Application of a Novel Fullerene-Containing Copolymer to Electroluminescent Devices

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The optical properties of a soluble fullerene (C_{60})-containing copolymer, $(PS)_x C_{60}(PMMA)_y$, were investigated. We employed the $(PS)_x C_{60}(PMMA)_y$ in a polymer electroluminescent device as a hole-injecting layer. The forward-biased ITO/poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene]/$(PS)_x C_{60}(PMMA)_y$/Al device showed strongly quenched electroluminescence. In contrast, when the device was operated in reverse-bias direction, the luminescence and the yield were enhanced. The turn-on voltage of the reverse-biased device was −2.6 V. The quantum efficiency and the emitted light power were improved by ≈5 and ≈20 times, respectively, compared with those of the single-layer device.

Inroduction

Since buckminsterfullerene (C_{60}) consisting of all carbons was discovered in 1985, it has received a great deal of attention because of its potential applications in a variety of fields.[1] In addition, the development of the mass production method of C_{60} in 1990 triggered a great deal of research studies concerning the C_{60}-related materials.[2–4] Especially, C_{60} possesses several different optoelectronic and electro-optic properties:[5–9] For instance, when C_{60} is excited by a frequency-doubled Nd: YAG laser with 8-ns pulses, it shows an optical limiting response.[7] It has been reported that the light-emitting diodes (LEDs) prepared from the blend film of a C_{60} adduct, T_h-hexapyrrolidin, poly(N-vinylcarbazole), and 2,5-bis-(4-naphthyl)-1,3,4-oxadiazole, exhibited white electroluminescence (EL).[9] However, C_{60} is so poorly soluble in common organic solvents except for a few

aromatic ones[10] that many attempts have been made to overcome this defect.[11,12]

The best way to improve its solubility in organic solvents and the miscibility with other materials is chemical modification by attaching it to polymers. The resulting polymers might be of the "pearl necklace" or "pendent chain" type that differ as to the point of C_{60} attachment to the polymer chain.[3] Dai et al. have reported the covalent attachment of C_{60} onto 1,4-polydiene chains through lithiation of polymer chains with *sec*-butyllithium (BuLi).[13] Polyfullerenes in the form of so-called "flagellenes" were prepared by the reaction of C_{60} with a living polystyrene. The general formula was given as (polystyrene (PS))$_x C_{60}$ with x between 1 and about 10.[14]

In this article, we present the optical absorption (Abs) and photoluminescent (PL) properties of a newly synthesized soluble C_{60}-containing polymer. Its Abs and PL spectra were investigated in both solution and solid states. Finally, we demonstrate the electrical and electroluminescent (EL) properties of the multilayer devices where the C_{60}-containing polymer was employed as a hole-injecting material. Although pristine[15] and lightly n-doped C_{60}[16] and its derivative[9] have been used for the

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emitting material of EL devices, the C_{60}-containing polymer has not been employed as a hole-injecting layer (HIL) in EL devices. Generally, charge (hole or electron)-injecting/-transporting materials have been used to balance the charge injection in an organic EL device.[17,18] We also confirmed that the bipolar recombination zone for the hole-majority-carrier EL device be located very close to the metal cathode.

Experimental Section

Synthesis of Polymers. *sec*-BuLi-initiated polymerization of styrene was carried out in cyclohexane at 30 °C under high vacuum using a break-seal technique. All the reactions were carried out by the procedure which was modified based on the literature reported by Ederle and Mathis.[19] Poly(styryl)lithium was reacted with purified C_{60} in cyclohexane/THF cosolvent. Purified THF was then delivered into the reactor after complete removal of the solvents from the living polymer solution, followed by distillation of methyl methacrylate (MMA) to synthesize a heteroarm star copolymer, $(PS)_xC_{60}$-$(PMMA)_y$. Polymerization was carried out at −78 °C for 6 h in THF, followed by termination with degassed methanol. All the products were precipitated in excess methanol and dried in a vacuum oven at 25 °C for at least 48 h prior to characterization. Details of the synthesis procedure and the results of characterization are described elsewhere.[20] Poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH−PPV) was also prepared by following the procedures in the literature.[21]

UV/Vis Absorption and Photoluminescence. $(PS)_xC_{60}$-$(PMMA)_y$ was dissolved in dichloroethane and then it was spin-cast on quartz substrates to obtain neat films. Optical absorption and photoluminescence (PL) spectra of the dilute solutions (10^{-5} M) and films were measured by using a Hewlett-Packard 8452A diode array spectrophotometer and an ISS PC1 photon-counting spectrofluorometer, respectively.

