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1,3-Bis(cyanomethoxy)calix[4]arene capped CdSe quantum dots for the fluorogenic sensing of fluorene†

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Capping of 1,3-bis(cyanomethoxy)-*tert*-butylcalix[4]arene (CAD) onto CdSe quantum dots (QDs) was characterized by a fluorescence enhancement of the QDs ($\lambda_{em} = 580$ nm) upon surface interaction with the phenolic moiety of CAD. CAD@QD showed selective and sensitive 1.67 fold fluorescence enhancement in the presence of fluorene among fifteen PAHs. The fluorescence enhancement was characterized by monolayer adsorption of fluorene on to the surface of CAD@QD. The limit of detection for fluorene was observed to be 0.8 nM. This method was used and compared with detection of fluorene in spiked respirable dust (PM₁₀) samples collected during an open biomass (stubble) burning event.

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Introduction

Polynuclear aromatic hydrocarbons (PAHs) are a family of pollutants emitted involuntarily during the combustion processes in our daily lives including cooking, domestic heating, smoking, charbroiling meat, and open fires (including forest fires & open biomass burning, incense and candle emissions).¹ PAHs are used to make dyes, plastics, and pesticides and some are even used in medicines² and they find their way into the human body commonly through air, soil, water and food.³ PAHs have been reported to be potential carcinogens and mutagens.⁴ Thus, the United States Environmental Protection Agency (USEPA) has regulated this class of chemicals in ambient air, water and soil to a trace level.⁵ The analysis of PAHs in environmental samples are presently being carried out using extraction followed by high performance liquid chromatography (HPLC) with a UV-vis/fluorescence detector⁶ and Gas Chromatography-Mass Spectrometry/Flame Ionization Detector (GC-MS/FID).^{2,7} However, these methods vary from matrix to matrix, are costly, time consuming and require skilled manpower. Thus, there is a dire need for simple, cost-effective, real-time field analysis of PAHs with low detection limits.

Fluorogenic sensing is a key approach, for selective and sensitive detection of analyte. Fluorogenic sensing of metal and anion have been widely studied, but few reports exists in the sensing of organic analytes.⁸ Sensing of aromatic analytes is based on the phenomenon of inclusion, whereby the chemosensor has a receptor moiety comprising of a cavity having potential for formation of inclusion complex. These inclusion based chemosensor receptor moieties exploit weak intermolecular bonding with the analyte of interest. Container molecules which form inclusion complex with small organic molecules include, cyclodextrins,⁹ calixarenes,¹⁰ cucurbiturils and pillararenes.¹¹ Of these, calixarenes are a versatile class of compounds which have significantly been studied for inclusion behaviour.⁸ Calix[4]arenes have the advantage of easy scalable synthesis, easy derivatization on lower rim, upper rim and bridging methylene moieties, with significant conformational control during derivatization.¹² Optical sensors based on functionalized calix[4]arene have widely been studied for the recognition of cations,¹³ anions¹⁴ and various neutral analytes.¹⁴ However, there have been limited studies on the fluorogenic recognition behavior of calix[4]arene based receptors for small organic molecules of environmental interest. The limitation is partly accounted to the challenges in designing of suitable fluorogenic derivatives of calix[4]arene for the relay of inclusion complexation.

Recently with the understanding of the optical properties of quantum dots (QDs), there have been surge in the fluorescent sensors based on QDs.^{8,15} Quantum dots have various advantages over organic fluorogenic moieties like broad excitation, narrow and size tuneable emission spectra and high quantum yield with reduced susceptibility to photobleaching and high photochemical stability.¹⁶ Apart from the optical features, QDs provide the flexibility in designing of the receptor QD association, whereby the receptor can be held on the surface of QD by

