Excimer Probes



# An Anthracene Excimer Fluorescence Probe on Mesoporous Silica for Dual Functions of Detection and Adsorption of Mercury (II) and Copper (II) with Biological In Vivo Applications

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Dual functional activity by the same organic-inorganic hybrid material toward selective metal ion detection and its adsorption has drawn more attraction in the field of sensing. However, most of the hybrid materials in the literature are either for sensing studies or adsorption studies. In this manuscript, a fluorescent active hybrid material SiO<sub>2</sub>@PBATPA is synthesized by covalent coupling of anthracene-based chelating ligand N,N'-(propane-1,3-diyl) bis(N-(anthracen-9-ylmethyl)-2-((3-(triethoxysilyl)propyl) amino) acetamide) (PBATPA) within the mesopores of newly synthesized cubic mesoporous silica. The synthetic strategy is designed to form an exclusively intramolecular excimer on a solid surface, which is then used as a sensory tool for selective detection of metal ions through fluorescence quenching by the destruction of excimer upon metal ion binding. The dual functions of sensing and adsorption studies show selectivity toward Hg<sup>2+</sup> and Cu<sup>2+</sup> among various metal ions with detection limits of 37 and 6 ppb, respectively, and adsorption capacities of 482 and 246 mg g<sup>-1</sup>, respectively. This material can be used as a sensory cum adsorbent material in real food samples and living organisms such as the brine shrimp Artemia salina without any toxic effects from the material.

## 1. Introduction

Metal ion toxicity is a well-known environmental issue and possesses a challenge for their early detection and removal. With increasing metal based industrial activity, these metal ions most often present in the industrial effluents and finally enters into the food chain system, threatening human health and the ecosystem.<sup>[1]</sup> Though copper is considered as one of the essential transition metal ion required for various metabolic functions, but could be toxic to human health and

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microorganisms when overused. Therefore, it is also present in the U.S. Environmental Protection Agency's (EPA's) list of priority pollutants considering its hazardous nature.<sup>[2]</sup> The recommended level of intake of Copper is limited to 1.3 mg per day by the World Health Organization (WHO). But Mercury and its compounds are highly toxic, dangerous and can cause many serious diseases.<sup>[3]</sup> The Minamata disease resulted in a disastrous effect in Minamata Bay of Japan due to accumulation methylmercury.<sup>[4]</sup> Owing to the adverse effects of Mercury, the threshold limits in drinking water have limited to 2  $\mu$ g L<sup>-1</sup> by WHO. Therefore, simultaneous detection and removal of toxic metal ions from the aqueous system have gained more attention due to their serious impact on environmental remediation.<sup>[5]</sup> In this regard, many organic-inorganic hybrid materials got more importance over organic probes only as they can be easily recycled and devoid of any dissolu-

tion issues as compared to many organic fluorescence probes. Also, the same organic molecule cannot be used for both purposes as sensory probes need hydrophilic motif whereas, an extractant needs hydrophobic motif. Because of the possibility of these dual functional activities by the same functionalized material, they have attracted more attention over sensory probes only. Therefore, many mesoporous solid supports bearing fluorogenic organic motif with appropriate binding sites are used to achieve both sensory and adsorption properties simultaneously. The various properties of Silica such as easiness for chemical modification, good thermal and chemical stability, large surface area, and tunable pore sizes makes it an attractive candidate for solid support.<sup>[6]</sup> The fluorogenic chelating motif is the recognition unit responsible for the selective metal ion recognition and binding. Among various polyaromatic fluorophores, anthracenes are one of the important blue fluorescent materials that display well-defined monomer and excimer emissions.<sup>[7]</sup> Although traditional cognition on excimer as fluorescence quencher is different from recent views as efficient fluorescence materials observed in several cases with red-shifted emission spectra and long lifetimes compared to their monomers.<sup>[8]</sup> Owing to the above advantages, excimers has drawn attraction of scientific researchers due to their significant roles in chemo- and biosensors and

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white OLED.<sup>[9]</sup> The photophysical properties due to excimer formation or destruction upon complexation is a detection tool most often used for sensory applications.<sup>[10]</sup> As the conformational changes of the receptor have a profound effect on intensity ratio of excimer to monomer emission  $(I_{\rm F}/I_{\rm M})$ , they can be instrumental as sensory probe material for metal ion detection and biological molecules.<sup>[11]</sup> Though excimer formation by anthracene is a well-known process in solution<sup>[12]</sup> but relatively rare on nanoporous solid surfaces<sup>[13]</sup> as compared to pyrene and naphthalene.<sup>[14]</sup> In the case of pyrene, it is also documented that ground-state pairing leads to static excimer emission when attached to silica surface even at low surface coverages.<sup>[15]</sup> It is also well known that intramolecular excimer formation is desirable as compared to intermolecular excimer formation for sensory applications.<sup>[16]</sup> It is also documented that intramolecular excimer formation of diphenylalkanes (Ph- $(CH_2)n$ -Ph) is possible if n = 3, though this may not be held so rigorously.<sup>[17]</sup>

Considering the above facts about excimer formation, we were interested in taking advantage of intramolecular excimer formation on a solid surface as a sensory tool for simultaneous applications of metal ion detection and removal as part of our research interest. Therefore, we synthesized mesoporous cubic SiO<sub>2</sub> as the solid support through a sol–gel technique in the presence of tetraethyl orthosilicate (TEOS), NH<sub>3</sub>, and hexadecyltrimethylammonium bromide (CTAB), following a modified procedure.<sup>[18]</sup> Then we have successfully fabricated a new anthracene-based receptor N,N'-(propane-1,3-diyl) bis(N-(anthracen-9-ylmethyl)-2-((3-(triethoxysilyl)propyl) amino) acetamide) (PBATPA) (with two anthracene motifs at 1,3

position of 1,3-diaminopropane) on the mesoporous silica surface to get the final material (SiO<sub>2</sub>@PBATPA). This fluorogenic material shows excimer based emissions used for dual functions of selective detection and adsorption of  $Hg^{2+}$  and  $Cu^{2+}$  ions in the presence of various metal ions. This strategy can be helpful in tuning the emission of the probe material as observed here from blue (monomer) to green (excimer) for need-based applications. As an application, this material can be used as a fluorescence probe for detection of the above metal ions in the living organism like *Artemia salina* as a biological platform.

To best of our knowledge, this material represents a rare example of anthracene derived heterogeneous excimer-based sensory probe for  $Hg^{2+}$  and  $Cu^{2+}$  which can be used as a probe in living organisms without any toxicity. This material also can detect and adsorb the above toxic metal ions in real food samples. Therefore, the dual functional activity of selective detection and removal by the same material with recyclability of the material represent an ideal remediation system.

## 2. Results and Discussion

### 2.1. Synthesis and Characterization

The synthetic procedure for the material  $SiO_2$ @PBATPA is expressed in **Scheme 1**, and the details are explained in the Experimental Section. The mesoporous silica was synthesized by a modified method using CTAB as structure



Scheme 1. Synthetic scheme for mesoporous silica, ligand PBATPA, and final probe material SiO<sub>2</sub>@PBATPA.







