Supporting Information

Effect of Central Linkages on Mesophase Behavior of Imidazolium-Based Rod-like Ionic Liquid Crystals

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Content

1. Additional textures of LC phases

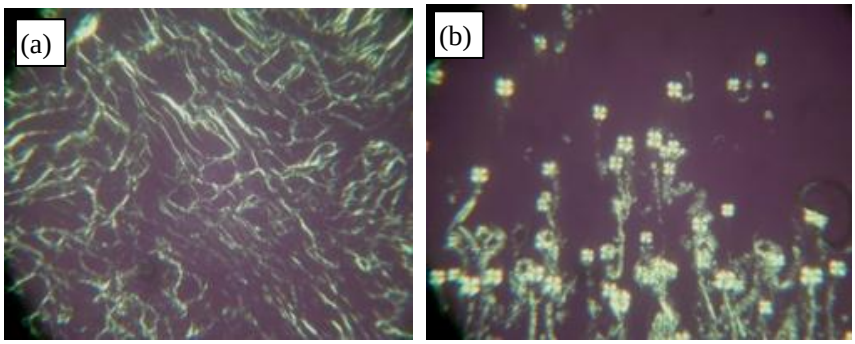


Fig. S1 Textures between crossed polarizers: (a) SmA phase of **E1^{12}/12** at T = 125 °C; (b) oily streaks texture of **E3^{12}/5** (crossed polarizers) at T = 83 °C (dark areas represent homeotropically aligned regions).

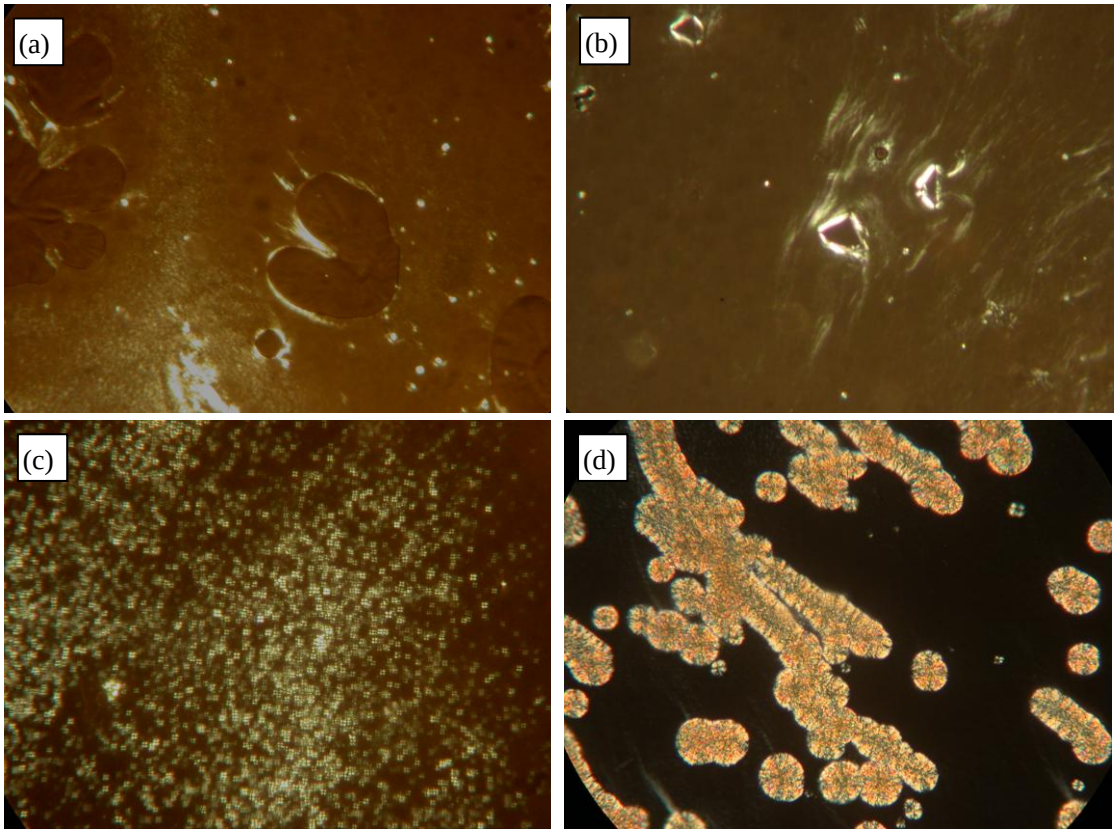


Fig. S2 Texture of the SmA phases of (a) **E3^{14}/5** at T = 46 °C; (b) **E3^{14}/6** at T = 60 °C; (c) **A3^{16}/4** at T = 92 °C (d) after shearing at T = 89 °C, bright regions are crystalline,

dark regions represent the homeotopically aligned SmA phase.

2. Additional XRD data

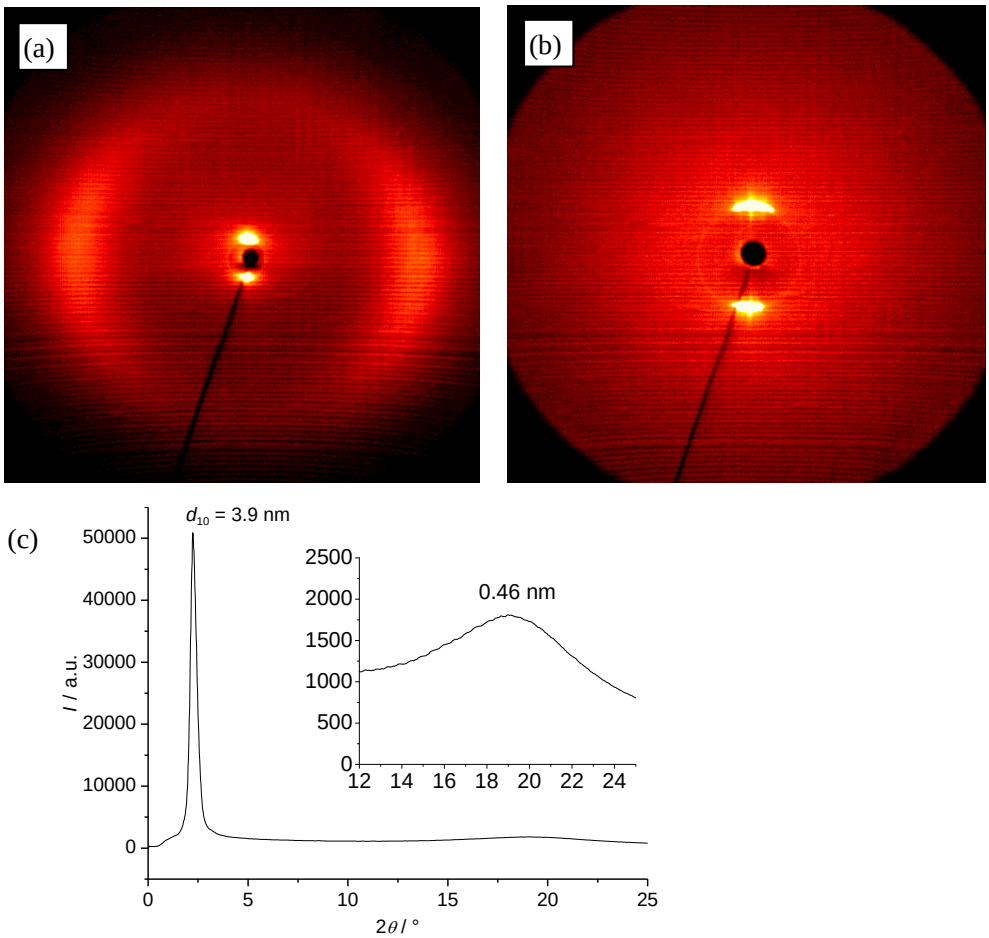


Fig. S3 X-ray diffraction pattern of an aligned sample of the SmA phase of compound **A1^{12}/0** at T = 165 °C, (a) wide angle pattern and (b) small angle pattern (c) plot of the diffraction pattern, the inset shows the diffuse scattering in the wide angle region.

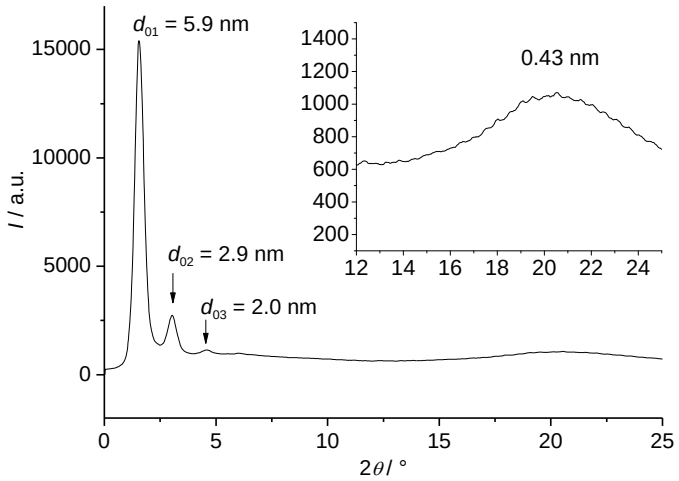


Fig. S4 WAXS diffraction pattern of the SmA phase of compound **E1**^{12}**/4** at T = 80 °C, the inset shows the diffuse scattering in the wide angle region.

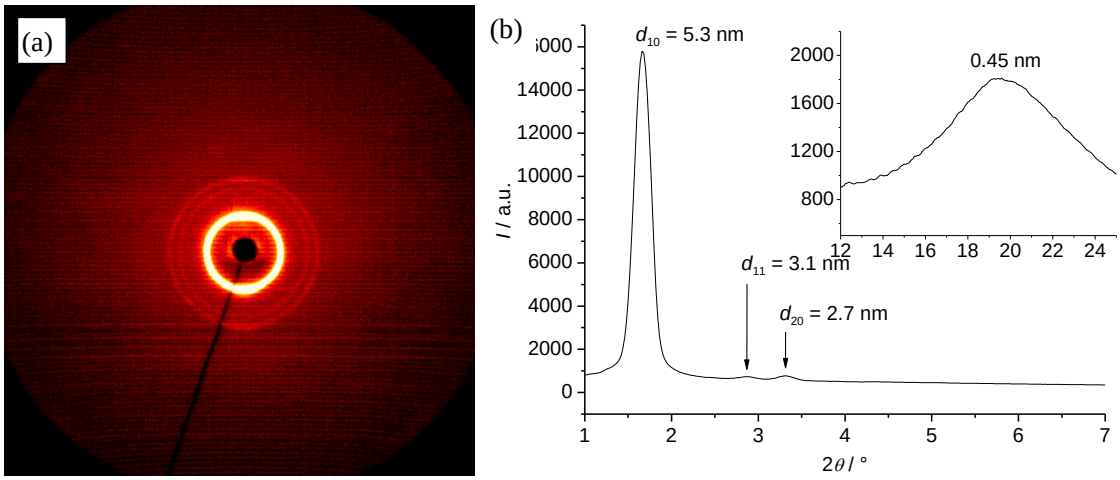


Fig. S5 X-ray diffraction pattern of the Col$_{hex}$ phase of compound **E2**^{16}**/3** at T = 100 °C, (a) small angle pattern, (b) θ-scan, inset diffuse scattering in the wide angle region.

