Supplementary Information:

# Tuning of luminescence color of π-conjugated liquid crystals through co-assembly with ionic liquids

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**Table of Contents:**

## 1. Experimental section

### Materials and Synthesis

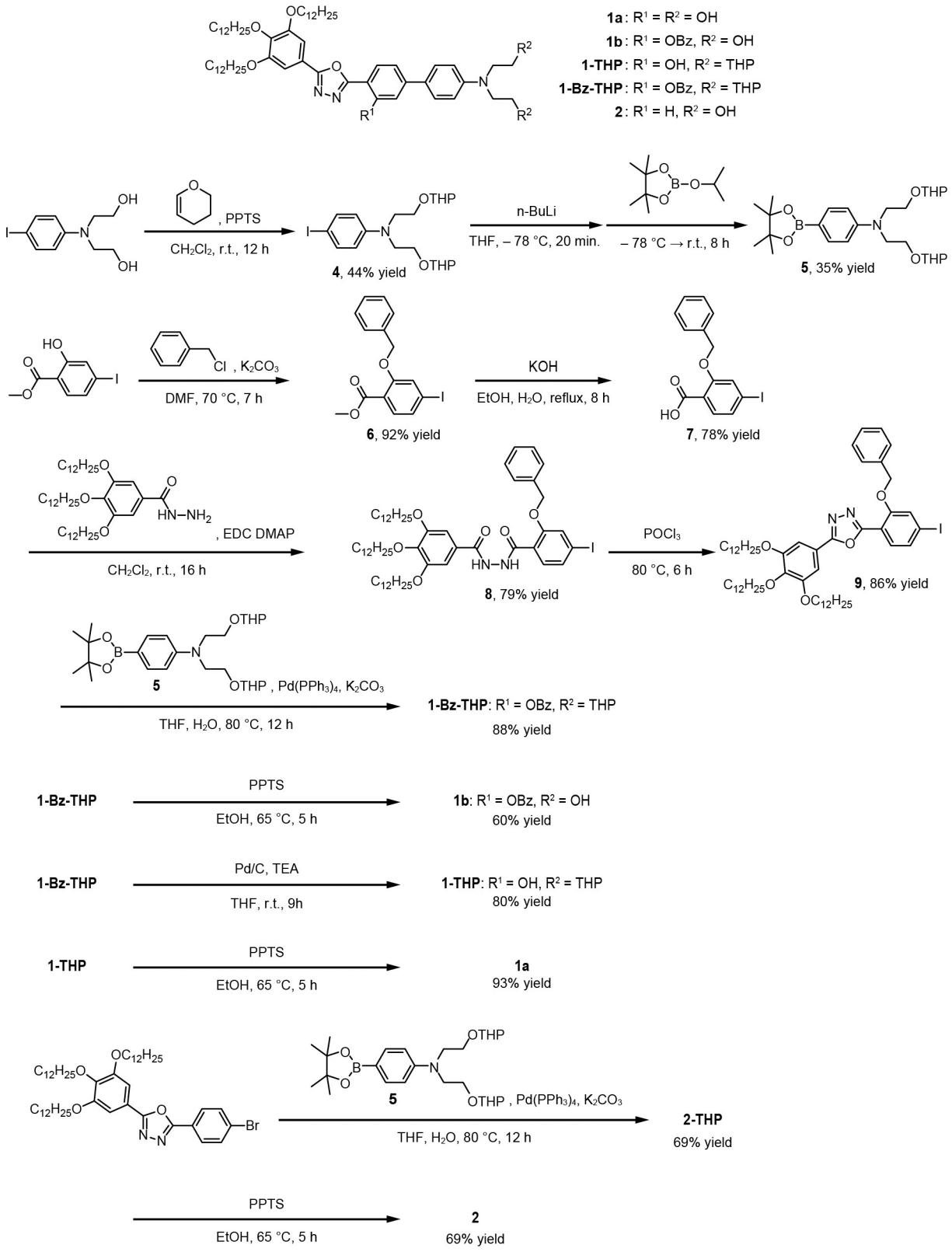
All reagents and solvents were purchased from Aldrich, Tokyo Kasei, and Kanto Chemicals. All of the reactions were carried out under argon atmosphere in dry solvents. Silica gel column chromatography was carried out with silica gel 60 from Kanto Chemicals (silica gel 60, spherical, 40–50 μm). Recycling preparative GPC was carried out with a Japan Analytical Industry LC-9201 chromatograph.

### General Procedures

$^{1}H$ and $^{13}C$ NMR spectra were obtained using a JEOL JNM-LA400 spectrometer in $CDCl_3$ solutions (400 and 100 MHz for $^{1}H$ NMR and $^{13}C$ NMR, respectively). Chemical shifts for $^{1}H$ and $^{13}C$ NMR were referenced to $Me_4Si$ ($\delta$ = 0.00) and $CDCl_3$ ($\delta$ = 77.00) as internal standards, respectively and are expressed in ppm ($\delta$), multiplicity, coupling constant (Hz), and relative intensity. Mass spectra were obtained using a Bruker Daltonics Autoflex Speed using dithranol as the matrix. Elemental analyses were carried out with an Exeter Analytical Inc. CE-440 Elemental Analyzer. Polarizing optical microscopic images were obtained with an Olympus BX51 equipped with a Mettler FP82 hot stage. Differential scanning calorimetry (DSC) measurements were performed on a NETZCH DSC204 Phoenix calorimeter at a scanning rate of 10 K $min^{-1}$. X-ray diffraction measurements were carried out on a Rigaku RINT2500 with a heating stage using Ni-filtered Cu Kα radiation (1.54 Å). The IR measurements were conducted on a JASCO FTIR-6100 and IRT-5000 using $CaF_2$ plates. Absorption spectra were measured with a JASCO V-670 spectrophotometer equipped with an integrating sphere unit ISN-800T. Emission spectra were recorded on a JASCO FP-6500 spectrofluorometer equipped with a hot stage. The absolute photoluminescence quantum yields were measured with a JASCO FP-8300 spectrofluorometer equipped with an integrating sphere unit ILF–835 ($\lambda_{ex}$ = 365 nm).

