Electronic Supplementary Material (ESI) for Chemical Science.

DNA-templated control of chirality and efficient energy transport in supramolecular DNA architectures with aggregation-induced emission

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Supporting Information

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1. Materials and methods

Solvents and reagents

Used Chemicals had the purification grade “for synthesis”, used solvents for synthesis, optical spectroscopy or analysis the grade “HPLC” or “pro analysis”. Water for the sample preparation was deionized and ultrafiltrated by a *Millipore Direct 8/16* from MERCK MILLIPORE. Unmodified and Atto dye-modified D-configured DNA-strands were obtained HPLC-purified and lyophilized from METABION. The L-configured DNA-strands were synthesized, described in the DNA synthesis part.

NMR spectroscopy

The NMR spectra were recorded on a *Bruker Advanced 400* or *Bruker Advanced 500*. The samples were dissolved in 0.5 mL denatured solvent from EURISOTOP. The chemical shifts are given in parts per million (ppm) relative to the standard tetramethylsilan (TMS). The spectra were calibrated against the ^{1}H- residues of the incompletely deuterated solvents.

Mass spectrometry

FAB-Mass spectra were measured on a FINNIGAN *MAT95 spectrometer*. MALDI-TOF spectra were recorded on a SHIMADZU *AXIMA Confidence spectrometer*. ESI-mass spectra recorded on a THERMOFISHER SCIENTIFIC *Q Exactive (Orbitrap)*.

Optical spectroscopy

Absorption spectra were recorded on a *Lambda 750* from PERKIN ELMER with a *PTP-6+6 Peltier System*. The fluorescence was determined on a *Fluoromax-4* from HORIBA SCIENTIFIC with an *AC 200 thermostat* from THERMO SCIENTIFIC. All samples were excited at 341 nm. Absolute fluorescence quantum yields were measured with a *Quantaurus QY C11347* from HAMAMATSU (λ_{exc} = 389 nm).

Circular dichroism was measured on a JASCO *J-810* Spectropolarimeter with the *peltier-element PTC-423S* (100 nm/min, 4 accumulations). FDCD spectra were recorded with a JASCO *J-1500* CD spectrometer (0.2 nm resolution, 4 accumulations) equipped with a filter system and a *PML-534 detector* in a perpendicular positioning to the excitation light path. The Long pass filter was chosen according to the emission spectrum of the Tpe chromophore.

2. Synthesis

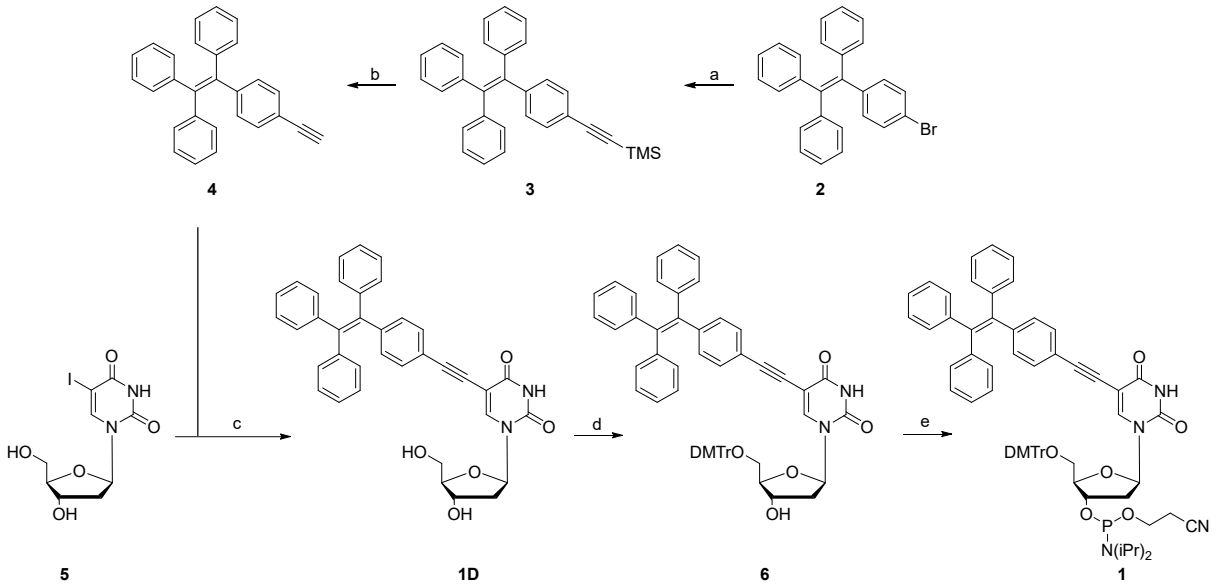

Figure S1. a) TMS-acetylene, $PdCl_2(PPh_3)_2$, CuI, PPh_3, THF/Et_3N, 60 °C, 19 h, 84%; b) KOH, THF/MeOH, r.t., 19 h, quant.; c) $Pd(PPh_3)_4$, CuI, DMF, Et_3N, 60 °C, 19 h, 81%; d) DMTrCl, pyridine, r. t., 19 h, 70%; e) $iPr_2NP(Cl)OCH_2CH_2CN$, DIPEA, DCM, r.t., 3h, 88%.

The synthesis of the acetylene-modified Tpe **4** was prepared according to the literature. [1]

Synthesis of Tpe-modified 5-Iodo-2′-deoxyuridine 1D

A mixture of 0.40 g **4** (1.12 mmol, 1.00 eq.), 0.44 g 5-Iodo-2′-deoxyuridine **5** (1.23 mmol, 1.10 eq.) and 0.04 mg CuI (0.22 mmol, 0.20 eq.) was dissolved in 5 mL dry DMF and 0.39 mL triethylamine (2.81 mmol, 2.50 eq.) was added under argon. The reaction mixture was degassed through injection of argon under stirring for 10 min. After addition of 0.26 g $Pd(PPh_3)_4$ (0.22 mmol, 0.20 eq.) the reaction mixture was stirred by 60 °C for 19 h. Afterwards the solvents were removed under reduced pressure. The crude product was dissolved in DCM, washed with brine and dried over sodium sulfate. The solvent was again removed under reduced pressure. The crude product was purified by flash-column chromatography (silica, DCM:MeOH = 1:0 – 20:1). The desired product **1D** could be obtained as a white solid in a yield of 81% (0.53 g, 0.91 mmol).

^{1}H-NMR (500 MHz, DMSO): δ = 11.67 (s, 1H), 8.35 (s, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.09 (m, 9H), 7.00 – 6.94 (m, 8H), 6.12 (t, *J* = 6.5 Hz, 1H), 5.25 (d, *J* = 4.2 Hz, 1H), 5.14 (t, *J* = 4.7 Hz, 1H), 4.24 (p, *J* = 4.2 Hz, 1H), 3.80 (q, *J* = 3.3 Hz, 1H), 3.70 – 3.50 (m, 2H), 2.22 – 2.04 (m, 2H).

^{13}C-NMR (126 MHz, DMSO): δ = 161.4, 149.4, 143.8, 143.6, 142.9, 142.7, 141.4, 139.8, 131.0, 130.7, 130.7, 130.6, 128.0, 127.9, 127.8, 126.8, 126.7, 120.4, 98.1, 91.7, 87.6, 84.8, 82.8, 69.9, 60.8, 40.2.

HR-MS (FAB): m/z calculated $C_{37}H_{30}N_2O_5^+$ [M^+] = 582.2155; found = 582.2154.

The L-configured nucleoside **1L** was synthesized in the same manner and the spectroscopic data was identical.

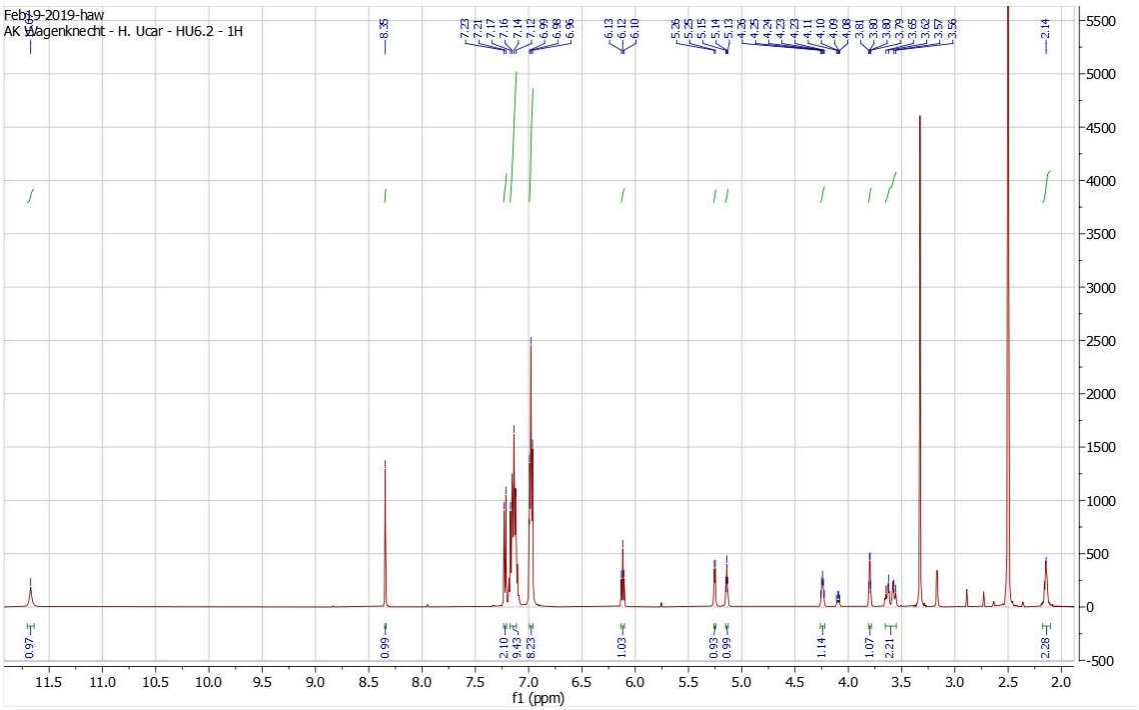

Figure S2. ^{1}H-NMR spectrum (500 MHz, DMSO) of **1D**.

