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ORIGINAL PAPER: SUPRAMOLECULAR MATERIALS

The fluorescence study of a styryl dye supramolecular complexes with cucurbit[6]uril and cucurbit[7]uril included in gels

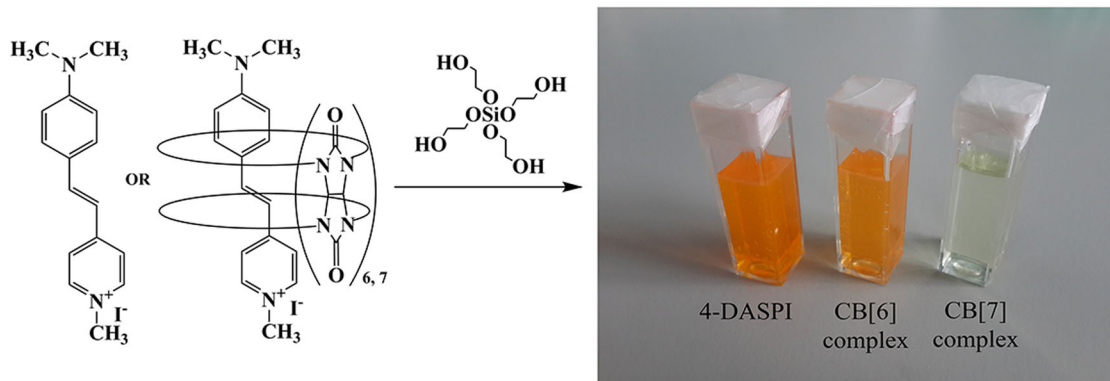Alexander V. Koshkin[1] · Nadezhda A. Aleksandrova[1] · Denis A. Ivanov[1]

Abstract The fluorescence properties of the silica gels based on tetrakis(2-hydroxyethyl)orthosilicate containing supramolecular complexes of the trans-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide were studied. For the first time the fluorescent gels with organic supramolecular complexes were synthesized by direct addition of cucurbit[6]uril and cucurbit[7]uril 4-trans-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide complexes into the reaction mixture. The comparison of spectral properties of free dye containing gels with complex containing ones showed complexes to be stable in the reaction conditions.

Graphical Abstract

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1 Introduction

Due to their manifestation of additive properties, cyclodextrin- and cucurbituril-based supramolecular complexes containing organic dyes have been drawing attention of researchers for several decades. A subject of a special interest here is photophysical properties and sensor characteristics of cucurbituril complexes with organic fluorophores. Adding dyes into complex structures often allows to drastically change their fluorescent properties [1].

In spite of a great number of research works dedicated to the behavior of cucurbituril complexes in water and other solvents [2, 3], the literature sources contains few if no instances of obtaining and analyzing properties of solid materials or gels containing supramolecular complexes of organic dyes. The main reason of that is the reversibility of complex formation and, as a result, a narrow range of conditions for the complexes existence. Used as solvents in common methods of making tetraalkyl ortosilicates based gels, the alcohol-water mixtures leading to disruption of

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supramolecular complexes. Moreover, tetraalkyl ortosilicates hydrolysis requires acidic or basic media, which is a negative factor influencing complex stability. Consequently, deriving siliceous materials containing cucurbituril complexes by means of sol-gel synthesis is rather a challenge.

Dedicated literature sources mention a water soluble precursors for a sol–gel synthesis- tetrakis(2-hydroxyethyl) orthosilicate (THEOS) requiring no acidic or basic catalysts in the reaction mixture. There are some successful examples of adding quantum dots and cyclodextrin into gels based on this compound [4, 5]. It was suggested that carrying out a synthesis of gels on the base of these compounds in the presence of cucurbituril complexes containing styryl dye would allow obtaining and analyzing optical properties of hybrid materials.

4-DASPI styryl dye **1** was chosen as a fluorophore (Fig. 1). The choice of this dye was determined by the fact that the growth of viscosity of local surrounding of 4-DASPI molecules is accompanied by substantial changes in its fluorescence spectra [6, 7]. As in the process of gelation the viscosity of the media changes [8, 9], we can expect substantial changes in optical properties of the system while the gel-process occurs. Moreover, complex formation involving cucurbituril is also accompanied with a substantial change of dye fluorescence spectra [10, 11], which significantly simplifies the analysis of experimental data.

