# Electronic Supplementary Information

# Selective detection of $Al^{3+}$ and citric acid with a fluorescent amphiphile

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**TABLE OF CONTENTS**

## 1. General

All chemicals and solvents were purchased from standard suppliers and used without further purification. Stock solutions of dye **3** (1 mM) and dye **4** (105 μM) were prepared in 10 mM MOPS buffer (pH 7.0) and stock solution of histidine (100 mM) was prepared in bidistilled water. Stock solutions of analytes (2 mM and 10 mM) were prepared in methanol. $NiCl_2$, $ZnCl_2$, $AlCl_3$, $CuCl_2$, $CaCl_2$, KCl, NaCl, AgCl, $Ga(acac)_3$, $Cd(NO_3)_2$, $Fe(ClO_4)_2$, $Co(C_2H_3O_2)_2$ salts were used to prepare metal stock solutions. All solutions were stored at 4 °C. MOPS buffer (10 mM MOPS buffer, pH 7.0) was prepared by dissolving 3−(N−morpholino) propanesulfonic acid in bidistilled water. HCl and NaOH solutions were used to adjust the pH of the buffer. Fluorescence measurements were performed on a Varian Cary Eclipse fluorescence spectrophotometer at room temperature. Absorption spectra were measured on a Cary 50 bio spectrometer (Varian). Quartz cuvettes were used for the absorbance and fluorescence measurements. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Advance DPX 400 and 800 instruments at 25 °C. Multiplicities of the $^1$H NMR signals are assigned as following: s (singlet), d (doublet), t (triplet), m (multiplet). DLS measurements were performed with Zetasizer nano ZS90 (Malvern) instrument. High resolution mass spectra were recorded with a waters Q−TOF Ultima (ESI−TOF) instrument.

## 2. Syntheses

### Synthesis of Compound 1

Compound **1** was synthesized in a similar fashion as described in the literature:[1] Dodecanoyl chloride (231 μL, 0.97 mmol) was added under $N_2$ to a stirred solution of 2,4-dimethyl pyrrole (200 μL, 1.94 mmol) in dry $CH_2Cl_2$ (50 mL). After 4 h, triethylamine (0.71 mL, 6.31 mmol) and $BF_3xOEt_2$ (0.86 mL, 6.80 mmol) were added. After stirring for 30 minutes, the mixture was washed with water (3 x 50 mL) and dried over $Na_2SO_4$. The solvent was the removed under vacuum and the product was purified by column chromatography ($SiO_2$; eluent: EtOAc:Hexane, 1:20) to give compound **1** as a red solid (210 mg, ~0.52 mmol, ~27%). The product contained small impurities but it was used without further purification. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.81 (t, $J$ = 7.0 Hz, 3 H, $CH_3$), 1.16−1.30 (m, 14 H, $CH_2$), 1.35−1.46 (m, 2 H, $CH_2$), 1.49−1.59 (m, 2 H, $CH_2$), 2.32 (s, 6 H, $CH_3$), 2.43 (s, 6 H, $CH_3$),

2.80−2.86 (m, 2 H, $CH_2$), 5.96 (s, 2 H, CH) . ESI−MS calcd. for $C_{24}H_{37}BF_2N_2$ [(M+H)] m/z = 403.3101 found 403.3109.

**Synthesis of Compound 2**

Compound **2** was synthesized in a similar fashion as described in the literature:[1] Stearoyl chloride (490 μL, 1.46 mmol) was added under $N_2$ to a stirred solution of 2,4-dimethyl pyrrole (300 μL, 2.91 mmol) in dry $CH_2Cl_2$ (100 mL). After 4 h, triethylamine (1.01 mL, 7.28 mmol) and $BF_3xOEt_2$ (1.29 mL, 10.2 mmol) were added. After stirring for 30 minutes, the mixture was washed with water (3 x 100 mL) and dried over $Na_2SO_4$. The solvent was the removed under vacuum and the product was purified by column chromatography ($SiO_2$; eluent: EtOAc:Hexane, 1:20) to give compound **2** as a red solid (354 mg, ~0.73 mmol, ~25%). The product contained small impurities but it was used without further purification. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 0.81 (t, $J$ = 7.0 Hz, 3 H, $CH_3$), 1.18−1.32 (m, 26 H, $CH_2$), 1.36−1.46 (m, 2 H, $CH_2$), 1.51−1.61 (m, 2 H, $CH_2$), 2.34 (s, 6 H, $CH_3$), 2.44 (s, 6 H, $CH_3$), 2.83−2.89 (m, 2 H, $CH_2$), 5.98 (s, 2 H, CH) . ESI−MS calcd. for $C_{30}H_{49}BF_2N_2Na$ [(M+Na)] m/z = 509.3860 found 509.3844.

## 3. UV and fluorescence measurements

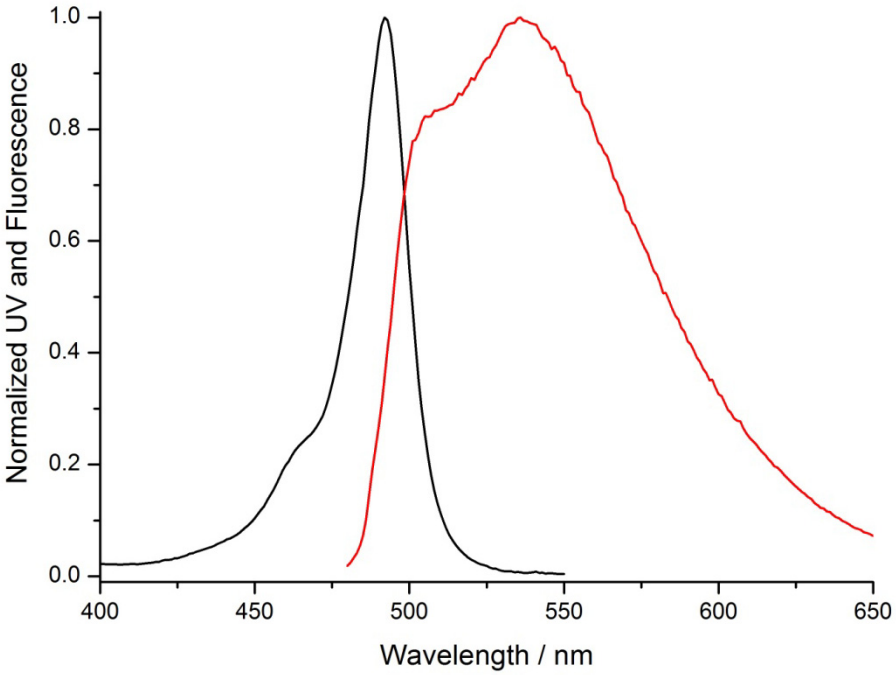


**Figure S1.** Normalized UV (black) and fluorescence (red) spectra ($\lambda_{ex}$: 490 nm) of buffered aqueous solutions (10 mM MOPS, pH 7.0) containing dye **3** (4.0 µM).

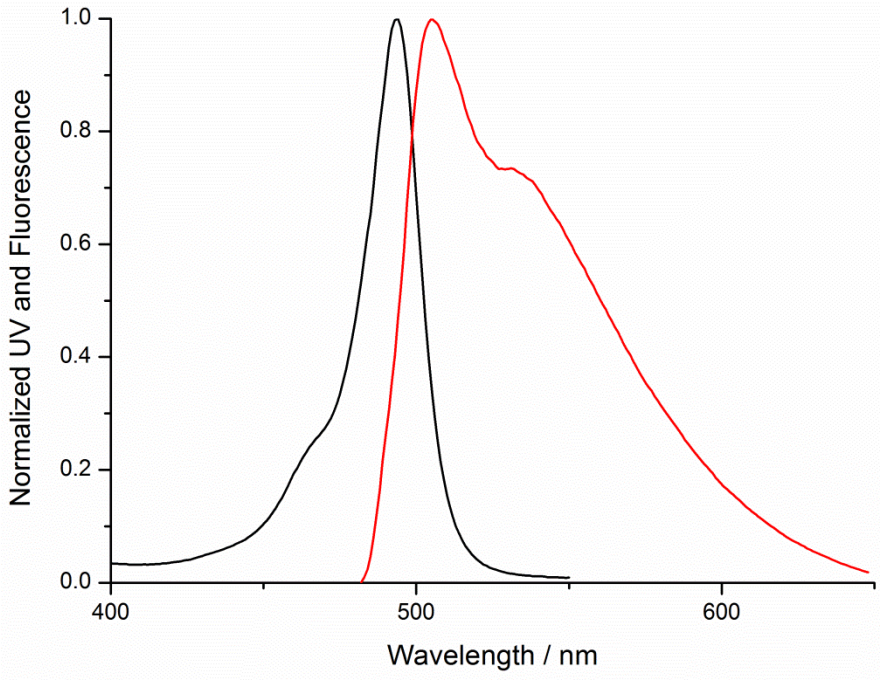


**Figure S2.** Normalized UV (black) and fluorescence (red) spectra ($\lambda_{ex}$: 490 nm) of buffered aqueous solutions (10 mM MOPS, pH 7.0) containing dye **4** (4.0 µM).

