Engineering of Layer-by-Layer Coated Capsules with the Prospect of Materials for Efficient and Directed Electron Transfer

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Abstract: Intermolecular electron transfer is investigated in a dye-doped polyelectrolyte (PE) multilayer film. Hollow PE capsules, with a mean diameter of 2 μm, were prepared by stepwise adsorption of a pyrene (PY)-labeled polyanion and various polycations onto charged colloids and subsequent dissolution of the colloidal core. The high concentration of dye molecules within the capsule wall and the control of the medium polarity on a nanometer length scale are proposed to facilitate light-induced charge separation over distances of a few nanometers. In particular, a PY-labeled poly(styrene sulfonate) (PSS-PY) has been synthesized and used as polyanion for the polyelectrolyte capsule preparation. A polarity gradient across the wall of the PE shells is assumed to be achieved by adsorbing diverse polycations at different film positions. The high effective film area followed by high optical density of the PE capsule solution enables time-resolved optical spectroscopy. Using pulsed excited state absorption (ESA) the transient absorption peaks of the radical anion and cation state of pyrene were measured, respectively. In the presence of additional electron donor (or acceptor) molecules in the capsule solution the pyrene anion (cation) is observed in the ESA spectra, while both transient states are seen if no additional molecules are present. These results are interpreted as an electron transfer from pyrene to the donor (acceptor) molecule or between two pyrene molecules. An asymmetry of the electron donor and electron acceptor efficiency was observed when multilayer shells were used that are supposed to carry an internal polarity gradient.

Introduction

Photosynthetic organisms are the most elegant and complex molecular devices available in nature. Plants, algae, and photosynthetic bacteria have developed efficient systems to harvest the sunlight and to transfer this energy to reaction centers where photoinduced redox processes occur.[1] The functional molecules involved in the photosynthetic machinery are organized with high precision with respect to intermolecular distances and orientations. Furthermore, the environment of the reactive units is organized in order to facilitate the charge transfer via local electrical fields.[2] The control of the supramolecular structure of redox-active sites and the design of the surrounding medium constitutes the general and central problem in the development of artificial photosynthetic systems. It is one of the challenging tasks of modern chemistry to build

supramolecular structures that have the precision and reproducibility required for the formation of such functional molecular devices.[3]

Among several strategies utilized to achieve structural control on the supramolecular level the layer-by-layer self-assembly technique[4] (L-by-L) is an attractive approach for developing nanostructured systems. Although the resulting films are mostly amorphous, there is still layering which allows the control of the interlayer distances with a precision on the angstrom level.[5,6] This feature was utilized to build up functional film structures for the study of energy[7,8] (ET) and electron[9] (CT) transfer reactions.

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To take into account the whole complexity of the mechanism underlying the natural photosynthetic process, a separate approach for ET and CT studies is desirable, as well as for the various and specific factors influencing each process. One of these factors in CT reactions is constituted by the local environment of the redox-active molecules.[10] In particular, the rate and, hence, efficiency of a charge transfer process increase with increasing solvent polarity.[11−14] Thus, an amplification of the electron transfer efficiency can be expected if the polarity of the surrounding medium is not constant, but obeys a gradient. This may be accomplished with the help of an interface between two phases of different polarity, like for example two different liquids.[15] For solid state materials a method has to be found that allows to structure, on the nanometer length scale, material properties that are equivalent to the solvent polarity (e.g., dielectric constant). The layer-by-layer deposition of different polyelectrolytes is thought to be an ideal candidate to provide a tool for the fabrication of a transparent matrix with an internal gradient of solvent polarity. For planar polyelectrolyte films assembled by poly(styrene sulfonate) (PSS) and different polycations it has been shown that the polarity of polyelectrolyte multilayer films can be varied very efficiently by simply changing the kind of polycation used for the multilayer buildup process.[16] This method allows the control of local solvent polarity in a thickness range of less than 2 nm, and it has been extended in this work to the adsorption of PEs onto melamine formaldehyde (MF) colloids. In particular, as polyanion for the PE adsorption a PY-labeled poly(styrene sulfonate) (PSS-PY) has been synthesized and successively adsorbed with different polycations in a sequence where an internal polarity gradient has been obtained across the film together with the immobilization of PY molecules at defined positions. To remove the Rayleigh scattering of the colloidal suspension, the MF colloidal template has been dissolved after film formation by a known procedure[17] to obtain hollow PE capsules. It is a great advantage of the L-by-L technique that PE films can be built on colloidal particles[18,19] with almost the same structural properties as can be obtained in planar films. Dissolution of the colloidal core after film deposition further allows the preparation of hollow polyelectrolyte shells[17] of spherical shape. Such a shell solution provides a large surface area per volume, which facilitates any spectroscopic investigations that require high optical densities of hosted light-absorbing molecules.

The most frequently used method to investigate photoinduced electron transfer reactions is static or time-resolved fluorescence detection. These measurements provide rate constants for the transfer reactions and hence indirect information about the pathways of the electron transfer.[20] A more direct method is based on the time-resolved detection of the charged state of the reactants. These states are transient and observable during the lifetime of the charge transfer state. A method to probe these states is by looking at the transient absorption spectra of the charged molecules (excited state absorption, ESA). Experimentally, the spectra are measured by a pump−probe technique, using a white light pulse to record the absorption spectrum. The transient excited state spectra can be analyzed by comparison with ground state spectra of chemically prepared radical ions.[21]

In this work, hollow polyelectrolyte capsules which are built up using PSS-PY as polyanion are doped with two different dye molecules that confer an alternative electron donor or acceptor behavior to the PY molecules. The electron transfer from or to PY is proven by transient excited state absorption (ESA) measurements. These systems are promising for the investigation of photoinduced unidirectional intermolecular electron transfer processes which are influenced by polarity and a gradient of polarity of the environment.

Experimental Section

Materials. Dispersions of monodispersed weakly cross-linked melamine formaldehyde (MF) particles with a diameter of 1.96 μm were purchased from Microparticles GmbH, Berlin, Germany. These particles decompose into oligomers at pH values below 1.6 and have been used as templates for the formation of hollow polyelectrolyte capsules. The polyelectrolytes used for the MF particle coating were poly(ethylenimine) (PEI), M_w 55 000, poly(allylamine hydrochloride) (PAH), M_w 50 000−65 000, and poly(diallyldimethylammonium chloride) (PDADMAC), M_w 200 000−350 000, as polycations, and poly-(styrenesulfonic acid) (PSS), M_w 70 000, as polyanion. All were purchased from Aldrich Chemical Co. and used as received, except for PSS, which was dialyzed (Millipore GmbH, France, Filter type: PBGC 07610, molar weight exclusion 10000 g/mol) against Milli-Q water and freeze-dried. For the synthesis of the pyrene (PY)-labeled poly(styrenesulfonic acid) (PSS-PY), M_w 30 000, unsubstituted PY, M_w 202.26, (purity > 99%), was obtained from Aldrich Chemical Co. and used without further purification. 1,4-Styrenesulfonic acid, sodium salt hydrate (SS), M_w 206.20 (purity 99%), and 1,1′-azobis(cyclohexanecarbonitrile) (purity 98%) were also purchased from Aldrich Chemical Co. and used as received. N,N′-Dimethylaniline (DMA), M_w 121.18 (purity 99%), and 3,4-vinylpyridine (VPd), M_w 105.14 (purity 96%), were used respectively as donor and acceptor molecules for PY and obtained from Aldrich Chemical Co. The chemical structures of the polymers and the dye molecules are shown in Figure 1.

