

Liquid-Crystalline Perylene Bisimide Derivatives Bearing an Azacrown Ether Ring Complexing with Alkaline Metal Ions

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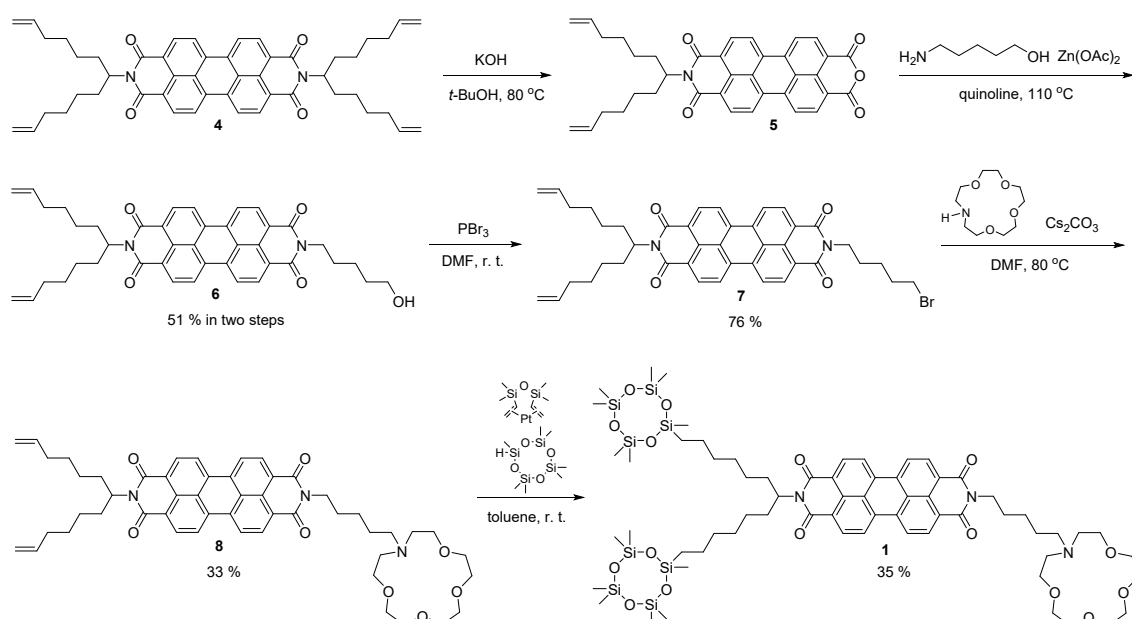
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Synthesis of materials

General

All ^1H NMR spectra were recorded on a Varian UNITY INOVA400NB spectrometer. FT-IR measurements were conducted on a JASCO FT/IR-660 Plus spectrometer. MALDI-TOF Mass spectra were measured by Bruker Ultraflex III without matrix. Perylene tetracarboxylic acid anhydride and the Karstedt catalyst were purchased from Tokyo Chemical Industry and Gelest Inc., respectively. Zinc acetate, quinoline, and toluene (commercially available from Wako Pure Chemical Industries) were used without purification. Silica gel was purchased from Kanto Chemicals. Gel permeation chromatography was performed by the recycle HPLC LC-200 (Japan Analytical Industry Company).



Scheme S1 Synthesis of compound **1**.

N-(1,12-Tridecadien-7-yl)-*N'*-(5-hydroxypentyl)perylene-3,4,9,10-tetracarboxylic bisimide (**6**)

□ Compound **4** (1.33 g, 2.33 mmol) and zinc acetate were dissolved in quinoline (30 ml). 5-amino-1-pentanol (0.52 g, 4.99 mmol) was added to the solution and the resulting solution was heated at 110 °C for 10 hours. The reaction mixture was cooled to room temperature and poured into a solution of hydrochloric acid (10 %). The produced precipitates were filtered and washed with water and methanol. The residual solids were purified by a silicagel column chromatography using a mixture of dichloromethane and methanol (30:1). The crude product was dissolved in dichloromethane and the solution was poured into methanol. The resulting red precipitates were collected. Red crystalline powder (0.76 g) was obtained in the yield of 51 %.

