Electronic Supplementary Material (ESI) for ChemComm.

Modulation of aggregation-induced emission by sequence-selective assembly of cyanostilbene in supramolecular DNA architectures

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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 DNA strands were obtained HPLC-purified and lyophilized from METABION.

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

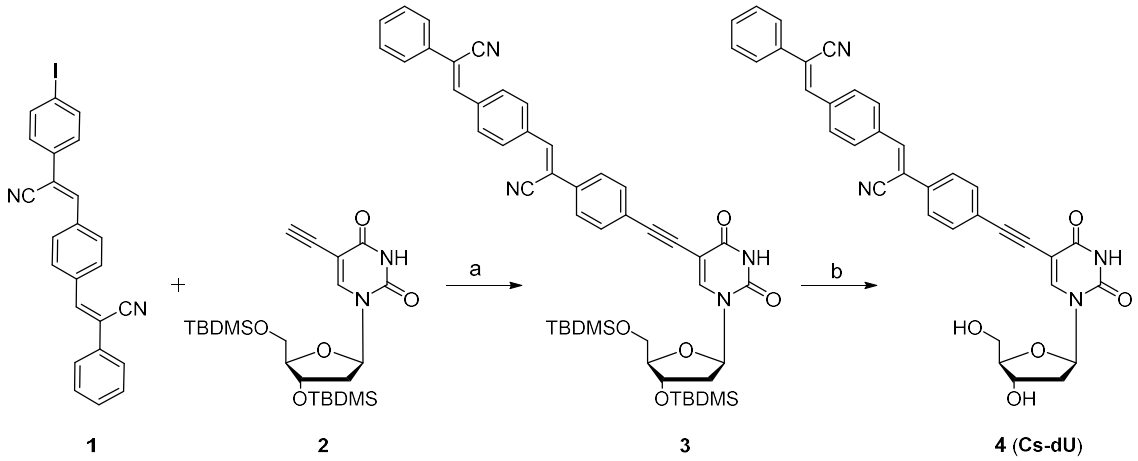
FAB-Mass spectra were measured on a FINNIGAN *MAT95 spectrometer*. MALDI-TOF spectra were recorded on a SHIMADZU *AXIMA Confidence spectrometer*. ESI-mass spectra recorded on a THERMOFISHER SCIENTIFIC *Q Exactive (Orbitrap)*.

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).

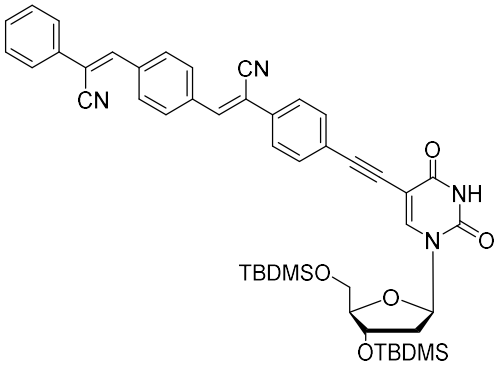
Circular dichroism was measured on a JASCO *J-810* Spectropolarimeter with the *peltier-element PTC-423S* (100 nm/min, 4 accumulations). FDCD spectra were recorded with a JASCO *J-1500* CD spectrometer (0.2 nm resolution, 4 accumulations) equipped with a filter system and a *PML-534 detector* in a perpendicular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

2. Synthesis of Cs-dU



Scheme S1. Synthesis of compound **4** (**Cs-dU**). a) $PdCl_2(PPh_3)_2$, CuI, PPh_3, DMF, Et_3N, 90 °C, 4 h, 32%; b) $Et_3N{\cdot}HF$, THF, r.t., 19 h, 56%.

Compound 3



$C_{47}H_{54}N_4O_5Si_2$
811.14 g/mol

In a Schlenk flash, compound **1**[1] (210 mg, 0.460 mmol, 1.00 equiv.), compound **2**[2] (220 mg, 0.460 mmol, 1.00 equiv.) and CuI (3.50 mg, 18.0 nmol, 0.04 equiv.) were lyophilized overnight. The solid residues were dissolved in abs. DMF (10 mL) and abs. Et_3N (0.260 mL, 187 mg, 1.83 mmol, 4.00 equiv.) and degassed by an Argon flow. $Pd(PPh_3)_4Cl_2$ (6.40 mg, 30.0 nmol, 0.06 eqiv.) was added. The reaction mixture was heated at 90 °C for 4 h. The solvent was removed under vacuum and the residue was prepurified by column chromatography (silica gel, CH_2Cl_2+MeOH 0-2 %). The product was finally purified by preparative thin layer chromatography (silica gel, CH_2Cl_2+MeOH 5 %) and obtained as yellow solid compound in a yield of 32 % (119 mg, 0.147 mmol).

