Electronic Supplementary Information

Rotaxanation as a sequestering template to preclude incidental metal insertion in complex oligochromophores

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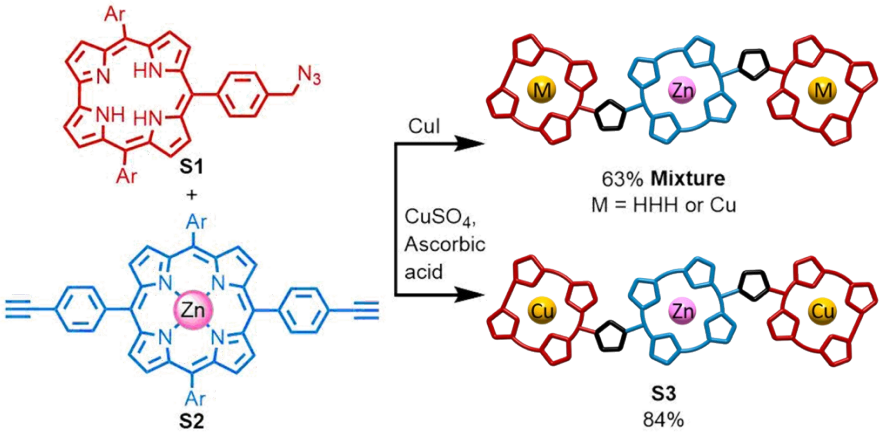
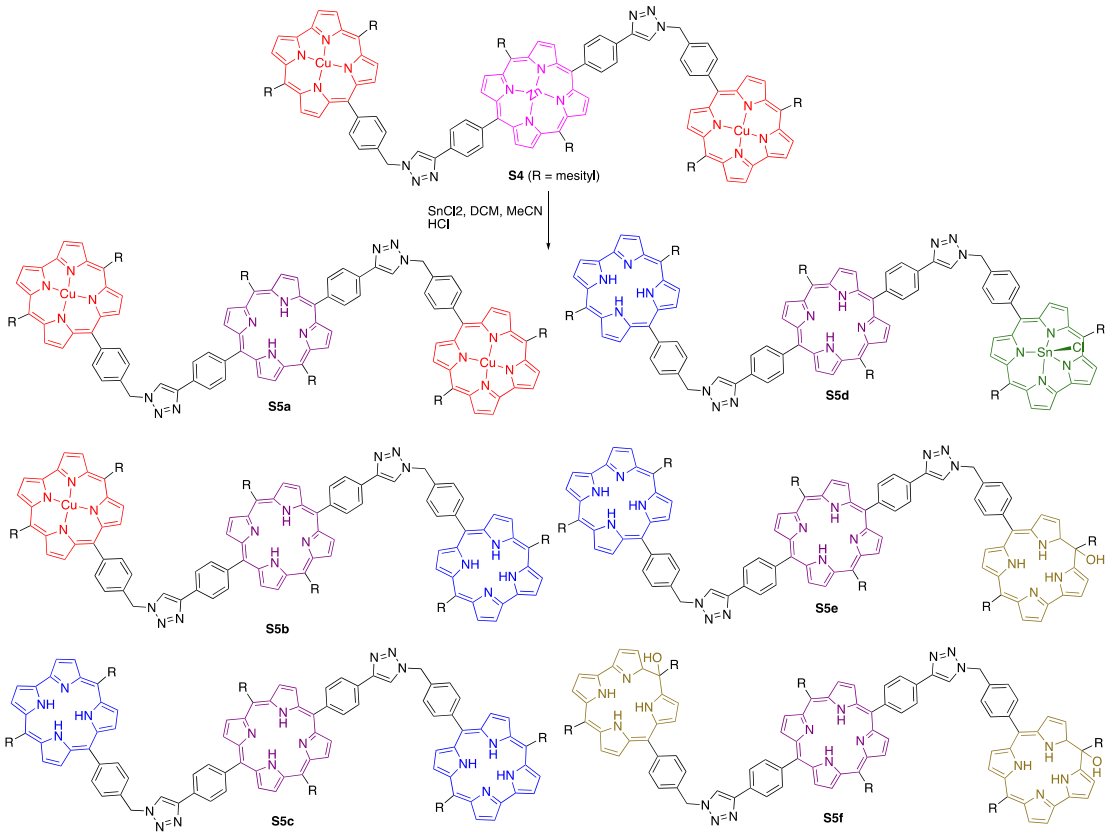
Copper catalyzed click reaction followed by reductive demetallation

Since the catalytic activity of the click reaction derives from copper of oxidation state +1, CuI was employed as catalyst. The click reaction with free base corrole **S1** diacetylenyl zinc porphyrin **S2** was successful (63%) but partial and fully copper metalated conjugates were isolated. The purification of different derivatives of fully non-metalated, single metalated and double metalated corroles was not possible since copper center does not change the size or polarity of the conjugates much. Disproportionation of Cu(I) to metallic copper and Cu(II) was fast enough compared to the click reaction to facilitate copper metalation of corrole moieties. Corrole could also be metalated by the released copper ion after the click reaction. When access of $CuSO_4$ was used in the presence of ascorbic acid, fully metalated corroles-porphyrin triad **S3** was isolated in high yield (84%).



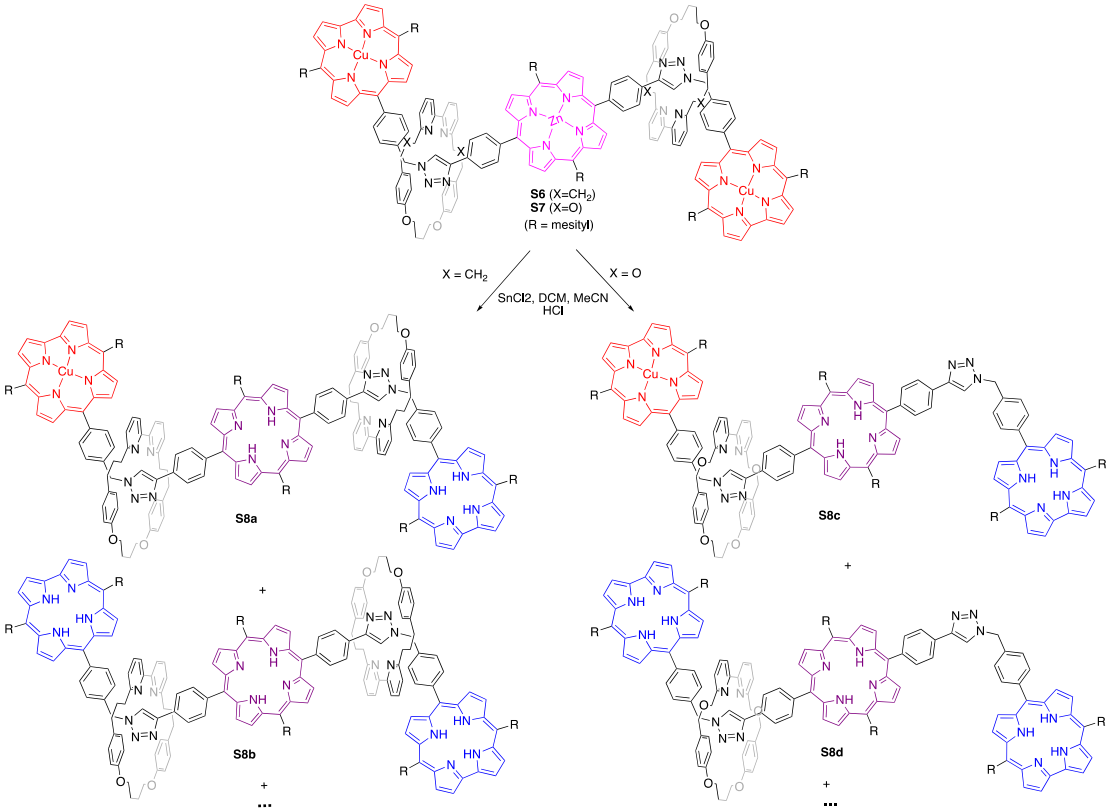
Scheme S1: Copper catalyzed click reaction of free base corrole and zin porphyrin using CuI and $CuSO_4$ as catalysts.

The pure free base corrole-porphyrin conjugates could not be obtained *via* click reaction starting from non-metalated precursors. We change the strategy to the reductive demetalation of the copper corrole-porphyrin conjugates described in previous reports.[1] When **S4** undergo the reductive metalation procedure[2] with $SnCl_2$ and HCl a number of mixtures of different products were observed on mass spectroscopy depending on the reaction time (Scheme 2). First observed product was of course the zinc demetalated product **S5a** with unreacted starting material. When the reaction continues first copper demetalation was observed but still in a mixture of starting material, **S5a** and **S5b**. After 2h the first indication of the presence of fully freebase **S5c** was observed but the mixture still contains **S5a** and **S5b**. The double copper demetalation occurred slower than our expectation and we were unable to purify each of the product because of the small difference in polarity and size. Therefore, the reaction was continued for a longer reaction time. When no more copper derivatives were observed, the other unexpected products were present, *i.e.* tin inserted derivative **S5d** and isocorrole derivatives **S5e** and **S5f**. Again, we cannot purify the obtained products. The different concentrations of reductant and acid (HCl in ethanol, HCl in ether) all gave the same inseparable mixtures.



Scheme S2: Reductive demetalation of **S4**

The same observations were made when rotaxane **S6** was subjected to the same reaction conditions resulting in a similar rotaxane derivative mixture (Scheme 3, left). Under the previously described demetalation condition on **S7**, containing a benzyl ether moiety in the macrocycle, not only provide the unwanted mixture but also the partially and fully non-interlocked derivatives were observed. The benzylic ether moiety was not stable under such reductive acidic condition and the macrocycle was decomposed (Scheme S3, right). When the reaction was carried on for longer reaction time a mixture of non-interlocked products as in Scheme S2 were observed.



Scheme S3: Reductive demetalation of rotaxane copper corrole zinc porphyrin conjugates.

These observations entirely changed our synthetic strategy using rotaxane unit as a sacrificial template toward fully freebase corrole porphyrin conjugates (see main manuscript).

References

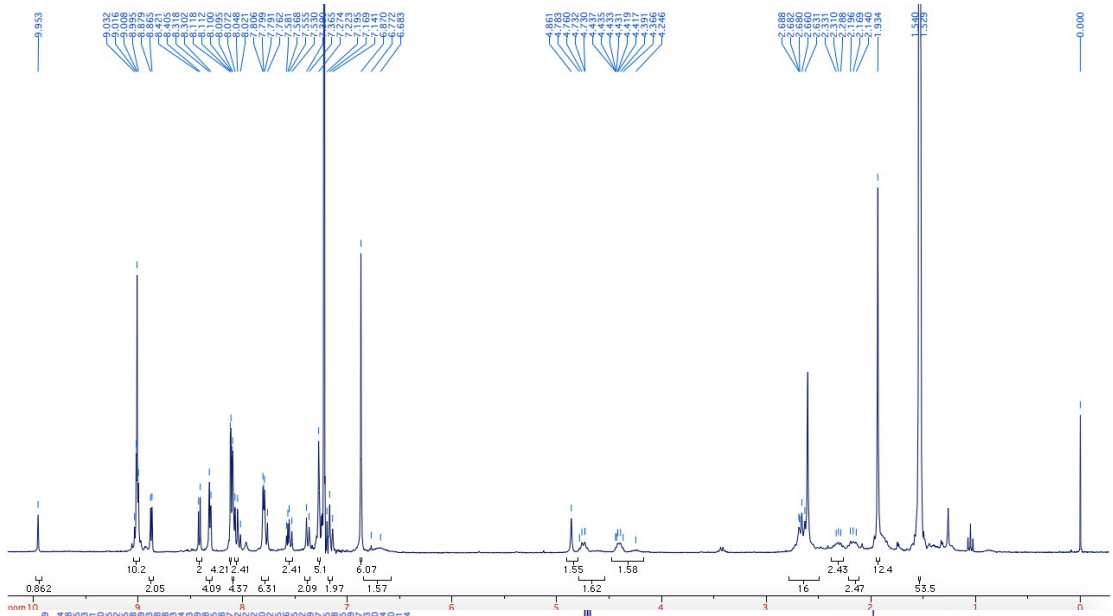
1. T. H. Ngo, D. Zieba, W. A. Webre, G. N. Lim, P. A. Karr, S. Kord, S. Jin, K. Ariga, M. Galli, S. Goldup, J. P. Hill and F. D'Souza, *Chem.*, 2016, **22**, 1301.
2. T. H. Ngo, W. Van Rossom, W. Dehaen, M. Maes, *Org. Biomol. Chem.* 2009**, *7***, 439.

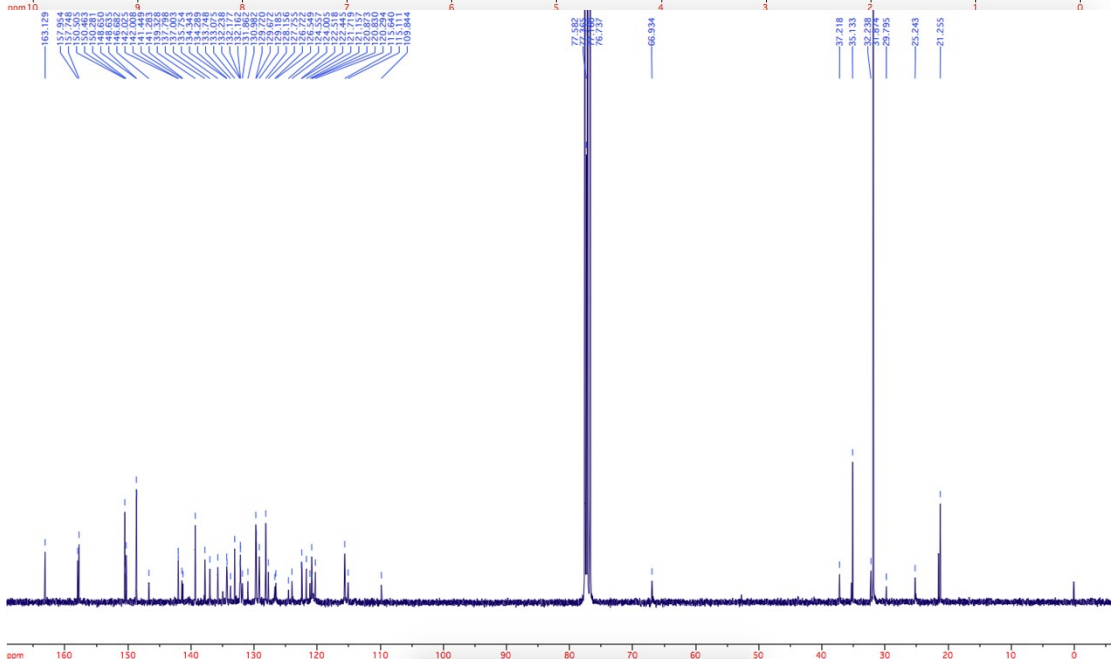
Synthetic procedure and characterization

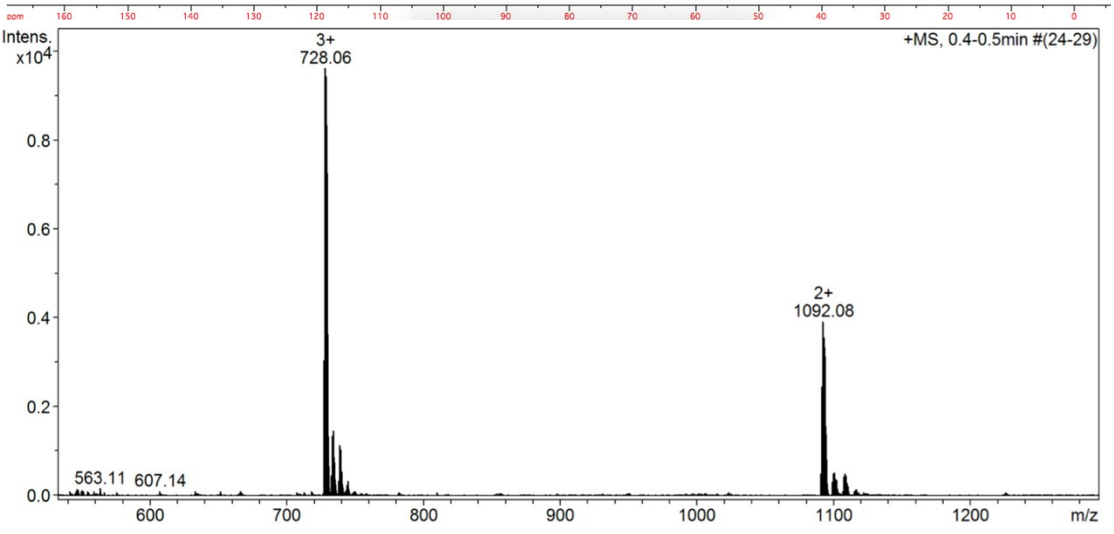
Diad 5a

To a solution of porphyrin **2** (19 mg, 1.83×10^{-5} mol) and azidocorrole **1** (40 mg, 5.02×10^{-5} mol) in 10 mL dichloromethane was added the preprepared mixture of $[Cu(CH_3CN)_4]PF_6$ (6.8mg, 1.82×10^{-5} mol) and macrocycle **4a** (17.5 mg, 3.66×10^{-5} mol) in 2 mL DCM. The solution was stirred at room temperature under N_2 atmosphere. A drop of diisopropylethylamine was added. The reaction was monitored using tlc. After completion, the solvent was evaporated under reduced pressure. Purification by size extrusion chromatography (Biobeads SX-1) eluting with chloroform afforded diad **5a** (37 mg, 93%) as a purple solid.

