Electronic Supplementary Material (ESI) for Analytical Methods.


*Electronic Supporting Information for*

# Detection of Bisphenol A and Derivatives in Human Urine via Cyclodextrin-Promoted Fluorescence Modulation

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**ANALYTE DETAILS**

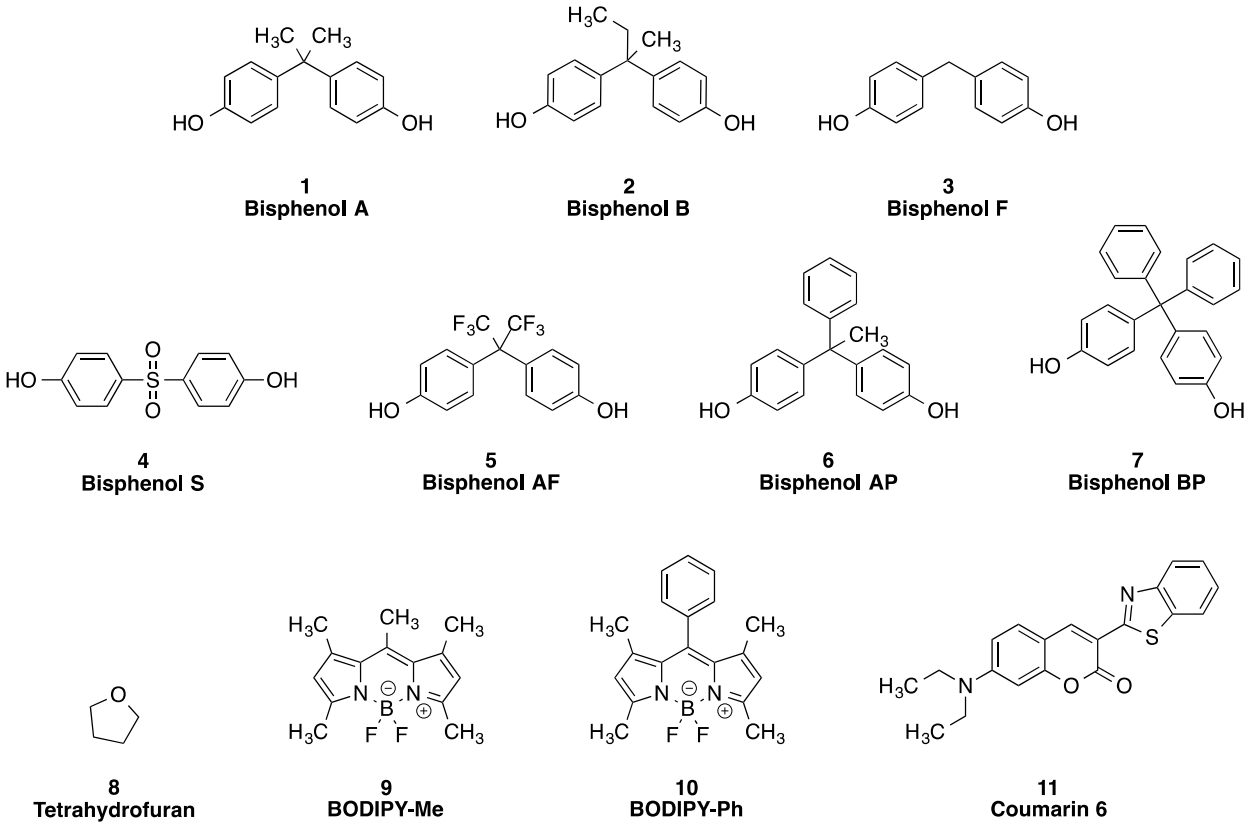


**Figure S1:** Structures of analytes **1-7**, control analyte **8**, and fluorophores **9-11**

**Table S1:** Final solution concentrations of analytes and fluorophores

| Compound | Volume Added (µL) | Final Concentration (µM) |
|---|---|---|
| **1** | 50 | 84.24 |
| **2** | 50 | 79.36 |
| **3** | 50 | 96.04 |
| **4** | 50 | 76.84 |
| **5** | 50 | 57.19 |
| **6** | 50 | 66.23 |
| **7** | 50 | 54.57 |
| **8** | 50 | 266.7 |
| **9** | 100 | 14.67 |
| **10** | 100 | 10.11 |
| **11** | 100 | 10.98 |

**SUMMARY TABLES**

**SUMMARY TABLES FOR FLUORESCENCE MODULATION EXPERIMENTS**

**Buffer**

**Table S2:** Fluorescence modulation results for each analyte in buffer

| Analyte | Fluorophore | Fluorescence Modulation |
|---|---|---|
| **1** | **9** | 1.19 ± 0.01 |
| | **10** | 1.03 ± 0.002 |
| | **11** | 1.06 ± 0.004 |
| **2** | **9** | 1.20 ± 0.001 |
| | **10** | 0.86 ± 0.01 |
| | **11** | 1.08 ± 0.01 |
| **3** | **9** | 1.68 ± 0.01 |
| | **10** | 0.68 ± 0.01 |
| | **11** | 1.07 ± 0.01 |
| **4** | **9** | 1.19 ± 0.004 |
| | **10** | 0.84 ± 0.003 |
| | **11** | 1.07 ± 0.002 |
| **5** | **9** | 1.18 ± 0.002 |
| | **10** | 0.83 ± 0.004 |
| | **11** | 1.07 ± 0.003 |
| **6** | **9** | 1.19 ± 0.01 |
| | **10** | 0.84 ± 0.01 |
| | **11** | 1.07 ± 0.003 |
| **7** | **9** | 1.18 ± 0.01 |
| | **10** | 0.81 ± 0.01 |
| | **11** | 1.09 ± 0.004 |
| **8** | **9** | 1.17 ± 0.01 |
| | **10** | 1.03 ± 0.01 |
| | **11** | 1.09 ± 0.01 |

**Urine**

**Table S3:** Fluorescence modulation results for each analyte in urine

| Analyte | Fluorophore | Fluorescence Modulation |
|---|---|---|
| **1** | **9** | 1.36 ± 0.02 |
| | **10** | 1.03 ± 0.002 |
| | **11** | 1.08 ± 0.004 |
| **2** | **9** | 1.36 ± 0.02 |
| | **10** | 0.95 ± 0.001 |
| | **11** | 1.08 ± 0.01 |
| **3** | **9** | 1.85 ± 0.01 |
| | **10** | 0.92 ± 0.01 |
| | **11** | 1.08 ± 0.004 |
| **4** | **9** | 1.34 ± 0.01 |
| | **10** | 0.92 ± 0.01 |
| | **11** | 1.08 ± 0.004 |
| **5** | **9** | 1.38 ± 0.01 |
| | **10** | 0.94 ± 0.01 |
| | **11** | 1.07 ± 0.004 |
| **6** | **9** | 1.39 ± 0.01 |
| | **10** | 0.99 ± 0.01 |
| | **11** | 1.05 ± 0.01 |
| **7** | **9** | 1.36 ± 0.01 |
| | **10** | 0.90 ± 0.004 |
| | **11** | 1.08 ± 0.01 |
| **8** | **9** | 1.32 ± 0.003 |
| | **10** | 1.09 ± 0.01 |
| | **11** | 1.08 ± 0.004 |

**SUMMARY TABLES FOR LIMIT OF DETECTION EXPERIMENTS**

**Buffer**

**Table S4:** Limits of detection for analytes with fluorophore **9** in buffer

| Analyte | Fluorophore | Equation | $R^2$ | LOD (μM) |
|---|---|---|---|---|
| **1** | **9** | y = 0.0026x + 1.0307 | 0.9998 | 6.61 ± 0.21 |
| **2** | **9** | y = 0.0027x + 1.0177 | 0.99763 | 0.57 ± 0.01 |
| **3** | **9** | y = 0.007x + 0.8928 | 0.99774 | 0.049 ± 0.00 |
| **4** | **9** | y = 0.0032x + 1.0078 | 0.99905 | 1.16 ± 0.00 |
| **5** | **9** | y = 0.0037x + 1.0299 | 0.99671 | 1.18 ± 0.02 |
| **6** | **9** | y = 0.0037x + 0.9999 | 0.99822 | 1.70 ± 0.06 |
| **7** | **9** | y = 0.0044x + 0.9972 | 0.99802 | 1.11 ± 0.03 |

**Urine**

**Table S5:** Limits of detection for analytes with fluorophore **9** in urine

| Analyte | Fluorophore | Equation | $R^2$ | LOD (μM) |
|---|---|---|---|---|
| **1** | **9** | y = 0.0043x + 1.0826 | 0.99573 | 7.96 ± 0.11 |
| **2** | **9** | y = 0.0044x + 0.9991 | 0.99798 | 9.50 ± 0.13 |
| **3** | **9** | y = 0.009x + 0.9322 | 0.99197 | 2.01± 0.06 |
| **4** | **9** | y = 0.0042x + 0.9673 | 0.9969 | 2.29 ± 0.00 |
| **5** | **9** | y = 0.0049x + 1.0074 | 0.99773 | 2.50 ± 0.03 |
| **6** | **9** | y = 0.0042x + 1.016 | 0.99108 | 9.66 ± 0.13 |
| **7** | **9** | y = 0.0043x + 1.0434 | 0.9815 | 0.79 ± 0.02 |

## SUMMARY TABLES FOR ARRAY GENERATION EXPERIMENTS

### Buffer

**Table S6:** Results of array generation in buffer

Jackknifed Classification Matrix

| | Analyte 1 | Analyte 2 | Analyte 3 | Analyte 4 | Analyte 5 | Analyte 6 | Analyte 7 | Analyte 8 | %correct |
|---|---|---|---|---|---|---|---|---|---|
| Analyte 1 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 100 |
| Analyte 2 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 100 |
| Analyte 3 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 100 |
| Analyte 4 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 100 |
| Analyte 5 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 100 |
| Analyte 6 | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 100 |
| Analyte 7 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 100 |
| Analyte 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 100 |
| Total | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 100 |

Cumulative Proportion of Total Dispersion

| | | |
|---|---|---|
| 0.925 | 0.988 | 1.000 |

### Urine

**Table S7:** Results of array generation in urine

Jackknifed Classification Matrix

| | Analyte 1 | Analyte 2 | Analyte 3 | Analyte 4 | Analyte 5 | Analyte 6 | Analyte 7 | Analyte 8 | %correct |
|---|---|---|---|---|---|---|---|---|---|
| Analyte 1 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 100 |
| Analyte 2 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 100 |
| Analyte 3 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 100 |
| Analyte 4 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 100 |
| Analyte 5 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 100 |
| Analyte 6 | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 100 |
| Analyte 7 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 100 |
| Analyte 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 100 |
| Total | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 100 |

Cumulative Proportion of Total Dispersion

| | | |
|---|---|---|
| 0.810 | 0.994 | 1.000 |

**SUMMARY TABLES FOR GC-MS CHARACTERIZATION**

**Table S8:** GC-MS results for urine

| Time (min) | NIST Compound ID |
|---|---|
| 10 | 6-methyl-3-cyclohexen-1-carboxaldehyde |
| 10.25 | 2,4,4-Trimethyl-1-hexene |
| 12 | 2-Methylbenzoxazol |
| 12.4 | Dehydromevalonic lactone |
| 12.5 | 1-methyl-2-piperidinone |
| 12.6 | Dodecane |
| 12.8 | Mannosamine |
| 13.1 | 1-Butyrylpyrrolidine |
| 13.25 | Carbonic acid, eicosyl prop-e-en-2-yl ester |
| 13.3 | 2-Isopopyl-5-methyl-1-hexanol |
| 13.45 | 11-Methyldodecanol |
| 13.5 | 1,4-Diethylhexyl dichloroacetate |
| 13.55 | Dodecyl nonyl ether |
| 13.65 | 2,4-Dimethylheptane |
| 13.7 | 2,3,5-Trimethyldecane |
| 13.75 | 3,8-Dimethyldecane |
| 13.85 | Tetradecane |
| 13.95 | Propanoic acid, 2-methyl-, 3-hydroxy-2,2,4-trimethylpentyl ester |
| 15 | Hexadecane |
| 15.1 | Acetaminophen |
| 15.2 | Cyclohexyl laurate |
| 15.4 | Benzophenone |
| 15.6 | 2-hexyldecanol |
| 16 | 3,7,11,15-Tetramethyl-2-hexadecene |
| 16.15 | 2-Methylhexacosane |
| 16.25 | 1-(15-Methylhexadecanoyl)pyrrolidine |
| 18.3 | Bis(tridecyl) phthalate |
| 18.4 | 5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1',2'-d]pyrazine |
| 18.5 | Dodecanamide |
| 22.8 | Hexadecanamide |
| 29.5 | 9-Octadecenamide |
| 44 | Diisooctyl phthalate |

**SUMMARY TABLE FOR MIXTURE FLUORESCENCE MODULATION EXPERIMENTS**

**Table S9:** Fluorescence modulation results for analyte mixtures in urine

| Analyte | Analyte | Fluorophore 9 | Fluorophore 10 | Fluorophore 11 |
|---|---|---|---|---|
| **1** | **2** | 1.06 ± 0.05 | 1.11 ± 0.004 | 1.07 ± 0.002 |
| **1** | **3** | 1.12 ± 0.05 | 1.10 ± 0.004 | 1.09 ± 0.0003 |
| **1** | **4** | 1.10 ± 0.03 | 1.09 ± 0.01 | 1.06 ± 0.003 |
| **1** | **5** | 1.02 ± 0.08 | 1.09 ± 0.01 | 1.07 ± 0.002 |
| **1** | **6** | 1.07 ± 0.02 | 1.10 ± 0.001 | 1.05 ± 0.003 |
| **1** | **7** | 1.03 ± 0.05 | 1.07 ± 0.002 | 1.05 ± 0.004 |
| **2** | **3** | 1.00 ± 0.09 | 1.12 ± 0.002 | 1.08 ± 0.001 |
| **3** | **4** | 1.07 ± 0.07 | 1.09 ± 0.01 | 1.08 ± 0.004 |
| **3** | **5** | 1.03 ± 0.08 | 1.10 ± 0.01 | 1.08 ± 0.01 |
| **6** | **7** | 0.99 ± 0.07 | 1.08 ± 0.002 | 1.06 ± 0.003 |

## SUMMARY TABLES FOR MIXTURE ARRAY GENERATION EXPERIMENTS

**Table S10:** Results of array generation for analytes mixtures in urine

Jackknifed Classification Matrix

| | Analytes 1 and 2 | Analytes 1 and 3 | Analytes 1 and 4 | Analytes 1 and 5 | Analytes 1 and 6 | Analytes 1 and 7 | Analytes 2 and 3 |
|---|---|---|---|---|---|---|---|
| Analytes 1 and 2 | 4 | 0 | 0 | 0 | 0 | 0 | 0 |
| Analytes 1 and 3 | 0 | 4 | 0 | 0 | 0 | 0 | 0 |
| Analytes 1 and 4 | 0 | 0 | 4 | 0 | 0 | 0 | 0 |
| Analytes 1 and 5 | 0 | 0 | 0 | 4 | 0 | 0 | 0 |
| Analytes 1 and 6 | 0 | 0 | 0 | 0 | 4 | 0 | 0 |
| Analytes 1 and 7 | 0 | 0 | 0 | 0 | 0 | 4 | 0 |
| Analytes 2 and 3 | 0 | 0 | 0 | 0 | 0 | 0 | 4 |
| Analytes 3 and 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Analytes 3 and 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Analytes 6 and 7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Total | 4 | 4 | 4 | 4 | 4 | 4 | 4 |

Jackknifed Classification Matrix (Contd.)

| | Analytes 3 and 4 | Analytes 3 and 5 | Analytes 6 and 7 | %correct |
|---|---|---|---|---|
| Analytes 1 and 2 | 0 | 0 | 0 | 100 |
| Analytes 1 and 3 | 0 | 0 | 0 | 100 |
| Analytes 1 and 4 | 0 | 0 | 0 | 100 |
| Analytes 1 and 5 | 0 | 0 | 0 | 100 |
| Analytes 1 and 6 | 0 | 0 | 0 | 100 |
| Analytes 1 and 7 | 0 | 0 | 0 | 100 |
| Analytes 2 and 3 | 0 | 0 | 0 | 100 |
| Analytes 3 and 4 | 4 | 0 | 0 | 100 |
| Analytes 3 and 5 | 0 | 4 | 0 | 100 |
| Analytes 6 and 7 | 0 | 0 | 4 | 100 |
| Total | 4 | 4 | 4 | 100 |

Cumulative Proportion of Total Dispersion

| | | |
|---|---|---|
| 0.766 | 0.998 | 1.000 |

## SUMMARY TABLE FOR BINDING CONSTANT MEASUREMENTS

**Table S11:** UV/Visible spectroscopy binding constants for analytes **1-7** with γ-cyclodextrin

| Analyte | Concentration (M) | $\lambda_{max}$ (nm) | Equation | $R^2$ | $K_a$ ($M^{-1}$) |
|---|---|---|---|---|---|
| **1** | $1.01 \times 10^{-4}$ | 284 | y = 0.0005x + 11.906 | 0.9586 | $3.22 \times 10^4 \pm 6.81 \times 10^3$ |
| **2** | $1.02 \times 10^{-4}$ | 285 | y = 0.0005x + 11.473 | 0.9595 | $2.37 \times 10^4 \pm 2.72 \times 10^3$ |
| **3** | $5.18 \times 10^{-5}$ | 286 | y = 0.0003x + 7.7833 | 0.9861 | $1.39 \times 10^4 \pm 1.15 \times 10^4$ |
| **4** | $5.07 \times 10^{-5}$ | 297 | y = 0.0005x + 9.9003 | 0.901 | $1.79 \times 10^4 \pm 1.98 \times 10^3$ |
| **5** | $5.15 \times 10^{-5}$ | 280 | y = 0.0001 + 11.405 | 0.9471 | $7.83 \times 10^4 \pm 1.97 \times 10^3$ |
| **6** | $5.30 \times 10^{-5}$ | 287 | y = 0.0002x + 9.1613 | 0.9414 | $5.99 \times 10^4 \pm 3.83 \times 10^3$ |
| **7** | $5.02 \times 10^{-6}$ | 250 | y = 00003x + 3.4255 | 0.9553 | $1.06 \times 10^5 \pm 9.27 \times 10^2$ |

## SUMMARY FIGURES

## SUMMARY FIGURES FOR FLUORESCENCE MODULATION EXPERIMENTS

The black line represents the emission from the fluorophore, and the red line represents the emission from the analyte and fluorophore mixed together in buffer or urine. All X-axes measure the emission from 470 nm to 800 nm, and all Y-axes have been normalized so that the fluorescence emission is on a scale of 0.0 to 1.0.

