Electronic Supplementary Material (ESI) for RSC Advances.

1,3-Bis(cyanomethoxy)calix[4]arene Capped CdSe Quantum Dots for Fluorogenic Sensing of Fluorene

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Supplementary Materials

Experimental Section

1. **Synthesis of CdSe QD**

CdSe QD was synthesized using CdO as precursor via procedure described by Yu and Peng[1]. To a three-necked flask was added 0.0127 g of CdO (0.1 mmol), 0.1140 g of stearic acid (0.4 mmol), 1.94 g of TOPO, 2.25 g of ODA and heated with stirring to 280-290^{0}C under N_2 environment. The red coloured CdO dissolved to give a colourless homogenous solution under inert condition. On the other hand, Se stock solution was prepared by adding 0.079 g of Se, 300 µL of TOP and 1.876 g of ODE at 150^{0}C. The black suspended selenium dissolved to give colourless homogenous solution under N_2 environment. The Se stock solution was introduced swiftly by a syringe into the Cd precursor solution maintained at 280^{0}C. The colour of the solution changed to red immediately. The red coloured solution was left under stirring for nucleation upto 1-5 min at 280^{0}C by Ostwald ripening process. The nucleation and seeding was quenched by rapid cooling of the reaction mixture under ice cold condition and precipitating using acetone. The precipitate was collected by centrifugation at 5000 rpm for 10 min. The precipitation with acetone and $CHCl_3$ (1:1, *v/v*) four times furnished the desired CdSe QD. The purified CdSe QD was re-dispersed in $CHCl_3$ and finally a solution with a concentration of 120 nM were prepared for further investigation.

2. **Characterization**

Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with alumina gel coated aluminum sheet (fluorescent indicator UV_{254}).

2.1 Optical Characterization. UV-visible spectra were recorded on PC based Shimadzu UV-2450 spectrophotometer using 3 mL quartz cuvettes, with the help of software UV probe 2.43 in

the spectrum mode. Fluorescence spectra were recorded on a PC based Synergy H1 Microplate reader with the help of Gen 5 software using biotek biocell plate and 1 mL quartz cuvette. The emission spectra were recorded between 350 and 700 nm. All the experimental parameters were kept constant throughout. The fluorescence spectra of PAHs are recorded with 120 nM CAD@QD.

2.2 Nuclear Magnetic Resonance (NMR) Spectroscopic Characterization. The ^{1}H NMR spectra analyses were carried out using JEOL JNM ECS400 (400 MH_Z). The ^{1}H NMR titration were carried out with CAD, QD, CAD@QD and CAD@QD with fluorene.

2.3 Fourier Transform Infrared Spectroscopy Characterization. FTIR were measured with a Bruker, Tensor 27 Spectrometer in the wave number range 600-4000 cm^{-1}. The liquid samples were prepared in $CHCl_3$ and directly applied on ZnSe ATR FTIR assembly for recording Attenuated Transmission Reflectance (ATR) spectra of the solution.

2.4 Transmission Electron Micrograph Characterization. TEM were recorded by a FEI Tecnai S Twin electron microscope operating at 200 kV. The samples are dropped onto a small carbon coated copper mesh, dried and left at room temperature so that the samples dispersed homogeneously on the carbon film among the tiny pores of the copper mesh. The images were characterized for their particle sizes using the ImageJ2© software.

2. 5 Extraction and Cleanup

The ambient air suspended particulate matter sample collected on glass fibre filter papers (GFA) were extracted using Soxhlet extraction method. The exposed filter papers were shredded into small pieces and transferred into a clean cellulose-extraction thimble and inserted into a Soxhlet assembly. The assembly was fitted with an extraction flask containing 200 mL of cylcohexane as solvent and extracted for 24 h at the rate of 2

