

Organic light-emitting devices based on solution-processible quinolato-complex supramolecules

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ABSTRACT

This paper discusses a new type of supramolecular material tris{5-*N*-[3-(9H-carbazol-9-yl)propyl]-*N*-(4-methylphenyl)amino-sulfonyl-8-hydroxyquinolato} aluminum(III), Al(SCarq)₃, which we synthesized using three 5-*N*-[3-(9H-carbazol-9-yl)propyl]-*N*-(4-methylphenyl)amino-sulfonyl-8-hydroxyquinoline as bidentate ligands. The peak photoluminescence in the solid phase appears at 488 nm. In cyclic voltammetric measurement, two oxidation peaks, which were obtained at –5.6 and –5.9 eV, correspond to HOMO sites of carbazolyl and aluminum quinolates, respectively. In the investigation of solid morphological thin film, the flat surface was investigated using an atomic force microscope. The root mean square (rms) and mean roughness (R_a) were respectively measured to be 0.427 and 0.343 nm. For the fabrication of organic light-emitting devices (OLEDs) using spin-coating techniques, the turn-on voltage and maximum luminescence of the optimized electroluminescence device, glass/ITO (20 nm)/PEDOT:PSS (75 nm)/Al(SCarq)₃ (85 nm)/BCP (8 nm)/LiF (1 nm)/Al (200 nm), were respectively 9.6 V and 35.0 cd m⁻². Due to the electroplex formation between the carbazole (electron-donor) and the aluminum quinolates (electron-acceptor) moieties under an applied DC bias, the chromaticity of electroluminescence shifted to green-yellow with 1931 CIE_{x,y} (0.40, 0.47).

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1. Introduction

Since 1987, Tang and VanSlyke discovered the first high efficiency organic light-emitting devices (OLEDs) based on tris(8-quinolinolato)aluminum (Alq₃) [1]. Most small molecules-based OLEDs were fabricated using thermal evaporation techniques. Because of the relative ease of synthesis and purification, small molecules of guest-host dopant systems based on Alq₃ are particularly suitable for fabrication of full color OLEDs [2]. On the contrary, solution processed small molecule OLEDs are rare except for a few relatively large frameworks of dendriatic molecules [3,4], dye dispersed polymers [5], and oligomers [6]. In pushing the small molecule OLED fabrication technology forward large area substrates, there exists a need to simplify the manufacturing process and to reduce the cost of these highly efficient doped devices. Development of OLEDs fabrication technology via solution processible small molecule materials offers a simple alternative and also

opens up exciting possibilities for inkjet printing fabrication similar to what has been demonstrated in PLEDs [7].

Although there are several materials utilized in device fabrication using spin-coating, such as dendrimers [4] and light-emitting polymers [8], little research has been done on a solution-process based on six-coordinated aluminum quinolate complexes without a polymeric backbone or matrix [9–12].

In the development of OLEDs, a wide band-gap of host materials is required for sensitizing various dopants. According to the semi-empirical approach of the Zerner International Neglect of Differential Overlap (ZINDO) theory [13], the band-gap of the quinolato aluminum complexes is tunable by introducing an electron-withdrawing group at C5 in 8-hydroxyquinoline. The corresponding derivatives with sulfonamide substituent were also demonstrated by Hopkins et al. [14]. However, these complexes cannot be sublimated because they are limited in thermal process. To overcome this problem and promote its applications in OLEDs, we have derived a novel solution-processible host material, meridional tris(5-*N*-ethyl-anilinesulfonamide-8-quinolato-N₁O₈) aluminum, Al(Saq)₃. Electroluminescence (EL) was demonstrated by the solution process. However, due to the absence of hole-transporting ability, its electroluminescent was observed to be noticeably suppressed [15].

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In this study, based on Al(Saq)₃, we attempt to promote the hole-transporting ability and EL performance in devices by introducing a well-known hole-transporting moiety, carbazole, into the bidentate quinoline to produce a novel and functionalized tris[5-*N*-(3-carbazylpropyl)-*p*-methylaniline-sulfonyl-8-hydroxyquinolato] aluminum(III)—hereby abbreviated as Al(SCarq)₃. All properties of Al(SCarq)₃ are characterized and discussed.

2. Experimental

2.1. General comments

All chemicals used in this research are commercially available. Tetrahydrofuran (THF) was distilled from Na/benzophenone. Al(Saq)₃ was prepared according to our previous work [15]. ¹H NMR was recorded with a Varian Unity-300 MHz spectrometer or AS-500 MHz NMR spectrometer. Elemental analyses on the samples were obtained using a HERAEUS CHN-OS RAPID. The thermal properties were determined by means of differential scanning calorimetry (DSC, Seiko SSC 5200).