**Buffer**

Analyte **1**

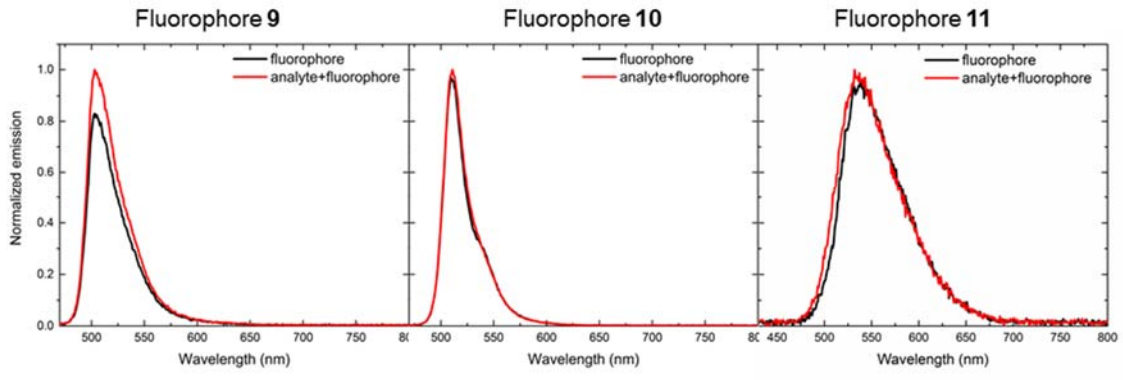


**Figure S2:** Fluorescence modulation of analyte **1** in buffer

Analyte **2**

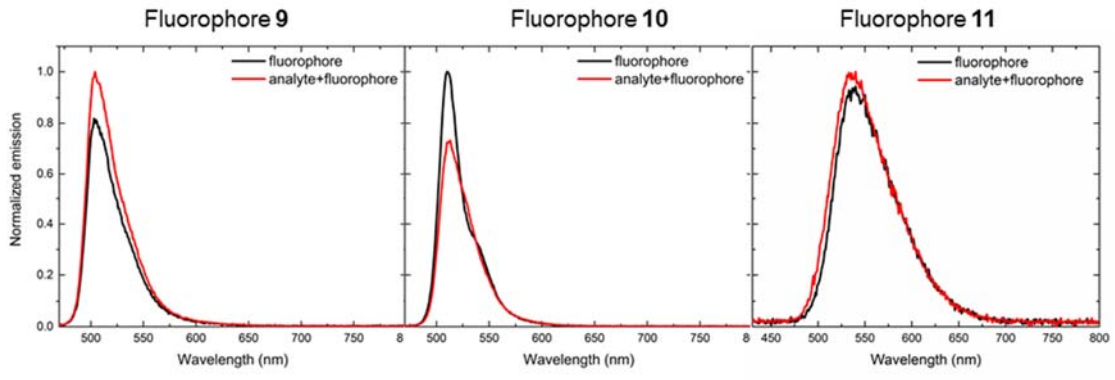


**Figure S3:** Fluorescence modulation of analyte **2** in buffer

Analyte **3**

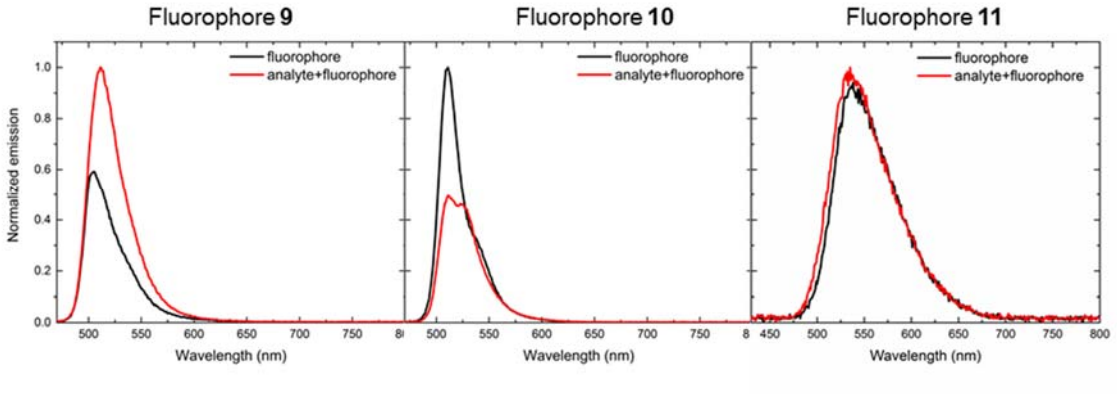


**Figure S4:** Fluorescence modulation of analyte **3** in buffer

Analyte **4**

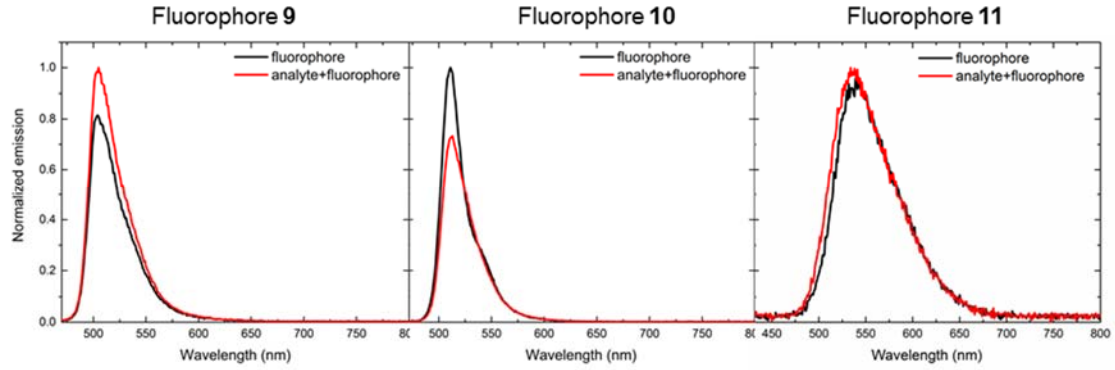


**Figure S5:** Fluorescence modulation of analyte **4** in buffer

Analyte **5**

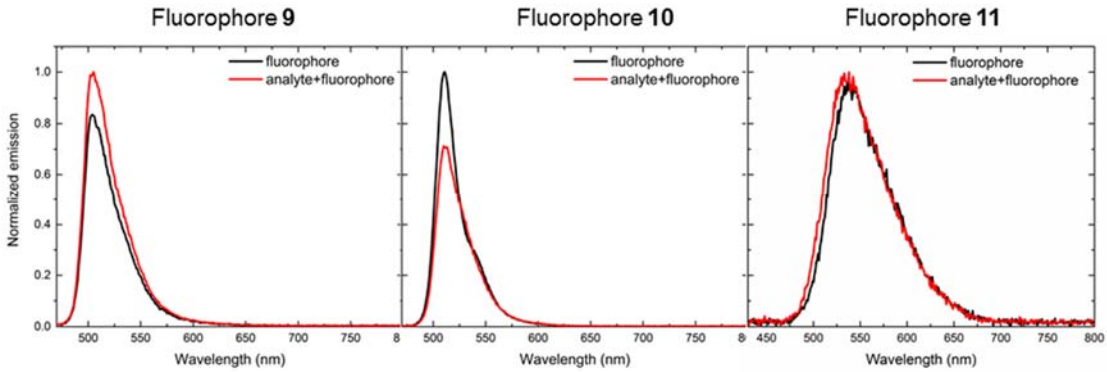


**Figure S6:** Fluorescence modulation of analyte **5** in buffer

Analyte **6**

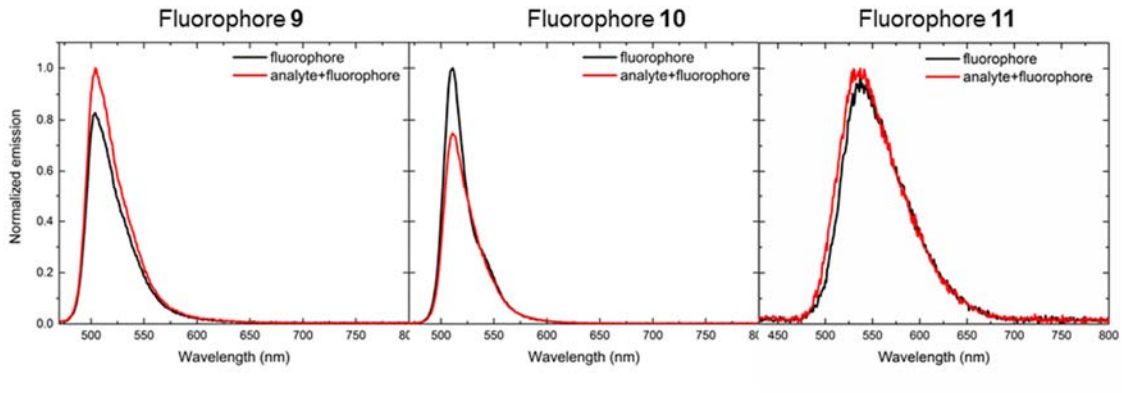


**Figure S7:** Fluorescence modulation of analyte **6** in buffer

Analyte **7**

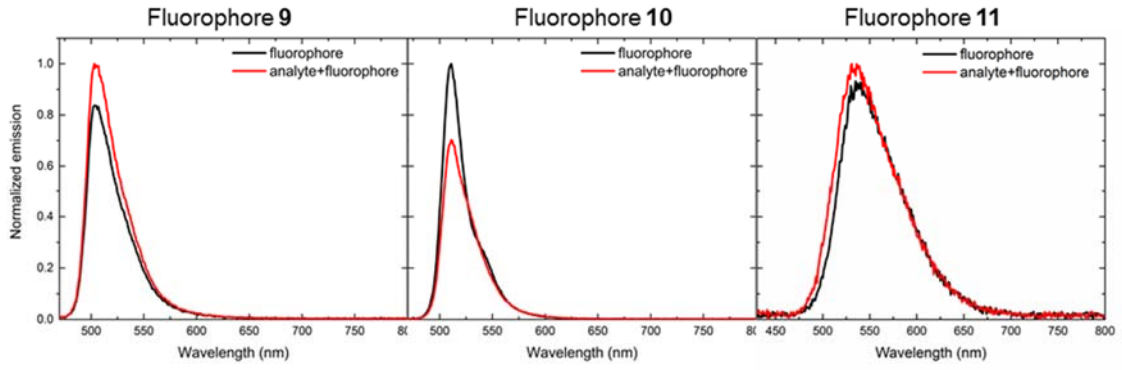


**Figure S8:** Fluorescence modulation of analyte **7** in buffer

Analyte **8**

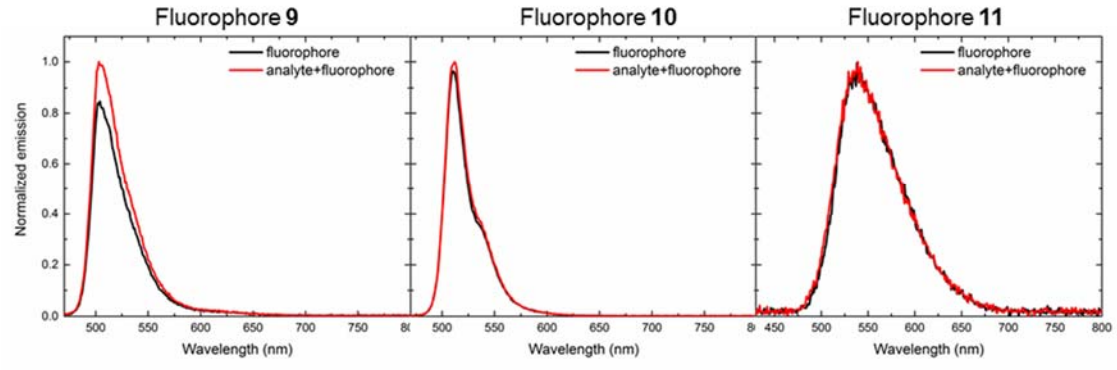


**Figure S9:** Fluorescence modulation of control analyte **8** in buffer

**Urine Experiments**

Analyte **1**

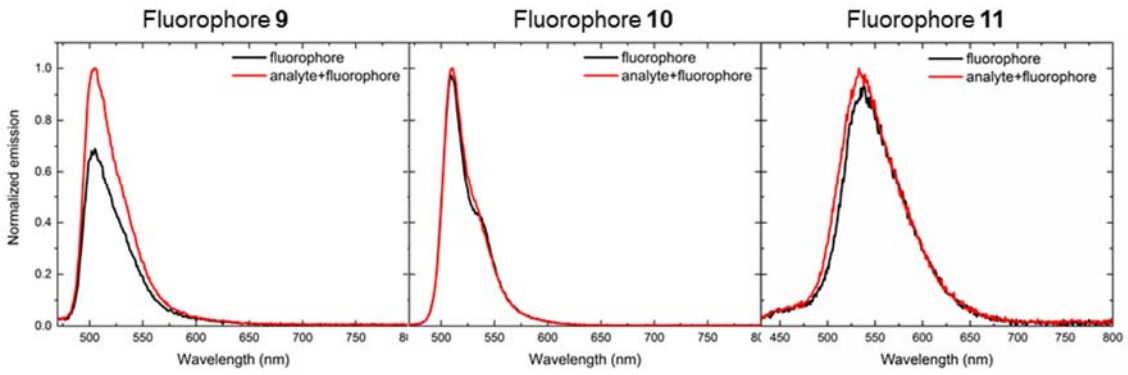


**Figure S10:** Fluorescence modulation of analyte **1** in urine

Analyte **2**

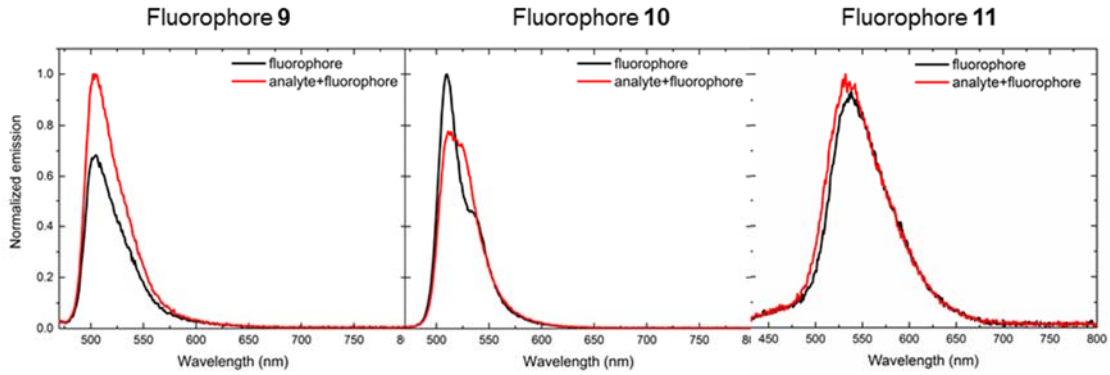


