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# Room Temperature Solid-State Synthesis of a Conductive Polymer for Applications in Stable I<sub>2</sub>-Free Dye-Sensitized Solar Cells

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A solid-state polymerizable monomer, 2,5-dibromo-3,4-propylenedioxythiophene (DBProDOT), was synthesized at 25 °C to produce a conducting polymer, poly(3,4-propylenedioxythiophene) (PProDOT). Crystallographic studies revealed a short interplane distance between DBProDOT molecules, which was responsible for polymerization at low temperature with a lower activation energy and higher exothermic reaction than 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) or its derivatives. Upon solid-state polymerization (SSP) of DBProDOT at 25 °C, PProDOT was obtained in a self-doped state with tribromide ions and an electrical conductivity of 0.05 S cm<sup>-1</sup>, which is considerably higher than that of chemically-polymerized PProDOT ( $2 \times 10^{-6}$  S cm<sup>-1</sup>). Solid-state <sup>13</sup>C NMR spectroscopy

# Introduction

Conducting polymers have received considerable attention for various applications such as photovoltaic cells, organic fieldeffect transistors (OFETs), organic light-emitting diodes (OLEDs), and sensors because of their controllable conductive and optical properties.<sup>[1-7]</sup> Among these, heterocyclic conducting polymers have become the most important materials owing to their high conductivity, easy modification, and good processability.<sup>[8-10]</sup> There are various polymerization methods used for the synthesis of heterocyclic conducting polymers: 1) oxidative polymerization, including chemical polymerization with an oxidant, electrochemical polymerization,<sup>[11-13]</sup> vaporphase polymerization,<sup>[14,15]</sup> and solution casting polymerization;<sup>[16,17]</sup> 2) chemical coupling polymerization with a catalyst;<sup>[18]</sup> and 3) solid-state polymerization (SSP).<sup>[19]</sup> Although oxidative and chemical coupling polymerizations have been extensively researched, SSP has rarely been reported.<sup>[20-25]</sup> SSP is a unique synthetic method for well-ordered, highly conductive polymers in films or bulk states without catalysts or solvent. In this regard, new polymerization methods with new materials are very important in materials science and fabrication because they directly affect the electrical and optical properties of the resultant polymers for desired applications. In SSP, polymerization occurs in crystalline states and thus short distances between the monomers are important to lower the activation energy for polymerization. Thus, dihalogenated heterocyclic monomers are a good choice of monomer for SSP owing to their crystalline nature and the short distance between molecules in their crystalline state, which ensures an exothermic reand DFT calculations revealed polarons in PProDOT and a strong perturbation of carbon nuclei in thiophenes as a result of paramagnetic broadening. DBProDOT molecules deeply penetrated and polymerized to fill nanocrystalline TiO<sub>2</sub> pores with PProDOT, which functioned as a hole-transporting material (HTM) for I<sub>2</sub>-free solid-state dye-sensitized solar cells (ssDSSCs). With the introduction of an organized mesoporous TiO<sub>2</sub> (OM-TiO<sub>2</sub>) layer, the energy conversion efficiency reached 3.5% at 100 mW cm<sup>-2</sup>, which was quite stable up to at least 1500 h. The cell performance and stability was attributed to the high stability of PProDOT, with the high conductivity and improved interfacial contact of the electrode/HTM resulting in reduced interfacial resistance and enhanced electron lifetime.

action with low activation energy for polymerization. The conductivity, crystallinity of the resultant polymer, and polymerization rate are controlled by the polymerization temperature. As dihalogenated heterocyclic monomers can easily penetrate nanopores, they are important tools in the formation of hole transporting channels in dye-sensitized solar cells (DSSCs).<sup>[26,27]</sup>

DSSCs represent a credible alternative to conventional crystalline silicon solar cells owing to their high energy conversion efficiency (>10%) and low production costs.<sup>[28-33]</sup> There has also been considerable interest in developing l<sub>2</sub>-free solid-state DSSCs (ssDSSCs) using hole-transporting materials (HTMs) owing to the potential to decrease the overall weight of the cells and provide long-term durability and flexibility.<sup>[34-43]</sup> The presence of l<sub>2</sub> can decrease the durability and photocurrent of the devices owing to the sublimation of l<sub>2</sub> and incident light absorption by l<sub>2</sub>. Furthermore, l<sub>2</sub> can act as an oxidizing agent, which corrodes the metals, such as grid metal Ag and Pt, of the counter electrode. An l<sub>2</sub>-containing quasi-solid-state DSSC

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with the N719 dye showed poor stability (35% decrease of energy conversion efficiency) after one week at 80°C.<sup>[30]</sup> Recently, we reported the preparation of a high efficiency (ca. 6.8% at 100 mW cm<sup>-2</sup>), I<sub>2</sub>-free ssDSSCs using solid-state polymerizable conductive polymers as effective HTMs.<sup>[26,27]</sup> The solution of dihalogenated heterocyclic monomers deeply penetrated the nanopores of the TiO<sub>2</sub> layer to form a well-packed nanostructure after solvent evaporation. Upon heating at 60°C, SSP resulted in improved interfacial contact properties between TiO<sub>2</sub> and the conducting polymers.

