Novel cationic water-soluble polyfluorene derivatives with ion-transporting side groups for efficient electron injection in PLEDs

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Abstract

Synthesis of cationic water-soluble polyfluorene derivatives with various side groups, which are used as electron injecting layers in polymer light emitting diodes, is described. Neutral polyfluorene derivatives containing bromo-alkyl terminal groups were synthesized by a palladium catalyzed Suzuki coupling reaction. The bromo-alkyl terminal groups in the neutral polyfluorenes were quaternized by treatment with a trimethyl amine solution. When a high work-function metal such as Ag is used as a cathode in a light emitting diode with an ITO/PEDOT:PSS/MEH-PPV/water-soluble polyfluorene/Ag configuration, effects of these water-soluble polyfluorenes on the device performance were investigated. In the case of poly[[9,9-bis((6-(N,N,N-trimethylammonium)hexyl)-2,7-fluorene))-alt-(9,9-bis(2-(2-methoxyethoxy)ethyl)-fluorene)] Dibromide (WPF-oxy-F) containing ethylene oxide groups as the electron injecting layer, the electroluminescence efficiency of light emitting devices was significantly enhanced by about two orders of magnitude compared to that of a device without an electron injecting layer because migration of bromide ions via the ethylene oxide side groups led to large space charge. As a result, the injection barrier could be reduced between the emitting layer and Ag cathode resulting high electroluminescence efficiency.

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1. Introduction

Since their introduction, polymer light emitting diodes (PLEDs) [1] based on conjugated polymer [2,3] have attracted continuous attention due to the possibility of fabricating flexible, low cost and high efficiency displays. For over a decade, synthesis and characterization of many types of conjugated polymers have been reported, in attempts to enhance efficiency and stability of PLEDs. In particular, among the various conjugated polymers, water-soluble conjugated polymers have also been
extensively investigated due to their environment-friendly water-soluble nature and multilayer formation capability with organic soluble conjugated polymers. Consequently, many water-soluble conjugated polymers have been reported, including polythiophene [4], poly(p-phenylene) [5,6], poly(phenylenevinylene) [7–9], poly(phenylene ethylene) [10] and polyfluorene derivatives [11–13]. They have also been used in a variety of optoelectronic devices such as DNA-sensors [14] using energy transfer [7,8,10] and photovoltaic cells [9] and emitting layers [5,15] or electron injecting layers (EIL) [11–13] in PLEDs.

In PLEDs, high efficiency at low operating voltage and high stability can be achieved through efficient and balanced injection of carriers [16,17]. It is well-known, that the carrier injection is dependent on energy barrier height between the emitting layer and the metal. Thus, low work-function metals such as Ca, Ba, etc. are used to enhance electron injection into organic materials. However, such metals are not stable in air and sometimes may react with and diffuse into organic materials, leading to the deterioration of the device. To complement the weakness of low work-function metals, a stable Al metal cathode together with LiF is used as a bilayer cathode in PLEDs [18,19].

Water-soluble polymers are considered to be potential candidates for the electron injecting layer in PLEDs because a multi-layer structure can be produced without damage to the underlying organic soluble polymer films. Deng et al. [20] reported that the EL efficiency in a PLED with an Al cathode was enhanced by blending water-soluble poly(ethylene glycol) into the MEH-PPV. Guo et al. [21] also reported that inserting water-soluble poly(ethylene oxide) between the emitting layer and the Al cathode improved device efficiency because the built-in potential was increased by interfacial interaction between oxygen atoms in poly(ethylene oxide). Recently, a bilayer cathode consisting of a water-soluble conjugated polymer and Al or Au [11–13] has also been applied to an emitting layer. Due to the enhancement in interfacial dipole between the emitting layer and the metal cathode, it has been reported that this bilayer cathode could improve electron injection.

