

Electronic Supplementary Information

Array-based sensing of purine derivatives with fluorescent dyes

Ziya Köstereli and Kay Severin*

*Institut des Sciences et Ingénierie Chimiques,
École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland.
Fax: +41(0)21 6939305; Tel: +41(0)21 6939302; E-mail: kay.severin@epfl.ch*

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1. ^1H NMR titration experiments

NMR titration experiments were performed to determine the binding constant of the dye MPTS to caffeine and theophylline. The first titration experiment (Figure S1) was performed with MPTS in the presence of different amount of caffeine ($[\text{MPTS}] = 1.0 \text{ mM}$; $[\text{caffeine}] = 1.0 - 20.0 \text{ mM}$) and the second titration (Figure S2) was performed with MPTS in the presence of theophylline ($[\text{MPTS}] = 1.0 \text{ mM}$; $[\text{theophylline}] = 1.0 - 20.0 \text{ mM}$). The labelled signals were used to calculate the apparent binding constant using Wineqnmr software. A 1:1 binding model was employed, which is an approximation because self-aggregation and higher order complexes are not accounted for. The derived binding was 98 M^{-1} for MPTS-caffeine and 120 M^{-1} for MPTS-theophylline.

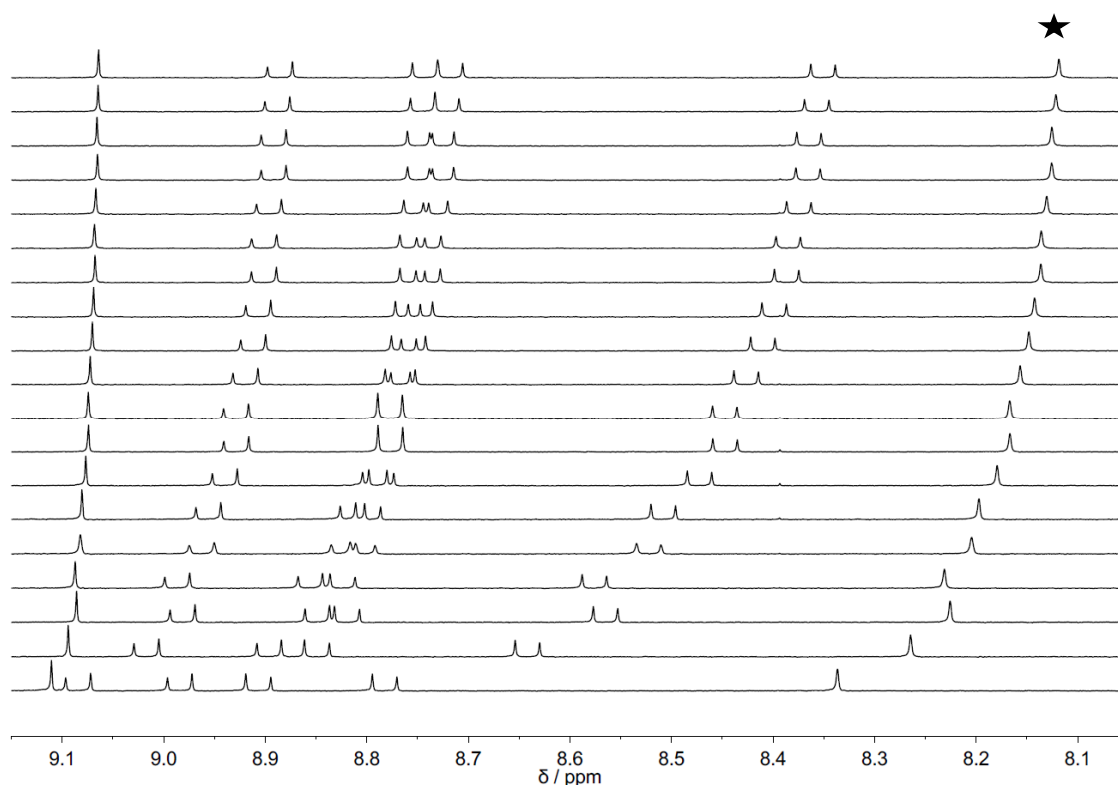


Figure S1. Aromatic part of the ^1H NMR spectra of solutions containing MPTS (1.0 mM) and different amounts of caffeine (1.0 – 20.0 mM) in D_2O .

