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Highly Efficient Electron-Transporting/Injecting and Thermally Stable Naphthyridines for Organic Electrophosphorescent Devices

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A series of 1,8-naphthyridine derivatives is synthesized and their electrontransporting/injecting (ET/EI) properties are investigated via a multilayered electrophosphorescent organic light-emitting device (OLED) using fac-tris(2phenylpyridine)iridium [Ir(ppy)3] as a green phosphorescent emitter doped into a 4,4'-N,N'-dicarbazolebiphenyl (CBP) host with 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (a-NPD) as the hole-transporting layer, and poly(arylene ether sulfone) containing tetraphenylbenzidine (TPDPES) doped with tris(4-bromophenyl)ammonium hexachloroantimonate (TBPAH) as the hole-injecting layer. The turn-on voltage of the device is 2.5 V using 2,7-bis[3-(2-phenyl)-1,8-naphthyridinyl]-9,9-dimethylfluorene (DNPF), lower than that of 3.0 V for the device using a conventional ET material. The maximum current efficiency (CE) and power efficiency (PE) of the DNPF device are much higher than those of a conventional device. With the aid of a hole-blocking (HB) and exciton-blocking layer of bathocuproine (BCP), 13.2-13.7% of the maximum external quantum efficiency (EQE) and a maximum PE of 50.2-54.5 Im W⁻¹ are obtained using the naphthyridine derivatives; these values are comparable with or even higher than the 13.6% for conventional ET material. The naphthyridine derivatives show high thermal stabilities, glasstransition temperatures much higher than that of aluminum(III) bis(2-methyl-8-quinolinato)-4-phenylphenolate (BAlq), and decomposition temperatures of 510–518 °C, comparable to or even higher than those of Alq₃.

1. Introduction

The generation of light in an organic light-emitting device (OLED) is the consequence of the recombination of holes and electrons injected from the electrodes to the organic light-emitting layer.

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The efficiency of an OLED therefore depends on the recombination efficiency of holes with electrons and the photoluminescence quantum yield of the emitter. An internal quantum efficiency (IQE) of 25% (corresponding to ≈5% external quantum efficiency (EQE)) can be obtained in a fluorescent emitter from the 1/4 singlet spin states. If a phosphorescent emitting material is used, the remaining 3/4 triplet spin states can also emit light, therefore 100% of the IQE (corresponding to $\approx 20\%$ of the EQE) can theoretically be obtained in an electrophosphorescent device.^[1,2] In the case of green electrophosphorescence, factris(2-phenylpyridine)iridium [Ir(ppy)₃] is a highly efficient electrophosphorescence emitter, and 100% photoluminescence quantum yields have been reported by Adachi and co-workers.^[3]

Organic semiconductors are generally better *p*-type conductors than they are *n*-type conductors (i.e., the hole mobility is much higher (around 1000 times) than the electron mobility of an organic semiconducting material),^[4] holes are much easier to transport than electrons in an OLED, therefore electron transport is

the limiting factor for the IQE of an OLED. To obtain a highefficiency electrophosphorescent device, it is crucial to develop highly efficient electron-transporting (ET) materials. Although tris(8-hydroxyquinoline)aluminum (Alq₃)^[5] and its analogs

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aluminum(III) bis(2-methyl-8-quinolinato)-4-phenylphenolate $(BAlq)^{[6]}$ are efficient ET materials, the triplet energies (E_T) of Alg₃ and BAlg are 2.0 eV^[7] and 2.2 eV^[6] respectively, both lower than the value of 2.4 eV for $Ir(ppy)_{3}$.^[8] Thus, they cannot effectively block the triplet exciton from the emitter layer of an Ir(ppy)₃-based electrophosphorescent device without combining with hole-blocking (HB) and exciton-blocking materials with wide energy gaps and high $E_{\rm T}$ values. HB materials with wide energy gaps (e.g., bathocuproine (BCP),^[9] bathophenanthroline,^[10] oxadiazoles,^[11,12] triazoles,^[13] and 1,3,5-tris(N-phenylbenzimidazol-2-yl-benzene),^[14] have been used to improve the efficiency of electrophosphorescent devices. Recently, Kido and coworkers reported a series of phenylpyrimidines^[15,16] and phenylpyridines^[17,18] as ET and HB materials with very high electron mobilities and higher $E_{\rm T}$ values than that of Ir(ppy)₃. An EQE of 29% and a power efficiency (PE) of 133 lm W^{-1} at 100 cd m⁻² were obtained using bis-4,6-(3,5-di-3-pyridylphenyl)-2-methylpyrimidine.^[15] With the aid of the out-coupling method, the PE can be further increased.^[19] However, the thermal stability of ET materials needs to be improved.

