Supplementary Material (ESI) for Analyst

SUPPORTING INFORMATION

Multiplexed energy transfer mechanisms in a dual function quantum dot for zinc and manganese

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Calculations

Quantum Yield

The quantum yield of QD_{540} and QD_{620} was estimated from Eq. (1):

$$\phi_S = \phi_R \frac{A_R(\lambda_R)}{A_S(\lambda_S)} \frac{n_S^2}{n_R^2} \frac{I_S}{I_R}$$

where ϕ_R is the quantum yield of the reference, $A_S(\lambda_S)$ is the absorbance of the sample (QD) and $A_R(\lambda_R)$ the absorbance of a reference solution at the excitation wavelength, n_S and n_R are the refractive index of the medium of the sample and the reference, respectively, and I_S and I_R the area under the emission spectrum of sample and reference, respectively.

The quantum yield of the QD_{540} and QD_{620} were calculated by using fluorescein ($\phi_R = 0.95$)[1] and rhodamine B ($\phi_R = 0.31$)[2] as reference in aqueous solution, respectively. For the calculation of the quantum yield of QD_{540} the excitation wavelength used to obtain the emission spectra was 450 nm, and for QD_{620} was 520 nm. $A_S(\lambda_S)$ and $A_R(\lambda_R)$ were the values of absorbance at these wavelengths, respectively. The experimental calculated quantum yields were 0.22 and 0.25 for QD_{540} and QD_{620}, respectively

Resonance Energy Transfer

The resonance energy transfer (RET) efficiency depends on many parameters, such as the distance between the donor and the acceptor; the spectral overlap of the donor emission spectrum and the acceptor absorption spectrum; and the relative orientation of the donor emission dipole moment and the acceptor absorption dipole moment. The efficiency depends on the donor-to-acceptor separation distance *r* with an inverse 6th power law due to the dipole-dipole coupling mechanism[1]:

$$E = \frac{1}{1 + (r/R_0)^6}$$

being R_0 the distance between the donor and acceptor that yields 50 % energy-transfer efficiency. To characterize the RET process between QDs and the complex zincon-Zn^{2+}, the Förster distance, R_0, can be calculated as[1] (Eq (3)):

$$R_0^6 = 8.8 \times 10^{23} \cdot \kappa^2 \cdot n_D^{-4} \cdot Q_D \cdot J$$

where Q_D is the quantum yield of the donor in the absence of acceptor, n_D is the refractive index of the medium, and κ^2 is an orientation factor, depending on the relative orientation of the donor and acceptor dipoles. $\kappa^2 = 2/3$ is the value for randomly orientation dipoles. The overlap integral J is a quantitative measure of donor-acceptor spectral overlap integrated over all wavelengths λ, an is defined as[1]:

$$J = \int f_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda$$

where f_D and ε_A represent the donor emission spectrum (normalized and dimensionless) and acceptor absorption spectrum, respectively.

By using our experimental data, the R_0 values obtained for QD_{540}-zincon-Zn^{2+} and QD_{620}-zincon-Zn^{2+} pairs were 41.5 and 47.6 Å, respectively.

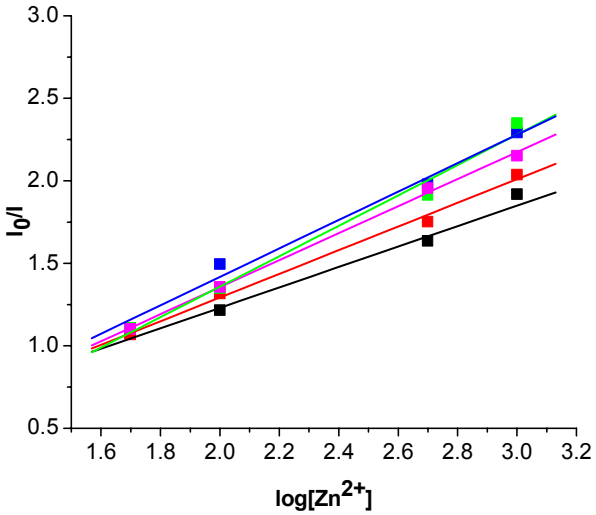

Figure SI.1. Response of QD_{540}-zincon conjugates toward Zn^{2+} at different ionic strengths. TRIS buffer concentration (pH 7.5): 5mM (black), 10 mM (red), 25 mM (blue), 50 mM (green), and 100 mM (pink).