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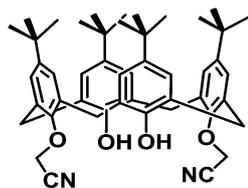
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covalent or non-covalent interaction. Lower rim carboxylic acid substituted and upper rim sulphonate functionalized calix[*n*] arene ($n = 4, 6, 8$)¹⁷ have extensively been studied for capping of CdSe QDs. Few quantum dot capped calixarene derivatives have been studied for inclusion complex based fluorogenic relay of organic analytes.^{8,11} Li *et al.* reported a similar sol-gel derived silica nanospheres coated with calix[4]arene and calix[7]arene CdTe QDs as luminescent probe for methomyl.¹⁸ Recently Carrillo-Carrión *et al.* (2011) studied CdSe/ZnS non-covalently coated with calix[8]arene as a fullerene (C₆₀) nanosensor and demonstrated its use in the liquid-liquid extraction based analysis of the analyte in river water sample.¹⁹ These studies suggest use of calixarene, its lower rim carboxylate or upper rim sulphonate functionalized derivatives as suitable substrates for sensing of aromatic analytes based on inclusion of analyte in the π -basic cavity of the calixarene. However, with the recent advancement in the influence of the photophysical behaviour of quantum dot by various organic functional moieties²⁰ like thioether,²¹ carboxylates,²² sulphonates,²³ amine,²⁴ pyridine,²⁵ phenols²⁶ and phosphine oxides,²⁷ and the unfavourable electrostatic interactions in sulphonated/carboxylated calix[4]arene for inclusion of neutral molecules, the non-polar calix[4]arene derivatives are suitable receptors for inclusion based sensing. Thus, the present work investigates the CdSe QD surface interaction with lower rim functionalized 1,3-bis(cyanomethoxy)-*tert*-butylcalix[4]arene (CAD) and its PAH sensing behavior. The sensing behavior of the CAD@QD were further evaluated for PAH sensing in ambient air PM₁₀ samples.



1,3-Bis(cyanomethoxy)-*tert*-butylcalix[4]arene (CAD)

Materials and methods

Details provided in ESI.†

Synthesis of CdSe QDs

CdSe QDs were synthesized by the method described by Peng and coworkers using CdO as precursor²⁸ (details provided in ESI†).

Synthesis of CAD@CdSe QDs

The CAD capped QD was prepared by addition of CAD solution to a solution of CdSe QDs in CHCl₃. To a 1 mL solution of TOPO-capped QD (120 nM), was added 1–20 μ L of CAD solution (1 mM) in CHCl₃. The mixture was placed for vortex mixing at room temperature for about 30 min. Upon dispersion, the mixture was sonicated for 30 min using an ultrasonic bath at room temperature. The resulting mixture (CAD@QD) were

treated with concentration of 20 μ M CAD and 120 nM w.r.t. CdSe QDs and used for further spectroscopic studies and characterization.

Fluorescence titration

The fluorescence titration of CAD and PAH with QD and CAD@QD, respectively were carried out. To a 1 mL solution of 120 nM solution of CdSe QD in CHCl₃, was added 1–20 μ L of 1 mM CAD solution in CHCl₃.

The CAD@QD stock solution was prepared by addition of 20 μ L of CAD to 120 nM QD solution in CHCl₃. The solution w.r.t. CAD is 10 μ M against the QD concentration of 120 nM. The stock solution was diluted to 10 nM w.r.t. CdSe QD and used for fluorescence titration. To a 10 nM solution of CAD@QD w.r.t. the QD, was added 1–10 μ L of 1 μ M PAH solution.

Sampling and monitoring of ambient air

Sampling was performed during the October 2015 at Naruwana, Bathinda, Punjab, India (latitude 30.163806° and longitude 74.896031°) as shown in ESI Fig. S1.† The respirable fraction of ambient air particulate matter (PM₁₀) was collected on USEPA glass fibre (GFA) filter paper of dimension 20.3 \times 25.4 cm². The samples were collected during biomass burning at a flow rate >1.0 m³ min⁻¹ for a continuous period of 8 h using respirable dust sampler APM 460BL, Envirotech India Pvt Ltd. The particles were collected with glass fibre filters, desiccated and weighed till constant weight, before and after sample collection. Analysis of the filter paper containing PM₁₀ was performed according to USEPA TO 13A norm.⁷

Extraction & cleanup and GC-MS analysis of PAHs

Extraction & cleanup and GC-MS analysis of the PAHs extract was carried out as provided in ESI.†

Fluorescence study of PM₁₀ extract and spiked extract

The PM₁₀ extract was diluted in CHCl₃ to 10, 100 and 1000 times dilutions. The solution thus prepared were spiked with fluorene upto 20 nM and were studied for fluorescence sensing of fluorene. The samples were then subjected to fluorescence analysis at an excitation wavelength of 350 nm and the fluorescence emission were recorded with wavelength range between 400–700 nm.

