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A Dual-Polymer Electrochromic Device with High Coloration Efficiency and Fast Response Time: Poly(3,4-(1,4-butylene-(2-ene)dioxy)thiophene)–Polyaniline ECD

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Dedicated to Professor Eun Lee on the occasion of his retirement and 65th birthday

Abstract: A new dual-polymer electrochromic device (ECD) composed of poly(3,4-(1,4-butylene-(2-ene)dioxy)thiophene) (PBueDOT) and polyaniline (PANI) with a hydrophobic molten salt electrolyte has been developed. To build this system, an alkylenedioxy ring in the BueDOT backbone was expanded to include a strongly electron-donating alkylenedioxy bridge, and the thickness and surface morphology of the corresponding PBueDOT film were controlled systematically. Not only the dual-electrochromic-polymer–electrode system, but also the expanded alkylenedioxy ring in the BueDOT backbone, synergistically improved the electrochromic performance. From the coloration efficiency (CE) value calculations, we found that the CE was enhanced up to 930 cm^2 C^{-1}. Furthermore, these ECDs showed an extremely fast response time of less than 80 ms.

Keywords: dual-polymers • electrochromic devices • fast response time • high coloration efficiency • PEDOT

Introduction

Semiconducting conjugated polymers have been widely used as materials in light-emitting diodes,[1] solar cells,[2] electrochromic devices (ECDs),[3] field-effect transistors,[4] and chemo-/biosensors.[5] Among them, poly(3,4-ethylenedioxythiophene) (PEDOT) has been by far the most-extensively studied as a cathode-coloring electrode owing to its small electron band gap ($E_g = 1.6$ eV at 775 nm), low redox potentials (which confer not only exceptional stability to the oxidatively charged PEDOT, but also high conductivity), good optical transparency in the visible spectrum, and fast response time between the neutral and doped states.[6] Based on these advantageous properties, many applications of PEDOT have been rapidly developed.[7] For example, PEDOT was suggested as a promising candidate for electrochromic applications, including smart windows, variable-reflectance mirrors, and optical lenses.[8] However, to meet the increasing demand for ECDs with enhanced electrochromic performance, several attempts have been made to design new PEDOT-based materials.[9] As the most-representative examples, Reynolds and co-workers[10] and Kumar and co-workers[11] synthesized the EDOT analogs like 3,4-propylenedioxythiophene (ProDOT) and 3,4-(1,4-butylenedioxy)thiophene (BuDOT) and studied the general factors influ-

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encing the electrochromic behaviors of corresponding polymer ECDs. As a result, it has been clearly demonstrated that attaching a strongly electron-donating alkylenedioxy bridge across the 3- and 4-positions of the EDOT backbone can prevent linkage defects during electrochemical polymerization and add electron density to the aromatic ring. This is the reason why the oxidation potentials of the monomer and polymer were significantly lowered and why the stability of the oxidized state and band-gap could be altered.[10–11,12e] Moreover, they found that larger alkylenedioxy rings and more-bulky substituents resulted in the separation of the polymer backbones from each other upon polymerization, which facilitated a more-expanded morphology and allowed the counter-ions to be transported more easily within the film. However, whilst substantial research has been performed on EDOT derivatives, there are still some drawbacks, such as poor synthetic processes and low monomer yields. In addition, the syntheses of EDOT derivatives with rings larger than 7-membered remain a challenge owing to their associated torsional, transannular, and large-angle strain.

Herein, we report the first large-ring EDOT derivatives composed of eight-membered rings and substituent with high synthetic yields. Moreover, of the derivatives, the 3,4-(1,4-butylene-(2-ene)dioxy)thiophene (BueDOT) was electrochemically polymerized on indium-doped tin-oxide (ITO) glass with different thicknesses to identify the optimum film-thickness and surface morphology of the electrode for their high electrochromic properties. In order to maximize the electrochromic properties, we constructed a dual-polymer ECD, in which poly-BueDOT (PBueDOT) and polyaniline (PANI) were employed as complementary coloring electrodes. It has been suggested that the dual-polymer ECD system gives rise to a synergistic effect on electrochromism owing to its electrochemical reversibility and compatibility between the polymer electrodes.[12] The electrochemical and optical behaviors of the dual-polymer ECDs were investigated quantitatively with respect to the thickness and surface morphology of new PEDOT-derivative electrodes.