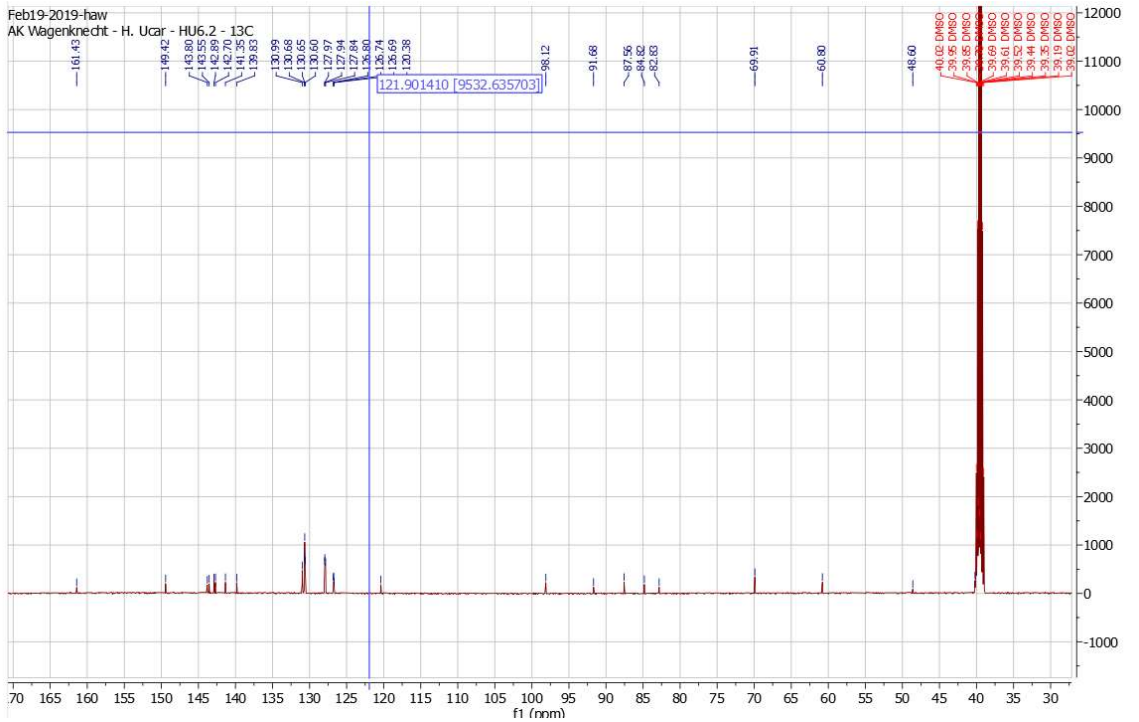

Figure S3. ^{13}C-NMR spectrum (126 MHz, DMSO) of **1D**.

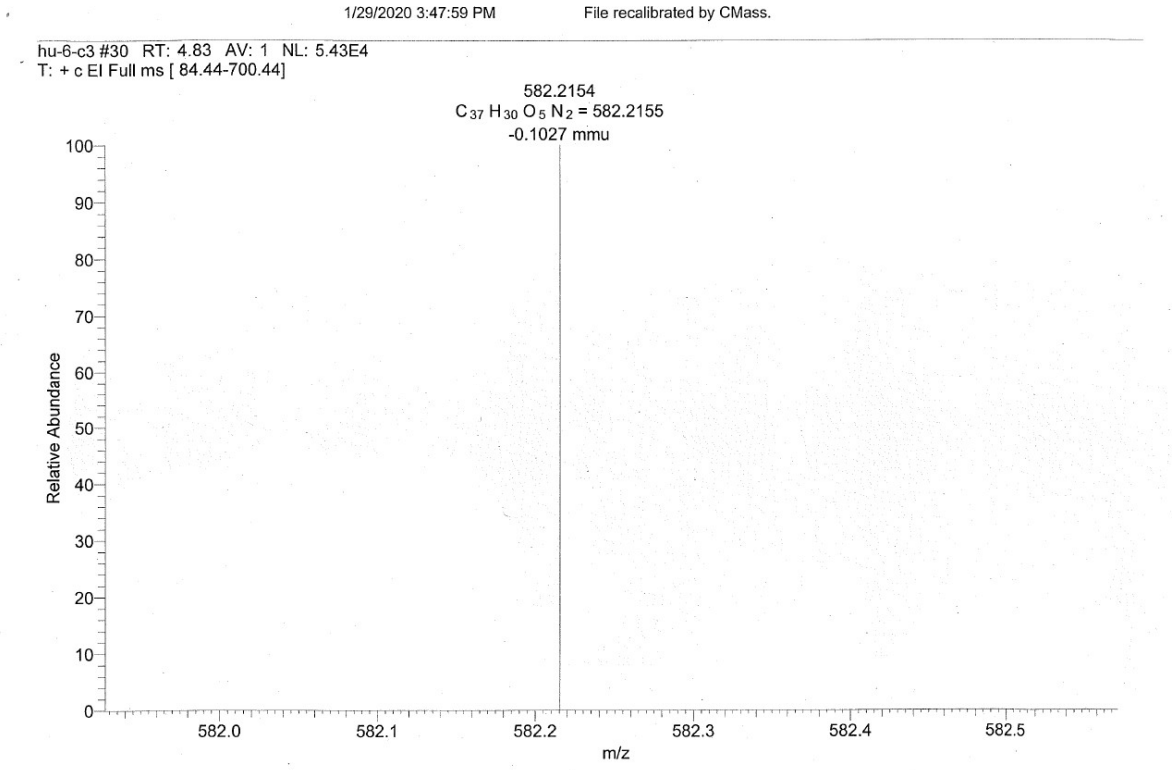

Figure S4. HR-MS (FAB) analysis of **1D**.

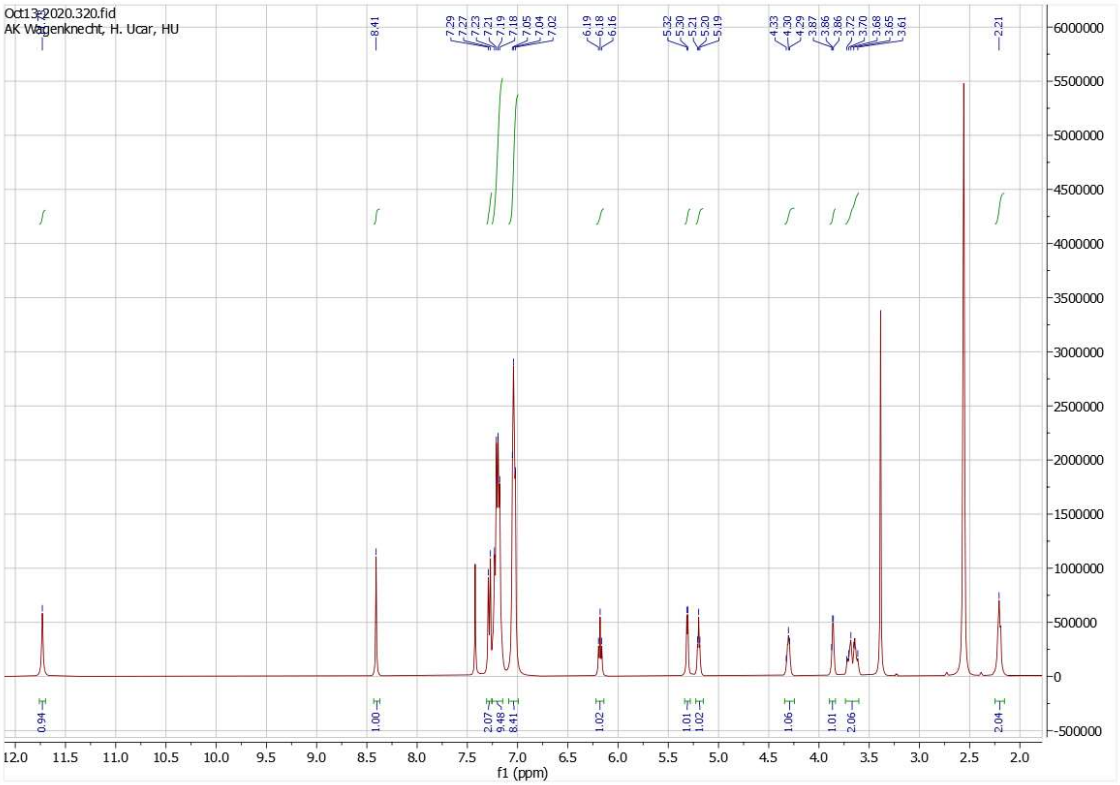

Figure S5. ^{1}H-NMR spectrum (400 MHz, DMSO) of **1L**.

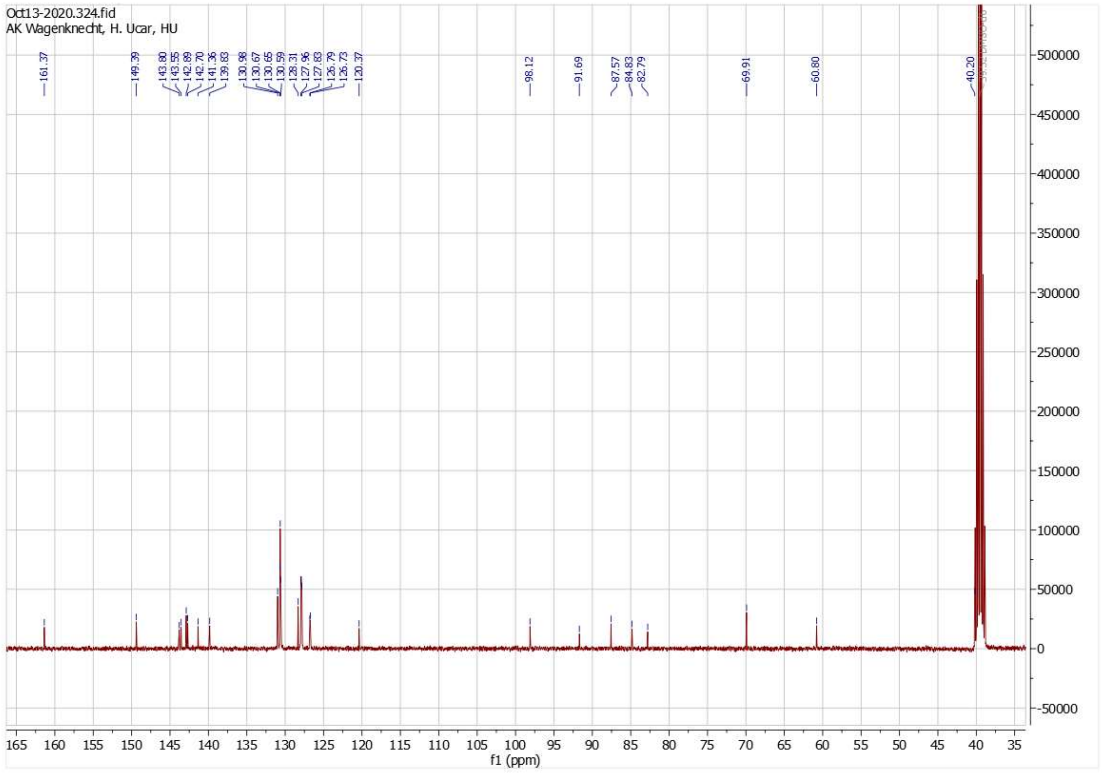

Figure S6. ^{13}C-NMR spectrum (126 MHz, DMSO) of **1L**.

