## Alcohol-Processable Organic Amorphous Electrolytes as an Effective Electron-Injection Layer for Organic Light-Emitting Diodes

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**Abstract:** A new series of monoammonium-based organic electrolytes with the tetrafluoroborate  $(BF_4^-)$  counteranion have been synthesized. Replacing the pendant ethyl groups in the fluorenyl unit with 4-ethoxyphenyl groups dramatically improves both solubility and morphological stability. The characterization of the alcohol-processable amorphous ionic compounds as an electron-injection layer in organic light-emitting diodes (OLEDs) reveals that the organic electrolyte that comprises a rigid linear-conjugated unit

**Keywords:** amorphous materials • electrolytes • electron injection • molecular devices • solution processability provides better device performance, with respect to its counterpart containing a branched bulky moiety. The capability of these compounds to facilitate electron injection from air-stable aluminum metal is preliminarily discussed on the basis of the investigations of the electron-only devices and photovoltaic experiments.

### Introduction

The quest for low-cost, large-area, organic light-emitting devices under electrical excitation has stimulated considerable research on solution-processed functional materials and device technologies.<sup>[1,2]</sup> Among others, an intriguing development was the finding that conjugated polymer electrolytes<sup>[3–8]</sup> and later their small-molecule counterparts<sup>[9–13]</sup> can facilitate electron injection from air-stable cathode metals such as aluminum. Furthermore, electrolyte materials that show processability from alcoholic solvents allow their utilization as an electron-injection layer (EIL), thereby providing the least perturbation over the bottom emissive layer, which generally consists of hydrophobic luminophors.

Recently, we reported an alcohol-processable small-molecule electrolyte based on a monoammonium salt that featured an amorphous morphology (Scheme 1 a). Notably, the spin-cast thin film affords effective electron injection from the Al metal, thus leading to device efficiency that approaches that of the Ba/Al cathode.<sup>[11]</sup>

In this contribution, we describe further a comparative study on a new series of small-molecule electrolytes with the  $BF_4^-$  counteranion (Scheme 1b), which is known to have

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better electrochemical stability. With respect to compound 3, compounds 1 and 2 consist of a rigid linear-conjugated



Scheme 1. a) The small-molecule electrolyte described in Ref. [11], and b) the chemical structures of compounds **1–3**.

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Scheme 2. Synthesis route to compounds 1 and 2. i) [Pd(PPh<sub>3</sub>)<sub>4</sub>], 2M Na<sub>2</sub>CO<sub>3</sub> aqueous solution, toluene, ethanol, reflux; ii) *n*BuLi, THF, -78 °C; iii) 2-iso-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaboralane; iv) 1,3-dibromopropane, K<sub>2</sub>CO<sub>3</sub>, DMF, 80 °C; v) bis(pinacolato)diborane, KOAc, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], diox-ane, 90 °C; vi) *N*,*N*-dimethylethylamine, THF, methanol; and vii) NaBF<sub>4</sub>, THF, methanol, H<sub>2</sub>O.

unit. The effects of the chemical structure on the resulting material properties such as solubility and electron injection in OLEDs are discussed.

The synthesis of compounds 1-3 is straightforward and outlined in Schemes 2 and 3, respectively. A mono-Suzuki coupling of 4-methoxyphenylboronic ester (4) with 2,7-dibromo-9,9-diethylfluorene (5) and 2,7-dibromo-9,9-di(4ethoxylphenyl)fluorene (6) leads to compounds 7 and 8, respectively, which undergo successive lithiation-boronation reactions to give Suzuki reagents 9/10.

Treatment of 6-bromonaphth-2-ol with an excess amount of 1,3-dibromopropane in the presence of  $K_2CO_3$  produces 2-(3-bromopropoxy)-6-bromonaphthalene (11). A one-pot catalytic boronation of compound 11 affords Suzuki reagent 12,<sup>[14]</sup> which further reacts with compound 5 to yield compound 13.

