Supporting Informations

for

Mesityl Phenanthroline-Modified 2'-Deoxyuridine for Heteroleptic Complexes in Metal Ion-Mediated Assembly of DNA

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1. Materials and methods

Commercial available chemicals and dry solvents were used without further purification unless otherwise mentioned. TLC was performed on Fluka silica gel F254 coated aluminium foil. Flash chromatography was carried out using Silica Gel 60 from Merck (43 – 60 μm). Reagents and controlled pore glass (CPG) (1 μmol) for DNA synthesis were purchased from ABI and Glen Research. DNA counter strands were ordered at metabion. Spectroscopic measurements were recorded in Na-P*i* buffer solution (10 mM, pH = 7,2) using quartz glass cuvettes (10 mm). Absorption spectra were recorded on a Varian Cary 100 spectrometer equipped with a 6x6 cell changer unit. Fluorescence was measured on a Jobin–Yvon Fluoromax 3 fluorimeter with a step width of 1 nm and an integration time of 0.2 s. All spectra were recorded at 20 °C with an excitation and emission band pass of 3 nm and were corrected for Raman emission from the buffer solution. Gel electrophoresis experiments were carried out on a Bio-Rad Mini-PROTEAN Tetra Cell with a vertical 8 x 10 cm unit on 25% polyacrylamide/8.3M urea gel. Tris-boric acid buffer without EDTA (pH = 8.6) was used.

2. Synthesis of the phenanthroline building block

2,9-bis-mesityl-3-ethynyl-phenanthroline (**1**) and DMT-protected 5-Iodo-deoxyuridine was synthesized according to literature.[1,2]

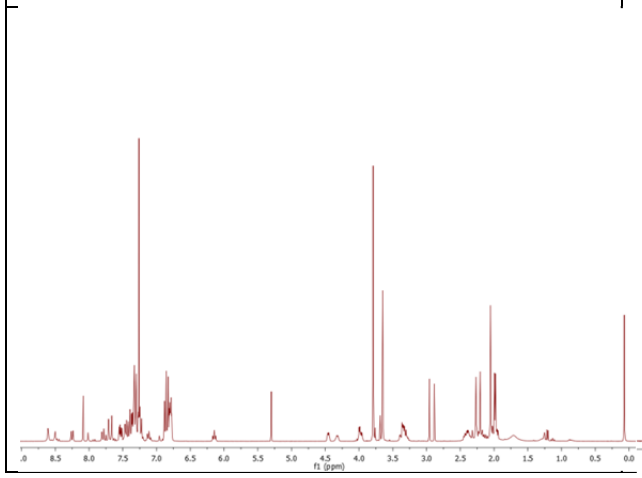
5-[(2,9-dimesityl-1,10-phenanthrolin-3-yl)ethynyl]-5'-O-[(bis-(4-methoxyphenyl)(phenyl)methoxy]-2'-deoxyuridine (2)

