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

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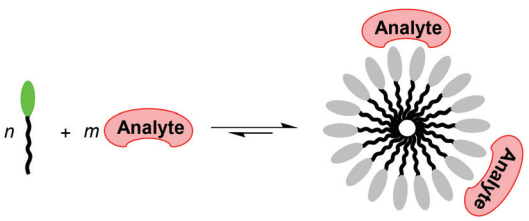
An amphiphilic fluorescent dye with a disulfonated BODIPY head group and a heptadecyl side chain is described. In buffered aqueous solution, the amphiphile can form aggregates with a critical micelle concentration of ~20 μM. The aggregation of the dye is associated with a strong quenching of its fluorescence. Al^{3+} promotes aggregation, whereas other metal ions have a much smaller effect, in particular when histidine is added as masking agent. The Al^{3+}-induced aggregation can be used to sense Al^{3+} in the low micromolar concentration range with high selectivity. Furthermore, we demonstrate that a dye–Al^{3+} mixture can be used as a sensing ensemble for the detection of citric acid. The assay allows quantifying the citric acid content of commercial beverages such as energy drinks.

Introduction

The analyte-induced aggregation of photoluminescent molecules has been used extensively for sensing purposes. Recently published examples include optical sensors for the detection of pyrophosphate,[1] biogenic amines,[2] oxalic acid,[3] DNA,[4] Hg^{2+},[5] K^+,[6] ATP,[7] heparin,[8] pH,[9] glucose,[10,11] and Mg^{2+}.[12] Luminescent polymers[1–5] have often been used in this context, but other types of compounds such as metal complexes,[7b–9] fluorescent amphiphiles,[7a,10] quantum dots,[11] and polypyridyl ligands[12] have been employed as well. Conceptually, this sensing approach is complementary to the analyte-induced *disassembly* of receptor-dye aggregates, commonly referred to as indicator displacement assays (IDAs).[13] We have recently shown that amphiphiles with polysulfonated fluorescent head groups can be employed as molecular probes for the detection of spermine[14] and aminoglycosides.[15] In both cases, the polycationic analytes are assumed to undergo a multivalent interaction[16] with the anionic amphiphile, thereby facilitation micellation. This process is associated with a change of the optical properties of the fluorescent head group, thereby allowing the detection of the analyte (Scheme 1).

We hypothesized that a similar approach could be used for the detection of Al^{3+} ions. Sensing of Al^{3+} is of interest because of its pharmacological effects. At high doses, Al^{3+} can be neurotoxic.[17] Furthermore, the accumulation of Al^{3+} in the human body has been associated with Alzheimer's disease.[18] Given its biological relevance, it is not surprising that numerous optical probes for Al^{3+} have been reported.[19–22] However, these sensing systems often require substantial amounts of organic co-solvents[21,22b,c] or they suffer from interference from other metal ions.[20a,d,f] So far, there are few studies about the detection of Al^{3+} by analyte-induced aggregation of fluorophores.[22] Below, we show that an amphiphilic dye with a disulfonated BODIPY head group and a heptadecane side chain can be used to sense low micromolar concentrations of Al^{3+} in buffered aqueous solution with high selectivity. Furthermore, we show that an amphiphile–Al^{3+} mixture can be used as a sensing ensemble for the detection of citric acid.[23]



Scheme 1 The analyte-induced aggregation of amphiphiles can be used for sensing purposes if aggregation induces a change in the optical properties of the amphiphile.

Results and discussion

For our studies, we synthesized the amphiphilic dyes **3** and **4** containing a disulfonated BODIPY head group and alkyl side chains of different lengths (**3**: undecyl; **4**: heptadecyl). The dyes were obtained by sulfonation of the easily accessible precursors **1** and **2** with chlorosulfonic acid in analogy to a known

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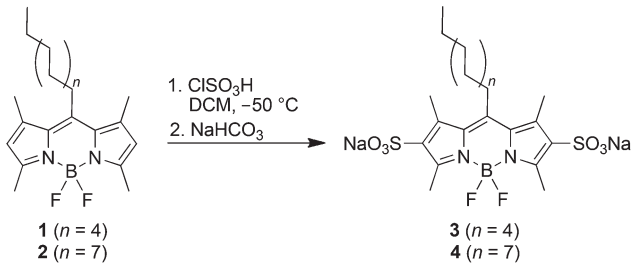

Scheme 2 Synthesis of the fluorescent dyes **3** and **4**.

