

Established in 1959

# Luminescent quantum clusters of noble metals

## T. Pradeep

#### Department of Chemistry Indian Institute of Technology Madras Chennai 600 036

 $Au_{25}$ ,  $Au_{23}$ ,  $Au_{22}$ ,  $Au_8$  and  $Ag_8$ 

Symposium on Surfaces and Catalysis, SSCU, IISc., July 26, 2010



Acknowledgements M.A. Habeeb Muhammad E.S. Shibu Tumu Udaya Bhaskara Rao Kamalesh Choudhari Lourdu Xavier

S.K. Pal, SNBS, Kolkata G.U. Kulkarni, JNCASR, Bangalore R. V. Omkumar, RGCBT, Thiruvananthapuram Nano Mission, Department of Science and Technology Monolayer Protected Metal Nanoparticles Monolayer Protected Clusters (MPCs)



N. Sandhyarani and T. Pradeep, Int. Rev. Phys. Chem. 2003

#### **Phosphine Capped Gold Clusters**



 Au<sub>55</sub> [P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>12</sub>Cl<sub>6</sub> - a gold cluster of unusual size, Schmid, G.; Pfeil, R.; Boese, R.; Brandermann, F.; Meyer, S.; Calis, G. H. M.; Van der Velden.; Jan W. A. Chemische Berichte 1981, 114, 3634.

Synthesis and x-ray structural characterization of the centered icosahedral gold cluster compound [ Au<sub>13</sub> (PMe<sub>2</sub>Ph)<sub>10</sub>Cl<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub>; the realization of a theoretical prediction, Briant, C. E.; Theobald, B. R. C.; White, J. W.; Bell, L. K.; Mingos, D. M. P.; Welch, A. J. Chem. Commun. 1981, 5, 201.

 Synthesis of water-soluble undecagold cluster compounds of potential importance in electron microscopic and other studies in biological systems, Bartlett, P. A.; Bauer, B.; Singer, S. J. Am. Chem. Soc. 1978, 100, 5085.

#### **Molecular Clusters**





• 28 kDa Alkanethiolate-Protected Au Clusters Give Analogous Solution Electrochemistry and STM Coulomb Staircases, Ingram, R. S.; Hostetler, M. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J.; Whetten, R. L.; Bigioni, T. P.; Guthrie, D. K.; First, P. N. J. Am. Chem. Soc. 1997, 119, 9279.

 Isolation of Smaller Nanocrystal Au Molecules: Robust Quantum Effects in Optical Spectra, Schaaff, T. G.; Shafigullin, M. N.; Khoury, J. T.; Vezmar, I.; Whetten, R. L.; Cullen, W. G.; First, P. N.; Gutierrez-Wing, C.; Ascensio, J.; Jose-Yacaman, M. J. J. Phys. Chem. B 1997, 101, 7885.

 Optical Absorption Spectra of Nanocrystal Gold Molecules, Alvarez, M. M.; Khoury, J. T.; Schaaff, T. G.; Shafigullin, M. N.; Vezmar, I.; Whetten, R. L. J. Phys. Chem. B 1997, 101, 3706. Isolation and Selected Properties of a 10.4 kDa Gold:Glutathione Cluster Compound, Schaaff, T. G.; Knight, G.; Shafigullin, M. N.; Borkman, R. F.; Whetten, R. L. J. Phys. Chem. B 1998, 102, 10643.

• Controlled Etching of Au:SR Cluster Compounds, Schaaff, T. G.; Whetten, R. L. J. Phys. Chem. B 1999, 103, 9394.

• Giant Gold-Glutathione Cluster Compounds: Intense Optical Activity in Metal-BasedTransitions, Schaaff, T. G.; Whetten, R. L. J. Phys. Chem. B 2000, 104, 2630.

Near-Infrared Luminescence from Small Gold Nanocrystals, Bigioni, T. P.; Whetten, R. L.; Dag, O. J. Phys. Chem. B 2000, 104, 6983.

Properties of a Ubiquitous 29 kDa Au:SR Cluster Compound. Schaaff, T. G.; Shafigullin, M. N.; Khoury, J. T.; Vezmar, I.; Whetten, R. L. J. Phys. Chem. B 2001, 105, 8785.

Visible to Infrared Luminescence from a 28-Atom Gold Cluster, Link, S.; Beeby, A.; FitzGerald, S.; El-Sayed, M. A.; Schaaff, T. G.; Whetten, R. L. J. Phys. Chem. B 2002, 106, 3410.

• All-Aromatic, Nanometer-Scale, Gold-Cluster Thiolate Complexes, Price, R. C.; Whetten, R. L. J. Am. Chem. Soc. 2005, 127, 13750.

