Electronic Supporting Information

Design, Synthesis, and Study of Benzobis- and Bibenz(imidazolium)-Based Fluorescent, Ionic Liquid Crystals

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General Considerations. Unless otherwise noted, all reactions were performed under ambient atmosphere. All starting materials and solvents were of reagent quality and used as received from commercial sources. 1,3,5,7-Tetra(dodecyl)benzobis(imidazolium) dibromide (**3**) as well as salts **1a** and **1b** were prepared as previously described.[1] CH_2Cl_2 was distilled from CaH_2 under N_2 atmosphere prior to use. ^1H and ^{13}C NMR spectra were recorded using a Varian Unity Plus 300 or 600 spectrometers. Chemical shifts (δ) are given in ppm and are referenced downfield from $(CH_3)_4Si$ using the residual solvent peak as an internal standard (^1H: $CDCl_3$, 7.24 ppm; DMSO-d_6, 2.49 ppm; ^{13}C: $CDCl_3$, 77.0 ppm; DMSO-d_6, 39.5 ppm). Coupling constants are expressed in hertz (Hz). ^{19}F NMR spectra were acquired on a Varian 300 MHz DirectDrive spectrometer and referenced to an external standard (^{19}F: $CFCl_3$, 0 ppm). To quantify the extent of the anion metathesis reactions that produced BF_4 or PF_6 salts, a known quantity of 1,2-dibromo-4,5-difluorobenzene ($\delta = -136.3$ ppm) was added as an internal standard. HRMS (ESI, CI) were obtained with a VG analytical ZAB2-E instrument. UV-vis spectra were recorded using a Perkin Elmer Lambda 35 spectrometer. Emission spectra were recorded using a QuantaMaster Photon Technology International fluorometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a Mettler-Toledo TGA/SDTA851e and DSC823e, respectively, under an atmosphere of nitrogen at a temperature scan rate of 10 °C min^{-1}. The decomposition temperature (T_d) was defined as the temperature at which 10% weight loss was observed. Melting points were obtained by DSC. Polarized light microscopy (PLM) studies were performed with a Leica DMRXP polarizing light microscope equipped with an Optronics digital camera at 100x magnification. Variable temperature powder X-ray diffraction (VT-PXRD) analyses were performed using an Inel CPS 120 diffraction system with monochromated Cu Kα X-ray radiation. The system is equipped with a programmable capillary furnace (accuracy ± 3 °C) for variable temperature analyses. All XRD spectra were calibrated against silver behenate (d_{100} = 58 Å) in a thin wall, boron enriched, glass capillary tube identical to that in which the samples were analyzed. This permits accuracy to within 1 Å of the observed values up to the d-value indicated for the d_{100} plane for silver behenate.

1,3,5,7-Tetra(hexadecyl)benzobis(imidazolium dibromide (2Br). A 30 mL vial was charged with **1a** (250 mg, 1.58 mmol), DMF (10 mL), sodium bicarbonate (1.30 g, 15.8 mmol), and a stir bar, and then sealed with a Teflon-lined cap. The resulting mixture was then stirred in an oil bath thermostated to 110 °C for 1 h. After cooling the mixture to ambient temperature, 1-bromohexadecane (7.70 mL, 25.3 mmol) was added. The vial was then re-sealed and stirred in an oil bath thermostated to 110 °C for 48 h. The hot reaction mixture was then filtered to remove excess sodium bicarbonate and the filtrate was added to excess diethyl ether (250 mL). The resulting precipitate was collected via filtration, triturated with acetone to remove residual DMF, and then dried under reduced pressure to afford 1.75 g (92% yield) of the desired product as an off-white powder. m.p. = 43.0 °C. ^1H NMR (400 MHz, 1:1 DMSO-d_6:$CDCl_3$ v/v): 10.21 (s, 2H), 9.05 (s, 2H) 4.61 (t, J = 13.6, 8H), 1.97 (br, 8H), 1.31-1.09 (m, 116H), 0.81 (t, J = 13.6, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-d_6:$CDCl_3$ v/v): 145.4, 130.1, 99.2, 47.4, 31.2, 29.0, 28.9, 28.8, 28.6, 28.5, 28.4, 25.8, 22.0, 13.7. HRMS m/z calcd for $C_{72}H_{136}N_4$ [M^{+2}]: 528.5383; found: 528.5377.

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[1] Boydston, A. J.; Williams, K. A.; Bielawski, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 12496.

1,3,5,7-Tetra(hexadecyl)benzobis(imidazolium) bis(tetrafluoroborate) (2BF$_4$). A 7.5 mL vial was charged with **2Br** (316 mg, 0.260 mmol), triethyloxonium tetrafluoroborate (117 mg, 1.04 mmol), dry CH_2Cl_2 (5 mL), and a stir bar then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added. The reaction mixture was then stirred for an additional hour. The resulting solution was poured into excess diethyl ether (50 mL) which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 273 mg (85% yield) of the desired product as a white powder. m.p. = 70.5 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 10.13 (s, 2H), 8.97 (s, 2H) 4.58 (br, 8H), 1.96 (br, 8H) 1.30-1.18 (m, 104H), 0.81 (br, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 145.4, 130.1, 99.2, 47.3, 31.2, 29.0, 28.9, 28.8, 28.6, 28.5. 28.4, 25.7, 22.0, 13.7. ^{19}F NMR (282 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): –147.8, –150.3 ppm. HRMS m/z calcd for $C_{72}H_{136}N_4$ [M^{+2}]: 528.5383; found: 528.5377.

1,3,5,7-Tetra(hexadecyl)benzobis(imidazolium) bis(methylsulfate) (2MeSO$_4$). A 7.5 mL vial was charged with **2Br** (586 mg, 0.480 mmol), dimethyl sulfate (0.10 mL, 1.1 mmol), dry CH_2Cl_2 (5 mL), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture at ambient temperature for 12 h, it was poured into excess diethyl ether (50 mL), which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 520 mg (84% yield) of the desired product as a tan powder. m.p. = 91.5 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 10.11 (s, 2H) 8.93 (s, 2H), 4.59 (t, *J* = 14 Hz, 8H), 3.18 (s, 6H), 1.96 (t, *J* = 13.2 Hz, 8H), 1.30-1.11 (m, 104H), 0.81 (t, *J* = 14.6 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 145.5, 130.1, 99.0, 56.2, 47.3, 31.2, 29.0, 28.9, 28.8, 28.6, 28.5, 28.4, 25.8, 22.0, 13.7. HRMS m/z calcd for $C_{72}H_{136}N_4$ [M^{+2}]: 528.5383; found: 528.5377.

1,3,5,7-Tetra(hexadecyl)benzobis(imidazolium) bis(hexafluorophosphate) (2PF$_6$). A 7.5 mL vial was charged with **1Br** (400 mg, 0.31 mmol), triethyloxonium hexafluorophosphate (240 mg, 0.97 mmol), dry CH_2Cl_2 (5 mL), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added. The reaction mixture then stirred for an additional hour. The resulting solution was poured into excess diethyl ether (50 mL) which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 429 mg (99% yield) of the desired product as a white powder. m.p. = 32.5 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$): 10.23 (s, 2H) 9.06 (s, 2H), 4.61 (br, 8H), 1.98 (br, 8H), 1.32-1.19 (m, 104 H), 0.83 (t, *J* = 13.6 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$): 145.3, 130.1, 99.2, 47.4, 31.2, 29.0, 28.9, 28.8, 28.6, 25.5, 28.4, 25.8, 22.0, 13.6. ^{19}F NMR (282 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): –149.8 ppm. ^{31}P NMR (121 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): –144.9 (sept, $J_{P\text{-}F}$ = 706 Hz) ppm. HRMS m/z calcd for $C_{72}H_{136}N_4$ [M^{+2}]: 528.5384; found: 528.5377.