In our previous work,<sup>[26,27]</sup> 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) and 2,5-dibromo-3,4-ethylenedithiathiophene (DBEDTT) monomers reported by Meng et al.<sup>[19]</sup> were used to produce conducting polymers as HTMs, poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3,4-ethylenedithiathiophene) (PEDTT), respectively (Scheme 1a). However, these



Scheme 1. (a) Solid-state polymerizable monomer structures of DBEDOT and DBEDTT. (b) Synthesis of DBProDOT and polymerization of PProDOT. Monomer synthesis: i) 1,3-propanediol, *p*-TSA, toluene, 100 °C, 48 h; ii) *N*-bromo-succinimide (NBS), chloroform/acetic acid=3:1, 0 °C to 25 °C, 1 h. Polymer synthesis: iii) room temperature to 45 °C.

monomers require a very long polymerization time (several months to two years) at low temperatures such as 25°C. For the commercialization and mass production of I2-free ssDSSCs, device heating is to be avoided to save energy, the fabrication process needs to be simplified, and the damage by heat to the dye during HTM synthesis should be reduced. To this end, we designed a new solid-state, polymerizable monomer, 2,5-dibromo-3,4-propylenedioxythiophene (DBProDOT), to synthesize a conducting polymer, poly(3,4propylenedioxythiophene) (PPro-DOT), at room temperature. The DBProDOT crystals could be polymerized at 25 °C because of the short distance between the monomers, lower activation

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energy, and higher exothermic reaction for polymerization compared to DBEDOT. Herein, we report the synthesis of a monomer and its crystallographic analysis, polymerization at room temperature inside nanopores of TiO<sub>2</sub>, and application to long-term stable I<sub>2</sub>-free ssDSSCs for the formation of HTMs.

# **Results and Discussion**

## Solid-state polymerization (SSP)

Careful control of crystal formation is of pivotal importance in solid-state polymerizable monomers because the crystal forms can directly affect the electrical and optical properties of the resultant conducting polymers. Here, DBProDOT was synthesized by a facile synthetic method (Scheme 1 b), which involved the bromination of 3,4-propylenedioxythiophene (ProDOT) and recrystallization from ethanol. The DBProDOT crystals (0.1–0.5 g) were incubated at room temperature (25 °C) for five days in a closed vial for the SSP synthesis of PProDOT. In the PProDOT-X notation, X represents reaction temperature.

To investigate the crystalline properties, XRD studies were performed on DBProDOT and PProDOT-25 (Figure 1a). The XRD pattern of DBProDOT showed sharp and strong diffraction peaks at  $2\theta = 12.8$ , 13.2, 20.1, 20.7, 21.6, 24.0, 24.4, 27.8, 30.4, and 37.3°, which indicate a well-ordered crystalline structure. The diffraction peak at 24.0° corresponds to a *d* spacing of 3.70 Å, which is assigned to the interplane distance between DBProDOT monomers in the stack. Although this value is slightly larger than that of DBEDOT (3.50 Å), it is among the shortest distances between DBProDOT monomers is similar to



**Figure 1.** (a) XRD patterns of the DBProDOT crystal and PProDOT-25. (b) Solid-state CP-MAS <sup>13</sup>C NMR spectra of DBProDOT and PProDOT-25. (c) UV-Vis-NIR spectra of PProDOT-25 coated on a glass slide and N719-dye-adsorbed TiO<sub>2</sub> on FTO glass. Inset: Magnified spectrum of PProDOT-25. (d) Isothermal DSC curves of DBProDOT at 25, 35, and 45 °C. Inset: Arrhenius plot of the SSP reaction.

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the van der Waals distance (3.70 Å). The difference ( $\Delta d$ ) between the crystalline distance ( $d_c$ ) and the van der Waals distance ( $d_v$ ) is 0 and 0.2 Å for DBProDOT and DBEDOT, respectively. Therefore, a short distance between the bromine atoms in the crystalline molecules facilitates polymerization at room temperature. The broad diffraction peak at 21.8° was only observed in PProDOT-25, which corresponds to a *d* spacing of 4.07 Å and is assigned to the interplane distance between the PProDOT molecules in the stack. The reduced crystalline order and increased interplane distance in PProDOT may be because of the tribromide (Br<sub>3</sub><sup>-</sup>) dopants between the polymer crystal lattice, which form spontaneously upon SSP.

The single crystals of DBProDOT were recrystallized from ethanol to produce white, needle-like crystals (Figure S1, Supporting Information). The single-crystal XRD data for DBProDOT was collected at low temperature (200 K) because of its low melting point (Table S1, the Supporting Information). The unit cell of DBProDOT contained two independent molecules with symmetric molecular structures (Figure 2a). DBProDOT comprises a planar thiophene ring and a protruding dioxypropylene ring, which cause distances between the DBProDOT molecules longer than those between the DBProDOT molecules. The DBProDOT crystal revealed two packing types with  $\pi$ - $\pi$  stacking and a herringbone pattern (Figure 2b). The C–C bond lengths of DBProDOT corroborated the calculated values of DBProDOT [B3LYP/6-31G(d), Table S3 in the Supporting Information]



**Figure 2.** (a) Crystal structure of DBProDOT; Oak Ridge thermal ellipsoidal plot (ORTEP) diagram, the bond lengths between DBProDOT atoms, and two independent molecules in the unit cell. (b) Crystal packing diagram of DBProDOT with short intermolecular contacts between Br atoms. The thermal ellipsoids were set to 25% probability level.

mation]. The shortest intermolecular S···S, S···Br, and Br···Br distances are 3.65, 3.72, and 3.91 Å, respectively, which are similar to the van der Waals radii of S (1.80 Å) and Br (1.85 Å). The short intermolecular Br···Br distance and short interplane distance (3.70 Å) are responsible for the SSP of DBProDOT at low temperature.

The structural changes from the monomer to polymer were investigated using solid-state cross-polarization magic angle spinning (CP-MAS) <sup>13</sup>C NMR spectroscopy (Figure 1 b). The PProDOT polymer showed two strong peaks at 74 and 33 ppm and very weak peaks at 148 and 126 ppm. In contrast, the DBProDOT monomer showed clear and sharp peaks at 151, 126, 75, and 34 ppm, which are slightly different from those of PProDOT. Through SSP, the DBProDOT monomers are polymerized to produce Br<sub>3</sub><sup>-</sup>-doped PProDOT, which has polarons as a result of the delocalization of electrons in PProDOT.<sup>[19]</sup> Thus, the effect of the paramagnetic broadening strengthened the carbon nuclei of the thiophenes, primarily because of the conjugation of conductive polymers and weak carbon nuclei of the dioxypropylene bridge. The NMR spectrum of the chemically polymerized PProDOT (CP-PProDOT) doped with FeCl<sub>4</sub>could not be measured owing to the strong paramagnetic broadening.<sup>[20]</sup>

The ordered structure of the conductive polymer chains is a key factor in the determination of their electrical conductivities. Compared to other polymerization methods, such as oxi-

> dative polymerization and chemical coupling polymerization, SSP of heterocyclic conjugated rings starts from monomers with a well-ordered, solid-state crystal structure. The electrical conductivity of PPro-DOT-25 and PProDOT-45 without any treatments or additives reached 0.05 and 0.002 S cm<sup>-1</sup>, respectively, which is significantly higher than that of CP-PProDOT  $(2 \times 10^{-6} \text{ S cm}^{-1})$ . Therefore, there is a strong dependence of the ordered structure of the conductive polymer on reaction temperature and polymerization method.

