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Fluorescent Ethenyl- and Ethynyl-dimesitylboranes Derived from 5-(Dimethylamino)-*N*-(prop-2-ynyl)naphthalene-1-sulfonamide

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Two new fluorescent ethenyl- and ethynyl-dimesitylboranes functionalized with a dansyl group 1 and 2 have been synthesized in good yields. Compound 1 was prepared by the hydroboration of 5-(dimethylamino)-N-(prop-2-ynyl)naphthalene-1-sulfonamide I with dimesitylborane (HB(Mes)₂) in dry tetrahydrofuran at room temperature, and compound 2 was synthesized by Pd-catalyzed cross-coupling of I with 4-I-C₆H₄B(Mes)₂. Both organoborane compounds 1 and 2 have been characterized by infrared spectroscopy, NMR spectroscopy, and mass spectrometry. The molecular structures of I and 1 were confirmed by X-ray crystallography. The electronic absorption and redox properties of 1 and 2 were investigated. They both exhibit large positive solvatochromism and their emission spectra have been recorded in a range of organic solvents with the fluorescence maxima exhibiting large bathochromic shifts in highly polar solvents, indicative of charge transfer which leads to large dipole moments in the excited state. The application of 1 as a blue fluorescent dopant in doped guest–host organic light-emitting diodes is also described.

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Introduction

The current search for new luminescent materials is a result in part of their potential for use in electroluminescent (EL) displays.^[1] In recent years, there has been considerable interest in both academia and industry in developing blue organic lightemitting devices (OLEDs), and the realisation of blue electroluminescence is an important step for possible application of these materials in flat-panel full-colour displays.^[2] It is well known that the EL efficiency, colour, and operational stability of blue OLEDs can be significantly improved with the use of a guest–host doped emitter.^[3] There have been several recent developments in blue-doped emitter systems, including the utilization of 2-methyl-9,10-di(2-napthyl)anthracene (MADN) as a blue host.^[4]

Electronic and electro-optical materials that contain electronrich organic molecules have attracted much attention.^[5] New routes to electron-deficient systems have also been developed, taking advantage of the fact that three-coordinate boron is isoelectronic and isostructural with a carbocation.^[6] These organoboron compounds have interesting optical, electronic, and structural properties with a wide range of applications,^[6] including fluoride ion sensors,^[7] non-linear optical materials,^[8] and both single and two-photon fluorescence.^[9] They can also serve as emissive and/or electron-transport layers in OLEDs.^[10] As with many other low-coordinate systems, a common strategy in the synthesis of three-coordinate boranes is to provide kinetic stability by blocking the approach of nucleophiles with sterically demanding substituents while maintaining conjugation with other unsaturated hydrocarbon substituents.^[6,10] Bulky aryl moieties such as the mesityl (2,4,6-trimethylphenyl) group are particularly effective, as steric congestion around boron results in the formation of propeller-like structures where the *ortho*substituents on the aryl ligands form a cage around the vacant p_z orbital.

Many endeavours have been made to employ fluorescent labels such as anthracene,^[8b,9c,11] acridone,^[12] and fluorene^[13] for the design of various novel optoelectronic materials. However, the 5-(dimethylamino)naphthalene-1-sulfonyl (dansyl) chromophore has been less explored.^[14] In view of the high luminescence quantum yield and high photochemical resistance to bleaching of the auxiliary dansyl unit,^[14] we expect that a properly derivatized molecule, such as 5-(dimethylamino)-N-(prop-2-ynyl)naphthalene-1-sulfonamide I could be employed to attach a fluorescent label to the B(Mes)₂ moiety through an acetylide linkage, which is likely to exhibit rich photophysical and optoelectronic properties. In the present article, we describe the synthesis, spectroscopic, structural, and photophysical properties of two new fluorescent compounds that incorporate the dansyl and dimesitylborane moieties. Preliminary studies of such compounds as dopants in a guest-host blue-doped emitter system will be discussed.

