Organic Electronic Devices

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A Small-Molecule Zwitterionic Electrolyte without a π-Delocalized Unit as a Charge-Injection Layer for High-Performance PLEDs**

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Conjugated organic optoelectronic materials have attracted significant attention owing to their application in light-emitting diodes (LEDs), solar cells, thin-film transistors, optically amplified biosensor assays, and other areas.[1] For organic optoelectronic devices, interfacial modification between the organic material and the electrode is a crucial issue and becomes one of the most important research focal points, since charge injection/extraction affect device performance greatly.[2] Excellent charge injection leads to a lower turn-on voltage and higher efficiency in organic LEDs.[3] In the case of organic solar cells, good interface properties result in a higher short-circuit current and a higher open-circuit voltage, which are the most important factors for solar-cell performance.[4]

Among the many kinds of solution-processable interfacial-modification materials,[4a,b,5] conjugated polyelectrolytes (CPEs) and oligoelectrolytes (OEs) containing a π-delocalized backbone with pendant groups that can be ionized have attracted great interest. Their solubility in polar solvents enables the fabrication of multilayer polymer-based devices by the solution-processing approach.[6a–g] The reported performance of devices based on CPEs/OEs is comparable to that of devices based on the conventional Ca/Ba electrode. However, mobile counterions, such as Na^+, Br^-, and tetrasubstituted borates,[6a,b,7] which can migrate during device operation, make the device mechanism more complicated and seriously affect the device turn-on time.[1h,8]

In recent years, conjugated zwitterionic materials have attracted great interest as a new kind of charge-injection materials owing to their unique chemical structure, in which both the positive and the negative ions are combined. As the ions are not mobile, the device response time is improved significantly. Furthermore, the solubility of the materials in polar solvents is good enough for multilayer-device fabrication as a result of the presence of the charged groups.[2a] In 2009, Bazan and co-workers reported small-molecule zwitterionic materials synthesized by the addition of iodoalkanes to sodium tetrakis(1-imidazolyl)borate ($NaBIm_4$); the device response time and performance were comparable to those of the Ba/Al electrode.[6d] In a previous study,[9] one of our research groups reported a conjugated polyelectrolyte with a fluorene-based zwitterionic sulfoammonium structure and no free counterions. When this zwitterionic polymer known as "$F(NSO_3)_2$" (**CPE1**) was used as the electron-injection layer, devices based on poly(9,9′-dioctylfluorene-*co*-benzothiadiazole) (F8BT) as the emitter showed very fast response times; moreover, both efficiency and brightness were considerably improved (by a factor of more than 2) in comparison with standard calcium-based devices. Huang and co-workers independently reported a fluorene-based zwitterionic polymer, "PF_6NSO",[3a] the luminance efficiency of which was as high as 23.8 cdA with poly[2-(4-(3′,7′-dimethyloctyloxy)-phenyl)-*p*-phenylenevinylene] (P-PPV) as the emitter. The overall device performance was much better than that of the neutral precursor and of conventional CPEs with mobile ions. Recently, Huang, Bazan, and co-workers reported a series of amine *N*-oxide functionalized CPEs. These materials showed similar device performance to that of the Ba/Al electrode in PLEDs. In the case of polymer solar cells, the V_{oc} value and the fill factor of the polymer solar cells were increased significantly.[3b] Besides the conjugated zwitterionic electrolytes mentioned above, only few examples of conjugated zwitterionic derivatives have been developed in the past, and the research has not been extended to the investigation of such materials as the injection layer in electronic devices.[10a,b]

At present, most of the reported electrolyte interfacial-modification materials based on zwitterions or mobile ions have been conjugated polymers/oligomers. Research results on small molecules are limited.[6h] Small-molecular semiconductors offer several intrinsic advantages over conjugated polymers/oligomers in organic electronic applications. They can be synthesized readily without complex C–C coupling and polymerization reactions, are monodisperse in nature with well-defined chemical structures, and are synthetically well-reproducible. For charge-injection materials, reported studies mainly focused on π-delocalized structures, since such structures are considered crucial for the conducting properties of conjugated materials. Herein, we report a series of

