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Supporting Information

for

Dynamic DNA architectures: Spontaneous DNA strand exchange and self-sorting driven by perylene bisimide interactions

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1. Materials and Methods

All chemicals and solvents were purchased from abcr, Alfa Aesar, TCI and Sigma Aldrich and were used without further purification. Reagents for oligonucleotide synthesis and controlled pore glass (CPG) (1 µmol) were purchased from Applied Biosystems and Glen Research. Spectroscopic measurements were recorded in 10 mM Na-Pi buffer solution (pH = 7) with 250 mM NaCl using quartz glass cuvettes (10 mm). Absorption spectra were recorded on a Varian Cary 100 spectrometer equipped with a 6×6 cell changer unit. All spectra were recorded at 20 °C. Fluorescence was measured with a Jobin-Yvon Fluoromax 3 fluorimeter with a step width of 1 nm and an integration time of 0.2 s. All spectra were recorded with an excitation and emission bandpass of 3 nm and are corrected for Raman emission from the buffer solution. MALDI-TOF mass spectra were measured at the Karlsruhe Institute of Technology on a BIFLEX-IV from Bruker Daltonics in negative ionization mode. CD data were collected with a JASCO J-815 spectropolarimeter equipped with a Julabo FP35 Refrigerated/Heating Circulator. The spectra represent the average of two accumulations recorded between wavelengths of 850 and 230 nm at 0.5 nm intervals, spectral band width of 5 nm, response time of 8 s and a scan-rate of 20 nm/min.

2. Synthetic and experimental procedures

The Oligonucleotides were prepared on an Expedite 8909 synthesizer from Applied Biosystems using standard phosphoramidite chemistry. For phosphoramidite 1 the coupling time was enhanced from 96 to 460 s, for phosphoramidtes 2 and 3 to 2060 s and for phosphoramidte 4 to 1060 s. To avoid precipitation during the DNA synthesis, 1-4 were dissolved in CH_2Cl_2 (0.1 M).
After preparation, the oligonucleotides were cleaved off the resin and deprotected by treatment with conc. NH_4OH at 55 °C for 18 h. The oligonucleotides were purified by reverse phase HPLC using the following conditions: A = NH_4OAc buffer (50 mM, pH = 6.5); B = acetonitrile; flow rate 2.5 mL/min, UV/vis detection at 260 nm, 550 nm, 600 nm and 700 nm (optional to the sequence; self-complementary strands at 40 °C). Finally the oligonucleotides were lyophilized and quantified by their absorbance in DMSO at 494 nm (1), 572 nm (2), 547 nm (3) or 438 nm (4) on a Varian Cary 100 spectrometer. Duplexes were prepared by heating the modified oligonucleotides in presence of no, for self-complementary strands, or 1.2 equiv. of unmodified complementary strand to 90 °C, followed by cooling to room temperature. All melting temperatures were determined by the change of absorbance at 260 nm using the following conditions: 2.5 µM dsDNA, 10 mM NaPi buffer, 250 mM NaCl, heating/cooling rate 0.7 °C/min, data interval 0.5 °C.

1 and *N*-(2-Ethylhexyl)-*N'*-[3-*O*-dimethoxytrityl-2-(*S*)-hydroxypropyl]-1,7-dibromoperylene-3,4:9,10-tetracarboxylic Acid Bisimide were synthesized according to literature procedure.[1, 2]

***N*-(2-Ethylhexyl)-*N*'-(3-*O*-dimethoxytrityl-2-(*S*)-hydroxypropyl)-1,7-dimethoxyperylene-3,4:9,10-tetracarboxylic Acid Bisimide (2):**
A mixture of 200 mg *N*-(2-Ethylhexyl)-*N'*-[3-*O*-trityl-2-(*S*)-hydroxypropyl]-1,7-dibromoperylene-3,4:9,10-tetracarboxylic Acid Bisimide (0.19 mmol, 1.0 equiv.), 1.6 mL methanol and 266 mg K_2CO_3 (1.9 mmol, 10 equiv.) in 20 mL dry DMF was heated to 120 °C for 1 h. The solvent was removed under reduced pressure and the residue was dissolved in 10 mL CH_2Cl_2. The organic layer was washed with H_2O (3×10 mL) and then dried over Na_2SO_4. Column chromatography (CH_2Cl_2:acetone 20:1) yielded a purple solid (151 mg, 0.16 mmol, 84%). R_f (CH_2Cl_2:acetone 20:1) = 0.53.

***N*-(2-Ethylhexyl)-*N*'-(3-*O*-dimethoxytrityl-2-(*S*)-[(2-cyanoethoxy)-*N,N*-(di*iso*propylamino)-phosphanyloxy]-propyl)-1,7-dimethoxyperylene-3,4:9,10-tetracarboxylic Acid Bisimide:**
108 mg **3** (0.12 mmol, 1.0 equiv.) were stirred in 5.0 mL dry CH_2Cl_2 and 90 µL dry DIPEA (65 mg, 0.89 mmol, 6.0 equiv.) for 15 min. Then 128 µL 2-Cyanoethyl *N,N*-di*iso*propylchlorophosphoramidite (136 mg, 0.58 mmol, 5.0 equiv.) were added. After 5 h the dark reddish solution was purified through column chromatography (CH_2Cl_2:acetone 20:1). The solution was concentrated to dryness and lyophilized with 1.5 mL benzene. The resulting purple foam (87 mg, 0.076 mmol, 66%) was dissolved in CH_2Cl_2 and used for automated DNA synthesis. R_f (CH_2Cl_2:acetone 20:1) ≈ 0.85.

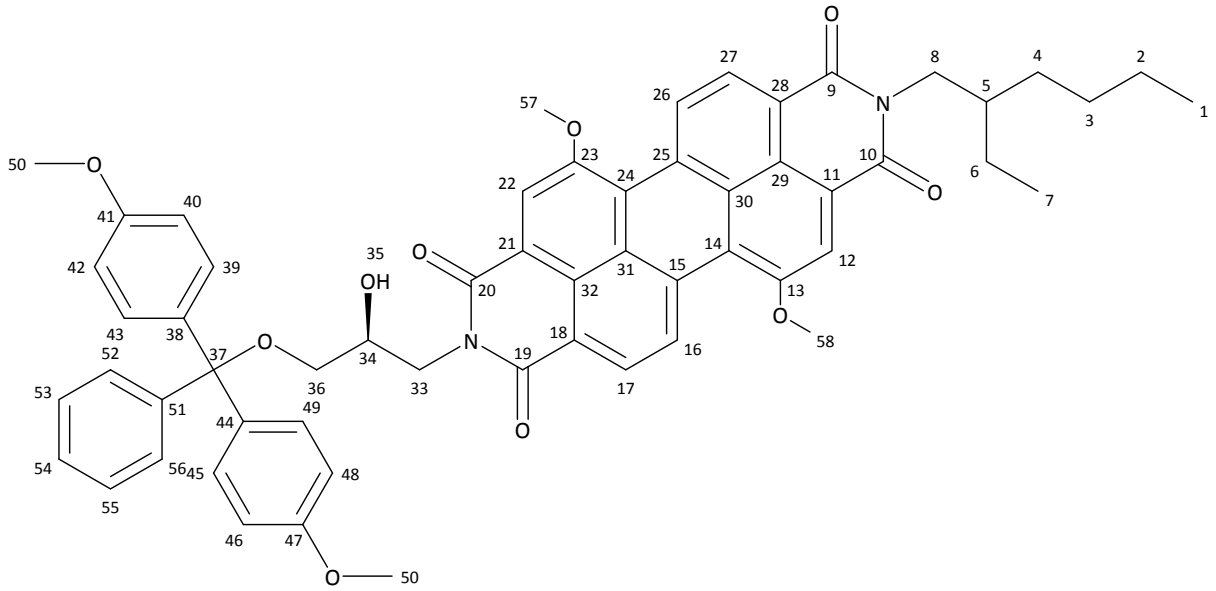
***N*-(2-Ethylhexyl)-*N*'-(3-*O*-dimethoxytrityl-2-(*S*)-hydroxypropyl)-1,7-diphenoxyperylene-3,4:9,10-tetracarboxylic Acid Bisimide (3):**
A mixture of 440 mg *N*-(2-Ethylhexyl)-*N'*-[3-*O*-trityl-2-(*S*)-hydroxypropyl]-1,7-dibromoperylene-3,4:9,10-tetracarboxylic Acid Bisimide (0.42 mmol, 1.0 equiv.), 321 mg phenol (3.4 mmol, 8.0 equiv.) and 593 mg K_2CO_3 (4.3 mmol, 10 equiv.) in 10 mL dry DMF was heated to 120 °C for 20 min. After cooling down to rt 10 mL H_2O were added and stirred for 15 min. The dark red precipitate was filtered and washed with H_2O (3×10 mL). The residue was dissolved in 10 mL CH_2Cl_2 and purified via column chromatography (CH_2Cl_2:acetone 50:1). The purification yielded a purple solid (378 mg, 0.36 mmol, 84%). R_f (CH_2Cl_2:acetone 20:1) = 0.65.

***N*-(2-Ethylhexyl)-*N*'-(3-*O*-dimethoxytrityl-2-(*S*)-[(2-cyanoethoxy)-*N,N*-(di*iso*propylamino)-phosphanyloxy]-propyl)-1,7-diphenoxyperylene-3,4:9,10-tetracarboxylic Acid Bisimide:**
92 mg **3** (0.087 mmol, 1.0 equiv.) were stirred in 5.0 mL dry CH_2Cl_2 and 80 µL dry DIPEA (58 mg, 0.57 mmol, 6.6 equiv.) for 15 min. Then 100 µL 2-Cyanoethyl *N,N*-di*iso*propylchlorophosphoramidite (106 mg, 0.45 mmol, 5.2 equiv.) were added. After 4 h the dark reddish solution was purified through column chromatography (CH_2Cl_2:acetone 20:1). The solution was concentrated to dryness and lyophilized with 1.5 mL benzene. The resulting purple foam (78 mg, 0.065 mmol, 71%) was dissolved in CH_2Cl_2 and used for automated DNA synthesis. R_f (CH_2Cl_2:acetone 20:1) ≈ 0.85.

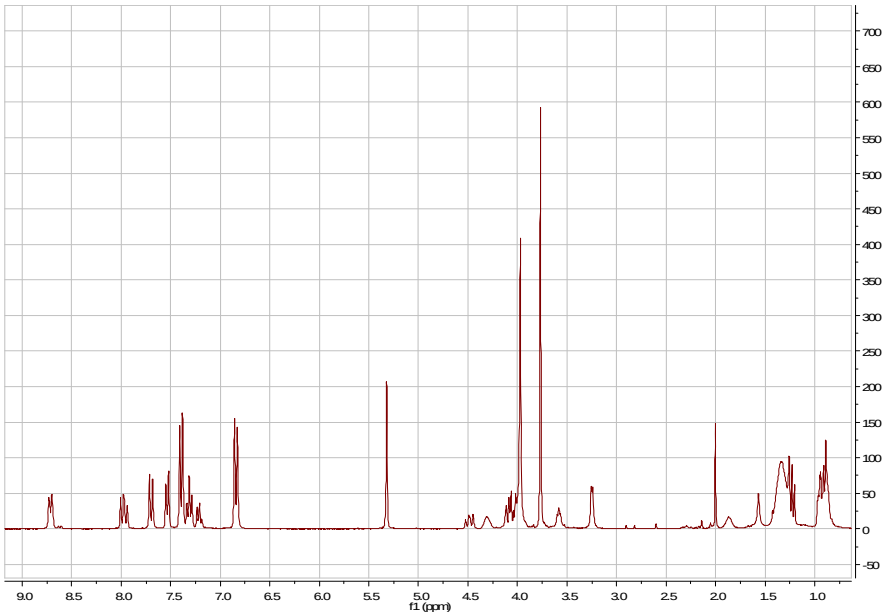
***N*-(2-Ethylhexyl)-*N*'-(3-*O*-dimethoxytrityl-2-(*S*)-hydroxypropyl)-1,7-di-(*N'',N'''*-dimethylamino)-perylene-3,4:9,10-tetracarboxylic Acid Bisimide (4):**
A mixture of 195 mg *N*-(2-Ethylhexyl)-*N'*-[3-*O*-trityl-2-(*S*)-hydroxypropyl]-1,7-dibromoperylene-3,4:9,10-tetracarboxylic Acid Bisimide (0.19 mmol, 1.0 equiv.), 1.0 mL pyridine and 5.0 mL dimethylamine solution (2.0 M in THF, 10 mmol, 53 equiv.) in 10 mL dry DMF was heated to 90 °C for 72 h. The solvent was removed under reduced pressure and the residue was dissolved in 10 mL CH_2Cl_2 and purified via column chromatography (CH_2Cl_2:acetone 20:1). The purification yielded a green solid (73 mg, 0.076 mmol, 40%). R_f (CH_2Cl_2:acetone 20:1) = 0.48.

***N*-(2-Ethylhexyl)-*N*'-(3-*O*-dimethoxytrityl-2-(*S*)-[(2-cyanoethoxy)-*N,N*-(di*iso*propylamino)-phosphanyloxy]-propyl)-1,7-di-(*N'',N'''*-dimethylamino)-perylene-3,4:9,10-tetracarboxylic Acid Bisimide:**
141 mg **4** (0.15 mmol, 1.0 equiv.) were stirred in 5.0 mL dry CH_2Cl_2 and 123 µL dry DIPEA (88.8 mg, 0.88 mmol, 6.0 equiv.) for 15 min. Then 163 µL 2-Cyanoethyl *N*,*N*-di*iso*propylchlorophosphoramidite (173 mg, 0.73 mmol, 5.0 equiv.) were added. After 2 h the dark green solution was purified through column chromatography (CH_2Cl_2:acetone 20:1). The solution was concentrated to dryness and lyophilized with 1.5 mL benzene. The resulting green foam (93 mg, 0.080 mmol, 55%) was dissolved in CH_2Cl_2 and used for automated DNA synthesis. R_f (CH_2Cl_2:acetone 20:1) ≈ 0.85.