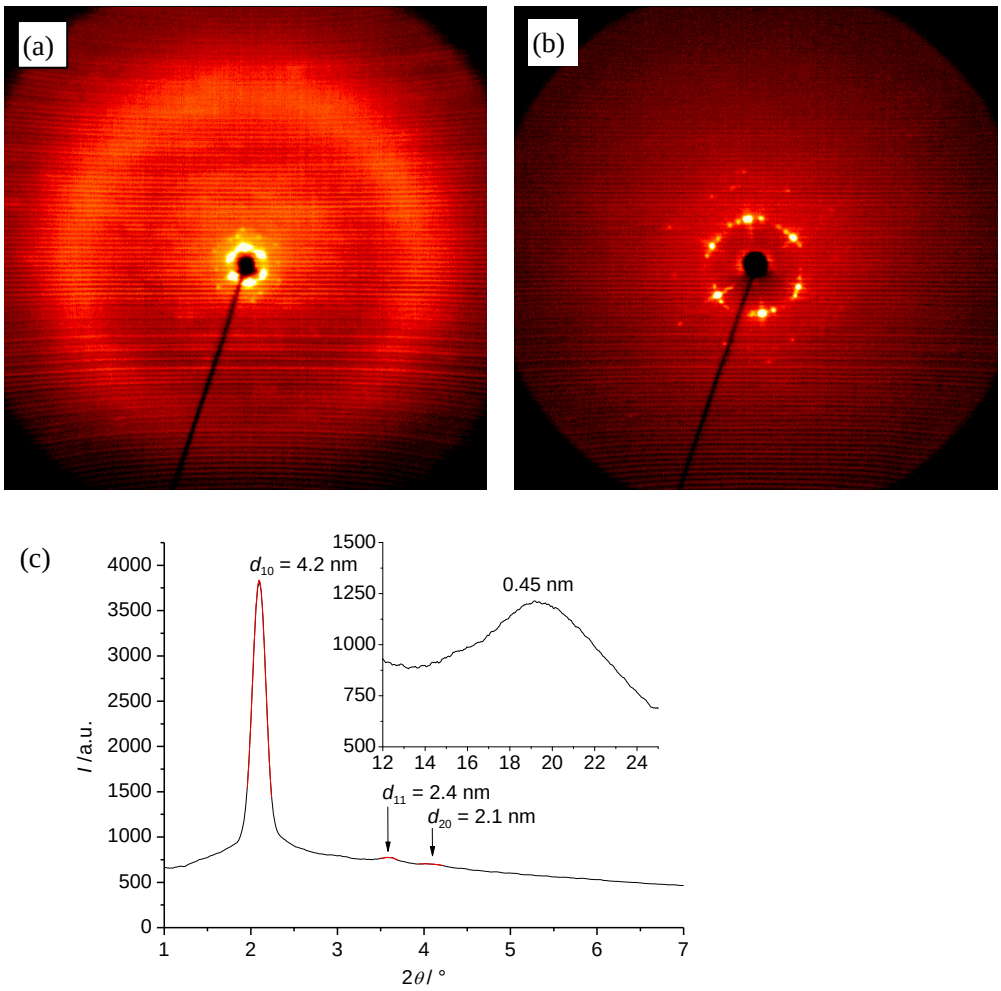


Fig. S6 X-ray diffraction pattern of the Col$_{hex}$ phase of compound **E3**^{12}**/4** at T = 100 °C,

(a) wide angle pattern; (b) small angle pattern and (c) θ-scan, the inset shows the diffuse scattering in the wide angle region.

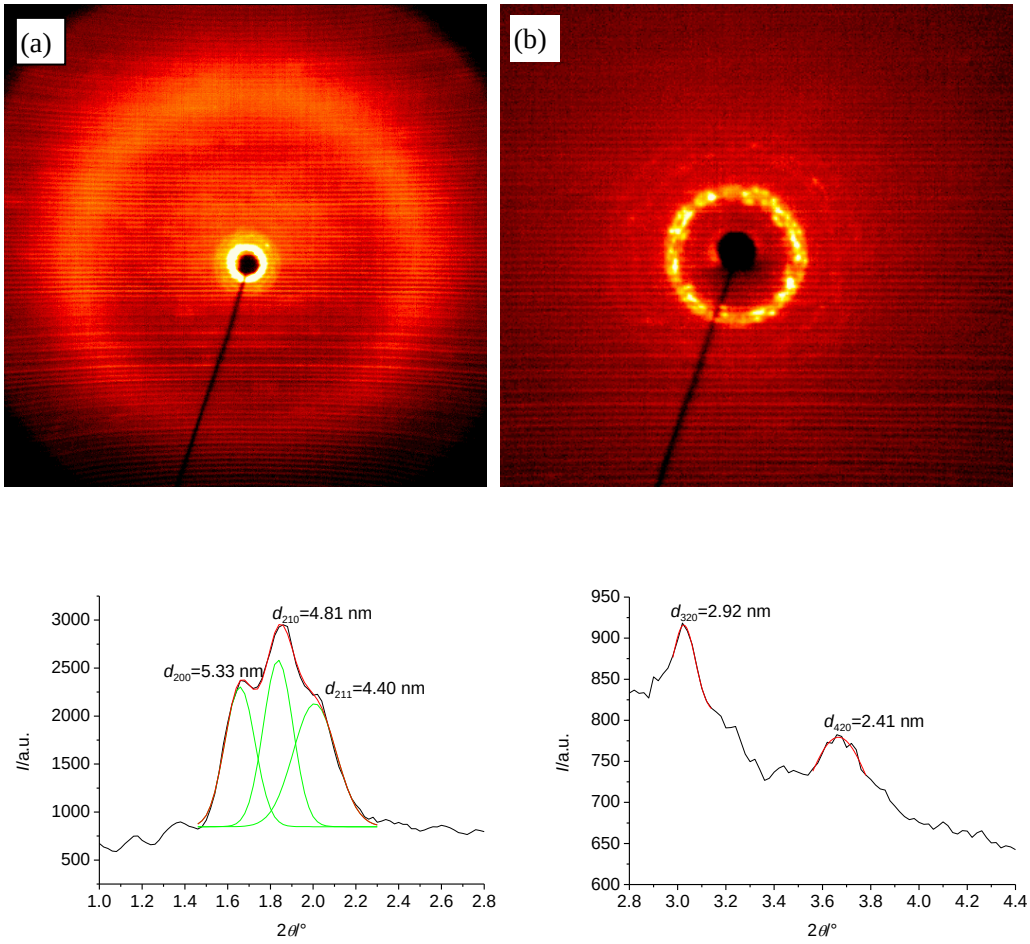


Fig. S7 X-ray diffraction pattern of the Cub_I phase of compound **E3^{16}/4** at T = 100 °C, (a) wide angle pattern and (b) small angle pattern, (c,d) scans over distinct regions of the small angle scattering.

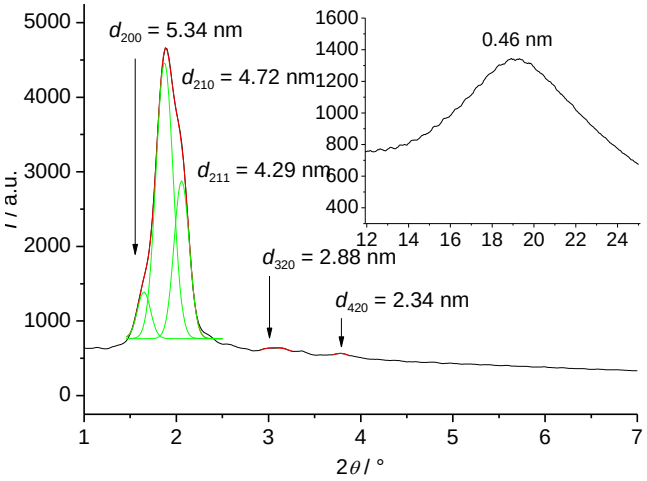


Fig. S8 SAXS diffraction pattern of the Cub/*Pm*3*n* phase of **E3^{16}/3** at *T* =120 °C, the inset shows the diffuse scattering in the wide angle region.

Table S1 Crystallographic data[a]

Comp.	*T* /°C	Phase	θ_{obs}/^{o}	d_{obs}/nm	*hkl*/*n*	d_{calc}/nm	d_{obs}-d_{calc}	*d*,*a*/nm
A1^{12}/0	165	SmA	1.14 9.57	3.89 0.46	1 diff	-	-	*d* = 3.89
A1^{18}/0	140	SmA	0.94 9.50	4.72 0.47	1 diff	-	-	*d* = 4.72
E1^{12}/4	80	SmA	0.75 1.51 2.27 10.27	5.86 2.92 1.95 0.43	1 2 3 diff	5.86 2.93 1.95	0.00 -0.01 0.00	*d* = 5.86
E1^{12}/12	100	SmA	1.10 2.19 9.84	4.02 2.02 0.45	01 02 diff	4.02 2.01	0.00 0.01	*d* = 4.02
E2^{16}/3	100	Col_{hex}	0.84 1.43 1.66 9.87	5.30 3.08 2.67 0.45	10 11 20 diff	5.30 3.06 2.65	0.00 0.02 0.02	*a* = 6.12
A3^{12}/2	140	Col_{hex}	1.20 9.70	3.70 0.46	10 diff			*a* = 4.27
A3^{16}/2	140	Col_{hex}	1.11 9.59	4.00 0.46	10 diff			*a* = 4.62
E3^{12}/4	100	Col_{hex}	1.05 1.79 2.07 9.78	4.22 2.47 2.13 0.45	10 11 20 diff	4.22 2.44 2.11	0.00 0.03 0.03	*a* = 4.87
E3^{14}/4	120	Col_{hex}	1.03 9.75	4.28 0.56	10 diff	-	-	*a* = 4.94
E3^{16}/4	120	Col_{hex}	1.01 9.65	4.38 0.46	10 diff	-	-	*a* = 5.06

[a] θ_{obs} = experimental scattering angle; d_{obs} = experimental and d_{calc} = calculated *d* spacing; *hkl*/*n* = assigned indices for Col_{hex}, Cub phases / order of reflection for SmA phases, parameter used: lattice parameters used to calculate d_{calc} with an error of the calculated parameters in the order of 0.1 nm, diff = diffuse wide angle scattering.

