Application of *N*,*N*,*N*′,*N*′-Tetrasubstituted 1,3-Bis(4-aminophenyl)azulenes to Hole-injecting Materials for Durable Organic EL Devices without Color Fade

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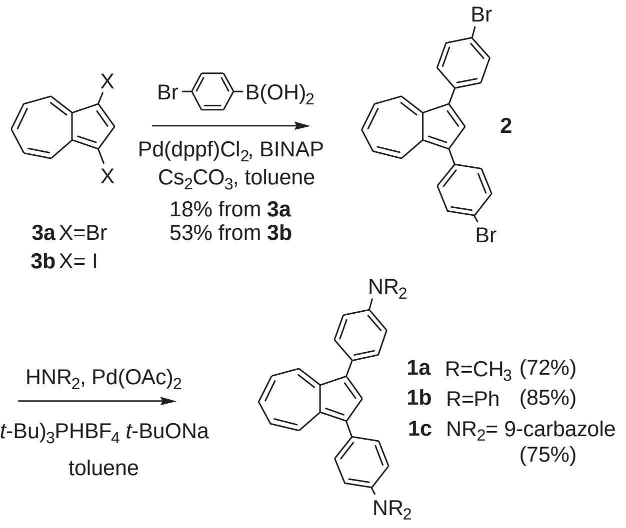
The title 1,3-bis(aminophenyl)azulenes were synthesized from 1,3-dihaloazulene in two steps involving the Suzuki cross-coupling with 4-bromophenylboronic acid and subsequent Pd-catalyzed amination. Their HOMO energy levels were estimated to be comparable to that of the widely used hole-injecting (HI) material, copper phthalocyanine. The application of these diamines to HL materials in organic electroluminescent (EL) devices was also studied as non-cyanine and non-polyamine substance.

Organic electroluminescent (organic EL) devices[1] have emerged as a propitious novel technology for the next generation of flat and thin panel displays, overcoming the drawbacks of contemporary electronic displays, such as low power-efficiency, narrow view angle, and a lack of brightness and flexibility. Recent interest in developing practical EL devices for long-term use with high power-efficiency is focused on those with a multi-layered structure which comprises hole-injecting, hole-transporting, light-emitting, hole-blocking, and electron-injecting layers between the indium–tin–oxide (ITO) electrode and the cathode. A hole-injecting layer (HIL) has been used to intermediate between the ITO electrode and a hole-injecting layer (HTL) to demonstrate higher operational half-life time compared with that without HIL.[2] Several materials, such as copper phthalocyanine (CuPc)[2a] and aryl-substituted tetraamine,[2b,2c] were reported for HIL mateials. Among these, CuPc was introduced by Kodak researchers and was a widely used material. However, CuPc itself has strong absorption in a visible light range so that the device containing it shows color fade, particularly at a range of 550–700 nm, depending on the thickness. In the meantime, azulene has relatively high HOMO and low LUMO energy levels and is colored, but its extinction coefficient for the visible absorption is small. Thus, we designed that CuPc could be replaced by an azulene derivative with less number of amino substituents. We herein report synthesis of the title diamine derivatives having an azulene as a core π-electron chromophore and their application to the HIL materials, which overcomes this shortcoming of CuPc, as a novel non-phthalocyanine and non-polyamine substance.

The diaminoazulene derivatives **3** were synthesized from 1,3-dihaloazulene by a straightforward way of Pd-catalyzed Suzuki coupling[3,4] with 4-bromophenylboronic acid and subsequent Pd-catalyzed amination reaction[5] (Scheme 1). The structures of **1a**–**1c** and **2** were characterized by spectroscopic and combustion analyses.[6] The yield of **2** with 1,3-diiodoazulene **3b** was much better than that with 1,3-dibromoazulene under the conditions with Pd(dppf)Cl$_2$, BINAP and Cs$_2$CO$_3$ in refluxing toluene.[7] Amination of **2** was achieved by the method of Fu et al. with amine, Pd(OAc)$_2$, (t-Bu)$_3$PHBF$_4$, and NaO-t-Bu[8] in good yields.[9] These azulenes **1a**–**1c** are green in color and have mainly two strong absorption bands at 230–250 and 320–350 nm, and the broad band at 600–650 nm. The latter band in a visible range have small extinction coefficients of ≈200 which are far weaker than that of CuPc. Oxidation potentials of **1a**–**1c** were measured by cyclic voltammetry in dichloromethane con-



Scheme 1.

