Highly Photoluminescent Metal–Polymer Complexes prepared with a Facile Chemical Vapor Deposition Polymerization Process

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Received October 31, 2007
Revised Manuscript Received February 28, 2008

Metal complexes have been commonly used as efficient emitting materials in multilayer small molecule organic light-emitting diodes. Particularly, the metalquinolate series, Mq_3, where M is metal and q_3 is tris-(8-hydroxyquinoline), have been intensively and extensively studied.[1–5] Metal complexes also play an important role in polymer light-emitting diodes, blending with a polymer matrix to form a host–guest system to improve quantum efficiencies and tune emission colors. The internal quantum efficiency of such systems may approach 100% because of the strong spin-orbit coupling induced by the central heavy metal atom.[6] The spin-orbit coupling enhances the intersystem crossing and mixing of the singlet and triplet states necessary for radiative relaxation through either Förest or Dexter energy transfer mechanism.[7,8] Although significant improvements in device efficiency have been achieved, the performance of such blend systems of metal complex and polymer may suffer from aggregation of phosphor, concentration quenching, and phase separation. More importantly, the synthetic procedures for metal complexes are quite complicated, and the subsequent purification steps are often a tough task.[9]

In this work, a direct complexing of metal, Zn, with polymer, poly(*p*-phenylene vinylene) (PPV), achieved in a cofed chemical vapor deposition polymerization (CVDP) process, produced a highly photoluminescent metal–polymer complex, that showed a 2 orders of magnitude improvement in PL quantum yield over the pristine polymer. To the best of our knowledge, this is the first example for prepareation of metal–polymer complexes with a CVDP process. In the process, the monomer precursor, *di*-chloro-*p*-xylene,[10a,b] was introduced into a high-temperature furnace where zinc powders were situated for zinc vapor supply. The mixed vapors passed through the furnace and exited to a low temperature deposition chamber. The collected deposits were then thermally converted in a N_2 atmosphere at 270 °C for 14 h to form conjugation structures. The formation of polymer conjugates during the thermal conversion process can be monitored with FTIR spectra collected at increasing conversion times as discussed in Figure S4 of the Supporting Information. The Zn vapor level was controlled by adjusting the location of the Zn powder within the furnace. Locations closer to the furnace center were hotter and gave higher Zn concentrations for the complexing. Products with three different Zn levels were produced and compared. Through adjustment of the Zn powder location, three Zn powder heating temperatures of 700, 500, and 300 °C were realized (see the Supporting Information, Scheme S2), leading to Zn/PPV complexes of three different Zn concentrations, 6.8 wt %, 0.63 wt %, and negligible, respectively (see the Supporting Information, Figure S5).

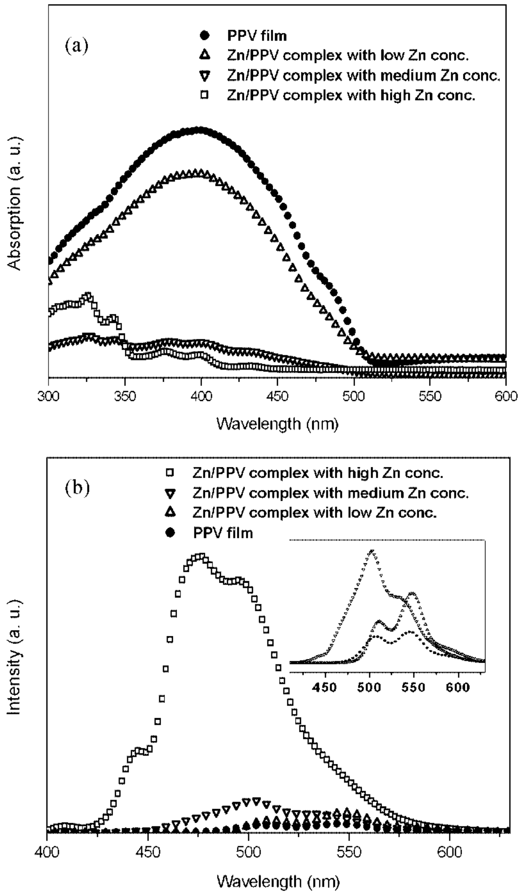

Figure 1. (a) UV–visible absorption and (b) photoluminescence spectra for pristine PPV and Zn/PPV complex films. Inset of (b) is for the low PL intensity samples. Excitation wavelength: 330 nm.