^{1}H−NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 9.95 (s, 1H, $H_{triazole}$), 9.03−9.00 (m, 10H, H_{ar}+H_β), 8.87 (d, ^3J(H,H) = 4.2 Hz, 2H, H_β), 8.41 (d, ^3J(H,H) = 4.8 Hz, 2H, H_β), 8.31(d, ^3J(H,H) = 4.8 Hz, 4H, H_β), 8.12−8.02 (m, 10H, H_{ar}), 7.81−7.79 (m, 6H, H_{ar}), 7.58−7.53 (m, 2H, H_{ar}), 7.38 (d, ^3J(H,H) = 7.5Hz, 2H, H_{ar}), 7.27 (s, 5H, H_{ar}), 7.20−7.14 (m, 2H, H_{ar}), 6.87(s, 6H, H_{ar}), 6.77−6.68 (m, 2H,H_{CH2}), 4.86 (s, 2H, $H_{macrocycle}$), 478−4.73 (m, 2H, H_{OCH2}), 4.44−4.25 (m, 4H, $H_{macrocycle}$), 2.69−2.63 (m, 16H, $H_{macrocycle}$ +$H_{mesityl}$), 2.33−2.31 (m, 2H, $H_{macrocycle}$), 2.20−2.24 (m, 2H, $H_{macrocycle}$), 1.93(s, 12H, $H_{mesityl}$), 1.54 (s, 54H, H_{tBu}) ppm. ^{13}C−NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 163.1, 158.0/157.7, 150.5/150.3, 148.7/148.6, 146.7, 142.0, 141.4/141.3, 139.3, 137.8, 137.0 (CH), 135.8, 134.3 (CH), 133.7, 133.1, 132.2 (CH), 131.9 (CH), 131.0, 129.7 (CH), 128.2 (CH), 127.8 (CH), 126.7 (CH), 124.6, 124.0 (CH), 122.5/122.4, 121.7 (CH), 121.2, 120.9/120.8 (CH), 120.3(CH), 115.6 (CH), 115.1 (CH), 109.8, 77.4, 66.9 (CH_2), 37.2 (CH_2), 35.1 (CH_2), 32.2, 31.9 (CH_3), 29.8 (CH_2), 25.2 (CH_2), 21.3 (CH_3) ppm. MS (ESI): calc: 1092.07 [M+2H^{2+}]; found: 1092.08; calc: 728.38 [M+3H^{3+}]; found: 728.06.



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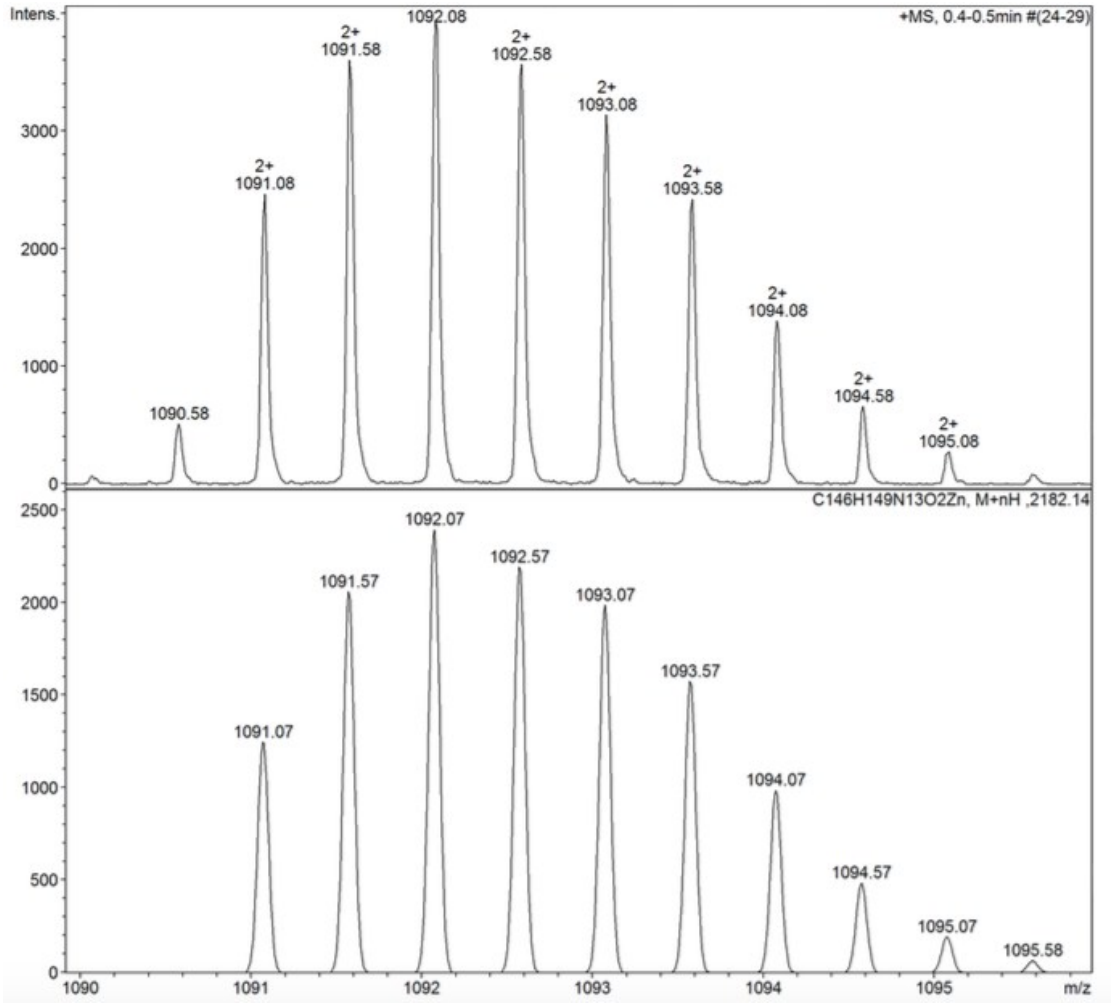
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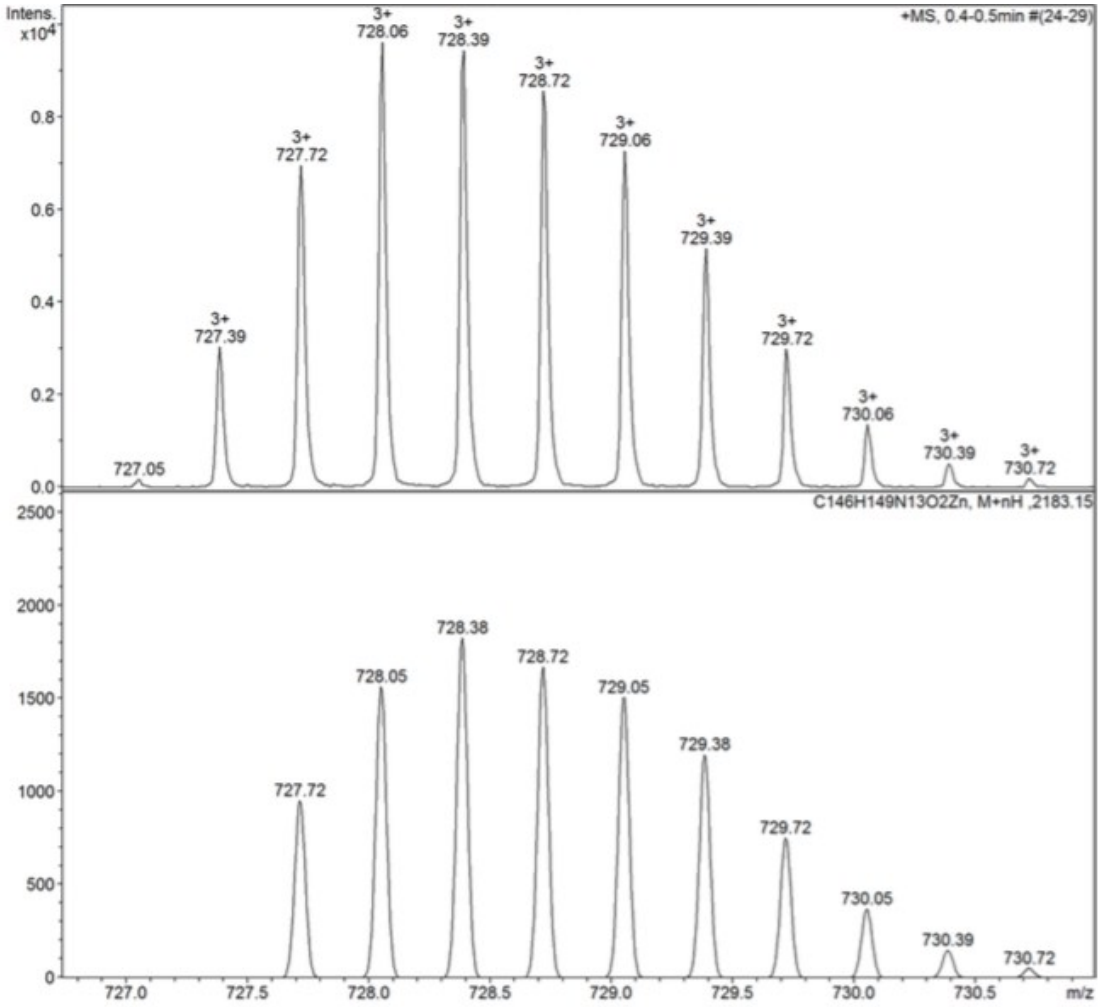
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729.05
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m/z

Generic Display Report

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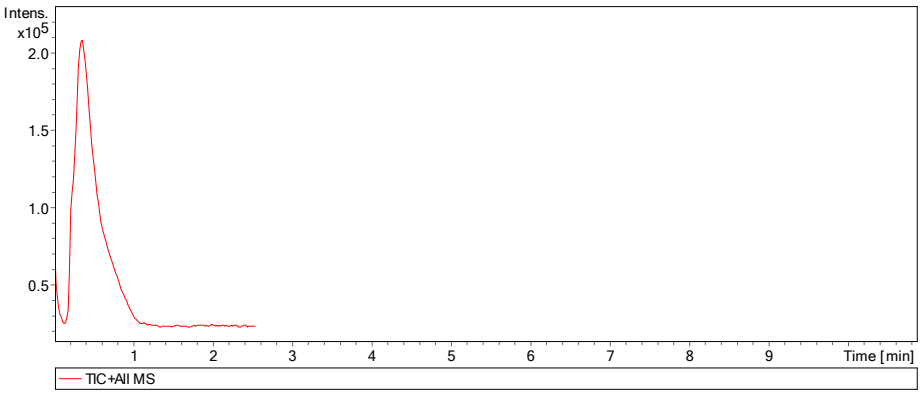
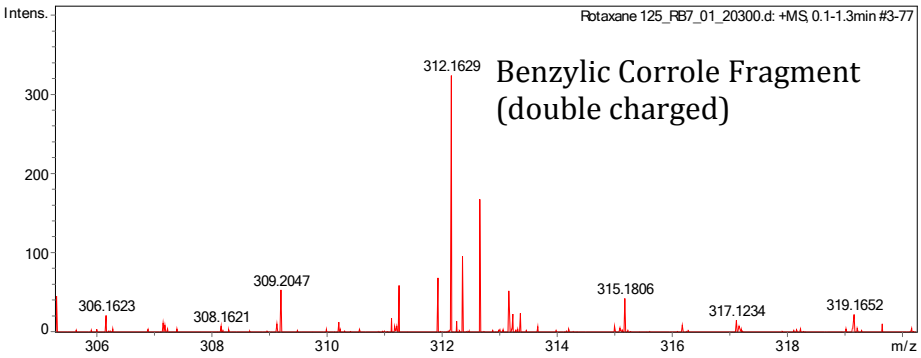
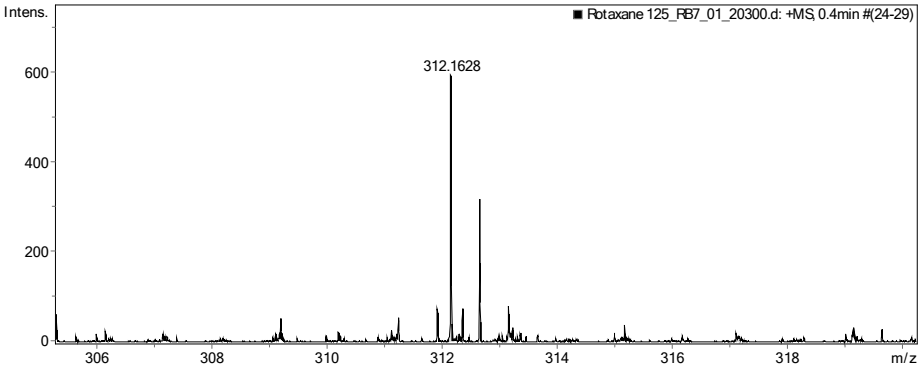