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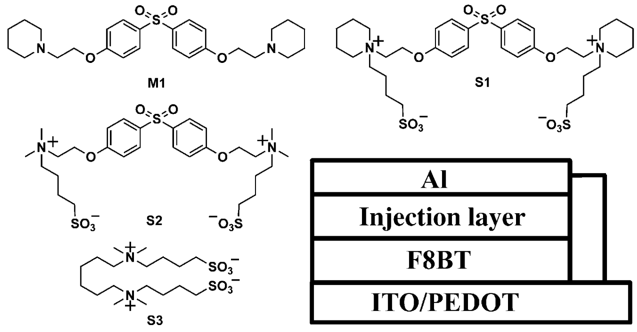
small-molecule zwitterionic materials (SMZWs) with and without π-delocalized groups (Scheme 1). These materials have superior electron-injection characteristics; they outperform Ca electrodes. Furthermore, for the first time, we found that a zwitterionic material without any π-delocalized unit showed excellent device performance.



Scheme 1. Structures of the small-molecule zwitterionic materials used in this study and the device structure. ITO = indium tin oxide, PEDOT = poly(3,4-ethylenedioxythiophene).

The SMZWs were synthesized by quaternization of the neutral precursor with 1,4-butane sultone in a THF/methanol solvent mixture. The precursors used were 1,1′-(2,2′-(4,4′-sulfonylbis(1,4-phenylene)bis(oxy))bis(ethane-1,2-diyl))-dipiperidine (**M1**), 2,2′-(4,4′-sulfonylbis(1,4-phenylene)bis(oxy))bis(*N*,*N*-dimethylethanamine) (**M2**), and N^1,N^1,N^6,N^6-tetramethylhexane-1,6-diamine (**M3**). The resulting zwitterionic products **S1**, **S2**, and **S3** were highly soluble in methanol and dimethyl sulfoxide (see the Supporting Information). The neutral precursors chosen for this study had a sulfonyl and a tertiary amine group and were thus similar to sulfoammonium zwitterions in their chemical structure but without any charges. The materials were tested with the device structure: ITO/PEDOT/F8BT/injection layer/Al (Scheme 1). The corresponding device with Ca/Al as the electrode was also fabricated for comparison.

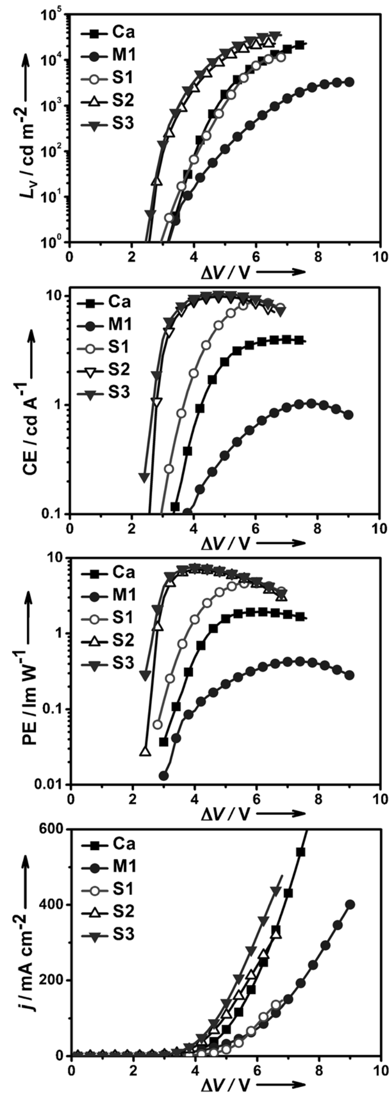


Figure 1. Luminance (L_v), current efficiency (CE), power efficiency (PE), and current density (j) as a function of voltage for PLEDs with the device structure: ITO/PEDOT:PSS/F8BT(100 nm)/SMZW or **M1** or Ca/Al. PSS = poly(4-vinylbenzenesulfonic acid).

