



β -Cyclodextrin and calix[4]arene-25,26,27,28-tetrol capped carbon dots for selective and sensitive detection of fluoride

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ABSTRACT

In this work we have designed a novel system based on carbon dots prepared from chitosan gel capped with β -cyclodextrin and calix[4]arene-25,26,27,28-tetrol for sensitive and selective detection of fluoride ions in aqueous media. Fluorescent carbon dots prepared from chitosan gel when capped with β -cyclodextrin and calix[4]arene-25,26,27,28-tetrol results in quenching of its fluorescence intensity. Introduction of F^- ions to carbon dots capped with β -cyclodextrin and calix[4]arene-25,26,27,28-tetrol system results in enhancement and restoration of fluorescence intensity leading to detection of F^- ion. Minimum detection limit was determined to be $\sim 6.6 \mu M$. The detection is selective as with other halide ions i.e. Cl^- , Br^- and I^- and hydroxyl ion (OH^-), there is observed decrease of fluorescence intensity. A possible mechanism to justify the observation is also discussed in the paper.

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1. Introduction

Fluoride is an essential element for maintaining proper human health. A specific amount of fluoride plays an important role in dental care and bone health of human beings. On the other hand an excess amount of fluoride is toxic to all forms of living beings leading to severe gastric and kidney disorders, dental and skeletal fluorosis and causes damage to the DNA. According to the World Health Organization (WHO) the maximum permissible limit of F^- in drinking water is set at 1.5 mg L^{-1} . Although a variety of methods for F^- detection has been reported, such as ion chromatography (IC) (Villagrán, Deetlefs, Pitner, & Hardacre, 2004), ^{19}F NMR (Duong, Ackerman, Ying, & Neil, 1998), fluoride selective electrodes, fluorescence capillary electrophoresis (Albin, Weinberger, Sapp, & Moring, 1991), colorimetric technique based on La(III), Ce(III) and Zr(IV) complexes with dye compounds (Gao, Zheng, Shang, & Xu, 2007), fluoride sensors based on fluorescence resonance energy transfer etc., but unfortunately, the low sensitivity, poor reproducibility,

high cost, the use of organic solvents as the detection medium, instability and the environmental pollution caused by the use of organic dyes and semiconductor quantum dots have led to limitations in their practical applicability. Therefore the search for environmentally benign alternatives for fluoride detection is the need of the hour.

Fluorescence spectroscopy has recently emerged as a very useful analytical tool due to its simple, inexpensive and rapid nature (Aragay, Pons, & Merkoci, 2011; Chadha & Zhao, 2013). Whereas other sophisticated analytical techniques like atomic absorption spectroscopy (AAS), inductively coupled plasma-mass spectrometry (ICPMS), mass spectroscopy (MS), X-ray fluorescence spectroscopy and potentiometric methods require extensive sample preparation, fluorescence spectroscopy on the contrary is non-invasive and bio-friendly for the detection of chemical, environmental and biological substances with enhanced sensitivity and low detection limit. Most importantly the greatest advantage of a fluorescent probe is intracellular detection (Dasary et al., 2013). Thus, continuous efforts are going on for the development of fluorescent and colorimetric sensors, for selective and sensitive detection of analytes.

Semiconductor nanoparticles i.e. quantum dots (QDs), have been regarded as one of the major breakthroughs in material science in the last two decades (Freeman & Willner, 2012; Kumar, Srivastava, & Dutta, 2013). QDs are known as zero-dimensional colloidal materials comprising of elements from the periodic

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groups II–IV, III–V or IV–VI (Zhu et al., 2013). QDs have successfully replaced traditional fluorophores, as they allow for improved photostability, multi-targeting, and improved brightness making them useful for biological applications such as conjugation with proteins and DNA and as desirable fluorescent labels. QDs have also been found to possess interesting electro-chemiluminescent properties (Song, Qin, He, Fan, & Chen, 2010). In spite of all these advantages, a major limitation of conventional QDs is their necessary use of heavy metals such as cadmium thus limiting their use for *in vivo* biological applications. Therefore the search for non-hazardous substitutes came into demand.