## Synthesis

*N,N*-Bis(2-hydroxyethyl)-4-iodoaniline[S1] and 3,4,5-tris(dodecyloxy)benzhydrazide[S2] were obtained according to the reported procedures.



**4-Iodo-*N*,*N*-bis[2-[(tetrahydro-2*H*-pyran-2-yl)oxy]ethyl]-benzenamine (4)**. A mixture of *N*,*N*-Bis(2-hydroxyethyl)-4-iodoaniline (911 mg, 2.97 mmol), 3,4-dihydro-2*H*-pyran (2496 mg, 29.7 mmol), and pyridinium *p*-toluenesulfonate (149.2 mg, 0.594 mmol) in $CH_2Cl_2$ (10 ml) was stirred for 13 h at room temperature. Brine was added to the mixture, and the solution was extracted with $CHCl_3$ two times. The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was purified by flush column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 1:0 to hexane/ethyl acetate = 6:1) to afford **4** (622 mg, 44%) and the product was used without further purification.

**Compound 5**. Compound **4** (620 mg, 1.30 mmol) was dissolved in anhydrous THF (7 ml) and *n*-Butyl lithium hexane solution (1.65 M, 0.98 ml, 1.56 mmol) was added to the solution at –78 °C. After stirring the solution at –78 °C for 20 min, isopropoxyboronic acid pinacol ester (315 mg, 1.70 mmol) was added dropwise to the reaction mixture. Stirring at room temperature for 8h, sat. $NH_4Cl$ aqueous solution was added. After the evaporation of the solvent, $CH_2Cl_2$ was added and washed with sat. $NH_4Cl$ aqueous solution and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was purified by flush column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 1:0 to hexane/ethyl acetate = 6:1) to afford to afford **5** as colorless viscous liquid (220 mg, 35%). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 4.61–4.53 (m, 2H), 3.93–3.78 (m, 4H), 3.72–3.56 (m, 6H), 3.50–3.44 (m, 2H), 1.87–1.77 (m, 2H), 1.77–1.63 (m, 2H), 1.63–1.46 (m, 8H), 1.32 (s, 12H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 150.07, 136.29, 110.76, 99.15, 99.12, 83.10, 64.71, 62.24, 50.87, 30.58, 25.37, 24.80, 19.47. MS (MALDI-TOF): *m/z* 476.42 $[M + H]^+$; calcd. 476.32.

**Compound 6**. A mixture of methyl 4-iodosalicylate (3.00 g, 10.8 mmol), benzyl chloride (1.64 g, 12.9 mmol), and $K_2CO_3$ (4.47 g, 32.4 mmol) in anhydrous DMF (20 ml) was degassed and refilled with argon. After stirring for 7 h at 70 °C, the mixture was cooled to room temperature. The mixture was poured into ethyl acetate/hexane (4/1) solution and washed with sat. $NH_4Cl$ aqueous solution (3 times) and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated. The resulting residue was purified by flash

column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 1:0 to hexane/ethyl acetate = 9:1) to afford **6** as colorless liquid (3.65 g, 92%). $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.54–7.45 (m, 3H), 7.45–7,29 (m, 5H), 5.14 (s, 2H), 3.88 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 166.11, 158.24, 136.02, 132.86, 129.90, 128.56, 127.95, 126.83, 123.20, 120.18, 99.78, 70.84, 52.08. MS (MALDI-TOF): *m/z* 391.03 [M + Na]$^{+}$; calcd. 390.98.

**Compound 7**. A mixture of **6** (3.65 g, 9,93 mmol) and KOH (1.23 g, 21.85 mmol) in EtOH (50 ml) and water (2 ml) was stirred for 8 h under reflux. After removing the solvent, the residue was poured into a mixture of 5% hydrochloric acid/ethyl acetate/ $CH_2Cl_2$. The organic phase was extracted and washed with water. The organic layer was dried over anhydrous $MgSO_4$, filtrated, and evaporated. The product was recrystallized from $CHCl_3$/hexane, and dried under vacuum to provide **7** as a white solid (2.75 g, 78%). $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 10.60 (s, 1H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.52–7.47 (m, 2H), 7.47–7.39 (m, 5H), 5.25 (s, 2H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 165.15, 157.23, 134.68, 133.81, 131.77, 129.33, 129.18, 128.94, 128.01, 122.59, 117.77, 101.56, 72.56. MS (MALDI-TOF): *m/z* 377.09 [M + Na]$^{+}$; calcd. 376.96. Anal. Calcd for $C_{14}H_{11}IO_3$: C, 47.48; H, 3.13; N, 0%; found: C, 47.66; H, 2.75; N, 0.24%.

**Compound 8**. A mixture of **7** (1.35 g, 3.81 mmol), 3,4,5-tris(dodecyloxy)benzhydrazide (2.50 g, 3.63 mmol), EDC (1.39 g, 7.26 mmol), and DMAP (88.6 mg, 0.73 mmol) in dry $CH_2Cl_2$ (40 mL) was stirred for 16 h at room temperature. The reaction mixture was poured into water and the solution was extracted with $CHCl_3$, and washed with brine. The organic phase was dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was purified by flush column chromatography on silica gel (eluent: gradient from $CHCl_3$/hexane = 3:1 to $CHCl_3$/hexane = 9:1) to afford **8** as white solid (2.94 g, 79%). $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 10.75–10.71 (m, 1H), 9.27–9.23 (m, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.55–7.35 (m, 7H), 7.02 (s, 2H), 5.35 (s, 2H), 4.00 (t, *J* = 6.6 Hz, 6H), 1.84–1.72 (m, 6H), 1.52–1.39 (m, 6H), 1.39–1.21 (m, 48H), 0.91–0.85 (m, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 163.23, 160.67, 156.52, 153.14, 141.52, 134.54, 133.29, 131.12, 129.05, 128.84, 127.79, 126.13, 122.55, 119.01, 105.57, 99.90, 73.46, 71.87, 69.17, 31.93, 30.33, 29.72, 29.65, 29.58, 29.42, 29.38,

29.31, 26.06, 26.03, 22.69, 14.12. MS (MALDI-TOF): *m/z* 1048.28 $[M + Na]^+$; calcd. 1047.57. Anal. Calcd for $C_{57}H_{89}IN_2O_6$: C, 66.78; H, 8.75; N, 2.73%; found: C, 66.91; H, 8.85; N, 2.39%.

