

Photochromism and hydrolysis of aromatic Schiff base *N,N'*-bis(salicylidene)-*p*-phenylenediamine (BSP) studied in heterogeneous environments

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Abstract A photochromic symmetric Schiff base, *N,N'*-bis(salicylidene)-*p*-phenylenediamine has been studied by means of stationary spectroscopic absorption and emission techniques in the IR and UV-vis spectral range in heterogeneous environments: microporous and mesoporous molecular sieves and micellar systems. The intermolecular hydrogen bonds between the molecule studied and silanol groups in mesoporous material have led initially to the stabilization of the cis-keto tautomer and later to a very effective hydrolysis. Persisting two-step color changes have been found to occur after the UV irradiation of the molecule studied encapsulated in microporous and mesoporous molecular sieves.

Keywords Schiff bases · Photochromism · MCM-41 · Hydrolysis · Micelle

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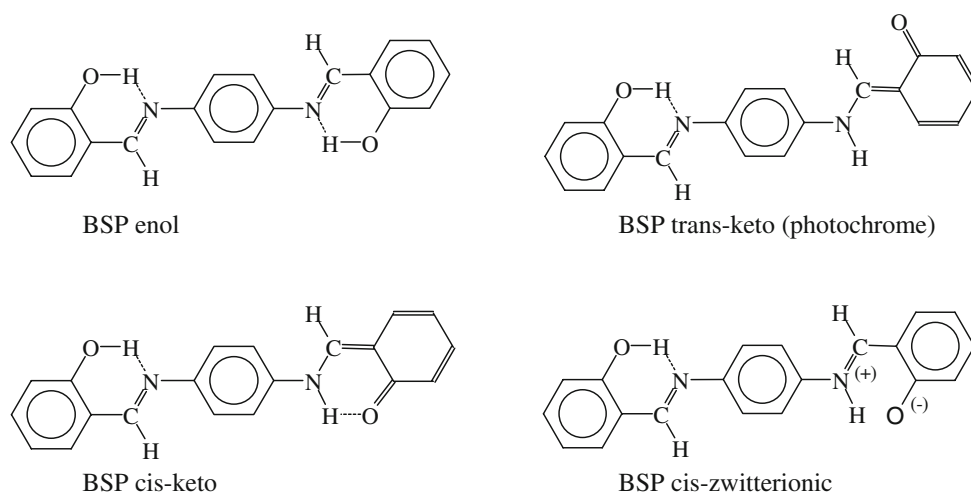
Introduction

Zeolites and MCM-41 as host materials are found to be convenient media to control the photochemical reactions of the organic species. The molecules adsorbed in their cavities and channels very often exhibit the photophysics and photochemistry drastically different from those in solutions [1]. Recently, nanosized microporous zeolite material with incorporated molecules exhibiting tautomerism due to the excited state intramolecular proton transfer (ESIPT) reaction has been studied [2, 3]. If the particle sizes are small enough and their concentration is not too high it is possible to obtain a colloidal solution that is transparent enough to permit the transmission spectroscopic studies [2, 3].

N,N'-bis(salicylidene)-*p*-phenylenediamine (BSP) is a symmetric aromatic Schiff base belonging to the family of salicylideneaniline (SA), see Scheme 1. The photochromism of the molecules from this family attracts much interest because of possible applications, e.g. in molecular memories and switches [4]. According to our knowledge there are only a few reports on the spectroscopic properties of photochromic Schiff bases in zeolites and MCM-41 [5–9] and none in micelles. Therefore, we report here the measurements of BSP in heterogeneous environments: in mesoporous silica (MCM-41), microporous aluminosilicates (zeolites) and micelles. The studies for BSP should be also relevant for a large group of aromatic Schiff bases (at least those belonging to the SA family).

The simplest and commonly assumed photochromic cycle of SA family in solution is the following [10, 11]. After the excitation of the initial enol tautomer ESIPT takes place leading to the excited keto tautomer (cis-keto or its zwitterionic form, see Scheme 1) exhibiting a characteristic, strongly Stokes shifted, fluorescence band. Then, after the structural changes (rotation around C=C and/or

Scheme 1 Different tautomers of the BSP molecule (for simplicity all structures are presented as planar ones)



C–N bond) involving the cleavage of the intramolecular hydrogen bond, the long-lived photochromic tautomer (trans-keto or its zwitterionic form, see Scheme 1) in the ground state is generated. The lifetime of the latter is in the order of microsecond and millisecond at room temperature [10, 11] but can increase up to minutes and hours at lower temperatures [12, 13].