T.l.c. (CH_2Cl_2+MeOH (2 %)): R_f = 0.25

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.65 (d, *J* = 5.4 Hz, 1H, **6-CH_{dU}**), 8.10 (d, *J* = 4.0 Hz, 1H, **CH_{CDS}**), 8.00 (s, 1H, **CH_{CDS}**), 7.76 (d, *J* = 8.5 Hz, 1H, **CH_{CDS}**), 7.70-7.62 (m, 2H, **CH_{CDS}**), 7.60-7.53 (m, 1H, **CH_{CDS}**), 7.50-7.33 (m, 7H, **CH_{CDS}**), 7.30-7.20 (m, 2H, **CH_{CDS}**), 6.47-6.20 (m, 1H, **1'-CH_{dU}**), 4.43 (tt, *J* = 5.3, 2.5 Hz, 1H, **3'-CH_{dU}**), 4.01 (dq, *J* = 4.6, 2.2 Hz, 1H, **4'-CH_{dU}**), 3.93 (ddd, *J* = 11.4, 6.6, 2.4 Hz, 1H, **5'-$CH_{2,\,dU}$**), 3.78 (ddd, *J* = 11.4, 5.3, 2.2 Hz, 1H, **5'-$CH_{2,\,dU}$**), 2.35 (ddt, *J* = 13.0, 5.8, 3.0 Hz, 1H, **2'-$CH_{2,\,dU}$**), 2.06 (dddd, *J* = 13.3, 7.7, 5.9, 3.7 Hz, 1H, **2'-$CH_{2,\,dU}$**), 0.97-0.82 (m, 18H, **$CH_{3,\,TBDMS}$**), 0.18-0.09 (m, 6H, **Si-$CH_{3,\,TBDMS}$**), 0.09-0.04 (m, 6H, **Si-$CH_{3,\,TBDMS}$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.3 (**4-$C_{q,\,dU}$**), 149.1 (**2-$C_{q,\,dU}$**), 143.4 (**CH_{CDS}**), 142.7 (**CH_{CDS}**), 141.1 (**CH_{CDS}**), 140.7 (**CH_{CDS}**), 140.6 (**CH_{CDS}**), 135.8 (**C_q**), 135.3 (**C_q**), 134.2 (**C_q**), 132.5 (**CH_{CDS}**), 132.4 (**CH_{CDS}**), 130.4 (**CH_{CDS}**), 130.0 (**CH_{CDS}**), 129.9 (**CH_{CDS}**), 129.8 (**CH_{CDS}**), 129.6 (**CH_{CDS}**), 129.3 (**CH_{CDS}**), 129.3 (**CH_{CDS}**), 129.0 (**CH_{CDS}**), 126.3 (**CH_{CDS}**), 126.2 (**CH_{CDS}**), 126.0 (**CH_{CDS}**), 124.4 (**C_q**), 119.6 (**C_q**), 117.8 (**C_q**), 115.2 (**C_q**), 113.3 (**C_q**), 112.4, 100.1 (**C_q**), 100.0, 93.1 (**$C_{C\equiv C}$**), 88.7 (**4'-CH_{dU}**), 86.2 (**1'-CH_{dU}**), 82.7 (**$C_{C\equiv C}$**), 77.5, 77.2 (**3'-CH_{dU}**), 76.8, 72.6 (**C_q**), 63.1 (**5'-$CH_{2,\,dU}$**), 42.3 (**2'-$CH_{2,\,dU}$**), 37.2 (**C_q**), 32.1 (**C_q**), 30.2 (**C_q**), 29.8 (**C_q**), 29.5 (**C_q**), 27.2 (**$CH_{3,\,TBDMS}$**), 26.2 (**$CH_{3,\,TBDMS}$**), 25.9 (**$CH_{3,\,TBDMS}$**), 22.8 (**$CH_{3,\,TBDMS}$**), 19.9 (**$CH_{3,\,TBDMS}$**), 18.6 (**$CH_{3,\,TBDMS}$**), 18.1 (**$CH_{3,\,TBDMS}$**), 14.3 (**$CH_{3,\,TBDMS}$**), -4.5 (**$CH_{3,\,TBDMS}$**), -4.7 (**$CH_{3,\,TBDMS}$**), -5.1 (**$CH_{3,\,TBDMS}$**), -5.3 (**$CH_{3,\,TBDMS}$**).

MS (MALDI-TOF): m/z cald. $C_{47}H_{54}N_4O_5Si_2$ [M^+] = 810.36, found = 810.06.

