Blue-Green Light Emission from Self-Assembled Bipyridinium Thin Films

Haipeng Zheng,* Ruifeng Zhang, Ying Wu, and Jiacong Shen
Key Laboratory for Supramolecular Structure & Spectroscopy, Department of Chemistry,
Jilin University, Changchun 130023, P.R. China

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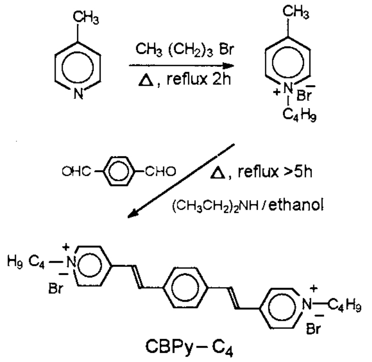
The photoluminescence (PL) properties of a short ribbon-like conjugated bipyridinium and its application in the design and fabrication of organic LED devices were discussed.

Organic/polymer-based light-emitting devices (LEDs) have recently attracted a great deal of attention due to their operation at relatively low voltages with good quantum efficiency and the possibility to chemically tune the energy gap to control the emission color.[1-3] Most of these LEDs are constructed by thin films of both thermally evaporated small molecule systems[4-7] as well as various spin-coated conjugated polymers[8-10] such as poly(phenylene vinylene) (PPV) and its derivatives. While it is difficult to control the thickness and homogeneity of polymer films with this spin-coated technique.

Rubner and his colleagues[11] first fabricated LEDs based on ultrathin multilayer heterostructures of PPV and non-conjugated polymers through layer-by-layer molecular self-assembly, which is indeed a powerful method to process conjugated polymers into ultrathin multilayer films with controlled thickness and molecular architecture. Since this initial disclosure, a number of other groups have utilized this technique to construct LEDs with PPV precursor materials[12,13] and fully conjugated polyions — poly(pyridinium vinylene) (PPyV).[14] However, the LEDs fabricated from PPV-precursor/poly(styrene-4-sulfonate) (PSS) or PPV-precursor/poly(methacrylic acid) (PMA) multilayer films exhibited the different emission peaks, intensity and the different electrical properties due to interlayer interactions in the self-assembled multilayer heterostructures.[12] For PPyV system,[14] the photoluminescence (PL) and electroluminescence (EL) spectra of the LED devices of PPyV/PSS films had no relation to the interlayer interactions, but all showed a wide emission (its half-width is about 150 nm) and emitted orange-red light, resulting from the strong π-π^* interactions among the long conjugated main chains and different kinds of molecular aggregations. Recently we successfully constructed the LEDs by using a short ribbon-like conjugated bipyridinium and PSS, which exhibit narrow and blue-green light emission. In this paper we report the PL and EL properties of the conjugated bipyridinium with two butyl groups (CBPy-C_4) for the fabrication of LEDs.

CBPy-C_4 was synthesized as follows. 1-buty, 4-methyl pyridinium bromide (BMPB) was first prepared by reflux of 4-picoline and 1-bromobutane for 2 h. Then 5.1 g of BMPB and 3.35 g of phthalaldehyde in ethanol was added diehylamine (5 mL) slowly, and reflowed for over 5 h. The precipitated product CBPy-C4 was filtered and recrystallized from ethanol and dried under vacuum to give yellow crystals. (11.2 g, 76% yield) Elem. Anal. Found: C, 60.34; H, 6.07; N, 5.05; Br, 28.54%. Calcd for $C_{28}H_{34}Br_2N_2$: C, 60.22; H, 6.09; N, 5.02; Br, 28.67%. Here CBPy-C_4 can be regarded as a special oligomer of PPV or PPyV. This short ribbon-like electrolyte is suited for film growth by electrostatic interactions with PSS to assemble highly uniform films like other dye-polyion systems[15] and has a good fluorescence quantum yield (φ = 0.82).



The deposition process was carried out according to our previous work: To charge the substrate and improve the adhesion of the film to the substrate, the solution of 0.1 vol% polyethylene-imine (PEI) in millipore water at pH 7~8 was also used. The multilayer films were prepared by charging the substrate first with PEI for 20 min, rinsing with pure water and drying. Then the substrate was dipped into 0.01 M PSS solution for 10 min, followed by immersion in 0.01 M CBPy-C_4 solution for 10 min, rinsing and drying after each dipping. This sequence is repeated until the desired number of bilayers are built up. The CBPy-C_4 cast film (100~200 nm) was prepared by dipping the CBPy-C_4 ethanol solution (10^{-5} M) on a quartz slide at 50 °C under the saturated ethanol atmosphere for over 10 h.