BSP molecule has been initially studied in the solid state, in which it shows its thermochromic properties [14, 15]. On contrary, BSP in solution exhibits photochromic behavior and the spectroscopic properties of cis-keto and trans-keto forms are very similar to those of SA [10, 11]. Because of its symmetry, BSP has been also recently studied in the aspects of fluorescent nanoparticles [16] and multi-component material design [17]. Theoretical calculations predict the additivity of the photochemical properties of the two subunits: the change in one subunit does not alter significantly the features of the other [17]. Recently, we have studied BSP by means of stationary and time-resolved (on femto- and picosecond time scale) absorption and emission methods in nonpolar, polar and protic solvents [18, 19]. One of the most important findings was the observation of another ultrafast deactivation channel in the excited enol tautomer (competing with ESIPT reaction) and the solvent dependant ground state equilibrium between the enol and cis-keto tautomers. With increasing the proton donating ability of the solvent the long wavelength absorption band with maximum around 450 nm assigned to the cis-keto form occurs.

Experimental

BSP was synthesized by conventional condensation of *p*-phenylenediamine and salicylaldehyde. The sample was additionally recrystallized from CHCl_3 . All measurements

were performed at room temperature. The following solvents were used: acetonitrile (ACN, for fluorescence, Merck), hexane (HEX, for HPLC, Merck), ethanol (EtOH, 99.8%, POCh), and methanol (MeOH, for HPLC, Merck). Cetyltrimethylammonium bromide (CTAB, Fluka), triton-X 100 (TX, Aldrich) and sodium dodecyl sulphate (SDS, Aldrich) were used as micelle forming surfactants. CTAB forms cationic, SDS anionic and TX non-ionic micelles in aqueous solutions (purified and deionised water was used).

The synthesis of colloidal MCM-41 mesoporous molecular sieves was performed following the procedure described in [20], from sodium silicate (Aldrich) using Pluronic P123 (poly (ethylene oxide)–*block*-poly (propylene oxide)–*block*-poly (ethylene oxide)—(EO₂₀PO₇₀EO₂₀; $M_{av} = 5800$) Basf) as the structure directing agent. Three grams of sodium silicate were dissolved in deionised water and after adjusting the pH to 3 (using HCl), poured into a water solution containing P123 (molar ratios of Si/P123 = 48 and Si/H₂O = 0.00019). The resultant mixture was kept at room temperature for 24 h without stirring. The product was washed repeatedly by centrifugation (at 4,000 rpm) and redispersed in water, than dried and calcined at 773 K.

Conventional mesoporous molecular sieves of MCM-41 type were synthesized by hydrothermal method according to the procedure described in [21, 22]. The synthesis was carried out in the presence of cetyltrimethylammonium chloride (Aldrich) as a surfactant, from mixtures containing aluminium and silica sources. The reactant mixture consisted of sodium silicate (27% SiO₂ in 14% NaOH, Aldrich) for the preparation of MCM-41 and additionally appropriate amount of aluminium sulphate (POCh) for AIMCM-41 material. The ratio of Si/Al in the gel was assumed as 64. The gel formed from these components was stirred for about 0.5 h. The pH was adjusted to 11, then distilled water was added. The gel was loaded into a stoppered polypropylene bottle and heated without stirring

at 373 K for 24 h. The mixture was then cooled down to room temperature and the pH level was adjusted to 11. This reaction mixture was heated again to 373 K for 24 h to produce highly ordered samples. The resulting precipitated product was washed with distilled water, dried in the air at ambient temperature, and the surfactant in the solid was removed by calcination at 823 K, 2 h in helium flow and 14 h in the air under static conditions.

Hydrogen forms of MCM-41 materials as well as NaY (Katalistiks) were obtained *via* cation exchange with NH_4^+ ions and calcination of the modified samples at 673 K for 2 h. The ion exchange was performed using a conventional method, i.e. stirring of the solid in aqueous solution of NH_4Cl (0.05 M) for 5 h at 323 K. This procedure was repeated two times. The ammonium ions content in the solution corresponded to the number of aluminium atoms in the material. In the case of silicate MCM-41 the same concentration of solution was used. After the ion exchange procedure, the solid was washed with distillate water to remove chloride ions in the filtrate.

