Supporting information

Oligo(3-methoxythiophene)s as Water-Soluble Dyes for Highly Lustrous Gold- and Bronze-Like Metal-Effect Coatings and Printings

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Table of Contents

Supplementary Note
1. Materials S2
2. Comment on the Dopant Species S2
3. General Instrumentation and Analytical Methods S3
4. Instrumentation and Method of Film Characterization. S2
5. Formation of Stain Region S3
6. Coloration of Oligomer Powder S3

Supplementary Discussion
7. $^1$H NMR and FT-IR Measurements of Oligomers S4
8. GPC analyses of Oligomers S6
9. EDX Analyses of Films S8
10. External Appearance of Coating Films under a Low Illumination Condition S9
11. Cross-Sectional Analyses of Films S9
12. Preparation and Optical Characterization of Coating Solutions S10
13. Preparation of Samples for XRD Measurements S13
14. Thermogravimetric Analysis S14
15. Measurements of Optical Constants for Films Subjected to Dehydrating Treatments S14
16. Dissolution Behavior of Films with and without the Dehydrating Treatments S16
17. Effect of Dehydration Treatment on the Molecular Orientation Characteristic in Film 2 S17
18. Electric Conductivity of Films S18
19. Supplementary References S19

Supplementary Movie S1 file description
20. Caption for Movie S1 file S22
Supplementary Note

Materials. 3-Methoxythiophene (>98%) was purchased from Wako Pure Chemical Industries, Ltd. Anhydrous iron(III) chloride (Wako Pure Chemical Industries, Ltd., >95%) and iron(III) chloride hexahydrate (Kanto Chemical Co., Inc. >99%) were used as oxidizing agents for oligomerizing the 3-methoxythiophene. Methanol (>99.8%) and acetonitrile (>99.7%) were obtained from Kanto Chemical Co., Inc. Distilled-deionized water and nitromethane (>98.0%, Tokyo Chemical Industry) were used as solvents for the coating solutions. The glass plates (S1225, Matsunami Glass Industry) were cleaned by sonication in acetone for 10 min prior to use. The 0.1-μm-thick layers of metallic gold and copper were deposited on individual glass plates by using a vacuum-evaporation system (VPC-260F, ULVAC KIKO Inc.).

Comment on the Dopant Species. It may be assumed that the concentration of FeCl₃ having high reaction activity may be always higher in an acetonitrile solution containing anhydrous iron (III) chloride than in the solution containing iron (III) chloride hexahydrate during the oligomerization reaction. This assumption is made by considering that the crystal waters in iron (III) chloride hexahydrate interact with a central iron ion and inhibit the reaction with 3-methoxythiophene and that the crystal waters gradually dissolve in an acetonitrile solvent with the lapse of time, resulting in gradual release of active FeCl₃ into the acetonitrile solution. The released FeCl₃ will be consumed by the reaction with 3-methoxythiophene and its concentration may be kept low. On the other hand, the concentration of Cl⁻ in the solution increases as the following oligomerization reaction proceeds:

\[(n \cdot \text{MeOT})^{n+} + \text{MeOT} + 2\text{FeCl}_3 \rightarrow \{(n+1) \cdot \text{MeOT}\}^{(n+1)+} + 2\text{H}^+ + (2-x)\text{Cl}^- + 2\text{FeCl}_2\]

where MeOT, n, and x denote 3-methoxythiophene unit, the degree of oligomerization, and doping level, respectively. It is reported that FeCl₄⁻ is formed in water and ether by the following reaction:\(^{1}\)

\[\text{HCl} + \text{FeCl}_3 \rightarrow \text{HFeCl}_4\]

In addition, the formation of HFeCl₄ is promoted with a higher ratio of Cl⁻/Fe³⁺ in water and water/ethanol mixed solvent systems,\(^{2}\) indicating that the lower the concentration of active FeCl₃, the more HFeCl₄ is generated. Thus, for the oligomerization using iron (III) chloride hexahydrate, HFeCl₄ may be easily generated and FeCl₄⁻ was also doped in Oligomer 2 together with Cl⁻, while for the oligomerization using anhydrous iron (III) chloride, FeCl₄⁻ may be hardly produced due to the high concentration of active FeCl₃ (i.e., low ratio of Cl⁻/Fe³⁺), leading to the exclusive doping of Cl⁻ in Oligomer 1.