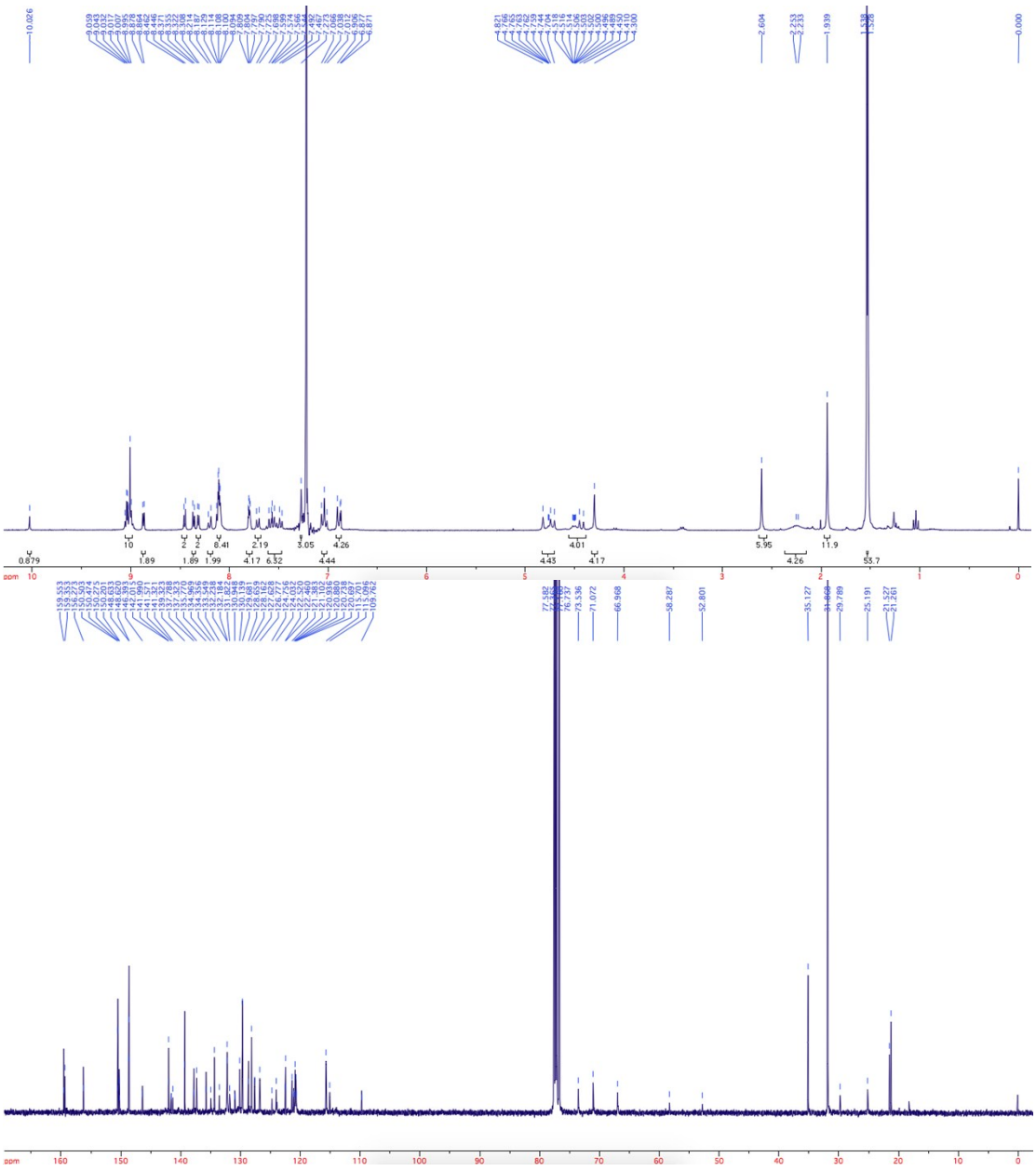


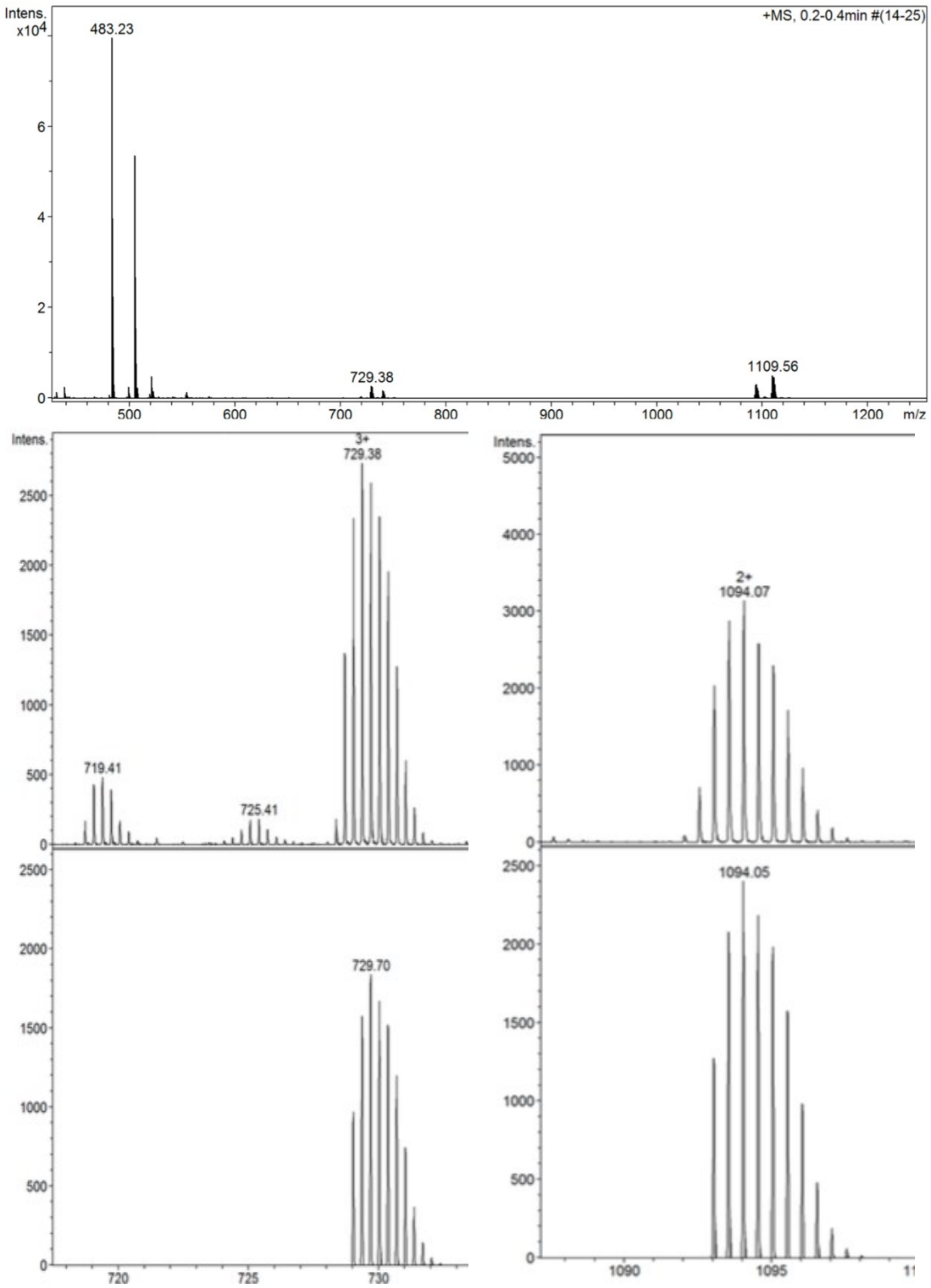


Diad 5b

To a solution of porphyrin **2** (20 mg, 1.92×10^{-5} mol) and azidocorrole **1** (40 mg, 5.02×10^{-5} mol) in 10 mL dichloromethane was added the preprepared mixture of $[Cu(CH_3CN)_4]PF_6$ (7.1 mg, 1.9×10^{-5} mol) and macrocycle **4b** (18.4 mg, 3.8×10^{-5} mol) in 2 mL DCM. The solution was stirred at room temperature under N_2 atmosphere. A drop of diisopropylethylamine was added. The reaction was monitored using t.l.c. After completion, the solvent was evaporated under reduced pressure. Purification by size extrusion chromatography (Biobeads SX-1) eluting with chloroform afforded diad **5b** (42 mg, quantitative) as a purple solid.

^{1}H−NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 10.03 (s, 1H, $H_{triazole}$), 9.06−9.00 (m, 10H, H_{ar}+H_β), 8.87 (d, ^3J(H,H) = 4.2 Hz, 2H, H_β), 8.45 (d, ^3J(H,H) = 4.8 Hz, 2H, H_β), 8.37(d, ^3J(H,H) = 4.8 Hz, 2H, H_β), 8.32 (d, ^3J(H,H) = 4.2 Hz, 2H, H_β), 8.20 (d, ^3J(H,H) = 8.1 Hz, 2H, H_{ar}), 8.13−8.09 (m, 8H, H_{ar}), 7.81−7.79 (m, 4H, H_{ar}), 7.71 (d, ^3J(H,H) = 8.1 Hz, 2H, H_{ar}), 7.60−7.47 (m, 6H, H_{ar}),7.27 (s, 3H, H_{ar}), 7.07−7.01 (m, 4H, H_{ar}), 6.91−6.87 (m, 4H, H_{ar}+H_{CH2}), 4.81−4.70 (m, 4H, H_{OCH2}), 4.52−4.41 (m, 4H, $H_{macrocycle}$), 4.30 (s, 4H, $H_{macrocycle}$), 2.60 (s, 6H, $H_{mesityl}$), 2.25−2.23 (m, 4H, $H_{macrocycle}$), 1.94(s, 12H, $H_{mesityl}$), 1.54 (s, 54H, H_{tBu}) ppm. ^{13}C−NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 159.5/159.4, 156.3, 150.5/150.2, 148.6, 146.4, 142.0, 141.6/141.3, 139.3, 137.78, 137.3 (CH), 135.8, 135.0, 134.4 (CH), 133.6, 132.2 (CH), 131.8, 130.9 (CH), 130.2, 129.7 (CH), 128.7, 128.2 (CH), 127.7 (CH), 126.8 (CH), 124.8 (CH), 124.0 (CH), 122.5, 121.4 (CH), 121.1, 120.9/120.7 (CH), 115.7 (CH), 115.1 (CH), 109.8, 77.4 (CH), 73.5 (CH_2), 71.1 (CH_2), 67.0 (CH_2), 58.3 (CH_2), 52.8 (CH_2), 35.1 (CH_2), 31.9 (CH_2), 29.8 (CH_2), 25.2 (CH_2), 21.5 (CH_3), 21.3 (CH_3) ppm. MS (ESI): calc: 1094.05 [M+2H^{2+}]; found: 1094.07; calc: 729.70 [M+3H^{3+}]; found: 729.38.

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2+
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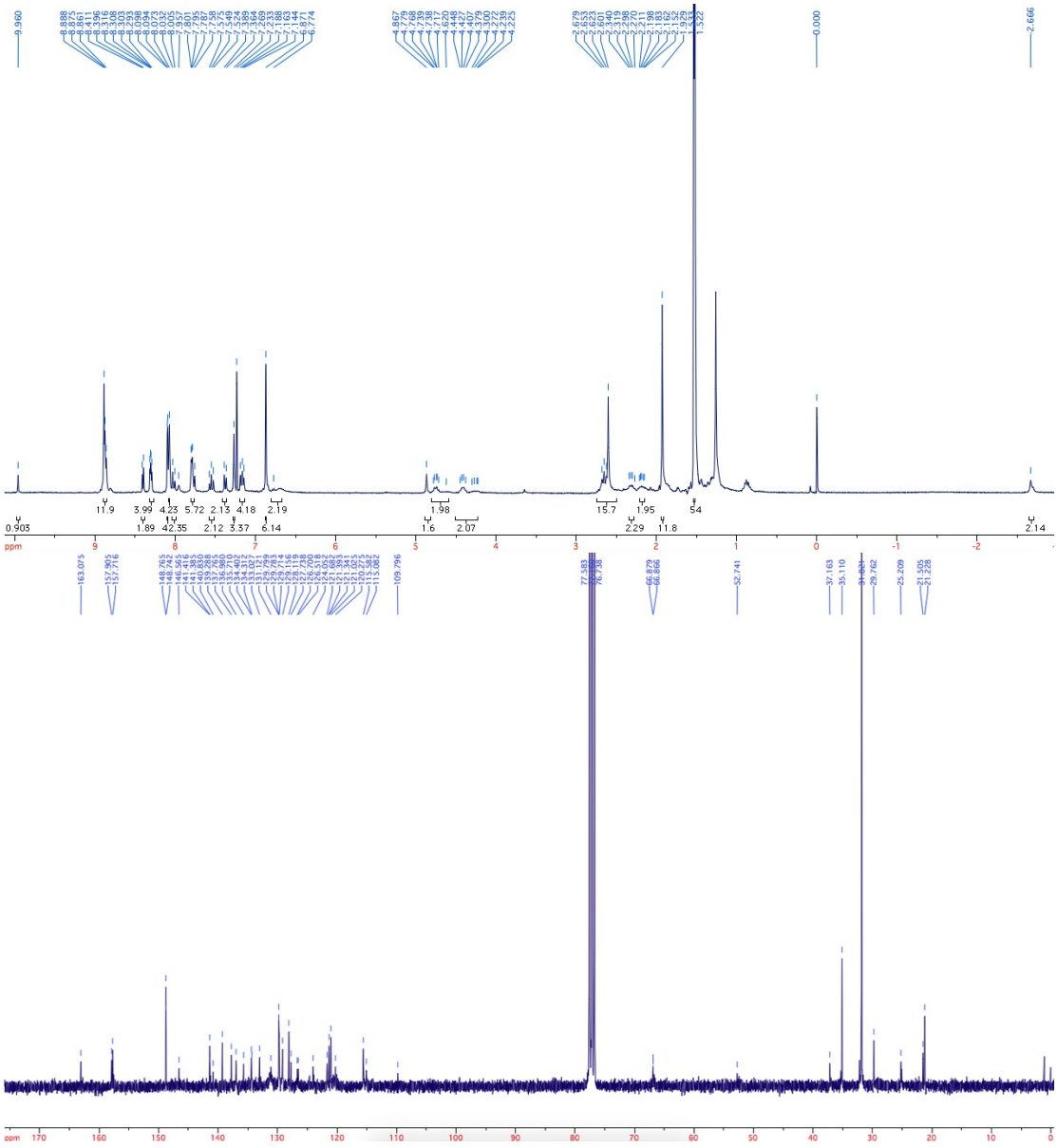
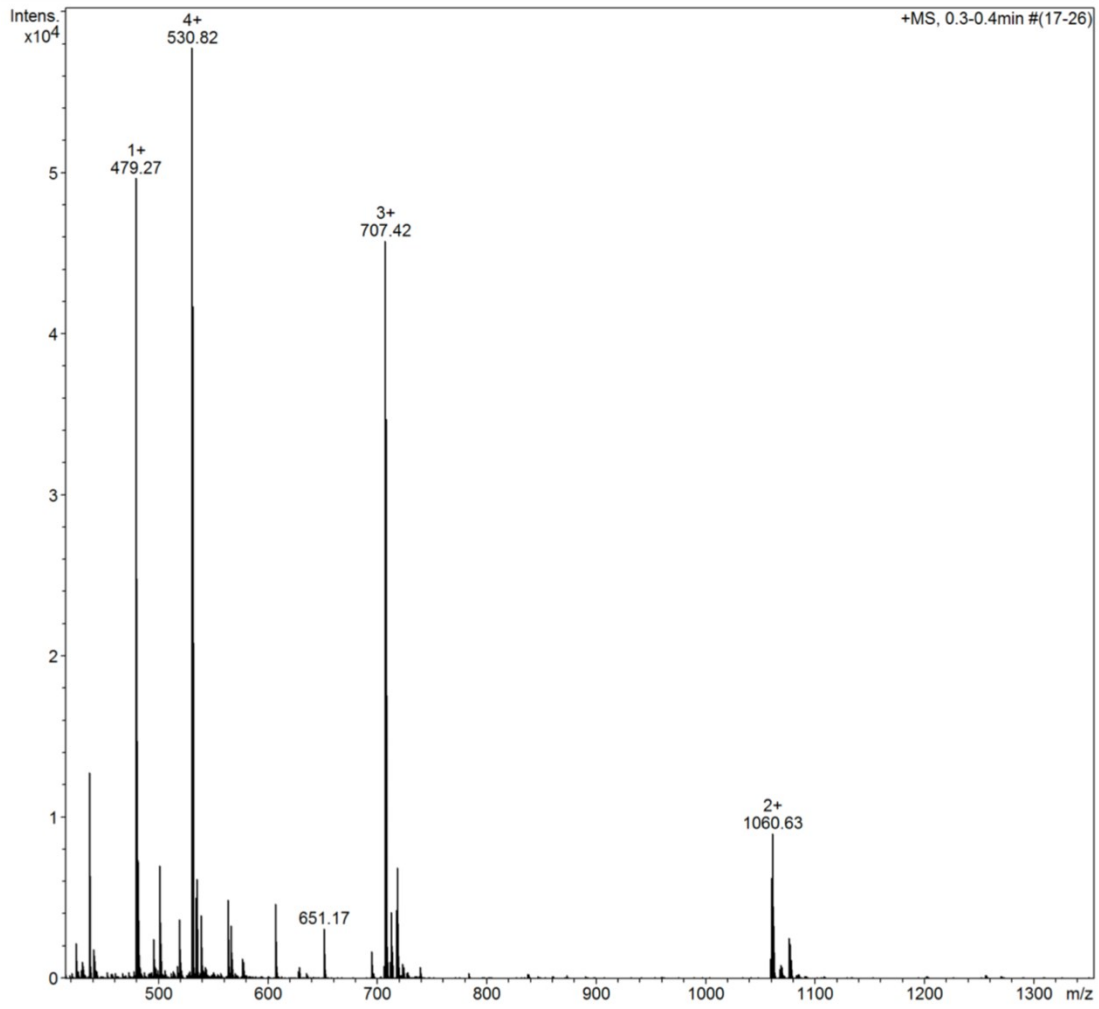
729.70
1094.05

Diad 6

To the solution of **diad 5a** (21 mg, 9.6×10^{-6} mol) in 10 mL DCM was added $HBr{\cdot}PPh_3$ (20 mg, 5.83×10^{-5} mol). The mixture was stirred for 10 min and washed with water and brine. Purification by size extrusion chromatography (Biobeads SX-1) eluting with chloroform afforded **diad 6** (18mg, 88%) as a purple solid.
^{1}H−NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=9.95 (s, 1H, $H_{triazole}$), 8.89−8.86 (m, 12H, H_{ar}+H_{β}), 8.45 (d, ^{3}J(H,H) = 4.5 Hz, 2H, H_{β}), 8.32−8.28 (m, 4H, H_{β}), 8.10− 7.96(d, ^{10}H, H_{ar}+H_{β}), 8.80−7.76 (m, 6H, H_{ar}+H_{β}), 7.56−7.52 (m, 2H, H_{ar}), 7.37 (d, ^{3}J(H,H) = 7.5Hz, 2H, H_{ar}), 7.27 (s, 3H, H_{ar}), 7.19−7.14 (m, 4H, H_{ar}), 6.87(s, 6H, H_{ar}), 6.77−6.68 (m, 2H,H_{CH2}), 4.87 (s, 2H, $H_{macrocycle}$), 478−4.62 (m, 2H, H_{OCH2}), 4.45−4.23 (m, 4H, $H_{macrocycle}$), 2.68−2.62 (m, 10H, $H_{macrocycle}$), 2.60 (s, 6H, $H_{mesityl}$), 2.34−2.27 (m, 2H, $H_{macrocycle}$), 2.21−2.15 (m, 2H, $H_{macrocycle}$), 1.93(s, 12H, $H_{mesityl}$), 1.53 (s, 54H, H_{tBu}) ppm. ^{13}C−NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 163.1, 157.9/157.7, 148.8/148.7, 146.6, 141.4, 140.8, 139.3, 137.8, 137.0 (CH), 135.7, 134.4/134.4 (CH), 133.0, 131.1, 129.8/129.7 (CH), 128.1 (CH), 127.7 (CH), 126.7/126.5 (CH), 124.1 (CH), 121.7 (CH), 121.4, 121.3 (CH), 121.0, 120.3(CH), 115.6 (CH), 115.1 (CH), 109.8, 66.9 (CH_2), 52.7 (CH_2), 37.2 (CH_2), 35.1 (CH_2), 31.0 (CH_3), 29.8 (CH_2), 25.2 (CH_2), 21.5 (CH_3), 21.2 (CH_3) ppm. MS (ESI): calc: 707.42 [M+2H^{2+}]; found: 707.41; calc: 530.82 [M+4H^{4+}]; found: 530.81.