In order to achieve this, we designed and synthesized a series of naphthyridine derivatives, based on the electronwithdrawing properties of the naphthyridine moiety and its high thermal stability. Naphthyridines are widely used as antibacterial substances.^[20] Very recently, Liao et al.^[21] reported a series of 4-hydroxy-1,5-naphthyridine-based group-III metal chelates as deep-blue emitters for OLEDs. In this paper, we report a series of thermally stable 1,8-naphthyridine derivatives with highly efficient ET properties, which also have HB properties and energy gaps (2.94-3.33 eV) much wider than that of Alq₃. Efficient ET properties can therefore be expected from the electron-withdrawing naphthyridine moiety, and holes and/or excitons injected from the emitter layer can be expected to be effectively blocked because of the wide energy gaps. Fluorene and anthracene moieties were introduced to improve the thermal stabilities of the compounds. Their ET and HB properties were investigated via multilayered devices using Ir(ppy)₃ as the phosphorescent emitter.

2. Results and Discussion

2.1. Syntheses

The 1,8-naphthyridine moiety was synthesized from nicotinamide. 2-(3'-Pyridyl)pyrido[2,3-*d*]pyrimidine and 2-aminonicotinaldehyde were obtained, and then 2-(3-bromophenyl)-1,8-naphthyridine was obtained via a Friedlander reaction.^[22] Finally, naphthyridine derivatives, 2,7-bis[3-(2-phenyl)-1,8-naphthyridinyl]-9,9dimethylfluorene (DNPF) and 9,10-bis[3-(1,8-naphthyridin-2-yl) phenyl]anthracene (DNPA) were synthesized through a Suzuki– Miyaura cross-coupling reaction^[23] by introducing fluorene and anthracene moieties, as shown in **Scheme 1**.

2.2. Physical Properties

The absorption spectra of the films, which were deposited by high-vacuum (10⁻⁶ Torr) thermal evaporation on quartz, are shown in Figure 1. The absorption peaks at around 335 nm for DNPF and 332 nm for DNPA can be assigned to the π - π * transitions of the naphthyridine moiety. There were peaks at 362 nm (shoulder), 382 nm, and 404 nm for DNPA, which can be attributed to absorptions of the anthracene moiety.^[24] According to calculations based on the absorption edges, the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) energy gap (E_{α}) of DNPF is 3.33 eV, and that of DNPA is 2.94 eV, both wider than that of Alq₃ (2.70 eV). The energy gap of DNPF is even wider than that of BAlq (3.00 eV);^[25] the values are listed in Table 1. The HOMO energy levels of the synthesized naphthyridine derivatives are deeper than that of Alq₃ (i.e., its I_p (5.85–5.93 eV), measured by atmospheric ultraviolet (UV) photoelectron spectroscopy, is larger than that of Alq₃ (5.70 eV)). The $E_{\rm T}$ level of DNPF was found to be 2.33 eV from the onset of the phosphorescent spectrum in the film state under excitation by a nitrogen laser (337 nm) at 4.2 K, which is higher than those of 2.03 eV for Alq₃ and 2.18 eV for BAlq. It is therefore expected that the triplet exciton in the emitting layer



Scheme 1. Syntheses of naphthyridine derivatives.



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Figure 1. UV-vis absorption spectra of naphthyridine films.

might be more effectively blocked by DNPF than by Alq_3 and BAlq.