#### **Abstract in Chinese:**

本文合成了一系列带有 BF4 阴离子的单铵基电解质分子。当芴 基单元上的乙基侧链由 4-乙氧基苯基取代后,所生成的目标产 物,不仅溶解性能改善(醇溶性),而且薄膜形貌稳定性也显 著提高。电致发光器件测试结果表明,相对于含有枝状芳基单 元的离子化合物,具有线性共轭单元的非晶态分子离子化合 物,作为电子注入层,能够提供更好的器件性能。基于单电子 载流子器件以及光伏实验,初步讨论了上述分子电解质协助 AI 金属注入电子的特性。 Subsequently, coupling of Suzuki reagents 9/10 with compound 13 gives compounds 14 and 15. Quaternization of compounds 14 and 15 with ice-cooled *N*,*N*-dimethylethyla-





Scheme 3. Synthesis route to compound 3, analogue of compounds 1 and  $2^{[11]}$ 

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mine affords the precursor  $Br^-$  salts **16/17** in approximately 95% yield. The target compounds **1** and **2** are obtained by adding an excess amount of aqueous NaBF<sub>4</sub> solution to **16** and **17** in methanol. Compound **3** was prepared analogously from 3,5-dibromophenol.<sup>[11]</sup>

Noticeably, replacement of the counteranion  $Br^-$  with  $BF_4^-$  results in a remarkable downshift of the proton signals in the ammonium cation  $[-OCH_2CH_2CH_2*N(CH_3*)_2 (CH_2*CH_3)]$  in the <sup>1</sup>H NMR spectra, which serves as an indicator for the chemical conversion (see Figure S1 in the Supporting Information).

The solubility of the electrolytes 1-3 in alcoholic solvents was checked in an attempt to process from an orthogonal solvent against the emissive layer. Replacement of the ethyl groups in the fluorenyl unit by 4-ethoxyphenyl groups produced a considerable increase in solubility, consistent with our recent observation.<sup>[15a]</sup> Thus, whereas 0.5 mg of compound **1** was difficult to solubilize in 1 mL of methanol under heating, 2 mg of **2** became soluble. On the other hand, compound **3** had a similar solubility to **2**.

#### **Results and Discussion**

#### **Optical Properties**

The UV/Vis absorption and photoluminescence (PL) spectra of solutions of compounds 1-3 in CH<sub>2</sub>Cl<sub>2</sub> (approximately  $10^{-5}$  mol L<sup>-1</sup>) and as films are shown in Figure 1, and the relevant data are summarized in Table 1.

Compounds 1 and 2 show similar absorption and PL spectra in solution with  $\lambda_{max}^{abs}$  at approximately 356 nm and  $\lambda_{max}^{em}$  at 400 and 420 nm, excited at the absorption maxima. In thin films, these emission maxima are redshifted by approximately 10 nm to approximately 412 and 433 nm, respectively, whereas a well-resolved low-energy emission shoulder emerges at approximately 460 nm.

In contrast, compound **3** possesses a shorter absorption maximum  $(\lambda_{\text{max}}^{\text{abs}})$  at 285 nm and emission maximum  $(\lambda_{\text{max}}^{\text{em}})$  at 361 nm in solution due to the limited  $\pi$  conjugation. The absorption and emission maxima are shifted respectively to approximately 298 and 374 nm in thin solid films.

#### **Thermal Properties**

Thermal gravimetric analysis (TGA) shows that compounds 1–3 decompose at approximately 350 °C, which corresponds to about 5% weight loss (see Figure S2 in the Supporting Information). Differential scanning calorimetry (DSC) measurements suggest that compound 1 is crystalline in the solid state; it melts at 265 °C during the first heating run and re-

melts at 260 °C after crystallization upon cooling. However, compound 2 is intrinsically amorphous and shows a high class transition temperature  $(T_{i})$  of around

shows a high glass transition temperature  $(T_g)$  of around 152 °C for the first heating run. Thus, in addition to increasing solubility, replacement of the pendent ethyl groups with 4-ethoxyphenyl moieties is greatly beneficial to morphologi-



Figure 1. UV/Vis and PL spectra of solutions of compounds 1-3 in  $CH_2Cl_2$  and as films on quartz.

