Supporting information available for

Fused π-Conjugated Imidazolium Liquid Crystals: Synthesis, Self-Organization, and Fluorescent Properties

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S1. Materials and instruments

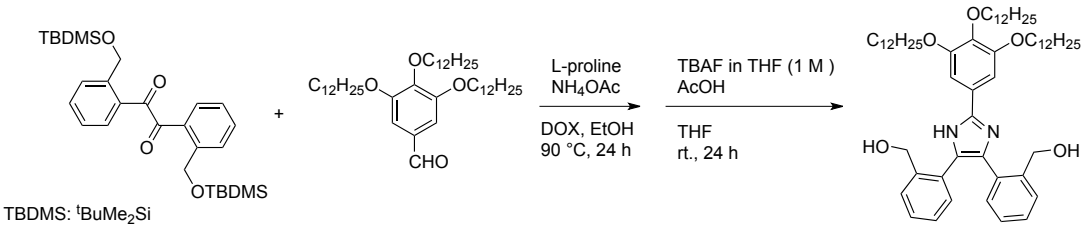
All organic materials were obtained from commercial suppliers and used without purification. Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) was purchased from Kanto Chemical Co. Lithium bis(trimethylsilyl)amide (LiHMDS) solution in tetrahydrofuran (THF) (1.0 M), silver trifluoromethanesulfonate (AgOTf), and triethyloxonium tetrafluoroborate ($Et_3O \cdot BF_4$) solution in CH_2Cl_2 (1.0 M) were purchased from Sigma-Aldrich Co. Anhydrous THF (without stabilizer) and CH_2Cl_2 were purchased from Kanto Chemical Co. Other solvents were dried following to standard methods and distilled before use under the nitrogen atmosphere.

^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) spectroscopies were obtained on a Bruker Avance 200 and Ascend 400 FT-NMR spectrometers in deuterated solvents. Tetramethylsilane (^{1}H-NMR, δ 0.00) and solvent residual peaks (^{1}H-NMR and ^{13}C-NMR) were used as an internal standard. Elemental analyses (EA) were performed on an Elementar vario EL cube. Differential scanning calorimetry (DSC) were measured on a Seiko Instruments Inc. DSC 220C at the heating and cooling rate of 5 °C/min under the nitrogen flow (25 mL/min). Polarizing optical microscope (POM) images were obtained on an Olympus BX50 at the heating and cooling rate of 5 °C/min.

Variable-temperature X-ray diffraction (VT-XRD) analyses were carried out on a Rigaku FR-E X-ray diffractometer equipped with a Rigaku R-axis IV two-dimensional detector using an imaging plate. Beams of 0.3-mm collimated Cu-Kα radiation (λ = 0.154 nm) were used as X-rays, and the camera length was set at 300 mm. Single crystal X-ray structure analysis was performed on a Bruker Smart ApexII Ultra. Ultraviolet-visible (UV-vis) absorption and fluorescence emission spectra in solution state were recorded on a Shimadzu UV-1650 spectrophotometer and a Shimadzu RF-5300 spectrofluorometer, respectively, using a 10 mm quartz cell. Fluorescence quantum yields (QY) were determined relative to quinine sulfate in 0.05 M H_2SO_4 having a QY of 0.55. UV-vis absorption and fluorescence emission spectra in solid state were recorded on a Shimadzu UV-3150 spectrophotometer with a calibrated integrating sphere system and a HORIBA FluoroMax-4 spectrofluorometer, respectively. Absolute QYs in solid state were determined using an a calibrated integrating sphere system. Fluorescence lifetime measurements were performed on a confocal laser scanning microscope (NX-3DFLIM-N03, Tokyo Instruments, Japan) equipped with an objective lens (MPLFLN ×50; numerical aperture = 0.30, Olympus, Japan) and a streak camera (C10627-03, Hamamatsu Photonics., Japan). A 375 and 420 nm TiSa laser (Mai Tai VF-TIS, Spectra-Physics, Inc.) was used as the excitation source as the frequency-doubled light modulated at 8 MHz through a pulse picker (Model3980, Spectra-Physics, Inc.).

S2. Syntheses of fused π-conjugated imidazolium compounds

4,5-Bis(2'-(hydroxymethyl)phenyl)-2-(3",4",5"-tridecyloxyphenyl)imidazole (Typical procedure)



TBDMS: $^{t}BuMe_2Si$

A mixture of 1,2-bis(2'-(*t*-butyldimethylsiloxymethyl)phenyl)ethane-1,2-dione[1] (0.50 g, 1.0 mmol), 3,4,5-tridodecyloxybenzaldehyde[2] (0.99 g, 1.5 mmol), L-proline (18 mg, 0.15 mmol), and ammonium acetate (3.0 g, 39 mmol) in EtOH (4 mL) and 1,4-dioxane (2 mL) was heated at 90 °C for 24 h. Water was added and an aqueous phase was extracted with CH_2Cl_2. The combined organic phase was rinsed with brine and dried over $MgSO_4$. The solvent was removed and the remaining brown solid was dissolved in a mixture of THF (95 mL), TBAF solution in THF (1 M, 4.5 mL), and AcOH (0.26 mL) to stir at room temperature overnight. The solvent was removed and dissolved in CH_2Cl_2 that was rinsed with sat. aqueous $NaHCO_3$ and dried over $MgSO_4$. The solvent was removed and the crude product was purified by SiO_2 column chromatography (hexane : ethyl acetate = 8 : 3, Rf = 0.40) to obtain a yellow solid (0.53 g, 59% yield).

^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ ppm 0.79 - 0.98 (m, 9 H) 1.26 (br. s., 48 H) 1.47 (br. s., 6 H) 1.77 (d, *J*=6.82 Hz, 6 H) 4.00 (q, *J*=6.06 Hz, 6 H) 4.59 (br. s., 2 H) 4.75 (br. s., 2 H) 7.04 (s, 2 H) 7.10 (br. s., 2 H) 7.21 (br. s., 2 H) 7.26 - 7.37 (m, 2 H) 7.45 (br. s., 2 H) 11.68 (br. s., 1 H)

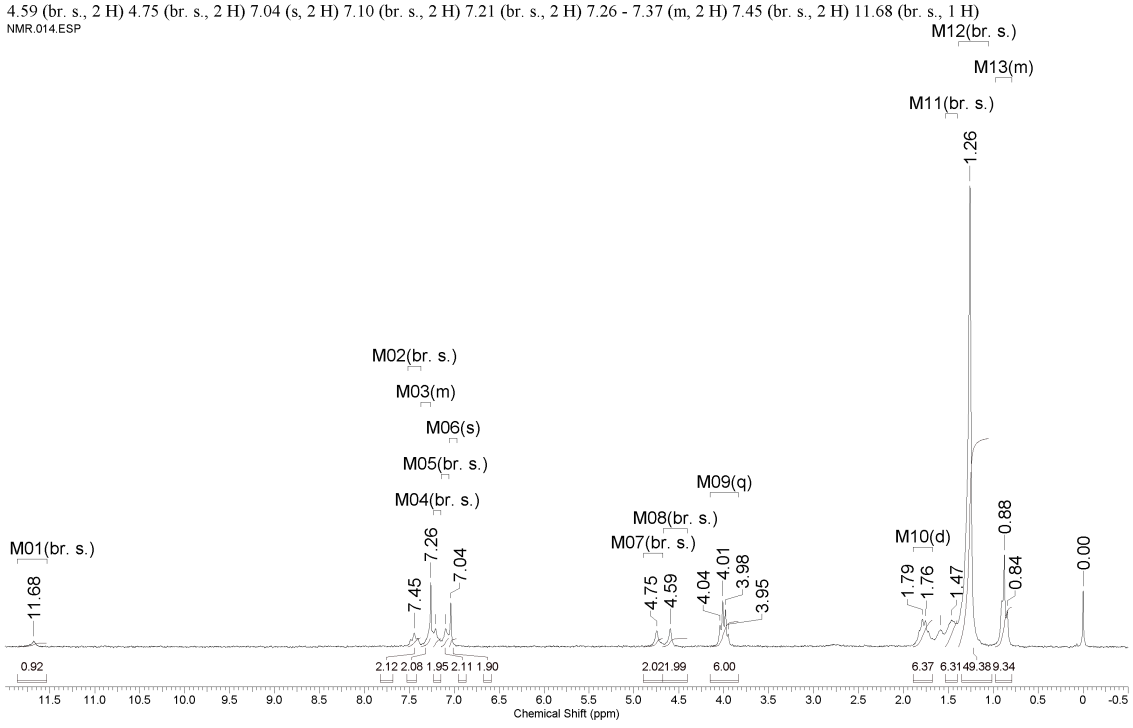


Figure S1. ^{1}H-NMR spectrum of 4,5-bis(2'-(hydroxymethyl)phenyl)-2-(3",4",5"-tridecyloxyphenyl)imidazole in $CDCl_3$.

4,5-Bis(2'-(hydroxymethyl)phenyl)-2-(3",4",5"-trioctyloxyphenyl)imidazole

This compound was synthesized in a similar manner to that of

4,5-bis(2'-(hydroxymethyl)phenyl)-2-(3",4",5"-tridecyloxyphenyl)imidazole.

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.83 - 0.95 (m, 9 H) 1.20 - 1.40 (m, 24 H) 1.40 - 1.55 (m, 6 H) 1.69 - 1.87 (m, 6 H) 3.93 - 4.08 (m, 6 H) 4.58 (br. s., 2 H) 4.73 (br. s., 2 H) 6.96 - 7.25 (m, 8 H) 7.41 (d, *J*=7.34 Hz, 1 H) 7.45 (d, *J*=7.34 Hz, 1 H) 11.75 (br. s., 1 H)

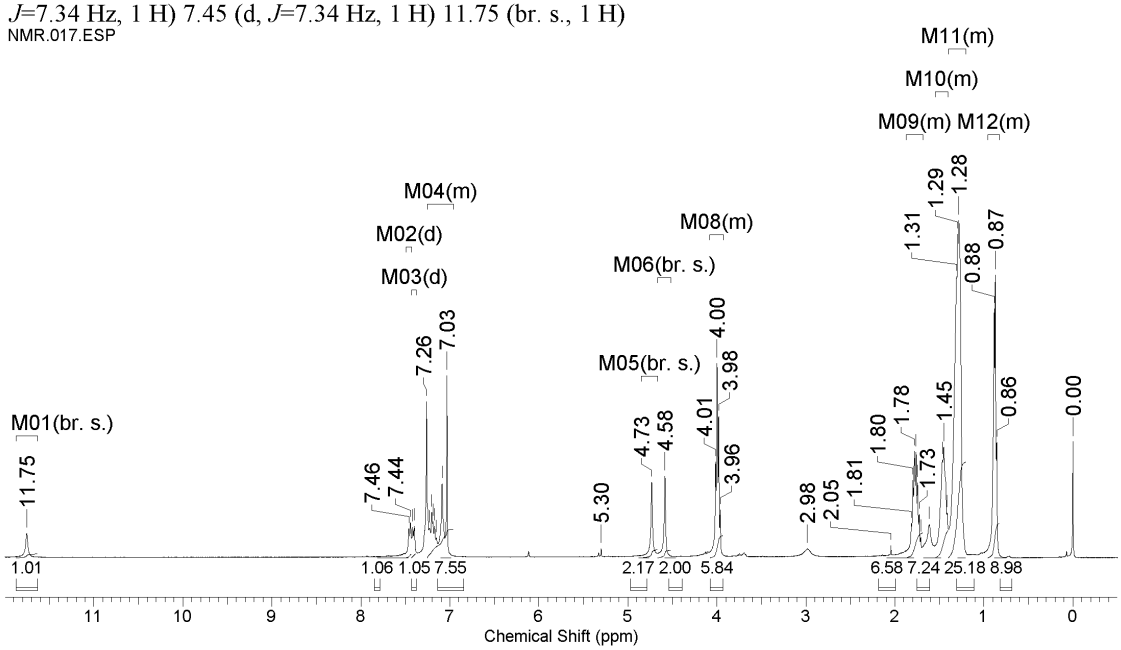


Figure S2. ^{1}H-NMR spectrum of

4,5-bis(2'-(hydroxymethyl)phenyl)-2-(3",4",5"-trioctyloxyphenyl)imidazole in $CDCl_3$.

4,5-Bis(2'-(hydroxymethyl)phenyl)-2-(3",4",5"-trihexadecyloxyphenyl)imidazole

This compound was synthesized in a similar manner to that of 4,5-bis(2'-(hydroxymethyl)phenyl)-2-(3",4",5"-tridecyloxyphenyl)imidazole.

^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ ppm 0.81 - 0.95 (m, 9 H) 1.25 (s, 72 H) 1.48 (br. s., 6 H) 1.77 (d, *J*=5.56 Hz, 6 H) 4.00 (d, *J*=6.32 Hz, 6 H) 4.54 - 4.82 (m, 4 H) 7.04 (s, 9 H) 7.33 - 7.60 (m, 1 H) 11.64 (s, 1 H)

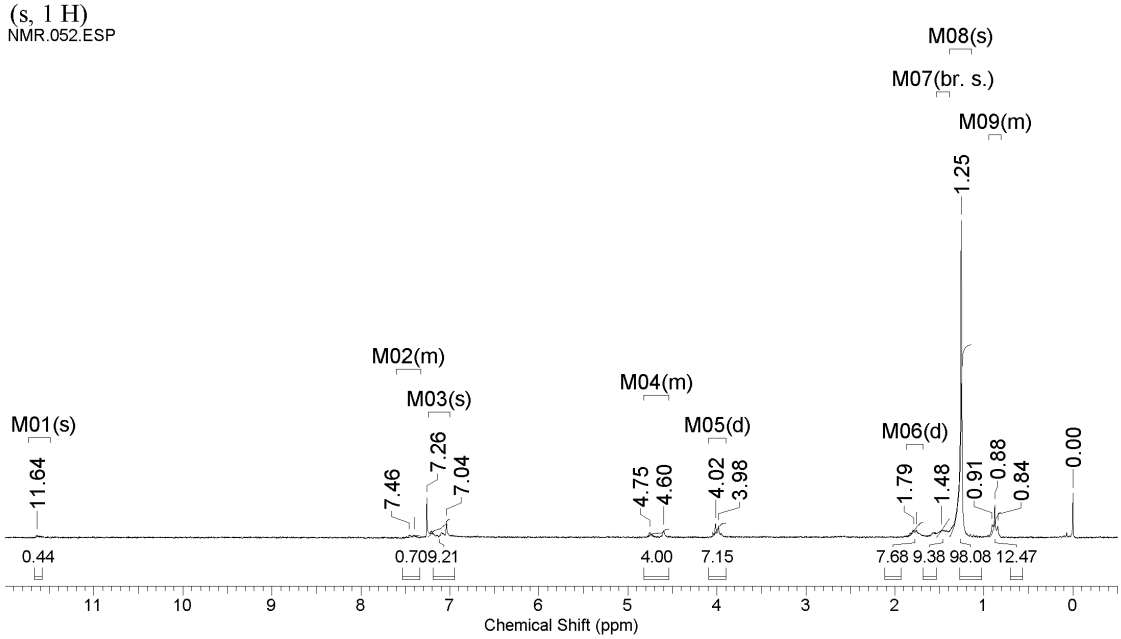


Figure S3. ^{1}H-NMR spectrum of 4,5-bis(2'-(hydroxymethyl)phenyl)-2-(3",4",5"-trihexadecyloxyphenyl)imidazole in $CDCl_3$.

4,5-Bis(2'-(hydroxymethyl)phenyl)-2-(3",4"-didodecyloxyphenyl)imidazole

This compound was synthesized in a similar manner to that of

4,5-bis(2'-(hydroxymethyl)phenyl)-2-(3",4",5"-tridecyloxyphenyl)imidazole.

^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ ppm 0.76 - 0.97 (m, 6 H) 1.26 (br. s., 32 H) 1.46 (br. s., 4 H) 1.79 (br. s., 4 H) 3.91 - 4.12 (m, 4 H) 4.66 (br. s., 4 H) 6.85 - 6.95 (m, 1 H) 7.13 (br. s., 4 H) 7.18 - 7.22 (m, 1 H) 7.27 - 7.51 (m, 5 H) 11.72 (br. s., 1 H)

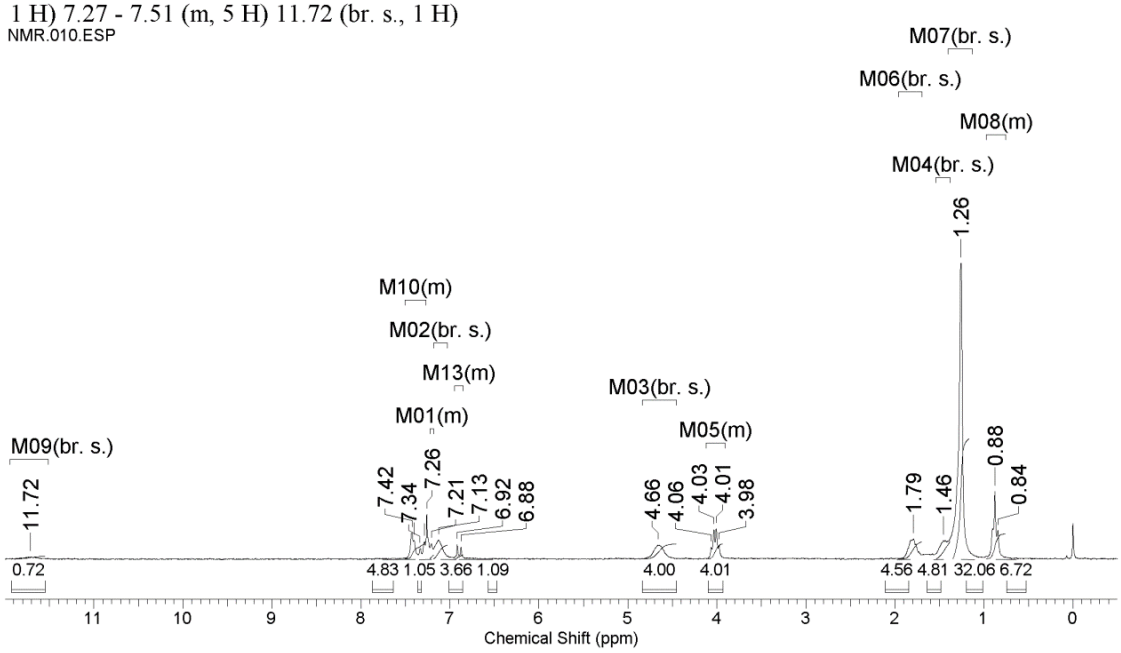
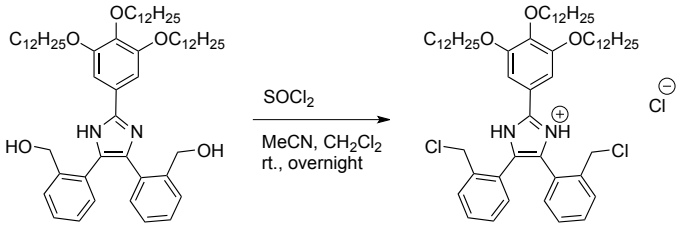


Figure S4. ^{1}H-NMR spectrum of

4,5-bis(2'-(hydroxymethyl)phenyl)-2-(3",4"-didodecyloxyphenyl)imidazole in $CDCl_3$.

