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Electrostatic interactions of cationic dyes with negatively charged polyelectrolytes in aqueous solution

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Abstract

The electrostatic binding of the cationic dyes rhodamine 6G (R6G), acridine orange (AO), bisindolenylpentamethine (Cy5) and 1,1′-diethyl-2,2′-cyanine (PIC) to the anionic polyelectrolyte polystyrene sulfonate (PSS) was investigated by absorption and fluorescence spectroscopy. R6G exhibits little changes in the absorption and fluorescence spectra upon binding to PSS. Adsorption of Cy5 to PSS shifts the absorption 10 nm to the red, if the dye/polymer ratio (*D*/*P*) is below 0.1. This is caused by polarization of the extended π-electron system through the PSS charges. Larger *D*/*P* ratio results in the formation of H-aggregates. Transition dipole interactions between the dye molecules shifts the absorption band to higher energy and quenches the fluorescence. This effect is even more pronounced in case of AO bound to PSS. Adsorption of the non-fluorescent dye PIC on PSS lead to a narrow fluorescence emission caused by formation of PIC J-aggregates. The J-aggregates requires a sterical fit of the aggregate structure to PSS binding sites, which is optimal fulfilled at a *D*/*P* ratio of 0.55. Adsorption of more dye destroys the J-aggregates again, which is explained by a model of the J-aggregate–PSS complex. The study of competitive binding between AO, Cy5 and poly(allylamine) hydrochloride (PAH) onto PSS showed comparable binding constants for the dyes but a remarkably higher one for PAH.

Keywords: Intermolecular interactions; Dye aggregates; J-aggregate fluorescence; Dye–polyelectrolyte complexes

1. Introduction

The electrostatic field around polyelectrolyte chains results in attraction of many kinds of inorganic and organic molecules. Therefore, polyelectrolytes are used in a wide variety of technical applications, such as sewage treatment [1], mineral flotation [2], papermaking [3,4], etc. Polyelectrolytes are adsorbed on oppositely charged interfaces, which is a very straightforward and convenient method to fabricate thin layers with defined functionality [5]. Since the alternating deposition of polyanions and polycations onto surfaces was developed 10 years ago [5], the research activities on such ordered polyelectrolyte complexes (layer by layer LbL films) increased rapidly. The use of soluble spherical templates allows the preparation of a new type of hollow polyelectrolyte capsules by subsequent removal of the core [6,34]. Such capsules could be used in drug formulation and in the control of crystal nucleation and growth in compartmentalized systems [7].

In order to study the formation of the hollow polyelectrolyte capsules, to investigate their surface charges and free binding sites by non-destructive methods such as optical absorption, emission spectroscopy and confocal microscopy, interactions of dye molecules with polyelectrolytes and their complexes have to be understood. The binding behavior and stoichiometry depend on the nature of both dyes and polyelectrolytes and cannot be generalized [8]. The negatively charged dyes 6-carboxyfluoresceine and pyrene tetrasulfonate were used to investigate positive charges of LbL films on colloids [9,10]. However, little is known about negative charges on the surface and in the interior of LbL films and capsules. In order to develop a system for the determination of negative charges in hollow capsules, we monitored the electrostatic binding of four cationic dyes on PSS using fluorescence and absorption measurements. PSS is one of the mostly used polymers for the preparation of polyelectrolyte layers and polyelectrolyte shells [6,34]. As dyes, we have used 3,6-bis(dimethyl-amino)-acridinium chloride (AO), rhodamine 6G (R6G), 2-[5-[1,3-dihydro-3,3-dimethyl-1-methyl-2*H*-indol-2-ylidene]-penta-1,3-dienyl]-3,3-dimethyl-1-methyl-3*H*-indolium tetrafluoro-borate (Cy5) and the non-fluorescent dye 1,1′-diethyl-2,2′-cyanine bromide (PIC), which forms fluorescent J-aggregates at high

