Suppprementary Information Available for

Synthesis of Green and Blue Fluorescent Ladder-Type Conjugated Imidazolium Compounds

Koji Takagi,* Yohei Ito, Kazuma Kusafuka, and Masanori Sakaida

Department of Materials Science and Engineering,

Graduate School of Engineering, Nagoya Institute of Technology,

Gokiso, Showa, Nagoya 466-8555 Japan

*To whom all correspondence should be addressed

Phone: +81-52-735-5264, Email: takagi.koji@nitech.ac.jp

Contents

1. General

1-1. Materials All reactions were performed under dry nitrogen atmosphere unless otherwise noted. *N*-Bromosuccinimide (NBS) was purchased from Tokyo Chemical Industry. Dry tetrahydrofuran (THF), lithium alminum hydride (LAH), *n*-butyllithium solution (BuLi, 1.6 M in hexane), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and 2-(hydroxymethyl)phenylboronic acid were purchased from Kanto Chemical. Dry diethyl ether (Et_2O), triisopropyl borate ($B(O^iPr)_3$), lithium bis(trimethylsilyl)amide solution (LiHMDS, 1.0 M in THF), and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) were purchased from Sigma-Aldrich. Thionyl chloride was purchased from Nacalai tesque. 2-Bromophenylacetic acid was purchased from Matrix Scientific. These reagents were used as received. Acetonitrile (AN) and *N*,*N*-dimethylformamide (DMF) were dried and distilled according to the general methods.

1-2. Instrumentation ^1H and ^{13}C nuclear magnetic resonance (^1H-NMR and ^{13}C-NMR) spectra were recorded on a Bruker Avance 200 FT-NMR spectrometer using tetramethylsilane (^1H-NMR, δ 0.00) and $CDCl_3$ (^{13}C-NMR, δ 77.0) as internal reference peaks. Infrared (IR) spectra were recorded on a Jasco FT-IR 460Plus spectrophotometer in the attenuated total reflection (ATR) method. Melting points (Mp) were determined on a Yanagimoto micro melting point apparatus MP-500D and were uncorrected. Elemental analyses (EA) were performed on a Elementar vario EL cube in the CHN mode. High resolution electrospray mass spectra (HRMS) spectra were performed on a Waters Synapt G2 HDMS in the positive and negative modes. Ultraviolet (UV) and photoluminescence (PL) spectra were recorded on a Shimadzu UV-1650PC spectrophotometer and a Shimadzu RF-5300PC spectrofluorometer, respectively, using a 1 cm quartz cell. Fluorescence quantum yields (QYs) in solution were determined relative to quinine sulfate in 0.1 M H_2SO_4 with QY of 0.55.

2. Synthesis and characterization of M1-M4

2-1. 4,5-Bis(2’-(2”-hydroxymethyl)phenyl)-2-octylimidazole (M1) To a flask containing 4,5-dibromo-2-octylimidazole (1.69 g, 5.00 mmol) and 2-(hydroxymethyl)phenylboronic acid (2.28 g, 15.0 mmol) in THF (84 mL) were added 2 M aqueous Na_2CO_3 (20 mL) and $Pd(PPh_3)_4$ (173 mg, 0.150 mmol), and the mixture was heated to reflux for 24 h. After saturated aqueous NH_4Cl was added, an aqueous phase was extracted with $CHCl_3$. The combined organic phase was dried over $MgSO_4$ and the solvents were removed by rotary evaporator. The crude product was purified by SiO_2 chromatography using hexane/ethyl acetate (2:3 in volume) (Rf=0.45) to obtain a pale yellow solid. The product was further purified by recrystallization from hexane/ethyl acetate to obtain a colorless solid in 1.16 g (59% yield). Mp. 110–112 °C. HRMS (ESI) *m*/*z* calcd for $C_{25}H_{32}N_2O_2Na$ [**M1**+Na]$^+$: 415.2361. Found: 415.2361. Elemental analysis calcd (%) for $C_{25}H_{32}N_2O_2$: C, 76.49; H, 8.22; N, 7.14. Found: C, 76.38; H, 8.26; N, 7.08.

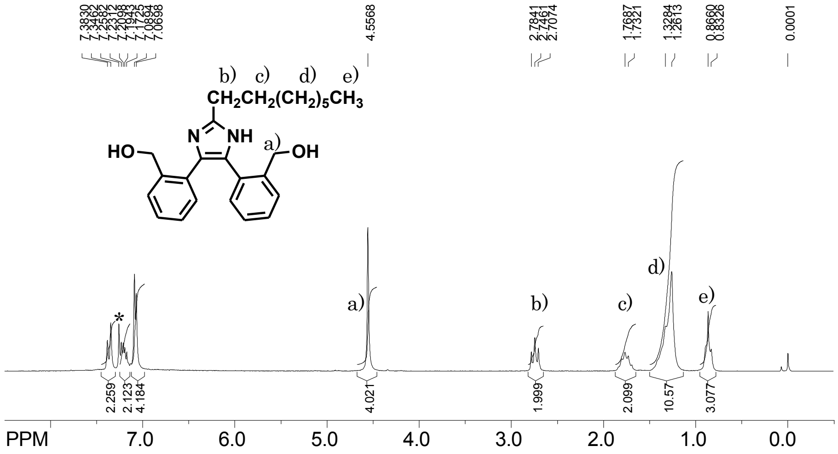


Figure S1. ^{1}H-NMR spectrum of 4,5-bis(2’-(2”-hydroxymethyl)phenyl)-2-octylimidazole (**M1**) in $CDCl_3$.

δ: 7.36 (d, *J*=7.4 Hz, 2H), 7.24–7.13 (m, 2H), 7.12–7.00 (4H), 4.56 (s, 4H), 2.75 (t, *J*=7.8 Hz, 2H), 1.77 (m, 2H), 1.50–1.13 (10H), 0.87 (br, 3H).

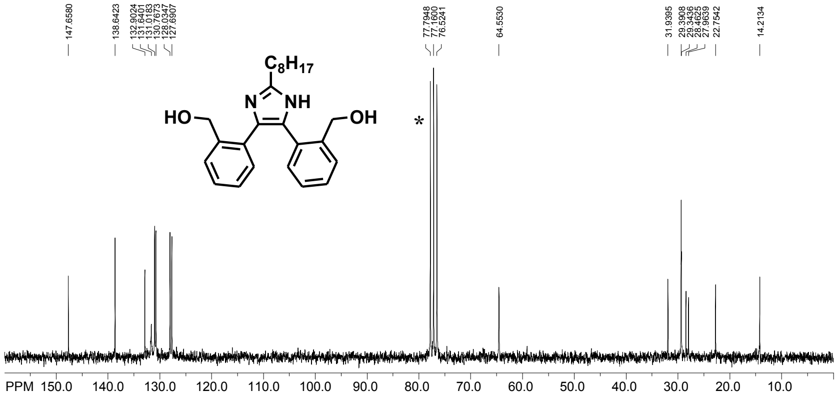


Figure S2. ^{13}C-NMR spectrum of 4,5-bis(2'-(2"-hydroxymethyl)phenyl)-2-octylimidazole (**M1**) in $CDCl_3$.

δ: 147.7, 138.6, 132.9, 131.6, 131.0, 130.8, 128.0, 127.7, 64.6, 31.9, 29.4, 29.3, 28.5, 28.0, 22.8, 14.2.

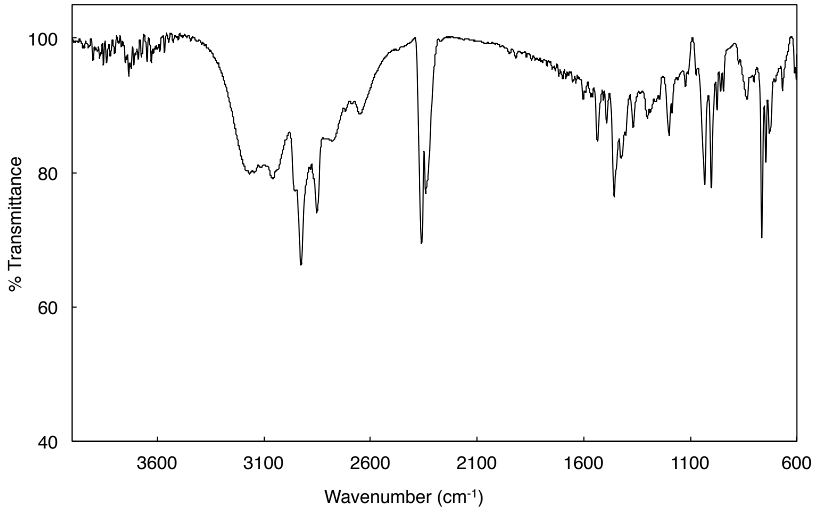


Figure S3. IR spectrum of 4,5-bis(2'-(2"-hydroxymethyl)phenyl)-2-octylimidazole (**M1**).

cm^{-1}: 3735, 3057, 2927, 2851, 1535, 1457, 1201, 1032, 1001, 764, 745.

