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Self-Assembled Monolayers Made of 6-(5-((6-((5-hexylthiophen-2yl)ethynyl)-9,10-bis(phenylethynyl)anthracen-2-yl)ethynyl)thiophen-2-yl)hexyl 3-(Triethoxysilyl)Propylcarbamate for Ultrathin Film Transistors

Dong Uk Heo,[†] Joo Bin Lee,[†] Yoon Deok Han,[‡] Jinsoo Joo,[‡] Hosuk Lee,[§] Hosun Lee,[§] and Dong Hoon Choi*^{,†}

[†]Department of Chemistry, Research Institute for Natural Sciences, and [‡]Department of Physics, Korea University, Seoul 136-701, South Korea

[§]Department of Applied Physics, Kyung Hee University, Yongin 446-701, South Korea

ABSTRACT: A new functionalized triethoxysilane bearing an X-shaped, anthracene-based semiconducting molecule on one arm was designed and synthesized as a precursor for the preparation of a self-assembled monolayer (SAM) on a SiO₂ substrate. 3-Isocyanatopropyl triethoxysilane was reacted with a monohydroxyl-terminated X-shaped, anthracene-based semiconducting molecule in the presence of tin catalyst. The 6-(5-((6-((5-hexylthiophen-2-yl)ethynyl)-9,10-bis(phenylethynyl)anthracen-2-yl)ethynyl)thiophen-2-yl)hexyl 3-(triethoxysilyl)propylcarbamate (BATHT-TEOS) was found to be stable and



sufficiently reactive to form organic monolayers on hydroxylated SiO₂ surfaces. The structures and properties of these SAMs were investigated using X-ray photoelectron spectroscopy, UV-vis absorption spectroscopy, photoluminescence (PL) spectroscopy, laser scanning confocal microscopy-PL spectrometry, and spectroscopic ellipsometry. In this work, BATHT-SAM was employed as an interfacial layer on SiO₂ to fabricate ultrathin film transistors (UTFTs, active layer thickness ~ 16.09 nm). The device UTFT-I, made of 0.06 wt % 5,5'-(9,10-bis(phenylethynyl)anthracene-2,6-diyl)bis(ethyne-2,1-diyl)bis(2hexylthiophene) (BATHT) solution on an n-octyltrichlorosilane-SAM/SiO₂ layer, showed no gate effect for the carrier transport behavior; however, the device UTFT-II, fabricated on BATHT-SAM/SiO₂, exhibited field effect mobilities of 0.04 cm² V^{-1} s⁻¹ ($I_{on/off} \sim 6.3 \times 10^3$ to 1.0×10^4). This can be attributed to the effect of BATHT-SAM inducing uniform coverage and ordering of BATHT molecules as an upper layer.

1. INTODUCTION

Organic thin film transistors (OTFTs) have attracted a great deal of interest over the past decade because of their potential application to low-cost printed electronics and large-area flexible electronic devices. In particular, fabrication techniques such as inkjet printing, microcontact printing, and roll-to-roll processing of soluble organic semiconductors have enabled the realization of high-performance solution-processed OTFTs in large-scale devices.

In the past, many research groups have observed that the performance of OTFTs can be significantly improved by treating the insulator surface with self-assembled monolayer (SAMs) using *n*-octyltrichlorosilane (OTS), *n*-octadecyltrichlorosilane (ODTS),^{1,2} aminopropyltrimethoxysilane,³ fluoroalkyltrichlorosilane (FTS),⁴ and phenyltrichlorosilane (PTCS).⁵ The modification of the dielectric surface via a SAM provides alternative means for the crystalline semiconducting molecules to achieve optimum crystallinity and edge-on molecular ordering for the facilitation of charge carrier transport in TFTs.⁶

The first chemically prepared SAM was proposed in the 1980s, which thereafter inspired more advanced research to be carried out on its formation and unique properties.^{7,8} Since then, SAMs have been employed in numerous electronic devices that have multiple interfaces in order to enhance the corresponding device performance. Attempts have been made to modify the wettability of the material surface,9 to tune the work function of metals,^{10,11} to achieve cascade energy-level alignment^{12,13} to make the carrier transport more efficient, and to facilitate the fabrication of very thin dielectric layers in TFTs.^{14,15}