1 (92.0 mg, 209 μmol), DMT protected I-dU (151 mg, 230 μmol) was dissolved in 10 mL dry DMF under Argon-Atmosphere. Afterwards, $Pd(PPh_3)_4$ (48.3 mg, 42 μmol), CuI (7.95 mg, 42 μmol) and dry Et_3N (289 μL) were added. The reaction mixture was stirred at 60 °C overnight. The solvent was evaporated and the crude product was first purified by flash chromatography (CH_2Cl_2:MeOH 100:1 + 0.1 % Et_3N – 50:1 + 0.1 % Et_3N). Finally **2** was isolated after flash chromatography on reversed phase (MeOH:H_2O 9:1 – MeOH) as a light ocher solid (121 mg, 0,124, yield: 60 %).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.49 (d, *J* = 8.9 Hz, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 8.09 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.48 - 7.33 (m, 9H), 6.88 (s, 2H), 6.86 (s, 2H), 6.79 (m, 4H), 6.14 (t, *J* = 6.5 Hz, 1H), 4.46 (m, 1H), 4.32 (m, 1H), 3.98 (m, 2H), 3.65 (s, 6H), 3.37 – 3.33 (m, 2H), 2.43 (m, 1H), 2.27 (s, 3H), 2.21 (s, 3H), 2.05 (s, 6H), 1.99 (s, 3H), 1.98 (s, 3H)
^{13}C-NMR (126 MHz, DMSO) δ 160.77, 160.52, 159.97, 159.55, 158.08, 150.03, 144.98, 144.76, 144.26, 139.21, 137.77, 136.87, 136.68, 136.59, 136.53, 135.46, 135.38, 135.13, 129.72, 128.33, 128.16, 127.96, 127.91, 127.63, 127.36, 127.16, 126.72, 126.28, 125.67, 118.76, 113.29, 98.27, 89.10, 87.08, 85.82, 85.80, 84.87, 70.50, 69.88, 63.73, 55.07, 45.76, 20.81, 20.76, 20.01, 19.58, 19.48.
NMR EI-MS m/z (calcd.) = 968.41[M-H$^+$]; m/z (found) = 968.4 [M-H$^+$]

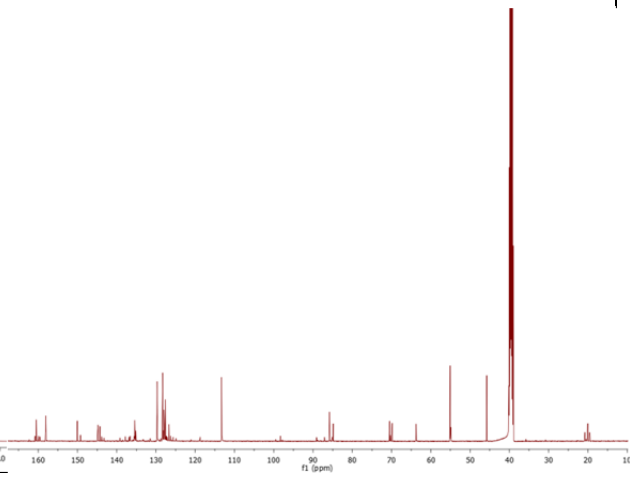
5-[(2,9-dimesityl-1,10-phenanthrolin-3-yl)ethynyl]-3'-O-[(2-cyanoethoxy)(diisopropylamino)phosphinyl]-5'-O-[(bis-(4-methoxyphenyl)(phenyl)methoxy]-2'-deoxyuridine (3)

2 (60 mg, 0.062 mmol) was dissolved in 1.5 mL dry CH_2Cl_2 under Argon-Atmosphere. Dry N,N-diisopropylethylamine (52.6 μL, 0.310 mmol) and 2-cyanoethyl N,N-diisopropylchlorophosphoramidite (55.2 μL, 0.248 mmol) were added and the mixture was stirred at room temperature for 4 h. After purification by flash chromatography (CH_2Cl_2:Acetone 4:1) **4** was isolate as a colorless solid (43.5 mg, 0.037 mmol, yield: 60%).
^{31}P NMR (101 MHz, d6-DMSO) δ 149.62.

