Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary Information

Amine-rich Carbon Nanodots as a Fluorescence Probe for Methamphetamine Precursors

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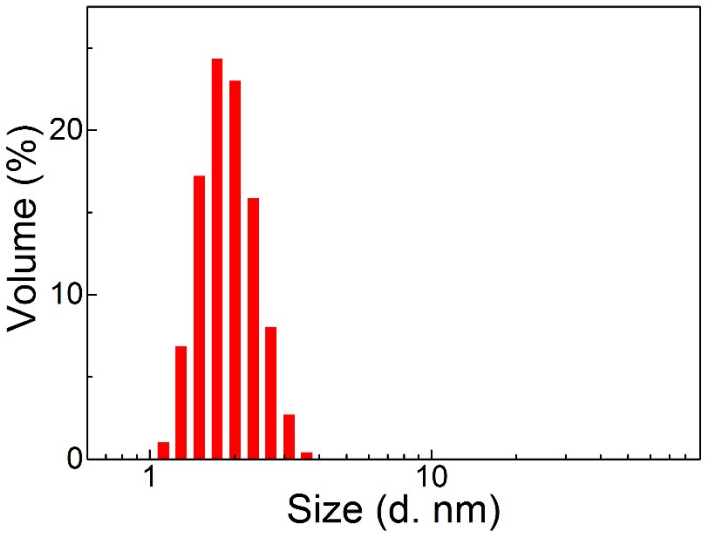