Results and discussion

Characterization of QD and CAD@QD

Distally substituted 1,3-bis(cyanomethoxy)-*tert*-butylcalix[4]arene (CAD)²⁹ and CdSe QD²⁸ were synthesized and characterized using the method reported in literature. The UV-vis absorption spectrum of the QD in the dispersed CHCl₃ media was characterized by an absorption peak at 580 nm (ESI Fig. S2†). Based on the UV-vis characteristic and using plasmonic equation,³⁰ the size of the quantum dot was calculated to be 3.8 nm and extinction co-efficient 2.04×10^5 per mol. Based on the extinction co-efficient per mol QD, the observed



concentration of the solution was 120 nM. The capping of CAD derivative on CdSe QD was carried out in CHCl_3 as dispersion medium with stirring followed by sonication.

Fig. 1(A and B) shows the Transmission Electron Microscope (TEM) images and histograms of QD and CAD@QD. All diameters are a measure of the major axis. A histogram showing the results of 100 individual measurements of the diameters of QDs from the TEM micrograph is depicted in Fig. 1(C and D). The measured mean diameter of QD and CAD@QD obtained with an average of 2.5 ± 0.5 and 2.8 ± 0.5 nm, respectively. From the TEM images it is quite evident that the QD and CAD@QD are both well dispersed and there is a coating of CAD on the surface of QD.

The binding behaviour of the CAD on the surface of QD were also studied using fluorescence spectroscopy. The QD (120 nM) was characterized by a fluorescence emission at $\lambda_{\text{em}} = 580$ nm when excited at 350 nm in CHCl_3 as given in Fig. 2. The full-width-at-half-maximum (FWHM) of 25 nm was observed for QD, is below 30 nm, which indicates narrow size range distribution of these QDs.³⁰ The change in the fluorescence spectra of QD upon addition of increasing aliquot of CAD in CHCl_3 is depicted in Fig. 2. Upon addition of CAD (1–20 μM) fluorescence enhancement was observed in the emission due to QD at $\lambda_{\text{max}} = 580$ nm. This behaviour could be accounted to the interaction of CAD with the surface of the nanocolloid QD upon adsorption of CAD.³¹ Similar fluorescence enhancement have been observed in case of pyridine and amine nitrogen upon interaction with QD surface.³² To investigate the binding of CAD to the surface of QD FTIR spectroscopy and ^1H NMR of CAD and CAD@QD were investigated as given in ESI Fig. S3 and S4.† However, no significant changes were observed in both the studies, except for the presence of an interaction of CAD phenolic hydroxyl group with the QD surface leading to broadening of the phenolic proton singlet in ^1H NMR. Further, the di-propoxy derivative of CAD (1–20 μM) (PCAD)^{14b} was used for fluorescence titration with QD (ESI Fig. S5†). An insignificant fluorescence quenching of the QD was observed upon addition of PCAD (1–10 nM) to QD. This suggests that interaction between the CAD and the QD surface occurs through proton exchange.³³