All organic solvents used for spectroscopy measurements were of UV spectroscopic grade and used without further purification, while reagent grade solvents were used for the polymer synthesis. The ultrapure water used in all experiments was obtained by reversed osmosis followed by ion-exchange and filtration (Milli-Q purification system, Millipore, France) with a specific resistance better than 18 MΩ cm. Cuvettes (45 × 12.5 × 3 mm, five windows, light path 1 × 1 cm, and two windows 1 cm × 1 mm, respectively) were made of quartz Suprasil (Hellma Optik, Jena, Germany).

Synthesis of Pyrene-Labeled Poly(styrenesulfonic acid) (PSS-PY). The PSS-PY random copolymer was synthesized via radical polymerization of 3-vinylpyrene and styrenesulfonic acid in dimethylformamide. 3-Vinylpyrene was obtained employing the procedure of Tanikawa et al.[22] The PSS-PY synthesis was optimized to increase the molar

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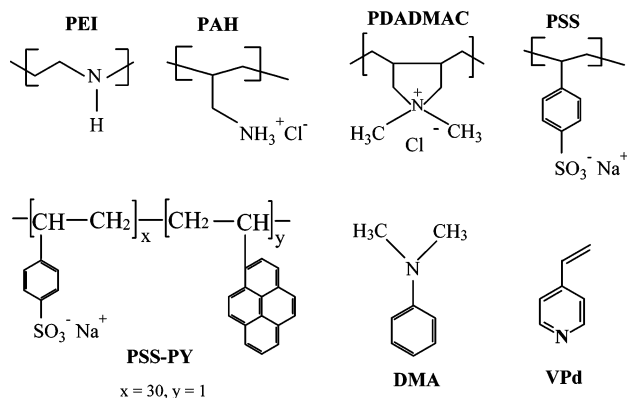(21) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: New York, 1988.

Figure 1. Chemical structures of the monomer units of poly(ethylenimine) (PEI), poly(allylamine hydrochloride) (PAH), poly(styrenesulfonic acid) (PSS), and poly(diallyldimethylammonium chloride) (PDADMAC). The fluorescent dye molecules were poly(styrenesulfonic acid) labeled with pyrene (PSS-PY), 3,4-vinylpyridine (VPd), and *N,N′*-dimethylaniline (DMA).

ratio of PY in the copolymer. A more efficient radical initiator (1,1′-azobis(cyclohexanecarbonitrile)) was employed to initiate the radical reaction, and the polymerization was performed at 80 °C for 24 h. By elementary analyses a dye loading of 1 PY/30 PSS was calculated, which is remarkably high compared to the values available in the literature up to now (1 PY/250 PSS).[23] The molar ratio of 1 PY/30 PSS was necessary in order to obtain enough dye optical density into the PE hollow capsules for detection of the transient absorption spectra.

Assembly of Polyelectrolyte Multilayers onto Colloids. Multilayer films were formed on the positively charged MF particles by sequential absorption of polyanions and polycations. All polyelectrolyte multilayer films consisted of *n* assembled PSS-PY/polycation *bilayers*. The term *bilayer* is used here without reference to the internal structure of the PE films. After adsorption of four bilayers (as described later) the coated particles were treated in HCl solution (0.1 M, pH = 1.1) to decompose the MF particles.[17] The produced MF oligomers and excess HCl were washed off until a neutral pH was again established by successive centrifugation/wash/redispersion cycles. The suspension light scattering decreased by roughly 80% upon dissolution of the template. In the case of films of 12 bilayers (see Results section) the removal of the colloidal core was already performed after four bilayers and adsorption of additional PSS-PY/polycation bilayers was successively completed onto the hollow polyelectrolyte capsules. Hollow spheres of PSS-PY/poly(ethylenimine) could not be produced, because dissolution of the MF core caused collapse of the PE shells into a unique polymer aggregate. Thus, adsorption of these PE layers was carried out on preformed PSS/PAH hollow shells (three bilayers).

For the assembly of polyelectrolytes onto colloidal templates, an aqueous MF particle suspension (25 mL) of concentration 1.5 mg/mL was prepared, and PSS, or PSS-PY, was first added. In the case of PSS as first layer, 3.2 mL of an aqueous 5×10^{-3} M (monomer) PSS solution containing 0.5 M NaCl was mixed into the particle suspension, while for adsorption of the PY-labeled PSS onto the MF colloids 3.2 mL of an aqueous 6.24×10^{-3} M (with respect to the repeat unit) PSS-PY solution containing 0.5 M NaCl was added. After a few minutes and a gentle shake the dispersion was centrifuged at ca. 4000*g* for 5 min and the supernatant removed (ca. 25 mL), and after dispersion of the deposited particles in the few milliliters remaining volume, water was added (25 mL) and the suspension gently shaken. The centrifugation/wash/redispersion cycle was repeated three times to ensure removal of free polyelectrolyte from solution. Using the same procedure additional polyelectrolyte layers were deposited. For aqueous solutions

of the polycations concentrations of 10^{-2} M (monomer) were used for PAH and PDADMAC, while a 5×10^{-2} M (monomer) concentration was necessary for adsorption of PEI. When PSS-PY was not adsorbed as first layer onto the MF particles but used as successive building layer with polycations, a concentration of 7.8×10^{-4} M (with respect to the repeat unit) had to be employed in order to obtain a successful negative recharging of the polycation outermost layer as measured by ζ-potential (see Results section). All solutions contained 0.5 M NaCl.

Electrophoretic Mobility (EPM) Measurements. Electrophoretic mobilities of the bare and coated MF particles, as well as of PE hollow capsules, were measured with a Malvern Zetasizer 4. The mobility *u* was converted into a ζ-potential by using the Smoluchowski relation $\zeta = u\eta/\epsilon$, where η and ε are the viscosity and permittivity of the solution, respectively. All ζ-potential measurements were performed on coated MF particles or hollow PE capsules redispersed in air-equilibrated Millipore water (pH ≈ 5.6).

Absorption and Fluorescence Measurements. UV/vis spectra were recorded with a Varian Cary-5 UV/vis spectrophotometer. Steady state fluorescence spectra were recorded using a Spex Fluorolog-2 (model FL-2T2) spectrofluorometer (ISA, Olching, Germany) at room temperature. Emission spectra of PY in the PE hollow capsules were measured in a front face arrangement. The excitation wavelength used throughout the experiments was 348 nm, and the excitation and emission slit widths were both adjusted to a resolution of 0.8 nm.

