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SUPPORTING INFORMATION

Title: Synthesis and Avidin Binding of Ruthenium Complexes Functionalized with a Light-Cleavable Free Biotin Moiety

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1. Synthesis and Characterization

1.1. NMRs and numbering of the synthesized compounds

1.1.1. N’’-(acetyl-L-methionine)-N’-biotinyl-3,6-dioxaoctane-1,8-diamine (**1**)

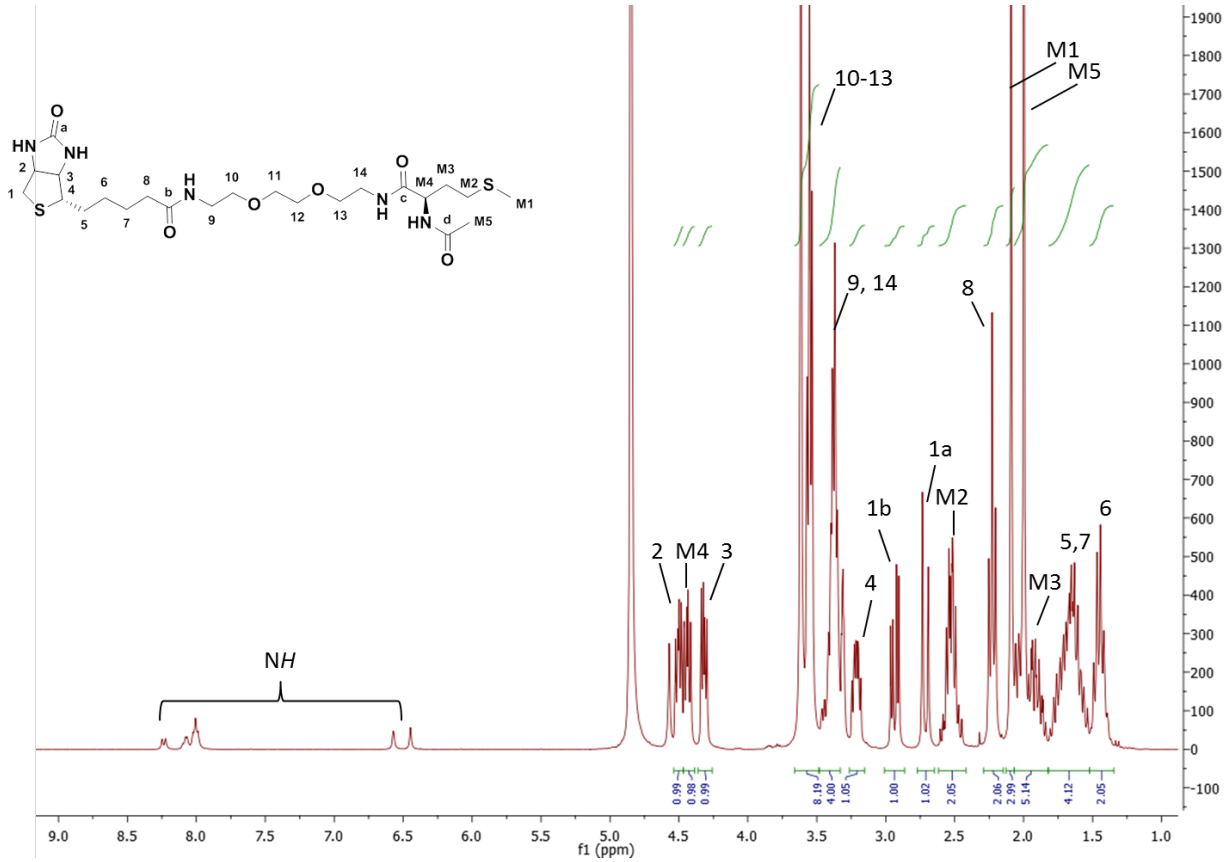

Figure S 1: 1H NMR (300 MHz, dMeOH) of compound 1.