Recently fluorescent carbon nanoparticles (CPs) or carbon dots (CDs) have emerged as promising substitutes for heavy-metal-containing semiconductor-based QDs (Chowdhury, Gogoi, & Majumdar, 2012; Jaiswal, Ghosh, & Chattopadhyay, 2012; Liu, Liu, & Zhang, 2011; Sun et al., 2006; Zhang et al., 2013a,b). Some of their advantages include low cytotoxicity, good stability, easy preparation, excellent photostability, favourable biocompatibility, good water solubility and environmental friendliness. Therefore a great deal of research is being carried out regarding their synthesis, properties and applications. While most of the common applications of CDs include bioimaging photoreduction of metals and optoelectronic devices, recently another area of their application as fluorescent sensors for analytical applications is being explored (Dong et al., 2012). Therefore the need for the development of specifically functionalized carbon dots (CDs) FL probes with high quantum yield and better selectivity has become very important for making them promising candidates for analytical applications. There are already some reports in literature of using functionalized CDs as FL probe for their use as chemical sensors. For example Wang, Periasamy, and Chang (2013) used photoluminescent carbon dots on reduced graphene oxide (C-dots@RGO) probe for sensitive and selective detection of acetylcholine. Wei, Xu, Ren, Xuab, and Qu (2012) showed metal ion sensor with high potassium selectivity and tunable dynamic range by using an ion-selective crown ether and fluorescence resonance energy transfer from carbon dots to graphene. Qu et al. have synthesized carbon dots from hydrothermal synthesis route using dopamine as source and shown that carbon dots can serve as a very effective fluorescent sensing platform for label-free sensitive and selective detection of Fe^{3+} ions and dopamine (Qu, Wang, Ren, & Qu, 2013). Zhang et al. (2013a,b) demonstrated green preparation of graphitic carbon quantum dots (GCQDs) as a fluorescent sensing platform for the highly sensitive and selective detection of Fe^{3+} . Dong et al. (2012) demonstrated polyamine-functionalized carbon dots as fluorescent probes for selective and sensitive detection of copper ions. Similarly Salinas-Castillo et al. (2013) showed use of carbon dots for copper detection with down and up-conversion fluorescent properties. In the present study we have designed a novel system based on carbon dots capped with β -cyclodextrin and calix[4]arene-25,26,27,28-tetrol for sensitive and selective detection of fluoride ions in aqueous media. Macromolecules are considered as ideal species for targeting specific analytes based on their structures (Collins & Choi, 1997). A great deal of research has been centred on the detection of heavy metals employing the host-guest chemistry of cyclodextrins (Ueno, Ikeda, Ikeda, Ikeda, & Toda, 1999; Ishikawa, Kunitake, Matsuda, Otsuka, & Shinkai, 1989). Calixarenes on the other hand are a class of macrocyclic compounds obtained by the reaction between *p*-substituted phenol and formaldehyde in basic medium, which has a π -electron rich hydrophobic cavity formed by benzene rings. The cavity size can be modified with specific functional groups for selective recognition of metal ions (Ishikawa et al., 1989; Talanova, Elkarim, Talanov, & Bartsch, 1999). Kim et al. (2004) and Lee, Kim, Kim, Lee, and Kim (2004) have developed a series of calix[4]arene-based fluorescent chemosensors for Pb^{2+} detection. Kim et al. (2004) and Lee et al. (2004) reported a new fluorescent

chemosensor with two different types of cation binding sites on the lower rims of a 1,3-alternate calix[4]arene. Although a good deal of research has been done on carbon dots based sensors for heavy metal detection, as discussed in earlier paragraph, the use of similar systems for anion detection is still lagging behind. Fluorescent CDs have already been used for fluoride ion detection as reported recently (Liu et al., 2013). The F^- probe reported is based on a heavy metal i.e. zirconium which is the main disadvantage of using such probes. Moreover, even though the sensitivity of the Zr based fluorescent probe for F^- ions is quite satisfactory, but it is a fluorescence turn-off probe for F^- ions, whereas the system we report herein is a fluorescence turn-on probe in presence of fluoride ions. For fluorescence-based detection of anions, fluorescence enhancement (turn-on) is preferable to fluorescence quenching (turn-off) because the former lessens the chance of other fluorescent quenchers existing in samples. Thus we feel our system is more advantageous for detection of F^- ions in aqueous media.

The system we have chosen for selective detection of fluoride ions (F^-) is fluorescent carbon dots prepared from chitosan gel since they show unique electrochemical properties including ability of electron transfer and are environmentally green. Chitosan is a linear co-polymer polysaccharide consisting of β (1–4)-linked 2-amino-2-deoxy-D-glucose (D-glucosamine) and 2-acetamido-2-deoxy-D-glucose (N-acetyl-D-glucosamine) units. The fluorescent carbon dots prepared from chitosan were capped with macromolecules like β -cyclodextrin and calix[4]arene-25,26,27,28-tetrol. This results in changes in the emission properties of such capped carbon dots. Such capped carbon dots viz. (CDs/ β -cd) and (CDs/C[4]A) showed increased PL intensity exclusively in the presence of F^- .