1,3-Dihydro-4,5-bis(2'-(chloromethyl)phenyl)-2-(3",4",5"-tridodecyloxyphenyl)imidazolium chloride (Typical procedure)



To a solution of 4,5-bis(2'-(hydroxymethyl)phenyl)-2-(3",4",5"-tridecyloxyphenyl)imidazole (0.53 g, 0.59 mmol) in CH_3CN (36 mL) and CH_2Cl_2 (28 mL) was added $SOCl_2$ (0.42 mL, 5.9 mmol), and the mixture was stirred overnight at room temperature. After the solvent was removed, a greenish brown solid was obtained quantitatively which was directly used for the next reaction.

^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ ppm 0.86 (br. s., 9 H) 1.24 (br. s., 54 H) 1.77 (br. s., 6 H) 4.03 (br. s., 6 H) 4.60 (br. s., 4 H) 6.83 (br. s., 6 H) 7.00 (br. s., 2 H) 7.40 (br. s., 2 H) 14.25 (br. s., 2 H)

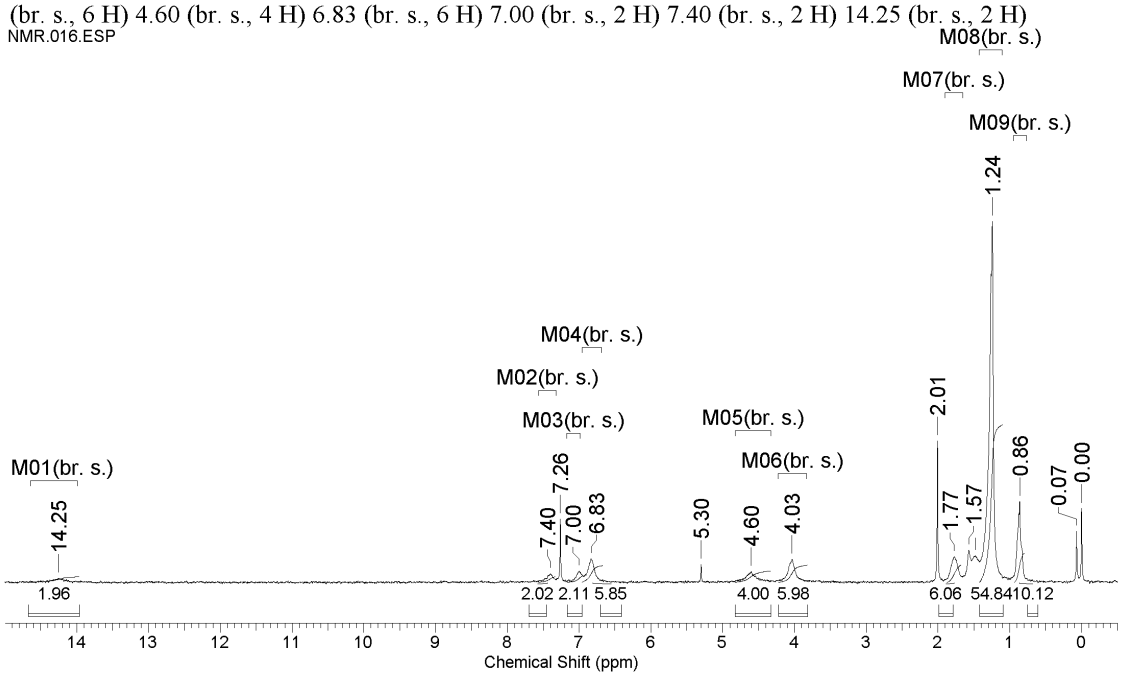


Figure S5. ^{1}H-NMR spectrum of 1,3-dihydro-4,5-bis(2'-(chloromethyl)phenyl)-2-(3",4",5"-tridodecyloxyphenyl)imidazolium chloride in $CDCl_3$.

1,3-Dihydro-4,5-bis(2'-(chloromethyl)phenyl)-2-(3",4",5"-trioctyloxyphenyl)imidazolium chloride

This compound was synthesized in a similar manner to that of 1,3-dihydro-4,5-bis(2'-(chloromethyl)phenyl)-2-(3",4",5"-tridodecyloxyphenyl)imidazolium chloride.

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.79 - 0.95 (m, 9 H) 1.17 - 1.41 (m, 24 H) 1.48 (d, *J*=6.60 Hz, 7 H) 1.78 (d, *J*=5.87 Hz, 6 H) 4.03 (br. s., 6 H) 4.59 (br. s., 4 H) 6.79 (br. s., 6 H) 6.89 - 7.07 (m, 2 H) 7.39 (br. s., 2 H) 14.25 (br. s., 2 H)

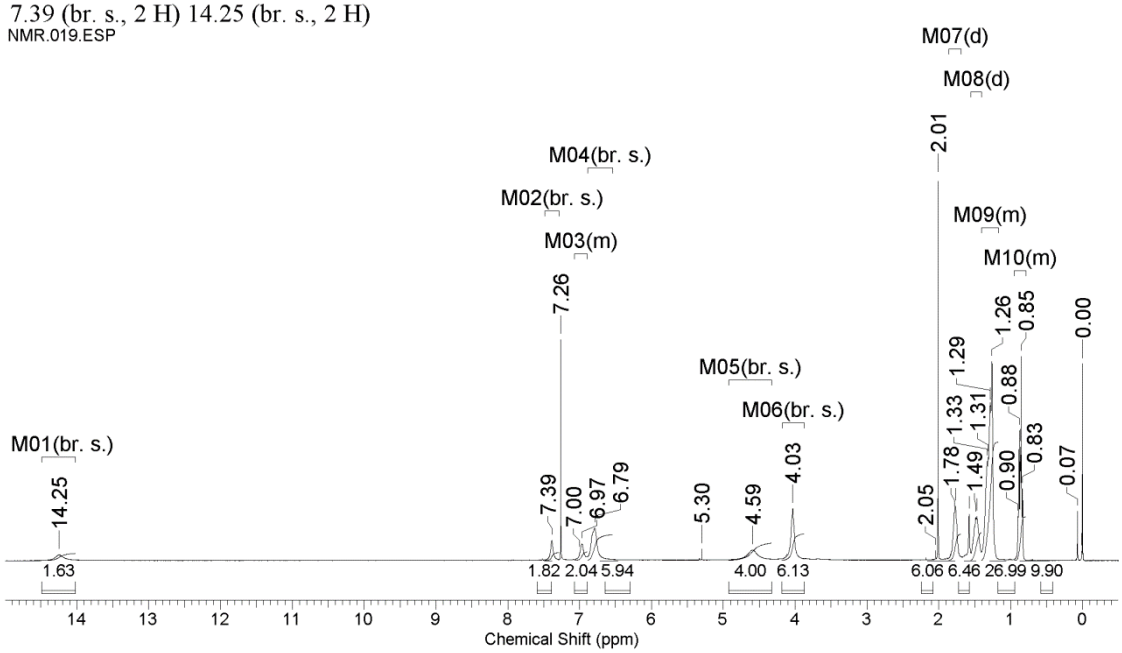


Figure S6. ^{1}H-NMR spectrum of 1,3-dihydro-4,5-bis(2'-(chloromethyl)phenyl)-2-(3",4",5"-trioctyloxyphenyl)imidazolium chloride in $CDCl_3$.

1,3-Dihydro-4,5-bis(2'-(chloromethyl)phenyl)-2-(3",4",5"-trihexadecyloxyphenyl)imidazolium chloride

This compound was synthesized in a similar manner to that of 1,3-dihydro-4,5-bis(2'-(chloromethyl)phenyl)-2-(3",4",5"-tridodecyloxyphenyl)imidazolium chloride.

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.87 (t, *J*=6.72 Hz, 9 H) 1.25 (d, *J*=5.14 Hz, 72 H) 1.48 (d, *J*=6.60 Hz, 6 H) 1.77 (br. s., 6 H) 4.03 (br. s., 6 H) 4.62 (br. s., 4 H) 6.74 - 7.13 (m, 8 H) 7.43 (br. s., 2 H) 13.99 - 14.49 (m, 2 H)

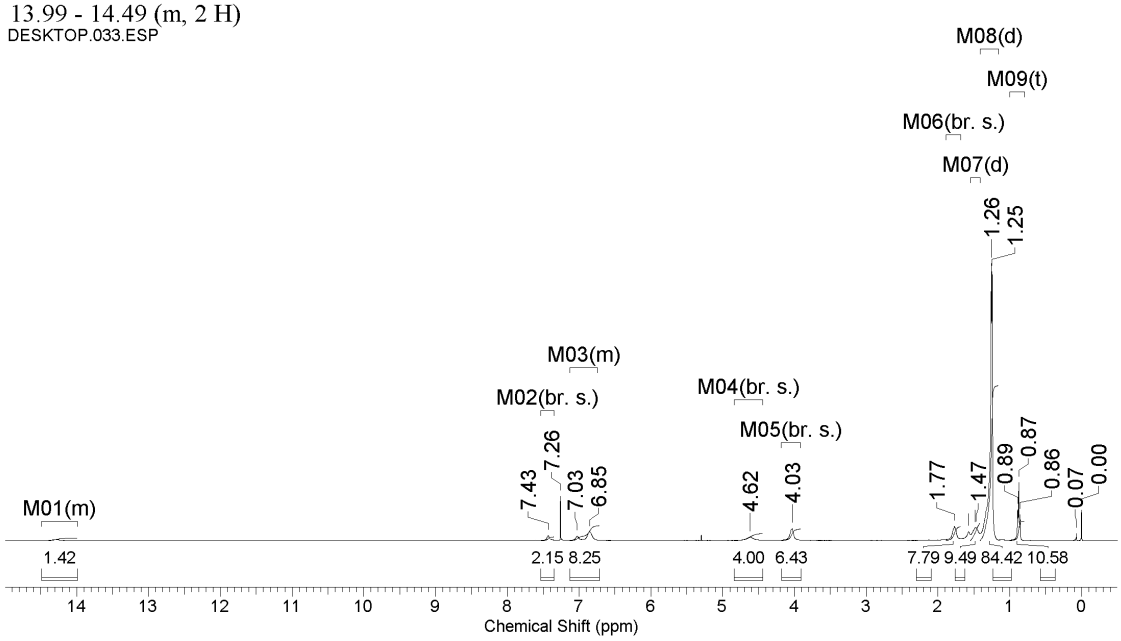


Figure S7. ^{1}H-NMR spectrum of 1,3-dihydro-4,5-bis(2'-(chloromethyl)phenyl)-2-(3",4",5"-trihexadecyloxyphenyl)imidazolium chloride in $CDCl_3$.

1,3-Dihydro-4,5-bis(2'-(chloromethyl)phenyl)-2-(3",4"-didodecyloxyphenyl)imidazolium chloride

This compound was synthesized in a similar manner to that of 1,3-dihydro-4,5-bis(2'-(chloromethyl)phenyl)-2-(3",4",5"-tridodecyloxyphenyl)imidazolium chloride.

^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ ppm 0.87 (d, *J*=2.53 Hz, 6 H) 1.26 (d, *J*=4.80 Hz, 32 H) 1.41 - 1.55 (m, 4 H) 1.83 (br. s., 4 H) 4.03 (br. s., 4 H) 4.62 (br. s., 4 H) 6.84 (br. s., 6 H) 6.99 (br. s., 2 H) 7.59 - 7.93 (m, 3 H) 14.12 (br. s., 2 H)

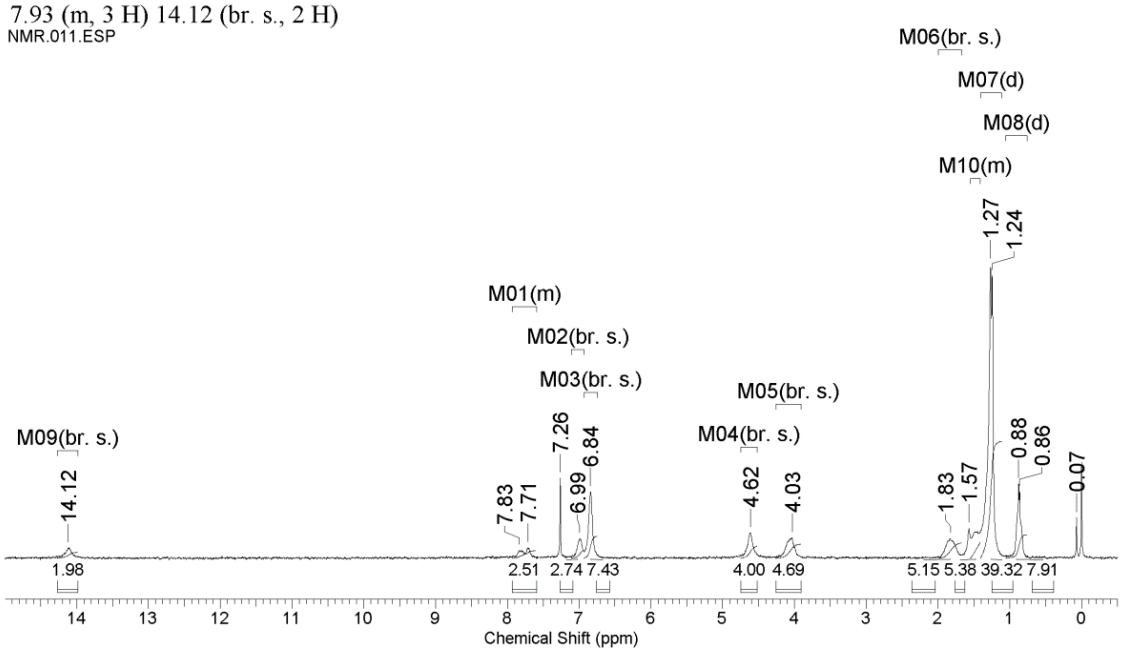
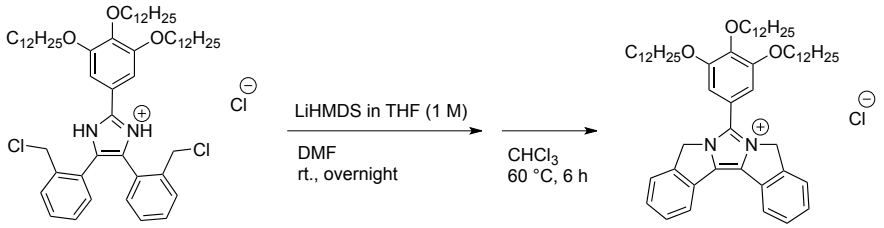


Figure S8. ^{1}H-NMR spectrum of 1,3-dihydro-4,5-bis(2'-(chloromethyl)phenyl)-2-(3",4"-didodecyloxyphenyl)imidazolium chloride in $CDCl_3$.

