Electronic Supporting Information

Luminescent Imidazolium-Naphtalene Salts in Liquid and Solid States.

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NMR, UV-Vis, IR and Elemental Analysis

3a

^{1}H NMR (300 MHz, Chloroform-*d*) δ 10.65 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.05 – 7.98 (m, 1H), 7.92 (d, *J* = 7.3 Hz, 1H), 7.72 – 7.56 (m, 4H), 7.50 (s, 2H), 4.78 (t, *J* = 7.4 Hz, 2H), 2.05 (q, *J* = 7.4 Hz, 2H), 1.37 (d, *J* = 55.1 Hz, 10H), 0.88 (t, 3H). ^{13}C NMR (75 MHz, Chloroform- *d*) δ 13.72, 22.23, 25.93, 28.67, 28.71, 30.12, 31.33, 50.16, 120.34, 123.17, 123.87, 124.34, 124.94, 127.27, 127.36, 128.43, 128.50, 130.32, 131.19, 133.79, 137.27. ν_{max}/cm^{-1}: 3059 (C-H aromatic), 2924 and 2851 (C-H aliphatic), 1545 (C=C aromatic). UV/Vis (CH_2Cl_2): λ_{max} (ε L.mol^{-1}.cm^{-1}) = 283 nm (7200), 228 nm (37300). Elemental analysis for $C_{21}H_{27}BrN_2$, Cacld: C, 65.11; H, 7.03; N, 7.23 %. Found: C, 64.95; H, 7.01; N, 7.33 %.

3b

^{1}H NMR (300 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 6.8 Hz, 2H), 7.69 – 7.57 (m, 4H), 7.56 – 7.47 (m, 2H), 4.71 (t, *J* = 7.5 Hz, 2H), 2.05 (q, *J* = 7.6, 7.2 Hz, 2H), 1.48 – 1.25 (m, 10H), 0.88 (t, 3H). ^{13}C NMR (75 MHz, Chloroform- *d*) δ 13.83, 22.34, 26.02, 28.76, 28.81, 30.08, 31.43, 50.57, 120.51, 123.26, 124.03, 124.65, 125.10, 127.34, 127.44, 128.63, 128.66, 130.28, 131.41, 133.90, 136.80. ν_{max}/cm^{-1}: 3054 (C-H aromatic), 1422 (C=C aromatic). UV/Vis (CH_2Cl_2): λ_{max} (ε L.mol^{-1}.cm^{-1}) = 364 nm (500), 283 nm (8500), 228 nm (41400). Elemental analysis for $C_{21}H_{27}I_{0.93}N_{2\cdot0.07}Br$, Cacld: C, 58.51; H, 6.31; N, 6.50 %. Found: C, 58.52; H, 6.38; N, 6.27 %.

3c

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.79 (s, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 8.01 (dd, *J* = 6.3, 3.3 Hz, 1H), 7.74 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.69 – 7.39 (m, 6H), 4.42 (t, *J* = 7.6 Hz, 2H), 2.06 – 1.93 (m, 2H), 1.33 (d, *J* = 32.1 Hz, 10H), 0.88 (t, 3H). ^{13}C NMR (75 MHz, Chloroform- *d*) δ 13.96, 22.50, 26.15, 28.79, 28.93, 29.77, 31.58, 50.59, 120.51, 122.91, 124.47, 124.55, 125.18, 127.61, 127.61, 128.69, 128.86, 130.43, 131.63, 134.03, 135.89. ν_{max}/cm^{-1}: 3073 (C-H aromatic), 2928 and 2855 (C-H aliphatic), 1552 (C=C aromatic), 843 (PF_6^-). UV/Vis (CH_2Cl_2): λ_{max} (ε L.mol^{-1}.cm^{-1}) = 282 nm (6900), 228 nm (31300). Elemental analysis for $C_{21}H_{27}F_6N_2P$, Cacld: C, 55.75; H, 6.02; N, 6.19 %. Found: C, 55.73; H, 6.07; N, 5.82 %.

3d

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.03 (d, *J* = 1.7 Hz, 1H), 8.09 – 7.97 (m, 2H), 7.75 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.66 – 7.56 (m, 4H), 7.49 (tt, *J* = 3.7, 2.1 Hz, 2H), 4.44 (t, *J* = 7.5 Hz, 2H), 1.97 (q, *J* = 7.3 Hz, 2H), 1.44 – 1.23 (m, 10H), 0.87 (t, 3H). ^{13}C NMR (75 MHz, Chloroform- *d*) δ 13.94, 22.47, 26.12, 28.80, 28.92, 29.95, 31.56, 50.47, 120.51, 123.05, 124.38, 124.54, 125.17, 127.50, 127.53, 128.67, 128.70, 130.51, 131.46, 133.99, 136.41.

ν_{max}/cm^{-1}: 3055 (C-H aromatic), 1423 (C=C aromatic), 1053 (BF_4^-). UV/Vis (CH_2Cl_2): λ_{max} (ε L.mol^{-1}.cm^{-1}) = 282 nm (7200), 228 nm (33000). Elemental analysis for $C_{21}H_{27}BF_4N_{2.0.12}H_2O$, Cacld: C, 63.63; H, 6.93; N, 7.07 %. Found: C, 63.62; H, 6.85; N, 7.15 %.

3e

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 8.06 – 7.98 (m, 1H), 7.72 – 7.52 (m, 6H), 7.48 – 7.43 (m, 1H), 4.42 (t, *J* = 7.6 Hz, 2H), 2.00 (q, *J* = 7.4 Hz, 2H), 1.46 – 1.21 (m, 10H), 0.88 (t, 3H).

^{13}C NMR (75 MHz, Chloroform- *d*) δ 13.91, 22.45, 26.07, 28.72, 28.87, 28.87, 29.87, 31.53, 50.65, 119.70, 120.32, 123.02, 124.54, 124.62, 125.12, 127.61, 127.63, 128.75, 128.86, 130.33, 131.73, 134.09, 136.09. ν_{max}/cm^{-1}: 3054 (C-H aromatic), 1422 (C=C aromatic), 1350 and 1140 ((CF3SO2)2N-). UV/Vis (CH_2Cl_2): λ_{max} (ε L.mol^{-1}.cm^{-1}) = 283 nm (7600), 228 nm (33000). Elemental analysis for $C_{23}H_{27}F_6N_3O_4S_2$, Cacld: C, 47.01; H, 4.63; N, 7.15 %. Found: C, 46.99; H, 4.67; N, 7.17 %.

4a

1H NMR (300 MHz, Chloroform-d) δ 10.61 (s, 1H), 8.09 (d, J = 8.3 Hz, 1H), 8.01 (s, 1H), 7.92 (dd, J = 7.4, 1.1 Hz, 1H), 7.71 – 7.56 (m, 4H), 7.53 – 7.45 (m, 2H), 4.77 (t, J = 7.4 Hz, 2H), 2.05 (q, J = 7.4 Hz, 2H), 1.26 (s, 18H), 0.89 (t, 3H). 13C NMR (75 MHz, Chloroform- d) δ 13.94, 22.50, 26.18, 28.95, 29.16, 29.28, 29.38, 29.44, 29.46, 30.29, 31.74, 50.48, 120.52, 123.00, 123.03, 123.94, 124.66, 125.21, 127.47, 128.65, 128.73, 130.52, 131.42, 134.03, 137.72. □max/cm-1: 3059 (C-H aromatic), 2921 and 2849 (C-H aliphatic), 1510 (C=C aromatic). UV/Vis (CH2Cl2): λmax (ε L.mol-1.cm-1) = 283 nm (7100), 228 nm (35700).

Elemental analysis for C25H35BrN2, CacId: C, 67.71; H, 7.96; N, 6.32 %. Found: C, 67.73; H, 8.06; N, 6.40 %.

