Electronic Supplementary Information

Phase-transfer Extraction for the Fast Quantification of Perchlorate Anions in Water

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1. Materials

Chemicals were purchased from Sigma-Aldrich or J&K Scientific and were used without further purification. Anion-free dodecabencylbambus[6]uril (**BnBU**) was prepared according to published procedure.[1] Water was of MilliQ quality unless mentioned otherwise.

The UV/Vis spectral measurements were performed at room temperature using 1-cm quartz cuvettes. The absorption spectra were recorded with a CARY 60 spectrophotometer from Agilent Technologies.

The ^{1}H NMR measurements were performed on a Bruker Avance III 300 spectrometer with working frequency 300.15 MHz, using deuterated chloroform purchased from Aldrich on the highest quality. All experiments were recorded at 303.15 K. NMR chemical Shifts (δ) are reported in ppm using the residual solvent signal as a reference for the measured spectra ($CDCl_3$ - ^{1}H = 7.26 ppm).

2. General procedures

The ability of the different anions and cations to extract **Luc^{2+}** were studied under UV/Vis spectroscopy. Titration experiments were performed where small additions of concentrated solutions of the different salts (Fig. S2 to S14) where added into a two-phase solution of 20 μM **Luc^{2+}** in water and 50 μM **BnBU** in DCM. The disappearance of the dye from water reflects each salt's potential as interference for the determination of perchlorate.

For the extraction experiments, solutions were prepared in 8 mL vials where 0.1 mM stock solution of **Luc**$(NO_3)_2$ was diluted to 3 mL with the sample of interest for a final concentration of 20 μM and its absorbance was measured. Then, 3 mL of 50 μM **BnBU** solution in DCM was added to the vial and it was shaken vigorously on a vortex for 30 seconds in order to mix the two phases. The vial was left aside for 10-15 minutes approximately for the phases to separate before collecting the aqueous phase, which absorbance was measured once more. The difference between initial and final absorbances at 369 nm was employed to calculate the total concentration of perchlorate anions in the sample according to the calibration curve previously obtained (Fig. S6).

In order to perform NMR experiment, a Hamiltonian syringe was employed for the collection of the organic phase, which was dried under vacuum to remove any trace of solvents prior dissolving the remaining solid in deuterated chloroform.

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1. V. Havel and V. Sindelar, ChemPlusChem, 2015, 80, 1601-1606.

3. Extraction experiments

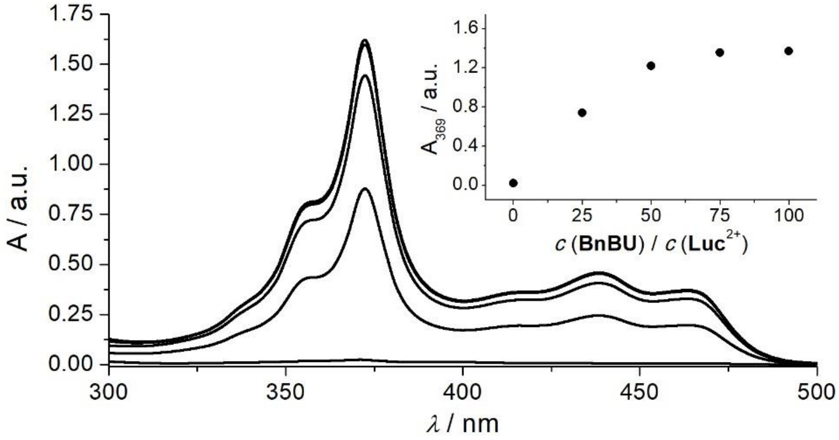


Fig. S1 Changes in the UV-Vis absorption spectra of the dichloromethane layer (3 mL), in the course of the extraction of Lucigenin nitrate from the water phase (3 mL, c(**Luc**(NO_3)$_2$) = 20 µM) upon adding the increasing amount of **BnBU** solution in dichloromethane (c = 20 mM). The extraction experiment showed that at least 75 eq of **BnBU** (1.5 mM) are required to fully dissolve **Luc**(NO_3)$_2$ in dichloromethane due to its high hydrophilicity. For the system proposed in the main text (2.5 eq of **BnBU**) only 5% of **Luc** will be present in the organic phase at the beginning of the experiments.

