Supporting Information Materials

Black and purple metal-like lustrous films from anion-doped poly(3-alkoxyselenophene) dyes

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Experimental Procedures

General

All reactions were conducted under an argon atmosphere unless otherwise specified. 3-Methoxythiophene, 1-butanol, and 1,2-dimethoxyethane were distilled and dried over 4 Å molecular sieves before use. Other materials were used as received without purification. 3-Methoxythiophene (>98%), iron(III) perchlorate n-hydrate (anhydride content = 70.0%), acetic acid (>99.7%), bromine (>99.0%), methanol (super dehydrated, >99.8%), copper(I) iodide (>95.0%), lithium bromide monohydrate (98.0% ~ 102.0%), magnesium sulfate (anhydrous, >98.0), sodium bicarbonate (>99.0%), sodium hydrogensulfite (64.0~67.4% as SO_2), zinc powder (>90.0%), and 4 Å molecular sieves were purchased from FUJIFILM Wako Pure Chemical. Nitromethane (>98.0%), selenophene (>98.0%), 1,2-diethoxyethane (>99.0%), and hydrobromic acid (>47.0%) were purchased from the Tokyo Chemical Industry. copper(II) tetrafluoroborate hexahydrate (≤25.8% Cu) and sodium hydride (60%, dispersion in Paraffin Liquid) was purchased from Sigma-Aldrich Co. Acetonitrile (>99.7%), acetone (>99.0%), methanol (>99.5%), ethanol (94.8~95.8%), 1-butanol (>99.0%), *N*-methyl-2-pyrrolidone (for high performance liquid chromatography, >99.0%), sodium (lump, in kerosene, >99.0%), diethyl ether (>99.5%), propylene carbonate (>99.0%), dichloromethane (>99.5%), and hexane (>96.0%) were purchased from Kanto Chemical Co., Inc. Flash column chromatography was performed using Silica Gel 60 (spherical, 40–50 μm), purchased from Kanto Chemical Co., Inc. The glass plate (S1225, Matsunami Glass Ind., Ltd.) used as a substrate for film deposition was sonicated following order in acetone, ethanol, and acetone for 10 minutes prior to use.

Characterization

^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra were obtained using a Bruker AVANCE III-400M (400 MHz) spectrometer with $CDCl_3$ as the solvent unless otherwise specified. $CHCl_3$ (δ = 7.26) was used as an internal standard for ^{1}H NMR spectra, and $CDCl_3$ (δ = 77.16) was used as an internal standard for ^{13}C NMR spectra. HR-APCI mass spectra were recorded on an Exactive Orbitrap MS (Thermo Fisher Scientific) with an ESI source.

Synthesis of 3-bromoselenophene

3-Bromoselenophene was synthesized with a modification of previous report.[1] To a mixture of selenophene (3.6 mL, 42 mmol), hydrobromic acid (47%, 15 mL) and diethyl ether (10 mL), a hydrobromic acid solution (47%, 18 mL) of bromine (8.3 mL, 0.16 mol) was added dropwise over a period of 1 hour at 0 °C. After stirring at 45 °C overnight, the reaction was quenched by adding saturated $NaHSO_3$ solution and extracted with CH_2Cl_2. The organic layer was then washed with 1 M KOH solution, saturated $NaHCO_3$ solution (three times), followed by drying over anhydrous $MgSO_4$. The organic phase was filtrated and concentrated under reduced pressure. The resulting brown liquid (16.2 g) contains 2,3,5-tribromoselenophene and 2,3,4,5-tetrabromoselenophene was used in the next step without further purification.

The mixture of above brown liquid (16.2 g), acetic acid (21 mL, 0.37 mol), distilled water (60 mL), and zinc dust (15 g, 0.23 mol) was stirring at 70 °C overnight. After filtration, the mixture was added distilled water and extracted CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ solution, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting brown solution was purified by vacuum distillation (3.6 Torr, 43 °C) to afford 3-bromoselenophene as a colorless solution (5.5 g, 62%). In addition, a brown transparent liquid of 3,4-dibromoselenophene (1.93 g) was recovered as a residue after the distillation. The ^1H and ^{13}C NMR data of 3-bromoselenophene[2] and 3,4-dibromoselenophene[3] are consistent with those previously reported.

Synthesis of 3-methoxyselenophene

Sodium hydride (0.49 g, 21 mmol) was washed with a small amount of hexane and dried under reduced pressure. 1,2-Dimethoxyethane (15 mL) and methanol (0.80 mL, 20 mmol) were then added and stirred for 30 minutes at room temperature. 3-Bromoselenophene (1.6 g, 7.6 mmol) and copper(I) iodide (2.3 g, 12 mmol) were added. The reaction mixture was refluxed for 5 days at 85 °C. After filtration to remove precipitates, water was added to the filtrate, and the mixture was extracted with diethyl ether. The combined organic phase was washed with saturated brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography using hexane as eluent to give 3-methoxyselenophene (0.92 g, 75%) as colorless liquid.

3-methoxyselenophene: ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 5.6, 2.8 Hz, 1H), 7.10 (dd, J = 5.6, 1.8 Hz, 1H), 6.68 (dd, J = 2.8, 1.8 Hz, 1H), 3.80 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 159.7, 128.5, 123.6, 97.9, 57.0. HRMS (APCI-TOF) *m/z* calcld for C_5H_7OSe 162.9657 $[M + H]^+$; found 162.9657.

