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9,10-Bis(bipyridyl, pyridylphenyl, phenylpyridyl, and biphenyl)anthracenes Combining High Electron Transport and Injection, Efficiency and Stability in Fluorescent Organic Light-emitting Devices

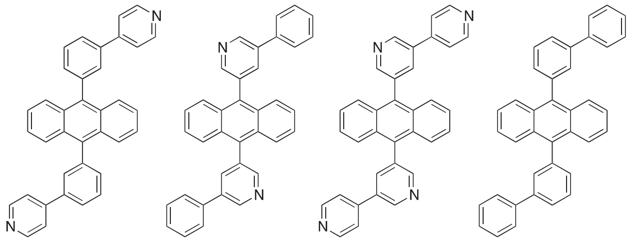
Jae-Jin Oh,[1] Yong-Jin Pu,*[1,2] Hisahiro Sasabe,[1,2] Ken-ichi Nakayama,[1,2] and Junji Kido*[1,2]
[1]*Department of Organic Device Engineering, Yamagata University, 4-3-16 Johnan, Yonezawa, Yamagata 992-8510*
[2]*Research Center for Organic Electronics, Yamagata University, 4-3-16 Johnan, Yonezawa, Yamagata 992-8510*

(Received July 6, 2011; CL-110571; E-mail: pu@yz.yamagata-u.ac.jp, kid@yz.yamagata-u.ac.jp)

A series of anthracene derivatives, 9,10-bis(bipyridyl, pyridylphenyl, phenylpyridyl, and biphenyl)anthracenes, were synthesized. They exhibited properties of small electron injection barrier from cathode in electron-only devices, high electron mobility from time-of-flight measurement, and high efficiency and stability of OLEDs.

Organic light-emitting devices (OLEDs) are charge injection devices, requiring the simultaneous supply of both electrons and holes to a light-emitting material sandwiched between two electrodes.[1] One of the issues in achieving high quantum efficiency is to balance the number of holes and electrons. Because the hole mobility in the OLED is usually much higher than the electron mobility under the same electric field,[2] development of electron-transporting materials with high mobility is necessary. The hole- and electron-transporting molecules, 4,4′-bis[1-naphthyl(phenyl)amino]-1,1′-biphenyl (NPD) and tris(8-quinolinolato)aluminum (Alq_3), commonly used in OLEDs, have hole and electron mobilities that differ by a factor of ca. 1000 (ca. 10^{-3} and ca. $10^{-6}\,cm^2\,V^{-1}\,s^{-1}$ for holes and electrons, respectively). The electron-transport materials (ETMs) should have the abilities of electron transport and injection, hole block, and electrochemical stability. In addition to the widely used Alq_3, various derivatives of siloles,[3,4] oxadiazoles,[5] oligopyridine,[6,7] etc. have been reported to have high electron mobility and performance in OLEDs as an ETM. 9,10-Diphenylanthracene-based derivatives have been used as a highly efficient host material in fluorescent OLEDs[8] and have high electrochemical stability, which is an advantage for device lifetime in OLED application.[9] However, there are few reports of ETM based on 9,10-diphenylanthracene structure, except a very recent report by Qiu et al.[10] In this work, we synthesized four kinds of 9,10-bis(biaryl)anthracene derivatives containing pyridyl group, 9,10-bis[3-(pyridin-4-yl)phenyl]anthracene (**PyPhAnt**), 9,10-bis(5-phenylpyridin-3-yl)anthracene (**PhPyAnt**), 9,10-bis(3,4′-bipyridin-5-yl)anthracene (**PyPyAnt**), and 9,10-bis(biphenyl-3-yl)anthracene (**PhPhAnt**), shown in Figure 1. They exhibited high electron mobility in time-of-flight measurement, good electron injection properties from cathode in an electron-only device, and high efficiencies in fluorescent OLEDs. In addition to this improvement, the device lifetime was much improved with **PyPhAnt**, compared with a device with Alq_3 as an ETM. **PyPhAnt** showed no trade-off performance between the efficiency and lifetime of the device.