2.2. Synthesis

2.2.1. *N*-[3-(9*H*-carbazole-9-yl)propyl]-*N*-(4-methylphenyl)amine (2)

In a 250-mL round-bottom flask fitted with a magnetic stirrer, condenser, and N₂ inlet were placed *p*-methylaniline (2.97 g, 27.76 mmol), 9-(3-bromopropyl)-9*H*-carbazole (compound **1** [16], 5.00 g, 17.35 mmol), calcium carbonate (1.74 g, 17.40 mmol), and acetonitrile (100 mL) with stirring. The reactants were refluxed for 36 h and then cooled at room temperature. The solid formed was filtered off and then the filtrate was concentrated under reduced pressure with heating at 100 °C to remove the solvent. Thereafter, the residual crude product was flashed through silica gel (eluent: hexane/ethyl acetate = 6/1) to produce **2** (4.49 g, yield 82.5%). ¹H NMR (300 MHz, CDCl₃) δ 1.927–2.00 (m, 2H), 2.16 (s, 3H), 3.13 (t, 2H), 3.60 (bs, 1H), 4.20 (t, 2H), 6.43 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 7.13–7.24 (m, 4H), 7.33–7.39 (m, 2H), 8.04 (d, *J* = 7.7 Hz, 2H). FT-IR (KBr) 3052, 2717, 2847, 1597, 1516, 1497, 1479, 1451, 1362, 1335, 1315, 1230, 788, 749, 724, 698 cm⁻¹. MS-El (*m/e*, rel. intensity) 314 (M⁺, 97.7), 315 (M⁺+1, 17.02). Anal. Calcd for C₂₂H₂₂N₂: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.31; H, 7.44; N, 8.64.

2.2.2. 5-*N*-[3-(9*H*-carbazole-9-yl)propyl]-*N*-(4-methylphenyl)aminesulfonyl-8-hydroxyquinoline (3)

In a 100-mL round-bottom flask fitted with a magnetic stirrer, a condenser, and a N₂ inlet were placed 8-hydroxyquinoline-5-sulfonyl chloride [17] (2.00 g, 8.21 mmol) with 20 mL of dichloromethane. Triethylamine (3.41 mL), compound **2** (3.09 g, 9.84 mmol), and dichloromethane (10 mL) mixtures were added slowly into the reactor. The reaction mixture was heated to reflux for 24 h. The solution was then filtered, and the solid byproduct was removed. Solvent was stripped off by rotary vapor, the solid was crystallized in ethyl acetate/methanol (1:1), and white crystals were collected to yield 3.33 g (65.0%). Mp 144–145 °C. ¹H NMR (300 MHz, CDCl₃) δ 2.02–2.10 (m, 2H), 2.33 (s, 3H), 3.66 (t, *J* = 6.6 Hz, 2H), 4.35 (t, *J* = 7.5 Hz, 2H), 6.48 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 7.18–7.30 (m, 6H), 7.37–7.44 (m, 2H), 7.99–8.11 (m, 3H), 8.37 (d, *J* = 11.1 Hz, 1H), 8.75 (d, *J* = 4.4 Hz, 1H). FT-IR (KBr) 3359 (br), 3041, 2936, 2878, 1744, 1594, 1518, 1500, 1483, 1452, 1403, 1372, 1342, 1326, 1225, 1202, 1190, 1152, 1130, 1065, 749, 721, 682 cm⁻¹. MS-El (*m/e*): 521 (M⁺), 522 (M⁺+1). Anal. Calcd for C₃₁H₂₇N₃O₃S: C, 71.38; H, 5.22; N, 8.06; O, 9.20; S, 6.15. Found: C, 71.12; H, 5.04; N, 8.44.

2.2.3. Tris[5-*N*-[3-(9*H*-carbazole-9-yl)propyl]-*N*-(4-methylphenyl)amine-sulfonyl-8-hydroxyquinolato] aluminum(III) (4)

