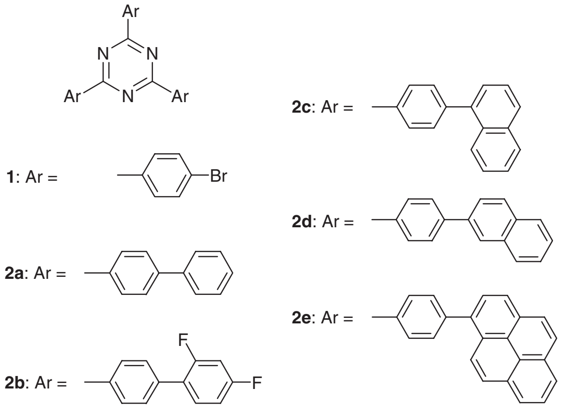
High Electron Drift Mobility in an Amorphous Film of 2,4,6,-Tris[4-(1-naphthyl)phenyl]-1,3,5-triazine

Tsutomu Ishi-i, Kentaro Yaguma,[†] Thies Thiemann, Masataka Yashima,[††] Kazunori Ueno,[††] and Shuntaro Mataka*
Institute for Materials Chemistry and Engineering (IMCE), Kyushu University, 6-1 Kasuga-kohen, Kasuga 816-8580
[†]*Department of Molecular and Material Sciences, Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-kohen, Kasuga 816-8580*
[††]*OL Development Div. 1, Advanced Device Technology Development Center, Canon Inc., 30-2, Shimomaruko 3-Chome, Ohta-ku, Tokyo 146-8501*

(Received June 30, 2004; CL-040770)

2,4,6-Tris[4-(1-naphthyl)phenyl]-1,3,5-triazine exhibited a high electron drift mobility of 8.0×10^{-4} cm^2 V^{-1} s^{-1}.

Organic light-emitting diodes (OLEDs) have been of much interest because of their application in new emissive displays. Generally, OLEDs are fabricated by three thin layers of hole-transporting, emissive, and electron-transporting materials sandwiched between an ITO-cathode and a metal-anode.[1] Currently, one of the most important challenges in OLED development is the design of electron-transporting materials. Here, a number of criteria have to be fulfilled to obtain high performance electron-transporting materials: i) electron affinity, ii) amorphous film-forming property, iii) thermal and electrochemical stability, iv) hole-blocking property, and v) high electron drift mobility.[2] In particular, the last feature is significantly reflected in OLED device performance, because the electron drift mobility is usually smaller by two to three orders of magnitude compared to the hole drift mobility, leading to high operation voltage.[3] Alq$_3$ [aluminum tris(8-hydroxyquinolinate)], which has been used practically as an electron-transporting material in OLED, exhibits low electron drift mobility of 1.4×10^{-6} cm^2 V^{-1} s^{-1}.[4] Only a few electron-transporting materials such as silole[5] and bathophenanthroline[6] were reported to have a high electron mobility of $\approx 10^{-4}$ cm^2 V^{-1} s^{-1}. Here, we report the high electron drift mobility of 8.0×10^{-4} cm^2 V^{-1} s^{-1} of tris[4-(1-naphthyl)phenyl]-1,3,5-triazine (**2c**).



Triazine derivatives **2a**–**2e** were obtained by using Suzuki coupling reactions of 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (**1**) with the corresponding aromatic boronic acids in the presence of a Pd (0) catalyst (Scheme 1).[7] The key synthetic intermediate **1** was prepared by trimerization of 4-bromobenzonitrile in a modified procedure in this work (see Supporting Information).[8]

In CV measurements, **2a**–**2e** show a one-electron reversible reduction couple to exhibit their electrochemical stabilities. The reduction potentials observed around –2.09 to –2.14 V (vs Fc/Fc$^+$) suggest that the electron affinity of the triazine core is affected slightly by the terminal groups through the phenylene spacer (Table 1).

Table 1. Physical properties (half-wave reduction potential ($E_{1/2}^{\mathrm{red}}$)[a], and melting and glass transition temperatures (T_{m} and T_{g})[b] of triazine derivatives **2a**–**2e**

Compound	$E_{1/2}^{\mathrm{red}}$ (V vs Fc/Fc$^+$)	T_{m} /°C	T_{g} /°C
2a	−2.12	284	—
2b	−2.09	240	—
2c	−2.14	309	133
2d	−2.10	315	—
2e	−2.10	296	—

[a]Determined by cyclic voltammetry in dichloromethane (5×10^{-4} M) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate at scan rate of 100 mV s^{-1}. [b]Determined by differential scanning calorimetry measurement at heating and cooling rate of 10 °C min^{-1}.

