Electronic Supporting Information

Potentiometric measurements. All the pH metric measurements (pH = -log [H^+]) were performed by using a water-thermostatted 5 ml titration vessel; the potentiometric titrations were carried out in degassed 0.1 mol dm^{-3} NMe_4NO_3 solutions, at 298.1 K by using the procedure which have been already described.[1] The combinated Ingold 405 S7/120 electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free NMe_4OH solutions and determining the equivalent point by the Gran's method[2] which allows to determine the standard potential E^o, and the ionic product of water (pK_w = 13.83(1) at 298.1 K in 0.1 mol dm^{-3} NMe_4NO_3). All equilibria involved in the studied systems were determined under the present experimental conditions in order to obtain a consistent set of data. Protonation constants of L ligands and substrates, formation constants of dinuclear Zn(II) complexes with L and formation constant of the UpU, UpA and U ternary complexes are supplied in Tables S1 and S2. The formation constants of the binary Zn(II) complexes with L have been previously determined in 0.1 M NMe_4Cl at 298.1 K.[1] The low solubility of the UpU complexes in this ionic medium lead us to study Zn(II) complexation in a different ionic medium (NMe_4NO_3 0.1 M, 298.1 K). The stability of the Zn(II) complexes with L, however, are very similar to that previously reported.[1] In the experiments to determine the stability of the Zn(II) complexes with L the ligand concentration was 5 x 10^{-4} mol dm^{-3}, while the Zn(II) concentration was varied in the range 5x10^{-4} - 1x10^{-3} mol dm^{-3}. In the experiments to determine the formation constants of the complexes with nucleosides or ribodinucleotides, L and Zn(II) concentrations were 5x10^{-4} and 1x10^{-3}, respectively, while the concentration of the substrates was varied from 5x10^{-4} to 5x10^{-3}. At least three measurements (about 150 data points each one) were performed for each system in the pH range 2.5-10.5 and the relevant e.m.f. data were treated by means of the computer program HYPERQUAD[3] which furnished the relevant equilibrium constants reported in Table S1 and S2.

Spectrofluorimetric measurements. UV-vis and steady state fluorescence emission spectra were recorded respectively on a Perkin-Elmer Lambda 25 and LS-55 spectrometers at 298.1 K. 0.01 M HNO_3 and NMe_4OH solutions were used to adjust the pH, which was measured on a Metrohm 713 pH meter.

Measurements of the florescence decay lifetimes were carried out by utilizing ultrashort pulses (duration ≈ 100 fs at 1 KHz repetition rate) from a regenerative amplifier Ti:sapphire laser system equipped with an optical parametric generator and amplifier (OPG-OPA). Non-linear sum frequency and second harmonic generation in BBO crystals provide tunable light pulses in the 240 to 800 nm spectral range[5]. The fluorescence was collected by a quartz lens and focused onto the photocathode of a Hamamatsu R2809U-microchannel plate photomultiplier after passing through a

proper set of coloured filters. The selected spectral intervals are: 300-375nm, 410-470 nm and 500-575 (FWHH). The output of the photomultiplier was amplified and connected to the 50 Ω input of a digital oscilloscope (LeCroy Mod.9370M 1 GHz band pass). The very reproducible instrumental function, obtained by measuring the light scattering from a latex solution, resulted slightly asymmetric with a time duration (FWHH) of 950 ps. The experimental fluorescence signals are treated in a deconvolution/fitting process and are reproduced by a single or dual-exponential function.

^{1}H NMR measurements. ^{1}H NMR spectra in D_2O solutions at different pH values were recorded at 298 K in a Varian 300 MHz spectrometer. In the NMR titrations small amounts of 0.01 M NaOD or DCl solutions were used to adjust the pD. The pH was calculated from the measured pD values using the relationship: pH = pD - 0.40[4]

(1) Lodeiro, C.; Parola, A. J.; Pina, F.; Bazzicalupi C.; Bencini, A.; Bianchi A.; Masotti, A.; Giorgi, C.; Valtancoli B. *Inorg. Chem.*, **2001**, *40*, 2968-2975.

(2) Gran, G. *Analyst* (London), **1952**, *77*, 661. Rossotti F. J.; H. Rossotti, *J. Chem. Educ.* **1965**, *42*, 375.