> According to the measurements, approximately 1.1 mg PProDOT per 1 cm<sup>2</sup> of the TiO<sub>2</sub> layer was appropriate for deep infiltration into the TiO<sub>2</sub> pores without significant deposition on the TiO<sub>2</sub> surface. Thus, a PProDOT-25 film with 1.1 mg cm<sup>-2</sup> was prepared on a glass slide and its ultraviolet-visible-near infrared (UV-Vis-NIR) spectrum was measured (Figure 1 c). The PProDOT-25 film showed a broad peak maximum at approximately 730 nm. The UV-Vis-NIR spectrum of a N719-dye-adsorbed TiO<sub>2</sub> film with 0.4 mg cm<sup>-2</sup> was also measured and showed strong light absorption at 300, 400, and 530 nm. Thus, the PProDOT synthesized by SSP hardly affected the incident light absorption of the N719 dye. Notably, the solid-state polymerizable monomers at room temperature reported by Patra et al.<sup>[25]</sup> overlapped with the dye absorption, which implies reduced effectiveness as HTM for ssDSSCs.

> The polymerization temperature is a key parameter because it directly determines the reaction rate of

SSP, which affects the conductivity of the resultant polymer. The conductivity of PProDOT decreased with the increase in reaction temperature because the ordered crystalline structure collapsed at high temperatures owing to the low melting point of the monomer (47 °C). Isothermal differential scanning calorimetry (DSC) curves of DBProDOT were measured at 25, 35, and 45 °C (Figure 1 d). The DSC curves showed a large full width at half maximum (ca. 500 min) with exothermic heat flow that involved part-to-part polymerization of micro-sized DBProDOT crystals.<sup>[20,21,23]</sup> The heat of polymerization ( $\Delta H_p$ ) was  $-12.2\pm0.7$  kcal mol<sup>-1</sup> (1 kcal = 4.2 kJ). The activation energy was calculated using the Arrhenius equation [Eq. (1)]:

$$\ln(k) = \ln(1/t_{1/2}) = \ln(A) - E_a/RT$$
(1)

where *k* is the rate constant,  $t_{1/2}$  is the time taken by SSP for half conversion, *A* is the pre-exponential factor,  $E_a$  is the SSP activation energy, *R* is the ideal gas constant, and *T* is the absolute temperature for SSP. Using Equation (1), the  $E_a$  of DBPro-DOT was determined to be  $10.8 \pm 1.1 \text{ kcal mol}^{-1}$  ( $R^2 = 0.981$ ). The SSP process was fast owing to the high *t* value of DBPro-DOT at room temperature, without the additional heat energy. Thus, the full conversion time of DBProDOT (five days) was less than that of DBEDOT (one to two months) at room temperature (22–25 °C).<sup>[20]</sup>

#### Calculation of energies required for the elementary reaction

To elucidate the reaction mechanism, the energy of each structure was calculated by using the Gaussian 03 program by using DFT at the B3LYP/6-31G(d) level (Scheme 2 and Table S2).<sup>[44]</sup> The dimerization of DBProDOT was exothermic at 11.9 kcal mol<sup>-1</sup>, releasing more energy than the dimerization of DBEDOT (11.2 kcal mol<sup>-1</sup>) and dibromothiophene (8.3 kcal mol<sup>-1</sup>, Figure 2a). In radical polymerization in the dark, the homolytic cleavage energy of a C–Br bond in DBProDOT was 87.0 kcal mol<sup>-1</sup>, which barely progresses at room temperature. The electron donating dioxypropylene ring in DBProDOT stabilized the cation of the heterolytic cleavage of the C–Br bond in oxidative polymerization. In Figure 2b, the first step for the



production of a DBProDOT carbocation by bromine requires a high activation energy of 115.2 kcal mol<sup>-1</sup>, which makes it the rate-determining step. Nonetheless, this value is smaller than that for the DBEDOT reaction. The second step for the production of a dimerized carbocation releases 11.0 kcal mol<sup>-1</sup>, and the last step for the release of bromine is exothermic with 116.1 kcal mol<sup>-1</sup>. Thus, SSP for DBProDOT is an energetically favorable process and is autocatalyzed by the bromide ions Br<sup>-</sup> and Br<sub>3</sub><sup>-</sup>. Despite the ordered structure of PProDOT and steric bulkiness, the activation energy of the oligomerized carbocations is less than that of the dimerized carbocations, mainly because of the formation of a stable delocalized structure in the oligomer.<sup>[20]</sup>