extractions per hour. After extraction, the sample extract was concentrated to near 2 mL under reduced pressure on a 40^{o}C water bath using a rotary evaporator. Concentrated sample extracts were cleaned with column chromatography using a glass column (25 cm x 10 mm id) packed with silica gel and Na_2SO_4. Briefly, the column was packed with silicagel in n-hexane and an approximate 2 cm length of Na_2SO_4 was added on the top. The column was tapped to settle the silicagel, and hexane was eluted at a flow rate of approximately 2 mL min^{-1} and discarded. Before loading the sample extract, the column was pre-eluted with 40 mL of cyclohexane. The column was further eluted with 25 mL of cyclohexane and discarded. Subsequently, the column was eluted with 25 mL of chloroform/cyclohexane (2:3 v/v) into a concentration flask. This eluted fraction containing PAHs was concentrated to less than 1 mL using as water bath with under vacuo. Finally, the solvent was evaporated completely with $CHCl_3$. The sample dilutions and the sample dilutions spiked with fluorene (2 μgL^{-1}) were prepared for analysis by fluorescence using CAD@QD.

2.5 GC-MS analysis of PAH

The ambient air particulate matter sample extracted in $CHCl_3$ for various compounds were run on in Shimadzu QP 2010 Ultra, GC-MS. The chromatograph was equipped with a 30-m fused silica capillary column, DB-5 (0.2 mm, ID, 0.25 μm film thickness) with helium as a carrier gas (1.0 mL min^{-1}). The column temperature was programmed from 70^{0}C with 2 min hold time followed by a ramping rate at 25^{0}C min^{-1} upto 150^{0}C followed by ramping at 3^{0}C min^{-1} upto 200^{0}C and 8^{0}C min^{-1} upto 280^{0}C. Sample was injected in the splitless mode. Data for quantitative analysis was acquired in the electron impact (EI)

mode (70 eV) with the ion source maintained at 200^0C. The ramping was followed subsequently with a hold time of 10 min at this temperature. The detector and interface were maintained at 290^0C and 280^0C, respectively. The solvent cut time was kept at 7 min.

3. Langmuir Monolayer Binding Isotherm

According to the Langmuir equation, the surface of QDs consists of a finite number of binding sites. Each of the binding sites can absorb one CAD molecule from the solution and the fraction of occupied sites is defined as θ. The rate of binding of CAD to the surface of CdSe QD is proportional to the CAD concentration (C) in the solution and fraction of available binding sites is given by 1-θ. The rate of binding, R_b, of CAD on the surface is expressed as

$$R_b = K_b C (1-\theta) \quad \textbf{(1)}$$

The rate of desorption of CAD from the surface depends only on the fraction of occupied binding sites and is expressed as

$$R_d = K_d \theta \quad \textbf{(2)}$$

The rate of binding is equal to the rate of desorption at equilibrium

$$K_d\theta = K_b C (1-\theta) \quad \textbf{(3)}$$

The equation can be solved for θ as a function of the ratio $B = K_b / K_d$

$$\theta = (BX) / (1 + BX) \quad \textbf{(4)}$$

The fraction of occupied binding sites, θ, is related to the ratio between the signals obtained at given CAD concentration I and the maximum intensity I_{max}.

$$\theta = I / I_{max} \quad \textbf{(5)}$$

Therefore, an expression that related the CAD concentration, C, to the signal intensity can be written as

$$I / I_{max} = (BC) / (1 + BC) \quad \textbf{(6)}$$

The equation can be linearized to take the form

$$C / I = (1 / B\, I_{max}) + (1 / I_{max})\, C \quad \textbf{(7)}$$

Figure S1: Sampling site location for ambient air monitoring during biomass burning in November 2015 at Narwana, Bathinda, Punjab, India.