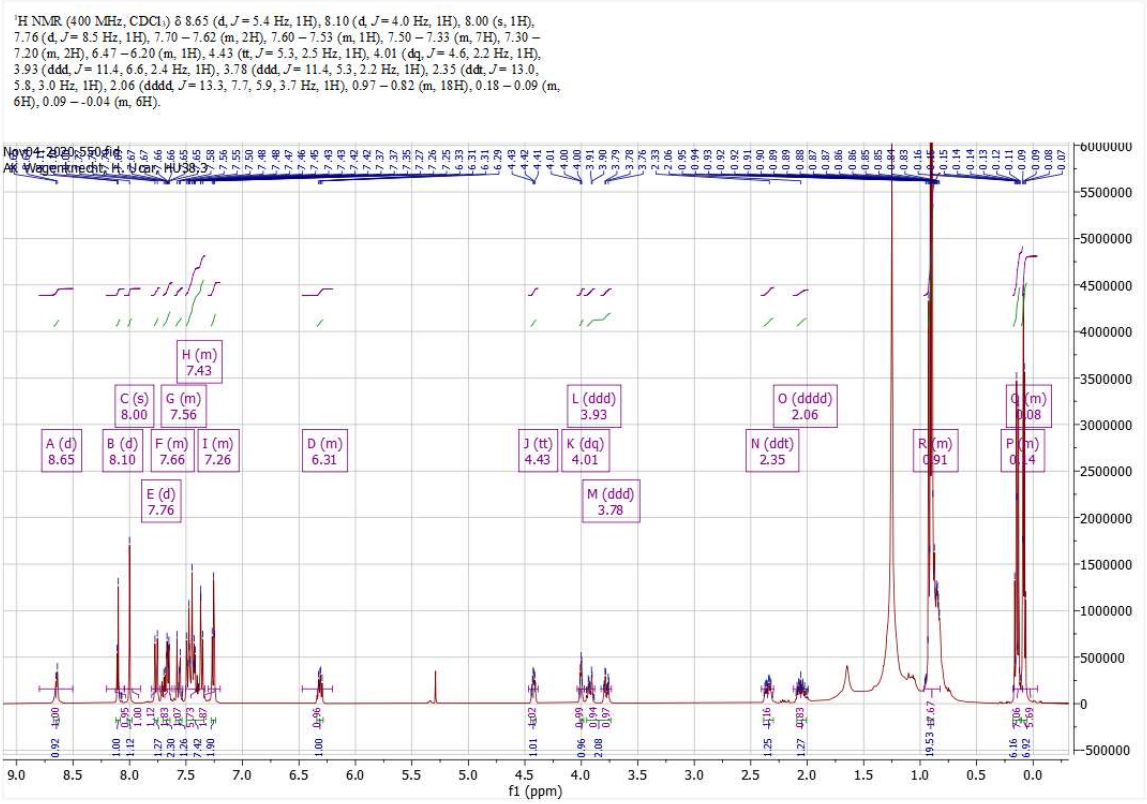


Figure S1. Image of **^{1}H NMR** (400 MHz, $CDCl_3$) of compound **3**.

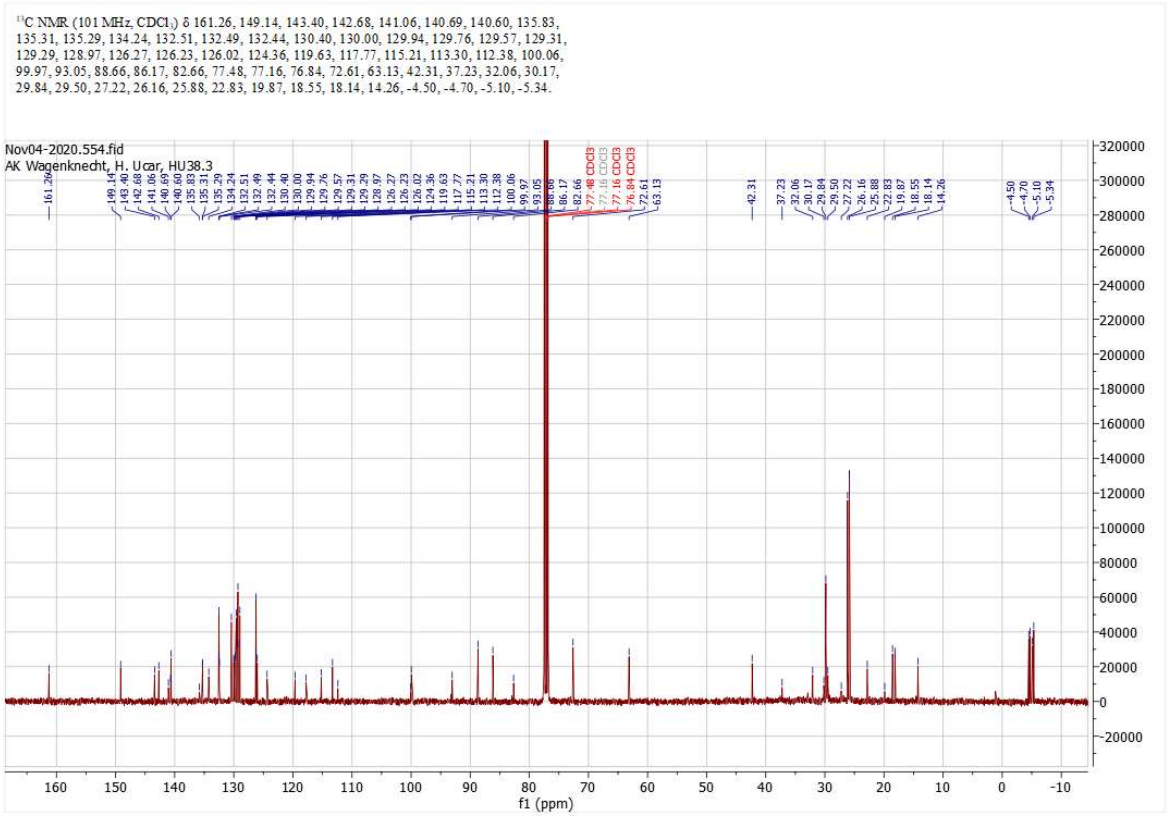
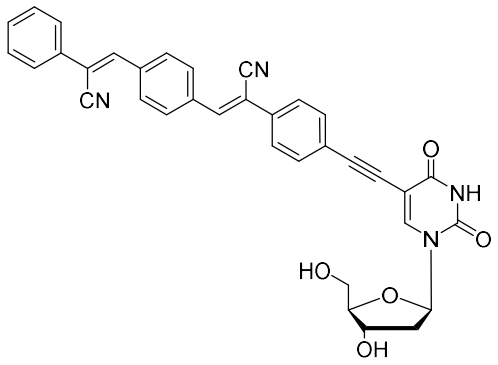