Fused imidazolium chloride with three dodecyloxy chains (3C12Cl) (Typical procedure)



To a solution of 1,3-dihydro-4,5-bis(2'-(chloromethyl)phenyl)-2-(3",4",5"-tridodecyloxyphenyl)imidazolium chloride (0.58 g, 0.59 mmol) in DMF (68 mL) was added LiHMDS solution in THF (1 M, 1.2 mL) at 0 °C, and the mixture was stirred overnight at room temperature. After the solvent was removed, water and $CHCl_3$ were added in the separating funnel. An aqueous phase was extracted with $CHCl_3$. The combined organic phase was rinsed with brine and dried over $MgSO_4$. The solvent was removed and the remaining solid was dissolved in $CHCl_3$ (30 mL) to be heated to 60 °C for 6 h. After the solvent was removed, the remaining solid was dissolved in $CHCl_3$ to be poured in ethyl acetate to obtain a colorless solid (0.24 g, 44% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.84 - 0.92 (m, 9 H) 1.21 - 1.41 (m, 48 H) 1.46 - 1.57 (m, 6 H) 1.73 - 1.89 (m, 6 H) 4.08 (t, *J*=6.48 Hz, 2 H) 4.23 (t, *J*=6.11 Hz, 4 H) 5.89 (s, 4 H) 7.45 - 7.51 (m, 4 H) 7.52 - 7.58 (m, 2 H) 7.67 (d, *J*=7.58 Hz, 2 H) 7.84 (d, *J*=7.58 Hz, 2 H)

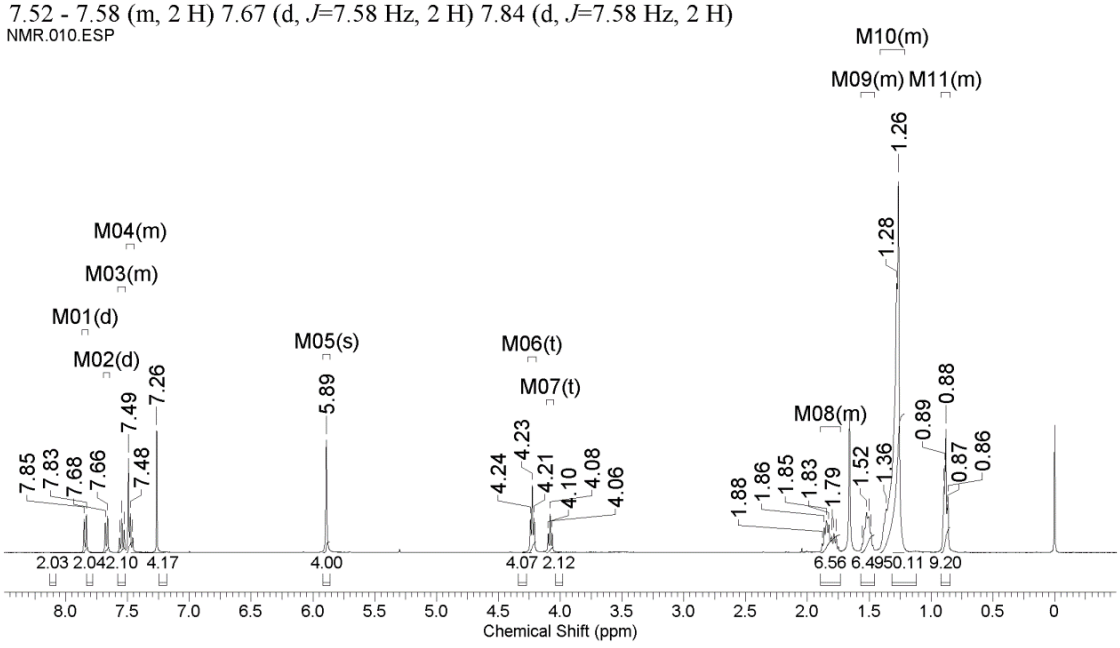


Figure S9. ^{1}H-NMR spectrum of **3C12Cl** in $CDCl_3$.

Fused imidazolium chloride with three octyloxy chains (3C8Cl)

This compound was synthesized in a similar manner to that of **3C12Cl**.

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.84 - 0.95 (m, 9 H) 1.23 - 1.42 (m, 24 H) 1.46 - 1.58 (m, 6 H) 1.74 - 1.91 (m, 6 H) 4.08 (t, *J*=6.60 Hz, 2 H) 4.23 (t, *J*=6.24 Hz, 4 H) 5.89 (s, 4 H) 7.43 - 7.56 (m, 6 H) 7.66 (d, *J*=7.34 Hz, 2 H) 7.83 (d, *J*=7.58 Hz, 2 H)

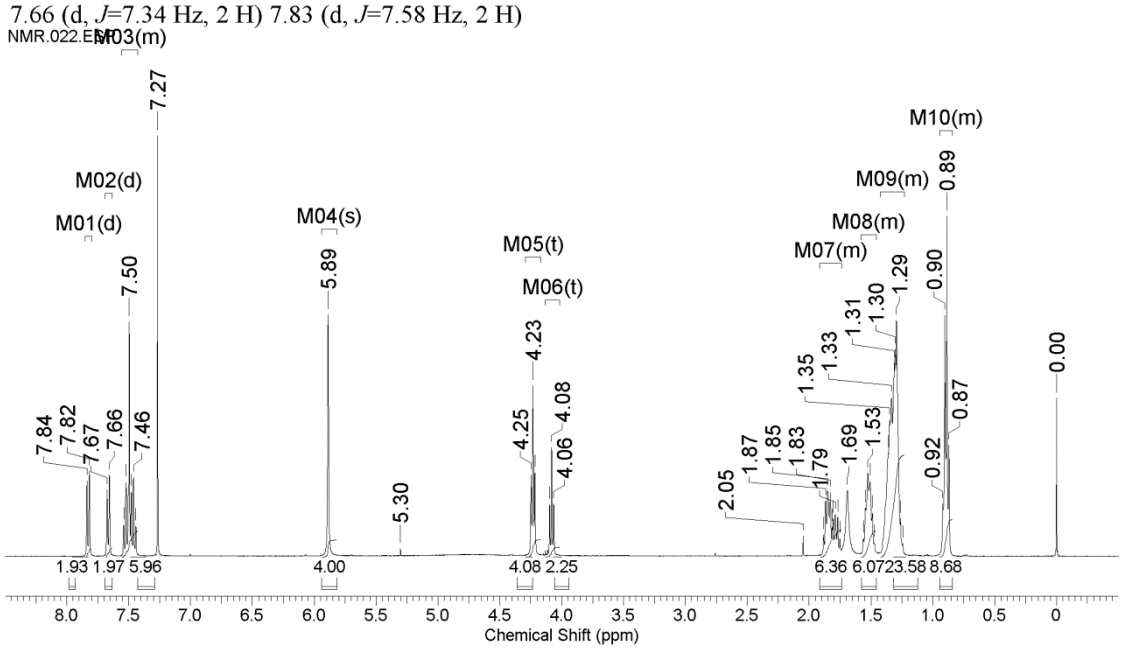


Figure S10. ^{1}H-NMR spectrum of **3C8Cl** in $CDCl_3$.

Fused imidazolium chloride with three hexadecyloxy chains (3C16Cl)

This compound was synthesized in a similar manner to that of **3C12Cl**.

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.88 (t, *J*=6.60 Hz, 9 H) 1.21 - 1.41 (m, 72 H) 1.47 - 1.57 (m, 7 H) 1.73 - 1.89 (m, 6 H) 4.08 (s, 2 H) 4.23 (t, *J*=6.11 Hz, 4 H) 5.89 (s, 4 H) 7.45 - 7.51 (m, 4 H) 7.54 (d, *J*=7.34 Hz, 2 H) 7.67 (d, *J*=7.58 Hz, 2 H) 7.85 (d, *J*=7.58 Hz, 2 H)

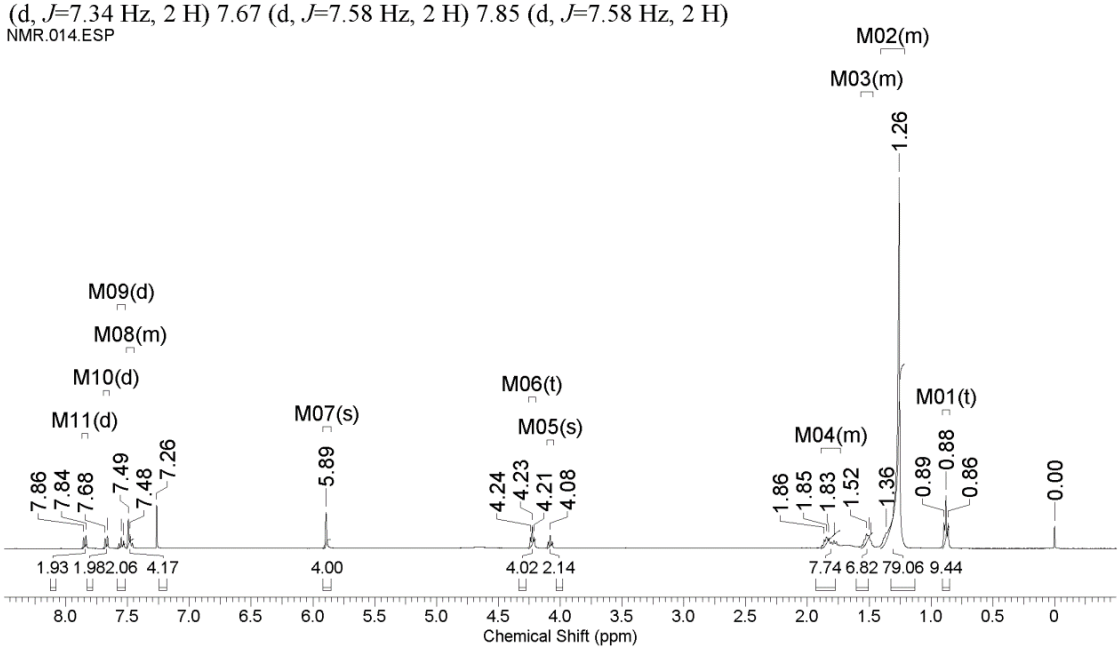


Figure S11. ^{1}H-NMR spectrum of **3C16Cl** in $CDCl_3$.

Fused imidazolium chloride with two dodecyloxy chains (2C12Cl)

This compound was synthesized in a similar manner to that of **3C12Cl**.

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.85 - 0.92 (m, 6 H) 1.28 (d, *J*=6.36 Hz, 32 H) 1.43 - 1.55 (m, 4 H) 1.75 - 1.88 (m, 4 H) 3.97 (t, *J*=6.60 Hz, 2 H) 4.24 (t, *J*=6.24 Hz, 2 H) 5.78 (br. s., 4 H) 7.08 (d, *J*=8.56 Hz, 1 H) 7.33 (br. s., 4 H) 7.61 (br. s., 2 H) 7.70 (br. s., 2 H) 7.76 (d, *J*=1.96 Hz, 1 H) 7.98 (d, *J*=8.56 Hz, 1 H)

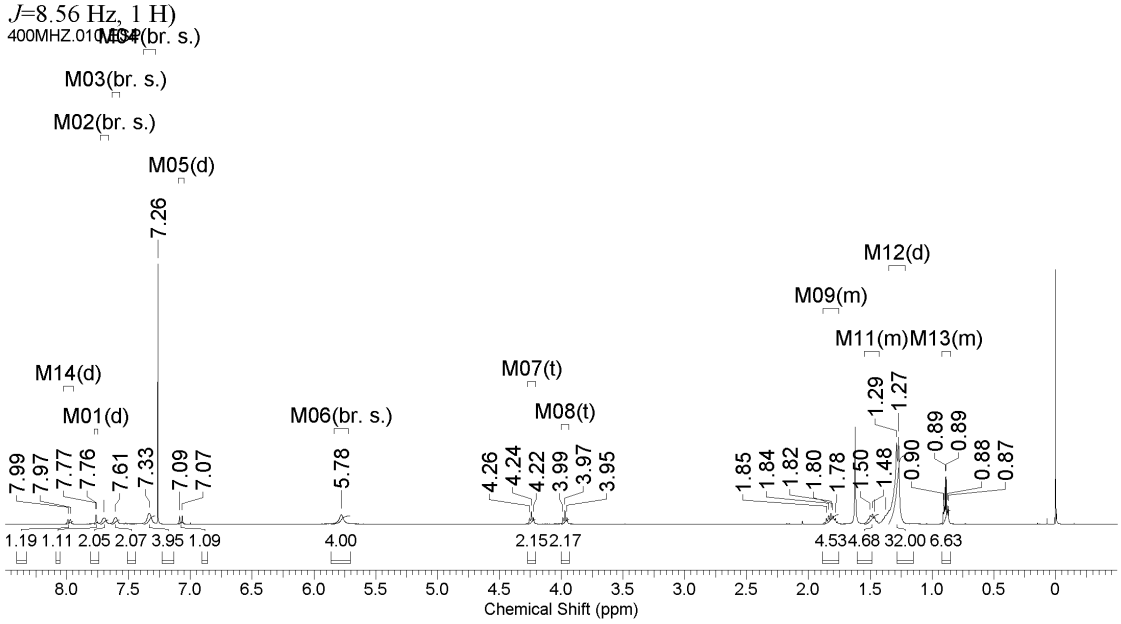
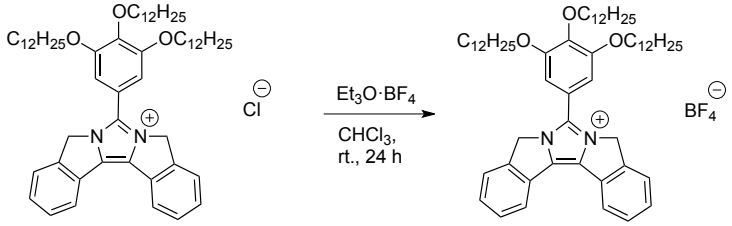


Figure S12. ^{1}H-NMR spectrum of **2C12Cl** in $CDCl_3$.

Fused imidazolium tetrafluoroborate with three dodecyloxy chains (3C12BF4) (Typical procedure)



To a solution of **3C12Cl** (50 mg, 55 μmol) in $CHCl_3$ (2 mL) was added $Et_3O{\cdot}BF_4$ solution in CH_2Cl_2 (1 M, 66 μL), and the mixture was stirred at room temperature for 24 h. After water was added, an aqueous phase was extracted with CH_2Cl_2. The combined organic phase was washed with water and dried over $MgSO_4$. The solvent was removed to obtain a colorless solid (42 mg, 80% yield). Anal Calcd for $C_{59}H_{89}BF_4N_2O_3$: C 73.73, H 9.33, N 2.91 %; Found: C 73.70, H 9.50, N 2.89 %.

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.84 - 0.94 (m, 9 H) 1.28 (d, *J*=5.87 Hz, 48 H) 1.50 (dt, *J*=14.43, 7.21 Hz, 6 H) 1.73 - 1.87 (m, 6 H) 4.05 (t, *J*=6.60 Hz, 2 H) 4.10 (t, *J*=6.24 Hz, 4 H) 5.48 (s, 4 H) 7.08 (s, 2 H) 7.39 - 7.44 (m, 2 H) 7.44 - 7.50 (m, 2 H) 7.61 (d, *J*=7.34 Hz, 2 H) 7.73 (d, *J*=7.58 Hz, 2 H)

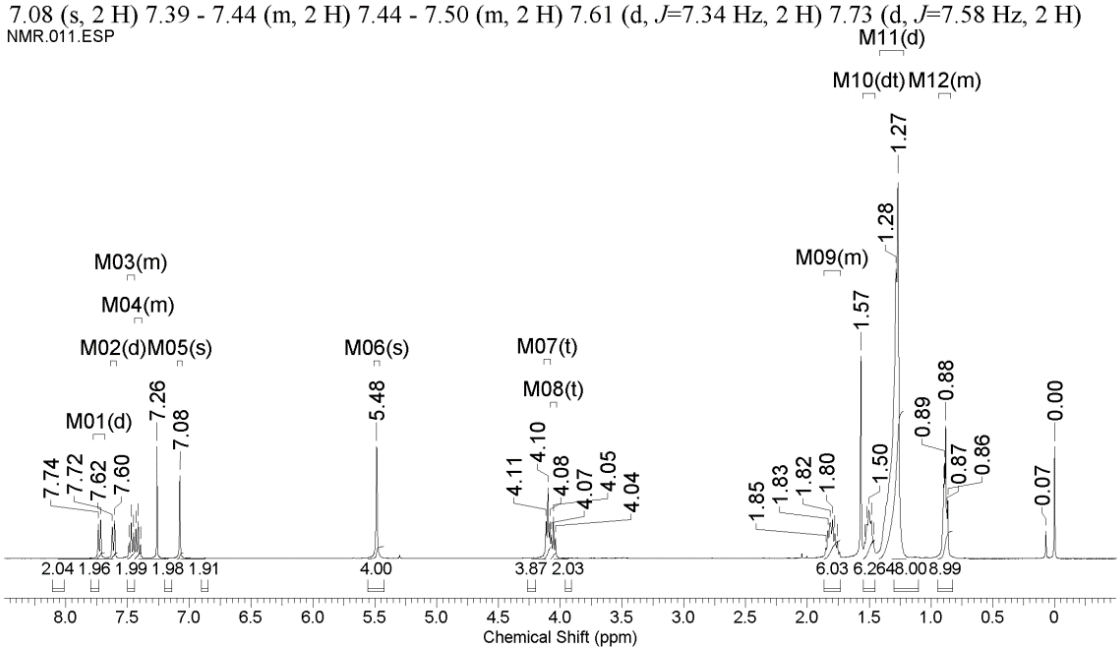


Figure S13. ^{1}H-NMR spectrum of **3C12BF4** in $CDCl_3$.

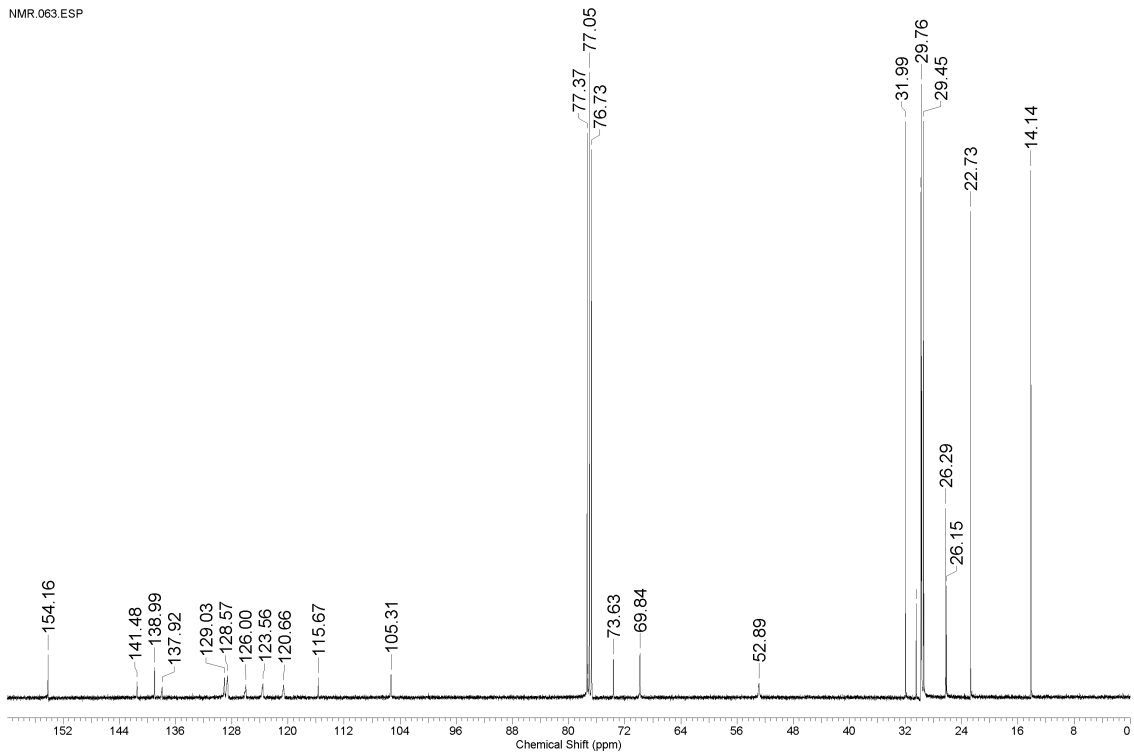


Figure S14. ^{13}C-NMR spectrum of **3C12BF4** in $CDCl_3$.

