Articles

Synthesis of a Pyrene-Labeled Polyanion and Its Adsorption onto Polyelectrolyte Hollow Capsules Functionalized for Electron Transfer

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A multilayer system is built up that enables vectorial electron transfer along a polarity gradient. For this, pyrene is covalently coupled to a polyeclectrolyte that can then be incorporated into polyelectrolyte multilayers by layer-by-layer technology. High pyrene labeling (1:30) allows for high chromophore density in the film (1/10 nm^3), which is necessary for efficient electron transfer. The photophysical properties of the covalently coupled dye do not differ much from those of the well-known free pyrene, except that the high local pyrene concentration yields considerable excimer emission. The multilayer is built in the form of the wall of hollow capsules of micrometer dimensions. This enables kinetic studies due to the high specific area and also gives perspectives for further development of the system for light harvesting and energy storage in the inside, in analogy to natural photosynthesis. Quantitative charge transfer across the capsule shell is demonstrated by means of fluorescence quenching studies.

Introduction

Photoelectric energy conversion is an important and interesting process for harvesting solar energy or for converting optical and electrical information. Among the many possibilities to achieve this, those mimicking natural photosynthesis are most promising. This includes basically a supramolecular array of chromophores responsible for light harvesting and funneling of photon energy to reaction centers. The charge separation takes place before an electron is transferred across a membrane of almost 5 nm thickness. Then this electron transfer is converted into storable chemical energy.

In an effort to mimic the natural system composites of carotenoids, porphyrines and quinones have been arranged in supramolecular assemblies with increasing success as regards to efficiency.[1−3] Also sol−gel glasses, zeolites, micelles, vesicles, or Nafion membranes have been used to build up the membrane by consecutive adsorption of oppositely charged polyelectrolytes.[4−7] This enables building the membrane also as a gradient material varying the composition over nanometer distances along the surface normal. This has been made use of to create polarity gradients that may enable vectorial electron transfer. Another possibility would be to incorporate different chromophores along the membrane. In this work we will concentrate on the problem of inserting chromophores in the membrane in sufficiently high concentration to enable electron transfer between the dyes. To be able at a later stage to insert the chromophore at a specific location, we coupled the chromophore to a polyelectrolyte. We concentrate here on building an electron transfer array and this essentially involves the following tasks:

(1) prepare a copolymer with sufficiently high dye density,

(2) understand the optical properties of the dye for different substitution,

(3) arrange the functional molecule in a polarity gradient, and

(4) prove the existence of electron transfer in the chromophore array.

We use pyrene as the dye because of its well-known photophysics and because of its large excited-state lifetime, which enables photoinduced charge generation with high yield. As the system, we study multilayer capsules, since due to their high surface-to-volume ratio they can be studied by time- and space-resolved optical spectroscopy. In a later stage this system could be extendable to obtain a storable product via the electron-transfer reaction, but this work will, as a first step, concentrate on the above topics.

Experimental Section

Materials. Dispersions of monodispersed weakly cross-linked melamine formaldehyde (MF) particles with a diameter

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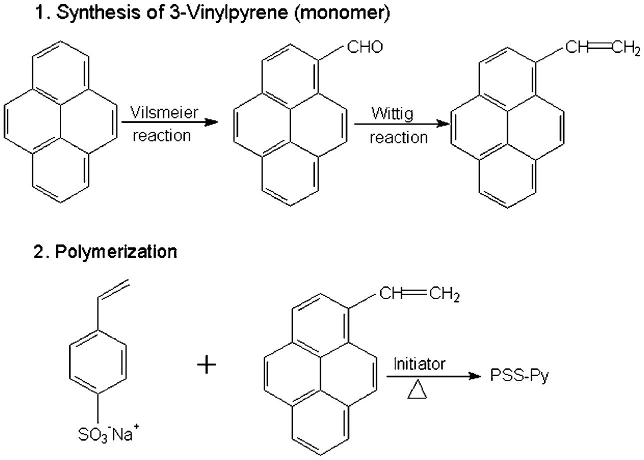
Scheme 1. Synthesis of PSS−Py



of 1.96 μm were purchased from Microparticles GmbH, Berlin, Germany. 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) were purchased from Aldrich Chemical Co.