The thermal properties of the naphthyridine derivatives were measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Table 1). The glass-transition temperature (T_g) and decomposition temperature (T_d) of DNPA are 180 °C and 518 °C, respectively, both higher than those of Alq₃.^[26] The T_d of DNPF is higher than that of Alq₃; although the T_g is lower than that of Alq₃ (175 °C), it is still as high as 150 °C. The T_g values of the synthesized naphthyridine derivatives are much higher than that of BAlq (92 °C).^[27] The higher thermal stability of DNPA than that of DNPF can be attributed to the higher thermal stability of the anthracene moiety compared with that of the fluorene moiety. These results indicate that the thermal stabilities of the synthesized naphthyridines are high enough for them to be used in OLEDs.

2.3. Device Properties

To study the ET properties of the naphthyridine derivatives, phosphorescent devices were fabricated using a 20 nm layer of 10:1 (wt) poly(arylene ether sulfone) containing tetraphenylbenzidine (TPDPES) doped with tris(4-bromophenyl)ammonium hexachloroantimonate (TBPAH) (TPDPES:TBPAH) as the hole-injecting material, a 30 nm layer of 4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (α -NPD) as the hole-transporting material, and a 30 nm layer of emitting material (EM) consisting of Ir(ppy)₃ (6 wt%) as the phosphorescent emitter, codeposited with 4,4'-*N*,*N*'-dicarbazolebiphenyl (CBP) as the host material.

 Table 1. Physical properties of naphthyridine derivatives.

A 30 nm layer of DNPF or BAlq (reference device) as the ET and HB combined layer was then deposited on the surface of the EM. Another HB layer, namely a 10 nm layer of BCP, and a 20 nm layer of DNPF or DNPA as the ET layer were then deposited on the EM surface. For comparison, a 10 nm layer of BCP together with a 20 nm layer of Alq₃ as the HB material and ET material, respectively, were deposited as a reference device. Finally, a 0.5 nm layer of LiF and a 100 nm layer of Al were deposited as the cathode. The emitting area was defined, using a shadow mask, to be 0.2 cm × 0.2 cm. The device architecture is shown in **Figure 2**.

The current-density-voltage curves are shown in Figure 3; the current density of the DNPF device at low voltage is higher than that of the BAlq device, and the turn-on voltage of the DNPF device is 2.5 V, lower than that of 3.0 V for the BAlq device. This indicates that the EI ability of DNPF is higher than that of BAlq. The luminance of the DNPF device is also higher than that of the BAlq device. The driving voltage of 3.7 V for the DNPF device at 100 cd m⁻² is much lower than that of 5.3 V for the BAlq device. Accordingly, the current efficiency (CE) and PE are higher than those of the BAlq device, especially at low current densities, as shown in Figure 4. The maximum CE and PE of the DNPF device are 19.6 cd A⁻¹ at 4.0 V and 18.9 lm W⁻¹ at 3.0 V, respectively, much higher than those of 12.5 cd A^{-1} at 12.0 V and 4.0 lm W^{-1} at 3.0 V for the BAlq device. The device performances are listed in Table 2. Although a 5.39% EQE was obtained for the DNPF device, higher than that of 3.69% for the BAlq device, these values are still not high enough for an electrophosphorescent device. This might be interpreted in terms of the low $E_{\rm T}$ of 2.33 eV of the DNPF, deduced from the phosphorescence spectrum, and that of 2.18 eV for BAlq, both lower than the 2.42 eV for Ir(ppy)₃, so triplet excitons cannot be blocked effectively because of the longer diffusion paths of triplet excitons than those of singlet excitons. The higher efficiency of the DNPF device at low current densities than that of the BAlq device might be because the E_{T} level of DNPF is higher than that of BAlq. In addition, holes cannot be effectively blocked because of the insufficiently deep HOMO level of 5.9 eV for DNPF and BAlq.^[25]

To improve the blocking effect for triplet excitons and holes in the device, a 10 nm layer of BCP with an E_T 2.5 eV higher than that of Ir(ppy)₃ and a much-deeper HOMO level of 6.5 eV was inserted between the emitter and the ET layers. For comparison, Alq₃ was chosen as the ET material. From the current-density–voltage curves (**Figure 5**), we found that the current density of BCP/DNPA was larger than that of

| Material | T _g [°C] | T _d [°C] | E _a [eV] | I _p [eV] | E _g [eV] | E _T [eV] | Reference |
|----------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|-----------|
| DNPF | 150 | 510 | 2.60 | 5.93 | 3.33 | 2.33 | This work |
| DNPA | 180 | 518 | 2.91 | 5.85 | 2.94 | | This work |
| BAlq | 92 | | 2.90 | 5.90 | 3.00 | 2.18 | [6,25,27] |
| Alq ₃ | 175 | 508 | 3.00 | 5.70 | 2.70 | 2.03 | [7,26] |
| Ir(ppy) ₃ | | | 3.00 | 5.60 | 2.60 | 2.42 | [8] |

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Figure 2. Chemical structures of organic materials used and OLED structure.