The equipment for stationary measurements in solution was the same as described in our previous papers [19]. Briefly, the stationary UV-vis absorption spectra were measured with a UV-VIS-550 (Jasco) spectrophotometer. The steady-state fluorescence emission spectra and the fluorescence excitation spectra were recorded with a modified SPF-500 (Aminco-Bowman) spectrofluorimeter (with the single-photon counting detection). All fluorescence spectra were corrected for the wavelength sensitivity of the detection system and the excitation spectra were corrected for the excitation lamp intensity.

The apparatus used for the time-resolved emission measurements (Time Correlated Single Photon Counting—TCSPC) was described in details earlier [23]. The repetition rate of the laser system for the time-resolved emission measurements (Ti: Sapphire) was set at 4 MHz providing pulses of about 1 ps duration. The temporal resolution of the spectrofluorimeter was about 1 ps, and the spectral resolution was 9 nm.

A Bruker FTIR Vector 22 spectrometer was used to detect infrared spectra of the solid state powder MCM-41 samples. The resolution was selected to be 2 cm^{-1} and the number of scans was 64. The samples were dispersed in KBr pellet (1 mg of the sample and 200 mg of KBr) with slight grinding. FTIR measurements were performed at room temperature.

UV-Vis spectra of solid state powder samples were obtained with a Cary 300 spectrometer (Varian). The Kubelka–Munk function ($F(R)$) was used to convert reflectance measurements into equivalent absorption spectra using the reflectance of SPECTRALON as a reference. Spectra were recorded at room temperature in the 200–800 nm range.

The effect of irradiation of the sample powders was measured using the 200 W output of a high pressure mercury lamp. Two colored filters of transmission for wavelength $<400\text{ nm}$ and $>500\text{ nm}$ were used for ultra-violet or visible irradiation, respectively.

Results and discussion

Our initial idea was to synthesize a mesoporous MCM-41 material with the particle size of less than 100 nm to obtain a colloidal solution that is transparent enough to permit the transmission spectroscopic studies like for microporous molecular sieves [2]. However, our attempt with the mesoporous colloidal material was not fully successful. We obtained MCM-41 crystals in which the particles of less than 100 nm in size were coexisting with much larger assemblies (see the images from the transmission and scanning electron microscopy in Fig. S1 in the supplementary information) and their ratio was difficult to estimate. After adding the MCM-41 material to the solution of BSP (concentration of about 10^{-4} M) in ACN or HEX (several mg per 10 mL of the solution) the diffusion of BSP into the channels of MCM-41 and its adsorption took place in the time scale of several hours. Part of the particles formed a colloidal solution, while the heavier rest dropped down. Therefore, the solution was used for the transmission spectroscopic measurements, while the larger particles of molecular sieves with encapsulated BSP were used (after stirring and drying) for the solid state spectroscopic studies.

The stationary transmission absorption studies revealed that the initial (after several tens of minutes to single hours) changes in the BSP spectrum involve the appearance of the cis-keto tautomer band with a maximum around 450 nm (in pure ACN and HEX only the enol tautomer band with maximum around 370 nm is present), see Fig. 1a. The red shifted band is even better observed in the excitation emission spectrum (emission of cis-keto tautomer measured at 550 nm), see Fig. 1b, since the influence of the scattered light from the colloidal particles is smaller. The probable explanation of the presence of the red shifted band is the stabilization of the BSP cis-keto tautomer by the intermolecular hydrogen bonds with the MCM-41 silanol (Si–O–H) groups, like it was observed in homogenous alcohol solutions [19]. It can be compared with the results of the solid state studies of SA in zeolites [5] whose authors concluded that the proton donating ability of zeolites (where both silanol groups as well as Brønsted acid sites are present) is between that of trifluoroethanol and hexafluoroisopropanol and depends on the ratio of Si/Al. Our results show that in mesoporous silica of MCM-41 type (where no Al atoms are present) the ability to form hydrogen bonds with Schiff bases is similar (the keto to

