SUPPORTING INFORMATION

Syntheses of novel multi-cationic PEG-based ionic liquids

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Experimental Section

General remarks.

All reagents were commercially available and used without purification. Solvents used were of spectroscopic grade. ^{1}H and ^{13}C NMR analyses were performed on a Bruker Avance DPX 200 MHz, Bruker Avance AM 300 MHz or Bruker AC-400 MHz and are reported in *ppm* and calibrated using residual undeuterated solvents as an internal reference. Data are reported as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in *Hz*, integration. The molecular weight of the poly(ethylene glycol)s were determined by MALDI mass spectrometry. MALDI-TOF MS mass spectra were acquired on Ultraflex III (Bruker) in positif mode. The irradiation source was a solid-state laser. The α-cyano-4-hydroxycinnamic acid (CHCA) was used as matrix. A solution of CHCA (10 mg/ml) and the solution containing the product to analyze were mixed in a ratio of 10:1 v/v. A 1 µL aliquot of the matrix/product mixture was deposited and air dried. External mass calibrations were performed with a standard peptide mixture. For MeO-PEG_{350}-Br (**13**)[1] a solution of sodium

iodide (10 mg/ml) was also added (CHCA/product solution/NaI, 10/1/1 v/v/v). Analyses were recorded in reflector mode. Mass spectra were analyzed with FlexAnalysis software. Mass spectra (electrospray ionization mode, ESI-MS) were recorded on a Micromass (Manchester, UK) Q-TOF quadrupole mass spectrometer fitted with an electrospray interface. The mass spectrometer was calibrated in the positive- and negative-ion ESI mode. Samples were dissolved in a H_2O/CH_3CN (50/50 v/v) mixture. Microwave-assisted reactions were performed in sealed vessels with a Biotage Initiator 60 EXP® instrument. The temperature was measured with an IR sensor on the outer surface of the reaction vial. Steady state shear experiments were measured by using the Physica UDS 200 rheometer (Paar Physica Instrument) with a cone plate geometry (plate diameter, 40 mm; cone angle, 2°; gap, 0.05 mm). The temperature was set with a Pelletier controller. MeO-PEG-350-Br (**13**) and $[(mPEG_{350})_2NMe_2][Br]$ (**1**) were previously described[1] and showed identical spectral data to those reported in the literature.

MeO-PEG-350-Br (13). Commercial MeO-PEG-350-OH (6.573 g, 15,39 mmol) was dried and degassed under dynamic vacuum at 120°C overnight. Then, anhydrous 1,4-dioxane (50 ml) was added at room temperature and under argon atmosphere, to the degassed reaction vessel and the mixture was frozen twice in a liquid nitrogen bath under dynamic vacuum. The frozen solution was left to warm up to room temperature until all solid was liquefied. The vacuum freezing/defreezing step was repeated three times. The solution was cooled to 0°C, Et_3N (7.7 ml, 44.33 mmol) was added, followed by PBr_3 (5 g, 18.47 mmol) added dropwise under argon atmosphere and under stirring. The reaction mixture was heated to 50°C and stirred for 24 hours. The 1,4-dioxane was eliminated by evaporation *in vacuo* and the crude oil obtained was diluted with water (50 ml) and treated with aqueous Na_2CO_3 5% (22 ml) till neutral pH. The aqueous layer was washed with $CHCl_3$ (3 x 20 ml), the organic layer was collected and dried over $MgSO_4$, filtered and evaporated *in vacuo* affording pure MeO-PEG-350-Br **13** (5.984 g, 97% yield) as a yellow liquid. ^{1}H NMR (300 M*Hz*, $CDCl_3$)[1] δ (ppm): 3.78 (t, 2H, OCH_2CH_2Br), 3.64-3.59 (m, 32H, -$[OCH_2CH_2O]_n$-), 3.44 (t, 2H, OCH_2CH_2Br), 3.35 (s, 3H, OCH_3). ^{13}C NMR (300 M*Hz*, $CDCl_3$)[1] δ (ppm): 71.93 (CH_3OCH_2), 71.21 ($CH_3OCH_2CH_2$), 70.66 (-$[OCH_2CH_2O]_n$-), 70.58 ($CH_2OCH_2CH_2Br$), 70.53 (OCH_2CH_2Br), 59.04 (CH_2Br), 30.32 (CH_3O). MALDI TOF (+)[1] *m/z*: 468.459/470.461 $[M+Na]^+$.

