Electronic Supplementary Information for

Array-based detection of isomeric and analogous analytes employing synthetically modified fluorophore attached β-cyclodextrin derivatives

Sauradip Chaudhuri, Dana J. DiScenza, Benjamin Smith, Reid Yocum, Mindy Levine

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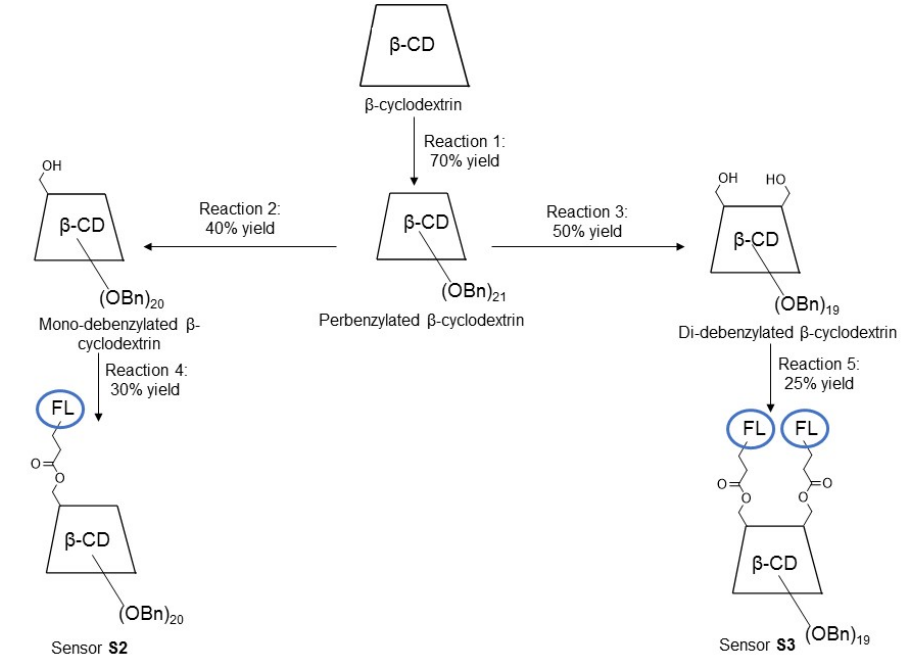
MATERIALS AND METHODS

All of the reagents were obtained from Sigma Aldrich or Fisher Scientific and used without further purification, unless otherwise noted. β-cyclodextrin was dried in the oven prior to use. Reagent grade solvents (99.9% purity) were used for the synthetic reactions. Column chromatography was performed in a Yamazen AKROS-Automatic TLC Smart Flash Chromatography System. ^{1}H and ^{13}C NMR spectra were recorded in a 400 MHz Bruker AVANCE and 500 MHz Varian NMR spectrometer, with assistance from Dr. Al Bach. Mass spectra were recorded in a Bruker Omniflex MALDI-TOF instrument with 2,5-dihydroxybenzoic acid as a matrix at the Department of Chemistry Instrumentation Facility (DCIF) at the Massachusetts Institute of Technology (MIT), with samples run by Dr. Li Li. All of the fluorescence measurements were performed using a Shimadzu RF 5301 spectrophotometer. Both the excitation and emission slit widths were 3 nm. All of the fluorescence spectra were integrated vs. wavenumber on the X-axis using Origin Pro Version 9.1 software. All arrays were generated using SYSTAT Version 13.

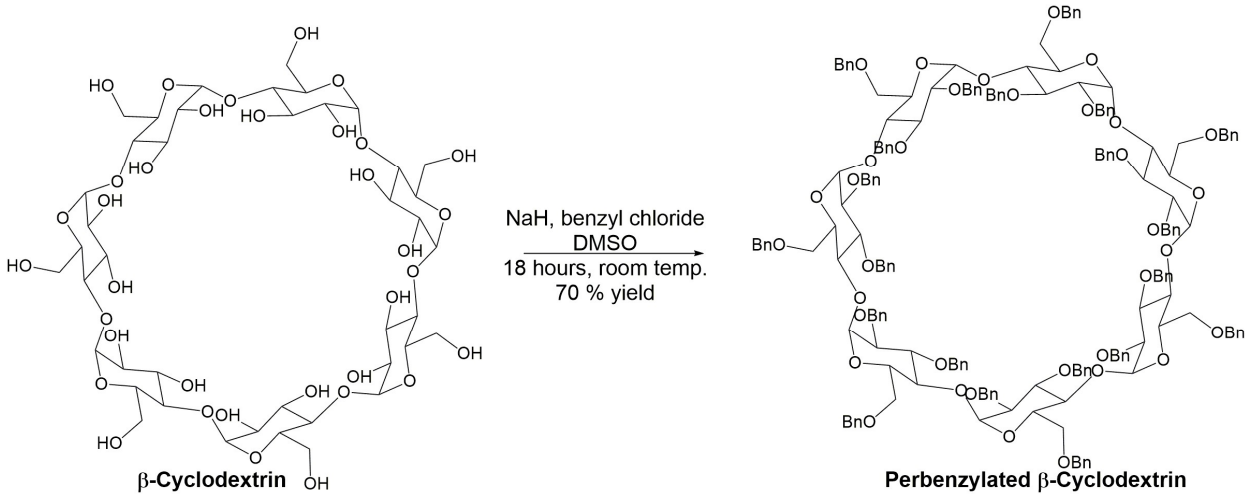
DETAILED PROCEDURES

DETAILED SYNTHETIC PROCEDURES

Overall Synthetic Scheme:



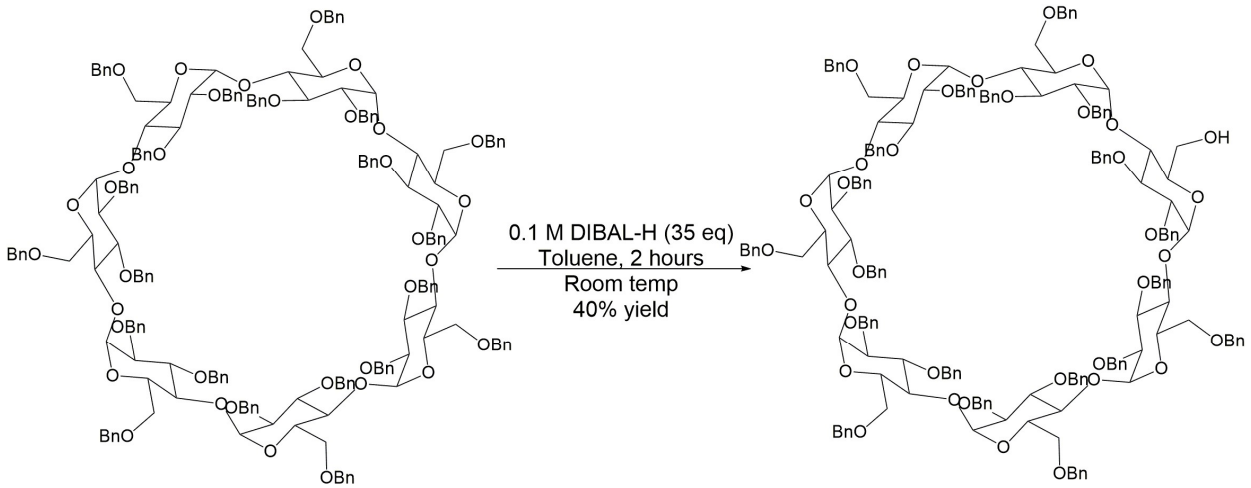
Reaction 1: Synthesis of Perbenzylated β-Cyclodextrin



To a stirred solution of oven-dried β-cyclodextrin (2.00 g, 1.76 mmol, 1.0 eq.) in DMSO (100 mL) under nitrogen, sodium hydride (2.60 g, 65 mmol, 36 eq.) was added carefully. The solution was allowed to stir for one hour at room temperature, after which time benzyl chloride (18.5 mL, 65 mmol, 36 eq.) was added over the course of one hour. The reaction mixture was stirred for 18 hours at room temperature, followed by the addition of methanol (20 mL). The reaction mixture was then diluted with water (200 mL) and extracted with diethyl ether (3 x 200 mL). The combined organic layers were washed with brine (200 mL), dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via column chromatography (25-40% v/v gradient elution of ethyl acetate/hexanes) to obtain a white foamy compound, perbenzylated β-cyclodextrin, (3.6 g, 70 % yield) after being dried under high vacuum. ^{1}H NMR

(400 MHz, $CDCl_3$): δ = 3.52 (dd, $^3J_{2,3}$ = 9.2 Hz, $^3J_{2,1}$ = 3.3 Hz, 7 H; 2-H), 3.58 (d, ^2J = 10.6 Hz, 7 H; 6-H), 3.98-4.10 (m, 28 H; 3-H, 4-H, 5-H, 6-H), 4.39, 4.43 (AB, $J_{A,B}$ = 12.2 Hz, 14 H; C*H*$_2$Ph), 4.50, 4.54 (AB, $J_{A,B}$ = 12.8 Hz, 14 H; C*H*$_2$Ph), 4.81, 5.11 (AB, $J_{A,B}$ = 11.0 Hz, 14 H; C*H*$_2$Ph), 5.22 (d, $^3J_{1,2}$ = 3.3 Hz, 7 H; 1-H), 7.15-7.30 (m, 105 H; aromatic-H) ppm; ^{13}C NMR (100 MHz, CDCl3): δ = 69.2, 71.4, 72.6, 73.2, 75.4, 78.6, 78.7, 80.8, 98.4, 126.9-128.3, 138.1, 138.3, 139.2 ppm; MS (MALDI-TOF): m/z = 3050.49 $[M+Na]^+$ (Calculated for $C_{189}H_{196}O_{35}$ + Na+ = 3050.55).

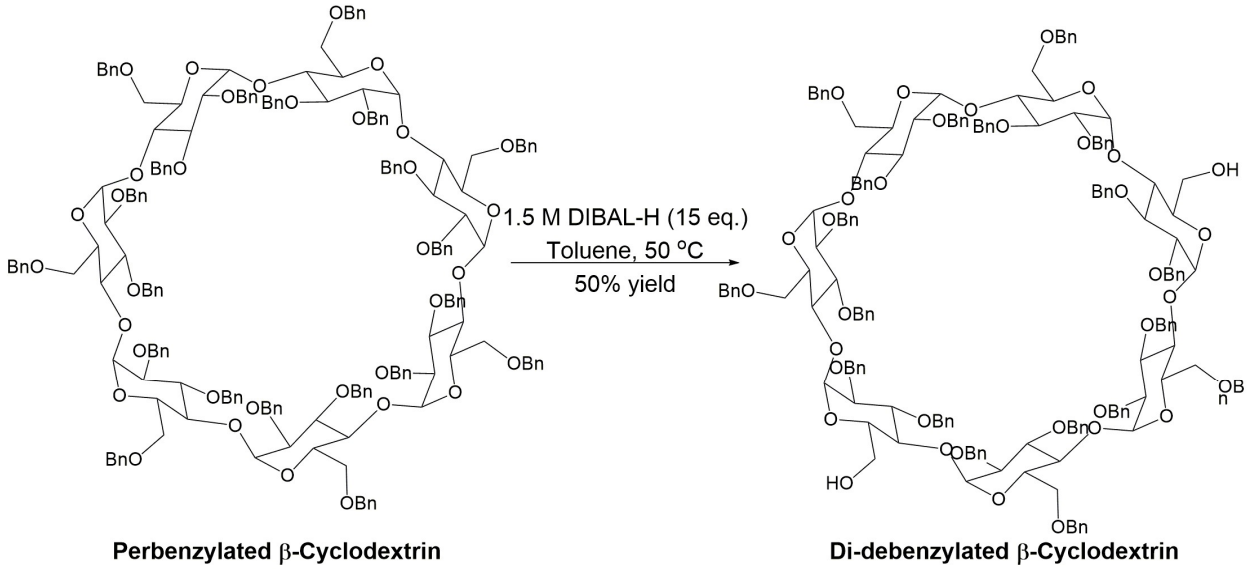
Reaction 2: Synthesis of Mono-debenzylated β-cyclodextrin:



Perbenzylated β-Cyclodextrin **Mono-debenzylated β-Cyclodextrin**

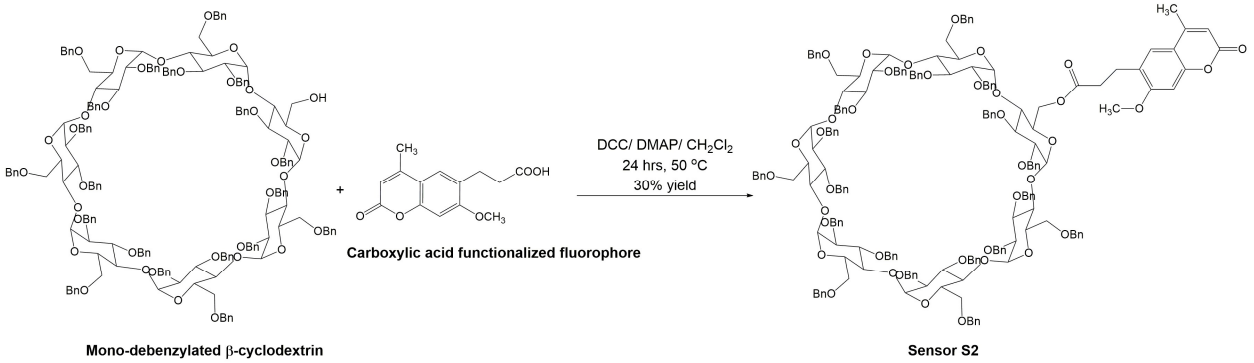
To a stirred solution of perbenzylated β-cyclodextrin (600 mg, 0.2 mmol, 1.0 eq.) in anhydrous toluene (65 mL) under nitrogen, diisobutylaluminum hydride (DIBAL-H) (4.7 mL, 7.0 mmol, 35 eq.) was added dropwise to a final concentration of 0.1 M. The reaction mixture was allowed to stir for 2 hours at room temperature, after which the complete disappearance of starting material was observed via TLC analysis (25% v/v ethyl acetate/hexane). The reaction mixture was cooled to 0 ^oC and hydrolyzed via the addition of 10% aqueous HCl (15 mL) for 15 minutes. The crude product was extracted with ethyl acetate (100 mL), treated with anhydrous Na_2SO_4 and dried under reduced pressure. Purification via column chromatography (1:3 ethyl acetate/hexane gradient elution) led to a white compound, mono-debenzylated β-cyclodextrin (250 mg, 40 % yield). ^{1}H NMR (400 MHz, CDCl3): δ = 2.48 (br s, 1 H; OH), 3.34-4.07 (m, 42 H; 7x2-H, 7x3-H, 7x4-H, 7x5-H, 14x6-H), 4.27-4.51 (m, 24H; C*H*$_2$Ph), 4.60-4.75 (m, 10H; C*H*$_2$Ph), 4.88-5.01 (m, 6H; 6x1-H), 5.08-5.18 (m, 4 H; C*H*$_2$Ph), 5.25 (dd, $^3J_{1,2}$ = 12.0, 4.0 Hz, 2 H; C*H*$_2$Ph), 5.36 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H; 1x1-H), 7.04-7.30 (m, 100 H; aromatic-H) ppm; ^{13}C NMR (100 MHz, CDCl3): δ = 61.6, 68.8, 69.2, 69.3, 69.4, 71.4, 71.5, 71.6, 71.7, 71.7, 71.8, 71.9, 72.5, 72.6, 72.7, 72.7, 72.9, 73.0, 73.3, 73.4, 73.4, 74.8, 75.0, 75.1, 75.3, 75.8, 75.9, 75.9, 76.0, 77.4, 77.7, 78.1, 78.8, 79.0, 79.1, 79.5, 79.6, 79.9, 80.1, 80.9, 81.0, 81.0, 81.1, 98.0, 98.3, 98.4, 98.4, 98.6, 98.8, 98.9, 127.0-128.4, 137.9, 138.1, 138.2, 138.2, 138.2, 138.3, 138.3, 138.4, 138.5, 138.5, 139.0, 139.1, 139.3, 139.3, 139.4, 139.4 ppm; MS (MALDI-TOF): m/z = 2960.29 $[M+Na]^+$ (Calculated for $C_{182}H_{190}O_{35}$ + Na = 2960.43).