^1H -NMR (400 MHz, CDCl_3) δ = 8.20-8.57 (m, 8H), 5.77 (ddt, 2H, J = 6.8, 10.0, 16.8 Hz), 5.13-5.22 (m, 1H), 4.84-5.00 (m, 4H), 4.15 (t, 2H, J = 7.4 Hz), 3.70 (t, 2H, J = 6.4 Hz), 2.21-2.36 (m, 2H), 2.04

(q, 4H, J = 6.7), 1.87-1.97 (m, 2H), 1.65-1.85 (m, 8H), 1.23-1.59 (m, 11H)

FT-IR (ATR) : ν = 3507, 3076, 2926, 2858, 1693, 1645, 1593, 1438, 1404, 1338, 1250, 1164, 993, 907, 855, 809, 746 cm^{-1} ; elemental analysis (%) calculated for $\text{C}_{42}\text{H}_{42}\text{N}_2\text{O}_5$: C, 77.04; H, 6.47; N, 4.28; O, 12.22; found: C, 76.78; H, 6.77; N, 4.37.

***N*-(1,12-Tridecadien-7-yl)-*N'*-(5-bromopentyl)perylene-3,4,9,10-tetracarboxylic bisimide (7)**

PBr_3 (0.30 ml, 3.16 mmol) was added dropwise to DMF at 0 °C and the resulting suspension was stirred for 1 hour. To the suspension, a DMF solution of compound **6** (0.80 g, 1.22 mmol in DMF 10 ml) was added and the suspension was stirred for 17 hours. Water (75 ml) was added to the reaction mixture to form red precipitates. The precipitates were filtered off and washed with water and methanol. The crude product was purified by a silicagel column chromatography using an elutant consisting of dichloromethane and methanol (20:1). The product was dissolved in dichloromethane and the solution was poured into methanol. Red crystalline powders of compound **7** were obtained in the yield of 76 % (0.66 g).

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 8.34-8.63 (m, 8H), 5.76 (ddt, 2H, J = 6.4, 10.4, 17.2 Hz), 5.14-5.23 (m, 1H), 4.84-4.98 (m, 4H), 4.17 (t, 2H, J = 7.6 Hz), 3.46 (t, 2H, J = 6.8 Hz), 2.23-2.34 (m, 2H), 1.86-2.08 (m, 8H), 1.79 (quin, 2H, J = 7.6 Hz) 1.56-1.65 (m, 4H), 1.23-1.50 (m, 9H)

FT-IR (ATR) : ν = 3567, 3074, 2926, 2857, 1693, 1649, 1594, 1578, 1437, 1404, 1338, 1247, 1176, 1125, 993, 907, 852, 809, 745, 628 cm^{-1} ; elemental analysis (%) calculated for $\text{C}_{42}\text{H}_{41}\text{BrN}_2\text{O}_4$: C, 70.29; H, 5.76; Br, 11.13; N, 3.90; O, 8.92; found: C, 69.42; H, 6.05; N, 3.98.

***N*-(1,12-Tridecadien-7-yl)-*N'*-(10-Hexyl-1,4,7,10-tetraoxa-13-azacyclopentadecane)perylene-3,4,9,10-tetracarboxylic bisimide (8)**

Compound **7** (1.00 g, 1.38 mmol), 1-aza-15-crown 5-ether (0.38g, 1.73 mmol), and Cs_2CO_3 (0.46 g, 1.41 mmol) were suspended in DMF (50 ml) and the reaction mixture was stirred at 80 °C for 16 hours. The reaction was quenched by the addition of water to the reaction mixture. The red precipitates which were formed at the quench were filtered off and washed with water and methanol. The crude product was purified by a silicagel column chromatography using an elutant consisting of dichloromethane and methanol (30:1). The product was dissolved in dichloromethane and poured into methanol. The resulting suspension was filtered, and red crystalline powders were collected. The yield was 33 % (0.39 g).