1.1.2. Bis(N-biotinyl)-3,6-dioxaoctane-1,8-diamine (**2**)

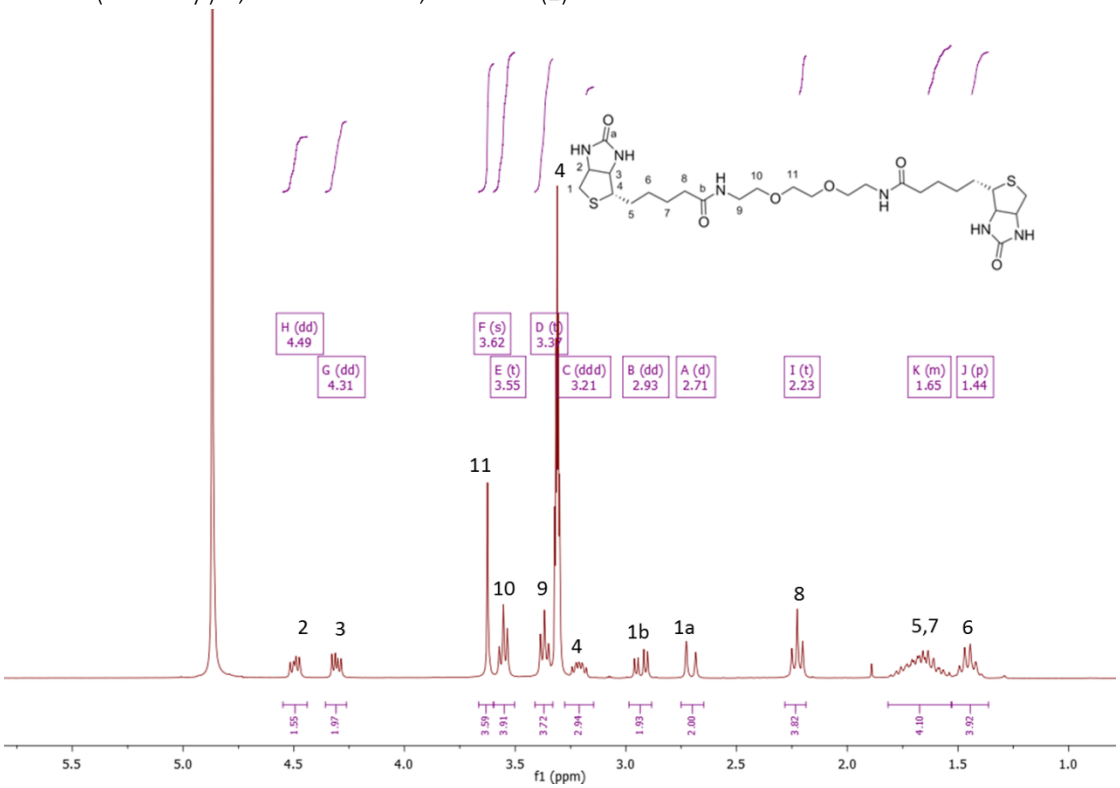

Figure S 2: ^{1}H NMR (300 MHz, dMeOH) ligand **2**.