Results and Discussion

Synthesis and Characterization

Scheme 1 summarizes the reaction pathways to all the compounds in this study. Ligand I was prepared by reacting dansyl chloride and propargylamine in a NEt₃/CH₂Cl₂ solvent mixture according to the literature method.^[14a] The terminal acetylene was hydroborated using HB(Mes)₂ in THF to obtain the *trans*-ethenyldimesitylborane 1 in 60%



Scheme 1. Synthetic routes to compounds I, 1, and 2.

vield.^[15] (p-Iodophenyl)dimesitylborane, prepared by reacting 1,4-diiodobenzene with BuⁿLi followed by reaction with dimesitylboron fluoride, was used in a Pd-catalyzed cross-coupling reaction with I to yield the dimesitylborylalkynyl compound 2 in moderate yield (46%).^[16] Compound 1 was purified by repeated recrystallization and compound 2 was purified by preparative TLC on silica plates followed by recrystallization. Both mesitylboranes are organic soluble and have been fully characterized by NMR and infrared (IR) spectroscopies and matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) high-resolution mass spectrometry (MS). Compounds 1 and 2 are thermally stable solids with onset decomposition temperatures of 296 and 328°C, respectively, as shown by thermogravimetric analysis (TGA). The crystalline borane, 1, did not exhibit a discernable glass transition. When 2 was heated, an endotherm as a result of melting was observed at 181°C, and upon cooling and re-heating, a glass transition was observed at 72°C.

Spectroscopic data (IR, ¹H and ¹³C NMR, and MS) for these new fluorophore-anchored mesitylboranes are in agreement with their formulation. The disappearance of the IR $\nu(C \equiv C)$ and $\nu (\equiv C-H)$ bands in 1 confirms that hydroboration of the alkyne unit occurred to give a vinyl boron compound. The IR spectrum of **2** displays a strong ν (C=C) absorption band at 2238 cm⁻¹, but absorption as a result of the terminal acetylenic C-H group of the ligand is absent. The ¹H NMR spectra of the new compounds show resonances that stem from the coordinated dansyl group, but the signals attributable to $-C \equiv CH$ for I (~1.92 ppm) are not observed. The ¹³C NMR spectroscopic data also give precise information about the structure of the compounds. In each case, the carbon resonances of the mesityl methyl group are clearly identified at ~ 21 and 23 ppm for both compounds. Notably, there are two distinct ¹³C NMR signals for the individual sp carbons in 2, in accordance with the formulation. The MALDI-TOF MS and elemental analytical data further support the formulation of these compounds. For 1 and 2, molecular ion peaks are observed at m/z 537 and 611 amu, respectively.

Single-crystal X-ray diffraction studies for I and 1 confirm their structures (Fig. 1). Important bond parameters are listed in Table 1. For both I and 1, there are two independent but structurally similar molecules in the unit cell. The propynyl group is attached to N(2) by a CH₂ bridge in I and has a typical C \equiv C bond length of 1.163(5) Å. The B–C bond lengths of 1 are 1.573(5) and 1.574(5) Å for the B–mesityl bonds and 1.577(5) Å for the boron–vinyl bond.

Photophysical and Redox Properties

The photophysical properties of boranes 1 and 2 have been studied in toluene at room temperature and the results are summarized in Table 2. Both 1 and 2 show similar structured absorption bands (\sim 322–324 nm). The absorption maxima exhibit negligible bathochromic solvatochromic shifts in solvents of increasing polarity, which is consistent with very small ground-state dipole moments. Fluorescence occurs in the blue region for compounds 1 and 2. Excitation of 1 and 2 in toluene solutions gave strong emission peaks located at 477 and 487 nm, respectively. The emission wavelengths of 1 and 2 are slightly red-shifted with respect to that of I (454 nm in toluene). These featureless luminescence spectra are independent of the excitation wavelength used. Because of their similar emission pattern, it is considered that the emission features in I and the dansylated boranes should have the same origin. In contrast to their absorption behaviour, 1 and 2 exhibit pronounced positive solvatochromism in their fluorescence spectra (Table 3), which can be attributed to highly polarized excited states. In other words, their emission spectra shift towards longer wavelengths with increasing polarity of the solvents. Solvent-dependent emission in solution has been frequently observed for three-coordinate organoboron compounds.^[15] As shown in Fig. 2, the shift of the emission maximum with solvents is dramatic in each case. For example, in the non-polar solvent, hexane, the emission maxima of 1 and 2 are located at 448 and 450 nm, while in dimethyl sulfoxide (DMSO), the emission maxima appear at 515 and 516 nm, respectively (Table 3). The fluorescence lifetimes of 1 and 2 are 14 and 12 ns, respectively.