MeO-PEG-750-Br (14). The synthesis was carried out as described for MeO-PEG-350-Br (**13**), by using commercial MeO-PEG-750-OH (9.381 g, 16.7 mmol), 70 ml of anhydrous 1,4-dioxane and reacting the mixture for 30 hours. The product MeO-PEG-750-Br **14** (6.953 g, 67% yield) was obtained as a deep yellow liquid. ^{1}H NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 3.80 (t, 2H, OCH_2CH_2Br), 3.64-3.59 (m, 32H, -$[OCH_2CH_2O]_n$-), 3.46 (t, 2H, OCH_2CH_2Br), 3.36 (s, 3H, OCH_3). ^{13}C NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 77.45 (CH_3OCH_2), 77.03 ($CH_3OCH_2CH_2$), 76.61 (-$[OCH_2CH_2O]_n$-), 71.94 ($CH_2OCH_2CH_2Br$), 70.57 (OCH_2CH_2Br), 59.06 (CH_2Br), 30.34 (CH_3O). ESI (+) *m/z*: 667.3 / 669.2 $[M+H]^+$.

MeO-PEG-350-NMe_2 (15). MeO-PEG-350-Br **13** (5.472 g, 13.50 mmol) was dried under vacuum overnight. Absolute ethanol (8 ml) was added under argon atmosphere and the solution was twice frozen in a liquid nitrogen bath. The frozen solution was left to warm up to room temperature and then kept at -15°C, before adding 3 equivalents of gaseous *N, N*-dimethylamine (1.826 g, 40.5 mmol). The reaction mixture was irradiated under microwave (80°C) for 30 minutes. Ethanol was evaporated *in vacuo* and the crude product was recovered with water. The aqueous layer was washed with chloroform (3 x 20 ml). The organic layer was dried over $MgSO_4$ and filtered. The solvent was eliminated by evaporation *in vacuo* affording pure product MeO-PEG-350-NMe_2 **15** (4.915 g, 99% yield) as a deep yellow liquid. ^{1}H NMR: (300 MHz, $CDCl_3$) δ (ppm) : 3.61-3.58 (m, 28H, -[CH_2CH_2O]$_7$), 3.54 (t, 2H, J = 5.9 *Hz*, OCH_2CH2NMe2), 3.34 (s, 3H, CH_3O), 2.47 (t, 2H, J = 5.9 *Hz*, -CH_2NMe_2), 2.22 (s, 6H, N(CH_3)$_2$); ^{13}C NMR: (300 MHz, $CDCl_3$) δ (ppm): 72.13 (*Me*OCH_2-), 70.77 (-[OCH_2CH_2O]$_7$-), 70.71 (MeOCH_2CH_2-), 70.57 (-CH_2OCH_2CH_2NMe_2), 69.52 (-OCH_2CH_2NMe_2), 59.22 (CH_3O), 59.01 (CH_2NMe_2), 46.06 (NMe_2) ; ESI (+) *m/z*: 368.2 $[M+H]^+$.

MeO-PEG-750-NMe_2 (16). The synthesis has been carried out as described previously for MeO-PEG-350-NMe_2 (**15**), by using MeO-PEG-750-Br (**14**) (2.953 g, 4.4 mmol), gaseous *N, N*-dimethylamine (0,698 g, 15.5 mmol, 3.5 equiv.) and anhydrous ethanol (4 ml). MeO-PEG-750-NMe_2 **16** (2.885 g, 96% yield) was obtained as a yellow liquid. ^{1}H NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 3.63 (m, -[OCH_2CH_2O]$_n$-), 3.54 (t, 2H, J = 6.0 *Hz*, OCH_2CH_2N), 3.34 (s, 3H, OCH_3), 2.47 (s, 6H, N(CH_3)$_2$);); ^{13}C NMR: (300 MHz, $CDCl_3$) δ (ppm): 71.94 (*Me*OCH_2-), 70.58 (-[OCH_2CH_2O]$_7$-), 70.38 (MeOCH_2CH_2-), 69.52 (-OCH_2CH_2NMe_2), 59.03 (CH_3O), 58.82 (CH_2NMe_2), 45.88 (NMe_2); MALDI TOF (+) *m/z*: 720.4 $[M+H]^+$.

