Towards Room-Temperature Ionic Liquid Crystals

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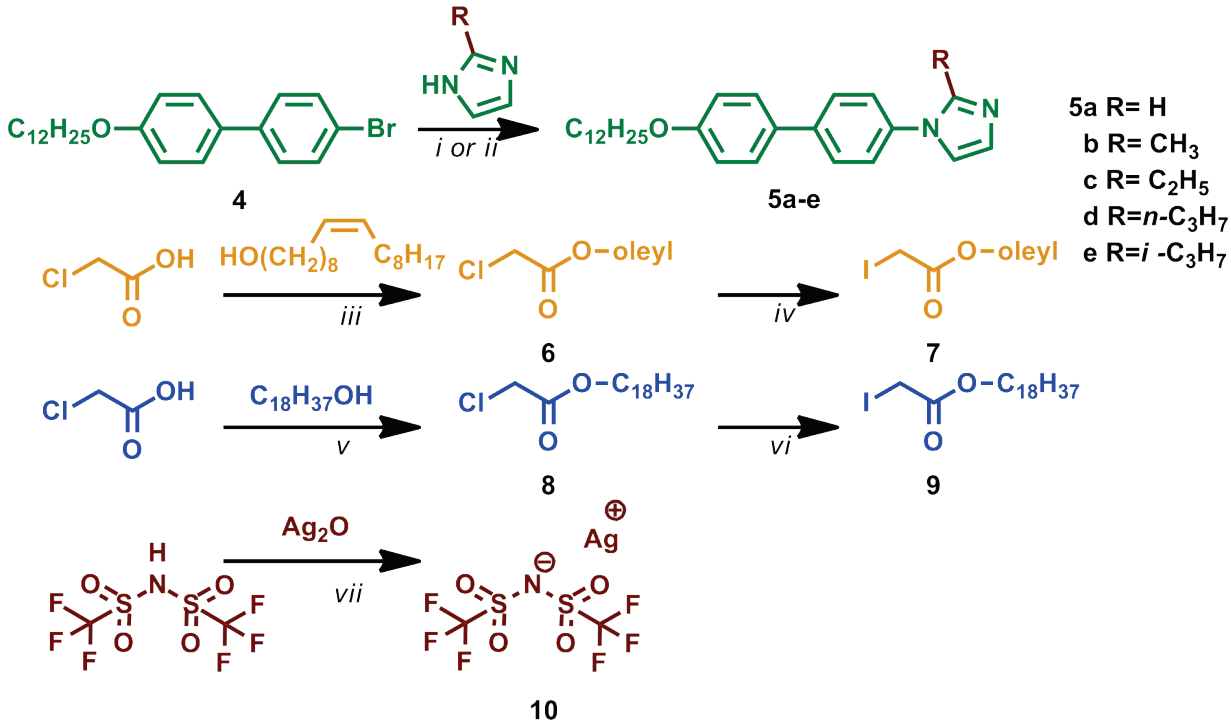
^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 (400 MHz) and a Bruker AC-300 (300 MHz) spectrometer. Spectra were recorded in $CDCl_3$. Chemical shifts are reported in ppm referenced against TMS, which was added as an internal reference. Optical microscopy was carried out on an Olympus BX60 microscope equipped with a Mettler FP82HT hot stage and digital camera using standard glass microscope slides. DSC experiments were performed on a TA Instruments DSC Q100.
HRMS (EI) measurements of ILC belonging to serie 1, were performed on a JEOL Accu TOF-CS instrument using acetonitrile as solvent.

Scheme S1: Synthesis of starting materials and ILC precursors

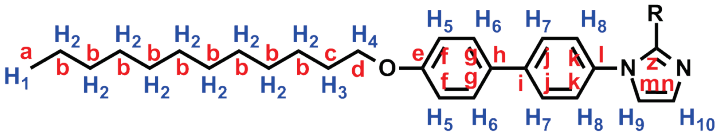


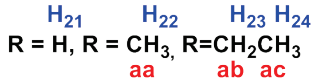
Key: (*i*) K_2CO_3, CuI, *N,N*-dimethylglycine, DMSO, 48-72 hrs at 110ºC; (*ii*) Cs_2CO_3, Cu_2O, 4,7-dimethoxy-1,10-phenanthroline, NMP, 110°C, 5 days reflux; (*iii, v*) PTSA, Toluene, 24 hrs, reflux; (*iv, vi*) NaI, acetone, rt, 8hrs; (*vii*) Ag_2O, toluene, reflux over night

*Synthesis of ILC precursors general procedure (***scheme S1, step *i, ii)***

ILC precursors 5a-5c

General procedure: 4-Bromo-4'-(dodecyloxy)-1,1'-biphenyl[1] (**4**) (1.82 mmol), imidazole , 2-methyl imidazole or 2-ethyl imidazole (3.38 mmol), CuI (0.19 mmol), dimethyl glycine (0.38 mmol), and K_2CO_3 (7.09 mmol), were stirred in 6 ml DMSO for 4 days at 110 ^{0}C. The crude product was precipitated in 500 ml of 1M NH_3 solution, extracted with CH_2Cl_2 and purified via column chromatography (SiO_2) using CH_2Cl_2/heptane 1:1 as the eluent to remove the starting material. To afford the final product, the polarity of the CH_2Cl_2 was increased from 0 →10% MeOH. Yield (**5a**): 62%, (**5b**): 64%, (**5c**): 60% yellow solid.





5a

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.89 (s, 1H, *H*$_{21}$), 7.64 (m, 2H, *H*$_8$), 7.52 (m, 2H, *H*$_6$), 7.43 (m, 2H, *H*$_7$), 7.31 (s, 1H, *H*$_9$ or *H*$_{10}$), 7.23 (s, 1H, *H*$_9$ or *H*$_{10}$), 6.99 (m, 2H *H*$_5$), 4.01 (t, 2H, J=6.6Hz, *H*$_4$), 1.77 (m, 2H, *H*$_3$), 1.40 (m, 18H, *H*$_2$), 0.90 (m, 3H, *H*$_1$). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 159.19 (e), 142.93 (l), 136.04 (z), 132.05 (i), 130.34 (h), 127.82 (g or j), 127.79 (g or j), 126.04 (k), 123.11 (m or n), 121.55 (m or n), 114.65 (f), 67.72 (d), 31.44 - 24.52 (b) , 13.65 (a).