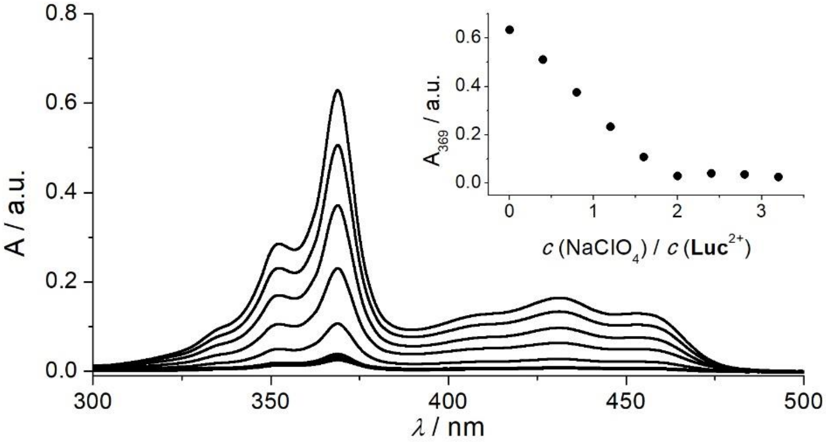


Fig. S2 Changes in the UV-Vis absorption spectra of the aqueous layer (3 mL), in the course of the extraction of **Luc**$^{2+}$ from the water phase (c(**Luc**(NO_3)$_2$) = 20 µM) into organic phase (DCM, c(**BnBU**) = 50 µM) upon adding the increasing amount of $NaClO_4$ solution (c = 5 mM).

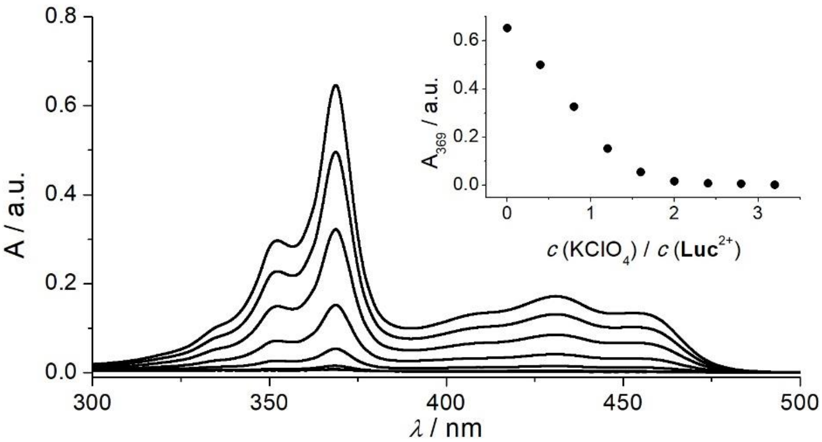


Fig. S3 Changes in the UV-Vis absorption spectra of the aqueous layer (3 mL), in the course of the extraction of **Luc**$^{2+}$ from the water phase (c(**Luc**$(NO_3)_2$) = 20 µM) into organic phase (DCM, c(**BnBU**) = 50 µM) upon adding the increasing amount of $KClO_4$ solution (c = 5 mM).

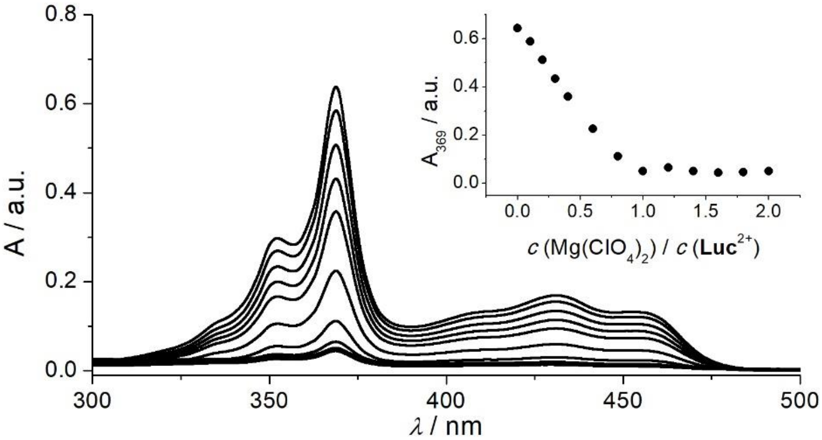


Fig. S4 Changes in the UV-Vis absorption spectra of the aqueous layer (3 mL), in the course of the extraction of **Luc**$^{2+}$ from the water phase (c(**Luc**$(NO_3)_2$) = 20 µM) into organic phase (DCM, c(**BnBU**) = 50 µM) upon adding the increasing amount of $Mg(ClO_4)_2$ solution (c = 2.5 mM).

