Novel Multifunctional Click-Dendrimers based on Calix[4]arene core with Poly-Amine Periphery: Synthesis, Aggregation and DNA CT Complexation

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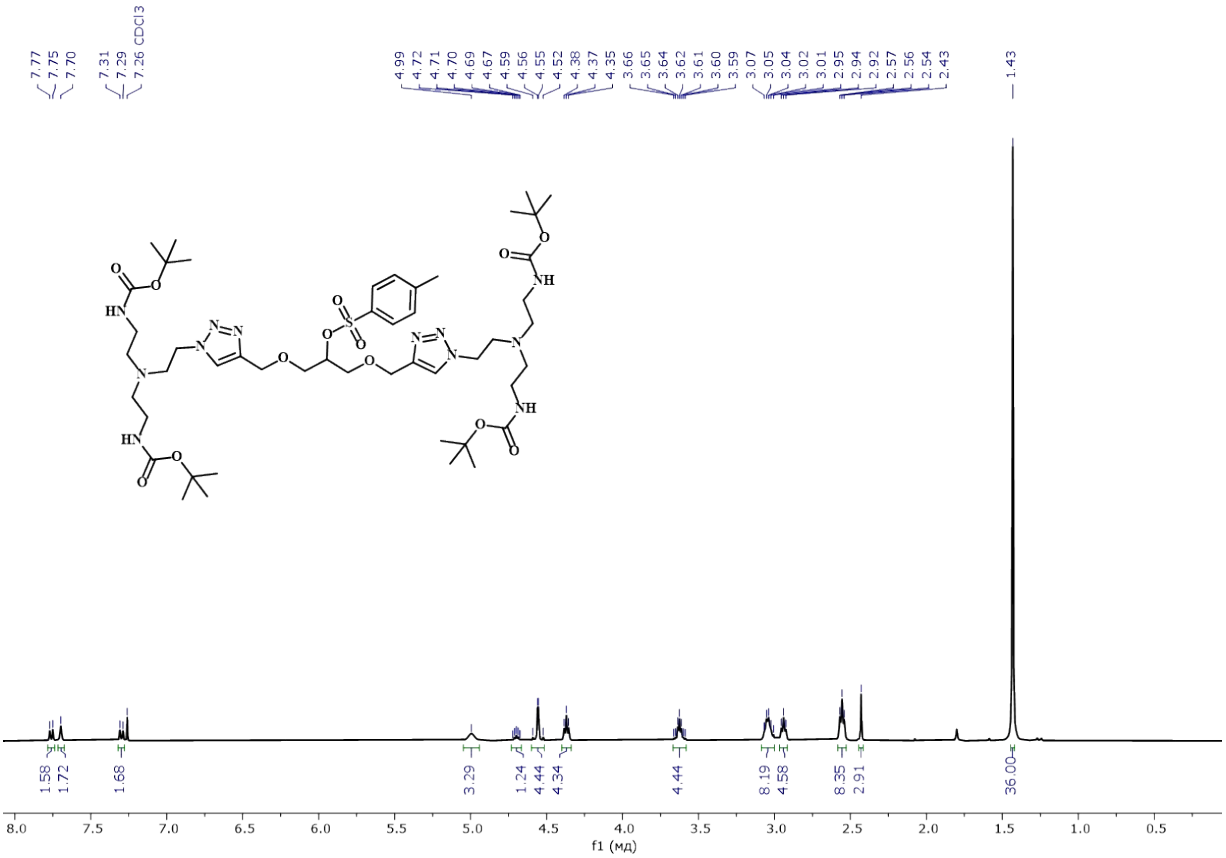
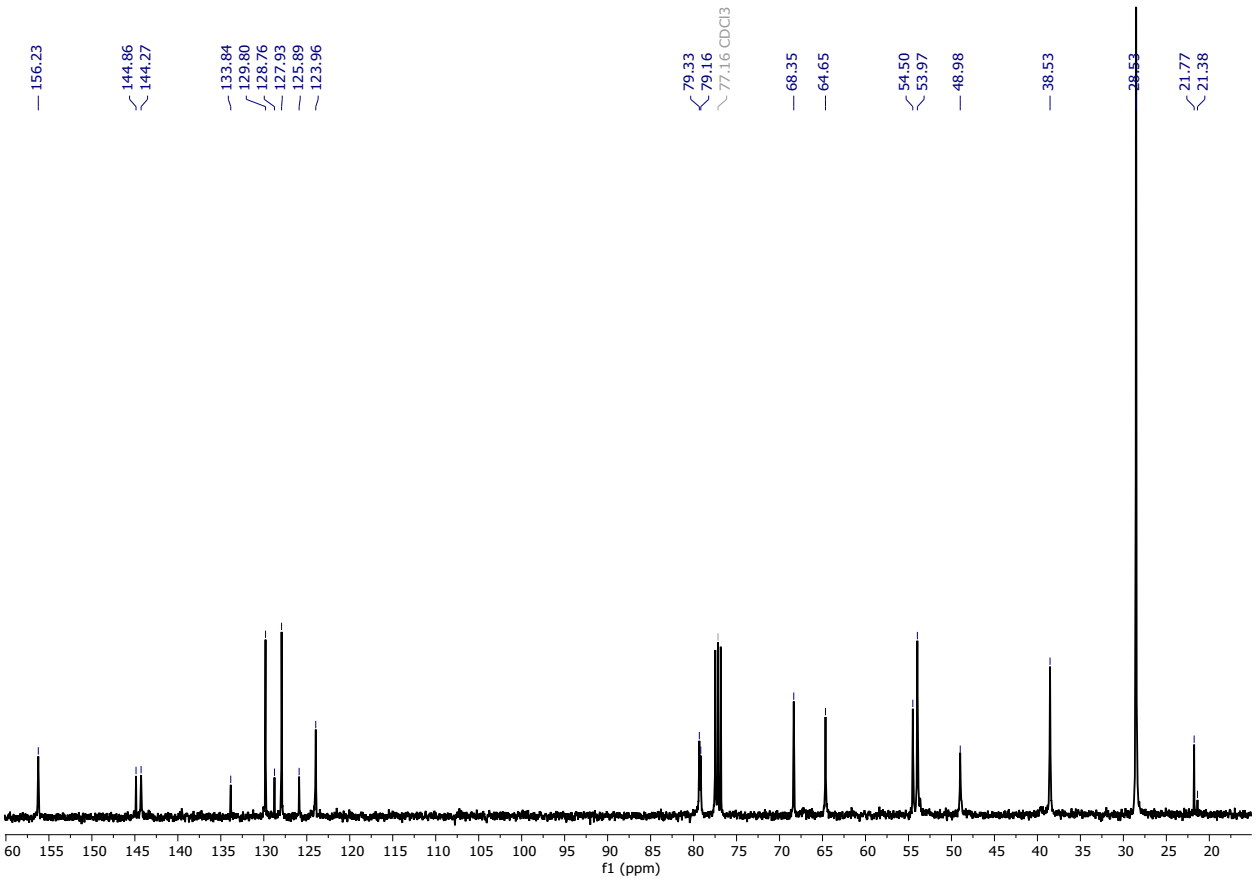
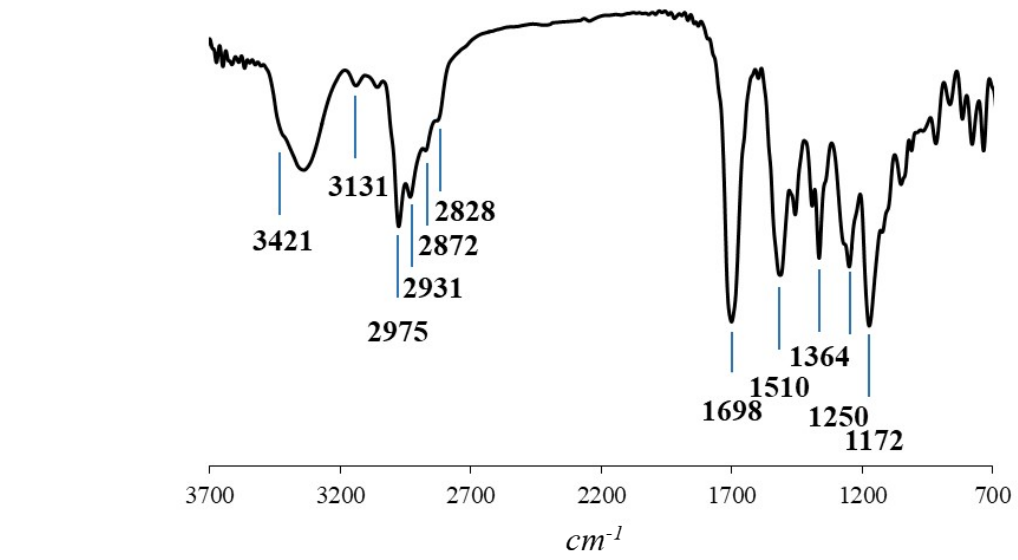
[b]. *Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, 8 Arbuzov Str., 420088 Kazan, Russia.*


7.77
7.75
7.70
7.31
7.29
7.26 CDCl3
4.99
4.72
4.71
4.70
4.69
4.67
4.59
4.56
4.55
4.52
4.38
4.37
4.35
3.66
3.65
3.64
3.62
3.61
3.60
3.59
3.07
3.05
3.04
3.02
3.01
2.95
2.94
2.92
2.57
2.56
2.54
2.43
1.43
1.58
1.72
1.68
3.29
1.24
4.44
4.34
4.44
8.19
4.58
8.35
2.91
36.00
f1 (мд)


156.23
144.86
144.27
133.84
129.80
128.76
127.93
125.89
123.96
79.33
79.16
77.16 CDCl3
68.35
64.65
54.50
53.97
48.98
38.53
28.53
21.77
21.38
f1 (ppm)



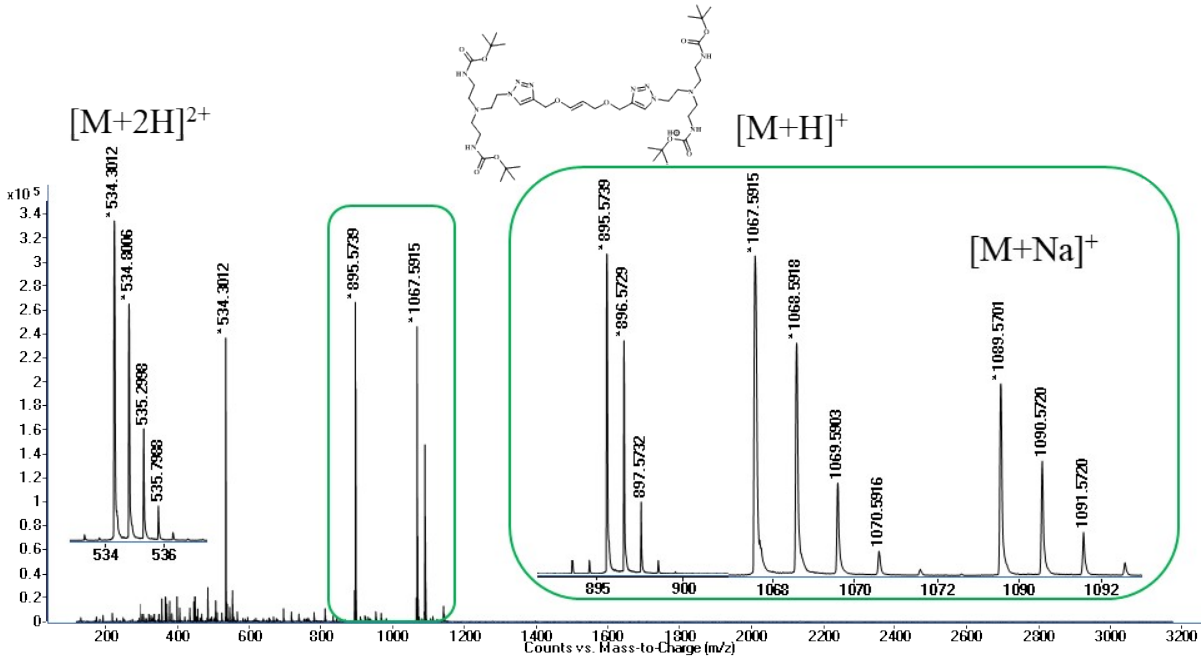
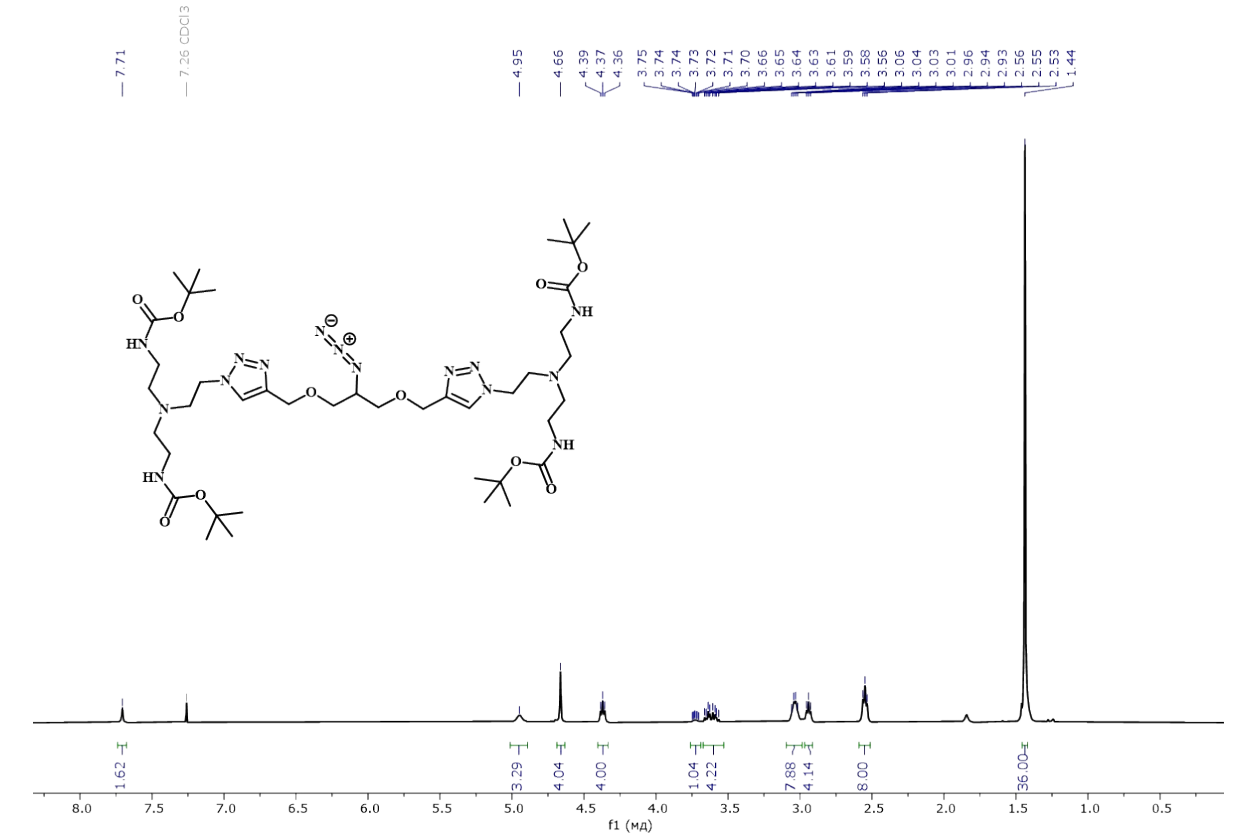
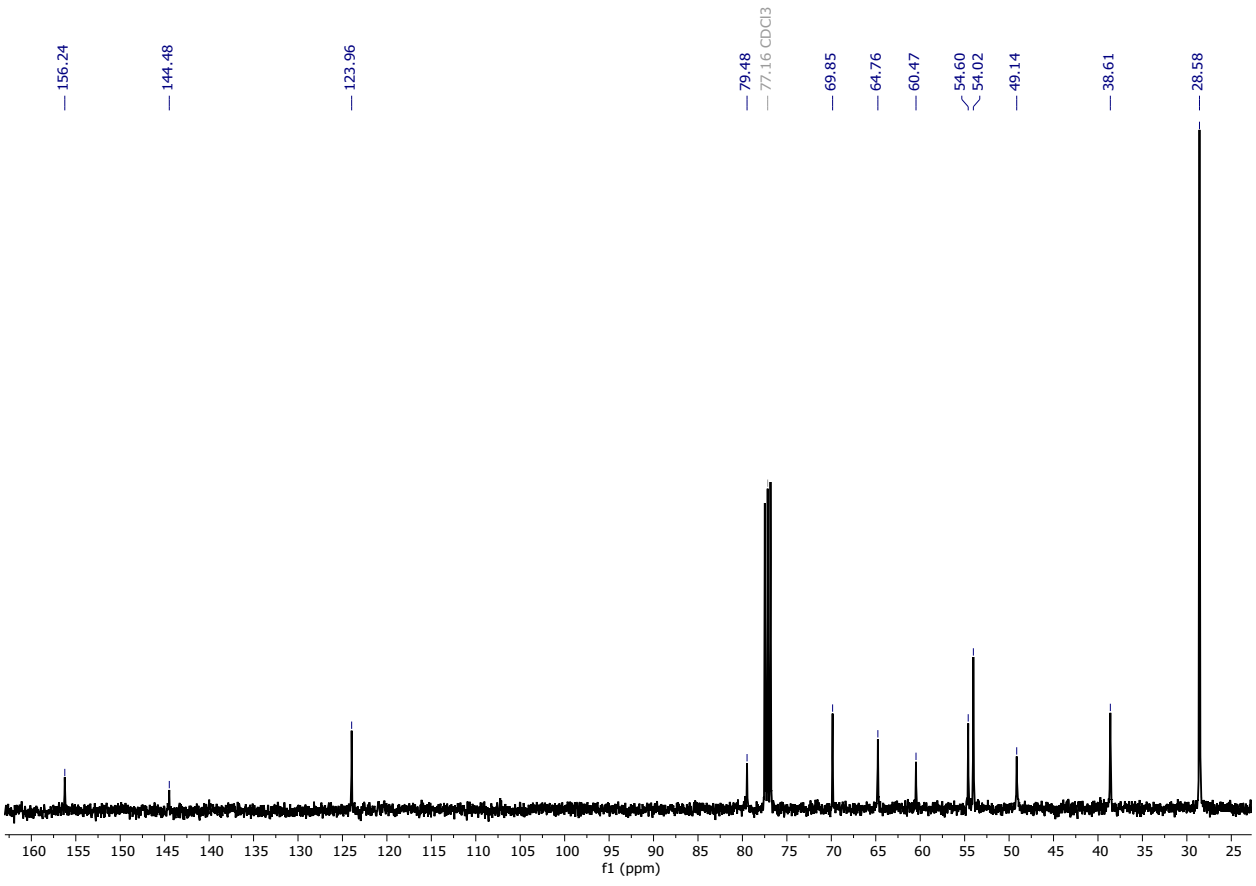