The anthracene derivatives were synthesized according to the procedures in Scheme S1.[17] 9,10-Bis(3-bromophenyl)anthracene and 9,10-bis(5-bromopyridin-3-yl)anthracene were obtained from 3,5-dibromopyridine and 1,3-dibromobenzene, respectively, by Suzuki coupling of 9,10-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anthracene. Another Suzuki coupling with the obtained bromophenyl- or bromopyridylanthracene and 4-pyridyl- or phenylboronic acid pinacol ester gave the target anthracene derivatives. The compounds were purified by temperature-gradient sublimation under flow of N_2 gas and characterized by ^{1}H NMR, mass spectrometry, and elemental analysis.



PyPhAnt **PhPyAnt** **PyPyAnt** **PhPhAnt**

Figure 1. Chemical structures of the compounds.

Table 1. Thermal and optoelectrochemical properties

	T_g /°C	T_c /°C	T_m /°C	$T_{d5\%}$ /°C	E_g[a] /eV	PL[b] /nm	I_p /eV	E_a[c] /eV
PyPhAnt	92	200	284	381	2.95	425	5.97	3.02
PhPyAnt	93	190	277	380	2.95	440	6.05	3.10
PyPyAnt	93	215	320	411	2.95	420	6.08	3.13
PhPhAnt	90	185	267	378	2.95	440	5.97	3.02

[a]Absorption edge of the film. [b]Film. [c]The difference between I_p and E_g.

Glass-transition temperatures (T_g) and thermal decomposition temperatures with loss of 5 wt % ($T_{d5\%}$) were measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. T_d's of the compounds were around 400 °C, and T_g's of the compounds were higher than 90 °C (Table 1). Although the T_g's are not different among the compounds, the melting point of only **PyPyAnt** was much higher than the others, probably because the four pyridine groups caused intermolecular hydrogen-bonding interaction. The UV absorption and PL spectrum of the films on a quartz substrate were measured (Figure S1).[17] All of the compounds exhibited similar absorption spectra and edges, so that their optical energy gaps were almost the same. The PL spectra were blue emission with wavelength maxima located around 425–440 nm. Ionization potentials (I_p's) were measured by atmos-

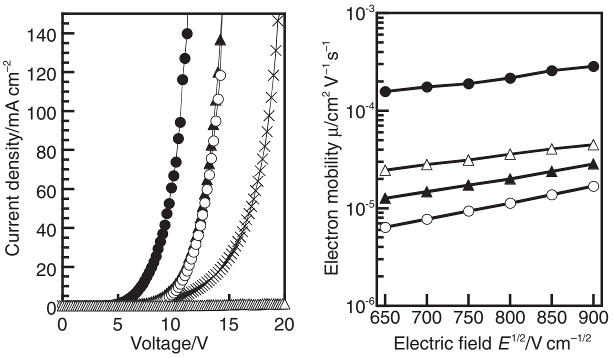


Figure 2. Left: current density–voltage plots of the electron-only decvices. Right: Electron mobility of the compounds. **PyPhAnt**: closed circle, **PhPyAnt**: open circle, **PyPyAnt**: closed triangle, **PhPhAnt**: open triangle, and Alq$_3$: cross.

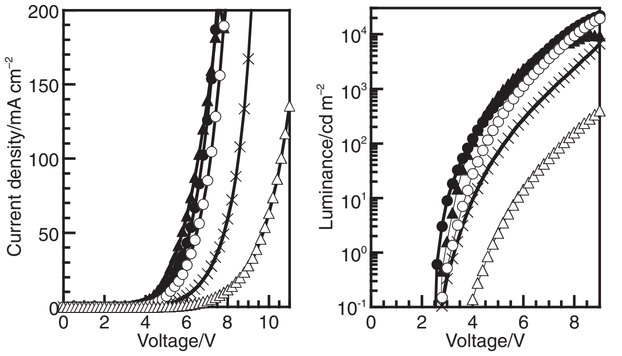


Figure 3. Current density–voltage (left) and luminance–voltage (right) plots of the device: ITO/NPD/Alq$_3$/ETM/LiF/Al. ETM: **PyPhAnt** (closed circle), **PhPyAnt** (open circle), **PyPyAnt** (closed triangle), **PhPhAnt** (open triangle), and Alq$_3$ (cross).

