Polymer Microcapsules

Photoinduced Vectorial Charge Transfer across Walls of Hollow Microcapsules**

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In photosynthesis, light is harvested by chromophores and transferred to reaction centers where a photoinduced charge separation and an electron transfer across a membrane of 5-nm thickness is effected. The electrical energy that is created is then converted into chemical energy, that is, products stored on both sides of the membrane.[1] There have been many attempts to mimic this process as photonic energy or information conversion devices.[2] However, to become technically attractive the system must also be sufficiently simple and easy to build up.

From the viewpoint of system design the electron-transfer chain is most demanding since it requires control of intermolecular distances with nanometer precision. Therefore this work intends to prepare a vectorial electron-transfer chain across a membrane that may later be coupled to a chemical-energy conversion and storage device. The membrane is built up by consecutive adsorption of alternatively charged polyelectrolytes. It exhibits a defined thickness, in most of the samples here of about 10 nm. The membrane represents the shell of a hollow capsule that has been prepared by adsorbing polyelectrolyte multilayers (PEMs) on a colloid that could later be destroyed.[3] We chose this highly versatile system since its constituent compounds and colloidal cores can determine the capsule size, and can also reversibly include macromolecules within the cores. Using appropriate polyelectrolytes, one can also build films with a polarity gradient over nanometer dimensions to direct charge transfer.[4]

We used pyrene as a chromophore in the films because of its well-known photophysical/chemical properties. Many donors and acceptors are known to enable very efficient electron transfer to and from pyrene because of its long excited-state lifetime.[5] We previously reported the synthesis of pyrene with the anionic polyelectrolyte polystyrenesulfonic acid (PSS) in a reasonably high concentration.[6] This should provide the possibility of sufficiently high chromophore density to enable electron transfer between different pyrene units, and indeed adding an oligomeric electron acceptor (polyviologen) allows the fluorescence quenching of pyrene to be observed, even for molecules inside the film. Scheme 1 a shows the structures of the polyelectrolytes used in the experiments. Scheme 1 b shows the model for electron trans-

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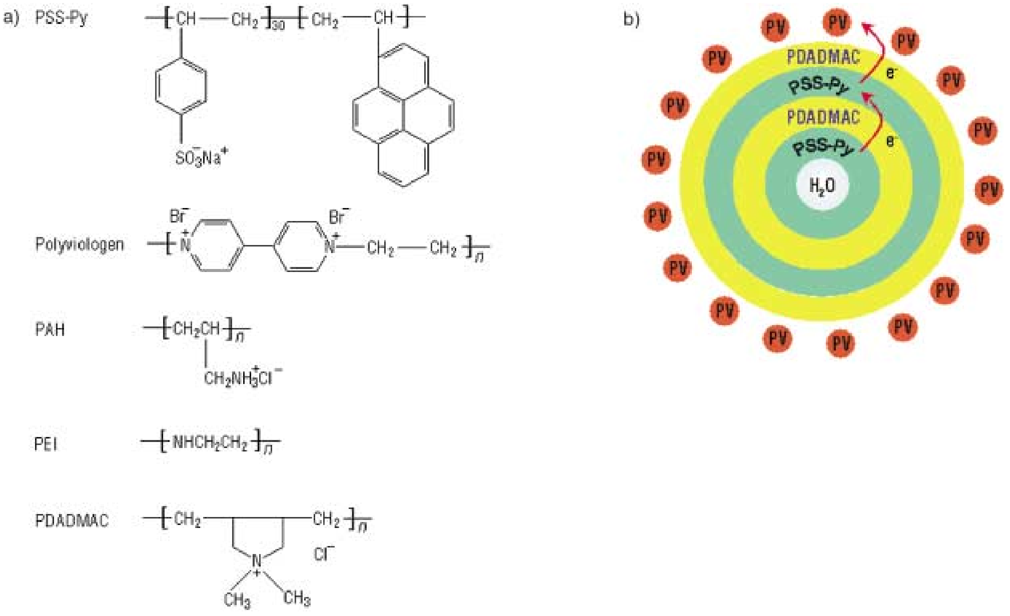


Scheme 1. a) Polymers used to build up the film and electron acceptor in the internal aqueous phase; b) electron transfer between components in the hollow capsule wall. The dimensions are not to scale as the capsule diameter is 1.96 μm and the wall thickness is 6 nm (12 nm in case of the experiment with a polarity gradient).

fer employed in this system. The previous results of pyrene quenching by polyviologen were interpreted as electron transfer, but there remain many unresolved issues:

- The electron acceptor used, polyviologen (PV), did not have a high molecular weight and a broad size distribution. This raises doubts whether a lower-molecular-weight fraction penetrates the film, thus quenching the nearby pyrene emission.
- From the concentration of pyrene in the film, one calculates an average chromophore distance of 2.7 nm.[6] This is rather large for electron transfer.
- Up to now information was basically derived from fluorescence quenching, but the remaining pyrene cation could not be detected. Also, no PV ionic species could be detected in transient absorption spectroscopy, probably due to a short lifetime.

