Supporting information for

Folding of phosphodiester-linked donor-acceptor oligomers into supramolecular tubes in water

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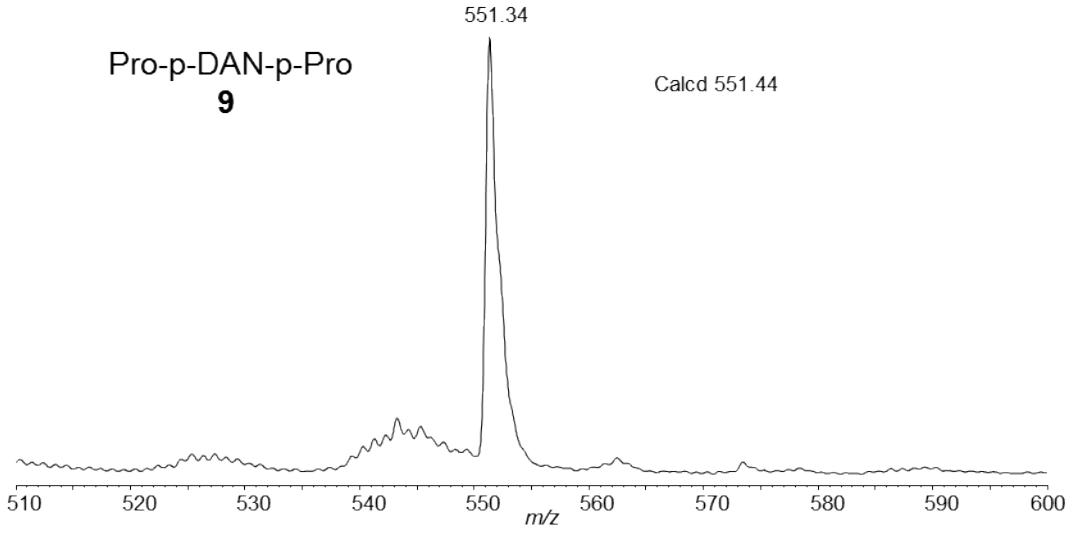
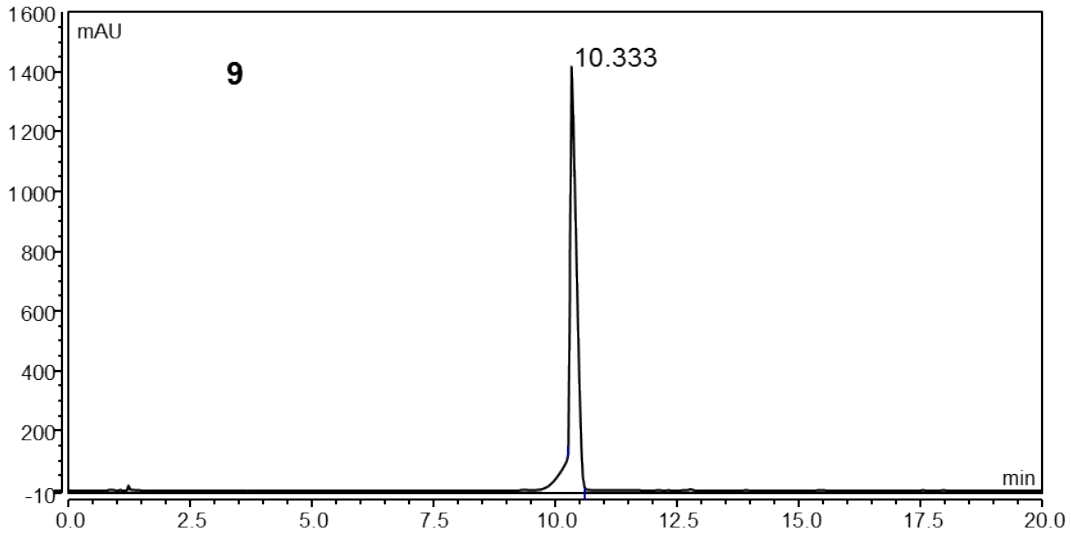
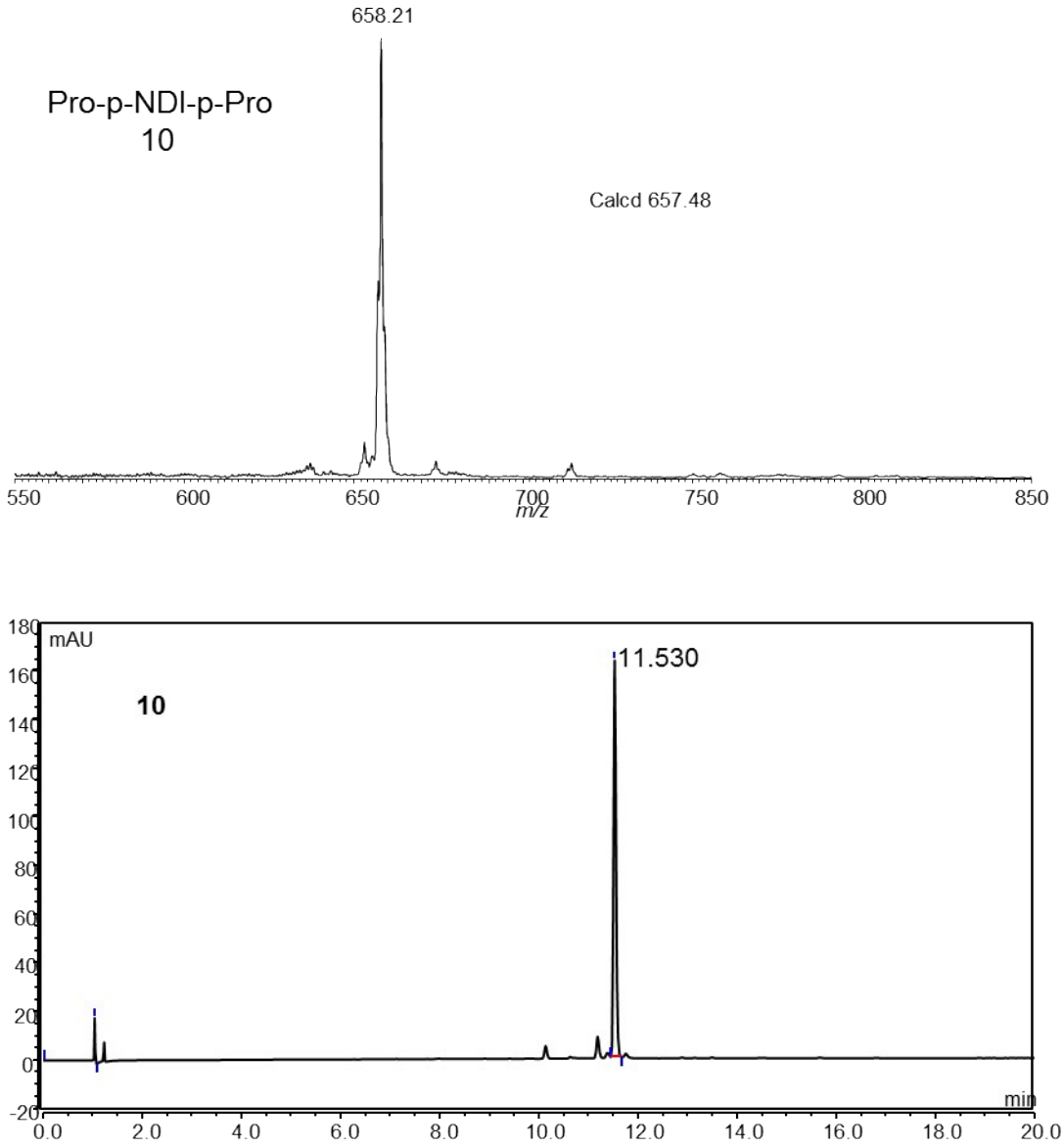
Figure S1. MALDI-TOF and RP C_{18} HPLC of 9.





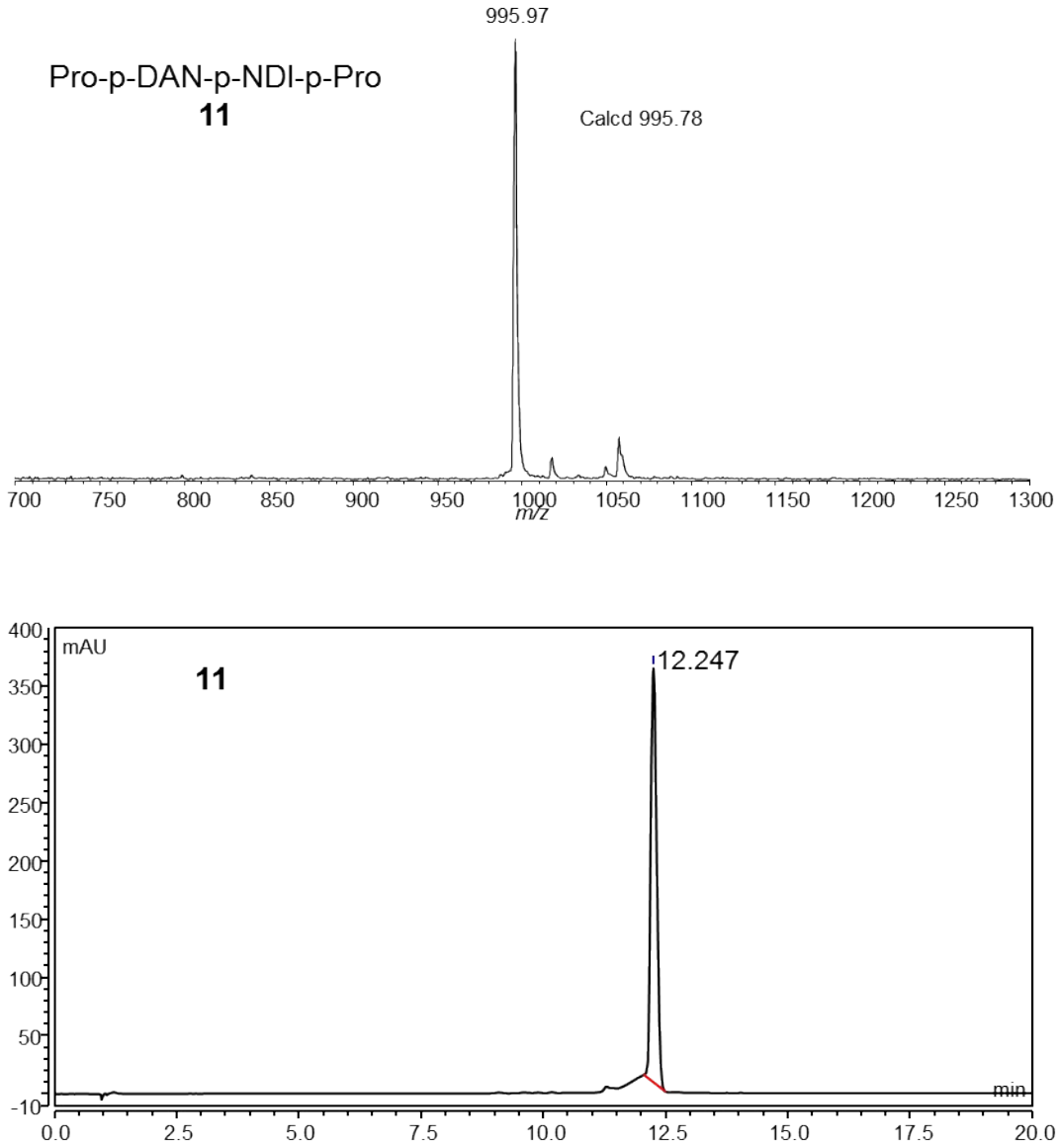
Linear gradient 8% to 32% of CH_3CN in 50 mM TEAAc buffer pH 7 over-20 min

Figure S2. MALDI-TOF and RP C_{18} HPLC of 10



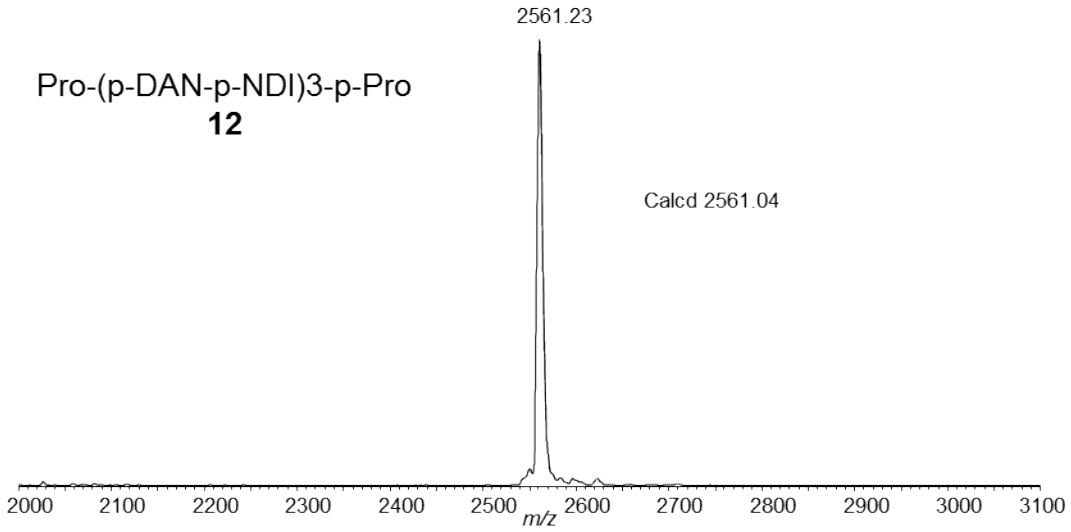
Linear gradient 0% to 40% of CH_3CN in 50 mM TEAAc buffer pH 7 over-20 min

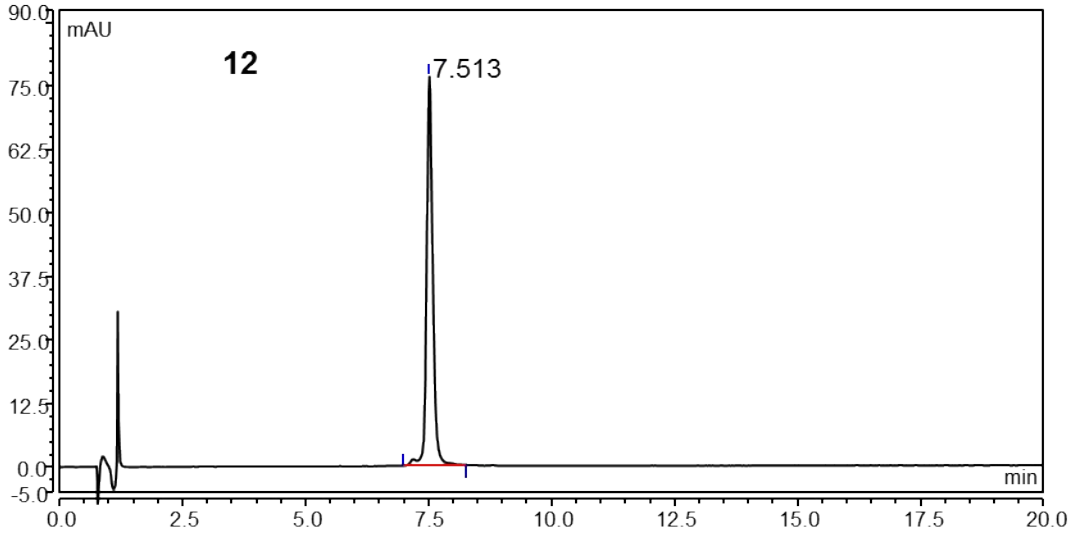
Figure S3. MALDI-TOF and RP C_{18} HPLC of 11



Linear gradient 8% to 32% of CH_3CN in 50 mM TEAAc buffer pH 7 over-20 min

Figure S4. MALDI-TOF and RP C_{18} HPLC of 12





Linear gradient 16% to 40% of CH_3CN in 50 mM TEAAc buffer pH 7 over-20 min

Fig. S5 Selected aromatic region of ^{1}H NMR of compounds 9-11 in D_2O at 25 °C. [9] = 3.9 mM, [10] = 2.7 mM and [11] = 2.7 mM.

