Electronic Supplementary Information for

Synthesis and evaluation of new modified diglycolamides with different stereochemistry for extraction of tri- and tetravalent metal ions

Laura Diaz Gomez[1], Andreas Wilden[1,*], Dimitri Schneider[1], Zaina Paparigas[1], Giuseppe Modolo[1], Maria Chiara Gullo[2], Jurriaan Huskens[2], Willem Verboom[2]

[1]Forschungszentrum Jülich GmbH, Institut für Energie–und Klimaforschung–Nukleare Entsorgung und Reaktorsicherheit (IEK-6), 52428 Jülich, Germany

[2]Laboratory of Molecular Nanofabrication, Department for Molecules & Materials, Mesa+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands

*corresponding author: a.wilden@fz-juelich.de

Table of Content

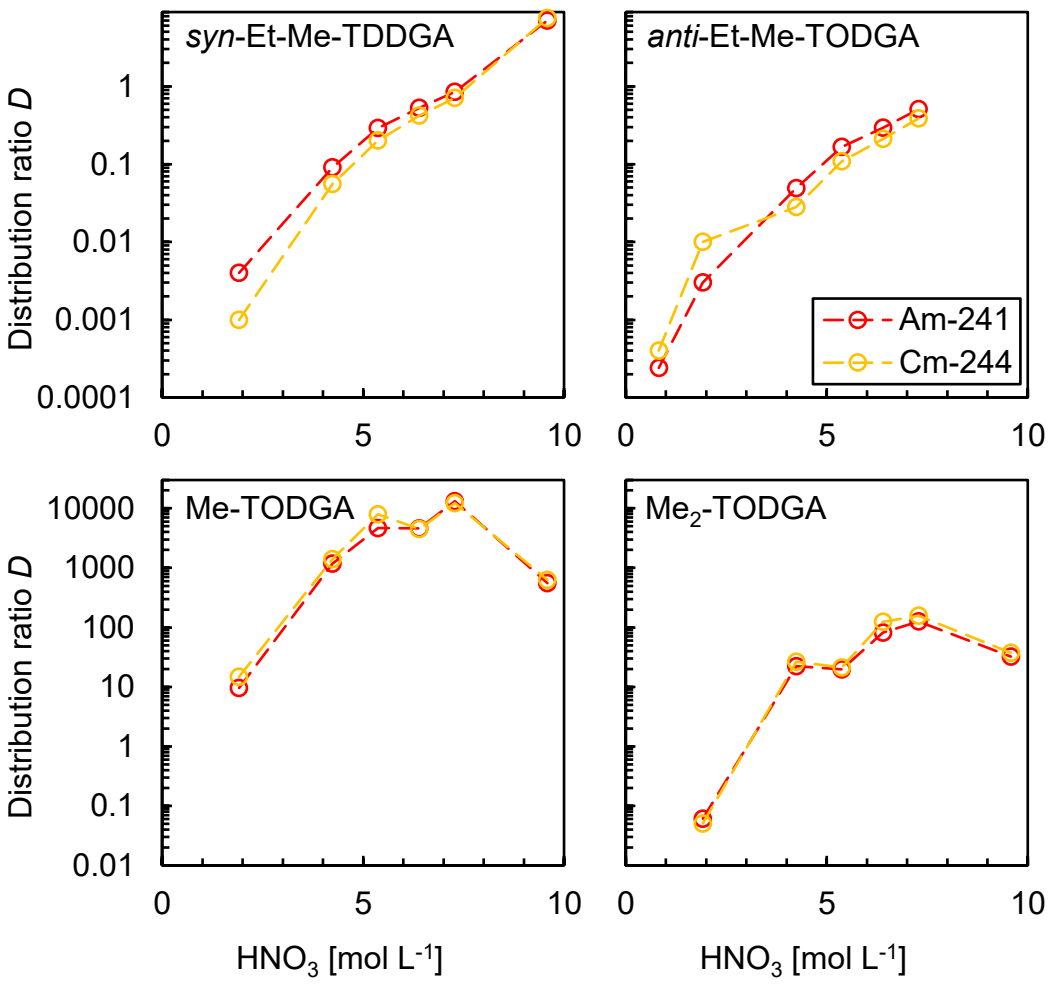

Fig. S1. Am(III) and Cm(III) distribution ratios *D* as a function of the HNO_3 concentration for different ligands (exp. conditions see main text Fig. 2). The data shown here is given in Table S1.