Table S2 Calculations of molecular volume (V_{mol}), volume of the (hypothetical) unit cells(V_{cell}) and number of molecules in these unit cells (n_{cell}).[a]

Comp.	phase	V_{cell} [nm^3]	V_{mol} [nm^3]	$n_{cell,cryst}$	$n_{cell,liq}$	n_{cell}
E2^{16}/3	Col$_{hex}$/*p6mm*	14.5	1.261	11.5	9.0	10.3
E3^{12}/4	Col$_{hex}$/*p6mm*	9.36	1.394	6.7	5.3	6.0
A3^{12}/2	Col$_{hex}$/*p6mm*	7.21	1.350	5.3	4.2	4.8
A3^{16}/2	Col$_{hex}$/*p6mm*	8.25	1.647	5.0	3.9	4.5
E3^{14}/4	Col$_{hex}$/*p6mm*	9.36	1.543	6.1	4.8	5.5
E3^{16}/3	Cub$_I$/*Pm*3*n*	1191	1.667	714	561	638
E3^{16}/4	Col$_{hex}$/*p6mm*	10.1	1.692	6.0	4.7	5.4
	Cub$_I$/*Pm*3*n*	1260		746	586	666

[a] V_{cell} = volume of the unit cell defined by the dimensions $a_{hex}^2 \times \sin(60°) \times 0.45$ nm for hexagonal phases and a_{cub}^3 for the cubic phases; V_{mol} = volume for a single molecule as calculated using the crystal volume increments;[S1] $n_{cell,cryst}$ = number of molecules in the unit cell, calculated according to $n_{cell,cryst} = V_{cell}/V_{mol}$ (average packing coefficient in the crystal is $k = 0.7$;[S2] $n_{cell,liq}$ = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient $k = 0.55$, calculated according to $n_{cell,liq} = 0.55/0.7 \times n_{cell,cryst}$; n_{cell} = in the LC phase estimated as the average of that in the $n_{cell,cryst}$ and $n_{cell,liq}$.

Table S3 Volumes of the molecular segments (V_{RC} = *C*-terminal alkyl chains; V_{RN} = *N*-terminal alkyl chains; V_{Ar} = aromatic units), and the related volume fractions *f*.

Comp.	V_{RC}	V_{RN}	V_{Ar}	f_{RC}	f_{RN}
E1^{6}/0	164.9		321.4	0.34	
E1^{12}/0	313.7		321.4	0.49	
E1^{16}/0	412.9		321.4	0.56	
E1^{18}/0	462.5		321.4	0.59	
E2^{16}/0	825.8		314.5	0.72	
E3^{12}/0	941.1		307.6	0.75	
E3^{14}/0	1089.9		307.6	0.78	
E3^{16}/0	1238.7		307.6	0.80	
E3^{18}/0	1387.5		307.6	0.82	
A1^{6}/0	164.9		326.4	0.34	
A1^{12}/0	313.7		326.4	0.49	
A1^{16}/0	412.9		326.4	0.56	
A1^{18}/0	462.5		326.4	0.59	
A2^{16}/0	825.8		319.5	0.72	
A3^{6}/0	494.7		312.6	0.61	
A3^{10}/0	792.3		312.6	0.72	

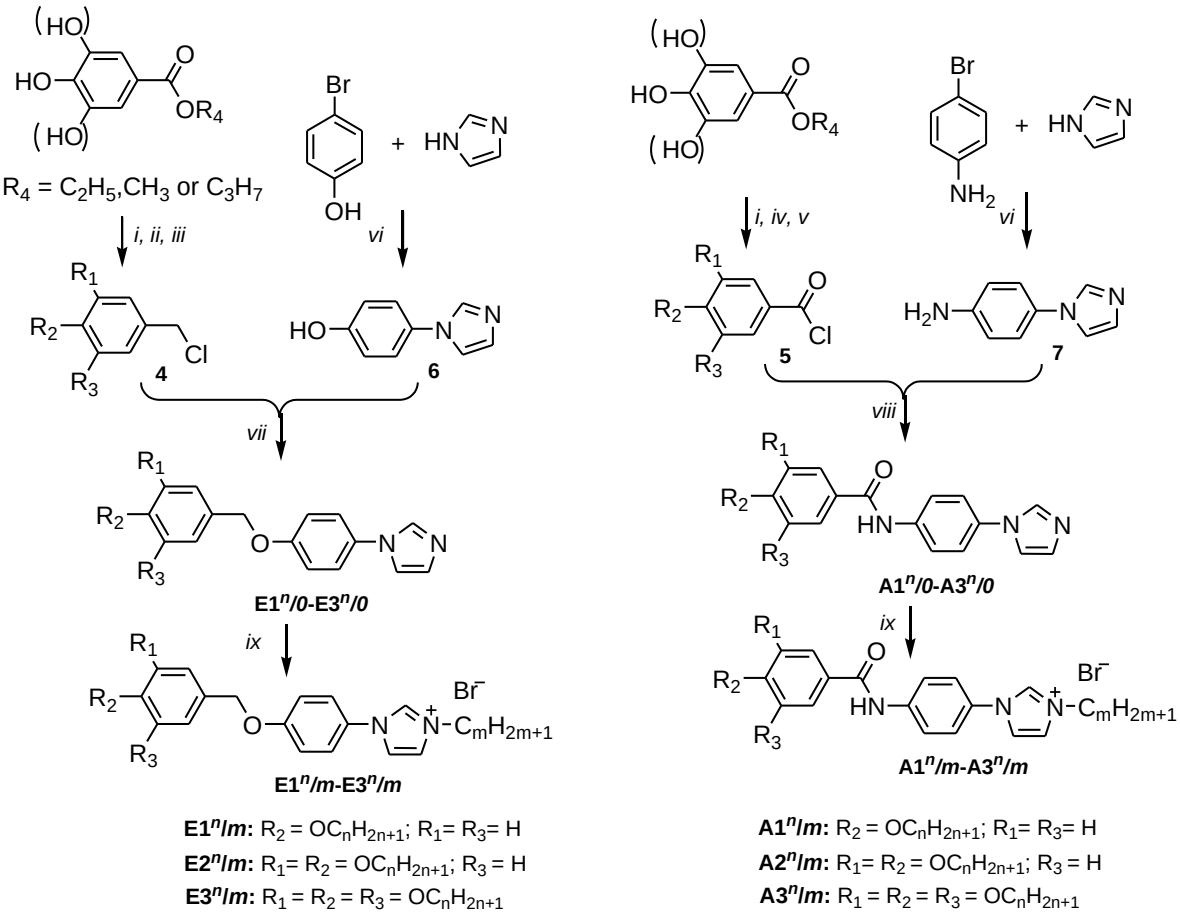
Table S3 continued

Comp.	V_{RC}	V_{RN}	V_{Ar}	f_{RC}	f_{RN}
A3^{12}/0	941.1		312.6	0.75	
A3^{14}/0	1089.9		312.6	0.78	
A3^{18}/0	1387.5		312.6	0.82	
E1^{12}/3	313.7	81.3	360.7	0.42	0.11
E1^{12}/4	313.7	106.1	360.7	0.40	0.14
E1^{12}/12	313.7	304.5	360.7	0.32	0.31
E1^{14}/12	363.3	304.5	360.7	0.35	0.30
E1^{16}/3	412.9	81.3	360.7	0.48	0.095
E1^{18}/6	462.5	155.7	360.7	0.47	0.16
C1^{12}/4	313.7	106.1	363.6	0.40	0.14
C1^{12}/12	313.7	304.5	363.6	0.32	0.31
C1^{18}/6	462.5	155.7	363.6	0.47	0.16
A1^{12}/4	313.7	106.1	365.7	0.40	0.14
A1^{16}/4	412.9	106.1	365.7	0.47	0.12
E2^{16}/3	825.8	81.3	353.8	0.65	0.064
E3^{12}/4	941.1	106.1	346.9	0.68	0.076
E3^{12}/5	941.1	130.9	346.9	0.66	0.092
E3^{14}/2	1089.9	56.5	346.9	0.73	0.038
E3^{14}/3	1089.9	81.3	346.9	0.72	0.054
E3^{14}/4	1089.9	106.1	346.9	0.71	0.069
E3^{14}/5	1089.9	130.9	346.9	0.70	0.083
E3^{14}/6	1089.9	155.7	346.9	0.68	0.098
E3^{16}/2	1238.7	56.5	346.9	0.75	0.034
E3^{16}/3	1238.7	81.3	346.9	0.74	0.049
E3^{16}/4	1238.7	106.1	346.9	0.73	0.063
E3^{16}/5	1238.7	130.9	346.9	0.72	0.076
E3^{18}/3	1387.5	81.3	346.9	0.76	0.045
E3^{18}/5	1387.5	130.9	346.9	0.74	0.070
A3^{12}/2	941.1	56.5	351.9	0.70	0.042
A3^{12}/3	941.1	81.3	351.9	0.68	0.059
A3^{16}/2	1238.7	56.5	351.9	0.75	0.034
A3^{16}/4	1238.7	106.1	351.9	0.73	0.063

3. Syntheses and analytical data

3.1 General Remarks

Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140 °C). Commercially available chemicals were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker–DRX-500 spectrometer. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer. Column chromatography was performed with merck silica gel 60 (230-400 mesh). The alkoxybenzyl chlorides **4** and alkoxybenzoyl chlorides **5** were prepared according to literature procedures.[S3,S4]



E1^n/*m*: $R_2 = OC_nH_{2n+1}$; $R_1 = R_3 = H$
E2^n/*m*: $R_1 = R_2 = OC_nH_{2n+1}$; $R_3 = H$
E3^n/*m*: $R_1 = R_2 = R_3 = OC_nH_{2n+1}$

A1^n/*m*: $R_2 = OC_nH_{2n+1}$; $R_1 = R_3 = H$
A2^n/*m*: $R_1 = R_2 = OC_nH_{2n+1}$; $R_3 = H$
A3^n/*m*: $R_1 = R_2 = R_3 = OC_nH_{2n+1}$

Scheme S1. Synthesis of the imidazolium bromides; Reagents and conditions: *i*) $C_nH_{2n+1}Br$, K_2CO_3, DMF, 90°C, overnight; *ii*) $LiAlH_4$, THF, 50°C, 4 h; *iii*) $SOCl_2$, DMF, THF, 5 h; *iv*) KOH, EtOH, reflux; *v*) $SOCl_2$, DMF, THF, reflux, 5 h; *vi*) K_2CO_3, CuI, DMF, N_2, reflux, 24 h; *vii*) K_2CO_3, DMF, 90°C, overnight; *viii*) NaH, DMF, 90°C, overnight; *ix*) $C_mH_{2m+1}Br$, toluene, reflux, 16 – 48 h.