2-2. 1,3-Dihydro-4,5-bis(2’-(2”-chloromethyl)phenyl)-2-octylimidazolium chloride (M2) To a flask containing **M1** (300 mg, 0.764 mmol) in AN (83 mL) was added $SOCl_2$ (16.3 mL, 225 mmol), and the mixture was stirred at room temperature overnight. The solvent and $SOCl_2$ were removed by diaphragm pump and the product was dried in vacuo to obtain a colorless solid in 401 mg (quantitative). Mp. 110–112 °C. HRMS (ESI) *m/z* calcd for $C_{25}H_{31}Cl_2N_2$ [**M2**–Cl]$^+$: 429.1864. Found: 429.1870.

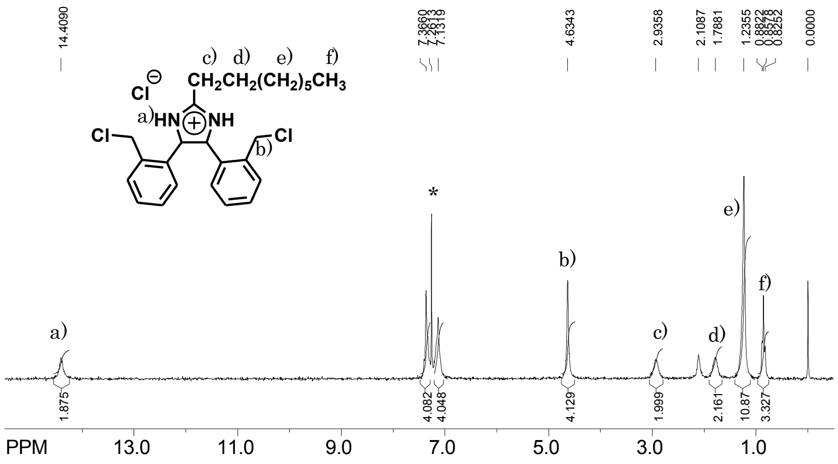


Figure S4. ^{1}H-NMR spectrum of 1,3-dihydro-4,5-bis(2’-(2”-chloromethyl)phenyl)-2-octylimidazolium chloride (**M2**) in $CDCl_3$.

δ: 14.4 (brs, 2H), 7.43–7.27 (4H), 7.22–7.02 (4H), 4.63 (s, 4H), 2.94 (br, 2H), 1.79 (m, 2H), 1.37–1.12 (10H), 0.86 (3H).

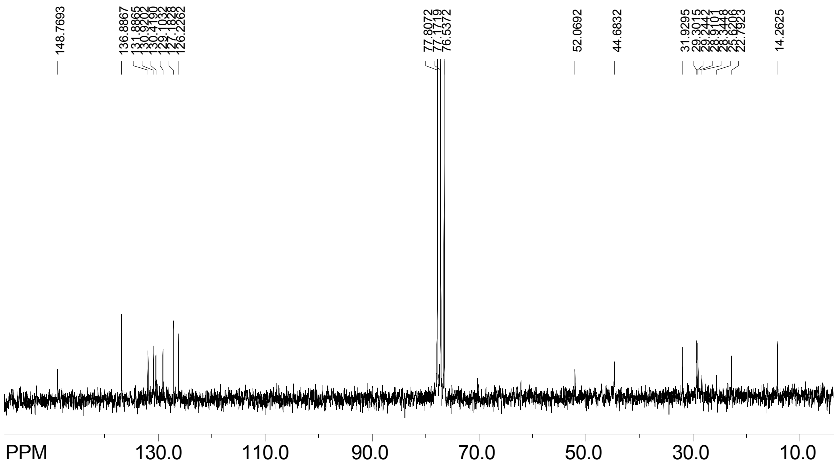


Figure S5. ^{13}C-NMR spectrum of 1,3-dihydro-4,5-bis(2’-(2”-chloromethyl)phenyl)-2-octylimidazolium chloride (**M2**).

δ: 148.8, 136.9, 131.9, 130.9, 130.4, 129.1, 127.2, 126.2, 52.1, 44.7, 31.9, 29.3, 29.2, 28.9, 28.3, 25.6, 22.8, 14.3.

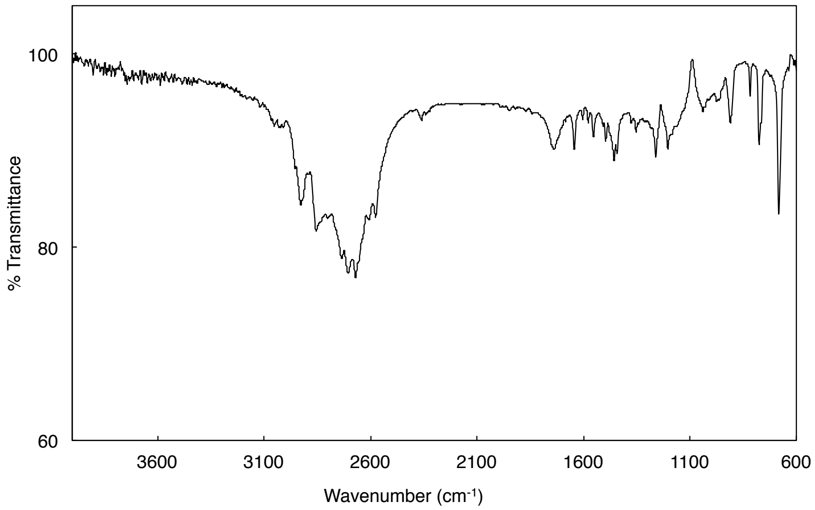


Figure S6. IR spectrum of 1,3-dihydro-4,5-bis(2’-(2”-chloromethyl)phenyl)-2-octylimidazolium chloride (**M2**).

cm^{-1}: 2927, 2854, 2704, 2670, 2576, 1740, 1643, 1552, 1496, 1456, 1260, 1203, 910, 775, 683.

2-3. Methylene-bridged imidazolium chloride (M3) To a flask containing **M2** (324 mg, 0.695 mmol) in DMF (80 mL) was added a THF solution of LiHMDS (1.39 mL, 1.39 mmol), and the mixture was stirred at room temperature overnight. After saturated aqueous NH_4Cl was added, an aqueous phase was extracted with $CHCl_3$. The combined organic phase was dried over $MgSO_4$ and the solvents were removed by rotary evaporator. The crude product was dissolved in $CHCl_3$ and poured into excess hexane to obtain a pale yellow solid in 223 mg (82% yield). Mp. 253–255 °C. HRMS (ESI) *m*/*z* calcd for $C_{25}H_{29}N_2$ [**M3**–Cl]$^+$: 357.2331. Found: 357.2340.

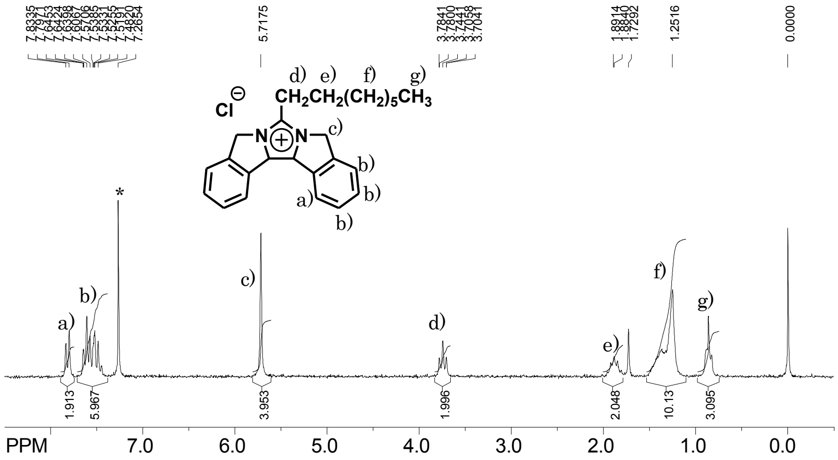


Figure S7. ^{1}H-NMR spectrum of methylene-bridged imidazolium chloride (**M3**) in $CDCl_3$.

δ: 7.82 (d, *J*=7.3 Hz, 2H), 7.67–7.43 (6H), 5.72 (s, 4H), 3.74 (t, *J*=7.7 Hz, 2H), 1.88 (m, 2H), 1.50–1.18 (10H), 0.86 (br, 3H).