Table S1. Am(III) and Cm(III) distribution ratios *D* and Am/Cm separation factors $SF_{Am/Cm}$ at different HNO_3 concentrations. Values in *italics* are associated with higher uncertainties and must be handled with care.

	syn-Et-Me-TDDGA			*anti*-Et-Me-TODGA			Me-TODGA			Me_2-TODGA		
HNO_3	*D*(Am)	*D*(Cm)	$SF_{Am/Cm}$	*D*(Am)	*D*(Cm)	$SF_{Am/Cm}$	*D*(Am)	*D*(Cm)	$SF_{Am/Cm}$	*D*(Am)	*D*(Cm)	$SF_{Am/Cm}$
0.82				*2.40E-04*	*4.00E-04*	*0.6*						
1.91	*4.00E-03*	*1.00E-03*	*4.0*	*3.00E-03*	*1.00E-02*	*0.3*	9.60E+00	1.47E+01	0.7	6.13E-02	5.06E-02	1.2
4.24	9.10E-02	5.55E-02	1.6	4.90E-02	2.80E-02	1.8	*1.18E+03*	*1.41E+03*	*0.8*	2.22E+01	2.63E+01	0.8
5.37	2.90E-01	2.01E-01	1.4	1.67E-01	1.09E-01	1.5	*4.65E+03*	*7.93E+03*	*0.6*	1.97E+01	2.12E+01	0.9
6.40	5.30E-01	4.20E-01	1.3	2.95E-01	2.10E-01	1.4	*4.61E+03*	*4.47E+03*	*1.0*	8.18E+01	1.25E+02	0.7
7.28	8.50E-01	7.10E-01	1.2	5.07E-01	3.88E-01	1.3	*1.32E+04*	*1.23E+04*	*1.1*	1.26E+02	1.58E+02	0.8
9.58	7.02E+00	7.53E+00	0.9				*5.58E+02*	*6.27E+02*	*0.9*	3.25E+01	3.74E+01	0.9

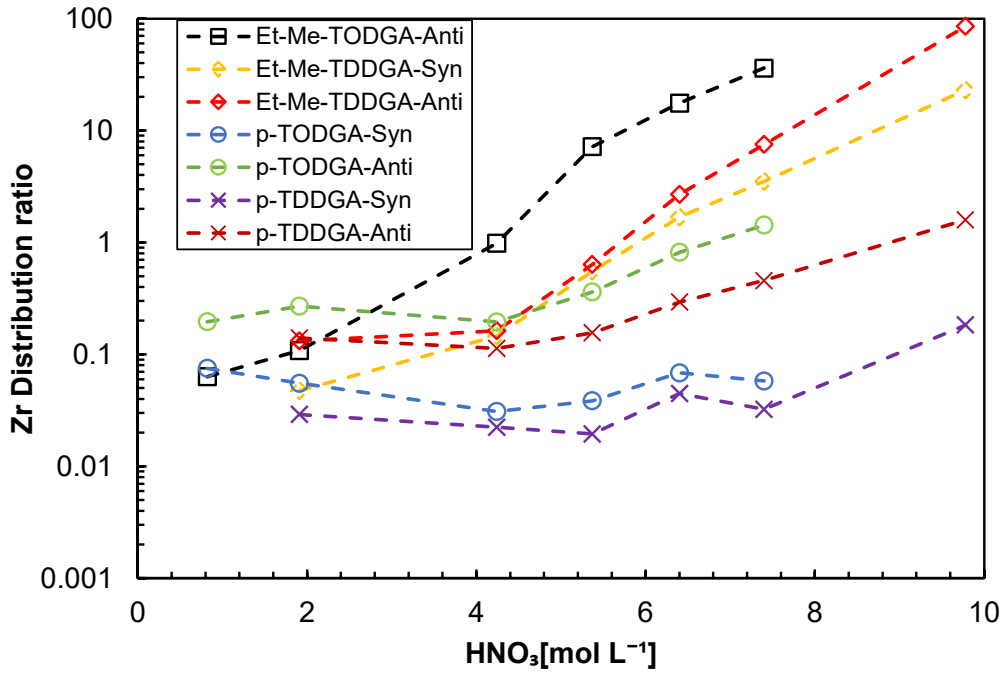

Fig. S2. Zr distribution ratios as a function of the HNO_3 concentration for the different extractants used in this study.

