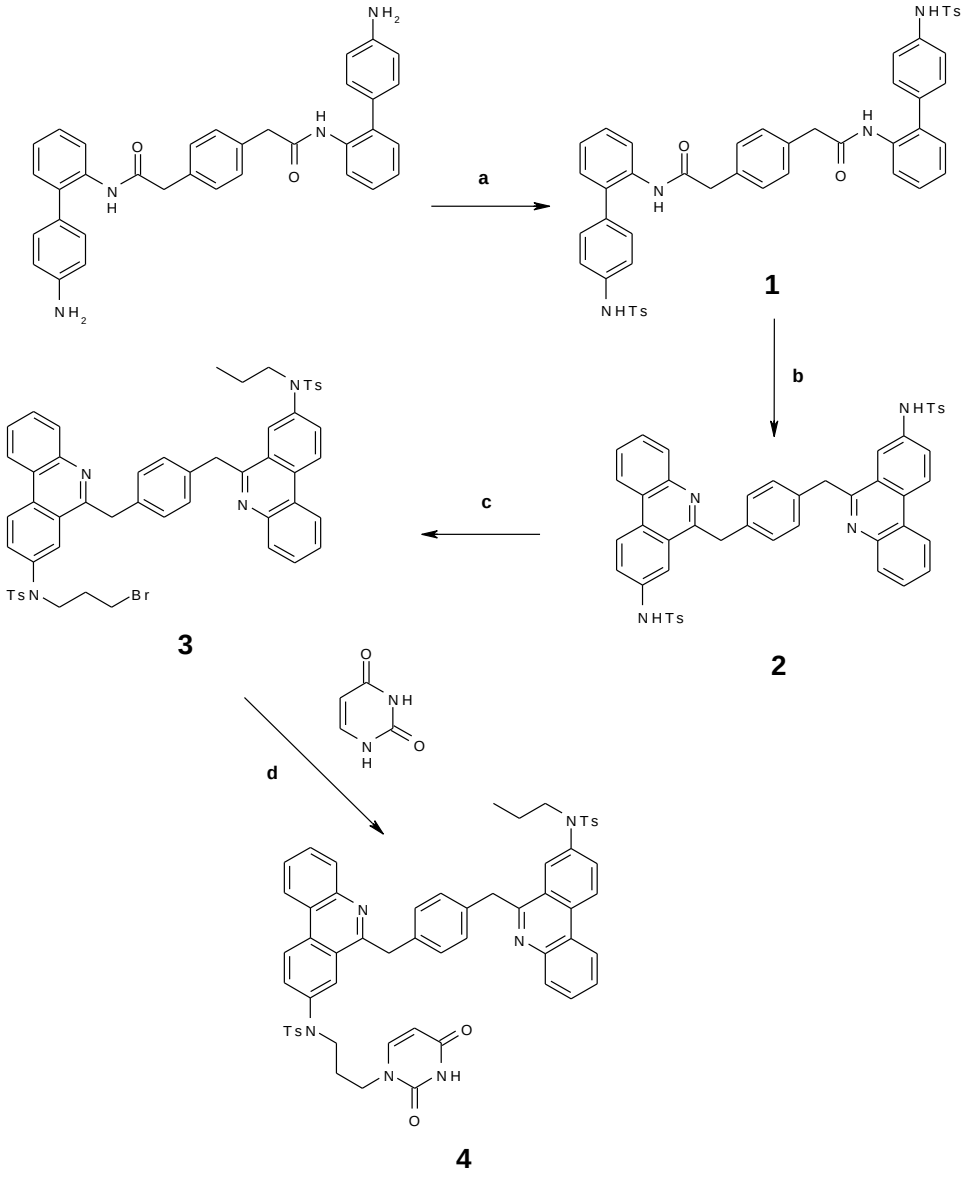
Supplementary Data

Synthesis

The general strategy that was used for the synthesis of the novel rigid asymmetric bis-phenanthridinium-nucleobase conjugate **7** was the same as for previously prepared flexible conjugates[1] and comprised asymmetric alkylation of the amino substituents of bis-phenanthridine **2** mono- with a dibromopropane, followed by the introduction of nucleobase uracil at the other end of one alkyl linker (Scheme 1), and finally by deprotection of tosylated compound

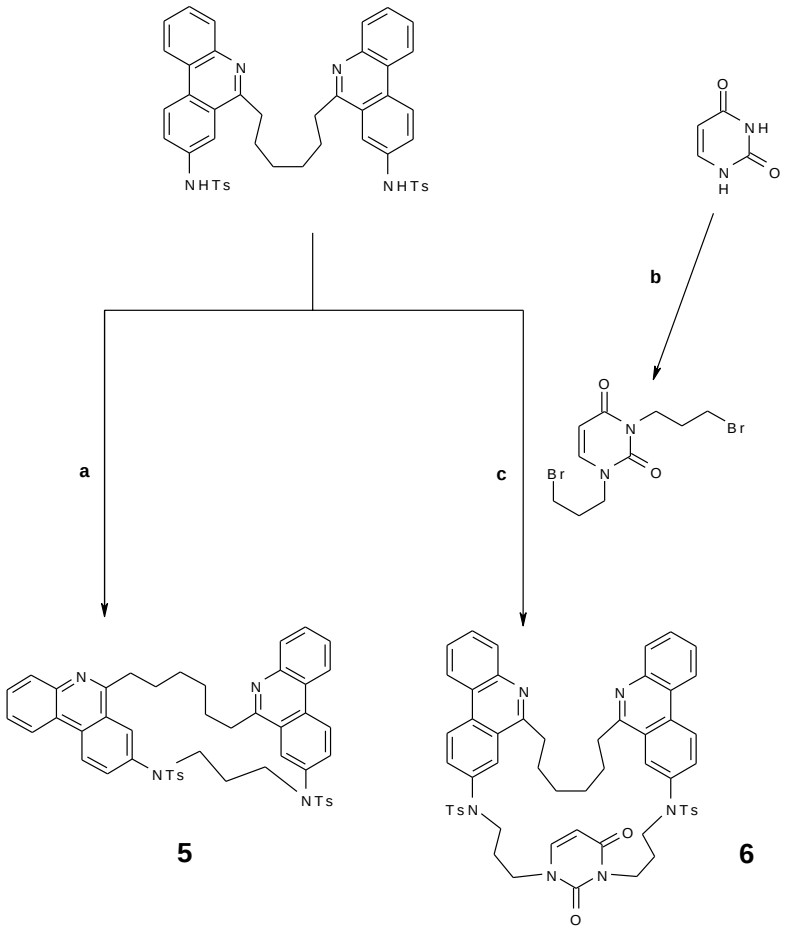
The compound **1** was prepared starting from *N,N'*-bis-[(4'-amino)-2-biphenylyl]-phenylenediacetamid[2] that was tosylated in pyridine. The bis-phenanthridine **2** was obtained by the Morgan-Walls reaction[3] based on the middle pyridine ring formation by intramolecular electrophilic cyclization of the bis-biphenylyl **1** using $POCl_3$. Then, one of two tosyl-amino groups of phenanthridine **2** was alkylated in the first reaction step over seven days in a dark and at room temperature, using small excess (1.5 eq) of 1-bromopropane. Afterwards, a large excess of potassium carbonate and 1,3-dibromopropane were added dropwise in situ, in order to obtain asymmetric compound **3**. Finally, the reaction of bromo-derivative **3** with large excess of uracil was performed under argon atmosphere at 40-50 °C in dry DMF in the presence of NaH, giving tosyl-protected conjugate **4**. Under these conditions the alkylation of uracil selectively occurred at N1 position**.** (Scheme 1).