Pyrene-labeled poly(styrenesulfonic acid) (PSS−Py) was synthesized according to the procedure of Tanikawa et al.[8,9]

Polyviologen (PV) was synthesized according to the literature.[10]

Solutions of PEI (1 mg/mL), PAH (1 mg/mL), PDADMAC (1 mg/mL), and PSS−Py (5 mg/mL) in water with NaCl (0.5 M) were prepared in all experiments.

Layer-by-Layer Self-Assembly on Colloid Particles. The first eight layers of polycation (PDADMAC) and polyanion (PSS−Py) were assembled onto the surface of MF by layer-by-layer adsorption.[11−15] Excess polyelectrolyte was removed by three repeated centrifugation (3000 rpm, 5 min)/washing/redispersion cycles in each depostion step. After that, hollow capsules could be obtained by dissolving the MF core in HCl (0.1 M).

The second step is to assemble eight layers of PSS−Py and PAH alternatively onto the surface of hollow capsules. The outer eight layers were composed of PSS−Py and PEI with the same protocol, but the speed of centrifugation was increased to 6000 rpm.

Characterization Methods. Absorption spectra were measured by a Varian Cary 4E UV−visible spectrophotometer. Steady-state fluorescence spectra were recorded at room temperature using a Spex Fluorolog-2 (model FL-2T2) spectrofluorometer (ISA, Olching, Germany). Confocal micrographs were taken with a confocal laser scanning microscope (CLSM) "Aristoplan" from Leica, equipped with a 100×oil immersion objective.

The capsule wall thickness was measured by scanning force microscopy (SFM), Nanoscope III Multimode SFM (Digital Instrument Inc., Santa Barbara, CA).

A bright-line hemacytometer (cell counting chamber) was used to count the amount of capsules in solution.

Results and Discussion

1. Photophysics and Photochemical Properties of PSS−Py and Precursors. The PSS−Py synthesis via radical polymerization was optimized to increase the molar ratio of pyrene in the copolymer. In this work, a molar ratio of 1 Py/30 PSS was obtained.

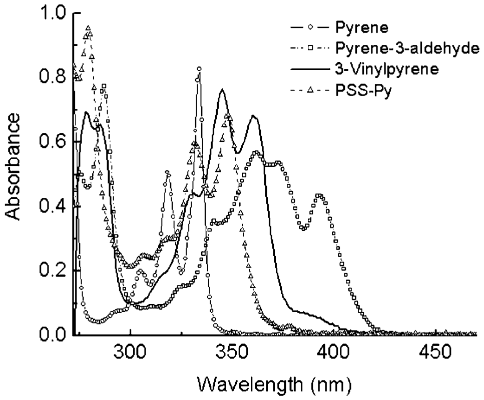


Figure 1. The UV absorption spectra of pyrene, pyrene-3-aldehyde, vinylpyrene, and PSS−Py, at 2×10^{-5} M, 25 °C.

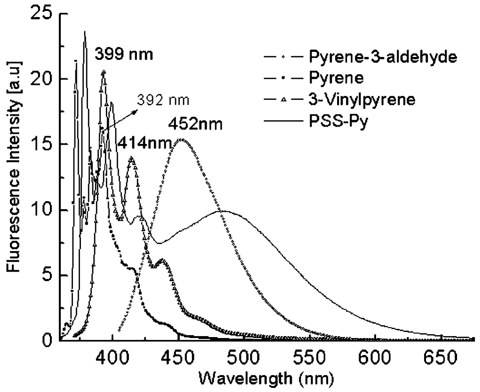


Figure 2. The emission spectra of pyrene, pyrene-3-aldehyde, 3-vinylpyrene, and PSS−Py, at 10^{-6} M, 25 °C.

Scheme 1 is the synthesis route. During the synthesis, the reaction is controlled by UV absorption and fluorescence spectra. Figure 1 shows the UV spectrum of the intermediates of the PSS−Py synthesis.

The maximal UV absorption of pyrene is at 335 nm. After the Vilsmeier reaction, an aldehyde group is attached to pyrene. Due to the conjugation of aldehyde with the ring of pyrene, pyrene-3-aldehyde should have a red shift. The maximal UV absorption of pyrene-3-aldehyde occurs at 396 nm. After the second step of the Wittig reaction, the aldehyde group was converted to a double bond. Compared to the pyrene, 3-vinylpyrene has an absorption maximum at 361 nm.