2. Materials and methods

2.1. Materials

Chitosan (low molecular weight, deacetylation $\geq 75.0\%$), β -cyclodextrin, calix[4]arene-25,26,27,28-tetrol and potassium iodide (KI) were purchased from Sigma Aldrich. Glycerol (98% purified), acetone ($\geq 99\%$ for synthesis), sodium hydroxide (NaOH), sodium fluoride (NaF), sodium chloride (NaCl), potassium bromide (KBr) were purchased from Merck. Glacial acetic acid (99.5%) used was purchased from Qualigens. The water used throughout the experiment was from a Milli-Q water purification system.

2.2. Synthesis of carbon dots (CDs) from chitosan hydrogel

Chitosan hydrogel was synthesized as reported earlier (Chowdhury et al., 2012). Briefly, 0.1 g of chitosan was taken in a beaker and 10 mL of a 1:3 mixture of 1% glacial acetic acid and glycerol was added to it and stirred with the help of a magnetic stirrer for 2 h at room temperature. To the resulting clear solution 300 μL of 5 N NaOH was added. Immediately a clear hydrogel was formed. The hydrogel was washed with plenty of water and stored in water.

CDs from chitosan gel were prepared by taking small amount of hydrogel and dissolving in 20 mL 0.1 M acetic acid and the resulting solution was micro-waved for 20 min. The formation of CDs was confirmed by bluish glow when placed under UV light.

2.3. Capping of the prepared CDs with β -cyclodextrin and calix[4]arene-25,26,27,28-tetrol

For the capping of CDs, 3 mL of CDs solution was taken and to it 400 μL of 2 mM β -cyclodextrin solution in water or 400 μL of 1.45 mM calix[4]arene-25,26,27,28-tetrol solution in acetone was

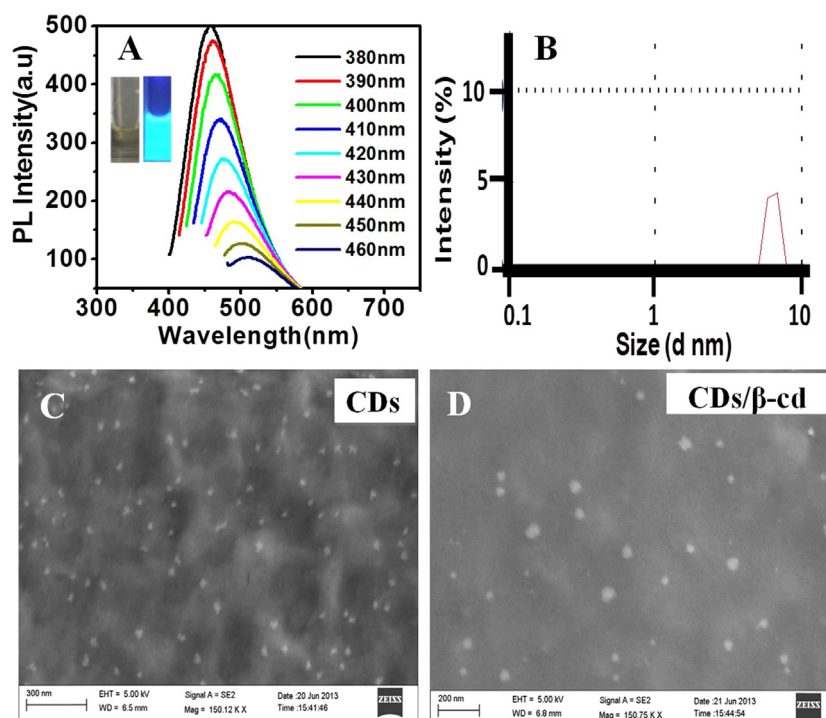


Fig. 1. (A) Photoluminescence emission spectra of carbon dots (CDs) obtained from chitosan gel at excitation wavelengths from 380 nm to 460 nm. Inset: photograph of the carbon dots solution at normal light and after illumination under a UV lamp. (B) Particle size distribution of the CDs obtained from DLS. (C) Representative SEM image of CDs. (D) Representative SEM image of CDs after capping with β -cyclodextrin(β -cd).

added dropwise with continuous stirring for 2 h at room temperature. The resultant solution obtained was then characterized by UV–visible spectroscopy, photoluminescence spectroscopy (PL), dynamic light scattering (DLS) and Fourier transformed infrared spectroscopy (FTIR).

2.4. Fluoride detection by CDs/ β -cd and CDs/C[4]A

The fluoride ion detection was monitored using a spectrofluorometer. The capped CDs i.e. CDs/ β -cd and CDs/C[4]A were taken in a quartz cuvette and NaF was added in amounts of 10 μ L and the corresponding fluorescence spectra was recorded at intervals of 2 min. Detection of other ions viz Cl^- , Br^- and I^- was also done in a similar way.