Scheme 1. The synthesis of asymmetric conjugate **4**; (a) TsCl / pyridine / 40-50 ºC; (b1) $POCl_3$ / 120 ºC (b2) NaOH / H_2O; (c1) $Br(CH_2)_2CH_3$ (1 eq) / K_2CO_3 / DMF / Ar / r.t. (c2) $Br(CH_2)_3Br$ (10 eq) / K_2CO_3 / DMF / Ar / r.t.; (d) NaH / DMF / Ar / 40-50 ºC

Flexible protected cyclobisintercaland **5** was obtained by alkylation of previously prepared bisphenathridine1. Bisphenanthridine1 was alkylated using small excess of 1,3-dibromopropane under high dilution conditions in order to obtain compound **5.** (Scheme 2). To obtain cyclobisintecaland **6,** uracil was alkylated in dry DMF in the presence of potassium carbonate. Resulted bromo-uracile derivative[4] reacted with bisphenathridine1 in dry DMF under basic conditions and inert atmosphere at 80-100

°C to give cyclic bisphenanthridine **6**, bridged by hexylene chaine as well as by uracil moiety. (Scheme 2)



Scheme 2. The synthesis of cyclobisphenanthridines **5** and **6**; (a) $Br(CH_2)_3Br$ (1.5 eq) / K_2CO_3 / DMF / Ar / r.t; (b) $Br(CH_2)_3Br$ (10 eq) / K_2CO_3 / DMF / Ar / r.t; (c) K_2CO_3 / DMF / Ar / r.t.

Tosyl-groups of **4-6** were removed by heating at 100 °C under acidic conditions, followed by neutralization using 5 M NaOH aqueous solution. Compounds **7-9** were found to be sufficiently soluble in water under acidic conditions (pH 5).

All here presented compounds (**1-9**), synthesized by modified procedures elaborated earlier for their close analogues [1, 2, 5, 6] have satisfying mass spectra and their structures were verified by detailed 1D and 2D NMR analysis.

Materials and methods

^{1}H NMR and ^{13}C NMR spectra were recorded on on Bruker Avance DRX 500 operating at 500 MHz. Chemical shifts (δ) are expressed in ppm, and *J* values in Hz. Signal multiplicities are denoted as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The electronic absorption spectra of newly prepared compounds were measured on a Varian Cary 100 Bio spectrometer in quartz cuvettes (1 cm). UV-Vis titration were performed on a Varian Cary 100 Bio spectrometer. IR spectra were recorded on a Perkin–Elmer 297 instrument using KBr pellets. Fluorescence spectra were recorded on Varian Cary Eclipse fluorimeter. CD spectra were recorded on JASCO J815 spectrophotometer using appropriate 1 cm path quartz cuvettes Mass spectra were obtained using Applied Biosystems 4800 *Plus* MALDI TOF/TOF™ Analyzer. Preparative thin layer chromatography (TLC) was carried out using Kieselgel HF_{254} "Merck". Melting points were determined on Kofler apparatus and are uncorrected. All products were characterized by NMR, IR, ESI-MS or HRMS. Hygroscopic character of compounds yielded elemental analyses with non–stoichiometric amounts of water – however, since NMR spectra of final compounds were in accordance with other, previously prepared close analogues, proposed structures were not questionable.

***N,N'*-bis-[(4'-tosylamino)-2-biphenylyl]-phenylenediacetamide (1)**

Solution of tosyl-chloride (3.04 g, 15.9 mmol) in 15 ml of pyridine was added dropwise during 1 h to the ice-cold solution of *N,N'*-bis-[(4'-amino)-2-biphenylyl]-phenylenediacetamid[2](1.4 g, 2.66 mmol) in 15 ml of pyridine. After adding was completed, reaction mixture heated at 50-60 ºC during 4 h. Subsequently, reaction mixture was allowed to cold and then poured into water. Therefore light yellow solid precipitated. Pure compound **1** was obtained by TLC as white solid (1.26 g, 57 %), additionally recrystallized from MeOH. R_f (SiO_2, 2 % MeOH in CH_2Cl_2) = 0.20; mp 259-260 °C; ^{1}H-NMR (DMSO-d_6) δ: 2.29 (s, Ts-CH_3, 6 H), 3.66 (s, CH_2, 4 H), 7.11 (d, Ts, 4H, *J* = 8.6 Hz), 7.23-8.63 (m, Ar-H, 28 H), 9.35 (s, NH-CO, 2 H), 10.39 (s, NH-Ts, 2 H) ppm; ^{13}C-NMR (DMSO-d_6) δ: 20.95, 42.28, 119.19, 125.89, 126.74, 126.81, 127.55, 129.06, 129.54, 129.76, 130.04, 133.88, 133.93, 134.60, 135.49, 136.95, 137.00, 143.29. 169.51; IR (KBr) ν: 3362, 3144, 3030, 2922, 2856, 2363,

1655, 1610, 1585, 1445, 1340, 1340, 1340, 1227, 1157, 1092, 914, 831, 814, 766, 704, 663, 636, 571, 546, 482 cm^{-1}; Anal. Calcd for $C_{48}H_{42}N_4O_6S_2$ (Mr 835.02 $gmol^{-1}$) × 1/2 H_2O: C 68.25, H 5.09, N 6.63 %; Found: C 68.35, H 5.13, N 6.65 %; (MALDI / TOF-HRMS) m/z: 835.2625 (cald. for $C_{48}H_{42}N_4O_6S_2$: 835.2619).

