

Electroluminescence of different colors from polycation/CdTe nanocrystal self-assembled films

Mingyuan Gao,^{a)} Constanze Lesser, Stefan Kirstein,^{b)} and Helmuth Möhwald
*Max-Planck-Institut für Kolloid- und Grenzflächenforschung, am Mühlenberg 2, 14476 Golm,
Potsdam, Germany*

Andrey L. Rogach and Horst Weller
Institut für Physikalische Chemie, Universität Hamburg, Bundesstrasse 45, D-20146 Hamburg, Germany

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Water soluble thiol capped CdTe nanocrystals are assembled into ultrathin films in combination with poly(diallyldimethylammonium chloride) (PDDA) by the self-assembly method of layer-by-layer adsorption of oppositely charged polyelectrolytes. Electroluminescent devices, which produce different color emissions, are fabricated by sandwiching CdTe/PDDA films between indium-tin-oxide (ITO) and aluminum electrodes using CdTe nanocrystals of different sizes. It is shown that the electroluminescence (EL) spectra of the CdTe/polymer films are nearly identical to the photoluminescence spectra of the corresponding CdTe nanocrystals in aqueous solutions. The devices produce room-light visible light output with an external quantum efficiency up to 0.1%. Light emission is observed at current densities of 10 mA/cm² and at low onset voltages of 2.5–3.5 V, which depends on the thickness of the film indicating field-dependent current injection. A variation of the EL efficiency with the size of the CdTe particles is observed and explained by the size dependent shift of the CdTe energy levels with respect to the work function of the electron injecting Al electrode. This is confirmed by the behavior of two-layer devices prepared from two differently sized CdTe particles being spatially separated, i.e., one size CdTe near ITO and the other size CdTe near Al by using the self-assembly method. © 2000 American Institute of Physics. [S0021-8979(00)06404-5]

I. INTRODUCTION

Recently it has been demonstrated by several groups that nanocrystalline materials of the II–VI semiconductors can be used as an emitting material in the preparation of thin film electroluminescence devices.^{1–6} Semiconductor nanocrystals exhibit many unique properties which are promising for the improvement of electroluminescence devices: first, the color of emission can easily be tuned by varying the size of the particles, while their chemical properties remain nearly the same. Therefore, one device fabricating procedure can be adopted for different size nanocrystals to produce different color emissions.^{1–3} Second, high fluorescence quantum yield and photochemical stability can be achieved by careful modification of the nanocrystal surface, and this may favor the efficiency of the device.^{7–11} Third, the thermal stability is expected to be higher for inorganic nanocrystals than for organic materials. Moreover, it was demonstrated recently that CdSe nanoparticles can improve the stability of poly(phenylene vinylene) (PPV) electroluminescence when they are combined in a two-layer structure.⁵ Fourth, the recombination of charge carriers at semiconducting nanoparticles is not restricted by the spin statistics. The energy of the

lowest exciton state of the particles is split by only a few meV into different levels for different mutual spin orientations of the electron or hole states.¹² Therefore, even if charge carriers form a forbidden spin combination, it can easily be brought to a radiative state by thermal activation.¹³

The layer-by-layer self-assembly method has been proved to be a very simple approach to combine semiconductor nanocrystals with various organic materials in order to build homogenous ultrathin films.^{14–16} This technique facilitates the buildup of multilayer structures from different materials, which is especially advantageous for the fabrication of sophisticated electro-optical devices.^{5,6,17–19} However, for the use of semiconducting nanocrystals an ionic surface is the prerequisite for alternate adsorption with polyelectrolytes from aqueous solutions by the layer-by-layer self-assembly method. In our previous work, CdSe nanocrystals were prepared with the particle surface being capped by thiolactic acid.^{5,6} We failed to vary the color of photoluminescence as well as electroluminescence of the CdSe, due to broad particle size distribution and the existence of surface defects. The latter also caused broadening of the spectra and low fluorescence quantum efficiency. Recently, we have prepared CdTe nanocrystals that show a narrow excitonic emission by a similar synthesis method employing thioglycolic acid as a stabilizing agent. Thus, the color of photoluminescence of the CdTe nanocrystals can be tuned from green to red simply by prolonging the refluxing time during the preparation of the nanocrystals. In the best case, the fluores-

^{a)} Author to whom correspondence should be addressed. Present address: Lehrstuhl für Photonik und Optoelektronik, Sektion Physik, Universität München, Amalienstr. 54, 80799 München; electronic mail: Mingyuan.Gao@Physik.Uni-Muenchen.de

^{b)} Present address: Institut für Physik, Humboldt-Universität zu Berlin, Invalidenstr. 110, 10115 Berlin.

cence quantum yield reaches 18%.⁹ This high quantum yield and the wide range of variable emission colors make the CdTe nanocrystalline materials very promising for the use as emitters in electroluminescence applications.

