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Andreas F Thünemann

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Electroluminescent Polyelectrolyte−Surfactant Complexes

Andreas F. Thünemann*

*Fraunhofer Institute for Applied Polymer Research, Geiselbergstrasse 69, D-14476 Golm,
Germany, and Institute of Theoretical Physics II, Heinrich Heine University,
Düsseldorf, Universitätsstr. 1, D-40225 Düsseldorf, Germany*

Dirk Ruppelt

Max Planck Institute of Colloids and Interfaces, Am Mühlenberg, D-14476 Golm, Germany

Polyelectrolyte complexes of poly(1,4-phenyleneethynylene carboxylate) (PPE) with 10 different cationic counterions were prepared. The counterions differed in their amphiphilicity, their headgroups (ammonium, pyridinium and sulfonium), and their alkyl chain lengths. It is shown that the optical properties of the PPE complexes depend on the nature of their counterions: The peak wavelength of the electroluminescence shifts from 430 to 515 nm for single-layer light-emitting diodes (LEDs) when the counterions were changed from tetraethylammonium to sulfonium ions. All the PPE complexes with amphiphile counterions displayed ordered mesophases. They are smectic A or smectic B-like in the solid state at room temperature with long periods of 2.38–4.27 nm. By contrast, no mesomorphous structures were found for the PPE complexes with nonamphiphilic counterions. All complexes were investigated by using differential thermal analysis, small- and wide-angle X-ray scattering techniques, and fluorescence spectroscopy.

Introduction

Conjugated polymeric materials have been the subject of intense academic and industrial research for their use in LEDs in the past decade. The work on organic LEDs has been summarized in a number of reviews.[1–6] Typically, polymers in organic LEDs have a conjugated backbone and normally are nonionic. On the other hand, it has been shown that polyelectrolytes such as polyaniline, in its form as an emeraldine salt, increase the hole transport via the indium tin oxide electrode in LEDs. As a result, the light-emitting characteristics of the LEDs are strongly improved.[7] It was shown recently that polyelectrolytes are useful in forming stepped and graded electronic profiles, leading to remarkably efficient single-layer polymeric LEDs.[8] Furthermore, it is well-known that complexes of polyelectrolytes and surfactants form interesting nanostructured materials in the solid state.[9–11] The first example of the combination of a rigid-rod-like polyelectrolyte and a surfactant into a material that is useful for the fabrication of LEDs was given by Neher et al.[12] Recently we reported on a nanostructured PPE complex, dihexadecyldimethylammonium−poly(1,4-phenylene-
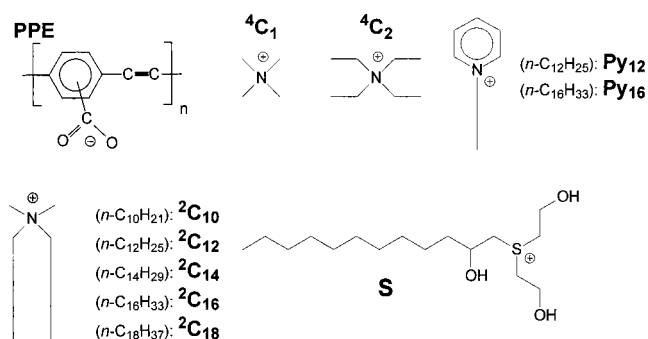

Figure 1. The molecular structures of the compounds used for complexation: poly(*p*-phenyleneethynylene carboxylate) (PPE**)**, tetramethylammonium ($^4C_1$), tetraethylammonium ($^4C_2$), dialkyldimethylammonium ($^2C_{10}$, $^2C_{12}$, $^2C_{14}$, $^2C_{16}$, $^2C_{18}$), alkyl-pyridinium (Py$_{12}$, Py$_{16}$**)**, and 2-hydroxy-*S,-S*(bis(2-hydroxyethyl)dodecylsulfonium (S).

ethynylene carboxylate). This material displays blue electroluminescence in single-layer LEDs with low turn-on points.[13] In this paper we report on further complexes of PPE with a number of different counterions. The molecular structures of the compounds are given in Figure 1. We focused on the solid-state structures of the complexes and their optical properties.

