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### Article

# Entrapping Atomically Precise Clusters in Cyclodextrin-Functionalized Aminoclay Sheets: Synthesis and Enhanced Luminescence

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**ABSTRACT:** In this article, a unique covalently linked aminoclay substrate, grafted with  $\beta$ -cyclodextrin (AC-CD), was prepared to entrap luminescent silver nanoclusters. Chemically synthesized aminoclay (AC) sheets grafted with  $\beta$ -cyclodextrins ( $\beta$ -CDs) were used to develop a supramolecular entity. Here, we grafted  $\beta$ -CD onto aminoclays using cyanuric chloride as a linker. The AC-CD material was thoroughly characterized using Fourier transform infrared spectros-copy (FTIR), powder X-ray diffraction (PXRD), and transmission electron microscopy (TEM). The grafting ratio of  $\beta$ -CD onto AC-CD was determined using the phenolphthalein inclusion protocol. The as-prepared functionalized clay (AC-CD) is an effective and attractive material for entrapping a luminescent silver chalcogenide cluster stabilized by 4-(*t*-butyl)benzyl mercaptan (Ag<sub>56</sub>Se<sub>13</sub>S<sub>15</sub>@ SBB<sub>28</sub> shortened as Ag<sub>2</sub>Se@SBB). The cluster AC-CD (AC-CD $\cap$ Ag<sub>2</sub>Se@SBB) supramolecular nanocomposite is based on specific host–guest interactions



involving  $\beta$ -CD of AC-CD and SBB of a silver cluster. Entrapment of the cluster into the  $\beta$ -CD cavity was verified using optical absorption, luminescence spectroscopy, XRD, and TEM. The entrapment resulted in enhanced luminescence and stability of the cluster. Such a dispersible nanocomposite system exhibiting intense luminescence will be useful in creating novel materials for various applications such as sensors, optoelectronic devices, etc.

## INTRODUCTION

Atomically precise metal nanoclusters (NCs) are an emerging class of materials and have attracted tremendous attention due to their unique physical and chemical properties.<sup>1-3</sup> NCs having a core size <3 nm possess exceptional geometric and electronic structures and exhibit intriguing properties such as strong photoluminescence, high catalytic activity, facile surface tailorability, and good photostability, which are different from bulk nanoparticles, with diameter >3 nm. Manipulating such functional materials is an important aspect of nanocluster chemistry.<sup>4-12</sup> In view of their exciting properties and applications, a large number of differently sized clusters of noble metals (Ag and Au) have been synthesized although those of silver are of poor stability. Therefore, synthetic modifications are needed to increase the stability of NCs. Mixed chalcogenide silver clusters or alloy NCs composed of more than two metals have gained research interest in recent years.<sup>4-6</sup> Alloying could increase their stability and photophysical properties, which opens up a broader window for their applications.' Hybrid nanocomposites have received attention in view of their simple preparation, lightweight, mechanical strength, flexible behavior, layered structures, etc.<sup>13-15</sup> Nanoclusters can also be incorporated in scaffolds such as polymers, 2D materials, etc., and such materials exhibit different physical properties due to additional influences of the matrix on their

electronic structure.<sup>16–18</sup> The important features observed in such clusters are greater stability, strong luminescence, etc., which occur when these clusters are anchored on suitable supports.<sup>19–21</sup> Consequently, such materials are used in fluorescence bioimaging including that of cancer cells, along with the detection of analytes such as ascorbic acid (AA), dopamine (DA), and uric acid (UA).<sup>17,18</sup> For a wide range of applications, there is a need to use tailored or functional clays as supports that would be highly dispersible in water.

