Electronic Supplementary Information

1. Determination of the formation constant K for the Zn(II) – nucleotide complex


\[ NMP + Zn^{2+} \rightleftharpoons NMP^* , \]

where NMP is a nucleotide and NMP* is a fluorescent nucleotide – Zn complex, the formation constant K is given by

\[ K = \frac{[NMP^*]}{([NMP] - [NMP^*]) \cdot ([Zn^{2+}] - [NMP^*])} \approx \frac{[NMP^*]}{([NMP] - [NMP^*]) \cdot [Zn^{2+}]}, \]

since the fixed Zn^{2+} concentration (1mM) is much larger than the nucleotide’s concentrations. Rearranging the formula, we obtain a ratio between the concentration of complexed nucleotides and the total concentration of nucleotides:

\[ \frac{[NMP^*]}{[NMP]} = \frac{K[Zn^{2+}]}{1 + K[Zn^{2+}]} = \frac{1}{1 + 1/K[Zn^{2+}]} . \]

This expression holds for all concentrations of nucleotides providing that [NMP]«<[Zn^{2+}]. Now we can write the complex concentrations normalized to the first (the lowest) concentration, which equals the normalized fluorescence intensity, as a linear function of the normalized total nucleotide’s concentrations:

\[ \frac{[NMP^*]_N}{[NMP^*]_1} = \frac{I_N}{I_1} = \frac{1}{1 + 1/K[Zn^{2+}]} [NMP]_N . \]

By plotting \( \frac{I_N}{I_1} \) versus \( \frac{[NMP]_N}{[NMP]_1} \), we can obtain the constant K from a linear fit.
Fig. S1  Fluorescence spectra of four nucleotide – Zn(II) complexes with increasing nucleotide’s concentrations between $1 \times 10^{-5}$ M and $1 \times 10^{-4}$ M. The concentration of Zn ions was held constant – 1 mM.
Fig. S2  The normalized fluorescence intensities of four nucleotides – Zn(II) complexes as functions of the normalized total nucleotide’s concentrations. The reaction constants K were calculated from the slopes of the linear fits.
2. Absorption Spectra

Fig. S3  Absorption spectra of four DNA nucleotides in 10 mM Tris-HCl buffer pH 9 without (black curves) and with 1 mM ZnCl$_2$ added (blue curves). The spectra were recorded with HP 8453 UV-Vis spectrophotometer.
3. Excitation Spectra

**2'-deoxyguanosine 5'-monophosphate (dGMP)**

\[ \lambda_{em} = 360 \text{ nm} \]

**2'-deoxyadenosine 5'-monophosphate (dAMP)**

\[ \lambda_{em} = 360 \text{ nm} \]

**2'-deoxycytidine 5'-monophosphate (dCMP)**

\[ \lambda_{em} = 360 \text{ nm} \]

**Thymidine 5'-monophosphate (TMP)**

\[ \lambda_{em} = 360 \text{ nm} \]

\[ \lambda_{em} = 395 \text{ nm} \]

\[ \lambda_{em} = 380 \text{ nm} \]

**Fig. S4** Excitation spectra of four DNA nucleotides in 10 mM Tris-HCl buffer, pH 9, without (upper frame) and with 1 mM ZnCl\(_2\) added (lower frame). The spectra were recorded with Perkin-Elmer LS 55 spectrofluorometer.
4. Time-decay

Samples: Calf Thymus (CT) DNA, 2'-deoxyguanosine 5'-monophosphate (dGMP), 2'-deoxyadenosine 5'-monophosphate (dAMP) in 10 mM Tris-HCl buffer pH 9; 1 mM ZnCl₂.

Measurements: Time Correlated Single Photon Counting (TCSPC) with Fluorolog 3 (Horiba Jobin Yvon) spectrofluorometer. Excitation wavelength \( \lambda_{\text{ex}} = 294 \) nm; emission wavelength \( \lambda_{\text{em}} = 400 \) nm (special thanks to dr. Miroslav Dramičanin, Vinča Institute of Nuclear Sciences, Serbia, for his assistance).

Fig. S5 A fluorescence time-decay of Zn(II) - Calf-Thymus DNA complex. The decay is fitted with a double-exponential function.

Fig. S6 Fluorescence time-decay of Zn(II) – 2'-deoxyguanosine 5'-monophosphate (dGMP) (left) and Zn(II) – 2'-deoxyadenosine 5'-monophosphate (dAMP) (right) complexes.