Figure S2. Image of **^{13}C NMR** (101 MHz, $CDCl_3$) of compound **3**.

Figure S3. Image of HR-MS (ESI) of compound **3**.

Compound 4 (Cs-dU)



$C_{35}H_{26}N_4O_5$
582.62 g/mol

In a Schlenk flask, compound **24** (200 mg, 0.250 mmol, 1.00 equiv.) was dissolved in abs. THF (10 mL) and $Et_3N{\cdot}HF$ (201 mL, 198 mg, 1.23 mmol, 5.00 equiv.). The reaction mixture was stirred at r.t. overnight. The solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 (500 mL) and washed with sat. $NaHCO_3$ solution (3×150 mL). The organic phase was dried with Na_2SO_4. The solvent was removed under vacuum. The residue was purified by chromatography (silica gel, CH_2Cl_2+MeOH 0-3 %). The product was obtained as yellow solid in a yield of 56% (81.6 mg, 0.140 mmol).

T.l.c. (CH_2Cl_2+MeOH 5 %): R_f = 0.31

^{1}H NMR (400 MHz, DMSO) δ = 8.40 (d, *J* = 5.2 Hz, 1H, **6-CH_{dU}**), 8.20 (s, 1H), 8.11 (d, *J* = 12.1 Hz, 3H, **CH_{CDS}**), 7.99 (s, 1H, **CH_{CDS}**), 7.89-7.72 (m, 4H, **CH_{CDS}**), 7.64-7.40 (m, 5H, **CH_{CDS}**), 7.39-7.34 (m, 1H, **CH_{CDS}**), 6.14 (q, *J* = 6.0 Hz, 1H, **1'-CH_{dU}**), 4.26 (t, *J* = 4.8 Hz, 1H, **4'-CH_{dU}**), 3.81 (p, *J* = 4.4, 3.9 Hz, 1H, **5'-$CH_{2,dU}$**), 3.63 (dqd, J = 20.2, 9.1, 8.4, 4.0 Hz, 2H, **5'-$CH_{2,dU}$**), 2.17 (q, *J* = 4.8, 3.9 Hz, 2H, **2'-$CH_{2,dU}$**).

^{13}C NMR (101 MHz, DMSO) δ = 162.1, 144.2 (**6-CH_{dU}**), 142.1 (**CH_{CDS}**), 141.7 (**CH_{CDS}**), 135.7 (**C_q**), 135.4 (**C_q**), 133.6 (**C_q**), 133.3 (**C_q**), 132.0 (**CH_{CDS}**), 131.8 (**CH_{CDS}**), 130.2 (**CH_{CDS}**), 129.7 (**CH_{CDS}**), 129.6 (**CH_{CDS}**), 129.3 (**CH_{CDS}**), 129.2 (**CH_{CDS}**), 129.1 (**CH_{CDS}**), 126.2 (**CH_{CDS}**), 126.0 (**CH_{CDS}**), 125.9 (**CH_{CDS}**), 117.7 (**C_q**), 117.5 (**C_q**), 111.6 (**C_q**), 110.8 (**C_q**), 97.9 (**C_q**), 87.6 (**5'-$CH_{2,dU}$**), 84.9 (**1'-CH_{dU}**), 69.9 (**4'-CH_{dU}**), 60.8 (**5'-$CH_{2,dU}$**), 40.2 (**2'-$CH_{2,dU}$**).

HR-MS (ESI): m/z cald. for $C_{35}H_{26}N_4O_5^+$ [M^+] = 582.1903, found = 582.1869.