One such scaffold is aminoclay (AC). It is a tailored organoclay having smaller micron-sized pieces of single clay sheets, which have a 2:1 trioctahedral phyllosilicate structure (also known as T-O-T structure).<sup>22,23</sup> In this structure, two tetrahedral aminopropyl-functionalized silica sheets sandwich octahedral brucite sheets on both sides by covalent bonding to give an approximate unit cell composition formulated as  $[H_2N(CH_2)_3]_8Si_8Mg_6O_{16}(OH)_4$ .<sup>23</sup> It is protected with amine groups on both sides and is prominently water-soluble. AC has

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multifaceted applications and is utilized for the stabilization of metal NPs,<sup>24</sup> catalysis,<sup>25,26</sup> light harvesting,<sup>27</sup> drug delivery,<sup>28,29</sup> energy devices,<sup>30</sup> and many other applications. It forms nanocomposite hydrogels and films with suitable polymers and macromolecules by acting as a cross-linker.<sup>31</sup> The terminal amine groups in AC can be functionalized with various chemically reactive species. One such functionalization can be performed with cyclodextrins (CDs), resulting in CDfunctionalized AC, labeled as AC-CD. CDs are cyclic oligosaccharides, consisting of glucopyranose subunits joined together by  $\alpha$ -1,4 glycosidic bonds. Typical cyclodextrins contain several glucose monomers ranging from six to eight units in a ring and are known as  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrins, respectively. CDs have a hydrophobic (lipophilic) central core cavity with hydrophilic outer surfaces.<sup>32</sup> They can form molecular inclusion complexes with hydrophobic compounds of suitable molecular sizes.<sup>33–35</sup> CDs enhance stability,<sup>36</sup> solubility,<sup>37,38</sup> bioavailability,<sup>39</sup> functionality,<sup>40–42</sup> and controlled release of the guest molecules<sup>43,44</sup> and are being used in food, <sup>45,46</sup> essential oils, <sup>47–49</sup> cosmetics, <sup>50</sup> pharmaceuticals, <sup>51–53</sup> and agrochemicals.<sup>54,55</sup>

Recently, we have reported supramolecular interactions between atomically precise clusters and cyclodextrins using specific host-guest interactions.<sup>21,56,57</sup> Strong inclusion interactions between the inner cavity of cyclodextrin and ligand molecules have been probed experimentally using various spectroscopic techniques and have been further analyzed by density functional theory calculations and molecular modeling.

In this work, we have prepared AC-CD $\cap$ Ag<sub>2</sub>Se@SBB through functionalized CDs, where Ag<sub>2</sub>Se@SBB is an atomically precise silver chalcogenide cluster and  $\cap$  symbolizes an inclusion complex (Ag<sub>2</sub>Se@SBB included in AC-CD is symbolized as AC-CD $\cap$ Ag<sub>2</sub>Se@SBB). A mixed chalcogenide silver cluster has been used because of its good stability and efficient luminescence compared to silver clusters. In our approach, we have derivatized AC, first, with CD so that the clay surfaces are effectively functionalized with CDs, rendering them receptive to entities such as the 4-(*t*-butyl)benzyl group, which protects the cluster core. Such incorporation enhances the luminescent property of the cluster. These materials are likely to be biocompatible as both aminoclays and CDs have this property and may be useful for many applications.

#### EXPERIMENTAL SECTION

**Materials.** All chemicals were of analytical grade and were used without further purification. Silver acetate (CH<sub>3</sub>COOAg), 4-*tert*-butylbenzyl mercaptan (BBSH), Se powder (100 mesh, 99.5%), octadecene (ODE, 90%), and 3-aminopropyltriethoxysilane (APTES) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH), sodium bicarbonate (NaHCO<sub>3</sub>), tetrahydrofuran (THF), and cyanuric chloride (CC) were purchased from Rankem. Magnesium chloride hexahydrate (MgCl<sub>2</sub>· 6H<sub>2</sub>O; 98%) and toluene were obtained from Merck (India). Absolute ethanol (99.99%) was purchased from Changshu Hongsheng Fine Chemicals (China). Glassware used was cleaned thoroughly in aqua regia, rinsed with distilled water, and dried in an oven prior to use. Millipore deionized water (~18.2 M $\Omega$ ) was used, wherever required.