#### Formation of HTMs for I<sub>2</sub>-free ssDSSCs at room temperature

The I2-free ssDSSCs were constructed with fluorine-tin-oxide-(FTO)-coated glass, an interfacial TiO<sub>2</sub> layer, an N719-dye-adsorbed nanocrystalline TiO<sub>2</sub> layer, pore-filled PProDOT as an HTM, and a Pt-coated FTO counter electrode (Figure 3a). A conventional compacted TiO<sub>2</sub> layer (CC-TiO<sub>2</sub>) was used as a control sample, whereas an organized mesoporous TiO<sub>2</sub> (OM-TiO<sub>2</sub>) layer was introduced to reduce the interfacial resistance and improve light transmittance. The 550 nm-thick, transparent OM-TiO<sub>2</sub> layer was synthesized through a sol-gel process using an amphiphilic graft copolymer (see the Supporting Information for details) as an interfacial layer.<sup>[27,45,46]</sup> After casting an ethanol solution containing DBProDOT on the dye-adsorbed TiO<sub>2</sub> photoelectrode, SSP occurred to produce PProDOT at room temperature. The cross-sectional scanning electron microscopy (SEM) images of the TiO<sub>2</sub> photoelectrode (Figure 3b) clearly show the deep penetration of PProDOT into the 11  $\mu$ mthick nanocrystalline TiO<sub>2</sub> layer to result in improved interfacial contact of the electrode/HTM. The 550 nm-thick OM-TiO<sub>2</sub> layer also had good interfacial contact on the FTO glass without defects. As shown in Figure 4a and b, the OM-TiO<sub>2</sub> layer exhibited high porosity with good interconnectivity compared to the uniformly dense CC-TiO<sub>2</sub> layer. The average pore diameter was approximately 40-70 nm. After in situ SSP of DBProDOT in the TiO<sub>2</sub> pores, the nanocrystalline TiO<sub>2</sub> layer was completely filled without defects (Figures 4c and d and S8).

> Three types of devices were fabricated using two interfacial layers and PProDOT polymerized at different temperatures; an OM-TiO<sub>2</sub> layer with PProDOT-25 (OM-PProDOT-25), a CC-TiO<sub>2</sub> layer with PProDOT-25 (CC-PPro-DOT-25), and a CC-TiO<sub>2</sub> layer with PProDOT-45 (CC-PProDOT-45). We controlled the electrical conductivity of the HTM by control of the SSP temperature using same monomer. The cur-(J–V) rent density-voltage curves, incident photon-to-current efficiency (IPCE), and elec-

Scheme 2. (a) Calculated energy for dimerization of DBProDOT. (b) Proposed mechanism for the autocatalyzed initiation of the SSP of DBProDOT.

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Figure 3. (a) Facile fabrication process for I2-free ssDSSCs using conductive polymers as HTMs. i) Solid-state polymerizable monomer crystal formation with complete penetration by drop casting and drying of DBProDOT or DBEDOT solutions. ii) Simple SSP of DBProDOT penetrated the cell at room temperature. iii) SSP of DBEDOT penetrated the cell at 60 °C. iv) Application of the counter electrode on the nanocrystalline TiO<sub>2</sub> layer. (b) Cross-sectional SEM images of the TiO<sub>2</sub> photoelectrode with HTMs and the magnified interface between the OM film and nanocrystalline TiO<sub>2</sub> layer.

trochemical impedance spectroscopy (EIS) were measured at 100 mW cm<sup>-2</sup>, as shown in Figure 5, and the results are summarized in Table 1. The J-V curves of OM-PProDOT-25 showed a short circuit current  $(J_{sc})$  of 10.0 mA cm<sup>-2</sup>, an open circuit voltage ( $V_{0c}$ ) of 0.63 V, and an energy conversion efficiency ( $\eta$ ) of 3.5%, which were greater than those of CC-PProDOT-25 and CC-PProDOT-45. The IPCE spectrum in Figure 5b also shows the large quantum efficiency of OM-PProDOT-25 in the visible wavelength region from 350-700 nm. These results illustrate that the use of the OM-TiO<sub>2</sub> layer and PProDOT synthesized at low temperature effectively improved the cell efficiency.

To understand the cell performance, the internal resistance and charge-transfer kinetics of the devices were investigated by using EIS analysis (Figure 5 c). Two semicircles were observed in the Nyquist plots of the EIS spectra (0.05-10<sup>5</sup> Hz) consisting of three components: ohmic resistance  $(R_s)$ , chargetransfer resistance at the interface of the counter electrode/

HTM  $(R_a)$ , and charge-transfer resistance at the interface of the photoelectrode/HTM ( $R_{\rm b}$ ). The  $R_{\rm a}$ values of OM-PProDOT-25 and CC-PProDOT-25 were not significantly different, but that of CC-PProDOT-45 was much greater. The R<sub>a</sub> value is largely dependent on the conductivity of HTM and the interfacial contact of the

Table 1. Performances and EIS results of $I_2$ -free ssDSSCs fabricated with different interfacial layers and SSP temperatures.									
Samples	V <sub>oc</sub> [V]	J <sub>sc</sub> [mA cm <sup>-2</sup> ]	FF	η [%]	R <sub>s</sub> [Ω]	R <sub>a</sub> [Ω]	$R_{ m b}$ [ $\Omega$ ]	$\omega_{min}$ [Hz]	$ au_{ m r}$ [ms]
OM-PProDOT-25 CC-PProDOT-25 CC-PProDOT-45	0.63 0.61 0.61	10.0 8.2 5.2	0.56 0.56 0.56	3.5 2.8 1.8	16.1 16.7 15.3	38.6 38.0 54.3	57.1 61.3 85.2	25.1 33.7 45.4	39.8 29.7 22.0

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counter electrode/HTM. The  $R_{\rm b}$ value of OM-PProDOT-25 was less than that of CC-PProDOT-25 and CC-PProDOT-45, which demonstrates that the OM-TiO<sub>2</sub> layer results in reduced resistance at the photoelectrode/HTM interface.

Based on the EIS model, the minimum angular frequency  $(\omega_{\min})$  of the impedance semicircles at the middle frequencies in the Bode phase plots (Figure 5 d) can be used to estimate the effective electron lifetime for recombination  $(\tau_r)$ according to the following equation:  $\tau_{\rm r} = 1/\omega_{\rm min}$ . Introduction of the OM-TiO<sub>2</sub> layer and PProDOT synthesized at low temperature resulted in the longest  $\tau_r$  (39.8 ms), which indicates enhanced electron transfer with reduced electron recombination.

The long-term stability of the I2-free ssDSSCs with PProDOT was investigated as a function of time without perfect encapsulation under vacuum (Figure 6). Epoxy resin was used for cell fix-



Figure 4. Surface SEM images of (a) the CC-TiO<sub>2</sub> layer on the FTO glass, (b) OM-TiO<sub>2</sub> layer on the FTO glass, (c) nanocrystalline TiO<sub>2</sub> layer, and (d) nanocrystalline TiO<sub>2</sub> layer with conducting polymers.