## 4. Determination of the critical micelle concentration (cmc)

A stock solution of dye **4** (105 µM) was prepared in 10 mM MOPS buffer (pH 7.0). Aliquots of the stock solutions of dye **4** were diluted with MOPS buffer (10 mM MOPS, pH 7.0). The fluorescence spectra of the resulting solutions were recorded at RT ($\lambda_{ex}$: 490 nm). The fluorescence emission maxima of solutions of dye **4** shift from 504 to 534 nm upon increasing the concentration from 0.21 to 105 µM (Fig. 1 in the main text). The cmc was determined by linear extrapolation as described in the literature.[2] A value of cmc = 20 µM was obtained (Fig. 1 in the main text). For dye **3**, no evidence for aggregation was observed in the concentration range between 1 µM and 1 mM.

## 5. Dynamic light scattering (DLS) measurements and Nile Red study

For the DLS measurements, a solution of dye **4** (50 µM) in buffer (10 mM MOPS, pH 7.0) was prepared and then filtered (PTFE filter, 0.22 µM). The solution contained polydisperse aggregates according to the measurements, but the results met the data quality criteria. For dye **3**, we were not able to detect aggregate by DLS.

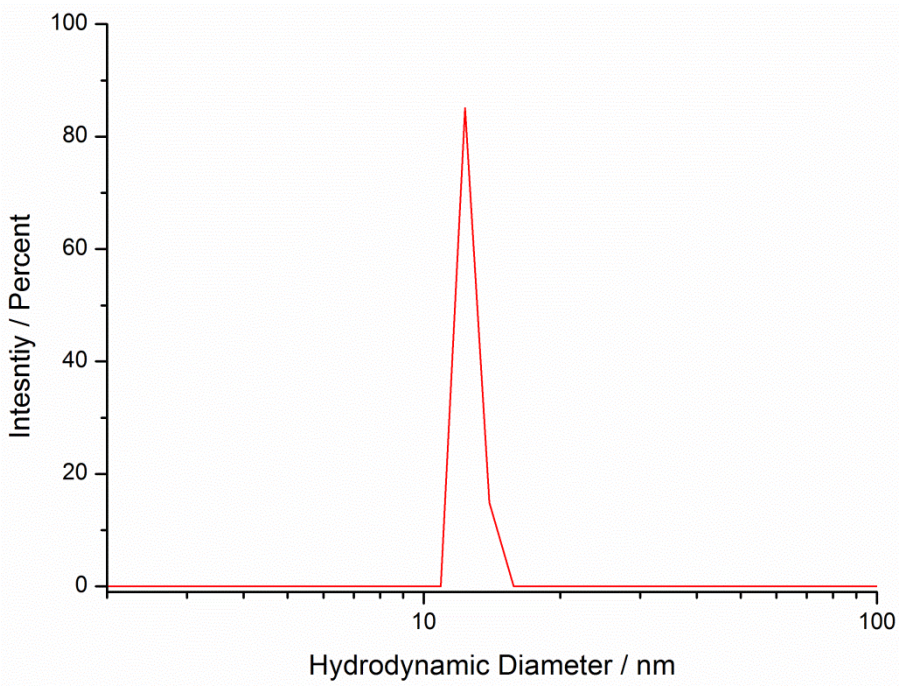


**Figure S3.** The size distribution of dye **4** aggregates as determined by DLS (average size is ~ 13 nm)

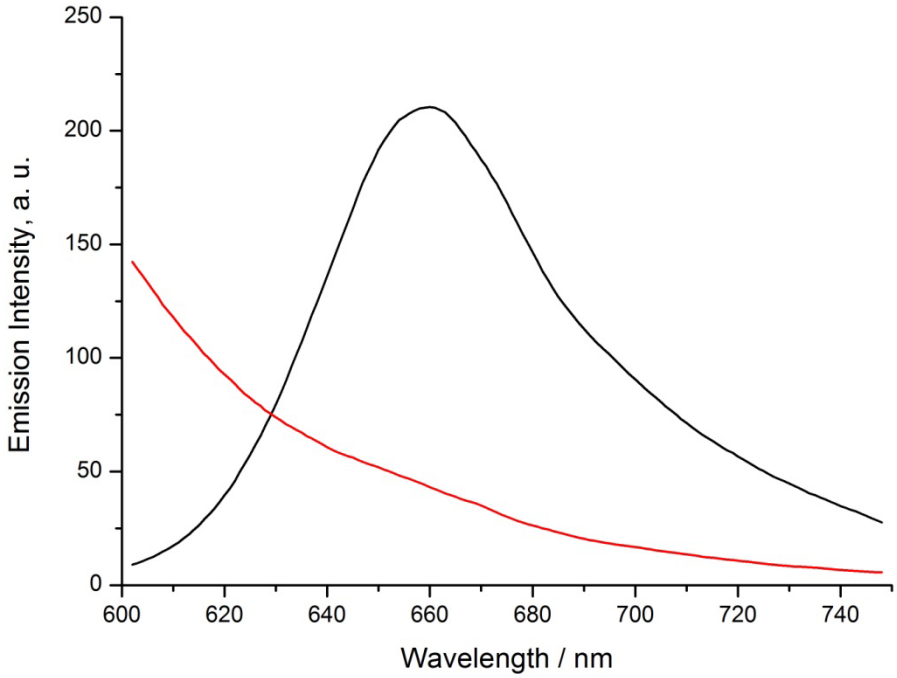


**Figure S4.** Fluorescence spectra ($\lambda_{ex}$: 520 nm) of buffered aqueous solutions (10 mM MOPS, pH 7.0) of Nile Red (6.0 μM) and dye **4** (4.0 μM) in the absence (red) and in the presence (black) of $Al^{3+}$ (60 μM).

## 6. Sensing Studies

Stock solutions of dye **3** (1.0 mM) and dye **4** (105 μM) were prepared in MOPS buffer (10 mM, pH 7.0) and stock solutions of the metal salts ($NiCl_2$, $ZnCl_2$, $AlCl_3$, $CuCl_2$, $Cd(NO_3)_2$: 2 mM; $NiCl_2$, $ZnCl_2$, $AlCl_3$, $CuCl_2$, $CaCl_2$, KCl, NaCl, AgCl, $Ga(acac)_3$, $Cd(NO_3)_2$, $Fe(ClO_4)_2$, $Co(C_2H_3O_2)_2$: 10 mM) were prepared in methanol. Stock solutions of histidine (100 mM) and carboxylic acid analytes (citric acid: 20 mM; citric acid, adipic acid, aspartic acid, glutamic acid, lactic acid, maleic acid, succinic acid, tartaric acid: 100 mM) were prepared in bidistilled water. The samples were prepared by mixing aliquots of the corresponding stock solutions with MOPS buffer in quartz cuvettes. The final volume of all samples was 1.5 mL. The fluorescent signal was measured 3 minutes after sample preparation. A Varian Cary Eclipse fluorescence spectrophotometer was employed for these measurements. Dye **3** (4.0 μM) was used in control experiments with the same analytes. A mixture of dye **4** (4.0 μM) and $AlCl_3$ (120 μM) in buffered aqueous solutions (10 mM MOPS, pH 7.0) was used as a sensing system for citric acid detection.