Results and Discussion

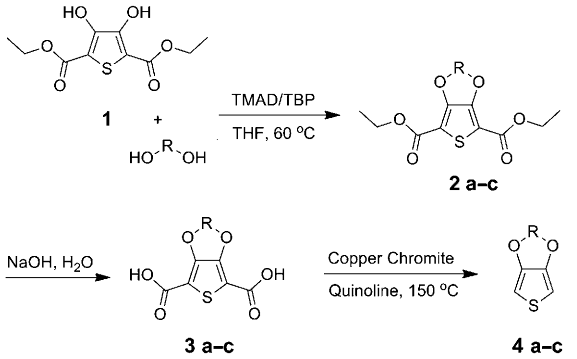
New EDOT-Derivative Series

The most-common industrially applied synthetic route for EDOT derivatives was the double Williamson etherification of 3,4-dihydroxy-2,5-thiophenedicarboxylic acid diethyl ester with 1,2-dihaloethanes under basic conditions.[6,10a–c] However, recently, in order to increase yields and the number and/or the length of functional groups, as well as stereochemical tolerance, the Mitsunobu reaction[13] has been used as a key step in the synthesis of a series of EDOT or ProDOT derivatives because it allows the conversion of primary and secondary alcohols with nucleophiles into a variety of functional groups, such as esters, using a redox combination of a trialkyl or triarylphosphine and a dialkyl azodicarboxylate. In reports by the Reynolds[10d,g] and Bäuerle groups,[14] the key step was the Mitsunobu reaction between diols and 3,4-dihydroxy-2,5-thiophenedicarboxylic acid diethyl ester **1** by means of diethylazodicarboxylate/triphenylphosphine (DEAD/TPP) and diisopropyl azodicarboxylate/tributylphosphine (DIAD/TBP), respectively. However, the scope of the Mitsunobu reaction is limited by the steric congestion of the alcohols and the acidity of the nucleophiles ($pK_a <$ 13).

To overcome these drawbacks, Tsunoda et al. invented a versatile Mitsunobu reagent system of *N,N,N′,N′*-tetramethylazodicarboxamide (TMAD) and tributylphosphine (TBP) that was successful for nucleophiles with a pK_a value of up to 13.5 and for a variety of steric environments.[15] This TMAD/TBP system successfully provided large-ring EDOT derivatives (Scheme 1, Table 1). The 8-membered compounds **2a–c** were obtained in excellent yields; these were then saponified in NaOH/H_2O followed by decarboxylation with copper chromite in quinoline to yield the final monomers **4a–c**.

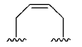
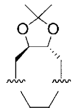
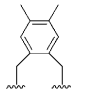
Abstract in Korean:

본 논문에서는 새로운 PEDOT 유도체를 합성하여 이를 박막화 하고, 상호보완적인 PANI 박막과의 조합을 통해 향상된 전기변색 특성을 (변색효율: 930 cm² C⁻¹, 반응속도: 약 80 ms) 가지는 고분자 전기변색소자를 개발하였다.



Scheme 1. Mitsunobu reaction of **1** with 1,*n*-alkyl diols for the large ring 3,4-ethylenedioxythiophenes (EDOTs).

Table 1. Mitsunobu reaction of **1** with 1,*n*-alkyl diols for the large-ring 3,4-ethylenedioxythiophenes (EDOTs).

