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Conjugated Dendrimers with Electrical Bistability for Organic Memory Application

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Introduction

Dendrimers are monodisperse and highly branched tree-like functional macromolecules.¹⁻³ Due to their well-defined and unique structure, dendrimers have attracted tremendous attention for a variety of applications. Recently, conjugated dendrimers have been widely studied for electronic applications such as light-emitting diode, light-harvesting, and two-photon absorption materials.⁴⁻⁸ Dendritic architectures provide several unique advantages as electronic materials. They can be synthesized in high purity with monodispersity in molecular weight just as low molecular weight species. In addition, just like polymers, several multifunctional moieties can be incorporated in one molecule to modulate electronic properties. A spin-coating is also applicable for thin-film fabrication of dendrimers. Therefore, dendritic molecules have been attractive for application as electronic materials. Lately, organic memory devices have attracted much attention due to their advantages such as low-cost, easy processing, flexibility, 3-D stacking, and large area fabrication.⁹⁻¹² For organic memory application, materials should have electrical bistability, i.e. the low-conductivity state (OFF state) and the high-conductivity state (ON state), suitable retention time at either state, and switchability between the two states under a suitable bias condition.^{13,14} Since the early observation of a voltage-induced switching phenomenon in organic materials,¹⁵⁻¹⁸ several systems with

electrical bistability have been investigated such as charge transfer complexes and conjugated polymers.¹⁹⁻³⁰ In addition, organic memory devices have been demonstrated with organic donor molecules and acceptors such as Au nanoparticle, fullerene, or Eu complex.³¹⁻³⁶ Other examples include polyimides with donor-acceptor moieties.^{37,38} For the donor-acceptor systems, a charge transfer between donor and acceptor was proposed for the memory mechanism. Therefore, we reasoned that an electrical bistability would be effectively realized with the π -conjugated dendrimers in which donors and acceptors are covalently linked. In this work, as a part of our effort to develop dendritic materials with electrical bistability,^{39,40} we report on the synthesis and characteristics of electrical bistability of the π -conjugated dendrimers that contain triarylamine at the core as a donor and peripheral triazine or stilbene as an acceptor.

Experimental

Materials and Instruments. Anhydrous *N,N'*-dimethylacetamide (DMAC) and other chemicals from Aldrich were used as received. 2,4-Bis(4-*tert*-butylphenyl)-6-(4-vinylphenyl)-1,3,5-triazine and 1,3-bis((*E*)-4-*tert*-butylstyryl)-5-vinylbenzene were synthesized following the literature procedure.^{8,41} ¹H and ¹³C NMR spectra were recorded on Varian UNITY INOVA 400 at 400 and 100 MHz, respectively. FT-IR spectra were obtained using Perkin-Elmer System 2000 FR-IR spectrophotometer. MALDI-TOF spectra were obtained using Voyager Biospectrometry time of flight mass spectrometer (Perspective Biosystem) operated at 25 kV accelerating voltage in reflector mode with positive ionization. Dithranol was used as the matrix. Elemental analysis data were obtained using CE Instrument EA 1110. UV-vis spectra were recorded on Hewlett-Packard 8452A spectrophotometer. Photoluminescence spectra were obtained using Shimadzu RF-5301PC spectrofluorophotometer.

Device Fabrication and Test. ITO-coated glass plates were washed and treated by oxygen plasma prior to use as a substrate. On the top of the substrate, a 1,2-dichloroethane solution of the conjugated dendrimers (1 wt%) was spin-coated at a speed in the range of 1,800-2,000 rpm for 60 sec and dried at 120 °C in vacuum for 30 min. A 2-nm-thick LiF alloy was vacuum-deposited on the organic layer as a blocking layer. Then, top aluminum electrode was then vacuum-deposited on the layer at 5×10^{-6} Torr. The device of top and bottom electrode had an area of 0.3×0.3 mm². The electrical characteristics of the device were measured by using a current/voltage source measurement unit (Keithly 2400).

Synthesis of 3Stb-TAD. A DMAC solution (20 mL) of 1,3-bis((*E*)-4-*tert*-butylstyryl)-5-vinylbenzene (1.00 g, 2.38 mmol), tris(4-bromophenyl)amine (0.33 g, 0.68 mmol), sodium carbonate (0.22 g, 2.08 mmol), 2,6-di-*tert*-butylresol (0.15 g,

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0.68 mmol), and *trans*-di(μ -acetato)bis[*o*-(di-*o*-tolylphosphino)-benzyl]dipalladium (II) (0.01 g, 0.01 mmol) was stirred at 130 °C for 24 h under nitrogen. After cooling, the solution was poured into a mixture of methylene chloride and distilled water. The organic layer was separated and filtered through silica gel. After removal of the solvent, the residue was precipitated into methylene chloride/methanol (1:10, v/v) to give 3Stb-TAD as a yellow solid. (Yield 0.42 g, 41%), mp 220 °C.

