RESEARCH ARTICLE

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# Accurate Thermal Resection of Atomically Precise Copper Clusters to Achieve Near-IR Light-Driven $CO_2$ Reduction

*Jian-Peng Dong, Jun-Kang Li, Huan Zhang, Yue Xu, Shu-Na Zhao, Gang Li, Rui Wang,* Bo Li,* and Shuang-Quan Zang**

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- Henan Key Laboratory of Crystalline Molecular Functional Materials
  College of Chemistry
  Zhengzhou University
  Zhengzhou 450001, P. R. China

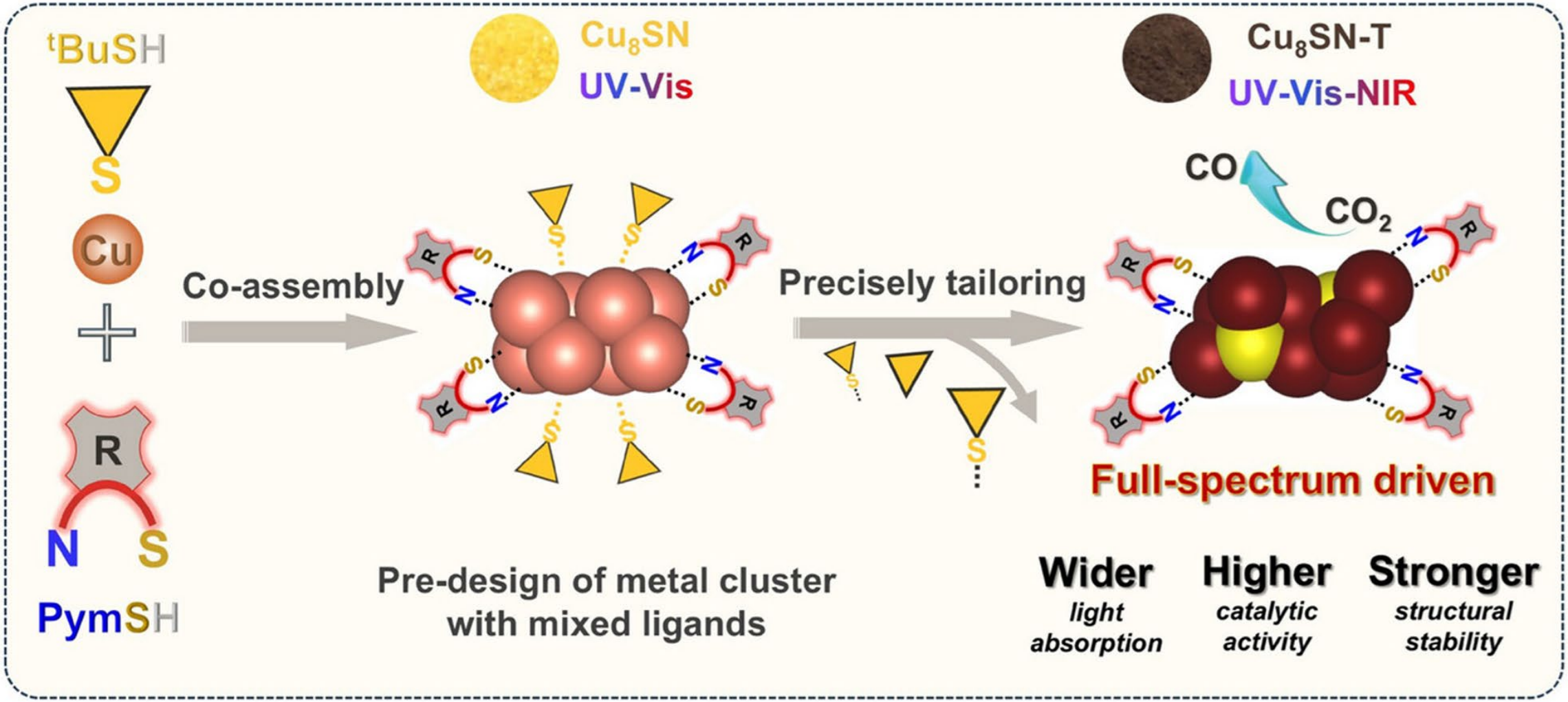
- College of Chemistry and Pharmaceutical Engineering
  Nanyang Normal University
  Nanyang 473061, P. R. China

Paper presentation

Subrata Bag

10th May, 2025

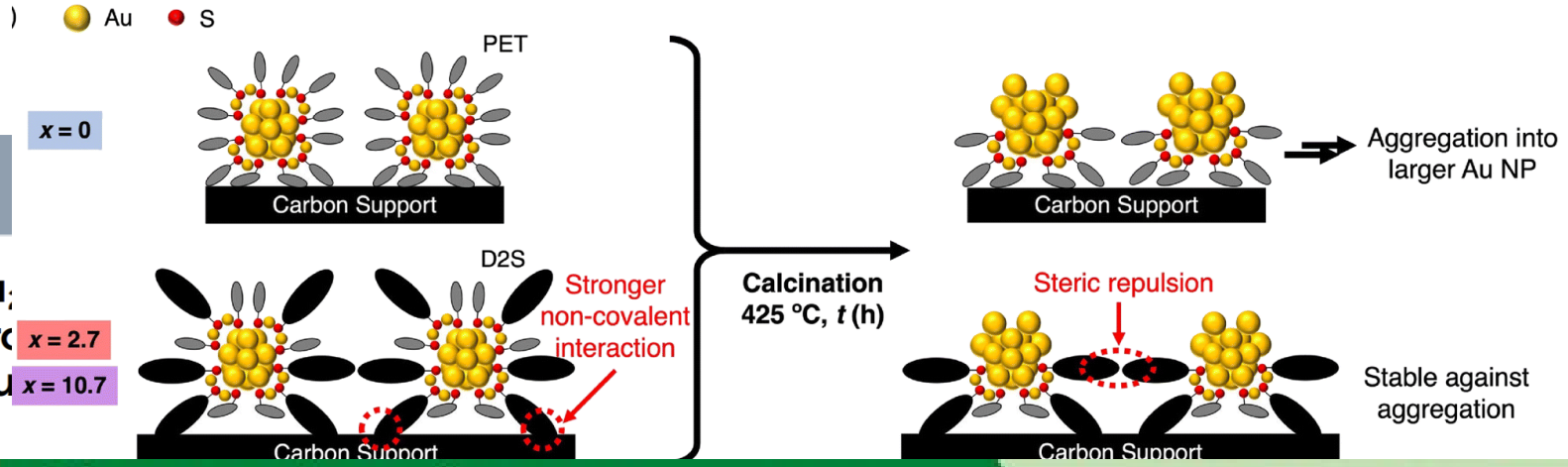
# Abstract


tBuSH
S
Cu
R
N
S
PymSH
Co-assembly
Cu8SN
UV-Vis
Pre-design of metal cluster
with mixed ligands
Precisely tailoring
Cu8SN-T
UV-Vis-NIR
CO
CO2
Full-spectrum driven
Wider
light
absorption
Higher
catalytic
activity
Stronger
structural
stability

# Background

Nanoscale

PAPER




Check for updates

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**Carbon-supported Au; decorated with dendr loading weight and du ution reaction†**