1,4-Bis-[(8-tosilaminofenantridin-6-il)-metil]benzen (2)

Compound **2** was obtained by suspending of *N,N'*-bis-[(4'-tosylamino)-2-biphenylyl]-phenylenediacetamide **1** *N* (1.2 g; 1.4 mmol) in 8 ml $POCl_3$ and heating reaction mixture at 100-110 °C during 3 h. Mixture was allowed to cold and poured into ice, and afterwards was made alkaline (pH = 8-9) by addition of 3 M NaOH water solution. Yellow solid precipitated and was filtered and washed with water to give pale yellow powder (1.3 g; 86 %); R_f (SiO_2,10 % MeOH in CH_2Cl_2) = 0.33; mp >300 ºC; ^{1}H-NMR (DMSO-d_6) 2.13 (s, Ts-CH_3, 6 H), 4.52 (Phen-CH_2), 7.05 (d, Ts, 4H, J = 8.2 Hz), 7.25 (s, Ar-H, 4H), 7.48 (d, Ts, 4 H, J = 8.4 Hz), 7.58 (dd, 2 H, Phen-9, $J_{7\text{-}9}$ = 2.2 Hz), 7.62 (t, 2 H, Phen-2), 7.68 (t, 2 H, Phen-3), 8.01 (d, 2H, Phen-4, $J_{3\text{-}4}$ = 7.9 Hz), 8.14 (d, 2H, Phen-7), 8.58 (d, 2H, Phen-1, $J_{1\text{-}2}$ = 8.2 Hz), 8.68 (d, 2H, Phen-10, $J_{9\text{-}10}$ = 9.1 Hz) ppm; ^{13}C-NMR (DMSO-d_6) δ: 156.26, 143.30, 137.39, 136.98, 129.51, 129.20, 128.70, 128.62, 128.36, 126.97, 126.57, 125.09, 124.39, 123.34, 123.00, 122.19, 60.21, 20.78 ppm; IR (KBr) ν: 3447, 3288, 2922, 2361, 2343, 1618, 1541, 1504, 1420, 1385, 1300, 1157, 1092, 970, 947, 891, 833, 816, 762, 667, 581, 542, 459, 419 cm^{-1}; (MALDI / TOF-HRMS) m/z: 799.2430 (cald. for $C_{48}H_{38}N_4O_4S_2$: 799.2407).

1-{[8-(3-bromopropyltosyl)aminophenanthridine-6-il]-methyl}-4-{[8-(propyltosyl)aminophenanhtridine-6-il]-methyl}benzene (3)

1-bromopropane (45 μl, 0.5 mmol, 1 equivalent) and K_2CO_3 (69 mg, 0.5 mmol, 1 equivalent) were suspended in dry DMF (5 ml). To this suspension, solution of 1,4-bis-[(8-tosilaminofenantridin-6-il)-metil]benzen (**2**) (400 mg, 0.5 mmol, 1 equivalent) in dry DMF (5 ml) was added dropwise during 10 min. and the reaction mixture was stirred during 7 days under argon atmosphere at room temperature. Then, 1,3-dibromopropane (512 μl, 5.14 mmol, 10 equivalents) and K_2CO_3 (690 mg, 5 mmol, 10 equivalents) were added to reaction mixture, that was stirred during next two days under argon atmosphere at room temperature. Water and CH_2Cl_2 were added to this

suspension, the water layer was washed twice with CH_2Cl_2, organic extracts were dried over Na_2SO_4 and evaporated, yielding 280 mg of light brown solid residue. Pure compound **3** was obtained by TLC (SiO_2, 2% MeOH in CH_2Cl_2, R_f = 0.37) as white solid (90 mg, 19 % yield) and recrystallized from from methanol; mp 207-209 ºC; ^{1}H-NMR ($CDCl_3$) δ: 0.62 (t, CH_3, 3H, *J* = 7.4 Hz), 1.06 (m, CH_2-propyl chain, 2 H), 1.59 (m, CH_2-propylene chain, 2 H), 2.31 (s, Ts-CH_3, 6 H), 3.11 (t, CH_2Br, 2 H, *J* = 5.8 Hz), 3.38 (t, NCH_2-propyl chain, 2 H, *J* = 6.7 Hz), 3.55 (t, NCH_2-propylene chain, 2 H, *J* = 6.5 Hz), 4.45 (s, Ar-CH_2, 2 H), 4.46 (s, Ar-CH_2, 2 H), 7.03 (br-s, Ar, 4H), 7.20 (br-s, Ts, 4 H), 7.37 (m, Ts, 4H), 7.45-7.48 (m, Phen-9, 2 H), 7.62-7.77 (m, Phen-2, Phen-3, Phen-7, 6 H), 8.16 (d, Phen-4, 2 H, $J_{3\text{-}4}$ = 7.8 Hz), 8.45-8.54 (m, Phen-1, Phen-10, 4 H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 10.82 (CH_3), 21.17 (Ts-CH_3), 21.55, 29.63, 31.11, 42.41, 42.59, 49.06, 52.17, 122.09, 123.24, 123.52, 123.52, 123.70, 123.77, 125.37, 126.55, 127.03, 127.09, 127.77, 127.84, 128.77, 128.87, 129.10, 129.21, 129.45, 129.56, 129.91, 129.95, 130.75, 131.04, 131.15, 131.80, 132.43, 132.61, 134.60, 134.75, 135.05, 137.04, 137.12, 137.86, 137.99, 143.59, 143.93, 159.61, 159.67 ppm; IR (KBr) ν: 3448, 3067, 2959, 2924, 2853, 2361, 2343, 1655, 1578, 1508, 1458, 1344, 1161, 1090, 1020, 968, 812, 766, 725, 708, 667, 586, 548, 473 cm^{-1}; Anal. Calcd for $C_{54}H_{49}BrN_4O_4S_2$ (Mr 962.05 $gmol^{-1}$) × CH_3OH: C 66.39, H 5.33, N 5.63 %; Found: C 66.55, H 5.35, N 5.81 %; (MALDI / TOF-HRMS) m/z: 961.2406 (cald. for $C_{54}H_{49}BrN_4O_4S_2$: 961.2451).

