SUPPLEMENTARY MATERIAL

Efficient Detection of Phthalate Esters in Human Saliva via Fluorescence Spectroscopy

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ANALYTE DETAILS

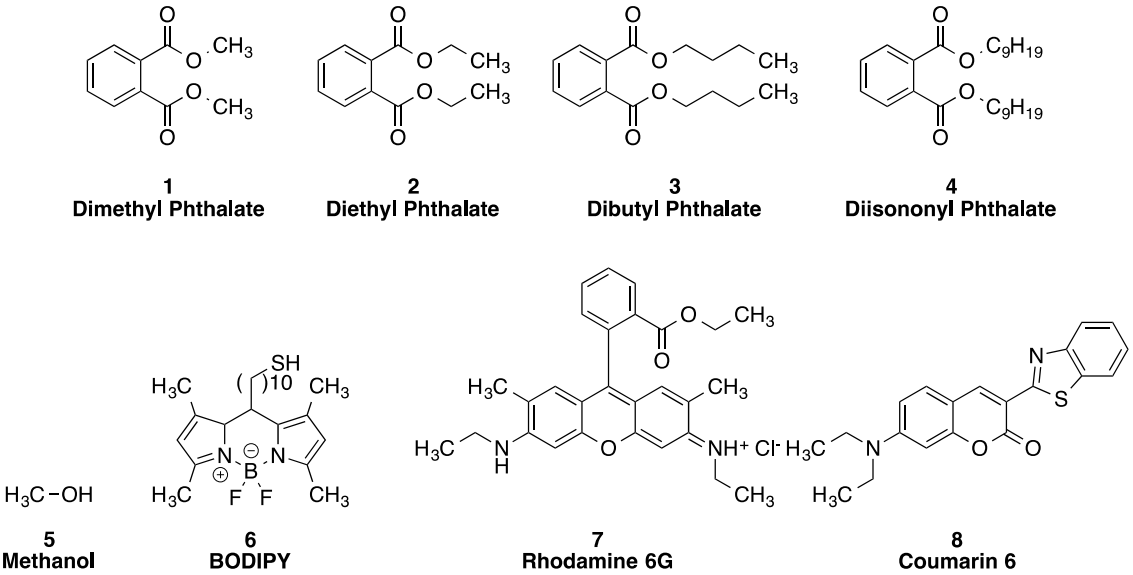

Figure S1: Structures of analytes **1-4**, control analyte **5**, and fluorophores **6-8**

Table S1: Final solution concentrations of analytes and fluorophores

Compound	Concentration (mg/mL) in methanol	Volume (µL)	Final Concentration (µM)
1	1.0	20	39.6
2	1.0	20	34.6
3	1.0	20	27.6
4	1.0	20	18.4
5	1.0	20	240.1
6	0.1	100	9.5
7	0.1	100	8.1
8	0.1	100	11.0

SYNTHESIS OF FLUOROPHORE 6

The synthesis of BODIPY **6** was performed according to literature-reported procedures:

Shepherd, J. L.; Kell, A.; Chung, E.; Sinclair, C. W.; Workentin, M. S.; Bizzotto, D. *J. Am. Chem. Soc.* **2004**, *126*, 8329-8335.

Reaction 1:

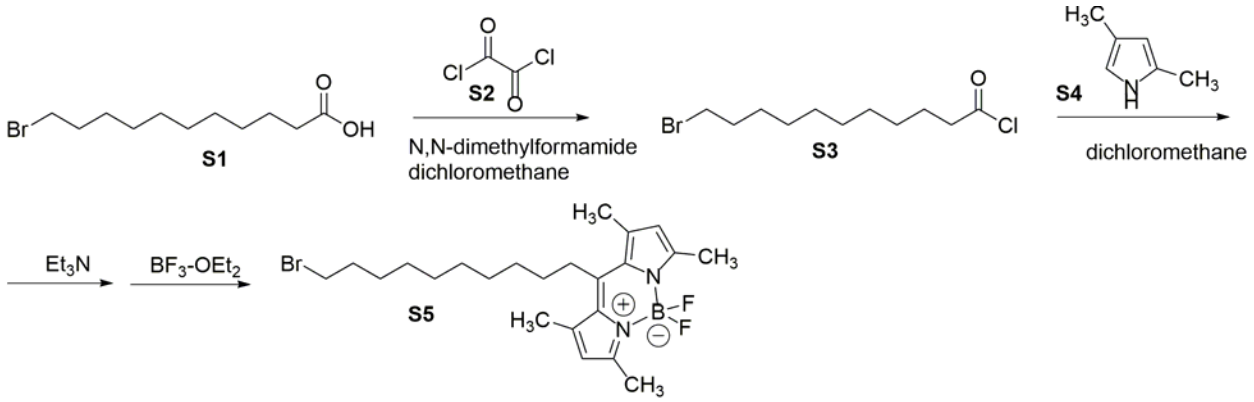

Figure S2: Synthetic pathway to structure **S5**

Procedure: 2.0 grams of 11-bromoundecanoic acid **S1** (7.54 mmol, 1.0 eq.) was combined with 2 drops of *N*,*N*-dimethylformamide in 40 mL of dichloromethane. 1.0 gram of oxalyl chloride **S2** (7.88 mmol, 1.05 eq.) was dissolved in 5.0 mL of dichloromethane and added dropwise. The reaction mixture was stirred for one hour, then the crude mixture was concentrated on the rotary evaporator and dried on a vacuum overnight to remove any unreacted oxalyl chloride. The resulting acid chloride **S3** was dissolved in 50 mL of dichloromethane. 0.772 mL of 2,4-dimethylpyrrole **S4** (7.50 mmol, 0.99 eq.) was dissolved in 5.0 mL of dichloromethane and added to the reaction mixture. The resulting reaction mixture was heated to reflux for 3 hours under a nitrogen atmosphere, during which time the mixture became a dark red color. After three hours, the reaction mixture was cooled to room temperature and solvent was removed on the rotary evaporator until approximately 5.0 mL of the dichloromethane solution remained. 200 mL of *n*-hexanes were added to the flask, and the mixture was cooled overnight in the freezer at -20 ºC. The hexanes were decanted from the insoluble oil and precipitate. The resulting crude product was dissolved in 75 mL of toluene and heated to 80 ºC. 1.0 mL of triethylamine (7.17 mmol, 0.95 eq.) was added and the solution immediately turned light yellow. 1.0 mL of boron trifluoride etherate (8.10 mmol, 1.07 eq.) was then added and the reaction mixture was stirred at 80 ºC for 30 minutes, during which time the color of the mixture darkened and became fluorescent. The reaction mixture was cooled to room temperature, and the product was extracted 3 times with brine (50 mL each time). The organic layer was dried over sodium sulfate, filtered, and concentrated. The crude product was purified by flash chromatography (1:1 dichloromethane: hexanes) to yield the desired product in 28% yield (comparable to the literature-reported 24% yield).

Reaction 2:

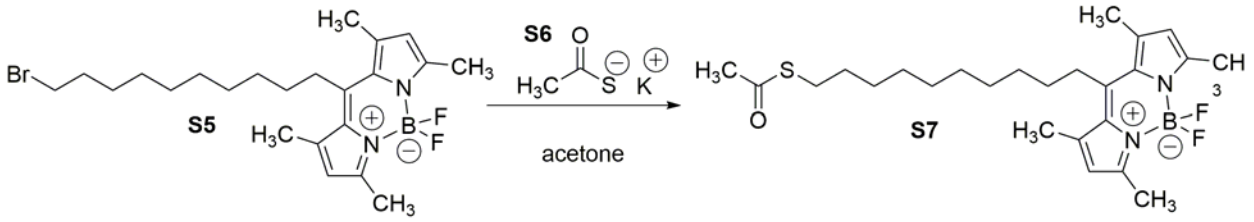

Figure S3: Synthetic pathway to structure **S7**

Procedure: Compound **S5** (0.968 g, 2.07 mmol, 1.0 eq.) and compound **S6** (0.27 grams, 2.36 mmol, 1.14 eq.) were dissolved in 50 mL of acetone. The reaction mixture was heated to reflux for two hours. After two hours, the reaction mixture was cooled to room temperature, acetone was removed, and the crude solid was re-dissolved in dichloromethane and washed with water. The organic extract was dried over sodium sulfate, filtered and concentrated, to yield compound **S7** in 97% yield (0.932 grams).

Reaction 3:

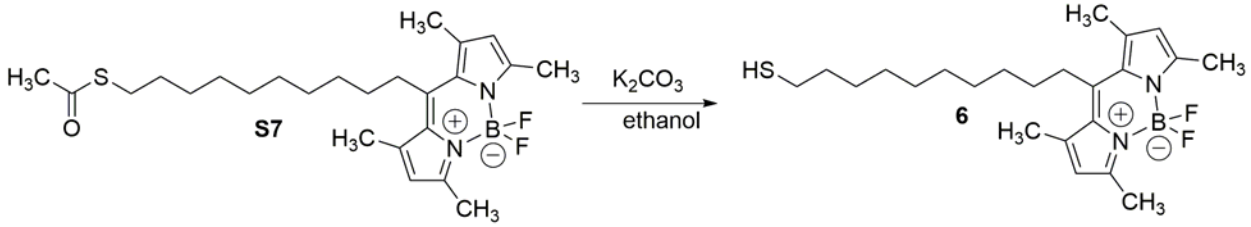

Figure S4: Synthetic pathway to compound **6**

Procedure: Compound **S7** (0.932 grams, 2.01 mmol, 1.0 eq.) was dissolved in 150 mL of anhydrous ethanol that was purged with nitrogen. Potassium carbonate was added, and the reaction mixture was warmed to 30 ºC. The reaction mixture was stirred under nitrogen for 4 hours at 30 ºC. The contents of the flask were poured over 40 mL of aqueous saturated ammonium chloride, at which point the solution turned bright orange. The product was extracted with dichloromethane and washed several times with water. The organic layer was dried over sodium sulfate, filtered, and concentrated. The product was purified via flash chromatography (1:1 dichloromethane: hexanes) to yield compound **6** in 76% yield (674 mg).

^{1}H NMR OF FLUOROPHORE 6

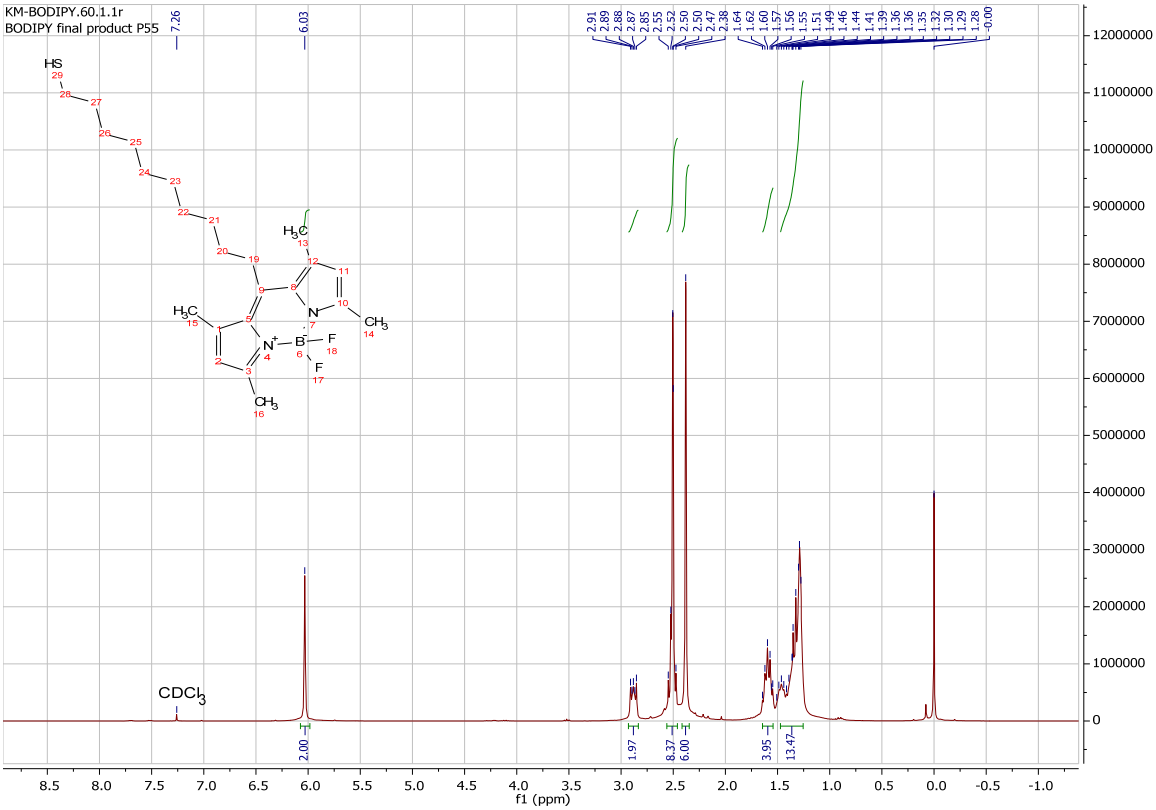

Figure S5: ^{1}H NMR spectrum of fluorophore **6**

SUMMARY TABLES

SUMMARY TABLE FOR FLUORESCENCE MODULATION EXPERIMENTS

Table S2: Fluorescence modulation results for analytes in buffer and saliva

Cyclodextrin	Analyte	Fluorophore 6		Fluorophore 7		Fluorophore 8	
		Buffer	Saliva	Buffer	Saliva	Buffer	Saliva
α-CD	**1**	0.98 ± 0.02	1.15 ± 0.02	0.99 ± 0.00	0.98 ± 0.00	1.72 ± 0.06	0.77 ± 0.07
α-CD	**2**	1.12 ± 0.04	1.06 ± 0.06	0.99 ± 0.00	0.99 ± 0.00	1.04 ± 0.04	0.97 ± 0.02
α-CD	**3**	1.15 ± 0.04	1.12 ± 0.02	1.00 ± 0.00	1.00 ± 0.00	1.08 ± 0.08	0.95 ± 0.03
α-CD	**4**	2.62 ± 0.06	1.95 ± 0.02	1.00 ± 0.00	1.00 ± 0.00	1.72 ± 0.06	1.82 ± 0.03
α-CD	**5**	0.96 ± 0.01	0.99 ± 0.01	0.97 ± 0.00	0.99 ± 0.00	0.97 ± 0.08	0.94 ± 0.02
β-CD	**1**	1.15 ± 0.02	1.09 ± 0.02	1.00 ± 0.00	1.01 ± 0.00	1.00 ± 0.00	0.99 ± 0.00
β-CD	**2**	1.01 ± 0.00	0.99 ± 0.02	0.99 ± 0.00	1.00 ± 0.00	1.00 ± 0.00	1.01 ± 0.00
β-CD	**3**	1.27 ± 0.01	1.11 ± 0.03	0.99 ± 0.00	1.00 ± 0.01	1.00 ± 0.00	1.00 ± 0.00
β-CD	**4**	3.96 ± 0.12	1.69 ± 0.15	1.00 ± 0.00	1.02 ± 0.00	1.05 ± 0.00	1.09 ± 0.00
β-CD	**5**	1.19 ± 0.08	1.13 ± 0.03	1.00 ± 0.00	0.99 ± 0.00	0.99 ± 0.00	1.00 ± 0.00
PBS	**1**	1.43 ± 0.03	1.21 ± 0.04	0.98 ± 0.00	0.98 ± 0.00	1.12 ± 0.03	0.94 ± 0.07
PBS	**2**	1.07 ± 0.01	1.11 ± 0.02	0.98 ± 0.00	0.99 ± 0.00	0.92 ± 0.03	1.12 ± 0.05
PBS	**3**	1.77 ± 0.05	1.20 ± 0.03	0.99 ± 0.00	0.98 ± 0.00	1.11 ± 0.02	0.96 ± 0.02
PBS	**4**	2.16 ± 0.04	1.77 ± 0.15	0.98 ± 0.00	0.98 ± 0.00	2.26 ± 0.04	2.39 ± 0.08
PBS	**5**	1.14 ± 0.04	0.96 ± 0.08	0.97 ± 0.00	0.99 ± 0.00	0.94 ± 0.02	0.96 ± 0.01

