

Ambipolar Carrier Transport in Amorphous Bis(triazinyl)arenes and Their Application in OLED

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Bis(4,6-diaryl-1,3,5-triazin-2-yl)arenes were prepared for new semiconductive materials, and their thermal and morphological natures were characterized. The glass formation properties of the materials were discussed with respect to the effect of the substituents and the molecular conformations. The carrier mobility measurement revealed that the bis-triazines showed ambipolar carrier transport capabilities in the films. We also demonstrated to fabricate an organic light emitting diode using the bis-triazine as an electron transport layer.

Key words: triazine, mobility, amorphous, OLED

1. INTRODUCTION

Since the first report of an organic light-emitting diode (OLED),¹ development of organic materials bearing carrier transport capability which could attribute to high performance in the device is being emphasized. An approach for those from synthetic viewpoint is to construct efficient π -conjugation system with relevant building blocks,² like vinylenes, ethynylenes, arylene and heteroarylenes.

1,3,5-Triazine nucleus is an attractive block for the electric material³⁻⁵ because of the enhanced electron affinity by inductive effect of three nitrogen atoms as well as its synthetic accessibility that has been well explored in the fields of agro- and medicinal chemistry. Additionally, 1,3,5-triazine derivatives are often utilized in flame retardants,⁶ suggesting that materials based on triazine nuclei would show good thermal stability.

We synthesized oligoaromatic compounds in which two diaryl-1,3,5-triazine cores are bridged by various aromatic hydrocarbons for new conductive materials. In this article, we discuss effects of molecular structures of the bis-triazines on the physical properties and carrier transport capabilities. The application in an OLED as an electron transport layer is also demonstrated.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

We modified reported synthetic procedures⁷ of mono-1,3,5-triazine compounds for bis(4,6-diaryl-1,3,5-triazin-2-yl)arenes (BTAr): arenedicarbonyl dichloride (4.0 mmol) and benzonitrile (16 mmol) were dissolved in ethanol-free chloroform (80 mL) under Ar. To the solution, antimony(IV) chloride (8.0 mmol) was added drop-wise at 0 °C. The mixture was refluxed for 12 h. After cooling, all volatiles were removed under vacuo, and the resulting yellow solid of bis(oxadiazinium) salt was finely crushed under an Ar stream. To vigorous stirred 28%-NH₃ aqueous solution (300 mL), the salt was carefully added at 0 °C. White precipitate of desired bis(triazinyl)arene was

immediately formed, and resulted suspension was stirred for additional 1 h at room temperature. The precipitate was collected by suction and washed with water and methanol. Column chromatography (SiO₂, chloroform-hexane) and recrystallization from suitable organic solvent(s) gave BTAr as white solid. Obtained products were further purified by the train-sublimation⁸ except compound 2 from which trace impurity was removed by recycle HPLC manner.

BTB 1: ¹H NMR (CDCl₃): δ 7.62-7.71 (m, 10H), 7.96 (d, J = 8.4 Hz, 4H), 8.83-8.89 (m, 8H), 8.95 (d, J = 8.4 Hz, 4H).

BTB 2: ¹H NMR (CDCl₃): δ 0.90 (t, J = 7.3 Hz, 12H), 1.27-1.43 (m, 8H), 1.53-1.70 (m, 8H), 2.69 (t, J = 7.7 Hz, 8H), 7.33 (d, J = 8.2 Hz, 8H), 7.84 (d, J = 8.4 Hz, 4H), 8.63 (d, J = 8.2 Hz, 8H), 8.82 (d, J = 8.4 Hz, 4H).

BTmP 3: ¹H NMR (CDCl₃): δ 1.37 (s, 36H), 7.58 (d, J = 8.6 Hz, 8H), 7.72 (t, J = 7.8 Hz, 1H), 8.37 (d, J = 8.6 Hz, 8H), 8.90 (dd, J = 7.8, 1.8 Hz, 2H), 10.22 (brs, 1H).

BTNp 4: ¹H NMR (CDCl₃): δ 1.35 (s, 36H), 7.55 (d, J = 8.6 Hz, 8H), 7.61 (dd, J = 6.7, 3.4 Hz, 2H), 8.50 (s, 2H), 8.65 (d, J = 8.6 Hz, 8H), 9.05 (dd, J = 6.7, 3.4 Hz, 2H).