Experimental Section

Materials. Poly(2-ethylhexyloxycarbonyl-1,4-phenyleneethynylene) without diine defects was synthesized by the route described by Heitz and Häger.[14] The molecular weight was determined by GPC and found to be M_w = 20 000 g/mol and M_n = 10 000 g/mol. The poly(1,4-phenyleneethynylene carboxylate) was prepared from poly(2-ethylhexyloxycarbonyl-1,4-phenyleneethynylene) by hydrolysis as described elsewhere.[15] The compounds tetramethylammonium hydroxide ($^4C_1$), tetraethylammonium hydroxide ($^4C_2$), didecyldimethylammonium bromide

* Corresponding author. E-mail: andreas.thuenemann@ fhg.iap.de.

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($^2C_{10}$), didodecyldimethylammonium bromide ($^2C_{12}$), dimethyldidetradecylammonium bromide ($^2C_{14}$), dihexadecyldimethylammonium bromide ($^2C_{16}$), dimethyldioctadecylammonium bromide ($^2C_{18}$), dodecylpyridinium bromide (Py$_{12}$), hexadecylpyridinium bromide (Py$_{16}$), chloroform (HPLC grade), and tetrahydrofurane (HPLC grade) were delivered from Aldrich and used as received. The sulfonium surfactant (2-hydroxy-*S,S*-(bis-(2′-hydroxyethyl)dodecyl sulfonium, S) acetate salt was synthesized by the route described by Putlitz et al.[16]

Complex Preparation. For complex preparation 1 mmol of the polymer, calculated with respect to the monomer units, and 1 mmol of the surfactant were dissolved in a NaOH solution (pH 9), heated to 70 °C, and treated with ultrasound for 10 min. The polymer is water-soluble and can be complexed at a basic pH value, where its carboxylic acid groups are deprotonated. Both, the polymer and amphiphile solutions were heated to 70 °C again and the polymer solution was added dropwise to the strongly stirred surfactant solution. The brownish precipitate was centrifuged and washed several times with hot water to remove formed salts. The yields were 79% (PPE-$^2C_{10}$), 80% (PPE-$^2C_{12}$), 85% (PPE-$^2C_{14}$), 92% (PPE-$^2C_{16}$), 89% (PPE-$^2C_{18}$), 65% (PPE-Py$_{12}$), 89% (PPE-Py$_{16}$), and 58% (PPE-S). Elemental analysis of all complexes resulted in sodium contents of lower than 0.1% and bromide contents of lower than 0.1%. Therefore, we can exclude the presence of salts as well as a surplus of surfactant (by Br$^-$) or noncomplexed repeat units (by Na$^+$). The stoichiometry of the complexes is therefore 1:1 with respect to the charges. The complexes PPE-$^4C_1$ and PPE-$^4C_2$ did not precipitate from the aqueous solutions. They were prepared by mixing 1% equimolar aqueous solutions of PPE and the ammonium hydroxide and then stirring the mixture for 1 h. This was followed by removing the water in a vacuum. The LED structure was produced by spin-coating, using commercial indium tin oxide (ITO) glass (Merck) and a 1% w/w solution of the complexes in chloroform (HPLC grade). A drop of complex solution was deposited onto the ITO glass. The sample was then rotated for 30 s at a spinning rate of 2500 s^{-1}. By this procedure films of the complexes with thicknesses of 140 nm ± 20 nm were obtained. The thicknesses of the active layers were determined using X-ray reflectivity[17] and the surface profiler Dektak 3 ST from Veeco Instruments. After solvent evaporation an aluminum top contact was vapor deposited. Device characterization was performed in the forward-bias configuration (with ITO positive); the emitted light was detected through the transparent ITO electrode and substrate.