**Compound 9**. A mixture of **8** (500 mg, 0.487 mmol) and $POCl_3$ (1.5 ml) was stirred at 80 °C for 6 h. After cooling to room temperature, the reaction mixture was poured into water and neutralized with aqueous NaOH solution. The resulting precipitate was collected by filtration and dried. The residue was purified by flush column chromatography on silica gel (eluent: hexane/ethyl acetate = 6:1) to afford **9** as white solid (0.420 g, 86%). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.54–7.46 (m, 4H), 7.38–7.27 (m, 3H), 7.24 (s, 2H), 5.23 (s, 2H), 4.03 (t, *J* = 6.6 Hz, 2H), 3.92 (t, *J* = 6.6 Hz, 4H), 1.84–1.72 (m, 6H), 1.55–1.39 (m, 6H), 1.39–1.21 (m, 48H), 0.91–0.85 (m, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 164.98, 162.86, 156.69, 153.55, 141.27, 135.77, 131.55, 130.55, 128.67, 128.08, 126.82, 122.78, 118.54, 113.47, 105.44, 98.79, 73.58, 70.80, 69.27, 31.92, 30.33, 29.73, 29.69, 29.64, 29.59, 29.40, 29.36, 29.29, 26.05, 22.68, 14.11. MS (MALDI-TOF): *m/z* 1008.11 $[M + H]^+$; calcd. 1007.57. Anal. Calcd for $C_{57}H_{87}IN_2O_5$: C, 67.97; H, 8.71; N, 2.78%; found: C, 68.20; H, 8.89; N, 2.60%.

**Compound 1-Bz-THP**. A mixture of **9** (423 mg, 0.421 mmol), **5** (220 mg, 0.463 mmol), and $K_2CO_3$ (290 mg, 2.10 mmol) in THF (6 ml) and $H_2O$ (6 ml) was bubbled by argon. To the mixture, $Pd(PPh_3)_4$ (19.4 mg, 0.0168 mmol) was added, and the mixture was stirred at 80 °C for 12 h. After the evaporation of the solvent, $CHCl_3$ was added and washed with water, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was purified by flush column chromatography on silica gel (gradient from eluent: hexane/chloroform = 1:9 to hexane/chloroform = 0:1) to afford compound **1-Bz-THP** (455 mg, 88%). $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 9.2 Hz, 2H), 7.38–7.27 (m, 7H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.33 (s, 2H), 4.61–4.57 (m, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 3.96–3.93 (m, 6H), 3.87–3,83 (m, 2H), 3.74–3.62 (m, 6H), 3.53–3.48 (m, 2H), 1.91–1.68 (m, 10H), 1.65–1.41 (m, 14H), 1.41–1.20 (m, 48H), 0.90–0.86 (m, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 164.56, 163.57, 157.02, 153.49, 148.06, 145.99, 140.99, 136.61, 130.83, 128.58, 127.94, 127.80, 126.97, 126.82, 118.90, 118.88, 111.96,

111.02, 110.77, 105.32, 99.16, 73.55, 70.48, 69.21, 64.74, 62.27, 51.10, 31.91, 30.60, 30.33, 29.73, 29.68, 29.63, 29.58, 29.40, 29.35, 29.29, 26.05, 25.38, 22.67, 19.46, 14.10. MS (MALDI-TOF): *m/z* 1228.89 $[M + H]^+$; calcd. 1229.57.

**Compound 1b**. A mixture of **1-Bz-THP** (455 mg, 0.370 mmol) and pyridinium *p*-toluenesulfonate (18.61 mg, 0.074 mmol) in EtOH (20 ml) was stirred at 65 °C for 4.5 h. After the evaporation of the solvent, $CHCl_3$ was added and washed with sat. $NaHCO_3$ aqueous solution, water, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was purified by flush column chromatography on silica gel (gradient from eluent: hexane/ethyl acetate = 1:1 to hexane/ethyl acetate = 1:4) and crystallization from ethyl acetate and hexane to afford compound **1b** (234 mg, 60%). $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.57–7.52 (m, 4H), 7.37–7.28 (m, 7H), 6.81 (d, *J* = 9.2 Hz, 2H), 5.32 (s, 2H), 4.03 (t, *J* = 6.8 Hz, 2H), 3.96–3.93 (m, 8H), 3.68 (t, *J* = 4.8 Hz, 4H), 2.82 (s, 2H), 1.82–1.73 (m, 6H), 1.50–1.42 (m, 6H), 1.40–1.24 (m, 48H), 0.90–0.86 (m, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 164.62, 163.52, 157.04, 153.53, 148.10, 145.81, 141.09, 136.55, 130.88, 128.60, 127.98, 127.91, 127.86, 126.84, 118.98, 118.80, 112.75, 111.19, 110.91, 105.39, 73.59, 70.51, 69.25, 60.71, 55.11, 31.92, 30.33, 29.74, 29.69, 29.64, 29.59, 29.41, 29.36, 29.31, 26.07, 22.68, 14.10. MS (MALDI-TOF): *m/z* 1061.16 $[M + H]^+$; calcd. 1060.77. Anal. Calcd for $C_{67}H_{101}N_3O_7$: C, 75.88; H, 9.60; N, 3.96%; found: C, 75.86; H, 9.82; N, 3.79%.