Synthesis of 3-butoxyselenophene

Sodium hydride (0.84 g, 35 mmol) was washed with a small amount of hexane and dried under reduced pressure. 1,2-Dimethoxyethane (20 mL) and *n*-butanol (7.4 mL, 81 mmol) were then added and stirred for 30 minutes at room temperature. 3-Bromoselenophene (3.2 g, 15 mmol) and copper(I) iodide (4.6 g, 24 mmol) were added. The reaction mixture was refluxed for 4 days at 85 °C. After filtration to remove precipitates, water was added to the filtrate, and the mixture was extracted with diethyl ether. The combined organic phase was washed with saturated brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography using hexane as eluent to give 3-butoxyselenophene (2.3 g, 76%) as colorless liquid.

3-butoxyselenophene: ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 5.8, 2.6 Hz, 1H), 7.10 (dd, J = 5.6, 1.6 Hz, 1H), 6.65 (dd, J = 2.4, 1.6 Hz, 1H), 3.94 (t, J = 6.6 Hz, 2H), 1.79–1.72 (m, 2H), 1.53–1.43 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 159.0, 128.2, 124.0, 98.2, 69.6, 31.4, 19.4, 14.0. HRMS (APCI-TOF) *m*/*z* calcld for $C_8H_{13}OSe$ 205.0126 $[M + H]^+$; found 205.0127.

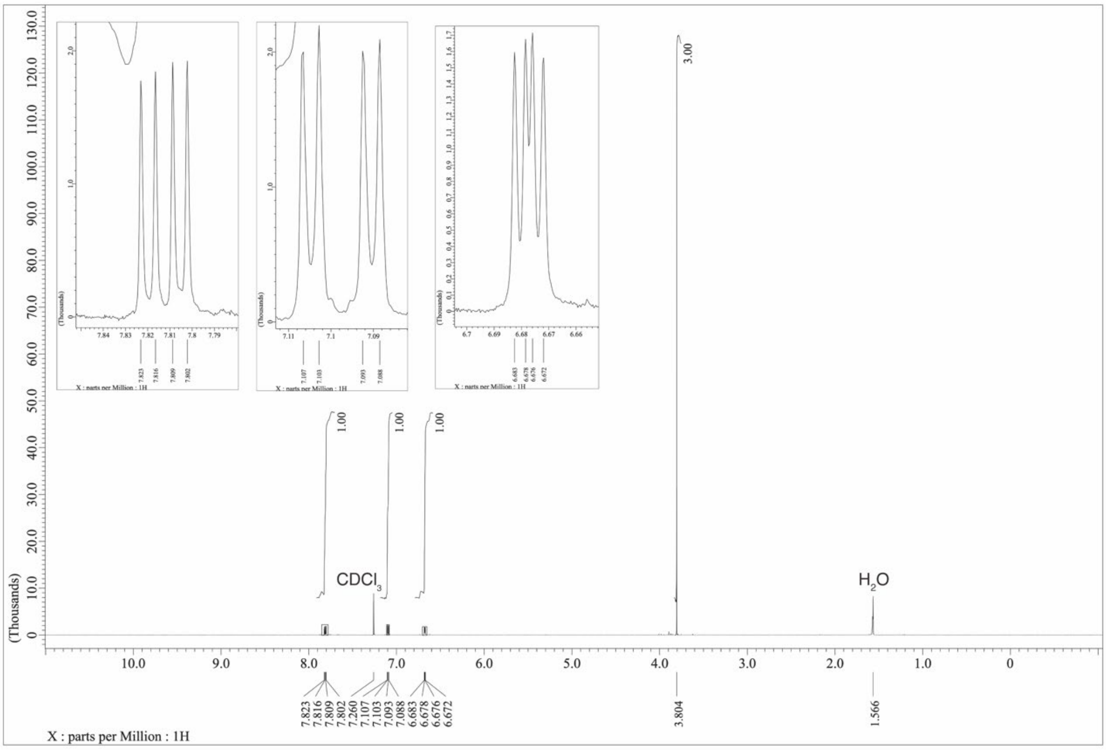

Figure S1. ^{1}H NMR spectrum of 3-methoxyselenophene in CDCl$_3$.

