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# PAPER

# Highly luminescent $\pi$ -conjugated dithienometalloles: photophysical properties and their application in organic light-emitting diodes<sup>†</sup>

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We have disclosed the photophysical and electroluminescent properties of a series of hetero-annulated  $\pi$ -conjugated dithieno[3,2-*b*:2',3'-*d*]metallole derivatives incorporating Ge, Si, P, and S atoms as a bridging center. The influence of the hetero-annulated structures on their photophysical properties has been investigated systematically by UV/vis and photoluminescence (PL) spectroscopy, transient PL measurements, and DFT calculations. All these compounds show bright fluorescence with high quantum yields both in solutions and in doped thin films with a host matrix. Furthermore, the OLEDs employing the dithienometallole emitters exhibit high external quantum efficiencies of ~6% at a practical brightness.

# Introduction

Luminescent organic and organometallic materials have gained a tremendous amount of attention during the last two decades, with respect to practical applications in organic electronics such as organic light-emitting diodes (OLEDs).<sup>1-3</sup> The control of their photophysical and electronic properties is one of the key issues in the optimization of these functional materials for the applications. In this regard, new synthetic approaches have been explored to produce luminescent  $\pi$ -conjugated materials incorporating main-group elements. Especially, metalloles,<sup>4</sup> which are hetero-annulated  $\pi$ -conjugated molecules, are attracting renewed interest because of their unusual electronic structure and resulting unique optoelectronic properties. Siloles<sup>5</sup> and their fused derivatives<sup>6</sup> (e.g., silafluorene) are the most important silicon-containing  $\pi$ -conjugated materials exhibiting high electron-transport and photoluminescent properties.<sup>5,6</sup> An effective  $\sigma^* - \pi^*$  hyperconjugation between the  $\sigma^*$  orbital of the heteroatom and the  $\pi^*$  orbital of the parent framework lowers the lowest unoccupied molecular orbital (LUMO) energy level,5,6 making it possible to utilize these compounds as n-type electrontransport materials, which is hardly realized in carbon-based analogues.

Recently, various types of metalloles containing boron,<sup>7</sup> phosphorus,<sup>8</sup> and sulfur<sup>9</sup> bridging elements have also emerged as a new building module of organic semiconductors. The incorporation of the hetero-bridged architecture into the  $\pi$ -conjugated framework is a fascinating approach to tailor the electronic properties and hence to develop photo- and electro-functional materials.<sup>7-9</sup> Despite these recent progresses, metalloles possessing a high degree of  $\pi$ -conjugation have been very weakly studied as an emitter in OLEDs so far.<sup>6b-d,8a,b</sup>

In this paper, we report a detailed study on the structural and photophysical properties of a family of luminescent  $\pi$ -conjugated dithieno[3,2-*b*:2',3'-*d*]metalloles incorporating germanium,



**Fig. 1** Chemical structures of luminescent  $\pi$ -conjugated dithieno[3,2b:2',3'-d]metalloles incorporating group 14–16 elements.

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silicon, phosphorus, and sulfur atoms as the bridging center (Fig. 1), together with their application as an emitting material in OLEDs. These building modules, conjoining two thiophene rings and a central heteroatom *via* annulations, allow modulation of the electronic functionality of the materials by virtue of their  $\sigma^*$ - $\pi^*$  interactions and high planarity of the *syn*-configured bithiophene unit. We envision that the versatile molecular design of luminescent  $\pi$ -conjugated dithienometalloles will offer great promise for their application in OLEDs because the device performance can be further enhanced by an appropriate design of the hetero-bridged architectures.

#### **Results and discussion**

#### Synthesis and characterization

The syntheses of Ge-BT, Si-BT, PO-BT, and SO<sub>2</sub>-BT were achieved by Suzuki-Miyaura cross-coupling of the corresponding dibromo-precursors with two equivalents of phenylboronic acid in the presence of  $Pd(PPh_3)_4$  as a catalyst (see ESI<sup>†</sup>). The synthetic protocol used to obtain Si-BT was previously established by Ohshita, Kunai, and coworkers.<sup>6h-j</sup> The synthesis of PO-BT was reported by Baumgartner and coworkers.<sup>8d-f</sup> Since the selective oxidation of thiophene rings can increase effectively its electron affinity,<sup>10</sup> we also chose to target the dithienothiophene-S,S-dioxide derivative SO<sub>2</sub>-BT. After conventional purifications including column chromatography and recrystallization, the obtained materials were further purified by temperature gradient sublimation under vacuum, and were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, mass spectrometry, and elemental analysis (see ESI<sup>†</sup>).