[(mPEG$_{350}$)$_2$NMe_2][Br] (1). MeO-PEG-350-Br **13** (5.836 g, 14.4 mmol) was dried under vacuum overnight. A solution of MeO-PEG-350-NMe_2 **15** (4.915 g, 13.57 mmol) in anhydrous tetrahydrofuran (7 ml) was added to MeO-PEG-350-Br **13** under argon atmosphere. The solution was frozen twice in liquid nitrogen under dynamic vacuum. When the solution reached room temperature, the vessel was irradiated under microwave (120°C) for 1 hour. The solvent was evaporated *in vacuo* and the crude was recovered in $CHCl_3$. The organic layer was washed with water (30 ml) and neutralized at pH = 7 with aqueous Na_2CO_3 5%. The organic layer was dried over $MgSO_4$ and filtered. The chloroform was concentrated *in vacuo* affording pure ionic liquid [(mPEG$_{350}$)$_2$NMe_2][Br] **(1)** (97% yield) as a viscous deep orange liquid. ^{1}H NMR (300 M*Hz*, $CDCl_3$)[1] δ (ppm): 3.80 (t, 8H, OCH_2CH_2N), 3.69-3.54 (m, 64H, -[OCH_2CH_2O]$_n$-), 3.55-3.44 (m, 8H, OCH_2CH_2N), 3.37 (s, 6H, OCH_3), 2.00 (s_{broad}, 6H, N(CH_3)$_2$).^{13}C NMR (300 M*Hz*, $CDCl_3$)[1] δ (ppm): 77.45 (CH_3OCH_2), 77.03 (CH_3OCH_2CH_2), 76.61 (-[OCH_2CH_2O]$_n$-), 71.94 (OCH_2CH_2N), 70.57 (OCH_2CH_2N), 59.06 (OCH_3), 30.34 (CH_3NCH_3). ESI (+)[1] *m/z*: 778.50 $[M+H]^+$.

[(mPEG$_{750}$)$_2$NMe_2][Br] (2). The synthesis was carried out as already described for [(mPEG$_{350}$)$_2$NMe_2][Br] (**1**), but in neat conditions, heating together MeO-PEG-750-NMe_2 **16** (2.203 g, 3.48 mmol) and MeO-PEG-750-Br **14** (2.322 g, 3.48 mmol) under microwave irradiation at 120°C for 1 hour. [(mPEG$_{750}$)$_2$NMe_2][Br] (**2**) was obtained as a viscous clear

liquid (75% yield). ^{1}H NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 3.63-3.57 (m, 124H, -[OCH_2CH_2O]$_n$-), 3.49-3.47 (m, 4H, OCH$_2$CH_2N), 3.31 (s, 6H, OCH_3), 2.85 (s, 6H, N(CH_3)$_2$); ^{13}C NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 77.89 (CH_3OCH_2), 73.00 ($CH_3OCH_2CH_2$), 72.33 (O*C*H$_2$CH$_2$N), 70.72 (-[O*C*H$_2$CH$_2$O]$_n$-), 70.60 (OCH$_2$*C*H$_2$N), 53.31 (O*Me*), 30.79 (N*Me*$_3$). ESI (+) *m/z*: 1306.8 $[M+H]^+$, 676.1 $[M+2H]^{2+}$, 524.4 $[M+3H]^{3+}$

[(mPEG$_{350}$NMe$_2$)$_2$(CH$_2$CH$_2$)$_x$][Br] x=1, **(3).**[1] MeO-PEG$_{350}$-Br (**13**) (1 g, 2.46 mmol) was dried under vacuum and then heated at 60°C under dynamic vacuum for 30 min. *N,N,N',N'*-tetramethylethylenediamine (135 μL, 0.9 mmol) and absolute ethanol (0.5 ml) were added. After two cycles of freezing/defreezing in a liquid nitrogen bath, the reaction mixture was left to reach 70°C and stirred at this temperature for 72 hours under nitrogen atmosphere. Ethanol was eliminated by evaporation *in vacuo* and the product was precipitated by addition of ether. After decantation, ether was eliminated by evaporation and the product was recovered in chloroform, that was evaporated *in vacuo*. Dicationic bis-PEG$_{350}$-IL, x=1 (**3**) (80% yield) was obtained as a viscous colourless liquid. ^{1}H NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 4.67 (m, 4H, NCH_2CH_2N), 3.99 (s$_{broad}$, 8H, OCH_2CH$_2$N), 3.81-3.45 (m, 64H, -[OCH_2CH_2O]$_n$-), 3.45-3.32 (m, 8H, OCH$_2$CH_2N), 3.35 (s, 6H, OCH_3), 2.79 (s$_{broad}$, 12H, N(CH_3)$_2$). ^{13}C NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 77.47 (CH_3OCH_2), 77.05 ($CH_2OCH_2CH_2$), 76.62 (-[O*C*H$_2$*C*H$_2$O]-), 71.89 (O*C*H$_2$CH$_2$N), 70.46 (OCH$_2$*C*H$_2$N), 64.72 (*C*H$_2$N(CH$_3$)$_2$), 59.02 (O*C*H$_3$), 52.61 (N(*C*H$_3$)). MALDI TOF (+) *m/z*: 734.11 $[M+H]^+$.