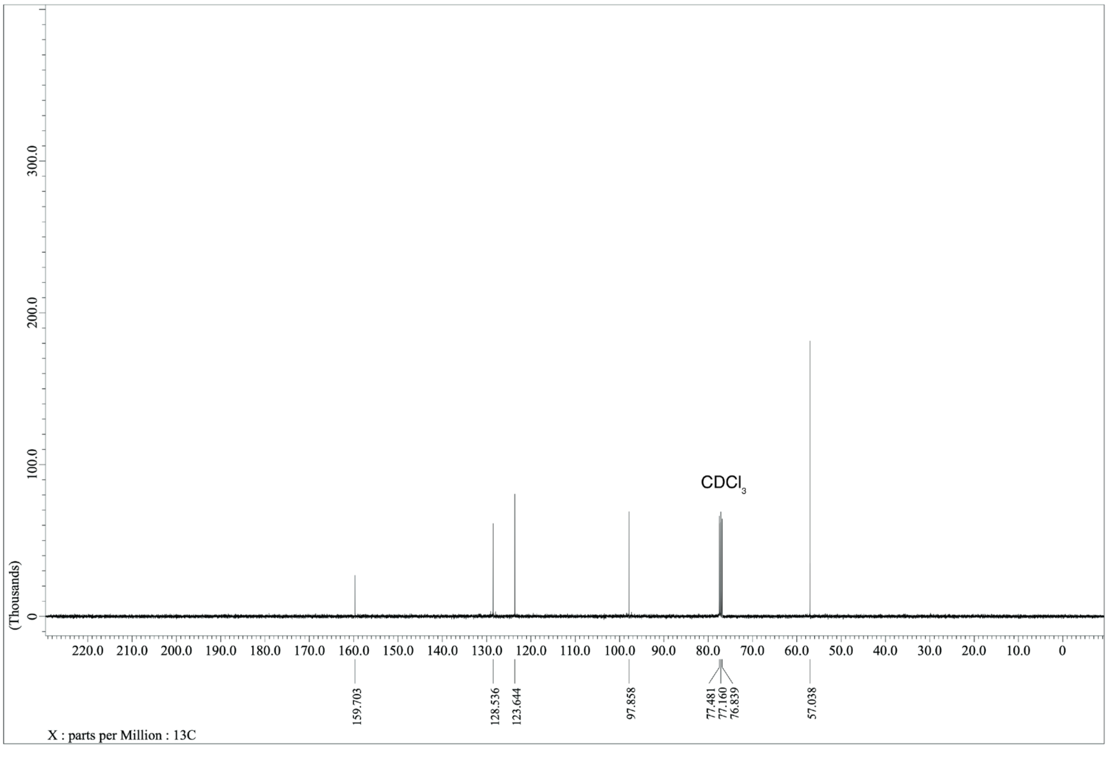

Figure S2. ^{13}C NMR spectrum of 3-methoxyselenophene in CDCl$_3$.

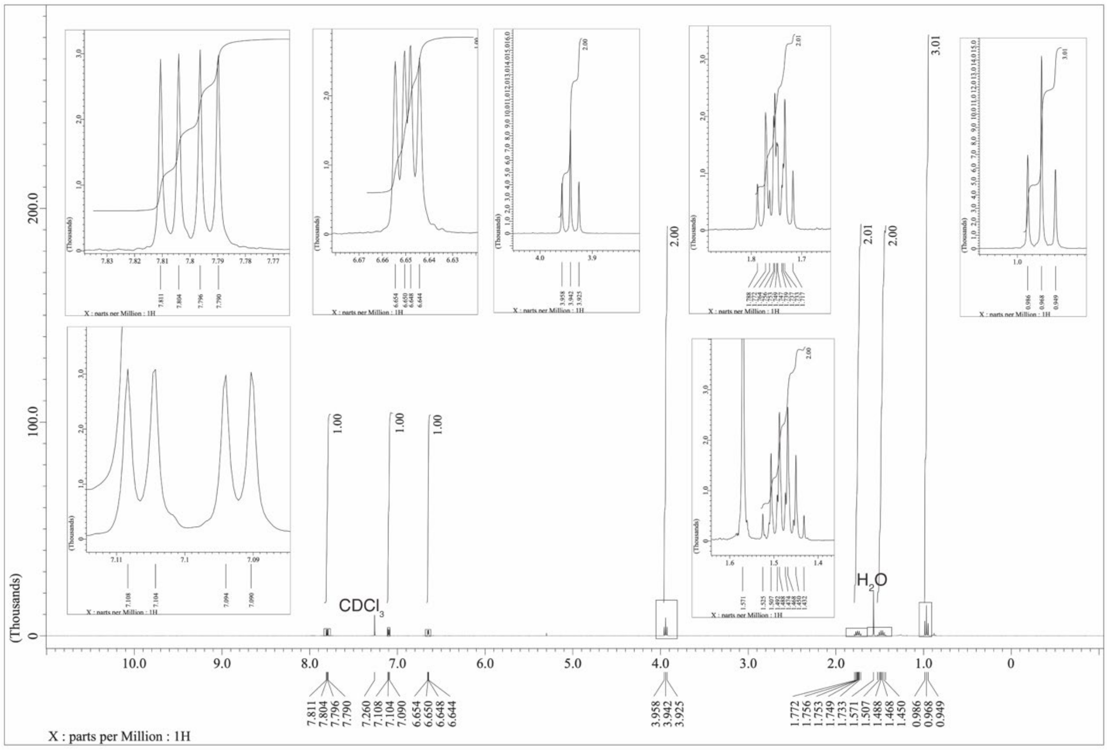

Figure S3. ^{1}H NMR spectrum of 3-butoxyselenophene in $CDCl_3$.