Methods. The differential scanning calorimetry measurements were performed on a Netzsch DSC 200. The samples were examined at a scanning rate of 10 K min^{-1} by applying two heating scans and one cooling scan in the temperature range of −100 to 130 °C. The numbers of crystalline CH$_2$ groups in the side chain, n_c, were estimated using the equation $n_c = \Delta H_m / k$. The value of k is 3 kJ/mol for the methylene group; ΔH_m is − 30 kJ/mol. The method for the determination of the values has been described in detail for a series of polyelectrolyte-surfactant complexes in a separate work.[18] Wide-angle X-ray scattering (WAXS) measurements were carried out with a Nonius PDS120 powder diffractometer in transmission geometry mode. A FR590 generator was used as the source of Cu Kα radiation. Monochromatization of the primary beam was achieved by means of a curved Ge crystal, and the scattered radiation was measured with a Nonius CPS120 position-sensitive detector. The resolution of this detector in 2θ is 0.018°. The scattering vector s is defined as $s = 2/\lambda \sin\theta$, where 2θ is the angle between the primary beam and the scattered beam. Small-angle X-ray scattering (SAXS) measurements were carried out with an X-ray vacuum camera with pinhole collimation (Anton Paar, Austria, Model A-8054) equipped with image plates (type BAS III, Fuji). The image plates were read with a MAC Science Dip-Scanner (type IPR-420) and IP
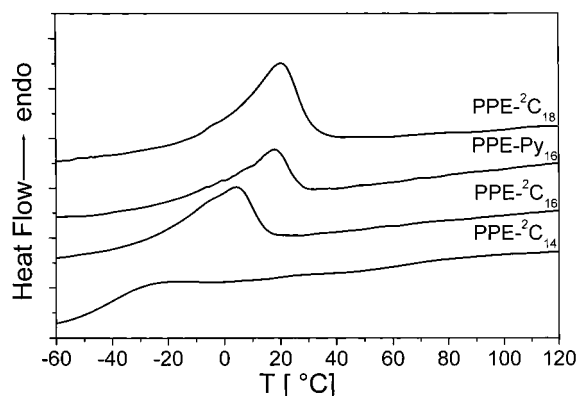
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Figure 2. DSC traces of PPE-$^2C_{14}$, PPE-$^2C_{16}$, PPE-Py$_{16}$, and PPE-$^2C_{18}$.

reader (type DIPR-420). The theoretical values of the long periods, l, of the lamellar complexes were calculated by using the Tanford[19] formula $l = 0.15 + 0.127n$, as used earlier for the calculation of the long spacing of lamellar polyelectrolyte amphiphile complexes by Dreja and Lennartz.[20] X-ray reflectivity was performed with a $\theta/2\theta$ instrument (Sot/Superman DF4, $U = 40$ kV, $I = 30$ mA, $\lambda = 0.154$ nm). The beam divergence of the incoming beam was 0.1°, the resolution in 2θ was 0.05°. A secondary monochromator selected the Cu Kα lines, and a scintillation counter served as detector. The luminescence of complex films was analyzed using a Perkin-Elmer LS-50B luminescence spectrometer with a solid-state sample holder. Excitation spectra were collected within the range of 250−470 nm. The emission wavelength was 500 nm, and the slits were 10/10 mm. Emission spectra were collected in the range of 390−700 nm, excitation wavelength 380 nm, slits 10/10 mm.