3.2 Intermediates

Compound 6: 4-(1*H*-imidazol-1-yl)phenol[S5] : A flame-dried Schlenk test tube with a magnetic stirring bar was charged with CuI (0.38g, 2mmol), K_2CO_3(2.76g, 20mmol), 1H-imidazole (0.85g, 12.5mmol), 4-bromo-phenol (1.73g, 10 mmol) and DMF (2 mL) under N_2. A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N_2. The reaction mixture was stirred for 30 min at RT, and then heated to reflux for 24 h. The reaction mixture was then cooled to RT, diluted with 10-20 mL of H_2O, filtered to remove the solvent. The residue was dissolved with ethyl acetate and washed with brine. The organic extracts were concentrated and the resulting residue was purified by column chromatography (petroleum ether: ethyl acetate = 1:1) to yield **6** as a pale yellow solid (1.21 g, 75%, mp: 183-185 °C, Lit.: 196-198 °C[S6]).

Compound 7: 4-(1*H*-imidazol-1-yl) aniline[S5] : A flame-dried Schlenk test tube with a magnetic stirring bar was charged with CuI (380mg, 2mmol), K_2CO_3 (2.76g, 20mmol), 1H-imidazole (0.95g, 14mmol), 4-bromo-phenylamine (1.72g, 10 mmol) and DMF (2 mL) under N_2. A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N_2. The reaction mixture was stirred for 30 min at RT, and then heated to reflux for 24 h. The reaction mixture was then cooled to RT, diluted with 10 - 20 mL of H_2O, filtered to remove the solvent. The residue was dissolved with ethyl acetate and washed with brine. The organic extracts were concentrated and the resulting residue was purified by column chromatography (petroleum ether: ethyl acetate = 1:1) to yield **7** as a white solid (1.39g, 88%). ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 7.73 (1H, s, imidazole-H), 7.18-7.14(4H, t, Ar-H and imidazole-H), 6.74(2H, d, Ar-H, J = 8.5 Hz), 3.88(2H, s, NH_2).

3.3 Phenylbenzylether based 1-phenyl-1*H*-imidazoles (1E^n/0 – 3E^n/0)

General procedure for the etherification of 4 with benzylchlorides 6[S7]**:** To a mixture of K_2CO_3 (1.1 mmol), 4-(1H-imidazol-1-yl)phenol **6** (1 mmol) in dry DMF (20 mL), the appropriate alkoxybenzyl chloride (1.1 mmol) was added under an N_2 atmosphere. The mixture was heated to 90 °C and stirred for 16 h. After the reaction was complete (TLC), the mixture was cooled to RT, and extracted with ethyl acetate (3 × 30 mL). The combined extracts were washed with H_2O (5 × 20 mL), dried over $MgSO_4$, then the solvent was removed in *vacuo*. The residue was purified by chromatography (petroleum ether: ethyl acetate = 2:1), (Yield: 59 - 91%, for analytical data see **Table S3**).

Table S3 Analytical data of compounds **E1^n/0 –E3^n/0**

Comp.	
E1^6/0	colourless crystals; yield: 91%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 7.75 (1H, s, imidazole-H), 7.34 (2H, d, Ar-H, *J* = 6.7 Hz), 7.28 (2H, d, Ar-H, *J* = 6.7 Hz), 7.18 (2H, d, imidazole-H), 7.04 (2H, d, Ar-H, *J* = 6.6 Hz), 6.92 (2H, d, Ar-H, *J* = 6.6 Hz), 5.01 (2H, s, $ArCH_2O$), 3.96 (2H, t, $ArOCH_2$, *J* = 4.7 Hz), 1.78 (2H, m, $ArOCH_2CH_2$), 1.51-1.45 (2H, m, CH_2), 1.40-1.26 (4H, m, $2CH_2$), 0.90 (3H, t, CH_3, *J* = 6.2 Hz); elemental analysis calcd (%) for $C_{22}H_{26}N_2O_2$ (350.45): C 75.40, H 7.48, N 7.99; found: C 75.18, H 7.72, N 8.21.
E1^{12}/0	colourless crystals; yield: 79%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 7.75 (1H, s, imidazole-H), 7.33 (2H, d, Ar-H, *J* = 7.0 Hz), 7.28 (2H, d, Ar-H, *J* = 6.7 Hz), 7.18 (2H, d, imidazole-H), 7.03 (2H, d, Ar-H, *J* = 7.0 Hz), 6.90 (2H, d, Ar-H, *J* = 6.7 Hz), 5.00 (2H, s, $ArCH_2O$), 3.95 (2H, t, $ArOCH_2$, *J* = 6.4 Hz), 1.79-1.74 (2H, m, $ArOCH_2CH_2$), 1.52-1.24 (18H, m, $9CH_2$), 0.87 (3H, t, CH_3, *J* = 6.3 Hz); elemental analysis calcd (%) for $C_{28}H_{38}N_2O_2$ (434.61): C 77.38, H 8.81, N 6.45; found: C 77.69, H 9.17, N 6.82.
E1^{16}/0	colourless crystals; yield: 68%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 7.75 (1H, s, Ar-H), 7.34 (2H, d, Ar-H, *J* = 7.6 Hz), 7.28 (2H, d, Ar-H, *J* = 8.6 Hz), 7.18 (2H, d, imidazole-H), 7.05 (2H, d, Ar-H, *J* = 8.3 Hz), 6.92 (2H, d, Ar-H, *J* = 8.1 Hz), 5.01 (2H, s, $ArCH_2O$), 3.96 (2H, t, $ArOCH_2$, *J* = 6.4 Hz), 1.79-1.74 (2H, m, $ArOCH_2CH_2$), 1.45-1.25 (26H, m, $13CH_2$), 0.90 (3H, t, CH_3, *J* = 7.0 Hz); Elemental Analysis calcd (%) for $C_{32}H_{46}N_2O_2$(490.72): C 78.32, H 9.45, N 5.71; found: C 77.02, H 9.35, N 6.04.
E1^{18}/0	colourless crystals; yield: 59%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 7.76 (1H, s, imidazole-H), 7.34 (2H, d, Ar-H, *J* = 8.2 Hz), 7.29 (2H, d, Ar-H, *J* = 8.6 Hz), 7.20 (2H, d, imidazole-H), 7.05 (2H, d, Ar-H, *J* = 8.6 Hz), 6.92 (2H, d, Ar-H, *J* = 8.3 Hz), 5.02 (2H, s, $ArCH_2O$), 3.96 (2H, t, $ArOCH_2$, *J* = 6.5 Hz), 1.79-1.76 (2H, m, $ArOCH_2CH_2$), 1.67-1.63 (2H, m, CH_2), 1.44-1.25 (28H, m, $14CH_2$), 0.88 (3H, t, CH_3, *J* = 6.3 Hz); elemental analysis calcd (%) for $C_{34}H_{50}N_2O_2$ (518.77): C 78.72, H 9.71, N 5.40; found: C 78.48, H 9.55, N 5.73.
E2^{16}/0	colourless crystals; yield: 74%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 7.76 (1H, s, imidazole-H), 7.29 (2H, d, Ar-H, *J* = 8.8 Hz), 7.19 (2H, d, imidazole-H), 7.05 (2H, d, Ar-H, *J* = 8.8 Hz), 6.96 (1H, s, Ar-H), 6.94 (1H, d, Ar-H, *J* = 9.3 Hz), 6.88 (1H, d, Ar-H, *J* = 8.1 Hz), 5.00 (2H, s, $ArCH_2O$), 4.02-3.98 (4H, m, $2ArOCH_2$), 1.84-1.78 (4H, m, $2ArOCH_2CH_2$), 1.62-1.25 (52H, m, $26CH_2$), 0.88 (6H, t, $2CH_3$, *J* = 6.5 Hz); elemental analysis calcd (%) for $C_{48}H_{78}N_2O_3$ (731.14): C 78.85, H

	10.75, N 3.83; found: C 78.53, H 10.98, N 3.67.
E3^{12}/0	colourless crystals; yield: 77%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 7.77 (1H, s, imidazole-H), 7.30 (2H, d, Ar-H, *J* = 8.8 Hz), 7.20 (2H, d, imidazole-H), 7.05 (2H, d, Ar-H, *J* = 8.8 Hz), 6.63 (2H, s, Ar-H), 4.99 (2H, s, $ArCH_2O$), 3.99-3.94 (6H, m, $3ArOCH_2$), 1.83-1.72 (6H, m, $3ArOCH_2CH_2$), 1.48-1.26 (54H, m, $27CH_2$), 0.88 (9H, t, $3CH_3$, *J* = 6.5 Hz); elemental analysis calcd (%) for $C_{52}H_{86}N_2O_4$ (803.25): C 77.75, H 10.79, N 3.49; found: C 78.01, H 10.51, N 3.17.
E3^{14}/0	colourless crystals; yield: 59%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 7.76 (1H, s, imidazole-H), 7.29 (2H, d, Ar-H, *J* = 8.5 Hz), 7.19 (2H, d, imidazole-H), 7.05 (2H, d, Ar-H, *J* = 8.5 Hz), 6.62 (2H, s, Ar-H), 4.98 (2H, s, $ArCH_2O$), 3.98-3.95 (6H, m, $3ArOCH_2$), 1.79-1.72 (6H, m, 3 $ArOCH_2CH_2$), 1.46-1.26 (66H, m, $33CH_2$), 0.87 (9H, t, $3CH_3$, *J* = 6.5 Hz); elemental analysis calcd (%) for $C_{58}H_{98}N_2O_4$ (887.40): C 78.50, H 11.13, N 3.16; found: C 78.40, H 10.83, N 3.50.
E3^{16}/0	colourless crystals; yield: 79%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 7.77 (1H, s, imidazole-H), 7.29 (2H, d, Ar-H, *J* = 8.4 Hz), 7.20 (2H, d, imidazole-H), 7.05 (2H, d, Ar-H, *J* = 8.4 Hz), 6.62 (2H, s, Ar-H), 4.98 (2H, s, $ArCH_2O$), 3.99-3.93 (6H, m, $3ArOCH_2$), 1.80-1.74 (6H, m, $3ArOCH_2CH_2$), 1.46-1.25 (78H, m, $39CH_2$), 0.87 (9H, t, $3CH_3$, *J* = 6.2 Hz); elemental analysis calcd (%) for $C_{64}H_{110}N_2O_4$ (971.57): C 79.12, H 11.41, N 2.88; found: C 79.62, H 11.27, N 2.67.
E3^{18}/0	colourless crystals; yield: 73%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 7.79 (1H, s, imidazole-H), 7.30 (2H, d, Ar-H, *J* = 8.8 Hz), 7.19 (2H, d, imidazole-H), 7.05 (2H, d, Ar-H, *J* = 8.8 Hz), 6.62 (2H, s, Ar-H), 4.98 (2H, s, $ArCH_2O$), 3.99-3.93 (6H, m, $3ArOCH_2$), 1.81-1.74 (6H, m, $3ArOCH_2CH_2$), 1.46-1.25 (90H, m, $45CH_2$), 0.87 (9H, t, $3CH_3$, *J* = 6.6 Hz); elemental analysis calcd (%) for $C_{70}H_{122}N_2O_4$ (1055.73): C 79.64, H 11.65, N 2.65; found: C 79.90, H 11.48, N 2.96.