Kosuke Sakamoto, Shinya Masuda,

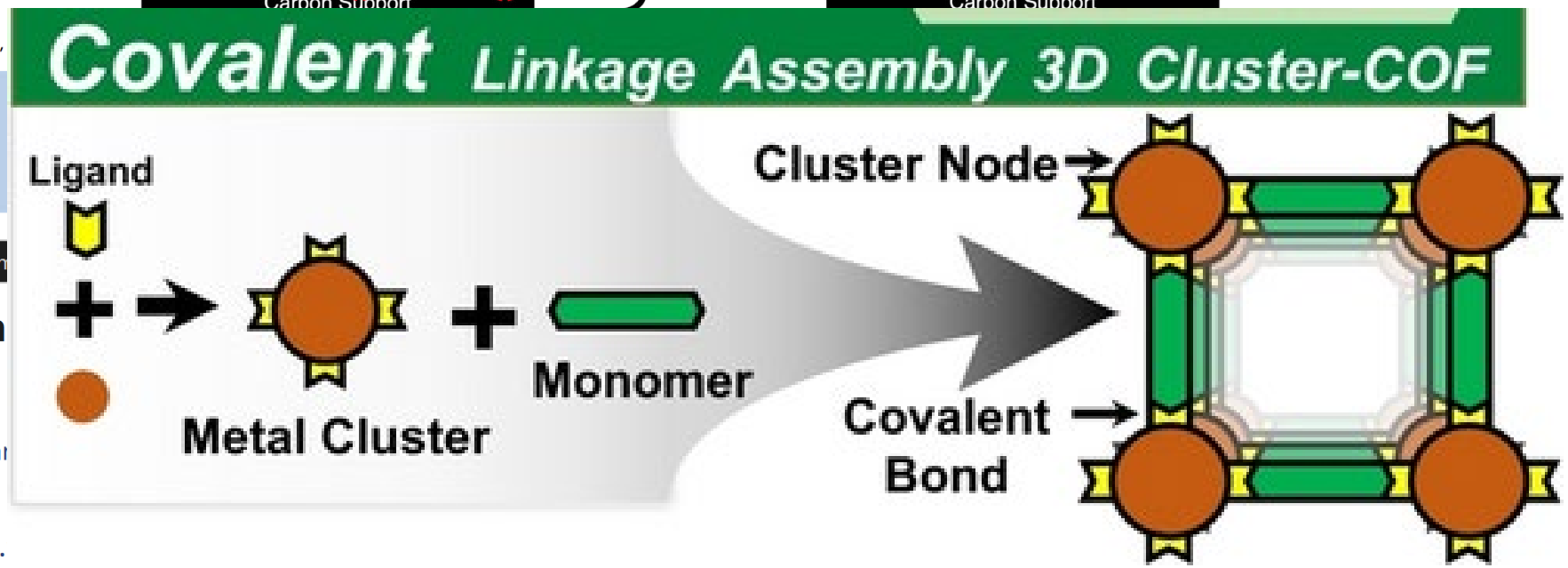
Angewandte International Edition Chemie

Research Article | Angewandte Chemie International Edition hon

**3D Cluster-Based Covalent Organ $CO_2$ Photoreduction**

Yue Xu, Jian-Peng Dong, Le Wang, Rong-Li Geng, Rui War Thomas C. W. Mak

First published: 18 February 2025 | https://doi.org/10.



# Motivation

- Increasing $CO_2$ percentage in atmosphere became threat to human civilization, $CO_2$ reduction is the most reliable approach to solve this problem.
- Using solar energy to get rid off from global warming is one of the dream of scientists.
- Uses of metal nanocluster's potential in such noble work is inspiring to all the researcher working with nanocluster.

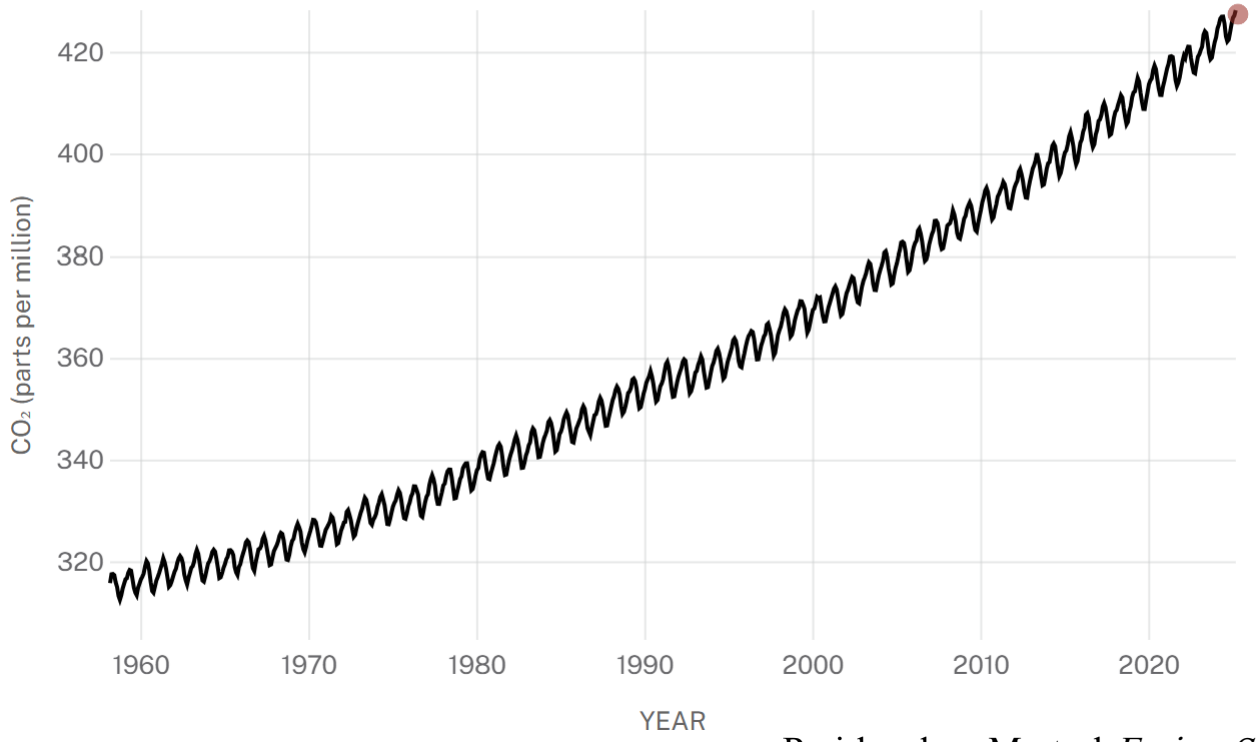
# Why this paper?