In this paper, the experimental results on electroluminescence of CdTe nanocrystals inserted into thin films of the nonconjugated polyelectrolyte poly(diallyldimethylammonium chloride) (PDDA) are presented. Single-layer devices with the structure indium-tin-oxide (ITO)//poly(ethylenimine) (PEI)(CdTe/PDDA)**n*//Al were prepared using differently sized CdTe nanocrystals which exhibited green, yellow, orange, and red color photoluminescence, respectively. Efforts were made to understand the mechanism of charge injection and to probe the location of the recombination zone of the charge carriers by combining different size nanocrystals in one device.

II. EXPERIMENT

A. Synthesis of CdTe nanocrystals

The CdTe colloidal solutions were prepared using the reaction between Cd²⁺ and NaHTe in aqueous solution as described previously⁹ in the presence of thioglycolic acid (RSH) as the stabilizing agent. The molar ratio of Cd²⁺:Te²⁻:RSH was 1:0.47:2.43. A colloidal solution with a CdTe concentration of 0.01305 M was prepared (here and elsewhere: referring to Cd²⁺). The final pH value of it was 11.4 after the reaction was completed. No fluorescence was observed. Fluorescence of the solution appeared under reflux and could be tuned in color by prolonging the refluxing time. Four fractions (I, II, III and IV) were extracted at different times in the course of reflux. The photoluminescence of these four samples was located at 549 nm (FWHM, 72 nm), 589 nm (FWHM, 78 nm), 622 nm (FWHM, 88 nm) and 655 nm (FWHM, 92 nm), respectively. For the preparation of the self-assembled films, the concentration of the particles was 6.5 × 10⁻⁴ M and the pH value of the particle solutions was controlled in the range of 6.3 ± 0.2. The optimized fluorescence quantum yield of CdTe I, CdTe II, CdTe III and CdTe IV are estimated to be 18%, 16%, 10%, and 9%, respectively.

After storage of the particles in the refrigerator for more than ½ yr a small shift of the maximum of the emission spectra was observed towards longer wavelengths. This shift depends on the initial size of the particles. For example, the photoluminescence of CdTe I shifts from 534 nm (FWHM, 51 nm) to 549 nm (FWHM, 72 nm), whereas practically no shift was seen for solution IV. All CdTe solutions were used in the electroluminescence investigations without any further treatment to narrow the size distribution.

B. Preparation of CdTe/polycation self-assembled films

The film preparation was performed following the standard layer-by-layer adsorption technique invented by Decher.¹⁴ The process started with dipping an intensively cleaned substrate first into a solution of PEI to deposit a first layer of polycation. Afterwards, the sample was dipped into a solution of CdTe particles (pH=6.3±0.2) for 20 min,

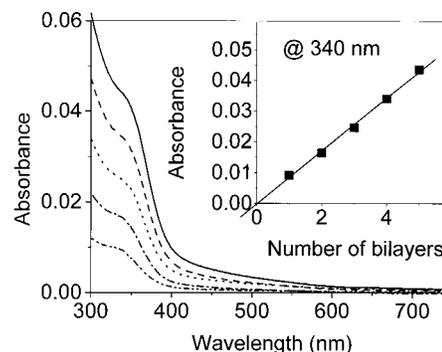


FIG. 1. Absorption spectra of one-, two-, ..., five-bilayer of CdTe/PDDA films. The pH value of the CdTe solution was controlled at 6.3 ± 0.2 during the film preparation. (Insert) Absorbance at the shoulder position of 340 nm vs the number of bilayers.

rinsed with water, then dipped into a solution of polycation (concentration of 1 mg/m³) for 20 min, and rinsed with water again. Such a deposition cycle resulted in one “bi-layer” of adsorbed CdTe/polymer material. This cycle was repeated *n* times to obtain a film of *n* bilayer. However, we want to emphasize that the term bilayer does not express a real two-layer structure that consists of two different sheets stacked on each other. Instead, as we have shown in former x-ray reflectivity studies on CdSe/polymer films,⁵ the resulting film structure of several bilayers looks more like a homogeneous mixture of the particles and the polymer.