Taking these issues into account, the purpose of this paper is to confirm the previous conclusions and to provide more information on the mechanism. The influence of the local environment is assessed by varying the type of polyelectrolyte and film surface, as well as the chromophore density and film architecture. Having established the mechanism we finally demonstrate the existence of vectorial electron transfer.

Figure 1 shows the emission spectra for pyrene after the addition of PV for a solution of hollow capsules containing PSS-Py in the walls, where the outer surface is either negatively (Figure 1 a) or positively charged (Figure 1 b). The vibrational structure of the monomer, as well as the shoulder near 480 nm due to the excimer, can be clearly observed. The latter is indicative of a rather high pyrene content because excimer formation is not expected as a result of molecular diffusion, rather only due to dye proximity within the polymer matrix. Both monomer and excimer emission are quenched by PV, and the corresponding intensity change is given in the insets of Figure 1 as a function of PV concentration. In both cases one observes complete quenching, but the amount of PV necessary for this varies by a

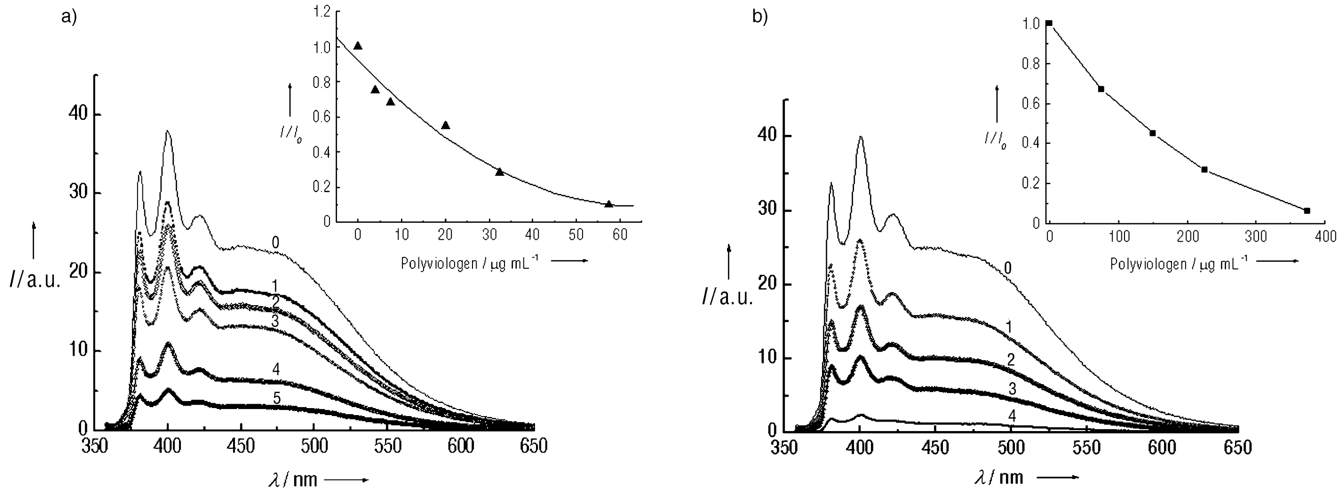


Figure 1. a) Fluorescence spectra of 2-mL hollow capsules (1.96 μm) in water. The shells are composed of (PSS-Py/PDADMAC)$_3$/PSS-Py. PV concentration: 1) 3.96, 2) 7.5, 3) 20, 4) 32.5, 5) 57.5 μg mL^{-1}; b) Fluorescence spectra of 2-mL hollow capsules (1.96 μm) in water. The shells are composed of (PSS-Py/PDADMAC)$_3$. PV concentration: 1) 75, 2) 150, 3) , 4) 375 μg mL^{-1}.

factor of five. This can be qualitatively understood by assuming a PV adsorption equilibrium between the film surface and the bulk. For positively charged PV this equilibrium is shifted towards the bulk if the surface is also positively charged, thus requiring a higher PV concentration for quenching. In the alternate case of PV diffusion into the film, the net surface charge would be less relevant, as previously shown for diffusing low-molecular-weight dyes.[7] We also changed the cationic polymer used for film build-up from poly(diallyldimethylammonium chloride) (PDADMAC) to poly(allylamine hydrochloride) (PAH) and poly(ethylenimine) (PEI). However, the PV concentrations necessary for quenching were very similar, again indicating that the effect is not due to PV in the interior of the film but to PV on the surface. Another strong argument against PV penetrating into the film has been presented by preparing a multilayer architecture with PSS-Py in two double layers interlaced by a pyrene-free double layer. In this case only the outer PSS-Py layer can be quenched.