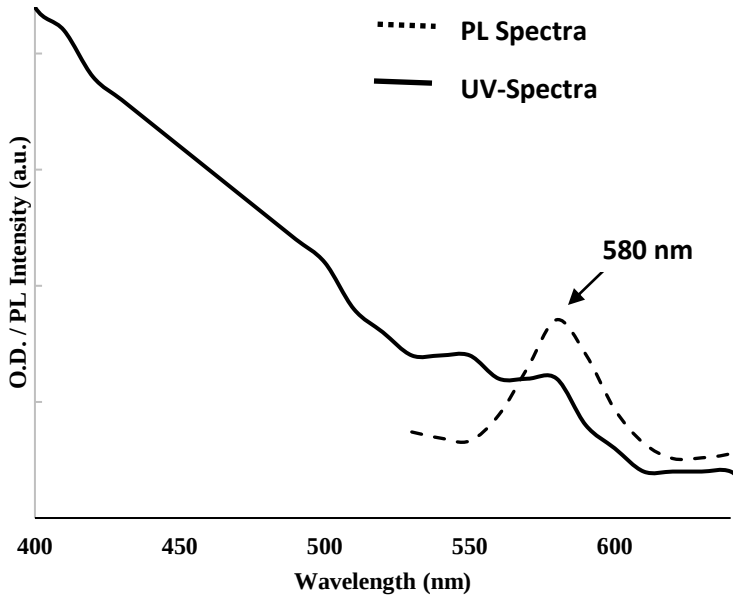

Figure S2: Absorbance (solid line) and fluorescence (dashed line) spectra of QD 120 nM concentration.

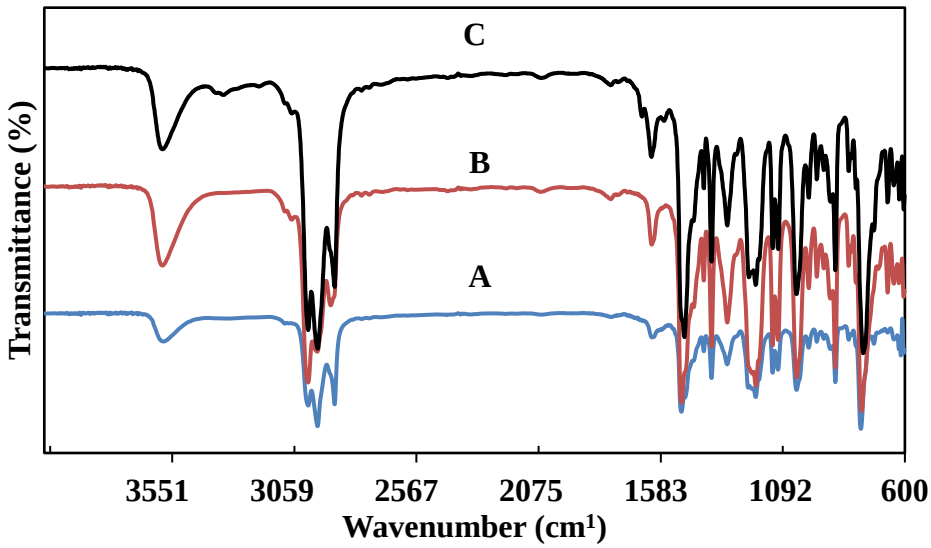

Figure S3: ATR-FTIR spectra of **(A)** CdSe QD **(B)** CAD and **(C)** CAD@QD in $CHCl_3$.