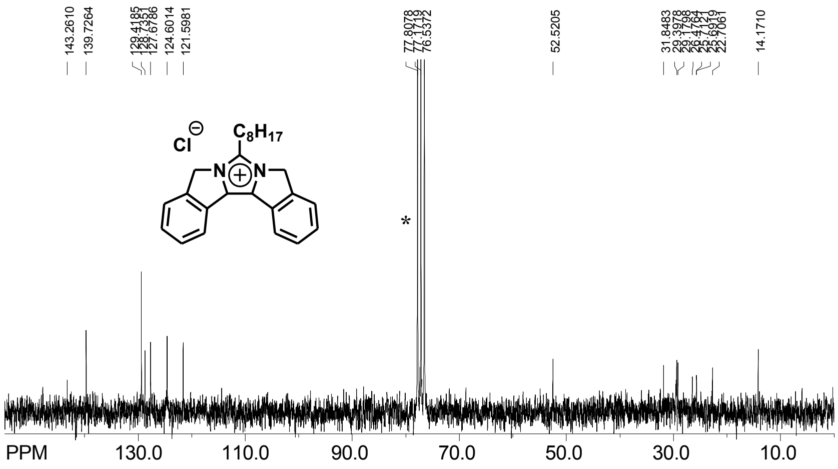


Figure S8. ^{13}C-NMR spectrum of methylene-bridged imidazolium chloride (**M3**) in $CDCl_3$.

δ: 143.3, 139.7, 129.4, 128.7, 127.7, 124.6, 121.6, 52.5, 31.8, 29.4, 29.2, 26.4, 25.7, 25.7, 22.7, 14.2.

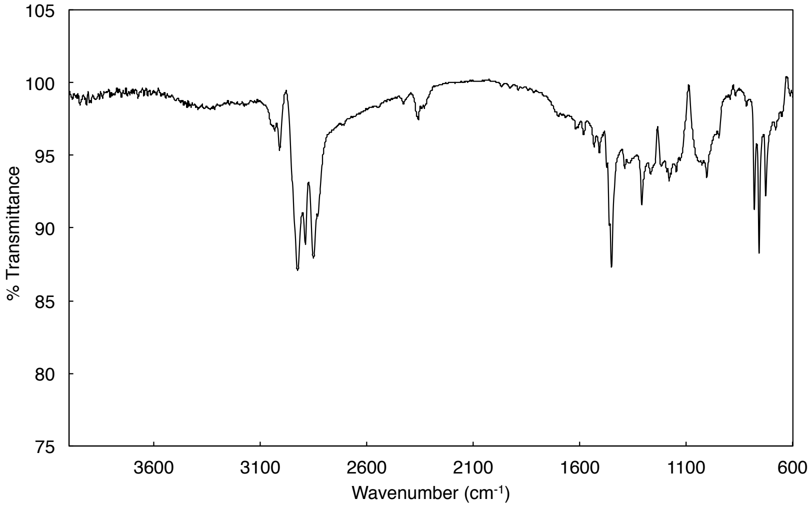


Figure S9. IR spectrum of methylene-bridged imidazolium chloride (**M3**).

cm^{-1}: 3388, 2925, 2854, 1469, 1303, 1268, 1111, 1026, 756, 655.

2-4. Methylene-bridged imidazolium bis(trifluoromethanesulfonyl)imide (M4) To a flask containing **M3** (27 mg, 69 μmol) in $CHCl_3$ (3.8 mL) was added an aqueous solution (5.3 mL) of LiTFSI (1.5 g, 5.3 mmol), and the mixture was vigorously stirred at room temperature overnight. After two layers were separated, an aqueous phase was extracted with $CHCl_3$. The combined organic phase was dried over $MgSO_4$ and the solvents were removed by rotary evaporator. The product was dried in vacuo to obtain a pale brown solid in 38 mg (87% yield). Mp. 116–119 °C. HRMS (ESI) *m*/*z* calcd for $C_{25}H_{29}N_2$ [**M4**–TFSI]$^+$: 357.2331. Found: 357.2327. HRMS (ESI) *m*/*z* calcd for $C_2F_6NO_4S_2$ [TFSI]$^-$: 279.9173. Found: 279.9180.

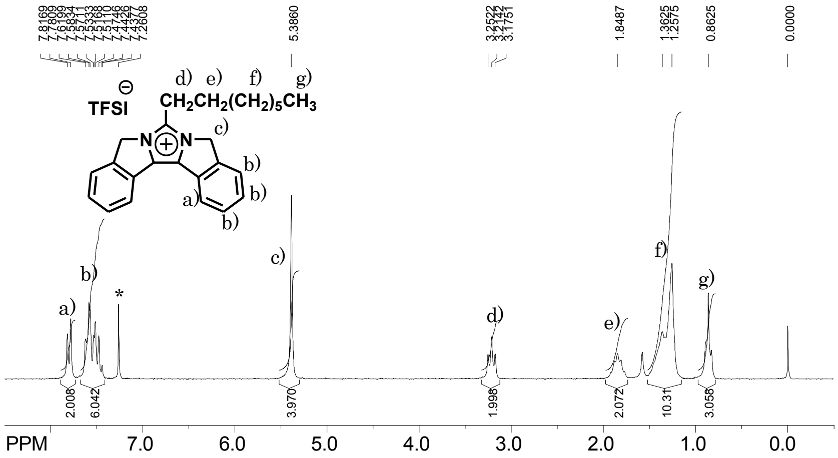


Figure S10. ^{1}H-NMR spectrum of methylene-bridged imidazolium bis(trifluoromethanesulfonyl)imide (**M4**) in $CDCl_3$.

δ: 7.80 (d, *J*=7.3 Hz, 2H), 7.70–7.38 (6H), 5.39 (s, 4H), 3.21 (t, *J*=7.7 Hz, 2H), 1.85 (m, 2H), 1.52–1.17 (10H), 0.86 (br, 3H).

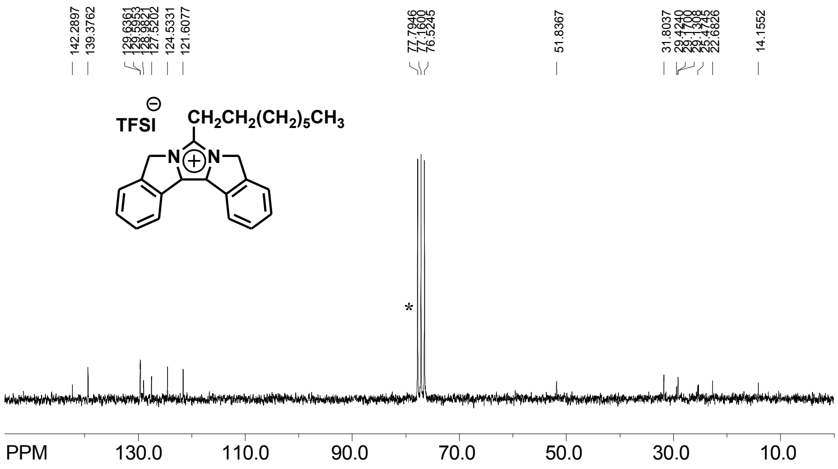


Figure S11. ^{13}C-NMR spectrum of methylene-bridged imidazolium bis(trifluoromethanesulfonyl)imide (**M4**) in $CDCl_3$.

δ: 142.3, 139.4, 129.6, 129.6, 129.0, 127.5, 124.5, 121.6, 51.8, 31.8, 29.4, 29.2, 29.1, 25.5, 22.7, 14.2.

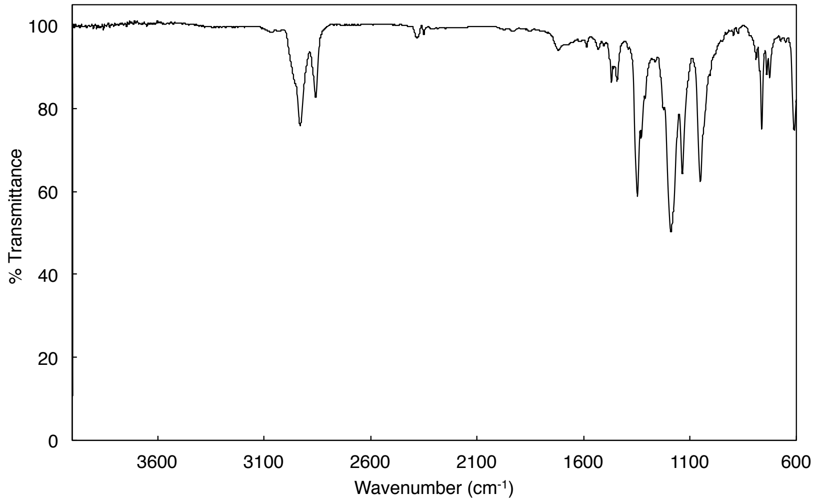


Figure S12. IR spectrum of methylene-bridged imidazolium bis(trifluoromethanesulfonyl)imide (**M4**).

cm^{-1}: 2929, 2857, 1468, 1346, 1189, 1135, 1050, 763, 739, 725, 610.

3. Synthesis and characterization of E1-E4

3-1. 2,4,6-Tris(2’-(2”-hydroxyethyl)phenyl)boroxin To a flask containing LAH (1.76 g, 46.5 mmol) and Et_2O (75 mL) was added dropwise a solution of 2-bromophenylacetic acid (10.0 g, 46.5 mmol) in Et_2O (35 mL) at 0 °C, and the mixture was heated to reflux for 5 h. Then celite 545 (4.0 g), THF (1.8 mL), distilled water (1.8 mL), and 15% aqueous NaOH (5.4 mL) were added at 0 °C. After the mixture was stirred for 2 h, the precipitate was filtered off. The filtrate was concentrated to driness and dried in vacuo to obtain 2-bromophenethyl alcohol as a colorless liquid in 8.70 g (93% yield).