2 Experimental part

2.1 Materials

Trans-4-[4-(dimethylamino)styryl]-1-methylpyr-idiniumiodide (Aldrich), cucurbit[6]uril (CB[6]) (Aldrich), cucurbit[7]uril (CB[7]) (Aldrich), tetraethoxysilane (Aldrich), ethylene glycol (Chimmed) and metanol (Aldrich) were used without additional purification.

2.2 Dye and complex solutions preparation

To prepare aqueous solutions of 4-DASPI dye **1** and its complexes in required concentration 2.6×10^{-5} mol/l, aqueous (Milipore water-based) stock solutions **1**, CB[6] or CB[7] in the concentration of 1×10^{-4} mol/l were used. Complex solutions were made by adding of the required amount of CB[6] or CB[7] stock solution into the dye aqueous solution at a mole ratio of 1:1.2. Excess of cucurbituril was required to shift equilibrium in the solution towards complex formation. As the commercially available cucurbiturils usually contains some amount of acid, to ensure equal pH conditions, the control on the pH of the solution was made by using Mettler Toledo SevenEasy pH-meter. The pH range of all solutions was in the range of 6.5–6.6.

2.3 THEOS synthesis procedure

Synthesis of the THEOS was carried out in accordance with the method described in the paper [12]. A mixture of 59.4 ml (0.267 mol) tetraethoxysilane and 60 ml (1.05 mol) ethylene glycol was prepared, and then it had been stirred for 20 h while having been heated to 140 °C in the inert atmosphere. Reaction monitoring was carried out by measuring the resulting amount of ethyl alcohol evolved during the reaction. The ethyl alcohol distillation stopped when its amount reached 38.8 ml (30.8 g) of 62.2 ml theoretically possible. The remains of ethyl alcohol were removed from the reaction mixture by the vacuum distillation. The resultant, THEOS, was a 89.24 g of viscous transparent liquid. The purity of the reaction product was determined by means of ^{1}H NMR spectroscopy and found to be 94 %. The reaction product was used to make a gels without additional purification.

2.4 General procedure of gels preparation

To make a THEOS–based gels containing **1**, 1000, 500 or 250 mcl THEOS was vigorously mixed with 800, 1300 or 1550 mcl of water correspondingly and 1200 mcl of the dye **1** aqueous solution in the concentration of 2.6×10^{-5} mol/l in a standard disposable fluorometric plastic cuvettes (ray path length is 1 cm). The resulting concentration of the dye in the reaction mixture was 1.04×10^{-5} mol/l. The cuvettes were hermetically covered with parafilm and held at the temperature of 24 °C. 24 h later, the solution transforms into a gel state, and the derived gels were transparent, lightly opaque solids of yellowish orange colour.

Analogically, samples of gels containing cucurbituril complexes were made. The concentration of stock solutions of **1**:CB[6] and **1**:CB[7] complexes was 2.6×10^{-5} mol/l, and the concentration of the complexes in the gel was 1.04×10^{-5} mol/l.

2.5 Fluorescence and ^{1}H NMR spectra measurements

The analysis of fluorescent properties of the fluorescent gels were carried out by use of Shimadzu 5301PC spectrofluorimeter. Registration of the fluorescence spectra was carried out immediately after the reaction mixture preparation, then 24 h and 7 days later after the reaction had begun.

Spectral data required for kinetics of the fluorescence intensity on time were obtained by use of Avantes 2048 fibre optic spectrometer. Registration of the fluorescence spectra was carried out every 30 min for the first 24 h after the sample was prepared and once an hour during the following 6 days.