4b

^{1}H NMR (300 MHz, Chloroform-*d*) δ 10.09 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.05 – 7.95 (m, 2H), 7.73 – 7.48 (m, 6H), 4.71 (t, *J* = 7.5 Hz, 2H), 2.06 (p, *J* = 7.6 Hz, 2H), 1.26 (s, 18H), 0.94 – 0.83 (t, 3H). ^{13}C NMR (75 MHz, Chloroform- *d*) δ 13.92, 22.47, 26.11, 29.13, 29.25, 29.35, 29.41, 29.43, 30.13, 31.70, 50.72, 120.58, 123.25, 124.06, 124.76, 125.18, 127.42, 127.50, 128.70, 128.73, 130.34, 131.48, 133.98, 136.84. ν_{max}/cm^{-1}: 3054 (C-H aromatic), 2929 and 2856 (C-H aliphatic), 1422 (C=C aromatic). UV/Vis (CH_2Cl_2): λ_{max} (ε L.mol^{-1}.cm^{-1}) = 283 nm (8100), 230 nm (25300). Elemental analysis for $C_{25}H_{35}IN_{2.0.3}H_2O$, CacId: C, 60.55; H, 7.24; N, 5.65 %. Found: C, 60.56; H, 7.23; N, 5.55 %.

4c

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.71 (s, 1H), 8.10 – 7.96 (m, 2H), 7.70 – 7.44 (m, 7H), 4.35 (t, *J* = 7.6 Hz, 2H), 1.95 (q, *J* = 7.6 Hz, 2H), 1.25 (s, 18H), 0.87 (t, 3H). ^{13}C NMR (75 MHz, Chloroform- *d*) δ 14.05, 22.63, 26.22, 28.91, 29.28, 29.35, 29.47, 29.57, 29.81, 31.86, 50.63, 120.54, 122.91, 124.47, 124.61, 125.22, 127.63, 127.65, 128.70, 128.89, 130.46, 131.65, 134.05, 135.92. ν_{max}/cm^{-1}: 3163 (C-H aromatic), 2919 and 2852 (C-H aliphatic), 1514 (C=C aromatic), 820 (PF_6^-). UV/Vis (CH_2Cl_2): λ_{max} (ε L.mol^{-1}.cm^{-1}) = 283 nm (7100), 229 nm (27300). Elemental analysis for $C_{25}H_{35}F_6N_2P_{.0.1}H_2O$, CacId: C, 58.84; H, 6.95; N, 5.49 %. Found: C, 58.83; H, 7.07; N, 5.54 %.

4d

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.05 (s, 1H), 8.11 – 7.98 (m, 2H), 7.77 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.67 – 7.57 (m, 4H), 7.52 – 7.46 (m, 2H), 4.45 (t, *J* = 7.5 Hz, 2H), 1.98 (q, *J* = 7.5 Hz, 2H), 1.26 (s, 18H), 0.87 (t, 3H). ^{13}C NMR (75 MHz, Chloroform- *d*) δ 14.00, 22.58, 26.18, 28.91, 29.24, 29.33, 29.44, 29.53, 29.54, 29.98, 31.81, 50.50, 120.54, 123.04, 124.38, 124.57, 125.19, 127.51, 127.56, 128.68, 128.73, 130.54 (quaternary C), 131.47, 134.01, 136.46. ν_{max}/cm^{-1}: 3055 (C-H aromatic), 2929 and 2857 (C-H aliphatic), 1422 (C=C aromatic), 1053 (BF4-). UV/Vis (CH_2Cl_2): λ_{max} (ε L.mol^{-1}.cm^{-1}) = 283 nm (7100), 229 nm (26700). Elemental analysis for $C_{25}H_{35}BF_4N_2$, CacId: C, 66.67; H, 7.83; N, 6.22 %. Found: C, 66.50; H, 7.98; N, 6.28 %.

4e

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.94 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 8.03 – 7.97 (m, 1H), 7.70 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.67 – 7.56 (m, 4H), 7.53 (t, *J* = 1.8 Hz, 1H), 7.48 – 7.43 (m, 1H), 4.40 (t, *J* = 7.6 Hz, 2H), 2.00 (p, *J* = 7.5 Hz, 2H), 1.26 (s, 18H), 0.87 (t, 3H). ^{13}C NMR (75 MHz, Chloroform- *d*) δ 13.92, 22.47, 26.11, 29.13, 29.25, 29.35, 29.41, 29.43, 30.13, 31.70, 50.72, 120.58, 123.25, 124.06, 124.76, 125.18, 127.42, 127.50, 128.70, 128.73, 130.34, 131.48, 133.98, 136.84. ν_{max}/cm^{-1}: 3054 (C-H aromatic), 2929 and 2856 (C-H aliphatic), 1422 (C=C aromatic). UV/Vis (CH_2Cl_2): λ_{max} (ε L.mol^{-1}.cm^{-1}) = 283 nm (8100), 230 nm (25300). Elemental analysis for $C_{25}H_{35}IN_{2.0.3}H_2O$, CacId: C, 60.55; H, 7.24; N, 5.65 %. Found: C, 60.56; H, 7.23; N, 5.55 %.