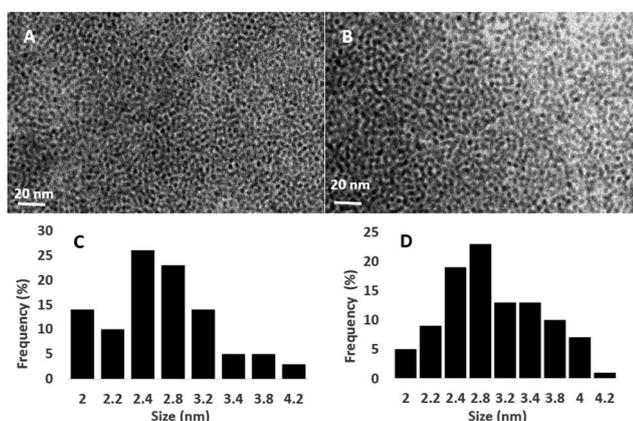


Fig. 1 TEM images of (A) QD and (B) CAD@QD at 20 nm scale. Particle size histograms of (C) QD and (D) CAD@QD.

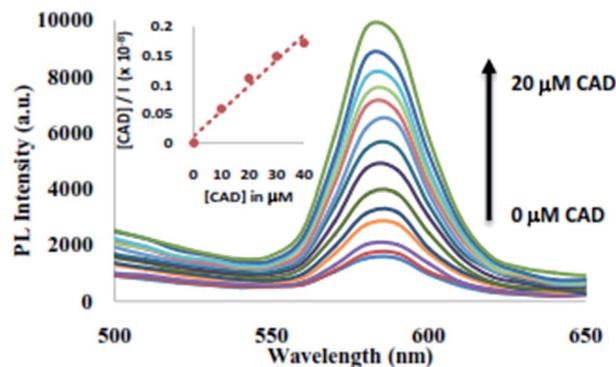


Fig. 2 Fluorescence emission spectra of QD (10 nM) upon addition of CAD (0–20 μM). Inset: linear fitting for Langmuir monolayer adsorption of CAD on to the surface of QD.

The fluorescence enhancement of QD upon addition of CAD in CHCl_3 solution was studied for the Langmuir monolayer adsorption isotherm.³⁴ The linear expression for Langmuir monolayer adsorption was studied using eqn (7) (ESI†). The plot of the Langmuir isotherm is shown in inset of Fig. 2 was obtained using $[\text{CAD}]/I$ vs. $[\text{CAD}]$. The equilibrium binding constant, B was found to be $3.77 \times 10^6 \text{ M}^{-1}$. The calculated equilibrium binding constant is much greater than those reported for TOPO binding on CdSe quantum dot,³⁵ thus it seems that CAD displaces the TOPO competitively from the QD surface.

PAH sensing behavior of CAD@QD

Fluorescence is a sensitive technique for detection of analyte, as it is influenced by the immediate environment of the fluorophore. The fluorescence sensing behaviour of CAD@QD (10 nM w.r.t. QD) was carried out in CHCl_3 as solvent with various PAH namely, fluorene (FLU), naphthalene (NAP), phenanthrene (PHE), pyrene (PYN), fluoranthene (FLA), anthracene (ANT), benzo[*a*]anthracene (BAN), benzo[*b*]fluoranthene (BFL), benzo[*a*]pyrene (BAL), benzo[*ghi*]perylene (BGP), benzo[*k*]fluoranthene (BKF), chrysene (CHR), dibenzo[*a,h*]anthracene (DAN), indeno[1,2,3-*cd*]pyrene (ICP) and acenaphthene (ACT). Influence of background fluorescence of PAHs on the fluorescence spectra of QD and CAD@QD, was ascertained by performing fluorescence titration of all the PAHs to either solvent or CdSe QD as given in ESI Fig. S6 and S7.† Studies indicate no significant emission of all the 15 PAHs was observed in the emission range of the CdSe QD. Further, upon addition of 10 nM of each PAH to CdSe QD, no change in the fluorescence of the quantum dot was observed. Similarly, fluorescence titration of TOPO capped QD (10 nM) were also carried out with various PAHs. The results of these study indicate no significant change in the fluorescence behaviour of the TOPO capped QD (10 nM) upon addition of various PAH (10 nM) as analytes in CHCl_3 . Further, the fluorescence emission of CAD@QD (10 nM) in presence of 10 nM PAH solution are as given in Fig. 3 (ESI Fig. S8†). A significant fluorescence enhancement was observed upon addition of 10 nM FLU to CAD@QD in CHCl_3 . However in