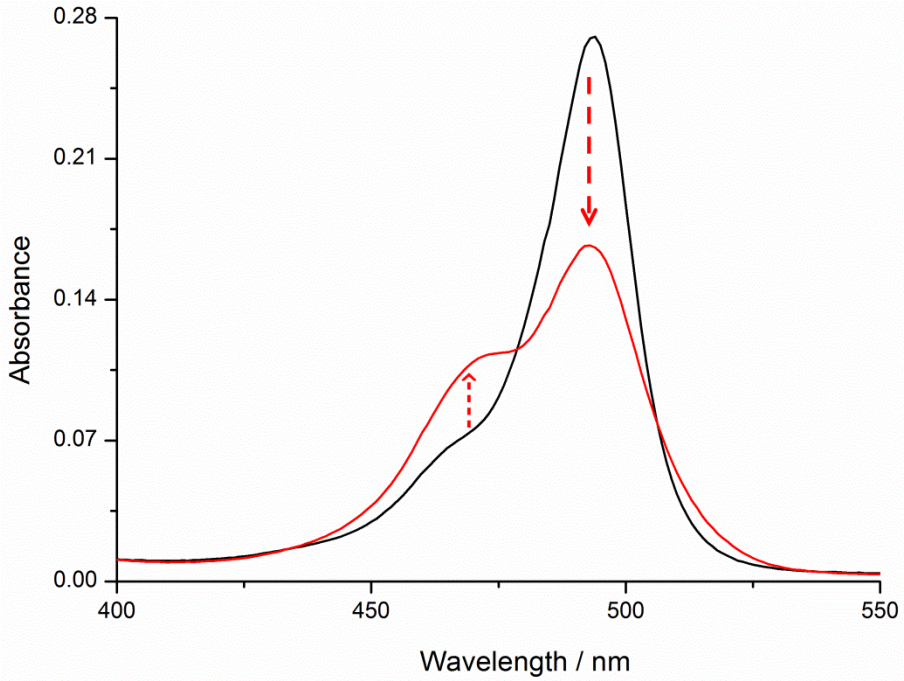


**Figure S5.** Absorption spectra of buffered aqueous solutions (10 mM MOPS, pH 7.0, $H_2O$ with 0.6 vol% MeOH) containing dye **4** (4.0 μM) and histidine (5.0 mM) in the absence (black) and in the presence (red) of $Al^{3+}$ (60 μM).

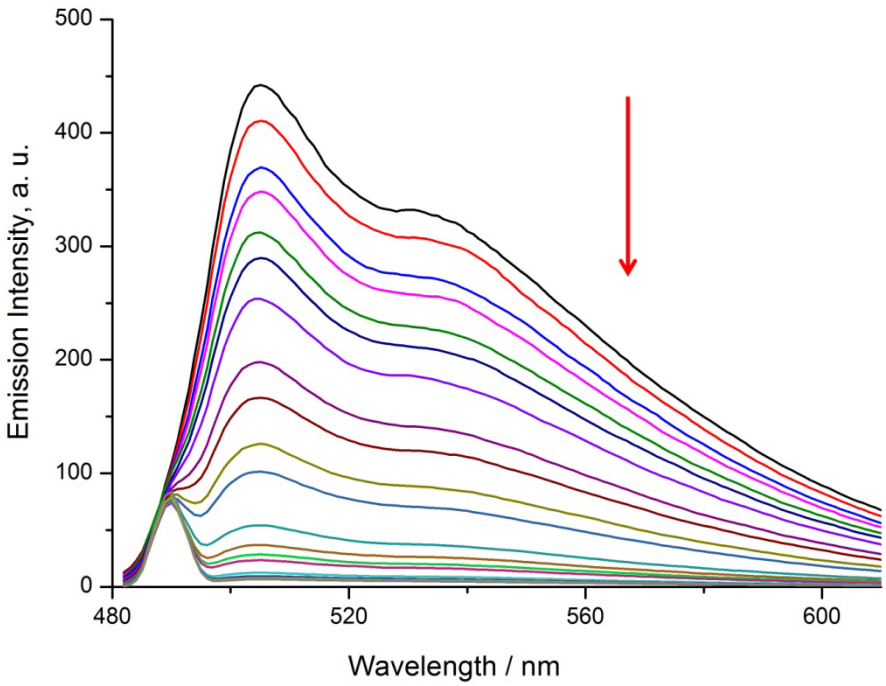


**Figure S6.** Fluorescence emission spectra ($\lambda_{ex}$ = 490 nm) of buffered aqueous solutions (10 mM MOPS, pH 7.0, $H_2O$ with 0−1.3 vol% MeOH) containing dye **4** (4.0 μM), histidine (5.0 mM), and different amounts of $Al^{3+}$ (0−156 μM).

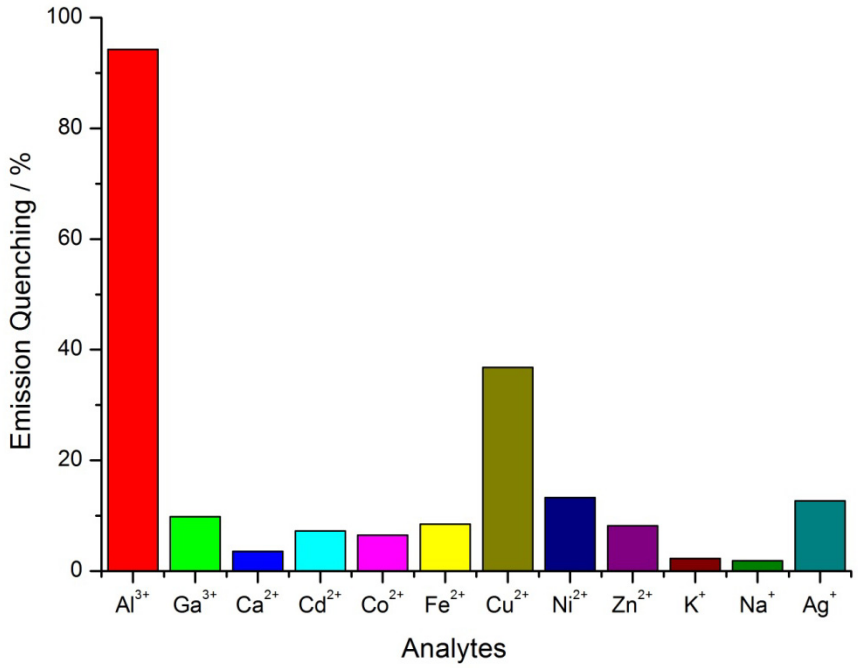


**Figure S7.** Fluorescence emission quenching ($\lambda_{ex}$ = 490 nm; $\lambda_{em}$ = 505 nm) of buffered aqueous solutions (10 mM MOPS, pH 7.0, $H_2O$ with 0.6 vol% MeOH) of dye **4** (4.0 μM) in the presence of different metal cations (60 μM).

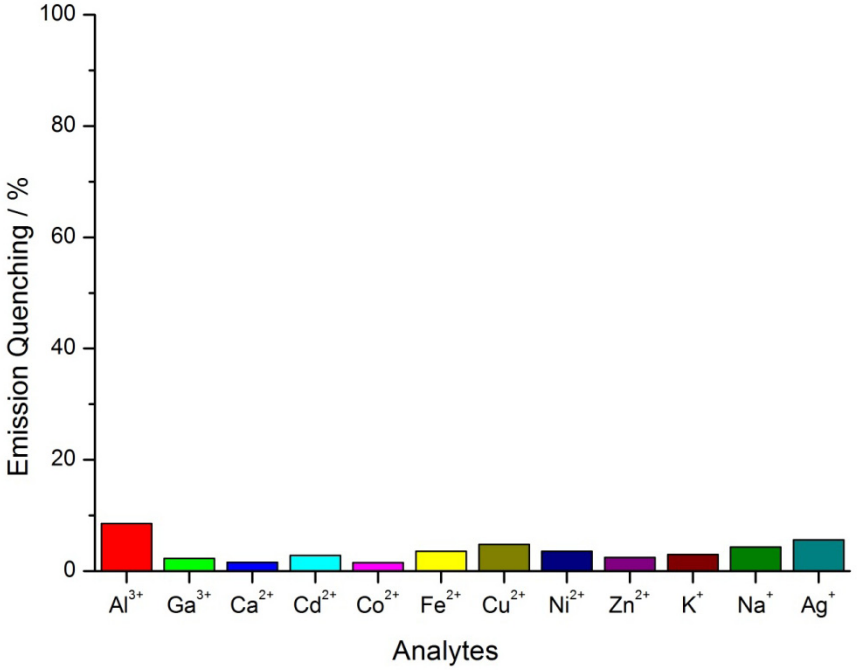


**Figure S8.** Fluorescence emission quenching ($\lambda_{ex}$ = 490 nm; $\lambda_{em}$ = 505 nm) of buffered aqueous solutions (10 mM MOPS, pH 7.0, $H_2O$ with 0.6 vol% MeOH) of dye **3** (4.0 μM) in the presence of different metal cations (60 μM).