**Methods.** Synthesis of Aminoclay (AC). Aminoclay (AC) was synthesized by previously reported methods.<sup>22,23</sup> In a typical procedure, magnesium chloride (2.52 g, 10.86 mmol) was dissolved in ethanol (60 mL). To this ethanolic solution of

magnesium chloride, 3-aminopropyltriethoxysilane (3.9 mL, 17.55 mmol) was added dropwise, resulting in the formation of a white slurry. This mixture was kept on stirring for 36 h, and the solution was centrifuged at 5000 rpm. The white precipitate obtained was washed several times using ethanol (150 mL) to remove the unreacted moieties. The pure product was dried at room temperature for 12 h and then ground to obtain the product in a powder form.

Synthesis of Monochlorotriazinyl- $\beta$ -cyclodextrin (MCT- $\beta$ -CD). MCT- $\beta$ -CD was synthesized as per the conventional method.<sup>40,58</sup> In this case, 5.50 g of cyanuric chloride was dispersed in 30 mL of cold water using sodium dodecyl sulfate (SDS) as an emulsifier and the solution was kept on stirring at 0 °C. To this, 12 mL of sodium hydroxide (5 mol L<sup>-1</sup>) was added dropwise to adjust the pH around 8. Then, 11.35 g of  $\beta$ -CD solution was gradually added to the above solution and the reaction mixture was kept on stirring for 24 h at 10 °C overnight until a transparent solution was obtained. To this, 10 mL of acetone was added for precipitation, desalted by 2 mL of DMF, and again precipitated by 10 mL of acetone. The product was obtained in a powder form by drying at 40 °C.

Synthesis of Cyclodextrin-Functionalized Aminoclay (AC-CD). Initially, 3 wt % AC solution was activated using 0.02 w/w NaHCO<sub>3</sub> and was kept on stirring for 1 h. To this solution, 1 wt % MCT- $\beta$ -CD was gradually added and stirred for 24 h at room temperature. The reaction mixture was centrifuged, and the precipitated product obtained was washed several times with ethanol. The final purified product in powder form was obtained by freeze-drying. The weight percentage of AC, sodium bicarbonate concentration, temperature, and reaction time effectively influence the  $\beta$ -CD grafting ratio. The reaction conditions optimum for the synthesis of higher inclusion ratio of  $\beta$ -cyclodextrin-grafted aminoclay (AC-CD) were achieved.

Synthesis of Luminescent  $Ag_{56}Se_{13}S_{15}@SBB_{28}$  ( $Ag_2Se@SBB$ ) Nanocluster. The  $Ag_2Se@SBB$  cluster was synthesized by an already reported method by our group.<sup>59</sup> CH<sub>3</sub>COOAg (0.1 mmol) and BBSH (4 mmol) were added to 5 mL of ODE in a 100 mL three-necked round-bottomed flask under argon (Ar) flow at 60 °C. Ar purging was continued for 30 min at this temperature. Then, the reaction mixture was heated to 90 °C, the Se powder (0.05 mmol) was added to this mixture under constant stirring, and the reaction was continued for 2 h. The reaction mixture was then cooled to room temperature and purified by washing with methanol and subsequent centrifugation. The  $Ag_2S$  nanocluster was stable for a week at room temperature, and this stability was enhanced to more than a month by keeping at low temperatures (4 °C).

Synthesis of Atomically Precise Clusters in Cyclodextrin-Functionalized Aminoclay (AC-CD $\cap$ Ag\_Se@SBB). Native Ag\_Se@SBB (2 mg) was dissolved in 3 mL of THF/H<sub>2</sub>O (3:1) solution, and to this, AC-CD (5 wt %) solution was added. Both the cluster and composite were dispersible in 3:1 THF/H<sub>2</sub>O. The mixture was sonicated for about 10 min. The reaction was allowed to proceed with continuous stirring for 3 h at room temperature with intermittent sonication for 1 min every 30 min intervals. The final product AC-CD $\cap$ Ag<sub>2</sub>Se@SBB hybrid nanostructure was repeatedly washed, purified by decantation, and then dried. Further, the reaction product was washed with ethanol to remove any unbound AC-CD, AC, and CD.