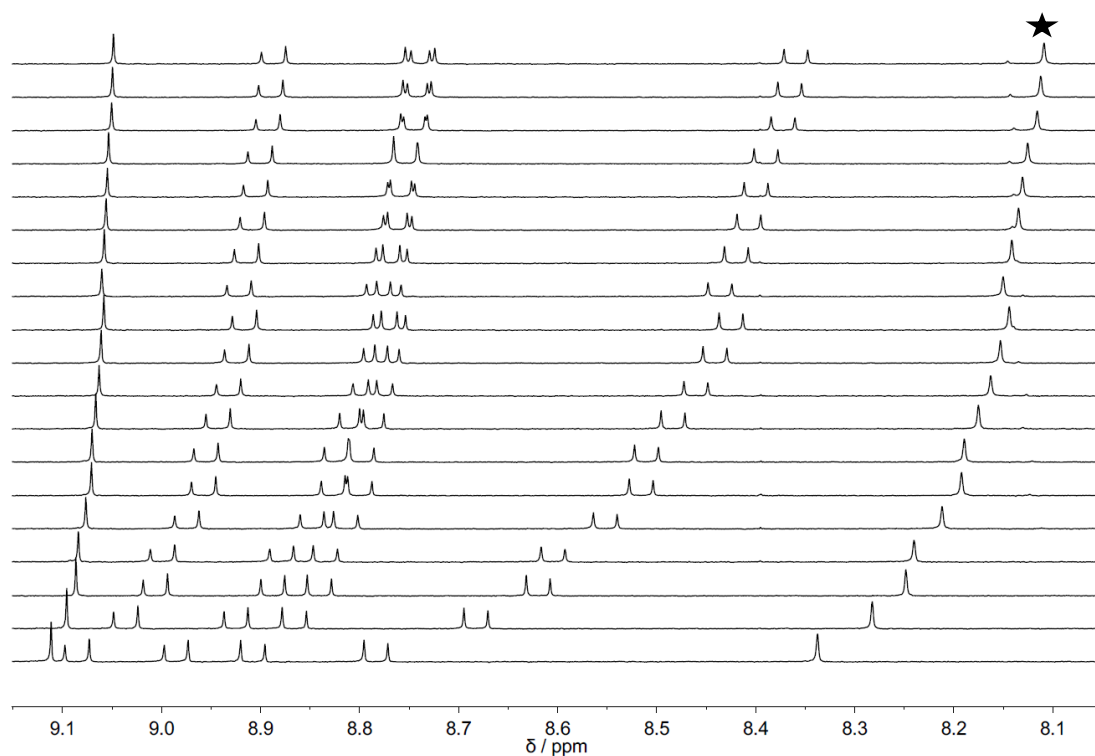


Figure S2. Aromatic part of the ^1H NMR spectra of solutions containing MPTS (1.0 mM) and different amounts of theophylline (1.0 – 20.0 mM) in D_2O .

2. Sensing studies:

Thirteen different analytes (caffeine, theophylline, theobromine, xanthine, hypoxanthine, paraxanthine, 8-chlorotheophylline, 6-mercaptopurine, cladribine, adenosine, guanosine, ATP and penciclovir) were employed ($[\text{dye}]_{\text{final}} = 2.0 \mu\text{M}$; $[\text{analyte}]_{\text{final}} = 1.0 \text{ mM}$, 20 mM MOPS buffer, pH 7.0). The Figures S3–S10 show the fluorescence emission spectra for the different dye-analyte combinations. For the multivariate analyses, only selected wavelengths were employed (see main text).