**Figure 5.** Performances of  $l_2$ -free ssDSSCs with a conducting polymer at 100 mW cm<sup>-2</sup> (a) *J–V* curves, (b) IPCE plots, (c) Nyquist plots, and (d) Bode phase plots of each device. Two different interfacial layers and SSP temperatures are compared.



Figure 6. Normalized cell efficiency of OM-PProDOT-25 maintained in room light as a function of time.

ation, and O<sub>2</sub> remained in the cell. There have been few reports on the long-term stability of ssDSSCs with conducting polymers because conducting polymers synthesized by electrochemical or chemical polymerization methods are highly sensitive to the environment, such as O<sub>2</sub>. Interestingly, an  $\eta$  value of 3.5% for OM-PProDOT-25 was maintained within  $\pm$  15% for 1500 h, which is one of the highest long-term stability values demonstrated in I<sub>2</sub>-free ssDSSCs fabricated with HTM.<sup>[30]</sup> Furthermore, the long-term stability could not be obtained from the liquid-state DSSC without a conducting polymer because of imperfect encapsulation. The excellent long-term stability might be a result of the lower sensitivity of PProDOT synthesized by the SSP method.

# Conclusions

A new solid-state polymerizable monomer at room temperature, 2,5-dibromo-3,4-propylenedioxythiophene (DBProDOT), and the corresponding conducting polymer, poly(3,4-propylenedioxythiophene) (PProDOT), were synthesized and characterized using XRD, solid-state crosspolarization magic angle spinning (CP-MAS) <sup>13</sup>C NMR and UV-Vis-NIR spectroscopy, and isothermal DSC analysis. PProDOT-25 (prepared at a reaction temperature of 25°C) doped with tribromide ions showed an electrical conductivity of 0.05 S cm<sup>-1</sup> without treatment, which was higher than that of PProDOT-45 (0.002 S cm<sup>-1</sup>) or CP-PProDOT  $(2 \times 10^{-6} \,\text{S}\,\text{cm}^{-1})$  and indicates the effectiveness of low-temperature solid-state polymerization solid-state (SSP). The CP-MAS<sup>13</sup>C NMR spectrum shows the presence of polarons in PProDOT and the strong effect of paramagnetic broadening on the carbon nuclei of the thio-

phenes. DBProDOT was also observed to have a low activation energy, high exothermic reaction, and short interplane distance, which suggest the reaction mechanism of SSP at low temperature. PProDOT deeply infiltrated the 11 µm-thick nanocrystalline TiO<sub>2</sub> layer and functioned as a HTM in I<sub>2</sub>-free ssDSSCs, which was confirmed by SEM analysis. The ssDSSC fabricated with a PProDOT-25 and 550 nm-thick OM-TiO<sub>2</sub> layer exhibited a high cell efficiency reaching 3.5% at 100 mW cm<sup>-2</sup> because of the high conductivity of HTM and the reduced interfacial resistance of the electrode/HTM. Importantly, the obtained efficiency was maintained within  $\pm$ 15% for 1500 h without perfect sealing, which indicates excellent long-term stability of the device with solid-state polymerized HTMs.

# **Experimental Section**

# Materials

3,4-Dimethoxythiophene, 1,3-propanediol, p-toluenesulfonic acid (p-TSA), NBS, iron(III) chloride (FeCl<sub>3</sub>), poly(vinyl chloride) (PVC,  $M_{\rm w} = 97\,000$  g mol<sup>-1</sup>), poly(oxyethylene methacrylate) (POEM), poly-(ethyleneglycol) methyl ether methacrylate ( $M_{\rm p} = 475 \text{ g mol}^{-1}$ ), titanium(IV) isopropoxide (TTIP), hydrogen chloride solution (HCl, 37 wt %), 1,1,4,7,10,10-hexamethyltriethylene tetramine (HMTETA), copper(I) chloride (CuCl), anhydrous toluene, acetic acid, chloroform, ethanol, acetonitrile (ACN), isopropyl alcohol (IPA), 4-tert-butylpyridine (TBP), lithium bistrifluoromethanesulfonimide (LiTFSI), lithium iodide (Lil), 1-methyl-3-propyl-imidazolium iodide (MPII), chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>), and titanium bis(ethyl acetoacetate) were purchased from Aldrich. Tetrahydrofuran (THF), N-methyl-2-pyrrolidone (NMP), and methanol were purchased from J. T. Baker. TiO<sub>2</sub> paste (Solaronix, D20) and N719 dye were purchased from Solaronix. The FTO glass (8  $\Omega$  per square) was purchased from Pilkington Co. Ltd. Silica gel (60-230 mesh, Merck) was used to purify the products. All solvents and chemicals were reagent grade and used as received without further purification.

3,4-Dimethoxythiophene (5.00 g, 34.7 mmol) and excess 1,3-propanediol (13.2 g, 173 mmol) were dissolved in anhydrous toluene (500 mL) and *p*-TSA (0.2 g) was added to the mixture at room temperature under an argon atmosphere. The mixture was heated to 100 °C for 12 h. The mixture was concentrated, washed with 5% potassium hydroxide aqueous solution (500 mL×1) and water (500 mL×2) to remove excess starting materials and extracted with ethyl ether (200 mL×3). The organic layer was dried with anhydrous magnesium sulfate, filtered, and evaporated. The crude white oil was purified by column chromatography by using a mixture of petroleum ether/ethyl ether =4:1 as an eluent to obtain 3.03 g (56%) of product as a white powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =6.53 (s, J=5 Hz, 2H; Th-H), 4.08 (t, J=5 Hz, 4H; -O- $CH_2$ -), 2.20 ppm (m, 2H;  $-CH_2$ - $CH_2$ - $CH_2$ -); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =150.45, 106.37, 71.21, 33.86 ppm.