**Figure 1.** A,B) FESEM images cubic SiO<sub>2</sub>; C,D) FESEM images of cubic SiO<sub>2</sub>@PBATPA; E) low angle and broad angle PXRD of SiO<sub>2</sub>, and SiO<sub>2</sub>@ PBATPA; F) N<sub>2</sub> adsorption/desorption isotherms of SiO<sub>2</sub>, SiO<sub>2</sub>@NH<sub>2</sub>, and SiO<sub>2</sub>@PBATPA.

directing template. The surface modification of above cubic mesoporous silica was done by two synthetic approaches [cubic SiO<sub>2</sub> $\rightarrow$  SiO<sub>2</sub>@NH<sub>2</sub> $\rightarrow$  SiO<sub>2</sub>@PBATPA (steps A and B) or cubic SiO<sub>2</sub> $\rightarrow$  SiO<sub>2</sub>@PBATPA (step F)]. In the latter method, the ligand ATPAA was synthesized first and then fabricated to confirm the formation of same product SiO2@PBATPA through various characterization data. In this work, the product from the first approach was used for most of the studies. The reason for synthesizing ligand PBATPA first in the second approach is to understand the complexation behavior of the ligand toward metal ions through mass spectral analysis discussed later. The final material SiO2@PBATPA was characterized through various analytical techniques like scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), solid state <sup>13</sup>C NMR, <sup>29</sup>Si NMR, Fourier transform infrared spectroscopy (FT-IR), and Brunauer-Emmett-Teller (BET) surface measurements.

#### 2.1.1. Structural Characterization

Structural characterization of cubic mesoporous silica  $(SiO_2)$ and final SiO<sub>2</sub>@PBATPA material carried out through low angle PXRD, SEM, TEM, and N<sub>2</sub> adsorption-desorption isotherms. The SEM images of both silica  $(SiO_2)$  (**Figure 1**A,B) and  $SiO_2$ @ PBATPA material (Figure 1C,D) shows cubic morphology with uniform particle sizes in the range of 280–350 nm. In case of the SiO<sub>2</sub>@PBATPA material, surfaces are quite irregular indicating that functionalization of the ligand on the SiO<sub>2</sub> surface. The broad angle PXRD patterns of cubic silica (SiO<sub>2</sub>) and the functionalized material (Figure 1E) shows the similar broadband at  $2\theta = 22^{\circ}$  indicating the amorphous nature of both materials.<sup>[19]</sup> Low angle PXRD patterns of both the materials (Figure 1E) shows a strong diffraction peak at  $2\theta = 1.55^{\circ}$ , and three weak diffraction peaks at  $2\theta = 3.99^\circ$ , 5.68°, and 6.65° with the corresponding crystal plane d-spacing of 5.67, 2.21, 1.55, and 1.32 nm, respectively. The low angle strong diffraction peak indicates the porous nature of synthesized materials. To investigate the BET surface area, pore size distribution (PSD), and pore volume for the cubic SiO<sub>2</sub> particle, SiO<sub>2</sub>@NH<sub>2</sub>, and SiO<sub>2</sub>@PBATPA, N<sub>2</sub> adsorption-desorption experiment carried out (Figure 1F; Table 1). It is observed that cubic  $SiO_2$  and SiO<sub>2</sub>@NH<sub>2</sub> exhibit type-IV isotherm which is the characteristic of the mesoporous material.<sup>[20]</sup> On the other hand, for material SiO<sub>2</sub>@PBATPA, the isotherm devoid of any capillary condensation, as observed for type-I isotherm, suggesting a decrease in pore size after functionalization. The various physicochemical parameters such as BET surface area, pore size distribution, and pore volume (Figure S1, Supporting Information) gradually decreases from cubic SiO<sub>2</sub> (927 m<sup>2</sup> g<sup>-1</sup>, 0.8884 cm<sup>3</sup> g<sup>-1</sup>, 3.8 nm)

 Table 1. Surface areas, pore volumes, and pore diameters of the synthesized materials.

Material	Surface area [m <sup>2</sup> g <sup>-1</sup> ]	Pore volume [cm <sup>3</sup> g <sup>-1</sup> ]	Pore diameter [nm]
SiO <sub>2</sub>	927.48	0.8884	3.8
SiO <sub>2</sub> @NH <sub>2</sub>	385.59	0.3933	3.3
SiO <sub>2</sub> @PBATPA	4.20	0.0667	1.1





Figure 2. A-C) TEM images of cubic SiO<sub>2</sub>; D-F) TEM images of cubic SiO<sub>2</sub>@PBATPA material.

to SiO<sub>2</sub>@NH<sub>2</sub> (385 m<sup>2</sup> g<sup>-1</sup>, 0.3933 cm<sup>3</sup> g<sup>-1</sup>, 3.3 nm) to SiO<sub>2</sub>@ PBATPA (4.20 m<sup>2</sup> g<sup>-1</sup>, 0.0667 cm<sup>3</sup> g<sup>-1</sup>, 1.11 nm) respectively, clearly suggest that functionalization happened inside the mesopores.<sup>[21]</sup>

The TEM images of SiO<sub>2</sub> and SiO<sub>2</sub>@PBATPA materials (Figure 2) are also in good agreement with similar morphological observations in SEM studies with particle sizes of 250–340 nm. As the pore size decreases from nanopores (3.8 nm) in cubic SiO<sub>2</sub> to micropores (1.11 nm) in SiO<sub>2</sub>@PBATPA, the pores are not visible in the TEM image of SiO<sub>2</sub>@PBATPA and are also in good compliance with pore size distribution studies from N<sub>2</sub> adsorption–desorption experiment.

#### 2.1.2. Surface Characterization

Surface characterization of final SiO<sub>2</sub>@PBATPA material carried out through FT-IR, solid-state <sup>13</sup>C CP (MAS), and <sup>29</sup>Si NMR spectrum, and TGA. FT-IR spectrum for SiO<sub>2</sub> (**Figure 3**A) displays bands at 3432, 1640, 1062, and 793 cm<sup>-1</sup> while SiO<sub>2</sub>@NH<sub>2</sub> shows bands at 3438, 2930, 2880, 1631, 1560, 1327, 1062, 793, and 694 cm<sup>-1</sup>. The additional peaks at 694, 1631, and 1560 cm<sup>-1</sup> due to N–H stretching and bending vibrations<sup>[22]</sup> are observed for the SiO<sub>2</sub>@NH<sub>2</sub>, whereas the extra bands at 1489, 2930, and 2880 cm<sup>-1</sup> is from the (3-Aminopropyl) triethoxysilane (APTES) group<sup>[23]</sup> assigned for the C–H stretching and bending

vibrations. The band at 1327 cm<sup>-1</sup> is for C–N vibration of alkyl amine.<sup>[24]</sup> Comparison of FT-IR spectra of SiO<sub>2</sub>@NH<sub>2</sub> and SiO<sub>2</sub>@PBATPA material (Figure 3B) reveals some similar bands at 1062, 793, 2930, and 2880 cm<sup>-1</sup> due to Si–O–Si, Si–OH, and –C–H vibration of –(CH<sub>2</sub>)<sub>3</sub>– groups respectively. The additional bands at 1665 and 1580 cm<sup>-1</sup> found in material SiO<sub>2</sub>@PBATPA due to the existence of "C=O" stretching of the amide group and NH deformation vibration respectively.<sup>[25]</sup> The above results provide strong evidence in favor of covalent attachment of ligand PBATPA on the silica surface.