Compound 2

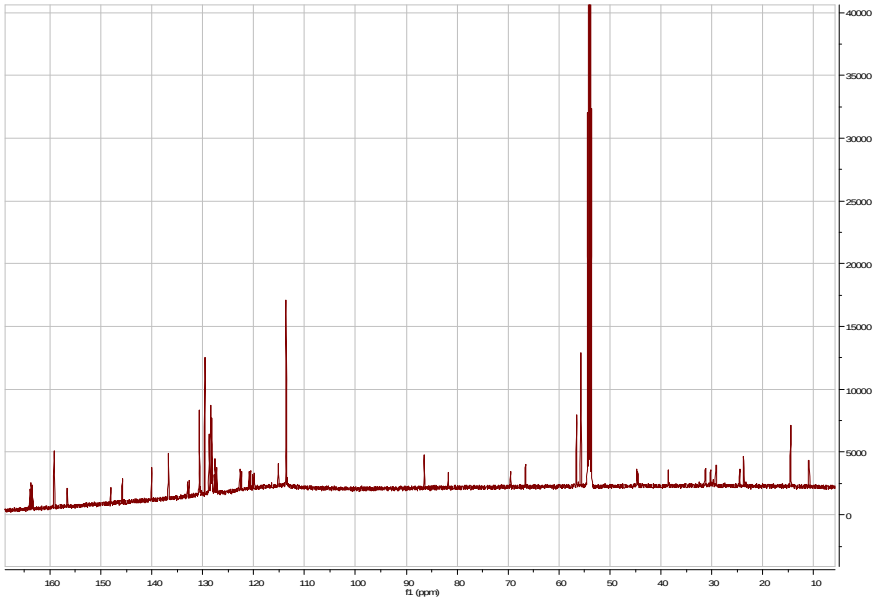


^{1}H-NMR



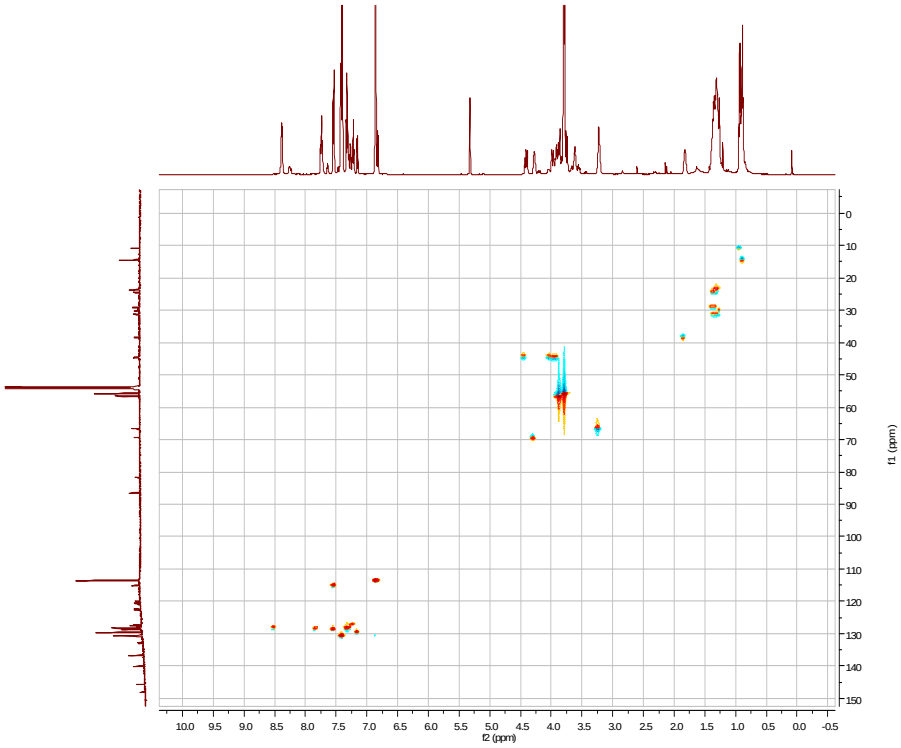
(600 MHz, CD_2Cl_2) δ 8.71 (m, 2H, 16/26), 7.99 (d, *J* = 8.5 Hz, 1H, 17), 7.95 (d, *J* = 8.5 Hz, 1H, 27), 7.71 (s, 1H, 22), 7.68 (s, 1H, 12), 7.54 (d, *J* = 7.7 Hz, 2H, 52/56) , 7.40 (d, *J* = 8.4 Hz, 4H, 39/43/45/49), 7.31 (t, *J* = 7.7 Hz, 2H, 53/55), 7.22 (t, *J* = 7.7 Hz, 1H, 54), 6.84 (d, *J* = 8.4 Hz, 4H, 40/42/46/48), 4.48 (dd, *J* = 13.2, 9.5 Hz, 1H, 33a), 4.33-4.26 (m, 1H, 34), 4.12-4.00 (m, 3H, 8/33b), 3.97 (s, 6H, 57/58), 3.77 (s, 6H, 50), 3.58-3.52 (bs, 1H, 35), 3.24-3.18 (m, 2H, 36), 1.87-1.81 (m, 1H, 5), 1.40-1.30 (m, 8H, 2/3/4/6), 0.97-0.80 (m, 3H, 7), 0.89-0.85 (m, 3H, 1).

^{13}C-NMR

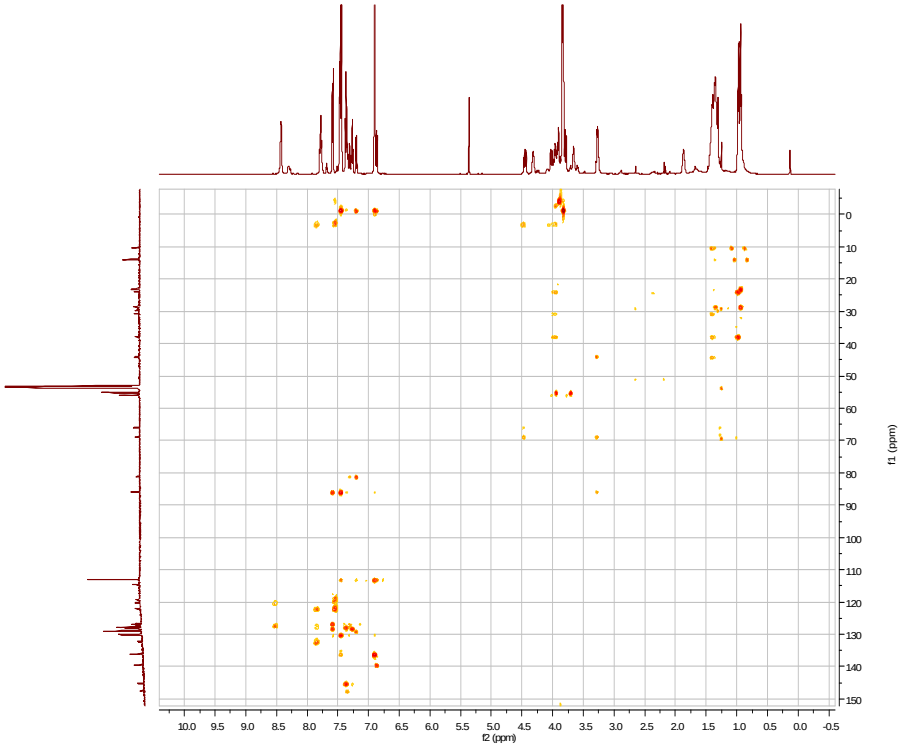


(151 MHz, CD_2Cl_2) δ = 163.9(19), 163.7 (9), 163.6(20), 163.4 (10), 159.3 (41/47), 156.5 (13/23), 145.8 (51), 136.7 (40/42/46/48), 133.0, 132.7 (arom.), 130.7 (39/43/45/49), 128.7 (52/56), 128.4 (53/55), 128.3 (16/26), 128.2, 127.7, 127.4, 127.3 (arom.), 127.2 (54), 122.7, 122.6, 122.4, 120.9, 120.6, 120.1 (arom.), 115.1 (12/22), 113.6 (40/42/46/48), 86.5 (37), 69.5 (34), 66.6 (36), 56.6 (57/58), 55.7 (50), 44.7 (8), 44.5 (33), 38.4 (5), 31.2 (4), 29.3 (3), 24.5 (6), 23.7 (2), 14.5 (1), 10.8 (7).

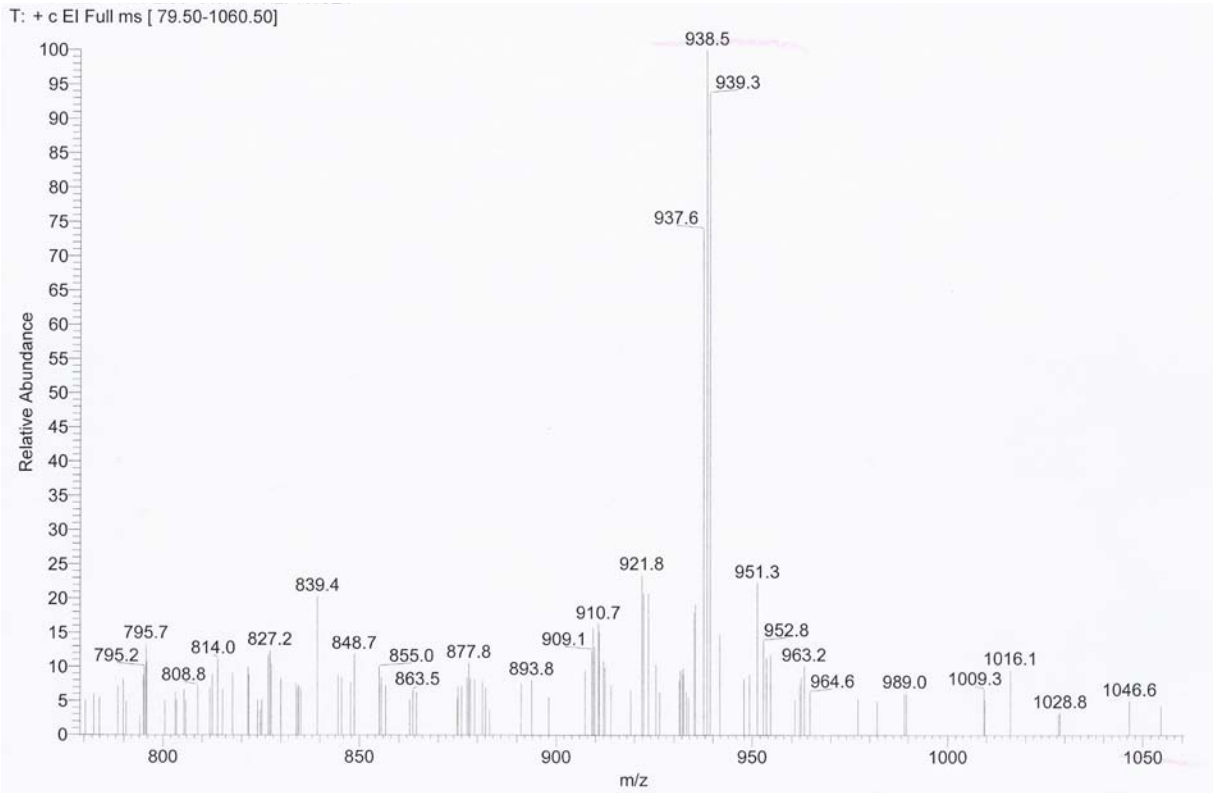
HSQC



HMBC


f2 (ppm)
f1 (ppm)

FAB-MS


T: + c EI Full ms [79.50-1060.50]
Relative Abundance
m/z
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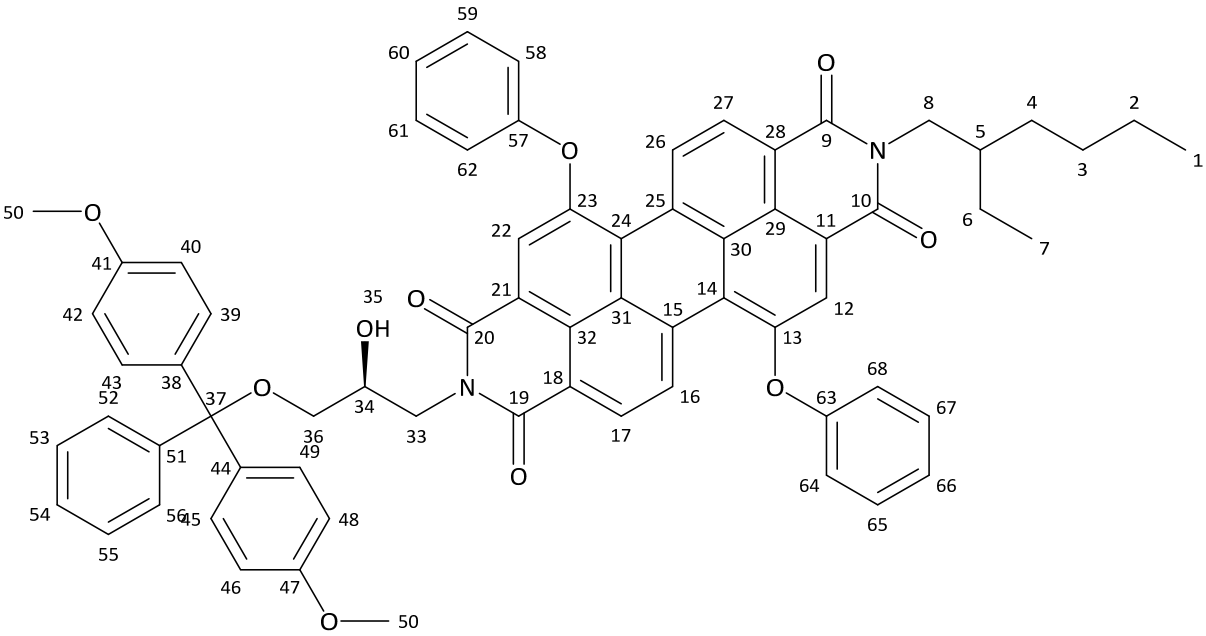
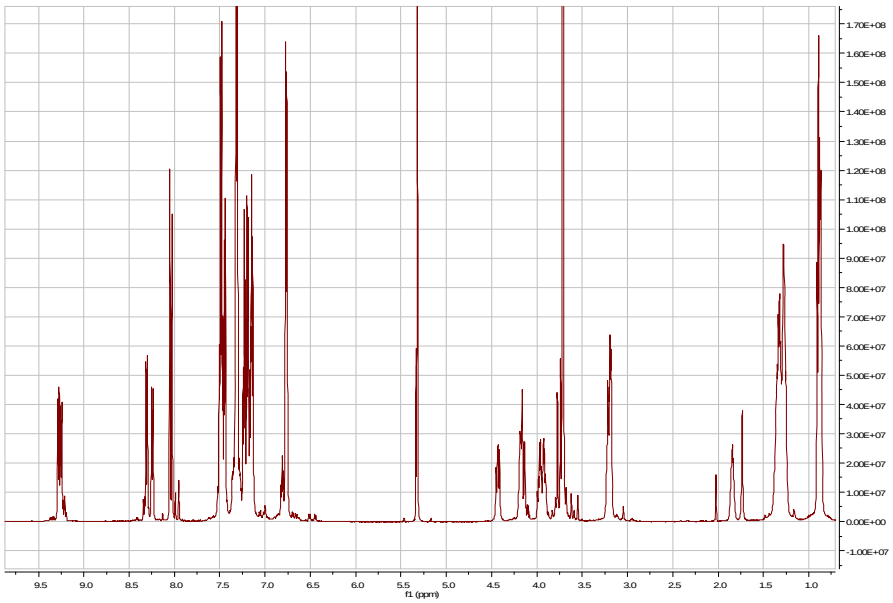
939.3
937.6
921.8
951.3
839.4
910.7
795.7
795.2
814.0
827.2
848.7
855.0
877.8
909.1
952.8
963.2
808.8
863.5
893.8
964.6
989.0
1009.3
1016.1
1028.8
1046.6

Compound 3

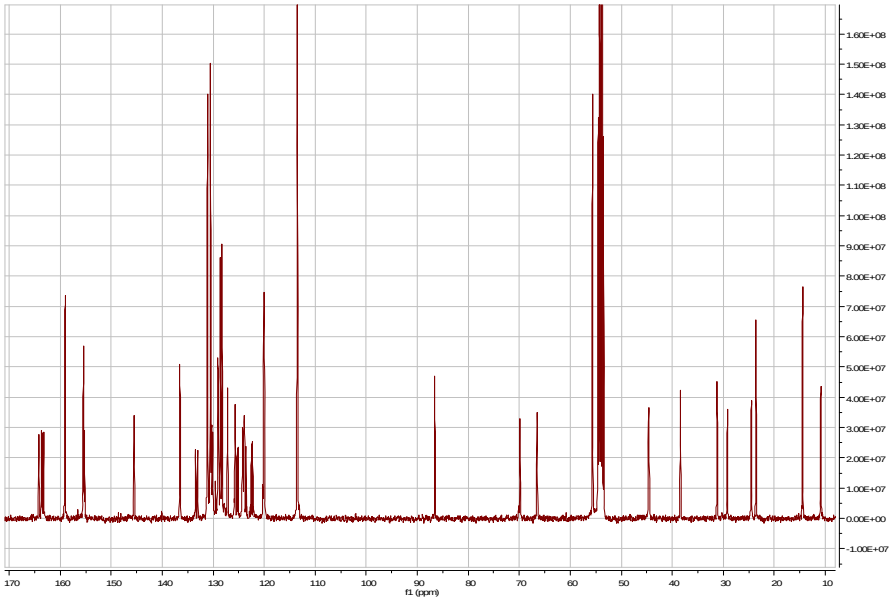


^{1}H-NMR



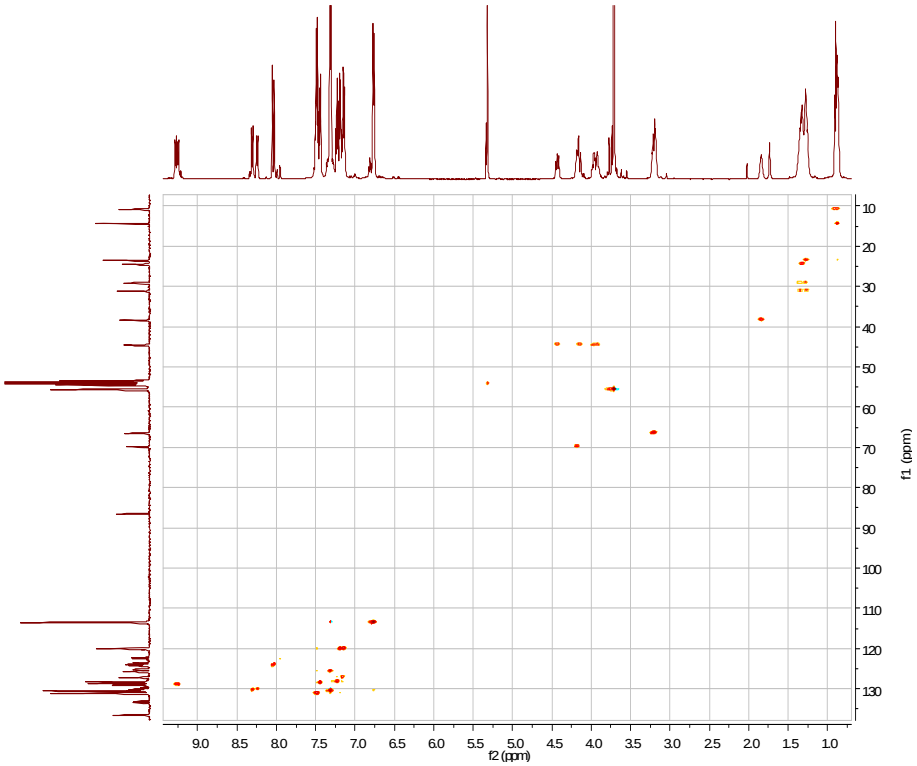
(600 MHz, CD_2Cl_2) δ 9.28 (d, *J* = 8.2 Hz, 1H, 16), 9.25 (d, *J* = 8.2 Hz, 1H, 26), 8.31 (d, *J* = 8.2 Hz, 1H, 17), 8.24 (d, *J* = 8.2 Hz, 1H, 27), 8.05 (s, 1H, 22), 8.03 (s, 1H, 12), 7.51-7.46 (m, 4H, 59/61/65/67), 7.45 (d, *J* = 7.9 Hz, 2H, 52/56), 7.34-7.30 (m, 6H, 39/43/45/49/60/66), 7.23 (t, *J* = 7.6 Hz, 2H, 53/55), 7.20-7.13 (m, 5H, 54/58/62/64/68), 6.78-6.75 (m, 4H, 40/42/46/48), 4.43 (dd, *J* = 13.6, 8.3 Hz, 1H, 33a), 4.20-4.15 (m, 2H, 33b/34), 3.99 – 3.94 (m, 1H, 8a), 3.94-3.90 (m, 1H, 8b), 3.71 (s, 6H, 50), 3.24-3.17 (m, 3H, 35/36), 1.84 (p, *J* = 6.6 Hz, 1H, 5), 1.37 – 1.26 (m, 8H, 2/3/4/6), 0.91 – 0.86 (m, 6H, 1/7).

