# Synthesis of Hole-Transporting Hydrazone Dendrimers

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Hole-transporting aromatic hydrazone dendrimers were synthesized by convergent method. Structures of dendrimers were characterized by NMR, IR, GC/MS (FAB$^+$), and elemental analysis.

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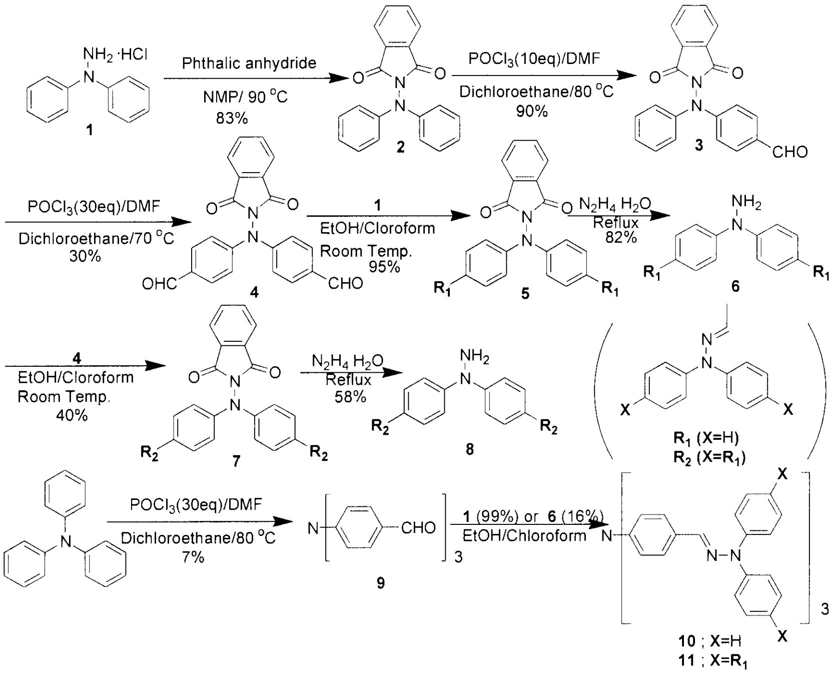
Aromatic hydrazone molecules dispersed in a binder polymer[1] or attached to the polymer chain as a pendant group[2] are used as the main constituent of electrophotographic devices due to their excellent hole-transporting property.[1,2] To further enhance the hole-transporting ability, new material system which does not involve inactive polymeric components and thus provides higher concentration of hydrazone moiety is needed. Dendritic molecular architecture is considered useful for this purpose because both the compact globular structure and good processibility are normally guaranteed.[3] In this work, we report novel spin-coatable dendrimers consisting of branched aromatic hydrazone moieties. Dendrimer syntheses were carried out by the convergent method as outlined in Scheme 1. Protecting of hydrazine group by phthalic anhydride and the Vilsmeyer formylation of aromatic ring were repeatedly applied for these convergent syntheses. From the commercially available first generation dendron **1**, second and third generation dendrons (**6** and **8**, respectively) were successfully synthesized. Core group **9** was synthesized by Vilsmeyer–Haack formylation of triphenylamine in a single step. Condensation reaction of **9** with dendrons **1** and **6** yielded first and second generation dendrimers **10** and **11** in 99% and 16% yields, respectively. However, reaction of **9** and **8** did not give third generation dendrimer presumably due to the equilibrium nature of condensation reaction and the severe steric hindrance of **8**.

Structures of hydrazine dendrimers **10** and **11** were characterized by NMR, FT-IR, elemental analysis, and GC/MS.[4] Aromatic hydrazone dendrimers **10** and **11** were very soluble in common organic solvents such as chlorobenzene, chloroform, and DMF. This contrasts to the rather limited solubility of linear hydrazone molecules originating from their high crystallinity. Aromatic hydrazone dendrimers **10** and **11** were amorphous materials which formed excellent optical films by spin-coating. These films were clear, transparent, homogeneous, and mechanically tough. Glass transition temperature of **11** was measured to be 164 °C, however that of **10** was not detected by DSC.