The electrochemical properties of 1 and 2 were investigated by cyclic voltammetry in THF. The potentials were measured against Ag/AgCl as the reference electrode and each measurement was calibrated with the ferrocene/ferrocenium (Fc/Fc⁺) redox system as an internal standard. The reduction



Fig. 1. Molecular structures of one of the two independent molecules of I (left) and 1 (right).

Table 1. Selected bond lengths [Å] and angles [°] for compounds I and 1

gth [Å]	Bond angle [°]			
Co	mpound I			
1.428(2)	O(1)–S(1)–O(2)	119.7(2)		
1.428(2)	C(12)-S(1)-N(2)	107.5(1)		
1.615(3)	S(1)-N(2)-C(13)	121.1(2)		
1.452(4)	N(2)-C(13)-C(14)	114.2(3)		
1.473(5)	C(13)-C(14)-C(15)	178.7(4)		
1.163(5)				
Co	mpound 1			
1.431(3)	O(1)-S(1)-O(2)	118.9(2)		
1.436(3)	C(8)–S(1)–N(2)	106.8(2)		
1.614(3)	S(1)-N(2)-C(13)	124.7(3)		
1.577(5)	N(2)-C(13)-C(14)	110.9(3)		
1.573(5)	C(16)-B(1)-C(25)	123.6(3)		
1.574(5)	C(15)-B(1)-C(16)	120.5(3)		
1.312(5)	C(15)-B(1)-C(25)	115.8(3)		
	gth [Å] Co 1.428(2) 1.428(2) 1.615(3) 1.452(4) 1.473(5) 1.163(5) Co 1.431(3) 1.436(3) 1.614(3) 1.577(5) 1.573(5) 1.574(5) 1.312(5)	$\begin{array}{c c} \mbox{gth} [\mathring{A}] & \mbox{Bond angle} [\degree \\ \hline \\ \mbox{Compound I} \\ 1.428(2) & O(1)-S(1)-O(2) \\ 1.428(2) & C(12)-S(1)-N(2) \\ 1.615(3) & S(1)-N(2)-C(13) \\ 1.452(4) & N(2)-C(13)-C(14) \\ 1.473(5) & C(13)-C(14)-C(15) \\ 1.163(5) \\ \hline \\ \hline \\ \mbox{Compound I} \\ 1.431(3) & O(1)-S(1)-O(2) \\ 1.436(3) & C(8)-S(1)-N(2) \\ 1.614(3) & S(1)-N(2)-C(13) \\ 1.577(5) & N(2)-C(13)-C(14) \\ 1.573(5) & C(16)-B(1)-C(25) \\ 1.574(5) & C(15)-B(1)-C(16) \\ 1.312(5) & C(15)-B(1)-C(25) \\ \hline \end{array}$		

Table 2. Photophysical data for 1 and 2

Compound	pmpound $\lambda_{max} [nm]^A$			$\lambda_{em} \ [nm]^C$		
	Toluene	Film				
1	322 (5.8)	322	3.39	477 (20, 14)		
2	287 (2.0), 324 (2.7)	287, 324	3.28	487 (18, 12)		

^AExtinction coefficients $(10^4 \text{ M}^{-1} \text{ cm}^{-1})$ are shown in parentheses.

