# Aggregation induced non-emissive-to-emissive switching of molecular platinum clusters

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# **Experimental Section**

# Materials

Chloroplatinic acid hydrate (H<sub>2</sub>PtCl<sub>6</sub>· H<sub>2</sub>O, 99.995 %), reduced glutathione (L-GSH,  $\geq$  98 %), sodium borohydride (NaBH<sub>4</sub>, 99 %, trace metal basis), chitosan (deacetylated, from shrimp shells  $\geq$  75 %), cadmium (II) acetate dihydrate (Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>· 2H<sub>2</sub>O  $\geq$  98%), mercuric chloride (HgCl<sub>2</sub>, 99%), ferrous chloride (FeCl<sub>2</sub>, 98%), zinc (II) chloride (ZnCl<sub>2</sub>, 99.99 %) and alcohols were purchased from Sigma-Aldrich. Triethylamine (Et<sub>3</sub>N, 99 %), was purchased from Spectrochem. Ethanol (absolute) was purchased from Emsure. All acids were purchased from Finar. All chemicals were used as received. High conducting arsenic doped n-type Si(111) with resistivity < 5 mΩ-cm purchased from Sillicon Valley Microelectronics (SVM) Incorporation, USA and Quartz substrates were purchased from Tedpella. Inc, USA.

# Synthesis of glutathione protected platinum cluster

Aqueous solutions of  $H_2PtCl_6$ ·  $H_2O$  (0.5 mmol) and L-reduced Glutathione (1.5 mmol) were mixed together and stirred for 2 h at 0 °C. An ice-cold aqueous solution of NaBH<sub>4</sub> (3 mmol) was added drop wise under vigorous stirring. The solution was allowed to react for 4 h. A golden yellow solution was obtained which on precipitation with methanol gave a fine yellow powder. The as-synthesized Pt-SG NC was purified by repeated washing with methanol and dried for further characterizations.

# Preparation of Pt cluster incorporated bio-composite film

0.24 g of chitosan was starred in 10 mL of distilled water containing 5 % glacial acetic acid. Insoluble substances were removed by filtration through a medium-pore-sized glass funnel to yield chitosan solution. 1.16 g of Pt-SG cluster was added to the chitosan solution and stirred to obtain a homogeneous solution. 20 mL of this NC-embedded chitosan solution was then poured onto a plastic Petridis and dried at 40 °C for 24 h.

# **Sensing experiments**

## Acid base sensing

10 mL of HCl or Et<sub>3</sub>N solvent was taken to a glass vial. A piece of film was placed on a holder, exposed to the vapors by placing the holder on the top of the vial, and equilibrated for 15 min.

## **Temperature sensing**

Samples were iteratively heated and cooled using a temperature-controlled cell holder connected to a circulation bath and mounted within a fluorimeter. During annealing, samples were heated from 5 °C to 65 °C at a rate of ~1 °C min<sup>-1</sup> with an equilibration time of 15 min

followed by cooling down to 5 °C at the same rate. This constitutes one cycle and 135 min was needed to complete one cycle. Four additional cycles were applied for each set of experiments. The AIE property of the Pt-SG clusters can be tuned by varying the temperature. The aqueous solution of Pt-SG cluster was slowly heated from 5 °C to 65 °C. An increase in temperature leads to a decrease in the emission intensity of Pt-SG cluster and when the temperature was decreased, the emission intensity was restored accordingly. This emission switching operations were repeated for five consecutive cycles by implementing multiple heating and cooling segments between 5 °C and 65 °C. This repeatability of the emission intensity against temperature shows that the Pt-SG clusters have excellent thermosensitivity against temperature variations and have a wide scope in the field of nanothermometry (Figure S4).

## Metal ion sensing

Metal ion induced aggregation was studied using several metal salts such as cadmium nitrate tetrahydrate (Cd(NO<sub>3</sub>)<sub>2</sub>· 4H<sub>2</sub>O), zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>· 6H<sub>2</sub>O), mercuric chloride dihydrate (HgCl<sub>2</sub>· 2H<sub>2</sub>O), ferrous chloride (FeCl<sub>2</sub>), with [M<sup>2+</sup>]: [GSH] is 1: 2. Metal salts (50  $\mu$ L) were added to the 3 mL Pt-SG cluster in aqueous medium.