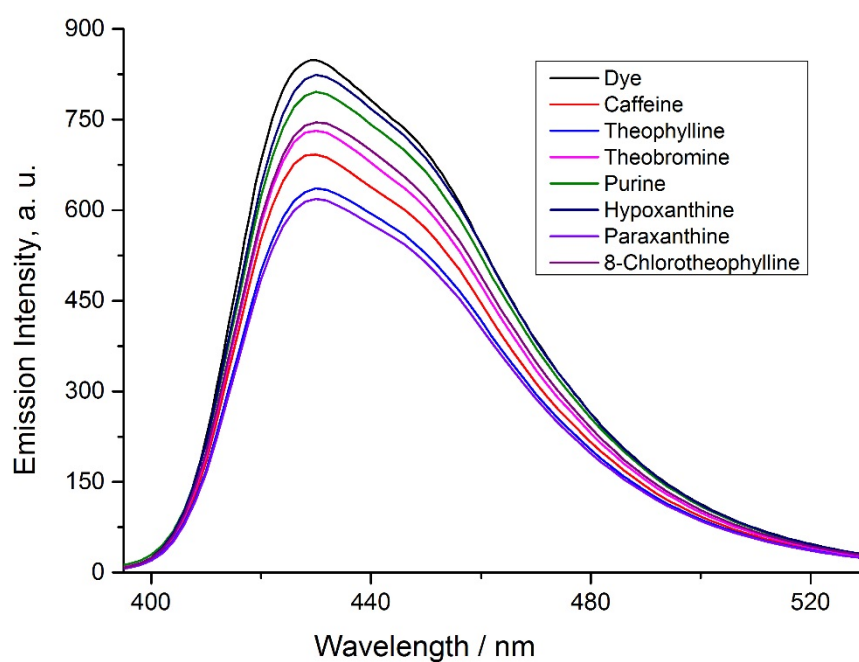


Figure S3. Fluorescence emission spectra (λ_{ex} : 350 nm) of solutions containing a mixture of MPTS and different analytes ([MPTS] = 2.0 μM , [analyte] = 1.0 mM; 20 mM MOPS, pH 7.0).

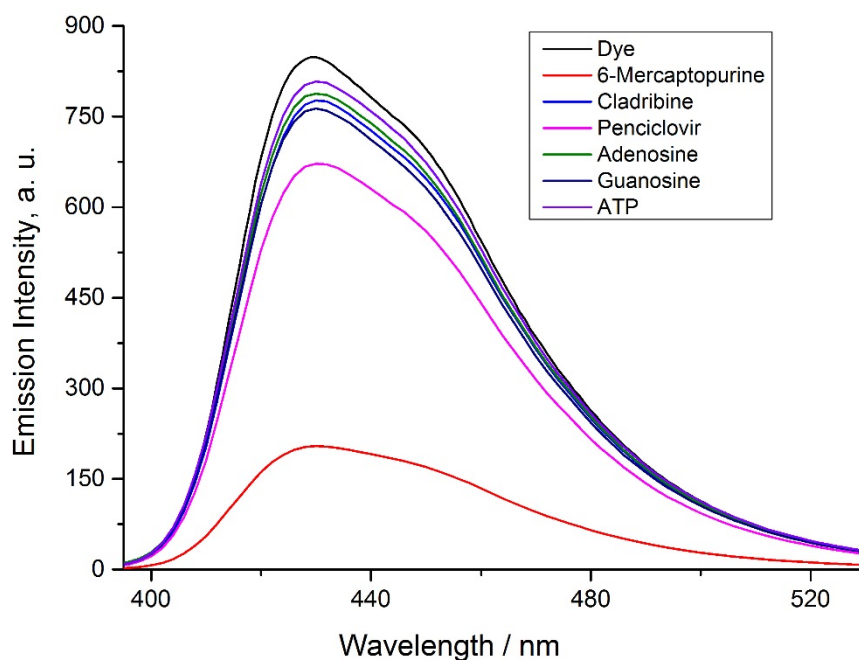


Figure S4. Fluorescence emission spectra (λ_{ex} : 350 nm) of solutions containing a mixture of MPTS and different analytes ([MPTS] = 2.0 μM , [analyte] = 1.0 mM; 20 mM MOPS, pH 7.0).