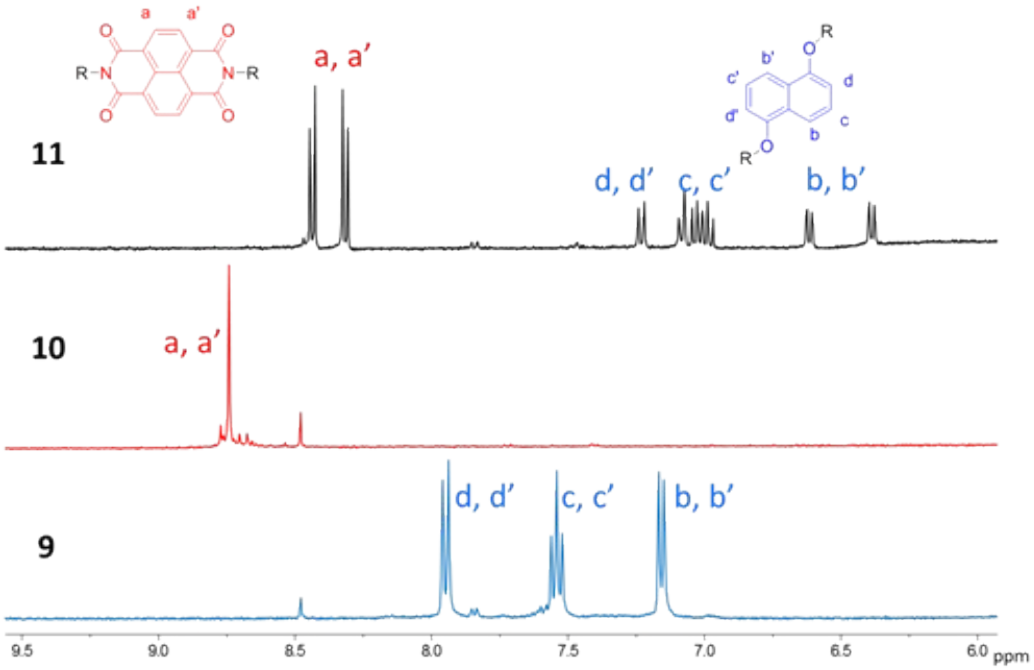


Fig S6: NMR spectrum of 11 at 2.7 mM in D_2O A) at 25 °C, Difference of the chemical shifts with a variation of temperature from 25 °C to 85 °C (arbitrary calibrated) B) of NDI's aromatic protons and C) of DAN's aromatic protons around 6.5 ppm.

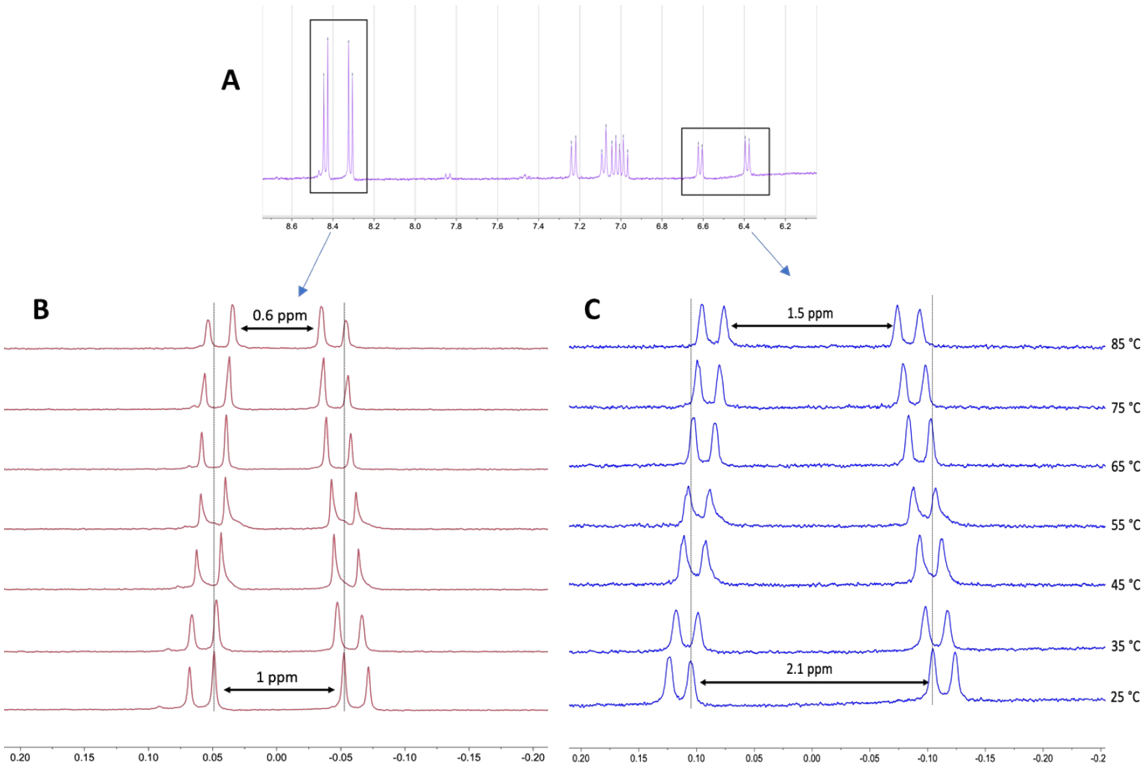


Fig. S7. A) UV-Vis spectra of oligomer 12 (33 µM) at 25 °C (red curve) and at 85 °C (black curve) in water B) Zoom of the charge-transfer band of 12 at 25 °C (red curve) and at 85 °C (black curve).

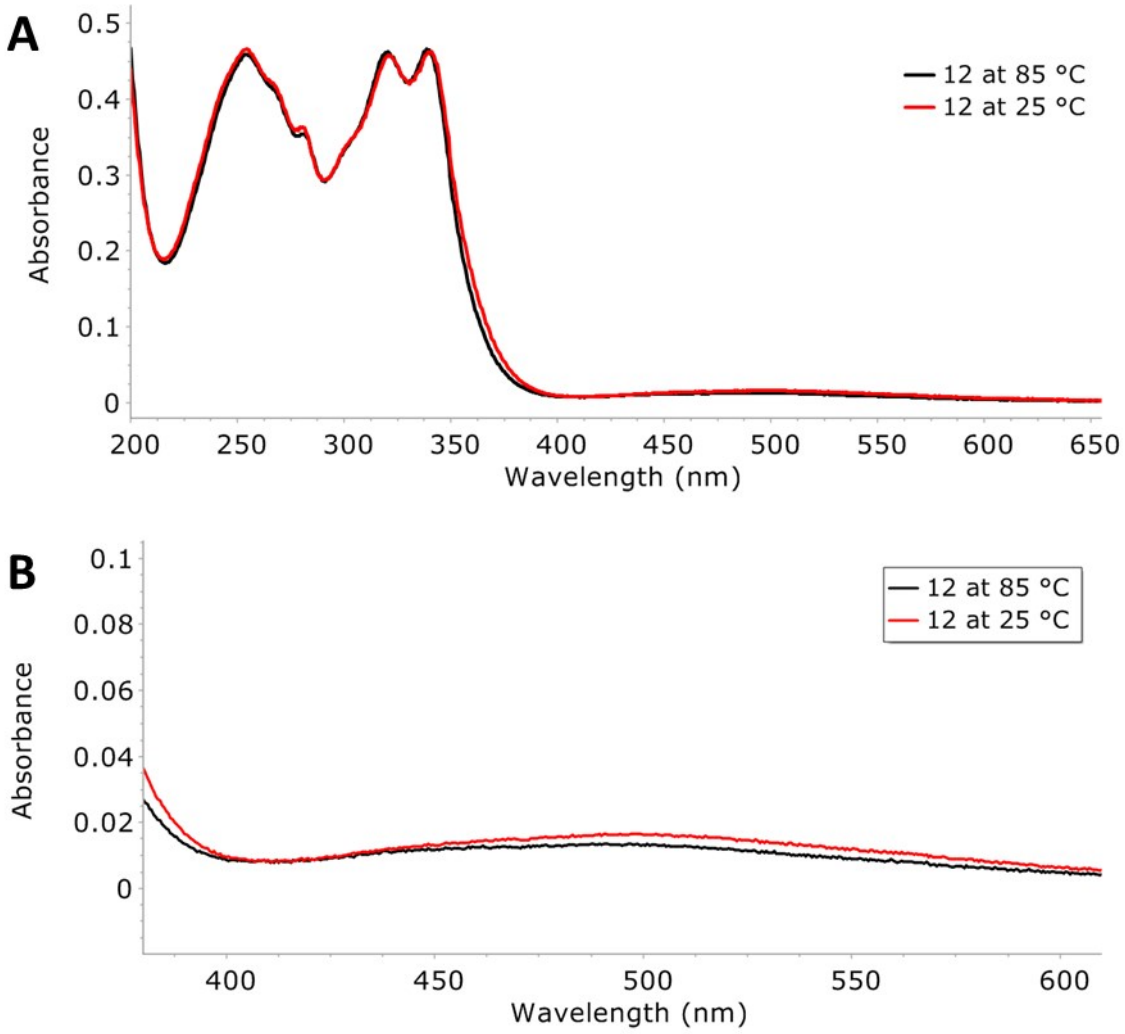


Fig. S8. Fluorescence emission spectra of compounds 9, 10 and 12 (15 µM in water). top: λ_{ex}= 296 nm Bottom: λ_{ex} = 363 nm.