Fig. S1. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), FT-IR and HRESI MS spectra of compound **6.**


7.71
7.26 CDCl3
4.95
4.66
4.39
4.37
4.36
3.75
3.74
3.74
3.73
3.72
3.71
3.70
3.66
3.65
3.64
3.63
3.61
3.59
3.58
3.56
3.06
3.04
3.03
3.01
2.96
2.94
2.93
2.56
2.55
2.53
1.44
1.62
3.29
4.04
4.00
1.04
4.22
7.88
4.14
8.00
36.00
f1 (мд)


156.24
144.48
123.96
79.48
77.16 CDCl3
69.85
64.76
60.47
54.60
54.02
49.14
38.61
28.58
f1 (ppm)

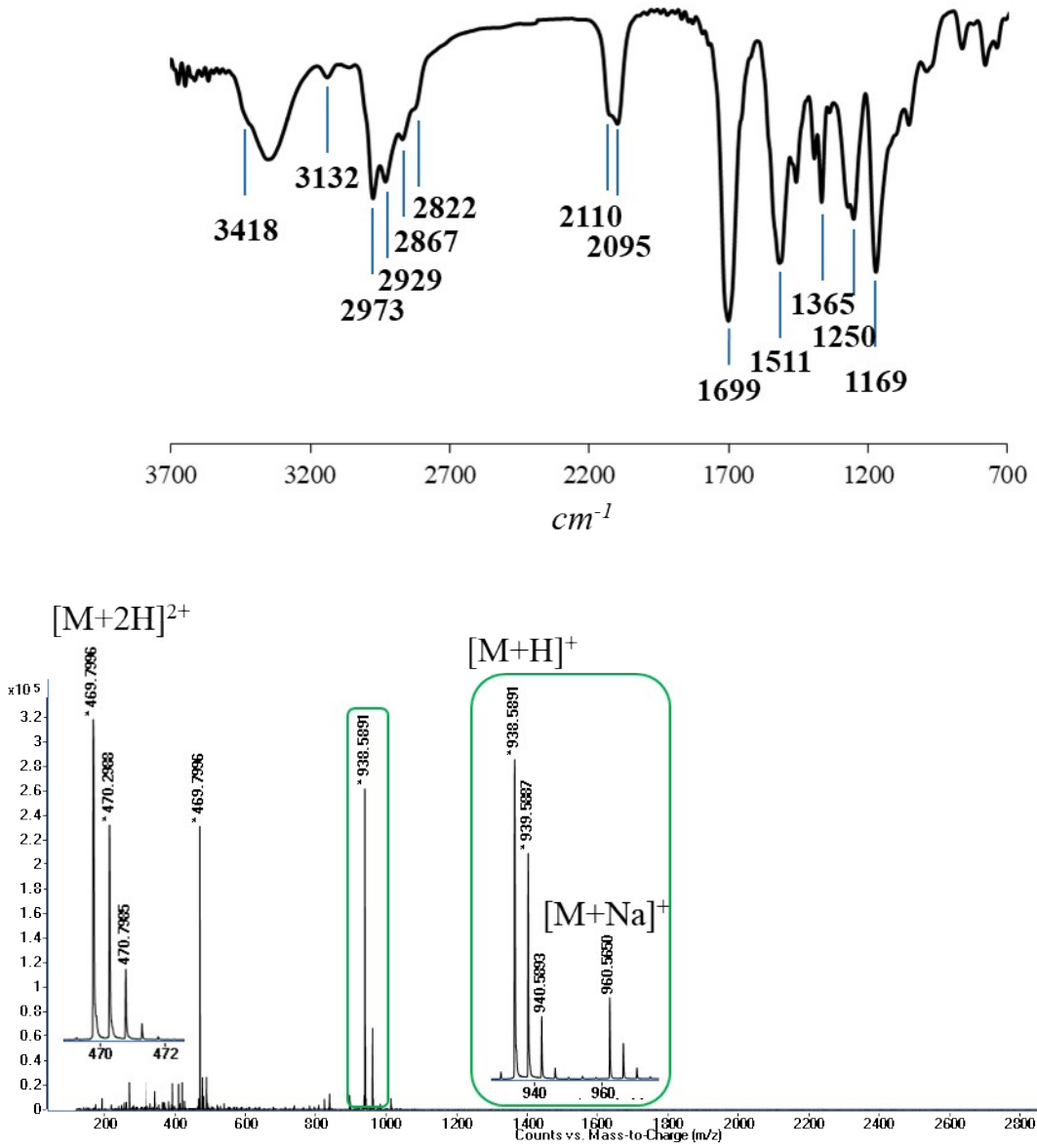
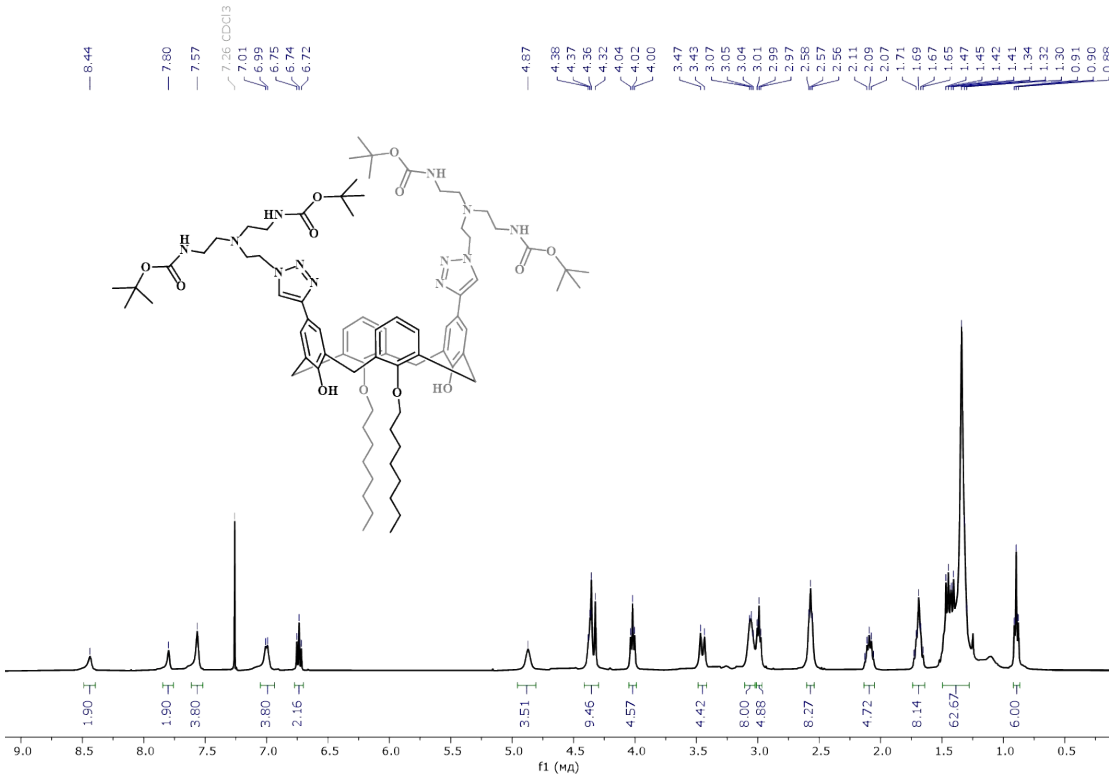
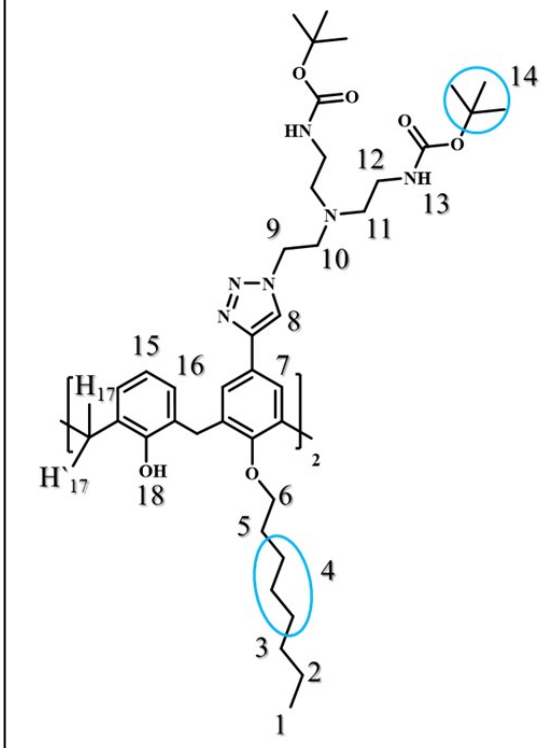
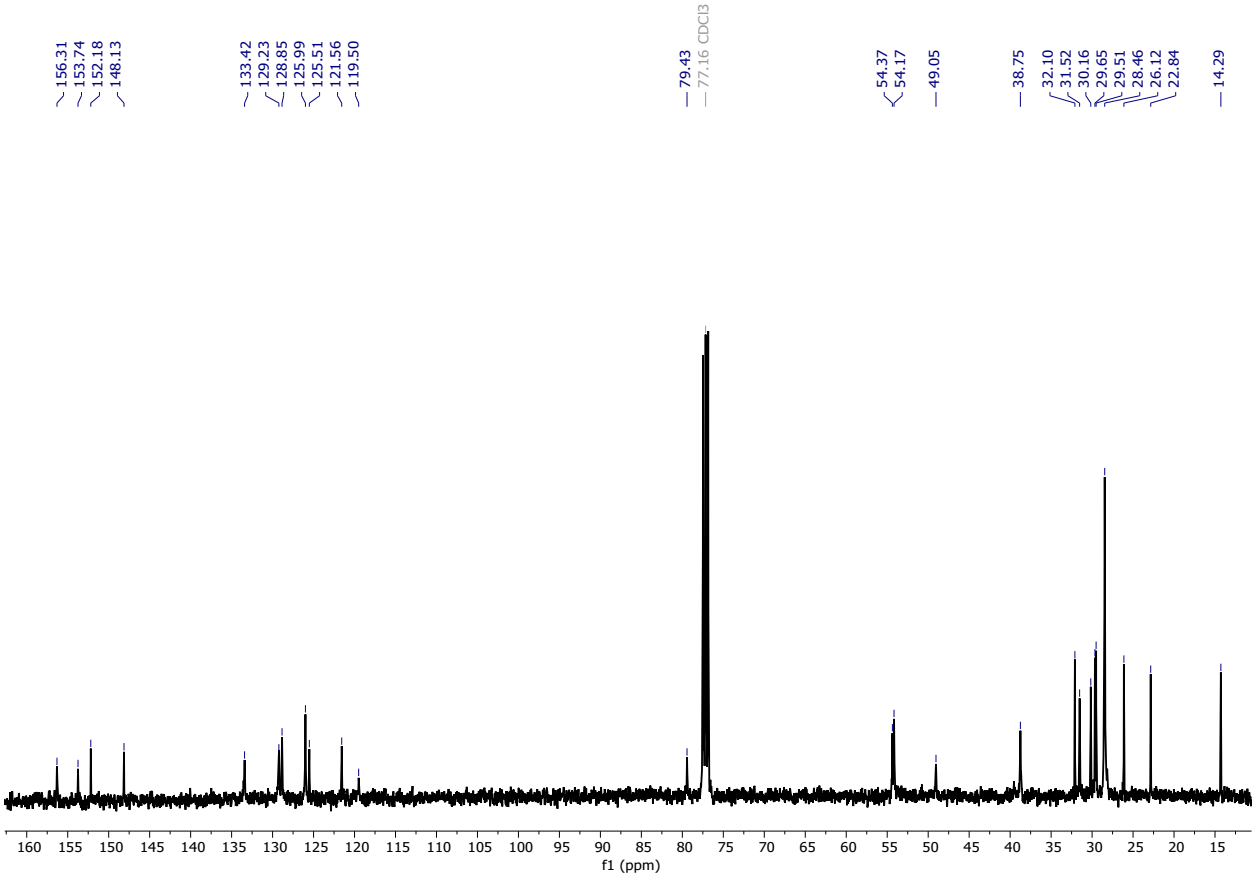
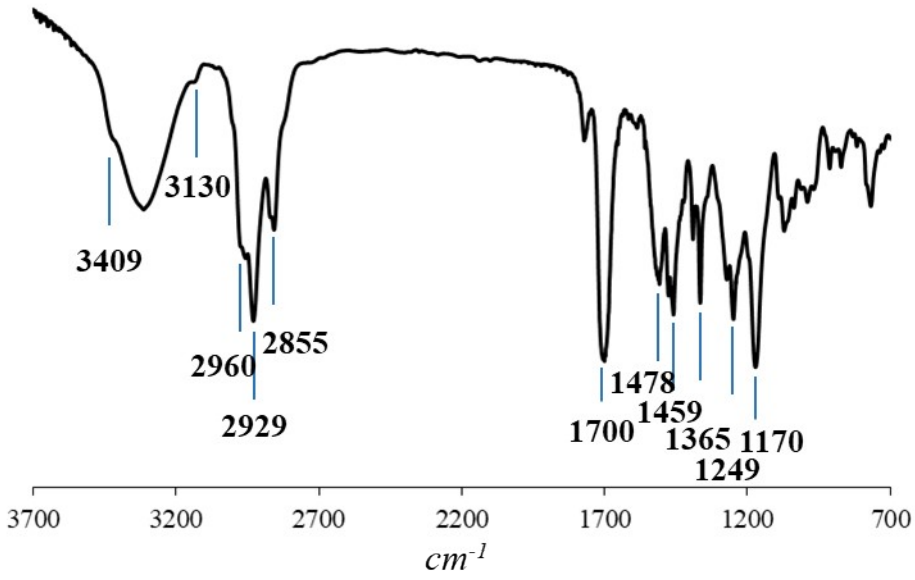


Fig. S2. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), FT-IR and HRESI MS spectra of compound **7.**



	№ H	δ, ppm
	1	0.90
	2+3	1.73-1.65
	4+14	1.47-1.30
	5	2.13-2.06
	6	4.02
	7	7.57
	8	7.80
	9+H_{17}	4.38-4.32
	10	2.99
	11	2.57
	12	3.07-3.04
	13	4.87
	15	6.74
	16	7.00
	H`$_{17}$	3.45
	18	8.44


156.31
153.74
152.18
148.13
133.42
129.23
128.85
125.99
125.51
121.56
119.50
79.43
77.16 CDCl3
54.37
54.17
49.05
38.75
32.10
31.52
30.16
29.65
29.51
28.46
26.12
22.84
14.29
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)


3409
3130
2960
2855
2929
1700
1478
1459
1365
1170
1249
3700 3200 2700 2200 1700 1200 700
cm-1