As mentioned above, to improve device performance using an interface dipole effect, the electron injecting layer should contain both ionic and polar groups such as oxygen side groups. In this study, we synthesized new three types of water-soluble polyfluorene derivatives with co-monomers with oxide side groups and without it. PLEDs were fabricated using these polymers as an electron injecting layer. A high work-function metal such Ag was used as a cathode. The findings show that such water-soluble polyfluorene derivatives can be used as an electron injecting layer inserted between the emitting layer and the Ag cathode, leading to a significant enhancement in the device performance. A possible mechanism about enhancement of the device was deduced from this study. Mobile bromide ions could be migrated under the applied bias via the ethylene oxide side groups which had an ion-transporting properties. So, the accumulation of mobile Br⁻ ions and positive ammonium salt near the electrodes induced ion space charge in the electron injecting layer. As a result, the effective injection barrier could be reduced by large space charge between the emitting layer and Ag cathode.

2. Results and discussion

2.1. Synthesis and characterization

The scheme for the preparation of water-soluble polyfluorene is shown in Scheme 1. Compound (1) was prepared using a method similar to the literature procedure [22]. Tetrabutylammoniumbromide (TBAB) as a phase transfer catalyst and 2,7-dibromofluorene and were dissolved in 1,6-dibromo-hexane as the solvent. To eliminate two protons at the 9-position of 2,7-dibromofluorene, a KOH solution was injected into the solution. The solution was stirred at 75 °C for 1 h. The color of the reaction mixture became yellow. The reaction mixture was extracted with dichloromethane, and evaporated. The reaction mixture was distilled under vacuum to remove the excess 1,6-dibromohexane. The product was purified by column chromatography using hexane and dichloromethane as an eluent. Pure (1) was obtained as a white solid in a 84% yield.

Compound (2) was prepared according to the published procedures [23]. 2,7-Dibromo-9,9-bis(6-bromohexyl)-fluorene (1) was dissolved in THF. To eliminate the two bromides at the 2,7-position of 2,7-dibromo-9,9-bis(6-bromohexyl)-fluorene, this solution was cooled to −80 °C and t-BuLi was carefully added to the solution. The elimination of the two bromides was confirmed thought GC/MS spectrometry while the solution was stirred for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was rapidly added to the solution. The reaction
mixture was warmed to room temperature and the mixture was extracted with 300 mL ether. The product was purified by column chromatography using hexane and ethylacetate as the eluent. The product (2) was a yellowish-white solid, produced in a 70% yield.

Neutral polymers PXF, PmXF and PF-oxy-F were synthesized from monomers via Suzuki coupling reaction. Each monomer was dissolved in THF. A 2 M K$_2$CO$_3$ solution was added and 1 mol% Pd(PPh$_3$)$_4$ was added to the solution, followed by refluxing for 3 days. The reaction mixture
was slowly cooled to room temperature. The reaction mixture was poured into a mixture of methanol and water. The precipitate was collected and redissolved in chloroform and slowly poured into stirred methanol. The precipitation process was repeated several times. The molecular weight of the polymer was determined by gel permeation chromatography. The number average molecular weight (Mn) of the neutral polymers PXF and PmXF and PF-oxy-F were determined by gel permeation chromatography. Mn were 12,000, 17,000 and 16,000, respectively.

Water-soluble polyfluorenes, WPXF, WPmXF and WPF-oxy-F were ionized using a trimethylamine solution. Neutral polymers PXF, PmXF and PF-oxy-F were dissolved in THF. A trimethylamine solution was added into the solution which was then stirred at rt for 24 h. The solubility of the ionic polymer was reduced in THF and the polymer precipitated during this period. Water was added to the solution to dissolve the precipitate. The solution was evaporated and the residue was collected and dried under vacuum overnight and then redissolved in methanol. The solution was slowly poured into stirred ether to give the ionic polymer. All the polymers were characterized by $^1$H NMR. After quaternization, a new peak around 3.00–3.06 ppm appeared in $^1$H NMR, which shows hydrogens in trimethyl amine groups.

The thermal properties of the neutral polymers PXF, PmXF and PF-oxy-F were characterized. Fig. 1 shows degradation temperature. TGA showed a 5% weight loss of PXF, PmXF and PF-oxy-F at 277, 307 and 271 °C, respectively. The temperature of the 5% weight loss of WPXF, WPmXF and WPF-oxy-F was similarly found at around 206 °C. After quaternization, the quaternized polymers showed a degradation temperature lower than those of the neutral polymers PXF, PmXF and PF-oxy-F, because they have weak parts which are amine salts [15].

