

Spirocycle-Incorporated Triphenylamine Derivatives as an Advanced Organic Electroluminescent Material

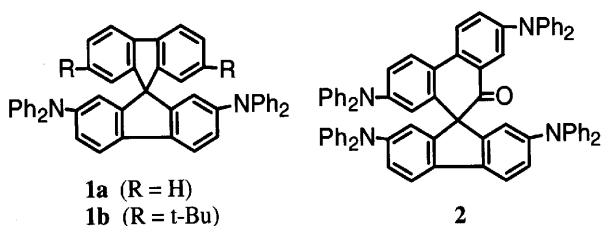
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For multi-color organic electroluminescent (EL) devices, new triphenylamine compounds attached to a spirocyclic framework were prepared from 2,7-bis(diphenylamino)-9-fluorenone. These amines showed exceedingly high Tg's or thermal stability as well as good electrochemical properties and sufficient EL characteristics, allowing practical application.

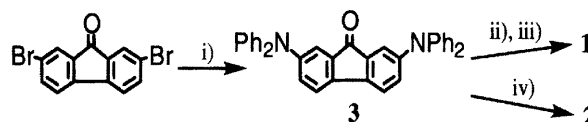
An organic electroluminescent (EL) devices¹ has been initiated into practical use as a mono-color device and new materials thermally stable in particular are expected for a coming multi-color device. Various triphenylamine derivatives have been elaborated as the hole-transport material.²⁻⁸ For example, *N,N'*-diphenyl-*N,N'*-di(*m*-tolyl)benzidine (TPD)³ shows excellent EL characteristics, but is lacking the thermal stability as illustrated by its glass transition temperature Tg as low as 60 °C; α -NPD⁴ a naphthalene substitute to TPD exhibited the satisfactory Tg of 96 °C. Starburst shaped triphenylamine derivatives invented by Shirota *et al.*⁵ have deserved the commercial application owing to the capability to form good amorphous solid films as well.

To improve the low thermal stability of TPD, we focused on the spirocompounds like **1** and **2** in view of the high melting points of the parent hydrocarbons and also recent application to electronic materials.^{9,10} New triphenylamine compounds incorporated into spiro-bi-9-fluorene (**1**) or a spiro-ketone (**2**) were found to possess exceedingly high Tg's and EL characteristics enough to allow practical use as the hole-transport material of future organic EL devices.



Preparation of **1** and **2** relied on the use of 2,7-bis(diphenylamino)-9-fluorenone **3** (Scheme 1). This was obtained from the requisite dibromide in 71 % yield by the amination using palladium acetate/tri-*tert*-butylphosphine (the Tosoh catalyst).¹¹ Synthesis of spiro-bifluorenes **1a** and **1b** were attained by coupling **3** with *o*-lithiobiphenyls, derived from the corresponding bromides **4** with BuLi in ether, followed by acid-treatment of the resulting crude alcohols in boiling acetic acid. Spiroketonic amine **2** was obtained in 70% isolated yield by heating **3** in triethyl phosphite;¹² the one-pot reaction involves apparently the pinacol coupling of **3** and subsequent pinacol rearrangement of the resultant diol.¹³

Scheme 1.



i) Ph_2NH , *t*-BuONa, $\text{Pd}(\text{OAc})_2/t\text{-Bu}_3\text{P}$ cat (0.1 mol%), xylene, reflux. ii) 2-bromobiphenyl or 2-bromo-4,4'-di-*tert*-butylbiphenyl (**4**), BuLi, THF, -70 °C $\rightarrow$ 0 °C. iii) MeSO_3H cat, AcOH reflux. iv) $\text{P}(\text{OEt})_3$, 140 °C, 1d.

Table 1. Thermal and electrochemical properties and EL characteristics for triphenylamine derivatives

Compound	Tg/°C ^a	Ea/V ^b	Luminance (V=100, V ^c) (max, $\times 100\text{cd/m}^2$)
TPB	70	0.72	4.1 ^d 20 (13V) ^d
1a	111	0.62	7.1 10 (14V)
1b	122	0.60	7.2 12 (16V)
2	141	0.76	6.5 15 (16V)

^a Tg's were determined with DSC rate of 10 °C/min.

^b First anodic peak potential, CH_2Cl_2 0.01 M, 0.1 M TBAP, scan rate 0.1 V/s.

^c See text. ^d Values with TPD.

The thermal properties of spiro-amines, **1** and **2**, were examined by the DSC analysis and the electrochemical ones by cyclic voltammetry (CV). The electroluminescent characteristics of **1** and **2** were obtained as a typical multi-layered devices. As a reference compound, *N,N,N',N'*-tetraphenylbenzidine (TPB) was used (Table 1). The observed Tg's of **1** and **2** are all over 110 °C, exceeding those of TPD and TPB. The present spirocompounds apparently have high Tg's enough for practical use as compared to α -NPD and non-cyclic or related amine derivatives.¹⁰ Therefore, the critical drawback of TPD is resolved, and spiroamines **1** and **2** would be thermally stable in keeping their solid thin films in EL devices.

Two or three successive waves of quasi-symmetry were observed in each CV of **1** and **2**. The first oxidation peaks of **1** and **2** appeared at 0.6-0.8 V vs. Ag/AgCl electrode. The wave analysis indicates a reversible formation of cation radicals;¹⁴ e.g., the cathodic and anodic peak current ratio at the first oxidation wave was 0.99 for **1b**, whereas that for TPB being 0.89. Thus, the cation radicals from **1** and **2** are electrochemically stable in solution.

Multi-layered EL devices for **1** and **2** were fabricated by vapor deposition onto the transparent ITO glass substrate (**1** 60

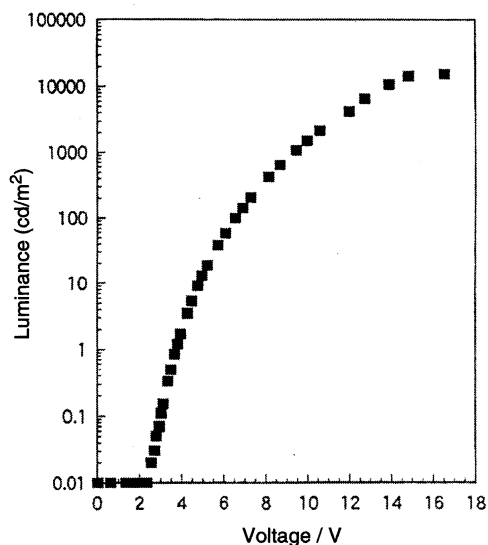


Figure 1. Luminance characteristic of **2** in the EL device.

nm / tris(8-quinolinolate)aluminum (Alq_3) 60 nm / metallic electrode Mg-Ag). By applying the electric voltage, a green emission due to Alq_3 was observed at 530 nm. For evaluating EL characteristics, we measured the applied voltage required for obtaining a practical level of luminance 100 cd/m^2 , i.e., V-100 (the lower the better) together with the maximum luminance before break-down of devices (see Figure 1 for **2**).

From Table 1, the luminances of spiroamines **1** and **2** are shown to be comparable to those of the standard TPD.¹⁵ The devices for **1** and **2** could be derived at a voltage lower than 10 V, clearly having the advantage of organic EL devices.

In conclusion, spirocyclic triphenylamines **1** and **2** prepared here have overcome the TPD's drawback in Tg, so that being expectable as a new hole-transport material.¹⁶ Based on the simple synthesis, spirocyclic ketone derivative **2** is proposed to be promising for coming multi-color EL devices.

References and Notes

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