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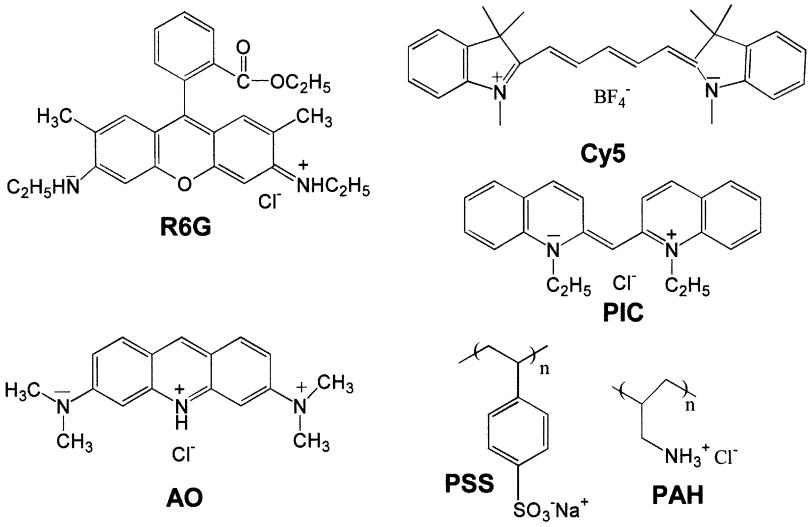

Scheme 1. Chemical structures of rhodamine 6G (R6G), acridine orange (AO), bisindolenylpentamethine (Cy5), 1,1′-diethyl-2,2′-cyanine (PIC), sodium polystyrene sulfonate (PSS), poly(allylamine) chloride (PAH).

concentration in water or on surfaces (Scheme 1) [11–14]. Several cationic species have to date been used with PSS to form LbL films [15–17] and in particular the polycation poly(allylamine) hydrochloride (PAH). To check if the positive polyelectrolyte interferes with the dyes at adsorption to PSS, we monitored also the interaction of the dyes with PAH as well as the competitive binding between dye and PAH to PSS.

2. Experimental

2.1. Materials

Cy5 dye was donated by Prof. W. Grahn (TU Braunschweig). PIC was purchased as bromide salt (NK-1046, Nippon Shisiko Kenkyusho, Japan). R6G chloride, acridine orange (AO) chloride and PAH (MW 8000–11 000 g/mol) were purchased from Aldrich and were used without further purification. PSS (MW 70 000 g/mol, purchased from Aldrich) was dialyzed against milli-Q-water and lyophilized before use. The water used in all experiments was prepared in a three stage Millipore milli-Q Plus 185 purification system and had a resistivity higher than 18.2 mΩ cm. The polymer concentration is given by the amount of sulfonate groups per volume.

2.2. Fluorescence and absorption spectroscopy

Absorption was measured using a Varian Cary qe UV–visible spectrophotometer between 200 and 800 nm. Absorption spectra of dilute aqueous solutions ($0–2 \times 10^{-5}$ M) were in good agreement with those reported in the literature [19,20]. Fluorescence spectra were obtained using a Spex Fluorolog 1680 Double Spectrometer. Both excitation and emission bandwidths were set at 1.0 nm. All measurements were performed on air-equilibrated solutions at 25°C. Experiments were typically performed by adding polyelectrolyte to a solution containing probe. Some of the titration curves were measured on a HTM 7000-plate reader from Perkin Elmer.

3. Results and discussion

3.1. Interaction of PSS with R6G

Rhodamine dyes are some of the most studied fluorescent probe molecules with numerous applications in biology and biochemistry. In order to avoid uncertainties in the binding behavior of the carboxylic group of rhodamine B, we chose the dye derivative 6G because it has exactly one positive binding site (see Scheme 1) [18]. The maximum absorption for R6G in aqueous solution is observed at 524 nm ($\varepsilon = 81\,000\,\mathrm{l\,mol^{-1}\,cm^{-1}}$) for the monomer and at 498 nm for the H-aggregate (sometimes also called dimer) [19,20]. The weak shoulder at 500 nm in the monomer absorption is ascribed to a vibronic transition of the monomer band and a H-aggregate content of ≈5%. In water, the monomer emits at 551 nm. The H-aggregate is non-fluorescent.