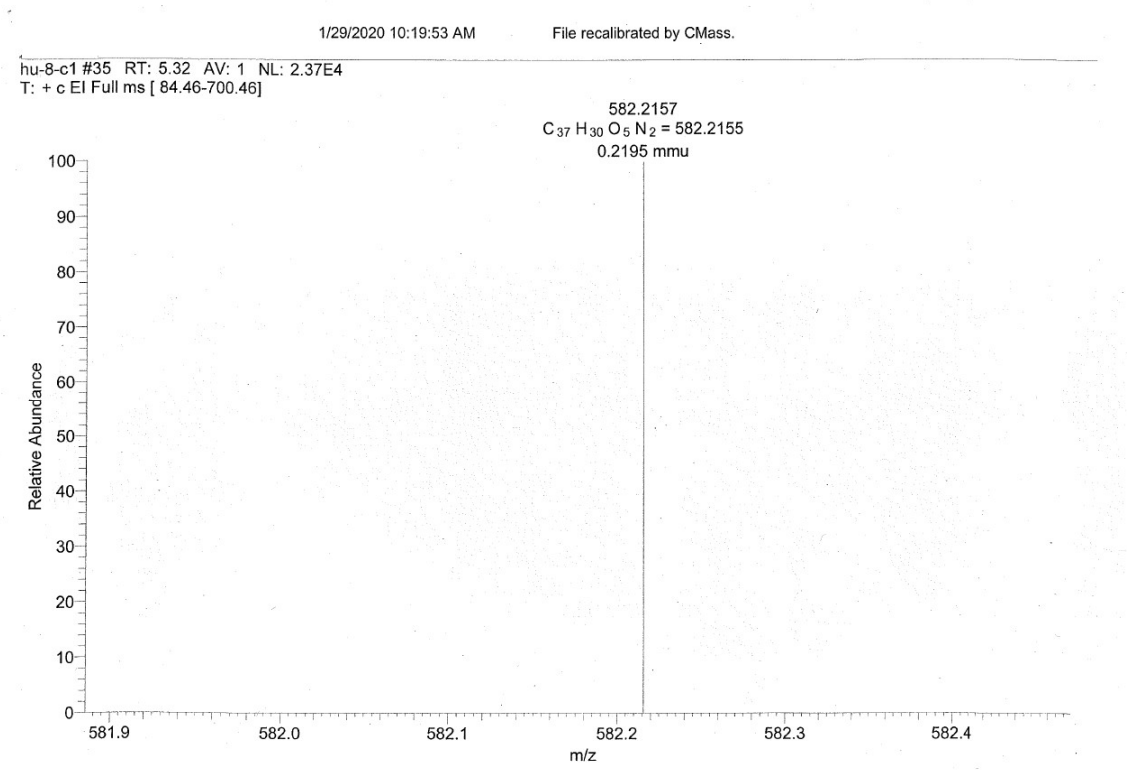

Figure S7. HR-MS (FAB) analysis of **1L**.

Compound 6

The compound **1D** (0.30 g, 0.51 mmol, 1.00 eq.) was lyophilized from benzene overnight. Afterwards it was dissolved in 5 mL dry pyridine under argon. After addition of 0.23 g 4,4′-dimethoxytrityl chloride (0.67 mmol, 1.30 eq.) the reaction mixture was stirred overnight. MeOH (2 mL) was added to the reaction and the solvents were removed under reduced pressure. The crude product was purified by flash-column chromatography (silica, DCM:MeOH = 99:1 + 0.1% NEt_3). The desired product was obtained as pale yellow solid in a yield of 70% (0.32 g, 0.36 mmol).

TLC (DCM/MeOH (1%)): R_f = 0.186

^{1}H-NMR (500 MHz, DMSO) δ = 11.73 (s, 1H), 8.02 (s, 1H), 7.37 (d, J = 9.0 Hz, 2H), 7.30 – 7.24 (m, 4H), 7.22 (t, J = 7.8 Hz, 2H), 7.15 – 7.10 (m, 10H), 7.02 – 6.92 (m, 6H), 6.88 (s, 4H), 6.81 (t, J = 8.9 Hz, 4H), 6.13 (t, J = 6.7 Hz, 1H), 5.34 (d, J = 4.4 Hz, 1H), 4.56 – 4.11 (m, 1H), 3.95 (dt, J = 5.5, 3.1 Hz, 1H), 3.63 (s, 6H), 3.18 (ddd, J = 44.6, 10.6, 3.9 Hz, 2H), 2.34 – 2.16 (m, 2H).

^{13}C-NMR (126 MHz, DMSO) δ = 161.4, 158.0, 149.3, 144.6, 143.4, 142.9, 142.9, 142.8, 142.7, 141.2, 139.8, 135.5, 135.3, 130.7, 130.7, 130.6, 130.6, 129.7, 129.6, 128.3, 127.9, 127.9, 127.8, 127.5, 126.7, 126.6, 120.2, 113.2, 99.5, 98.5, 98.5, 91.9, 86.0, 85.9, 85.1, 82.1, 81.1, 70.5, 63.7, 55.0.

HR-MS (ESI): m/z calculated for $C_{58}H_{48}N_2O_7^+$ [M^+] = 884,3462; found = 884.3455.

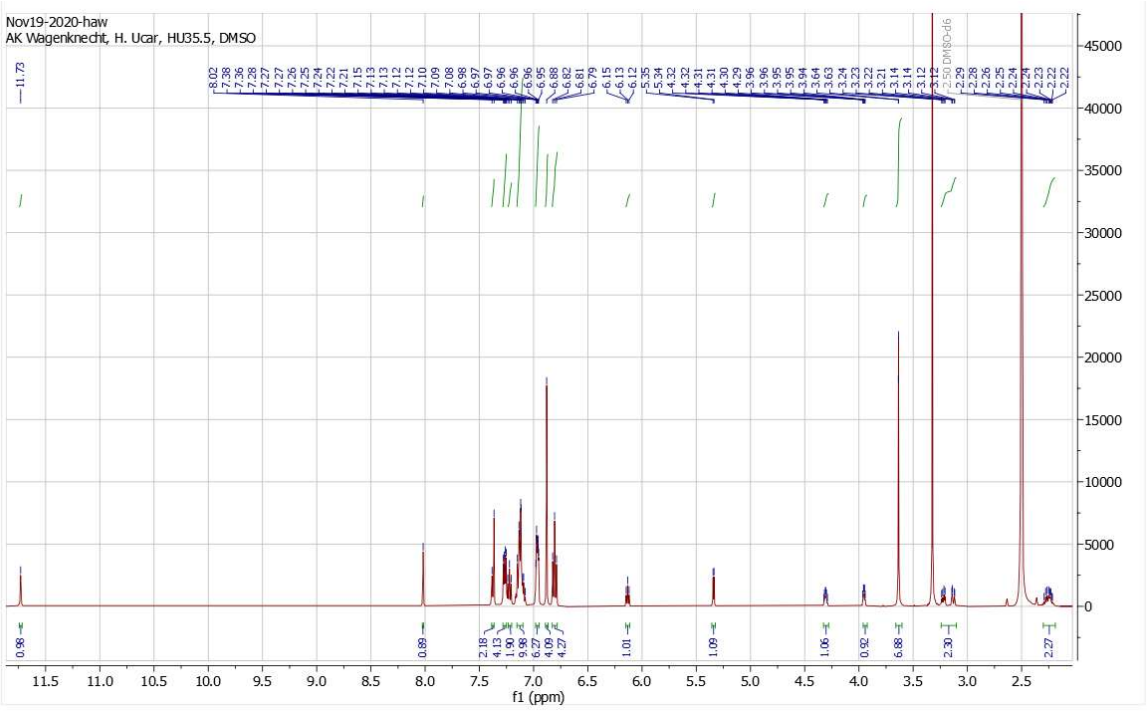

Figure S8. ^{1}H-NMR spectrum (500 MHz, DMSO) of **6**.

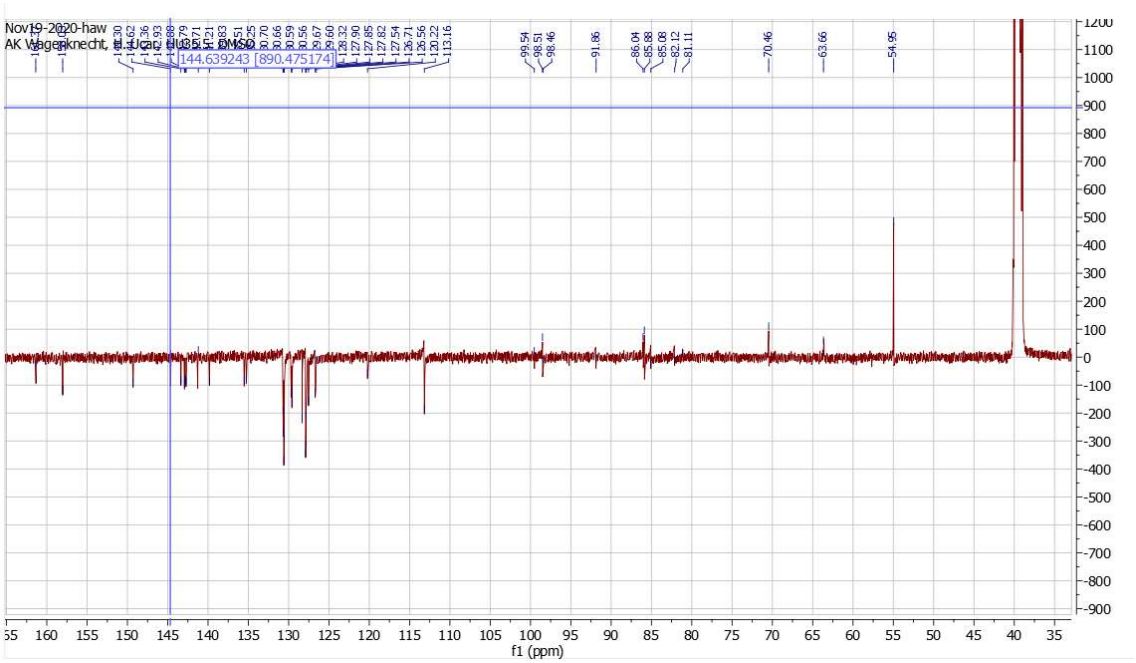

Figure S9. ^{13}C-NMR spectrum (126 MHz, DMSO) of **6**.

