

# WRITE-UP FOR PMR FELLOWSHIP FROM NOV 2024- NOV 2025

## External Teaching Assistantship: Sri Venkateswara College of Engineering, Tirupati

- Modern Engineering Materials
- Structure and Bonding Models
- Instrumental Methods and its Applications
- Polymer Chemistry

## Achievements

- *Best Poster Award* by RSC Publications in 13th Asian and Oceanian Photochemistry Conference (APC), 2025.

## Research Progress

### Chapter 1: Introduction

This chapter provides a broad introduction to chirality, nanoscale chirality, and different methods used for chiral detection. The subsequent section narrows down to the key nanomaterials of interest, chiral metal clusters. We describe their fundamental characteristics and highlight their potential roles in emerging applications. Additionally, we emphasize the significance and necessity of developing chiral metal clusters.

### Chapter 2: (a) Biomolecule-assisted Circularly Polarized Thermally Activated Delayed Luminescence in Copper Iodide Hybrid Clusters

We report the synthesis and chiral analysis of enantiomerically pure copper-iodide clusters exhibiting strong optical activity in both ground and excited states. Using L- and D-isomers of a chiral ligand yielded metal clusters with mirror-image circular dichroism and circularly polarized luminescence signals. Structural validation through single-crystal XRD, powder XRD, and XPS, supported by chiroptical and computational studies, established a distinct structure-property relationship. Photoluminescence studies revealed long excited-state lifetimes, with the rare occurrence of circularly polarized thermally activated delayed luminescence. This work also offers key insights into excited-state chirality in copper clusters, encouraging further exploration of similar effects in other metal systems.

**Reference:** Dutta C, Maniappan S, Kumar J. Delayed luminescence guided enhanced circularly polarized emission in atomically precise copper nanoclusters, *Chemical Science*, **2023**, *14*, 5593-601.

#### **(b) Optically Active Dual-emissive Gold Clusters Featuring Circularly Polarized Phosphorescence**

Enantiomerically pure gold clusters with dual-emission properties, encompassing both fluorescence and phosphorescence, were synthesized using a straightforward and efficient method. Detailed investigations revealed that the triplet-state emission exhibited chiral luminescence, leading to circularly polarized phosphorescence observable in both solution and solid states. The gold clusters also demonstrated aggregation-induced emission enhancement (AIEE), where the emission intensity was significantly enhanced upon aggregation. Notably, the aggregated clusters retained their chiral characteristics, resulting in circularly polarized phosphorescence. These findings highlight the potential of such materials for applications in chiral optoelectronics, sensing, and display technologies.

**Reference:** Dutta C, Maniappan S, Kumar J. Dual emissive optically active gold nanoclusters endowed with circularly polarized phosphorescence, *Chemical Communications*, **2023**, *59*, 13735-8.

#### **Chapter 3: Intrinsic Chirality and Thermoresponsive Behaviour in Gold Cluster Assemblies**

A simple strategy was employed to synthesize inherently chiral cluster assemblies by introducing a positively charged chiral dopant during the formation of negatively charged achiral clusters, resulting in enhanced luminescence and mirror-image chiral absorption. Notably, the nanostructures displayed intriguing thermoresponsive behaviour, where temperature served as a probe to modulate their chiroptical properties. This study provides comprehensive thermodynamic and mechanistic insights and represents the first report on the synthesis of intrinsically chiral Au cluster assemblies.

**Reference:** Dutta C, Nataraajan RV, Kumar J. Intrinsically chiral thermoresponsive assemblies from achiral clusters: enhanced luminescence and optical activity through tailor-made chiral additives, *Chemical Science*, **2025** *16*, 1722-9.

#### **Chapter 4: (a) pH Guided Chiral Inversion and Amplification of Intrinsically Chiral Gold Cluster Aggregates**

This study presents a straightforward pH-guided approach for synthesizing intrinsically chiral gold cluster aggregates stabilized by amino acids. Depending on the pH, amino acids exist in distinct protonation states and engage in various non-bonding interactions, resulting in the formation of diverse cluster assemblies. By modulating the pH from acidic to zwitterionic to

basic conditions, two successive chiral inversions accompanied by AIEE were achieved. This work reports the highest chiral anisotropy observed for gold clusters to date.

**Reference:** Dutta C., Kumar J. pH guided pathways trigger tailoring of chiral luminescence in enantiomeric gold cluster assemblies, *Chemical Science*, **2025**, *16*, 18713-18721.

### **(b) Additive Driven Strategy for Chiral Inversion and Amplification in Bimetallic Cluster Aggregates**

Chiral inversion and amplification were accomplished through an additive-driven strategy, leading to the formation of well-defined cluster-assembled materials (CAMs). Remarkably, both chiral and achiral additives were employed to induce and control the chiral transformation within the assemblies. This approach not only enabled precise modulation of chiroptical behaviour but also resulted in the highest chiral anisotropy values observed for clusters so far.

**Reference:** Dutta C., Mandal A, Shukla A, Hemaprabha E, Nakashima T, Kumar J. Supramolecular Engineering of Cluster-Assembled Materials for Amplification and Dynamic Modulation of Chiral Luminescence, *Angewandte Chemie International Edition*, **2025**, *64*, e202511554.

### **Chapter 5: Emergence of Negative Nonlinear Chiroptical Response from Metal Cluster Aggregates**

This study highlights chiral modulation governed by the optical purity of the protecting ligands. An unusual and rarely reported chiral behaviour dependent on enantiomeric purity was observed, wherein variations in enantiomeric excess led to divergent thermodynamic pathways.

**Reference:** *Manuscript under preparation...*

### **Chapter 6: Design and Synthesis of Optically Active Platinum Clusters**

After successfully exploring the chemistry of gold, silver, and copper clusters, our research focus has now shifted toward the less-explored platinum clusters. The current investigation is centered on the synthesis and exploring the chiroptical behaviour of chiral Pt clusters.

## **Publications (Nov 2023- Nov 2024)**

1. Dutta, C., Kumar, J., *Chem. Sci.*, **2025**, *16*, 18713-18721.
2. Dutta, C., Mandal, A., Shukla, A., Hemaprabha, E., Nakashima, T., Kumar, J., *Angew. Chem. Int. Ed.*, **2025**, *137*, e202511554.
3. Dutta, C., Nataraajan, R. V., Kumar, J., *Chem. Sci.*, **2025**, *16*, 1722-1729.

4. Jha, S., Mehra, K. S., Mondal, P. K., **Dutta, C.**, Kumar, J., Ramalingam, S. S., Jeyaraman, S., *J. Phys. Chem. Lett.*, **2025**, *16*, 12237–12245.