For the most common application of SAMs to OTFTs, the SAM can modulate the surface property of the insulator through the introduction of hydrophobic molecules. Thus, vacuum-processed pentacene and rubrene molecules on OTS-SAM/SiO₂/Si have shown good coverage and provided robust crystalline films.^{16,17}

Received: May 23, 2012 Revised: June 28, 2012 Published: June 29, 2012 Recently, field-effect transistors (FETs) that use only a semiconductor-containing SAM as an active layer have been demonstrated and combined into integrated circuits after preparing dimethylchlorosilane-functionalized oligothiophenes.^{18–22} This single molecular layer that contains semiconducting moieties can be fabricated onto the insulator surface quite efficiently.

A few more examples of SAM-based FETs based on hydroxyl-functionalized acenes and thiophenes have already been reported. $^{23-27}$ Although the available literature suggests that the use of merely a monolayer of an organic semiconductor can control the molecular alignment and significantly decrease the material expense for a single device, spontaneous self-assembly remains challenging for realizing large-area and practical applications for these devices.

In this work, we present new solution-processed OTFTs fabricated onto a **BATHT**-SAM/SiO₂/Si gate insulator. **BATHT** was deposited onto **BATHT**-SAM/SiO₂/Si by spincoating using an unusually dilute solution (0.06 wt %) for an active layer. The semiconducting moiety in **BATHT**-SAM is identical to the **BATHT** molecules used as the upper coated active layer. The absorption and photoluminescence (PL) spectral behaviors of the fabricated **BATHT**-SAM on the substrate were investigated in detail.

Ultrathin film transistors (UTFTs) from the **BATHT**-SAM/ SiO₂/Si were subsequently fabricated and the device performances measured and compared to those of TFTs fabricated onto OTS-treated SiO₂. The combination of the **BATHT** monolayer (t = 2.10 nm) and upper film (t = 16.09 nm) coated with **BATHT** provided successful charge transport properties in the UTFT devices. The output and transfer curves were measured to yield a saturated mobility of around 0.04 cm² V⁻¹ s⁻¹ ($I_{on/off} \approx 6.3 \times 10^3$ to 1.0×10^4).

2. EXPERIMENTAL SECTION

2.1. Synthesis. All commercially available starting materials and solvents were purchased from Aldrich, TCI, or Acros Co. and were used without further purification. 2,6-Dibromo-9,10-bis-(phenylethynyl)anthracene (1), 2-ethynyl-5-hexylthiophene (2), and 6-(5-ethynylthiophen-2-yl)hexan-1-ol (4) were synthesized using the following literature procedures.^{28–30}

2-((6-Bromo-9,10-bis(phenylethynyl)anthracen-2-yl)ethynyl)-5hexylthiophene, 3. An oven-dried 250 mL round-bottomed flask (RBF) was charged with a magnetically stirred solution of 2,6dibromo-9,10-bis(phenylethynyl)anthracene, 1 (3.00 g, 5.6 mmol), bis(triphenylphosphine) palladium(II) dichloride (0.196 g, 0.28 mmol), and copper iodide (0.053 g, 0.28 mmol) in a mixture of freshly distilled THF (80 mL), triethylamine (35 mL), and diisopropylamine (25 mL). 2-Ethynyl-5-hexylthiophene (0.97 g, 5.03 mmol) was then added and the mixture heated at 80 °C for 6 h. After completing the reaction, the solution was poured into methanol and the precipitates collected. The crude solid was purified by silica-gel column chromatography using a mixture of methylene chloride (MC) and hexane as an eluent (MC/hexane = 1:3 v/v). Further precipitation afforded pure 2-((6-bromo-9,10-bis(phenylethynyl)anthracen-2-yl)ethynyl)-5-hexylthiophene, 3 (yield = 1.1 g, 30%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.72 (d, J = 1.96 Hz, 1H), 8.67 (s, 1H), 8.51 (d, J = 9.00 Hz, 1H), 8.44 (d, J = 9.00 Hz, 1H), 7.78 (m, 4H), 7.63 (m, 2H), 7.47 (m, 6H), 7.22 (d, J = 3.52 Hz, 1H), 6.73 (d, J = 3.52 Hz, 1H), 2.85 (t, J = 7.84 Hz, 2H), 1.74 (m, 2H), 1.41 (m, 6H), 0.92 (t, J = 7.04 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 149.01, 132.85, 132.56, 131.78, 128.60, 127.28, 124.39, 122.98, 121.77, 120.29, 117.43, 103.28, 93.04, 85.56, 31.55, 30.29, 28.73, 22.59, 14.10. LR-MS (FAB) m/z (M⁺): calcd for C₄₂H₃₁BrS, 646.13; found, 648.10. Anal. Calcd for C42H31BrS: C, 77.89; H, 4.82; S, 4.95. Found: C, 77.80; H, 4.91; S, 5.01.