SUMMARY TABLE FOR LIMIT OF DETECTION EXPERIMENTS

Table S3: Limits of detection for analytes **1-4** with β-cyclodextrin and fluorophore **6**

Analyte	Matrix	Fluorophore	Equation	R^2	LOD (μM)
1	Buffer	**6**	y = 0.0033x + 1.0568	0.9938	8.63 ± 1.63
	Saliva	**6**	y = 0.0027x + 1.0765	0.9091	17.06 ± 1.11
2	Buffer	**6**	y = 0.0083x + 0.9858	0.9807	2.22 ± 0.02
	Saliva	**6**	y = 0.0061x + 1.0103	0.9896	2.78 ± 0.19
3	Buffer	**6**	y = 0.0094x + 1.0153	0.9968	1.02 ± 0.02
	Saliva	**6**	y = 0.0067x + 1.0391	0.9803	1.46 ± 0.16
4	Buffer	**6**	y = 0.0565x + 0.6971	0.9920	0.09 ± 0.00
	Saliva	**6**	y = 0.0499x + 1.0748	0.9862	0.42 ± 0.09

SUMMARY TABLES FOR ARRAY GENERATION EXPERIMENTS

Buffer Experiments

α-cyclodextrin

Table S4: Results of array generation in buffer with α-cyclodextrin

Jackknifed Classification Matrix

	Analyte 1	Analyte 2	Analyte 3	Analyte 4	Analyte 5	%correct
Analyte 1	4	0	0	0	0	100
Analyte 2	0	4	0	0	0	100
Analyte 3	0	0	4	0	0	100
Analyte 4	0	0	0	4	0	100
Analyte 5	0	0	0	0	4	100
Total	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.976	0.997	1.000

β-cyclodextrin

Table S5: Results of array generation in buffer with β-cyclodextrin

Jackknifed Classification Matrix

	Analyte 1	Analyte 2	Analyte 3	Analyte 4	Analyte 5	%correct
Analyte 1	4	0	0	0	0	100
Analyte 2	0	4	0	0	0	100
Analyte 3	0	0	4	0	0	100
Analyte 4	0	0	0	4	0	100
Analyte 5	0	0	0	0	4	100
Total	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.935	0.999	1.000

PBS

Table S6: Results of array generation in buffer without cyclodextrin

Jackknifed Classification Matrix

	Analyte 1	Analyte 2	Analyte 3	Analyte 4	Analyte 5	%correct
Analyte 1	4	0	0	0	0	100
Analyte 2	0	4	0	0	0	100
Analyte 3	0	0	4	0	0	100
Analyte 4	0	0	0	4	0	100
Analyte 5	0	0	0	0	4	100
Total	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.887	0.992	1.000

Saliva Experiments

α-cyclodextrin

Table S7: Results of array generation in saliva with α-cyclodextrin

Jackknifed Classification Matrix

	Analyte 1	Analyte 2	Analyte 3	Analyte 4	Analyte 5	%correct
Analyte 1	4	0	0	0	0	100
Analyte 2	0	4	0	0	0	100
Analyte 3	0	0	4	0	0	100
Analyte 4	0	0	0	4	0	100
Analyte 5	0	0	0	0	4	100
Total	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

1.000	1.000	1.000

β-cyclodextrin

Table S8: Results of array generation in saliva with β-cyclodextrin

Jackknifed Classification Matrix

	Analyte 1	Analyte 2	Analyte 3	Analyte 4	Analyte 5	%correct
Analyte 1	4	0	0	0	0	100
Analyte 2	0	4	0	0	0	100
Analyte 3	0	0	4	0	0	100
Analyte 4	0	0	0	4	0	100
Analyte 5	0	0	0	0	4	100
Total	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.992	0.999	1.000

PBS

Table S9: Results of array generation in saliva without cyclodextrin

Jackknifed Classification Matrix

	Analyte 1	Analyte 2	Analyte 3	Analyte 4	Analyte 5	%correct
Analyte 1	4	0	0	0	0	100
Analyte 2	0	4	0	0	0	100
Analyte 3	0	0	4	0	0	100
Analyte 4	0	0	0	4	0	100
Analyte 5	0	0	0	0	4	100
Total	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.948	0.996	1.000

SUMMARY TABLES FOR GC-MS EXPERIMENTS

Table S10. Results of GC-MS characterization of saliva

Sample Type	Retention Time (min)	NIST Compound ID
Doped Standard	6.73	Dimethyl phthalate
	7.29	Diethylphthalate
	8.56	Dibutylphthalate
Undoped Sample	16.15	Caffeine
	18.55	2-methylnonadecane
	19.40	7-n-hexyleicosane
	20.40	9-octylheptadecane
	21.65	10-methyleicosane
	23.25	Bis(tridecyl)phthalate
	24.45	7-methyldocosane
	24.80	11-decyltetracosane

SUMMARY TABLES FOR MIXTURE FLUORESCENCE EXPERIMENTS

Table S11: Fluorescence modulation results for analyte mixtures in buffer and saliva

Cyclodextrin	Analyte	Analyte	Fluorophore 6		Fluorophore 7		Fluorophore 8	
			Buffer	Saliva	Buffer	Saliva	Buffer	Saliva
α-CD	**1**	**2**	0.99 ± 0.01	1.10 ± 0.02	1.00 ± 0.00	0.98 ± 0.00	0.98 ± 0.04	0.25 ± 0.02
α-CD	**1**	**3**	1.06 ± 0.01	1.07 ± 0.03	0.99 ± 0.00	0.99 ± 0.00	2.88 ± 0.10	0.28 ± 0.02
α-CD	**1**	**4**	1.73 ± 0.05	1.52 ± 0.05	0.99 ± 0.00	1.01 ± 0.00	1.30 ± 0.05	1.44 ± 0.01
α-CD	**2**	**3**	1.03 ± 0.01	1.20 ± 0.03	0.99 ± 0.00	0.99 ± 0.00	0.98 ± 0.03	0.24 ± 0.02
α-CD	**2**	**4**	1.63 ± 0.02	1.62 ± 0.04	1.00 ± 0.00	1.01 ± 0.00	1.48 ± 0.01	1.52 ± 0.01
α-CD	**3**	**4**	1.10 ± 0.01	1.20 ± 0.03	0.99 ± 0.00	1.01 ± 0.00	1.99 ± 0.05	1.13 ± 0.08
β-CD	**1**	**2**	1.02 ± 0.01	1.12 ± 0.01	0.99 ± 0.00	0.99 ± 0.00	0.99 ± 0.00	0.99 ± 0.00
β-CD	**1**	**3**	1.07 ± 0.01	1.19 ± 0.03	0.98 ± 0.00	0.99 ± 0.00	1.00 ± 0.00	0.98 ± 0.00
β-CD	**1**	**4**	1.64 ± 0.02	1.38 ± 0.07	0.99 ± 0.00	1.01 ± 0.00	1.02 ± 0.00	1.03 ± 0.00
β-CD	**2**	**3**	1.19 ± 0.01	1.08 ± 0.02	0.99 ± 0.00	1.00 ± 0.00	0.99 ± 0.00	0.99 ± 0.00
β-CD	**2**	**4**	1.48 ± 0.01	1.46 ± 0.04	0.99 ± 0.00	1.01 ± 0.00	1.03 ± 0.00	1.02 ± 0.00
β-CD	**3**	**4**	1.50 ± 0.03	1.47 ± 0.08	0.99 ± 0.00	1.00 ± 0.00	1.02 ± 0.00	1.02 ± 0.00
PBS	**1**	**2**	1.46 ± 0.08	1.12 ± 0.03	0.98 ± 0.00	0.99 ± 0.00	0.93 ± 0.04	0.87 ± 0.05
PBS	**1**	**3**	1.63 ± 0.03	1.12 ±0.01	0.97 ± 0.00	1.00 ± 0.00	0.98 ± 0.06	0.70 ± 0.10
PBS	**1**	**4**	1.34 ± 0.03	1.33 ± 0.08	0.99 ± 0.00	0.99 ± 0.00	1.41 ± 0.12	1.75 ± 0.02
PBS	**2**	**3**	1.52 ± 0.03	1.04 ± 0.05	0.98 ± 0.00	0.99 ± 0.00	0.89 ± 0.02	0.93 ± 0.03
PBS	**2**	**4**	1.17 ± 0.02	1.23 ± 0.07	0.99 ± 0.00	0.99 ± 0.00	1.31 ± 0.10	1.72 ± 0.01
PBS	**3**	**4**	1.51 ± 0.14	1.36 ± 0.08	0.99 ± 0.00	1.00 ± 0.00	1.83 ± 0.06	1.78 ± 0.01

SUMMARY TABLES FOR MIXTURE ARRAY GENERATION EXPERIMENTS

Buffer Experiments

α-cyclodextrin

Table S12: Results of array generation for mixtures in buffer with α-cyclodextrin

Jackknifed Classification Matrix

	Analytes 1 and 2	Analytes 1 and 3	Analytes 1 and 4	Analytes 2 and 3	Analytes 2 and 4	Analytes 3 and 4	%correct
Analytes 1 and 2	4	0	0	0	0	0	100
Analytes 1 and 3	0	4	0	0	0	0	100
Analytes 1 and 4	0	0	4	0	0	0	100
Analytes 2 and 3	0	0	0	4	0	0	100
Analytes 2 and 4	0	0	0	0	4	0	100
Analytes 3 and 4	0	0	0	0	0	4	100
Total	4	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.771	0.904	1.000

β-cyclodextrin

Table S13: Results of array generation for mixtures in buffer with β-cyclodextrin

Jackknifed Classification Matrix

	Analytes 1 and 2	Analytes 1 and 3	Analytes 1 and 4	Analytes 2 and 3	Analytes 2 and 4	Analytes 3 and 4	%correct
Analytes 1 and 2	4	0	0	0	0	0	100
Analytes 1 and 3	0	4	0	0	0	0	100
Analytes 1 and 4	0	0	4	0	0	0	100
Analytes 2 and 3	0	0	0	4	0	0	100
Analytes 2 and 4	0	0	0	0	4	0	100
Analytes 3 and 4	0	0	0	0	0	4	100
Total	4	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.713	0.995	1.000

PBS

Table S14: Results of array generation for mixtures in buffer with PBS

Jackknifed Classification Matrix

	Analytes 1 and 2	Analytes 1 and 3	Analytes 1 and 4	Analytes 2 and 3	Analytes 2 and 4	Analytes 3 and 4	%correct
Analytes 1 and 2	4	0	0	0	0	0	100
Analytes 1 and 3	0	4	0	0	0	0	100
Analytes 1 and 4	0	0	4	0	0	0	100
Analytes 2 and 3	0	0	0	4	0	0	100
Analytes 2 and 4	0	0	0	0	4	0	100
Analytes 3 and 4	0	0	0	0	0	4	100
Total	4	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.952	0.985	1.000

Saliva Experiments

α-cyclodextrin

Table S15: Results of array generation for mixtures in saliva with α-cyclodextrin

Jackknifed Classification Matrix

	Analytes 1 and 2	Analytes 1 and 3	Analytes 1 and 4	Analytes 2 and 3	Analytes 2 and 4	Analytes 3 and 4	%correct
Analytes 1 and 2	1	0	0	3	0	0	25
Analytes 1 and 3	0	4	0	0	0	0	100
Analytes 1 and 4	0	0	4	0	0	0	100
Analytes 2 and 3	1	0	0	3	0	0	75
Analytes 2 and 4	0	0	0	0	4	0	100
Analytes 3 and 4	0	0	0	0	0	4	100
Total	2	4	4	6	4	4	83

Cumulative Proportion of Total Dispersion

0.943	1.000	1.000

β-cyclodextrin

Table S16: Results of array generation for mixtures in saliva with β-cyclodextrin

Jackknifed Classification Matrix

	Analytes 1 and 2	Analytes 1 and 3	Analytes 1 and 4	Analytes 2 and 3	Analytes 2 and 4	Analytes 3 and 4	%correct
Analytes 1 and 2	4	0	0	0	0	0	100
Analytes 1 and 3	0	4	0	0	0	0	100
Analytes 1 and 4	0	0	4	0	0	0	100
Analytes 2 and 3	0	0	0	4	0	0	100
Analytes 2 and 4	0	0	0	0	4	0	100
Analytes 3 and 4	0	0	0	0	0	4	100
Total	4	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.994	1.000	1.000

