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Synthesis of N,N,N',N'-tetrasubstituted 1,3-bis(4-aminophenyl)azulenes and their application to a hole-injecting material in organic electroluminescent devices

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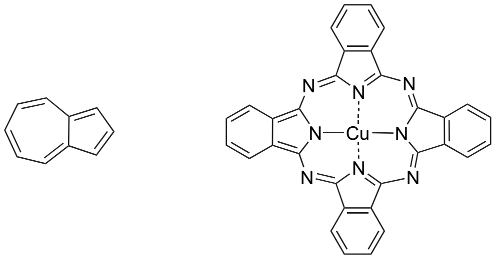
Abstract—After a preliminary search of the reaction conditions for the Suzuki–Miyaura cross-coupling of haloazulenes with arylboronic acids, the title compounds were synthesized either by the direct coupling reaction between 1,3-dihaloazulene and the corresponding *N*,*N*-disubstituted 4-aminophenylboronic acids or by a two-step sequence involving the cross-coupling with 4-bromophenylboronic acid and subsequent Pd-catalyzed amination. Application of the title diamines to a hole-injecting material in organic electroluminescent devices was carried out to provide their prominent characteristics as a novel durable, non-cyanine and non-polyamine substance without color fade. The diamine derivatives, extended by an ethynyl unit between the azulenyl core and the 4-aminophenyl moiety, were also synthesized and found, unfortunately, unsuitable for vacuum deposition in preparing a multilayer composite.

1. Introduction

Azulene (**1**) constructed by two odd membered rings, an isomer of naphthalene, appertains to a typical non-alternant hydrocarbon (Chart 1).[1] It appears blue in color because of its relatively narrow HOMO–LUMO gap and the reduced mutual repulsion between the unpaired electrons at the first excited state based on the nature of the coefficients of the HOMO and LUMO inherently accompanied with non-alternant hydrocarbons,[2] and the color has fascinated physical and synthetic organic chemists for a long time.[3] While azulene and its derivatives were used as anti-inflammatory and antiulcer agents extensively in the fields of medicinal chemistry for a long time,[4] their application in material science has been less pronounced despite their attractive color. There is only scattered literature on their applications in material science. There are some reports on azulene-containing polymers as a conductive material[5] and an amperometric biosensor,[6] azulene derivatives as non-linear optics[7] and near-infrared quencher.[8] Independently, we have studied the synthesis of the title azulene derivatives and applied them to a material in organic electroluminescent (organic EL) devices.[9]



azulene, 1 **CuPc, 2**

Chart 1.

Organic EL devices have received much attention in recent years because of their application in flat and thin panel displays, overcoming the drawbacks of contemporary electronic displays.[10,11] Recent interest in developing practical EL devices for long-term use with high power-efficiency is focused on those with a multilayered structure, which

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Keywords: Azulenes; Suzuki–Miyaura reaction; Amination; Organic electroluminescent device; Hole-injecting material.

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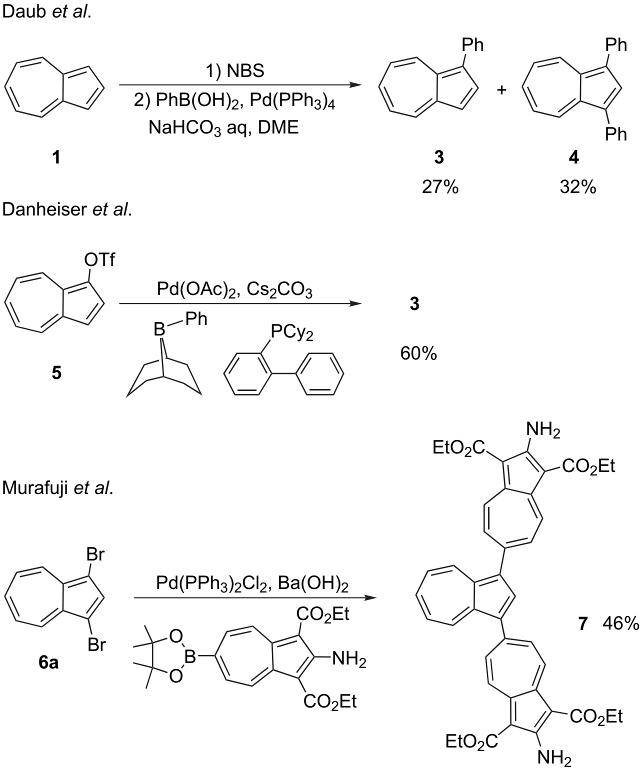
comprises hole-injecting, hole-transporting, light-emitting, hole-blocking, and electron-injecting layers between the indium-tin-oxide (ITO) electrode and the cathode. A hole-injecting layer (HIL) has been used to intermediate between the ITO electrode and a hole-transporting layer (HTL) to demonstrate greater operational half-life time compared with that without HIL.[12] Several materials, such as copper phthalocyanine (CuPc, **2**)[12c] and aryl-substituted tetraamine,[12a,b,e] were reported for this purpose. 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. Azulene has relatively high HOMO and low LUMO energy levels and is colored, but its extinction coefficient for visible absorption is small. Thus, we undertook a design where CuPc could be replaced by an azulene derivative with less number of amino substituents. In this paper, we disclose the synthetic study of the cross-coupling between haloazulenes and arylboronic acids, and describe the full detailed synthesis of the title diamines containing 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.

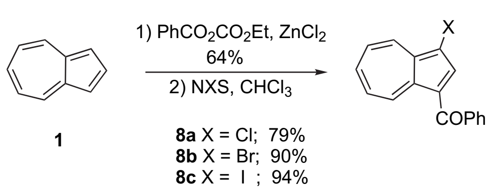
2. Results and discussion

2.1. Synthesis of 1-aryl-3-benzolylazulenes as preliminary experiments for the Suzuki–Miyaura cross-coupling reaction of haloazulenes

In 1997, Daub et al. reported the first example of the Suzuki–Miyaura cross-coupling reaction[13] of bromoazulenes (Scheme 1).[14] After bromination of azulene with *N*-bromosuccinimide, the products were subjected to the Suzuki–Miyaura cross-coupling reaction with phenylboronic acid and $Pd(PPh_3)_4$ as a catalyst to give a mixture of 1-phenyl- and 1,3-diphenylazulenes (**3** and **4**) in yields of 27 and 32%, respectively. Later, Danheiser et al. found efficient coupling with azulenyl triflate and *B*-phenyl-9-BBN[15] and Murafuji et al. disclosed the double cross-coupling of azulenylboronic acids and 1,3-dibromoazulene (**6a**) in better yields than that of **4** reported by Daub et al.,[16] though both methods required expensive reagents and the manipulation of azulene substrates and the yields were not necessarily satisfactory.[17] Since we focused on an efficient Suzuki–Miyaura coupling of 1,3-dihaloazulenes for the synthesis of HTL materials, we had begun with a preliminary search of the reaction conditions for the cross-coupling between haloazulenes and arylboronic acids. We chose 1-benzoyl-3-haloazulenes (**8**) as an initial substrate to avoid any obstacles on the process because an electron-withdrawing substituent like a benzoyl group is known to accelerate the oxidative addition of the palladium(0) reagent in Suzuki–Miyaura coupling. The substrates **8a**–**c** were prepared by halogenation of 1-benzoylazulene (**7**) with *N*-halosuccinimide (Scheme 2). We applied various reaction conditions with $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, and $Pd(dppf)Cl_2$[18] as a catalyst and phenylboronic acid for **8**. The results are shown in Table 1. At first, we used bromide **8b** as a substrate (entries 1–6). The reaction under the conditions with **8b**, $Pd(dppf)Cl_2$, BINAP, and Cs_2CO_3[19] (entry 5) provided the product **9** in a good yield, and iodide **8c** under the same conditions was transformed to **9** also in a good yield (entry 8) but not chloride **8a** (entry 7). Although, we applied the Fu's reaction conditions[20] for chloride **8a** with $Pd_2(dba)_3$,[21] $(t\text{-Bu})_3PHBF_4$, and CsF, the yield of **9** was as low as 20% (entry 9). We also examined the reactions of **8b** and **c** with various arylboronic acids under the conditions of the entries 5 and 8 in Table 1. The results are shown in Table 2. Satisfactory yields of the corresponding aryl-substituted products were found either from **8b** or **c**. The yields from **8c** were slightly better than those from **8b** except in the case of the 4-dibenzofurylboronic acid. With this knowledge of the satisfactory reaction conditions with $Pd(dppf)Cl_2$, BINAP, and Cs_2CO_3 in hand, synthesis of 1,3-diarylazulenes from 1,3-dihaloazulenes was undertaken next.



Scheme 1.

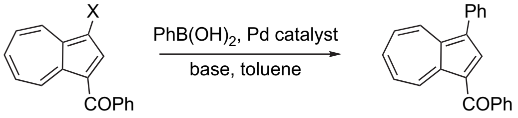


Scheme 2.