5b

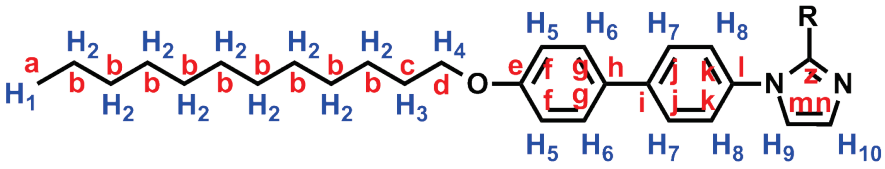
^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.64 (m, 2H, *H*$_8$), 7.54 (m, 2H, *H*$_6$), 7.33 (m, 2H, *H*$_7$), 7.05 (d, 1H, J=1.4Hz, *H*$_9$ or *H*$_{10}$), 7.04 (d, 1H, J=1.4Hz, *H*$_9$ or *H*$_{10}$), 7.00 (m, 2H, *H*$_5$), 4.02 (t, 2H, J=6.6Hz, *H*$_4$), 2.40 (s, 3H, *H*$_{22}$), 1.82 (m, 2H, *H*$_3$), 1.36 (m, 18H, *H*$_2$), 0.92 (m, 3H, *H*$_1$). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 159.22 (e), 146.06 (z), 143.48 (l), 132.13 (i), 130.53 (h), 127.82 (g or j), 127.79 (g or j), 126.04 (k), 123.11 (m or n), 121.55 (m or n), 114.65 (f), 67.72 (d), 31.43-24.52 (b), 13.65 (a), 12.45 (aa).

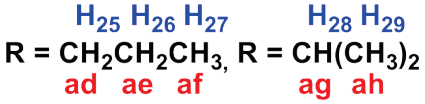
5c

7.75 (m, 3H, *H*$_8$ + *H*$_9$ *or* *H*$_{10}$), 7.69 (m, 2H, *H*$_7$), 7.54 (m, 2H, *H*$_6$), 7.30 (t, 1H, J=2.1Hz, *H*$_9$ *or* *H*$_{10}$), 7.01 (m, 2H, *H*$_5$), 4.01 (t, 2H, J_3=6.6Hz, *H*$_4$), 3.15 (q, 2H, J=7.7Hz, *H*$_{23}$), 1.71 (q, 2H, J=6.8Hz, *H*$_3$), 1.39 (m, 18H, *H*$_2$), 1.13 (t, 3H, J=7.7Hz, *H*$_{24}$), 0.89 (t, 3H, J=6.9Hz, *H*$_1$). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 159.27 (e), 149.78 (z), 143.64 (l), 132.13 (i), 130.44 (h), 127.82 (g + j), 126.07 (k), 123.15 (m or n), 121.97 (m or n), 114.67 (f), 67.74 (d), 31.44 - 24.51 (b), 19.14 (ab), 13.65 (a), 11.01 (ac).

ILC precursors 5d-5e:

General procedure: 4-bromo-4'-(dodecyloxy)-1,1'-biphenyl[1] (**4**) (8.61 mmol), propyl imidazole or 2-isopropyl imidazole (16.8 mmol), Cu_2O (0.57 mmol), 4,7-dimethoxy-1,10-phenanthroline[2] (0.9 mmol), and Cs_2CO_3 (12.5 mmol), stirred in 10 ml of *N*-methylpyrrolidone (NMP), 110^{o}C, for 5 days. The crude product was precipitated in 500 ml of 1M NH_3 solution, extracted with CH_2Cl_2 and purified via column chromatography (SiO_2) by following the same procedure for precursors **5a-5c**. Yield **(5d)** 68% **(5e)** (37%) of a tan solid.





5d

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.64 (m, 2H, H_8), 7.55 (m, 2H, H_6), 7.32 (m, 2H, H_7), 7.08 (d, 1H, J=1.2Hz, H_9 or H_{10}), 7.00 (m, 3H, H_5 + H_9 or H_{10}), 4.01 (t, 2H, J=6.6Hz, H_4), 2.65 (m, 2H, H_{25}), 1.77 (m, 4H, H_3 + H_{26}), 1.40 (m, 18H, H_2), 0.90 (m, 6H, H_1 + H_{27}). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 159.27 (e), 148.81 (z), 143.59 (l), 132.22 (i), 130.42 (h), 127.82 (g or j), 127.78 (g or j), 126.16 (k), 123.15 (m or n), 122.01 (m or n), 114.67 (f), 67.74 (d), 31.44-24.51 (b + ae), 20.28 (ad), 13.64 (a), 13.36 (af)

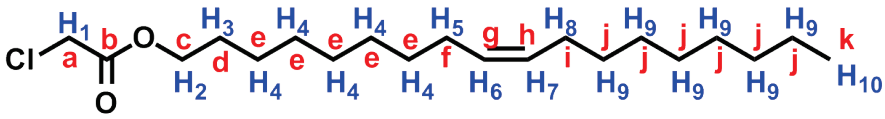
5e

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.63 (m, 2H, H_8), 7.53 (m, 2H, H_6), 7.30 (m, 2H, H_7), 7.07 (d, 1H, J=1.2Hz, H_9 or H_{10}), 6.99 (m, 2H, H_5), 6.94 (d, 1H, J=1.3Hz, H_9 or H_{10}), 4.00 (t, 2H, J=6.7Hz, H_4), 3.02 (m, 1H, H_{28}), 1.80 (m, 2H, H_3), 1.37 (m, 24H, H_2 + H_{29}), 0.88 (t, 3H, J=6.9Hz, H_1). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 159.35 (e), 150.82 (z), 143.95 (l), 132.37 (i), 130.29 (h), 127.83 (g or j), 127.55 (g or j), 126.86 (k), 124.03 (m or n), 122.79 (m or n), 114.70 (f), 67.75 (d), 31.43-24.51 (b), 19.81 (ag), 13.64 (ah+a).

Synthesis of starting materials

Oleyl chloroacetic acid (6) - (scheme S1, step *iii*)

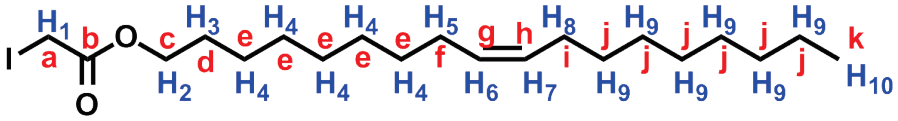
Oleyl alcohol (technical grade: apprx. 85% cis and 15% trans) (32 mmol) and 2-chloroacetic acid (40 mmol) were dissolved in 100 ml toluene. A catalytic amount of *para*-toluene sulfonic acid was added, the mixture was refluxed overnight while water was removed using a Dean-Stark trap. The solvent was removed via rotary evaporation and 100 ml hexane was added to the resulting mixture. The solution was washed (x3) with a saturated $NaHCO_3$ solution, dried over magnesium sulfate and the solvent was removed via rotary evaporation. Yield: 90%.^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 5.34 (m, 2H, H_6 + H_7), 4.35 (s, 2H, H_1), 4.13 (t, 2H, J=6.7Hz, H_2), 1.99 (m, 4H, H_5 + H_8), 1.65 (m, 2H, H_3), 1.32 (m, 22H, H_4 + H_9), 0.88 (t, 3H, J=6.3Hz, H_{10}). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 168.38 (b), 129.51 (g or h), 129.29 (g or h), 65.77 (c), 59.16 (a), 32.13-22.21 (e + j), 13.64 (k).



