

*Dedicated to the memory of  
Professor Mircea D. Banciu (1941–2005)*

## NEW ELECTRON-TRANSPORTING AND HOLE-BLOCKING MATERIAL BASED ON HEXAATRIPHENYLENES WITH SIX AROMATIC GROUPS

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Hexaazatriphenylenes HAT-ph with six phenyl and HAT-biph with six biphenyl functional groups at the peripheral positions were designed, and prepared as electron-transporting as well as hole-blocking materials in OLEDs. When HAT-ph and HAT-biph were used as the electron-transporting layer in suitable OLED devices, good OLED performance was achieved.

### INTRODUCTION

Organic light-emitting diodes (OLEDs) have attracted much interest because of their application in emissive displays. Generally, OLEDs are composed of three thin layers of hole-transporting, emitting, and electron-transporting materials sandwiched between an ITO cathode and a metal anode.<sup>1</sup> Currently, one of the most important challenges in OLED development is the design of electron-transporting and hole-blocking materials.<sup>2</sup> Here, a number of criteria have to be fulfilled to obtain high performance electron-transporting materials: i) high electron affinity, ii) suitable amorphous film-forming property, iii) good thermal and electrochemical stability, iv) good hole-blocking property, and v) high electron mobility. Hexaazatriphenylene (HAT) derivatives can be viewed as potential candidates for new electron-transporting materials because of their electron-deficient nature arising from the three pyrazine rings. Introduction of six aromatic functional groups at the peripheral positions of the hexaazatriphenylene core offers valuable advantages as electron-transporting materials: i) the electron affinity can be tuned by the six aromatic groups, improving electron injection, electron-transporting, and hole-blocking performances and ii) the steric effect of the functional groups can be useful to prevent crystallization, leading to the formation of stable amorphous films. Here, we report that star-burst HAT derivatives with six functional aromatic groups really work as electron-transporting as well as hole-blocking material in OLEDs.

### RESULTS AND DISCUSSION

Compounds HAT-ph and HAT-biph, which have six phenyl and six biphenyl groups, respectively, were obtained by the condensation reaction of the corresponding diaryldiketones with hexaaminobenzene<sup>3</sup> in

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refluxing acetic acid. Similarly, tetraazaphenanthrene TAP-biph, which has two pyrazine rings and four biphenylene units, was prepared from tetraaminobenzene.<sup>4</sup>

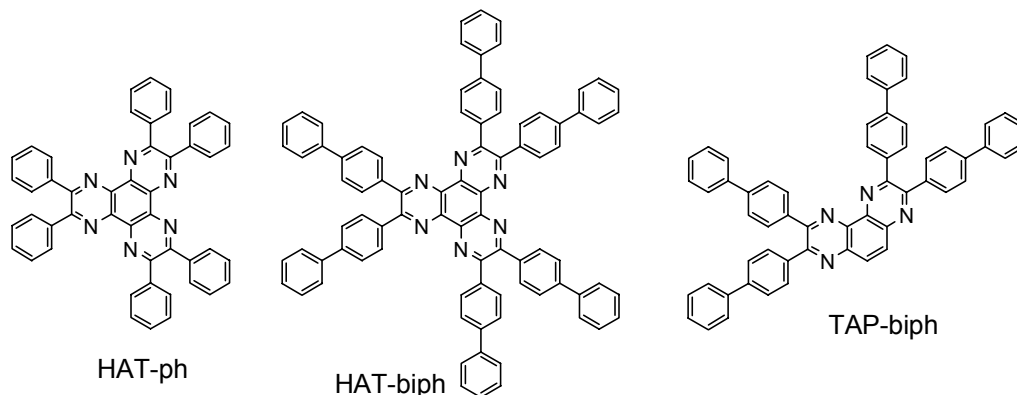


Chart 1.