The solid-state structures of **Ge–BT**, **Si–BT**, and **SO<sub>2</sub>–BT** have been determined by single-crystal X-ray analysis (Fig. 2). The rigid tricyclic dithienometallole units are completely planar, independent of the bridging heteroatom. The dihedral angles between the central tricyclic unit and the peripheral phenyl rings range from 4 to 14°, suggesting that an effective  $\pi$ -conjugation is preserved over the entire molecular structure. In all these molecules, each heteroatom center (Ge, Si, S) adopts a distorted tetrahedral geometry with endocyclic angles of 89.6° for C–Ge–C (in **Ge–BT**), 92.06° for C–Si–C (in **Si–BT**), and 92.24° for C–S–C (in **SO<sub>2</sub>–BT**), which are much smaller than the standard value (109.5°) of an sp<sup>3</sup>-hybridized silicon or carbon atom.

To better understand the electronic effects of the heterobridged structures, we have performed density functional theory



**Fig. 2** ORTEP drawings of the X-ray structures (50% probability ellipsoids) of **Ge–BT**, **Si–BT**, and **SO<sub>2</sub>–BT**: (a) top view and (b) side view. Hydrogen atoms are omitted for clarity (see ESI†).



**Fig. 3** Frontier orbital distributions for dithieno[3,2-*b*:2',3'-*d*]metalloles derived from DFT calculations (B3LYP/6-31G(d)/LANL2DZ).

(DFT) calculations for the dithienometalloles (Fig. 3). The highest occupied molecular orbital (HOMO) of these molecules is expanded over the whole  $\pi$ -conjugated molecular framework without obvious participation of the heteroatom orbitals. In contrast, it is found that the bridging heteroatom center substantially affects the lowest unoccupied molecular orbital (LUMO) of the dithienometallole systems;  $\sigma^* - \pi^*$  interactions can operate to stabilize the LUMO energy levels (vide infra). For these materials, the HOMO energy levels have been determined experimentally by means of photoelectron spectroscopy, and subsequently their LUMO energy levels can be deduced from the HOMO energy levels and the optical energy gaps  $(E_{\alpha})$  (Table 1). **SO<sub>2</sub>–BT** possesses the most electron-deficient  $\pi$ -system, providing a low-lying LUMO energy level (-3.58 eV). Thus, modulation of the electronic character or energy levels can be attained by varying the hetero-bridged scaffold for this class of materials.

#### **Photophysical properties**

UV/vis absorption and photoluminescence (PL) spectra of Ge-BT, Si-BT, PO-BT, and SO<sub>2</sub>-BT have been measured in CH<sub>2</sub>Cl<sub>2</sub> solution, and the photophysical data are summarized in Table 1. The absorption spectra of these compounds are very similar, giving the absorption peaks ( $\lambda_{abs}$ ) in the range of 400– 420 nm (see ESI<sup>†</sup>), which are assigned to  $\pi$ - $\pi$ <sup>\*</sup> transition of the  $\pi$ -conjugated backbone. In the PL spectra (Fig. 4a), **PO-BT** and SO<sub>2</sub>-BT exhibit structureless emissions with the emission peak  $(\lambda_{em})$  at 529 and 509 nm, respectively, which takes place at a lower energy with a larger Stokes shift, compared to those of Ge-BT ( $\lambda_{em}$  = 483 nm) and Si–BT ( $\lambda_{em}$  = 493 nm). An intriguing photophysical feature is that the annulated dithienometalloles present much higher PL quantum yields ( $\Phi_{PL}$ ) than that of the non-bridged parent compound, 5,5'-diphenyl-2,2'-bithiophene (BT).<sup>11</sup> Incorporation of the bridging heteroatom results in a remarkably increased  $\Phi_{PL}$  and excited-state lifetime, as well as in