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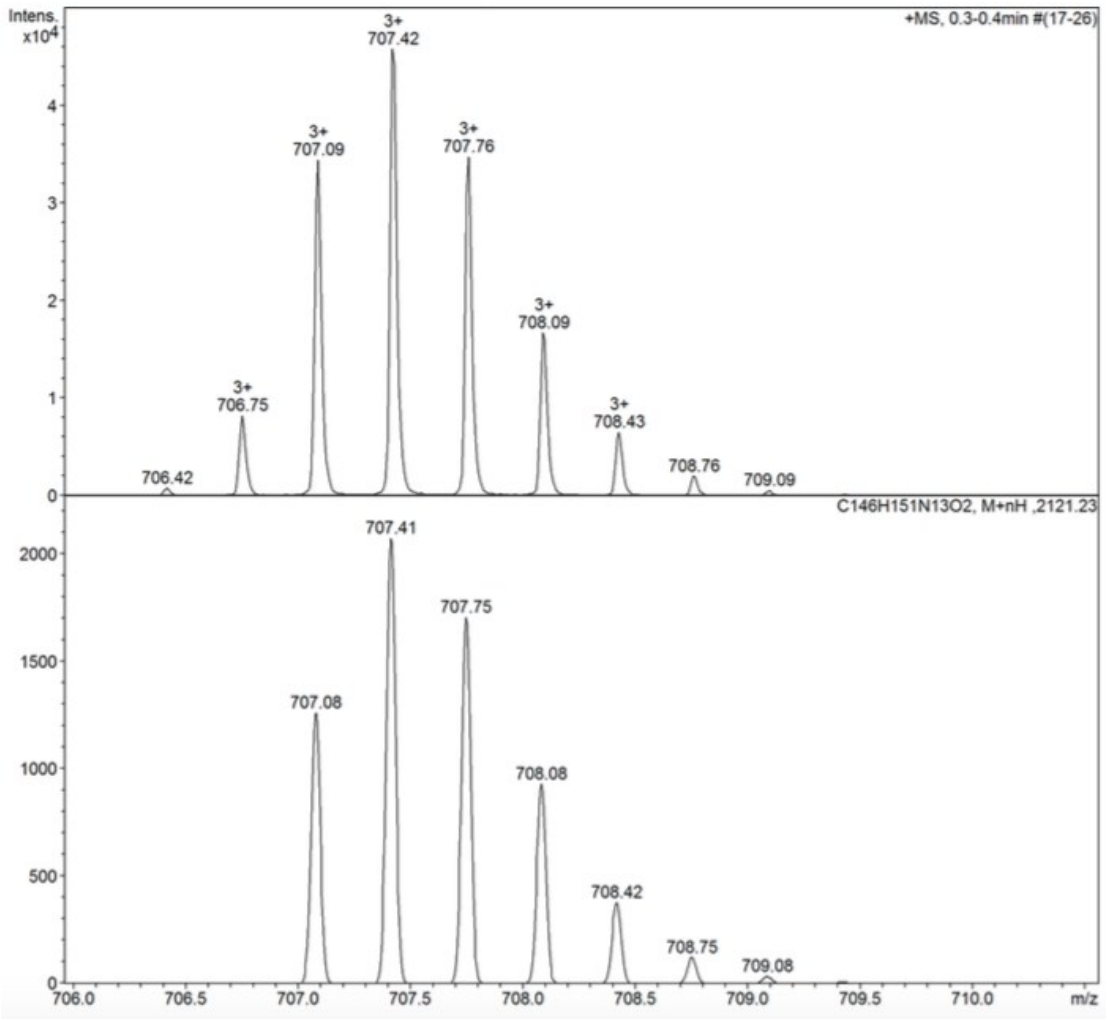
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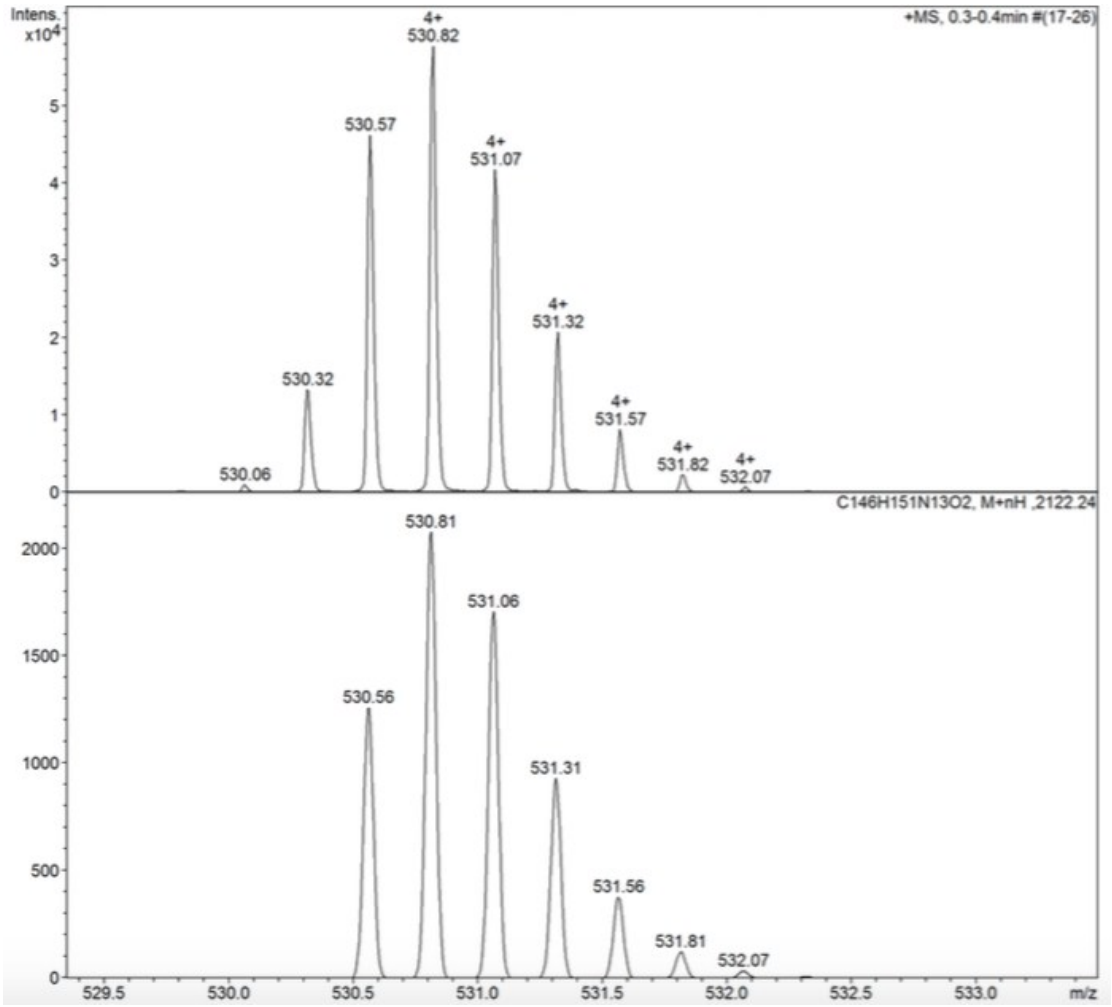
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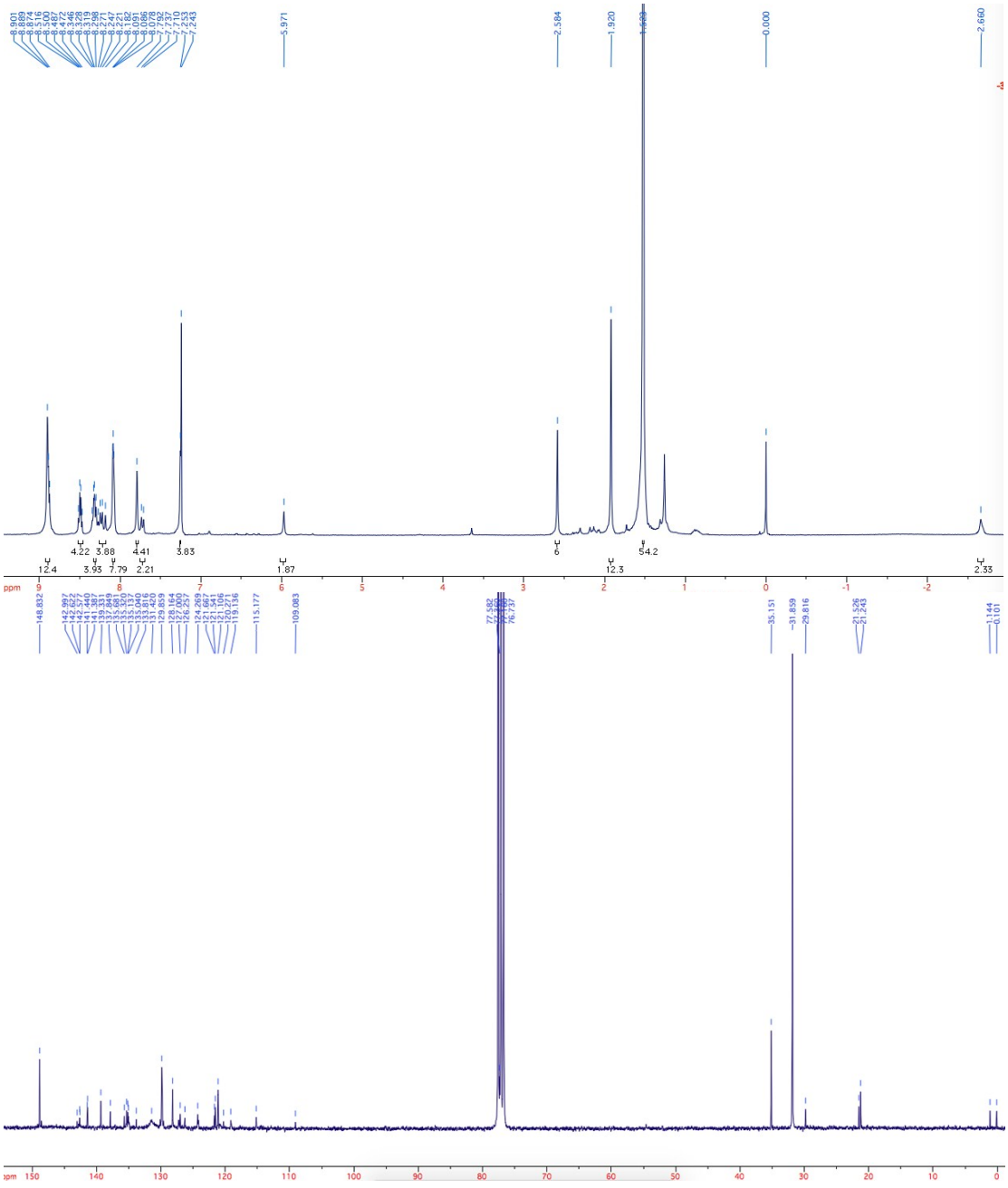
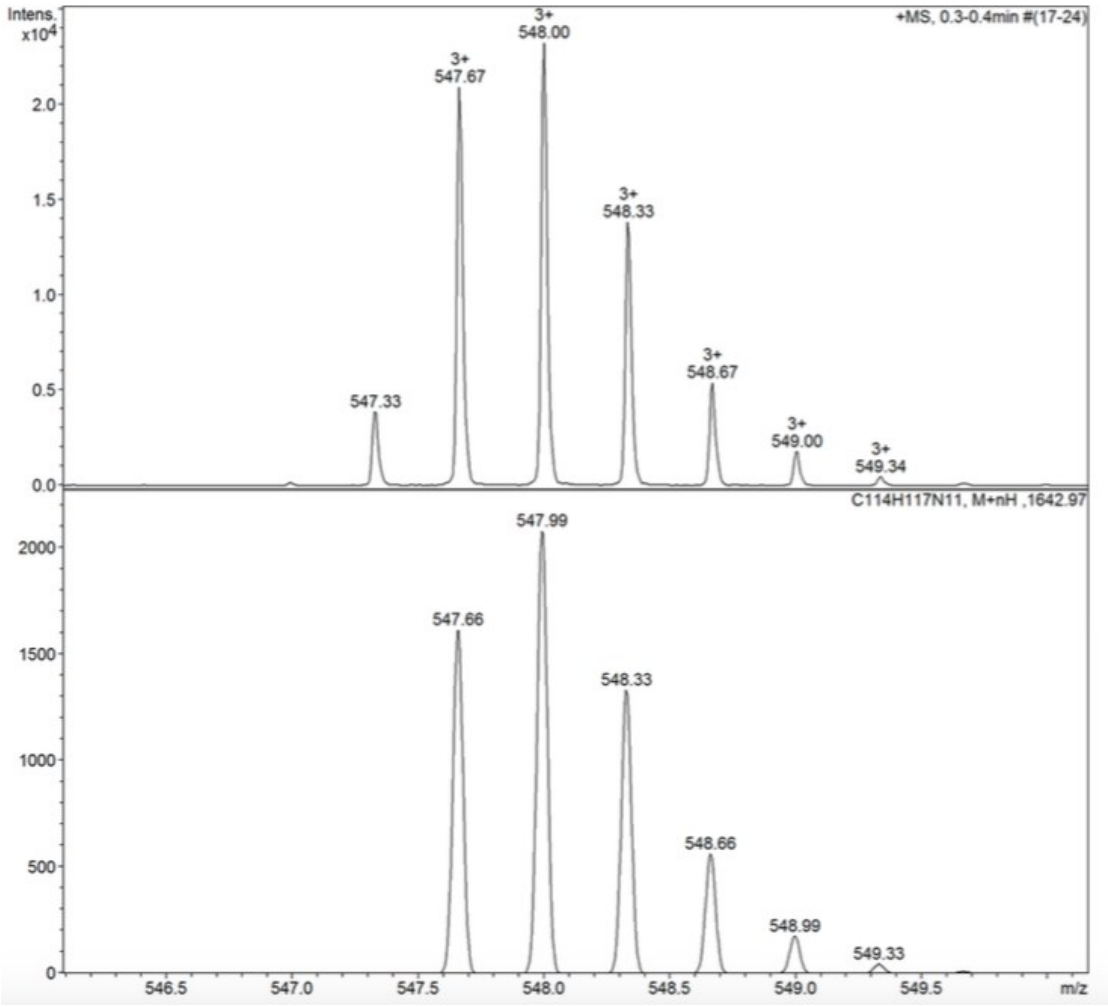
531.5
532.0
532.5
533.0
m/z

Diad 7

To the solution of **diad 5b** (16.6 mg, 7.59 × 10^{-6} mol) in 10 mL DCM was added HBr•PPh_3 (20 mg, 5.83 × 10^{-5} mol). The mixture was stirred for 1h min and washed with water and brine. Purification by size extrusion chromatography (Biobeads SX-1) eluting with chloroform afforded diad **7** (10 mg, 82%) as a purple solid.

^{1}H−NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=8.90−8.89 (m, 16H, H_β), 8.52−8.47 (m, 4H, H_{ar}), 8.35−8.18 (m, 10H, H_{ar}), 8.09−8.08 (m, 10H, H_{ar}), 7.79 (s, 6H, H_{ar}), 7.72 (d, ^3J(H,H) = 8.4 Hz, 2H, H_{ar}), 7.25 (s, 4H, H_{ar}) , 5.97 (s, 2H, H_{CH2}), 2.58 (s, 6H, $H_{mesityl}$), 1.92(s, 12H, $H_{mesityl}$), 1.52 (s, 54H, H_{tBu}), -266 (s_{br}, 2H, NH) ppm. ^{13}C−NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 148.8, 143.0, 142.6, 141.4, 139.3, 137.8, 135.7, 135.3/135.1/135.0 (CH), 133.8, 131.4 (CH), 129.8 (CH), 128.2 (CH), 127.0 (CH), 126.3 (CH), 124.3 (CH), 121.7/121.5 (CH), 121.1 (CH), 120.3 (CH), 119.1, 115.2 (CH), 109.1, 77.4 (CH), 66.9, 35.2, 31.9 (CH_3), 29.8 (CH_2), 21.5 (CH_3), 21.2 (CH_3) ppm. MS (ESI): calc: 821.48 [M+2H^{2+}]; found: 821.49; calc: 547.99 [M+3H^{3+}]; found: 548.00.

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x10^4
+MS, 0.3-0.4min #(17-24)
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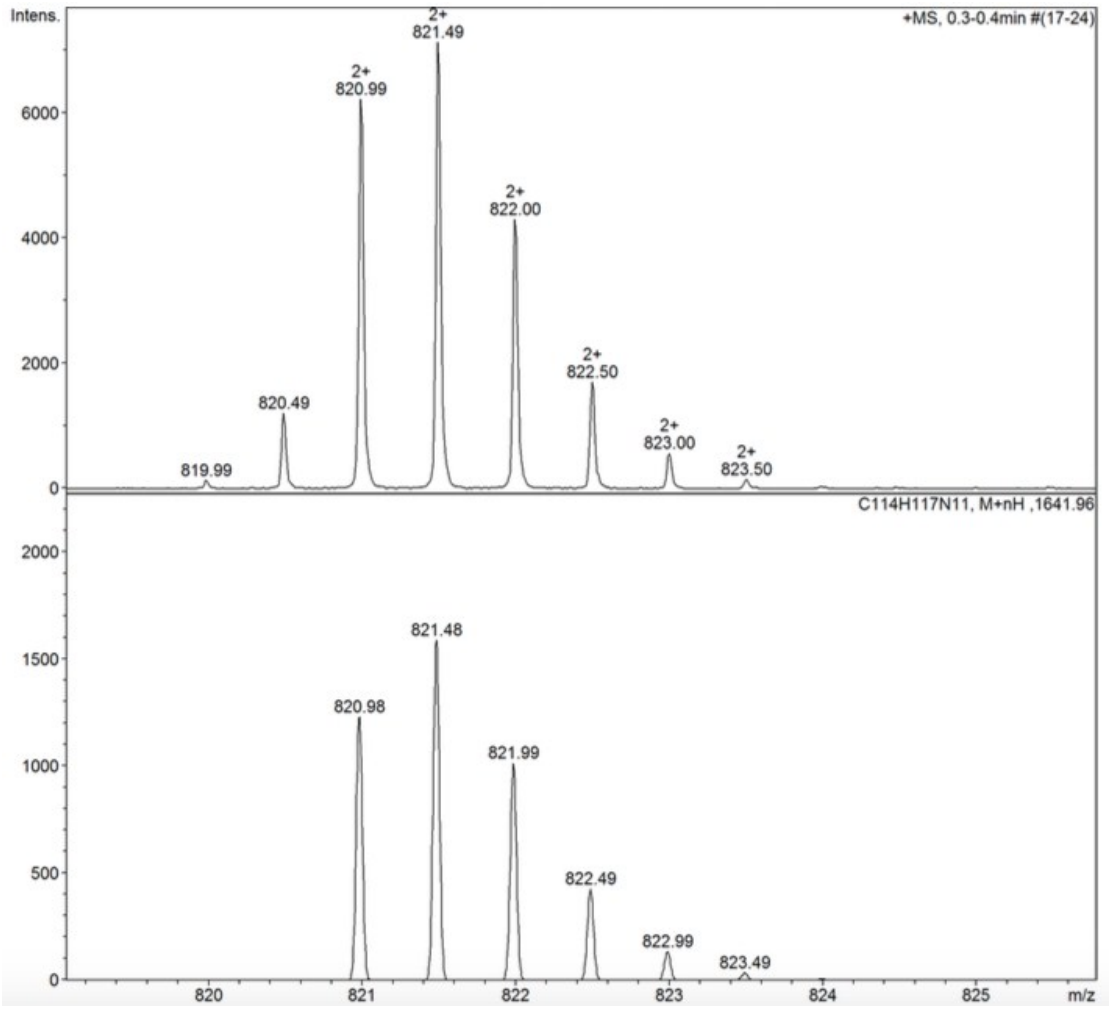
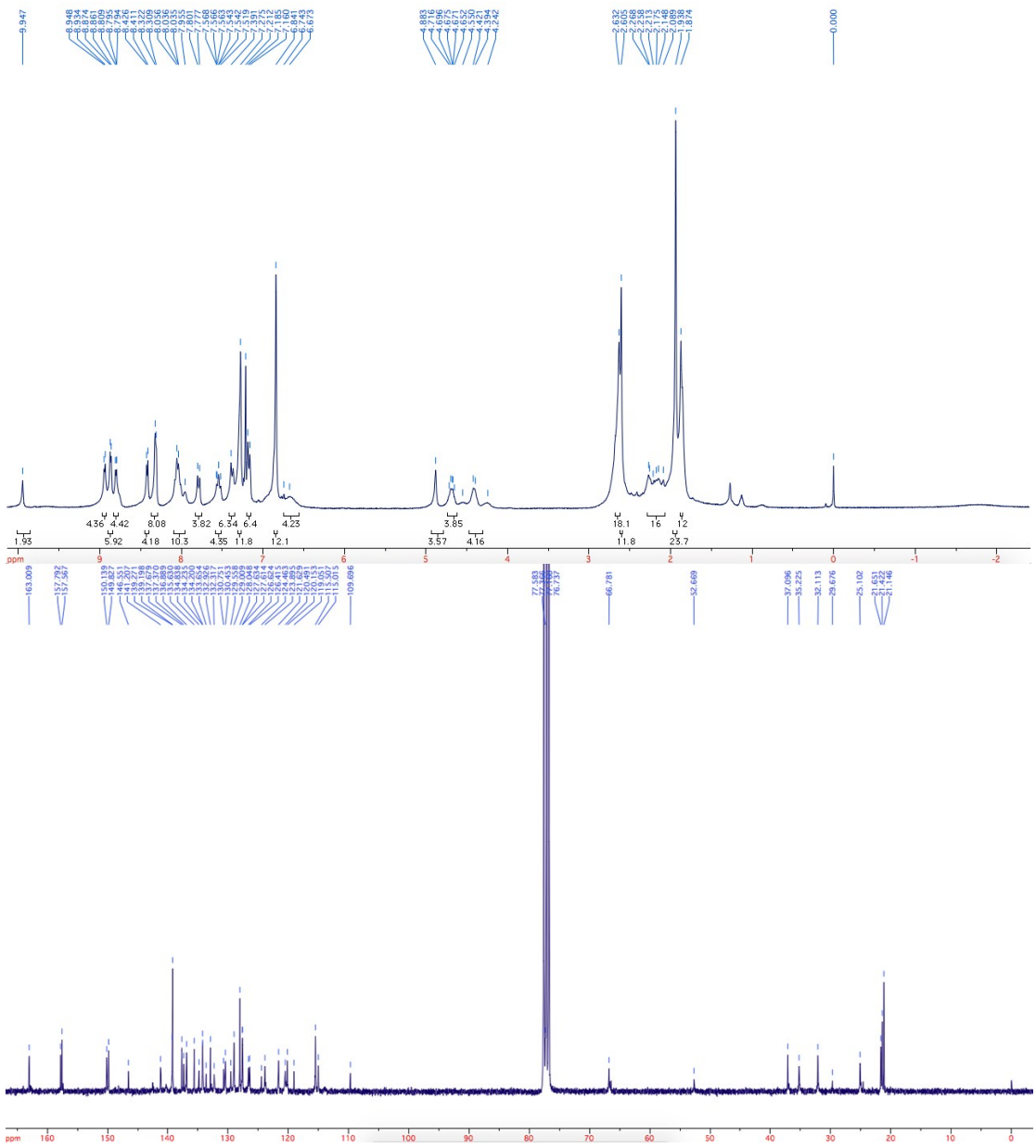
548.00
3+
547.67
3+
548.33
3+
548.67
547.33
3+
549.00
3+
549.34
C114H117N11, M+nH ,1642.97
547.99
547.66
548.33
548.66
548.99
549.33
m/z