1,3,5,7-Tetra(octyl)benzobis(imidazolium) bis(tetrafluoroborate) (3). A 30 mL vial was charged with **1a** (250 mg, 1.58 mmol), CH_3CN (10 mL), sodium bicarbonate (1.3 g, 15.8 mmol), potassium iodide (2.6 g, 16 mmol), 1-bromooctane (4.4 mL, 25.3 mmol) and a stir bar, and then sealed with a Teflon-lined cap. The resulting mixture was stirred in an oil bath thermostated to 80 °C for 96 h. After cooling to ambient temperature, the residual solvent was removed under reduced pressure. The residue was triturated with hexanes, collected via filtration and dried under high vacuum to afford crude 1,3,5,7-tetra(octyl)benzobisimidazolium dibromide. A separate 7.5 mL vial was charged with the crude salt, dry CH_2Cl_2 (5 mL), triethyloxonium tetrafluoroborate (531 mg, 4.74 mmol), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, the solvent was removed under reduced pressure. The residue was triturated with hexanes and then dried under reduced pressure to afford 1.07 g (87% yield) of the desired product as a tan powder. m.p. = 86.3 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-d_6:$CDCl_3$ v/v): 10.02 (s, 2H), 8.87 (s, 2H), 4.55 (br, 8H), 1.96 (br, 8H), 1.32-1.21 (m, 40H), 0.82 (t, J = 13.2 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-d_6:$CDCl_3$ v/v): 145.3, 130.2, 98.6, 47.3, 31.1, 28.5, 28.4, 28.3, 25.8, 22.0, 13.7. ^{19}F NMR (282 MHz, 1:1 DMSO-d_6:$CDCl_3$ v/v): –147.5, –150.0 ppm. HRMS m/z calcd for $C_{40}H_{72}N_4$ [M^{+2}] 304.2879; found 304.2873.

1,3,5,7-Tetra(decyl)benzobis(imidazolium) bis(tetrafluoroborate) (4). A 30 mL vial was charged with **1a** (250 mg, 1.58 mmol), CH_3CN (10 mL), sodium bicarbonate (1.3 g, 15.8 mmol), potassium iodide (2.6 g, 15.8 mmol), 1-bromodecane (5.3 mL, 25.3 mmol) and a stir bar, and then sealed with a Teflon-lined cap. The resulting mixture was stirred in an oil bath thermostated to 80 °C for 96 h. After cooling to ambient temperature, the residual solvent was removed under reduced pressure. The residue was triturated with hexanes, collected via filtration, and dried under high vacuum to afford crude 1,3,5,7-tetra(decyl)benzobisimidazolium dibromide. A separate 7.5 mL vial was charged with the crude salt, dry CH_2Cl_2 (5 mL), triethyloxonium tetrafluoroborate (531 mg, 4.74 mmol), dry CH_2Cl_2 (5 mL), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, the solvent was removed under reduced pressure. The residue was triturated with hexanes and then dried under reduced pressure to afford 1.41 g (97% yield) of the desired product as a tan powder. m.p. = 87.3 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-d_6:$CDCl_3$ v/v): 10.04 (s, 2H), 8.88 (s, 2H), 4.55 (t, J = 14 Hz, 8H), 1.96 (t, J = 12.8 Hz, 8H), 1.32-1.20 (m, 56H), 0.82 (t, J = 13.6 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-d_6:$CDCl_3$ v/v): 145.3, 130.1, 98.8, 47.3, 31.2, 28.9, 28.8, 28.6, 28.5, 28.3, 25.8, 22.0, 13.7. ^{19}F NMR (282 MHz, 1:1 DMSO-d_6:$CDCl_3$ v/v): –147.6, –150.1 ppm. HRMS m/z calcd for $C_{48}H_{88}N_4$ [M^{+2}] 360.3494; found 360.3499.

1,3,5,7-Tetra(dodecyl)benzobis(imidazolium) bis(tetrafluoroborate) (5). A 30 mL vial was charged with **1a** (100 mg, 0.63 mmol), CH_3CN (7 mL), sodium bicarbonate (531 mg, 6.3 mmol), 1-bromododecane (0.9 mL, 3.7 mmol) and a stir bar, and then sealed with a Teflon-lined cap. The resulting mixture was stirred in an oil bath thermostated to 80° C for 72 h. After cooling to ambient temperature, the residual solvent was removed under reduced pressure. The residue was triturated with hexanes, collected via filtration, and dried under high vacuum to afford crude 1,3,5,7-tetra(dodecyl)benzobisimidazolium dibromide. A separate 7.5 mL vial was charged with the crude salt, dry CH_2Cl_2 (5 mL), triethyloxonium tetrafluoroborate (212 mg, 1.9 mmol), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, the solvent was removed under reduced pressure. The residue was triturated with hexanes and then dried under reduced pressure to afford 667 mg (98% yield) of the desired product as a white powder. m.p. = 84.6 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): 10.43 (s, 2H), 9.28 (s, 2H), 4.66 (t, *J* = 14 Hz, 8H), 1.95 (br, 8H), 1.27-1.15 (m, 72H), 0.78 (t, *J* = 13.6 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$): 145.4, 130.1, 99.6, 47.5, 34.2, 31.3, 29.0, 28.98, 28.9, 28.7, 28.6, 25.8, 22.1, 13.8. ^{19}F NMR (282 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): –148.0, –150.5 ppm. HRMS m/z calcd for $C_{48}H_{88}N_4$ [M^{+2}] 360.3494; found 360.3499.

1,3,5,7-Tetra(tetradecyl)benzobis(imidazolium) bis(tetrafluoroborate) (6). A 30 mL vial was charged with **1a** (350 mg, 2.2 mmol), DMF (10 mL), sodium bicarbonate (1.9 g, 22.1 mmol), and a stir bar, and then sealed with a Teflon-lined cap. The resulting mixture was then stirred in an oil bath thermostated to 110 °C for 1 h. After cooling the mixture to ambient temperature, 1-bromotetradecane (5.3 mL, 17.7 mmol) was added. The vial was then re-sealed and stirred in an oil bath thermostated to 110 °C for an additional 48 h. The hot reaction mixture was then filtered to remove excess sodium bicarbonate, and the filtrate was added to excess diethyl ether (250 mL). The solids which precipitated were collected via filtration, triturated with acetone to remove residual DMF, and dried under high vacuum to afford crude 1,3,5,7-(tetradecyl)benzobisimidazolium dibromide. A separate 7.5 mL vial was charged with the crude salt, dry CH_2Cl_2 (5 mL), triethyloxonium tetrafluoroborate (740 mg, 6.7 mmol), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added and the mixture stirred an additional 1 h. The mixture was then poured into excess diethyl ether which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 1.98 g (82% yield) of the desired product as a white powder. m.p. = 32.2 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): 10.46 (s 2H), 9.22 (s, 2H) 4.67 (t, *J* = 14 Hz, 8H), 1.98 (br, 8H) 1.29-1.16 (m, 88H), 0.79 (t, *J* = 13.6 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): 145.3, 130.1, 99.5, 47.5, 31.2, 285.7, 22.0, 13.7. ^{19}F NMR (282 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): –147.7, –150.2 ppm. HRMS m/z calcd for $C_{64}H_{120}N_4$ [M^{+2}] 472.4757; found 472.4751.