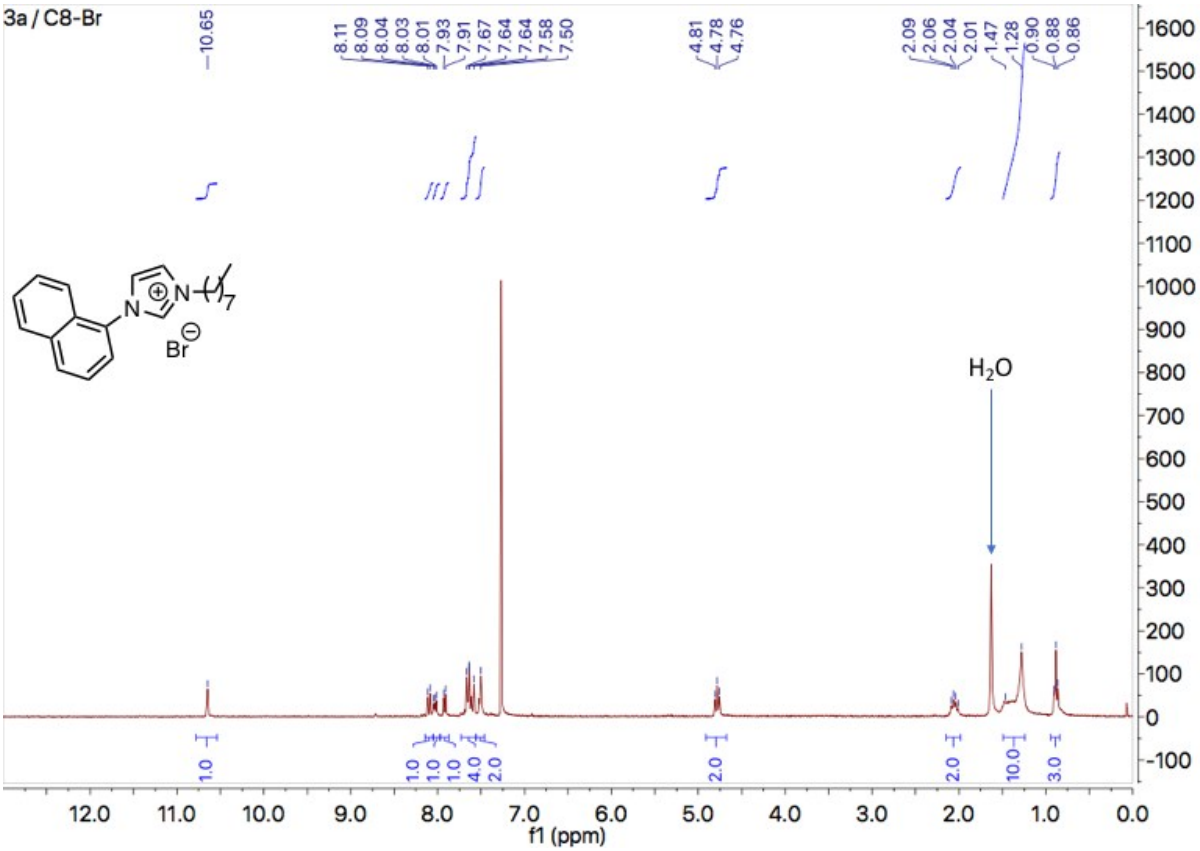

*Figure S1 - **3a** ^{1}H NMR Spectrum 300MHz in $CDCl_3$*

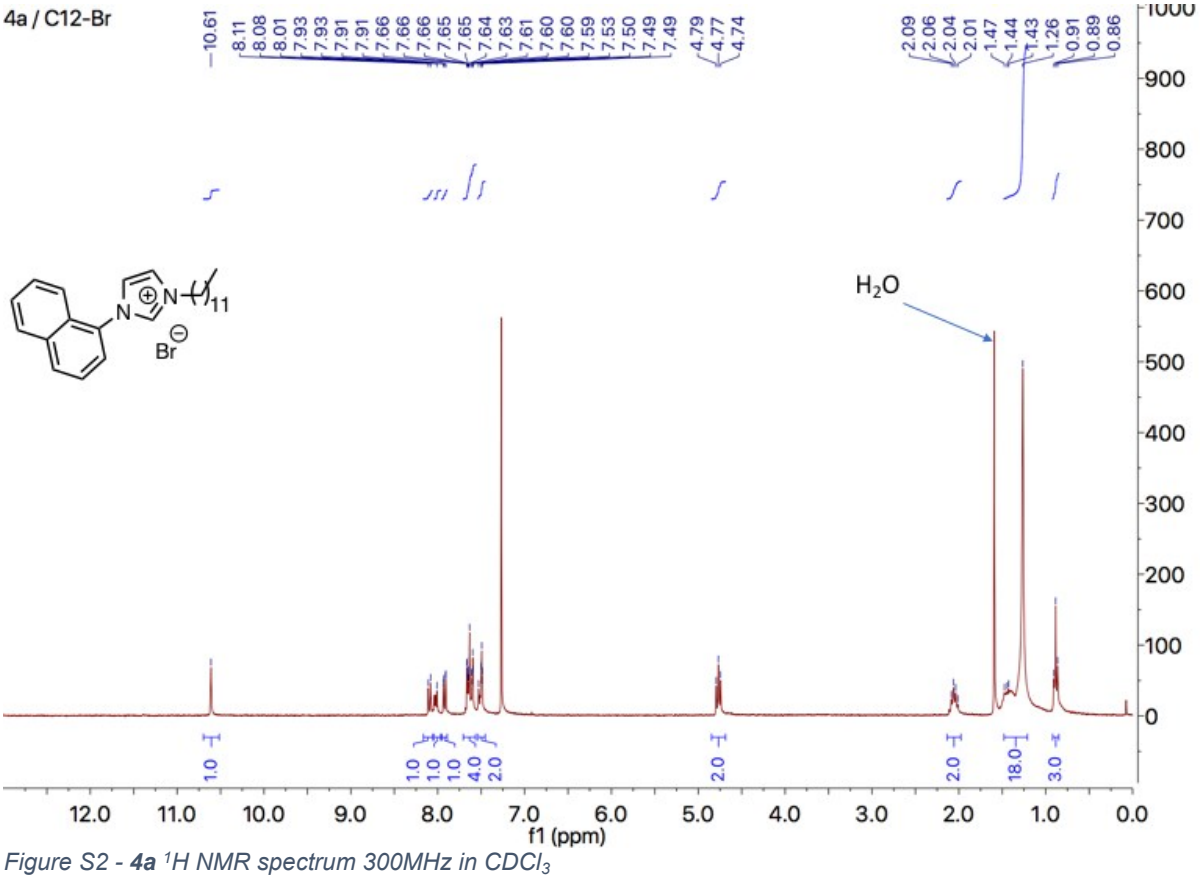

*Figure S2 - **4a** ^{1}H NMR spectrum 300MHz in $CDCl_3$*

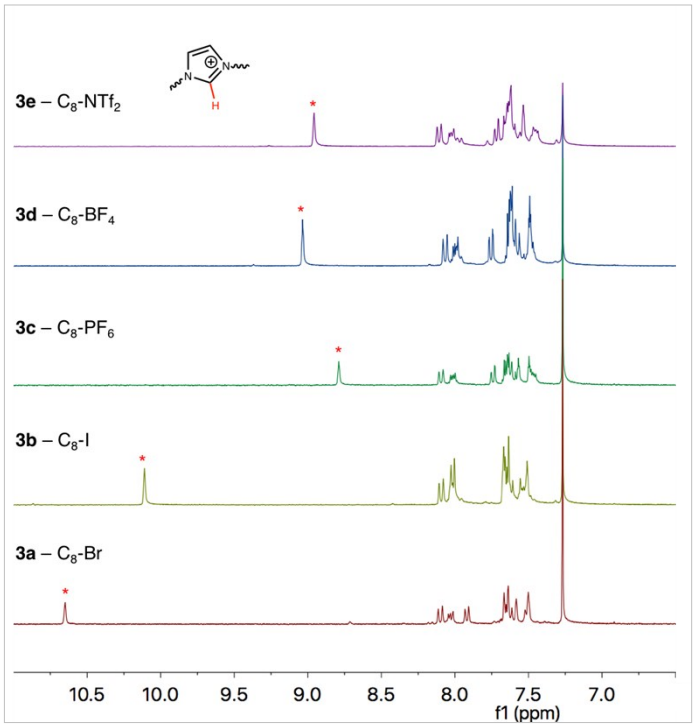

Figure S3 -^{1}H NMR 300 MHz in $CDCl_3$ - Aromatic & Imidazolium proton section 6.0 to 11 ppm

TGA Studies

The TGA measurements were carried out with a Q50 apparatus of TA Instruments, at a scanning rate of 5 C min^{-1} and with air as purge gas.