3.4 Phenylbenzylether based imidazolium bromides (E1^n/*m*-E3^n/*m*)

General procedure for alkylation reaction: Compound **E1^n/0** (0.27 mmol), toluene (5 mL), corresponding *n*-bromoalkane (2.7 mmol, 10 eq./**E1^n/0**), were heated to reflux for 18-48 h. After the reaction was complete (TLC), the mixture was cooled to RT, and the solvent was removed in *vacuo*. The residue was purified by column chromatography (silica gel, chloroform: methanol = 30:1). (Yield: 40 - 97%, for analytical data see **Table S4**).

Table S4 Analytical data of compounds **E1^{n}/*m*-E3^{n}/*m***

Comp.	
E1^{12}/3	pale yellow crystals; yield: 40%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.04 (1H, s, imidazole-H), 7.69 (2H, d, Ar-H, *J* = 8.8 Hz), 7.50 (1H, s, imidazole-H), 7.41 (1H, s, imidazole-H), 7.33 (2H, d, Ar-H, *J* = 8.5 Hz), 7.11 (2H, d, Ar-H, *J* = 8.8 Hz), 6.91 (2H, d, Ar-H, *J* = 8.5 Hz), 5.02 (2H, s, $ArCH_2O$), 4.54 (2H, t, NCH_2, *J* = 7.3 Hz), 3.95 (2H, t, $ArOCH_2$, *J* = 6.6 Hz), 2.08-2.02 (2H, m, NCH_2CH_2), 1.79-1.76 (2H, m, $ArOCH_2CH_2$), 1.45-1.26 (18H, m, $9CH_2$), 1.04 (3H, t, CH_3, *J* = 7.4 Hz), 0.88 (3H, t, CH_3, *J* = 6.5 Hz); elemental analysis calcd (%) for $C_{31}H_{45}BrN_2O_2$ (557.60): C 66.77, H 8.13, N 5.02; found: C 67.02, H 8.54, N 4.82.
E1^{12}/4	colourless crystals; yield: 63%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.02 (1H, s, imidazole-H), 7.69 (2H, d, Ar-H, *J* = 8.1 Hz), 7.55 (1H, s, imidazole-H), 7.47 (1H, s, imidazole-H), 7.33 (2H, d, Ar-H, *J* = 7.8 Hz), 7.10 (2H, d, Ar-H, *J* = 8.1 Hz), 6.91 (2H, d, Ar-H, *J* = 7.7 Hz), 5.01 (2H, s, $ArCH_2O$), 4.58 (2H, t, NCH_2, *J* = 7.1 Hz), 3.96 (2H, t, $ArOCH_2$, *J* = 6.3 Hz), 1.98-1.95 (2H, m, NCH_2CH_2), 1.79-1.76 (2H, m, $ArOCH_2CH_2$), 1.46-1.26 (20H, m, $10CH_2$), 0.98 (3H, t, CH_3, *J* = 7.2 Hz), 0.88 (3H, t, CH_3, *J* = 5.9 Hz); elemental analysis calcd (%) for $C_{32}H_{47}BrN_2O_2$ (571.63): C 67.24, H 8.29, N 4.90; found: C 67.03, H 8.56, N 5.17.
E1^{12}/12	colourless crystals; yield: 73%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.04 (1H, s, imidazole-H), 7.69 (2H, d, Ar-H, *J* = 8.9 Hz), 7.50 (1H, s, imidazole-H), 7.38 (1H, s, imidazole-H), 7.33 (2H, d, Ar-H, *J* = 8.6 Hz), 7.11 (2H, d, Ar-H, *J* = 8.9 Hz), 6.91 (2H, d, Ar-H, J = 8.6 Hz), 5.02 (2H, s, $ArCH_2O$), 4.57 (2H, t, NCH_2, *J* = 7.3Hz), 3.96 (2H, t, $ArOCH_2$, *J* = 6.6 Hz), 1.97-1.94 (2H, m, NCH_2CH_2), 1.79-1.76 (2H, m, $ArOCH_2CH_2$), 1.45-1.24 (36H, m, $18CH_2$), 0.89-0.86 (6H, m, $2CH_3$); elemental analysis calcd (%) for $C_{40}H_{63}BrN_2O_2$ (682.41): C 70.25, H 9.29, N 4.10; found: C 70.60, H 8.98, N 3.94.
E1^{14}/12	colourless crystals; yield: 66%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.06 (1H, s, imidazole-H), 7.69 (2H, d, Ar-H, *J* = 8.6 Hz), 7.50 (1H, s, imidazole-H), 7.38 (1H, s, imidazole-H), 7.33 (2H, d, Ar-H, *J* = 8.0 Hz), 7.11 (2H, d, Ar-H, *J* = 7.6 Hz), 6.92 (2H, d, Ar-H, *J* = 8.0 Hz), 5.02 (2H, s, $ArCH_2O$), 4.56 (2H, t, NCH_2, *J* = 7.3Hz), 3.96 (2H, t, $ArOCH_2$, *J* = 5.5 Hz), 1.97-1.94 (2H, m, NCH_2CH_2), 1.79-1.76 (2H, m, $ArOCH_2CH_2$),, 1.45-1.25 (40H, m, $20CH_2$), 0.87 (6H, t, $2CH_3$, *J* = 6.8 Hz); elemental analysis calcd (%) for $C_{42}H_{67}BrN_2O_2$ (711.90): C 70.86, H 9.49, N 3.94; found: C 71.01, H 9.47, N 4.14.
E1^{16}/3	colourless crystals; yield: 70%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.04 (1H, s, imidazole-H), 7.69 (2H, d, Ar-H, *J* = 8.8 Hz), 7.50 (1H, s, imidazole-H), 7.41 (1H, s, imidazole-H), 7.33 (2H, d, Ar-H, *J* = 8.5 Hz),

	7.11 (2H, d, Ar-H, *J* = 8.8 Hz), 6.91 (2H, d, Ar-H, *J* = 8.5 Hz), 5.02 (2H, s, $ArCH_2O$), 4.54 (2H, t, NCH_2, *J* = 7.3 Hz), 3.95 (2H, t, $ArOCH_2$, *J* = 6.6 Hz), 2.08-2.02 (2H, m, NCH_2CH_2), 1.79-1.76 (2H, m, $ArOCH_2CH_2$), 1.45-1.26 (26H, m, $13CH_2$), 1.04 (3H, t, CH_3, *J* = 7.4 Hz), 0.88 (3H, t, CH_3, *J* = 6.5 Hz); elemental analysis calcd (%) for $C_{35}H_{53}BrN_2O_2$ (613.71): C 68.50, H 8.70, N 4.56; found: C 68.31, H 8.38, N 4.90.
E1[18]/6	colourless crystals; yield: 43%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.06 (1H, s, imidazole-H), 7.69 (2H, d, Ar-H, *J* = 8.9 Hz), 7.51 (1H, s, imidazole-H), 7.39 (1H, s, imidazole-H), 7.33 (2H, d, Ar-H, *J* = 8.5 Hz), 7.11 (2H, d, Ar-H, *J* = 8.9 Hz), 6.92 (2H, d, Ar-H, *J* = 8.5 Hz), 5.02 (2H, s, $ArCH_2O$), 4.56 (2H, t, NCH_2, *J* = 7.3Hz), 3.96 (2H, t, $ArOCH_2$, *J* = 6.6 Hz), 1.97-1.94 (2H, m, NCH_2CH_2), 1.79-1.76 (2H, m, $ArOCH_2CH_2$), 1.45-1.25 (36H, m, $18CH_2$), 0.88 (6H, t, $2CH_3$, *J* = 6.6 Hz); elemental analysis calcd (%) for $C_{40}H_{63}BrN_2O_2$ (683.84): C 70.25, H 9.29, N 4.10; found: C 70.48, H 9.62, N 3.29.
E2[16]/3	colourless crystals; yield: 70%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 10.91 (1H, s, imidazole-H), 7.70 (2H, d, Ar-H, *J* = 8.9 Hz), 7.59 (1H, s, imidazole-H), 7.55 (1H, s, imidazole-H), 7.11 (2H, d, Ar-H, *J* = 8.9 Hz), 6.95-6.92 (2H, t, 2Ar-H), 6.87 (1H, d, Ar-H, *J* = 8.0 Hz), 4.99 (2H, s, $ArCH_2O$), 4.53 (2H, t, NCH_2, *J* = 8.3 Hz), 4.01-3.98 (4H, m, $2ArOCH_2$), 2.05-2.00 (2H, m, NCH_2CH_2), 1.83-1.78 (4H, m, $2CH_2$, $2ArOCH_2CH_2$), 1.46-1.25 (52H, m, $26CH_2$), 1.03 (3H, t, CH_3, *J* = 7.3 Hz), 0.88 (6H, m, $2CH_3$, *J* = 6.4 Hz); elemental analysis calcd (%) for $C_{51}H_{85}BrN_2O_3$ (854.13): C 71.72, H 10.03, N 3.28; found: C 71.38, H 10.29, N 3.59.
E3[12]/4	colourless crystals; yield: 74%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.09 (1H, s, imidazole-H), 7.71 (2H, d, Ar-H, *J* = 8.9 Hz), 7.57 (1H, s, imidazole-H), 7.48 (1H, s, imidazole-H), 7.12 (2H, d, Ar-H, *J* = 9.0 Hz), 6.61 (2H, s, Ar-H), 4.98 (2H, s, $ArCH_2O$), 4.56 (2H, t, NCH_2, *J* = 7.4 Hz), 3.99-3.93 (6H, m, $3ArOCH_2$), 1.98-1.94 (2H, m, NCH_2CH_2), 1.83-1.73 (6H, m, $3CH_2$, $3ArOCH_2CH_2$), 1.47-1.25 (56H, m, $28CH_2$), 0.98 (3H, t, CH_3, *J* = 7.4 Hz)，0.87 (9H, m, $3CH_3$, *J* = 6.7 Hz). ^{13}C-NMR (125MHz, $CDCl_3$), δ (ppm): 160.4, 153.8 (2C), 138.7, 136.7, 131.2, 128.0, 123.8 (2C), 122.7, 120.8, 116.9, (2C) 106.6 (2C), 73.9, 71.3, 69.6 (2C), 50.7, 32.7, 32.3, 30.8-29.7 (multicarbon in alkyl chain), 26.5, 23.1, 19.9, 14.9, 14.5, 13.9; elemental analysis calcd (%) for $C_{56}H_{95}BrN_2O_4$ (940.27): C 71.53, H 10.18, N 2.98; found: C 71.81, H 10.42, N 3.19.
E3[12]/5	colourless crystals; yield: 74%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.09 (1H, s, imidazole-H), 7.71 (2H, d, Ar-H, *J* = 8.8 Hz), 7.51 (1H, s, imidazole-H), 7.40 (1H, s, imidazole-H), 7.13 (2H, d, Ar-H, *J* = 8.7 Hz),