PBS

Table S17: Results of array generation for mixtures in saliva with PBS

Jackknifed Classification Matrix

	Analytes 1 and 2	Analytes 1 and 3	Analytes 1 and 4	Analytes 2 and 3	Analytes 2 and 4	Analytes 3 and 4	%correct
Analytes 1 and 2	4	0	0	0	0	0	100
Analytes 1 and 3	0	4	0	0	0	0	100
Analytes 1 and 4	0	0	4	0	0	0	100
Analytes 2 and 3	0	0	0	4	0	0	100
Analytes 2 and 4	0	0	0	0	4	0	100
Analytes 3 and 4	0	0	0	0	0	4	100
Total	4	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.989	1.000	1.000

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 the fluorophore mixed together in buffer or saliva. 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 Experiments

Analyte **1** – Fluorophore **6**

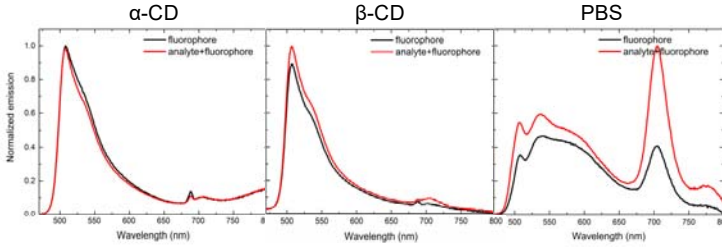

Figure S6: Fluorescence modulation of fluorophore **6** with analyte **1** in buffer

Analyte **1** – Fluorophore **7**

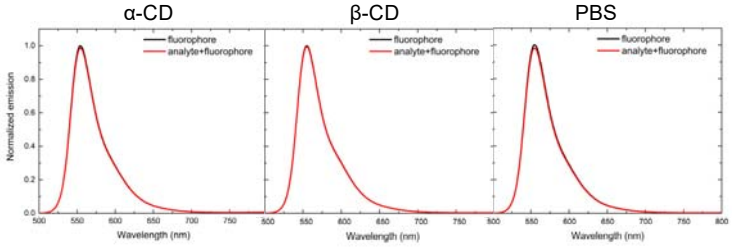

Figure S7: Fluorescence modulation of fluorophore **7** with analyte **1** in buffer

Analyte **1** – Fluorophore **8**

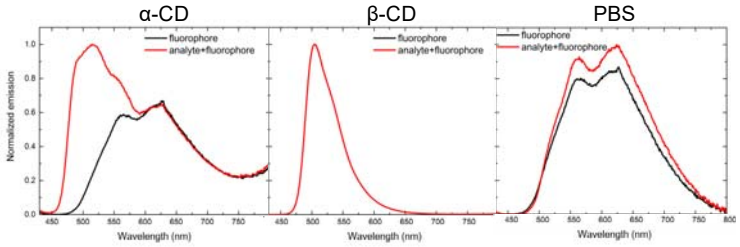

Figure S8: Fluorescence modulation of fluorophore **8** with analyte **1** in buffer

Analyte **2** – Fluorophore **6**

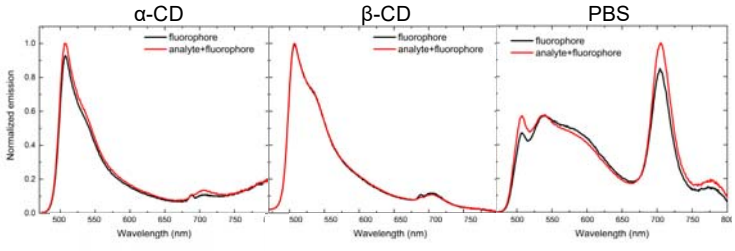

Figure S9: Fluorescence modulation of fluorophore **6** with analyte **2** in buffer

Analyte **2** – Fluorophore **7**

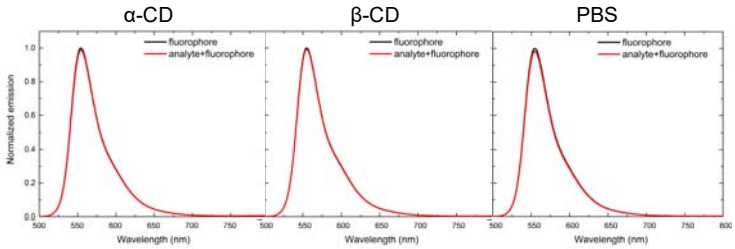

Figure S10: Fluorescence modulation of fluorophore **7** with analyte **2** in buffer

Analyte **2** – Fluorophore **8**

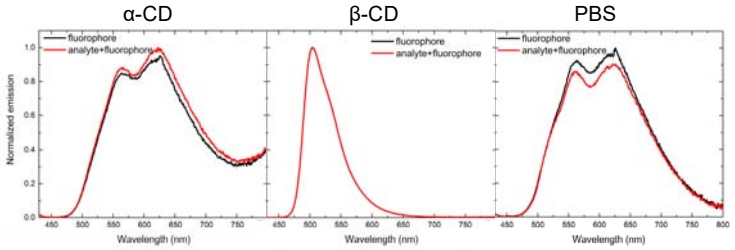

Figure S11: Fluorescence modulation of fluorophore **8** with analyte **2** in buffer

Analyte **3** – Fluorophore **6**

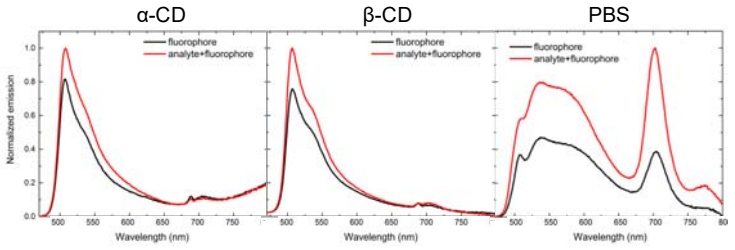

Figure S12: Fluorescence modulation of fluorophore **6** with analyte **3** in buffer

Analyte **3** – Fluorophore **7**

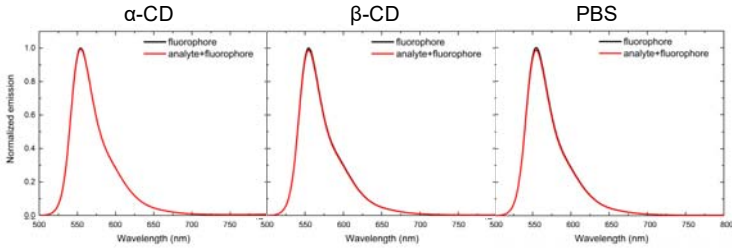

Figure S13: Fluorescence modulation of fluorophore **7** with analyte **3** in buffer

Analyte **3** – Fluorophore **8**

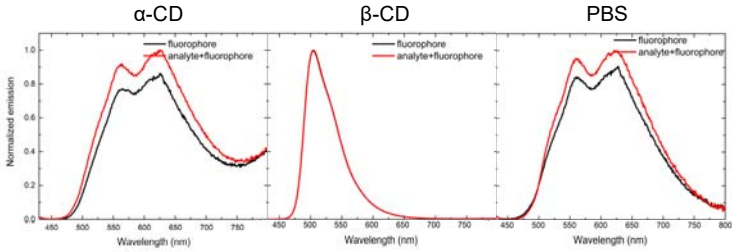

Figure S14: Fluorescence modulation of fluorophore **8** with analyte **3** in buffer

Analyte **4** – Fluorophore **6**

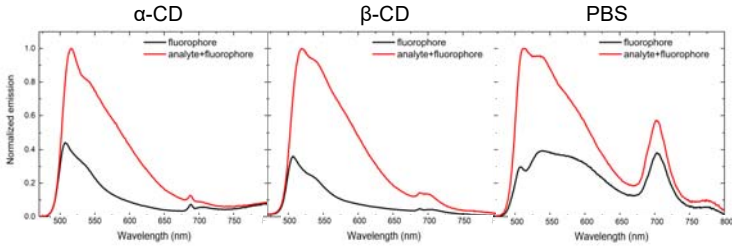

Figure S15: Fluorescence modulation of fluorophore **6** with analyte **4** in buffer

Analyte **4** – Fluorophore **7**

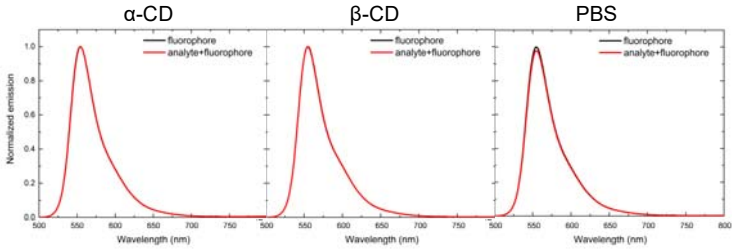

Figure S16: Fluorescence modulation of fluorophore **7** with analyte **4** in buffer

Analyte **4** – Fluorophore **8**

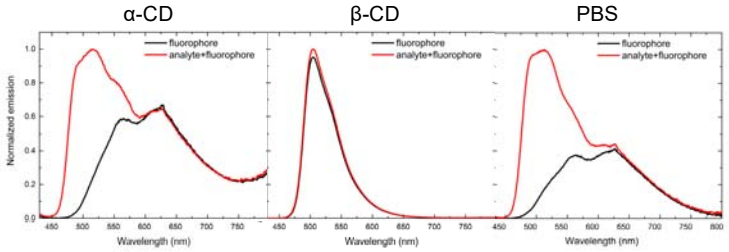

Figure S17: Fluorescence modulation of fluorophore **8** with analyte **4** in buffer

Analyte **5** – Fluorophore **6**

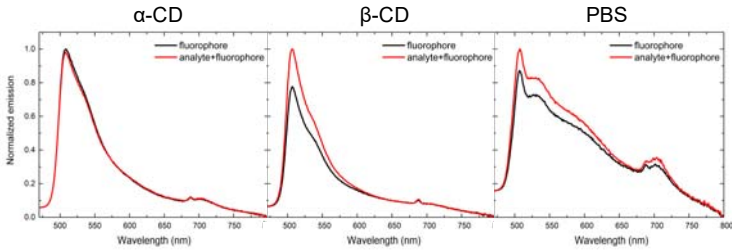

Figure S18: Fluorescence modulation of fluorophore **6** with analyte **5** in buffer

Analyte **5** – Fluorophore **7**

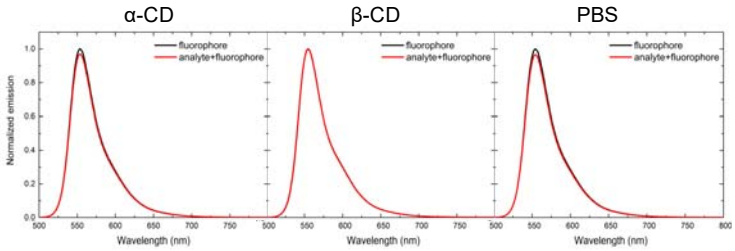

Figure S19: Fluorescence modulation of fluorophore **7** with analyte **5** in buffer

Analyte **5** – Fluorophore **8**

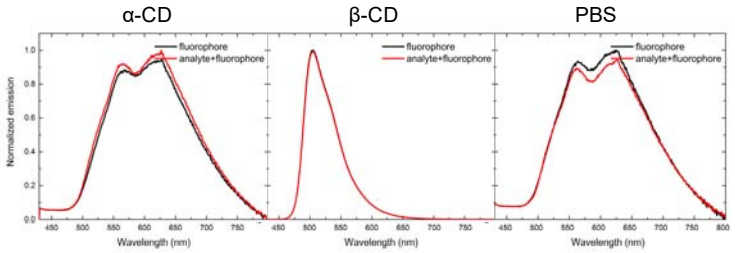

Figure S20: Fluorescence modulation of fluorophore **8** with analyte **5** in buffer

Saliva Experiments

Analyte **1** – Fluorophore **6**

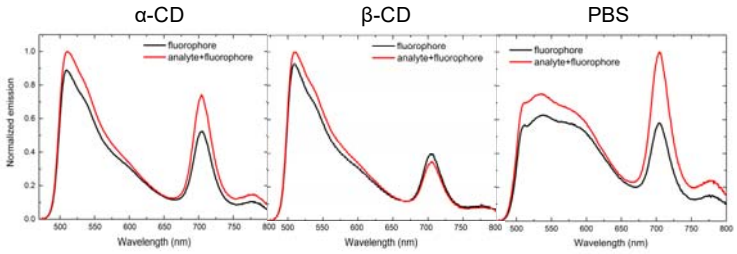

Figure S21: Fluorescence modulation of fluorophore **6** with analyte **1** in saliva

Analyte **1** – Fluorophore **7**

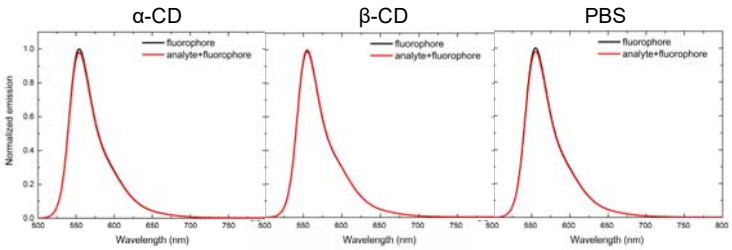

Figure S22: Fluorescence modulation of fluorophore **7** with analyte **1** in saliva

Analyte **1** – Fluorophore **8**

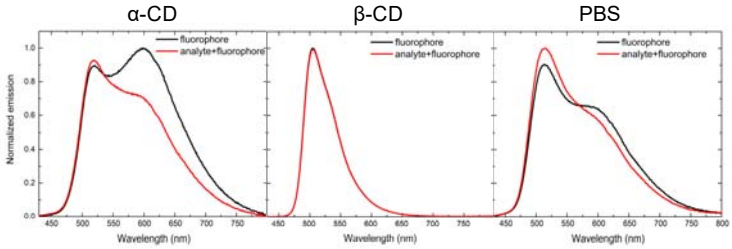

Figure S23: Fluorescence modulation of fluorophore **8** with analyte **1** in saliva