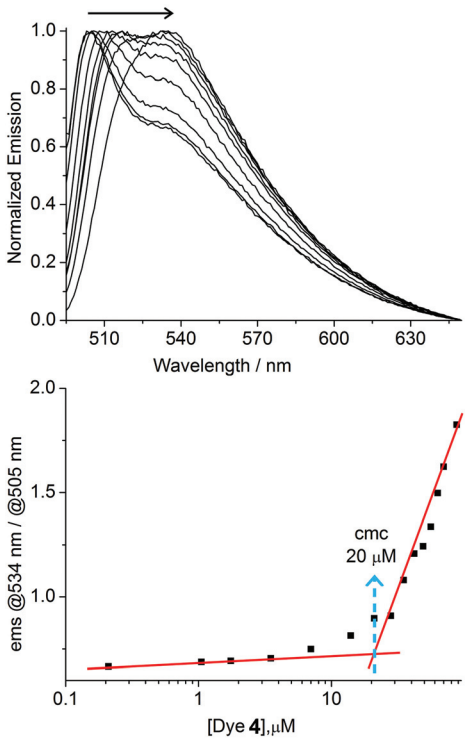

Fig. 1 Top: normalized fluorescence emission spectra (λ_{ex} = 490 nm) of buffered aqueous solutions (10 mM MOPS, pH 7.0) containing different amounts of dye **4** (0.21–105 μM). Bottom: relative fluorescence intensity at 534 and 505 nm of the same solutions.

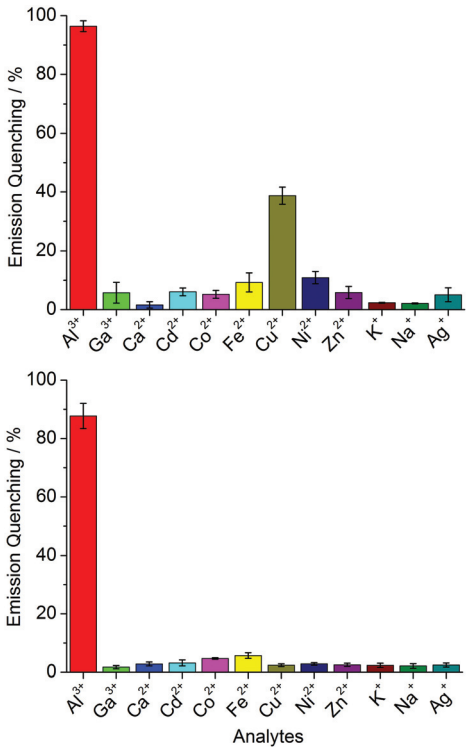

Fig. 2 Top: fluorescence emission quenching (λ_{ex} = 490 nm; λ_{em} = 505 nm) of buffered aqueous solutions (10 mM MOPS, pH 7.0, H_2O with 0.6 vol% MeOH) of dye **4** (4.0 μM) in the presence different metal cations (60 μM). Bottom: measurements in the presence of the masking agent histidine (5.0 mM). The values are averages of three independent measurements.

procedure (Scheme 2).[24] The sulfonated BODIPY was chosen as fluorescent head group because of the high quantum yield of this fluorophore. Furthermore, we expected an emission maximum of higher than 500 nm, which would be well suited for sensing applications because of reduced interference from background fluorescence.[25]

Both amphiphiles were characterized by NMR spectroscopy and mass spectrometry. The aggregation of the dyes in buffered aqueous solution (10 mM MOPS buffer, pH 7.0) was investigated by concentration-dependent fluorescence spectroscopy. For dye **4**, we observed a shift of the fluorescence emission maximum from 504 to 534 nm ($\lambda_{ex.}$ = 490 nm) upon increasing the concentration from 0.21 to 105 μM (Fig. 1, top). A critical micelle concentration (cmc) of ~20 μM was determined by linear extrapolation of the relative fluorescence emission intensity at 534 and 505 nm (Fig. 1, bottom).

Similar experiments were performed with dye **3** having a shorter undecyl side chain. No evidence for aggregation was observed in the concentration range between 1 μM and 1 mM. The formation of micellar aggregates by dye **4** at concentrations above 20 μM was substantiated by dynamic light scattering (DLS) experiments. At a concentration of [**4**] = 50 μM, we were able to observe aggregates with an average hydrodynamic diameter of ~13 nm (see ESI†).