A 200-mL flask fitted with a N₂ inlet, a septum, and a stir bar was flame-dried and cooled under N₂. Compound **3** (1.50 g, 2.88 mmol) was added along with anhydrous THF (60 mL). A hexane solution of triethylaluminum (1.1 mL, 15, w/w%) was added via syringe. A yellow solution with blue-green fluorescence was immediately visible. The reaction was stirred at room temperature for 48 h. The crude product was recrystallized in THF to afford yellow solid (1.39 g, yield 91.1%) of **4**. Mp 219–220 °C. *T*_g = 154.1 °C. ¹H NMR (300 MHz, CDCl₃) δ 1.94–2.08 (m, 6H), 2.29 (s, 3H), 2.34 (s, 3H), 2.380 (s, 3H), 3.54–3.60 (m, 2H), 3.64–3.68 (m, 2H), 3.74–3.76 (m, 2H), 4.26 (t, *J* = 4.2 Hz, 2H), 4.31 (t, *J* = 4.5 Hz, 2H), 4.36 (t, *J* = 4.8 Hz, 2H), 6.90–6.94 (q, 6H), 6.97–7.08 (m, 13H), 7.23–7.17 (m, 8H), 7.35–7.43 (m, 9H), 8.04–8.11 (m, 9H), 8.44 (d, *J* = 5.4 Hz, 1H), 8.51–8.56 (m, 3H), 8.65 (d, *J* = 2.7 Hz, 1H), 8.69 (d, *J* = 2.1 Hz, 1H). FT-IR (KBr) 3049, 2924, 2850, 1599, 1576, 1498, 1484, 1463, 1494, 1373, 1332, 1233, 1201, 1166, 1153, 1136, 816, 750, 723, 701, 657, 545, 425 cm⁻¹. The molecular weight was characterized by Bruker Biflex III with the matrix-assisted laser desorption/ionization (MALDI) [18] method which revealed no extraneous peak other than the desired parent *m/e* = 1589.8. Anal. Calcd for C₉₃H₇₈AlN₉O₉S₃: C, 70.30; H, 4.95; N, 7.93; O, 9.06; S, 6.05; Al, 1.70. Found: C, 70.28; H, 4.72; N, 7.55.

2.3. Photoluminescence (PL)

For solution investigation, the compound was dissolved in 1,2-dichloroethane (*c* = 10⁻³–10⁻⁴ mol L⁻¹). For solid-phase investigations of pure compounds, thin films of 1,2-dichloroethane solution (1.0 wt.%) were spin-coated. UV–vis absorption spectra were measured with an HP spectrophotometer by using either the solutions in cuvettes of 10 mm path length or the solid thin film coated on quartz plates. PL spectra were recorded with an Acton Research Spectra Pro-150 spectrometer. For PL experiments, the excitation wavelength was set at the absorption maximum of the complex.

2.4. Device fabrication

The two different device structures, ITO/PEDOT:PSS/Al(SCarq)₃/LiF/Al and ITO/PEDOT:PSS/Al(SCarq)₃/BCP/LiF/Al, were prepared for EL measurement in the following manner. For all structures, the indium-tin-oxide (ITO, sheet resistance is 20 Ω □⁻¹) glass substrates were cleaned ultrasonically with detergent, de-ionized water, *iso*-propanol and methanol. After cleaning, poly(3,4-ethylenedioxythiophene)/poly(styrene)-sulfonate (PEDOT:PSS, obtained from Bayer) aqueous solution was spin-coated at 3000 rpm onto the cleaned ITO substrates and baked at 110 °C for 24 h. The neat Al(SCarq)₃ were subsequently spin-coated on the PEDOT layer at 2500 rpm to give the film typically 85 nm thick. The 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 8 nm), lithium fluoride (LiF, 1 nm) and Al layer (200 nm) were sequentially deposited at 1 × 10⁻⁶ Torr. The emitting area of the device was 3 mm × 3 mm. The voltage-current-luminance characteristics were measured using an optical power meter (PR-650) and a digital source meter (Keithley 2400). The EL spectra were carried out in an ambient atmosphere after encapsulation.