3. Results and discussion

Carbon dots (CDs) were prepared from chitosan hydrogel by the method developed and reported by our laboratory. As CDs are fluorescent materials photoluminescence properties were investigated. Fig. 1A shows the photoluminescence (PL) spectra of CDs excited at different wavelengths. It was observed that with increase in the excitation wavelength from 380 nm to 460 nm, the emission from CDs gradually shifted to higher wavelengths accompanied with decreased fluorescence intensity. This red shift of emission from CDs has also been reported previously by us and other groups. It was observed that excitation at 380, 390, 400, 410, 420, 430, 440, 450 and 460 nm resulted in emission at 458, 461, 465, 471, 476, 484, 490, 498 and 511 nm, respectively.

As far as the PL mechanism of CDs is concerned it is believed that both the quantum size effect and surface defects contribute to PL. The inset in Fig. 1A shows photograph of CDs solution when viewed under normal light and UV lamp. The particle size of CDs was determined by dynamic light scattering (DLS) measurement. The DLS data showed the average particle sizes of CDs are ~ 8.3 nm.

The zeta potential of CDs was determined to be 29 mV indicating the positive charge on the CDs.

Capping of CDs was carried out using β -cyclodextrin (β -cd) and calix[4] arene-25,26,27,28-tetrol (C[4]A). Representative SEM image of β -cd capped CDs is shown in Fig. 1D. SEM image of C[4]A capped CDs is shown and discussed in Supplementary material (Fig. S2). It is evident from the SEM images that particle size of CDs becomes bigger after capping. The increased particle size of CDs after capping with β -cd and C[4]A was also confirmed by DLS measurement. The size of CDs after capping with β -cd and C[4]A was also determined by DLS.

The DLS data is shown in Supplementary material. The average size of CDs after capping with β -cd and C[4]A was determined to be ~ 44 nm and ~ 83.6 nm, respectively (Fig. S1, Supplementary material). It was observed that the PL intensity decreased with capping of CDs.

Fig. 2A shows the photoluminescence (PL) spectra of CDs capped with β -cyclodextrin (β -cd) and calix[4] arene-25,26,27,28-tetrol (C[4]A) and excited at 380 nm. The emission spectrum clearly shows that there is decrease in the fluorescence intensity (quenching) after capping with both β -cd and C[4]A. While excitation at 380 nm resulted in emission of 457 nm with bare carbon dots (CDs), CDs capped with β -cyclodextrin (β -cd) and calix[4]arene-25,26,27,28-tetrol (C[4]A) showed emission at 462 nm and 461 nm, respectively. The respective fluorescence quantum yields for CDs, CDs/ β -cd and CDs/C[4]A were determined using quinine sulfate in water as the reference standard. While the CDs showed a quantum yield value of 30.6%, the value was decreased to 23.2% after capping with β -cd and further to 21.066% after capping with C[4]A. We tried to study the interactions of the capping agents used i.e. β -cyclodextrin and calix-4-arene-25,26,27,28-tetrol to the carbon dots. For this we determined the association constants of the capping agents used to the carbon dots by using UV–visible spectroscopy for the titration experiments (Thordarson, 2011) (detailed procedure and graphs in Supplementary material, Fig. S4). From these experiments the association constants of β -cyclodextrin and