**Compound 1-THP**. A mixture of **1-Bz-THP** (690 mg, 0.561 mmol) and palladium 10% on carbon (120 mg) in THF (30 ml) and trimethylamine (1 ml) was stirred at r.t. for 9 h. Insoluble palladium on carbon was filtered off through a pad of celite by using a suction funnel. The filtrate was concentrated by evaporation. The residue was purified by flush column chromatography on silica gel (eluent: chloroform) to afford **1-THP** as pale yellow solid (0.510 g, 80%). $^1$H NMR ($CDCl_3$, 400 MHz): δ 10.18 (s, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.34–7.32 (m, 3H), 7.25–7.22 (m, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.63–4.59 (m, 2H), 4.12–4.03 (m, 6H), 3,98–3.90 (m, 2H), 3.89–3.81 (m, 2H), 3.74–3.60 (m, 6H), 3.54–3.47 (m, 2H), 1.91–1.67 (m, 10H), 1.64–1.57 (m, 4H), 1.55–1.45 (m, 10H), 1.43–1.24 (m, 48H), 0.91–0.86 (m, 9H). $^{13}$C NMR ($CDCl_3$, 100

MHz): δ 164.18, 163.18, 157.91, 153.65, 148.17, 146.47, 141.65, 127.95, 126.67, 126.59, 117.96, 117.71, 114.11, 111.97, 105.62, 105.51, 99.18, 73.67, 69.43, 64.80, 62.29, 51.10, 31.93, 30.62, 30.34, 29.70, 29.64, 29.58, 29.41, 29.37, 29.33, 26.08, 25.40, 22.69, 19.47, 14.11. MS (MALDI-TOF): *m/z* 1139.30 $[M + H]^+$; calcd. 1138.84. Anal. Calcd for $C_{70}H_{111}N_3O_9$: C, 73.84; H, 9.83; N, 3.69%; found: C, 73.99; H, 10.12; N, 3.42%.

**Compound 1a**. A mixture of **1-THP** (410 mg) and pyridinium *p*-toluenesulfonate in EtOH (30 ml) and THF (30 ml) was stirred for 6 h at 65 °C. After evaporation of the solvent, water and $CHCl_3$ were added to the resulting residue. Organic layer was extracted and washed with sat. $NaHCO_3$ aqueous solution, water, and brine. The organic phase was dried over anhydrous $Na_2SO_4$, filtered, and evaporated. The residue was purified by crystallization from ethyl acetate and hexane to afford **1a** as pale yellow solid (324 mg, 93%). $^1$H NMR ($CDCl_3$, 400 MHz): δ 10.19 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.33–7.31 (m, 3H), 7.23 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.79 (d, *J* = 9.2 Hz, 2H), 4.10–4.04 (m, 6H), 3.93 (t, *J* = 4.8 Hz, 4H), 3.67 (t, *J* = 4.8 Hz, 4H), 1.90–1.74 (m, 6H), 1.55–1.45 (m, 6H), 1.44–1.25 (m, 48H), 0.90–0.86 (m, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 164.10, 163.22, 157.89, 153.65, 148.10, 146.17, 141.66, 128.00, 127.64, 126.72, 117.90, 117.78, 114.29, 112.74, 105.87, 105.50, 73.69, 69.43, 60.81, 55.14, 31.93, 30.33, 29.70, 29.64, 29.58, 29.41, 29.37, 29.33, 26.09, 22.69, 14.11. MS (MALDI-TOF): *m/z* 971.25 $[M + H]^+$; calcd. 970.72. Anal. Calcd for $C_{60}H_{95}N_3O_7$: C, 74.26; H, 9.87; N, 4.33%; found: C, 74.32; H, 10.13; N, 4.12%.

**Compound 2-THP**. A mixture of 2-(4-bromophenyl)-5-(3,4,5-tridodecyloxyphenyl)-1,3,4-oxadiazole (452 mg, 0.530 mmol), **5** (277 mg, 0.583 mmol), and $K_2CO_3$ (366 mg, 2.65 mmol) in THF (10 ml) and $H_2O$ (8 ml) was bubbled by argon. To the mixture, $Pd(PPh_3)_4$ (24.5 mg, 0.0211 mmol) was added, and the mixture was stirred at 80 °C for 7 h. After the evaporation of the solvent, $CHCl_3$ was added and washed with water twice, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was purified by flush column chromatography on silica gel (gradient from eluent: hexane/chloroform = 1:9 to hexane/chloroform = 0:1) to afford compound **2-THP** (412 mg, 69%). $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.14 (d,

*J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.33 (s, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.66–4.54 (m, 2H), 4.13–4.02 (m, 6H), 3.98–3.91 (m, 2H), 3.90–3.81 (m, 2H), 3.77–3.60 (m, 6H), 3.53–3.46 (m, 2H), 1.91–1.66 (m, 10H), 1.66–1.44 (m, 14H), 1.44–1.20 (m, 48H), 0.91–0.84 (m, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 164.56, 164.50, 153.58, 147.98, 144.26, 141.26, 127.88, 127.31, 126.86, 126.25, 121.13, 118.67, 112.05, 105.40, 99.18, 73.61, 69.37, 64.78, 62.28, 51.10, 31.92, 30.61, 30.33, 29.70, 29.64, 29.58, 29.41, 29.39, 29.36, 26.08, 25.39, 22.68, 19.47, 14.11. MS (MALDI-TOF): *m/z* 1123.57 $[M + H]^+$; calcd. 1122.84.

**Compound 2**. A mixture of **2-THP** (412 mg, 0.367 mmol) and pyridinium *p*-toluenesulfonate (18.4 mg, 0.073 mmol) in EtOH (20 ml) was stirred at 65 °C for 8 h. After the evaporation of the solvent, $CHCl_3$ was added and washed with sat. $NaHCO_3$ aqueous solution, water, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was purified by crystallization from ethyl acetate and from acetone to afford compound **2** (242 mg, 69%). $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.8 Hz,2H), 7.53 (d, *J* = 9.2 Hz, 2H) 7.31 (s, 2H), 6.79 (d, *J* = 9.2 Hz, 2H), 4.12–4.02 (m, 6H), 3.96–3.89 (m, 4H), 3.66 (t, *J* = 4.8 Hz, 4H), 3.35 (s, 2H), 1.92–1.74 (m, 6H), 1.56–1.44 (m, 6H), 1.44–1.21 (m, 48H), 0.91–0.85 (m, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 164.54, 164.48, 153.58, 147.96, 144.04, 141.30, 127.90, 127.73, 127.33, 126.35, 121.26, 118.54, 112.78, 105.39, 73.64, 69.38, 60.73, 55.17, 31.93, 30.33, 29.70, 29.64, 29.58, 29.42, 29.37, 26.09, 22.69, 14.11. MS (MALDI-TOF): *m/z* 955.02 $[M + H]^+$; calcd. 954.73. Anal. Calcd for $C_{60}H_{95}N_3O_6$: C, 75.51; H, 10.03; N, 4.40%; found: C, 75.46; H, 10.18; N, 4.65%.

