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Synthesis and Properties of Amorphous Hole Transport Materials of Triphenylamine Based Trihydrazones

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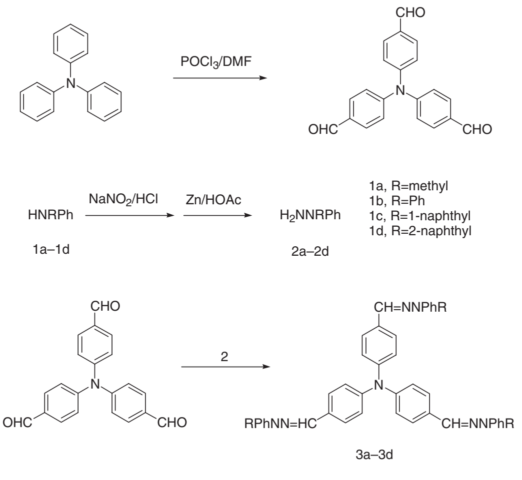
A novel class of amorphous state triphenylamine-based trihydrazones were synthesized by condensation reaction of tris(*p*-formylphenyl)amine with *N*-methyl-*N*-phenyl hydrazine, *N*,*N*-diphenylhydrazine, *N*-1-naphthyl-*N*-phenyl-hydrazine, and *N*-2-naphthyl-*N*-phenyl-hydrazine, respectively, and characterized using different scanning calorimetry (DSC) and cyclic voltammetry (CV).

Recently, amorphous molecular materials, having stable amorphous phase above room temperature, have been thoroughly investigated because of their excellent processability, transparency, inexistence of grain boundaries and isotropic properties. They were extensively used in organic photoconductors (OPCs), light-emitting diodes (OLEDs), field effect transistors and solid solar cells.[1–4] Among these materials, the most widely studied are hole transporting materials (HTMs). Polymers with hole transport moieties on their side or main chains,[5,6] and molecularly doped systems, where small molecular hole transport compounds are dispersed in polymer binders, can easily form amorphous state. Most of them often show lower charge transfer mobility compared to small molecular HTMs owing to lower concentration of active moieties. However, small molecular HTMs often suffer from poor thermal stability, and easy recrystallization when they are allowed to stand at ambient temperature or heated above the glass state, which limit their use in photoelectric devices. It is much important to design and synthesize small molecular HTMs with high glass transition temperatures (T_gs) and stable amorphous state. It is well known that many compounds can be transformed into amorphous state by fast cooling from the melt. Generally, the amorphous materials should contain non-planar chemical structures, which can prevent easy packing of molecules and hence hinder crystallization. In addition, increasing number of conformer and incorporation of bulky substitutes in the molecule also improve the formation of amorphous state. In order to increase the glass transition temperature, there are some effective measures such as incorporation of bulky substitutes in the molecules, increasing molecular size and enhancing intermolecular interaction, which can hinder molecular motions. Shirota and co-workers synthesized a series of 'burst star' hole transport materials containing aromatic amine groups, which form amorphous film on cooling from the melt.[7,8] Josef et al. designed spiro-linked molecular hole-transporting materials, which show organic glass state with high thermal stability due to their high T_gs.[9] Some other HTMs were also reported recently.[10–16] For the most of these materials reported by now, however, the amorphous states can be achieved only by cooling from the melt, showing relatively low stability. Only a limited number of compounds can completely form amorphous state, and don't show melting or crystallization in the differential scanning calorimetry (DSC) up to decomposition temperature. Here, we report, for the first time, the syntheses and properties of novel triphenylamine-based trihydrazones, triphenylamine-4,4′,4″-tricarbalaldehyde tris(*N*-methyl-*N*-phenylhrdrazone) (**3a**), triphenylamine-4,4′,4″-tricarbalaldehyde tris(*N*,*N*-diphenylhrdrazone) (**3b**), triphenylamine-4,4′,4″-tricarbalaldehyde tris(*N*-1-naphthyl-*N*-phenyl-drazone) (**3c**), and triphenylamine-4,4′,4″-tricarbalaldehyde tris(*N*-2-naphthyl-*N*-phenyl-hrdrazone) (**3d**), respectively. As shown in Scheme 1, these compounds were synthesized by condensation reaction of tris(*p*-formylphenyl)amine with *N*-methyl-*N*-phenyl hydrazine, *N*,*N*-diphenylhydrazine, *N*-1-naphthyl-*N*-phenyl-hydrazine, and *N*-2-naphthyl-*N*-phenyl-hydrazine, respectively. Tris(*p*-formyl-phenyl)amine,[17] synthesized through Vilsmeier formylation of triphenylamine, reacted with these different hydrazines with yield of 80, 77, 60, and 58%, respectively. The hydrazines were obtained by nitrosation and reduction reaction of corresponding diamines. The compounds (**3a**–**3d**) were purified by chromatography, and confirmed by ^{1}H NMR.