1.1.3. [{Ru(tpy)(bpy)}$_2$(**1**)]Cl$_4$ –compound [**5**]Cl$_4$

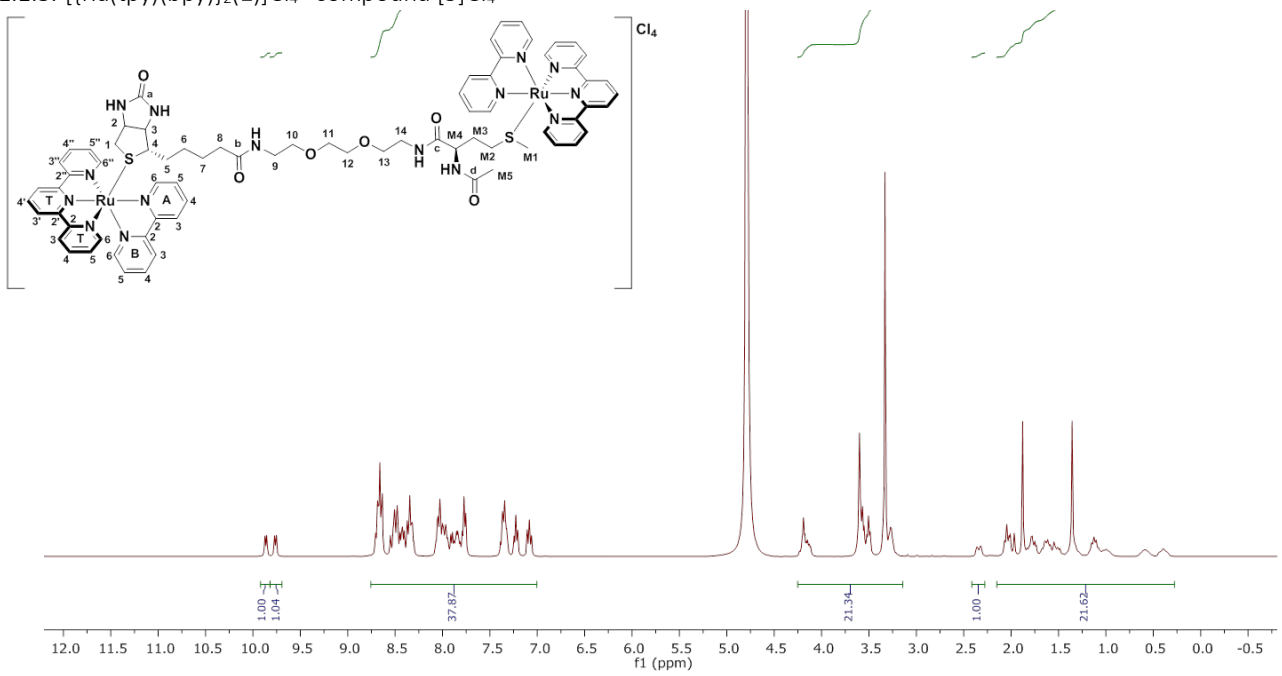

Figure S 3: ^{1}H NMR (300 MHz, dMeOH) complex [**5**]Cl$_4$.

1.1.4. [Ru(tpy)(bpy)(**1**)]Cl_2 –compound [**6**]Cl_2 (as mixture with complex [**7**]$_2$)

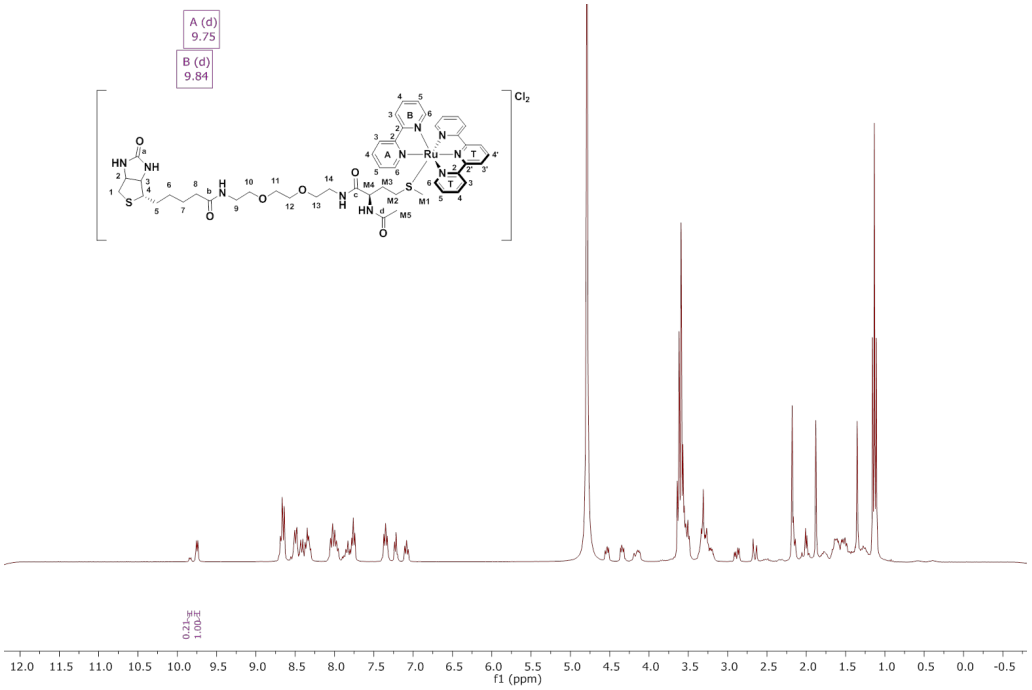

Figure S 4: ^{1}H-NMR of complex [**6**]Cl_2. The small dd signal at 9.84 indicates the formation of the regioisomere, complex [**7**]Cl_2.

1.1.5. [Ru(tpy)(bpy)(**2**)]$(PF_6)_2$ – (compound [**8**]$(PF_6)_2$)