3. Result and discussion

3.1. Synthesis and characterization of Al(SCarq)₃ complex

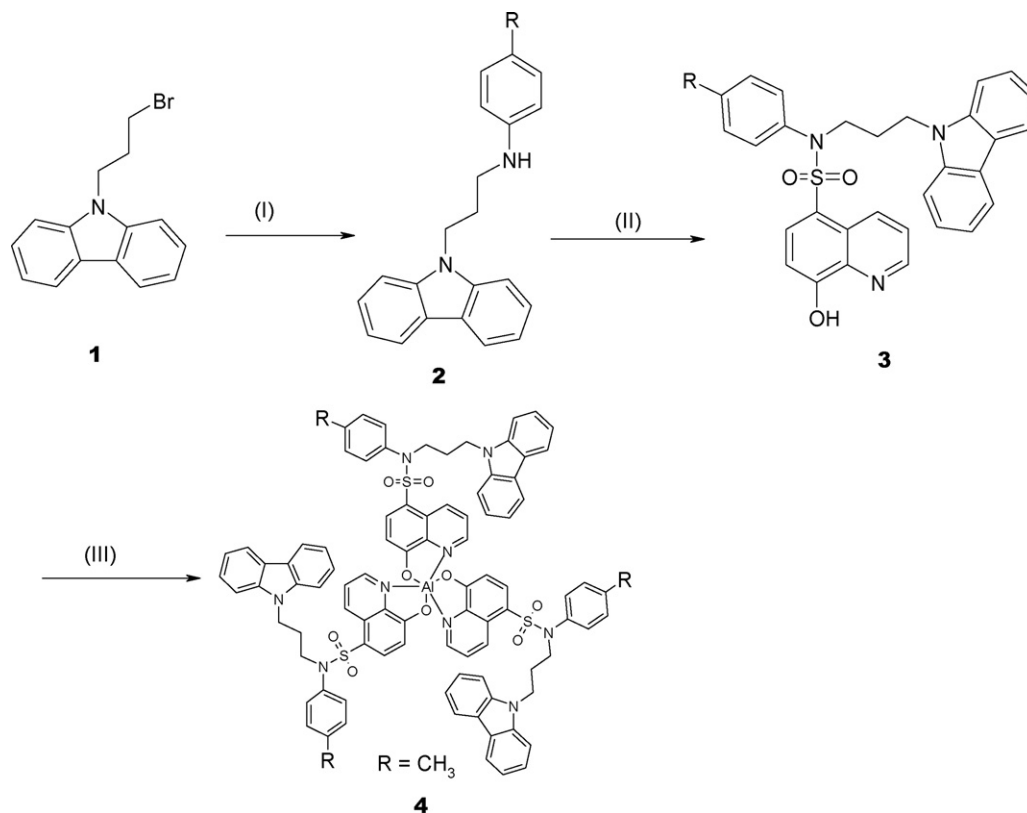
The chemical structure and the synthetic procedure of the supramolecular Al(SCarq)₃ are illustrated in Scheme 1. Via S_N2 reaction, carbazole, and *p*-methylaniline were connected with a propyl spacer to enable *N*-[3-(9*H*-carbazole-9-yl)propyl]-*N*-(4-methylphenyl)amine (**2**) which reacted further with 8-hydroxyquinoline-5-sulfonyl chloride to obtain 5-*N*-[3-(9*H*-carbazole-9-yl)propyl]-*N*-(4-methylphenyl)aminesulfonyl-8-hydroxyquinoline (**3**). Finally, reacting ligand **3** with triethylaluminum produced the desired six-coordinated Al(SCarq)₃ (**4**). This functionalized supramolecule has good solubility in a variety of common organic solvent, such as 1,2-dichloroethane, THF, and dimethyl sulfoxide (DMSO). In our study, it was also found that the solubility of this organometallic complex significantly improved when R was replaced instead of H by methyl group (–CH₃) as shown in Scheme 1.

3.2. Cyclic voltammetric measurement

To realize the highest occupied molecular orbitals (HOMOs) energy levels, the oxidation electrochemical behavior of Al(SCarq)₃ was examined by using cyclic voltammetry (CV) on Pt electrodes in 1,2-dichloroethane. Here, (Bu)₄NBF₄ and Ag/AgCl (saturated) were utilized as the supporting electrolyte and the reference electrode, respectively. The potential values were reported with respect to the ferrocene standard. The functionalized Al(SCarq)₃ showed three stepwise-oxidation waves, which peaked at 1.54, 1.02 and 0.96 V, as shown in Fig. 1. Evidently, the inserted propyl spacer cannot only separate the conjugated system between the core and carbazolyl, but also keeps their individual redox potential constant. Therefore, two HOMOs energy levels were measured using CV, and their corresponding values, carbazolyl and core, were –5.6 and –5.9 eV, respectively.

3.3. Net thin films of Al(SCarq)₃ formed by solution-process

High quality thin film formation is essential for the potential use of solution-processible materials in manufacturing organic devices.



Scheme 1. Synthesis of the Alq_3 -based supramolecule. (I) *p*-Methylaniline/ K_2CO_3 /acetonitril/reflux, (II) 8-hydroxyquinoline-5-sulfonylchloride/ CH_2Cl_2 /triethyl amine, and (III) triethylaluminum/THF.

Fig. 2 shows the AFM image of the solid thin film morphology coated with 1.0 wt.% $\text{Al}(\text{SCarq})_3$ in 1,2-dichloroethane. The AFM image reveals that the film is flat and pin-hole-free. Its root mean square (rms) and mean roughness (R_a) are 0.427 and 0.343 nm, respectively. The thin film phase prepared by spin-coating is presumably possible for most small molecular materials due to the formation of intermolecular hydrogen bonding or physically entanglement. The better $\text{Al}(\text{SCarq})_3$ thin film obtained by solution process could be due to two factors. First, the intermolecular entanglement occurred

from the packing of sulfonamide groups at C-5 of the quinolate ring. This was also demonstrated by Cheng et al. [15] and Qiao et al. [19]. Second, it could be the magnitude of the molecular weight, $\text{Mw} = 1589.8 \text{ g mol}^{-1}$, which increased since carbazoles were introduced into the $\text{Al}(\text{SCarq})_3$. Thus, the viscosity of the solution increased. As a result, high quality thin-films can be obtained at lower concentration than that of $\text{Al}(\text{Saq})_3$.