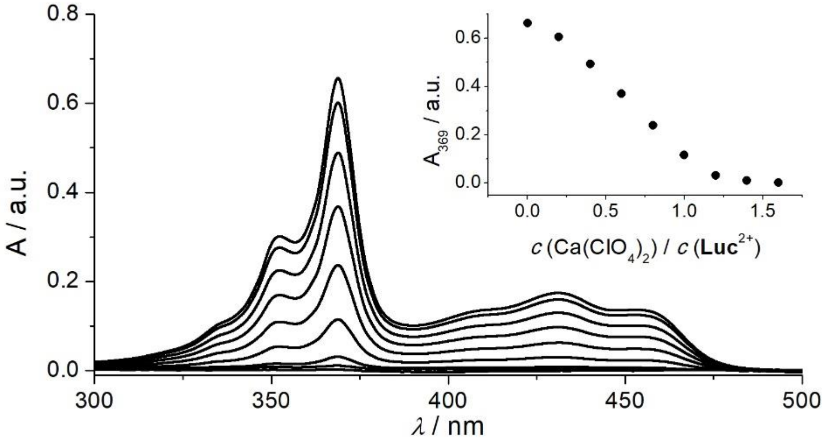
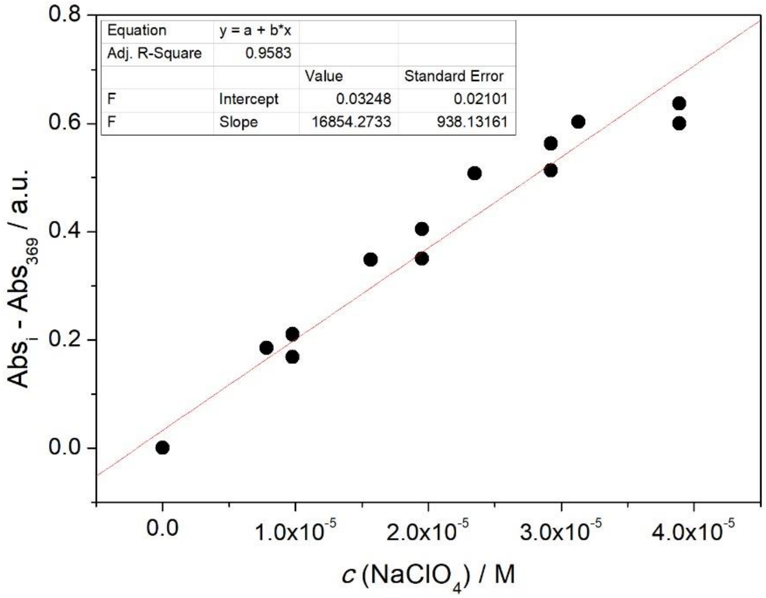


Fig. S5 Changes in the UV-Vis absorption spectra of the aqueous layer (3 mL), in the course of the extraction of **Luc**$^{2+}$ from the water phase (c(**Luc**(NO$_3$)$_2$) = 20 µM) into organic phase (DCM, c(**BnBU**) = 50 µM) upon adding the increasing amount of Ca(ClO$_4$)$_2$ solution (c = 2.5 mM).



Equation	y = a + b*x		
Adj. R-Square	0.9583		
		Value	Standard Error
F	Intercept	0.03248	0.02101
F	Slope	16854.2733	938.13161

Fig. S6 Calibration curve obtained from 3 individual solutions of NaClO$_4$ in pure water at 369 nm. The calibration curved was obtained from the correlation between concentration of NaClO$_4$ added and the difference between Absorbance of **Luc**$^{2+}$ in water before and after addition of NaClO$_4$.