1,3,5,7-Tetra(pentadecyl)benzobis(imidazolium) bis(tetrafluoroborate) (7). A 30 mL vial was charged with **1a** (200 mg, 1.2 mmol), DMF (10 mL), sodium bicarbonate (1 g, 12.6 mmol), and a stir bar, and then sealed with a Teflon-lined cap. The resulting mixture was then stirred in an oil bath thermostated to 110 °C for 1 h. After cooling the mixture to ambient temperature, 1-bromopentadecane (3 mL, 10 mmol) was added. The vial was then re-sealed and stirred in an oil bath thermostated to 110 °C for an additional 48 h. The hot reaction mixture was then filtered to remove excess sodium bicarbonate, and the filtrate was added to excess diethyl ether (250 mL). The solids which precipitated were collected via filtration, triturated with acetone to remove residual DMF, and dried under high vacuum to afford crude 1,3,5,7-tetra(pentadecyl) benzobisimidazolium dibromide. A separate 7.5 mL vial was charged with the crude salt, dry CH_2Cl_2 (5 mL), triethyloxonium tetrafluoroborate (740 mg, 6.7 mmol), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added and the mixture stirred an additional 1 h. The mixture was then poured into excess diethyl ether which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 1.5 g (99% yield) of the desired product as a white powder. m.p. = 35.4 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-d_6:CDCl$_3$ v/v): 10.36 (s, 2H), 9.13 (s, 2H), 4.64 (br, 8H), 1.99 (br, 8H), 1.30-1.17 (m, 96H) , 0.80 (t, J = 13.6 Hz, 12H. ^{13}C NMR (125 MHz, 1:1 DMSO-d_6:CDCl$_3$ v/v): 145.1, 130.1, 99.5, 47.6, 29.0, 28.9. 28.8, 28.6, 28.5, 25.8, 22.0, 13.6. ^{19}F NMR (282 MHz, 1:1 DMSO-d_6:CDCl$_3$ v/v): –148.1, –150.6 ppm. HRMS m/z calcd for $C_{68}H_{128}N_4$ [M^{+2}] 500.5069; found 500.5064.

1,3,5,7-Tetra(octadecyl)benzobisimidazolium bis(tetrafluoroborate) (8). A 30 mL vial was charged with **1a** (200 mg, 1.2 mmol), DMF (10 mL), sodium bicarbonate (1.06 g, 12.6 mmol), and a stir bar, and then sealed with a Teflon-lined cap. The resulting mixture was then stirred in an oil bath thermostated to 110 °C for 1 h. After cooling the mixture to ambient temperature, 1-bromooctadectane (3.5 mL, 10.1 mmol) was added. The vial was then re-sealed and stirred in an oil bath thermostated to 110 °C for an additional 48 h. The hot reaction mixture was then filtered to remove excess sodium bicarbonate, and the filtrate was added to excess diethyl ether (250 mL). The solids which precipitated were collected via filtration, triturated with acetone to remove residual DMF, and dried under high vacuum to afford crude 1,3,5,7-tetra(octadecyl) benzobisimidazolium dibromide. A separate 7.5 mL vial was charged with the crude salt, dry CH_2Cl_2 (5 mL), triethyloxonium tetrafluoroborate (404 mg, 3.6 mmol), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added and the mixture stirred an additional 1 h. The mixture was then poured into excess diethyl ether which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 1.3 g (82% yield) of the desired product as a white powder. m.p. = 30.2 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-d_6:CDCl$_3$ v/v): 10.08 (s, 2H), 8.91 (s, 2H), 4.56 (t, J = 14 Hz, 8H), 1.96 (br, 8H), 1.30-1.19 (m, 120H) 0.82 (t, J = 13.6 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-d_6:CDCl$_3$): 145.4, 130.1, 98.9, 47.3, 31.2, 29.0, 28.9, 28.8, 28.6, 28.4, 24.3, 25.7, 22.0, 13.7. ^{19}F NMR (282 MHz, 1:1 DMSO-d_6:CDCl$_3$ v/v): –147.9, –150.4 ppm. HRMS m/z calcd for $C_{80}H_{152}N_4$ [M^{+2}] 584.6009; found 584.6003.

1,1′,3,3′-Tetra(hexadecyl)-5,5′-bibenzimidazolium dibromide (9Br). A 30 mL vial was charged with **1b**, (200 mg, 0.85 mmol), DMF (10 mL), sodium bicarbonate (717 mg, 8.5 mmol), and a stir bar, and then sealed with a Teflon-lined cap. The resulting mixture was then stirred in an oil bath thermostated to 110 °C for 1 h. After cooling the mixture to ambient temperature, 1-bromohexadecane (4.2 mL, 13.7 mmol) was added. The vial was then re-sealed and stirred in an oil bath thermostated to 110 °C for an additional 48 h. The hot reaction mixture was then filtered and the filtrate was poured into excess diethyl ether (250 mL), causing solids to precipitate. The resulting precipitate was collected via filtration, triturated with acetone to remove residual DMF, and then dried under reduced pressure to afford 990 mg (90% yield) of the desired product as an off-white powder. m.p. = 28.4 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-d_6:CDCl$_3$ v/v): 10.23 (s, 2H), 8.68 (s, 2H), 8.01 (br, 4H), 4.71 (br, 4H), 4.53 (br, 4H), 1.94 (br, 8H), 1.31-1.13 (m, 104H), 0.79 (t, J = 14 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-d_6:CDCl$_3$ v/v): 142.2, 142.1, 137.9, 131.8, 130.6, 126.4, 113.6, 112.9, 47.2, 47.0, 31.2, 28.97, 28.95, 29.93, 28.86, 28.83, 28.79, 28.73, 28.6, 28.5, 28.4, 25.8, 22.0, 13.7. HRMS m/z calcd for $C_{78}H_{140}N_4$ [M^{+2}] 566.5541; found 566.5534.

1,1′,3,3′-Tetra(hexadecyl)-5,5′-bibenzimidazolium bis(tetrafluoroborate) (9BF$_4$). A 7.5 mL vial was charged with **9Br** (200 mg, 0.12 mmol), triethyloxonium tetrafluoroborate (70 mg, 0.62 mmol), dry CH_2Cl_2 (5 mL), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added. The reaction mixture then stirred for an additional hour. The resulting solution was poured into excess diethyl ether (50 mL) which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 183 mg (90% yield) of the desired product as a white powder. m.p. = 84.5 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 10.06 (s, 2H), 8.56 (s, 2H), 8.0 (br, 4H), 4.66 (br, 4H), 4.51 (br, 4H), 1.94 (br, 8H), 1.29–1.16 (m, 104H), 0.79 (t, *J* = 14 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 142.2, 142.1, 137.9, 131.8, 130.6, 126.4, 113.6, 112.9, 47.2, 47.0, 31.2, 28.97, 28.95, 29.93, 28.86, 28.83, 28.79, 28.73, 28.6, 28.5, 28.4, 25.8, 22.0, 13.7. ^{19}F NMR (282 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): –148.2, –148.3 ppm. HRMS m/z calcd for $C_{78}H_{140}N_4$ [M^{+2}] 566.5544; found 566.5534.

1,1′,3,3′-Tetra(hexadecyl)-5,5′-bibenzimidazolium bis(methyl sulfate) (9MeSO$_4$). A 7.5 mL vial was charged with **9Br** (300 mg, 0.23), dimethyl sulfate (0.1 mL, 1.1 mmol), dry CH_2Cl_2 (5 mL), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added. The reaction mixture then stirred for an additional hour. The resulting solution was poured into excess diethyl ether (50 mL) which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 280 mg (89% yield) of the desired product as a white powder. m.p. = 90.8 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 9.88 (s, 2H), 8.41 (s, 2H), 8.05 (br, 4H), 4.58 (br, 4H), 4.52 (br, 4H), 3.97 (s, 6H), 1.94 (br, 8H), 1.28-1.21 (m, 104H), 0.82 (br, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 142.5, 137.9, 131.7, 130.7, 126.4, 113.8, 112.2, 52.9, 46.9, 46.8, 31.2, 29.0, 28.9, 28.87, 28.83, 28.8, 28.7, 28.6, 28.5, 28.43, 28.4, 25.7, 25.6, 22.0, 21.7, 13.7. HRMS m/z calcd for $C_{78}H_{140}N_4$ [M^{+2}] 566.5538; found 566.5534.