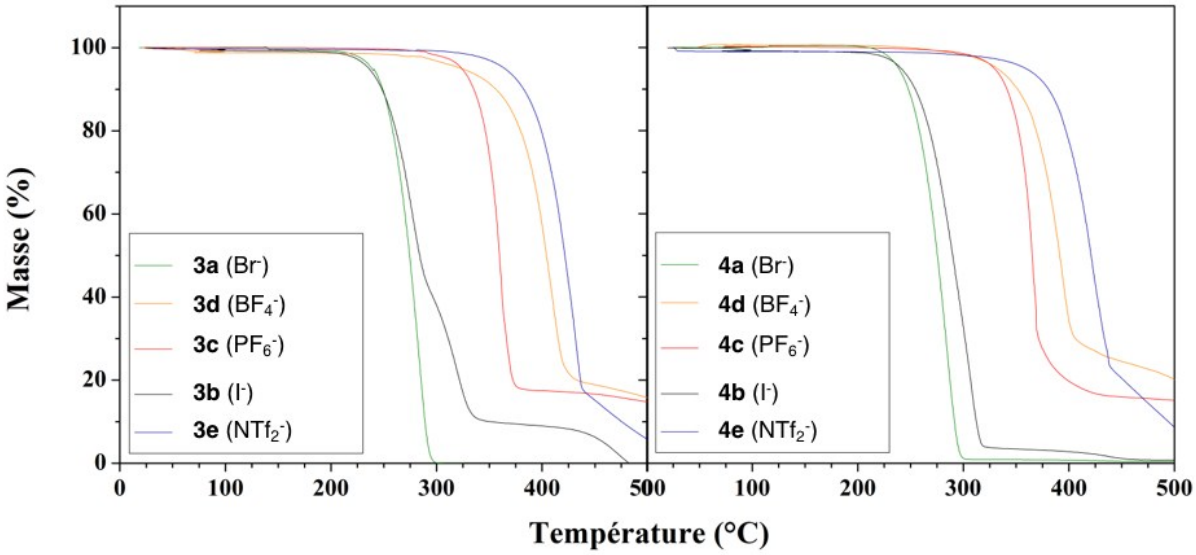

Figure S4 - TGA Curves

SAXS Studies

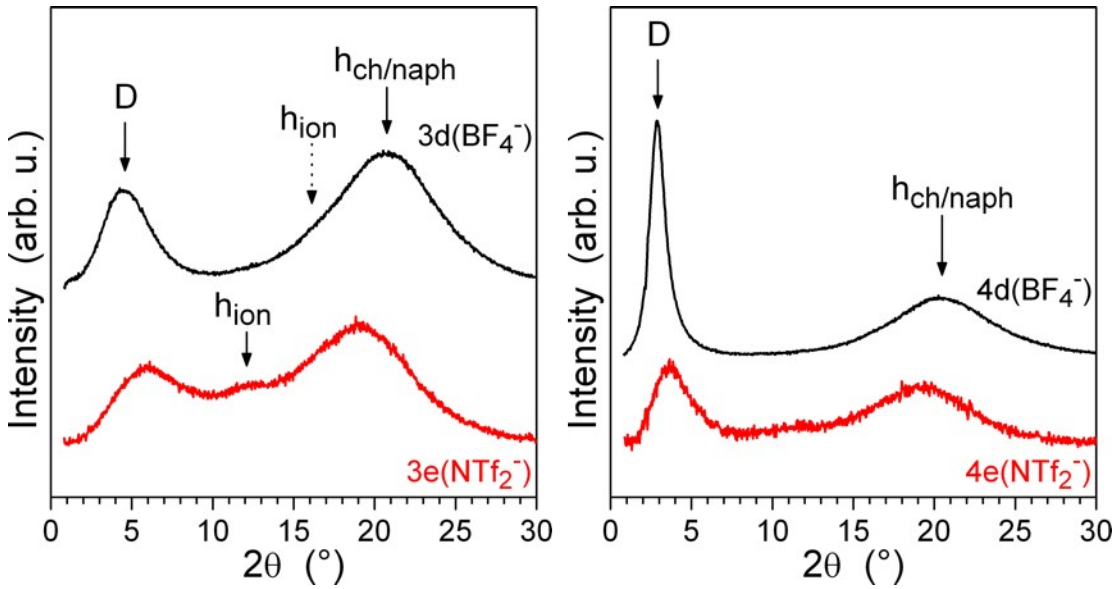

Figure S5 : SAXS patterns of the room temperature ionic liquids from series 3 and 4, with respectively octyl (left) and dodecyl (right) substituents: the liquid 3d(BF_4^-) and 3e(NTF_2^-) exhibit a local-range structure of same configuration as the homologue crystalline 3a(Br^-) that consists in the nanosegregation of ionic moieties and mixed naphthyl/alkyl substituents into strata, with only variation of the strata periodicity D (3d: 19-19.5 Å, 3e: 15-16 Å) and of the molecular area A_{mol}, ratio of molecular volume V_{mol} and D, (3d: 30-31 $Å^2$, 3e: »50 $Å^2$) reflecting the different sizes of anions and superficies of ionic arrangements (average spacing h_{ion} » ÖA_{mol} for the ideal square arrangement); the liquid 4d(BF_4^-) and 4e(NTF_2^-) develop an even more pronounced stratification, but the molecular organization could not be clarified without knowing the crystalline structure of parent 4a-c, from which usable single-crystals could not be grown.

The SAXS pattern was obtained with a transmission Guinier-like geometry, using a linear focalized monochromatic Cu $K_{\alpha 1}$ beam, from a sealed-tube generator (600 W) equipped with a bent quartz monochromator, and a curved Inel CPS120 counter gas-filled detector. The liquid was filled in a sealed cell and exposed for 5 hours ; the empty cell contribution was subtracted.

X-ray Crystallography

Crystal data and structure refinement for **3a** (CCDC 1856447)

Identification code:	ldmlh180511
Empirical formula:	$C_{21}H_{27}BrN_2$
Formula weight:	387.35
Temperature:	173(2) K
Wavelength:	0.71073 A
Crystal system, space group:	Monoclinic, P $2_1/c$
Unit cell dimensions:	a = 17.7618(11) A alpha = 90 deg.
b = 8.5269(3) A	beta = 112.281(2) deg.
c = 14.2656(9) A	gamma = 90 deg.
Volume:	1999.25(19) A^3
Z, Calculated density:	4, 1.287 Mg/m^3
Absorption coefficient:	2.060 mm^{-1}
F(000):	808
Crystal size:	0.20 x 0.18 x 0.15 mm
Theta range for data collection:	1.239 to 27.388 deg.
Limiting indices:	-23<=h<=22, -10<=k<=10, -18<=l<=18
Reflections collected / unique:	34724 / 4527 [R(int) = 0.1428]
Completeness to theta = 25.242:	100.0 %
Absorption correction:	Semi-empirical from equivalents
Max. and min. transmission:	0.84847 and 0.68467
Refinement method:	Full-matrix least-squares on F^2
Data / restraints / parameters:	4527 / 0 / 218
Goodness-of-fit on F^2:	1.186
Final R indices [I>2sigma(I)]:	R1 = 0.0824, wR2 = 0.1396
R indices (all data):	R1 = 0.1539, wR2 = 0.1675
Extinction coefficient:	n/a
Largest diff. peak and hole:	0.545 and -0.426 $e.A^{-3}$

Table S2. Atomic coordinates ($x.10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for ldmlh180511. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	4547(3)	4569(6)	2866(4)	33(1)
C(2)	4114(3)	2172(5)	2911(4)	34(1)
C(3)	4777(3)	2400(5)	3759(4)	34(1)
C(4)	3316(3)	3825(5)	1400(4)	34(1)
C(5)	3499(3)	4143(6)	572(4)	40(1)
C(6)	2860(4)	4390(6)	-365(4)	49(2)
C(7)	2078(4)	4260(6)	-462(4)	48(2)
C(8)	1873(3)	3934(6)	376(4)	42(1)
C(9)	1053(4)	3813(7)	299(5)	57(2)
C(10)	880(4)	3559(8)	1127(5)	63(2)
C(11)	1501(3)	3421(7)	2090(5)	53(2)
C(12)	2297(3)	3501(6)	2203(4)	41(1)
C(13)	2506(3)	3739(5)	1345(4)	37(1)
C(14)	5777(3)	4621(6)	4467(4)	36(1)
C(15)	6536(3)	3886(6)	4410(4)	37(1)
C(16)	7306(3)	4611(7)	5165(4)	46(1)
C(17)	8079(3)	3910(7)	5101(4)	48(1)
C(18)	8164(4)	4173(8)	4106(5)	60(2)
C(19)	8910(4)	3457(8)	4012(5)	70(2)
C(20)	8922(5)	3657(11)	2966(7)	109(3)
C(21)	9613(5)	2986(12)	2777(7)	118(3)
N(1)	3970(2)	3547(4)	2359(3)	33(1)
N(2)	5043(2)	3909(4)	3717(3)	31(1)
Br(1)	4195(1)	8228(1)	3520(1)	44(1)

Table S3. Bond lengths [A] and angles [deg] for ldmlh180511.