6-(5-((6-((5-Hexylthiophen-2-yl)ethynyl)-9,10-bis(phenylethynyl)anthracen-2-yl)ethynyl) thiophen-2-yl)hexan-1-ol, 5. An oven-dried 250 mL RBF was charged with a magnetically stirred solution of 3 (0.90 g, 1.4 mmol), bis(triphenylphosphin) palladium(II) dichloride (0.049 g, 0.069 mmol), and copper iodide (0.013 g, 0.069 mmol) in a mixture of freshly distilled THF (80 mL), triethylamine (35 mL), and diisopropylamine (25 mL). 6-(5-Ethynylthiophen-2-yl)hexan-1-ol (0.434 g, 2.08 mmol) was then added and the mixture heated at 80 °C for 6 h. After completing the reaction, the solution was poured into methanol and the precipitates collected. The crude solid was purified by silica-gel column chromatography using a mixture of MC and hexane (1:2 v/v) as an eluent. Further purification via precipitation afforded pure compound 5 (yield = 0.76 g, 71%). ¹H NMR (400 MHz, $CDCl_3$: δ (ppm) 8.74 (s, 2H), 8.58 (d, J = 9.00 Hz, 2H), 7.82 (d, J =7.84 Hz, 4H), 7.65 (d, J = 9.00 Hz, 2H), 7.48 (m, 6H), 7.22 (d, J = 3.52 Hz, 2H), 6.73 (d, J = 3.88 Hz, 2H), 3.68 (q, J = 6.64 Hz, 2H), 2.86 (m, 4H), 1.74 (m, 4H), 1.59 (m, 2H), 1.43 (m, 6H), 1.33 (m, 4H), 1.25 (t, J = 5.12 Hz, 2H), 0.92 (t, J = 6.68 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 187.33, 132.54, 131.83, 131.49, 128.57, 124.44, 123.09, 118.21, 104.75, 85.91, 85.55, 62.94, 32.62, 31.53, 30.18, 28.78, 25.46, 22.57. LR-MS (FAB) m/z (M⁺): calcd for C54H46OS2, 774.30; found, 774.57. Anal. Calcd for C54H46OS2: C, 83.68; H, 5.98; S, 8.27. Found: C, 83.55; H, 6.08; S, 8.20.

6-(5-((6-((5-Hexvlthiophen-2-vl)ethvnvl)-9,10-bis(phenvlethvnvl)anthracen-2-yl)ethynyl) thiophen-2-yl)hexyl 3-(Triethoxysilyl)-Propylcarbamate, 7. Compound 5 (0.20 g, 0.258 mmol) and dibutyltin dilaurate (0.46 mL, 0.774 mmol) were dissolved in 13 mL of distilled THF under an argon atmosphere. 3-Isocyanatopropyl triethoxysilane (ICPTEOS; 0.19 mL, 0.77 mmol) was added dropwise to the mother solution before the mixture was kept at 65 °C for 3 h. The mixture was poured into 200 mL of distilled hexane to collect the precipitates, with this precipitation procedure repeated for further purification. The product was dried under vacuum at room temperature for 24 h and stored in a vacuum desiccator before being used further (yield = 0.10 g, 38%). ¹H NMR (300 MHz, $CDCl_3$: δ (ppm) 8.77 (s, 2H), 8.62 (d, J = 9.06 Hz, 2H), 7.82 (d, J =7.98 Hz, 4H), 7.63 (d, J = 9.06 Hz, 2H), 7.51 (m, 6H), 7.22 (d, J = 3.57 Hz, 2H), 6.73 (d, J = 3.57 Hz, 2H), 4.05 (t, J = 6.86 Hz, 2H), 3.85 (q, J = 7.14 Hz, 6H), 3.17 (t, J = 6.86 Hz, 2H), 2.83 (t, J = 7.68 Hz, 4H), 1.65 (m, 8H), 1.34 (m, 10H), 1.25 (t, J = 6.87 Hz, 9H), 0.93 (t, J = 7.14 Hz, 3H), 0.66 (t, J = 8.52 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 149.23, 132.78, 132.08, 128.82, 123.36, 118.47, 103.26, 93.37, 86.07, 85.72, 58.69, 32.14, 31.79, 28.97, 27.86, 22.82, 18.53, 14.33, 13.82. LR-MS (FAB) m/z (M⁺): calcd for C₆₄H₆₇NO₅S₂Si, 1021.42; found, 1021.43. Anal. Calcd.for C₆₄H₆₇NO₅S₂Si: C, 75.18; H, 6.61; N, 1.37; S, 6.27. Found: C, 76.43; H, 6.76; N, 1.45; S, 5.68.