Aliquots of R6G were added to a solution of 1.43×10^{-7} M PSS in water. We compared the fluorescence spectra with those obtained from a PSS-free solution of the same dye concentration (Fig. 1). Differences in shape and position of the absorption and fluorescence bands were small, but the fluorescence intensity diminished by 30% when dye molecules adsorbed on PSS chains. This relatively weak quenching efficiency compared to AO (see below) might be caused by the bulky phenyl group of the rhodamine dye preventing a close packing and effective H-aggregate formation

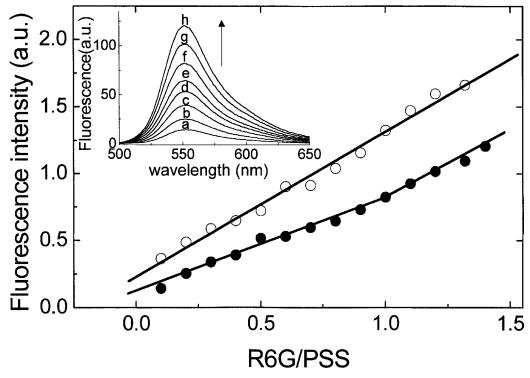

Fig. 1. Fluorescence intensity of R6G at $\lambda_{em} = 551$ nm as a function of the molar ratio of dye to polyelectrolyte (R6G/PSS). Filled circles: the amount of PSS is kept constant ([PSS] $= 1.4 \times 10^{-7}$ M) and aliquots of dye are added. Open circles: PSS-free solution of the same dye concentration. Inset: corresponding fluorescence spectra ($\lambda_{exc} = 490$ nm) of an increasing concentration of R6G in 1.4×10^{-7} M solution of PSS: (a) $D/P = 0$, (b) $D/P = 0.2$, (c) $D/P = 0.4$, (d) $D/P = 0.6$, (e) $D/P = 0.8$, (f) $D/P = 1$, (g) $D/P = 1.2$, (h) $D/P = 1.4$.

of R6G along the PSS chain. Hayakawa et al. [18] reported a decreased fluorescence due to R6G aggregation in the polyion domain of dextran sulfate through hydrophobic interactions. They attributed the leftover fluorescence to either R6G monomers remaining in bulk solution or to bound but isolated monomers. R6G cannot be used for the determination of free anionic binding sites of PSS because of the small influence of the polyanion on the fluorescence and absorption spectra of the dye. However, R6G is successfully used as coloration agent for fluorescence microscopy due to its relatively high fluorescence yield in the adsorbed state.

3.2. Interaction of PSS with Cy5

Applications for the dye Cy5 can be found in photography [21] (sensibilizator agent) or as chromophore for dye lasers [22]. It is also increasingly used for investigations on biological systems due to its low energy absorption ($\lambda_{max} = 638$ nm) and fluorescence ($\lambda_{max} = 656$ nm) in water and to a high absorption coefficient of 220 000 l mol^{-1} cm^{-1} [13]. Aliquots of a 10^{-5} M solution of Cy5 were added stepwise to a 3.5×10^{-6} M solution of PSS in water. The absorption spectrum of the Cy5 dye depends in a complex way on the *D*/*P* ratio (Fig. 2a). If the ratio is below 0.1, no changes are observed in the shape of the absorption band, but the absorption maximum is shifted from 638 nm in pure water to 648 nm for the adsorbed dye. This shift is caused by electrostatic interactions of the isolated dye molecule with PSS. An asymmetric binding of the extended chromophore to the negative charge of PSS perturbs the symmetry of the delocalized π-electron system, yielding an increase of the ground state energy and a bathochromic shift of the absorption [23]. This result shows that Cy5 is completely adsorbed onto the polyelectrolyte on well-separated binding sites. For increasing *D*/*P* ratio above 0.1, the absorption band at

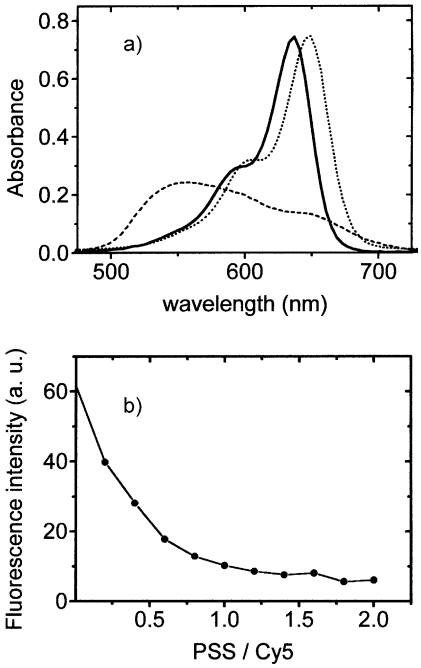

Fig. 2. (a) Absorption spectra of a 3.5×10^{-6} M solution of Cy5 in water at different dye/PSS ratio: Cy5 in water (solid line), Cy5/PSS = 0.1 (dotted line), Cy5/PSS = 1 (dashed line). (b) Evolution of the fluorescence intensity at $\lambda_{em} = 654$ nm as a function of the PSS to dye ratio ($\lambda_{exc} = 610$ nm, [Cy5] $= 5 \times 10^{-6}$ M).