Oleyl iodoacetic acid (7) - (scheme S1, step *iv*)

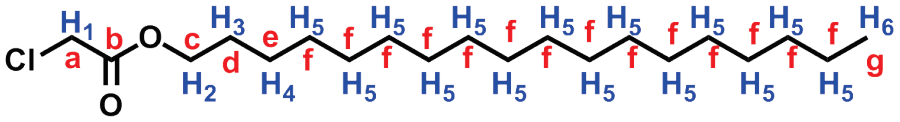
A mixture of NaI (100 mmol) and compound **6** (60 mmol) was stirred in acetone (50 ml) overnight at room temperature and protected from the light. The solution was filtered and the solvent was removed via rotary evaporation. The resulting oil was dissolved in heptane,

washed (x2) with aqueous $Na_2S_2O_5$ and (x2) with water, and dried over magnesium sulfate. The product was purified via column chromatography (SiO_2) using CH_2Cl_2/heptane 1:1 as the eluent. The solvent was removed via rotary evaporation yielding a clear oil. Yield: 99%. ^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 5.34 (m, 2H, H_6 + H_7), 4.13 (t, 2H, J=6.7Hz, H_2), 3.68 (s, 2H, H_1), 1.99 (m, 4H, H_5 + H_8), 1.65 (m, 2H, H_3), 1.32 (m, 22H, H_4 + H_9), 0.88 (t, 3H, J=6.3Hz, H_{10}). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 168.38 (b), 129.51 (g or h), 129.29 (g or h), 65.77 (c), 32.13-22.21 (e + j), 15.23 (a), 13.64 (k).



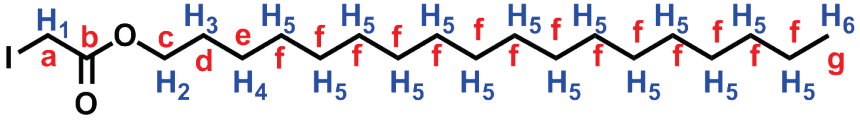
Octadecyl chloroacetic acid (8) - (scheme S1, step *v*)

Octadecanol (32 mmol) and 2-chloroacetic acid (40 mmol) were dissolved in 100 ml of toluene. The reaction was set it up and the crude product purified following the same procedure given (***step iii***). Yield: 92%.^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 4.35 (s, 2H, H_1), 4.17 (t, 2H, J=6.7Hz, H_2), 1.63 (m, 2H, H_3), 1.38 (m, 30H, H_4+H_5), 0.88 (t, 3H, J=6.3Hz, H_6). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 168.38 (b), 65.77 (c), 59.21 (a), 32.13-22.21 (e + f), 13.64 (g).



Octadecyl iodoacetic acid (9) - (Scheme S1, step *vi*)

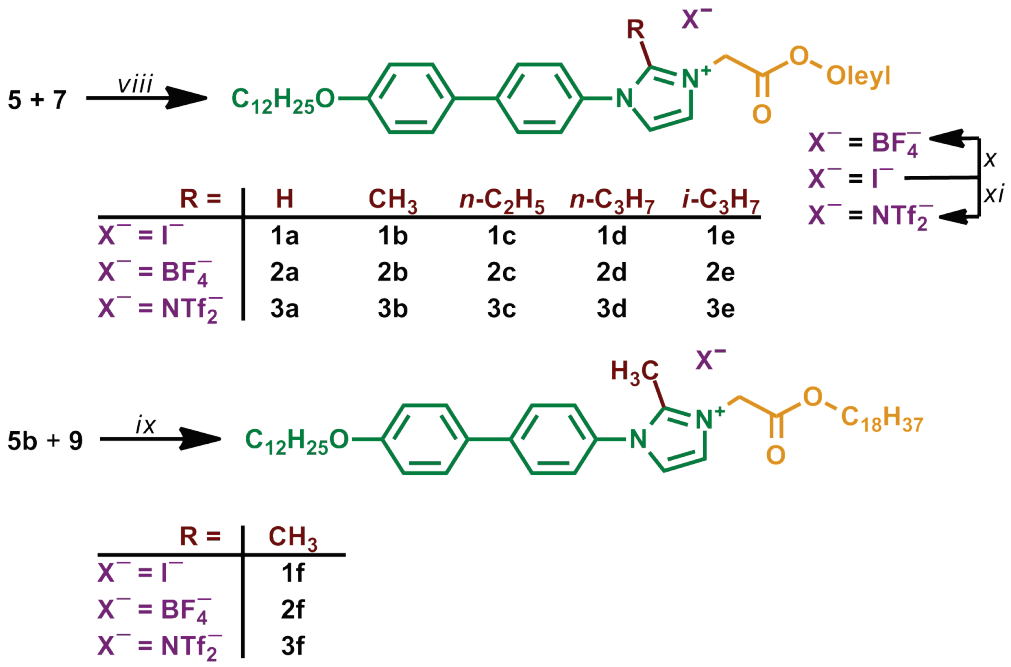
A mixture of NaI (100 mmol) and compound **8** (60 mmol) was stirred in acetone (50 ml) The reaction was set it up and the crude product purified following the same procedure given (***step iv***). Yield: 95%. ^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 4.17 (t, 2H, J=6.7Hz, H_2), 3.66 (s, 2H, H_1), 1.63 (m, 2H, H_3), 1.38 (m, 30H, H_4+H_5), 0.88 (t, 3H, J=6.3Hz, H_6). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 168.38 (b), 65.77 (c), 32.13-22.21 (e + f), 15.23 (a), 13.64 (g).



Synthesis of $AgNTf_2$ (10) - (Scheme S1, step *vii*)

$HNTf_2$ (12.6 mmol) and Ag_2O (6.3 mmol) were dissolved in 50 ml toluene. The mixture was refluxed overnight and water was removed using a Dean-Stark trap. The solution was concentrated, filtrated and the solvent was removed via rotary evaporation. The resulting brown powder was dissolved in ether and precipitated in $CHCl_3$. The precipitate was collected via filtration, washed with $CHCl_3$, and dried in vacuum to obtain the product as a white powder. Yield: 59%.

Scheme S2: Synthesis of ILC and ion exchange



R =	H	CH_3	*n*-C_2H_5	*n*-C_3H_7	*i*-C_3H_7
$X^- = I^-$	1a	1b	1c	1d	1e
$X^- = BF_4^-$	2a	2b	2c	2d	2e
$X^- = NTf_2^-$	3a	3b	3c	3d	3e

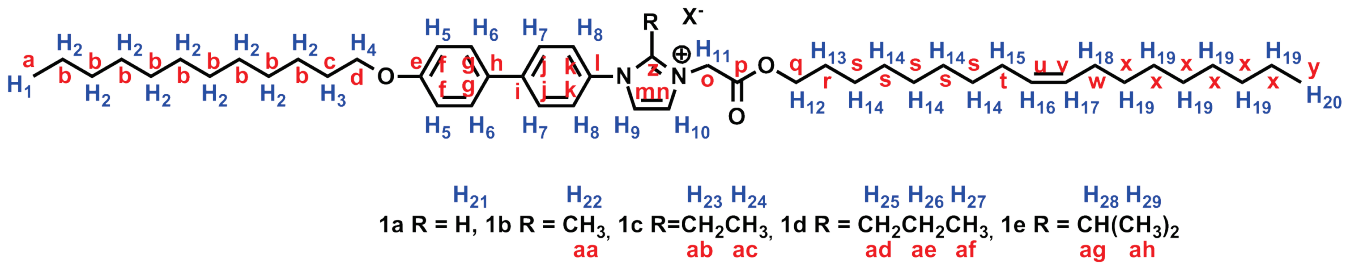
R =	CH_3
$X^- = I^-$	1f
$X^- = BF_4^-$	2f
$X^- = NTf_2^-$	3f

(viii) toluene, 100 °C, 10hrs; (ix) $NaBF_4$ (aq) multiple washes; (vii) $AgNTf_2$, methanol.