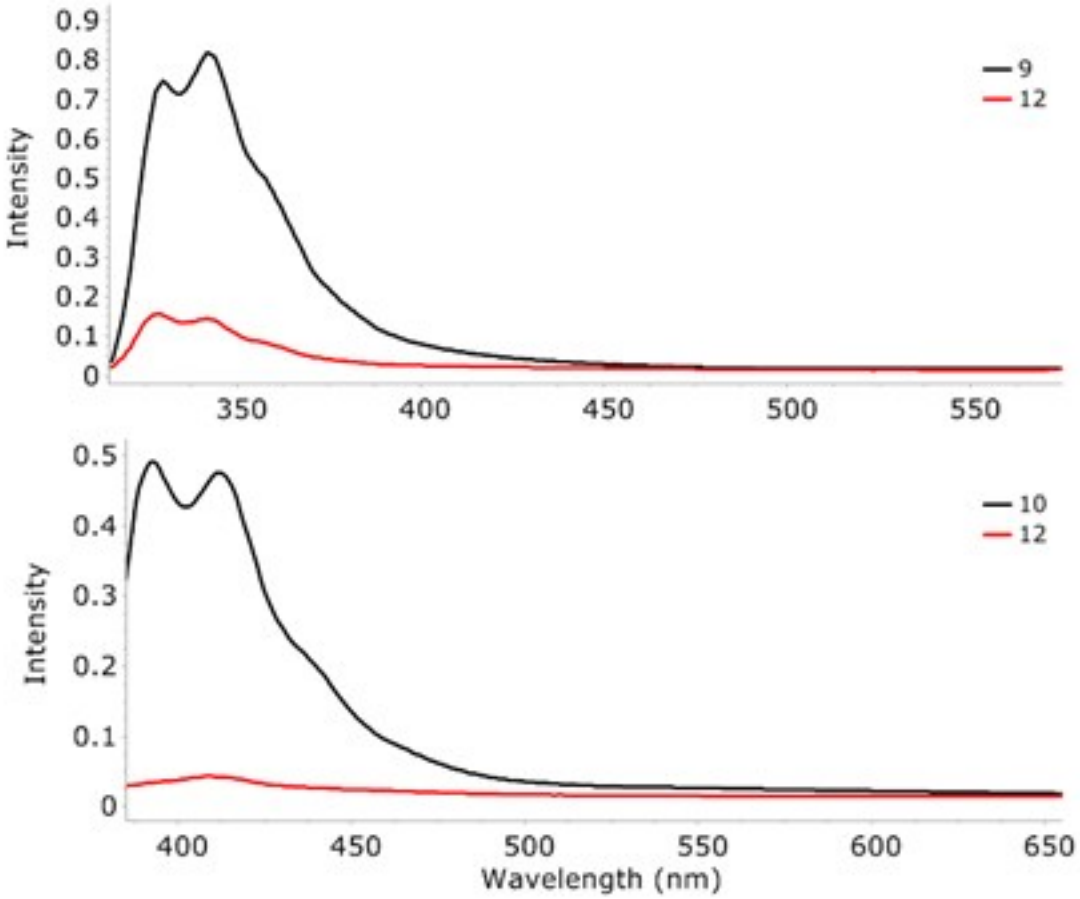


Figure S9. AFM images (height) of 9 at 45 μM in water after 1 d

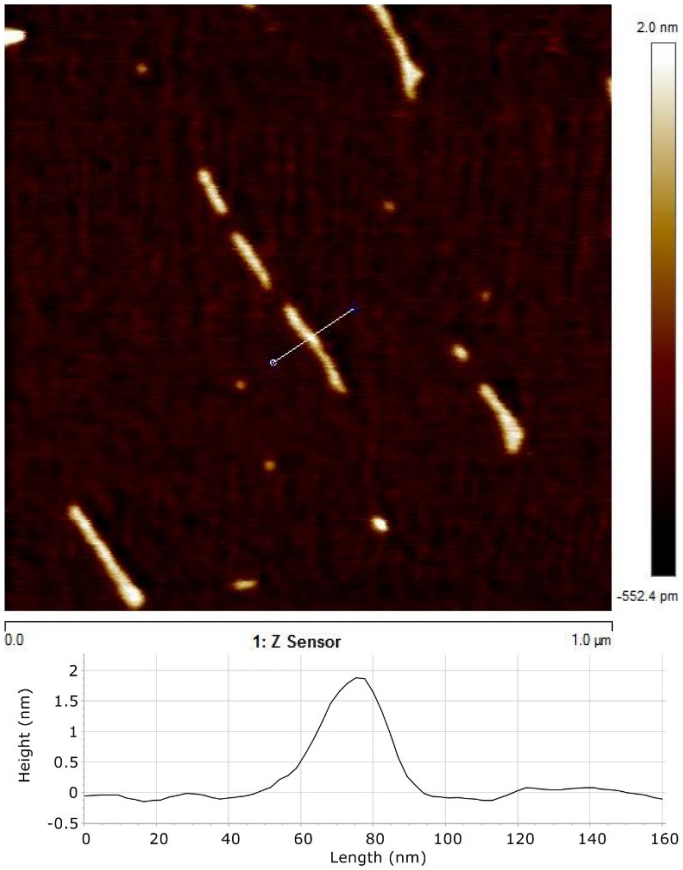


Figure S10. AFM images (height) of 10 at 45 μM in water after 1 d

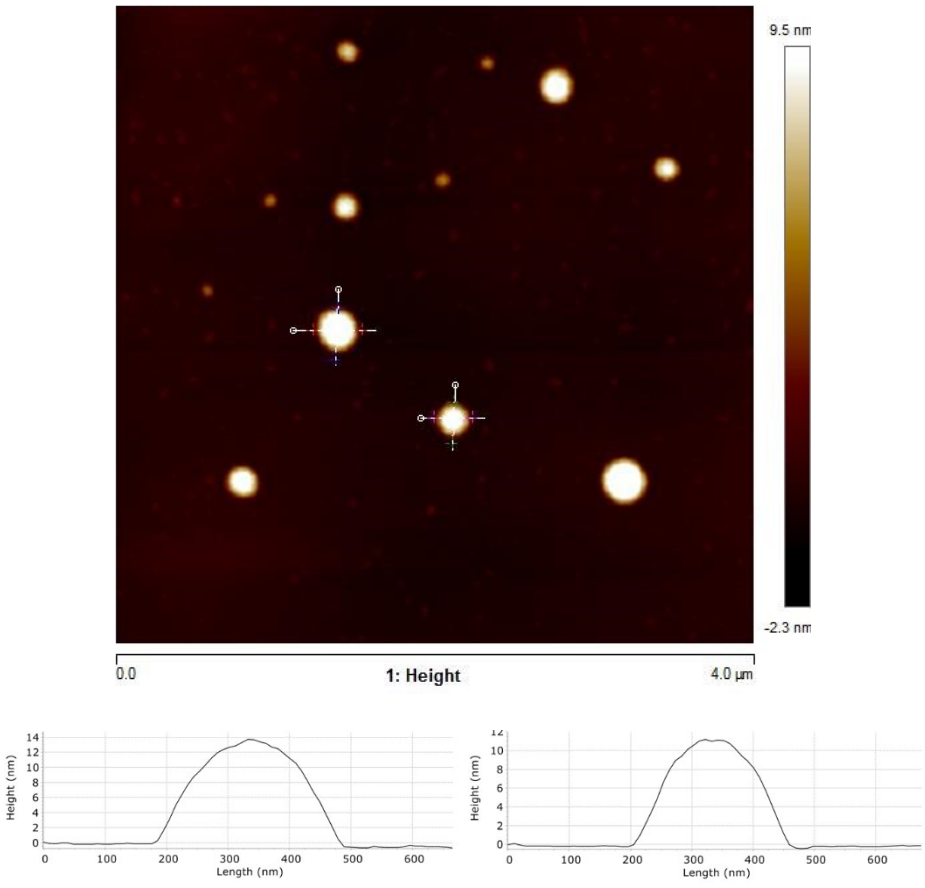


Figure S11. AFM images (height) of 9 + 10 at 45 µM each in water after 1 d

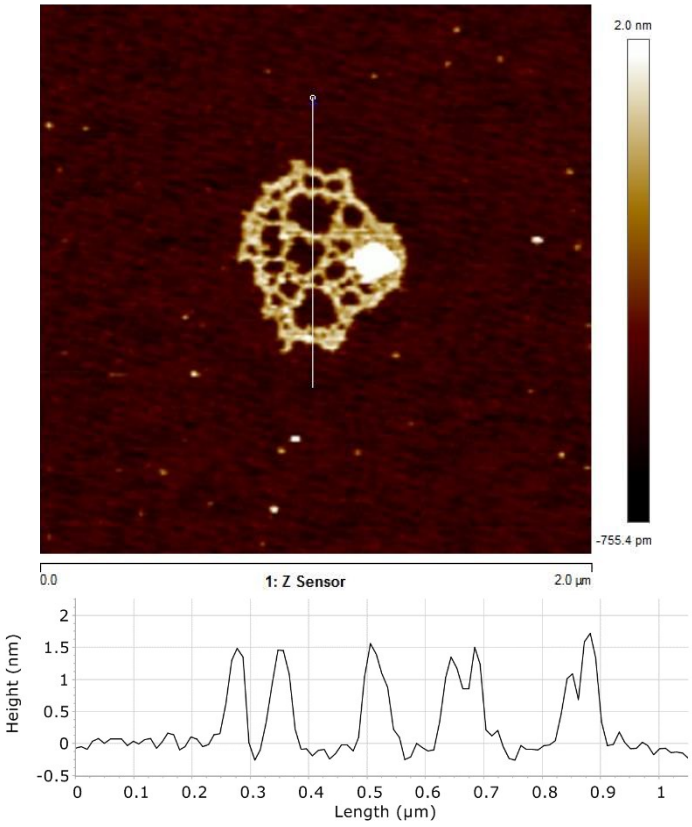


Figure S12. AFM images (height) of 11 at 45 µM in water after 1 d

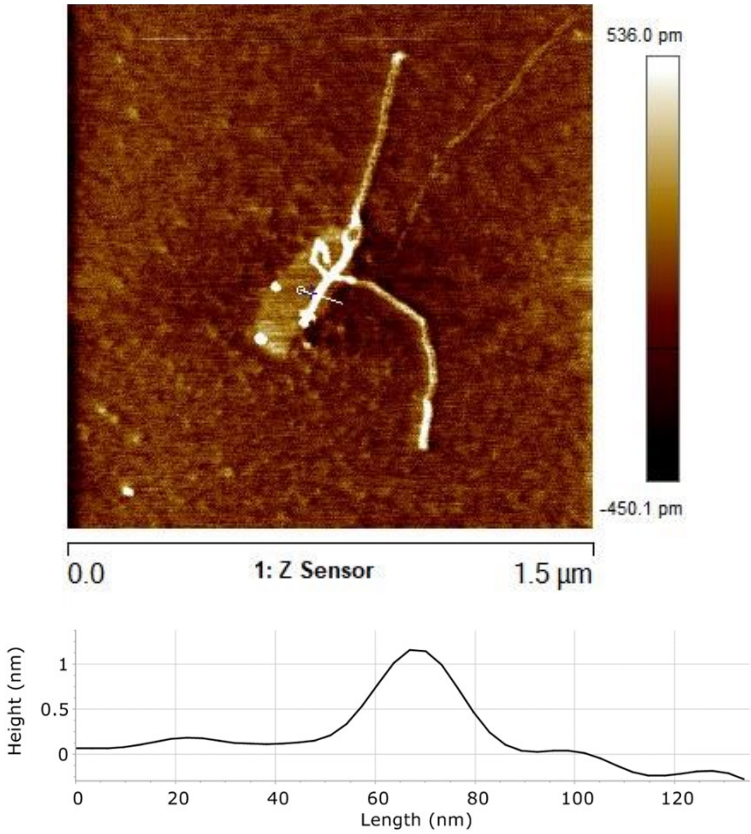


Figure S13. AFM images (height) **of 12 at 1 µM in water after 1 d**

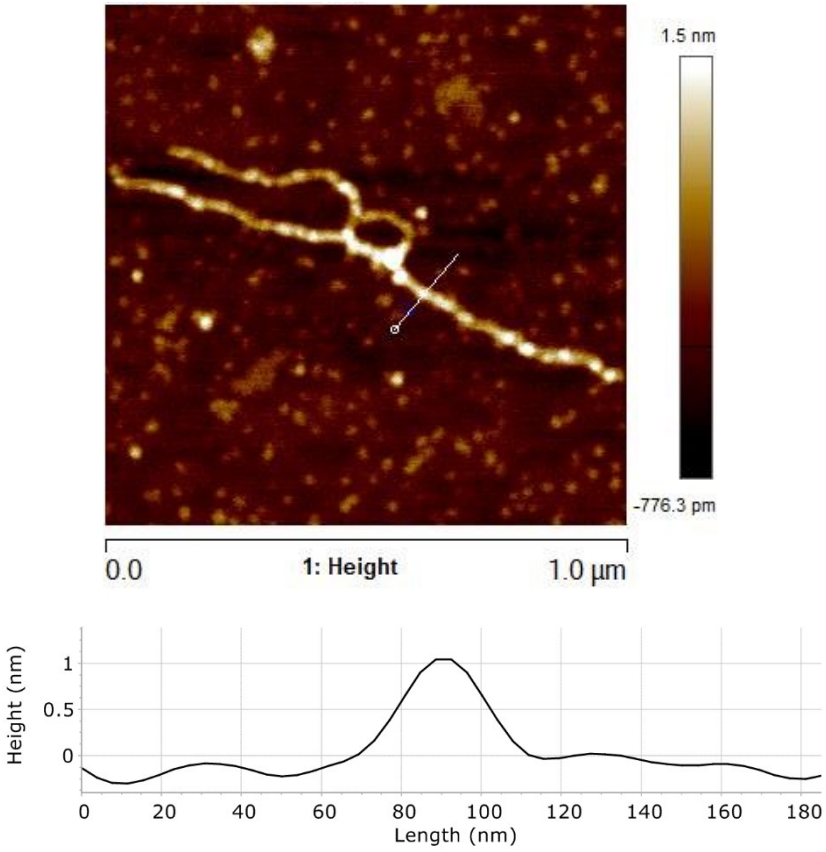


Figure S14. AFM images (height) of 12 at 15 µM in water after 1 d

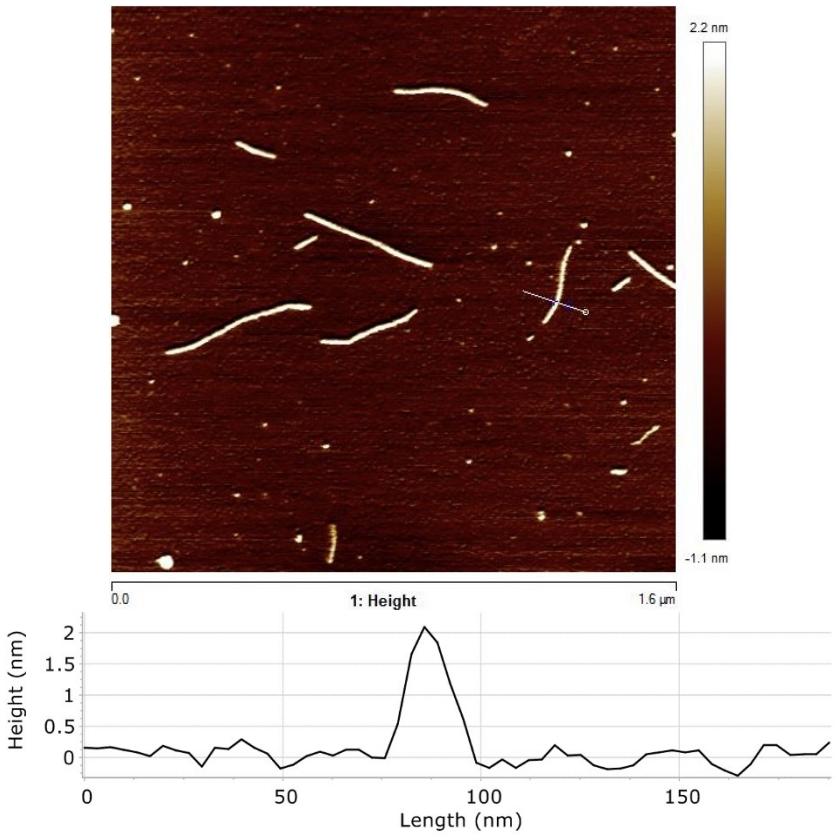


Figure S15 AFM images (height) of 12 at 30 µM after 1 d

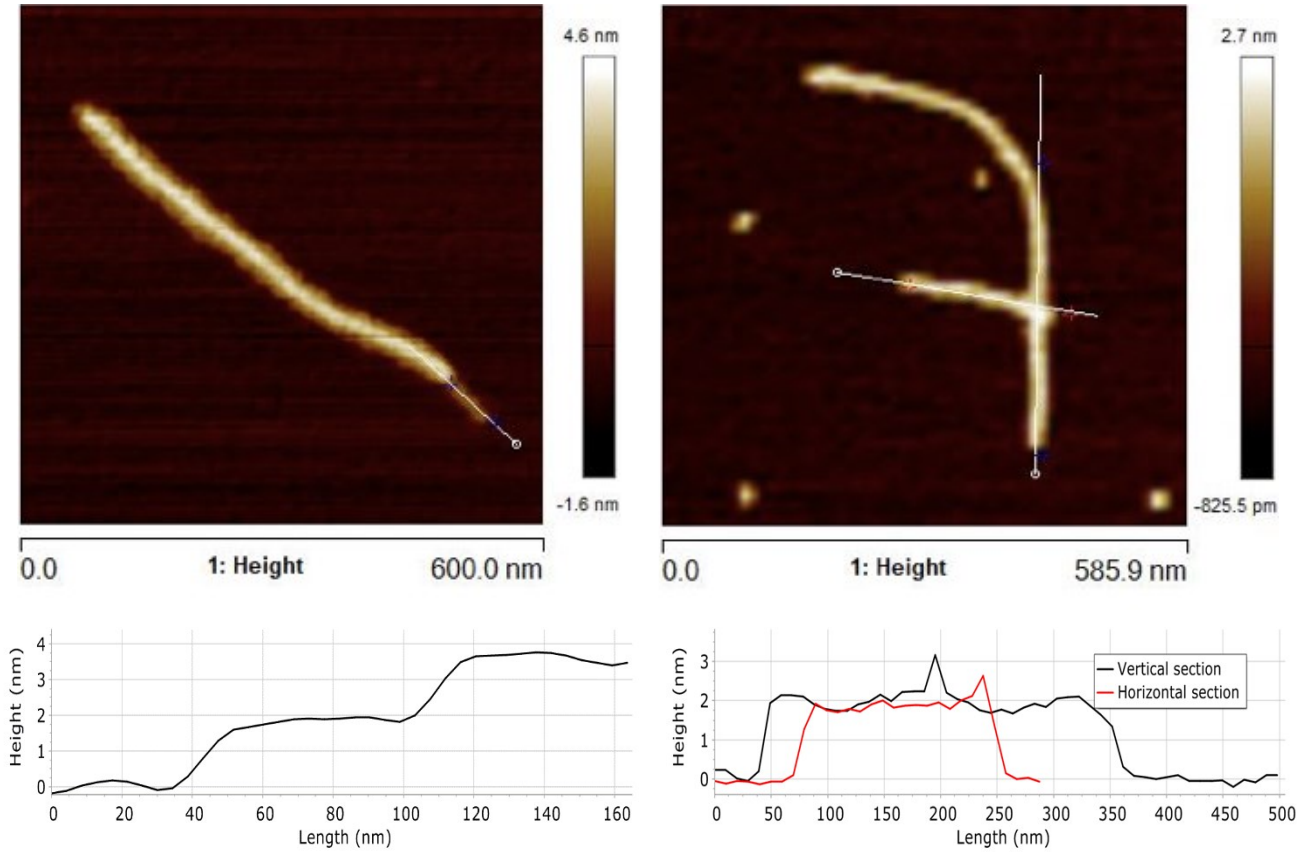


Figure S16 AFM images (height) of 12 at 15 µM after 3 days (left) and 7 d (right)

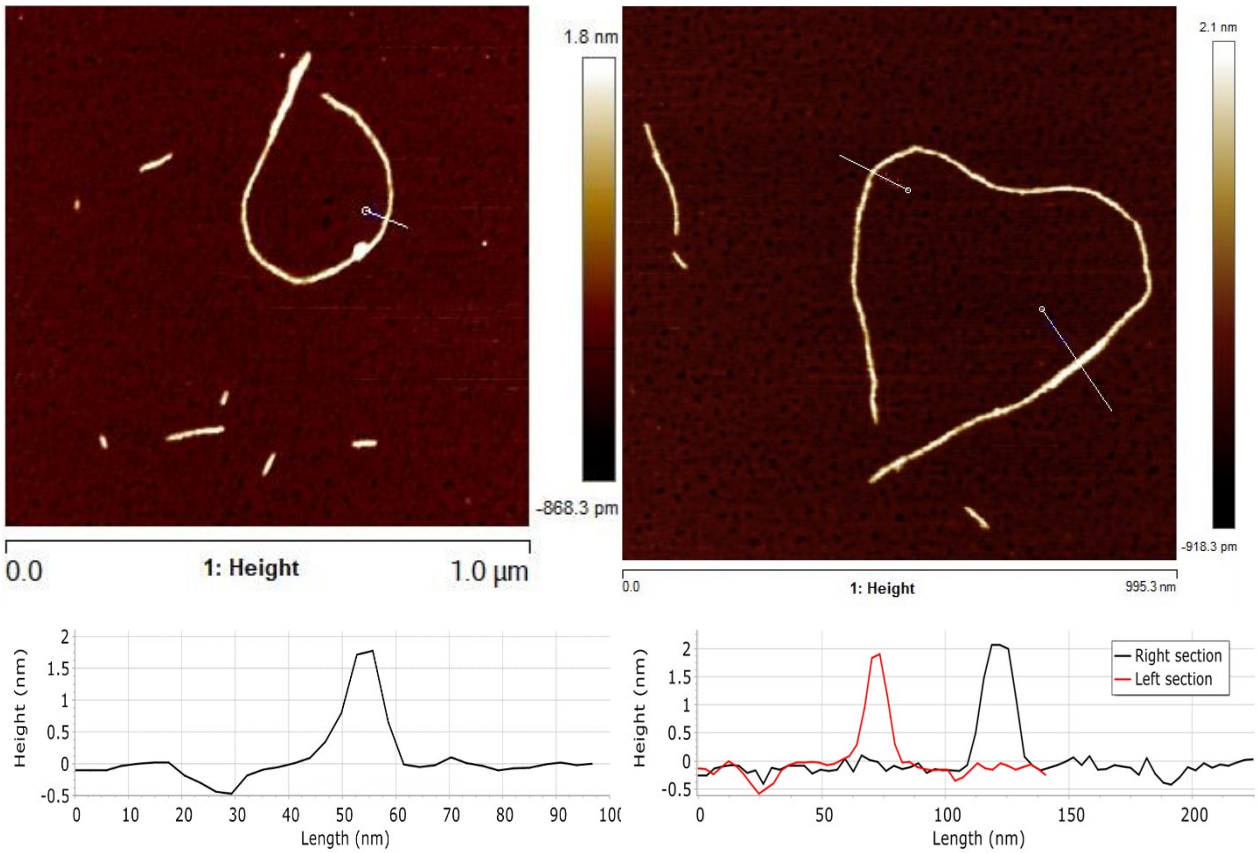


Figure S17 AFM images (height) of 12 at 15 µM after 3 days at 4 °C (left) and then after heating 1h to 80°C (right)

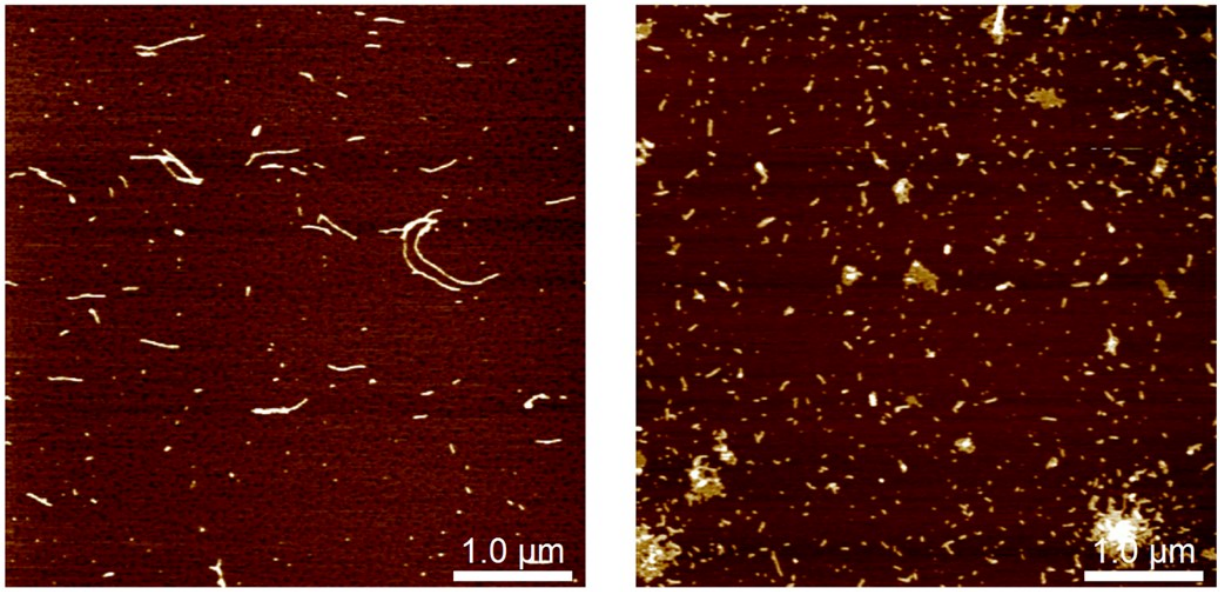


Figure S18. Negative-stained TEM image of 12 at 30 µM after 1 day in water with 2% uranyl acetate solution for staining.