**Scheme 1**. Synthesis of Dendrons and Dendrimers.

UV–visible absorption maxima were observed at 400 nm and 418 nm for the dendrimers **10** and **11** in chloroform solutions. Cut-off wavelengths of these dendrimers were 444 nm and 487 nm corresponding to the HOMO to LUMO excitation energies of 2.8 eV and 2.5 eV for **10** and **11**, respectively. Red-shifted absorption of **11** over that of **10** suggests that the dendritic structure provides partial conjugation of hydrazone branches. According to this conjugation effect, ionization potential (IP) of **11** was also measured to be higher than that of **10** by 0.1 eV. Cyclic voltametry measurements were carried out with dendrimers coated on an ITO electrode in a 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) in acetonitrile at a constant scan rate of 20 mV/s using a three-electrode cell and potentiostat assembly. Actual IP values of **10** and **11** measured by cyclic voltametry were 5.1 eV and 5.2 eV, respectively. To attest the hole transporting properties of **10** and **11**, we fabricated multilayer EL devices ITO/dendrimer (**10**,**11**)(60nm)/$Alq_3$(90nm)/Al and also ITO/PVK (60nm)/$Alq_3$(90nm)/Al as a control. All these devices showed strong green emission from $Alq_3$ layer. At 10 V, brightness of devices with hole transporting layer of **10**, **11** and PVK were $2.8 \times 10^{-2}$ μW, $1.3 \times 10^{-3}$ μW, and $2.9 \times 10^{-3}$ μW, and the quantum efficiencies were $2.93 \times 10^{-2}$%, $1.28 \times 10^{-2}$%, and $1.35 \times 10^{-2}$%, respectively. We could see that the quantum efficiencies and the luminance properties of the synthesized dendrimers were higher than, or at least comparable to that of PVK. Compared to the turn-on voltage of control device (5.0 V), those of multi layer devices using **10** and **11** dendrimer layers were significantly lowered to be 2.5 V and 4.5 V, which suggests good hole-injecting and transporting properties of aromatic hydrazone dendrimers. Much lower turn-on voltage of the device containing the layer of **10** over those of **11** and control is considered to originate from the lower IP value (5.1 eV) of **10** which matches better to the Fermi level of ITO anode whose work function is 4.8 eV.

## References and Notes

1 J. Mort and G. Pfister, “Electronic Properties of Polymers,” Wiley, New York (1982).

2 M. Döbler, C. Weder, P. Neuenschwander, and U. W. Suter, *Macromolecules*, **31**, 6184 (1998).

3 G. R. Newkome, C. N. Moorefield, and F. Vögtle, “Dendritic Molecules,” VCH, Weinheim (1996).

4 Structure characterization of **10** and **11**. **10** ; $^1$H NMR ($CDCl_3$) δ 7.49 (d, 6H), 7.31 (t, 12H), 7.08 (m, 28H); IR (KBr window, cm$^{-1}$) 1597 (ν C=N); Anal. Found : C, 82.26; H, 5.137; N, 11.80%; M$^+$, 828. Calcd for $C_{57}H_{45}N_7$ : C, 82.68; H, 5.48; N, 11.84%; M, 828. **11** ; $^1$H NMR ($CDCl_3$) δ 8.60 (d, 6H), 7.66 (m, 24H), 7.43 (t, 24H), 7.18 (m, 51H) ; IR (KBr window, cm$^{-1}$) 1590 (ν C=N); Anal. Found: C, 79.12; H, 4.832; N, 13.76%; M$^+$, 1993. Calcd for $C_{135}H_{105}N_{19}$ : C,81.34; H, 5.31; N, 13.35%; M, 1993.