General Instrumentation and Analytical Methods. The FT-IR transmission spectra of samples (KBr pellets) were recorded using a Jasco FT/IR-410 spectrometer. Gel permeation chromatography
(GPC) measurements were conducted using a Waters Corporation system equipped with a PDA 996 photodiode array detector (UV 270 nm) and two Shodex KF-806M columns (Showa Denko). 1-Methy-2-pyrrolidone (for high performance liquid chromatography, procured from Kanto Chemical Co., Inc.) was used as the eluent containing 0.01 M lithium bromide (elution rate, 0.4 ml min⁻¹); polystyrene standards were used for calibration. UV-vis absorption measurements were carried out using a Hitachi U-3000 spectrophotometer.

**Instrumentation and Method of Film Characterization.** The contents of sulfur, chlorine, and iron were determined by energy dispersive X-ray (EDX) analysis using a scanning electron microscope (JEOL, model JSM-6510A) equipped with an EDX unit (JED-2300 EDS); the doping level, defined as the atomic concentration ratio Cl/S, was calculated. The acceleration voltage, integration time, and working distance were set to 15 keV, 180 s, and 10 mm, respectively. The analyzed area of the EDX measurements in this study was taken as about 2 mm × 2 mm. Such large-area analyses should average the distribution of elements. UV-vis reflection spectra were obtained using a JASCO MSV-370 spectrometer in which the incident and reflection angles were at 23° from the vertical position. The spectra were recorded at room temperature using an evaporated aluminum film as the reference material. Observations of films were made using an optical microscope (VHX-5000, KEYENCE). The lustrous feature of the films was demonstrated by the optical micrographic images. The illumination was carried out using a ring type lighting system attached to the microscope. In taking photographs of films, the distance between the light source and the sample, the illumination angle, and the photographing angle were adjusted so as to become almost the same. Out-of-plane X-ray diffraction (XRD) measurements were performed using a diffractometer (X’Pert MRD, Malvern Panalytical) equipped with a CuKα (λ = 1.5406 Å) source in the 2θ/ω scan mode. The electric conductivity of the films was measured by a four-point-probe method using a resistivity meter (Loresta-GP MCP-T600 with an MCP-TP06P probe, Mitsubishi Chemical Analytech). Each electric conductivity value was averaged from five measurements made at different positions on the film surface. The thickness of the film was measured using a surface profile measuring system (Dektak 3030, Sloan, now Veeco).

**Formation of Stain Region.** During the drying process, after casting the coating solutions, the solutions were dried from the periphery to the center of the glass plate. The colors within the central regions of Films 1 and 2 were reddish brown and reddish purple, respectively. Additionally, the central regions displayed a large surface roughness and no luster. The drying process can be explained by the mechanistic model proposed by Kajiya *et al.*³ They observed the drying process of a polymer solution drop on a substrate in detail and revealed that the process took place in the following three stages. First, the droplet evaporates and the contact angle decreases with the
contact line fixed. Second, the droplet shrinks, keeping the contact angle constant. Finally, the contact line is pinned and the droplet starts to be deformed. This final stage involves the piling of the polymer by the outward capillary flow and the buckling of the crust layer. These processes are accompanied by the formation of a dimple around the droplet center, depending on the solution and ambient conditions. The formation of the center parts of Films 1 and 2 can be reasonably explained on the basis of the above model.

**Coloration of Oligomer Powder.** When Oligomer 3 is used, an edge-on dominant film and a face-on dominant film were both produced. As reported, they display a gold-like color and a reddish-purple color with poor luster. Therefore, it can be assumed that Oligomer 1 can also produce an edge-on lamellar crystallite structure displaying a gold-like color and a face-on lamellar crystallite structure displaying reddish-purple color. In addition, it is thought that the edge-on lamella crystallites and face-on lamella crystallites are present in equal proportions in the powder of Oligomer 1. Therefore, based on the principle of additive mixture of colors, Oligomer 1 powder may appear to be brown since color mixing of reddish-purple and yellow provides brown (the gold-like color is approximately yellow); this supports the observation that Oligomer 1 powder presented with a brown color.