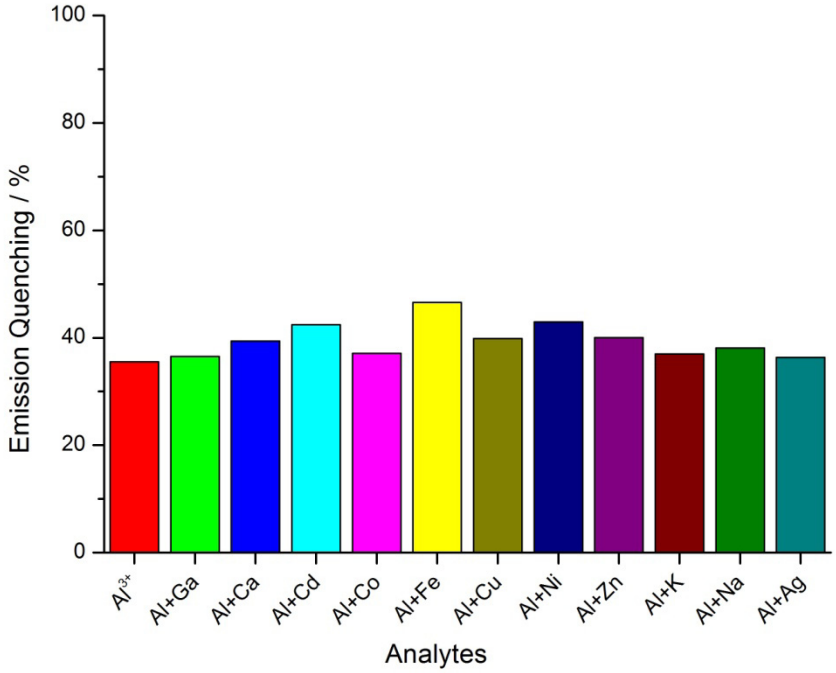


**Figure S9.** Fluorescence emission quenching ($\lambda_{ex}$ = 490 nm; $\lambda_{em}$ = 505 nm) of buffered aqueous solutions (10 mM MOPS, pH 7.0, $H_2O$ with 0.4 vol% MeOH) containing dye **4** (4.0 μM), histidine (5.0 mM), $Al^{3+}$ (20 μM) and different metal cations (20 μM).

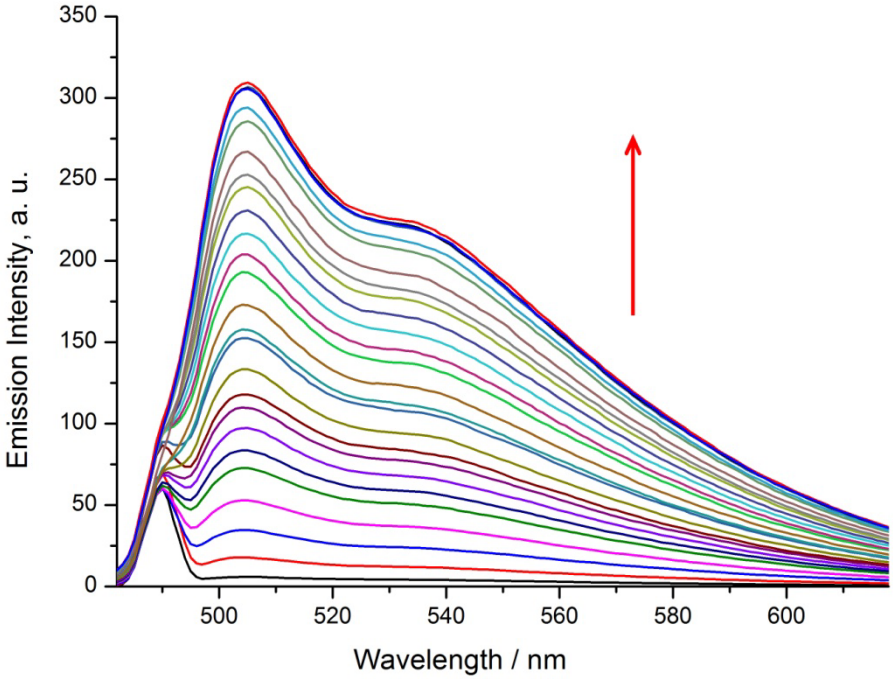


**Figure S10.** Fluorescence emission spectra ($\lambda_{ex}$ = 490 nm; $\lambda_{em}$ = 505 nm) of buffered aqueous solutions (10 mM MOPS, pH 7.0, $H_2O$ with 1.2 vol% MeOH) containing dye **4** (4.0 μM), $Al^{3+}$ (120 μM), and different amounts of citric acid (0−400μM).

## 7. Determination of Citric Acid in Commercial Beverages

The following commercial beverages were used for study: energy drink 1 (Denner energy drink), energy drink 2 (Migros energy drink, sugar free), energy drink 3 (Red Bull, sugar free), soft drink (Yedigun from Pepsi Co.), ice tea (Lipton ice tea, peach), mineral water (Henniez drinking water).

$^1$H NMR spectroscopy in combination with isopropanol as internal standard was used to determine the concentration of citric acid in the samples. First, a reference sample containing 50 mM citric acid and 50 mM isopropanol in a mixture of $H_2O$ and $D_2O$ (9:1) was analyzed by $^1$H NMR spectroscopy. The citric signals at 2.75 ppm and 2.97 ppm and the isopropanol signal at 1.10 ppm were integrated as a calibration set. For the analysis of the beverages, we have mixed 0.9 mL of the respective drink with 0.10 mL of $D_2O$ and 3.85 µL of isopropanol ($conc._{final}$ = 50 mM). The concentration of citric acid was then determined by integration of the citric acid and isopropanol peaks while taking into account the relative signal intensities of the reference sample. Three independent measurements were performed for each sample. A representative spectrum for each type of sample is shown in Figures S15−S21.

For the fluorescence measurements, we have added 5.0 µL of the respective beverage to buffered aqueous solutions (10 mM MOPS, pH 7.0, $H_2O$ with 1.2 vol% MeOH, final volume: 1.5 mL) containing dye **4** (4.0 µM) and $AlCl_3$ (120 µM). After 3 minutes, a fluorescence spectrum was recorded and the emission intensity at 505 nm was determined ($\lambda_{ex}$ = 490 nm). The signal intensity was converted into a concentration value by using the calibration curve shown in the main text (Fig. 4). Three independent measurements were performed for each sample.

## 8. NMR Spectra

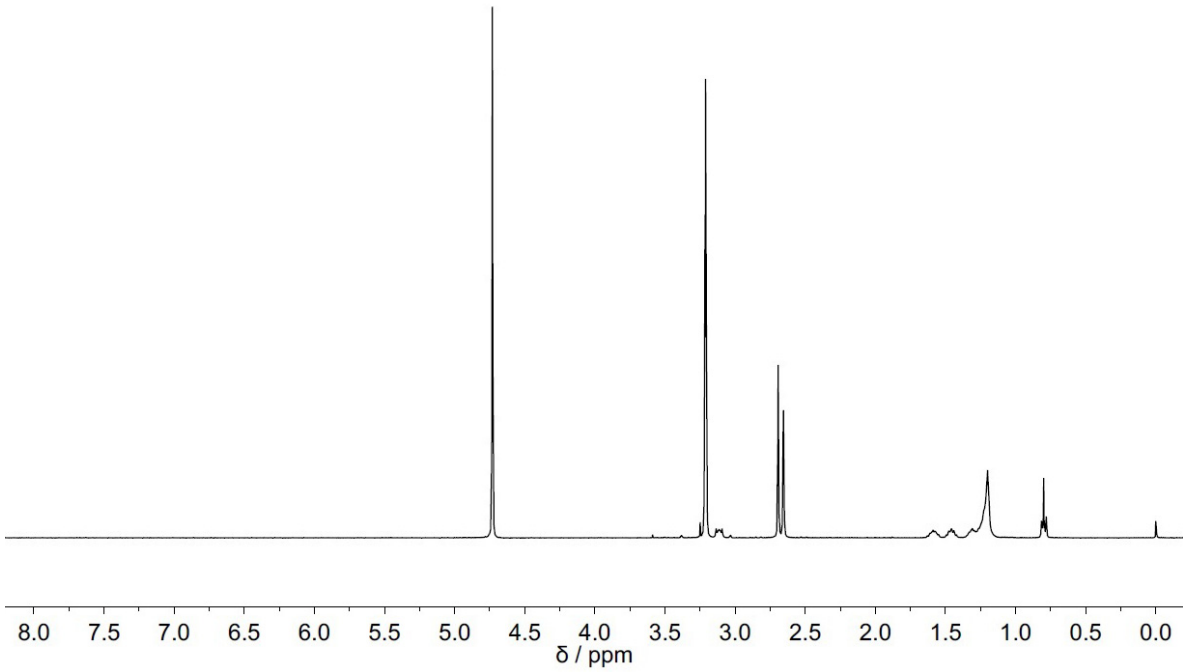


**Figure S11.** $^{1}$H NMR (400 MHz, $CD_3OD$) spectrum of dye **3**. The peaks at 3.25 ppm and 4.75 ppm correspond to the solvent.