^BEstimated from the onset wavelength of the solid-state optical absorption. ^CToluene (290 K). Fluorescence quantum yields [%] and lifetimes [ns] shown in parentheses (Φ_F , τ_F) were measured in toluene relative to quinine sulfate in 1.0 N H₂SO₄ and 9,10-diphenylanthracene in cyclohexane.

potentials (E_{red}) and optical bandgaps (E_g) were used to determine the HOMO and LUMO energy levels using the equations $E_{LUMO} = -(E_{red} + 4.8)$ and $E_{HOMO} = -(E_{ox} - E_{red})$ eV, which were calculated using the internal standard ferrocene value of -4.8 eV with respect to the vacuum level.^[17] Each of them shows an irreversible reduction peak at -2.55 and 2.54 V, respectively,

 Table 3. Absorption and emission maxima of 1 and 2 in different solvents

Solvent	Compo	ound 1	Compound 2		
	λ_{max}	λ_{em}	λ_{max}	λ_{em}	
Hexane	320	448	321	450	
CCl ₄	318	464	323	462	
Toluene	318	477	323	481	
CH_2Cl_2	318	503	321	500	
Ethanol	318	510	321	510	
DMSO	325	515	324	516	

and this can be attributed to the reduction of the boron centre. Hence, the calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies for 1 (2) are -5.64 (-5.54) and -2.25 eV (-2.26 eV), respectively.

Electroluminescent Behaviour

Initially, it was noted that a blue-emitting OLED device based on a neat emissive layer of 1 showed a poor EL efficiency with luminance yield $\eta_L = 0.83 \text{ cd } \text{A}^{-1}$ and power efficiency $\eta_{\rm P} = 0.21 \, {\rm Im \, W^{-1}}$. From the similar photoluminescence (PL)/electroluminescence (EL) spectra (Fig. 3), it is concluded that the emissive states of both EL and solid PL are identical and the absence of aggregation or π -stacking is apparent. In the present study, blue-doped devices A-E were used instead. Typical multilayer EL devices A-C were constructed using dopant 1 with indium tin oxide (ITO) as the anode, 4,4',4'-tris[2-*N*-naphthyl-*N*-phenylamino]triphenylamine (2-TNATA, 60 nm) as the hole-injection material, 4,4'-bis[N-(1-naphthyl)-Nphenylamino]biphenyl (NPB, 10 nm) as the hole-transporting material, and MADN (40 nm) as the host material for blue dopants. Tris[8-hydroxyquinolinato]aluminum (Alq3) was used as the electron-transporting layer and LiF/Al as the bi-layer cathode (Fig. 4). Devices D,E were similarly fabricated using 1,3,5-tris[N-(phenyl)benzimidazole]benzene (TPBI)^[18] as the hole blocker and electron transporter instead of Alq3. Different



Fig. 2. Photoluminescence spectra of (a) 1 and (b) 2 in different solvents.



Fig. 3. Solid-state PL and neat-emissive layer electroluminescent (EL) spectra of 1.

dopant concentrations were used to obtain the optimum weight percentages for devices with the highest efficiencies. Fig. 5 depicts the current–voltage–luminance (I–V–L) characteristics of devices **A**–**C** and EL efficiency versus current density curves for device **A**. The turn-on voltages ($V_{\text{turn-on}}$) observed for such devices are ~4.0 V. There are no undesirable emission peaks from Alq₃ in each case but a slight blue-shift in the EL maximum was noted for the blue-doped devices relative to the one without the MADN host. The pertinent EL characteristics of devices **A**–**E** are summarized in Table 4. The maximum blue EL efficiency of device **A** can reach 2.5 cd A⁻¹ and 1.2 lm W⁻¹ at 20 mA cm⁻² and 6.7 V at 3 wt.-% doping concentration with Commission Internationale de L'Eclairage colour coordinates of (0.17, 0.12). The corresponding external quantum efficiency is ~2.4%. Fig. 6 depicts the EL performance of device **D** and **E** at the same doping level. Optimization of the devices **D** and **E** at the same doping level. Optimization of the device efficiencies using other host systems and the applicability of **1** for the electron-transport layer warrants further examination.

Conclusions

We have studied the chemistry and optoelectronic properties of two new mesitylborane compounds anchored with fluorescent dansyl termini through the hydroboration and cross-coupling reactions based on the dansylated alkyne unit. The spectroscopic, structural, and electrochemical properties of these compounds were examined and interestingly, their emission spectra display significant solvent-induced shifts characteristic of highly polar excited states. These fluorescent materials hold promise for blue light generation and have also found potential applications in dopant-based blue OLEDs.