1,1′,3,3′-Tetra(hexadecyl)-5,5′-bibenzimidazolium bis(hexafluorophosphate) (9PF$_6$). A 7.5 mL vial was charged with **9Br** (300 mg, 0.23 mmol), triethyloxonium hexafluorophosphate (173 mg, 0.70 mmol), dry CH_2Cl_2 (5 mL), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added. The reaction mixture was then stirred for an additional hour. The resulting solution was poured into excess diethyl ether (50 mL) which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 309 mg (95% yield) of the desired product as a white powder. m.p. = 31.1 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 10.07 (s, 2H), 8.60 (s, 2H), 8.04 (t, *J* = 4.8 Hz, 4H), 4.67 (t, *J* = 14 Hz, 4H), 4.52 (t, *J* = 13.6 Hz, 4H), 1.95 (q, *J* = 21.6 Hz, 8H), 1.30-1.16 (m, 104H), 0.80 (t, *J* = 13.6 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 142.2, 142.1, 137.9, 131.8, 130.6, 126.4, 113.6, 112.9, 47.2, 47.0, 31.2, 28.97, 28.95, 29.93, 28.86, 28.83, 28.79, 28.73, 28.6, 28.5, 28.4, 25.8, 22.0, 13.7. ^{19}F NMR (282 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): –149.9 ppm. ^{31}P NMR (121 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): –145.3 (sept, $J_{P\text{-}F}$ = 704 Hz)ppm. HRMS m/z calcd for $C_{78}H_{140}N_4$ [M^{+2}] 566.5544; found 566.5539.

1,1′,3,3′-Tetra(octyl)-5,5′-bibenzimidazolium bis(tetrafluoroborate) (10). A 30 mL vial was charged with **1b** (200 mg, 0.85 mmol), CH_3CN (8 mL), sodium bicarbonate (717 mg, 8.5 mmol), 1-bromooctane (2.3 mL, 13.7 mmol), and a stir bar, and then sealed with a Teflon-lined cap. The resulting mixture was then stirred in an oil bath thermostated to 80 °C for 72 h. The hot reaction mixture was filtered to remove excess sodium bicarbonate, and the filtrate was added to excess diethyl ether (250 mL). The solids which precipitated were collected via filtration, triturated with acetone to remove residual DMF, and dried under high vacuum to afford crude 1,1′,3,3′-tetra(octyl)-5,5′-bibenzimidazolium dibromide. A separate 7.5 mL vial was charged with the crude salt, dry CH_2Cl_2 (5 mL), triethyloxonium tetrafluoroborate (286 mg, 2.6 mmol), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added. The reaction mixture then stirred for an additional hour. The resulting solution was poured into excess diethyl ether (50 mL) which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 722 mg (99% yield) of the desired product as an off-white powder. m.p. = 218.8 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): 10.23 (s, 2H), 8.67 (s, 2H), 8.01 (br, 4H), 4.71 (br, 4H), 4.53 (br, 4H) 1.95 (br, 8H), 1.33-1.16 (m, 40H), .078 (t, *J* = 17 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$): 142.2, 137.9, 131.8, 130.6, 126.4, 113.6, 112.8, 47.2, 47.0, 31.0, 28.8, 28.7, 28.41, 28.4, 28.3, 25.8, 22.0, 13.6. ^{19}F NMR (282 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): –145.8, –148.3 ppm. HRMS m/z calcd for $C_{46}H_{76}N_4$ [M^{+2}] 342.3034; found 342.3030.

1,1′,3,3′-Tetra(decyl)-5,5′-bibenzimidazolium bis(tetrafluoroborate) (11). A 30 mL vial was charged with **1b** (100 mg, 0.43 mmol), CH_3CN (6 mL), sodium bicarbonate (358 mg, 4.3 mmol), 1-bromodecane (0.5 mL, 2.1 mmol) and a stir bar, and then sealed with a Teflon-lined cap. The hot reaction mixture was then filtered to remove excess sodium bicarbonate, and the filtrate was added to excess diethyl ether (250 mL). The solids which precipitated were collected via filtration, triturated with acetone to remove residual DMF, and dried under high vacuum to afford crude 1,1′,3,3′-tetra(decyl)-5,5′-bibenzimidazolium dibromide. A separate 7.5 mL vial was charged with the crude salt, dry CH_2Cl_2 (5 mL), triethyloxonium tetrafluoroborate (144 mg, 1.3 mmol), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added. The reaction mixture then stirred for an additional hour. The resulting solution was poured into excess diethyl ether (50 mL) which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 413 mg (99% yield) of the desired product as an off-white powder. m.p. = 93.4 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): 9.84 (s, 2H), 8.36 (s, 2H), 8.05 (br, 4H) 4.54-4.50 (m, 8H), 1.94 (br, 8H), 1.32-1.21 (m, 56H), 0.81 (t, *J* = 12 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): 142.5, 137.9, 131.7, 130.7, 126.4, 113.9, 112.1, 48.6, 46.7, 32.0, 29.6, 29.4, 29.2, 26.6, 22.8, 14.5. ^{19}F NMR (282 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): –146.2, –148.7 ppm. HRMS m/z calcd for $C_{54}H_{92}N_4$ [M^{+2}] 398.3658; found 398.36555.

1,1′,3,3′-Tetra(dodecyl)-5,5′-bibenzimidazolium bis(tetrafluoroborate) (12). A 30 mL vial was charged with **1b** (200 mg, 0.85 mmol), CH_3CN (8 mL), sodium bicarbonate (717 mg, 8.5 mmol), 1-bromododecane (3.2 mL, 13.7 mmol) and a stir bar, and then sealed with a Teflon-lined cap. The resulting reaction mixture was stirred in an oil bath thermostated to 80 °C for 72 h. The hot reaction mixture was then filtered to remove excess sodium bicarbonate, and the filtrate was added to excess diethyl ether (250 mL). The solids which precipitated were collected via filtration, triturated with acetone to remove residual DMF, and dried under high vacuum to afford crude 1,1′,3,3′-tetra(dodecyl)-5,5′-bibenzimidazolium dibromide. A separate 7.5 mL vial was charged with the crude salt, dry CH_2Cl_2 (5 mL), triethyloxonium tetrafluoroborate (286 mg, 2.6 mmol), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added. The reaction mixture then stirred for an additional hour. The resulting solution was then poured into excess diethyl ether (50 mL) which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 900 mg (98% yield) of the desired product as a white powder. m.p. = 89.5 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 9.84 (s, 2H), 8.37 (s, 8H), 8.09 (t, *J* = 21.6 Hz, 4H), 4.53 (q, *J* = 30.4 Hz, 8H), 1.94 (br, 8H), 1.32-1.18 (m, 72H) 0.85-0.80 (m, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 142.5, 137.9, 131.7, 130.7, 126.4, 113.9, 112.1, 46.9, 31.2, 30.9, 28.92, 28.9, 28.85, 28.8, 28.6, 28.4, 25.7, 22.0, 13.7. ^{19}F NMR (282 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): $\delta = -146.4, -148.9$ ppm. HRMS m/z calcd for $C_{62}H_{108}N_4$ [M^{+2}] 454.4284; found 454.4282.