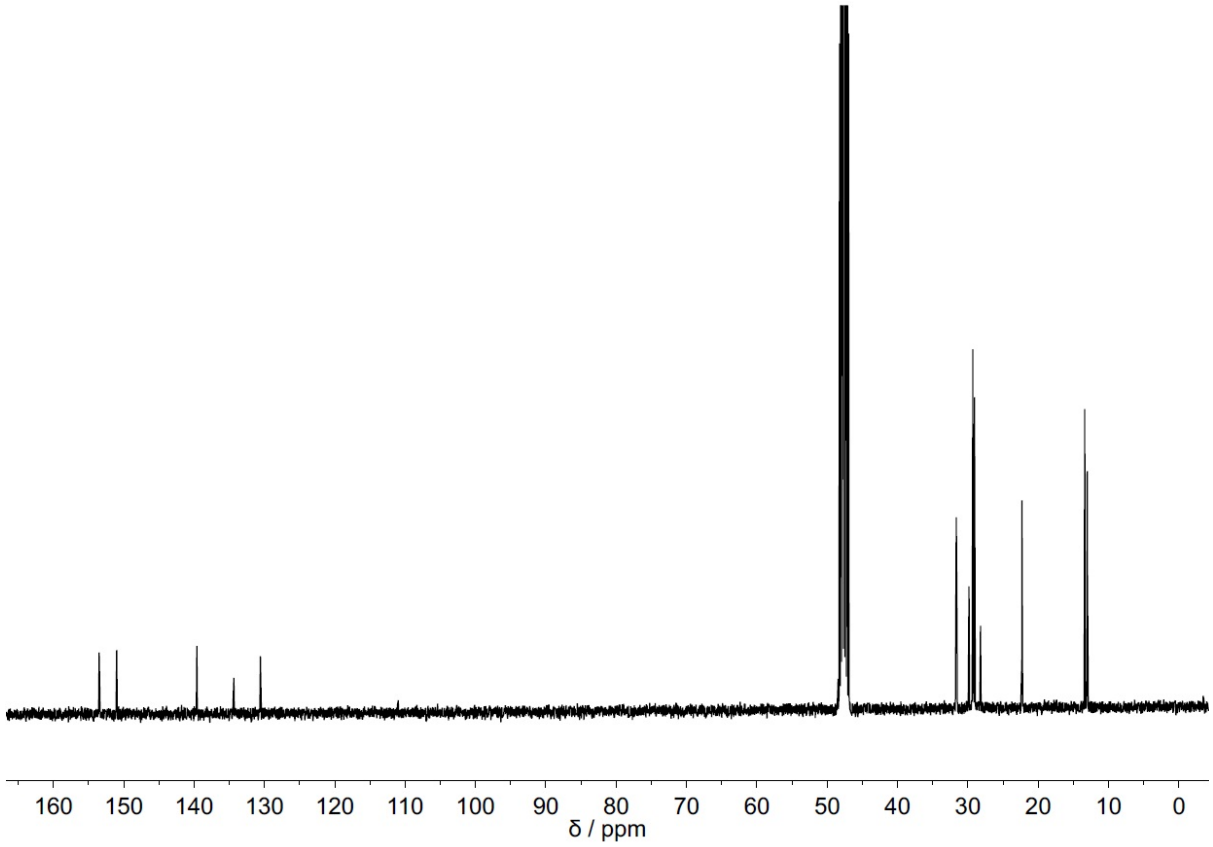


**Figure S12.** $^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of dye **3**. The peak at 49 ppm corresponds to the solvent.

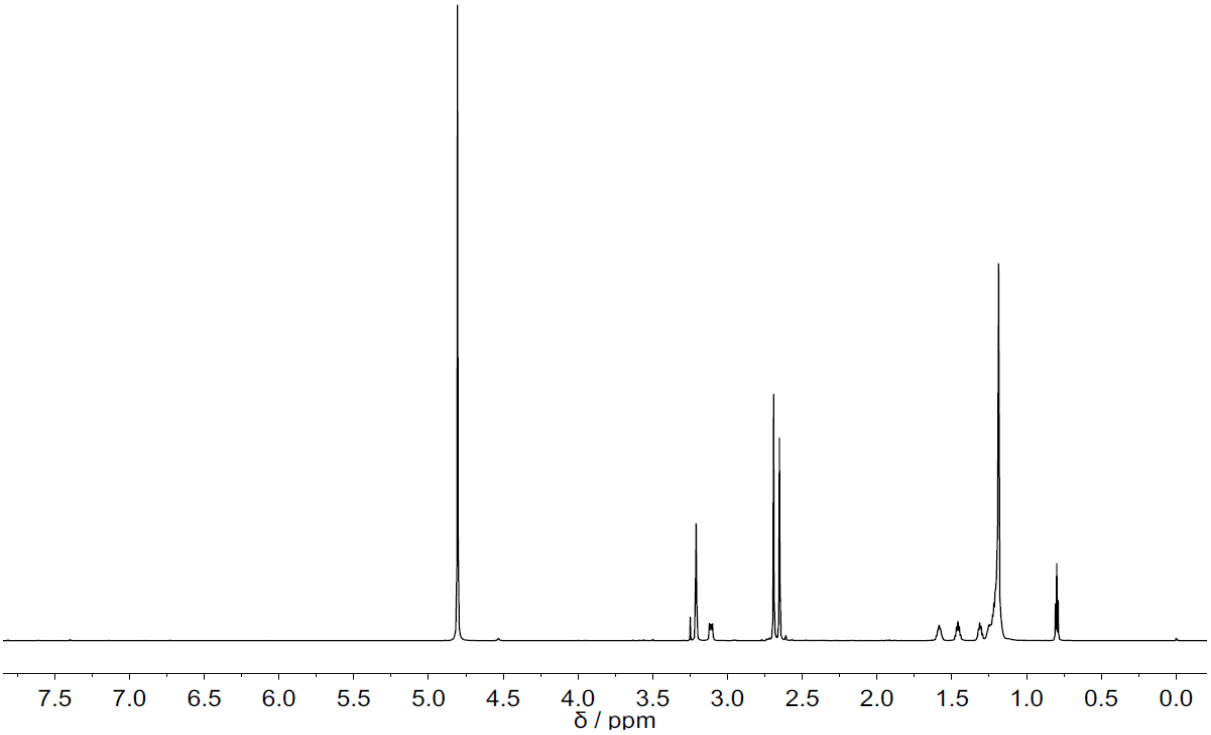


**Figure S13.** $^{1}$H NMR (800 MHz, $CD_3OD$) spectrum of dye **4**. The peaks at 3.25 ppm and 4.75 ppm correspond to the solvent.

