Electroluminescence from an Organic−Inorganic Perovskite Incorporating a Quaterthiophene Dye within Lead Halide Perovskite Layers

Konstantinos Chondroudis and David B. Mitzi*

IBM T. J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

Received September 2, 1999

Organic−inorganic hybrids are a technologically important class of materials, offering the possibility of combining useful properties of both organic and inorganic components within a single molecular composite. Optical and electrical properties of organic materials, for example, can be tuned relatively easily by modifying their molecular structure. Their ease of processing, plasticity, and low price make organic materials attractive for a number of applications (e.g., field-effect transistors, light-emitting devices, etc.). Lack of robustness, thermal stability, and low electrical mobility, however, inhibit their use in many of the same applications. These latter properties are offered by inorganic materials. By synthesizing organic−inorganic composites, the best of both worlds can potentially be obtained within a single material. An example of an organic−inorganic LED (OILED), based on CdSe nanoparticles dispersed in different polymers has recently been fabricated, although such devices currently operate only at low temperatures or at room temperature with very low efficiencies (0.001−0.01%).[1,2]

The layered organic−inorganic perovskites are a subclass of the organic−inorganic hybrids and have recently attracted substantial interest due to their unique electrical, magnetic, and optical properties.[3] They are crystalline compounds that self-assemble into a multilayer structure in which two-dimensional layers of corner-sharing MX_6 octahedra alternate with layers of aliphatic or aromatic ammonium cations. The simplest and most common examples of hybrid perovskites have the general formula $(R-NH_3)_2MX_4$ (M = divalent metal, X = halogen). The ammonium groups hydrogen bond to the inorganic sheet halogens, with the organic tails extending into the space between the layers and holding the structure together via van der Waals interactions. A similar layered perovskite structure is stabilized by diammonium cations, yielding compounds with the general formula $(H_3N-R-NH_3)MX_4$ (Figure 1).[3−6] In these systems, there is no van der Waals gap between the layers since the ammonium groups of each organic layer hydrogen bond to two adjacent inorganic layers.

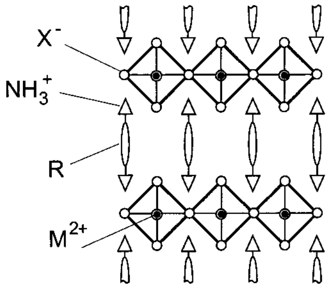
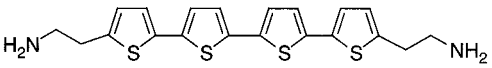


Figure 1. Schematic of the structure of the $(H_3N-R-NH_3)MX_4$ perovskite family.

Chart 1. Single AEQT Dye Molecule Designed for Insertion into the Layered Perovskite Structure



Many Pb(II) and Sn(II) halide-based hybrid layered perovskites form self-assembling multiquantum well structures, with semiconducting metal halide sheets alternating with generally much wider band gap organic layers. Their interesting physical properties, which include strong room-temperature photoluminescence,[7,8] third-harmonic generation,[9] and polariton absorption,[10] arise from excitons in the inorganic sheets. The excitons display large binding energies (>300 meV) and oscillator strengths.[7,10] These attributes make them potentially attractive as emitter materials in electroluminescent devices. Devices prepared using perovskites of the $(R-NH_3)_2PbI_4$ family with phenethylammonium $(C_6H_5C_2H_4-NH_3)^+$ or cyclohexenylethylammonium $(C_6H_9C_2H_4NH_3)^+$ cations as the organic component, exhibit efficient electroluminescence when driven at 24 V. Unfortunately, the strong electroluminescence is observed only at liquid nitrogen temperatures, rendering such devices impractical for display applications.[11,12] The drop off in efficiency at room-temperature arises, most probably, from thermal quenching of the excitons.

To address the issue of room-temperature electroluminescence in these compounds, we designed and synthesized a relatively complex dye cation, on the basis of an oligothiophene moiety and ethylammonium units, to replace the optically inert (in the visual spectrum) alkyl or simple aromatic component within the layered perovskite structure. The molecule (Chart 1), 5,5‴-bis-(aminoethyl)-2,2′:5′,2″:5″,2‴-quaterthiophene ($H_2N-C_2H_4C_{16}H_8S_4C_2H_4NH_2$), was designed with a long, narrow profile to "fit" in the available space of a $(H_3N-R-NH_3)MX_4$-type structure. An ethylammonium group connected to the 2-position of each terminal thiophene provides for the hydrogen bonding of the molecule to

---

(1) Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. *Nature* **1994**, *370*, 354.

(2) Dabbousi, B. O.; Bawendi, M. G.; Onitsuka, O.; Rubner, M. F. *Appl. Phys. Lett.* **1995**, *66*, 1316.