The thermal properties of these compounds were studied us-



Scheme 1. Synthetic routes of **3a**–**3d**.

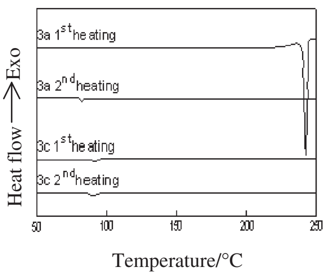


Figure 1. DSC curves of **3a** and **3c**.

Table 1. DSC and CV data of compounds **3a**–**3d**

Compound	T_g /°C[a]	T_m /°C[a]	λ_{max} /nm[b]	E_{ox} /V[c]
3a	74	247	252.3, 332.0, 359.5,	0.17
3b	81	241	286.1,332.7, 362.5, 382.7	0.22
3c	86	no	283.8, 331.4, 358.9, 381.0	0.23
3d	87	no	270.6, 335.1, 360.7, 384.1	0.23

[a] Obtained from differential scanning calorimetry (DSC) measurement; no: T_g or T_m not detected. [b] Measurement in CH_2Cl–CH_2Cl solution. [c] All data were reported relative to ferrocene which has an oxidation potential at 0.58 V relative to Ag/$AgNO_3$. The sweeping voltage is from −100 to 1000 mV, and the scan rate is 100 mV/s.

ing differential scanning calorimetry (DSC). The glass transition temperature (T_g), melting temperature (T_m) and recrystallization temperature (T_c) are summarized in Table 1. **3a** and **3b** are crystalline and show a clear endothermic melting peak on first heating at 247 and 241 °C, respectively. They form amorphous state after cooling from the melt. Upon second heating, they show glass transition at 74 and 81 °C, respectively, no crystallization was observed even they were heated above T_g over 300 °C. It is very interesting that, **3c** and **3d** didn't show any endothermic melting peaks on first and also on second heating up to 300 °C where they began to decompose. Although we attempted to crystallize them from solution, they showed only amorphous state with T_g at 86 and 87 °C, respectively, which means that **3c** and **3d** possess higher stability compared with **3a** and **3b**. As reported in the literature, triphenylamine possess non-planar chemical structure with N atom deviating from the plane of the bonded C atoms with a dihedral angle of about 75° between any phenyl rings of the triphenylamine molecules.[18] Their glass transition temperatures increase from 74 to 86 °C with their different hydrazine substitutes changing from *N*-methyl-*N*-phenylhydrazine to *N*-1-naphthyl-*N*-phenylhydrazine in the triphenylamine molecules, whereas **3c** and **3d** almost possess same T_gs around 86 °C with *N*-1-naphthyl-*N*-phenylhydrazine and *N*-2-naphthyl-*N*-phenylhydrazine substitutes, respectively. Because of large substitutes in **3c** and **3d**, which can hinder regular arrangement and motion of their molecules and lead to formalization of amorphous state, they show only glass state. We assume that **3c** and **3d** are suitable materials to form stable amorphous glassy film, which can be formed directly by solution coating.