**Supplementary Discussion**

**H NMR and FT-IR Measurements of Oligomers.** Oligomer 1 and Oligomer 2 were dissolved in DMSO-$d_6$, and the $^1$H NMR spectra were recorded. According to previous reports, the spectra were recorded after the dissolution state reached equilibrium (roughly three days after solution preparation). Figure S1 shows the spectra of Oligomer 1 (a) and Oligomer 2 (b). These spectra exhibited peaks assigned to the methoxy protons (4.02 ppm) and the aromatic protons (7.16 ppm). These assignments were based on the chemical shifts and integration area of the proton peaks. Spectra c and d in Figure S1 show the expanded NMR spectra in the regions occupied by the methoxy protons and aromatic protons of Oligomer 1 and Oligomer 2, respectively. The methoxy peak has a shoulder, indicating that the oligomers are composed of a mixture of head-to-tail (HT) and head-to-head (HH) linkages along the main chain of the oligomer. The aromatic proton peak has a poor S/N ratio, indicative of a likely composition of four triads (HT-HT, HT-HH, TT-HT, and TT-HH triads) according to both previous studies on poly(3-alkylthiophene) and the above result on the methoxy protons. The small signal at ~6.5 ppm is assumed to correlate with the 2-position on the terminal 5-substituted 3-methoxythiophene ring; this assumption was based on the $^1$H NMR spectrum of the 3-methoxythiophene monomer. The even smaller signal at ~8.1 ppm may be
assigned to the 5-proton on the terminal 4-substituted 3-methoxythiophene ring, estimated based on the $^1$H NMR chemical shift using a ChemNMR program in a CS ChemBioDraw Ultra version 13.0 (PerkinElmer Co.). The complete assignment of the aromatic proton signals should be performed after obtaining high-resolution two-dimensional spectra. Studies to characterize the regiochemistry of the oligomers are planned in the near future. These NMR results strongly suggest that the oligomers are oligo(3-methoxythiophene)s. The signals at 2.55 and 3.40 ppm in spectra a and b are attributed to the residual protons of both DMSO and water, respectively.

Curves a, b and c in Figure S2 show the FT-IR spectra of Oligomer 1, Oligomer 2 and 3-methoxythiophene monomer, respectively. The $C_\beta$-H in-plane deformation band at 1065 cm$^{-1}$ was observed in all spectra; however, the $C_\alpha$-H in-plane bending peaks at 1238 and 1158 cm$^{-1}$,

![Figure S1. $^1$H NMR spectra of the DMSO-d$_6$ solutions prepared by dissolving (a) Oligomer 1 and (b) Oligomer 2; the expanded $^1$H NMR spectrum of methoxy and aromatic protons for (c) Oligomer 1 and (d) Oligomer 2.](image-url)
visible in curve c, were not observed in curves a and b. The peak at 1258 cm⁻¹ – observed in all spectra – is assigned to the C-O-C stretching of the methoxy group.¹⁵ These results are consistent with the assumption that the oligomers consist of the linked 3-methoxythiophene structures.

**Figure S2.** FT-IR spectra of KBr pellets containing (a) Oligomer 1, (b) Oligomer 2 and (c) 3-methoxythiophene. The pellets were prepared by mixing KBr and the respective oligomer sample.