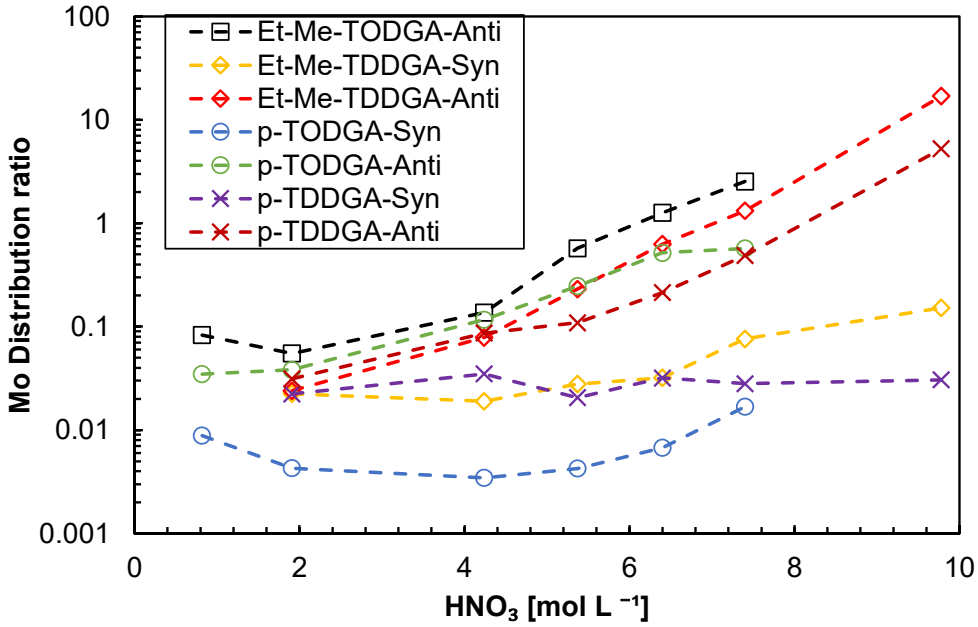

Fig. S3. Mo distribution ratios as a function of the HNO_3 concentration for the different extractants used in this study.

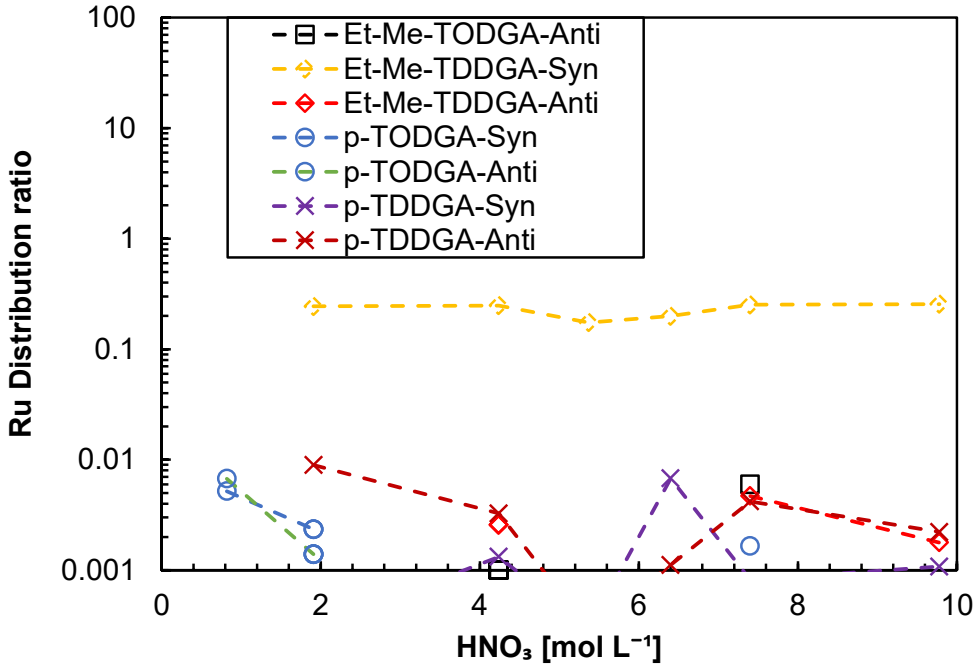

Fig. S4. Ru distribution ratios as a function of the HNO_3 concentration for the different extractants used in this study.

