Novel hole-transporting materials based on triphenylamine for organic electroluminescent devices

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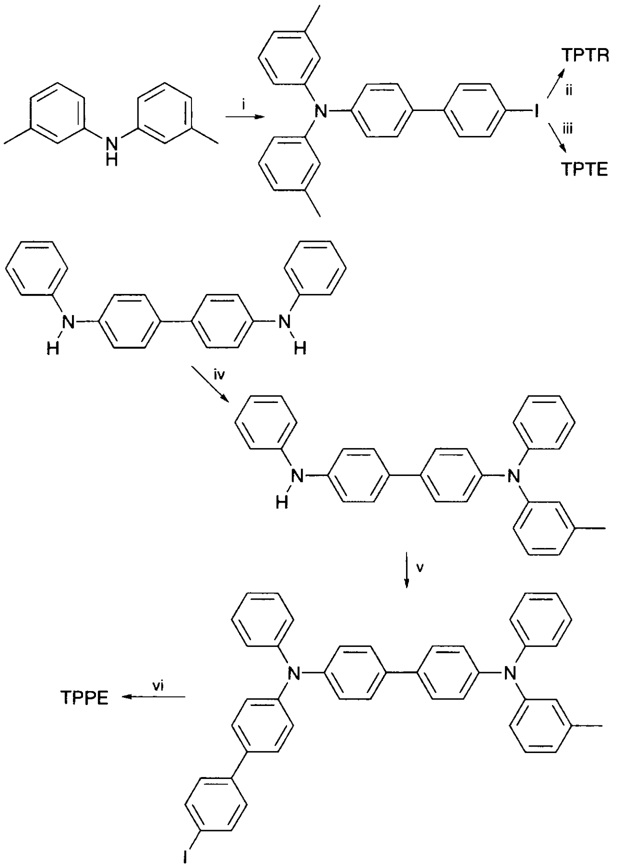
Oligomeric triphenylamines having high glass transition temperatures are synthesized for use in thermally stable organic electroluminescent devices.

Electroluminescent (EL) devices fabricated from multilayers of organic materials have great potential for use in full colour flat panel displays as a result of their various emission colours, low drive voltage and high efficiency.[1–9] Recent studies have focused on improving the durability of EL devices, as substantial device degradation, such as decreasing of luminance and increasing drive voltage, is observed during continuous operation.[10] Several studies have shown that the degradation of the EL devices is attributable to morphological change resulting from the thermal instability of the amorphous organic layers used in the EL devices. *N,N′*-Diphenyl-*N,N′*-(*m*-tolyl)benzidine (TPD) has been used most widely as the hole-transporting layer in EL devices due to its high carrier mobility and amorphous film-forming ability.[11] However, it is observed that the morphology of vapour-deposited TPD films changes even at ambient temperature.[12] Such morphological change of the TPD film is also caused by heating during operation of the device. Morphological change could be promoted by the movement of molecules due to rapid molecular motion near the glass transition temperature (T_g). Therefore, hole-transporting materials having high T_gs are required for organic EL devices to have a long lifetime.

Recently, Shirota and co-workers synthesized a novel hole-transport 'starburst' shaped molecule with a high T_g (150 °C), 4,4′,4″-tricarbazoyltriphenylamine (TCTA).[13,14] They fabricated an EL cell consisting of indium tin oxide (ITO)–TCTA–tris(8-hydroxyquinoline-*n*-yl)aluminum (Alq3) and Mg–Ag,



Scheme 1 *Reagents*: i, 4,4′-diiodobiphenyl, 33%; ii, *p*-toluidine, 30%; iii, *N,N′*-diphenylbenzidine, 75%; iv, *m*-iodotoluene, 16%; v, 4,4′-diiodobiphenyl, 47%; vi, *p*-toluidine, 51%