Entry	R	Product	Yield [%][a]	M.p. [°C]
1		**2a**, **3a**, **4a**	78, 82, 66	80, >250, ~[b]
2		**2b**, **3b**, **4b**	86, 82, 73	146, >250, ~[b]
3		**2c**, **3c**, **4c**	97, 69, 44	148, >250,116

[a] Yield of isolated product. [b] Product was a pale-yellow oil.

Electrochemical- and Electrochromic Properties of PBueDOT ECDs

Of the synthetic monomers investigated, poly(3,4-(1,4-butylene-(2-ene)dioxy)thiophene (**4a**; PBueDOT) films were only obtained from the potentiostatic method by applying $E=1.4$ V for $t=10$–30 s. This result shows that monomers with both eight-membered rings and other substituents on the EDOT backbone are difficult to polymerize onto ITO glass because of the low planarity of the alkylenedioxy ring caused by the steric hindrance of the terminal groups and poor adhesion to the ITO glass.[16] Considering the above factors, steric hindrance and adhesion, upon electrochemical polymerization of monomers onto ITO, we then selected BueDOT as a model precursor to synthesize the polymer-ECD and ascertained their physical and electrochromic properties.

To elucidate the optimum thickness and surface morphology of the electrode for high-quality ECDs, the thickness of the deposited PBueDOT films was controlled by varying the deposition time of the electrochemical polymerization (10 s, 20 s, and 30 s, hereafter abbreviated as PBueDOT10, PBueDOT20, and PBueDOT30, respectively). First, the thickness and the detailed surface morphology of the PBueDOT layers were investigated by cross-sectional scanning electron microscope (SEM). As shown in Figure 1 (left), the thickness of the PBueDOT10, PBueDOT20, and PBueDOT30 layers was determined to be approximately 100, 230, and 380 nm, respectively; this result indicates that the PBueDOT layer became thicker upon lengthening the electrochemical polymerization time. Furthermore, no defects were observed between the ITO substrate and the PBueDOT layer, which suggests that the layer of electroactive polymer adhered well to the electrode surface. Figure 1 (right) shows a surface morphology comprised of bundled rod-like structures for the PBueDOT layers. Based on the formation mechanism for the interconnected and branched networks on the surface of the layers, as well as the thickness of the deposited polymer film, Figure 1 (right) could be explained as follows:[17] 1) After a small amount of PBueDOT was deposited, the surface began to roughen, leading to an increase in surface area and porosity (Figure 1 a). 2) Upon further PBueDOT deposition, the surface became increasingly rough and eventually formed a loosely bound open structure, resulting in a highly porous surface area (Figure 1 b). 3) Afterwards, as the deposition-time increased, the pores were filled with additional PBueDOT, leading to a decrease in surface roughness and porosity (Figure 1 c). It has also been reported that an increase in surface area and pore growth of the electrode causes a lowering in the impedance, as well as an improvement in conductivity. On the other hand, if the surface morphology of the electrode begins to become dense, the lithium diffusion onto the film becomes more difficult.[17] Therefore, it is important to properly control the thickness and surface morphology of the electrode. In this study, PBueDOT20 showed a maximum surface area corresponding to the highest conductivity. This would lead to a fast response time and an effective color change with a small amount of power consumption, which is of particular importance for display devices.

