.4$ Hz, 1H), 7.15 (s, 2H), 7.76 (d, $J = 8.4$ Hz, 1H), 7.77 (s, 1H), 7.84 (d, $J = 8.4$ Hz, 1H), 8.11 (s, 1H). MALDI-TOF: *m*/*z*, 632.9.

SPOII: SPOII (1,3,3,4,5-pentamethyl-9′-hydroxy-spiro(indoline-2,3′-[3*H*]naphtha[2,1-*b*][1,4]oxazine)) was synthesized by the condensation of 1,3,3,4,5-pentamethyl-α-methyleneindoline and 2,7-dihydroxy-1-nitrosonaphthalene, and the structure was confirmed by ^{1}H NMR, and mass spectra.

^{1}H NMR (600 MHZ, CD_3CN, 298 K) δ 1.28 (s, 3H), 1.32 (s, 3H), 2.23 (s, 3H), 2.27 (s, 3H), 2.69 (s, 3H), 6.46 (s, 1H), 6.78 (d, $J = 8.8$ Hz, 1H), 6.91 (s, 1H), 7.00 (d, $J = 8.8$ Hz, 1H), 7.32 (s, 1H), 7.64 (d, $J = 8.8$ Hz 1H), 7.69 (d, $J = 8.8$ Hz 1H), 7.75 (s, 1H), 7.79 (s, 1H). MALDI-TOF: *m*/*z*, 371.5.

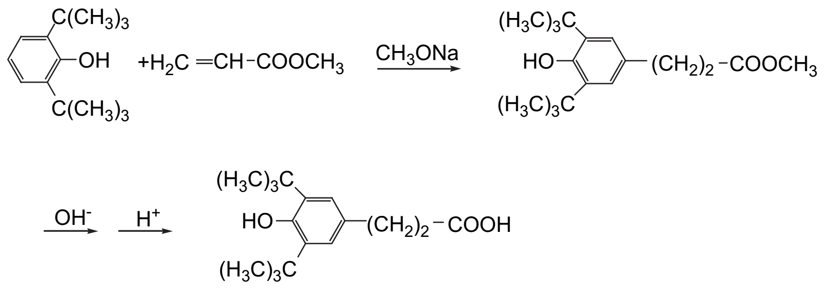
2.3. Calculation of the chemical yields for the protonated merocyanine (PMCH)

To a solution of SPOI in deuterated acetonitrile ($c = 3.81 \times 10^{-3}$ mol L^{-1}), equimolar amount of trifluoro-acetic acid was added, and the protonated merocyanine (PMCH) was formed. ^{1}H NMR results indicate that new peaks appeared at $\delta = 3.97$, 1.42, and 4.17 ppm, stemming from N–CH_3, –CH_3 and –OCH_3 in PMCH, respectively, the position of



Compound **III**

Scheme 2.



Compound **IV**

Scheme 3.

whose are $\delta = 2.72$, 1.32 and 3.78 ppm, respectively, for SPOI. The integrations of the O–CH_3 signal were 0.888 and 2.879 in PMCH and SPOI, respectively, and the chemical yields can be calculated as follows: $0.888/(0.888 + 2.879) = 0.24$. Similarly, from the other signals the chemical yields can be also calculated. The original concentration of PMCH ($c = 8.98 \times 10^{-4}\ \mathrm{mol\,L^{-1}}$) can be calculated from the chemical yield.

Similarly, the chemical yield for SPOII to corresponding PMCH is calculated, which is 0.22, and the PMCH concentration of SPOII is $8.76 \times 10^{-4}\ \mathrm{mol\,L^{-1}}$.

2.4. Determination of thermal decay rate constant

The integrated form of the first-order rate law is

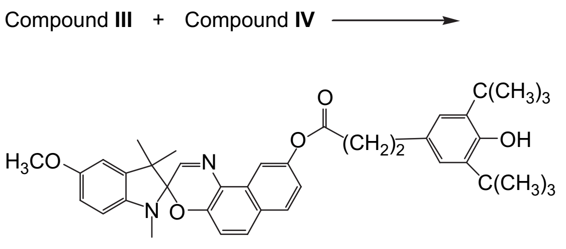
$$[\mathrm{PMC}]_t = [\mathrm{PMC}]_0\,\mathrm{e}^{-kt}$$

For waterchromism:

$$[\mathrm{WP}]_t = [\mathrm{WP}]_0\,\mathrm{e}^{-kt}$$

Here, k is the rate constant; $[\mathrm{PMC}]_0$ and $[\mathrm{PMC}]_t$ are the concentrations of PMC present at right after UV irradiation and at time t, respectively; $[\mathrm{WP}]_0$ and $[\mathrm{WP}]_t$ are the concentrations of waterchromic product (WP) just after waterchromism and at time t, respectively.