# **Au**<sub>102</sub>

Au<sub>102</sub>(p-MBA)<sub>44</sub>



Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. Structure of a Thiol Monolayer–Protected Gold Nanoparticle at 1.1 Å Resolution *Science* **2007**, *318*, 430.

How to make them?

#### Polyacrylamide gel electrophoresis (PAGE)



Negishi, Y.; Nobusada, K.; and Tsukuda, T. Glutathione-Protected Gold Clusters Revisited: Bridging the Gap between Gold(I)-Thiolate Complexes and Thiolate-Protected Gold Nanocrystals. *J. Am. Chem. Soc.* **2005**, *127*, 5261-70.

# Au<sub>25</sub>SG<sub>18</sub>

Synthesis: Au<sub>25</sub> clusters can be preferentially populated by dissociative excitation of larger precursors



Scheme showing the synthesis of  $Au_{25}SG_{18}$  clusters

E. S. Shibu et al. J. Phys. Chem. C. 2008







FTIR spectrum: The peak at 2526 cm<sup>-1</sup> of glutathione due to -SH stretching frequency is absent in IR spectrum of Au<sub>25</sub> suggesting the ligand binding on cluster surface.

#### 1H NMR spectrum: There is one-to-one

correspondence between the two spectra, except that the  $\beta$ CH<sub>2</sub> resonance (labeled as C) disappears completely in the cluster which is expected as it is close to the cluster surface. All the observed resonances have been broadened in view of their faster relaxation and non-uniform distribution of ligands.





#### XPS spectrum

TEM image: The clusters are seen only faintly since the size is ~1 nm. Some of the individual clusters are shown by circles. There are also cluster aggregates which upon extended electron beam irradiation fuse to form bigger particles



#### Perumal Ramasamy et al. J. Mater. Chem., 2009, 19, 8456.

#### With Arindam Banerjee

Ligand Exchange of Au<sub>25</sub>











Lecoultrea, S.; Rydlo, A.; F elixb, C.; Harbich, W. Eur. Phys. J. D, 2009 DOI: 10.1140/epjd/e2008-00290-0

	Cluster	Q.Yield			
	$\begin{array}{l} Au_{10}(SG)_{10} \\ Au_{11}(SG)_{11} \\ Au_{11}(SG)_{11} \end{array}$	1*10-4	Precursor Using other ligands	v developed clusters using Au <sub>25</sub> as precursor	
	Au <sub>15</sub> (SG) <sub>13</sub>	2*10-4			
	Au <sub>18</sub> (SG) <sub>14</sub>	4*10 <sup>-3</sup>		Cluster	Q. Yield
	Au <sub>22</sub> (SG) <sub>16</sub>	4*10 <sup>-3</sup>		Au <sub>22</sub>	4.0*10-2
	Au <sub>22</sub> (SG) <sub>17</sub>	2*10-3		Au <sub>23</sub>	1.3*10 <sup>-2</sup>
	Au <sub>25</sub> (SG) <sub>18</sub>	1.9*10-3			
	Au <sub>29</sub> (SG) <sub>20</sub>	3*10-3		Au <sub>31</sub>	1.0*10-2
	$Au_{33}(SG)_{22} Au_{35}(SG)_{22}$	2*10-3		Au <sub>8</sub> (SG) <sub>8</sub>	1.5*10-1
	$\begin{array}{c} Au_{38}(SG)_{24,} \\ Au_{39}(SG)_{24} \end{array}$	2*10-3		Res., 1(2008) 333-340.	
			• 2. Chemistry A European Journal. (2009).		
••	Gold nanoparticles	1*10-10	3. ACS Applied Materials and Interfaces (2009)		terfaces (2009)

#### FRET between Au<sub>25</sub> and Dansyl Chromophore



Approaches Used for the Functionalization of Dansyl Chromophore on the Au<sub>25</sub> Cluster.

Habeeb Muhammmed et al. J. Phys. Chem. C 2008, 112, 14324.



Scheme 1. Formation of the three sub-nanoclusters from Au SG by core etching by two routes. 25 18 Photographs of the cluster aqueous solutions under UV light are also given.

#### Habeeb Muhammed et al. Chem. Euro. J. 2009, 15, 10110.



Comparison of the optical absorption features of Au  $_{25}^{SG}$  (green trace) with Au OT (grey trace), Au  $_{x}^{SG}$  (pink trace) and Au MPTS (purple trace). The arrows show the absorption peaks of the clusters due to intra band transitions. The spectra are shifted vertically for clarity. Dotted lines indicate the threshold of absorption. Inset shows the photographs (under white light) of the water-toluene bi-phasic mixture before (A) and after (B) reaction at 55 °C (interfacial etching) for 1 h.