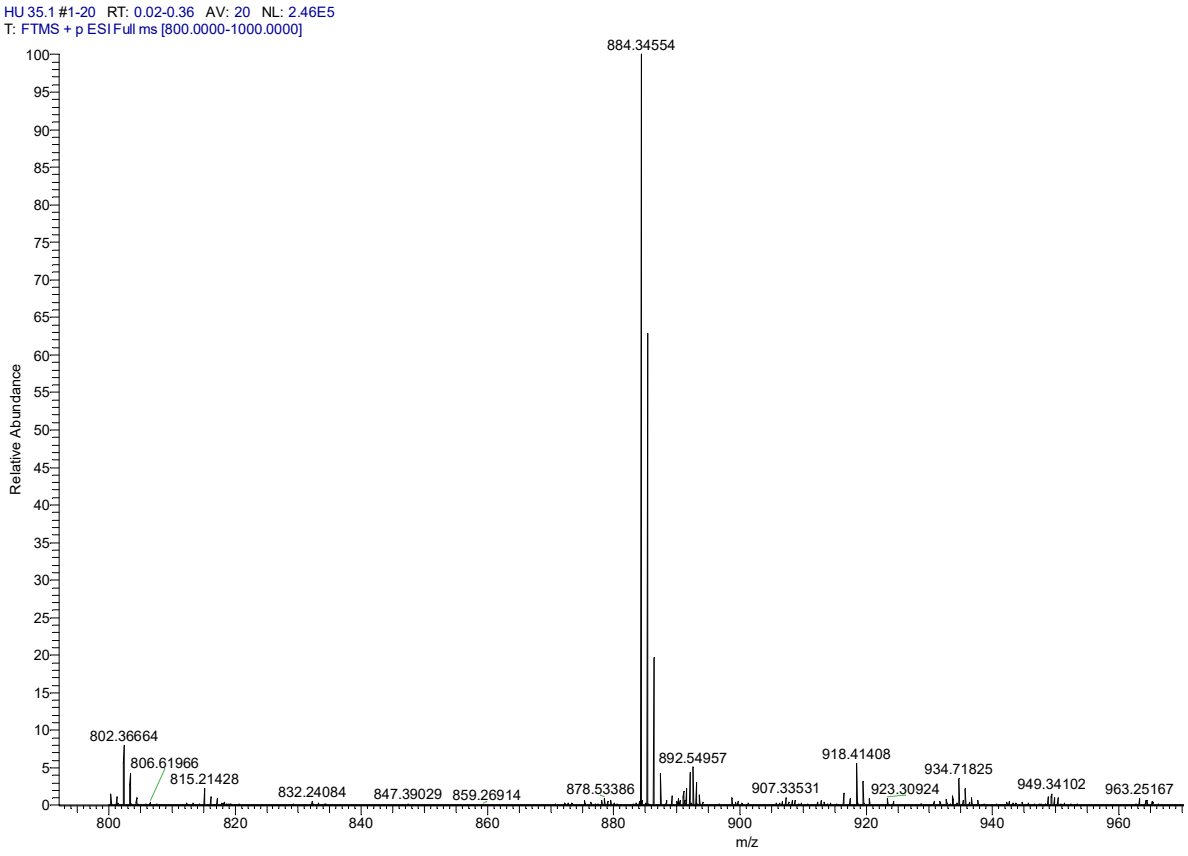

Figure S10. HR-MS (ESI) analysis of **6**.

Compound 1

The compound **6** (0.30 g, 0.34 mmol, 1.00 eq.) was lyophilized from benzene overnight. Afterwards it was dissolved in 5 mL dry DCM under argon. After addition of 0.18 mL N,N-diisopropylethylamine (0.13 g, 1.02 mmol, 3.00 eq.) and 0.11 mL 2-cyanoethyl-N,N-diisopropylchlorophosphoramidite (0.12 g, 0.51 mmol, 1.50 eq.) the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was purified by flash-column chromatography (silica, DCM:acetone = 5:1 + 0.1 % NEt_3). The desired product was obtained as pale yellow solid in a yield of 88 % (0.35 g, 0.30 mmol).

TLC (DCM/Aceton 5:1): R_f = 0.89

^{31}P-NMR (162 MHz, MeOD): δ = 148.5, 148.2.

HR-MS (ESI): m/z calculated for $C_{67}H_{65}N_4O_8P^+$ [M^+] = 1084.4540; found = 1084.4533.

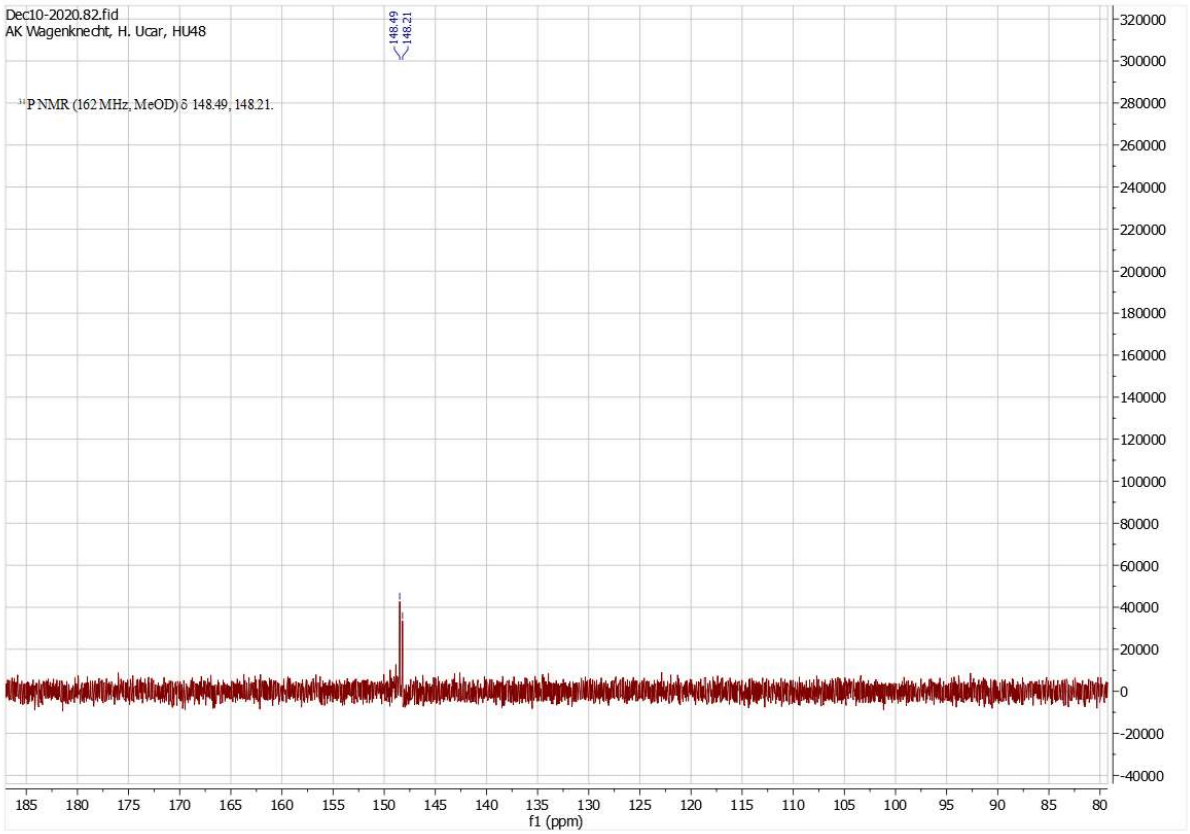

Figure S11. ^{31}P-NMR spectrum (162 MHz, MeOD) of **1**.

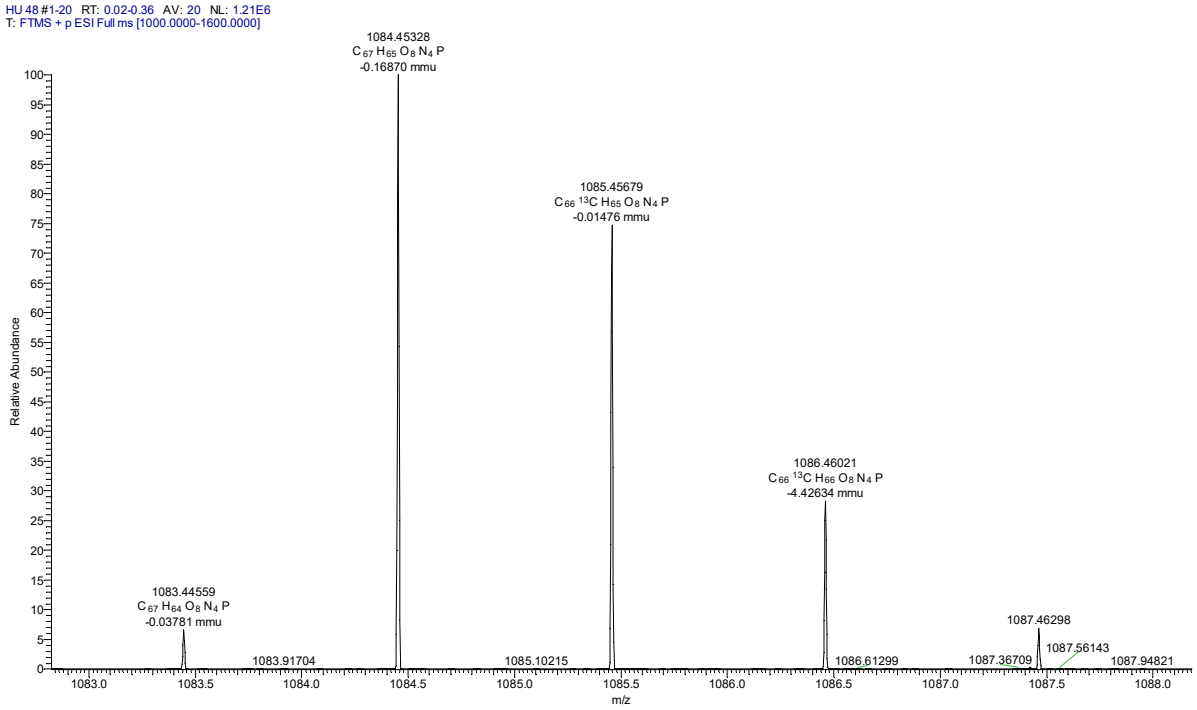

Figure S12. HR-MS(ESI) analysis of **1**.