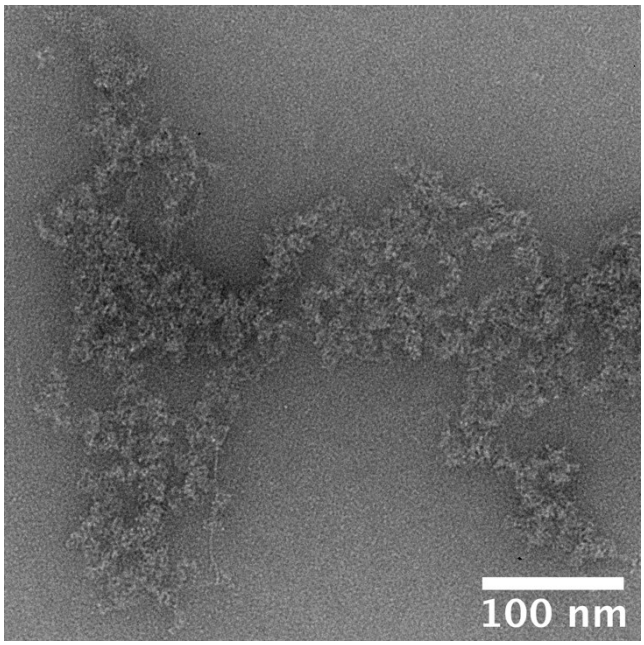


Figure S19. Negative-stained TEM image of 12 at 15 µM after 1 day in 10 mM phosphate buffer pH 7 and 10 mM NaCl with 2% uranyl acetate solution for staining.

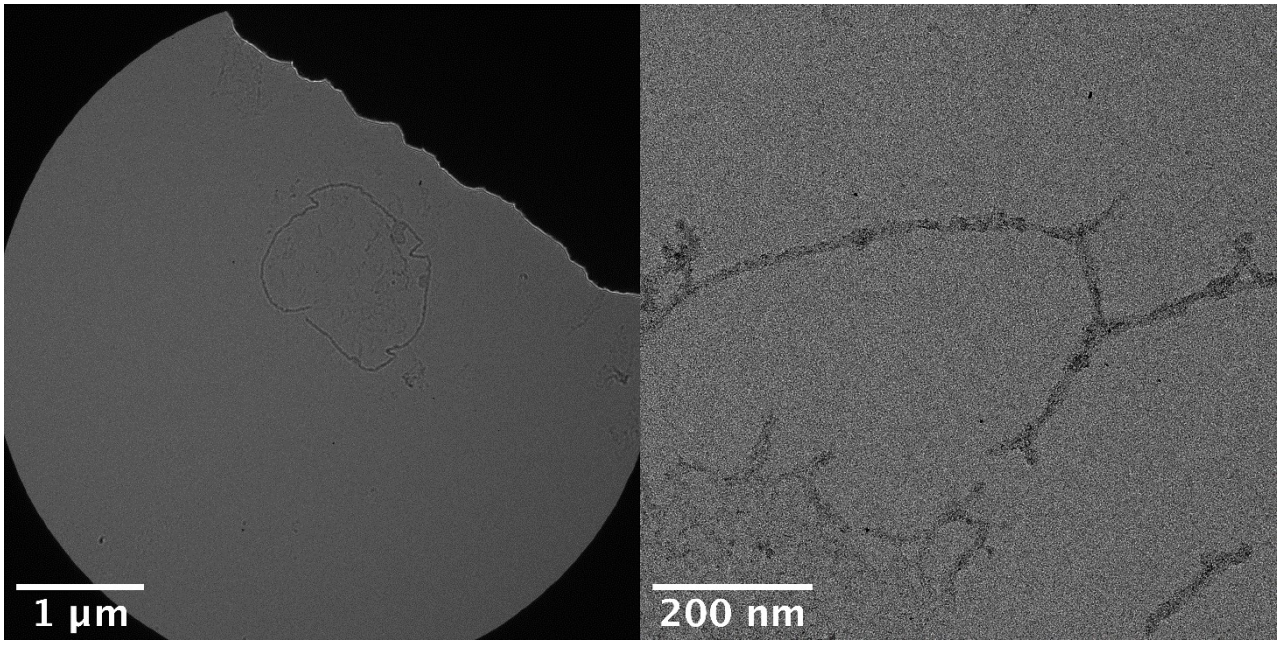
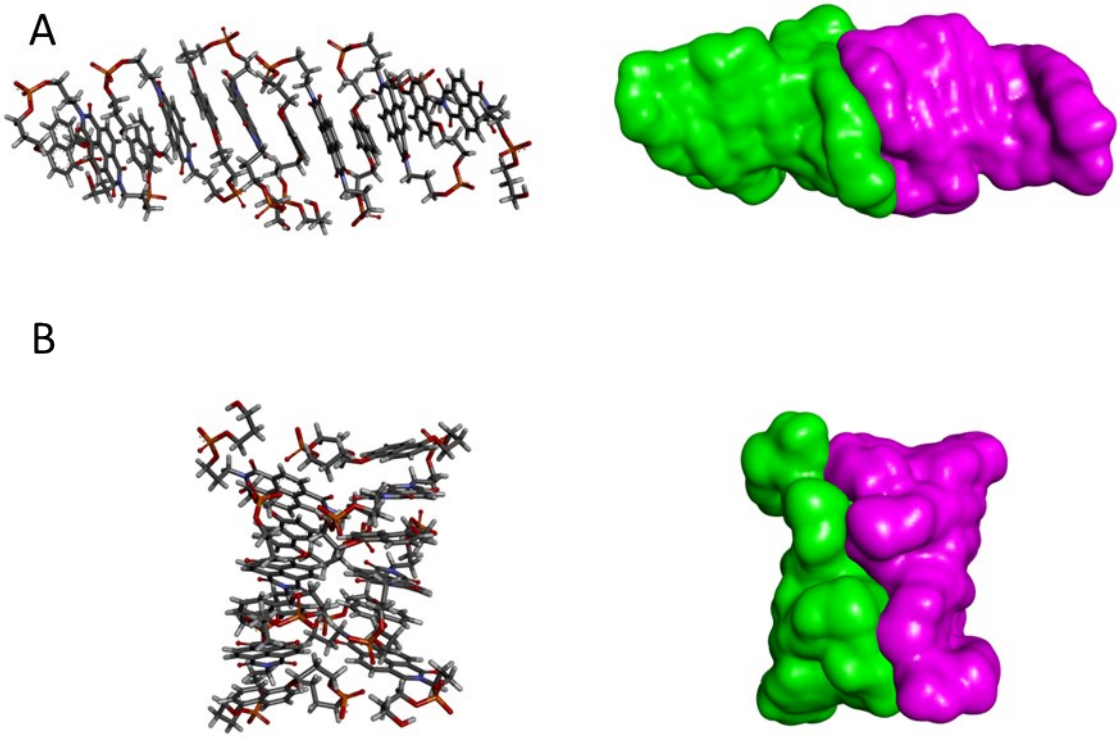


Figure S20. Molecular modeling of two foldamers 12.

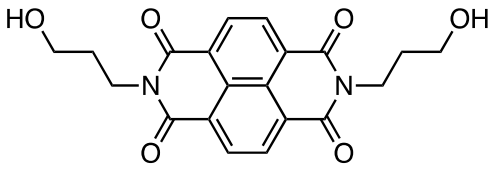


A) According to a longitudinal interaction (ΔE= -32.504 kcal/mol) and B) according to a lateral interaction (ΔE= -76.152 kcal/mol).

Materials and methods

All reactions were performed under an atmosphere of argon. Pyridine, CH_3CN, DIEA was distilled over CaH_2, CH_2Cl_2 was distilled over P_2O_5, CH_3CN and CH_2Cl_2 were conditioned with molecular sieve of respectfully 3 Å and 4 Å, EtOH (absolute) was dried on Al_2O_3, other solvents were commercial and used without further distillation. Column chromatography was performed by using silica gel (40-63 μm). For acid sensitive compounds the silica was pretreated with solvents containing 1-5% NEt_3. The ^{1}H NMR spectra were recorded at 298 K on a 400, 500 or 600 MHz spectrometer of BRUKER© with BBFO beacon in the indicated solvents, chemical shifts are expressed in parts per million relative to the residual solvent protons as internal standards. Coupling constants are expressed in Hertz (Hz). Chloroform (δ = 7.26 ppm), MeOH (δ = 4.87 ppm), H_2O (δ = 4.79 ppm) and DMSO (δ = 3.33 and 2.5 ppm) were used as an internal standard for $CDCl_3$, MeOD, D_2O, DMSO-d_6, respectively. The ^{13}C NMR chemical shifts are reported in ppm relative to TMS (δ = 0.0). ^{31}P NMR chemical shifts are reported in ppm relative to H_3PO_4 (δ= 0.0) as an external standard. High-resolution (HR-ESI-QToF) mass spectra were recorded using Q-ToF Micromass© spectrometer, phosphoramidite compound spectra were recorded on Synapt G2-S, with a source temperature of 373 K and a desolvation temperature of 323 K. Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification.

Synthesis of *N,N'*-di (3-hydroxypropyl)-1,8,4,5-Naphthalenetetracarboxylic Diimide 2.

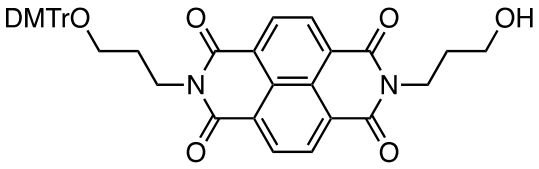


Chemical Formula: $C_{20}H_{18}N_2O_6$

1,8,4,5-Naphthalenetetracarboxylic dianhydride **1** (5 g, 18.64 mmol) was poured in 220 mL of absolute ethanol. The reaction mixture was heated to reflux for 30 min, then 3-amino-propan-1-ol (4.22 mL, 56.0 mmol) was added. The reaction was stirred and monitored for 18 h by TLC (CH_2Cl_2/MeOH 7:3, v/v) and then was cooled to room temperature. The mixture was poured into 500 mL of ice-cold water, and the pink precipitate was filtered, and washed with 150 mL of ice-cold solvent, water, ethanol, diethyl ether. The product **2** was dried up overnight in a desiccator with NaOH and P_2O_5. Yield: 6.92 g, 97 %, pink powder.

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 8.61 (s, 4H, H-Ar), 4.52 (s, 2H, OH), 4.11 (t, J = 8 Hz, 4H, CH_2-N), 3.52 (t, J = 8 Hz, 4H, CH_2-OH), 1.82 (p, J = 8 Hz, 4H, R-CH_2-R). **^{13}C NMR** (100 MHz, DMSO-d_6): 162.4 (CONR), 130.1 (C-H Ar), 126.0 (C Ar), 125.8 (C Ar), 58.8 (C-OH), 37.9 (C-N), 30.6 (C-(CH2)2). **HR-ESI-QToF MS** (positive mode): m/z calcd for $C_{20}H_{19}N_2O_6$ $[M+H]^+$: 383.1243 found 383.1242.

Synthesis of *N*-[3-(dimethoxytrityloxy)propyl]-*N'*- (3-hydroxypropyl)-1,8,4,5,-Naphthalenetetracarboxylic Diimide 3.

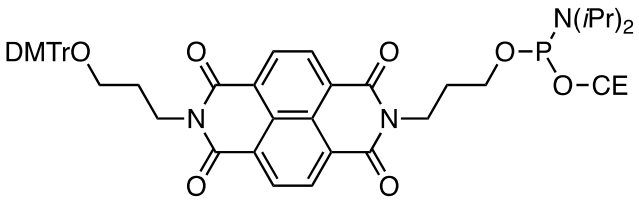


Chemical Formula: $C_{41}H_{36}N_2O_8$

N-[3-(dimethoxytrityloxy)propyl]-*N'*-(3-hydroxypropyl)-1,4,5,8-Naphthalenetetracarboxylic Diimide **2** (1.8 g, 4.71 mmol) was coevaporated with dry pyridine and dissolved in 40 mL of dry pyridine, then 50 mL of acetonitrile was added to completely solubilize **2**. After that DMTr-Cl (1.60 g, 4.71 mmol) dissolved into 100 mL of dry pyridine was added dropwise over one hour. The reaction was monitored by TLC (Cyclohexane/AcOEt/Net_3 7:2.5/0.5, v/v) and stirred for 2 h, after that 5 drops of water were added. The solvents were partially evaporated and the mixture was dissolved in 120 mL of CH_2Cl_2, and washed twice with 100 mL of a saturated solution of $NaHCO_3$. The aqueous phase was washed with 50 mL of CH_2Cl_2. The organic phases were dried over $Na2SO_4$, filtered and evaporated under vacuum. The compound **3** was purified by chromatography on silica gel column (Cyclohexane/AcOEt 7:3, v/v with 1% of NEt_3). Yield: 972 mg, 38 %, orange foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.70 (dd, J = 12 Hz, J = 8 Hz, 4H, H-Ar), 7.32 (d, J = 8 Hz, 2H, trityl), 7.17 (m, 6H, trityl), 7.13 (td, J = 8 Hz, J = 4 Hz, 1H, trityl), 6.63 (td, J = 8 Hz, J = 4 Hz, 4H, trityl), 4.38 (t, J = 8 Hz, 2H, CH_2-N), 4.34 (t, J = 8 Hz, 2H, CH_2-N), 3.72 (s, 6H, O-Me), 3.66 (t, J = 8Hz, 2H, CH_2-OH), 3.22 (t, J = 8 Hz, 2H, CH_2-ODMTr), 2.10 (p, J = 8 Hz, 2H, R-CH_2-R), 2.03 (p, J = 8 Hz, 2H, R-CH_2-R). **^{13}C NMR** (100 MHz, $CDCl_3$): 163.6, 162.8, 158.3, 144.7, 136.4, 131.2, 130.8, 130.0, 128.3, 127.7, 127.1, 126.9, 126.8, 126.7, 126.2, 112.9, 86.2, 62.3, 59.3, 55.3, 39.3, 37.7, 31.1, 28.5. **HR-ESI-QToF MS** (positive mode): m/z calcd for $C_{41}H_{37}N_2O_8$ $[M+H]^+$: 685.2550 found 685.2576.

Synthesis of *N*-[(3-dimethoxytrityloxy)propyl]-*N'*-{3-[(2-cyanoethyl *N,N*-diisopropyl phosphoramidite)]propyl}-1,8,4,5-Naphthalenetetracarboxylic Diimide 4.



