

Supplementary Materials

Contamination- and Perturbation-Free Fluorescent Monitoring of Zn^{2+} in Suspensions using Crown Ether-Functionalized Magnetic Nanoparticles

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1. Supplementary information regarding ICP-OES measurements

Sample solutions were measured in simultaneous, multielement mode by a Labtest Plasmalab ICP-spectrometer (Labtest Equipment Company, USA) with a 40-channel Paschen-Runge vacuum polychromator with photomultiplier detectors, using 27 MHz argon plasma. Instrument settings were the following, forward power: 1.3 kW, sample introduction with a “OneNeb” nebulizer (Agilent Technologies, USA), cyclonic spray chamber and Gilson peristaltic pump (Gilson Company, USA) at 1 mL min⁻¹ sample flow rate, observation height: 13.5 mm, integration time: 5 s. Limit of quantitation for Ag was 0.025 mg·L⁻¹, (wavelength: 328.068 nm), for Ca was 0.03 mg·L⁻¹, (wavelength: 422.673 nm), for Co was 0.019 mg·L⁻¹, (wavelength: 238.892 nm), for Cu was 0.025 mg·L⁻¹, (wavelength: 224.700 nm), for K was 0.05 mg·L⁻¹, (wavelength: 766.491 nm), for Mg was 0.0005 mg·L⁻¹, (wavelength: 279.553 nm), for Na was 0.19 mg·L⁻¹, (wavelength: 589.592 nm), for Pb was 0.13 mg·L⁻¹, (wavelength: 220.353 nm), and for Zn was 0.005 mg·L⁻¹, (wavelength: 213.856 nm).

2. Composition of river water samples

The river water samples were collected from river Danube in Budapest (GPS coordinates: 47°29'06.5"N 19°03'11.8"E, 2021.02.16. 10⁰⁰). The metal ion compositions were determined by ICP-OES method after filtering and acidifying the samples by nitric acid (**Table S1**).

Table S1. Metal ion composition of the investigated river water samples determined by ICP-OES

Elements	River water (mg·L ⁻¹)
Ag	<0.02
Al	<0.09
As	<0.07
B	<0.01
Ba	0.03
Be	<0.01
Bi	<0.19
Ca	59.8
Cd	0.01
Co	<0.02
Cr	<0.02
Cu	<0.02
Fe	0.07
Hg	<0.01
K	3.21
Li	<0.06
Mg	12.20
Mn	<0.01
Mo	<0.02
Na	19.9
Ni	<0.04
P	0.43

Pb	0.01
S	12.5
Sb	<0.13
Se	<0.23
Sn	<0.08
Sr	0.23
Ti	<0.01
V	<0.02
W	<0.09
Zn	0.05
Zr	<0.02

3. Composition of the pumpkin seed flour

The composition of the commercially available pumpkin seed flour can be found in **Table S2**.

Table S2. Composition of the investigated pumpkin seed flour calculated for 100 g

Components	Pumpkin seed flour (mg/100 g)
Protein	40000
Fibre	6000
Carbohydrates	1500
Total fat	14000
Ash	4900
Calcium	65
Iron	22
Magnesium	810
Phosphorus	1700
Zinc	12
Copper	2
Manganese	5
Potassium	1200
Sodium	436
Sulphur	63
Chloride	58
Vitamins and other trace elements	

4. UV-calibration for determining the concentration of fluoroionophore 1 in solution

The ratio of the immobilized ionophore was determined based on UV-calibration in chloroform (**Figure S1** and **Figure S2**).