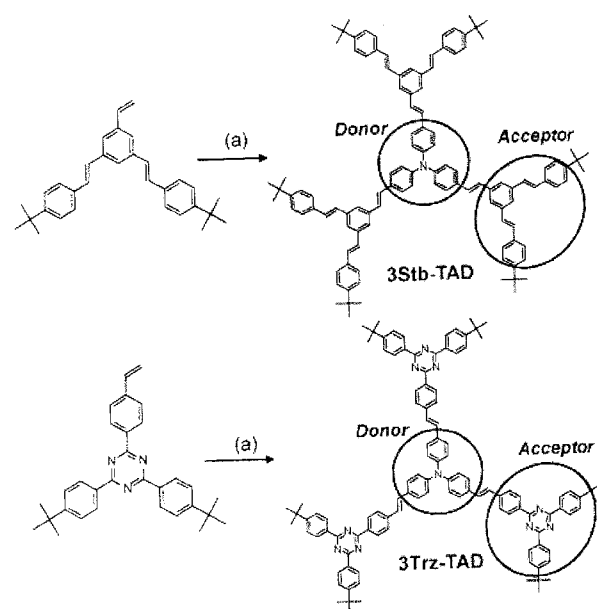
¹H NMR (400 MHz, CDCl₃) δ 1.33 (s, 54H, *t*-Bu), 7.09 (d, J=16 Hz, 3H, N-Ph₃-CH=CH-), 7.12 (d, J=16 Hz, 3H, N-Ph₃-CH=CH-), 7.13-1.18 (m, 6H, N-Ph₃-), 7.19 (d, J=16 Hz, 3H, N-Ph₃-CH=CH-), 7.21 (d, J=16 Hz, 3H, N-Ph₃-CH=CH-), 7.42 (d, J=8.4 Hz, 12H, -Ph-*t*Bu), 7.48-7.56 (m, 15H, N-Ph₃- and =CH-Ph-CH=), 7.51 (d, J=8.4 Hz, 12H, -Ph-*t*Bu); ¹³C NMR (100.64 MHz, CDCl₃) δ 31.28, 34.64, 123.53, 124.08, 125.64, 126.29, 127.11, 127.55, 127.63, 128.96, 132.15, 134.46, 138.18, 146.76, 150.90; IR (KBr): ν =3028, 2963, 2869, 1584, 1505, 1321, 1263, 1321, 1263, 1178, 1102, 1019, 961, 848, 805; MS (MALDI-TOF) calcd for C₁₁₄H₁₁₇N 1501.19, found 1501.51 [m]⁺ Anal. Calcd for C₁₁₄H₁₁₇N: C, 91.21; H, 7.86; N, 0.93. Found: C, 91.18; H, 7.90; N, 0.81.

Synthesis of 3Trz-TAD. A DMAC solution (20 mL) of 2,4-bis(4-*tert*-butylphenyl)-6-(4-vinylphenyl)-1,3,5-triazine (1.00 g, 2.23 mmol), tris(4-bromophenyl)amine (0.31 g, 0.64 mmol), sodium carbonate (0.20 g, 1.92 mmol), 2,6-di-*tert*-butylcresol (0.14 g, 0.64 mmol), and *trans*-di(μ -acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl] dipalladium(II) (0.01 g, 0.01 mol) was stirred at 130 °C for 24 h under nitrogen. After cooling, the solution was poured into a mixture of methylene chloride and distilled water. The organic layer was separated and filtered through silica gel. After removal of the solvent, the residue was precipitated into methylene chloride/methanol (1:10, v/v) to give 3Trz-TAD as a yellow solid. (Yield 0.62 g, 61 %), mp 202 °C.

¹H NMR (400 MHz, CDCl₃) δ 1.42 (s, 54H, *t*-Bu), 7.14 (d, J=16.1 Hz, 3H, -Ph-CH=CH-Ph-N-), 7.18 (d, J=8.4 Hz, 6H, -Ph-N-), 7.26 (d, J=16.1 Hz, 3H, -Ph-CH=CH-Ph-N-), 7.52 (d, J=8.8 Hz, 6H, -Ph-N-), 7.61 (d, J=8.8 Hz, 12H, -Trz-Ph-*t*Bu), 7.69 (d, J=8.4 Hz, 6H, -Trz-Ph-CH=CH-), 8.65 (d, J=8.4 Hz, 12H, -Trz-Ph-*t*Bu), 8.76 (d, J=8.4 Hz, 6H, -Trz-Ph-CH=CH-); ¹³C NMR (100.64 MHz, CDCl₃) δ 31.23, 35.08, 124.32, 125.65, 126.45, 126.84, 127.81, 128.75, 129.29, 129.81, 132.00, 133.70, 135.27, 141.42, 146.90, 155.91, 170.96, 171.39; IR (KBr): ν =2961, 2906, 1580, 1507, 1371, 1280, 1190, 1108, 1017, 959, 820; MS (MALDI-TOF) calcd for C₁₁₁H₁₀₈N₁₀ 1582.15, found 1582.18 Anal. Calcd for C₁₁₁H₁₀₈N₁₀: C, 84.27; H, 6.88; N, 8.85. Found: C, 83.93; H, 7.10; N, 8.51.