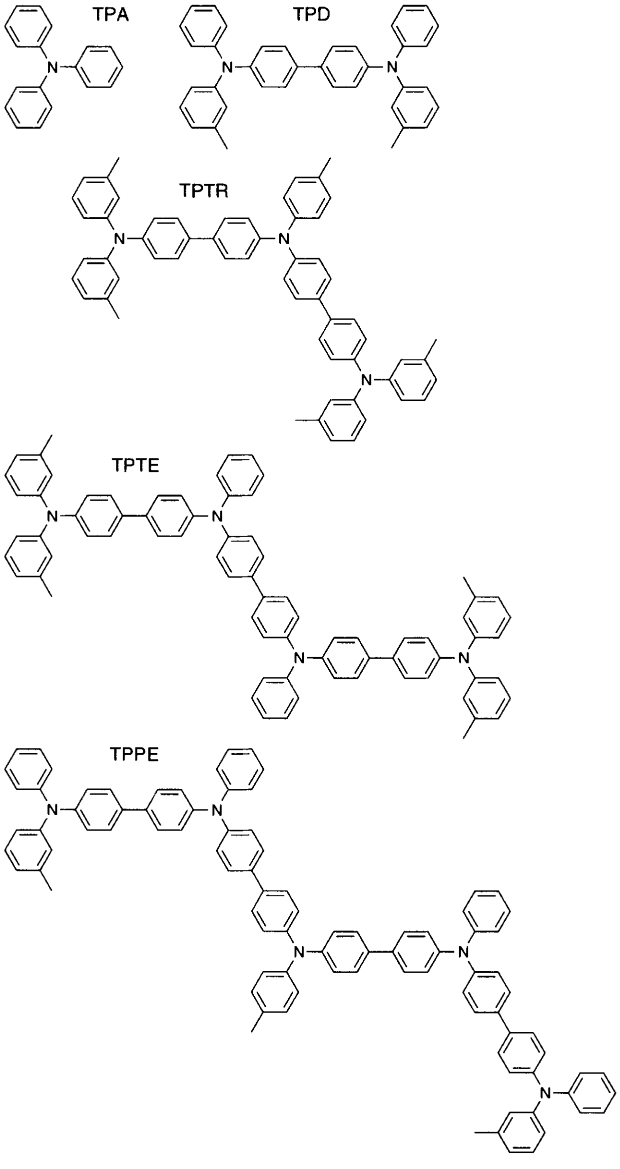


Fig. 1 Structure of the oligomeric TPAs

using TCTA as the hole-transporting material. However, the driving voltage of the EL device (turn-on voltage, *ca.* 10 V) was higher than that of the device using TPD (4 V) as the hole-transporting material.[1,13]

More recently, we have designed and synthesized novel hole-transporting molecules with high T_gs, based on triphenylamine (TPA) which have good hole-transporting characteristics. By oligomerization of TPA, the T_g of the oligomeric triphenylamines can be increased with increasing molecular weight as a result of the restriction of molecular motion. In this communication, we report the synthesis of linear oligomeric TPAs (oligomerization number, *n*; *n* = 2–5) and the thermal and optical properties of the films prepared by conventional vacuum-deposition. The performance of the EL device fabricated using one of the TPAs is also presented.

Fig. 1 shows the structure of TPA oligomers. The dimer of TPA is referred to as TPD. The trimer is referred to as TPTR, the tetramer as TPTE and the pentamer as TPPE. Oligomeric TPAs were synthesized through an Ullmann coupling reaction between the corresponding primary or secondary arylamine and aryl iodide in the presence of a copper catalyst and potassium carbonate at 160 °C in xylene or decalin for 40 h under nitrogen (Scheme 1). To promote the reaction, 18-crown-6 was used as a phase transfer catalyst. All the compounds were purified by column chromatography over silica gel. Each purified sample gave only one spot on TLC (hexane–chloroform on activated silica gel). The oligomeric TPAs were obtained as white powders, were soluble in benzene, toluene, chloroform and THF and were stable in air.

The thermal properties of the oligomeric TPAs were studied by differential scanning calorimetry (DSC). Before the measurement, all compounds were melted at 300 °C and cooled rapidly to room temperature to form glassy samples. Then, the samples were heated again at a rate of 10 °C min^{-1}. There was no exothermic pattern of TPA oligomers corresponding to the crystallization observed in starburst molecules.[14] However, the T_gs of the compounds that were observed were characteristic of amorphous materials. Fig. 2 shows the relationship between the oligomerization number (*n*) of the TPAs and the T_g. The value of T_g shifted to a high temperature as *n* increased, *e.g.* the T_g for TPTR was 130 °C and for TPTE was 140 °C. These values are much higher than that of TPD (T_g 60 °C). This result indicates that the oligomerization of TPA has an effect on the value of T_g.