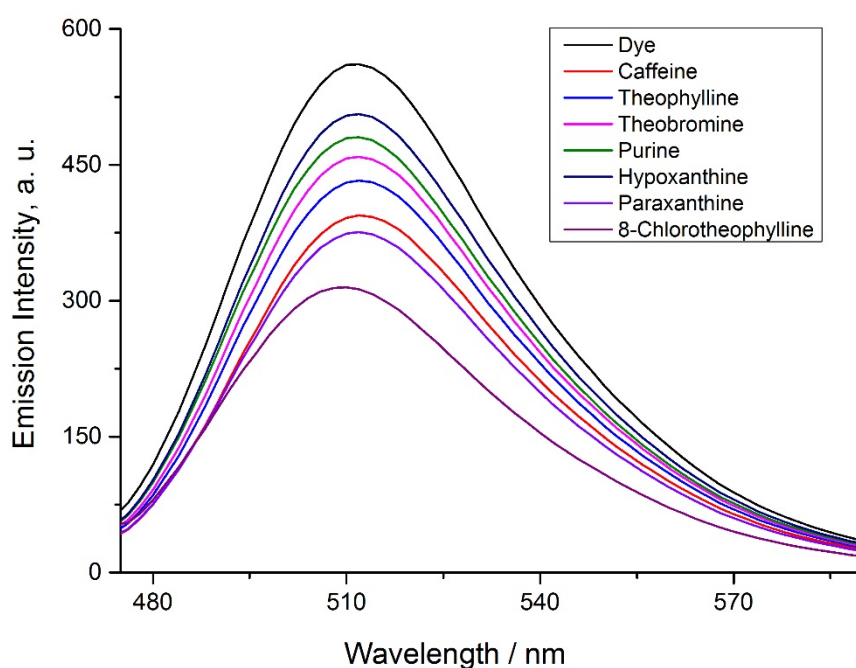


Figure S5. Fluorescence emission spectra (λ_{ex} : 460 nm) of solutions containing a mixture of HPTS and different analytes ([HPTS] = 2.0 μM), [analyte] = 1.0 mM; 20 mM MOPS, pH 7.0).

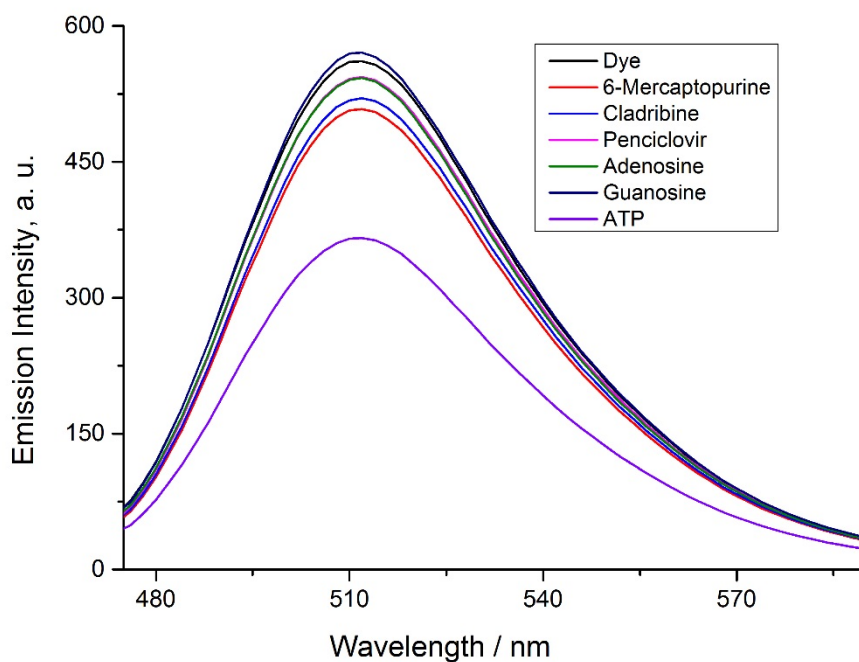


Figure S6. Fluorescence emission spectra (λ_{ex} : 460 nm) of solutions containing a mixture of HPTS and different analytes ([HPTS] = 2.0 μM), [analyte] = 1.0 mM; 20 mM MOPS, pH 7.0).