		$CH_2Cl_2$ solution (10 <sup>-5</sup> M)						Doped thin film in TBADN				
	HOMO $(eV)^a$	LUMO $(eV)^b$	$E_{\rm g}~({\rm eV})^b$	$\overline{\lambda_{abs}} (nm)^c$	$\lambda_{\rm em}  ({\rm nm})$	$\Phi_{\mathrm{PL}}$ (%) <sup>d</sup>	$\tau$ (ns) <sup>e</sup>	$k_{\rm r}  (10^8  {\rm s}^{-1})$	$k_{\rm nr}  (10^8  {\rm s}^{-1})$	$\lambda_{\rm em}  ({\rm nm})$	$\Phi_{\mathrm{PL}}$ (%) <sup>d</sup>	$\tau$ (ns) <sup>e</sup>
Ge-BT Si-BT PO-BT SO <sub>2</sub> -BT BT	-5.60 -5.59 -5.44 -5.82 f	-3.00 -3.04 -2.96 -3.58 f	2.60 2.55 2.48 2.24 f	401 408 419 414 370	483 493 529 509 455	50 81 75 90 13	1.3 2.8 6.0 5.7 0.3	3.9 2.9 1.3 1.6 4.3	3.9 0.7 0.4 0.2 29	466 479 531 519 440	70 86 90 94 18	2.9 3.6 8.9 5.7 0.6

Table 1 Photophysical properties of dithieno[3,2-b:2',3'-d]metallole derivatives and the corresponding non-bridged analogue BT

<sup>*a*</sup> Determined by photoelectron spectroscopy. <sup>*b*</sup> LUMO = HOMO +  $E_g$ , the values of  $E_g$  were estimated from the absorption onset of thin films. <sup>*c*</sup> Only the lowest energy absorption maxima are given. <sup>*d*</sup> Absolute PL quantum yield measured using an integrating sphere. <sup>*e*</sup> PL lifetime. <sup>*f*</sup> Not determined.

red-shifted emission (Table 1). The hetero-bridged structure would prevent structural relaxation in the excited state by comparison with the non-bridged **BT**, and therefore suppress non-radiative decay. The trend of  $\Phi_{PL}$  is **SO<sub>2</sub>-BT** > **Si-BT** > **PO-BT** > **Ge-BT** in CH<sub>2</sub>Cl<sub>2</sub> solution.

The transient PL signals for the dithienometalloles (Fig. 4b) exhibit monoexponential decay with the lifetime in the range of 1–6 ns, indicative of their fluorescent origin. One can calculate the radiative  $(k_r)$  and non-radiative  $(k_{nr})$  decay rates from the data of  $\tau (= 1/(k_r + k_{nr}))$  and  $\Phi_{PL} (= k_r/(k_r + k_{nr}))$ , as listed in Table 1. While the radiative decay rates of all these compounds



**Fig. 4** (a) PL spectra and (b) PL decay profiles for **Ge–BT**, **Si–BT**, **PO–BT**, **SO<sub>2</sub>–BT**, and **BT** in CH<sub>2</sub>Cl<sub>2</sub> solution after excitation at 405 nm at 293 K.

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are in the same order of magnitude  $(10^8 \text{ s}^{-1})$ , the non-radiative rates are observed to decrease considerably in the case of **Si–BT**, **PO–BT**, and **SO<sub>2</sub>–BT**, by introducing the rigid hetero-bridged structure. It is noteworthy that the suppression of non-radiative decay processes leads to progressive enhancement of the luminescent properties for the dithienometalloles. As for **Ge–BT**, a relatively large  $k_{nr}$  value should mainly be ascribed to the intersystem crossing into the triplets manifold, as a consequence of the heavy-atom effect of germanium.

Since the present hetero-bridged  $\pi$ -conjugated compounds were being developed as emitting materials for OLEDs, it is of importance to investigate their PL properties not only in solution but also in doped thin films with a host matrix. We have employed 2-tert-butyl-9,10-di(2-naphthyl)anthracene (TBADN)<sup>12</sup> as a host material for Ge-BT, Si-BT, PO-BT, and SO<sub>2</sub>-BT guest emitters on account of its ambipolar ability,<sup>13</sup> wide energy gap, and spectral overlap between the emission of TBADN and the absorption of the guest emitters. With the doping concentration of 3 wt%, the emission from the TBADN host centered around 440 nm disappears under photoexcitation (see ESI<sup>†</sup>), confirming the occurrence of efficient Förster-type energy transfer from the host to the guest emitters. The  $\Phi_{\rm PL}$ values of the thin films tend to depress at higher doping concentrations (>6%) owing to concentration quenching.<sup>14</sup> The 3 wt% dithienometallole:TBADN codeposited films give  $\Phi_{PL}$  of 70–94% and  $\tau$  of 2–9 ns (Table 1). Of great interest, the  $\Phi_{\rm PL}$ values are higher than those recorded in solution, which should arise from the restriction of intramolecular fragmental rotation in the solid state.