**Characterization.** Ultraviolet–visible (UV–vis) spectra were measured using a PerkinElmer Lambda 25 instrument in the range 200–1100 nm. Fourier transform infrared spectra

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(IR) were recorded using a PerkinElmer Spectrum One spectrometer. Powder X-ray diffraction (XRD) was recorded using a Bruker D8 Advance X-ray diffractometer. Matrixassisted desorption ionization mass spectrometry (MALDI MS) studies were conducted using a Voyager DE PRO biospectrometry workstation (Applied Biosystems) matrixassisted laser desorption ionization (MALDI) time-of-flight (TOF) mass spectrometer. The matrix used was trans-2-[3-(4*t*-butylphenyl)-2-methyl-2-propenylidene] malononitrile. The electrospray ionization mass spectrometric (ESI MS) measurements were done using a Thermo Scientific LTQ XL ESI MS, within a mass range of m/z 100-4000. High-resolution transmission electron microscopy (HR TEM) was conducted to study the morphology using a JEOL 3010 ultrahighresolution analytical electron microscope operated at 200 kV. TEM samples were prepared as dispersions in ethanol, dropcasted on carbon-coated copper grids, and then allowed to dry at room temperature. Luminescence measurements were carried out on a Horiba Jobin Yvon NanoLog spectrometer. The slit width for excitation and emission was set at 2 nm. Fluorescence decay profiles were measured using a timecorrelated, single-photon-counting spectrometer (Horiba Jobin Yvon). A diode laser source ( $\lambda_{ex}$ , 460 nm), having a pulse repetition rate of 1 MHz, was used for excitation. The instrument response function (IRF) for the 460 nm excitation was 1.28 ns. The decay curves were collected at wavelengths near to the emission maxima and analyzed with IBH DAS6 software with proper fitting. During fitting, the  $\chi^2$  values were adjusted within the valid range.

## RESULTS AND DISCUSSION

Aminoclay is an exfoliated and sheetlike nanoclay, which exhibits a low-angle reflection and is having a bilayer



**Figure 1.** (A) FTIR spectra of (i) MCT- $\beta$ -CD, (ii) aminoclay, and (iii) AC-CD. (B) XRD pattern of (i) aminoclay and (ii) AC-CD with the inset showing the expanded view in the low-angle region corresponding to the  $d_{001}$  position. (C, D) TEM images of AC-CD.

arrangement of propylamino groups consistent with a  $d_{001}$  interlayer spacing of 1.6 nm.<sup>22</sup> PXRD shows various reflections at higher angles, viz.,  $d_{020,110}$  and  $d_{060}$ . The  $d_{060}$  is a characteristic reflection, which affirms the formation of 2:1