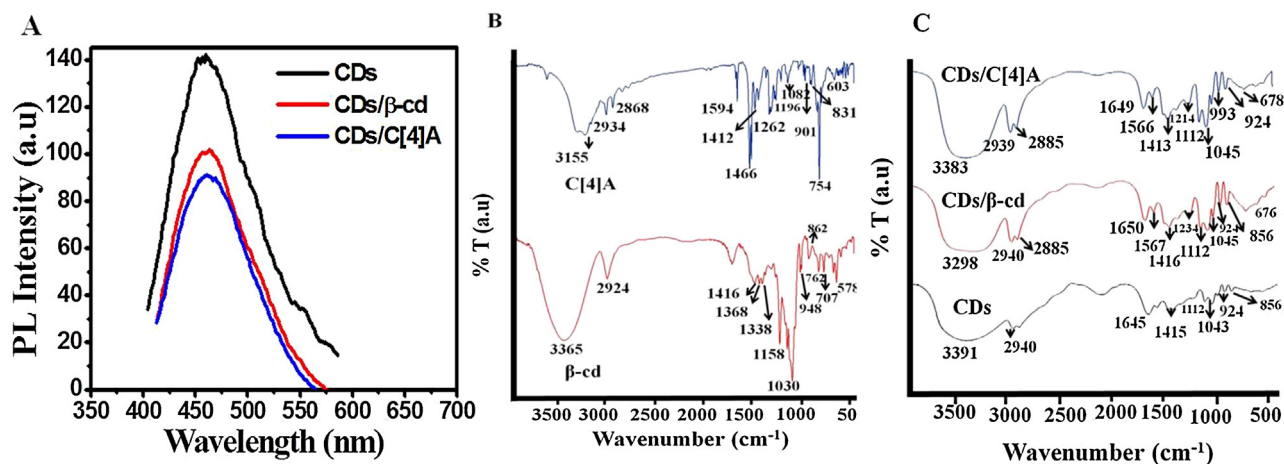


Fig. 2. (A) Photoluminescence emission spectra of carbon dots (CDs), CDs/β-cd and CDs/C[4]A at excitation wavelengths of 380 nm. (B) Stacked FTIR spectra of β-cyclodextrin and calix[4]arene-25,26,27,28-tetrol. (C) Stacked FTIR spectra of CDs, CDs/β-cd and CDs/C[4]A.

calix-4-arene-25,26,27,28-tetrol to the carbon dots were found to be 1.0014 M^{-1} and 0.988 M^{-1} , respectively. From the same plot concentration of capping agent used i.e. β-cyclodextrin and calix-4-arene-25,26,27,28-tetrol at the point of saturation were determined to be 0.44 mM and 0.32 mM, respectively. From the concentration, percentage loading of β-cd and C[4]A were determined to be 63.28% and 61.34%, respectively. CDs capped with β-cyclodextrin (CDs/β-cd) and calix[4] arene-25,26,27,28-tetrol (CDs/C[4]A) were also characterized by FTIR. Fig. 2B shows the FTIR of β-cyclodextrin and calix[4]arene-25,26,27,28-tetrol. The frequencies for β-cd observed at 3365 cm^{-1} , 2924 cm^{-1} , 1158 cm^{-1} , 1338 cm^{-1} and 1045 cm^{-1} correspond to the symmetric and anti-symmetric stretching of —OH , CH_2 , C—C , C—O and bending vibration of O—H , respectively. The main peaks of C[4]A include stretching vibration at 3155 cm^{-1} (—OH) and 1650 (aromatic C=C).

Fig. 2C shows the stacked FTIR spectrum of CDs/β-cd and CDs/C[4]A plotted together with bare CDs. The presence of main peak 1650 cm^{-1} of aromatic C=C in CDs/C[4]A along with other peaks of CDs shows the successful capping of the carbon dots (CDs) with C[4]A. Similarly CDs/β-cd has all the peaks of β-cd mostly the common peaks of —OH , —CH_2 — and C—C are present both in β-cd and CDs. The FTIR spectrum of CDs shows broad 3400 cm^{-1} peak due to —OH and —NH_2 of chitosan present in CDs, 2940 cm^{-1} and 2881 cm^{-1} due to H—C—H asymmetric and symmetric stretch. Peaks at 1415.64 and 1645 cm^{-1} arise due to presence of —CH_2 deformation and N—H bending, respectively.

Detection of fluoride was studied through the fluorescence emission properties of CDs/β-cd and CDs/C[4]A. Fig. 3A shows the stacked photoluminescence (PL) spectra of CDs, after capping with β-cd and addition of fluoride. It is evident from the spectrum