Fig. S1. Hydrodynamic size of A-CDs measured by DLS

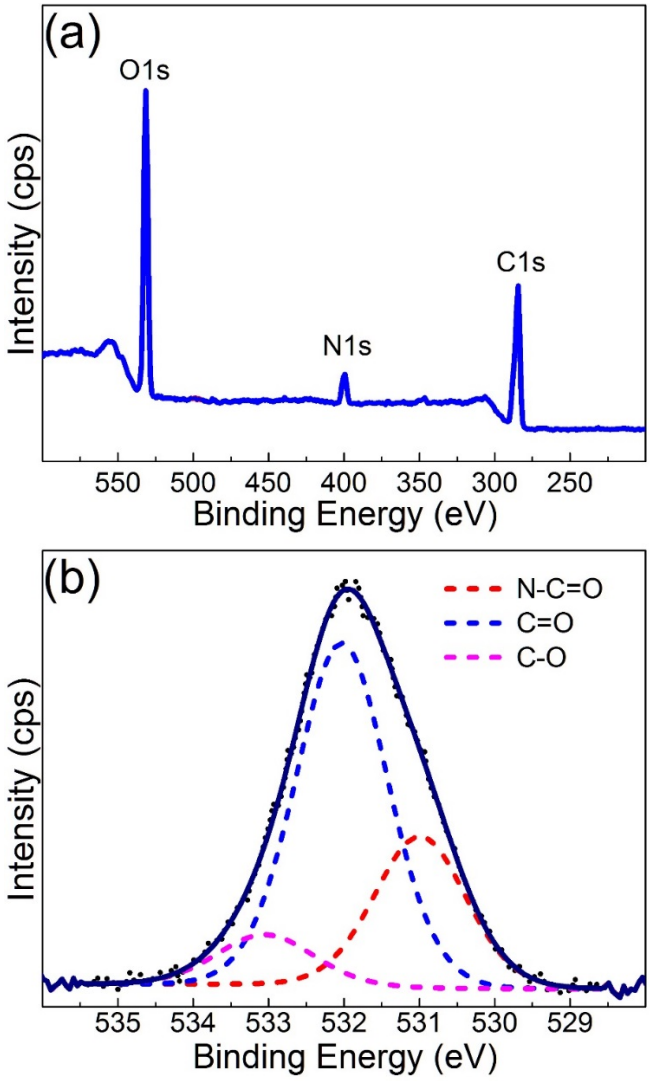

Fig. S2. XPS (a) survey and (b) O1s spectra of A-CDs

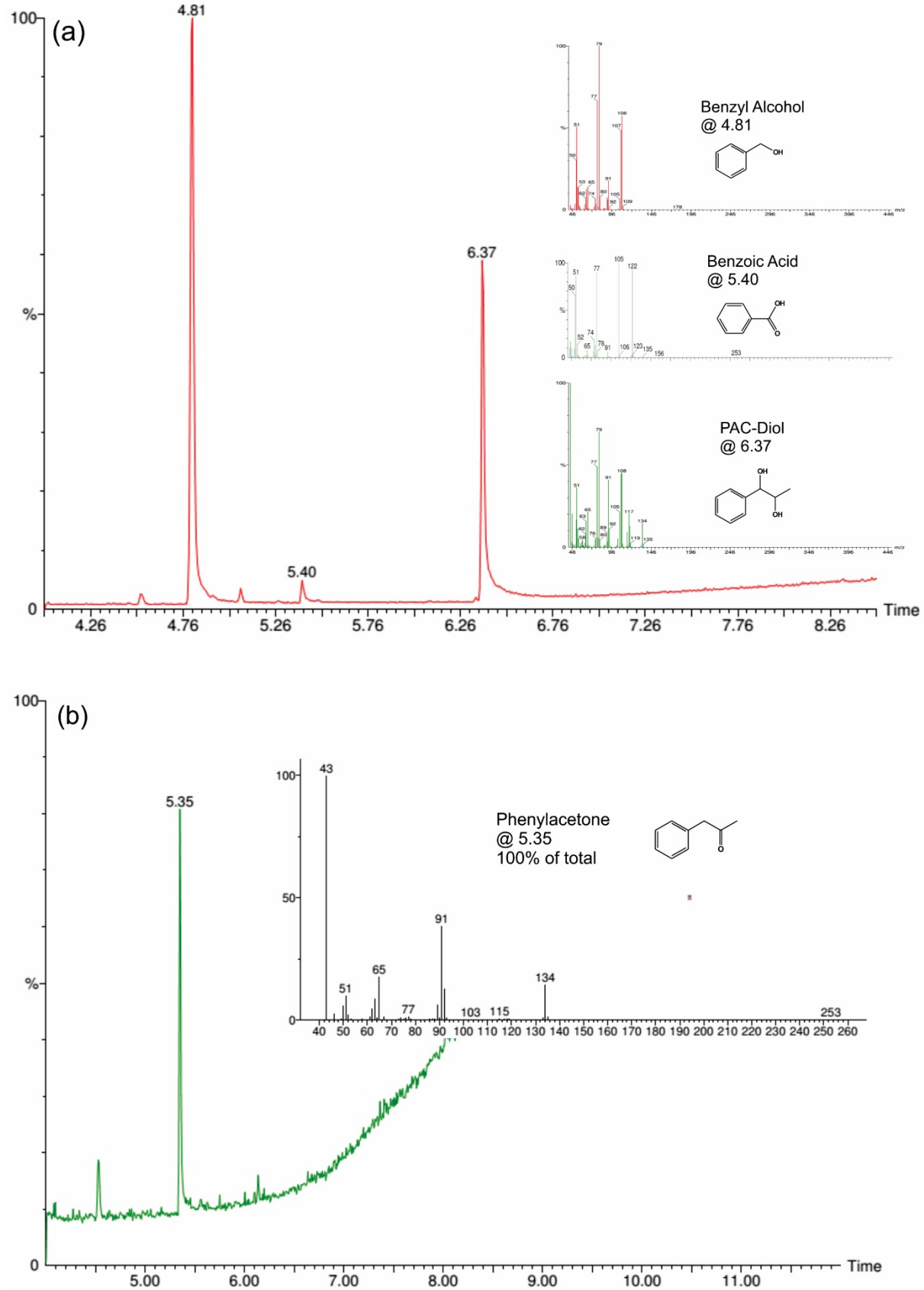

Fig. S3. GC-MS of (a) Phenylpropan-1,2-diol (PAC-Diol) and (b) Phenylpropan-2-one (Phenylacetone, P2P)