We hypothesized that metal cations could induce the aggregation of **4**. Therefore, we have measured the fluorescence spectra of solutions containing dye **4** in the presence of different metal salts ([M^{n+}] = 60 μM; stock solutions in MeOH). For these studies, a dye concentration of [**4**] = 4.0 μM was chosen. This value is slightly below the cmc of the amphiphile. Most metal salts had a very small effect on the fluorescence emission. For $CuCl_2$ and for $AlCl_3$, however, substantial fluorescence quenching was observed (Fig. 2, top). The most pronounced change was found for $AlCl_3$, the addition of which resulted in nearly complete quenching of the fluorescence.

Control experiments with dye **3** support the hypothesis of analyte-induced aggregation. Only minor fluorescence quenching was observed with Al^{3+} (see ESI, Fig. S8†), indicating that a simple complexation between the BODIPY head group and

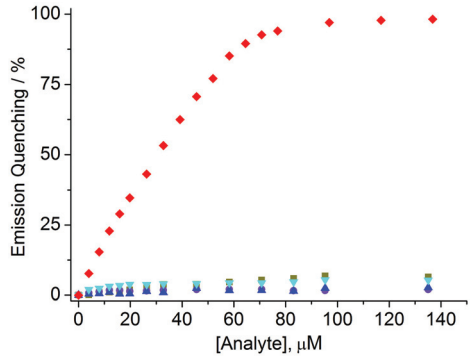

Fig. 3 Fluorescence emission quenching (λ_{ex} = 490 nm; λ_{em} = 505 nm) of buffered aqueous solutions (10 mM MOPS, pH 7.0, H_2O with 0–1.3 vol% MeOH) containing dye **4** (4.0 μM), histidine (5.0 mM), and different amounts of Al^{3+} (red symbols), Cd^{2+} (cyan symbols), Cu^{2+} (olive symbols), Ni^{2+} (blue symbols), or Zn^{2+} (violet symbols). The data points are averages of three independent measurements. The errors are less than 4%.

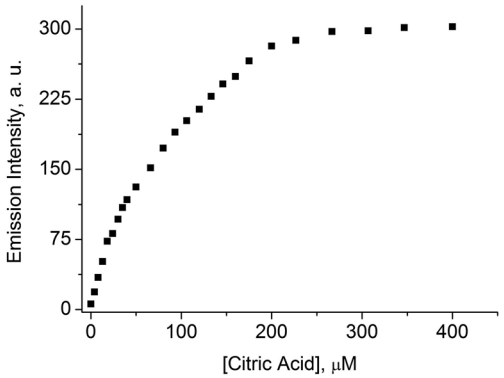

Fig. 4 Fluorescence emission intensity (λ_{ex} = 490 nm; λ_{em} = 505 nm) of buffered aqueous solutions (10 mM MOPS, pH 7.0, H_2O with 1.2 vol% MeOH) containing dye **4** (4.0 μM), Al^{3+} (120 μM), and different amounts of citric acid (0–400 μM). The data points are averages of three independent measurements. The errors are less than 4%.

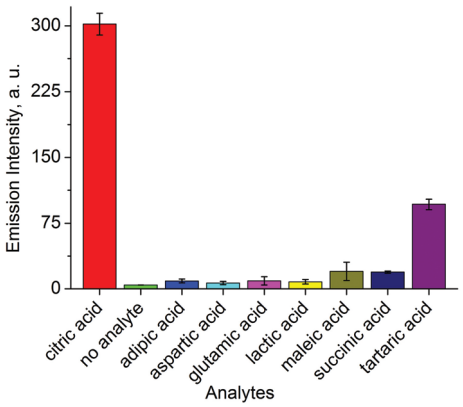

Fig. 5 Fluorescence emission intensity (λ_{ex} = 490 nm; λ_{em} = 505 nm) of buffered aqueous solutions (10 mM MOPS, pH 7.0, H_2O with 1.2 vol% MeOH) of dye **4** (4.0 μM) and Al^{3+} (120 μM) in the presence different analytes (400 μM). The values are averages of three independent measurements.