#### **Characterization techniques**

The emission spectra were recorded using a Horiba JobinYvon-Fluorolog 3 spectrofluorimeter. All the steady-state emission studies were carried out by exciting the sample at 400 nm. Quantum yields at different EtOH: H<sub>2</sub>O mixtures were recorded in a FluoroMax-3 (HORIBA, JobinYvon) fluorimeter equipped with a xenon lamp with a quartz cuvette of 1 cm optical path length. Fluorescence lifetimes were measured by using a time-correlated single-photon counting (TCSPC) fluorescence spectrometer. In this setup, samples were excited with a 377 nm (IBH Nanoleds) pulsed picosecond diode laser (~75 ps pulse width) with a repetition rate of ~1 MHz. Appropriate band pass filters are used to block the excitation light during the fluorescence signal collection. The fluorescence signal collected at 90 ° angle to the excitation beam maintaining magic angle polarization (54.7 °) with a band pass of 4 nm. Fluorescence signal at 725 nm was dispersed through a monochromator (IBH, model MCG-910 IB) and detected by using a cooled micro-channel plate photomultiplier (Hamamatsu, 5000-U-09). The full width at half maximum (FWHM) of the instrument response function (IRF) is 270 ps and the resolution is 28 ps/channel. The global lifetime analysis software, IBH DAS6, was used for decay processing where the deconvolution technique was used to calculate the decay of the fluorophore by using the measured decay data and the instrument response function. The

excellence of the fitted data was judged from the obtained  $\chi^2$  and weighted residuals where all the data were analyzed, fitted and plotted by using "Origin-8.0" software.

# Quantum yield measurement

We have measured the fluorescence quantum yield of the aggregation induced metal cluster by recording absorbance and fluorescence of both reference (Cy5) and aggregated nanocluster (NC) at 5 different concentration. By comparing the slopes ( $^{Slope} = ^{Fluorescence} / _{Absorbance}$ ) of Cy5 and Pt-SG cluster at different Ethanol: H<sub>2</sub>O mixtures, we have measured their quantum yield by using the following equation and are listed below

 $\frac{QY \text{ of } Cy5}{QY \text{ of } Pt - SG \text{ } NC} = \frac{Slope \text{ of } Cy5}{Slope \text{ of } Pt - SG \text{ } NC}$ 

# AFM and STM measurements

High conducting arsenic doped n-type Si (111) with resistivity  $< 5 \text{ m}\Omega$ -cm were used as substrates to deposit Pt-SG cluster film for STM and AFM study. Quartz substrates were used to measure the UV-Visible absorption spectrum of Pt-SG in its thin film form. Si was cleaned by ultra-sonication following standard protocol to clean these by soap solution, deionized water (DI water), and acetone: PA (1:1) mixture. DI water (collected from milli-Q direct 8 system) with resistivity 18.2 MQ-cm was used for the entire study. Cleaned substrates were kept in a mixer of ammonium hydroxide and hydrogen peroxide solution with ratio 3: 1 (v/v) for 3 h to make their surface hydrophilic. These substrates were rinsed thoroughly using DI water. Pt-SG clusters were dissolved in DI water with concentration 3 mg/mL and spin coated over the cleaned hydrophilic substrates with 3000 rpm for 30 s and annealed the film in vacuum oven at 100 °C for 1 h and allowed to cool down to room temperature before going for further characterizations.

# **Computational methods**

To elucidate the unusual excitation characteristics of Pt-based NC, we have carried out density functional theory (DFT) and time-dependent density functional perturbation theory (TD-DFT) calculations using G09 software.<sup>1</sup> All geometries optimization and TD-DFT computation were carried out by using hybrid B3LYP functional<sup>2</sup> using G09 software. To include scalar relativistic effect for platinum (Pt), we have used LANL2DZ pseudopotential<sup>3</sup> and 6-31G (D) basis set<sup>4</sup> for all other atom. We have further performed normal-mode analysis to verify the absence of any second-order saddle point of all optimized ground state structures. The TD-DFT

calculation was performed based on the optimized ground state geometries to analyze optical properties of this cluster. IEF-PCM solvation was used (ethanol solvent) during the TD-DFT calculation.<sup>5</sup>

#### Methods to calculate degree of aggregation

The degree of aggregation was guided by the polarity of the mixed solvent, that can be

$$f_e = \frac{V_{EtOH}}{V_{(EtOH + H_2 0)}}.$$

controlled by volume fraction  $(f_e)$  of ethanol in the mixture,

# **Density of states measurements**

Spin coated thin films of Pt-SG cluster with two different concentrations 1.0 and 3.0 mg/mL in DI water were used to observe the surface coverage on substrate by recording the AFM topography images. Among these, 3 mg/mL gave the uniform film with better coverage. Tapping mode AFM image of the film of 1.0 & 3.0 mg/mL solution are shown in Figure S4. Presence of Pt-SG clusters on top of substrate was confirmed again from STM topographic images as shown in inset of figure 4b. After achieving good topographic images, tunneling current-voltage (I-V) characteristics were measured on different locations of cluster thin film to study its electrical property as thin film. STM tip voltage was scanned from -3V to +3V between the Si(111) substrate and STM tip for making I-V measurements.