Table S1. Zeta potential of A-CDs at different pHs

pH	PL Intensity (a.u.)	Fitting parameters of PL decay (Intensity contribution, %)				Zeta potential, (ζ , mV)
		τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	χ2	
1	63	1.09 (9%)	4.48 (62%)	10.08 (29%)	1.047	2.4
3	148	1.37 (9%)	5.49 (68%)	11.95 (23%)	1.013	-14.3
5	155	1.32 (9%)	5.33 (70%)	11.84 (21%)	1.031	-20.4
7	165	1.27 (9%)	5.27 (68%)	11.22 (23%)	1.107	-22.0
9	170	1.33 (9%)	5.29 (67%)	11.15 (24%)	1.067	-32.1
11	157	1.22 (9%)	4.92 (59%)	9.98 (32%)	1.062	-45.0
13	79	1.11 (17%)	4.21 (54%)	10.48 (29%)	1.131	-36.7

The fluorescence decay curves were fitted by using a three-exponential function in Eq. S1

$$R(t) = A + B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2} + B_3 e^{-t/\tau_3} \quad \text{(S1)}$$

Where A is the background value, B_χ is normalized amplitude and τ_χ is the decay time constant of each component

Table S2. Detection limits of the analytes

Drugs	Slope, m	Intercept, b	Corr. Coeff., r	Standard deviation, σ	Detection Limit (mg mL^{-1})	
					95.4%	99.7%
PAC-Diol (pre-precursor)	5.3	3.6×10^{-2}	0.993	3.54×10^{-3}	0.001	0.002
P2P (precursor)	3.4	2.0×10^{-2}	0.996	3.28×10^{-3}	0.002	0.003

Table S3. Fluorescence lifetime and zeta potential changes by PAC-Diol and P2P

Concentration	PAC-Diol				P2P			
	FL Lifetime (ns)			ζ (mV)	FL Lifetime (ns)			ζ (mV)
	τ_1	τ_2	τ_3		τ_1	τ_2	τ_3	
0.000 mg/mL	1.34 (8%)	5.30 (74%)	11.18 (18 %)	-23.8	1.12 (10%)	4.64 (59%)	12.66 (31%)	-20.5
0.005 mg/mL	1.21 (7%)	4.98 (68%)	10.07 (25%)	-16.4	1.09 (9%)	4.56 (60%)	12.64 (31%)	-22.1
0.025 mg/mL	0.94 (8%)	4.68 (62%)	9.71 (30%)	-18.4	0.89 (9%)	4.31 (57%)	12.34 (34%)	-44.1
0.050 mg/mL	0.67 (9%)	4.37 (61%)	9.63 (30%)	-22.7	0.77 (11%)	4.35 (57%)	12.82 (32%)	-46.1
0.075 mg/mL	0.65 (16%)	4.17 (53%)	9.35 (31%)	-28.3	0.62 (11%)	3.95 (52%)	12.01 (37%)	-47.8
0.100 mg/mL	0.58 (19%)	4.18 (53%)	9.80 (28%)	-30.5	0.60 (17%)	3.98 (48%)	11.57 (35%)	-48.2