Having convincingly shown that PV does not penetrate the film the question remains about how the charge transfers to PV after excitation of an arbitrary pyrene unit in the film. There may be energy transfer to a pyrene unit near the surface followed by electron transfer, or electron transfer from the excited molecule. For energy transfer one may envisage two different mechanisms:

Transfer according to a dipolar mechanism (Förster transfer[8]) is highly improbable for this system since it depends on the overlap integral between pyrene absorption and emission spectra; this is essentially zero. In addition the oscillator strength for the longest wavelength absorption is very low.

Transfer according to the Dexter mechanism[9] cannot a priori be ruled out. This mechanism relies on the overlap integral of the wave functions of the excited states and should consequently be of short range. However, it also depends on the overlap of the pyrene absorption and emission spectra, which is very small. Although quantum chemical calculations are not available, the intermolecular distance of 2.7 nm is probably too large for this process to compete with radiative emission with a lifetime of about 100 ns.

The argument against Dexter transfer may also hold against electron transfer because this process also depends on the overlap of wave functions, in this case of anions. However, the relevant time is the lifetime of the pyrene anion, which is much longer in the rather polar PEM. That the transfer mechanism is due to short range interactions of chromophores and that the pyrene density can not be greatly reduced without losing electron-transfer capability can be deduced from the experiment whose results are shown in Figure 2. Here, the build-up of layers was achieved using a mixture of PSS-Py and PSS in varying ratios for the middle of three bilayers and measuring the quenching at saturating PV concentration. The fluorescence intensity as a function of PV concentration (Figure 2 a) can be grouped into two types of curves. They either decay towards zero intensity (for high pyrene content) or they decay only to about half the initial intensity. This is displayed more quantitatively in Figure 2 b, where the intensity at high PV concentration is plotted versus PSS-Py/PSS-Py + PSS ratio in the middle layer. The two regimes are thus divided more clearly. In films with only one type of polycation, for a PSS-Py content below 70 % the transfer chain is interrupted, for higher pyrene content it operates equally well. This means that a pyrene labeling of PSS below 2 % would not have been tolerable, and also that the average inter-chromophore distance could not be increased by more than 10 %, that is, not above 3 nm. With respect to this dilution experiment, all systems with other polycations are very similar. However, if one prepares a film with a polarity gradient the threshold where the chain is interrupted can be shifted by about 15 %. Figure 2 b also contains the data for such a film that has been designed to exhibit the highest polarity at the exterior, as previously measured with pyrene probes.[4] Apparently for concentra-

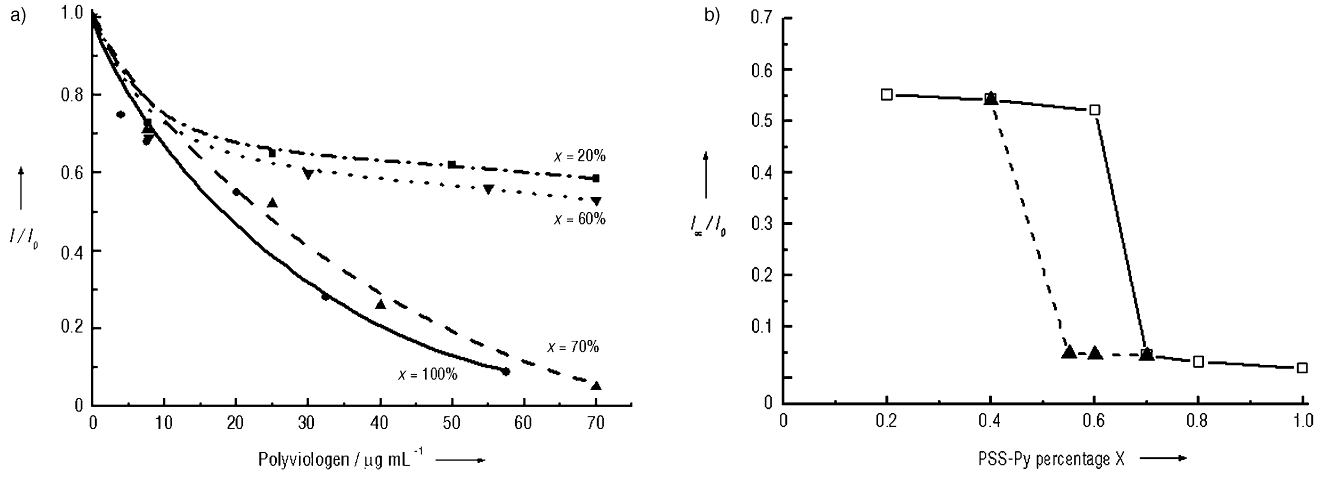
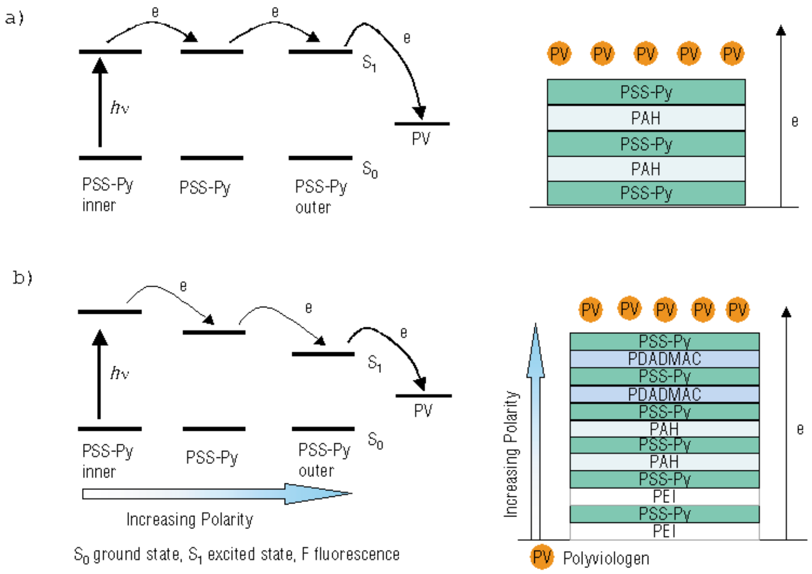