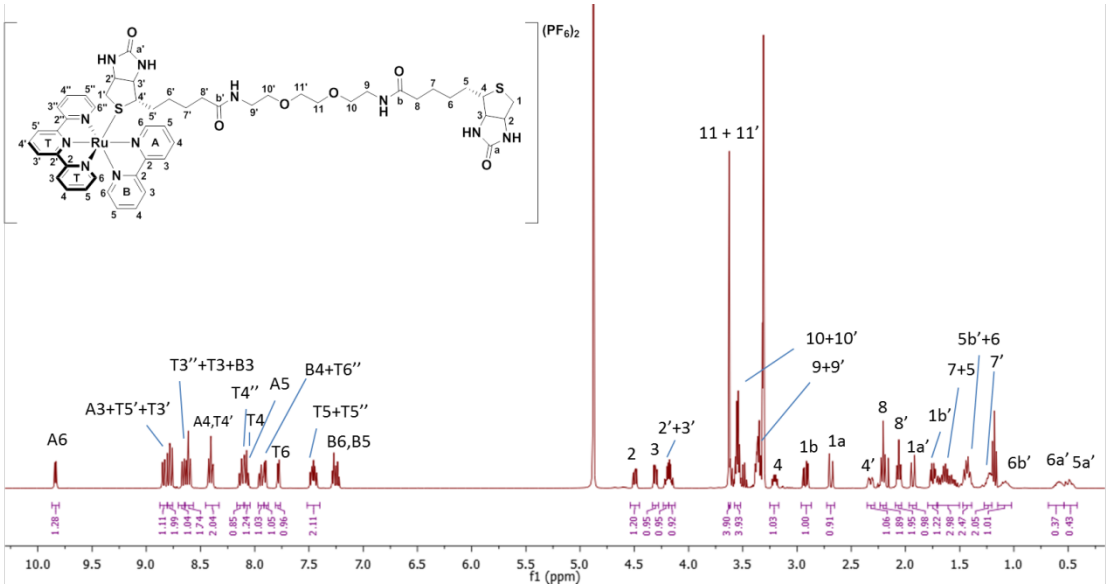

Figure S 5: ^{1}H NMR (400 MHz, dMeOH) of complex [**8**]Cl_2

1.2. Analytical scale synthesis of [Ru(tpy)(bpy)(**1**)]$(PF_6)_2$ – (compound [**6**]$(PF_6)_2$)

Table S1. Results of the reaction of ligand **1** with [Ru(tpy)(bpy)(OH_2)]$(PF_6)_2$ in H_2O under different conditions.[a] Isomeric ratios were obtained from ^{1}H NMR measurements (in D_2O or MeOD, 300 MHz) after workup of the reaction by silica column chromatography.

			NMR yield	
	Temperature (K)	**Time (h)**	**[6]$^{2+}$**	**[7]$^{2+}$**
A	333	48	61%	39%
B	353	48	83%	17%
C	Reflux	48	84%	16%
D	Reflux	2	63%	37%

[a] Conditions: [$RuOH_2$] = 5.0 mM, [**1**] = 25 mM, in H_2O:acetone (3:1) solution, under argon, in the dark.