Analyte **2** – Fluorophore **6**

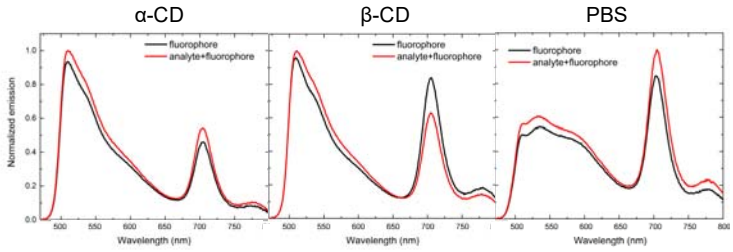

Figure S24: Fluorescence modulation of fluorophore **6** with analyte **2** in saliva

Analyte **2** – Fluorophore **7**

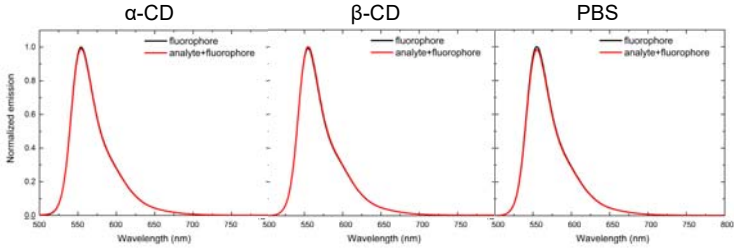

Figure S25: Fluorescence modulation of fluorophore **7** with analyte **2** in saliva

Analyte **2** – Fluorophore **8**

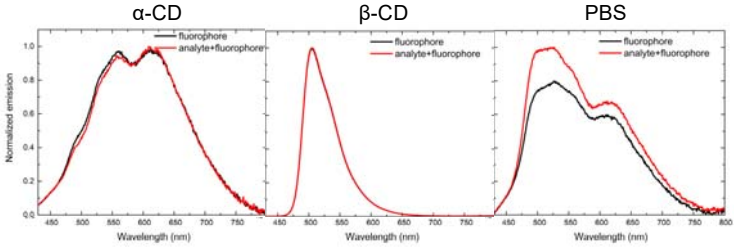

Figure S26: Fluorescence modulation of fluorophore **8** with analyte **2** in saliva

Analyte **3** – Fluorophore **6**

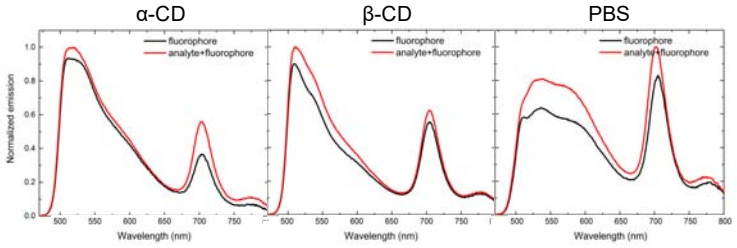

Figure S27: Fluorescence modulation of fluorophore **6** with analyte **3** in saliva

Analyte **3** – Fluorophore **7**

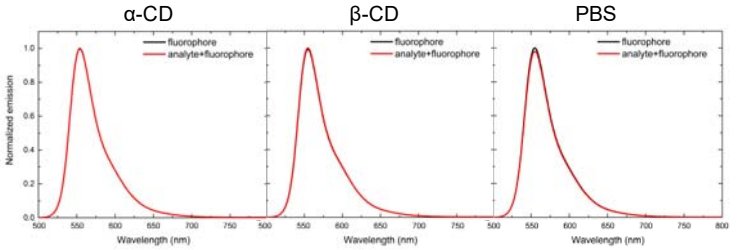

Figure S28: Fluorescence modulation of fluorophore **7** with analyte **3** in saliva

Analyte **3** – Fluorophore **8**

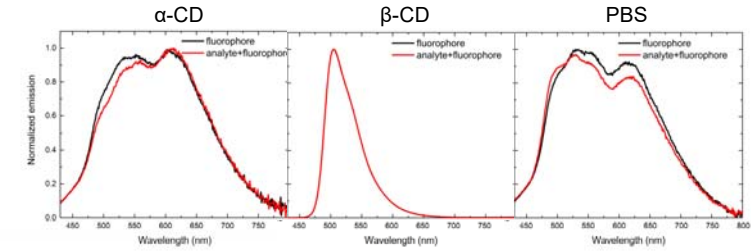

Figure S29: Fluorescence modulation of fluorophore **8** with analyte **3** in saliva

Analyte **4** – Fluorophore **6**

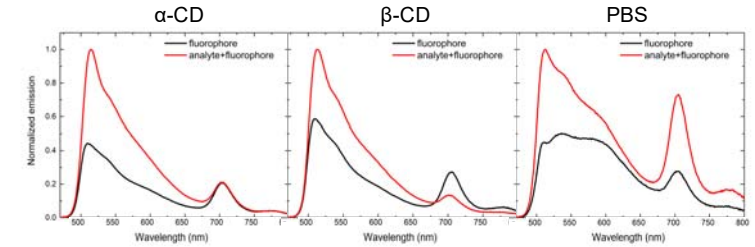

Figure S30: Fluorescence modulation of fluorophore **6** with analyte **4** in saliva

Analyte **4** – Fluorophore **7**

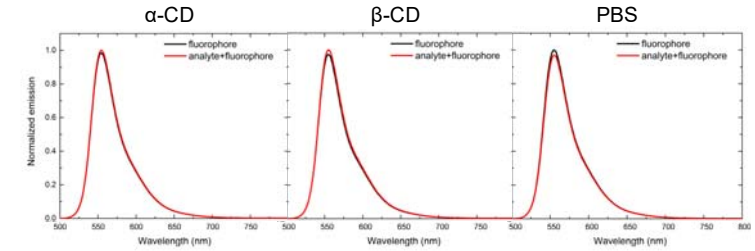

Figure S31: Fluorescence modulation of fluorophore **7** with analyte **4** in saliva

Analyte **4** – Fluorophore **8**

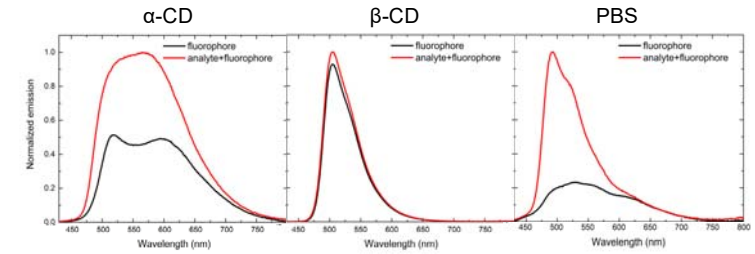

Figure S32: Fluorescence modulation of fluorophore **8** with analyte **4** in saliva

Analyte **5** – Fluorophore **6**

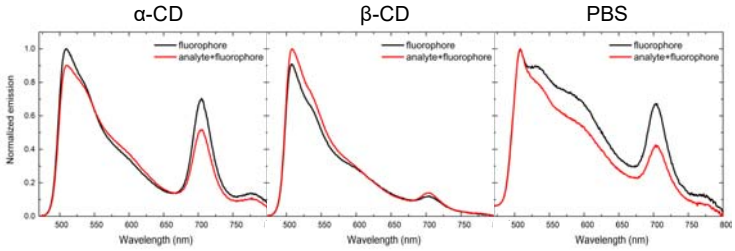

Figure S33: Fluorescence modulation of fluorophore **6** with analyte **5** in saliva

Analyte **5** – Fluorophore **7**

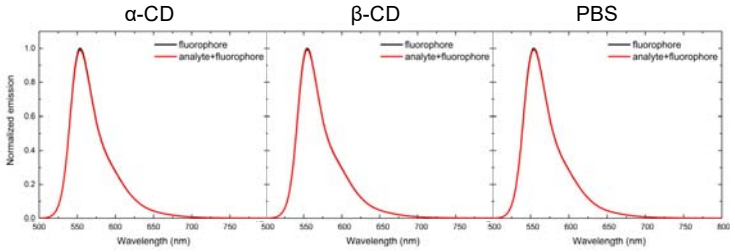

Figure S34: Fluorescence modulation of fluorophore **7** with analyte **5** in saliva

Analyte **5** – Fluorophore **8**

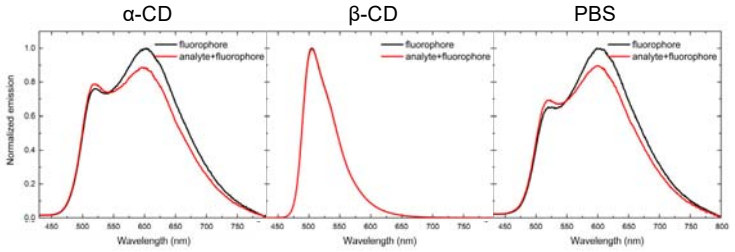

Figure S35: Fluorescence modulation of fluorophore **8** with analyte **5** in saliva

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 fluorescence modulation ratio (F/F_0) on the Y-axis, and the analyte concentration in micromolar on the X-axis.

Buffer Experiments

Analyte **1** – Fluorophore **6**

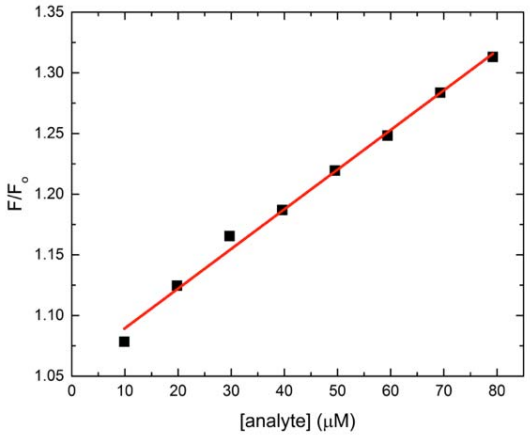

Figure S36: Limit of detection for analyte **1** with fluorophore **6** and β-cyclodextrin in buffer

Analyte **2** – Fluorophore **6**

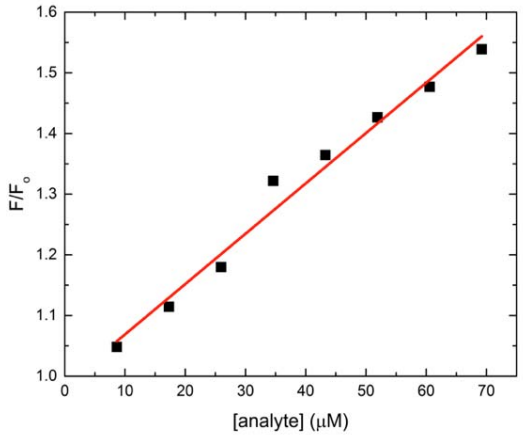

Figure S37: Limit of detection for analyte **2** with fluorophore **6** and β-cyclodextrin in buffer

Analyte **3** – Fluorophore **6**

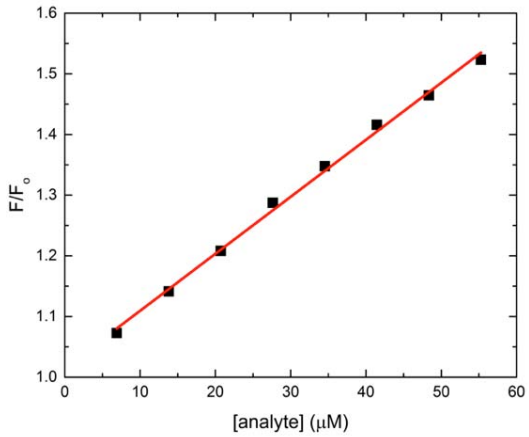

Figure S38: Limit of detection for analyte **3** with fluorophore **6** and β-cyclodextrin in buffer

Analyte **4** – Fluorophore **7**

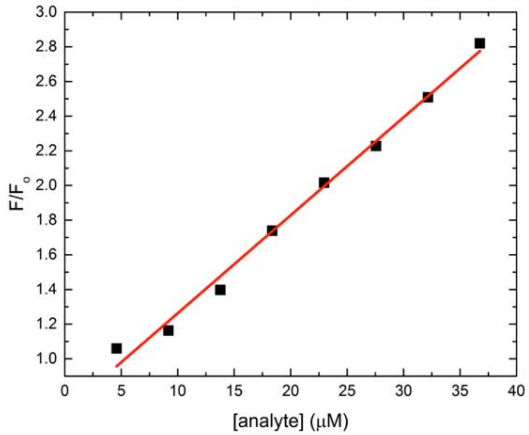

Figure S39: Limit of detection for analyte **4** with fluorophore **6** and β-cyclodextrin in buffer

Saliva Experiments

Analyte **1** – Fluorophore **6**

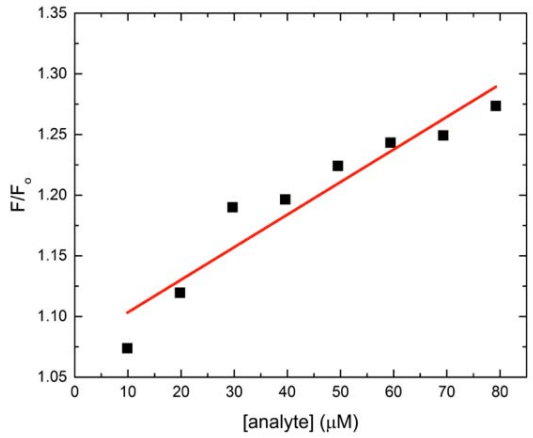

Figure S40: Limit of detection for analyte **1** with fluorophore **6** and β-cyclodextrin in saliva

Analyte **2** – Fluorophore **6**

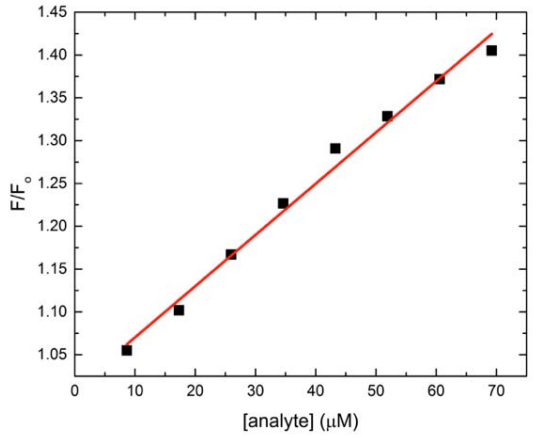

Figure S41: Limit of detection for analyte **2** with fluorophore **6** and β-cyclodextrin in saliva