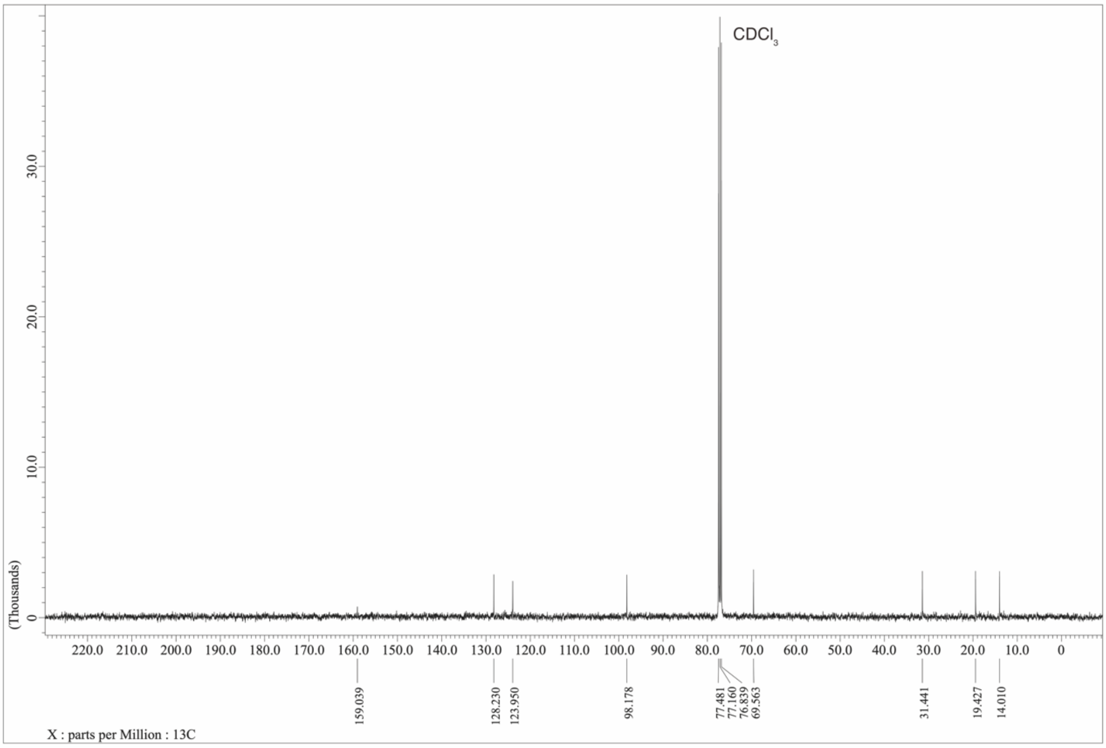

Figure S4. ^{13}C NMR spectrum of 3-butoxyselenophene in $CDCl_3$.

Table S1 Summary of molecular weight of anion-doped poly(3-alkoxyselenophene)s.

Oligomer	M_w[a]	M_n[a]	M_w/M_n[a]	M_p[b]	DP_w[c]	DP_n[d]	DP_p[e]
MeOSe_ClO$_4$	2480	1450	1.7	1110	15.6	9.1	7.0
BuOSe_ClO$_4$	2660	1470	1.8	1210	13.2	7.3	6.0
MeOSe_BF$_4$	2190	1380	1.6	1080	13.8	8.7	6.8
BuOSe_BF$_4$	1850	1150	1.6	1240	9.2	5.7	6.2

[a] Determined by GPC relative to polystyrene standards. [b] Molecular weight corresponding to the main peak in the differential molecular weight distribution curve. [c] Polymerization degree calculated from M_w. [d] Polymerization degree calculated from M_w. [e] Polymerization degree calculated from M_p.

Table S2 Summary of EDX analyses of anion-doped poly(3-alkoxyselenophene) films.[a]

Oligomer	C (mass%)	O (mass%)	F (mass%)	Cl (mass%)	Se (mass%)	Doping level (%)
MeOSe_ClO$_4$	66	26	-	1.5	7.5	20
BuOSe_ClO$_4$	74	17	-	1.6	7.6	21
MeOSe_BF$_4$	65	13	9.6	-	13	18
BuOSe_BF$_4$	72	8.0	10	-	9.0	28