Figure 1 shows the UV–visible (Hitachi, U-3300) and PL (Hitachi, F-4500) spectra of these Zn/PPV complexes. Blue shifts in both spectra are evident, with the emission color changing from yellow, to green, and to sky blue with increasing Zn concentration. The pronounced blue shift at

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10.1021/cm703115q CCC: $40.75

Table 1. PL Quantum Yields

sample	film thickness[a] (nm)	Q_s (%)	relative Q_s
pristine PPV film	~90	0.5	1.0
Zn/PPV complex with low Zn concentration	~80	1.1	2.1
Zn/PPV complex with medium Zn concentration	~90	7.3	14.0
Zn/PPV complex with high Zn concentration	~70	37.0	70.5

[a] The film thicknesses were estimated from cross-section SEM images.

medium and high Zn concentrations was a direct result of the enlarged bandgap, corresponding to reduction in polymer conjugation length, caused by the perturbation of conjugation by the Zn/PPV complexing. The evident vibronic structure below 450 nm in the absorption spectra implies the more disordered film conformation, whereas the broadening of the PL spectra came from the wider conjugation length distribution, both attributable to the Zn/PPV complexing.

The Huang–Rhys parameter, defined as the ratio between the intensities of the 0–1 and 0–0 transitions in PL spectra, $S = I_{0-1}/I_{0-0}$, increases from 1.2 to 2.8 with increasing Zn concentration, implying more disordered structure in metal complexed films.[11] The Huang–Rhys parameter can also be related to the conjugation length of the polymer, shorter conjugation lengths giving rise to larger S.[12] Note that shorter conjugation lengths lead to more localized π-electrons and enlarge the bandgap. The presence of the complexed Zn enhances the energy transfer of excitons through the strong spin-orbit coupling that eases the intersystem crossing during exciton diffusion and thus favors the radiative recombination.[13,14] Furthermore, with the direct complexing of metal with the polymer main chain, it is possible to increase the triplet energy level to suppress the luminescence quenching.[9,15] Other possibilities also exist, for example, the metal–polymer complexing may lead to a lesser extent of interchain interactions from which improvement in PL quantum yield results.[16] Further investigation is required to clarrify this issue. A 71-fold improvement in PL quantum yield was achieved for the Zn/PPV complex film of high Zn concentration over the pristine PPV (Table 1).

To confirm the Zn/PPV complexing, we conducted solid ^{13}C NMR (Bruker, DSX400WB) and Raman spectroscopy (homemade, excitation source is JDS uniphase 1100 series He−Ne laser with JYHoriba BX41 confocal microscope). Solid NMR spectra can be used to infer molecular structures of the sample. As for Raman spectroscopy, the frequency of the absorption peak increases with increasing bond strength and atomic mass, whereas the intensity increases with increasing bond polarizability and dipole moment.[17,18]

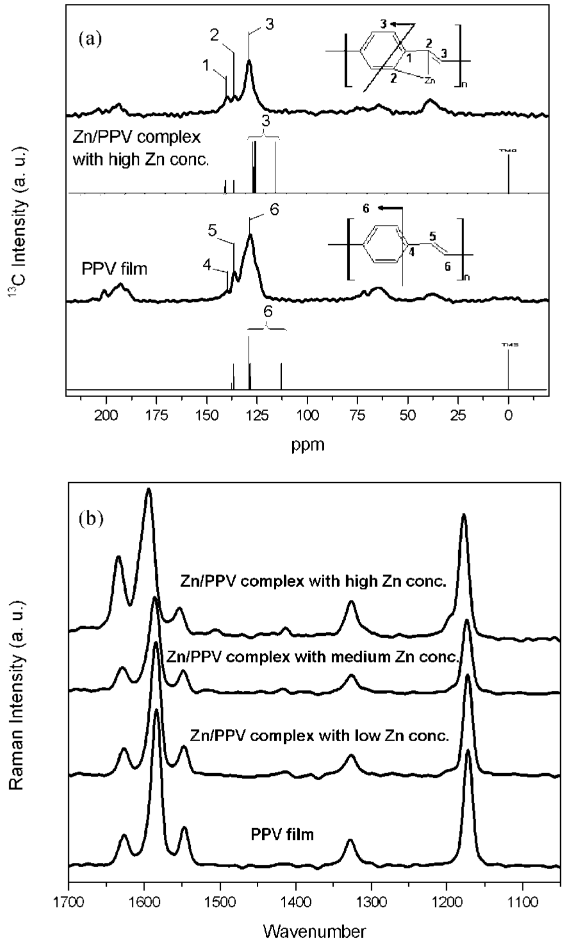

Figure 2. (a) Solid NMR spectra and (b) Raman spectra for pristine PPV and Zn/PPV complex films. Excitation wavelength: 632.8 nm.