C(1)-N(2)	1.325(6)
C(1)-N(1)	1.330(6)
C(1)-H(1)	0.9500
C(2)-C(3)	1.344(7)
C(2)-N(1)	1.381(6)
C(2)-H(2)	0.9500
C(3)-N(2)	1.380(6)
C(3)-H(3)	0.9500
C(4)-C(5)	1.366(7)
C(4)-C(13)	1.413(7)
C(4)-N(1)	1.439(6)
C(5)-C(6)	1.403(7)
C(5)-H(5)	0.9500
C(6)-C(7)	1.347(8)
C(6)-H(6)	0.9500
C(7)-C(8)	1.404(7)
C(7)-H(7)	0.9500
C(8)-C(9)	1.421(8)
C(8)-C(13)	1.423(7)
C(9)-C(10)	1.346(9)
C(9)-H(9)	0.9500
C(10)-C(11)	1.403(8)
C(10)-H(10)	0.9500
C(11)-C(12)	1.363(7)
C(11)-H(11)	0.9500
C(12)-C(13)	1.422(7)
C(12)-H(12)	0.9500
C(14)-N(2)	1.468(6)
C(14)-C(15)	1.517(6)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.515(7)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.532(7)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.500(8)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.511(8)
C(18)-H(18A)	0.9900

C(18)-H(18B)	0.9900
C(19)-C(20)	1.510(10)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-C(21)	1.469(11)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
N(2)-C(1)-N(1)	109.1(4)
N(2)-C(1)-H(1)	125.4
N(1)-C(1)-H(1)	125.4
C(3)-C(2)-N(1)	107.5(4)
C(3)-C(2)-H(2)	126.3
N(1)-C(2)-H(2)	126.3
C(2)-C(3)-N(2)	107.1(4)
C(2)-C(3)-H(3)	126.5
N(2)-C(3)-H(3)	126.5
C(5)-C(4)-C(13)	122.3(5)
C(5)-C(4)-N(1)	118.9(5)
C(13)-C(4)-N(1)	118.8(4)
C(4)-C(5)-C(6)	118.8(5)
C(4)-C(5)-H(5)	120.6
C(6)-C(5)-H(5)	120.6
C(7)-C(6)-C(5)	121.1(5)
C(7)-C(6)-H(6)	119.4
C(5)-C(6)-H(6)	119.4
C(6)-C(7)-C(8)	121.2(5)
C(6)-C(7)-H(7)	119.4
C(8)-C(7)-H(7)	119.4
C(7)-C(8)-C(9)	122.5(5)
C(7)-C(8)-C(13)	119.0(5)
C(9)-C(8)-C(13)	118.4(5)
C(10)-C(9)-C(8)	120.8(5)
C(10)-C(9)-H(9)	119.6
C(8)-C(9)-H(9)	119.6
C(9)-C(10)-C(11)	121.0(6)
C(9)-C(10)-H(10)	119.5
C(11)-C(10)-H(10)	119.5
C(12)-C(11)-C(10)	120.4(6)
C(12)-C(11)-H(11)	119.8
C(10)-C(11)-H(11)	119.8

C(11)-C(12)-C(13)	120.2(5)
C(11)-C(12)-H(12)	119.9
C(13)-C(12)-H(12)	119.9
C(4)-C(13)-C(12)	123.6(5)
C(4)-C(13)-C(8)	117.5(5)
C(12)-C(13)-C(8)	119.0(5)
N(2)-C(14)-C(15)	110.6(4)
N(2)-C(14)-H(14A)	109.5
C(15)-C(14)-H(14A)	109.5
N(2)-C(14)-H(14B)	109.5
C(15)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	108.1
C(16)-C(15)-C(14)	112.0(4)
C(16)-C(15)-H(15A)	109.2
C(14)-C(15)-H(15A)	109.2
C(16)-C(15)-H(15B)	109.2
C(14)-C(15)-H(15B)	109.2
H(15A)-C(15)-H(15B)	107.9
C(15)-C(16)-C(17)	112.7(4)
C(15)-C(16)-H(16A)	109.0
C(17)-C(16)-H(16A)	109.0
C(15)-C(16)-H(16B)	109.0
C(17)-C(16)-H(16B)	109.0
H(16A)-C(16)-H(16B)	107.8
C(18)-C(17)-C(16)	114.3(5)
C(18)-C(17)-H(17A)	108.7
C(16)-C(17)-H(17A)	108.7
C(18)-C(17)-H(17B)	108.7
C(16)-C(17)-H(17B)	108.7
H(17A)-C(17)-H(17B)	107.6
C(17)-C(18)-C(19)	115.4(5)
C(17)-C(18)-H(18A)	108.4
C(19)-C(18)-H(18A)	108.4
C(17)-C(18)-H(18B)	108.4
C(19)-C(18)-H(18B)	108.4
H(18A)-C(18)-H(18B)	107.5
C(20)-C(19)-C(18)	112.6(6)
C(20)-C(19)-H(19A)	109.1
C(18)-C(19)-H(19A)	109.1
C(20)-C(19)-H(19B)	109.1
C(18)-C(19)-H(19B)	109.1

H(19A)-C(19)-H(19B)	107.8
C(21)-C(20)-C(19)	117.6(7)
C(21)-C(20)-H(20A)	107.9
C(19)-C(20)-H(20A)	107.9
C(21)-C(20)-H(20B)	107.9
C(19)-C(20)-H(20B)	107.9
H(20A)-C(20)-H(20B)	107.2
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(1)-N(1)-C(2)	107.9(4)
C(1)-N(1)-C(4)	125.9(4)
C(2)-N(1)-C(4)	126.2(4)
C(1)-N(2)-C(3)	108.4(4)
C(1)-N(2)-C(14)	126.2(4)
C(3)-N(2)-C(14)	125.3(4)

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for ldmlh180511. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [\ h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12\ ]$

	U11	U22	U33	U23	U13	U12
C(1)	40(3)	28(3)	36(3)	1(2)	21(3)	0(2)
C(2)	41(3)	24(3)	41(3)	3(2)	19(3)	1(2)
C(3)	38(3)	24(2)	47(3)	5(2)	23(3)	3(2)
C(4)	41(3)	27(2)	30(3)	-1(2)	10(2)	2(2)
C(5)	47(3)	37(3)	41(3)	1(2)	20(3)	5(2)
C(6)	76(4)	35(3)	41(3)	6(2)	27(3)	-1(3)
C(7)	57(4)	45(3)	31(3)	0(2)	4(3)	1(3)
C(8)	43(3)	38(3)	38(3)	1(2)	9(3)	2(3)
C(9)	40(4)	63(4)	55(4)	-2(3)	3(3)	5(3)
C(10)	35(3)	77(5)	74(5)	-1(4)	16(4)	6(3)
C(11)	44(4)	65(4)	53(4)	0(3)	21(3)	10(3)
C(12)	37(3)	44(3)	38(3)	-3(2)	11(3)	6(2)
C(13)	42(3)	29(3)	42(3)	-3(2)	19(3)	5(2)
C(14)	34(3)	38(3)	32(3)	-6(2)	10(2)	-7(2)
C(15)	32(3)	42(3)	32(3)	-3(2)	8(2)	-1(2)
C(16)	39(3)	55(3)	40(3)	-5(3)	12(3)	-2(3)
C(17)	39(3)	54(3)	46(3)	4(3)	11(3)	-2(3)
C(18)	49(4)	71(4)	65(4)	11(3)	26(3)	8(3)
C(19)	57(4)	77(5)	90(5)	23(4)	42(4)	16(3)
C(20)	91(6)	150(8)	120(7)	64(6)	77(6)	47(6)
C(21)	99(7)	170(10)	96(7)	35(6)	50(6)	26(6)
N(1)	35(2)	27(2)	37(2)	-1(2)	15(2)	1(2)
N(2)	33(2)	31(2)	31(2)	-4(2)	14(2)	1(2)
Br(1)	61(1)	34(1)	38(1)	4(1)	19(1)	5(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ldmlh180511.

	x	y	z	U(eq)
H(1)	4596	5605	2652	39
H(2)	3802	1237	2726	41
H(3)	5016	1662	4288	41
H(5)	4049	4196	629	48
H(6)	2981	4652	-940	59
H(7)	1657	4392	-1111	58
H(9)	623	3912	-344	69
H(10)	328	3472	1058	76
H(11)	1365	3272	2667	64
H(12)	2713	3398	2857	49
H(14A)	5776	4470	5155	43
H(14B)	5777	5763	4339	43
H(15A)	6536	2747	4545	44
H(15B)	6528	4022	3717	44
H(16A)	7318	4453	5858	55
H(16B)	7298	5754	5041	55
H(17A)	8558	4370	5647	58
H(17B)	8084	2767	5226	58
H(18A)	8172	5318	3992	72
H(18B)	7676	3742	3561	72
H(19A)	9402	3952	4514	84
H(19B)	8928	2324	4172	84
H(20A)	8417	3188	2473	131
H(20B)	8903	4794	2819	131
H(21A)	10123	3406	3272	177
H(21B)	9569	3261	2091	177
H(21C)	9609	1842	2843	177

Table S6. Torsion angles [deg] for ldmlh180511.