Al^{3+} is *not* responsible for the optical changes observed for **4**. Experiments with the solvatochromic probe Nile Red are in line with these results. When Al^{3+} was added to solutions containing dye **4** (4.0 μM) and Nile Red (6.0 μM), an increased fluorescence at 660 nm was observed (see ESI, Fig. S4†). This increase can be attributed to the encapsulation of Nile Red in a hydrophobic domain.[26] Because of the low concentration of dye **4** under sensing conditions, we were not able to confirm aggregation by DLS.

In order to enhance the selectivity for Al^{3+}, we explored different masking agents. The amino acid histidine, a known chelate ligand for transition metal ions,[27] was found to give good results. In the presence of 5.0 mM histidine, none of the metal ions gave a significant fluorescence change apart from Al^{3+} (Fig. 2, bottom). For the latter, an emission quenching of nearly 90% was observed.

Fluorescence titration experiments with solutions of **4** and different amounts of $AlCl_3$, $CuCl_2$, $ZnCl_2$, $NiCl_2$, and $Cd(NO_3)_2$ (0–135 μM) showed that it is possible to selectively sense low micromolar concentrations of Al^{3+} with a detection limit of approximately 3 μM ($3\sigma_o$) (Fig. 3). The good selectivity was further confirmed by measuring the fluorescence of solutions containing dye **4** (4.0 μM), histidine (5.0 mM), $AlCl_3$ (20 μM) and an additional metal salt (20 μM). In all cases a fluorescence quenching of around 40% was observed (ESI, Fig. S9†).

Citric acid is known to bind Al^{3+} with high affinity and selectivity.[20c,28] Therefore, it seemed possible to use citric acid for the disassembly of dye **4**–Al^{3+} aggregates. This is indeed the case. When citric acid was added to a buffered aqueous solution containing dye **4** (4.0 μM) and $AlCl_3$ (120 μM), an increased fluorescence emission at 505 nm was observed (Fig. 4), suggesting the formation of monomeric **4**. It is thus possible to use a mixture of **4** and Al^{3+} as a sensing ensemble for the detection of citric acid *via* a turn-on fluorescence signal.[29] The titration data depicted in Fig. 4 could be used to sense citric acid in the low micromolar concentration range with a detection limit of approximately 5 μM ($3\sigma_o$).

The selectivity of this assay turned out to be very good. Several biological relevant carboxylic acids were tested (400 μM), most of which gave a negligible optical response (Fig. 5). Only tartaric acid resulted in a fluorescence signal, but its intensity was only 1/3 of that of citric acid. We have also tested the influence of glucose, fructose, or sucrose (400 μM in each case) on the sensing system. These carbohydrates gave a negligible fluorescence response.

The good selectivity and sensitivity of our citric acid assay prompted us to examine the possibility to detect and quantify citric acid in commercial beverages. Three energy drinks, two soft drinks, and one mineral water were chosen as representative samples. First, we have determined the content of citric acid in these samples by ^1H NMR spectroscopy. This analytical technique is well suited for such an analysis because the signals of the CH_2 group of citric acid are well separated in the

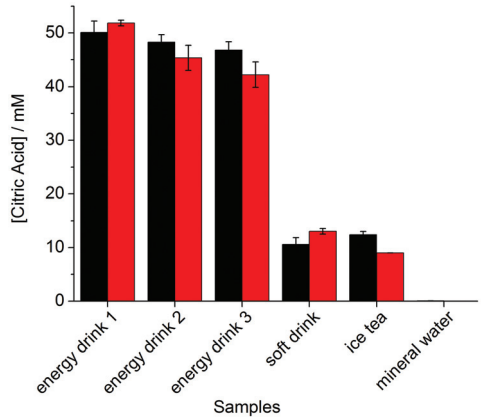

Fig. 6 Concentration of citric acid in drinks as determined by ^{1}H NMR spectroscopy (black bars) and by the dye **4**–Al^{3+} sensing ensemble (red bars). Experimental details are given in the ESI.†

spectra, allowing for a reasonably precise integration (see ESI†). We then determined the citric acid concentration of the samples using a mixture of dye **4** and $AlCl_3$ as a sensing ensemble. The fluorescence signal was converted into a concentration value by using the calibration curve depicted in Fig. 4. As shown in Fig. 6, the match between the values obtained by NMR and by fluorescence spectroscopy is remarkably good.