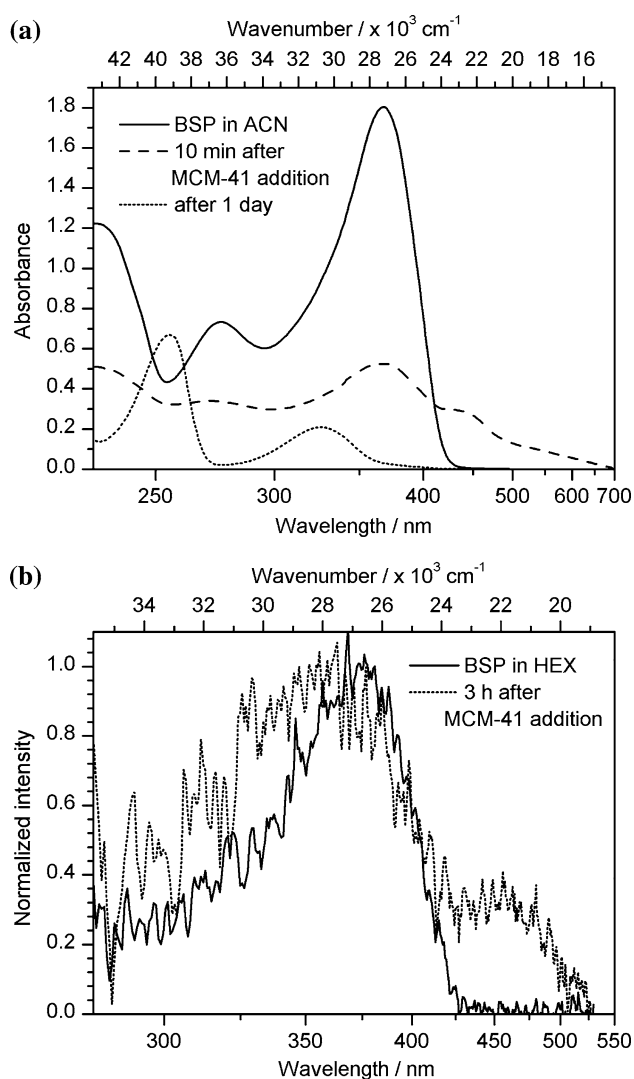


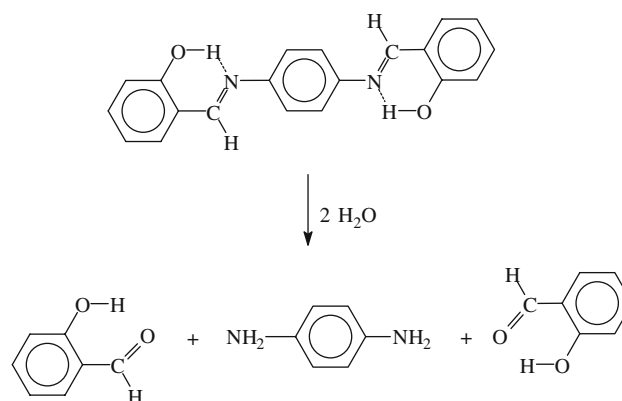
Fig. 1 Effect of adding MCM-41 sieves on the stationary absorption spectra of BSP in ACN (a) and on the fluorescence excitation spectra of BSP in HEX (b), the emission wavelength is 550 nm

enol absorbance ratio for BSP is 0.24 in trifluoroethanol [19] and 0.72 in hexafluoroisopropanol).

After several hours the absorption spectrum of BSP in colloidal MCM-41 drastically changes (Fig. 1a). Both visible bands decrease and new UV bands with maxima at 325 and 255 nm appear (in HEX the latter band has a double maximum). The excitation of these bands leads to the blue shift of the fluorescence from 570 nm (BSP in ACN [19]) to about 520 nm (Fig. S2). Such changes could be most probably assigned to the hydrolysis process of BSP that takes place in MCM-41 channels [9]. The hydrolysis of Schiff bases was observed for SA when water was added to the solutions in protic or acid solvents [24, 25]. It is usually explained by the water attack on the C=N bond of the Schiff base molecule which is weakened by the intermolecular hydrogen bond between the nitrogen atom and the

solvent or by the protonation of nitrogen. In BSP, the molecular decomposition by the presence of water leads to one *p*-phenylenediamine and two salicylaldehyde molecules (Scheme 2). Indeed, the stationary absorption and emission spectra of salicylaldehyde [25, 26] match the data obtained by us for BSP in MCM-41 (one day after preparing). We performed also the fluorescence lifetime measurements which yielded the values of about 40 ps in ACN when excited at 365 nm, close to the lifetimes obtained for salicylaldehyde in different solvents (50–75 ps) [27]. The shortening of the fluorescence lifetime might be caused by the interplay of the emission from salicylaldehyde and that of non-decomposed BSP (10 ps in ACN [18]). Moreover, we also obtained the same changes in BSP absorption spectrum when water was added to protic solutions (Fig. S3). It should be noted that the hydrolysis process was also observed when the additionally dried HEX was used as a solvent and MCM-41 molecular sieves were used just after the high temperature activation (dehydration). Therefore, even traces of water (if any) or silanol groups in neighborhood are enough to cause the BSP hydrolysis catalyzed in MCM-41 cavities. It is worthy to note that silanol groups in MCM-41 can take part in the chemical reactions with the adsorbed molecules (e.g. CO [28, 29]). When smaller amount of mesoporous material was added to the BSP solution, the equilibrium between BSP and salicylaldehyde was reached, reflected in the absorption and emission spectra.