Confocal Laser Scanning Microscopy (CLSM). Confocal micrographs were obtained by a Leica TCS NT confocal scanning system (Leica, Germany) mounted to a Leica Aristoplan. A 100×/1.4−0.7 oil immersion objective was used. For the observation of capsule sizes and shapes 6-carboxyfluorescein (6-CF) was used as fluorescent label and the standard filter settings for fluorescein excitation and emission were used. The outermost layer of the investigated PE capsules was always a polycation, so that a drop of the particle suspension was directly put onto a glass microscope slide for image acquisition.

Nanosecond Transient Absorption Measurements. Transient absorption (TA) spectra from high surface area PE capsules were obtained by using a laser pump−probe setup as described elsewhere.[24,25] The sample excitation was performed using a 340 nm, 12 ns pulsed dye laser (Lambda Physik FL 2002) that was pumped by a 308 nm, 11.9 ns pulsed XeCl excimer laser (Lambda Physik LPX 200, 180 mJ/pulse). Part of the excimer laser light (ca. 10%) was used to produce broadband fluorescence light from dye solutions for probing the excited states. The temporal evolution of the pulse was measured with a vacuum photodiode and a sampling oscilloscope (Tektronics TDS 620A). The pulse energy was measured with a laser probe Rm 6600 Universal Radiometer. The pump light was focused to a spot of 500 μm in diameter as determined by a microscope and a CCD chip. The probe light spot on the sample was 300 μm, being completely covered by the excitation spot over the whole path length of 1 mm. The probe light intensity was checked to be low enough not to induce nonlinear effects in the sample by itself. The two beams were arranged to pass the sample cells in an anti-collinear way. Excitation took place with intensities of ca. 4×10^{24} photons/(cm² s).

After passing the excited sample the probe light was collected to a 50 cm Jarrell Ash polychromator and detected on a cooled CCD chip (OMA). The dynamics of the detection system was 6.5×10^3. The spectral resolution was set to 2.5 nm. By this OMA system the pump−probe spectra and an additional reference spectrum were recorded simultaneously for each laser pulse. The excited state absorption (ESA) spectra shown in this paper were calculated as 1 − (transmission with excitation/transmission without excitation). The whole spectral range of the transient absorption was covered by combining the spectra obtained from different fluorescence dyes, each covering a range of 100−200 nm. Typical samples used for the transient absorption

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spectroscopy consisted of 90 mg of the PE capsules suspended in 3 mL of Millipore water. To achieve this high particle concentration, a solution with 1.5 mg/mL was prepared and concentrated by solvent evaporation.

Results

Hollow Polyelectrolyte Capsules of Multilayered Material and Their Characterization. In a previous paper,[16] we have shown that the solvent polarity probed by unsubstituted PY molecules adsorbed into bilayers of PSS/PEI is lower than the one recorded for PSS/PAH or PSS/PDADMAC bilayers. According to these results, one would expect that the film polarity of the layer sequence [PSS/PEI]$_4$/[PSS/PAH]$_4$/[PSS/PDAD-MAC]$_4$ would increase from left to right. On the basis of this finding, and in order to study electron transfer processes in a material with an internal polarity gradient, a 12-bilayer film of the type [PSS-PY/PDADMAC]$_4$/[PSS-PY/PAH]$_4$/[PSS-PY/PEI]$_4$ was assembled onto MF colloidal particles. The PY-labeled copolymer was used whether to juxtapose dye molecules at fixed position within the multilayer assembly or to have chromophores exhibiting either electron donor or acceptor behavior, depending on the kind of dyes used for doping the PE hollow capsules. It is known in fact that PY behaves as an electron acceptor in the presence of dimethylaniline (DMA), but it exhibits an electron donor behavior in the presence of vinylpyridine (VPd). As will be presented later these two dye molecules were used in combination with PSS-PY for electron transfer investigations into the capsules. The PSS-PY/PDADMAC layers were assembled at first onto the MF particles in order to have an increase of the system polarity from the outer PSS-PY/PEI layers toward the interior of the polyelectrolyte capsules. Dissolution of the MF core was performed after deposition of the four PSS-PY/PDADMAC bilayers. The remaining PE layers were adsorbed onto the hollow PE shells. At higher multilayer numbers the film permeability decreases, which impedes the proper release of MF oligomers through the capsule wall.[26]

In addition to the multilayer samples with the proposed polarity gradient, capsules were prepared that consist of four bilayers of PSS-PY/PDADMAC, PSS-PY/PAH, or PSS-PY/PEI, respectively. Again, the MF core was removed by treating with 0.1 M HCl solution.[12] The PSS-PY/PEI layers were assembled onto preformed hollow PE capsules of [PSS/PAH]$_3$, because in the presence of PEI the procedure to dissolve the MF core gave rise to precipitation of the polyelectrolyte walls into a unique polymer aggregate as observed by CLSM (data not shown).

The assembly of PSS-PY/polycation bilayers was first followed by electrophoretic measurements (EPM). Figure 2 shows the ζ-potential as a function of polyelectrolyte layer number for the assembly of the 12 bilayers with internal polarity gradient. The two vertical lines have been drawn to mark the changeover between the layers of different material. The positively charged (uncoated) MF particles yield a ζ-potential of about +45 mV in water. The presence of PSS-PY (anionic) causes a reversal in ζ-potential (-35.2 mV). Subsequent deposition of PDADMAC onto the previous PSS-PY adsorbed layer again reverses the ζ-potential. Alternating ζ-potentials (in sign) are observed with the further deposition of each oppositely

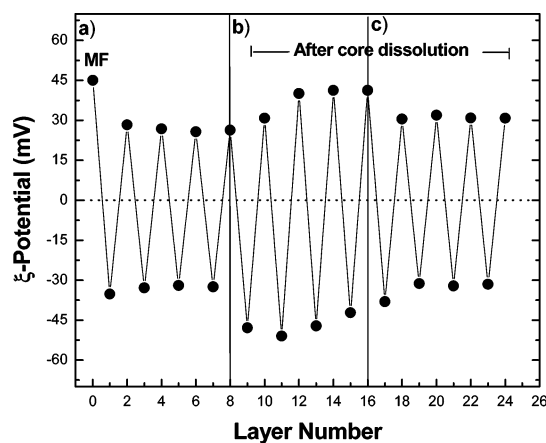**Figure 2.** ζ-Potential as a function of PE layer number for the assembly of 12 bilayers with an internal polarity gradient ([PSS-PY/PDADMAC]$_4$/[PSS-PY/PAH]$_4$/[PSS-PY/PEI]$_4$): (a) ζ-potential for PSS-PY/PDADMAC-coated positively charged MF particles; after dissolution of the MF core, the alternating ζ-potentials (in sign) for the successive adsorption of [PSS-PY/PAH]$_4$ (b) and [PSS-PY/PEI]$_4$ (c) on preformed hollow PE capsules. The even layer numbers correspond to PDADMAC, PAH, or PEI deposition and the odd layer numbers to PSS-PY deposition.