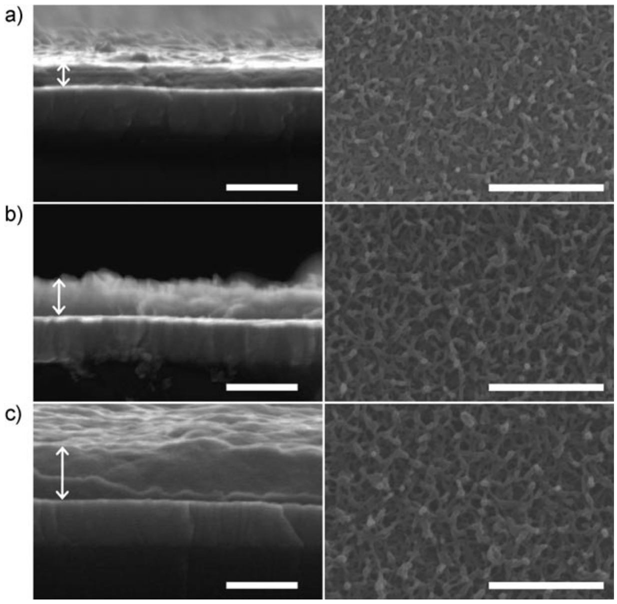


Figure 1. The thickness of PBueDOT electrodes with different electrochemical polymerization times (left; scale bar: 500 nm, magnification: 70 K) and the surface morphology (right; scale bar: 1 μm, magnification: 70 K): a) PBueDOT10, b) PBueDOT20, and c) PBueDOT30.

To investigate the influence of structural modification of the PEDOT backbone on electrochemical and electrochromic properties, we have studied the cyclic voltammetry (CV) profiles and UV/Vis absorbance/transmittance spectra for the PBueDOT electrodes. (see the Supporting Information, Figure S1, Figure S2, and Figure S3) As revealed by the voltammograms, all of the PBueDOT electrodes showed similar curve shapes to that of the PEDOT electrode, thus suggesting that as the potential of the electrode changed, the intrinsic redox reactions of PBueDOT were found to be similar to that of PEDOT. However, upon replacing the alkylene bridge of the EDOT backbone with a butylenes group, positive shifts of two consecutive oxidation (approximately −0.8 V and 0 V) and reduction (approximately −0.9 V and −0.3 V) peak potentials were induced, thereby indicating that PBueDOT has a higher ionization potential than PEDOT, owing to the higher resistance resulting from the large alkylene dioxy rings between the polymer backbones, and that the neutral state should therefore be more stable in air.[9e] On the other hand, for all of the PBueDOT electrodes, the absorbance of π–π* transition was essentially similar to that of the PEDOT electrode, as the color changed from an almost transparent sky blue color in the oxidized state to opaque dark blue color in the neutral state.[8–9,18] Furthermore, the obtained optical band-gap onsets of approximately 1.7 eV (725 ~ 745 nm in absorption edge) were nearly identical to the PEDOT, thereby implying that the ring-expansion of an alkylenedioxy ring in the

EDOT backbone had little influence on the nature of the polymer.[9,18]

From the CV and UV/Vis transmittance analysis, the coloration efficiency (CE, η)—defined as the ratio of the change in transmittance with log scale at a specified wavelength (optical density change, ΔOD) to the integrated electronic charge (Q)—was calculated for the individual PBueDOT devices,[12] as summarized in Table 2. The CE values for PBueDOT10, PBueDOT20, and PBueDOT30 were determined to be 88.8 cm^2 C^{-1}, 147 cm^2 C^{-1}, and 120 cm^2 C^{-1}, respectively, thereby indicating that highly porous PBueDOT20 exhibited the highest optical contrast with a small amount of charge injection or extraction, thereby allowing the faster switching rates in a narrow potential window.[10e] This result is surely due to the fact that the thickness and surface morphology of the electrode can influence the electronic interaction between intercalated lithium ions and coloration layer. In this regard, the electrochemical polymerization time for the PBueDOT electrode could be optimized as 20 s, with a film thickness of approximately 230 nm, which is in good accordance with the SEM results. Expansion of the alkylenedioxy ring within the EDOT backbone was made in an attempt to improve the optical properties of the conducting polymer ECD, no remarkable enhancement was observed in the CE value when compared to PEDOT or PEDOT-derived ECDs reported previously.[9e,10a–b,e]

Table 2. Transmittance deference (ΔT), integrated charge (Q), optical density (ΔOD), and coloration efficiency (η) of the devices in this study.