**GPC Analyses of Oligomers.** Figure S3 shows the gel permeation chromatograms – relating the absorbance and retention time under illumination with 270 nm light – of Oligomer 1 and Oligomer 2. The molecular-weight distribution curves showed a broad distribution extending from 630 to 10000 grams/mol for Oligomer 1 and extending from 800 to 16000 grams/mol for Oligomer 2. The solid black curve shows the measured value. The weight-averaged molecular weight ($M_w$), the number-averaged molecular weight ($M_n$), and polydispersity ($M_w/M_n$) values obtained from GPC analyses are contained in Table 1 of the text. These GPC chromatograms always display a shoulder peak within the shorter retention time domain. Deconvolution of the GPC chromatograms was carried out using the Pro 2018 program (OriginLab Corp., Northampton, MA, USA). The solid red curves in the figures show these deconvoluted curves. The values $M_{w1}$ and $M_{w2}$ for the weight-average molecular weight – calculated from peaks of the deconvoluted curves – are provided in Table S1. Interestingly, the molecular weight calculated from the two isolated waveforms differed by a factor of two. This indicates that one of the oligomers is a nonaggregated species, while the other is a dimer. In our previous report¹⁶, Oligomer 3 was expected to form a π-dimer in nitromethane, based on results of both viscosity measurements and UV-vis absorption measurements; the aforementioned GPC results indicate the existence of the π-dimer. Based on the above results, the molecular weight values provided in the in-text Table 1 are the average values of the nonaggregated species of the oligomers and their π-dimers.
Figure S3. Gel permeation chromatograms (solid black curves) of (a) Oligomer 1, (b) Oligomer 2, and (c) Oligomer 3. Solid red curves in each figure show the results of deconvolution of the measured chromatograph into the most probable distributions. The broken green curve represents the fitted cumulative molecular weight distribution. Deconvolution was carried out using the Gram-Charlier function in the OriginPro 2018 program (OriginLab. Corp., Northampton, MA, USA).
EDX Analyses of Films. A 2.0 mg sample of Oligomer 1 or Oligomer 2 was dissolved in 0.50 ml water to prepare a 0.40 wt% coating solution. Then, 0.45 ml of each coating solution was collected by micropipette. Coating films were obtained by drop casting the solution samples on transparent conductive glass plates (indium-tin-oxide coated glass) measuring 15 mm × 15 mm; transparent conductive glass was used to reduce possible surface charging effects during analysis of the film samples. The thickness of Film 1 and Film 2 was 3.0 and 2.2 μm, respectively. The accelerating voltage of the applied electron beam was 15 kV, the working distance was 10 mm, the magnification was 30x, the EDX measurement area was approximately 2×2 mm², and the EDX cumulation time was 180 s. Measurements were taken at 3 different locations in the film plane. The atomic concentration ratios of Cl/S and Fe/S and their standard deviations were determined in reference to an atomic ratio of sulfur set to 1. Table S2 shows the measurement results for each film measured in this way. Almost no Fe was detected in either Film 1 or Film 3; these films were primarily doped with Cl⁻ and ClO₄⁻, respectively. However, Film 2 displays a high ratio of Fe, indicating that FeCl₄⁻ is included as a dopant. Simple calculations show that FeCl₄⁻ and Cl⁻ are included in Film 2 at ratios of 0.13 and 0.17, respectively. The sum of these dopant ratios is 0.30, which is the doping level of Film 2 (see Table 1 in the text). Tanaka et al.¹⁷ suspended FeCl₃ in chloroform and synthesized a dark red poly(3-methoxythiophene) by adding 3-methoxythiophene to the suspension. Elemental analysis results indicated that poly(3-methoxythiophene) contains both FeCl₄⁻ and Cl⁻ as dopants at ratios of 0.16 and 0.11 relative to each monomer unit, respectively. That is, FeCl₄⁻ is also included as a dopant, supporting the hypothesis that Oligomer 2 may contain both Cl⁻ and FeCl₄⁻ as dopants.

All the results of ¹H NMR, FT-IR, GPC, and EDX analyses were consistent with our expectation that
Oligomers 1 and 2 are comprised of oligo(3-methoxythiophene) partially doped with Cl\(^{-}\)/FeCl\(_4^{-}\).

**Table S2.** EDX Analyses of Films\(^a\)

| Element | Film 1  | Film 2  | Film 3  |
|---------|---------|---------|---------|
| S       | 1.00    | 1.00    | 1.00    |
| Cl      | 0.29 ± 0.01 | 0.69 ± 0.02 | 0.26 ± 0.02 |
| Fe      | 0.01 ± 0.00 | 0.13 ± 0.01 | 0.00 ± 0.00 |

\(^a\) Each value was averaged from three measurements made at different positions on the film surface.

**External Appearance of Coating Films under a Low Illumination Condition.** The appearance of lustrous objects changes depending on the illumination intensity. Therefore, films were photographed in lower illumination conditions (Figure S4) than those in Figure 1 of the text. The strong luster can be observed by the clear reflection of a stainless-steel ruler placed next to the film. Additionally, the color tone of the film is highlighted by the reduced illumination; the photographs show that Film 1 and Film 2 display a gold-like and a bronze-like color, respectively.