1-{[8-(3-(urac-1-il)propyltosyl)aminophenanhtridine-6-il]-methyl}-4-{[8-(propyltosyl)aminophenanthridine-6-il]-methyl}benzene (4)

Uracil (99 mg, 0.88 mmol, 10 equivalents) that was previously dried, and NaH (35 mg, 60% w.w., 0.88 mmol, 10 equivalents) were suspended in dry DMF (5 ml) and stirred during 1 h in argon atmosphere at room temperature. To this suspension, a solution of 1-{[8-(3-bromopropyltosyl)aminophenanthridine-6-il]-methyl}-4-{[8-(propyltosyl)aminophenanhtridine-6-il]-methyl}benzene **(3)** (85 mg; 0.088 mmol) in dry DMF (10 ml) was added dropwise and the reaction mixture was stirred during 48 hours under argon atmosphere at 50 °C. Then, water and CH_2Cl_2 were carefully added to this suspension. The water layer was washed twice with CH_2Cl_2, organic extracts were dried over Na_2SO_4 and evaporated, yielding solid residue (68 mg) that was

purified by TLC (SiO_2, 10% MeOH in CH_2Cl_2, R_f = 0.46). Compound **4** was obtained as white solid (20 mg, 23 %yield) that was additionally recrystallized from MeOH; mp 153-156 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.66 (t, CH_3, 3H, *J* = 7.81 Hz), 1.11 (m, CH_2-propyl chain, 2 H), 1.49 (t, CH_2-propylene chain, 2 H, *J* = 6.5 Hz), 2.38 (s, Ts-CH_3, 3 H), 2.40 (s, Ts-CH_3, 3 H), 3.40 (t, NCH_2-propyl chain, 2 H, *J* = 6.7 Hz), 3.45 (t, NCH_2-propylene chain, 2 H, *J* = 6.3 Hz), 3.50 (t, CH_2-uracil-propylene chain, 2H, *J* = 6.7 Hz), 4.43 (s, Ar-CH_2, 2 H), 4.48 (s, Ar-CH_2, 2 H), 5.57 (d, uracil-5, 1 H, $J_{5\text{-}6}$ = 7.9 Hz), 7.02-7.06 (m, Ar, uracil-6, 5 H), 6.91 (d, uracil-6, 1H), 7.18 (d, Ts, 4H, *J* = 8.1 Hz), 7.21 (d, Ts, 4H, *J* = 8.1 Hz), 7.35-7.38 (m, Ts, 4 H) 7.47 (m, Phen-9, 2H), 7.64-7.76 (m, Phen-2, Phen-3, Phen-7, 6 H), 8.15 (br s, Phen-4, 2 H), 8.46 (d, Phen-1, 2 H, $J_{1\text{-}2}$ = 8.1 Hz), 8.50-8.54 (m, Phen-10, 2 H), 9.24 (s, U-NH, 1 H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 10.81 (CH_3), 21.18 (CH_2-propyl chain), 21.50 ($TsCH_3$), 21.52 ($TsCH_3$), 27.07 (CH_2-uracil-propylene chain), 45.95 (CH_2-uracil). 47.61 (NCH_2-propylene chain), 52.07 (NCH_2-propyl chain), 61.47 (Ar-CH_2), 69.11(Ar-CH_2), 102.01 (uracil-5), 114.59, 121.11, 122.02, 122.06, 123.16, 123.26, 123.49, 123.82, 125.32, 125.35, 126.62, 126.72, 127.17, 127.67, 127.72, 127.78, 127.83, 128.72, 128.83, 129.22, 129.31, 129.40, 129.45, 129.50, 129.59, 129.68, 132.77, 134.1, 135.01, 143.61, 144.13, 144.75, 150.48, 159.45, 159.6, 163.45 ppm; IR (KBr) ν: 3448, 2924, 2853, 2363, 2345, 1718, 1686, 1655, 1560, 1541, 1508, 1458, 1163, 1090, 812, 766, 669, 550, 471, 459 cm^{-1}; (MALDI / TOF-HRMS) m/z: 993.3466 (cald. for $C_{58}H_{52}N_6O_6S_2$: 993.3463).

2,6-Ditosyl-2,6-diaza-1,7(8,6)-diphenanthridinacyclotridecaphane (5)

1,3-dibromopropane (20 µl, 0.193 mmol, 1.5 equivalents) and K_2CO_3 (53 mg, 0.386 mmol, 3 equivalents) were suspended in dry DMF (20ml). To this suspension, solution 1,6-bis-(8-tosylaminophenantridine-6-il)-hexane1 (100 mg; 0.128 mmol 1 equivalent) in dry DMF (5 ml) was added dropwise during 10 min. and the reaction mixture was stirred during 5 days under argon atmosphere at room temperature. Water and CH_2Cl_2 were added to this suspension, the water layer was washed twice with CH_2Cl_2, organic extracts were dried over Na_2SO_4 and evaporated, yielding light brown solid. Solid residue was purified was by TLC (SiO_2, 10% MeOH in CH_2Cl_2, R_f = 0.35) to give white solid **5**, additionally recrystallized from MeOH (27 mg, 26 %