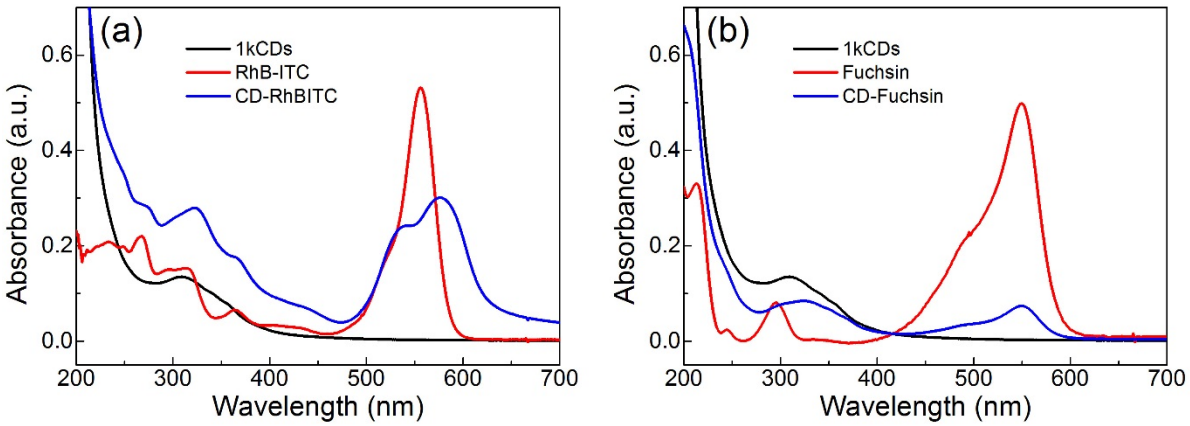

Fig. S4. UV-Vis absorption of (a) rhodamine B isothiocynate and A-CD conjugate and (b) fuchsin and A-CD conjugate

A-CDs were conjugated with –NH2 reactive dye, Rhodamine B isothiocynate (RhB-ITC) and –COOH reactive dye, fuchsin-basic. 1mL of the each dye solution prepared at 1M was introduced to 10mL A-CDs followed by 1 hr reaction at room temperature. The mixture was then purified by dialysis in order to remove excessive dye. The amount of dye linked by A-CDs was calculated by using Beer-Lambert Law and extinction coefficient (ε) of the dyes[1,2]. The Beer-Lambert Law is expressed in terms of extinction coefficient (ε), concentration of samples (C) and light path length (l), Therefore molar concentration of the dye linked by A-CDs can by derived by Eq. (S2)

$$C_{Dye} = \frac{Abs_{Dye}}{\varepsilon_{Dye}(M \cdot cm) \cdot l(cm)} \qquad \text{(S2)}$$

Table S4. Concentration of the dye conjugated by A-CDs

Sample	Dye abs. peak, (Abs, nm)	Absorption, (a.u.)	Light path length (l, cm)	Extinction Coefficient, (ε, M·cm)	Concentration of dye linked by A-CDs (M)
RhB-ITC-CDs	555	0.254	1	106000[3]	$2.4 \cdot 10^{-6}$
Fuchsin-CDs	544	0.074	1	85000[4]	$8.7 \cdot 10^{-7}$

1. J. A. Dean and N. A. Lange, *Lange's handbook of chemistry*, McGraw-Hill, 1992.
2. W. M. Haynes, *CRC Handbook of Chemistry and Physics, 93rd Edition*, Taylor & Francis, 2012.
3. M. Beija, C. A. Afonso and J. M. Martinho, *Chem. Soc. Rev.*, 2009, 38, 2410-2433.

4. European Committee for Clinical Laboratory Standards, *Dye standards, Part II.8: New Fuchsin (CI 42520)*, *Histochem. J.*, 1992, 24, 240-242.