To further confirm the formation of SiO<sub>2</sub>@PBATPA material, both solid state <sup>29</sup>Si CP (MAS) and <sup>13</sup>C CP (MAS) NMR studies were done. Both the materials SiO<sub>2</sub>@NH<sub>2</sub> and SiO<sub>2</sub>@ PBATPA shows three peaks at 12, 24, and 45 ppm in <sup>13</sup>C CP (MAS) NMR spectrum (**Figure** 4A) which can be assigned to three methylene groups,  $-(CH_2)_3-.^{[26]}$  Some additional peaks between 92–162 and 180 ppm in SiO<sub>2</sub>@PBATPA are due to the presence of arene and carbonyl carbons, respectively.<sup>[27]</sup> The <sup>29</sup>Si CP (MAS) NMR (Figure 4B) shows  $Q_n$  type signals (-94, -102, -110 ppm) for silanol group in all the three compounds and  $T_n$  type signals (-50 to -70 ppm) for SiO<sub>2</sub>@NH<sub>2</sub> and SiO<sub>2</sub>@PBATPA due to silicon atoms of the organic linker 3-APTES.<sup>[28]</sup>

The loading of the organic motif on cubic silica surface was studied by TGA measurements. The TGA of  $SiO_2@NH_2$  and  $SiO_2@PBATPA$  (Figure 5) show three weight loss regions



**Fransmittance** %

3438 Si-OH



4000 3500 3000 2500 2000 1500 1000 500 4000 3500 3000 2500 2000 1500 1000 500 Wavenumber (cm<sup>-1</sup>) Wavenumber (cm<sup>-1</sup>)

Figure 3. A) Comparison of FT-IR spectra of SiO<sub>2</sub> and SiO<sub>2</sub>@NH<sub>2</sub>; B) SiO<sub>2</sub>@NH<sub>2</sub> and SiO<sub>2</sub>@PBATPA.

between 33-218, 218-440, and 440-800 °C. The foremost regions show a weight loss of -17.29% and -11.92% in SiO<sub>2</sub>@ NH2 and SiO2@PBATPA, respectively, owing to desorption of physically adsorbed aqueous molecule on the surface of the materials. The higher value with the SiO<sub>2</sub>@NH<sub>2</sub> is probably due to the existence of hydrophilic NH2 groups which leads to more water adsorption.<sup>[29]</sup> The weight loss of the second region showing -16.18% in SiO<sub>2</sub>@PBATPA material compared to -2.41% in SiO<sub>2</sub>@NH<sub>2</sub> due to more organic content in SiO<sub>2</sub>@ PBATPA material. The last regions show similar weight losses for both the materials SiO<sub>2</sub>@NH<sub>2</sub> (-6.42%) and SiO<sub>2</sub>@PBATPA (-6.63%) due to the destruction of organosilicate frameworks.

#### 2.2. Sensing Studies

To determine the working pH condition with this material for sensing and adsorption studies, the UV-Vis absorption studies were done in the pH range of 2-10 in aq. buffer medium to know the stability of the material. It is observed that this material shows its original absorption bands in the pH range of 5–10 but in the lower pH range (2–5), a new band at 300 nm appears due to protonation of NH groups at ligand sites (SiO<sub>2</sub>@PBATPA-H<sup>+</sup>) (Figure 6A). As the materials surface charges sensitive to the pH of the suspension which also affects adsorption capacities, the zeta potential at different pH ranges were evaluated (Figure 6B). It is observed that though zeta potential does not change much from neutral to higher pH range but a more positive value was observed at lower pH range owing to protonation of ligand motif in the material.<sup>[30]</sup> Though the material is stable at higher pH, considering the formation of metal hydroxides at higher pH range (>8), the neutral pH (≈7; Na<sub>2</sub>HPO<sub>4</sub>: NaH<sub>2</sub>PO<sub>4</sub>) was considered for all analytical and adsorption studies.

To examine the sensing ability of material toward various metal ions both UV-Vis and fluorescence investigations were done in the aqueous buffer system at pH 7 (Na<sub>2</sub>HPO<sub>4</sub>:NaH<sub>2</sub>PO<sub>4</sub>). The UV–Vis spectrum of SiO<sub>2</sub>@PBATPA material shows three typical peaks of anthracene moiety<sup>[31]</sup> at 354, 375, and 395 nm along with peaks at 254 and 268 nm. In the presence of  $Cu^{2+}$  and  $Hg^{2+}$  metal ions, the anthracene peaks remain intact, but the peak position at lower wavelength



Figure 4. A) <sup>13</sup>C solid CP NMR for SiO<sub>2</sub>@NH<sub>2</sub> and SiO<sub>2</sub>@PBATPA; B) <sup>29</sup>Si CP (MAS) NMR of SiO<sub>2</sub> SiO<sub>2</sub>@NH<sub>2</sub>, and SiO<sub>2</sub>@PBATPA.

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Figure 5. TGA of  $SiO_2@NH_2$  and  $SiO_2@PBATPA$  material.

got shifted with increasing in absorbance (Figure 7A). But no changes were observed with all other metal ions (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, and  $Cd^{2+}$ ). Likewise, the fluorescence spectra of suspended SiO<sub>2</sub>@ PBATPA (0.5 mg/2 mL) in aqueous buffer medium shows characteristic monomeric peaks at 445, 417, and 395 nm ( $\lambda_{em}$ ) and a strong excimer emission band at 510 nm ( $\lambda_{em}$ ) upon excitation at 395 nm ( $\lambda_{ex}$ ) (Figure 7B). The band at 510 nm probably due to an intramolecular excimer formation ( $\pi$ - $\pi$  stacking of aromatics) whose intensity ratio ( $I_{\text{excimer}}/I_{\text{monomer}} = 1.17-1.07$ ) does not change much with concentration variation as shown in Figure 7C.<sup>[10c,e]</sup> After addition of Cu<sup>2+</sup> and Hg<sup>2+</sup> ions  $(100 \times 10^{-6} \text{ M})$  to a suspension of SiO<sub>2</sub>@PBATPA, both the monomeric and excimer peak quenched dramatically with a more pronounced effect on the latter whereas no drastic changes were observed with other relevant metal ions (Figure 7B). Though solid surface appended anthracene-based hybrid materials are known in the literature, but excimer formation is not

observed in these cases.<sup>[32]</sup> Though only a few reports on such systems with excimer formation is known but never used as a sensory tool for detection of metal ions.<sup>[13]</sup> In our case due to the presence of two anthracene motifs at 1,3 position leads to a ground-state pairing to exhibit excimer emission.

To determine the Stern–Volmer quenching constant  $(K_{sv})^{[33]}$ of SiO<sub>2</sub>@PBATPA material toward metal ions (Hg<sup>2+</sup>, Cu<sup>2+</sup>) fluorescence titration was done with the incremental addition of these metal ions into the aqueous suspended solution of SiO<sub>2</sub>@PBATPA material with a saturation concentration of  $100 \times 10^{-6}$  M (Figure 8A,D). The Stern–Volmer plots of both metal ions ( $Hg^{2+}$ ,  $Cu^{2+}$ ) shows a straight line with linear fitting (Figure 8B,E), which indicates a static mechanism<sup>[5a,e]</sup> where the quencher (metal ions) binds the fluorophore in the ground state forming a nonfluorescent complex, also in good agreement with UV-Vis spectral changes. More details about fluorescence sensing mechanism of SiO2@PBATPA material toward these metal ions are discussed later in probable mechanism section. Considering a linear fitting, a linear Stern-Volmer equation  $F_0/F = 1 + K_{sv}$  [Mn<sup>+</sup>] was used. In this equation,  $F_0$  represents the original fluorescence intensity of material SiO<sub>2</sub>@PBATPA, and F is the final fluorescence intensity of material after the addition of increment amount of metal ions (Hg<sup>2+</sup> and Cu<sup>2+</sup>),  $K_{sv}$  is the Stern–Volmer constant which is the slope of linear plot found to be  $1.2563 \times 10^4$  and  $1.5332 \times 10^4$  M<sup>-1</sup>, respectively. To determine the limit of detection (LOD)<sup>[5a,e]</sup> for Hg<sup>2+</sup> and Cu<sup>2+</sup> ions, incremental addition of low concentrations (1  $\times$  10<sup>-6</sup>–5  $\times$  $10^{-6}$  M) of above metal ions to the aqueous suspension of SiO2@PBATPA material were made in deionized water at  $pH \approx 7$  and the fluorescence quenching was recorded (Figure S2, Supporting Information). The LOD calculations for the metal ions (Hg<sup>2+</sup> and Cu<sup>2+</sup>) found to be 37 and 5.44 ppb respectively using the equation LOD = 3 S.D./S. Where S.D. is the standard deviation, calculated from three blank reading of SiO<sub>2</sub>@ PBATPA material and S is the slope of linear plot between fluorescence intensity and metal ions concentrations (Figure S2, Supporting Information). The Stern–Volmer constant ( $K_{sv}$ ), limit of detection and correlation factor  $(R^2)$  for individual  $Hg^{2+}$  ions and  $Cu^{2+}$  ions are listed in Table 2. A competitive



Figure 6. UV–Vis spectra of SiO<sub>2</sub>@PBATPA at different pH range; B) change of zeta potential value of SiO<sub>2</sub>@PBATPA surface with the change in pH of the solution.