Synthesis of ILC: serie 1

Alkylation reaction with oleyl iodide: ILC (1a-1e) -General procedure (Scheme S2, step *viii*)

About 200 mg (~0.5 mmol) of the ILC precursor (**5a-5e**) and an excess (1.5 eq.) of the iodoacetic ester (compound **7**) were stirred in a Schlenk tube under argon atmosphere. Toluene (3 mL) was added and the mixture was stirred for 12 hours at 80 °C (compounds **1a, 1b**) or 100 °C (compounds **1c-1e**). The mixture was precipitated in heptane and separated by centrifugation and decantation. The solids were dissolved in CH_2Cl_2 and washed with aqueous $Na_2S_2O_5$ (x2), water (x2) and concentrated NaI (x1), dried ($MgSO_4$) and the solvent was evaporated. The crude product was precipitated in pentane from CH_2Cl_2 (x3) and purified via column chromatography (SiO_2) using CH_2Cl_2 as the eluent to remove the starting material. To afford the final product the polarity of the mobile phase was gradually increased from 0 → 10% methanol.



ILC 1a

Yield: 80% ^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 10.72 (m, 1H, *H_{21}*), 7.80 (m, 2H, *H_8*), 7.76 (m, 2H, *H_7*), 7.54 (m, 1H, *H_9 or H_{10}*), 7.53 (m, 2H, *H_6*), 7.48 (m, 1H, *H_9 or H_{10}*), 7.00 (m, 2H, *H_5*), 5.64 (s, 2H, *H_{11}*), 5.36 (m, 2H, *H_{16}+H_{17}*), 4.26 (t, 2H, J_3=6.8Hz, *H_{12}*), 4.01 (t, 2H, J_3=6.6Hz, *H_4*), 2.00 (m, 4H, *H_{15}+H_{18}*), 1.82 (t, 2H, J_3=6.8Hz, *H_{13}*), 1.71 (t, 2H, J_3=7.3Hz, *H_3*), 1.40 (m, 40H, *H_2+H_{14}+H_{19}*), 0.88 (m, 6H, *H_1+H_{20}*). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.39 (p), 159.19 (e), 142.93 (l), 136.04 (z), 132.05 (i), 130.34 (h), 129.50 (u or v), 129.28 (u or v), 128.01 (g or j), 127.71 (g or j), 123.97 (m or n), 121.96 (k), 119.69 (m or n), 114.63 (f), 67.72 (d), 66.87 (q), 50.63 (o), 31.44 - 22.22 (b + s + x) , 13.65 (a + y).
HRMS (EI) m/z calcd. $C_{47}H_{73}N_2O_3^+$ (cation): 713.56212, found 713.56051

ILC 1b

Yield: 77% ^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.92 (m, 1H, *H_9* or *H_{10}*), 7.72 (m, 2H, *H_8*), 7.64 (m, 2H, *H_7*), 7.51 (m, 2H, *H_6*), 7.35 (m, 1H, *H_9 or H_{10}*), 6.99 (m, 2H, *H_5*), 5.47 (s, 2H, *H_{11}*), 5.33 (m, 2H, *H_{16}+H_{17}*), 4.23 (t, 2H, J=6.9Hz, *H_{12}*), 4.00 (t, 2H, J=6.6Hz, *H_4*), 2.75 (s, 3H, *H_{22}*), 1.98 (m, 4H, *H_{15}+H_{18}*), 1.80 (p, 2H, J=6.5, *H_{13}*), 1.68 (m, 2H, *H_3*), 1.38 (m, 40H, *H_2+H_{14}+H_{19}*), 0.91 (m, 3H, *H_1 + H_{20}*), 0.86 (t, 3H, J=6.9Hz, *H_1* or *H_{20}*). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.61 (p), 159.22 (e), 146.06 (z), 143.48 (l), 132.13 (i), 130.53 (h), 129.52 (u or v), 129.26 (u or v), 127.82 (g or j), 127.79 (g or j), 126.04 (k), 123.11 (m or n), 121.55 (m or n), 114.65 (f), 67.72 (d), 66.67 (q), 50.69 (o), 31.43-22.13 (b + s + x), 13.65 (a or y), 13.56 (a or y), 12.45 (aa).
HRMS (EI) m/z calcd. $C_{48}H_{75}N_2O_3^+$ (cation): 727.58387, found 727.58175

ILC 1c

Yield: 82% ^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.75 (m, 3H, *H_8 + H_9 or H_{10}*), 7.69 (m, 2H, *H_7*), 7.54 (m, 2H, *H_6*), 7.30 (t, 1H, J=2.1Hz, *H_9 or H_{10}*), 7.01 (m, 2H, *H_5*), 5.43 (d, 2H, J=3.6Hz, *H_{11}*), 5.36 (m, 2H, *H_{16}+H_{17}*), 4.26 (t, 2H, J=6.8Hz, *H_{12}*), 4.02 (t, 2H, J=6.6Hz, *H_4*), 3.15 (q, 2H, J=7.7Hz, *H_{23}*), 2.01 (m, 4H, *H_{15}+H_{18}*), 1.82 (q, 2H, J=6.7Hz, *H_{13}*), 1.71 (q, 2H, J=6.8Hz, *H_3*), 1.39 (m, 40H, *H_2+H_{14}+H_{19}*), 1.13 (t, 3H, J=7.7Hz, *H_{24}*), 0.89 (t, 3H, J=6.9Hz, *H_1 or H_{20}*), 0.88 (t, 3H, J=6.9Hz, *H_1 or H_{20}*). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.86 (p), 159.27 (e), 149.78 (z), 143.64 (l), 132.13 (i), 130.44 (h), 129.53 (u or v), 129.26 (u or v), 127.82 (g + j), 126.07 (k), 123.15 (m or n), 121.97 (m or n), 114.67 (f), 67.74 (d), 66.71(q), 50.61 (o), 31.44 -22.21 (b + s + x), 19.14 (ab), 13.65 (a + y), 11.01 (ac).
HRMS (EI) m/z calcd. $C_{49}H_{77}N_2O_3^+$ (cation): 741.59342 found 741.59071

ILC 1d

Yield: 83% ^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.75 (d, 1H, J=2.1Hz, *H_9 or H_{10}*), 7.74 (m, 2H, *H_8*), 7.67 (m, 2H, *H_7*), 7.54 (m, 2H, *H_6*), 7.30 (d, 1H, J=2.2Hz, *H_9 or H_{10}*), 7.01 (m, 2H, *H_5*), 5.39 (s, 2H, *H_{11}*), 5.34 (m, 2H, *H_{16}+H_{17}*), 4.25 (t, 2H, J=6.8Hz, *H_{12}*), 4.01 (t, 2H, J=6.6Hz, *H_4*), 3.09 (m, 2H, *H_{25}*), 1.99 (m, 4H, *H_{15}+H_{18}*), 1.81 (m, 2H, *H_{13}*), 1.70 (m, 2H, *H_3*), 1.42 (m, 42H, *H_2+H_{14}+H_{19}+H_{26}*), 0.87 (m, 9H, *H_1+H_{20}+H_{27}*). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.84 (p), 159.27 (e), 148.81 (z), 143.59 (l), 132.22 (i), 130.42 (h), 129.54 (u or v),