Thus, k is the slope of the straight line obtained through the plot of $\ln([\mathrm{PMC}]_0[\mathrm{PMC}]_t^{-1})$ versus t, or $\ln([\mathrm{WP}]_0[\mathrm{WP}]_t^{-1})$ versus t.



SPOI

Scheme 4.

2.5. The energy values (Hartree) of PMCH with one and two water molecules calculated by the program B3LYP/6-31G(d)

The TTC isomer of PMCH: −1035.5116809.
PMCH with one water molecule: −1111.9466459.
PMCH with two water molecules: −1188.3077551.

3. Results and discussion

3.1. Waterchromism of protonated photomerocyanine

The colorless acetonitrile solution of SPOI ($3.81 \times 10^{-3}\ \mathrm{mol\,L^{-1}}$) turned red after the addition of an equimolar amount of hydrochloric acid or trifluoro-acetic acid, and the absorption maximum shifted from $\lambda_{\max} = 320$ nm to $\lambda_{\max} = 510$ nm (line 1 and line 2 in Fig. 1, respectively). From the ^{1}H NMR spectra of SPOI in deuterated acetonitrile before and after addition of an equimolar amount of trifluoro-acetic acid, we can see that after the addition of trifluoro-acetic acid to the deuterated acetonitrile solution a new peak centered at $\delta = 9.8$ was found, which is for the hydrogen of hydroxyl in PMCH [12–14]. Both the absorption and ^{1}H NMR suggest the formation of PMCH upon addition of

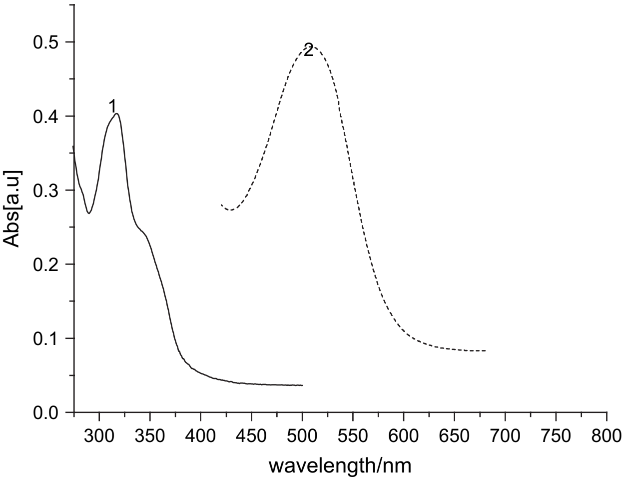


Fig. 1. UV–vis absorption spectra of SPO (line 1) and PMCH in acetonitrile (line 2).

acid, and the chemical yield of PMCH in this process is 0.24 (see Section 2.3).

When PMCH solution (9.14×10^{-4} mol L^{-1}, 0.1 mL) was added to a mixture (5 mL) of acetonitrile and water, the solution experienced a stepwise color modulation from red to purple and then eventually blue with the volume ratio of water (X_w) changing from $X_w = 0$ to 1 (Fig. 2a). In other words, by adjusting the ratio of water to acetonitrile, the color of PMCH solution can be modulated in a simple way.

Visible absorption spectra were used to identify the chemical species formed during waterchromism (Fig. 2b). With increased content of water in the mixture of water and acetonitrile, the absorption band of PMCH became weaker and that corresponding to the waterchromic product (WP) gradually dominated. The ultimate blue WP in water presents two absorption maximum peaks at $\lambda_{max} = 580$ nm and 628 nm. An isosbestic point is observed at $\lambda_{max} = 550$ nm, indicating that only two species are concerned in the waterchromism. In addition, the relative absorption intensity of WP to PMCH (A_{WP}/A_{PMCH}) shows a linear relationship with the relative content of water to PMCH ([H_2O]/[PMCH]) as shown in Fig. 3. This observation indicates that the color of the protonated merocyanine dye is related to the content of water.