Fused imidazolium tetrafluoroborate with three octyloxy chains (3C8BF4)

This compound was synthesized in a similar manner to that of **3C12BF4**. Anal Calcd for $C_{47}H_{65}BF_4N_2O_3$: C 71.20, H 8.26, N 3.53 %; Found: C 71.03, H 8.54, N 3.40 %.

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.84 - 0.95 (m, 9 H) 1.24 - 1.42 (m, 24 H) 1.50 (quin, *J*=7.34 Hz, 6 H) 1.73 - 1.87 (m, 6 H) 4.02 - 4.15 (m, 6 H) 5.50 (s, 4 H) 7.09 (s, 2 H) 7.40 - 7.46 (m, 2 H) 7.46 - 7.53 (m, 2 H) 7.62 (d, *J*=7.34 Hz, 2 H) 7.75 (d, *J*=7.58 Hz, 2 H)

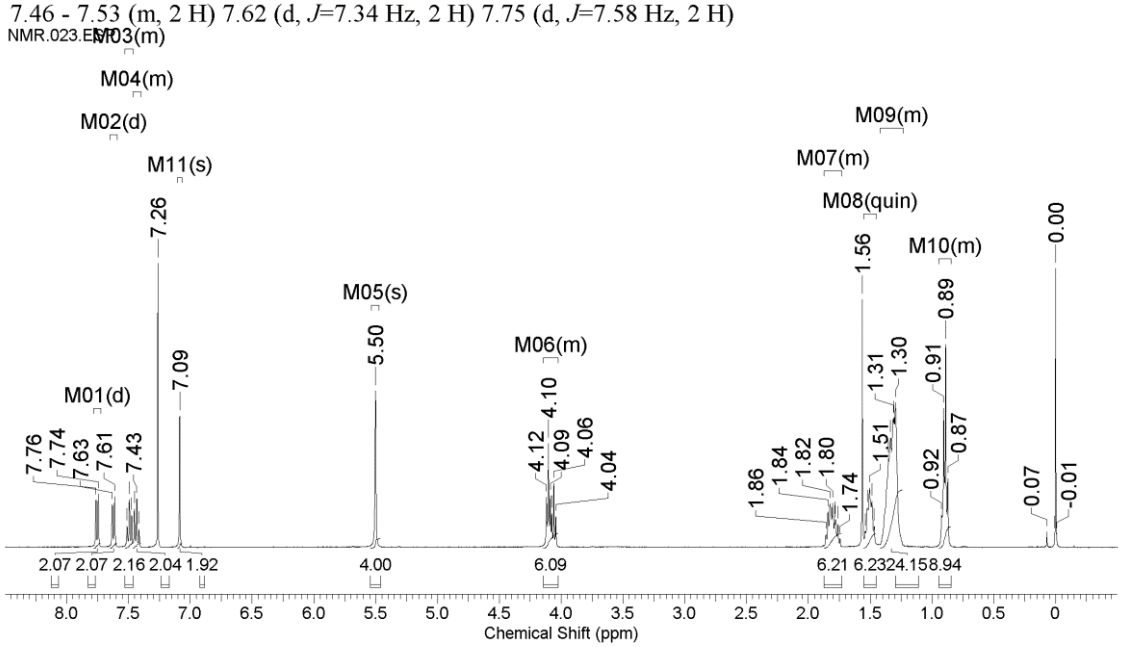


Figure S15. ^{1}H-NMR spectrum of **3C8BF4** in $CDCl_3$.

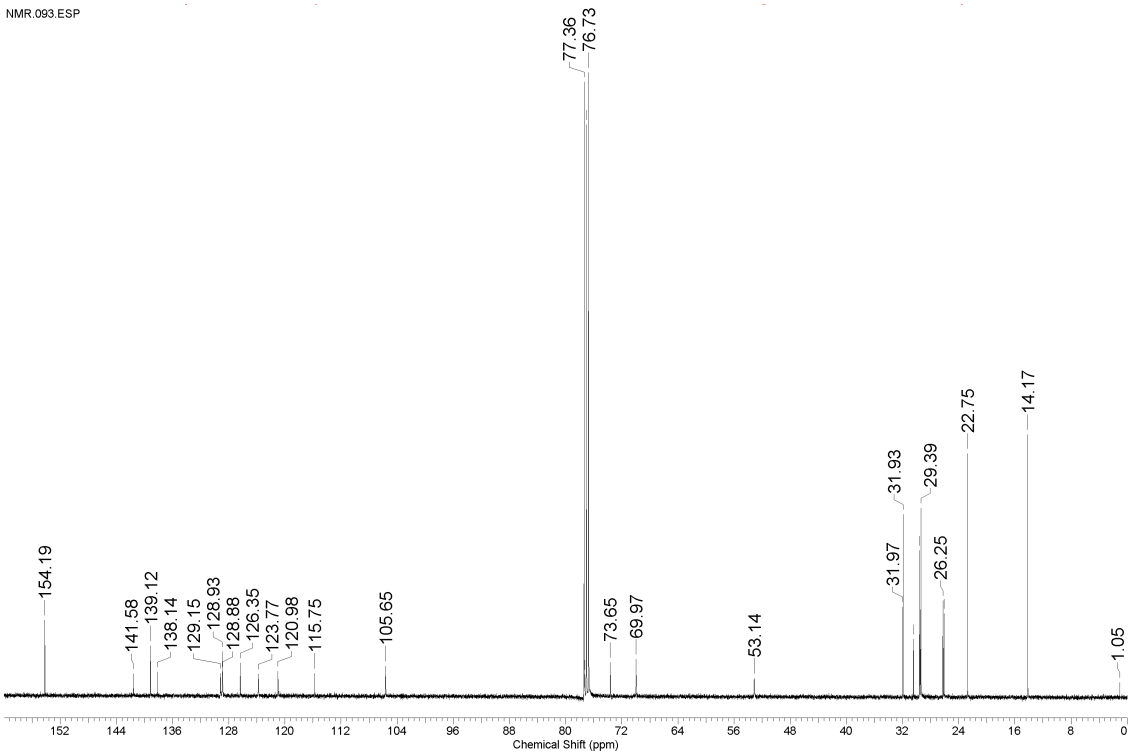


Figure S16. ^{13}C-NMR spectrum of **3C8BF4** in $CDCl_3$.

Fused imidazolium tetrafluoroborate with three hexadecyloxy chains (3C16BF4)

This compound was synthesized in a similar manner to that of **3C12BF4**. Anal Calcd for $C_{71}H_{113}BF_4N_2O_3$: C 75.50, H 10.08, N 2.48 %; Found: C 75.29, H 10.51, N 2.41 %.

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.84 - 0.93 (m, 9 H) 1.26 (s, 72 H) 1.45 - 1.54 (m, 6 H) 1.73 - 1.87 (m, 6 H) 4.06 (t, *J*=6.48 Hz, 2 H) 4.10 (t, *J*=6.11 Hz, 4 H) 5.52 (s, 4 H) 7.09 (s, 2 H) 7.47 (d, *J*=7.58 Hz, 2 H) 7.50 - 7.56 (m, 2 H) 7.63 (d, *J*=7.58 Hz, 2 H) 7.79 (d, *J*=7.58 Hz, 2 H)

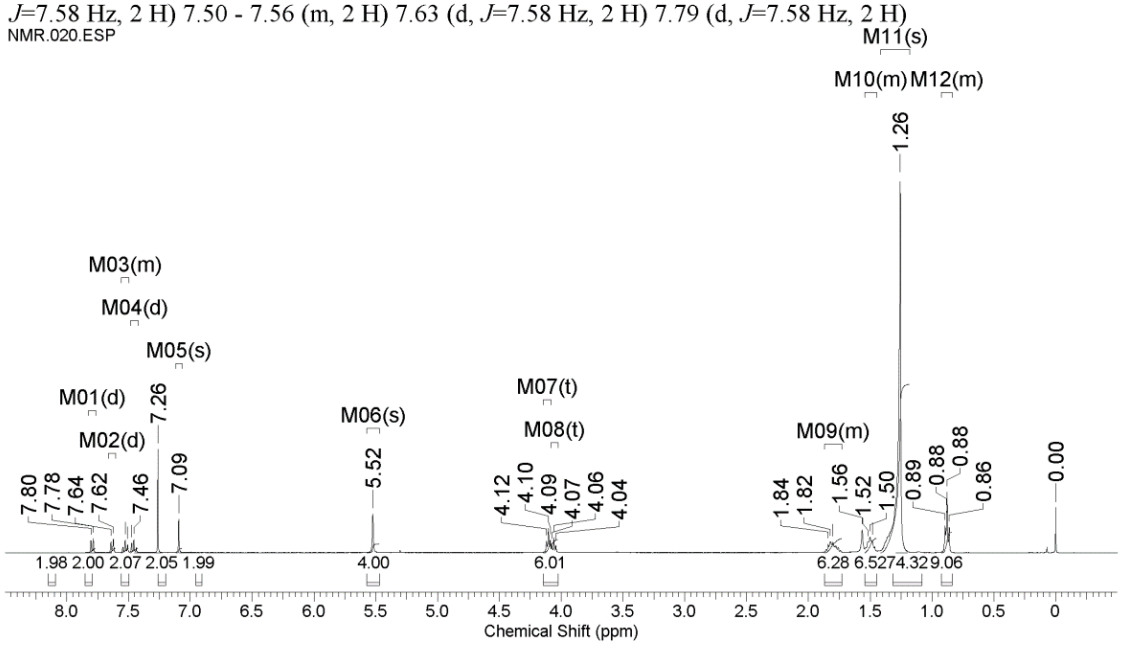


Figure S17. ^{1}H-NMR spectrum of **3C16BF4** in $CDCl_3$.

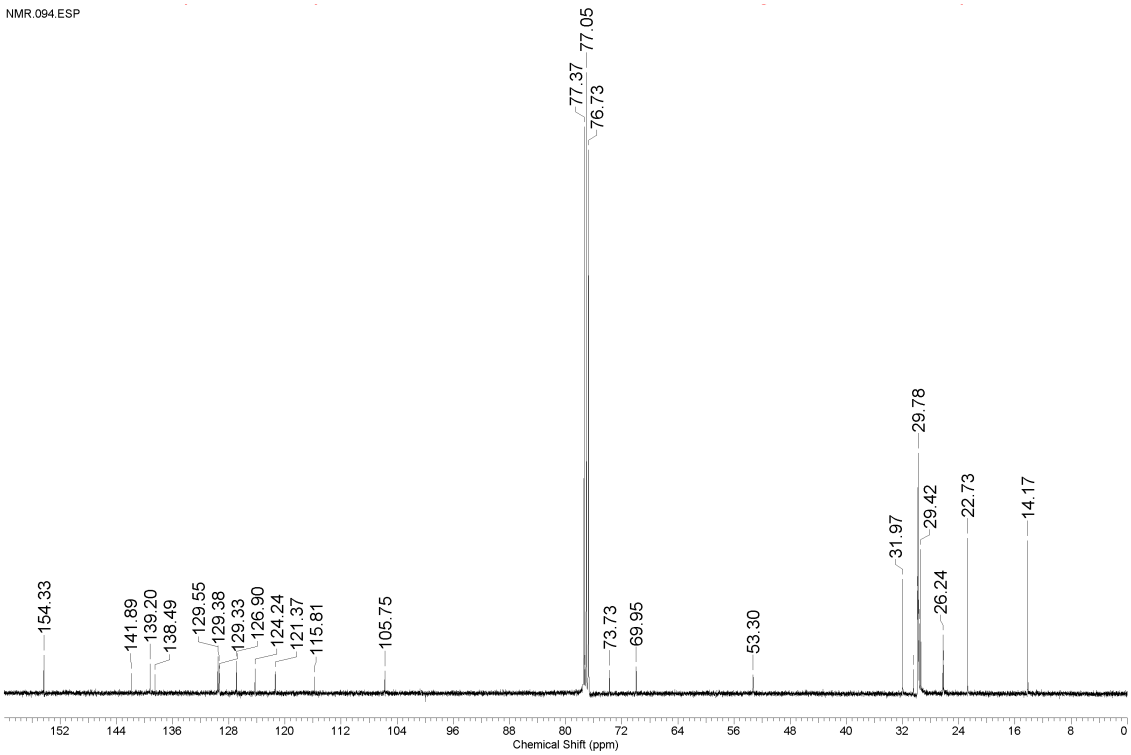


Figure S18. ^{13}C-NMR spectrum of **3C16BF4** in $CDCl_3$.

Fused imidazolium tetrafluoroborate with two dodecyloxy chains (2C12BF4)

This compound was synthesized in a similar manner to that of **3C12BF4**. Anal Calcd for $C_{47}H_{65}BF_4N_2O_2$: C 72.62, H 8.43, N 3.61 %; Found: C 72.39, H 8.64, N 3.51 %.

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.84 - 0.94 (m, 6 H) 1.28 (d, *J*=5.38 Hz, 32 H) 1.43 (br. s., 4 H) 1.65 - 1.83 (m, 4 H) 3.80 (t, *J*=6.48 Hz, 2 H) 4.03 (t, *J*=6.24 Hz, 2 H) 5.44 (s, 4 H) 6.96 (d, *J*=8.56 Hz, 1 H) 7.30 (s, 1 H) 7.34 - 7.43 (m, 4 H) 7.55 (d, *J*=8.31 Hz, 1 H) 7.62 (d, *J*=6.85 Hz, 2 H) 7.66 (d, *J*=6.85 Hz, 2 H)

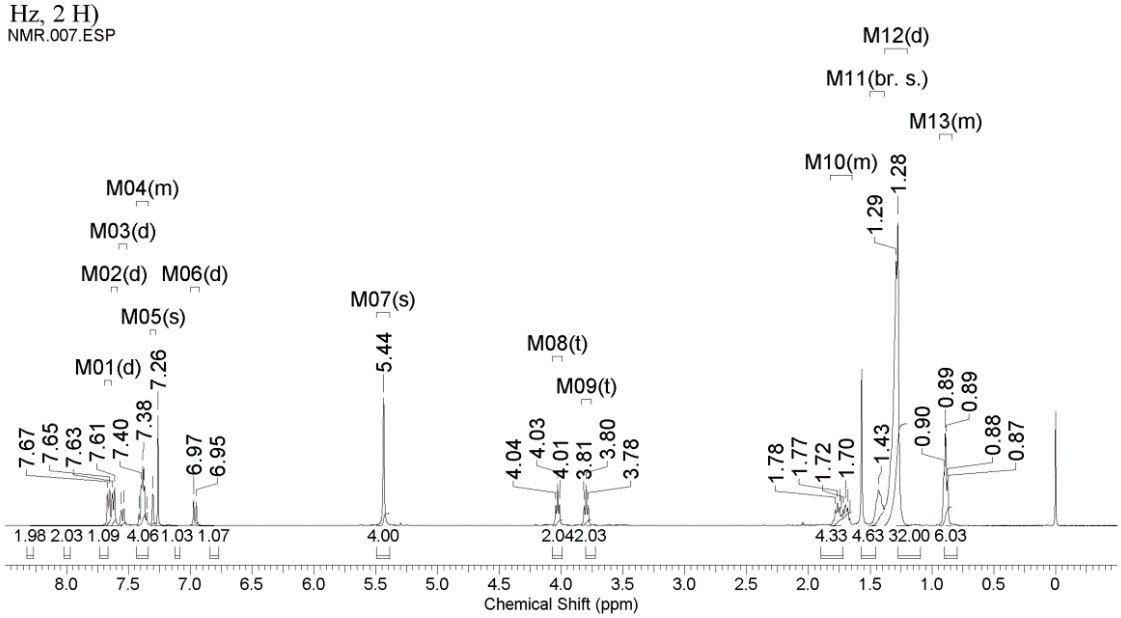


Figure S19. ^{1}H-NMR spectrum of **2C12BF4** in $CDCl_3$.