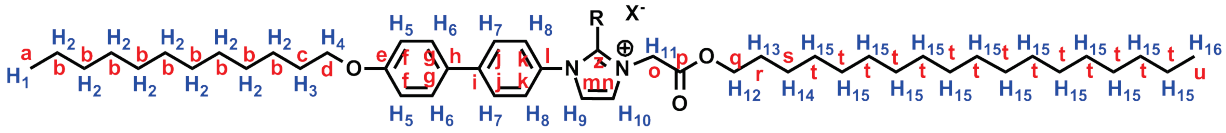
129.25 (u or v), 127.82 (g or j), 127.78 (g or j), 126.16 (k), 123.15 (m or n), 122.01 (m or n), 114.67 (f), 67.74 (d), 66.69 (q), 50.61 (o), 31.44-22.21 (b + s + x + ae), 20.28 (ad), 13.64 (a + y), 13.36 (af).
HRMS (EI) m/z calcd. $C_{50}H_{79}N_2O_3^+$ (cation): 755.60907, found 755.60708

ILC 1e

Yield: 60% ^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.87 (d, 1H, J=2.2Hz, *H_9 or H_{10}*), 7.75 (m, 2H, *H_8*), 7.59 (m, 2H, *H_7*), 7.55 (m, 2H, *H_6*), 7.20 (d, 1H, J=2.2Hz, *H_9 or H_{10}*), 7.02 (m, 2H, *H_5*), 5.52 (s, 2H, *H_{11}*), 5.36 (m, 2H, *H_{16}+H_{17}*), 4.27 (t, 2H, J=6.8Hz, *H_{12}*), 4.02 (t, 2H, J=6.6Hz, *H_4*), 3.38 (m, 1H, *H_{28}*), 2.00 (m, 4H, *H_{15}+H_{18}*), 1.82 (m, 2H, *H_{13}*), 1.72 (m, 2H, *H_3*), 1.40 (m, 40H, *H_2+H_{14}+H_{19}*), 1.36 (d, 6H, J=7.2Hz, *H_{29}*), 0.88 (t, 6H, J=6.9Hz, *H_1+H_{20}*). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.88 (p), 159.35 (e), 150.82 (z), 143.95 (l), 132.37 (i), 130.29 (h), 129.55 (u or v), 129.26 (u or v), 127.83 (g or j), 127.55 (g or j), 126.86 (k), 124.03 (m or n), 122.79 (m or n), 114.70 (f), 67.75 (d), 66.80 (q), 50.81 (o), 31.43-22.21 (b + s + x), 19.81 (ag), 13.64 (ah+a).
HRMS (EI) m/z calcd. $C_{50}H_{79}N_2O_3^+$ (cation): 755.60907, found 755.60681

Alkylation reaction with octadecyl iodide: **ILC 1f (Scheme S2, step *ix*)**

About 200 mg of the ILC precursor (**5b**) and an excess of 2-iodoacetic octadecane (0.77 mmol), (compound **9**), were stirred in 3 ml of toluene. The reaction was set it up and the crude product purified by following the procedure given (***step viii***).



1f R = CH_3,

ILC 1f

Yield: 80% ^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.92 (m, 1H, *H_9* or *H_{10}*), 7.72 (m, 2H, *H_8*), 7.64 (m, 2H, *H_7*), 7.51 (m, 2H, *H_6*), 7.35 (m, 1H, *H_9 or H_{10}*), 6.99 (m, 2H, *H_5*), 5.54 (s, 2H, *H_{11}*), 4.25 (t, 2H, J=6.9Hz, *H_{12}*), 4.01 (t, 2H, J=6.6Hz, *H_4*), 2.75 (s, 3H, *H_{17}*), 1.68 (m, 2H, *H_3*), 1.63 (m, 2H, *H_{13}*)1.38 (m, 48H, *H_{14}+H_{15}+H_2*), 0.86 (t, 6H, J=6.9Hz, *H_{16}+H_1*). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.61 (p), 159.22 (e), 146.06 (z), 143.48 (l), 132.13 (i), 130.53 (h), 127.82 (g or j), 127.79 (g or j), 126.04 (k), 123.11 (m or n), 121.55 (m or n), 114.65 (f), 67.72 (d), 66.67 (q), 50.69 (o), 31.43-22.13 (b + s + t), 13.65 (a or u), 13.56 (a or u), 12.45 (aa).
HRMS (EI) m/z calcd. $C_{48}H_{77}N_2O_3^+$ (cation): 729.59342, found 729.59060

Synthesis of ILC series 2

BF_4^- metathesis with $NaBF_4$: ILC (2a-2f)-General procedure (scheme S2, step *x*)

About 100mg of the ILC (**1a-1f**) was dissolved in CH_2Cl_2. The solution was washed with aqueous $NaBF_4$ (x3) and water (x3) dried ($MgSO_4$) and the solvent was evaporated. A concentrated solution of the product was prepared in CH_2Cl_2, filtered (0.2 μm pores), the solvent was evaporated and the final product dried for 24h under vacuum.

ILC 2a

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 9.38 (s, 1H, H_{21}), 7.74 (m, 2H, H_8), 7.65 (m, 2H, H_7), 7.56 (t, 1H, J=1.8Hz, H_9 *or* H_{10}), 7.51 (m, 3H, H_6+H_9 *or* H_{10}), 6.99 (m, 2H, H_5), 5.36 (m, 2H, H_{16}+H_{17}), 5.29 (m, 2H, H_{11}), 4.25 (t, 2H, J=6.9Hz, H_{12}), 4.01 (t, 2H, J=6.6Hz, H_4), 1.99 (m, 4H, H_{15}+H_{18}), 1.81 (m, 2H, H_{13}), 1.70 (m, 2H, H_3), 1.35 (m, 40H, H_2+H_{14}+H_{19}), 0.88 (t, 6H, J=6.9Hz, H_1+H_{20}). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.39 (p), 159.19 (e), 142.93 (l), 136.04 (z), 132.05 (i), 130.34 (h), 129.50 (u or v), 129.28 (u or v), 128.01 (g or j), 127.71 (g or j), 123.97 (m or n), 121.96 (k), 119.69 (m or n), 114.63 (f), 67.72 (d), 66.87 (q), 50.63 (o), 31.44 - 22.22 (b + s + x) , 13.65 (a + y).