3.4. Absorption and photoluminescence

For comparison and characterization, the optical spectra of $\text{Al}(\text{SCarq})_3$ and $\text{Al}(\text{Saq})_3$ are plotted in Fig. 3. As shown in Fig. 3a, the spectrum of $\text{Al}(\text{SCarq})_3$ exhibits characteristic absorption bands of carbazole groups and the core of aluminum quinolate at 332, 346, and 376 nm, respectively. In the normalized PL spectra, as shown in Fig. 3c and e, features of $\text{Al}(\text{Saq})_3$ and $\text{Al}(\text{SCarq})_3$ are almost the same in diluted solution, and their corresponding peaks are 481 and 483 nm. In solid PL, similar features of $\text{Al}(\text{Saq})_3$ and $\text{Al}(\text{SCarq})_3$ were observed at 489 and 488 nm, respectively. However, it is clearly observed that a shoulder appeared on the long-wave side in Fig. 3d. In our previous study on $\text{Al}(\text{Saq})_3$ crystalloid, we found that sizeable gaps existed between the central metal and ligands [20]. Therefore, the electron-donating group (carbazoyl) could be attracted easier and inserted into the electron-withdrawing core (aluminum quinolates) in $\text{Al}(\text{SCarq})_3$. As a result, the emission formed from excimer on the long-wave side is depicted in Fig. 3d. However, similar phenomena has not been observed in both $\text{PVK}/\text{Al}(\text{Saq})_3$ [15] and $\text{PVK}/\text{tris}(5\text{-piperidinylsulfonamide-8-quinolinolato-N}_1\text{,O}_8)\text{aluminum} [\text{Al}(\text{QS})_3]$ [14] hybridized thin films. It presented that carbazoles pended on PVK were confined in the poly(vinylene) backbone. Thus, the formation of exciplex was suppressed [21].

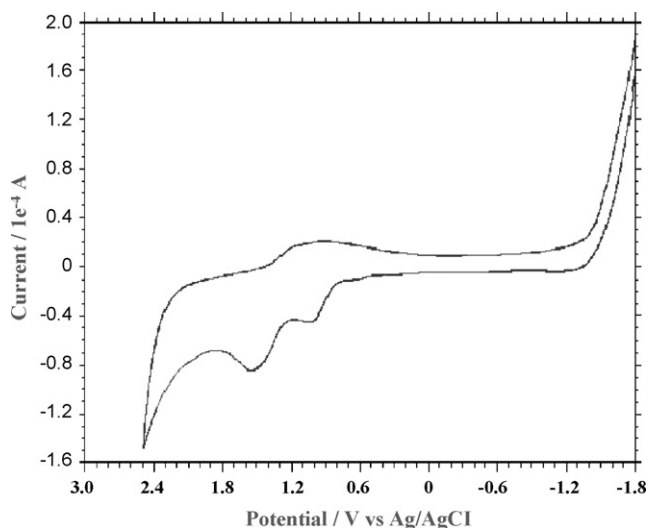


Fig. 1. Cyclic voltammogram of $\text{Al}(\text{SCarq})_3$ (1 mM) complex in 1,2-dichloroethane with $(\text{Bu}_4)\text{NBF}_4$ (0.1 M) as the supporting electrolyte.

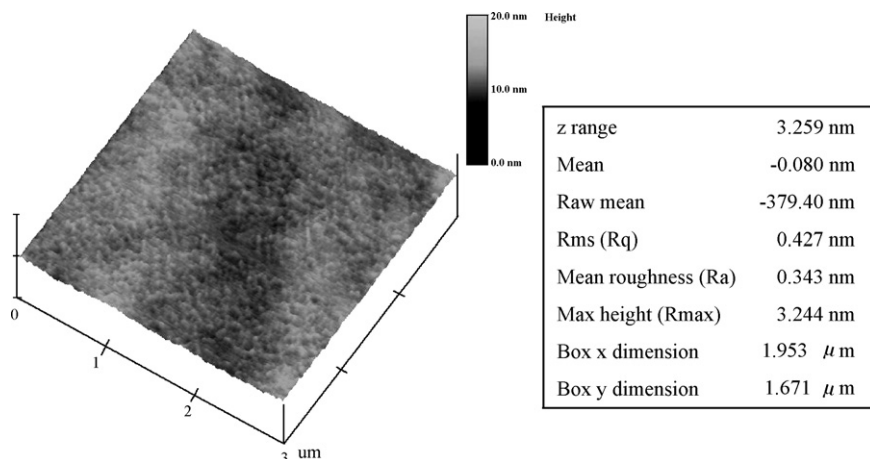


Fig. 2. AFM image of Al(SCarq)₃ thin film, spin-coated from 1,2-dichloroethane.