In the solid state powder samples of BSP in MCM-41 no indications of hydrolysis products were found. Probably, the products of hydrolysis are not anchored in the MCM-41 channels and diffuse into the solvent. The maximum of the long-wavelength absorption band (measured by diffuse reflectance UV-vis spectroscopy) is equal 415 nm (Fig. 2) which is red shifted by $2,900\text{ cm}^{-1}$ with respect to that of the BSP enol band in solution (370 nm). There are at least two possible explanations of this fact. The red shift of the absorption band (by $1,600\text{ cm}^{-1}$) was observed in another



Scheme 2 Hydrolysis of BSP

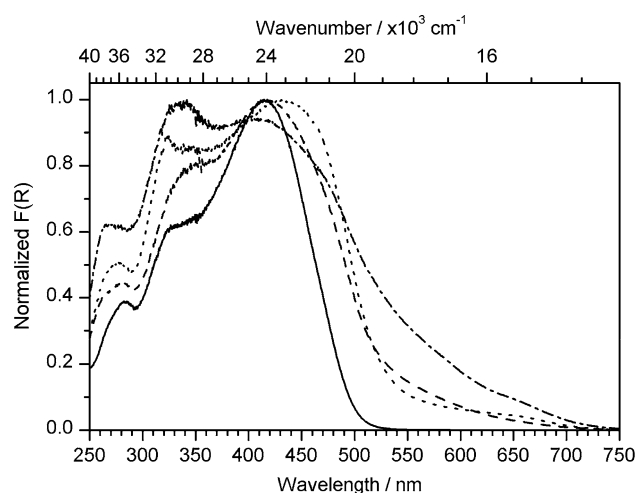


Fig. 2 Diffuse reflectance spectroscopy of BSP in MCM-41 crystal powder: before irradiation (*solid line*), after 2 h of UV irradiation (*dotted line*), 8 days after the irradiation (*dashed line*) and after 2 h of additional UV irradiation (*dashed and dotted line*)

symmetric Schiff base in MCM-41 [7] and explained by the reduction of HOMO-LUMO band gap of the enol tautomer due to the molecular orbital confinement in MCM-41 channels. On the other hand, the red shift of the absorption band of SA in NaY zeolites (from 350 to 400 nm) was interpreted as a result of the presence of SA in the cis-zwitterionic form in zeolite microcavities [8] (instead of the enol form present in solution), see Scheme 1. The solid state IR studies performed by us indicate that the latter rationalization should rather be applied to BSP. The infrared spectra of BSP in MCM-41 reproduce mainly the characteristic features of the host material, however the new bands of BSP can be found at 1,618 and 1,636 cm^{-1} (see Fig. 3). The strongest band of the crystal powder of BSP is located at 1,612 cm^{-1} (Fig. 3) and should be probably assigned to the C=N stretching vibration. There are no accurate literature data for BSP vibrations in this spectral region. However, for the parent SA molecule the C=N vibrations of the enol form were found at 1,620 cm^{-1} , the C=O vibrations of the keto form at 1,650 cm^{-1} , and the C=NH⁺ vibrations of the zwitterionic form at 1,635 cm^{-1} (in the IR spectra) or 1,640 cm^{-1} (in the Raman spectra) [5, 8, 30–32]. Therefore, the observed value of 1,636 cm^{-1} should be most probably assigned to the C=NH⁺ vibrations. It can be also noted that we do not observe any bands of the main vibration of salicylaldehyde at 1,670 cm^{-1} (C=O) [33].