Results and Discussion

Thermal Properties. The thermal properties of all complexes were investigated by using differential scanning calorimetry. It was found that none of the complexes showed a glass transition, which is probably due to the high ionic character of the materials in combination with the rigid-rod-like polymeric backbone. Melting peaks were found for alkyl chain lengths longer than 12 in the series of the double-chain surfactant containing complexes. The complex PPE-$^2C_{14}$ displays a melt transition with a maximum (onset in parentheses) at −27 °C (−50 °C), PPE-$^2C_{16}$ at 5 °C (−28 °C), and PPE-$^2C_{18}$ at 20 °C (−6 °C) (see Figure 2). The endothermic transitions were attributed to the melting of the crystalline side chains, which are the alkyl tails of the surfactants. As described in the Experimental Section, we calculated the amount of crystalline CH$_2$ groups to be 8% (PPE-$^2C_{14}$), 15% (PPE-$^2C_{16}$), and 20% (PPE-$^2C_{18}$) present in the structures below the individual melt transition of each complex. The complex PPE-Py$_{16}$ displays a melt transition with a maximum at 18 °C (−8 °C) and approximately 10% crystalline CH$_2$ groups. No crystallinity was detected for the other complexes in the temperature range from −100 to 150 °C.

Molecular and Supramolecular Structure. Wide- and small-angle X-ray measurements were undertaken in order to obtain further information on the molecular and supramolecular structures of the complexes. The wide-angle diagrams of the complexes revealed that only two of the 10 complexes, PPE-$^2C_{18}$ and PPE-Py$_{16}$, contained crystalline side chains at 16 °C, the temperature at which the X-ray measurements were carried out. It can be seen, for example, that an amorphous halo was present in the

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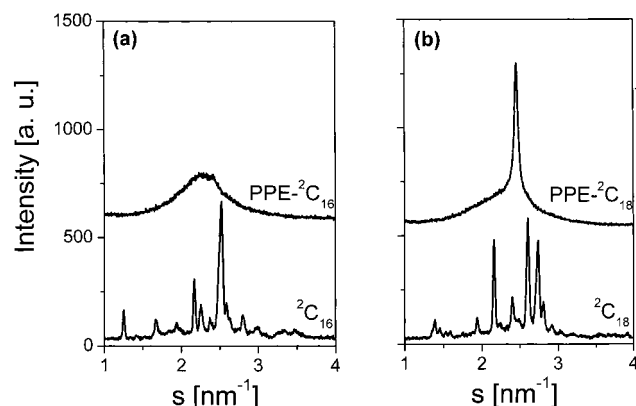(20) Dreja, M.; Lennartz, W. *Macromolecules* **1999**, *32*, 3528−3530

Figure 3. Wide-angle X-ray scattering diagrams of $^2C_{16}$, PPE-$^2C_{16}$ (a) and $^2C_{18}$, PPE-$^2C_{18}$ (b). For clarity, the curves of PPE-$^2C16$ and PPE-$^2C18$ have been vertically shifted.
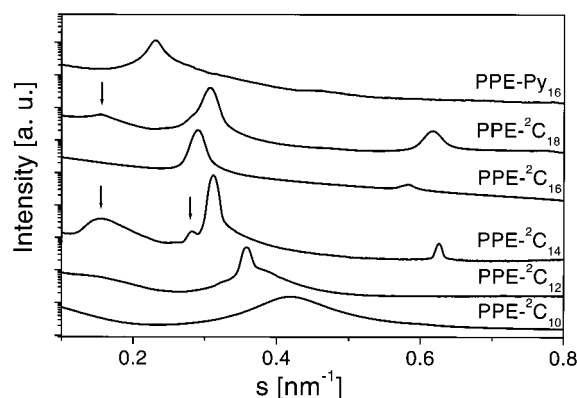

Figure 4. Small-angle X-ray scattering diagrams of the PPE complexes with double-chain surfactants: PPE-$^2C_{10}$, PPE-$^2C_{12}$, PPE-$^2C_{14}$, PPE-$^2C_{16}$, PPE-$^2C_{18}$, and PPE-Py$_{16}$. The arrows indicate the nonlamellar reflections attributed to periodic undulations of the lamellar surfaces.

