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Electrochemical-Coupling Layer-by-Layer (ECC−LbL) Assembly

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Supporting Information

ABSTRACT: Electrochemical-coupling layer-by-layer (ECC−LbL) assembly is introduced as a novel fabrication methodology for preparing layered thin films. This method allows us to covalently immobilize functional units (e.g., porphyrin, fullerene, and fluorene) into thin films having desired thicknesses and designable sequences for both homo- and heteroassemblies while ensuring efficient layer-to-layer electronic interactions. Films were prepared using a conventional electrochemical setup by a simple and inexpensive process from which various layering sequences can be obtained, and the photovoltaic functions of a prototype p/n heterojunction device were demonstrated.

One of the most successful strategies for preparing functional nanosystems using organic components is construction of controlled layer formations on solid substrates, as seen in various pioneering examples from photoelectronic devices[1] to biorelated applications.[2] Of the many thin-film preparation methods, layer-by-layer (LbL) assembly[3] could be the most versatile technique, as it permits us to assemble a variety of substances into nanometric films in a controlled manner using simple, inexpensive procedures. While LbL assembly is mostly conducted using noncovalent electrostatic interactions between layering components, several pioneering methodologies have employed covalent bonding to provide robust films.[4] As a novel approach, we here introduce the concept of molecular coupling into LbL technology. Coupling reactions,[5] including those due to Heck and Suzuki, have been used to connect appropriate molecules through extremely stable carbon−carbon bonds. Recently, Rydzek et al. reported pioneering research on electrochemically triggered click coupling for LbL assembly[6a] and one-pot film preparation.[6b]

Herein we report the addition of another strategy for electrochemical-coupling layer-by-layer (ECC−LbL) assembly based on a direct coupling reaction. As shown in Figure 1, we selected *N*-alkylcarbazole dimerization[7] as a coupling reaction that can be induced through electrochemical stimuli from an electrode surface beneath the films without the use of additional reactants. Because *N*-alkylcarbazoles and their dimers have large hole-transport mobilities,[8] electrochemical signals can be transmited to the top layer in their films. This clean, reagentless process is especially useful for constructing covalently linked layer-controlled thin films on a sensitive device surface. In addition, unlike other electropolymerizable precursors such as aniline and thiophene, the resulting di-*N*-alkylcarbazole is transparent in the visible light region[9] and thus does not impair the optical or electrical properties of the active moieties in the film. We synthesized several carbazole derivatives carrying distinctive donor (**PZ4C** and **F4C**) and acceptor (**C_{60}1C** and **C_{60}2C**) moieties.[10] Controlled layering of these monomers in both homo- and hetero-ECC−LbL assemblies was demonstrated, and clear indications of interlayer interactions were obtained. The assembled films had fine flat structures, and preliminary measurements demonstrated their functionality as photocurrent conversion devices.

Electrochemical coupling of *N*-alkylcarbazoles was performed using cyclic voltammetry (CV) apparatus in order to precisely control the layer thickness, as continuous application of a constant potential made control of the film thickness problematic. Homotype ECC−LbL assemblies that were prepared from the porphyrin monomer **PZ4C** through potential sweeps between −0.6 and 1.0 V vs Ag/Ag$^+$ at 200 mV/s on indium tin oxide (ITO) in a 0.5 mM CH_2Cl_2 solution resulted in regular film growth, as demonstrated by UV−vis spectroscopy (Figure 2A; the layer dependence is shown in Figure 2B) and CV (Figure 2C). The latter behaviors included successive increases of the reversible oxidation waves due to porphyrin at 0.53 V ($E_{1/2}$) and 0.79 V ($E_{1/2}$),[11] overlapped with the dicarbazole oxidation wave,[7,12] as well as an irreversible wave for carbazole coupling (>0.8 V).[7,12] The other units, fullerene **C_{60}2C** (0.7 mM) and fluorene **F4C** (0.5 mM), also exhibited regular film growth [Figure 2D(a) and Figure 2E, respectively]. In these three cases, linear increases in reduction currents with coupling cycle (Figure 2F) and homogeneous surface textures in atomic force microscopy (AFM) images[10] were confirmed, as well as UV−vis spectra with peak shifts and broadening, possibly due to chromophore aggregation.[10] However, films of mono-*N*-alkylcarbazole-substituted fullerene derivative **C_{60}1C** (2.0 mM) did not grow under the same conditions [Figure 2D(b)], suggesting the crucial role of multiple substitution with *N*-alkylcarbazole groups in enabling interlayer coupling for successful ECC−LbL homoassembly.