400

Wavelength (nm)

450

500

Table 1. UV/Vis absorption, photoluminescence (PL), and thermal data for compounds 1–3.

350

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	UV/Vis $(\lambda_{max}^{abs} [nm])^{[a]}$		PL $(\lambda_{\max}^{em} [nm])^{[a]}$		$T_{\rm m}$ [°C]	$T_{\rm d}  [^{\circ}\mathrm{C}]^{[\mathrm{b}]}$	$T_{\rm g}$ [°C]		
	solution	solid	solution	solid					
1	356	344	400, 420	412, 433, 460 (sh)	265	351	-		
2	357	358	400, 421	411, 433, 460 (sh)	-	353	152		
3	285	298	361	375	_	345	143		

[a] In CH<sub>2</sub>Cl<sub>2</sub> solution ( $\approx 10^{-5}$  mol L<sup>-1</sup>). [b] Corresponding to 5% weight loss.

300

cal stability. As expected from our previous study,<sup>[11]</sup> compound **3** exhibits an inherent  $T_g$  of 143 °C.

#### **Electron-Injecting Properties in OLEDs**

On the basis of their amorphous morphology and processability in methanol, compounds **2** and **3** were evaluated as an

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---- Solution UV/Vis

electron-injecting layer (EIL) in OLEDs. In addition to a solution-processable molecular red emitter,<sup>[15]</sup> the OLED characterization was also conducted on a polymer emitter (P-PPV) (Scheme 4). The electrolyte was processed from methanol ( $2 \text{ mgmL}^{-1}$ ) at a spin speed of 2000 rpm. Similar devices that involved an Al cathode devoid of the EIL were fabricated for purposes of comparison.



x = 0.04 mol% y = 0.48 mol% z = 0.48 mol%

Scheme 4. The chemical structures of the molecular and polymer emitters.

The device characteristics of the red-light-emitting diodes (ITO/PEDOT:PSS/PVK/red emitter/cathode; ITO = indium-tin oxide; PEDOT:PSS = poly(3,4-ethylenedioxy-thiophene)poly(styrenesulfonate); PVK = poly(vinyl carbazole)) are shown in Figure 2, and the relevant data are summarized in Table 2. The Al device devoid of EIL shows the highest turn-on voltage of 6.0 V, defined at a luminance of  $1 \text{ cdm}^{-2}$ . In contrast, the turn-on voltage is considerably reduced to 3.2 V with a thin layer of the electrolyte between the emitting layer and Al cathode. The enhanced electron injection by the ionic compounds is further supported by the presence of a higher current density when the devices are turned on relative to the reference device (Figure 2a).

The OLED that contained compound **2** produced the highest performance: maximum luminance efficiency  $(LE_{\rm max}) = 1.92 \text{ cd A}^{-1}$  ( $\eta_{\rm EXE}^{\rm max} = 2.48 \%$ , EXE = external device efficiency) versus 1.70 cd A<sup>-1</sup> ( $\eta_{\rm EXE}^{\rm max} = 2.2 \%$ ), for the **3**/Al device and 0.19 cd A<sup>-1</sup> for the Al device at approximately 20 mA cm<sup>-2</sup>. Whereas the luminance (L)=202 cd m<sup>-2</sup>, LE = 0.93 cd A<sup>-1</sup>, and V=7.6 V for the **3**/Al device; and L = 236 cd m<sup>-2</sup>, LE = 1.25 cd A<sup>-1</sup>, and V=6.8 V for the **2**/Al device. The latter parameters are nearly comparable to those reported for a device with a Ba/Al cathode.<sup>[15a]</sup> No EL emission occurs from the electrolytes, thus yielding pure red emission with  $\lambda_{\rm max}^{\rm EL}$  at 622 nm (Figure 3).