charged polyelectrolyte, suggesting that stepwise polyelectrolyte multilayer growth occurs on the particles (Figure 2, part a) as well as on the hollow capsules (Figure 2, parts b and c) for all kinds of adsorbed layers. The ζ-potential approaches, within the error of the mobility measurements, a constant value characteristic for both the negative and the positive polyions forming the outermost layer. Similar plots are obtained also for the separate assembly of the [PSS-PY/PDADMAC]$_4$, [PSS-PY/PAH]$_4$, and [PSS-PY/PEI]$_4$ onto the MF particles (data not shown). No quantitative conclusions are made from the ζ-potential values obtained because the ζ-potential depends on the polyelectrolyte conformation at the surface.[27,28]

To obtain further evidence for the multilayer film formation on MF particles, the growth of four bilayers of PSS-PY/PAH formed by sequential adsorption of PSS-PY and PAH was examined by using steady state fluorescence spectroscopy. A typical series of emission spectra for the formation of PSS-PY/PAH multilayers is shown in Figure 3. The spectra depict the PY emission after PSS-PY (solid spectra) and PAH (dotted spectra) deposition, respectively. The fluorescence intensity clearly increases with number of adsorbed PSS-PY layers. Additionally, the emission of the PSS-PY/PAH multilayers is slightly larger when PSS-PY is deposited as the outermost layer. Less than 6% of the PSS-PY monomer emission is lost when PAH is adsorbed next after a layer of PSS-PY (see inset of Figure 3). Such a stepwise decrease in fluorescence intensity is often observed[29,30] and is due to depletion of the last layer upon addition of the successive one. However, it could also be explained by a loss of particles during the centrifugation/washing/redispersion cycle.

The linear growth of shell thickness was confirmed by atomic force microscopy measurements performed on [PSS-PY/PDAD-

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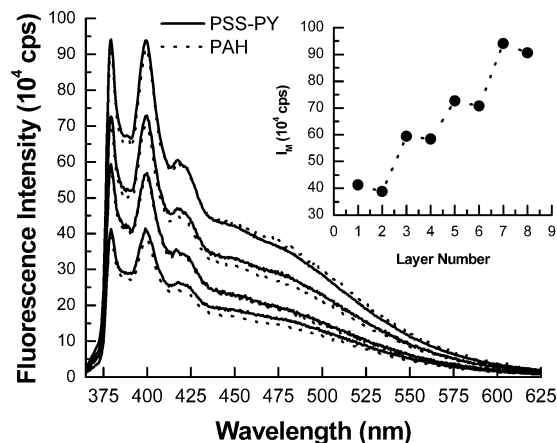
Figure 3. Emission spectra of four PSS-PY/PAH bilayers (on MF particles) measured after each deposition cycle. The solid spectra are recorded after PSS-PY adsorption; the dotted spectra, after PAH deposition. In the inset the monomer intensity of the dye versus layer number is displayed.
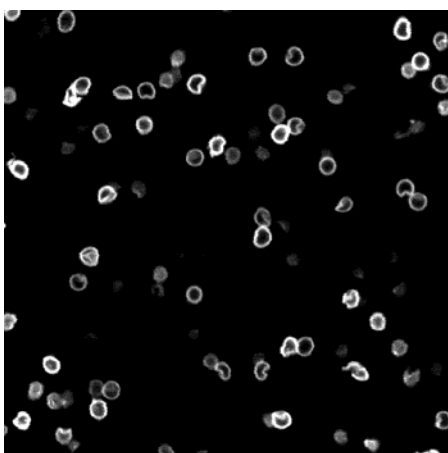

Figure 4. Confocal laser scanning microscopy (CLSM) image of hollow capsules of [PSS-PY/PDADMAC]$_4$/[PSS-PY/PAH]$_4$/[PSS-PY/PEI]$_4$ dispersed into a water solution containing 6-carboxyfluorescein (6-CF). The image size is $500 \times 500 \ \mu m^2$.

MAC]$_4$/[PSS-PY/PAH]$_4$/[PSS-PY/PEI]$_4$ hollow PE capsules and on each capsule of the three single-layer combination. The shell wall thickness of the 12 bilayers is roughly three times higher (31−40 nm) than that of the four bilayers of PSS-PY/polycation (values vary between 11 and 15 nm depending on the kind of assembly), as expected for a linear multilayer growth.[31]

Upon dissolution of the MF core and removal of MF oligomers by washing the capsules, the multilayers were kept intact as investigated by confocal laser scanning microscopy (CLSM). Figure 4 illustrates a typical CLS micrograph of the 12-bilayer hollow PE capsules in aqueous solution. The capsules were visualized by the fluorescence of the negatively charged dye 6-carboxyfluorescein (6-CF), which was added to the suspension at a concentration of ca. 10^{-6} M. The 6-CF is absorbed by the PE film, which allows the imaging of the shape of the capsules.[32] It is seen that the majority of the capsules exhibit a spherical shape in solution. Only a few of them are distorted, probably due to the osmotic pressure.[33]
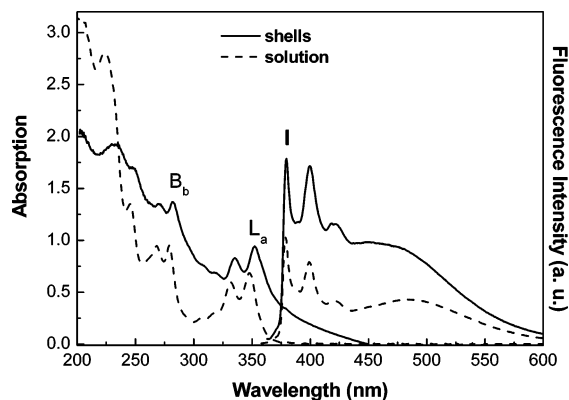
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Figure 5. Absorption (left ordinate) and fluorescence (right ordinate) spectra of aqueous PSS-PY solution (dotted lines) and hollow polyelectrolyte capsules (solid lines). The capsules were of the type [PSS-PY/PDADMAC]$_4$/[PSS-PY/PAH]$_4$/[PSS-PY/PEI]$_4$.

The optical response of PSS-PY was investigated by UV−vis and fluorescence spectroscopy. Figure 5 shows the optical spectra of PSS-PY, which was simply dissolved in water solution (dotted lines), and the spectra of a solution of PE hollow capsules of 12 bilayers with an internal polarity gradient (solid lines). The PSS-PY absorption (left ordinate) of both the water solution and the hollow capsules is clearly identified by the peaks between 250 and 400 nm, which are characteristic for the third and second pyrene transitions (B$_b$ band and L$_a$ band). The PSS-PY absorption spectrum for PE hollow capsules (solid line) is slightly shifted toward longer wavelengths with respect to the PSS-PY water solution (dotted line). The strong background intensity observed for the capsules results from light scattering. The fluorescence emission spectra (right ordinate) of PSS-PY in both water solution (dotted line) and PE hollow capsules (solid line) resemble the shape of pyrene fluorescence emission with the characteristic vibronic progression of the monomers, followed by a broad emission from 450 to 550 nm due to excimer formation. A characteristic feature of the fluorescence spectra of PSS-PY compared to unsubstituted PY is the loss of resolution in the vibronic fine structure of pyrene, consisting normally of five vibronic bands. The loss in fine structure of the vibronic levels is accompanied by lower sensitivity to the environmental polarity.