trioctahedral Mg-phyllosilicate (Figure S1). The planar layered structure is supported by TEM images, which display aminoclay sheets having lateral size in microns. Further, aminoclay is grafted with  $\beta$ -CD, but native  $\beta$ -CD and aminoclay do not show any kind of interaction with each other. For the interaction to occur,  $\beta$ -CD is functionalized with a monochlorotriazinyl (MCT) group. MCT is known for its capability to form covalent bonds with nucleophilic groups. Monochlorotriazinyl- $\beta$ -cyclodextrin (MCT- $\beta$ -CD) is synthesized by reacting  $\beta$ -CD with cyanuric chloride, and their interaction is analyzed by FTIR and ESI MS. The FTIR spectra of  $\beta$ -CD, cyanuric chloride, and MCT- $\beta$ -CD are compared in Figure S2. In the case of MCT- $\beta$ -CD, the stretching between 1500 and 860 cm<sup>-1</sup> is characteristic for  $\beta$ -CD. The stretching frequency of 1464 cm<sup>-1</sup> is attributed to the C=N bond, and the stretching at 810 cm<sup>-1</sup> corresponds to the C-Cl bond of cyanuric chloride. The additional peak at 1580 cm<sup>-1</sup> confirms the ester bond formation, which binds the triazine ring of cyanuric chloride with  $\beta$ -CD. ESI MS of MCT- $\beta$ -CD is also performed, exhibiting the peaks at m/z 1286.42 and 1308.42, which correspond to the formation of a monosubstituted product, and the peaks at m/z 1436.16 and 1459.32 are assigned to the formation of a disubstituted product. This indicates that  $\beta$ -CD has been functionalized by MCT.

Aminoclay is then grafted with MCT- $\beta$ -CD by substituting the chlorine atom with the  $-NH_2$  group of the aminoclay. The grafting of MCT- $\beta$ -CD onto the surface of aminoclay is verified by FTIR, XRD, and TEM studies (Figure 1). FTIR spectrum of aminoclay shows the characteristic peaks at 3425, 1630, 1145, and 1037 cm<sup>-1</sup>. The peaks at 1630 and 2017 cm<sup>-1</sup> correspond to the primary amine group and its protonated form. The  $-NH_2$  group of the aminoclay reacts by substituting the chlorine atom of MCT- $\beta$ -CD (Figure 2). The IR spectrum of the aminoclay conjugated with MCT- $\beta$ -CD (AC-CD) shows the disappearance of the primary amine peak at 1630 and 2017 cm<sup>-1</sup>. The spectrum of the AC-CD possesses peaks attributed to MCT- $\beta$ -CD and also due to aminoclay. The peaks at 560, 863, and 1750 cm<sup>-1</sup> are the characteristic bands for MCT- $\beta$ -CD, and the peak at 1037 cm<sup>-1</sup> corresponds to the Si–O–Si stretching of the aminoclay.

Powder X-ray diffraction analyses of AC and AC-CD were carried out to investigate the extent of exfoliation in AC, and the results are presented in Figure 1B. The XRD pattern of AC-CD exhibits a change in peak position in the low-angle region. The diffraction peak corresponding to the  $d_{001}$  plane shifts from  $6^{\circ}$  in AC to 5.25° in AC-CD. This decrease in the XRD peak position of the  $\beta$ -CD-grafted aminoclay can be related to the increase in the interlayer spacing. The functionalization of AC with  $\beta$ -CD changed the XRD profile significantly from amorphous to crystalline, which is evident from the disappearance of the broad hump at a  $2\theta$  value of 22.30° and appearance of sharp diffraction peaks at  $2\theta \sim 17.30$ , 26.50, and 29.25°. This could be due to the grafting of  $\beta$ -CD onto AC, which leads to the exfoliation and intercalation of  $\beta$ -CD onto the sheets of aminoclay, which results in the ordered arrangement of the AC-CD hybrid material, thereby increasing crystallinity.

TEM images of AC-CD in Figure 1C,D show morphological features and reveal the precise and sharp sheetlike structures. The close assembly of functionalized clay layers emerges due to the chemical interaction of hydroxylated edges between adjacent layers. The functionalization of aminoclay with  $\beta$ -CD does not distort the layered sheet structure.

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Figure 2. Schematic representation of entrapment of atomically precise clusters in cyclodextrin-functionalized aminoclay (AC-CD).



**Figure 3.** (A) Photographs of phenolphthalein solutions with increasing concentrations of AC-CD,  $\beta$ -cyclodextrin, and aminoclay. Color change is observed for AC-CD and  $\beta$ -cyclodextrin. However, no change in color is seen in aminoclay-added solutions. (B) UV absorbance of PHTH/AC-CD solutions with increasing AC-CD concentration. (C) Curves of absorbance vs concentrations of (i)  $\beta$ -CD, (ii) AC-CD, and (iii) aminoclay.