^{1}H NMR spectra for precursor purity characterization were collected on «Bruker Avance-400» ^{1}H NMR
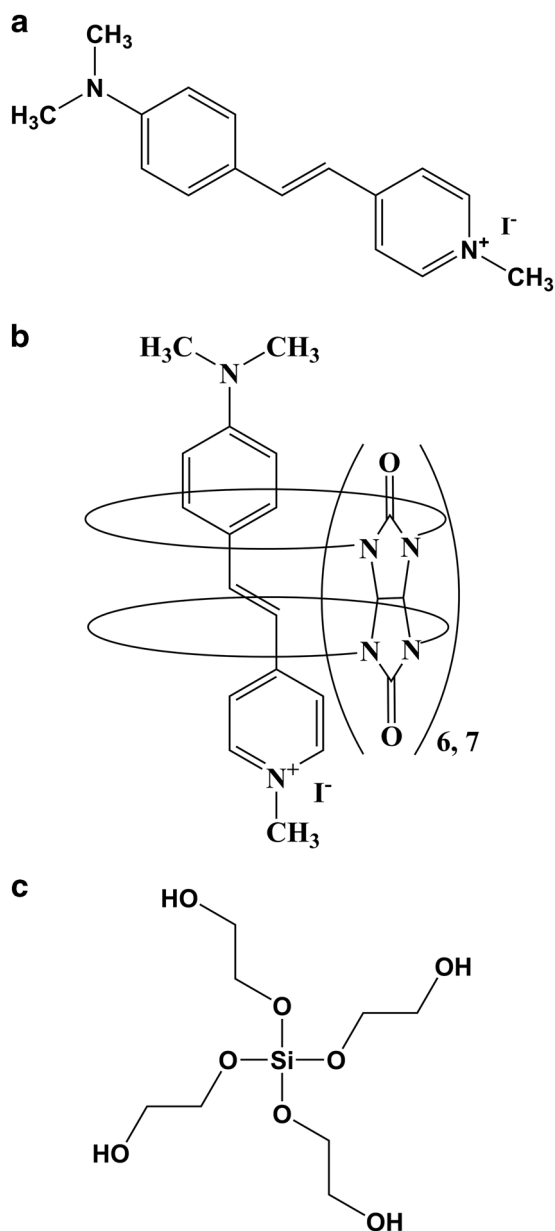
Fig. 1 Molecular structures of 4-DASPI (a); 4-DASPI cucurbituril complexes (b); THEOS (c)

spectrometer (working frequency 400 MHz), using CDCl$_3$ as solvent. TMS was used as internal standard.

3 Results and discussion

3.1 Spectral properties of dye 1 and its complexes in water

Adding of the cucurbiturils into the dye **1** solution resulted in substantial changes in fluorescence spectra intensity. Figure 2 shows the fluorescence spectra of the solution of
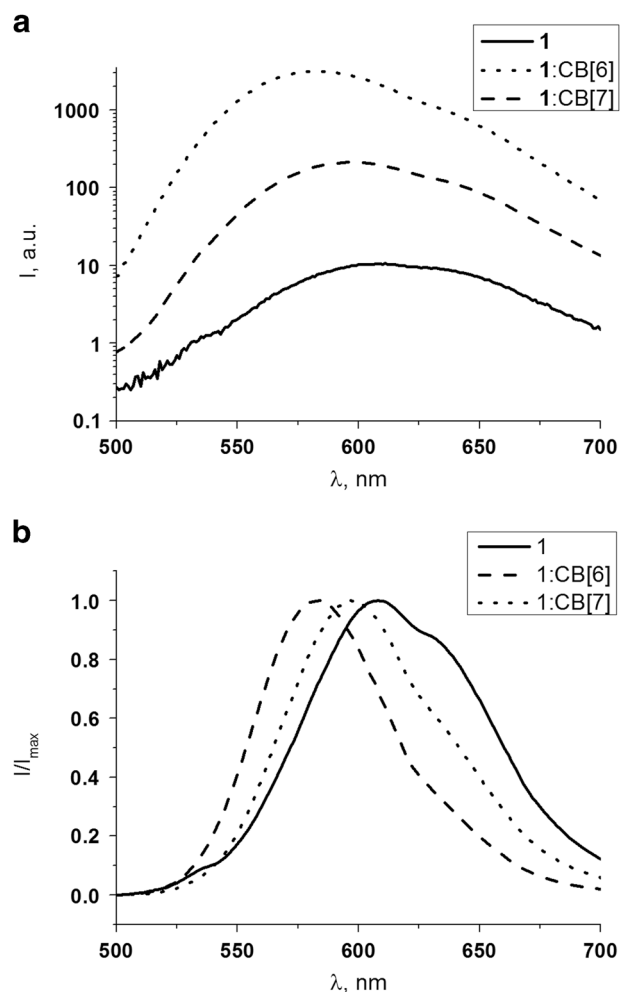

Fig. 2 Fluorescence spectra of dye **1** and its **1**:CB[6] and **1**:CB[7] complexes in water, the excitation wavelength is 450 nm (**a**), normalized fluorescence spectra of dye **1** and its **1**:CB[6] and **1**:CB[7] complexes in water (**b**)

the dye **1** and its **1**:CB[6] complex excited at the wavelength of 450 nm and **1**:CB[7] complex under the excitation at the wavelength of 325 nm. The difference in excitation wavelength values is explained by the fact that there is hardly any absorption of **1**:CB[7] complex within 450 nm range.