**Figure S11:** Fluorescence modulation of analyte **2** in urine

Analyte **3**

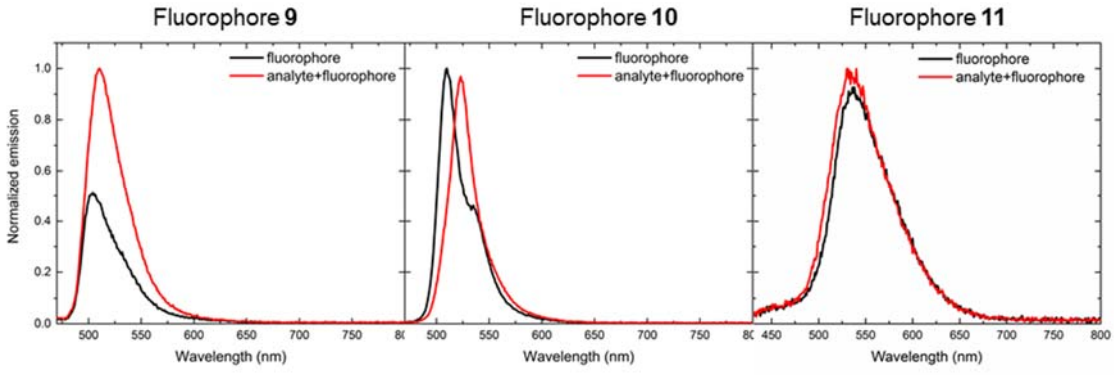


**Figure S12:** Fluorescence modulation of analyte **3** in urine

Analyte **4**

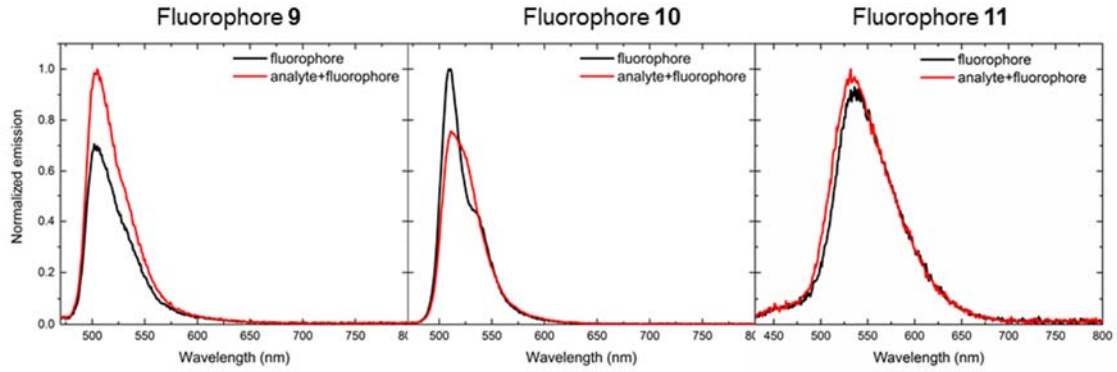


**Figure S13:** Fluorescence modulation of analyte **4** in urine

Analyte **5**

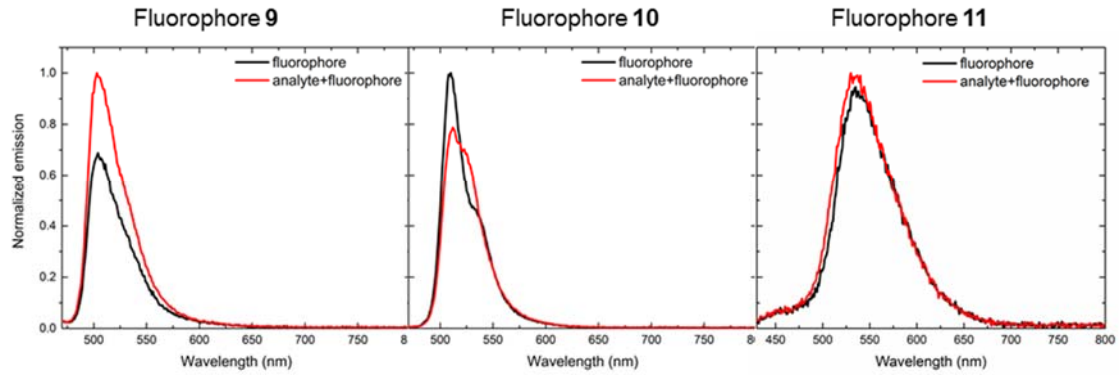


**Figure S14:** Fluorescence modulation of analyte **5** in urine

Analyte **6**

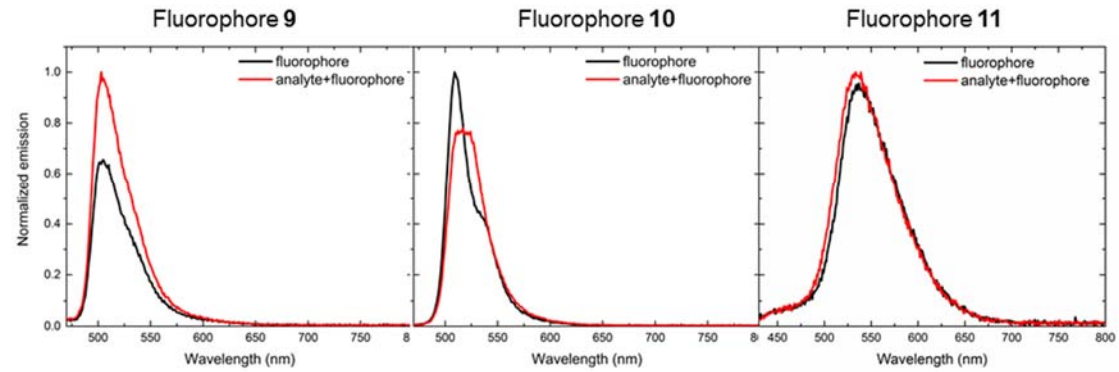


**Figure S15:** Fluorescence modulation of analyte **5** in urine

Analyte **7**

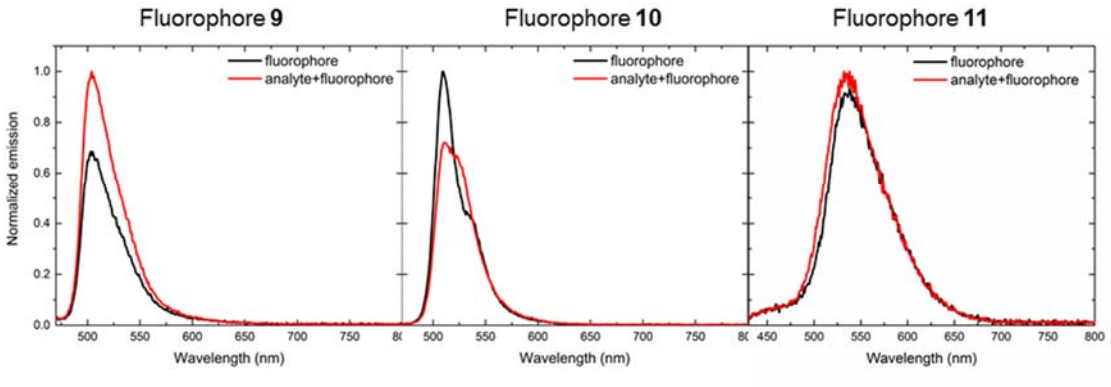


**Figure S16:** Fluorescence modulation of analyte **7** in urine

Analyte **8**

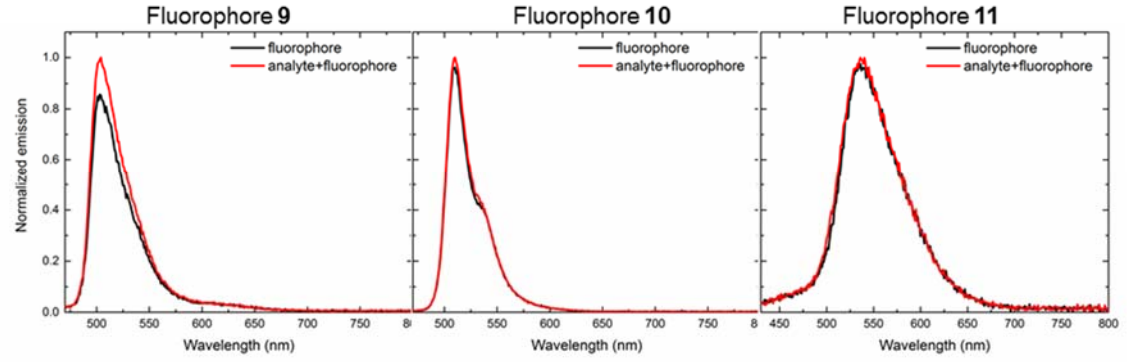


**Figure S17:** Fluorescence modulation of control analyte **8** in urine

## SUMMARY FIGURES FOR LIMIT OF DETECTION EXPERIMENTS

Limits of detection were calculated following literature-reported procedures:

Cheng, D.; Zhao, W.; Yang, H.; Huang, Z.; Liu, X.; Han, A. Detection of Hg2+ by a FRET ratiometric fluorescent probe based on a novel BODIPY-RhB system. *Tetrahedron Lett*. **2016**, *57*, 2655-2659.

We plotted the ratio of $Fl_{analyte}/Fl_{blank}$ on the Y-axis, and the analyte concentration in micromolar on the X-axis.