Table 1: Summary of the performance of PLEDs with the device structure: ITO/PEDOT/F8BT/cathode.

Cathode	V_{on}[a]	Maximum CE [cd A^{-1}]	Maximum L_v [cd m^{-2}]	Maximum PE [lm W^{-1}]
Ca/Al	3.1	4.0	22916	1.9
M1/Al	3.1	1.0	3248	0.4
S1/Al	2.9	8.8	11395	4.7
S2/Al	2.5	9.9	22819	7.0
S3/Al	2.4	10.4	35093	7.5
CPE1	2.4	9.9	50382	6.6

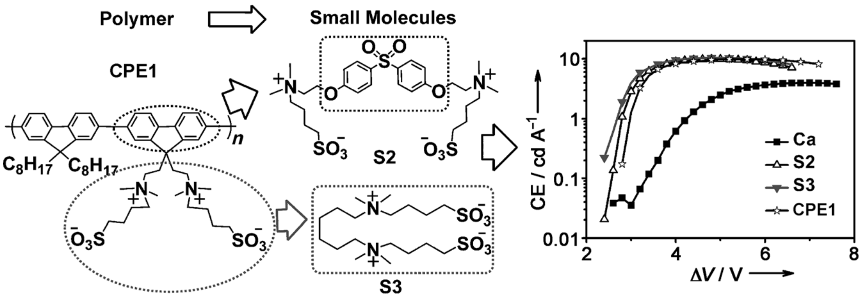
[a] V_{on} is the voltage at which the brightness reached 1 cd m^{-2}.

The device characteristics of luminance (L) versus voltage (V) and current efficiency (CE) versus voltage are shown in Figure 1. The turn-on voltage of the devices (voltage at which the brightness reached 1 cd m^{-2}) for **S1**, **S2**, **S3**, **M1**, and Ca/Al was 2.4, 2.5, 2.9, 3.1, and 3.1 V, respectively (Table 1). In the case of **M1**, the chemical structure of which is similar to that of a sulfoammonium zwitterion, the device showed poorer overall performance, including its turn-on voltage (V_{on}), brightness, and efficiency. The quaternization of **M1** to give **S1** led to an impressive improvement in performance: the turn-on voltage decreased by 0.2 V, the brightness was improved by a factor of 3.5, and the current efficiency was improved by a factor of 9. The current efficiency of the device with **S1** were even twice as high as those for the Ca-based device at all operation voltages, but the device current was lower than that of the Ca-based device. This improvement in performance can be ascribed to the insertion of a layer of a zwitterionic material, which should also alleviate light-emission quenching induced by metal electrodes. The maximum current efficiency reached 8.8 cd A^{-1} (at 6.0 V) and a power efficiency (PE) of 4.7 lm W^{-1} (at 5.8 V). This result indicates that the formation of a zwitterionic structure is crucial for the electron injection.

In the material **S1**, there are long alkyl groups on the sulfobetaine zwitterionic structure. According to previous studies, dipole formation is induced by the insertion of a zwitterionic layer between the Al electrode and the active layer; the resulting shift in the vacuum level is the main contributing factor for device improvement.[6d,9] The steric bulk of the big alkyl groups on **S1** may affect dipole formation at the interface. We synthesized **S2** with smaller alkyl groups and observed a further improvement in device performance relative to that of the **S1**-based device: the brightness was improved by a factor of 2 and reached 22 819 cd m^{-2}, and the power efficiency reached 7.0 lm W^{-1} (Table 1). Since the turn-on voltage decreased significantly from 2.9 to 2.5 V, the overall performance is superior to that of the **S1**-based device, especially at a low operation voltage (2.5–6.0 V). These results indicate better charge injection for the **S2**-based device, the efficiency of which is similar to that found with our previously reported zwitterionic polymer electrolyte **CPE1**.[9] They imply that small molecules are also excellent and competitive candidates for the electron-injection layer.