![Figure S4](image)

**Figure S4.** External appearance of (a) Film 1 and (b) Film 2 under a low-illumination condition.

**Cross-Sectional Analyses of Films.** Figure S5 shows the obtained AFM images of the surfaces of Films 1-3, and the cross-sectional analyses. The average value was calculated assuming that the length of the blue bar in the cross-sectional profiles is indicative of the particle size (or fiber diameter). Results were corrected using the method described in the Methods section of the text. As a result, the particle size was estimated to be 10 nm or smaller, and the fiber diameter was estimated to be approximately 10 nm.
**Preparation and Optical Characterization of Coating Solutions.** In applying the coating solutions, we should understand the dissolution state of the oligomers in water. Generally, anion-doped states are generated in the oxidized conjugated polymers, and the generated charges are considered to be stored as cation radicals (polarons) and dications (bipolarons).\(^{18-21}\) Also, there have been some reports on the cation radicals and dications of oligothiophenes whose electronic spectra were demonstrated,\(^{22-28}\) and the existence states of the cationic species were discussed.

Hill *et al.*\(^{22,23}\) synthesized terminally-blocked oligothiophenes (oligomerization degree, \(n\), of 2 or 3) and carried out their electrooxidation in acetonitrile. They then investigated the temperature and concentration dependencies of the electronic spectra of the acetonitrile solutions, revealing the presence of electrooxidation-produced cationic radical \(\pi\)-dimers in addition to the expected monomeric cation radicals and dications. The \(\pi\)-dimers, with paired spins, are hypothetically formed by the dimerization of cation radicals.\(^{22-24}\) \(2\)-oligothiophen e\(^*\) \(\rightleftharpoons\) (oligothiophene)\(^{2+}\). Yu *et al.*\(^{28}\) synthesized various terminally-blocked oligothiophenes with methoxy substituents \((n = 2 – 6)\), and prepared their cation radicals by the electrooxidation in both acetonitrile and dichloromethane. Measurements of the electronic spectra indicate that the oligomers spectra in acetonitrile displayed differences in both shape and peak position from those in dichloromethane. Interpretation of these results suggest that the oligomers with cation radicals were mainly \(\pi\)-dimers and unaggregated species in acetonitrile and dichloromethane, respectively. The \(\pi\)-dimers are mainly formed in polar
solvents (typically, acetonitrile with a Gutmann's donor number, DN, of 14.1) as they can better disperse the charge and minimize coulombic repulsions between cation radicals in the π-dimers.\textsuperscript{24,25,28} However in low-polarity solvents (e.g., dichloromethane with a DN of 0),\textsuperscript{30} cation radicals are mainly unaggregated species. Additionally, it was reported that π-dimer formation was enhanced for longer oligomers,\textsuperscript{24,28} and indeed it was suggested that a thiophene oligomer (n = 12) π-dimerized. It was also demonstrated that water-soluble oligothiophenes (n = 2 and 4) formed π-stacks – larger aggregates with overlapped π-systems – in water (DN ≈ 33).\textsuperscript{29} The DN value is a measure of the ability of solvent to solute cationic species, and is likely the best measure in the present case.

Based on these previous reports, we carried out UV-vis absorption measurements. Coating solutions were prepared by dissolving 5.0 mg samples of Oligomers 1 and 2 in 2.5 ml water. Figure S6 shows the spectra of Oligomers 1 (a and b) and 2 (c and d) measured in water and dichloromethane, respectively. The aqueous solutions of Oligomers 1 and 2 were prepared by aqueous dilution of the above coating solutions by a factor of 120. The dichloromethane solutions containing Oligomers 1 and 2 were prepared by adding a 1.5 mg sample of Oligomers 1 and 2 to 15 ml dichloromethane, followed by 30 s of sonication and filtering the residues. The observed spectral shapes of the oligomers contained in water were quite different from those in dichloromethane. Considering that water is a highly polar solvent (DN ≈ 33), it is natural to assume that the aqueous oligomers exist as π-dimers and/or π-stacks. Supporting this assumption, the spectral shapes of the aqueous oligomers are analogous those of the π-dimers (α,ω-dimethylquinquethiophene and α,ω-dimethylsexithiophene) substituted with four methoxy groups in acetonitrile.\textsuperscript{24,28} The spectral shapes of the oligomers in dichloromethane showed similarities to those of the cation radical monomers of the analogues in dichloromethane.\textsuperscript{24,28} Additionally, Figure S3 shows that Oligomers 1 and 2 form π-dimers in the GPC solvent, N-methyl-2-pyrrolidone (DN = 27.3).\textsuperscript{29} These results support the conclusion that the Oligomers 1 and 2 form π-dimers and/or π-stacks in the aqueous coating solutions.