**Buffer**

Analyte **1**- Fluorophore **9**

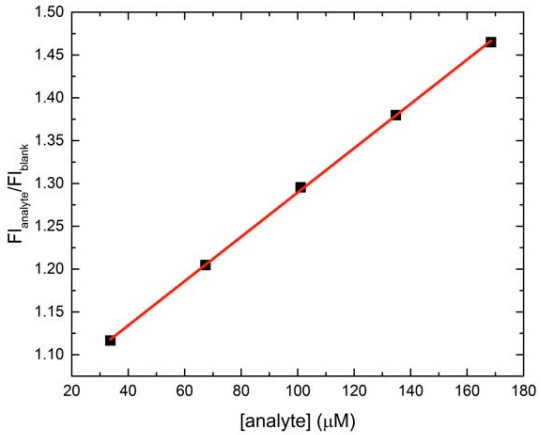


**Figure S18:** Limit of detection for analyte **1** in buffer

Analyte **2**- Fluorophore **9**

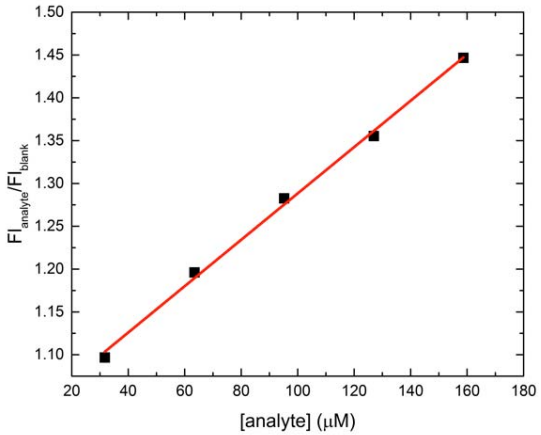


**Figure S19:** Limit of detection for analyte **2** in buffer

Analyte **3**- Fluorophore **9**

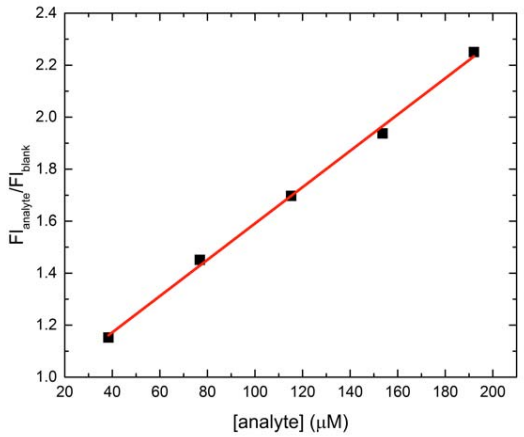


**Figure S20:** Limit of detection for analyte **3** in buffer

Analyte **4**- Fluorophore **9**

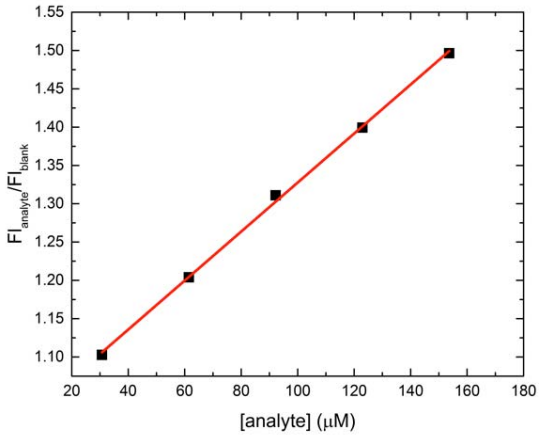


**Figure S21:** Limit of detection for analyte **4** in buffer

Analyte **5**- Fluorophore **9**

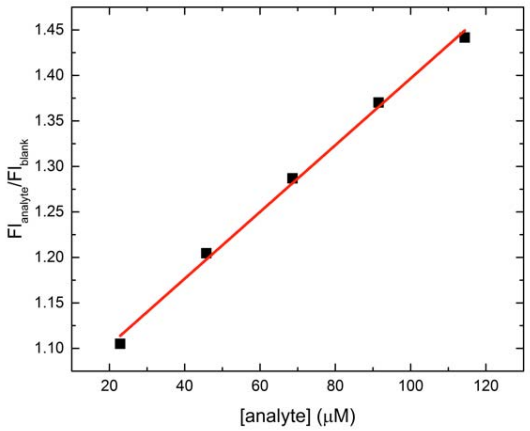


**Figure S22:** Limit of detection for analyte **5** in buffer

Analyte **6**- Fluorophore **9**

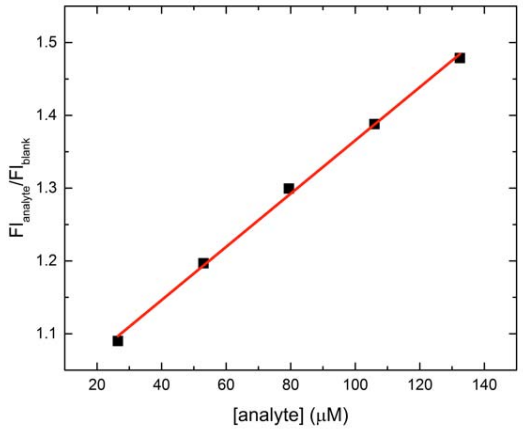


**Figure S23:** Limit of detection for analyte **6** in buffer

Analyte **7**- Fluorophore **9**

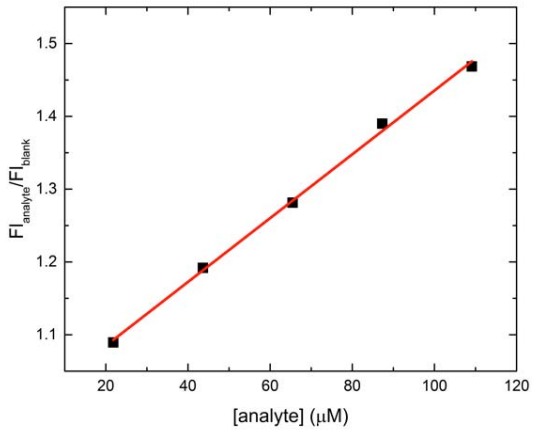


**Figure S24:** Limit of detection for analyte **7** in buffer

**Urine**

Analyte **1**- Fluorophore **9**

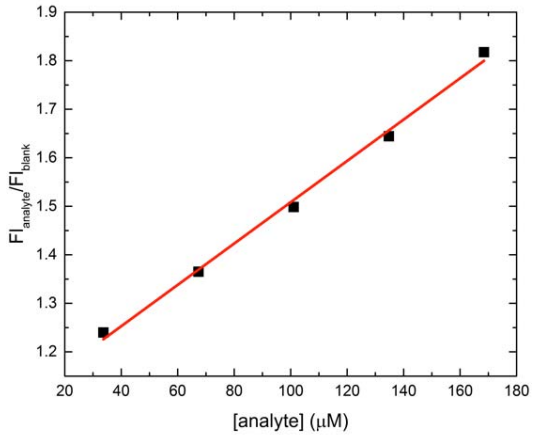


**Figure S25:** Limit of detection for analyte **1** in urine

Analyte **2**- Fluorophore **9**

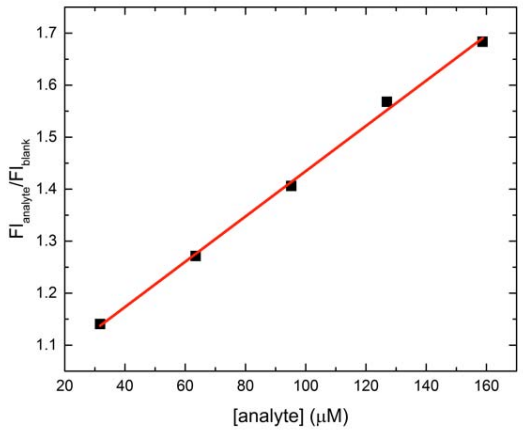


**Figure S26:** Limit of detection for analyte **2** in urine

Analyte **3**- Fluorophore **9**

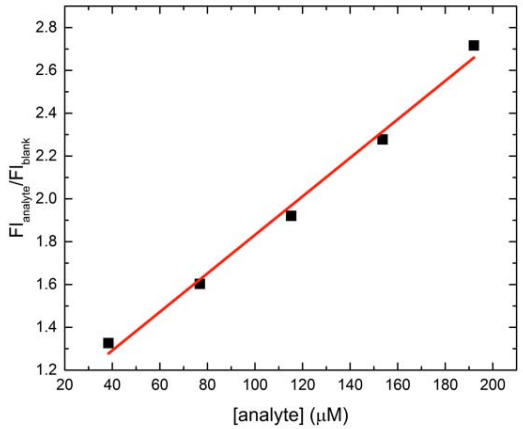


**Figure S27:** Limit of detection for analyte **3** in urine

Analyte **4**- Fluorophore **9**

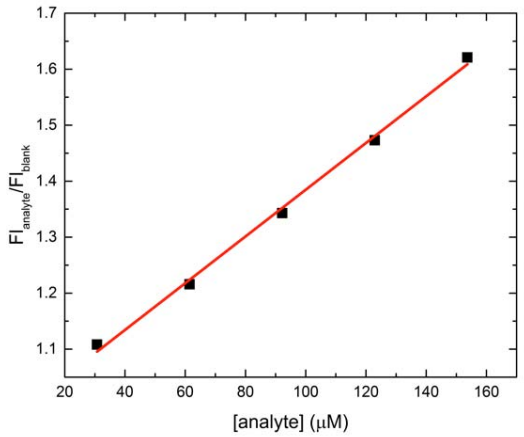


**Figure S28:** Limit of detection for analyte **4** in urine

Analyte **5**- Fluorophore **9**

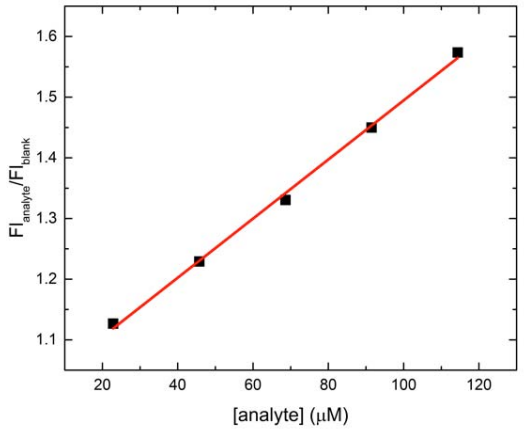


**Figure S29:** Limit of detection for analyte **5** in urine

Analyte **6**- Fluorophore **9**

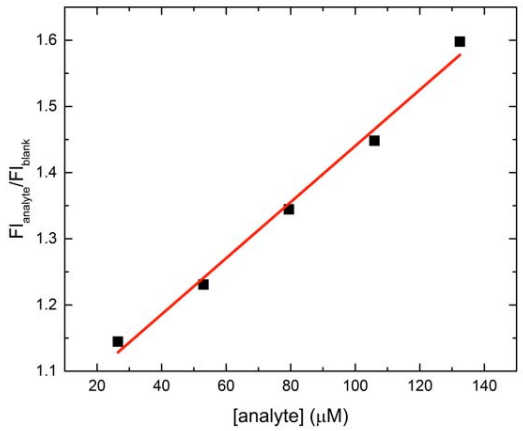


**Figure S30:** Limit of detection for analyte **6** in urine

Analyte **7**- Fluorophore **9**

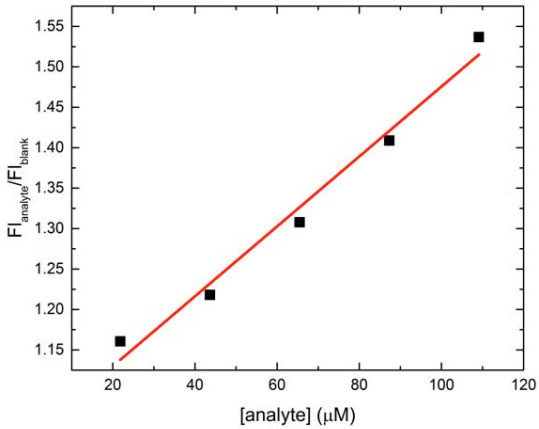


**Figure S31:** Limit of detection for analyte **7** in urine

## SUMMARY FIGURES FOR ARRAY GENERATION EXPERIMENTS

Results from linear discriminant analyses of the fluorescence responses were plotted with SCORE (1) values on the X-axis and SCORE (2) values on the Y-axis.

**Buffer**

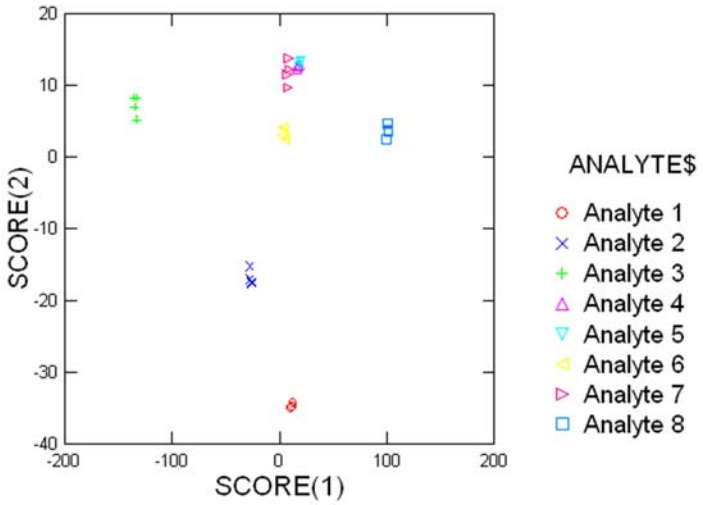


**Figure S32:** Linear discriminant analysis of fluorescence responses for analytes **1-8** with fluorophores **9-11** in buffer

**Urine**

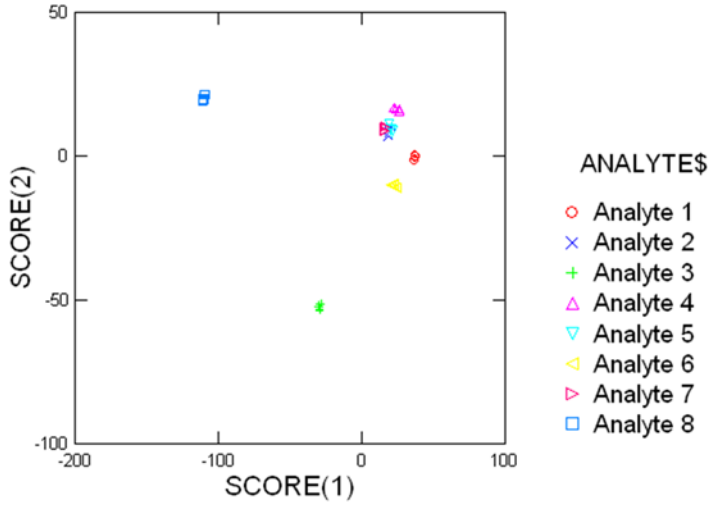


**Figure S33:** Linear discriminant analysis of fluorescence responses for analytes **1-8** with fluorophores **9-11** in urine

**SUMMARY FIGURES FOR GC-MS CHARACTERIZATION**

An undoped urine sample was run on the GC-MS, and results and compound identification of those experiments are shown below:

Urine – Undoped Sample – 10 min

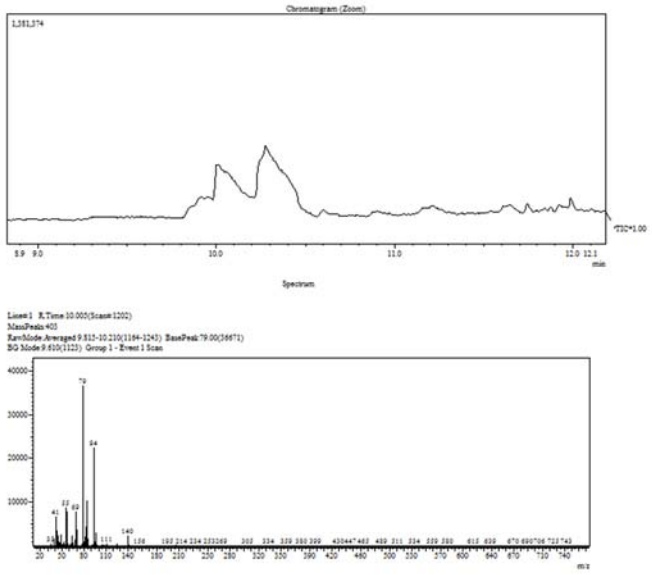

**Figure S34:** GC-MS trace for urine for undoped sample at 10 minutes

**NIST compound ID:** 6-methyl-3-cyclohexen-1-carboxaldehyde

Urine – Undoped Sample – 10.25 min

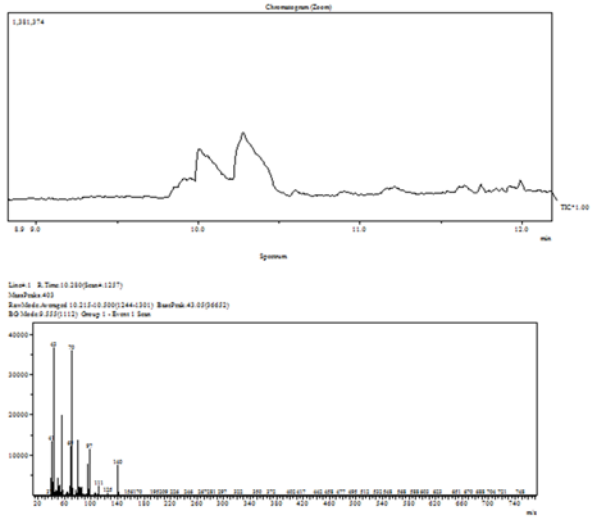

**Figure S35:** GC-MS trace for urine for undoped sample at 10.25 minutes

**NIST compound ID:** 2,4,4-Trimethyl-1-hexene

Urine – Undoped Sample – 12 min

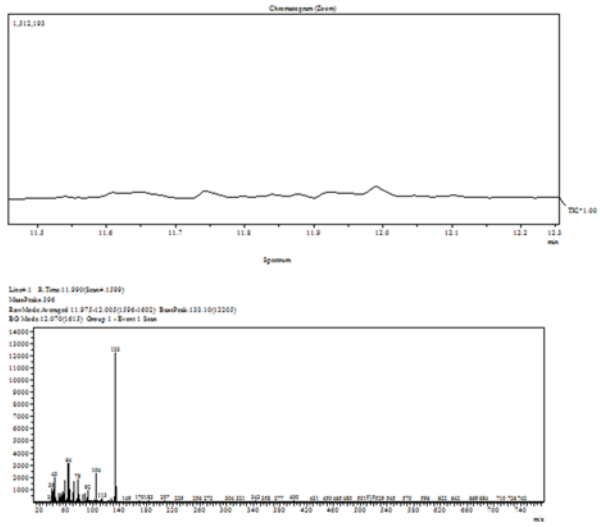

**Figure S36:** GC-MS trace for urine for undoped sample at 12 minutes

**NIST compound ID:** 2-Methylbenzoxazol

Urine – Undoped Sample – 12.4 min

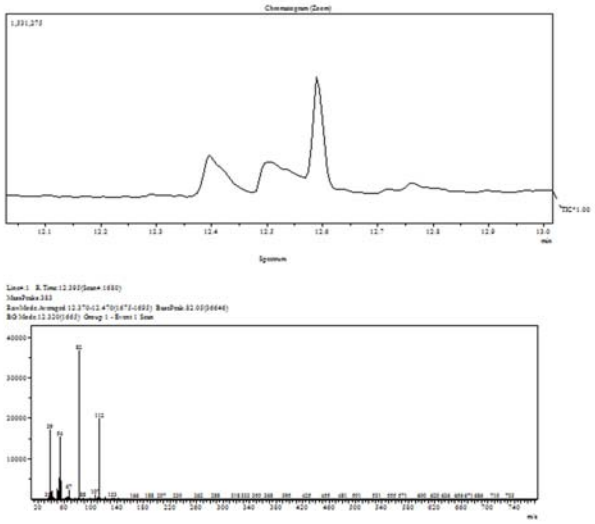

**Figure S37:** GC-MS trace for urine for undoped sample at 12.4 minutes

**NIST compound ID:** Dehydromevalonic lactone

Urine – Undoped Sample – 12.5 min

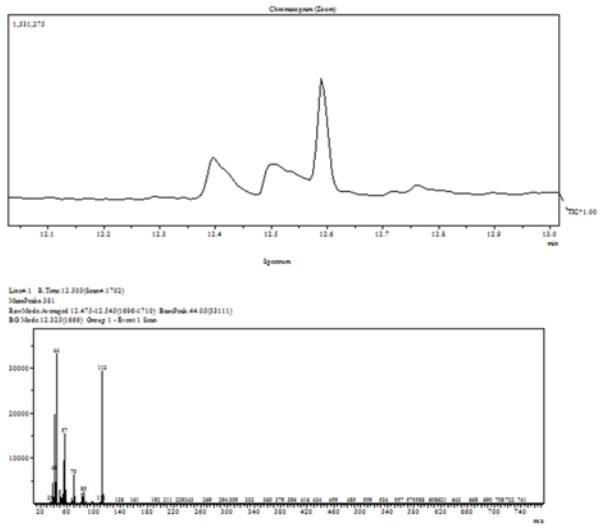

**Figure S38:** GC-MS trace for urine for undoped sample at 12.5 minutes

**NIST compound ID:** 1-methyl-2-piperidinone

Urine – Undoped Sample – 12.6 min

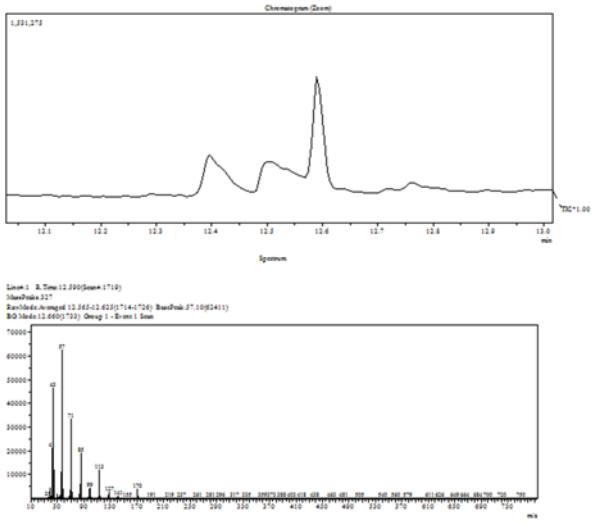

**Figure S39:** GC-MS trace for urine for undoped sample at 12.6 minutes

**NIST compound ID:** Dodecane

Urine – Undoped Sample – 12.8 min

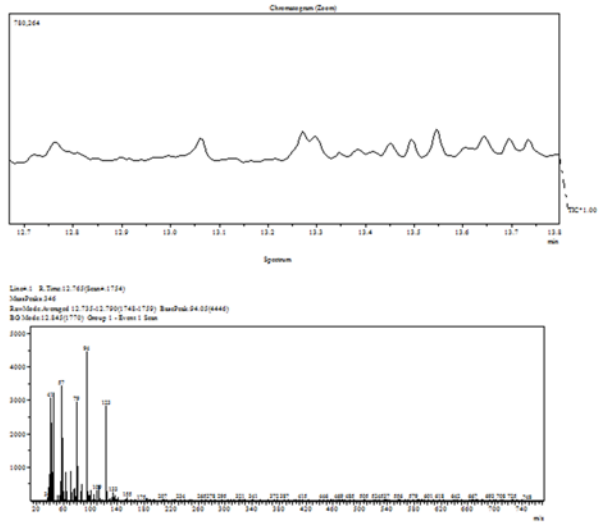

**Figure S40:** GC-MS trace for urine for undoped sample at 12.8 minutes

**NIST compound ID:** Mannosamine

Urine – Undoped Sample – 13.1 min

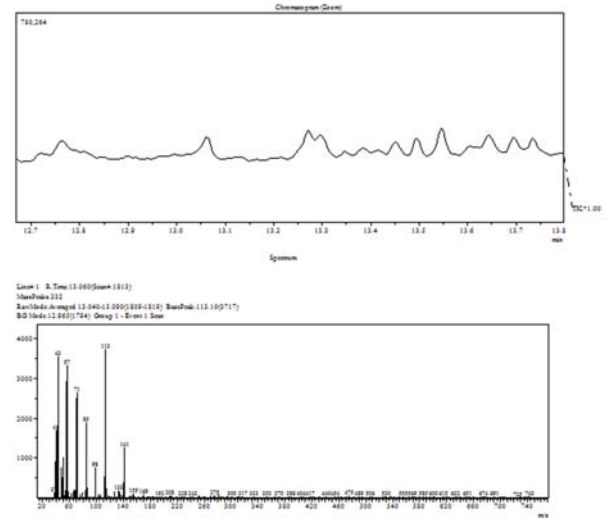

**Figure S41:** GC-MS trace for urine for undoped sample at 13.1 minutes

**NIST compound ID:** 1-Butyrylpyrrolidine

Urine – Undoped Sample – 13.25 min

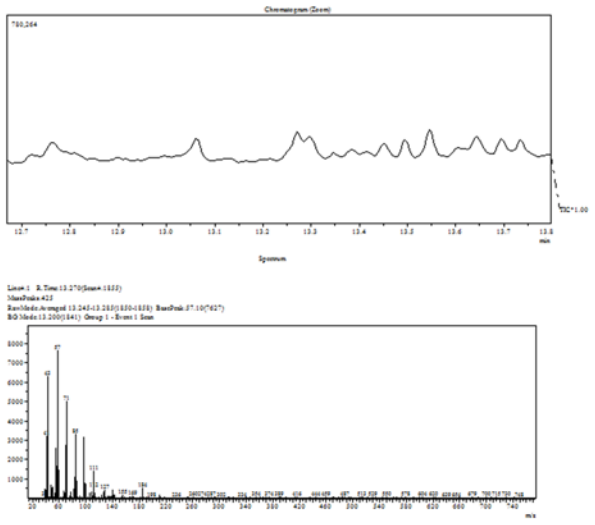

**Figure S42:** GC-MS trace for urine for undoped sample at 13.25 minutes

**NIST compound ID:** Carbonic acid, eicosyl prop-e-en-2-yl ester

Urine – Undoped Sample – 13.3 min

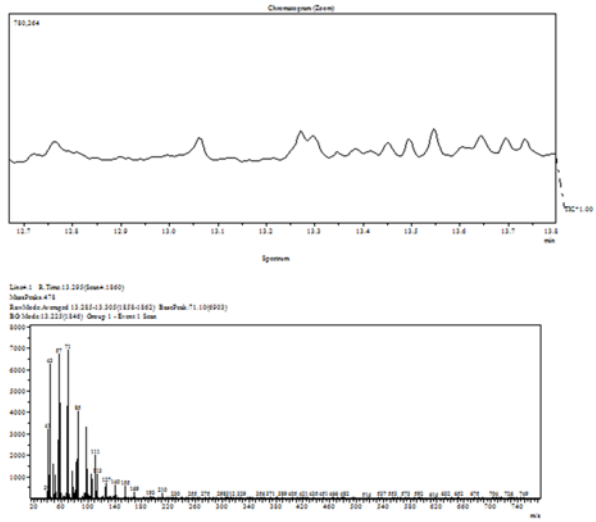

**Figure S43:** GC-MS trace for urine for undoped sample at 13.3 minutes

**NIST compound ID:** 2-Isopopyl-5-methyl-1-hexanol

Urine – Undoped Sample – 13.45 min

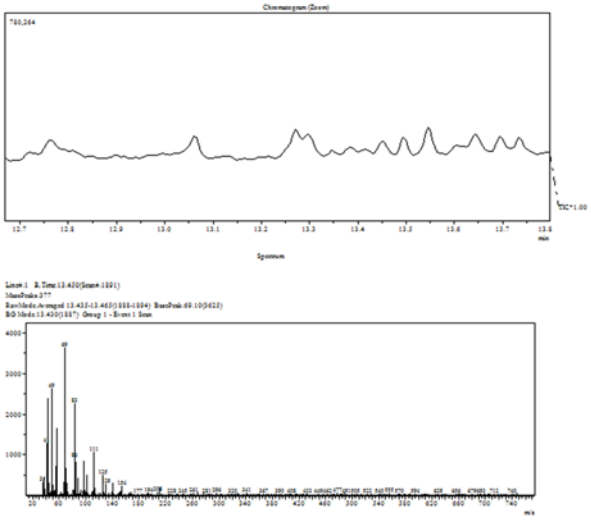

**Figure S44:** GC-MS trace for urine for undoped sample at 13.45 minutes

**NIST compound ID:** 11-Methyldodecanol

Urine – Undoped Sample – 13.5 min

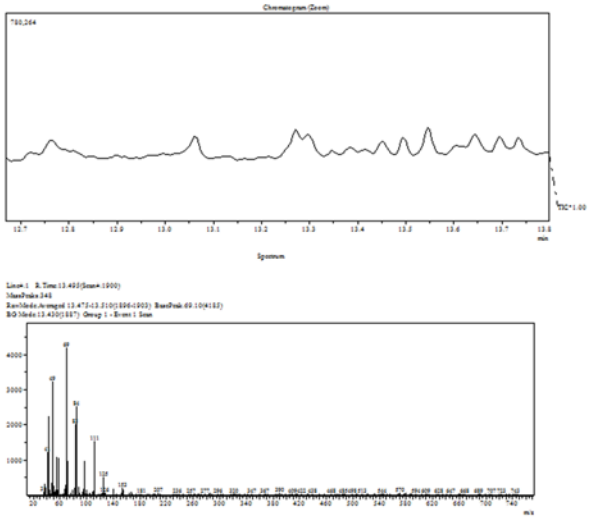

**Figure S45:** GC-MS trace for urine for undoped sample at 13.5 minutes

**NIST compound ID:** 1,4-Diethylhexyl dichloroacetate

Urine – Undoped Sample – 13.55 min

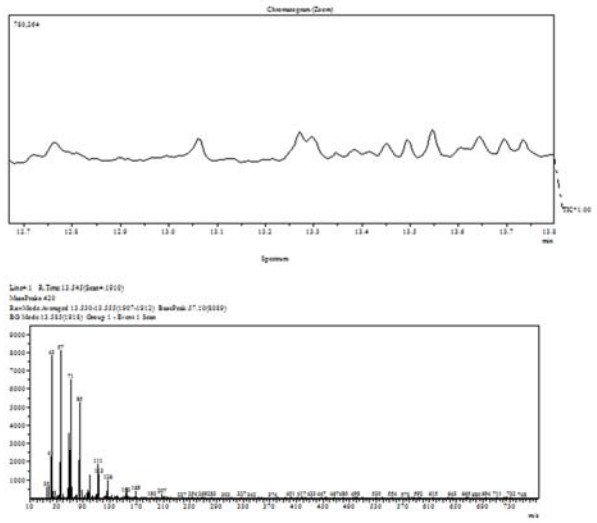

**Figure S46:** GC-MS trace for urine for undoped sample at 13.55 minutes

**NIST compound ID:** Dodecyl nonyl ether

Urine – Undoped Sample – 13.65 min

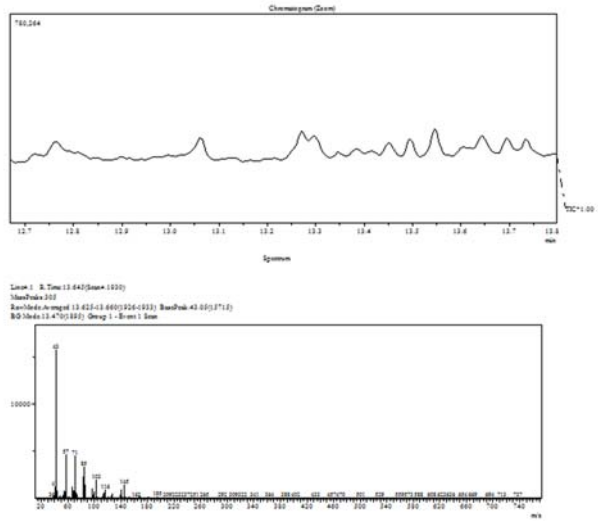

**Figure S47:** GC-MS trace for urine for undoped sample at 13.65 minutes

**NIST compound ID:** 2,4-Dimethylheptane

Urine – Undoped Sample – 13.7 min

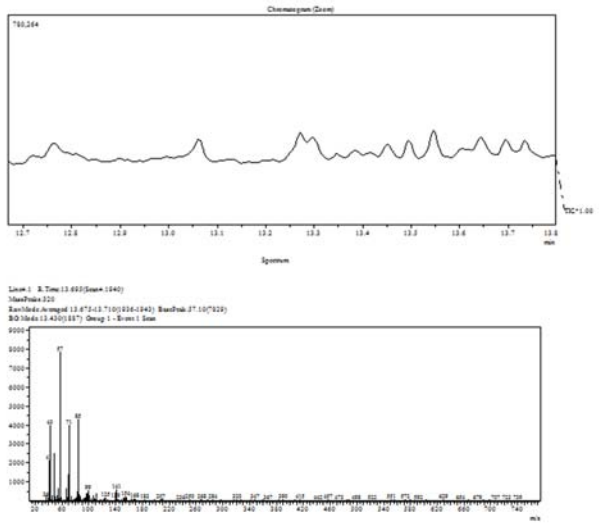

**Figure S48:** GC-MS trace for urine for undoped sample at 13.7 minutes

**NIST compound ID:** 2,3,5-Trimethyldecane

Urine – Undoped Sample – 13.75 min

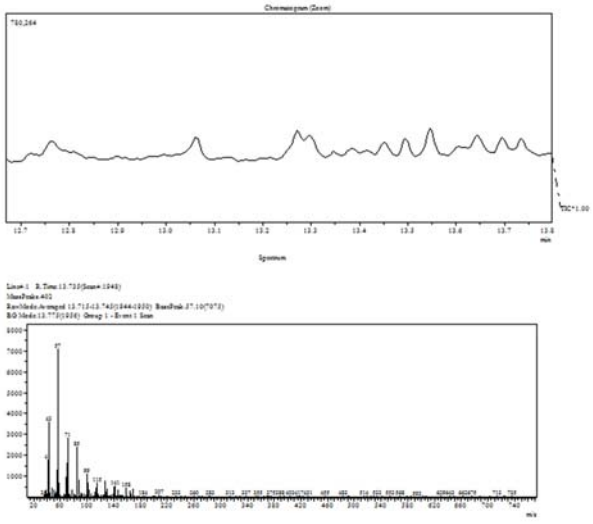

**Figure S49:** GC-MS trace for urine for undoped sample at 13.75 minutes

**NIST compound ID:** 3,8-Dimethyldecane

Urine – Undoped Sample – 13.85 min

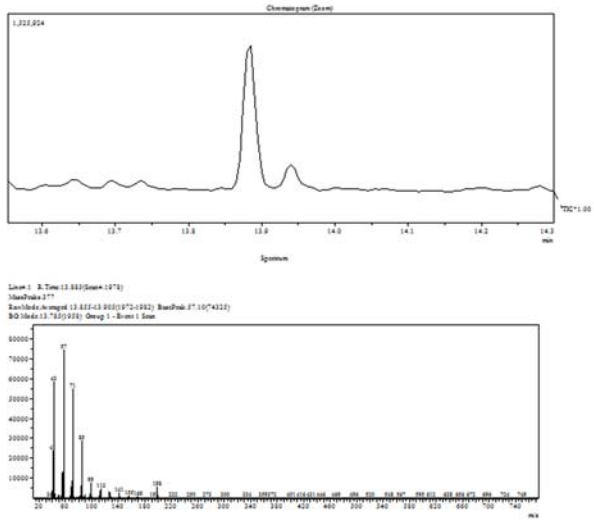

**Figure S50:** GC-MS trace for urine for undoped sample at 13.85 minutes

**NIST compound ID:** Tetradecane

Urine – Undoped Sample – 13.95 min