Experimental

General Procedures

The preparations of organoborane compounds were carried out under a nitrogen atmosphere with the use of standard inert atmosphere and Schlenk techniques, but no special precautions were taken to exclude oxygen during workup. Solvents were predried and distilled from appropriate drying agents. All chemicals, unless otherwise stated, were obtained from commercial sources and used as received. Preparative TLC was performed on 0.7 mm silica plates (Merck Kieselgel 60 GF₂₅₄) prepared in our laboratory. The starting compounds (p-iodophenyl)dimesitylborane^[15] and 5-(dimethylamino)-N-(prop-2-ynyl)naphthalene-1-sulfonamide^[14a] were prepared by the reported procedures. Infrared spectra were recorded as CH₂Cl₂ solutions in a CaF₂ cell (0.5 mm path length) on a Nicolet Magna 550 Series II FTIR spectrometer. NMR spectra were measured in CDCl3 on a Varian INOVA 400 MHz FT NMR spectrometer. Chemical shifts were quoted relative to $SiMe_4(\delta 0)$ for both ¹H and ¹³C nuclei. The MALDI-TOF high-resolution mass spectra were recorded on an Autoflex Bruker MALDI-TOF system. Electronic absorption spectra were obtained with a Hewlett Packard 8453 diode array UV-vis spectrometer. The solution emission spectra and lifetimes of the compounds were measured on a Photon Technology International Fluorescence QuantaMaster Series QM1 spectrophotometer. The fluorescence quantum yields were determined in toluene solutions at 293 K against quinine sulfate in 0.1 N H₂SO₄ and 9,10diphenylanthracene in cyclohexane.^[19] The decay curves were analyzed using a Marquardt-based non-linear least-squares fitting routine and were shown to follow a single-exponential function in each case according to $I = I_0 + A \exp(-t/\tau)$. For solidstate emission, the photoluminescence measurement system consisted of a monochromator (Acton SpectraPro 500i) attached



Fig. 4. The general structures of the blue-doped blue organic light-emitting devices (OLED) devices and the molecular structures of the relevant compounds used in these devices.

to a photomultiplier tube (PMT) (Hamamatsu R636-10) as the detector. The signal from the PMT was first pre-amplified by the pre-amplifier (Princeton Applied Research 5182), and then it was processed by the lock-in amplifier (Stanford Research Systems SR830 DSP Lock-in Amplifier) and recorded by the computer. The excitation source used was a N2 pulse 337 nm continuous laser (Spectra-Physics 337201-01). The excitation light source was directed to the sample by optics and the emission from the sample was collected and focussed by a lens onto the input slit of the monochromator system. Cyclic voltammetry experiments were performed with a Princeton Applied Research model 273A potentiostat. A conventional three-electrode configuration consisting of a glassy carbon working electrode, a Pt-wire counter electrode, and an Ag/AgCl reference electrode (0.1 M in acetonitrile) was used. The solvent in all measurements was deoxygenated THF and the supporting electrolyte was 0.1 M [Bu₄N]PF₆. Ferrocene was added as a calibrant after each set of measurements and all potentials reported were quoted with reference to the Fc/Fc⁺ couple. Thermal analyses were performed with Perkin-Elmer Pyris Diamond DSC and Perkin-Elmer TGA6 thermal analyzers at a scanning rate of 20° C min⁻¹.

