Supplementary Information


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Materials and Methods

All solvents were dried before use according to standard procedures. Unless specifically indicated, all other chemicals and reagents used in this study were purchased from commercial sources and used as received. $^1$H- and $^{13}$C-NMR spectra were recorded on Agilent MR 400, Varian DirectDrive 400 or Agilent VNMRS 500 spectrometers using TMS as an internal reference. Mass spectra were measured on a Thermo Scientific TSQ Quantum GC and Micromass Autospec Ultima. Viscosity measurements were carried out with an Ubbelohde micro dilution viscometer (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 293 K in chloroform. Melting points were determined using a Gallenkamp instrument with 1°C/min. temperature increment under ambient conditions.

Synthesis

**Compound 3**

Compound 2 (1.36 g, 2.97 mmol), 11-bromo-1-undecanol (0.68 g, 2.7 mmol), and DMAP (4-dimethylaminopyridine) (39.5 mg, 0.32 mmol) were dissolved in 15 mL dichloromethane (DCM) under a N$_2$ atmosphere. Then, DCC (N,N'-dicyclohexylcarbodiimide) (0.67 g, 3.2 mmol) in 5 mL dichloromethane (DCM) was added to the mixture. The reaction mixture was stirred for 24 h and the precipitate was removed by filtration. The remaining solution was washed with 0.5 N HCl (50 mL), saturated aqueous NaHCO$_3$ (50 mL) and water (50 mL) before being dried over Na$_2$SO$_4$ and taken to dryness under vacuum. Column chromatography (silica gel, DCM/hexanes: 80/20, R$_f$ = 0.78) afforded a white solid (1.2 g, 64.3%). M.p. 93-94°C; $^1$H-NMR (400 MHz, CDCl$_3$, 25°C, TMS): δ = 7.42 (brs, 2H, pyrrole-NH), 7.08 (brs, 2H, pyrrole-NH), 5.89 (m, 8H, pyrrole-CH), 4.12 (t, $J = 4.1$ Hz, 2H, -OCH$_2$), 3.39 (t, $J = 3.4$ Hz, 2H, Br-CH$_2$), 1.84 (m, 2H, -CH$_2$), 1.72 (s, 3H, meso-CH$_3$), 1.61 (m, 2H, -CH$_2$), 1.52-1.49 (m, 18H, meso-CH$_3$), 1.26 ppm (brm, 14H, -CH$_2$); $^{13}$C-NMR (100 MHz, CDCl$_3$, 25°C, TMS): δ = 172.9, 139.1, 138.5, 138.1, 131.7, 104.9, 103.1, 103.0, 102.8, 77.3, 77.2, 77.1, 76.9, 76.7, 65.7, 47.3, 35.2, 35.2, 34.0, 32.8, 29.6, 29.4, 29.3, 29.1, 29.0, 28.8, 28.5, 28.3, 28.1, 25.8, 25.0 ppm; ESI MS: m/z calcd for C$_{39}$H$_{58}$BrN$_4$O$_2$ [M + H]$^+$: 691.35812; found 691.35823; elemental analysis calcd. (%) for C$_{39}$H$_{58}$BrN$_4$O$_2$: C 67.71, H 8.01, N 8.10; found C 68.11, H 7.89, N 8.17.

**Compound 4**

Compound 3 (0.33 g, 0.5 mmol) and 1,2-dimethylimidazole (0.14 g, 1.4 mmol) were dissolved in dry acetonitrile (25 mL). The mixture was then stirred at 70°C for 1 day. After completion of the reaction (as
inferred from TLC analysis), the acetonitrile was removed under vacuum. Then, 2 mL DCM were added to the remaining dark colored oily mixture and the resulting solution was added drop-wise to ethyl acetate. This caused precipitation of the product, which was then washed with excess ethyl acetate three times. This afforded 3 as a pale yellow solid in 93% yield (0.35 g). M.p. decomposes over 175°C; ¹H-NMR (400 MHz, CDCl₃, 25°C, TMS): δ = 9.30 (br, 4H, pyrrole-NH), 7.77 (brs, 1H, imidazolium-CH), 6.63 (brs, 1H, imidazolium-CH), 5.70 (brm, 8H, pyrrole-CH₂), 4.21 (t, J = 4.1 Hz, 2H, -OCH₂), 3.88 (t, J = 3.4 Hz, 2H, Br-CH₂), 2.68 (brs, 3H, imidazolium-CH₃), 2.13 (brs, 3H, imidazolium-CH₃), 1.90 (s, 3H, meso-CH₃), 1.70-1.64 (brm, 22H, -CH₂ + meso-CH₃), 1.26 ppm (brm, 14H, -CH₂); ¹³C-NMR (126 MHz, DMSO-d₆, 25°C, TMS): δ = 173.9, 144.6, 139.9, 139.0, 138.8, 132.6, 122.7, 121.3, 104.3, 102.3, 102.1, 102.0, 72.6, 65.0, 60.7, 47.3, 35.1, 34.9, 34.8, 30.6, 30.3, 29.6, 29.3, 28.9, 28.5, 28.2, 26.0, 25.6, 24.0, 9.5 ppm; ESI MS: m/z calcd for C₄₄H₆₃N₆O₂ [M−Br + H]^+: 708.50383; found 708.50382; elemental analysis calcd. (%) for C₄₄H₆₃BrN₆O₂: C 67.07, H 8.06, N 10.67; found C 67.35, H 7.96, N 10.81.