Table 1. The oxidation potentials and estimated HOMO energy levels of CuPc and **1a**–**1c**

Compound	$E_{\mathrm{ox}1/2}$ (V vs Fc/Fc$^+$)[a] E^1_{ox}	E^2_{ox}	HOMO (eV)[b]
CuPc	0.46		5.3
1a	0.42	1.02	5.2
1b	0.38	0.94	5.2
1c	0.51	0.89	5.3

[a]Corrected values from the E_{ox} (V vs SCE) by substracting the E_{ox} value (0.48 V in dichloromethane, 0.50 V in *N*,*N*-dimethylformamide) of ferrocene in the same conditions. CuPc was measured in *N*,*N*-dimethylformamide and **1a**–**1c** were in dichloromethane. [b]HOMO energy values were obtained from oxidation potentials (E^1_{ox}) against ferrocene and calculated by taking the HOMO energy value of ferrocene to be 4.8 eV with respect to zero energy level.

taining 0.1 M tetrabutylammonium perchlorate. The HOMO energy levels of **1a**–**1c** were estimated from the first oxidation potentials ($E_{ox}{}^{1}$), which are comparable to that of CuPc (Table 1). It should be noted that the HOMO energy levels of **1a** and **1b** intermediate between those of HTL materials, such as TPD (5.4–5.5 eV),[10] α-NPD (5.4 eV)[11] and TPTE (5.3 eV),[12,13] and the work function of the ITO electrode (4.6–5.0 eV),[2d] and that of **1c** is the same as that of TPTE, suggesting that **1a**–**1c** can be used as HIL materials in organic EL devices.[14]

Transmittance of visible light through the thin films (10 nm) of **1a**–**1c** on quartz was compared with that of CuPc. While reduction of less than 15% of the initial light intensity in the 550–750 nm range through the film of **1a**–**1c** was observed, 20–30% of the light in the same range was diminished through the film of CuPc.[15] Indeed, color fade was not observed with the film of **1a**–**1c**, as expected from their visible absorption spectra. A preliminary application for EL devices was examined with the multilayered structure depicted in Figure 1. The initial characteristics and half-life time are shown in Table 2. Although the initial luminance with **1a**–**1c** was slightly lower than that with CuPc, the half-life time with **1a**–**1c** was much longer than that of CuPc. While operation with a low initial voltage retards degradation of a device in general,[1d] the device with **1a** unusually shows higher initial voltage and longer half-life time. Probably the relatively greater hole drift mobility of **1a** compared with those of **1b** and **1c**[16] may overcome its defect.

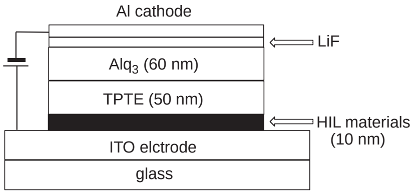


Figure 1. The organic EL architecture investigated.

Table 2. The characteristics of the EL devices with CuPc and **1a**–**1c** as HIL materials at 11 mA cm^{-2}

HIL materials	Initial luminance /cd cm^{-2}	Initial voltage /V	Half-life time/h
1a	578	8.42	630
1b	567	5.52	400
1c	543	5.09	600
CuPc	602	7.35	150

In summary we have prepared novel derivatives of 1,3-bis(aminophenyl)azulenes from 1,3-dihaloazulenes in two steps involving the Suzuki cross-coupling and Pd(OAc)$_2$-catalyzed amination and demonstrated that these compounds can be used as hole-injecting materials in EL devices with longer half-life time than the widely used CuPc and without color fade.