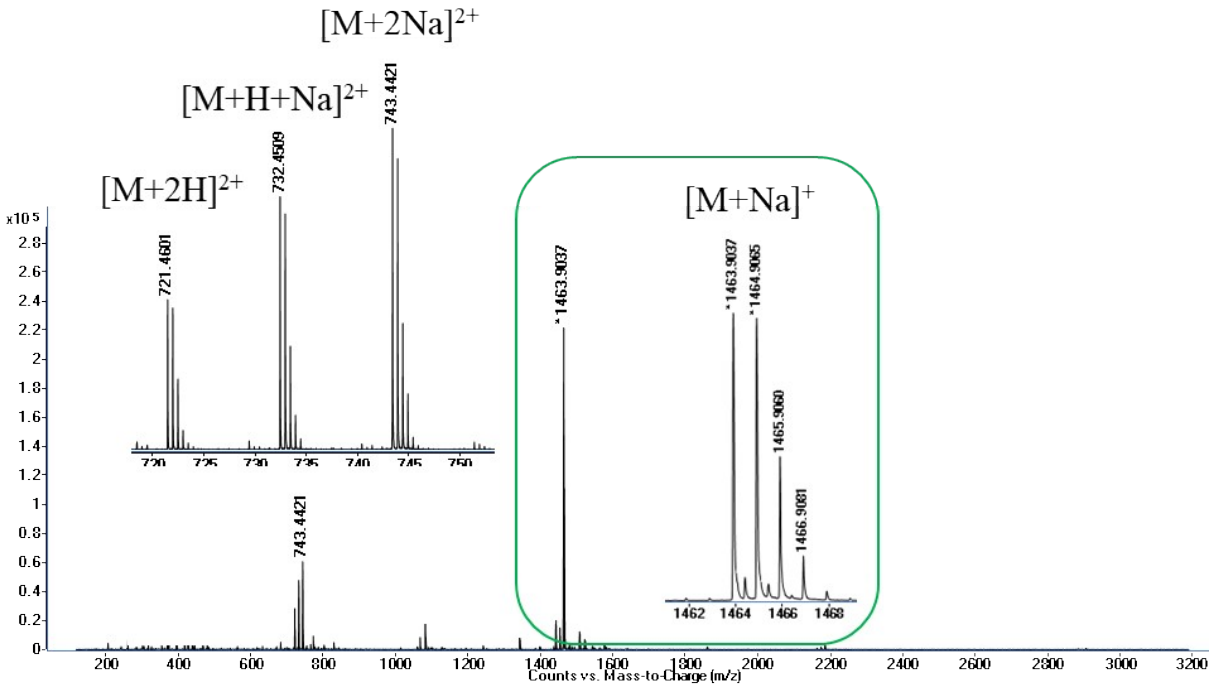
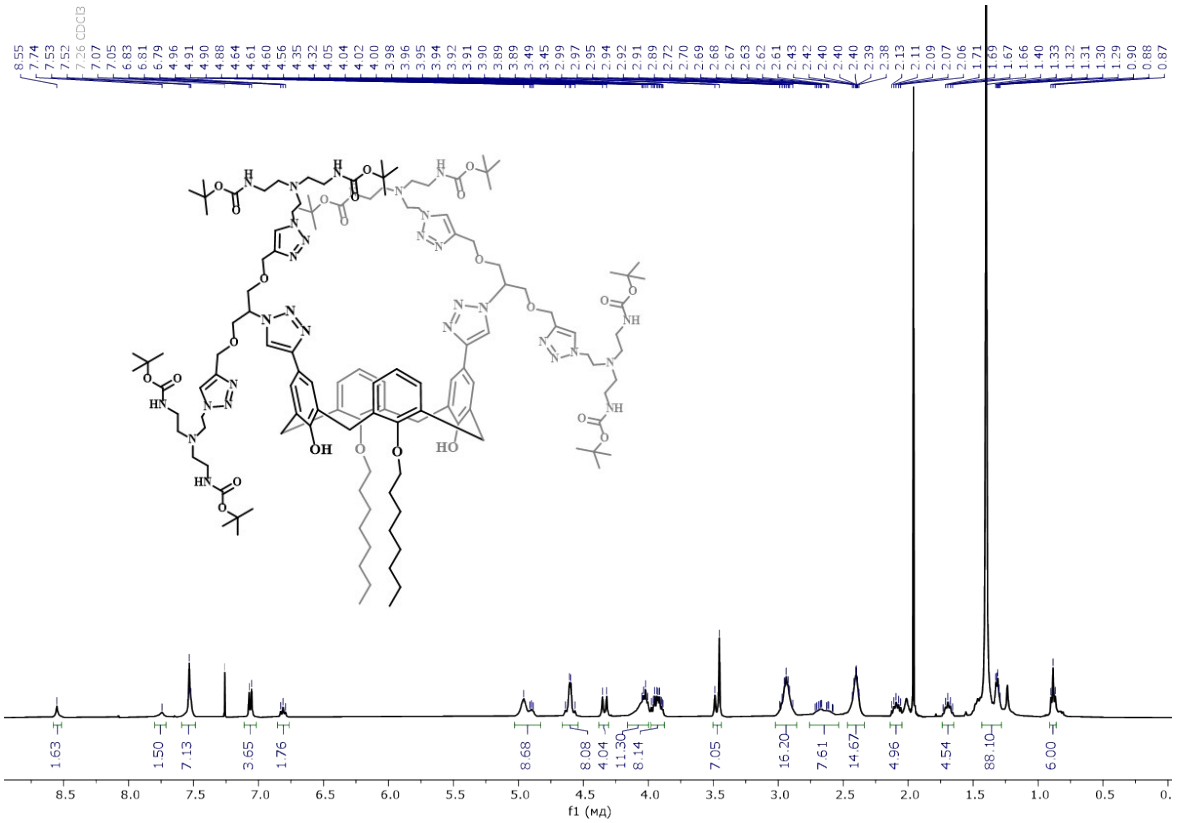
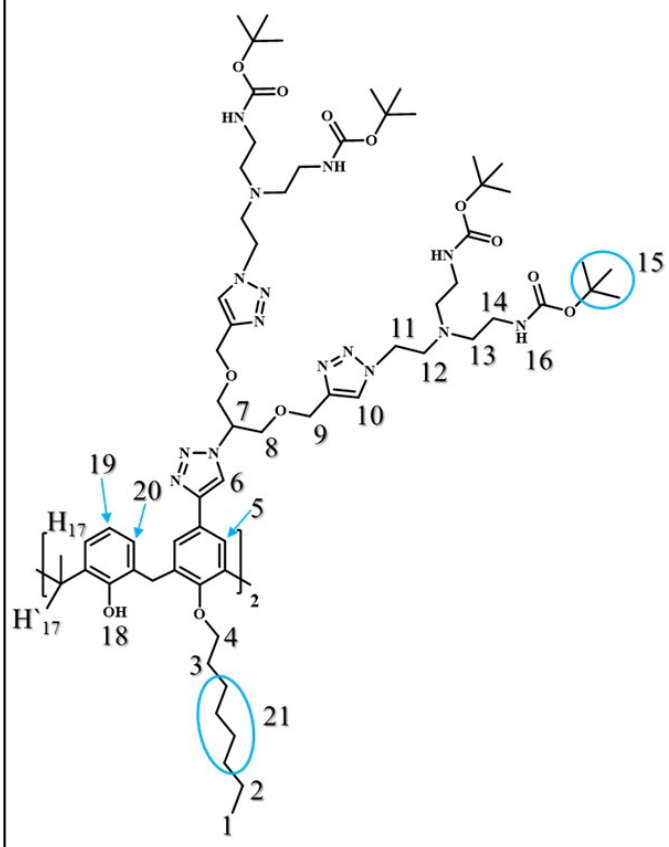


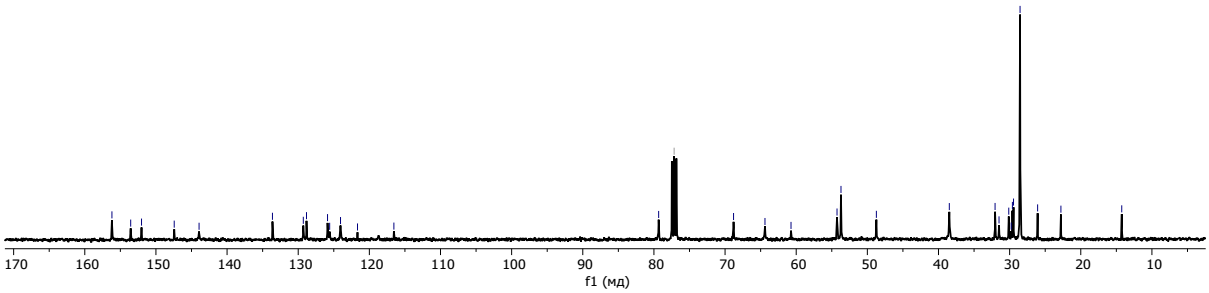
Fig. S3. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), FT-IR and HRESI MS spectra of compound **8**.

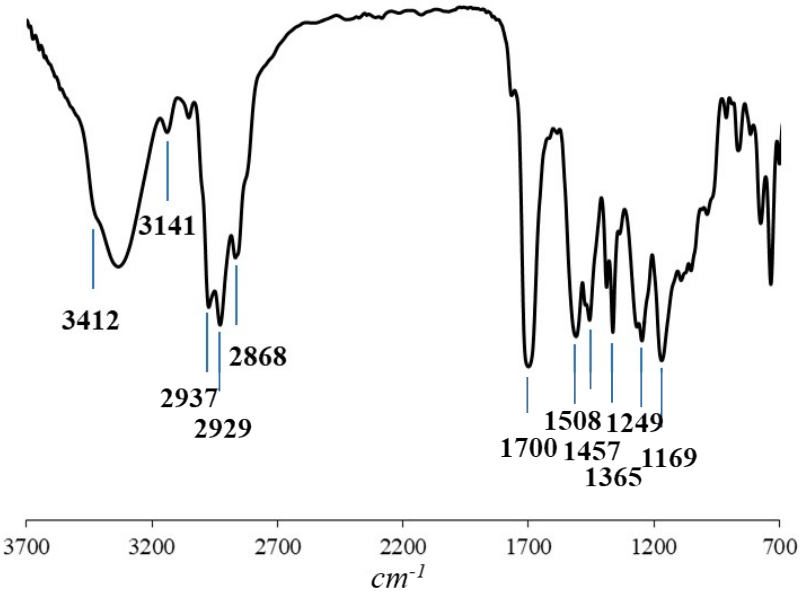




№ H	δ, ppm
1	0.88
2	1.73-1.66
3	2.13-2.06
4+11	4.05-4.00
5+10	7.53
6	7.74
7+16	4.96-4.88
8	3.98-3.89
9	4.64-4.56
11	4.36
12	2.72-2.58
13	2.43-2.38
14	2.99-2.89
15+21	1.40-1.29
H_{17}	4.33
$H`_{17}$	3.47
18	8.55
19	6.81
20	7.06


156.18
153.55
152.02
147.43
143.94
133.62
129.28
128.84
125.88
125.58
124.05
121.66
116.55
79.33
77.16 CDCl3
68.81
64.39
60.73
54.26
53.71
48.73
38.48
32.05
31.49
30.12
29.78
29.61
29.45
28.53
26.07
22.79
14.24


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (мд)


3412
3141
2937
2929
2868
1700
1508
1457
1365
1249
1169
3700
3200
2700
2200
1700
1200
700
cm-1

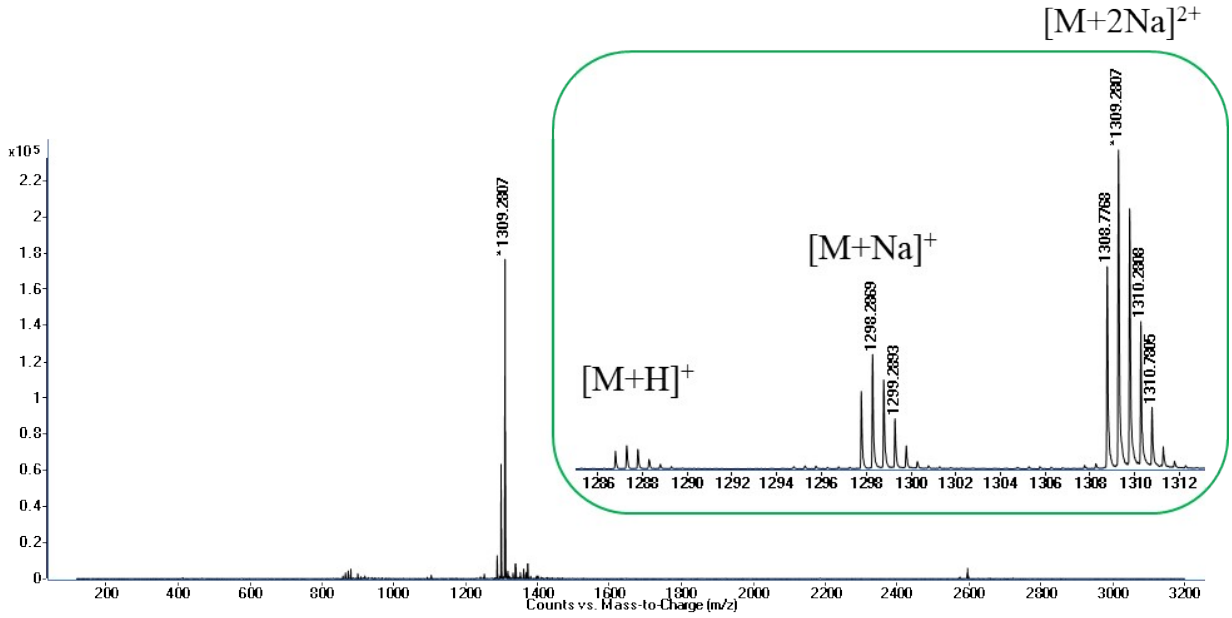
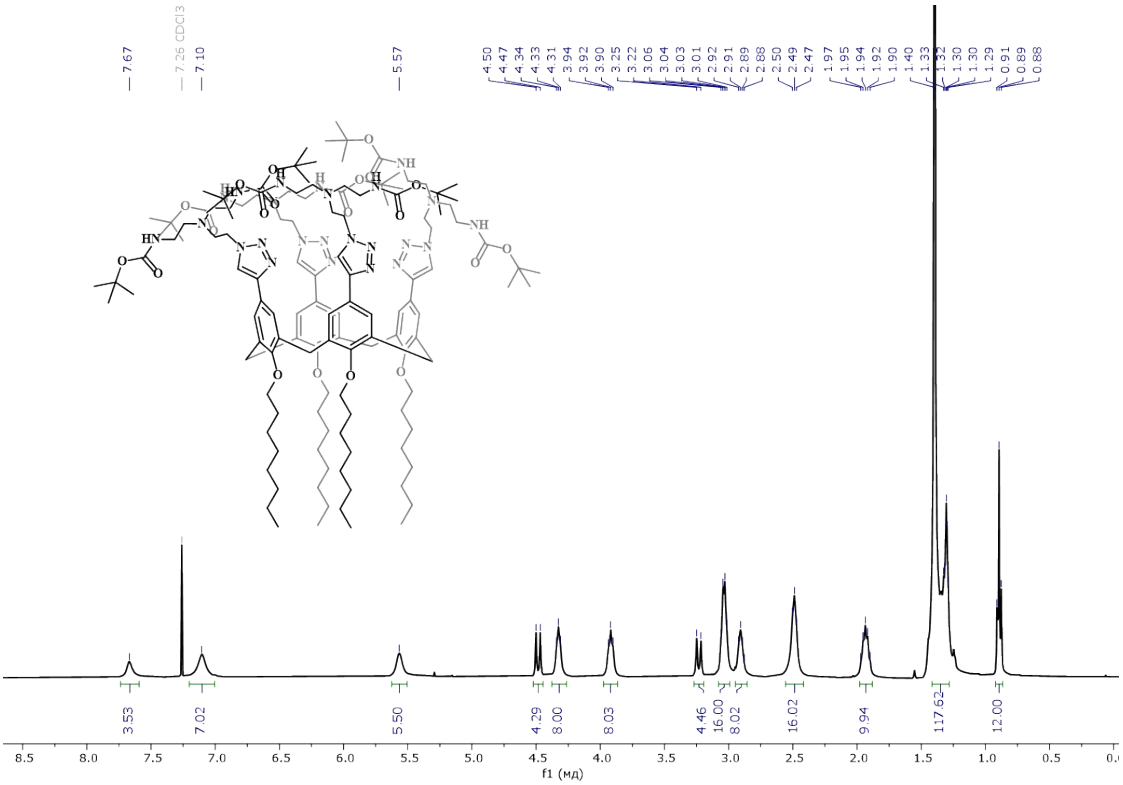
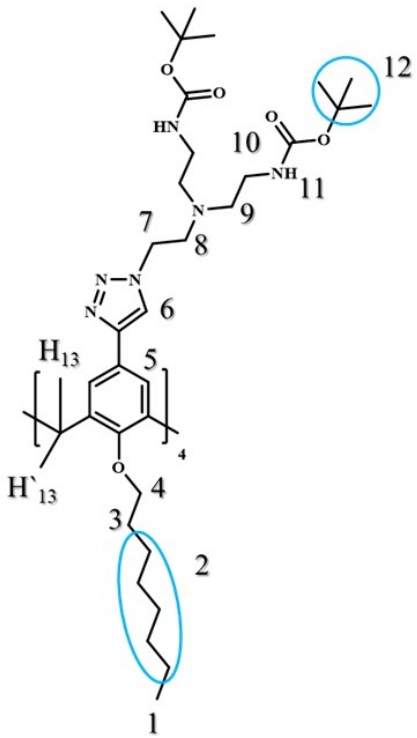
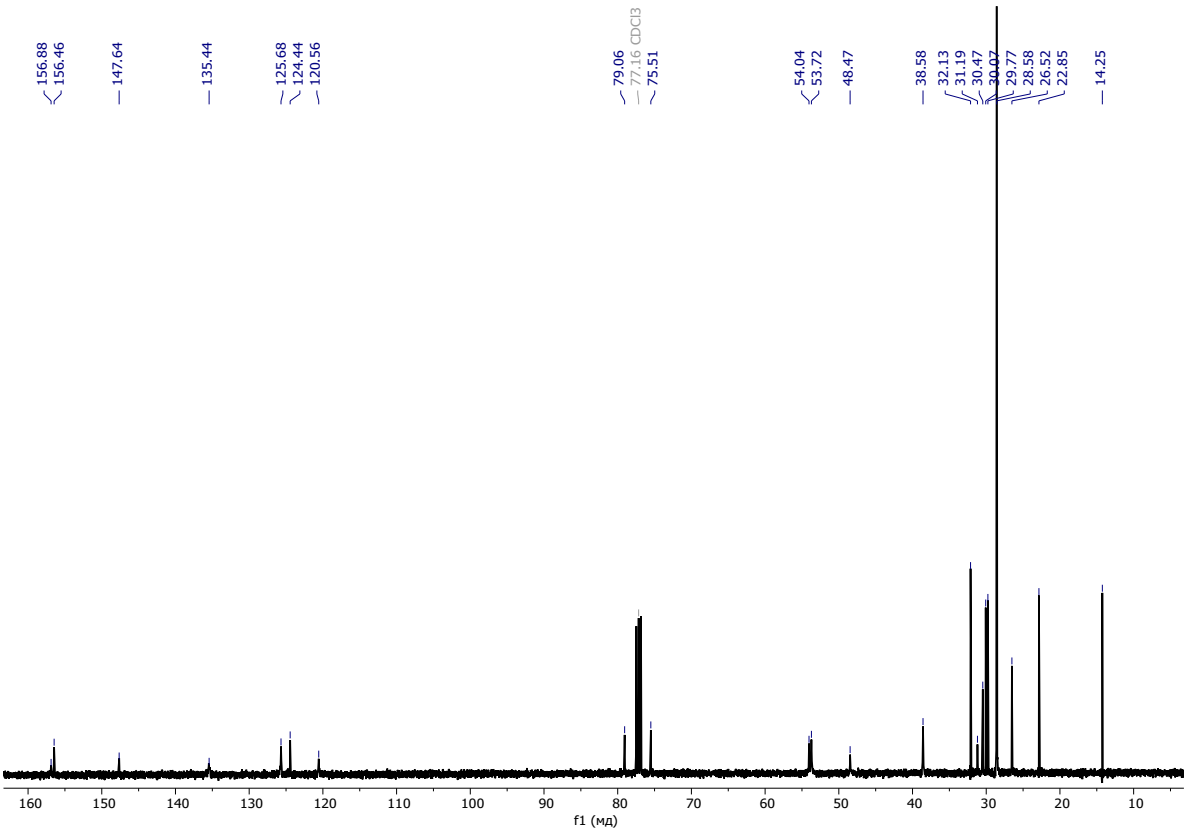