Figure 3. Current-density-voltage (left) and luminance-voltage (right) curves of devices: ITO/TPDPES:TBPAH 20 nm/α-NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/LiF/Al (\odot); and ITO/TPDPES:TBPAH 20 nm/α-NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/DNPF 30 nm/LiF/Al (\odot).



Figure 4. CE-current-density (left) and PE-current-density (right) curves of devices. ITO/TPDPES:TBPAH 20 nm/ α -NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/LiF/Al (\odot); and ITO/TPDPES:TBPAH 20 nm/ α -NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/LiF/Al (\odot).



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Table 2. Performances of devices without additional HB layer.

| ET | Turn-on voltage [V] | Max Luminance [cd m ⁻² @ V] | Max PE [Im W ⁻¹ @ V] | Max CE [cd A ⁻¹ @ V] | Max EQE [%] |
|------|------------------------|---|------------------------------------|------------------------------------|-------------|
| DNPF | 2.5 | 65817 @ 14.5 | 18.9 @ 3.0 | 19.6 @ 4.0 | 5.39 |
| BAlq | 3.0 | 70143 @ 13.5 | 4.0 @ 3.0 | 12.5 @ 12.0 | 3.69 |

BCP/Alq₃, and the current density of BCP/DNPF increased to be larger than that of BCP/Alq₃with increasing operating voltage. These results indicate that the ET/EI abilities of naphthyridines are comparable or even higher than that of Alq₃. These results might be explained by the presence of the electron-withdrawing naphthyridine moiety.^[21] To confirm this, electron-only devices of DNPF, DNPA, and Alq₃ were fabricated with the structure of indium tin oxide (ITO)/BCP 10 nm/DNPF, DNPA, or Alq₃ 90 nm/LiF/Al; BCP acted as an HB layer to prevent hole injection from the ITO layer to the ET laver. The electron-current densities of both DNPF and DNPA were higher than that of Alq₃ (Figure 6). This indicates that the ET capabilities of DNPF and DNPA are definitely higher than that of Alq₃. This is consistent with the result that the electron mobility of a 1,5-naphthyridine Al(III) chelate is 10^{-4} cm² V⁻¹ s⁻¹, higher than that of 10^{-5} cm² V⁻¹ s⁻¹ for Alg₃, as previously reported.^[21]

The luminance–voltage curves (Figure 5) show that the BCP/ DNPA device exhibits a higher luminance than that of the BCP/ Alq₃ device, and the BCP/DNPF device shows a comparable luminance to that of the BCP/Alq₃ device. The naphthyridine devices show maximum luminances of 115 880 cd m⁻² at 12.0 V for the DNPA device and 102 480 cd m⁻² at 13.0 V for the DNPF device, both higher than that of 99 704 cd m⁻², at a higher voltage of 13.5 V, for the Alq₃ device.

The plots of CE versus current density (Figure 7) showed a higher CE for the BCP/DNPF device than for the BCP/Alq₃

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Figure 6. Current-density–voltage curves of devices: ITO/BCP10 nm/ DNPF (○), DNPA (●), or Alq₃ (○) 90 nm/LiF/Al.