Analyte **3** – Fluorophore **6**

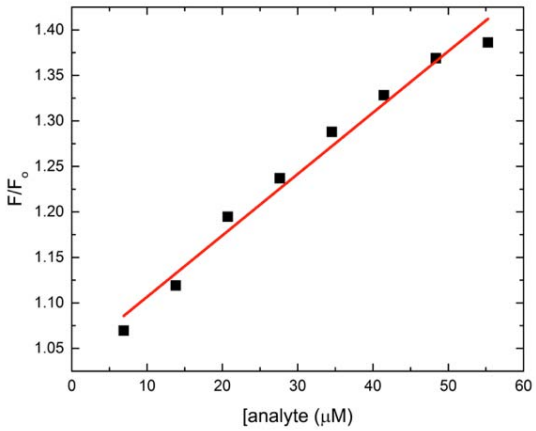

Figure S42: Limit of detection for analyte **3** with fluorophore **6** and β-cyclodextrin in saliva

Analyte **4** – Fluorophore **6**

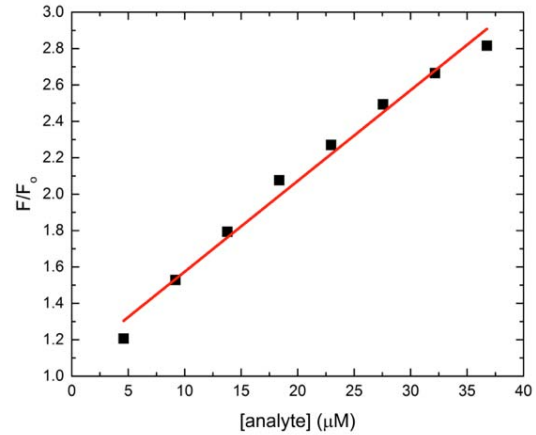

Figure S43: Limit of detection for analyte **4** with fluorophore **6** and β-cyclodextrin in saliva

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 Experiments

α-cyclodextrin

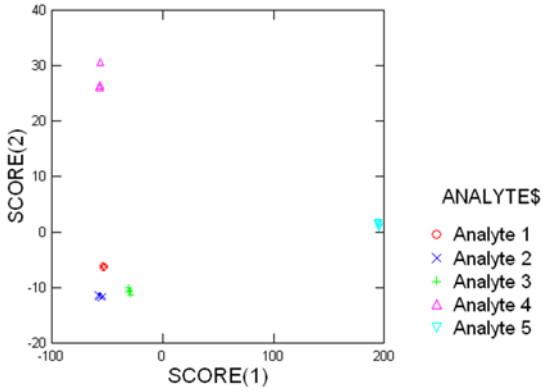

Figure S44: Linear discriminant analysis of fluorescence responses for analytes **1-5** with fluorophores **6-8** with α-cyclodextrin in buffer

β-cyclodextrin

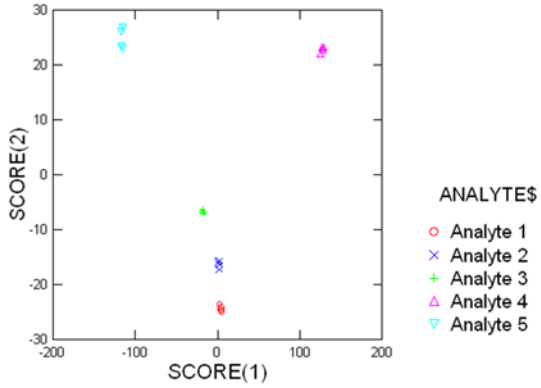

Figure S45: Linear discriminant analysis of fluorescence responses for analytes **1-5** with fluorophores **6-8** with β-cyclodextrin in buffer

PBS

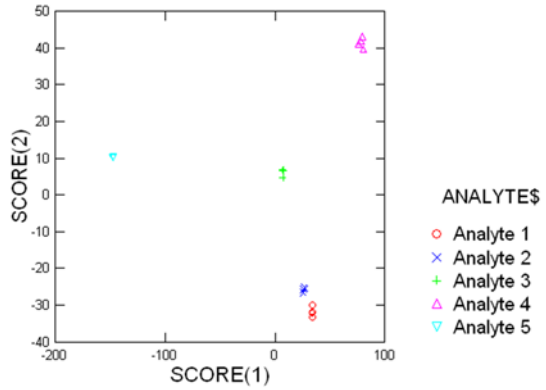

Figure S46: Linear discriminant analysis of fluorescence responses for analytes **1-5** with fluorophores **6-8** without cyclodextrin in buffer

Saliva Experiments

α-cyclodextrin

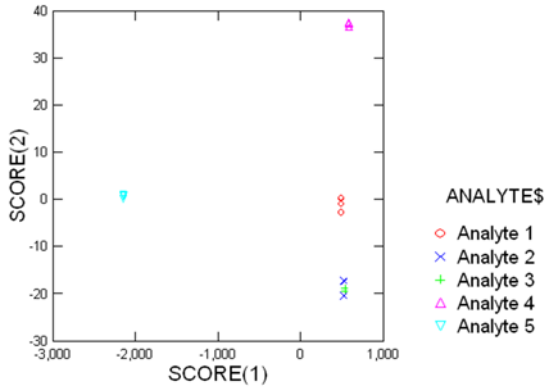

Figure S47: Linear discriminant analysis of fluorescence responses for analytes **1-5** with fluorophores **6-8** with α-cyclodextrin in saliva

β-cyclodextrin

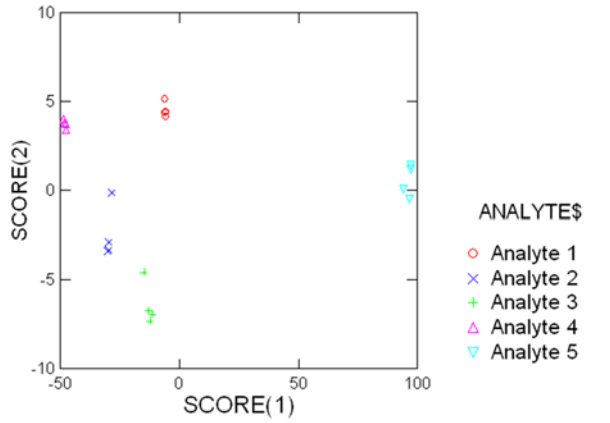

Figure S48: Linear discriminant analysis of fluorescence responses for analytes **1-5** with fluorophores **6-8** with β-cyclodextrin in saliva

PBS

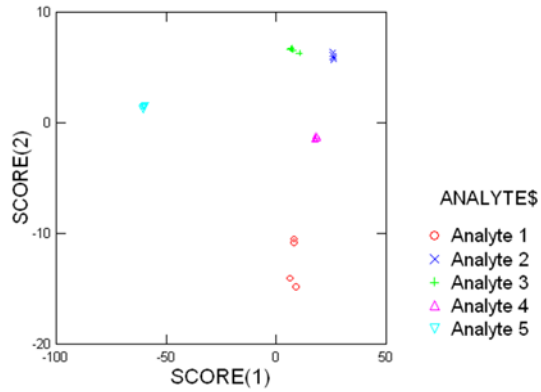

Figure S49: Linear discriminant analysis of fluorescence responses for analytes **1-5** with fluorophores **6-8** without cyclodextrin in saliva

SUMMARY FIGURES FOR MIXTURE 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 buffer or saliva. 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 Experiments

Analyte **1** – Analyte **2** – Fluorophore **6**

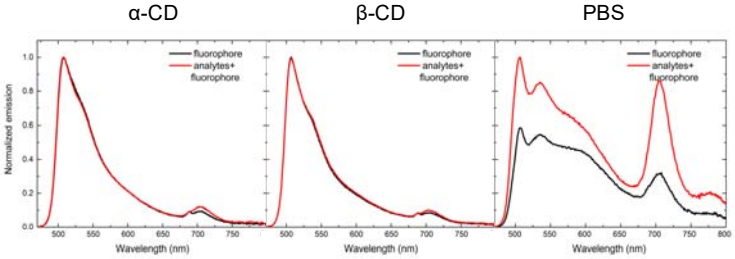

Figure S50: Fluorescence modulation of fluorophore **6** with analytes **1** and **2** in buffer

Analyte **1** – Analyte **2** – Fluorophore **7**

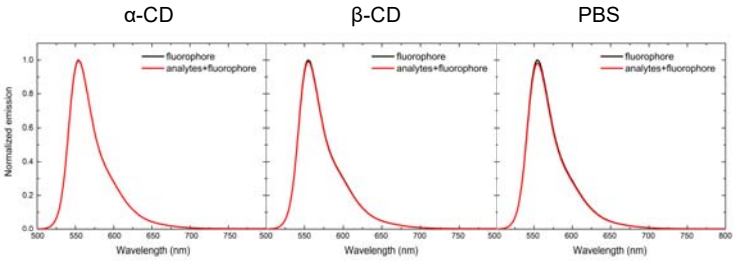

Figure S51: Fluorescence modulation of fluorophore **7** with analytes **1** and **2** in buffer

Analyte **1** – Analyte **2** – Fluorophore **8**

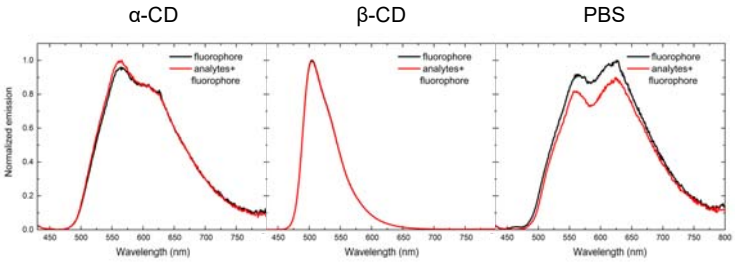

Figure S52: Fluorescence modulation of fluorophore **8** with analytes **1** and **2** in buffer

Analyte **1** – Analyte **3** – Fluorophore **6**

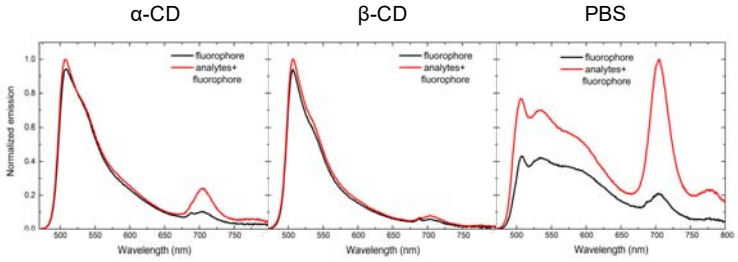

Figure S53: Fluorescence modulation of fluorophore **6** with analytes **1** and **3** in buffer

Analyte **1** – Analyte **3** – Fluorophore **7**

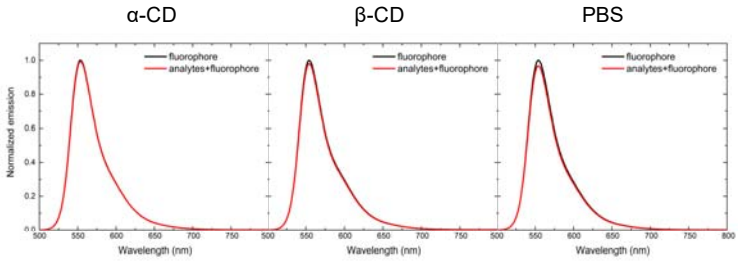

Figure S54: Fluorescence modulation of fluorophore **7** with analytes **1** and **3** in buffer

Analyte **1** – Analyte **3** – Fluorophore **8**

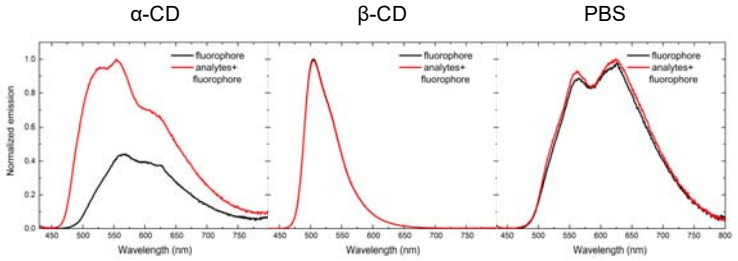

Figure S55: Fluorescence modulation of fluorophore **8** with analytes **1** and **3** in buffer

Analyte **1** – Analyte **4** – Fluorophore **6**

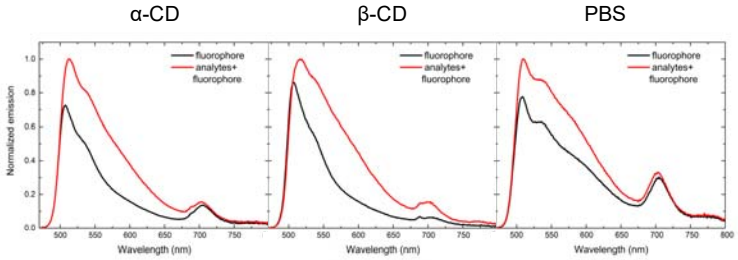

Figure S56: Fluorescence modulation of fluorophore **6** with analytes **1** and **4** in buffer

Analyte **1** – Analyte **4** – Fluorophore **7**

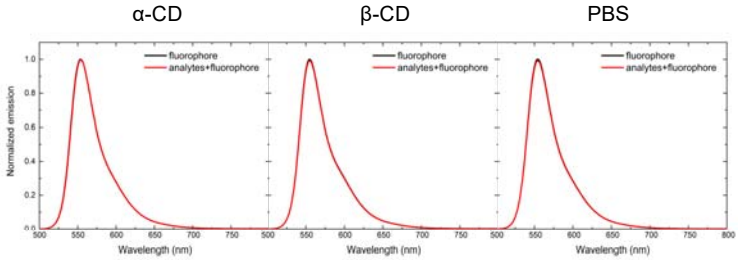

Figure S57: Fluorescence modulation of fluorophore **7** with analytes **1** and **4** in buffer