N(1)-C(2)-C(3)-N(2)	-0.8(5)
C(13)-C(4)-C(5)-C(6)	-0.1(7)
N(1)-C(4)-C(5)-C(6)	179.0(4)
C(4)-C(5)-C(6)-C(7)	-2.5(7)
C(5)-C(6)-C(7)-C(8)	2.5(8)
C(6)-C(7)-C(8)-C(9)	179.1(5)
C(6)-C(7)-C(8)-C(13)	0.0(8)
C(7)-C(8)-C(9)-C(10)	-177.4(6)
C(13)-C(8)-C(9)-C(10)	1.7(9)
C(8)-C(9)-C(10)-C(11)	0.6(10)
C(9)-C(10)-C(11)-C(12)	-1.7(9)
C(10)-C(11)-C(12)-C(13)	0.5(8)
C(5)-C(4)-C(13)-C(12)	-176.2(5)
N(1)-C(4)-C(13)-C(12)	4.7(7)
C(5)-C(4)-C(13)-C(8)	2.5(7)
N(1)-C(4)-C(13)-C(8)	-176.6(4)
C(11)-C(12)-C(13)-C(4)	-179.6(5)
C(11)-C(12)-C(13)-C(8)	1.7(7)
C(7)-C(8)-C(13)-C(4)	-2.4(7)
C(9)-C(8)-C(13)-C(4)	178.4(5)
C(7)-C(8)-C(13)-C(12)	176.3(5)
C(9)-C(8)-C(13)-C(12)	-2.8(7)
N(2)-C(14)-C(15)-C(16)	179.2(4)
C(14)-C(15)-C(16)-C(17)	-178.6(4)
C(15)-C(16)-C(17)-C(18)	62.9(7)
C(16)-C(17)-C(18)-C(19)	-178.4(5)
C(17)-C(18)-C(19)-C(20)	175.5(7)
C(18)-C(19)-C(20)-C(21)	-179.1(8)
N(2)-C(1)-N(1)-C(2)	-0.7(5)
N(2)-C(1)-N(1)-C(4)	179.9(4)
C(3)-C(2)-N(1)-C(1)	0.9(5)
C(3)-C(2)-N(1)-C(4)	-179.6(4)
C(5)-C(4)-N(1)-C(1)	62.2(6)
C(13)-C(4)-N(1)-C(1)	-118.6(5)
C(5)-C(4)-N(1)-C(2)	-117.2(5)
C(13)-C(4)-N(1)-C(2)	62.0(6)
N(1)-C(1)-N(2)-C(3)	0.2(5)
N(1)-C(1)-N(2)-C(14)	177.3(4)
C(2)-C(3)-N(2)-C(1)	0.4(5)
C(2)-C(3)-N(2)-C(14)	-176.7(4)
C(15)-C(14)-N(2)-C(1)	-106.5(5)
C(15)-C(14)-N(2)-C(3)	70.1(6)

Table S7. Hydrogen bonds for ldmlh180511 [A and deg.] - Symmetry transformations used to generate equivalent atoms: #1 x,y-1,z #2 -x+1,-y+1,-z+1 #3 -x+1,y-1/2,-z+1/2.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1)...Br(1)	0.95	2.78	3.383(5)	122.4
C(2)-H(2)...Br(1)#1	0.95	2.78	3.463(4)	129.1
C(3)-H(3)...Br(1)#2	0.95	2.90	3.648(5)	136.2
C(5)-H(5)...Br(1)#3	0.95	3.00	3.878(5)	154.0
C(14)-H(14A)...Br(1)#2	0.99	2.97	3.747(5)	136.6
C(15)-H(15B)...Br(1)#3	0.99	3.03	3.920(5)	149.9

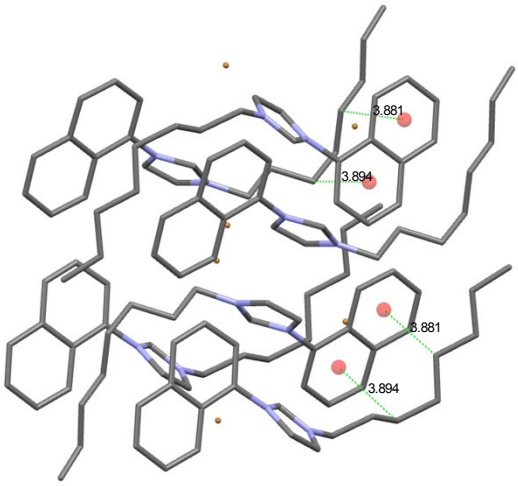

Figure S6 - ORTEP View, Capped stick view of assembly of molecules of 3a in the packing showing the naphtalene groups "sandwiched" by the alkyl chains and vice-versa the alkyl chains "sandwiched" by the napthalene cores. The shortest distances between the centroids Cg1 and Cg2 and the alkyl chain are represented. H-atoms are omitted for clarity.

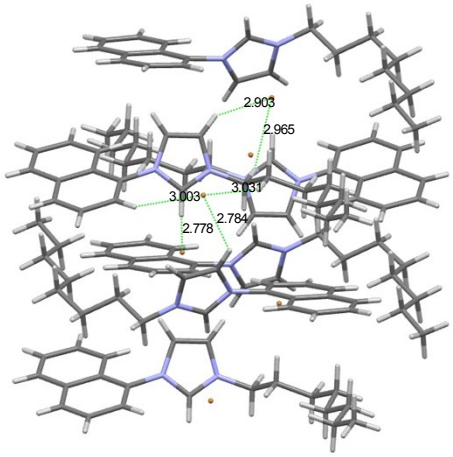

Figure S7 - ORTEP View, Capped stick view of the packing of 3a showing the CH weak interactions with bromide anions and distance values.

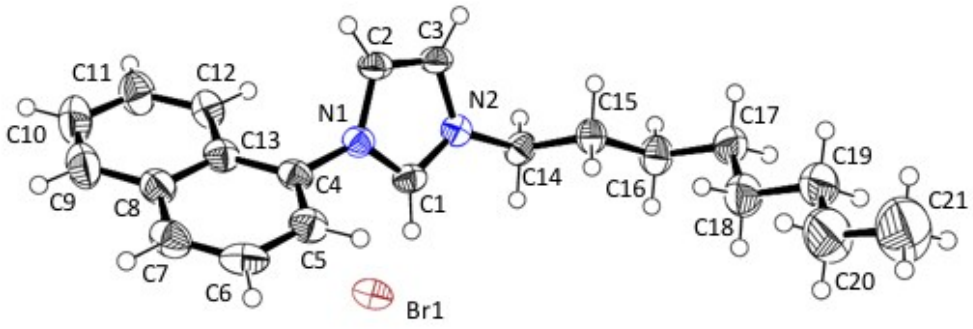

Figure S8 - ORTEP View of compound 3a with labelling scheme. The ellipsoids are drawn with 50% probability.