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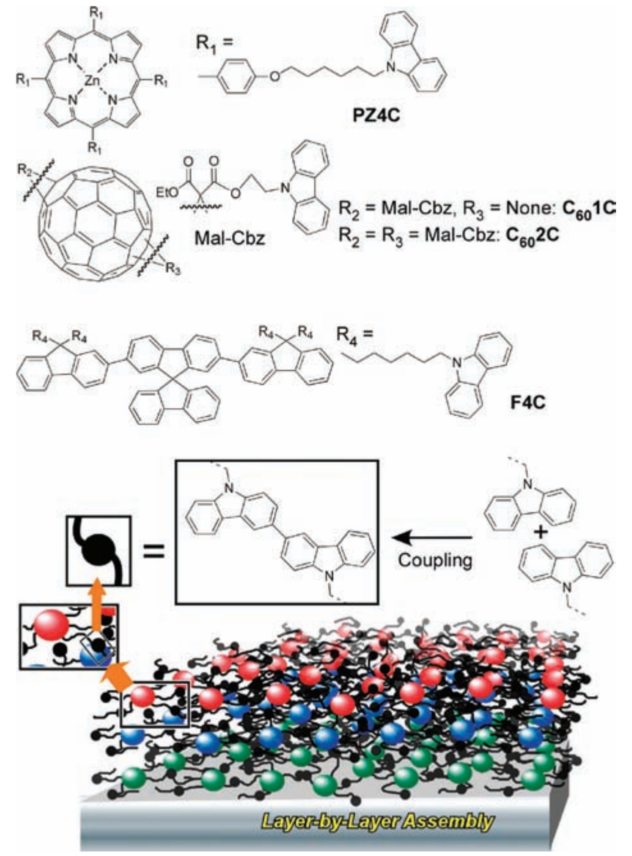

Figure 1. Molecules used for electrochemical-coupling layer-by-layer (ECC−LbL) assembly through cross-linking of peripheral *N*-alkylcarbazole units.

For the first example of ECC−LbL heteroassembly, alternate layers of **PZ4C** and **C_{60}2C** were prepared by CV sweeps between −0.6 and 1.0 V at 200 mV/s (two cycles for each of the **PZ4C** and **C_{60}2C** layers) with an intervening CH_2Cl_2 washing. While constant film growth (except for the initial few layers) was confirmed by measuring the UV−vis absorbance at 500 nm, the absorbance at 437 nm for the porphyrin Soret band exhibited a switching behavior (Figure 3A,B). Similar switching behavior in **PZ4C/C_{60}2C** assemblies was observed in CV measurements (Figure 3C) where the peak currents for porphyrin oxidation were switched upon **C_{60}2C** assembly. These features reveal that **PZ4C** and **C_{60}2C** interact electronically (as donor and acceptor, respectively) between the layers.[13] The smooth surface morphology of this heteroassembly was confirmed by AFM observation.[10] Another porphyrin−fullerene assembly composed of **PZ4C/C_{60}1C** did not exhibit the large peak reduction in the Soret band intensity due to electronic interactions (Figure 3D).[10] This was probably due to inefficient incorporation of the monosubstituted **C_{60}1C** as a result of the lack of interlayer coupling.

Other ECC−LbL heteroassemblies, **F4C/C_{60}2C** (Figure 3E) and **F4C/PZ4C** (Figure 3F), similarly exhibited both constant film growth and interlayer interactions. Figure 3G,H shows the results for three-component assembled **F4C/PZ4C/C_{60}2C** ECC−LbL films. Constant film growth was indicated by regular increases in absorbance at 355 and 500 nm. Interlayer interactions were clearly detected through the periodic changes in the porphyrin Soret band intensity at 437 nm. As seen in changes of absorption at 437 nm (Figure 3G), assemblies of **PZ4C**, **C_{60}2C**, and **F4C** in regular sequence induced the appearance of porphyrin (red plots), electronic interactions with the fullerene (blue plots), and intact adsorption of fluorene (green plots), respectively, that were regularly repeated. These results confirm the general applicability of the ECC−LbL technique for construction of various components into regular layered structures where the required assembly sequence can be guaranteed. In all of the heteroassemblies, spectral shifts due to interlayer interactions were observed. This characteristic is indispensable in the design of organic device applications that require significant interactions between functional units embedded in different layers.