2.2. Synthesis of various 1,3-diarylazulenes including the title azulenes

From 1,3-dibromo- and 1,3-diiodoazulenes, **6a** and **b**, 1,3-diarylazulenes, **4** and **11**, were synthesized under the reaction conditions with $Pd(dppf)Cl_2$, BINAP, and Cs_2CO_3 (Table 3). In general the yields from iodide **6b** are better than those from bromide **6a** except in the case of the reaction

Table 1. The Suzuki–Miyaura cross-coupling of 1-benzoyl-3-haloazulenes with phenylboronic acid under various conditions



8a-c **9**

Entry	X (**8**)	Pd catalyst and additive[a]	Base[b]	Reaction time (h)[c]	Yield of **9** (%)[d]
1	Br (**8b**)	$Pd(PPh_3)_4$	Cs_2CO_3	2	55
2	Br (**8b**)	$Pd(PPh_3)_2Cl_2$, PPh_3	Cs_2CO_3	1	55
3	Br (**8b**)	$Pd(dppf)Cl_2$	Cs_2CO_3	16	74
4	Br (**8b**)	$Pd(dppf)Cl_2$	K_2CO_3	30	38
5	Br (**8b**)	$Pd(dppf)Cl_2$, BINAP	Cs_2CO_3	2	87
6	Br (**8b**)	$Pd(dppf)Cl_2$, BINAP	K_2CO_3	2	46
7	Cl (**8a**)	$Pd(dppf)Cl_2$, BINAP	Cs_2CO_3	4	40
8	I (**8c**)	$Pd(dppf)Cl_2$, BINAP	Cs_2CO_3	2	90
9	Cl (**8a**)	$Pd_2(dba)_3$, $(t\text{-Bu})_3PHBF_4$, CsF[e]	Cs_2CO_3	26	20

[a] Pd catalyst (5 mol %) and 2 equiv of phenylboronic acid to **8** were used.

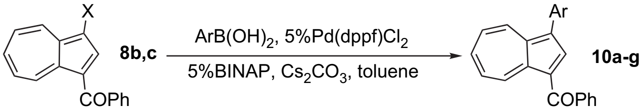
[b] Base (4 equiv) was used.

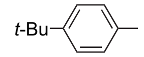
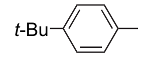
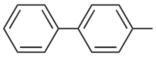
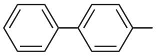
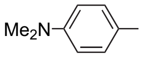
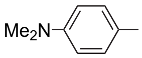
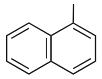
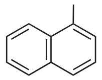
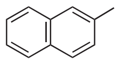
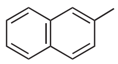
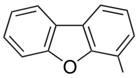
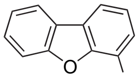
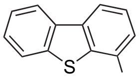
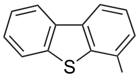
[c] Reaction was done in refluxing toluene.

[d] Isolated yield after chromatographic purification.

[e] Pd catalyst and the ligand (12 mol %), and 2 equiv of phenylboronic acid were used. The reaction was carried out at 90 °C in dioxane as a solvent.

Table 2. The Suzuki–Miyaura cross-coupling of 1-benzoyl-3-haloazulenes with various arylboronic acids under the conditions with $Pd(dppf)Cl_2$, BINAP, and Cs_2CO_3 in refluxing toluene[a]



Entry	X (**8**)	Ar	Reaction time (h)	Product	Yield (%)[b]
1	Br (**8b**)		3	**10a**	63
2	I (**8c**)		3	**10a**	74
3	Br (**8b**)		3	**10b**	89
4	I (**8c**)		3	**10b**	97
5	Br (**8b**)		3.5	**10c**	61
6	I (**8c**)		3.5	**10c**	65
7	Br (**8b**)		1.5	**10d**	81
8	I (**8c**)		1.5	**10d**	86
9	Br (**8b**)		1.5	**10e**	80
10	I (**8c**)		1.5	**10e**	92
11	Br (**8b**)		1	**10f**	86
12	I (**8c**)		1	**10f**	73
13	Br (**8b**)		1	**10g**	82
14	I (**8c**)		1	**10g**	83

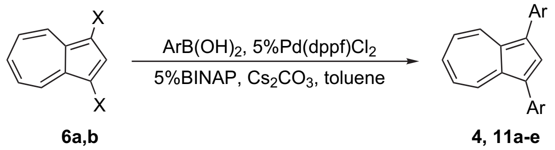
[a] Pd catalyst and BINAP (5 mol %), 2 equiv of arylboronic acid to **8**, and 4 equiv of Cs_2CO_3 were used.

[b] Isolated yield after chromatographic purification.

with 4-(*N*,*N*-dimethylamino)phenylboronic acid, which required a longer reaction time (entry 8). Although some yields of 1,3-diarylazulenes **11** from **6b** (entries 2, 6, and 10) were good, other yields were relatively low. In these double Suzuki–Miyaura reactions, thus, the second couplings are assumed to be comparatively deactivated by the first aryl substituents.

We obtained the amine-substituted 1,3-diphenylazulene derivatives **11c–e**, all of which we had designed as primitive hole-injecting materials. For these diamines, we also applied a stepwise method, which involves the cross-coupling with 4-bromophenylboronic acid (**12**) and subsequent Pd-catalyzed amination (Scheme 3). The synthetic intermediate, 1,3-bis(4-bromophenyl)azulene (**11f**), was prepared by the Suzuki–Miyaura coupling under similar reaction conditions in 18% yield from **6a** or 53% yield from **6b**. The amination[22] of **11f** using $Pd(OAc)_2$ as a catalyst was carried out under Fu's reaction conditions with $(t\text{-Bu})_3PHBF_4$ as a ligand and *t*-BuONa as a base in toluene.[20] In a case where volatile dimethylamine was used, the reaction was carried out in a sealed tube to give 72% yield of **11c**. Other derivatives,

Table 3. The Suzuki–Miyaura cross-coupling of 1,3-dihaloazulenes with various arylboronic acids under the conditions with Pd(dppf)Cl_2, BINAP, and Cs_2CO_3 in refluxing toluene[a]



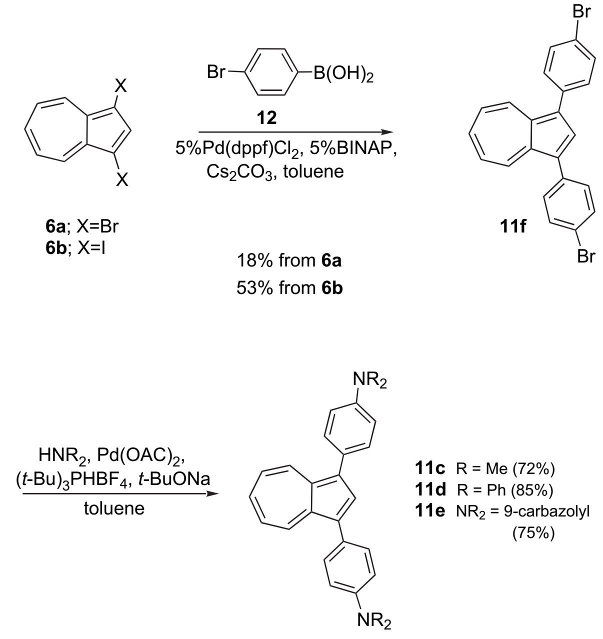
Entry	X (**6**)	Ar	Reaction time (h)	Product	Yield of **9** (%)[b]
1	Br (**6a**)	Ph–	2	**4**	61
2	I (**6b**)	Ph–	2	**4**	90
3	Br (**6a**)	4-Ph–C_6H_4–	3	**11a**	7
4	I (**6b**)	4-Ph–C_6H_4–	4	**11a**	35
5	Br (**6a**)	1-Naphthyl–	2	**11b**	43
6	I (**6b**)	2-Naphthyl–	2	**11b**	75
7	Br (**6a**)	4-(Me_2N)–C_6H_4–	24	**11c**	23
8	I (**6b**)	4-(Me_2N)–C_6H_4–	24	**11c**	10
9	Br (**6a**)	4-(Ph_2N)–C_6H_4–	2	**11d**	40
10	I (**6b**)	4-(Ph_2N)–C_6H_4–	1	**11d**	80
11	Br (**6a**)	4-Cz–C_6H_4–[c]	2	**11e**	22
12	I (**6b**)	4-Cz–C_6H_4–[c]	2	**11e**	24

[a] Pd catalyst and BINAP (5 mol %), 3 equiv of arylboronic acid to **6**, and 4 equiv of base were used.

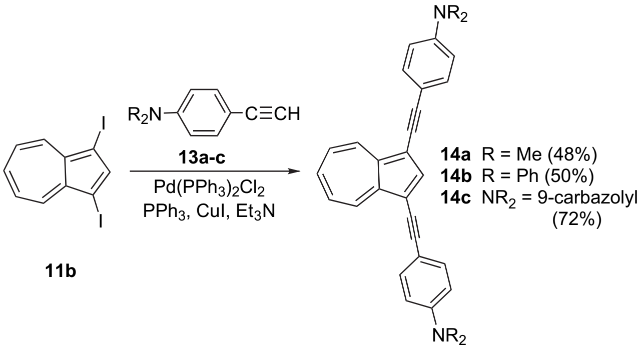
[b] Isolated yield after chromatographic purification.

[c] Cz means a 9-carbazolyl group.

11d and **11e**, were obtained with the corresponding amines by conventional heating under atmosphere of argon in 85 and 75% yields, respectively. Although the two-step yields are not attractive as compared with those of the direct method, the amination can provide a divergent protocol for preparing a variety of the amine derivatives from a single intermediate. We also prepared similar diamine derivatives, **14a–c**, which are extended by an ethynyl unit between phenyl and the azulene moieties, by the Sonogashira reaction[23] of **11b** with the corresponding acetylene compounds, **13a–c**, as shown in Scheme 4.