[(mPEG$_{350}$NMe$_2$)$_2$(CH$_2$CH$_2$)$_x$][Br], x=3, (**4**)**.** Commercial *N,N,N',N'*-tetramethyl-1,6-hexanediamine (328 μL, 1.53 mmol) and absolute ethanol (1 ml) were added to MeO-PEG$_{350}$-Br (**13**) (2.0 g, 4.93 mmol) previously dried as described before. After two cycles of freezing/defreezing in a liquid nitrogen bath, the reaction mixture was heated to 70°C and stirred at this temperature for 12 hours under nitrogen atmosphere. The solution was treated in the same experimental conditions as described for dicationic bis-PEG$_{350}$-IL, x=1 (**3**), affording dicationic bis-PEG$_{350}$-IL, x=3 (**4**) (75% yield) as a viscous colourless liquid. ^{1}H NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 4.67 (m, 4H, NCH_2CH_2N), 3.95 (s$_{broad}$, 8H, OCH_2CH$_2$N), 3.83-3.54 (m, -[OCH_2CH_2O]$_n$-), 3.54-3.45 (m, 8H, OCH$_2$CH_2N), 3.35 (s, 6H, OCH_3), 2.79 (s$_{broad}$, 12H, N(CH_3)$_2$), 2.50 s$_{broad}$, 12H, N(CH$_3$)$_2$), 1.99 (s$_{broad}$,4H, CH_2NMe$_2$), 1.55 (s$_{broad}$, 4H, Me$_2$NCH$_2$CH_2CH$_2$CH$_2$CH_2CH$_2$NMe$_2$), 1.23 (s$_{broad}$, 4H, Me$_2$NCH$_2$CH$_2$CH_2CH_2CH$_2$CH$_2$NMe$_2$). ^{13}C NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 77.25 (CH_3OCH_2), 76.62 (-[O*C*H$_2$*C*H$_2$O]-), 71.92 (O*C*H$_2$CH$_2$N), 70.52 (OCH$_2$*C*H$_2$N), 70.27, 65.08 (*C*H$_2$N(CH$_3$)$_2$), 59.03 (O*C*H$_3$), 52.11 (NMe$_2$), 21.60. MALDI TOF (+) *m/z*: 811.60 $[M+H]^+$, 431.3 $[M+2H]^{2+}$.

Br-PEG-400-Br (17). Commercial HO-PEG-400-OH (6.583 g, 15.85 mmol) was dried and degassed at 120°C under dynamic vacuum overnight. Anhydrous 1,4-dioxane (33 ml) was added at room temperature and the solution was frozen twice in a liquid nitrogen bath under dynamic vacuum. Then the reaction mixture was kept at 0°C for 2 hours. Under stirring, PBr_3 (5 g, 18.47 mmol) was added and the solution heated at 50°C for 20 hours. The solvent was evaporated *in vacuo* and the crude product was recovered in water (30 ml) and chloroform (30 ml). Aqueous Na_2CO_3 5% (37 ml) was added till neutral pH. The organic layer was dried over

$MgSO_4$ and filtered. The $CHCl_3$ was eliminated by evaporation *in vacuo* affording pure Br-PEG-400-Br (**17**) (8.48 g, 99% yield) as a pale white liquid. ^{1}H NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 3.79 (t, 4H, J = 6.0 *Hz*, OCH_2CH_2Br), 3.64-3.59 (m, 32H, -$[OCH_2CH_2O]_n$-), 3.45 (t, 4H, J = 6.0 *Hz*, OCH_2CH_2Br). ^{13}C NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 68.92 (OCH_2CH_2Br), 66.30 (-$[OCH_2CH_2O]_n$-), 64.80 (OCH_2CH_2Br), 28.05 ($CH_2OCH_2CH_2Br$). ESI (+) *m/z*: 451.0/453.0/455.0 $[M+H]^+$ or MALDI TOF(+) *m/z*: 605.1/607.1/609.1 $[M+H]^+$.