Photoinduced Electron Transfer in High Surface Area Polyelectrolyte Hollow Capsules. It is well established that the fluorescence of pyrene is effectively quenched by pyridinium halides, such as VPd,[34] by electron transfer. On the other hand, DMA is well known as a strong electron-donating molecule.[34] Therefore, it is expected that in a mixed solution of PY and DMA pyrene behaves as an electron acceptor (A), while in association with VPd the PY plays the role of an electron donor (D). Since PY can serve as both donor and acceptor, charge transfer reactions between adjacent PY molecules are also possible. Figure 6 shows steady state fluorescence spectra obtained from an aqueous solution of pure PSS-PY in which either VPd or DMA was added in similar amount. The PY emission intensity is clearly quenched in the presence of VPd as well as in the presence of DMA, suggesting that CT occurs also for this system where PY is covalently bound to the

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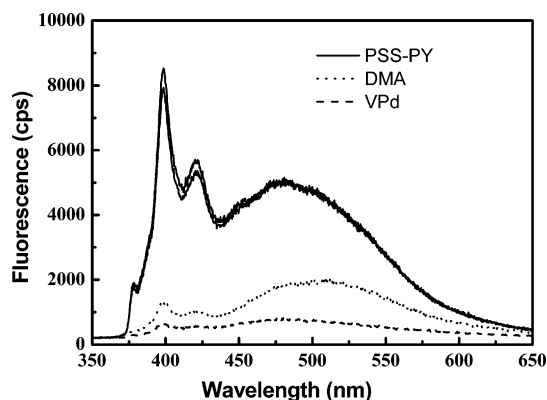
Figure 6. Steady state measurements of PSS-PY fluorescence quenching in aqueous solution by addition of DMA (dotted line) and VPd (dashed line). The quencher molecules were added in large excess with respect to the PY molecules.
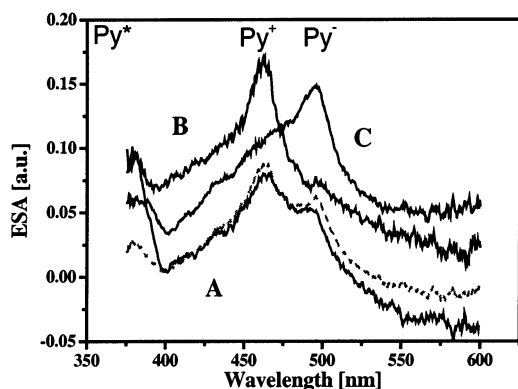

Figure 7. Excited state absorption (ESA) spectra of PSS-PY aqueous solutions in the absence or presence of electron acceptor (Vpd) and donor (DMA) molecules for pyrene. Optical excitation by a 340 nm pump pulse (intensity: 5×10^{24} photons/(cm^2 s)): (A) PSS-PY aqueous solution (3 mg/mL), (B) aqueous solution of PSS-PY (1.5 mg/mL) plus VPd (0.25 mg/mL), (C) aqueous solution of PSS-PY (1.5 mg/mL) plus DMA (50% vol). The dashed line represents a spectrum calculated by 1/2(B + C).

polymer. The intensity of the PY monomer is reduced by a larger factor than the intensity of the excimers, which is an indication that the charge transfer starts from the monomer excitation and is in competition with the rate of excimer formation.

The charge separation after photoexcitation was veryfied by transient excited state absorption (ESA) of PY, as depicted in Figure 7. First, the ESA spectrum of a PSS-PY aqueous solution was measured for samples in the absence of any electron donor or acceptor molecules (Figure 7, spectrum A). Three bands are identified at 380, 460, and 495 nm, respectively. By addition of the electron acceptor VPd to the polymer solution, the PSS-PY transient spectrum exhibits only one band centered at 461 nm (Figure 7, spectrum B), while in the presence of the donor DMA only the band at 495 nm is observed (Figure 7, spectrum C). The absorption bands at 460 nm (B) and at 495 nm (C) have been identified as a characteristic feature of the pyrene radical cation (PY$^+$) and anion (PY$^-$), respectively. This was concluded from comparison with ground state absorption spectra of pyrene radicals.[21] Therefore these spectra are considered to be representative for a PY$^+$−VPd$^-$ and a PY$^-$−DMA$^+$ state, respectively. The transition at 380 nm observed in spectrum A is assigned to the neutral excited state PY*. It is interesting to note that in the case of A, where no electron acceptor or donor is present, the spectrum is similar to a superposition of the PY$^+$
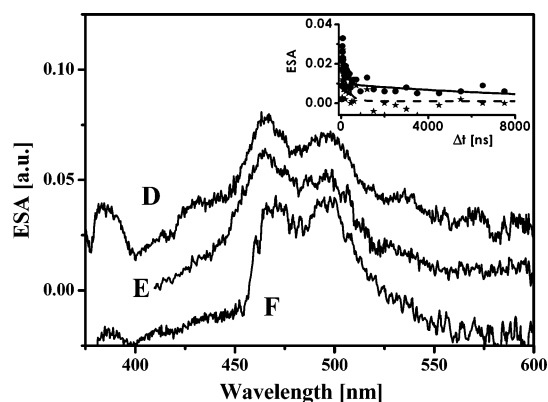

Figure 8. ESA spectra of aqueous solutions of polyelectrolyte hollow capsules (all 90 mg/mL), prepared by PSS-PY and different polycations. Experimental conditions are as in Figure 7. (D) [PSS-PY/PDADMAC]$_4$, (E) [PSS-PY/PEI]$_4$, (F) [PSS-PY/PAH]$_4$. The spectra are shifted vertically relative to each other for better visibility. The inset shows the decay of the ESA signal in D at 470 nm (circles) and 500 nm (stars) on a logarithmic scale together with a biexponential fit (straight line, $t_1 = 163$ ns, $t_2 = 10731$ ns) and a monoexponential fit (dashed line, $t = 254$ ns).

and PY$^-$ spectra. This indicates the existence of inter-pyrene charge transfer transitions of the type PY−PY → PY$^+$−PY$^-$.