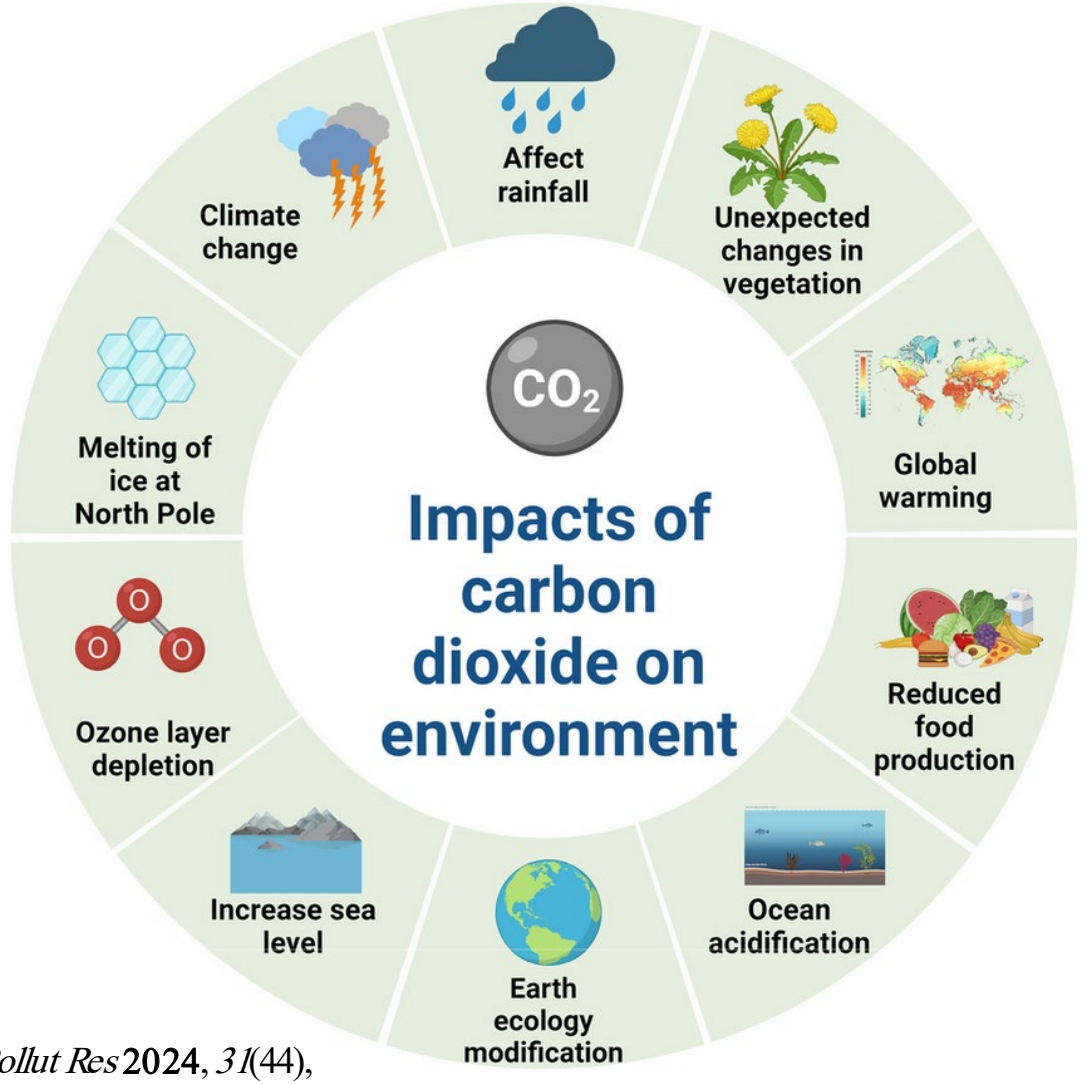
- This article provides a comprehensive analytical essence of how selective ligand removal change the properties of NC drastically and enhance cluster's catalytic properties.
- This article widen the window of catalysis using nanocluster which enhance the relevance of nanocluster.