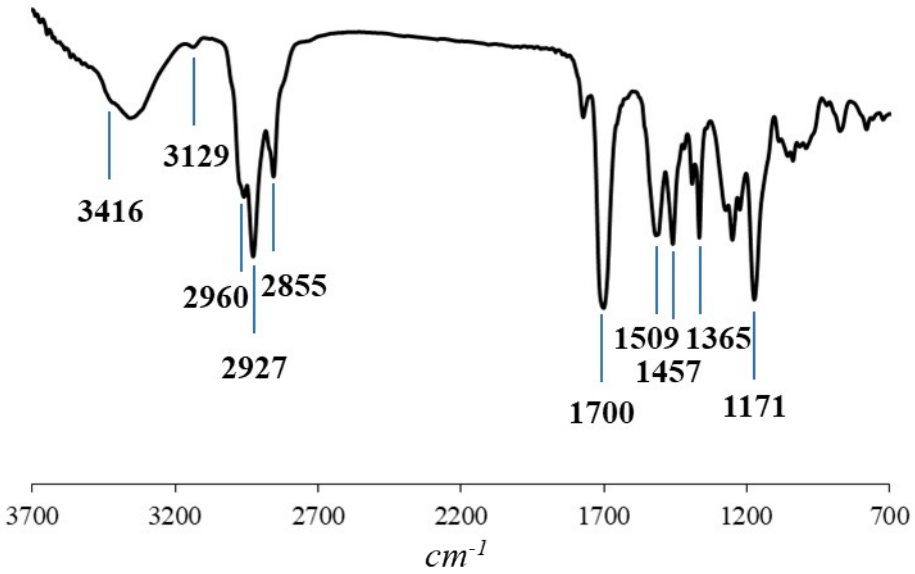
Fig. S4. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), FT-IR and HRESI MS spectra of compound **9**.





№ H	δ, ppm
1	0.89
2+12	1.40-1.29
3	1.94
4	3.92
5	7.10
6	7.67
7	4.33
8	2.91
9	2.49
10	3.06-3.01
11	5.57
H_{13}	4.49
$H`_{13}$	3.24


156.88
156.46
147.64
135.44
125.68
124.44
120.56
79.06
77.16 CDCl3
75.51
54.04
53.72
48.47
38.58
32.13
31.19
30.47
30.07
29.77
28.58
26.52
22.85
14.25
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (мд)


3416
3129
2960
2855
2927
1700
1509
1457
1365
1171
3700
3200
2700
2200
1700
1200
700
cm-1

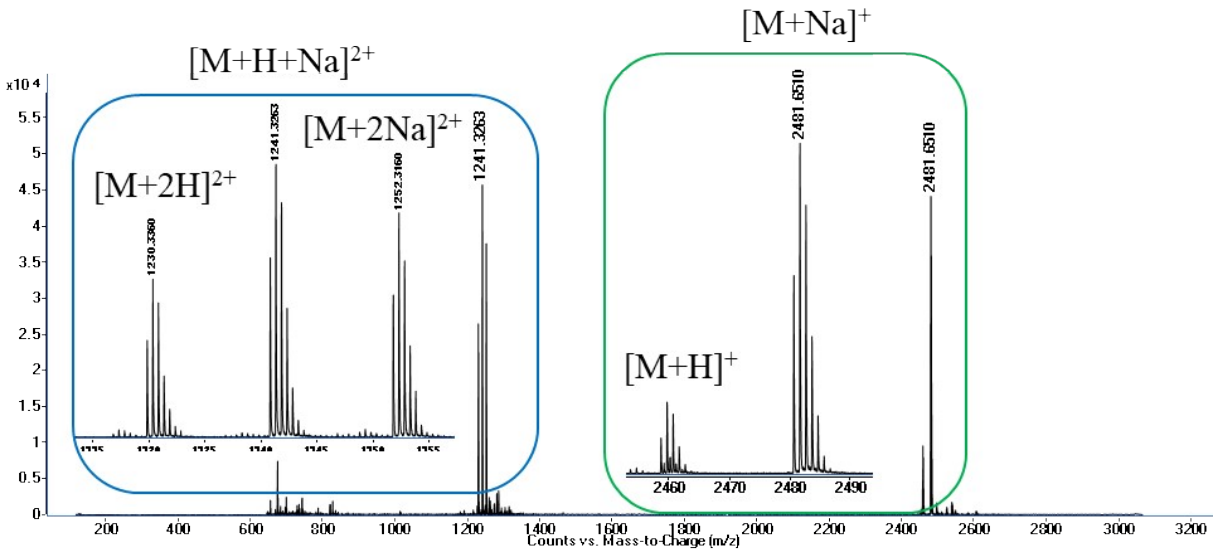
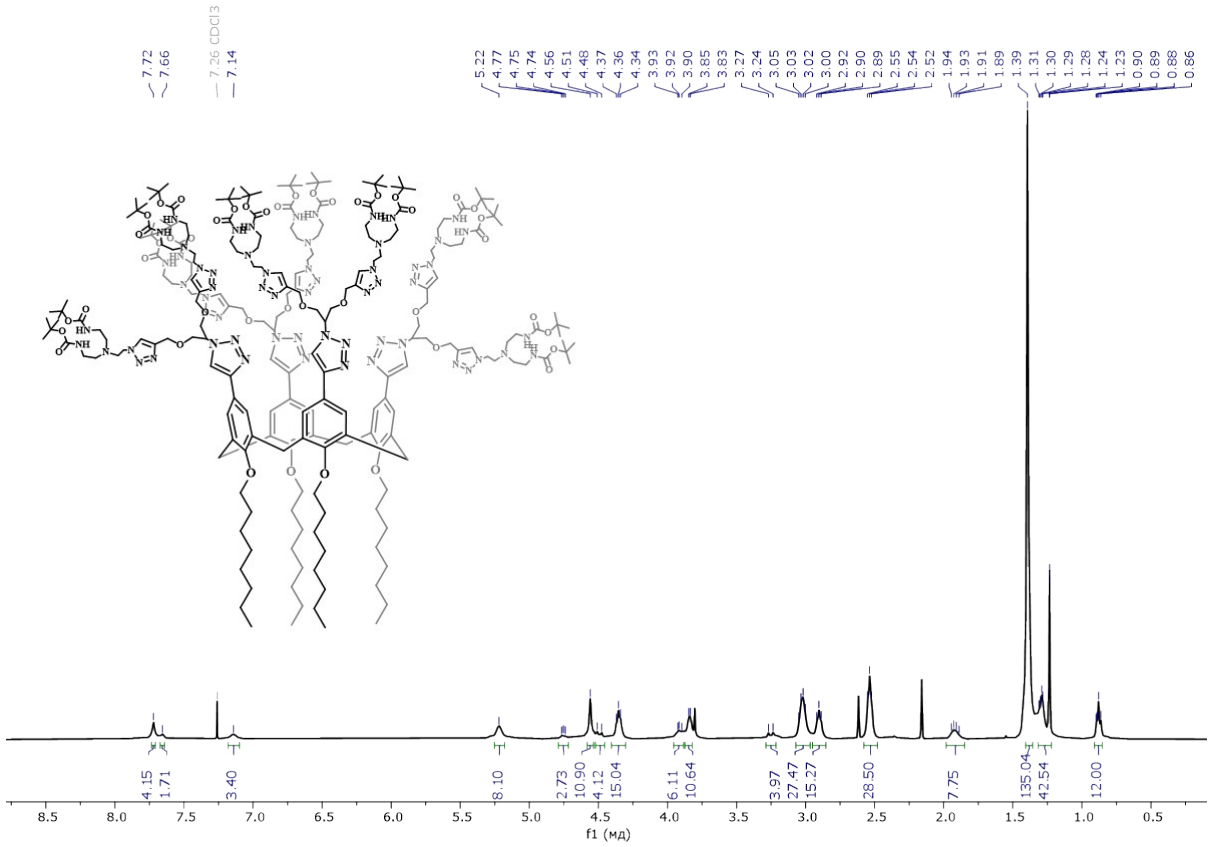
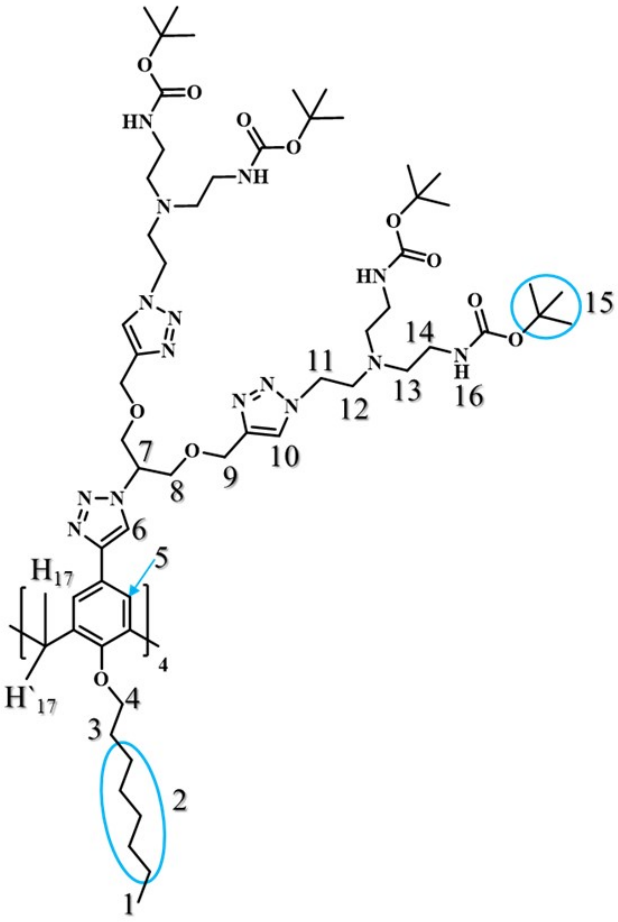
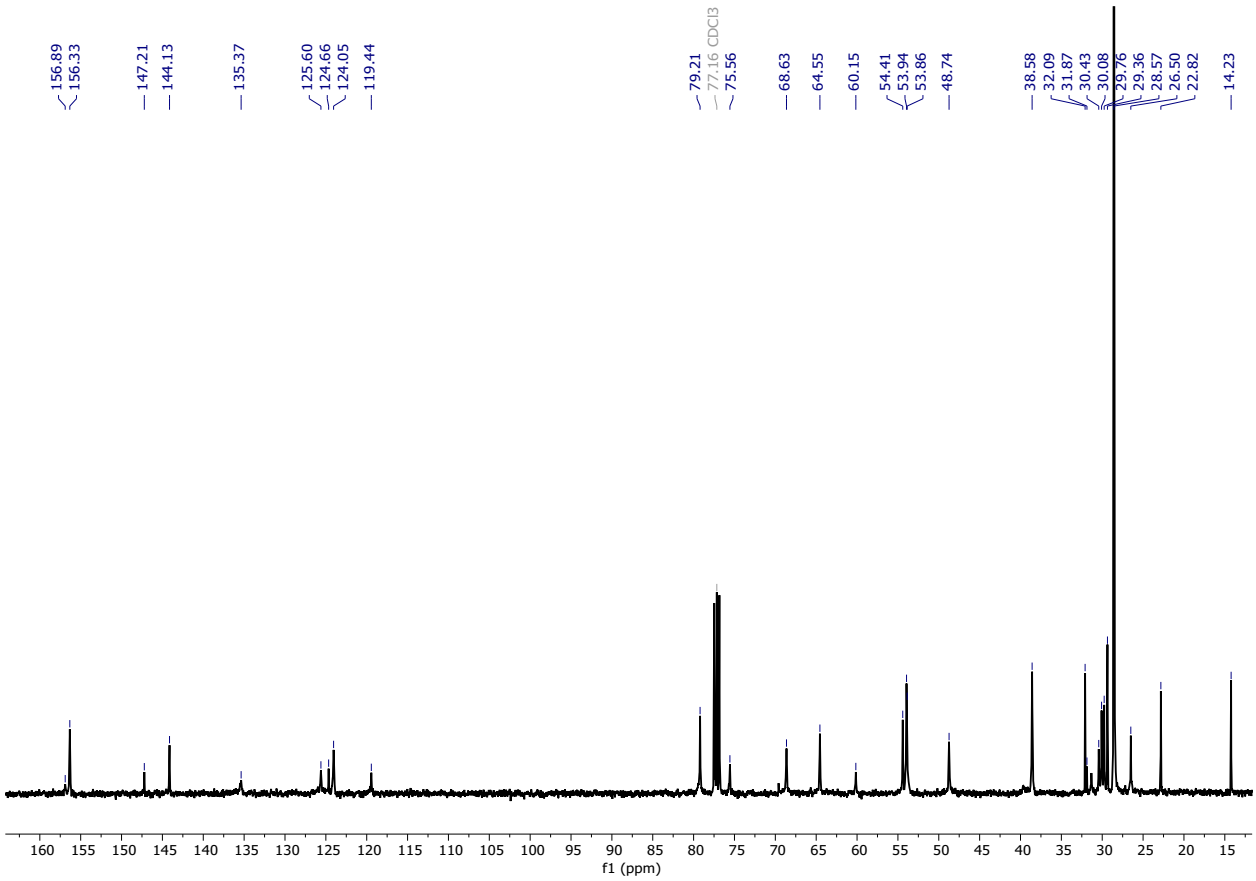


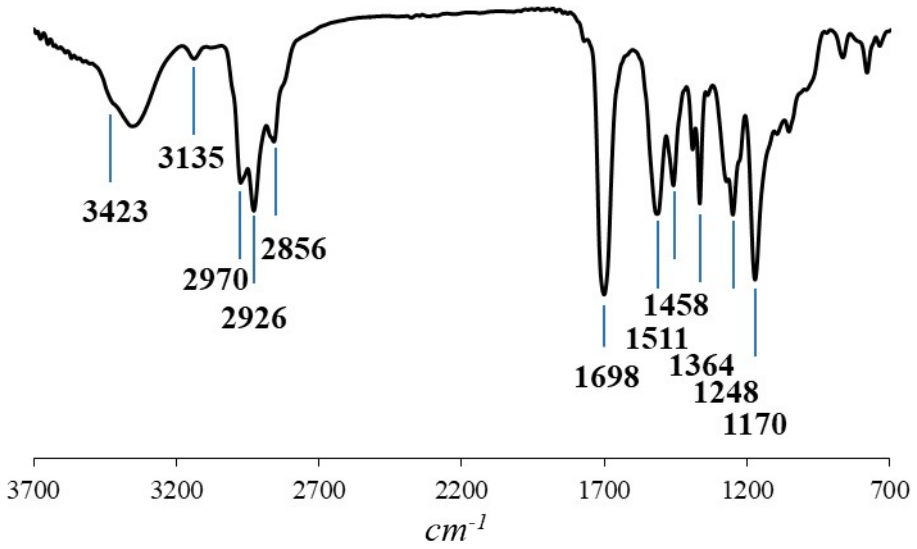
Fig. S5. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), FT-IR and HRESI MS spectra of compound **10**.