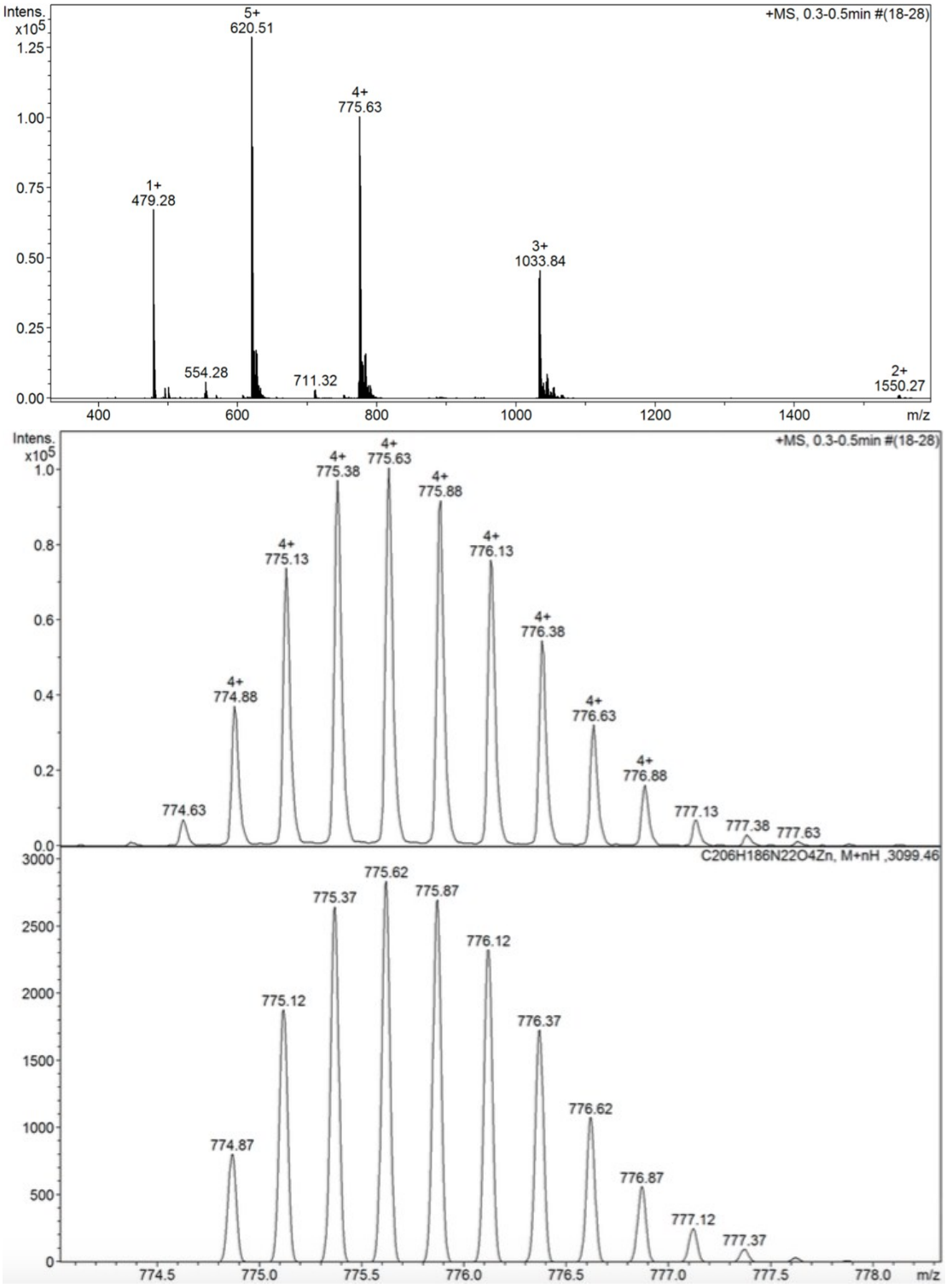

Intens.
+MS, 0.3-0.4min #(17-24)
2+
821.49
2+
820.99
2+
822.00
2+
822.50
2+
823.00
2+
823.50
820.49
819.99
6000
4000
2000
0
C114H117N11, M+nH ,1641.96
821.48
820.98
821.99
822.49
822.99
823.49
2000
1500
1000
500
0
820
821
822
823
824
825
m/z

Rotaxanated triad 8a

To a solution of porphyrin **2** (16 mg, 2.04 × 10^{-5} mol) and azidocorrole **1** (54 mg, 8.11 × 10^{-5} mol) in 10 mL dichloromethane was added the preprepared mixture of $[Cu(CH_3CN)_4]PF_6$ (15.2 mg, 4.07 × 10^{-5} mol) and macrocycle **5a** (29.2 mg, 6.10 × 10^{-5} mol) in 2 mL DCM. The solution was stirred at room temperature under N_2 atmosphere. A drop of diisopropylethylamine was added. The reaction was monitored using t.l.c. After completion, the solvent was evaporated under reduced pressure. Purification by size extrusion chromatography (Biobeads SX-1) eluting with chloroform afforded triad **8a** (47.4 mg, 76%) as a purple solid.

^{1}H−NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=9.95 (s, 2H, $H_{triazole}$), 8.94 (d, ^3J(H,H) = 4.2 Hz, 4H, H_β), 8.87 (d, ^3J(H,H) = 3.9 Hz, 6H, H_β), 8.81−8.79 (m, 4H, H_β), 8.42 (d, ^3J(H,H) = 4.5 Hz, 4H, H_β), 8.32 (d, ^3J(H,H) = 3.9 Hz, 8H, H_β), 8.06−7.96 (m, 10H, H_{ar}), 7.79 (d, ^3J(H,H) = 7.2 Hz, 4H, H_{ar}), 7.57−7.52 (m, 4H, H_{ar}), 7.38 (d, ^3J(H,H) = 7.5 Hz, 6H, H_{ar}), 7.28 (s, 12H, H_{ar}), 7.21−7.16 (m, 6H, H_{ar}), 6.84 (s, 12H, H_{ar}), 6.67 (s_{br}, 2H, H_{CH2}), 4.88 (s, 4H, $H_{macrocycle}$), 4.72−4.55 (m, 4H, $H_{macrocycle}$), 4.42−4.24 (m, 4H, $H_{macrocycle}$), 2.63−2.61 (m, 30H, $H_{mesityl}$+$H_{macrocycle}$), 2.27−2.09 (m, 16H, $H_{macrocycle}$), 1.94 (s, 24H, $H_{mesityl}$), 1.88 (s, 12H, $H_{mesityl}$) ppm. ^{13}C−NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 163.0, 157.8/157.6, 150.1, 149.8, 146.5, 141.2, 139.3/139.2, 137.7, 137.4, 136.9 (CH), 135.6, 134.8, 134.2 (CH), 133.7, 132.9, 132.3 (CH), 130.8, 130.5 (CH), 129.6, 129.0 (CH), 128.4 (CH), 127.6 (CH), 126.6/126.5 (CH), 124.5 (CH), 123.9 (CH), 121.6 (CH), 120.5 (CH), 120.2 (CH), 119.1, 115.5 (CH), 115.0 (CH), 109.7, 77.4 (CH), 66.8 (CH_2), 52.7 (CH_2), 37.1 (CH_2), 35.2 (CH_2), 32.1 (CH_2), 29.7, 25.1 (CH_2), 21.6 (CH_3), 21.4 (CH_3), 21.1 (CH_3) ppm. MS (ESI): calc: 1033.82 [M+3H^{3+}]; found: 1033.84; calc: 775.62 [M+4H^{4+}]; found: 775.63.

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x10^5
+MS, 0.3-0.5min #(18-28)
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620.51
4+
775.63
1+
479.28
3+
1033.84
554.28
711.32
2+
1550.27
m/z
4+
775.38
4+
775.88
4+
775.13
4+
776.13
4+
776.38
4+
774.88
4+
776.63
4+
776.88
774.63
777.13
777.38
777.63
C206H186N22O4Zn, M+nH ,3099.46
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775.87
776.12
775.12
776.37
776.62
774.87
776.87
777.12
777.37

Generic Display Report

Analysis Info		Acquisition Date	10/22/2015 2:44:37 PM
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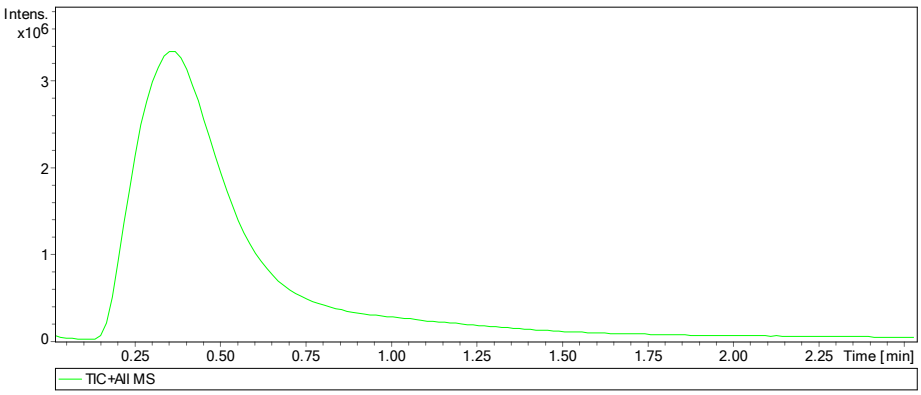
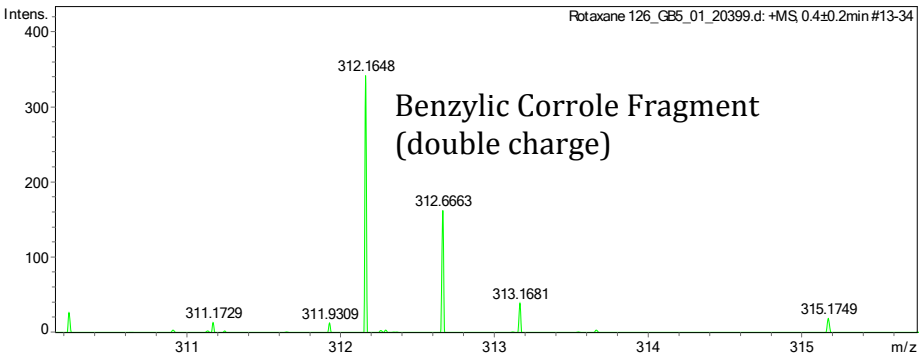
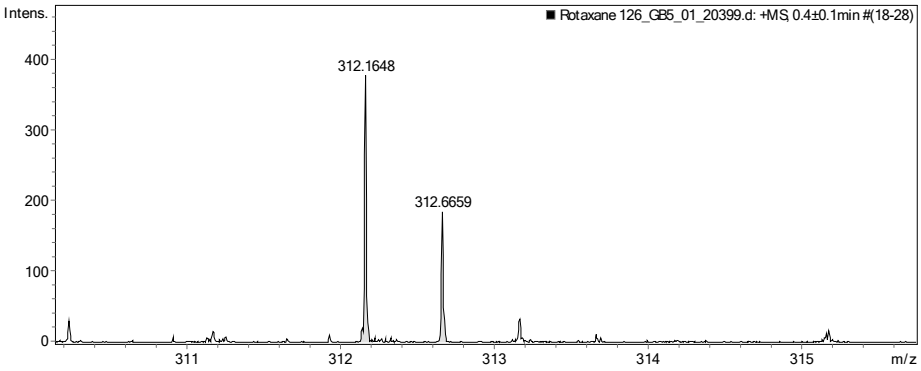
Method	soton fia high ms.m	Operator	MSWEB@SOTON.AC.UK
Sample Name	Rotaxane 126	Instrument	maXis
Comment			