2.2. Optical and electrochemical properties

The optical properties of the three types of water-soluble polyfluorenes are shown in Fig. 2. UV–vis-absorption spectra were measured in the solid-state. A film was prepared using a 0.5 wt% solution of WPXF, WPmXF and WPF-oxy-F in methanol and water (methanol:water = 3:7), which was spin coated on the glass and baked at 120 °C for 5 min. The absorption onset and absorption maximum of WPXF appeared at 376 and 340 nm, respectively. In the case of WPmXF, the absorption onset and absorption maximum appeared at 403 and 365 nm. The absorption of WPmXF was shifted to longer wavelength than WPXF due to two electron-donating methoxy groups in WPmXF [24]. The absorption onset and absorption maximum of WPF-oxy-F appeared at 435 and 392 nm, respectively. The optical band gap values of WPXF, WPmXF and WPF-oxy-F were 3.2, 3.0 and 2.8 eV, respectively. In the case of WPXF and WPmXF, the optical band-gap was slightly higher than WPF-oxy-F due to their shorter conjugation length. The bond between the xylene and the fluorene unit in WPXF and WPmXF were tilted by steric hindrance [25].

The HOMO and LUMO of WPXF, WPmXF and WPF-oxy-F were measured by cyclic voltam-
metry. Cyclic voltammetry was performed in 0.1 mol/L of Bu4NClO4 in an acetonitrile solution. WPXF, WPmXF and WPF-oxy-F were spin coated on the ITO as a working electrode. A platinum wire was used as a counter electrode and silver wire was used as a reference electrode.

Fig. 3 shows oxidation potentials of WPXF, WPmXF and WPF-oxy-F. The HOMO and LUMO of WPXF, WPmXF and WPF-oxy-F were calculated from the UV–vis absorption on-set and cyclic voltammograms. The HOMO and LUMO of WPXF were 5.4 and 2.2 eV, and those of WPmXF were calculated to be 5.3 and 2.3 eV, respectively. In the case of WPF-oxy-F, the HOMO and LUMO were estimated to be 5.1 and 2.3 eV.

2.3. Device properties

Each WPXF, WPmXF and WPF-oxy-F was used as an electron injection layer in PLEDs with the configuration of ITO/PEDOT:PSS/MEH-PPV/water-soluble polymer/Ag. Fig. 4 shows EL spectra for each device. Due to the location of the recombination zone in the bulk of EL polymer, the EL spectra was almost identical, when an amino-terminated conjugated polymer was used as an electron injecting layer.

All devices were fabricated from the same batch and were measured under air. Device efficiency was determined by measuring the light output only in the front direction. As shown in Fig. 5a and b, the turn-on voltage of a device with a Ag cathode was 6.6 V, and the external quantum efficiency was less than 0.005% with a luminance of 84 cd m\(^{-2}\) at 13.8 V. Because an injection of electron from Ag cathode was not efficient according to high injection barrier between MEH-PPV and Ag cathode.

However, when WPXF, WPmXF and WPF-oxy-F were used as an electron injection layer, the turn-on voltage was reduced to around 3.8, 3.5 and 3.1 V, respectively, and the external quantum efficiency significantly increased by about one to two order of magnitude. This enhancement of efficiency measuring the light output only in the front direction was comparable to reported device [13] measuring that all direction in an integrating sphere. In the case of WPXF used as an electron injection layer, when it was inserted between the emitting polymer (MEH-PPV) and Ag, the operating voltage was reduced and external quantum efficiency and luminance efficiency were 3.8 V, 0.01% and 0.03%, respectively. In the case of WPmXF, the operating voltage, external quantum efficiency and luminance efficiency was 3.5 V, 0.02% and 0.04%, all of them were slightly enhanced compared to WPXF. As WPmXF has two oxygen side groups that enhance the dipole moment, the performance of the device with WPmXF was slightly enhanced. For a device with a WPF-oxy-F layer inserted between the MEH-PPV and Ag, the operating voltage was reduced to 3.1 V and external quantum efficiency, power efficiency and luminance efficiency were higher than WPXF and WPmXF (Table 1).

