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Electrochemical Deposition of End-Capped Triarylamine and Carbazole Dendrimers: Alternate Technique for the Manufacture of Multilayer Films

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Spin-coating is a convenient, simple, and inexpensive method for manufacturing OLED (organic light-emitting device) structures.[1] In the preparation of multilayer devices, however, spin-coating has the disadvantage that it is a wet procedure that may partially dissolve preexisting layers. One approach used to protect existing layers against interfacial erosion by the organic solvents used in the spin-casting of subsequent layers is to subject the existing layer to a posttreatment procedure such as a cross-linking process[2] based on photopolymerization[3] driven by irradiation of UV light or thermal annealing.[4]

Dendritic molecules have been proposed as alternative materials for convenient solution processing. The spherelike rigid structures of these molecules enable the easy fabrication of homogeneous films by casting.[5] In addition, dendrimeric precursors exhibit properties that are desirable for OLED applications, such as amorphous structure, high moldability, and high thermal stability.[6] Recently, we found that carbosilane dendrimers adorned with either triarylamine or carbazole units in their periphery exhibit novel electrochemical behavior in which the electrochemical deposition is controlled by dendrite generation. In addition, the deposited layers remained intact in the depositing solvent, methylene chloride, allowing a second layer to be deposited on top of the first layer. In the present study, we sought to establish the

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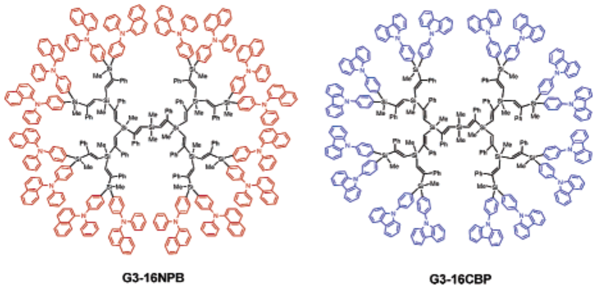
Chart 1



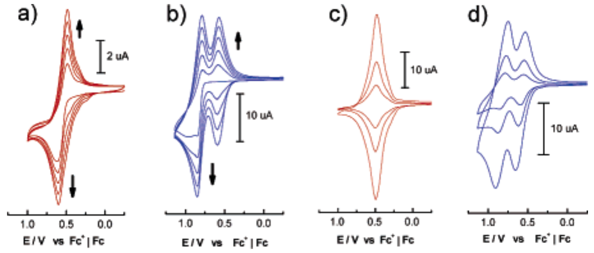


Figure 1. CVs on a Pt electrode in a CH_2Cl_2 solution of (a) **G3-16NPB** and (b) **G3-16CBP** containing 0.1 M Bu_4NBF_4 with $\upsilon = 0.1$ V s^{-1} during the first 5 cycles, and CVs of a Pt electrode modified with (c) **G3-16NPB** ($\Gamma_{NPB} = 2.8 \times 10^{-8}$ mol cm^{-2}) and (d) **G3-16CBP** in CH_2Cl_2/Bu_4NBF_4 with $\upsilon = 0.025$, 0.05, and 0.1 V s^{-1} (from inside to outside), respectively.

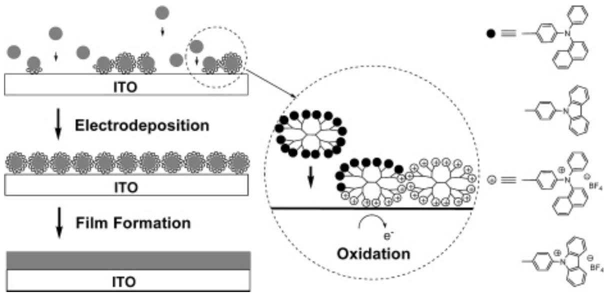


Figure 2. Electrodeposition mechanism of NPB and CBP dendrimers.