Br-PEG-600-Br (18). The synthesis and work-up were performed in the same experimental conditions previously described for the synthesis of Br-PEG-400-Br (**17**) using HO-PEG-600-OH (8.402 g, 15.37 mmol) in 50 ml of anhydrous 1,4-dioxane, affording pure product Br-PEG-600-Br **18** (8.716 g, 84% yield) as a viscous white liquid. ^{1}H NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 3.79 (t, 4H, J = 6.0 *Hz*, OCH_2CH_2Br), 3.64-3.59 (m, 32H, -$[OCH_2CH_2O]_n$-), 3.46 (t, 4H, J = 6.0 *Hz*, OCH_2CH_2Br). ^{13}C NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 71.69 (OCH_2CH_2Br), 71.51 (-$[OCH_2CH_2O]_n$-), 71.14 (OCH_2CH_2Br), 71.06 ($CH_2OCH_2CH_2Br$), 30.81. MALDI TOF (+) *m/z*: 829.2 $[M+H]^+$.

Me_2N-PEG-400-NMe_2 (19). Br-PEG-400-Br (**17**) (8.47 g, 15.72 mmol) was dried under vacuum overnight, then absolute ethanol (5.4 ml) was added under argon atmosphere. The solution was frozen twice in liquid nitrogen and then kept at -15°C, before adding 4 equivalents of gaseous *N, N*-dimethylamine (2.83 g, 62.86 mmol). The solution was irradiated under microwave for 30 minutes at 80°C. The ethanol was then concentrated *in vacuo* and the residue recovered in water (30 ml) and chloroform (3 x 30 ml) by adding 5% aqueous Na_2CO_3 (37 ml). The organic layer was dried over $MgSO_4$ and filtered. $CHCl_3$ was eliminated by evaporation *in vacuo* and Me_2N-PEG_{400}-NMe_2 (**19**) (7.39 g, 50% yield) was obtained as a pale yellow liquid. ^{1}H NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 3.63-3.51 (s_{broad}, 32H, -$[OCH_2CH_2O]_n$-), 2.48 (t, 4H, J = 5.76 *Hz*, OCH_2CH_2Br), 2.23 (s, 12H, NMe_2);^{13}C NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 77.26 ($MeOCH_2$), 70.56 (OCH_2CH_2N), 70.36 (OCH_2CH_2N), 69.07 (-$[OCH_2CH_2O]_n$-), 58.70 (OMe), 45.72 (NMe_2). ESI (+) *m/z*: 235.1 $[M+2H]^{2+}$.

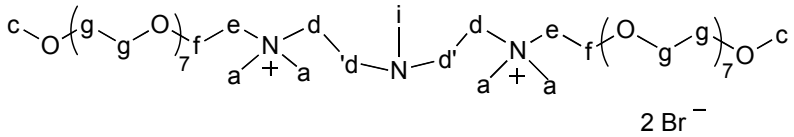
Me_2N-PEG-600-NMe_2 (20). The reaction was carried out as previously described for the synthesis of Me_2N-PEG-400-NMe_2 (**19**) starting from Br-PEG-600-Br (**18**) (4.361 g, 6.48 mmol) and irradiating the reaction mixture under microwave at 120°C for 1 hour. After usual treatment and extraction, pure Me_2N-PEG-600-NMe_2 (**20**) (2.488 g, 60% yield) was obtained as a pale pink liquid. ^{1}H NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 3.57-3.51 (s_{broad}, 52H, -$[OCH_2CH_2O]_n$-), 2.48 (t, 4H, J = 5.78 *Hz*, OCH_2CH_2Br), 2.23 (s, 12H, NMe_2); ^{13}C NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 70.56 (OCH_2CH_2N), 70.36 (OCH_2CH_2N), 69.10 (-$[OCH_2CH_2O]_n$-), 58.71 (OMe), 45.76 (NMe_2). MALDI TOF (+) *m/z*: 755.5 $[M+H]^+$, ESI (+)*m/z*: 345.2 $[M+2H]^{2+}$

$[(mPEG_{350}NMe_2)_2(PEG_{400})][Br]$ (5). Me_2N-PEG-400-NMe_2 (**19**) (1.21 g, 2.36 mmol) MeO-PEG-350-Br (**13**) (2.86 g, 7 mmol) were placed into a microwave reactor. The reaction mixture was frozen twice into a liquid nitrogen bath under dynamic vacuum and allowed to react under microwave irradiation at 120°C for 1 hour without solvent.