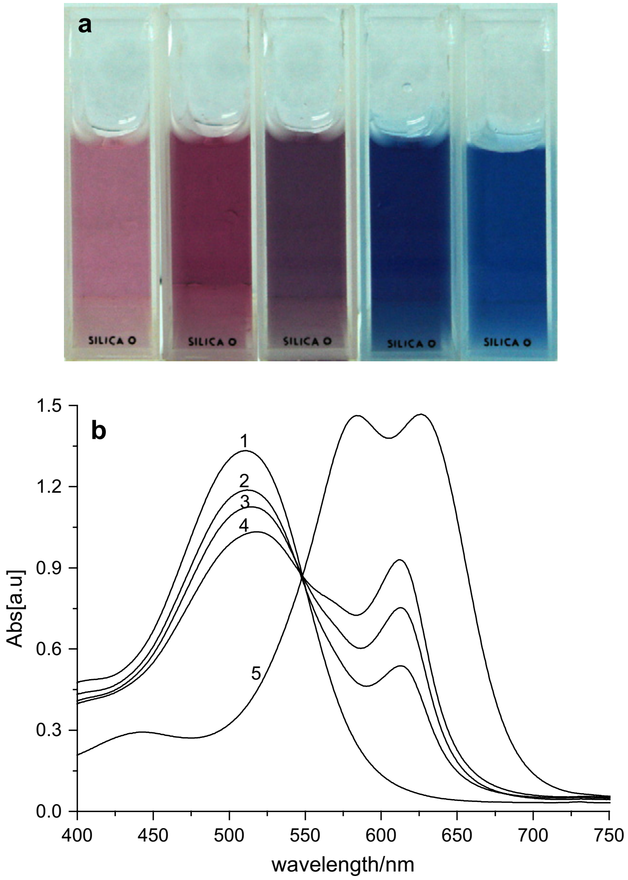


Fig. 2. (a) Photographs of color change for PMCH in mixtures of water and acetonitrile with different X_w; (b) UV–vis absorption spectra of the PMCH solution (8.98×10^{-4} mol L^{-1}) upon addition of mixture of acetonitrile and water at $X_w = 0$ (line 1), 0.2 (line 2), 0.4 (line 3), 0.6 (line 4), and 1(line 5).

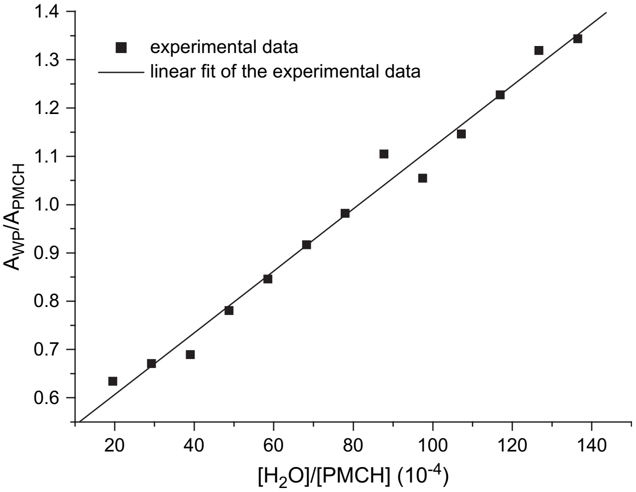


Fig. 3. Linear correlations between the relative absorption intensity of WP to PMCH (A_{WP}/A_{PMCH}) and the relative content of water to PMCH ([H_2O]/[PMCH]).

3.2. Characteristic effect of water on PMCH

3.2.1. UV–vis absorption spectra

Furthermore, similar experiments were carried out by replacing water with typical organic Lewis base, such as aniline or pyridine. Blue solution can also be obtained. The blue solution presents similar absorption spectra to PMC in acetonitrile, i.e., only one peak with a maximum at around $\lambda_{max} = 630$ nm, which may experience blue shift with increased polarity of the solvent [15], as displayed by Fig. 4. What's more, the blue solution is thermal bleaching, namely, quickly became colorless, and the colorless solution presents identical absorption spectra to SPO. Based on the above experimental data, we concluded that the blue solution is PMC when organic Lewis bases were used instead of water in the experiments. From the absorption difference between WP and PMC we can see that water has different effect on PMCH from the typical organic Lewis base.

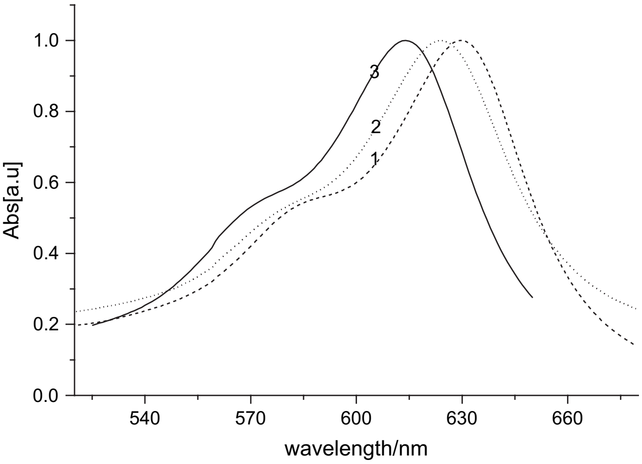


Fig. 4. The normalized UV–vis absorption spectra of PMCH in aniline (line 1), pyridine (line 2) and acetonitrile (line 3).