(3) For a recent review, see: Mitzi, D. B. *Prog. Inorg. Chem.* **1999**, *48*, 1.

(4) Halvorson, K.; Willet, R. D. *Acta Crystallogr.* **1988**, *C44*, 2071.

(5) Garland, J. K.; Emerson, K.; Pressprich, M. R. *Acta Crystallogr.* **1990**, *C46*, 1603.

(6) Willet, R. D.; Riedel, E. F. *Chem. Phys.* **1975**, *8*, 112.

(7) Ishihara, T.; Takahashi, J.; Goto, T. *Solid State Commun.* **1989**, *69*, 933.

(8) Papavassiliou, G. C.; Koutselas, I. B. *Synth. Met.* **1995**, *71*, 1713.

(9) Calabrese, J.; Jones, N. L.; Harlow, R. L.; Herron, N.; Thorn, D. L.; Wang, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2328.

(10) Fujita, T.; Sato, Y.; Kuitani, T.; Ishihara, T. *Phys. Rev.* **1998**, *B57*, 12428.

(11) Hattori, T.; Taira, T.; Era, M.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1994**, *65*, 676.

(12) Era, M.; Morimoto, S.; Tsutsui, T.; Saito, S. *Chem. Phys. Lett.* **1996**, *254*, 103.

10.1021/cm990561t CCC: $18.00

the adjacent perovskite sheets. Successful incorporation into the perovskite structure yields ($H_3NC_2H_4C_{16}H_8S_4$-$C_2H_4NH_3)PbX_4$ (X = Cl, Br, I) [(AEQT)PbX_4 hereafter]. Details of the preparation, X-ray single-crystal structure and properties of these compounds have been published elsewere.[3,13] By fabricating OILEDs (organic–inorganic light emitting devices) incorporating these hybrid perovskites, we were successful in obtaining relatively efficient room-temperature electroluminescence.

Due to the difficulty of solubilizing oligothiophenes in common solvents used for the lead halides, as well as substrate wetting problems with those solvents that are appropriate for the two components, spin-coated films were not found to be suitable for device fabrication. Instead, thin films of (AEQT)$PbCl_4$ were deposited by a recently described single source thermal ablation method (SSTA).[14,15] The as-deposited films lacked the spectroscopic features of a layered perovskite structure, indicating a poorly formed inorganic framework.[15] After deposition, the films were therefore annealed on a digitally controlled hot plate under inert conditions. The optimum device performance was obtained when the films were annealed at 115 °C for 5 min. The UV–vis absorption spectrum of the annealed SSTA films exhibited the characteristic exciton absorption (331 nm) for the lead chloride-based perovskite framework.[3,16] The films had a featureless X-ray powder diffraction pattern, suggesting a small grain size or short-range ordering of the perovskite structure. Higher annealing temperatures resulted in a gradual increase of the grain size, as observed previously for a related system.[15]

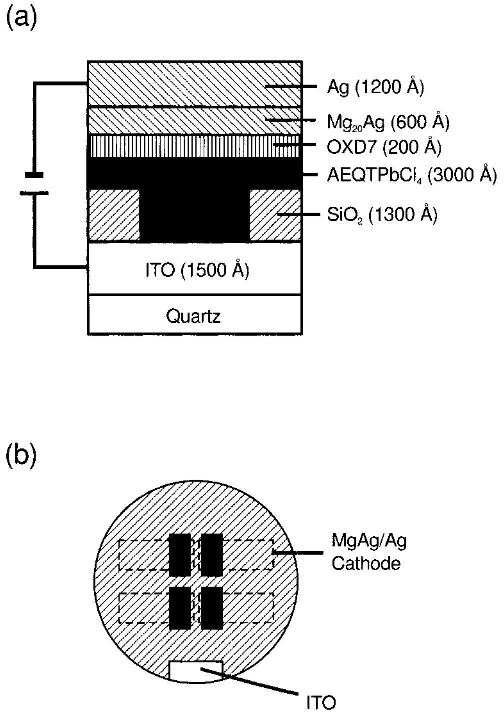


Figure 2. (a) Cross-section of the OILED device structure (not to scale) and (b) a circular quartz substrate containing four devices (bottom view).