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 8.26-8.63 (m, 8H), 5.75 (ddt, 2H, J = 6.8, 10.0, 16.8 Hz), 5.13-5.22 (m, 1H), 4.83-4.98 (m, 4H), 4.16 (t, 2H, J = 7.6 Hz), 4.08 (t, 2H, J = 6.6 Hz), 3.58-3.76 (m, 15H), 3.50-3.40 (m, 4H), 2.21-2.33 (m, 2H), 1.99-2.04 (m, 4H), 1.19-1.96 (m, 20H)

FT-IR (ATR) : ν = 3524, 3074, 2923, 2855, 1693, 1648, 1593, 1577, 1507, 1437, 1404, 1338, 1248, 1176, 1125, 993, 907, 852, 809, 745, 623, 432 cm^{-1} ; elemental analysis (%) calculated for

***N*-(1,12-Di(1,1,3,3,5,5,7,7-heptamethylcyclotetrasiloxanyl)tridecan-7-yl)-*N'*-(10-Hexyl-1,4,7,10-tetraoxa-13-azacyclopentadecane)perylene-3,4,9,10-tetracarboxylic bisimide (1)**

Compound 8 (60 mg, 0.070 mmol) and 1,1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane (66 mg, 0.233 mmol) were dissolved in toluene (10 ml). To the solution, the Karstedt catalyst (1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum (0), 2.1 at%, xylene solution, 5 μ l) (5 μ l) was added and the reaction solution was stirred at room temperature for 20 hours. Solvent was evaporated and residual red solids were purified by a silicagel column chromatography using an elutant consisting of dichloromethane and methanol (20:1). The product was purified a gel permeation chromatography. Red-black waxy solids were obtained in the yield of 32 % (32 mg). \square

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 8.55-8.70 (m, 8H), 5.12-5.24 (m, 1H), 4.21 (t, 2H, $J = 7.6$ Hz), 4.09 (t, 2H, $J = 6.4$ Hz), 3.60-3.73 (m, 18H), 3.51-3.43 (m, 4H), 2.17-2.31 (m, 2H), 1.69-1.94 (m, 7H), 1.47-1.58 (m, 2H), 1.18-1.39 (m, 18H), 0.43-0.50 (m, 4H), 0.004-0.065 (m, 42H)

FT-IR (ATR) : $\nu = 2960, 2924, 2857, 1694, 1655, 1595, 1578, 1438, 1404, 1341, 1257, 1051, 802, 745$ cm^{-1} ; elemental analysis (%) calculated for $\text{C}_{66}\text{H}_{105}\text{N}_3\text{O}_{16}\text{Si}_8$: C, 55.78; H, 7.45; N, 2.96; O, 18.01; Si, 15.81; found: C, 55.65; H, 7.63; N, 2.95.