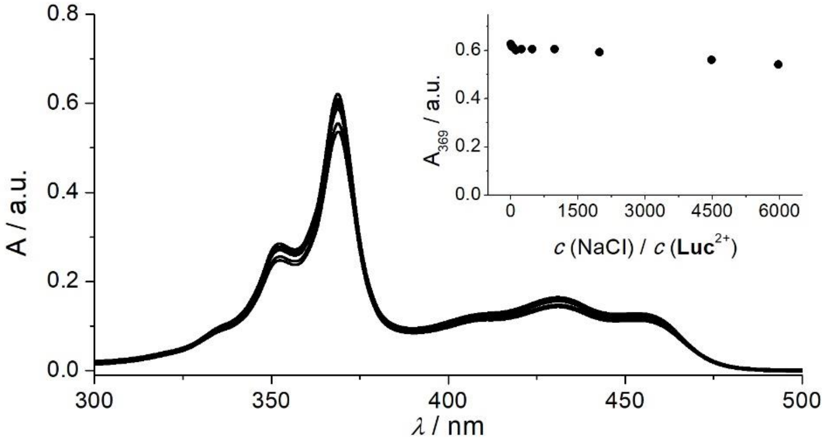


Fig. S7 Changes in the UV-Vis absorption spectra of the aqueous layer (3 mL), in the course of the extraction of **Luc**$^{2+}$ from the water phase (c(**Luc**(NO_3)$_2$) = 20 µM) into organic phase (DCM, c(**BnBU**) = 50 µM) upon adding the increasing amount of NaCl solution (c = 1 M).

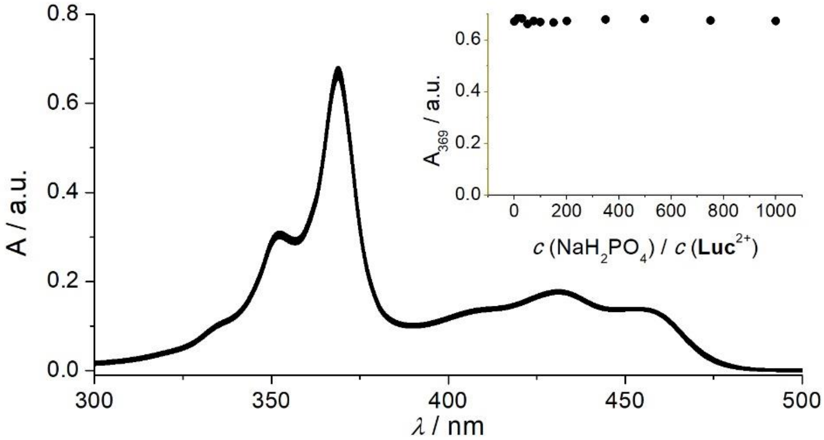


Fig. S8 Changes in the UV-Vis absorption spectra of the aqueous layer (3 mL, pH = 5.9), in the course of the extraction of **Luc**$^{2+}$ from the water phase (c(**Luc**(NO_3)$_2$) = 20 µM) into organic phase (DCM, c(**BnBU**) = 50 µM) upon adding the increasing amount of NaH_2PO_4 solution (c = 0.5 M, pH final = 4.7).

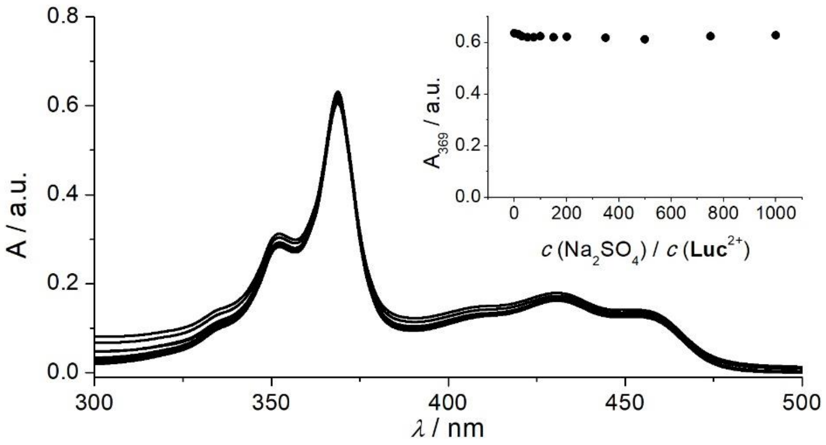


Fig. S9 Changes in the UV-Vis absorption spectra of the aqueous layer (3 mL), in the course of the extraction of **Luc**$^{2+}$ from the water phase (c(**Luc**(NO$_3$)$_2$) = 20 μM) into organic phase (DCM, c(**BnBU**) = 50 μM) upon adding the increasing amount of Na$_2$SO$_4$ solution (c = 0.5 M).