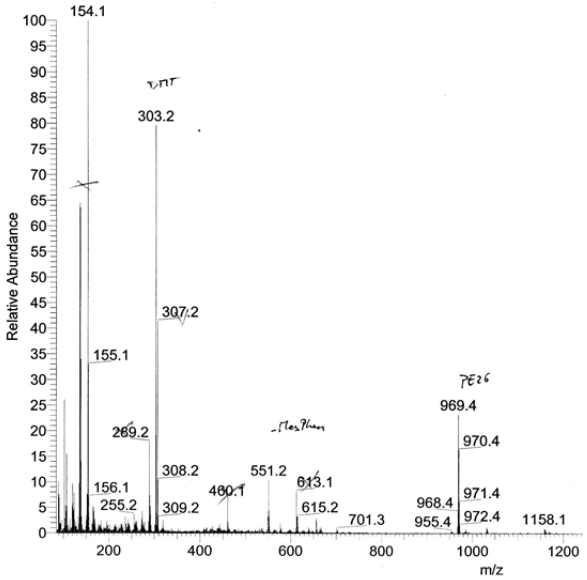
^{1}H NMR of **2**



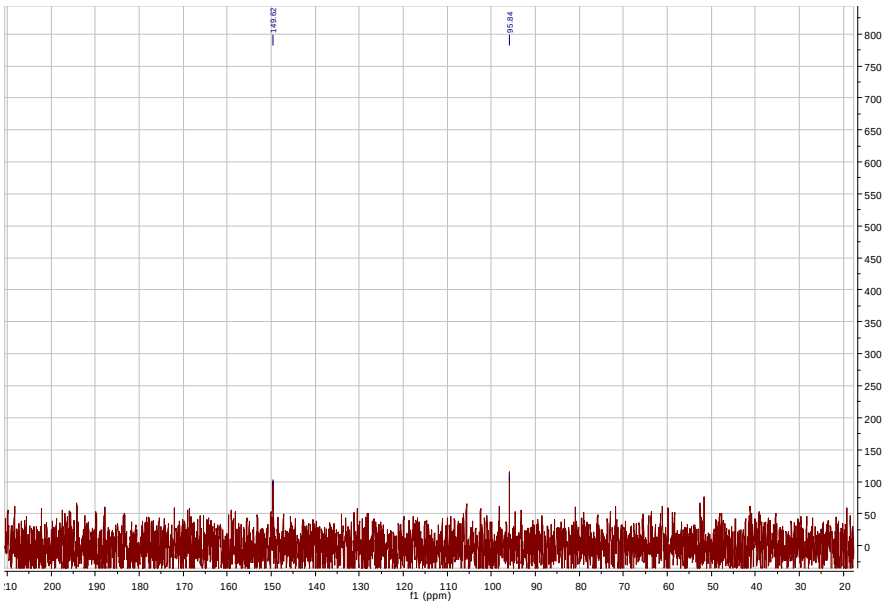
^{13}C NMR of **2**



EI-MS of **2**



^{31}P NMR of **3**



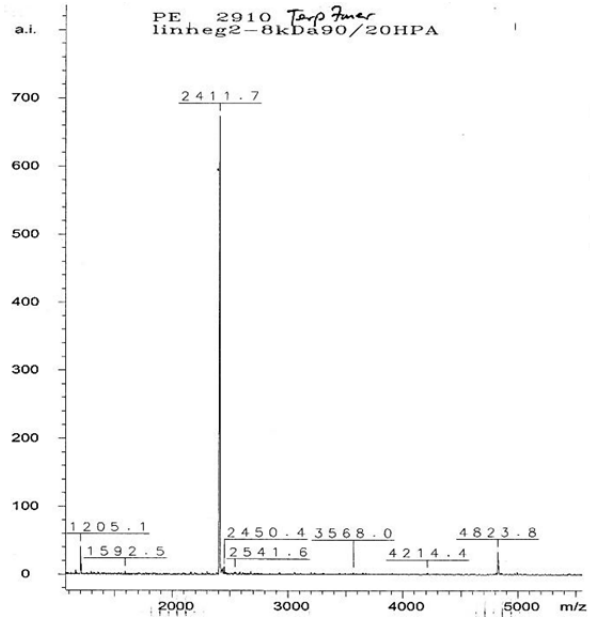
3. Synthesis and characterization of DNA1-2