1,1′,3,3′-Tetra(tetradecyl)-5,5′-bibenzimidazolium bis(tetrafluoroborate) (13). A 30 mL vial was charged with **1b** (200 mg, 0.85 mmol), DMF (8 mL), sodium bicarbonate (717 mg, 8.5 mmol), and a stir bar, and then sealed with a Teflon-lined cap. The resulting mixture was then stirred in an oil bath thermostated to 110 °C for 1 h. After cooling the mixture to ambient temperature, 1-bromotetradecane (4.1 mL, 13.7 mmol) was added. The vial was then re-sealed and stirred in an oil bath thermostated to 110 °C for an additional 48 h. The hot reaction mixture was filtered to remove excess sodium bicarbonate, and the filtrate was added to excess diethyl ether (250 mL). The solids which precipitated were collected via filtration, triturated with acetone to remove residual DMF, and dried under high vacuum to afford crude 1,1′,3,3′-tetra(tetradecyl)-5,5′-bibenzimidazolium dibromide. A separate 7.5 mL vial was charged with the crude salt, dry CH_2Cl_2 (5 mL), triethyloxonium tetrafluoroborate (286 mg, 2.6 mmol), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added. The reaction mixture then stirred for an additional hour. The resulting solution was poured into excess diethyl ether (50 mL) which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 938 g (89% yield) of the desired product as a white powder. m.p. = 73.0 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 10.06 (s, 2H), 8.57 (s, 2H), 8.00 (br, 4H), 4.66 (br, 4H), 4.51 (br, 4H), 1.94 (q, *J* = 14.4 Hz, 8H), 1.30-1.15 (m, 88H), 0.79 (t, *J* = 13.6 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*$_6$:$CDCl_3$ v/v): 142.2, 138.0, 131.8, 130.7, 126.5, 113.7, 112.6, 47.1, 47.0, 31.3, 29.02, 29.0, 28.98, 28.94, 28.92, 28.87, 28.83, 28.76, 28.68, 28.51, 28.45, 25.8, 22.0, 13.7. ^{19}F NMR (282

MHz, 1:1 DMSO-d_6:CDCl$_3$ v/v): –146.2, –148.7 ppm. HRMS m/z calcd for $C_{70}H_{124}N_4$ [M^{+2}] 510.4914; found 510.4908.

1,1′,3,3′-Tetra(pentadecyl)-5,5′-bibenzimidazolium bis(tetrafluoroborate) (14). A 30 mL vial was charged with **1b** (200 mg, 0.85 mmol), DMF (8 mL), sodium bicarbonate (717 mg, 8.5 mmol), and a stir bar, and then sealed with a Teflon-lined cap. The resulting mixture was then stirred in an oil bath thermostated to 110 °C for 1 h. After cooling the mixture to ambient temperature, 1-bromopentadecane (2 mL, 6.8 mmol) was added. The vial was then re-sealed and stirred in an oil bath thermostated to 110 °C for an additional 48 h. The hot reaction mixture was then filtered to remove excess sodium bicarbonate, and the filtrate was added to excess diethyl ether (250 mL). The solids which precipitated were collected via filtration, triturated with acetone to remove residual DMF, and dried under high vacuum to afford crude 1,1′,3,3′-tetra(pentadecyl)-5,5′-bibenzimidazolium dibromide. A separate 7.5 mL vial was charged with the crude salt, dry CH_2Cl_2 (5 mL), triethyloxonium tetrafluoroborate (286 mg, 2.6 mmol), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added. The reaction mixture then stirred for an additional hour. The resulting solution was poured into excess diethyl ether (50 mL) which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 952 mg (86% yield) of the desired product as a white powder. m.p. = 85.6 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-d_6:CDCl$_3$ v/v): 10.01 (s, 2H), 8.55 (s, 2H), 7.99 (br, 3H), 4.65 (t, *J* = 14 Hz, 4H), 4.50 (t, *J* = 14 Hz, 4H), 1.94 (q, *J* = Hz, 8H), 1.31-1.16 (m, 96H), 0.80 (t, *J* = 14 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*6:CDCl$_3$): 142.2, 142.1, 137.9, 131.8, 130.6, 126.4, 113.6, 112.9, 47.2, 47.0, 31.2, 28.97, 28.95, 29.93, 28.86, 28.83, 28.79, 28.73, 28.6, 28.5, 28.4, 25.8, 22.0, 13.7. ^{19}F NMR (282 MHz, 1:1 DMSO-d_6:CDCl$_3$ v/v): –145.8, –148.3 ppm. HRMS m/z calcd for $C_{74}H_{132}N_4$ [M^{+2}] 538.5228; found 538.5220.

1,1′,3,3′-Tetra(octadecyl)-5,5′-bibenzimidazolium bis(tetrafluoroborate) (15). A 30 mL vial was charged with **1b** (200 mg, 0.85 mmol), DMF (8 mL), sodium bicarbonate (717 mg, 8.5 mmol), and a stir bar, and then sealed with a Teflon-lined cap. The resulting mixture was then stirred in an oil bath thermostated to 110 °C for 1 h. After cooling the mixture to ambient temperature, 1-bromooctadecane (4.6 mL, 13.7 mmol) was added. The vial was then re-sealed and stirred in an oil bath thermostated to 110 °C for an additional 48 h. The hot reaction mixture was then filtered to remove excess sodium bicarbonate, and the filtrate wasadded to excess diethyl ether (250 mL). The solids which precipitated were collected via filtration, triturated with acetone to remove residual DMF, and dried under high vacuum to afford crude 1,1′,3,3′-tetra(octadecyl)-5,5′-bibenzimidazolium dibromide. A separate 7.5 mL vial was charged with the crude salt, dry CH_2Cl_2 (5 mL), triethyloxonium tetrafluoroborate (286 mg, 2.6 mmol), and a stir bar, and then sealed with a Teflon-lined cap. After stirring the resulting mixture for 12 h at ambient temperature, methanol (3 mL) was added. The reaction mixture was then stirred for an additional hour. The resulting solution was poured into excess diethyl ether (50 mL) which caused solids to precipitate. The solids were collected via filtration and dried under reduced pressure to afford 992 mg (82% yield) of the desired product as a white powder. m.p. = 50.0 °C. ^{1}H NMR (400 MHz, 1:1 DMSO-d_6:CDCl$_3$ v/v): 10.00 (s, 2H), 8.56 (s, 2H), 8.06 (br, 4H), 4.64 (br, 4H), 4.52, (br, 4H), 1.95 (br, 8H), 1.31-1.17 (m, 120H), 0.81 (t, *J* = 13.6 Hz, 12H). ^{13}C NMR (125 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): 142.4, 137.9, 131.8, 130.7, 126.4, 113.8, 112.5, 47.0, 46.9, 31.2, 29.0, 28.98, 28.9, 28.87, 28.83, 28.8, 28.7, 38.6, 28.5, 28.4, 25.8, 25.7, 22.0, 13.7. ^{19}F NMR (282 MHz, 1:1 DMSO-*d*$_6$:CDCl$_3$ v/v): –145.8, –148.3 ppm. HRMS m/z calcd for $C_{86}H_{156}N_4$ [M^{+2}] 622.6166; found 622.6160.