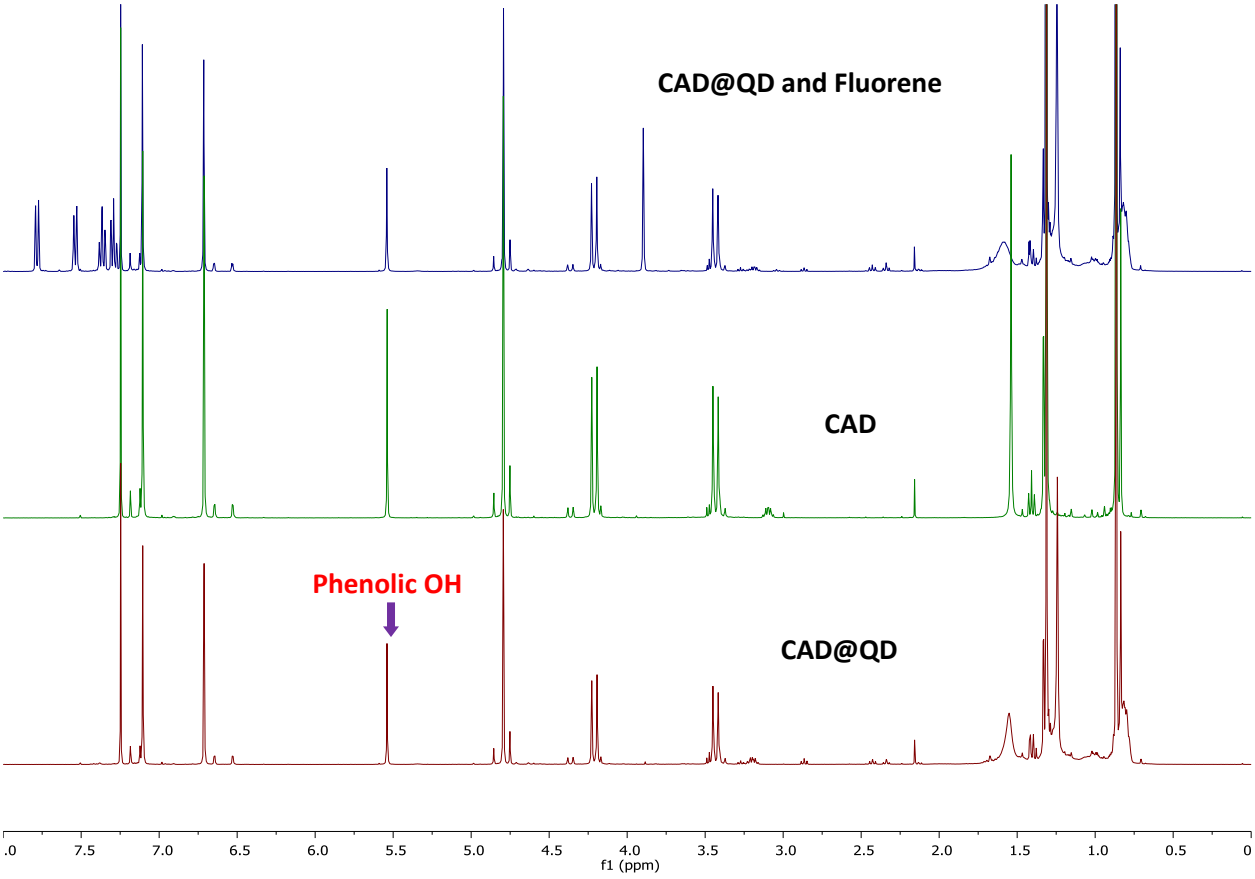

Figure S4: Stacked ^1H NMR spectra of CAD, CAD@QD and Fluorene interaction in $CDCl_3$with TMS as internal standard (i.s.)