It is clear that CB[6] adding into the dye **1** solution leads to a rise in the fluorescence intensity by two values accompanied by a simultaneous hypsochromic shift of the fluorescence band maximum by 24 nm. Adding of CB[7] into the dye **1** solution resulted in a significantly lower growth of the fluorescence intensity within 590 nm range, however, a wide peak corresponding to **1**:CB[7] complex appeared within 360 nm range.

Analysis of the dye **1** and it's complexes absorption spectra showed the addition of cucurbit[6]uril to the dye solution not to affect on the position of the maximum and form of the spectrum, whereas the addition of cucurbit[7] uril resulted in disappearing of the long wavelength band at
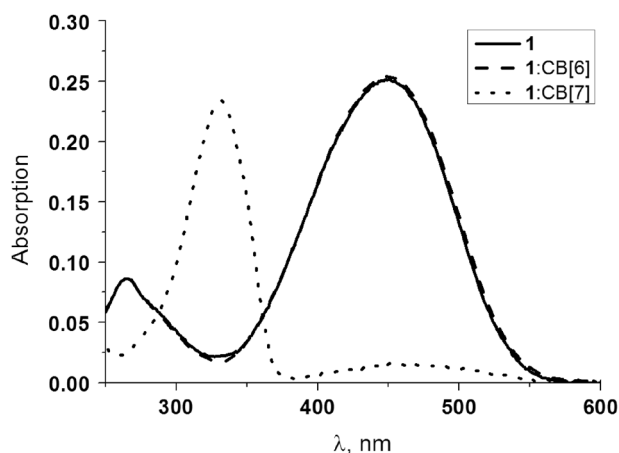
Fig. 3 Absorption spectra of the dye **1** and its complexes

450 nm and formation of the short wavelength band at 320 nm (Fig. 3). This fact explains lack of the fluorescence signal while irradiating the solution of the **1**:CB[7] complex at 450 nm. Such spectral changes could be attributed to the protonation of the dye inside CB[7] cavity [11]. The measurements of dye **1** pK_a showed an increase upon **1**:CB[6] complex formation [10]. It is possible to suppose the reason of protonation of the dye **1** in **1**:CB[7] complex to be the same, but more strong influence of CB[7] allowing protonation to occur even in buffer solution with pH 7.4 as it was shown in [11]. This should explain the difference of the spectral behavior of the complexes in our experimental conditions.

Also, it should be noted the protonated dye **1** to be capable to form 1:2 complexes with CB[7] while working with more than 1 equivalent of CB[7]. Fortunately, the fluorescent spectra of 1:1 and 1:2 complexes are shown to be the same [11], so the formation of 1:2 complex will not interfere the fluorescent determination of the free dye **1** presence in silica gel. This making **1**:CB[7] a good choice to ensure the complex integrity in the silica gel. Indeed, the significant changes of the absorption and fluorescence spectra together with intensity of the fluorescence while **1**:CB[7] complex formation is quite a rare case [13], the specific protonation of dye in complex allows to clearly distinguish between bound and unbound dye.

3.2 Spectral properties of the gels with unbound dye **1**

The analysis of the spectral properties of dye **1** in the gelation process showed that there was a substantial rise in the fluorescence intensity immediately after adding the dye into the reaction mixture (Fig. 4a). However, mixing all of components was followed by almost no changes in the spectrum form or fluorescence maximum position. This can
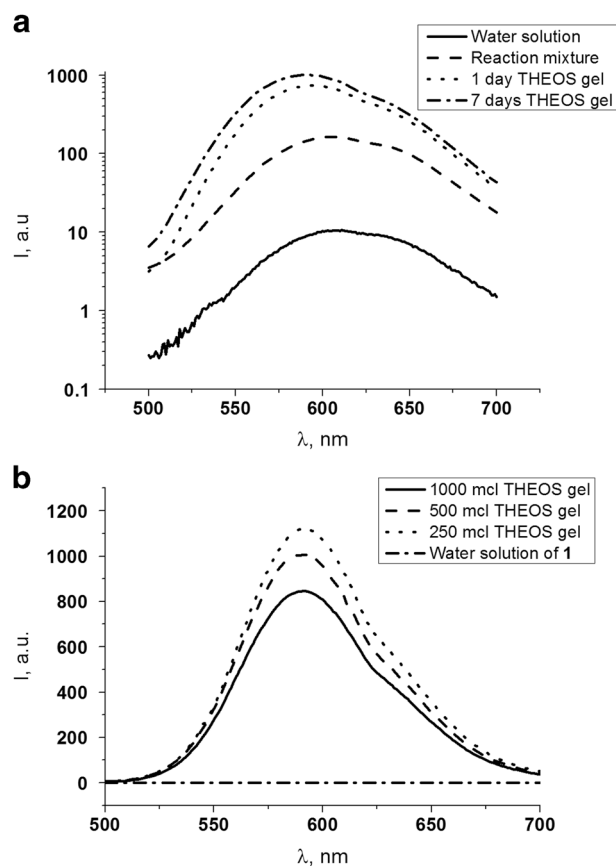