# **OLED** device performances

The high PL efficiency of the  $\pi$ -conjugated dithienometalloles in doped films suggests that they are promising candidates for the fabrication of efficient OLEDs. To this end, multilayer OLEDs have been fabricated with the following device configuration (Fig. 5): ITO/4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl]biphenyl diamine ( $\alpha$ -NPD, 40 nm)/3 wt% dithienometallole:TBADN (30 nm)/4,7diphenyl-1,10-phenanthroline (BPhen, 50 nm)/LiF (0.8 nm)/Al (80 nm), where  $\alpha$ -NPD serves as the hole-transporting layer, BPhen functions as the hole-blocking and electron-transporting layer, and LiF is the electron-injection material. As schematically shown in Fig. 5, the LUMO and HOMO levels of TBADN (-2.8 eV and -5.8 eV, respectively) as a host are above and below those of the dithienometalloles, respectively, implying that



**Fig. 5** Energy-level diagram of OLED devices (top) and chemical structures of the materials used for the devices (bottom).

the guest emitters will possibly trap electrons and holes. Moreover, the BPhen layer possessing a deep HOMO level effectively prevents hole leakage and allows a better confinement of charge carriers and excitons within the emitting layer.

Fig. 6 displays the current density-voltage (J-V) and luminance-voltage (L-V) characteristics and the external quantum efficiencies ( $\eta_{ext}$ ) of the OLEDs featuring Ge-BT, Si-BT, PO-BT, and SO<sub>2</sub>-BT as emitters. The electroluminescence (EL) properties are summarized in Table 2, which are dependent on the optoelectronic features of the hetero-bridged scaffold. The EL spectra testify the emission exclusively from the dithienometallole emitters (Fig. 6a); no emission from the TBADN host is observed. All of the devices exhibit good OLED performances, as they possess a low turn-on voltage (V<sub>ON</sub>) of 2.8-2.9 V and a high maximum luminance  $(L_{\text{max}})$  exceeding 26 000 cd  $m^{-2}$  (Fig. 6b). Among the devices, the SO<sub>2</sub>-BT-based one shows the highest external EL quantum efficiency ( $\eta_{ext}$ ) of 6.1% (Fig. 6c), which is greater than those of the devices based on **Ge–BT** ( $\eta_{\text{ext}} = 3.4\%$ ), **Si–BT** (5.2%), and **PO–BT** (4.0%), as well as conventional fluorescent OLEDs. Notably, even when the luminance reaches 10 000 cd m<sup>-2</sup>, the  $\eta_{ext}$  of the SO<sub>2</sub>–BT-based device still remains nearly 6%, indicative of a balanced injection and the transport of holes and electrons in the device, at high current densities.

As for the SO<sub>2</sub>-BT-based OLED, the theoretical value of the external EL quantum efficiency,  $\eta_{\text{ext}}$ , can be estimated to be 4.7% using the following equation:  $\eta_{\text{ext}} = \gamma \times \eta_{\text{st}} \times \Phi_{\text{PL}} \times \eta_{\text{out}}$ .<sup>15</sup> Therein, the charge balance factor  $(\gamma)$ , the production efficiency of spin-allowed excitons ( $\eta_{st}$ ), the quantum yield of the SO<sub>2</sub>-**BT**:TBADN film ( $\Phi_{\rm PL}$ ), and the light out-coupling efficiency  $(\eta_{out})$  could be assumed as approximately 1, 0.25, 0.94, and 0.2,<sup>16</sup> respectively. As a result, the experimentally obtained  $\eta_{ext}$  of 6.1% exceeds the theoretical limit for the present system. A plausible origin accounting for a relatively high EL efficiency is outcoupling enhancement by orientation of the luminescent molecules within the emitting layer. Recently, it has been revealed that the emission dipoles of linearly  $\pi$ -extended fluorescent<sup>17a-c</sup> or phosphorescent<sup>17d</sup> molecules are not isotropic but aligned horizontally on the surface of the OLEDs, giving rise to an increase of  $\eta_{\rm out}$ .<sup>17</sup>