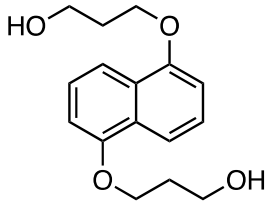
Chemical Formula: $C_{50}H_{53}N_4O_9P$

N-[3-(dimethoxytrityloxy)propyl]-*N'*-(3-hydroxypropyl)-1,4,5,8-Naphthalenetetra-carboxylic Diimide **3** (550 mg, 0.8 mmol) was dissolved in 20 mL of dry dichloromethane, then DIEA (0.696 mL, 3.21 mmol) after that 2-Cyanoethyl N,N-diisopropyl-chlorophosphoramidite (342.19 mg, 1.45 mmol), were added. The reaction mixture was stirred and monitored for 3 h by TLC (Cyclohexane/AcOEt/NEt_3 5:4.5:0.5, v/v/v), after that the reaction was quenched with few drops of water. The reaction mixture was extracted with 50 mL

$NaHCO_3$ twice, the aqueous phase was extracted again with 20 mL of dichloromethane, then the reunited organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. The compound **4** was purified by chromatography on silica gel column (Cyclohexane/AcOET 8:2 v/v with 5% NEt_3): 682 mg, 97%, orange-green foam.

^{1}H NMR (400 MHz, $CDCl_3$) : δ (ppm) = 8.72 (dd, J = 8 Hz, J = 4 Hz, 4H, H-Ar), 7.34 (d, J = 8 Hz, 2H, trityl), 7.18 (m, 6H, trityl), 7.13 (m, 1H, trityl), 6.66 (d, J = 8 Hz, 4H, trityl), 4.34 (m, 4H, CH_2-N), 3.86 (m, 4H, cyanoethyl), 3.74 (s, 6H, O-Me), 3,60 (m, 2H, R-CH_2-R), 3.22 (t, J = 8 Hz, 2H, CH_2-O-P), 2.66 (t, J = 8 Hz, 2H, CH_2-ODMTr), 2.10 (m, 4H, R-CH_2-R), 1.18 (d, 12H, CH_3 isoprop). **^{13}C NMR** (100 MHz, $CDCl_3$): 163.6, 162.6, 158.1, 144.6, 136.2, 130.6, 130.6, 129.8, 128.1, 127.6, 126.6, 126.6, 126.5, 126.3, 112.7, 86.0, 62.0, 61.5, 61.3, 58.5, 58.3, 55.1, 45.3, 45.2, 43.1, 43.0, 39.1, 38.3, 29.8, 29.7, 28.3, 24.6, 24.6, 24.5, 22.9, 22.8, 20.4, 20.3. **^{31}P NMR** (100 MHz, $CDCl_3$): 147.81. **HR-ESI-QToF MS** (positive mode): m/z calcd for $C_{50}H_{54}N_4O_9P$ $[M+H]^+$: 885.3628 found 885.3631.

Synthesis of 1,5-Bis(3-hydroxypropoxy)naphthalene 6.

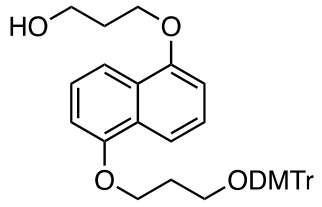


Chemical Formula: $C_{16}H_{20}O_4$

1,5-dihydroxynaphthalene **5** (2.5 g, 15.6 mmol) was dissolved in 120 mL of degassed dry acetonitrile, then K_2CO_3 (10.79 g, 78.0 mmol) was added and the reaction mixture was heated to reflux for 1 h, then KI (5.18 g, 31.2 mmol) and 3-chloropropan-1-ol (5.18 mL, 62.4 mmol) were added. The reaction was monitored by TLC (MeOH/CH_2Cl_2 0.3:9.7, v/v) and performed under high agitation and heat. After 24 h, the reaction is stopped and cooled at room temperature, the reaction mixture was filtered and the residue was washed with 250 mL of warm acetonitrile. The filtrate was evaporated under vacuum until dryness, then the residue was triturated with 150 mL of room temperature diethyl ether, filtered, and then washed with 150 mL of near frozen diethyl ether resulting in **6** as a powder. Yield: 4.23 g, 98 %, yellow-green powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.70 (d, J = 8 Hz, 2H, $C_{2,6}$-H), 7.37 (t, J = 8 Hz, 2H, $C_{3,7}$-H), 6.97 (d, J = 8 Hz, 2H, $C_{4,8}$-H), 4.59 (t, J = 8 Hz, 2H, OH), 4.19 (t, J = 8 Hz, 4H, CH_2-OR), 3.65 (dd, J = 8 Hz, J = 2 Hz, 4H, CH_2-OH), 1.99 (p, J = 8 Hz, 4H, R-CH_2-R). ^{13}C NMR (100 MHz, $CDCl_3$): 154.0, 126.0, 125.4, 113.5, 105.7, 64.8, 57.4, 32.2. **HR-ESI-QToF MS** (positive mode): m/z calcd for $C_{16}H_{20}O_4$ $[M]^{+\cdot}$: 276.1362 found 276.1362.

Synthesis of 1-(3-dimethoxytrityloxypropoxy)-5-(3'-hydroxypropoxy)naphthalene 7.

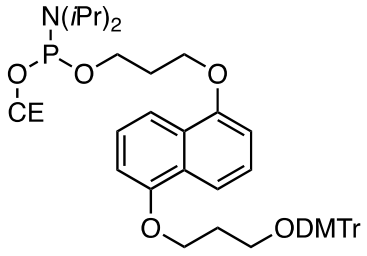


Chemical Formula: $C_{37}H_{38}O_6$

1,5-Bis(3-hydroxypropoxy)naphthalene **6** (2.13 g, 7.71 mmol) was dissolved in 100 mL of dry pyridine, then DMTr-Cl (2.61 g, 7.71 mmol) dissolved in 100 mL of dry pyridine was added dropwise in 2 h, and stirred for 2 h, the reaction was monitored with TLC (Cyclohexane/AcOEt, 8:2, v/v), , Then 5 drops of water were added and the reaction solution was reduced under vacuum. The mixture was then dissolved in 120 mL of CH_2Cl_2 and washed twice with 100 mL of a saturated solution of $NaHCO_3$, both aqueous phases were washed again with 50 mL of CH_2Cl_2. The resulting organic phases were dried over Na_2SO_4, filtered and evaporated under vacuum. The compound **7** was purified by chromatography on silica gel column (Cyclohexane/AcOEt 7:3, v/v with 1% of NEt_3). Yield: 1086 mg, 49 %, orange foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.8 (d, J = 8 Hz, 1H, C_2-H), 7.72 (d, J = 8 Hz, 1H, C_6-H), 7.45 (td, J = 8 Hz, J = 2 Hz, 2H, trityl), 7.37 (d, J = 8 Hz, 1H, C_3-H), 7.33 (td, J = 8 Hz, J = 2,4 Hz, 4H, trityl), 7.30 (d, J = 8 Hz, 1H, C_3-H), 7.23 (tt, J = 8 Hz, J = 2 Hz, 2H, C_4-H and C_8-H), 7.17 (tt, J = 8 Hz, J = 1,6 Hz, 1H, trityl), 6.86 (d, J = 8 Hz, 2H, trityl), 6.75 (td, J = 8 Hz, J = 2 Hz, 4H, trityl), 4.30 (m, 4H, CH_2-OR), 3.98 (t, J = 8 Hz, 2H, CH_2-OH), 3.73 (s, 6H, O-Me), 3.39 (t, J = 8 Hz, 2H, CH_2-ODMTr), 2.20 (m, 4H, R-CH_2-R). **^{13}C NMR** (100 MHz, $CDCl_3$): 158.8, 155, 154.7, 145.7, 136.9, 130.5, 130.4, 128.6, 128.2, 127.2, 127.0, 125.8, 125.4, 115.2, 114.3, 113.5, 113.5, 113.4, 105.9, 105.8, 86.4, 66.2, 65.4, 61, 60.3, 55.6, 32.6, 30.5. **HR-ESI-QToF MS** (positive mode): m/z calcd for $C_{37}H_{38}O_6$ $[M]^+$: 578.2668 found 578.2662.

Synthesis of 2-cyanoethyl ((3-(5-(3-dimethoxytrityloxy)propoxy)naphthalen-1-yloxy)propyl) diisopropylphosphoramidite 8.



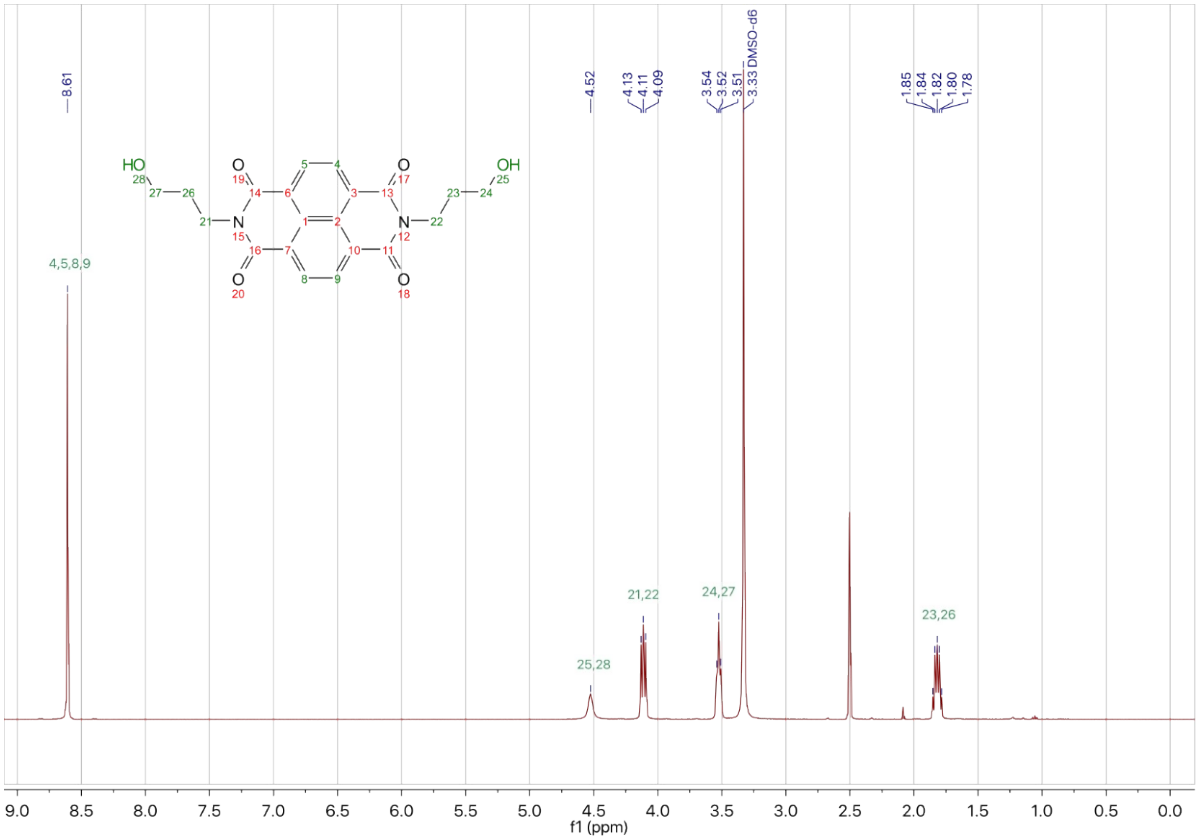
Chemical Formula: $C_{46}H_{55}N_2O_7P$

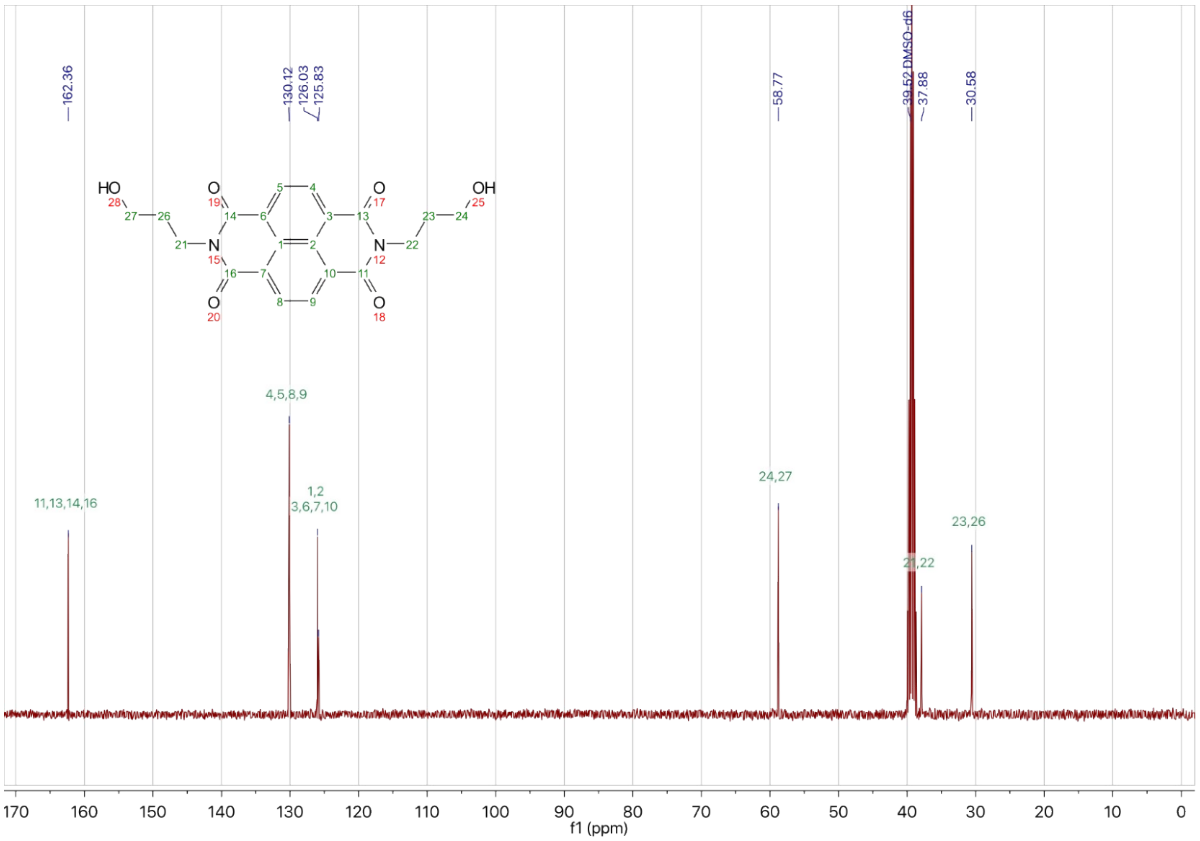
The compound **7** (266 mg, 0.46 mmol) was dissolved in 20 mL of dry dichloromethane, then was added DIEA (0.320 mL, 1.84 mmol) and 2-cyanoethyl *N,N*-diisopropyl-chloro phosphoramidite (130 mg, 0.55 mmol), the reaction was stirred and monitored for 3 h by TLC (Cyclohexane/AcOEt/NEt_3, 5:4.5:0.5, v/v/v), after that the reaction was quenched with few drops of water. The reaction mixture was extracted with 50 mL $NaHCO_3$ twice, the aqueous phase was extracted again with 20 mL of dichloromethane, then the reunited organic phase

was dried over Na_2SO_4, filtered, and concentrated under vacuum. The compound **8** was purified by chromatography on silica gel column (Cyclohexane/AcOET 8:2, v/v with 5% NEt_3). 344 mg, 96 %, yellow-green oil.