Figure 2. a) Fluorescence intensity as a function of PV concentration for a multilayer with dilution of the pyrene concentration in the middle layer PSS-Py/PDADMAC/(PSS-Py)$_x$ (PSS)$_{1-x}$/PDADMAC/PSS-Py; b) fluorescence intensity I_∞ measured at high PV concentration as a function of pyrene content x for hollow capsules in water for the system described in a) (full line). The dotted line shows the measurement with a polarity gradient for a film architecture: (PSS-Py/PEI)$_2$ [(PSS-Py)$_x$ (PSS)$_{1-x}$/PAH)]$_2$ (PSS-Py/PDADMAC)$_2$.

tions near the threshold ($x \sim 0.6$) the polarity gradient is needed to direct the electron transfer. This is another strong argument in favor of electron transfer versus Dexter transfer.

In conclusion, we have shown the existence of photoinduced vectorial electron transfer from the film to the surface and argued that it is most probably due to electron transfer within the film (Scheme 2). There still remains an unresolved issue concerning the large hopping distance of approximately 3 nm. One possible explanation for this may be a superexchange mechanism, which has been discussed for similar cases involving DNA.[10] In our system the conjugated bonds of polystyrene may be involved, and we plan reference experiments with PEM without conjugation. We could also show that for a suitable composition, electron transfer between identical molecules can be directed by creating a polarity gradient. Hence we have performed experiments on a system that is not defined at the nanometer level but is very versatile and thus provides a means not only for applications but also for further understanding of these interesting mechanisms.



Scheme 2. Left: Energy level scheme for electron transfer in the absence (a) and presence (b) of a polarity gradient. It has been shown[4] by measuring the vibronic structure of pyrene emission that the local polarity is highest for PSS/PDADMAC and lowest for PSS/PEI. However, the numbers cannot unequivocally be converted into a dielectric constant, and therefore we give energy levels only qualititatively; right: architecture corresponding to the energy-level schemes.

Experimental Section

Dispersions of monodisperse weakly cross-linked melamine formaldehyde (MF) particles with a diameter of 1.96 μm were purchased from Microparticles GmbH (Berlin). Poly(diallyldimethylammonium chloride) (PDADMAC, $M_w = 200000$–350000) was purchased from Aldrich Chemical Co. Pyrene-labeled poly(styrenesulfonic acid) (PSS-PY) was synthesized according to the procedure of Tanikawa et al.[11] Polyviologen (PV) was synthesized according to the literature procedure.[12] Solutions of PDADMAC(1 mg mL^{-1}), PEI (1 mg mL^{-1}), PAH (1 mg mL^{-1}), and PSS-Py (5 mg mL^{-1}) in water with NaCl (0.5 M) were prepared in all experiments.

Layer-by-layer self-assembly on colloid particles: Polycation (PDADMAC) and polyanion (PSS-Py) were assembled onto the surface of MF by layer-by-layer adsorption.[3] Excess polyelectrolytes were removed by three repeated centrifugation (3000 rpm, 5 min)/washing/redispersion cycles in each deposition step. After obtaining the desired layers, hollow capsules could be obtained by dissolving the MF core in HCl (0.1 M). The final capsule concentration was 5×10^7 mL^{-1}.

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). Some experiments were performed under nitrogen, however, there was no noticeable variation with those experiments carried out in air.

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