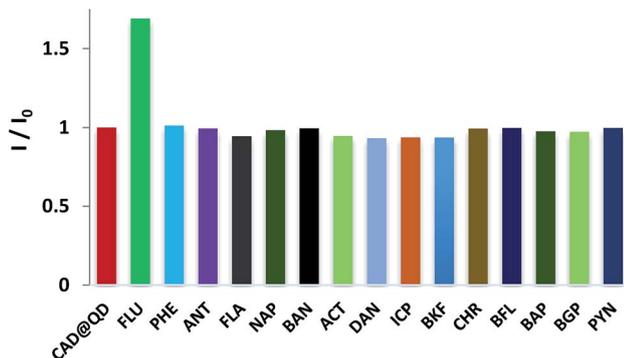


Fig. 3 Fluorescence intensity change (I/I_0) of CAD@QD (10 nM) upon addition of 10 nM of different PAHs (FLU, PHE, ANT, FLA, NAP, BAN, ACT, DAN, ICP, BKF, CHR, BFL, BAP, BGP, PYN) in CHCl_3 .

presence of other PAHs, CAD@QD did not show any significant change in fluorescence emission (ESI Fig. S9†). Thus confirming the selective sensing behaviour of CAD@QD for fluorene to be characteristic of the calix[4]arene on the QD surface. The CAD@QD showed varied response to the PAH sensing, which could be due to the improper orientation of calix[4]arene inclusion cavity of CAD upon surface binding on to QD.

Further, fluorescence titrations of CAD@QD was carried out with fluorene (10 nM). Upon addition of increasing amount of fluorene to the CAD@QD (10 nM), a fluorescence enhancement was observed with the emission band centred at $\lambda_{\text{em}} = 580$ nm. The fluorescence intensity of CAD@QD increased linearly with increase in concentration of fluorene and maximum enhancement was observed at 10 nM fluorene concentration (Fig. 4). The significant fluorescence enhancement upto 1.67 folds was observed upon binding of fluorene (10 nM) to CAD@QD (10 nM). Thus, from these results, it is envisaged that the resulting fluorescence enhancement of CAD@QD in the presence of fluorene, could be accounted to the interaction of fluorene with CAD in CHCl_3 solution.

To establish the mode of binding between the CAD@QD and fluorene, ^1H NMR titration were carried out in CDCl_3 , which indicated no shift in the fluorene or the CAD protons. Further, fluorescence titration of CAD (1 μM) upon addition of fluorene

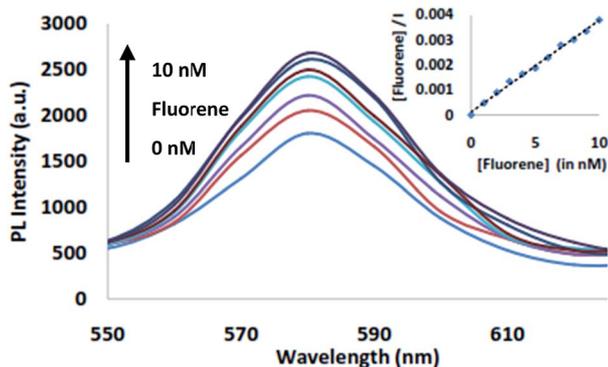


Fig. 4 Change in fluorescence of CAD@QD upon addition of 10 nM of fluorene in CHCl_3 ($\lambda_{\text{ex}} = 350$ nm). Inset: linear fitting for Langmuir monolayer adsorption of fluorene on to the surface of CAD@QD.

(1–10 μM) and fluorene (1 μM) upon addition of CAD (1–10 μM) was carried out (ESI Fig. S10 and S11†). The later addition showed a significant change in the fluorescence spectra of fluorene. A significant fluorescence quenching of the fluorene fluorescence at $\lambda_{\text{em}} = 420$ nm was observed upon excitation at 350 nm with the addition of CAD solution (ESI Fig. S11†). Thus, CAD interacts with the fluorene in CHCl_3 by weak supramolecular interactions which results in the sensing of fluorene by CAD.