**Grafting Ratio of**  $\beta$ **-CD.**  $\beta$ -CD is known to form an inclusion complex with phenolphthalein, and this complexation fades the pink color (Figure 3). The grafting ratio of  $\beta$ -CD was measured by the phenolphthalein (PHTH) inclusion method.<sup>60</sup> The PHTH molecule undergoes deprotonation in alkaline media (above a pH of 8.2). This causes an opening

of the lactone ring of the molecule and results in an increase in the delocalization of  $\pi$ -electrons, which changes its color from colorless to pink. PHTH forms a host-guest inclusion complex with  $\beta$ -CD. Binding of PHTH results in the transformation of a pink-colored trigonal sp<sup>2</sup>-conjugated system to a colorless tetrahedral sp<sup>3</sup>-lactonoid form (Figure



Figure 4. (A) UV-vis absorption and (B) emission spectra of the cluster and AC-CD $\cap$ Ag<sub>2</sub>Se@SBB. (C) XRD pattern of (i) AC-CD, (ii) cluster, and (iii) AC-CD $\cap$ Ag<sub>2</sub>Se@SBB. (D, E) TEM images and (F) photograph of AC-CD $\cap$ Ag<sub>2</sub>Se@SBB.



Figure 5. Time-resolved fluorescence decay profile of  $Ag_2Se@SBB$  and  $AC-CD\cap Ag_2Se@SBB$  in a 3:1 THF/H<sub>2</sub>O solution.

S3).<sup>61</sup> In the experiment on the grating ratio measurement, we have taken a fixed amount of PHTH and different amounts of AC-CD.

A freshly prepared solution of 0.1 mM PHTH in 0.02 M NaHCO<sub>3</sub> buffer was used for all of the measurements. Different concentrations of AC-CD suspensions were mixed with this PHTH solution, and the resulting mixtures were kept for stirring overnight. An alkaline solution of PHTH exhibits an absorption maximum at 580 nm, responsible for the pink color of phenolphthalein (Figure 3A,B).

In the experiment on the grafting ratio measurement, we have taken different amounts of AC-CD. With increasing concentration of AC-CD, the intensity of the pink color decreases as shown in Figure 3A. This is due to its complexation with phenolphthalein. Accordingly, the absorbance intensity at 552 nm decreases (Figure 3B). The decrease in absorbance intensity with an increase in  $\beta$ -CD concentration follows an exponential behavior, which yields a linear relationship between ln(Abs of PHTH) and ln( $\beta$ -CD concentration) (Figure 3C). PHTH does not interact electrostatically with aminoclay as aminoclay is positively charged due to amine groups on its surface (Figures S4 and \$5). Thus, the amount of phenolphthalein anchored in the cavity of  $\beta$ -CD is used to determine the weight percentage of  $\beta$ -CD in AC-CD and the average grafting ratio of  $\beta$ -CD in the AC-CD is 4.15 wt %.

Supramolecular Functionalization of the AC-CD Composite with the Ag<sub>2</sub>Se@SBB Cluster. The supramolecular interaction between the Au<sub>25</sub> cluster protected by 4-(*t*-butyl)benzyl mercaptan (Au<sub>25</sub>SBB<sub>18</sub>) and CD yielding Au<sub>25</sub>SBB<sub>18</sub> $\cap$ CD<sub>n</sub> (n = 1, 2, 3, and 4;  $\cap$  represents supramolecular inclusion) was reported earlier by our group.<sup>57</sup> To further explore this kind of interaction, we have treated AC-CD, having molecular recognition properties of cyclodextrin, with the Ag<sub>2</sub>Se@SBB cluster to build a luminescent supramolecular structure. Ag<sub>2</sub>Se@SBB is a red luminescent cluster protected with a 4-(*t*-butyl)benzyl mercaptan (SBB) ligand