3. DNA preparation

The L-configured DNA-template strands (L-A_{20} & L-T_{20}) and the Tpe-modified DNA strands **Tpe1a**, **Tpe1b**, **Tpe2a** and **Tpe2b** were synthesized on a *H-6 DNA/RNA Synthesizer* from K&A LABORGERÄTE using the standard protocol. The strands **Tpe1a** and **Tpe2b** were prepared with a longer coupling time of 500 s (3 pulses) and a higher concentration of the phosphoramidite (0.1 M). The ß-L-deoxyadenosine/ ß-L-deoxythymidine phosphoramidites (0.067 M) and the CPG-colums (1 µmol, 500 Å) loaded with the first nucleobase are commercially available and were purchased from CHEMGENES. The 5'-terminal DMT protecting group was not removed during synthesis. The cleavage of the DNA strands from the CPG resin were achieved by heating the strands in 0.7 mM conc. aqueous ammonia solution (>25 %, trace select, FLUKA) to 60 °C for 16 h. The solvents were removed under reduced pressure and the DNA was purified using *Glen-Pak™ DNA Purification Cartridges* from GLEN RESEARCH with the manufacturer given standard procedure. As final step the DNA was further purificated by reverse phase HPLC purification using the following conditions: A = NH_4OH buffer (50 mM), B = MeCN; gradient = 0-30 % in 30 min (L-A_{20} and L-T_{20}); 0-50 % in 50 min (**TPE1a**, **TPE1b**, **TPE2a** and **TPE2b**). The HPLC runs were carried out on a THERMO FISCHER SCIENTIFIC (*Dionex UltiMate3000 auto sampler*, *software Chromeleon 7*) with a *VDSpher OptiBio PUR 300 S18-SE-column* (250 x 10 mm, 5 µm) and a flow rate of 2.5 mL/min. The DNA-strands were dissolved in water. The concentrations were determined spectrometric with a *Nanodrop ND-100* spectrophotometer by their absorbance at 260 nm. Duplexes of TPE-modified DNA were prepared by heating the chromophore-modified strands in the presence of 1.0 eq. unmodified or with atto dye modified complementary strands to 90 °C, hold this temperature for 5 min and then slowly cooling to RT.

Table S1. MS analyses and extinction coefficients of the used DNA strands.

DNA	**$[M]^+$ calc. [g/mol]**	**$[M]^+$ found [g/mol]**	**ε_{260} [$mM^{-1}cm^{-1}$]**
L-A_{20}	6199.2	6197.4	277.2
L-T_{20}	6019.0	6020.4	158.4
TPE1a	6404.1	6403.3	203.6
TPE1b	6404.1	6405.5	203.6
TPE2a	6744.3	6749.8	219.1
TPE2b	6744.3	6745.8	219.1
1D			23.4

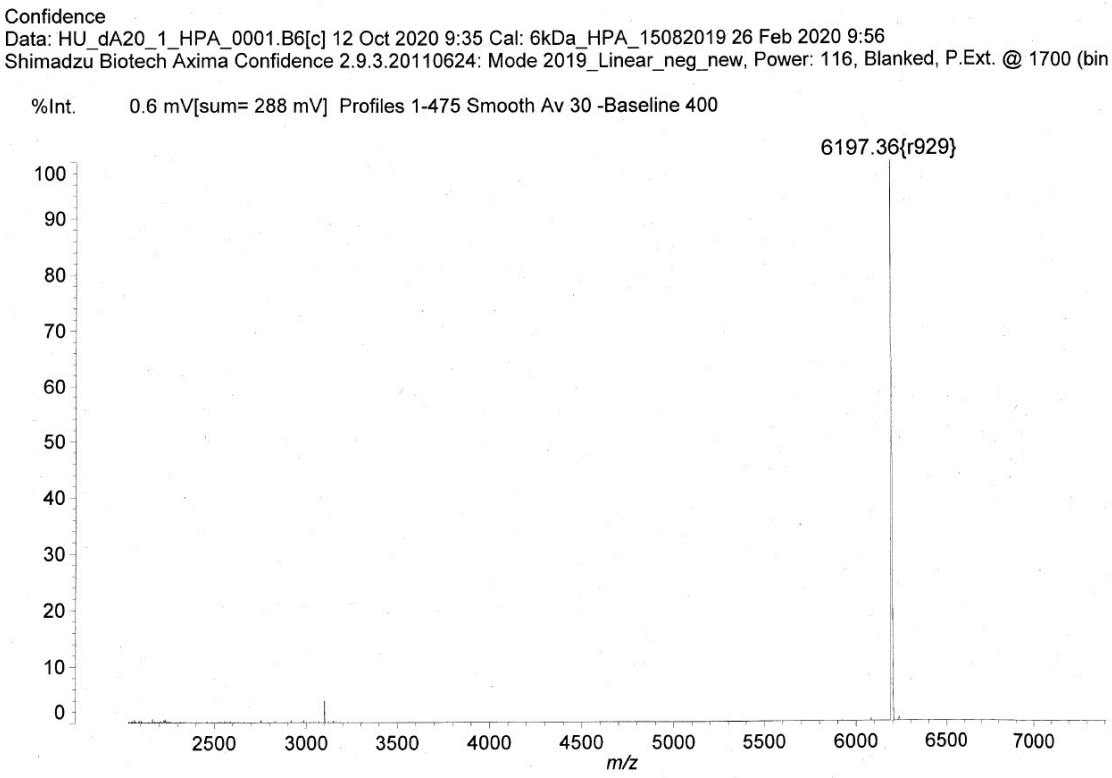

Figure S13. MS (MALDI) analysis of L-A_{20}.

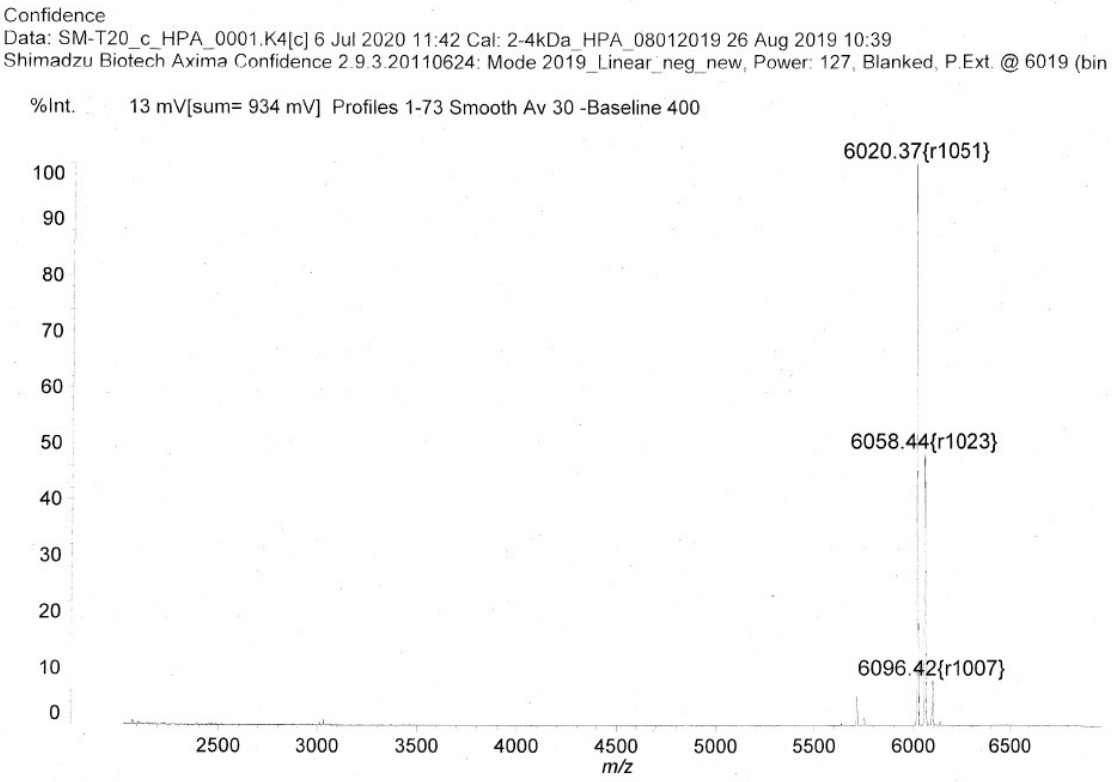

Figure S14. MS (MALDI) analysis of L-T_{20}.