In the case of WPF-oxy-F and WPmXF, EL efficiency was higher than that of WPXF. Especially, in the case of WPF-oxy-F, very large enhancement was observed. As two ethylene oxygen side groups in WPF-oxy-F at 9-position led to an interaction between the Ag cathode and the lone-pair electrons.
on the oxygen atoms [20,21], the effective charge injection barrier could be reduced between the MEH-PPV and the Ag cathode. As can be seen from Table 1, due to the lowering of the injection barriers to electronic carrier injection by enhancing interface dipole formation according to interaction between oxygen atom and Ag cathode, when WPmXF and WPF-oxy-F containing oxygen atoms were inserted between the MEH-PPV and the Ag cathode, the device efficiencies were significantly more improved compared to that of WPXF without containing oxygen side groups. These results indicate that our water-soluble polymers, when used as electron injecting layer, greatly enhance electron injection. As ammonium bromide salts of water-soluble polyfluorenes in the vicinity of the Ag cathode induce dipole moments [11–13], the effective charge injection barrier could be reduced.

The effective work-function of the cathode could be measured by photovoltaic measurement of the open-circuit voltage ($V_{oc}$) across the device [26]. Fig. 6 shows photovoltaic measurement for each device, under AM1.5 irradiation (100 mW cm$^{-2}$). As the anode of each device was identical, the effective work-function of the cathode influenced the open-circuit voltage. In the case of the MEH-PPV/Ag device, the open-circuit voltage

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**Table 1**

<table>
<thead>
<tr>
<th>EIL</th>
<th>Turn-on voltage (V)</th>
<th>$I_{\text{max}}$ Luminance (cd m$^{-2}$)</th>
<th>Quantum efficiency (%)</th>
<th>Luminance efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>–</td>
<td>6.5</td>
<td>86 (at 13.8 V)</td>
<td>0.005 (at 14.0 V)</td>
<td>0.01 (at 14.0 V)</td>
</tr>
<tr>
<td>WPXF</td>
<td>3.8</td>
<td>418 (at 5.4 V)</td>
<td>0.01 (at 5.4 V)</td>
<td>0.03 (at 5.4 V)</td>
</tr>
<tr>
<td>WPmXF</td>
<td>3.5</td>
<td>502 (at 4.6 V)</td>
<td>0.02 (at 4.6 V)</td>
<td>0.04 (at 4.6 V)</td>
</tr>
<tr>
<td>WPF-oxy-F</td>
<td>3.1</td>
<td>1768 (at 5.8 V)</td>
<td>0.2 (at 6.0 V)</td>
<td>0.4 (at 6.0 V)</td>
</tr>
</tbody>
</table>

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**Fig. 5.** (a) $I$–$V$ characteristic of each device. (b) $L$–$V$ characteristic of each device. (c) LE–$V$ characteristic of each device.

**Fig. 6.** Photovoltaic characteristics of each device.
was close to zero. When WPXF, WPmXF and WPF-oxy-F were used as an electron injecting layer, the $V_{oc}$ was found to be 0.11, 0.17 and 0.27 V, respectively. The $V_{oc}$ of the devices with electron injecting layer was higher than those without it because of improvement of interface dipole formation and consequent lower injection barriers. Therefore, the EL efficiency was increased and turn-on voltage was decreased.

In the case of WPF-oxy-F with two ethylene oxide side groups, EL efficiency was significantly enhanced. It has been reported that because ethylene oxide groups were able to transport mobile ion [27], poly(ethylene oxide) could be used as a solid-state ionic transporting material in light emitting electrochemical cells (LEC) [28,29]. LECs show low turn-on voltage and high efficiency, even thought LEC have a slow response time due to low ionic mobility in the solid-state electrolyte. A mechanism of enhanced EL efficiency, in case of WPF-oxy-F, could be attributed to ethylene oxide side groups. So, luminance of each device was measured as a function of time. As can be seen from Fig. 7, as soon as the bias applied to each device, a slow increase in luminance of WPF-oxy-F was observed compared with other cases, implying Br$^{-}$ ion migration through the ethylene oxide groups in WPF-oxy-F.