Results and Discussion

Synthesis of Conjugated Dendrimers. The conjugated



Scheme I. Synthesis of conjugated dendrimers (a) tris(4-bromophenyl)amine, *trans*-di(μ -acetato)bis[*o*-(di-*o*-tolylphosphino)-benzyl]dipalladium, Na₂CO₃, DMAC.

dendrimers, 3Stb-TAD and 3Trz-TAD, were synthesized via Heck coupling of tris(4-bromophenyl)amine respectively with 1,3-bis((*E*)-4-*tert*-butylstyryl)-5-vinylbenzene and 2,4-bis(4-*tert*-butylphenyl)-6-(4-vinylphenyl)-1,3,5-triazine as shown in Scheme I. The dendrimers were characterized by using ¹H and ¹³C NMR, FT-IR spectra, elemental analysis, and MALDI-TOF mass spectrometry. All the compounds were soluble in methylene chloride, chloroform, THF, and 1,2-dichloroethane.

Photophysical Properties of Conjugated Dendrimers.

The absorption spectra of the conjugated dendrimers in methylene chloride (10⁻⁶ M) are shown in Figure 1. The absorption spectrum of 3Stb-TAD showed maxima at 320 nm due to the peripheral stilbene moiety, and 400 nm due to the

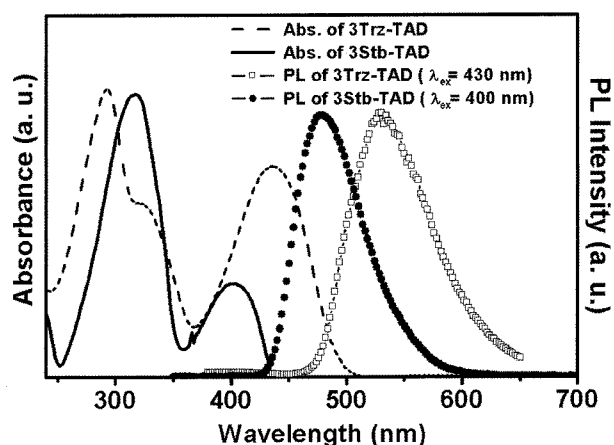


Figure 1. Absorption and PL spectra of 3Stb-TAD and 3Trz-TAD.

conjugation of stilbene branch and triphenylamine moieties. The absorption spectrum of 3Trz-TAD showed absorption maxima at 292 nm due to the peripheral triazine moiety, 430 nm due to the conjugated moiety of stilbene branch and triphenylamine units, and a shoulder at around 326 nm (Figure 1).³⁸ The photoluminescence (PL) spectra of the dendrimers in methylene chloride (10^{-5} M) are also shown in Figure 1. The PL spectra of 3Stb-TAD ($\lambda_{ex}=400$ nm) and 3Trz-TAD ($\lambda_{ex}=430$ nm) showed the emission at 478 and 530 nm, respectively.

I-V-R Characteristics of the Devices (ITO/Dendrimers/LiF/Al). The current-voltage-resistance (*I-V-R*) characteristics of the samples were investigated by using a two-terminal single layer device (ITO/dendrimer/LiF/Al) fabricated through the following procedure. On the top of a clean 80 nm-thick ITO-coated glass, a 1,2-dichloroethane solution of the dendrimer (1 wt%) was spin-coated at a speed of 1,800 rpm. The film thickness was 50 nm. A 2 nm-thick LiF layer was vacuum-deposited onto the organic layer as a blocking layer, and then Al was deposited with a thickness of 80 nm as a top electrode. The LiF layer blocks the diffusion of Al atoms into the organic layer during thermal vapor deposition of Al electrode.⁴² The device had an area of 0.09 mm². The *I-V-R* characteristics of the device for 3Stb-TAD and 3Trz-TAD are shown in Figure 2. The voltage scans for all the devices started from number 1 to 6. Only when a negative bias was applied, the device could be switched

from the OFF to the ON state. When a positive bias was first applied to the device, the transition did not occur. The *I-V-R* data of 3Stb-TAD in Figure 2(a) show that, during the first scan from 0 to -3.6 V, the high resistance and low current state (OFF state) was maintained. At around -3.6 V (set-on voltage), the current of the device suddenly increased to -2.8×10^{-5} A with abrupt decrease of the resistance. This result indicates that a transition occurred from the low conductivity (OFF state) to high conductivity state (ON state), which corresponds to “writing” process in a memory device. The resistance of the device in the OFF state was more than four orders of magnitude higher than that in the ON state. During the scan from 3 to 4, the state of the device was maintained in the ON state. At around +2.9 V (set-off voltage), the device of the ON state returned to the OFF state, which corresponds to an “erasing” process in a memory device.