**Compound 5**

1-Bromodecan (0.50 g, 2.3 mmol) and 1,2-dimethylimidazole (0.65 g, 6.8 mmol) were dissolved in 1-propanol (50 mL). The mixture was then stirred at reflux for 1 day. After completion of the reaction (as inferred from TLC analysis) the solvent was removed under vacuum. Excess diethyl ether was added drop-wise to the remaining oily mixture, causing precipitation of the product, which was then washed with excess diethyl ether. This afforded 6 as a white solid 96% yield (0.69 g). M.p. 74-75°C; ¹H-NMR (400 MHz, CDCl₃, 25°C, TMS): δ = 7.70 (d, J = 7.7 Hz, 1H, -CH), 7.40 (d, J = 7.4 Hz, 1H, -CH), 4.17 (t, J = 4.2 Hz, 2H, -CH₂), 4.02 (s, 3H, -CH₃), 2.81 (s, 3H, -CH₃), 1.81 (m, 2H, -CH₂), 1.31-1.24 (brm, 16H, -CH₂), 0.86 (t, J = 0.9 Hz, 3H, -CH₃) ppm; ¹³C-NMR (100 MHz, CDCl₃, 25°C, TMS): δ = 123.0, 120.9, 49.1, 36.2, 31.8, 29.8, 29.4, 29.3, 29.2, 29.0, 26.4, 22.6, 14.1, 11.1 ppm; ESI MS: m/z calcd for C₁₅H₂₉N₂ [M−Br]: 237.2350; found 237.2330; elemental analysis calcd. (%) for C₁₅H₂₉BrN₂: C 56.78, H 9.21, N 8.83; found C 56.91, H 9.35, N 8.90.
NMR spectra

**Compund 3**

![NMR spectrum of compound 3](image)

**Figure S1.** $^1$H-NMR (400 MHz) spectrum of 3 recorded in CDCl$_3$.

![NMR spectrum of compound 3](image)

**Figure S2.** $^{13}$C-NMR (101 MHz) spectrum of 3 recorded in CDCl$_3$. 
**Compound 4**

*Figure S3.* $^{1}$H-NMR (400 MHz) spectrum of 4 recorded in CDCl$_3$.

*Figure S4.* $^{13}$C-NMR (125 MHz) spectrum of 4 recorded in DMSO-$d_6$.  

S5
**Compound 5**

Figure S5. $^1$H-NMR (400 MHz) spectrum of 5 recorded in CDCl$_3$.

Figure S6. $^{13}$C-NMR (101 MHz) spectrum of 5 recorded in CDCl$_3$. 
**Titration and Dilution NMR Spectra**

**Figure S7.** Partial $^1$H-NMR (400 MHz) spectral titration of 5 (6.3 mM) with 1 in CDCl$_3$. Peak labels: Imidazolium –CH$_3$ peaks (£ and ©) and –CH peaks (Θ and O); alkyl –CH$_2$ (□).

**Figure S8.** Dilution $^1$H-NMR (400 MHz) spectral study of 4 in DMSO-$d_6$/CDCl$_3$ (2.5/97.5). Peak labels: Imidazolium –CH$_3$ peaks (£ and ©) and –CH peaks (Θ and O); alkyl –CH$_2$ (□); pyrrole –CH (£).
Figure S9. \(^1\)H-NMR spectral titration of 4 (6.3 mM) with 5 in CDCl\(_3\). Peak labels: Imidazolium –CH\(_3\) peaks (○ and ●) and –CH peaks (□ and △); alkyl –CH\(_2\) (■); pyrrole –CH (□).
**Mass Spectra**

**Compound 3**

*Figure S10.* HRMS spectrum of compound 3 (715.33879 = [M + H + Na]+).