Figure 2a shows the solid ^{13}C NMR spectra (100 MHz, δ) of the pristine PPV and Zn/PPV films, with the corresponding simulated spectra from ACD/ChemSketch placed underneath for comparison. Peak 3, located around 128.9 ppm, came from carbon atoms of the aromatic ring and vinylene not connected to Zn. It is slightly sharper than the corresponding peak 6 (128.3 ppm) as it should as suggested by the simulation. Peak 2 (136.1 ppm) are contributions from carbon atoms connected to Zn, whereas peak 1 (139.7 ppm) from the carbon atom located opposite to Zn. The differences in chemical shift and relative intensity existing between peaks 1 and 2 and corresponding peaks 4 and 5, respectively, were apparently caused by the complexing of Zn with the polymer backbone. The Raman spectra, excited at 632.8 nm, are presented in Figure 2b. Several points can be observed from the spectra. First, the incorporation of Zn leads to increase in system mass and thus band shifts to higher wavenumbers, e.g., the C=C stretching of the vinylene group from 1582

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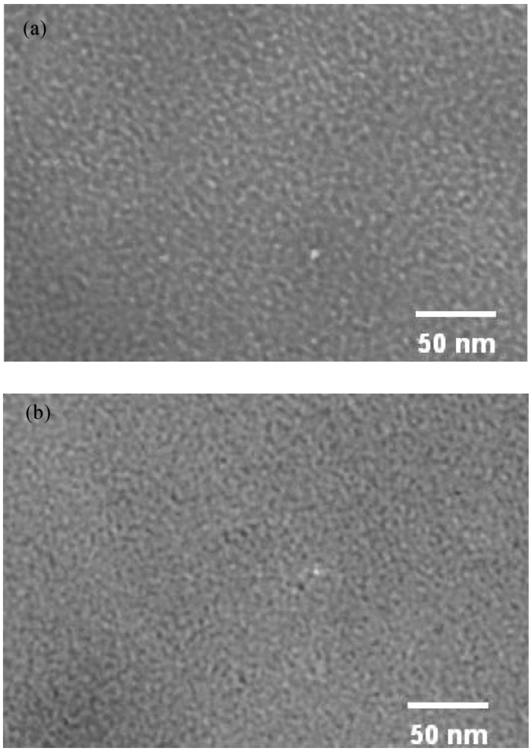

Figure 3. Top view TEM images for (a) pristine PPV film and (b) Zn/PPV complex film.

cm^{-1} for PPV films to 1593 cm^{-1} for Zn/PPV films of high Zn concentration. Second, a shoulder develops on the peak of 1195 cm^{-1} with increasing Zn incorporation. The peak of 1195 cm^{-1} is due to C−H stretching, which is influenced when Zn is complexed to the PPV main chain. Third, the intensity[19,20] of the C−C stretching of the aromatic ring at 1630 cm^{-1} is significantly increased, implying an increase in polarizability for enhancement of charge carrier mobility around the unit.[21,22] It has been reported that for PPV the decrease in Raman band intensity ratio of I_{1548}/I_{1626} indicated more disordered chains and shorter conjugation length. In the present work, I_{1548}/I_{1626} decreases with increasing Zn incorporation, giving the same trend in chain conformation and conjugation length as the Huang–Rhys parameter did. In addition, TEM (JEOL JEM-200CX) images (Figure 3) seem to support the proposal of more disordered chain structures for Zn/PPV complexing films. XRD (MAC Science MXP18, Cu Kα) patterns (see Figure S2 in the Supporting Information) of the PPV and Zn/PPV complex films indicates that there was an absence of appreciable Zn or ZnO phases in the films, a further support for the Zn/PPV complexing.

In conclusion, highly photoluminescent Zn/PPV complex films were successfully prepared with direct complexing of Zn to PPV in a facile CVDP process for the first time. A 2 orders of magnitude improvement in PL quantum yield was achieved through this metal complexing. The present approach can be readily extended to other photoluminescent metal–polymer systems.

Acknowledgment. The authors thank the National Science Council of the Republic of China (Taiwan) for financial support under Grant NSC 95-2221-E-007-193. The assistance offered by Prof. Keh-Chyang Liu for Raman experiments and Prof. An-Chung Su for discussions on vibrational spectra is greatly appreciated.

Supporting Information Available: Experimental details, PL spectra with Gaussian deconvolution analyses, XRD patterns, FTIR spectra, and SEM EDS analyses (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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