Votage (V)

8 10 12 14 16 18 20 22

1000

100

10

0.1 0.01 1E-3 1E-4 1E-5 1E-6

0 2 4 6

Current Density (mA/cm²)

DNPF 90 nm

DNPA 90 nn

device at low current densities. The BCP/DNPA device showed a comparable performance to that of the BCP/Alq₃ device; the device performances are listed in Table 3. Maximum EQEs of 13.2-13.7% (Figure 8) were obtained for the naphthyridine devices, corresponding to maximum CEs of 48.2-52.4 cd A⁻¹ and maximum PEs of 50.2-54.4 lm W⁻¹; these values are comparable to or even higher than those of the BCP/Alq₃ device. Because the E_T of 2.3 eV for DNPF is higher than that of 2.0 eV for Alq₃, triplet excitons in the device might be more effectively blocked in the BCP/DNPF device than in the BCP/Alq₃ device as a result of the longer diffusion paths of the triplet excitons than those of the singlet excitons, as a result of diffusion to the ET layer, giving a higher efficiency. The turn-on voltages of the BCP/DNPF and BCP/DNPA devices are the same as that of the BCP/Alq₃ device, and no additional peak was observed for the naphthyridine device, the same as in the case of the BCP/Alq₃ device (Figure 9). These results indicate that naphthyridines are suitable for use as ET materials for green electrophosphorescent devices.



Figure 5. Current-density–voltage (left) and luminance–voltage (right) curves of devices: ITO/TPDPES:TBPAH 20 nm/α·NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/BCP 10 nm/Alq₃ 20 nm/LiF/Al (○); ITO/TPDPES:TBPAH 20 nm/α·NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/BCP 10 nm/DNPF 20 nm/LiF/Al (●); ITO/TPDPES:TBPAH 20 nm/α·NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/BCP 10 nm/DNPA 20 nm/LiF/Al (○).



Figure 7. CE-current-density (left) and PE-current-density (right) curves of devices: ITO/TPDPES:TBPAH 20 nm/α·NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/BCP 10 nm/Alq₃ 20 nm/LiF/Al (○); ITO/TPDPES:TBPAH 20 nm/α·NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/BCP 10 nm/DNPF 20 nm/LiF/Al (●); ITO/TPDPES:TBPAH 20 nm/α·NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/BCP 10 nm/DNPA 20 nm/LiF/Al (○).



Figure 8. EQE–current-density curves of devices: ITO/TPDPES:TBPAH 20 nm/ α -NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/BCP 10 nm/Alq₃ 20 nm/ LiF/Al (\odot); ITO/TPDPES:TBPAH 20 nm/ α -NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/BCP 10 nm/DNPF 20 nm/LiF/Al (\bullet); ITO/TPDPES:TBPAH 20 nm/ α -NPD 30 nm/CBP:6%Ir(ppy)₃ 30 nm/BCP 10 nm/DNPA 20 nm/ LiF/Al (\odot).

3. Conclusions

A series of 1,8-naphthyridine derivatives were synthesized and their ET/EI properties in green electrophosphorescent devices were investigated. The turn-on voltage of the DNPF device was lower than that of the BAlq device as a result of the higher EI ability of the naphthyridine derivative DNPF compared with that of the conventional ET material BAlq. The maximum CE and PE of the DNPF device were 19.6 cd A⁻¹ and 18.9 lm W⁻¹, much higher than those of 12.5 cd A⁻¹ and 4.0 lm W⁻¹ for the BAlq device; this might be the result of the higher $E_{\rm T}$. With the aid of an HB and exciton-blocking layer of BCP, 13.2–13.7% maximum EQEs with maximum PEs of 50.2–54.5 lm W⁻¹,



Figure 9. EL spectra of devices: ITO/TPDPES:TBPAH 20 nm/ α -NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/BCP 10 nm/Alq₃ 20 nm/LiF/Al (dashed line); ITO/TPDPES:TBPAH 20 nm/ α -NPD 30 nm/CBP:6% Ir(ppy)₃ 30 nm/BCP 10 nm/DNPF 20 nm/LiF/Al (solid line).

comparable to or even higher than those of the BCP/Alq₃ device, were obtained using the naphthyridine derivatives as ET materials. Because of the higher E_T of 2.33 eV for DNPF compared with that of 2.03 eV for Alq₃, triplet excitons in the device might be more effectively blocked in the BCP/DNPF device

 Table 3. Performances of devices with HB layer of BCP.