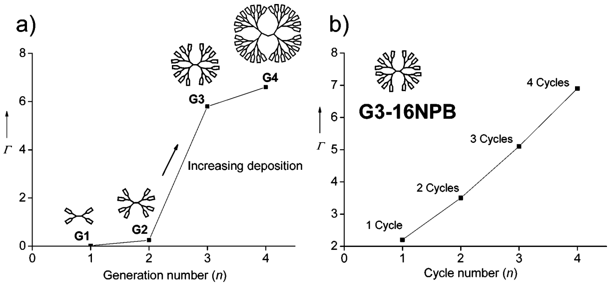


Figure 3. (a) Surface coverage ($\Gamma = 1 \times 10^{-9}$ mol cm^{-2}) of ITO modified with a film deposited in CH_2Cl_2 solution containing 0.5 mmol **G*n*-2^{n+1}NPB**/0.1 M Bu_4NBF_4 with $\upsilon = 0.1$ V s^{-1} for 5 cycles and (b) the linear relationship between the deposited surface coverage and the CV cycle number.

suitability of this electrochemical deposition technique for use in the construction of multilayer OLEDs, which cannot be fabricated via conventional spin-coating with a polymeric precursor. Thus, the electrochemical deposition-based process could potentially offer an ideal combination of deposition control on the one hand and multilayer fabrication on the other. We report herein the novel electrochemical deposition behavior of triarylamine or carbazole end-capped carbosilane dendrimers of the type **G*n*-2^{n+1}NPB** or **G*n*-2^{n+1}CBP** and their use for the formation of multilayer structures of the type used in OLEDs.

End-capped triarylamine or carbazole dendrimers of the type **G*n*-2^{n+1}NPB** or **G*n*-2^{n+1}CBP** were prepared through divergent synthesis on the basis of the reaction of diethenyl propagating carbosilane dendrimers with suitable functional groups such as the naphthylphenylaminophenyl (NPB) or carbazolylphenyl (CBP) unit (see Figures S1 and S2 of the Supporting Information).The electrochemical deposition behavior of end-capped triarylamine/carbazole dendrimers has not been previously reported, although arylamine[7] and carbazole[8] units are known to undergo electrochemical polymerization upon oxidation. In the case of end-capped NPB dendrimers, effective deposition is observed from the third generation **G3-16NPB**, whereas for the end-capped CBP dendrimers, deposition started even in the first generation, **G1-4CBP**. To maximize the film growth, we optimized the deposition process for each NPB or CBP end-capped dendrimer by using the third generation of the dendrimer, as shown in Figure 1.

For example, the electrochemical deposition of **G3-16NPB** was clearly shown by increases in both the anodic and cathodic peak currents during continuous cyclic voltammetric (CV) scans (Figure 1a). Well-defined reversible surface redox waves ($E_{1/2} = 0.49$ V vs Fc$^+$Fc, $\Gamma = 2.8 \times 10^{-8}$ mol cm^{-2}) were obtained in fresh CH_2Cl_2/0.1 M Bu_4NBF_4 solution after successive potential sweep cycles (Figure 1c). It bears two diagnostics of surface-immobilized CV, specifically, 11 mV of the potential peak difference and a linear relationship of peak currents depending on the potential scan rate (υ). Likewise, similar CVs of electrodeposition were also clear for **G3-16CBP** by continuous potential scans (Figure 1b). The growth of surface-immobilized CBP dendrimers was also confirmed by the presence of two diagnostic redox peaks (Figure 1d).

For the third-generation dendrimers, a thick film was deposited on the electrode surface because higher-generation dendrimers contain highly charged species and hence have an increased tendency toward good film formation.[9] In particular, in the case of the peripheral NPB dendrimers, such an increase in deposition is apparent as the dendrimer generation increases (see Figure 3a). An additional advantage of electrochemical deposition is that the film thickness can be controlled by varying the number of redox cycles in the CV. A linear relationship between the thickness of the

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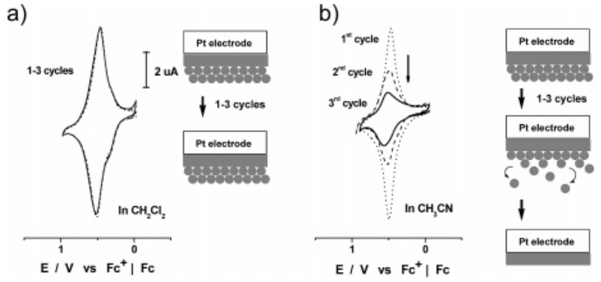

Figure 4. CVs and scheme of the **G3-16NPB** film-modified Pt electrode in)a) CH_2Cl_2 and)b) CH_3CN solution containing 0.1 M Bu_4NBF_4 after holding the electrode potential at 1.0 V for 100 s.

deposited film and the number of CV cycles is observed for the NPB dendrimers (see Figure 3b).