Table 1. Lifetime Values of Ag₂Se@SBB and AC-CD∩Ag₂Se@SBB

sample	$ au_1$ (ns)	$ au_2$ (ns)	$\tau_3$ (ns)	B1	B2	B3	$\chi^2$	average lifetime (ns)
Ag <sub>2</sub> Se@SBB	5.21	0.93	13.13	43.29	5.96	50.75	1.18	5.10
AC-CD∩Ag₂Se@SBB	1.85	6.63	15.23	10.43	54.76	34.81	1.13	6.49

and has been thoroughly characterized. This cluster displays UV–vis absorption features at 445 and 570 nm as shown in Figure S6A. From the MALDI MS of the cluster in negative ion mode, a peak with m/z 12.5 kDa is observed similar to the earlier report.<sup>59</sup> The Ag<sub>2</sub>Se@SBB shows red luminescence with an emission maximum at 625 nm, and the TEM image shows that the cluster is monodisperse with an average size of 2 nm as shown in Figure S6C,D. The schematic preparation of the AC-CD $\cap$ Ag<sub>2</sub>Se@SBB supramolecular nanocomposite from AC-CD and Ag<sub>2</sub>Se@SBB is shown in Figure 2. It can be seen that the functionalization of AC with MCT- $\beta$ -CD yields AC-CD and its supramolecular self-assembly with the Ag<sub>2</sub>Se@SBB cluster results in a highly luminescent AC-CD $\cap$ Ag<sub>2</sub>Se@SBB nanohybrid. AFM images of AC-CD are shown in Figure S7.

The AC-CD∩Ag<sub>2</sub>Se@SBB nanocomposite is characterized by UV-vis, PXRD, and TEM. UV-vis spectral features of the nanocomposite show absorption bands at 447 and 573 nm, which are blue-shifted by 2 and 3 nm, respectively, as compared to the cluster (Figure 4A). This could be due to the interaction of the cluster with AC-CD. This indicates that the cluster features are retained in the nanocomposite. Photoluminescence (PL) of the cluster and cluster-embedded AC-CD are measured in the solution phase using the following concentration: 5 mg of the sample in 2 mL of the THF and water 3:1 mixture. PL measurements are carried upon exciting the samples at a wavelength of 440 nm. The luminescence profiles of the native cluster and cluster-embedded AC-CD are shown in Figure 4B. The emission spectra marked in black and red correspond to the native cluster and cluster-embedded AC-CD, respectively. The shapes of the emission curves are almost similar having emission maximum at 625 nm; however, clusterembedded AC-CD shows higher emission intensity and is about 1.4 fold higher as compared to that of the pristine cluster. The origin of luminescence in a nanocomposite is from the cluster as the native AC-CD is nonluminescent. Enhanced luminescence in the nanocomposite could be due to the encapsulation of the cluster in the CD cavities of AC-CD, which provides a rigid support to the cluster and therefore prevents nonradiative energy loss. The powder XRD patterns of AC-CD, Ag<sub>2</sub>Se@SBB, and AC-CD∩Ag<sub>2</sub>Se@SBB are shown in Figure 4C. The XRD pattern of the Ag<sub>2</sub>Se@SBB cluster exhibits a broad peak and is similar to the reported one.<sup>59</sup> The powder XRD patterns of AC-CD∩Ag<sub>2</sub>Se@SBB show the diffraction peaks characteristic of AC-CD. However, the lowangle peak observed for AC-CDAg2Se@SBB splits and gets shifted to a low-angle range from 5.25 to 5.15° as compared to AC-CD (inset of Figure 4C). These results suggest the existence of a layered structure in the AC-CD Ag2Se@SBB nanocomposite, which is supported by the TEM micrograph (Figure 4D). TEM micrographs (Figure 4D,E) also show that the cluster is dispersed in AC-CD∩Ag<sub>2</sub>Se@SBB. The cluster gets incorporated only into the CD of the functionalized aminoclay (AC-CD) as the 4-(t-butyl)benzyl group of the SBB ligand on Ag<sub>2</sub>Se@SBB acts as a recognition site for a stable host-guest inclusion complex with CD.57 The photograph of powdered AC-CD∩Ag<sub>2</sub>Se@SBB shows red luminescence under UV light (Figure 4F). A luminescent AC-CD∩Ag<sub>2</sub>Se@ SBB nanocomposite is obtained in bulk amounts.