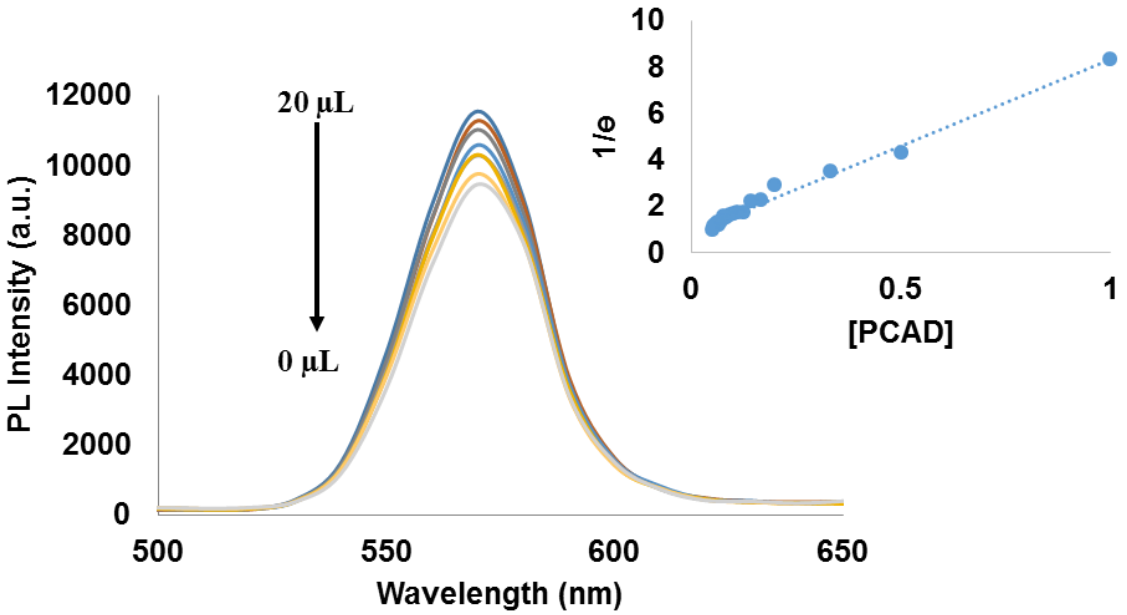

Figure S5: Fluorescence emission spectra of QD (120 nM) upon addition of CAD (0-20 µL). Inset: Linear fitting for Langmuir monolayer adsorption of PCAD on to the surface of QD.