Fig. 4 Changes in the fluorescence intensity of the dye **1** during the ageing of the gel made with 500 mcl of the THEOS (**a**), the fluorescence spectra of the dye **1** in the gels with different amount of the THEOS 7 days later after the gelation was started (**b**). Dye **1** concentration in all samples was 1.04×10^{-5} mol/l

be explained by the raised viscosity of dye molecules surrounding, which nevertheless remains unstructured.

The gelation process is followed by a further growth of the intensity in the fluorescence spectra accompanied by a hypsochromic shift of the fluorescence band maximum by 16 nm. The gelation appears to be accompanied by the change of the local surrounding of the dye molecules due to building up a compact lattice of non-polar THEOS fragments. In this case, the bathochromic shift of the fluorescence band maximum can be correlated to displacement of the residue of water from the nearest dye surrounding followed by its replacement by less polar gel fragments. The effect of the fluorescence intensity rise was observed even 7 days later after the gelation had been started.

The amount of the THEOS taken to make the gel samples also influenced fluorescence intensity of the samples. An increase of the THEOS amount in the reaction mixture leads to a fall in the fluorescence intensity of the gel samples (Fig. 4b). One of the possible explanations of the fluorescence intensity decrease with the increase of THEOS concentration is the concentration quenching of the dye **1**
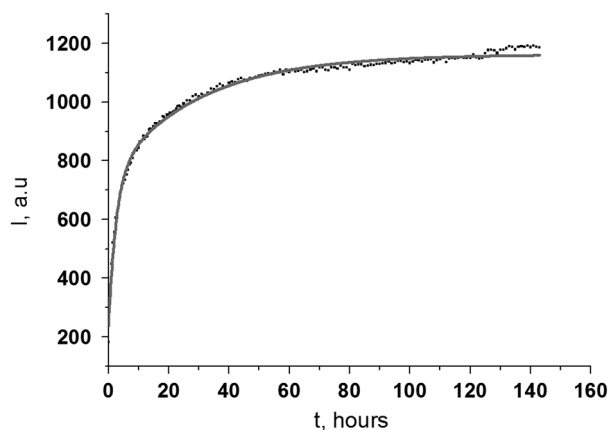
Fig. 5 Dynamics of fluorescence change of the gel sample prepared from 500 mcl of the THEOS in the presence of dye **1**. Experimental data and approximation curve are shown

fluorescence as a result of the formation of pores of smaller size.

To estimate the time required for building up a three-dimensional lattice of the gel and its influence on the fluorescence intensity of the dye in the gels, we have studied a dependence of the fluorescence intensity at the wavelength of 590 nm on time and carried out an approximation of the experimental data (Fig. 5).

It is clear that the process of changing the fluorescence intensity of the gel sample containing 500 mcl of THEOS has still been continuing even 1 week later after the reaction had started. The experimental data were approximated by biexponential rule with correlation coefficient equaled to 0.992. It points at two processes—quick building up of a three-dimensional lattice finishing approximately in 20 h and a slow process of gel maturation continuing for quite a long period of time. Thus, to carry out a further comparative analysis of the fluorescent properties of the dye **1** and its complexes in the gel, we used the fluorescence spectra of the samples obtained immediately after the reaction mixture was prepared and those derived 24 h and 7 days later.