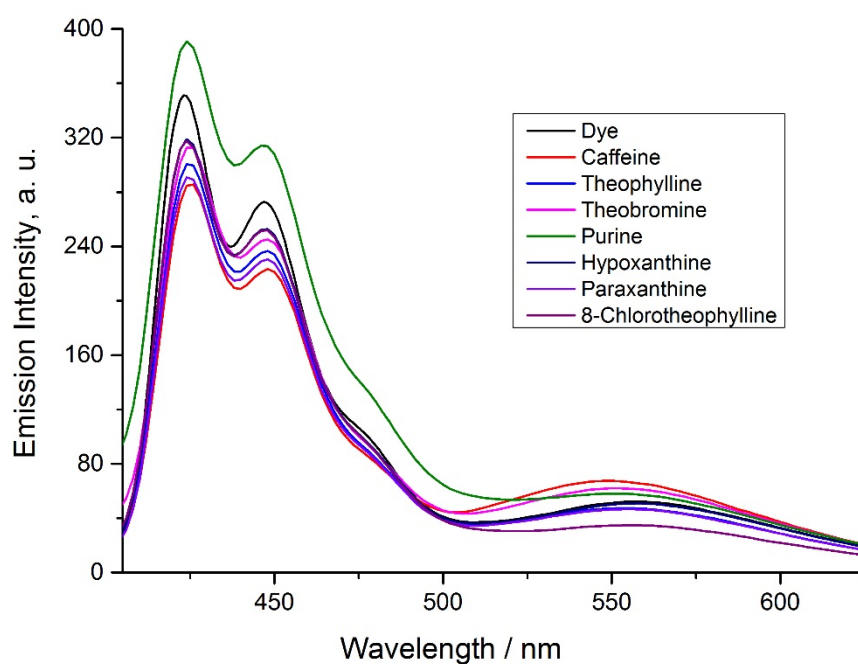


Figure S7. Fluorescence emission spectra (λ_{ex} : 350 nm) of solutions containing a mixture of TDS and different analytes ($[\text{TDS}] = 2.0 \mu\text{M}$), $[\text{analyte}] = 1.0 \text{ mM}$; 20 mM MOPS, pH 7.0).

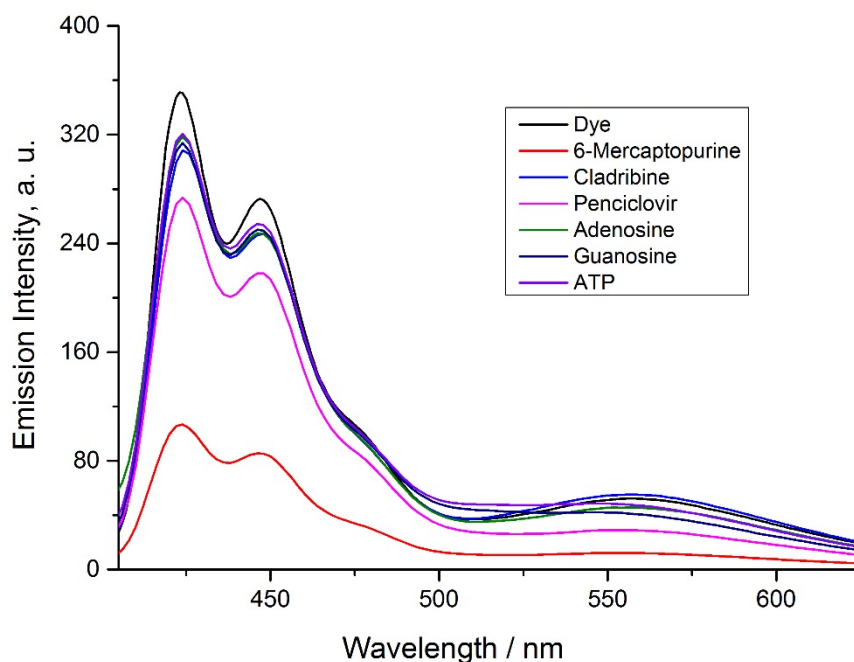


Figure S8. Fluorescence emission spectra (λ_{ex} : 350 nm) of solutions containing a mixture of TDS and different analytes ($[\text{TDS}] = 2.0 \mu\text{M}$), $[\text{analyte}] = 1.0 \text{ mM}$; 20 mM MOPS, pH 7.0).