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

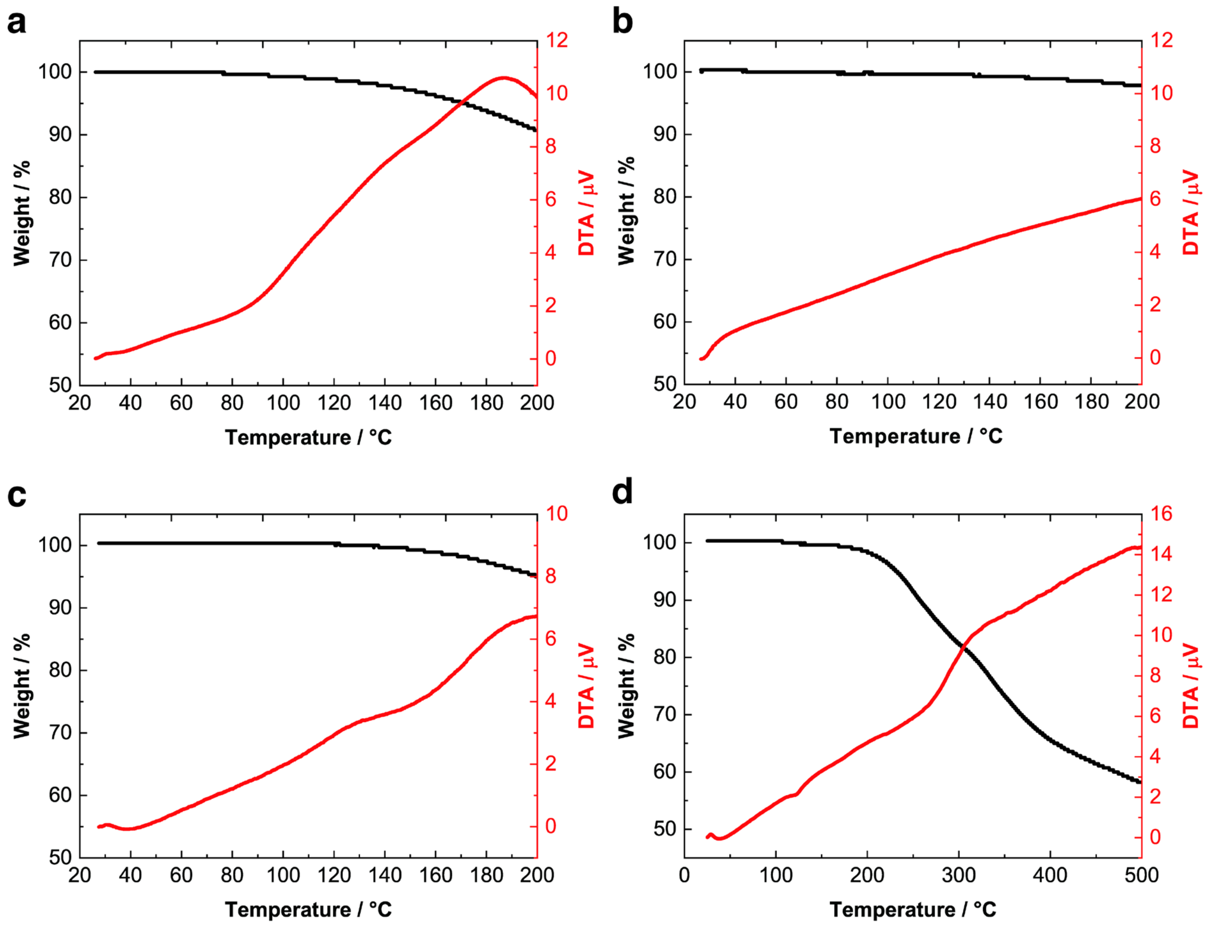

Figure S5. TG-DTA curves for (a) **MeOSe_ClO$_4$**, (b) **MeOSe_BF$_4$**, (c) **BuSe_ClO$_4$**, and (d) **BuOSe_BF$_4$** measured at a heating rate of 10 °C/min under N_2 flow.

Table S3 Summary of Thermal properties.

Polymer	T_{d5} (°C)
MeOSe_ClO$_4$	171
BuOSe_ClO$_4$	187
MeOSe_BF$_4$	271
BuOSe_BF$_4$	235

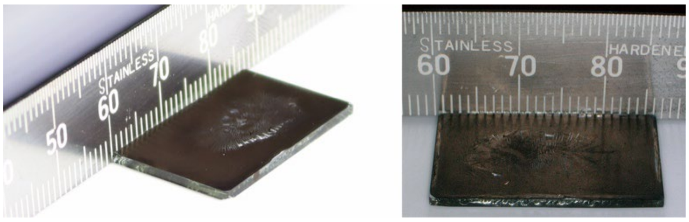

Figure S6. Photograph (left) and digital microscope image (right) of **MeOSe_ClO$_4$** coating film prepared from nitromethane coating solution.

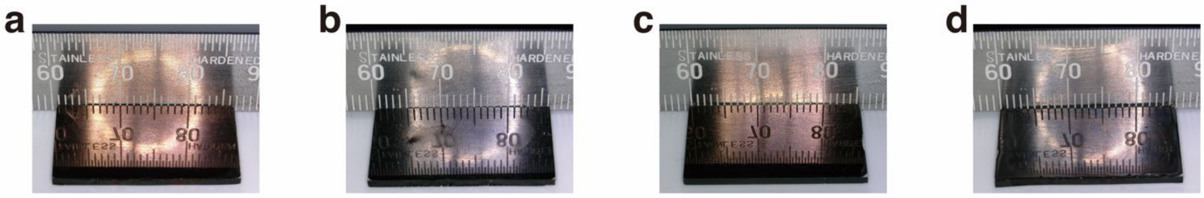

Figure S7. Digital microscope images of (a) **MeOSe_ClO$_4$**, (b) **MeOSe_BF$_4$**, (c) **BuSe_ClO$_4$**, and (d) **BuOSe_BF$_4$** coating film prepared from propylene carbonate coating solutions of corresponding polymer.