3.2.2. Kinetic results

Thermal bleaching dynamics was also investigated to further distinguish WP, which reverts to SPO (Fig. 5). WP exhibits first-order kinetics as PMC does [16] but the kinetic rate constant (k, see Section 2.4), however, is different. The decay of PMC (line 1), with $k = 1.05 \times 10^{-2}\ s^{-1}$, is faster than that of WP (line 2, $k = 3.00 \times 10^{-3}\ s^{-1}$), both the solvents are a mixture of water and acetonitrile with $X_w = 0.4$. Furthermore, the decay rate of WP depends on the content of water. The rate constant of WP decreases from $k = 3.00 \times 10^{-3}\ s^{-1}$ to $2.00 \times 10^{-3}\ s^{-1}$ when X_w increases from 0.4 to 1 in the mixture (lines 2, 3, and 4).

3.3. The mechanism of waterchromic process (discussions)

Both the absorption spectra and thermal bleaching suggest that water has an effect on PMCH, and not simply induced to PMC as typical organic Lewis base does. The waterchromic process is proposed by the following equation:

$$\text{PMCH} + n\text{H}_2\text{O} \rightleftharpoons \text{WP} \quad (1)$$

According to Eq. (1), when a small amount of water exists as compared to PMCH, the equilibrium shifts to the left, thus, PMCH is expected to be the major species in the system and the solution should be a red color. When the content of water increases, the equilibrium shifts to the right, and both the red PMCH and blue WP coexist in the system so that the solution shows a purple color. When water is excessive, WP will be the predominant species, and the solution exhibits a blue color. This reasoning agrees well with the experimental results.

^{1}H NMR spectra of SPO and PMCH were measured in CD_3CN to investigate the mechanism of waterchromism. The signal at $\delta = 9.8$ ppm is assigned to the hydroxyl group in PMCH as mentioned above. The intensity (integration of signal) decreased after water was added to the PMCH solution [17,18]. This change indicates that the interaction between the hydroxyl group in PMCH and water is responsible for the formation of WP. It is known that the oxygen atom in water molecule is negatively charged, while PMCH bears a hydroxyl group, with an electron deficient positively charged H-atom. Hydrogen bonds between the oxygen atom of the water molecule and the H-atom of the hydroxyl group of PMCH are the most plausible specific interaction between the components.

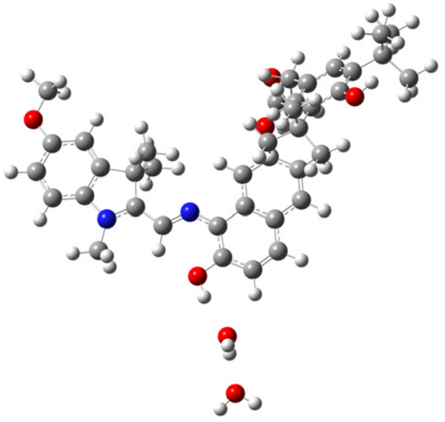


Fig. 6. The calculated molecular structure of WP.

Molecular modeling (B3LYP/6-31G(d)) was adopted to verify this assumption. Energy values of PMCH with one and two water molecules were calculated in the gaseous phase, and the investigation was centered on the four transoid isomers of PMCH since the cisoid ones were considered to be unstable compared with transoid isomers [15,19]. Calculation suggests that the most stable isomer for PMCH is also TTC isomer: *trans–trans–cis* of the three bonds between indolyl and naphthyl groups and the hydrogen atom of the hydroxyl group

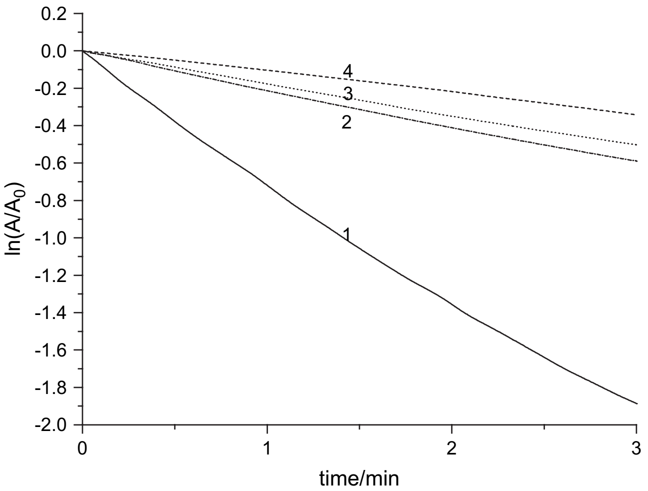


Fig. 5. Thermal bleaching kinetics of PMC in mixture of water and acetonitrile with $X_w = 0.4$ (line 1), and the WP at $X_w = 0.4$ (line 2), 0.6 (line 3), and 1 (line 4). The monitoring wavelengths were at 614 nm, 612 nm, 612 nm, and 628 nm, respectively. PMC was obtained by 30 s irradiation of SPO using a 500 W high pressure mercury lamp.