DSC thermograms of 1:1 complexes of compound with LiOTf, NaOTf, and KOTf

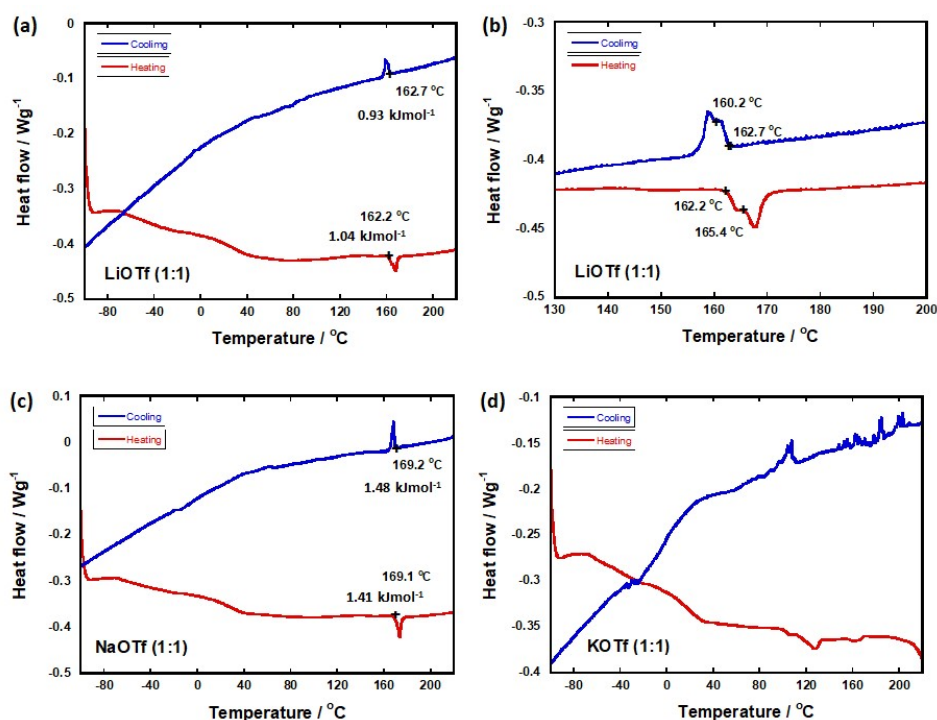


Figure S1. DSC thermograms of mixtures of compound 1 with alkaline metal triflates. (a) Complex with LiOTf. (b) Enlarged graph of the thermograms of the complex of compound 1 and LiOTf. (c) Complex with NaOTf. (d) Complex with KOTf.

X-ray diffraction of compound **1** and the complexes with LiOTf, NaOTf, and KOTf

Table S1 Compound **1** at 85 °C (lattice constants: $a = 42.7 \text{ \AA}$, $b = 32.9 \text{ \AA}$)

$2\theta / \text{deg}$	$d(\text{exp}) / \text{\AA}$	hkl	$d(\text{calc.}) / \text{\AA}$
3.39	26.1	1 1 0	26.1
4.14	21.4	2 0 0	21.4
5.94	14.9	1 2 0	15.4
25.46	3.5	0 0 1	---

Table S2 1:1 complex of compound **1** with LiOTf at r. t. (lattice constants: $a = 61.0 \text{ \AA}$, $b = 105.7 \text{ \AA}$)

$2\theta / \text{deg}$	$d(\text{exp}) / \text{\AA}$	hkl	$d(\text{calc.}) / \text{\AA}$
1.67	52.8	1 1 0	52.8
2.90	30.5	2 0 0	30.5
4.20	21.0	3 0 0	20.3
4.90	18.0	2 5 0	17.4
25.33	3.5	0 0 1	---

Table S3 1:1 complex of compound **1** with NaOTf at r. t. (lattice constants: $a = 63.6 \text{ \AA}$, $b = 108.2 \text{ \AA}$)

$2\theta / \text{deg}$	$d(\text{exp}) / \text{\AA}$	hkl	$d(\text{calc.}) / \text{\AA}$
1.61	54.8	1 1 0	54.8
2.77	31.8	2 0 0	31.8
4.17	21.2	3 0 0	21.2
4.89	18.1	2 5 0	17.9
25.08	3.6	0 0 1	---