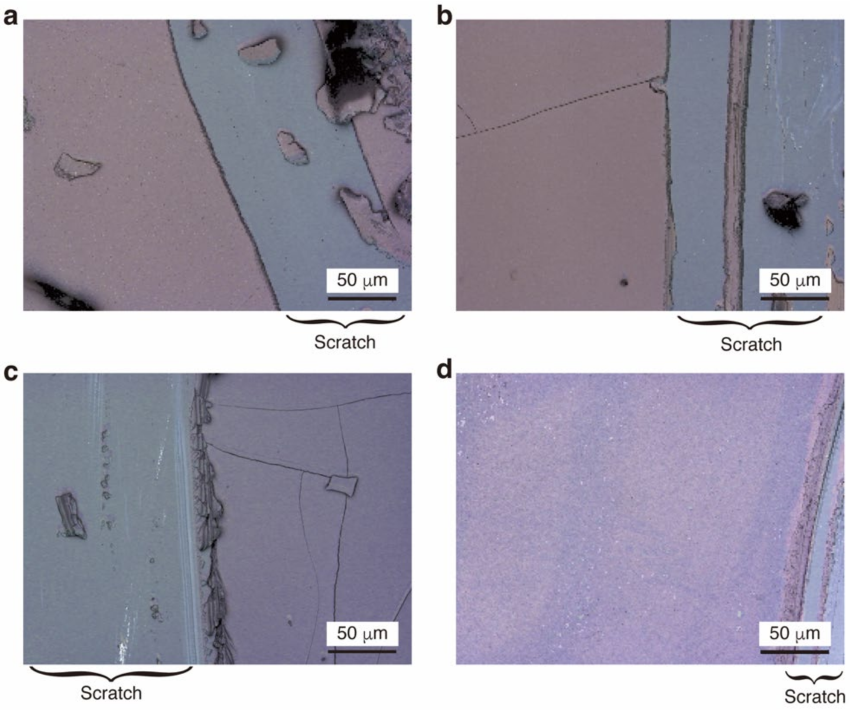

Figure S8. Laser-scanning microscope images of (a) **MeOSe_ClO$_4$**, (b) **MeOSe_BF$_4$**, (c) **BuSe_ClO$_4$**, and (d) **BuOSe_BF$_4$** coating film prepared from propylene carbonate coating solutions of corresponding polymer. Each image contains intentionally added scratches to measure film thickness.

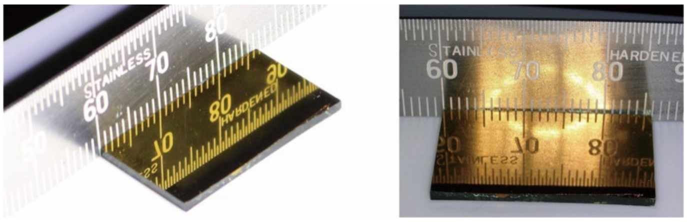

Figure S9. Photograph (left) and Digital microscope image (right) of **MeOT_ClO$_4$** coating film prepared from propylene carbonate coating solution.

Table S4 Summary of the film properties of the aniondoped poly(3-methoxythiophene)

Polymer	Film thickness (μm)^a	*Rq* (μm)^a	σ (S cm^{-1})^b	Pencil hardness
MeOT_ClO$_4$	2.87	0.04	7.6 x 10^{-5}	B

^{a}Determined via CLSM. ^{b}The electric conductivity of film was determined by measuring the sheet resistance via the double ring method using a resistivity meter.

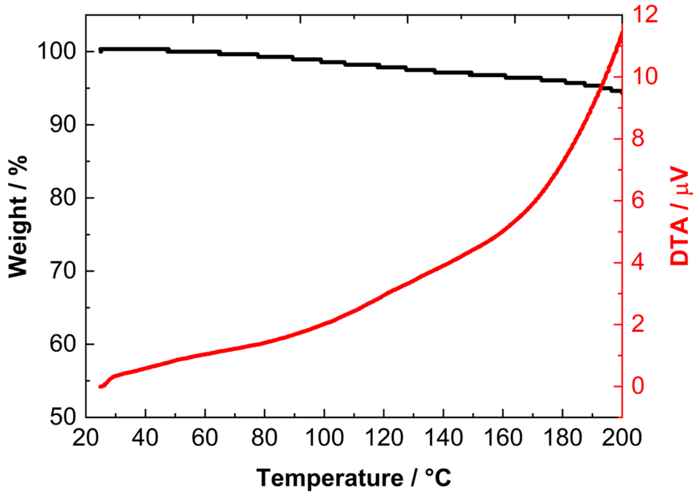

Figure S10. TG-DTA curves for **MeOT_ClO$_4$** measured at a heating rate of 10 °C/min under N$_2$ flow.