(3) Gans, P.; Sabatini, A.; Vacca, A. *Talanta*, **1996**, *43*, 807-812.

(4) Covington, A. K.; Paabo, M.; Robinson R. A.; Bates, R. G. *Anal. Chem.* **1968,** *40*, 700

(5) Neuwahl, F.V.R.; Bussotti, L.; Foggi, P. *Res. Adv. In Photochem & photobiol.*; **2000**, *1*, 77-93.

Table S1. Protonation constants of ligand L and pK_a of the substrates (NMe_4NO_3 0.1 M, 298.1 K)

Equilibrium	Log K
$L + H^+ = [HL]^+$	9.40(1)[a]
$[HL]^+ + H^+ = [H_2L]^{2+}$	8.6(1)
$[H_2L]^{2+} + H^+ = [H_3L]^{3+}$	7.43(1)
$[H_3L]^{3+} + H^+ = [H_4L]^{4+}$	4.12(1)
$[H_4L]^{4+} + H^+ = [H_5L]^{5+}$	2.19(2)

substrate	pK_a [b]
Uridine (U)	9.29(1)[c]
Guanidine (G)	9.19(1)[c]
Adenosine (A)	3.60(1)[c]
Citidine (C)	4.22(1)[c]

Substrate	pK_{a1} [d]	pK_{a2} [d]
UpU	9.62(1)[e]	9.31(1)
GpG	9.59(1)[e]	9.27(1)
ApA	3.78(1)[e]	3.10(1)
CpC	4.53(1)[e]	3.71(1)
UpA	9.4(1)	4.6(1)

[a]: the values are very similar to those previously determined in 0.1 M NMe_4Cl (see Lodeiro, C.; Parola, A. J.; Pina, F.; Bazzicalupi C.; Bencini, A.; Bianchi A.; Masotti, A.; Giorgi, C.; Valtancoli B. *Inorg. Chem.*, **2001**, *40*, 2968-2975. [b]: in the case of U and G the pK_a values are referred to deprotonation of the substrate, i. e, to the equilibria $X(H_{-1})^- + H^+ = X$ (X = U or G), while in the case of cytidine and adenosine are related to protonation of the substrate, i. e. to equilibria of the type $X + H^+ = XH^+$ (X = A or C) [c]: the values are in good agreement with those previously reported (for uridine see: Nagy, Z; Sovago, I, *Dalton Trans,* **2001**, 2467; for guanosine, cytidine and adenosine see: Taylor, S.; Buncel, E.; Norris, A.; *J. Inorg. Biochem.,* **1981,** *15*, 131). [d] in the case of UpU and GpG the pK_{a1} and pK_{a2} values are referred to deprotonation of the substrate, i. e, to the equilibria $X(H_{-2})^{3-} + H^+ = X(H_{-1})^{2-}$ and $X(H_{-1})^{2-} + H^+ = X^-$ (X = UpU or GpG), while in the case of CpC and ApA are related to protonation of the substrate, i. e to equilibria of the type $X + H^+ = XH^+$ and $XH^+ + H^+ = XH^{2+}$ (X = ApA or CpC). In the case of UpA the pK_{a1} value is related to deprotonation of the substrate, while the pK_{a2} value refers to protonation of the substrate. [e]: the values are in good agreement with those previously reported by Ogasawara N; Inoue, Y, *J. Am. Chem. Soc.*, **1976,** *98,* 7048.

Table S2. Stability constants of the Zn(II) complexes (log K) with L (NMe_4NO_3 0.1M, 298.1 K)[a]