2.2. Instrumental Analysis. ¹H NMR spectra were recorded on Varian Mercury 400 and 300 MHz NMR spectrometers using deuterated chloroform purchased from Cambridge Isotope Laboratories, Inc. Elemental analyses were performed using an EA1112 (Thermo Electron Corp.) elemental analyzer. Low-resolution mass spectrometry (LR-MS) was performed using a JMS-700 MStation mass spectrometer (JEOL, Tokyo, Japan; resolution of 60 000 and m/z range at full sensitivity of 2400).

2.3. UV–Vis Absorption and PL Spectroscopy. Absorption spectra of the solution (solvent = 1×10^{-5} mol L⁻¹ chloroform) and film samples were obtained using a UV–vis spectrometer (HP 8453, photodiode array type) in the wavelength range 190–1100 nm. PL spectra of the solutions and films were acquired at room temperature using a Hitachi F-7000 FL spectrophotometer.

2.4. Laser Confocal Microscopy–PL Spectroscopy (LCM-PL). Nanoscale PL images and spectra were taken for the **BATHT**-SAM and its surface measured spot by spot using a customized laser confocal microscope (Nano-Focus Ltd., Albatross) built around an inverted optical microscope (Axiovert 200, Zeiss GmbH). The 488-nm line of an unpolarized argon (Ar) ion laser was used for PL excitation. The **BATHT**-SAM was placed on a glass substrate, which was then mounted onto an *xy*-scan stage (PSIA XE-120) of the confocal microscope. The spot size of the focused laser beam on the sample was



Figure 1. Structures of TFT devices. (a) UTFT-I: BATHT/OTS-SAM/SiO₂/Si and (b) UTFT-II: BATHT/BATHT-SAM/SiO₂/Si.





estimated to be about 190 nm. The scattered light was collected with the same objective lens and with the excitation laser light filtered out using a long-pass edge-filter. The measured PL signal was focused to a multimode fiber (core size = $100 \ \mu m$) that acted as a pinhole for the confocal detection. The other end of the multimode fiber was connected to the photomultiplier tube for the PL image, or the input slit of a 0.3-m-long monochromator (Acton Spectra Pro 300i) equipped with a cooled charge coupled device (Acton PIXIS 100) for measurement of the PL spectra. For all confocal PL measurements performed in this work, the laser power incident on the sample and the acquisition time for each PL spectrum were fixed at 3 μ W and 1 s, respectively.

2.5. Contact Angle Measurements. A Phoenix 300Plus instrument with an automatic liquid dispenser was employed to measure contact angles at ambient temperature. Static water contact angles were measured using a $4-\mu L$ droplet of deionized water at three different locations on a film. Data are reported as the average of these individual measurements.

2.6. Spectroscopic Ellipsometry. Ellipsometric angles Ψ and Δ were measured using spectroscopic ellipsometry with incidence angles of 65°, 70°, and 75°. A variable angle spectroscopic ellipsometer (Woollam Inc., VASE model) was employed with an autoretarder in the spectral range between 1.0 and 5.0 eV.