After the irradiation of BSP in MCM-41 with the UV light (wavelength <400 nm) the initially yellow powder becomes orange within minutes and after further irradiation (within hours) changes its color into dark-red. The changes are accompanied by the increase in the intensity of the long-wavelength band (550–700 nm) in the diffuse

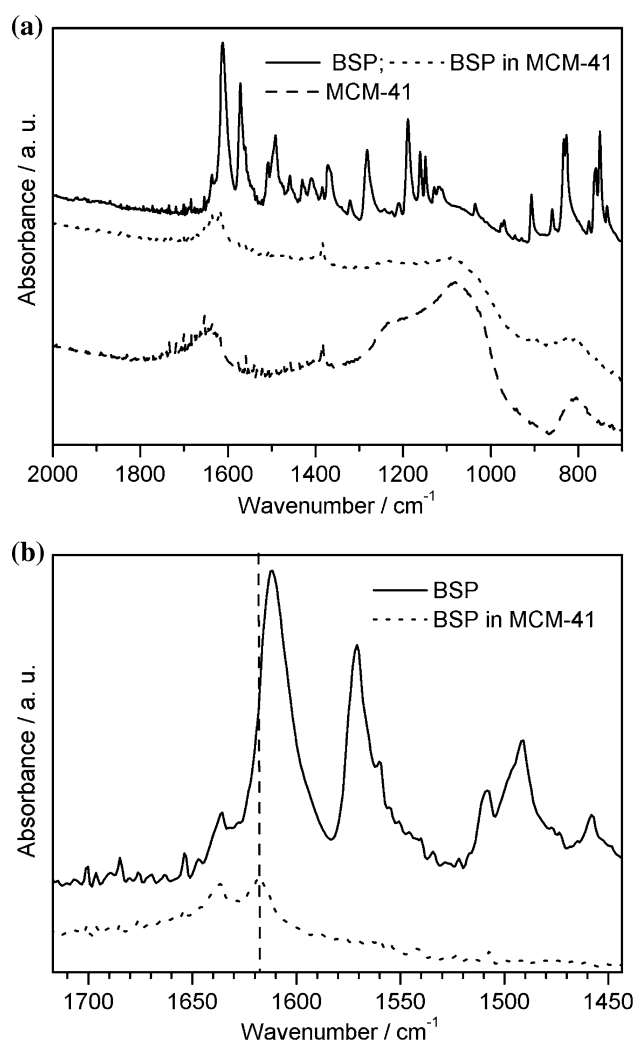


Fig. 3 The infrared spectra of BSP, MCM-41 and BSP in MCM-41 in the whole spectral range investigated (**a**) and in the narrowed range where the vibrations characteristic of BSP appear (**b**)

reflectance spectra of the sample, see Fig. 2. The intensity of this band does not decrease neither when the sample studied is kept for several days in the dark nor when it is irradiated with visible light (wavelength >500 nm). Therefore, the lifetime of such a photochromic form (probably trans-keto tautomer) is very long. It should be emphasized that the BSP crystals are thermochromic [14, 15] and we also confirmed that the UV irradiation of the crystal powder of BSP causes almost no change in its spectrum (Fig. S4). Therefore, the encapsulation of BSP in mesoporous molecular sieves drastically changes its photochromic properties in solid state.

Persistent color changes were also observed for SA in zeolites [8] and for the thermochromic Schiff base N-(5-chlorosalicylidene)aniline in MCM-41 [6]. The new observation in our work is that the light-induced modification of absorption spectra is a two step process: at first a

new band with a maximum around 450 nm appears, which then decomposes within tens of minutes partially into the further long-wavelength band (550–700 nm) and partially to the initial form with a maximum at 415 nm (see Fig. 2). Having in mind the position of the ground state absorption of different BSP tautomers in solution this transient unstable form can be assigned to the cis-keto tautomer.

Finally, we have also performed preliminary measurements of BSP encapsulated in MCM-41 material modified by the presence of the acidic centers H–Al–MCM-41 and H–Si–MCM-41 as well as in microporous HNaX zeolite. The exemplary diffuse reflectance spectra are presented in Fig. S5. In all cases after irradiation the long-wavelength band appears together with the short wavelength bands below 350 nm. In MCM-41 with acidic centers the short wavelength light-induced bands grow to higher intensities than in silica MCM-41.

Next, we report the measurements of BSP in micro-heterogeneous micelles. The maximum concentration of BSP in three micellar systems (TX, CTAB, SDS) deduced from the absorbance at maximum of the enol band (370 nm) was about 1×10^{-6} M when the concentration of the surfactants in water was 0.15 M (in TX we performed also measurements for 0.45 M and the BSP concentration was slightly higher with the results being the same). The solubility of BSP in pure water was below 1×10^{-7} M. Therefore, it can be safely assumed that the signals obtained originate from the BSP molecules inside the micelles and that not more than one BSP molecule is present in one micelle [34].