The Oligonucleotides were synthesized on an Expedite 8909 synthesizer from Applied Biosystems (ABI) using standard phosphoramidite chemistry. Synthesis was performed using longer coupling time of 900 s and a higher concentration of the phosphoramidites (0.1 M in MeCN) for modified building blocks. After preparation, the oligonucleotides were cleaved off the resin and deprotected by treatment with conc. NH_4OH at 50°C for 10 h. The oligonucleotides were purified by reverse phase HPLC using the following conditions: A = NH_4OAc buffer (50 mM, pH = 6.5); B = acetonitrile; gradient 0 – 20 % B over 40 min for **DNA1** and 0 – 50% over 40 min for **DNA2**, flow rate 2.5 mL/min, UV/vis detection at 260 nm, 325 nm (**DNA1**) or 334 nm (**DNA2**). Finally the oligonucleotides were lyophilized and quantified by their absorbance in 10 mM sodium phosphate buffer at 260 nm on a Varian Cary 100 spectrometer.

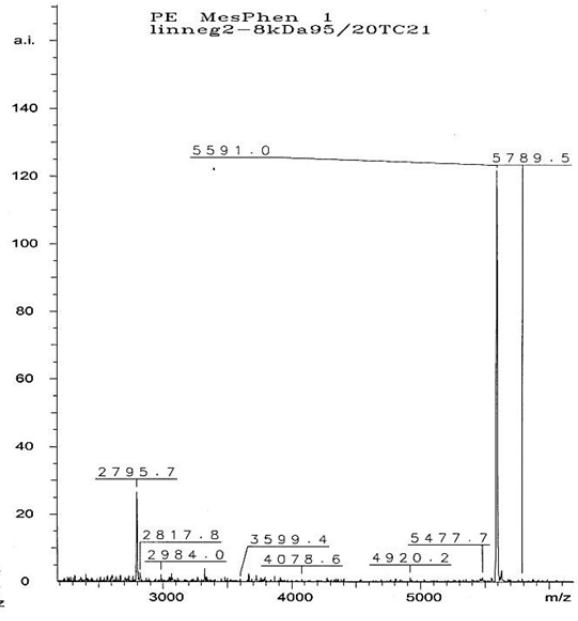
Table S1: MALDI MS data and extinction coefficients of modified DNA.

Sample	calculated [g/mol]	found [g/mol]	ε_{260} [L*mmol^{-1}*cm^{-1}]
DNA1	2409.8	2411.7	89.1
DNA2	5588.6	5591.0	177.4

MALDI MS of **DNA1**



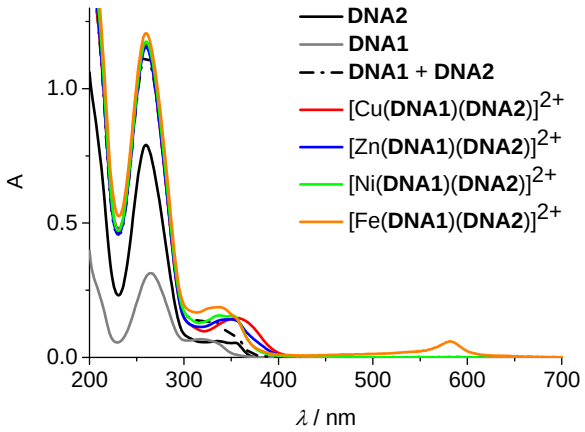
DNA2



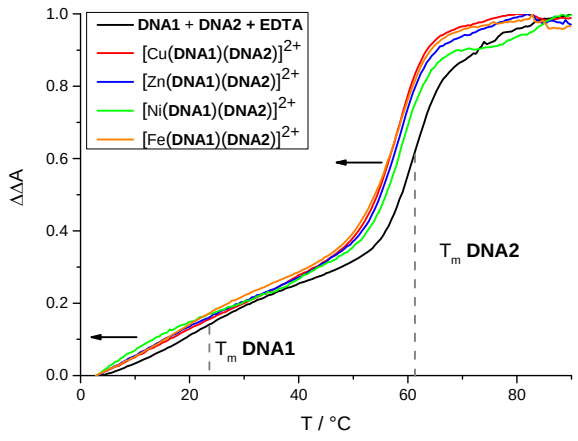
4. Preparation of heteroleptic complexes for

To remove any divalent metal **DNA1** and **DNA2** were treated for 1 h with chelex-100. The oligonucleotides were incubated with 1 eq of their counter strands in 10 mM NaPi-buffer (pH = 7.2) for 10 min at 90 °C. 1.1 eq. $M(II)SO_4$ (M = Cu, Zn, Fe, Ni) were added to **DNA2.** Afterwards 1 eq. **DNA1** were added and incubated for 30 min at room temperature.