2.7. X-ray Photoelectron Spectroscopy (XPS). An ESCALAB 220i-XL X-ray photoelectron spectrometer was employed to perform elemental analysis of the film surface ($E_p = 1486.7 \text{ eV}$). The typical pressure of the chamber during analysis was less than 6×10^{-10} mbar. All XPS spectra were measured with a pass energy of 58.7 eV and an energy step of 0.125 eV. The data were collected at 45° to the normal of the sample surface.

2.8. Atomic Force Microscopy (AFM). An advanced scanning probe microscope (XE-100, PSIA) operating in a tapping mode with a silicon cantilever was used to characterize the surface topographies of the samples. The monolayer and spin-coated films were prepared using

the corresponding solutions and the surface coverage and roughness of the SAM on the SiO_2/Si dielectric layer investigated.

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2.9. TFT Fabrication. To fabricate the TFTs and characterize their performance, a bottom-gate top-contact device geometry was employed. To fabricate the active layer, a solution of **BATHT** was prepared with unusually low concentration (~0.06 wt %). The solution was spin-coated onto OTS-treated SiO₂/Si (UTFT-I) or **BATHT**-SAM/SiO₂/Si (UTFT-II) (see Figure 1).

Source and drain electrodes were then thermally evaporated (100 nm) through a shadow mask with a channel width and length of 1500 and 50 μ m, respectively.

All field-effect mobilities were extracted from the saturation regime using the relationship $\mu_{\rm sat} = (2I_{\rm DS}L)/(WC(V_{\rm G}-V_{\rm th})^2)$, where $I_{\rm DS}$ is the saturation drain current, C is the capacitance of the dielectric, $V_{\rm G}$ is the gate bias, and $V_{\rm th}$ is the threshold voltage. The device performance was evaluated using a 4200-SCS semiconductor characterization system under ambient conditions.

3. RESULTS AND DISCUSSION

3.1. Synthesis and SAM Formation. The two-dimensional (2-D) π -conjugated molecule 5,5'-(9,10-bis-(phenylethynyl)anthracene-2,6-diyl)bis(ethyne-2,1-diyl)bis(2-hexylthiophene) (**BATHT**) and its analogue, 5, which bears a hydroxyl group, were synthesized to prepare **BATHT-TEOS**. The monohydroxyl-terminated **BATHT**, 5, was synthesized by deprotecting the acetate group of compound 4. Compound 5 was tethered to one arm of triethoxysilane via a simple carbamate forming reaction. **ICPTEOS**, 6, is very reactive toward a hydroxyl group, yielding carbamate-containing **BATHT** molecules in the presence of dibutyltin dilaurate (DBTDL) in dried THF at 60 °C (Scheme 1). Using the synthesized **BATHT-TEOS**, hydrolysis and condensation

reactions were performed in dried toluene on the SiO₂/Si insulator layer (temperature = 100 °C, concentration of **BATHT-TEOS** solution = 0.6 mM). Upon grafting of the **BATHT-TEOS** onto the SiO₂, any unreacted **BATHT-TEOS** was thoroughly removed by sonication.

3.2. Surface Characterization of BATHT-SAM on SiO₂/ **Si.** After fabricating **BATHT**-SAM on SiO₂/Si, the placement of **BATHT** molecules on SiO₂/Si was confirmed by XPS, spectroscopic ellipsometry, contact angle measurements, AFM, absorption spectroscopy, and LCM-PL.

First, XPS provided the elemental composition within the substrate-bearing **BATHT** moieties (scan range = 0-1200 eV).

The samples were prepared by immersing SiO_2/Si substrate into the **BATHT-TEOS** solution (solvent = 0.6 mM dried toluene) at 100 °C for 5 h before being dried at room temperature for 6 h under vacuum. XPS spectra of **BATHT-TEOS**-treated SiO₂/Si and bare SiO₂/Si are shown in Figure 2.



Figure 2. XPS spectra of bare SiO₂/Si (A) and **BATHT-TEOS** treated SiO₂/Si substrate (B). Insets: Image of water droplet (4 μ L) on the substrate and magnified spectra in the range of 390–409 eV.

From the sample treated with the **BATHT-TEOS** solution, there can be observed a significant intensity increase in the C(1s) peak at 284 eV and the existence of an N(1s) peak at 399 eV (see Figure 2B, inset). This therefore provides evidence that the **BATHT-TEOS** was successfully grafted onto the SiO₂/Si substrate.