^{13}C-NMR

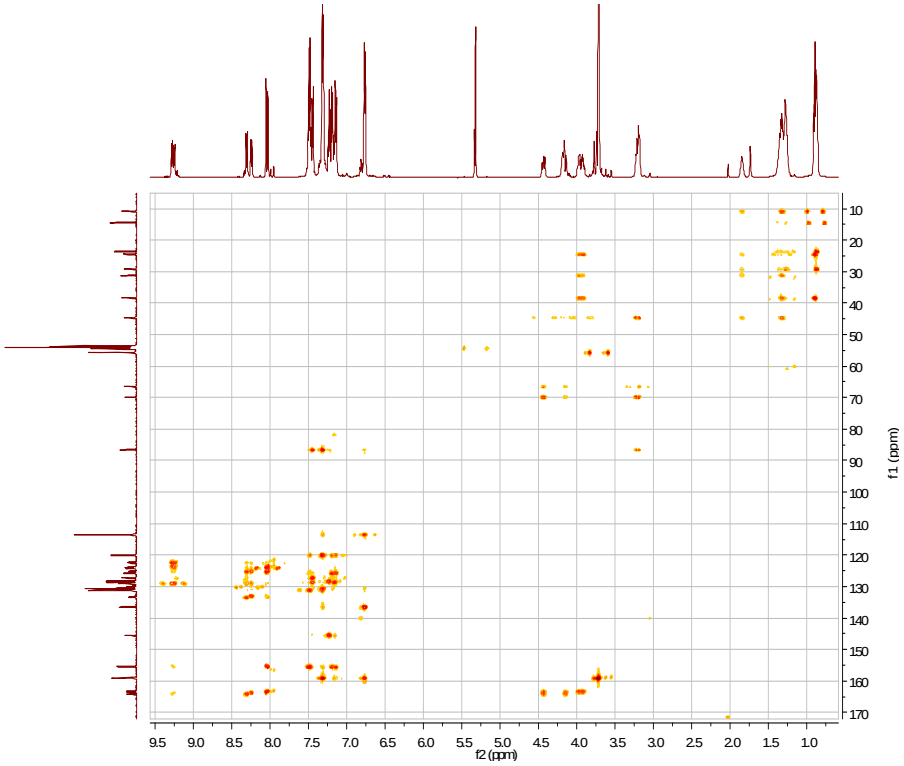


(100 MHz, CD_2Cl_2) δ = 164.2(19), 163.7(9), 163.5(20), 163.2(10), 159.1 (41/47), 155.5 (13/57/63), 155.3 (23), 145.5 (51), 136.5 (38/44), 133.4, 133.0 (arom.), 131.1 (59/61/65/67), 130.5 (39/43/45/49), 130.3 (17), 130.1 (27), 129.1 (26), 129.0 (16), 128.6 (52/56), 128.3 (53/55), 127.2 (54), 125.7 (60/66), 125.3, 125.1, 124.3, 124.2 (arom.), 124.2 (22), 124.0 (12), 123.9, 123.6, 122.5, 122.3 (arom.), 120.0 (58/62/64/68), 113.5 (40/42/46/48), 86.6 (37), 69.9 (34), 66.5 (36), 55.7 (50), 44.6 (8/33), 38.4 (5), 31.2 (4), 29.2 (3), 24.5 (6), 23.6 (2), 14.4 (1), 10.9 (7).

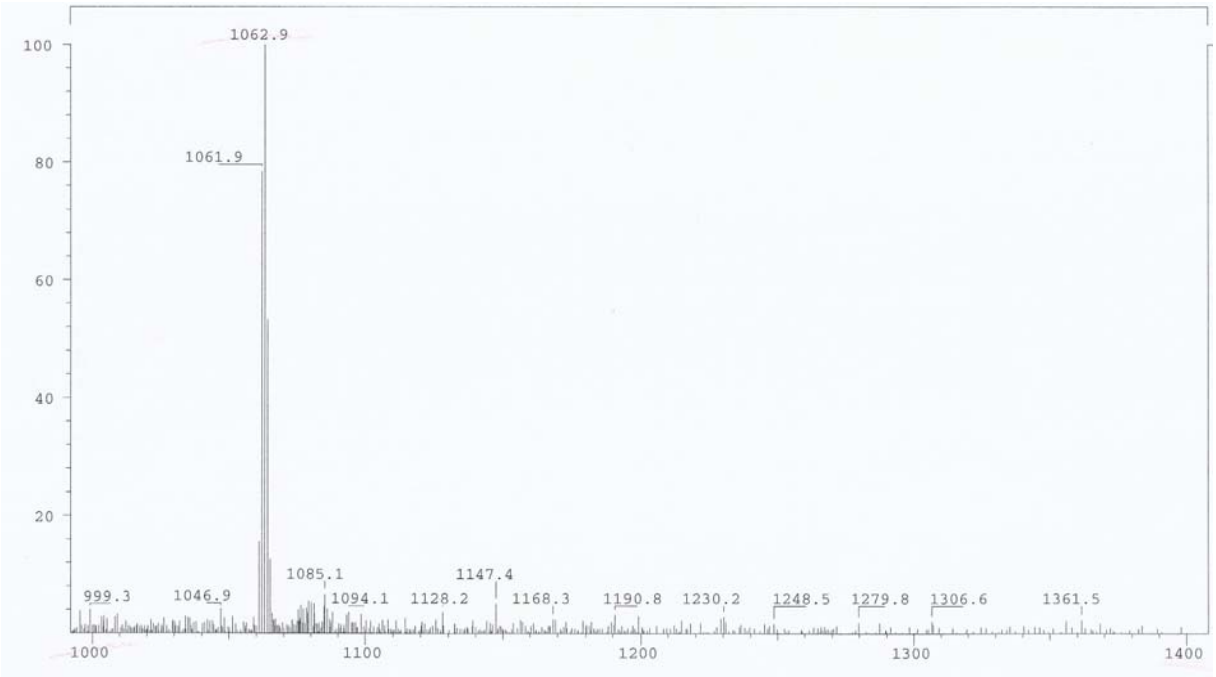
HSQC



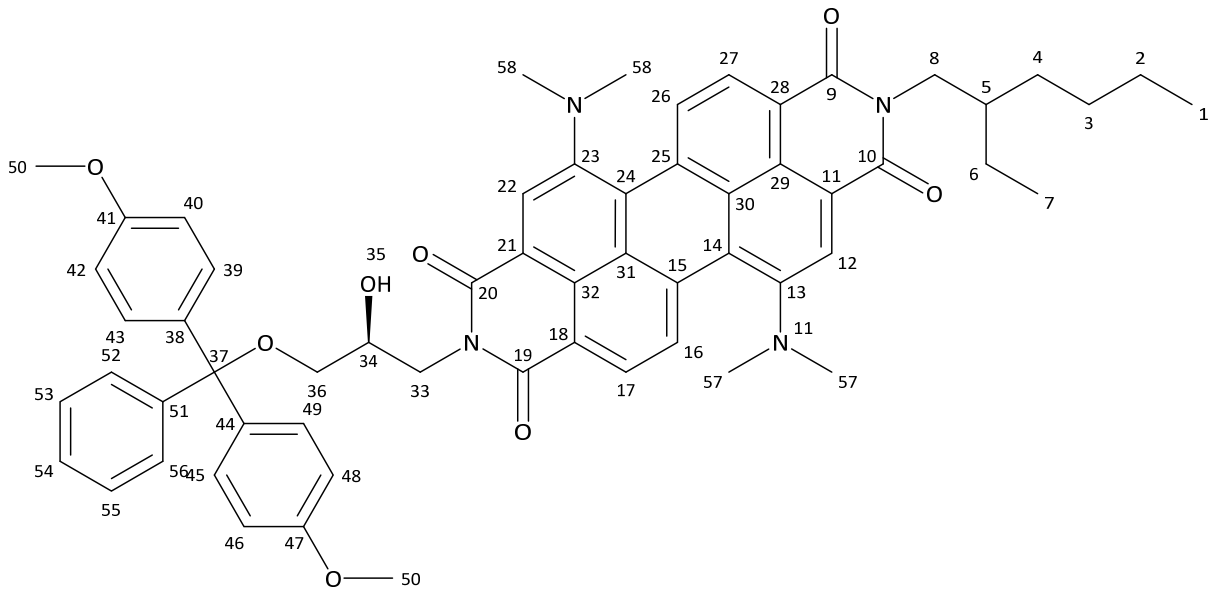
HMBC


f1 (ppm)
f2 (ppm)

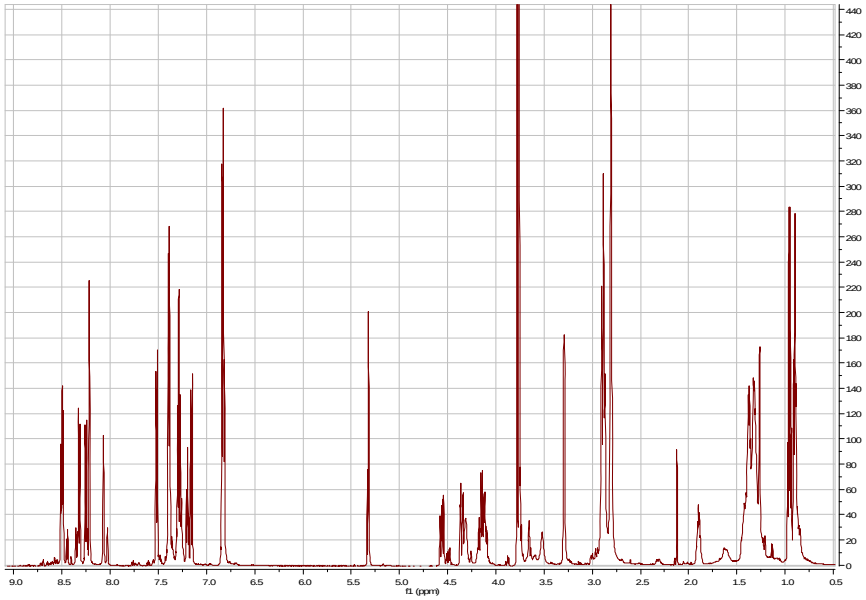
FAB-MS


1062.9
1061.9
999.3
1046.9
1085.1
1094.1
1128.2
1147.4
1168.3
1190.8
1230.2
1248.5
1279.8
1306.6
1361.5

Compound 4

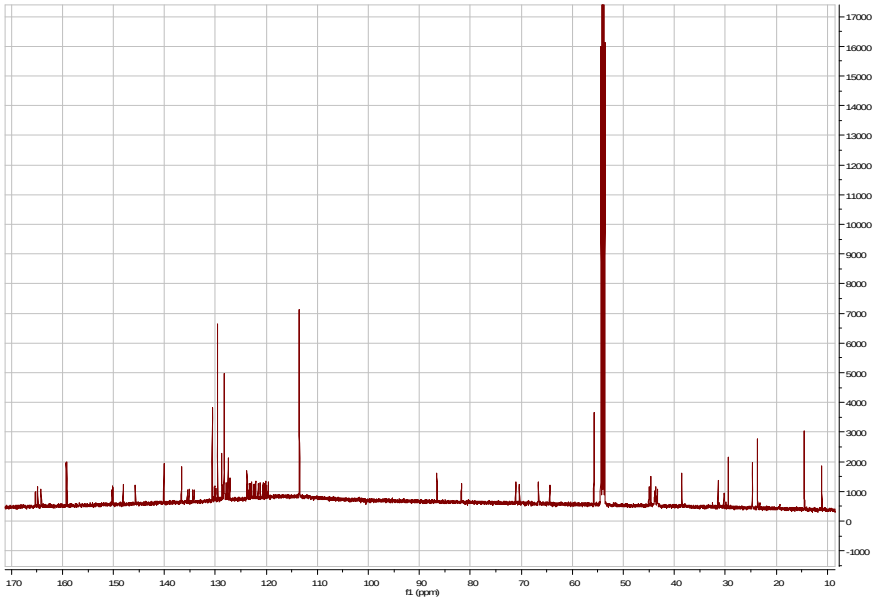


^{1}H-NMR



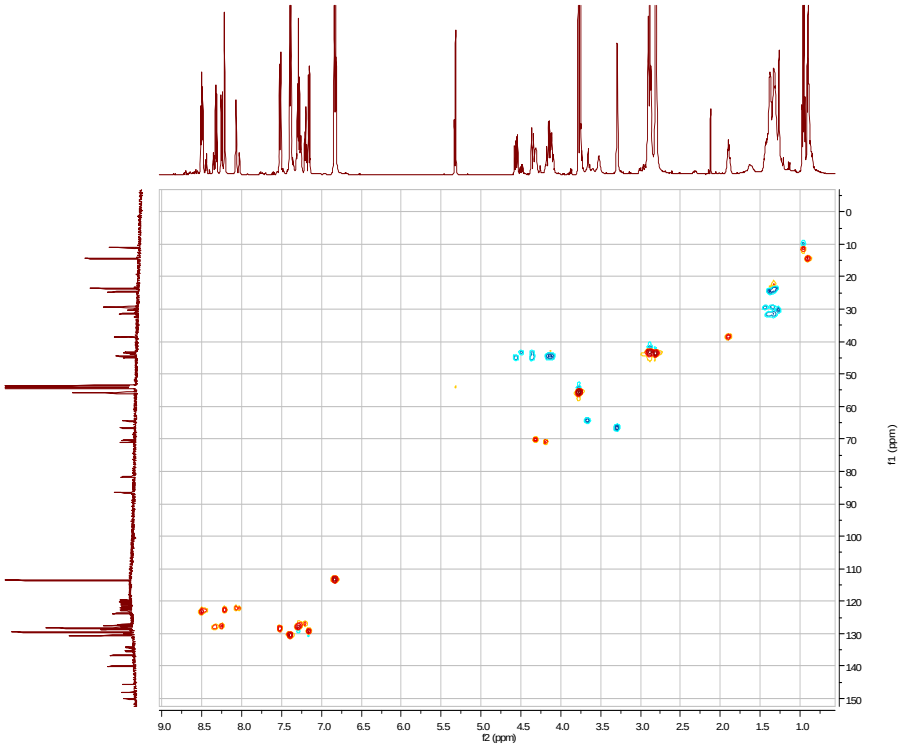
(600 MHz, CD_2Cl_2) δ 8.51 (m, 2H, 16/26), 8.32 (d, *J* = 8.0 Hz, 1H, 17), 8.25 (d, *J* = 8.0 Hz, 1H, 27), 8.22 (s, 1H, 22), 8.07 (s, 1H, 12), 7.53-7.51 (m, 2H, 52/56), 7.40-7.38 (m, 4H, 39/43/45/49), 7.30-7.27 (m, 2H, 53/55), 7.20 (t, *J* = 7.4 Hz, 1H, 54), 6.85-6.81 (m, 4H, 40/42/46/48), 4.56 (dd, *J* = 13.6, 8.8 Hz, 1H, 33a), 4.36 (dd, *J* = 13.6, 3.6 Hz, 1H, 33b), 4.33-4.29 (bs, 1H, 35), 4.20 – 4.08 (m, 3H, 8/34), 3.76 (s, 6H, 50), 3.29 (d, *J* = 4.8 Hz, 2H, 36), 2.89 (s, 6H, 58), 2.81 (s, 6H, 57), 1.90 (p, *J* = 6.2 Hz, 1H, 5), 1.42-1.30 (m, 8H, 2/3/4/6), 0.98-0.94 (m, 3H, 7), 0.92-0.88 (m, 3H, 1).