Thermogravimetry analysis (TGA) and differential thermal analysis (DTA) were carried out under a N₂ stream (50 mL min⁻¹) at a heating rate of 5 °C min⁻¹. The differential scanning calorimetry (DSC) thermograms were obtained at scanning rates of 5-10 °C min⁻¹ under a flow of N₂ (30 mL min⁻¹).

2.2 Time-of-flight measurements

Carrier mobilities were measured using single-layer type samples with a vacuum deposited film of a BTAr on an anode. For sample preparation, films were fabricated by conventional vacuum deposition on pre-cleaned indium-tin oxide (ITO)-coated glass substrates under a vacuum of

10^{-4} Pa. Aluminum cathodes of 100 nm thick were deposited through a shadow mask, creating an active area of 2×2 mm². The devices were encapsulated in N₂-glove box. For carrier generation, a N₂ laser (337 nm) with 0.6 ns pulse width was used. Under an applied dc bias, the transient photocurrent as a function of time was measured with a series load resistor and was recorded with a digital storage oscilloscope.

2.3 Organic light-emitting diodes

EL devices were fabricated on pre-cleaned ITO-coated glass sheets under a vacuum of 10^{-4} Pa. Deposition rates of organics were typically 0.5 nm min⁻¹. Copper phthalocyanine (CuPc), 4,4-Bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl (NPD) and tris(8-hydroxyquinolino)aluminum (Alq₃) were used as a hole injection layer, a hole transport layer (HTL) and an emitting layer (EML) in all devices, respectively. The BTAr was employed as an electron transport layer (ETL) followed by deposition of Al cathode. Structure of the device was [ITO/CuPc(25 nm)/NPD(40 nm)/Alq₃(40 nm)/BTAr(20 nm)/LiF(1 nm)/Al(100 nm)]. LED area of the device was 2×2 mm².

3. RESULT AND DISCUSSION

3.1 Materials

The synthesis of BTAr is depicted in Fig. 1. Starting from appropriate bis-acid chlorides and arynitriles, Sb(V) promoted trimerization reaction produced bis(oxadiazinium) hexachloroantimonates as bright yellow-red solids, followed by ammonolysis to give desired BTAr 1-4. This simple procedure provided various BTAr bearing substituted aryl moieties (4-*tert*-butylphenyl, 4-butylphenyl and parent phenyl) on the 4,6-position of 1,3,5-triazine rings and a linkage group (4,4'-biphenylene, 1,3-phenylene and 1,4-naphthylene). It should be noted that sterically hindered 1,4-naphthylene could be successfully introduced as a linker to produce BTNp 4 in the same manner.

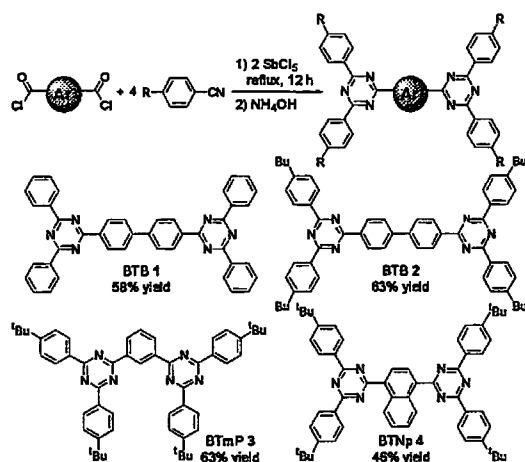


Fig 1. Synthesis of Bis-triazine compounds 1-4.

Optical properties of synthesized BTAr 1-4 are listed in Table I. All compounds exhibited bluish violet-blue emissions by irradiation of UV in the dilute solutions

(CHCl₃). Triaryl-1,3,5-triazine unit is often responsible for blue luminescence.^{3,4} However we found that conjugation (or non-conjugation) of triazine nuclei in the BTAr through the linking aromatic also had a great influence on emission intensity and energy. The lack of strong electronic interaction of triazine nuclei in BTmP 3, in which *m*-phenylene was a linker, significantly weaken the intensity of photoluminescence compared to other compounds, although the emission energy was nearly equal to that corresponded to core chromophore of triphenyltriazine. On the other hand, electron-rich 1,4-naphthylene group that gave *p*-phenylene-type π -conjugation to BTNp 4 showed about 40 nm red-shift of the emission maxima relative to the biphenylene- and *m*-phenylene-linked compounds.