7.72
7.66
7.26 CDCl3
7.14
5.22
4.77
4.75
4.74
4.56
4.51
4.48
4.37
4.36
4.34
3.93
3.92
3.90
3.85
3.83
3.27
3.24
3.05
3.03
3.02
3.00
2.92
2.90
2.89
2.55
2.54
2.52
1.94
1.93
1.91
1.89
1.39
1.31
1.30
1.29
1.28
1.24
1.23
0.90
0.89
0.88
0.86
4.15
1.71
3.40
8.10
2.73
10.90
4.12
15.04
6.11
10.64
3.97
27.47
15.27
28.50
7.75
135.04
42.54
12.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (мд)



№ H	δ, ppm
1	0.88
2+15	1.39-1.28
3	1.94-1.89
4	3.93-3.90
5	7.14
6	7.66
7	4.77-4.74
8	3.85-3.83
9	4.56
10	7.72
11	4.36
12	2.90
13	2.54
14	3.05-3.00
16	5.22
H_{17}	4.50
$H`_{17}$	3.26


156.89
156.33
147.21
144.13
135.37
125.60
124.66
124.05
119.44
79.21
77.16 CDCl3
75.56
68.63
64.55
60.15
54.41
53.94
53.86
48.74
38.58
32.09
31.87
30.43
30.08
29.76
29.36
28.57
26.50
22.82
14.23
f1 (ppm)


3423
3135
2970
2926
2856
1698
1511
1458
1364
1248
1170
cm-1

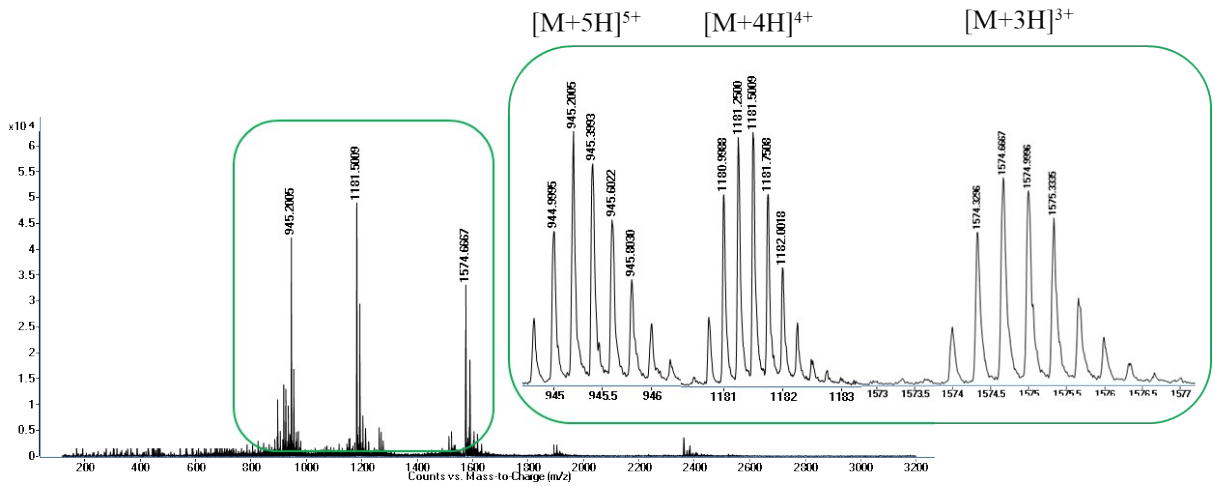
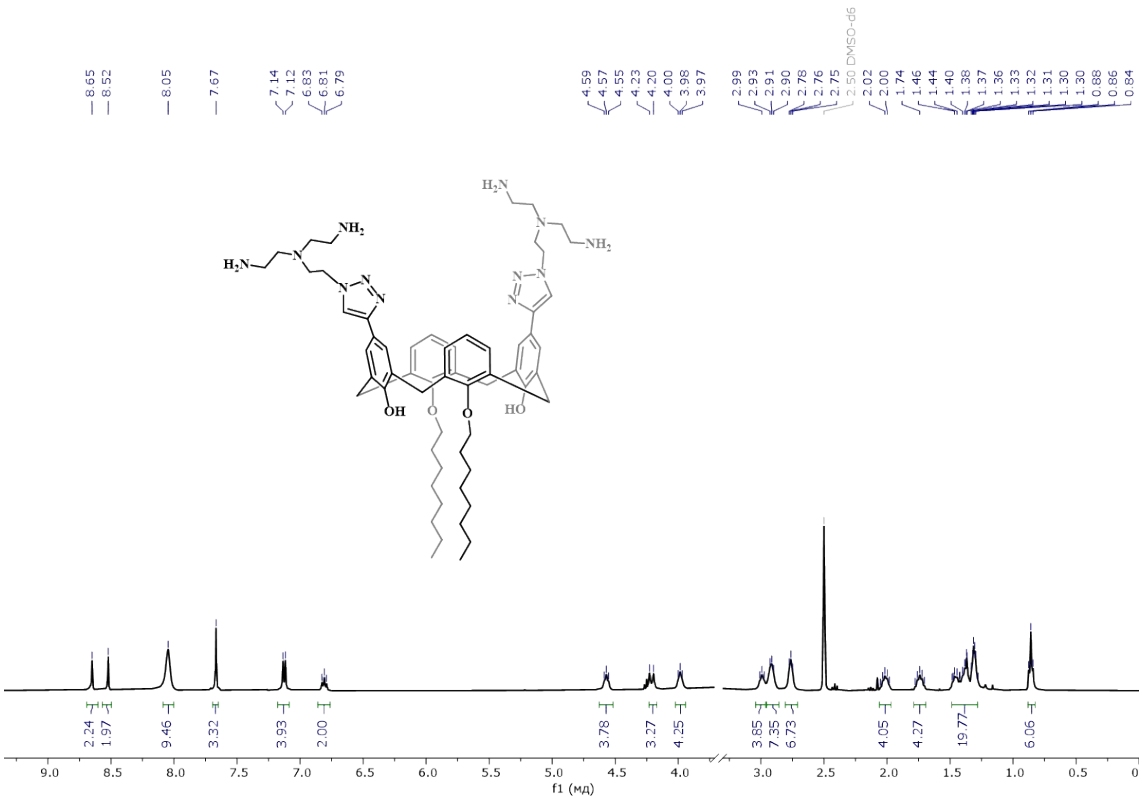
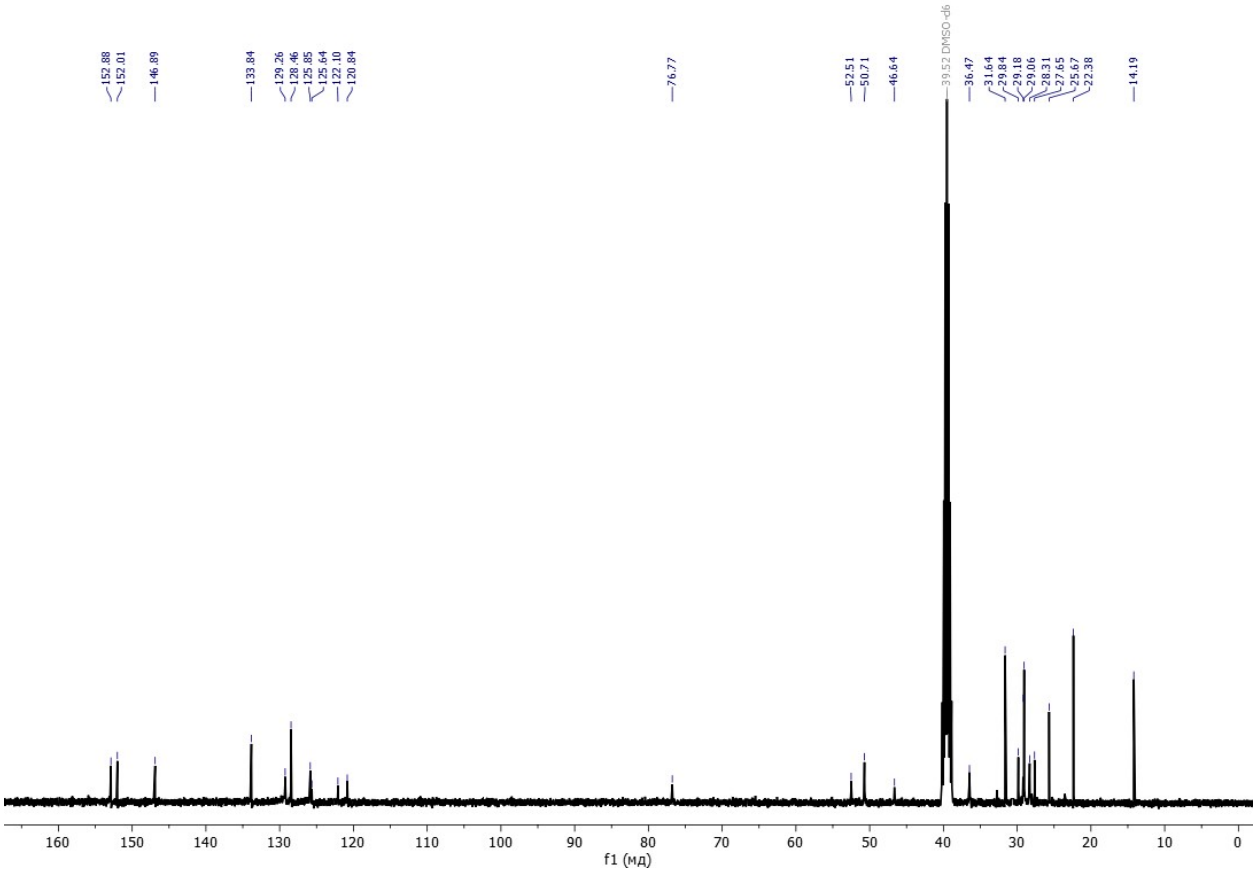


Fig. S6. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), FT-IR and HRESI MS spectra of compound **11**.


8.65
8.52
8.05
7.67
7.14
7.12
6.83
6.81
6.79
4.59
4.57
4.55
4.23
4.20
4.00
3.98
3.97
2.99
2.93
2.91
2.90
2.78
2.76
2.75
2.50 DMSO-d6
2.02
2.00
1.74
1.46
1.44
1.40
1.38
1.37
1.36
1.33
1.32
1.31
1.30
1.30
0.88
0.86
0.84
H2N
NH2
N
N
N
N
N
OH
O
O
HO
2.24
1.97
9.46
3.32
3.93
2.00
3.78
3.27
4.25
3.85
7.35
6.73
4.05
4.27
19.77
6.06
f1 (мд)


152.88
152.01
146.89
133.84
129.26
128.46
125.85
125.64
122.10
120.84
76.77
52.51
50.71
46.64
39.52 DMSO-d6
36.47
31.64
29.84
29.18
29.06
28.31
27.65
25.67
22.38
14.19
f1 (мд)

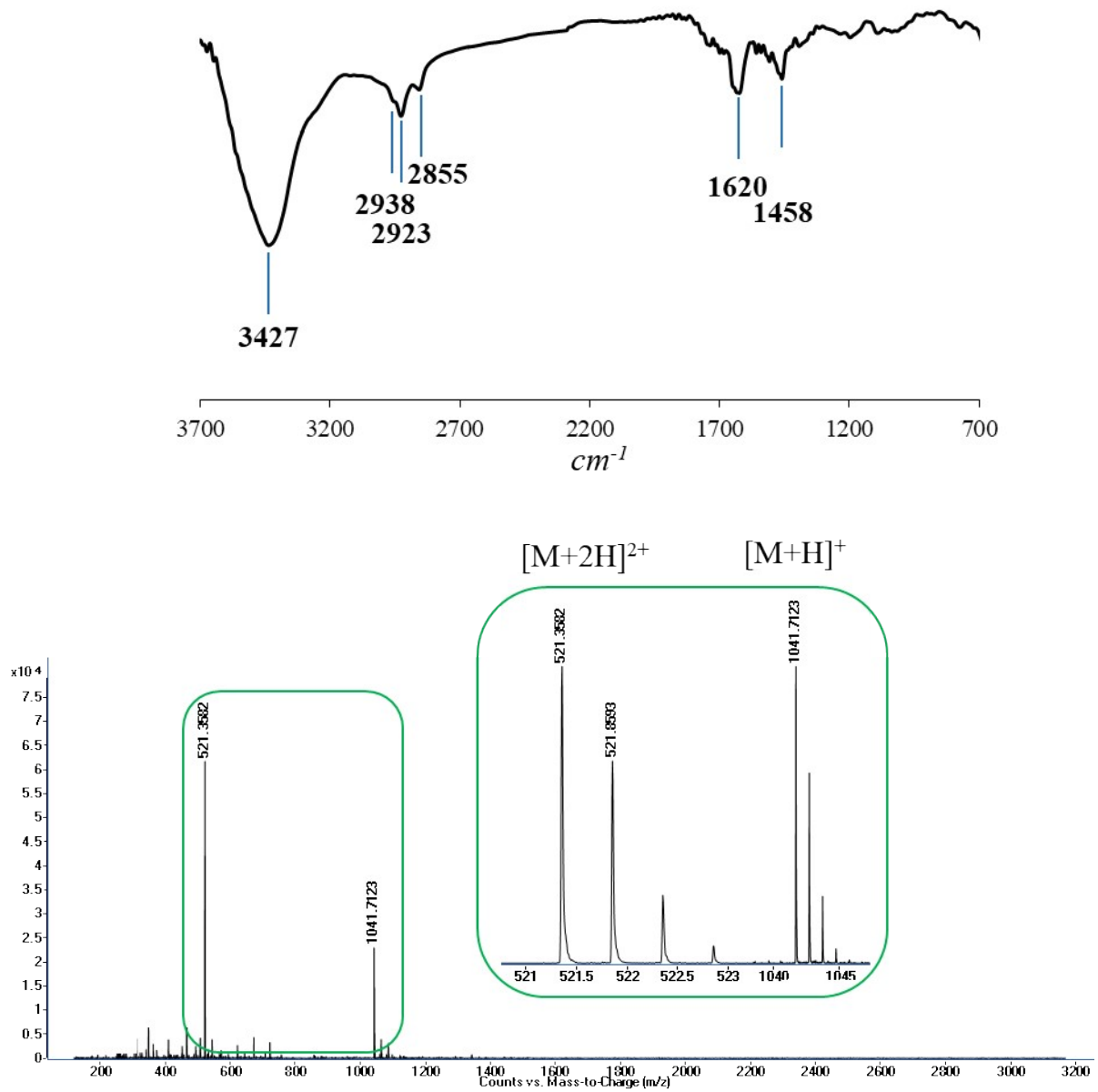
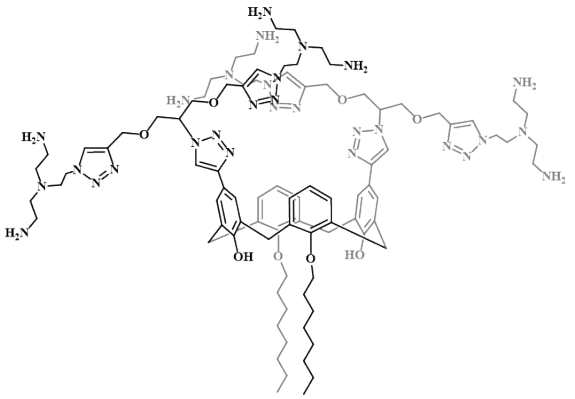
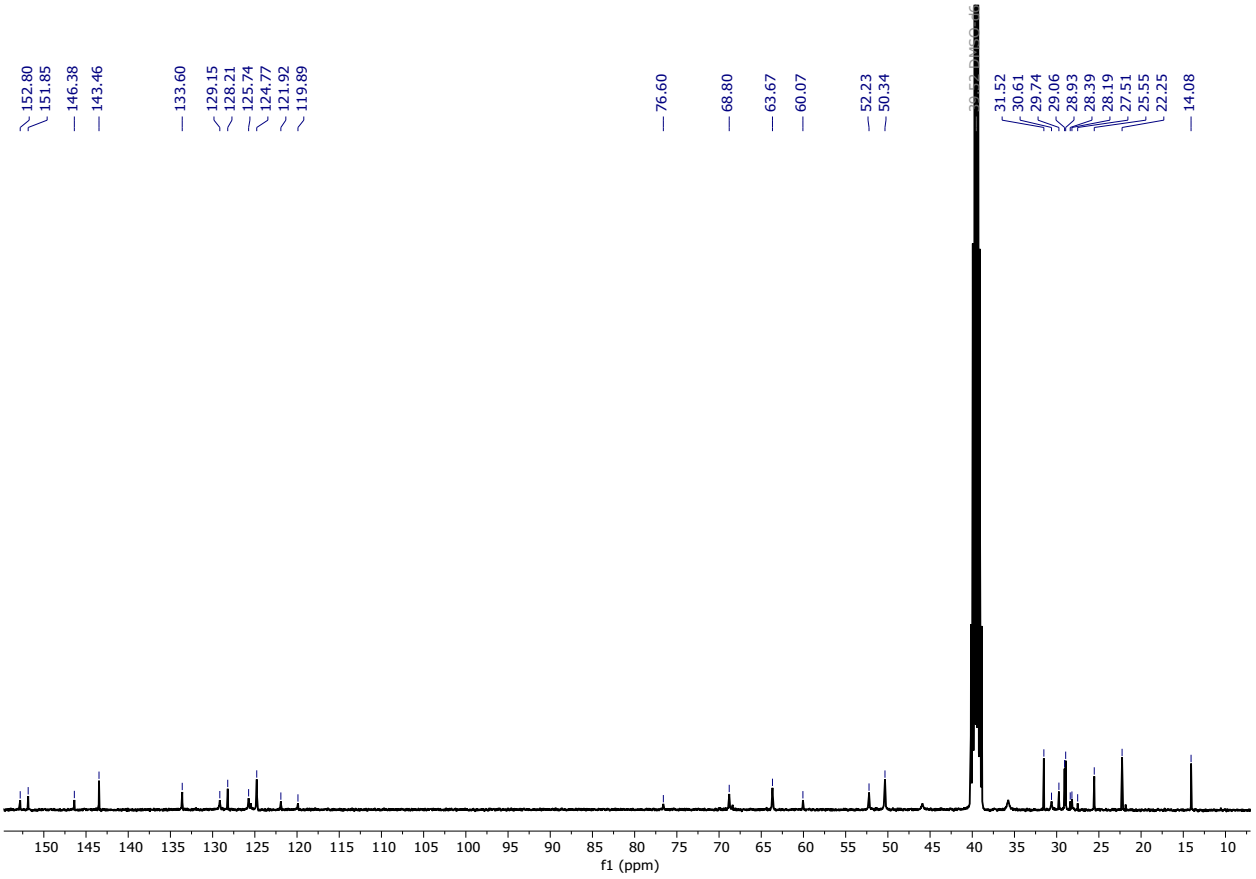


Fig. S7. ^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6), FT-IR and HRESI MS spectra of compound **12**.