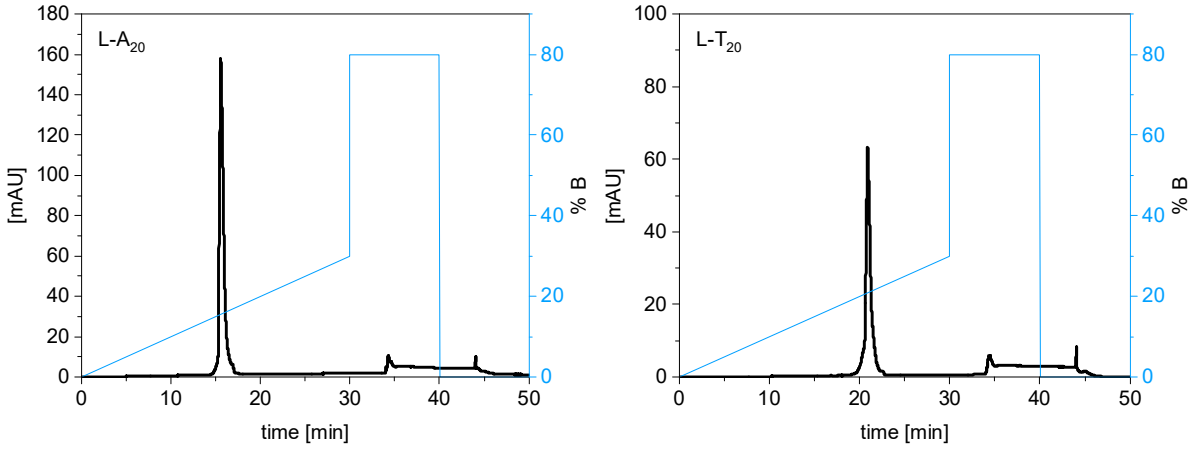

Figure S15. HPLC analyses of L-A_{20} (left) and L-T_{20} (right).

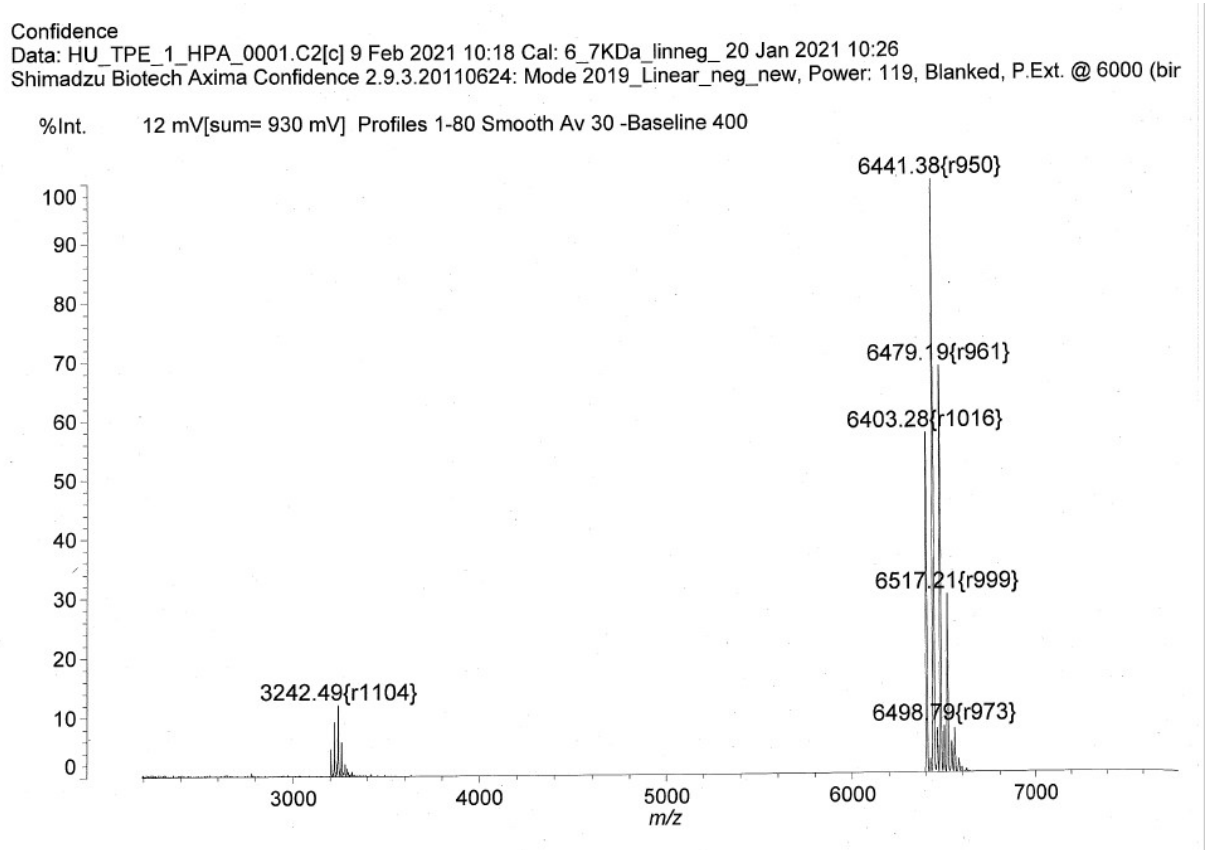

Figure S16. MS (MALDI) analysis of **TPE1a**.

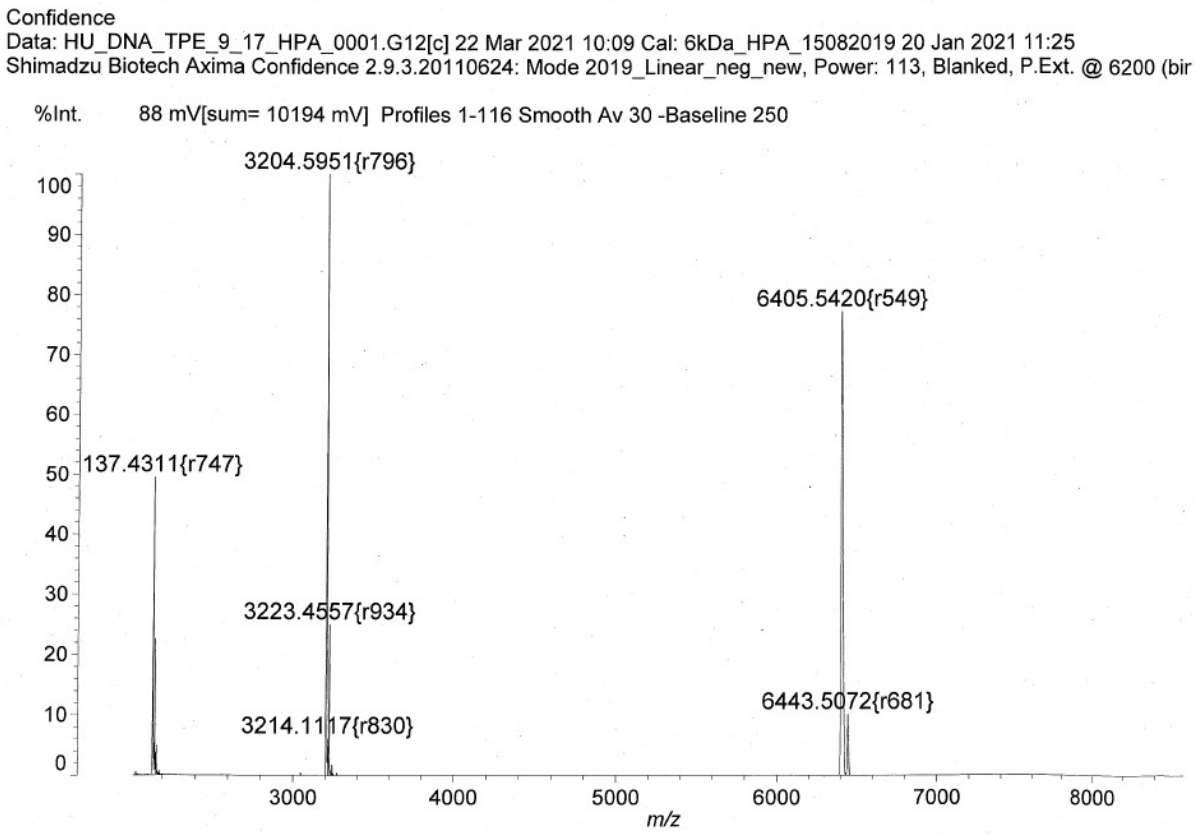

Figure S17. MS (MALDI) analysis of **TPE1b**.

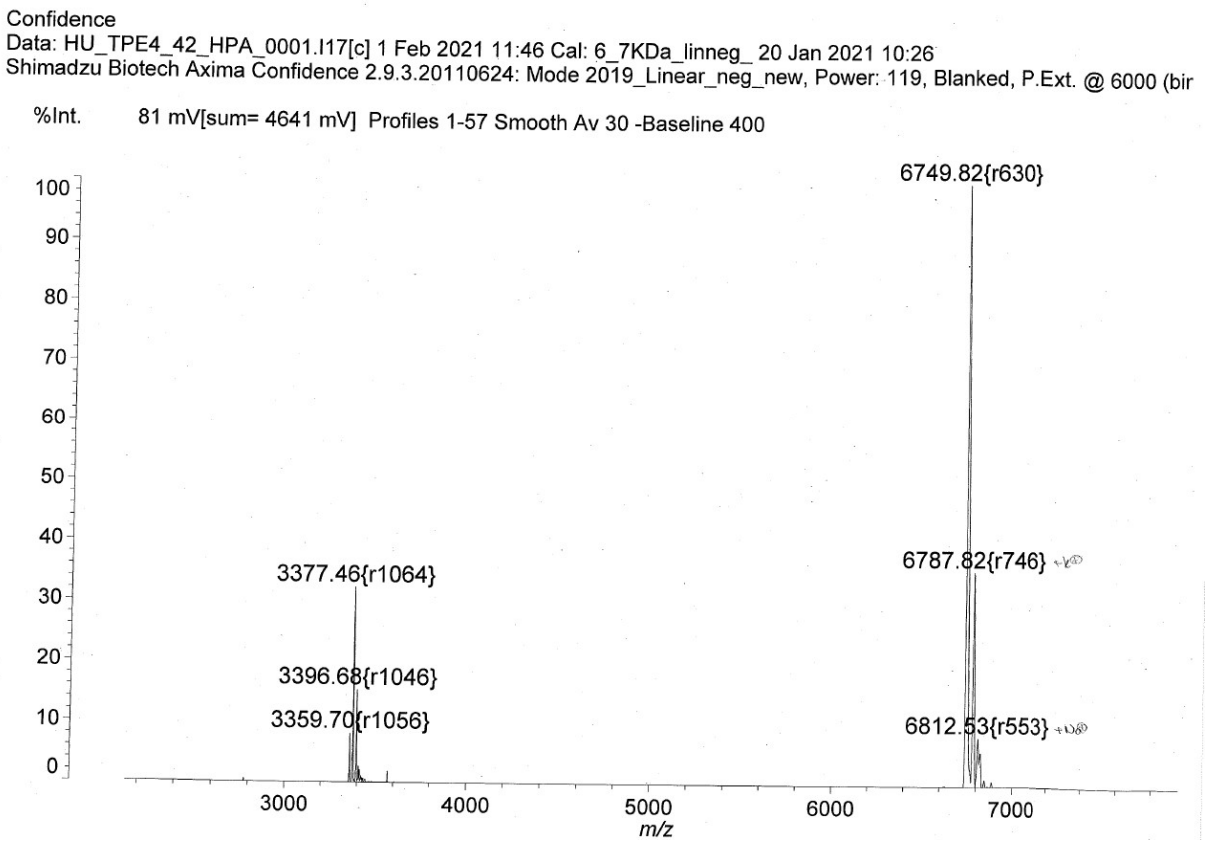

Figure S18. MS (MALDI) analysis of **TPE2a**.