Table I. Optical Properties of BTAr 1-4

	BTB 1	BTB 2	BTmP 3	BTNp 4
Photo luminescence, $\lambda_{\text{em}} / \text{nm}^a$	393	392	398	438
Relative PL intensity (a. u.)	70	55	1	1450
HOMO-LUMO gap, E_g / eV^b	3.4	3.4	3.9	3.1

^a 1.0×10^{-5} M in CHCl₃. ^b Evaluated from the onsets of absorption spectra.

We estimated HOMO-LUMO gap (E_g) of compound 1-4 from the onset of the absorption spectra. The largest E_g was observed in BTmP 3 (3.9 eV) due to the weak interaction of triazine cores in meta-conjugated backbone. Compound 1 and 2, which had the same 4,4'-biphenylenic linker, exhibited an identical value (3.4 eV) regardless of substituents on the peripheral phenyl groups. Relatively narrow energy gap of 3.1 eV in BTNp 4 was presumably caused by delocalization of HOMO in the electron-rich linker part. Thus, these results raise the possibility of tuning E_g in a series of bis-triazines simply by choosing a relevant aromatic linkage.

3.2 Thermal properties

Results of TGA and DTA of BTAr 1-4 are shown in Table II. All compounds except BTB 2 showed good heat-resistance and started to evaporate slightly around 400 °C. No thermal decomposition of those occurred during heating up to 500 °C. The sufficient volatility and thermal stability of compound 1, 3, 4 are advantageous to using them in thin-film devices which are formed by thermal vacuum deposition method. On the other hand, BTB 2 decomposed in the heating process, where the temperature of 5% weight-loss ($T_{5\%}$) is 288.7 °C. A reason for the low thermal stability of BTB 2 would be that peripheral butyl groups in the molecule broke up before evaporating.

Table II. Thermal Properties of BTAr 1-4

	$T_{5\%}^a$	T_g^b	T_{c1}^c	T_{c2}^c	T_m^d (°C)
BTB 1	—	—	—	—	361.5
BTB 2	288.7	57.8	98.7	—	259.4
BTmP 3	—	146.2	183.9	226.7	334.8
BTNp 4	—	165.8	—	—	311.4

^a 5% Weight loss temperature. ^b Glass transition temperature.

^c Crystallization temperature. ^d Melting point.

Next, the glass-forming properties and phase transition of BTAr 1-4 were studied by DSC experiments. Glassy samples of BTB 2 and BTmP 3

were prepared by rapid cooling from isotropic states on a dry ice-cooled aluminum block. When the resulted glasses were heated under a N_2 stream at a rate of $10\text{ }^\circ\text{C min}^{-1}$, both samples showed well-defined glass transitions at 57.8 and $146.2\text{ }^\circ\text{C}$, respectively (Fig. 2). The large difference of glass transition temperatures (T_g s) should be responsible to their peripheral alkyl substituents; bulky *tert*-Bu groups on compound 3 may prevent reorientation of the molecules in the glassy state more strongly than normal alkyl chains on 2. Interestingly, BTmP 3 displayed well-resolved two recrystallization peaks ($T_{c1} = 183.9\text{ }^\circ\text{C}$, $T_{c2} = 226.7\text{ }^\circ\text{C}$) followed by a sharp melting peak of $334.8\text{ }^\circ\text{C}$. No observation of endothermic peaks between T_{c1} and T_{c2} indicated that the first metastable crystalline state directly transformed to the stable crystal phase. While glassy organic materials often have polymorphism,^{9,10} such a phenomenon of crystal-to-crystal phase transition is still rare.

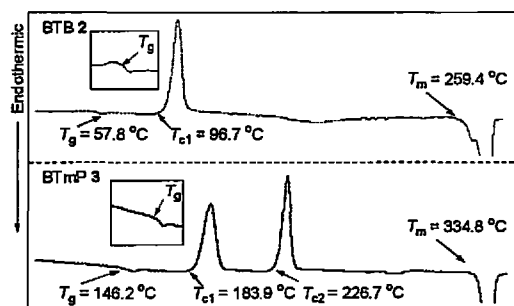


Fig. 2 DSC curves for BTB 2 (upper) and BTmP 3 (lower) at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Each endothermic peak at T_g is enlarged for clarity in insets.