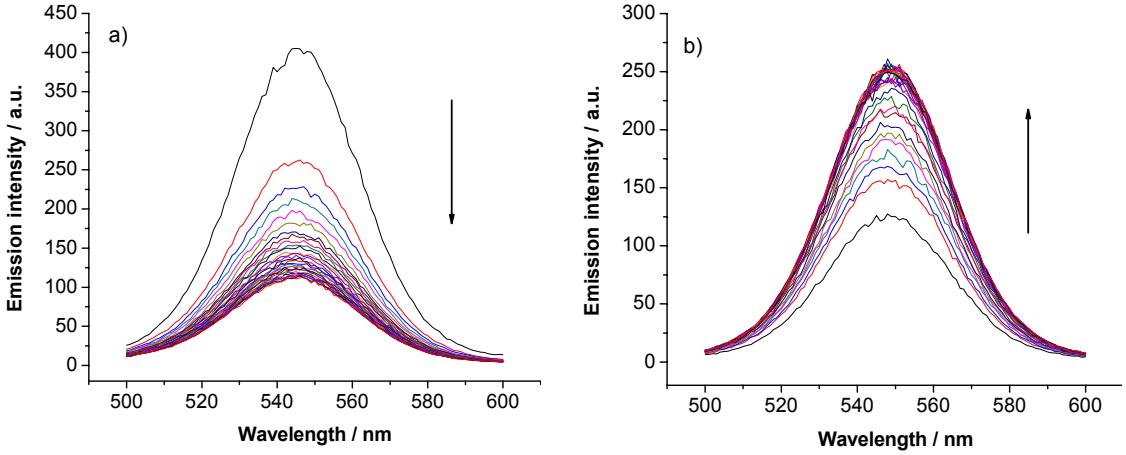

Figure SI-2. Response of QD_{540}-zincon conjugates towards a) Zn^{2+} and b) Mn^{2+} (TRIS pH 7.5) with time. Every spectrum was scanned every 20 seconds.

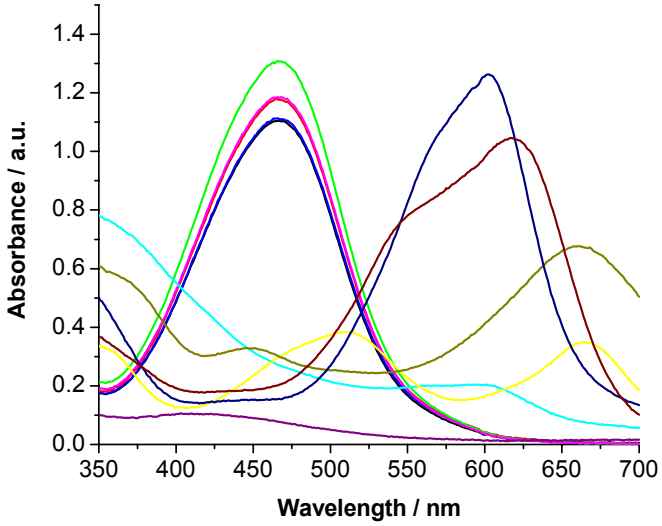

Figure SI.3. Absorption spectra of zincon before (black) and after addition of different metal ion in solution (TRIS pH 7.5): Ca^{2+} (red), Mg^{2+} (blue), K^{+} (green), Na^{+} (pink), Fe^{2+} (cyan), Ni^{2+} (yellow), Co^{2+} (dark yellow), Cu^{2+} (dark blue), Mn^{2+} (purple), and Zn^{2+} (brown).

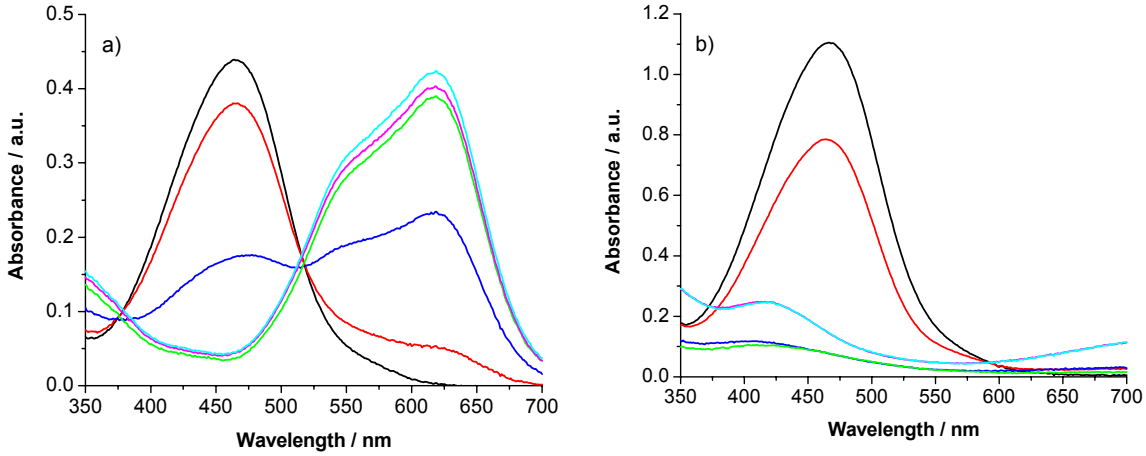

Figure SI-4. Absorption spectra of zincon (black) and a) zincon-Zn^{2+} complex, and b) zincon-Mn^{2+} complex in solution at different pHs. pH: 6.2 (red), 7.0 (blue), 7.5 (green), 8.2 (pink) and 8.8 (cyan).

REFERENCES

[1] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, 2nd Ed., Kluwer Academic/Plenum Publishers, New York, London, Moscow, Dordrecht, 1999.

[2] D. Magde, G.E. Rojas, and P. Seybold, Solvent Dependence of the Fluorescence Lifetimes of Xanthene Dyes. Photochem. Photobiol. 70, 737, 1999.