[(mPEG$_{350}$NMe$_2$)$_2$(PEG$_{400}$)][Br] (**5**) was obtained without purification in 96% yield. ^{1}H NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 3.91 (m, 16 H), 3.63-3.55 (s$_{broad}$, 136H, -[OCH_2CH_2O]$_n$-), 3.48 (m, 8H), 3.39 (m, 12H), 3.31 (s, 12H, NMe$_2$); ^{13}C NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 77.25, 71.93, 70.56 (O*C*H$_2$CH$_2$N), 70.31, 67.09 (-[O*C*H$_2$*C*H$_2$O]$_n$-), 65.17, 64.59 (OCH$_2$*C*H$_2$N), 59.04 (NMe$_2$); 58.71 (OCH$_2$*C*H$_2$N), 45.76 (OMe). MALDI TOF (+) *m/z*: 1011.7 [M+H]$^+$.

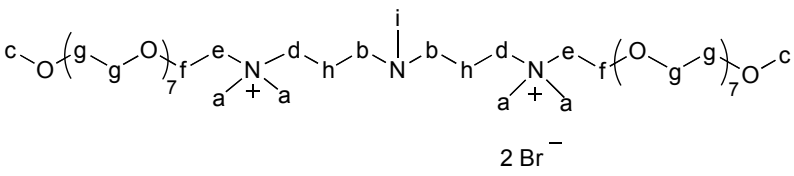
[(mPEG$_{350}$NMe$_2$)$_2$(PEG$_{600}$)][Br] (6). Me$_2$N-PEG-600-NMe$_2$ (**20**) (2.148 g, 3.11 mmol) and MeO-PEG-350-Br (**13**) (3.29 g, 6.22 mmol) were reacted as previously described for the synthesis of [(mPEG$_{350}$NMe$_2$)$_2$(PEG$_{400}$)][Br] (**5**), without solvent under microwave irradiation. The final compound [(mPEG$_{350}$NMe$_2$)$_2$(PEG$_{600}$)][Br] (**6**) was obtained as a brown viscous liquid (3.15 g, 73% yield). ^{1}H NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 3.92 (m, 8H), 3.63-3.57 (s$_{broad}$, 108H, -[OCH_2CH_2O]$_n$-), 3.49 – 3.46 (m, 8H), 3.35 (m, 12H), 3.31 (s, 12H, NMe$_2$), 2.60 (s, 6H, OMe); ^{13}C NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 77.35, 71.89, 70.52 (O*C*H$_2$CH$_2$N), 70.36, 66.84 (-[O*C*H$_2$*C*H$_2$O]$_n$-), 65.14, 64.62 (OCH$_2$*C*H$_2$N), 58.98 (NMe$_2$), 58.71 (OCH$_2$*C*H$_2$N), 44.14 (OMe). ESI (+) *m/z*: 638.30 [M+H+Na]$^{2+}$, 645.90 [M+H+K]$^{2+}$

[(mPEG$_{350}$)$_2$(PMDT)][Br] (**7**)**.** Pentamethyldiethylenetriamine (PMDT, 1.0 equiv.) was reacted with MeO-PEG$_{350}$-Br (**13**) (3.5 equiv.) in neat conditions. The reaction mixture was stirred four days at room temperature. The crude was triturated with hexane to eliminate unreacted MeO-PEG$_{350}$-Br **13**. The organic layer was recovered and the residue was evaporated *in vacuo* to afford 10 g of [(mPEG$_{350}$)$_2$(PMDT)][Br] **7** quantitatively.



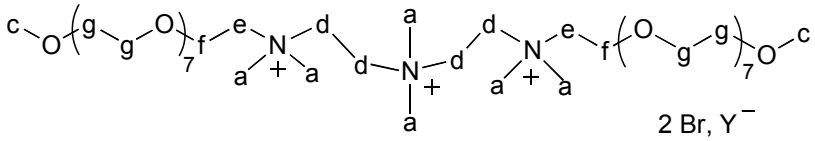
^{1}H NMR (300 M*Hz*, D_2O) δ (ppm): 3.88-3.96 (m, 12H, H$_{d,e,f}$), 3.63 (m, 56H, [OCH$_2$CH$_2$O]$_7$, H$_g$), 3.31 (m, 6H, OCH_3, H$_c$), 3.14 (s, 12H, (CH_3)$_2$N, H$_a$), 2.91 (m, 4H, H$_{d'}$), 2.30 (m, 3H, H$_i$); ESI (+) *m/z* 734.6 [M+H]$^+$. ^{13}C NMR (300 M*Hz*, D_2O) δ (ppm): 71.9 (O*C*H$_2$CH$_2$N, C$_f$), 70.99 (OCH$_2$*C*H$_2$N, C$_e$), 70.65 (-[O*C*H$_2$*C*H$_2$O]-, C$_g$), 64.21 (*C*H$_2$NMe$_2$, C$_d$), 63.95 (*C*H$_2$CH$_2$NMe$_2$, C$_{d'}$) 60.4 (OMe, C$_c$), 52.2 (NMe$_2$, C$_a$), 31.2 (NMe, C$_i$). MALDI (+) *m/z* : 734.50 [M+H]$^+$.