In a next step we investigated the electron transfer behavior of PSS-PY embedded in hollow capsules built from different polycations. In Figure 8 the spectra are shown for hollow shells of [PSS-PY/PDADMAC]$_4$ (spectrum D), [PSS-PY/PEI]$_4$ (spectrum E), and [PSS-PY/PAH]$_4$ (spectrum F). The measurements were disturbed by strong scattering of the samples, which is more pronounced at shorter wavelengths. Therefore, in some cases the spectra contain no reliable data in the blue region and are cut below a certain wavelength. As the excited state spectra of a chromophore strongly depend on covalent substituents,[35,36] these spectra are not compared to those of isolated pyrene molecules but those of PSS-PY in solution as given in Figure 7. The shape of all three spectra is similar to that of spectrum A in Figure 7, indicating neutral PY* and PY$^+$−PY$^-$ charge transfer states. Admittedly, the relative intensity of the 380 nm peak is smaller than in Figure 7, which indicates that the charge transfer states are favored in the shells. This conclusion is strengthened by the time dependence of the signal that is shown in the inset of Figure 8: As a function of the delay time between pump and probe pulse, the two peaks in the spectra at 470 and 500 nm, respectively, decrease differently. While the 470 nm peak, representing Py$^+$, decreases biexponentially with lifetimes of $t_1 = 160$ ns and $t_2 = 10700$ ns, the 500 nm peak, representing Py$^-$, decays much faster and monoexponentially with a lifetime of $t = 250$ ns. To avoid any distortion of the spectra due to the different decay times, all spectra presented in this paper were measured at $t = 0$, i.e., without an appreciable delay between pump and probe pulse.

In Figures 9 and 10, measurements are presented where DMA or VPd molecules were added to the capsule solution. The spectra of [PSS-PY/PDADMAC]$_4$ (spectrum G), [PSS-PY/PEI]$_4$ (spectrum H), and [PSS-PY/PAH]$_4$ (spectrum I) in the presence of the electron acceptor VPd are shown in Figure 9. All three spectra exhibit only a maximum at around 460 nm, which represents the PY$^+$−VPd$^-$ state as in the case of the pure PSS-

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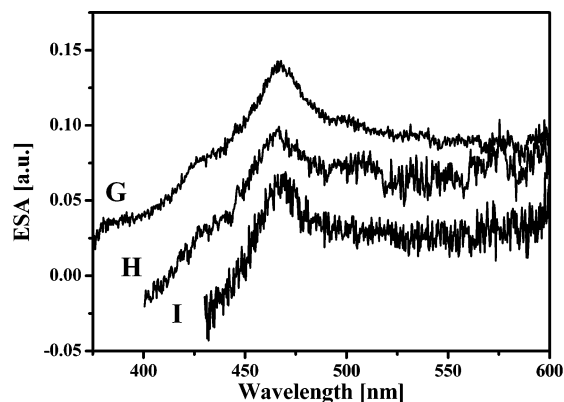
Figure 9. ESA spectra of aqueous suspensions of polyelectrolyte shells after addition of the electron acceptor VPd. Pump pulse was at 340 nm with 5×10^{24} photons/(cm^2 s). (G) [PSS-PY/PDADMAC]$_4$ (72 mg/mL) plus VPd (0.1 mg/mL), (H) [PSS-PY/PEI]$_4$ (90 mg/mL) plus VPd (9.3 mg/mL), (I) [PSS-PY/PAH]$_4$ (72 mg/mL) plus VPd (0.1 mg/mL).
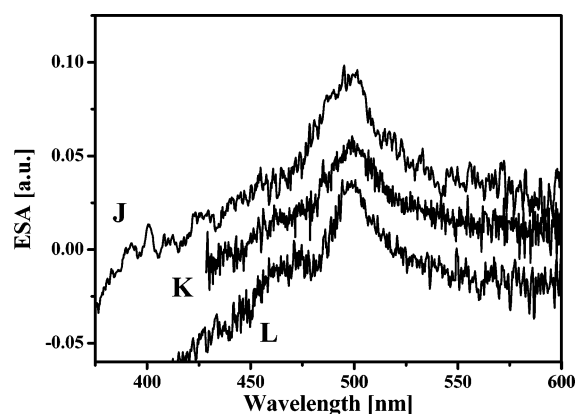

Figure 10. ESA spectra of aqueous suspensions of polyelectrolyte shells after addition of the electron donor DMA. Pump pulse was at 340 nm with 5×10^{24} photons /(cm^2 s). (J) [PSS-PY/PDADMAC]$_4$ (45 mg/mL) plus DMA (50% vol), (K) [PSS-PY/PEI]$_4$ (72 mg/mL) plus DMA (20% vol), (L) [PSS-PY/PAH]$_4$ (45 mg/mL) plus DMA (50% vol).

Table 1. Summary of Particle and the Respective Electron Donor or Acceptor Concentrations

spectrum	polyelectrolyte shells	[shell],[a] mg/mL	[VPd], mg/mL	[DMA], vol %
G	[PSS-PY/PDADMAC]$_4$	72	0.1	
H	[PSS-PY/PEI]$_4$	90	9.3	
I	[PSS-PY/PAH]$_4$	72	0.1	
J	[PSS-PY/PDADMAC]$_4$	45		50
K	[PSS-PY/PEI]$_4$	72		20
L	[PSS-PY/PAH]$_4$	45		50
O	multicomposite[b]	48	0.1	
P	multicomposite	30		50

[a] The given PE shell concentration is the one of MF particles present in the aqueous solution before hollow capsule fabrication by MF removal. [b] The PE shells of 12 bilayers of the type [PSS-PY/PDADMAC]$_4$/[PSS-PY/PAH]$_4$/[PSS-PY/PEI]$_4$ are named as multicomposite.

PY of spectrum B in Figure 7. The absorbance of the PY$^+$ state is similar for all three spectra. However, one has to mention that for the (PSS-PY/PEI)$_4$ system a concentration of VPd was used that was 100 times higher than the concentration used for the other two systems; see Table 1.

After addition of the electron donor DMA the typical PY$^-$–DMA$^+$ spectra arise. In Figure 10 the spectra of [PSS-PY/PDADMAC]$_4$ (spectrum J), [PSS-PY/PEI]$_4$ (spectrum K), and [PSS-PY/PAH]$_4$ (spectrum L) are presented as recorded after
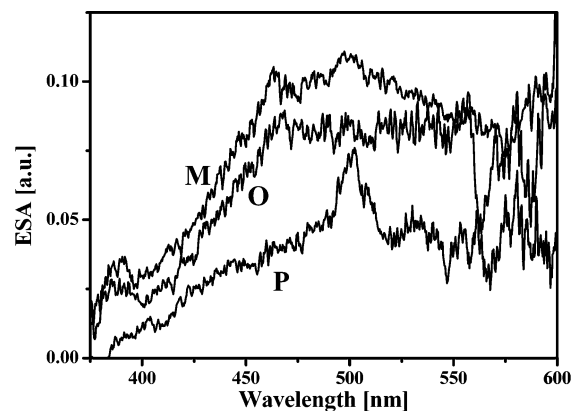
Figure 11. ESA spectra of aqueous solutions of polyelectrolyte multicomposite shells of the type [PSS-PY/PDADMAC]$_4$/[PSS-PY/PAH]$_4$/[PSS-PY/PEI]$_4$. Pump pulse was at 340 nm with 5×10^{24} photons/(cm^2 s). (M) Multicomposite shells in water (60 mg/mL), (O) multicomposite shells in water (48 mg/mL) plus VPd (0.1 mg/mL), (P) multicomposite shells in water (30 mg/mL) plus DMA (50% vol).

addition of DMA. All three spectra exhibit a pronounced maximum at 495 nm, which is typical for the pyrene anion PY$^-$. Again, the absorbance at the PY$^-$ transition is of comparable intensity for the three systems. But opposite of the case of VPd, a lower concentration of DMA was used for the (PSS-PY/PEI)$_4$ system than for the other two systems.