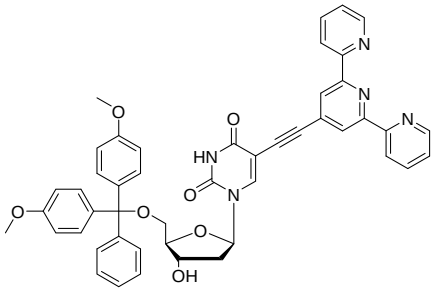
5. Full range UV/vis spectra



6. Melting temperature curves

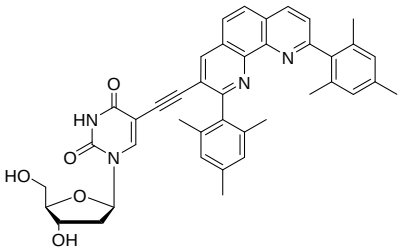


7. MALDI mass spectra of heteroleptic nucleoside complexes



4

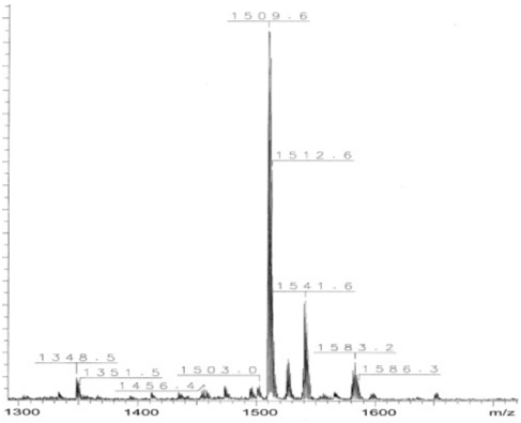
785,28 g/mol



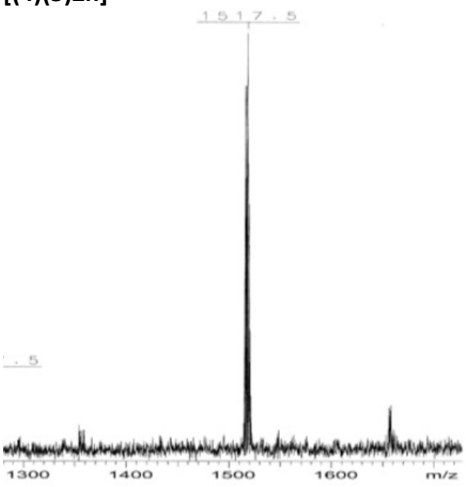
5

666,28 g/mol

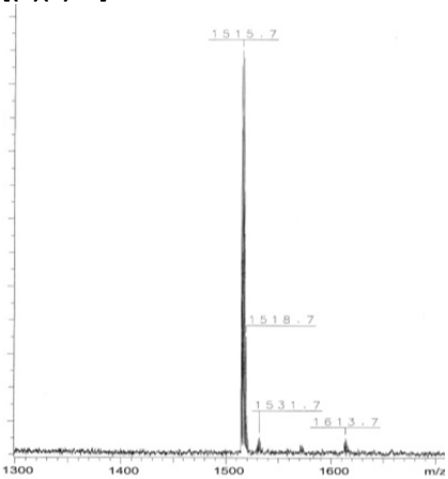