Different polycations were used to optimize the film preparation with respect to the particle density and fluorescence efficiency of the nanocrystals within the solid films. The polycations, such as PEI, poly(allylamine hydrochloride) (PAH) and PDDA, were commercial products (Aldrich) and used without further purification. It was found that the strongest particle fluorescence and reasonable density in the film could be achieved by using PDDA.²⁰ No films could be formed using the precursor of PPV as polycation as it was used previously in combination with CdSe particles.^{5,6,20} The pre-PPV was found to be incompatible with the low pH of the particle solution because it tends to be converted to PPV and loses its positive charges on the polymer backbone during the deposition process. Hence, the film preparation stopped prematurely.

A good linear relationship between the absorbance and number of bilayers of the films was obtained for (CdTe/PDDA)**n* in a large range of pH values. A set of absorption spectra of CdTe/PDDA of different bilayer films is presented in Fig. 1. A linear increment of the absorbance against the number of bilayers suggests that an equal amount of CdTe is adsorbed after each dipping cycle, which results in the buildup of a homogenous film. This is also confirmed by preliminary x-ray investigations (not shown here).

C. Electroluminescence measurements

Light-emitting devices (LEDs) were made by sandwiching the CdTe/PDDA film in between Al and ITO electrodes. ITO glass (Balzers) with conductivity of 63 Ω/□ was used as a substrate. As we reported before, PEI was used to cover

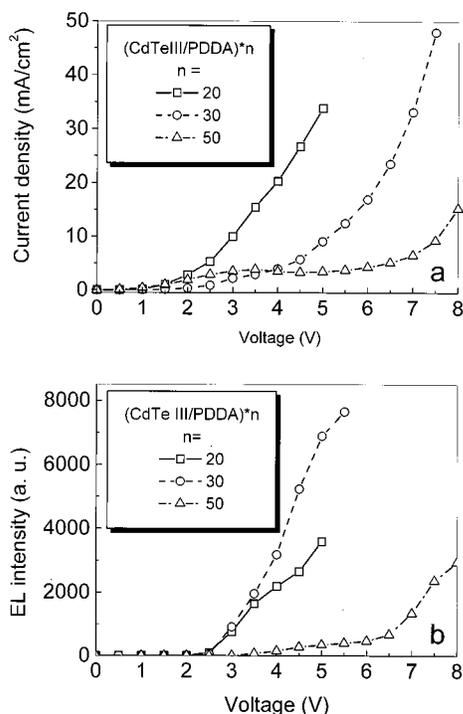


FIG. 2. (a) I - V characteristics of $(\text{CdTe III/PDDA})^*n$ films sandwiched between ITO and aluminum electrodes, with $n=20, 30, 50$. (b) Electroluminescence intensities of the above films vs externally applied voltage.

the ITO glass, thereafter an alternate dipping process was performed using PDDA and CdTe to build films with a different number of bilayers. A round shaped aluminum electrode of 3 mm in diameter, 120 ± 15 nm in thickness was evaporated on top of the film.

Current-voltage (I - V) measurements were performed with the help of a Keithley 617 electrometer/voltage source. Electroluminescence spectra were captured simultaneously with a spectrometer consisting of a monochromator (SP275, Acton) and a thermoelectrically cooled charge coupled device camera (S&I). The light was collected by an optical fiber bundle with its one end mounted in front of the LED and the other end connected to the spectrometer.

III. RESULTS AND DISCUSSION

A. Electroluminescence of CdTe/PDDA films with different thickness

Electroluminescence devices were prepared with a different number of CdTe/PDDA bilayers in order to investigate the influence of the film thickness on the electronic properties. The fraction III of the CdTe solution was used which emits at 622 nm. In Fig. 2 the current density (a) and electroluminescence intensity (luminosity) (b) is drawn versus the applied voltage for three different samples of $(\text{CdTe III/PDDA})^*n$ with $n=20, 30$, and 50, respectively. Here, and for all other experiments presented in the text, the positive terminal was connected to the ITO electrode. An increase in electroluminescence intensity was observed for the 30-bilayer film compared to the 20-bilayer sample. However, the intensity was much lower for the sample of 50

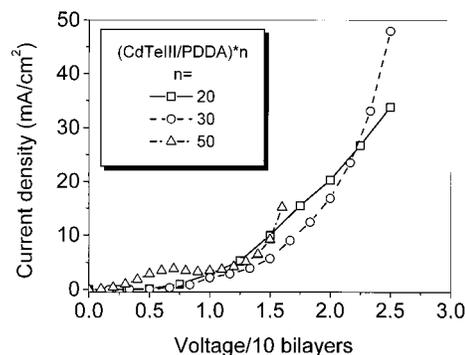


FIG. 3. Current densities of the films of $(\text{CdTe III/PDDA})^*n$ with $n=20, 30$, and 50 vs electric field. The electric field was expressed in units of voltage/ten bilayers.

bilayers. This nonmonotonic behavior is not seen in the I - V curves in Fig. 2(a). Instead, a clear increase of turn-on voltage with the sample thickness can be found.