Reaction 3: Synthesis of Di-debenzylated β-cyclodextrin:



To a stirred solution of perbenzylated β-cyclodextrin (1.2 g, 0.4 mmol, 1.0 eq.) under nitrogen, DIBAL-H (4.0 mL, 6.0 mmol, 15 eq.) was added dropwise. The reaction mixture was stirred for 6 hours at 50 °C until a complete disappearance of starting material was observed via TLC analysis. After an additional 15 minutes of stirring, the reaction mixture was cooled to 0 °C and hydrolyzed by vigorously stirring with 10 % aqueous HCl (15 mL) for 20 minutes. The crude product was extracted with ethyl acetate (100 mL), treated with anhydrous Na_2SO_4 and dried under reduced pressure. Purification via column chromatography (1:3 ethyl acetate/hexanes) led to a white compound di-debenzylated β-cyclodextrin (566 mg, 50 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.69 (br s, 1 H ; OH), 2.78 (br s, 1 H; OH), 3.44-3.54 (m, 5 H; 5x2-H), 3.60-4.15 (m, 37 H; 2x2-H, 7x3-H, 7x4-H, 7x5-H, 14x6-H), 4.44-4.88 (m, 33 H; CH_2Ph), 4.89 (d, $^3J_{1,2}$ = 3.3 Hz, 1 H ; 1-H), 4.98 (d, $^3J_{1,2}$ = 3.7 Hz, 1H ; 1-H), 5.00 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H; 1-H), 5.02 (d, $^3J_{1,2}$ = 3.4 Hz, 1 H ; 1-H), 5.04 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H ; 1-H), 5.06 (d, ^2J = 12.3 Hz, 1 H ; CH_2Ph), 5.21-5.25 (m, 3 H; 3xCH_2Ph), 5.30 (d, ^2J = 10.7 Hz, 1 H;CH_2Ph), 5.56 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H; 1-H), 5.67 (d, $^3J_{1,2}$ = 3.7 Hz, 1 H; 1-H), 7.12-7.33 (m, 95H; aromatic-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.6, 69.5, 69.6, 71.2, 71.6, 72.0, 72.1, 72.9, 73.2, 73.25, 73.3, 73.9, 74.1, 76.1, 76.4, 77.6, 79.0, 79.7, 80.6, 80.9, 81.0, 81.6, 81.7, 97.6, 97.7, 98.2, 126.3-128.3, 137.7, 137.8, 137.9, 138.2, 138.6, 137.7, 139.2 ppm; MS (MALDI-TOF): m/z = 2870.1 $[M+Na]^+$ (Calculated for $C_{175}H_{184}O_{35}$ + Na = 2870.31).

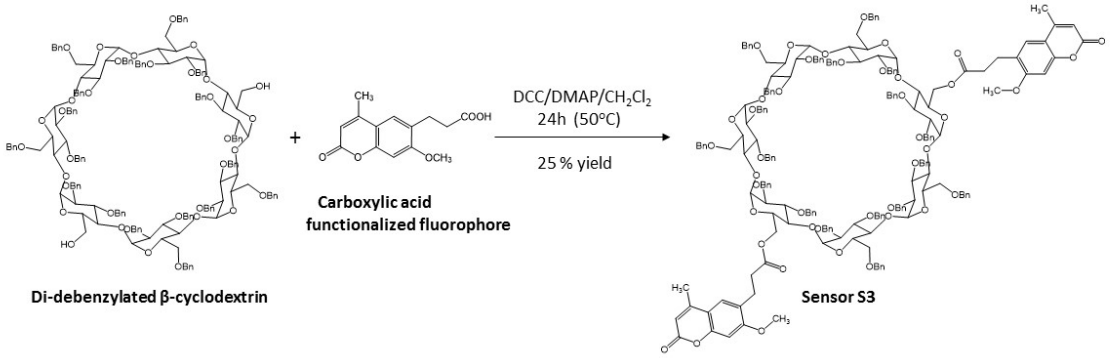
Reaction 4: Synthesis of Sensor S2:



A mixture of mono-debenzylated β-cyclodextrin (100 mg, 0.034 mmol, 1.0 eq.), carboxylic acid functionalized fluorophore (10.5 mg, 0.04 mmol, 1.17 eq.), *N,N'*-dicyclohexylcarbodiimide (DCC) (8.3 mg, 0.04 mmol, 1.17 eq.) and 4-dimethylaminopyridine (DMAP) (0.5 mg, 0.004 mmol, 0.1 eq.) in

dichloromethane (1 mL) was stirred at 50 °C for 24 hrs. The mixture was filtered, treated with 5% aqueous acetic acid (2 x 3 mL) and extracted with dichloromethane (2 x 4 mL). The combined organic layer was dried under anhydrous Na_2SO_4 and subjected to solvent removal under reduced pressure. The crude product was purified via column chromatography (1:3 ethyl acetate/hexanes) to yield a white amorphous compound **sensor S2** (32 mg, 30% yield). ^{1}H NMR (500 MHz, d_6-acetone): δ = 2.31 (s, 3 H; ArC*H*$_3$), 2.62 (m, 2 H; C*H*$_2$FL3), 2.93 (t, $^3J_{1,2} = {}^3J_{1,2'} = 10.0$ Hz, 2 H; C*H*$_2$CHFL3), 3.43-3.50 (m, 7 H; 2-H), 3.62-3.74 (m, 7 H; 6-H), 3.84 (br t, 2 H; 6-H), 3.89 (s, 3 H; OC*H*$_3$), 3.92-4.16 (m, 26 H; 3-H, 4-H, 5-H, 6-H), 4.40-4.62 (m, 26 H; C*H*$_2$Ph), 4.75-4.78 (m, 7 H; C*H*$_2$Ph), 5.09-5.13 (m, 7 H; C*H*$_2$Ph), 5.16 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H; 1-H), 5.27 (dd, $^3J_{1,2}$ = 10, 3.5 Hz, 2 H; 1-H), 5.30 (m, 3 H; 1-H), 5.33 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H; 1-H), 6.02 (s, 1 H; C*H*=CCH$_3$), 6.86 (s, 1 H; ArH), 7.12-7.33 (m, 80 H; PhH), 7.48 (s, 1 H; ArH) ppm; ^{13}C NMR (125 MHz, d_6-acetone): δ = 17.8, 25.3, 33.6, 55.7, 63.5, 69.5, 69.8, 71.7, 71.9, 72.4, 72.7, 73.0, 75.2, 78.3-79.4, 80.8-81.1, 97.8-98.0, 98.2, 98.7, 98.7, 111.5, 112.8, 124.5, 125.6, 126.8, 127.29-128.25, 138.6, 138.7-138.8, 139.5-139.6, 152.8, 154.3, 160.1, 160.6, 172.0 ppm; MS (MALDI-TOF): m/z = 3204.57 $[M+Na]^+$ (Calculated for $C_{196}H_{202}O_{39}$ + Na = 3204.67).

Reaction 5: Synthesis of Sensor S3:



A mixture of di-debenzylated β-cyclodextrin (100 mg, 0.035 mmol, 1.0 eq.), carboxylic acid functionalized fluorophore (21.0 mg, 0.08 mmol, 2.34 eq.), *N,N'*-dicyclohexylcarbodiimide (16.5 mg, 0.08 mmol, 2.34 eq.) and 4-dimethylaminopyridine (1.1 mg, 0.008 mmol, 0.2 eq.) in dichloromethane (1 mL) was stirred at 50 °C for 24 hrs. The mixture was filtered, treated with 5% aqueous acetic acid (2 x 3 mL) and extracted with dichloromethane (2 x 4 mL). The combined organic layer was dried under anhydrous Na_2SO_4 and subjected to solvent removal under reduced pressure. The crude product was purified via column chromatography (1:3 ethyl acetate: hexanes) to lead to a white amorphous compound **Sensor S3** (30 mg, 25 % yield). ^{1}H NMR (500 MHz, d_6-acetone): δ = 2.31 (s, 6 H; ArC*H*$_3$), 2.62 (m, 4 H; C*H*FL3), 2.93 (m, 4 H; C*H*CHFL3), 3.44-3.51 (m, 7 H; 2-H), 3.62-3.74 (m, 7 H; 6-H), 3.82-3.89 (multiplet overlapped, 4 H; 6-H), 3.89 (singlet overlapped, 6 H; OC*H*$_3$), 3.94-4.16 (m, 24 H; 3-H, 4-H, 5-H, 6-H), 4.41-4.64 (m, 26H; C*H*$_2$Ph), 4.74-4.78 (m, 6H; C*H*$_2$Ph), 5.08-5.12 (m, 6H; C*H*$_2$Ph), 5.22 (dd, $^3J_{1,2}$ = 8.5, 3.5 Hz, 2H; 1-H), 5.26 (m, 3 H; 1-H), 5.29 (m, 2 H; 1-H), 6.01 (s, 2 H; C*H*=CCH$_3$), 6.86 (s, 2 H; ArH), 7.06-7.30 (m, 80 H; PhH), 7.46 (d, $^3J_{1,2}$ = 6.5 Hz, 2H; ArH) ppm; ^{13}C NMR (125 MHz, d_6-acetone): δ = 17.8, 24.6, 25.2-25.4, 25.6, 25.8, 30.6, 32.1, 33.5, 34.1, 55.7, 63.5, 69.3-69.8, 71.6-73.1, 75.2, 78.3-79.4, 80.7-81.0, 97.9-98.7, 111.5, 112.7, 125.4-125.5, 126.8, 127.3-128.3, 138.6, 138.7-138.8, 139.4-139.6, 152.7, 154.3, 160.0, 160.6, 172.1 ppm; MS (MALDI-TOF): m/z = 3358.82 $[M+Na]^+$ (Calculated for $C_{203}H_{208}O_{43}$ + Na = 3358.40).

DETAILED PROCEDURES FOR FLUORESCENCE MODULATION EXPERIMENTS

Fluorescence emission spectra were obtained using a Shimadzu RF-5301PC spectrophotofluorimeter with 3 nm excitation and 3 nm emission slit widths. In a quartz cuvette, 0.5 mL of **S1**, **S2**, or **S3** solutions (5 μM in DMSO) and 2 mL of DI water were combined. Then, the solution was excited at 320 nm, and the fluorescence emission spectra were recorded. Repeat measurements were recorded for four separate trials.

The fluorescence emission spectra were integrated vs. wavenumber on the X-axis, and fluorescence modulation was measured by the ratio of integrated emission of the fluorophore in the presence of the analyte to integrated emission of the fluorophore in the absence of the analyte, as shown in Equation 1:

$$\text{Fluorescence Modulation} = Fl_{\text{analyte}} / Fl_{\text{blank}} \quad \text{(Eq. 1)}$$

Where Fl_{analyte} is the integrated fluorescence emission of the fluorophore in the presence of 10 μL of analyte (1 mg/mL in THF), and Fl_{blank} is the integrated fluorescence emission of the fluorophore in the absence of the analyte.

DETAILED PROCEDURES FOR ARRAY GENERATION EXPERIMENTS

Array analysis was performed using SYSTAT 13 statistical computing software with the following settings:

(a) Classical Discriminant Analysis

(b) Grouping Variable: Analytes

(c) Predictors: **S1**, **S2**, and **S3**

(d) Long-Range Statistics: Mahal

DETAILED PROCEDURES FOR LIMIT OF DETECTION EXPERIMENTS

The limit of detection (LOD) is defined as the lowest concentration of analyte at which a signal can be detected. To determine this value, the following steps were performed for each cyclodextrin-analyte combination. In a quartz cuvette, 0.5 mL of **S1**, **S2**, or **S3** solutions (5 μM in DMSO) and 2 mL of deionized (DI) water were combined. Then, the solution was excited at 320 nm, and the fluorescence emission spectra were recorded starting at 330 nm. Six repeat measurements were taken.

Next, 2 μL of analyte (1 mg/mL in THF) was added, and again the solution was excited at the fluorophore's excitation wavelength, and the fluorescence emission spectra were recorded. Six repeat measurements were taken. This step was repeated for 4 μL of analyte, 6 μL of analyte, 8 μL of analyte, 10 μL of analyte, 12 μL of analyte, 14 μL of analyte, 16 μL of analyte, 18 μL of analyte, 20 μL of analyte.

All of the fluorescence emission spectra were integrated vs. wavenumber on the X-axis, and calibration curves were generated. The curves plotted the analyte concentration in μM on the X-axis, and the fluorescence modulation ratio on the Y-axis. The curve was fitted to a straight line and the equation of the line was determined.

The limit of detection is defined according to Equation S2:

$$LOD = 3(SD_{blank})/m \quad \text{(Eq. S2)}$$

Where SD_{blank} is the standard deviation of the blank sample and m is the slope of the calibration curve. In cases where the slope of the trendline was negative, the absolute value of the slope was used to calculate the LOD. In all cases, the LOD was calculated in μM.

DETAILED PROCEDURES FOR THE HPLC ANALYSIS OF S2 AND S3

The HPLC analysis of the cyclodextrin-fluorophore covalent hosts was performed on a Waters Acquity® Arc™ system using a Waters 2998 Photo Diode Array (PDA) detector and a Cortecs® C18 2.7 µm 4.6x50 mm column. The solvent systm was an isocratic solution of 0.1% formic acid in acetonitrile, run at a rate of 1 mL/minute for 5 minutes. All samples were prepared in the same solution of 0.1% formic acid in acetonitrile. The PDA detector was set to collect from 210-400 nm.