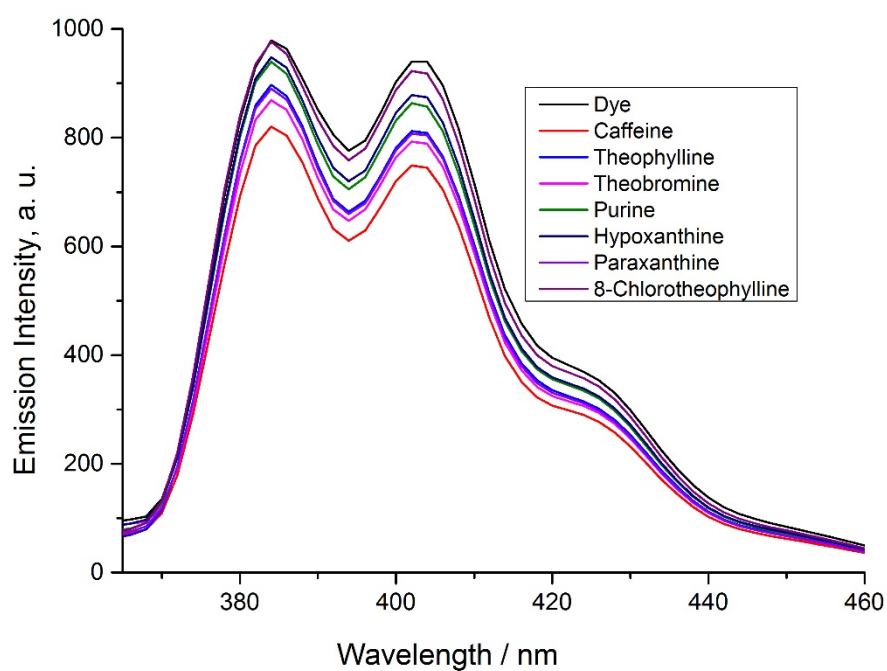


Figure S9. Fluorescence emission spectra (λ_{ex} : 364 nm) of solutions containing a mixture of PTS and different analytes ([PTS] = 2.0 μM), [analyte] = 1.0 mM; 20 mM MOPS, pH 7.0).

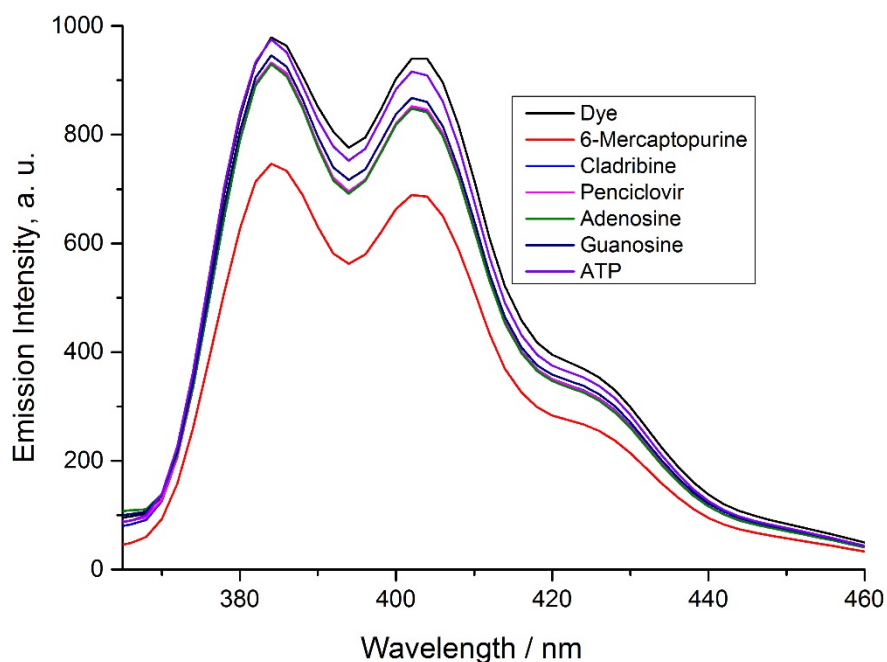


Figure S10. Fluorescence emission spectra (λ_{ex} : 364 nm) of solutions containing a mixture of PTS and different analytes ([PTS] = 2.0 μM), [analyte] = 1.0 mM; 20 mM MOPS, pH 7.0).