yield); mp 223-225 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.44 (br s, CH_2-propyl chain, 4 H), 1.57 (br s, CH_2-hexylene-chain, 4 H), 1.87 (t, CH_2-propyl chain, 2 H, J = 6.9 Hz), 2.25 (s, Ts-CH_3, 6 H), 3.12 (t, CH_2-hexylene-chain, 4 H, J = 7.6 Hz), 3.65 (t, NCH_2, 4 H), 6.92 (d, Ts, 4H, J = 8.0 Hz), 7.17 (d, Ts, 4H), 7.55 (dd, Phen-9, 2 H, $J_{7\text{-}9}$ = 2.0 Hz, $J_{9\text{-}10}$ = 8.8 Hz), 7.60-7.66 (m, Phen-2, Phen-7, 4 H), 7.75 (dt, Phen-3, 2 H, $J_{3\text{-}4}$ = 7.8 Hz, $J_{1\text{-}3}$ = 1.3 Hz), 8.12 (d, Phen-4, 2 H,), 8.46 (dd, Phen-1, 2 H, $J_{1\text{-}2}$ = 8.2 Hz), 8.58 (d, Phen-10, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ: 21.44 (Ts-CH_3), 28.68 (CH_2-propyl chain), 28.94 (CH_2-hexylene-chain), 29.35 (CH_2-hexylene-chain), 36.41 (CH_2-hexylene-chain), 48.45 (NCH_2), 122.05, 122.96, 123.88, 125.22, 125.71, 126.96, 127.57, 129.35, 129.45, 130.79, 132.43, 134.15, 138.08, 143.92, 162.04 ppm; IR (KBr) ν: 3454, 2928, 2858, 2361, 2343, 1653, 1541, 1508, 1458, 1356, 1167, 1149, 1090, 1067, 943, 810, 762, 710, 662, 592, 546, 419, 407, 397, 351 cm^{-1}; (MALDI / TOF-HRMS) m/z: 819.3003 (cald. for $C_{49}H_{46}N_4O_4S_2$: 819.3033).

2,10-Ditosyl-2,10-diaza-6(3,1)-uracil-1,11(8,6)-diphenanthridinacycloheptadecaphane (6)

1,3-bis-(3-bromopropyl)-uracil[4] (136 mg, 0.386 mmol, 1.5 equivalents) and K_2CO_3 (178 mg, 1.28 mmol, 5 equivalents) were suspended in dry DMF (80ml). To this suspension, solution 1,6-bis-(8-tosylaminophenantridine-6-il)-hexane[1] (200 mg; 0.257 mmol 1 equivalent) in dry DMF (70 ml) was added dropwise during 10 min. The reaction mixture was stirred during 2 days under argon atmosphere at room temperature, and next 2 days at 80-100 °C. Water and CH_2Cl_2 were added to this suspension, the water layer was washed twice with CH_2Cl_2, organic extracts were dried over Na_2SO_4 and evaporated, yielding light brown oily residue. Residue was purified by TLC (SiO_2, 5% MeOH in CH_2Cl_2, R_f = 0.35). Obtained light oil was trituated with water to give precipitate that was filtered, washed with water and dried. Pure compound **6** was obtained as white solid (130 mg, 52 % yield), that was additionally recrystallized from MeOH (27 mg, 26 %); mp 142-145 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.53 (br s, CH_2-hexylene-chain, 4 H), 1.81 (br s, CH_2-hexylene-chain, 2 H), 1.90 (m, CH_2-hexylene-chain, CH_2-propylene chain (b), 4 H), 2.00 (t, CH_2-propylene chain (a), 2 H), 2.35 (s, Ts-CH_3, 3 H), 2.39 (s, Ts-CH_3, 3 H), 3.25 (br s, CH_2-hexylene-chain (a), 2 H), 3.38 (br s, CH_2-hexylene-chain (b), 2 H), 3.68 (t,

NCH_2-propylene chain (b), 2 H, J = 6.3 Hz), 3.76 (t, NCH_2-propylene chain (a), 2 H, J = 6.0 Hz), 3.91 (t, CH_2-uracil-propylene chain (a), 2H, J = 6.1 Hz), 4.04 (t, CH_2-uracil-propylene chain (b), 2H, J = 6.7 Hz), 5.77 (d, uracil-5, 1 H, $J_{5\text{-}6}$ = 7.8 Hz), 7.15 (d, Ts, 2H, J = 7.9 Hz), 7.20 (d, Ts, 4H, J = 7.9 Hz), 7.30-7.36 (m, Ts, Phen-9, uracil-6, 7 H), 7.61 (m, Phen-2, 2 H), 7.72 (m, Phen-3, 2 H), 7.83 (s, Phen-7 (a), 1 H), 8.12 (br s, Phen-4, 2 H), 8.28 (s, Phen-7 (b), 1 H), 8.42-8.47 (m, Phen-1, Phen-10, 3 H), 8.54 (d, Phen-1, 1 H, $J_{1\text{-}2}$ = 8.8 Hz) ppm; ^{13}C-NMR ($CDCl_3$) δ: 21.51 ($TsCH_3$), 25.34 (CH_2-propylene chain b), 27.03 (CH_2-propylene chain a), 29.44 (CH_2-hexylene-chain), 29.51 (CH_2-hexylene-chain), 29.74 (CH_2-hexylene-chain), 29.9 (CH_2-hexylene-chain), 38.49 (CH_2-hexylene-chain), 46.51 (CH_2-uracil-propylene chain b). 47.01 (NCH_2-propylene chain a), 47.29 (CH_2-uracil-propylene chain a). 47.34 (NCH_2-propylene chain b), 101.59 (uracil-5), 121.99, 122.99, 123.09, 123.33, 123.67 (Phen-1), 125.16, 125.45 (Phen-7 a), 126.64 (Phen-7 b), 127.56, 127.67, 127.74, 129.11, 129.5, 129.57, 132.29, 133.94, 134.64, 137.24, 142.67, 143.67, 144.03, 151.58, 162.1, 163.29 ppm; (MALDI / TOF-HRMS) m/z: 971.3629 (cald. for $C_{56}H_{54}N_6O_6S_2$: 971.3619).

1-{[8-(3-(urac-1-il)propyl)aminophenanhtridine-6-il]-methyl}-4-{[8-(propyltosyl)aminophenanthridine-6-il]-methyl}benzene (7)