DSC Thermograms

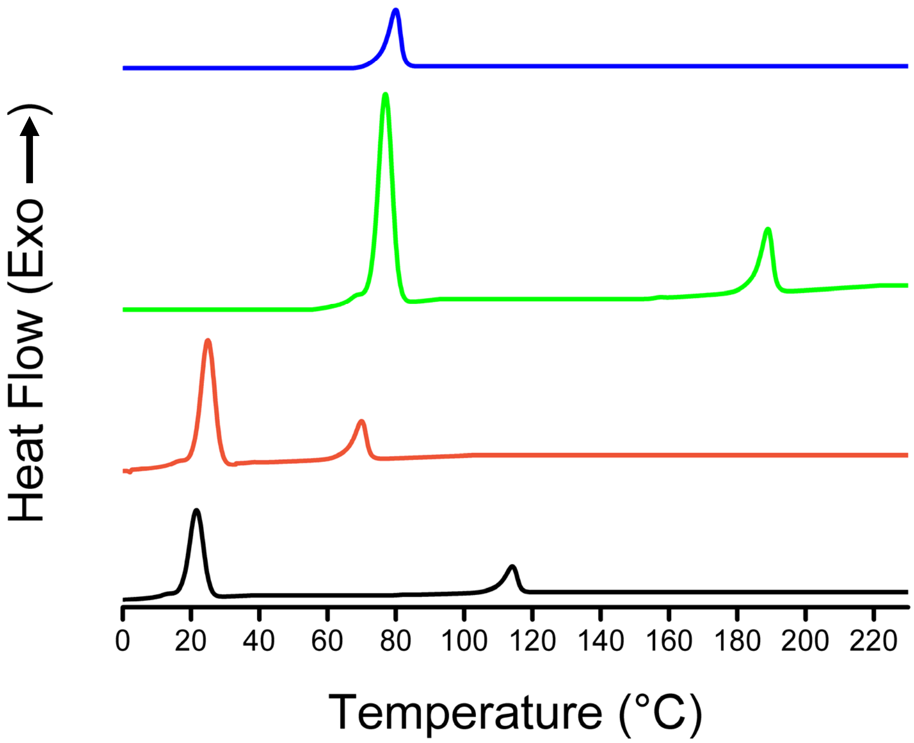


Figure S1. DSC thermograms of **9MeSO$_4$** (blue), **9BF$_4$** (green), **9PF$_6$** (orange), and **9Br** (black). Data shown were collected from the third cooling cycle at a rate of 10 °C min^{-1} under nitrogen.

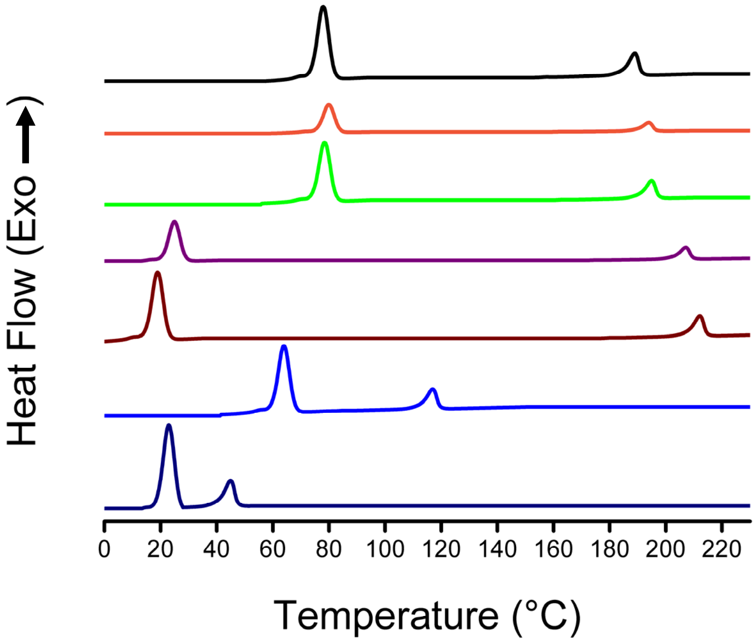


Figure S2. DSC thermograms of **3** (black), **4** (orange), **5** (green), **6** (pruple), **7** (brown) **2BF$_4$** (blue) and **8** (navy). Data shown were collected from the third cooling cycle at a rate of 10 °C min^{-1} under nitrogen.

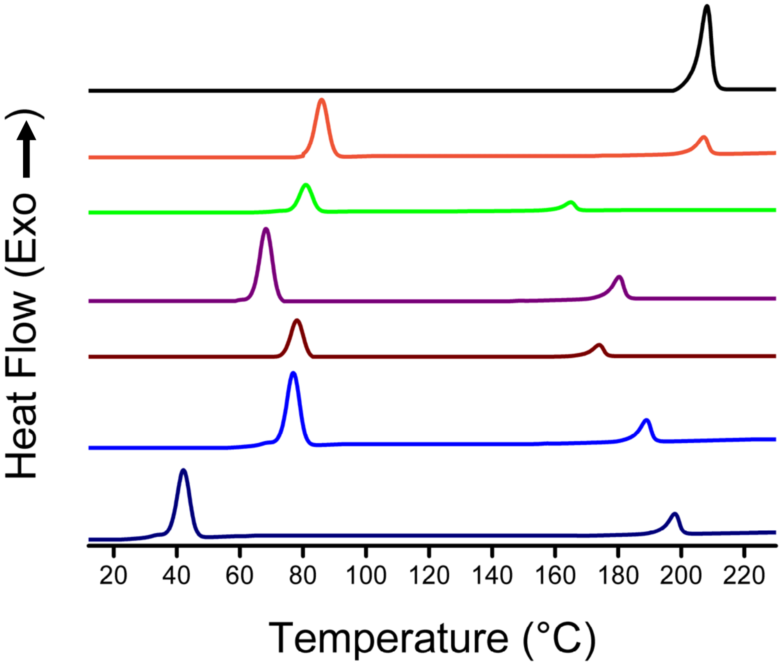


Figure S3. DSC thermograms of **9** (black), **10** (orange), **11** (green), **12** (purple), **13** (brown) **2BF$_4$** (blue) and **14** (navy). Data shown were collected from the third cooling cycle at a rate of 10 °C min^{-1} under nitrogen.

Selected Polarized Light Microscope (PLM) Images

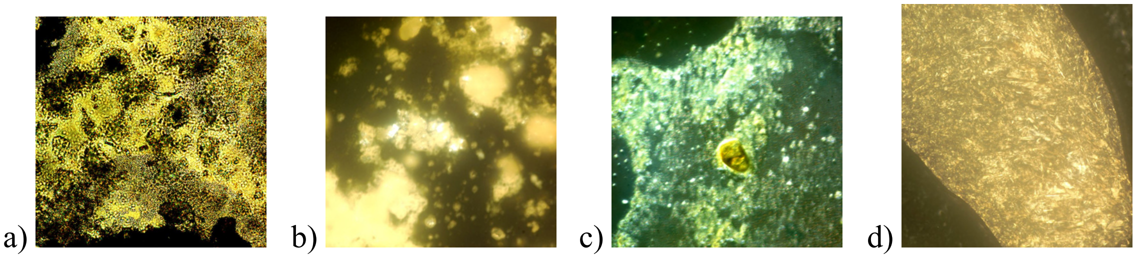


Figure S4. PLM images of the mesophases of BBI salts a) **4**, b) **5**, c) **6**, d) **8** as recorded on the second cooling cycle.

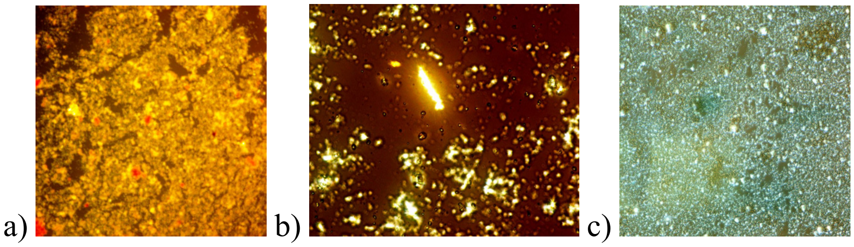


Figure S5. PLM images of the mesophases of BBI salts a) **2Br**, b) **2BF$_4$**, and c) **2PF$_6$** as recorded on the second cooling cycle.