Device Fabrication. Multilayer polymer light-emitting devices composed of MEH−PPV and $(PS)_xC_{60}(PMMA)_y$ layers were fabricated as follows: 60-nm-thick emitting MEH−PPV films were spin-cast from the 1,2-dichloroethane solution on indium−tin oxide (ITO)-coated glass substrates. $(PS)_xC_{60}$-$(PMMA)_y$ film with a 10-nm thickness was spin-coated from the solution dissolved in dimethyl formamide (DMF) on top of the emissive layer, followed by baking in a vacuum oven at 150 °C for 1 h. Finally, the Al cathode was deposited with a 150-nm thickness by thermal evaporation under $\approx 10^{-6}$ Torr.

Electroluminescence. The electrical and luminescent characteristics of the device were measured by using a current/voltage source measurement unit (Keithley 236) and an optical power meter (Newport 1830-C) connected to a photodiode (Newport 818-UV). EL spectra were measured using an ISS PC1 photon-counting spectrofluorometer equipped with the photomultiplier tube (Hamamatsu R928) as a detector.

Results and Discussion

Absorption spectra of the copolymer in the UV/visible region are different from those of pristine C_{60}. Initially, we examined the optical absorption spectrum of $(PS)_xC_{60}$-$(PMMA)_y$ in dilute dichloroethane solution as shown in
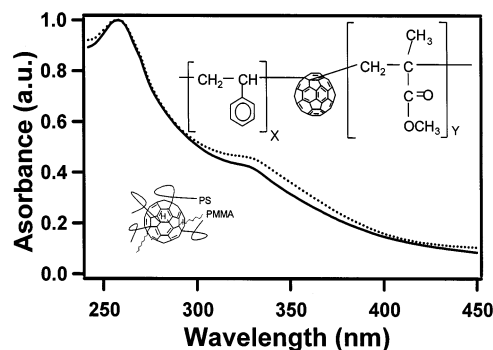

Figure 1. Normalized optical absorption spectra of $(PS)_x$$C_{60}$-$(PMMA)_y$ in dilute dichloroethane solution (solid line) and solid film (dotted line) spin-cast from the solution. The inset shows the chemical structure of the copolymer.

Figure 1. It has been reported that the absorption spectrum of pristine C_{60} ranges from 250 to 400 nm with two peaks at 260 and 330 nm, which represent h_u-t_{1g} dipole-allowed electronic transitions.[22,23] On the optical absorption spectrum of the copolymer in solution, we observed a strong absorption at 260 nm, which may mainly originate from the absorption by polystyrene.[24] Therefore, we determined the existence of C_{60} by the peak at 330 nm, not by the one at 260 nm. $(PS)_xC_{60}$-$(PMMA)_y$ showed a clear absorption peak exactly at 330 nm. We also observed the broadening of allowed C_{60} bands (250−400 nm), especially the band around 330 nm as reported elsewhere.[25] The broadening of the electron excitations at 260 and 330 nm is correlated with the nature of the complex and the coordination of C_{60}.[25] Figure 1 also shows the optical absorption spectrum of the solid film spin-cast from the dichloroethane solution. It is obvious that the spectrum of the film is very similar to that of the solution, which demonstrates that there is no aggregation in the ground state.