Our results based on **M1**, **S1**, and **S2** indicate that the zwitterionic part of the molecule plays an important role in charge injection. We were interested to find out whether small molecules without conjugated π-delocalized structures were also suitable. The conjugated backbone of the polymer/oligomer electrolyte undoubtedly affects the device performance significantly, as observed previously.[7c] We wanted to know whether conjugated π-delocalized units were indispensable for the charge-injection function, since most reported electrolyte interfacial-modification materials have a typical conjugated π-delocalized unit, such as a fluorene, phenyl, or imidazole group. We therefore synthesized the zwitterionic material **S3**, which does not contain a conjugated unit (Scheme 1). To our surprise, devices based on **S3** as the electron-injection layer showed superior performance even to that of **S2**. The turn-on voltage was 2.4 V, which is the lowest observed for these materials, the current density was much higher than that of the Ca-based device, and the brightness reached a maximum of 35 093 cd m^{-2} at 6.8 V with a high current efficiency of 7.4 cd A^{-1}. The highest current efficiency and power efficiency were 10.4 cd A^{-1} and 7.5 lm W^{-1}, respectively (Table 1). The brightness was 3365 cd m^{-2} at 4 V with a corresponding current efficiency of 9.5 cd A^{-1} (7.5 lm W^{-1}).

Scheme 2 describes the differences in the chemical structures of the polymer **CPE1** and the small molecules **S2** and **S3**, and the efficiencies of the devices with these materials as the electron-injection layer. Details of device performance are also summarized in Table 1 for comparison. When the fluorene unit of the functional part of polymer **CPE1** was substituted for a sulfonyldiphenol unit, the device containing the resulting small molecule **S2** showed comparable efficiency to that of the polymer-based device. In the case of **S3**, in which the fluorene or sulfonyldiphenol unit has been completely removed and only the charged group is left, the device showed a 13.6 % improvement in the power efficiency (from 6.6 to 7.5 lm W^{-1}) and a 5 % improvement in the current efficiency (from 9.9 to 10.4 cd A^{-1}). Our results clearly show that, at least for sulfoammonium zwitterionic interfacial materials, π-delocalized structures are not absolutely necessary for the electron-injection function. However, the π-delocalized structures may still be useful for the device performance. For example, the presence of a conjugated polymer/oligomer backbone results in a better film-forming ability; it could also improve the dipole at the interface further or the optical properties of the device.



Scheme 2. Structures of the polymer **CPE1** and the small-molecule zwitterionic materials **S2** and **S3** with the corresponding device efficiencies.

We also found that the small-molecule zwitterionic materials resulting from quaternization of the neutral precursors showed an improved film-forming ability. The improvement could be ascribed to the interaction of zwitterionic structures in the different molecules and the resulting cross-linking or partial cross-linking.[10c] We also investigated polymer solar cells fabricated with these zwitterionic materials as the electron-extraction layer; however, we have unfortunately not observed obvious device improvement in the P3HT:PCBM-based polymer solar cells so far (P3HT = poly(3-hexylthiophene), PCBM = phenyl-C61-butyric acid methyl ester). A plausible reason for this lack of improvement is that the nonpolar and crystalline properties of P3HT could lead to a wetting problem. The use of a different active polymer or device structure should overcome this problem. We will come back to this issue in the future.

In summary, we have synthesized a series of novel small-molecule zwitterionic materials with and without a π-delocalized structure. Device performance was considerably improved in comparison with that of Ca-based devices when these materials were used as the electron-injection layer in PLEDs. Our results indicate that the zwitterionic nature of the molecules is important for charge injection. They also strongly suggest that π-delocalized structures are not necessary for the electron-injection function. For the further mechanistic study of zwitterionic materials, an effect of the electrical and optical properties induced by the π-delocalized structure on device performance could be ruled out; the function of the π-delocalized part and the zwitterionic part of the molecules could be identified separately. As **S1**, **S2**, and **S3** are in fact typical ionic liquids in terms of their chemical structure, solid ionic liquids may be promising alternative candidates for charge-injection materials in organic electronic devices. The results of this study will lead to broader approaches to the design of charge-injection materials, simpler synthetic procedures for efficient charge-injection materials, and advances in mechanistic studies of polymer/small-molecule electrolytes as charge-injection materials.

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