To gain direct insight into the electron-injection properties of compounds 2 and 3, the electron-only devices (ITO/ Al/red emitter (100 nm)/cathode) were fabricated. The J-V



Current Density (mA cm -)

Figure 2. a) *J*–*V*–*L* and b) *LE*–*J* characteristics of the OLEDs: ITO/PE-DOT:PSS/PVK/red emitter/cathode (Al, **2**/Al, and **3**/Al).

Table 2.	The summary	of OLED	data concerning	different	cathodes.

EML	Cathodes	$\frac{LE_{\rm max}}{[{\rm cd}{\rm A}^{-1}]}$	$@\approx 20 \text{ mA cm}^{-2}$				$V_{ ext{turn-on}}$ $[V]^{[a]}$
			V	L	LE	EXE	
			[V]	$\left[ cdm^{-2} ight]$	$\left[ cd A^{-1} \right]$	[%]	
rad	<b>2</b> /Al	1.92	6.8	236	1.25	1.62	3.2
amittan	3/Al	1.70	7.6	202	0.93	1.21	3.2
emitter	Al	0.19	8.4	32	0.16	0.21	6.0
	<b>2</b> /Al	16.6	6.2	2777	14.0	4.59	2.4
P-PPV	3/Al	13.0	7.0	2100	10.4	3.41	2.6
	Al	0.95	8.6	199.8	0.95	0.31	4.8

[a] At a luminance of  $1 \text{ cdm}^{-2}$ .

characteristics show that the electron-only device that includes **2** exhibits a constantly larger current density than the **3**-based device (Figure 4), thus giving rise to improved EL characteristics with higher luminous efficiency and lower working voltage. The reference Al device has the least electron current density, particularly at high voltages, which suggests that electron injection is hindered.

The characterization of the OLEDs that contain the polymer emitter (ITO/PEDOT:PSS/P-PPV/cathode) further sup-

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Figure 3. EL spectra of the OLEDs: ITO/PEDOT:PSS/PVK/red emitter/ cathode (2/Al and 3/Al).



Figure 4. *J*–*V* characteristics of the electron-only devices: ITO/Al/red emitter (100 nm)/cathode (Al, **2**/Al, and **3**/Al).

ports the notion that compound **2** is a more effective electron-injection material. Thus, at around 20 mA cm<sup>-2</sup>, L = 2777 cdm<sup>-2</sup>, LE = 14.0 cdA<sup>-1</sup>, and V = 6.2 V for the **2**/Al device, whereas L = 2100 cdm<sup>-2</sup>, LE = 10.4 cdA<sup>-1</sup>, and V = 7.0 V for the **3**/Al device (Table 2 and Figure 5).

The reduction of the built-in potential of the OLED has been considered to contribute to the enhanced electron injection on account of the formation of a favorable dipole provided by the thin interfacial layer.<sup>[16]</sup> Therefore, photovoltaic measurements were carried out to estimate the builtin potentials of the devices (ITO/PEDOT:PSS/PVK/red emitter/cathode).

Under white-light illumination, the devices that consisted of **2**/Al and **3**/Al cathodes show an open-circuit voltage ( $V_{oc}$ ) of 1.5 and 1.3 V, respectively (Figure 6). By contrast, the  $V_{oc}$ of the reference Al device was considerably lower than the expected value of around 1.0 V.<sup>[4b]</sup> Nevertheless, the loss of  $V_{oc}$  suggests an existing large energy barrier for electron transport across the interface between the neat Al cathode and molecular red-emitter layer.<sup>[17]</sup>

Finally, it is interesting to observe that compound 2 provides largely improved device efficiency, with respect to



Figure 5. a) *J*–*V*–*L* and b) LE–*J* characteristics of the OLEDs: ITO/PE-DOT:PSS/P-PPV/cathode (Al, **2**/Al, and **3**/Al).



Figure 6. Current density/voltage curves for the devices: ITO/PE-DOT:PSS/PVK/red emitter/cathode (Al, **2**/Al, and **3**/Al), under white-light irradiation.