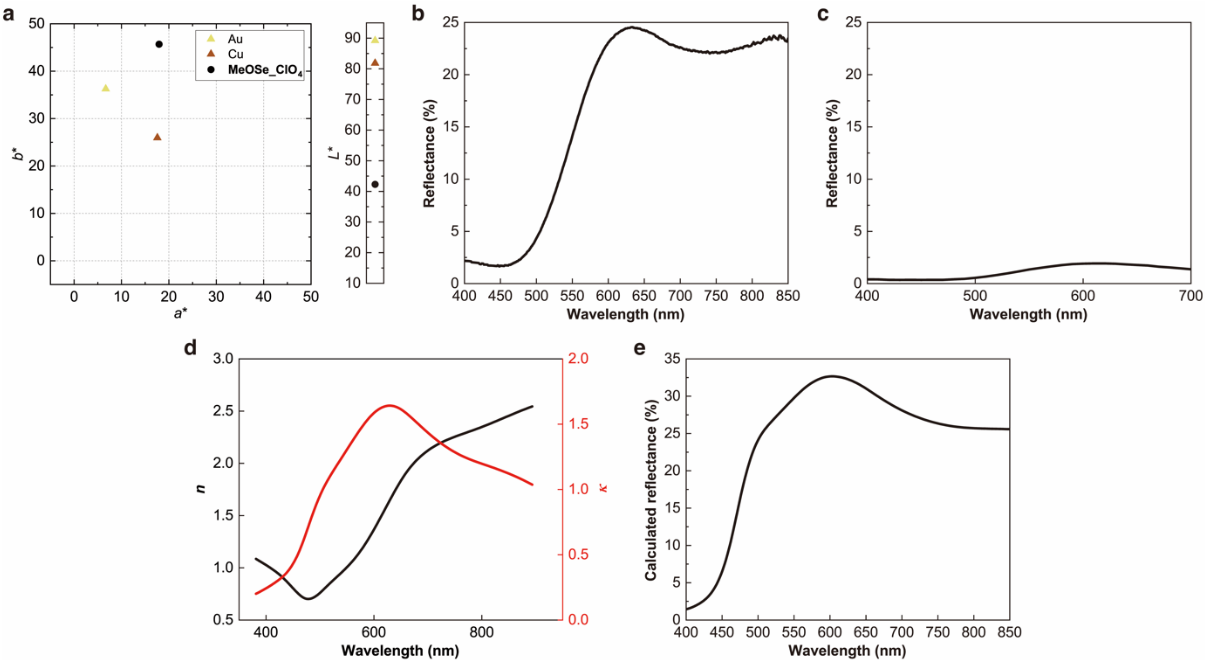

Figure S11. (a) Values of *a**, *b**, and *L** according to a CIELab color system of **MeOT_ClO$_4$** film with vacuum-evaporated gold and copper films. (b) Specular reflection, (c) diffuse reflection (d) refractive index (*n*) and extinction coefficient (*κ*), and (e) calculated reflection spectra for **MeOT_ClO$_4$** films.

Table S5 Summary of chromaticity measurement using *L*a*b** color space.

Film	*L**	*a**	*b**
MeOSe_ClO$_4$	27.48	10.32	4.85
BuOSe_ClO$_4$	22.95	2.86	−1.60
MeOSe_BF$_4$	26.5	10.71	6.19
BuOSe_BF$_4$	22.72	6.96	−2.27
MeOT_ClO$_4$	42.29	17.93	45.70
Au[a]	89.23	6.68	36.26
Cu[a]	81.82	17.57	25.95

[a] Vacume-evaporated metal film.

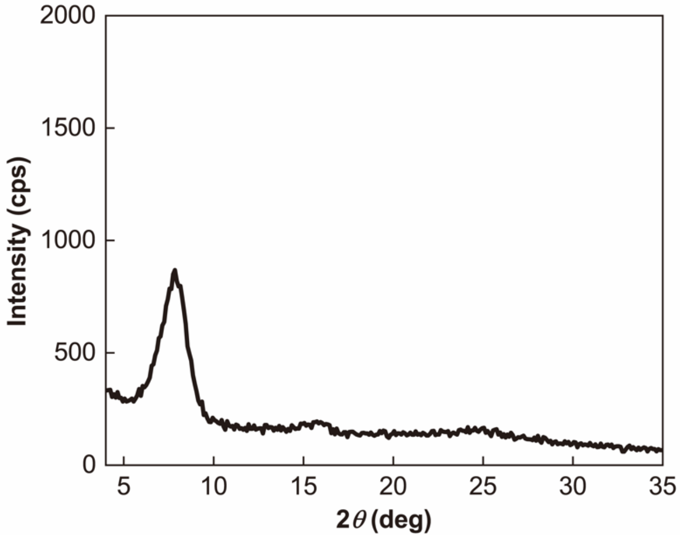

Figure S12. X-ray diffraction patterns of **MeOT_ClO$_4$** film.

Table S6 Crystallographic properties of anion-doped poly(3-alkoxyselenophene) films.

Film	2*θ* (°)[a]	*a* (nm)[b]	*I* (cps)[c]	FWHD (°)[d]	2*θ* (°)[e]	*b* (nm)[f]	*D* (nm)[g]
MeOSe_ClO$_4$	7.89	1.12	503	2.29	24.8	0.358	3.97
BuOSe_ClO$_4$	5.71	1.54	820	1.01	24.4	0.366	10.9
MeOSe_BF$_4$	7.58	1.16	738	2.29	25.0	0.356	3.97
BuOSe_BF$_4$	5.81	1.51	1540	0.6	24.6	0.362	25.3

[a] Peak position corresponding to the edge-on lamellar interlayer spacing. [b] The value of the lamellar interlayer distance. [c] Diffracted X-ray intensity for the peak corresponding to the edge-on lamellar interlayer spacing. [d] The full width at half-depth of the peak corresponding to the edge-on lamellar interlayer spacing. [e] Peak position corresponding to the face-on lamellar interlayer spacing. [f] The value of the stacking distance. [g] Crystallite size.