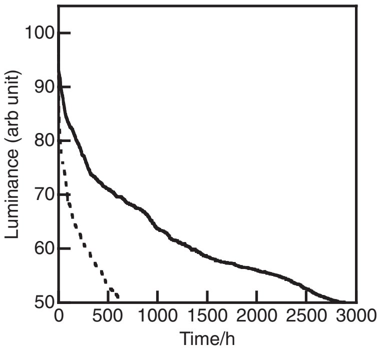


Figure 4. Stability of the devices: ITO/NPD/Alq$_3$/ETM/LiF/Al. ETM: **PyPhAnt** (solid line) and Alq$_3$ (dashed line).

pheric ultraviolet photoelectron yield spectroscopy. The I_p's of the compounds with attached pyridine groups directly on anthracene, **PhPyAnt** and **PyPyAnt**, were higher than that of the compounds with attached phenyl groups on anthracene, **PyPhAnt** and **PhPhAnt**, because of the electrophilicity of the pyridine group.

Figure 2 (left) shows the current density–voltage characteristics of the electron-only devices, of which structure was ITO/4,6-bis[3,5-(dipyrid-4-yl)phenyl]-2-methylpyrimidine (B4PYMPM)[6] (20 nm)/**PyPhAnt**, **PhPyAnt**, **PyPyAnt**, **PhPhAnt**, or Alq$_3$ (150 nm)/LiF (0.5 nm)/Al, where B4PYMPM was used as a hole-blocking layer. The devices of **PyPhAnt**, **PhPyAnt**, and **PyPyAnt** having pyridine group showed much lower driving voltage than the device with Alq$_3$. On the other hand, the device of **PhPhAnt** having no pyridine group showed no current response. This demonstrates that the pyridine group of the compounds enhanced the electron injection from LiF/Al cathode. Electron affinities, E_a's, of the compounds were almost the same around 3.0–3.1 eV, and there was no correlation between the order of these E_a's and the order of electron injection barrier in the electron only device. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the compounds were calculated by density functional theory. The frontier orbitals of the compounds are shown in Figure S2.[17] Both the HOMO and LUMO of the compounds are located only on the anthracene moiety. Their LUMO energy levels are similar, and their order also cannot explain the order of the electron injection barrier. In the electron injection process, Li ion in LiF is expected to be reduced to Li metal by the thermally activated Al during vacuum deposition[11–13] and interact with the pyridine group of electron-transporting materials as an electron donor.[14] **PyPhAnt** bearing a pyridine group at the outside of the molecule showed the lowest turn-on voltage, suggesting that the positions of the pyridine ring affect the specific affinity with cathode metal or metal halide to determine the barrier height for the electron injection.

Electron transport properties of the compounds were investigated by time-of-flight (TOF) measurement. The device structure was ITO/anthracene derivatives (5.0 μm)/Al (80 nm), and the transient photocurrent signals were dispersive (Figure S3).[17] Figure 2 (right) shows the electron mobility of the films as a function of the square root of the electric field. The electron mobility of the compounds was much higher than that of Alq$_3$: 1.3–2.9 × $10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ for **PyPyAnt**, 6.4 × 10^{-6}–1.7 × $10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ for **PhPyAnt**, and 2.5–4.5 × $10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ for **PhPhAnt**. Particularly, **PyPhAnt** shows the highest electron mobility of 1.6–2.8 × $10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. This value is higher than that of well-known electron-transporting materials, 1,3-bis[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazo-5-yl]-benzene (OXD-7)[5] and 2,2′,2″-(1,3,5-benzenetriyl)tris(1-phenyl-1*H*-benzimidazole) (TPBI)[15] and comparable to that of high electron-transporting silole compound, 2,5-bis(2,2′-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenylsilole (PyPySPyPy)[3] and oligopyridine compound, 1,3,5-tris(2,2′-bipyridin-6-yl)benzene (BPyB).[16]