ILC 2b

^{1}H-NMR, 300 MHz, $CDCl_3$, δ ppm: 7.71 (m, 2H, H_8), 7.56 (d, 1H, J=2.2Hz, H_9 *or* H_{10}), 7.51 (m, 4H, H_7+H_6), 7.30 (d, 1H, J=2.2Hz, H_9 *or* H_{10}), 6.99 (m, 2H, H_5), 5.33 (m, 2H, H_{16}+H_{17}), 5.14 (s, 2H, H_{11}), 4.22 (t, 2H, J=6.9Hz, H_{12}), 4.01 (t, 2H, J=6.6Hz, H_4), 2.56 (s, 3H, H_{22}), 1.98 (m, 4H, H_{15}+H_{18}), 1.81 (m, 2H, H_{13}), 1.68 (m, 2H, H_3), 1.38 (m, 40H, H_2+H_{14}+H_{19}), 0.90 (m, 6H, H_1+H_{20}). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.93 (p), 159.19 (e), 145.80 (z), 143.29 (l), 132.28 (i), 130.58 (h), 129.51 (u or v), 129.28 (u or v), 127.81 (g or j), 127.77 (g or j), 125.80 (k), 122.94 (m or n), 121.53 (m or n), 114.63 (f), 67.71 (d), 66.57 (q), 49.08 (o), 31.43-22.14 (b + s + x), 13.64 (a or y), 13.57 (a or y), 10.07 (aa).

ILC 2c

^{1}H-NMR, 300 MHz, $CDCl_3$, δ ppm: 7.71 (m, 2H, H_8), 7.56 (d, 1H, J=2.2Hz, H_9 *or* H_{10}), 7.52 (m, 4H, H_7+H_6), 7.29 (d, 1H, J=2.2Hz, H_9 *or* H_{10}), 6.98 (m, 2H, H_5), 5.35 (m, 2H, H_{16}+H_{17}), 5.15 (s, 2H, H_{11}), 4.22 (t, 2H, J=6.9Hz, H_{12}), 4.00 (t, 2H, J=6.6Hz, H_4), 2.98 (q, 2H, J=7.5Hz, H_{23}), 1.99 (m, 4H, H_{15}+H_{18}), 1.81 (m, 2H, H_{13}), 1.68 (m, 2H, H_3), 1.39 (m, 40H, H_2+H_{14}+H_{19}), 1.07 (t, 3H, J=7.7Hz, H_{24}), 0.87 (t, 6H, J=6.7Hz, H_1+H_{20}). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 166.20 (p), 159.20 (e), 149.39 (z), 143.37 (l), 132.31 (i), 130.53 (h), 129.50 (u or v), 129.28 (u or v), 127.81 (g + j), 125.92 (k), 123.13 (m or n), 122.01 (m or n), 114.63 (f), 67.71 (d), 66.53 (q), 48.97 (o), 32.14-22.21 (b +s + x), 17.15 (ab), 13.64 (a + y), 10.54 (ac).

ILC 2d

^{1}H-NMR, 300 MHz, $CDCl_3$, δ ppm: 7.73 (m, 2H, H_8), 7.54 (m, 4H, H_7+H_6), 7.46 (d, 1H, J=2.1Hz, H_9 *or* H_{10}), 7.26 (d, 1H, J=1.6Hz, H_9 *or* H_{10}), 7.00 (m, 2H, H_5), 5.36 (m, 2H, H_{16}+H_{17}), 5.14 (s, 2H, H_{11}), 4.25 (t, 2H, J=6.8Hz, H_{12}), 4.01 (t, 2H, J=6.6Hz, H_4), 2.94 (m, 2H, H_{25}), 1.98 (m, 4H, H_{15}+H_{18}), 1.81 (m, 2H, H_{13}), 1.70 (m, 2H, H_3), 1.41 (m, 42H, H_2+H_{14}+H_{19}+H_{28}), 0.86 (m, 9H, H_1+H_{20}+H_{29}). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 166.14

(p), 159.26 (e), 148.61 (z), 143.55 (l), 132.25 (i), 130.43 (h), 129.54 (u or v), 129.25 (u or v), 127.81 (g + j), 126.04 (k), 122.91 (m or n), 121.94 (m or n), 114.67 (f), 67.74 (d), 66.65 (q), 49.12 (o), 31.44-22.22 (b + s + x + ae), 20.10 (ad), 13.65 (a + y), 13.26 (af).

ILC 2e

^{1}H-NMR, 300 MHz, $CDCl_3$, δ ppm: 7.73 (m, 2H, H_8), 7.52 (m, 5H, H_7+H_6+ (H_9 *or* H_{10})), 7.19 (d, 1H, J=2.2Hz, H_9 *or* H_{10}), 7.01 (m, 2H, H_5), 5.36 (m, 2H, H_{16}+H_{17}), 5.22 (s, 2H, H_{11}), 4.25 (t, 2H, J=6.8Hz, H_{12}), 4.01 (t, 2H, J=6.6Hz, H_4), 3.32 (m, 1H, H_{28}), 1.98 (m, 4H, H_{15}+H_{18}), 1.81 (m, 2H, H_{13}), 1.70 (m, 2H, H_3), 1.38 (m, 40H, H_2+H_{14}+H_{19}), 1.30 (d, 9H, J=7.2Hz, H_{29}), 0.87 (t, 6H, J=6.6Hz, H_1+H_{20}). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 166.16 (p), 159.31 (e), 150.73 (z), 143.82 (l), 132.47 (i), 130.40 (h), 129.54 (u or v), 129.25 (u or v), 127.82 (g or j), 127.50 (g or j), 126.80 (k), 123.54 (m or n), 122.76 (m or n), 114.67 (f), 67.75 (d), 66.71 (q), 49.52 (o), 31.44-22.22 (b + s + x), 19.17 (ag), 13.65 (ah).

ILC 2f

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.92 (m, 1H, H_9 or H_{10}), 7.72 (m, 2H, H_8), 7.64 (m, 2H, H_7), 7.51 (m, 2H, H_6), 7.35 (m, 1H, H_9 *or* H_{10}), 6.99 (m, 2H, H_5), 5.54 (s, 2H, H_{11}), 4.25 (t, 2H, J=6.9Hz, H_{12}), 4.01 (t, 2H, J=6.6Hz, H_4), 2.75 (s, 3H, H_{17}), 1.68 (m, 2H, H_3), 1.63 (m, 2H, H_{13})1.38 (m, 48H, H_{14}+H_{15}+H_2), 0.86 (t, 6H, J=6.9Hz, H_{16}+H_1). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.61 (p), 159.22 (e), 146.06 (z), 143.48 (l), 132.13 (i), 130.53 (h), 127.82 (g or j), 127.79 (g or j), 126.04 (k), 123.11 (m or n), 121.55 (m or n), 114.65 (f), 67.72 (d), 66.67 (q), 50.69 (o), 31.43-22.13 (b + s + t), 13.65 (a or u), 13.56 (a or u), 12.45 (aa).

Synthesis of ILC: series 3

NTf_2^- metathesis with $AgNTf_2$ (3a-3f) -General procedure (scheme S2, step *xi*)

About 100 mg of the ILC (**1a-1e**) was dissolved in MeOH and a solution of $AgNTf_2$ in MeOH was slowly added. A yellow precipitate was formed, removed via filtration, and the solvent via rotary evaporation. The resulting solid was dissolved in CH_2Cl_2 and washed with aqueous $LiNTf_2$ (x2) and water (x2), dried ($MgSO_4$) and the solvent was evaporated. A concentrated solution of the product was prepared in CH_2Cl_2, filtered (0,2 μm pores), the solvent was removed and the final product dried for 24h under vacuum.