X-ray diffraction patterns of complexes of compound **1** with KOTf

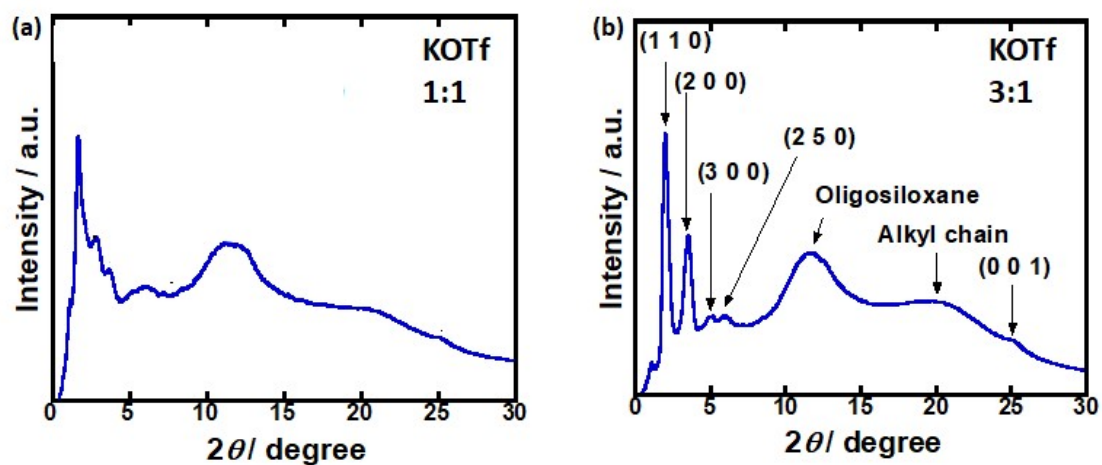


Figure S2. (a) X-ray diffraction pattern of a mixture of compound **1** and KOTf at room temperature in a molar ratio of 1:1 and (b) that in a molar ratio of 3:1.

Table S4 3:1 complex of compound **1** with KOTf at r. t. (lattice constants: $a = 61.6 \text{ \AA}$, $b = 111.1 \text{ \AA}$)

$2\theta / \text{deg}$	$d(\text{exp}) / \text{\AA}$	hkl	$d(\text{calc.}) / \text{\AA}$
1.64	53.9	1 1 0	53.9
2.87	30.8	2 0 0	30.8
3.72	23.7	2 3 0	23.7
5.22	16.9	3 4 0	16.5
5.97	14.8	4 1 0	15.3
7.08	12.5	5 0 0	12.3
25.17	3.5	0 0 1	---

Fluorescence spectra of compound 1, 1:1 complexes of compound 1 with LiOTf and NaOTf, and 1:1 mixture of compound 1 and KOTf

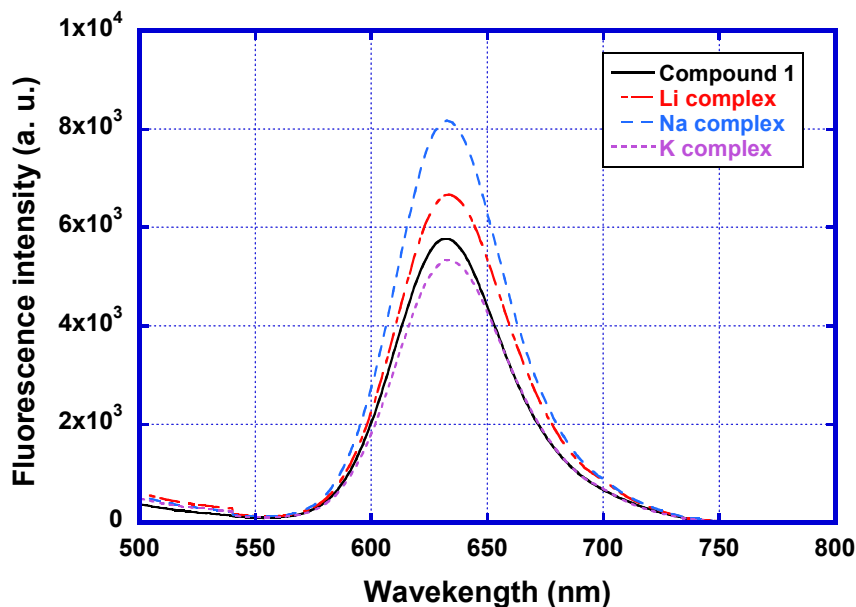


Figure S3 Fluorescence spectra of compound 1, 1:1 complexes of compound 1 with LiOTf and NaOTf, and 1:1 mixture of compound 1 and KOTf in thin film states (wavelength of the excitation light was 360 nm).