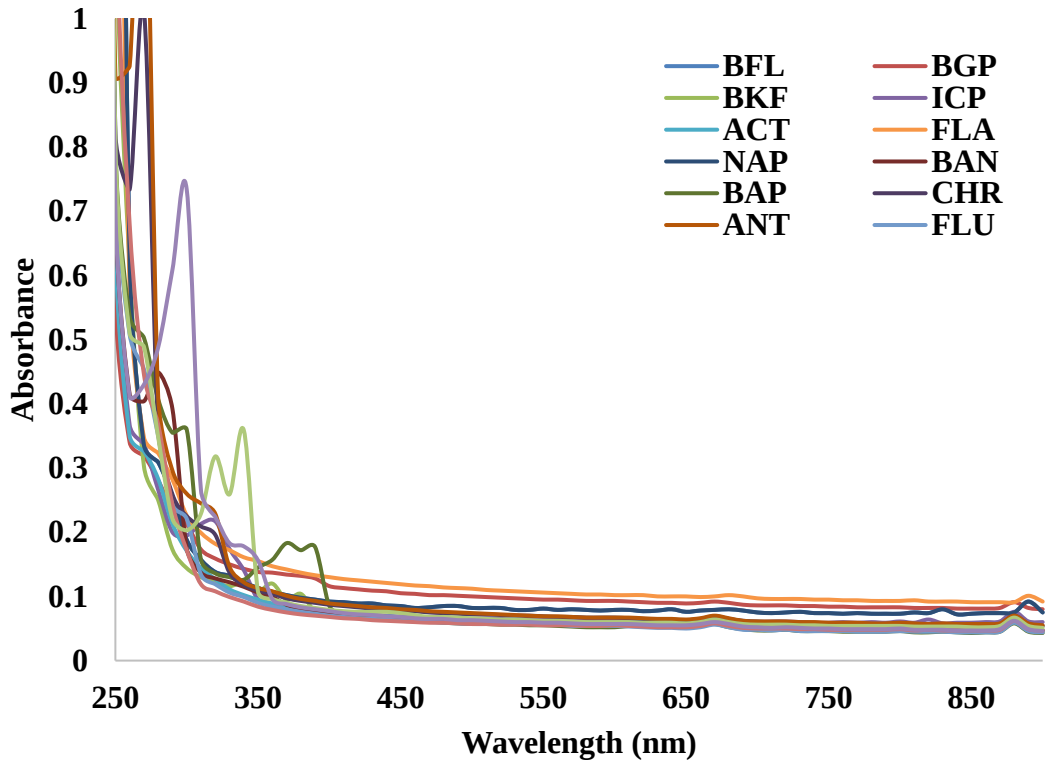

Figure S6: Absorbance spectra of PAHs (1000 nM) in $CHCl_3$

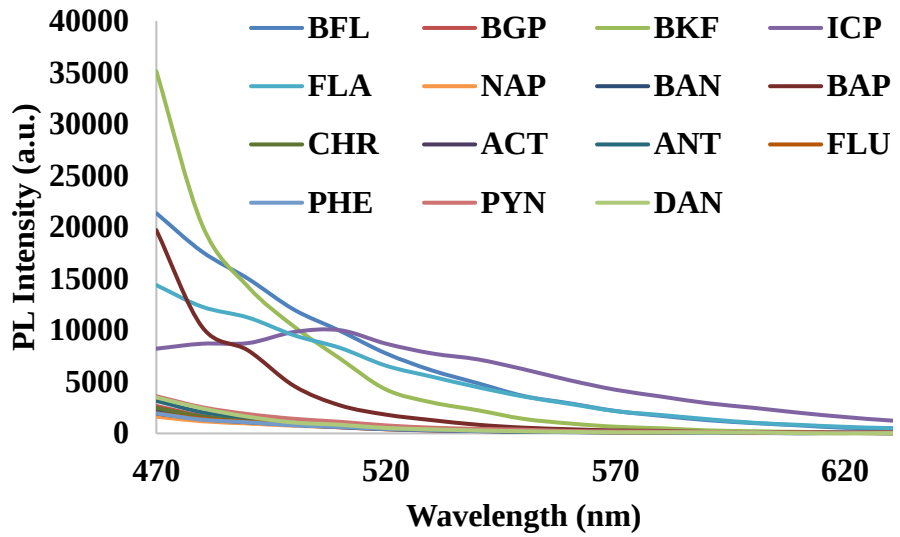

Figure S7: Fluorescence spectra of PAHs (1000 nM) in $CHCl_3$ (λ_{ex}=350 nm)

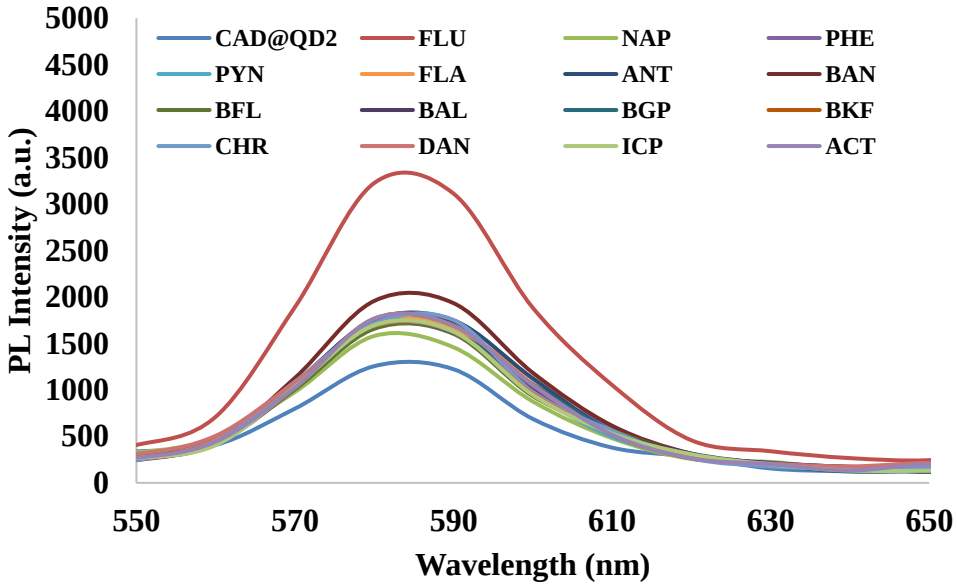

Figure S8: PL spectra of CAD@QD (10 nM) and fifteen PAHs (FLU, NAP, PHE, PYN, FLA, ANT, BAN, BFL, BAL, BGP, BKF, CHR, DAN, ICP and ACT) at 10 nM concentration of each in $CHCl_3$ (λ_{ex} = 350 nm)