3. Multivariate analyses

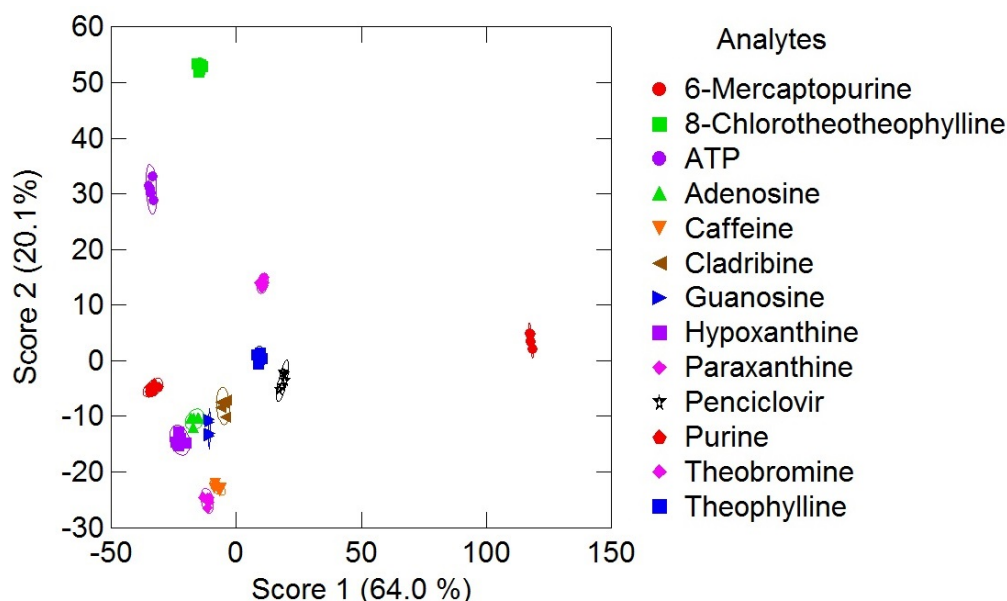


Figure S11. Two-dimensional LDA score plot with confidence ellipsoids ($p = 0.8$) for the analysis of thirteen different purine derivatives ($[\text{dye}]_{\text{final}} = 2.0 \mu\text{M}$; $[\text{analyte}]_{\text{final}} = 1.0 \text{ mM}$). The data were obtained as described in the main text.