As described above, the shape of the UV-vis absorption spectra provides information on the aggregation behavior of the oligomers. Additional information was provided by the differences in the position of absorption maxima. In Figure S6, aqueous Oligomers 1 and 2 showed the absorption maxima at 558 and 620 nm, respectively. This indicates that the latter oligomer has a longer effective conjugation length than the former, expected from the higher polymerization degree of Oligomer 2 compared to Oligomer 1 (Table S1). This difference in the absorption maxima was also related to the differences in peak position in the optical extinction spectrum (see Figure 3 in the text), in which Oligomers 1 and 2 have peaks at 620 and 720 nm, respectively. This implies that Film 2 reflects more lights in orange (590 – 620 nm) and red (620 – 750 nm) regions, explaining why Film 2 developed a lustrous bronze-like color, while Film 1 exhibited a lustrous gold-like color.
Figure S6. Solution spectra of oligomers. UV-vis absorption spectra of Oligomer 1 in (a) water and (b) dichloromethane. UV-vis absorption spectra of Oligomer 2 in (c) water and (d) dichloromethane. UV-vis absorption spectra of Oligomer 3 in (e) nitromethane and (f) dichloromethane.

The dissolution state of Oligomer 3 in the nitromethane-based coating solution was also investigated. Oligomer 3 was insoluble in water and slightly soluble in dichloromethane. The
curves e and f in Figure S6 show the spectra of Oligomer 3 solutions with nitromethane and dichloromethane, respectively. The former solution was prepared by dissolving an 11 mg sample of Oligomers 3 in 1.1 ml nitromethane, followed by a 1200-fold dilution. The latter solution was prepared by adding a 1.5 mg sample of Oligomer 3 to 15 ml dichloromethane, followed by 30 s of sonication and filtering the residues. The shape and peak (shoulder) positions of curves e and f were nearly identical to those of b and d, suggesting that the cationic radicals of Oligomer 3 remain as unaggregated species in these solvents. This result was anticipated due to the small DN values of both nitromethane (DN = 2.7) and dichloromethane (DN = 0).

**Preparation of Samples for XRD Measurements.** 180 mg of either Oligomer 1 or 2 was dissolved in 60 ml water to prepare the respective 0.30 wt% coating solution. Then, 3.0 ml samples of each coating solution were applied to 19-20 glass slides, each slide measuring 26 mm × 76 mm. These samples were then dried in a desiccator containing silica gel for 17 h to prepare gold-like and bronze-like lustrous films (Figure S7a and c). The metal-like lustrous regions of the 19-20 coating film samples were removed by abrasion with a spatula, obtaining Powders 1 and 2 derived from Oligomers 1 and 2, respectively (Figure S7b and d).

**Figure S7.** Preparation of film samples for powder X-ray diffraction measurements. Photographs of large-area film samples: (a) Film 1; (c) Film 2. Photographs of powder samples obtained by abrasively removing the metal-like lustrous region of (b) Film 1 and (d) Film 2.
Thermogravimetric Analysis. The thermogravimetric (TG) analyses were performed with a Shimadzu DTG-60H thermal analyzer. The experiments were carried out under a nitrogen stream with a heating rate of 20 K/min. The result obtained for Oligomer 1 (Figure S8) showed a typical thermogravimetry curve during which a three-step loss of weight was observed. The first loss was only slight (0.85 wt%), occurring from ~288-470 K due to the evaporation of moisture trapped in the conducting polymer.\textsuperscript{31,32} The second loss occurred in ~470-700 K, possibly attributable to the degradation of the skeletal oligomethoxythiophene backbone structure. The final loss was attributed to the overflow of some oligomers decomposing from the sample.