SUMMARY TABLES

FLUORESCENCE MODULATION SUMMARY TABLES

Analyte	S1	S2	S3
benzyl alcohol	1.00 ± 0.00	1.04 ± 001	0.98 ± 0.01
o -cresol	1.01 ± 0.00	0.82 ± 0.01	0.88 ± 0.01
m -cresol	0.99 ± 0.00	0.90 ± 0.00	1.05 ± 0.02
p -cresol	1.01 ± 0.01	0.87 ± 0.01	0.75 ± 0.01

Analyte	S1	S2	S3
1-methylcyclohexanol	1.01 ± 0.00	0.89 ± 0.00	1.07 ± 0.05
cis -2-methylcyclohexanol	1.01 ± 0.00	0.90 ± 0.00	0.97 ± 0.01
cyclohexylmethanol	1.01 ± 0.00	0.99 ± 0.03	0.77 ± 0.06
trans -2-methylcyclohexanol	0.99 ± 0.00	0.89 ± 0.00	1.14 ± 0.01

Analyte	S1	S2	S3
DDD	1.00 ± 0.00	0.93 ± 0.01	1.33 ± 0.03
DDE	1.01 ± 0.00	0.95 ± 0.01	1.07 ± 0.04
o,p -DDT	0.99 ± 0.01	1.08 ± 0.01	1.04 ± 0.05
p,p -DDT	0.98 ± 0.01	1.17 ± 0.01	1.35 ± 0.05

Analyte	S1	S2	S3
n -hexanes	1.00 ± 0.00	1.01 ± 0.01	0.94 ± 0.02
2-methylpentane	1.05 ± 0.00	1.06 ± 0.00	0.93 ± 0.02
3-methylentane	0.98 ± 0.00	1.09 ± 0.01	0.95 ± 0.02
2,3-dimethylbutane	1.00 ± 0.00	0.99 ± 0.01	1.01 ± 0.01
1-methylcyclopentane	1.03 ± 0.01	1.03 ± 0.02	0.89 ± 0.01

Analyte	S1	S2	S3
PCB3	1.03 ± 0.00	1.06 ± 0.06	0.85 ± 0.01
PCB29	1.01 ± 0.01	1.02 ± 0.04	0.98 ± 0.03
PCB52	1.01 ± 0.00	1.07 ± 0.04	0.89 ± 0.02
PCB77	1.05 ± 0.00	0.56 ± 0.01	0.98 ± 0.01
PCB209	1.00 ± 0.01	0.92 ± 0.03	1.14 ± 0.02

LIMIT OF DETECTION SUMMARY TABLE

Analyte	Host	Equation	R^2	LOD (μM)
p,p -DDT	**S1**	y = 0.0094x + 1.0385	0.939	0.39
p,p -DDT	**S2**	y = 0.011x + 0.971	0.9406	0.51
p,p -DDT	**S3**	y = 0.0188x + 0.9592	0.9547	2.20
o -Cresol	**S1**	y = 0.0018x + 1.0195	0.9748	4.97
Benzyl alcohol	**S2**	y = 0.0032x + 0.932	0.8521	8.34
o -Cresol	**S3**	y = -0.0026x + 0.7242	0.9893	11.79
Cyclohexylmethanol	**S1**	y = 0.01x + 0.9866	0.9708	1.17
Cyclohexylmethanol	**S2**	y = -0.0031x + 0.9648	0.9405	1.85
1-Methylcyclohexanol	**S3**	y = 0.0012x + 0.942	0.9236	26.30
2-Methylpentane	**S1**	y = 0.0026x + 0.9776	0.9555	2.20
3-Methylpentane	**S2**	y = 0.0017x + 1.0775	0.9864	15.74
1-Methylcyclopentane	**S3**	y = 0.0038x + 0.7209	0.9421	19.82
PCB 77	**S1**	y = 0.0116x + 1.0153	0.8832	0.29
PCB 209	**S2**	y = -0.0077x + 0.8402	0.9655	0.88
PCB 209	**S3**	y = 0.0079x + 1.0621	0.8686	4.59

SUMMARY TABLES FOR ARRAYS

All analytes

Jackknifed Classification Matrix

	1-methylcyclohe-xanol	1-methylcyclope-ntane	2,3-dimethylbut-ane	2-methylpentane	3-methylpentane	DDD	DDE
1-methylcyclohexanol	4	0	0	0	0	0	0
1-methylcyclopentane	0	4	0	0	0	0	0
2,3-dimethylbutane	0	0	4	0	0	0	0
2-methylpentane	0	0	0	4	0	0	0
3-methylpentane	0	0	0	0	4	0	0
DDD	0	0	0	0	0	4	0
DDE	0	0	0	0	0	0	4
benzyl alcohol	0	0	0	0	0	0	0
cis-2methylcyclohexanol	0	0	0	0	0	0	0
cyclohexylmethanol	0	0	0	0	0	0	0
m-cresol	0	0	0	0	0	0	0
n-hexanes	0	0	0	0	0	0	0
o-cresol	0	0	0	0	0	0	0
opDDT	0	0	0	0	0	0	0
p-cresol	0	0	0	0	0	0	0
pcb209	0	0	0	0	0	0	0
pcb29	0	0	0	0	0	0	0
pcb3	0	0	0	0	0	0	0
pcb52	0	0	0	0	0	0	0
pcb77	0	0	0	0	0	0	0
ppDDT	0	0	0	0	0	0	0
trans-2methylcyclohexano	0	0	0	0	0	0	0
Total	4	4	4	4	4	4	4

Jackknifed Classification Matrix (Contd.)

	benzyl alcohol	cis-2methylcycl-ohexanol	cyclohexylmetha-nol	m-cresol	n-hexanes	o-cresol	opDDT	p-cresol	pcb209
1-methylcyclohexanol	0	0	0	0	0	0	0	0	0
1-methylcyclopentane	0	0	0	0	0	0	0	0	0
2,3-dimethylbutane	0	0	0	0	0	0	0	0	0
2-methylpentane	0	0	0	0	0	0	0	0	0
3-methylpentane	0	0	0	0	0	0	0	0	0
DDD	0	0	0	0	0	0	0	0	0
DDE	0	0	0	0	0	0	0	0	0
benzyl alcohol	4	0	0	0	0	0	0	0	0
cis-2methylcyclohexanol	0	4	0	0	0	0	0	0	0
cyclohexylmethanol	0	0	4	0	0	0	0	0	0
m-cresol	0	0	0	4	0	0	0	0	0
n-hexanes	0	0	0	0	4	0	0	0	0
o-cresol	0	0	0	0	0	4	0	0	0
opDDT	0	0	0	0	0	0	4	0	0
p-cresol	0	0	0	0	0	0	0	4	0
pcb209	0	0	0	0	0	0	0	0	4
pcb29	0	0	0	0	0	0	0	0	0
pcb3	0	0	0	0	0	0	0	0	0
pcb52	0	0	0	0	0	0	0	0	0
pcb77	0	0	0	0	0	0	0	0	0
ppDDT	0	0	0	0	0	0	0	0	0
trans-2methylcyclohexano	0	0	0	0	0	0	0	0	0
Total	4	4	4	4	4	4	4	4	4

Jackknifed Classification Matrix (Contd.)

	pcb29	pcb3	pcb52	pcb77	ppDDT	trans-2methylcy-clohexano	%correct
1-methylcyclohexanol	0	0	0	0	0	0	100
1-methylcyclopentane	0	0	0	0	0	0	100
2,3-dimethylbutane	0	0	0	0	0	0	100
2-methylpentane	0	0	0	0	0	0	100
3-methylpentane	0	0	0	0	0	0	100
DDD	0	0	0	0	0	0	100
DDE	0	0	0	0	0	0	100
benzyl alcohol	0	0	0	0	0	0	100
cis-2methylcyclohexanol	0	0	0	0	0	0	100
cyclohexylmethanol	0	0	0	0	0	0	100
m-cresol	0	0	0	0	0	0	100
n-hexanes	0	0	0	0	0	0	100
o-cresol	0	0	0	0	0	0	100
opDDT	0	0	0	0	0	0	100
p-cresol	0	0	0	0	0	0	100
pcb209	0	0	0	0	0	0	100
pcb29	4	0	0	0	0	0	100
pcb3	0	4	0	0	0	0	100
pcb52	0	0	4	0	0	0	100
pcb77	0	0	0	4	0	0	100
ppDDT	0	0	0	0	4	0	100
trans-2methylcyclohexano	0	0	0	0	0	4	100
Total	4	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.908	0.994	1.000

Aromatics

Jackknifed Classification Matrix

	benzyl alcohol	m-cresol	o-cresol	p-cresol	%correct
benzyl alcohol	4	0	0	0	100
m-cresol	0	4	0	0	100
o-cresol	0	0	4	0	100
p-cresol	0	0	0	4	100
Total	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.859	0.950	1.000

Pesticides

Jackknifed Classification Matrix

	DDD	DDE	opDDT	ppDDT	%correct
DDD	4	0	0	0	100
DDE	0	4	0	0	100
opDDT	0	0	4	0	100
ppDDT	0	0	0	4	100
Total	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.995	1.000	1.000

Alkanes

Jackknifed Classification Matrix

	1-methylcyclope-ntane	2,3-dimethylbut-ane	2-methylpentane	3-methylpentane	n-hexanes	%correct
1-methylcyclopentane	4	0	0	0	0	100
2,3-dimethylbutane	0	4	0	0	0	100
2-methylpentane	0	0	4	0	0	100
3-methylpentane	0	0	0	4	0	100
n-hexanes	0	0	0	0	4	100
Total	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.767	0.930	1.000

Aliphatic alcohols

Jackknifed Classification Matrix

	1-methylcyclohe-xanol	cis-2methylcycl-ohexanol	cyclohexylmetha-nol	trans-2methylcy-clohexano	%correct
1-methylcyclohexanol	4	0	0	0	100
cis-2methylcyclohexanol	0	4	0	0	100
cyclohexylmethanol	0	0	4	0	100
trans-2methylcyclohexano	0	0	0	4	100
Total	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.775	0.990	1.000

PCBs

Jackknifed Classification Matrix

	pcb209	pcb29	pcb3	pcb52	pcb77	%correct
pcb209	4	0	0	0	0	100
pcb29	0	4	0	0	0	100
pcb3	0	0	4	0	0	100
pcb52	0	0	0	4	0	100
pcb77	0	0	0	0	4	100
Total	4	4	4	4	4	100

Cumulative Proportion of Total Dispersion

0.806	0.996	1.000

1:1 binary mixtures of analytes 5-8

Jackknifed Classification Matrix

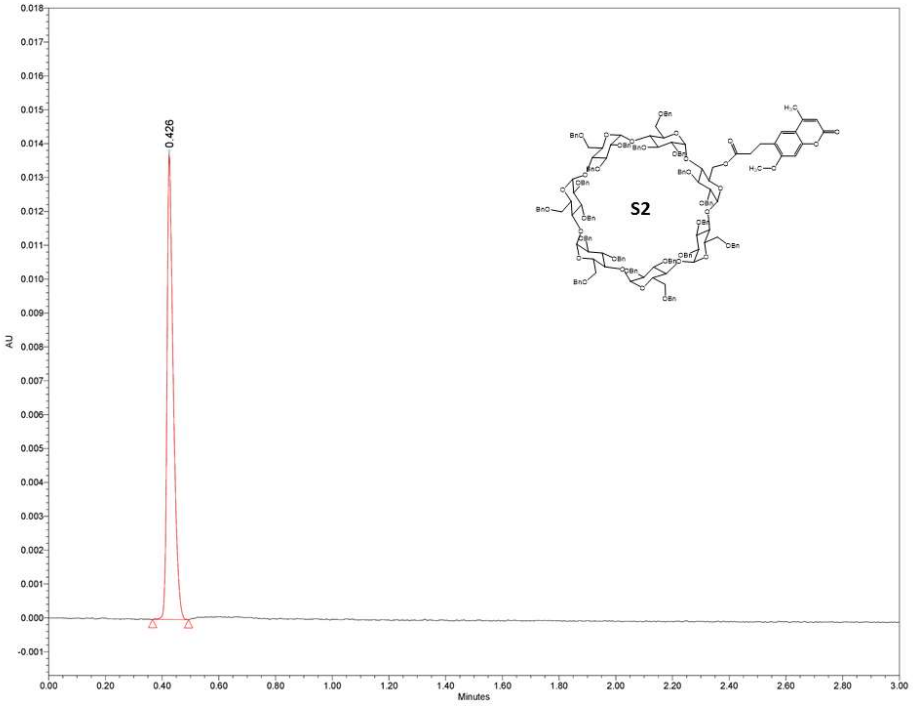
	BA-M	BA-O	BA-P	M-P	O-M	O-P	%correct
BA-M	2	0	0	0	0	2	50
BA-O	0	4	0	0	0	0	100
BA-P	1	0	3	0	0	0	75
M-P	0	0	0	4	0	0	100
O-M	0	0	0	0	4	0	100
O-P	1	0	0	0	0	3	75
Total	4	4	3	4	4	5	83

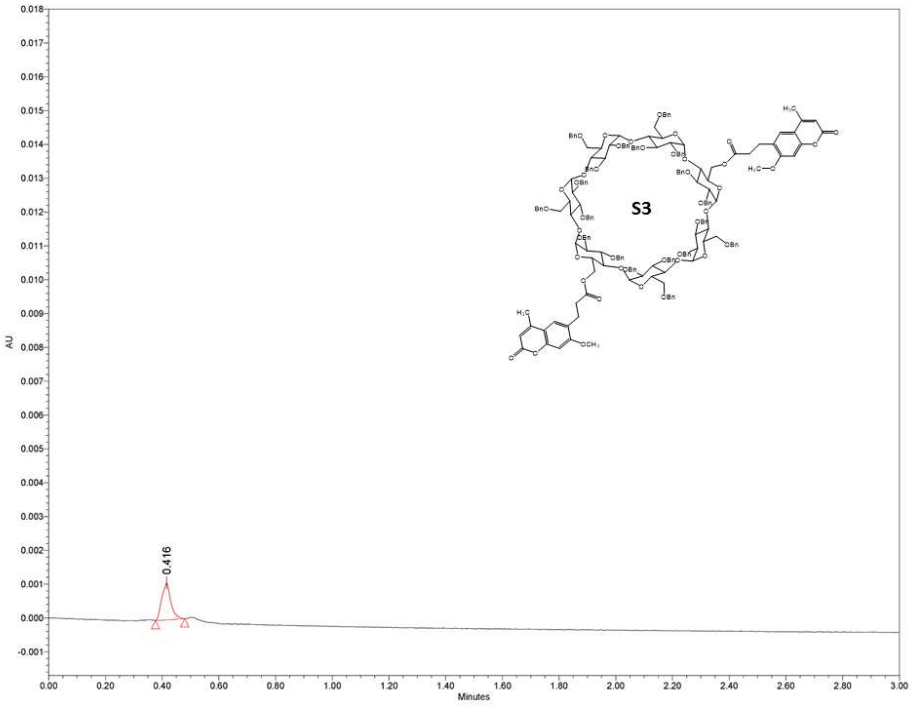
Cumulative Proportion of Total Dispersion