Analyte **1** – Analyte **4** – Fluorophore **8**

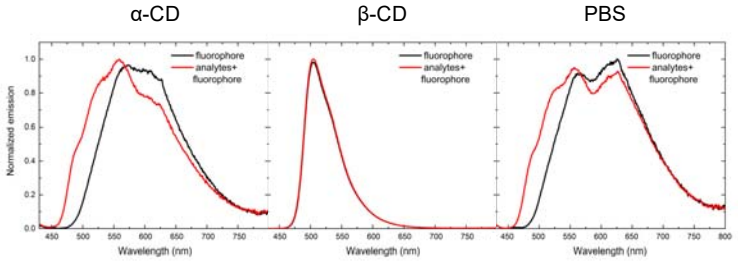

Figure S58: Fluorescence modulation of fluorophore **8** with analytes **1** and **4** in buffer

Analyte **2** – Analyte **3** – Fluorophore **6**

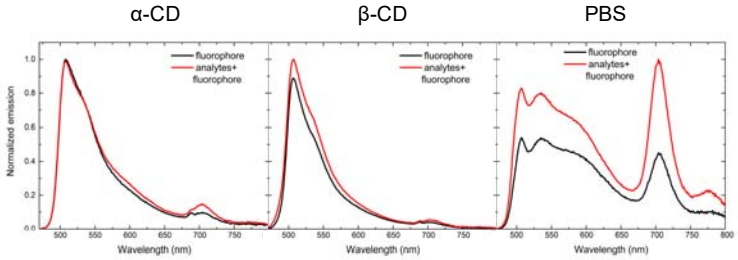

Figure S59: Fluorescence modulation of fluorophore **6** with analytes **2** and **3** in buffer

Analyte **2** – Analyte **3** – Fluorophore **7**

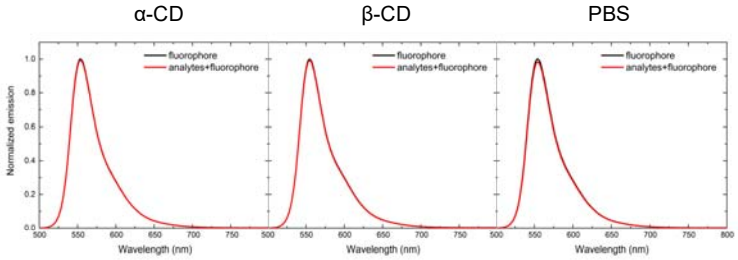

Figure S60: Fluorescence modulation of fluorophore **7** with analytes **2** and **3** in buffer

Analyte **2** – Analyte **3** – Fluorophore **8**

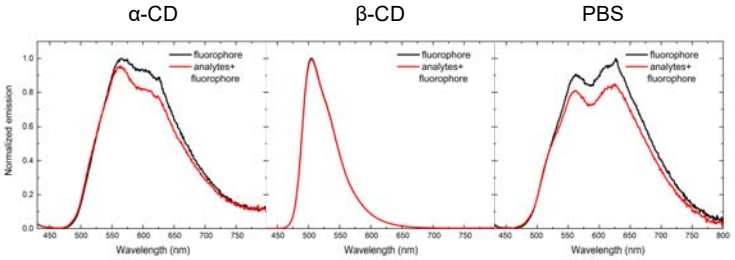

Figure S61: Fluorescence modulation of fluorophore **8** with analytes **2** and **3** in buffer

Analyte **2** – Analyte **4** – Fluorophore **6**

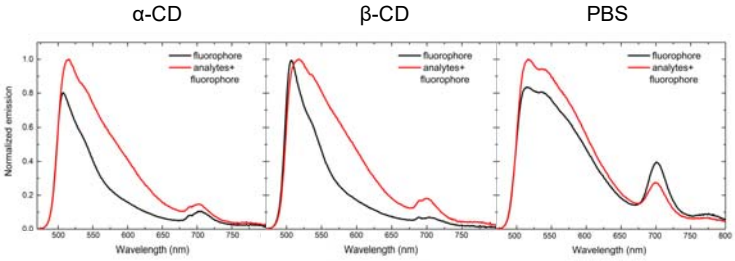

Figure S62: Fluorescence modulation of fluorophore **6** with analytes **2** and **4** in buffer

Analyte **2** – Analyte **4** – Fluorophore **7**

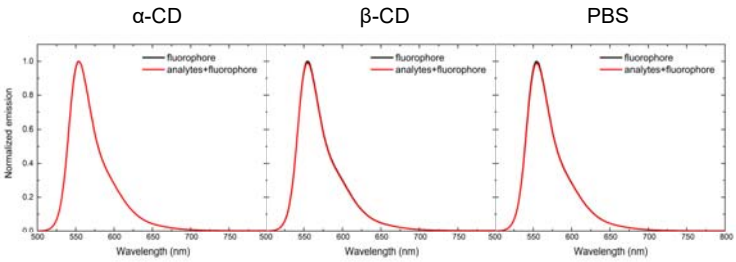

Figure S63: Fluorescence modulation of fluorophore **7** with analytes **2** and **4** in buffer

Analyte **2** – Analyte **4** – Fluorophore **8**

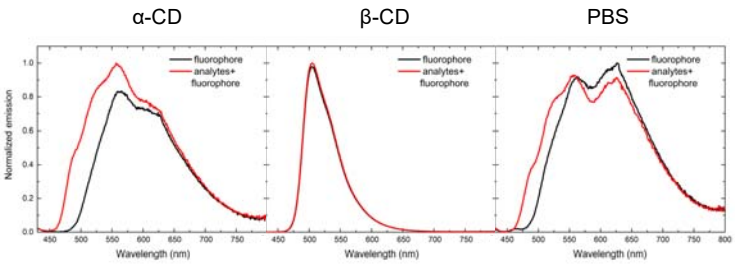

Figure S64: Fluorescence modulation of fluorophore **8** with analytes **2** and **4** in buffer

Analyte **3** – Analyte **4** – Fluorophore **6**

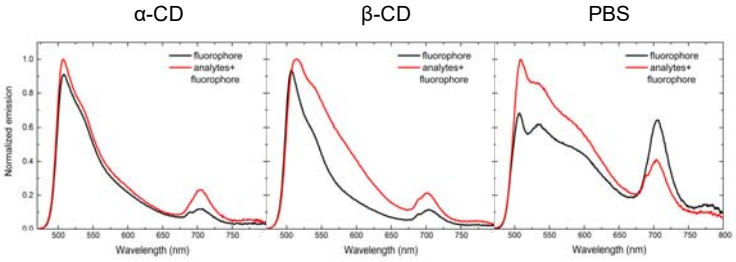

Figure S65: Fluorescence modulation of fluorophore **6** with analytes **3** and **4** in buffer

Analyte **3** – Analyte **4** – Fluorophore **7**

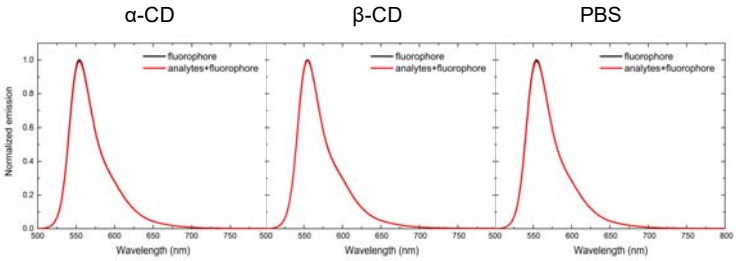

Figure S66: Fluorescence modulation of fluorophore **7** with analytes **3** and **4** in buffer

Analyte **3** – Analyte **4** – Fluorophore **8**

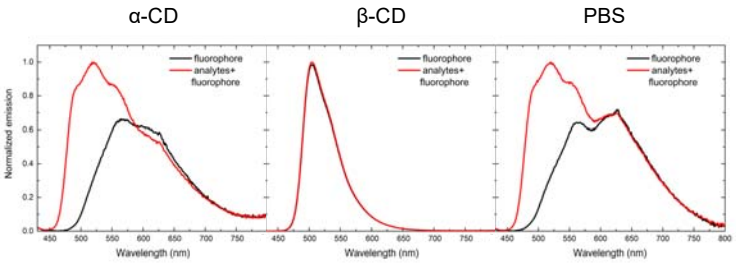

Figure S67: Fluorescence modulation of fluorophore **8** with analytes **3** and **4** in buffer

Saliva Experiments

Analyte **1** – Analyte **2** – Fluorophore **6**

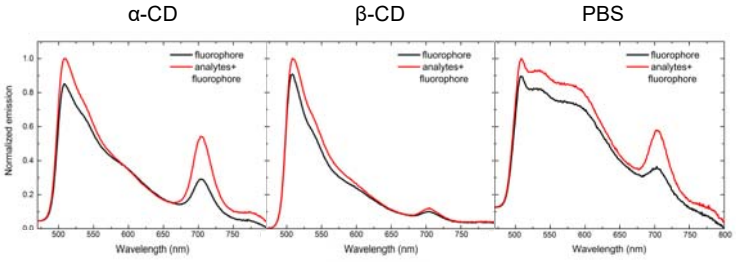

Figure S68: Fluorescence modulation of fluorophore **6** with analytes **1** and **2** in saliva

Analyte **1** – Analyte **2** – Fluorophore **7**

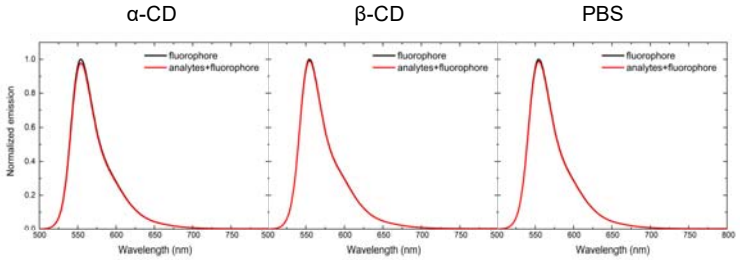

Figure S69: Fluorescence modulation of fluorophore **7** with analytes **1** and **2** in saliva

Analyte **1** – Analyte **2** – Fluorophore **8**

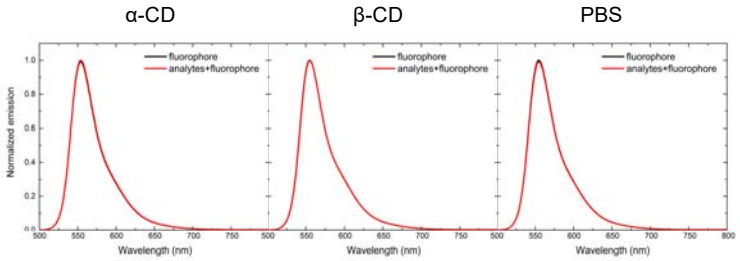

Figure S70: Fluorescence modulation of fluorophore **8** with analytes **1** and **2** in saliva

Analyte **1** – Analyte **3** – Fluorophore **6**

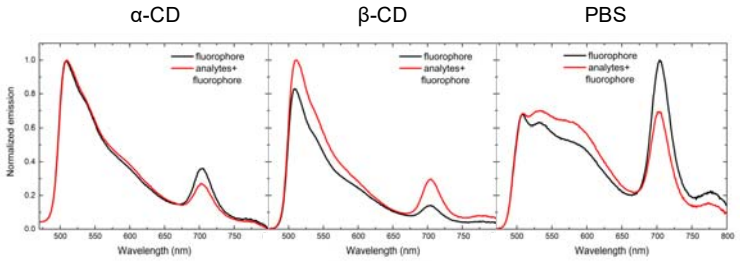

Figure S71: Fluorescence modulation of fluorophore **6** with analytes **1** and **3** in saliva

Analyte **1** – Analyte **3** – Fluorophore **7**

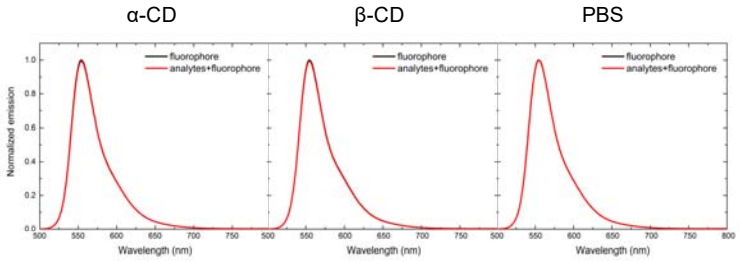

Figure S72: Fluorescence modulation of fluorophore **7** with analytes **1** and **3** in saliva

Analyte **1** – Analyte **3** – Fluorophore **8**

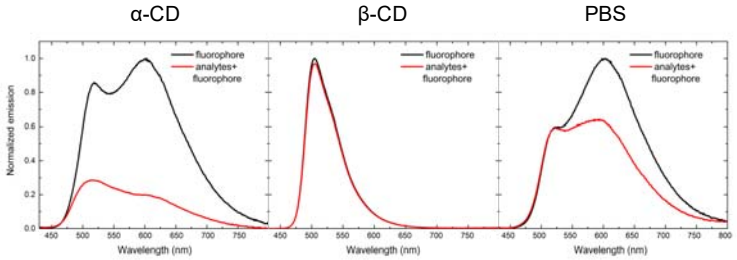

Figure S73: Fluorescence modulation of fluorophore **8** with analytes **1** and **3** in saliva

Analyte **1** – Analyte **4** – Fluorophore **6**

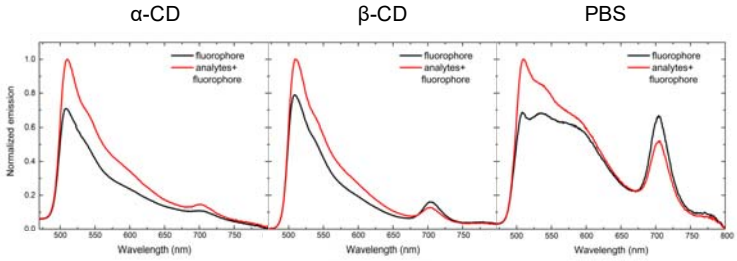

Figure S74: Fluorescence modulation of fluorophore **6** with analytes **1** and **4** in saliva