When a crystalline sample of BTNp 4 was heated at a rate of $5\text{ }^\circ\text{C min}^{-1}$, it melted at $311.4\text{ }^\circ\text{C}$ to give an isotropic liquid (Fig. 3). No recrystallization occurred on successive slow cooling ($5\text{ }^\circ\text{C min}^{-1}$), and a stable amorphous glass was formed. On the second heating at the same rate, it showed clear T_g at $165.8\text{ }^\circ\text{C}$. The bulky *tert*-Bu groups attribute to form the amorphous glass for BTNp 4, also being shown for BTmP 3. Additionally, the steric hindrance of 1,4-naphthylene linker would induce conformational distortion along triazine-naphthylene-triazine axial. BTB 1, which had biphenylenic structure and no alkyl substituents, was highly crystalline and did not form any glasses even with rapid cooling of the melted sample. These revealed that the incorporation of both bulky alkyl group and distorted scaffold significantly enhanced the glass forming property of materials.

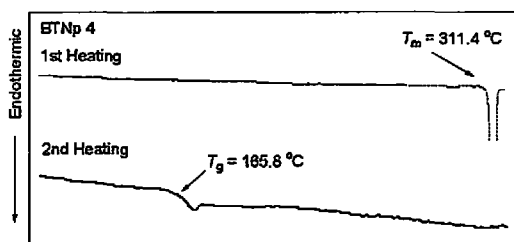


Fig. 3 DSC curves for BTNp 4 at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$.

3.3 Time-of-flight measurements

TOF technique¹¹ is a powerful method in order to obtain the direct evidence of the carrier transport capabilities. The measurement was performed for the electron transport of BTNp 4 at first. A homogeneous film of 4 ($2.0\text{ }\mu\text{m}$ thick) was vapor deposited onto ITO glass substrate, followed by 100 nm of aluminum electrode. Ensuring a small penetration depth for the light, irradiation of N_2 laser to the sample generated a packet of carriers, which drifted across the film of BTNp 4 under an externally applied bias voltage. The TOF transient signal for electron in film of BTNp 4 is shown in Fig. 4.

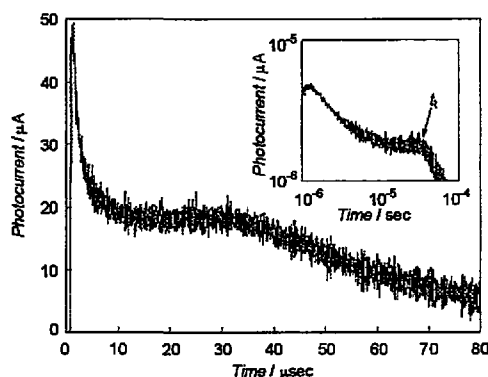


Fig. 4 Representative TOF transient for electron in BTNp 4 sample ($2.0\text{ }\mu\text{m}$ thick, $E = 3.3 \times 10^5\text{ V cm}^{-1}$, $30\text{ }^\circ\text{C}$). The inset shows a double logarithmic plot.

The photocurrent signal showed a characteristic current plateau followed by a drop. The plateau clearly indicated that the material has nature of nondispersive electron transport, that is, the packet of electrons traveled with a constant drift velocity then reached the electrode keeping a certain density. The transit time t_t was determined from the intersection of the slopes in the double-logarithmic plot (inset of Fig. 4). The electron mobility μ_e for BTNp 4 was in range of 10^{-5} to $10^{-4}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, which was determined using the relation $\mu = d/(t_t \times E)$ where the E is the electric field and d is the thickness of the film. The electron mobility of BTNp 4 is 10-100 times larger than that of Alq₃,¹² which is the most widely employed as an electron transport material in OLEDs.