648 nm vanished and a new broad absorption band centered at 555 nm was formed. This large hypsochromic absorption shift is typical for dye H-aggregates [24]. It is caused by transition dipole interactions between two or more chromophores (H-aggregates) arranged parallel to each other with a small dislocation (Fig. 3) [25]. The interaction of two transition dipoles M1 and M2 yield an energetic splitting of the excited state in two components m_+ and m_-. In case of parallel alignment of the molecules, the absorption and emission from one energy level is forbidden because the resulting transition moment $m_- = \mathrm{M1} - \mathrm{M2} = 0$. Only the state $m_+ = \mathrm{M1} + \mathrm{M2}$ can be populated. In H-aggregates the allowed m_+ state has a higher energy than the m_- state and the excited monomer (Fig. 3), leading to the observed

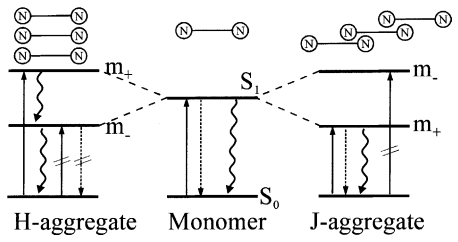

Fig. 3. Model of molecule orientation and transition dipole interactions in dye H- and J-aggregates and the resulting absorption and fluorescence properties. The dumbbells model the dye molecules, solid arrows mark the absorption, broken arrows the fluorescence and wavy arrows the internal conversion, crossed lines are forbidden transitions. m_+ and m_- are the splitted excitonic states whereas only m_+ is allowed for light transitions.

hypsochromic shift of the absorption energy with respect to the monomer. The m_+ state does not show fluorescence due to fast internal conversion process to the non-emitting m_- state. Therefore, formation of H-aggregates should quench the Cy5 emission efficiently. This was investigated by titration of a 5×10^{-6} M solution of Cy5 with PSS. The fluorescence ($\lambda_{exc} = 635$ nm, $\lambda_{em} = 670$ nm) was detected (Fig. 2b). In contrast to the absorption, where both intensity and position of the band are affected, only the intensity of the fluorescence band varies. The fluorescence quenching reached 85% of the initial value at a *D*/*P* ratio of 1.0. The equivalence point is not sharp, pointing to a rather weak binding of the dye to PSS. In a control experiment, the H-aggregate was excited at 555 nm, and no fluorescence was detected. This result indicates that the remaining fluorescence intensity is caused either by separated dye molecules bound to the polymer or by free dye molecules in solution.

This mechanism of self-quenching of dye molecules by H-aggregate formation is known for other dye/polyelectrolyte systems [9,10]. It can be used for quantitative determination of charges on polyelectrolytes and their complexes if the binding constant is high and the available binding sites are in close vicinity.

3.3. Interaction of PSS with AO

AO (Scheme 1) is known to undergo a change of the absorption and fluorescence spectra in the visible region (metachromasia) upon binding to biopolymers and to synthetic polyelectrolytes [26]. This property has been successfully exploited in the staining of biological tissues, where, for instance, DNA stained with AO shows green fluorescence while RNA shows a red one [26]. At the AO concentration used for our experiments (5×10^{-6} M), the absorption spectrum of AO in water exhibits a main transition at 492 nm and a shoulder at 470 nm. These bands are attributed, respectively, to the AO monomer and to a superposition of the vibronic band of the monomer and the H-aggregate absorption. In order to obtain linear titration curves, which can be easily evaluated, we titrated an aqueous solution of 5×10^{-6} M AO with PSS. The vice versa titration of PSS with AO yielded nonlinear curves, which cannot be used for the determination of free sulfonate groups. As the polymer to dye ratio increased, we observed a strong quenching of the fluorescence at 534 nm and a parallel decrease in the absorption intensity at 492 nm. Simultaneously, a weak fluorescence band at 657 nm appeared (Fig. 4a). The plot of the fluorescence intensity against the PSS concentration showed a linear decrease until the equivalence point is reached. Past the equivalence point, the fluorescence remains constantly low at ≈10% of the initial value (Fig. 3a, inset). This behavior is similar to what was observed with Cy5. H-aggregate formation and self-quenching of the adsorbed AO contribute to the decrease in fluorescence intensity. The sharpness of the equivalence point (Fig. 4a, inset) and the efficient quenching revealed a larger binding constant as for