	6.61 (2H, s, Ar-H), 4.99 (2H, s, $ArCH_2O$), 4.57 (2H, t, NCH_2, *J* = 7.3 Hz), 3.99-3.93 (6H, m, $3ArOCH_2$), 1.99-1.94 (2H, m, NCH_2CH_2), 1.81-1.71 (6H, m, $3CH_2$, $3ArOCH_2CH_2$), 1.48-1.28 (58H, m, $29CH_2$), 0.91-0.86 (12H, m, $4CH_3$); elemental analysis calcd (%) for $C_{57}H_{97}BrN_2O_4$ (954.30): C 71.74, H 10.25, N 2.94; found: C72.01, H 10.58, N 2.39.
E3^{14}/2	colourless crystals; yield: 73%;^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.08 (1H, s, imidazole-H), 7.69 (2H, d, Ar-H, *J* = 8.8 Hz), 7.50 (1H, s, imidazole-H), 7.44 (1H, s, imidazole-H), 7.12 (2H, d, Ar-H, *J* = 8.8 Hz), 6.60 (2H, s, Ar-H), 4.99 (2H, s, $ArCH_2O$), 4.64 (2H, q, NCH_2, *J* = 7.4 Hz), 3.99-3.93 (6H, m, $3ArOCH_2$), 1.81-1.72 (6H, m, $3CH_2$, $3ArOCH_2CH_2$), 1.66 (3H, t, CH_3, *J* = 7.3 Hz), 1.47-1.25 (66H, m, $33CH_2$), 0.87 (9H, t, $3CH_3$, *J* = 6.4 Hz); elemental analysis calcd (%) for $C_{60}H_{103}BrN_2O_4$ (996.37): C 72.33, H 10.42, N 2.81; found: C 72.77, H 10.92, N 2.41.
E3^{14}/3	colourless crystals; yield: 97%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.10 (1H, s, imidazole-H), 7.71 (2H, d, Ar-H, *J* = 8.8 Hz), 7.51 (1H, s, imidazole-H), 7.42 (1H, s, imidazole-H), 7.12 (2H, d, Ar-H, *J* = 8.8 Hz), 6.61 (2H, s, Ar-H), 4.99 (2H, s, $ArCH_2O$), 4.54 (2H, q, NCH_2, *J* = 7.4 Hz), 3.99-3.93 (6H, m, $3ArOCH_2$), 2.04-2.00 (2H, m, NCH_2CH_2), 1.81-1.72 (6H, m, 3 $ArOCH_2CH_2$), 1.47-1.25 (66H, m, $33CH_2$), 1.05 (3H, t, CH_3, *J* = 7.3 Hz), 0.89-0.82 (9H, m, $3CH_3$); elemental analysis calcd (%) for $C_{61}H_{105}BrN_2O_4$ (1010.40): Elemental Analysis: C 72.51, H 10.47, N 2.77; found: C 72.90, H 10.79, N 3.03.
E3^{14}/4	colourless crystals; yield: 85%;^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.15 (1H, s, imidazole-H), 7.71 (2H, d, Ar-H, *J* = 8.8 Hz), 7.49 (1H, s, imidazole-H), 7.37 (1H, s, imidazole-H), 7.12 (2H, d, Ar-H, *J* = 8.9 Hz), 6.60 (2H, s, Ar-H), 4.99 (2H, s, $ArCH_2O$), 4.59 (2H, t, NCH_2, *J* = 7.4 Hz), 3.99-3.93 (6H, m, $3ArOCH_2$), 1.98-1.94 (2H, m, NCH_2CH_2), 1.83-1.71 (6H, m, $3ArOCH_2CH_2$), 1.47-1.25 (68H, m, $34CH_2$), 0.99 (3H, t, CH_3, *J* = 7.3 Hz), 0.88 (9H, m, $3CH_3$, *J* = 6.5 Hz); elemental analysis calcd (%) for $C_{62}H_{107}BrN_2O_4$ (1024.43): Elemental Analysis: C 72.69, H 10.53, N 2.73; found: C 72.31, H 10.22, N 2.47.
E3^{14}/5	colourless crystals; yield: 67%;^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.23 (1H, s, imidazole-H), 7.73 (2H, d, Ar-H, *J* = 8.6 Hz), 7.47 (1H, s, imidazole-H), 7.36 (1H, s, imidazole-H), 7.13 (2H, d, Ar-H, *J* = 8.3 Hz), 6.61 (2H, s, Ar-H), 5.00 (2H, s, $ArCH_2O$), 4.59 (2H, t, NCH_2, *J* = 7.4 Hz), 4.00-3.96 (6H, m, $3ArOCH_2$), 2.02-1.98 (2H, m, NCH_2CH_2), 1.82-1.72 (6H, m, $3CH_2$, $3ArOCH_2CH_2$), 1.48-1.28 (70H, m, $35CH_2$), 0.93-0.88 (12H, m, $4CH_3$); elemental analysis calcd (%) for $C_{63}H_{109}BrN_2O_4$ (1038.45): C 72.87, H 10.58, N 2.70; found: C 72.48, H

	10.91, N 3.09.
E3^{14}/6	colourless crystals; yield: 93%;^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.13(1H, s, imidazole-H), 7.71 (2H, d, Ar-H, *J* = 8.7 Hz), 7.48 (1H, s, imidazole-H), 7.36 (1H, s, imidazole-H), 7.13 (2H, d, Ar-H, *J* = 7.8 Hz), 6.60 (2H, s, Ar-H), 4.99 (2H, s, $ArCH_2O$), 4.57 (2H, t, NCH_2, *J* = 7.3 Hz), 3.99-3.93 (6H, m, $3ArOCH_2$), 1.98-1.94 (2H, m, NCH_2CH_2), 1.82-1.72 (6H, m, $3CH_2$, $3ArOCH_2CH_2$), 1.47-1.25 (72H, m, $36CH_2$), 0.88 (12H, m, $4CH_3$, *J* = 7.0 Hz); elemental analysis calcd (%) for $C_{64}H_{111}BrN_2O_4$ (1052.48): C 73.04, H 10.63, N 2.66; found: C 73.41, H 10.97, N 2.98.
E3^{16}/2	colourless crystals; yield: 88%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 10.92 (1H, s, imidazole-H), 7.69 (2H, d, Ar-H, *J* = 8.7 Hz), 7.54 (1H, s, imidazole-H), 7.52 (1H, s, imidazole-H), 7.13 (2H, d, Ar-H, *J* = 8.7 Hz), 6.61 (2H, d, Ar-H, *J* = 8.0 Hz), 4.99 (2H, s, $ArCH_2O$), 4.64 (2H, q, NCH_2, *J* = 7.0 Hz), 3.99-3.93 (6H, m, $3ArOCH_2$), 1.81-1.74 (6H, m, 3 $ArOCH_2CH_2$), 1.66 (3H, t, CH_3, *J* = 7.3 Hz), 1.45-1.25 (78H, m, $39CH_2$), 0.87 (9H, t, $3CH_3$, *J* = 6.3 Hz); elemental analysis calcd (%) for $C_{66}H_{115}BrN_2O_4$ (1080.53): C 73.36, H 10.73, N 2.59; found: C 73.71, H 10.39, N 2.21.
E3^{16}/3	colourless crystals; yield: 40%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.12 (1H, s, imidazole-H), 7.71 (2H, d, Ar-H, *J* = 8.9 Hz), 7.49 (1H, s, imidazole-H), 7.38 (1H, s, imidazole-H), 7.13 (2H, d, Ar-H, *J* = 9.0 Hz), 6.61 (2H, s, Ar-H), 4.99 (2H, s, $ArCH_2O$), 4.55 (2H, t, NCH_2, *J* = 7.3 Hz), 3.99-3.93 (6H, m, $3ArOCH_2$), 2.06-2.02 (2H, m, NCH_2CH_2), 1.81-1.71 (6H, m, $3ArOCH_2CH_2$), 1.47-1.25 (78H, m, $39CH_2$), 1.05 (3H, t, CH_3, *J* = 7.4 Hz), 0.88 (9H, t, $3CH_3$ *J* = 6.6 Hz); elemental analysis calcd (%) for $C_{67}H_{117}BrN_2O_4$ (1094.56): C 73.52, H 10.77, N 2.56; found: C 73.87, H 10.43, N 2.19.
E3^{16}/4	colourless crystals; yield: 54%;^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.19 (1H, s, imidazole-H), 7.71 (2H, d, Ar-H, *J* = 8.9 Hz), 7.47 (1H, s, imidazole-H), 7.34 (1H, s, imidazole-H), 7.13 (2H, d, Ar-H, *J* = 8.9 Hz), 6.61 (2H, s, Ar-H), 4.99 (2H, s, $ArCH_2O$), 4.59 (2H, t, NCH_2, *J* = 7.3 Hz), 3.99-3.93 (6H, m, $3ArOCH_2$), 1.98-1.94 (2H, m, NCH_2CH_2), 1.82-1.72 (6H, m, $3CH_2$, $ArOCH_2CH_2$), 1.48-1.25 (80H, m, $40CH_2$), 1.00 (3H, t, CH_3, *J* = 7.4 Hz), 0.88 (9H, m, $3CH_3$, *J* = 6.5 Hz); elemental analysis calcd (%) for $C_{68}H_{119}BrN_2O_4$ (1108.59): C 73.67, H 10.82, N 2.53; found: C 73.29, H 11.02, N 2.81.
E3^{16}/5	colourless crystals; yield: 93%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.12 (1H, s, imidazole-H), 7.71 (2H, d, Ar-H, *J* = 8.8 Hz), 7.48 (1H, s, imidazole-H), 7.27 (1H, s, imidazole-H), 7.13 (2H, d, Ar-H, *J* = 9.0 Hz), 6.61 (2H, s, Ar-H), 4.99 (2H, s, $ArCH_2O$), 4.58 (2H, t, NCH_2, *J* = 7.3