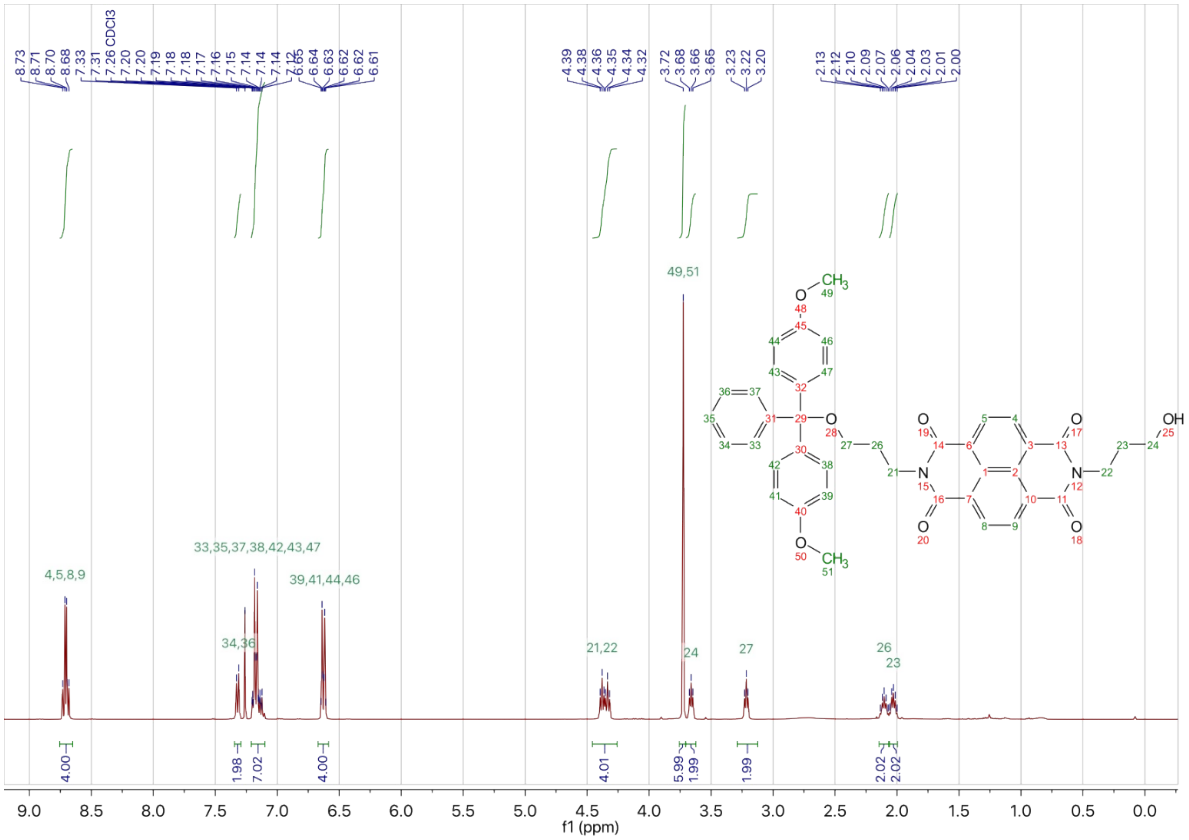
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.82 (d, J = 8 Hz, 1H, Naph-H), 7.69 (d, J = 8 Hz, 1H, Naph-H), 7.43 (m, 2H, trityl), 7.35 (d, J = 8 Hz, 1H, Naph-H), 7.30 (m, 4H, trityl), 7.28 (d, J = 8 Hz, 1H, Naph-H), 7.22 (tt, J = 8 Hz, J = 4 Hz, 2H, trityl), 7.16 (tt, 1H, trityl), 6.85 (d, J = 4 Hz, 1H, Naph-H), 6.83 (d, J = 4 Hz, 1H, Naph-H), 6.74 (td, J = 8 Hz, J = 4 Hz, 4H, trityl), 4.29 (d, J = 8 Hz, 2H, CH_2-OR), 4.25 (d, J = 8 Hz, 2H, CH_2-OR), 3.88 (m, 4H, CH_2 cyanoethyl), 3.73 (s, 6H, O-Me), 3.60 (m, 2H, CH isopropyl), 3.38 (t, J = 8 Hz, 2H, CH_2-O-P), 2.57 (t, J = 8 Hz, 2H, CH_2-ODMTr), 2.21 (m, 4H, R-CH_2-R), 1.17 (dd, J = 8 Hz, J = 4 Hz, 12H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): 158.3, 154.5, 154.4, 145.3, 136.5, 130.0, 128.2, 127.7, 126.7, 126.6, 125.1, 125, 114.5, 114.1, 113.0, 105.4, 105.3, 85.9, 65, 64.7, 60.5, 60.3, 59.9, 58.4, 58.2, 55.2, 43.1, 43.0, 31.2, 30.1, 29.7, 24.7, 24.6, 24.6, 20.4, 20.3. **^{31}P NMR** (100 MHz, $CDCl_3$): 147.58 **HR-ESI-QToF MS** (positive mode): *m/z* calcd for $C_{46}H_{58}N_2O_8P$ $[M+H_3O]^+$: 797.3931 found 797.3929.

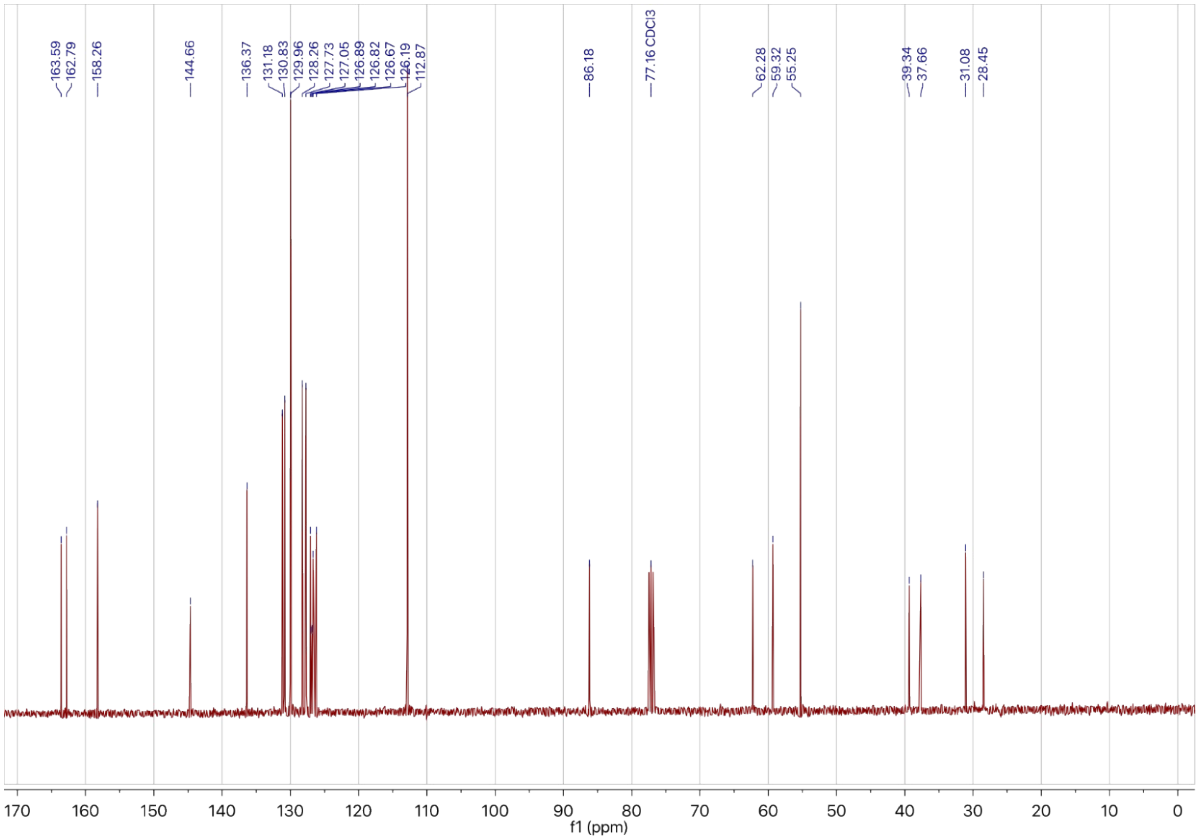
^{1}H and ^{13}C-NMR spectra of 2 in DMSO-d_6



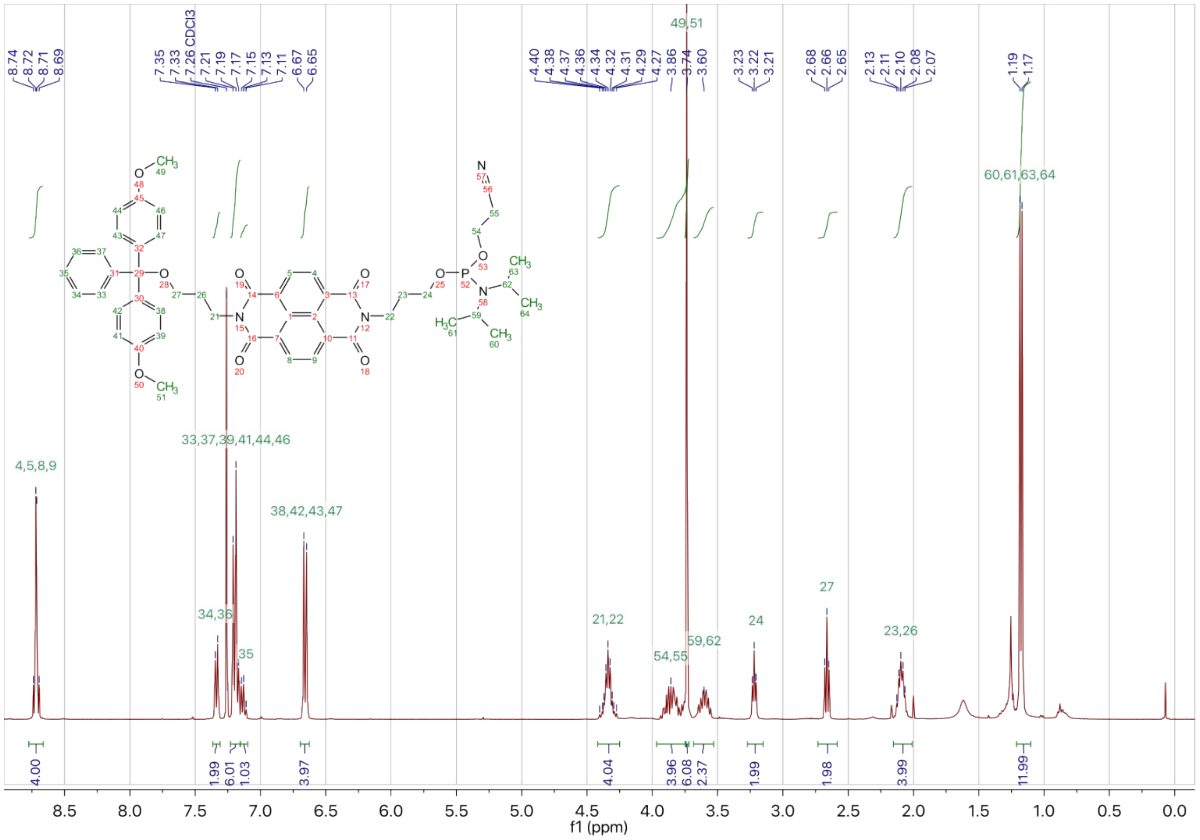


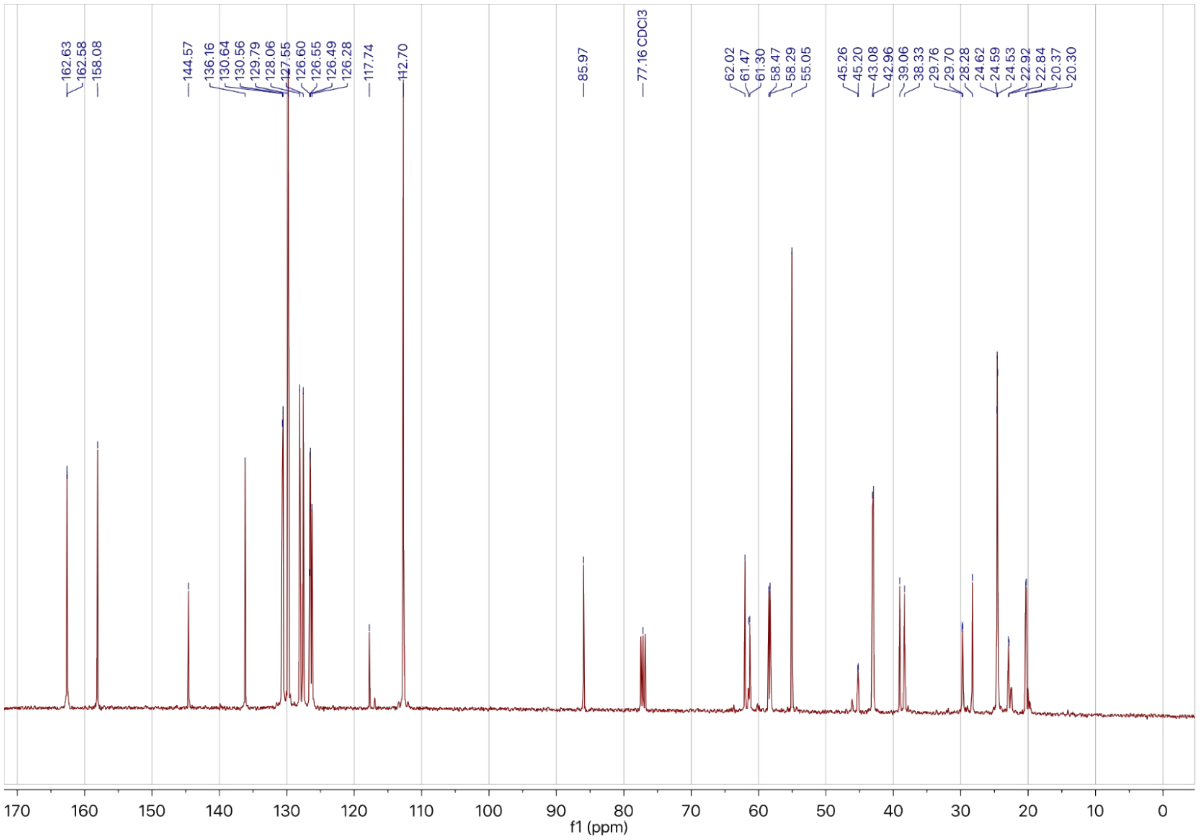
^{1}H and ^{13}C-NMR spectra of 3 in $CDCl_3$