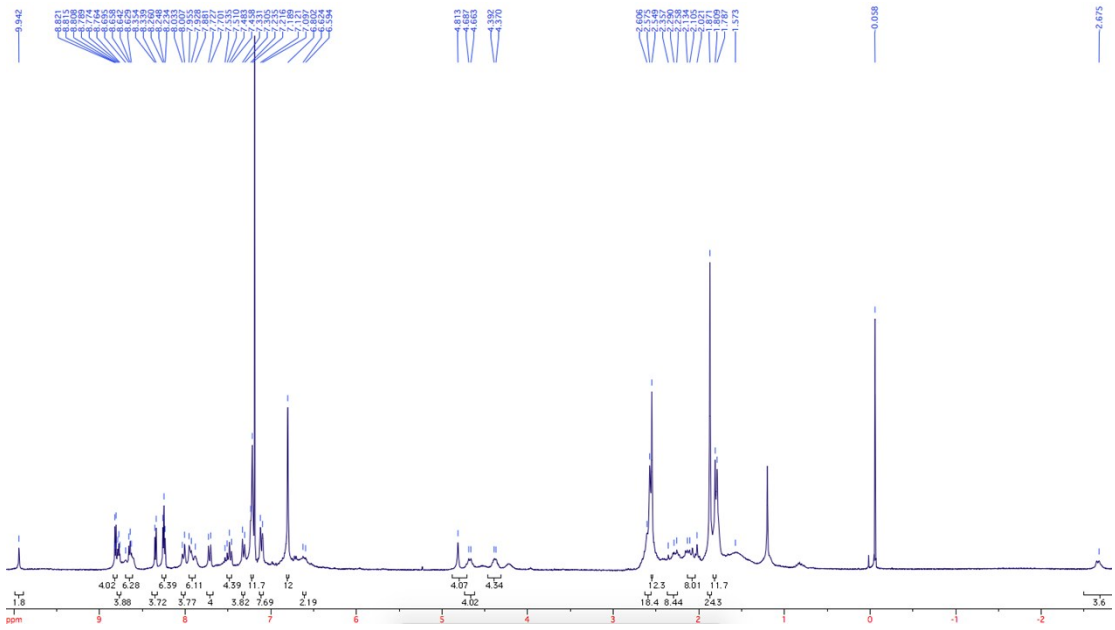


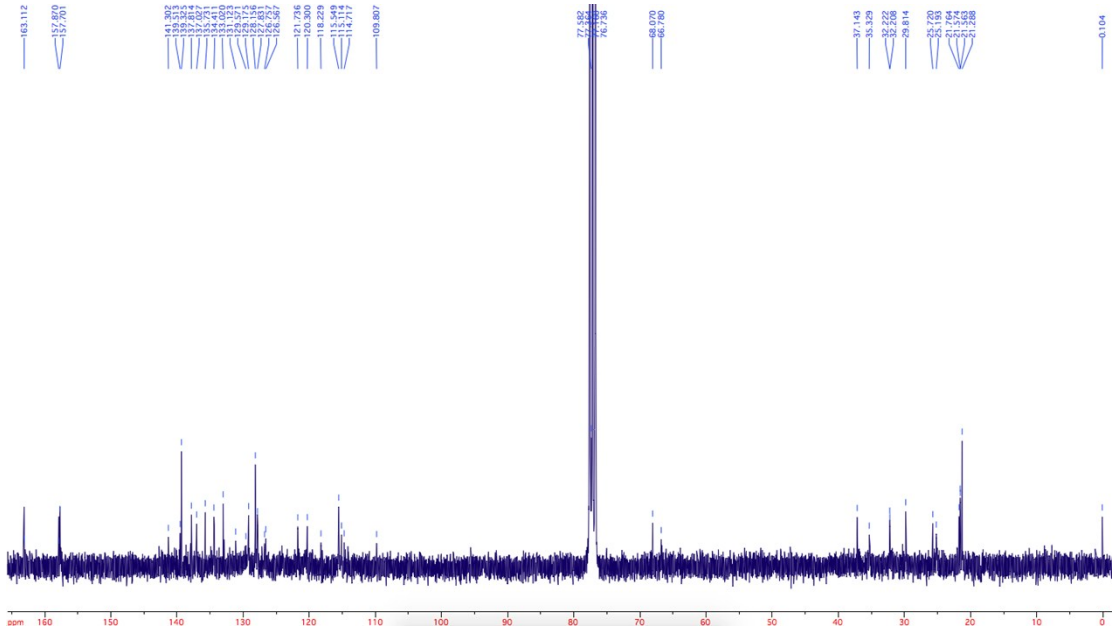


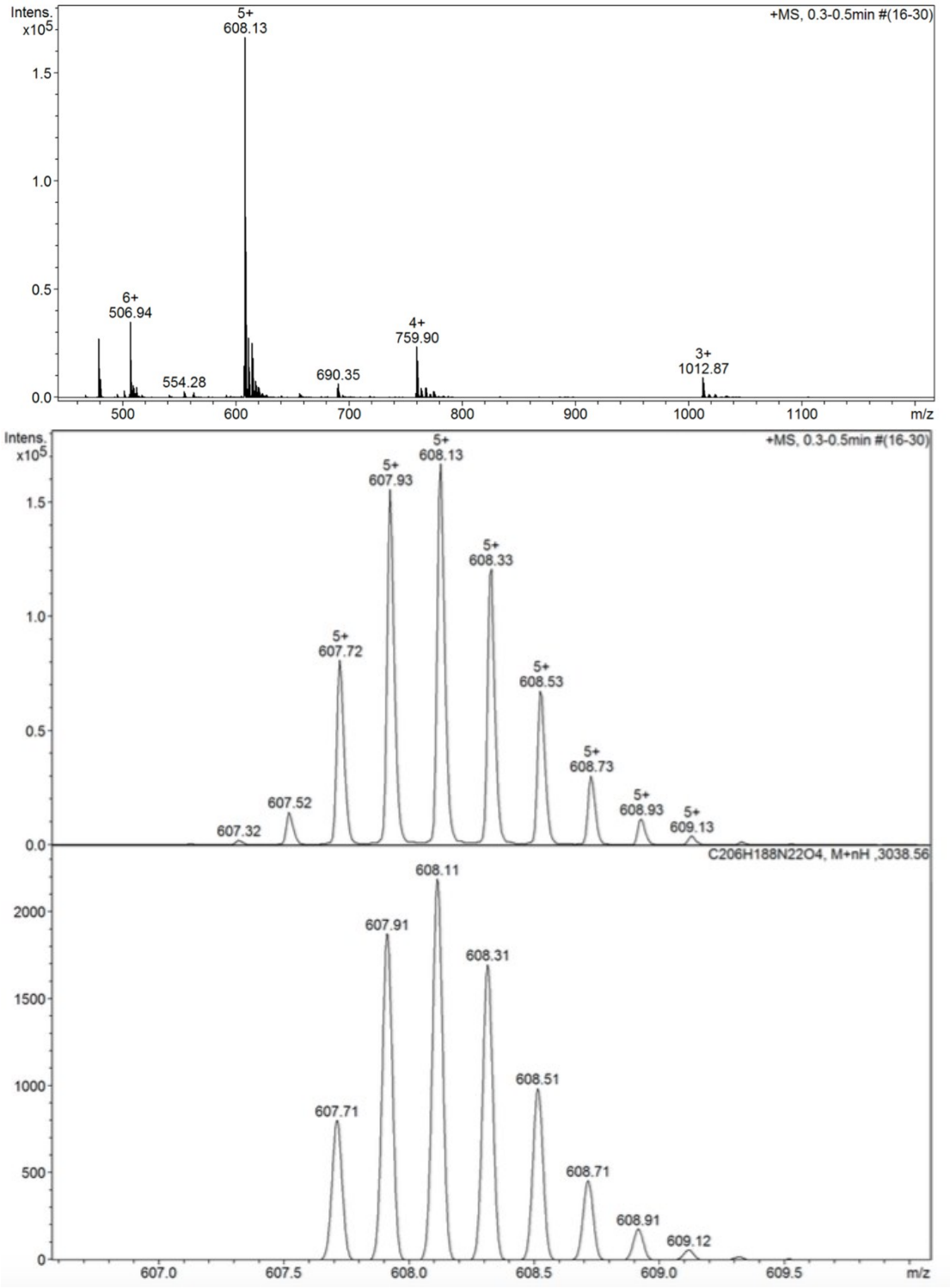
Rotaxanated triad 8b

To the solution of triad **8a** (20 mg, 6.51×10^{-6} mol) in 10 mL DCM was added HBr•PPh_3 (20 mg, 5.83×10^{-5} mol). The mixture was stirred for 10 min and washed with water and brine. Purification by size extrusion chromatography (Biobeads SX-1) eluting with chloroform afforded free base triad **8b** (18.5mg, 94%) as a purple solid.

^{1}H−NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=9.94 (s, 2H, $H_{triazole}$), 8.82−8.63 (m, 14H, H_β), 8.35 (d, ^3J(H,H) = 4.5 Hz, 4H, H_β), 8.26−8.23 (m, 6H, H_β), 8.02 (d, ^3J(H,H) = 7.5 Hz, 4H, H_{ar}), 7.96−7.88 (m, 6H, H_{ar}+H_β), 7.71 (d, ^3J(H,H) = 7.8 Hz, 4H, H_{ar}), 7.54−7.46 (m, 4H, H_{ar}), 7.32 (d, ^3J(H,H) = 7.8 Hz, 4H, H_{ar}), 7.24−7.22 (m, 12H, H_{ar}), 7.16 (d, ^3J(H,H) = 7.2 Hz, 8H, H_{ar}), 6.80 (s_{br}, 12H, H_{CH2}), 6.61 (s_{br}, 2H, H_{CH2}), 4.81 (s, 4H, $H_{macrocycle}$), 4.67−4.58 (m, 4H, $H_{macrocycle}$), 4.39−4.28 (m, 4H, $H_{macrocycle}$), 2.61−2.55 (m, 30H, $H_{mesityl}$+$H_{macrocycle}$), 2.36−2.02 (m, 16H, $H_{macrocycle}$), 1.87 (s, 24H, $H_{mesityl}$), 1.81 (s, 12H, $H_{mesityl}$), -2.68 (s_{br}, 2H, H_{NH}) ppm. ^{13}C−NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 163.1, 157.9/157.7, 141.3, 139.5/139.3, 137.8, 137.0 (CH), 135.7, 134.4 (CH), 133.0, 131.1, 132.3, 129.6, 129.2 (CH), 128.2 (CH), 127.8 (CH), 126.7/126.6 (CH), 124.2 (CH), 121.7 (CH), 120.3 (CH), 118.2, 115.5 (CH), 115.1 (CH), 114.7, 109.8, 77.4 (CH), 68.1, 66.8 (CH_2), 37.1 (CH_2), 35.3 (CH_2), 32.2 (CH_2), 29.8, 25.7 (CH_2), 25.2, 21.8 (CH_3), 21.6 (CH_3), 21.3 (CH_3) ppm. MS (ESI): calc: 608.11 [M+5H^{5+}]; found: 608.13.






Intens.
x10^5
+MS, 0.3-0.5min #(16-30)
5+
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6+
506.94
554.28
690.35
4+
759.90
3+
1012.87
m/z
5+
607.93
5+
608.33
5+
607.72
5+
608.53
5+
608.73
607.52
607.32
5+
608.93
5+
609.13
C206H188N22O4, M+nH ,3038.56
608.11
607.91
608.31
608.51
607.71
608.71
608.91
609.12

Generic Display Report

Analysis Info		Acquisition Date	10/22/2015 2:48:32 PM
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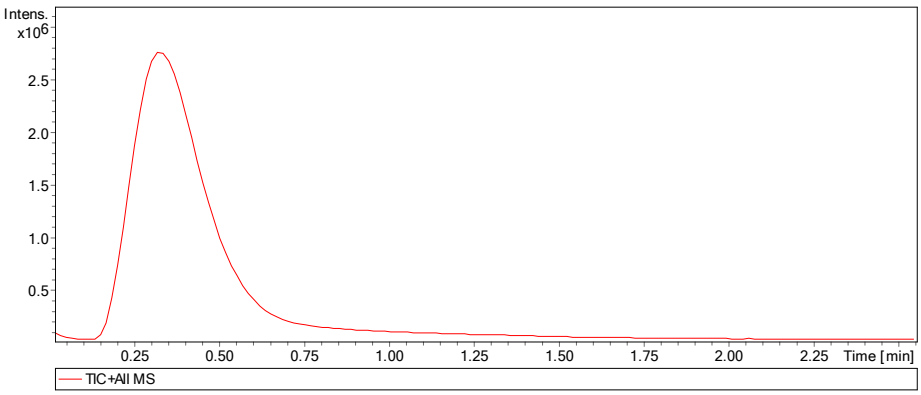
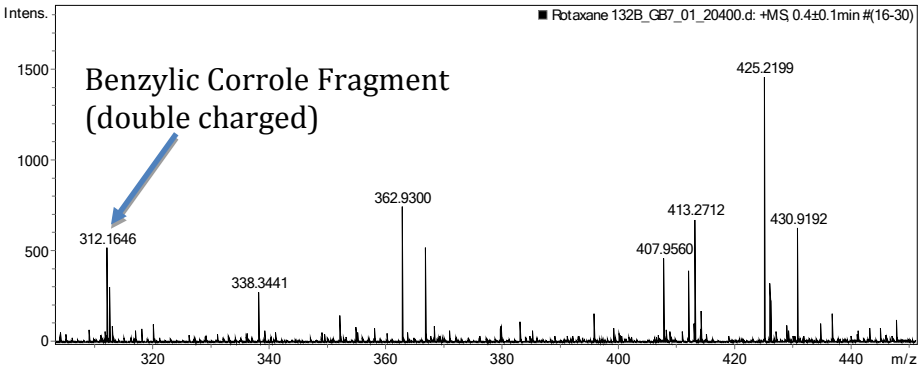
Method	soton fia high ms.m	Operator	MSWEB@SOTON.AC.UK
Sample Name	Rotaxane 132B	Instrument	maXis
Comment			

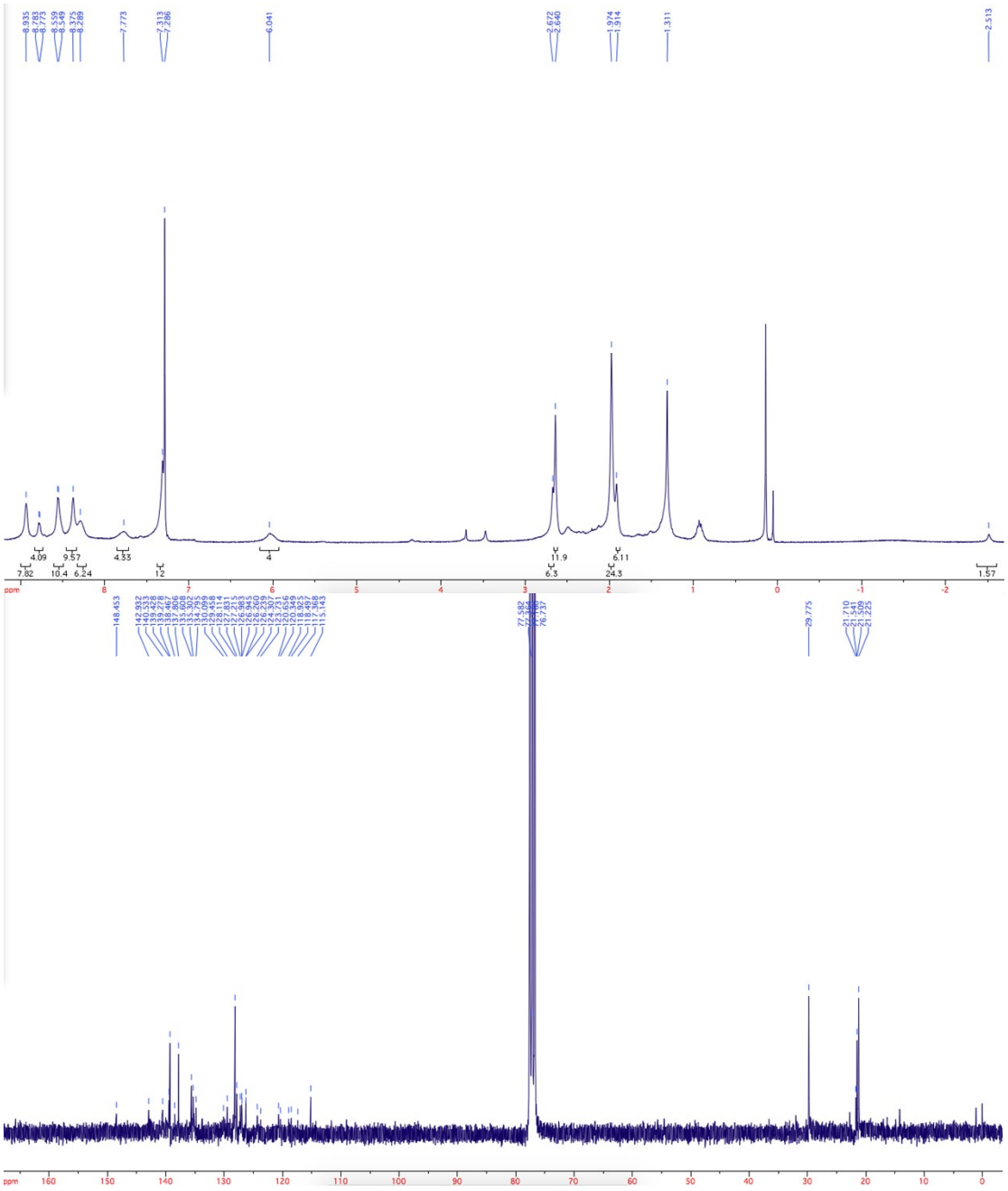


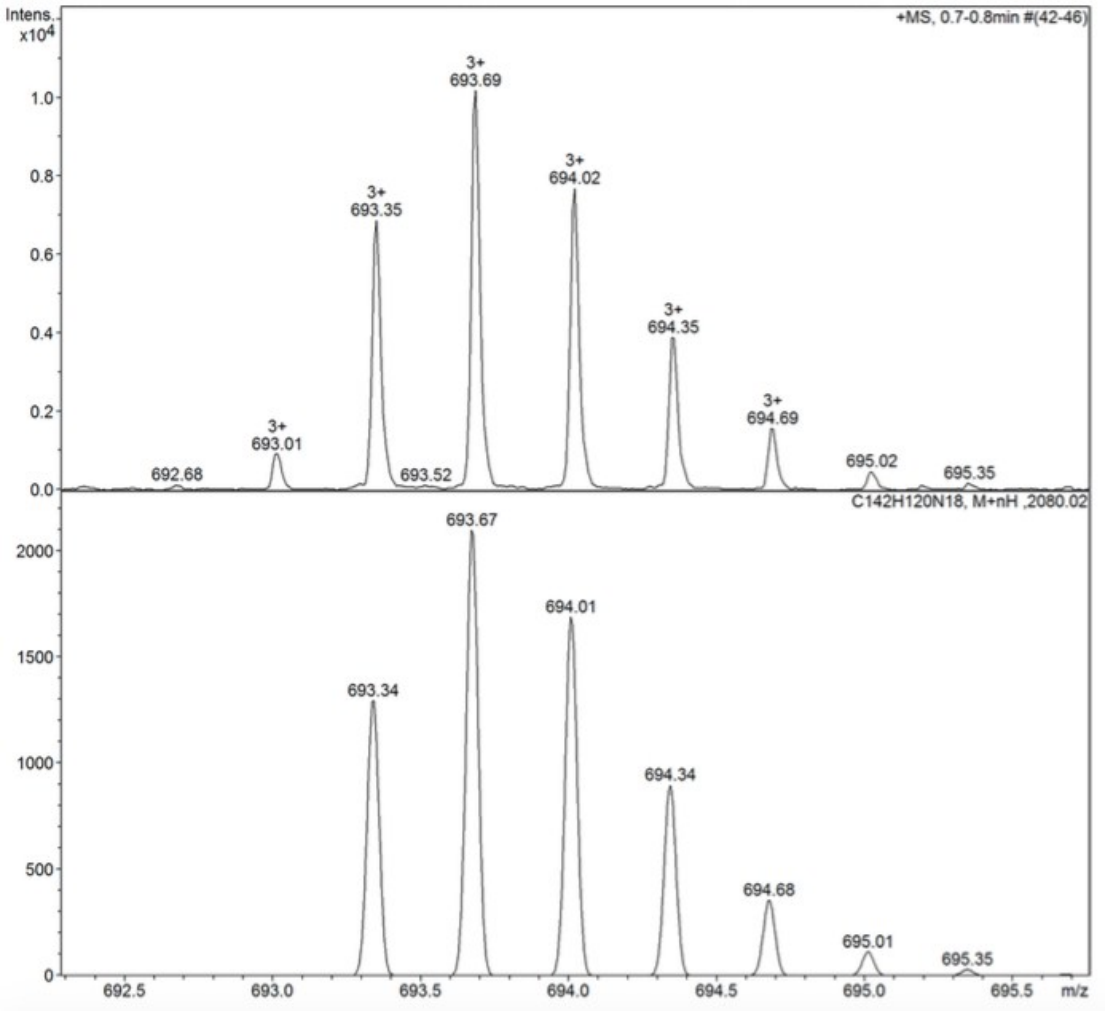


Free base triad 9

To a solution of porphyrin **2** (6 mg, 7.4 × 10^{-6} mol) and azidocorrole **1** (20 mg, 2.96 × 10^{-5} mol) in 10 mL dichloromethane was added the preprepared mixture of $[Cu(CH_3CN)_4]PF_6$ (5.5 mg, 1.48 × 10^{-5} mol) and macrocycle **5b** (14 mg, 2.96 × 10^{-5} mol) in 2 mL DCM. The solution was stirred at room temperature under N_2 atmosphere. A drop of diisopropylethylamine was added. The reaction was monitored using t.l.c. After completion, the solvent was evaporated under reduced pressure affording rotaxanated diad with ether moiety containing macrocycle as a purple solid. The obtained product was not further purified but subjected to following step.
The unpurified compound was dissolved in 10 mL DCM followed by the addition of $HBr{\bullet}PPh_3$ (20 mg, 5.83 × 10^{-5} mol). The mixture was stirred for 10 min and washed with water and brine. Purification by size extrusion chromatography (Biobeads SX-1) eluting with chloroform afforded triad **9** (8.8 mg, 57%) as a purple solid.