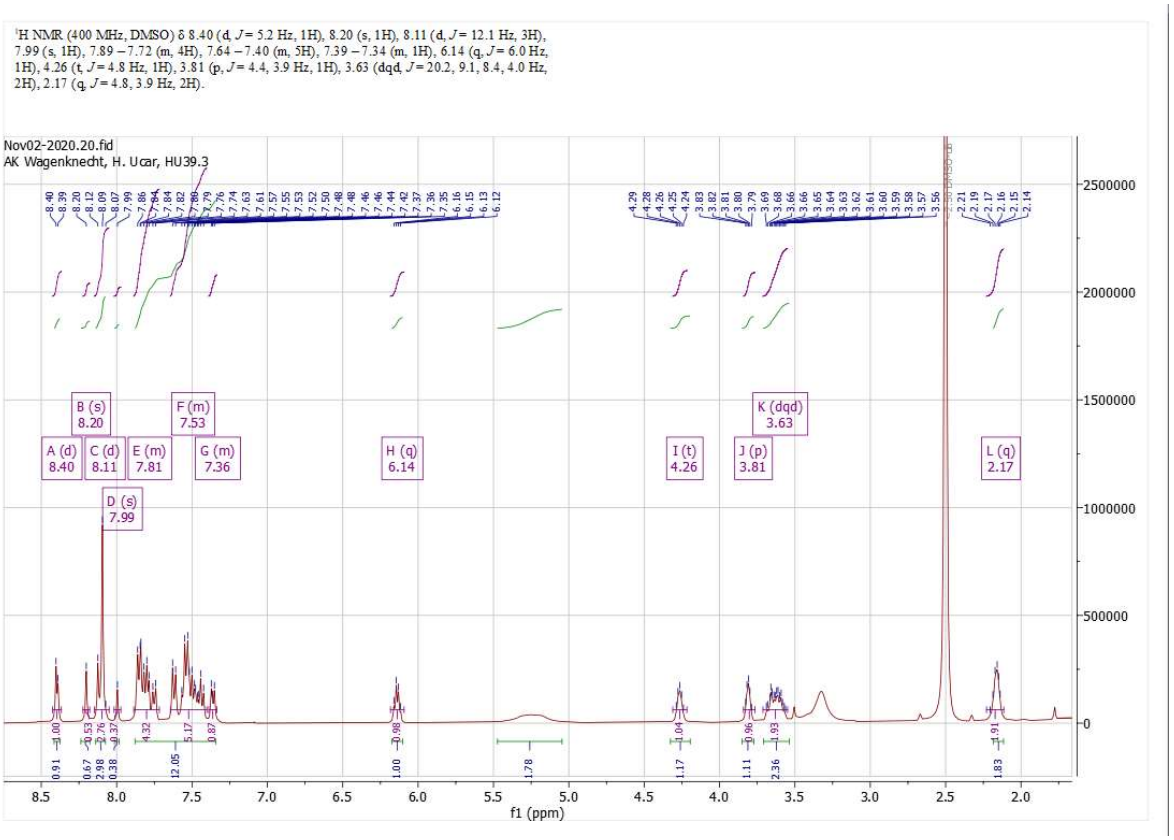


Figure S4. Image of ^{1}H NMR (400 MHz, DMSO) of compound **3**.