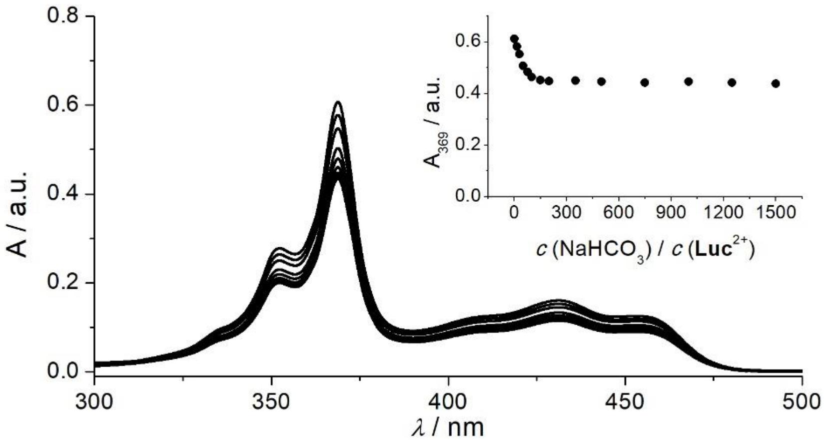


Fig. S10 Changes in the UV-Vis absorption spectra of the aqueous layer (3 mL, pH = 6.0), in the course of the extraction of **Luc**$^{2+}$ from the water phase (c(**Luc**(NO$_3$)$_2$) = 20 μM) into organic phase (DCM, c(**BnBU**) = 50 μM) upon adding the increasing amount of NaHCO$_3$ solution (c = 0.5 M, pH at 150 eq = 8.6, pH final = 8.7).

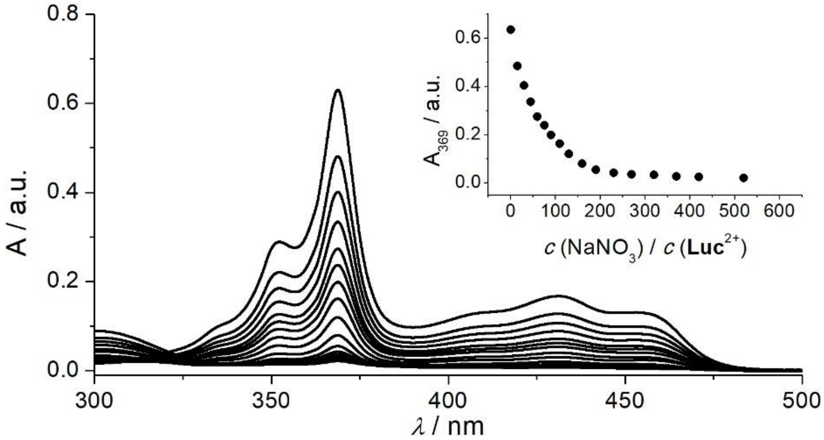


Fig. S11 Changes in the UV-Vis absorption spectra of the aqueous layer (3 mL), in the course of the extraction of **Luc**$^{2+}$ from the water phase (c(**Luc**(NO_3)$_2$) = 20 µM) into organic phase (DCM, c(**BnBU**) = 50 µM) upon adding the increasing amount of $NaNO_3$ solution (c = 0.5 M).

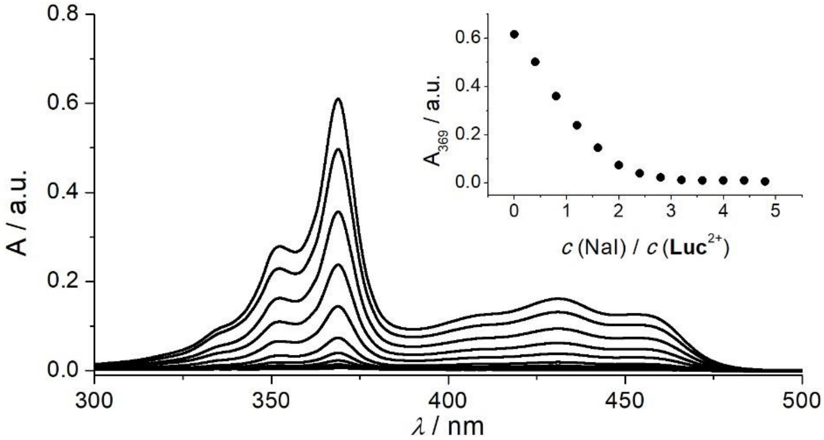


Fig. S12 Changes in the UV-Vis absorption spectra of the aqueous layer (3 mL), in the course of the extraction of **Luc**$^{2+}$ from the water phase (c(**Luc**(NO_3)$_2$) = 20 µM) into organic phase (DCM, c(**BnBU**) = 50 µM) upon adding the increasing amount of NaI solution (c = 5 mM).