There is also further corroborative evidence of SAM deposition onto the SiO_2/Si surface. For example, significant differences in the measured contact angles can be observed for the two above-mentioned samples (see the insets of Figure 2). After **BATHT**-SAM deposition, a contact angle of 82° was

measured (work of adhesion = 82.14 mN/m) as a result of the imposed hydrophobicity on the surface of the SiO_2/Si .

For further precise characterization, spectroscopic ellipsometry measurements were performed for the ultrathin films on the SiO₂/Si with incidence angles of 65°, 70°, and 75° using a variable angle spectroscopic ellipsometer (VASE) with an autoretarder in the spectral range 1.0–5.0 eV. In order to carry out the VASE study, two samples on SiO₂/Si were fabricated: (a) **BATHT**-SAM/SiO₂/Si (Sample I) and (b) spin-coated **BATHT** solution (0.06 wt %)/**BATHT**-SAM/SiO₂/Si (Sample II). The use of multiple incident angles increases the accuracy in determining the dielectric function of the layer from the ellipsometric angles Ψ and Δ . The ellipsometric angles were fitted using a parametric optical constant (POC) model.³¹

Assuming three phases for the **BATHT**-SAM layer, SiO_2 , and Si substrate, the refractive index and extinction coefficient of the **BATHT**-SAM were estimated using layer modeling analysis. In the case of a molecular layer of **BATHT** on a **BATHT**-SAM, four phases were assumed: **BATHT** layer, **BATHT**-SAM layer, SiO_2 , and Si substrate, and the refractive index and extinction coefficient of the **BATHT** layer was estimated with a fixed thickness for the **BATHT**-SAM using layer modeling analysis.

A POC model was adopted for the line shape of the dielectric function ($\varepsilon^* = \varepsilon_1 + i\varepsilon_2$) of the organic layer,³¹ where the complex refractive index, (n + ik), is the square root of the dielectric function ε . Figure 3c summarizes the layer models for (a) Sample I and (b) Sample II.

To model the surface roughness layer, we used an effective medium approximation with components comprised of a mixture of the main layer and voids. The effective dielectric function was calculated according to the Bruggeman effective medium approximation (EMA):³²

$$f_{\min} \frac{\varepsilon_{\min} - \varepsilon^{\text{eff}}}{\varepsilon_{\min} + 2\varepsilon^{\text{eff}}} + f_{\text{void}} \frac{\varepsilon_{\text{void}} - \varepsilon^{\text{eff}}}{\varepsilon_{\text{void}} + \varepsilon^{\text{eff}}} = 0$$
(1)

where the effective dielectric function of the roughness layer is denoted by ε^{eff} and dielectric functions (volume fractions) of the main layer and voids are denoted, respectively, as $\varepsilon_{\text{main}}(f_{\text{main}})$ and $\varepsilon_{\text{void}}(f_{\text{void}})$. We fixed $f_{\text{void}} = 0.5$ for simplicity.

Figure 3a,b shows the measured complex refractive indices of the films for (a) Sample I and (b) Sample II. The standard critical point (SCP) model assumes a simple parabolic dispersion relationship for the valence and conduction bands of semiconductors, as developed by Cardona³³ and Aspnes.³⁴ This model provides accurate critical point (CP) parameters such as the energy threshold, broadening, amplitude, and excitonic phase angle and can be applied to polymers.³² The SCP line shape equation is given by³⁵

$$\varepsilon(E) = C - Ae^{i\Phi}(E - E_{\rm th} + i\Gamma)^n \tag{2}$$

where the CP is described by the amplitude *A*, threshold energy $E_{\rm th}$, broadening Γ , and excitonic phase angle Φ . The exponent *n* takes the values of -1/2 for one-dimensional (1-D), 0 [logarithmic, i.e., $\ln(E - E_{\rm th} + i\Gamma)$] for 2-D, and 1/2 for 3-D CPs. Discrete excitons are represented by n = -1. Here, the excitonic phase angle, Φ , represents coupling between the discrete exciton states and continuum band states. To remove the background contribution, the second derivative of the dielectric function with respect to energy $(d^2\varepsilon/dE^2)$ is fitted using the SCP model. The best matched lowest optical gap

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Figure 3. Refractive index and extinction coefficient vs photon energy. The best match complex refractive index of the films for fabricated (a) Sample I and (b) Sample II. (c) Configurations of the multilayer in the samples: (i) Sample I and (ii) Sample II.