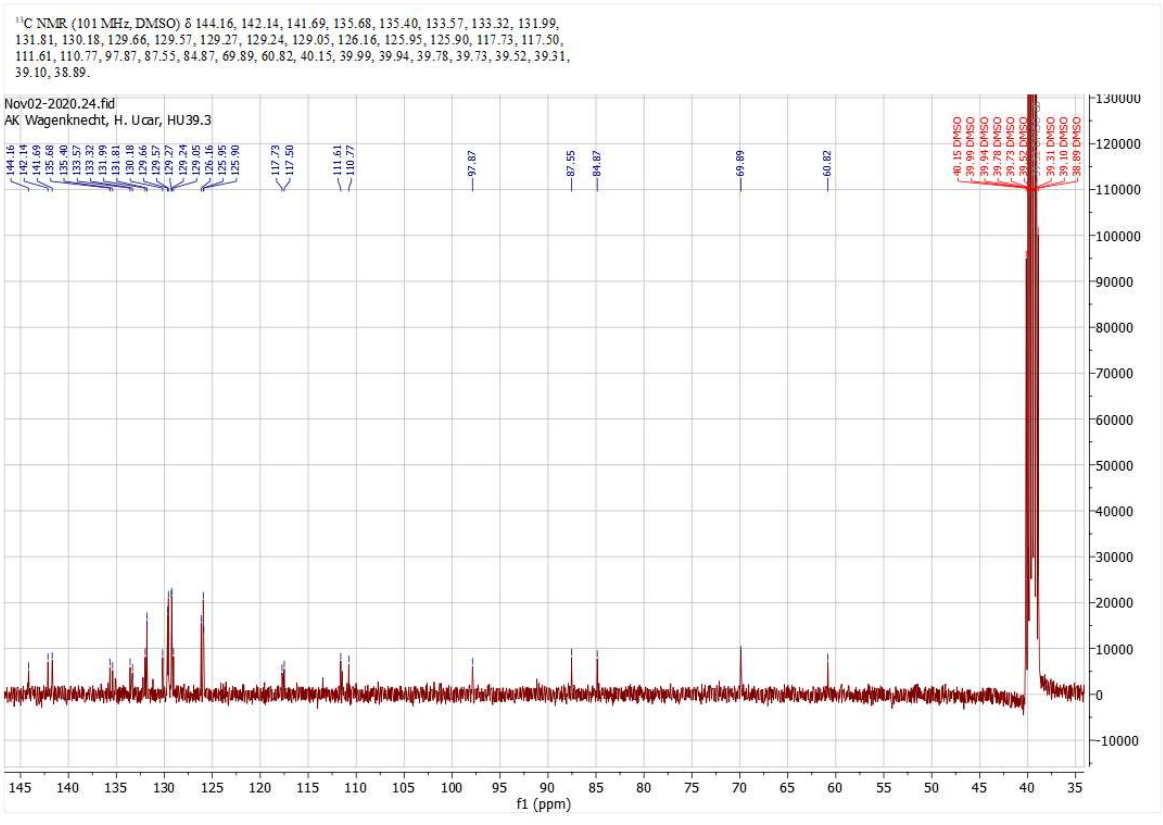


Figure S5. Image of **^{13}C NMR** (101 MHz, $CDCl_3$) of compound **3**.

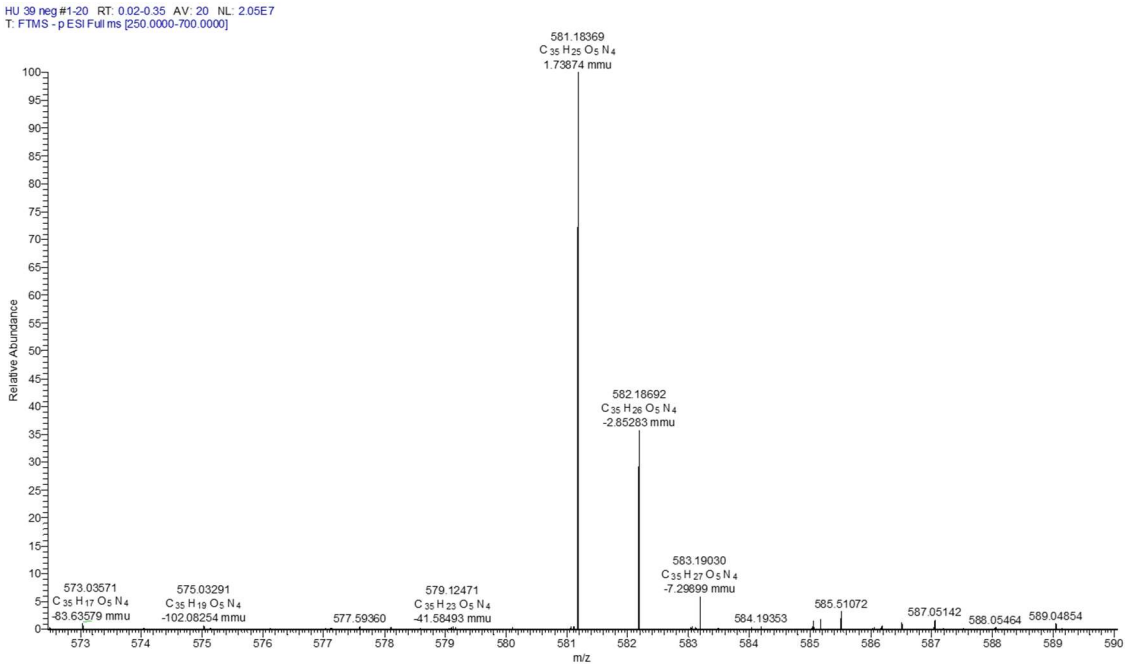


Figure S6. Image of HR-MS (ESI) of compound **4**.

3. Additional optical spectroscopy

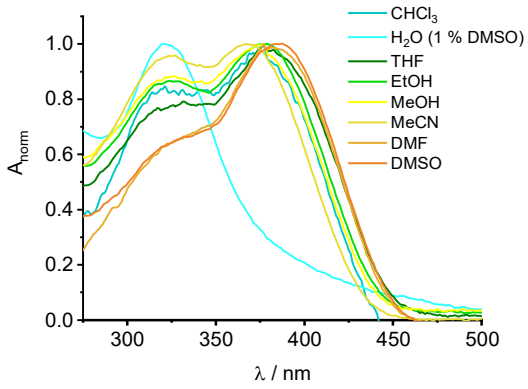


Figure S7. UV/Vis absorbance of **Cs-dU** (37.5 µM) in in different solvents, 1 h incubated at r.t..

Table S1. Fluorescence quantum yields Φ_f and maxima of **Cs-dU** (37.5 µM) in different solvents. 1 h incubated at r.t., λ_{exc} = 390 nm.

Solvent	Φ_f	λ_{max} [nm]
H_2O (1 % DMSO)	0.07	490
$CHCl_3$	0.24	493
THF	0.72	514
EtOH	0.35	516
MeOH	0.20	522
MeCN	0.35	529
DMF	0.31	547
DMSO	0.24	559

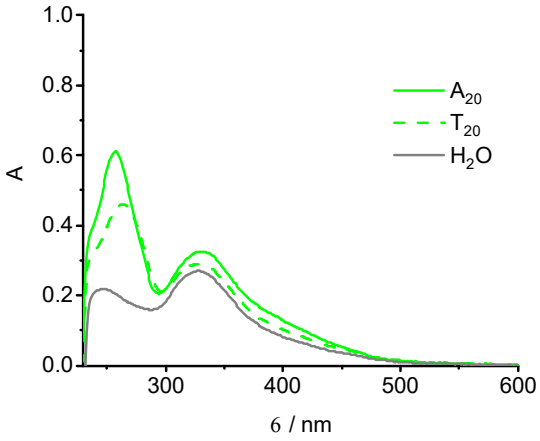


Figure S8. UV/Vis absorption of **Cs-dU** without and with A_{20} (and T_{20} in comparison),1.25 µM DNA in H_2O (1 % DMSO), 25 µM **Cs-dU**, 250 mM NaCl, 1 h at r.t, λ_{exc} = 360 nm.