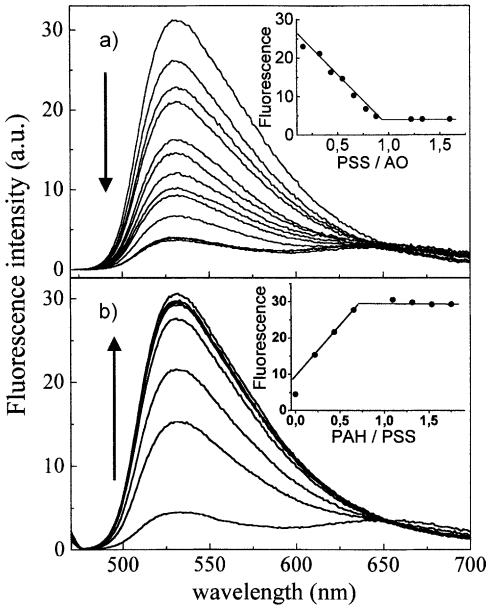

Fig. 4. (a) Fluorescence spectra of 10^{-6} M AO in water at increasing concentration of PSS. The inset shows the dependence of fluorescence intensity on the titration grade. (b) The addition of PAH to a 1:1 complex of AO and PSS lead to an increase of the fluorescence intensity by release of the AO until the value of the pure AO is reached at a PAH/PSS ratio of ≈1 (see inset).

Cy5. Since, the dye titration should be used mainly for the investigation of PAH/PSS layers, we checked if the addition of PAH to an AO solution influences the fluorescence behavior of the dye. As expected the presence of a polycation has no influence on the fluorescence of positively charged dye molecules. This result confirms that AO interacts only with negatively charged polyelectrolytes make it well suited for the quantitative determination of PSS charges.

The binding efficiency of PSS to the dye and to the polycation PAH was compared. A 1:1 complex between AO and PSS was titrated with PAH (Fig. 4b). The fluorescence intensity of the AO increased until 95% of the initial intensity of the free dye was reached at the equivalence point. As expected, the bound AO was quantitatively released from the PSS because of the higher binding strength of the polycation [25]. This behavior allows the determination of negative charges of polyelectrolyte complexes by back-titration, which can be more accurate. In addition, it should be possible to discriminate between polymers inside and outside the semi-permeable capsules.

3.4. Aggregation of PIC on PSS

The monomeric PIC dye ($\lambda_{max} = 523$ nm, $\varepsilon = 77\,000\,\mathrm{l\,mol^{-1}\,cm^{-1}}$) [24] does not exhibit fluorescence, due to fast thermal deactivation by the flip–flop motion of the two chinolyl ring systems, which are twisted to each other (see Scheme 1). However, at concentrations above 7×10^{-4} M, the PIC dye forms fluorescent aggregates [27].

They exhibit a narrow absorption band at 572 nm and a strong fluorescence with almost no Stokes shift at 575 nm. Such aggregates are called J-aggregates [23]. They consist of long threads in which two alternating sites of PIC molecules are stacked parallel to each other with a large dislocation of the molecules (see Fig. 6a) [27]. Such arrangement decreases the energy of the m_+ state below the excited state of the monomer and the m_- state explaining the red shift of the absorption and the intense fluorescence (see Fig. 3). It is well known that adsorption of cyanine dyes on surfaces [28–30] or on polyelectrolytes [31] supports the aggregation process. For example, Horng and Quitevis [28] reported the typical J-aggregate fluorescence for a complex between PIC and polyvinyl sulfonate. However, for adsorption to PSS the authors did not found J-aggregation, which was explained by steric reasons in the voluminous PSS chain [29,31].