The fluorescence enhancement of the CAD@QD in presence of fluorene was studied by Langmuir isotherm for monolayer adsorption of fluorene in the inclusion cavity of CAD@QD in dispersed phase in CHCl_3 .³⁴ The plot of concentration of fluorene ($[\text{fluorene}]$) versus $[\text{fluorene}]/I$ was found to be a linear as shown in inset Fig. 4. The coefficient of the linear fit is 0.996, which indicates a monolayer adsorption of fluorene on CAD@QD. The plot of the Langmuir isotherm is shown in inset of Fig. 4 was obtained using $[\text{fluorene}]/I$ vs. $[\text{fluorene}]$. The equilibrium binding constant, B was found to be $4 \times 10^9 \text{ M}^{-1}$. The limit of detection of PAH fluorene using CAD@QD was found to be 0.8 nM. Earlier Sehatnia *et al.* studied PAH sensing behavior of calix[4]arene moieties functionalized on upper rim, which showed a detection limit of upto 25 μM with a binding based fluorescence quenching as the sensor relay phenomenon.³⁶ Thus, the present method has a good sensitivity for detection of fluorene using CAD@QD, which would be useful in developing a quantitative methods for environmental and food sample analysis.

Ambient air PM_{10} PAH analysis

In order to check the feasibility of the CAD@QD for fluorene analysis and monitoring, ambient air samples of respirable suspended particulate matter (PM_{10}) were collected during the open biomass burning in the agricultural fields near Bathinda city. PM_{10} were collected using a respirable dust sampler on a glass fibre filter. The filter was then Soxhlet extracted and precleaned for PAH.³⁷ The GC-MS analysis of the extracted samples showed the presence of various trace residues of organics during the open biomass burning process (ESI Fig. S12†). The GC-MS spectrograph of the PM_{10} extracted samples showed the presence of trace residues namely isopropyl-5-methylphenol, 1*H*-isoindole-1,3(2*H*)-dione, 2,4-di-*tert*-butylphenol, 5-phenylpentanoic acid, 1-nitro- β -*D*-arabino-furanose tetraacetate, 3-[2-tetrahydropyranloxy]-1-butyne, acetosyrignone, 1-amino-2-hydroxy-3,5-nitrobenzene, 5,6-dihydro-2-methoxy-2*H*-pyran, 5-butyldihydro-4-methylfuranone, 2-methoxy-1,3,4-trimethyl-benzene and ergost-3-en-3-ol. These are characteristic fragmented oxidized products of the lignocellulosic material of biomass during the open burning process.³⁸ The GC-MS analysis showed no traces of any PAHs. The matrix solution was diluted 10, 100 and 1000 times. This organic loaded matrix with various dilutions were spiked with fluorene upto a concentration of 20 nM and subjected to the analysis of fluorene upon 10 times dilution with 10 nM CAD@QD in CHCl_3 . The concentration of fluorene as determined in the triplicate analysis of the sample and were found to



be 0.56 (± 0.21), 1.21 (± 0.30), 1.68 (± 0.22) and 1.78 (± 0.25) nM with the extract 10, 100 and 1000 times diluted extract, respectively. A significantly high organic loading of the sample showed a fluorescence quenching indicating reduced/competitive binding of fluorene under a higher organic loaded ambient air particulate matter matrix.

Conclusions

1,3-Bis(cyanomethoxy)-*tert*-butylcalix[4]arene (CAD) capped on CdSe QD shows selective fluorogenic response for the PAH fluorene with a detection limit well below the environmental permissible limits. The PAH sensing was selectively observed in CAD@QD ($\lambda_{em} = 580$ nm) which is accounted to the orientation of calix[4]arene on the quantum dot surface. Further this sensor was subjected to fluorogenic sensing of fluorene in ambient air monitoring in the sensing event, however upon dilution upto 100 and 1000 times there is significant lowering of the interference and actual determined fluorene is close to the expected value. Thus, a reliable analysis of fluorene could be carried out.

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