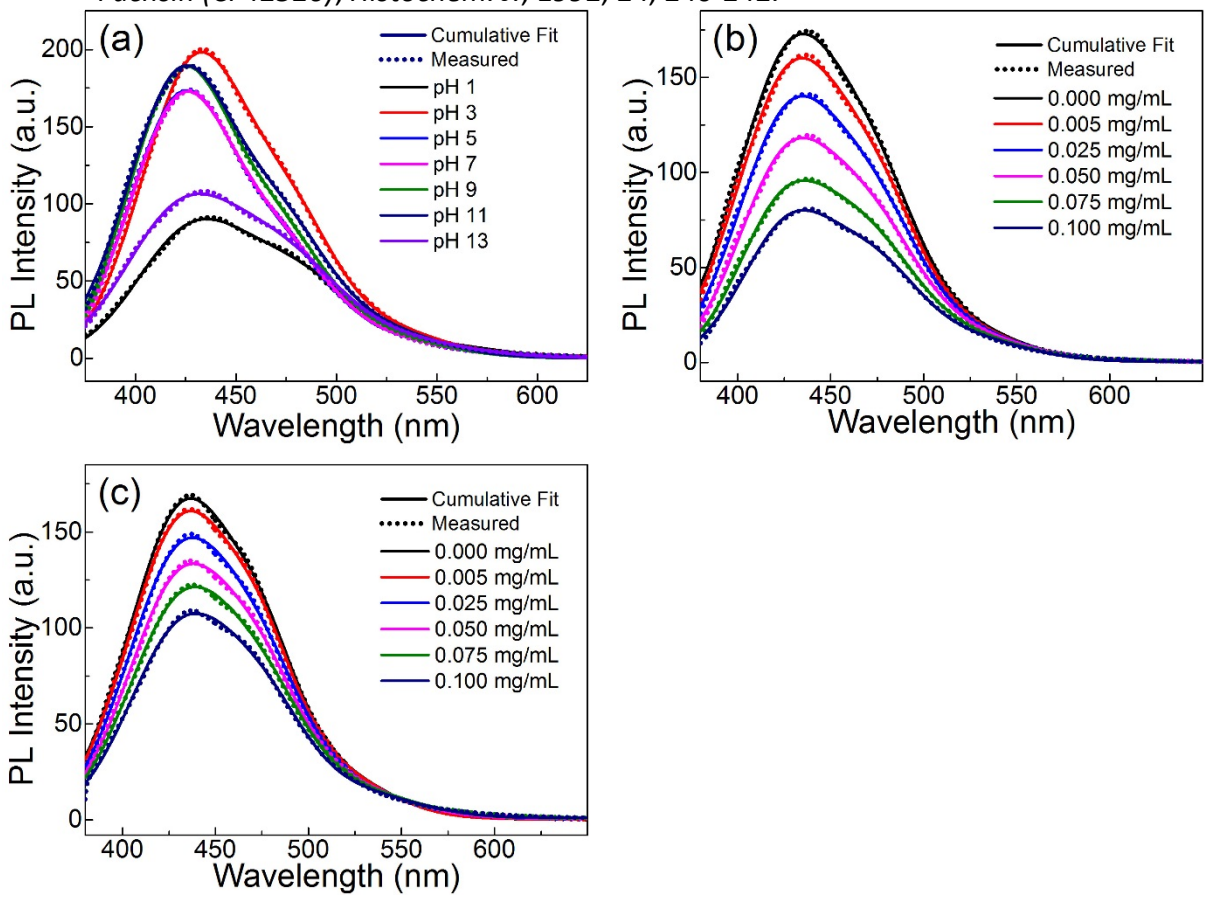

Fig. S5. Measured photoluminescence intensity and cumulative fitting spectra of (a) pH effects, (b) PAC-diol and (c) P2P samples