It should be noted that not only electron transport but also hole transport was observed in the film of BTNp 4. At the opposite bias voltage, the TOF measurement of BTNp 4 sample gave a transient signal for hole. Although defined current plateau did not appear and it was interpreted as dispersive transport, the hole mobility μ_h was estimated to be 10^{-6} – $10^{-5}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, which was somewhat smaller than μ_e for BTNp 4. Ambipolar carrier transport in amorphous systems was previously reported in the literatures, where many of the "ambipolar" carrier transport materials consisted of plural chromophores to transport the both carriers.^{10,13} In contrast to them, BTNp 4 with a single type of chromophore realized ambipolar transport.

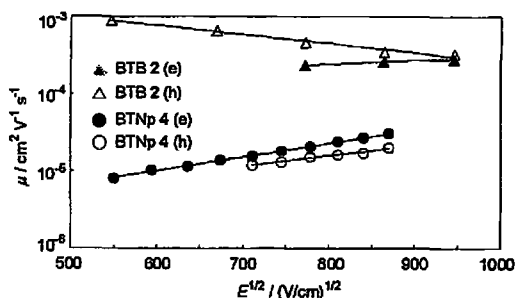


Fig. 5 Electron and hole mobilities versus $E^{1/2}$ for BTB 2 and BTNp 4.

To examine the carrier transport capability of BTB 2, a TOF sample was prepared by spin-coat method to avoid thermal decomposition of the material in vacuum deposition process. Interestingly, the nature of ambipolar carrier transport was also found in 2, and fairly high mobilities for both carriers were determined to be in the range of 10^{-4} – 10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, although the both transports were dispersive. The smaller carrier mobilities of compound 4 than BTB 2 may be due to weak intermolecular interaction caused by bulky substituents, which would enlarge the distance between the chromophores in the condensed state and disturb the hopping of photoinduced carriers.

The mobilities for compound 2 and 4 are plotted in Fig. 5 as a function of square root of the electric field. All mobilities showed relatively small dependence on electric field. A reasonable electric field regime is expected to be ca. 10^6 V cm^{-1} for working OLEDs¹⁴ that have typical structures (total thickness of organic layers is 150–200 nm). In such a large electric field, the electron mobilities for both compounds are high enough to operate EL devices.

3.4 Organic light-emitting diodes

Considering various properties described above, such as thermal stability, volatility, morphology, and carrier transport capability, we concluded that BTNp 4 was the most suitable candidate for the following device studies. Because we were interested in the conductive behavior of the material in thin film rather than optimum device performance, we employed a simplified device structure: [ITO/CuPc(25 nm)/NPD(40 nm)/Alq₃(40 nm)/BTNp 4(20 nm)/LiF(1 nm)/Al(100 nm)], where BTNp 4, Alq₃ and NPD were used as an ETL, an EML and a HTL, respectively. The EL spectrum was nearly equal to PL emission of Alq₃, and no bluish EL corresponded to BTNp 4 was observed (Fig. 6). These indicated that recombination of carriers took place only in EML, and that BTNp 4 layer could work as an electron transport layer.

A turn-on voltage (defined as the voltage required to give a luminance of 1 cd m^{-2}) of 5.0 V in the device was relatively high and the brightness was marginal ($\sim 400 \text{ cd m}^{-2}$, inset of Fig. 6). It suggested that electron injection from a cathode

to BTNp 4 layer may be inhibited by mismatching of energy levels between the organic segment and cathode. The effort for developing the material to facilitate the electron injection is now in progress.

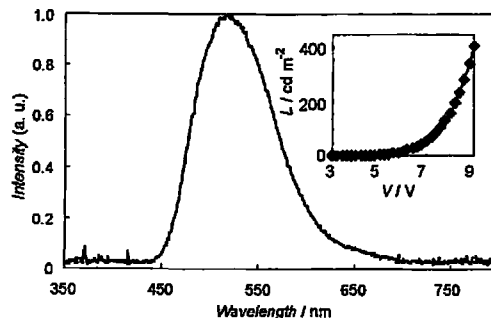


Fig. 6 EL spectra for the device; the inset shows luminance-voltage (L-V) characteristic.

4. CONCLUSIONS

Bis(1,3,5-triazinyl)arenes with structural variety were successfully prepared for the new organic semiconductive materials. Some of them exhibited excellent thermal and morphological stabilities, and ambipolar carrier transport capabilities were observed. The OLED study using BTNp 4 confirmed that the bis-triazines could be utilized as an electron transport segment in the organic thin-film device.

5. REFERENCES

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