Figure 2 shows the photoluminescence (PL) and PL excitation spectra (PLE) of the $(PS)_xC_{60}(PMMA)_y$ solid film cast from the dichloroethane solution on a quartz substrate. We measured the PL spectra at different excitation wavelengths as shown in the figure. As the excitation wavelength becomes longer, the emission peak wavelength also shifts to longer wavelengths. This kind of excitation wavelength-dependent emission typically indicates an inhomogeneous distribution of emitting sites.[26,27] Although the film absorbs the excitation source light at 260 nm most strongly, the emission is strongest when the film is excited at 280 nm. The fluorescence spectrum obtained while exciting the film at 260 nm is similar to that of the polystyrene reference, although the spectrum of the copolymer film is spectrally broadened. The emission peak wavelength of monomeric styrene units was 300 nm, as observed on the PL spectrum of pure polystyrene in a dilute dichro-

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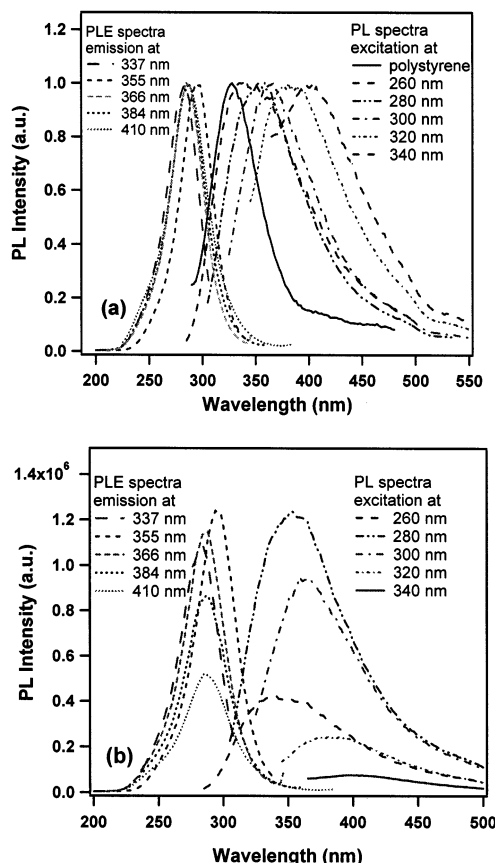
Figure 2. Photoluminescence (PL) and PL excitation spectra (PLE) of the $(PS)_xC_{60}(PMMA)_y$ solid film cast from the dichloroethane solution on a quartz substrate: (a) normalized spectra; (b) real spectra.

ethane solution (10^{-5} M). However, the emission peak of the polystyrene film was observed at 328 nm, as can be seen in Figure 2a, which indicates that the solid state emission of polystyrene comes predominantly from intermolecular excimers.[24,28] The spectral broadening of the copolymer implies that the energy level of the intermolecular excimers has a distribution.

While the fluorescence spectral features are similar, the fluorescent yield of the copolymer is lower ($\approx$67%) than that of neat polystyrene, as reported elsewhere,[28] which can be attributed to the quenching through the intramolecular excited-state energy transfer:[27-29] The C$_{60}$-containing sites may act as energy traps. To find out the origin of the fluorescence, we measured the PLE spectra by recording the PL intensities at different emission wavelengths while changing the excitation wavelength. The observed PLE spectra are all the same irrespective of the emission wavelengths. But this does not imply that all emission originated from the excitation at 280 nm. As Figure 2b shows, the absolute PL intensity over the whole wavelength range of emission was the strongest when the film was excited at 280 nm. The PLE spectra measured at various emission wavelengths reflect only the emission triggered by the excitation at 280 nm.