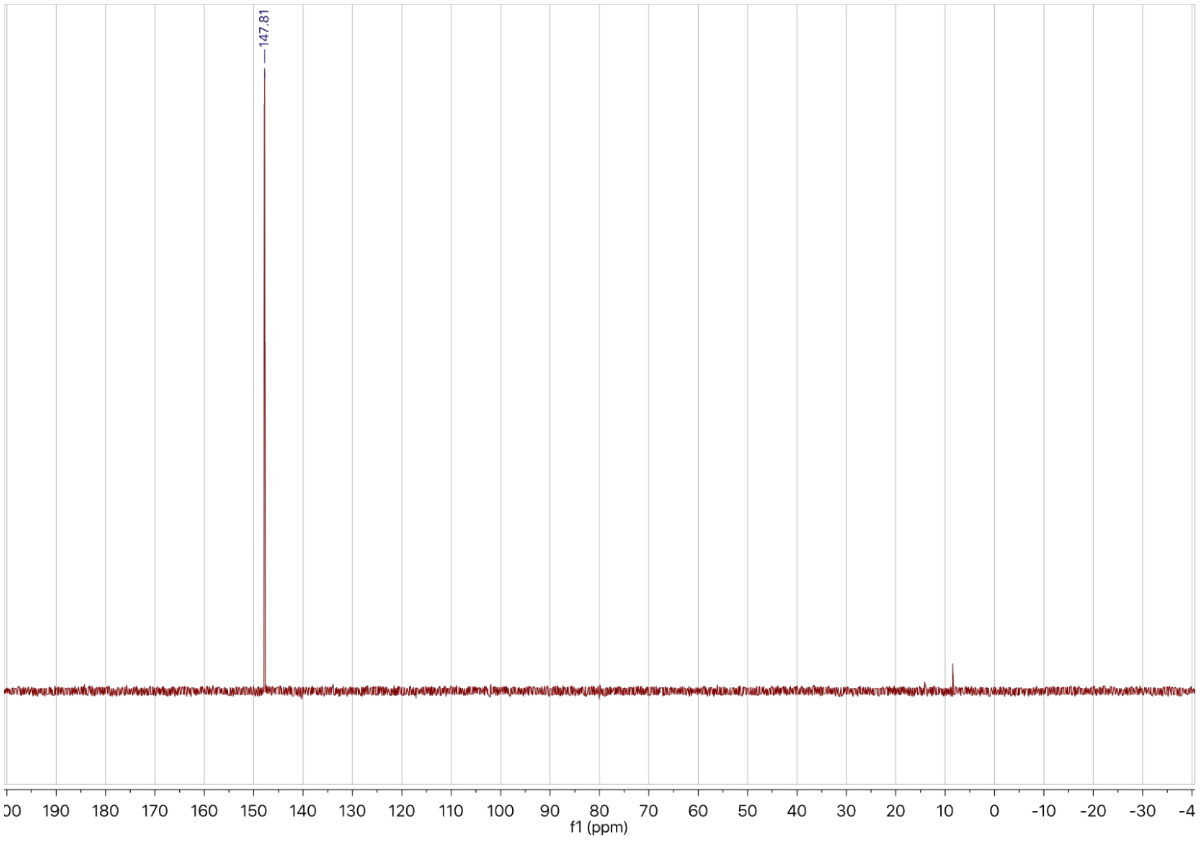




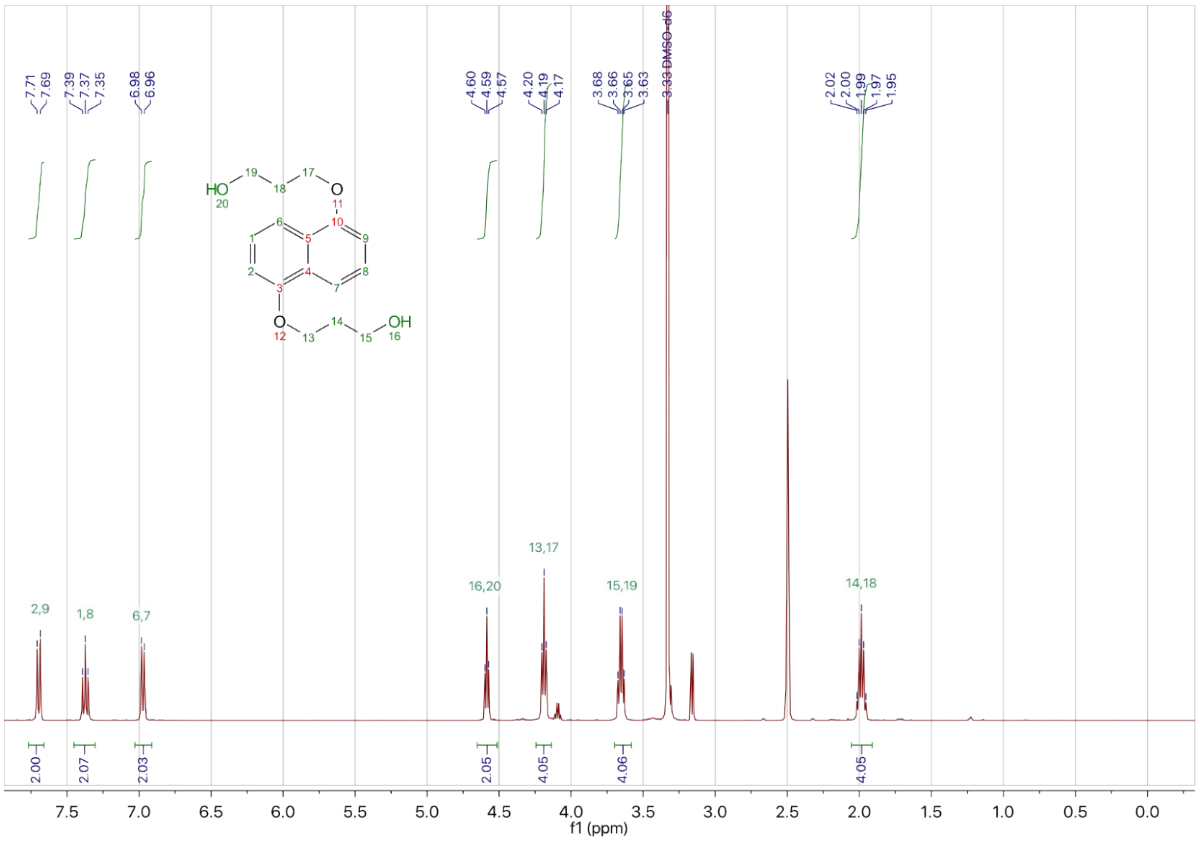
^{1}H, ^{13}C and ^{31}P-NMR spectra of 4 in $CDCl_3$

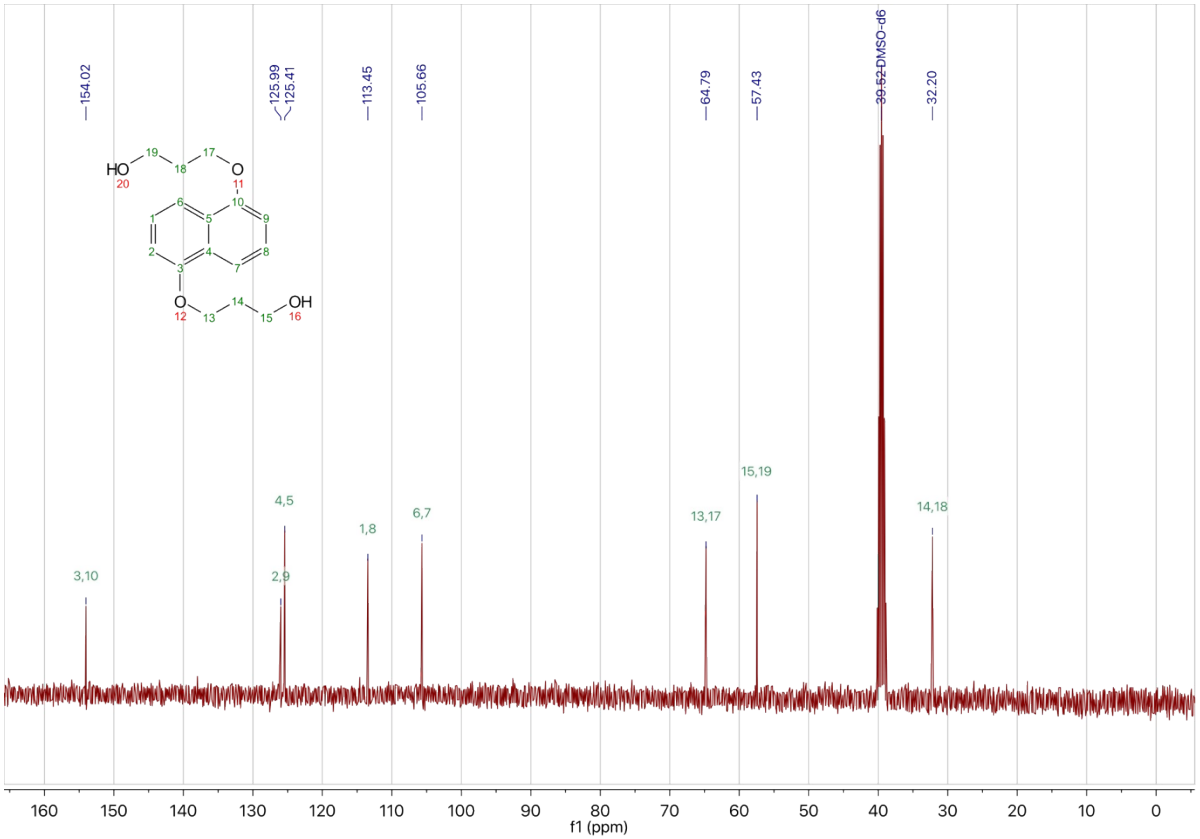




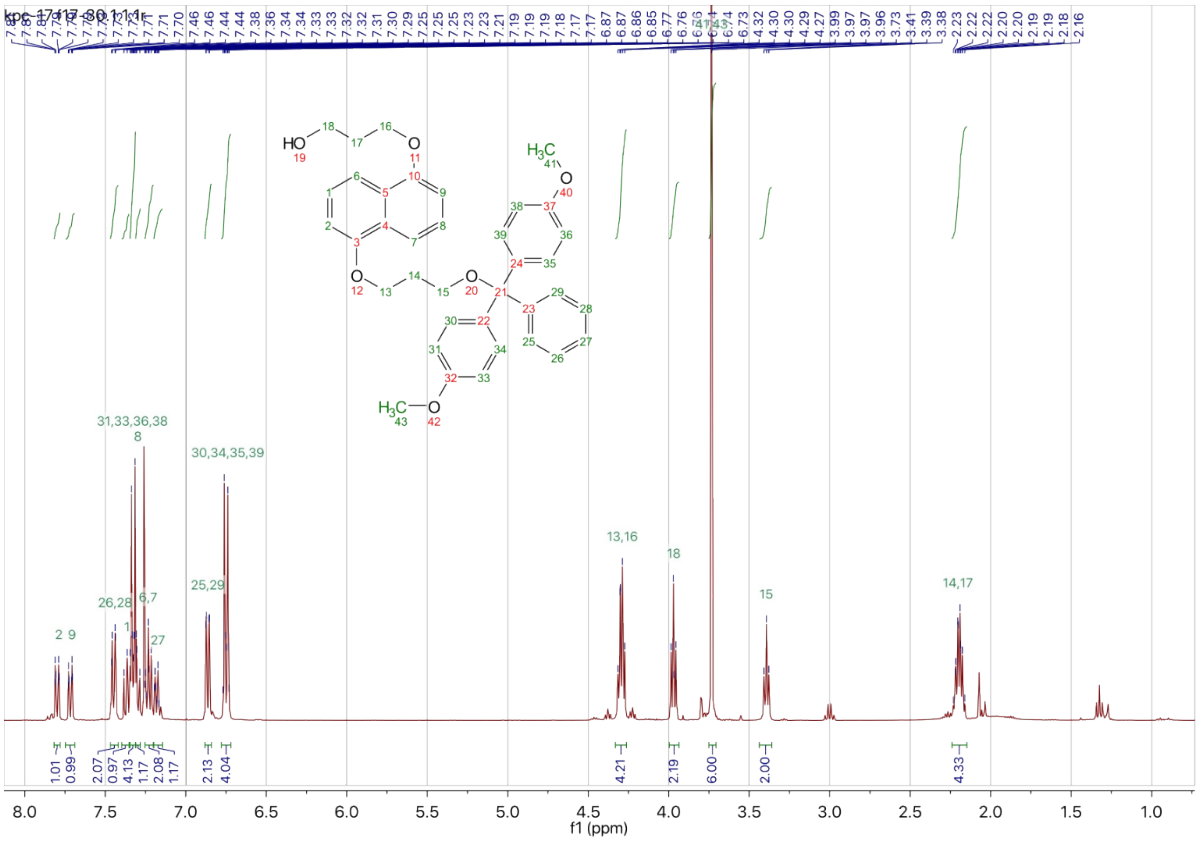


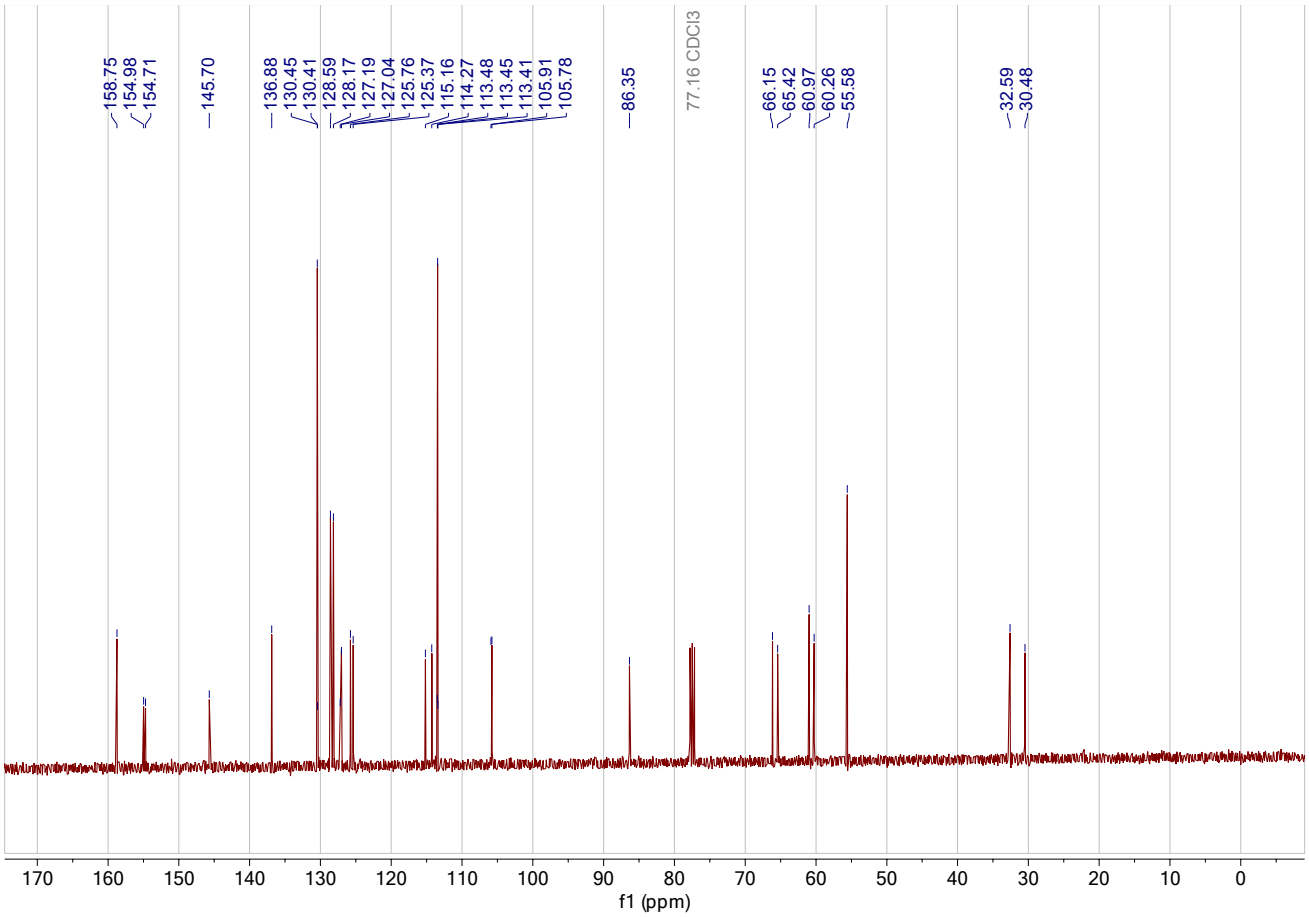
^{1}H and ^{13}C-NMR spectra of 6 in DMSO-d_6