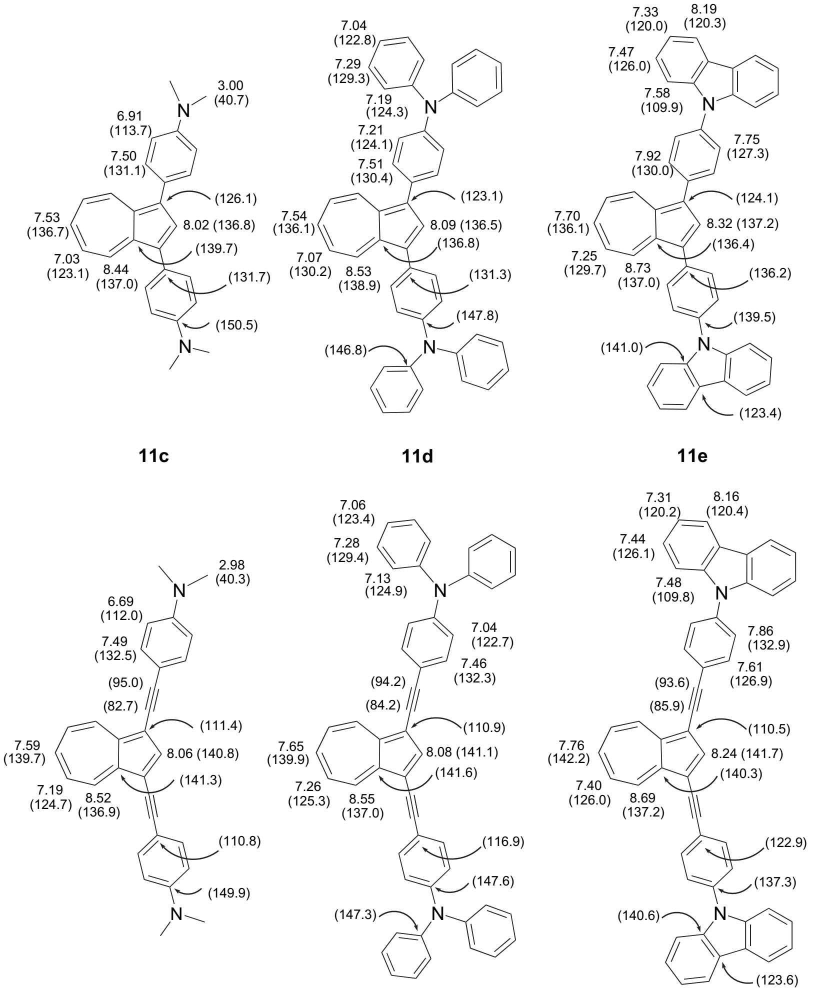
Scheme 3.



Scheme 4.

2.3. Structure and physical properties of *N,N,N′,N′*-tetrasubstituted 1,3-bis(4-aminophenyl)- and 1,3-bis(4-aminophenylethynyl)azulenes

The structures of three *N,N,N′,N′*-tetrasubstituted 1,3-bis(4-aminophenyl)azulenes and three *N,N,N′,N′*-tetrasubstituted 1,3-bis(4-aminophenylethynyl)azulenes were characterized by spectroscopic and combustion analyses. Signals in the ^1H and ^{13}C NMR spectra were assigned by correlations based on their two-dimensional H–H COSY, NOESY, HMQC, and HMBC spectra; the results are shown in Figure 1. A higher field shift of azulenyl protons in the ^1H NMR spectra of **11c** and **14a** compared with those of the others may be ascribed to a stronger electron-donating effect of the dimethylamino group. All of them were isolated as green solids and have mainly three strong absorption bands at 230–250, 320–350, and 370–410 nm, and a broad band at 600–700 nm. The latter band in a visible range has small extinction coefficients of ≈200, which are far weaker than that of CuPc. The results are promising for overcoming the color fade observed in the device using CuPc (vide infra). Electrochemical oxidation of **11c–e** and **14a–c** was examined by cyclic voltammetry in dichloromethane containing 0.1 M tetrabutylammonium perchlorate. The diamines **11c–e** showed two oxidation potentials ($E_{ox}{}^1$ and $E_{ox}{}^2$) and the differences between them are more than 0.38 V, which are large enough for the purpose of organic EL applications. The diamines **14b**,**c** were very sensitive to electrochemical oxidation. While diamines **14b**,**c** provided quasi-reversible voltammograms with one oxidation potential,[24] the diamine **14a** did not show any clear oxidation potential in its voltammogram and a significant amount of an insoluble substance was observed at the electrode surface after scans. The HOMO energy levels of these compounds were estimated from the first oxidation potentials (Table 4).[25] Those of **11c** and **d** are slightly less than that of CuPc, that of **11e** is the same, and those of **14b**,**c** are slightly greater. It should be noted that the HOMO energy levels of **11c** and **d** intermediate between those of HTL materials, such as TPD (5.4–5.5 eV),[26] α-NPD (5.4 eV),[27] TPTE (5.3 eV),[28,29] and the work function of the ITO electrode (4.6–5.0 eV),[12b] and that of **11e** is the same as that of TPTE, suggesting that these compounds can be used as HIL materials in organic EL devices (Chart 2).[30] Since the diamine derivatives, **14a–c**, were found to decompose during vacuum deposition in OLED fabrication besides possessing slightly greater HOMO energy levels than some of the HTL materials, only the derivatives, **11c–e**, were further examined for application to HIL material.



11c **11d** **11e**

14a **14b** **14c**

Figure 1. Assignment of ^{1}H and ^{13}C chemical shifts. Carbon shifts are in parentheses.

2.4. Application of *N*,*N*,*N*′,*N*′-tetrasubstituted 1,3-bis(4-aminophenyl)azulenes as a hole-injecting material in organic EL devices

Transmittance of visible light through the films of **11c–e** on quartz was first examined. Reduction of the transmittance with the 100 nm film of CuPc was very clear. Similarly, transmittance of visible light through the thin film (100 nm) of **11c–e** on quartz was compared with that of 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 **11c–e**. A thinner film was also examined; reduction of less than 15% of the initial light in the range through the thin film (10 nm) of **11c–e** was observed, 20–30% of the light was diminished through that of CuPc. As expected from their visible absorption spectra, indeed color fade was not observed with the thin film of **11c–e**. Then, an application for EL devices was investigated with the multilayered structure **A**, which emits green light, depicted in Figure 2. The initial characteristics, the CIE chromatocity coordinate, EL peak, and half-life time are shown in Table 5. There is no clear difference in CIE chromatocity coordinate and EL peak between the HIL materials. Although, the initial luminance with **11c–e** was slightly lower than that with CuPc, the half-life time with **11c–e** was much longer than that of CuPc. While operation with a low initial voltage retards degradation of a device in general,[12d] the device with **11c** unusually shows higher initial voltage and longer half-life time. Probably the relatively greater hole drift mobility of **11c** compared with those of **11d** and **e**[31] may overcome its defect. Since reduction of

Table 4. Oxidation potentials and estimated HOMO energy levels of CuPc, **11c–e**, and **14a–c**

Compounds	$E_{\mathrm{ox}\ 1/2}$ (V vs Fc/Fc^{+})[a]		HOMO (eV)[b]
	$E_{\mathrm{ox}}{}^{1}$	$E_{\mathrm{ox}}{}^{2}$	
CuPc	0.46		5.3
11c	0.42	1.02	5.2
11d	0.38	0.94	5.2
11e	0.51	0.89	5.3
14a	—[c]	—[c]	—
14b	0.62	—[c]	5.4
14c	0.55	—[c]	5.4

[a] Corrected values from the E_{ox} (V vs SCE) by subtracting the E_{ox} value of ferrocene (0.48 V in dichloromethane, 0.50 V in *N*,*N*-dimethylformamide) in the same conditions. CuPc was measured in *N*,*N*-dimethylformamide and others were in dichloromethane.

[b] HOMO energy values were obtained from oxidation potentials ($E_{\mathrm{ox}}{}^{1}$) against the value of ferrocene and calculated by taking the HOMO energy value of ferrocene to be 4.8 eV with respect to zero energy level.

[c] E_{ox} was not clearly observed.

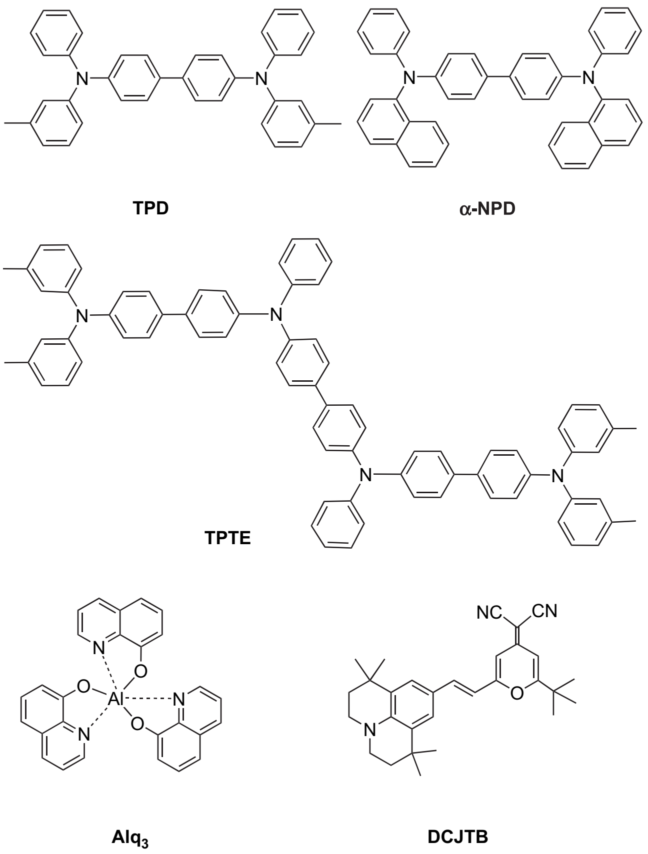


Chart 2. Structures of the dopant and hole-transporting and light-emitting materials used in our study.

light at a range of 500–800 nm through the thin films of **11c–e** was clearly shown, we also examined another multilayered structure **B**, which emitted the orange light by using DCJTB[32] as a dopant, depicted in Figure 2. The characteristics of the luminescence are shown in Table 6. Although we have not checked the half-life time with this structure, the device with **11c** indicated the most effective performance among them. With these results in hand, we now are advancing to the development of a more practical application, which will be reported elsewhere in due course.