The UV-VIS spectra of the multilayer films of CBPy-C_4/PSS on quartz are shown in Figure 1. The insert clearly shows a linear relationship between the absorbance of the multilayers at different wavelengths and the number of layers present, which indicates the vertical periodic structure of the self-assembled

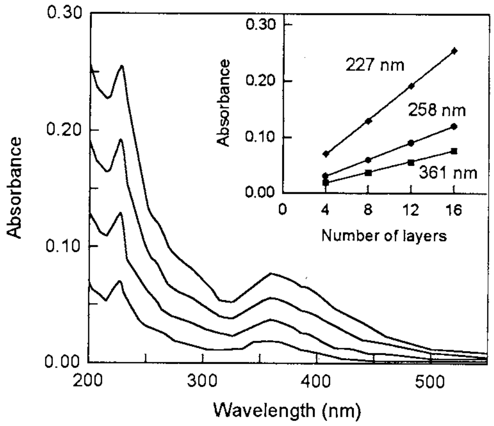


Figure 1. UV-VIS spectra of the CBPy-C_4/PSS multilayer films with 4, 8, 12 and 16 bilayers, respectively. Insert is absorbance *vs.* number of layers at 227, 258, and 361 nm.

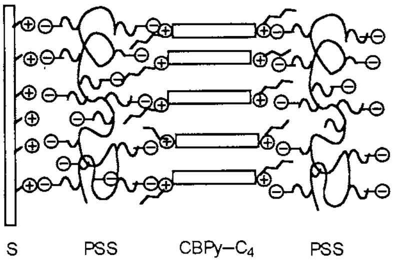


Figure 2. The proposed structure model of the multilayer alternating films.

alternating films. At the same time, extrapolation of the linear lines through, or very close to, the zero point which proves the monomolecule-layer deposition process.[16] The possible structure model of the CBPy-C_4/PSS multilayer films is proposed in Figure 2. Aqueous CBPy-C_4 at 10^{-5} M with PSS gives λ_{max} at 370 nm. Spectra of CBPy-C_4 in the films show blue shifts, suggesting that CBPy-C_4 molecules form H aggregates.

Both CBPy-C_4 powder and its cast film exhibit a wide emission peak at about 520 nm (see Figure 3), but the PL spectra of the self-assembled CBPy-C_4/PSS multilayer films excited at 361 nm all exhibit narrow peaks at 468 nm and their half-width is 75 nm, which is alike that of CBPy-C_4 aqueous solution, indicating that chromophores in H aggregates tend to form the higher excited state, so the emission of the multilayer films becomes more blue-shift than that of the CBPy-C_4 cast film. It is also found that the emission intensity at 468 nm is almost linearly dependent on the number of CBPy-C_4/PSS bilayers.

ITO glass was used as the substrate for the multilayer films of CBPy-C_4/PSS, onto which aluminum was evaporated directly as another electrode. Seen from the current-voltage (*I-V*) curves, the ITO/(CBPy-C_4/PSS)$_n$/Al devices (n=8, 12, 16) all show classical rectifying behaviors. An obvious correspondence between film thickness and threshold voltage can be seen that the threshold voltage required to operate the device increases with increasing film thickness. Figure 4 is the *I-V* data obtained from the ITO/(12-bilayer CBPy-C_4/PSS film)/Al device. EL of blue-green light at 470 nm is observed when a potential of 7.5 V or higher was applied to ITO. This device exhibits a relatively high threshold voltage which may be related to the arrangement of the CBPy-C_4 molecules in the multilayer films.

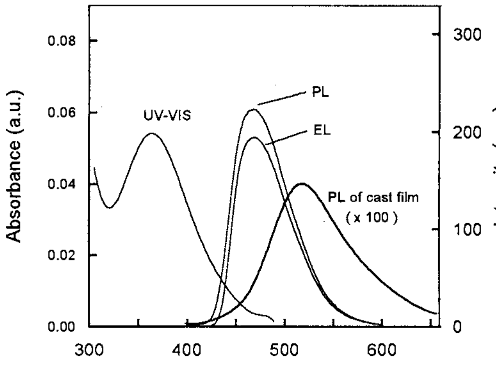


Figure 3. The UV-VIS, PL, and EL spectra of the 12-bilayer CBPy-C_4/PSS film, and the PL curve of CBPy-C_4 cast film.

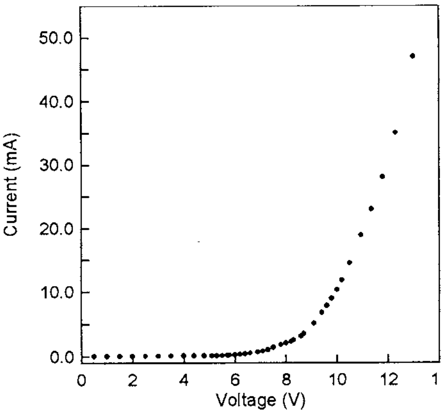


Figure 4. Current-voltage plots of ITO/(12-bilayer CBPy-C_4/PSS)/Al devices.

The PL and EL spectra are basically identical as shown in Figure 3, and there is a little overlap between the absorption and luminescence spectra implying almost no self-absorption in the multilayer films. When the luminance levels are in 10~50 cd/m^2, they have obvious increasing tendency as the applied voltage increases. The device exhibits the maxium brightness (about 47 cd/m^2) when the applied voltage is 13 V.

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