# Introduction

DIRECT MEASUREMENTS: 1958-PRESENT

Data source: NOAA, measured at the Mauna Loa Observatory



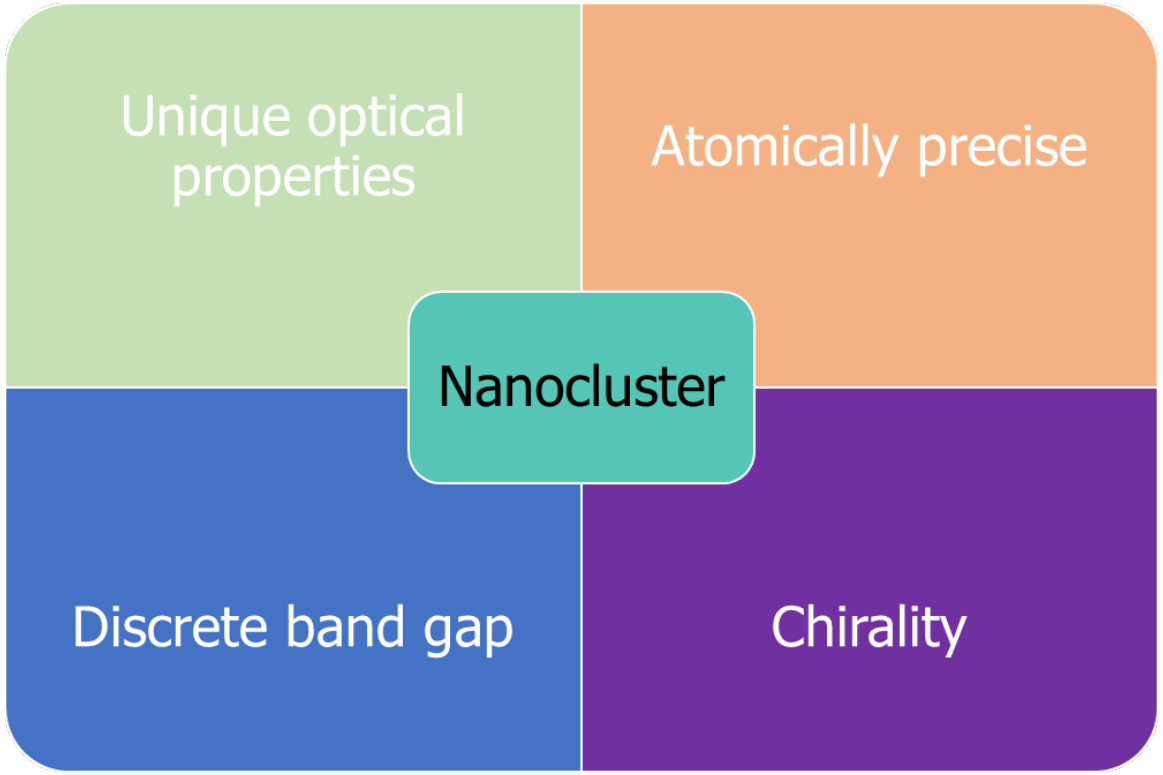



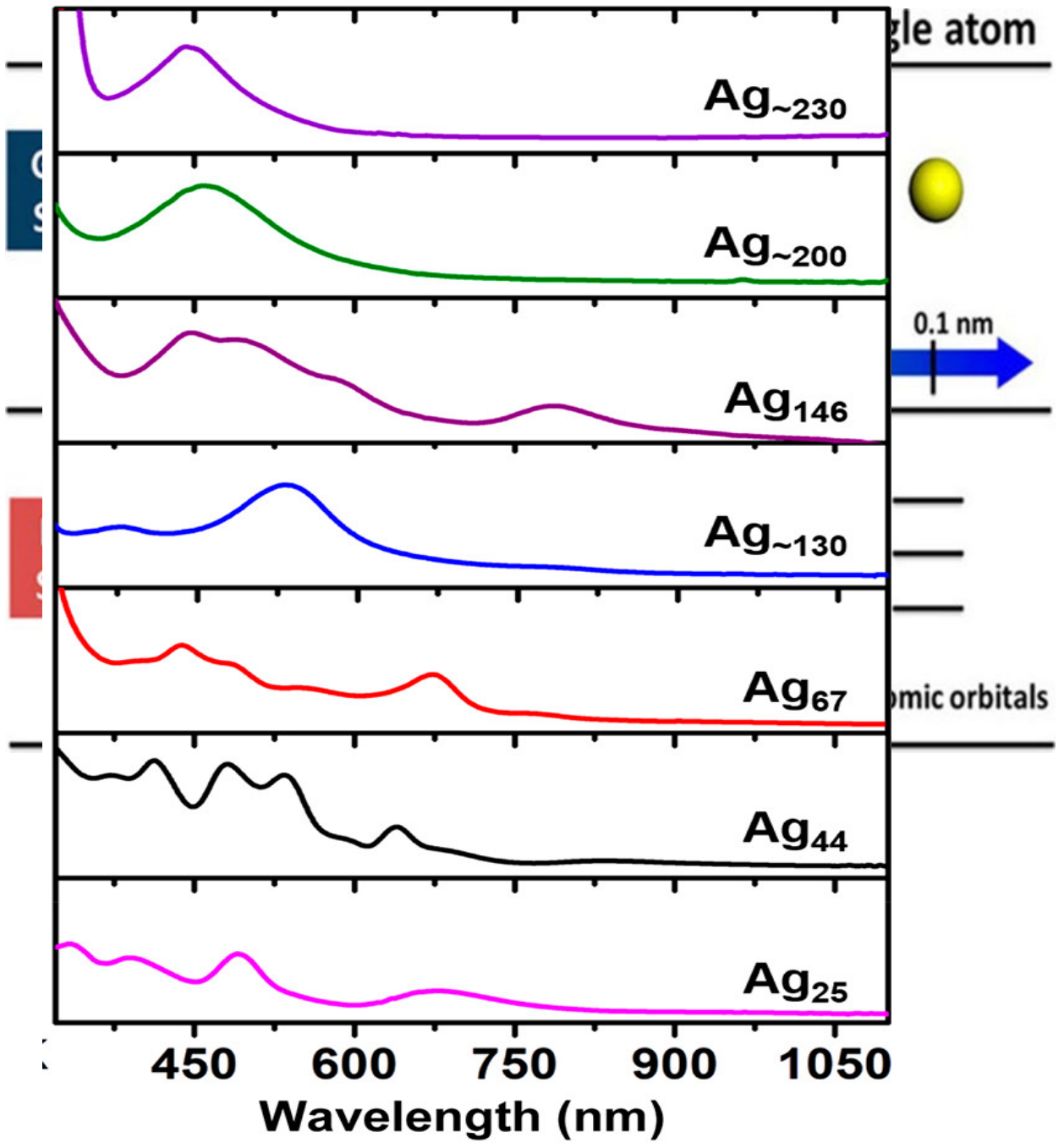

Ravichandran, M; et. al. *Environ Sci Pollut Res* 2024, *31*(44), 55895–55916.

# Introduction

What is Nanocluster?

**Nanoclusters** are atomically precise, crystalline materials most often existing on the 0-2 nanometer scale



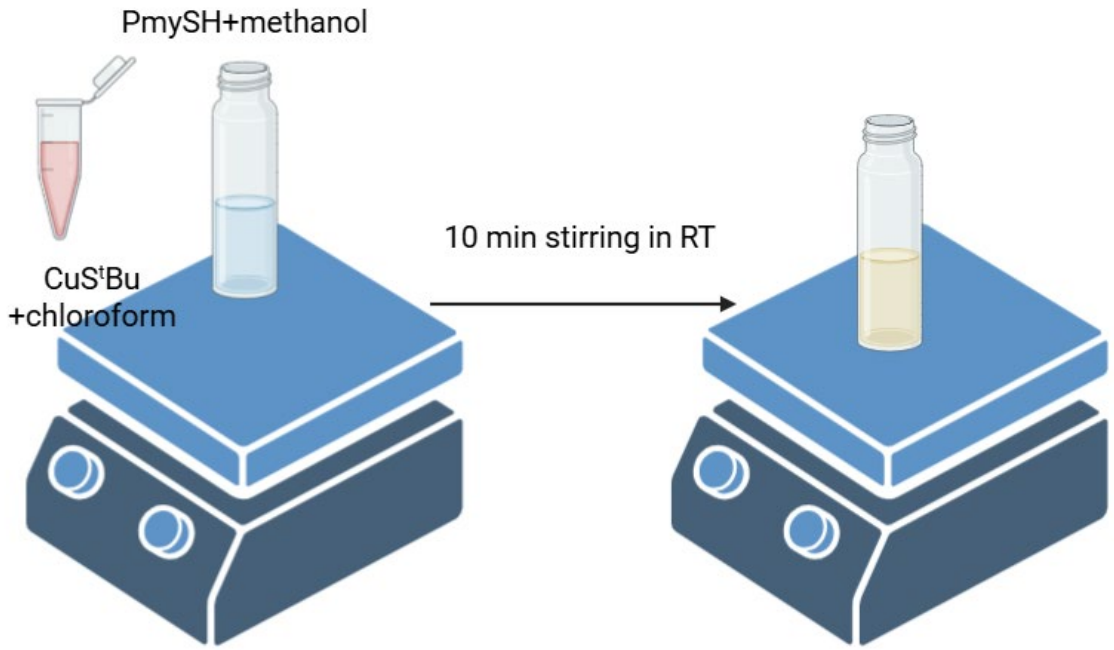



# Introduction

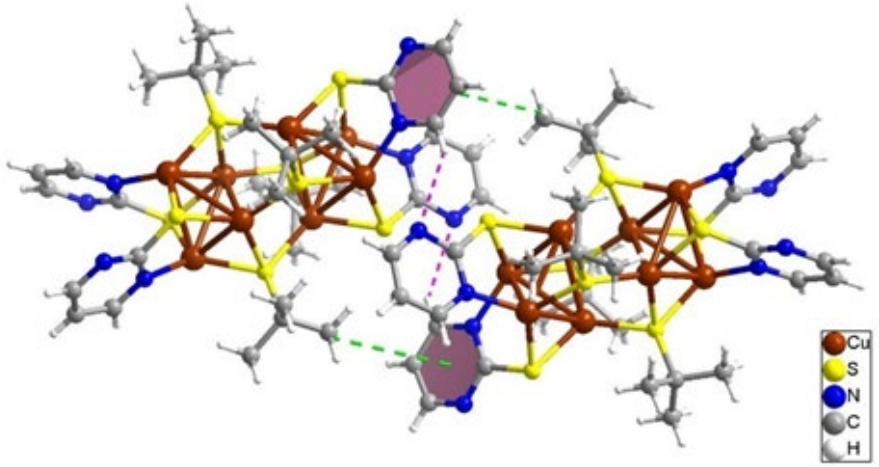
- Various types of materials namely metal organic framework (MOF), g-CN, metal nitrides, metal sulfides etc. have been used to reduce $CO_2$ but the efficiency is lower than the threshold over which practically it can be implemented.
- The limiting reason for low efficiency is their adsorption is limited to the certain range of wavelength of solar spectrum.
- Nanoclusters are one of the materials among those which has drawn maximum attention.
- Ligand makes clusters stable but less active due to non-accessibility of metal atom.
- Selective removal of ligands can prohibit the aggregation of cluster and enhance the catalytic efficiency by making metal atom accessible.