Compound **7** was obtained by heating solution of 1-{[8-(3-(urac-1-il)propyltosyl)aminophenanhtridine-6-il]-methyl}-4-{[8-(propyltosyl)aminophenanthridine-6-il]-methyl}benzene **4** (20 mg, 0.02 mmol) in mixture of 1 ml conc. H_2SO_4 and 2 ml conc. acetic acid under reflux at 80-100 °C for 2 h. Reaction mixture was cooled, poured on ice and made alkaline (pH = 8-9) by addition of 2 M NaOH. The obtained yellow-brown solid was precipitated, filtered and washed with lots of water to afford pure compound **7** (8 mg, 57 % yield); mp 140-143 ºC; R_f (SiO_2, 10% MeOH in CH_2Cl_2) = 0.48; ^{1}H-NMR (DMSO-d_6) δ: 0.79 (t, CH_3, 3H, J = 7.4 Hz), 1,41 (m, CH_2-propyl chain, 2 H), 1.80 (t, CH_2-propylene chain, 2 H, J = 6.5 Hz), 2.92 (m, NCH_2-propyl chain, 2 H), 3.01 (m, NCH_2-propylene chain, 2 H), 3.68 (t, CH_2-uracil-propylene chain, 2H, J = 6.7 Hz), 4,48 (s, Ar-CH_2, 2 H), 4.48 (s, Ar-CH_2, 2 H), 5.55 (d, uracil-5, 1 H, $J_{5\text{-}6}$ = 7.7 Hz), 6.20 (br s, NH, 2H), 7.00 (d, Phen-7, 1 H, $J_{7\text{-}9}$ = 2.1 Hz), 7.05 (d, Phen-7, 1 H, $J_{7\text{-}9}$ = 1.6 Hz), 7.17-7.22 (m, Ar,

Phen-9, 6 H), 7.51-7.56 (m, Phen-2, Phen-3, uracil-6, 5 H), 7.92 (m, Phen-4, 2 H), 8.43-8.49 (m, Phen-1, Phen-10, 4 H), 11.27 (s, uracil-NH, 1 H) ppm; ^{13}C-NMR (DMSO-d_6) δ: 11.68 (CH_3), 21.57 (CH_2-propyl chain), 27.79 (CH_2-uracil-propylene chain), 41.93, 42.07, 44.61, 45.99, 101.15, 103.62, 103.93, 120.17, 121.41, 121.47. 123.07, 123.43, 123.69, 123.79, 124.40, 124.47, 126.42, 126.54, 126.71, 128.77, 128.84, 129.23, 137.31, 137.37, 141.46, 141.56, 145.80, 145.86, 148.2, 148.47, 151.22, 159.25, 164.09, 172.44 ppm; IR (KBr) ν: 3414, 2957, 2926, 2853, 2365, 2345, 1684, 1655, 1618, 1558, 1541, 1508, 1458, 1420, 1387, 1340, 1259, 1232, 1144, 1024, 824, 760, 719, 669, 621, 569, 548 cm^{-1}; (MALDI / TOF-HRMS) m/z: 685.3314 (cald. for $C_{44}H_{40}N_6O_2$: 685.3286).

2,6-Diaza-1,7(8,6)-diphenanthridinacyclotridecaphane (8)

Compound **(8)** was obtained as described for **7**; 2,6-ditosyl-2,6-diaza-1,7(8,6)-diphenanthridinacyclotridecaphane **5** (30 mg, 0.037 mmol) in 1 ml conc. H_2SO_4 and 2 ml conc. acetic acid gave yellow powder gave yellow powder **8** (15 mg, 78 % yield); mp 165-170 ºC; R_f (SiO_2, 10% MeOH in CH_2Cl_2) = 0.52; ^{1}H-NMR (DMSO-d_6) δ: 1.56 (br s, CH_2-hexylene-chain, 4 H), 1.84 (br s, CH_2-hexylene-chain, 4 H), 2.01 (t, CH_2-propyl chain, 2 H, J = 6.49 Hz), 3.15 (br s, CH_2-hexylene-chain, 4 H), 3.42 (ps q, NCH_2, 4 H, J = 6.1 Hz), 6.24 (br s, NH, 2H), 7.26 (d, Phen-7, 2H, $J_{7\text{-}9}$ = 2.1 Hz), 7.55 (dd, Phen-9, 2 H, $J_{9\text{-}10}$ = 8.9 Hz), 7.50 (m, Phen-2, Phen-3, 4 H), 7.86 (m, Phen-4, 2 H), 8.44 (m, Phen-1, 2 H), 8.46 (d, Phen-10, 2 H) ppm; ^{13}C NMR (DMSO-d_6) δ: 20.53 (CH_2-propyl chain), 28.81 (CH_2-hexylene-chain), 29.07 (CH_2-hexylene-chain), 35.11 (CH_2-hexylene-chain), 40.31 (NCH_2), 103.01 (Phen-7), 119.86 (Phen-9), 121.13 (Phen-1), 122.62, 123.58 (Phen-10), 123.93, 126.01 (Phen 2 ili Phen 3), 126.05 (Phen 2 ili Phen 3), 126.64, 128.78 (Phen-4),141.42, 148.43, 161.11 ppm; IR (KBr) ν: 3462, 2928, 2856, 2361, 2343, 1653, 1624, 1541, 1508, 1458, 1385, 1265, 1205, 1128, 824, 760, 716, 679, 669, 654, 617, 592, 548, 517, 501, 473, 457 cm^{-1}; (MALDI / TOF-HRMS) m/z: 511.2874 (cald. for $C_{35}H_{34}N_4$: 511.2856).

Compound **(8)** was obtained as described for **7**; 2,6-ditosyl-2,6-diaza-1,7(8,6)-diphenanthridinacyclotridecaphane **5** (30 mg, 0.037 mmol) in 1 ml conc. H_2SO_4 and 2 ml conc. acetic acid gave yellow powder gave yellow powder **8** (15 mg, 78 % yield); mp 165-170 ºC; R_f (SiO_2, 10% MeOH in CH_2Cl_2) = 0.52; ^{1}H-NMR (DMSO-d_6) δ:

1.56 (br s, CH_2-hexylene-chain, 4 H), 1.84 (br s, CH_2-hexylene-chain, 4 H), 2.01 (t, CH_2-propyl chain, 2 H, J = 6.49 Hz), 3.15 (br s, CH_2-hexylene-chain, 4 H), 3.42 (ps q, NCH_2, 4 H, J = 6.1 Hz), 6.24 (br s, NH, 2H), 7.26 (d, Phen-7, 2H, $J_{7\text{-}9}$ = 2.1 Hz), 7.55 (dd, Phen-9, 2 H, $J_{9\text{-}10}$ = 8.9 Hz), 7.50 (m, Phen-2, Phen-3, 4 H), 7.86 (m, Phen-4, 2 H), 8.44 (m, Phen-1, 2 H), 8.46 (d, Phen-10, 2 H) ppm; ^{13}C NMR (DMSO-d_6) δ: 20.53 (CH_2-propyl chain), 28.81 (CH_2-hexylene-chain), 29.07 (CH_2-hexylene-chain), 35.11 (CH_2-hexylene-chain), 40.31 (NCH_2), 103.01 (Phen-7), 119.86 (Phen-9), 121.13 (Phen-1), 122.62, 123.58 (Phen-10), 123.93, 126.01 (Phen 2 ili Phen 3), 126.05 (Phen 2 ili Phen 3), 126.64, 128.78 (Phen-4),141.42, 148.43, 161.11 ppm; IR (KBr) ν: 3462, 2928, 2856, 2361, 2343, 1653, 1624, 1541, 1508, 1458, 1385, 1265, 1205, 1128, 824, 760, 716, 679, 669, 654, 617, 592, 548, 517, 501, 473, 457 cm^{-1}; (MALDI / TOF-HRMS) m/z: 511.2874 (cald. for $C_{35}H_{34}N_4$: 511.2856).