^{13}C-NMR

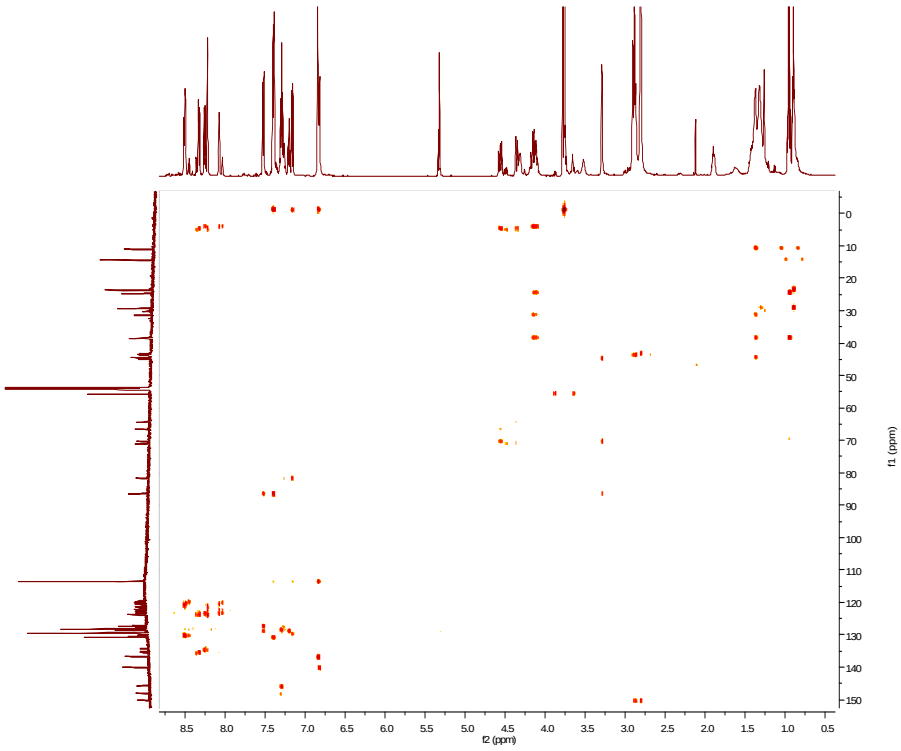


(151 MHz, CD_2Cl_2) δ = 164.9 (19/20), 164.2 (9/10), 159.2 (41/47), 150.1 (13/23), 145.8 (51), 136.7 (38/44), 135.2, 134.4 (arom.), 130.6 (39/43/45/49), 130.2, 129.9 (arom.), 128.7 (52/56), 128.3 (53/55), 128.2 (17), 128.0 (27), 127.2 (54), 123.6 (16/26), 122.9 (22), 122.5 (12), 122.3, 122.2, 121.6, 121.2, 120.7, 120.4, 120.2, 119.6 (arom.), 113.6 (40/42/46/48), 86.6 (37), 70.4 (34), 66.7 (36), 55.7 (50), 44.9 (33), 44.6 (8), 43.6 (58), 43.3 (57), 38.6 (5), 31.4 (4), 29.4 (3), 24.7 (6), 23.7 (2), 14.5 (1), 11.1 (7).

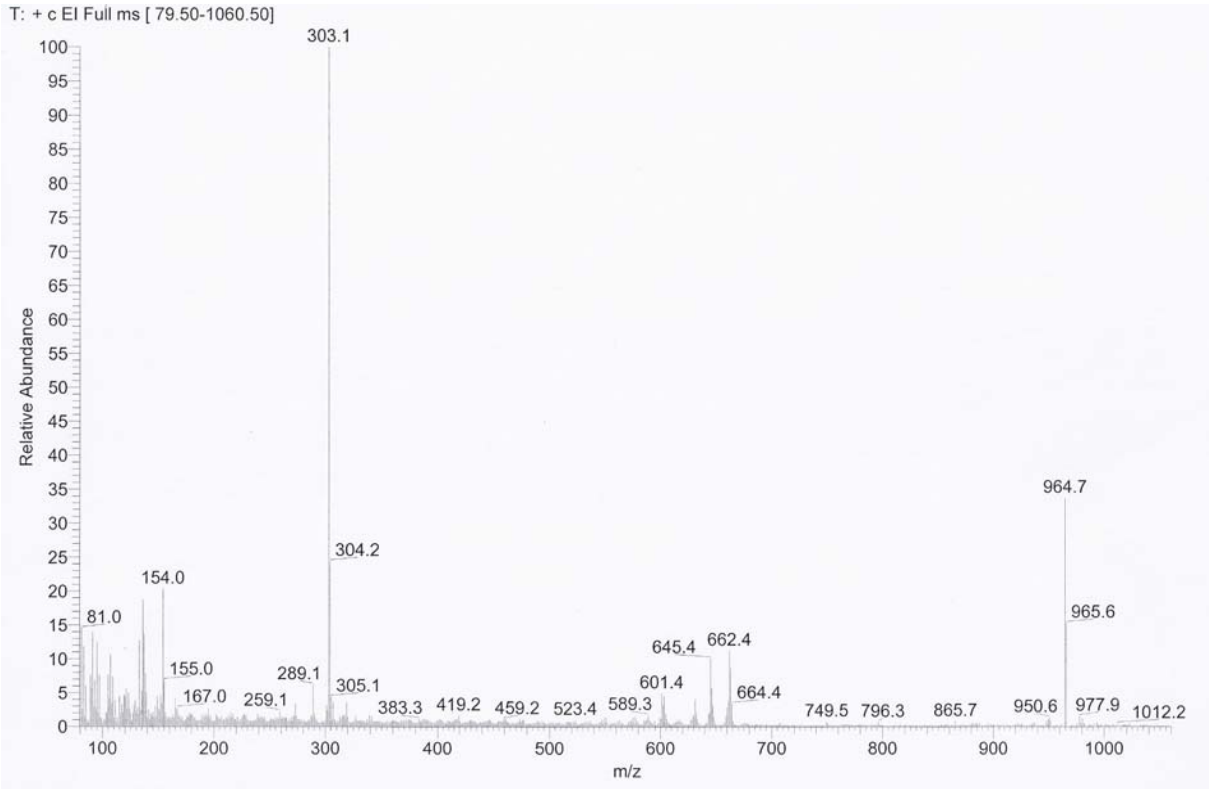
HSQC



HMBC


f2 (ppm)
f1 (ppm)

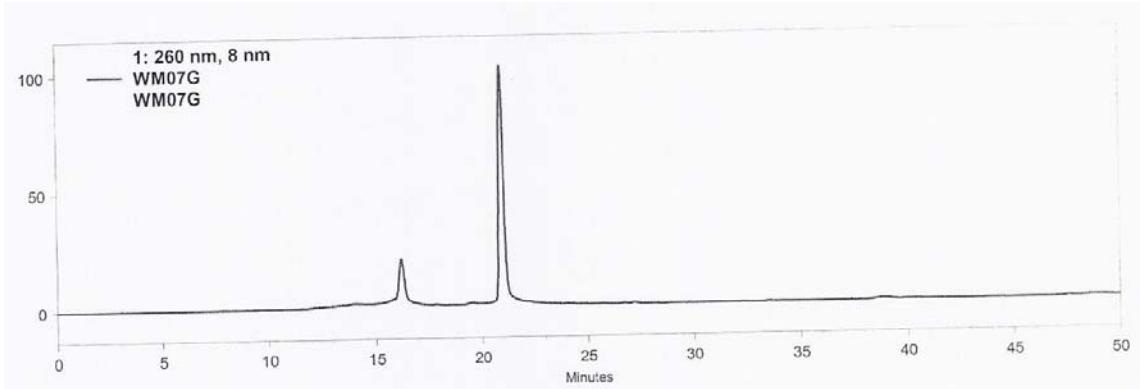
FAB-MS

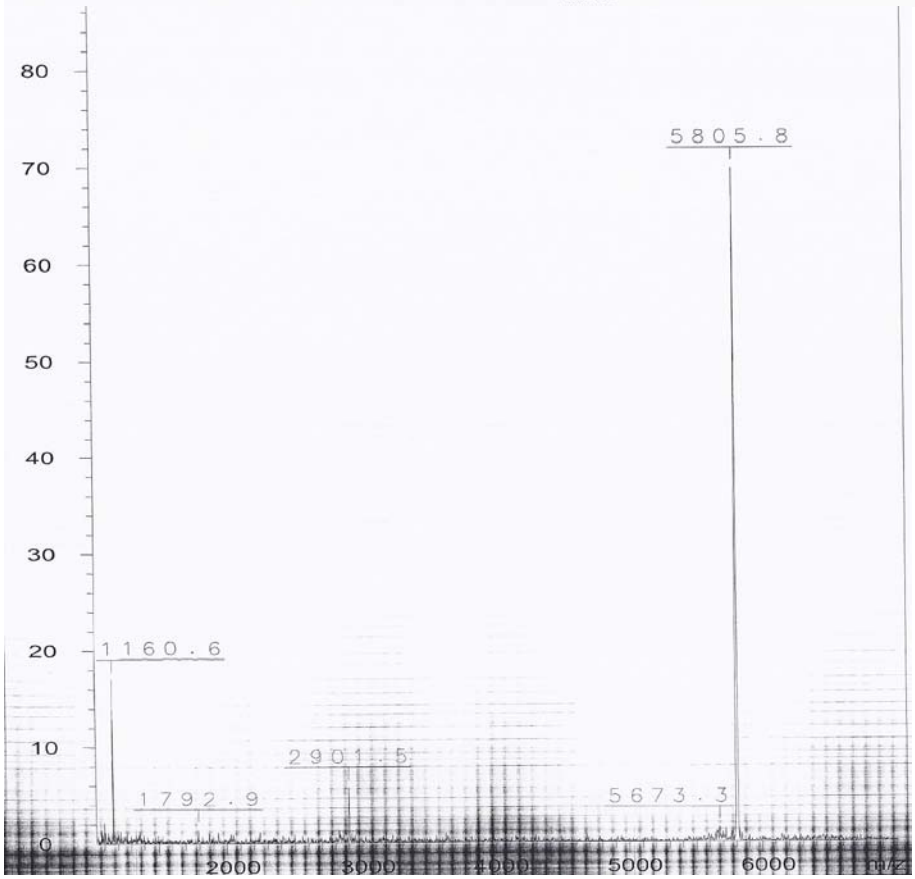

T: + c EI Full ms [79.50-1060.50]
Relative Abundance
m/z
303.1
304.2
154.0
81.0
155.0
167.0
259.1
289.1
305.1
383.3
419.2
459.2
523.4
589.3
601.4
645.4
662.4
664.4
749.5
796.3
865.7
950.6
964.7
965.6
977.9
1012.2

MALDI MS Data of modified DNA

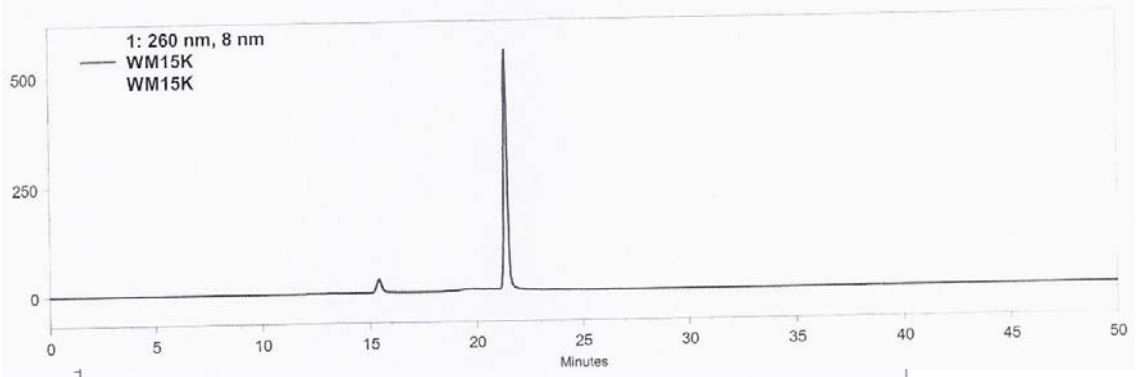
mass	calculated / g·mol^{-1}	found / g·mol^{-1}
DNA1	5806.5	5805.8
DNA2	5866.6	5868.5
DNA3	5990.7	5993.8
DNA4	5892.7	5893.8
DNA5	5483.5	5484.8
DNA6	5543.5	5546.0
DNA7	5667.7	5671.5
DNA8	5569.6	5572.9

DNA1





DNA2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WM15K
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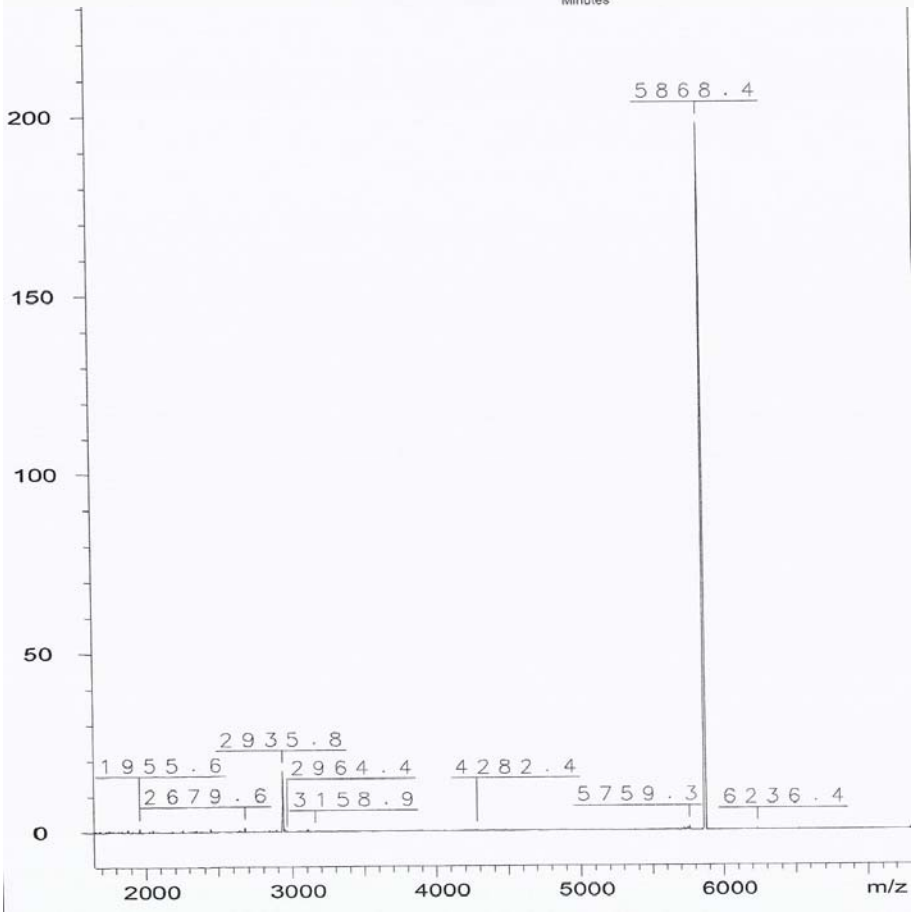
250
0
0
5
10
15
20
25
30
35
40
45
50
Minutes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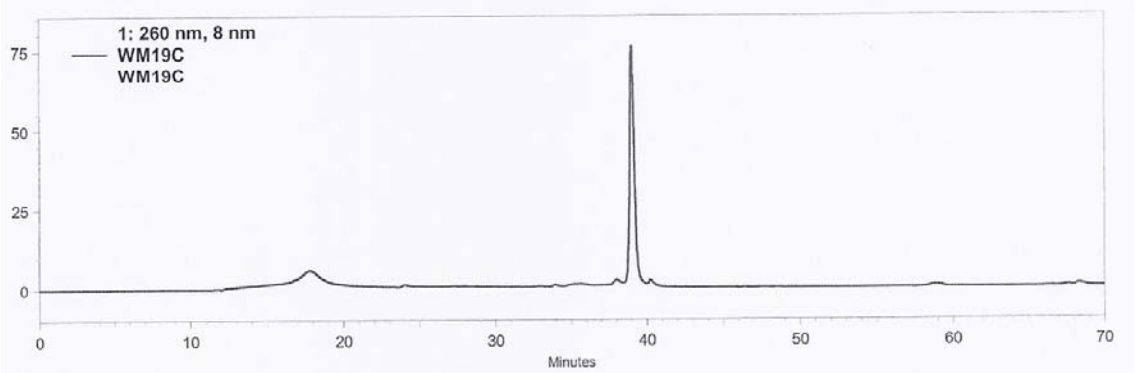
150
100
50
0
2935.8
1955.6
2964.4
4282.4
2679.6
3158.9
5759.3
6236.4
2000
3000
4000
5000
6000
m/z