The device structure employed can be seen in Figure 2. It consists of a circular ($^3/_4$ in. diameter), optically polished quartz substrate on which ITO was e-beam deposited (1500 Å, 14 Ω/square). To avoid shorting between the anode and cathode, 1300 Å of SiO_2 were e-beam-deposited on top of the ITO through contact masks that defined four rectangular areas (3 × 1 mm) of exposed ITO. The patterned substrates were cleaned by ultrasonication for 5 min in each of the following: 1% w/v aqueous detergent solution, acetone, and methanol, and then boiled in methanol for 5 min. They were dried in a 120 °C oven and subjected to an O_2 plasma (30 W, 120 mTorr, 4 min). A 3000 Å (AEQT)$PbCl_4$ film was deposited at 10^{-7} Torr in a SSTA vacuum chamber, followed by annealing. Subsequently, 200 Å of the electron-transporting 1,3-bis[4-(*tert*-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD7 hereafter) were vacuum deposited by resistive heating at 10^{-7} Torr. To complete the devices, an alloy of $Mg_{20}Ag$ was deposited by coevaporation from two separate sources (600 Å, 10^{-7} Torr). Another 1200 Å of Ag were deposited on top to inhibit oxidation. The MgAg/Ag cathode was deposited through contact masks with rectangular 2 × 7 mm openings, with the openings at a 90° angle to the exposed ITO areas, therefore defining an active device area of 1 × 2 mm (Figure 2b). It should be noted that the vacuum system employed is connected to the antechamber of a nitrogen-filled glovebox, allowing preparation of the devices under completely inert conditions. The devices were encapsulated using a cover glass and epoxy glue.[17] All measurements were performed in ambient conditions, outside the glovebox. Thickness measurements were performed using a Tencor P-10 surface profilometer. The efficiency of the devices was measured using an Optronic Laboratories Inc. integrating sphere and a UV-enhanced silicon detector equipped with a photopic filter (the apparatus was calibrated against NIST standards).

Figure 3a shows the current–voltage (I–V) and electroluminescence–voltage characteristics for the OILED structure. Bright green light (530 nm) was observed in a well-lit room when the devices were forward biased under ambient conditions. A low turn-on voltage of about 5.5 V was observed. Both the I–V and EL–V curves follow a similar pattern, indicating a relatively balanced electron and hole injection.[18] The electroluminescence spectrum corresponds well to the photoluminescence spectrum of (AEQT)$PbCl_4$ (Figure 3b), as well as to that of the dye salt AEQT·2HCl.[13] The maximum efficiency was 0.1 lm/W at 8V and 0.24 mA (power conversion efficiency 0.11%). Devices with a 600 Å (AEQT)$PbCl_4$ film had a lower turn-on voltage of 4.8 V compared to the devices with a 3000 Å emission layer. Interestingly, even with the thicker film, the turn-on voltage remains low (5.5 V). Further studies are under way to elucidate the role of the inorganic and organic layers on the charge injection and transport properties of the hybrid. The fact that thicker layers of the emission layer can be used, compared to conventional OLEDs (typically <600 Å), should improve device reli-

---

[13] Mitzi, D. B.; Chondroudis, K.; Kagan, C. R. *Inorg. Chem.*, in press.

[14] Mitzi, D. B.; Prikas, M. T.; Chondroudis, K. *Chem. Mater.* **1999**, *11*, 542.

[15] Chondroudis, K.; Mitzi, D. B. *Chem. Mater.*, in press.

[16] Ishihara, T.; Hirasawa, M.; Goto. T. *Jpn. J. Appl. Phys.* **1995**, *Suppl. 34-1*, 71.

[17] Burrows, P. E.; Bulovic, V.; Forrest, S. R.; Sapochak, L. S.; McCarty, D. M.; Thompson, M. E. *Appl. Phys. Lett.* **1994**, *65*, 2922.

[18] Pei, Q.; Yang, Y. *Chem. Mater.* **1995**, *7*, 1568.

