Synthesis of a New Cross-Linkable Perfluorocyclobutane-Based Hole-Transport Material

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ABSTRACT
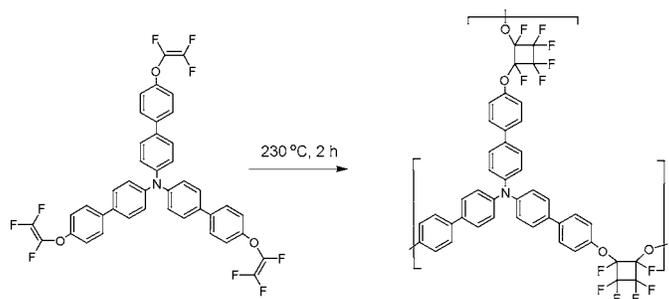
A new curable arylamine containing a perfluorocyclobutane (PFCB) structure without an acidic group was synthesized. The material was thermally cured on ITO after spin-coating. The polymer showed excellent solvent resistance, high thermal stability, high transparency, and good surface smoothness.

Polymer light-emitting diodes (PLEDs) have been extensively investigated for possible use in flat panel displays.[1] However, the successful development of PLEDs requires improvements in factors such as lifetime, efficiency, and stability. To improve the efficiency of PLEDs, the balance of charge injection and transport from each electrode is an important factor. For balanced charge injection, multilayer architectures, for example, the introduction of both hole- and electron-transporting layers, are required.[2] In the case of PLEDs, multilayer structures can be fabricated using a solution process such as spin-coating. A number of hole injection/transporting polymers have been reported. Among these, the development of poly(styrenesulfonate)-doped poly-(3,4-ethylenedioxythiophene) (PEDOT-PSS) has indeed led to a dramatic improvement in lifetime as well as luminous efficiency.[3] Although the PEDOT-PSS shows excellent

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performance, it has some disadvantages, one of which is the formation of an unstable interface between the ITO and PEDOT-PSS.[4] Moreover, the high conductivity of the PEDOT-PSS is undesirable, when used in pixilated displays.[5] Recently, new hole transporting materials (HTM) for replacing the PEDOT-PSS have been reported, because the long-term stability of such devices remain an issue for commercialization.[5−7]

Scheme 1
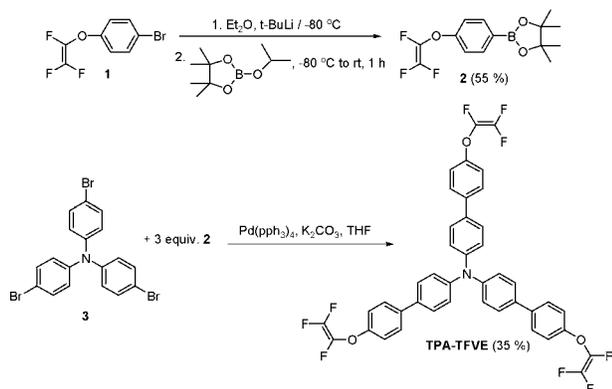
An organic solvent resistant cross-linkable hole transporting layer (HTL) would be an alternative to water soluble PEDOT-PSS.[6] Especially, perfluorocyclobutane (PFCB) based hole transporting polymers have many advantages and the properties of these polymers are suitable for applications to PLEDs.[5,7] PFCB polymers are synthesized by the radical mediated thermal cyclopolymerization of trifluorovinyl ethers (TFVE). These polymers are known to lead to increased processability, durability, chemical resistance, thermal stability, and optical properties.[8] Thus, PFCB polymers would be suitable for use in various applications such as polymer photonic devices,[9] low dielectric coatings,[10] and light-emitting diodes.[5,7]

In this paper, we report on the preparation of a new curable HTM-containing PFCB. When heated, this monomer undergoes cyclopolymerization, producing PFCB polymers. The optical, electrochemical, and surface properties of this PFCB-based HTM were investigated.