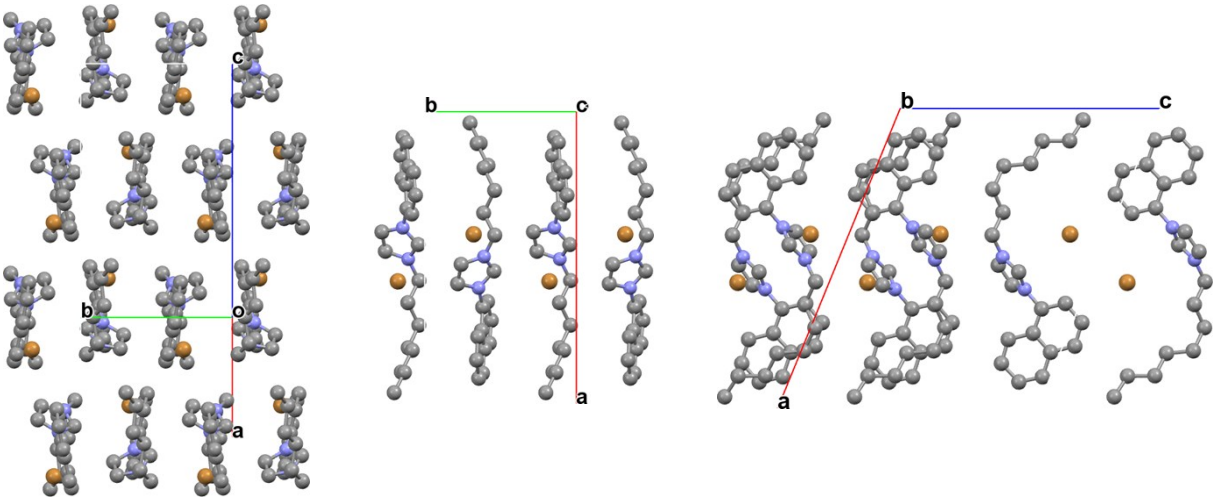

*Figure S9 - self-assembly of **3a** in the crystal phase, left: molecular layer parallel to the **b**×**c** plane, constituted by rows aligned on b-axis and superposed along c-axis; middle: row viewed from side (along c-axis) with head-to-tail association of molecules into acentral ionic ribbon and in two side-ribbons of intercalated naphthyl and alkyl substituents (spacing of molecules within the row: b/2 = 4.263 Å); right: view along b-axis of the successive staggered rows (spacing of rows: c/2 = 7.133 Å), which design an ionic double-layer and intercalated layers of strongly tilted substituents (tilt angles from layer normal: 58° for chains and 47° for naphthalene).*

Excitation & Emission

The molar attenuation coefficient ε (L.mol^{-1}.cm^{-1}) were calculated at the maximum absorbance wavelength λ_{max} (nm) and are reported in table **1**. All materials present luminescent properties, as such their fluorescent quantum yields were determined with a Hamamatsu absolute PL quantum Yield spectrometer (C11347).

Steady-state emission spectra were recorded on a Horiba Jobin−Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation, and emission monochromators (2.1 nm mm−1 of dispersion; 1200 grooves mm−1) and a TBX-04 single photon-counting detector. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Photoluminscence quantum yields measurements were performed by using an integrated sphere, Quantaurus C11347 (Hamamatsu, Japan) exciting the sample at λexc between 260 and 350 nm.

Time-resolved measurements were performed using the time-correlated single-photon-counting (TCSPC) PicoHarp300 or the Multi-Channel Scaling (MCS) electronics NanoHarp 250 of the PicoQuant FluoroTime 300 (PicoQuant GmbH, Germany), equipped with a PDL 820 laser pulse driver. A pulsed laser diode was used to excite the sample and mounted directly on the sample chamber at 90°. The photons were collected by a PMA-C-192 photomultiplier(PMT) single-photon-counting detector. The data were acquired by using the commercially available software EasyTau (PicoQuant GmbH, Germany), while data analysis was performed using the commercially available software FluoFit (PicoQuant GmbH, Germany).

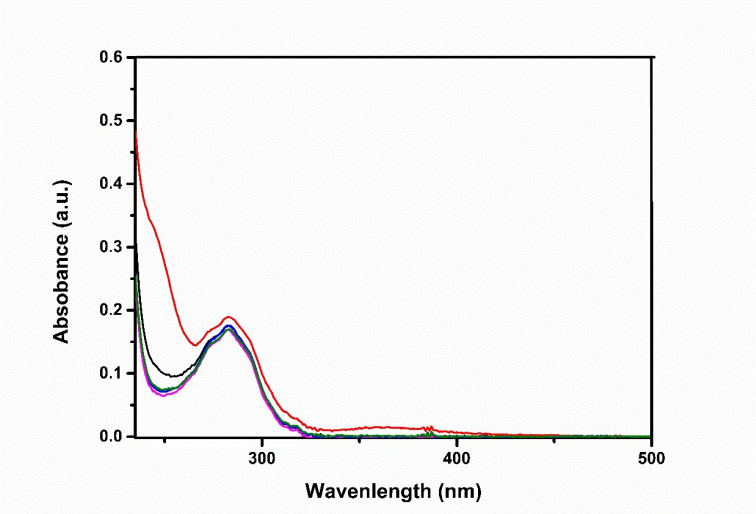

*Figure S10 - Absorption spectra of compounds **3a** (black line), **3b** (red line), **3c** (blue line), **3d** (pink line), and **3e** (green line) in dichloromethane ($2 \cdot 10^{-5}$M).*

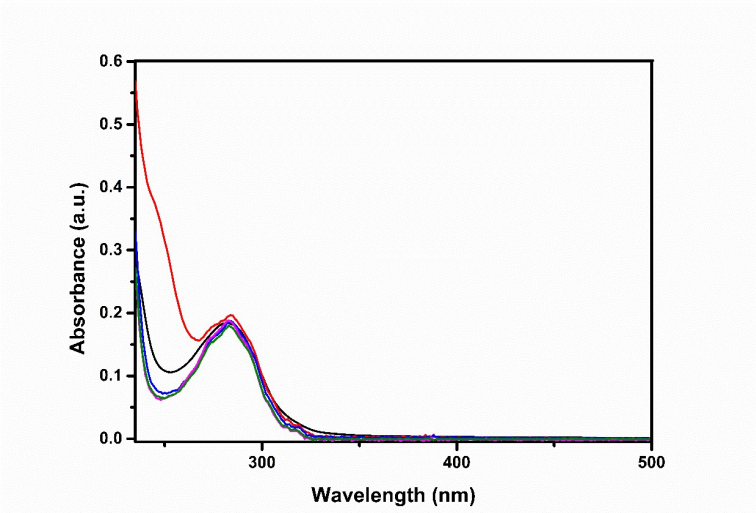

*Figure S11 - Absorption spectra of compounds **4a** (black line), **4b** (red line), **4c** (blue line), **4d** (pink line), and **4e** (green line) in dichloromethane ($2 \cdot 10^{-5}$M).*

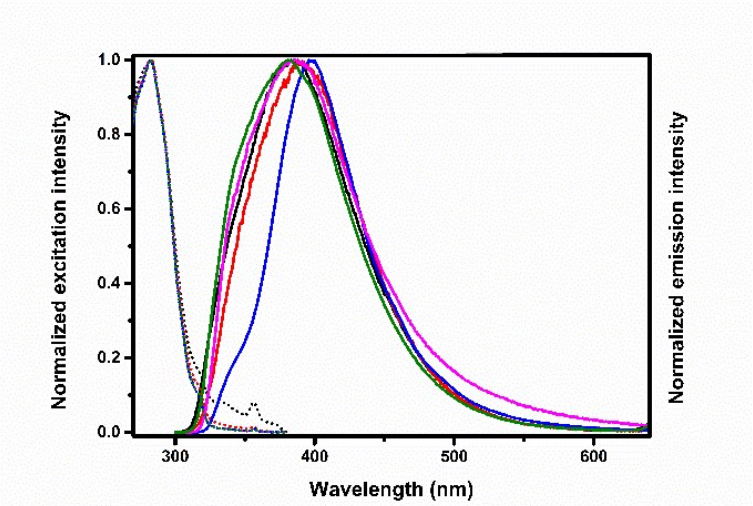

*Figure S12 - Excitation (dotted lines, λ_{Em} = 400 nm) and emission (full lines, λ_{Exc} = 280 nm) of **3a** (black line), **3b** (red line), **3c** (blue line), **3d** (pink line) and **3e** (green line) in solution (dichloromethane, 10^{-5}M)*