Preparation of Compound 1

In a glove box, a solution of dimesitylborane^[20] (1.0 mmol, 260 mg) in THF (20 mL) was added dropwise to a flask that contained a solution of ligand I (1.0 mmol, 288 mg) in THF (20 mL) and the mixture was stirred for 3 days. The solvent was removed under vacuum, and Et₂O (2 × 20 mL) was added to extract the product. The crude product was recrystallized from

hexane/CH₂Cl₂ (1/1, v/v) to yield white crystals of **1** (320 mg, 60%) (Found: C 71.8, H 7.2, N 5.2. $C_{33}H_{39}BN_2O_2S \cdot H_2O$ requires C 71.2, H 7.4, N 5.0%). $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.52–8.56 (m, 2H, Ar), 8.23–8.34 (m, 2H, Ar), 7.46–7.58 (m, 2H, CH vinyl), 7.15–7.19 (m, 1H, Ar), 6.76 (s, 4H, Mes), 6.67 (m, 1H, Ar), 4.95 (m, 1H, NH), 3.75 (m, 2H, NHCH₂), 2.90 (s, 6H, N(CH₃)₂), 2.28 (s, 6H, *p*-Mes), 2.04 (s, 12H, *o*-Mes). $\delta_{\rm C}$ (100.3 MHz, CDCl₃) 151.98, 149.55, 140.51, 133.70, 130.54, 129.85, 129.55, 128.54 (Ar + vinyl), 141.51, 140.34, 138.68, 128.16 (Mes), 46.85 (NHCH₂), 45.37 (N(CH₃)₂), 23.15, 21.11 (Mes). *m/z* (MALDI-TOF) 537.2756 (calc. 537.2753) (M⁺).

Preparation of Compound 2

Ligand I (100 mg, 0.35 mmol), (p-iodophenyl)dimesitylborane (157 mg, 0.35 mmol), Pd(PPh₃)₂Cl₂ (5 mg), and CuI (1.3 mg) were added to a nitrogen-purged flask and then NEt₃ (50 mL) was added to the mixture through a cannula. The reaction mixture was stirred at room temperature. After 1 day, the mixture was refluxed at 80°C for 6 h. The solvent was then removed under vacuum. The crude product was dissolved in CH₂Cl₂ and purified on preparative silica TLC plates with CH₂Cl₂ as eluent. From the yellow band ($R_{\rm F}$ 0.60) 2 was obtained as an off-white solid (98 mg, 46%) (Found: C 74.5, H 6.7, N 4.3. $C_{39}H_{41}BN_2O_2S \cdot H_2O$ requires C 74.3, H 6.9, N 4.4%). ν_{max} $(CH_2Cl_2)/cm^{-1}$ 2238 (C=C). δ_H (400 MHz, CDCl₃) 8.43 (d, J 8.4, 1H, Ar), 8.33–8.28 (m, 2H, Ar), 7.56 (t, J 8, 1H, Ar), 7.46 (t, J 8, 1H, Ar), 7.29 (d, J 8, 2H, Ar), 7.13 (d, J 8, 1H, Ar), 6.85 (d, J 8, 2H, Ar), 6.81 (s, 4H, Mes), 5.11 (t, J 6.4, 1H, NH), 4.04 (d, J 6.4, 2H, NHCH₂), 2.78 (s, 6H, N(CH₃)₂), 2.30 (s, 6H, *p*-Mes), 1.95 (s, 12H, *o*-Mes). δ_C (100.3 MHz, CDCl₃) 152.05, 135.60, 134.50, 130.78, 129.92, 128.51, 125.05, 123.18, 118.51, 115.08 (Ar), 141.35, 140.66, 138.83, 128.17 (Mes), 85.00, 84.57 (C \equiv C), 45.26 (N(CH₃)₂), 33.85 (NHCH₂), 23.32, 21.16 (Mes). *m/z* (MALDI-TOF) 611.2944 (calc. 611.2910) (M⁺).

X-Ray Crystallography

Single crystals of 1 suitable for X-ray crystallographic analyses were grown by slow evaporation of its solution in CH_2Cl_2 /hexane at room temperature. The crystals were chosen and mounted on a glass fibre using epoxy resin. Crystal data, data collection parameters, and results of the analyses are listed in Table 5.









Fig. 6. Luminance (\blacksquare) and power (\bullet) efficiencies versus current density curves of blue organic light-emitting devices (OLED) device **D**.