***N*-(1,12-Di(1,1,3,3,5,5,7,7-heptamethylcyclotetrasiloxanyl)tridecan-7-yl)-*N'*-(3,6,9-trioxodecane-1-yl)perylene-3,4,9,10-tetracarboxylic bisimide (8)**

• ¹H-NMR (400 MHz, CDCl₃) δ = 8.45-8.64 (m, 10H), 5.12-5.20 (m, 1H), 4.43 (t, 2H, J = 6.0 Hz), 3.84 (t, 2H, J = 6.0 Hz), 3.72 (dd, 2H, J = 3.2, 5.8 Hz), 3.63 (dd, 2H, J = 3.2, 6.0 Hz), 3.58 (dd, 2H, J = 3.2, 6.0 Hz), 3.45 (dd, 2H, J = 3.2, 6.2 Hz) 3.29 (s, 3H), 2.18-2.26 (m, 2H), 1.82-1.88 (m, 4H), 1.19-1.43 (m, 20H), 0.45-0.47 (dd, 4H J = 8.0, 7.2 Hz), 0.02-0.05 (m, 42H) ppm; ¹³C-NMR (100 MHz, CDCl₃) δ = 163.9, 163.8, 135.2, 135.1, 134.8, 134.7, 132.4, 131.9, 131.8, 130.1, 129.9, 126.9, 126.8, 123.7, 123.5, 72.6, 71.4, 71.2, 70.8, 68.6, 59.7, 55.6, 39.9, 33.8, 33.1, 30.1, 27.7, 23.6, 17.8, 1.5, 1.4 ppm; IR (ATR) ν = 2961, 2923, 2857, 1694, 1648, 1594, 1577, 1507, 1438, 1403, 1343, 1257, 1196, 1178, 1053, 851, 800, 744, 695, 632, 552, 487, 432 cm⁻¹; elemental analysis (%) calculated for C₆₆H₁₀₅N₃O₁₆Si₈: C, 55.78; H, 7.45; N, 2.96; O, 18.01; Si, 15.81; found: C, 55.65; H, 7.63; N, 2.95.

