Review of Recent Advancements in Thiolate Chemistry

Thiolate chemistry has been a subject of intense research due to its significant role in various fields, including materials science, catalysis, and biological systems. This report aims to provide a comprehensive overview of the latest advancements in thiolate chemistry, focusing on the synthesis, applications, and mechanistic understanding of thiolate compounds and thiolate-protected nanoclusters.

Thiolation via Sulfur Electrophiles

One of the significant advancements in thiolate chemistry is the development of new methodologies for thiolation using sulfur electrophiles. The review by Wei, Gao, Chang, and Jiang (2022) highlights the umpolung strategy for the synthesis of S-containing compounds. This approach involves designing a series of sulfur electrophiles for diverse thiolation reactions. The methodologies summarized in the review include thiofunctionalization of alkenes or alkynes, insertion of carbene precursors, C-S cross-coupling, and electrophilic substitution. These methods have been developed to incorporate thio groups with regio- and stereoselectivity, which is crucial for the synthesis of complex molecules (Wei, Gao, Chang, & Jiang, 2022).

Thiolate-Protected Gold Nanoclusters

The control of single-ligand chemistry on thiolated Au25 nanoclusters has been explored, as reported in Nature Communications (2020). This study provides insights into the influence of ligands on the properties of gold nanoclusters, which are essential for applications in catalysis and materials science. The precise control over the ligand shell can lead to the development of nanoclusters with tailored properties for specific applications (Nature Communications, 2020).

Furthermore, the review by Liang, Chen, Mo, Wu, and Xiao (2023) discusses the current advances in solar-powered photoredox catalysis using atomically precise thiolate-protected gold nanoclusters. These nanoclusters serve as light-harvesting antennas due to their unique atomic stacking, quantum confinement effect, and discrete energy band structure. The review emphasizes the importance of understanding the charge transport characteristics of metal nanoclusters in photocatalysis, which is crucial for the development of efficient solar energy conversion systems (Liang et al., 2023).

Molecular Reactivity of Thiolate-Protected Noble Metal Nanoclusters

The molecular reactivity of thiolate-protected noble metal nanoclusters has been the subject of a review by Yao, Wu, Liu, Lin, Yuan, and Xie (2021). The review discusses the synthesis, self-assembly, and applications of these nanoclusters, focusing on their molecular interactions and reactions. The noble metal nanoclusters exhibit molecule-like properties due to quantum confinement effects, which make them suitable for applications in sensors, biomedicine, and catalysis. The review also highlights the importance of synthesis and characterization techniques in understanding the active sites and molecular interactions of these nanoclusters (Yao et al., 2021).

Ligand Exchange Reactions on Thiolate-Protected Gold Nanoclusters

Ligand exchange reactions on thiolate-protected gold nanoclusters have been reviewed by Wang and Bürgi (2021). This post-synthesis modification method extends the functionality of nanoclusters. The review provides background on the synthesis and structure of various gold clusters and discusses the SN2-like mechanism of ligand exchange. The flexibility of the gold-sulfur interface allows for the introduction of various functionalities to the nanoclusters, which is essential for their application in diverse fields (Wang & Bürgi, 2021).

Thiol-Addition Reactions and Their Applications

The development of probes for thiols has been an active research area due to the biological importance of thiols. A review by Yin, Huo, Zhang, Martínez-Máñez, Yang, Lv, and Li (2013) summarizes thiol-addition reactions and their applications in thiol recognition. The reactions are classified into four types based on their addition mechanisms and are coupled to color and/or emission changes. The use of thiol-addition reactions provides a simple and straightforward procedure for the preparation of thiol-sensing probes (Yin et al., 2013).

Conclusion

The advancements in thiolate chemistry have led to the development of new synthetic methodologies, a deeper understanding of molecular reactivity, and the exploration of applications in catalysis and materials science. The precise control over thiolation reactions and the functionalization of thiolate-protected nanoclusters are pivotal for the advancement of this field. The reviews discussed in this report provide a comprehensive insight into the current state of thiolate chemistry and its potential for future research and applications.

References

- Liang, H., Chen, Q., Mo, Q., Wu, Y., & Xiao, F. (2023). Atomically precise thiolate-protected gold nanoclusters: current advances in solar-powered photoredox catalysis. Journal of Materials Chemistry A, 11, 9401. https://pubs.rsc.org/en/content/articlelanding/2023/ta/d3ta01154b
- Nature Communications. (2020). Control of single-ligand chemistry on thiolated Au25 nanoclusters. Nature Communications, 11, Article number: 5498. https://www.nature.com/articles/s41467-020-19327-2
- Wang, Y., & Bürgi, T. (2021). Ligand exchange reactions on thiolate-protected gold nanoclusters. Nanoscale Advances, 3, 2710. https://pubs-rsc-org-443.vpnm.ccmu.edu.cn/en/content/articlelanding/2021/na/d1na00178g
- Wei, Y., Gao, W., Chang, H., & Jiang, X. (2022). Recent advances in thiolation via sulfur electrophiles. Organic Chemistry Frontiers, 9, 6684. https://pubs.rsc.org/en/content/articlelanding/2022/go/d2go01447e
- Yao, Q., Wu, Z., Liu, Z., Lin, Y., Yuan, X., & Xie, J. (2021). Molecular reactivity of thiolate-protected noble metal nanoclusters: synthesis, self-assembly, and applications. Chemical Science, 12, 99. https://pubs.rsc.org/en/content/articlelanding/2021/sc/d0sc04620e
- Yin, C., Huo, F., Zhang, J., Martínez-Máñez, R., Yang, Y., Lv, H., & Li, S. (2013). Thiol-addition reactions and their applications in thiol recognition. Chemical Society Reviews, 42, 6032. https://pubs.rsc.org/en/content/articlelanding/2013/cs/c3cs60055f