In Fig. 3 the current is plotted against the electric field. The field strength is expressed in units of voltage per 10 bilayers which roughly corresponds to 0.3×10^5 V/cm, assuming an average thickness of 3 nm per bilayer. It is clearly seen that the I - V curves of the different samples fall into one line, which indicates a field driven current. The field dependence of I - V characteristics is typical for a tunneling mechanism which is usually taken into consideration for the charge carrier injection from the electrodes into the organic material.²¹ However, in our case the nanocrystals are isolated from each other by the polyelectrolyte and thus, the internal charge transport can also be considered as a hopping transport which is mediated by the external electric field.

An interesting behavior is observed for the I - V curve of the 50-bilayer film. The current density presents an early increase as a shoulder in the range from 2 to 6 V, in contrast to the curve of the 30-bilayer film. At the moment, we do not know the reason responsible for this current shoulder. It may be due to some electrochemical reactions which are not evident in the case of thinner films. This current shoulder vanishes in subsequent voltage sweeps accompanied by a decrease in electroluminescence intensity.

B. Electroluminescence of different size CdTe particles in CdTe/PDDA films

The electroluminescence emission of samples consisting of 30 bilayers of CdTe/PDDA was clearly visible at room light when a current density of ~ 10 mA/cm² was applied. Different color emission was achieved by using different size CdTe nanocrystals. A set of electroluminescence spectra together with the fluorescence spectra of the corresponding aqueous solutions of CdTe are presented in Fig. 4. The maxima of the electroluminescence (EL) spectra in the lower frame are set to the same values as that of the photoluminescence (PL) spectra of the corresponding samples shown in the upper frame, and the relative intensities are set to arbitrary values for clarity of the presentation. It can be seen that the EL and PL spectra are nearly identical, except for a small

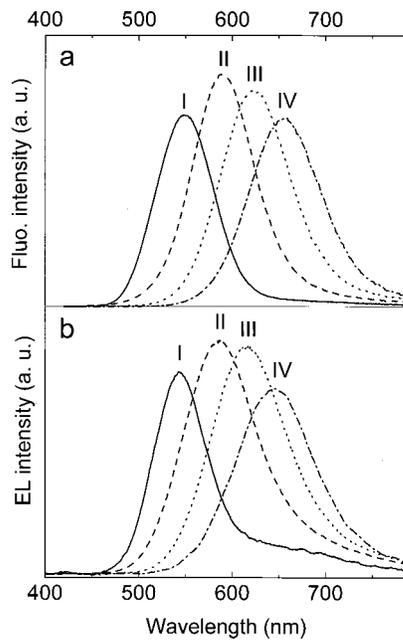


FIG. 4. (a) Fluorescence spectra of CdTe aqueous solutions excited at 400 nm. (b) Electroluminescence spectra of (CdTe/PDDA)*30 films. The spectra recorded from CdTe I, CdTe II, CdTe III and CdTe IV were labeled I, II, III, and IV, respectively.

red tail appearing in the EL spectra of the films made from the smaller particles, i.e., CdTe I and CdTe II.

It was also observed that the stability of the devices was increasing with the size of the nanocrystals used for the device fabrication. Moreover, the external quantum efficiency increases monotonically as the nanocrystal size is increasing. The relative EL quantum efficiencies (RQEs) are listed in Table I. In Figs. 5(a) and 5(b) the EL intensity and the current density against the applied voltage of 30-bilayer CdTe/PDDA film systems containing different size CdTe are presented. The turn-on voltage, above which EL can be observed, falls in the range of 2.5–3.5 V for all devices. The smaller the nanocrystal size is, the higher the voltage needed to produce current through the samples and light out of the films. For samples CdTe I, CdTe II and CdTe III a monotonic increase of the luminosity and the current density with particle size can be observed. The device of particle fraction IV exhibits extraordinary low current and luminosity.