| ET | Turn-on voltage [V] | Max Luminance [cd m ⁻² @ V] | Max PE [Im W ⁻¹ @ V] | Max CE [cd A ⁻¹ @ V] | Max EQE [%] |
|------------------|------------------------|---|------------------------------------|------------------------------------|----------------|
| Alq ₃ | 3.0 | 99704 @ 13.5 | 53.4 @ 3.0 | 50.1 @ 3.5 | 13.6 |
| DNPF | 3.0 | 102480 @ 13.0 | 54.5 @ 3.0 | 52.4 @ 3.5 | 13.7 |
| DNPA | 3.0 | 115880 @ 12.0 | 50.2 @ 3.0 | 48.2 @ 3.5 | 13.2 |



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than in the BCP/Alq₃ device, resulting in a higher efficiency. The naphthyridine derivatives have high thermal stabilities, even higher than those of Alq₃, and have potential applications as ET materials for green electrophosphorescent devices.

4. Experimental Section

General: The ¹H NMR spectra were recorded using a JEOL 270 (270 MHz) spectrometer. Electron-ionization mass spectrometry (EI-MS) was performed using a JEOL JMS-K9 mass spectrometer. UV-vis spectra were measured using a Shimadzu UV-3150 UV-vis/near-IR spectrophotometer. Photoluminescence spectra were obtained using a FluroMax-2 (Jobin-Yvon-Spex) luminescence spectrometer. DSC was performed on a Perkin-Elmer Diamond DSC Pyris instrument under a nitrogen atmosphere at a heating rate of 20 °C min⁻¹. TGA was performed using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹. The HOMO levels were determined using atmospheric UV photoelectron spectroscopy (Rikken Keiki AC-1). Phosphorescence spectra were measured using a streak camera (Hamamatsu Photonics, C4334) at 4.2 K. Electroluminescence (EL) spectra were obtained using an optical multichannel analyzer PMA 10 (Hamamatsu). The luminance was measured using a Topcon BM-8 luminance meter at room temperature under an ambient atmosphere.

Synthesis of 2,7-Dibromo-9,9-dimethylfluorene (1): The synthesis procedure was a modified version of a previously reported method.^[28] Methyl iodide (32.8 g, 0.231 mol) was added dropwise to a solution of 2,7-dibromofluorene (26.6 g, 0.082 mol) and sodium methoxide (12.5 g, 0.231 mol) in dimethyl formamide (500 mL), under nitrogen at 0–5 °C. Then the reaction mixture was stirred using a mechanical stirrer for 12 h. Water was added to quench the reaction, the mixture was extracted with ethyl acetate and finally purified on a column with *n*-hexane as the solvent; **1** was obtained as a white solid in an 86% yield, and identified using NMR spectroscopy. The synthesis is shown in Scheme 1. ¹H NMR (270 MHz, CDCl₃, δ): 7.538 (dd, 4H, J = 3.7 Hz, 5.7 Hz), 7.465 (d, 2H, J = 8.2 Hz), 1.464 (s, 6H).

2,2'-(9,9-Dimethyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-Synthesis of tetramethyl-1,3,2-dioxaborolane) (2): 1 (10.56 g, 0.03 mol) was dissolved in 400 mL of dehydrated diethyl ether with agitation under a flow of nitrogen. Then n-butyl lithium (2.44 M in n-hexane, 31 mL, 0.075 mol) was added to the solution after cooling to -78 °C using dry-ice. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16 mL, 0.078 mol) was added to the reaction solution after 2 h at -78 °C. The reaction was continued for 12 h after the temperature was back up to room temperature. Finally, 100 mL of water were added to quench the reaction. The product was extracted with diethyl ether, and purified by column chromatography (solvent: ethyl acetate:*n*-hexane = 1:9), and identified by ^{1}H NMR spectroscopy. The product 2 was obtained as a white solid in a 60.5% yield. The synthesis is shown in Scheme 1. ¹H NMR (270 MHz, CDCl₃, δ): 7.883 (s, 2H), 7.809 (d, 2H, J = 7.8 Hz), 7.759 (d, 2H, J = 8.0 Hz), 1.537 (s, 6H), 1.377 (s, 24H).