Analyte **1** – Analyte **4** – Fluorophore **7**

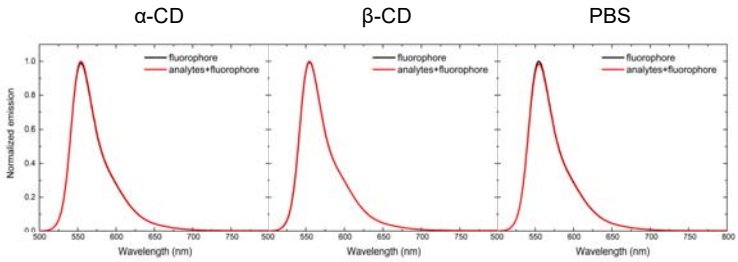

Figure S75: Fluorescence modulation of fluorophore **7** with analytes **1** and **4** in saliva

Analyte **1** – Analyte **4** – Fluorophore **8**

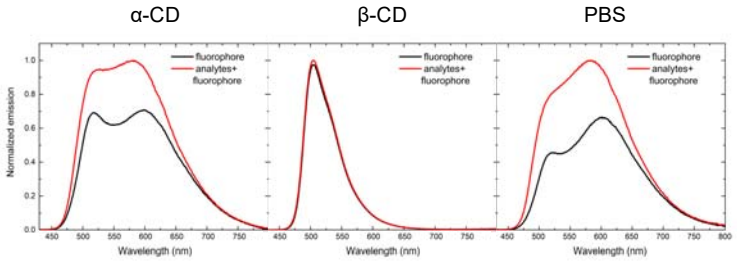

Figure S76: Fluorescence modulation of fluorophore **8** with analytes **1** and **4** in saliva

Analyte **2** – Analyte **3** – Fluorophore **6**

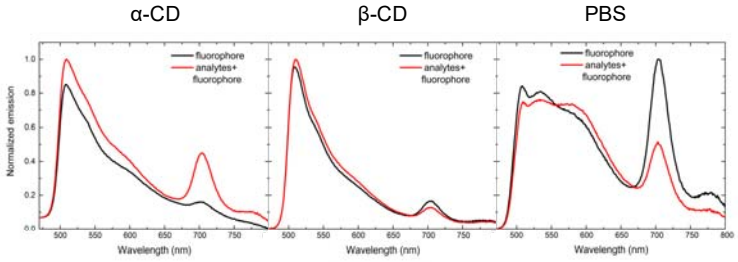

Figure S77: Fluorescence modulation of fluorophore **6** with analytes **2** and **3** in saliva

Analyte **2** – Analyte **3** – Fluorophore **7**

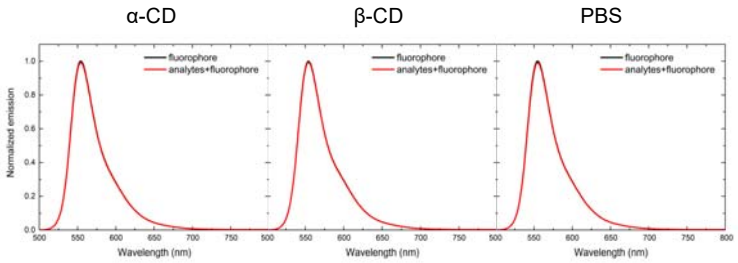

Figure S78: Fluorescence modulation of fluorophore **7** with analytes **2** and **3** in saliva

Analyte **2** – Analyte **3** – Fluorophore **8**

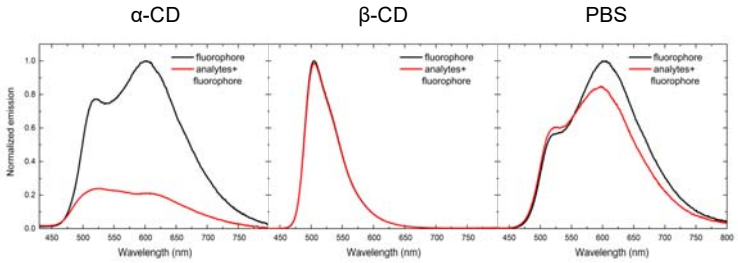

Figure S79: Fluorescence modulation of fluorophore **8** with analytes **2** and **3** in saliva

Analyte **2** – Analyte **4** – Fluorophore **6**

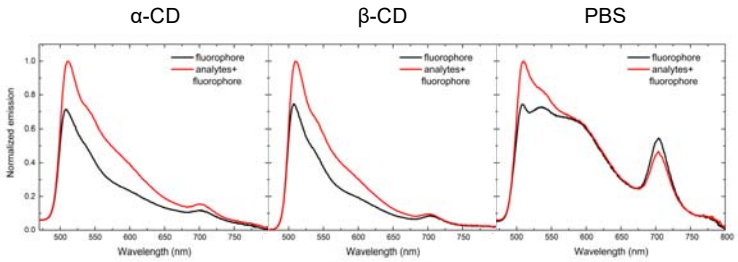

Figure S80: Fluorescence modulation of fluorophore **6** with analytes **2** and **4** in saliva

Analyte **2** – Analyte **4** – Fluorophore **7**

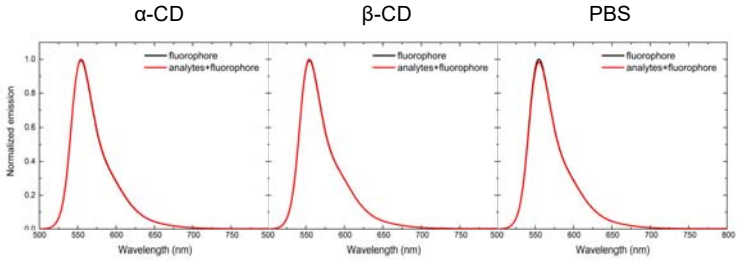

Figure S81: Fluorescence modulation of fluorophore **7** with analytes **2** and **4** in saliva

Analyte **2** – Analyte **4** – Fluorophore **8**

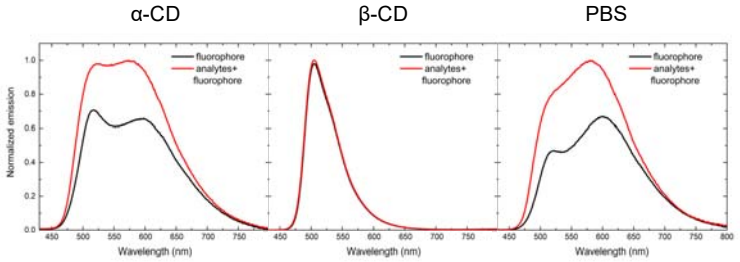

Figure S82: Fluorescence modulation of fluorophore **8** with analytes **2** and **4** in saliva

Analyte **3** – Analyte **4** – Fluorophore **6**

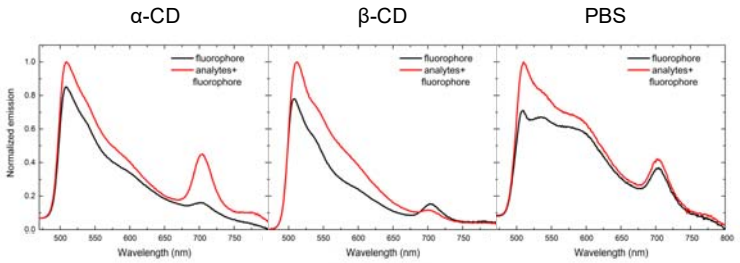

Figure S83: Fluorescence modulation of fluorophore **6** with analytes **3** and **4** in saliva

Analyte **3** – Analyte **4** – Fluorophore **7**

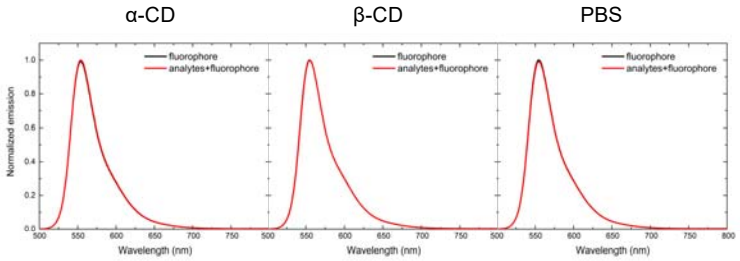

Figure S84: Fluorescence modulation of fluorophore **7** with analytes **3** and **4** in saliva

Analyte **3** – Analyte **4** – Fluorophore **8**

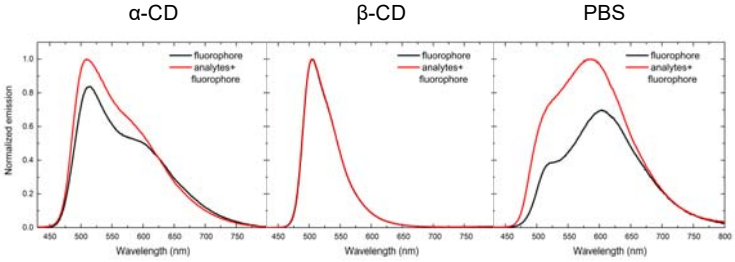

Figure S85: Fluorescence modulation of fluorophore **8** with analytes **3** and **4** in saliva

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.

Buffer Experiments

α-cyclodextrin

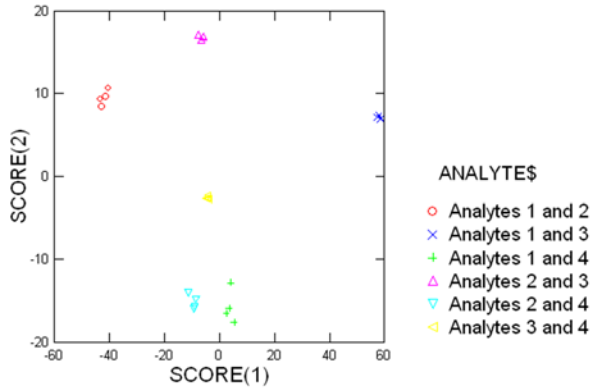

Figure S86: Linear discriminant analysis of fluorescence responses for analytes mixtures with fluorophores **6-8** with α-cyclodextrin in buffer

β-cyclodextrin

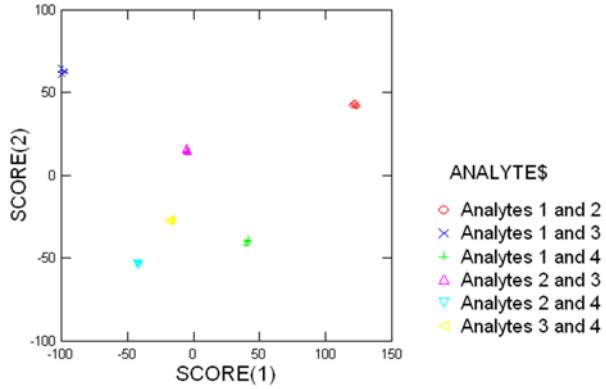

Figure S87: Linear discriminant analysis of fluorescence responses for analytes mixtures with fluorophores **6-8** with β-cyclodextrin in buffer

PBS

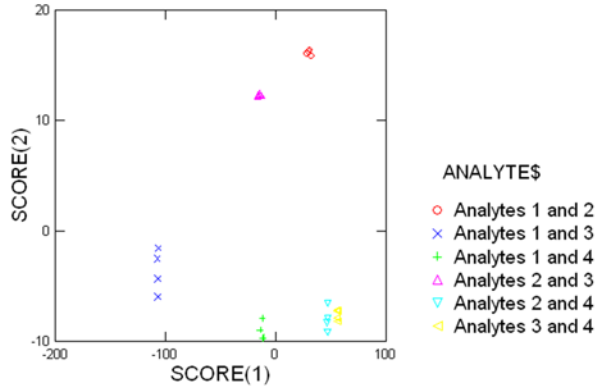

Figure S88: Linear discriminant analysis of fluorescence responses for analytes mixtures with fluorophores **6-8** without cyclodextrin in buffer

Saliva Experiments

α-cyclodextrin

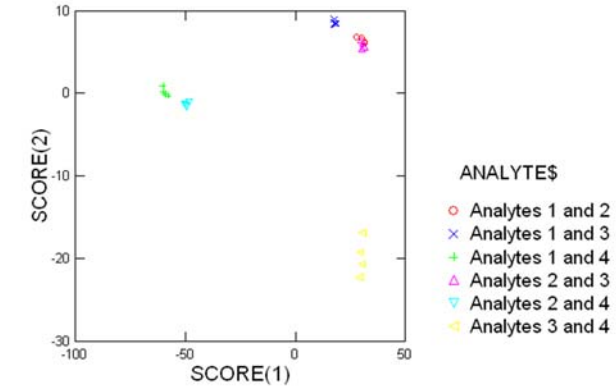

Figure S89: Linear discriminant analysis of fluorescence responses for analytes mixtures with fluorophores **6-8** with α-cyclodextrin in saliva

β-cyclodextrin

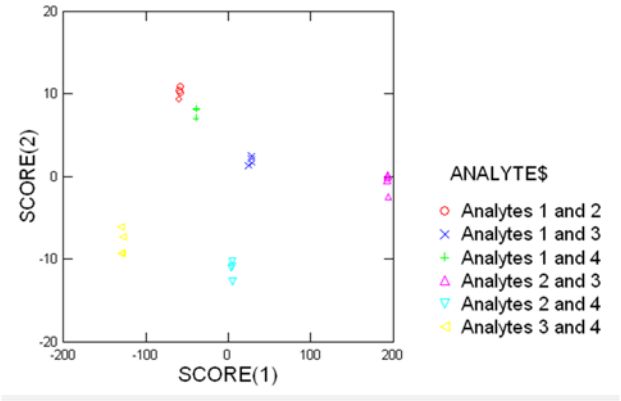

Figure S90: Linear discriminant analysis of fluorescence responses for analytes mixtures with fluorophores **6-8** with β-cyclodextrin in saliva

PBS

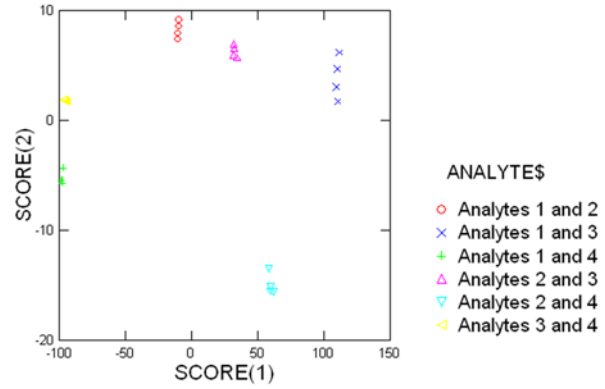

Figure S91: Linear discriminant analysis of fluorescence responses for analytes mixtures with fluorophores **6-8** without cyclodextrin in saliva