2.50 DMSO-d6
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (мд)


152.80
151.85
146.38
143.46
133.60
129.15
128.21
125.74
124.77
121.92
119.89
76.60
68.80
63.67
60.07
52.23
50.34
39.52 DMSO-d6
31.52
30.61
29.74
29.06
28.93
28.39
28.19
27.51
25.55
22.25
14.08
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

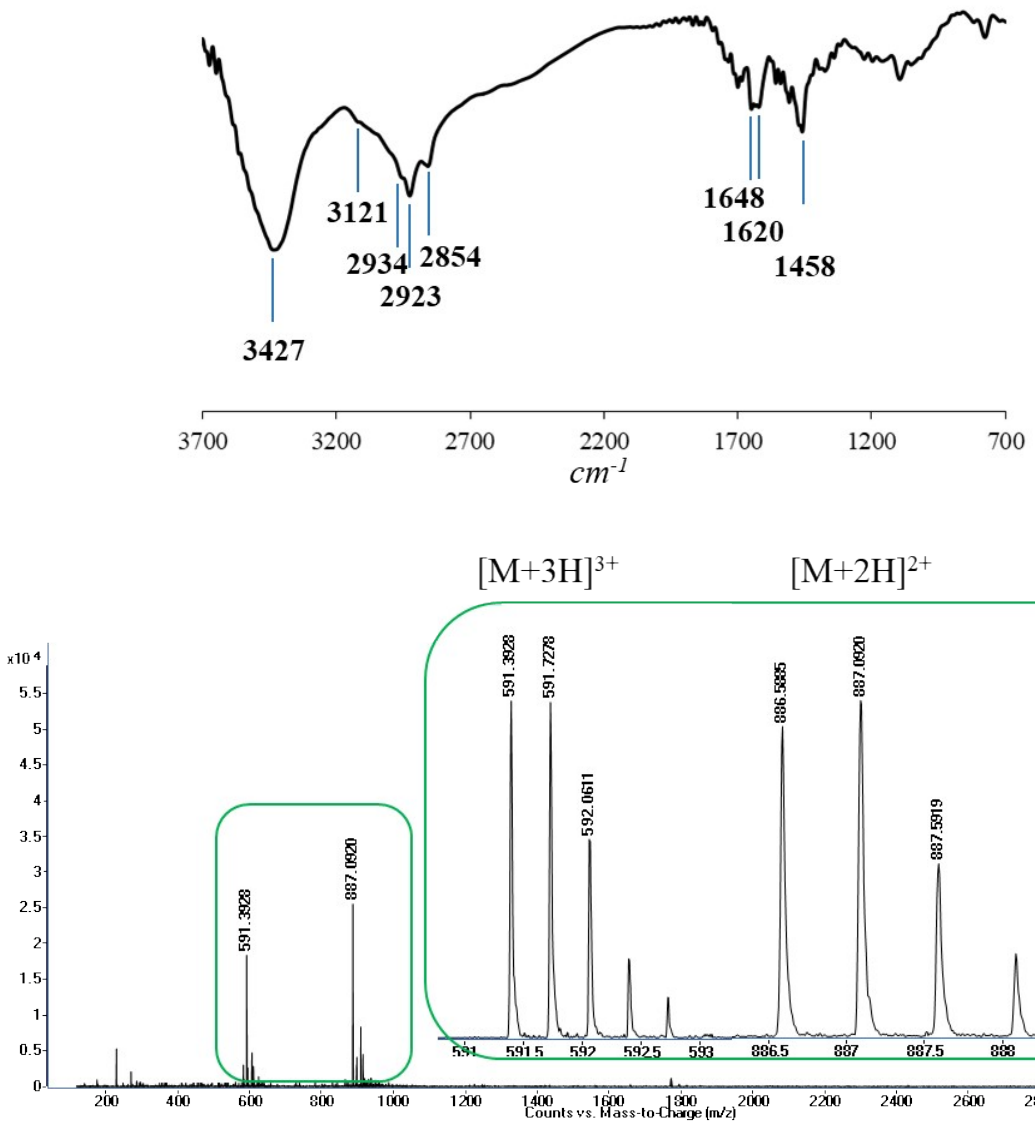
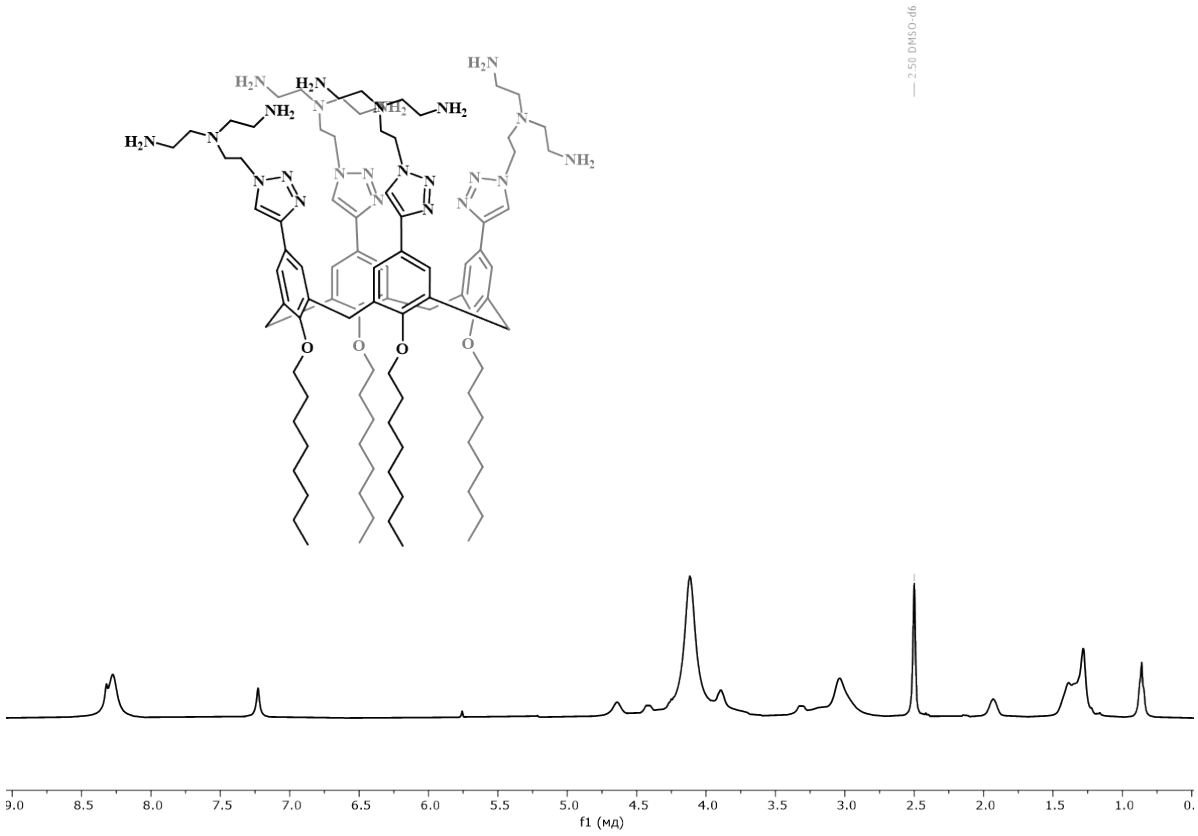
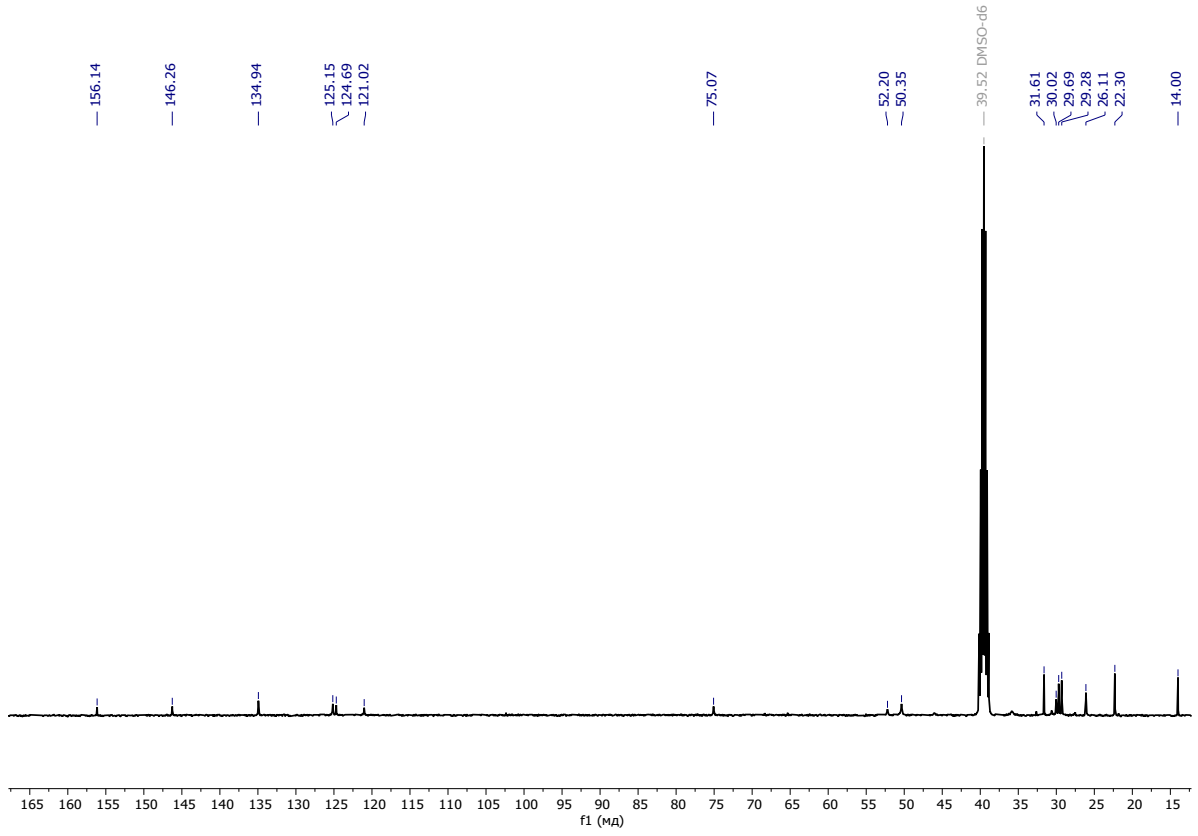


Fig. S8. ^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6), FT-IR and HRESI MS spectra of compound **13**.


2.50 DMSO-d6
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.
f1 (мд)


156.14
146.26
134.94
125.15
124.69
121.02
75.07
52.20
50.35
39.52 DMSO-d6
31.61
30.02
29.69
29.28
26.11
22.30
14.00
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (мд)

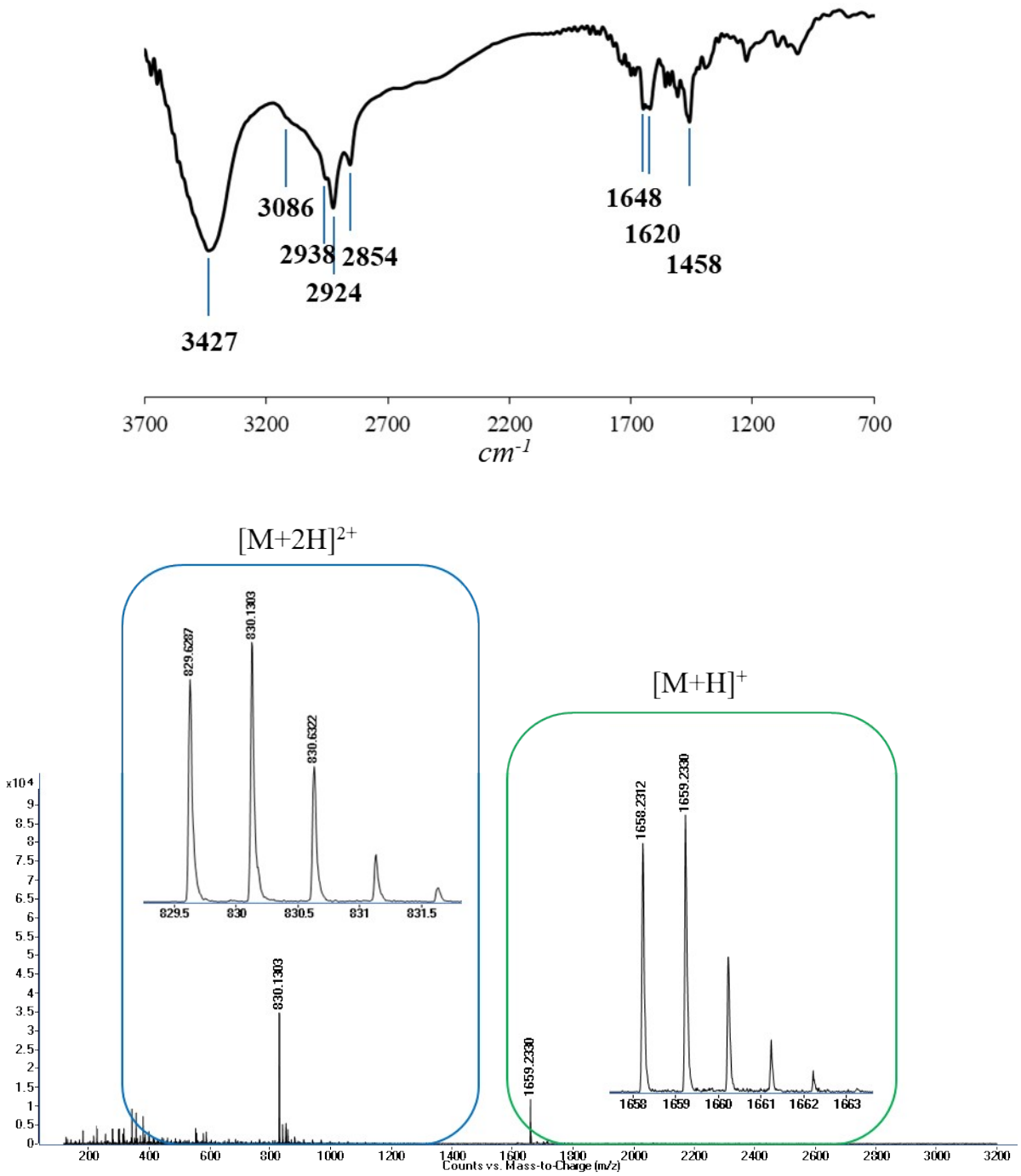
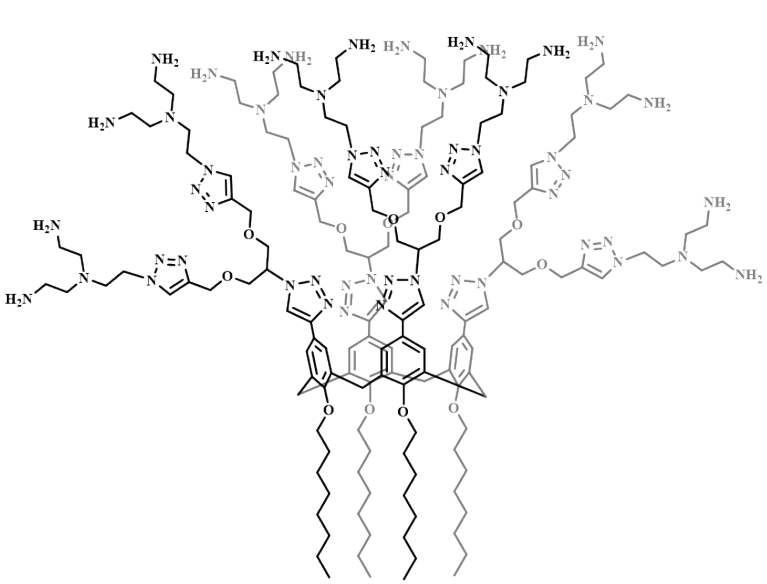
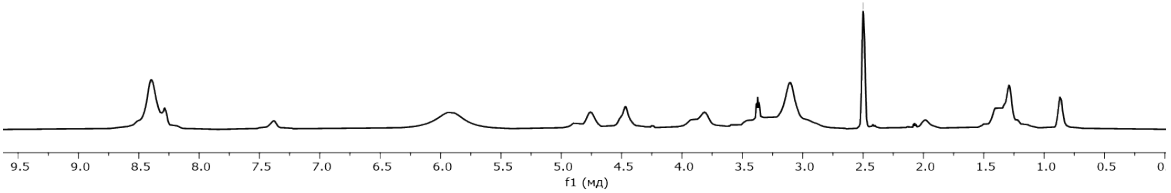
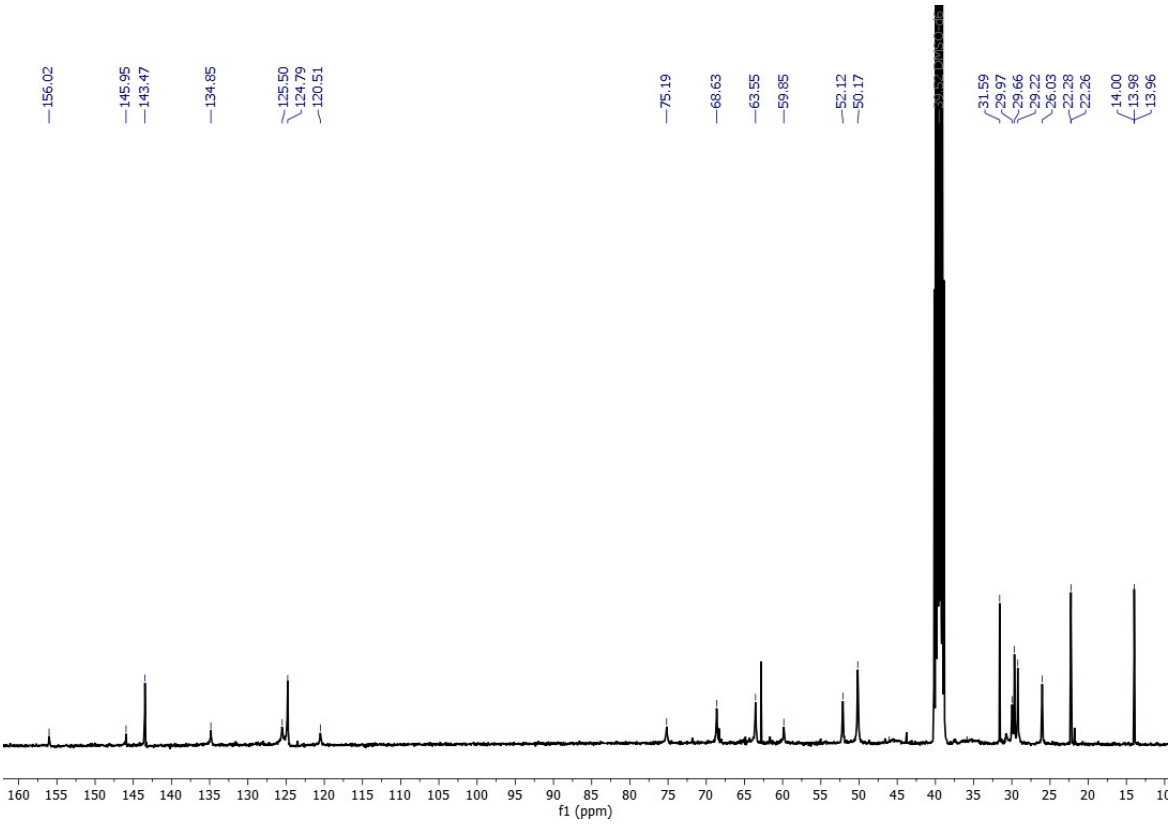


Fig. S9. ^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6), FT-IR and HRESI MS spectra of compound **14**.