0.889	0.981	1.000

SUMMARY FIGURES

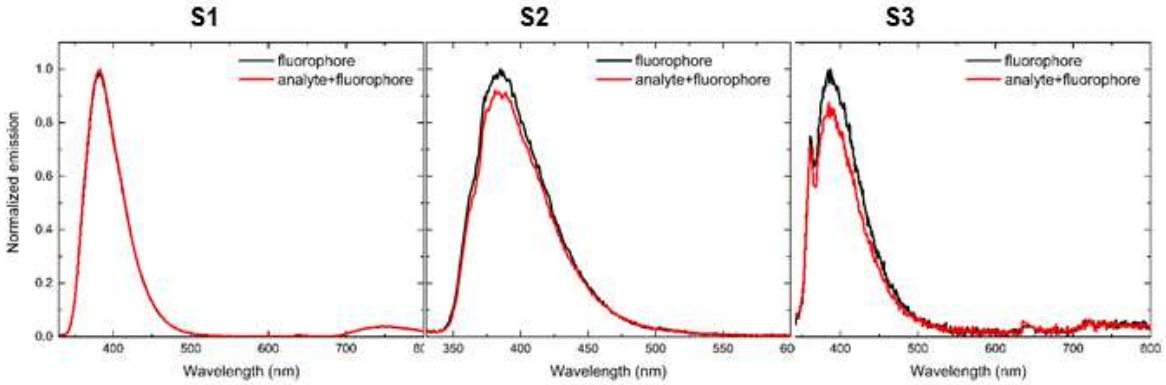
SUMMARY FIGURES FOR HPLC ANALYSIS OF COMPOUNDS S2 AND S3