Figure 4. UV-vis absorption (A) and photoluminescence (B) spectra of a solution and film of compound 5, and those of BATHT-SAM on glass: dashed-dotted-dashed line (solution of 5), dotted line (film of 5), solid line (BATHT-SAM/glass), and dashed line (BATHT (0.06 wt %)/BATHT-SAM/glass). (C) LCM-PL spectra of BATHT-SAM/glass with each measurement position. Inset: PL image of BATHT-SAM on glass substrate indicating the separately measured spots with yellow circles.

energies are 2.322 and 2.288 eV for (a) Sample I and (b) Sample II, respectively.

Figure 4A shows the UV-vis absorption spectra of BATHT-SAM, BATHT/BATHT-SAM/glass, and solution and film samples of compound 5. From this figure it can be seen that the solution spectrum of 5 shows absorption maxima at 461 and 489 nm, whereas that of the film of 5 shows increased

broadening and a bathochromic shift to reduced bandgap energy.

In a previous study carried out by us, a film of BATHT was found to exhibit J-aggregation behavior, with absorption maxima at 481 and 504 nm showing highly resolved vibronic transitions.²⁸ On the other hand, the spectrum for BATHT-SAM/glass shows no spectral characteristics that are specific to



Figure 5. AFM topographic images (10 μ m × 10 μ m) of A: bare SiO₂/Si, and B: BATHT-SAM/SiO₂/Si (after 5 h immersion of silicon wafer in BATHT-TEOS solution).



Figure 6. AFM topographic images (10 μ m × 10 μ m) of A: BATHT/BATHT-SAM/SiO₂/Si, B: BATHT/OTS-SAM/SiO₂/Si, and C: BATHT/SiO₂/Si.

this aggregation behavior. This may be attributed to the anchoring of one end of the peripheral group to the glass substrate which thus prevents J-aggregation behavior from occurring. When the extremely thin film of **BATHT** was coated onto the **BATHT**-SAM, the peak at 522 nm was clearly observed; therefore, **BATHT** molecules in the upper layer were associated via a J-aggregation manner.

Corresponding emission spectra can be seen in Figure 4B. The spectra of **BATHT**-SAM and of the thin film of **5** show very broad spectra whose emission maximum is around 622 nm, which can be assigned to excimer formation between the **BATHT** molecules. The SAM prepared after 5 h of immersion exhibited almost negligible emission at 540 nm but with a dominant emission observed at 622 nm. The thin **BATHT** film on **BATHT**-SAM/glass shows a clear emission peak at 540 nm, which corresponds to the absorption band at 522 nm, indicating that the J-aggregation peak results from a small Stokes shift. This experiment also provides strong evidence that the specific arrangement of the **BATHT** is aided by the **BATHT**-SAM.

A series of PL spectra obtained using a LCM-PL spectrometer are provided in Figure 4C. In order to investigate the uniformity of **BATHT**-moieties in the monolayer, the measured area was varied and the corresponding PL spectra superimposed onto each other. The variation in emission maximum wavelengths and intensities were monitored. No significant variation in these parameters was observed for the **BATHT**-SAM on the glass substrate, supportive of the notion that there is uniformity of the **BATHT**-SAM on the glass substrate. The inset in Figure 4C is an LCM-PL image which



Figure 7. Electrical characterization for OTFTs of UTFT-II. A: plot of drain current $(-I_{DS})$ versus drain-source voltage (V_{DS}) . B: plot of $-I_{DS}$ and $-I_{DS}^{1/2}$ versus gate voltage (V_G) , $V_{DS} = -120$ V. The performances were measured at ambient conditions.

visibly shows the uniformity through the surface of the monolayer.

In order to provide further clear evidence of the obtained surface, we recorded the AFM topographic image of the **BATHT**-SAM that had been prepared by the 5 h immersion of SiO_2/Si into the **BATHT-TEOS** solution, with comparison made to the image of the bare substrate.

As can be seen in Figure 5, the surface image is clearly changed after **BATHT-TEOS** deposition compared to that of the bare SiO_2/Si substrate. Crystalline domains are observed in the **BATHT-SAM**/SiO₂/Si.