3.3 Gel samples with **1**:CB[6] complex

Adding **1**:CB[6] complex solution into the reaction mixture resulted in substantial changes in the fluorescence spectrum of the complex. Figure 6a shows the fluorescence spectra of the complex aqueous solution and complex aqueous solution in the presence of 500 mcl of THEOS amount of time later after the preparation of the reaction mixture. It is clear that adding THEOS into the system leads to a sharp fall of the fluorescence intensity accompanied by an insignificant hypsochromic shift of the fluorescence band maximum position. A more significant effect of the fluorescence band maximum shift followed the process of gelation. The
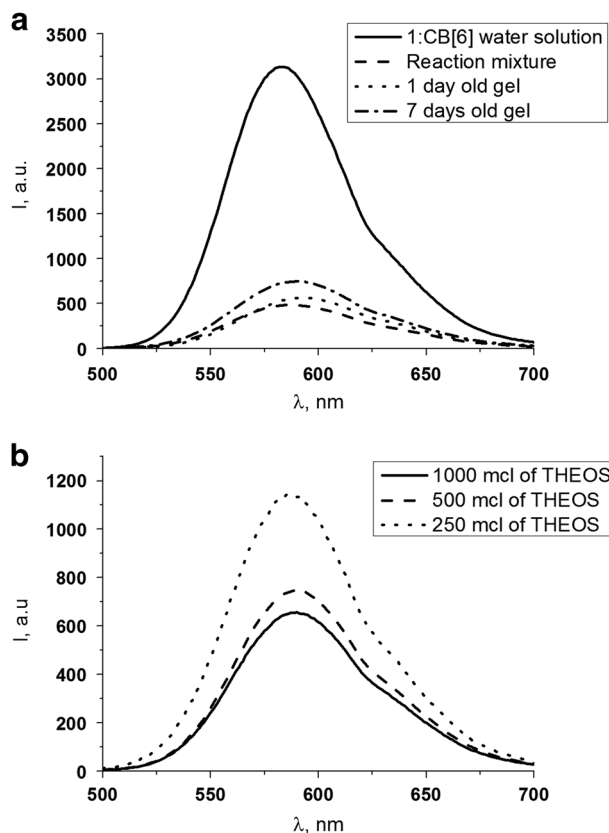

Fig. 6 Fluorescence spectra of **1**:CB[6] complex solution in water, in the reaction mixture, in the gel immediately after the process of its formation and in the gel 1 week later. The concentration of **1**:CB[6] complex was 1×10^{-5} mol/l (**a**); fluorescence spectra of the 7 day old gels with **1**:CB[6] complex prepared from different amount of the THEOS (**b**)

fluorescence maximum shift of the complex in water in relation to its reference spectrum equaled 11 nm. However, 1 week later after the preparation of the gels the registered fluorescence band maximum value was within 590 nm range (8 nm hypsochromic shift in relation to its starting position). As the maximum values of the fluorescence spectra of the pure dye **1** and **1**:CB[6] complex in the gel are close (590 and 591 nm correspondingly), it is impossible to make a precise conclusion of the complex structure integrity.

As in the case with the gels derived by use of pure dye **1**, as the amount of THEOS the reaction mixture rises, the fluorescence intensity of the gels falls (Fig. 6b).

To better understand the behavior of the **1**:CB[6] complex in the reaction media, the titration of complex solution (1×10^{-5} mol/l) with THEOS was carried out (Fig. 7a). The experimental data were processed according to the Stern–Volmer law, the results are show on Fig. 7b. The linear approximation of the data was made with correlation coefficient 0.997. Based on the obtained data, it is possible to conclude the addition of THEOS to **1**:CB[6] complex
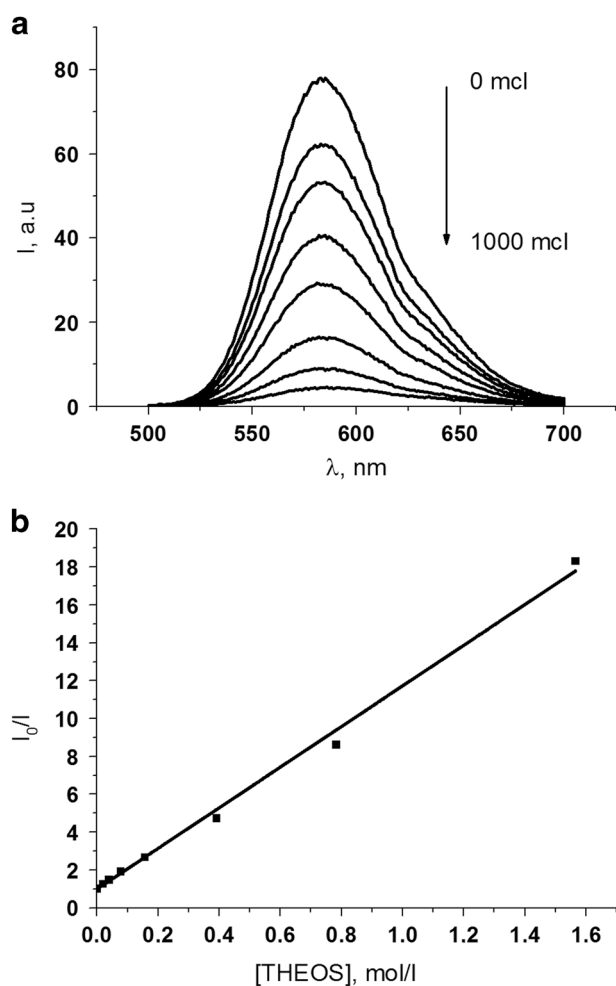
a

b

Fig. 7 Fluorescence spectra of the fluorescence quenching of 1:CB[6] in presence of increasing amounts of THEOS (**a**); Stern–Volmer quenching plots (**b**)