We titrated an aqueous solution of 10^{-5} M PSS with aliquots of PIC and followed the evolution of the absorption and fluorescence spectra. Up to a *D*/*P* ratio of 0.25, no effect on the absorption or fluorescence behavior of the dye was observed (Fig. 5, inset) pointing to the adsorption of mainly monomeric species on the polymer chain. At higher titration grade, we observed the growth of a sharp band at 571 nm in the absorption spectrum and a narrow fluorescence peak centered at 575 nm (Fig. 5) which are characteristic features of PIC J-aggregates. The growth of the J-band is remarkably faster than the increase of the PIC concentration (Fig. 5, inset). This means, the addition of few PIC molecules induces a transition from random distributed PIC molecules on the PSS chain to well-ordered J-aggregates. The J-band reached a maximum intensity at a *D*/*P* ratio of 0.55. Further addition of PSS lead to a fast decrease of the J-band.

The stability of the J-aggregate/PSS adduct was investigated by dilution experiments. The fluorescence of the PSS–PIC aggregate complex was observed down to a PIC concentration of 4×10^{-6} M. Hence, the use of PSS as a counterion instead of chloride increases the stability of PIC aggregates in aqueous solution by more than 150 times. The strong stabilization [23] of the J-aggregate and the *D*/*P* ratio of almost 2:3 imply a good steric match of the aggregate structure and the PSS binding sites. The arrangement of the PIC molecules in long threads obtained from single crystal X-ray analysis [32,33] was compared with a calculated structure model of isotactic PSS (Fig. 6a) [30]. The distance of 0.68 nm between the positive charges in PIC threads matches fairly well with the 0.62 nm distance between the negative charges of one side of the trigonal arranged sulfonate groups of isotactic PSS. Cryo-Electron-Microscopy has shown recently that PIC J-aggregates consists of six of such double strands arranged in cylinders of 2.3 nm in diameter and 350 nm in lengths (Fig. 6b) [27]. Such structure can be well-stabilized by surrounding of three PSS polymer chains, whereby only two of the three possible charges of PSS can be used for the PIC aggregate which corresponds well to the

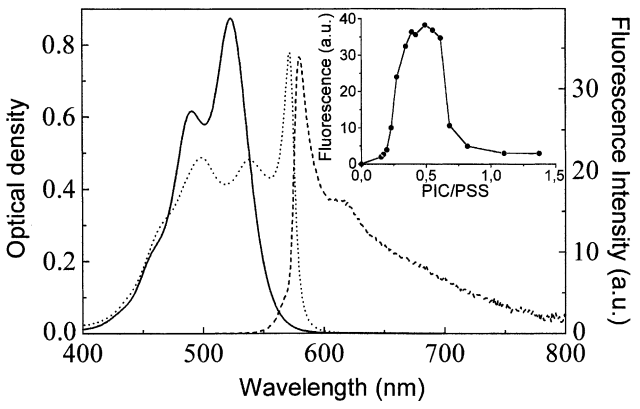

Fig. 5. Absorption of a 10^{-5} M solution of PIC monomer (solid) and of a 2:3 *D*/*P* complex with PSS (dotted). Fluorescence spectra (dashed) of the complex ($\lambda_{exc} = 520$ nm). The inset shows the fluorescence intensity ($\lambda_{em} = 575$ nm) as a function of the *D*/*P* ratio during the titration of a 10^{-5} M PSS solution with PIC.