When a bias was applied to PLEDs, mobile bromide ions would move away from the cathode to near the MEH-PPV layer. Because MEH-PPV is hydrophobic and does not include ion stabilizing groups, penetration of bromide ions and damage to the MEH-PPV layer is unlikely. The positive ammonium ion would be accumulated near the cathode. However, these positive ions would not diffuse into the cathode due to the covalent bonding between positive ammonium ions and massive poly-electrolyte. When the operational stability was compared, PLEDs with WPF-oxy-F/Ag cathode were more stable than those with reactive Ca cathode alone under ambient conditions.

For further investigation, current of the device with WPF-oxy-F was measured as a function of time. In Fig. 8, when a forward bias was applied to a device with WPF-oxy-F at +5 V for 20 s, the current of the device gradually increased. After applying a reverse bias to the device at −1 V for 20 s, and applied a forward bias at +5 V again, the pattern of current increasing was identical to the first state. When a forward bias was applied to this device again and the diffused bromide ion may have returned to the original state. Therefore, the pattern of increasing current was identical to the first cycle.

These results indicated that the accumulation of mobile Br$^{-}$ ions and positive ammonium salt near the electrodes induced an increase in ion space charge. As a result, the injection barrier to electronic carrier injection was reduced, due to the ionic space charge near the electrodes [31–33]. Similar as the LEC cases, due to the ion-transporting ethylene oxide groups of WPF-oxy-F, mobile bromide ions could migrate more easily via the ethylene oxide side groups compared to WPXF and WPmXF without ethylene oxide side groups, so when WPF-oxy-F
was used as an electron injecting layer, EL efficiency was significantly enhanced. The studies of LECs using this polymer as a light emitting layer will be reported in future communications.

3. Conclusions

Cationic water-soluble polyfluorene derivatives with various co-monomers were successfully synthesized. When they were used as an electron injecting layer with a high work-function Ag cathode in a PLED, EL efficiency was improved, due to the reduced electron injection barrier. Especially, in the case where WPF-oxy-F containing ethylene oxide side groups was inserted between MEH-PPV and Ag cathode, the EL efficiency was significantly enhanced by about two orders of magnitude because of ionic transporting properties of the ethylene oxide side groups leading to large space charge. Water-soluble conjugated polymers containing ethylene oxide groups could be promising candidate materials for high efficiency PLED applications.

4. Experimental

4.1. Characterization and measurements

Materials were characterized by $^1$H, $^{13}$C NMR spectroscopy (JEOL JNM-LA300WB 300 MHz). Thermal properties were confirmed by thermogravimetric analysis (TGA; TA-2050) at a heating rate of 10 °C min$^{-1}$ under nitrogen. Elemental analyses were carried out by the Korea Basic Science Institute, Seoul Branch Analytical Laboratory (Elemental analysis; CE Instruments Flash EA 1112 series). Absorption spectra were measured using a UV–vis spectrophotometer (Varian spectrometer, Carry1E). Molecular weight was confirmed by gas chromatography mass spectrometry (GC/MS; Shimadzu, GCMS-QP2010) and by gel permeation chromatography (GPC, Futees, NS2001). The current–voltage–luminescence characteristics of the devices were measured using a Keithley 237 Source Measurement Unit and an optical power meter (Newport, 1835C) with a calibrated photodiode (Newport, 818 UV). Photocurrent–voltage measurements were performed using an Autolab PGSTAT30 Potentiostat/Galvanostat (Solartron, 1287A) under AM1.5 irradiation (100 mW cm$^{-2}$) by xenon light source (Müller).

4.2. Materials

All starting materials and 1,4-dibromo-2,5-dimethylbenzene (3) and 1,4-dibromo-2,5-dimethoxybenzene (4) were obtained from Aldrich Chemical Co. and were used without further purification except THF, which was dried by refluxing over sodium.