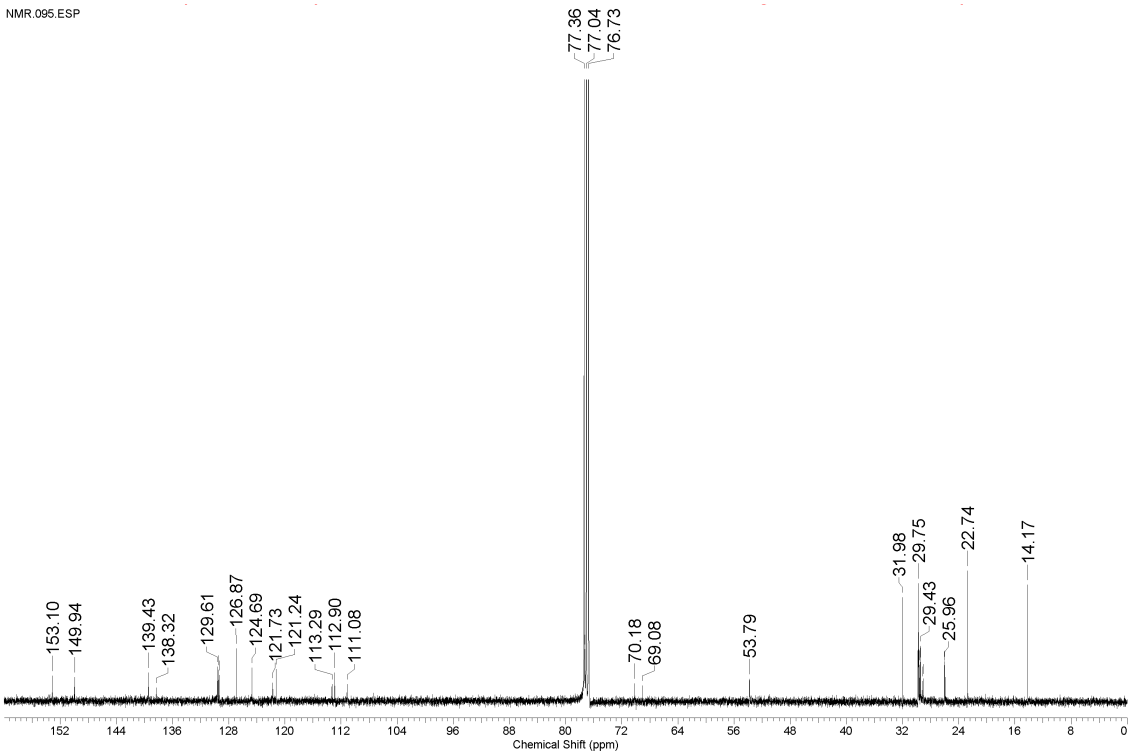
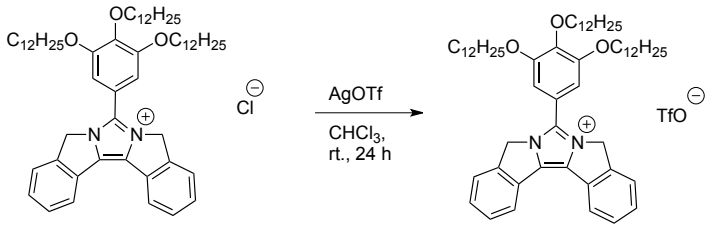


Figure S20. ^{13}C-NMR spectrum of **2C12BF4** in $CDCl_3$.

Fused imidazolium trifluoromethanesulfonate with three dodecyloxy chains (3C12OTf)



To a solution of **3C12Cl** (50 mg, 55 μmol) in $CHCl_3$ (3 mL) was added AgOTf (21 mg, 83 μmol), and the mixture was stirred at room temperature for 24 h. After solvent was removed, the crude product was purified by SiO_2 column chromatography ($CHCl_3$: MeOH = 6 : 1, Rf = 0.59) to obtain a colorless solid (51 mg, 91% yield). Anal Calcd for $C_{60}H_{89}F_3N_2O_6S$: C 70.42, H 8.77, N 2.74, S 3.13 %; Found: C 70.45, H 8.93, N 2.56, S 2.99 %.

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.83 - 0.94 (m, 9 H) 1.19 - 1.43 (m, 48 H) 1.45 - 1.55 (m, 6 H) 1.73 - 1.89 (m, 6 H) 4.04 - 4.15 (m, 6 H) 5.59 (s, 4 H) 7.15 (s, 2 H) 7.46 - 7.53 (m, 2 H) 7.54 - 7.60 (m, 2 H) 7.64 (d, *J*=7.58 Hz, 2 H) 7.86 (d, *J*=7.58 Hz, 2 H)

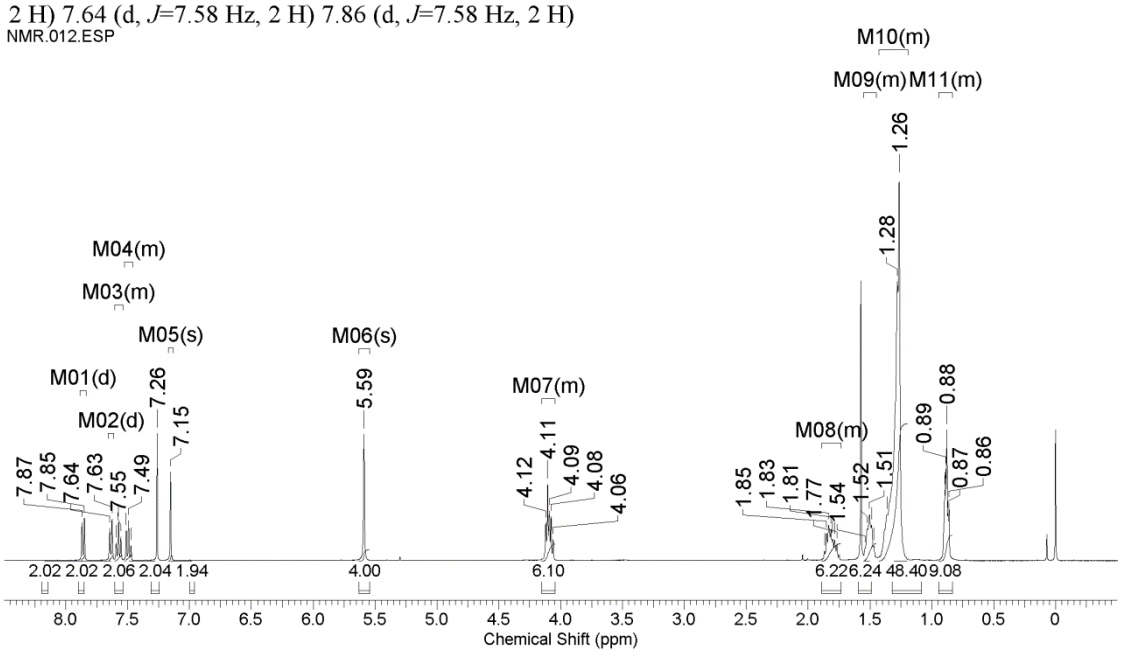


Figure S21. ^{1}H-NMR spectrum of **3C12OTf** in $CDCl_3$.

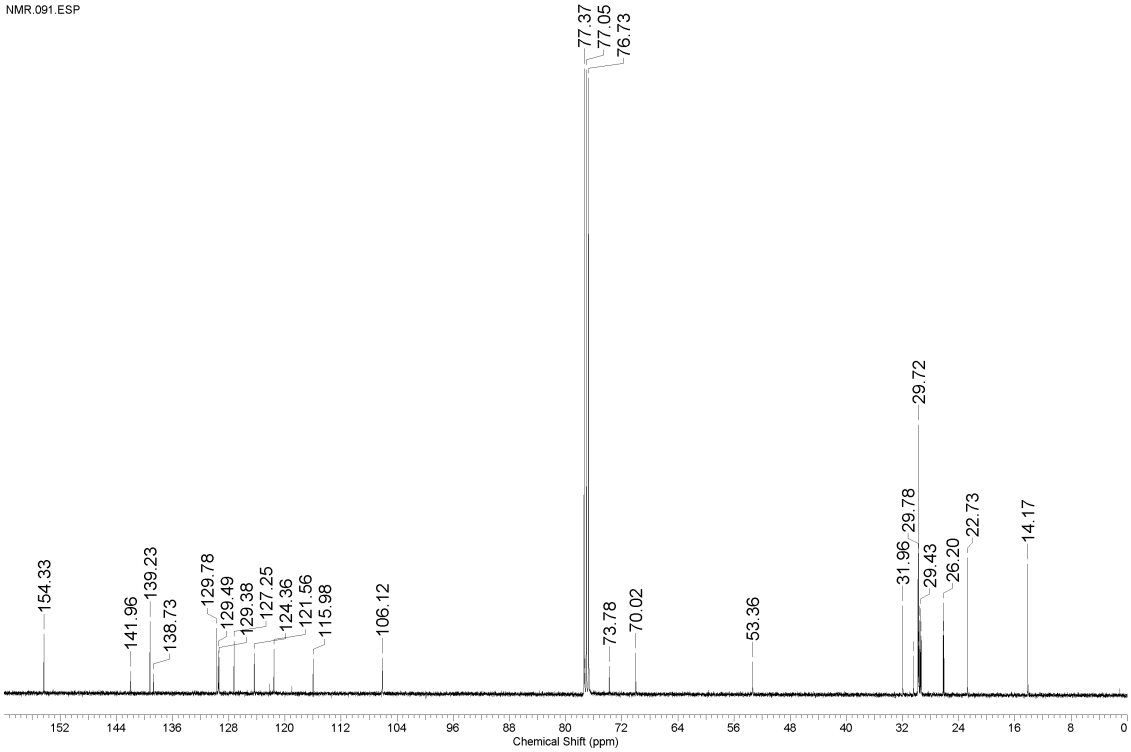
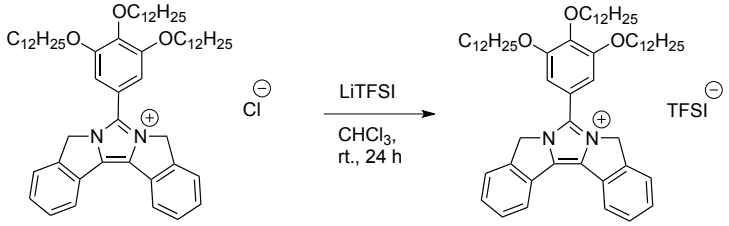


Figure S22. ^{13}C-NMR spectrum of **3C12OTf** in $CDCl_3$.

Fused imidazolium bis(trifluoromethanesulfonyl)imidate with three dodecyloxy chains (3C12TFSI)



To a solution of **3C12Cl** (51 mg, 56 μmol) in $CHCl_3$ (3 mL) was added a solution of LiTFSI (1.2 g, 5.3 mmol) in distilled water (4.2 mL), and the mixture was stirred at room temperature for 24 h. An aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and solvent was removed to obtain a colorless solid (59 mg, 93% yield). Anal Calcd for $C_{61}H_{89}F_6N_3O_7S_2$: C 63.46, H 7.77, N 3.64, S 5.55 %; Found: C 63.53, H 7.82, N 3.50, S 5.49 %.

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.84 - 0.93 (m, 9 H) 1.20 - 1.43 (m, 48 H) 1.46 - 1.54 (m, 6 H) 1.75 - 1.90 (m, 6 H) 4.09 (q, *J*=6.77 Hz, 6 H) 5.55 (s, 4 H) 7.06 (s, 2 H) 7.49 - 7.57 (m, 2 H) 7.58 - 7.66 (m, 4 H) 7.90 (d, *J*=8.07 Hz, 2 H)

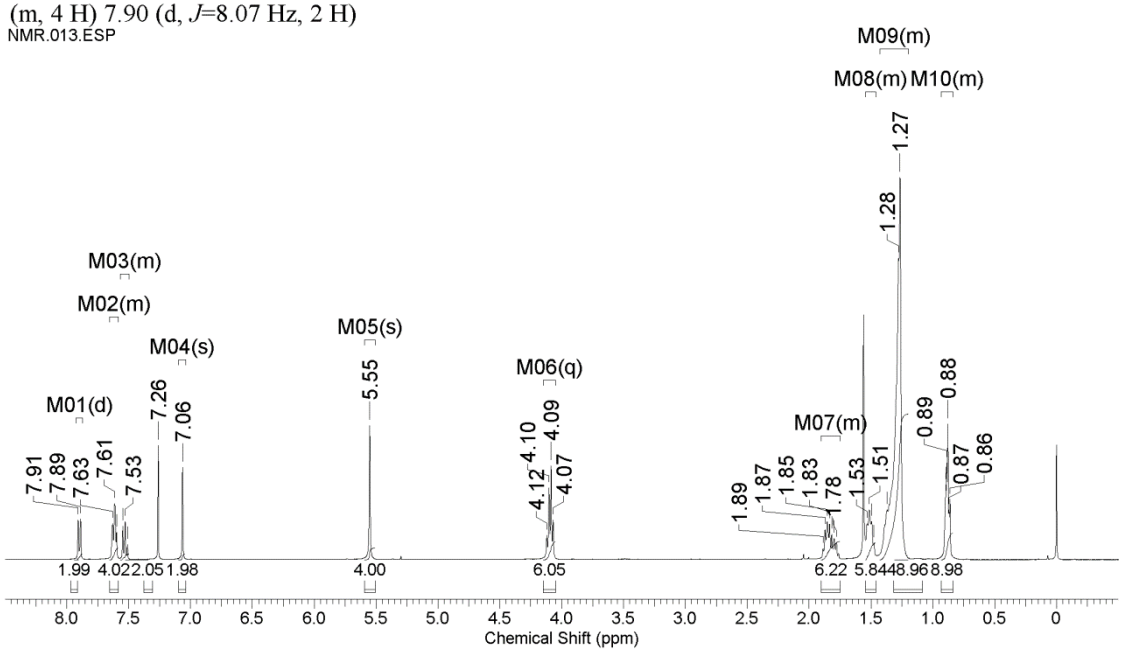


Figure S23. ^{1}H-NMR spectrum of **3C12TFSI** in $CDCl_3$.

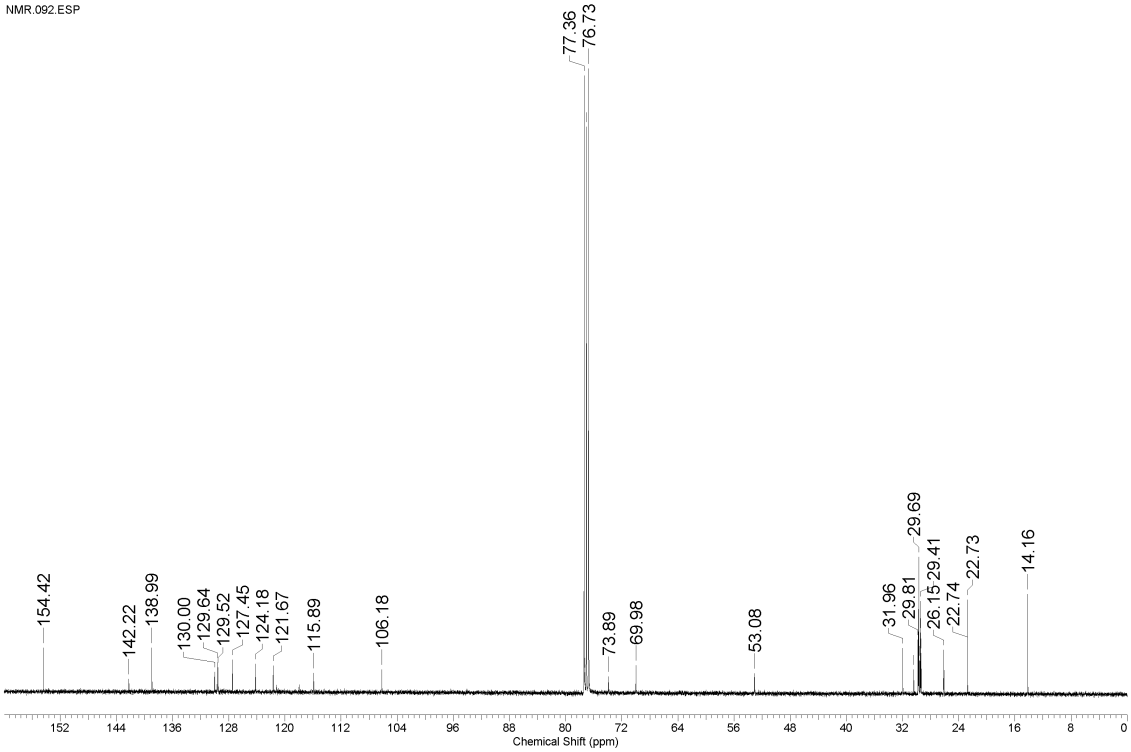
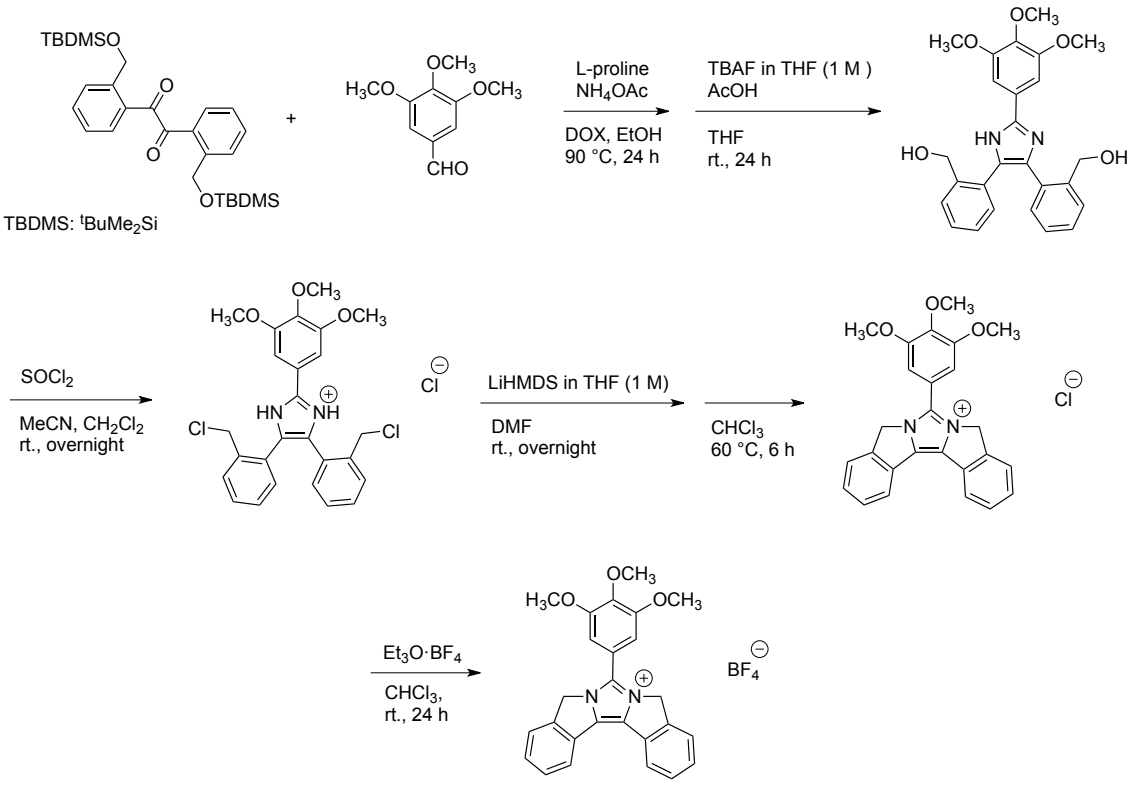


Figure S24. ^{13}C-NMR spectrum of **3C12TFSI** in $CDCl_3$.