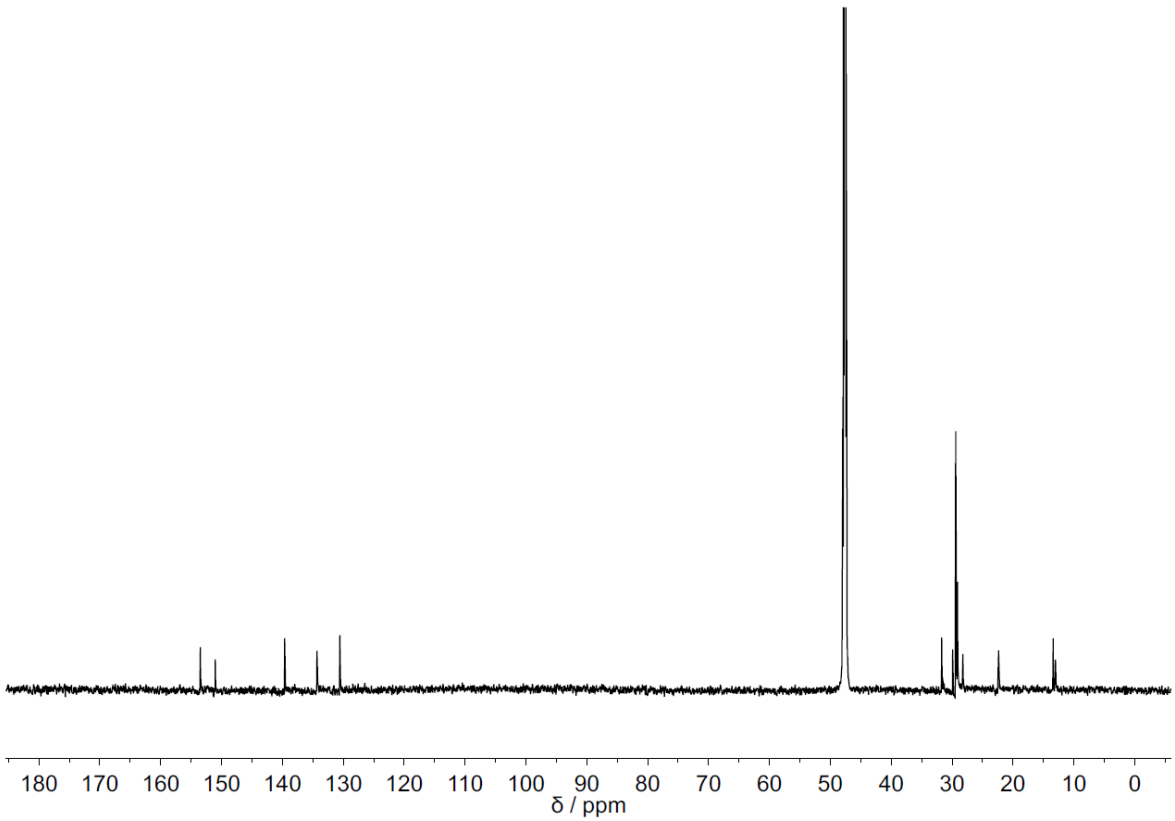


**Figure S14.** $^{13}$C NMR (200 MHz, $CDCl_3$) spectrum of dye **4**. The peak at 49 ppm corresponds to the solvent.

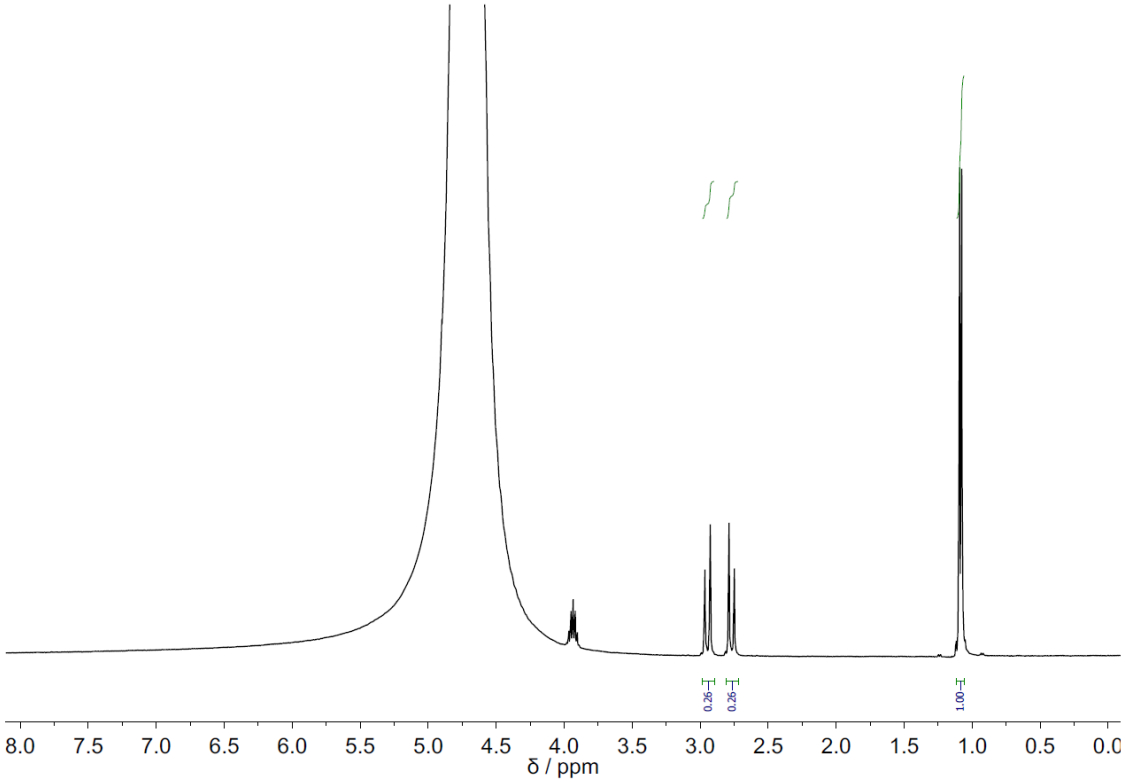


**Figure S15.** $^{1}$H NMR (400 MHz, 90% $H_2O$ : 10% $D_2O$) spectrum of citric acid (50 mM) and isopropanol (50 mM, 3.85 µL). The peak at 4.75 ppm corresponds to the solvent.

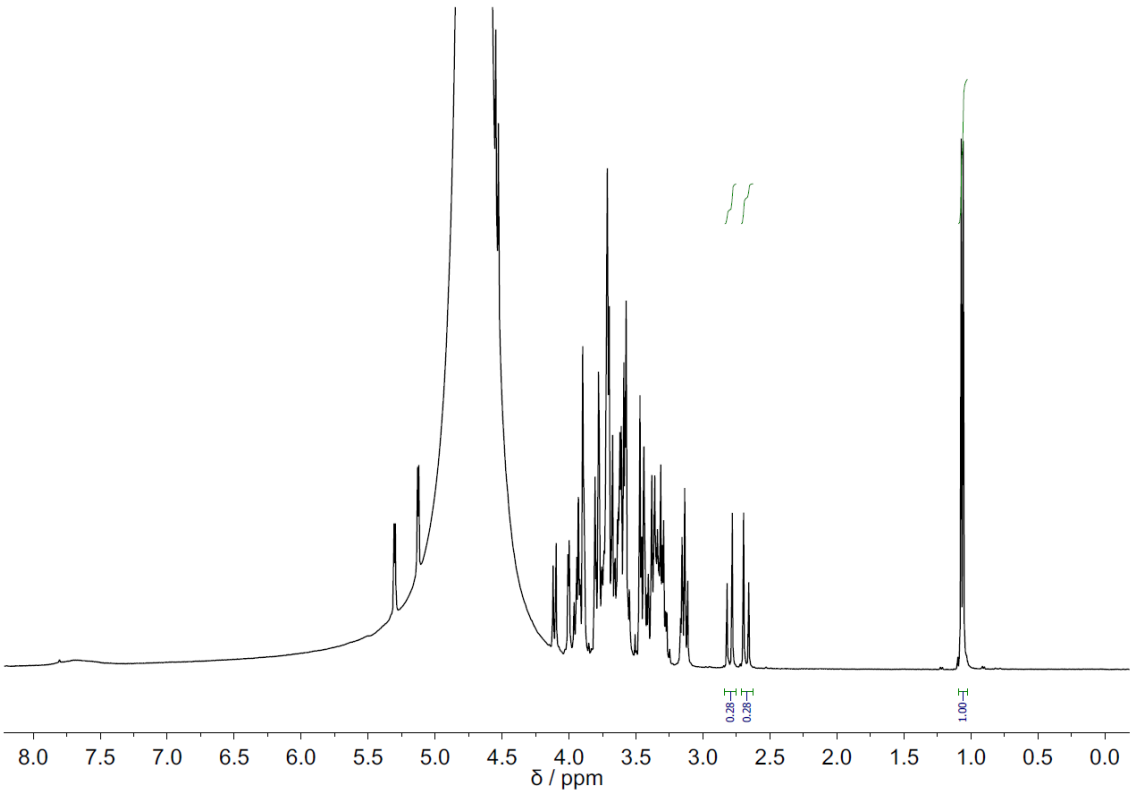


**Figure S16.** $^{1}$H NMR (400 MHz) spectrum of a solution containing energy drink 1 (90%), $D_2O$ (10%) and isopropanol (50 mM, 3.85 µL). The peak at 4.75 ppm corresponds to the solvent.