![Thermogravimetric Analysis Curve](image)

**Figure S8.** Thermogravimetric analysis curve of a 10.3 mg sample of Oligomer 1 at 20 K min\textsuperscript{-1}.

Measurements of Optical Constants for Films Subjected to Dehydrating Treatments. We measured the refractive index spectra (Figure S9a) and extinction spectra (Figure S9b) of Film 1-TA, Film 1-LP, Film 1-LH, and Film 1 using ellipsometry (see Methods in the text). Comparing the on-set wavelength of each refractive index spectrum, we found that the wavelength increased in the following order: Film-1-TA < Film 1-LP < Film 1-LH < Film 1; thusly, dehydration treatment blue shifted the wavelength spectrum. A similar blue shift was also observed in both the rising wavelength and the peak wavelength for the extinction spectrum. The order of these rising wavelengths was consistent with the above order from the reflection spectrum (Figure 5 in the text). The peak values increased in the expected order: Film 1-TA < Film 1-LP < Film 1-LH < Film 1. This magnitude relationship is also consistent with the order of the measured peak reflectance values of the specular reflection spectra (Figure 5 in the text). Therefore, the calculated reflection spectrum (Figure S9c) – obtained by substituting the n and κ values into equation (1) in the text – successfully reproduced the measured reflection spectrum. Reflective amplitude ratio angle of s- and
Figure S9. Effect of dehydration treatment on optical properties of film samples. (a) Refractive index spectra of Film 1-TA (solid red line), Film 1-LP (solid green line), Film 1-LH (solid blue line), and Film 1 (i.e., as-prepared film, dashed black line). (b) Extinction spectra of Film 1-TA (solid red line), Film 1-LP (solid green line), Film 1-LH (solid blue line), and Film 1 (dashed black line). (c) Calculated reflection spectra of Film 1-TA (solid red line), Film 1-LP (solid green line), Film 1-LH (solid blue line), and Film 1 (dashed black line). (d) Refractive index spectra of Film 2-TA (solid red line) and Film 2 (i.e., as-prepared film, dashed black line). (e) Extinction spectra of Film 2-TA (solid red line) and Film 2 (dashed black line). (f) Calculated reflection spectra of Film 2-TA (red line) and Film 2 (black line). (g) Measured reflection spectra of Film 2-TA (solid red line) and Film 2 (dashed black line).

\( p \)-polarization (\( \psi \)) and phase difference of \( s \) - and \( p \)-polarization (\( \Delta \)) were both obtained at incident angles of 65°, 70° and 75° in the ellipsometry of this study; \( n \) and \( \kappa \) values were determined using these \( \psi \) and \( \Delta \) values. Therefore, it is thought that the optical constants displayed birefringence due to molecular alignment within the measured films. The calculated reflection spectrum differed from
the experimental value in a wavelength region near 500 nm, likely caused by the aforementioned birefringence.

We conducted the same investigation as that described above for both Film 2 and Film 2-TA. The results indicated that — similar to the above — the blue shifts observed in the rising wavelength of the refractive index spectrum (Figure S9d) and in the extinction spectrum (Figure S9e) are due to the dehydration treatment. Also, a reduction in peak reflectance in the calculated reflection spectrum (Figure S9f) occurred after dehydration treatment. This behavior was consistent with that of the measured specular reflection spectrum (Figure S9g).

**Dissolution Behavior of Films with and without the Dehydrating Treatments.** Films 1 and 1-TA were placed in a petri dish containing water, and dissolution behaviors were observed after 1 minute, shown in Figure S10. The gold-like color completely disappeared from Film 1, apparently dispersing as purple solubilized material. Alternatively, only the central stain region of Film 1-TA became a dissolved purple solubilized material. Film 2 samples — after being subjected to both non-annealing and annealing treatment (80°C, 1 h) — almost completely dissolved within 2 min after addition to water; for samples annealed at 80°C for 17 h, the bronze-like lustrous region did not dissolve even after 2 min (Figure S12).

![Figure S10](image1.png)

**Figure S10.** Dissolution behavior of film samples. (a) Photograph of Film 1 after a 1 min immersion in a water-filled laboratory dish. During the immersion, the laboratory dish was hand shaken. After a lapse of two minutes, the sample was removed from the water. No film remained on a glass plate. (b) Photograph of Film 1-TA treated as described above. The film part having a gold-like luster remained on a glass plate even after the sample was immersed for two minutes, while the stained region dissolved within water.
Effect of Dehydration Treatment on the Molecular Orientation Characteristic in Film 2. A 3.0 mg sample of Oligomer 2 was added to 1 ml water and underwent sonication at 50 °C for 20 min to prepare a 0.30 wt% coating solution. Next, a 0.60 ml coating solution was fractionated using a micropipette, which was then applied to glass plates measuring 25 mm × 15 mm. These samples were kept in a desiccator containing silica gel (~6%RH) for 17 h to obtain Film 2. Film 2-TA was prepared by thermal annealing Film 2 at 80 °C for 1 h under ordinary pressure. Figure S11 shows the out-of-plane XRD measured with 2θ/ω mode for both Film 2 and Film 2-TA. The signal attributed to the edge-on lamella interlayer distance of Film 2 was observed at 2θ = 8.27°, yet was shifted to 2θ = 9.95° by annealing treatment. These values correspond to lamellar interlayer distances of 1.07 nm and 0.89 nm, respectively. This indicates that dehydration effectively shortens the lamellar interlayer distance, as discussed for Film 1 in the text. The signal intensity is approximately 1/4 after annealing, suggesting a decrease in the amount of edge-on lamella.