## Synthesis of the DBProDOT crystal

ProDOT (0.7 g, 4.48 mmol) was dissolved in a mixture of chloroform (150 mL) and acetic acid (50 mL). NBS (1.75 g, 9.86 mmol, 2.2 equiv) was slowly added to the mixture at 0°C under an Ar atmosphere, and the mixture was stirred at 25 °C for 1 h. The organic layer was neutralized with 5% potassium hydroxide solution (250 mL $\times$ 1) and washed with distilled water (250 mL $\times$ 3). The mixture was dried with anhydrous magnesium sulfate, filtered, and then evaporated. The light yellow powder was recrystallized from ethanol to produce white needle-like crystals (1.36 g, 97%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>2</sub>):  $\delta = 4.18$  (t, J = 5 Hz, 4H;  $-O-CH_2-$ ), 2.26 ppm (m, J=5 Hz, 2H; -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 147.53$ , 92.29, 71.46, 33.32 ppm; CP-MAS <sup>1</sup>H NMR (500 MHz, solid state):  $\delta = 5.34$  (O–CH<sub>2</sub>–), 1.97 ppm (–CH<sub>2</sub>–CH<sub>2</sub>– CH<sub>2</sub>--); CP-MAS  $^{13}\text{C}$  NMR (125 MHz, solid state):  $\delta\!=\!150.62,\ 130.73,$ 75.03, 34.06 ppm; EIMS: m/z (%): 316 (52) [M]<sup>+</sup>, 314 (100), 312 (51); HRMS (EI): m/z: calc. for C<sub>7</sub>H<sub>6</sub>Br<sub>2</sub>O<sub>2</sub>S 311.8455 [M]<sup>+</sup>; found 311.8454; elemental analysis calc. (%) for  $C_7H_6Br_2O_2S$  313.9943: C 26.78, H 1.93, O 10.19, S 10.21; found: C 26.88, H 2.00, O 10.00, S 10.36.

## Synthesis of PProDOT Using SSP

DBProDOT (0.2 g) was put in a vial and placed in an oven at room temperature (22–25 °C) for five days, 35 °C for three days, or 45 °C for two days. During the process, the color of the monomer crystal changed from white to black, and brown bromine vapor formed on the vial surface. For the film preparation, DBProDOT dissolved in ethanol (1 wt% solution) was drop-cast on the slide glass by evaporating the solvent at room temperature, and SSP was performed in an oven at 25 °C. The drop-cast quantity was the same amount used for ssDSSCs fabrication. CP-MAS <sup>1</sup>H NMR (500 MHz, solid state):  $\delta$  = 5.44 (–O–CH<sub>2</sub>–), 1.93 ppm (–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–); CP-MAS <sup>13</sup>C NMR (125 MHz, solid state):  $\delta$  = 147.55, 126.36, 74.06, 32.66 ppm.

### Fabrication of the CC-TiO<sub>2</sub> Layer

The 200 nm-thick CC-TiO<sub>2</sub> layer was prepared by spin-coating a titanium bis(ethyl acetoacetate) solution (2 wt% in *n*-butanol) on FTO glass at 2000 rpm for 25 s, followed by calcination at 450 °C for 30 min.

### Fabrication of the OM-TiO<sub>2</sub> Layer

The OM-TiO<sub>2</sub> film was prepared by using an optimized mixture of synthesized amphiphilic PVC-g-POEM graft copolymer, TTIP, water and HCI. HCI was slowly added to TTIP while stirring vigorously, and distilled water was added to the mixture. The molar composition of the mixture was TTIP/H<sub>2</sub>O/HCI = 2:1:1. Separately, PVC-g-POEM graft copolymer (0.05 g) was dissolved in THF (1.5 mL) and added to the mixture (0.6 mL). The final mixture was aged while stirring at room temperature overnight and spin-coated on the FTO glass at 2000 rpm for 20 s (SMSS Delta 80BM spin coater). Upon calcination at 450 °C for 30 min, the organic chemicals were completely removed to produce the OM-TiO<sub>2</sub> thin film.

## Fabrication of I<sub>2</sub>-free ssDSSCs

The I<sub>2</sub>-free ssDSSCs were fabricated by drop-casting a monomer in ethanol onto the photoelectrode and covering with a Pt-coated counter electrode using a previously reported procedure.  $^{\left[ 26,27\right] }$  For the preparation of Pt counter electrodes, a H<sub>2</sub>PtCl<sub>6</sub> solution (7 mM in IPA) was drop-cast on the conductive FTO glass; the glass was heated to 450 °C, which was maintained for 30 min, and then cooled to 30 °C for 8 h. The TiO<sub>2</sub> paste was cast onto the interfacial layer of photoelectrodes coated with CC-TiO<sub>2</sub> or OM-TiO<sub>2</sub> film by using a doctor-blade technique, dried at 50 °C for 30 min, which was followed by successive sintering at 450 °C for 30 min and cooling to 30°C within 8 h. Nanocrystalline TiO<sub>2</sub> films were immersed in the N719 solution (0.5 mm in ethanol) at room temperature for 24 h. The monomer solution was prepared by dissolving DBProDOT in ethanol. The 1 and 3 wt% solutions were directly cast onto the photoelectrodes. After drying the solvent, the DBProDOT-filled TiO<sub>2</sub> photoelectrodes were subjected to SSP to produce PProDOT at 25°C for five days or 45°C for two days. A drop of the mixture solution [MPII (1.0  $\ensuremath{\mathsf{M}}\xspace),$  TBP (0.2  $\ensuremath{\mathsf{M}}\xspace),$  and LiI (0.2  $\ensuremath{\mathsf{M}}\xspace)$  in ethanol] was cast onto the dye-adsorbed TiO<sub>2</sub> photoelectrodes with HTM. After evaporation of the solvent in a vacuum oven, sandwich-type ssDSSCs were fabricated by clipping two electrodes and sealing with epoxy resin. The active area was 0.25  $\text{cm}^2$  (0.5  $\text{cm} \times 0.5$  cm).