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6 Selected properties of **1a**: green microcrystals; mp 152–154 °C. ^{1}H NMR ($CDCl_3$) δ 3.00 (s, 12H), 6.91 (dm, $J = 8.6$ Hz, 4H), 7.03 (t, $J = 9.8$ Hz, 2H), 7.50 (dm, $J = 8.6$ Hz, 4H), 7.53 (t, $J = 9.8$ Hz, 1H), 8.02 (s, 1H), 8.44 (d, $J = 9.8$ Hz, 2H). UV–vis (CH_2Cl_2) λ max 236 ($\log \varepsilon = 4.42$), 279 (4.54), 312 (4.78), 384 (4.23), 657 (2.51). **1b**: green needles; mp 279–281 °C. ^{1}H NMR ($CDCl_3$) δ 7.04 (t, $J = 8.0$ Hz, 4H), 7.07 (t, $J = 10.0$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 8H), 7.21 (d, $J = 8.8$ Hz, 4H), 7.29 (t, $J = 8.0$ Hz, 8H), 7.51 (d, $J = 8.8$ Hz, 4H), 7.54 (t, $J = 10.0$ Hz, 4H), 8.09 (s, 1H), 8.53 (d, $J = 10.0$ Hz, 2H). UV–vis (CH_2Cl_2) λ max 230 ($\log \varepsilon = 4.53$), 244sh (4.51), 303 (4.71), 330 (4.71), 347sh (4.63), 395sh (4.63), 577sh (2.32), 636 (2.45), 698sh (2.33). **1c**: green needles; mp 261–263 °C. ^{1}H NMR ($CDCl_3$) δ 7.25 (t, $J = 9.8$ Hz, 2H), 7.33 (tm, $J = 7.7$ Hz, 4H), 7.47 (tm, $J = 7.7$ Hz, 4H), 7.58 (d, $J = 7.7$ Hz, 4H), 7.70 (t, $J = 9.8$ Hz, 1H), 7.75 (d, $J = 8.1$ Hz, 4H), 7.92 (d, $J = 8.1$ Hz, 4H), 8.19 (d, $J = 7.7$ Hz, 4H), 8.32 (s, 1H), 8.73 (d, $J = 9.8$ Hz, 2H). UV–vis (CH_2Cl_2) λ max 242 ($\log \varepsilon = 4.92$), 288sh (4.68), 294 (4.78), 316 (4.74), 337sh (4.49), 377 (4.05), 390sh (4.01), 407 (3.25), 462 (2.79), 584sh (2.15), 617 (2.27), 653sh (2.10).
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11 α-NPD is 4,4′-bis[*N*-(α-naphtyl)-*N*-phenylamino]biphenyl; the HOMO energy level was obtained from photoelectron measurements.
12 TPTE is 4,4′-bis{*N*-[*N*,*N*-di(*m*-tolyl)-4′-aminobiphenyl]-*N*-phenylamino}biphenyl; the HOMO energy level was obtained from photoelectron measurements.
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14 Since two methods for determining HOMO levels of the HIL and HTL materials are different from each other, comparison of the two HOMO levels is tentative so far.
15 Reduction of the transmittance with the 100 nm thick film of CuPc was much clear. Similarly, transmittance of visible light through the thin film (100 nm) of **1a**–**1c** on quartz was compared with CuPc. While only 20–30% of the light in the 500–800 nm range passed through the film of CuPc, more than 80% of the light in all of the visible range passed through the film of **1a**–**1c**.
16 Hole drift mobilities of **1a**–**1c** are 1.0×10^{-5}, 1.0×10^{-6}, and 1.0×10^{-6} cm^2 V^{-1} s^{-1}, respectively.