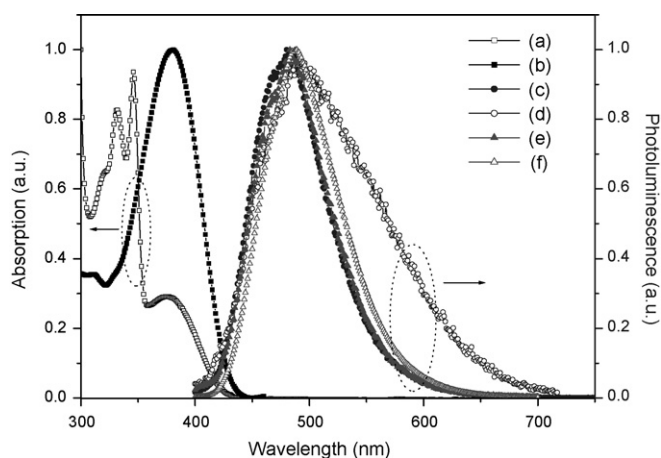


Fig. 3. Comparison of optical properties of Al(SCarq)₃ and Al(Saq)₃. UV–vis absorption: (a) Al(SCarq)₃ thin solid film, and (b) Al(Saq)₃ thin solid film. Photoluminescence spectra: (c) Al(SCarq)₃ in 1,2-dichloroethane; (d) Al(SCarq)₃ thin solid film, (e) Al(Saq)₃ in 1,2-dichloroethane; (f) Al(Saq)₃ thin solid film.

3.5. Electroluminescence

The EL behaviors were characterized by using device architectures as shown in Fig. 4. The well-known hole-injection layer poly(3,4-ethylenedioxythiophene)/poly(styrene)-sulfonate (PEDOT:PSS) [22] was inserted to reduce the energy barrier between the active layer and the anode. To study EL

performance, the hole-blocking layer, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), was added into device b.

The EL spectra of the devices are shown in Fig. 5, and their corresponding current–voltage–brightness (*I*–*V*–*B*) characters are also illustrated. Identical features of EL spectra were observed in device a and device b. However, the intensity of device b is higher than that of device a. According to the energy diagram illustrated in Fig. 4, the BCP layer in device b could confine the charges and excitons within the desired regions for improved emission in these kinds of solution-process-based devices [23]. As a result, more excitons were generated at the active layer in device b than that of device a. In *I*–*V*–*B* characterization, the turn-on voltage of device a and device b are 9.8 and 9.6 V, respectively. Their corresponding current efficiencies are respectively 0.25 and 0.18 cd A⁻¹ at 5 mA cm⁻². The maximum luminescences are 35.0 cd m⁻² at 25.2 V and 19.2 cd m⁻² at 26.4 V, respectively. Although the hole blocker utilized in device b caused high current density with identical driving voltage, the luminescence was higher than that of device a.

In addition, the broadened EL feature of both devices appeared at 572 nm with the full width at half maximum (FWHM) of 184 nm. Their Commission Internationale de L'Éclairage (CIE) coordinates are (0.40, 0.47), and the chromaticity of EL is almost independent of the driving voltage. However, the EL spectra related to that of the PL were substantially red-shifted, and it was inferred that emission in the red region in our devices may arise from the singlet electroplex (Carbazole⁺/Core⁻)^{*} [24,25]. The electroplex can be regarded as a pair of statistically independent carbazole groups and the chromophoric core, in which one has an excess electron (core⁻), while another one has a hole (carbazole⁺). Fig. 6 schemati-