Table 1 Intensity of the fluorescence of the gels with dye **1** or **1**:CB [6] prepared from different THEOS amount

Fluorophore	Amount of THEOS (mcl)	λ max (nm)	I_{max} a.u.
1	250	591	1207
1:CB[6]	250	589	1136
1	500	591	895
1:CB[6]	500	590	746
1	1000	593	796
1:CB[6]	1000	587	733

solution does not result in the complete complex destruction as the release of fluorescent dye **1** from the complex should lead to the nonlinearity of the approximation.

The comparative analysis of the fluorescence intensity of the gels made by use of pure dye **1** and samples containing **1**:CB[6] complexes carried out at the wavelength of 590 nm showed that in all the cases the fluorescence intensity of the
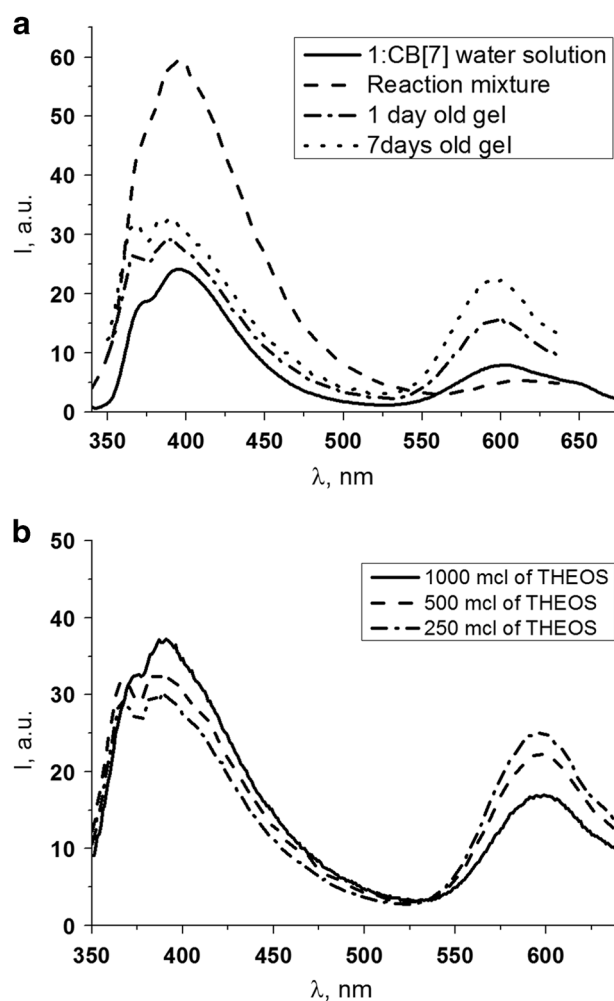
a

b

Fig. 8 Fluorescence spectra of **1**:CB[7] complex solution in water, reaction mixture and gels of different age. The concentration of **1**:CB [7] complex was 1×10^{-5} mol/l (**a**); fluorescence spectra of **1**:CB[7] complex in 7 day old gels made by use of the THEOS in different concentrations (**b**)

samples containing the complex was lower than that of analogical samples containing the dye **1** (Table 1).

From the measurement results, it follows the viscosity of dye molecules surrounding in the gels made by use of the pure dye **1** to be higher than in the gels derived by use of **1**: CB[6] complex. As a whole, the obtained data show that adding complexes into gel is accompanied with a substantial change in **1**:CB[6] complex structure, but no full complex disruption follows. Cucurbituril molecules are in close proximity to the dye **1** molecules, which gives the fluorophore a freedom of swinging motions and results in a fall in the fluorescence intensity of the system.