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**Figure 7.** A) UV–Vis spectra of SiO<sub>2</sub>@PBATPA material with various metal ions in neutral buffer solution (Na<sub>2</sub>HPO<sub>4</sub>:NaH<sub>2</sub>PO<sub>4</sub>). B) Fluorescence spectra of SiO<sub>2</sub>@PBATPA in the presence of various metal ions in the aqueous medium at neutral pH (7.0) with an excitation at 395 nm. C) Fluorescence spectra of SiO<sub>2</sub>@PBATPA at different concentrations with excitation at 355 nm.

fluorescence study with five equivalent molar excess of other metal ions shows similar quenching result that of the control experiments with  $Hg^{2+}$  ions and  $Cu^{2+}$  ions (Figure 8C,F).

#### 2.2.1. Possible Sensing Mechanism

As discussed above the fluorescence spectra of this material (0.5 mg/4 mL) shows three weak anthracene monomeric peak at 395, 417, 445 nm, and a strong excimer peak at 510 nm due to intramolecular  $\pi$ - $\pi$  stalking interactions at excitation at 355 nm. In the presence of excess Cu<sup>2+</sup> and Hg<sup>2+</sup> (300 × 10<sup>-6</sup> M) the intensity of both monomeric and excimer peak decreases simultaneously (**Figure 9**A). The monomer fluorescence

quenching may be due to the photoelectron transfer (PET) from anthracene to the amide carbonyl group.<sup>[10c]</sup> But the quenching of excimer emission may be due to conformational change upon metal ion complexation resulting in the destruction of excimer.<sup>[10c]</sup> As a result, in this conformation, parallel stalking of two anthracene units is not possible as shown in Figure 9B.

To determine the binding constant and number of binding sites for such quenching interaction between SiO<sub>2</sub>@PBATPA material and Hg<sup>2+</sup> and Cu<sup>2+</sup> ion, we used Scatchard equation:  $Log\{(F_0 - F)/F\} = Log K_b + n Log [Q].^{[34,5a]}$  Here, Q is the concentration of Hg<sup>2+</sup> and Cu<sup>2+</sup> ions,  $F_0$  and F represent the fluorescence intensity of the material before and after the addition of Hg<sup>2+</sup> and Cu<sup>2+</sup> ions (values were taken from fluorescence titration studies),  $K_b$  is the binding constant, and "n" is the



**Figure 8.** A) Fluorescence titration with increasing concentration of  $Hg^{2+}$ . B) The linear Stern–Volmer plot with  $Hg^{2+}$ . C) Competitive fluorescence spectra in the presence of excess other metal ions with  $Hg^{2+}$ . D) Fluorescence titration with increasing concentration of  $Cu^{2+}$ . E) The linear Stern–Volmer plot with the  $Cu^{2+}$  ion. F) Competitive fluorescence spectra in the presence of excess other metal ions with  $Cu^{2+}$ .

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Table 2. The detection parameters from fluorescence studies for  ${\rm Hg}^{2+}$  and  ${\rm Cu}^{2+}$  ions.

Analytes	K <sub>sv</sub> [м <sup>-1</sup> ]	LOD	R <sup>2</sup>
Hg <sup>2+</sup>	$1.5332 \times 10^4$	37 ppb (184.4 × 10 <sup>-9</sup> м)	0.9878
Cu <sup>2+</sup>	$1.2563\times10^4$	5.44 ppb (85 × 10 <sup>-9</sup> м)	0.9940

number of binding sites. The *K* and *n* can be calculated from the slope, and the intercept of the double logarithm regression curve of Log { $(F_0 - F)/F$ } verses Log [*Q*] which shows a linear fitting (**Figure 10**A,B). The calculated number of binding sites, binding constant, and the correlation factor ( $R^2$ ) for Cu(II) and Hg(II) ions are shown in **Table 3**.

The mass spectral analysis of ligand and ligand–metal chloride adducts also supports the formation 1:1 complex adduct. The electrospray ionization mass spectrometry (ESI-MS) of Ligand PBATPA-HgCl<sub>2</sub> (DMF solution) shows peaks at 1249 for [PBATPA-HgCl<sub>2</sub> + H<sup>+</sup>]<sup>+</sup> and 1379.95 for [PBATPA-HgCl<sub>2</sub>-DMF-H<sub>2</sub>O + K<sup>+</sup>] (Figure S3, Supporting Information). Similarly, PBATPA-CuCl<sub>2</sub> adduct shows peaks at 1332.61 for [PBATPA-CuCl<sub>2</sub>-2DMF-3H<sub>2</sub>O + Na<sup>+</sup>]<sup>+</sup> and 1348.56 for [PBATPA-CuCl<sub>2</sub>-2DMF-3H<sub>2</sub>O+K<sup>+</sup>]<sup>+</sup> (Figure S4, Supporting Information). Probably the complex undergo solvation due to presence of triethoxysilyl motif as observed earlier.<sup>[5e]</sup>

#### 2.3. Adsorption Studies

To evaluate various adsorption parameters and selectivity, the competitive adsorption experiments with all metal ions and batch adsorption experiments were carried out in aqueous buffer medium (pH 7) at room temperature. To examine the adsorption equilibrium times ( $Q_1$ ) with one of the representative cases for Cu<sup>2+</sup> with fixed concentrations of metal ion and adsorbent but variable treatment time shows an increase in adsorption capacity with time which gets saturated after 2 h (**Figure 11**A). So, in all experiments, the equilibrium adsorption time was kept a little upper side for 3 h. For the competitive

adsorption experiments, 100 mg of SiO2@PBATPA material was treated with 20 ppm of each metal ion mixed solution (50 mL) for 4 h at room temperature. After 4 h, the mixture was filtered, and the filtrate was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis to evaluate the final concentration of various metal ions. The adsorption/extraction efficiency was calculated by employing the equation %  $E = C_i - C_f / C_i \times 100$ ,<sup>[33]</sup> where % *E* is the extraction percentage,  $C_i$  and  $C_f$  are the initial and final concentration of metal ions in aqueous solution. It has been observed that only Hg2+ (98.20%) and Cu2+ (95.35%) ions got substantially extracted whereas for other relevant metal ions it was negligible (Table S1, Supporting Information). To calculation of experimental equilibrium adsorption capacity  $(Q_e)$  of SiO<sub>2</sub>@PBATPA material toward Hg<sup>2+</sup> and Cu<sup>2+</sup> ions, batch adsorption experiments were performed in aqueous buffer medium as discussed in the Experimental Section. The maximum equilibrium adsorption capacity  $(Q_e)$  calculated from the plot between  $Q_e$  versus  $C_e$ , using the adsorption isotherm equation  $Q_e = (C_1 - C_e) V / W$ <sup>[5a]</sup> where  $Q_e$  is the equilibrium adsorption capacity,  $C_{\rm I}$  and  $C_{\rm e}$  are the initial and final concentration of metal ions ( $Hg^{2+}$  and  $Cu^{2+}$ ) in aqueous solution, V is the volume of aqueous solution (*L*), and *W* is the weight of the material (g). From equilibrium adsorption isotherm (Figure 11B), the adsorption capacity for Hg (II) and Cu (II) ions by the material found to be 482 and 246 mg  $g^{-1}$ , respectively at room temperature.