Syntheses 2-(3'-Pyridyl)pyrido[2,3-d]pyrimidine of (3)and 2-Aminonicotinaldehyde (4): 3 and 4 were synthesized as described in the literature.^[29] A mixture of nicotinamide (73 g, 0.6 mol) and ammonium sulfamate (104 g, 0.9 mol) was heated to melting. After the solid was completely melted, the temperature was raised slowly to 200 $^\circ\text{C}.$ After complete solidification, the material was kept at 200 °C for 6 h. Water (300 mL) was used to wash the resultant material, followed by diethyl ether to remove nicotinonitrile; 3 was obtained as a white solid. The product 3 was refluxed in 2 N HCl for 8 h, NaOH was added to make the mixture alkaline, and the mixture was extracted with diethyl ether. The resulting **4** was obtained in a 16% yield. ¹H NMR (270 MHz, CDCl₃, δ , ppm): 3, 9.926 (dd, 1H, J = 0.7 Hz, 2.4 Hz), 9.589 (s, 1H), 9.336 (dd, 1H, J = 2.0 Hz, 4.3 Hz), 9.011 (m, 1H), 8.785 (dd, 1H, J = 2.0 Hz, 4.9 Hz), 8.381 (dd, 1H, J = 2.2 Hz, 8.1 Hz), 7.653 (dd, 1H, J = 4.3 Hz, 8.2 Hz), 7.509 (m, 1H); 4, 9.851 (s, CHO), 8.239 (dd, 1H, J = 2.1 Hz, 4.7 Hz), 8.001 (dd, 1H, J = 2.1 Hz, 7.7 Hz), 7.555 (s, NH₂), 6.738 (dd, 1H, J = 4.6 Hz, 7.5 Hz).

functional

Synthesis of 2-(3-Bromophenyl)-1,8-naphthyridine (5): A Friedlander reaction^[22] was used for the synthesis of 5. Sodium methoxide (1.08 g, 0.02 mol) was added to a solution of 4 (1.22 g, 0.01 mol) and 3-bromoacetylbenzene (1.99 g, 0.01 mol) in absolute ethanol (80 mL). The resultant solution was refluxed under nitrogen for 4.5 h, until no 4 was detected by thin-layer chromatography. Water was added to quench the reaction. Then the reaction mixture was extracted using chloroform, and purified on a column containing silica gel, with 9:1 chloroform:ethyl acetate as the eluent. Solid 5 was obtained in a 47% yield and identified using NMR spectroscopy. The synthesis is shown in Scheme 1. ¹H NMR (270 MHz, CDCl₃, δ): 9.171 (dd, 1H, *J* = 1.9 Hz, 4.2 Hz), 8.541 (t, 1H, *J* = 1.8 Hz), 8.317 (s, 1H), 8.285 (s, 1H), 8.234 (dd, 1H, *J* = 2.2 Hz, 8.4 Hz), 8.004 (d, 1H, *J* = 4.2 Hz, 8.0 Hz), 7.413 (t, 1H, *J* = 8.0 Hz).

Synthesis of 2, 7-Bis[3-(2-phenyl)-1,8-naphthyridinyl]-9,9-dimethylfluorene (DNPF): A standard Suzuki-Miyaura cross-coupling reaction^[23] was used to synthesize DNPF. Ethanol (100 mL) and Na2CO3 solution (2 M, 100 mL) were added to a solution of 2 (0.89 g, 2 mmol) and 5 (1.25 g, 4.4 mmol) in toluene (200 mL) under nitrogen with agitation. Then Pd(PPh₃)₄ (102 mg, 0.088 mmol) was added, and the resultant solution was refluxed for 12 h. Water was added to guench the reaction, and the mixture was then extracted with ethyl acetate, and purified by column chromatography with an eluent of ethyl acetate: chloroform = 1:9. A pale-yellow solid, DNPF, was obtained in an 83% yield (corresponding to an overall yield of 43.2% from 2,7-dibromofluorene). ¹H NMR $(270 \text{ MHz}, \text{CDCl}_3, \delta)$: 9.184 (dd, 2H, l = 2.1 Hz, 4.4 Hz), 8.659 (t, 2H, l= 1.7 Hz), 8.337 (s, 1H), 8.305 (s, 2H), 8.271 (d, 2H, J = 2.0 Hz), 8.241 (d, 1H, J = 1.7 Hz), 8.149 (s, 1H), 8.118 (s, 1H), 7.890 (s, 1H), 7.861 (s, 1H), 7.841 (t, 1H, / = 1.4 Hz), 7.809 (d, 3H, / = 0.9 Hz), 7.760 (d, 1H, J = 1.5 Hz), 7.731 (d, 1H, J = 1.6 Hz), 7.653 (t, 2H, J = 7.7 Hz), 7.515 (dd, 2H, J = 4.1 Hz, 8.0 Hz), 1.581 (s, 6H). EIMS m/z: [M⁺]calcd. for C43H30N4, 602.73; found: 603. Anal. calcd. for C43H30N4: C 85.69%, H 5.02%, N 9.30%; found: C 85.45%, H 5.26%, N 9.13%.