Characterization data of newly synthesized compounds

Ethyl (R)-2-(((S)-1-ethoxy-1-oxopropan-2-yl)oxy)butanoate (1A) and ethyl (S)-2-(((S)-1-ethoxy-1-oxopropan-2-yl)oxy)butanoate (1B)

1A: ^{1}H NMR (400 MHz, $CDCl_3$): d 1.04 (3H, t, *J* = 7.4 Hz, C*H*$_3$CH$_2$CH), 1.30 (6H, t, *J* = 7.2 Hz, C*H*$_3$CH$_2$OCO), 1.48 (3H, d, *J* = 6.8 Hz, C*H*$_3$CH), 1.74-1.91 (2H, m, CH$_3$C*H*$_2$CH), 3.95 (1H, t, *J* = 5.0 Hz, CH$_3$CH$_2$C*H),* 4.05 (1H, q, *J* = 6.8 Hz, CH$_3$C*H*), 4.15-4.29 (4H, m, CH$_3$C*H*$_2$OCO). ^{13}C NMR (100 MHz, $CDCl_3$): d 172.9, 172.6, 79.1, 74.0, 60.85, 60.79, 26.4, 18.7, 14.2, 14.19, 9.7. IR (ϑ_{max}/cm^{-1}): 2981.8, 2937.5, 1730.3, 1447.6, 1369.9, 1268.4, 1192.5, 1127.1, 1045.9, 1022.3. ESI-MS: *m/z* 255.61 [100%; $(M+Na)^+$].

1B: ^{1}H NMR (400 MHz, $CDCl_3$): d 0.99 (3H, t, *J* = 7.4 Hz, C*H*$_3$CH$_2$CH), 1.29 (6H, t, *J* = 7.2 Hz, C*H*$_3$CH$_2$OCO), 1.44 (3H, d, *J* = 6.8 Hz, C*H*$_3$CH), 1.75-1.86 (2H, m, CH$_3$C*H*$_2$CH), 3.89 (1H, t, *J* = 5.8 Hz, CH$_3$CH$_2$C*H),* 4.07 (1H, q, *J* = 6.8 Hz, CH$_3$C*H*), 4.21 (4H, q, *J* = 7.2 Hz, CH$_3$C*H*$_2$OCO). ^{13}C NMR (100 MHz, $CDCl_3$): d 172.4, 172.0, 80.1, 75.2, 60.9, 60.8, 26.0, 18.1, 14.2, 14.1, 9.6. IR (ϑ_{max}/cm^{-1}): 2981.8, 2937.5, 1730.3, 1447.6, 1369.9, 1268.4, 1192.5, 1127.1, 1045.9, 1022.3. ESI-MS: *m/z* 255.61 [100%; $(M+Na)^+$].

(R)-2-((S)-1-Carboxyethoxy)butanoic acid (2A)

^{1}H NMR (400 MHz, CD_3OD): d 1.02 (3H, t, *J* = 7.4 Hz, C*H*$_3$CH$_2$CH), 1.43 (3H, d, *J* = 6.8 Hz, C*H*$_3$CH), 1.71-1.9 (2H, m, CH$_3$C*H*$_2$CH), 3.96 (1H, t, *J* = 6.8 Hz, CH$_3$CH$_2$C*H*), 4.06 (1H, q, *J* = 6.8 Hz, CH$_3$C*H*). ^{13}C NMR (100 MHz, CD_3OD): d 175.0, 174.7, 78.5, 73.6, 25.9, 17.6, 8.5. IR (ϑ_{max}/cm^{-1}): 2980.3, 1704.7, 1465.2, 1450.4, 1419.5, 1246.2, 1161.8, 1131.7, 1069.8. ESI-MS: *m/z* 199.53 [100%; $(M+Na)^+$].