2.50 DMSO-d6
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (мд)


156.02
145.95
143.47
134.85
125.50
124.79
120.51
75.19
68.63
63.55
59.85
52.12
50.17
39.52
31.59
29.97
29.66
29.22
26.03
22.28
22.26
14.00
13.98
13.96
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

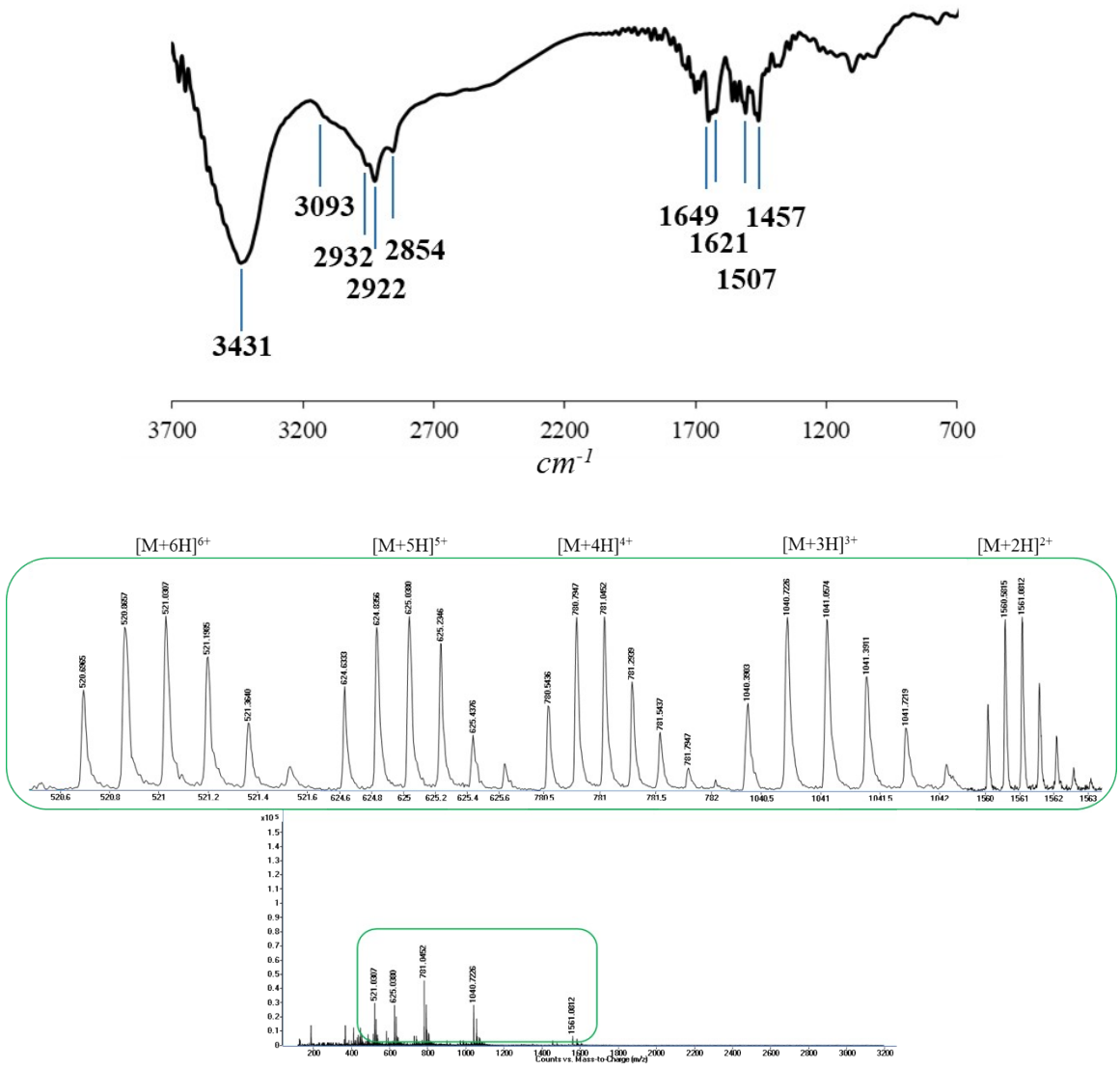


Fig. S10. ^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6), FT-IR and HRESI MS spectra of compound **15**.

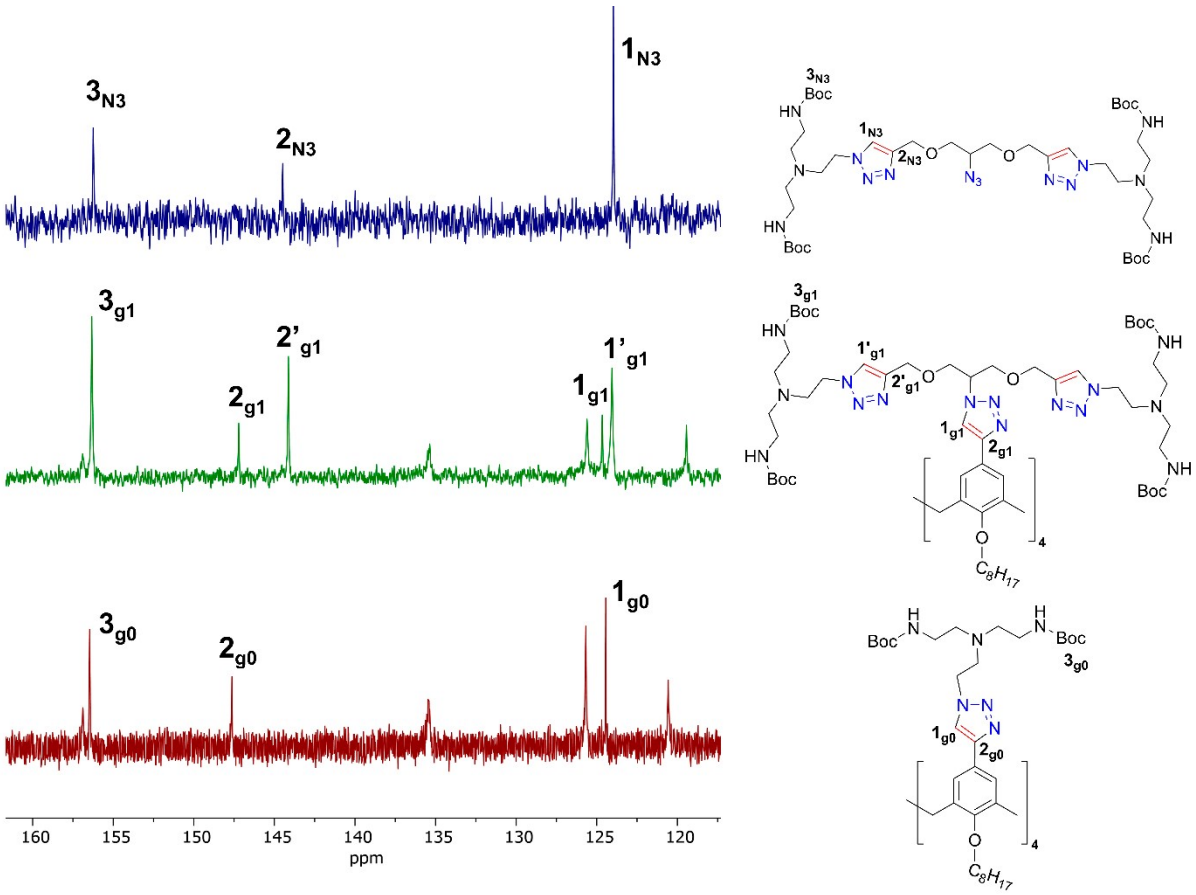


Fig. S11. ^{13}C NMR spectra of dendron **7** and Boc dendrimers **10** and **11** (101 MHz, $CDCl_3$).

	MP AES			
Dendrimer	**Entered dendrimers, g/L**	**Found copper, mg/L**	**Copper content in the sample, mg g^{-1}**	**RSD %**
13	50	0.76	0.015	0.32
15	45	0.85	0.019	0.66

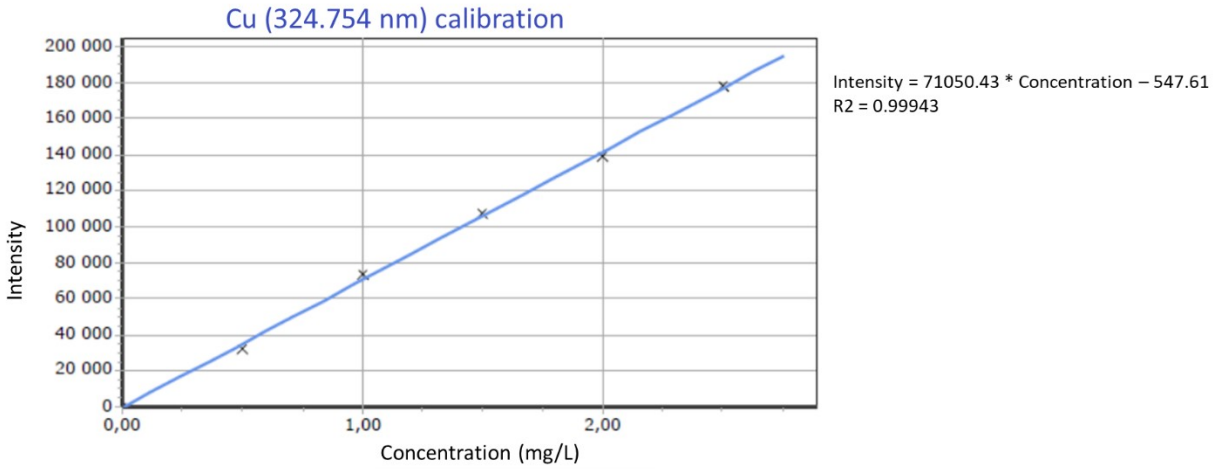


Fig. S12. MIP-AES calibration curve and copper content for compounds 13 and 15.

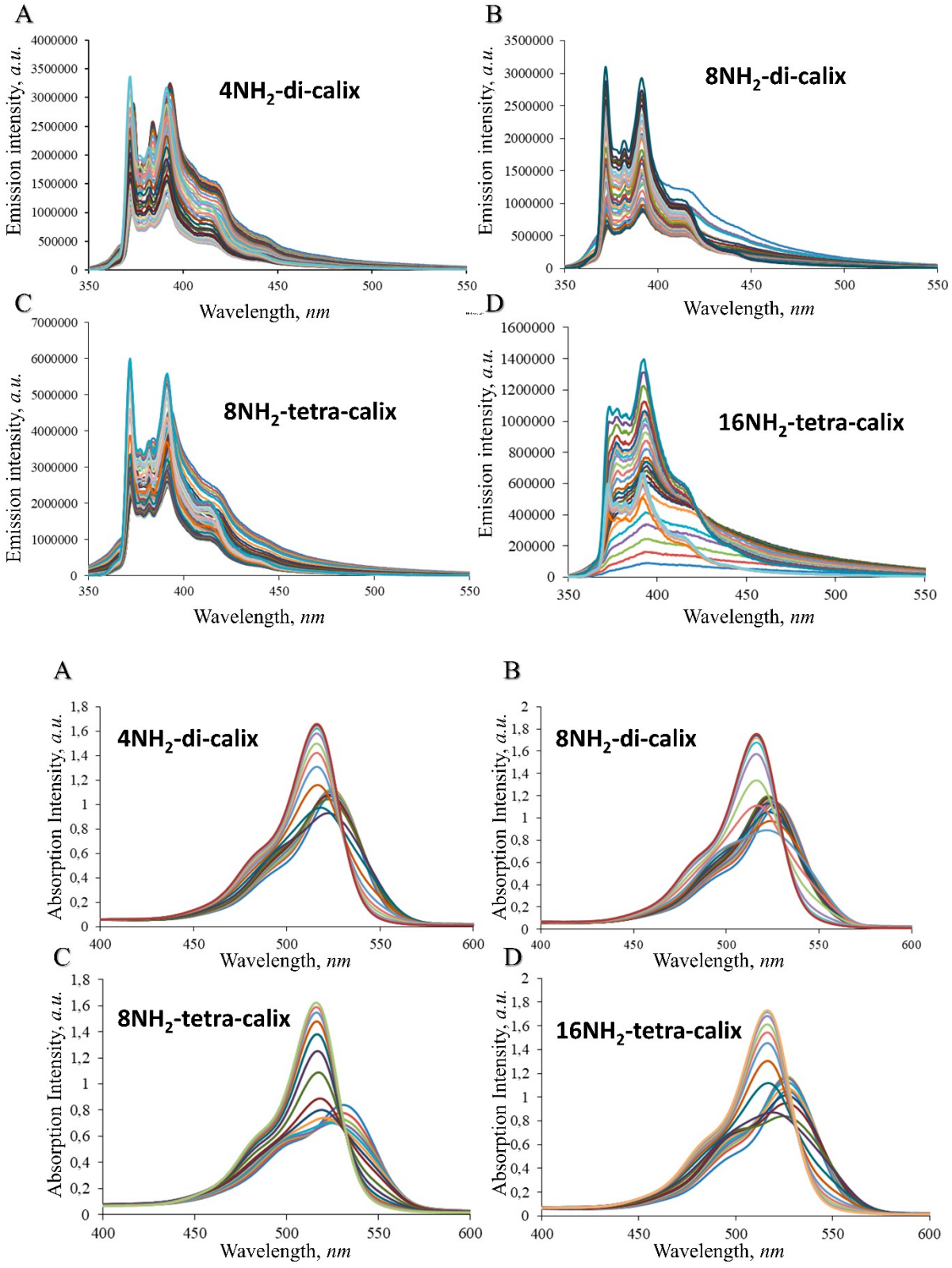
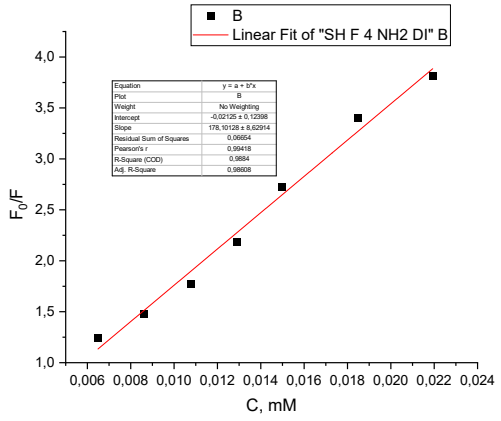


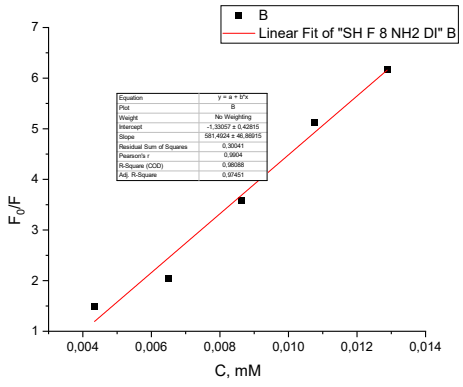
Fig. S13. Fluorescence emission of pyrene in aqueous solutions (upper graphs, A-D) and Eosin Y UV-vis spectra (lower graphs, A-D) in the presence of different amounts of aminocalxarenes. H_2O, 25 ºC, *C(Pyrene) = 1 μM, C(dendrimer) = 0.2-2000 μM; C(Eosin Y) = 20 μM, C(dendrimer) = 0. 3 - 250 μM.*

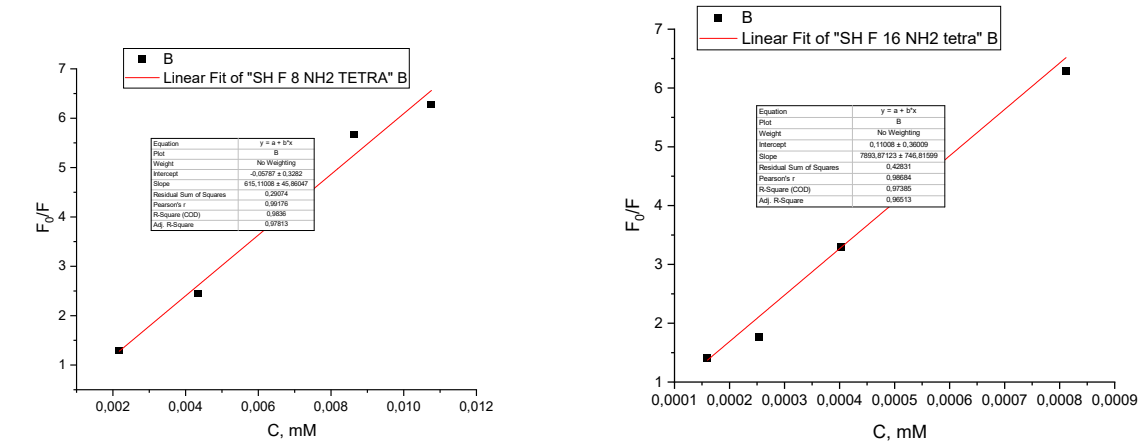
Model	Boltzmann	
Equation	y=A2+(A1-A2)/(1+exp((x-x0)/dx))	
Plot	$4NH_2$-di-calix	$8NH_2$-di-calix
A1	516±0.0756	516±0.109
A2	523±0.0834	523±0.0939
x0	0.0382	0.0359
Adj. R-Square	0.997	0.996