The redox behavior of the hole-transporting materials were characterised using cyclic voltammetry. The measurements were conducted at a Pt disc electrode in dichloromethane solution containing millimolar sample and 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. The potentials were recorded against Ag/$AgNO_3$ as reference electrode and each measurement was calibrated with ferrocene/ferrocenium (Fc) redox system as an internal standard. Their first oxidation potentials were listed in Table 1. The first oxidation step for each of **3a**–**3d** is reversible over the entire scan rate range of 50 to 200 mV/s with the peak height varying linearly with the scan rate and no changed positions of anodic and cathodic peaks. The first oxidation potential increases with the molecular size in the order **3a** (0.17 V) < **3b** (0.22 V) < **3c** (0.23 V) = **3d** (0.23 V). Their low oxidation potentials can function as good hole transport materials for use in the photoelectric devices.

A series of hole transport materials were designed and synthesized by consideration reaction of tris(*p*-formylphenyl) amine with different hydrazines. Among these compounds, **3c** and **3d**, with large substituent groups of *N*-1-naphthyl-*N*-phenyl hydrazine and *N*-2-naphthyl-*N*-phenyl hydrazine respectively in their molecules, show excellent stable amorphous states.

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References

1 D. M. Pai and J. Yanus, *Photogr. Sci. Eng.*, **27**, 14 (1983).
2 H. Tanaka, S. Tokito, Y. Taga, and A. Okada, *Chem. Commun.*, **1996**, 2175.
3 H. J. Bolink, C. Arts, V. V. Krasnikov, G. G. Maliaras, and G. Hadziioannou, *Chem. Mater.*, **9**, 1407 (1997).
4 J. Ostrauskaite, V. Voska, J. Antulis, V. Gaidelis, V. Jankauskas, and J. V. Grazulevicius, *J. Mater. Chem.*, **12**, 3469 (2002).
5 E. S. Kolb, R. A. Gaudiana, and P. G. Mehta, *Macromolecules*, **29**, 2359 (1996).
6 M. Redecker, D. C. Bradley, M. Inbasekaran, W. W. Wu, and E. P. Woo, *Adv. Mater.*, **11**, 241 (1999).
7 K. Katsuma and Y. Shirota, *Adv. Mater.*, **10**, 223 (1998).
8 Y. Shirota, *J. Mater. Chem.*, **10**, 1 (2000).
9 S. Josef, W. Frank, and B. Jacqueline, *Macromol. Symp.*, **125**, 121 (1997).
10 M. Thelakkat and H. W. Schmidt, *Adv. Mater.*, **10**, 219 (1998).
11 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissörte, J. Salbeck, H. Spreitzer, and M. Grätzel, *Nature*, **395**, 583 (1998).
12 S. Grigalevičius, V. Getautis, J. V. Grazulevičius, V. Gaidelis, V. Jankauskas, and E. Montrimas, *Mater. Chem. Phys.*, **72**, 395 (2001).
13 K. Okumota, K. Wayaku, T. Noda, H. Kageyama, and Y. Shirota, *Synth. Met.*, **111**, 473 (2000).
14 N. X. Hu, S. Xie, Z. D. Popovic, B. Ong, and A. M. Hor, *Synth. Met.*, **111**, 421 (2000).
15 D. E. Loy, B. E. Koene, and M. E. Thompson, *Adv. Funct. Mater.*, **12**, 245 (2002).
16 I. Y. Wu, J. T. Lin, Y. T. Tao, and E. Balasubramaniam, *Adv. Mater.*, **12**, 668 (2000).
17 H. Nam, D. H. Kang, J. K. Kim, and S. Y. Park, *Chem. Lett.*, **2002**, 897.
18 M. H. Huang, F. Kartona, B. Dunn, and J. I. Zink, *Chem. Mater.*, **14**, 5153 (2002).

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