With the aid of this novel electrochemical deposition method, NPB and CBP dendrimer films were grown onto an indium tin oxide (ITO) surface, as shown in Figure 2. The thickness of the deposited films was measured using a profilometer. The surface coverage of the deposited film was also determined by coulometric assay from the areas encompassed by CV's at low scan rates.[10] By comparison, $\Gamma = 1.9 \times 10^{-9}$ mol cm^{-2} reveals the thickness of 1.0 nm assuming the number of electron (n) is one for each triarylamine or carbazole unit. This indicates that the proposed technique may be a viable alternative method for constructing layers.

To obtain additional information on the sequence of film formation as well as the corresponding film stability, we attempted electrochemical exfoliation, as shown in Figure 4. The electrochemically deposited films were not removed in methylene chloride, whereas exfoliation was apparent in acetonitrile. These observations not only support the mechanism of film formation shown in Figure 2 but also establish that our deposition process is different from electrochemical polymerization.

To demonstrate the successive formation of multiple layers, we electrochemically deposited a second layer. The film of end-capped NPB dendrimers formed after electrodeposition of **G3-16NPB** was insoluble in methylene chloride. Therefore, to test the feasibility of successive deposition, we conducted a second electrochemical deposition with **G3-16CBP** onto the preformed NPB dendrimer film. The results of this electrochemical deposition are presented in Figure 5a and Figure S7 of the Supporting Information. In the depositions of the NPB and CBP dendrimer films, the potential scan ranges were varied to obtain films with similar thicknesses. A representative cross-sectional scanning electron microscope (SEM) image of the double-layer structure is shown in Figure 5b. These experimental data clearly establish that, using suitable dendrimer precursors, multilayer structures can be fabricated by applying successive electrochemical processes.

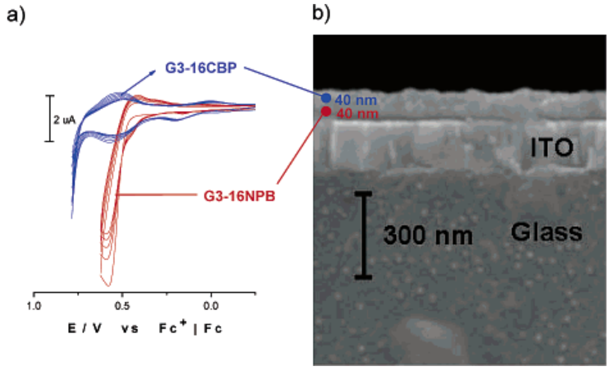

Figure 5. (a) CVs for the successive electrodeposition of NPB and CBP dendrimers and (b) a typical cross-sectional SEM image of the NPB/CBP dendrimer double-layer film.

In summary, we have demonstrated that (1) rigid ethenyl-linked carbosilane dendrimers adorned with NPB or CBP units were well-suited to electrochemical deposition. (2) Once electrochemically deposited, the dendrimer films remained intact in the depositing solvent. (3) The film thickness could be adjusted by varying the number of CV cycles. (4) Most importantly, multilayer films could be fabricated without causing any damage to the previous layer. The fabrication of OLEDs using this electrochemical deposition process as well as the optimization of such device structures is currently being investigated.

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Supporting Information Available: Experimental procedures and characterization data including NMR, SEC, and MALDI TOF data for the first to fourth generation dendrimers **G*n*-2^{n+1}NPB** and **G*n*-2^{n+1}CBP**; CVs for for a successively electrodeposited NPB and CBP dendrimer film. This material is available free of charge via the Internet at http://pubs.acs.org.

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