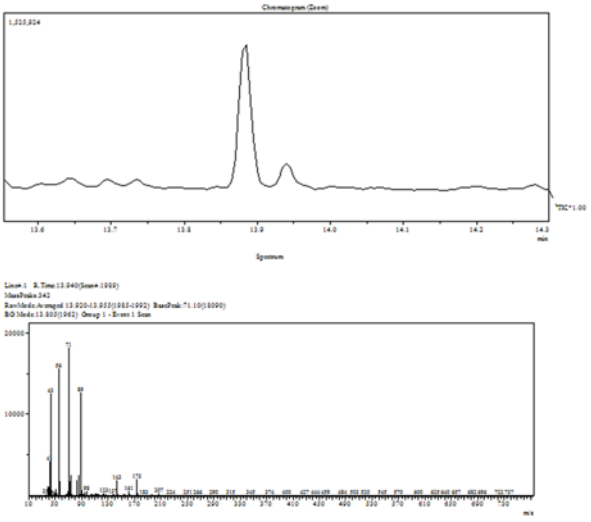

**Figure S51:** GC-MS trace for urine for undoped sample at 13.95 minutes

**NIST compound ID:** Propanoic acid, 2-methyl-, 3-hydroxy-2,2,4-trimethylpentyl ester

Urine – Undoped Sample – 15 min

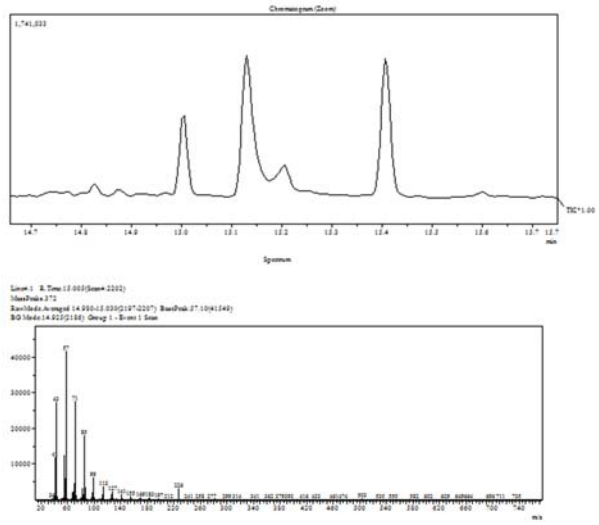

**Figure S52:** GC-MS trace for urine for undoped sample at 15 minutes

**NIST compound ID:** Hexadecane

Urine – Undoped Sample – 15.1 min

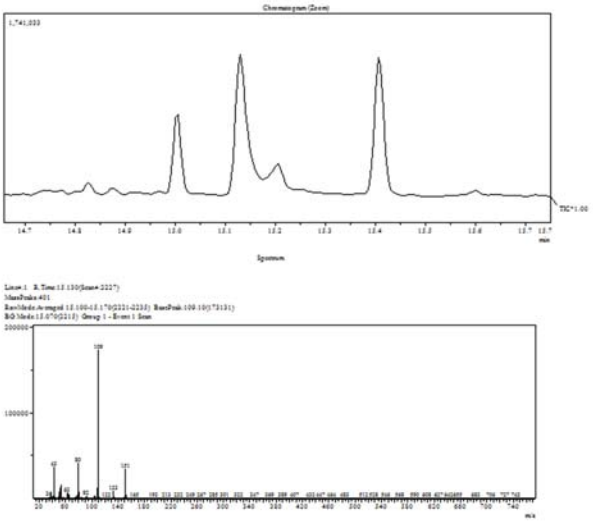

**Figure S53:** GC-MS trace for urine for undoped sample at 15.1 minutes

**NIST compound ID:** Acetaminophen

Urine – Undoped Sample – 15.2 min

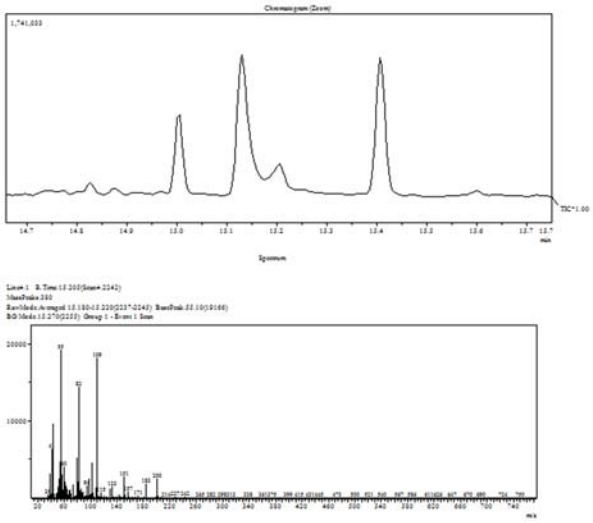

**Figure S54:** GC-MS trace for urine for undoped sample at 15.2 minutes

**NIST compound ID:** Cyclohexyl laurate

Urine – Undoped Sample – 15.4 min

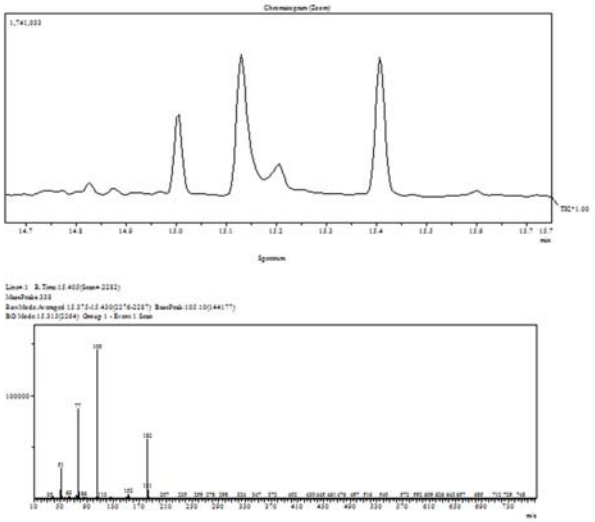

**Figure S55:** GC-MS trace for urine for undoped sample at 15.4 minutes

**NIST compound ID:** Benzophenone

Urine – Undoped Sample – 15.6 min

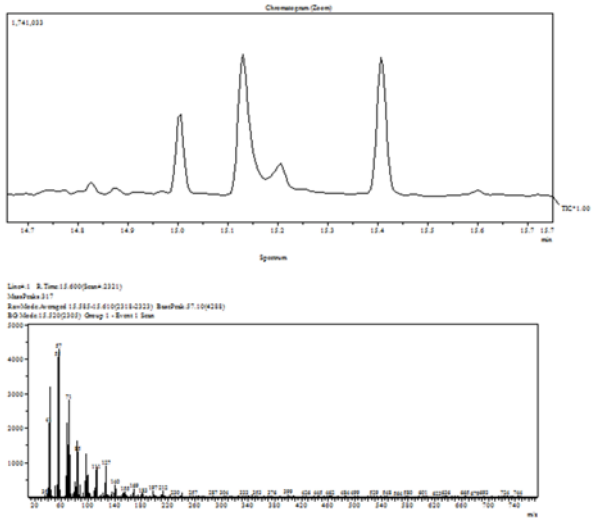

**Figure S56:** GC-MS trace for urine for undoped sample at 15.6 minutes

**NIST compound ID:** 2-hexyldecanol

Urine – Undoped Sample – 16 min

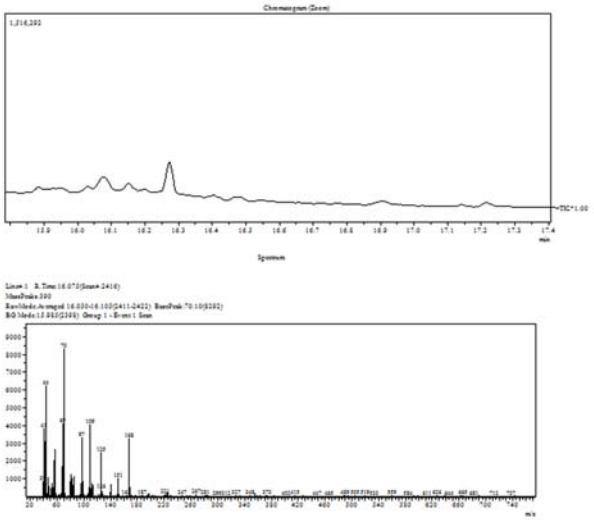

**Figure S57:** GC-MS trace for urine for undoped sample at 16 minutes

**NIST compound ID:** 3,7,11,15-Tetramethyl-2-hexadecene

Urine – Undoped Sample – 16.15 min

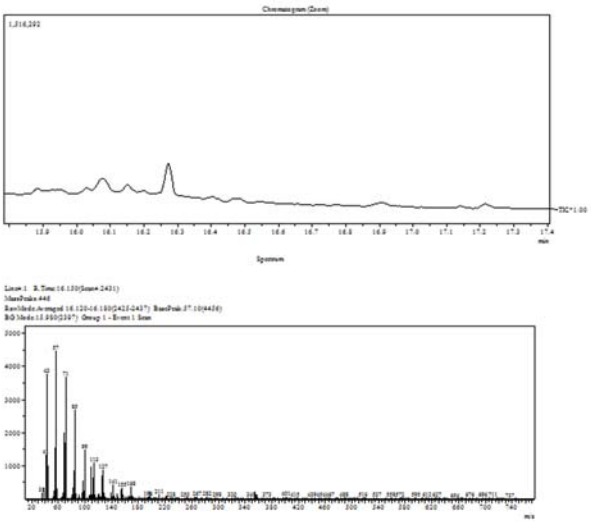

**Figure S58:** GC-MS trace for urine for undoped sample at 16.15 minutes

**NIST compound ID:** 2-Methylhexacosane

Urine – Undoped Sample – 16.25 min

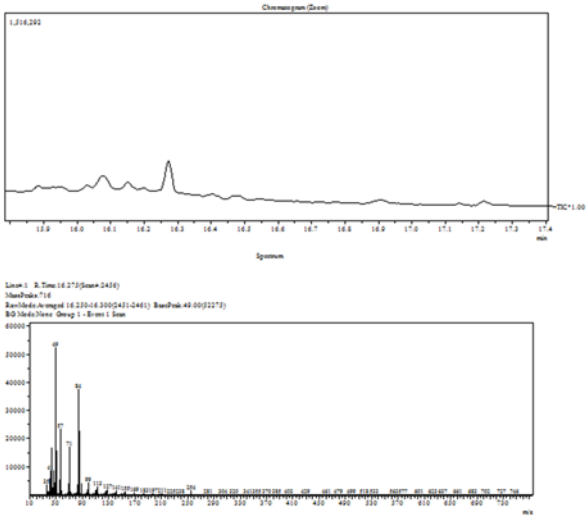

**Figure S59:** GC-MS trace for urine for undoped sample at 16.25 minutes

**NIST compound ID:** 1-(15-Methylhexadecanoyl)pyrrolidine

Urine – Undoped Sample – 18.3 min

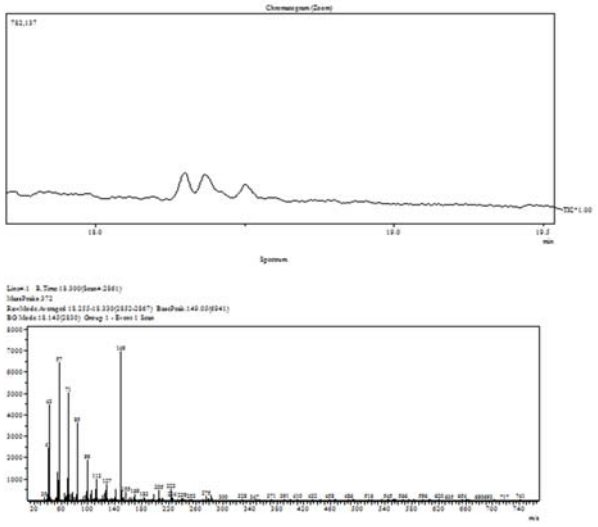

**Figure S60:** GC-MS trace for urine for undoped sample at 18.3 minutes

**NIST compound ID:** Bis(tridecyl) phthalate

Urine – Undoped Sample – 18.4 min

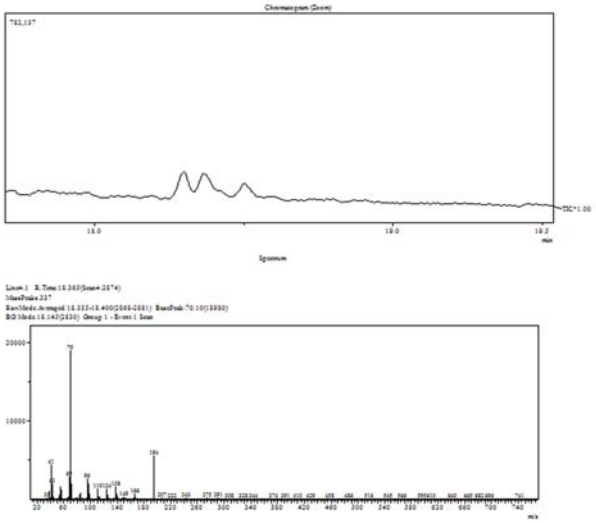

**Figure S61:** GC-MS trace for urine for undoped sample at 18.4 minutes

**NIST compound ID:** 5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1',2'-d]pyrazine

Urine – Undoped Sample – 18.5 min

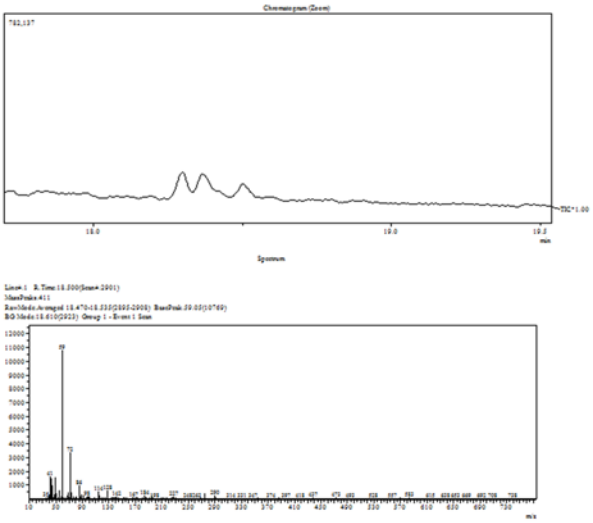

**Figure S62:** GC-MS trace for urine for undoped sample at 18.5 minutes

**NIST compound ID:** Dodecanamide

Urine – Undoped Sample – 22.8 min

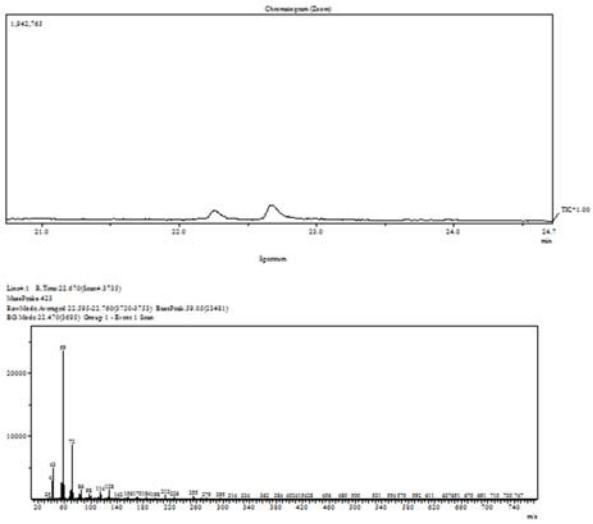

**Figure S63:** GC-MS trace for urine for undoped sample at 22.8 minutes

**NIST compound ID:** Hexadecanamide

Urine – Undoped Sample – 29.5 min

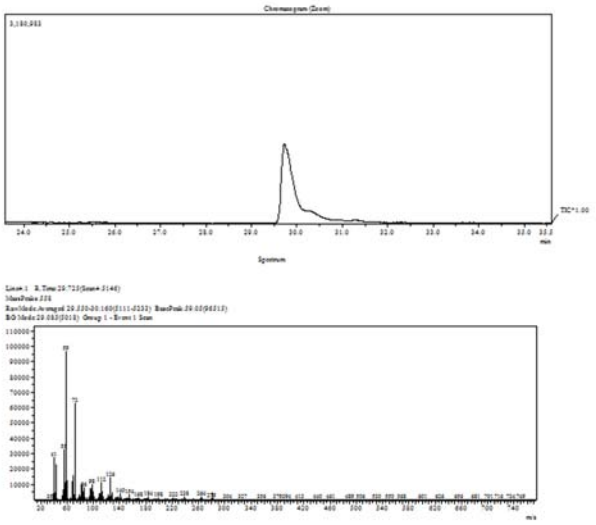

**Figure S64:** GC-MS trace for urine for undoped sample at 29.5 minutes

**NIST compound ID:** 9-Octadecenamide

Urine – Undoped Sample – 44 min

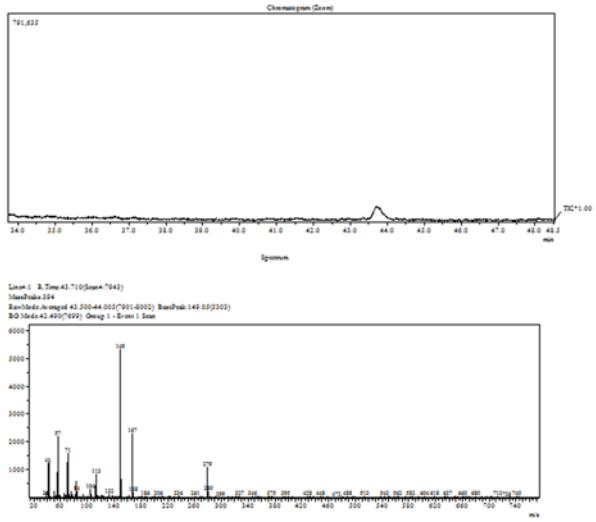

**Figure S65:** GC-MS trace for urine for undoped sample at 44 minutes

**NIST compound ID:** Diisooctyl phthalate

## SUMMARY FIGURES FOR MIXTURE FLUORESCENCE MODULATION EXPERIMENTS

The black line represents the emission from the fluorophore, and the red line represents the emission from the 1:1 binary analyte mixtures and the fluorophore mixed together in urine. All X-axes measure the emission from 470 nm to 800 nm, and all Y-axes have been normalized so that the fluorescence emission is on a scale of 0.0 to 1.0.