The synthetic scheme for the preparation of the TFVE-type monomer for a new HTM is shown in Scheme 1. Compound **1** was prepared as described previously[8b,9a] and is commercially available from Oak-wood Chemicals, Inc. Compound **2** was synthesized from **1** as follows. *tert*-Butyllithium was added dropwise to a solution of **1** in diethyl ether at −78 °C. The reaction mixture was stirred at −78 °C for 1 h, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was then added. Compound **2** was obtained as a colorless liquid in 55% yield. Compound **3** was prepared according to the published procedure.[11] **TPA-TFVE** was synthesized from **2** and **3** using the palladium-catalyzed Suzuki coupling method.[12] **TPA-TFVE** was obtained as a white powder in 35% yield. The **TPA-TFVE** was soluble in common organic solvents such as chlorobenzene, THF, and toluene. Due to the trifunctional TFVE of **TPA-TFVE**, it can be thermally cured.[8b]

Thermal properties were investigated by means of TGA and DSC. As shown in Figure 1, the endothermic peak of **TPA-TFVE** corresponds to its melting point. The broad exothermic peak in the DSC curve corresponds to its thermal polymerization.[8b] Exothermic peaks were found at about T_{onset} = 160 °C and T_{max} = 230 °C. The decomposition temperature (T_d) of the TPA-PFCB polymer was found to be 487 °C. Thus, the PFCB polymer has good thermal stability. After curing, a glass transition temperature was not detected before T_d, implying the existence of a high degree of cross-linking between the TFVE groups.

The **TPA-TFVE** was spin-coated onto a ITO substrate and then cured at 230 °C for 2 h under nitrogen. The resulting polymer showed high durability in common organic solvents such as chlorobenzene and toluene. We investigated the

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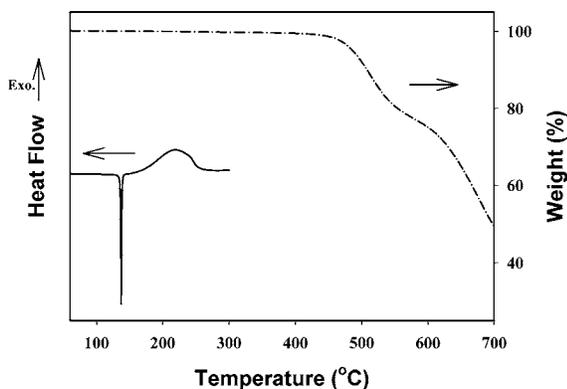
Figure 1. TGA (dash dot line) and DSC (solid line) curves of TPA-TFVE.

resistance of this new HTM to chlorobenzene via UV/vis spectroscopy as shown in Figure 2, and the data show that the cross-linked TPA-PFCB polymer is completely resistant to chlorobenzene and 2 h of heating is required to ensure complete curing (Figure 2, a vs b). Therefore, the polymer could be used to produce a multilayer structure using a solution process. The absorption spectra also verify that the
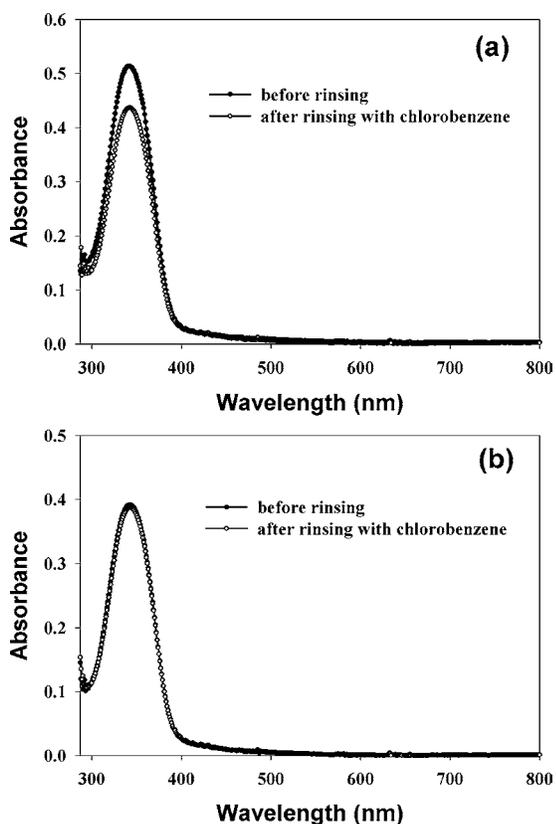
Figure 2. Absorption spectra of spin-coated TPA-TFVE films after curing for (a) 1 h and (b) 2 h before and after rinsing with chlorobenzene.