# Results and discussion

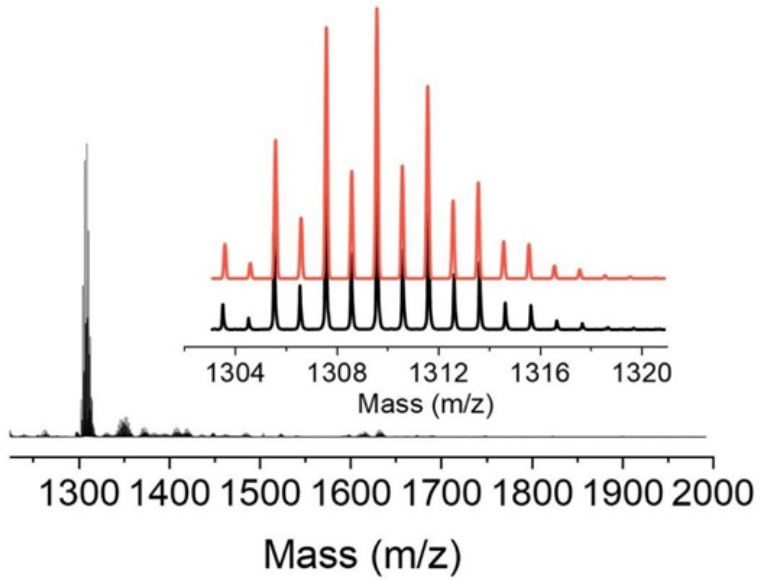
## Synthesis and characterization of $Cu_8(S^tBu)_4(PymS)_4$ [$Cu_8SN$]