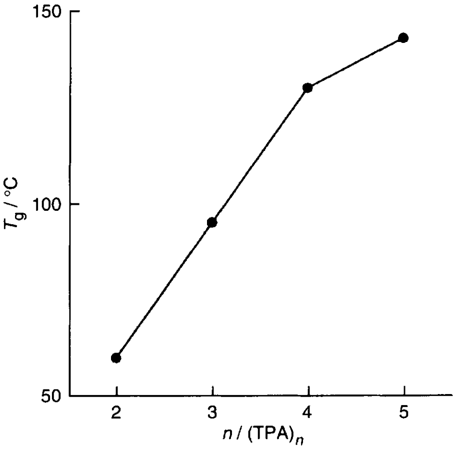


Fig. 2 Dependence of T_g on the oligomerization number (*n*)

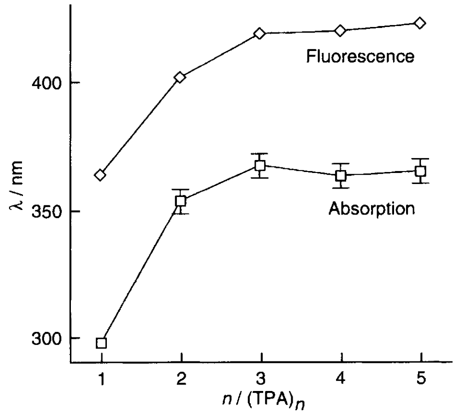


Fig. 3 Dependence of the absorption and fluorescence (λ_{ex} = 360 nm) maxima of the oligomeric TPAs on the oligomerization number (*n*). All the measurements were carried out on thin films of TPA oligomers on glass (thickness = 100 nm).

TPA oligomers were vaccum-deposited on glass substrates from a tungsten boat at 2–4 × 10^{-4} Pa at a rate of 3–4 nm min^{-1}. Transparent and smooth film were obtained for the oligomers without thermal decomposition. All the deposited films were found to be amorphous, as was observed by polarized microscopy. The TPTR and TPTE films were transparent and smooth, even at 100 °C, and no morphological change was observed. This is attributable to the high T_gs of these materials. The absorption and fluorescence spectrum maxima of the oligomeric TPA films are plotted against the oligomerization numbers (*n*) in Fig. 3. The absorption and fluorescence maxima were shifted to longer wavelength with increased *n*, however there was little change where *n* had a value greater than three.

We fabricated EL devices using oligomeric TPAs for the hole-transporting layer.[15] TPTE was used as the hole-transporting layer (thickness 70 nm), Alq3 as the emitting layer (thickness 70 nm), Mg–Ag (10 : 1) (180 nm) as the cathode and ITO as the anode. Luminescence from the device was observed from an applied voltage of 3.1 V, with an initial luminance exceeding 11 000 cd m^{-2} at 14 V. These results show that the hole-transporting properties of TPTE are almost comparable to those of TPD. This device could be operated at 100 °C for 100 h without serious degradation, whereas the device using TPD broke down after a few seconds at 100 °C. This excellent stability at high temperature is attributable to the high T_g of TPTE.

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Footnote

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References

1 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
2 C. Adachi, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, 1989, **55**, 1489.
3 C. Adachi, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, 1990, **57**, 1513.
4 Y. Hamada, C. Adachi, T. Tsutsui and S. Saito, *Jpn. J. Appl. Phys.*, 1992, **32**, 1812.
5 H. Tokaillin, M. Matsuura, H. Higashi, C. Hosokawa and T. Kusumoto, *Proc. SPIE Int. Soc. Opt. Eng.*, 1993, **38**, 1910.
6 J. Kido, K. Hongawa, K. Nagai and K. Okuyama, *Appl. Phys. Lett.*, 1994, 65, 2124.
7 J. H. Burroughs, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackey, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539.
8 Y. Yang and A. J. Heeger, *Appl. Phys. Lett.*, 1994, **64**, 1245.
9 D. R. Baignet, R. N. Marks, N. C. Greenheim, R. H. Friend, S. C. Moratti and A. B. Holmes, *Appl. Phys. Lett.*, 1994, **65**, 2636.
10 P. E. Burrows, V. Bulovic, S. R. Forrest, L. S. Spochak, D. M. McCarty and M. E. Thompson, *Appl. Phys. Lett.*, 1994, **65**, 2922.
11 M. Abkowitz and D. M. Pai, *Philos. Mag. B*, 1986, **53**, 193.
12 E. M. Han, L. M. Do, Y. Niidome and M. Fujihira, *Chem. Lett.*, 1994, 969.
13 Y. Kuwayama, H. Ogawa, H. Inada, N. Noma and Y. Shirota, *Adv. Mater.*, 1994, **6**, 677.
14 Y. Shirota, T. Kobata, N. Noma, *Chem. Lett.*, 1989, 1145.
15 S. Tokito, H. Tanaka, A. Okada, Y. Taga, *Appl. Phys. Lett.*, in the press.

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