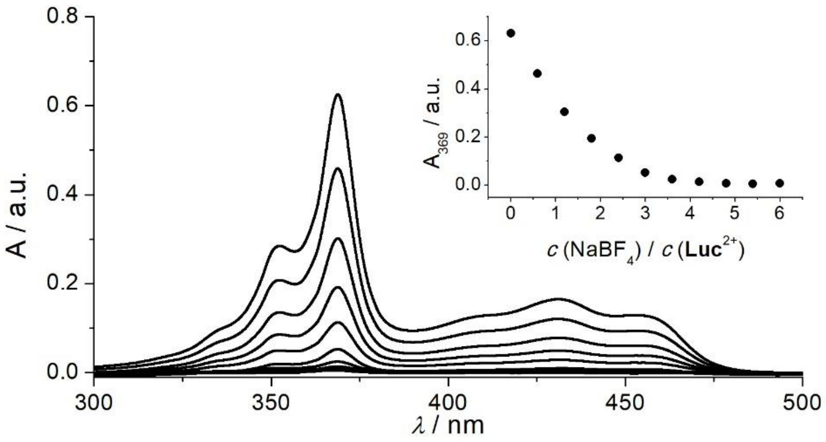


Fig. S13 Changes in the UV-Vis absorption spectra of the aqueous layer (3 mL), in the course of the extraction of **Luc**$^{2+}$ from the water phase (c(**Luc**(NO_3)$_2$) = 20 µM) into organic phase (DCM, c(**BnBU**) = 50 µM) upon adding the increasing amount of $NaBF_4$ solution (c = 15 mM).

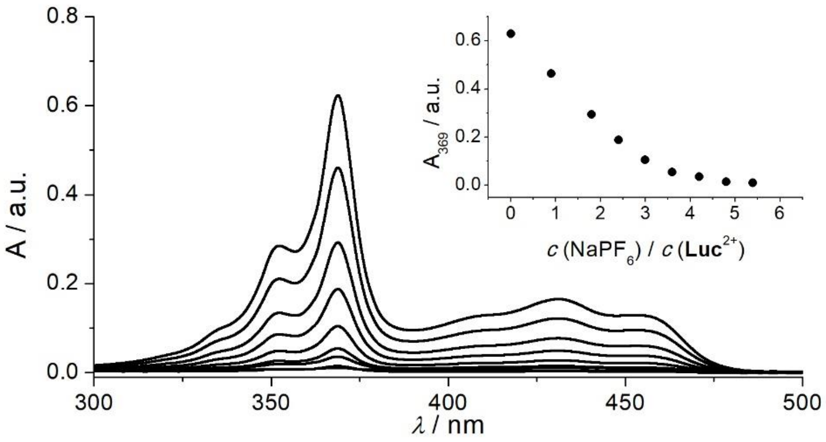


Fig. S14 Changes in the UV-Vis absorption spectra of the aqueous layer (3 mL), in the course of the extraction of **Luc**$^{2+}$ from the water phase (c(**Luc**(NO_3)$_2$) = 20 µM) into organic phase (DCM, c(**BnBU**) = 50 µM) upon adding the increasing amount of $NaPF_6$ solution (c = 15 mM).

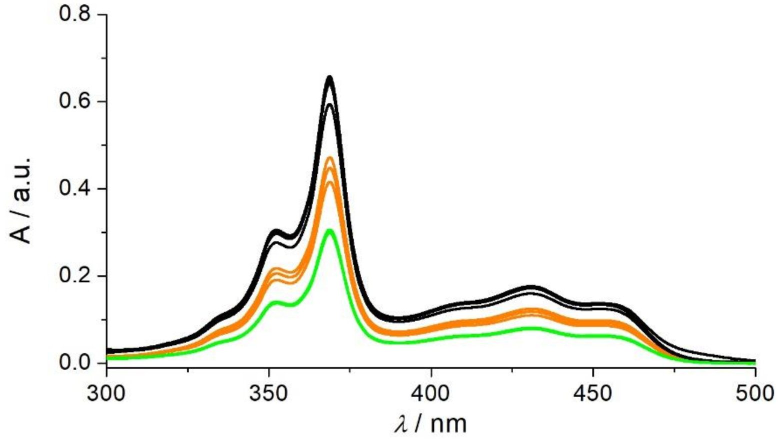


Fig. S15. Overlapped UV-Vis spectra of the aqueous layer (MilliQ water), before (black) and after extraction of **Luc^{2+}** for the 10 (orange) and 20 µM (green) concentrations of perchlorate. All the experiments were done in triplicates.