SC-XRD driven structure

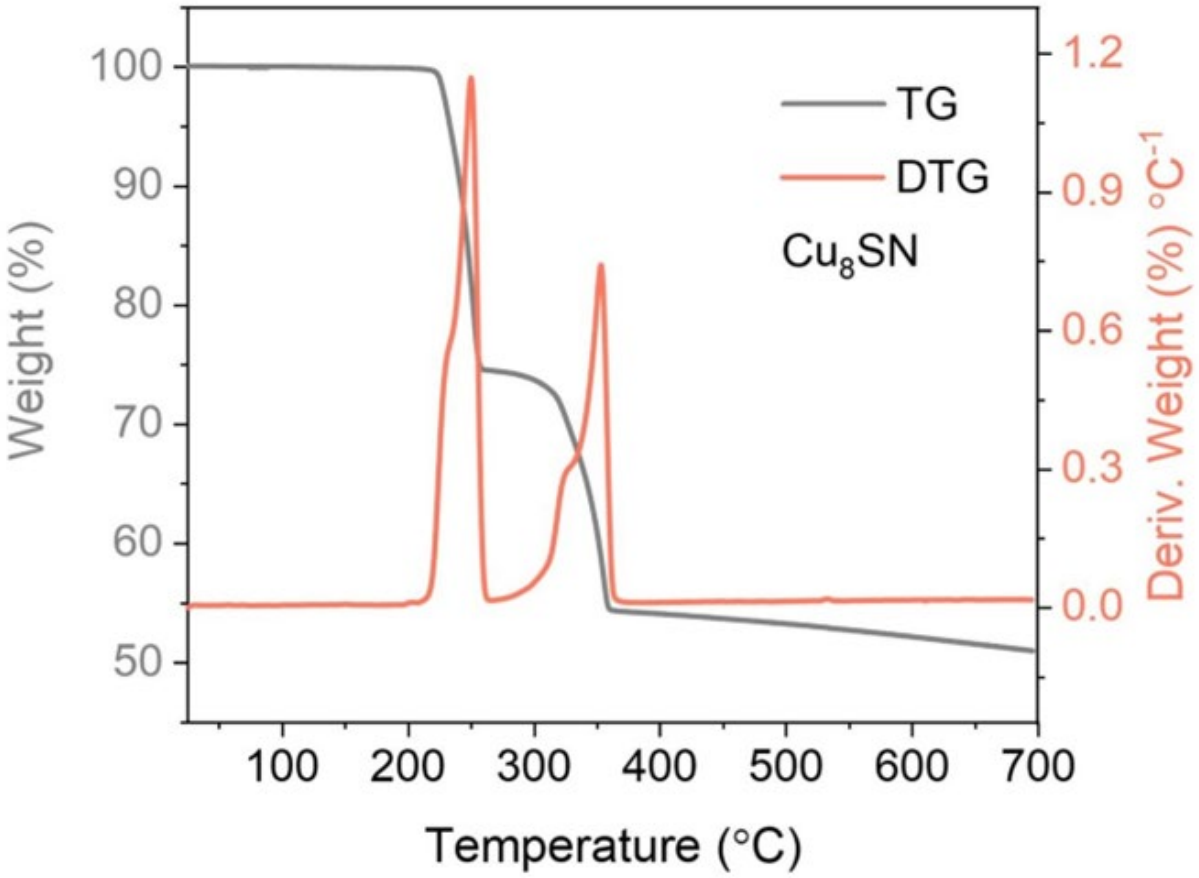



ESI-MS data



# Results and discussion

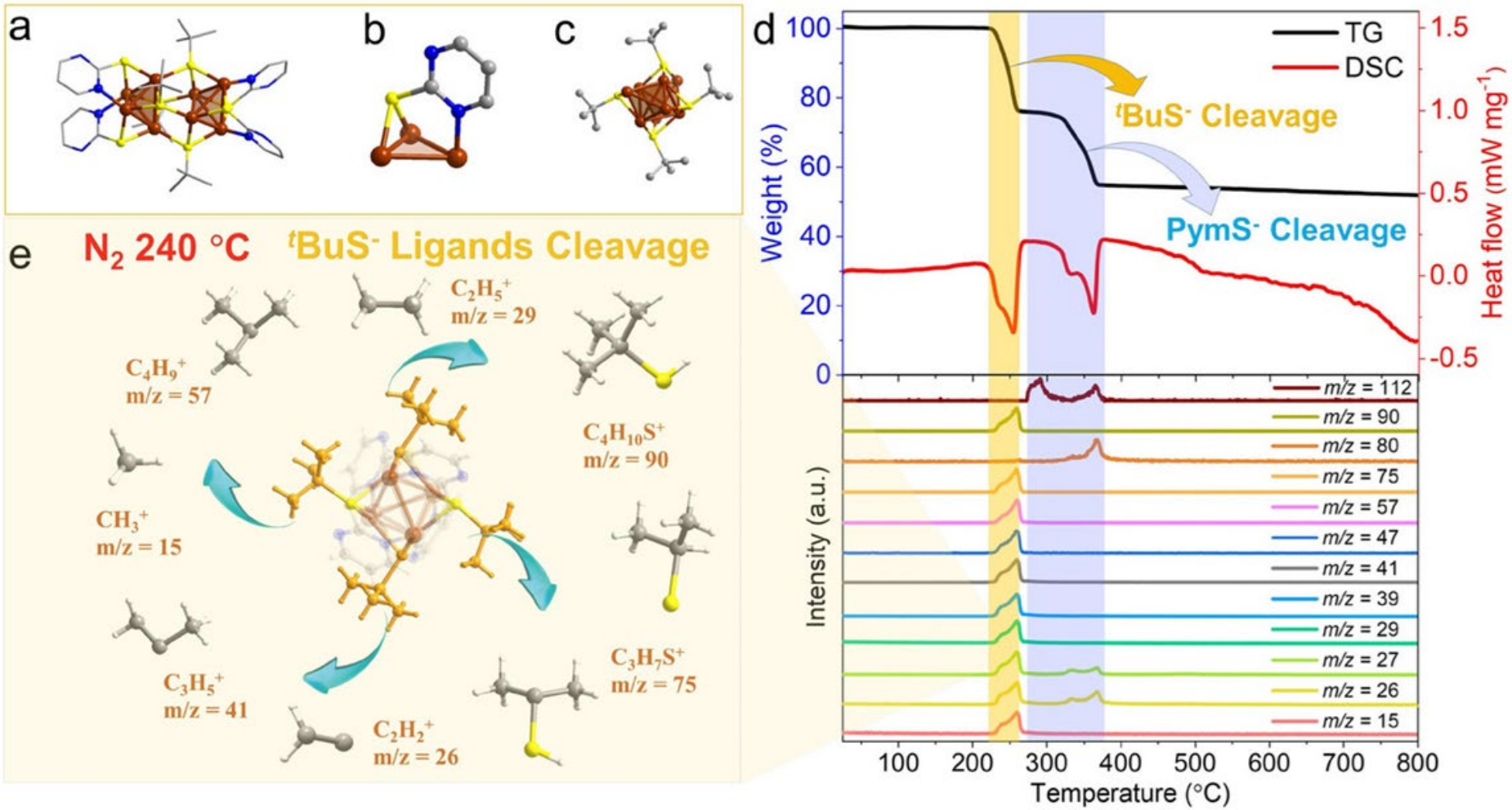
TGA analysis



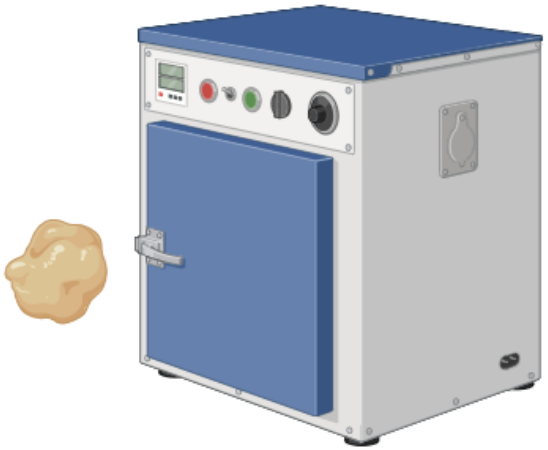

| Component | Formula Count | Mass (g/ mol) | Theoretical Mass % |
|---|---|---|---|
| Cu | 8 | 508.40 | 38.69% |
| S$^t$Bu | 4 | 356.68 | 27.15% |
| PymS | 4 | 448.60 | 34.16% |
| **Total** | | **1313.68** | 100% |

# Results and discussion

TG-MS data



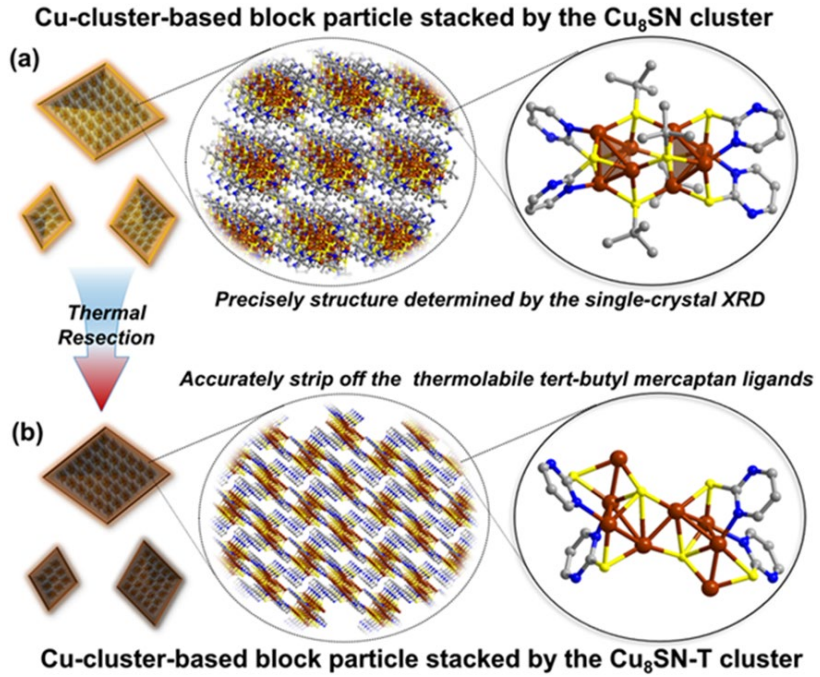
# Results and discussion

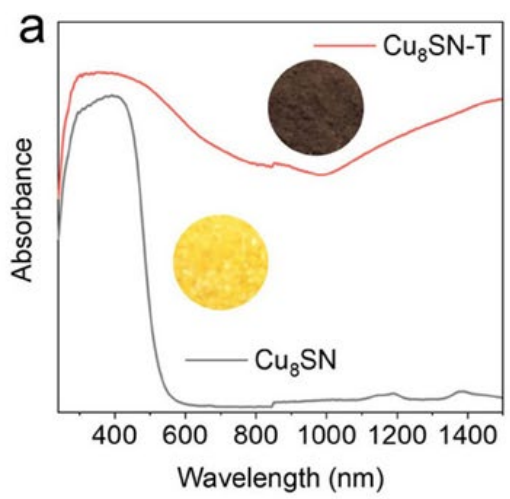


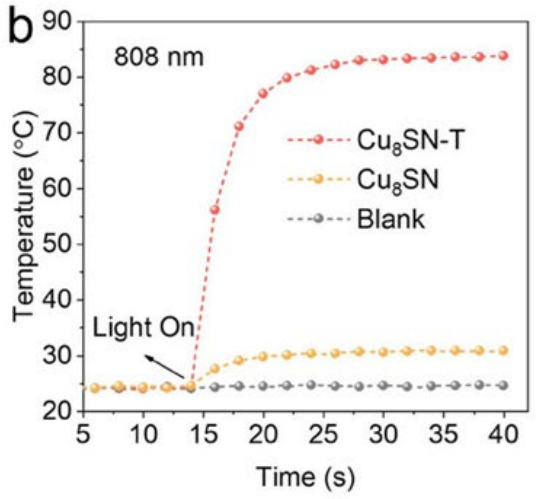
240° C
$N_2$ environment for 1 h

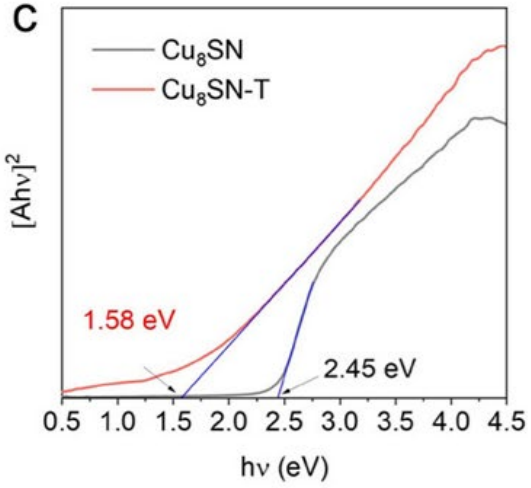
$Cu_8(S)_2(PymS)_4$ [$Cu_8$SN-T]

$Cu_8(S^tBu)_4(PymS)_4$ [$Cu_8$SN]