Model	Boltzmann	
Equation	y=A2+(A1-A2)/(1+exp((x-x0)/dx))	
Plot	$8NH_2$-tetra-calix	$16NH_2$-tetra-calix
A1	517±0.115	516±0.0161
A2	532±0.138	526±0.0178
x0	0.00665	0.0067
Adj. R-Square	0.998	0.999

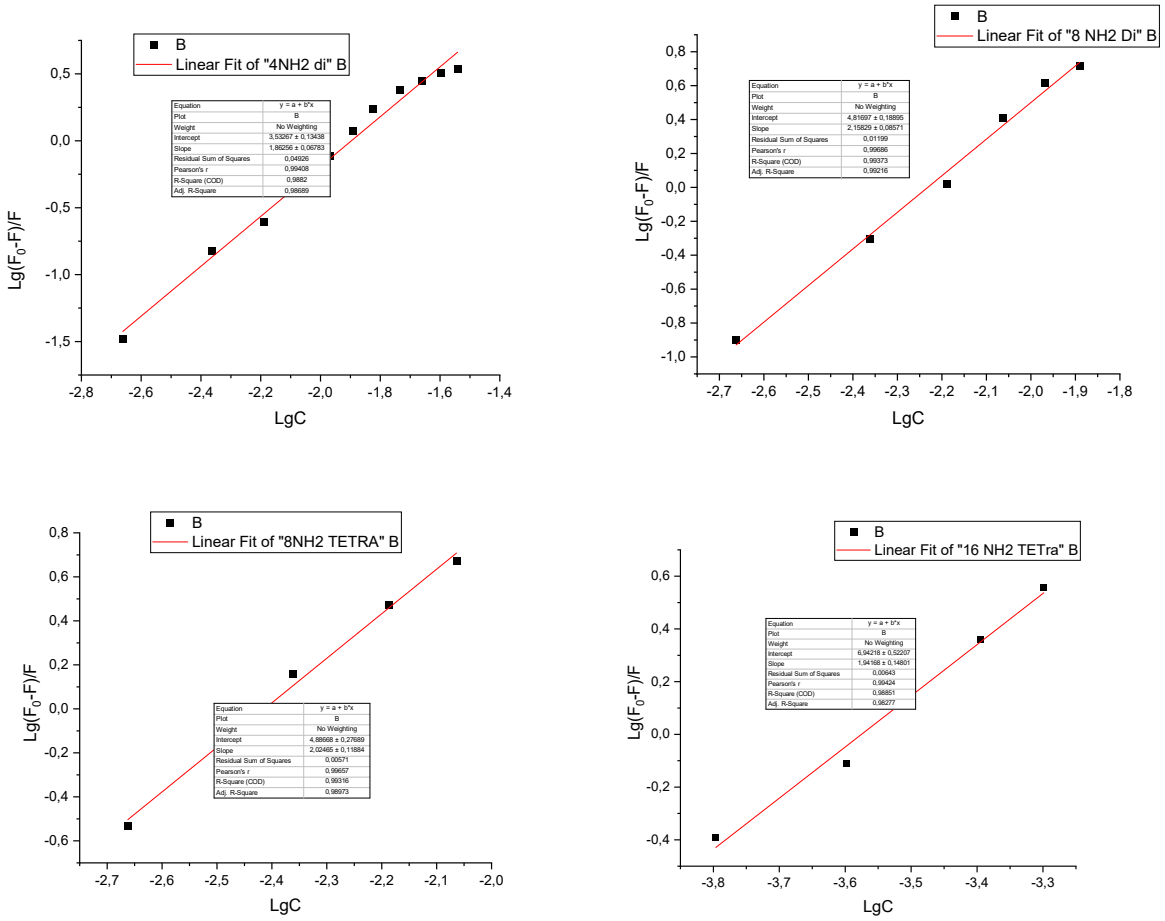
Fig. S14. Calculation data tables of decreasing sigmoid of the Boltzmann type showing the center of the sigmoid x0 (CAC) for amino-dendrimers by Eosin Y absorbance titration.





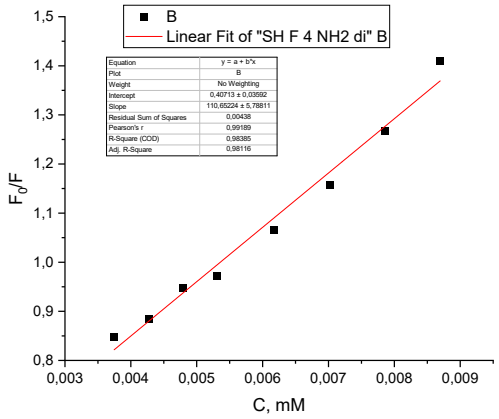


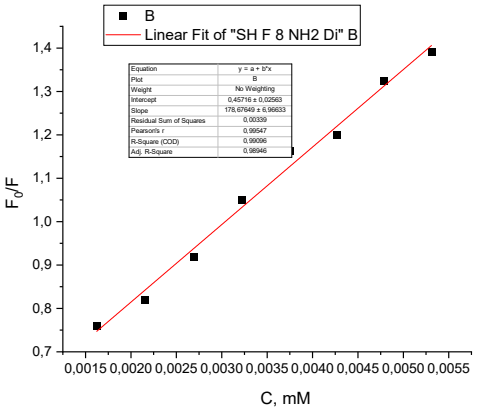
(A)

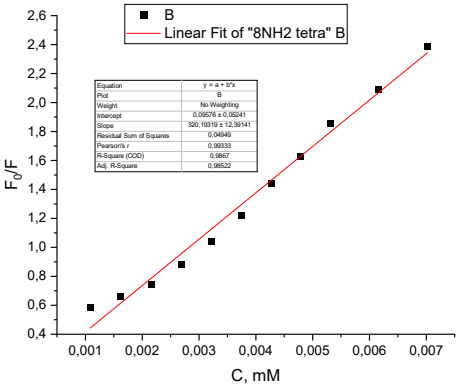


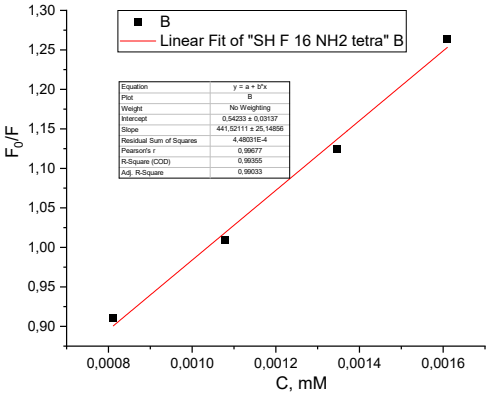
(B)

Fig. S15. (A) Stern-Volmer plots of CT-DNA – EthBr titrated with macrocycles **12-15**. (B) The plots of log ((F_0-F)/F) vs log[macrocycle] for **12-15**

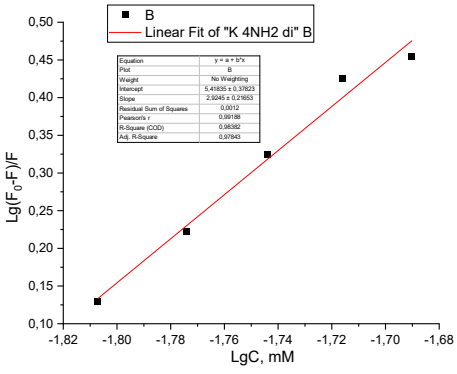

B
Linear Fit of "SH F 4 NH2 di" B
Equation y = a + b*x
Plot B
Weight No Weighting
Intercept 0,40713 ± 0,03592
Slope 110,65224 ± 5,78811
Residual Sum of Squares 0,00438
Pearson's r 0,99189
R-Square (COD) 0,98385
Adj. R-Square 0,98116
F0/F
C, mM

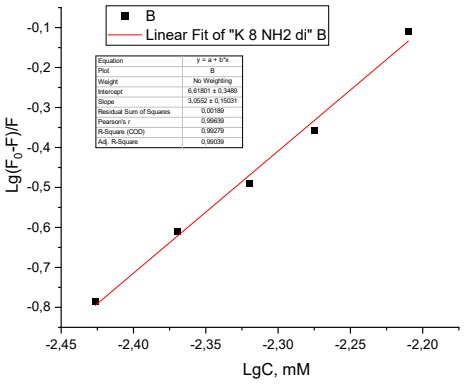

B
Linear Fit of "SH F 8 NH2 Di" B
Equation y = a + b*x
Plot B
Weight No Weighting
Intercept 0,45716 ± 0,02563
Slope 178,67649 ± 6,96633
Residual Sum of Squares 0,00339
Pearson's r 0,99547
R-Square (COD) 0,99096
Adj. R-Square 0,98946
F0/F
C, mM

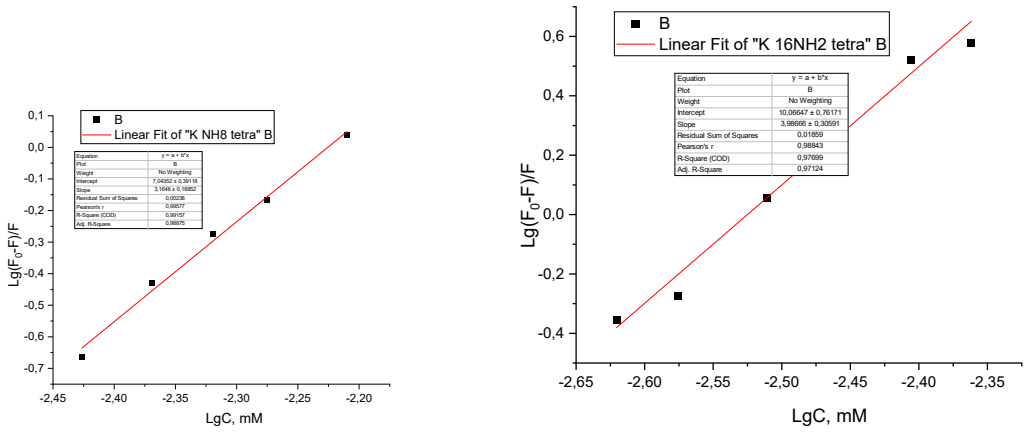

B
Linear Fit of "8NH2 tetra" B
Equation y = a + b*x
Plot B
Weight No Weighting
Intercept 0,09576 ± 0,05241
Slope 320,19319 ± 12,39141
Residual Sum of Squares 0,04949
Pearson's r 0,99333
R-Square (COD) 0,9867
Adj. R-Square 0,98522
F0/F
C, mM


B
Linear Fit of "SH F 16 NH2 tetra" B
Equation y = a + b*x
Plot B
Weight No Weighting
Intercept 0,54233 ± 0,03137
Slope 441,52111 ± 25,14856
Residual Sum of Squares 4,48031E-4
Pearson's r 0,99677
R-Square (COD) 0,99355
Adj. R-Square 0,99033
F0/F
C, mM

(A)


B
Linear Fit of "K 4NH2 di" B
Equation y = a + b*x
Plot B
Weight No Weighting
Intercept 5,41835 ± 0,37623
Slope 2,9245 ± 0,21653
Residual Sum of Squares 0,0012
Pearson's r 0,99198
R-Square (COD) 0,98382
Adj. R-Square 0,97843
Lg(F0-F)/F
LgC, mM


B
Linear Fit of "K 8 NH2 di" B
Equation y = a + b*x
Plot B
Weight No Weighting
Intercept 6,61801 ± 0,3489
Slope 3,0592 ± 0,15031
Residual Sum of Squares 0,00189
Pearson's r 0,99639
R-Square (COD) 0,99279
Adj. R-Square 0,99039
Lg(F0-F)/F
LgC, mM



(B)

Fig. S16. (A) Stern-Volmer plots of CT-DNA – DAPI titrated with macrocycles **12-15**. (B) The plots of log ((F_0-F)/F) vs log[macrocycle] for **12-15**

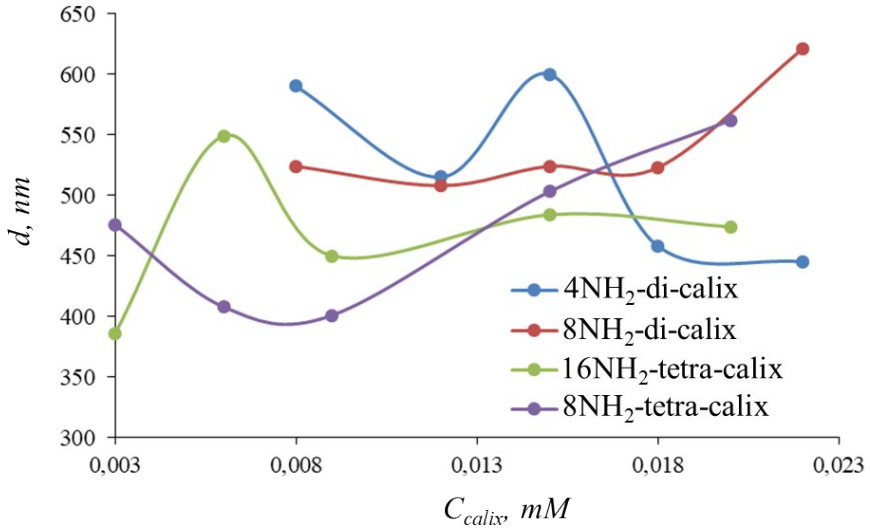


Fig. S17. The average diameter *vs* the concentration of amino-dendrimers.

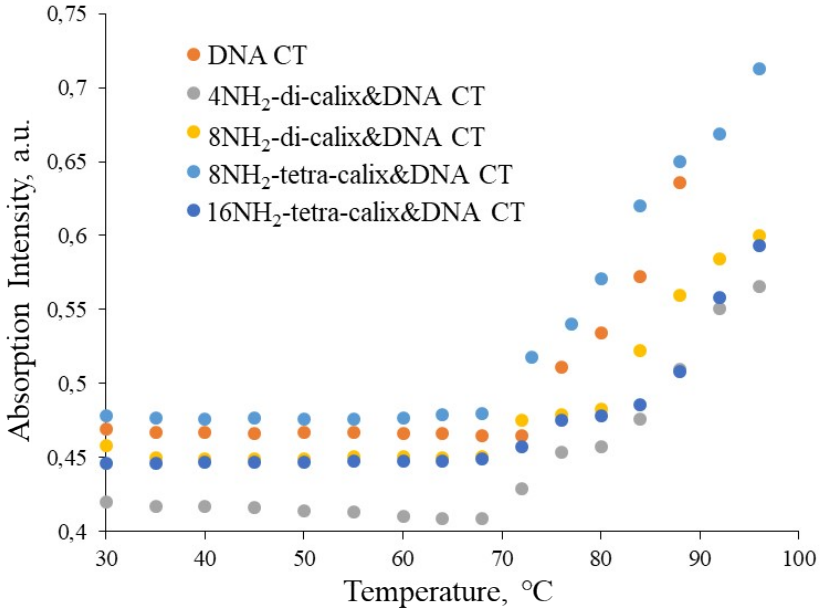


Fig. S18. Absorbance *vs* temperature in a CT DNA denaturation experiment. [DNA CT] = 45 μM, [dendrimer] = 1 μM.

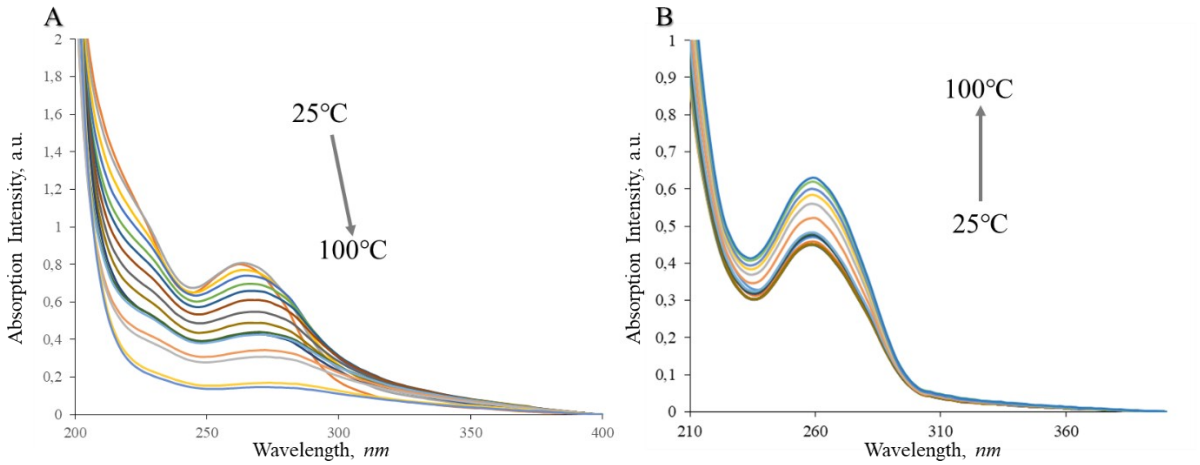


Fig. S19. UV-vis spectra of CT DNA in presence of $8NH_2$-tetra-calix at 18 μM (A) and 1 μM (B).