This size dependent behavior can be explained under the assumption that the structural properties of the samples, such as particle density and film thickness, are identical and do not change with the particle size. In this case the electronic and optical properties of the films are solely determined by the size dependence of the electronic states of the CdTe nanocrystals. Due to the quantum size effect, the energy

TABLE I. RQE of EL recorded from the ITO//PEI(CdTe/PDDA)*30//Al samples. The device structure of sample A is ITO//PEI(CdTe II/PDDA)*20/(CdTe IV/PDDA)*20//Al. The RQEs are normalized to that from CdTe I film.

Samples	CdTe I	CdTe II	CdTe III	CdTe IV	Sample A
RQE	1	1.8–2.2	1.8–2.2	5.7	3.2–5.7

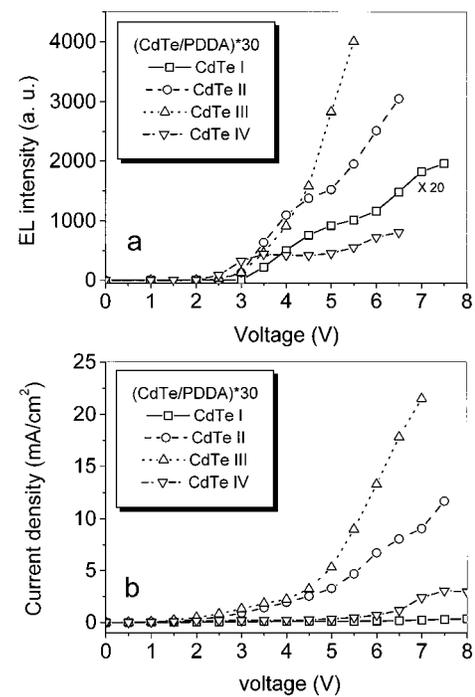


FIG. 5. (a) The electroluminescence intensities vs applied voltages from 30-bilayer CdTe/PDDA films consisting of different size nanocrystals, namely, CdTe I, CdTe II, CdTe III, and CdTe IV. (b) The corresponding I - V characteristics.

level of the electron state is shifted towards higher energies for smaller particles, while the energy of the hole state is shifted towards lower energies. Therefore, the difference of both energies, known as the band gap energy and represented by the absorption edge, is increasing for decreasing particle size. In our samples a clear blueshift of the absorption edge and the maximum of the PL emission on the order of 0.4 eV was observed comparing particles of CdTe I with CdTe IV. It was calculated theoretically by Efros²² for spherical CdTe crystallites that the lowest electron levels (bottom of conduction band) move faster to higher energy than the lowest hole levels (top of valance band) to lower energy when the particle size is decreased. Although the absolute positions of the energy levels of the particles are not known, it seems to be a reasonable assumption that the electron state is closer to the work function of the aluminum for large particles, and shifts to higher values for smaller particles. Thus, the injection efficiency of electrons significantly decreases when the particle size is reduced. As we will show below, the particles act as an electron transporting material, which means that electrons are the majority carriers. Therefore, the behavior of the I - V curves and EL intensity- V curves of CdTe I/PPDA, CdTe II/PDDA and CdTe III/PDDA in Fig. 5 can be assigned to the electron current which is controlled by the injection mechanism. However, an exception is observed for CdTe IV/PDDA, which gives lower rather than the expected higher current density and EL luminosity. At the moment, we still do not understand the reason, and investigations are currently in progress to interpret this nonmonotonic behavior.

The quantum efficiency and the stability of CdTe I film devices were very poor compared to the values observed with the films containing other particle fractions. The lower EL efficiency of small particles compared to larger ones is opposite to the PL behavior, where the small particles have the highest quantum efficiencies. This further indicates that the light output of these samples is mainly controlled by the electronic properties, which also depend on the particle size, and not by the optical properties. Similar behavior of small nanocrystals in electroluminescence was also observed by Mattoussi *et al.*¹ Moreover, they also found that a ZnS overcoating of CdSe nanocrystals did not enhance the EL efficiency, in contrast to the PL.

The low stability of the CdTe I may be caused by lower photostability of smaller CdTe nanocrystals. Because all the samples were prepared and measured in air, oxygen in the device could not be avoided. As it was proven before, the oxygen in the device will attack the nanocrystals when they are electrically excited, resulting in degradation of the nanocrystals.⁵ This degradation effect is more favorable for smaller particles due to the increment of energetic levels and thus, lower electron affinity of the electron state. The appearance of the red tail in the EL spectra of CdTe I, which is absent in the PL spectra, indicates that surface traps are created due to oxidation.