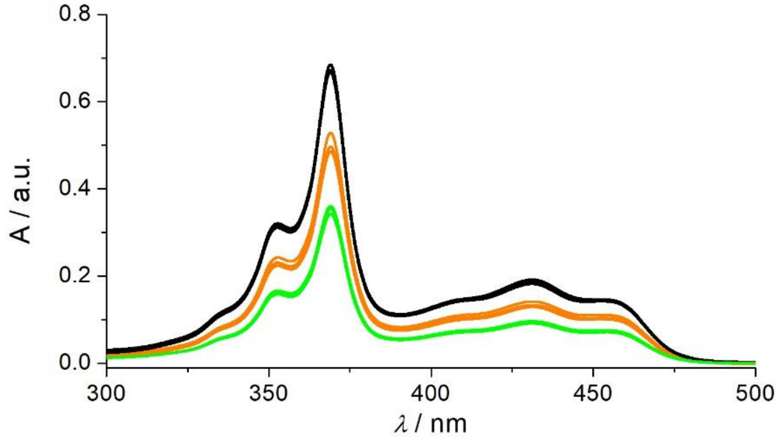


Fig. S16. Overlapped UV-Vis spectra of the aqueous layer (Saline water; *c*(NaCl) = 500 mM), before (black) and after extraction of **Luc^{2+}** for the 10 (orange) and 20 µM (green) concentrations of perchlorate. All the experiments were done in triplicates.

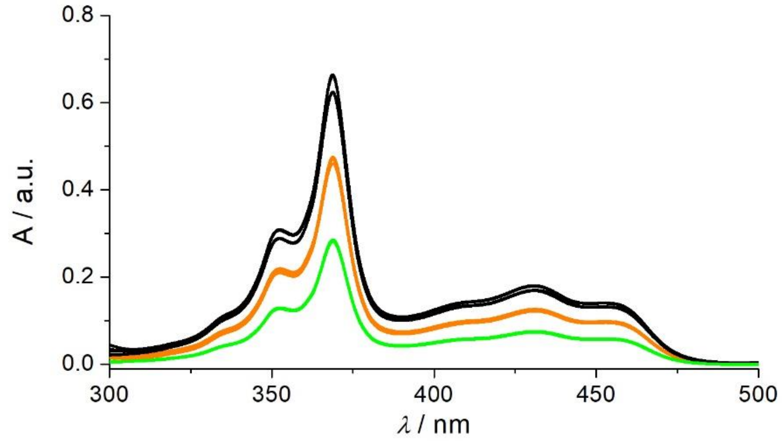


Fig. S17. Overlapped UV-Vis spectra of the aqueous layer (Plasma conditions; *c*(NaCl) = 100 mM, *c*($NaHCO_3$) = 20 mM), before (black) and after extraction of **Luc^{2+}** for the 10 (orange) and 20 µM (green) concentrations of perchlorate. All the experiments were done in triplicates.

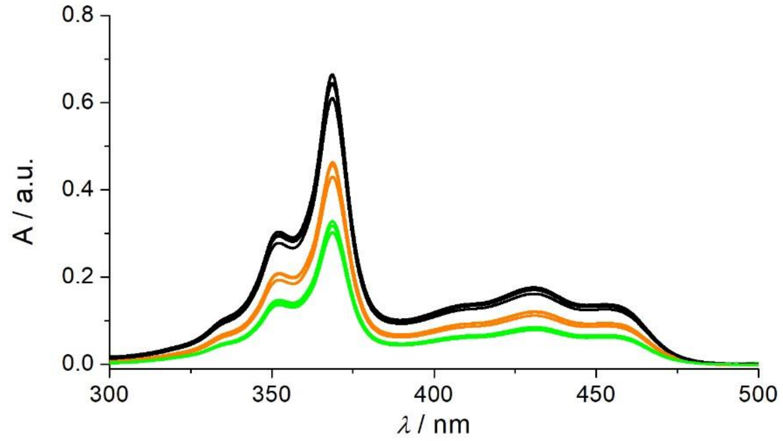


Fig. S18. Overlapped UV-Vis spectra of the aqueous layer (Mixture of salts), before (black) and after extraction of **Luc^{2+}** for the 10 (orange; *c*($CaCl_2$) = 5 µM, *c*(KH_2PO_4) = 10 µM, *c*(Na_2SO_4) = 5 µM, *c*($NaHCO_3$) = 10 µM, *c*($NaNO_3$) = 10 µM, *c*($Mg(ClO_4)_2$) = 5 µM) and 20 µM (green; *c*($CaCl_2$) = 10 µM, *c*(KH_2PO_4) = 20 µM, *c*(Na_2SO_4) = 10 µM, *c*($NaHCO_3$) = 20 µM, *c*($NaNO_3$) = 20 µM, *c*($Mg(ClO_4)_2$) = 10 µM) concentrations of perchlorate. All the experiments were done in triplicates.