In the DSC measurement, 1-naphthylphenyl derivative **2c** showed high glass transition temperature (T_{g}) at 133 °C. On the other hand, the glass transition could not be found in the other triazine derivatives **2a**, **2b** and **2d**, **2e** (Table 1). Thus, a combination of the star-burst core structure of 2,4,6-triaryl triazine derivative and the sterically crowded 1-naphtyl group is useful to prevent crystallization and to form an amorphous film.

From the facts described above, **2c** is expected as a new candidate of electron-transporting material. The electron-transporting capability of **2c** is measured by the conventional TOF technique. A single device was fabricated, in which **2c** (3.31-µm width) was coated on an ITO cathode by vapor-deposition technique, then it was covered with Al. After irradiation with a N$_2$ laser (337 nm), time-dependent photocurrent (I) was detectable and the transient photocurrent signal showed pseudo non-dispersive electron transport (Figure 1), suggesting that electron trapping due to energetic disorder is small in **2c**.[5,9]

Electron drift mobility (μ) was determined from Eq 1:

$$\mu = L^2/(t_{\mathrm{TR}} \times V) \qquad (1)$$

where L is the sample thickness, t_{TR} is the transit time determined from the inflection point on a log(I)-log(t) plot, and V

Copyright © 2004 The Chemical Society of Japan

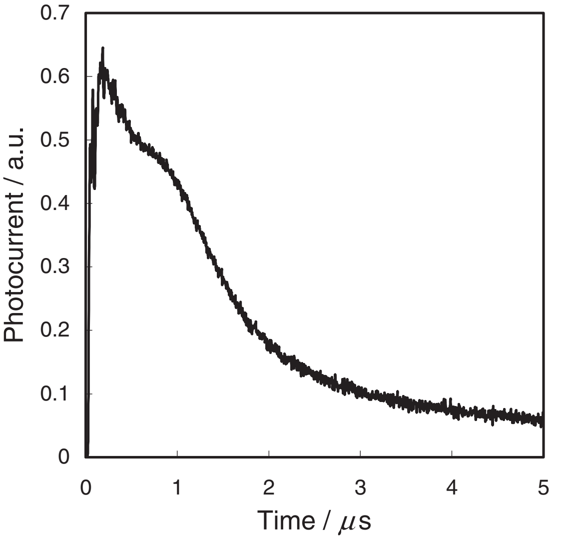


Figure 1. Transient photocurrent signal for a **2c** single device between ITO anode and Al cathode recorded at field $E = 3.8 \times 10^{-5}\,\mathrm{V\,cm^{-1}}$ and at 25 °C. The film thickness was 3.31 μm.

is the applied voltage. High electron drift mobility can be estimated for **2c** to be $8.0 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ at 25 °C ($3.8 \times 10^{-5}\,\mathrm{V\,cm^{-1}}$), depending on the temperature and the electric field in the range from 3.2×10^{-4} to $1.2 \times 10^{-3}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ (from -50 to 60 °C) and from 7.6×10^{-4} to $1.1 \times 10^{-3}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ (from 3.0×10^{-5} to $7.6 \times 10^{-5}\,\mathrm{V\,cm^{-1}}$).[10] The electron drift mobility of **2c** is 4 times as large as that ($2.0 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ at 27 °C/$6.4 \times 10^{-5}\,\mathrm{V\,cm^{-1}}$) of a silole-based material[5] and competes with bathophenanthroline[6] ($5.2 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ at 25 °C/$5.5 \times 10^{-5}\,\mathrm{V\,cm^{-1}}$).

In conclusion, 2,4,6-tris[4-(1-naphthyl)phenyl]-1,3,5-triazine is an attractive amorphous glassy electron-transporting material, which has high electron drift mobility of $8.0 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ at 25 °C ($3.8 \times 10^{-5}\,\mathrm{V\,cm^{-1}}$).

This work was financially supported in part by a Grant-in-Aid for Scientific Priority Area (No. 15750157) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References and Notes

1 For reviews of OLEDs see: a) U. Mitschke and P Bäuerle, *J. Mater. Chem.*, **10**, 1471 (2000). b) Y. Shirota, *J. Mater. Chem.*, **10**, 1 (2000). c) S. R. Forrest, D. D. C. Gradley, and M. E. Thompson, *Adv. Mater.*, **15**, 1043 (2003).

