DOCTORAL THESIS

Synthesis and characterization of electroluminescent bipolar small molecules and polymers

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Synthesis and Characterization of Electroluminescent Bipolar Small Molecules and Polymers

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Abstract

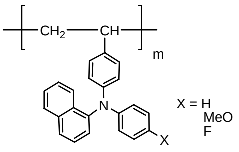
The launch of commercial electronic appliances incorporating organic light-emitting diode (OLED) as display has illustrated the suitability and wide-range application for this technology. There are, however, still a number of technical problems to be resolved in order for OLED to compete with lower cost LCDs. These problems including thermal stability, color purity and manufacturing yield, etc. Thermal stability of the transporting materials has been shown to correlate with the device stability. It is also desirable to develop a hole transport layer that has matching mobility compared to AlQ_3, which is one of the most widely used electron-transporting and green light-emitting material. From the manufacturing point of view, reducing the number of layers allows better control on the uniformity of the device, and minimizing interfacial diffusion, which are the causes for degradation and poor long term stability in OLEDs. The problem can be resolved by the development of multifunctional bipolar compounds, which contain an electron-transporting, a hole-transporting, as well as an emitting moiety. Finally, compared to green OLED, color purity of blue OLED have much room for improvement. It is much more difficult to produce strong blue emitting materials, owing to its large band-gap.

In this thesis, several series of side-chain hole-transporting and bipolar copolymers have been prepared using facile synthetic procedures. They are soluble in common organic solvents and have high glass-transition temperatures (132 – 178 ^{o}C). The IP of these polymers, P(X-NPA) (**Series I**), can be modified by the side-group subsitutent X (where X = F (5.39 eV) > H (5.37 eV) > MeO (5.23 eV)). The substituent changed the dipole moment of the molecule and hence the hole mobility as well. For the device (ITO/PEDOT:PSS/P(X-NPA) /AlQ_3/Ca/ Al), the hole mobility and energy barrier at the interface, P(X-NPA)/AlQ_3, are two factors affecting the device performance (maximum

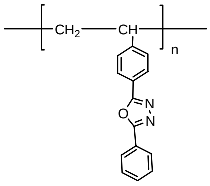
luminance = 6608 cd/m^2, current efficiency = 3.5 cd/A for X= MeO). For the bipolar copolymers (**Series II-III**), the inclusion of hole-blocking oxadiazole (OXA) units (HOMO = 6.04 eV), enhanced the current efficiency and maximum luminance of the OLED. The device performance improved from 3.5 cd/A and 6600 cd/m^2 (heterojunction device employing P(X-NPA), X = MeO) to 4.2 cd/A and 24000 cd/m^2 (heterojunction device employing P(MeONPA-co-OXA 82:18)). The introduction of a greenish yellow perylene repeating unit (**Series IV**) produced a color tunable PLED.

For bipolar compounds (**Series V-VII**), their respective homojunction OLEDs with or without a charge injection CuPc layer (ITO/XOT/Ca/Al or ITO/CuPc/XOT/Ca/Al) were studied. Both PyOT (**Series VI**) and TOTPD (**Series V**) shown excellent device performance (PyOT: 7500 cd/m^2 and 2.2 cd/A; TOTPD: 2000 cd/m^2 and 1.1 cd/A). TOTPD-base OLED has strong blue emission with EL spectrum centered at 478 nm corresponding to (0.164, 0.274) on CIE coordinates. This is one of the best results reported for single-layer small molecule-based OLED with EL maximum below 480 nm. Finally, a hybrid-OLED (HOLED) employing PPOT (**Series VI**) (ITO/PEDOT:PSS/ P(MeONPA)/PPOT/Ca/Al) was found to have a narrow EL peak (FWHM = 70 nm), centered at 449 nm [CIE coordinates (0.15, 0.13)] which was very close to the CIE coordinates required for a blue color chromaticity according to the National Television System Committee (NTSC) (0.14, 0.08). Its full width at half maximum (FWHM) at 70 nm is similar to the requirement for a monochromic light source (60 -70 nm).

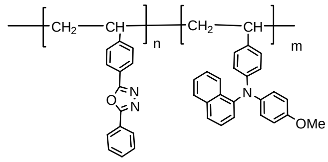
The chemical structures of the intermediates and final products were confirmed by ^{1}H NMR, HRMS (ESI) and/or FAB mass spectrometry and/or MALDI-TOF-HRMS. The optical, electrochemical and thermal properties of these new materials were studied by fluorescent and UV/Vis spectroscopy, cyclic voltammetry, DSC and TGA respectively. The organic light-emitting diodes (OLEDs) of the materials such as polymeric OLED (PLED), heterojunction OLED, homojunction OLED as well as hybrid OLED (HOLED) were successfully fabricated and their electroluminescent properties were measured.



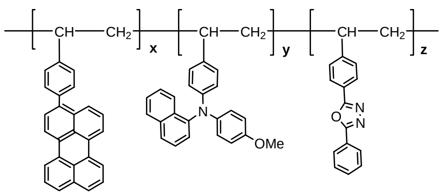
Series I) P(X-NPA)



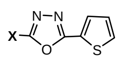
Series II) P(OXA)

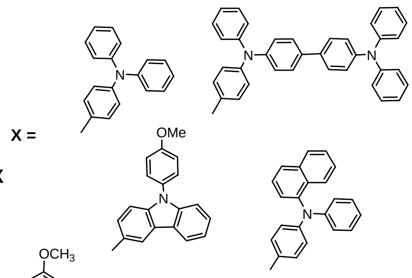


Series III) P(MeONPA-co-OXA)

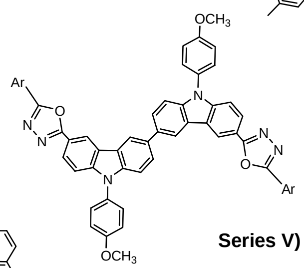


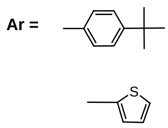
Series IV) P(MeONPA-co-OXA-co-Pery)



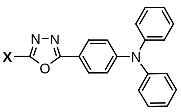


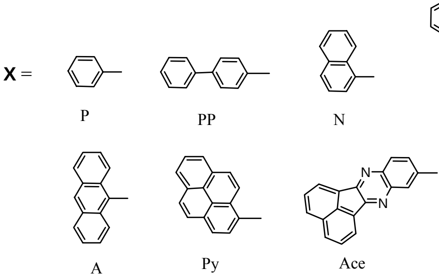
Series V) TOX



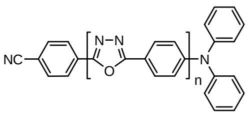


Series V) TOX



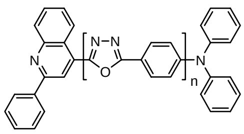


Series VI) XOT



n = 1 and 2

Series VII) CNPO(*n*)T



n = 1, 2 and 3

Series VII) PQO(*n*)T

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