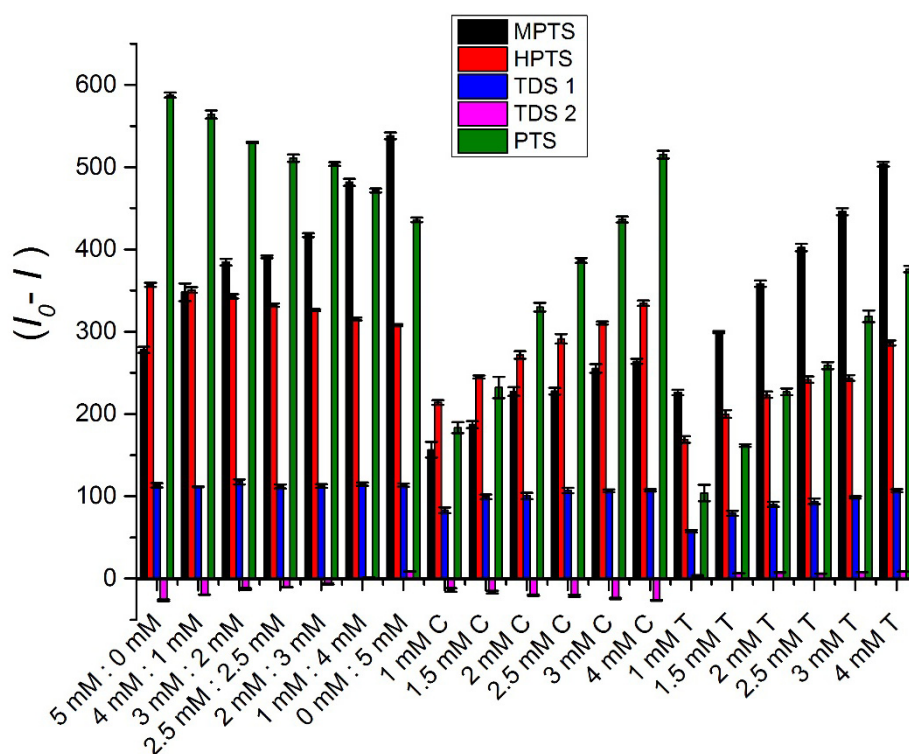


Figure S12. Changes of the fluorescence emission intensities of buffered aqueous solutions (20 mM MOPS, pH 7.0) containing the dyes MPTS (λ_{ex} : 350 nm, λ_{em} : 430 nm, black), HPTS (λ_{ex} : 460 nm, λ_{em} : 511 nm, red), TDS (λ_{ex} : 350 nm, λ_{em} : 424 nm, blue; λ_{em} : 546 nm, pink) or PTS (λ_{ex} : 364 nm, λ_{em} : 384 nm, green) upon addition of caffeine and/or theophylline at different concentrations and ratios ($[\text{dye}] = 2.0 \mu\text{M}$, $[\text{caffeine}] = 1.0 - 5.0 \text{ mM}$; $[\text{theophylline}] = 1.0 - 5.0 \text{ mM}$; $[\text{caffeine:theophylline mix}] = 5.0:0 \text{ mM} - 0:5.0 \text{ mM}$). The values represent averages of five independent measurements.

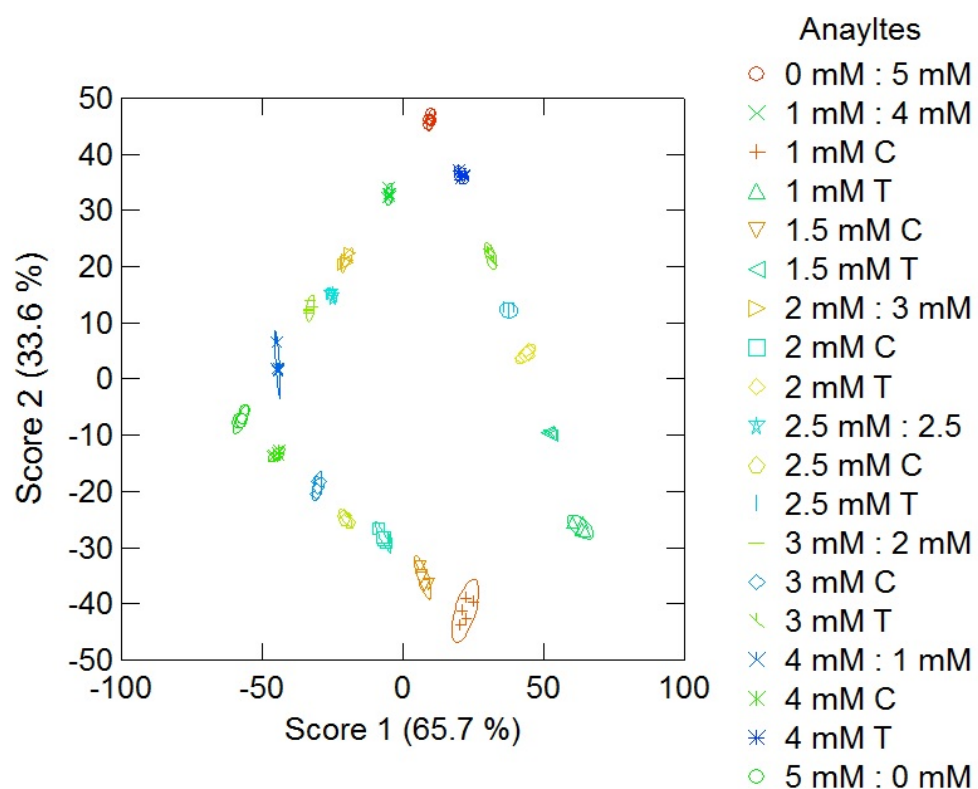


Figure S13. Two-dimensional LDA score plot with confidence ellipsoids ($p = 0.8$) for the analysis of samples containing caffeine and/or theophylline at different concentrations and ratios ([dye] = 2.0 μ M, [caffeine] = 1.0 – 5.0 mM; [theophylline] = 1.0 – 5.0 mM; [caffeine:theophylline mix] = 5.0:0 mM – 0:5.0 mM). The data were obtained as described in the main text.