^{1}H−NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 9.94 (s_{br}, 8H, H_β), 8.78 (d, ^3J(H,H) = 3.0 Hz, 4H, H_β), 8.55 (d, ^3J(H,H) = 3.0 Hz, 10H, H_β), 8.38 (s, 10H, H_{ar}+H_β), 8.29 (s_{br}, 6H, H_{ar}), 7.77 (s_{br}, 6H, H_{ar}), 7.31 (s, 12H, H_{ar}), 6.04 (s_{br}, 4H, H_{CH2}), 2.67 (s, 6H, $H_{mesityl}$), 2.64 (s, 12H, $H_{mesityl}$), 1.97 (s, 24H, $H_{mesityl}$), 1.91 (s, 12H, $H_{mesityl}$), -2.51 (s_{br}, 2H, H_{NH}) ppm. ^{13}C−NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 148.5, 142.9, 140.5, 139.4/139.3, 138.5, 137.8 (CH), 135.6, 135.3, 134.8 (CH), 130.1, 129.5, 128.1, 127.8 (CH), 127.2 (CH), 127.0/126.9 (CH), 126.2 (CH), 124.3 (CH), 123.7, 120.7, 120.3 (CH), 118.9, 118.5, 117.4, 115.1 (CH), 77.4 (CH), 29.8 (CH_2), 21.7 (CH_3), 21.5 (CH_3), 21.2 (CH_3) ppm. MS (ESI): calc: 693.67 [M+3H^{3+}]; found: 693.69.




Intens.
x10^4
+MS, 0.7-0.8min #(42-46)
3+
693.69
3+
694.02
3+
693.35
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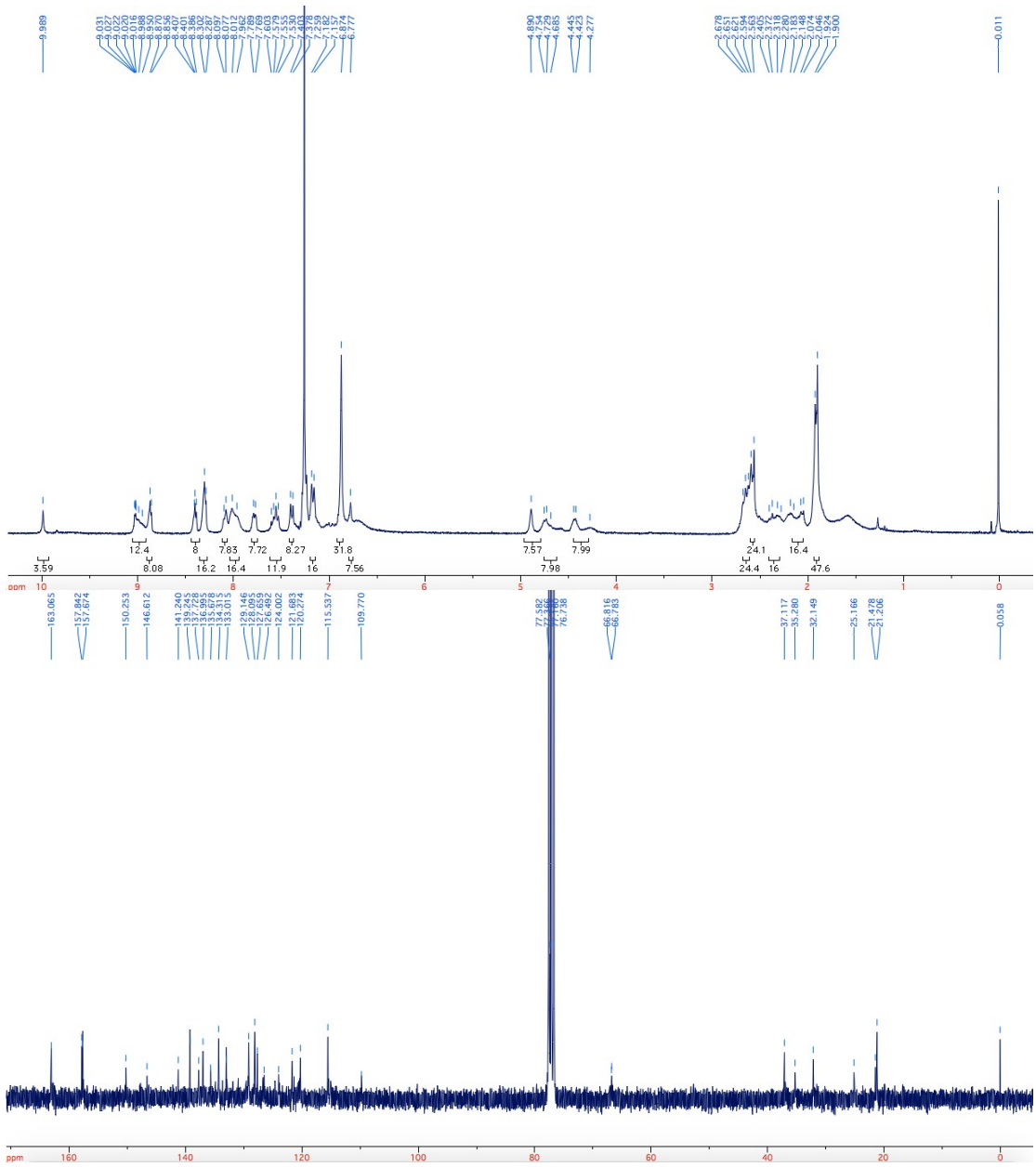
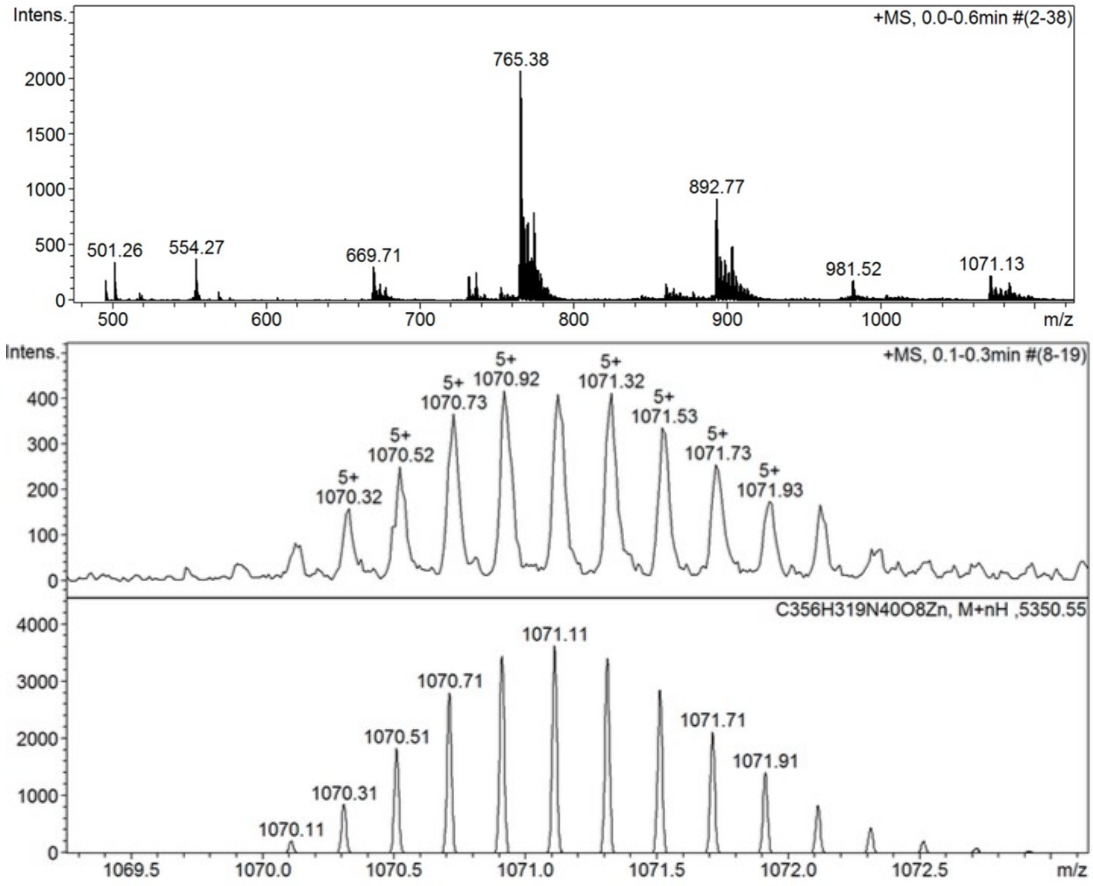
694.35
3+
694.69
3+
693.01
692.68
693.52
695.02
695.35
C142H120N18, M+nH ,2080.02
693.67
694.01
693.34
694.34
694.68
695.01
695.35
m/z

Rotaxanated pentad 10a

To a solution of zinc tetra-*meso*(4-ethynyl-phenyl)porphyrin (8.5 mg, 1.10×10^{-5} mol) and azidocorrole **1** (58.5 mg, 8.79×10^{-5} mol) in 10 mL dichloromethane was added the preprepared mixture of $[Cu(CH_3CN)_4]PF_6$ (16.3 mg, 4.37×10^{-5} mol) and macrocycle **5a** (31.5 mg, 6.58×10^{-5} mol) in 2 mL DCM. The solution was stirred at room temperature under N_2 atmosphere. A drop of diisopropylethylamine was added. The reaction was monitored using t.l.c. After completion, the solvent was evaporated under reduced pressure. Purification by size extrusion chromatography (Biobeads SX-1) eluting with chloroform afforded pentad **10a** (42 mg, 71%) as a purple solid.
^{1}H−NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 9.99 (s, 4H, $H_{triazole}$), 9.03−9.92 (m, 12H, H_β), 8.87 (d, ^3J(H,H) = 4.2 Hz, 8H, H_β), 8.41−8.39 (m, 8H, H_β), 8.30−8.29 (m, 16H, H_β+H_{ar}), 8.01−7.96 (m, 24H, H_{ar}), 7.79−7.77 (m, 8H, H_{ar}), 7.60−7.53 (m, 8H, H_{ar}), 7.39 (d, ^3J(H,H) = 7.5 Hz, 8H, H_{ar}), 7.17 (d, ^3J(H,H) = 7.5 Hz, 16H, H_{ar}), 6.87 (s, 32H, H_{ar}), 6.78 (s, 8H, H_{CH2}), 4.89 (s, 8H, $H_{macrocycle}$), 4.75−4.69 (m, 8H, $H_{macrocycle}$), 4.45−4.28 (m, 4H, $H_{macrocycle}$), 2.68−2.56 (m, 48H, $H_{mesityl}$+$H_{macrocycle}$), 2.40−2.28 (m, 16H, $H_{macrocycle}$), 2.18−2.05 (m, 16H, $H_{macrocycle}$), 1.92 (s, 48H, $H_{mesityl}$) ppm. ^{13}C−NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 163.1, 157.8/157.7, 150.3, 146.6, 141.2, 139.2, 137.7, 137.0 (CH), 135.7, 134.3 (CH), 133.0 (CH), 129.1 (CH), 128.1 (CH), 127.7 (CH), 126.5 (CH), 124.0 (CH), 121.7 (CH), 120.3 (CH), 115.5 (CH), 109.8, 77.4 (CH), 66.8 (CH_2), 37.1 (CH_2), 35.3 (CH_2), 32.1 (CH_2), 25.2 (CH_2), 21.5 (CH_3), 21.2 (CH_3) ppm. MS (ESI): calc: 1071.11 [M+5H^{5+}]; found: 1071.13.

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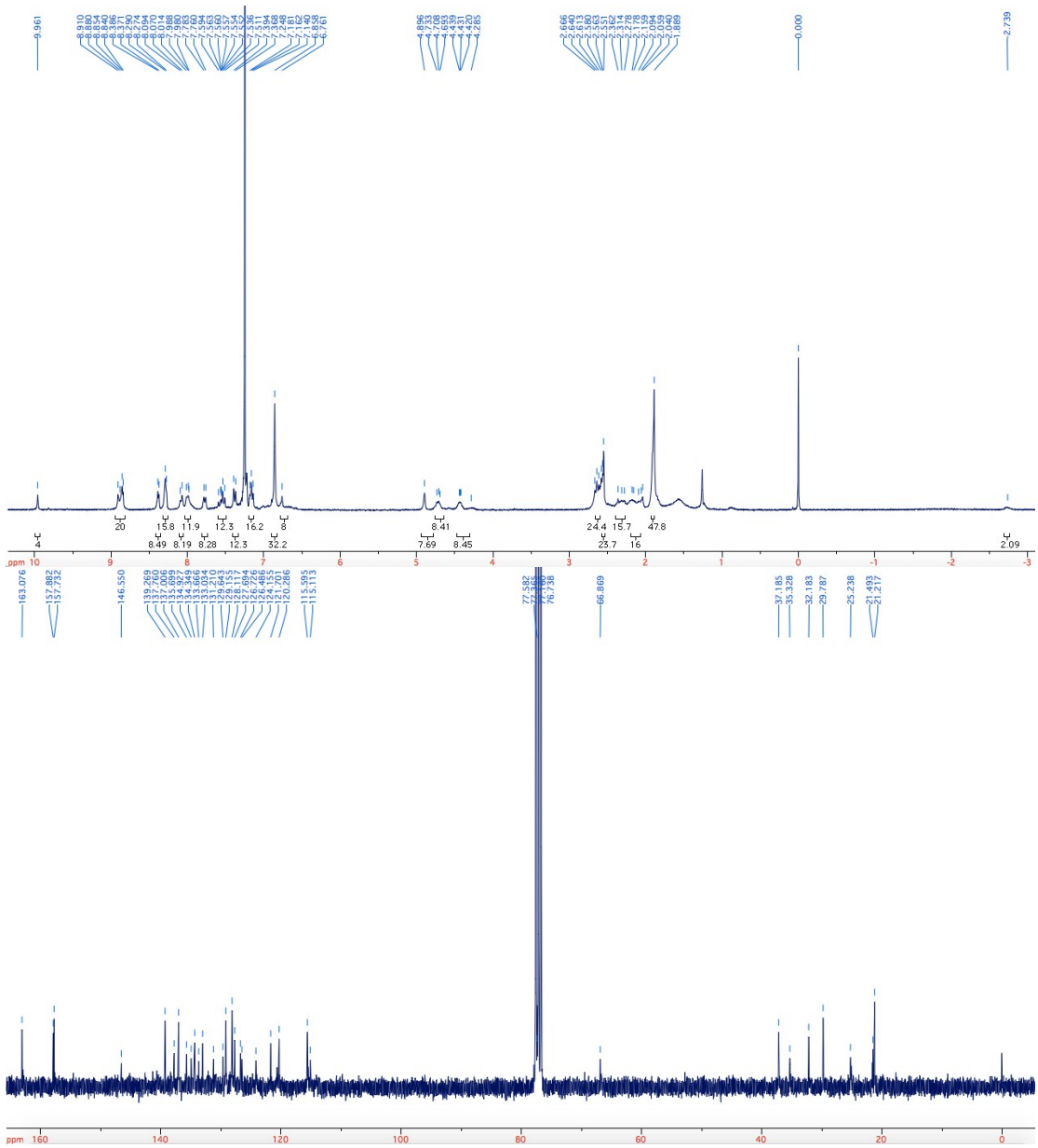
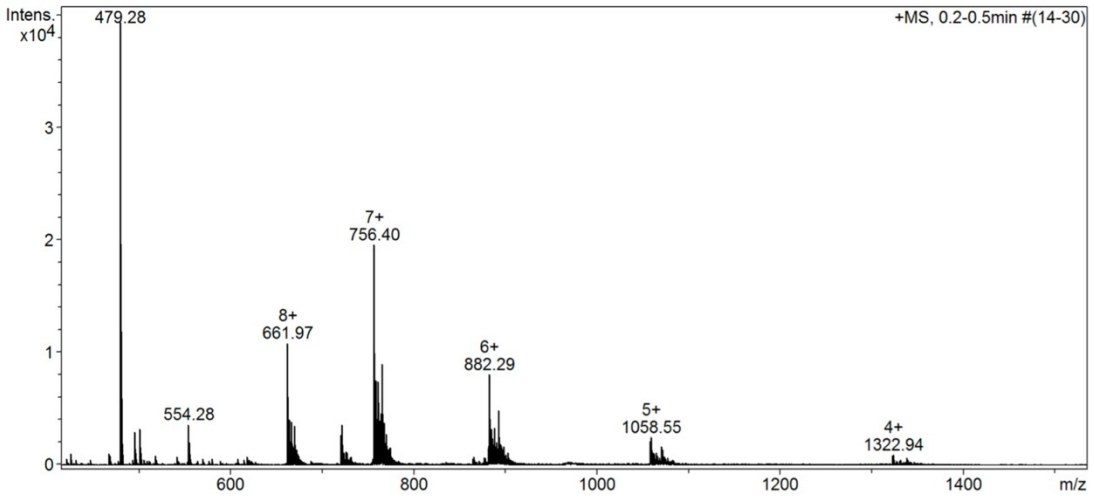
554.27
669.71
981.52
1071.13
m/z
Intens.
+MS, 0.1-0.3min #(8-19)
5+ 1070.32
5+ 1070.52
5+ 1070.73
5+ 1070.92
5+ 1071.32
5+ 1071.53
5+ 1071.73
5+ 1071.93
C356H319N40O8Zn, M+nH ,5350.55
1071.11
1070.71
1070.51
1071.71
1071.91
1070.31
1070.11
m/z