[(mPEG$_{350}$)$_2$(TMTAU)][Br] (**8**)**.** 2,6,10-trimethyl-2,6,10-triazaundecane (TMTAU, 1.0 equiv) was reacted with MeO-PEG$_{350}$-Br (**13**) (3.5 equiv.) in neat conditions, as already described for the synthesis of [(mPEG$_{350}$)$_2$(PMDT)][Br] (**7**). [(mPEG$_{350}$)$_2$(TMTAU)][Br] **8** was obtained in quantitative yield on a 10 g scale.



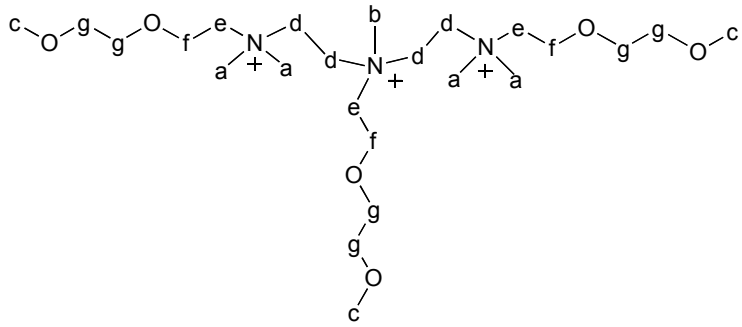
^{1}H NMR (300 M*Hz*, MeOD-d_4) δ (ppm): 4.05-3.94 (m, 12H, $H_{d,e,f}$), 3.66 (m, 56H, $[OCH_2CH_2O]_7$, H_g), 3.38 (m, 6H, OCH_3, H_c), 3.23 (s, 12H, $(CH_3)_2N$, H_a), 2.53 (m, 4H, H_b), 2.32 (m, 3H, H_i), 2.02 (m, 4H, H_h); ESI (+) *m/z* 394.9 $[M+Na+K]^{2+}$

[(mPEG$_{350}$)$_2$Me(PMDT)][Y] (9). The synthesis was performed by reacting pentamethyldiethylenetriamine (PMDT, 1.0 equiv.) with MeO-PEG$_{350}$-Br (**13**) (3.5 equiv.) in neat conditions. The reaction mixture was stirred 4 days at room temperature. After elimination of the MeO-PEG$_{350}$-Br **13** with hexane, ^{1}H NMR spectra indicated the formation of the product [(mPEG$_{350}$)$_2$(PMDT)][Br] **7,** arising from the bi-condensation reaction (singlet at 2.30 ppm corresponding to the CH_3 of the central amine). CH_3I (1.0 equiv.) was added and the reaction mixture was heated at 60°C for 6 days. [(mPEG$_{350}$)$_2$Me(PMDT)][Y] (**9**) was obtained in quantitative yield (disappearance of the singlet at 2.30 ppm) on a 10 g scale.



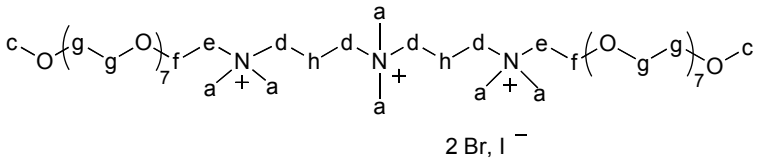
^{1}H NMR (300 M*Hz*, D_2O) δ (ppm): 4.69 and 4.09 (m, 16H, $H_{d,e,f}$), 3.60-3.49 (m, 56H, $[OCH_2CH_2O]_7$, H_g), 3.46 (m, 6H, OCH_3, H_c), 3.17 (s, 18H, $(CH_3)_2N$, H_a).