![Figure S11](image_url)

**Figure S11.** Effect of dehydration treatment on the molecular orientation of Film 2. XRD patterns of Film 2 (solid black line) and Film 2-TA (solid red line).
Figure S12. Dissolution behavior of film samples. (a) Photograph of Film 2 immersed in a laboratory dish filled with water for two minutes. During the immersion, the dish was hand-shaken. After a lapse of two minutes, the film completely dissolved in water. (b) Photograph of Film 2-TA prepared by thermal annealing at 80 °C for 1 h and then treated in the above manner. (c) Photograph of Film 2-TA annealed at 80 °C for 17 h and then treated in the above manner. The film part having a bronze-like luster remained on a glass plate even after the sample was immersed for 2 min.

**Electric Conductivity of Films.** When considering the electric conductivity of poly(3-alkythiophene) films containing lamellar crystallites, it is generally accepted that the π-π interchain stacking results in a significant improvement of charge carrier mobility along the stacking direction.\(^{33,34}\) We previously prepared two films – from ClO\(_4^-\)-doped 3-methoxythiophene oligomer samples – that mainly contain either edge-on or face-on lamellae, and measured their in-plane conductivities.\(^5\) The results indicated that the conductivity of the former film was 1.5×10\(^3\) times higher than that of the
latter. Based on these previous studies, it can be expected that Films 1 and 2 show relatively higher in-plane conductivity than Film 3 since the amount and size of the edge-on lamellar crystallite in the former two films are larger than those in Film 3. This expectation may be possible since the films have nearly the same doping level (29, 30, and 30% for Films 1, 2, and 3, respectively, see Table 1 in the text). In-plane conductivity ($\sigma$) measurements were carried out. Table S3 shows the measured $\sigma$ value and the thicknesses for Film 1, Film 2, and Film 3. Contrary to expectations, the $\sigma$ values of Films 1 and 2 were roughly two orders of magnitude lower than that of Film 3.

Wang et al. chemically prepared polypyrrole films and investigated the effect of dopant anion types on their electric conductivities.\(^3\) Their results indicated that polypyrrole films doped with chloride, $p$-toluenesulfonate, and anthraquinone-2-sulfonate exhibited conductivities of 0.64, 7.1, and 120 S/cm, respectively. The Raman, electron spin resonance, and UV-vis-NIR spectroscopic measurements revealed that the charge carriers in the anthraquinone-2-sulfonate-doped and chloride-doped films were mainly bipolarons (or dications) and polarons (or radical cations), respectively, suggesting that bipolarons have higher mobility than polarons. Based on this report, the lower conductivities of Films 1 and 2 may be explained by assuming that polarons are the dominate charge carriers, whereas bipolarons contribute more to the electric conduction of Film 3.

| Table S3. Electric Conductivity and Thickness of Film 1, Film 2, and Film 3$^a$ |
|------------------------|------------------|------------------|
| Film                  | $\sigma$ (S cm$^{-1}$) | Thickness (\(\mu\)m) |
| ---                   | ---               | ---               |
| Film 1                | $8.1 \times 10^{-4}$ | 1.7               |
| Film 2                | $6.8 \times 10^{-4}$ | 2.3               |
| Film 3                | $3.6 \times 10^{-2}$ | 2.2               |

$^a$ Each value was averaged from three measurements made at different positions on the film surface.

Supplementary References

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Supplementary Movie S1 file description

Caption for Movie S1 file. Dropping of a coating solution of Oligomer 1 on a glass plate measuring 25 mm × 15 mm and the subsequent curing process in the ambient atmosphere (24oC, 37%RH). The movie plays at 7360X real-time speed.