Table 1. Structure Properties of the PPE Complexes as Determined by X-ray Measurements and the Positions of the Maxima of the Electroluminescence Spectra

complex	long period (nm)	correlation length (nm)	structure	maximum in electroluminescence (nm)
PPE-$^4C_1$	a	a	amorphous	430
PPE-$^4C_2$	a	a	amorphous	430
PPE-$^2C_{10}$	2.38	11 ± 2	smectic A	440−450
PPE-$^2C_{12}$	2.80	70 ± 5	smectic A	440−450
PPE-$^2C_{14}$	3.20	170 ± 10	smectic A	480
PPE-$^2C_{16}$	3.45	65 ± 5	smectic A	440−450
PPE-$^2C_{18}$	3.25	60 ± 5	smectic B	440−450
PPE-Py$_{12}$	3.24	14 ± 2	smectic A	470
PPE-Py$_{18}$	4.27	50 ± 5	smectic B	480
PPE-S	3.33	≈10	smectic A	515

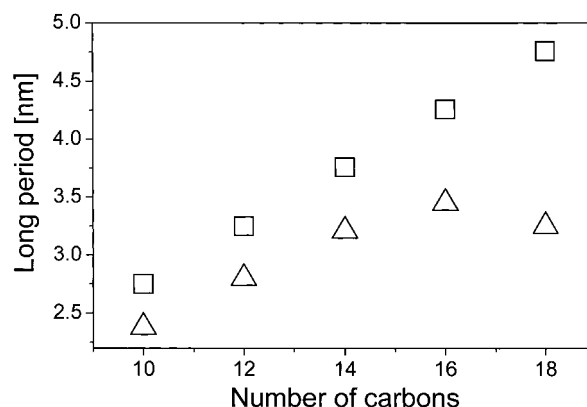^{a}No reflections were found in the small-angle scattering diagrams.

Figure 5. The long periods of the double-chain-containing surfactant complexes depend on the number of carbon atoms of the surfactant chains. The triangles represent the values determined by small-angle scattering measurements and the squares represent values that were calculated for a double-layer arrangement of the surfactant with extended alkyl chains.

wide-angle diagram of PPE-$^2C_{16}$ (Figure 3a, upper curve), while in addition to this an intense reflection was found in the wide-angle diagram of PPE-$^2C_{18}$ (Figure 3b, upper curve). By contrast, a number of sharp reflections were present in the diagrams of the pristine amphiphiles $^2C_{16}$ and $^2C_{18}$ (see Figure 3a,b, lower curves). Both amphiphiles are highly crystalline compounds at room temperature. It is a typical quality of polyelectrolyte−surfactant complexes that crystallinity in these complexes is absent or strongly reduced compared to the pristine surfactants.[21,22] No reflections were found in the small-angle scattering diagrams of the two complexes with the nonamphiphilic counterions (PPE-$^4C_1$ and PPE-$^4C_2$). In combination with the results from differential calorimetry and wide-angle scattering, we concluded that these complexes are amorphous materials in the temperature range from −100 to 150 °C. By contrast, reflections of equidistant positions are present in the small-angle diagrams of the other eight complexes that contain the amphiphilic counterions. Examples are shown in Figure 4. We interpret the scattering diagrams of these complexes as resulting from lamellar mesophases. The long periods of the complexes are summarized in Table 1. It can be seen that the long period varied from 2.38 nm (PPE-$^2C_{10}$) to 4.27 nm (PPE-Py$_{16}$). As expected, we observed that the repeat unit increases with the increasing chain length of