After polymerization, 3-vinylpyrene ceased to exist due to the conversion of its double bond. Compared to 3-vinylpyrene, the UV absorption of PSS−Py occurs at 348 nm. So according to the UV spectrum, different maximal UV absorption of the intermediates of pyrene could be observed during different reaction steps.

Figure 2 summarizes the fluorescence spectra of the intermediates of the synthesis of PSS−Py. The shifts of the short wavelength emission maxima roughly follow the shifts of the absorption maxima comparing pyrene, 3-vinylpyrene, and PSS−Py. These shifts can be at-

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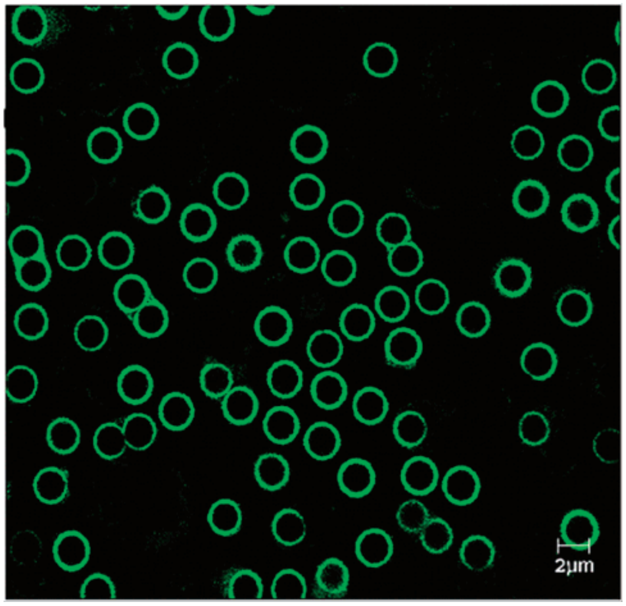
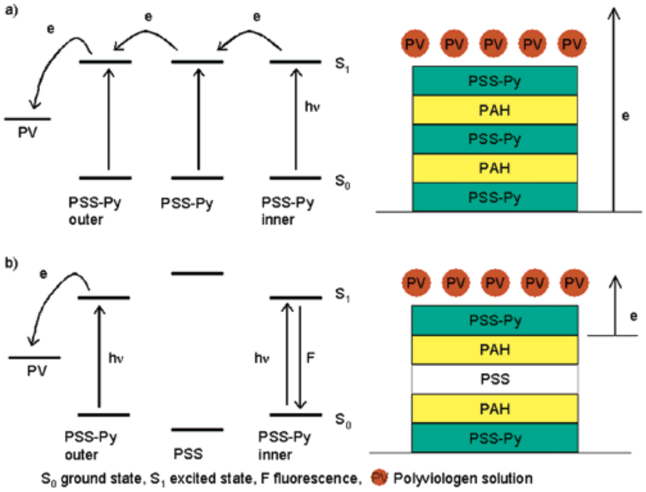


Figure 3. CLSM images of polarity gradient hollow capsules having 24 layers composed of (PSS−Py/PDAD)$_4$(PSS−Py/PAH)$_4$(PSS−Py/PEI)$_4$. Emission was at 517 nm, from fluorescein dye.

tributed to an energy change of the excited state. Also the broad maximum of the emission near 480 nm can be described as usual to the emission of the excimer formation. More difficultly and not unequivocally explained are the changes in the spectra of pyrene-3-aldehyde. There the absorption spectra are shifted drastically and the relative intensities of vibronic bands are altered so that one may derive that the configurations in the ground and excited state differ. In that case one would also expect a change in the vibronic structure of the emission: in the extreme case a broadening and a larger Stokes shift. This is indeed observed. Hence, the broad emission for pyrene-3-aldehyde at 450 nm is not due to an excimer but due to monomer with different equilibrium configuration in ground and excited state.

2. Polarity Gradient Hollow Capsules. In previous papers,[16,17] we showed that the micropolarity of unsubstituted Py molecules adsorbed into four preformed [PSS/PEI] bilayers is lower than the one recorded for dye molecules inserted into PSS/PAH or PSS/PDADMAC layers. According to these results, one would expect that by assembling the layer sequence [PSS/PEI]$_4$/[PSS/PAH]$_4$/[PSS/PDADMAC]$_4$ the polarity of the whole film would increase from left to right. By using 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 either to juxtapose dye molecules at a fixed position within the multilayer assembly or to have chromophores exhibiting simultaneously electron donor or acceptor behavior depending on the kind of dyes used for doping the PE hollow capsules.