(S)-2-((S)-1-Carboxyethoxy)butanoic acid (2B)

^{1}H NMR (400 MHz, CD_3OD): d 0.89 (3H, t, *J* = 7.4 Hz, C*H*$_3$CH$_2$CH), 1.31 (3H, d, *J* = 6.8 Hz, C*H*$_3$CH), 1.59-1.8 (2H, m, CH$_3$C*H*$_2$CH), 3.92 (1H, t, *J* = 7.0 Hz, CH$_3$CH$_2$C*H*), 4.04 (1H, q, *J* = 6.8 Hz, CH$_3$C*H*). ^{13}C NMR (100 MHz, CD_3OD): d 174.2, 173.4, 79.3, 74.7, 25.4, 17.0, 8.3. IR (ϑ_{max}/cm^{-1}): 2980.3, 1704.7, 1465.2, 1450.4, 1419.5, 1246.2, 1161.8, 1131.7, 1069.8. ESI-MS: *m/z* 199.53 [100%; $(M+Na)^+$].

(S)-2-(((S)-1-(Di-n-octylamino)-1-oxopropan-2-yl)oxy)-N,N-di-n-octylbutanamide (4B)
^{1}H NMR (400 MHz, $CDCl_3$): d 0.88-0.92 (12H, br s, $N(CH_2)_7CH_3$), 1.04 (3H, t, *J* = 7.2 Hz, CH_3CH_2CH), 1.29 (40H, s, $NCH_2CH_2(CH_2)_5CH_3$), 1.41 (3H, d, *J* = 6.4 Hz, CH_3CH), 1.52 (8H, br s, NCH_2CH_2), 1.67-1.83 (2H, m, CH_3CH_2CH), 3.05-3.32 + 3.48-3.55 (8H, m, $NCH_2CH_2(CH2)_5CH_3$), 4.09 (1H, br t, CH_3CH_2CH), 4.28 (1H, q, *J* = 6.6 Hz, CH_3CH). IR (ϑ_{max}/cm^{-1}): 2954.9, 2922.9, 2854.6, 1646.1, 1464.1, 1427.0, 1376.5, 1110.9. ESI-MS: *m/z* 646.83 [100%; $(M+Na)^+$].

(R)-N,N-Di-n-decyl-2-(((S)-1-(N,N-di-n-decylamino)-1-oxopropan-2-yl)oxy)butanamide (5A)
^{1}H NMR (400 MHz, $CDCl_3$): d 0.88-0.92 (12H, m, $NCH_2CH_2(CH_2)_7CH_3$), 1.06 (3H, t, *J* = 7.2 Hz, CH_3CH_2CH), 1.29 (56H, s, $NCH_2(CH_2)_7CH_3$), 1.41 (3H, d, *J* = 6.3 Hz, CH_3CH), 1.52 (8H, br s, $NCH_2CH_2(CH_2)_7CH_3$), 1.68-1.85 (2 H, m, CH_3CH_2CH), 3.05-3.32 + 3.48-3.56 (8H, m, $NCH_2CH_2(CH_2)_7CH_3$), 4.08 (1H, br t, CH_3CH_2CH), 4.28 (1H, q, *J* = 6.5 Hz, CH_3CH). IR (υ_{max}/cm^{-1}): ESI-MS: 757.65 *m/z* [100%; $(M+Na)^+$].

(S)-N,N-Di-n-decyl-2-(((S)-1-(N,N-di-n-decylamino)-1-oxopropan-2-yl)oxy)butanamide (5B)
^{1}H NMR (400 MHz, $CDCl_3$): d 0.88-0.95 (15H, m, $NCH_2CH_2(CH_2)_7CH_3$ + CH_3CH_2CH), 1.32 (59H, br s, $NCH_2(CH_2)_7CH_3$ + CH_3CH_2CH), 1.53 (8H, br s, $NCH_2CH_2(CH_2)_7CH_3$), 1.69-1.81 (2H, m, CH_3CH_2CH), 3.16-3.59 (8H, m, $NCH_2CH_2(CH_2)_7CH_3$), 4.16-4.21 (1H, br t, CH_3CH_2CH), 4.44 (1H, q, *J* = 6.5 Hz, CH_3CH). IR (ϑ_{max}/cm^{-1}): 2921.3, 2852.5, 1750.7, 1649.8, 1464.3, 1375.8, 1200.9, 1112.2. ESI-MS: 757.45 *m/z* [100%; $(M+Na)^+$].