## Characterization

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained by using a Bruker Biospin Avance II at 400 and 100 MHz, respectively, using tetramethylsilane (TMS) dissolved in CDCl<sub>3</sub> as a standard. Solid state <sup>1</sup>H and <sup>13</sup>C NMR spectra were acquired at 500 and 125 MHz, respectively, by using a Bruker Avance II with a 4 mm magic angle spinning probe with the spinning speed regulated at 7 kHz. The XRD data was collected by using a Rigaku Ultima Idiffractometer using CuK<sub>a</sub>  $(\lambda = 0.154 \text{ nm})$  radiation. UV-Vis-NIR spectra were obtained by using a Perkin-Elmer Lambda 750 spectrometer. FTIR spectra were collected by using a Bruker Tensor 37 FTIR Spectrometer with attenuated total reflectance (ATR). DSC was performed by using a Netzsch/DSC 200 F3 instrument under N<sub>2</sub> gas flow at a heating rate of 10°C min<sup>-1</sup>, and the DBProDOT monomer was placed in a tightly sealed Netzsch aluminum pan. The temperature was controlled in the isothermal mode at 25, 35, and 45 °C to determine the heat energy absorbed during SSP. Single-crystal XRD data was collected by using a Bruker AXS Smart Apex CCD diffractometer, MoK<sub>a</sub> ( $\lambda = 0.71073$  Å), T = 200 K, installed at the KBSI (Jeonju, Korea). PProDOT-25, PProDOT-45, and CP-PProDOT were pelletized to a 3 mm thickness for conductivity measurements. The conductivity of the samples was measured by using an electrochemical analyzer (CHI624B, CH Instruments Inc.) and a four-point probe

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(Jandel, UK). PProDOT and the dye-adsorbed TiO<sub>2</sub> films were weighed by using a microbalance (Sartorius CPA2P, resolution of 0.001 mg). All DFT calculations were performed using the Gaussian 03 program at the B3LYP/6-31G(d) level.<sup>[44]</sup> Photoelectrochemical performance characteristics were measured by using an electrochemical workstation (Keithley Model 2400) and a solar simulator (1000 W xenon lamp, Oriel, 91193). The light of the lamp was homogeneous (8 inch × 8 inch area) and adjusted by using a calibrated Si solar cell (Fraunhofer Institute for Solar Energy Systems, Mono-Si + KG filter, Certificate No. C-ISE269) to 1 sun (100 mW cm<sup>-2</sup>, AM1.5), and a NREL-calibrated Si solar cell (PV Measurements Inc.) was used to double-check the calibration. IPCE measurements were performed by using a 300 W Xe light source and a monochromator (Polaronix K3100 IPCE Measurement System, McScience). The morphology was observed by performing HR-SEM (SUPRA 55VP, Carl Zeiss).

CCDC 842924 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

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- [1] A. Shah, P. Torres, R. Tscharner, N. Wyrsch, H. Keppner, Science 1999, 285, 692-698.
- [2] J. Zaumseil, H. Sirringhaus, Chem. Rev. 2007, 107, 1296-1323.
- [3] S. Allard, M. Forster, B. Souharce, H. Thiem, U. Scherf, Angew. Chem. 2008, 120, 4138-4167; Angew. Chem. Int. Ed. 2008, 47, 4070-4098.
- [4] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **1990**, *347*, 539–541.
- [5] P. M. Beaujuge, J. R. Reynolds, Chem. Rev. 2010, 110, 268-320.
- [6] S. W. Thomas, G. D. Joly, T. M. Swager, Chem. Rev. 2007, 107, 1339– 1386.
- [7] R. Senadeera, N. Fukuri, Y. Saito, T. Kitamura, Y. Wada, S. Yanagida, Chem. Commun. 2005, 2259–2261.
- [8] P. A. Levermore, L. Chen, X. Wang, R. Das, D. D. C. Bradley, Adv. Mater. 2007, 19, 2379–2385.
- [9] Y. H. Kim, C. Sachse, M. L. Machala, C. May, L. Müller-Meskamp, K. Leo, Adv. Funct. Mater. 2011, 21, 1076–1081.
- [10] R. Charvet, S. Acharya, J. P. Hill, M. Akada, M. Liao, S. Seki, Y. Honsho, A. Saeki, K. Ariga, J. Am. Chem. Soc. 2009, 131, 18030–18031.
- [11] G. Sonmez, H. B. Sonmez, C. K. F. Shen, R. W. Jost, Y. Rubin, F. Wudl, Macromolecules 2005, 38, 669–675.
- [12] A. Kumar, D. M. Welsh, M. C. Morvant, F. Piroux, K. A. Abboud, J. R. Reynolds, Chem. Mater. 1998, 10, 896–902.
- [13] a) B. Kim, J. Kim, E. Kim, *Macromolecules* 2011, 44, 8791-8797; b) J. Kim,
   Y. Kim, E. Kim, *Macromol. Res.* 2009, 17, 791-796.
- [14] B. Winther-Jensen, K. West, Macromolecules 2004, 37, 4538-4543.
- [15] J. Kim, J. You, E. Kim, *Macromolecules* **2010**, *43*, 2322–2327.

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[16] B. Winther-Jensen, D. W. Breiby, K. West, Synth. Met. 2005, 152, 1-4.