Figure 6A–C displays the surface topographies of the samples of BATHT/BATHT-SAM/SiO₂/Si, BATHT/OTS-SAM/SiO₂/Si, and BATHT/SiO₂/Si, respectively, when a coating of a 0.06 wt % solution of BATHT is applied to the substrate. Because of the extremely low concentration of the spin-coated solution, Figures 6B,C shows very poor surface coverage, with only some islands observed to be occupied with BATHT molecules. However, the film surface in Figure 6A shows highly compact structures with good connectivity between molecular crystallites of BATHT. Therefore, the BATHT-SAM aided the formation of a good film, even when coating with a 0.06 wt % solution of BATHT.

3. 3. Organic Thin Film Transistors Made of BATHT Deposited on BATHT-SAM/SiO₂/Si. Bottom-gate, topcontact **BATHT**-SAM-based TFTs were fabricated to investigate the carrier transport behavior under ambient conditions. For fabrication of an active layer, a very dilute **BATHT** solution (0.06 wt % in chloroform) was prepared for spin coating. UTFT-I was prepared by coating the solution of **BATHT** onto OTS-SiO₂/Si, with the solution of **BATHT** coated onto **BATHT**-SAM/SiO₂/Si for the fabrication of UTFT-II.

The device characteristics of UTFT-I could not be observed at all. This is likely due to the lack of **BATHT** molecules on the surface (as shown by the AFM image in Figure 6B), with only discontinuous islands of **BATHT** molecules in this case. Therefore, a UTFT device could not be successfully realized on OTS-treated SiO₂/Si using the 0.06 wt % solution of **BATHT**. However, UTFT-II fabricated on **BATHT**-SAM/SiO₂/Si exhibited typical p-channel FET characteristics (see Figure 7). The mobility was obtained from the source (S)-drain (D) current–voltage curves ($I_{\rm DS}$ vs $V_{\rm DS}$) for the well-resolved saturation region. The saturated field-effect mobility, $\mu_{\rm FET}$, could then be calculated from the amplification characteristics using known equations that describe TFTs.

The annealing-free TFTs fabricated on **BATHT**-SAM/SiO₂/ Si exhibited interestingly high carrier mobilities of around 0.04 cm² V⁻¹ s⁻¹ with $I_{on/off} \sim 6.3 \times 10^3$ to 1.0×10^4 , with such high values obtained using only an ultrathin semiconducting layer. The improved performance of the UTFT-II can mainly be attributed to the improved crystallization on the surface of the **BATHT**-SAM which contains the identical semiconducting moieties to **BATHT**. This affords a densely packed geometry of erect **BATHT** moieties on the surface of the gate insulator.

Overall, the good performance of the UTFT device on BATHT-SAM/SiO₂/Si may be attributed to the presence of the single BATHT molecular layer placed between the overcoat of BATHT molecules and SiO₂, which supports a favorable, uniform conformation of molecules suitable for carrier transport. In addition, BATHT units generate strong intermolecular interactions and induce large overlaps between the π -orbitals of neighboring molecules, thus generating efficient channels for charge transport and resulting in high carrier mobility in the UTFT even though the thickness of the active layer is extremely small (~16.09 nm).

4. CONCLUSIONS

A new anthracene-based conjugated molecule containing triethoxysilane that is a precursor molecule for SAM fabrication was successfully synthesized. The molecules formed a uniform SAM layer onto the large surface of a gate insulator and also drove uniform alignment of **BATHT** molecules to the substrate. We successfully deposited **BATHT** molecules onto the surface of **BATHT**-SAM/SiO₂/Si and fabricated an unexpectedly compact thin-layer structure by spin coating using an unusually dilute solution. UTFT-II, fabricated on **BATHT**-SAM/SiO₂/Si, exhibited intriguingly high carrier mobility of around 0.04 cm² V⁻¹ s⁻¹, with $I_{on/off} \sim 6.3 \times 10^3$ to 1.0×10^4 .

AUTHOR INFORMATION

Corresponding Author

*E-mail: dhchoi8803@korea.ac.kr. Tel: +82-2-3290-3140. Fax: +82-2-925-4284.

Notes

The authors declare no competing financial interest.

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