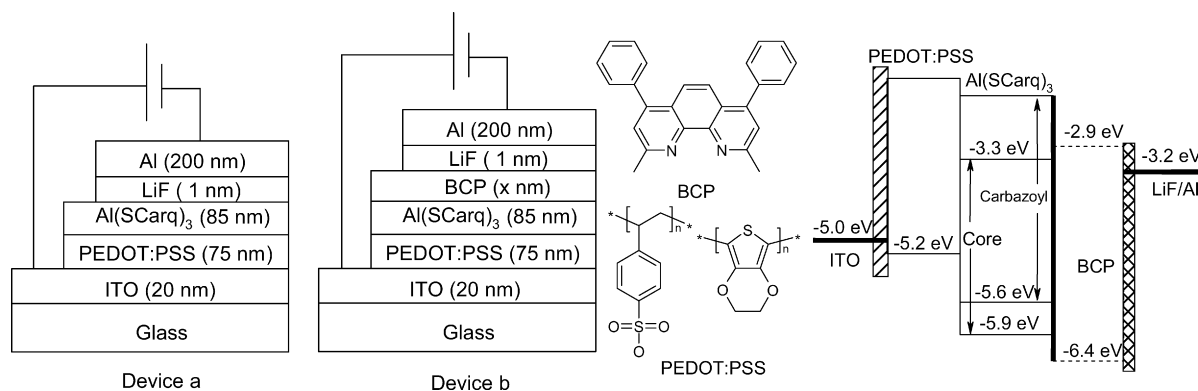


Fig. 4. Device architecture based on Al(SCarq)₃ as an active layer.

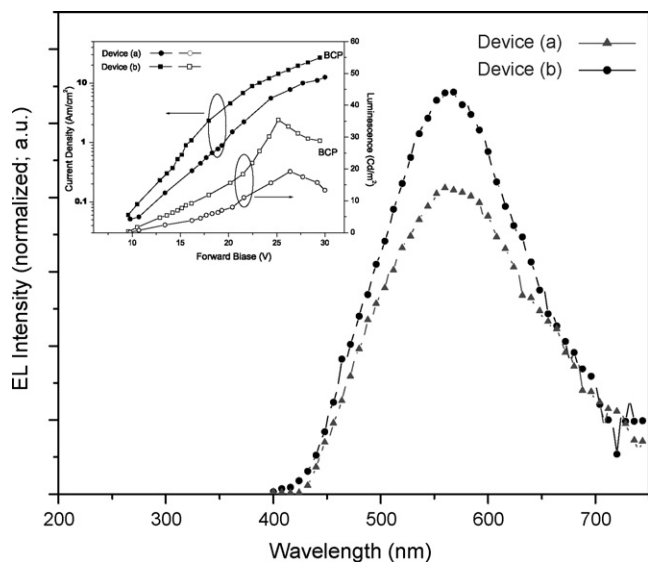


Fig. 5. Normalized EL spectra from electroluminescent devices: (a) single layer; (b) multilayer with BCP. The current–voltage–brightness curves of the corresponding devices were inserted at the right corner.

cally presents the electron configuration in the molecular orbitals of the Al(SCarq)₃ electroplex. For comparison, the electron configuration of exciplex is also presented. The energy of such a hole–electron pair trapped by the carbazole and the core should be lower than that of a singlet excited state of a single chromophoric core. As a result, direct cross recombination of the hole and the electron would lead to emission at longer wavelengths compared to the fluorescence of Al(SCarq)₃ in solution. The electroplex rather than exciplex of

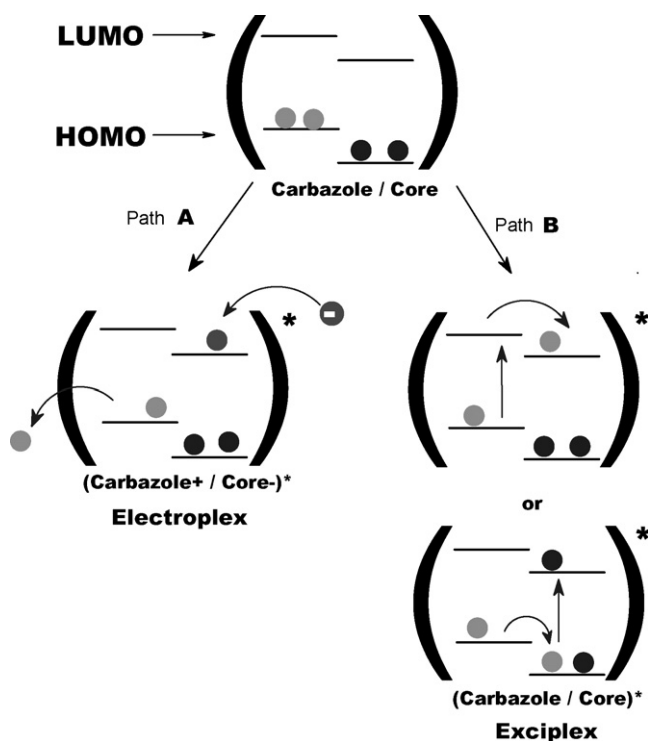


Fig. 6. Schematic representation for the electron configuration in the molecular orbitals of electroplex and exciplex of Al(SCarq)₃. Path A and path B were respectively driven by DC bias and photoexcitation.