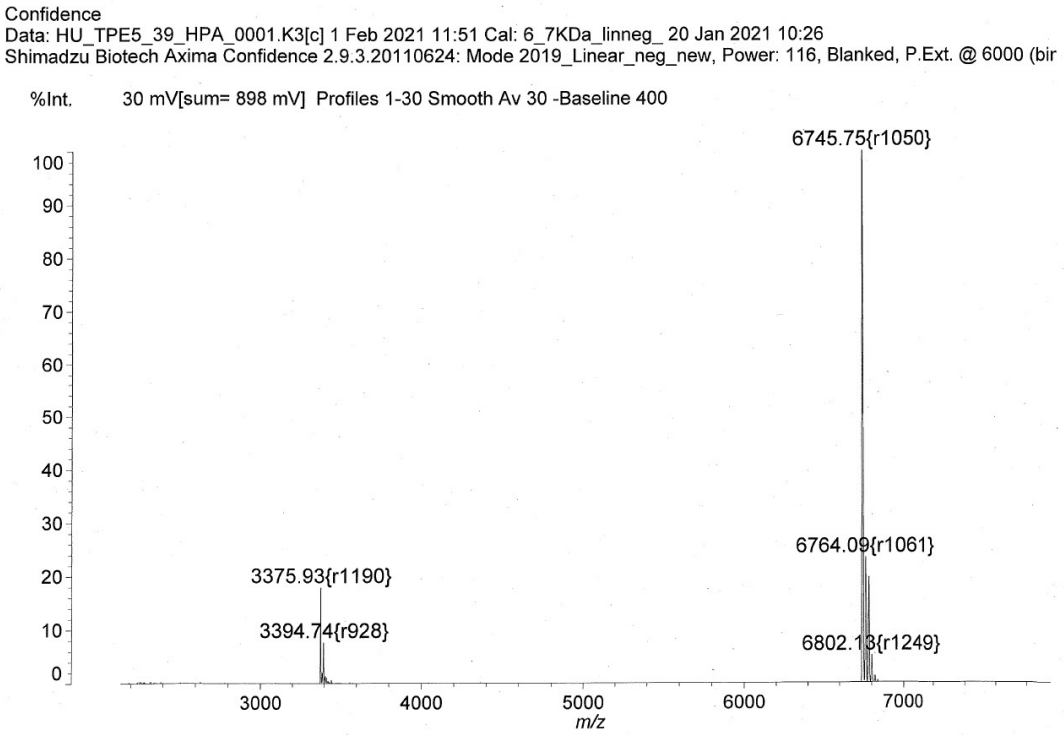

Figure S19. MS (MALDI) analysis of **TPE2b**.

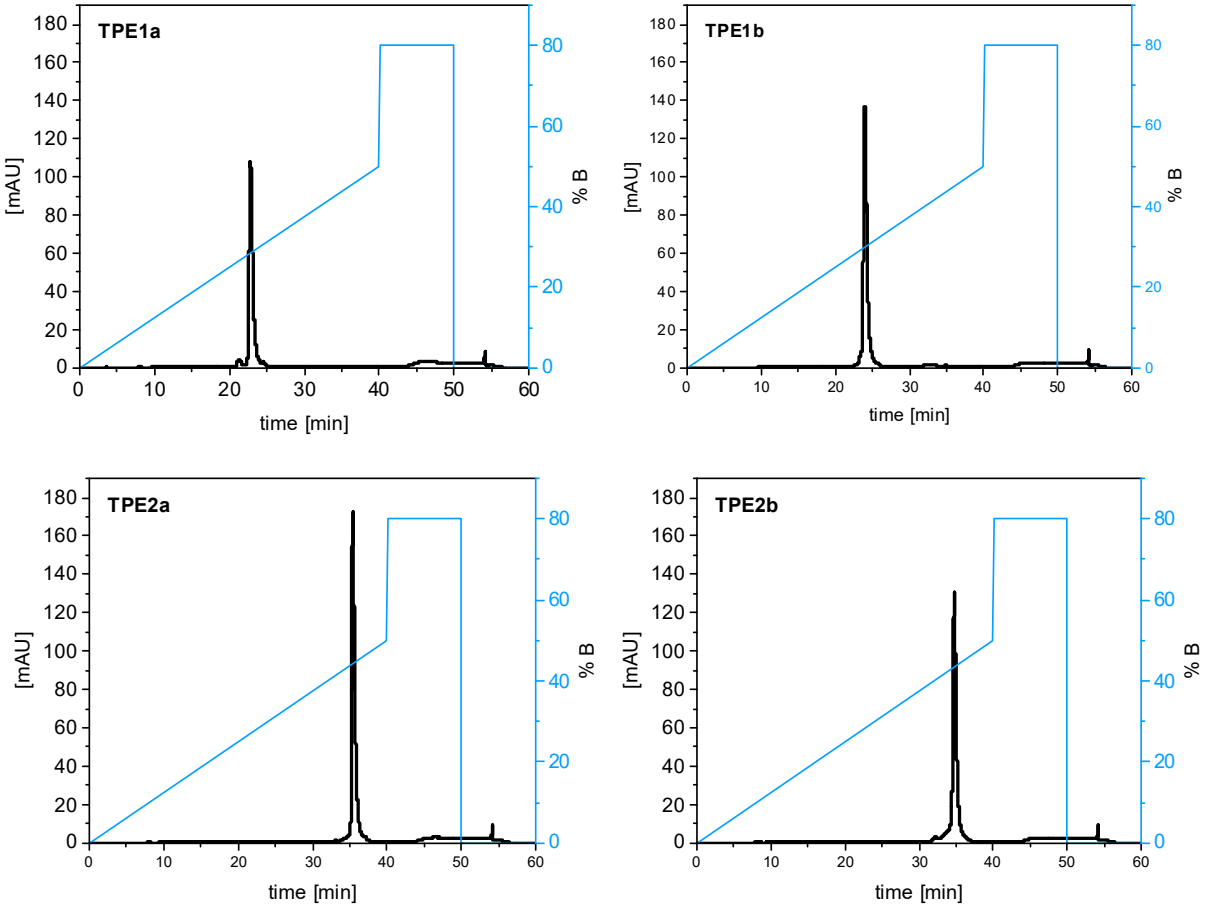

Figure S20. HPLC analyese of **TPE1a**, **TPE1b**, **TPE2a** and **TPE2b**.

4. Additional optical spectroscopy

Non-templated supramolecular assemblies

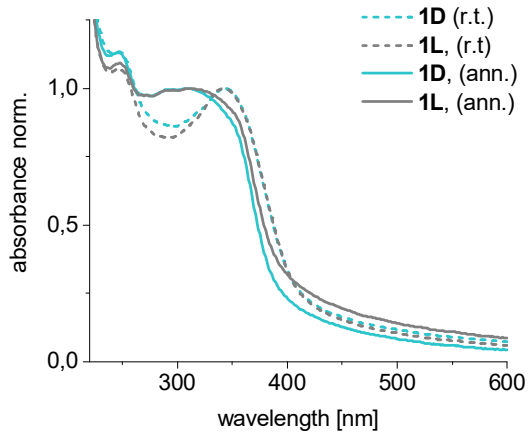

Figure S21. UV/Vis absorbance of the assemblies prepared with **1D** and **1L** in the absence of any DNA template (H_20, 0.9% **THF**) either at room temperature (dashed) or by annealing after heating to 90 °C for 5 min (solid).