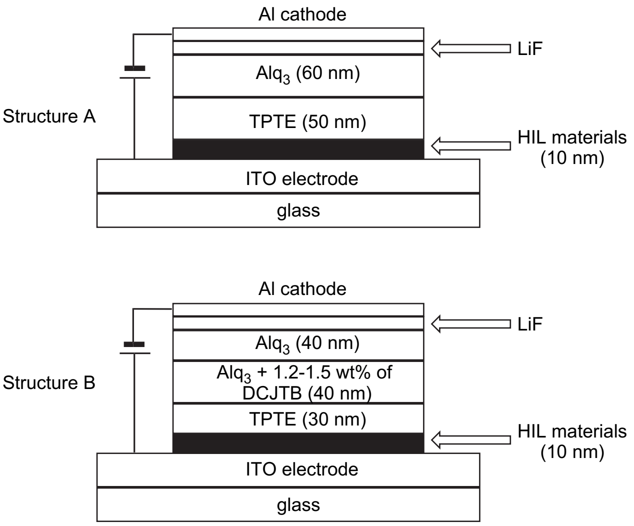


Figure 2. The investigated organic EL architectures.

Table 5. The characteristics of the EL devices (structure **A**) with CuPc and **11c–e** as HIL materials at 11 mA cm^{-2}

HIL materials	Initial luminance (cd cm^{-2})	Initial voltage (eV)	CIE[a] chromaticity coordinates		EL peak (nm)	Half-life time (h)
			x	y		
11c	578	8.42	0.336	0.524	526	630
11d	567	5.52	0.356	0.531	535	400
11e	543	5.09	0.355	0.534	538	600
CuPc	602	7.35	0.335	0.534	533	150

[a] Commission Internationale de L'Éclairage.

Table 6. The characteristics of the EL devices (structure **B**) with CuPc and **11c–e** as HIL materials at 11 mA cm^{-2}

HIL materials	Initial luminance (cd cm^{-2})	Initial voltage (eV)	CIE[a] chromaticity coordinates		EL peak (nm)
			x	y	
11c	444	9.95	0.610	0.379	620
11d	238	10.05	0.619	0.373	621
11e	299	6.71	0.609	0.384	614
CuPc	221	8.11	0.617	0.375	618

[a] Commission Internationale de L'Éclairage.

3. Summary

After a preliminary search of the reaction conditions for the Suzuki–Miyaura cross-coupling of haloazulenes with various arylboronic acids, bases, palladium catalysts, and additive ligands, the title compounds have been synthesized in moderate yields either by the direct coupling reaction between 1,3-dihaloazulene and the corresponding *N*,*N*-disubstituted 4-aminophenylboronic acids under the conditions with Pd(dppf)Cl_2, BINAP, and Cs_2CO_3 in refluxing toluene or by a two-step sequence involving the cross-coupling with 4-bromophenylboronic acid and subsequent Pd$(OAc)_2$-catalyzed amination with $(t\text{-Bu})_3PHBF_4$ and *t*-BuONa. We have also synthesized the derivatives extended by an ethynyl group between the azulenyl core and the aminophenyl group, *N*,*N*,*N*′,*N*′-tetrasubstituted 1,3-bis(4-aminophenylethynyl)azulenes **14a–c**, as a candidate for HIL material. Unfortunately, the latter derivatives were not appropriate for a fabrication process by vacuum deposition. Application of these title diamines, **11c–e**, to HIL material in organic electroluminescent devices was made to provide their prominent characteristics as a novel durable, non-cyanine, and non-polyamine substance without color fade.

4. Experimental

4.1. General

Melting points were measured on a Yanaco MP-3 and are uncorrected. IR spectra were recorded on a Perkin–Elmer Spectrum RX I spectrometer. UV spectra were measured on a Shimadzu UV-1600 spectrometer. ^1H and ^{13}C NMR were recorded with tetramethylsilane as an internal standard on a JEOL α400 or JEOL δECP-600 NMR. Mass spectra were measured on a JMS-700 mass spectrometer. Cyclic voltammograms were recorded on a Yanako P1100 instrument. Column chromatography was done with either Merck Kieselgel 60 Art 7734 or Wako Activated alumina. Toluene was purified by distillation from calcium hydride under a nitrogen atmosphere. Diphenylamine, dimethylamine aqueous solution, and carbazole were purchased from Tokyo Kasei Ind. Co., cesium carbonate was purchased from Kanto Chem. Inc., and BINAP (*rac*-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl), tetrakis(triphenylphosphine)palladium, bis-(triphenylphosphine)palladium dichloride, tris(dibenzylideneacetone)dipalladium, and [1,1′-bis(diphenylphosphino)-ferrocene]dichloropalladium (1:1 complex with dichloromethane) were purchased from Aldrich Co. and were used without purification. Various arylboronic acids were also purchased from Aldrich Co., except 4-[9-(carbazolyl)]-phenylboronic acid, which was prepared by the reported method.[33] Sodium *tert*-butoxide, palladium acetate, and copper iodide were purchased from Wako Chem. Co. and were used without purification. The ethynyl compounds **13a**,[34] **b**,[35] and **c**[36] were prepared from disubstituted 4-haloanilines by palladium-catalyzed Sonogashira coupling with trimethylsilylacetylene, followed by deprotection with K_2CO_3 in methanol according to their reported methods.[37] 1,3-Dihaloazulenes, **6a** and **b**, were prepared from azulene with *N*-iodo- and *N*-bromosuccinimides according to a literature procedure[38] and were purified by alumina chromatography before use.

4.2. Synthesis of 1-benzoyl-3-haloazulenes (8)

To a solution of 1-benzoylazulene (2.00 mmol), prepared by the method of Sugihara et al.,[39] in 10 ml of chloroform at 0 °C was added 3.00 mmol of *N*-halosuccinimide in several portions. After being stirred at 40 °C for 3 h, the reaction mixture was concentrated and the residue was purified by alumina column chromatography. Elution with chloroform–hexane (3:7) gave **8** as solids. Analytical samples were obtained by recrystallization from hexane–dichloromethane. Compound **8a** (X=Cl) (79%): green solids, mp 70–72 °C. ^{1}H NMR ($CDCl_3$) δ=9.69 (d, J=9.8 Hz, 1H), 8.59 (d, J=9.8 Hz, 1H), 7.97 (s, 1H), 7.91 (t, J=9.8 Hz, 1H), 7.84–7.81 (dm, J=6.8 Hz, 2H), 7.67–7.56 (m, 3H), 7.53–7.49 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$) δ=192.0, 140.9, 140.7, 140.0, 139.9, 139.7, 138.6, 136.2, 131.4, 129.5, 129.4, 128.2, 127.9, 122.5, 116.9; IR (KBr) ν_{max}=1655m, 1627s, 1595s, 1576m, 1561w, 1543m, 1525w, 1508w, 1498m, 1476w, 1458m, 1449w, 1417s, 1385s, 1342m, 1288m, 1237s, 1179, 1119w, 1026w, 977w, 958w, 919w, 867w, 801w, 781m, 742s, 706s, 671m, 637m, 587w, 565w cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}=242 (log ε=4.46), 280 (4.44), 317 (4.59), 393 (4.15), 406sh (4.14), 559 (2.88), 562 (2.88), 608sh (2.74), 650 (2.30) nm; MS (70 eV) *m/z* (rel int): 268 (M^+, 27), 267 (M^+−1, 17), 266 (M^+, 81), 265 (M^+−1, 6), 231 (M^+−1, 12), 202 (15), 191 (32), 190 (12), 189 (100), 161 (17), 126 (40). Anal. Calcd for $C_{17}H_{11}ClO$: C, 76.55; H, 4.16. Found: C, 76.78; H, 4.30.

Compound **8b** (X=Br) (90%): green microprizms, mp 93–96 °C (lit.[40] 88 °C). ^{1}H NMR ($CDCl_3$) δ=9.70 (d, J=10.0 Hz, 1H), 8.57 (d, J=10.0 Hz, 1H), 8.05 (s, 1H), 7.92 (t, J=10.0 Hz, 1H), 7.84–7.82 (dm, J=6.8 Hz, 2H), 7.67–7.57 (m, 3H), 7.53–7.49 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$) δ=191.9, 142.8, 140.8, 140.74, 140.71, 140.4, 139.6, 137.9, 131.5, 129.6, 129.5, 128.2, 127.9, 123.9, 104.6; IR (KBr) ν_{max}=1625s, 1594s, 1574s, 1533m, 1492s, 1456s, 1414m, 1379m, 1333m, 1285m, 1236m, 1178m, 1116m, 1072w, 1024m, 977w, 956w, 932w, 904m, 866m, 854m, 800m cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}=236 (log ε=4.42), 244 (4.45), 274sh (4.40), 282 (4.44), 307sh (4.51), 318 (4.57), 393 (4.11), 404 (4.10), 521sh (2.64), 555 (2.72), 581sh (2.66), 662sh (2.07) nm; MS (70 eV) *m/z* (rel int): 313 (M^++1, 18), 312 (M^+, 95), 311 (M^++1, 22), 310 (M^+, 100), 235 (90), 233 (91), 207 (10), 205 (11), 126 (84), 77 (19).