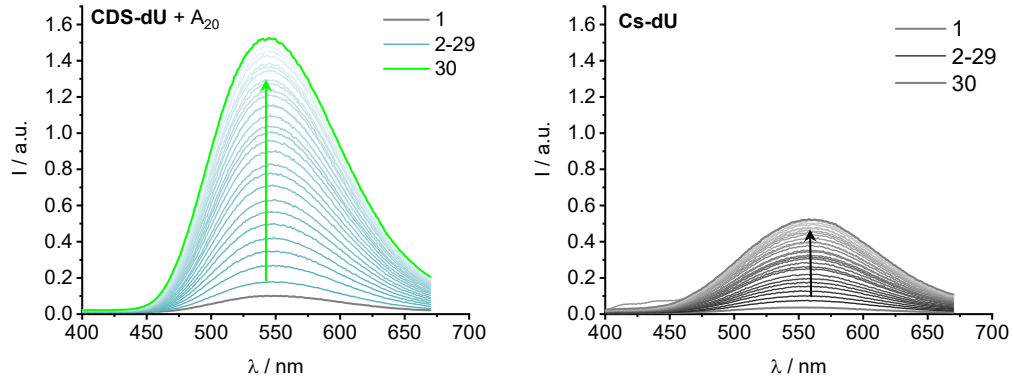


Figure S9. Fluorescence of **Cs-dU** with (left) and without A_{20} (right), 1.25 µM DNA in H_2O (1 % DMSO), 1-30 equiv (1 equiv.=1.25 µM) **Cs-dU**, 250 mM NaCl, 1 h at r.t, λ_{exc} = 360 nm.

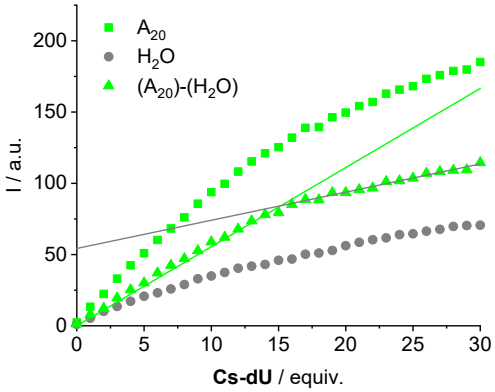


Figure S10. Fluorescence intensities of **Cs-dU**, 1.25 µM DNA in H_2O (1 % DMSO), 1-30 equiv (1 equiv.=1.25 µM) **Cs-dU**, 250 mM NaCl, 1 h at r.t, λ_{exc} = 360 nm. The green line was fitted to 1-15 equiv., the gray line was fitted to 16-30 equiv.

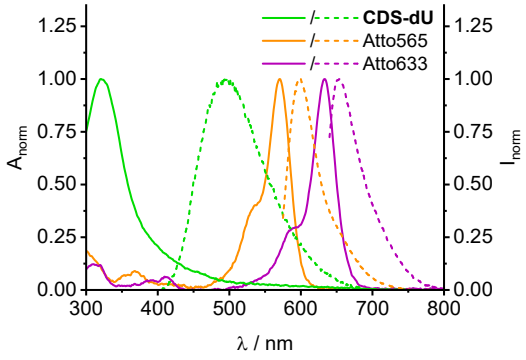


Figure S11. UV/Vis absorption (solid lines) and fluorescence (dashed lines) of **Cs-dU,** A_{20}-Atto565 and A_{20}-Atto633: 1.25 µM DNA in H_2O (1 % DMSO), 37.5 µM **Cs-dU**, 1 h incubated at r.t., λ_{exc} = 360 nm, 565 nm and 633 nm, respectively.

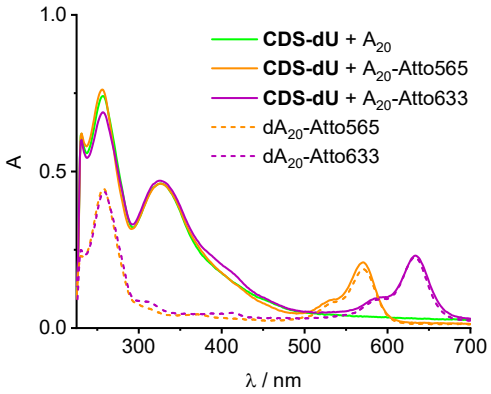


Figure S12. UV/Vis absorption of the assemblies of **CDS-dU** with the templates A_{20}, A_{20}-Atto565 and A_{20}-Atto633, and the UV/Vis absorption of A_{20}-Atto565 and A_{20}-Atto633 without **Cs-dU:** 1.25 µM DNA in H_2O (1 % DMSO), 37.5 µM **Ca-dU**, 250 mM NaCl, 1 h incubated at r.t..