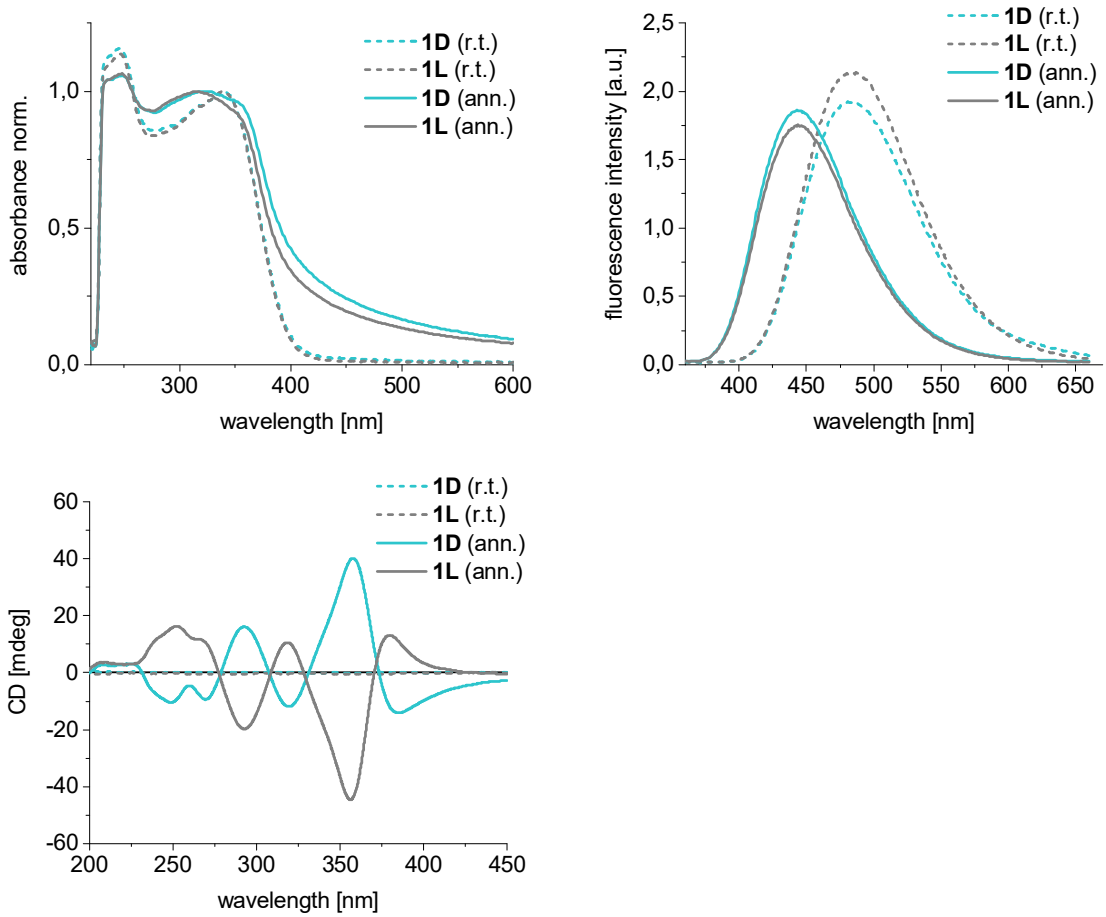

Figure S22. UV/Vis absorbance, emission and circular dicroism of the assemblies prepared with **1D** and **1L** in the absence of any DNA template (H_20, 0.9% **DMSO**) either at room temperature (dashed) or by annealing after heating to 90 °C for 5 min (solid).

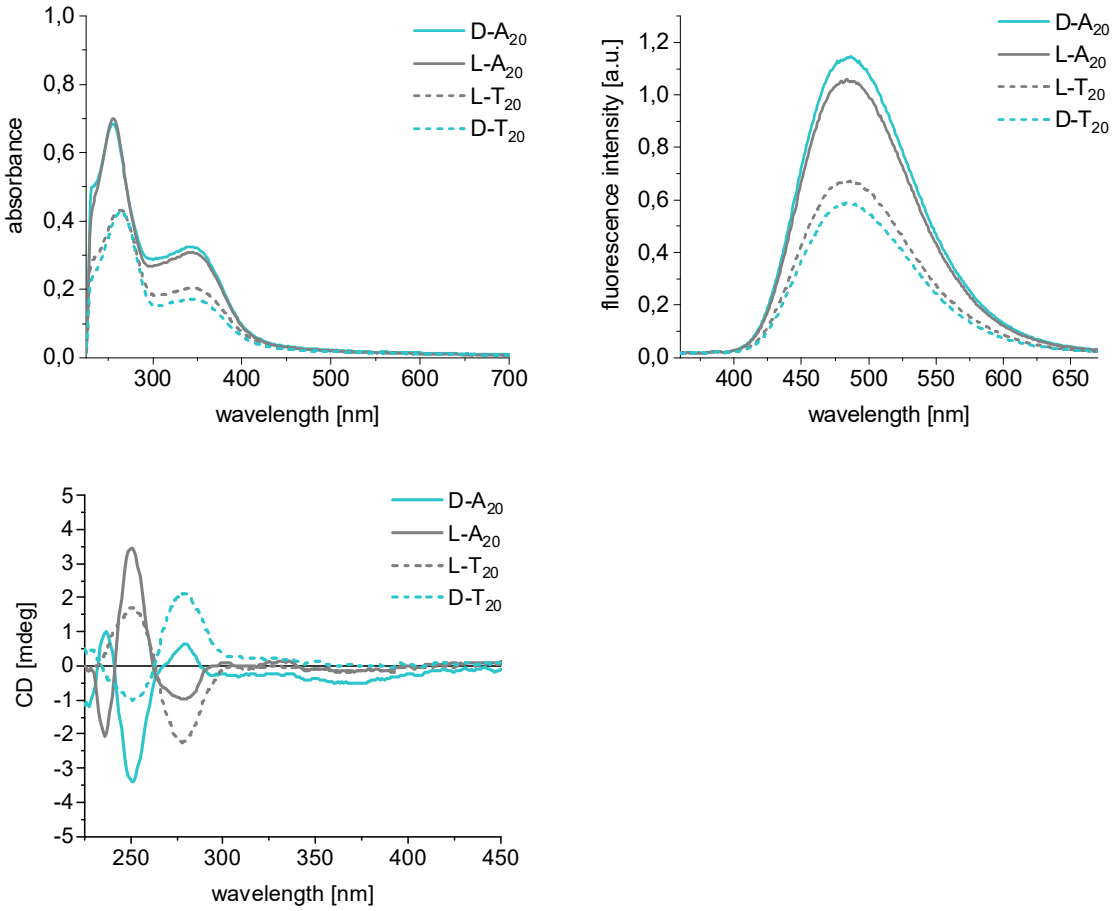

Figure S23. UV/Vis absorbance, fluorescence and circular dichroism of the DNA-templated assemblies of **1L** (1.25 µM DNA, 37.5 µM **1L**, 250 mM NaCl, 0.9 % DMSO, 1h incubated at r. t., 3 min at 16 000 g centrifuged, λ_{exc} = 341 nm).

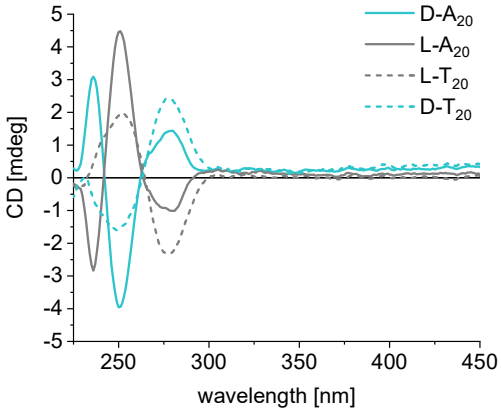

Figure S24. Circular dichroism of the DNA-templates in the absence of **1D** and **1L** (1.25 µM DNA, 250 mM NaCl, 0.9 % DMSO, 1h incubated at r. t).

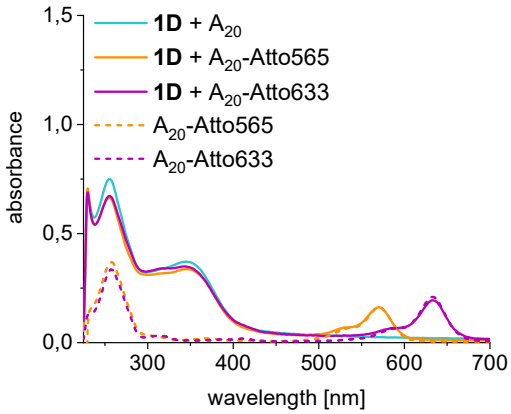

Figure S25. UV/Vis absorbance of the DNA-templated (with and without atto dye modification) assemblies of **1D** (1.25 µM DNA, 37.5 µM **1D**, 250 mM NaCl, 0.9 % DMSO, 1h incubated at r. t., 3 min at 16 000 g centrifuged).

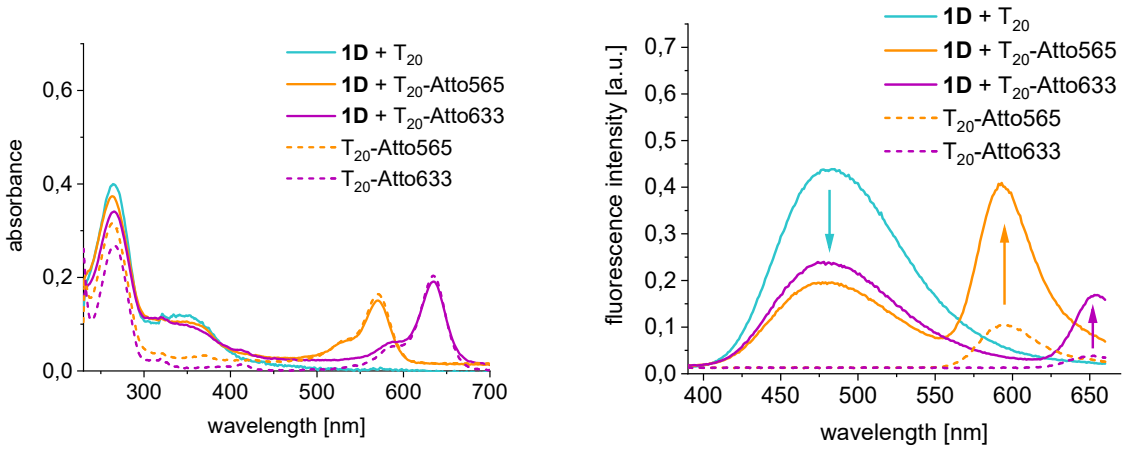

Figure S26. UV/Vis absorbance and fluorescence of the DNA-templated (with and without atto dye modification) assemblies of **1D** (1.25 µM DNA, 37.5 µM **1D**, 250 mM NaCl, 0.9 % DMSO, 1h incubated at r. t., 3 min at 16 000 g centrifuged).

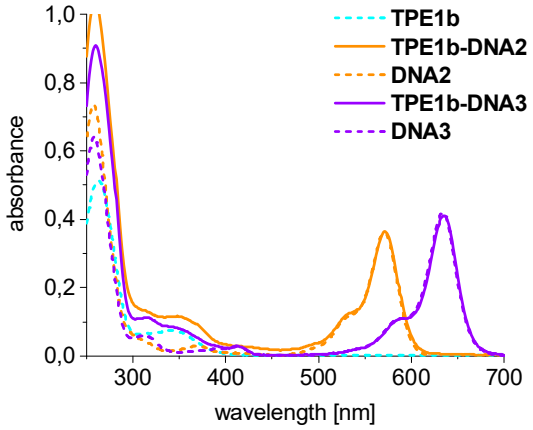

Figure S27. UV/Vis absorbance of the TPE-modified DNA single strand **TPE1b** and hybrids with atto dye modified counter strands **DNA2** and **DNA3** (c(**TPE1b**) = c(cs) = 2.5 µM, 250 mM NaCl, 10 mM NaPi buffer).

5. References

[1] J. Wang, J. Mei, E. Zhao, Z. Song, A. Qin, J. Z. Sun, B. Z. Tang, *Macromolecules* **2012**, *45*, 7692-7703.