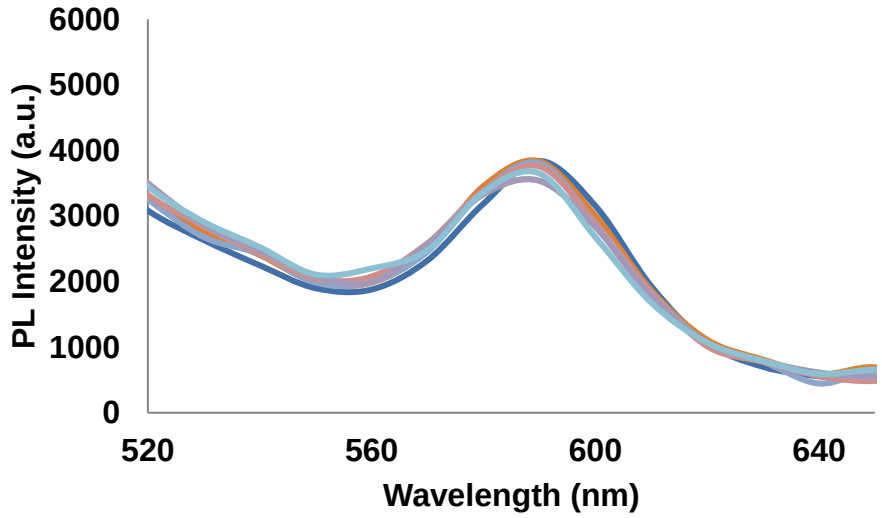

Figure S9: Fluorescence spectra of QD (120 nM) upon addition of FLU (0-10 nM) in $CHCl_3$ (λ_{ex} = 350 nm)

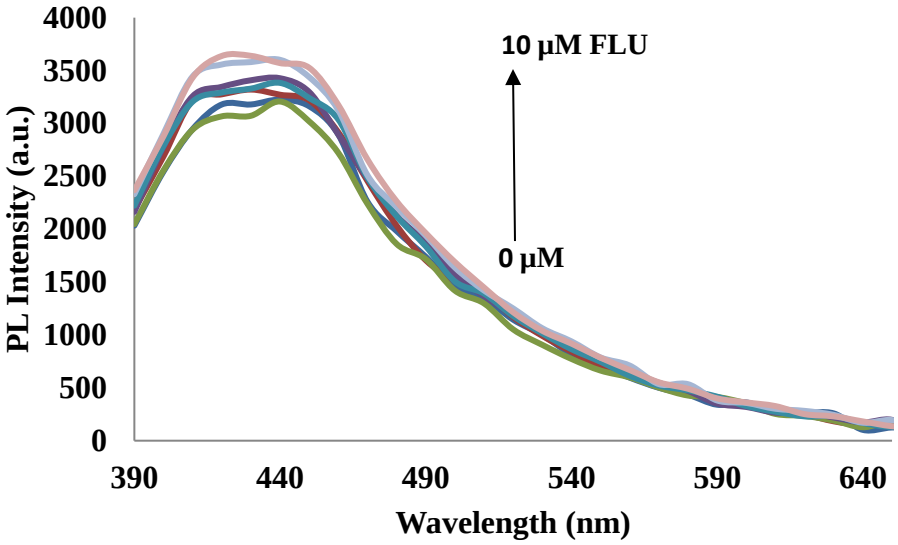

Figure S10: Fluorescence spectra of CAD (1 µM) upon addition of FLU (0-10 µM) in $CHCl_3$ (λ_{ex} = 360 nm)