polymer is transparent over the entire visible region (Figure S2, Supporting Information). As a result, the output of light from the emitting layer could be increased. The onset of absorption of the TPA-PFCB polymer was 395 nm which corresponds to 3.14 eV of the optical band-gap.

To assess the charge injecting properties and electrochemical stability of the polymer, cyclic voltammetry (CV) measurements of the polymer films coated on an ITO substrate were carried out (Figure S1, Supporting Information). The highest occupied molecular orbital (HOMO) energy was calibrated from the half-wave potential of ferrocene/ferrocenium (Fc) redox coupling which is 4.8 eV below vacuum.[13] The HOMO level appeared at 5.06 eV, and the LUMO level was estimated from the optical band-gap. The LUMO energy level of the polymer was determined to be 1.92 eV. In addition, the results of CV measurements of the polymer thin films on ITO substrates showed very good reversibility, indicating that the TPA-PFCB polymer has good electrochemical stability.

The surfaces of the TPA-PFCB film were investigated by atomic force microscopy (AFM). Surface morphology of polymer film is critical to the device performance.[6b] Figure 3 shows AFM images of the surface of PEDOT-PSS and TPA-PFCB film on the ITO. As can be seen, the surface of the TPA-PFCB film was much smoother than that of the PEDOT-PSS film. The root-mean-square (rms) roughness of the TPA-PFCB was 0.47 nm. In contrast, the rms roughness of PEDOT-PSS was 1.15 nm.
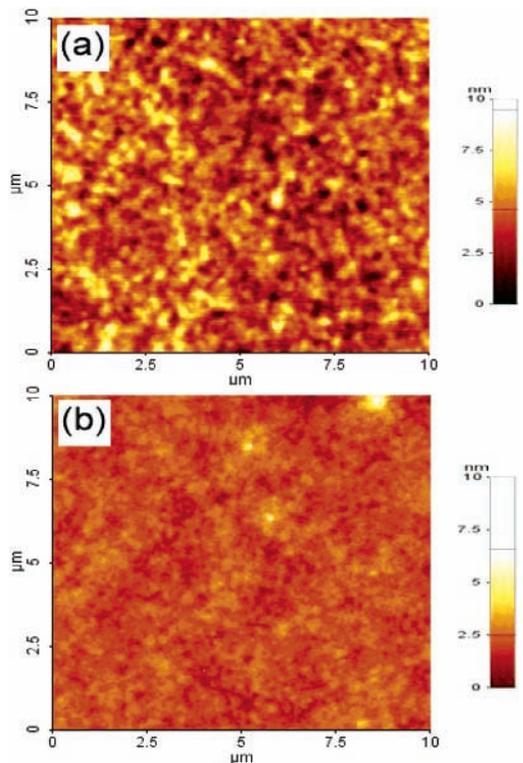
Figure 3. Atomic force microscopy images of (a) PEDOT-PSS and (b) TPA-PFCB thin films on ITO.
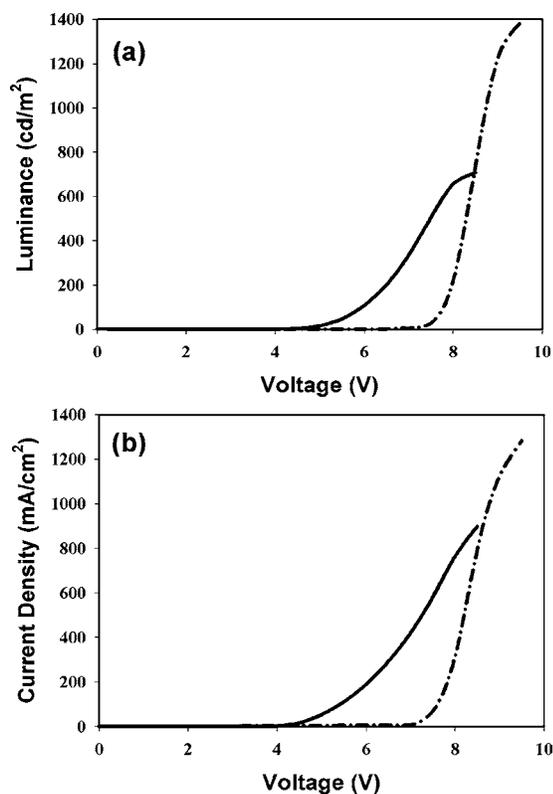
Figure 4. (a) Current density−voltage and (b) luminance−voltage diagrams of PLED of the structure ITO/HTL/PFO/Ba/Al. PEDOT-PSS (solid line) and TPA-PFCB (dash dot line) were used as a HTL.