The above experimental data were evaluated by the Langmuir and Freundlich adsorption isotherm models, which relates to heterogeneous surfaces. For a Langmuir adsorption isotherm, the following equation  $C_e/q_e = 1/K_L \cdot q_m + C_e/q_m$  was used.<sup>[5a]</sup> Where  $q_e$  and  $q_m$  are the equilibrium adsorption and maximum equilibrium adsorption capacity,  $C_e$  is the equilibrium concentration of metal ions (after adsorption, mg L<sup>-1</sup>),  $K_L$  (L mg<sup>-1</sup>) is the Langmuir adsorption constant. Similarly, the equation  $\ln q_e = \ln K_f + 1/n \ln C_e^{[5a]}$  was used for Freundlich adsorption isotherm model where  $K_F$  (L g<sup>-1</sup>) and n are the Freundlich constants. The various Langmuir and Freundlich adsorption parameter listed in **Table 4** and the adsorption isotherms are illustrated in (**Figure 12** and Figure S5, Supporting



**Figure 9.** A) The fluorescence spectra of SiO<sub>2</sub>@PBATPA showing quenching of monomeric and excimer emission peak with  $Cu^{2+}$  and  $Hg^{2+}$  ions. B) Schematic presentation of excimer on-off mechanism.







Figure 10. A) The Scatchard plot showing one binding site for Cu<sup>2+</sup>. B) The Scatchard plot showing one binding site for Hg<sup>2+</sup>.

Information). The above results show a better agreement with the Langmuir model which indicates monolayer adsorption occurred on the material surface.

To further support our claim and to track the adsorption process, energy dispersive X-ray spectroscopy (EDXs) was used. The EDX measurement of material obtained from competitive adsorption experiment indicates the presence of signals for Cu, Hg, and Cl elements along with C, O, Si, and N elements signify the adsorption of above metal chlorides (**Figure 13**). The dual functional activities of this material are comparable with most of the other materials known in the literature regarding extraction capability (adsorption capacity), selectivity, extraction time, detection limit (LOD) and recyclability (Table S2, Supporting Information).

#### 2.4. Recyclability Studies

As reusability of material is one of the crucial factors from the economic point of view, the reversibility nature of adsorption and desorption property was studied through absorbance spectral studies, zeta potential measurements, and adsorption studies. As a representative case for Cu (II), it is observed that the UV–Vis absorption band for SiO<sub>2</sub>@PBATPA material changes upon addition of metal ion due to complexation reaction forming SiO<sub>2</sub>@PBATPA@M (**Figure 14**A,C). Upon acidification (0.2 N HCl), the bands at 254 and 268 nm vanishes and a new peak at 300 nm appear due to decomplexation reaction and protonation of secondary amine nitrogens (SiO<sub>2</sub>@PBATPA-H<sup>+</sup>). Upon addition of dilute NaOH (0.2 N NaOH), the band at 300 nm vanishes and shifted back to the original position

Table 3. The various binding parameters from the Scatchard equation.

Metal ions	<i>К</i> <sub>b</sub> [м <sup>-1</sup> ]	Binding sites (n)	R <sup>2</sup>
Hg <sup>2+</sup>	$0.2149 \times 10^4$	0.7930	0.9876
Cu <sup>2+</sup>	$0.8425\times10^4$	0.9480	0.9905

for the material SiO<sub>2</sub>@PBATPA. Similar observations were also made with  $Hg^{2+}$  suggesting reversibility nature of metal binding and stripping process (Figure S6, Supporting Information). The reversibility nature of the material was also studied through acid–base treatments by measuring the zeta potential of isolated materials after treatments which shows similar zeta potential for original and regenerated material (–21.75 and –22.30 mV) due to the presence of electronegative donor atoms (Figure 14B). The acid treated material SiO<sub>2</sub>@PBATPA-H<sup>+</sup> shows a more positive value of zeta potential (+13.90 mV) due to protonation of organic amine functionality in the material. Based on these observations a probable mechanism is shown in Figure 14C.

The recyclability studies were also investigated through four cycles of adsorption/desorption of metal ions by acid-base treatments (Figure 15A and Figure S7, Supporting Information). For desorption process, 0.2 N HCl was used whereas for regeneration process 0.2 N NaOH solution was used. After every adsorption/desorption and regeneration process, the material was washed with deionized water. Every adsorption experiment was repeated thrice to minimize the experimental error. For one of the representative cases with Cu<sup>2+</sup> adsorption, it is noticed that the adsorption capacity falls by 1.62% after 1st cycle and 3.65% after 2nd cycle (Figure 15A) may be due to little damage of binding sites but later on uniform adsorption capacity was observed which shows that the material is stable enough for successive acidic stripping steps. The solidstate <sup>13</sup>C NMR spectra after the fourth cycle demonstrate the organic motif is intact and comparable with the original spectra (Figure 15B).

#### 2.5. Detection and Adsorption Studies in Real Samples

To evaluate the applicability of this probe material for detection of  $Cu^{2+}$  and  $Hg^{2+}$  in real samples, grape juice, and orange juice were considered for copper ion detection and conger eel fish was considered for mercury ion detection. Fruit juices were





Figure 11. A) The Equilibrium adsorption time with one of the representative case with  $Cu^{2+}$ . B) The Equilibrium adsorption capacity of SiO<sub>2</sub>@PBATPA material toward  $Cu^{2+}$  and  $Hg^{2+}$ .

centrifuged and filtered before use while Conger eel fish tissue was acid digested and filtered after neutralization as described in experimental section. Considering the low concentration of these metal ions in the real samples, spiked solutions were prepared with  $30 \times 10^{-6}$ ,  $40 \times 10^{-6}$ , and  $50 \times 10^{-6}$  M of metal ions ( $Cu^{2+}$  for fruit juice and  $Hg^{2+}$  for fish). Initially, fluorescence titrations of material SiO<sub>2</sub>@PBATPA (2 mg/2 mL) were carried out in water suspension in the presence of various concentrations of individual metal ions to plot the calibration curves. Then the emission intensities of the same material  $SiO_2@$ PBATPA (2 mg/2 mL) with various spiked solutions were recorded, and the concentration of metal ions was estimated from the calibration curves (Figures S8 and S9, Supporting Information). The results show that the obtained recoveries<sup>[35]</sup> are satisfactory in the range of 96-104% for copper ion in fruit juices and 102-106% for mercury ion in fish as shown in Table S3 (Supporting Information). For adsorption studies in these real samples, all the samples were digested and analyzed by ICP-OES analysis with and without spiking to know the initial total metal ion (Cu<sup>2+</sup> or Hg<sup>2+</sup>) concentrations correctly. For copper ion determination, raw fruit juices were treated with the material (10 mg in 10 mL), filtered and finally acid digested to know the final concentration after the adsorption process. Similarly, for mercury ion adsorption, the neutralized acid-digested fish liquor was treated with the material (10 mg in 10 mL) and after filtration analyzed to know the final concentration (Table S4, Supporting Information). It has been observed that around 60.11% and 68.88% of copper ion adsorbed by the material in grape and orange juices, respectively. These results are impressive considering the complex system, where the total copper ion may not be in free ion state to be adsorbed by the material. In the case of fish sample, 96.3% of mercury ion

removal was observed, as all the mercury ion is expected to be in free ion state in the acid-digested sample. These results demonstrate the potential application of the material to detect and adsorb these toxic metal ions in the real samples.