Compound **8c** (X=I) (94%): green solids, mp 109–111 °C. ^{1}H NMR ($CDCl_3$) δ=9.68 (d, J=9.8 Hz, 1H), 8.49 (d, J=9.8 Hz, 1H), 8.17 (s, 1H), 7.93 (t, J=9.8 Hz, 1H), 7.84–7.81 (dm, J=6.8 Hz, 2H), 7.72–7.56 (m, 3H), 7.53–7.49 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$) δ=191.9, 148.8, 144.1, 141.5, 140.7 (2C), 140.5, 138.8, 131.5, 129.9, 129.5, 128.3, 128.2, 126.3, 75.3; IR (KBr) ν_{max}=1654w, 1636w, 1616s, 1588w, 1573m, 1545w, 1529m, 1509w, 1491m, 1447m, 1414m, 1364m, 1329w, 1282m, 1233m, 1173w, 1129w, 1079w, 1036w, 1019m, 953w, 929w, 898m, 875w, 859s, 795w, 775m, 747s, 732w, 703m, 665m, 619w cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}=231 (log ε=4.53), 284 (4.50), 321 (4.58), 395 (4.15), 407 (4.15), 413 (3.97), 552 (2.90), 590sh (2.82), 638sh (2.28) nm; MS (70 eV) *m/z* (rel int): 358 (M^+, 100), 282 (10), 281 (86), 253 (10), 202 (18), 126 (49), 77 (12). Anal. Calcd for $C_{17}H_{11}IO$: C, 57.01; H, 3.10. Found: C, 57.37; H, 3.25.

4.3. The Suzuki–Miyaura cross-coupling reactions of 1-benzoyl-3-haloazulenes (8)

A mixture of **8** (0.300 mmol), Cs_2CO_3 (1.20 mmol), and arylboronic acid (0.600 mmol) in 10 ml of toluene was evacuated well. And either 0.015 mmol of the palladium catalyst or the same amount of both the palladium catalyst and an additive was added to the mixture. The flask was evacuated and refilled with argon five times. The mixture was heated at 110 °C until the halogen substrate was almost consumed. Then the resulting reaction mixture was poured into water and extracted with ether (30 ml×3). The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel to give the product.

Compound **9** (90%): 1-benzoyl-3-phenylazulene, dark purple microcrystals, mp 187–191 °C. ^{1}H NMR ($CDCl_3$) δ=9.77 (d, J=10.0 Hz, 1H), 9.71 (d, J=10.0 Hz, 1H), 8.17 (s, 1H), 7.90–7.84 (m, 3H), 7.66–7.47 (m, 9H), 7.34 (m, J=7.4 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$) δ=192.9, 142.2, 142.3, 141.3, 140.6, 140.3, 139.6, 137.3, 136.3, 131.2, 130.8, 129.7, 129.6, 129.1, 128.7, 128.1, 127.7, 127.0, 123.9 ppm; IR (KBr) ν_{max}=3050w, 3022w, 1617, 1594s, 1571s, 1524s, 1490s, 1421m, 1390m, 1365m, 1303w, 1236s, 1177w, 1113w, 1074w, 1018m, 910m, 894m cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}=238 (log ε=4.36), 256 (4.36), 296 (4.53), 316 (4.45), 407 (3.99), 515 (2.56), 556 (2.66), 600 (2.55) nm; MS (70 eV) *m/z* (rel int): 309 (M^++1, 24), 308

(M$^+$, 100), 232 (11), 231 (62), 203 (10), 202 (45), 126 (3), 77 (5). Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 89.48; H, 5.44.

Compound **10a** (74%): 1-benzoyl-3-(4-*tert*-butylphenyl)-azulene, green solids, mp 155–158 °C. ^{1}H NMR ($CDCl_3$) δ=9.75 (d, *J*=9.8 Hz, 1H), 8.74 (d, *J*=9.8 Hz, 1H), 8.16 (s, 1H), 7.88 (d, *J*=8.4 Hz, 2H), 7.85 (t, *J*=9.2 Hz, 1H), 7.62 (t, *J*=9.8 Hz, 1H), 7.58–7.45 (m, 4H), 7.52 (s, 4H), 1.39 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$) δ=192.9, 150.0, 142.43, 142.40, 141.3, 140.6, 140.2, 139.5, 137.4, 133.4, 131.2, 130.8, 129.6, 129.4, 129.0, 128.1, 127.6, 125.7, 123.8, 34.6, 31.4 ppm; UV–vis (CH_2Cl_2) λ_{max}=236 (log ε=4.44), 258 (4.40), 284 (4.50), 297 (4.58), 320 (4.46), 410 (4.03), 522 (2.60), 561 (2.69), 614 (2.52) nm; IR (KBr) ν_{max}=3023w, 2962w, 2868w, 1619s, 1595m, 1574m, 1531m, 1501m, 1446s, 1423s, 1389s, 1368s, 1299m, 1269m, 1235s, 1187m, 1174m, 1157m, 1099m, 1018m, 913m, 872m, 840s, 802s, 745s, 699s, 639s, 571m cm^{-1}; MS (70 eV) *m*/*z* (rel int): 365 (M$^+$+1, 29), 364 (M$^+$, 100), 350 (19), 349 (63), 287 (8), 257 (9), 228 (6), 202 (11), 105 (23), 77 (9). Anal. Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 88.80; H, 6.79.

Compound **10b** (97%): 1-benzoyl-3-(4-biphenylyl)azulene, dark green needless, mp 133–136 °C. ^{1}H NMR ($CDCl_3$) δ=9.78 (d, *J*=9.8 Hz, 1H), 8.77 (d, *J*=9.8 Hz, 1H), 8.21 (s, 1H), 7.90 (d, *J*=7.4 Hz, 2H), 7.88 (t, *J*=9.8 Hz, 1H), 7.74 (d, *J*=8.4 Hz, 2H), 7.62–7.69 (m, 5H), 7.46–7.60 (m, 6H), 7.38 (tm, *J*=7.4 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$) δ=192.9, 142.6, 142.3, 141.2, 140.7, 146.0, 140.4, 139.8, 139.6, 137.4, 135.3, 131.3, 130.3, 130.1, 129.6, 129.2, 128.9, 128.2, 127.8, 127.5, 127.4, 127.1, 124.0 ppm; UV–vis (CH_2Cl_2) λ_{max}=237sh (log ε=4.49), 244 (4.52), 309 (4.72), 409 (4.04), 516sh (2.58), 560 (2.65), 610sh (2.54) nm; IR (KBr) ν_{max}=3054w, 3029w, 2925w, 2852w, 1618s, 1596m, 1576m, 1531w, 1509w, 1488w, 1446m, 1424s, 1388m, 1361m, 1238s, 1184w, 1159w, 1019w, 913m, 846m, 807m, 766m, 746s, 727m, 696s, 656m cm^{-1}; MS (70 eV) *m*/*z* (rel int): 385 (M$^+$+1, 34), 384 (M$^+$, 100), 307 (44), 278 (19), 277 (17), 276 (20), 252 (6), 202 (10), 138 (3), 77 (7). Anal. Calcd for $C_{29}H_{20}NO$: C, 90.60; H, 5.24. Found: C, 90.52; H, 5.39.

Compound **10c** (65%): 1-benzoyl-3-{4-(*N*,*N*-dimethylamino)phenyl}azulene, brown solids, mp 146–149 °C. ^{1}H NMR ($CDCl_3$) δ=9.70 (d, *J*=9.6 Hz, 1H), 8.68 (d, *J*=9.6 Hz, 1H), 8.12 (s, 1H), 7.88 (d, *J*=6.8 Hz, 2H), 7.79 (t, *J*=9.6 Hz, 1H), 7.58–7.67 (m, 7H), 6.88 (d, *J*=6.8 Hz, 2H), 3.02 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$) δ=192.3, 150.8, 142.8, 142.3, 142.1, 141.4, 140.7, 139.7, 138.4, 132.1, 131.9, 131.0, 130.2, 129.3, 129.0, 128.2, 127.2, 124.4, 113.6, 40.6 ppm; UV–vis (CH_2Cl_2) λ_{max}=229 (log ε=4.35), 248 (4.38), 300 (4.63), 322 (4.75), 423 (3.86), 578 (2.65) nm; IR (KBr) ν_{max}=3022w, 2886w, 2803w, 1610s, 1573m, 1540s, 1507m, 1447m, 1420s, 1388s, 1349s, 1237s, 1200m, 1161m, 1019m, 945m, 912m, 823s cm^{-1}; MS (70 eV) *m*/*z* (rel int): 352 (M$^+$+1, 39), 351 (M$^+$, 100), 274 (11), 258 (7), 246 (7), 231 (6), 202 (28), 137 (9), 105 (8), 77 (11). Anal. Calcd for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99. Found: C, 85.36; H, 6.11; N, 4.07.

Compound **10d** (86%): 1-benzoyl-3-(1-naphthyl)azulene, purple solids, mp 180–182 °C. ^{1}H NMR ($CDCl_3$) δ=9.86 (d, *J*=9.7 Hz, 1H), 8.28 (d, *J*=9.7 Hz, 1H), 8.22 (s, 1H), 7.96–7.90 (m, 4H), 7.86 (t, *J*=9.7 Hz, 1H), 7.69 (t, *J*=9.7 Hz, 1H), 7.66 (d, *J*=8.8 Hz, 1H), 7.61–7.46 (m, 6H), 7.35–7.43 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$) δ=192.9, 144.0, 142.5, 142.1, 141.2, 140.2, 139.6, 137.7, 134.0, 133.8, 132.9, 131.2, 129.6, 129.3, 129.0, 128.7, 128.4, 128.1, 127.9, 127.7, 126.2, 126.1, 125.9, 125.4, 123.8 ppm; UV–vis (CH_2Cl_2) λ_{max}=233 (log ε=4.68), 247sh (4.61), 279 (4.62), 297sh (4.62), 304sh (4.67), 315 (4.71), 388sh (4.12), 405 (4.17), 514sh (2.70), 550 (2.82), 602sh (2.65) nm; IR (KBr) ν_{max}=3049w, 2370w, 2344w, 1621s, 1586m, 1574m, 1520m, 1425s, 1375s, 1303m, 1259m, 1236s, 1161m, 1132m, 1006m, 908m, 821s, 809s, 780m, 748s, 711m, 699m, 660m cm^{-1}; MS (70 eV) *m*/*z* (rel int): 359 (M$^+$+1, 43), 358 (M$^+$, 100), 281 (48), 253 (35), 252 (75), 126 (10), 105 (6), 77 (7). Anal. Calcd for $C_{27}H_{18}O$: C, 90.47; H, 5.06. Found: C, 90.25; H, 5.33.