High electron affinity as well as electrochemical stability of HATs and TAP are confirmed by cyclic voltammetry, which indicates one electron reversible reduction couple around -1.7 V (vs Ag/Ag<sup>+</sup>).<sup>5</sup> The reduction potential shifts more positive in the increasing order of HAT-biph (-1.66 V), HAT-ph (-1.68 V), and TAP-biph (-1.75 V), indicating that electron affinity of the three-pyrazine-ring system in HAT is higher than that of the two-pyrazine-ring system in TAP. No oxidation peak was observed in the cyclic voltammograms (~1.5 V), indicating *n*-type semiconducting property of HAT-biph, HAT-ph, and TAP-biph. TAP-biph, HAT-ph, and HAT-biph did form amorphous films on sublimation for the fabrication of devices, although in DSC measurements glass transition temperature could not be observed.

Devices OLEDs 1-3 with TAP-biph, HAT-ph, and HAT-biph as an electron-transporting material were fabricated. The device structure is ITO/FL-03 (11 nm)/Alq<sub>3</sub> (20 nm)/HAT or TAP (40 nm)/Al-Li (12 nm)/Al (150 nm), in which FL-03 [*N,N'*-bis(9,9-dimethyl-2-fluorenyl)-*N,N'*-diphenyl-4,4'-diaminobiphenyl] was used as a hole-transporting layer, Alq<sub>3</sub> [tris(8-quinolinonlate)aluminium] as an emitting material layer, HATs or TAP as an electron-transporting layer, Al-Li as a buffer layer, and Al as a cathode. A control device, OLED 4 (ITO/FL-03 (11 nm)/Alq<sub>3</sub> (60 nm)/Al-Li (12 nm)/Al (150 nm)) without the electron-transporting layer was prepared, in which Alq<sub>3</sub> was used as the emitting material layer as well as the electron-transporting layer (Table 1 and Fig. 1).

In OLEDs 1-4, green light is emitted from Alq<sub>3</sub> at 524 nm both in the presence and absence of the electron-transporting layer of TAP-biph, HAT-ph, and HAT-biph (Fig. 1). Nevertheless, TAP-ph, HAT-ph, and HAT-biph are themselves fluorescent in the solid state, and electroluminescence from the HAT- and TAP-chromophores was not observed. These results indicate that HATs and TAP act as electron-transporting as well as hole-blocking materials.

In the OLED 3 using HAT-biph, small turn-on-voltage of 5.1 V was required to obtain luminance of 300 cd, which was comparable to that (4.9 V) of the control device OLED 4 (Fig. 1-a and Table 1). In the OLED 3, maximum luminance reached a high value of 27,670 cd m<sup>-2</sup>, and high luminous power efficiency of 1.3 lm W<sup>-1</sup> was achieved, although the performances are less than those (49,095 cd m<sup>-2</sup> and 2.0 lm W<sup>-1</sup>) of OLED 4 (Table 1).<sup>6</sup> In contrast, OLED 1 using TAP-biph and OLED 2 using HAT-ph showed inferior performance in the turn-on-voltage, maximum luminance, and luminous power efficiency (Table 1).

Compared to OLED 4, current density is improved in OLEDs 1 and 3 (from 11.0 to 18.1 and 14.8 mA cm<sup>-2</sup>, respectively). The results indicate that electron injection ability of HAT and TAP layers with biphenyl groups is higher than that of Alq<sub>3</sub>. Another improvement is found in luminance efficiency (from 2.99 to 3.16 cd A<sup>-1</sup>) and quantum efficiency (from 0.93 to 0.96) in OLED 2, indicating more effective recombination at the emitting layer of OLED 2. The good luminance efficiency in OLED 2 was visualized in current density-luminance efficiency plot in Figure 1-c. Thus, HAT-ph with phenyl groups acts as better hole-blocking material than Alq<sub>3</sub> as well as HAT-biph and TAP-biph with biphenyl groups.<sup>7</sup>