Scheme 2. Scheme of PSS−Py Fluorescence Quenching by Polyviologen in Multilayers with PSS−Py in Each Anionic Layer (a) and with an Intermittent PSS Layer between the PSS−Py Films (b)[a]



[a] The energy levels are only schematic since no relaxation or local polarity effects are considered.

For the multilayer sequence of 12 bilayers, the PSS−Py/PDADMAC layer combination was assembled as a first sequence onto the MF particles in order to increase 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 four PSS−Py/PDADMAC bilayers, and additional PE layers were adsorbed onto hollow PE shells. By core dissolution at higher multilayer numbers the film permeability decreases, hindering the release of MF oligomers from the capsule wall. On the other hand, core dissolution is needed to reduce light scattering of the sample.

Figure 3 shows confocal laser scanning microscope (CLSM) images of polarity gradient capsules. These images provide strong evidence that hollow polarity gradient capsules were obtained. By UV measurements, strong pyrene absorption could be found. It proves that PSS−Py had been successfully inserted in the wall of the hollow capsules. To quantify the chromophore concentration in the capsules, we combine measurements of absorption spectra and particle counting by a bright-line hemacytometer. For a solution with 5.2×10^7 capsules/mL, we obtain a pyrene concentration (from PSS−Py) of 2.3×10^{15}/mL. Hence there are 4.4×10^7 chromophores/capsule. The wall thickness is about 36 nm, obtained by SFM measurement. The capsules with radius 1.0 μm and wall thickness 36 nm have a wall volume $V = 4\pi(10^3\ \mathrm{nm})^2 \times 36\ \mathrm{nm} = 4.5 \times 10^8\ \mathrm{nm}^3$. Thus the chromophore density amounts to

$$\rho_c = \frac{4.4 \times 10^7}{4.5 \times 10^8\ \mathrm{nm}^3} = \frac{1}{10\ \mathrm{nm}^3}$$

This concentration is nearly identical to the one previously derived for pyrene in planar multilayers.[17]

It is also intriguing to estimate characteristic distances d between chromophores. Assuming each pyrene is distributed in a sphere of 10 nm^3 with a radius

$$d = \sqrt[3]{\frac{3 \times 10\ \mathrm{nm}^3}{4\pi}} = 1.34\ \mathrm{nm}$$

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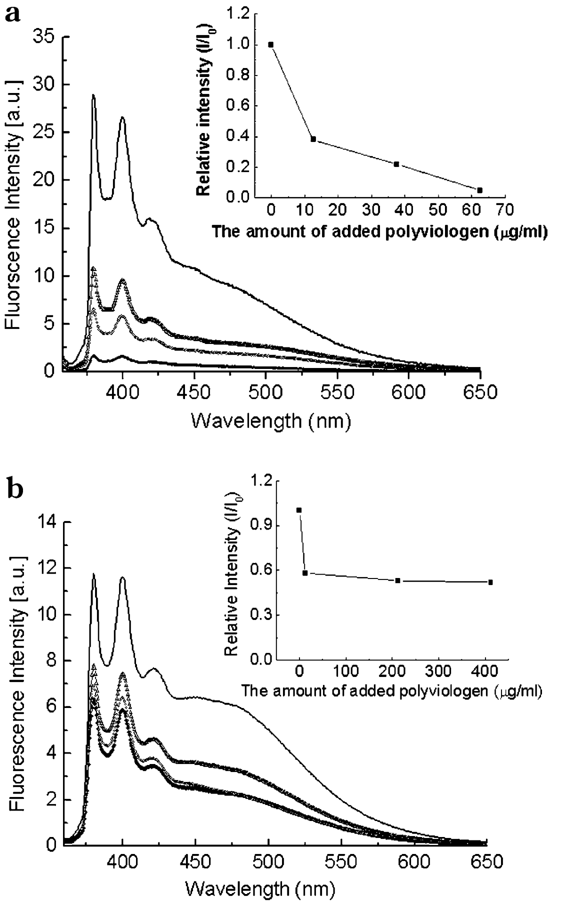