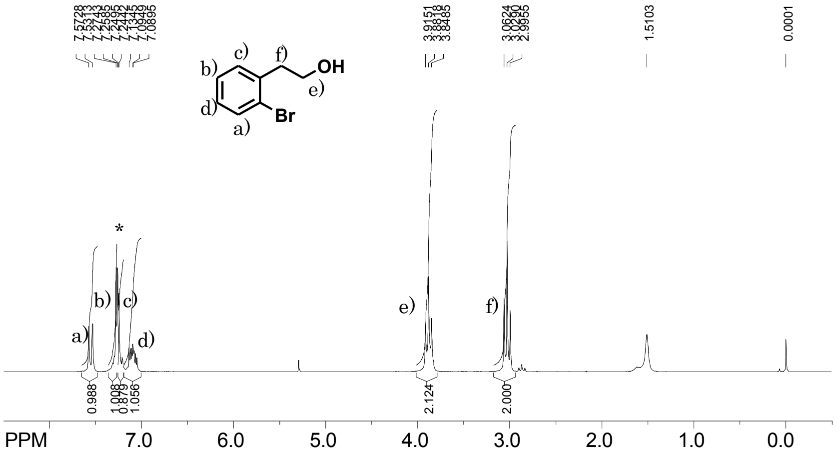


Figure S13. ^{1}H-NMR spectrum of 2-bromophenethyl alcohol in $CDCl_3$.

δ: 7.55 (d, *J*=8.3 Hz, 1H), 7.22–7.30 (2H), 7.03–7.14 (m, 1H), 3.88 (t, *J*=6.7 Hz, 2H), 3.03 (t, *J*=6.7 Hz, 2H).

To a flask containing 2-bromophenethyl alcohol (5.00 g, 24.9 mmol) and THF (300 mL) was added dropwise a hexane solution of BuLi (33.6 mL, 54.1 mmol) at –78 °C, and the mixture was stirred for 4 h. Then $B(O^iPr)_3$ (7.40 mL, 32.3 mmol) was added and the mixture was stirred overnight while gradually increasing to room temperature. After 1 M HCl was added, an aqueous phase was extracted with ethyl acetate. The combined organic phase was dried over $MgSO_4$ and the solvents were removed by rotary evaporator. The crude product was purified by SiO_2 chromatography using hexane/ethyl acetate (1:1 in volume) (Rf=0.60) to obtain a colorless liquid. The product was further purified by recrystallization from hexane to obtain a colorless solid in 1.21 g (33% yield). Mp. 59–62 °C. Elemental analysis calcd (%) for $C_{24}H_{27}B_3O_6$: C, 64.94; H, 6.13. Found: C, 65.33; H, 6.17.

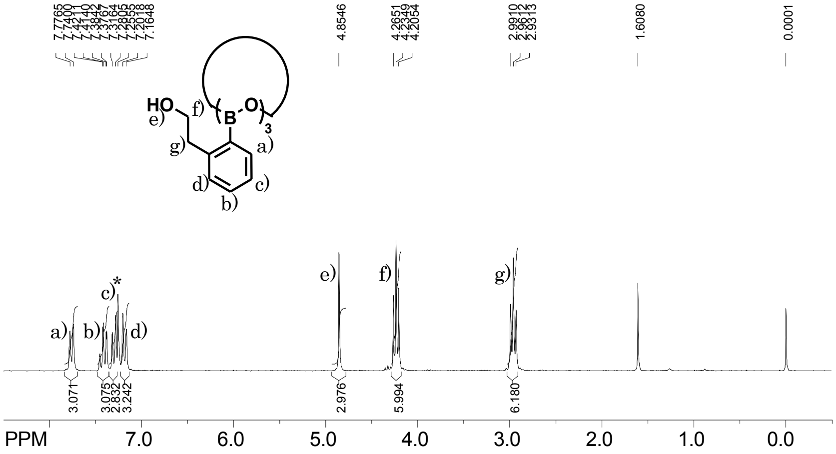


Figure S14. ^{1}H-NMR spectrum of 2,4,6-tris(2’-(2”-hydroxyethyl)phenyl)boroxin in $CDCl_3$.

δ: 7.75 (d, *J*=3.6 Hz, 3H), 7.47–7.36 (m, 3H), 7.30 (d, *J*=3.6 Hz, 3H), 7.18 (d, *J*=3.8 Hz, 3H), 4.85 (s, 3H), 4.23 (t, *J*=6.0 Hz, 6H), 2.96 (t, *J*=6.0 Hz, 6H).

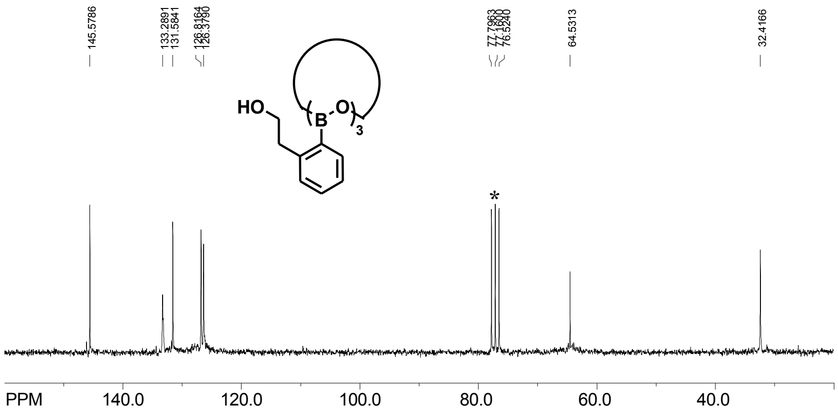


Figure S15. ^{13}C-NMR spectrum of 2,4,6-tris(2'-(2"-hydroxyethyl)phenyl)boroxin in $CDCl_3$.

δ: 145.6, 133.3, 131.6, 126.8, 126.4, 64.5, 32.4.

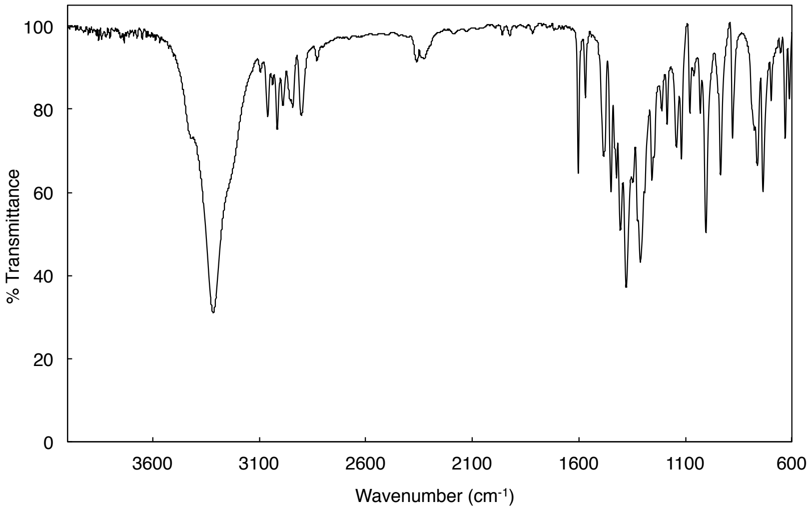


Figure S16. IR spectrum of 2,4,6-tris(2'-(2"-hydroxyethyl)phenyl)boroxin.

cm^{-1}: 3315, 3059, 3015, 2989, 2943, 2901, 1603, 1448, 1405, 1377, 1311, 1004, 736.

3-2. 4,5-Bis(2'-(2"-hydroxyethyl)phenyl)-2-octylimidazole (E1) To a flask containing 4,5-dibromo-2-octylimidazole (914 mg, 2.70 mmol) and 2,4,6-tris(2'-(2"-hydroxyethyl)phenyl)boroxin (1.26 g, 2.83 mmol) in THF (84 mL) were added 2 M aqueous Na_2CO_3 (11 mL) and $Pd(PPh_3)_4$ (156 mg, 0.135 mmol), and the mixture was heated to reflux for 24 h. After saturated aqueous NH_4Cl was added, an aqueous phase was extracted with $CHCl_3$. The combined organic phase was dried over $MgSO_4$ and the solvents were removed by rotary evaporator. The crude product was purified by SiO_2 chromatography using ethyl acetate (Rf=0.53) to obtain a pale yellow solid. The product was further purified by recrystallization from hexane/ethyl acetate to obtain a colorless solid in 615 mg (54% yield). Mp. 106–108 °C. HRMS (ESI) *m/z* calcd for $C_{27}H_{37}N_2O_2$ [**E1**+H]$^+$: 421.2855. Found: 421.2889. Elemental analysis calcd (%) for $C_{27}H_{36}N_2O_2$: C, 77.10; H, 8.63; N, 6.66. Found: C, 76.47; H, 8.78; N, 6.45.