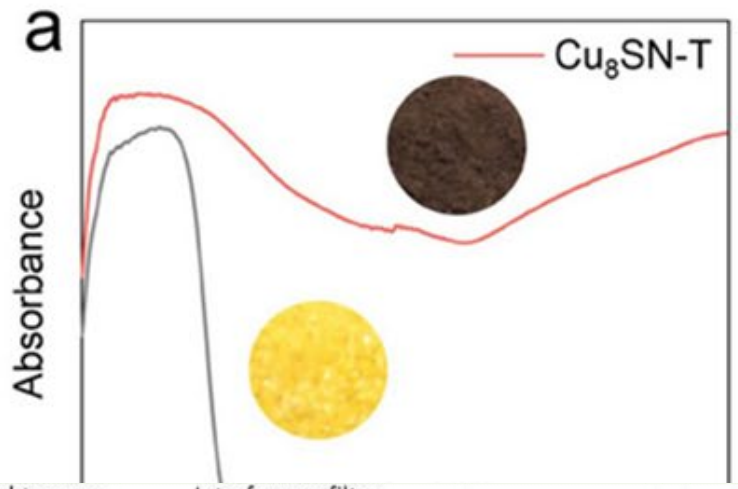



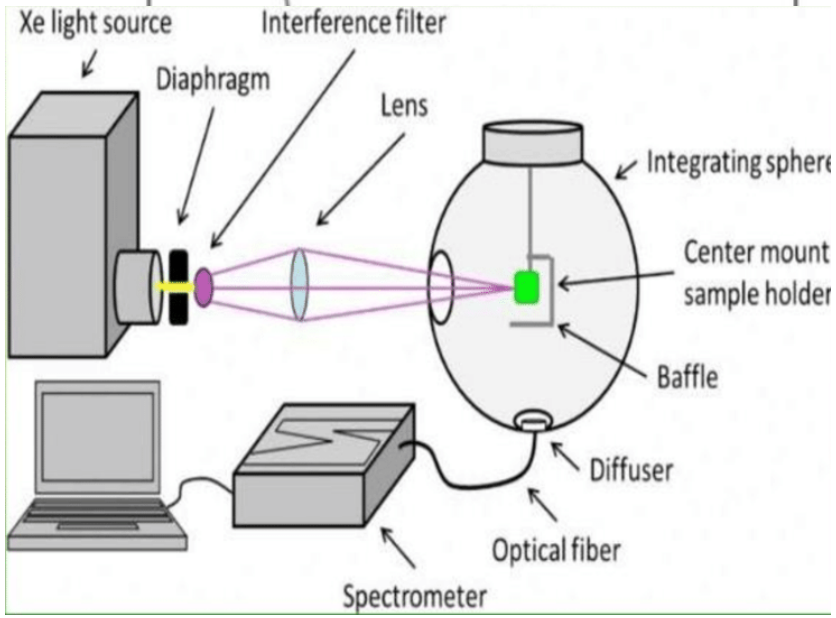



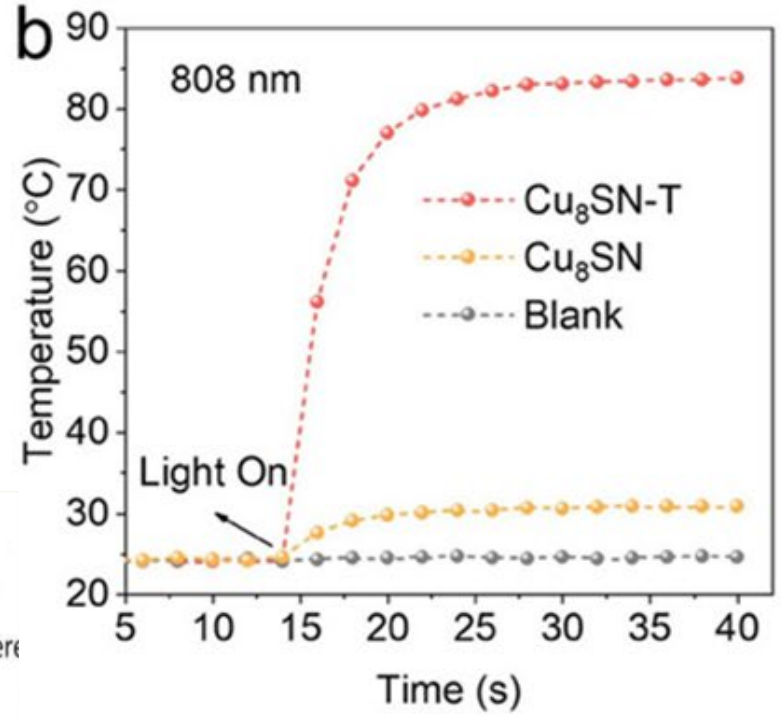
# Results and discussion

UV- Vis- NIR DRS data

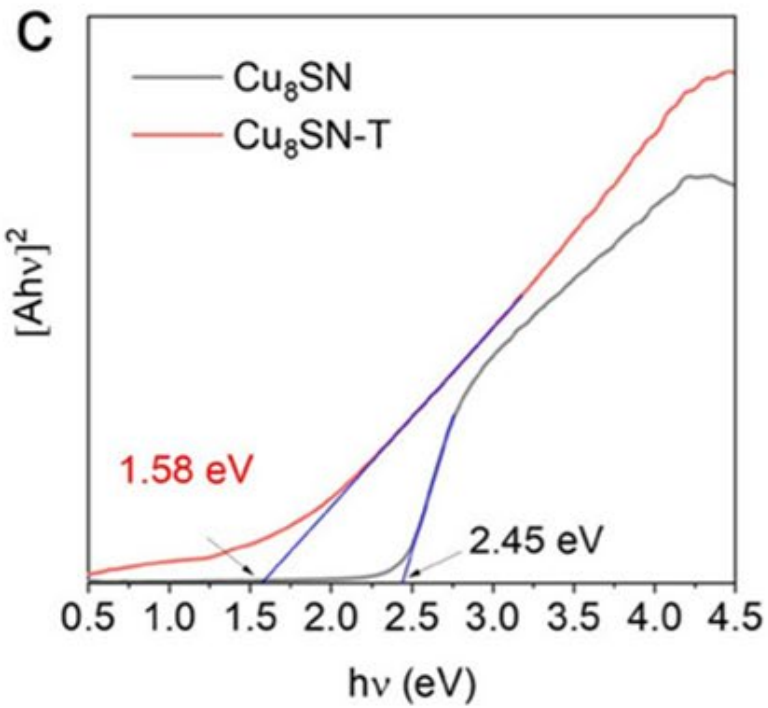



IR photothermal image



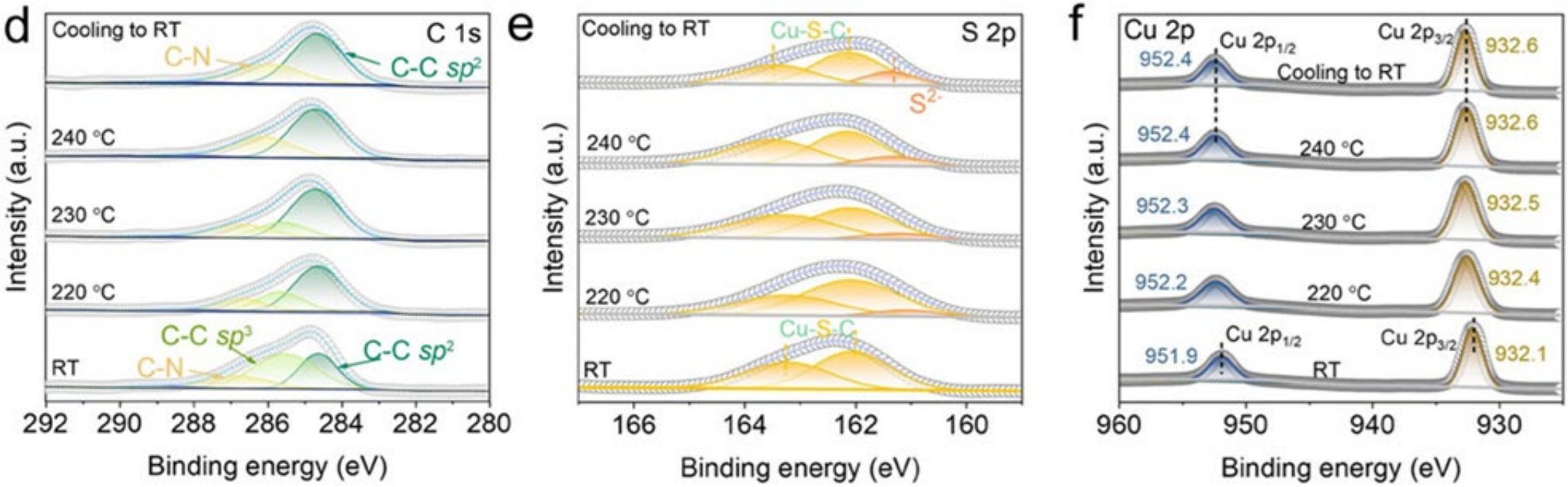

Tauc plot




$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

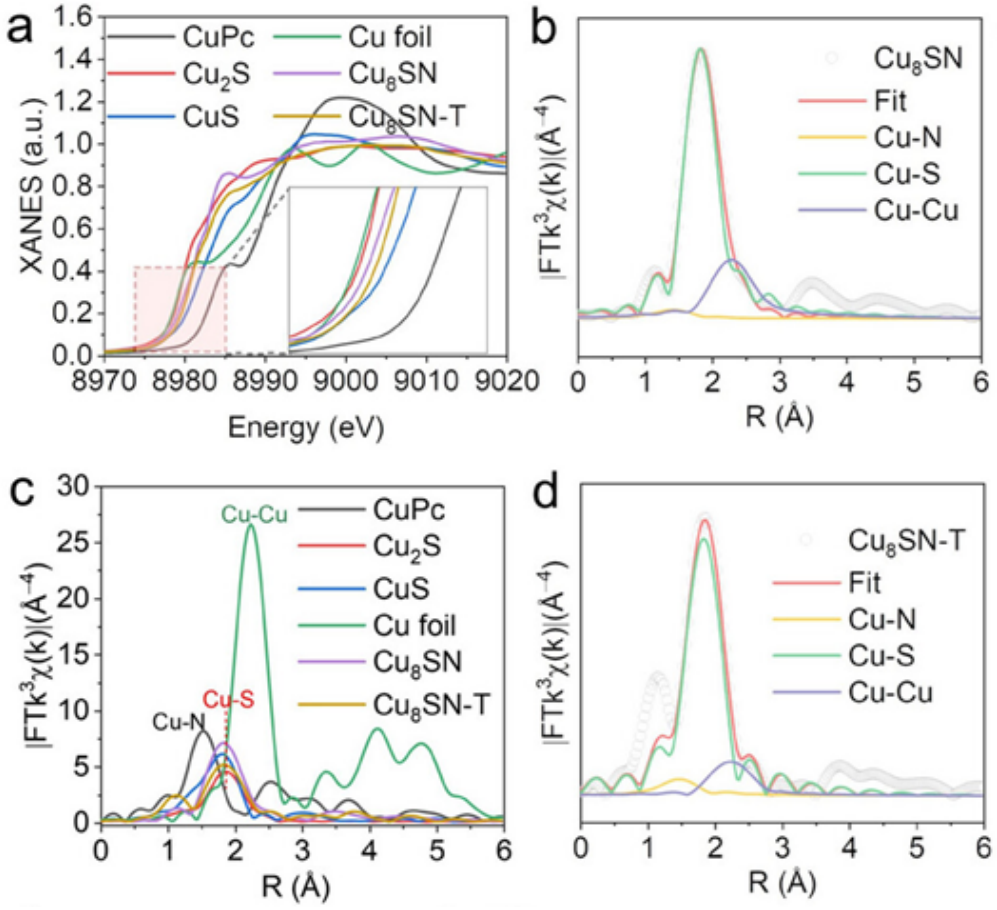
# Results and discussion

In situ XPS data during thermal resection