4.3. Synthesis

2,7-dibromofluorene and 2,7-dibromo-9,9-bis(2-(2-methoxyethoxy)ethyl)-fluorene (5) were prepared according to previously published procedures [34,35].

4.3.1. 2,7-Dibromo-9,9-bis(6-bromohexyl)-fluorene (1)

9.72 g of 2,7-dibromofluorene and 0.96 g of tetra-butylammoniumbromide (TBAB) were dissolved in 100 mL of 1,6-dibromohexane and 30 mL of a 45% KOH solution was then injected under nitrogen. The solution was stirred at 75 °C for 1 h. The reaction mixture was extracted with 300 mL dichloromethane and the resulting solution was evaporated. The reaction mixture was distilled under vacuum, to remove the 1,6-dibromohexane. The reaction mixture was purified by column chromatography using hexane and dichloromethane (hexane:dichloromethane = 95:5) as the eluent ($R_f = 0.37$). The final product was a white solid, produced in 84% yield. MP: 68–71 °C. $^1$H NMR (300 MHz; CDCl$_3$; Me$_4$Si): δ$_H$ 7.53 (d, 2H, $J = 6.0$, fluorene), 7.46 (dd, 2H, $J = 3.0$ and 6.0, fluorene), 7.44 (d, 2H, $J = 3.0$, fluorene), 3.30 (t, 4H, $J = 9.0$, –CH$_2$Br), 1.92 (t, 4H, $J = 9.0$, –CH$_2$–), 1.67 (t, 4H, $J = 9.0$, –CH$_2$–), 1.20 (m, 4H, –CH$_2$–), 1.08 (m, 4H, –CH$_2$–), 0.58 (m, 4H, –CH$_2$–). $^{13}$C NMR (300 MHz; CDCl$_3$; MeSi): δ$_C$ 23.37, 27.66, 28.86, 32.53, 33.75, 39.97, 55.22, 121.29, 121.64, 126.18, 130.42, 139.17, 152.29. Element Anal. Calcd. for C$_{25}$H$_{30}$Br$_4$: C, 46.15%; H, 4.61%. Found: C, 46.13; H, 4.59. m/z (EI) 649.95 (M$^+$).

4.3.2. 2,7-bis(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-(6-dibromomethyl)-fluorene (2)

Three grams of 2,7-dibromo-9,9-bis(6-bromomethyl)-fluorene (1) was dissolved in 150 mL of tetrahydrofuran. The solution was cooled to −80 °C and 6 mL of 1.7 M t-BuLi was injected under nitrogen followed by stirring for 1 h. 2.1 mL of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxo-
borolane was rapidly injected into the solution. The reaction mixture was warmed to room temperature and mixture was extracted with 300 mL of ether. The product was purified by column chromatography using hexane and ethylacetate (hexane:ethylacetate = 20:1) as the eluent (Rf = 0.14). The product was a yellowish-white solid, produced in 70% yield. MP: 117–121 °C. 1H NMR (300 MHz; CDCl3, Me4Si): δH 7.82 (d, 2H, J = 9.0, fluorene), 7.74 (s, 2H, fluorene), 7.72 (d, 2H, J = 9.0, fluorene), 3.25 (t, 4H, J = 9.0, –CH2Br), 1.98 (m, 4H, –CH2–), 1.62 (m, 4H, –CH2–), 1.39 (s, 24H, –CH3), 1.20 (m, 4H, –CH2–), 1.15 (m, 4H, –CH2–), 0.55 (m, 4H, –CH2–). 13C NMR (300 MHz, CDCl3, Me4Si): δC 23.43, 25.01, 27.78, 29.01, 32.73, 33.99, 39.99, 55.15, 83.92, 119.67, 129.00, 134.03, 144.15, 150.34. Element Anal. Calcd. for C37H54B2Br2O4: C, 55.15; H, 83.92; 119.67; 129.00; 134.03; 144.15; 150.34.