Compound **10e** (92%): 1-benzoyl-3-(2-naphthyl)azulene, dark purple plates, mp 116–118 °C. ^{1}H NMR ($CDCl_3$) δ=9.79 (d, *J*=10.0 Hz, 1H), 8.80 (d, *J*=10.0 Hz, 1H), 8.27 (s, 1H), 8.02 (s, 1H), 7.96 (d, *J*=8.8 Hz, 1H), 7.93–7.86 (m, 5H), 7.71 (dd, *J*=8.4, 1.6 Hz, 1H), 7.65 (t, *J*=10.0 Hz, 1H), 7.59–7.49 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$) δ=192.9, 142.5, 141.3, 140.8, 140.4, 139.7, 137.4, 133.8, 133.6, 132.4, 131.3, 130.8, 129.6, 128.4, 128.2, 128.1, 127.9, 127.8, 126.4, 126.0, 124.0 ppm; UV–vis (CH_2Cl_2) λ_{max}=229 (log ε=4.17), 256 (3.81), 290 (4.05), 304sh (4.02), 317 (3.99), 393sh (4.02), 398 (4.55), 409 (3.56), 516 (2.63), 518sh (2.65), 552 (2.71), 602 (2.55), 611sh (2.59), 749 (0.752) nm; IR (KBr) ν_{max}=3051w, 2371w, 2343w, 1615s, 1594m, 1572m, 1524m, 1501m, 1444m, 1421s, 1393s, 1332m, 1304m, 1234s, 1203m, 1176m, 1016m, 957m, 920m, 863m, 833s, 747s, 709s, 662s, 639m, 572m cm^{-1}; MS (70 eV) *m*/*z* (rel int): 359 (M$^+$+1, 29), 358 (M$^+$, 100), 281 (49), 253 (18), 252 (54), 126 (10), 77 (7). Anal. Calcd for $C_{27}H_{18}O$: C, 90.47; H, 5.06. Found: C, 90.27; H, 5.27.

Compound **10f** (86%): 1-benzoyl-3-(4-dibenzofuryl)azulene, purple plates, mp 204–205 °C. ^{1}H NMR ($CDCl_3$) δ=9.85 (d, *J*=9.9 Hz, 1H), 8.63 (d, *J*=9.9 Hz, 1H), 8.43 (s, 1H), 8.01 (d, *J*=7.7 Hz, 1H), 7.99 (d, *J*=7.5 Hz, 1H), 7.96 (d, *J*=7.5 Hz, 2H), 7.89 (t, *J*=9.9 Hz, 1H), 7.69 (t, *J*=9.9 Hz, 1H), 7.62 (d, *J*=7.5 Hz, 1H), 7.56 (t, *J*=7.5 Hz, 1H), 7.52–7.46 (m, 5H), 7.44 (t, *J*=7.5 Hz, 1H), 7.37 (t, *J*=7.5 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$) δ=192.8, 156.1, 154.0, 143.6, 142.6, 141.23, 141.16, 140.3, 139.7, 137.7, 131.3, 129.8, 129.5, 128.7, 128.1, 127.8, 127.3, 124.8, 124.7, 124.3, 124.2, 123.1, 120.9, 120.8, 119.5 ppm; UV–vis (CH_2Cl_2) λ_{max}=242 (log ε=4.60), 252sh (4.56), 291 (4.58), 313 (4.47), 394sh (3.90), 405 (3.92), 516sh (2.49), 550 (2.57), 599sh (2.42) nm; IR (KBr) ν_{max}=3050w, 2369w, 2344w, 1617s, 1575m, 1525m, 1449s, 1418s, 1388s, 1366s, 1307m, 1240s, 1185s, 1128m, 1018m, 940m, 840s, 814s, 748s, 710s, 651s, 611m, 563m cm^{-1}; MS (70 eV) *m*/*z* (rel int): 399 (M$^+$+1, 32), 398 (M$^+$, 100), 322 (14), 321 (55), 292 (29), 265 (11), 263 (24) 237 (5), 199 (4), 161 (4), 132 (4), 105 (4), 77 (10). Anal. Calcd for $C_{19}H_{18}O_2$: C, 87.42; H, 4.55. Found: C, 87.56; H, 4.73.

Compound **10g** (83%): 1-benzoyl-3-(4-dibenzothienyl)azulene, purple powder, mp 194–201 °C. ^{1}H NMR (CDCl$_3$) δ=9.87 (d, J=10.0 Hz, 1H), 8.54 (d, J=10.0 Hz, 1H), 8.41 (s, 1H), 8.21 (dm, J=7.6 Hz, 2H), 7.95 (dm, J=7.2 Hz, 2H), 7.91 (t, J=10.0 Hz, 1H), 7.80 (dm, J=8.0 Hz, 1H), 7.71 (t, J=10.0 Hz, 1H), 7.63–7.44 (m, 8H) ppm; ^{13}C NMR (CDCl$_3$) δ=192.9, 142.5, 142.4, 141.1, 140.1, 140.9, 140.5, 139.9, 139.5, 137.6, 136.2, 135.9, 131.4, 131.3, 129.7, 129.6, 128.8, 128.5, 128.2, 127.9, 126.9, 124.8, 124.5, 124.1, 122.7, 121.8, 120.5 ppm; UV–vis (CH$_2$Cl$_2$) λ_{max}=239 (log ε=4.66), 257sh (4.50), 282sh (4.45), 291 (4.47), 305sh (4.44), 392sh (3.90), 403 (3.92), 547 (2.65), 605sh (2.44) nm; IR (KBr) ν_{max}=3048w, 1617s, 1589m, 1574m, 1523m, 1509w, 1499w, 1480w, 1444s, 1420s, 1397s, 1358s, 1298m, 1241s, 1210m, 1166m, 1131m, 1099w, 1018m, 937m, 845m, 822m, 796m, 752s, 717m, 703m, 676m, 651m, 619m, 578w, 536w, 433w cm^{-1}; MS (70 eV) m/z (rel int): 415 (M$^+$+1, 32), 414 (M$^+$, 100), 338 (13), 337 (50), 309 (12), 308 (41), 306 (8), 276 (4), 207 (6), 169 (7), 154 (8), 77 (4). Anal. Calcd for C$_{29}$H$_{18}$OS: C, 84.03; H, 4.38. Found: C, 84.06; H, 4.55.

4.4. The Suzuki–Miyaura cross-coupling reactions of 1,3-dihaloazulenes (6)

To a solution of 0.500 mmol of 1,3-dihaloazulene in 10 ml of toluene were added 1.50 mmol of arylboronic acid, 15.6 mg (0.025 mmol) of BINAP, 20.4 mg (0.025 mmol) of Pd(dppf)Cl$_2$·CH$_2$Cl$_2$, and 489 mg (1.50 mmol) of Cs$_2$CO$_3$. This flask was evacuated and refilled with argon five times. The mixture was heated at 110 °C for several hours and then the resulting reaction mixture was poured into water and extracted with ether (30 ml×3). The combined organic layer was washed with brine and dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure and the residue was purified by chromatography to give a coupling product.

Compound **4** (90%): 1,3-diphenylazulene, green needles, mp 114–116 °C (lit. 100–102 °C;[14] 117–118 °C[41]). ^{1}H NMR (CDCl$_3$) δ=8.55 (d, J=9.8 Hz, 2H), 8.12 (s, 1H), 7.65 (d, J=7.2 Hz, 4H), 7.58 (t, J=9.8 Hz, 1H), 7.51 (t, J=7.2 Hz, 4H), 7.37 (tm, J=7.4 Hz, 2H), 7.12 (t, J=9.8 Hz, 2H) ppm.

Compound **11a** (35%): 1,3-bis(4-biphenylyl)azulene, green needles, mp 243–245 °C. ^{1}H NMR (CDCl$_3$) δ=8.62 (d, J=9.8 Hz, 2H), 8.21 (s, 1H), 7.72 (m, 12H), 7.61 (t, J=9.9 Hz, 1H), 7.49 (t, J=7.4 Hz, 4H), 7.38 (t, J=7.4 Hz, 2H), 7.16 (t, J=9.8 Hz, 2H) ppm; ^{13}C NMR (CDCl$_3$) δ=140.9, 139.3, 136.9, 139.1, 137.1, 136.3, 130.2, 128.8, 127.6, 127.4, 127.3, 127.1, 123.7 ppm; IR (KBr) ν_{max}=3033m, 2928w, 1594m, 1578s, 1570s, 1561s, 1544s, 1525m, 1509m, 1498w, 1482s, 1459m, 1425m, 1399m, 1365m, 1224w, 1076w, 1004m, 938w, 872w, 845s, 765s, 739s, 724s, 691s, 576m, 488w, 461w cm^{-1}; UV–vis (CH$_2$Cl$_2$) λ_{max}=228 (log ε=4.41), 240sh (4.37), 269sh (4.41), 315 (4.73), 388 (4.05), 483 (1.00), 571sh (1.39), 622 (1.51), 680sh (1.39), 762sh (0.81) nm; MS (70 eV) m/z (rel int): 433 (M$^+$+1, 38), 432 (M$^+$, 100), 430 (1), 415 (1), 352 (3), 339 (2), 326 (2), 276 (5), 252 (2), 216 (9), 202 (1), 152 (1), 77 (1). Anal. Calcd for C$_{34}$H$_{24}$: C, 94.35; H, 5.72. Found: C, 94.41; H, 5.59.