Reaction	Log K
$L + Zn^{2+} = [ZnL]^{2+}$	12.12(1)
$[ZnL]^{2+} + H^{+} = [ZnLH]^{3+}$	6.91(1)
$[ZnLH]^{3+} + H^{+} = [ZnLH_2]^{4+}$	5.08(2)
$[ZnL]^{2+} + OH^{-} = [ZnL(OH)]^{+}$	2.94(1)
$[ZnL(OH)]^{+} + OH^{-} = [ZnL(OH)_2]$	
$L + 2Zn^{2+} = [Zn_2L]^{4+}$	17.62(5)
$[Zn_2L]^{4+} + OH^{-} = [ZnL(OH)]^{3+}$	5.69(6)
$[Zn_2L(OH)]^{3+} + OH^{-} = [Zn_2L(OH)_2]^{2+}$	5.64(6)
$[Zn_2L]^{4+} + UpU(H_{-1})^{2-} = [Zn_2L{\cdot}UpU(H_{-1})]^{2+}$	8.0(1)
$[Zn_2L{\cdot}UpU(H_{-1})]^{2+} = [Zn_2L{\cdot}UpU(H_{-2})]^{+} + H^{+}$	-8.1(1)
$[Zn_2L]^{4+} + U(H_{-1})^{-} = [Zn_2L{\cdot}U(H_{-1})]^{3+}$	8.1(1)
$[Zn_2L{\cdot}U(H_{-1})]^{3+} + U(H_{-1})^{-} = [Zn_2L{\cdot}U(H_{-1})_2]^{2+}$	7.2(1)
$[Zn_2L]^{4+} + UpA(H_{-1})^{2-} = [Zn_2L{\cdot}UpA(H_{-1})]^{2+}$	6.1(1)
$[Zn_2L{\cdot}UpA(H_{-1})]^{2+} + UpA(H_{-1}) = [Zn_2L{\cdot}UpA(H_{-2})_2]^{+} + H^{+}$	4.9(1)

[a]: the stability of the binary complexes between Zn(II) and L, previously determined in 0.1 M NMe_4Cl at 298.1 K (Lodeiro, C.; Parola, A. J.; Pina, F.; Bazzicalupi C.; Bencini, A.; Bianchi A.; Masotti, A.; Giorgi, C.; Valtancoli B. *Inorg. Chem.*, **2001**, *40*, 2968-2975), have been determined again in the course of the present study in a different ionic medium (0.1 M NMe_4NO_3, 298.1 K), due to the low solubility of the UpU complexes in 0.1 M NMe_4Cl. The constant values, however, are in good accord to that previously reported.

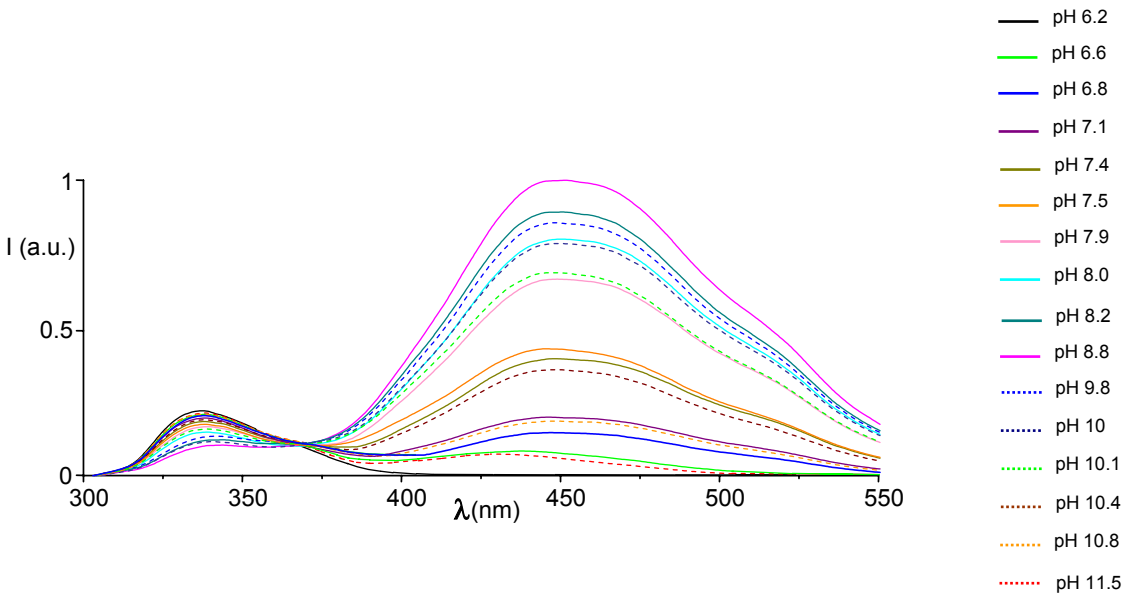

Figure S1. Fluorescence emission spectra recorded on solutions containing UpU and complex **1** at selected pH values ([UpU] = [**1**] = 2.5 x 10^{-5} M, λ_{exc} = 290 nm, T = 298 K).