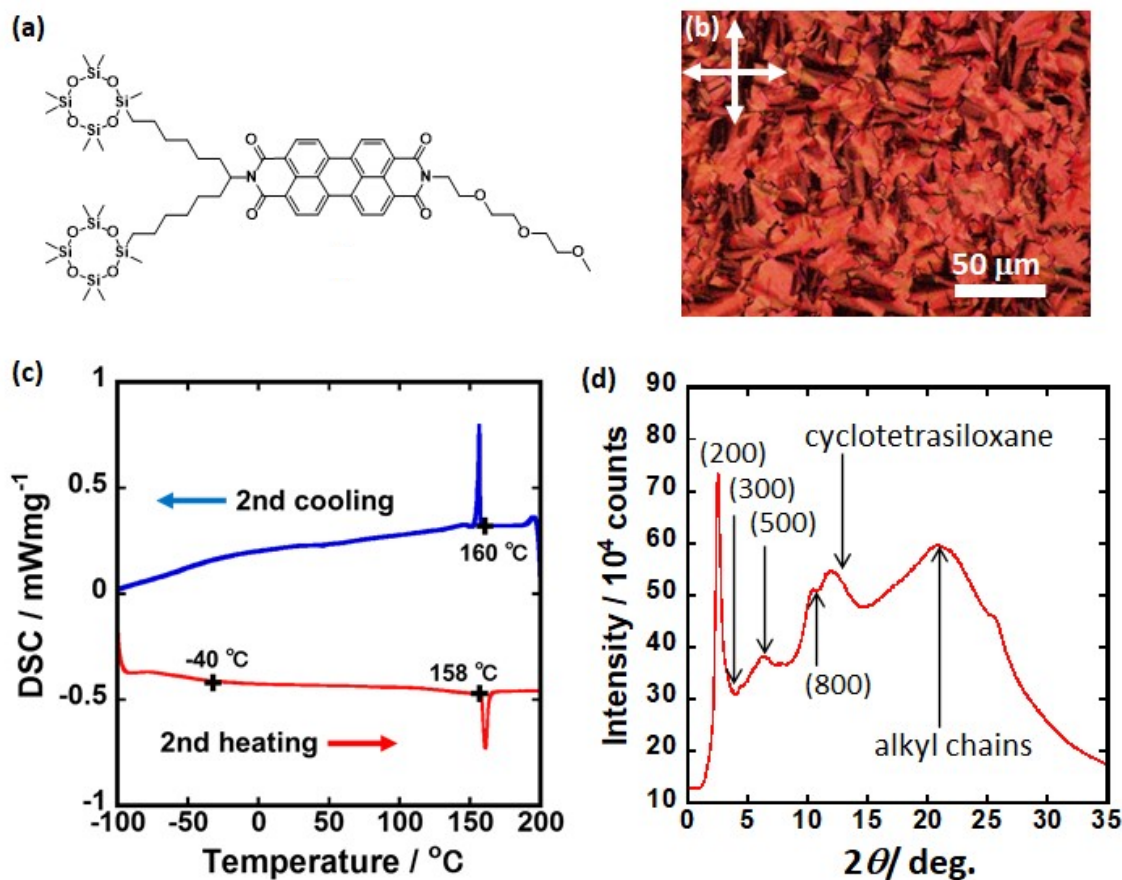


Figure S4 (a) Molecular structure of compound **8**. (b) Polarizing optical micrograph of compound **8** at 100 °C. (c) DSC thermograms of compound **8**. Heating and cooling rates were 10 Kmin⁻¹. (d) X-ray diffraction pattern of compound **8** at room temperature.

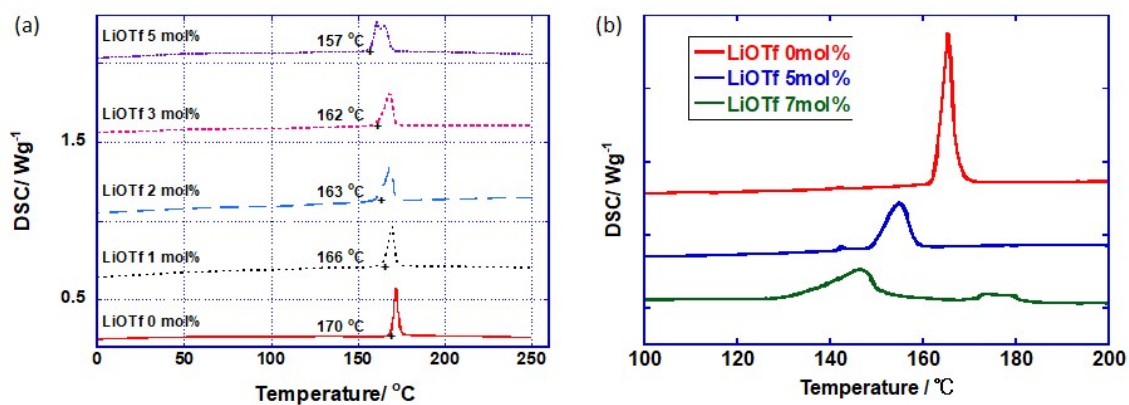


Figure S5 DSC thermograms of mixtures of (a) compound **7** and (b) compound **8** with LiOTf at a rate of 10 Kmin⁻¹ on heating.