Diethyl 2,2'-oxydipentanoate (6A and 6B)
6A: ^{1}H NMR (400 MHz, $CDCl_3$): d 0.95 (6H, t, *J* = 7.4 Hz, CH_3CH_2OCO), 1.30 (6H, t, *J* = 7.2 Hz, CH_3CH_2), 1.46-1.56 (4H, m, $CH_3CH_2CH_2CH$), 1.74-1.79 (4H, m, $CH_3CH_2CH_2CH$), 3.96 (2H, t, *J* = 6.2 Hz, $COCHO$), 4.15-4.28 (4H, m, CH_3CH_2OCO). ^{13}C NMR (100 MHz, $CDCl_3$): d 172.7, 77.7, 60.7, 35.3, 18.5, 14.2, 13.8. IR (ϑ_{max}/cm^{-1}): 2962.5, 2874.7, 1747.6, 1732.2, 1466.6, 1380.8, 1265.0, 1190.1, 1130.5, 1096.3, 1025.2. ESI-MS: *m/z* 297.64 [100%; $(M+Na)^+$].

6B: ^{1}H NMR (400 MHz, $CDCl_3$): d 0.95 (6H, t, *J* = 7.4 Hz, CH_3CH_2OCO), 1.30 (6H, t, *J* = 7.2 Hz, CH_3CH_2), 1.37-1.55 (4H, m, $CH_3CH_2CH_2CH$), 1.98-1.84 (4H, m, $CH_3CH_2CH_2CH$), 3.89 (2H, t, *J* = 6.2 Hz, $COCHO$), 4.20 (4H, q, *J* = 7.1 Hz, CH_3CH_2OCO). ^{13}C NMR (100 MHz, $CDCl_3$): d 172.2, 79.7, 60.8, 34.9, 18.5, 14.2, 13.8. IR (ϑ_{max}/cm^{-1}): 2960.8, 2875.2, 1750.4, 1730.8, 1466.5, 1368.3, 1271.5, 1185.6, 1128.3, 1028.2. ESI-MS: *m/z* 297.66 [100%; $(M+Na)^+$].

2,2'-Oxydipentanoic acid (7A)
^{1}H NMR (400 MHz, $CDCl_3$): d 0.97 (6H, t, *J* = 7.0 Hz, $CH_3CH_2CH_2CH$), 1.56 (4H, sext, *J* = 7.7 Hz, $CH_3CH_2CH_2CH$), 1.84 (4H, q, *J* = 6.1 Hz, $CH_3CH_2CH_2CH$), 4.1 (2H, t, *J* = 6.0 Hz, $CH_3CH_2CH_2CH$). ^{13}C NMR (100 MHz, $CDCl_3$): d 178.3, 77.3, 35.1, 18.3, 13.7. IR (ϑ_{max}/cm^{-1}): 2963.7, 2875.4, 1717.7, 1455.0, 1420.9, 1254.2, 1208.7, 1132.3, 1094.5. ESI-MS: *m/z* 241.57 [100%; $(M+Na)^+$].

2,2'-Oxydipentanoic acid (7B)
^{1}H NMR (400 MHz, $CDCl_3$): d 0.99 (6H, t, *J* = 7.4 Hz, $CH_3CH_2CH_2CH$), 1.50 (4H, sext, *J* = 7.4 Hz, $CH_3CH_2CH_2CH$), 1.82-1.87 (4H, q, *J* = 6.0 Hz, $CH_3CH_2CH_2CH$), 4.01 (2H, t, *J* = 6.0 Hz, $CH_3CH_2CH_2CH$). ^{13}C NMR (100 MHz, $CDCl_3$): d 175.8, 80.0, 34.5, 18.2, 13.8. IR (ϑ_{max}/cm^{-1}): 2960.6, 2875.4, 1715.6, 1380.24, 1212.7, 1123.8, 1092.7. ESI-MS: *m/z* 241.59 [100%; $(M+Na)^+$].

2,2'-Oxybis(N,N-di-n-octylpentanamide) (9A)
^{1}H NMR (400 MHz, $CDCl_3$): d ^{1}H NMR (400 MHz, $CDCl_3$): 0.85-0.97 (18H, m, $N(CH_2)_7CH_3$ + $CHCH_2CH_2CH_3$), 1.28-1.33 (44H, br s, $NCH_2CH_2(CH_2)_5CH_3$, $CHCH_2CH_2CH_3$), 1.44-1.55 (8H, m, $NCH_2CH_2(CH_2)_5CH_3$), 1.67-1.78 (4H, m, $CHCH_2CH_2CH_3$), 3.00-3.08, 3.09-3.15, 3.28-3.36, 3.50-3.57 (2H each, m, $CH_2CH_2(CH_2)_5CH_3$), 4.14 (2H, t, *J* = 6.4 Hz, $CHCH_2CH_2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): d 171.4, 75.5, 47.1, 46.1, 35.7, 31.8, 29.4, 29.3, 29.29, 29.2, 27.7, 27.1, 26.9, 22.6, 18.9, 14.1, 18.9, 14.1, 14.0. IR (ϑ_{max}/cm^{-1}): 2956.3, 2923.5, 2854.4, 1653.2, 1458.2, 1425.7, 1377.4, 1120.1, 1091. ESI-MS: *m/z* 687.61 [100%; $(M^+Na)^+$].