2 For selected references of electron-transporting materials see: a) J. Bettenhausen, P. Strohriegl, W. Brütting, H. Tokuhisa, and T. Tsutsui, *J. Appl. Phys.*, **82**, 4957 (1997). b) J. Kido, M. Kimura, and K. Nagai, *Chem. Lett.*, **1996**, 47. c) M. Jandke, P. Strohriegl, S. Berleb, E. Werner, and W. Brütting, *Macromolecules*, **31**, 6434 (1998). d) T. Noda and Y. Shirota, *J. Am. Chem. Soc.*, **120**, 9714 (1998). e) M. Redecker, D. D. C. Bradley, M. Jandke, and P. Strohriegl, *Appl. Phys. Lett.*, **75**, 109 (1999). f) S. B. Heidenhain, Y. Sakamoto, T. Suzuki, A. Miura, H. Fujikawa, T. Mori, S. Tokito, and Y. Taga, *J. Am. Chem. Soc.*, **122**, 10240 (2000).

3 P. Strohriegl and J. V. Gazulevicius, *Adv. Mater.*, **14**, 1439 (2002).

4 G. M. Kepler, P. M. Beeson, S. J. Jacobs, R. A. Anderson, M. B. Sinclair, V. S. Valencia, and P. A. Cahill, *Appl. Phys. Lett.*, **66**, 3618 (1995).

5 H. Murata, G. G. Malliaras, M. Uchida, Y. Shen, and Z. H. Kafafi, *Chem. Phy. Lett.*, **339**, 161 (2000).

6 S. Naka, H. Okada, H. Onnagawa, and T. Tsutui, *Appl. Phys. Lett.*, **76**, 197 (2000).

7 A typical procedure of **2c**: To a mixture of **1** (546 mg, 1 mmol) and tetrakis(triphenylphosphine) palladium (0) (150 mg, 5.0 mol %) in benzene (20 mL) were added 1-naphthylboronic acid (600 mg, 3.5 mmol) in ethanol (5 mL) and aqueous 2 M sodium carbonate solution (5 mL) under an argon atmosphere and the mixture was heated at 80 °C for 15 h. After the reaction mixture was evaporated in vacuo to remove benzene, it was filtered off and washed with water. The insoluble solid was dissolved in chloroform and washed with brine. The water layer was extracted with chloroform. The combined organic layers were dried over anhydrous magnesium sulfate and evaporated in vacuo to dryness. The residue was recrystallized from chloroform to give **2c** in 74% yield (508 mg, 0.74 mmol) as white powder: mp 312–313 °C; IR (KBr, cm^{-1}) 1608, 1570, 1364, 1180, 1019, 851, 436, 787, 772; ^{1}H NMR (CDCl$_3$) δ 7.48–7.60 (m, 12 H, naphthyl H), 7.77 (d, $J = 8.3$ Hz, 6 H, phenylene H), 7.91–8.01 (m, 9 H, naphthyl H), 8.99 (d, $J = 8.3$ Hz, 6 H, phenylene H); FAB–MS (NBA, positive) m/z 688 [$(\mathrm{M}+1)^+$]. Anal. $\mathrm{C_{51}H_{33}N_3 \cdot 0.05CHCl_3}$: C, 88.38; H, 4.80; N, 6.06. Found: C, 88.15; H, 4.86, N 6.05.

8 J. Pang, Y. Tao, S. Freiberg, X.-P. Yang, M. D'Iorio, and S. Wang, *J. Mater. Chem.*, **12**, 206 (2000).

9 Electron-transport in disordered glassy amorphous molecules occurs via a hopping mechanism. Many electron-transporting materials including heterocyclic rings resulted in dispersive electron transport,[2a,2e,6] which is attributed to dipolar disorder arising from a fluctuation of energy in electron hopping sites: P. M. Borsenberger and H. Bässler, *J. Chem. Phys.*, **95**, 5327 (1991).

10 Probably, the high electron mobility in **2c** is attributed to favored π-stacking among the molecules to enjoy the electron hopping even in the amorphous state, as it is known that some 1,3,5-triazine derivatives tend to aggregate via the π-stacking interactions: i.e. columnar liquid crystals. For triazine-based columnar liquid crystals see: a) C. Lee and T. Yamamoto, *Tetrahedron Lett.*, **42**, 3993 (2001). b) K. Pieterse, A. Lauritsen, A. P. H. J. Schenning, J. A. J. M. Vekeman, and E. W. Meijer, *Chem.—Eur. J.*, **9**, 5597 (2003). c) H. Lee, D. Kim, H.-K. Lee, W. Qiu, N.-K. Oh, W.-C. Zin, and K. Kim, *Tetrahedron Lett.*, **45**, 1019 (2004). d) H. Bock, A. Babeau, I. Seguy, P. Jolinat, and P. Destruel, *ChemPhysChem*, **2002**, 532.

Published on the web (Advance View) August 28, 2004; DOI 10.1246/cl.2004.1244