The *I-V-R* characteristics of 3Trz-TAD in which the triazine and triarylamine moieties are covalently linked are shown in Figure 2(b). Upon applying a negative bias, the resistance of the device started to decrease. At around -3.0 V, an abrupt increase of current and decrease of resistance occurred, which indicates that a transition was induced from the OFF to the ON state. The device returned to the OFF state at around +2.3 V. The retention time of the device for 3Stb-TAD and 3Trz-TAD exhibited around 100 min and 2 min, respectively (Figure 3). We are currently optimizing the dendritic architecture to increase the retention time.

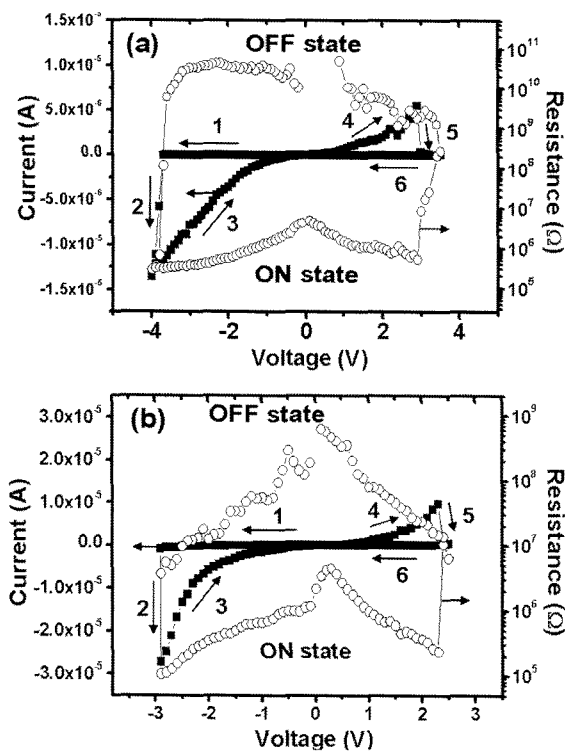


Figure 2. *I-V-R* characteristics of the device with ITO/dendrimer/LiF/Al structure (a) 3Stb-TAD, (b) 3Trz-TAD.

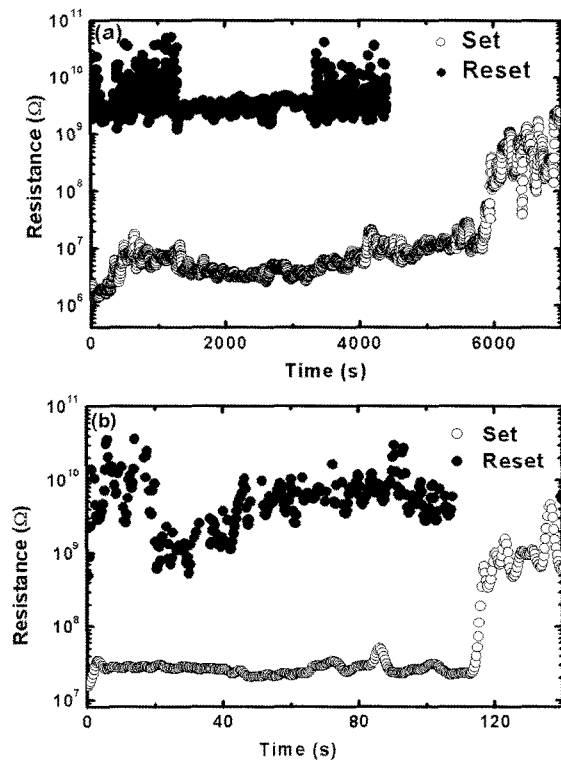


Figure 3. Retention time of the device (a) 3Stb-TAD, (b) 3Trz-TAD.

Conclusions

In summary, we have synthesized π -conjugated dendrimers in which donors and acceptors are covalently linked and demonstrated that they exhibited a clear electrical bistability. It is suggested that the electrical bistability would be due to charge transfer between donor and acceptor. The resistance of the device in the OFF state was more than four orders of magnitude higher than that in the ON state. These results provide potential of dendrimers for organic memory device application. The short retention time in organic materials is one of the subjects that should be improved for practical application. We are currently tuning the dendrimer structure to clarify the relationship between the structure and the memory characteristics.

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