As expected [35] the hydrolysis of BSP occurs, which is evidenced by the stationary absorption bands at 325 and 255 nm in anionic SDS and cationic CTAB (Fig. S6). Also, the relatively low concentration of BSP in micellar systems indicates that the hydrolysis products are formed. For BSP in TX it is difficult to observe these products since the absorption of TX reaches 320 nm. However, the characteristic band of BSP at around 370 nm is present, which means that in the non-ionic micelles the hydrolysis is not so dominant (Fig. S6). The incorporation of BSP into the micelles took place in the time scale of single days (without stirring). However, on even longer time scale (tens of days) further absorption changes were observed leading to the appearance of a new band at 500 nm (Figs. S6 and S7). These changes were observed also when the sample was kept in the dark but not when it was kept at low temperatures, thus they are of thermal character. Moreover, we also observed similar changes in alcohol and water mixtures. Due to the scattering of light, the 500 nm band is better visible in the fluorescence excitation spectra, see Fig. 4. The excitation at 500 nm leads to the emission with a maximum at around 600 nm, which is red-shifted

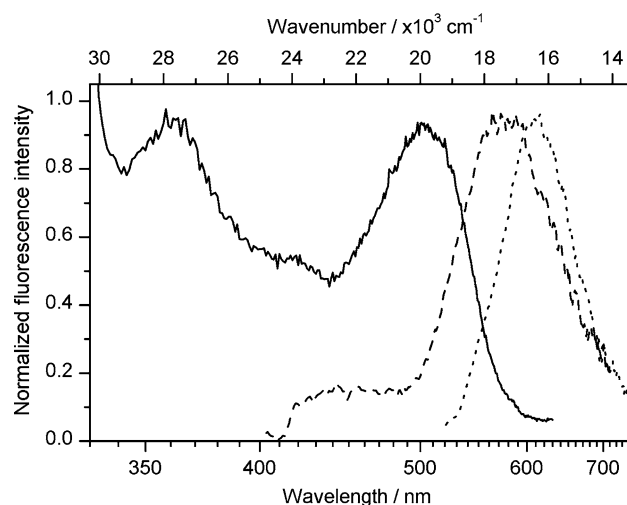


Fig. 4 Stationary fluorescence (dotted line—excitation at 500 nm, dashed line—excitation at 360 nm) and fluorescence excitation spectra (measured at 650 nm) of BSP in TX (1 month after BSP addition to the surfactant solution, concentration of detergent in water was 0.15 M)

with respect to the emission of the BSP cis-keto tautomer (Fig. 4).

It should be noted that the hydrolysis products are simultaneously the substrates for the BSP synthesis. Therefore, most probably an equilibrium between salicylaldehyde, *p*-phenylenediamine and BSP exist in solution and the new spectroscopic feature can originate from any of them. According to our knowledge, the hydrolysis products or their possible tautomers (stable in the ground state) do not exhibit any absorption band for wavelength longer than 400 nm. On the contrary, the positions of the new absorption and emission bands are similar to that the BSP photochromic form [11] (trans-keto tautomer). Therefore, the species responsible for the 500 nm absorption and 600 nm emission bands could be assigned to the complex of BSP photochrome tautomer and water molecules. In such efficiently stabilized trans-keto tautomer the hydrolysis process is probably suppressed.

Conclusions

The most important findings from this paper concerning the BSP molecules (probably also relevant for many other Schiff bases) are the following:

- (1) The intermolecular hydrogen bonds between BSP and silanol groups in mesoporous MCM-41 material (located in nonprotic solvent) lead initially to the stabilization of the BSP cis-keto form and later to a very effective hydrolysis of BSP.

- (2) Persisting color changes occur after the UV irradiation of the powder of BSP encapsulated in MCM-41 mesoporous sieves, while no color changes take place for the BSP crystal powder. The light-induced modification of absorption spectra is a two step process. Most probably, the initial cis-zwitterionic form of BSP is transferred to the cis-keto tautomer and later to the very stable trans-keto tautomer.
- (3) A long-term stabilization of a new BSP tautomer with long-wavelength absorption and emission is observed in micellar systems in water and alcohol-water mixtures.

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