The devices with the following structure: ITO/NPD (40 nm)/Alq$_3$ (40 nm)/**PyPhAnt**, **PhPyAnt**, **PyPyAnt**, **PhPhAnt**, or Alq$_3$ (20 nm)/LiF (0.5 nm)/Al (80 nm) were fabricated. Figure 3 shows current density–voltage–luminance characteristics. The device with **PyPhAnt**, **PhPyAnt**, and **PyPyAnt** with a pyridine group in an ETL showed lower driving voltage than that of the device with Alq$_3$, resulting in higher power efficiency (lm W^{-1}) (Table S1).[17] **PyPhAnt** also improved current efficiency compared with the Alq$_3$ device. On the other hand, the device with **PhPhAnt** with no pyridine group showed highest driving voltage and lowest efficiency, because of the poor

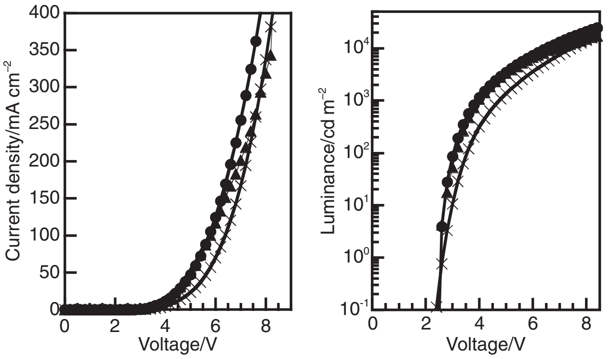


Figure 5. Current density–voltage and luminance–voltage characteristics of the device: ITO/NPD/MADN: 8 wt% rubrene/ETM/LiF/Al. ETM: **PyPhAnt** (closed circle), **PyPyAnt** (closed triangle), and Alq_3 (cross).

Table 2. Efficiencies of the devices with MADN host and rubrene dopant[a]

ETL	V_{on} /V	100 cd m^{-2} (1000 cd m^{-2})			
		Voltage /V	CE /cd A^{-1}	PE /lm W^{-1}	EQE /%
Alq_3	2.6	3.5 (4.7)	6.3 (6.1)	5.6 (4.1)	2.0 (1.9)
PyPhAnt	2.5	3.0 (3.9)	14 (11)	15 (8.5)	4.6 (3.4)
PyPyAnt	2.4	3.1 (4.0)	9.9 (9.1)	10 (7.2)	3.1 (2.9)

[a] V_{on}: at 1 cd m^{-2}, CE: current efficiency, PE: power efficiency, and EQE: external quantum efficiency.

electron injection ability of the cathode. Figure 4 shows the accelerated operation lifetime tests of the device with **PyPhAnt** and the device with Alq_3 and as an ETM, under the current density of 30 mA cm^{-2}. The initial luminance was 1370 cd m^{-2} for the device with **PyPhAnt** and 1170 cd m^{-2} for the device with Alq_3. The device with the anthracene compound **PyPhAnt** as an ETM exhibited 2880 h of much higher half-life (LT_{50}) than 660 h of the device with Alq_3 ETM. This anthracene compound, **PyPhAnt**, is thought to achieve the high efficiency and the long lifetime of the device simultaneously.

Yellow fluorescent devices with rubrene dopant and 2-methyl-9,10-bis(naphthalen-2-yl)anthracene (MADN) host were fabricated with the following structure: ITO/NPD (40 nm)/MADN: 8 wt% rubrene (20 nm)/**PyPhAnt**, **PyPyAnt**, or Alq_3 (40 nm)/LiF (0.5 nm)/Al (80 nm). Figure 5 shows the current density–voltage–luminance characteristics of the devices. The efficiencies of the device with **PyPhAnt** and **PyPyAnt**, summarized in Table 2, were much improved over the device with Alq_3. The EL spectrum of the device with Alq_3 (Figure S4)[17] showed a shoulder peak around 520 nm derived from Alq_3 emission, indicating the poor electron-transporting and injection properties of Alq_3. These results demonstrated that the 9,10-bis(pyridylphenyl)anthracenes can be useful as an ETM for the anthracene host in a fluorescent OLED to improve power efficiency and current efficiency.

In summary, new 9,10-bis(biaryl)anthracene-based electron-transporting materials were synthesized. The compounds having pyridine groups have both small electron injection barrier from cathode and high electron mobility. The compound **PyPhAnt** with outer pyridine showed longer lifetime of the device as an ETM, even with higher efficiency than the device with Alq_3.

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