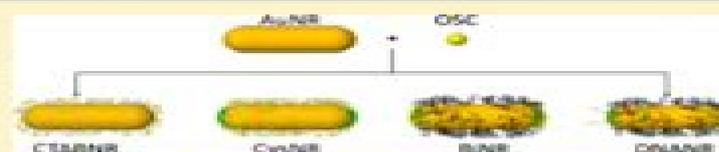


## Tuning Optical Properties of Functionalized Gold Nanorods through Controlled Interactions with Organic Semiconductors

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**ABSTRACT:** A novel nanohybrid assembly consisting of gold nanorods (AuNRs) and organic semiconductors (OSCs) to tune optical properties is presented. OSCs are bound to specific areas of the AuNRs (e.g., end or side) by controlling the surface chemistry of the AuNRs. AuNRs anisotropically functionalized with cetyltrimethylammonium bromide (CTAB), cysteine, poly(ethylene oxide) (PEO), and/or DNA, Rhodamine B (RhB) 5(6)-carboxyfluorescein (CF), or cyanine3 (Cy3) are incubated with the anisotropically functionalized AuNRs. The resulting optical properties of the dispersed AuNRs are characterized via steady-state UV–vis absorption and photoluminescence (PL) spectroscopies as a function of OSC concentration. We found that CF and RhB adsorb to the AuNR differently depending on the AuNR surface chemistry, which results in unique optical properties of the assembly. The distinctive spectra were used to determine the interaction between the OSC and the AuNR. Finally, we found that attaching Cy3 specifically to the ends of the AuNR via a DNA tether results in a larger emission quenching process than when Cy3 is not attached. This method of nanohybrid assembly can be extended to other metal nanostructures and OSCs. Its generic nature qualifies it as new methodology to precisely assemble nano- and molecular objects with controlled (opto)electronic properties.



## INTRODUCTION

The precise (self-)assembly of molecular components and nano-objects is essential for the realization of nanodevices with unique properties. It constitutes one of the foremost challenges in nanotechnology today. To date, much work has focused on the directed self-assembly of individual metal-nanoparticles (NPs) into organized structures, such as chains<sup>1–3</sup> and vesicles,<sup>4,5</sup> to tune their properties thanks to a diverse tool-kit allowing for the anisotropic functionalization of NPs. The anisotropic surface chemistry can be exploited to self-assemble molecular components at precise locations on the particle to create unique nanoarchitectures. Gold nanorods (AuNRs) are particularly attractive for use as a component in nanohybrid assemblies. AuNRs possess size and assembly dependent optical properties which have found use in cancer therapy,<sup>6</sup> biosensing,<sup>7</sup> surface enhanced Raman spectroscopy (SERS),<sup>8,9</sup> and solar cells<sup>10,11</sup> applications. Furthermore, AuNRs can be anisotropically functionalized. AuNRs have been anisotropically functionalized with functional ligands such as cysteine,<sup>12</sup> DNA,<sup>13</sup> polymers,<sup>14,15</sup> and alkanes.<sup>16</sup> The diverse array of functional groups allows for broad control over surface chemistry, surface charge, and ligand length along particular facets of the AuNRs.

Organic semiconductors (OSCs) are also attractive as smart components for nanohybrid assembly. OSCs, such as Rhodamine B (RhB) and 5(6)-carboxyfluorescein (CF), are used in a wide variety of applications such as sensors,<sup>17,18</sup> imaging,<sup>19,20</sup> and solar cells<sup>21</sup> due to their fluorescent properties. OSC fluorescence intensity and wavelength are tied to their concentration, charge, and complexation, which can be characterized through simple spectroscopic techniques. Donor/acceptor (D/A) complexes can be formed when OSCs interact with an electron acceptor, like AuNRs, resulting in the quenching of the emission of the OSC. The quenching process is D/A separation distance dependent, with smaller distances typically resulting in a larger emission quenching.<sup>22,23</sup> OSCs have been homogeneously assembled on the surface of AuNRs in the past,<sup>24–26</sup> but not, to the authors' knowledge, with control over the particular area of the AuNR (e.g., end or side) that the OSC is bound to. Furthermore, anisotropy in the AuNR surface coating would allow for precise tuning of the