# 2.6. Detection of Metal Ions in the Animal Model Brine Shrimp Artemia Nauplii

To examine the application of the above material as a sensory probe for detection of Cu<sup>2+</sup> and Hg<sup>2+</sup> in the living organism, in vivo fluorescence imaging was carried out with whole brine shrimp Artemia in the absence and presence of the above metal ions (Figure 16). Considering a cost-effective animal model for in vivo bioimaging studies Artemia was chosen as the biological platform.<sup>[36]</sup> For this purpose, hatched Artemia nauplii (50 organisms in 10 mL tube) taken in 10 mL seawater to which 100 µL (from 10 mg/10 mL stock solution) of the suspended SiO2@PBATPA aqueous solution was added and kept for 2 h. Fluorescence imaging shows that Artemia nauplii readily intake the fluorescent materials from the surrounding water and can accumulate it in the gastrointestinal (GI) tract supported by the observation of bright green colored staining of GI tract under the microscope (BX 53 OLYMPUS) (Figure 16C,D). The treated Artemia nauplii were then incubated in a 10 mL brine solution containing 100  $\mu L$  of 10  $\times$  10<sup>-6</sup> and 100  $\times$  10<sup>-6</sup>  $\,{}_{M}$  of Hg^{2+} and Cu<sup>2+</sup> ions and kept for 1 h. However, the Artemia treated with  $10 \times 10^{-6}$  M Hg<sup>2+</sup> and Cu<sup>2+</sup> displayed a weak green fluorescence staining of GI tract whereas, with  $100 \times 10^{-6}$  M Hg<sup>2+</sup> and Cu<sup>2+</sup> (Figure 16G,H) the green fluorescence staining of GI tract almost vanishes. These observations further support the fluorescence quenching of material in the presence of these metal

Table 4. The Langmuir and Freundlich adsorption parameter for analytes at 25 °C.

Analytes	Experimental	Langmuir linear isotherm		Freundlich linear isotherm			
	Qe	<i>q</i> <sub>max</sub> [mg g <sup>-1</sup> ]	K <sub>L</sub> [L g <sup>-1</sup> ]	R <sup>2</sup>	K <sub>F</sub>	п	R <sup>2</sup>
Hg <sup>2+</sup>	482	505	0.1548	0.9995	186.53	4.6360	0.9781
Cu <sup>2+</sup>	246	256	0.2019	0.9980	111.73	5.8736	0.9794







Figure 12. A) Langmuir adsorption isotherm for Cu<sup>2+</sup>. B) Langmuir adsorption isotherm for Hg<sup>2+</sup>.

ions as discussed in fluorescence sensing studies. Therefore, these results suggest that this material can be used to detect the presence of these toxic metal ions in living organisms and hence can be used as an in vivo sensory probe material.

#### 2.7. In Vivo Toxicity Studies in Shrimp Artemia Nauplii

To examine the toxicity of the material to the brine shrimp Artemia nauplii in vivo toxicity studies<sup>[37]</sup> were carried out in the presence of the material and metal ions (Hg<sup>2+</sup> or Cu<sup>2+</sup>). An aliquot of material, Cu<sup>2+</sup> and Hg<sup>2+</sup> that was used for in vivo sensing studies was used to check the lethality toward Artemia nauplii in different time duration. In the presence of material only (100 µL from 10 mg/10 mL stock solution added to 10 mL of seawater with 50  $\pm$  3 organisms), no significant mortality was observed in Artemia nauplii after 8 and 24 h. Whereas, in the presence of Cu<sup>2+</sup> or Hg<sup>2+</sup> (100  $\mu$ L from 100  $\times$  10<sup>-6</sup> M) in 10 mL of seawater, Artemia mortality was observed. In the case of copper ion only, mortality percentage (≈15%) was similar after 8 and 24 h. However, in the case of mercury, after 24 h, all treated Artemia nauplii were died (Figure S10, Supporting Information) due to the toxicity of metal ions. Similar results were also observed when metal ions added to the solution with materials and Artemia. When copper ion added to the solution with material and Artemia, it was observed that Artemia were healthy except few



**Figure 13.** EDX spectrum of isolated material from competitive adsorption experiments showing adsorption of metal chlorides (Cu and Hg).

numbers died after 24 h. Whereas, in the presence of mercury ion, movements were restricted totally after 24 h and all *Artemia* were found dead accounting for 100% mortality. Only *Artemia* without any treatment was treated as the negative control. These observations confirm the nontoxic nature of material but mortality observed in the presence of these metal ions.

## 3. Conclusion

In summary, a new functionalized mesoporous material was synthesized by covalent coupling of anthracene-based chelator within the mesopores of newly synthesized cubic mesoporous silica. PXRD, SEM, and TEM data suggests retention of a highly ordered cubic mesoporous structure after functionalization. A steady decrease in surface area, pore volume, and pore diameter from SiO<sub>2</sub> to SiO<sub>2</sub>@PBATPA from the N<sub>2</sub> sorption studies suggest grafting of chelating fluorophore inside the mesopores. Taking advantage of intramolecular excimer formation by anthracene motif on a solid surface as a sensory tool, selective detection of toxic metal ions like Cu<sup>2+</sup> and Hg<sup>2+</sup> were done through the fluorescence quenching mechanism. This material also shows high adsorption capacity toward above metal ions by complex formation supported by EDX analysis and mass spectral analysis of ligand-metal ion adducts. Recyclability of material up to four cycles shows the stability of the compound during adsorption, desorption, and regeneration by acid-base treatments supported by reversibility studies through UV-Vis absorption studies, zeta potential measurements and solid-state <sup>13</sup>C NMR studies. This material also shows a promising result in real samples and in vivo sensory probe studies for detection of above metal ions in a living organism like A. salina as a biological platform. Therefore, this material represents very rare example of excimer based heterogeneous sensory probe cum adsorbent material which can be recycled easily with simple acid-base treatments.

### 4. Experimental Section

*Materials*: All reagents and chemicals used here were of analytical grades. In all analytical experiments, deionized water was used.



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**Figure 14.** A) Reversible absorption spectral studies of SiO<sub>2</sub>@PBATPA material with one of the representative case (Cu<sup>2+</sup>) with acid–base treatments. B) Reversible zeta potential studies with acid–base treatments. C) Probable recycling mechanism of SiO<sub>2</sub>@PBATPA material during metal ion uptake, stripping and regeneration of material.

Solvents were dried in the laboratory as required. TEOS, APTES, CTAB, 1,3-diaminopropane, 9-anthracenecarboxaldehyde, bromoacetyl chloride, NaBH<sub>4</sub> were purchased from TCI chemical Private Ltd. For buffer solutions of pH 2–5, Na<sub>2</sub>HPO<sub>4</sub>/citric acid was used for pH 5–7, NaH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub> was used, for pH 8–10, KH<sub>2</sub>PO<sub>4</sub>/NaOH was used which were purchased from Merck group private Ltd. All metal chlorides were purchased from Spectrochem Private Ltd. All dry solvents (toluene, methanol, acetonitrile), anhydrous K<sub>2</sub>CO<sub>3</sub>, NaOH,

HCl (37%), dry  $N(\mbox{CH}_2\mbox{CH}_3)_3$  were purchased from SD Fine Chemical Private Ltd.

Instrumentation: Bruker Advance 500 MHz NMR was used to record <sup>13</sup>C and <sup>29</sup>Si solid CP NMR spectra. UV–Vis absorption studies were measured by Shimadzu UV 3101 PC spectrophotometer. Fluorescence spectra were recorded by using Edinburgh Instruments model Xe-900. FT-IR spectra were recorded using KBR disks on a Perkin-Elmer GX spectrophotometer (USA). Mass spectra were collected by using



Figure 15. A) The adsorption capacity of SiO<sub>2</sub>@PBATPA material toward Cu<sup>2+</sup> ions up to four cycles. B) Comparison of <sup>13</sup>C solid-state NMR of SiO<sub>2</sub>@ PBATPA after 4th cycle.