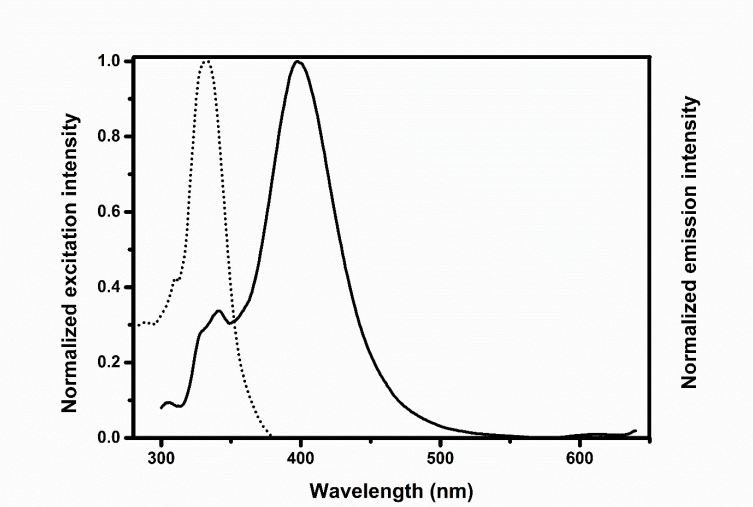

*Figure S13 - Excitation (dotted lines, λ_{Em} = 400 nm) and emission (full lines, λ_{Exc} = 280 nm) of **3a** in neat state, i.e. without solvent.*

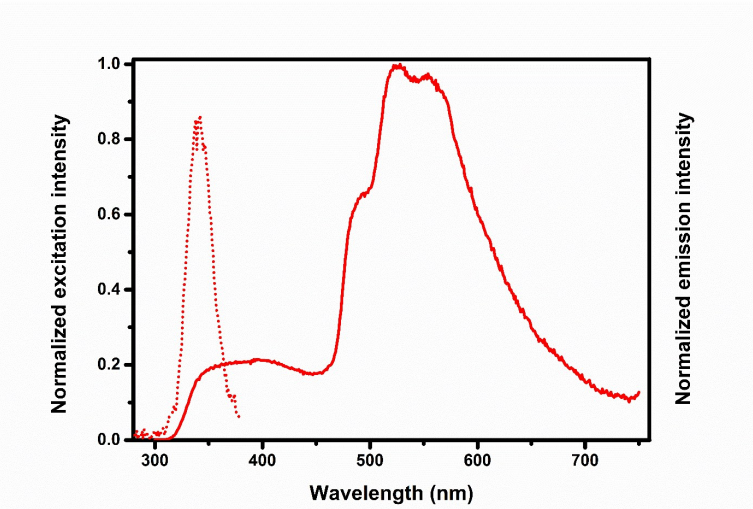

*Figure S14 - Excitation (dotted lines, λ_{Em} = 400 nm) and emission (full lines, λ_{Exc} = 280 nm) of **3b** in neat state, i.e. without solvent.*

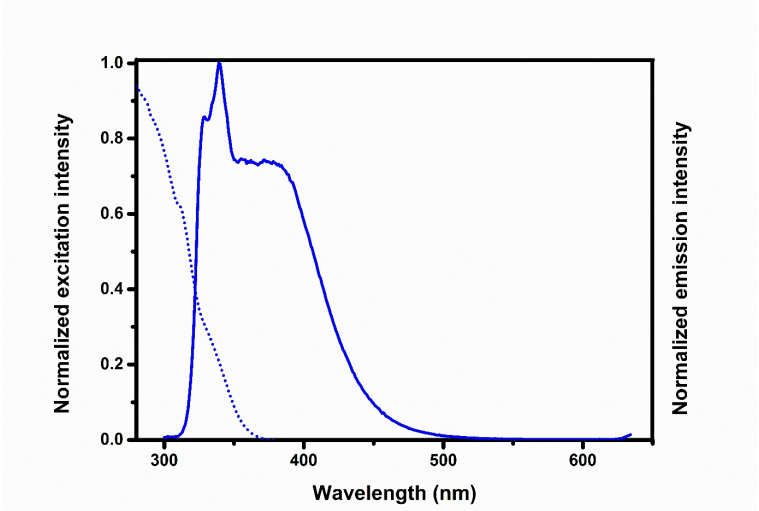

*Figure S15 - Excitation (dotted lines, λ_{Em} = 400 nm) and emission (full lines, λ_{Exc} = 280 nm) of **3c** in neat state, i.e. without solvent.*

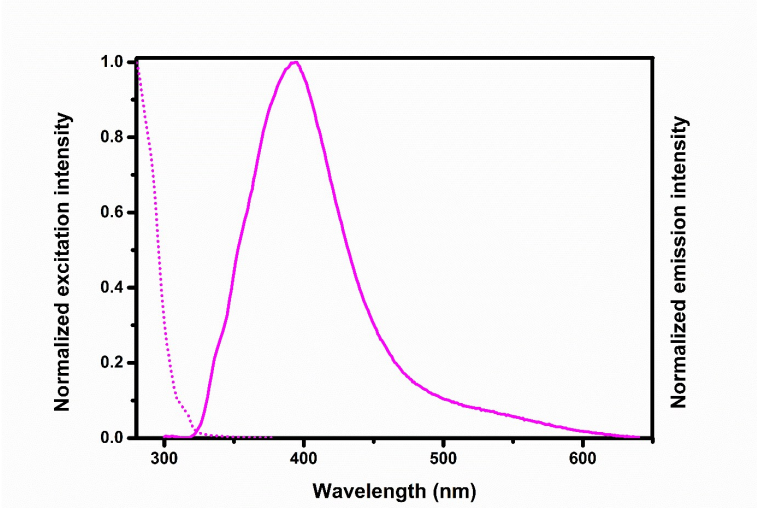

*Figure S16 - Excitation (dotted lines, λ_{Em} = 400 nm) and emission (full lines, λ_{Exc} = 280 nm) of **3d** in neat state, i.e. without solvent.*

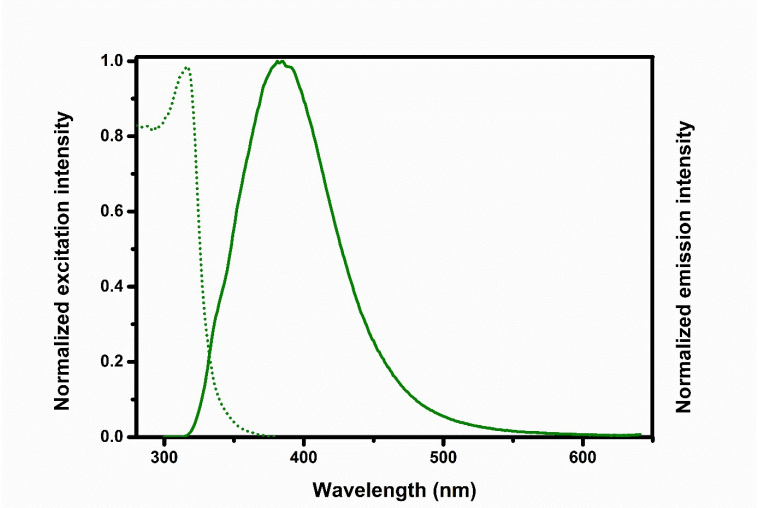

*Figure S17 - Excitation (dotted lines, λ_{Em} = 400 nm) and emission (full lines, λ_{Exc} = 280 nm) of **3e** in neat state, i.e. without solvent.*