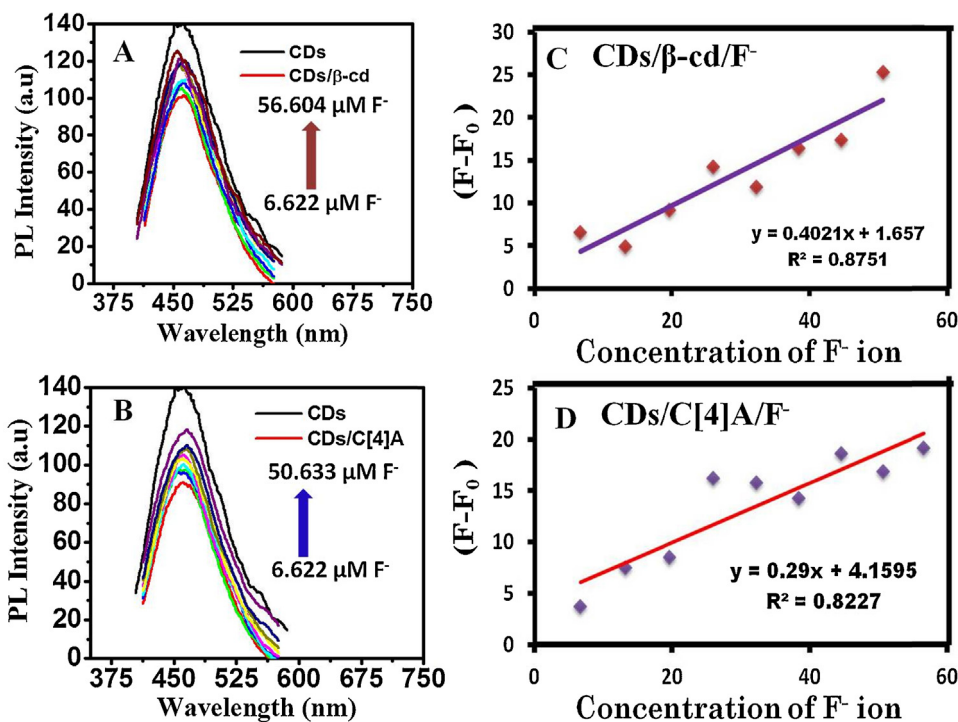


Fig. 3. Photoluminescence emission spectra of (A) CDs/β-cd and (B) CDs/C[4]A at different concentration of fluoride. (C) and (D) Linear curve fitting of the donor fluorescence intensity against different concentrations of fluoride. F_0 and F are the fluorescence intensity of CDs/β-cd or CDs/C[4]A at 380 nm in absence and presence of fluoride ion, respectively.

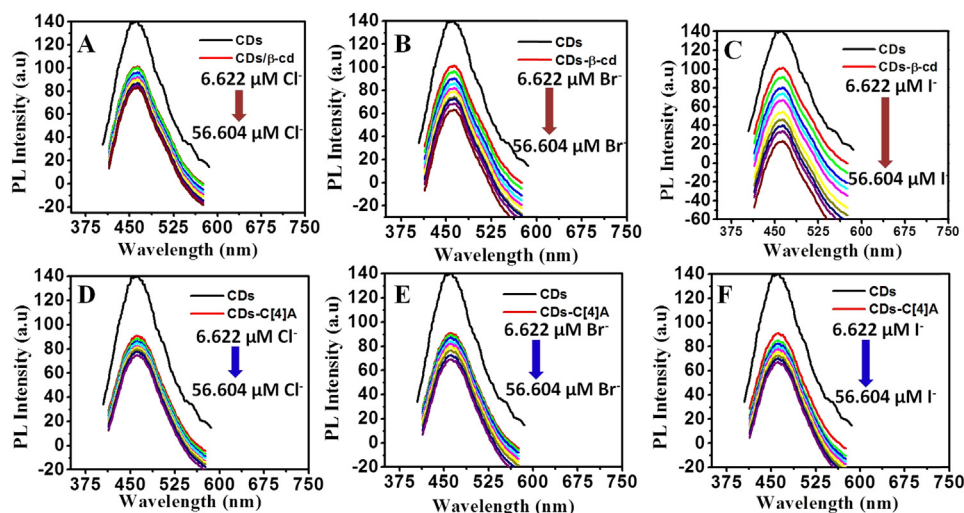


Fig. 4. Photoluminescence emission spectra of CDs/β-cd with different concentration of (A) chloride ion (Cl⁻), (B) bromide ion (Br⁻) (C) iodide ion (I⁻) and CDs/C[4]A with different concentration of (D) chloride ion (Cl⁻), (E) bromide ion (Br⁻) (F) iodide ion (I⁻).

that addition of fluoride results in gradual increase in emission intensity. It is clear from the plot that the fluorescence intensity increases in the concentration range 6.6–56.6 μM. The linear curve fitting of the donor fluorescence intensity against concentration of fluoride ion is shown in Fig. 3C. Similar behaviour in fluorescent intensity is observed for calix[4] arene-25,26,27,28-tetrol capped carbon dot system. Fig. 3B shows the stacked photoluminescence (PL) spectra of CDs, after capping with C[4]A and addition of fluoride. PL emission spectrum shows gradual increase in emission intensity on addition of fluoride. The plot shows that fluorescence intensity increases in linear fashion in concentration range 6.6–50.6 μM. The corresponding linear curve fitting obtained of the

donor fluorescence intensity against concentration of fluoride ion is shown in Fig. 3D. Similarly, as for the capping agents the association constants for binding of fluoride to the capped carbon dot systems were also determined by UV–visible spectroscopy. (detailed procedure and graphs in Fig. S5, Supplementary material). The values of association constants for binding of fluoride to CDs/β-cd and CDs/C[4]A were found to be 1.004 M⁻¹ and 0.730 M⁻¹, respectively.