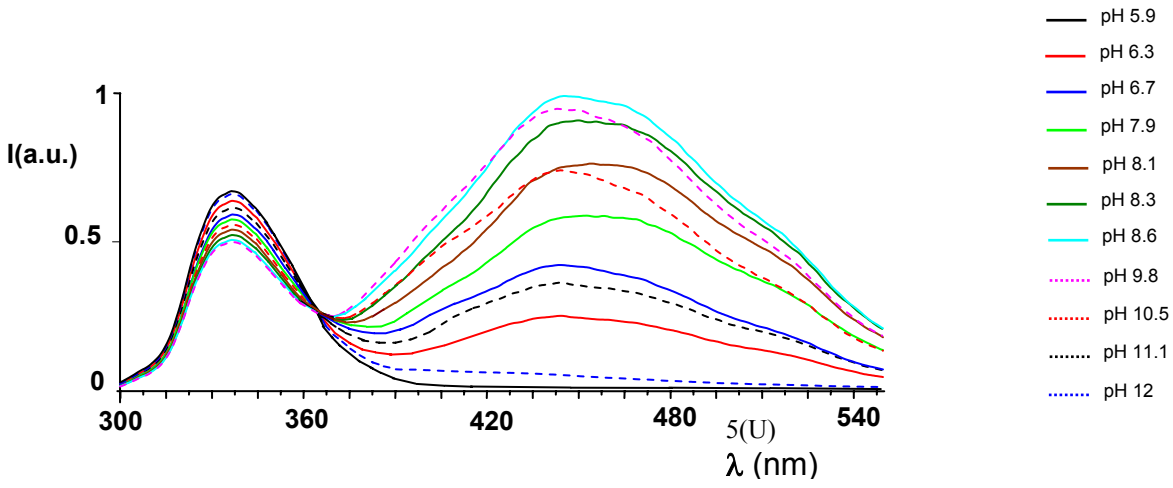

Figure S2. Fluorescence spectra recorded on solutions containing U and complex **1** at selected pH values ([**1**] = [U] = 2.5.10^{-5} M, [U] = 5·10^{-5} M λ_{exc} = 290 nm, T = 298.1 K)