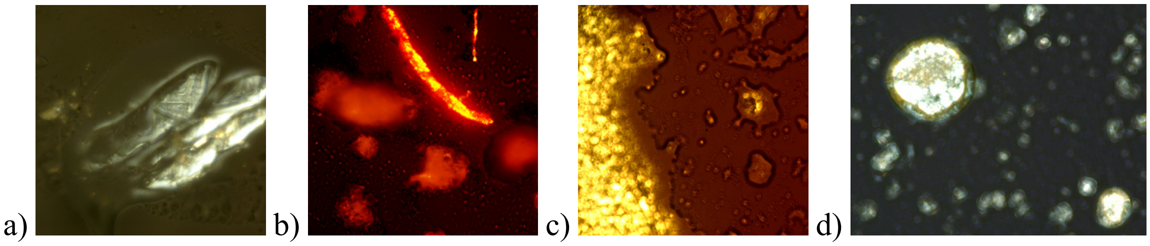


Figure S6. PLM images of the mesophases of BiBz salts a) **11**, b) **12**, c) **13**, d) **15** as recorded on the second cooling cycle.

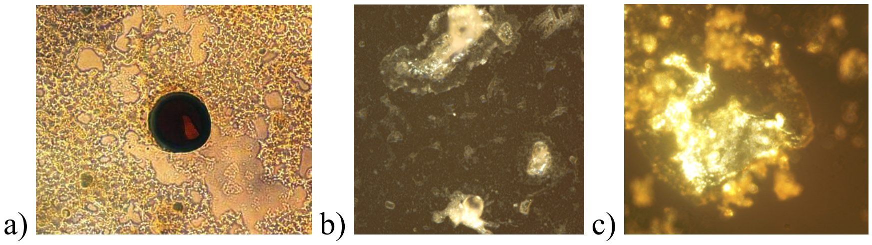


Figure S7. PLM images of the mesophases of BiBz salts a) **9Br**, b) **9BF$_4$**, and c) **9PF$_6$** as recorded on the second cooling cycle.

VT-PXRD Data

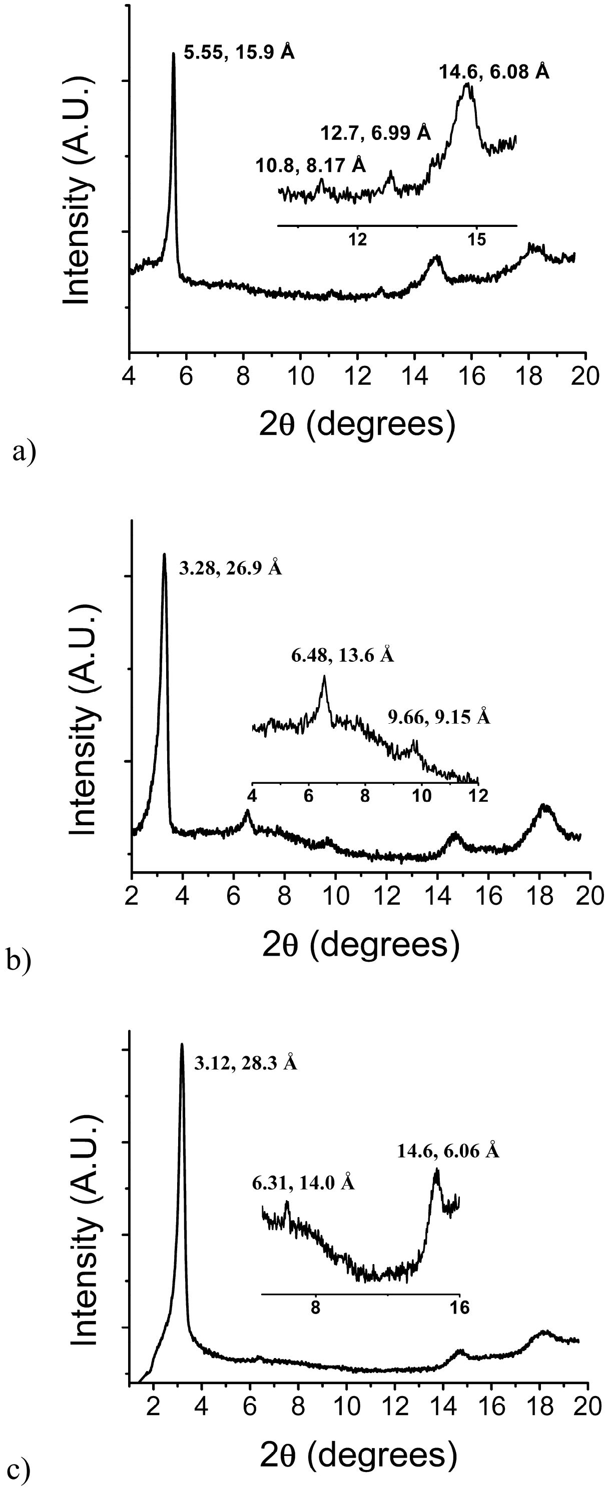


Figure S8. PXRD data for a) **3** at 140 °C, b) **6** at 150 °C, and c) **7** at 150 °C as recorded on the second cooling cycle.

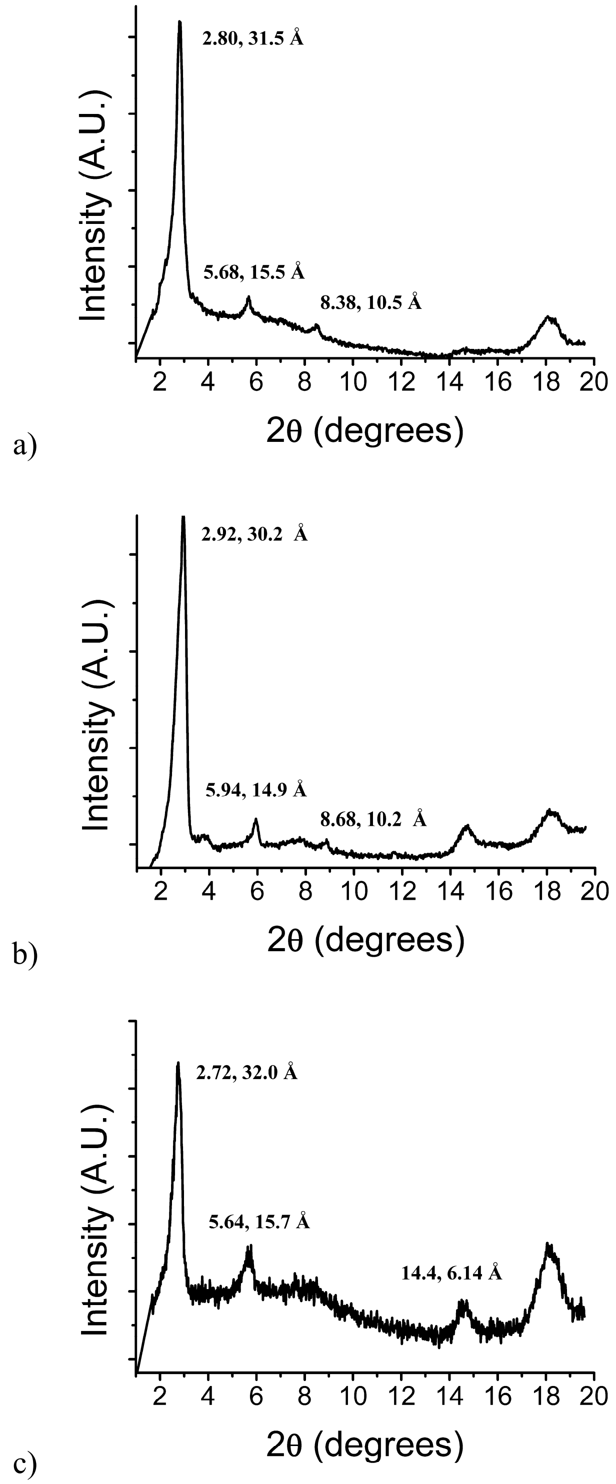


Figure S9. PXRD data for a) **2Br** at 150 °C, b) **2PF$_6$** at 75 °C, and c) **8** at 40 °C as recorded on the second cooling cycle.