## 2. Solvent effects on the photophysical properties of compounds 1a and 2

**Table S1.** Solvent effects on the photophysical properties of compounds **1a** and **2**.

| Solvent | $E_T(30)$ | $\Delta f$ | $\Delta f$" | **1a** | | | **2** | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $\lambda_{abs}{}^a$ | $\lambda_{em}{}^a$ | $\Phi_{PL}$ | $\lambda_{abs}{}^a$ | $\lambda_{em}{}^a$ | $\Phi_{PL}$ |
| cyclohexane | 30.9 | -0.001 | 0.126 | 354 | 398 | – | 347 | 391 | – |
| toluene | 33.9 | 0.013 | 0.176 | 369 | 428 | – | 358 | 423 | – |
| THF | 37.4 | 0.209 | 0.560 | 373 | 475 | – | 365 | 465 | – |
| chloroform | 39.1 | 0.149 | 0.431 | 366 | 449 | – | 355 | 446 | – |
| dichloromethane | 39.4 | 0.219 | 0.600 | 366 | 464 | 0.96 | 356 | 461 | 0.96 |
| DMF | 43.2 | 0.275 | 0.794 | 375 | 519 | – | 371 | 510 | – |
| DMSO | 45.1 | 0.265 | 0.797 | 374 | 522 | – | 375 | 523 | – |

[a] $\lambda_{abs}$: wavelengths of absorption maxima (nm); $\lambda_{em}$: wavelengths of emission maxima (nm).

The orientation polarizabilities are expressed as

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

$$\Delta f'' = \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{2n^2 + 4}$$

where, $\varepsilon$ and $n$ represent the relative dielectric constant and the refractive index of a solvent.

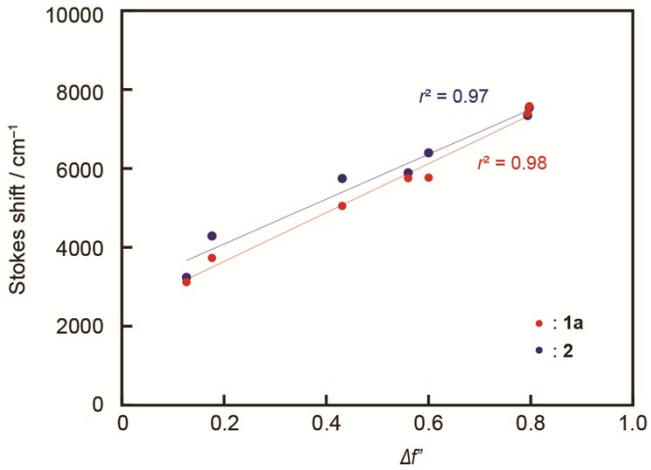



**Fig. S1** Lippert-Mataga correlations for compounds **1a** and **2** on the solvent polarity parameter $\Delta f$''. *r*: Correlation coefficient.

## 3. Liquid-crystalline properties of compound 1b

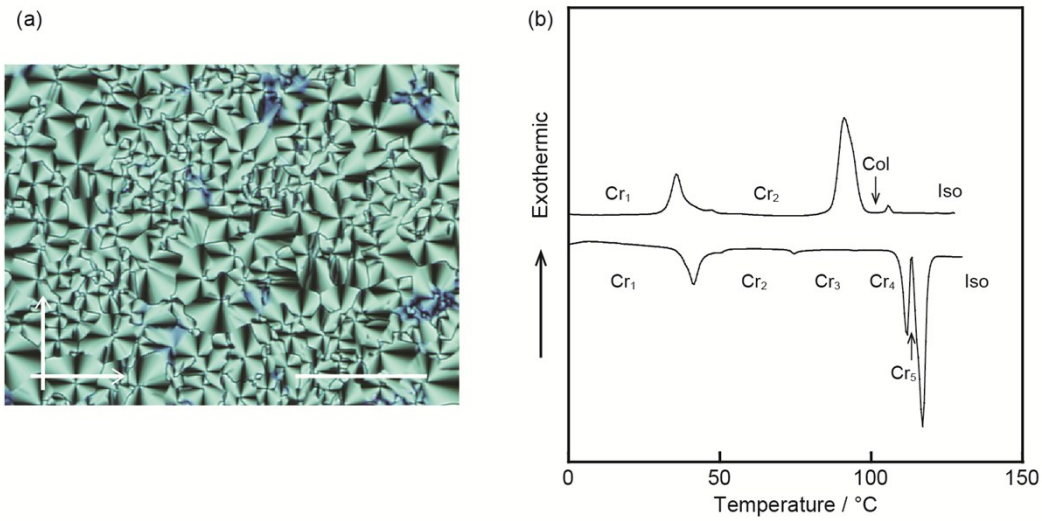



**Fig. S2** (a) A polarizing optical microscopic image of compound **1b** at 100 °C on the cooling process. Arrows indicate the directions of polarizer and analyzer axes. Scale bar: 100 μm. (b) DSC traces of compound **1b** at a scanning rate of 10 K $min^{-1}$. Cr: crystalline; Col: unidentified columnar, Iso: isotropic liquid.

## 4. Contact tests for compounds 1a and 3(X)

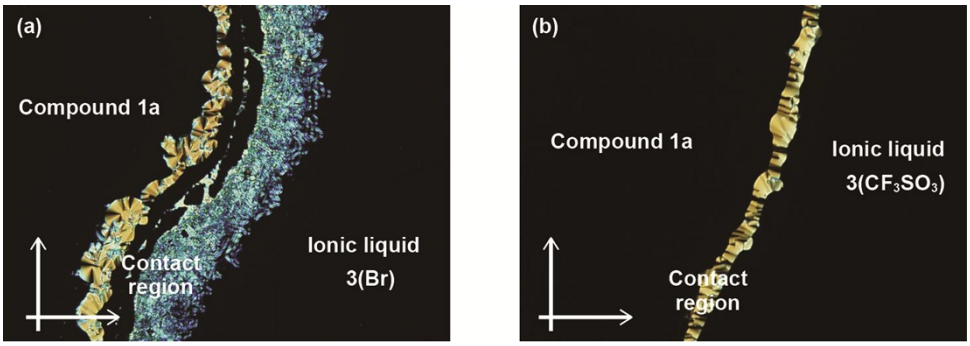



**Fig. S3** Polarizing optical microscopic images of the contact region: (a) compounds **1a** and **3(Br)** at 150 °C; (b) compounds **1a** and **3($CF_3SO_3$)** at 170 °C. Arrows indicate the directions of polarizer and analyzer axes.