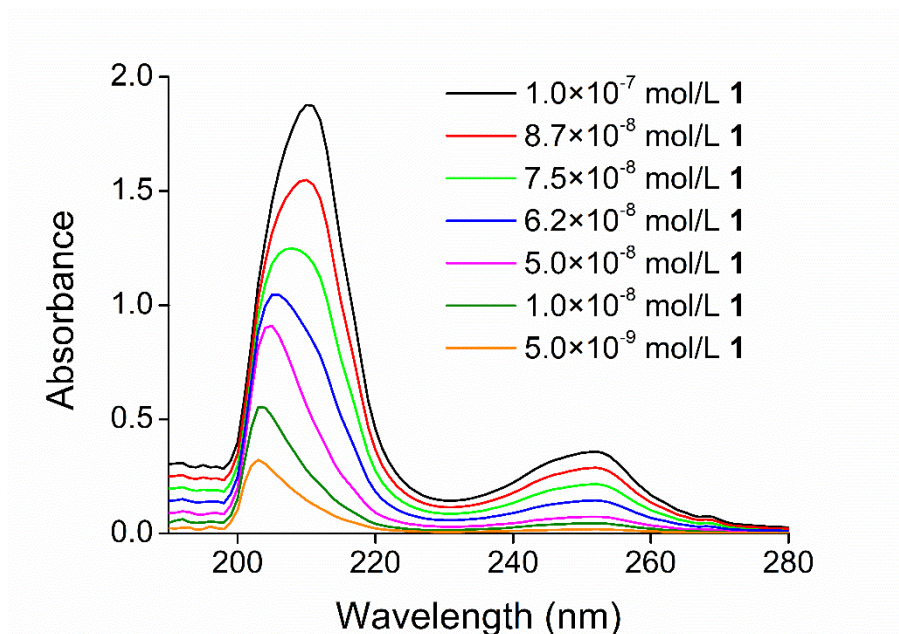


Figure S1. Concentration-dependent absorption of fluoroionophore 1 in chloroform

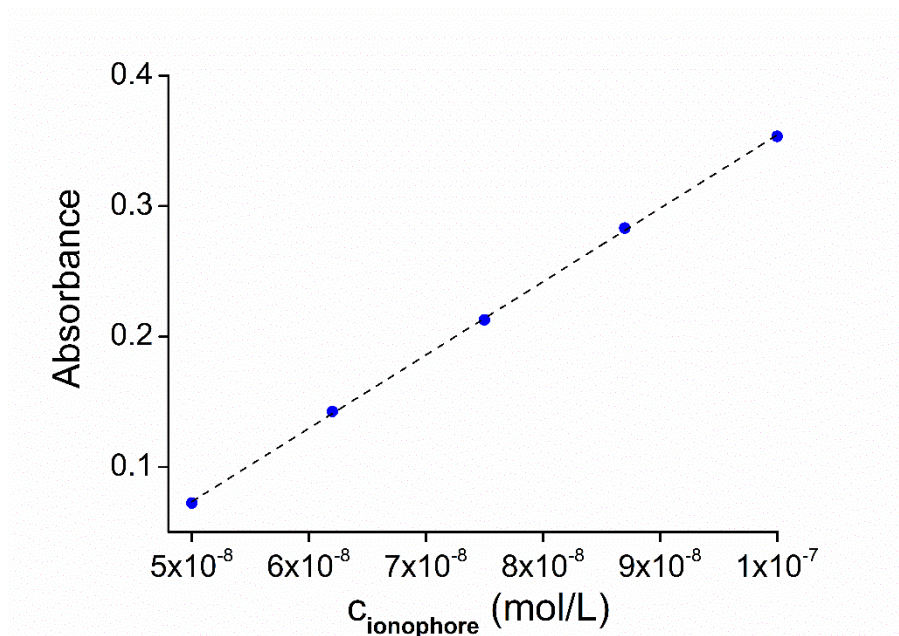


Figure S2. UV-absorbance-based calibration curve of fluoroionophore 1 at 250 nm used for calculating its concentration ($R^2 = 0.99$)

5. Determination of LOD

Detection limits were calculated based on data of the fluorescence titrations. To determine the signal-to-noise ratio, the fluorescence intensity of the sensor membrane was measured 9 times and the standard deviation of these blank measurements was determined as 9.0.

Three separate measurements of the emission intensity were performed in the presence of low concentrations of Zn^{2+} and the average of the intensities was plotted as a function of concentration to determine the slope of the linear regression (**Figure S3**).

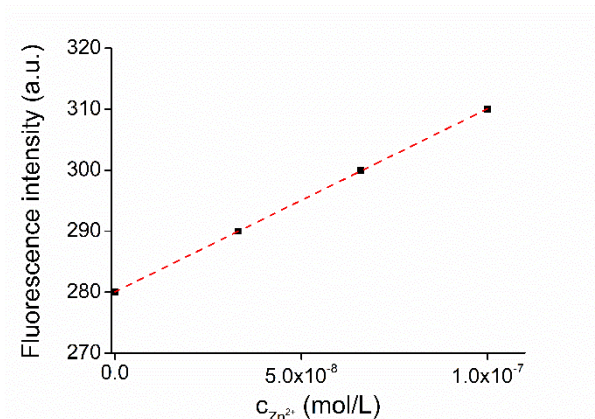


Figure S3. Linear regression for the optochemical responses in the presence of low concentrations of Zn^{2+}

The equation of the linear regression line is as follows: $F_{\text{obs}(370 \text{ nm})} = 3 \cdot 10^8 c_{\text{Zn}^{2+}} + 280$, $R^2=0.99$. The LOD was calculated with the following equation:

$$LOD = \frac{3d}{S} \quad (1)$$

where d is the standard deviation of the optical signal of the sensor membrane ($d=9.0$) and S is the slope of linear regression for the emission intensities as a function of the concentration of Zn^{2+} ($S=3 \times 10^8$).