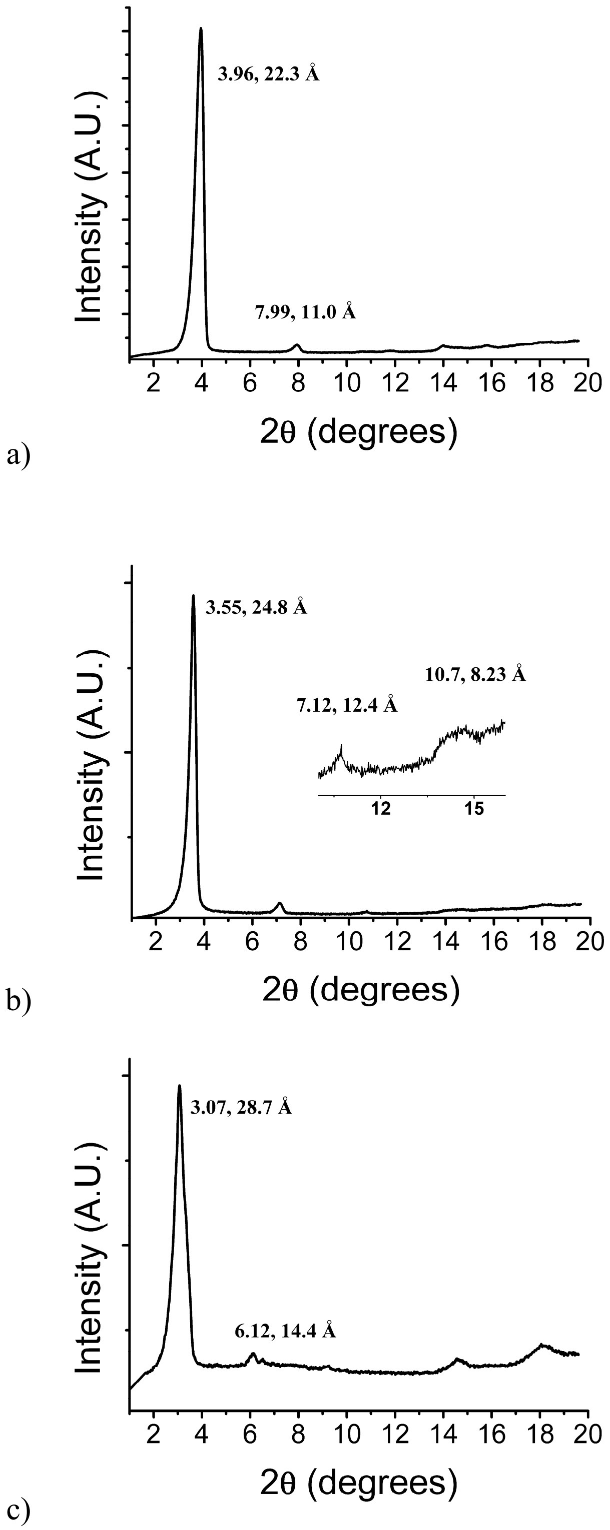
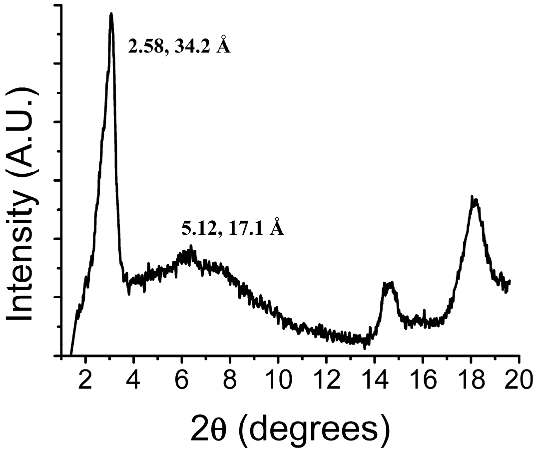
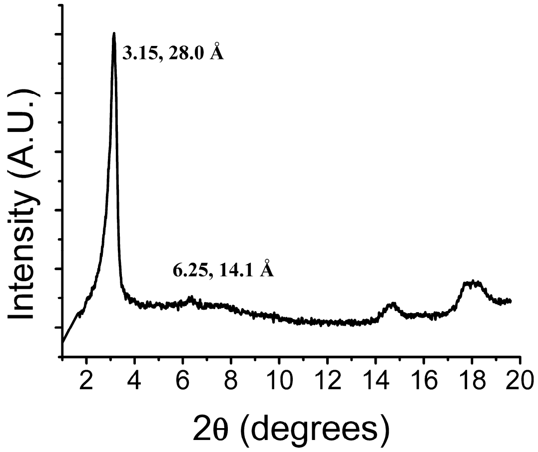


Figure S10. PXRD data for a) **11** at 145 °C, b) **12** at 130 °C, and c) **13** at 150 °C as recorded on the second cooling cycle.

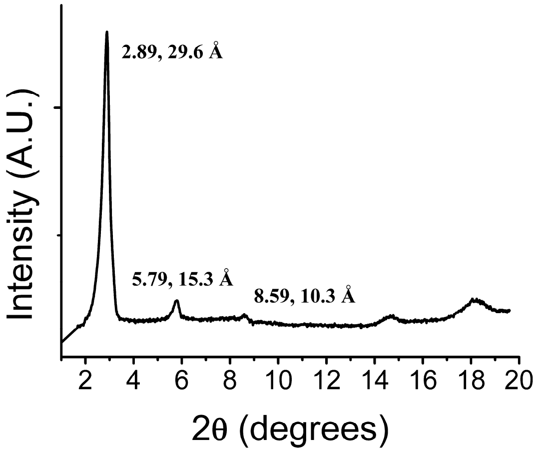


a)

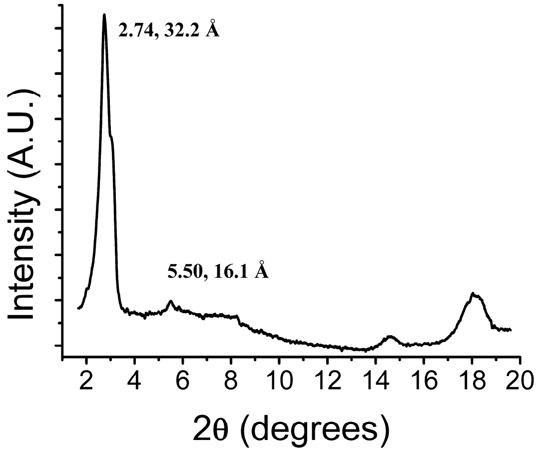


b)

Figure S11. PXRD data for a) **9Br** at 75 °C and b) **9PF$_6$** at 150 °C as recorded on the second cooling cycle.



a)



b)

Figure S12. PXRD data for a) **14** and b) **15** both at 140 °C as recorded on the second cooling cycl**e**.