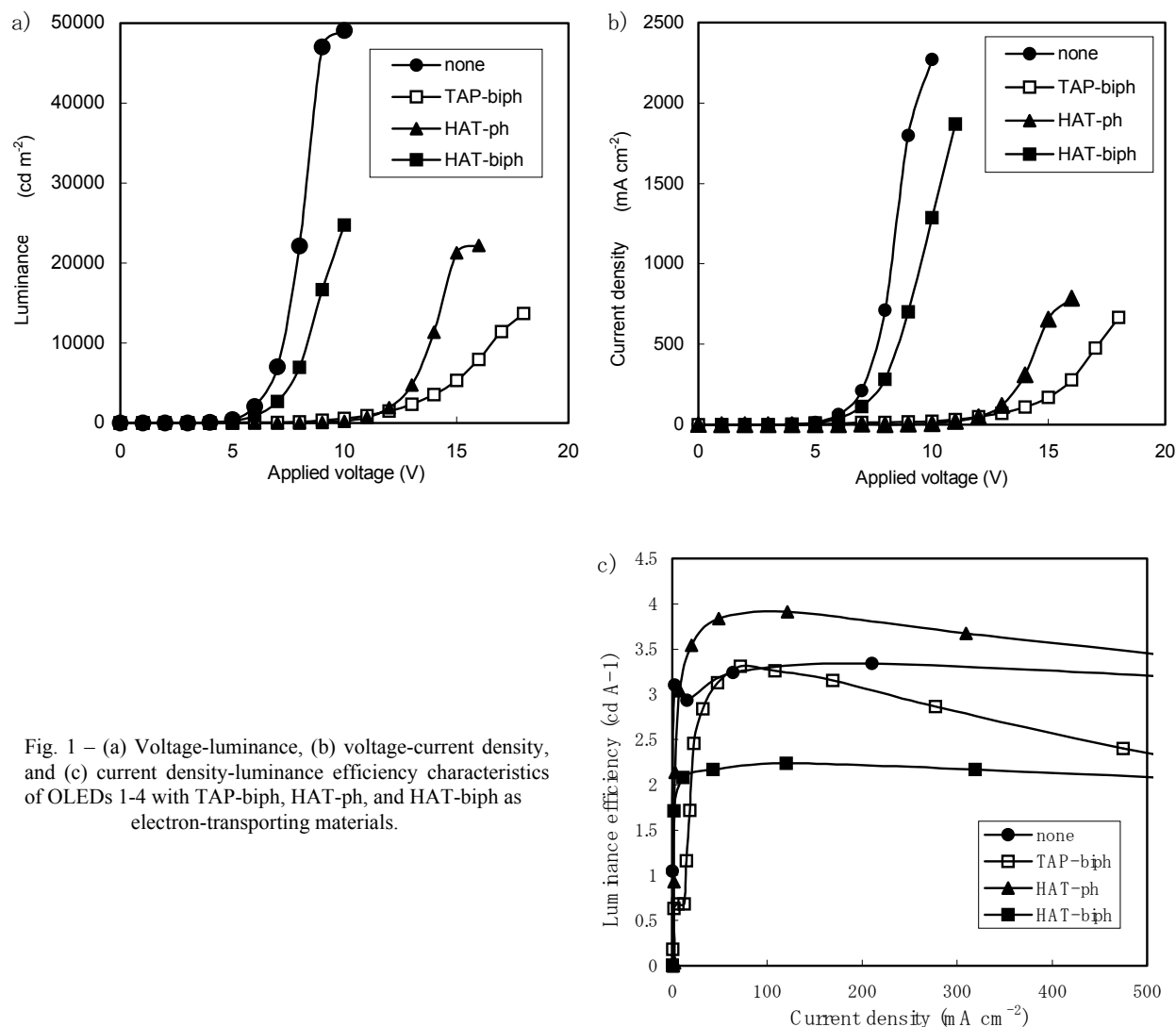


Fig. 1 – (a) Voltage-luminance, (b) voltage-current density, and (c) current density-luminance efficiency characteristics of OLEDs 1-4 with TAP-biph, HAT-ph, and HAT-biph as electron-transporting materials.