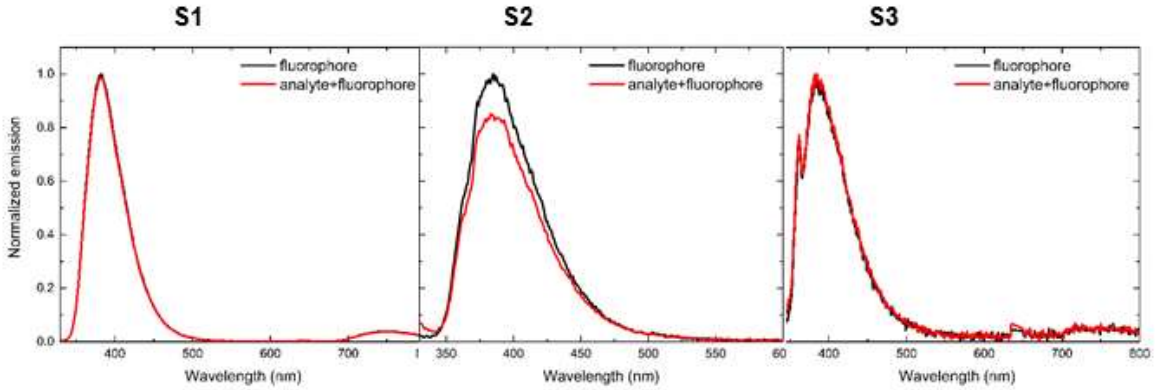


SUMMARY FIGURES FOR FLUORESCENCE MODULATION

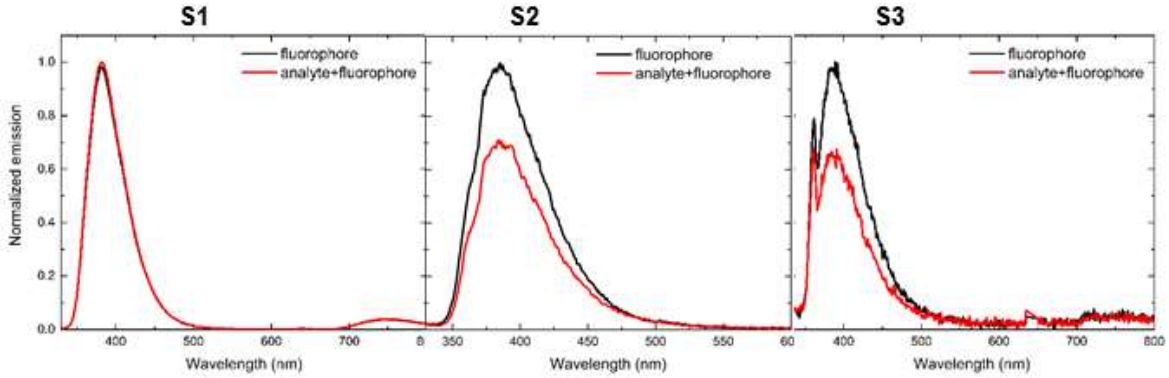
o-Cresol



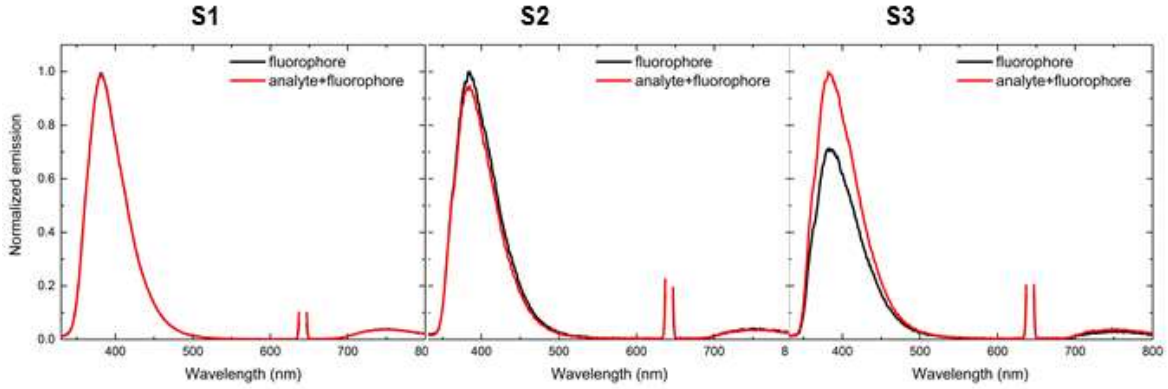
m-Cresol



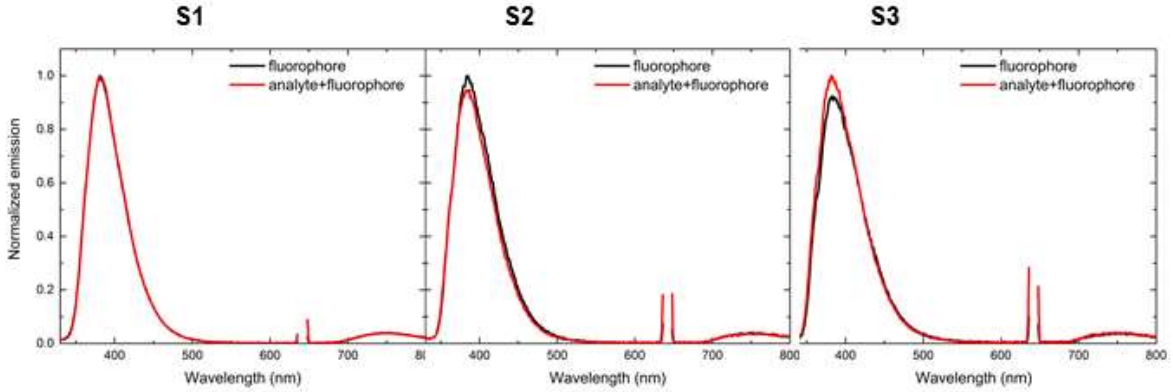
p-Cresol



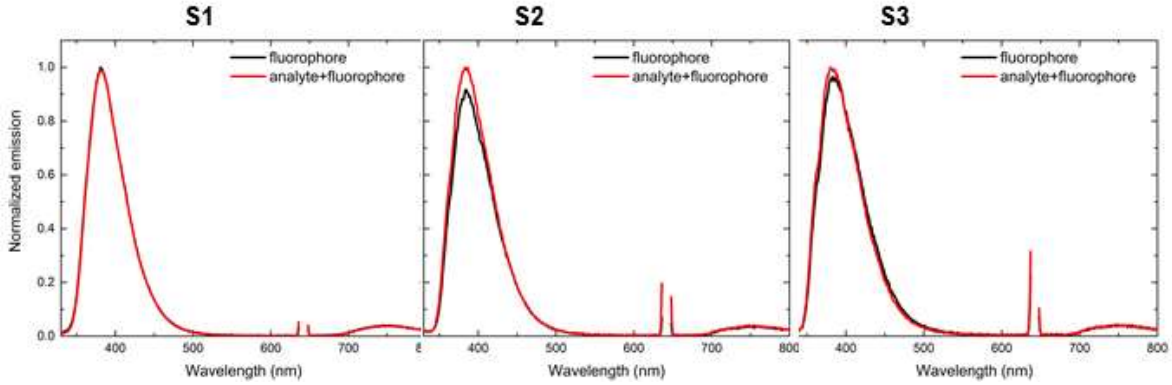
DDD



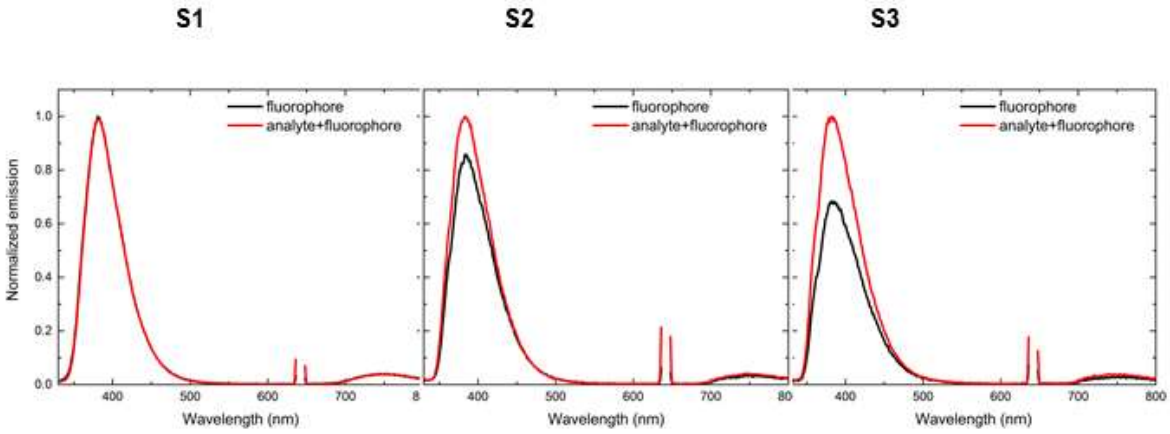
DDE



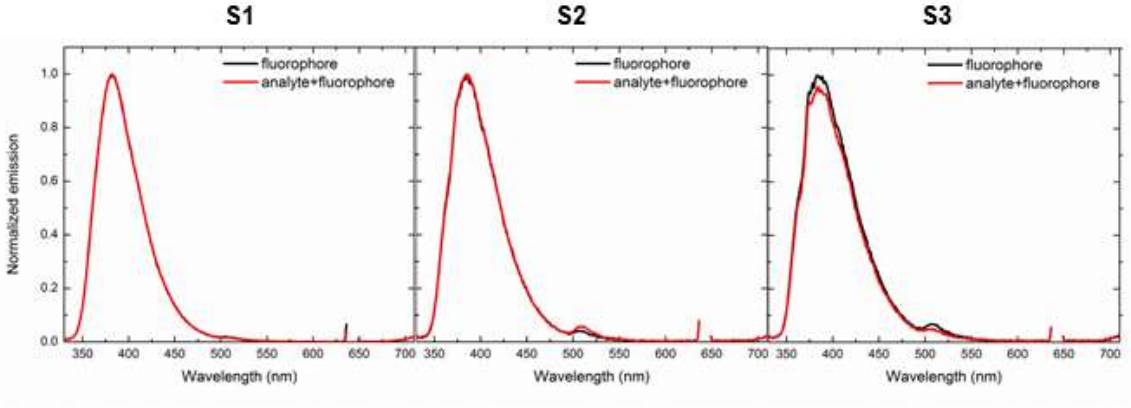
o,p-DDT



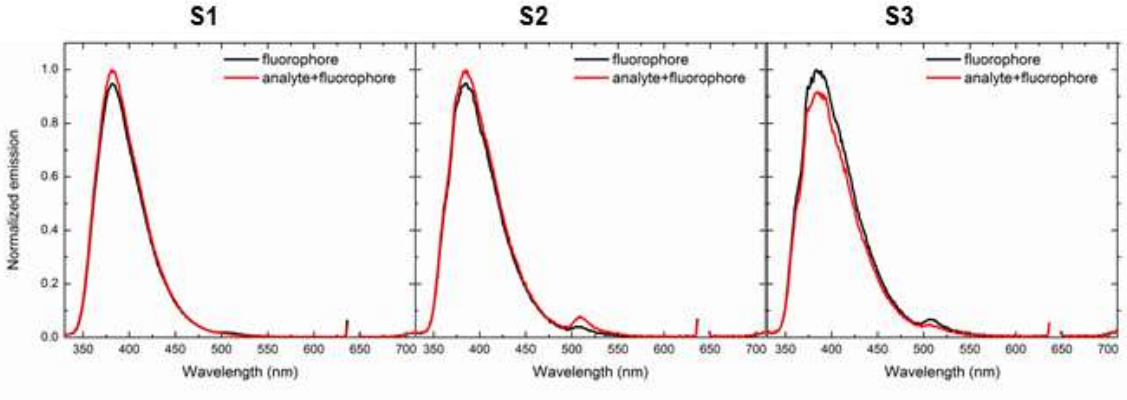
p,p-DDT



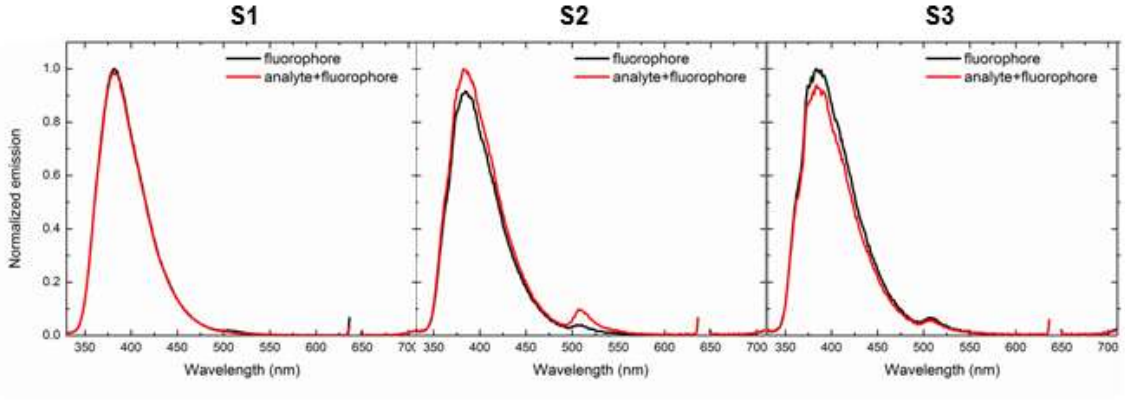
n-Hexanes



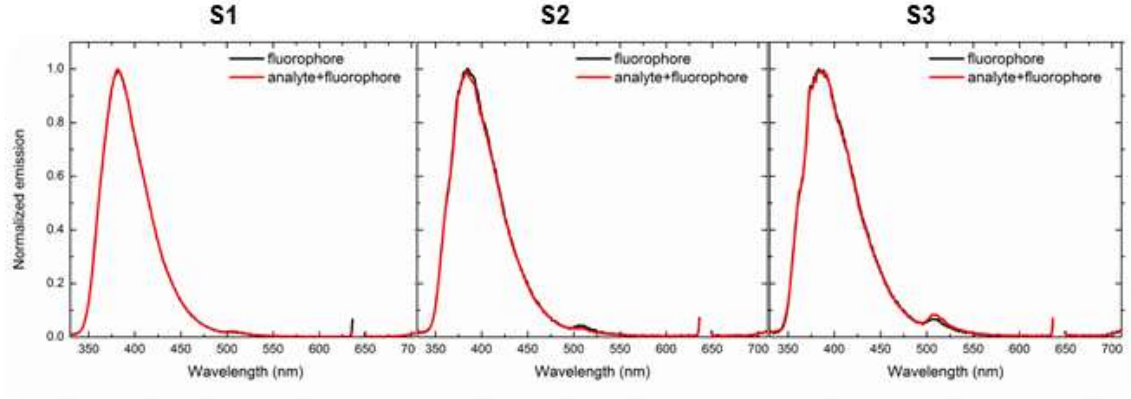
2-Methylpentane



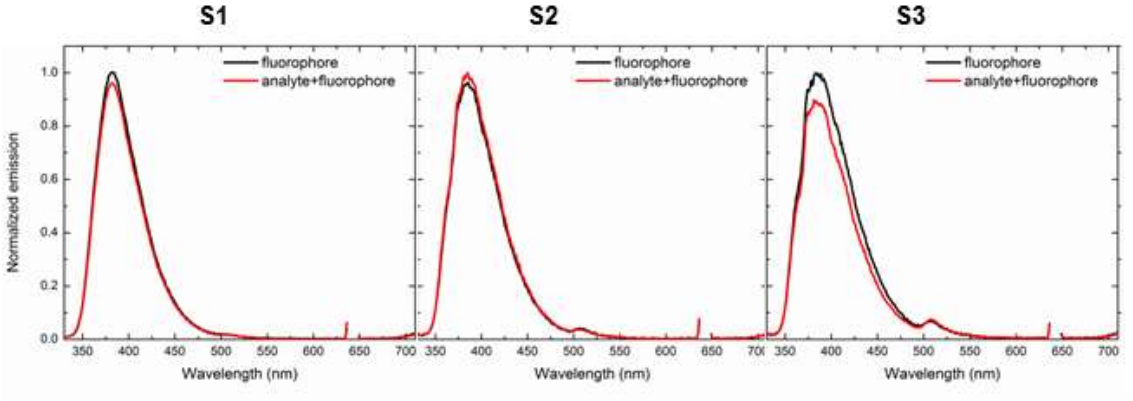
3-Methylpentane



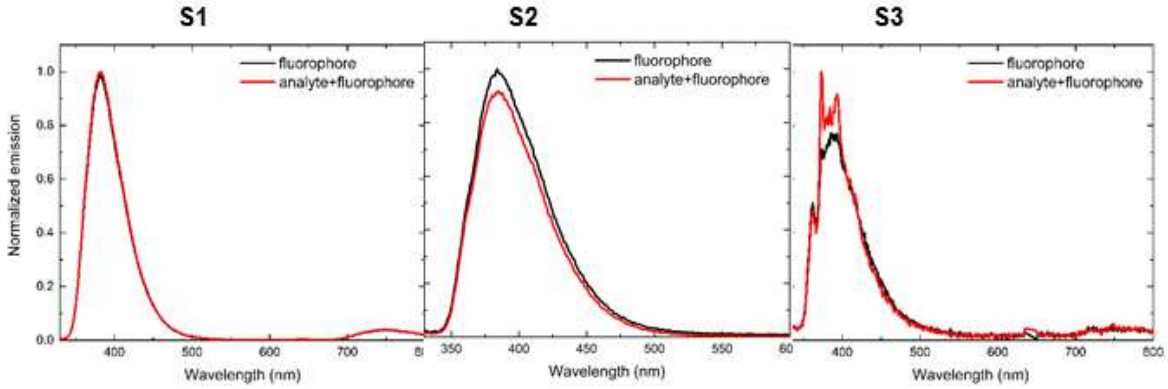
2,3-Dimethylbutane



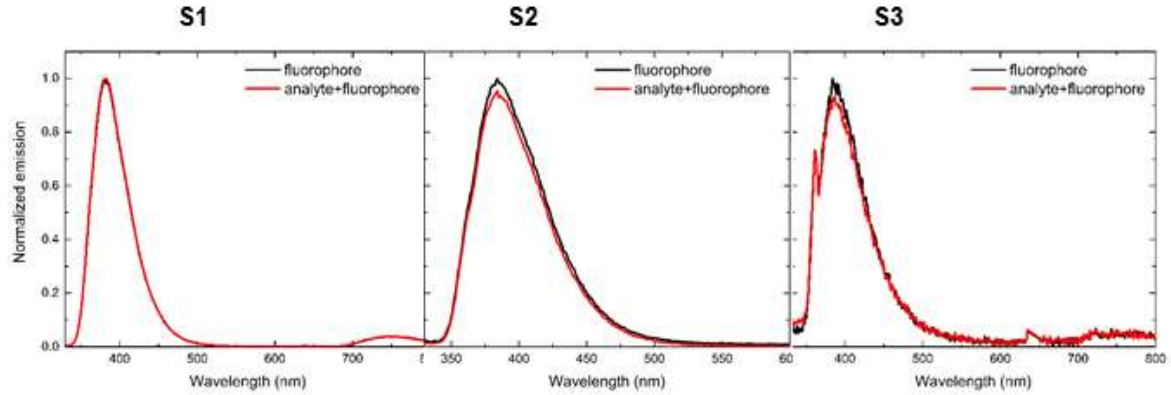
1-Methylcyclopentane



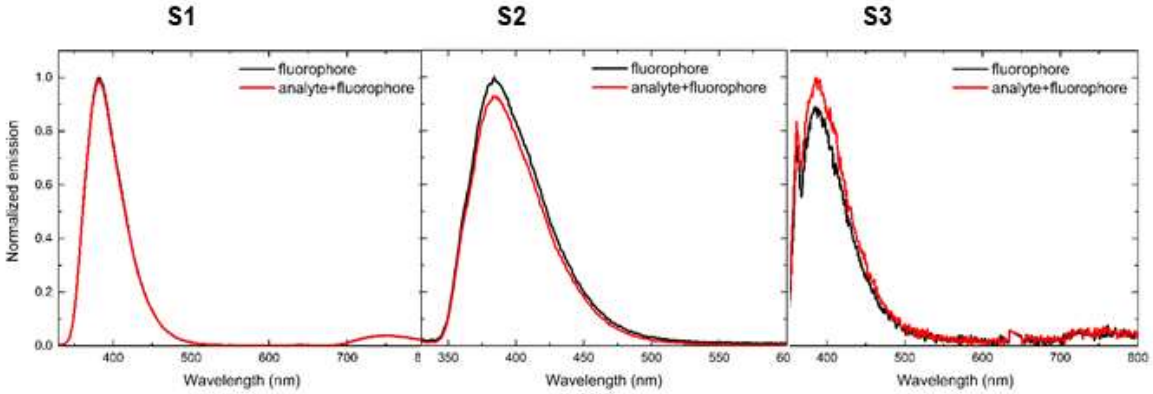
1-Methylcyclohexanol



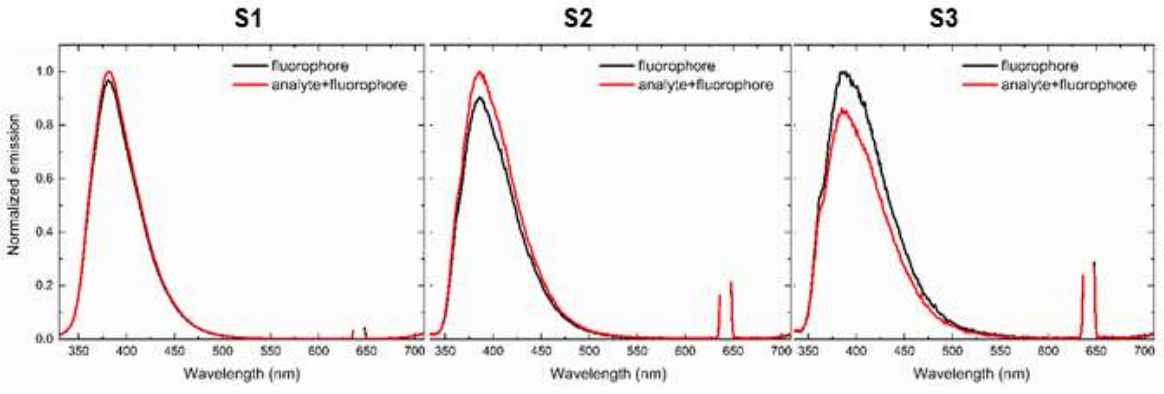
cis-2-Methylcyclohexanol



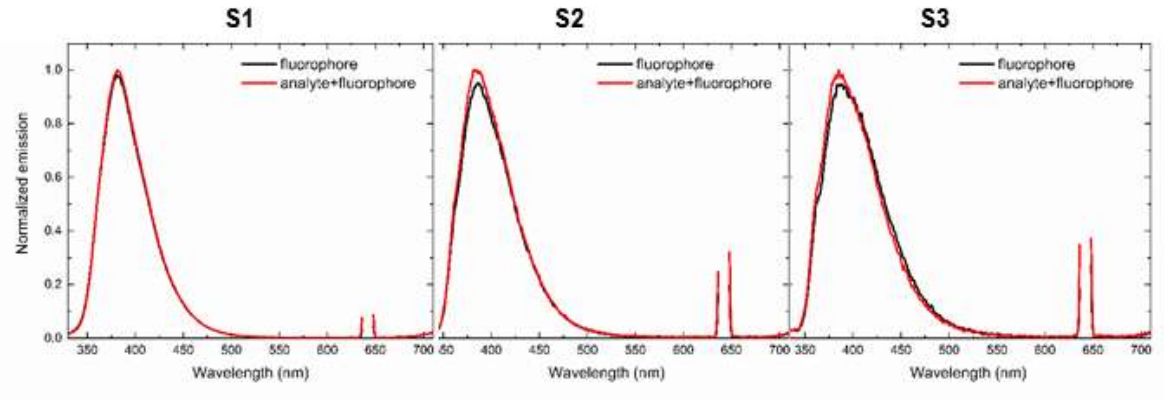
trans-2-Methylcyclohexanol



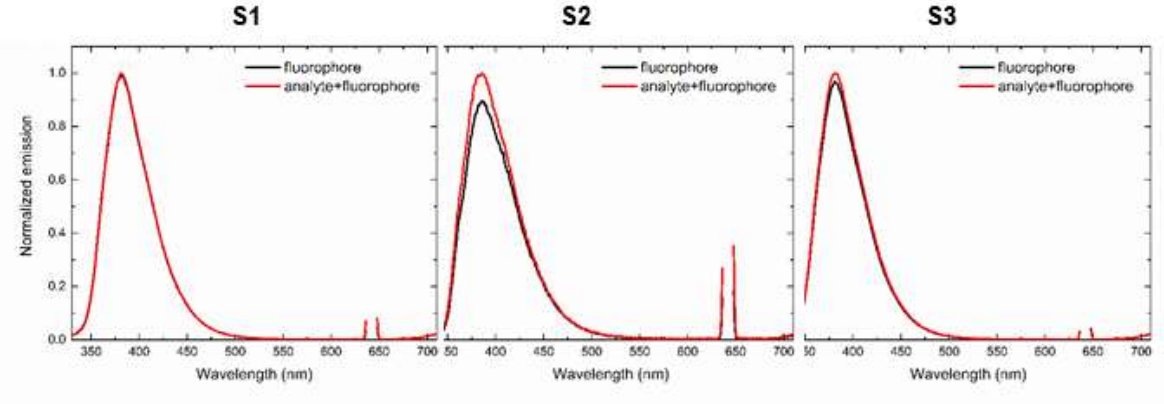
PCB3



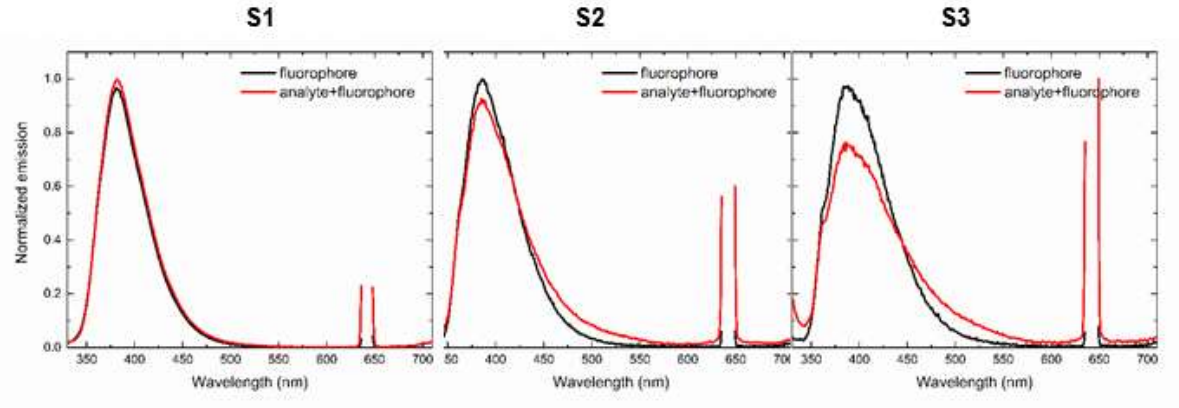