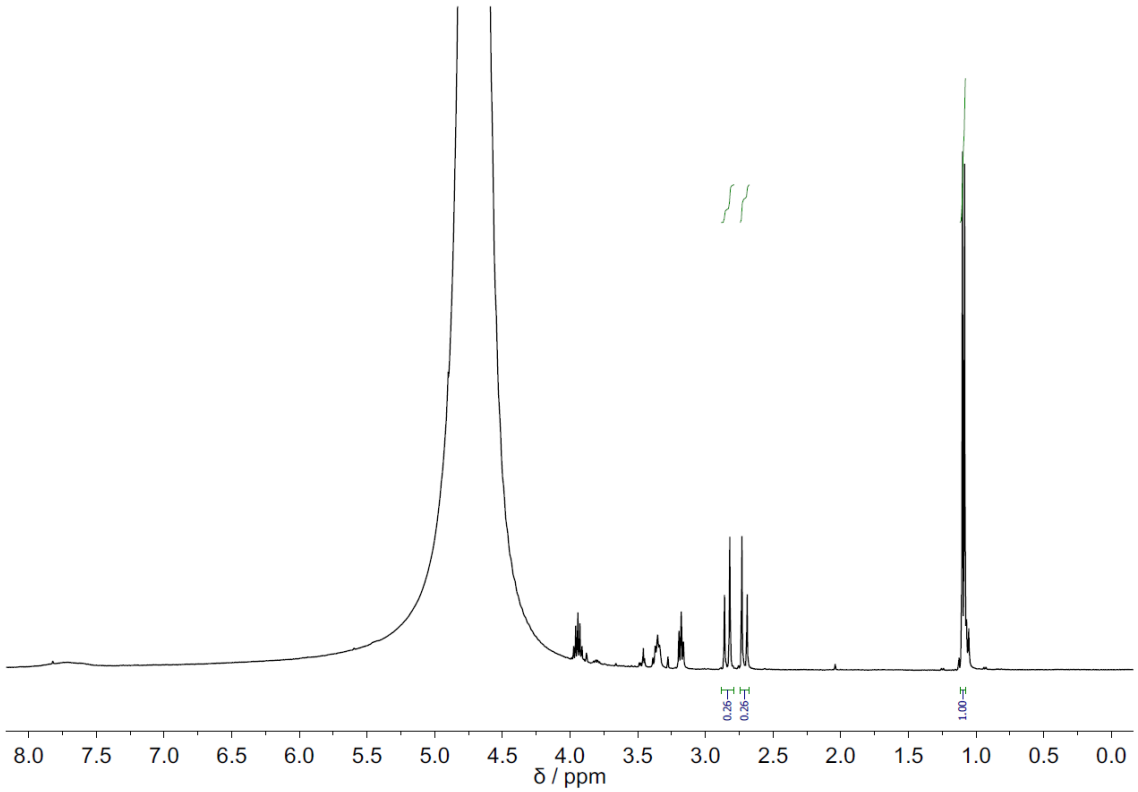


**Figure S17.** $^{1}$H NMR (400 MHz) spectrum of a solution containing energy drink 2 (90%), $D_2O$ (10%) and isopropanol (50 mM, 3.85 µL). The peak at 4.75 ppm corresponds to the solvent.

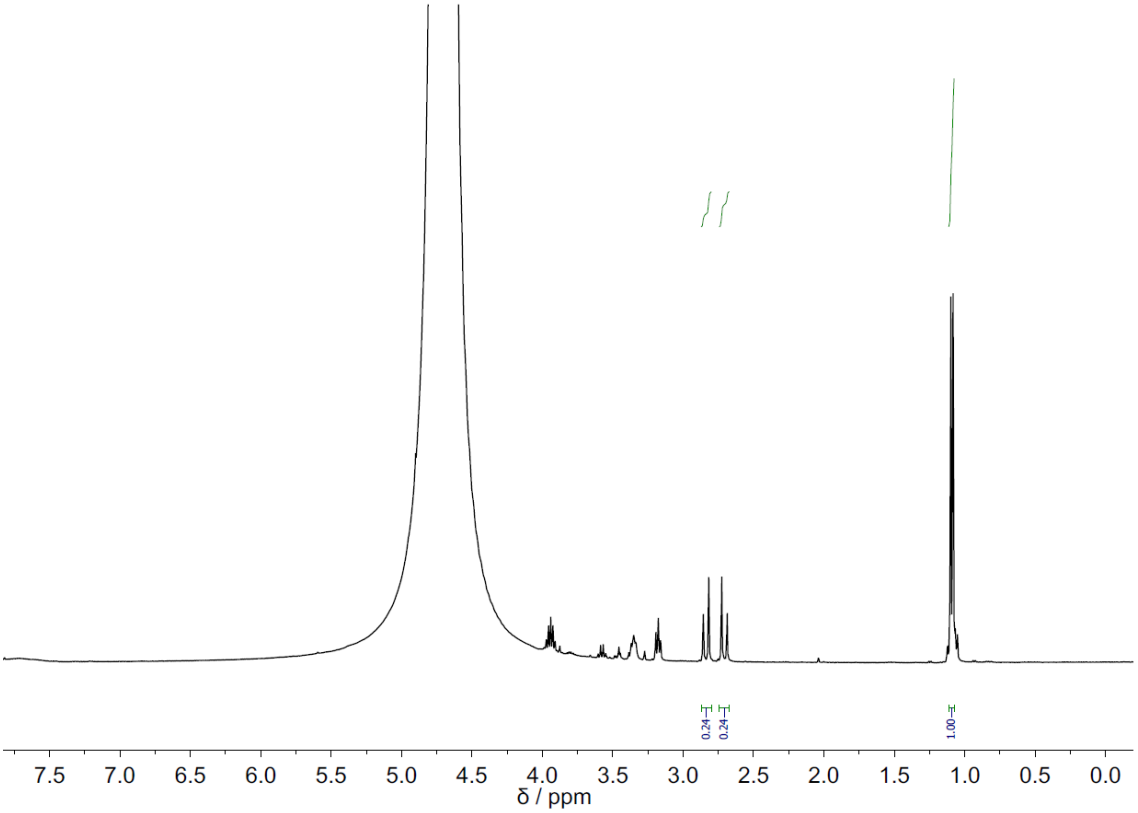


**Figure S18.** $^{1}$H NMR (400 MHz) spectrum of a solution containing energy drink 3 (90%), $D_2O$ (10%) and isopropanol (50 mM, 3.85 µL). The peak at 4.75 ppm corresponds to the solvent.