λ[a]	ΔT [%]	Q	ΔOD[b]	CE, η [cm^2 C^{-1}]
PBueDOT10	24	0.63	0.15	88.8
PBueDOT20	45	0.68	0.43	147
PBueDOT30	33	0.72	0.40	120
PBueDOT10-PANI	59	–	0.60	–
PBueDOT20-PANI	67	0.92	1.0	930
PBueDOT30-PANI	49	–	1.2	–

[a] $\lambda = 613$ nm for the single PBueDOT ECDs and $\lambda = 630$ nm for the dual polymer PBueDOT - PANI ECDs. [b] The optical densities (ΔOD) were measured under potentiostatic condition.

PBueDOT-PANI Dual-Polymer ECDs

It has been suggested that a dual-polymer ECD system using two complementary electrochromic electrodes could enhance electrochemical and electrochromic performances, such as optical contrast, switching time, and stability.[12] Therefore, in this study, a polyaniline (PANI) film was used as a complementary anodic electrode to the PBueDOT film during the oxidation and reduction processes.[12a–b] The thickness of the PANI layer was fixed to approximately 100 nm, which was found to be the optimal thickness based on our previous studies.[17a] The complementary electrochemical and electrochromic properties of the present dual-polymer ECDs were also investigated by CV profiles and UV/Vis transmittance spectra, as summarized in Table 2.

Figure 2 shows the UV/Vis transmittance spectra, which were obtained by applying a potential range between −0.6–0.8 V for 30 seconds/half cycle. The voltage was controlled using the same method as described above. The percentage transmittance difference (ΔT) at 630 nm for the PBueDOT20-PANI ECD with the best optical contrast among the samples was determined to be 67 %, which was significantly higher than 45 % for the single PBueDOT20 ECD; this result indicated that the dual-polymer ECD could show a synergetic electrochromic effect when they were properly coupled.

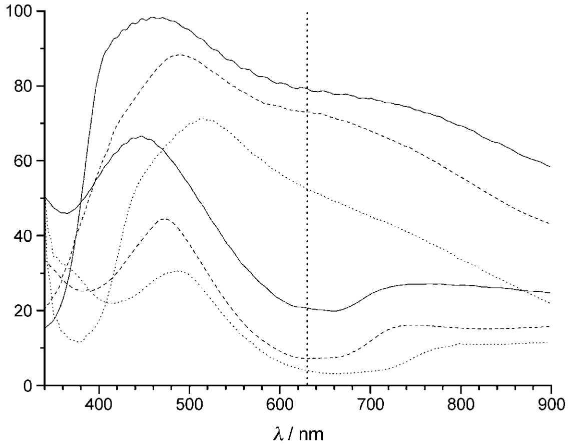


Figure 2. Percent UV/Vis transmittance (T) spectra of the PBueDOT-PANI ECDs. The solid lines (–), dashed lines (–), and dotted lines (•••••) represent the PBueDOT10-PANI, PBueDOT20-PANI, PBueDOT30-PANI ECDs, respectively. The upper and lower lines show the bleached and colored states for each sample.

As can be seen in Figure 3, 600 successive CV cycles were scanned for the PBueDOT20 and PANI films as working and counter electrodes, respectively, between −0.6 V–0.8 V at a scanning rate of 50 mV s^{-1}. As revealed by the evolution of the voltammograms, the PBueDOT20-PANI electrodes

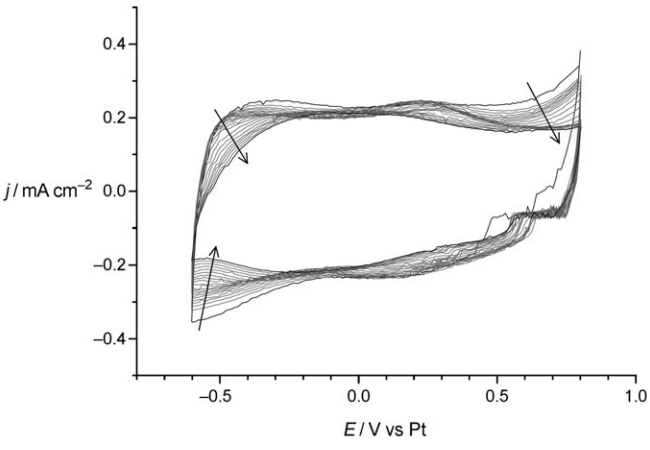


Figure 3. Cyclic voltammograms for the PBueDOT20-PANI electrodes as a function of repeated scans. The black cycles represent the first and the last (600th) scans.