## 5. Liquid-crystalline properties of the mixture of 2 and 3($BF_4$)

The pristine compound **2** forms only crystalline phases (Table 1). However the mixture of compound **2** and **3($BF_4$)** in the molar ratio of 8:2 exhibits the $Col_h$ phase (Fig. S4). In the SAXS patterns of the mixture at 130 °C in the molar ratio of 8:2, three peaks at 48.5 (100), 27.8 (110), and 24.1 Å (200) with reciprocal *d*-spacing ratio of 1:√3:2 were obtained (Fig. S4), confirming the formation of the $Col_h$ phase.

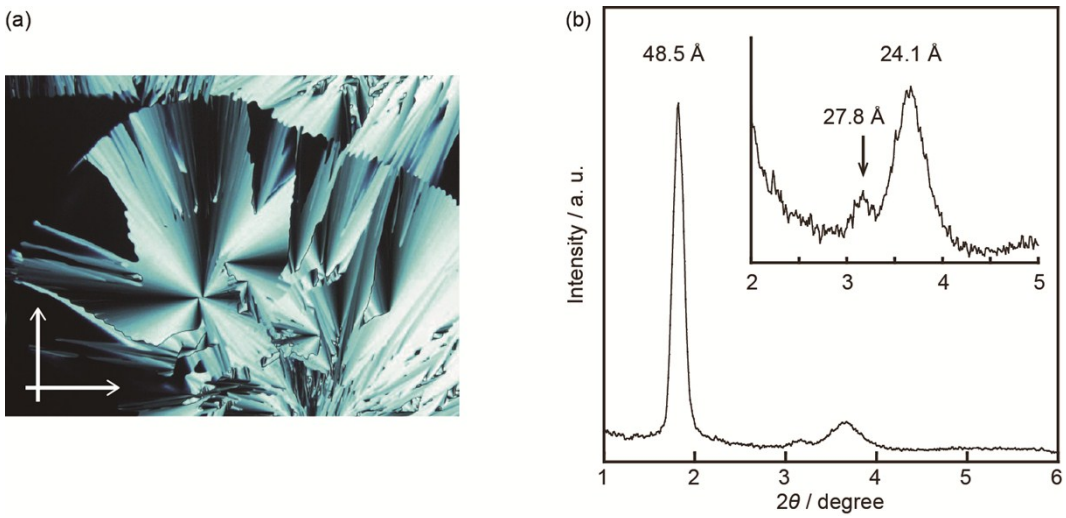



**Fig. S4** (a) A polarizing optical microscopic image of the mixture of compound **2** and **3($BF_4$)** in the $Col_h$ phase at 130 °C in the molar ratio of 8:2. (b) SAXS pattern of the mixture of compound **2** and **3($BF_4$)** in the $Col_h$ phase at 130 °C in the molar ratio of 8:2.

## 6. Liquid-crystalline properties of the mixture of 1a and 3($BF_4$)

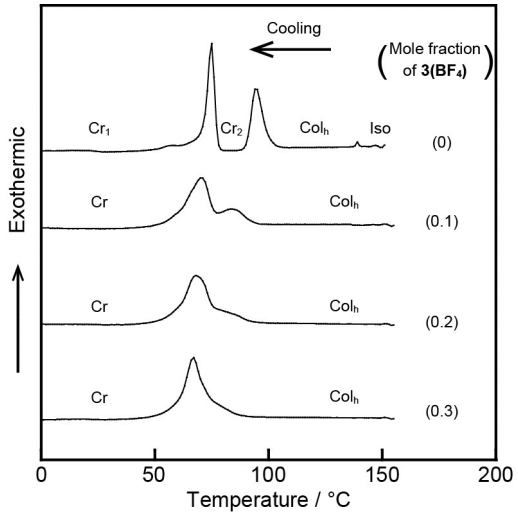



**Fig. S5** DSC traces of mixtures of compounds **1a** and **3($BF_4$)** with different molar ratio on cooling at a scanning rate of 10 K $min^{-1}$. The mole fraction of **3($BF_4$)** is shown in the parentheses. Cr: crystalline; $Col_h$: hexagonal columnar, Iso: isotropic liquid.