PCB29



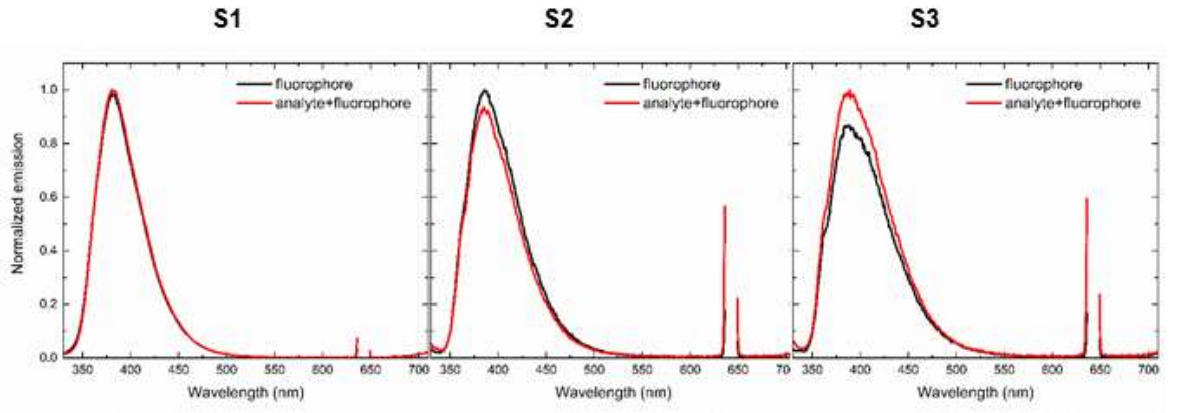
PCB52



PCB77

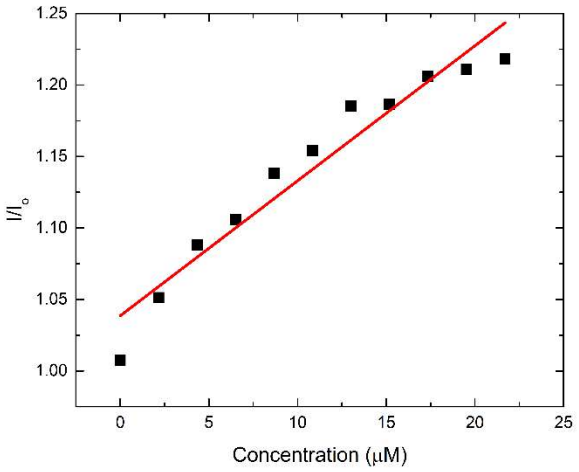


PCB209

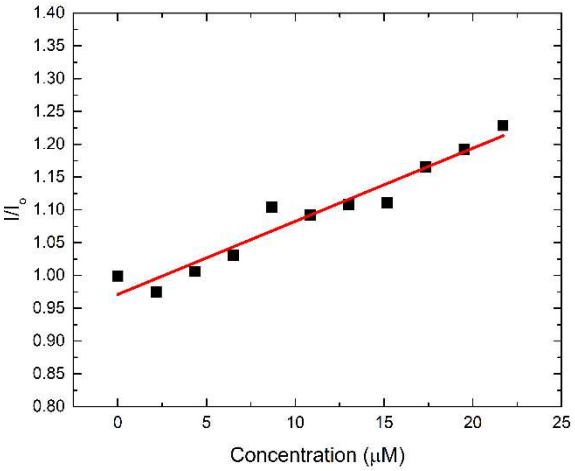


SUMMARY FIGURES FOR LIMIT OF DETECTION EXPERIMENTS

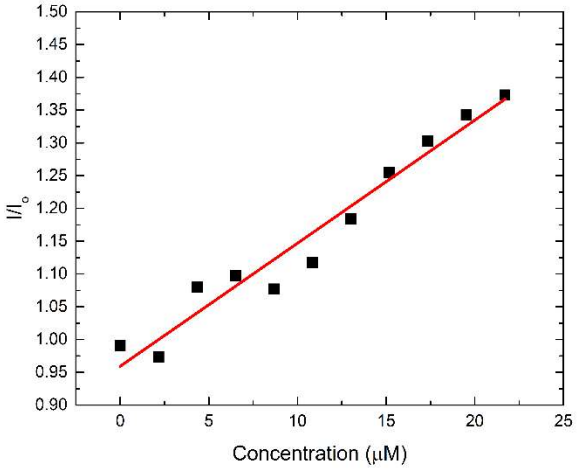
p,p-DDT – **S1**



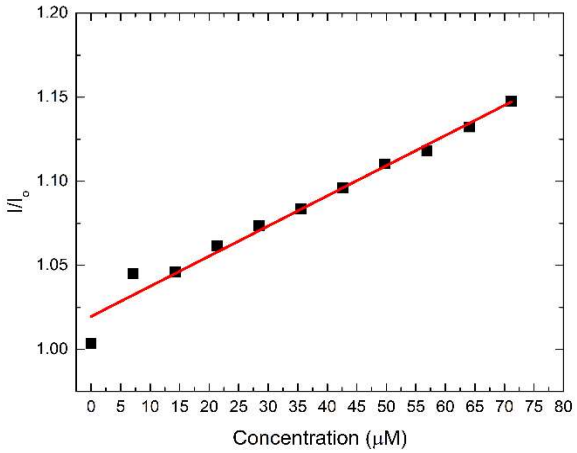
p,p-DDT – **S2**



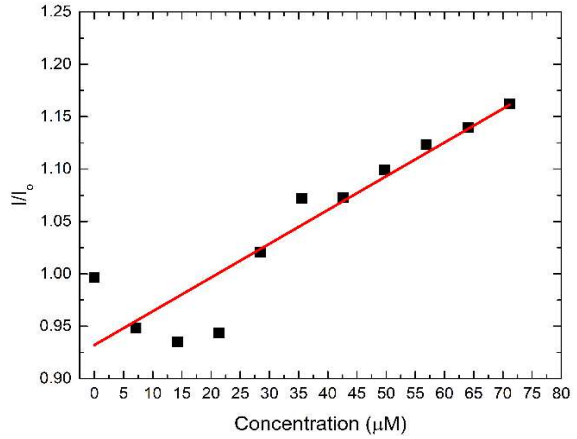
p,p-DDT – **S3**



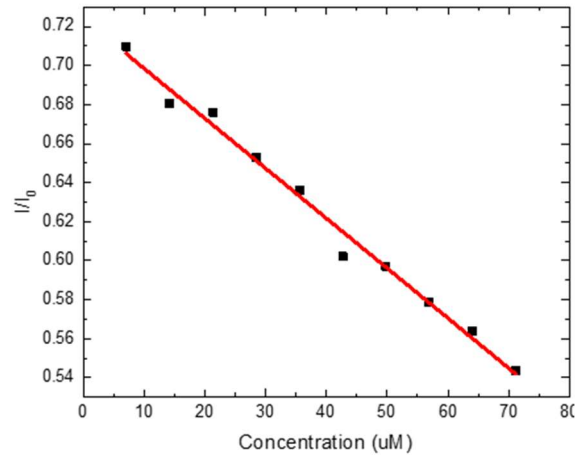
o-Cresol – **S1**



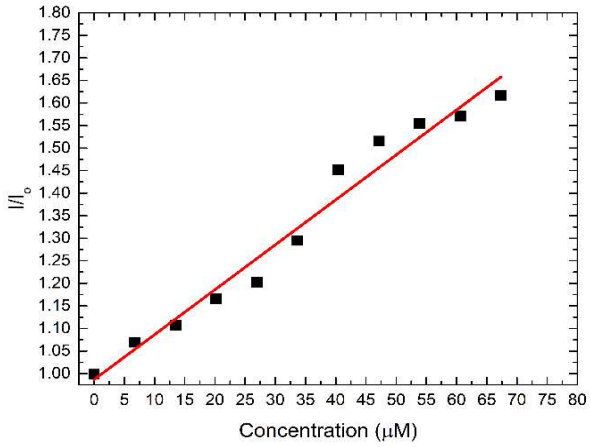
Benzyl alcohol – **S2**



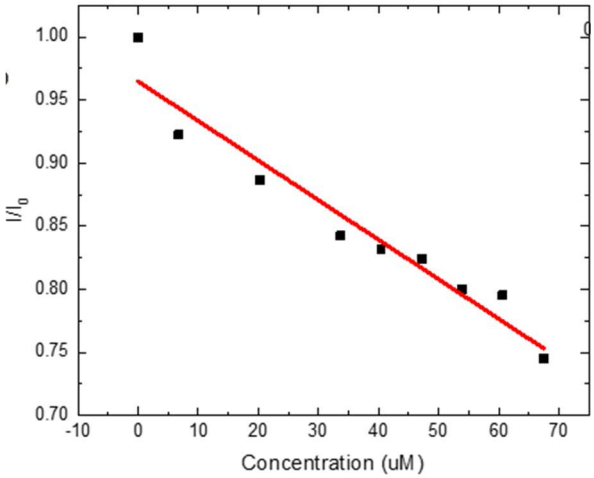
o-Cresol – **S3**



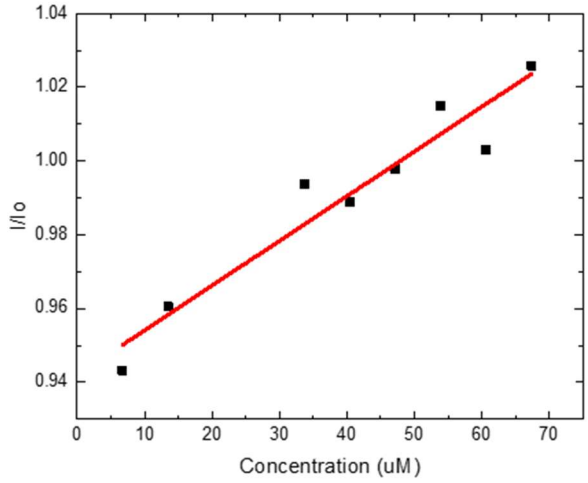
Cyclohexylmethanol – **S1**



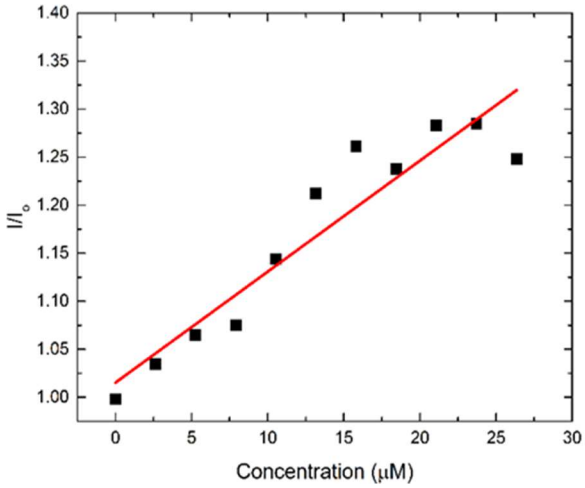
Cyclohexylmethanol – **S2**



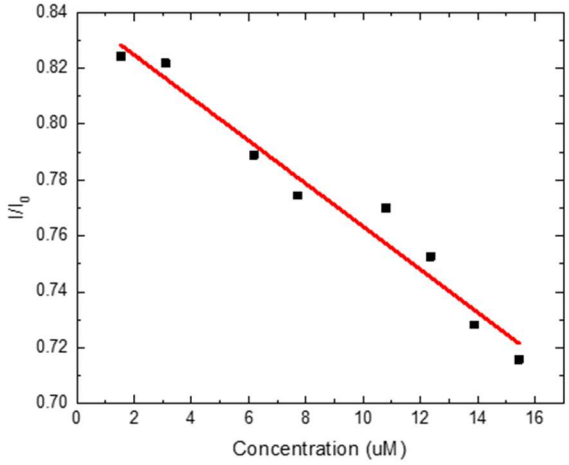
1-Methylcyclohexanol – **S3**



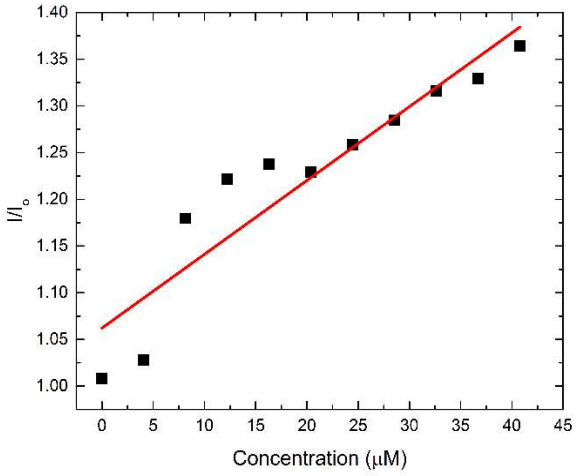
PCB77 – **S1**



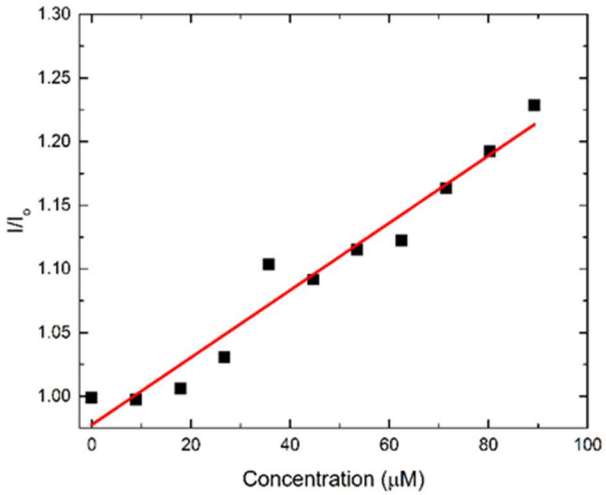
PCB209 – **S2**



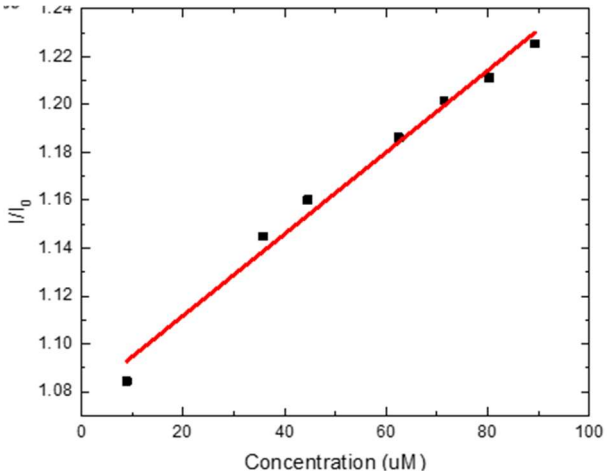
PCB209 – **S3**



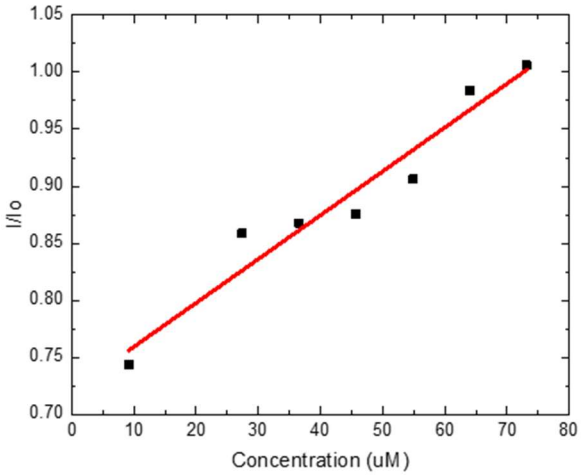