Synthesis of 9,10-Di(*m*-diacetylphenyl)anthracene (6): A Suzuki–Miyaura cross-coupling reaction similar to that described above was used for the synthesis of **6** from 9,10-dibromoanthracene (3.12 g, 9 mmol) and *m*-acetylphenylboronic acid (3.35 g, 20 mmol). The product was purified by column chromatography with an eluent of ethyl acetate:toluene = 1:20; a pale-yellow solid **6** was obtained in 90% yield. ¹H NMR (270 MHz, CDCl₃, δ): 8.205 (t, 1H, J = 1.9 Hz), 8.179 (t, 1H, J = 1.9 Hz), 8.085 (s, 2H), 7.740 (q, 4H, J = 7.6 Hz), 7.635 (dd, 4H, J = 3.0 Hz, 6.8 Hz), 7.374 (dd, 4H, J = 3.4 Hz, 7.2 Hz), 2.667 (s, 6H).

Svnthesis of 9,10-Bis[3-(1,8-naphthyridin-2-yl)phenyl)]anthracene (DNPA): The naphthyridine derivative DNPA was obtained via a Friedlander reaction as follows. Anhydrous ethanol (20 mL) and NaOCH₃ (0.432 mg, 8 mmol) were added to a suspension of 4 (0.513 g, 4.2 mmol) and 6 (0.829 mg, 2 mmol) in o-dichlorobenzene (100 mL). The resultant mixture was refluxed for 36 h, quenched using ice-water, extracted with chloroform, and purified by column chromatography with an eluent of ethyl acetate: chloroform = 1:9. DNPA was obtained in a 51% yield (corresponding to an overall yield of 45.9% from 9,10-dibromoanthracene). ¹H NMR (270 MHz, CDCl₃, δ): 9.161 (d, 2H, J = 5.0 Hz), 8.656 (d, 2H, J = 9.3 Hz), 8.397 (s, 2H), 8.257 (m, 4H), 8.100 (dd, 2H, J = 5.7 Hz, 8.6 Hz), 7.799 (m, 6H), 7.666 (d, 2H, J = 7.2 Hz), 7.499 (dd, 2H, J = 3.6 Hz, 7.9 Hz), 7.359 (dd, 4H, J = 2.9 Hz, 7.2 Hz). Anal. calcd. for C422H26N4: C 85.98%, H 4.47%, N 9.55%; found: C 85.61%, H 4.40%, N 9.36%. EIMS m/z: [M⁺]: calcd. for C₄₂H₂₆N₄, 586.68; found, 587.

Fabrication of Organic Electrophosphorescent Devices and Measurements: Organic layers were deposited by high-vacuum (10^{-6} Torr) thermal evaporation, as previously reported.^[30] Firstly, a 20 nm layer of 10:1 by weight of TPDPES:TBPAH was deposited via a dichloroethane solution as the hole-injecting layer before it was loaded into the evaporation system. Then, hole-transporting, EM, and HB/ET layers were sequentially deposited on the surface via thermal evaporation in a vacuum of 10^{-6} Torr. Finally, a 0.5 nm layer of LiF together with a 100 nm layer of Al were deposited as the cathode under a vacuum of 2×10^{-5} Torr. The emitting area was defined, using a shadow mask, to



be 0.2 cm \times 0.2 cm. The EQE was estimated based on luminance, EL spectra, and current densities.

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