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Figure S1: TEM images of Pt-SG cluster on aggregation in 93 % ethanol-water mixture.



**Figure S2:** a) Temperature dependent emission studies of aqueous solution of Pt-SG cluster, Inset shows the exponential decay of the luminescence intensity on increasing temperature. b) The recyclability of emission on multiple heating-cooling segments.

Lifetime	T <sub>1</sub>	Standard Error
Pt-SG in Solid state	7.98 x 10⁻ <sup>8</sup>	± 6.22x10 <sup>-10</sup>
Pt-SG in EtOH	8.11 x 10 <sup>-8</sup>	± 7.55x10 <sup>-10</sup>
Pt-SG in 7:3 EtOH:H <sub>2</sub> O	4.42 x 10 <sup>-8</sup>	± 3.76x10 <sup>-10</sup>
Pt-SG in 5:5 EtOH:H <sub>2</sub> O	2.64 x 10 <sup>-8</sup>	± 1.42x10 <sup>-10</sup>

**Table S1**: Emission lifetime for the ethanol induced aggregates.

**Table S2**: Relative QY for the ethanol induced aggregates.

C <sub>2</sub> H <sub>5</sub> OH : H <sub>2</sub> O	Measured QY (%)
6:4	0.007
7:3	0.12
8:2	0.21
9:1	0.32
10:0	1.99



**Figure S3**: Emission response of aqueous solution of Pt-SG cluster on the addition of different protic solvents.

Table S3. Protic solvents acceptance number and solvent-cluster interaction parameters.

Solvents	Acceptance number (AN)	Solvent-cluster (surface) interaction $(\delta_D)$ (mPa)
<sup>t</sup> Bu-OH	27.1	15.2
<sup>i</sup> Pr-OH	33.5	15.8
EtOH	37.9	15.8
MeOH	41.5	15.8

Table S4. Aprotic solvents acceptance number and solvent-cluster interaction parameters.

Solvents	Acceptance	Solvent-cluster (surface)
	number (AN)	interaction (δ <sub>D</sub> ) ( mPa)
DMA	13.6	16.8
Acetone	12.5	15.5
DMF	16	17.4
DMSO	19.3	18.4



**Figure S4:** AFM topographical image of Pt cluster films spin coated on Si substrate with solution concentration (a) 1.0 mg/mL (b) and 3 mg/mL. ((b) Shows better surface coverage as thin film).



Figure S5: Photograph of Pt-SG cluster on glass substrate: under visible and UV light.



**Figure S6**. a) Photograph of the Pt-SG composite film under visible and UV light. b) Emission spectra of the composite film on different loading of the cluster. c) Emission response of the composite film to HCl and  $Et_3N$  vapors.



**Figure S7**: UV-Vis absorption spectrum of Pt-SG-CS film. Inset: Absorption spectrum of Pt-SG cluster in aqueous medium.



Figure S8: SEM-EDAX of Pt-SG-CS film.



Figure S9: Photograph of the composite film on exposure to HCl and Et<sub>3</sub>N vapours.



**Figure S10**: Time dependent luminescence spectra of Pt-SG-CS film on exposure to HCl vapors.



Figure S11: Photograph of aqueous solution after dipping the acid-base exposed film in it.

Note: This experiments were performed by initially exposing the film to HCl vapors followed by dipping the film in aqueous solution. It was observed that the color of the solution turned yellow after the removal of the film, which indicates the weak interaction of the cluster with chitosan. Whereas on dipping the acid-base exposed film, no considerable color change was observed after the removal of film from water indicating the strong interaction of the cluster with chitosan.



Figure S12: Luminescence response of Pt-SG-CS film on exposure to various acids.



Figure S13: Luminescence switching of Pt-SG-CS film on exposure to HCl-Et<sub>3</sub>N vapours.