2-Methylpentane – **S1**



3-Methylpentane – **S2**

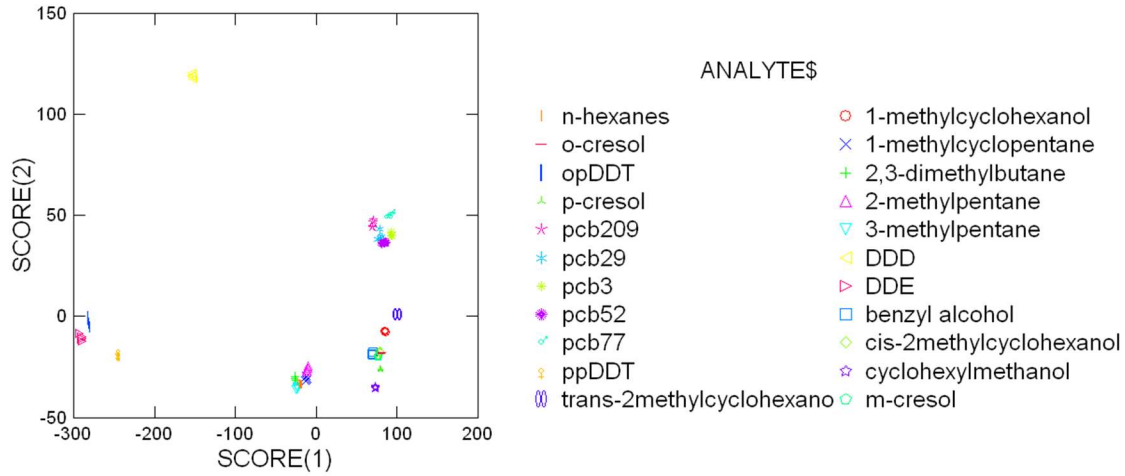


1-Methylcyclopentane – **S3**

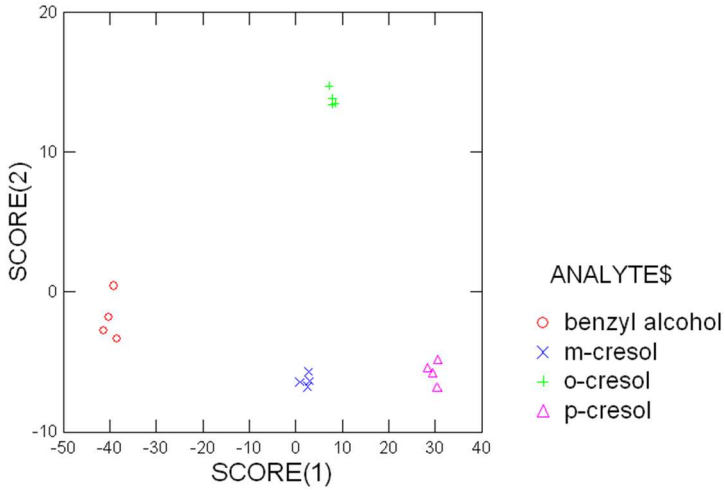


SUMMARY FIGURES FOR ARRAY GENERATION EXPERIMENTS

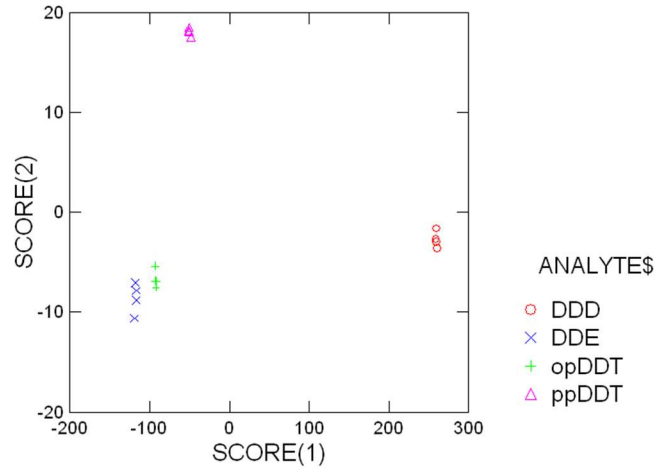
All Analytes



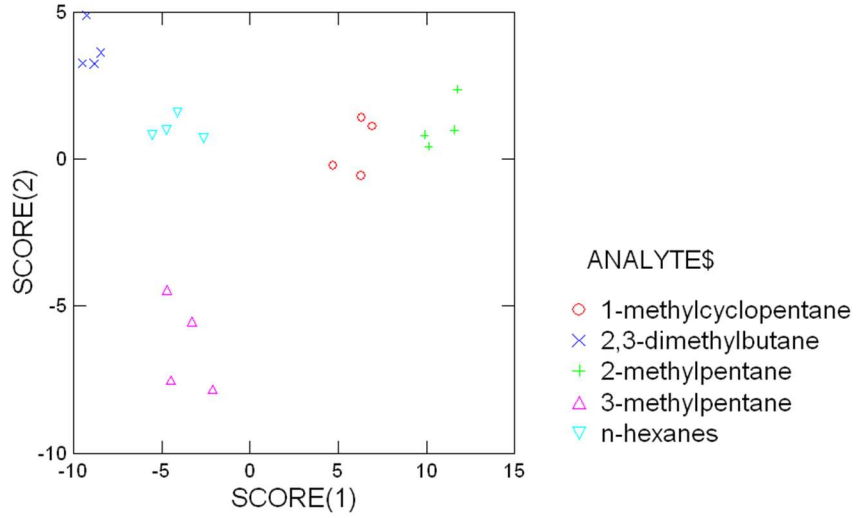
Aromatics



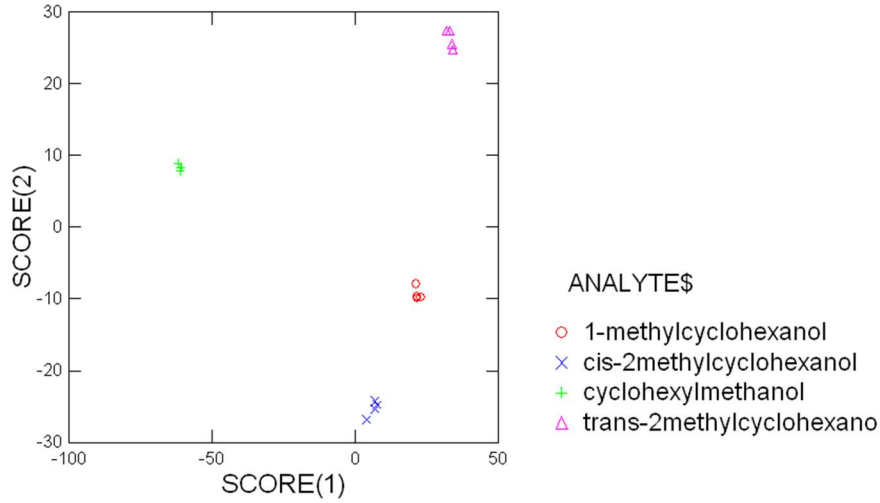
Pesticides



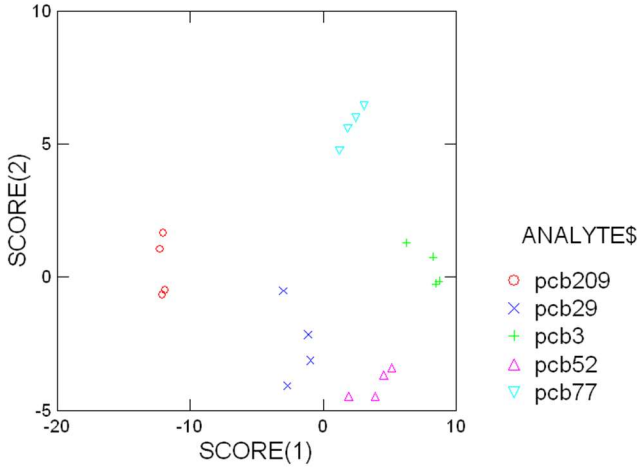
Alkanes



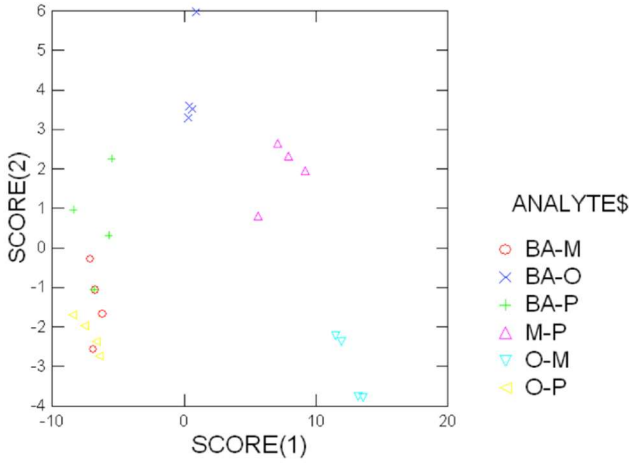
Alcohols



PCBs



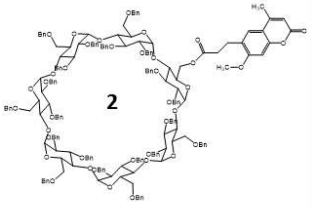
1:1 binary mixtures of analytes 5-8



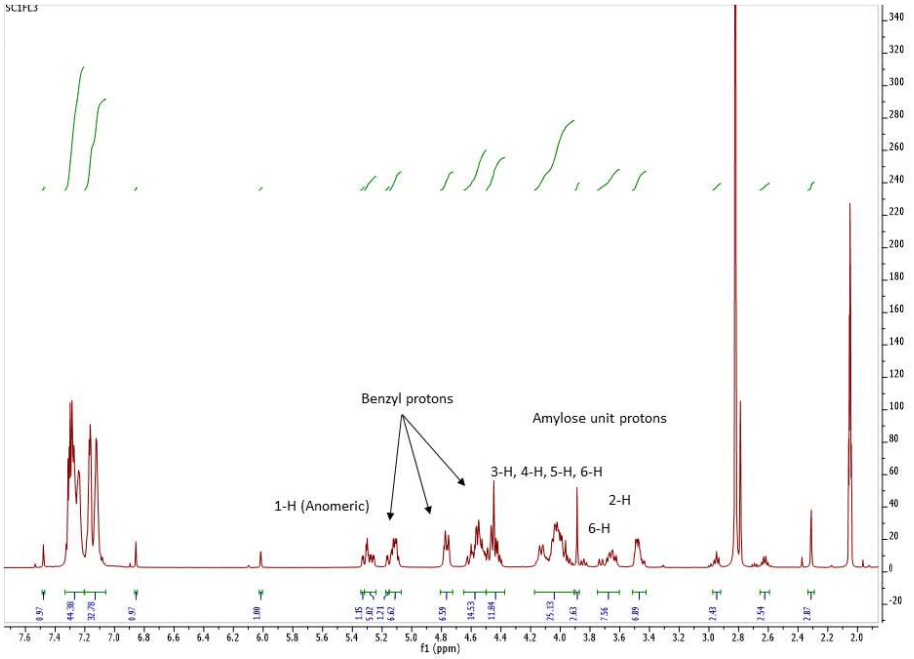
NMR SPECTRA OF ALL NEW COMPOUNDS

Compound **2**

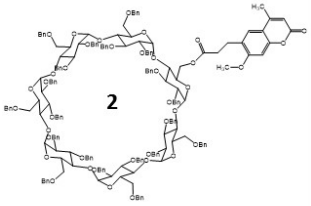
^{1}H NMR



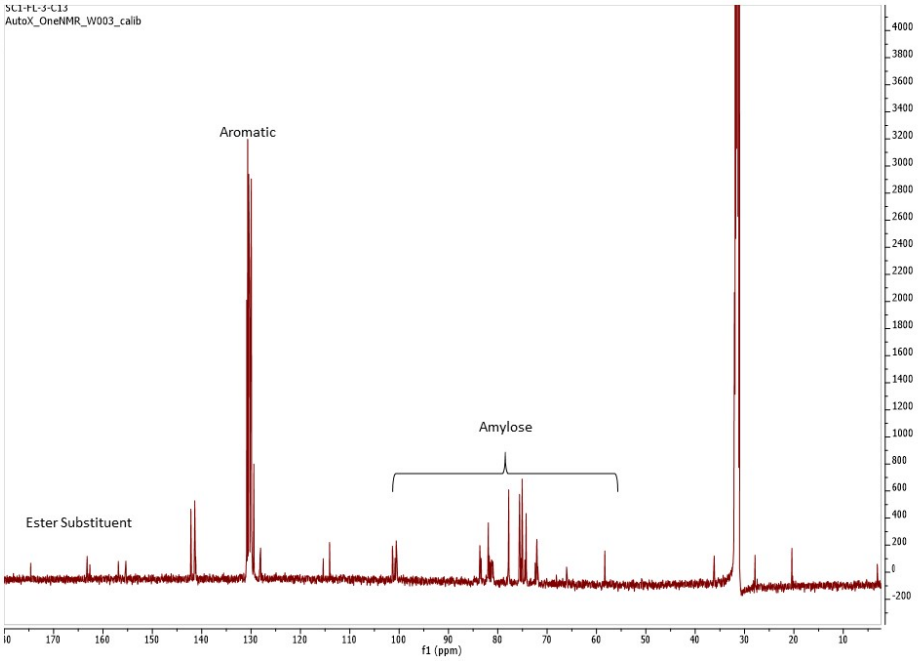
^{1}H – NMR Spectrum
(500MHz)



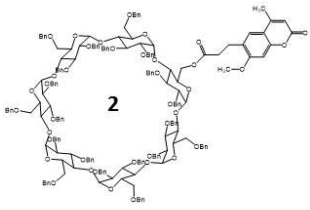
^{13}C NMR



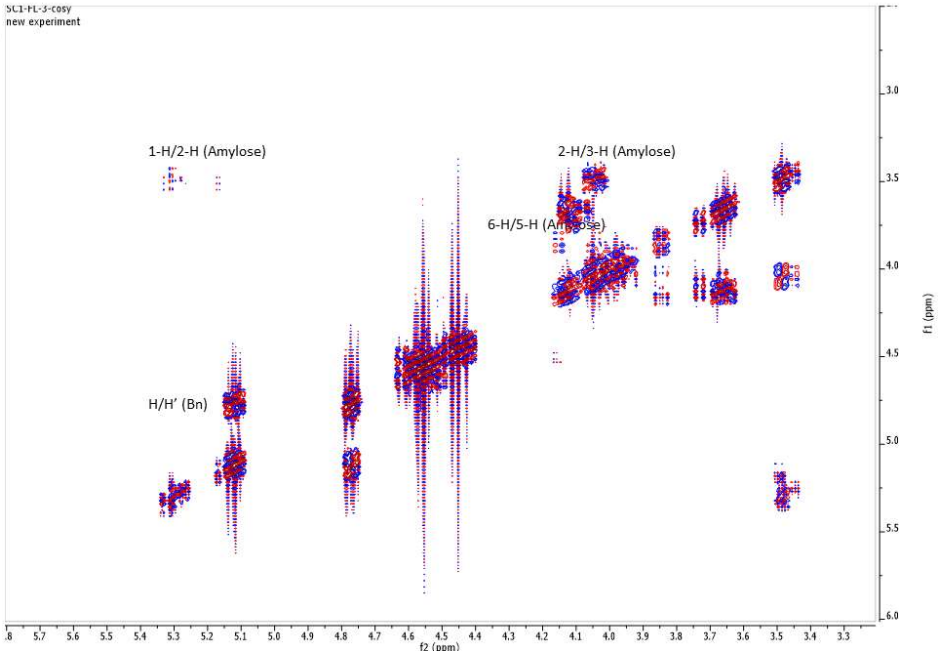
^{13}C – NMR Spectrum
(500MHz)



COSY NMR

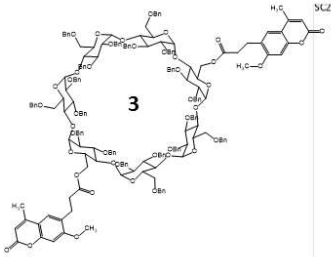


$^{1}H/^{1}H$ COSY – NMR Spectrum (500MHz)