**Fig. 6** Performance of multilayer OLEDs incorporating dithieno[3,2-b:2',3'-d]metalloles as emitters: (a) current density–voltage (inset: EL spectra operated at *ca.* 10 V), (b) luminance–voltage (inset: photographs showing EL emission), and (c) external EL quantum efficiency–current density characteristics of the devices.

 Table 2
 Summary of OLED performances<sup>a</sup>

Emitter	$\lambda_{\rm EL}~({\rm nm})$	$V_{\rm ON}\left({\rm V} ight)$	$L_{\rm max}~({\rm cd}~{\rm m}^{-2})$	$\eta_{\mathrm{ext,max}}$ (%)	CIE $(x,y)$
Ge–BT	490	2.8	29 700	3.4	0.17,0.39
Si–BT	502	2.9	26 100	5.2	0.18,0.42
PO–BT	520	2.8	43 800	4.0	0.29,0.57
SO2–BT	524	2.8	46 300	6.1	0.28,0.55

<sup>*a*</sup> Device configuration: ITO/α-NPD (40 nm)/3 wt% emitter:TBADN (30 nm)/BPhen (50 nm)/LiF (0.8 nm)/Al (80 nm). Abbreviations:  $\lambda_{EL}$ : EL maximum;  $V_{ON}$ : turn-on voltage at 1 cd m<sup>-2</sup>;  $L_{max}$ : maximum luminance;  $\eta_{ext,max}$ : maximum external EL quantum efficiency; CIE (*x*,*y*): Commission Internationale de l'Eclairage color coordinates measured at 10 mA cm<sup>-2</sup>.



Fig. 7 Polarized emission spectra from the edge of a 3 wt%  $SO_2$ -BT:TBADN film with a thickness of 100 nm on a quartz glass substrate (left) and optical setup used for the anisotropic PL measurements (right).<sup>16,18</sup> The electric field in TE mode is polarized parallel to the substrate and that in the TM mode is polarized in the plane perpendicular to it.

Accordingly, if the linear-shaped light-emitting SO<sub>2</sub>-BT molecules have a tendency towards horizontal orientation within the amorphous TBADN matrix, the out-coupling efficiency of the device will be enhanced. To verify this notion, we have measured polarized PL spectra from the edge of the SO<sub>2</sub>-BT:TBADN codeposited film (Fig. 7). The intensity of the transverse electric (TE) emission from the edge of the doped thin film is found to be much larger than that of the transverse magnetic (TM) emission. This result unambiguously indicates that the transition dipoles for emission lie preferentially parallel even in the isotropic TBADN host matrix on the substrate, leading to an enhancement of  $\eta_{out}$  of the OLEDs. The S=O groups in SO<sub>2</sub>-BT are orthogonal to the dithienothiophene plane (Fig. 2), but are sterically less hindered compared to the phenyl groups of the other dithienometallole emitters. It is anticipated that the preferential horizontal orientation of the emitting molecules in the doped films should be affected by steric effects of the orthogonal substituents.

Another possible mechanism causing such high  $\eta_{out}$  is triplettriplet annihilation (TTA), in which interactions between two triplet states lead to the production of one singlet excited state and one ground state.<sup>19</sup> To promote deeper insight, the transient EL responses have been examined for the **SO<sub>2</sub>–BT**-based device (see ESI†). While the delayed EL component originating from the TTA process can be observed at high current densities (*ca.* 10–100 mA cm<sup>-2</sup>), the contribution of the TTA in the EL efficiency is found to be negligible at low current densities less than 10 mA cm<sup>-2</sup>. Hence, the higher  $\eta_{ext}$  than the theoretical limit should predominantly be ascribed to the enhancement of outcoupling efficiency on account of horizontal orientation of the emitters in the devices.