It is essential to observe the selectivity of (CDs/β-cd) and (CDs/C[4]A) towards fluoride. Therefore PL emission properties of (CDs/β-cd) and (CDs/C[4]A) were studied in presence of other halide ions (Cl⁻, Br⁻, I⁻) and also in presence of OH⁻ (Fig. S3 Supplementary material). Fig. 4A shows the stacked photoluminescence

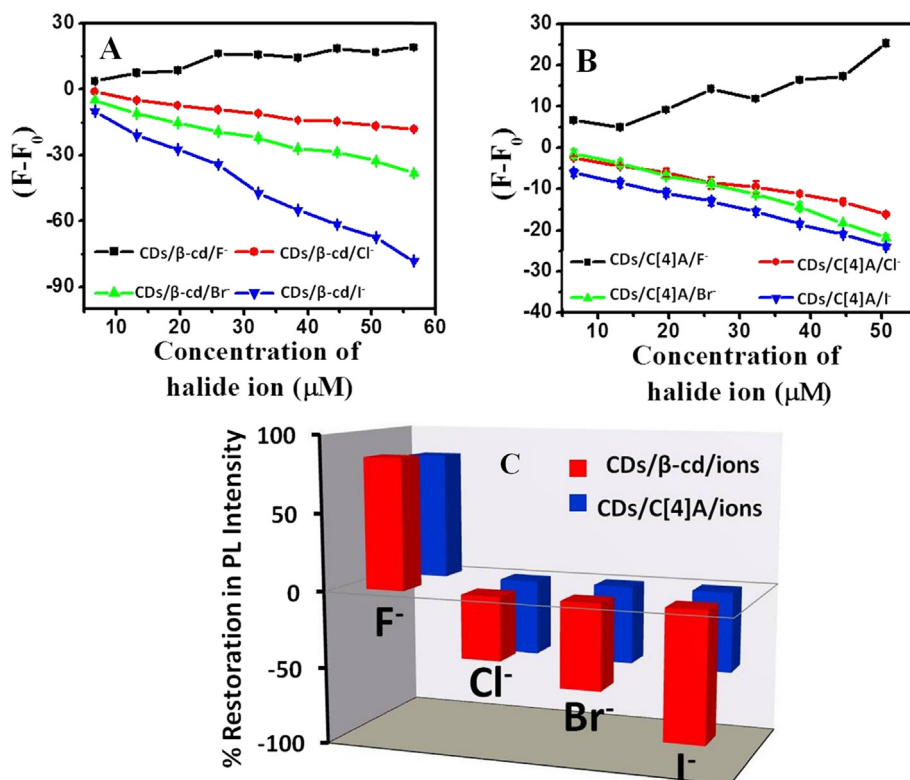


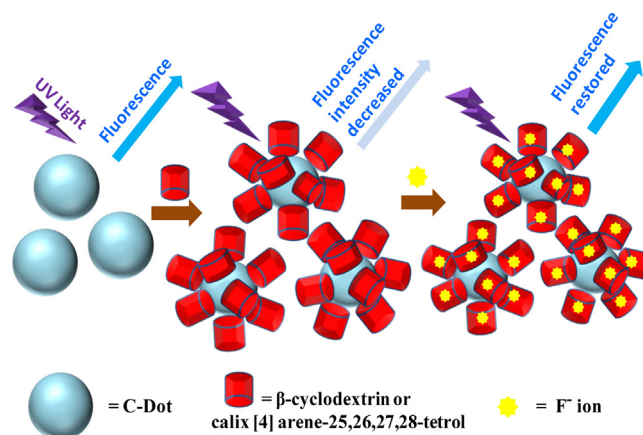
Fig. 5. Comparison plot of the donor fluorescence intensity against different concentration of Fluoride ion (F⁻), Chloride ion (Cl⁻), Bromide ion (Br⁻) and Iodide ion (I⁻) for (A) CDs/β-cd and (B) CDs/C[4]A. (C) Histogram plot of effect of different analytes (F⁻, Cl⁻, Br⁻, I⁻) on fluorescence intensity of CDs/β-cd and CDs/C[4]A.

(PL) spectra of CDs/ β -cd in the presence of different concentration of Cl^- . It is quite evident from the spectrum that presence of increased concentration of Cl^- (6.6–56.6 μM) results in quenching and hence decrease in PL intensity. Fig. 4B shows the stacked photoluminescence (PL) spectra of CDs/ β -cd in the presence of different concentration of Br^- . In this case too PL spectra depict that increased concentration of Br^- results in quenching and hence decrease in PL intensity. The PL spectra were monitored in the presence of 6.6–56.6 μM of Br^- . Fig. 4C shows the stacked photoluminescence (PL) spectra of CDs/ β -cd in the presence of different concentration of I^- . With I^- there is increased quenching of the PL intensity. It is observed that the PL quenching of CDs is maximum with I^- . Iodide has an intrinsic fluorescence quenching nature due to the heavy atom effect based on which a number of fluorescence turn-off probes for iodide have already been reported before (Du, Zeng, Ming, & Wu, 2013). Similarly Fig. 4D–F shows the stacked photoluminescence (PL) spectra of CDs/C[4]A in the presence of different concentration of Cl^- , Br^- and I^- , respectively. Fig. 5 shows the comparison plots of donor fluorescence intensity against different concentrations of halide ions added for (A) CDs/ β -cd and (B) CDs/C[4]A. The plot brings out the distinction in the PL emission intensity changes for different halides. While there is increase in PL intensity with F^- , there is observed gradual decrease in PL intensity of both the systems in the presence of Cl^- , Br^- and I^- .