DNA3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WM19C
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10
20
30
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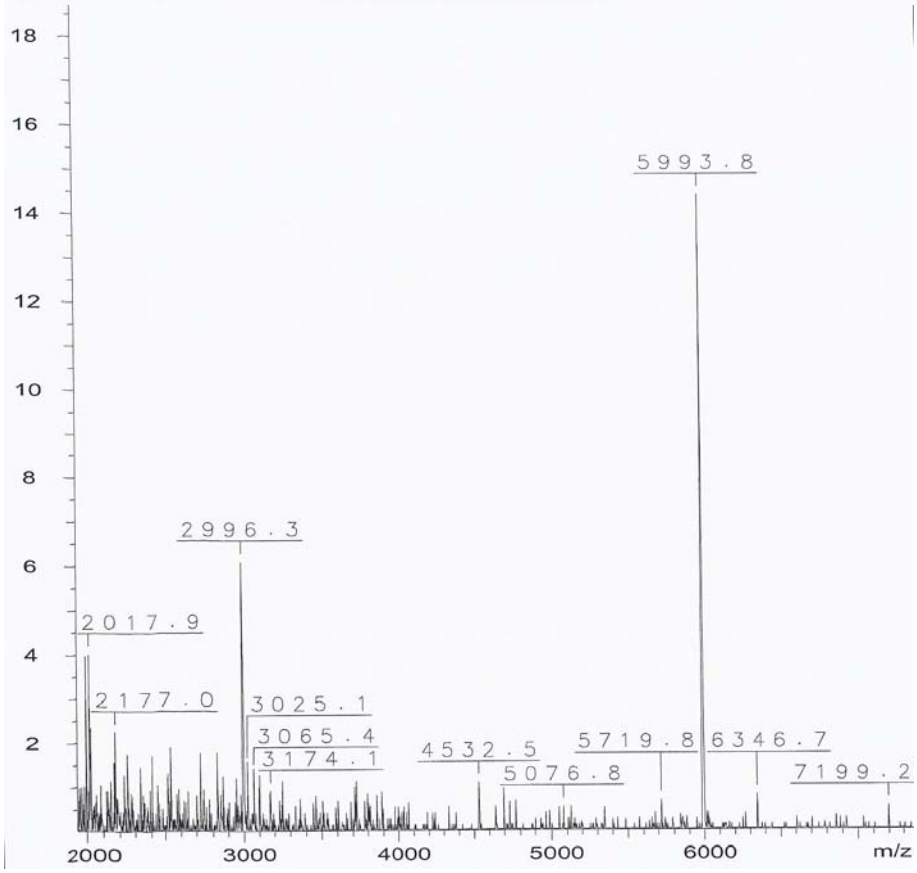
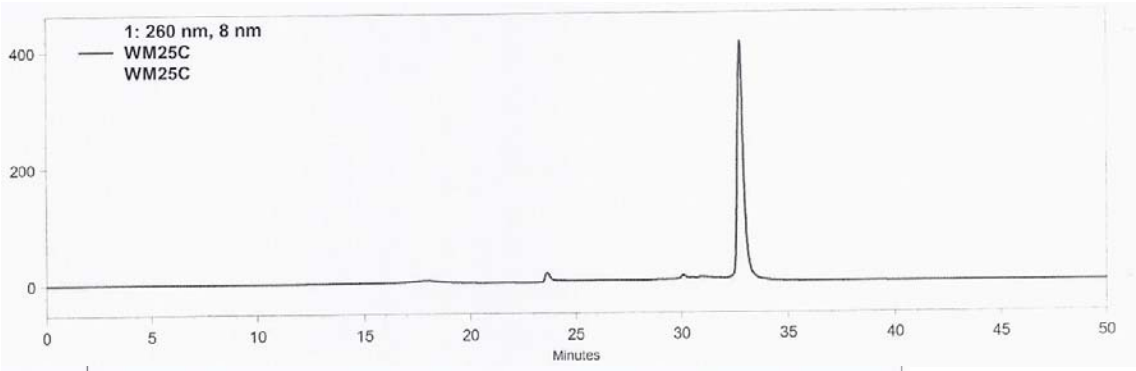
50
60
70
Minutes


18
16
14
12
10
8
6
4
2
5993.8
2996.3
2017.9
2177.0
3025.1
3065.4
3174.1
4532.5
5076.8
5719.8
6346.7
7199.2
2000
3000
4000
5000
6000
m/z

DNA4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WM25C
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200
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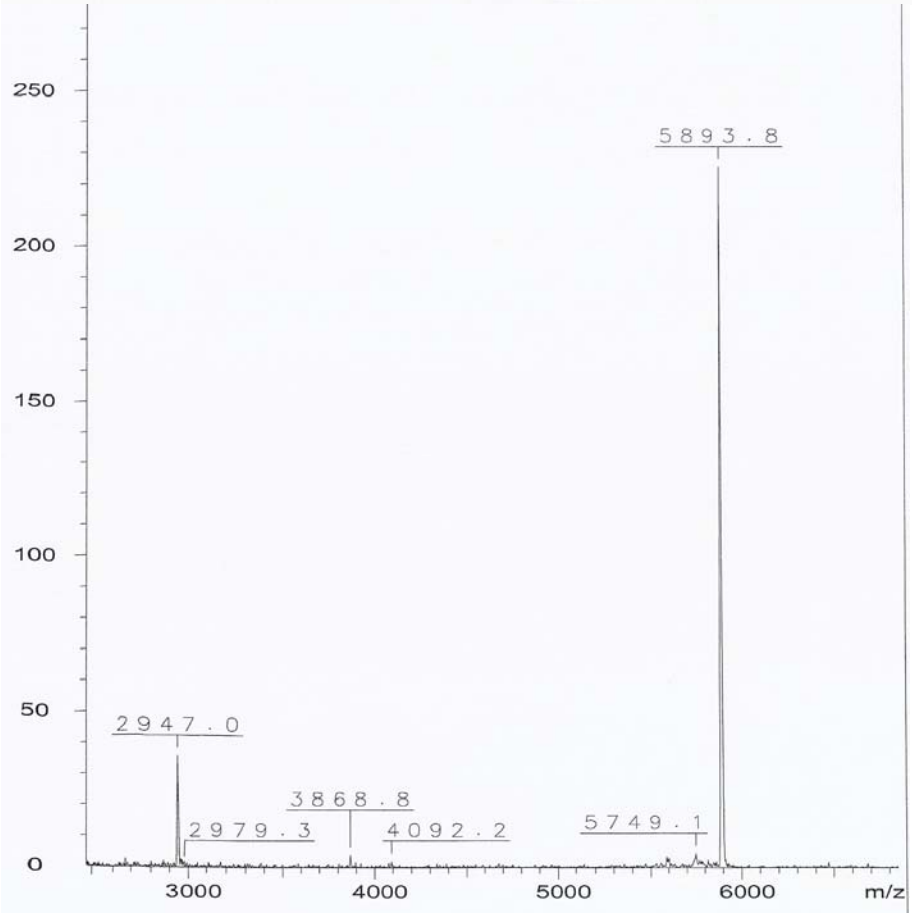
5
10
15
20
25
30
35
40
45
50
Minutes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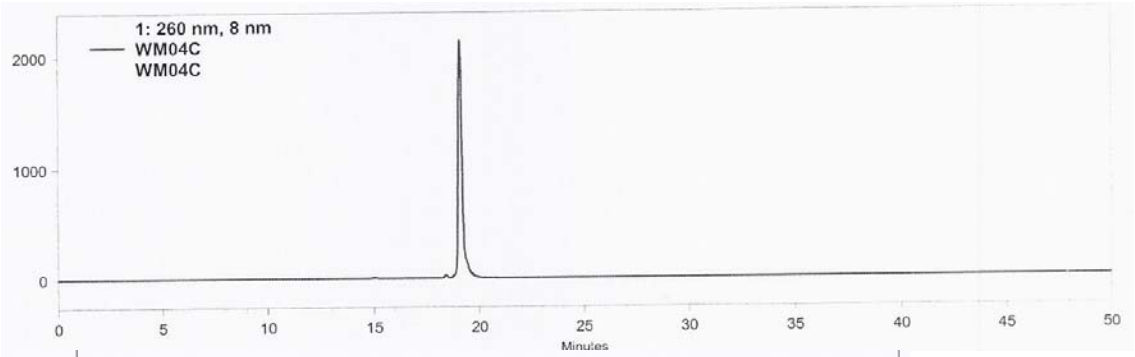
200
150
100
50
0
5893.8
2947.0
3868.8
2979.3
4092.2
5749.1
3000
4000
5000
6000
m/z

DNA5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WM04C
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1000
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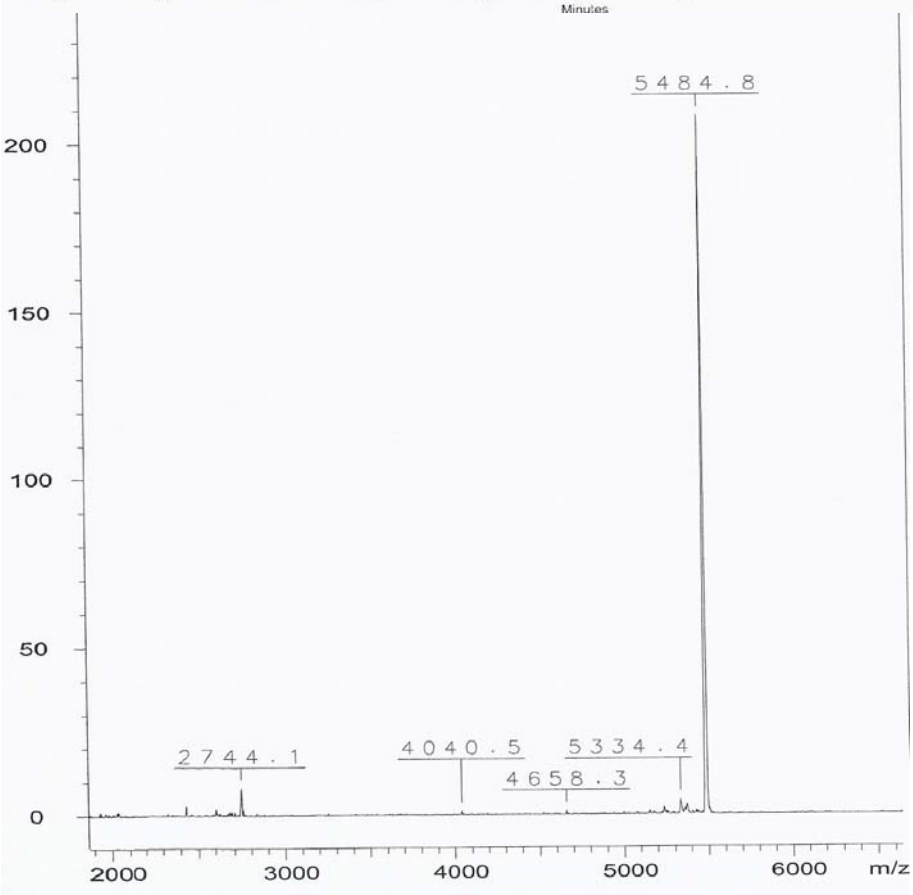
0
5
10
15
20
25
30
35
40
45
50
Minutes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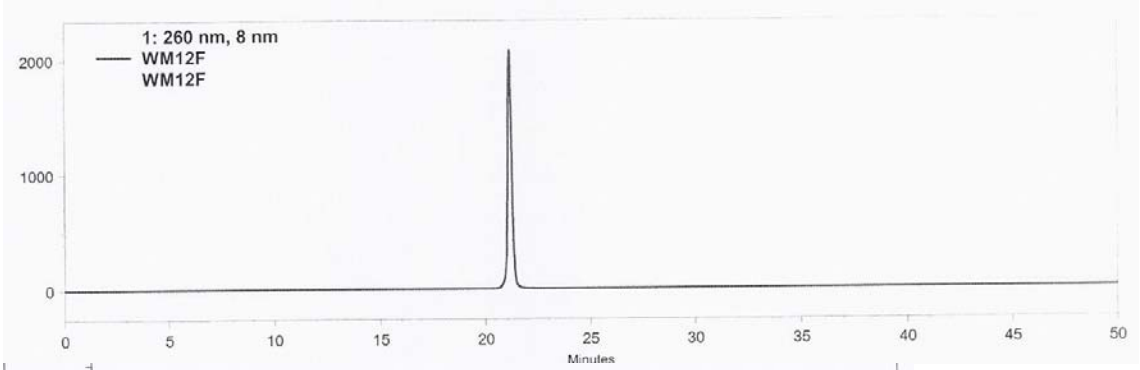
4040.5
5334.4
4658.3
2000
3000
4000
5000
6000
m/z

DNA6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WM12F
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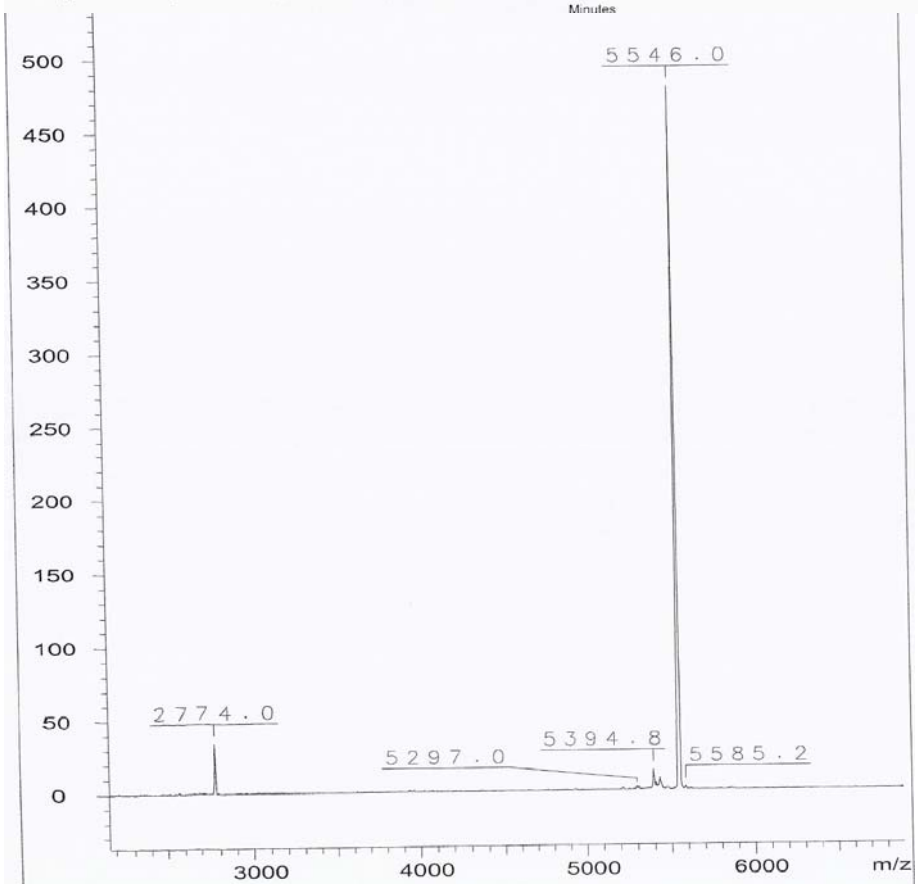
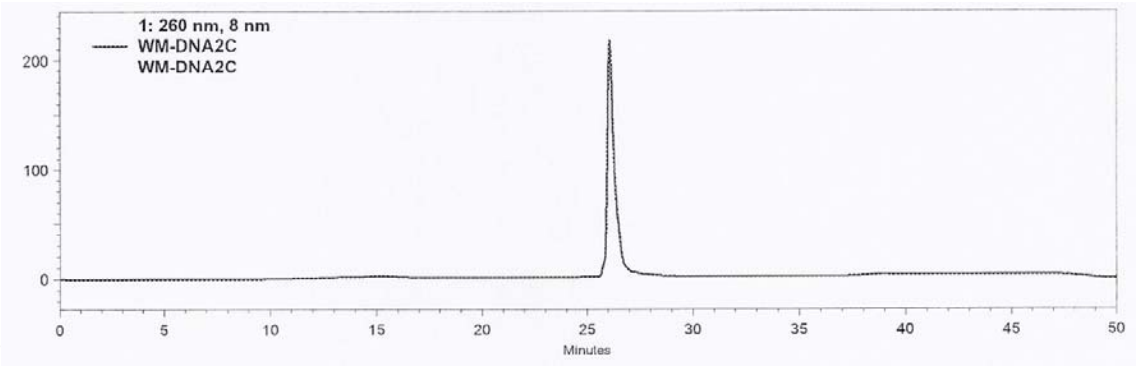
1000
0
0
5
10
15
20
25
30
35
40
45
50
Minutes