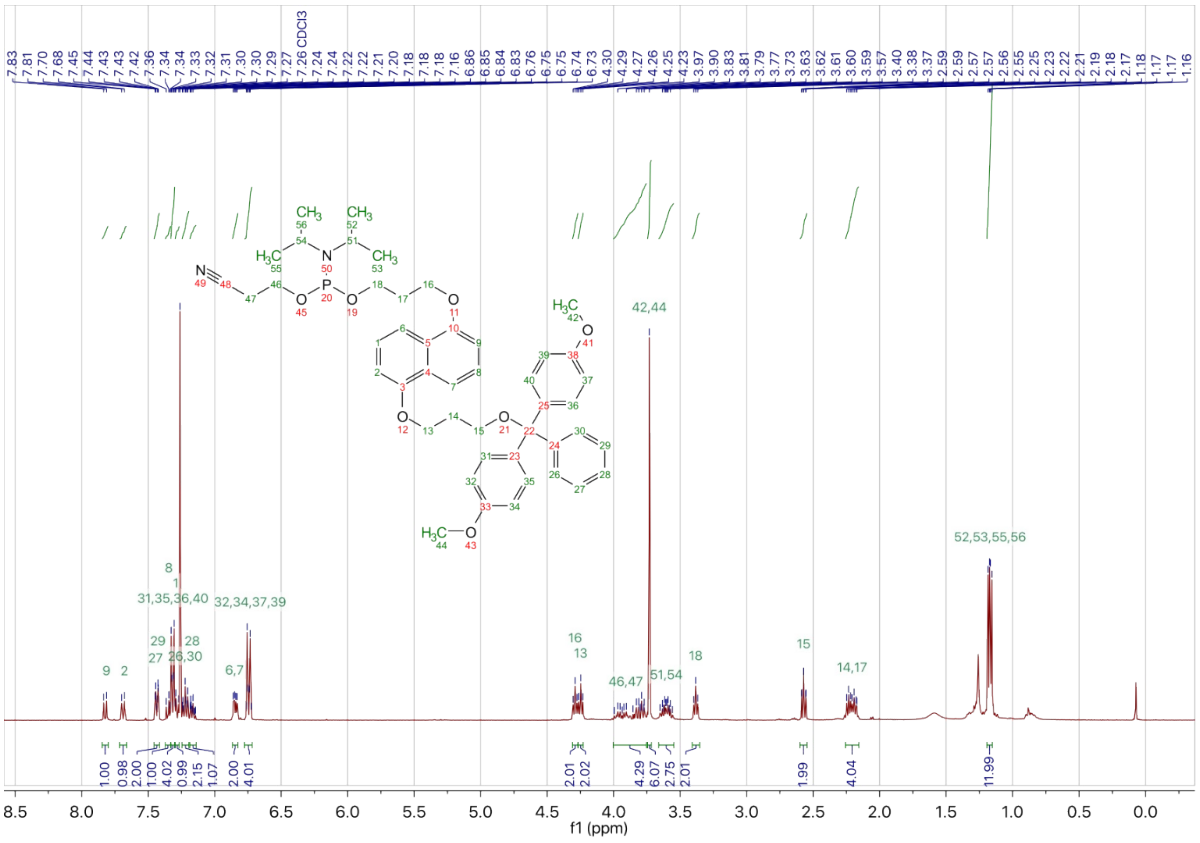


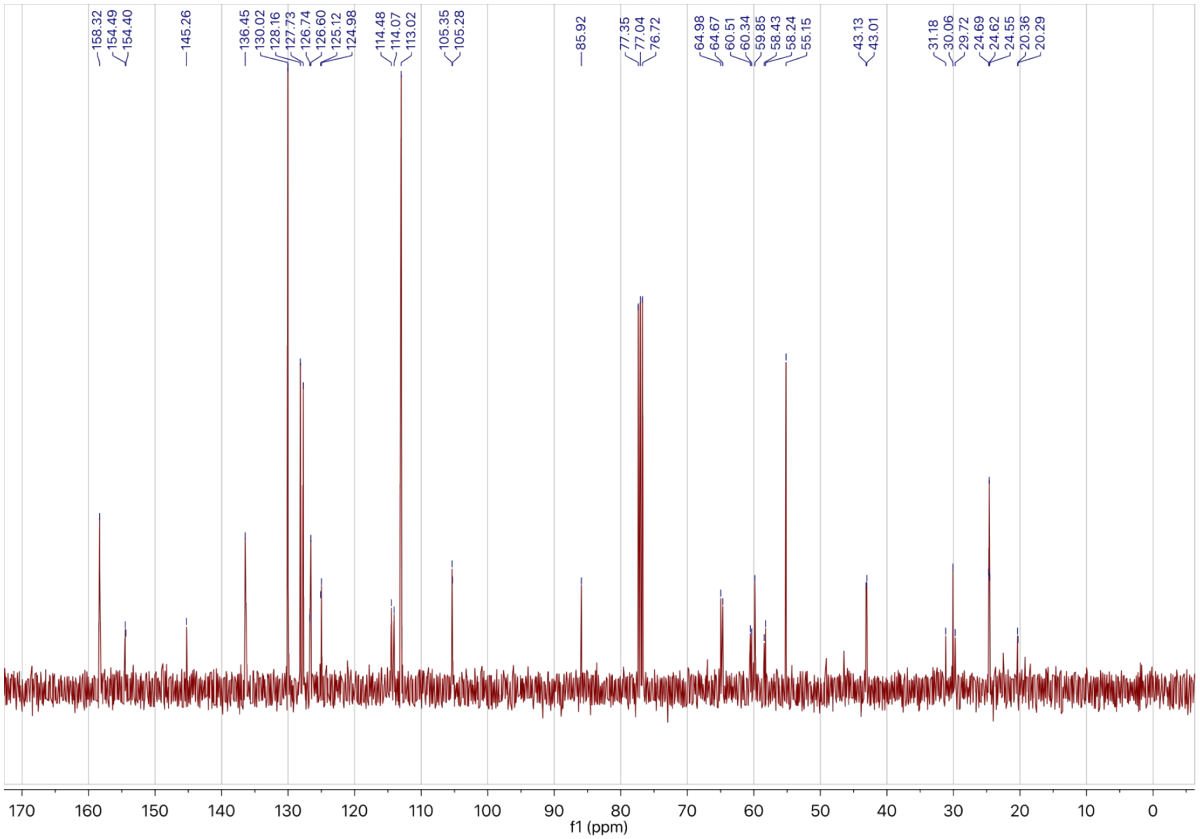
^{1}H and ^{13}C-NMR spectra of 7 in $CDCl_3$





^{1}H, ^{13}C and ^{31}P-NMR spectra of 8 in $CDCl_3$

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154.40
145.26
136.45
130.02
128.16
127.73
126.74
126.60
125.12
124.98
114.48
114.07
113.02
105.35
105.28
85.92
77.35
77.04
76.72
64.98
64.67
60.51
60.34
59.85
58.43
58.24
55.15
43.13
43.01
31.18
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20.29
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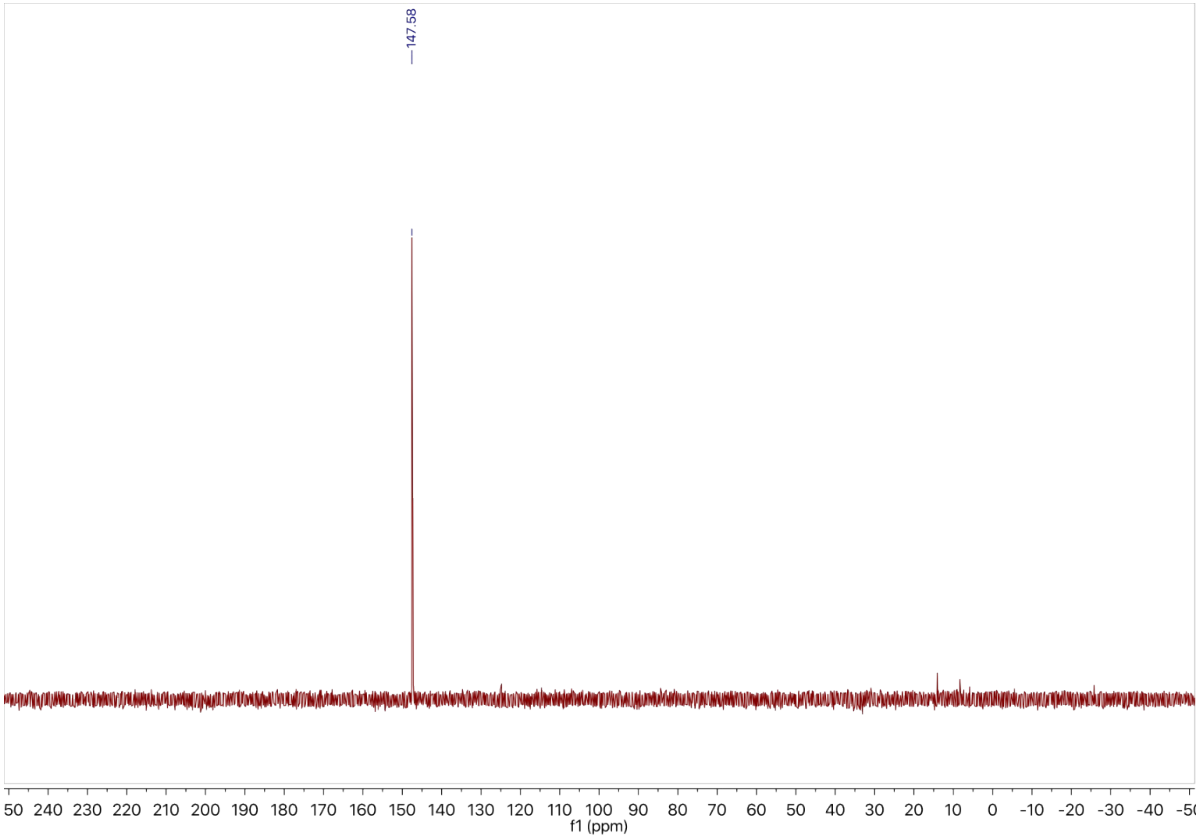
f1 (ppm)


147.58
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -5
f1 (ppm)

Oligomers synthesis

The solid-supported synthesis of oligonucleotides was performed on a 394 ABI DNA synthesizer. All conventional CPG columns, reagents and solvents for DNA synthesis were purchased from Link© technologies, ChemGenes© Corporation and Biosolve© Chimie. Propanediol solid support **14** and propanediol phosphoramidite **13** was prepared according to literature (F. Seela, K. Kaiser, Nucleic Acids Res. **1987**, *15*, 3113-3129).

The foldamers were elongated from the propanediol solid support **14** on an ABI 394 DNA synthesizer, with a 1 μmol scale cycle, according to standard phosphoramidite chemistry protocols. The detritylation step was performed for 65 s using 3 % TCA in CH_2Cl_2. For the coupling step, benzylmercaptotetrazole (0.3 M in anhydrous CH_3CN) was used as the activator with **4**, **8** or **13** phosphoramidites (0.1 M in CH_3CN, 3 min coupling time). The capping step was performed with acetic anhydride using commercially available solutions (Cap A: acetic anhydride:pyridine:THF 10:10:80 v/v/v and Cap B: 10 % *N*-methylimidazole in THF) for 10 s. The oxidation step was performed with a standard, diluted iodine solution (0.1 M I_2, THF:pyridine:water 90:5:5, v/v/v) for 15 s. Oligomers were deprotected and released from the CPG by treatment with a solution of 7N NH_3/MeOH for 24 h with orbital agitation. WARNING: Treatment with concentrated aqueous ammonia leads to degradation due to the opening of the imides of NDI. The CPG beads were washed with dry MeOH. The two fractions were pooled and dried on a speed vacuum.

Oligomers treatment and analysis

After cleavage, oligomers were purified by C_{18} reversed-phase HPLC (Macherey-Nagel, Nucleodur 250x10 mm, 5 μm) on a Dionex Ultimate 3000 system with Reodyn injector with a detector UV DAD 3000 at a flow rate of 5.0 mL/min. The conditions for the HPLC purification are specified in the section below. The resulting oligomers with triethylammonium cations were exchanged on a DOWEX 50W X2 conditioned with Na^+ cation affording oligomers as sodium form which is more soluble in water.

Reverse phase C18 HPLC of oligomers for purification

Compounds	Linear gradient	Retention time (min)
Pro-p-DAN-p-Pro **9**	8% to 32% of CH_3CN in 50 mM TEAAc buffer pH 7 over-20 min	12.20
Pro-p-NDI-p-Pro **10**	8% to 32% of CH_3CN in 50 mM TEAAc buffer pH 7 over-20 min	13.72

Pro-p-DAN-p-NDI-p-Pro **11**	8% to 32% of CH_3CN in 50 mM TEAAc buffer pH 7 over-20 min	13.93
Pro-(p-DAN-p-NDI)$_3$-p-Pro **12**	15% to 21% of CH_3CN in 50 mM TEAAc buffer pH 7 over-20 min	10.21

Table S1. Sequence of compounds 9-12.

Compound[a]		MALDI-TOF[b]	
		m/z Calcd	Found
9	Pro-p-DAN-p-Pro	551.44	551.34
10	Pro-p-NDI-p-Pro	657.48	658.21
11	Pro-p-DAN-p-NDI-p-Pro	995.78	995.97
12	Pro-(p-DAN-p-NDI)$_3$-p-Pro	2561.04	2561.23

[a] Pro= Propanol, p = phosphodiester. [b] $[M-H]^-$

NMR studies of **9**, **10** and **11** were performed in D_2O and calibrated at 4.79 ppm offset for spectra at 25°C. Due to the very low amount of material the ^{1}H-NMR spectra were limited to the aromatic protons. Furthermore, due to the water chemical shift close to those of methylene protons the integration of aliphatic protons was disturbed.

For **9**: ^{1}H NMR (400 MHz, D_2O): δ (ppm) = 7.95 (d, J = 8 Hz, 2H, $C_{2,6}$-H), 7.54 (t, J = 8 Hz, 2H, $C_{3,7}$-H), 7.16 (d, J = 8 Hz, 2H, $C_{4,8}$-H)

For **10**: ^{1}H NMR (400 MHz, D_2O): δ (ppm) = 8.74 (s, 4H, H-Ar)

For **11**: ^{1}H NMR (400 MHz, D_2O): δ (ppm) = 8.31 and 8.44 (2d, J = 8 Hz, 2 x 2H, H-Ar$_{NDI}$), 7.23 (d, J = 8 Hz, 1H, H-Ar$_{DAN}$), 7.03 (m, 3H, H-Ar$_{DAN}$), 6.62 (d, J = 8 Hz, 1H, H-Ar$_{DAN}$), 6.39 (d, J = 8 Hz, 1H, H-Ar$_{DAN}$).

Molar Extinction coefficients of 9, 10 and 12 in water at 25°C.

9	**10**	**12**
$\lambda_{296\ nm}$ 5 150 $M^{-1}.cm^{-1}$	$\lambda_{363\ nm}$ 10 300 $M^{-1}.cm^{-1}$	$\lambda_{296\ nm}$ 4 950 $M^{-1}.cm^{-1}$
$\lambda_{311\ nm}$ 3 150 $M^{-1}.cm^{-1}$	$\lambda_{382\ nm}$ 11 320 $M^{-1}.cm^{-1}$	$\lambda_{363\ nm}$ 4 860 $M^{-1}.cm^{-1}$
$\lambda_{324\ nm}$ 2 200 $M^{-1}.cm^{-1}$		$\lambda_{382\ nm}$ 4 860 $M^{-1}.cm^{-1}$
		CT $\lambda_{530\ nm}$ 300 $M^{-1}.cm^{-1}$

Foldamers preparation and storage. Compounds **9**, **10**, **11**, **12** were filtered on Chromafil Xtra H-PTFE-45/25 0,45 µm hydrophilic filter, evaporated and stored dry at -20 °C to avoid structuration in water, then were dissolved at 0.1 mM in water to withdraw the needed number of nanomols, this volume was then completed to 1 mL with water to obtain the needed concentration. This solution was then stored at 4 °C for the time required. The remaining solution was dried.

MALDI-ToF mass spectra were recorded on Axima© Assurance in negative mode, calibration was performed with a mixture of oligomers for reference, 2,4,6 Trihydroxyacetophenone (THAP) and anthranilic acid were used as matrix. Oligomers were dissolved with 200 µL of water and then 0.75 µL was mixed with 1 µL of THAP or anthranilic acid solution in 1/1 aqueous sodium citrate/acetonitrile. This mixture was then spotted on a MALDI plate and dried.

UV-Vis spectra were recorded on a VARIAN© Cary 300 Bio UV-Vis spectrophotometer at the indicated temperature. All oligomers were dissolved in 1 mL of water for spectra analysis in an UV cuvette with 1 cm of path-length at the specified concentration.

Fluorescence spectra was recorded on the J-1000 Series Circular Dichroism spectrophotometers from JASCO®. All oligomers were dissolved in 1 mL of water for spectra analysis and we used a 650 V beam with a slit of 2000 and a D.I.T of 2s with an UV cuvette with 1 cm of path length at the specified concentration.

Atomic force microscopy analyses were recorded using Nanoscope on three instruments: MultiMode 8 (Quantitative nanomecanics QNM) equipped with nanoscope V electronics in peak force mode. Bruker Dimension 3100 equipped with nanoscope IIIa quadrex electronics in tapping mode. Nanoman 5 equipped with nanoscope V electronics in tapping mode. We used 300-rtespa and Rfesp-75 probes from Bruker with a tip radius of 5 nm. The mica substrates of highest grade V1 mica discs 15 mm (Ted Pella, Inc.) were attached to a steel baseplate with carbon tape. For each analysis three drops of the aqueous solution containing our compounds was placed on a freshly cleaved mica surface and dried at room temperature for 30 minutes to 1 hour in a laminar flow cabinet.

Transmission Electron Microscopy Imaging in negative stain, 3 µL of the sample was deposited for 2 min onto a glow-discharged carbon-coated grids (Quantifoil Micro tools GmbH, Germany), stained for 60 s with a 2% (w/vol) aqueous uranyl acetate (Merck, France) solution, and then dried with ashless filter paper (VWR, France). All observations of EM-grids were carried out on a JEOL 2200FS FEG operating at 200 kV equipped with a 4k x 4k slow-scan CDD camera (Gatan inc.) under low-dose conditions (total dose of 20 electrons/Å2) in the zero-energy-loss mode with a slit width of 20 eV. Images were taken at a nominal magnification of 50,000 X, with defocus ranging from 0.6 to 2.5 µm.

Molecular modeling

The structure of the longitudinal and lateral arrangements has been optimized using a classical Monte Carlo conformational searching procedure as described in the BOSS software (1). For that purpose, the Spectroscopic Empirical Potential Energy function SPASIBA and the corresponding parameters

are used (2,3) Molecular graphics and analysis were performed using the Discovery Studio 2020 Client software, Dassault Systemes Biovia Corp.

1. W. L. Jorgensen, J. Tirado-Rives, *J. Comput. Chem*. **2005**, *26*, 1689-1700.
2. G. Vergoten, I. Mazur, P. Lagant, J. C. Michalski, J. P. Zanetta, *Biochimie* **2003**, *85*, 65-73.
3. P. Lagant, D. Nolde, R. Stote, G. Vergoten, M. Karplus, *J. Phys. Chem.* A **2004**, *108*, 4019-4029.