2,10-Diaza-6(3,1)-uracil-1,11(8,6)-diphenanthridinacycloheptadecaphane (9)

Compound **(9)** was obtained as described for **7**; 2,10-ditosyl-2,10-diaza-6(3,1)-uracil-1,11(8,6)-diphenanthridinacycloheptadecaphane **6** (50 mg, 0. 051 mmol) in 1 ml conc. H_2SO_4 and 2 ml conc. acetic acid gave yellow powder gave yellow powder **9** (20 mg, 56 % yield); mp 143-146 ºC; R_f (SiO_2, 10% MeOH in CH_2Cl_2) = 0.41; ^{1}H-NMR (DMSO-d_6) δ: 1.55 (br s, CH_2-hexylene-chain, 2 H), 1.65 (br s, CH_2-hexylene-chain, 2H) 1.82 (m, CH_2-propylene chain, 2 H), 1.88 (m, CH_2-hexylene-chain, 4 H), 1.99 (m, CH_2-propylene chain, 2 H), 3.16-3.23 (m, CH_2-hexylene-chain, NCH_2-propylene chain, 8 H), 3.91 (t, CH_2-uracil-propylene chain, 2H, J = 6.5 Hz), 3.96 (t, CH_2-uracil-propylene chain, 2H, J = 6.6 Hz), 5.71 (d, uracil-5, 1 H, $J_{5\text{-}6}$ = 7.9 Hz), 6.39 (t, NH, 1 H, J = 5.6 Hz), 6.43 (t, NH, 1 H, J = 5.5 Hz), 7.02 (dd, Phen-9, 1 H, $J_{7\text{-}9}$ = 1.6 Hz), 7.20-7.25 (m, Phen-7, Phen-9, 3 H), 7.31 (d, Phen-7, 1 H, $J_{7\text{-}9}$ = 2.0 Hz), 7.50-7.54 (m, Phen-2, Phen-3, 4 H), 7.74 (d, uracil-6, 1 H), 7.88 (m, Phen-4, 2 H), 8.48-8.51 (m, Phen-1, Phen-10, 4 H) ppm; ^{13}C-NMR (DMSO-d_6) δ: 26.65, 27.69, 28.82, 28.95, 29.17, 34.84, 35.27, 40.26, 40.55, 100.36, 101.63, 103.06, 121.36, 122.86, 122.97, 123.03, 123.73, 123.77, 124.06, 124.09, 126.37, 126.42, 126.57, 126.79, 128.34, 144.09, 148.01, 148.22, 148.64, 151.53, 160.78, 160.86, 161.30, 162.44 ppm; IR (KBr) ν: 3337, 3057, 2926, 2853, 2361, 2343, 1701, 1653, 1618, 1570, 1541, 1508, 1458, 1394, 1339, 1317, 1259, 1232, 1203, 1094, 1032, 824, 760, 723, 673, 565, 419,

397 cm^{-1}; (MALDI / TOF-HRMS) m/z: 663.3442 (cald. for $C_{42}H_{42}N_6O_2$: 663.3414).

Molecular modeling of compounds 7, 8 and 9

Each of the selected conjugates was placed in the center of the octahedral box filled with TIP3P type water molecules, a water buffer of 7Å was used and Cl^- ions were added to neutralize the systems. Geometry optimization and molecular dynamics (MD) simulations were accomplished using the AMBER10 program package[7]. The solvated molecules were geometry optimized using steepest descent and conjugate gradient methods, 2500 steps of each. During 300 ps of equilibration, the temperature was linearly incerasing from from 0 K to 300 K, and the volume kept constant. The equilibrated systems were subjected to 30 ns of the productive unconstrained molecular dynamics (MD) simulation at constant temperature and pressure (300 K, 1 atm). The time step during the simulation was 1 fs and the temperature was kept constant using Langevin dynamics with a collision frequency of 1 ps^{-1}. The simulations were accomplished using using Periodic Boundary Conditions (PBC). The Particle Mesh Ewald (PME) method was used for calculation of electrostatic interactions. In the direct space the pairwise interactions were calculated within the cutoff-distance of 11 Å.

All studied molecules were prepared in maximally folded shape with rings stacked conformations. During the MD simulations molecules retained their more or less stacking conformation with no water molecules accommodated within the two phenanthridinium units. The stacking interactions were most efficient between two phenanthridinium subunits. Compound **7** was stabilized by two intramolecular stacking interactions – face to face between uracil and phenanthridinium ring and face to edge between uracil and benzene ring. Molecules **8** and **9** were stabilized with intramolecular stacking interaction between two phenanthridinium rings. Compound **9** was additionally stabilized with one intramolecular H bond between uracil and neighbouring phenanthridinium ring. Obtained molecules are in accordance with the spectroscopic results.