CsF, a vacuum-deposited inorganic electron-injection material. For instance, at approximately 20 mA cm<sup>-2</sup>, L = 156 cd m<sup>-2</sup>, and LE = 0.80 cd A<sup>-1</sup> in the OLED structure (ITO/PEDOT:PSS/PVK/red emitter/CsF/Al; see Figure S3 in the Supporting Information).

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#### Conclusion

In summary, we have shown that replacement of pendant aliphatic chains by appropriate rigid bulky groups leads to a general increase in both the solubility and morphological stability of the organic electrolytes. Furthermore, the chemical structures of the compounds exert a distinct effect on the electron-injection properties. The choice of the emitting materials can be extended to some other interesting molecular emitters that show high solid-state PL efficiency and bipolar charge transport.<sup>[15b,18]</sup> In light of the general application potentialities in the field of organic optoelectronics including organic field-effect transistors and organic solar cells, this class of amorphous ionic molecular compounds that combines concise synthesis, facile purification, and alcohol processability should merit further research.

#### **Experimental Section**

#### General

All manipulations involving air-sensitive reagents were performed under an inert atmosphere of dry nitrogen. THF was dried over Na/benzophenone and distilled prior to use. All the intermediates were isolated and analyzed by TLC on silica gel. The syntheses of precursor compounds **16** and **17** are presented in the Supporting Information, as well as compound **21**, which was prepared by a modified procedure.<sup>[11]</sup> All other starting materials were purchased commercially and were used as received, unless otherwise specified.

#### Physical Measurements

<sup>1</sup>H NMR spectra were recorded with a Bruker AV 300 spectrometer with deuterated solvents as the internal reference. TOF-MS was performed with a KOMPACT MALDI mass spectrometer (Shimadzu/Kratos) in the positive-ion mode with a matrix of dithranol. ESI mass spectrometry was conducted with an Esquire HCT PLUS LC/MSn System in the positive electrospray ionization (ESI+) mode. UV/Vis absorption spectra were obtained with an HP 8453 spectrophotometer. Photoluminescence spectra were measured with a Jobin–Yvon spectrofluorometer JY Fluorolog-3 spectrofluorometer. TGA was conducted with a TG 209 F1 (NETZSCH) thermal analysis system under a heating rate of 20°Cmin<sup>-1</sup> from 30 to 550°C. DSC was run with a DSC 204 F1 (NETZSCH) thermal analysis system. The sample was heated from -60°C at a rate of 20°Cmin<sup>-1</sup>.

#### Synthesis of Compound 1

An excess amount of sodium tetrafluoroborate (1 g, 9.11 mmol) in water (5 mL) was added to a solution of compound **16** (0.23 g, 0.26 mmol) in mixed solvents of THF (30 mL) and methanol (30 mL). After the mixture was stirred at room temperature for 3 d, the solvents were removed under vacuum. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting white solid was redissolved in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub>, filtered, and reprecipitated with heptane. Yield: 0.22 g (93.6 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.41-0.52$  (m, 12 H), 1.39 (t, *J*=7.05 Hz, 3 H), 2.06–2.35 (m, 10 H), 3.12 (s, 6 H), 3.32–3.44 (m, 2 H), 3.48–3.51 (m, 2 H), 3.88 (s, 3 H), 4.12–4.25 (m, 2 H), 6.98–7.05 (m, 2 H), 7.12–7.19 (m, 2 H), 7.51–7.58 (m, 2 H), 7.61–7.69 (m, 8 H), 7.74–7.86 (m, 7 H), 8.03 ppm (s, 1 H); MALDI-TOF: *m*/*z* calcd: 804.48; found: 805.0 (100%) [*M*–BF<sub>4</sub>].