Figure 2. A) MALDI-MS of Au SG which shows bunch of peaks due to Au S clusters. B) A group of peaks with m/z spacing of 197 or 229 between the major peaks of the adjacent group of peaks. C) Expanded view of peaks due to Au S 23 18-23.



Comparison of the Au(4f) XPS spectra of  $Au_{22}$ ,  $Au_{23}$  and  $Au_{33}$  along with parent  $Au_{25}$ .



Comparison of the photoluminescence profiles of  $Au_{22}$ ,  $Au_{23}$  and  $Au_{33}$  along with parent  $Au_{25}$ . Photographs of the aqueous solutions of  $Au_{22}$  and  $Au_{23}$  under white light (A and C, respectively) and UV light (B and D, respectively) are also given.



Fluorescence decay pattern of  $Au_{25}$ ,  $Au_{31}$ ,  $Au_{23}$ , and  $Au_{22}$  collected at 630 nm.



Photoluminescene profile of Au<sub>23</sub> cluster before (pink trace) and after (orange trace) phase transfer. Emission of the cluster enhances considerably after the phase transfer. Photographs of the aqueoustoluene mixture containing the cluster before and after phase transfer under white light (A and B, respectively) and UV light (C and D, respectively). In C, only the interface is illuminated as the UV is attenuated as the sample was irradiated from the top



Schematic representation of the conjugation of streptavidin on Au  $\begin{array}{c} SG \\ 23 \end{array}$  by EDC coupling.



Fluorescence (A), bright field (B) and overlay of fluorescent and bright field images (C) of human hepatoma (HepG2) cells stained with streptavidin conjugated Au



**Bright field (A) and fluorescence (B) images of HepG2 cells stained with unconjugated Au**<sub>23</sub> clusters. **No fluorescence was observed from the cells after washing** 



Fluorescent microscopic images showing interaction of Au-BSA-FA NCs with different types of cell lines: a1-a2) FR-ve lung carcinoma A549 after 2 hours of incubation, b1-b2) FR-ve lung carcinoma A549 after 24 hours of incubation, c1-c2) FR+ve KB cells with unconjugated Au clusters, d1-d2) FR+ve KB cells with FA conjugated Au clusters at 2 hrs, e1-e2) 4 hrs and f1-f 2) 24 hrs of incubation [Archana R, Sonali S, Deepthy M et al. Molecular Receptor Specific, Non-toxic, Near-infrared Emitting Au Cluster-Protein Nanoconjugates for Targeted Cancer Imaging. Nanotechnology (2010)]

#### Archana et al. Nanotechnology 2010

## **Clusters for metal ion detection**



Water soluble red emitting clusters where treated with various metal ions with a final Concentration of 25 ppm. The emission was shifted to lower wavelength in case of silver ions and quenched completely in case of copper ions. The emission was an altered in case of other ions.

#### Habeeb Muhammed et al. Chem. Euro. J. 2009, 15, 10110.







С

300

D

300

50 100 150 200 250 Concentration of Zn<sup>2</sup> (µM)

50 100 150 200 250 Concentration of Cu<sup>+2</sup> (µM)

50

Ò

Ò

4x10<sup>6</sup>

4x10<sup>6</sup>





**3D image of CD showing the nanometer cavity** 



E. S. Shibu and T. Pradeep. Unpublished









#### **Clusters in proteins - BSA**



#### Habeeb Muhammed et al. Chem. Euro. J. 2010 Online

#### **Clusters in proteins -Lactoferrin**





Lourdu Xavier et al. Nanoscale (2010)





#### **Mechanism of growth**



Kamalesh Choudhari et al. Unpublished

# Interfacial etching





TUB Rao and T Pradeep, Angew. Chem. Int. Ed. (2010)













White light UV light T→→ RT

# Ag<sub>9</sub>MSA<sub>7</sub>



TUB Rao and T Pradeep, Submitted





Quantum clusters are interesting new materials They exhibit new properties and can be used for diverse applications Catalysis Environmental remediation Diagnostics Security

. . . . . . .



Interfacial Synthesis

DOI: 10.1002/anie.200907120

#### Luminescent Ag<sub>7</sub> and Ag<sub>8</sub> Clusters by Interfacial Synthesis\*\*

T. Udaya Bhaskara Rao and T. Pradeep\*

Dedicated to Professor Manjanath Subraya Hegde on the occasion of his 65th birthday

T. U. B. Rao and T. Pradeep, Angew. Chem. Int. Ed., 49 (2010) 3925 - 3929.





Nano Mission, Department of Science and Technology





# Thanks!