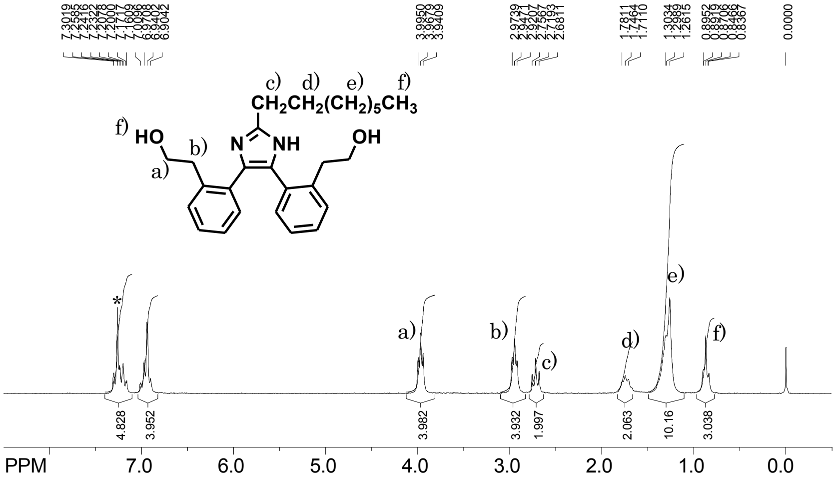


Figure S17. ^{1}H-NMR spectrum of 4,5-bis(2'-(2"-hydroxyethyl)phenyl)-2-octylimidazole (**E1**) in $CDCl_3$. δ: 7.35–7.13 (4H), 7.03–6.86 (4H), 3.97 (t, *J*=5.4 Hz, 4H), 2.95 (t, *J*=5.4 Hz, 4H), 2.72 (t, *J*=7.5 Hz, 2H), 1.75 (m, 2H), 1.26 (10H), 0.87 (br, 3H).

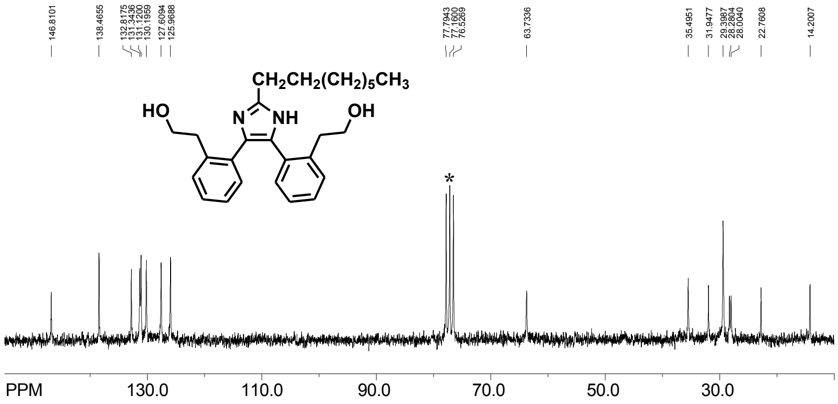


Figure S18. ^{13}C-NMR spectrum of 4,5-bis(2’-(2”-hydroxyethyl)phenyl)-2-octylimidazole (**E1**) in $CDCl_3$.

δ: 146.8, 138.5, 132.8, 131.3, 131.1, 130.2, 127.6, 126.0, 63.7, 35.5, 31.9, 29.4, 28.3, 28.0, 22.8, 14.2.

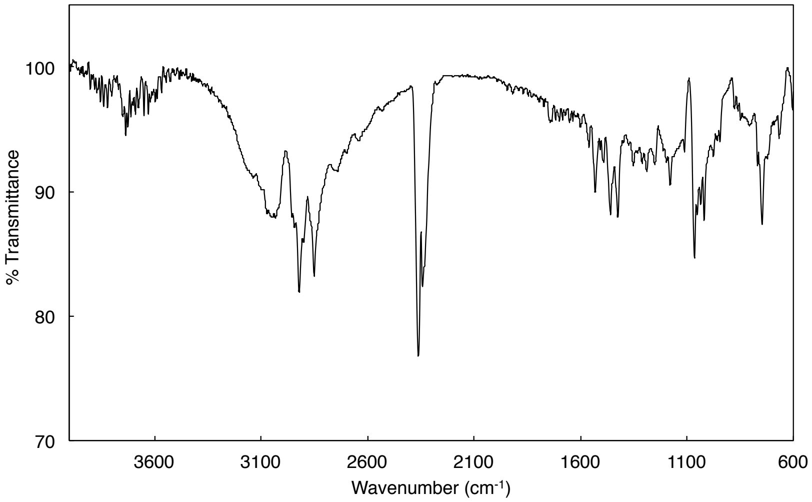


Figure S19. IR spectrum of 4,5-bis(2’-(2”-hydroxyethyl)phenyl)-2-octylimidazole (**E1**).

cm^{-1}: 3735, 3032, 2921, 2850, 1531, 1458, 1424, 1287, 1178, 1065, 1019.

3-3. 1,3-Dihydro-4,5-bis(2'-(2"-chloroethyl)phenyl)-2-octylimidazolium chloride (E2) To a flask containing **E1** (300 mg, 0.713 mmol) in AN (74 mL) was added $SOCl_2$ (10.4 mL, 142 mmol), and the mixture was stirred at room temperature overnight. The solvent and $SOCl_2$ were removed by diaphragm pump and the product was dried in vacuo to obtain a colorless solid in 365 mg (quantitative). HRMS (ESI) *m/z* calcd for $C_{27}H_{35}Cl_2N_2$ [**E2**–Cl]$^+$: 457.2177. Found: 457.2184.

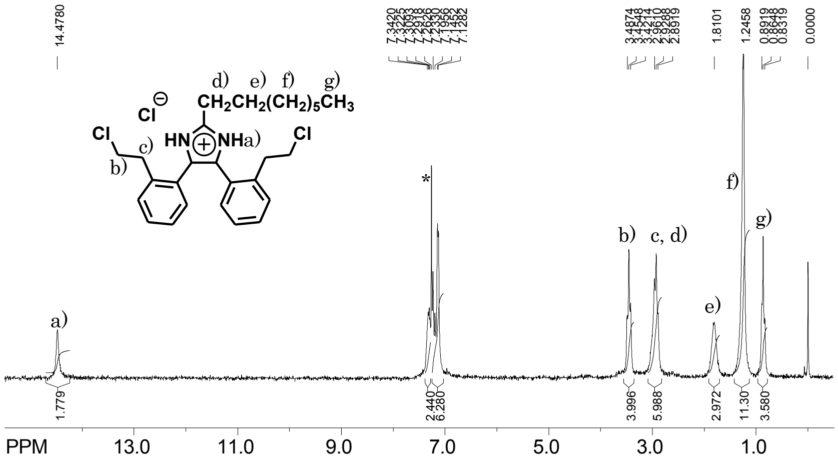


Figure S20. ^{1}H-NMR spectrum of 1,3-dihydro-4,5-bis(2'-(2"-chloroethyl)phenyl)-2-octylimidazolium chloride (**E2**) in $CDCl_3$.

δ: 14.5 (brs, 2H), 7.43–7.03 (8H), 3.45 (t, *J*=6.7 Hz, 4H), 2.93 (6H), 1.81 (m, 2H), 1.25 (10H), 0.86 (br, 3H).

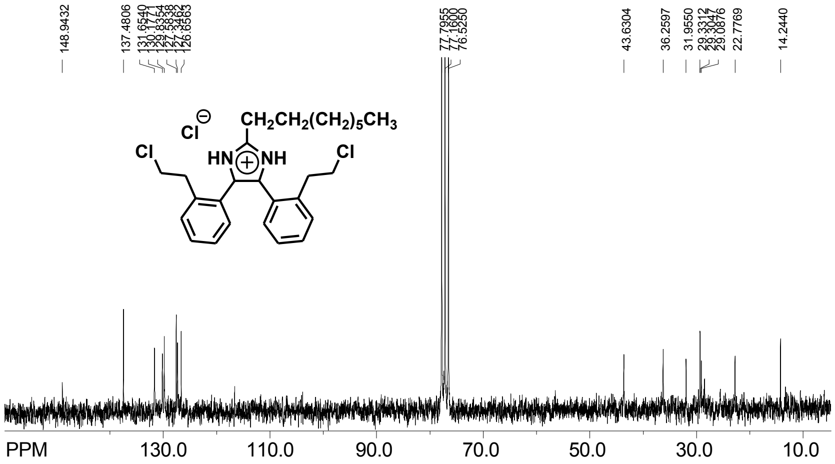


Figure S21. ^{13}C-NMR spectrum of 1,3-dihydro-4,5-bis(2'-(2"-chloroethyl)phenyl)-2-octylimidazolium chloride (**E2**).

δ: 148.9, 137.5, 131.7, 130.2, 129.8, 127.6, 127.3, 126.7, 43.6, 36.3, 32.0, 29.3, 29.3, 29.1, 22.8, 14.2.