[(4)(5)Ni]$^+$



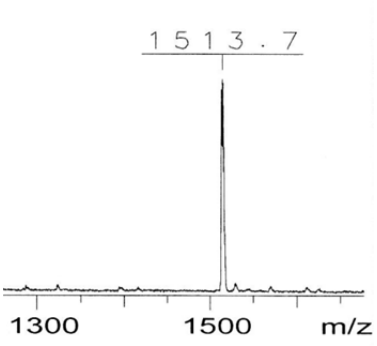
[(4)(5)Zn]$^+$



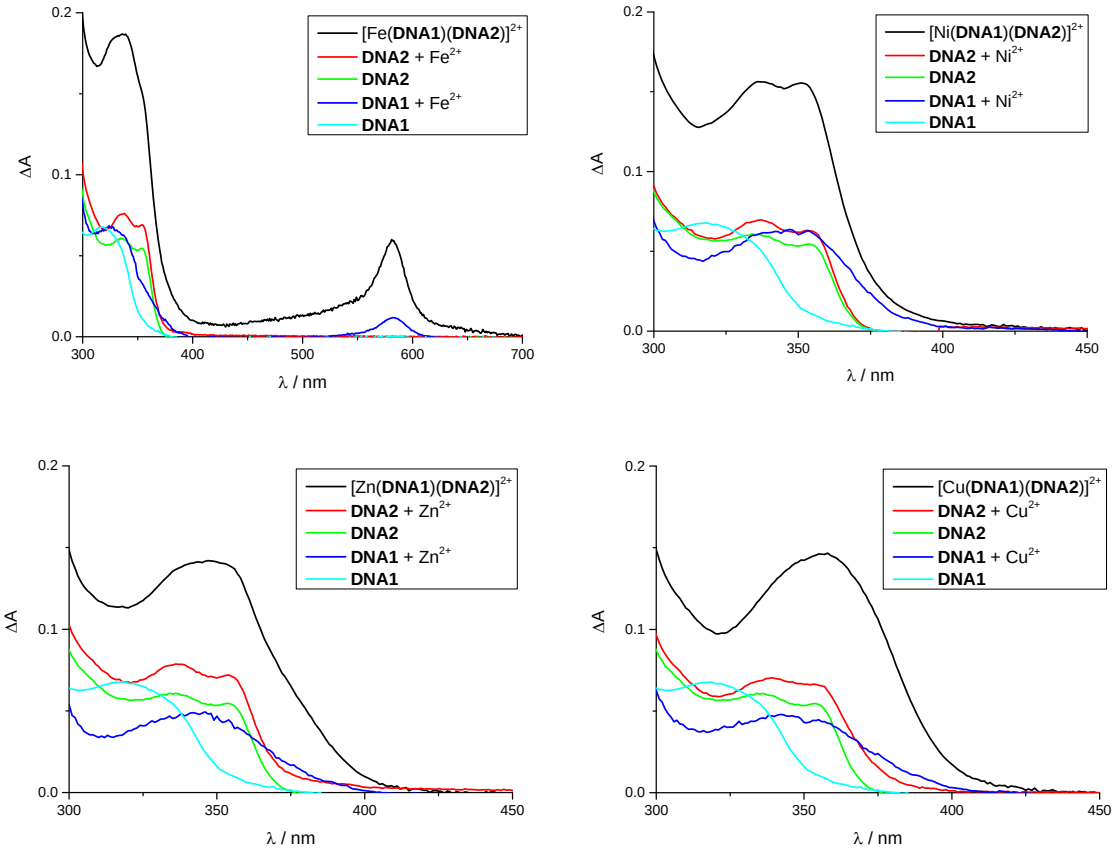
[(4)(5)Cu]$^+$



[(4)(5)Fe]$^+$



8. Additional single component spectra



9. References

[1] Schmittel, M.; Michel, C.; Wiegrefe, A.; Kalsani, V. *Synthesis* **2001**, 10, 1561-1567.
[2] R. H. E. Hudson, A. Ghorbani-Choghamarani, *Synlett* **2007**, 870-873.