[(mPEG$_{350}$)$_3$(PMDT)][Br] (**10**). Pentamethyldiethylenetriamine (PMDT) (1.0 equiv) and MeO-PEG$_{350}$-Br **13** (3.5 equiv.) were stirred, without solvent, for 4 days at room temperature, affording a yellow compact gel. Then, temperature was increased to 60°C, and stirring was continued for 6 days affording a yellow gel. Hexane was added to the crude and the mixture was washed with water. The aqueous layer was lyophilized affording [(mPEG$_{350}$)$_3$(PMDT)][Br] **(10)** in quantitative yield on a 10 g scale.



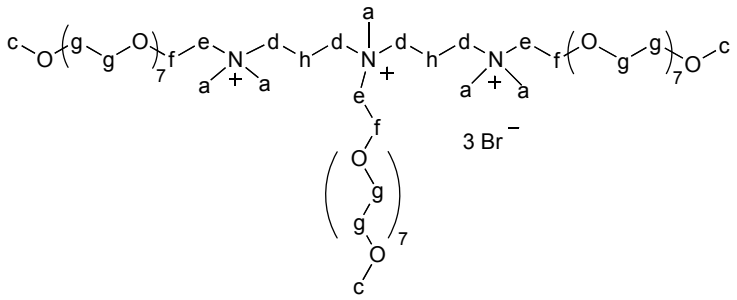
^{1}H NMR (300 M*Hz*, CD_3OD) δ (ppm): 3.93 (m, 20H, $H_{d,e,f}$), 3.63 (m, 84H, $[OCH_2CH_2O]_7$, H_g), 3.31 (s, 9H, OCH_3, H_c), 3.17 (m, 12H, NMe, H_a), 2.34 (m, 3H, NMe, H_b). ESI (+) *m/z* 577.9 $[M+2H].^{2+}$

[(mPEG$_{350}$)$_2$Me(TMTAU)][Y] (11). Prepared as already described for compound [(mPEG$_{350}$)$_2$Me(PMDT)][Br] (**9**) was used. The pure product was recovered in quantitative yield on a 10 g scale.



^{1}H NMR (300 M*Hz*, CD_3OD) δ (ppm): 3.90-3.70 (m, 16H, $H_{d,e,f}$), 3.67-3.41 (m, 56H, $[OCH_2CH_2O]_7$, H_g), 3.31 (s, 6H, OCH_3, H_c), 3.24 (m, 18H, NMe, H_a), 2.53 (m, 4H, $NCH_2CH_2CH_2N$, H_h). ^{13}C NMR (300 M*Hz*, $CDCl_3$) δ (ppm): 77.25, 72.5 (-[O*C*H_2*C*H_2O]-), 71.91 (O*C*H_2CH_2N), 70.48 (OCH_2*C*H_2N), 65.08 (*C*H_2NMe_2), 59.06 (OMe), 52.98 (NMe_2).

[(mPEG$_{350}$)$_3$(TMTAU)][Br] (12). 2,6,10-trimethyl-2,6,10-triazaundecane (1.0 equiv) and MeO-PEG$_{350}$-Br **13** (3.5 equiv.) were stirred, without solvent, for 4 days at room temperature, affording a yellow compact gel. Then, temperature was increased to 60°C, and stirring was continued for 6 days affording a yellow gel. Hexane was added to the crude and the mixture washed with water. The aqueous layer was lyophilized affording [(mPEG$_{350}$)$_3$(TMTAU)][Br] **(12)** in quantitative yield on a 10 g scale.



^{1}H NMR (300 M*Hz*, CD_3OD) δ (ppm): 4.02-3.85 (m, 20H, $H_{d,e,f}$), 3.66 (m, 84H, $[OCH_2CH_2O]_7$, H_g), 3.38 (s, 9H, OCH_3, H_c), 3.32 (m, 15H, NMe, H_a), 2.48 (m, 4H, $NCH_2CH_2CH_2N$, H_h); ^{1}H NMR (300 M*Hz*, MeOD-d_4) δ (ppm): 71.57, 69.79, 69.55, 64.25, 61.32, 59.21, 57.74, 51.68, 17.49; ESI (+) *m/z*: 555.3 $[M+2H]^{2+}$; MALDI QTOF (+) *m/z*: 1460 $[C_{62}H_{132}O_{24}N_3Br_2]^+$, 690.5 $[C_{62}H_{132}O_{24}N_3Br]^{2+}$, 434 $[C_{62}H_{132}O_{24}N_3]^{3+}$

Reference

[1] P. Petiot, C. Charnay, J. Martinez, L. Puttergill, F. Galindo, F. Lamaty, E. Colacino, *Chem. Comm.* **2010**, *46*, 8842.