Analyte **1** – Analyte **2**

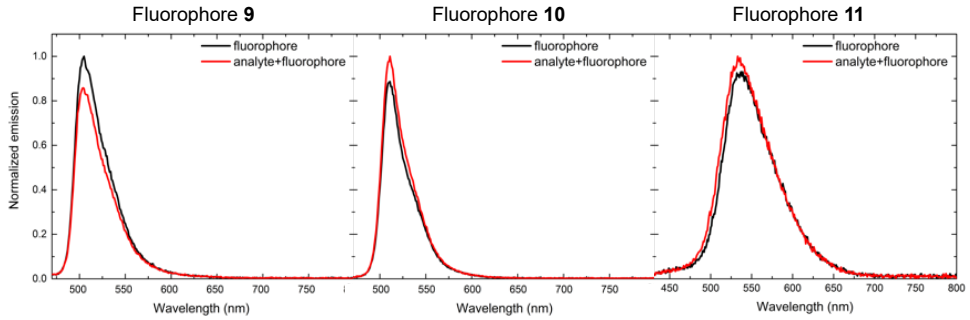


**Figure S66:** Fluorescence modulation of fluorophores **9-11** with analytes **1** and **2** in urine

Analyte **1** – Analyte **3**

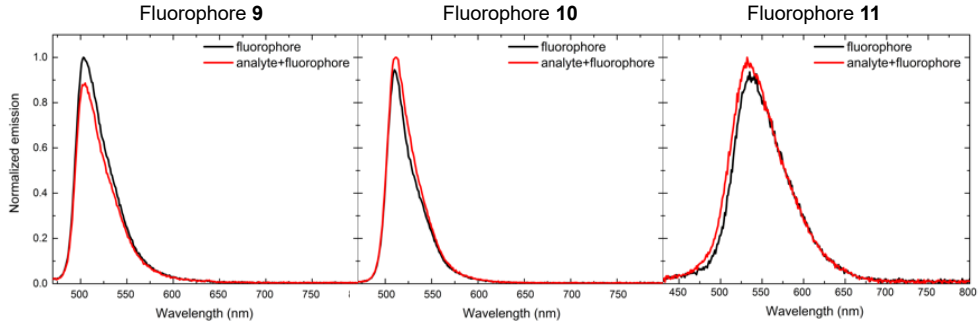


**Figure S67:** Fluorescence modulation of fluorophores **9-11** with analytes **1** and **3** in urine

Analyte **1** – Analyte **4**

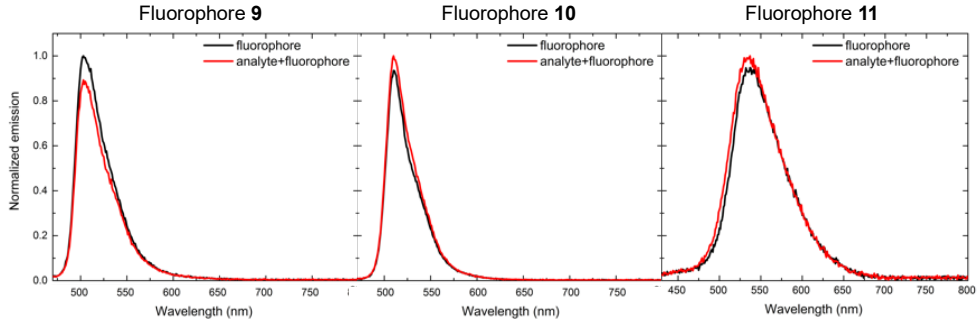


**Figure S68:** Fluorescence modulation of fluorophores **9-11** with analytes **1** and **4** in urine

Analyte **1** – Analyte **5**

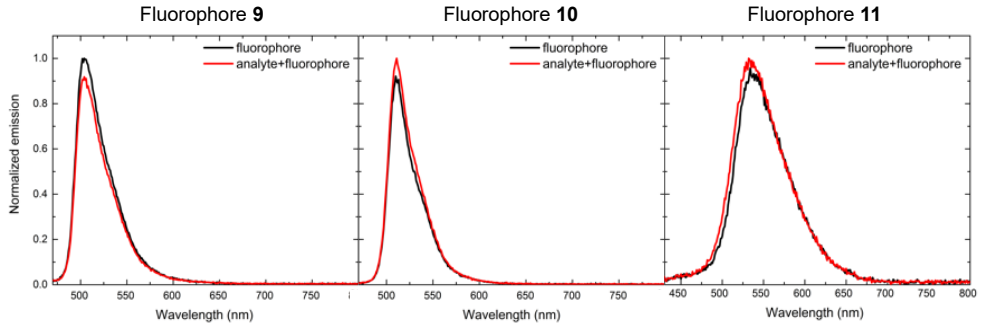


**Figure S69:** Fluorescence modulation of fluorophores **9-11** with analytes **1** and **5** in urine

Analyte **1** – Analyte **6**

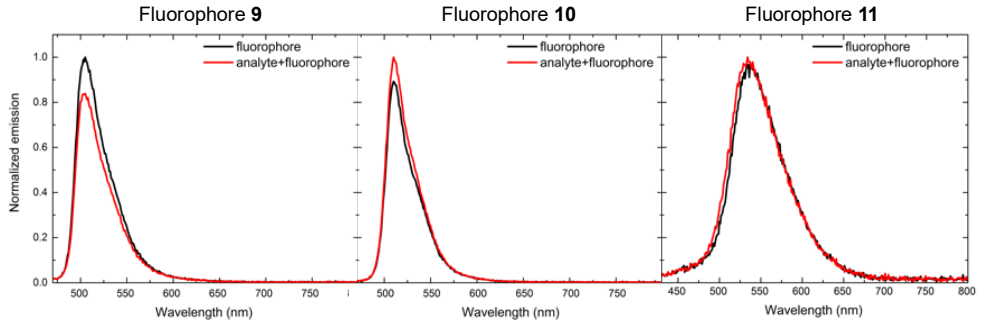


**Figure S70:** Fluorescence modulation of fluorophores **9-11** with analytes **1** and **6** in urine

Analyte **1** – Analyte **7**

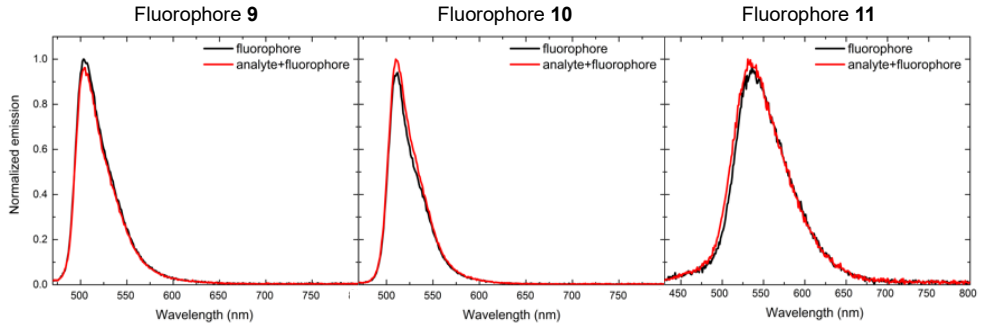


**Figure S71:** Fluorescence modulation of fluorophores **9-11** with analytes **1** and **7** in urine

Analyte **2** – Analyte **3**

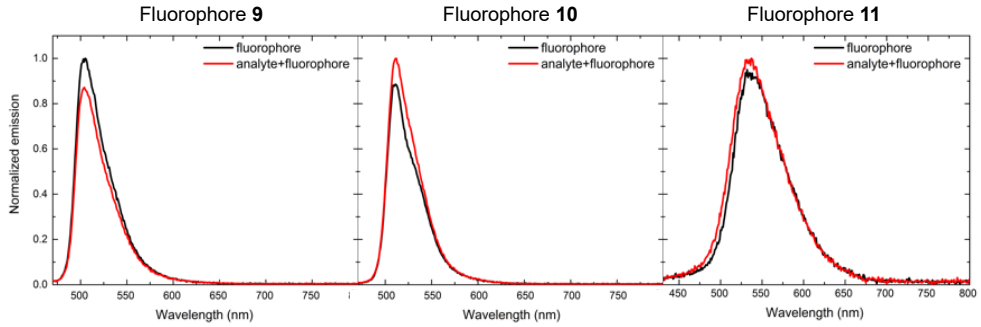


**Figure S72:** Fluorescence modulation of fluorophores **9-11** with analytes **2** and **3** in urine

Analyte **3** – Analyte **4**

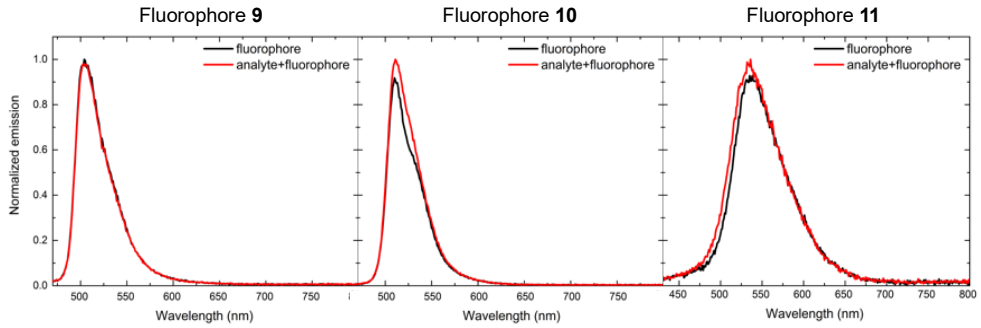


**Figure S73:** Fluorescence modulation of fluorophores **9-11** with analytes **3** and **4** in urine

Analyte **3** – Analyte **5**

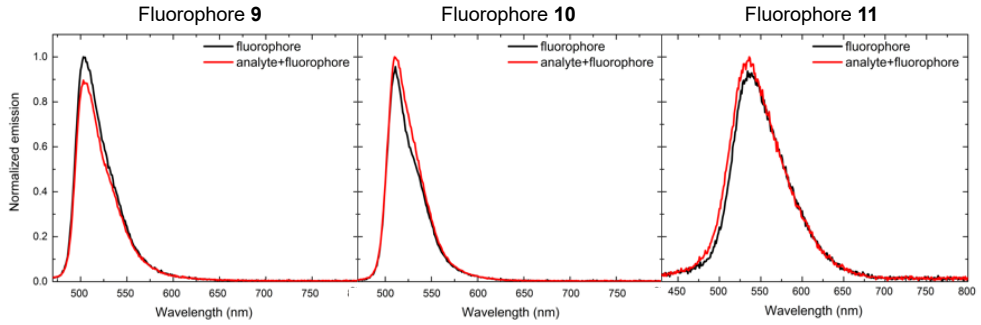


**Figure S74:** Fluorescence modulation of fluorophores **9-11** with analytes **3** and **5** in urine

Analyte **6** – Analyte **7**

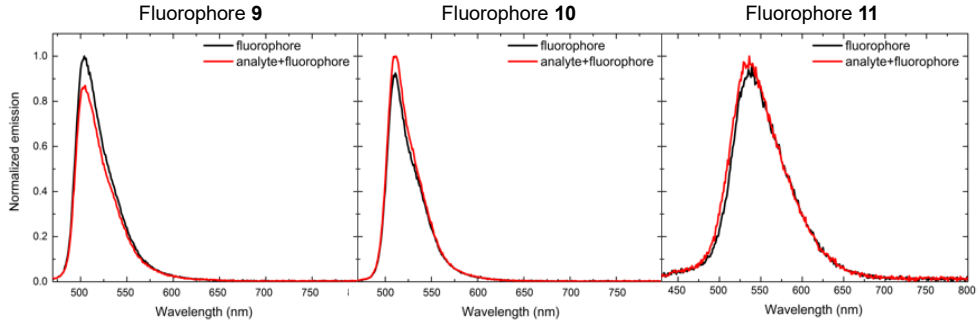


**Figure S75:** Fluorescence modulation of fluorophores **9-11** with analytes **6** and **7** in urine

**SUMMARY FIGURES FOR MIXTURE ARRAY GENERATION EXPERIMENTS**

Results from linear discriminant analyses of the fluorescence responses of binary analyte mixtures were plotted with SCORE (1) values on the X-axis and SCORE (2) values on the Y-axis.

**Urine**

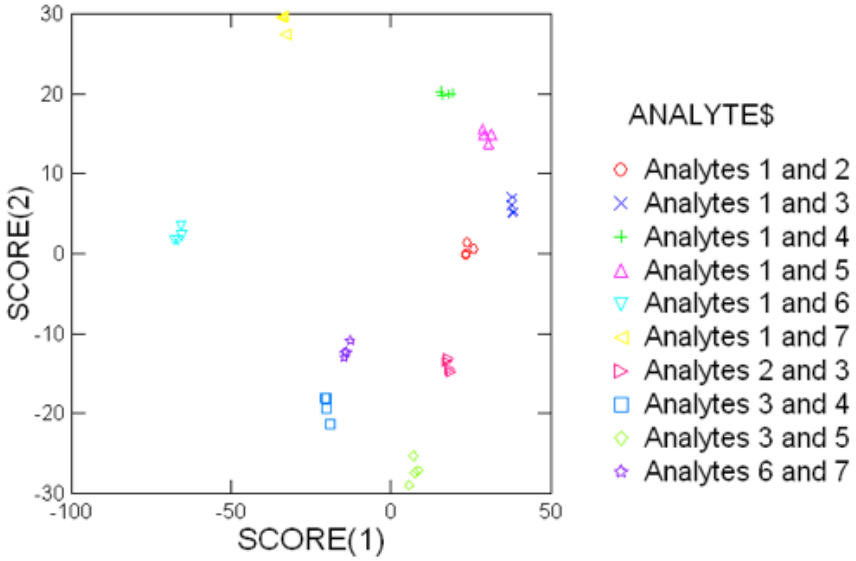


**Figure S76:** Linear discriminant analysis of fluorescence responses for analytes mixtures with fluorophores **9-11** in urine

## SUMMARY FIGURES FOR ELECTROSTATIC POTENTIAL MAPPING

All conformations shown were energy-minimized using Spartan 16 software. The red areas represent electron-rich regions and the blue areas represent electron-deficient regions.