Compound **11b** (75%): 1,3-bis(1-naphthyl)azulene, blue solids, mp 66–69 °C. ^{1}H NMR (DMSO-d_6 at 100 °C)[42] δ=8.17 (s, 1H), 8.14 (d, J=9.8 Hz, 2H), 7.90–8.05 (m, 4H), 7.78 (d, J=8.0 Hz, 2H), 7.70 (t, J=9.8 Hz, 1H), 7.65–7.70 (m, 4H), 7.54 (d, J=8.0 Hz, 2H), 7.45 (t, J=8.0 Hz, 2H), 7.19 (t, J=9.8 Hz, 2H) ppm; ^{13}C NMR (DMSO-d_6 at 100 °C) δ=139.4, 138.7, 137.2, 135.6, 133.8, 133.2, 132.2, 128.2, 127.8, 127.3, 126.9, 125.7, 125.3, 125.0, 123.2 ppm; UV–vis (CH$_2$Cl$_2$) λ_{max}=742sh (log ε=2.33), 662sh (2.87), 608 (2.96), 553sh (2.78), 384sh (3.37), 352sh (3.68), 311sh (3.93), 293 (4.06), 279sh (3.99), 268 (3.97), 229 (4.32) nm; IR (KBr) ν_{max}=3040m, 2949m, 2923m, 2852m, 1569s, 1543m, 1524w, 1507m, 1459m, 1437m, 1379m, 1354m, 1318w, 1261m, 1230w, 1158w, 1112m, 1009m, 967w, 947w, 925w, 801s, 776s, 741s, 647m, 579w, 553w cm^{-1}; MS (70 eV) m/z (rel int): 381 (M$^+$+1, 34), 380 (M$^+$, 100), 379 (13), 378 (9), 377 (12), 376 (13), 363 (9), 253 (6), 252 (15), 188 (7), 182 (7), 149 (3), 111 (3), 97 (3), 69 (4). Anal. Calcd for C$_{30}$H$_{20}$·1/3CH$_2$Cl$_2$: C, 89.12; H, 5.10. Found: C, 89.21; H, 5.10.[43]

Compound **11c** (23%): 1,3-bis[4-(*N*,*N*-dimethylamino)phenyl]azulene, green microcrystals, mp 152–154 °C. ^{1}H NMR (CDCl$_3$) δ=8.44 (d, J=9.8 Hz, 2H), 8.02 (s, 1H), 7.53 (t, J=9.8 Hz, 1H), 7.50 (dm, J=8.6 Hz, 4H), 7.03 (t, J=9.8 Hz, 2H), 6.91 (dm, J=8.6 Hz, 4H), 3.00 (s, 12H, CH$_3$) ppm; ^{13}C NMR (CDCl$_3$) δ=150.5, 139.7, 137.0, 136.8, 136.7, 131.7, 131.1, 126.1, 123.1, 113.7, 40.7 ppm; IR (KBr) ν_{max}=3021w, 2916m, 2882m, 2848m, 2798m, 1610s, 1562m, 1533s, 1502s, 1477m, 1443m, 1383m, 1353s, 1225s, 1195m, 1167m, 1125m, 1062m, 946s, 867m, 820s, 737s, 724s, 572m, 553m, 536m cm^{-1}; UV–vis (CH$_2$Cl$_2$) λ_{max}=236 (log ε=4.42), 279 (4.54), 312 (4.78), 384 (4.23), 657 (2.51) nm; MS (70 eV) m/z (rel int): 366 (M$^+$, 100), 350 (21), 183 (11). Anal. Calcd for C$_{26}$H$_{26}$N$_2$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.45; H, 7.24; N, 7.70.

Compound **11d** (80%): 1,3-bis[4-(*N*,*N*-diphenylamino)phenyl]azulene, green needles, mp 279–281 °C. ^{1}H NMR (CDCl$_3$) δ=8.53 (d, J=10.0 Hz, 2H), 8.09 (s, 1H), 7.54 (t, J=10.0 Hz, 1H), 7.51 (d, J=8.8 Hz, 4H), 7.29 (t, J=8.0 Hz, 8H), 7.21 (d, J=8.8 Hz, 4H), 7.19 (d J=8.0 Hz, 8H), 7.07 (t, J=10.0 Hz, 2H), 7.04 (t, J=8.0 Hz, 4H) ppm; ^{13}C NMR (CDCl$_3$) δ=147.8, 146.3, 138.9, 136.8, 136.5, 136.1, 131.3, 130.4, 130.2, 129.3, 124.4, 124.1, 123.1, 122.8 ppm; IR (KBr) ν_{max}=3034m, 3020m, 2956m, 2924s, 2852s, 1589s, 1570m, 1561m, 1543m, 1524m, 1509m, 1491s, 1459s, 1449m, 1439m, 1421m, 1408m, 1377m, 1364m, 1314m, 1271s, 1218m, 1174m, 1153m, 1109m, 1074m, 1027m, 936w, 896w, 871w, 840m, 749s, 694s, 670m, 619m, 573w, 548w, 528w, 511m, 497m cm^{-1}; UV–vis (CH$_2$Cl$_2$) λ_{max}=230 (log ε=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) nm; MS (70 eV) m/z (rel int): 614 (M$^+$, 100), 307 (15), 167 (13). Anal. Calcd for C$_{46}$H$_{34}$N$_2$·0.8H$_2$O: C, 87.81; H, 5.70; N, 4.45. Found: C, 87.76; H, 5.63; N, 4.40.

Compound **11e** (24%): 1,3-bis[4-(9-carbazolyl)phenyl]azulene, green needles, mp 261–263 °C; ^{1}H NMR (CDCl$_3$) δ=8.73 (d, J=9.8 Hz, 2H), 8.32 (s, 1H), 8.19 (d, J=7.7 Hz), 7.92 (d, J=8.1 Hz, 4H), 7.75 (d, J=8.1 Hz, 4H), 7.70 (t, J=9.8 Hz, 1H), 7.58 (d, J=7.7 Hz, 4H), 7.47

(tm, J=7.7 Hz, 4H), 7.33 (tm, J=7.7 Hz, 4H), 7.25 (t, J=9.8 Hz, 2H) ppm; ^{13}C NMR (CDCl$_3$) δ=141.0, 139.5, 137.2, 137.0, 136.4, 136.2, 136.1, 131.0, 129.7, 127.3, 126.0, 124.1, 123.4, 120.3, 120.0, 109.9 ppm; IR (KBr) ν_{max}=3036m, 1687m, 1673m, 1655m, 1638m, 1625m, 1596m, 1578m, 1561m, 1543m, 1524s, 1508s, 1499s, 1477s, 1449s, 1422s, 1377m, 1361s, 1313s, 1227s, 1169m, 1146m, 1106m, 1031m, 936m, 914m, 835s, 771w, 744s, 719s, 649m, 632m, 566m, 530m, 518m, 437m, 421m cm^{-1}; UV–vis (CH$_2$Cl$_2$) λ_{max}=242 (log ε=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) nm; MS (70 eV) m/z (rel int): 610 (M$^+$, 100), 305 (13), 276 (12), 241 (10), 166 (12). Anal. Calcd for $C_{46}H_{30}N_2\cdot 1.4H_2O$: C, 86.86; H, 5.20; N, 4.40. Found: C, 86.99; H, 5.08; N, 4.37.

Compound **11f** (53%): 1,3-bis(4-bromophenyl)azulene,[44] green needles, mp 192–194 °C. ^{1}H NMR (CDCl$_3$) δ=8.48 (d, J=9.8 Hz, 2H), 8.04 (s, 1H), 7.63 (d, J=8.4 Hz, 4H), 7.62 (t, J=9.8 Hz, 1H), 7.49 (d, J=8.4 Hz, 2H), 7.17 (t, J=9.8 Hz, 2H) ppm; ^{13}C NMR (CDCl$_3$) δ=139.4, 136.8, 136.7, 136.2, 135.9, 131.8, 131.3, 129.3, 124.1, 120.7 ppm; IR (KBr) ν_{max}=3040w, 2927m, 2846m, 1573s, 1561s, 1543s, 1525s, 1509m, 1498s, 1479s, 1459m, 1449m 1438m 1429m, 1409m, 1378m, 1362m, 1322m, 1293m, 1264m, 1219s, 1175m, 1138w, 1100m, 1074s, 1007s, 936m, 877w, 831s, 810s, 736s, 719m, 693w, 671w, 656w, 639w, 619w, 601w, 574m, 537m, 507m, 492w cm^{-1}; UV–vis (CH$_2$Cl$_2$) λ_{max}=228sh (log ε=4.24), 252 (4.33), 286sh (4.47), 304 (4.61), 324sh (4.37), 384 (3.92), 560sh (2.29), 614 (2.44), 637 (2.32), 7.49 (1.77) nm; MS (70 eV) m/z (rel int): 440 (M$^+$, 40), 438 (M$^+$, 100), 436 (M$^+$, 53), 278 (14), 276 (53), 274 (12), 202 (12), 138 (11). Anal. Calcd for $C_{22}H_{14}Br_2$: C, 60.31; H, 3.22. Found: C, 60.28; H, 3.34.

4.5. Alternative synthesis of 1,3-bis[4-(*N*,*N*-dimethylamino)phenyl]azulene (11c)

In a 20 ml pressure-resistant glass bottle was charged 100 mg (0.228 mmol) of **11f**, 8.0 mg (36 mmol) of palladium acetate, 20 mg (69 mmol) of (t-Bu)$_3$PHBF$_4$, 65.0 mg (0.676 mmol) of NaOBu-t, and 5 ml of toluene. The bottle was evacuated at −100 °C and 0.255 g (5.00 mmol) of dimethylamine, obtained from the aqueous solution by mixing with a NaOH solution, was introduced into the bottle at the same temperature. The resulting bottle was sealed and heated at 110 °C in an oil bath with occasional swirling for 7 days. The resulting reaction mixture was poured into water and extracted with ether (20 ml×3). The combined organic layer was washed with brine and dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure and the residue was chromatographed on neutral alumina with a 1:1 mixture of hexane and chloroform as eluent to give 61.0 mg (73%) of **11c** as green microcrystals.