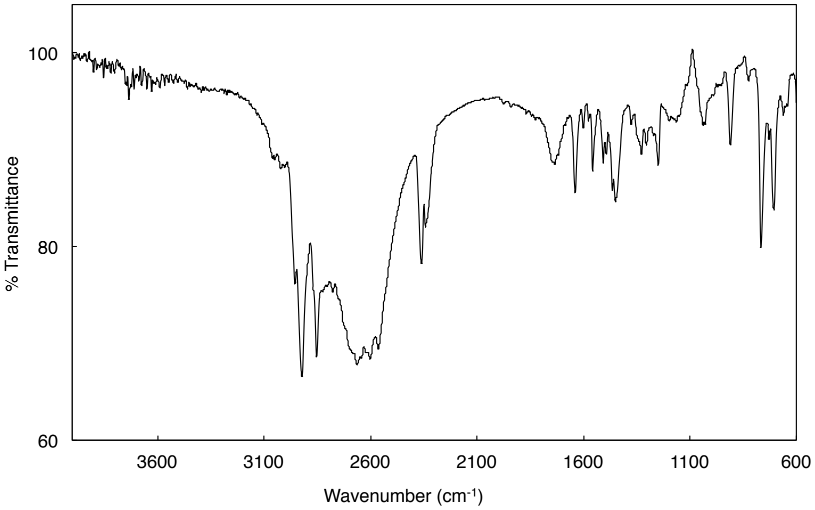


Figure S22. IR spectrum of 1,3-dihydro-4,5-bis(2'-(2"-chloroethyl)phenyl)-2-octylimidazolium chloride (**E2**).

cm^{-1}: 3735, 2922, 2852, 2662, 2602, 2562, 1733, 1638, 1557, 1507, 1449, 1327, 1248, 1038, 909, 767, 706, 661.

3-4. Ethylene-bridged imidazolium chloride (E3) To a flask containing **E2** (352 mg, 0.713 mmol) in DMF (84 mL) was added a THF solution of LiHMDS (1.42 mL, 1.42 mmol), and the mixture was stirred at room temperature overnight. After saturated aqueous NH_4Cl was added, an aqueous phase was extracted with $CHCl_3$. The combined organic phase was dried over $MgSO_4$ and the solvents were removed by rotary evaporator. The crude product was dissolved in $CHCl_3$ and poured into excess hexane to obtain a pale brown hygroscopic solid in 253 mg (84% yield). HRMS (ESI) *m*/*z* calcd for $C_{27}H_{33}N_2$ [**E3**–Cl]$^+$: 385.2638. Found: 385.2671.

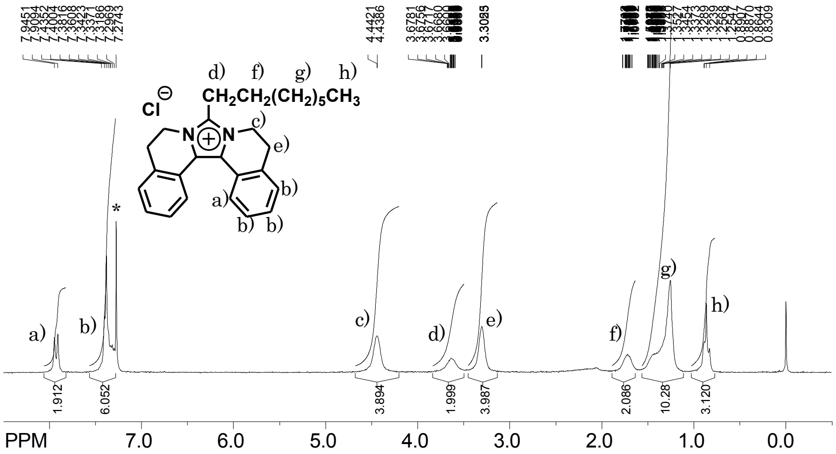


Figure S23. ^{1}H-NMR spectrum of ethylene-bridged imidazolium chloride (**E3**) in $CDCl_3$.

δ: 7.94 (d, *J*=7.1 Hz, 2H), 7.50–7.29 (6H), 4.44 (br, 4H), 3.63 (br, 2H), 3.30 (br, 4H), 1.72 (m, 2H), 1.53–1.14 (10H), 0.86 (br, 3H).

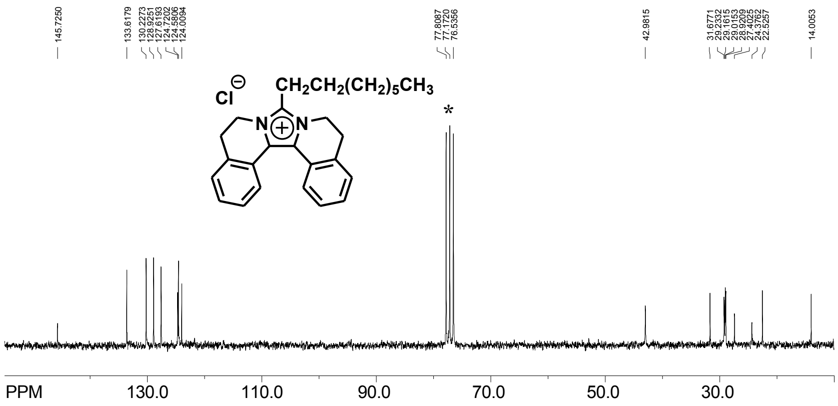


Figure S24. ^{13}C-NMR spectrum of ethylene-bridged imidazolium chloride (**E3**) in $CDCl_3$.

δ: 145.7, 133.6, 130.2, 128.9, 127.6, 124.7, 124.6,124.0, 43.0, 31.7, 29.2, 29.1, 29.0, 28.9, 27.4, 24.4, 22.5, 14.0.

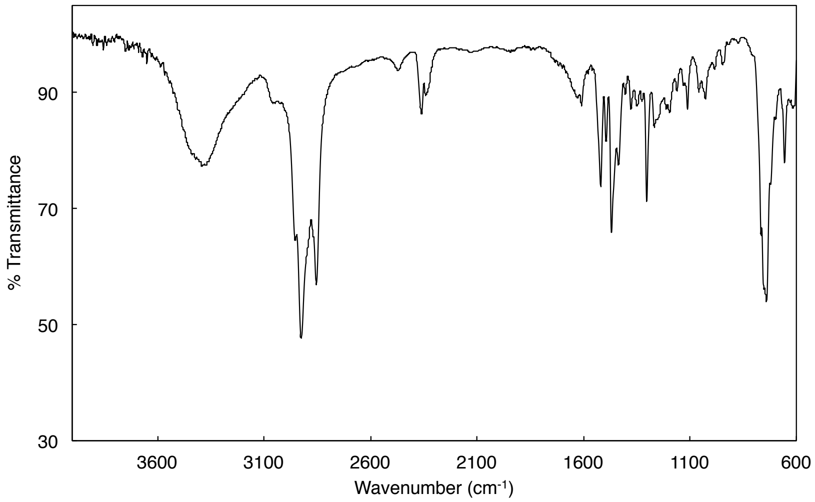


Figure S25. IR spectrum of ethylene-bridged imidazolium chloride (**E3**).

cm^{-1}: 3390, 2925, 2853, 1608, 1519, 1494, 1468, 1303, 1267, 1111, 1027, 741, 656.

3-5. Ethylene-bridged imidazolium bis(trifluoromethanesulfonyl)imide (E4) To a flask containing **E3** (36 mg, 86 μmol) in $CHCl_3$ (4.8 mL) was added an aqueous solution (6.7 mL) of LiTFSI (1.7 g, 6.1 mmol), and the mixture was vigorously stirred at room temperature overnight. After two layers were separated, an aqueous phase was extracted with $CHCl_3$. The combined organic phase was dried over $MgSO_4$ and the solvents were removed by rotary evaporator. The product was dried in vacuo to obtain a pale brown solid in 48 mg (83% yield). Mp. 95–97 °C. HRMS (ESI) *m/z* calcd for $C_{27}H_{33}N_2$ [**E4**–TFSI]$^+$: 385.2638. Found: 385.2659. HRMS (ESI) *m/z* calcd for $C_2F_6NO_4S_2$ [TFSI]$^-$: 279.9173. Found: 279.9177.

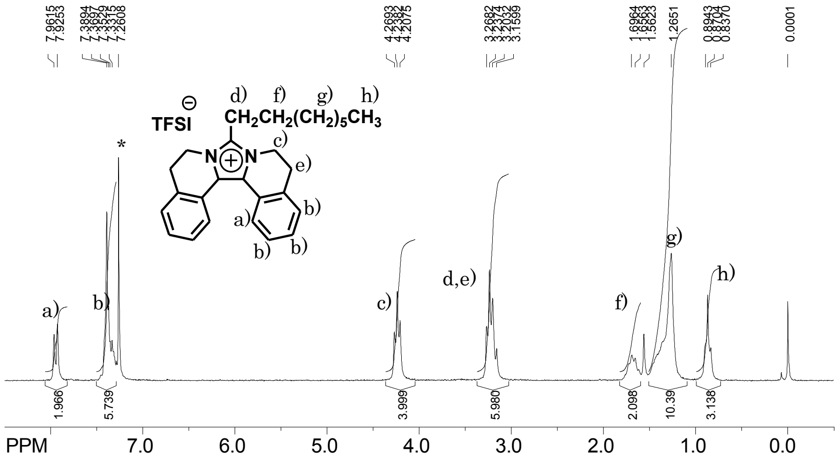


Figure S26. ^{1}H-NMR spectrum of ethylene-bridged imidazolium bis(trifluoromethanesulfonyl)imide (**E4**) in $CDCl_3$.