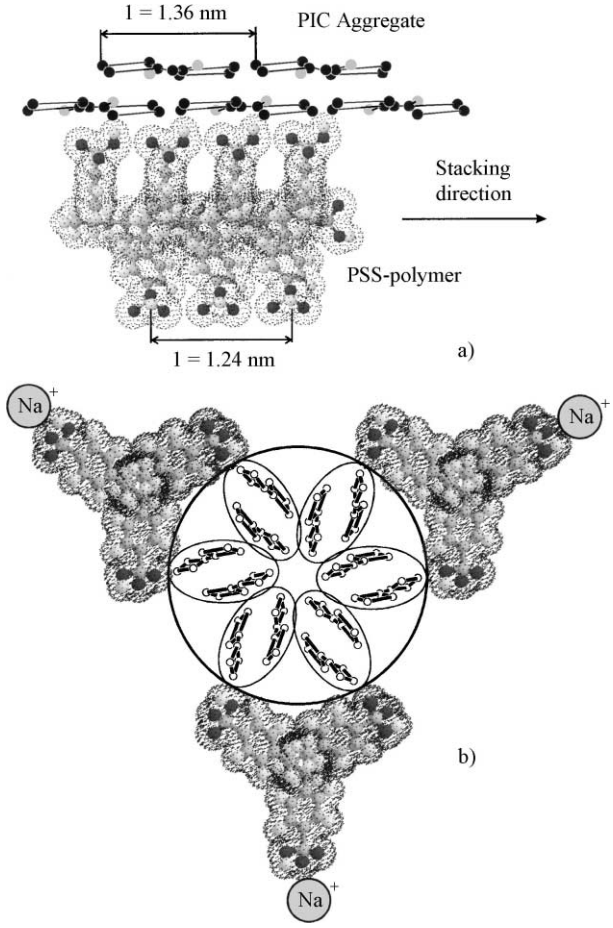

Fig. 6. (a) Side view of a PIC thread adsorbed on one side of the trigonal arranged sulfonate groups of isotactic PSS. The PIC molecules are shown simplified as coupled rectangles, marking the chinoline rings connected by the methine bridge (see Scheme 1). The molecular arrangement were taken from X-ray analysis of the single crystal [32]. The PSS structure were obtained by molecular modeling [30]. (b) Top view of a model of the J-aggregate/PSS complex. The shape of the J-aggregate was derived from Cryo-TEM measurements [27].

optimal *D*/*P* ratio of almost 2:3. The attachment of further PIC dye molecules beyond this ratio destroys the J-aggregate and leads to the observed fast decrease of the J-band.

Due to the nonlinearity of the J-aggregate formation, the PIC dye is not suited for the quantitative determination of negative charges of polyelectrolytes and their complexes. Nevertheless, the unique property of this dye to show fluorescence only in the aggregate form makes it well suited as coloration agent for fluorescence microscopy of strongly charged surfaces of synthetic or biological materials. An excess of the monomer will not perturb the fluorescence results. In addition, the very small half width of the fluorescence band allows an excellent separation from the fluorescence of other dyes in multicolor experiments.

4. Summary

The interaction of four different cationic dyes with the polyanion PSS was investigated in view of their use for the determination of the charge distribution in a new kind of capsules made by ordered polyelectrolyte complexes and for their coloration for laser scanning fluorescence microscopy. Interactions of dye molecules with PSS are governed by different mechanisms. Direct influence on the dye color by electrostatic binding to PSS was only observed for Cy5 due to the polarization of the extended π-system. All other effects were caused by transition dipole interactions between closely adsorbed dye molecules. The adsorption to PSS induced the formation of dye aggregates. The H-aggregate formation of Cy5 and AO led to self-quenching of the monomer fluorescence and, in case of Cy5, to a hypsochromic shift of the absorption band according to the Kasha theory [25]. The competitive adsorption of an excess of a Cy5 and AO mixture on PSS yielded a simultaneous deposition of both dye molecules pointing to only small differences in their binding constants. The PIC dye forms J-aggregates by adsorption to PSS. This results in an appearance of a J-fluorescence from non-fluorescent molecules. The supramolecular structure of the PIC aggregates fits well with the negative charge distribution along the PSS chain explaining the observed stabilisation of the J-aggregate by the polyanion PSS.

With exception of R6G, all of the dyes exhibit strong changes in their optical behavior by adsorption to PSS, which can be used for the titration of negative charges on polyelectrolytes. However, the origin of the optical effects are transition dipole interactions which require a small distance between the adsorbed dye molecules. Hence, high charge densities along the polymer chain are necessary in order to adsorb enough molecules for the formation of aggregates and to observe significant variations in the optical spectra. This makes the titration of polyelectrolyte complexes difficult. Since the polycations have larger binding constant as the dyes, the concentration of available binding sites is remarkably reduced by occupation of oppositely charged polyelectrolytes. Only the Cy5 dye shows a remarkable shift of absorption energy if adsorbed to the polymer chain as single molecule. However, the H-aggregate formation at higher dye concentration superimposed this effect and prevents the use of Cy5 for the quantitative charge determination.

The addition of PAH to the dye–PSS complexes released the dyes quantitatively from the adsorbed state on PSS. This could be used for the determination of charges by back-titration of adsorbed dye against PAH. The increase of the fluorescence intensity by the released molecules will be a sensitive measure of the equivalence point. On the other side, monovalent dyes are not well suited for the incorporation in polyelectrolyte layers because due to their weak binding they can be replaced easily by polyelectrolytes or can be washed out.

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