	Hz), 3.99-3.93 (6H, m, $3ArOCH_2$), 1.99-1.94 (2H, m, NCH_2CH_2), 1.81-1.72 (6H, m, $3CH_2$, $ArOCH_2CH_2$), 1.47-1.25 (82H, m, $41CH_2$), 0.92-0.86 (12H, m, $4CH_3$); elemental analysis calcd (%) for $C_{69}H_{121}BrN_2O_4$ (1122.61): C 73.82, H 10.86, N 2.50; found: C 73.49, H 10.49, N 2.78.
E3^{18}/3	colourless crystals; yield: 75%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.20 (1H, s, imidazole-H), 7.70 (2H, d, Ar-H, *J* = 7.8 Hz), 7.46 (1H, s, imidazole-H), 7.33 (1H, s, imidazole-H), 7.13 (2H, d, Ar-H, *J* = 8.9 Hz), 6.60 (2H, s, Ar-H), 4.99 (2H, s, $ArCH_2O$), 4.56 (2H, t, NCH_2, *J* = 6.8 Hz), 3.99-3.93 (6H, m, $3ArOCH_2$), 2.06-2.02 (2H, m, NCH_2CH_2), 1.81-1.72 (6H, m, 3 $ArOCH_2CH_2$), 1.47-1.25 (90H, m, $45CH_2$), 1.06 (3H, t, CH_3, *J* = 7.6 Hz), 0.88 (9H, m, $3CH_3$, *J* = 5.9 Hz); elemental analysis calcd (%) for $C_{73}H_{129}BrN_2O_4$ (1178.72): C 74.38, H 11.03, N 2.38; found: C 74.01, H 11.60, N 2.69.
E3^{18}/5	colourless crystals; yield: 99%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 11.11 (1H, s, imidazole-H), 7.71 (2H, d, Ar-H, *J* = 8.8 Hz), 7.49 (1H, s, imidazole-H), 7.37 (1H, s, imidazole-H), 7.13 (2H, d, Ar-H, *J* = 9.1 Hz), 6.61 (2H, s, Ar-H), 4.99 (2H, s, $ArCH_2O$), 4.57 (2H, t, NCH_2, *J* = 7.4 Hz), 3.99-3.93 (6H, m, $3ArOCH_2$), 1.99-1.94 (2H, m, NCH_2CH_2), 1.80-1.72 (6H, m, $3CH_2$, OCH_2CH_2), 1.47-1.25 (94H, m, $47CH_2$), 0.91-0.86 (12H, m, $4CH_3$); elemental analysis calcd (%) for $C_{75}H_{133}BrN_2O_4$ (1206.77): C 74.65, H 11.11, N 2.32; found: C 74.91, H 11.46, N 2.09.

3.5 Benzanilide based 1-phenyl-1*H*-imidazoles (A1^n/0 –A3^n/0)

General procedure for the amidation of 5 with benzoylchlorides 7[S8]**:** To a mixture of NaH (2 mmol), 4-(1*H*-imidazol-1-yl)aniline **7** (1 mmol) in dry DMF (20 mL), the appropriate alkoxybenzoyl chloride (1.1 mmol) was added under a N_2 atmosphere. The mixture was heated to 90 °C and stirred for 16 h. After the reaction was complete (TLC), the mixture was cooled to RT, and extracted with ethyl acetate (3 × 30 mL). The combined extracts were washed with H_2O (5 × 20 mL), dried over $MgSO_4$, then the solvent was removed in *vacuo*. The residue was purified by chromatography (petroleum ether: ethyl acetate = 2:1), (Yield: 53 - 75%, for analytical data see **Table S5**).

Table S5 Analytical data of compounds **A1^n/0 –A3^n/0**

Comp.	
A1^6/0	colourless crystals; yield: 58%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 8.44 (1H, s, imidazole-H), 7.87 (2H, d, Ar-H, *J* = 8.6 Hz), 7.78 (3H, t, Ar-H and imidazole-H), 7.35 (2H, d, Ar-H, *J* = 8.6 Hz), 7.27 (1H, s, CONH), 7.19 (1H, s, imidazole-H), 6.94 (2H, d, Ar-H, *J* = 8.6 Hz), 4.00 (2H, t, $ArOCH_2$, *J* = 6.5 Hz), 1.83-1.77 (2H, m, $ArOCH_2CH_2$), 1.47-1.43 (2H, m, CH_2), 1.35-1.26 (4H, m, $2CH_2$), 0.92 (3H, t, CH_3, *J* = 6.5 Hz); ^{13}C-NMR (125MHz, $CDCl_3$), δ (ppm): 165.9 (CO), 162.7, 138.2 , 136.0, 133.7, 130.7, 129.5 (2C), 126.8, 122.6 (2C), 121.9 (2C), 118.8, 114.9 (2C), 68.7, 31.9, 29.7, 29.5, 26.1, 22.9, 14.4; elemental analysis calcd (%) for $C_{22}H_{25}N_3O_2$ (363.45): C 72.70, H 6.93, N 11.56; found: C 72.33, H 6.60, N 11.21.
A1^{12}/0	colourless crystals, yield: 55%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 8.02 (1H, s, imidazole-H), 7.86 (2H, d, Ar-H, *J* = 8.5 Hz), 7.83 (1H, s, imidazole-H), 7.77 (2H, d, Ar-H, *J* = 8.5 Hz), 7.38 (2H, d, Ar-H, *J* = 8.6 Hz), 7.21 (1H, s, imidazole-H), 6.97 (2H, d, Ar-H, *J* = 8.6 Hz), 4.02 (2H, t, $ArOCH_2$, *J* = 6.5 Hz), 1.82-1.78 (2H, m, $ArOCH_2CH_2$), 1.47-1.26 (18H, m, $9CH_2$), 0.88 (3H, t, CH_3, *J* = 6.5 Hz); ^{13}C-NMR (125MHz, $CDCl_3$), δ (ppm): 165.7 (CO), 162.8, 138.1, 136.0, 133.8, 130.7, 129.5 (2C), 126.8, 122.7 (2C), 121.7 (2C), 118.8, 114.9 (2C), 68.8, 32.3, 30.0-29.5 (multicarbon in alkyl chain), 26.4, 23.1, 14.5; elemental analysis calcd (%) for $C_{28}H_{37}N_3O_2$ (447.61): C 75.13, H 8.33, N 9.39; found: C 75.41, H 8.80, N 9.91.
A1^{16}/0	colourless crystals, yield: 70%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 8.03 (1H, s, imidazole-H), 7.85 (2H, d, Ar-H, *J* = 8.1 Hz), 7.82 (1H, s, imidazole-H), 7.77 (2H, d, Ar-H, *J* = 8.4 Hz), 7.39 (2H, d, Ar-H, *J* = 8.3 Hz), 7.20 (1H, s, imidazole-H), 6.97 (2H,d, Ar-H, *J* = 8.2 Hz), 4.02 (2H, t, $ArOCH_2$, *J* = 6.3 Hz), 1.82-1.77 (2H, m, $ArOCH_2CH_2$), 1.46-1.23 (26H, m, $13CH_2$), 0.87 (3H, t, CH_3, *J* = 5.6 Hz) ; elemental analysis calcd (%) for $C_{32}H_{45}N_3O_2$ (503.72): C 76.30, H 9.00, N 8.34; found: C 76.07, H 8.81, N 8.78.
A1^{18}/0	colourless crystals, yield: 53%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 8.03 (1H, s, imidazole-H), 7.85 (2H, d, Ar-H, *J* = 8.7 Hz), 7.83 (1H, s, imidazole-H), 7.77 (2H, d, Ar-H, *J* = 8.7 Hz), 7.37 (2H, d, Ar-H, *J* = 8.7 Hz), 7.20 (1H, s, imidazole-H), 6.97 (2H, d, Ar-H, *J* = 8.7 Hz), 4.02 (2H, t, $ArOCH_2$, *J* = 6.6 Hz), 1.82-1.78 (2H, m, $ArOCH_2CH_2$), 1.47-1.25 (30H, m, $15CH_2$), 0.87 (3H, t, CH_3, *J* = 6.6 Hz); elemental analysis calcd (%) for $C_{34}H_{49}N_3O_2$ (531.77): C 76.79, H 9.29, N 7.90; found: C 76.45, H 9.53, N 7.73.
A2^{16}/0	colourless crystals, yield: 75%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 7.93 (1H, s, imidazole-H), 7.84 (1H, s, imidazole-H), 7.76 (2H, d, Ar-H, *J* = 8.6

	Hz), 7.49 (1H, s, CONH), 7.39 (3H, m, 3Ar-H), 7.21 (1H, s, imidazole-H), 6.91 (2H, s, Ar-H, *J* = 8.3 Hz), 4.8-4.04 (4H, m, $2ArOCH_2$), 1.86-1.84 (4H, m, $2ArOCH_2CH_2$), 1.66-1.25 (52H, m, $26CH_2$), 0.88 (6H, t, $2CH_3$, *J* = 6.3 Hz); elemental analysis calcd (%) for $C_{48}H_{77}N_3O_3$ (744.14): C 77.47, H 10.43, N, 5.65; found: C 77.81, H 10.81, N 5.92.
A3^6/0	pale yellow crystals, yield: 60%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 8.78 (1H, s, imidazole-H), 7.81-7.79 (3H, s, 2Ar-H and imidazole-H), 7.34 (2H, d, Ar-H, *J* = 8.5 Hz), 7.18 (1H, s, imidazole-H), 7.11 (2H, s, Ar-H), 4.02-3.95 (6H, m, $3ArOCH_2$), 1.79-1.73 (6H, m, $3ArOCH_2CH_2$), 1.47-1.31 (18H, m, $9CH_2$), 0.89 (9H, t, $3CH_3$, *J* = 4.8 Hz); ^{13}C-NMR (125MHz, $CDCl_3$), δ (ppm): 166.5(CO), 153.6 (2C), 142.1, 138.3, 135.9, 133.7, 130.6, 129.8, 122.5(2C), 121.8(2C), 118.8, 106.5 (2C), 73.9, 69.8 (2C), 32.1-29.7 (multicarbon in alkyl chain), 26.1, 23.0, 14.7, 14.5, 14.4; elemental analysis calcd (%) for $C_{34}H_{49}N_3O_4$ (563.77): C 72.43, H 8.76, N 7.45; found: C 72.80, H 8.77, N 7.57.
A3^{10}/0	pale yellow crystals, yield: 75%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 8.43 (1H, s, CONH), 7.99 (1H, s, imidazole-H), 7.83 (1H, s, imidazole-H), 7.79 (2H, d, Ar-H, *J* = 8.6 Hz), 7.37 (2H, d, Ar-H, *J* = 8.6 Hz), 7.20 (1H, s, imidazole-H), 7.09 (2H, s, Ar-H), 4.01-3.94 (6H, m, $3ArOCH_2$), 1.82-1.73 (6H, m, $3ArOCH_2CH_2$), 1.46-1.27 (42H, m, $21CH_2$), 0.87 (9H, t, $3CH_3$, *J* = 6.6 Hz). ^{13}C-NMR (125MHz, $CDCl_3$), δ (ppm): 166.3(CO), 153.7 (2C), 142.3, 138.1, 136.0, 133.8, 130.7, 129.8, 122.6 (2C), 121.9 (2C), 118.8, 106.6 (2C), 74.0, 69.9 (2C), 32.3-29.7 (multicarbon in alkyl chain), 26.5, 23.1, 14.5, elemental analysis calcd (%) for $C_{46}H_{73}N_3O_4$ (732.09): C 75.47, H 10.05, N 5.74; found: C 75.49, H 10.51, N 5.91.
A3^{12}/0	pale brownish crystals; yield: 68%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 8.08 (1H, s, imidazole-H), 7.89 (1H, s, imidazole-H), 7.77 (2H, d, Ar-H, *J* = 8.2 Hz), 7.37 (2H, d, Ar-H, *J* = 8.4 Hz), 7.21 (1H, s, imidazole-H), 7.07 (2H, s, Ar-H), 4.03-3.95 (6H, m, $3ArOCH_2$), 1.83-1.73 (6H, m, $3ArOCH_2CH_2$), 1.47-1.26 (54H, m, $27CH_2$), 0.88 (9H, t, $3CH_3$, *J* = 6.0 Hz); elemental analysis calcd (%) for $C_{52}H_{85}N_3O_4$ (816.25): C 76.52, H 10.50, N 5.15; found: C 76.52, H 10.63, N 5.59.
A3^{14}/0	pale brownish crystals; yield: 56%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 8.33 (1H, s, CONH), 7.89 (1H, s, imidazole-H), 7.78 (2H, d, Ar-H, *J* = 8.6 Hz), 7.35 (2H, d, Ar-H, *J* = 8.6 Hz), 7.25 (1H, s, imidazole-H), 7.20 (1H, s, imidazole-H), 7.09 (2H, s, Ar-H), 4.02-3.99 (6H, m, $3ArOCH_2$), 1.82-1.72 (6H, m, $3ArOCH_2CH_2$), 1.48-1.26 (66H, m, $33CH_2$), 0.88 (9H, t, $3CH_3$, *J* = 6.3 Hz); elemental analysis calcd (%) for $C_{58}H_{97}N_3O_4$ (900.41): C 77.37, H 10.86, N 4.67; found: C 77.39, H 11.07, N 4.69.
A3^{18}/0	colourless crystals; yield: 70%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 7.96