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the complexed surfactant. But the increase is not strictly linear, as was expected for a series of isomorphous lamellar structures. This can be seen in Figure 5 (triangles) for the series of the double-chain surfactant containing complexes. The increase of the long period is almost linear for PPE-$^2C_{10}$, PPE-$^2C_{12}$, and PPE-$^2C_{14}$. Then the increase from PPE-$^2C_{14}$ to PPE-$^2C_{16}$ reduces, and the long period of PPE-$^2C_{18}$ is even smaller than that of PPE-$^2C_{16}$. By comparison, the theoretical values of the long period with increasing alkyl chain length are given in Figure 5 (squares). It can be seen that the experimental values are slightly smaller than the theoretical values for the complexes containing the shorter alkyl chains (10, 12, 14, and 16). We interpret the scattering curves of the complexes as resulting from lamellar structures with the surfactants in a double-layer arrangement with the alkyl chains in a liquidlike state. The lamellar structures are similar to those of the polystyrene sulfonate alkylammonium complexes, described by Antonietti et al.[21] They showed that modifications of the lamellae, such as periodic undulations (waviness) of the lamellae surfaces, can be produced by varying of the alkyl chain lengths. The presence of undulations may be an explanation for the deviation of the linear increase of the long period. In the case of PPE-$^2C_{14}$ we were recently able to show that its lamellar mesophase consists of alternating ionic layers (1.3 nm) and nonionic layers (1.9 nm) with periodic undulations of a hexagonal symmetry and a maximum-to-maximum

distance of 7.5 nm.[23] The positions of the undulations in adjacent layers are not correlated with each other. Reflections resulting from undulations are marked by arrows in Figure 4. It was found that the structures do not follow a simple correlation in the series form PPE-$^2C_{10}$ to PPE-$^2C_{18}$. For example, for PPE-$^2C_{14}$, we were able to show a high probability of the existence of undulations. No indications of undulations are present in the scattering curve of PPE-$^2C_{16}$, while a weak reflection with a Bragg distance of about 6 nm in the curve of PPE-$^2C_{18}$ also indicates undulations for this complex. If we ignore the possibility of undulations, even though it is an interesting detail of the lamellar structures of the complexes, then we can classify the structures at 16 °C into three structural categories: amorphous (PPE-$^4C_1$, PPE-$^4C_2$), smectic A (PPE-$^2C_{10}$, PPE-$^2C_{12}$, PPE-$^2C_{14}$, PPE-$^2C_{16}$, PPE-Py$_{12}$, PPE-S), and smectic B (PPE-$^2C_{18}$, PPE-Py$_{16}$). Above the melt transition of the side chains at 20 and 18 °C, respectively, we assume that PPE-$^2C_{18}$ and PPE-Py$_{16}$ undergo an order−order transition from smectic B to smectic A. Skoulios et al. recently described a transition from a smectic B phase at a low temperature to a smectic A phase at a higher temperature for poly(vinyl sulfonate) alkylammonium complexes, which are morphologically similar to the PPE complexes.[24] We calculated the correlation lengths of the complexes in order to compare their degree of order. This was done by using the integral breadth of the (001) reflections.[25,26] It can be seen in Table 1 that the correlation lengths are in the range of 10−170 nm. We observed the phenomenon that the correlation lengths of the complexes with the shorter alkyl chains are lower than those of the complexes with the longer chains. For example, 14 nm was found for PPE-Py$_{12}$ and 50 nm for PPE-Py$_{16}$. But there is an exception: PPE-$^2C_{14}$. Its has the highest correlation length (170 nm). Probably this results from its additional ordering in the plane of the lamellae.