exhibited typical characteristics of a dual-polymer ECD, such as broad peak potentials of oxidation and reduction within a common and narrow voltage range.[9c,17a] Indeed, these electrodes nearly maintained their initial electroactivity even after 600 cycles. One thing to note here is that no peaks were seen for side-reactions, indicating that the PBueDOT20 and PANI electrodes are an excellent complementary pair in the electrochemical and electrochromic reactions, and thereby allowing an increase of the durability of ECD.[19] The high Q value of 0.93 for the PBueDOT20-PANI electrodes is an evidence that the reversible redox reactions are indeed occurring between these two conducting polymer electrodes (see the Supporting Information, Figure S4).

The CE and response-time analysis provide direct evidence for the advantages of not only the dual-polymer ECD system but also the structural modifications in EDOT. According to the CE value calculation from the results of UV/Vis transmittance spectra and CV profiles, a CE value of 930 $cm^2\,C^{-1}$ for the PBueDOT20-PANI ECD was calculated, and found to be superior to that for the PEDOT-PANI ECD or other PEDOT-based ECDs reported previously.[10–12,18] Such an enhancement of CE could be attributed to the fact that the current amplitude of the PBueDOT20-PANI electrodes was almost 10 times higher than that of PEDOT-PANI electrodes, thereby implying that a smaller electronic charge was required to affect bleaching or coloration of the present sample, which would lead to faster switching rates and more-pronounced optical changes in a narrow potential window.[10b,e]

Finally, optical-switching studies for the PBueDOT20-PANI ECDs were carried out by electric-circuit analysis. For this experiment, the voltage for a square-wave function (($\pm$0.9) V, 0.1 Hz) was employed in mimic switching with a function generator. The dynamic profile of electric voltage across the present samples corresponding to the current through a capacitor and a resistor was monitored and digitalized through an oscilloscope. According to the theory of determining an optical response based on the electric current generated into the device during switching,[12a,20] the current-response time for all samples of PBueDOT20-PANI ECDs was reproducibly determined to be approximately 80 ms (Figure 4), which was significantly faster than that for the previous PEDOT-PANI ECD or other conducting polymer ECDs.[9–11] This observation can presumably be attributed to the ease of charge transport during doping/de-doping resulting from porous polymer film morphology.[10b,18] Reviewing these results, we were able to greatly enhance the electrochemical and electrochromic performances of a PEDOT-based electrode by expanding the alkylenedioxy ring in the EDOT backbone.

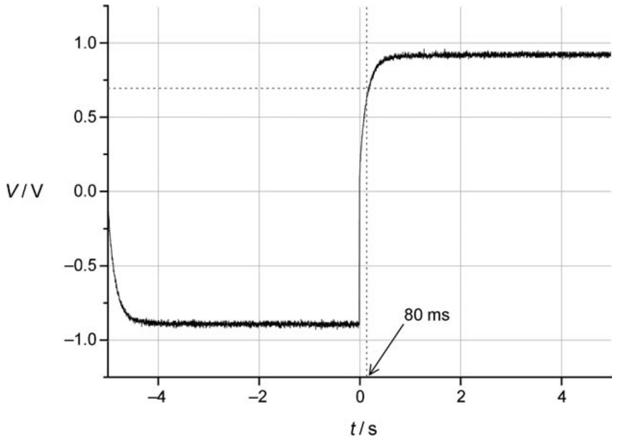


Figure 4. Dynamic voltage profile across the PBueDOT20-PANI ECDs.