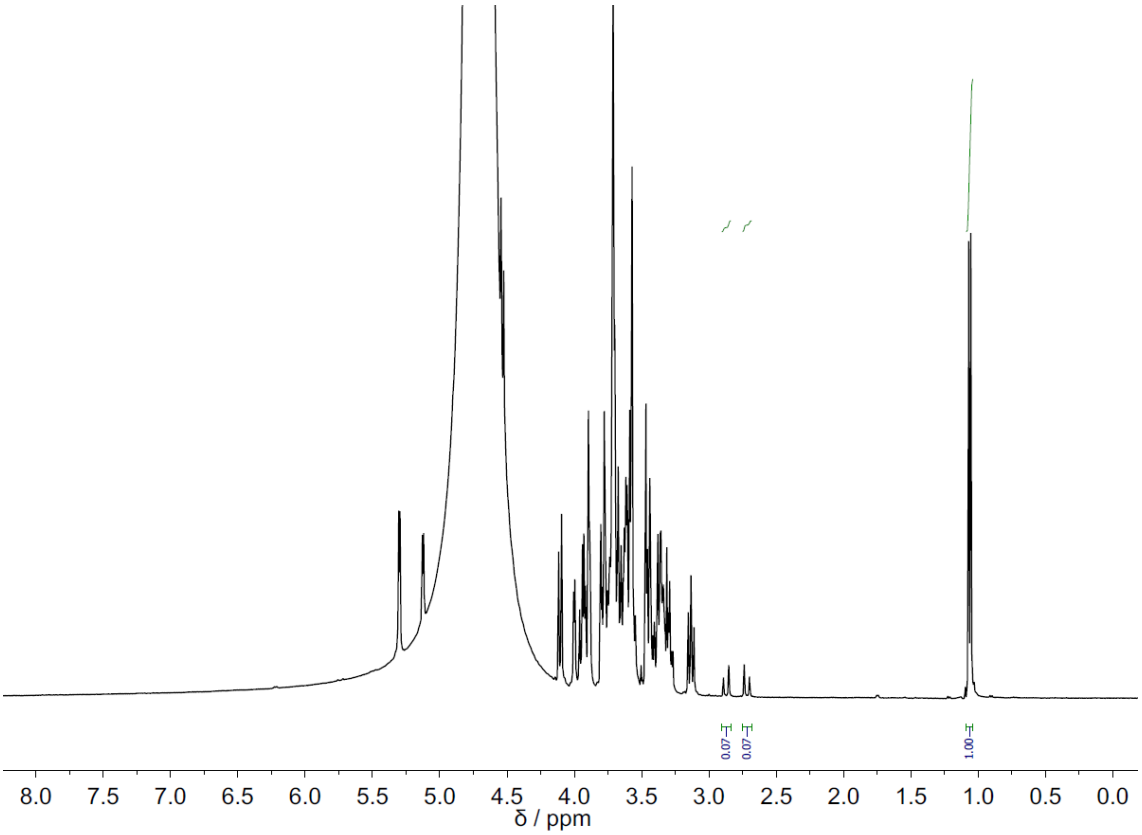


**Figure S19.** $^{1}$H NMR (400 MHz) spectrum of a solution containing soft drink (90%), $D_2O$ (10%) and isopropanol (50 mM, 3.85 µL). The peak at 4.75 ppm corresponds to the solvent.

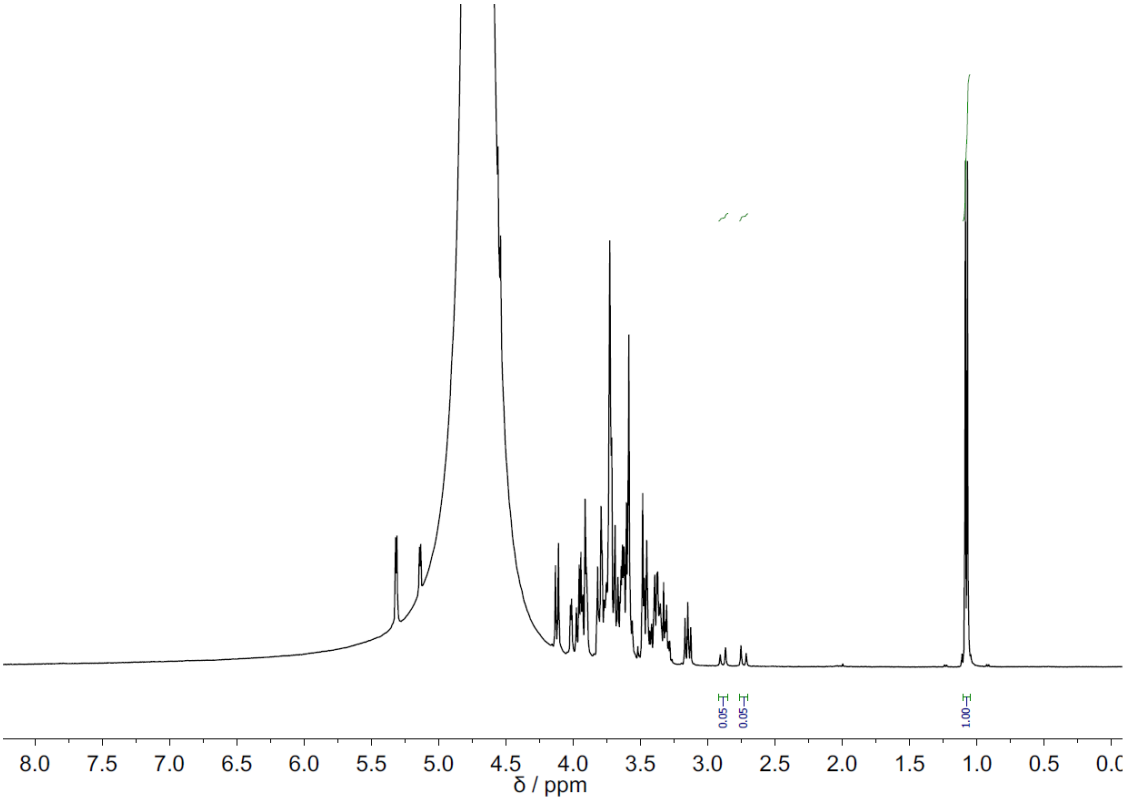


**Figure S20.** $^{1}$H NMR (400 MHz) spectrum of a solution containing ice tea (90%), $D_2O$ (10%) and isopropanol (50 mM, 3.85 µL). The peak at 4.75 ppm corresponds to the solvent.

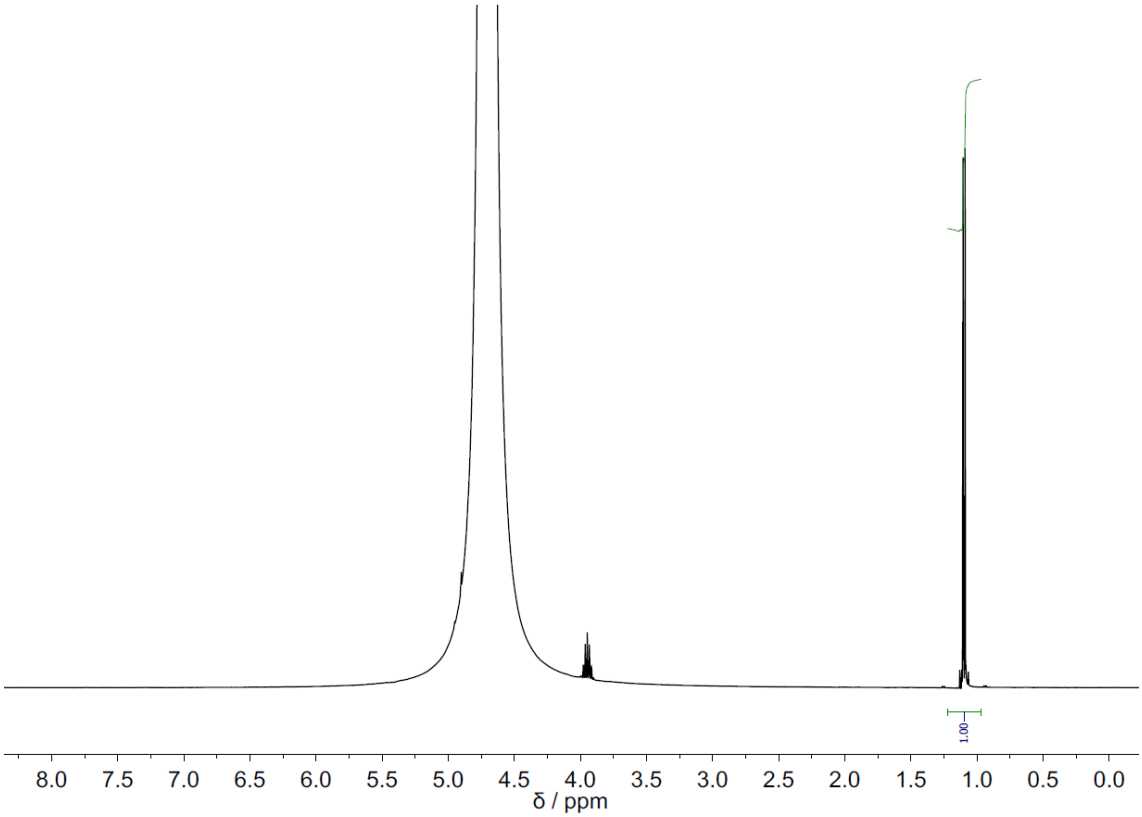


**Figure S21.** $^{1}$H NMR (400 MHz) spectrum of a solution containing mineral water (90%), $D_2O$ (10%) and isopropanol (50 mM, 3.85 µL). The peak at 4.75 ppm corresponds to the solvent.

## 9. References

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2 G. J. M. Koper, R. Eelkema and J. H. van Esch, *Angew. Chem. Int. Ed.*, 2011, **50**, 3421–3424.