Table S2. Fluorescence quantum yields of **Cs-dU** (donor) in the prescence of the acceptor (Φ_{DA}) in the DNA architectures **Cs-dU** + A_{20}-Atto565 und **Cs-dU** + A_{20}-Atto633, as well as the fluorescence quantum yields of the acceptor (Φ_A) during excitation of the donor at 389 nm.

	Φ_{DA} 400 - 550 nm	Φ_A 550 - 675 nm	Efficiency E $E = 1 - \frac{\Phi_{DA}}{\Phi_A}$
CDS-dU + A_{20}-Atto565	0.03	0.16	0.81
CDS-dU + A_{20}-Atto633	0.04	0.14	0.72

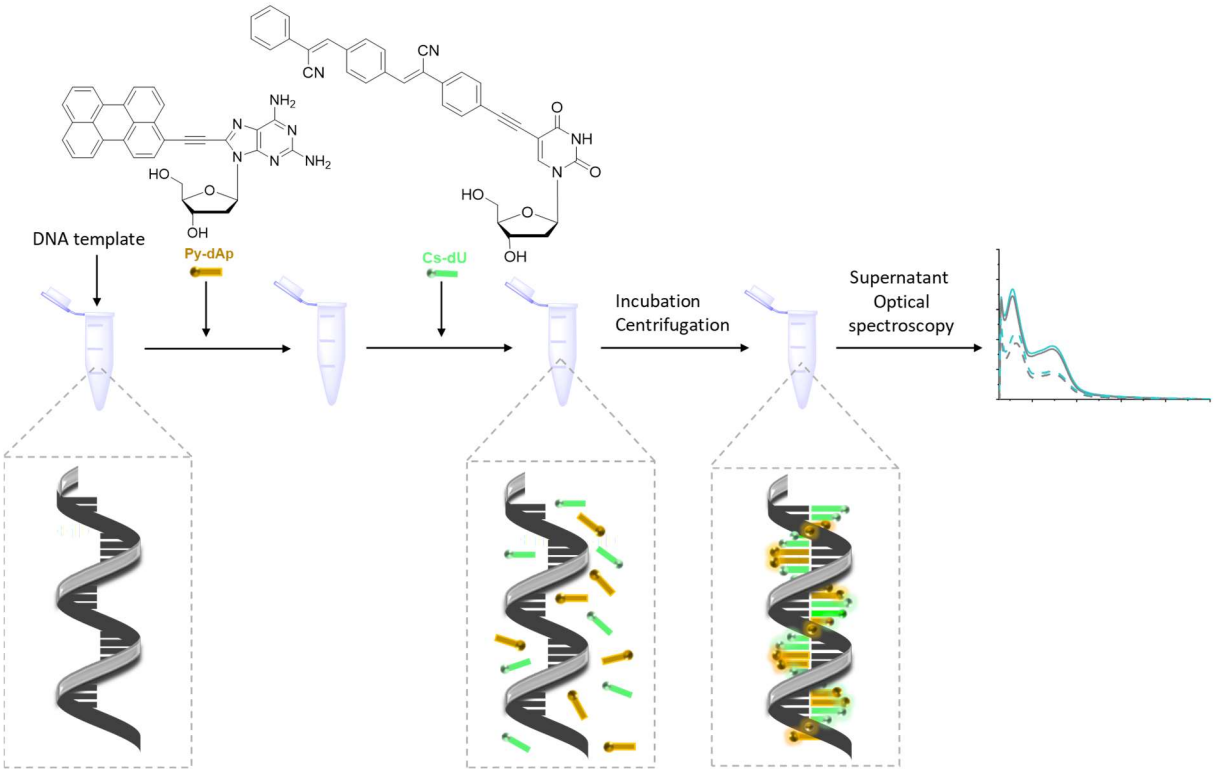


Figure S13. Preparation of supramolecular DNA architectures with **Cs-dU**, **Pe-dAp** and $(AATT)_5$, $(ATTT)_5$, $(AATT)_5$-Atto565/633, $(ATTT)_5$-Atto565/633 as DNA templates: 1.25 µM DNA template in water, 18.75 µM **Cs-dU** (from stock solution in DMSO), 18.75 µM **Pe-dAp** (from stock solution in DMSO) + 1 % DMSO, 250 mM NaCl, λ_{exc} = 360 nm), after incubation for 1 h at r.t. and centrifugation (1 min, 16,000 g).

4. References

[S1] S. Hayashi, R. Hirai , S.-i. Yamamoto, T. Koizumi, *Chem. Lett.,* 2018, **47**, 1003-1005.

[S2] J. Wang, J. Mei, E. Zhao, Z. Song, A. Qin, J. Z. Sun, B. Z. Tang, Macromolecules, 2012, **45**, 7692-7703.