Conclusions

A new series of large-ring alkoxy-substituted EDOT cyclic analogs was synthesized successfully by a Mitsunobu reaction, which provides a straightforward high yielding route to modifying the EDOTs. The molecular structures of the derivative series were characterized by ^1H and ^{13}C NMR spectroscopy, and by analysis of the melting point and mass spectra. Of the series, a single polymer 3,4-(1,4-butylene-(2-ene)dioxy)thiophene (PBueDOT) ECD was fabricated by electrochemical polymerization. Spectro-electrochemical analysis revealed that this ECD had an electronic band-gap of ca. 1.7 eV (725~745 nm) and a coloration efficiency (CE) of 147 $cm^2\ C^{-1}$, which was similar to the parent PEDOT ECD.

In the second part of the study, a dual-type complementary colored polymer ECD with enhanced coloration efficiency and fast response time was developed by employing the PBueDOT cathode with a controlled thickness and PANI anode, in combination with a hydrophobic lithium electrolyte. As expected, increasing the alkylenedioxy ring-size within the EDOT backbone improved the EC properties. In the optimal case where the 230 nm thickness PBueDOT electrode was used, the PBueDOT20-PANI ECD showed an ideally matched integrated charge of $Q = 0.93$ between −0.6 V and 0.8 V, a noticeable increase in coloration efficiency of 930 $cm^2\ C^{-1}$, and a faster than 80 ms in response time. Further investigations to enhance the optical contrast and long-term stability of a conducting-polymer-based ECD are underway, with an ultimate goal of constructing high quality ECDs for various optical-device applications.

Experimental Section

Characterization of 3,4-Ethylenedioxythiophene (EDOT) Derivatives

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Flash chromatography was carried out on silica gel 60 (230–400 mesh ASTM; Merck). Thin layer chromatography (TLC) was carried out using Merck 60 F^{254} plates with a thickness of 0.25 mm. Preparative TLC was performed using Merck 60 F^{254} plates with a thickness of 1 mm. Melting points were measured using a Büchi 530 melting point apparatus. ^1H NMR and ^{13}C NMR spectra were recorded using Bruker 250 MHz and Varian 500 MHz. Chemical shifts were given in ppm and coupling constants (J) in Hz.

*General Procedure for the Mitsunobu Reaction of Thiophene **1** and Diols*

3,4-dihydroxy-2,5-thiophenedicarboxylic acid diethyl ester **1** (130 mg, 0.5 mmol), diol (0.5 mmol), and tributylphosphine (TBP; 0.31 mL, 1.26 mmol) were added to tetrahydrofuran (THF; 5 mL) in a two-necked flask. With the exclusion of light, the system was then purged with argon. *N*,*N*,*N′*,*N′*-Tetramethylazodicarboxamide (TMAD; 0.215 g, 1.25 mmol) was dissolved in THF (10 mL) and added to the above solution over a period of 30 min via syringe. After the addition, the mixture was warmed to 60 °C for 36 h. The solvent was then removed under reduced pressure. The crude product was purified by column chromatography on silica gel (SiO_2, CH_2Cl_2) to give **2** as a white solid.

2a: 78 % yield. m.p. 80 °C. ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 1.25$ (t, $J = 7.1$ Hz, 6H), 4.20 (m, $J = 7.1$ Hz, 4H), 4.95 (d, $J = 3.3$ Hz, 4H), 5.87 ppm (m, $J = 3.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 13.98$, 60.91, 69.35, 117.48, 129.67, 150.45, 160.17 ppm. HRMS (EI) calcd for $C_{14}H_{16}O_6S$ $[M]^+$ 312.0668, found 312.0670.

*General Procedure for the Preparation of **3***

Under argon, **2** (2.4 mmol) and NaOH (0.4 g, 10 mmol) were stirred in water at 90 °C for 12 h. The resulting solution was cooled to room temperature and acidified with HCl (1.0 M) to precipitate a gray solid. The product was filtered, washed with water, and dried under vacuum to give **3**.