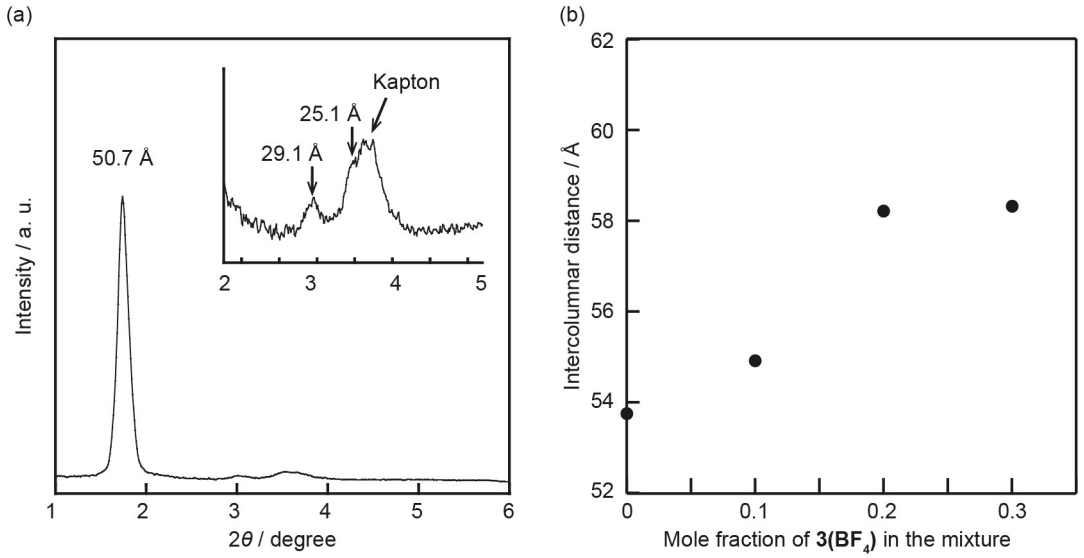



**Fig. S6** (a) A SAXS pattern of the mixture of **1a** and **3($BF_4$)** in the $Col_h$ in a 8:2 molar ratio at 130 °C. (b) Intercolumnar distance of mixtures of **1a** and **3($BF_4$)** in the $Col_h$ phase at 130 °C.

## 7. IR measurements

IR spectra were obtained to study the interactions of the hydroxyl groups at the π-conjugated moiety and the terminal diol moiety. Compound **1-THP** in the crystalline phase at room temperature shows a peak at 3258 $cm^{-1}$ (Fig. S7a), which can be ascribed to the -OH stretching band of hydroxyl group at the π-conjugated moiety forming an intramolecular hydrogen bond with the oxadiazole moiety. In the IR spectrum of compound **1b** in the $Col_h$ phase at 105 °C, a broad band centered at 3395 $cm^{-1}$ is due to the intermolecular hydrogen bonds of the diol groups whereas a shoulder around 3565 $cm^{-1}$ can be attributed the free -OH stretching band (Fig. S7b). Compound **1a** in the $Col_h$ phase at 130 °C shows the IR spectrum which is similar to the superposition spectrum of compounds **1-THP** and **1b** (Fig. S7c). A broad absorption band centered at 3412 $cm^{-1}$ and a shoulder around 3565 $cm^{-1}$ are ascribed to the -OH stretching bands of the diol group. A shoulder around 3209 $cm^{-1}$ is due to the intramolecular hydrogen bonds as observed for the compound **1-THP**. These results suggest that compound **1a** exhibits the $Col_h$ phase through nanosegregation. Diol moieties are organized at the center of the columns to form the intermolecular hydrogen bonds. As for the mixture of **1a** and **3($BF_4$)**, the absorption around 3547 $cm^{-1}$ becomes stronger as the mole fraction of compound **3($BF_4$)** increases (Fig. S7d–f). Compound **3($BF_4$)** does not show the corresponding peak (Fig. S7g). Therefore, this band appears through co-oraganization of compounds **1a** and **3($BF_4$)**. The absorption peak is close to that of the free -OH stretching band of compound **1a** (3565 $cm^{-1}$, Fig. S7c), and can be ascribed to the -OH stretching band of diol moiety forming the hydrogen bonds with $BF_4^-$.[S3] These observations indicate that the ionic liquids **3($BF_4$)** are organized inside the columns, of which $BF_4$ anions interact with the diol moieties of compound **1a**. The co-organization of compound **1a** and **3($BF_4$)** may promote nanosegregation between the ionophilic moieties and ionophobic moieties, resulting in the stabilization of the $Col_h$ phases.

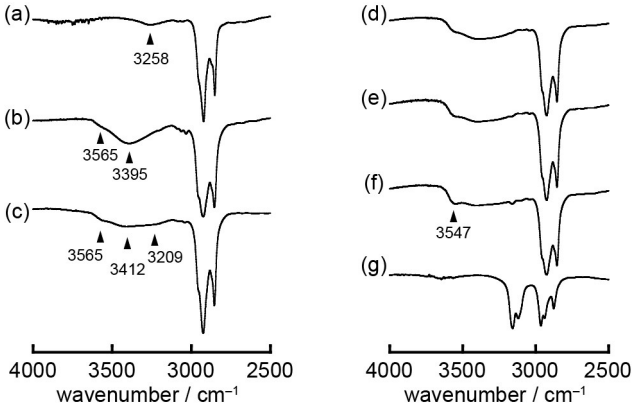



**Fig. S7** IR spectra for (a) **1-THP** in the crystalline phase at r.t.; (b) **1b** in the $Col_h$ phase at 105 °C; (c) **1a** in the $Col_h$ phase at 130 °C; (d) mixtures of **1a** and **3($BF_4$)** in a 9:1; (e) 8:2; and (f) 7:3 ratio in the $Col_h$ phase at 130 °C; (g) compound **3($BF_4$)** at 130 °C.

## 8. Liquid-crystalline properties and luminescence properties of the mixture of 1a and tetraethylammonium tetrafluoroborate ($[Et_4N]BF_4$)

To examine the effects of cationic moieties on the properties of the mixture, compound **1a** and tetraethylammonium tetrafluoroborate (**$[Et_4N]BF_4$**) (Fig. S8a) were mixed in the 9:1 molar ratio. The mixture of **1a** and **$[Et_4N]BF_4$** (**1a/$[Et_4N]BF_4$**) exhibits a fan-shaped texture at 130 ºC under polarizing optical microscope (Fig. S8b) indicating the formation of a columnar liquid-crystalline phase. The polarizing optical microscopic image of the mixture of **1a** and **$[Et_4N]BF_4$** turns to black at 155 ºC due to the phase transition to the isotropic liquid phase (Fig. S8c and Fig. S8f), while the mixture of **1a** and **3($BF_4$)** in the 9:1 molar ratio maintains the fan shaped-texture (Fig. S8d). The mixture of **1a** and **3($BF_4$)** in the 9:1 molar ratio starts melting above 155 ºC (Fig. S8e) and the phase transition to the isotropic liquids state completes at 180 ºC. Due to partial decomposition, it is difficult to determine the exact isotropization temperature of the mixture of **1a** and **3($BF_4$)**.