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# Gold Nanorods Synthesis And Modulation Of Optical Properties

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## **Table of Contents Gold Nanorods Synthesis And Modulation Of Optical Properties**

1. Understanding the eBook Gold Nanorods Synthesis And Modulation Of Optical Properties
  - The Rise of Digital Reading Gold Nanorods Synthesis And Modulation Of Optical Properties
  - Advantages of eBooks Over Traditional Books
2. Identifying Gold Nanorods Synthesis And Modulation Of Optical Properties
  - Exploring Different Genres
  - Considering Fiction vs. Non-Fiction
  - Determining Your Reading Goals
3. Choosing the Right eBook Platform
  - Popular eBook Platforms
  - Features to Look for in an Gold Nanorods Synthesis And Modulation Of Optical Properties
  - User-Friendly Interface
4. Exploring eBook Recommendations from Gold Nanorods Synthesis And Modulation Of Optical Properties
  - Personalized Recommendations
  - Gold Nanorods Synthesis And Modulation Of Optical Properties User Reviews and Ratings
  - Gold Nanorods Synthesis And Modulation Of Optical Properties and Bestseller Lists
5. Accessing Gold Nanorods Synthesis And Modulation Of Optical Properties Free and Paid eBooks
  - Gold Nanorods Synthesis And Modulation Of Optical Properties Public Domain eBooks
  - Gold Nanorods Synthesis And Modulation Of Optical Properties eBook Subscription Services
  - Gold Nanorods Synthesis And Modulation Of Optical Properties Budget-Friendly Options
6. Navigating Gold Nanorods Synthesis And Modulation Of Optical Properties eBook Formats

- ePub, PDF, MOBI, and More
  - Gold Nanorods Synthesis And Modulation Of Optical Properties Compatibility with Devices
  - Gold Nanorods Synthesis And Modulation Of Optical Properties Enhanced eBook Features
7. Enhancing Your Reading Experience
    - Adjustable Fonts and Text Sizes of Gold Nanorods Synthesis And Modulation Of Optical Properties
    - Highlighting and Note-Taking Gold Nanorods Synthesis And Modulation Of Optical Properties
    - Interactive Elements Gold Nanorods Synthesis And Modulation Of Optical Properties
  8. Staying Engaged with Gold Nanorods Synthesis And Modulation Of Optical Properties
    - Joining Online Reading Communities
    - Participating in Virtual Book Clubs
    - Following Authors and Publishers Gold Nanorods Synthesis And Modulation Of Optical Properties
  9. Balancing eBooks and Physical Books Gold Nanorods Synthesis And Modulation Of Optical Properties
    - Benefits of a Digital Library
    - Creating a Diverse Reading Collection Gold Nanorods Synthesis And Modulation Of Optical Properties
  10. Overcoming Reading Challenges
    - Dealing with Digital Eye Strain
    - Minimizing Distractions
    - Managing Screen Time
  11. Cultivating a Reading Routine Gold Nanorods Synthesis And Modulation Of Optical Properties
    - Setting Reading Goals Gold Nanorods Synthesis And Modulation Of Optical Properties
    - Carving Out Dedicated Reading Time
  12. Sourcing Reliable Information of Gold Nanorods Synthesis And Modulation Of Optical Properties
    - Fact-Checking eBook Content of Gold Nanorods Synthesis And Modulation Of Optical Properties
    - Distinguishing Credible Sources
  13. Promoting Lifelong Learning
    - Utilizing eBooks for Skill Development
    - Exploring Educational eBooks
  14. Embracing eBook Trends
    - Integration of Multimedia Elements
    - Interactive and Gamified eBooks

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