Table 5. Summary of crystal data for compounds I and 1

Parameter	Compound I	Compound 1		
Empirical formula	$C_{15}H_{16}N_2O_2S$	C33H39BN2O2S		
Molecular weight	288.36	538.53		
Crystal size [mm ³]	$0.30 \times 0.25 \times 0.21$	$0.26 \times 0.24 \times 0.10$		
Crystal system	Monoclinic	Triclinic		
Space group	$P 2_1/c$	$P \bar{I}$		
<i>a</i> [Å]	25.017(5)	11.478(2)		
<i>b</i> [Å]	8.020(2)	11.792(2)		
c [Å]	15.193(3)	21.952(4)		
α [°]	90	99.480(3)		
β [°]	107.08(3)	91.102(4)		
γ [°]	90	90.351(3)		
$U[Å^3]$	2913(1)	2929.9(9)		
μ (Mo _{Kα}) [mm ⁻¹]	0.225	0.143		
$D_{\text{calc}} [\text{g cm}^{-3}]$	1.315	1.221		
Ζ	8	4		
F(000)	1216	1152		
θ range [°]	1.70-25.00	1.88-25.00		
Reflections collected	14021	14066		
Unique reflections	5111	9965		
R _{int}	0.0396	0.0408		
Observed reflections $[I > 2\sigma(I)]$	3758	6246		
No. of parameters	365	711		
$R_1, wR_2 [I > 2\sigma(I)]$	0.0620, 0.1758	0.0716, 0.1674		
R_1 , wR_2 (all data)	0.0798, 0.1874	0.1217, 0.1955		
Goodness-of-fit on F^2	1.050	1.035		
Residual extrema in final diff. map $[e Å^{-3}]$	0.636 to -0.382	0.836 to -0.424		

 Table 4. EL performance of the doped blue-emitting devices at 20 mA cm⁻²

 CIE, Commission Internationale de L'Eclairage; EL, electroluminescent; EQE, external quantum efficiency

Device	V _{turn-on} [V]	x [%]	Voltage [V]	Luminance [cd m ⁻²]	Luminance yield [cd A ⁻¹]	Power efficiency [lm W ⁻¹]	EQE [%]	CIE(<i>x</i>)	CIE(y)	EL λ _{em} [nm]
A	4.0	3	6.7	494	2.5	1.2	2.35	0.17	0.12	439
В	4.0	5	6.8	483	2.4	1.1	2.17	0.17	0.13	440
С	4.0	7	6.8	436	2.2	1.0	2.05	0.17	0.12	440
D	4.1	3	7.3	434	2.2	0.9	2.82	0.16	0.08	436
Е	4.7	5	6.6	422	2.1	1.0	2.14	0.17	0.11	438

The diffraction experiments were carried out at 293 K on a Bruker Axs SMART 1000 CCD area-detector diffractometer using graphite-monochromated Mo_{K α} radiation (λ 0.71073 Å). The raw intensity data frames were integrated with the SAINT+ program using a narrow-frame integration algorithm.^[21] Corrections for Lorentz and polarization effects were also applied by SAINT+. For each analysis an empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS.^[22] The structures were solved by direct methods, and expanded by difference Fourier syntheses using the software SHELTXL.^[23] Structure refinements were made on F^2 by the full-matrix least-squares technique. In each case, all the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in their ideal positions but not refined. CCDC-654097 and CCDC-654098 contain the supplementary crystallographic data for this paper.

OLED Device Fabrication and Testing

Commercial ITO-coated glass with a sheet resistance of 20- $30 \Omega \text{ sq}^{-1}$ was used as the starting substrate. Before device fabrication, the ITO glass substrates were cleaned by ultrasonication in organic solvents followed by ozone treatment for 20 min.^[24] The device was fabricated layer by layer in a standard vacuum coater under a base vacuum of $\sim 10^{-6}$ torr. The deposition of the entire device was carried out without a vacuum break. The MADN:dopant emissive layer was co-deposited simultaneously with a series of controlled ratios. The laver thickness was monitored in situ using a quartz crystal oscillator. The characteristics of the I-V-L of the devices were measured with a PR650 spectrophotometer with a direct current source controlled by a computer in a dark room under ambient air conditions at room temperature. All measurements were completed within 20 min after the device was unloaded from the vacuum chamber.

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