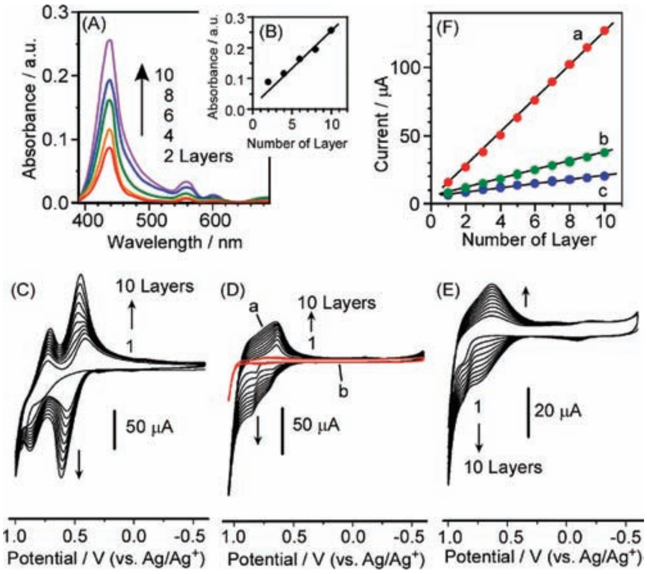

Figure 2. (A) UV−vis spectra and (B) absorbance at 438 nm for **PZ4C** ECC−LbL films. (C−E) Cyclic voltammograms of (C) **PZ4C**; (D) (a) **C_{60}2C** and (b) **C_{60}1C**; and (E) **F4C** ECC−LbL films. (F) Layer number dependence of the reduction current of dicarbazole (at 0.45−0.6 V) for ECC−LbL films: (a) **PZ4C**; (b) **F4C**; (c) **C_{60}2C**.

One attractive potential application of heterolayered films lies in thin-film photoelectronic devices, whose utility has been demonstrated previously.[14] A prototype p/n heterojunction device with the structure ITO/**PZ4C** (donor)/**C_{60}2C** (acceptor)/Al was fabricated using the ECC−LbL assembly method, and its photovoltaic properties were investigated. Its cross-sectional morphology was observed by scanning electron microscopy (Figure 4A), which revealed that the interfaces between each pair of layers were incredibly flat. The photovoltaic switching response of this film (Figure 4B), which was studied using pulsed single-wavelength (500 nm) irradiation at 10 s intervals, demonstrated repetitive and stable device performance of the p/n heterojunction composed of the **PZ4C/C_{60}2C** ECC−LbL assembly. Although decay of photocurrent occurred during each period of irradiation, possibly because of trapping of photogenerated carriers in defects caused by residual traces of the supporting electrolyte, regular photocurrent switching was realized, with instantaneous increases and decreases in the photocurrent during periods of irradiation and darkness, respectively. Next, the photovoltaic effect of this device, as characterized by its current density−voltage performance upon irradiation with white light (AM1.5), was investigated (Figure 4C). The anodic photocurrent increased monotonically with increasing positive bias at the ITO electrode from −0.5 to 2.0 V, whereas the dark current remained almost constantly zero, indicating photoconductive behavior. The open-circuit voltage under