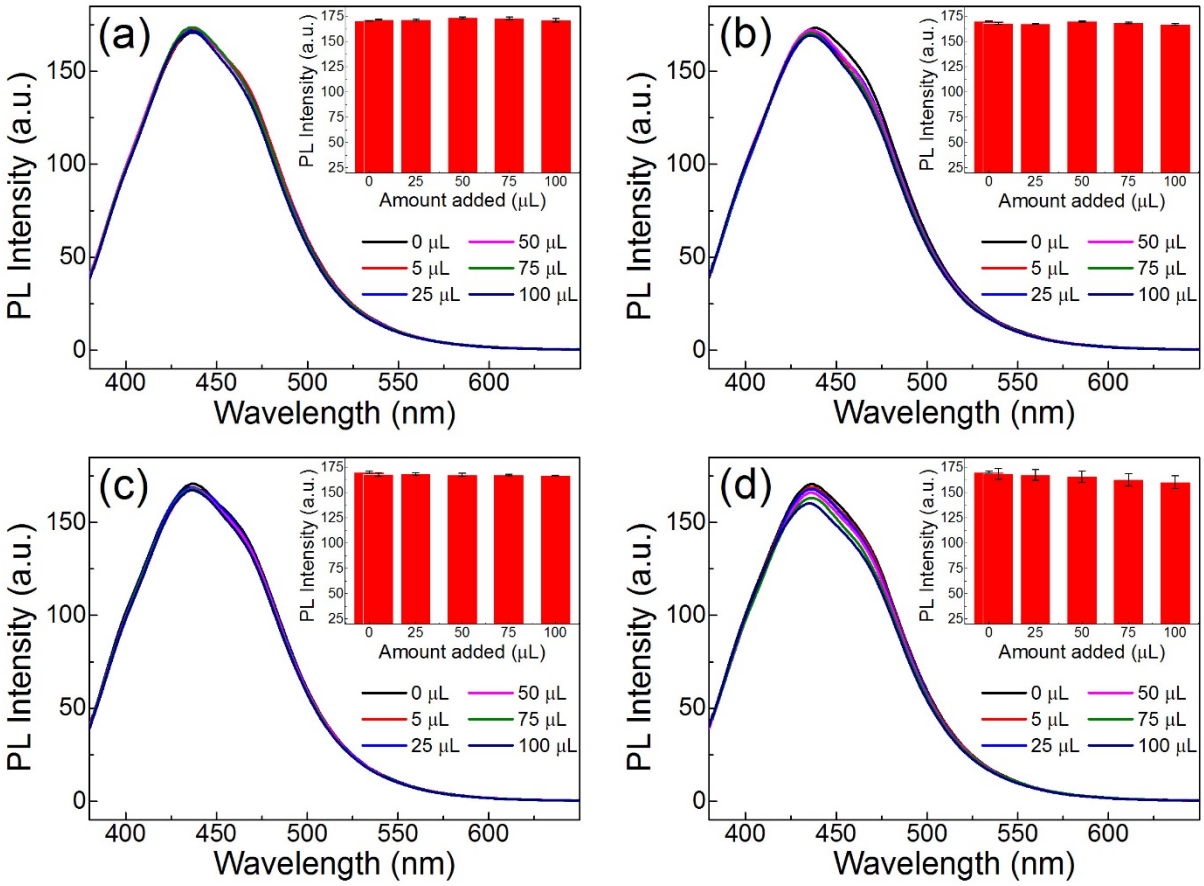

Fig. S6. Photoluminescence responses of A-CDs against (a) acetone, (b) ethanol, (c) methanol and (d) propylene glycol (1,2-propanediol)