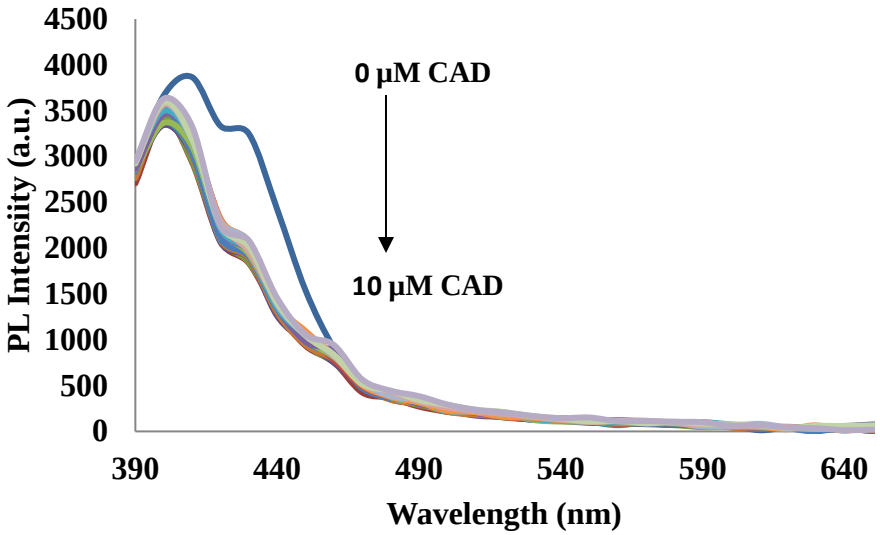

Figure S11: Fluorescence spectra of Fluorene (FLU) (1 µM) upon addition of CAD (0-10 µM) in $CHCl_3$ (λ_{ex} = 360 nm)

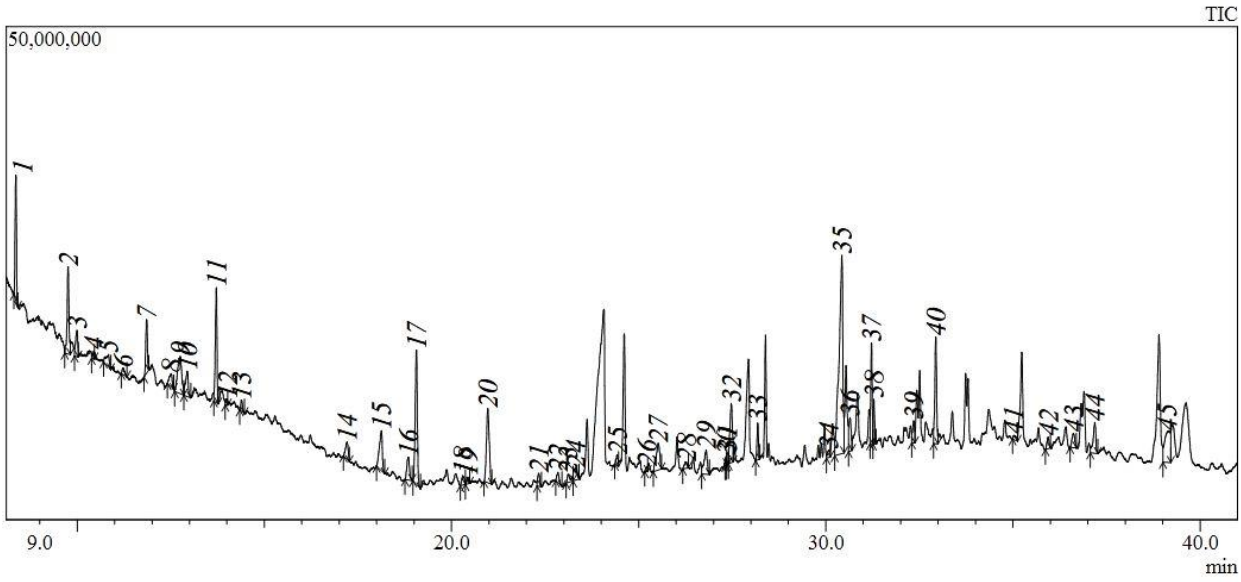

Figure S12: Extracted PM_{10} ambient air sample analysis during biomass burning by GC-MS analysis.

References

1. W. W. Yu and X. Peng, *Angew. Chem. Intl. Ed.*, 2002, **41**, 2368-2371.