$(PS)_xC_{60}(PMMA)_y$ is readily soluble in common organic solvents. Therefore, these materials can be applied to various optoelectronic devices such as EL, photorefractive, and photovoltaic devices and so forth. We employed the fullerene-containing copolymer, $(PS)_xC_{60}(PMMA)_y$, in the EL device as a hole-injecting material, which is the first, to the best of our knowledge. PMMA segments were incorporated to the copolymer to improve the interfacial adhesion between the copolymer and the metal cathode (Al). It has been reported that the chemical interaction between MMA moieties and metals enhances the interfacial adhesive strength.[30] The interaction between ionic materials and Al occurs in the form of a polymer–metal complex such as C–O–Al when the metal atoms are vapor-deposited on oxygen-containing polymers.[30,31] The interfacial adhesive strength between the copolymer and the metal was significantly enhanced through the C–O–Al complex formation. Another reason for the incorporation of PMMA segments lies in the high solubility of the copolymer in a polar solvent such as dimethyl formamide (DMF). PS segments were also incorporated to the copolymer for solubility in aromatic solvents. Although the high solubility of $(PS)_xC_{60}(PMMA)_y$ in common organic solvents makes it difficult to fabricate multilayer polymeric EL devices, we could fabricate multilayer structures because MEH–PPV, employed as an emitting materials, is insoluble in DMF.

To confirm the hole-injecting property of $(PS)_xC_{60}(PMMA)_y$, it is necessary to prepare a device of an ITO/$(PS)_xC_{60}(PMMA)_y$/MEH–PPV/Al structure. But this is almost infeasible because of the high solubility of $(PS)_xC_{60}(PMMA)_y$ in the solvents of MEH–PPV such as dichloroethane. Another reason that the device structure is inadequate for examining the hole-injection property is as follows: The energy level of the highest occupied molecular orbital (HOMO) of MEH–PPV is $\approx$4.9 eV below vacuum and ITO has a work function of $\approx$4.7 eV, resulting in a barrier of $\approx$0.2 eV at the anode,[32] while the barrier height at the MEH–PPV/Al interface is 1.2–1.6 eV.[32] Hole injection from ITO greatly surpasses electron injection from the Al electrode in a positively biased field. Therefore, the hole-injecting layer between ITO and MEH–PPV in the positively biased field could not contribute to the enhancement of brightness and efficiency in a ITO/HIL/MEH–PPV/Al device because of insufficient injection of the minority carrier (electrons).[33] Therefore, we tried to investigate the hole-injecting property of the copolymer layer by applying reverse bias to the ITO/MEH–PPV/$(PS)_xC_{60}(PMMA)_y$/Al device (ITO: cathode; Al: anode).[34]

First, we examined the electrical and luminescent characteristics of the ITO/MEH–PPV/$(PS)_xC_{60}(PMMA)_y$/Al device in forward bias (ITO: anode; Al: cathode), as shown in Figure 3, in which electrons are injected from the Al cathode. When C$_{60}$ is incorporated (or doped) in

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(34) A high work function material such as ITO is used as an anode and lower work function metals as the cathode. In this case, we call the bias field direction "forward-bias field". However, we used "reverse-bias field" in which the lower work function metal is used as the anode and the higher work function material as the cathode.
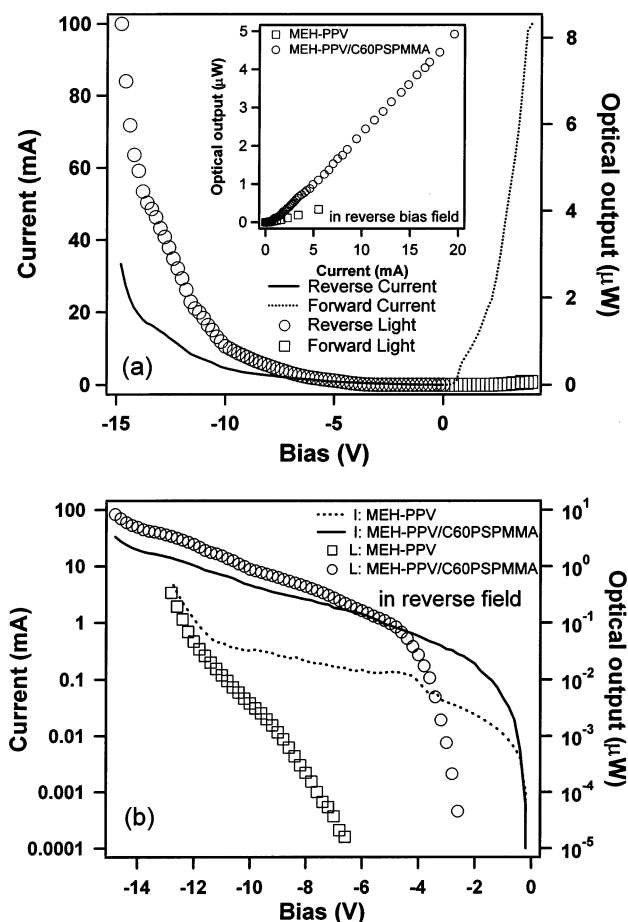
Figure 3. Current−voltage−luminance (I−V−L) characteristics of the ITO/MEH−PPV/(PS)$_x$C$_{60}$(PMMA)$_y$/Al device. (a) I−V−L curves of the device both in the forward- and reverse-biased field. The inset shows the relative quantum efficiency of the ITO/MEH−PPV/(PS)$_x$C$_{60}$(PMMA)$_y$/Al and the ITO/MEH−PPV/Al in the reverse-biased field. (b) Linear-log plots of I−V−L in the reverse-biased field.