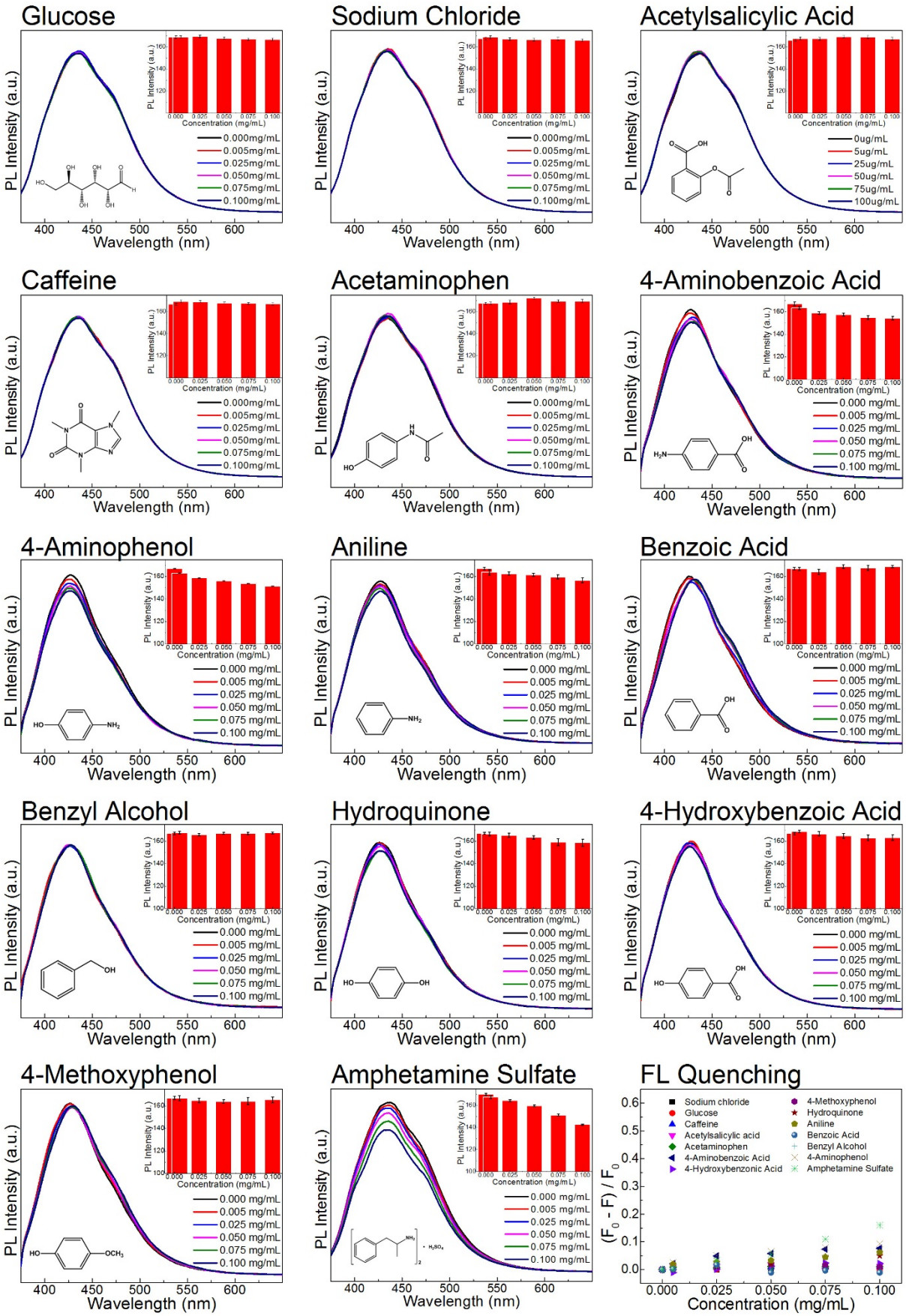

Fig. S7. Photoluminescence spectra and quenching of other molecules tested

Table S5. Percent quenched by analytes at 0.2 mg concentration in 2mL of A-CD solution

Chemicals	Concentration			Photoluminescence Int.		Percent Quenched (%)
	Mass (mg/mL)	Mol. mass (g/mol)	Mol (µmol/mL)	Initial	Final	
Phenylpropan-1,2-diol (PAC-Diol)	0.1	120.57	0.23	167.42	76.8	54
Phenylacetone (P2P)	0.1	136.340	0.27	169.01	107.77	36
Amphetamine Sulfate	0.1	368.490	0.27	170.02	142.58	16
Glucose	0.1	180.160	0.56	168.82	166.77	1
Aspirin	0.1	180.157	0.56	166.12	167.15	0
Caffeine	0.1	194.190	0.52	166.77	167.01	0
Paracetamol	0.1	151.163	0.66	167.26	169.40	0
4-Aminobenzoic acid	0.1	137.140	0.73	167.05	154.23	8
4-hydroxybenzoic acid	0.1	138.121	0.72	166.92	163.2	2
4-methoxyphenol	0.1	124.137	0.81	166.93	165.31	1
Hydroquinone	0.1	110.110	0.91	166.94	158.66	5
Aniline	0.1	93.130	1.07	167.00	156.59	6
Benzoic acid	0.1	122.120	0.82	167.02	168.88	0
Benzyl alcohol	0.1	108.140	0.93	166.98	167.32	0
4-Aminophenol	0.1	109.126	0.92	166.95	151.42	9

Note: Molar mass of PAC-Diol and P2P was derived from GC-MS data