C. Electroluminescence of two-layer structures containing different size particles

Since differently sized nanocrystals show nearly size-independent behavior with respect to the film preparation, particles of different size can easily be combined into one multilayer system by the layer-by-layer deposition method. Here, devices were prepared with two differently sized nanocrystals being positioned at different places along the vertical direction of the film, i.e., one film of 20 double layers of CdTe II/PDDA near the ITO electrode with another film of 20 double layers of CdTe IV/PDDA deposited on top of it before evaporation of the aluminum electrode (sample A). Another sample of the two-layer films was prepared with a reversed order (sample B). The electroluminescence spectra of both samples are presented in Fig. 6. The electroluminescence of such two-layer devices always showed emission from the layer close to the ITO electrode. This proves that the recombination zone of the charge carriers is located near the ITO side and indicates that electrons are the majority carriers, due to more favorable transportation or injection.

By comparing the efficiency of samples of the type ITO//PEI(CdTe II/PDDA)*30//Al with the efficiency of sample A (ITO//PEI(CdTe II/PDDA)*20/(CdTe IV/PDDA)*20//Al), it was found that the EL efficiency of CdTe II in the two-layer system is improved by at least a factor of 2 (see Table I). Hence, it can be concluded that placing larger particles near the Al electrode favors the EL efficiency of the smaller particles near the ITO side. On the contrary, the efficiency of sample B with reverse configuration was much lower than the efficiency of a (CdTe IV/PDDA)*30 single layer device. However, even in the unfavorable configuration, where the large particles are close to the ITO side, their EL intensity can be tuned by changing the size of the

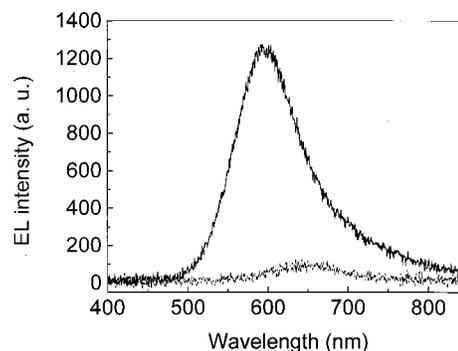


FIG. 6. Electroluminescence spectra of two-layer films consisting of two different sized nanocrystals: spectrum in solid line was recorded from ITO//PEI(CdTe II/PDDA)*20/(CdTe IV/PDDA)*20//Al, spectrum in dashed line from ITO//PEI(CdTe IV/PDDA)*20/(CdTe II/PDDA)*20//Al. The EL emissions were recorded under the same current densities with positive terminal of power source connected to the ITO electrode.

particles close to the Al electrode. This was observed by replacing the CdTe II particles within the layer close to aluminum with CdTe III particles. These findings further support the fact that electron injection dominates the quantum efficiency of the device. This coincides well with the results that single-layer films of smaller nanocrystals showed lower quantum efficiency than that made from larger ones due to the difficulties of charge carrier injection.

IV. CONCLUSIONS

Different color electroluminescence with room-light visible luminosity was successfully achieved by employing differently sized semiconducting nanocrystals in (CdTe/PDDA)**n* self-assembled film devices. The spectrum of the electroluminescence was nearly identical to that of fluorescence of the corresponding CdTe colloids in aqueous solutions. Moreover, all (CdTe/PDDA)**n* devices consisting of any size nanocrystals are characterized by a very small onset voltage for electroluminescence. The difference in the electroluminescence efficiency of the different CdTe film devices indicates that the electron injection is the dominating process in the (CdTe/PDDA)**n* devices. This is further supported by results obtained from composite films consisting of two layers built from different size CdTe nanocrystals. The *I*-*V* characteristics of the (CdTe/PDDA)**n* (*n*=20, 30, 50) films indicate that a tunneling mechanism might be applicable to describe the charge carrier injection. This makes it possible to improve the quantum efficiency of the smallest particle by using low work function metals as a cathode.²¹ In contrast to our previous observations from CdSe/PAH devices, the CdTe/PDDA system presents a low turn-on voltage. This indicates that the lowest energy level of the conduction band is lower in the case of CdTe than for CdSe, which favors electron tunneling into the film. Hence, by using CdTe instead of CdSe, thin film electroluminescent devices of high efficiency can be built using a simple and isolating polyelectrolyte. This is interesting not only with respect to possible technical applications, but also from a scientific point of view, since it allows the manufacturing of

novel composite materials of organic and inorganic compounds, whose optical and electronic properties are determined by inorganic components.

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