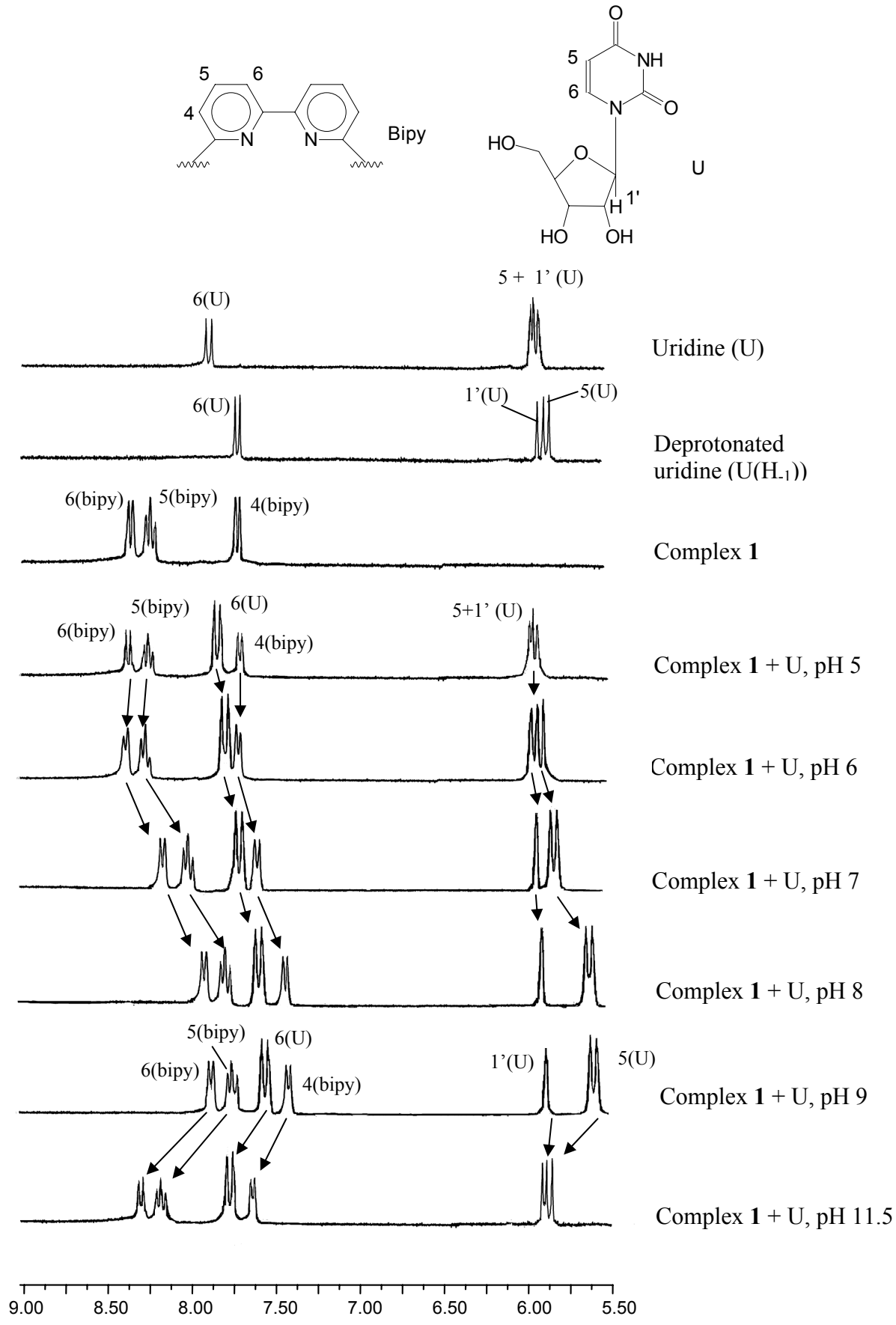

Figure S3. ^{1}H NMR spectra of uridine, deprotonated uridine, complex **1** and complex **1** in the presence of 2 eq. of uridine at different pH values at 318 K (the spectra of complex **1** in the presence of uridine display fluxionality at lower T values, avoiding a correct interpretation). The observed downfield shift of the ^{1}H signals of the nucleobase and dipyridine at pH 11.5 is due to hydroxide binding to complex **1,** which leads to detachment of the nucleoside from the dimetal complex.

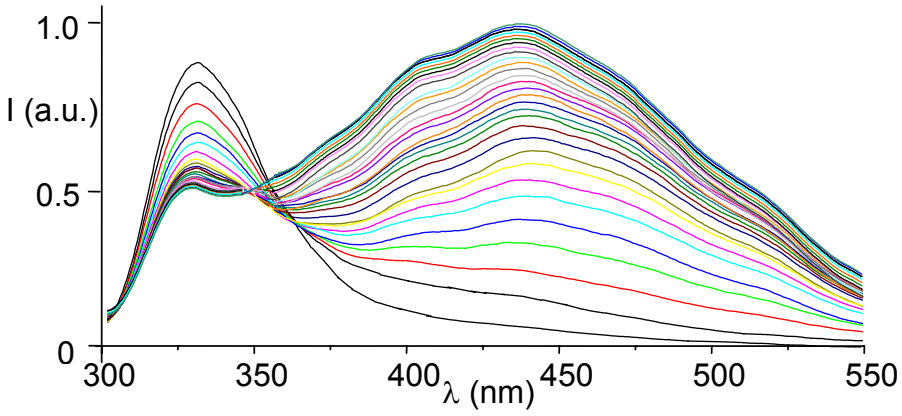

Figure S4. Fluorescence emission spectra of **1** in the presence of increasing amounts of UpA (0.2 eq each addition) at pH 9. ([1] = $2.5.10^{-5}$ M, λexc = 290 nm, 298.1 K).