*Figure S11.* ESIMS spectrum of compound 3.
**Compound 4**

**Figure S12.** ESI mass spectrum of 4.

<table>
<thead>
<tr>
<th>Obs. m/z</th>
<th>Calc. m/z</th>
<th>Charge</th>
<th>Abund</th>
<th>Formula</th>
<th>Ion/Isotope</th>
<th>Tgt Mass Error (ppm)</th>
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</tr>
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**Figure S13.** HRMS spectrum of 4.
**Compound 5**

![Graph 1](image1)

**Figure S14.** ESI mass spectrum of 5 determined in positive ionization mode.

![Graph 2](image2)

**Figure S15.** HRMS spectrum of 5.

<table>
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<tr>
<th>Obs. m/z</th>
<th>Calc. m/z</th>
<th>Charge</th>
<th>Abund</th>
<th>Formula</th>
<th>Ion/Isotope</th>
<th>Tgt Mass Error (ppm)</th>
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<td>M^+</td>
<td>15.15</td>
</tr>
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</table>
DOSY and 2-D NOESY NMR SPECTRA

Compound 4
Figure S16. DOSY NMR (600 MHz) spectra of 4 recorded in CDCl$_3$ at different concentrations.
Figure S17. DOSY NMR (600 MHz) spectra of 4 and 4 + 3.2 equiv. 5 recorded in CDCl₃.
Figure S18. 2D-NOESY spectrum of a DMSO-d$_6$/CDCl$_3$ (5/95) solution of compound 4 (116 mM). Imidazolium –CH$_3$ (⊗) and –CH peaks (Θ and O); pyrrole –CH (⊕); ester –CH$_2$ (★).
Stoichiometry and Association Constant Determinations

**Figure S19.** Molar ratio plot for the interaction of 1 with 5, indicating a 1:1 stoichiometry.

**Figure S20.** The chemical shift changes of the $-\text{CH}_3$ protons belonging to the imidazolium unit of 5 seen upon the addition of 1. The black solid line was obtained from non-linear curve fitting using the equation provided within the table present as an insert to the figure.
Calculated values of maximum polymerization degree (DP) at different concentrations of compound 4

Using the Carothers equation\textsuperscript{51} and assuming that the same average association constant holds for each successive step (isodesmic model) and that cyclic species can either be ignored or taken into account, the average degree of polymerization, DP, may be derived from the equilibrium constant $K_a$ and the initial monomer concentration as follows:\textsuperscript{52}

\[ DP = \frac{1}{(1 - p)} \]  
(1)

Where $p$ is defined as the extent of complexation,

\[ K_a = p[4]/(1 - p)^2[4]^2 \]

Solving this equation leads to

\[ DP = (K_a[4])^{1/2} \]  
(2)

<table>
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<tr>
<th>[4] (mM)</th>
<th>$\delta_{\text{observed}}^a$</th>
<th>$p^b$</th>
<th>$DP_{\text{max}}(\text{Eq. 1})$</th>
<th>$DP_{\text{max}}(\text{Eq. 2})$</th>
</tr>
</thead>
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<tr>
<td>0.94</td>
<td>3.084</td>
<td>0.611 ± 0.03</td>
<td>2.6 ± 0.013</td>
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</tr>
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<td>1.81</td>
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<td>3.24 ± 0.021</td>
<td>5.1 ± 0.033</td>
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<td>2.04</td>
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<tr>
<td>7.25</td>
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<td>0.869 ± 0.03</td>
<td>7.6 ± 0.117</td>
<td>10.2 ± 0.065</td>
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<tr>
<td>14.50</td>
<td>2.595</td>
<td>0.932 ± 0.03</td>
<td>14.7 ± 0.436</td>
<td>14.5 ± 0.093</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Imidazolium $-\text{CH}_3$ ($\delta\circ$) proton signals (observed at 4.017 ppm when uncomplexed). \textsuperscript{b} Calculated from $p = \Delta/\Delta_0$; standard errors reflect a potential error of 0.005 ppm in $\Delta$; the maximum chemical shift change of $-\text{CH}_3$ ($\delta\circ$) was estimated to be 2.490 ppm (Figure S32).
Figure S21. Partial $^1$H-NMR spectra (400 MHz, CDCl$_3$, room temperature) for 5 (1 mM) and 5 + 10 equiv. 1.

References