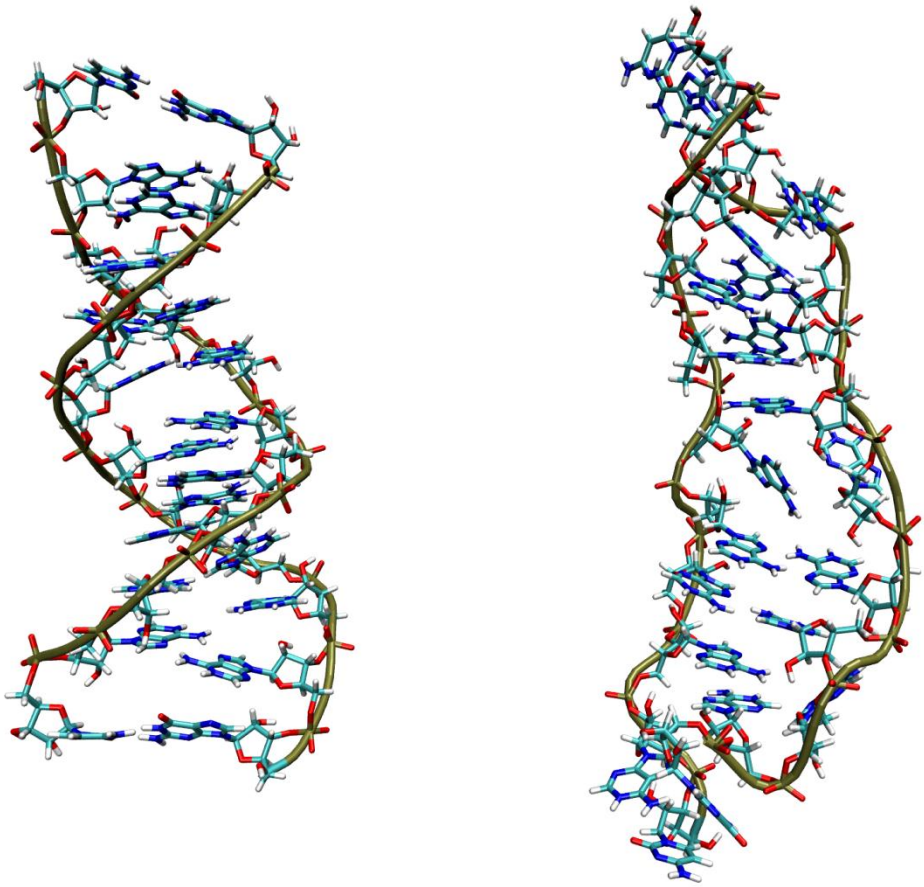


Figure S1: The model of poly rAH^+- poly rAH^+ double helix. Left – initial optimized structure; right – final optimized structure (after 24 ns of MD simulations).

Table S1. MM_PBSA calculated free energies for rAH^+ - rAH^+ in the complexes with **7** and **11**.

	*rAH^+ - rAH^+ from the complex with **7***		*rAH^+ - rAH^+ from the complex with ***11***	
Energy (kcal/mol)	MEAN	STD	MEAN	STD
ELE	-3599.74	28.92	-3183.85	32.70
VDW	-178.64	8.79	140.29	12.47
PBSUR	32.28	0.39	37.00	0.64

PBSOL	-1087.43	24.94	-1536.42	31.38
PBTOT	-3536.21	20.58	-3493.42	22.79

Table S2. Partial atomic charges for rAH^+ obtained by fitting to the electrostatic potential at the 6-31G(d) level of theory[8] of the rAH^+.

Charges from ESP fit	
P	1.152084
O1P	-0.542651
O2P	-0.553623
O5'	-0.359532
C5'	-0.132427
C4'	0.103212
O4'	-0.476126
C1	0.366287
N9	-0.399005
C8	0.403972
N7	-0.639266
C5	0.018186
C6	0.706746
N6	-0.958799
N1	-0.650846
C2	0.459180
N3	-0.628821
C4	0.582660
C3'	0.514659
C2'	0.264171
O3'	-0.903473
O2'	-0.704572
H51	0.231265
H52	0.074374
H4'	0.079978
H1'	0.126577
H8	0.170362
H61	0.448392
H62	0.485280
H1	0.447479
H2	0.132692
H3'	-0.159075
H21	-0.064228
H22	0.404887

Content of the rAH^+ parameter file used for the simulations of poly rAH^+-poly rAH^+.

```
MASS
OX         16.00     0.465   based on OS ether and ester oxygen
HX         1.008     0.135   based on HO hydroxyl group

BOND
CT-OX      320.0     1.410   based on CT-OS JCC,7,(1986),230; NUCLEIC ACIDS
HX-OH      553.0     0.960   based on HO-OH JCC,7,(1986),230; SUGARS,SER,TYR
CQ-NA      502.0     1.324   based on CQ-NC JCC,7,(1986),230; ADE
NC-H5      394.1     1.018
CT-HO      340.0     1.090
OH-H1      553.0     0.960

ANGLE
H1-CT-OX     50.0     109.50   based on  H1-CT-OS changed based on NMA nmodes
CT-CT-OX     50.0     109.50   based on  CT-CT-OS
CB-CA-NA     70.0     117.30   based on  CB-CA-NC
NC-CQ-NA     70.0     129.10   based on  NC-CQ-NC
H5-CQ-NA     50.0     115.45   based on  H5-CQ-NC
CA-NA-CQ     70.0     118.60   based on  CA-NC-CQ
CQ-NA-H      50.0     118.00   based on  CA-NA-H changed based on NMA nmodes
CA-NC-H5     50.0     118.00
CQ-NC-H5     50.0     118.00
OH-CT-HO     50.0     109.50   changed based on H1-CT-OH
CT-OH-H1     55.0     108.50   changed based on CT-OH-HO
CT-CT-HO     50.0     109.50   changed based on NMA nmodes
CT-CT-H0     50.0     109.50   changed based on NMA nmodes
O2-P-OS      45.0     102.60   changed based on OH-P-OS
O2-P-O2      45.0     102.60   changed based on OS-P-OS

DIHEDRAL
OX-CT-CT-OS    1   0.144    0.0    -3.   based on OS-CT-CT-OS parm98, TC,PC,PAK
OX-CT-CT-OS    1   1.175    0.0     2.   based on OS-CT-CT-OS Piotr et al.
H1-CT-CT-OX    1    0.25    0.0     1.   based on H1-CT-CT-OS Junmei et al, 1999
OX-CT-CT-OH    1   0.144    0.0    -3.   based on OS-CT-CT-OH parm98, TC,PC,PAK
OX-CT-CT-OH    1   1.175    0.0     2.   based on OS-CT-CT-OH parm98, TC,PC,PAK
X -NA-CQ- X    4    9.60   80.0     2.

NONBON
OX         1.6837          0.1700     based on OS OPLS ether
```

HX	0.6000	0.0157	based on HS W. Cornell CH3SH --> CH3OH FEP

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