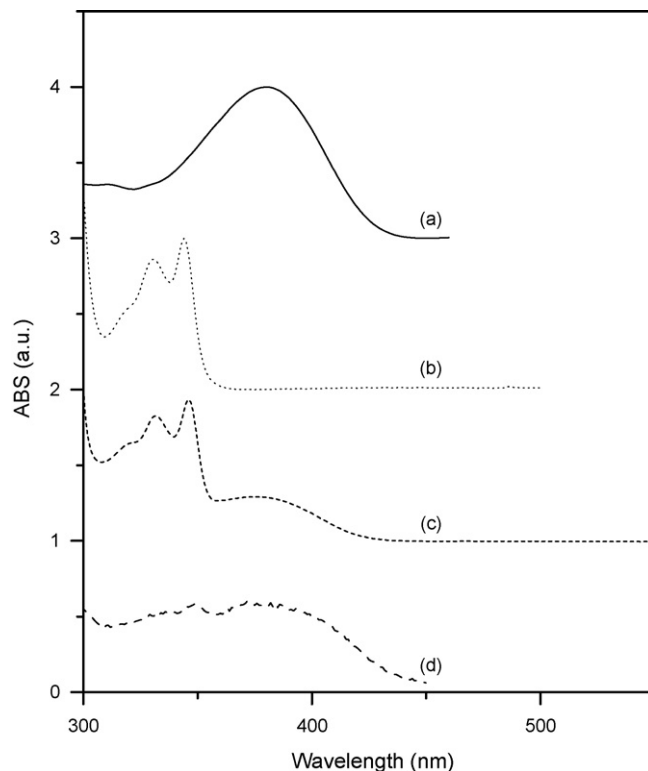


Fig. 7. Absorption spectra of thin films: (a) Al(Saq)₃, (b) PVK, and (c) Al(SCarq)₃. Here, (d) is the photoluminescence excitation spectrum of Al(SCarq)₃ at 572 nm.

Al(SCarq)₃ is favorably formed in EL devices because of the presence of an electric field. Similar disparity in the EL and PL spectra was also reported for other small molecules and polymer materials, where the radiative decay of the electromer (M^+/M^-)* or the electroplex (M^+/N^-)* was usually responsible for additional emission in EL. It is notable that previously reported electromers and electroplexes in the literature were usually formed at relatively high electric fields [26,27], while the electroplex of Al(SCarq)₃ in our experiment was detected at a relative low electric field starting from 9.6 V across a film thickness of 85 nm.

According to the mechanism proposed in Fig. 6, the emission level of Al(SCarq)₃ at 572 nm (around 2.2 eV) in Fig. 5 is very close to the energy gap between the HOMO energy level of carbazolyl groups, -5.6 eV, and the LUMO energy level of the core, -3.3 eV. To verify the mechanism of exciplex and electroplex formation, a series of optical spectra thin films were measured and are shown in Fig. 7. Absorptions of Al(Saq)₃ and PVK in thin solid film are shown in Fig. 7a and b, respectively. Their absorptions appear at 381, 331, and 344 nm, respectively. The spectrum of Al(SCarq)₃, which structurally combines carbazolyl groups and Al(Saq)₃, can be observed not only the absorption of Al(Saq)₃ at 376 nm, but also a shoulder on the left side. This was generated from carbazoles at 332 and 346 nm, as shown in Fig. 7c. For further exploration, excitation was also measured to trace back the exciplex energy as shown in Fig. 7d. Clearly, the feature of this spectrum is very similar to that of Fig. 7c. In Fig. 7, however, the intensity of the excitation is much lower than that of the inherent absorption of Al(SCarq)₃. Evidently, partial carbazole moieties physically interact with the core and generate weak exciplex emission in photoluminescence, as shown in Fig. 3d. This result implies that the EL emission at 572 nm is partially contributed from exciplex, but mostly from the emission energy coming from the electrically induced complex emission under an applied voltage.

In other words, some exciplex emission coexists with electrophex during the electroluminescence process. As a result, EL emission mainly appears at 572 nm, as shown in Fig. 5.

4. Conclusion

We have developed a new class of spin-coatable metallo-complex, Al(SCarq)₃ via molecular engineering. The improved EL performance of Al(SCarq)₃ was also demonstrated compared with that of Al(Saq)₃. However, the electrophex was formed between carbazoles and the chromophoric core under the applied electric field, and then the EL was quenched and shifted to yellow. Based on our study, current efficiency and luminance could be further improved by increasing the steric hindrance of hole-transporting moiety to suppress exciplex formation. Accordingly, the development of this type of solution-processible material would be of interest to the OLED community for development of next generation small molecule fabrication technology.

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