The mixture of **1a** and **$[Et_4N]BF_4$** and the mixture of **1a** and **3($BF_4$)** in 9:1 molar ratio also show difference in their luminescence spectra. A broad emission band with an emission peak ($\lambda_{em}$) at 489 nm is seen for the mixture of **1a** and **$[Et_4N]BF_4$** which is slightly red-shifted compared to compound **1a** alone ($\lambda_{em}$ = 483 nm), but the peak shift is not as large as that of the mixture of **1a** and **3($BF_4$)** ($\lambda_{em}$ = 497 nm) (Fig. S8g).

Polarizing optical microscopic observation and photoluminescence measurements indicate that introduction of both of **$[Et_4N]BF_4$** and **3($BF_4$)** stabilizes the liquid-crystalline columnar phases and the intramolecular charge transfer state of compound **1a**. The difference in stabilities of liquid-crystalline states and luminescence spectra suggests that the intermolecular interactions between compound **1a** and **3($BF_4$)** are stronger compared to that of **1a** and **$[Et_4N]BF_4$**.

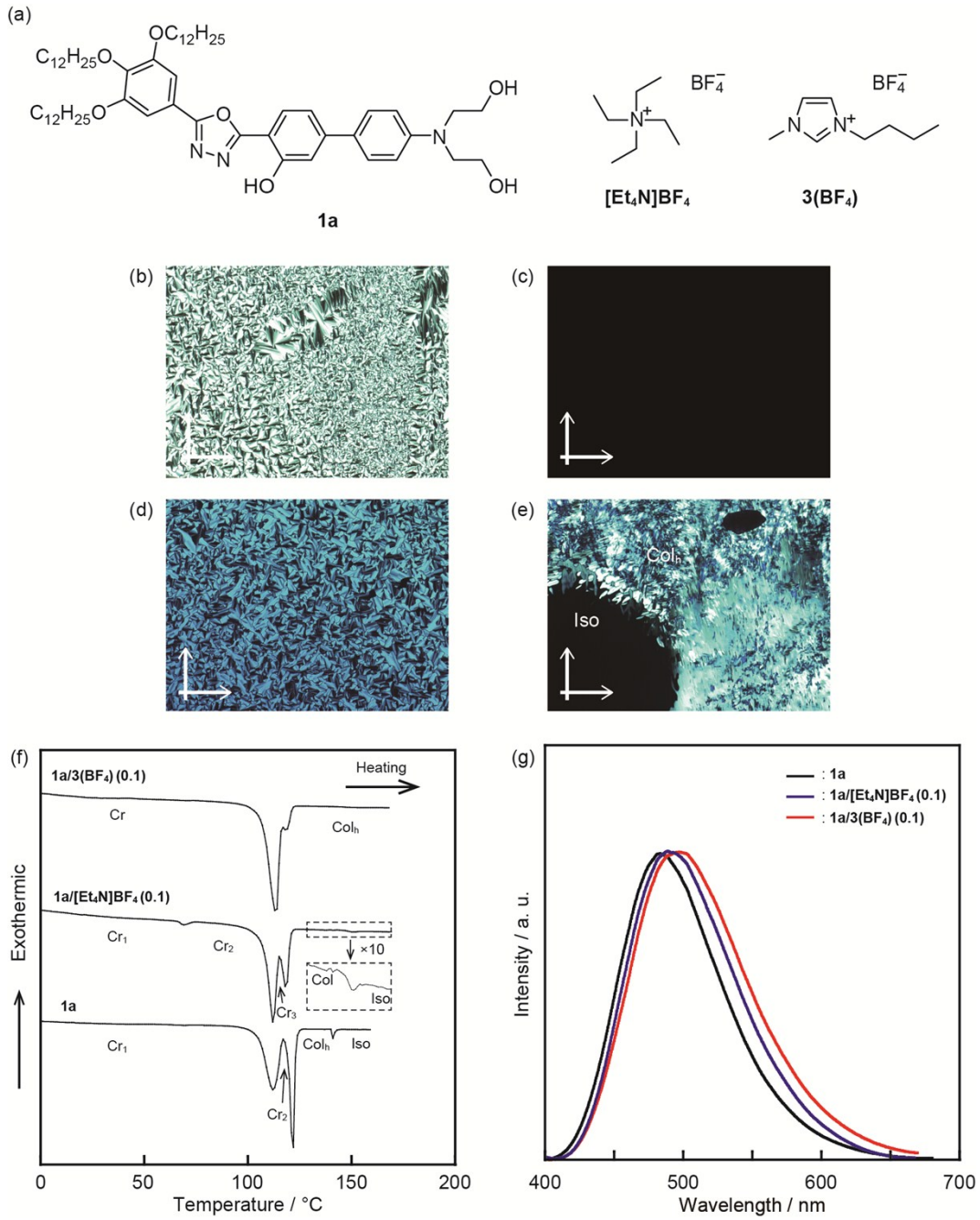



**Fig. S8** (a) Molecular structures of compound **1a**, tetraethylammonium tetrafluoroborate (**[Et$_4$N]BF$_4$**), and **3(BF$_4$)**. Polarizing optical microscopic images of the mixture of **1a** and **[Et$_4$N]BF$_4$** in the molar ratio of 9:1 at (b) 130 °C and (c) 155 °C, and the mixture **1a/3(BF$_4$)** in the 9:1 molar ratio at (d) 155 °C and (e) 165 °C. Arrows indicate the directions of polarizer and analyzer axes. (f) DSC traces of compound **1a**(bottom), the mixture of **1a** and **[Et$_4$N]BF$_4$** in the 9:1 molar ratio (middle), and the mixture of **1a** and **3(BF$_4$)** in the 9:1 molar ratio (top) on heating at a scanning rate of 10 K min$^{-1}$ on second heating. Cr: crystalline; Col$_h$: hexagonal columnar, Col: unidentified columnar; Iso: isotropic liquid. (g) Emission spectra of compound **1a** (black), the mixture of **1a** and **[Et$_4$N]BF$_4$** in the 9:1 molar ratio (blue), and the mixture of **1a** and **3(BF$_4$)** in the 9:1 molar ratio (red) in the Col phase at 130 °C ($\lambda_{ex}$ = 365 nm) The mole fraction of **[Et$_4$N]BF$_4$** and **3(BF$_4$)** is shown in the parentheses.

## 9. References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