Optical Properties. The optical properties of a number of poly(1,4-phenyleneethynylene)s in solution have been investigated by Bunz et al.[27] They found that their fluorescence properties depend to a large extent on the concentration of the polymer solution, which they interpreted as the result of the complex aggregation behavior of these polymers. The aggregation of PPE in its pristine state is highly complicated. According to Schnablegger et al. PPE is able to self-assemble, producing a hierarchy of structures in water as well as in tetrahydrofurane.[15] In contrast to the pristine PPE, we were able to show that the fluorescence emission of PPE-$^2C_{14}$ in solution of tetrahydrofurane is largely independent of its complex concentration.[23] This applies equally to the other PPE complexes. As in an earlier study we conclude that aggregates are present in the solution of the complexes, but the aggregates of the complexes are constant in their composition over a large range of concentrations (10^{-4}−10^{-2}% w/w). By contrast, we found that the photoluminescence of the complexes depends on the type of counterion. The emission spectra of thin films are given in Figure 6 as an example. The excitation wavelength was 380 nm. The positions of the emission maxima of the complexes depend on the nature of the headgroup. A shift was observed in the series PPE-$^4C_2$ (470 nm), PPE-$^2C_{18}$
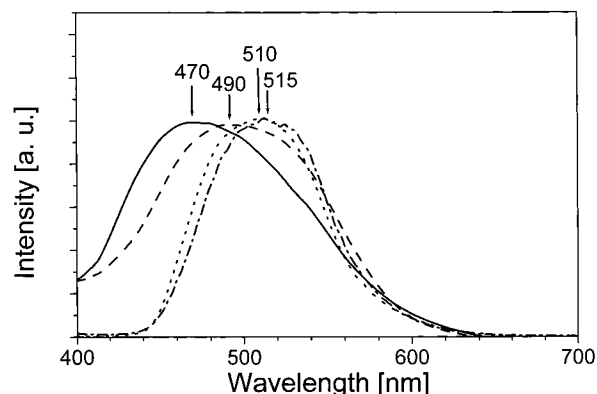
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Figure 6. The fluorescence emission spectra of PPE-$^4C_2$, (solid line), PPE-$^2C_{18}$ (dashed line), PPE-Py$_{16}$ (dotted line), and PPE-S (dash−dotted line). The emission maxima are indicated by arrows. The excitation wavelength is 380 nm.
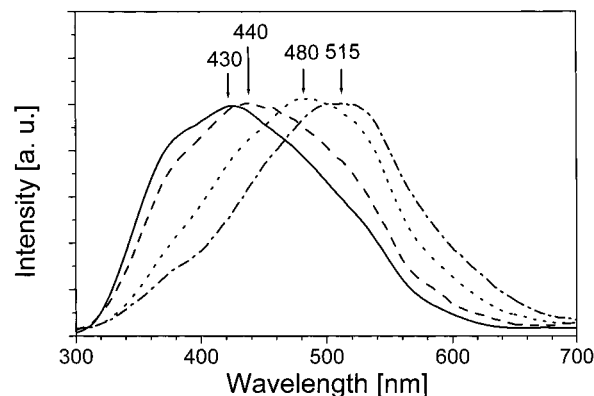

Figure 7. The electroluminescence spectra single-layer LEDs of PPE-$^4C_2$, (solid line), PPE-$^2C_{18}$ (dashed line), PPE-Py$_{16}$ (dotted line), and PPE-S (dash−dotted line). The emission maxima are indicated by arrows.

(490 nm), PPE-Py$_{16}$ (510 nm), and PPE-S (515 nm). The same sequence was found in the electroluminescence diagrams of single layer LEDs, which contain the complexes in the form of thin films (140 nm) as the active layer. It can be seen in Figure 7 that the shift of the maxima of the electroluminescence is larger than in the photoluminescence (85 nm instead of 45 nm). Curves of PPE-$^4C_2$ (430 nm), PPE-$^2C_{18}$ (440 nm), PPE-Py$_{16}$ (480 nm), and PPE-S (515 nm) are shown. The values of the position of the electroluminescence maxima are summarized in Table 1. It was also found that the positions of the maxima of the double-chain-containing complexes (between 440 and 450 nm) do not depend on the chain length. PPE-$^2C_{14}$ is an exception. Its maximum in the electroluminescence spectrum is found at 480 nm. This possibly results from its additional ordering in the plane of the lamellae, which leads to an increase in the conjugation lengths of the polymeric backbone.[23] Despite this exception, we conclude that the optical properties of the complexes are largely independent of the length of the alkyl chains, but they do depend on the nature of the ionic headgroup to a great extent. Tentatively, we interpret this shift of the fluorescence maxima as resulting from the polarizability of the ionic headgroups. Within the HSAB theory[28] the ammonium group is the hardest and least polarizable, followed by the pyridinium group and the sulfonium group, which is the softest, most polarizable group. Therefore, given the condition that the type of the mesomorphous