S3. Synthesis of model compound

The model compound with three methoxy group (**3C1BF4**) was synthesized according the following scheme. Anal Calcd for $C_{26}H_{23}N_3BF_4N_2O_3 \cdot 1/3H_2O$: C 61.93, H 4.73, N 5.56 %; Found: C 62.00, H 4.84, N 5.50 %.



^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 3.83 (s, 3 H) 3.97 (s, 6 H) 5.94 (s, 4 H) 7.46 (s, 2 H) 7.60 - 7.66 (m, 2 H) 7.66 - 7.73 (m, 2 H) 7.78 (d, *J*=7.34 Hz, 2 H) 8.28 (d, *J*=7.58 Hz, 2 H)

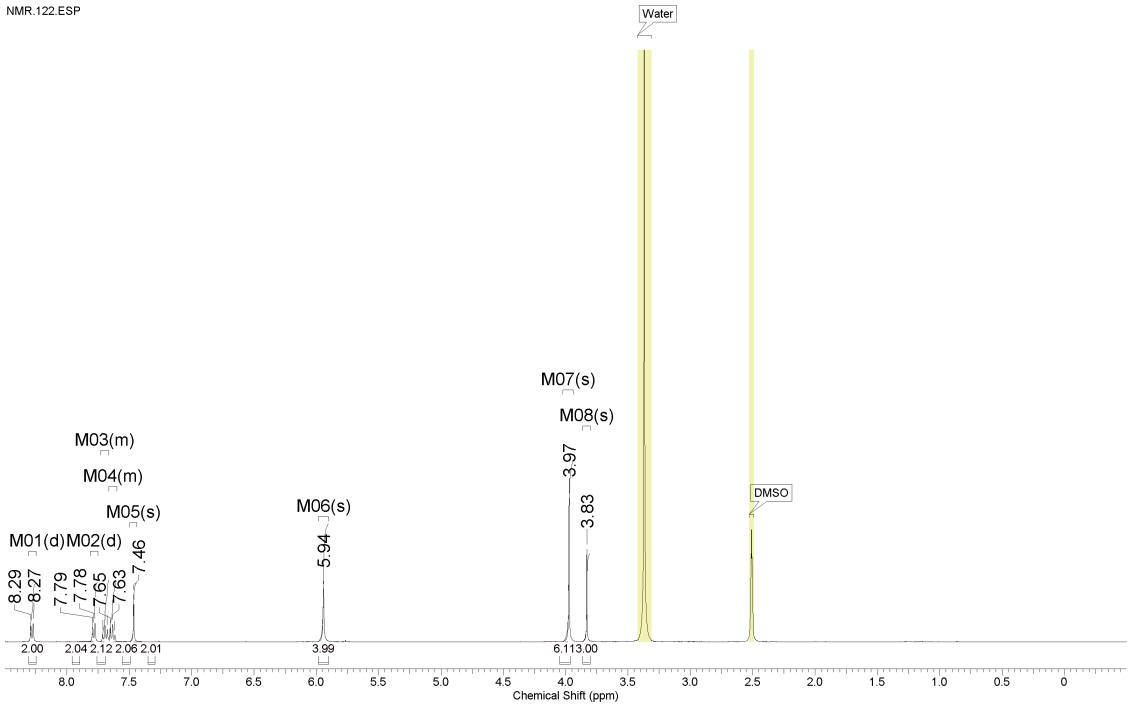


Figure S25. ^{1}H-NMR spectrum of **3C1BF$_4$** in DMSO-d$_6$.

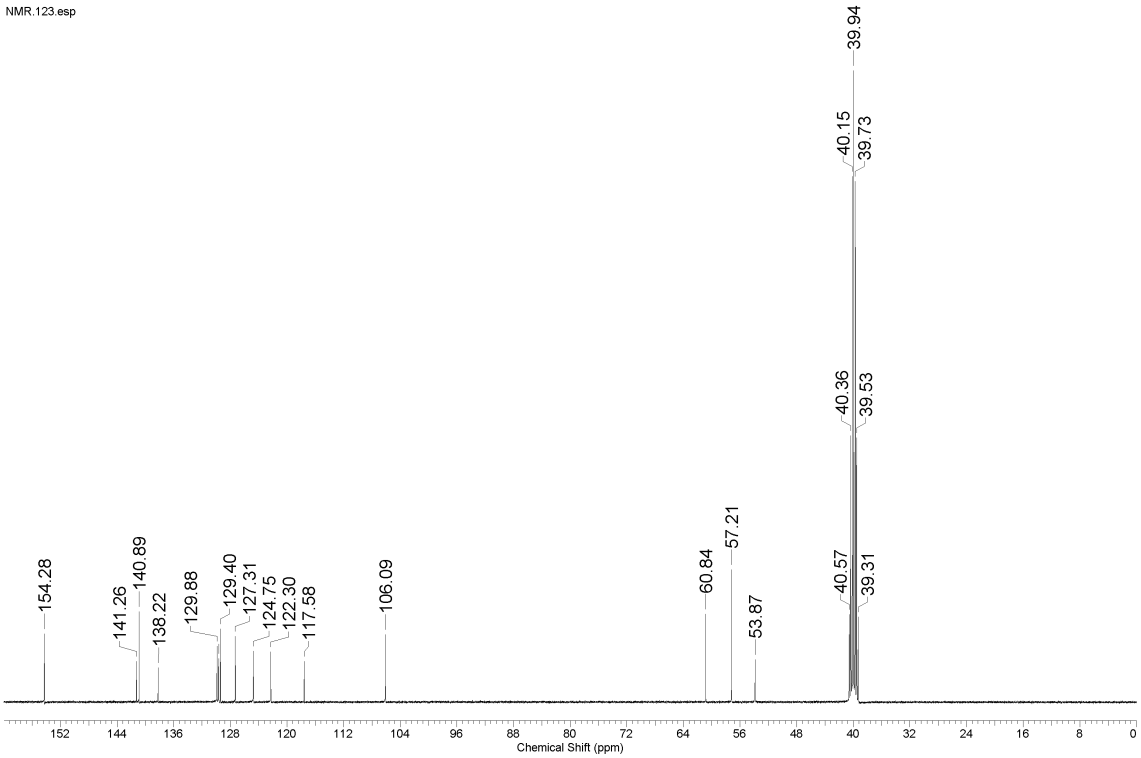
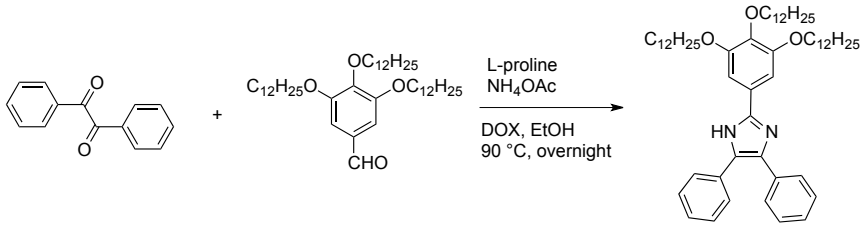


Figure S26. ^{13}C-NMR spectrum of **3C1BF$_4$** in DMSO-d$_6$.

S4. Synthesis of reference compound without fused structure

4,5-Diphenyl-2-(3',4',5'-tridecyloxyphenyl)imidazole



A mixture of benzil (64 mg, 0.30 mmol), 3,4,5-tridodecyloxybenzaldehyde[2] (0.30 g, 0.45 mmol), L-proline (5.3 mg, 0.05 mmol), and ammonium acetate (0.92 g, 12 mmol) in EtOH (2 mL) and 1,4-dioxane (1 mL) was heated at 90 °C overnight. Water was added and an aqueous phase was extracted with CH_2Cl_2. The combined organic phase was rinsed with brine and dried over $MgSO_4$. The solvent was removed and the crude product was purified by SiO_2 column chromatography (hexane : ethyl acetate = 10 : 1, Rf = 0.46) to obtain a pale yellow solid (0.16 g, 61% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.88 (t, *J*=6.60 Hz, 9 H) 1.26 (br. s., 48 H) 1.42 - 1.54 (m, 6 H) 1.70 - 1.87 (m, 6 H) 3.95 - 4.01 (m, 2 H) 4.02 (t, *J*=6.72 Hz, 4 H) 7.07 (s, 2 H) 7.24 (s, 1 H) 7.28 (s, 1 H) 7.31 - 7.35 (m, 2 H) 7.35 - 7.41 (m, 2 H) 7.42 - 7.49 (m, 2 H) 7.65 (d, *J*=7.34 Hz, 2 H) 9.36 (br. s., 1 H)

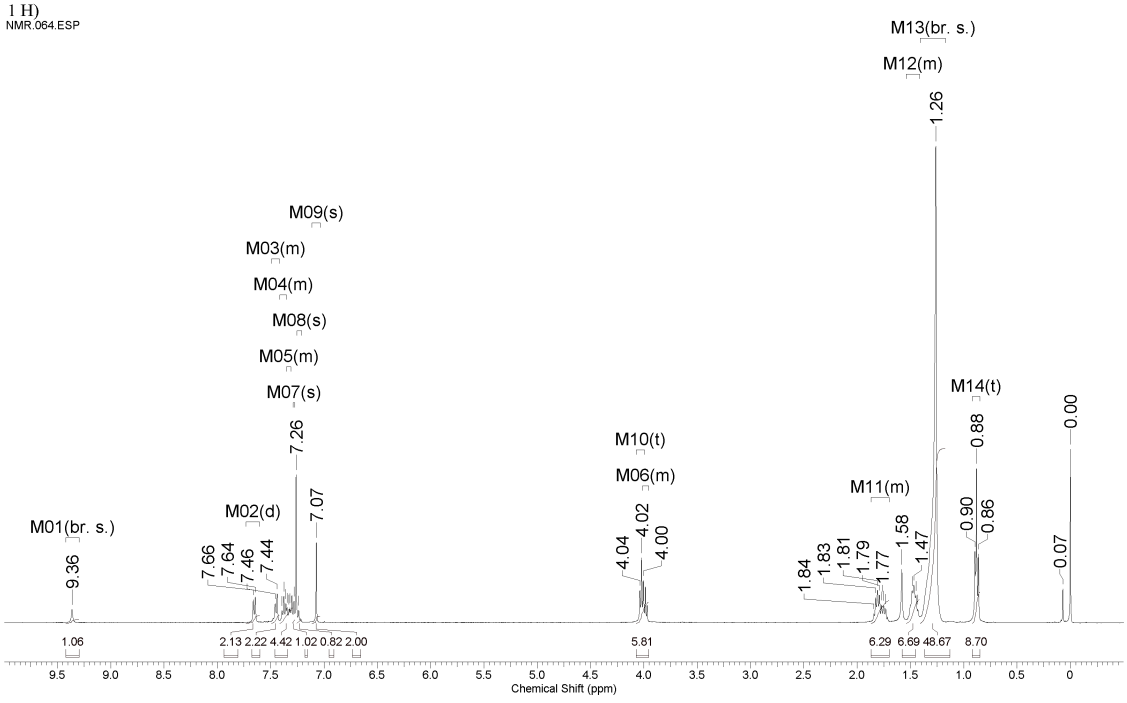
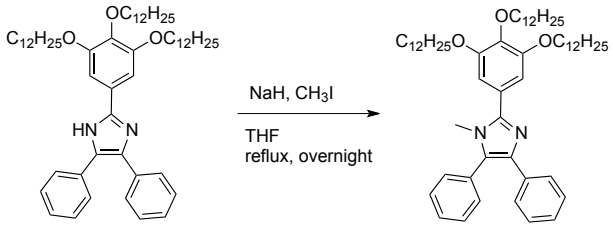


Figure S27. ^{1}H-NMR spectrum of 4,5-diphenyl-2-(3',4',5'-tridecyloxyphenyl)imidazole in $CDCl_3$.

4,5-Diphenyl-1-methyl-2-(3',4',5'-tridecyloxyphenyl)imidazole



To a THF solution (10 mL) of 4,5-diphenyl-2-(3',4',5'-tridecyloxyphenyl)imidazole (0.16 g, 0.19 mmol) was added NaH (24mg, 0.56 mmol) and CH_3I (79 mg, 0.55 mmol), and the mixture was refluxed overnight. After water was added, an aqueous phase was extracted with ethyl acetate. The combined organic phase was rinsed with sat. aqueous NH_4Cl and dried over $MgSO_4$. The solvent was removed and the crude product was purified by SiO_2 column chromatography (hexane : ethyl acetate = 10 : 1, Rf = 0.46) to obtain a pale yellow solid (0.10 g, 64% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.88 (t, *J*=6.72 Hz, 9 H) 1.19 - 1.41 (m, 48 H) 1.42 - 1.55 (m, 6 H) 1.71 - 1.88 (m, 6 H) 3.49 (s, 3 H) 3.97 - 4.03 (m, 2 H) 4.04 (t, *J*=6.60 Hz, 4 H) 6.89 (s, 2 H) 7.15 (d, *J*=7.34 Hz, 1 H) 7.17 - 7.24 (m, 2 H) 7.38 - 7.44 (m, 2 H) 7.44 - 7.51 (m, 3 H) 7.55 (d, *J*=7.34 Hz, 2 H)

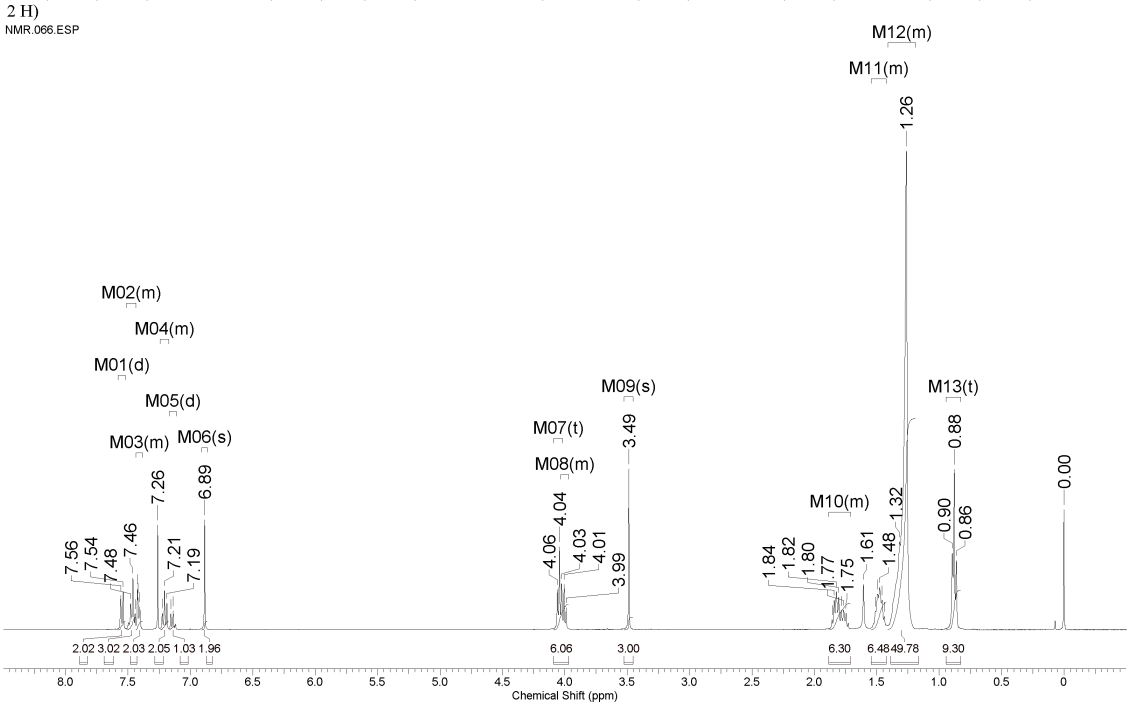
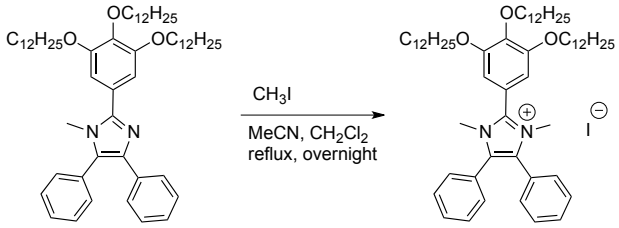


Figure S28. ^{1}H-NMR spectrum of 4,5-diphenyl-1-methyl-2-(3',4',5'-tridecyloxyphenyl)imidazole in $CDCl_3$.