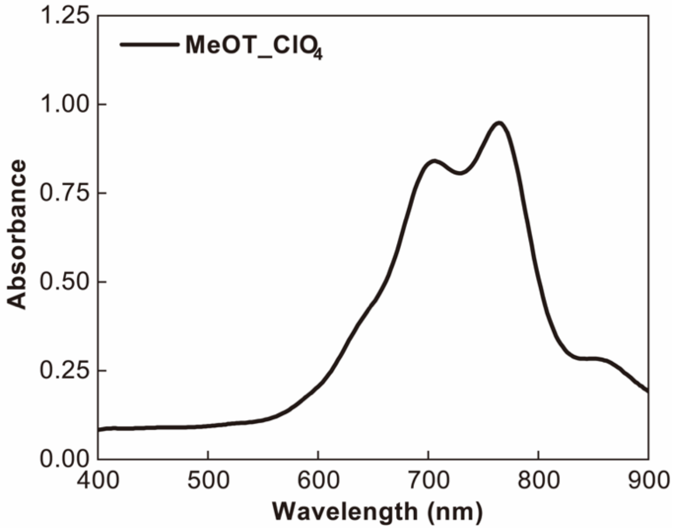

Figure S13. Ultraviolet-visible (UV-vis) spectra of diluted coating solution of **MeOT_ClO$_4$** in propylene carbonate.

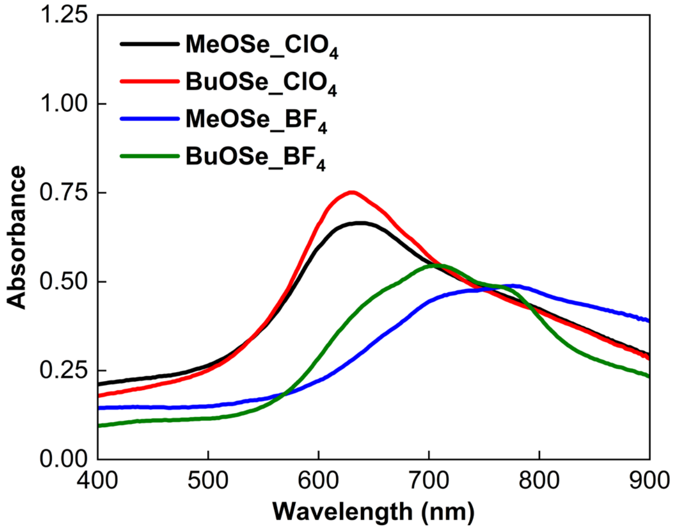

Figure S14. Ultraviolet-visible (UV-vis) spectra of undiluted coating solution of anion-doped poly(3-alkoxyselenophene)s in propylene carbonate.

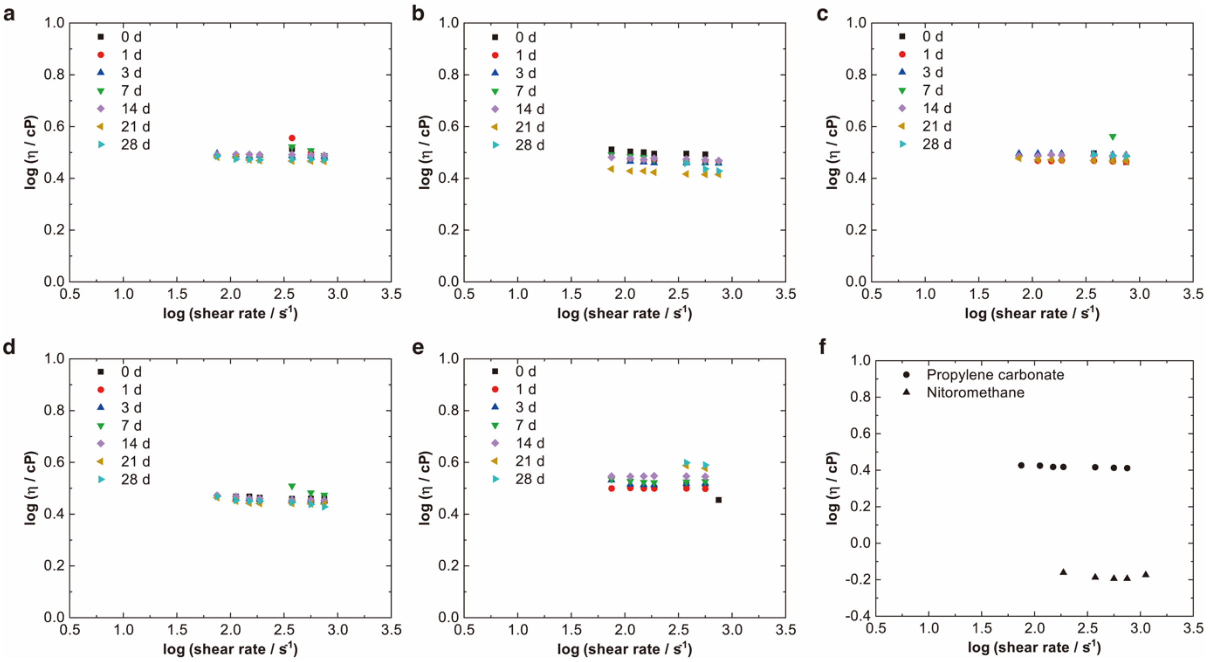

Figure S15. Logarithm of η vs the logarithm of γ for the propylene carbonate coating solutions of (a) **MeOSe_ClO$_4$**, (b) **BuOSe_ClO$_4$**, (c) **MeOSe_BF$_4$**, (d) **BuOSe_BF$_4$**, (e) **MeOT_ClO$_4$**, and (f) pure solvents.

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