The transient excited state absorption spectra of the 12-bilayer shells [PSS-PY/PDADMAC]$_4$/[PSS-PY/PAH]$_4$/[PSS-PY/PEI]$_4$ are given in Figure 11. The spectrum M was recorded without acceptor or donor molecules and shows the typical maximum of PY* at 385 nm and the two maxima of PY$^+$ at 460 nm and of PY$^-$ at 495 nm. The spectra O and P are recorded after addition of VPd and DMA, respectively. The relative concentration of VPd was roughly 2 times higher than in the case of spectra G and I in Figure 9, and the relative concentration of DMA was about 30% higher compared to the concentration used for the spectra J and L shown in Figure 10. It is clearly seen that the VPd has nearly no effect, and only the intensity of the PY$^+$ state seems to be slightly enhanced. On the other hand, the addition of DMA leads to a well-pronounced ESA spectrum of the pure PY$^-$ state. The PY$^+$ transition at 460 nm has completely vanished. This asymmetry of the transient absorption is observed only in the multilayer shells built from the sequence of different polyelectrolyte materials.

Discussion

In this work a pyrene-substituted polycation (PSS-PY) with a high load of PY is presented, and it is used to study the charge transfer behavior of pyrene in the environment of polyectrolyte materials. The PSS-PY is used as a polyanion for the layer-by-layer deposition technique to build homogeneous films with high concentration of pyrene. The investigation of the photophysical properties requires high optical density, which is achieved by adsorption of the polyelectrolytes on colloids.[18]

The regular and homogeneous formation of PE multilayers was deduced from the measurements of ζ-potentials (Figure 2) and fluorescence intensity (Figure 3). For the multicomposite shells of the type [PSS-PY/PDADMAC]$_4$/[PSS-PY/PAH]$_4$/[PSS-PY/PEI]$_4$ the ζ-potential was recorded during the whole deposition process. Since there is no significant change in

surface potential when the polycation is changed, it is justified to assume that the amount of PE material adsorbed is almost constant, independent of the polycation used for the multilayer buildup process. Hence, the PY density across the shell is nearly constant, which is an important prerequisite for the following charge transfer investigations. The fluorescence of PY during layer-by-layer deposition, as shown in Figure 3, suggests a linear growth rate of film material and film thickness. However, it is impossible to draw quantitative conclusions from fluorescence intensity data measured during deposition of layers of different polycations, since the PE materials show quenching of PY emission in varying quantity.

The small size of the colloids and their high concentration cause huge light scattering (Rayleigh scattering), which must be overcome by the optical density of the pyrene. The amount of PY seen by a light beam passing through the colloidal solution is proportional to the total surface area covered by the PE shells and the PY density within the films. In this case, dye concentration from a loading of 1 PY/30 PSS provided an optical density of 0.5−0.8, which is similar to the optical density due to the scattering losses (see Figure 5). Unfortunately, the mean PY density within the PE films cannot be calculated from the absorbance, since the concentration of shells is not known with sufficient accuracy. However, an estimate is obtained from the molecular volume of PY and the polyelectrolytes. Assuming 30 monomer units of PSS per one PY and taking into account that only every second layer of the PE is doped with PY, and taking into account that the PE may contain up to 30 mol % of water,[5] one can estimate the density of PY in the PE to be one chromophore per 9 nm^3, which is equal to an average distance between neighboring PY molecules of 2.1 nm. The same value was obtained from an independent estimate.[37] It is sufficient to compare this value with the size of PY molecules (0.7 nm) to see that a network of molecules with overlapping electron wave functions is present in the PE hollow capsules. Such a network is an indispensable prerequisite for electron transfer cascades between several neighboring PY molecules. A further consequence of the high PY concentration is the formation of excimers, as can be seen in Figure 3 from the broad emission in the wavelength range 450−550 nm.

The functionality of the photoinduced charge transfer is demonstrated by probing the transient charged states of PY. Therefore, the ability of PY to serve as an electron donor as well as an electron acceptor is utilized, and this behavior is actually detected by the measurements. A schematic view of the photophysical processes involved is depicted in Figure 12.

After photoexcitation of PY from the ground state (1 in Figure 12) a charge transfer is assumed to a neighboring molecule (2), which can be either an electron donor or acceptor molecule. After the charge transfer a transient charged state of the respective PY radical is observed, which lives for several microseconds. This charged state is probed by the ESA technique (3) by looking at the absorption spectrum using a probe pulse that is in coincidence with the pump pulse used for the photoexcitation. A charge transfer to neighboring PY molecules is assumed to be driven by energy steps due to different polarities of the local environment of the molecules. In Figure 12 this is indicated by the energy shift between the levels of the neighboring molecules.
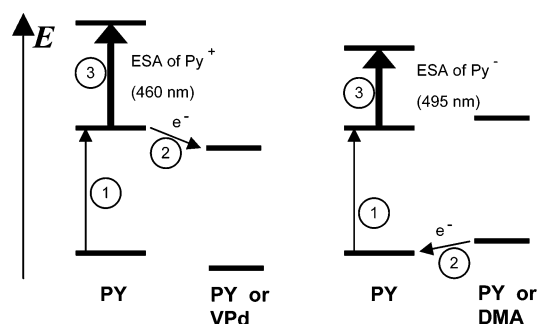
(37) Li, L.; Tedeschi, C.; Kurth, D.; Möhwald, H. *Chem. Mater.* (in press).

Figure 12. Schematic view of the processes involved for the observation of the excited state absorption spectra of pyrene radicals. After photoexcitation (1) a charge transfer occurs (2) to a neighboring molecule. The transient charged state of the PY is probed by the excited state absorption (ESA) (3). On the left, the charge transfer to an acceptor molecule is depicted, and on the right the same process is shown for donor molecules. The relative heights of the energy levels are arbitrary and not in scale. A relative shift of energy levels of identical PY molecules may be caused by different polarity of the local environment.

The experimental verification of the spectroscopic behavior of the transient excited states is best seen from the pure PSS-PY polyelectrolyte dissolved in aqueous solution, as shown in Figure 7. In the case where an electron acceptor or donor is present, the radical states of PY^+ (460 nm) and PY^- (495 nm) are detected, respectively. These radical states are the result of a charge transfer transition of either the type PY-VPd → PY^+−VPd^- or PY-DMA → PY^-−DMA^+. In both cases the electron is completely transferred from/to the pyrene. Similarly, transfer states of the type PY−PY → PY^+−PY^- are observed in the absence of donor or acceptor molecules. Although for this system a quantification of the PY density is not possible, it is reasonable to assume a much higher density than in the case of the PE shells. This is supported by the higher amount of excimer emission, as can be seen in Figure 6.