Figure 4. (a) Fluorescence spectra of 2 mL of hollow capsules (1.96 μm, 3.75 mg/mL) in water. The shells are composed of PSS−Py/PAH/PSS−Py/PAH/PSS−Py. PV concentration: (1) 12.5 μg/mL, (2) 37.5 μg/mL, (3) 62.5 μg/mL. (b) Fluorescence spectra of 2 mL hollow capsules (1.96 μm, 15 mg/mL) in water. The shells are composed of PSS−Py/PAH/PSS/PAH/PSS−Py. The adjacent PSS−Py layers are interlaced by insulating one PSS layer. PV concentration: (1) 12.5 μg/mL, (2) 212.5 μg/mL, (3) 412.5 μg/mL.

yields an average distance of two chromophores of 2.68 nm. This is presumably sufficient to enable electron-transfer considering chromophore dimensions of 1 nm, but it is also clear that concentrations about that large will be needed.

3. Photoinduced Electron Transfer across the Capsule Wall. To test if there is electron transfer between different pyrene chromophores, we performed the experiment sketched in Scheme 2. To a multilayer with PSS−Py as negatively charged component polyviologen was added, which is known to be a strong electron acceptor for excited state pyrene and hence quenches its fluorescence. If pyrene is now excited optically anywhere in the film, the fluorescence may be quenched if an electron can hop between excited states to finally arrive at the acceptor PV in solution (Scheme 2a). This is indeed observed in Figure 4a, where apparently the pyrene emission can be completely quenched. To prove that quenching is indeed due to charge transfer and not due to, for example, the oligomeric PV diffusing into the film, we varied the film composition according to Scheme 2b. Here between two PSS−Py layers a PSS layer without chromophore was inserted, and one expects this to block electron transfer. It would not change PV permeation if existing at all, because the 3 mol % labeling is not expected to significantly affect the structure of the PSS host. Hence, if quenching is due to electron transfer to PV, one expects the outer PSS−Py layer to exhibit fluorescence quenching, not the inner layer. The expected maximum fluorescence decrease by a factor of 2 is indeed observed (see Figure 4b). This demonstrates that we have constructed an electron relay, and obviously the simplicity of construction suggests many structural variations to manipulate electron transfer.

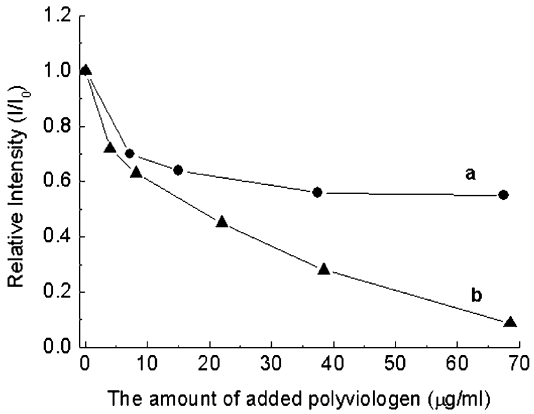

Figure 5. (a) Fluorescence intensity as a function of PV concentration for a multilayer with dilution of the pyrene concentration in the middle layer PSS−Py/PAH/(PSS−Py)$_{0.6}$-(PSS)$_{0.4}$/PAH/PSS−Py. (b) Fluorescence intensity as a function of PV concentration for a multilayer with dilution of the pyrene concentration in the middle of the polarity gradient film (PSS−Py/PEI)$_2$[(PSS−Py)$_{0.6}$(PSS)$_{0.4}$/PAH)]$_2$(PSS−Py/PDADMAC)$_2$.

To demonstrate the vectorial electron transfer, we prepared a multilayer where the middle anionic part is composed of (PSS−Py)$_{0.6}$/PSS$_{0.4}$. In this case, the dye intensity is too low to enable electron transfer, and this is why the fluorescence can be quenched only up to 0.5 (Figure 5a). However, if one prepares a multilayer with a composition yielding a polarity gradient, the fluorescence can be completely quenched at high PV concentration (Figure 5b). This indicates that vectorial electron transfer has indeed been achieved.

Conclusions

We have shown in this work that polyelectrolyte multilayers with high chromophore densities to allow for electron transfer between the dyes could be prepared, and we have shown that photoinduced electron transfer exists. This was possible by synthesizing polyelectrolytes with rather high dye content and assembling them in multilayers. The optical properties of the functional dyes can be understood as they deviate only little from those of the well-known molecular pyrene. It was also possible to build up gradient films allowing for vectorial electron transfer.

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