1,3-Dimethyl-4,5-diphenyl-2-(3',4',5'-tridecyloxyphenyl)imidazolium iodide



To a solution of 4,5-diphenyl-1-methyl-2-(3',4',5'-tridecyloxyphenyl)imidazole in CH_3CN (6 mL) and CH_2Cl_2 (3 mL) was added CH_3I (0.17 g, 1.2 mmol), and the mixture was refluxed overnight. Due to the incomplete conversion, the same protocol was repeated. After the solvent was removed, the crude product was purified by SiO_2 column chromatography ($CHCl_3$: MeOH = 6 : 1, Rf = 0.65) to obtain pale yellow solid (0.10 g, 83% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.88 (t, *J*=6.72 Hz, 9 H) 1.20 - 1.42 (m, 49 H) 1.45 - 1.55 (m, 6 H) 1.74 - 1.89 (m, 6 H) 3.59 (s, 6 H) 4.07 (t, *J*=6.48 Hz, 2 H) 4.12 (t, *J*=6.24 Hz, 4 H) 7.34 - 7.44 (m, 8 H) 7.62 (dd, *J*=7.46, 1.83 Hz, 4 H)

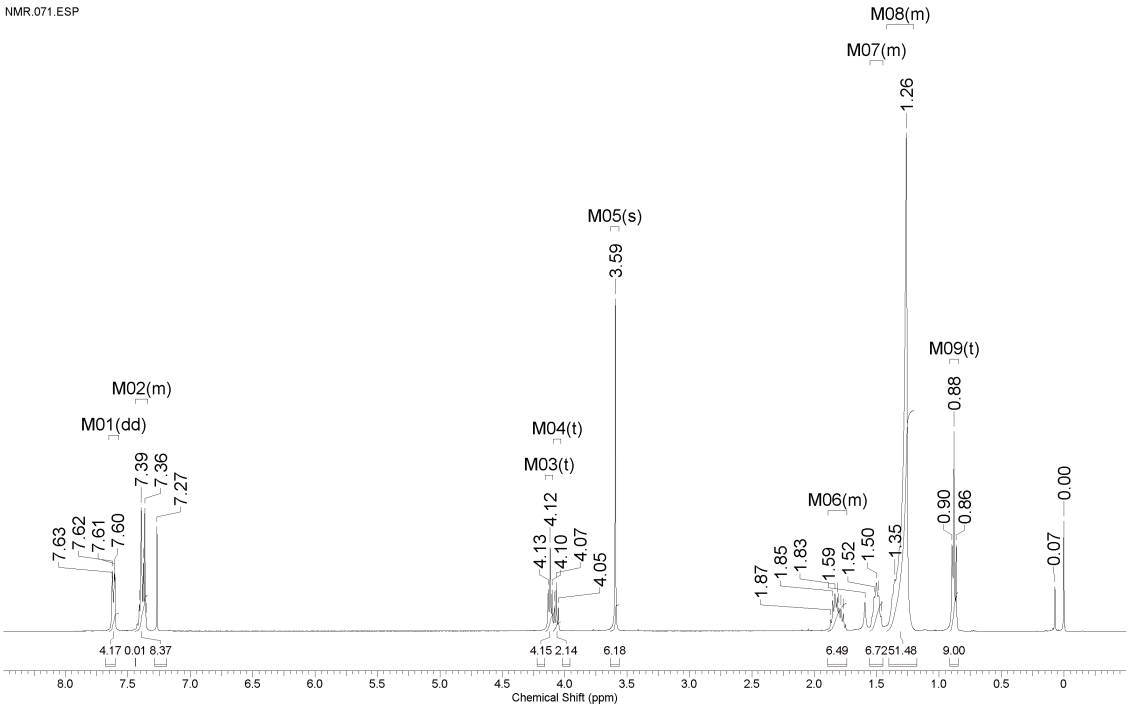
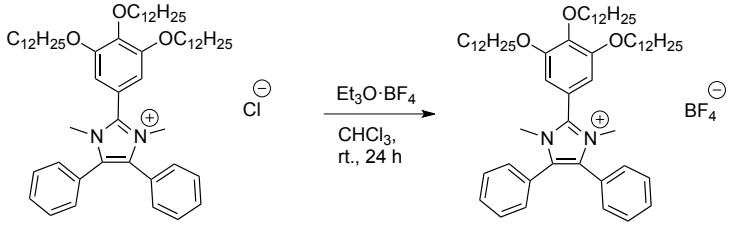


Figure S29. ^{1}H-NMR spectrum of 1,3-dimethyl-4,5-diphenyl-2-(3',4',5'-tridecyloxyphenyl)imidazolium iodide in $CDCl_3$.

1,3-Dimethyl-4,5-diphenyl-2-(3',4',5'-tridecyloxyphenyl)imidazolium tetrafluoroborate (3C12BF4ref)



To a solution of 1,3-dimethyl-4,5-diphenyl-2-(3',4',5'-tridecyloxyphenyl)imidazolium iodide (0.10 g, 0.10 mmol) in $CHCl_3$ (3 mL) was added $Et_3O{\cdot}BF_4$ solution in CH_2Cl_2 (1 M, 0.12 mL), and the mixture was stirred at room temperature for 24 h. After water was added, an aqueous phase was extracted with CH_2Cl_2. The combined organic phase was washed with water and dried over $MgSO_4$. The solvent was removed to obtain a pale yellow solid (82 mg, 87% yield). Anal Calcd for $C_{59}H_{93}BF_4N_2O_3$: C 73.42, H 9.71, N 2.90 %; Found: C 73.20, H 9.69, N 2.88 %.

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.88 (t, *J*=6.85 Hz, 9 H) 1.20 - 1.41 (m, 48 H) 1.44 - 1.55 (m, 6 H) 1.74 - 1.89 (m, 6 H) 3.56 (s, 6 H) 4.08 (q, *J*=6.28 Hz, 6 H) 7.02 (s, 2 H) 7.35 - 7.42 (m, 6 H) 7.44 - 7.50 (m, 4 H)

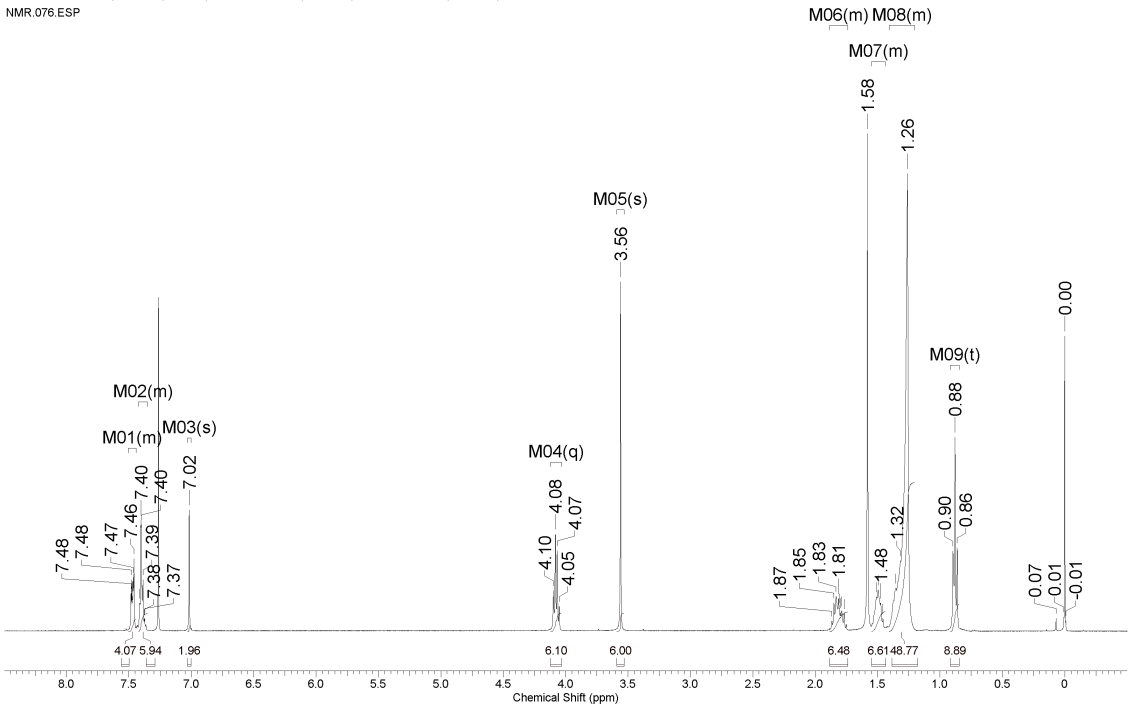


Figure S30. ^{1}H-NMR spectrum of **3C12BF4ref** in $CDCl_3$.

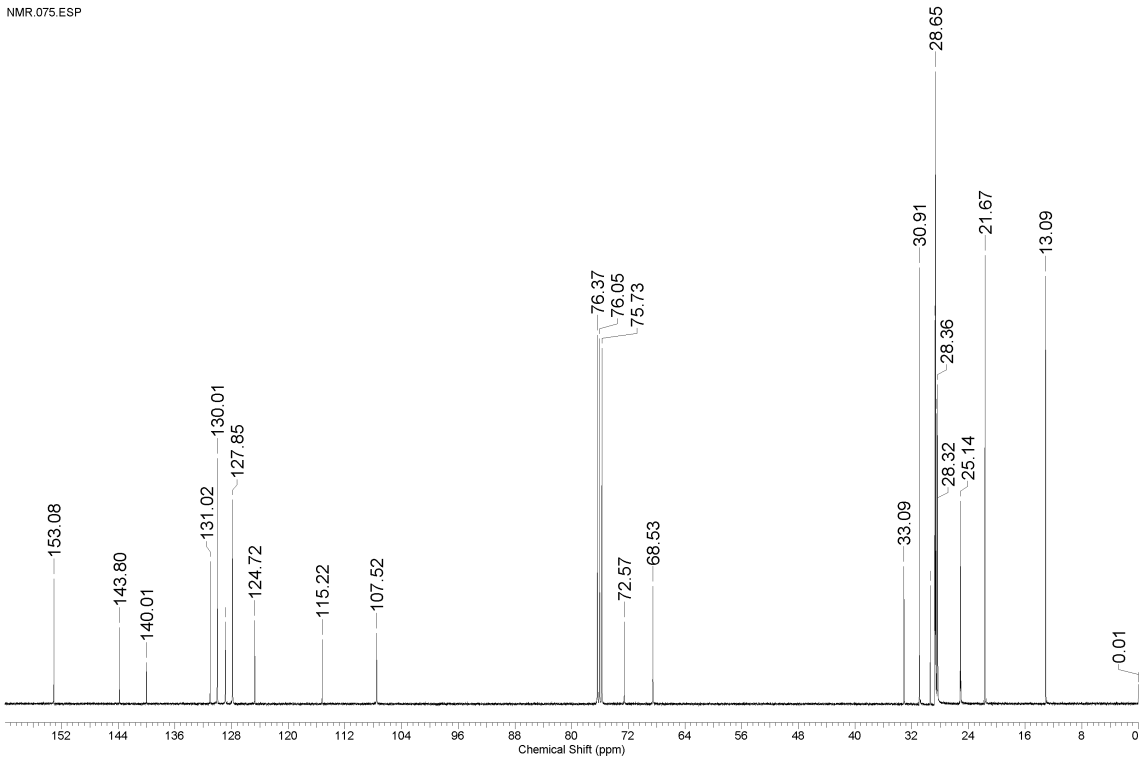


Figure S31. ^{13}C-NMR spectrum of **3C12BF4ref** in $CDCl_3$.

S5. Thermal properties

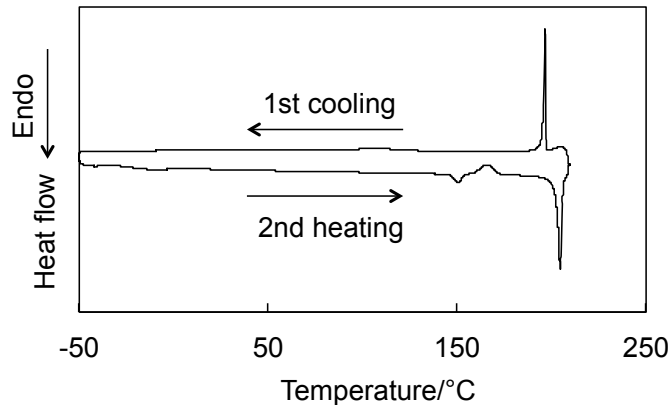


Figure S32. DSC thermogram of **3C8BF4** in first cooling and second heating processes at 5 °C/min.

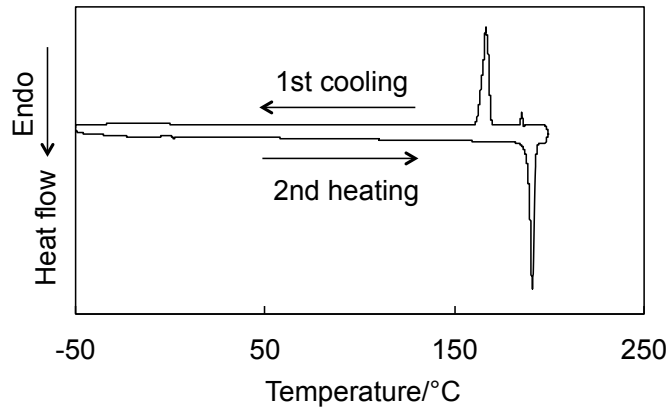


Figure S33. DSC thermogram of **2C12BF4** in first cooling and second heating processes at 5 °C/min.

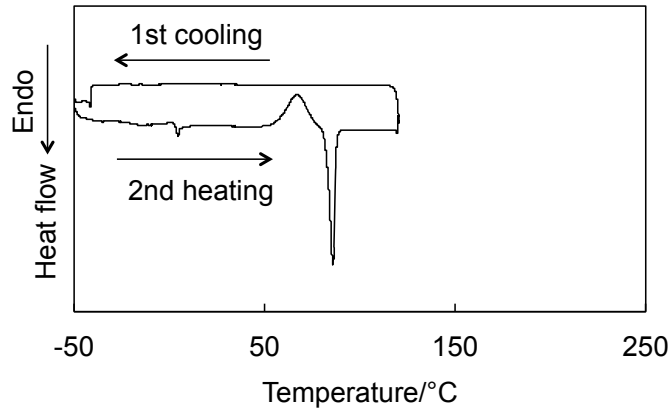


Figure S34. DSC thermogram of **3C12TFSI** in first cooling and second heating processes at 5 °C/min.

Table S1. Phase transition temperatures[a] (°C) and corresponding enthalpies ($kJ \cdot mol^{-1}$).

compound	thermal properties[b]
3C8BF4	Cr_1 150.2 (3.20) Iso 164.9 (–6.97) Cr_2 204.5 (23.3) Iso
2C12BF4	Cr 190.9 (50.8) Iso
3C12TFSI	Sc 66.2 (–20.3) Cr 85.6 (23.4) Iso

[a] Peak temperatures obtained by DSC measurement in the second heating process at 5 °C/min.

[b] Sc: supercooling, Cr: crystal, Iso: isotropic.

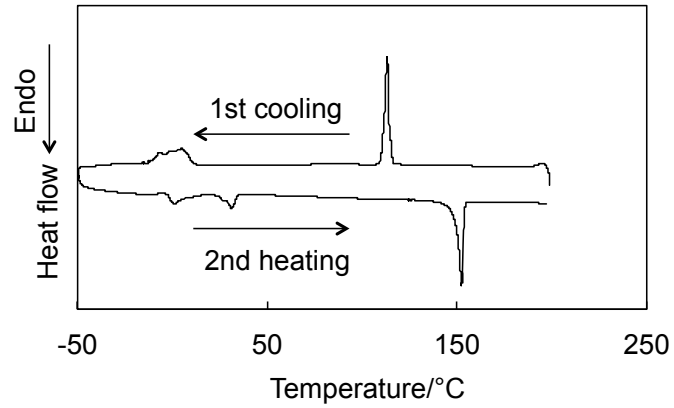


Figure S35. DSC thermogram of **3C12BF4ref** in first cooling and second heating processes at 5 °C/min.

S6. POM images

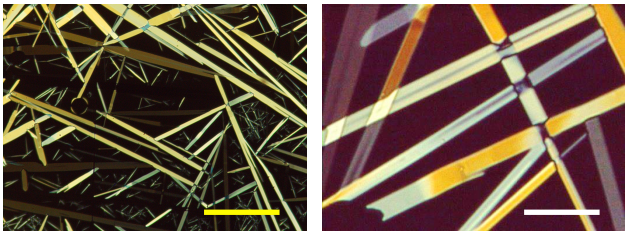


Figure S36. POM images of **3C8BF4** at 190 °C. Yellow and white scale-bars shown in images denote 200μm and 40μm, respectively.

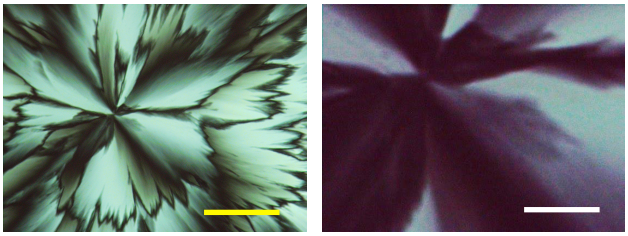


Figure S37. POM images of **2C12BF4** at 150 °C. Yellow and white scale-bars shown in images denote 200μm and 40μm, respectively.

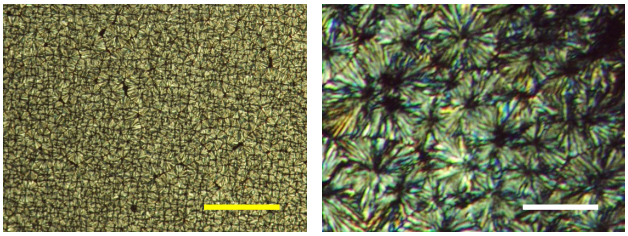


Figure S38. POM images of **3C12TFSI** at 25 °C. Images were captured after cooling from isotropic liquid and kept still standing for 1 day. Yellow and white scale-bars shown in images denote 200μm and 40μm, respectively.

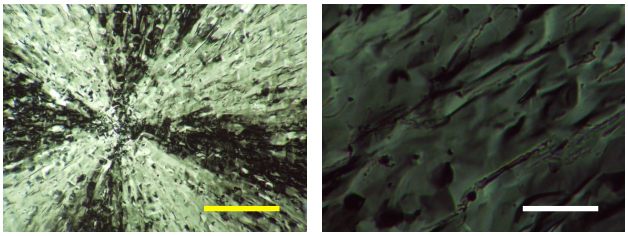


Figure S39. POM image of **3C12BF4ref** at 25 °C. Yellow and white scale-bars shown in images denote 200μm and 40μm, respectively.