If the concentration of donor or acceptor molecules is high enough to saturate the PY in a sense that the probability for the formation of PY^+−PY^- is negligible, pyrene molecules are only excited in one type of radical state. If the same PY concentration and the same light intensity for excitation are used for the system without additional donor or acceptor molecules, only 50% of the pyrene molecules are excited into the corresponding radical states. Hence, in a pure system the absorption intensity of the PY radical bands should be half of the intensities measured for the systems with donor or acceptor molecules. This is actually the case for the spectra given in Figure 7, where spectrum A can be reproduced in good coincidence by the spectrum calculated from 1/2(B + C), indicated by the dashed line. This observation strongly supports our interpretation of the ESA spectra.

The efficiency of the electron transfer processes, as measured by the optical density of the ESA radical bands, depends not only on the donor (acceptor) concentration but also on the material of the PE matrix where PY is embedded. As can be seen from the measurements of Figures 9 and 10 and the data presented in Table 1, similar optical densities are obtained by the usage of very different donor (or acceptor) concentrations. An extra low charge transfer efficiency has been found for the PSS-PY/PEI shells in the presence of the electron acceptor VPd. In this case a VPd concentration 100 times higher than the one used for other PE hollow capsules was necessary.

A remarkable asymmetry of the transfer efficiencies is observed for the multicomposite shells of 12 bilayers (Figure 11). In the case where VPd is added, the spectrum should be comparable to the spectra of Figure 9. For a quantitative comparison, one has to take into account that the PY content for the four-bilayer shells is only one-third of the PY content of the multicomposite shells. In the latter, the part of the film containing the PEI probably does not contribute to the PY-VPd states, since for the PSS-PY/PEI layers the transfer efficiency was 100 times lower. Therefore, spectrum O should give a signal that is twice as intense as that from spectra G to I, which is in contrast to the low signal observed here. If DMA is added to the multicomposite shells of 12 bilayers, the PY⁻ state is well resolved and the intensity corresponds to that measured for the four-bilayer shells of Figure 10. Again, the intensity is less than expected; however, the molar ratio of DMA compared to PY is lowered because of the higher thickness of the samples. Therefore, the overall efficiency seems to be enhanced in that case.

Partially this asymmetry can be explained by the asymmetric electron transfer behavior of those PY molecules that are located within the PSS-PY/PEI layers. However, this should lead to an asymmetric deviation of the ESA intensity which is on the order of 30%; the asymmetry observed here is much more pronounced. Although this effect is not fully understood at the present time and deserves further investigation, it can be ascribed to the asymmetric and inhomogeneous nature of the multicomposite hollow PE capsules.

In our previous investigations[16] it was shown that the polarity of PE multilayers can be varied over a large scale by the choice of the polycation. Therefore, the polarity of the multicomposite shells is expected to vary smoothly across the capsule wall. One may criticize the assumption that the investigated PE hollow capsules exhibit the same polarity measured in a previous paper for analogous planar PE films. In that work the micropolarity of multilayer films was investigated by using the fluorescence emission of PY, a polarity sensitive probe. The $\pi^* \rightarrow \pi$ emission spectrum of pyrene molecules inserted into preformed planar PE multilayer films exhibited the characteristic five well-resolved major vibronic bands between 370 and 400 nm, generally labeled I, II, III, ..., in progressive order. Due to coupling of the electronic and vibronic states,[38–40] the first vibronic band (labeled I) undergoes significant intensity enhancement with increasing solvent polarity compared to the third band (labeled III).[41,42] By the ratio of emission intensities of the vibronic bands I and III (indicated as I/III) measured into different PSS/polycation multilayers, the film polarity was macroscopically estimated as an average of the emission characteristic of the environment sensed by individual probe molecules.

By binding the PY probe to poly(styrenesulfonic acid) (PSS), the characteristic vibronic structure of the PY emission spectrum is partially lost, which makes the polymer-bound pyrene less useful to probe the micropolarity of the shells of hollow PE capsules. To overcome this problem, hollow PE shells prepared from unlabeled PSS and PDADMAC (or the other two poly-

cations, PAH and PEI) were doped with unsubstituted PY molecules, by adding PY molecules to the capsule solution in a concentration of 10^{-6} M. Apart from the difficulty coming from removal of PY molecules during the centrifugation/wash/redispersion cycle, detection of the film polarity by the PY scale was still possible and revealed values only slightly different from the one recorded previously for the corresponding planar films. The differences in the recorded PY values can be explained by the fact that a substantial amount of PY was present in the water solution. Therefore the recorded PY spectra are a superposition of two components: one that results from PY dissolved in the polyelectrolyte multilayers and another one that results from the PY dissolved in the aqueous phase. Additionally, water molecules may be contained in the hollow shells in a larger amount than was found for planar multilayer films,[5,6] and it is not excluded that a few MF oligomers are retained within the PE walls after dissolution of the colloidal template.[43] These factors influence the absolute value for the polarity given by PY. Nevertheless, the tendency of a more polar environment for PSS/PDADMAC layers with respect to the PSS/PAH and PSS/PEI layers could be confirmed, and therefore we conclude that there is a gradual change of solvent polarity across the multilayer shells of the type PSS-PY/PDADMAC]₄/[PSS-PY/PAH]₄/[PSS-PY/PEI]₄.

Since PY itself is a highly hydrophobic and hence apolar material, one should consider that the high load of the polyelectrolyte films with pyrene molecules could decrease the polarity of the shell material. However, in this case the polarity monitored by the PY should indicate this decrease, which however was never observed. Furthermore, the volume concentration of PY is less than 3%, which should not affect the polarity on average.

A further indication of the enhancement of charge separation due to the polarity gradient was found from very recent time-resolved transient ESA spectra that will be presented in detail in an upcoming publication. It was seen that in films without polarity gradient 30%−40% of the initially formed PY⁺ remains with a lifetime of about 10 μs, while the rest as well as the entire PY⁻ decays rapidly with the fluorescence lifetime. In contrast with this, in the films with gradient an equal amount of PY⁻ and PY⁺ remains observable with lifetimes of more than 50 μs. This gives rise to the conclusion that in the homogeneous materials charge separation is driven by local polarity variations, while a long-lived charge separation over long distances is observed in the case where a polarity gradient is present across the film.

Summary and Conclusions

In this paper we have demonstrated that it is possible to prepare hollow polyelectrolyte capsules with high content of pyrene molecules and have provided evidence for an internal polarity gradient across the shell wall. PY molecules are capable of photoinduced electron transfer reactions either to neighboring PY or to electron donor or acceptor molecules that are added to the capsule wall by adsorption from solution. The electron transfer was proven unambiguously by the transient excited stated absorption spectra of pyrene. The efficiency of this

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process depends not only on the donor (or acceptor) concentration but also on the polyelectrolyte material. An extra low charge transfer efficiency was observed for PSS-PY/PEI films in the presence of the electron acceptor VPd. The PY concentration in the films is large enough to enable a cascade of charge transfer reactions. Although we could not demonstrate clearly an effect of the polarity gradient on the charge transfer efficieny, it is expected that these materials may be used in future times to stabilize the direction of a charge transfer with distances that range over several molecules.