2. Photochemistry

2.1. Kinetics of photosubstitution study of [**8**]$(PF_6)_2$

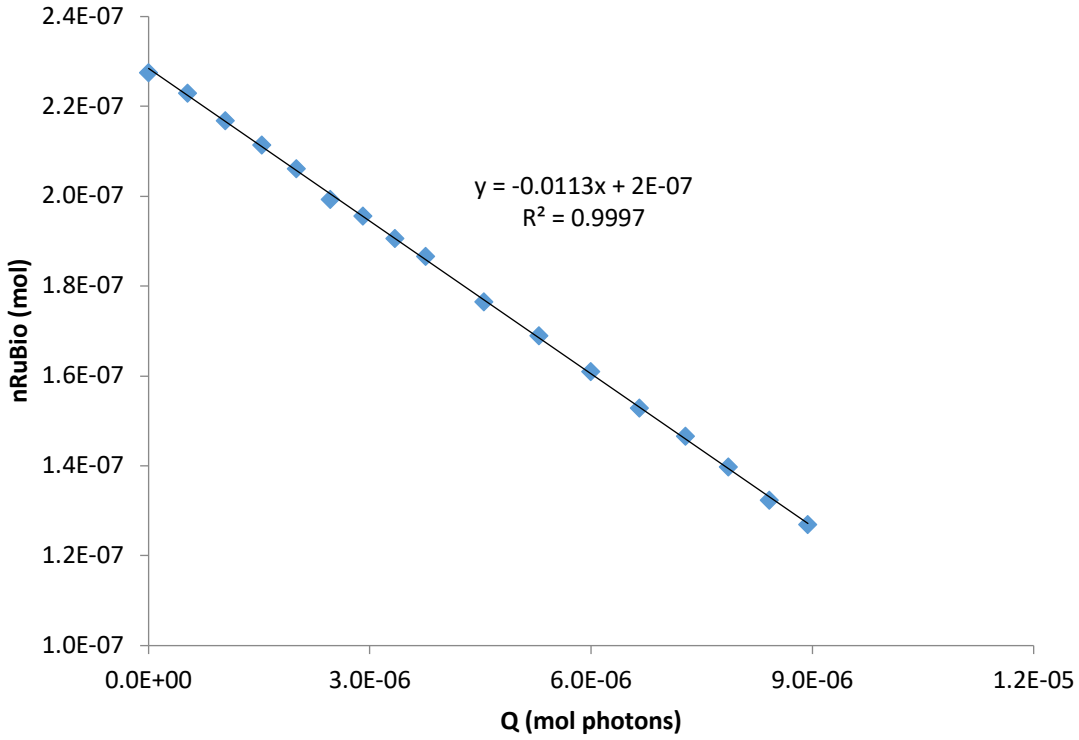

Figure S 6 Plot of the moles of the ruthenium thioether complex [**8**]$^{2+}$ *vs* the moles of photons Q absorbed by the complex.

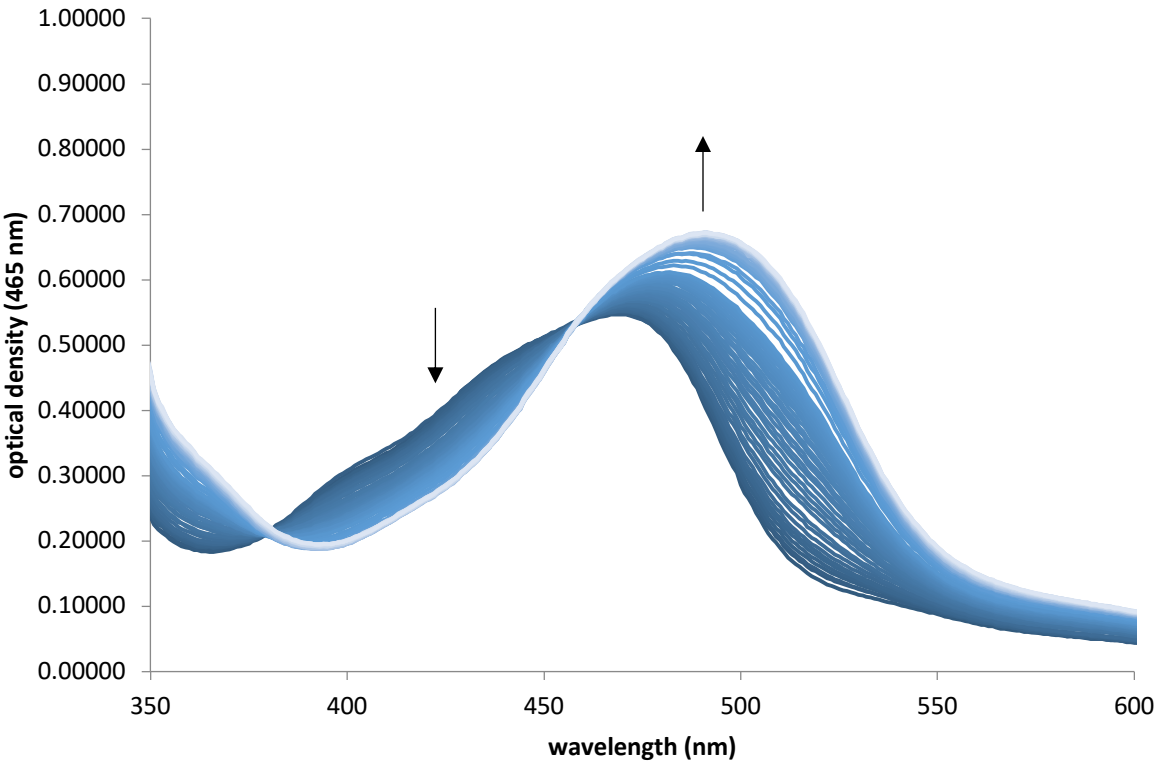

Figure S 7. Evolution of the UV-Vis spectra of a solution of [8](PF$_6$)$_2$ during blue light irradiation (λ = 465 nm, $\Delta\lambda_{1/2}$ = 25 nm). Conditions [Ru]$_0$ = 9.4×10^{-5} M in PBS solution (pH = 7.03, I = 50 mM), photon flux Φ_p = 1.87×10^{-8} (Einstein/s); photon flux Φ_p = 1.29×10^{-8} (Einstein/s). T = 298 K, irradiation pathlength: 3.00 cm, UV-vis absorbance pathlength: 1.00 cm.