**Analyte 1**

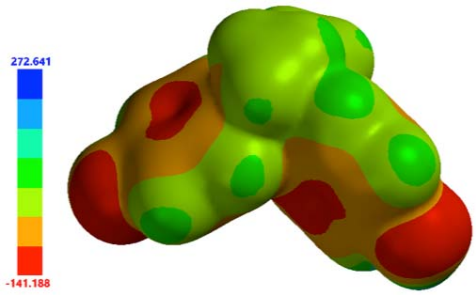


**Figure S77:** Electrostatic potential map of analyte **1**

**Analyte 2**

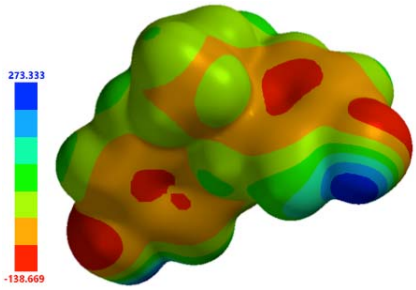


**Figure S78:** Electrostatic potential map of analyte **2**

**Analyte 3**

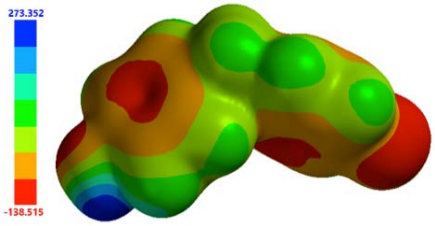


**Figure S79:** Electrostatic potential map of analyte **3**

**Analyte 4**

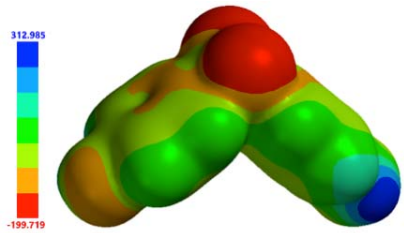


**Figure S80:** Electrostatic potential map of analyte **4**

**Analyte 5**

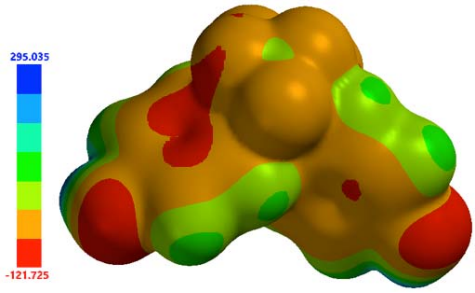


**Figure S81:** Electrostatic potential map of analyte **5**

**Analyte 6**

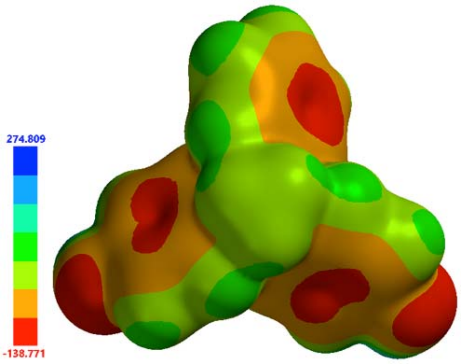


**Figure S82:** Electrostatic potential map of analyte **6**

**Analyte 7**

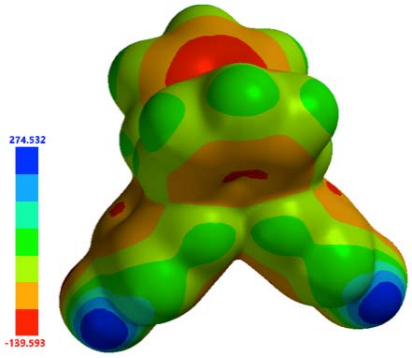


**Figure S83:** Electrostatic potential map of analyte **7**

**Analyte 8**

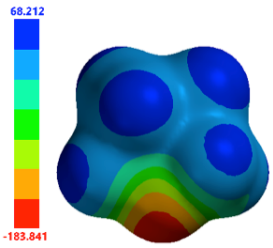


**Figure S84:** Electrostatic potential map of analyte **8**

**Fluorophore 9**

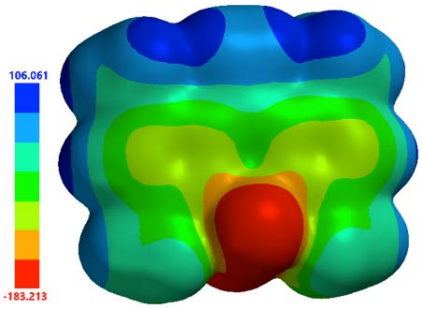


**Figure S85:** Electrostatic potential map of fluorophore **9**

**Fluorophore 10**

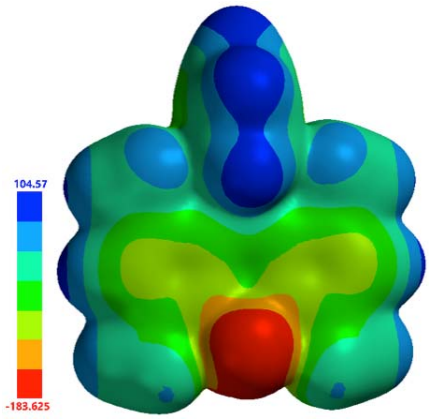


**Figure S86:** Electrostatic potential map of fluorophore **10**

**Fluorophore 11**

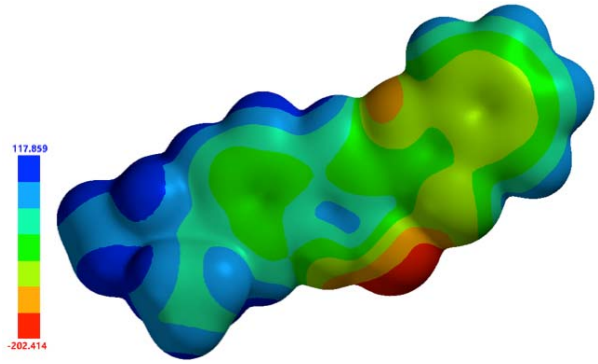


**Figure S87:** Electrostatic potential map of fluorophore **11**

## SUMMARY FIGURES FOR FLUOROPHORES 9-11 FLUORESCENCE EMISSION SPECTRA

The black line represents the emission from the fluorophore in the absence of cyclodextrin, and the red line represents the emission from the fluorophore in the presence of cyclodextrin in buffer or urine. All X-axes measure the emission from 470 nm to 800 nm, and all Y-axes have been normalized so that the fluorescence emission is on a scale of 0.0 to 1.0.

**Buffer**

Fluorophore **9**

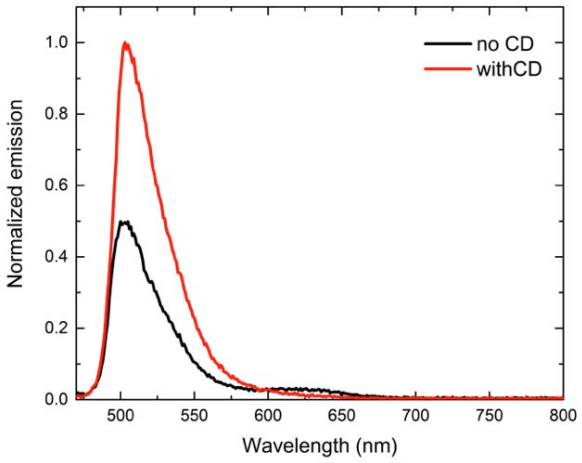


**Figure S88:** Fluorescence emission of fluorophore **9** in the absence and presence of cyclodextrin in buffer

Fluorophore **10**

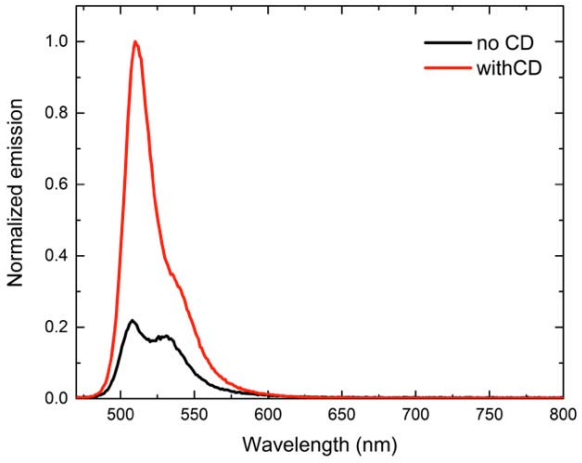


**Figure S89:** Fluorescence emission of fluorophore **10** in the absence and presence of cyclodextrin in buffer

Fluorophore **11**

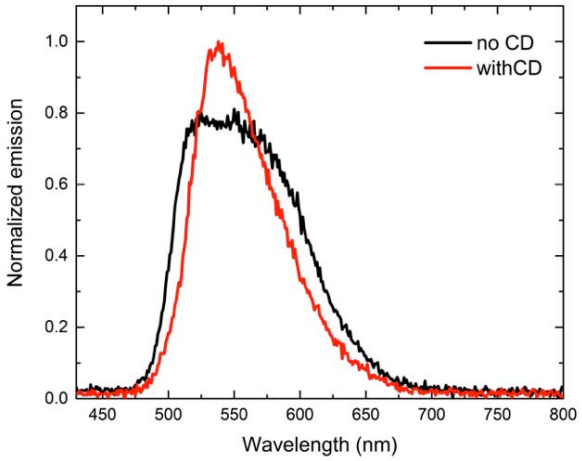


**Figure S90:** Fluorescence emission of fluorophore **11** in the absence and presence of cyclodextrin in buffer

**Urine**

Fluorophore **9**

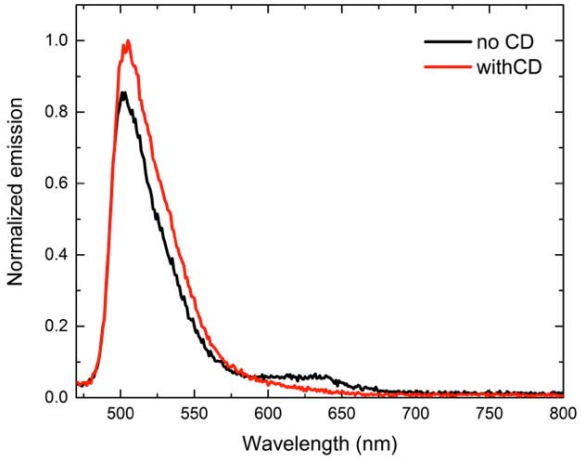


**Figure S91:** Fluorescence emission of fluorophore **9** in the absence and presence of cyclodextrin in urine

Fluorophore **10**

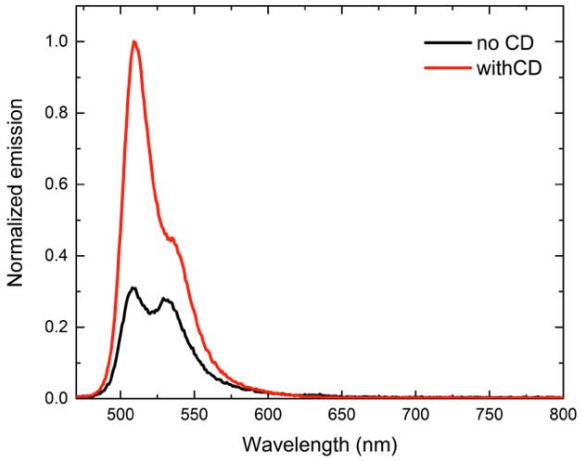


**Figure S92:** Fluorescence emission of fluorophore **10** in the absence and presence of cyclodextrin in urine

Fluorophore **11**

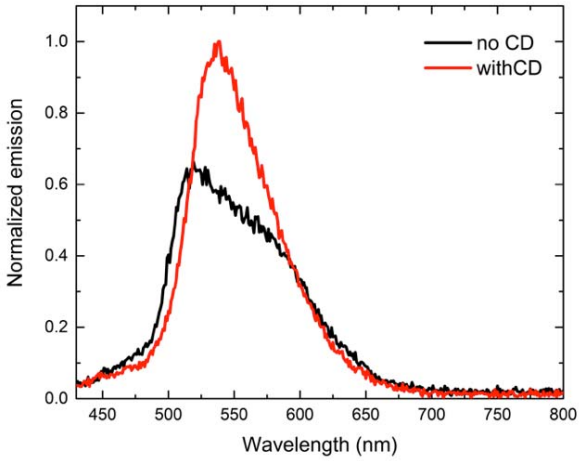


**Figure S93:** Fluorescence emission of fluorophore **11** in the absence and presence of cyclodextrin in urine

## SUMMARY FIGURES FOR BINDING CONSTANT EXPERIMENTS

Binding constants were calculated via UV/Visible spectroscopy following literature-reported procedures:

Tomiyasu, H.; Zhao, J. L.; Ni, X. L.; Zeng, X.; Elsegood, M. R. J.; Jones, B.; Redshaw, C.; Teat, S. J.; Yamato, T. Positive and negative allosteric effects of thiocalix[4]arene-based receptors having urea and crown ether moieties. *RSC Advances* **2015**, *5*, 14747-14755.

Figures represent double reciprocal Benesi-Hildebrand plots with the reciprocal change in absorbance (1/ΔA) on the Y-axis, and reciprocal γ-cyclodextrin concentration (1/[CD]) on the X-axis.

Analyte **1** – γ-cyclodextrin

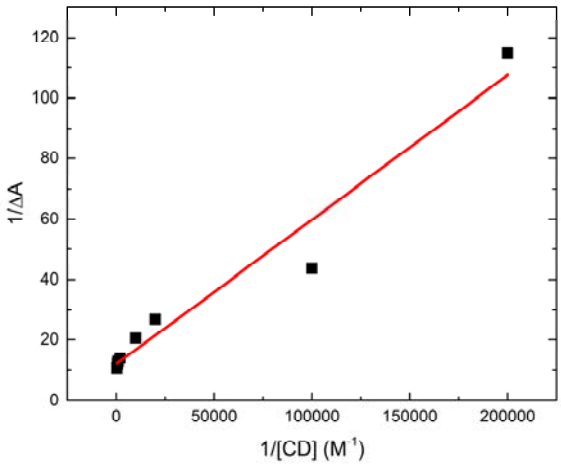


**Figure S94:** Double reciprocal Benesi-Hildebrand plot for analyte **1** with γ-cyclodextrin

Analyte **2** – γ-cyclodextrin

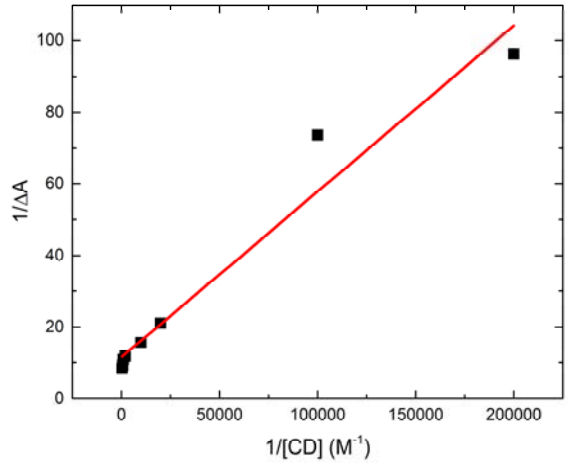


**Figure S95:** Double reciprocal Benesi-Hildebrand plot for analyte **2** with γ-cyclodextrin

Analyte **3** – γ-cyclodextrin

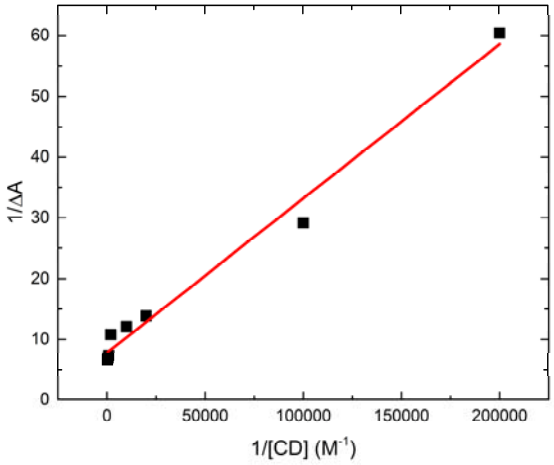


**Figure S96:** Double reciprocal Benesi-Hildebrand plot for analyte **3** with γ-cyclodextrin

Analyte **4** – γ-cyclodextrin

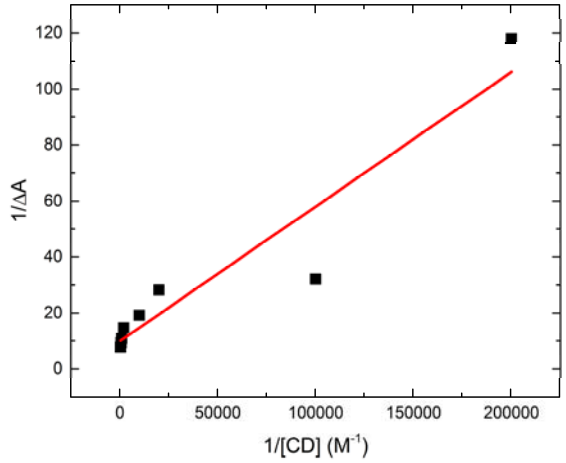


**Figure S97:** Double reciprocal Benesi-Hildebrand plot for analyte **4** with γ-cyclodextrin

Analyte **5** – γ-cyclodextrin

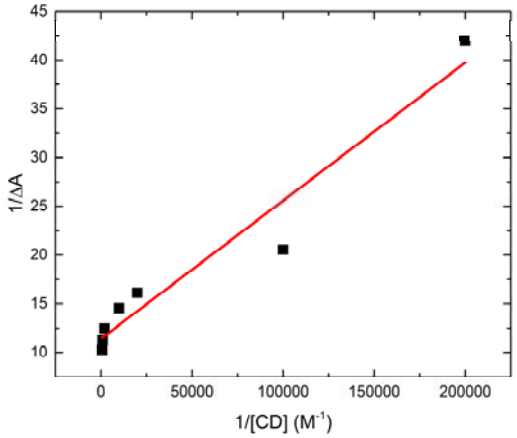


**Figure S98:** Double reciprocal Benesi-Hildebrand plot for analyte **5** with γ-cyclodextrin

Analyte **6** – γ-cyclodextrin

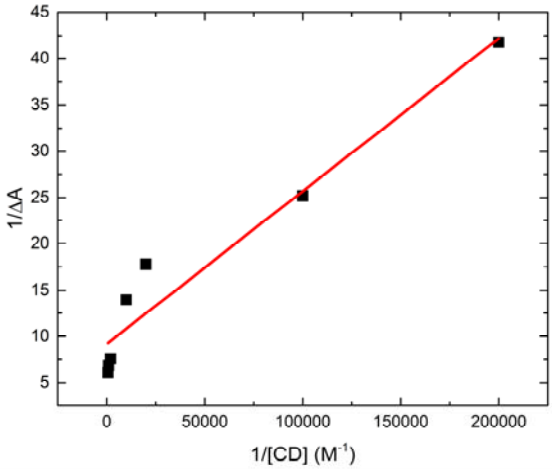


**Figure S99:** Double reciprocal Benesi-Hildebrand plot for analyte **6** with γ-cyclodextrin

Analyte **7** – γ-cyclodextrin

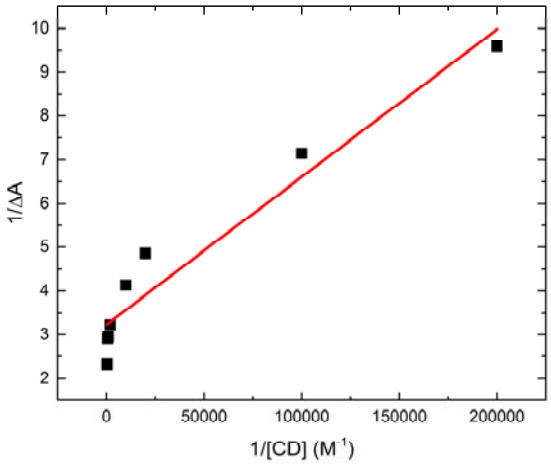


**Figure S100:** Double reciprocal Benesi-Hildebrand plot for analyte **7** with γ-cyclodextrin