2,2'-Oxybis(*N,N-*di*-n-*octylpentanamide) (9B)

^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): d 0.89-0.95 (18H, m, $N(CH_2)_7CH_3$ + $CHCH_2CH_2CH_3$), 1.30 (40 H, s, $NCH_2CH_2(CH_2)_5CH_3$), 1.3-1.4 (4H, m, $CHCH_2CH_2CH_3$), 1.5-1.73 (12H, m, $NCH_2CH_2(CH_2)_5CH_3$ + $CHCH_2CH_2CH_3$), 3.21-3.53 (8H, m, $NCH_2CH_2(CH_2)_5CH_3$), 4.29 (2H, t, *J* = 6.5 Hz, $CHCH_2CH_2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): d 171.6, 76.6, 46.8, 34.8, 31.8, 31.77, 29.4, 29.3, 27.4, 27.1, 26.9, 22.6, 18.9, 14.1, 14.0. IR (ϑ_{max}/cm^{-1}): 2956.1, 2923.6, 2854.2, 1651.9, 1458.8, 1426.7, 1377.3, 1111.2, 1085.3. ESI-MS: *m/z* 688.18 [100%; $(M+Na)^+$].

2,2'-Oxybis(*N,N-*di*-n-*decylpentanamide) (10A)

^{1}H NMR (400 MHz, $CDCl_3$): d 0.88-0.97 (18H, m, $N(CH_2)_7CH_3$ + $CHCH_2CH_2CH_3$), 1.29 (56H, br s, $NCH_2CH_2(CH_2)_7CH_3$), 1.44-1.78 (16H, m, $NCH_2CH_2(CH_2)_6CH_3$ + $CHCH_2CH_2CH_3$), 3.01-3.57 (8H, m, $NCH_2CH_2(CH_2)_7CH_3$), 4.13–4.16 (2H, m, $CHCH_2CH_2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): d 171.4, 75.4, 47.2, 46.1, 35.6, 31.9, 29.64, 29.59, 29.6, 29.5, 29.44, 29.41, 29.3, 27.6, 27.1, 27.0, 22.7, 18.9, 14.1, 14.0. IR (ϑ_{max}/cm^{-1}): 2956.2, 2921.4, 2852.8, 1653.3, 1465.4, 1425.7, 1376.9, 1121.0, 1089.7. ESI-MS: *m/z* 799.62 [100%; $(M+Na)^+$].

2,2'-Oxybis(*N,N-*di*-n-*decylpentanamide) (10B)

^{1}H NMR (400 MHz, $CDCl_3$): d 0.89-0.95 (18H, m, $N(CH_2)_7CH_3$ + $CHCH_2CH_2CH_3$), 1.29 (56H, br s, $NCH_2CH_2(CH_2)_7CH_3$), 1.5-1.73 + 2.00 (16H, m, $NCH_2CH_2(CH_2)_6CH_3$ + $CHCH_2CH_2CH_3$), 3.21-3.53 (8H, m, $NCH_2CH_2(CH_2)_7CH_3$), 4.33 (2H, t, *J* = 6.5 Hz, $CHCH_2CH_2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): d 171.1, 75.4, 47.4, 46.4, 34.5, 31.9, 31.9, 29.62, 29.60, 29.57, 29.53, 29.45, 29.42, 29.41, 29.3, 27.5, 27.1, 27.0, 22.7, 18.9, 14.1, 14.0. IR (ϑ_{max}/cm^{-1}): 2956.6, 2921.4, 2852.7, 1652.7, 1465.2, 1427.0, 1377.4, 1110.7, 1079.9. ESI-MS: *m/z* 799.58 [100%; $(M^+Na)^+$].