**Figure 16.** A) A brine Shrimp Artemia nauplii bright field image; B) Artemia nauplii under UV filter as negative control (blank); C,D) Artemia nauplii after intake of SiO<sub>2</sub>@PBATPA material (under UV filter); E) Artemia nauplii in the presence of  $10 \times 10^{-6}$  M Hg<sup>2+</sup>; F) Artemia nauplii in the presence of  $10 \times 10^{-6}$  M Cu<sup>2+</sup>; G) Artemia nauplii in the presence of  $10 \times 10^{-6}$  M Cu<sup>2+</sup>; C) Artemia nauplii in the presence of  $10 \times 10^{-6}$  M Cu<sup>2+</sup>; C) Artemia nauplii in the presence of  $10 \times 10^{-6}$  M Cu<sup>2+</sup>; C) Artemia nauplii in the presence of  $100 \times 10^{-6}$  M Cu<sup>2+</sup>.

Q-TOF Micro TM LC–MS instrument. ICP-OES analyses were measured through Perkin Elmer instrument (Optima 2000DV). Malvern instrument (Zetasizer, Nano series, Nano-ZS90) was used to measure the zeta potentials. TGA was performed by using a Mettler-Toledo (TGA/SDTA 851e) instrument in the air with a heating rate of 10 °C min<sup>-1</sup>. PXRD was measured by Miniflex-II (FD 41521) powder diffractometer (Rigaku, Japan). SEM was performed by Leo series 1430 VP instrument equipped with INCA. TEM was performed using a JEOL JEM 2100 microscope.

Synthesis-Synthesis of Cubic Mesoporous Silica: The synthesis of Cubic SiO<sub>2</sub> was performed with little modification of the reported method.<sup>[18]</sup> Typically, 2 g of CTAB surfactant was dissolved in 300 mL of deionized water and stirred for 1 h followed by addition of 10-12 mL of ammoniawater (28%) solution, forming a clear solution which was stirred further for another 1 h. Then a mixture of n-hexane (40 mL) and TEOS (10 mL) was added drop-wise to the above mixture for 45 min under vigorous stirring at a temperature of 45 °C. As the reaction proceeds a milky colloidal solution gradually formed and stirring continued for 12 h. The white product was collected by centrifugation and washed with deionized water and methanol. To remove CTAB surfactant template, the solid white product was dispersed into 200 mL methanol in the presence of 1 M HCl (8-10 mL) under reflux condition for 12 h. The above solvent extraction process was repeated 4-5 times, and finally, the sample was collected by centrifugation and washing with hot methanol 3-4 times. The above product was oven dried overnight at 80 °C and yielded 2.2 g of product (Scheme 1).

Synthesis—Preparation of 3-APTES Functionalized Silica (SiO<sub>2</sub>@NH<sub>2</sub>): Functionalization of above synthesized cubic silica with 3-APTES done by following a reported procedure.<sup>[38]</sup> For this, 1 g of cubic silica (SiO<sub>2</sub>) refluxed with 2.5 g of 3-APTES in toluene for 12 h under an inert atmosphere. The white solid (SiO<sub>2</sub>@NH<sub>2</sub>) was collected by centrifugation and repeatedly washed with excess toluene, hot methanol, and chloroform to removed excess unreactive 3-APTES and finally dried in the oven at 80 °C for 12 h to give 1.026 g of product (Scheme 1D).

Synthesis—Synthesis of N1,N3-bis(anthracen-9-ylmethyl)propane-1,3diamine (BPD): This compound was synthesized following a literature procedure<sup>[39]</sup> by a Schiff-base reaction between anthraldehyde and 1,3-propanediamine, followed by the reduction reaction in the presence of NaBH<sub>4</sub>.

Synthesis—Synthesis of N,N'-(propane-1, 3-diyl)bis(N-(anthracen-9ylmethyl)-2-bromoacetamide) (PBAB): To a 500 mL round bottom flask, BPD (2 g, 4.4 mmol) and triethylamine (1.12 g, 11 mmol) were taken in 250 mL of dry chloroform and stirred under cold condition (Ice-NaCl bath) with a temperature range of 0–5 °C for 30 min. After that bromoacetyl chloride (1.12 g, 11 mmol) was added dropwise to the above mixture and stirred for 3 h under cold condition followed by stirring at room temperature for 24 h. Formation of both sides substituted final product was monitored through TLC spotting and mass spectral analysis (Figures S11 and S12, Supporting Information). Then the organic part was extracted with brine and normal deionized water 3–4 times. The organic part was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed through the rotary evaporator. The crude was purified by recrystallization (2.20 g, 72%), which was used as it is in the second step.

Synthesis—Direct Functionalization of Ligand PBAB onto  $SiO_2@NH_2$  to Form  $SiO_2@PBATPA$ : In this procedure, 3 g of  $SiO_2@NH_2$  refluxed with PBAB ligand (1 g, 1.4 mmol) in the presence of anhydrous  $K_2CO_3$  (0.3982 g, 2.8 mmol,) in dry acetonitrile (200 mL) for 48 h at 80 °C. The crude material was separated by filtration and repeatedly washed with hot chloroform to removed excess unreactive PBAB ligand and finally washed with deionized water to removed excess  $K_2CO_3$ . The final compound was dried under a hot air oven at 80 °C for 2 h to yield 3.42 g of the compound. This final material  $SiO_2@PBATPA$  was characterized by various analytical techniques.

Synthesis—Synthesis of Ligand PBATPA and Functionalization on Cubic SiO<sub>2</sub> to Prepare SiO<sub>2</sub>@PBATPA: For the synthesis of ligand PBATPA, both PBAB and 3-APTES were refluxed in dry MeCN in the presence of K<sub>2</sub>CO<sub>3</sub> in an inert atmosphere. After 48 h, the solvent was removed by the rotary evaporator, and crude solid was dissolved in CHCl<sub>3</sub> and washed with water several times. Then the solvent was removed, and the solid was recrystallized from hot ethanol to give PBATPA ligand confirmed from the mass spectral analysis (Figures S13 and S14, Supporting Information). The above crude ligand (0.5 g) was refluxed with 1 g of cubic silica in dry toluene for 12 h under argon. Finally, the SiO<sub>2</sub>@PBATPA material was filtered off and thoroughly washed with CHCl<sub>3</sub>, deionized water and dried under vacuum for 48 h to give an off-white colored material (1.18 g). The analytical data for both methods confirms the formation of the same compound SiO<sub>2</sub>@PBATPA.

Synthesis—UV-Vis and Fluorescence Studies: For both UV-Vis and fluorescence studies, 0.5 mg of SiO<sub>2</sub>@PBATPA material was suspended

in 2 mL buffer solution and shaken well on a vortex shaker for 1 min to get a uniform suspension solution before any spectral studies. The suspension was taken in a 1 cm quartz cuvette, and before and after addition of various metal ions to the suspension the cuvette is shaken well, and the process was repeated for every spectrophotometric/ fluorescence reading. UV–Vis spectra were recorded in the range of 200–800 nm and fluorescence spectra were recorded in the range of 420–700 nm with an excitation wavelength of 395 nm. For LOD calculations, the fluorescent intensity was recorded by gradually adding 0–70  $\mu$ m solution of analytes to the SiO<sub>2</sub>@PBATPA suspension (0.5 mg/2 mL). The slope (S) was obtained from the fluorescence measurements were done to calculate the standard deviation (SD). The LOD was determined using the formula: LOD = (3SD/S).