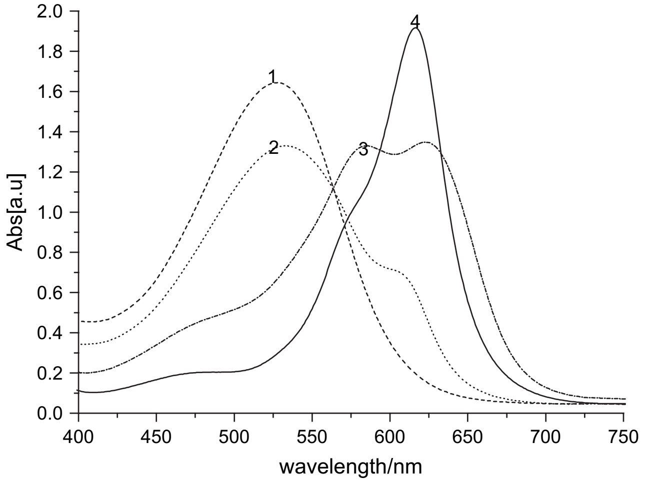


Fig. 7. Absorption spectra of protonated SPOII (8.76×10^{-4} mol L^{-1}, 0.1 mL) upon addition of mixtures of water and acetonitrile (3 mL) with different X_w from $X_w = 0$ (line 1), $X_w = 0.3$ (line 2), $X_w = 1$ (line 3) and the opened photomerocyanine (line 4).

has little effect on the isomerization. The complex of the TTC isomer with two water molecules presents the lowest energy (see Section 2.5). In the complex, one of the water molecules is attached to the hydroxyl group of PMCH via the hydrogen bond and the other water molecule is linked to the complex through hydrogen bond between the water molecules (Fig. 6). What's more, there is no change in the conformation of PMCH upon waterchromism. The length of the O–H bond in the complex is 97 pm, a little longer than that in PMCH (96 pm), while the length of the C–O bond in PMCH decreases from 136 pm to 126 pm upon the formation of the complex.

The different bleaching kinetics between WP and PMC (see Fig. 5) can be understood based on the waterchromic process. The WP exhibits slower decay than that of PMC, since the hydrogen bonding can suppress the thermal decay [20]. The thermal decay of WP depends on water content also, which is reasonable by taking account of the preferential solvation [21] and which is a common phenomenon in water–organic solvent binary mixtures, such as water and acetonitrile. At low water content, WP may be preferentially solvated by acetonitrile, thus the WP presents only one peak, similar to that of PMC (lines 2, 3 and 4 in Fig. 2b), suggesting the hydrogen bonds in the complex are weakened to some extent due to the solvation effect of acetonitrile. At high water content, WP is expected to be mainly solvated by water (line 5 in Fig. 2b), therefore WP presents the characteristic two peaks of the complex and the thermal decay becomes slower due to the complete recovery of the hydrogen bonds in the complex.

3.4. Waterchromism of another protonated photomerocyanine

Waterchromism was also observed for another protonated photomerocyanine of 1,3,3,4,5-pentamethyl-9′-hydroxy-spiro (indoline-2,3′-[3*H*]naphtha[2,1-*b*][1,4]oxazine) (Fig. 7). The red protonated photomerocyanine presents an absorption band centered at $\lambda_{max} = 530$ nm, and with increasing the content of water in the mixture of water and acetonitrile, a stepwise color change from red to purple to blue was also observed. The maximum absorption peak of WP was centered at $\lambda_{max} = 625$ nm and 585 nm, which is different from the opened form of SPOII ($\lambda_{max} = 615$ nm).

4. Conclusions

Solutions of PMCH in acetonitrile present a stepwise color modulation by the gradual addition of water, due to the gradual formation of a waterchromic product (WP). The relative absorption of WP to PMCH presents a linear relationship with the content of water. The structure of WP is a complex of PMCH with two water molecules via intermolecular hydrogen bonds.

Acknowledgements

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