Conclusions

The amphiphilic fluorescent dye **4** with a disulfonated BODIPY head group and a heptadecyl side chain can be used to sense Al^{3+} in the low micromolar concentration range with high selectivity. The optical response is due to analyte-induced aggregation of the dye. From an application point of view, it is noteworthy that the assay can be performed in aqueous solution at neutral pH without the need of large amounts of organic co-solvents. Citric acid, a known chelator for Al^{3+}, can reverse the aggregation of **4**. It is thus possible to use a mixture of **4** and Al^{3+} as a turn-on fluorescence sensor for citric acid. As proof of concept, we have shown that it is possible to detect the citric acid concentration in commercial beverages. Overall, our results provide further evidence for the utility of fluorescent amphiphiles in supramolecular analytical chemistry.

Experimental section

General

All chemicals and solvents were purchased from standard suppliers and used without further purification. 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. ^{1}H and ^{13}C NMR spectra were recorded on 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 a Zetasizer nano ZS90 (Malvern) instrument. High resolution mass spectra were recorded with a Waters Q-TOF Ultima (ESI-TOF) instrument. The dyes **1** and **2** were prepared in analogy to a known procedure (see ESI†).[24]

Synthesis of dye 3

A solution of chlorosulfonic acid (49.8 μL, 0.75 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 20 min under stirring to a cooled (−50 °C) solution of compound **1** (100 mg, 0.25 mmol) in CH_2Cl_2 (30 mL). The ice bath was then removed and the stirred mixture was warmed to RT, resulting in the formation of a red precipitate. The precipitate was isolated by filtration, washed with CH_2Cl_2, and redissolved in aqueous bicarbonate solution (10 mL, 40 mM). The solution was dried under vacuum. Purification by column chromatography (SiO_2; eluent: $CHCl_3$–MeOH–H_2O; 7 : 3 : 0.5) gave **3** as a red solid (61 mg, 87 μmol, 35%). ^{1}H NMR (400 MHz, CD_3OD): δ = 0.80 (t, J = 7.0 Hz, 3 H, CH_3), 1.15–1.35 (m, 14 H, CH_2), 1.46 (p, J = 8.0 Hz, 2 H, CH_2), 1.55–1.64 (m, 2 H, CH_2), 2.65 (s, 6 H, CH_3), 2.69 (s, 6 H, CH_3), 3.09–3.13 (m, 2 H, CH_2). ^{13}C NMR (100 MHz, CD_3OD): δ = 13.0, 13.03, 13.39, 22.32, 28.20, 29.06, 29.29, 29.31, 29.84, 31.55, 31.65, 130.57, 134.34, 139.61, 150.99, 153.49. ESI-MS calcd for $C_{24}H_{35}BF_2N_2O_6S_2$ $[(M - 2Na)^{-2}]$ m/z = 280.1001 found 280.1006.

Synthesis of dye 4

A solution of chlorosulfonic acid (39.9 μL, 0.60 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 20 min under stirring to a cooled (−50 °C) solution of compound **2** (100 mg, 0.20 mmol) in CH_2Cl_2 (30 mL). The ice bath was then removed and the stirred mixture was warmed to RT, resulting in the formation of a red precipitate. The precipitate was isolated by filtration, washed with CH_2Cl_2, and redissolved in aqueous bicarbonate solution (10 mL, 40 mM). The solution was dried under vacuum. Purification by column chromatography (SiO_2; eluent: $CHCl_3$–MeOH–H_2O; 7 : 3 : 0.5) gave **4** as a red solid (20.7 mg, 30 μmol, 15%). ^{1}H NMR (800 MHz, CD_3OD): δ = 0.80 (t, J = 7.0 Hz, 3 H, CH_3), 1.15–1.35 (m, 26 H, CH_2), 1.46 (p, J = 8.0 Hz, 2 H, CH_2), 1.55–1.61 (m, 2 H, CH_2), 2.65 (s, 6 H, CH_3), 2.69 (s, 6 H, CH_3), 3.10–3.12 (m, 2 H, CH_2). ^{13}C NMR (200 MHz, CD_3OD): δ = 13.0, 13.07, 13.39, 22.36, 28.21, 29.10, 29.27, 29.35, 29.38, 29.41, 29.90, 31.56, 31.69, 130.57, 134.32, 139.62, 151.02, 153.47. ESI-MS calcd for $C_{30}H_{47}BF_2N_2O_6S_2$ $[(M - 2Na)^{-2}]$ m/z = 322.1471 found 322.1469.

Fluorescence measurements

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.

Acknowledgements

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