a conjugated polymer, their fluorescence is strongly quenched.[35] Yoshino's group explained this phenomenon as follows: the photoexcited excitons on conjugated polymer chains are dissociated upon collision with C$_{60}$ molecules, with electrons being transferred from the conjugated polymer to C$_{60}$, to result in the formation of positive polarons of the conjugated polymer chains and negative polarons, C$_{60}^{-1}$.[35] Although we did not use C$_{60}$ as a dopant material, we also observed a large EL quenching in the forward-biased ITO/MEH−PPV/(PS)$_x$C$_{60}$(PMMA)$_y$/Al device. It has been suggested that MEH−PPV is a p-type or dominantly hole-transporting material so that the bipolar recombination zone for light emission is located near the cathode. Thus, to find out the location of the emitting zone in organic/polymer EL devices, several trials have been reported.[36] From this viewpoint, one of the reasons for the EL quenching may be the dissociation of excitons by C$_{60}$. Our result also supports that the recombination zone is very close to the cathode. Another possibility is the direct capturing of the injected electrons by C$_{60}$ before
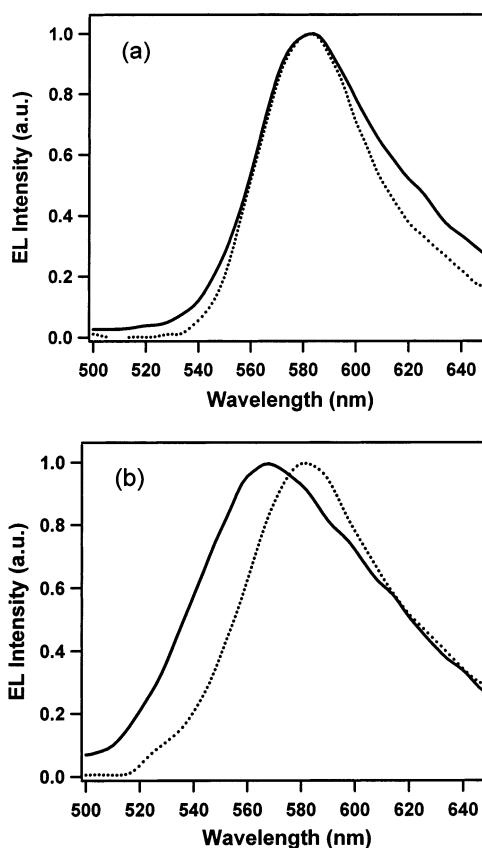

Figure 4. Electroluminescence (EL) spectra of (a) the ITO/MEH−PPV/Al and (b) the ITO/MEH−PPV/(PS)$_x$C$_{60}$(PMMA)$_y$/Al devices in both forward- (solid line) and reverse-biased (dotted line) fields.

they meet the holes for recombination. On the other hand, it was found that the current was larger than that of the single MEH−PPV device, although not shown in the figure, which mainly originates from the hole current, because C$_{60}$ can generate holes after capturing electrons.