Synthesis-Adsorption Experiments: To calculate various adsorption parameters and adsorption isotherms, batch adsorption experiments were carried out in the aqueous buffer solution at neutral pH following a reported method.<sup>[5e]</sup> In a typical experiment, various concentrations (20–200 ppm) of metal ions (Hg<sup>2+</sup> or Cu<sup>2+</sup>) in 50 mL aqueous suspension was treated with 5 mg SiO<sub>2</sub>@PBATPA material at neutral buffer (pH 7) for 3 h. Then the mixture was filtered through a polypropylene syringe filter after equilibrating for 3 h, and the filtrate was analyzed to get the equilibrium concentration  $(C_e)$  of the metal ions by ICP-OES analysis. The adsorption capacity ( $Q_e$ , mg g<sup>-1</sup>) of the SiO<sub>2</sub>@PBATPA material for the analytes was found from the equation  $Q_e = (C_1 - C_e)V/W_{ads}$ . In this equation,  $Q_e$ ,  $C_l$ , and  $C_e$  represents the equilibrium adsorption capacity (mg  $g^{-1}$ ), initial and final concentration of analytes (mg  $L^{-1}$ ), respectively. V and  $W_{ads}$  represents the volume of analyte solution (L), and weight of the adsorbent (g), respectively. All adsorption experiments were repeated thrice to reduce the experimental error. To calculate adsorption equilibrium time (Qt), the same amount of analytes (~200 ppm  $\rm Cu^{2+}$ ion solution was taken in five 50 mL glass vials) were treated with same amount of material (5 mg of SiO2@PBATPA) and subjected to different treatment times. The solutions were filtered after the treatment times of 30 min, 1, 2, 3, and 4 h and the filtrates were analyzed by ICP-OES measurements to calculate the equilibrium adsorption time.

Synthesis-Striping and Reusability Studies: For reusability studies of SiO<sub>2</sub>@PBATPA material toward metal ion adsorption/desorption and recyclability of the above material, simple acid-base treatments were carried out. One of the representative cases with  $\mathsf{Cu}^{2+}$  ion is mentioned here. Initially, various concentration cupric-ion aqueous solution ranging from ≈20-200 ppm taken in 50 mL glass vials (10 nos.), to which 5 mg SiO<sub>2</sub>@PBATPA material was added individually in a neutral buffer solution of pH 7 and stirred for 4 h. After that, these mixture solutions were centrifuged and the solid adsorbent and aqueous part separated by filtration through a syringe filter. The aqueous part was analyzed to measure the final concentration of cupric ions by ICP-OES analysis. This separated solid adsorbent was washed gently with deionized water to removed nonbound cupric ions. Then the material was treated with 0.2 N HCl (10 mL aqueous) for 5 min and Milli-Q water twice, and the filtrate was analyzed to determine the stripped metal ions. In the regeneration step, the above material treated with 0.2 N NaOH (10 mL aqueous) for 5 min and washed with water and dried for reuse. Each glass vials material undergoes similar acid-base treatments separately. The adsorption, desorption, and regeneration process was studied up to 4th cycles through calculation of adsorption capacity from each cycle. Adsorption capacities were evaluated separately for each cycle from the plot of adsorption isotherms.

Synthesis—Detection and Adsorption Studies in Real Samples: For detection and adsorption of copper ion in real samples both grape and orange juices were considered. For this purpose, around 5 mL of each juice were centrifuged at 5000 rpm for 30 min before filtration. Then  $1 \times 10^{-3}$  M stock solutions of copper ion was prepared in these juices separately as spiked solutions. Similarly,  $1 \times 10^{-3}$  M stock solution of copper ion were prepared in deionized water for fluorescence titrations of material SiO<sub>2</sub>@PBATPA (2 mg/2 mL) in the presence of various concentration of copper ion to plot the calibration curve. Then, the copper ion spiked juice solutions ( $30 \times 10^{-6}$ ,  $40 \times 10^{-6}$ ,  $50 \times 10^{-6}$  M) were used for fluorescence

titrations with the material (2 mg/2 mL), and the concentration of copper ion in these spiked solutions were estimated from the calibration curve (intensity vs concentration). For adsorption experiment, 10 mL of each juice after filtration were acid-digested and volume adjusted to 10 mL before the analysis by ICP-OES to know the initial concentration of total copper ions (1.434 ppm in grape juice, 0.587 ppm in orange juice). Each juice (10 mL) were treated with 10 mg of materials for 3h under a vibrating mixture, filtered and acid-digested and volume adjusted to 10 mL before the analysis to know the final concentration (0.572 ppm in grape juice and 0.183 ppm in orange juice). For mercury ion, Conger eel fish was considered, and the samples were prepared by acid-digestion of 2 g of fish tissue followed by neutralization with NaOH which was used for detection and adsorption studies. For detection studies,  $1 \times 10^{-3}$  M spiked fish solution with Hg<sup>2+</sup> was prepared. This mercury ion spiked fish solution  $(30 \times 10^{-6}, 40 \times 10^{-6}, 50 \times 10^{-6} \text{ m})$  was used for fluorescence titrations with the material (2 mg/2 mL), and the concentration of mercury ion in these spiked solutions were estimated from the calibration curve. For adsorption of mercury ion, initial concentration of mercury ion from aciddigested solution found to be 0.326 ppm. After 10 mL of the neutralized fish solution were treated with 10 mg of material and equilibrated for 3 h, the final concentration found to be 0.012 ppm from ICP-OES analysis. All the samples were spiked with a standard metal ion solution (6.061 ppm for  $Cu^{2+}$  and 16.240 for  $Hg^{2+}$ ) to know the correctness of the measurements. The differences of initial and final concentration were considered for adsorption percentage calculations.

Synthesis—In Vivo Metal Ion Detection Studies: A. salina cysts were taken out from the freeze and were allowed to hatch overnight in a vigorously aerated vessel under very high-intensity visible light. The next day hatched cysts produced Artemia larvae (nauplii) those larvae were then used for the experimental purpose. Using A. salina as animal model sensing experiment was done as described earlier with slight modification. Approximately 50 number of Artemia nauplii were taken in 10 mL of seawater and to which 100  $\mu$ L (from 10 mg/10 mL stock solution) of the suspended SiO<sub>2</sub>@PBATPA aqueous solution was added and kept for 2 h. The treated Artemia nauplii were then incubated in a 10 mL brine solution containing 100  $\mu$ L of 10  $\mu$ M and 100  $\mu$ M of Hg<sup>2+</sup> and Cu<sup>2+</sup> ions. Some organisms from the tube were transferred on a glass slide and viewed under BX53 OLYMPUS microscope under bright and fluorescent filters.

Synthesis—In Vivo Toxicity Studies: The hatched mature Artemia nauplii (50  $\pm$  3 nos.) were randomly collected with a sterile glass dropper and transferred into the test tubes with 10 mL of sterile seawater. In one set of experiments, 100  $\mu$ L of material suspension (10 mg/10 mL) was added to the test tubes and kept under light at room temperature, and numbers of live Artemia were counted after 8 and 24 h. Other sets of experiment were done similarly in the presence of 100  $\mu$ L of metal ions only (100  $\times$  10<sup>-6</sup> M) in 10 mL of sterile seawater and in the presence of both material and metal ions. All experiments were performed in triplicate with 50  $\pm$  3 nos. of Artemia under similar experimental conditions, and mortality percentage was calculated considering the standard deviations and using the formula: mortality percentage = (mortality observed – mortality of control)/(total no of artemia – mortality of control)  $\times$  100.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

## **Keywords**

anthracene, cubic mesoporous silica, detection and adsorption, excimer emission, mercury and copper ion

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