δ: 7.94 (d, *J*=7.1 Hz, 2H), 7.50–7.29 (6H), 4.24 (br, 4H), 3.27-3.16 (br, 6H), 1.66 (m, 2H), 1.53–1.14 (10H), 0.86 (br, 3H).

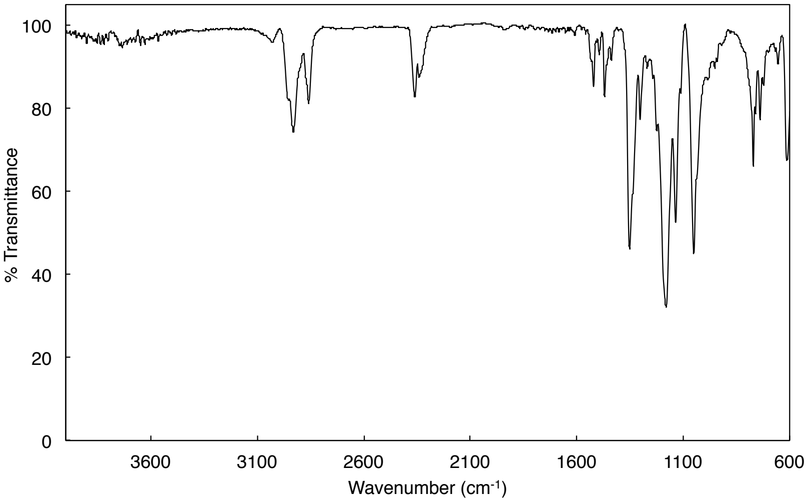


Figure S27. IR spectrum of ethylene-bridged imidazolium bis(trifluoromethanesulfonyl)imide (**E4**).

cm^{-1}: 2930, 2859, 1521, 1470, 1352, 1303, 1180, 1135, 1050, 770, 740, 655, 613.

4. Optical properties

Table S1. Optical properties of **M1**, **M2**, **M3**, **E1**, **E2**, and **E3** in DCM.

Compound	λabs/nm	λem/nm[c]	QY/%[d]
M1[a]	300	388	16
M2[a]	NA	NA	NA
M3[b]	290, 304, 319	321, 337, 356	39
E1[a]	282	379	13
E2[a]	NA	NA	NA
E3[b]	308	357	41

[a] $10\text{x}10^{-6}$ M. [b] $5 \text{ x } 10^{-6}$ M. [c] Excited at absorption maixima.
[d] Determined by using quinine sulfate (0.1 M H_2SO_4) as standard (QY=55%).

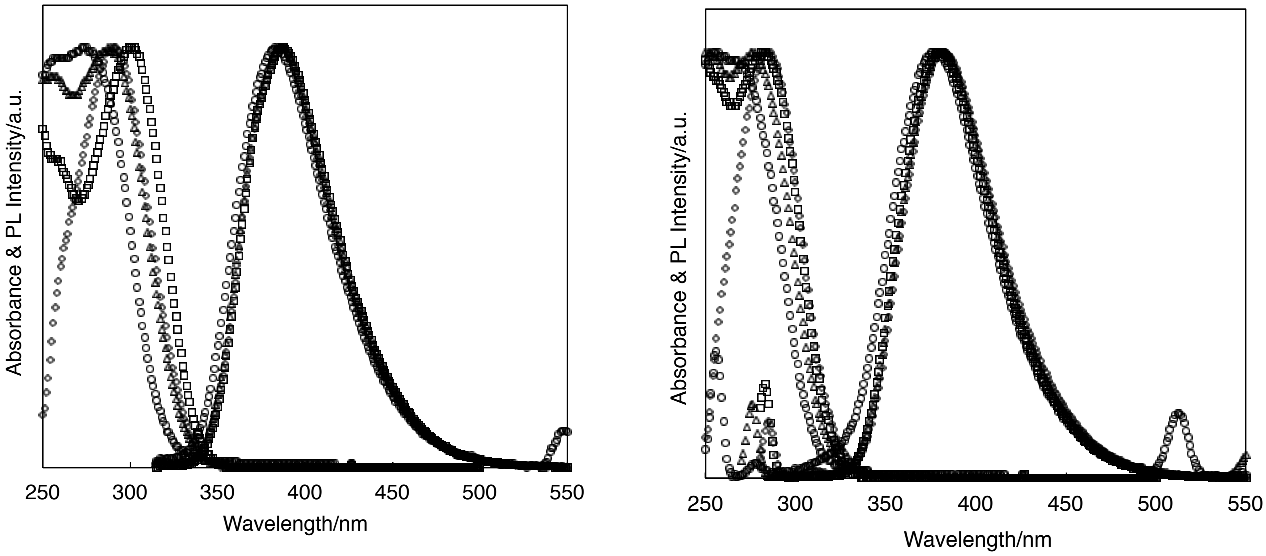


Figure S28. UV and PL spectra of **M1** (left) and **E1** (right) in MeOH (circle), AN (triangle), DCM (square), and THF (diamond).

Table S2. Optical properties of **M1** and **E1** in various solvents.[a]

Compound		MeOH	AN	DCM	THF
	λabs/nm	273	287	300	290
M1	λem/nm[b]	383	386	388	386
	QY/%[c]	3.8	12	16	10
	λabs/nm	255	275	282	284
E1	λem/nm[b]	378	380	379	382
	QY/%[c]	4.3	14	13	11

[a] 10×10^{-6} M. [b] Excited at absorption maixima.
[c] Determined by using quinine sulfate (0.1 M H_2SO_4) as standard (QY=55%).

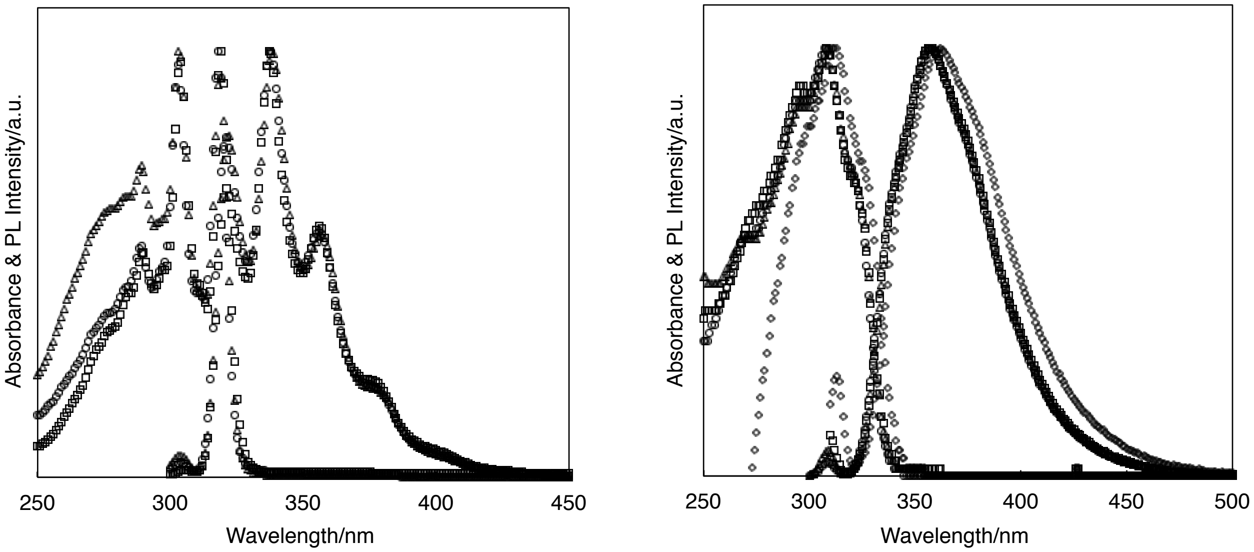


Figure S29. UV and PL spectra of **M3** (left) and **E3** (right) in MeOH (circle), AN (triangle), DCM (square), and THF (diamond).

Table S3. Optical properties of **M3** and **E3** in various solvents.

Compound		MeOH[a]	AN[a]	DCM[b]	THF[b]
M3	λabs/nm[c]	318	319	319	NA[f]
	λem/nm[d]	321	322	321	NA[f]
	QY/%[e]	62	70	39	NA[f]
E3	λabs/nm	308	308	308	312
	λem/nm	357	358	357	362
	QY/%[e]	60	57	41	12

[a] 1x10^{-6} M. [b] 5x10^{-6} M.
[c] Only the longest wavelengths are shown. [d] Only the shortest wavelengths are shown.
[e] Determined by using quinine sulfate (0.1 M H_2SO_4) as standard (QY=55%).
[f] Insoluble.