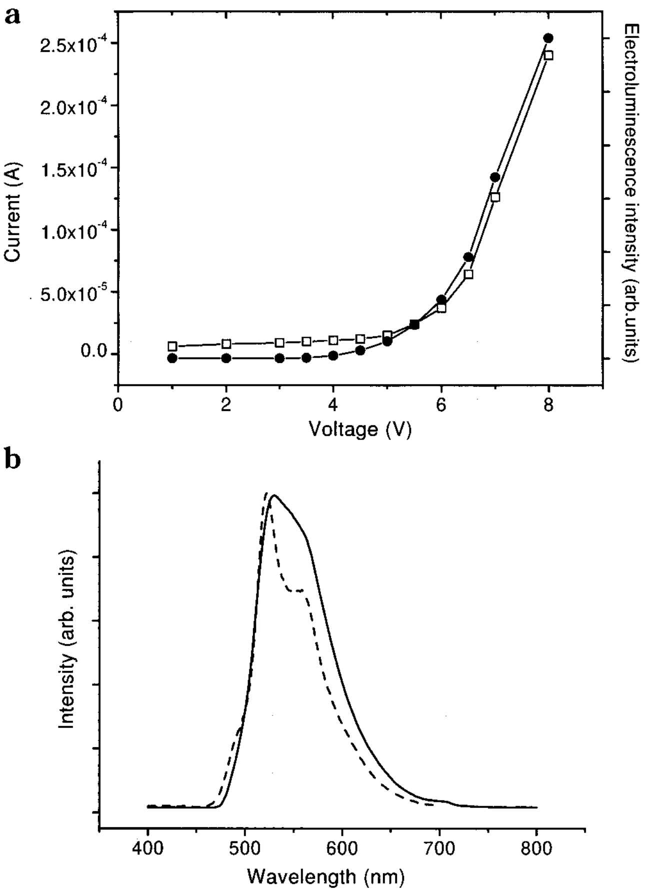


Figure 3. (a) Room-temperature current–voltage (I–V) (open squares) and electroluminescence–voltage (EL–V) (filled circles) characteristics of a ITO/(AEQT)$PbCl_4$ (3000 Å)/OXD7 (200 Å)/$Mg_{20}Ag$ (600 Å)/Ag (1200 Å) light emitting device, and (b) electroluminescence (solid line) and photoluminescence (broken line, excited at 360 nm) spectra of (AEQT)$PbCl_4$.

ability and lifetime since it becomes less prone to pinholes and shorts.

Previous attempts to utilize thin, purely organic, films of unsubstituted or alkyl- and silyl-substituted oligothiophenes in OLEDs, yielded devices with very low efficiencies.[19,20] Higher efficiencies were obtained from oligothiophenes substituted with triphenylamino groups (e.g., 0.03 lm/W for quaterthiophene[21] and 1.1 lm/W for terthiophene.[22]) It is interesting that even in the unoptimized devices of the current work, incorporation of the quaterthiophene derivative in the hybrid perovskites yielded more efficient devices (0.1 lm/W) than those achieved with triphenylamino-substituted quaterthiophene. Due to the self-assembling nature of the hybrids, their structure forms a perfectly alternating sequence of organic–inorganic layers at the molecular level, which may be advantageous for several reasons. First, artificially alternating sequences of organic and inorganic compounds have been used for preparing conventional OLEDs, using LiF and Alq_3.[23] It was found that there is a distinct improvement of the efficiency and the lifetime, attributed to better injection, transport, and recombination of the carriers. The self-assembling hybrid perovskites provide a much simpler way (i.e., a single evaporation step) of achieving this type of alternating structure. Furthermore, when the dye molecules are contained within the perovskite framework, the latter acts as a template, inducing a different molecular packing than that achievable in a purely organic film. This control over packing has the potential for reducing the quenching interactions between the dye molecules, thereby increasing their overall luminescence quantum efficiency. Finally, the hybrid perovskite films exhibit a high thermal stability (120–200 °C depending on the inorganic framework) against crystallization, providing for more robust films. For comparison, glass transition temperatures of materials used in conventional OLEDs vary from 60 °C for common molecules such as TPD, to ~95 °C for the substituted oligothiophenes,[22] up to150 °C for starbust molecules.[24]

In conclusion, room-temperature electroluminescence has been obtained from OILED devices employing a hybrid organic–inorganic perovskite as the emission layer. In contrast to earlier systems based on perovskites, the emission in these devices arises from the organic layer of the structure. The efficiency of these preliminary devices is very promising and higher values are expected by further fine-tuning of the device characteristics. Other inorganic frameworks, currently under study, along with further understanding of the role of the inorganic component, may provide for higher efficiencies. For example, devices with lead bromide (smaller band gap) perovskite sheets exhibited efficiencies 20–30 times lower than the ones with lead chloride, whereas preliminary results for devices with cadmium chloride (higher band gap) layers show efficiencies higher than 0.1 lm/W. Another important parameter is the organic ammonium cation component. By appropriate choice of the organic cation, higher luminescence efficiency and different emission colors (e.g., blue, red, etc.) necessary for full color display applications should be feasible. Appropriate modification[3] of common dye molecules should provide a vast repertoire of candidate molecules.

Acknowledgment. We are grateful to DARPA for support of this work under contract DAAL01-96-C-0095.

CM990561T

---

(19) Uchiyama, K.; Akimichi, H.; Hotta, S.; Noge, H.; Sakaki, H. *Synth. Met.* **1994**, *63*, 57.

(20) Neureiter, H.; Gebauer, W.; Vaterlein, C.; Sokolowski, M.; Bauerle, P.; Umbach, E. *Synth. Met.* **1994**, *67*, 173.

(21) Noda, T.; Ogawa, H.; Noma, N.; Shirota, Y. *Adv. Mater.* **1997**, *9*, 720.

(22) Noda, T.; Ogawa, H.; Noma, N.; Shirota, Y. *Appl. Phys. Lett.* **1997**, *70*, 699.

(23) Riess, W.; Riel, H.; Seidler, P. F.; Vestweber, H. *Synth. Met.* **1999**, *99*, 213.

(24) Kuwabara, Y.; Ogawa, H.; Inada, H.; Noma, N.; Shirota, Y. *Adv. Mater.* **1994**, *6*, 677.