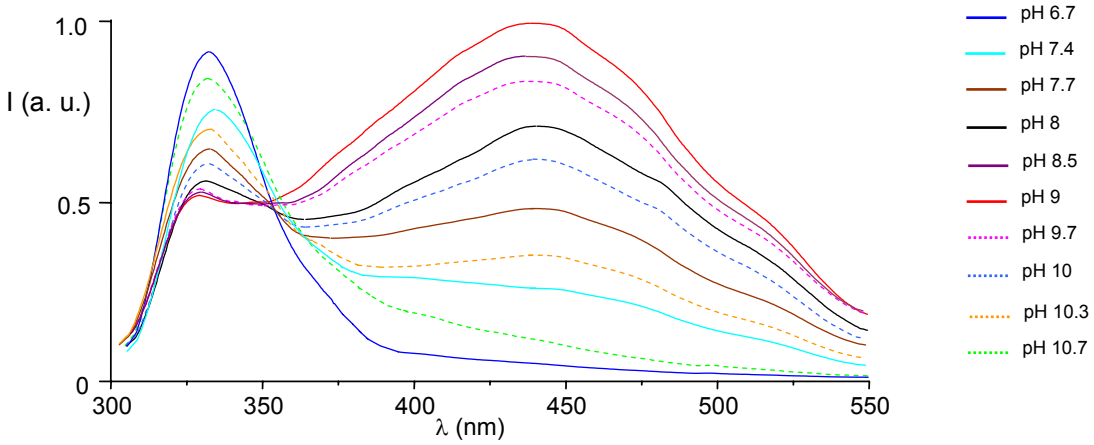

Figure S5. Fluorescence emission spectra recorded on solutions containing UpA and complex **1** at selected pH values ([UpA] = 1,25 x 10^{-4}, [**1**] = 2.5 x 10^{-5} M, λ_{exc} = 290 nm, T = 298 K).

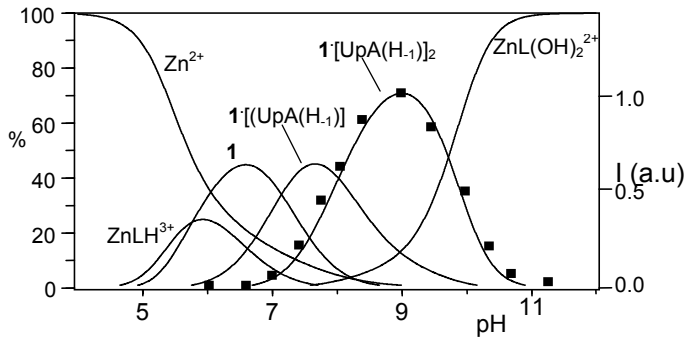

Figure S6. Emission intensity at 440 nm (•, right y axis) as a function of pH compared to the distribution curves of the complexes (solid curves, left y axis) for a system containing **1** and UpA ([**1**] = $2.5 \cdot 10^{-5}$ M, [UpA] = $1.25 \cdot 10^{-4}$ M, λ_{exc} = 290 nm, 298.1 K).

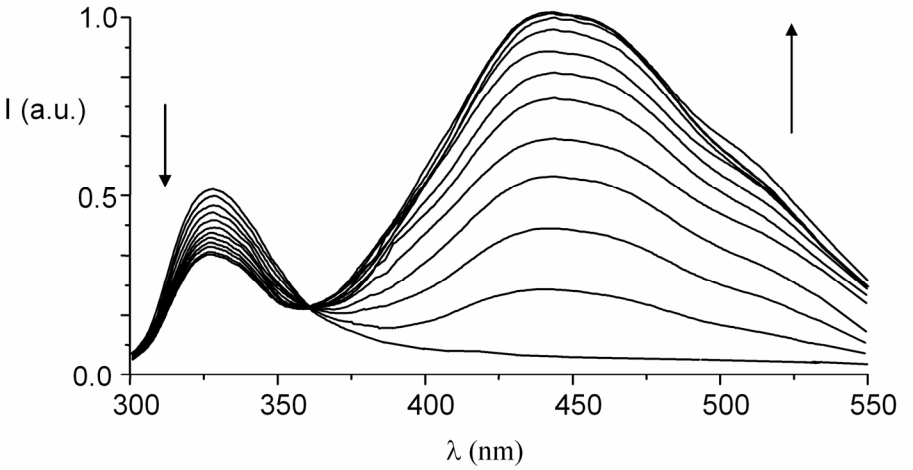

Figure S7. Fluorescence emission spectra of **1** in the presence of increasing amounts of 5'-AAUUAA-3' (0.25 eq each addition) at pH 8.5. ([**1**] = $2.5.10^{-5}$ M, λ_{exc} = 290 nm, 298.1 K).