Infrared absorption spectra of a spin-coated thin film of compound 1

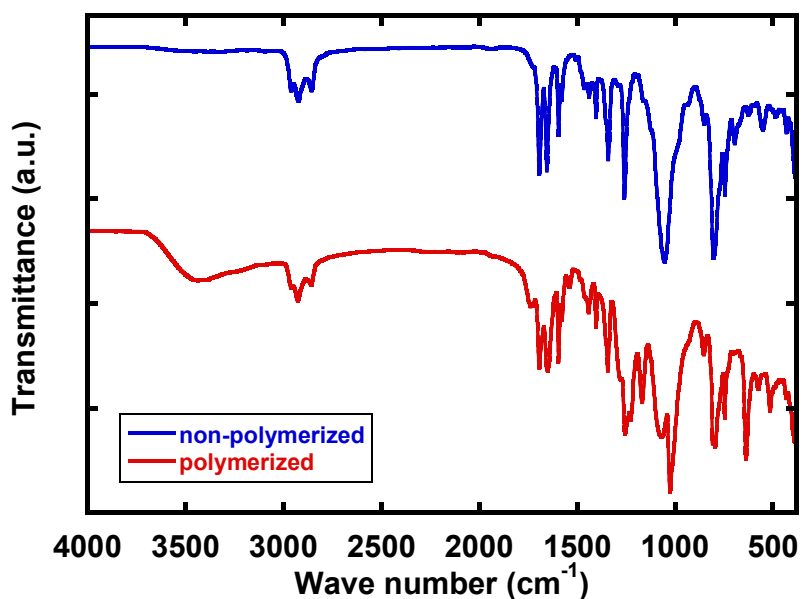


Figure S6. Infrared absorption spectra of spin-coated thin film of compound 1 before and after polymerization.

Fine structures in the surface morphology of the spin-coated films of complexes of compound 1 with LiOTf and NaOTf

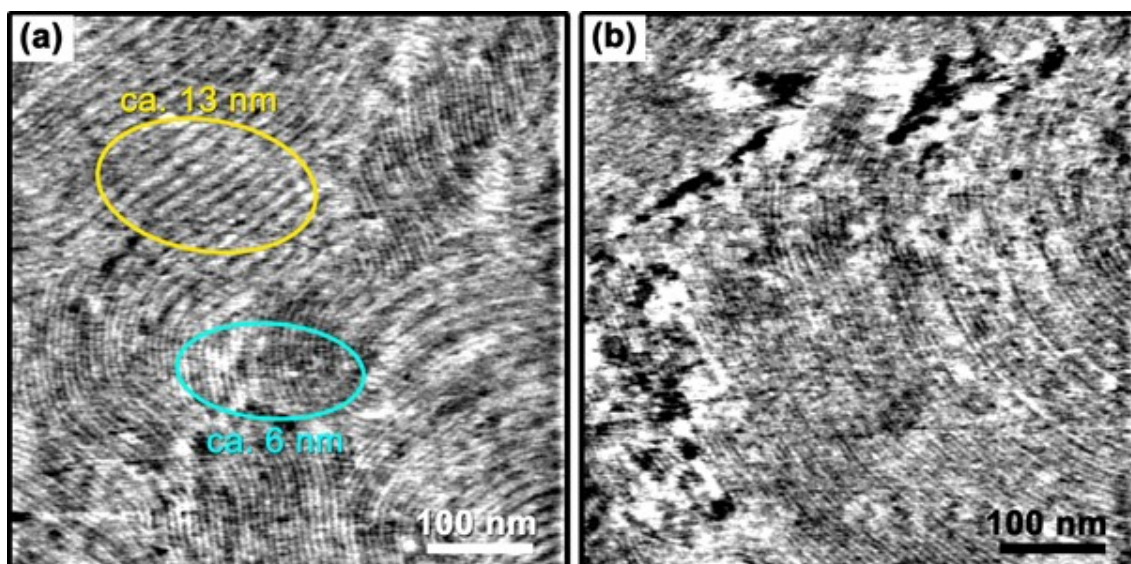


Figure S7 Magnified AFM phase images for the surface of the spin-coated films of the 1:1 complexes of compound 1 with LiOTf and NaOTf.