ILC 3a

^{1}H-NMR, 300 MHz, $CDCl_3$, δ ppm: 9.17 (t, 1H, J=1.6Hz, H_{21}), 7.74 (m, 2H, H_8), 7.59 (m, 3H, H_7+ H_9 *or* H_{10}), 7.55 (m, 1H, H_9 *or* H_{10}), 7.52 (m, 2H, H_6), 6.99 (m, 2H, H_5), 5.36 (m, 2H, H_{16}+H_{17}), 5.22 (s, 2H, H_{11}), 4.25 (t, 2H, J=6.8Hz, H_{12}), 4.01 (t, 2H, J=6.6Hz, H_4), 1.99 (m, 4H, H_{15}+H_{18}), 1.81 (m, 2H, H_{13}), 1.69 (m, 2H, H_3), 1.38 (m, 40H, H_2+H_{14}+H_{19}), 0.88 (t, 6H, J=6.7Hz, H_1+H_{20}). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.29 (p), 159.25 (e), 143.33 (l), 135.28 (z), 131.91 (i), 130.30 (h), 129.51 (u or v), 129.28 (u or v), 128.06 (g or j), 127.77 (g or j), 124.01 (m or n), 122.11 (k), 120.65 (m or n), 114.64 (f), 67.73 (d), 66.99 (q), 50.02 (o), 31.44-22.21 (b + s +x), 13.64 (a + y)

ILC 3b

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.76 (m, 2H, H_8), 7.54 (m, 4H, H_6+H_7), 7.42 (d, 1H, J=2.2Hz, H_9 *or* H_{10}), 7.31 (d, 1H, J=2.2Hz, H_9 *or* H_{10}), 7.01 (m, 2H, H_5), 5.36 (m, 2H, H_{16}+H_{17}), 5.12 (s, 2H, H_{11}), 4.25 (t, 2H, J=6.8Hz, H_{12}), 4.02 (t, 2H, J=6.6Hz, H_4), 2.57 (s, 3H, H_{22}), 2.00 (m, 4H, H_{15}+H_{18}), 1.82 (m, 2H, H_{13}), 1.71 (m, 2H, H_3), 1.39 (m, 40H, H_2+H_{14}+H_{19}), 0.88 (t, 6H, J=6.9Hz, H_1 or H_{20}). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.56 (p), 159.30 (e), 145.62 (z), 143.73 (l), 131.92 (i), 130.41 (h), 129.55 (u or v), 129.25 (u or v), 127.95 (g or j), 127.84 (g or j), 125.68 (k), 122.68 (m or n), 121.74 (m or n), 114.68 (f), 67.73 (d), 66.91 (q), 49.41 (o), 31.43-22.14 (b + s + x), 13.64 (a or y), 13.57 (a or y), 10.21 (aa).

ILC 3c

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.76 (m, 2H, H_8), 7.55 (m, 2H, H_6), 7.51 (m, 2H, H_7), 7.47 (d, 1H, J=2.2Hz, H_9 *or* H_{10}), 7.30 (d, 1H, J=2.2Hz, H_9 *or* H_{10}), 7.01 (m, 2H, H_5), 5.36 (m, 2H, H_{16}+H_{17}), 5.13 (s, 2H, H_{11}), 4.26 (t, 2H, J=6.9Hz, H_{12}), 4.02 (t, 2H, J=6.6Hz, H_4), 2.96 (q, 2H, J=7.7Hz, H_{23}), 1.99 (m, 4H, H_{15}+H_{18}), 1.82 (m, 2H, H_{13}), 1.71 (m, 2H, H_3), 1.40 (m, 40H, H_2+H_{14}+H_{19}), 1.14 (t, 3H, J=7.7Hz, H_{22}), 0.88 (m, 6H, H_1+H_{20}). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.78 (p), 159.32 (e), 149.17 (z), 143.80 (l), 131.92 (i), 130.36 (h), 129.54 (u or v), 129.26 (u or v), 127.94 (g or j), 127.84 (g or j), 125.81 (k), 122.93 (m or n), 122.19 (m or n), 114.68 (f), 67.74 (d), 66.87 (q), 49.15 (o), 32.13-22.21 (b + s +x), 17.23 (ab), 13.64 (a + y), 10.72 (ac).

ILC 3d

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.77 (m, 2H, H_8), 7.56 (m, 2H, H_6), 7.51 (m, 2H, H_7), 7.45 (d, 1H, J=2.2Hz, H_9 *or* H_{10}), 7.29 (d, 1H, J=2.2Hz, H_9 *or* H_{10}), 7.02 (m, 2H, H_5), 5.36 (m, 2H, H_{16}+H_{17}), 5.13 (s, 2H, H_{11}), 4.27 (t, 2H, J=6.8Hz, H_{12}), 4.02 (t, 2H, J=6.6Hz, H_4), 2.90 (m, 2H, H_{25}), 1.99 (m, 4H, H_{15}+H_{18}), 1.82 (m, 2H, H_{13}), 1.71 (m, 2H, H_3), 1.42 (m, 42H, H_2+H_{14}+H_{19}+H_{25}), 0.88 (m, 9H, H_1+H_{20}+H_{26}). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.77 (p), 159.32 (e), 148.15 (z), 143.73 (l), 132.00 (i), 130.32 (h), 127.89 (g or j)), 127.83 (g or j), 125.86 (k), 123.02 (m or n), 122.23 (m or n), 114.68 (f), 67.74 (d), 66.87 (q), 49.16 (o), 32.13-22.22 (b + s + x + ae), 20.05 (ad), 13.64 (a + y), 13.22 (af).

ILC 3e

^{1}H-NMR, 300 MHz, $CDCl_3$, δ ppm: 7.75 (m, 2H, H_8), 7.55 (m, 2H, H_6), 7.51 (m, 2H, H_7), 7.43 (d, 1H, J=2.2Hz, H_9 *or* H_{10}), 7.21 (d, 1H, J=2.2Hz, H_9 *or* H_{10}), 7.01 (m, 2H, H_5), 5.36 (m, 2H, H_{16}+H_{17}), 5.19 (s, 2H, H_{11}), 4.26 (t, 2H, J=6.8Hz, H_{12}), 4.02 (t, 2H, J=6.6Hz, H_4), 3.32 (m, 1H, H_{28}), 1.99 (m, 4H, H_{15}+H_{18}), 1.82 (m, 2H, H_{13}), 1.70 (m, 2H, H_3), 1.38 (m, 40H, H_2+H_{14}+H_{19}), 1.30 (d, 6H, J=7.2Hz, H_{29}), 0.88 (t, 3H, J=6.9Hz, H_1 or H_{20}), 0.87 (t, 3H, J=6.5Hz, H_1 or H_{20}). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.83 (p), 159.38 (e), 150.77 (z), 144.02 (l), 132.15 (i), 130.27 (h), 129.52 (u or v), 129.29 (u or v), 127.87 (g or j), 127.56 (g or j), 126.84 (k), 123.57 (m or n), 122.82 (m or n), 114.78 (f), 67.75 (d), 66.89 (q), 50.16 (o), 31.44-22.22 (b + s + x), 19.15 (ag), 13.62 (ah)