5546.0
2774.0
5297.0
5394.8
5585.2
500
450
400
350
300
250
200
150
100
50
0
3000
4000
5000
6000
m/z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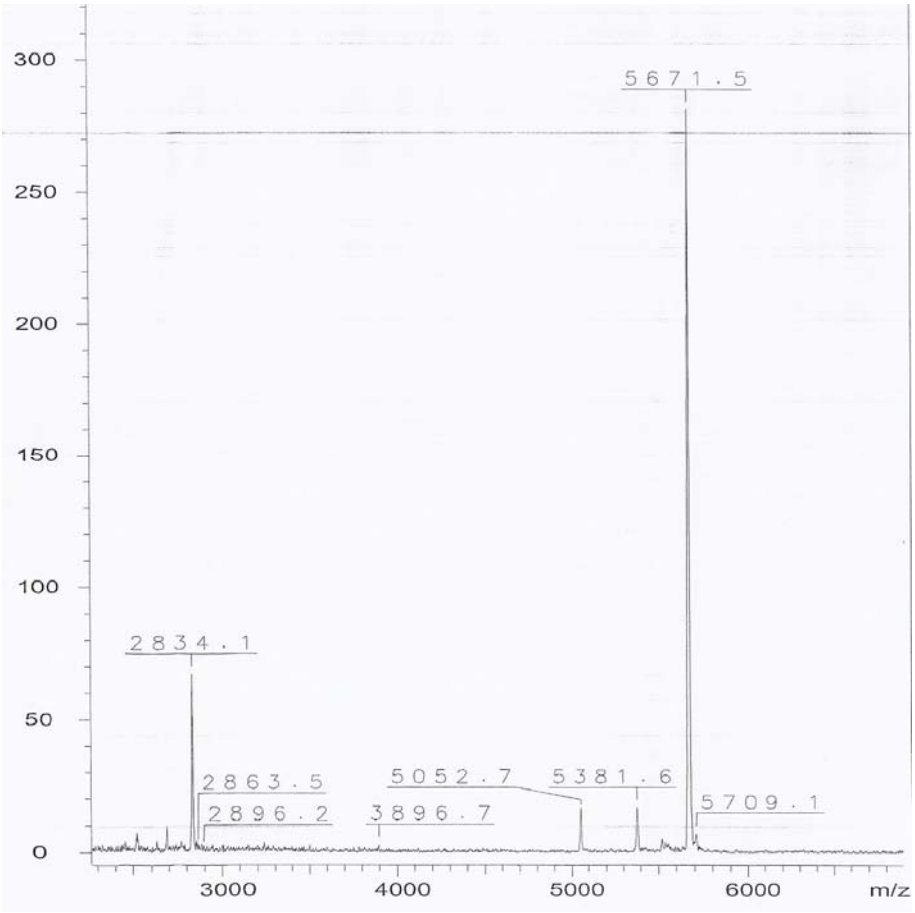
WM-DNA2C
WM-DNA2C
200
100
0
0
5
10
15
20
25
30
35
40
45
50
Minutes

DNA7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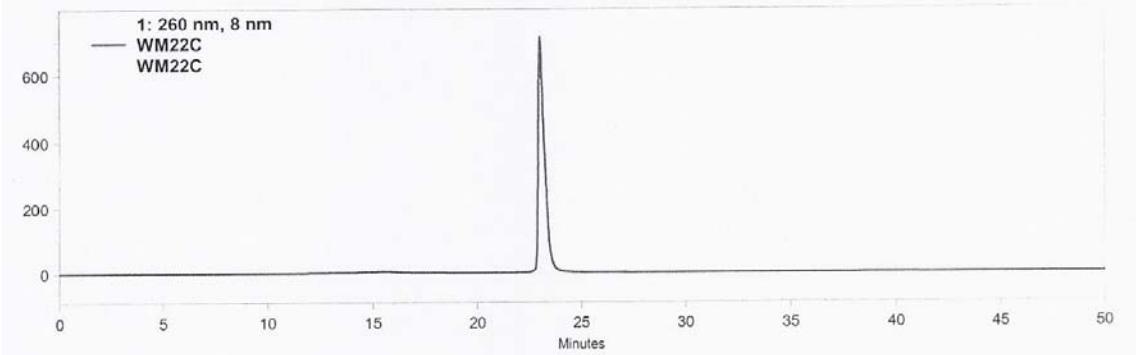
250
200
150
100
50
0
5671.5
2834.1
2863.5
2896.2
3896.7
5052.7
5381.6
5709.1
3000
4000
5000
6000
m/z

DNA8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WM22C
WM22C
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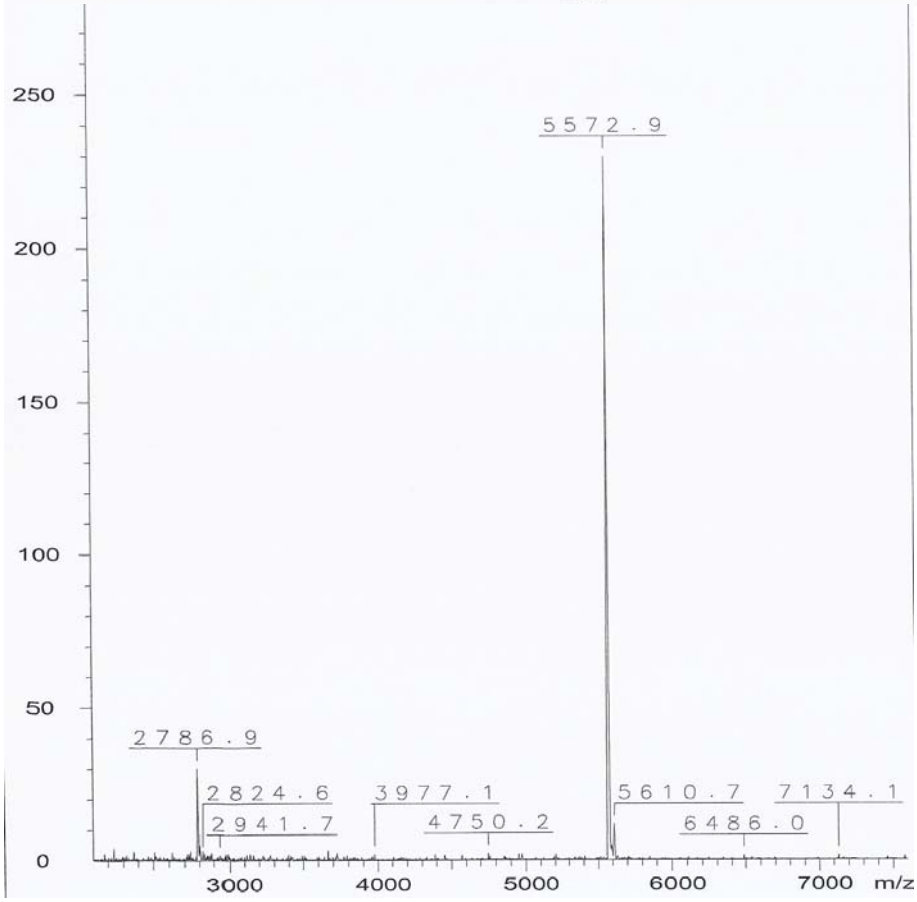
400
200
0
0
5
10
15
20
25
30
35
40
45
50
Minutes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200
150
100
50
0
5572.9
2786.9
2824.6
2941.7
3977.1
4750.2
5610.7
6486.0
7134.1
3000
4000
5000
6000
7000
m/z

3. UV/Vis absorption and fluorescence spectra of homodimers

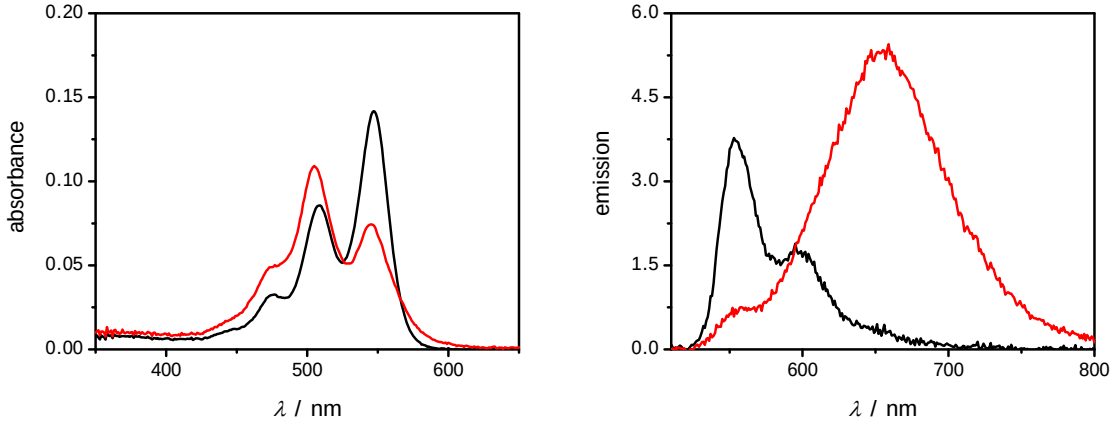

Figure S1: Comparison of **DNA1-1** (red) and **DNA5C** (black), 2.5 µM DNA in 10 mM buffer and 250 mM NaCl; left spectra show absorption and right spectra show fluorescence (λ_{exc} = 505 nm).

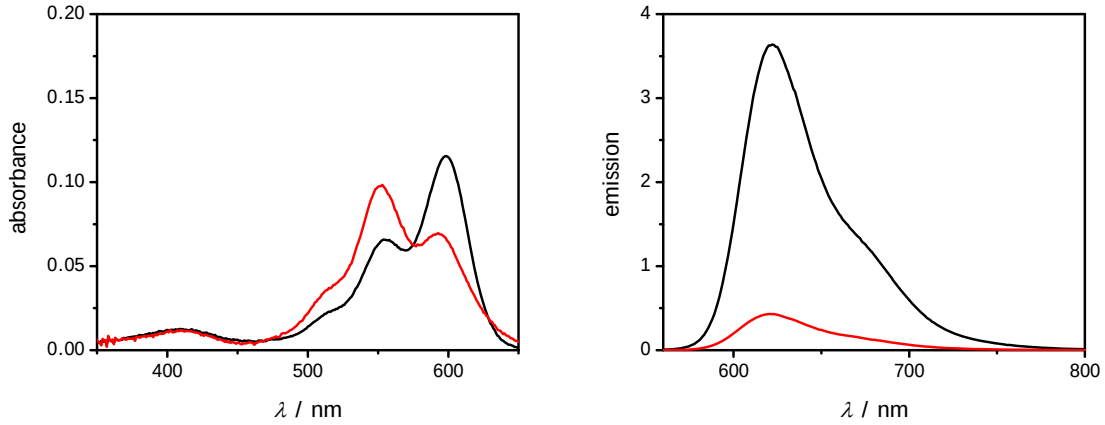

Figure S2: Comparison of **DNA2-2** (red) and **DNA6C** (black), 2.5 µM DNA in 10 mM buffer and 250 mM NaCl; left spectra show absorption and right spectra show fluorescence (λ_{exc} = 555 nm).

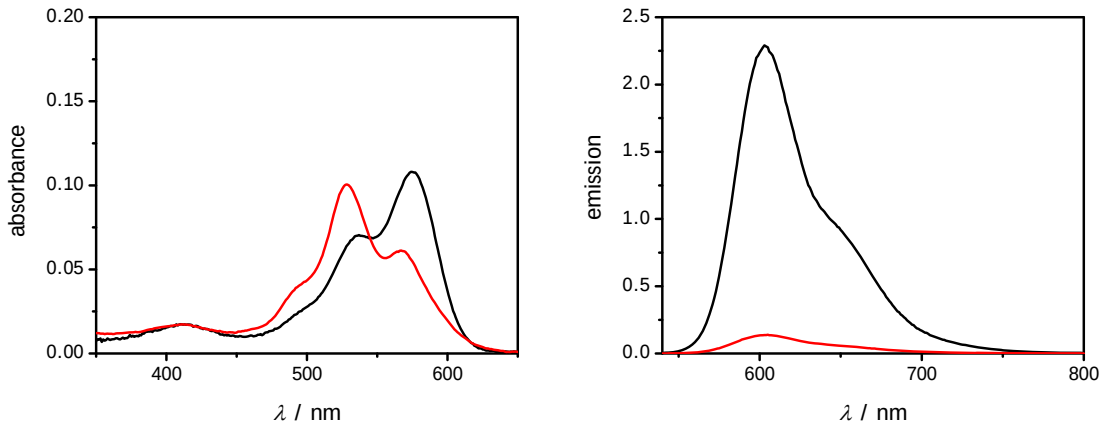

Figure S3: Comparison of **DNA3-3** (red) and **DNA7C** (black), 2.5 µM DNA in 10 mM buffer and 250 mM NaCl; left spectra show absorption and right spectra show fluorescence (λ_{exc} = 535 nm).

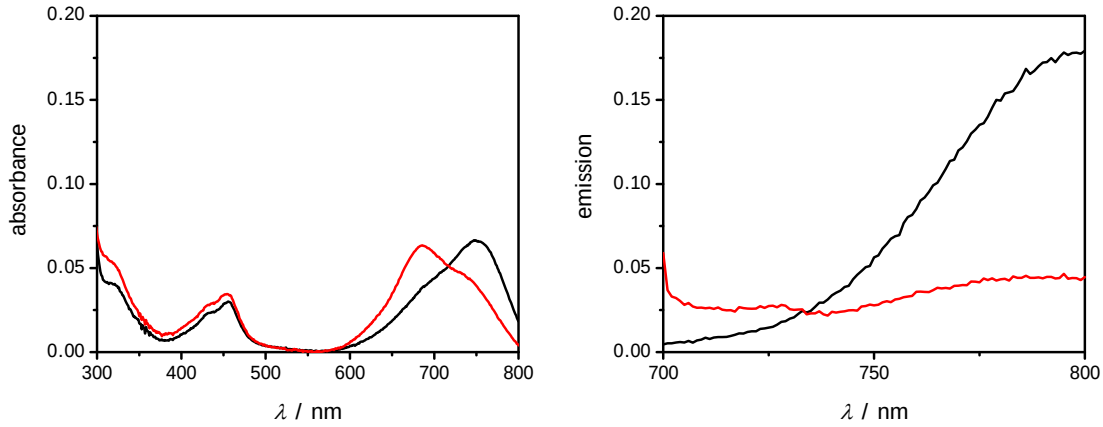

Figure S4: Comparison of **DNA4-4** (red) and **DNA8C** (black), 2.5 µM DNA in 10 mM buffer and 250 mM NaCl; left spectra show absorption and right spectra show fluorescence (λ_{exc} = 685 nm).