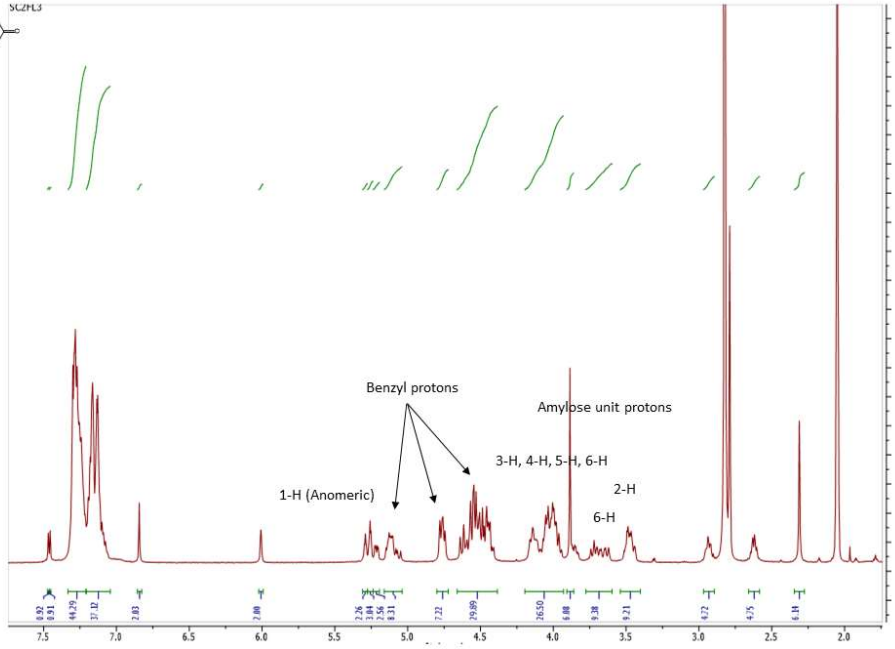


Compound **3**

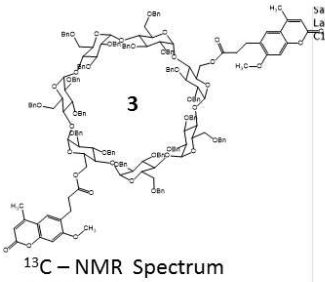
^{1}H NMR



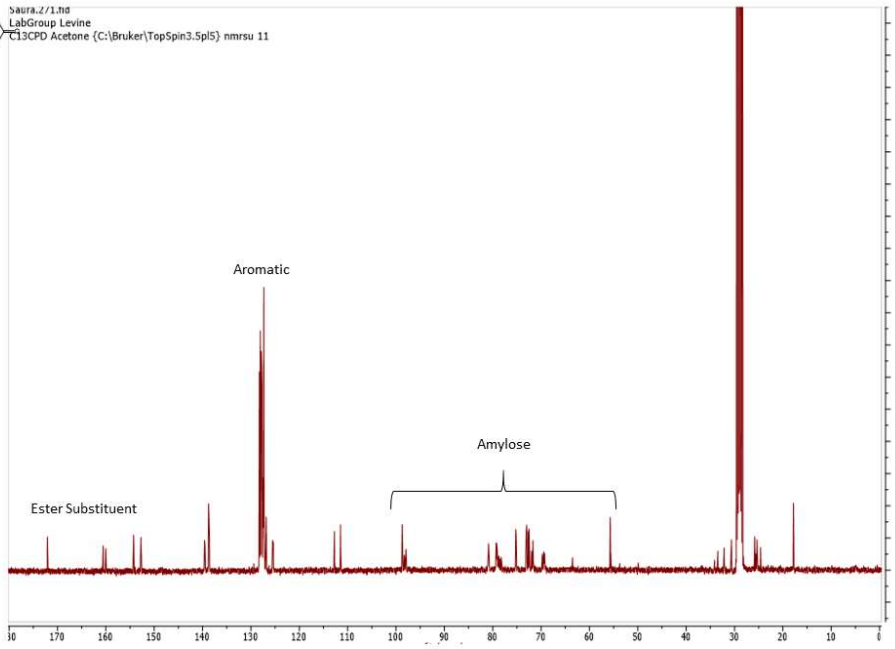
^{1}H – NMR Spectrum (500MHz)



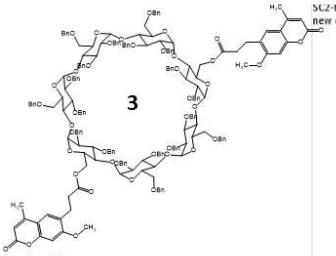
^{13}C NMR



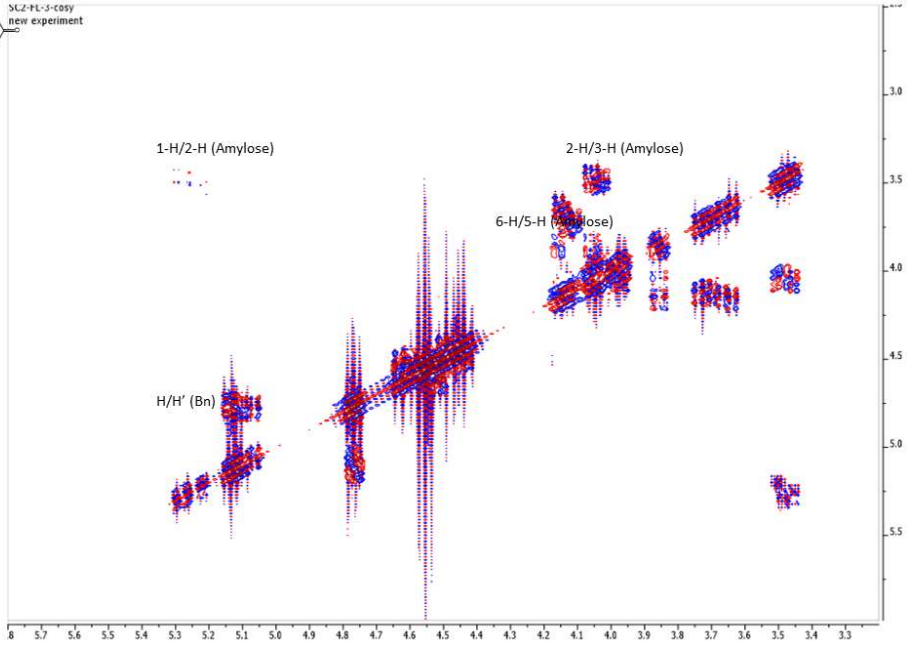
^{13}C – NMR Spectrum (500MHz)



COSY NMR



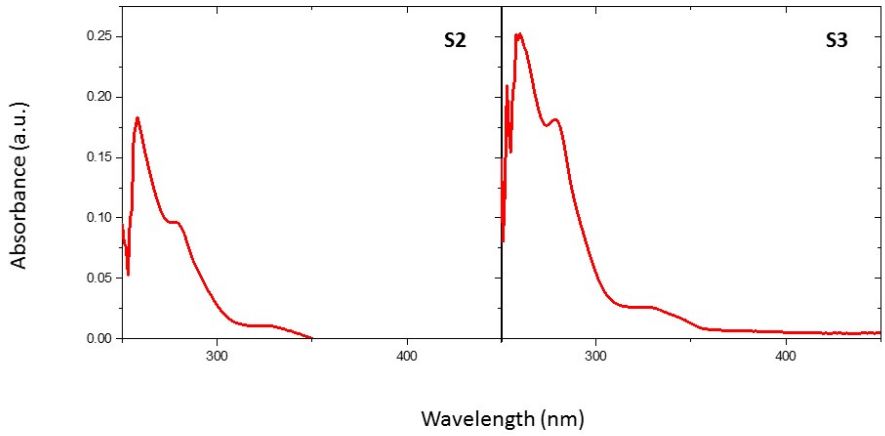
^{1}H/^{1}H COSY – NMR Spectrum (500MHz)



SPECTROSCOPIC INVESTIGATIONS OF SENSORS S1-S3

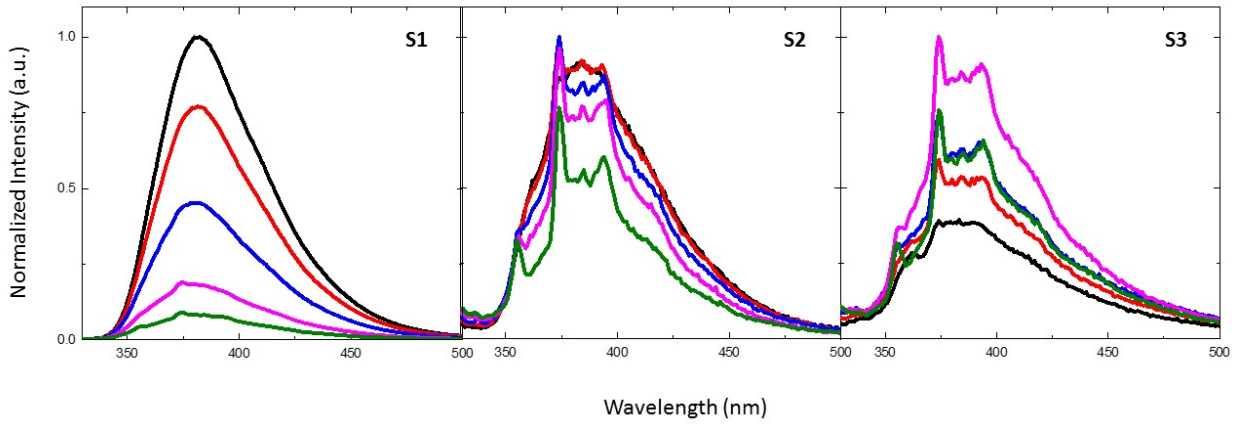
ABSORPTION SPECTRA

UV-Visible Absorption Spectra of **S2** and **S3** (1μM) in DMSO measured at room temperature:



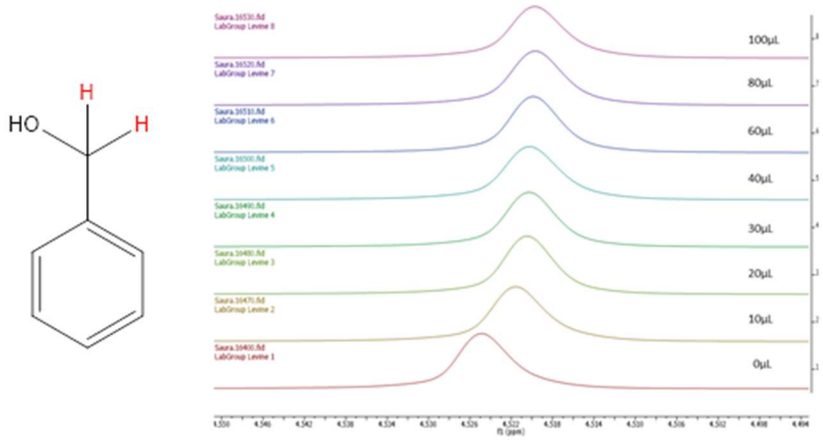
VARIATION OF FLUORESCENCE EMISSION OF SENSORS IN H_2O/DMSO MIXTURES

Fluorescence emission spectra of **S1**, **S2** and **S3** (at 1 μM concentration) in 80:20 (H_2O: DMSO) (black trace), 60:40 (H_2O: DMSO) (red trace), 40:60 (H_2O: DMSO) (blue trace), 20:80 (H_2O: DMSO) (purple trace), 0:100 (H_2O:DMSO) (green trace). (λ_{ex} = 320 nm). All spectra were recorded at room temperature.



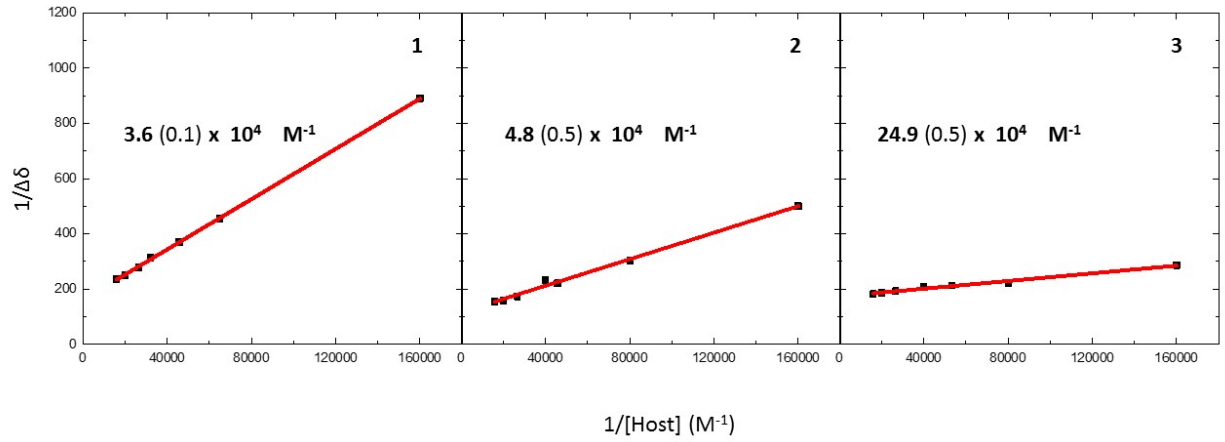
BENESI-HILDEBRAND PLOTS FOR NMR TITRATION

Analyte **5** (0.2 M in 0.4 mL D_2O) was titrated against 0 µL, 10 µL, 20 µL, 25 µL, 30 µL, 35 µL, 40 µL, 50 µL, 60 µL, 80 µL and 100 µL of the host (1 mg/mL dissolved in d_6-DMSO) in a clean dry NMR tube. The volume was adjusted to 0.5 mL final volume with the addition of d_6-DMSO. The ^{1}H-NMR spectra of the samples were recorded in 300 MHz Bruker AVANCE NMR Spectrometer at room temperature. The chemical shift of benzylic protons (highlighted in red in the figure below) were tracked, and the data was used to solve the Benesi-Hildebrand equation, below.



Benesi-Hildebrand Equation:

$$1/\Delta\delta = (1/ K_a \Delta\delta_{max})1/[H] + (1/\Delta\delta_{max}) \quad \text{(Eq. S3)}$$



Host	Equation	K_a (M^{-1})	$\Delta\delta_{max}$ (ppm)
1	y = 0.0045x + 162.97	3.6(0.1) x 10^4	0.0061
2	y = 0.0024x + 116.62	4.8(0.5) x 10^4	0.0085
3	y = 0.0007x + 173.27	24.9(0.5) x 10^4	0.0057

Benesi-Hildebrand plots for association constant calculations of analyte **5** with compounds **1**, **2** and **3** in 80:20 water-DMSO at room temperature. (H is the host; K_a is association constant; $\Delta\delta_{max}$ is maximum peak shift at infinite host concentration [H] = ∞; Δδ is the peak shift at a given host concentration. Values in parentheses indicate to the error in the K_a values from linear fit of the data points.)