4.6. Alternative synthesis of 1,3-bis[4-(*N*,*N*-diphenylamino)phenyl]- and 1,3-bis[4-(9-carbazoylyl)phenyl]-azulenes (11d and e)

To a solution of 110 mg (0.250 mmol) of **11f** in 7 ml of toluene were added 1.7 mg (7.5 mmol) of palladium acetate, 4.4 mg (15 mmol) of (t-Bu)$_3$PHBF$_4$, 72.1 mg (0.750 mmol) of NaOBu-t, and 0.75 mmol of the amine. This flask was evacuated and refilled with argon five times and then refluxed at 110 °C for 7 h. Then the resulting reaction mixture was poured into water and extracted with ether (20 ml×3). The combined organic layer was washed with brine and dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel to give the product.

4.7. Synthesis of *N*,*N*,*N*′,*N*′-tetrasubstituted 1,3-bis(4-aminophenylethynyl)azulenes (14a–c)

To a solution of 152 mg (0.400 mmol) of 1,3-diiodoazulene and 1.20 mmol of *N*,*N*-disubstituted 4-ethynylaniline in 15 ml of triethylamine were added 6.7 mg (0.010 mmol) of bis(triphenylphosphine)palladium dichloride, 11 mg (0.040 mmol) of triphenylphosphine, and 9.1 mg (0.048 mmol) of CuI. This flask was evacuated and refilled with argon five times and then refluxed at 50 °C for 5 h. Then the resulting reaction mixture was poured into water and extracted with ether (20 ml×3). The combined organic layer was washed with brine and dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel to give the product.

Compound **14a** (48%): 1,3-bis{4-(dimethylamino)phenylethynyl}azulene, mp 204–206 °C. ^{1}H NMR (CDCl$_3$) δ=8.52 (d, J=9.7 Hz, 2H), 8.06 (s, 1H), 7.59 (t, J=9.7 Hz, 1H), 7.49 (d, J=9.0 Hz, 4H), 7.19 (t, J=9.7 Hz, 2H), 6.69 (d, J=9.0 Hz, 4H), 2.98 (s, 12H) ppm; ^{13}C NMR (CDCl$_3$) δ=149.9, 141.3, 140.8, 139.7, 136.9, 132.5, 124.7, 111.9, 111.4, 110.8, 95.0, 82.7, 40.3 ppm; IR (KBr) ν_{max}=3448w, 2882w, 2793w, 2182w, 1892w, 1870w, 1846w, 1831w, 1812w, 1802w, 1794w, 1774w, 1751w, 1719m, 1702m, 1686m, 1674w, 1655w, 1638m, 1607s, 1571m, 1561w, 1532s, 1499m, 1476w, 1459w, 1438s, 1408w, 1389w, 1368s, 1286m, 1231m, 1187s, 1064m, 1003w, 948m, 867w, 805s, 754w, 726s, 670w, 644w, 575w, 549m, 517m cm^{-1}; UV–vis (CH$_2$Cl$_2$) λ_{max}=250 (log ε=4.38), 309sh (4.65), 341 (4.77), 412 (4.22), 665 (2.49) nm; MS (70 eV) m/z (rel int): 414 (M$^+$, 100), 262 (18). Anal. Calcd for $C_{30}H_{26}N_2\cdot 1/3H_2O$: C, 85.68; H, 6.39; N, 6.66. Found: C, 85.80; H, 6.34; N, 6.60.

Compound **14b** (50%): 1,3-bis{4-(diphenylamino)phenylethynyl}azulene, mp 152–153 °C. ^{1}H NMR (CDCl$_3$) δ=8.55 (d, J=9.7 Hz, 2H), 8.08 (s, 1H), 7.65 (t, J=9.7 Hz, 1H), 7.46 (d, J=8.8 Hz, 4H), 7.28 (t, J=8.0 Hz, 8H), 7.26 (t, J=9.7 Hz, 2H), 7.13 (d, J=8.0 Hz, 8H), 7.06 (t, J=8.0 Hz, 4H), 7.04 (d, J=8.8 Hz, 4H) ppm; ^{13}C NMR (CDCl$_3$) δ=147.6, 147.3, 141.6, 141.1, 139.9, 137.0, 132.3, 129.4, 125.3, 124.8, 123.4, 122.6, 116.9, 110.9, 94.2, 84.1 ppm; IR (KBr) ν_{max}=3448w, 3033m, 2189w, 1945w, 1924w, 1896w, 1870m, 1794w, 1774m, 1761w, 1719m, 1655m, 1638m, 1618w, 1587s, 1562w, 1543m, 1523w, 1509w, 1491s, 1459w, 1439w, 1389w, 1362w, 1315m, 1275s, 1175m, 1075w, 1028w, 893w, 861w, 834m, 752s, 728w, 695s, 646w, 618m, 575w, 511m, 475w cm^{-1}; UV–vis (CH$_2$Cl$_2$) λ_{max}=254 (log ε=4.48), 310 (4.68), 370 (4.84), 412sh (4.39), 650 (2.33) nm; MS (70 eV): m/z (rel int) 662 (M$^+$, 100), 331 (20). Anal. Calcd for $C_{50}H_{34}N_2$: C, 90.60; H, 5.17; N, 4.23. Found: C, 90.32; H, 5.34; N, 4.04.

Compound **14c** (72%): 1,3-bis(4-carbazolylphenylethynyl)-azulene, mp 214–216 °C. ^{1}H NMR ($CDCl_3$) δ=8.69 (d, J=9.8 Hz, 2H), 8.69 (d, J=9.8 Hz, 2H), 8.24 (s, 1H), 8.16 (dm, J=8.3 Hz, 4H), 7.87 (dm, J=8.3 Hz, 4H), 7.78 (t, J=9.8 Hz, 1H), 7.62 (dm, J=8.3 Hz, 4H), 7.58 (d, J=8.3 Hz, 4H), 7.44 (tm, J=8.3 Hz, 4H), 7.41 (t, J=9.8 Hz, 2H), 7.32 (t-like, J=8.3 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$) δ=142.2, 141.7, 140.2, 137.2, 137.2, 132.9, 126.9, 126.1, 126.0, 125.0, 123.6, 122.9, 120.4, 120.2, 110.5, 109.8, 93.6, 85.9 ppm; IR (KBr) ν_{max}=3048m, 3023m, 2927m, 2866m, 2193m, 1647w, 1637w, 1625m, 1598m, 1561m, 1524m, 1499s, 1477m, 1408m, 1390m, 1359s, 1334m, 1314m, 1293m, 1227s, 1182m, 1169m, 1148m, 1119m, 1104m, 1054w, 1028w, 1015m, 1003m, 929w, 914m, 883w, 825m, 772w, 746s, 722s, 669m, 658m, 624m, 574m, 565m, 537m, 491w, 459w, 445w, 435m, 421m cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}=239 (log ε=5.03), 259sh (4.81), 284sh (4.61), 294 (4.72), 331sh (4.83), 345 (4.91), 406 (4.21), 431sh (4.14), 574sh (2.51), 629 (2.27), 695sh (2.10), 781sh (1.78) nm; MS (70 eV) m/z (rel int): 658 (M$^+$, 100), 329 (28). Anal. Calcd for $C_{50}H_{30}N_2\cdot 0.8H_2O$: C, 89.21; H, 4.73; N, 4.16. Found: C, 89.17; H, 4.80; N, 3.87.

4.8. Cyclic voltammetry

A standard three-electrode cell configuration was employed using a glassy carbon disk working electrode, a Pt wire auxiliary electrode, and an Ag wire as an Ag/Ag$^+$ quasi-reference electrode. The reference electrode was calibrated at the completion of each measurement on a saturated calomel electrode (SCE). Cyclic voltammetry was measured in a dichloromethane solution for **11** and **14** with tetrabutylammonium perchlorate as a supporting electrolyte and a scan rate of 0.1 Vs^{-1} at 25 °C.

4.9. OLED fabrication

The OLED structures **A** and **B** employed in this study are shown in the inset of Figure 2.

Structure **A**: organic layers were fabricated by high-vacuum (10^{-7}–10^{-6} Torr) thermal evaporation onto a glass substrate precoated with an ITO layer with a sheet resistance of 10 Ω/square. Prior to use, the ITO was degreased with solvents and cleaned in an UV–ozone chamber before loading into the evaporation system. A 10 nm-thick CuPc, **11c**, **d**, or **e** as the HIL, a 50 nm-thick TPTE as the HTL, a 60 nm-thick Alq_3 as the light-emitting layer, a 0.5 nm-thick LiF as the electron-injecting layer, and a 150 nm-thick aluminum metal as a cathode were deposited on the substrate. Devices were encapsulated under nitrogen in a glass-to-glass epoxy sealed package.

Structure **B**: organic layers were fabricated by high-vacuum (10^{-7}–10^{-6} Torr) thermal evaporation onto a glass substrate precoated with an ITO layer with a sheet resistance of 10 Ω/square. Prior to use, the ITO was degreased with solvents and cleaned in an UV–ozone chamber before loading into the evaporation system. A 10 nm-thick CuPc, **11c**, **d**, or **e** as the HIL, a 30 nm-thick TPTE as the HTL, a 40 nm-thick Alq_3 with 1.2–1.5 wt% of DCJTB as the light-emitting layer, a 40 nm-thick Alq_3 and a 0.5 nm-thick LiF as the electron-injecting layer, and a 100 nm-thick aluminum metal as a cathode were deposited on the substrate. Devices were encapsulated under nitrogen in a glass-to-glass epoxy sealed package.

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