4. Time-dependent UV/vis absorption spectra

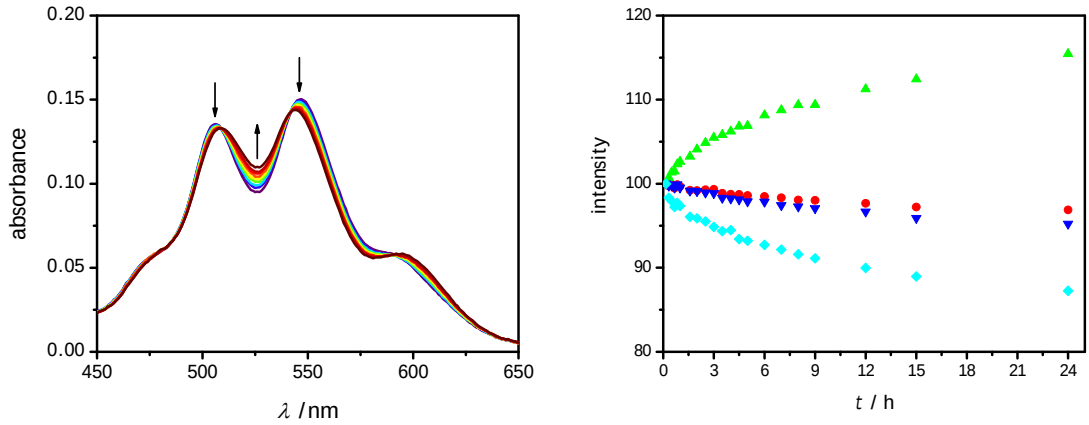

Figure S5: 2.5 µM **DNA1-1**, 2.5 µM **DNA2-2** in 10 mM buffer and 250 mM NaCl, left: time-dependent UV/vis spectra over 24 h at 50 °C, right: relative change of absorbance intensity of the absorption maxima at 506 nm (●), 526 nm (▲), 546 nm (▼) and 568 nm (♦).

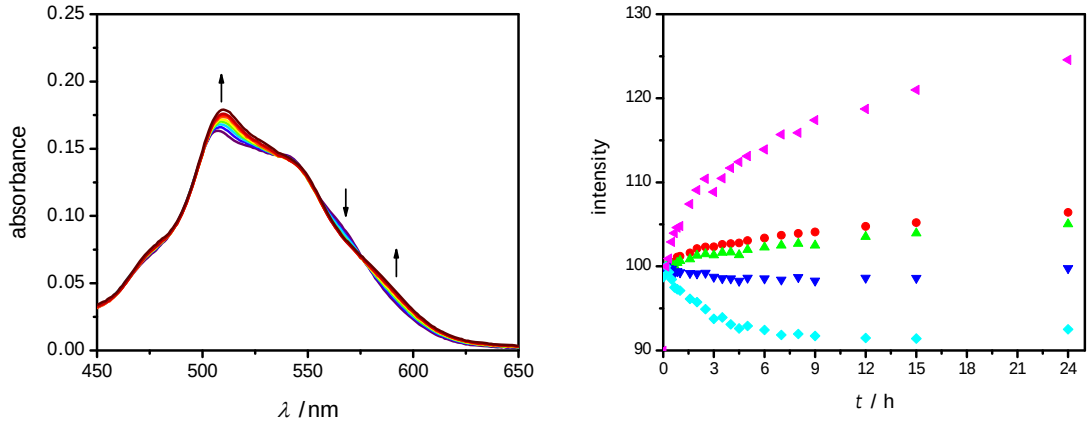

Figure S6: 2.5 µM **DNA1-1**, 2.5 µM **DNA3-3** in 10 mM buffer and 250 mM NaCl, left: time-dependent UV/vis spectra over 24 h at 50 °C, right: relative change of absorbance intensity of the absorption maxima at 506 nm (●), 526 nm (▲), 546 nm (▼), 568 nm (♦) and 592 nm (◄).

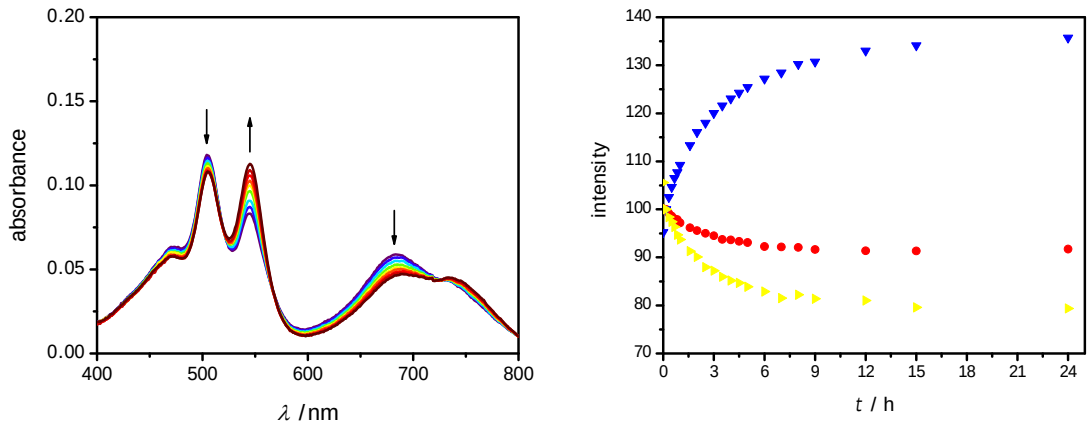

Figure S7: 2.5 µM **DNA1-1**, 2.5 µM **DNA4-4** in 10 mM buffer and 250 mM NaCl, left: time-dependent UV/vis spectra over 24 h at 50 °C, right: relative change of absorbance intensity of the absorption maxima at 506 nm (●), 546 nm (▼) and 685 nm (▶).

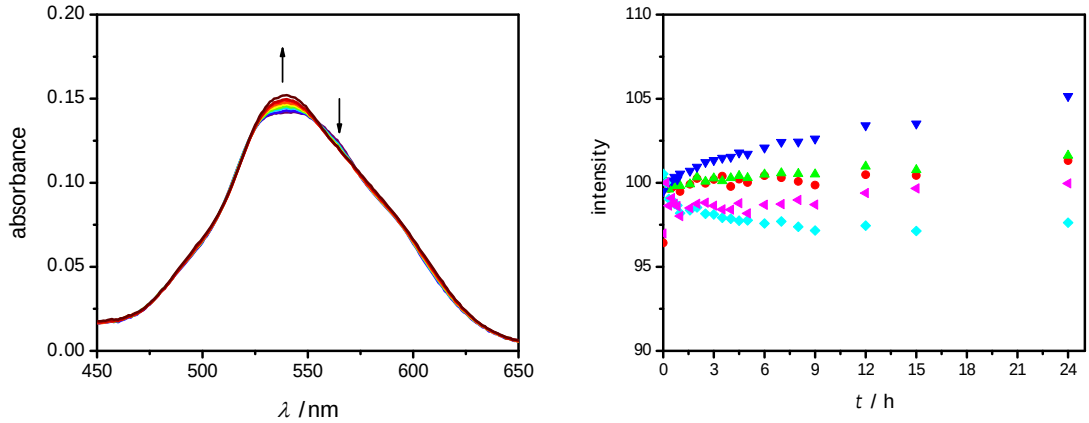

Figure S8: 2.5 µM **DNA2-2**, 2.5 µM **DNA3-3** in 10 mM buffer and 250 mM NaCl, left: time-dependent UV/vis spectra over 24 h at 50 °C, right: relative change of absorbance intensity of the absorption maxima at 506 nm (●), 526 nm (▲), 546 nm (▼), 568 nm (◆) and 592 nm (◀).

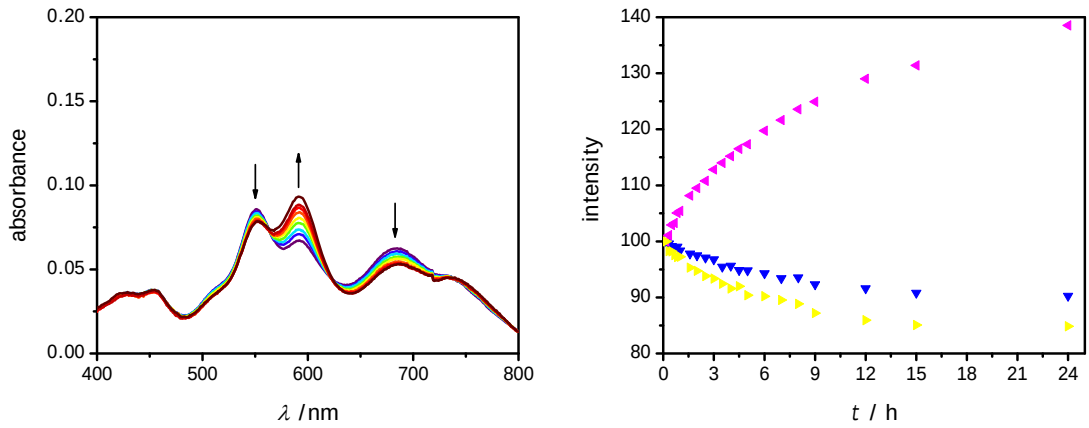

Figure S9: 2.5 µM **DNA2-2**, 2.5 µM **DNA4-4** in 10 mM buffer and 250 mM NaCl, left: time-dependent UV/vis spectra over 24 h at 50 °C, right: relative change of absorbance intensity of the absorption maxima at 546 nm (▼), 592 nm (◀) and 685 nm (▶).

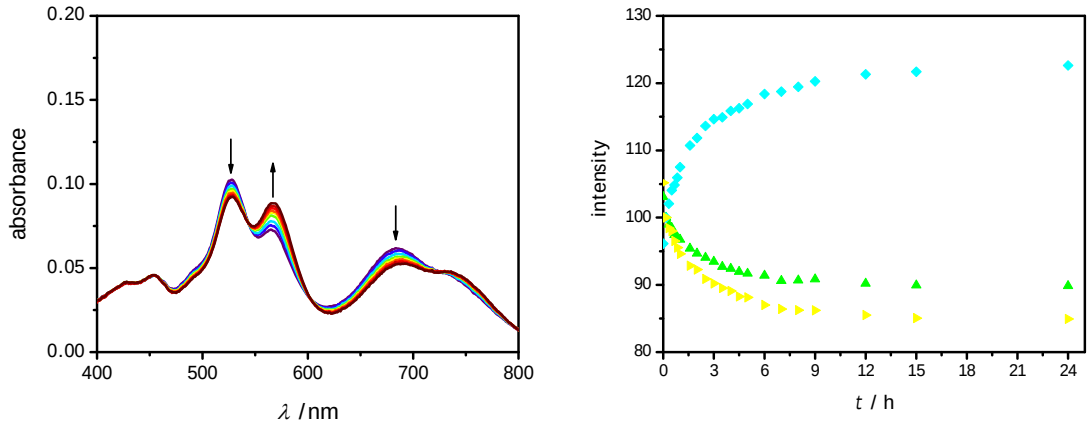

Figure S10: 2.5 µM **DNA3-3**, 2.5 µM **DNA4-4** in 10 mM buffer and 250 mM NaCl, left: time-dependent UV/vis spectra over 24 h at 50 °C, right: relative change of absorbance intensity of the absorption maxima at 526 nm (▲), 568 nm (♦) and 685 nm (▶).

5. Peak deconvolution

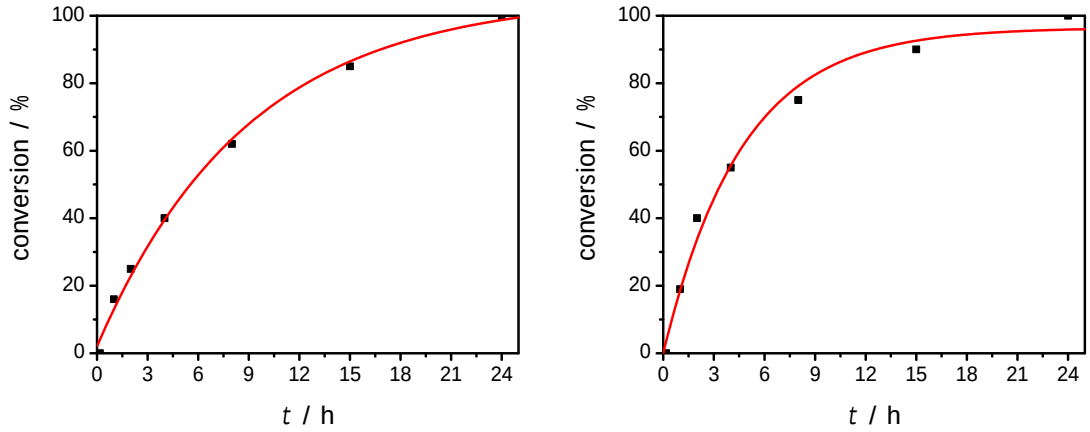

Figure S11: Exponential fit of the reaction rate for the formation of heterodimers after peak deconvolution, left: dsDNA1-2, right: dsDNA1-3.

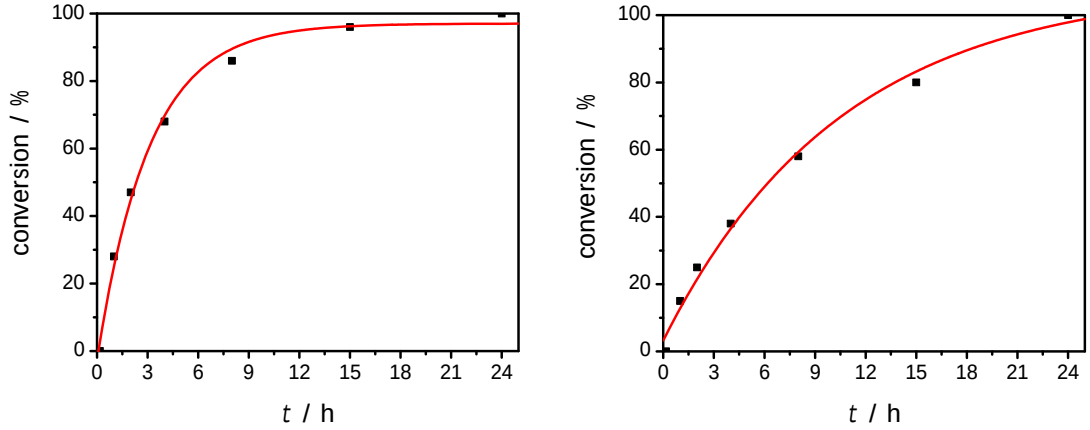

Figure S12: Exponential fit of the reaction rate for the formation of heterodimers after peak deconvolution, left: dsDNA1-4, right: dsDNA2-3.

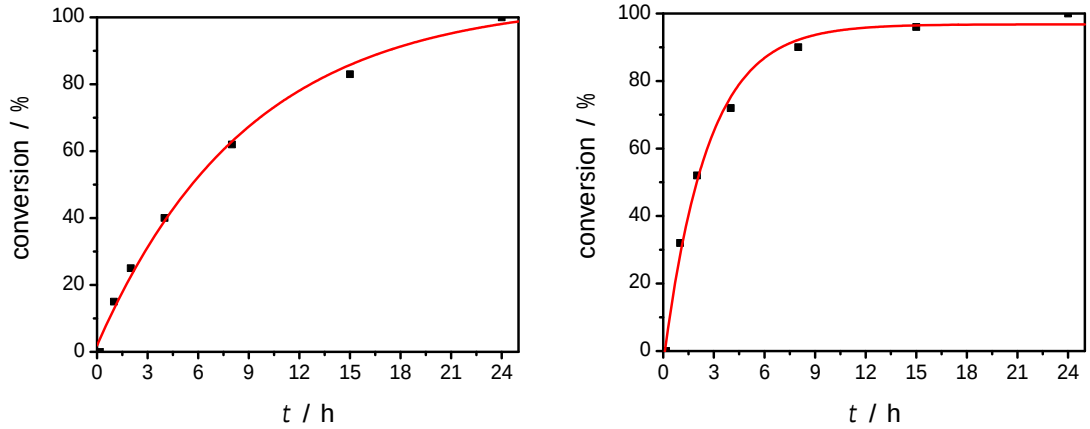

Figure S13: Exponential fit of the reaction rate for the formation of heterodimers after peak deconvolution, left: dsDNA2-4, right: dsDNA3-4.