To estimate the device performance of TPA-PFCB as a HTL, a PLED was fabricated with the device configuration ITO/TPA-PFCB (30 nm)/PFO (70 nm)/Ba (15 nm)/Al (130 nm). The performance of this device was then compared with a PEDOT-PSS based device. **TPA-TFVE** was spin-coated from a 1 wt % solution in chlorobenzene on an ITO substrate cleaned by a conventional process and cured at 230 °C for 2 h under nitrogen. Devices based on the PEDOT-PSS and TPA-PFCB showed the same EL spectra. This indicates that the emission properties were not affected when TPA-PFCB was used as a HTL. The current density−voltage−luminance (I−V−L) characteristics of the PEDOT-PSS based device and the PFCB based device are shown in Figure 4. The turn

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on voltage of the PEDOT-PSS and the TPA-PFCB were 5 and 7 V, respectively. The TPA-PFCB device as a HTL showed a higher turn on voltage than a PEDOT-PSS based device. The reason for this is probably due to the larger difference in energy barrier between the HOMO level of the emitting polymer and that of the TPA-PFCB than the corresponding PEDOT-PSS HOMO level (Figure S3, Supporting Information). However, the maximum luminance (L_{max}) and luminance efficiency (LE_{max}) were improved, when TPA-PFCB was used. The L_{max} and LE_{max} of the TPA-PFCB based device were 1500 cd/m^2 and 0.132 cd/A, respectively, compared with L_{max} = 710 cd/m^2 and LE_{max} = 0.091 cd/A for the PEDOT-PSS based device. This could be due to the greater electron blocking properties of the TPA-PFCB polymer than the PEDOT-PSS.[6b]

In summary, a newly designed PFCB-based HTM containing an arylamine was successfully synthesized. The resulting PFCB-based hole transporting polymer exhibits good thermal properties, solvent resistance, high transparency, and has good surface smoothness. The TPA-PFCB device as a HTL showed a higher turn on voltage than the PEDOT-PSS based device, but L_{max} and LE_{max} were improved when the TPA-PFCB polymer was employed. Although the performance of the TPA-PFCB based device was not as good as that of the device fabricated using PEDOT-PSS, the interface between ITO and TPA-PFCB is likely to be more stable than PEDOT-PSS due to the no acidity of TPA-PFCB. In addition, **TPA-TFVE** should be amenable for use as a cross-linking agent with various difunctional TFVE materials. Further improvements in PFCB polymers and device performance are under investigation, and other applications of **TPA-TFVE** as a cross-linking agent with various difunctional TFVE materials are currently underway.

Supporting Information Available: Synthetic procedures and characterization data for the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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