#### Synthesis of Compound 2

Prepared from 17 according to the procedure described for 1. Yield: 95.2 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =0.35–0.49 (m, 6H), 1.26–1.45 (m,

9H), 2.05–2.16 (m, 4H), 2.16–2.32 (m, 2H), 3.11 (s, 6H), 3.32–3.49 (m, 2H), 3.50–3.59 (m, 2H), 3.84 (s, 3H), 3.91–4.06 (m, 4H), 4.14–4.26 (m, 2H), 6.76–6.79 (m, 4H), 6.95 (d, *J*=8.67 Hz, 2H), 7.12–7.19 (m, 2H), 7.21–7.26 (m, 4H), 7.49–7.59 (m, 6H), 7.64–7.67 (m, 4H), 7.70–7.80 (m, 7H), 8.02 ppm (s, 1H); ESI-MS: *m*/*z* calcd: 988.53; found: 988.80 (100%) [*M*–BF<sub>4</sub>].

#### Synthesis of Compound 3

Prepared from **21** according to the procedure described for **1**. Yield: 96.4%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =1.33 (t, *J*=6.45 Hz, 3H), 2.18 (m, 2H), 3.06 (s, 6H), 3.35–3.50 (m, 4H), 4.14 (m, 2H), 7.18 (s, *J*=1.20 Hz, 2H), 7.42–7.57 (m, 16H), 7.65 (m, 3H), 7.81–7.90 (m, 12H), 8.06 ppm (d, *J*=7.95 Hz, 4H); MALDI-TOF: *m/z* calcd: 864.42; found: 864.31 (100%) [*M*–BF<sub>4</sub>].

#### OLED Fabrication and Characterizations

The potentiality of compounds **2** and **3** was studied in OLEDs [ITO/ PEDOT:PSS(40 nm)/PVK(x nm)/EML/**2**, **3**/Al(200 nm)], together with the reference device with the Al cathode (EML=red emitter (45 nm), x=40 nm; EML=P-PPV (80 nm), x=0 nm). Patterned (15  $\Omega$  square<sup>-1</sup>) indium-tin oxide (ITO)-coated glass substrates were cleaned with distilled water, acetone, detergent, distilled water, and 2-propanol successively in an ultrasonic bath. After treatment with oxygen plasma, PE-DOT:PSS (Baytron P4083, Bayer AG) was spin-coated from water at 3000 rpm onto the ITO substrate and dried in a vacuum oven at 80°C for 8 h. PVK (Aldrich, MW 1100000) was coated atop the PEDOT:PSS layer and dried at 100°C for approximately 15 min.

Subsequently, a thin film of the red emitter was spin-cast from *p*-xylene solution ( $25 \text{ mg mL}^{-1}$ ) at 3000 rpm and dried at 130 °C for around 10 min. By contrast, the polymer emitting layer P-PPV was spin-coated from *p*-xylene solution ( $6 \text{ mg mL}^{-1}$ ) at 1000 rpm. Compounds **2** and **3** were spin-cast atop the emitting layer from a methanol solution ( $2 \text{ mg mL}^{-1}$ ) at 2000 rpm. The CsF layer and the Al cathode were thermally deposited through a mask in vacuum ( $<3 \times 10^{-4}$  Pa) with the deposition speed and thickness monitored by a thickness/rate meter. All steps except the processing of PEDOT:PSS were performed in a glovebox. The active area of the device was 0.19 cm<sup>2</sup>.

The current density/luminance/voltage characteristics were measured with a Keithley 236 source measurement unit and a calibrated silicon photodiode. The EL spectra were collected with a PR-705 photometer. The photovoltaic measurements were carried out under the white-light illumination of a xenon lamp.

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#### **Molecular Devices**

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Alcohol-Processable Organic Amorphous Electrolytes as an Effective Electron-Injection Layer for Organic Light-Emitting Diodes



**Light work**: A thin layer of the alcohol-processable amorphous small-molecule electrolyte that features a linearconjugated unit (see scheme) provides improved electron injection from the Al metal and thus better organic lightemitting diode performance, unlike its counterpart that contains a rigid branched bulky moiety.

### **KK** These are not the final page numbers!