SUMMARY FIGURES FOR GC-MS EXPERIMENTS

Standard samples in which analyte was doped into the sample and then subjected to the GC-MS extraction/detection procedure are shown below:

Saliva – Doped Standard – 6.73 min

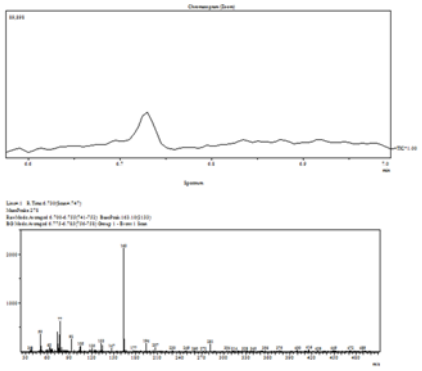

Figure S92: GC-MS trace for saliva dimethyl phthalate-doped standard at 6.73 minutes

NIST Compound ID: Dimethyl phthalate

Saliva – Doped Standard – 7.29 min

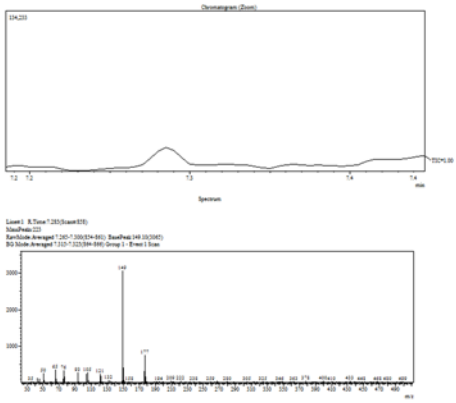

Figure S93: GC-MS trace for saliva diethyl phthalate-doped standard at 7.29 minutes

NIST Compound ID: Diethyl phthalate

Saliva – Doped Standard – 8.56 min

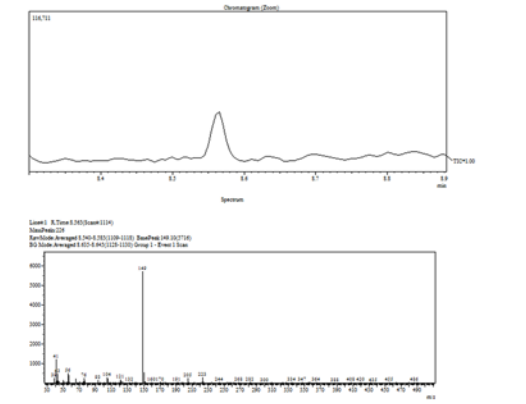

Figure S94: GC-MS trace for saliva dibutyl phthalate-doped standard at 8.56 minutes

NIST Compound ID: Dibutyl phthalate

Undoped samples were also run on the GC-MS, and the results and compound identification of those experiments are shown below:

Saliva – Undoped Sample – 16.15 min

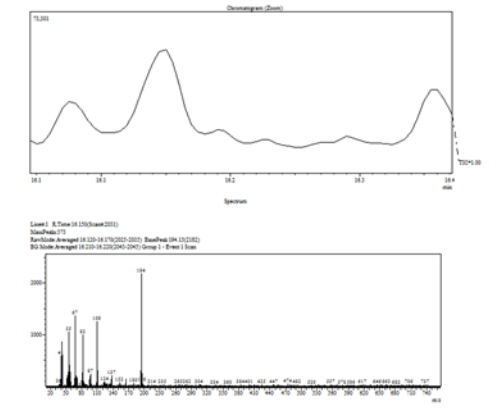

Figure S95: GC-MS trace for saliva for undoped sample at 16.15 minutes

NIST Compound ID: Caffeine

Saliva – Undoped Sample – 18.55 min

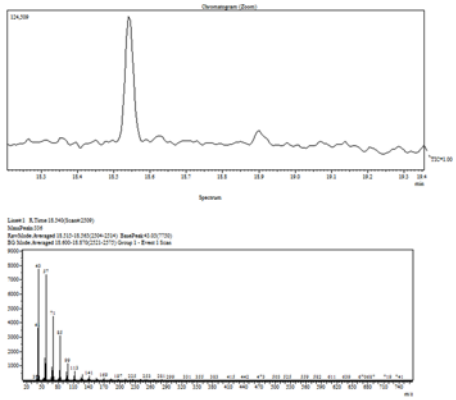

Figure S96: GC-MS trace for saliva for undoped sample at 18.55 minutes

NIST Compound ID: 2-methylnonadecane

Saliva – Undoped Sample – 19.40 min

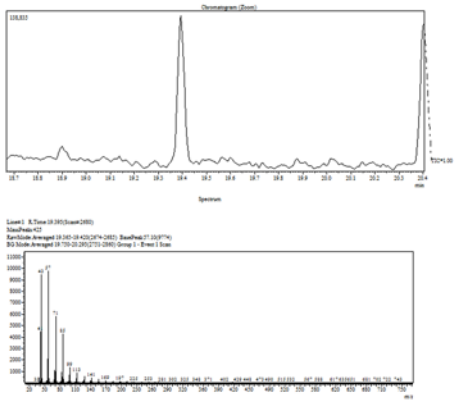

Figure S97: GC-MS trace for saliva for undoped sample at 19.40 minutes

NIST Compound ID: 7-n-hexyleicosane

Saliva – Undoped Sample – 20.40 min

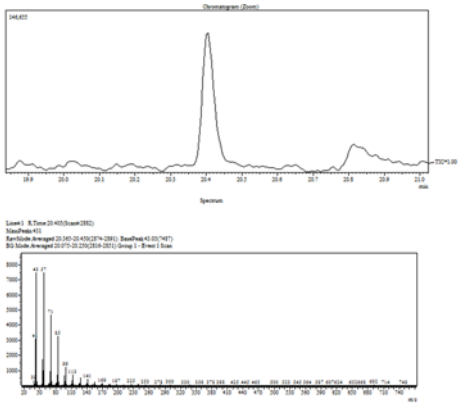

Figure S98: GC-MS trace for saliva for undoped sample at 20.40 minutes

NIST Compound ID: 9-octylheptadecane

Saliva – Undoped Sample – 21.65 min

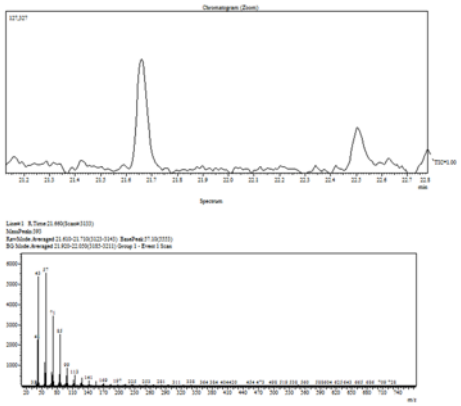

Figure S99: GC-MS trace for saliva for undoped sample at 21.65 minutes

NIST Compound ID: 10-methyleicosane

Saliva – Undoped Sample – 23.25 min

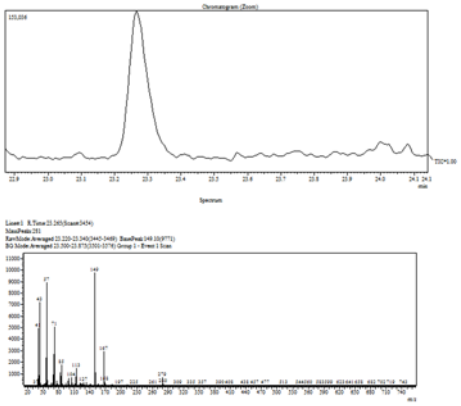

Figure S100: GC-MS trace for saliva for undoped sample at 23.25 minutes

NIST Compound ID: Bis(tridecyl)phthalate

Saliva – Undoped Sample – 24.45 min

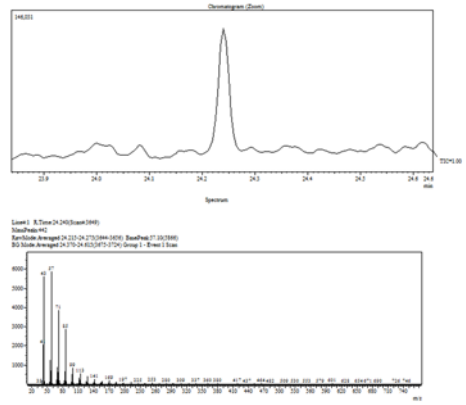

Figure S101: GC-MS trace for saliva for undoped sample at 24.45 minutes

NIST Compound ID: 7-methyldocosane

Saliva – Undoped Sample – 24.80 min

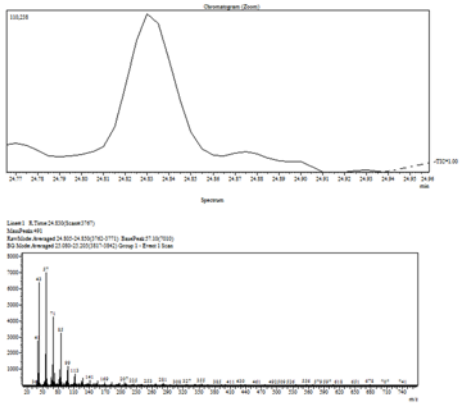

Figure S102: GC-MS trace for saliva for undoped sample at 24.80 minutes

NIST Compound ID: 11-decyltetracosane

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

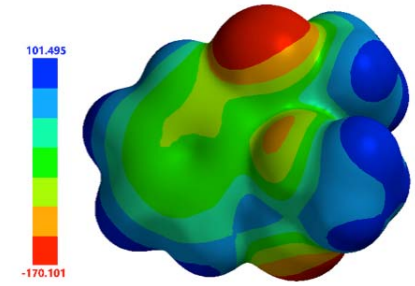

Figure S103: Electrostatic potential map of analyte **1**

Analyte 2

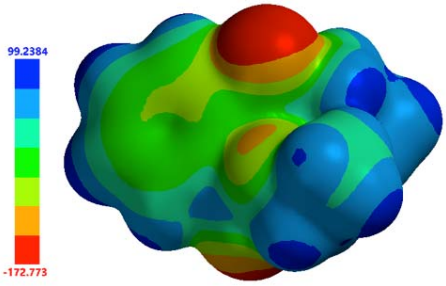

Figure S104: Electrostatic potential map of analyte **2**

Analyte 3

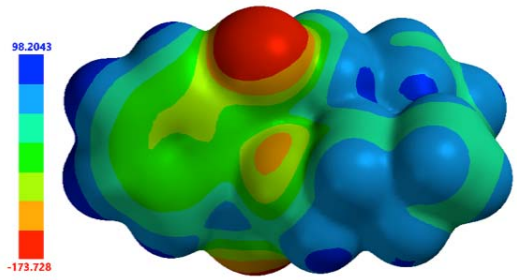

Figure S105: Electrostatic potential map of analyte **3**

Analyte 4

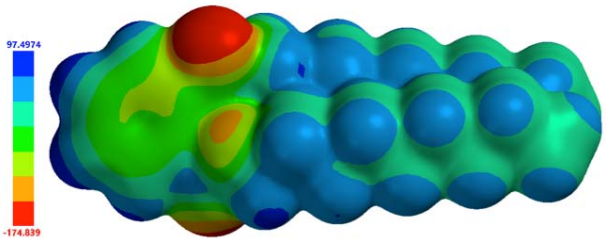

Figure S106: Electrostatic potential map of analyte **4**

Analyte 5

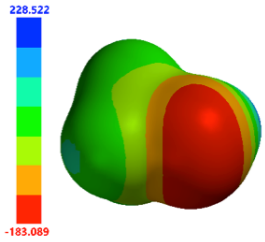

Figure S107: Electrostatic potential map of analyte **5**

Fluorophore 6

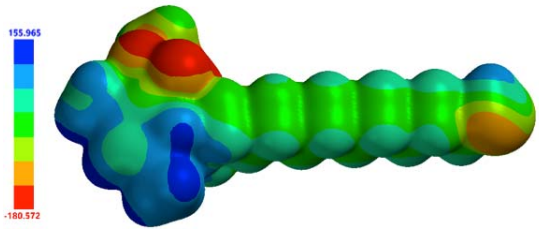

Figure S108: Electrostatic potential map of fluorophore **6**

Fluorophore 7

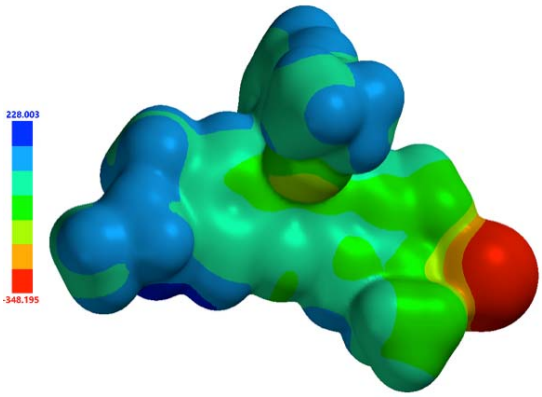

Figure S109: Electrostatic potential map of fluorophore **7**

Fluorophore 8

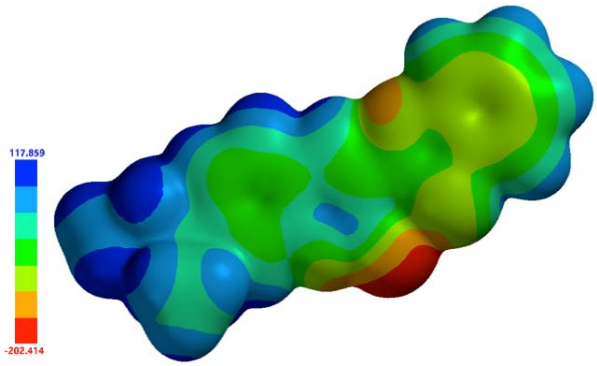

Figure S110: Electrostatic potential map of fluorophore **8**