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structure is the same, we conclude that the electrolumi-nescence spectra shift to higher wavelengths when the counterions become more polarizable. The counterions seem to influence the effective conjugation length of the polymeric backbone; hard counterions decrease it and soft counterions increase it. The reasons for the difference between photoluminescence (PL) and electroluminescence (EL) of the series of complexes, e.g. PPE-$^4C_1$ (470 nm PL, 430 nm EL) and PPE-$^2C_{18}$ (490 nm PL, 440 nm EL), are not yet clear.

From a material science point of view it is interesting that the emission properties of a conjugated polymer can be shifted simply by exchanging the counterions. It is conceivable that red, green, and blue LEDs could be produced by using one conjugated polymer and various counterions. Appropriate candidates for this may be cationic and anionic derivatives of poly(*p*-phenylenes).[29−31] Current−voltage diagrams of the LEDs from the PPE complexes were recorded in order to determine the voltage at which the LEDs start emitting light (turn-on point). It was found that the turn-on points of LEDs of all the complexes were around 6 V when the thickness of the active layer is 140 ± 20 nm. A typical current−voltage curve is shown in Figure 8. This finding was surprising, since we expected that the turn-on point would also depend on the nature of the counterion. It is known that the turn-on point of similarly prepared LEDs using the pristine polymer with covalently bound side groups, poly(2-ethylhexyloxycarbonyl-1,4-phenyleneethynylene), is around 21 V with an emission maximum at 557 nm.[32] The much lower turn-on point of the complexes compared to that of the analogues side-chain polymer is probably due to the highly ionic character of the complexes. Normally such low turn-on points need the support of an additional charge transport layer.[33] Unfortunately, we are not able at present to give a direct correlation between the structural proper-
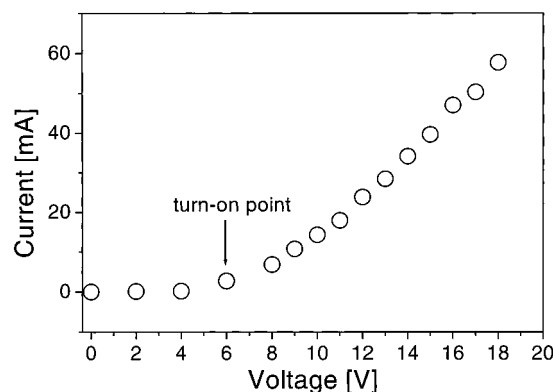

Figure 8. The current−voltage curve of single-layer LED with PPE-$^2C_{14}$ as the active layer. The layer thickness is 140 nm.

ties of the complexes (mesophase, crystallinity) and their optical properties (photoluminescence and electrolumi-nescence).

Conclusion

We have demonstrated that the optical properties of single-layer LEDs of PPE complexes depend on the nature of the counterions. The maximum of the electrolumines-cence can be shifted from 430 nm, when using hard counterions, to 515 nm, when using soft counterions. We suggest that it is, in principle, possible to produce single-layer LEDs that cover the entire visible spectrum by using only one polymer. The turn-on points of the LEDs are around 6 V for layer thicknesses of 140 nm. The complexes of PPE with amphiphilic counterions are either smectic A or smectic B at 16 °C with repeat units of 2.38−4.27 nm, while the complexes with nonamphiphilic counterions are amorphous. The correlation lengths of the lamellar structures vary between 10 and 170 nm.

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