Second, we investigated the electrical and luminescent properties of the ITO/MEH−PPV/(PS)$_x$C$_{60}$(PMMA)$_y$/Al device in reverse bias as shown in Figure. 3. The turn-on voltage for detectable light emission of the device was found at −2.6 V, while it was at −6.6 V for the single-layer MEH−PPV device. The turn-on voltage is close to the band gap of MEH−PPV (2.1 eV), although the energy barrier for hole injection is very high, judging from the band energy levels. This indicates that an effective energy-barrier lowering between the Al and the MEH−PPV has taken place.[37] The optical output was enhanced by ≈20 times compared with that of the single-layer device. The external quantum efficiency was also improved by ≈5 times (0.02% photons/electrons), which is a great improvement from that of the forward-biased single-layer device (0.008% photons/electrons). The enhanced optical output and quantum efficiency is attributed to the efficient hole-injecting property of the

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C_{60}-containing copolymer layer. The enhanced hole injection originates from the role of the negative C_{60}^- polarons near the anode (Al) that induce holes by dipole moments as explained elsewhere.[38] As shown in the inset of Figure 3, the device breaks down at a higher current level than the control single-layer device, which may be due to good adhesion at the polymer/Al interface by the chemical interaction of MMA moieties and Al metal.[30] It is noticeable that the incorporation of the $(PS)_xC_{60}(PMMA)_y$ layer at the hole-injecting contact changed the bias direction for more efficient light emission.

Figure 4 shows the EL spectra of the ITO/MEH−PPV/Al and the ITO/MEH−PPV/$(PS)_xC_{60}(PMMA)_y$/Al devices in both forward- and reverse-bias fields. For the ITO/MEH−PPV/Al device, the location of the emission maximum remains unchanged at 583 nm, irrespective of the direction of applied bias voltage. The emission spectral full-widths at half-maximum (fwhm) measured in both bias directions are not much different, but the fwhm in reverse bias is slightly narrower, which has been observed in other reports, although the authors did not mention this.[39] We consider this small difference may result from the shift of the recombination zone and the change of the width of exciton diffusion in the reverse-biased field. However, more fundamental and systematic works have to be done to clarify this speculation in the future. On the other hand, the EL spectrum of the forward-biased ITO/MEH−PPV/$(PS)_xC_{60}(PMMA)_y$/Al device has been blue-shifted and broadened as shown

in Figure 4b. We suggest a possible reason for this phenomenon: The spectral broadening implies that some parts of excitons decay in the region within MEH−PPV near the MEH−PPV/$(PS)_xC_{60}(PMMA)_y$ interface without being trapped by $(PS)_xC_{60}(PMMA)_y$, and the other excitons with higher energy are formed in a different way and then decay. The excitons near the $(PS)_xC_{60}(PMMA)_y$ layer dissociate into separate charges and the electrons are trapped in $(PS)_xC_{60}(PMMA)_y$, which generates opposite charges, holes. The holes from $(PS)_xC_{60}(PMMA)_y$ may recombine with the electrons of the MEH−PPV layer at the interface of MEH−PPV/$(PS)_xC_{60}(PMMA)_y$. This results in the blue-shifted and broadened emission spectrum. The spectrally blue-shifted emission may imply that the exciton dissociation by C_{60} takes place more prevalently than the direct capturing of injected electrons.

Summary and Conclusion

In the present study, we characterized the optical and electro-optical properties a highly soluble, fullerene (C_{60})-containing, heteroarm star copolymer, $(PS)_xC_{60}$-$(PMMA)_y$. $(PS)_xC_{60}(PMMA)_y$ was successfully employed as the hole-injecting layer of a polymer EL device. The quantum efficiency and the emitted light power were improved by ≈5 and ≈20 times compared to those of the single-layer device. We demonstrated the change of the bias direction for light emission of the EL device. This realization of EL devices with the C_{60}-containing polymer gives hope for its application in many different fields of optoelectronics such as photovoltaic devices, photorefractive devices, field-effect transistors, and so forth.

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