3.4 Gel samples with 1:CB[7] complex

Complex formation of the dye **1** with CB[7] hardly resulted in any changes in the fluorescence spectra of the solutions.
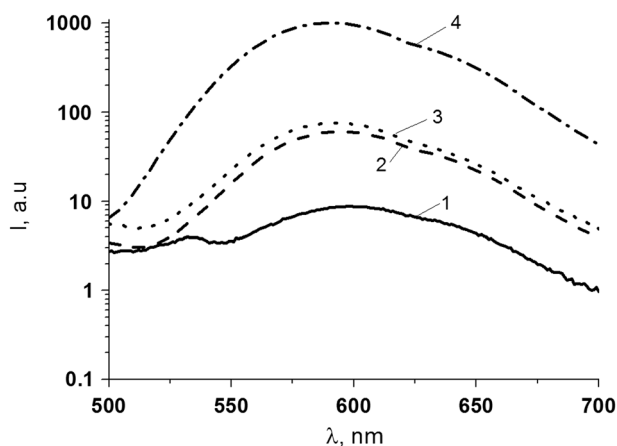
Fig. 9 Fluorescence spectra of the reaction mixture with 500 mcl of THEOS (*1*) and gels containing **1**:CB[7] complex 1 (*2*) and 7 days (*3*) after the beginning of the reaction and 7 days old gel with unbound dye **1** (*4*)

The fluorescence intensity of **1**:CB[7] complexes within 590 nm range is low (Fig. 2), so it was suggested that in the case of complex disruption in the process of gel formation there should be a substantial rise in fluorescence intensity of the samples.

Figure 8a demonstrates the fluorescence spectra of the gel sample with the unbound dye and **1**:CB[7] complex, obtained by the use of 500 mcl of the THEOS. Adding **1**:CB[7] complex solution was immediately followed by an increase in the fluorescence intensity within 360 nm range associated with the viscosity growth of complex surrounding. However, the changes within 590 nm range were extremely small, which definitely allows us to confirm the suggestion of the complex structure integrity in the sol-gel process conditions.

A significant change in the fluorescence spectrum was observed 24 hours later after the formation of the gel three-dimensional structure starts. The band intensity with the maximum value at 390 nm fell nearly to the initial value, while the band intensity with the maximum value at 366 nm remained higher as compared to the spectrum of **1**:CB[7] complex in water.

It should be noted that the fluorescence intensity within 590 nm is inversely proportional to THEOS concentration in the reaction mixture (Fig. 8b). As the analogical changes were same for gel samples with unbound dye, we carried out a comparative analysis of the fluorescence intensity of gel samples on the base of 500 mcl of THEOS containing **1**:CB[7] complex and analogical gel sample containing pure dye **1** to confirm the integrity of the complex structure in gel. From the data given in Fig. 9 it is clear that after the formation of a gel structure in the fluorescence spectra of the samples with **1**:CB[7] complex we observe the appearance of a band within 590 nm range proposed to correspond to the unbound dye.

However, fluorescence intensity of the samples with **1**:CB[7] complex is small as compared to the fluorescence intensity of the samples made by use of the pure dye **1**.

Since the conditions for the spectra obtaining and initial concentrations of the gel components were the same, the concentration of unbound dye in the samples containing **1**:CB[7] complex was calculated on the basis of the fluorescence intensity proportion and it equaled to 7.7×10^{-7} mol/l, which is more than one value lower than the initial concentration of **1**:CB[7] complex in the reaction mixture. Thus it can be said that almost all the dye in gel is contained in the form of a CB[7] complex.

4 Conclusion

Substantial changes in the intensity of the fluorescence spectrum of 4-DASPI styryl dye **1** in the process of complex formation with cucurbiturils and in process of gelation allowed us to use fluorescent analysis method to confirm the possibility of creating porous samples containing cucurbituril complexes. As opposed to the previously known methods of cucurbituril complexes production in gels consisting in covalent bonding of cucurbituril with a gel and following addition of a dye [14, 15], the method of direct embedding of a complex into a reaction mixture requires no chemical modification of cucurbiturils. Moreover, the absence of free fluorophore excess in the system allows to analyze the photophysical properties of supramolecular complexes in the gels. As the result of our experiment, we successfully prepared THEOS based gels containing complexes of cucurbiturils of different sizes with 4-DASPI styryl dye. Although stability constant of **1**:CB[6] and **1**:CB[7] complexes, 1.02×10^5 and 1.35×10^5 l/mol correspondingly [10, 11], are rather close, the behavior of these complexes in the conditions of sol-gel process significantly differs. The nature of different behavior of complexes and influence of complexes on a gel structure are to be a subject of the future research. However, the obtained data showing a possibility of a direct embedding of supramolecular complexes into gel, open wide prospects for an analysis of the possibility of preparing and using of the gels and xerogels containing organic fluorophore supramolecular complexes.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interests.

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