Table 1

Performance of OLEDs 1-4 with TAP-biph, HAT-ph, and HAT-biph as electron-transporting materials.

OLED	Electron-transporting layer	Maximum Luminance /cd m <sup>-2</sup> (Voltage/V)	Voltage /V	Luminous Power Efficiency/ lm W <sup>-1</sup>	Luminance Efficiency /cd A <sup>-1</sup>	Quantum Efficiency/%	Current Density /mA cm <sup>-2</sup>
1	TAP-biph	13,700 (18)	8.7	0.58	1.65	0.52	18.1
2	HAT-ph	22,850 (16)	10.1	0.96	3.16	0.96	9.5
3	HAT-biph	27,670 (11)	5.1	1.3	2.10	0.62	14.8
4	none	49,095 (10)	4.8	2.0	2.99	0.93	11.0

In conclusion, we have demonstrated that hexaatriphenylenes with six functional aromatic groups actually work as OLED electron-transporting as well as hole-blocking materials.

## EXPERIMENTAL

**General.** All melting points are uncorrected. IR spectra were recorded on a JASCO FT/IR-470 plus Fourier transform infrared spectrometer and measured as KBr pellets. <sup>1</sup>H NMR spectra were determined in CDCl<sub>3</sub> with a JEOL EX-270

spectrometer. Residual solvent protons were used as internal standard and chemical shifts ( $\delta$ ) are given relative to tetramethylsilane (TMS). The coupling constants ( $J$ ) are reported in hertz (Hz). Elemental analysis was performed at the Elemental Analytical Center, Kyushu University. Fast atom bombardment mass spectrometry (FAB-MS) spectra were recorded with a JEOL JMS-70 mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as a matrix. Cyclic voltammetry was performed with a BAS100B/W (CV 50W) electrochemical workstation, and by using a cell equipped with a glassy carbon as working electrode, a platinum wire as counter electrodes, and Ag/AgNO<sub>3</sub> as the reference electrode, and at scan rate of 100 mV sec<sup>-1</sup>. All electrochemical measurements were performed in dichloromethane solution ( $5 \times 10^{-4}$  mol cm<sup>-3</sup>) containing 0.10 mol cm<sup>-3</sup> tetra-*n*-butylammonium hexafluorophosphate at room temperature. Analytical TLC was carried out on silica gel coated on aluminum foil (Merck 60 F<sub>254</sub>). Column chromatography was carried out on silica gel (Wako C-300). Preparation of HAT-ph and HAT-biph was reported previously.<sup>3</sup>

**2,3,6,7-Tetrakis(biphenyl-4-yl)-1,4,5,8-tetraazaphenanthrene (TAP-biph).** A mixture of 1,2,3,4-tetraaminobenzene dihydrochloride<sup>4</sup> (211 mg, 1.00 mmol) and bis(biphenyl-4-yl)ethanedione<sup>3</sup> (724 mg, 2.0 mmol) in degassed ethanol (100 mL) and degassed acetic acid (100 mL) was heated at the refluxing temperature for 24 h under an argon atmosphere. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane. The organic layer was washed with saturated aqueous sodium hydrogencarbonate solution and with brine, dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was separated by silica gel column chromatography eluting with dichloromethane to give TAP-Biph in 46% yield (364 mg, 0.46 mmol): mp 320-321 °C; IR (KBr) 1603, 1546, 1520, 1487, 1448, 1367, 1248, 1101, 1007, 950, 845, 796, 765, 732; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.36-7.47 (m, 12 H, ArH), 7.65-7.68 (m, 16 H, ArH), 7.79-7.82 (m, 4 H, ArH), 7.88-7.91 (m, 4 H, ArH), 8.40 (s, 2H, ArH); FAB-MS (NBA, positive) 791 [(M+H)<sup>+</sup>]. Anal. Calcd for C<sub>58</sub>H<sub>38</sub>N<sub>4</sub>: C, 88.07; H, 4.84, N, 7.08. Found: C, 87.79; H, 4.84; N, 7.08.

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