Table S4. Optical properties of **M3**, **M4**, **E3**, and **E4** in DCM.[a]

Compound	λabs/nm	λem/nm	QY/%[b]
M3	290, 304, 319	322, 339, 356	39
M4	289, 304, 319	321, 337, 356	47
E3	308	357	41
E4	308	357	42

[a] $5\text{x}10^{-6}$ M.

[b] Determined by using quinine sulfate (0.1 M H_2SO_4) as standard (QY=55%).

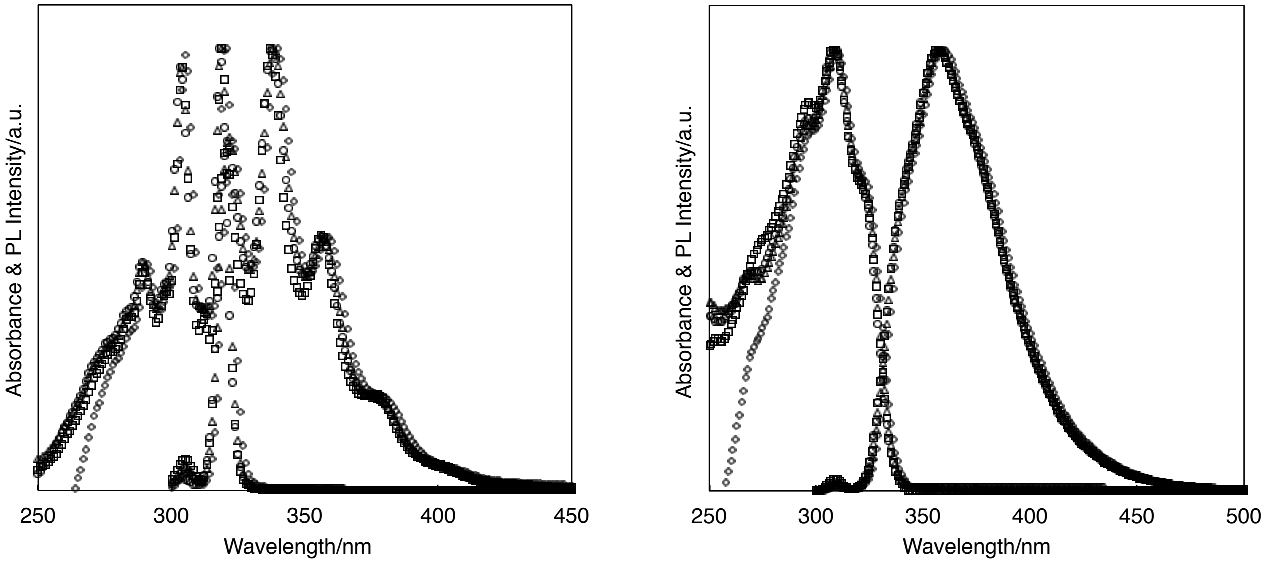


Figure S30. UV and PL spectra of **M4** (left) and **E4** (right) in MeOH (circle), AN (triangle), DCM (square), and THF (diamond).

Table S5. Optical properties of **M4** and **E4** in various solvents.

Compound		MeOH[a]	AN[a]	DCM[b]	THF[b]
M4	λabs/nm[c]	318	319	319	321
	λem/nm[d]	321	322	323	323
	QY/%[e]	49	62	47	59
E4	λabs/nm	308	308	308	310
	λem/nm	357	358	357	359
	QY/%[e]	50	51	42	52

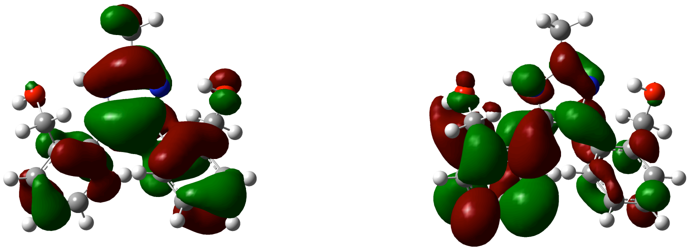
[a] $1\text{x}10^{-6}$ M. [b] $5\text{x}10^{-6}$ M.

[c] Only the longest wavelengths are shown. [d] Only the shortest wavelengths are shown.

[e] Determined by using quinine sulfate (0.1 M H_2SO_4) as standard (QY=55%).

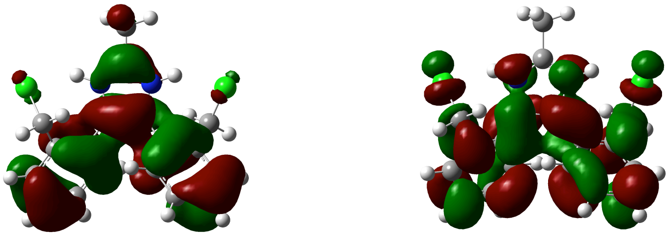
5. Theoretical calculation

M1



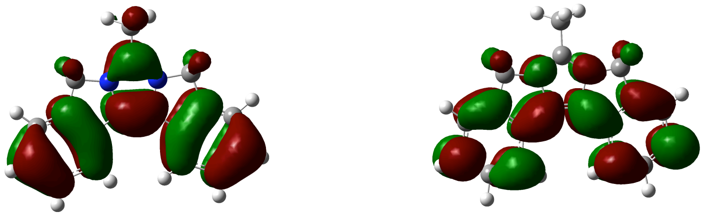
HOMO LUMO

M2



HOMO LUMO

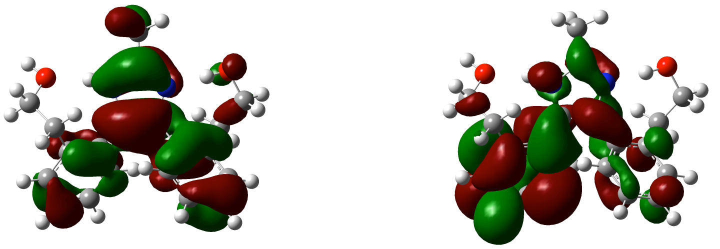
M3



HOMO LUMO

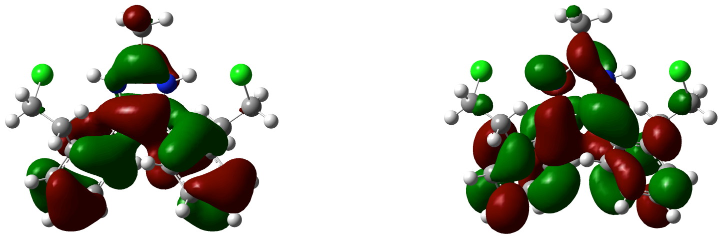
Figure S31. Frontier molecular orbitals for model of **M1**, **M2**, and **M3** without counter ion. Geometry optimization was performed using the Gaussian 09W program[1] with the DFT method employing the B3LYP hybrid functional and 6-31G* basis sets. The C_8H_{17} group was omitted and replaced with a methyl group for these calculations. The TD-DFT method was used to calculate the one electron excitation energies and oscillator strengths at the B3LYP/6-311+G** level.

E1



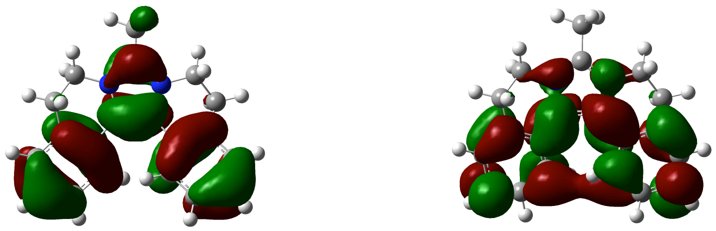
HOMO LUMO

E2



HOMO LUMO+1

E3



HOMO LUMO

Figure S32. Frontier molecular orbitals for model of **E1**, **E2**, and **E3** without counter ion. Geometry optimization was performed using the Gaussian 09W program[1] with the DFT method employing the B3LYP hybrid functional and 6-31G* basis sets. The C_8H_{17} group was omitted and replaced with a methyl group for these calculations. The TD-DFT method was used to calculate the one electron excitation energies and oscillator strengths at the B3LYP/6-311+G** level.

Table S6. Calculated absorption maxima and oscillator strengths.[a]

Compound	nm[b]	f
M1	319	0.22
M2	275	0.24
M3	295	0.66
E1	300	0.20
E2	256	0.13
E3	305	0.38

[a] Calculation was performed with DFT followed by TD-DFT methods at B3LYP/6-31G*//B3LYP/6-311+G** level of theory.

[b] Electronic transition from HOMO to LUMO except for **E2** (from HOMO to LUMO+1).

6. Reference

1. Gaussian 09W, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.