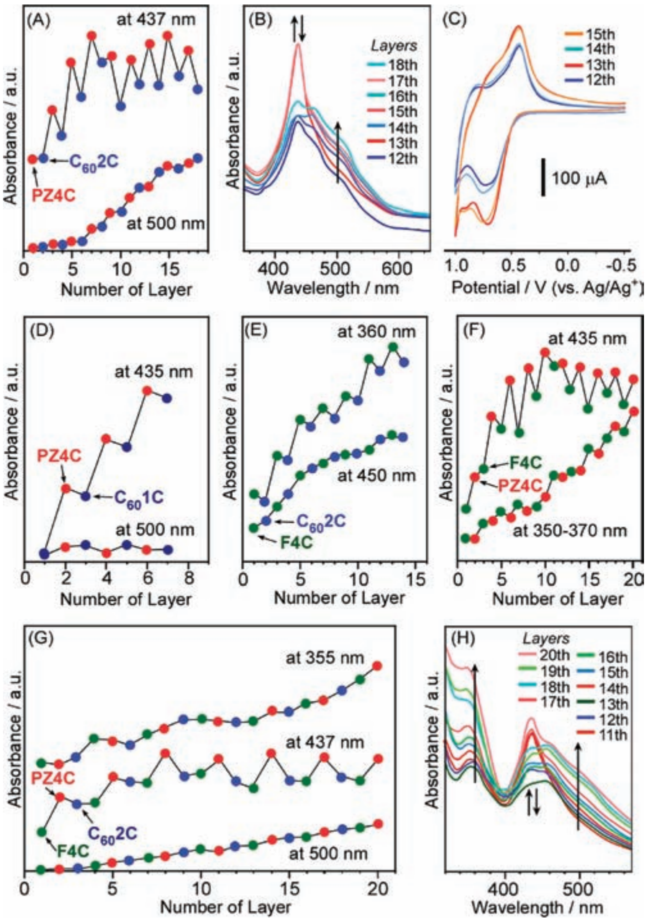

Figure 3. (A) Absorbance values, (B) UV−vis spectra, and (C) cyclic voltammograms of **PZ4C/C_{60}2C** ECC−LbL films with different numbers of layers. (D−F) Absorbance values as a function of the number of layers for (D) **PZ4C/C_{60}1C**, (E) **F4C/C_{60}2C**, and (F) **F4C/PZ4C** ECC−LbL films. (G) Absorbance values and (H) UV−vis spectra of **F4C/PZ4C/C_{60}2C** ECC−LbL films with different numbers of layers.

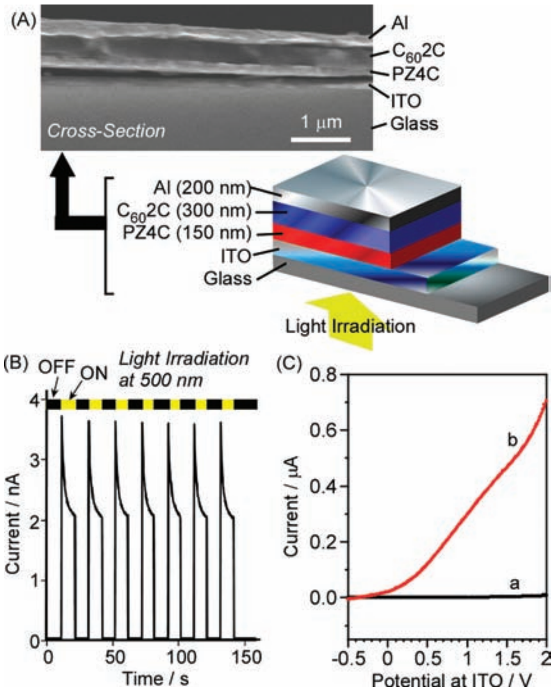

Figure 4. (A) Illustration and SEM image of the p/n heterojunction device consisting of a **C_{60}2C/PZ4C** ECC−LbL film. (B) Photocurrent switching of the p/n heterojunction device (2 mm × 2 mm) between irradiation and darkness from steady-state measurement at 10 s intervals with excitation at 500 nm. (C) Current density−voltage profiles of the p/n heterojunction device (2 mm × 2 mm) (a) in the dark and (b) under irradiation with AM1.5 white light.

irradiation with AM1.5 white light was measured to be 0.4 V. Thus, the fundamental properties of a photovoltaic device were demonstrated, although the conversion efficiency in this prototype device was still low (∼10^{-5}). Appropriate variation of the film structure and composition for broad optical absorption and low contact resistance and trapping density would improve the device performance.

Conventional methods of thin-film preparation, such as vacuum deposition and spin-coating, are limited in terms of which components can be applied, depending on their molecular weights and solubilities, respectively.[15] These factors are not necessarily obstacles to the ECC−LbL method. In this case, use of electrochemical *N*-alkylcarbazole coupling enabled us to fix cross-linked thin films at a substrate surface from solutions of the components. Functional moieties such as porphyrin and fullerene interacted within the film, indicating that the coupling reaction does not have a detrimental effect on the incorporated units. In addition, ECC−LbL processing may lead to improvements in processing time. Although the preparation of this p/n heterojunction device with a thickness of 500 nm took ∼30 min, the process time could easily be optimized to a few minutes by varying the electrochemical conditions, including the monomer concentrations, oxidation potential, and so on.

In conclusion, we have introduced electrochemical-coupling layer-by-layer (ECC−LbL) assembly as a methodology for the preparation of layered thin films. This method allowed us to use a simple and inexpensive process in a conventional electrochemical setup to immobilize functional units covalently into thin films having requisite thickness (number of layers) and sequence for both homo- and heteroassemblies while ensuring efficient layer-to-layer electronic communication. Because the reaction site for coupling is independent of the functional unit, this method is applicable in the presence of many kinds of organic functional groups. Therefore, the ECC−LbL approach should be a powerful method for constructing robust and well-designed organic layered structures with potential uses in various types of organic devices.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details, compound syntheses and characterization, and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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