# Conclusions

In summary, we have synthesized and characterized a series of hetero-annulated dithieno[3,2-*b*:2',3'-*d*]metalloles (**Ge–BT**, **Si–BT**, **PO–BT**, and **SO<sub>2</sub>–BT**) as new light-emitting materials. The versatile molecular design strategy provides access to a wide variety of luminescent hetero-annulated  $\pi$ -conjugated materials. The incorporation of heteroatoms into main  $\pi$ -systems allows their electronic structure and photophysical properties to be modulated effectively. The photoluminescent properties of the dithienometalloles are remarkable in terms of quantum yields,

compared with those of their non-bridged counterparts. The multilayer OLED devices employing the luminescent dithienometallole guest emitters, doped into a host matrix, have been fabricated and evaluated. We have achieved a high external EL efficiency of approximately 6% for the fluorescent OLED incorporating **SO<sub>2</sub>-BT** at a practical brightness. The polarized photoluminescence measurements indicated the possibility of the enhancement of the light out-coupling efficiency by the horizontal orientation of the emitting molecules in the devices.

# Experimental

# General procedure

Commercially available reagents and solvents were used without further purification unless otherwise noted. 3.3'-Dibromo-2.2'bithiophene and dithieno[3,2-b:2',3'-d]thiophene were purchased from Aldrich. If necessary, the compounds were purified by recycling preparative HPLC (LC-9130 NEXT, Japan Analytical Industry) on GPC columns. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance III 500 spectrometer. Chemical shifts of <sup>1</sup>H and <sup>13</sup>C NMR signals were quoted to tetramethylsilane ( $\delta = 0.00$ ) and CDCl<sub>3</sub> ( $\delta = 77.0$ ) as internal standards. Mass spectra were collected on a Waters 3100 mass spectrometer with an atmospheric solid analysis probe. Elemental analyses were carried out with a Yanaco MT-5 CHN corder. UV/Vis absorption and photoluminescence (PL) spectra were measured with a Shimadzu UV-2550 spectrometer and a JASCO FP-6500-ST spectrophotometer, respectively. PL quantum yields were measured using an integration sphere system coupled with a photonic multichannel analyzer (Hamamatsu Photonics C9920-02, PMA-11). The experimental HOMO energy levels of thin films were determined using a Riken-Keiki AC-2 photoelectron spectrometer (see ESI<sup>†</sup>); the LUMO energy levels were estimated by subtracting the optical energy gap from the measured HOMO energy levels. Transient PL decay curves were measured with a Hamamatsu Photonics Quantaurus-Tau spectrometer at room temperature. The density-functional theory (DFT) calculations were performed on the Gaussian 03 program package, using the B3LYP functional with the 6-31G(d)/LANL2DZ basis sets. The LANL2DZ effective core potential was applied for Ge atom and 6-31G(d) for other atoms.

#### X-ray crystallography

Single crystals of Ge–BT, Si–BT, and SO<sub>2</sub>–BT were obtained by slow diffusion of methanol vapour into their CHCl<sub>3</sub> solutions at room temperature. X-ray crystal analyses were made on a Rigaku VariMax with a Saturn 724+ system with graphite monochromated MoK $\alpha$  radiation. The structures were solved by direct methods (SIR2008) and refined by full-matrix least-square methods based on  $F^2$  (SHELXL-97). CCDC-875779 (Ge–BT), CCDC-875780 (Si–BT), and CCDC-875781 (SO<sub>2</sub>–BT) contain the supplementary crystallographic data for this paper.

#### **OLED** device fabrication and measurements

In a general procedure, indium-tin oxide (ITO)-coated glass substrates were cleansed with detergent, deionized water, acetone, and isopropanol, followed by UV-ozone treatment. Organic layers were successively deposited onto the ITO substrate by vacuum thermal evaporation at deposition rates of  $0.2-0.4 \text{ nm s}^{-1}$ . The layer thickness and the deposition rate were monitored *in situ* during the deposition by an oscillating quartz thickness monitor. LiF and Al cathodes were finally deposited through a shadow mask on the organic stacks. The current density–voltage–luminance characteristics and EL spectra of the devices were collected using a Keithley 2400 source measurement unit and a Hamamatsu Photonics PMA-12 photonic multichannel analyzer in an ambient condition. For edge photo-luminescence measurements of thin films, the sample was excited by an N<sub>2</sub> laser (337 nm), and the light emission was detected through a linear polarizer and an optical fiber scope connected to a spectrometer.

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