Lifetime Studies. To study the photoluminescence property of the AC-CD $\cap$ Ag<sub>2</sub>Se@SBB composite, photoluminescence lifetime measurements were recorded using a Horiba Jobin Yvon Fluorocube spectrometer in a time-correlated singlephoton-counting (TCSPC) arrangement with a 460 nm LED having a pulse repetition rate of 1 MHz as the light source. Photoluminescence lifetime curves were investigated by studying the emission wavelength ( $\lambda_{\rm em}$  625 nm) at an excitation wavelength,  $\lambda_{\rm ex}$  of 460 nm. Decay curves were investigated by nonlinear least-squares iteration using IBH DAS6 decay analysis software employing the following equation

$$I(t) = A_i \exp(-t/\tau_i)$$

where  $\tau_i$  is the luminescence lifetime and  $A_i$  is the amplitude of the corresponding decay.

Decay curves were fitted triexponentially and are shown in Figure 5. Average lifetimes for the cluster and entrapped cluster-based system (AC-CD∩Ag<sub>2</sub>Se@SBB) were found to be 5.10 and 6.49 ns, respectively, as shown in Table 1. The emission expected from the hybrid material arises from the sensitization of Ag<sub>2</sub>Se cluster sites, and these clusters possibly occupy the host sites close to the surface of aminoclay and cyclodextrin. Cluster interaction with AC-CD can also be evaluated by lifetime measurements. There are significant changes in the lifetime components, viz.,  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ . This change suggests a different environment around the Ag<sub>2</sub>Se cluster. This is further understood from the decay function  $\tau_{3}$ , which contributes highest to the total average lifetime. A higher lifetime decay component of the embedded cluster (AC-CD∩Ag<sub>2</sub>Se@SBB) compared to the free cluster indicates that the cluster moieties are highly protected to avoid crossrelaxation and vibrational coupling with the SBB ligand.

#### CONCLUSIONS

In summary, the grafting of  $\beta$ -cyclodextrin onto the surface of aminoclay was achieved. The as-synthesized AC-CD was shown to be an effective and attractive material for the functionalization of the clay with Ag<sub>2</sub>Se@SBB. The interactions between AC-CD and Ag<sub>2</sub>Se@SBB resulted in enhanced luminescence of the clusters. These supramolecular interactions were studied in detail by various spectroscopic techniques. We presented a methodology to functionalize AC-CD with luminescent clusters and observed the enhancement in the luminescence for the resulting nanocomposite system. Interlayer spacing between AC-CD layers was determined by various analytical techniques, such as XRD and TEM, and was found to be sufficient enough to accommodate the cluster in it. This material was highly stable. We believe that this stable luminescent material will be useful for various applications such as sensors, optoelectronic devices, etc.

## ASSOCIATED CONTENT

#### **1** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.9b07018.

XRD pattern of the aminoclay with TEM as the inset; FTIR, ESI MS, and schematic procedure for the synthesis of MCT- $\beta$ -CD, binding of phenolphthalein to cyclodextrin, UV–vis absorbance and calibration curves with different concentrations of  $\beta$ -CD; UV–vis absorbance and calibration curves with different concentrations of aminoclay; characterization of the Ag<sub>2</sub>Se@SBB cluster; AFM images of AC-CD (PDF)

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## Notes

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