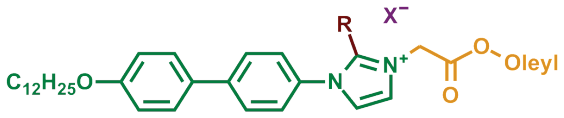
ILC 3f

^{1}H-NMR, 400 MHz, $CDCl_3$, δ ppm: 7.92 (m, 1H, H_9 or H_{10}), 7.72 (m, 2H, H_8), 7.64 (m, 2H, H_7), 7.51 (m, 2H, H_6), 7.35 (m, 1H, H_9 *or* H_{10}), 6.99 (m, 2H, H_5), 5.54 (s, 2H, H_{11}), 4.25 (t, 2H, J=6.9Hz, H_{12}), 4.01 (t, 2H, J=6.6Hz, H_4), 2.75 (s, 3H, H_{17}), 1.68 (m, 2H, H_3), 1.63 (m, 2H, H_{13})1.38 (m, 48H, H_{14}+H_{15}+H_2), 0.86 (t, 6H, J=6.9Hz, H_{16}+H_1). ^{13}C-NMR, 300 MHz, $CDCl_3$, δ ppm: 165.61 (p), 159.22 (e), 146.06 (z), 143.48 (l), 132.13 (i), 130.53 (h), 127.82 (g or j), 127.79 (g or j), 126.04 (k), 123.11 (m or n), 121.55 (m or n), 114.65 (f), 67.72 (d), 66.67 (q), 50.69 (o), 31.43-22.13 (b + s + t), 13.65 (a or u), 13.56 (a or u), 12.45 (aa).

Mesomorphic properties of ILC (DSC and OPM)

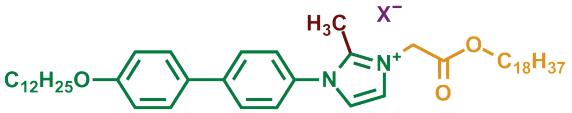
Phase transition enthalpies and entropies of series **2** and **3** are given in Tables 1and 2.

Scheme S3



R =	H	CH_3	*n*-C_2H_5	*n*-C_3H_7	*i*-C_3H_7
$X^- = BF_4^-$	2a	2b	2c	2d	2e
$X^- = NTf_2^-$	3a	3b	3c	3d	3e

Scheme S4



R =	CH_3
X = BF_4	2f
X = NTf_2	3f

Table S1. Mesomorphic properties of ILC for compounds **2a-2e** (**Scheme S3**) and **2f** (**Scheme S4**) containing BF_4 as counter ion

ILC	2a	2b	2c	2d	2e	2f
T(Cr-SmA)(°C)	76				63	59
ΔH(Cr-SmA) (kJ mol^{-1})	6.2				55	41.2
ΔS(Cr-SmA) (J mol^{-1} K^{-1})	18				163.5	124.4
T(SmA-Iso) (°C)	208	160	140	79	116	233
ΔH(SmA-Iso) (kJ mol^{-1})	1.6	2.2	1.8	0.2	2	2.8
ΔS(Cr-SmA) (J mol^{-1} K^{-1})	3.3	5	4.3	0.4	5.1	5.5

Table S2. Mesomorphic properties of ILC for compounds **3a-3e** (**Scheme S3**) and **3f** (**Scheme S4**) containing Ntf_2 as counter ion

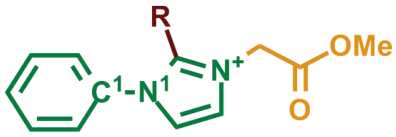
ILC	3a	3b	3c	3d[(a)]	3e	3f
T(Cr-SmA)(°C)	44	23	17	-2	-2	90
ΔH(Cr-SmA) (kJ mol^{-1})	27.2	7.7	29.5	13.4	13.1	53
ΔS(Cr-SmA) (J mol^{-1} K^{-1})	85.9	25.7	102.2	53.1	48	149.5
T(SmA-Iso)(°C)	99	83	55	7	25	110
ΔH(SmA-Iso)(kJ mol^{-1})	3	2.2	1.8	1.5	1.3	2.5
ΔS(SmA-Iso) (J mol^{-1} K^{-1})	8.1	6.3	5.6	5.3	4.5	6.7

(a) ILC **3d** is monotropic, it has a (Cr-Iso) phase transition at 35 °C / ΔH= 47.7 kJ/mol, Δ*S* = 153 J/mol K.

Molecular modelling

Our modeling studies were aimed to quantify the value in the rotational energy barrier (C_1-N_1) when the size of the lateral chain in the core (R) was increased. The structures were first subjected to structural minimization using Spartan software package (force field: Hartree-FockF 6-31G*) (scheme S4).

Scheme S5



Rotational energy barriers were calculated by rotating the C1-N1 bond 5° and subsequent minimization of the structure (same force field), maintaining the dihedral angle fixed. Energy barriers are given as the difference between the minimum and maximum energies after a rotation of 180 or 360 º. Crude data is given in Figure S1

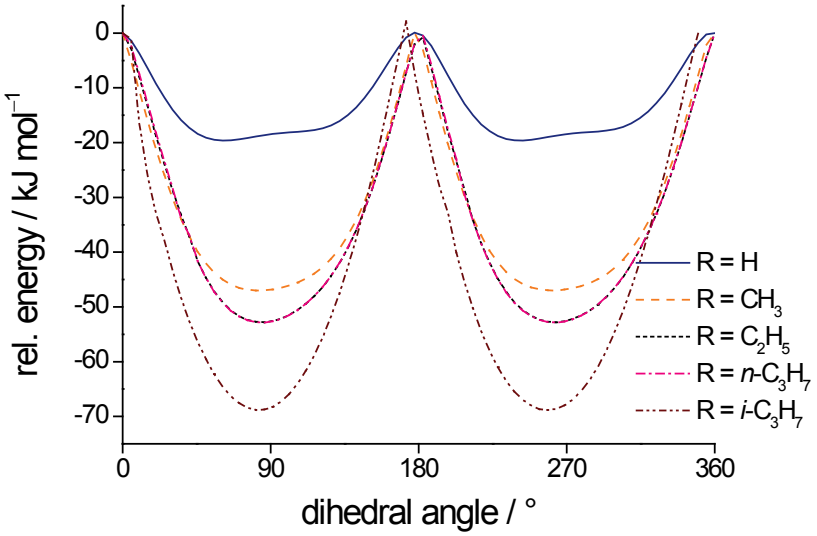


Figure S1: Energy barriers for ratations around the C1-N1 bond (scheme S5).

References

(1) P. H. J. Kouwer and T. M. Swager, *J. Am. Chem. Soc.*, 2007, **129**, 14042-14052.
(2) R. A. Altman and S. L. Buchwald, *Org. Lett.* 2006, **8**, 2779-2782.