In order to determine the concentration of perchlorate in an iodide containing solution, a combination of UV/Vis and NMR spectroscopies are necessary.

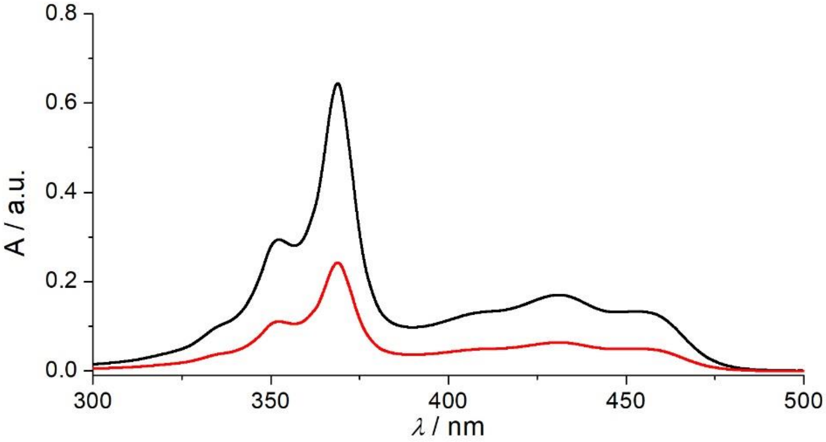


Fig. S19 Absorption spectra of the aqueous phase of the system for the extraction of **Luc**$^{2+}$ (c = 20 µM) from water to **BnBU** solution (DCM, *c* = 50 µM) before (black) and after (red) the addition of an aliquot from a $NaClO_4$: NaI (1:1.5) solution (c_{total} = 5 mM).

The use of the methodology resulted in a 92 % accuracy, as it detected 4.6 mM of total anion concentration in water.

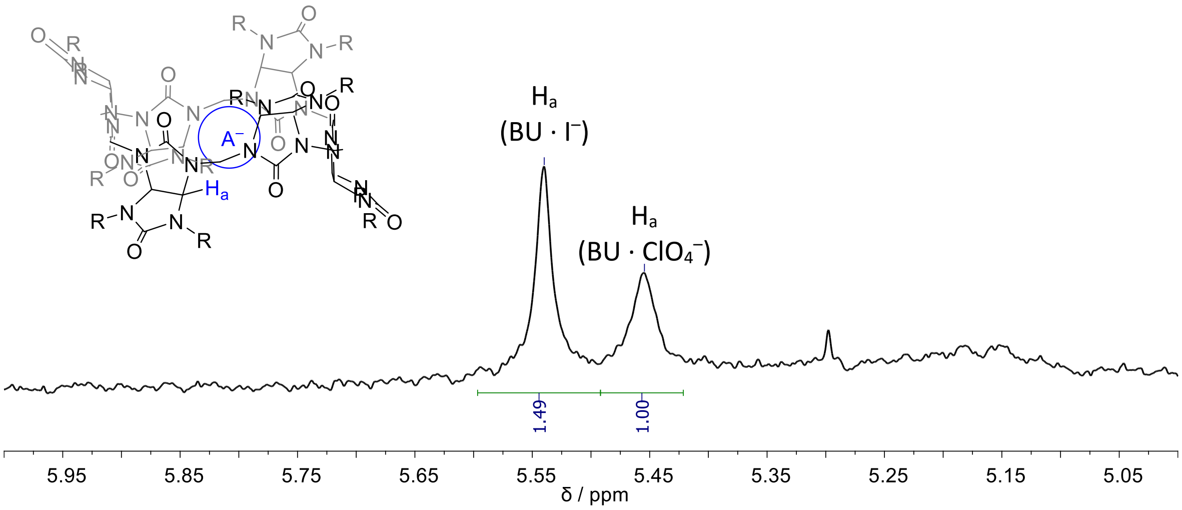


Fig. S20 ^{1}H NMR spectra (300 MHz, $CDCl_3$) of the organic phase of the system after the extraction of **Luc**$^{2+}$ from water with a $NaClO_4$: NaI (1:1.5) solution (c_{total} = 5 mM).

Finally, the NMR spectra showed the ratio between the two anionic species which corresponds to the ratio on the original sample.