3a: 82 % yield. m.p. > 250 °C. ^1H NMR ([D_6]DMSO, 250 MHz): $\delta = 5.02$ (d, $J = 3.2$ Hz, 4H), 6.03 (m, $J = 3.2$ Hz, 2H), 13.36 ppm (s, 2H). ^{13}C NMR ([D_6]DMSO, 62.5 MHz): $\delta = 69.20$, 118.15, 129.92, 150.03, 161.49 ppm. HRMS (FAB) calcd for $C_{10}H_8O_6S$ $[M]^+$ 256.0042, found 256.0043. DMSO = dimethyl sulfoxide.

*General Prodedure for the Preparation of **4***

3 (1.7 mmol) and copper chromite (0.13 g) were heated in quinoline at 150 °C for 20 h under argon. After cooling, the mixture was poured into an excess of HCl (1.0 M). The product was extracted with ether and washed with HCl (1.0 M) and water. The ether was removed under reduced pressure after drying the organic layer over anhydrous sodium sulfate. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/*n*-hexane, 1:1, v/v) to give **4**.

4a: Pale-yellow oil in 66 % yield. ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 4.87$ (d, $J = 3.3$ Hz, 4H), 5.90 (m, $J = 3.3$ Hz, 2H), 6.53 ppm (s, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 69.59$, 106.77, 129.60, 147.35 ppm. HRMS (EI) calcd for $C_8H_8O_2S$ $[M]^+$ 168.0245, found 168.0247.

Characterization of PBueDOT and PBueDOT-PANI ECDs

The physical, electrochemical, and optical characteristics of the electrodes were investigated by scanning electron microscopy (SEM; Hitachi S-4300), a potentiostat/galvanostat (WonATech WPG100), UV/Vis spectrophotometry (Perkin–Elmer lambda 35), and using electric circuit components such as a function generator and oscilloscope.

Preparation of PBueDOT and PANI ECDs

We prepared the $4.0 \times 2.5\ cm^2$ sized indium-doped tin oxide glass (ITO, Samsung Corning, ca. $19\ \Omega\,sq^{-1}$) as an electrode substrate by cleaning with a KOH solution (0.5 M) and deionized water, with subsequent drying under nitrogen gas. Copper-conducting tape (bought from 3M) was then attached to one side of the ITO glass to serve as a bus bar. Three electrodes were used for the electro-polymerization of conducting monomers: ITO glass as a working electrode, fluorine-doped tin oxide (FTO, Solems, ca. $15\ \Omega\,sq^{-1}$) glass as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode.

To fabricate the PBueDOT electrode, its monomer was electrochemically polymerized onto ITO glass using a deposition solution consisting of BueDOT (20 mM) monomer and tetrabutylammonium perchlorate (TBAP; 0.1 M) in acetonitrile under deposition conditions of 1.4 V (vs. SCE reference; all potentials in this study were quoted with respect to the reference) for various intervals of 10 s, 20 s, and 30 s.

The polyaniline film was also fabricated by electrochemical polymerization onto ITO glass in a deposition solution including aniline monomer (0.5 M) and H_2SO_4 (1.0 M) with deionized water under the deposition condition of 0.75 V for 60 s.[12a] All electrodes were then washed repeatedly with acetonitrile to remove the remaining monomer and oligomer on the surface.

Finally, a dual-polymer ECD (ITO | PBueDOT | | PANI | ITO, PBueDOT-PANI ECD) was prepared by assembling PBueDOT and PANI electrodes with the hydrophobic lithium electrolyte (hereafter abbreviated as LiTFSI-EtMeImTFSI), which was synthesized by mixing 10 wt % of lithium trifluorosulfonimide ($Li(CF_3SO_2)_2N$, Li TFSI) and hydrophobic molten salt (ethylmethylimidazolium trifluorosulfonimide, 1,3-EtMeIm TFSI).[21]

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