S7. VT-XRD analyses

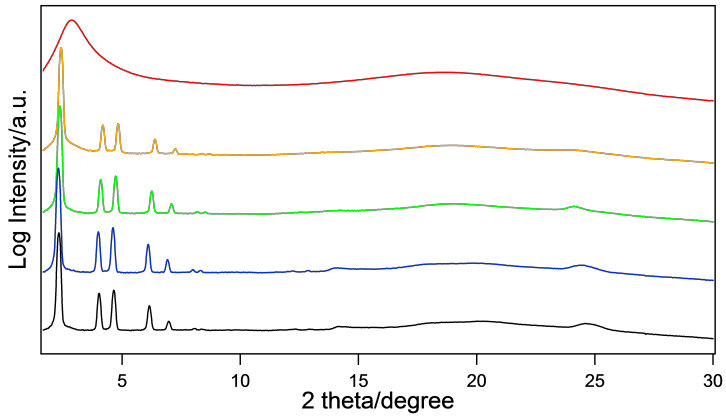


Figure S40. VT-XRD patterns of **3C12BF4** at 25 °C (black), 100 °C (blue), 140 °C (green), 180 °C (orange), and 220 °C (red).

Table S2. VT-XRD results for **3C12BF4** at each temperature.

	d_{obs} (100)/Å	a/Å	c/Å
180 °C	36.51	42.15	NA
140 °C	37.44	43.23	(6.32)
100 °C	38.41	44.35	6.26
25 °C	38.08	43.97	6.24

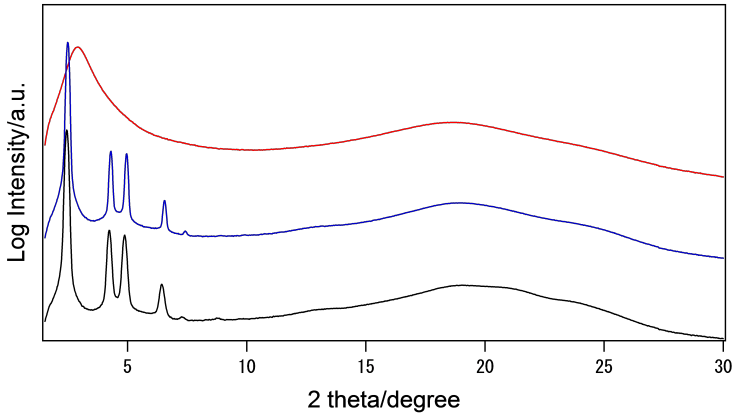


Figure S41. VT-XRD patterns of **3C12OTf** at 25 °C (black), 75 °C (blue), and 120 °C (red).

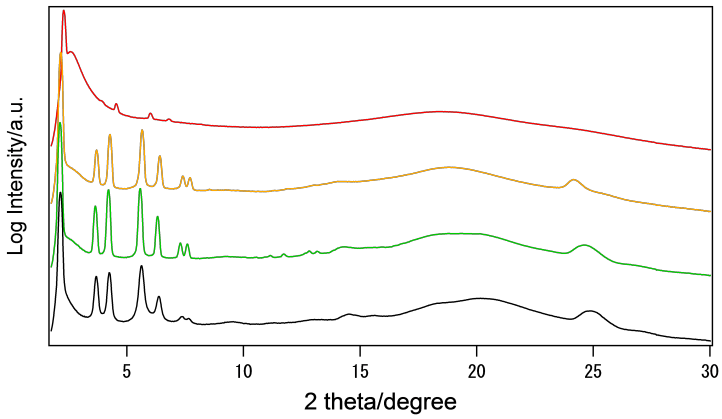


Figure S42. VT-XRD patterns of **3C16BF4** at 25 °C (black), 70 °C (green), 150 °C (orange), and 220 °C (red).

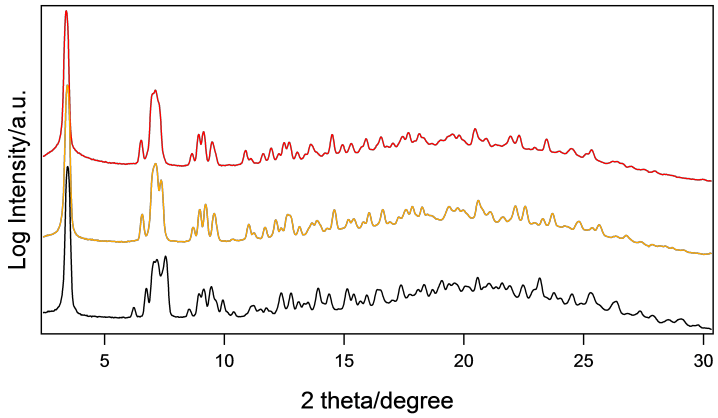


Figure S43. VT-XRD patterns of **3C8BF4** at 25 °C (black), 150 °C (orange), and 210 °C (red).

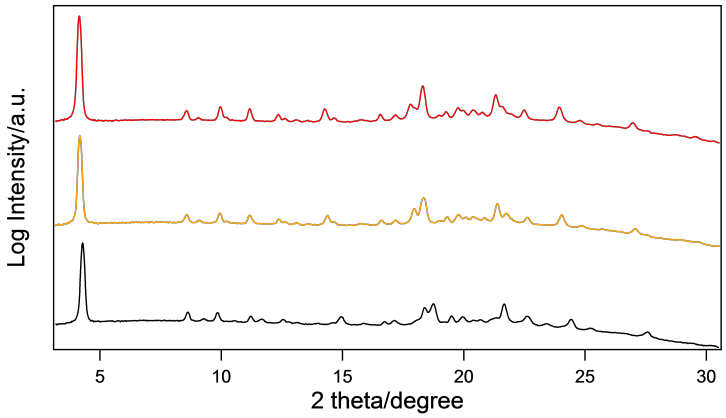


Figure S44. VT-PXRD patterns of **2C12BF4** at 25 °C (black), 100 °C (blue), 175 °C (orange), and 200 °C (red).

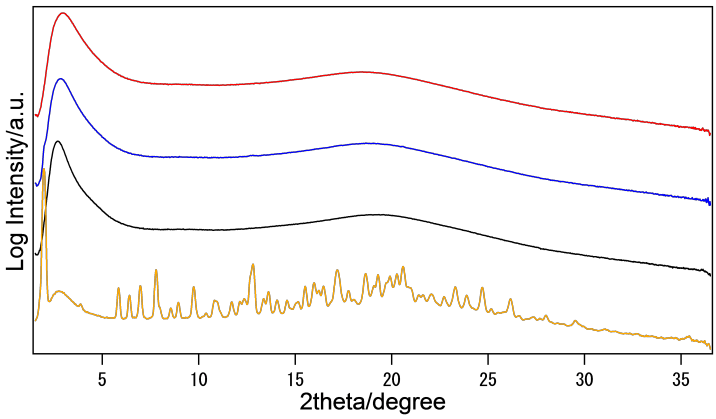


Figure S45. VT-XRD patterns of **3C12TFSI** at 25 °C (black), 75 °C (blue), and 120 °C (red). Orange line denotes a diffraction pattern of sample after standing at 75 °C for 1 h.

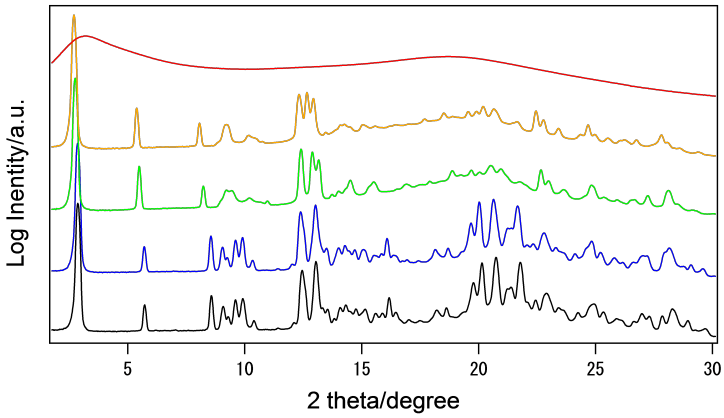


Figure S46. VT-XRD patterns of **3C12BF4ref** at 4 °C (black), 20 °C (blue), 50 °C (green), 130 °C (orange), and 180 °C (red).

S8. Single crystal X-ray structure

Measurement. Crystallographic data was collected on a CCD diffractometer with Cu Kα (λ = 1.54178 Å) radiation. Data collections were carried out at low temperature (173 K) using liquid nitrogen. All of the crystal structures were solved by direct methods with SHELXS-97 and refined with full-matrix least-squares SHELXL-2013.[3] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at their calculated positions.

Crystal data for 3C1BF4: $C_{26}H_{23}BF_4N_2O_3$, M_r = 498.27, Monoclinic, P_{21}/c, a = 12.5531(2), b = 12.7129(2), c = 15.2681(2) Å, V = 2260.00(6) Å^3, Z = 4, D_c = 1.461 Mg m^{-3}, $2\theta_{max}$ = 136.712°, T = 173 K, 14925 reflections measured, 4142 unique (R_{int} = 0.0174), μ = 0.996 mm^{-1}. The final R_1 and wR_2 were 0.0453 and 0.1266 ($I > 2\sigma(I)$), 0.0531 and 0.1345 (all data). CCDC 1437162

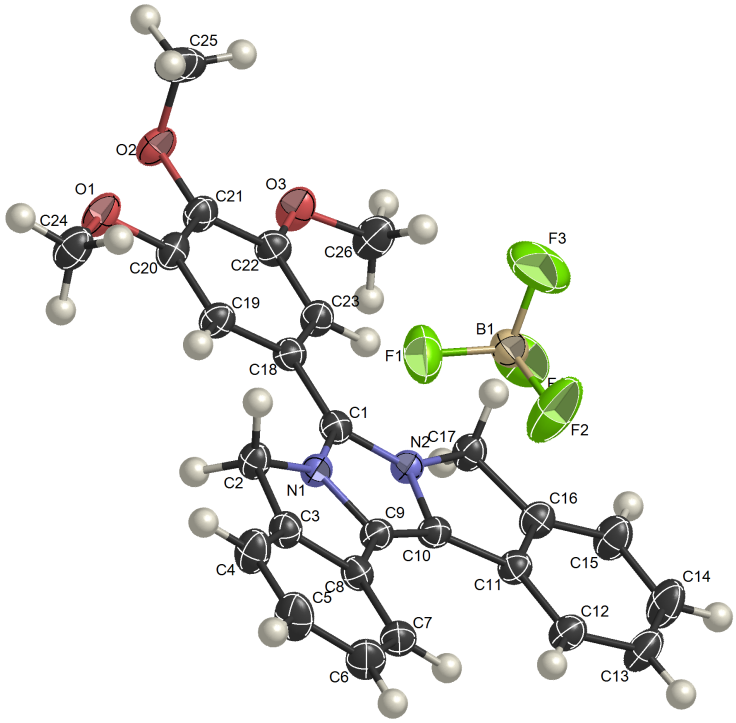


Figure S47. Thermal ellipsoidal model of **3C1BF4**. The ellipsoids are drawn at 50% probability level while isotropic hydrogen atoms are represented by spheres of arbitrary size. The labels of hydrogen atoms are omitted for clarity.

S9. Optical properties

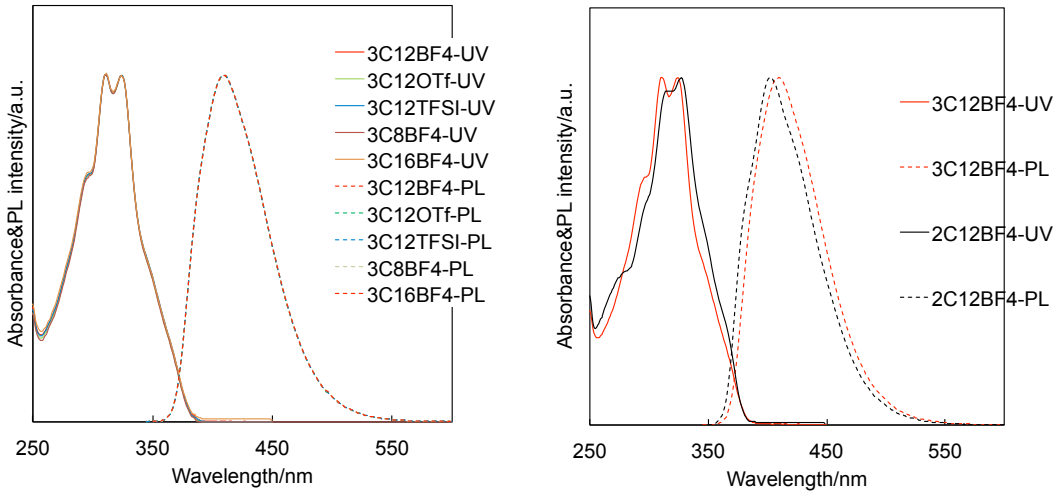


Figure S48. UV-vis and fluorescence spectra of five fused π-conjugated imidazolium compounds in DCM (10^{-5} M). Left: Influence of alkyl chain length and counter anion. Right: Influence of a number of alkoxy chains. The excitation wavelengths were that of the absorption maxima.

Table S3. Photophysical data of five fused π-conjugated imidazolium compounds in CH_2Cl_2 (10^{-5} M).

	λ_{abs}/nm	λ_{em}/nm	QY/%[a]
3C8BF4	311, 324	409	0.55
3C12BF4	311, 324	410	0.55
3C16BF4	311, 324	409	0.55
3C12OTf	311, 324	409	0.54
3C12TFSI	311, 324	409	0.52
2C12BF4	316, 327	403	0.78

[a] Relative fluorescence quantum yield determined using quinine sulfate as a standard (QY = 0.55).

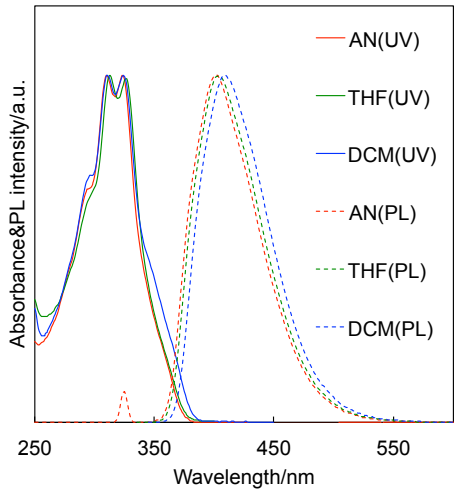


Figure S49. UV-vis and fluorescence spectra of **3C12BF4** in various solvents (10^{-5} M). AN: acetonitrile, THF: tetrahydrofuran, DCM: dichloromethane. The excitation wavelengths were that of the absorption maxima.

Table S4. Photophysical data of **3C12BF4** in various solvents (10^{-5} M).

	λ_{abs}/nm	λ_{em}/nm	QY/%[a]
AN	310, 324	401	0.82
THF	313, 326	404	0.57
DCM	311, 324	410	0.55

a Relative fluorescence quantum yield determined using quinine sulfate as a standard (QY = 0.55).

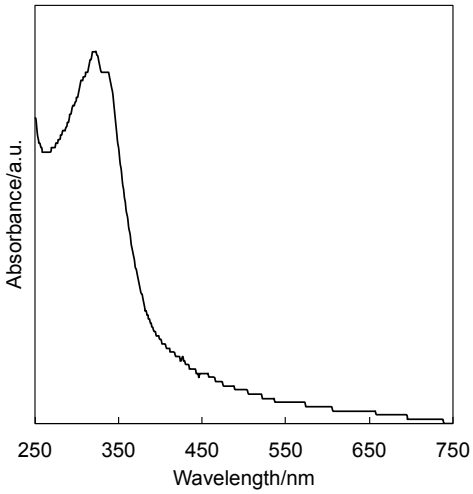


Figure S50. UV-vis spectrum of **3C12BF4** in solid state.

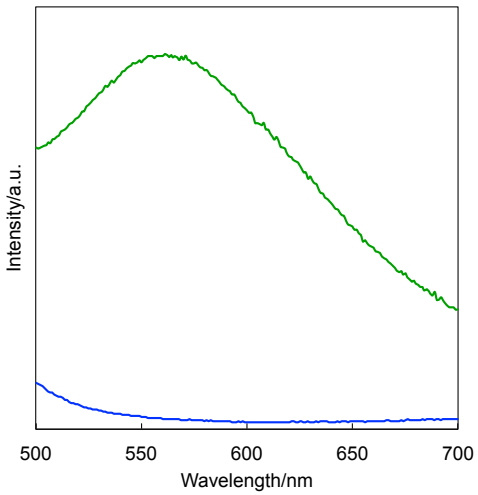


Figure S51. Fluorescence spectra of **3C12OTf** (blue line) and **3C16BF4** (green line) in solid state obtained by irradiating at 450 nm.

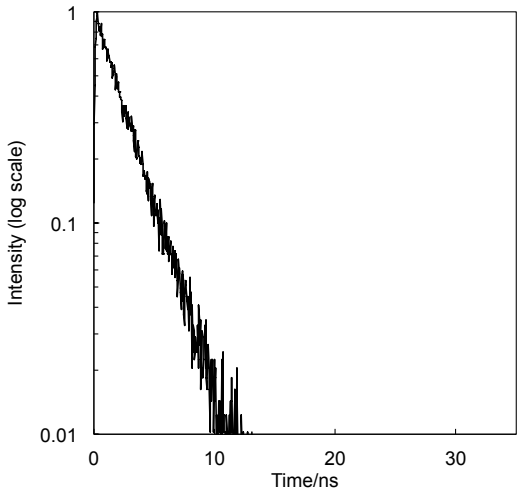


Figure S52. Fluorescence decay curve of **3C12BF4** in CH_2Cl_2 by irradiating at 375 nm and monitoring at 420 nm.

S10. References

1) K Takagi, K. Kusafuka, Y. Ito, K. Yamauchi, K. Ito, R. Fukuda, and M. Ehara *J. Org. Chem.*, **2015**, *80*, 7172–7183.
2) A. S. Achalkumar and C. V. Yelamaggad *Tetrahedron Lett.*, **2012**, *53*, 7108–7112.
3) A short history of SHELX. G. M. Sheldrick, *Acta Cryst*. 2008, **A64**, 112–122.