Rotaxanated pentad 10b

To the solution of pentad **10a** (18 mg, 3.36×10^{-6} mol) in 10 mL DCM was added HBr•PPh_3 (20 mg, 5.83×10^{-5} mol). The mixture was stirred for 10 min and washed with water and brine. Purification by size extrusion chromatography (Biobeads SX-1) eluting with chloroform afforded pentad **10b** (15.3 mg, 86%) as a purple solid.
^{1}H−NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 9.97 (s, 4H, $H_{triazole}$), 8.91−8.88 (m, 20H, H_β), 8.38 (d, ^3J(H,H) = 4.5 Hz, 8H, H_β), 8.28 (d, ^3J(H,H) = 4.8 Hz, 16H, H_{ar}+H_β), 8.08 (d, ^3J(H,H) = 7.2 Hz, 8H, H_{ar}), 8.01−7.99 (m, 12H, H_{ar}), 7.77 (d, ^3J(H,H) = 6.9 Hz, 8H, H_{ar}), 7.59−7.51 (m, 12H, H_{ar}), 7.38 (d, ^3J(H,H) = 7.8 Hz, 8H, H_{ar}), 7.18−7.14 (m, 16H, H_{ar}), 6.86 (s, 32H, H_{ar}), 6.76 (s, 8H, H_{CH2}), 4.90 (s, 8H, $H_{macrocycle}$), 4.73−4.69 (m, 8H, $H_{macrocycle}$), 4.44−4.29 (m, 4H, $H_{macrocycle}$), 2.67−2.55 (m, 48H, $H_{mesityl}$+$H_{macrocycle}$), 2.36−2.28 (m, 16H, $H_{macrocycle}$), 2.18−2.04 (m, 16H, $H_{macrocycle}$), 1.89 (s, 48H, $H_{mesityl}$), -2.74 (s_{br}, 2H, H_{NH}) ppm.
^{13}C−NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 163.1, 157.9/157.7, 146.6, 139.3, 137.8, 137.0 (CH), 135.7, 134.9, 134.3 (CH), 133.7, 133.0 (CH), 131.2, 129.6, 129.1 (CH), 128.1 (CH), 127.7 (CH), 126.5 (CH), 124.2 (CH), 121.7 (CH), 120.3 (CH), 115.6 (CH), 115.1, 77.4 (CH), 66.9 (CH_2), 37.2 (CH_2), 35.3 (CH_2), 32.2 (CH_2), 29.8, 25.2 (CH_2), 21.5 (CH_3), 21.2 (CH_3) ppm. MS (ESI): calc: 756.52 [M+7H^{7+}]; found: 756.40.

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5+
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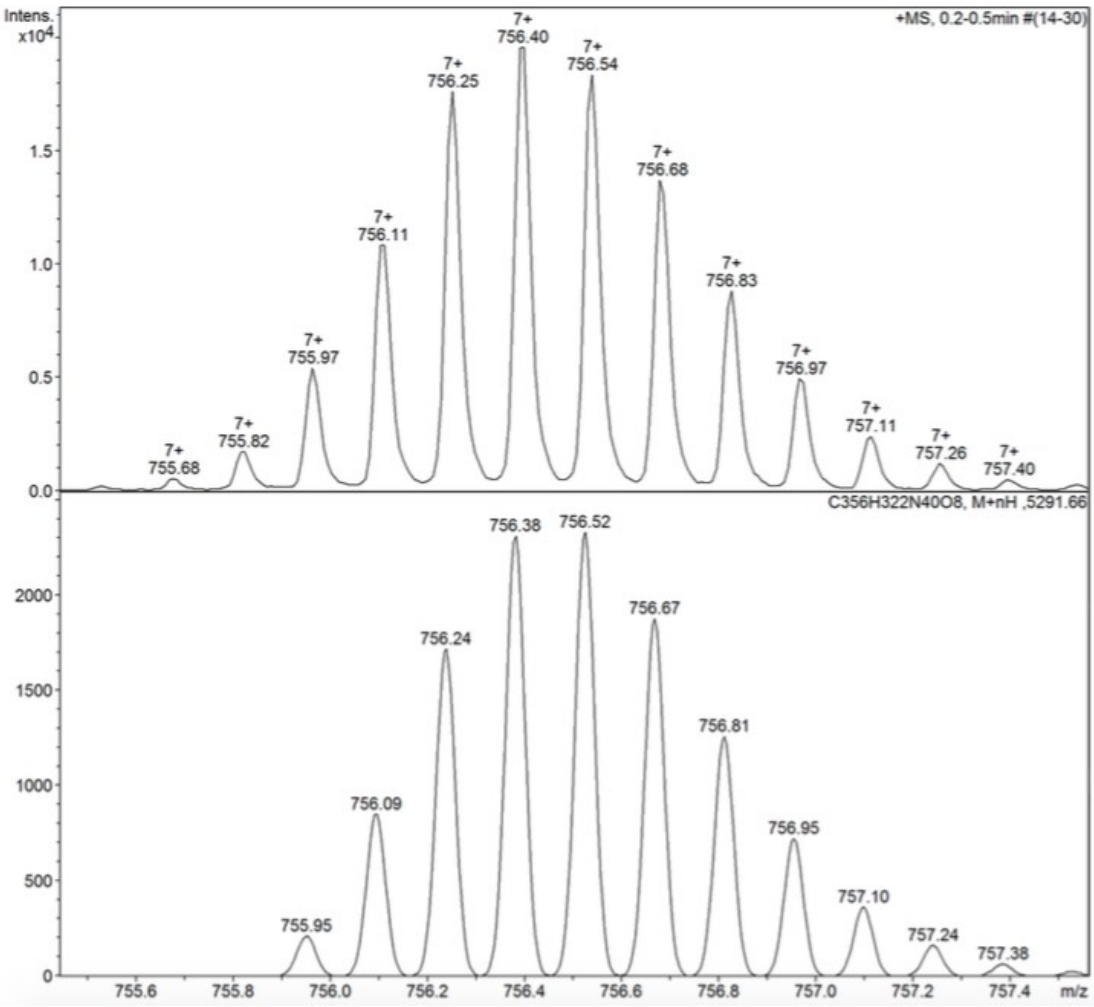
4+
1322.94
m/z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+MS, 0.2-0.5min #(14-30)
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7+ 756.25
7+ 756.40
7+ 756.54
7+ 756.68
7+ 756.83
7+ 756.97
7+ 757.11
7+ 757.26
7+ 757.40
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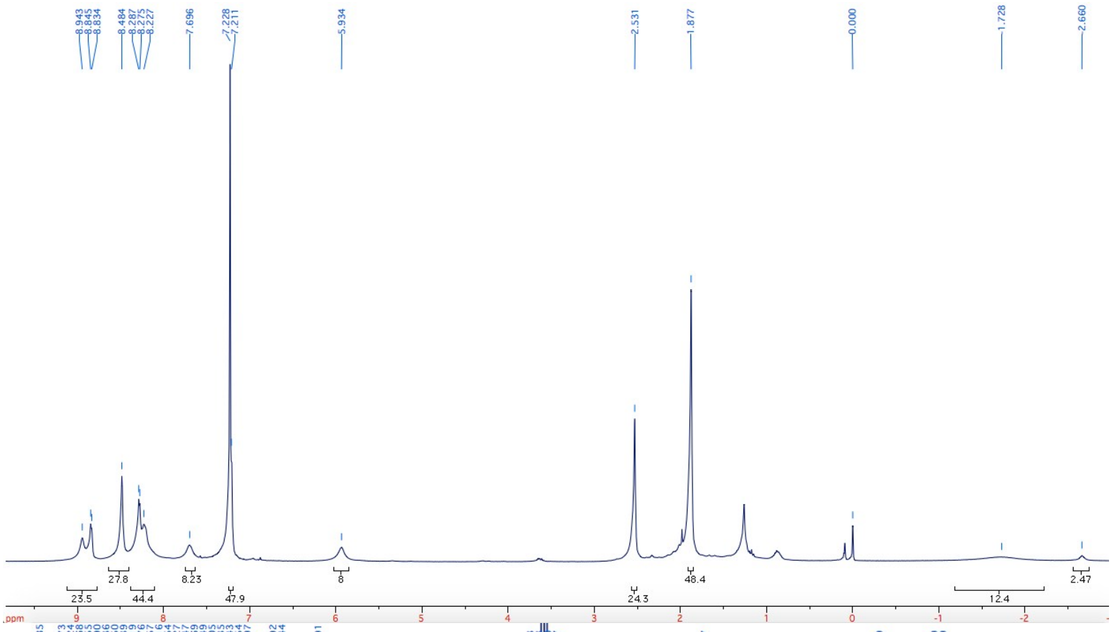
755.95
756.09
756.24
756.38
756.52
756.67
756.81
756.95
757.10
757.24
757.38
m/z

Free base pentad 11

To a solution of zinc tetra-*meso*(4-ethynyl-phenyl)porphyrin (5 mg, 6.46×10^{-6} mol) and azidocorrole **1** (34.4 mg, 5.17×10^{-5} mol) in 10 mL dichloromethane was added the preprepared mixture of $[Cu(CH_3CN)_4]PF_6$ (10.6 mg, 2.84×10^{-5} mol) and macrocycle **5b** (24 mg, 5.17×10^{-5} mol) in 2 mL DCM. The solution was stirred at room temperature under N_2 atmosphere. A drop of diisopropylethylamine was added. The reaction was monitored using t.l.c. After completion, the solvent was evaporated under reduced pressure affording rotaxanated pentad with ether moiety containing macrocycle as a purple solid. The obtained product was not further purified but subjected to following step.
The unpurified compound was dissolved in 10 mL DCM followed by the addition of $HBr{\bullet}PPh_3$ (20 mg, 5.83×10^{-5} mol). The mixture was stirred for 10 min and washed with water and brine. Purification by size extrusion chromatography (Biobeads SX-1) eluting with chloroform afforded pentad **11** (10.8 mg, 54%) as a purple solid.

^{1}H−NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 8.94−8.83(m, 24H, H_β), 8.48 (s, 28H, H_{ar}), 8.29−8.23 (m, 44H, H_{ar}+H_β), 7.70 (s_{br}, 8H, H_{ar}), 7.21 (s, 48H, H_{ar}), 5.93 (s_{br}, 8H, H_{CH2}), 2.53 (s, 24H, $H_{mesityl}$), 1.87 (s, 48H, $H_{mesityl}$), -1.73 (s_{br}, 12H, H_{NHcor}), -2.66 (s_{br}, 2H, H_{NH}) ppm.
^{13}C−NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 148.4, 143.0, 142.7, 140.6, 139.3, 137.8, 135.7(CH), 135.3/135.2(CH), 134.9, 133.8, 131.5, 130.3, 129.5, 128.1(CH), 127.3 (CH), 126.9 (CH), 126.3 (CH), 124.3 (CH), 120.7(CH), 120.4 (CH), 120.0, 115.2 (CH), 114.3, 109.1, 77.4 (CH), 54.5, 29.8 (CH_2), 21.5 (CH_3), 21.3 (CH_3) ppm. MS (ESI): calc: 675.72 [M+5H^{5+}]; found: 675.73.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1.877
0.000
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8
24.3
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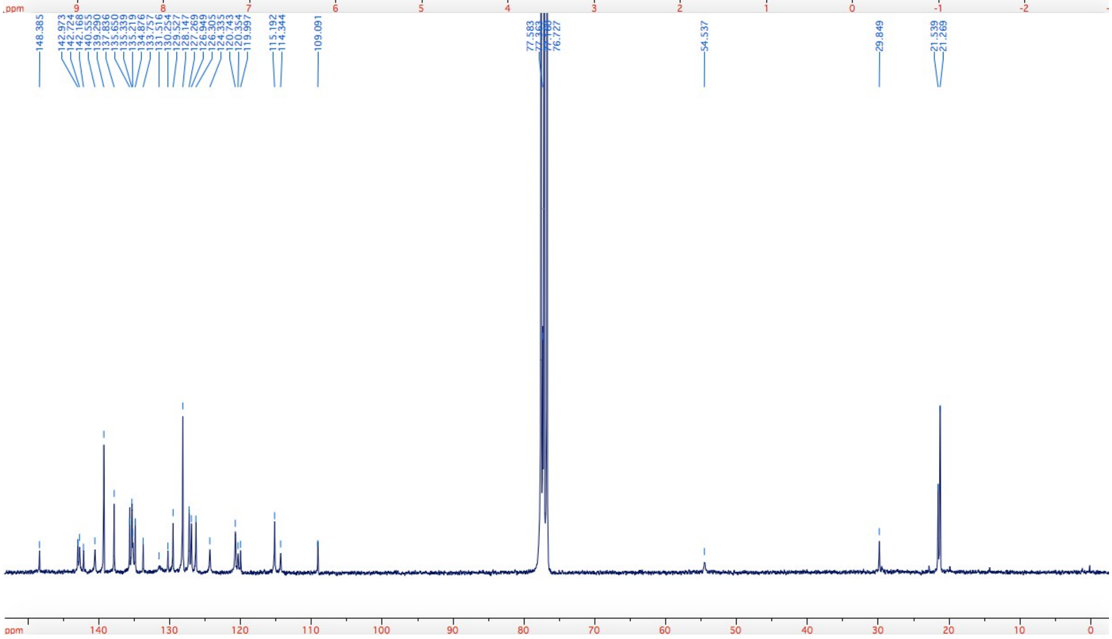
12.4
2.47
ppm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127.269
126.949
126.305
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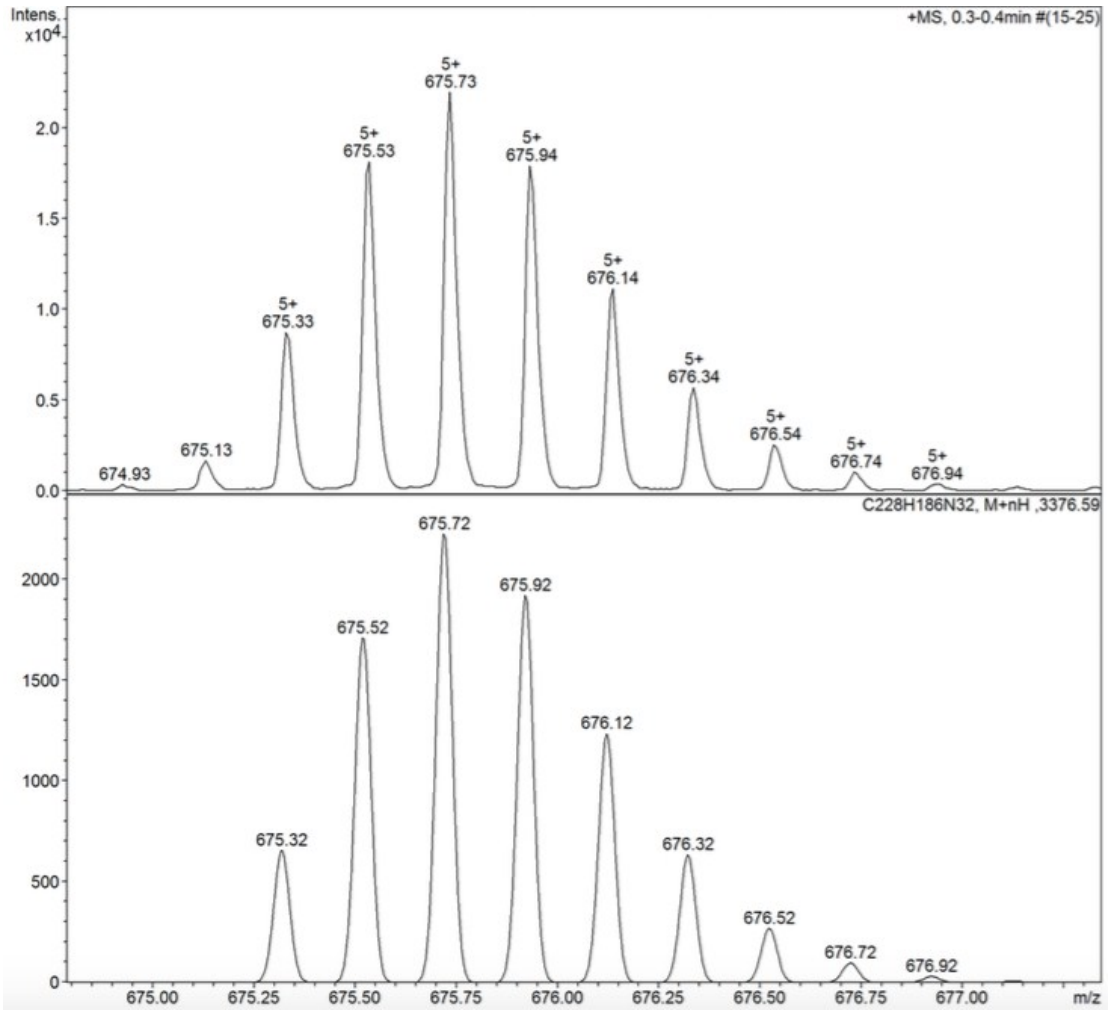
ppm


Intens.
x10^4
+MS, 0.3-0.4min #(15-25)
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675.73
5+
675.53
5+
675.94
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676.14
5+
675.33
5+
676.34
5+
676.54
5+
676.74
5+
676.94
675.13
674.93
C228H186N32, M+nH ,3376.59
675.72
675.92
675.52
676.12
675.32
676.32
676.52
676.72
676.92
m/z