6. Circular Dichroism

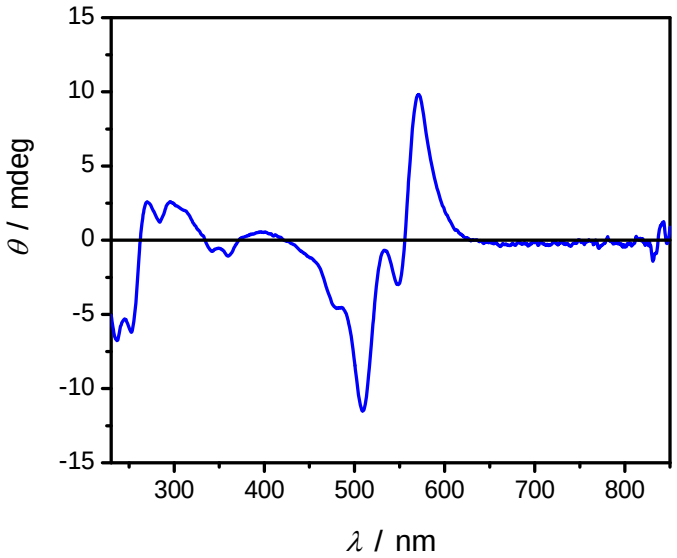

Figure S14: CD spectrum of dsDNA1-1.

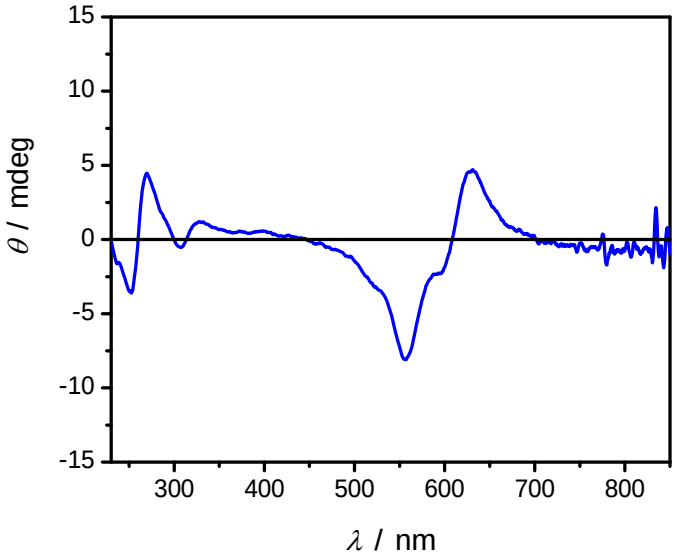

Figure S15: CD spectrum of dsDNA2-2.

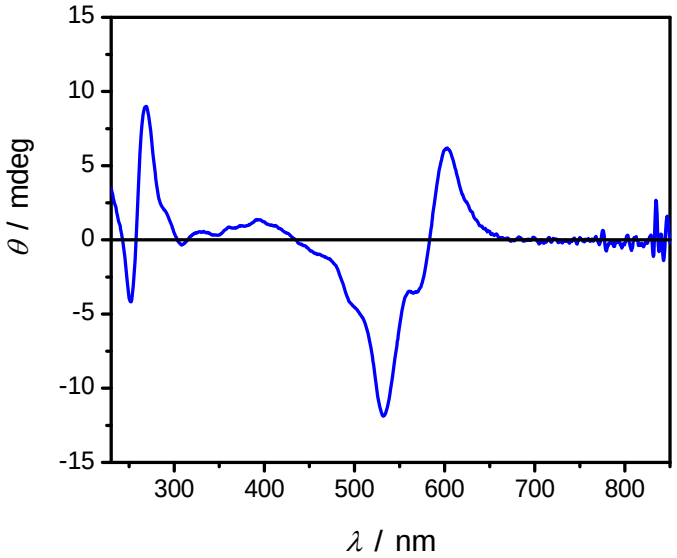

Figure S16: CD spectrum of dsDNA3-3.

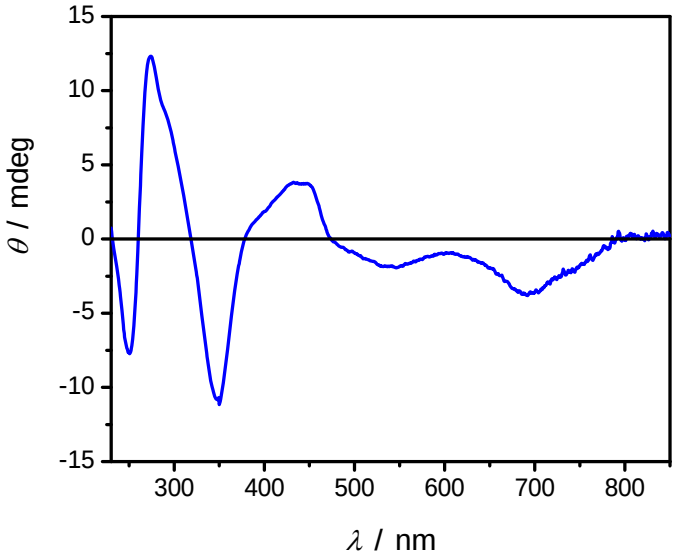

Figure S17: CD spectrum of dsDNA4-4.

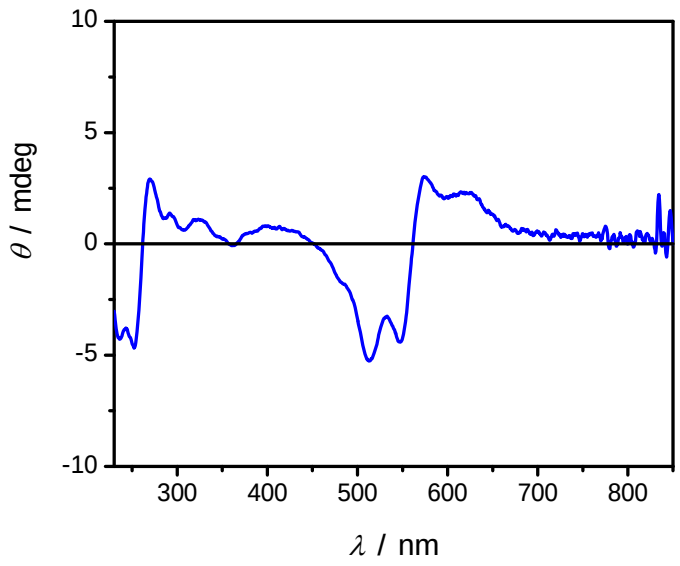

Figure S18: CD spectrum of dsDNA1-2.

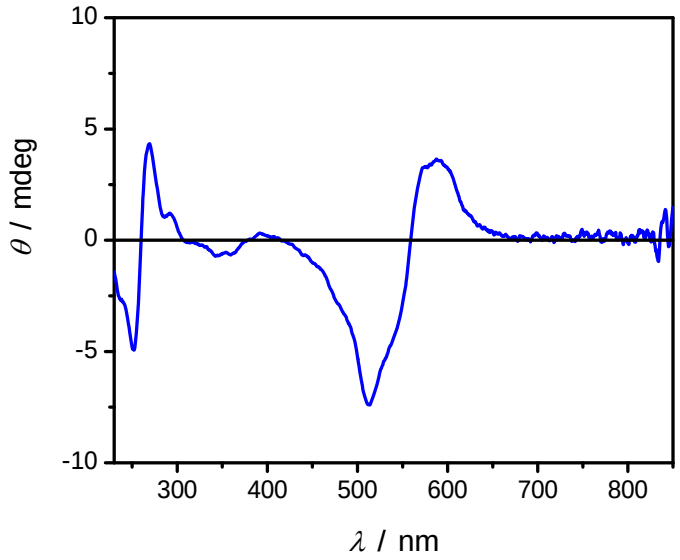

Figure S19: CD spectrum of dsDNA1-3.

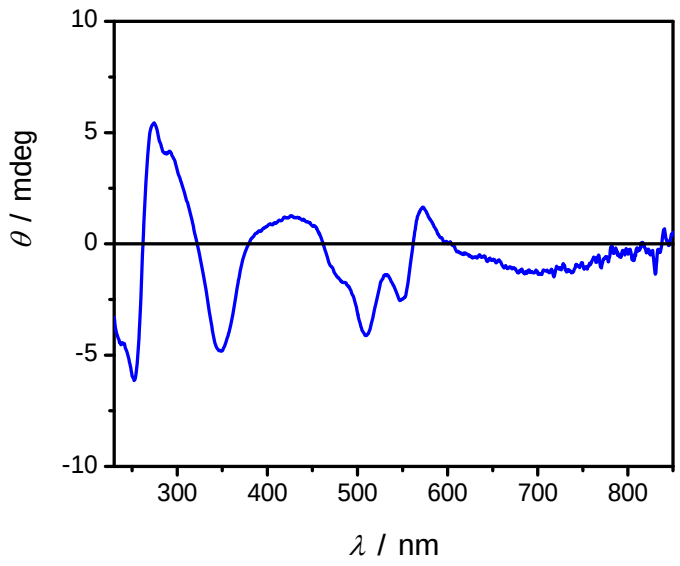

Figure S20: CD spectrum of dsDNA1-4.

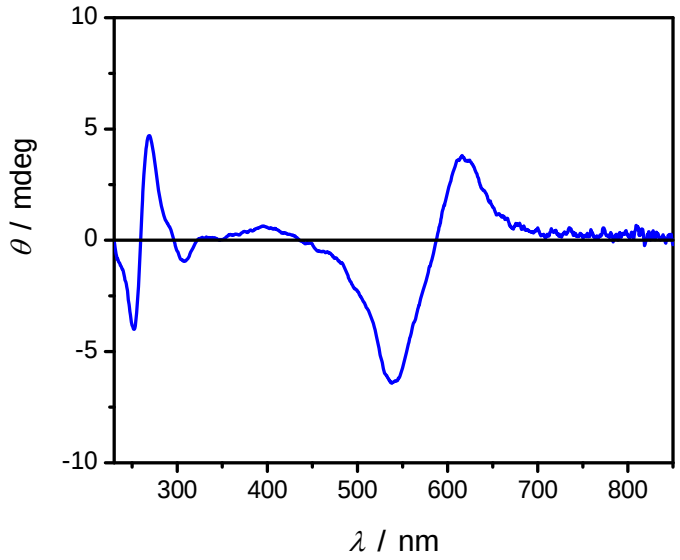

Figure S21: CD spectrum of dsDNA2-3.

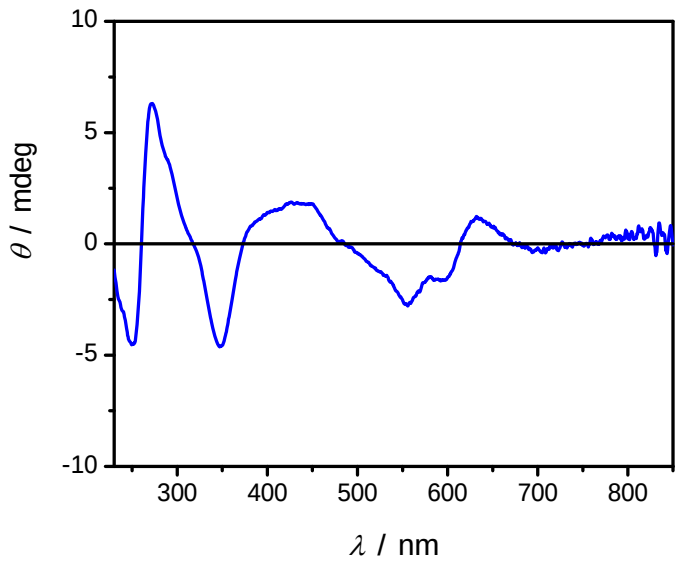

Figure S22: CD spectrum of dsDNA2-4.

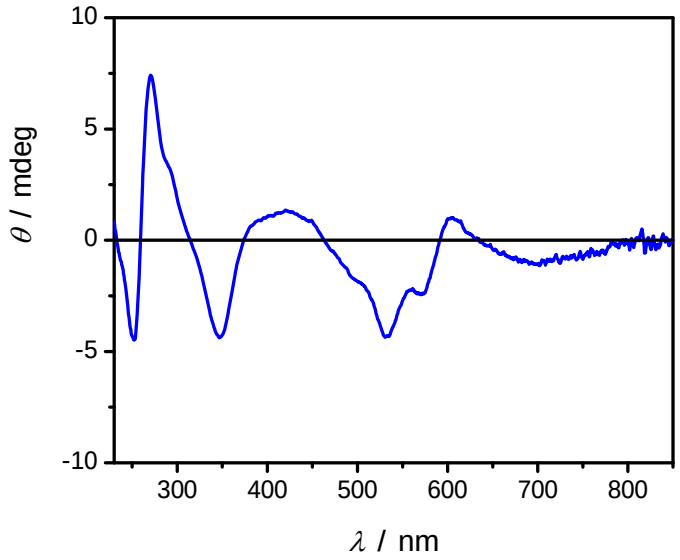

Figure S23: CD spectrum of dsDNA3-4.

7. Frontier Orbital Calculations

The HOMO and LUMO of the PBI chromophore were calculated with the semiempirical AM1 method and were obtained after full geometry optimization using the AMBER force field. The two substituents at the imide nitrogen were reduced to methyl groups.

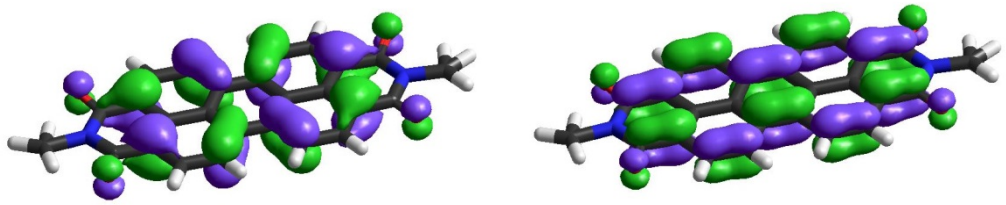

Figure S24: Calculated HOMO (left) and LUMO (right) of PBI **1**.

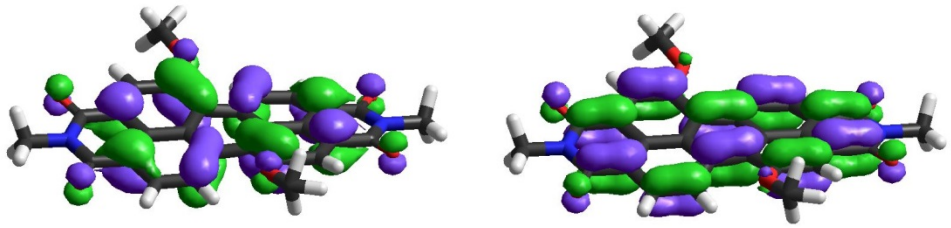

Figure S25: Calculated HOMO (left) and LUMO (right) of PBI **2**.

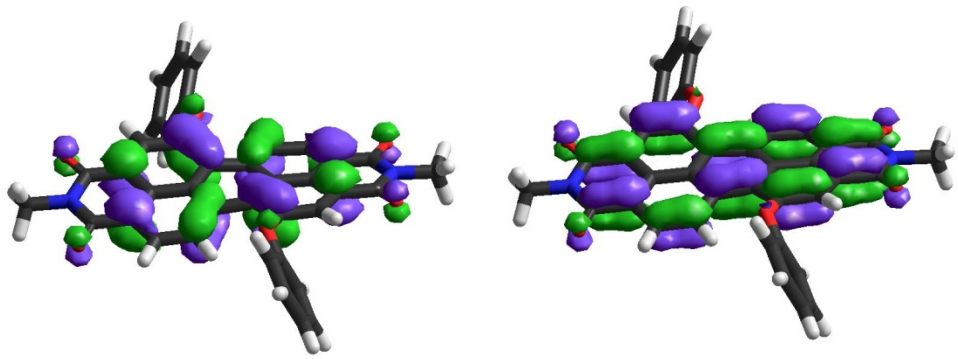

Figure S26: Calculated HOMO (left) and LUMO (right) of PBI **3**.

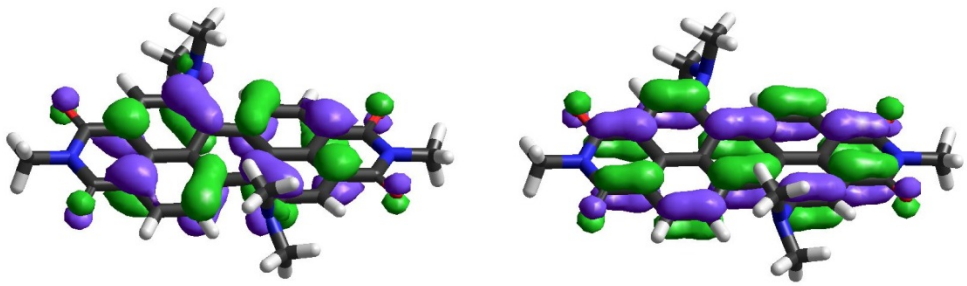

Figure S27: Calculated HOMO (left) and LUMO (right) of PBI **4**.

References

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