It is evident from the histogram plot of effect of different halides F^- , Cl^- , Br^- , I^- on fluorescence intensity of CDs/C[4]A and CDs/ β -cd (Fig. 5C), in the presence of other halide ions viz. Cl^- , Br^- , I^- there is decrease (quenching) in PL intensity. The plot demonstrates the selectivity of β -cd capped CDs (CDs/ β -cd) and C[4]A capped CDs exclusively towards F^- ion. The corresponding restoration of fluorescence intensities after addition of fluoride ions to both the systems viz. CDs/ β -cd and CDs/C[4]A and the corresponding decrease on addition of the other halide ions are tabulated in Table 1(A) for CDs/ β -cd and in Table 1(B) for CDs/C[4]A.

We want to mention here that a blank experiment was also performed to confirm the role of β -cd and C[4]A capped CDs in sensing of F^- ion. Fig. S6, Supplementary Material shows decrease of fluorescence intensity upon introduction of F^- ion on bare CDs. In fact bare CDs also show decrease in fluorescence intensity with other halide ions viz. Cl^- , Br^- and I^- (detail Fig. S6B–D, Supplementary Material). This demonstrates the selectivity of CDs/ β -cd and CDs/C[4]A towards detection of F^- ion.

The PL emission in CDs is due to recombination of photo-generated electron-hole pairs, which takes place predominantly on the surface of the CDs. In general it has been suggested that the interaction of molecules and ions with the surface atoms of the nanocrystal can affect the efficiency of the recombination of



Scheme 1. Mechanistic view of the proposed CD/ β -cd/ F^- and CD/C[4]A/ F^- complex formation resulting in enhancement in PL intensity used for detection of F^- ion.

electron-hole. Among the quenching mechanisms are inner filter effects, non-radiative recombination pathways and electron transfer processes, whereas enhancement of photoluminescence has been attributed primarily to passivation of trap states in the surface (Chen, Yu, Zhou, & Zhong 2004; Chen & Rosenzweig, 2002; Freeman, Finder, Bahshi, & Willner, 2009; Gattas-Asfura & Leblanc, 2003; Touceda-Varela et al., 2008). In our case when surface modification is carried out (i.e. capping of CDs) emission quenching is observed which can be attributed to non-radiative recombination pathway. In the presence of F^- , the F^- ion enters the cavity of β -cd and C[4]A resulting in the formation of β -cd/ F^- and C[4]A/ F^- as a result enhancement in emission intensity is observed which may be correlated to the structural changes of the capped carbon dot upon addition of F^- . This might lead to the generation of a new and efficient radiative path (Han & Haibing, 2008) involving the bound β -cd/ F^- and C[4]A/ F^- and results in the suppression of a non-radiative process as shown in Scheme 1.

4. Conclusion

In summary, in this work we have demonstrated a simple fluorescence based technique to detect selectively fluoride ion in μM concentration using cyclodextrin capped carbon dots and calix[4]arene-25,26,27,28-tetrol capped carbon dots. Such capped carbon dots viz. (CDs/ β -cd) and (CDs/C[4]A) show increased PL intensity exclusively in the presence of F^- . Minimum detection limit was determined to be $\sim 6.6 \mu\text{M}$. The present study will help in the development of fluorescence based sensors especially of anions as these techniques are still attracting great interest as a means to the development of optical sensors and intracellular probes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbpol.2014.09.083>.

Table 1

The restoration of fluorescence intensities after addition of fluoride ions and the corresponding decrease on addition of the other halide ions (A) for CDs/ β -cd and (B) for CDs/C[4]A.

A		
System	Ion	% Restoration of PL intensity
CDs/ β -cd	F^-	85.26
	Cl^-	−41.28
	Br^-	−55.50
	I^-	−83.90
B		
System	Ion	% Restoration of PL intensity
CDs/C[4]A	F^-	82.62
	Cl^-	−49.09
	Br^-	−51.14
	I^-	−52.46

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