4.3.4. Poly[(9,9-bis(4-(2-methoxyethoxy)ethyl)-fluorene)-alt-1,4-xylene] (PmXF)

0.74 g of 2, 0.26 g of 3 and 60 mL THF were placed in a two-neck flask under a nitrogen atmosphere. Twenty millilitres of 2 M K2CO3 solution was injected and 1 mol% of Pd(PPh3)4 was added to the solution. The reaction mixture was refluxed for 3 days. The reaction mixture was slowly cooled to room temperature. The reaction mixture was poured into a mixture of 250 mL of methanol and water (methanol:water = 4:1). The precipitate was collected, redissolved in chloroform and precipitated several times by adding methanol. The resulting polymer was a yellowish-white powder. (Yield 71%). 1H NMR (300 MHz; CDCl3, Me4Si): δH 7.81 (br, 2H, Ph), 7.40 (br, 6H, fluorene), 3.31 (br, 4H, –CH2Br), 2.38 (br, 6H, –CH3), 2.03 (br, 4H, –CH2–), 1.70 (br, 4H, –CH2–), 1.25 (br, 4H, –CH2–), 1.12 (br, 4H, –CH2–), 0.80 (br, 4H, –CH2–). Element Anal. Calcd. for C35H54Br2O4: C, 66.51; H, 6.24.

4.3.5. Poly[(9,9-bis(6-bromohexyl)-fluorene)-alt-1,4-xylene] (PF-oxy-F)

0.74 g of 2, 0.26 g of 4 and 60 mL THF were placed in a two-neck flask under a nitrogen atmosphere. Twenty millilitres of 2 M K2CO3 solution was injected and 1 mol% of Pd(PPh3)4 was added to the solution. The reaction mixture was refluxed for 3 days. The reaction mixture was slowly cooled to room temperature and poured into a mixture of 250 mL of methanol and water (methanol:water = 4:1). The precipitate was collected, redissolved in chloroform and precipitated several times by adding methanol. The resulting polymer was a yellowish-white powder. (Yield 70%). 1H NMR (300 MHz; CDCl3, Me4Si): δH 7.85 (br, 6H, fluorene), 7.73 (br, 6H, fluorene), 3.35 (br, 4H, –CH2Br), 3.29 (br, 6H, –OCH3), 2.95 (br, 4H, –CH2O–), 2.62 (br, 4H, –OCH2–), 2.50 (br, 4H, –CH2O–), 2.19 (br, 8H, –CH2–), 1.71 (br, 4H, –CH2–), 1.26 (br, 8H, –CH2–), 0.81 (br, 4H, –CH2–). Element Anal. Calcd. for C47H58Br2O4: C, 67.13%; H, 6.81%. Found: C, 67.27; H, 6.54.

4.3.6. Poly[(9,9-bis(6-(N,N,N-trimethylammonio)hexyl)-2,7-fluorene)-alt-1,4-xylene] Dibromide (WPXF)

0.25 g of PXF was dissolved in 100 mL of THF. Five millilitres of trimethylamine solution was added to the solution which was then stirred at rt for 24 h. The solubility of the ionic polymer was reduced in THF and precipitated during this period. Twenty millilitres of water was added to the solution in order to dissolve the precipitate. The solution was evaporated and the residue was redissolved in methanol. The ionic polymer was precipitated from ether. The ionic polymer was a yellowish powder. (Yield 89%). 1H NMR (300 MHz; CD3OD, Me4Si): δH 7.88 (br, 2H, Ph), 7.42 (br, 6H, fluorene), 3.23 (br, 4H, –CH2N–), 3.06 (br, 18H, –NCH3), 2.36 (br, 6H, –CH3), 2.16 (br, 4H, –CH2–), 1.64 (br, 4H, –CH2–), 1.21 (br, 8H,
was spin coated on the PEDOT:PSS layer as an emitting layer and baked at 150 °C for 20 min under air. A 0.5 wt% solution of WPXF or WPMXF or WPF-oxy-F in methanol was spin coated on the MEH-PPV layer as an electron injecting layer and baked at 120 °C for 5 min under air. Ag was deposited as the cathode through a shadow mask by thermal evaporation. The area of sample was 4.34 mm².

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