	(1H, s, imidazole-H), 7.84 (1H, s, imidazole-H), 7.76 (2H, d, Ar-H, *J* = 8.6 Hz), 7.39 (2H, d, Ar-H, *J* = 8.6 Hz), 7.27 (1H, s, CONH), 7.21 (1H, s, imidazole-H), 7.07 (2H, s, Ar-H), 4.05-4.01 (6H, m, $3ArOCH_2$), 1.84-1.74 (6H, m, $3ArOCH_2CH_2$), 1.48-1.25 (90H, m, $45CH_2$), 0.88 (9H, t, $3CH_3$, *J* = 6.4 Hz); elemental analysis calcd (%) for $C_{70}H_{121}N_3O_4$ (1068.73): C 78.67, H 11.41, N 3.93; found: C 78.61, H 11.81, N 4.10.

3.6 Benzanilide based imidazolium bromides (A1^n/*m*-A3^n/*m*)

General procedure for the alkylation reaction: Compound A**1**^{n}**/0** (0.27 mmol), toluene (5 mL), corresponding *n*-bromoalkane (2.7 mmol, 10 eq./A**1**^{n}**/0**), were heated to refluxed for 18 - 48 h. The residue was filtered and purified by column chromatography (silica gel, chloroform: methanol = 30:1), (Yield: 75-94 %, for analytical data see **Table S6**).

Table S6 Analytical data of compounds **A1**^{n}***/m*-A3**^{n}***/m***

Comp.	
A1^{12}/4	colourless crystals; yield: 75%; ^{1}H-NMR (500MHz, $CDCl_3$/DMSO), δ (ppm): 10.41 (1H, s, imidazole-H), 10.12 (1H, s, CONH), 8.13 (2H, d, Ar-H, *J* = 8.6 Hz), 8.03 (2H, d, Ar-H, *J* = 8.4 Hz), 7.90 (1H, s, imidazole-H), 7.74 (1H, s, imidazole-H)，7.67 (2H, d, Ar-H, *J* = 8.6 Hz), 6.96 (2H, d, Ar-H, *J* = 8.4 Hz), 4.46 (2H, t, NCH_2, *J* = 7.3 Hz), 4.03 (2H, t, $ArOCH_2$, *J* = 6.4 Hz), 1.99-1.96 (2H, m, NCH_2CH_2), 1.81-1.77 (2H, m, $ArOCH_2CH_2$), 1.47-1.27 (20H, m, $10CH_2$), 1.00 (3H, t, CH_3, *J* = 7.3 Hz), 0.87 (3H, t, CH_3, *J* = 6.9 Hz); elemental analysis calcd (%) for $C_{32}H_{46}BrN_3O_2$ (584.63): C 65.74, H 7.93, N 7.19; found: C 65.99, H 7.75, N 7.51.
A1^{16}/4	colourless crystals; yield: 81%; ^{1}H-NMR (500MHz, $CDCl_3$/DMSO), δ (ppm): 10.20 (1H, s, imidazole-H or CONH), 10.16 (1H, s, imidazole-H or CONH), 8.12 (2H, d, Ar-H, *J* = 8.8 Hz), 8.00 (2H, d, Ar-H, *J* = 8.6 Hz), 7.97 (1H, s, imidazole-H), 7.80 (1H, s, imidazole-H)，7.64 (2H, d, Ar-H, *J* = 8.8 Hz), 6.96 (2H, d, Ar-H, *J* = 8.7 Hz), 4.39 (2H, t, NCH_2, *J* = 7.3 Hz), 4.03 (2H, t, $ArOCH_2$, *J* = 6.4 Hz), 1.97-1.94 (2H, m, NCH_2CH_2), 1.81-1.78 (2H, m, $ArOCH_2CH_2$), 1.46-1.25 (28H, m, $14CH_2$), 1.01 (3H, t, CH_3, *J* = 7.4 Hz), 0.87 (3H, t, CH_3, *J* = 6.5 Hz); elemental analysis calcd (%) for $C_{36}H_{54}BrN_3O_2$ (640.74): C 67.48, H 8.49, N 6.56; found: C 67.24, H 8.42, N 6.51.
A3^{12}/2	colourless crystals; yield: 86%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 10.61 (1H, s, imidazole-H), 10.36 (1H, s, CONH), 8.23 (2H, d, Ar-H, *J* = 8.1 Hz), 7.60 (1H, s, imidazole-H), 7.44 (2H, d, Ar-H, *J* = 8.1 Hz), 7.36 (2H, s, Ar-H), 7.29 (1H, s, imidazole-H)，4.38 (2H, q, NCH_2, *J* = 7.3 Hz), 4.15-4.11

	(4H, m, $2ArOCH_2$), 3.99 (2H, t, $ArOCH_2$, *J* = 6.4 Hz), 1.79-1.71 (6H, m, $3ArOCH_2CH_2$), 1.59 (3H, t, CH_3, *J* = 7.3 Hz), 1.46-1.25 (54H, m, $27CH_2$), 0.86 (9H, t, $3CH_3$, *J* = 6.7 Hz); elemental analysis calcd (%) for $C_{54}H_{90}BrN_3O_4$ (925.21): C 70.10, H 9.80, N 4.54; found: C 70.13, H 9.84, N 4.75.
A3[12]/3	colourless crystals; yield: 94%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 10.60 (1H, s, imidazole-H), 9.67 (1H, s, CONH), 8.04 (2H, d, Ar-H, *J* = 8.5 Hz), 7.59 (1H, s, imidazole-H), 7.47 (2H, d, Ar-H, *J* = 8.3 Hz), 7.35 (2H, s, Ar-H), 7.28 (1H, s, imidazole-H), 4.30 (2H, t, NCH_2, *J* = 7.0 Hz), 4.15-4.11 (4H, m, $2ArOCH_2$), 4.00 (2H, t, $ArOCH_2$, *J* = 6.4 Hz), 1.98-1.94 (2H, m, NCH_2CH_2), 1.80-1.66 (6H, m, $3ArOCH_2CH_2$), 1.47-1.25 (54H, m, $27CH_2$), 1.00 (3H, t, CH_3, *J* = 7.2 Hz), 0.87 (9H, t, $3CH_3$, *J* = 7.0 Hz); elemental analysis calcd (%) for $C_{55}H_{92}BrN_3O_4$ (939.24): C 70.33, H 9.87, N 4.47; found: C 70.78, H 9.51, N 4.78.
A3[16]/2	colourless crystals; yield: 75%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm): 10.70 (1H, s, imidazole-H), 9.58 (1H, s, CONH), 8.05 (2H, d, Ar-H, *J* = 8.8 Hz), 7.55 (1H, s, imidazole-H), 7.49 (2H, d, Ar-H, *J* = 8.6 Hz), 7.34 (2H, s, Ar-H), 7.28 (1H, s, imidazole-H), 4.41 (2H, q, NCH_2, *J* = 7.3 Hz), 4.16-4.11 (4H, m, $2ArOCH_2$), 4.00 (2H, t, $ArOCH_2$, *J* = 6.4 Hz), 1.82-1.72 (6H, m, $3ArOCH_2CH_2$), 1.60 (3H, t, CH_3, *J* = 7.3 Hz), 1.49-1.25 (78H, m, $39CH_2$), 0.88 (9H, t, $3CH_3$, *J* = 6.4 Hz); elemental analysis calcd (%) for $C_{66}H_{114}BrN_3O_4$ (1093.53): C 72.49, H 10.51, N 3.84; found: C 72.41, H 10.83, N 3.47.
A3[16]/4	colourless crystals; yield: 85%; ^{1}H-NMR (500MHz, $CDCl_3$), δ (ppm)***:*** 10.73 (1H, s, imidazole-H), 9.58 (1H, s, CONH), 8.06 (2H, d, Ar-H, *J* = 8.7 Hz), 7.55 (1H, s, imidazole-H), 7.48 (2H, d, Ar-H, *J* = 8.6 Hz), 7.34 (2H, s, Ar-H), 7.23 (1H, s, imidazole-H), 4.34 (2H, t, NCH_2, *J* = 7.3 Hz), 4.15 (4H, t, $2ArOCH_2$, *J* = 6.0 Hz), 4.01 (2H, t, $ArOCH_2$, *J* = 6.4 Hz), 1.94-1.87 (2H, m, NCH_2CH_2), 1.83-1.73 (6H, m, $3ArOCH_2CH_2$), 1.48-1.25 (80H, m, $40CH_2$), 0.98 (3H, t, CH_3, *J* = 7.3 Hz), 0.88 (9H, t, $3CH_3$, *J* = 6.4 Hz); elemental analysis calcd (%) for $C_{68}H_{118}BrN_3O_4$ (1121.59): C 72.82, H 10.60, N 3.75; found: C 72.63, H 10.87, N 3.98.

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