- [17] J. Kim, J. You, B. Kim, T. Park, E. Kim, Adv. Mater. 2011, 23, 4168-4173.
- [18] I. Osaka, R. D. McCullough, Acc. Chem. Res. 2008, 41, 1202-1214.
- [19] H. Meng, D. F. Perepichka, F. Wudl, Angew. Chem. 2003, 115, 682–685; Angew. Chem. Int. Ed. 2003, 42, 658–661.
- [20] H. Meng, D. F. Perepichka, M. Bendikov, F. Wudl, G. Z. Pan, W. Yu, W. Dong, S. Brown, J. Am. Chem. Soc. 2003, 125, 15151–15162.
- [21] H. J. Spencer, R. Berridge, D. J. Crouch, S. P. Wright, M. Giles, I. McCulloch, S. J. Coles, M. B. Hursthouse, P. J. Skabara, *J. Mater. Chem.* 2003, 13, 2075 – 2077.
- [22] A. Patra, Y. H. Wijsboom, S. S. Zade, M. Li, Y. Sheynin, G. Leitus, M. Bendikov, J. Am. Chem. Soc. 2008, 130, 6734–6736.
- [23] M. Lepeltier, J. Hiltz, T. Lockwood, F. Belanger-Gariepy, D. F. Perepichka, J. Mater. Chem. 2009, 19, 5167–5174.
- [24] Y. H. Wijsboom, A. Patra, S. S. Zade, Y. Sheynin, M. Li, L. J. W. Shimon, M. Bendikov, Angew. Chem. 2009, 121, 5551–5555; Angew. Chem. Int. Ed. 2009, 48, 5443–5447.
- [25] A. Patra, Y. H. Wijsboom, G. Leitus, M. Bendikov, Chem. Mater. 2011, 23, 896–906.
- [26] a) J. K. Koh, J. Kim, B. Kim, J. H. Kim, E. Kim, Adv. Mater. 2011, 23, 1641– 1646; b) J. Kim, J. K. Koh, B. Kim, J. H. Kim, E. Kim, Angew. Chem. 2012, 124, 6970–6975; Angew. Chem. Int. Ed. 2012, 51, 6864–6869.
- [27] J. Kim, J. K. Koh, B. Kim, S. H. Ahn, H. Ahn, D. Y. Ryu, J. H. Kim, E. Kim, Adv. Funct. Mater. 2011, 21, 4633–4639.
- [28] B. O'Regan, M. Grätzel, Nature 1991, 353, 737-740.
- [29] M. Grätzel, Nature 2001, 414, 338-344.
- [30] P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi, M. Grätzel, Nat. Mater. 2003, 2, 402–407.
- [31] Z.-S. Wang, H. Kawauchi, T. Kashima, H. Arakawa, Coord. Chem. Rev. 2004, 248, 1381–1389.
- [32] a) I. K. Ding, J. Zhu, W. S. Cai, S. J. Moon, N. Cai, P. Wang, S. M. Zakeeruddin, M. Grätzel, M. L. Brongersma, Y. Cui, *Adv. Energy Mater.* **2011**, *1*, 52– 57; b) J. T. Park, D. K. Roh, W. S. Chi, R. Patel, J. H. Kim, *J. Ind. Eng. Chem.* **2012**, *18*, 449–455.
- [33] a) A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, Md. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science* 2011, *334*, 629–634; b) S. H. Ahn, H. W. Kim, S. H. Lee, W. S. Chi, J. R. Choi, Y. G. Shul, J. H. Kim, *Korean J. Chem. Eng.* 2011, *28*, 138–142.
- [34] a) D. Kuang, P. Wang, S. Ito, S. M. Zakeeruddin, M. Grätzel, J. Am. Chem. Soc. 2006, 128, 7732–7733; b) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Chem. Rev. 2010, 110, 6595–6663.
- [35] H. J. Snaith, A. J. Moule, C. Klein, K. Meerholz, R. H. Friend, M. Grätzel, *Nano Lett.* 2007, 7, 3372–3376.
- [36] a) S. Yanagida, Y. Yu, K. Manseki, Acc. Chem. Res. 2009, 42, 1827–1838;
   b) Y. Saito, T. Azechi, T. Kitamura, Y. Hasegawa, Y. Wada, S. Yanagida, Coord. Chem. Rev. 2004, 248, 1469–1478.
- [37] a) K.-J. Jiang, K. Manseki, Y.-H. Yu, N. Masaki, K. Suzuki, Y.-I. Song, S. Yanagida, Adv. Funct. Mater. 2009, 19, 2481–2485; b) Z. Yin, Q. Zheng, Adv. Energy Mater. 2012, 2, 179–218.
- [38] R. Zhu, C.-Y. Jiang, B. Liu, S. Ramakrishna, Adv. Mater. 2009, 21, 994– 1000.
- [39] X. Liu, W. Zhang, S. Uchida, L. Cai, B. Liu, S. Ramakrishna, Adv. Mater. 2010, 22, E150-E155.
- [40] X. Liu, Y. Cheng, L. Wang, L. Cai, B. Liu, Phys. Chem. Chem. Phys. 2012, 14, 7098-7103.
- [41] Y. Hao, X. Yang, M. Zhou, J. Cong, X. Wang, A. Hagfeldt, L. Sun, Chem-SusChem 2011, 4, 1601–1605.
- [42] M. Wang, S. Plogmaker, R. Humphry-Baker, P. Pechy, H. Rensmo, S. M. Zakeeruddin, M. Grätzel, *ChemSusChem* 2012, 5, 181–187.
- [43] H. Zhou, T. Fan, D. Zhang, ChemSusChem 2011, 4, 1344-1387.
- [44] Gaussian 03W, Version 6.1, M. J. Frisch, et al., Gaussian, Inc., Wallingford, CT, 2004.
- [45] S. H. Ahn, J. H. Koh, J. A. Seo, J. H. Kim, Chem. Commun. 2010, 46, 1935–1937.
- [46] S. H. Ahn, H. Jeon, K. J. Son, H. Ahn, W.-G. Koh, D. Y. Ryu, J. H. Kim, J. Mater. Chem. 2011, 21, 1772–1779.

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# **FULL PAPERS**

What a wait for solid state: 2,5-Dibromo-3,4-propylenedioxythiophene (DBProDOT), a new monomer that is a solid at room temperature, has been synthesized to produce poly(3,4-propylenedioxythiophene) (ssPProDOT). I<sub>2</sub>-free solid-state dye-sensitized solar cells with ssPProDOT exhibit exceptional longterm stability (> 1500 h) with an efficiency of 3.5% at 100 mW cm<sup>-2</sup>.



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Room Temperature Solid-State Synthesis of a Conductive Polymer for Applications in Stable I<sub>2</sub>-Free Dye-Sensitized Solar Cells