# Results and discussion

XAFS data

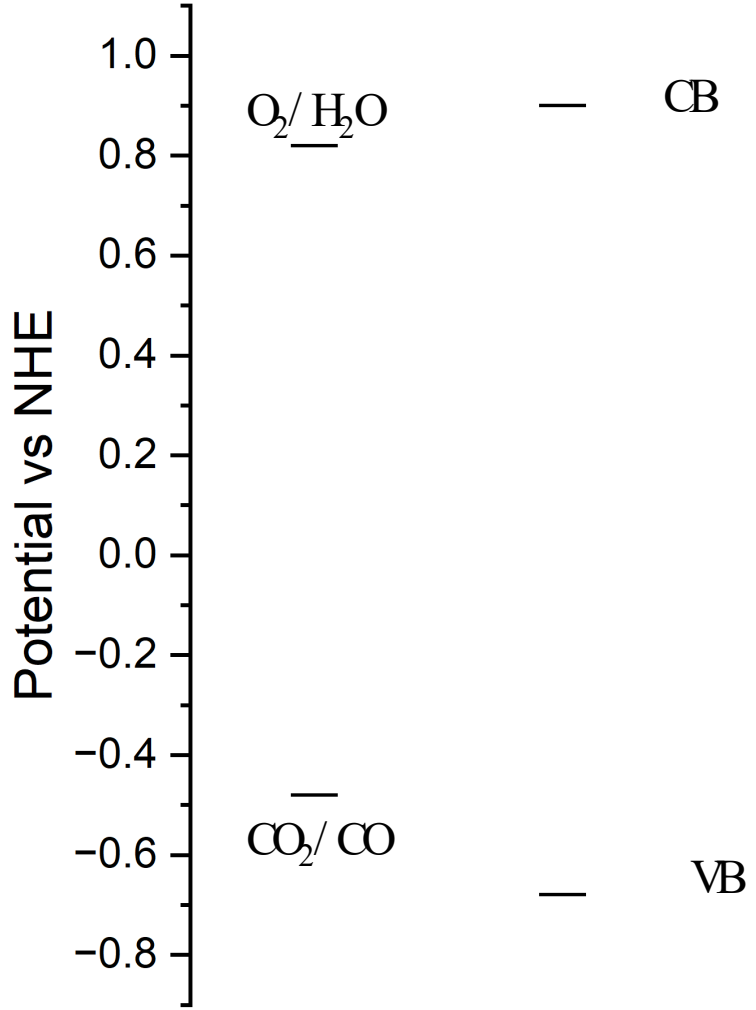



## Findings

- For $Cu_8SN$ the absorption edge is in between Cu foil and $Cu_2S$ and closer to the $Cu_2S$ revealing monovalent nature of Cu.
- EXAFS study reveals the ratio of Cu-N,Cu-S and Cu-Cu is 1:5:1 which support the predicted formula of $Cu_8SN$.
- And for $Cu_8SN$-T the ratio of Cu-N,Cu-S and Cu-Cu environment is 4:18:3 which supports the predicted formula for $Cu_8SN$-T too.

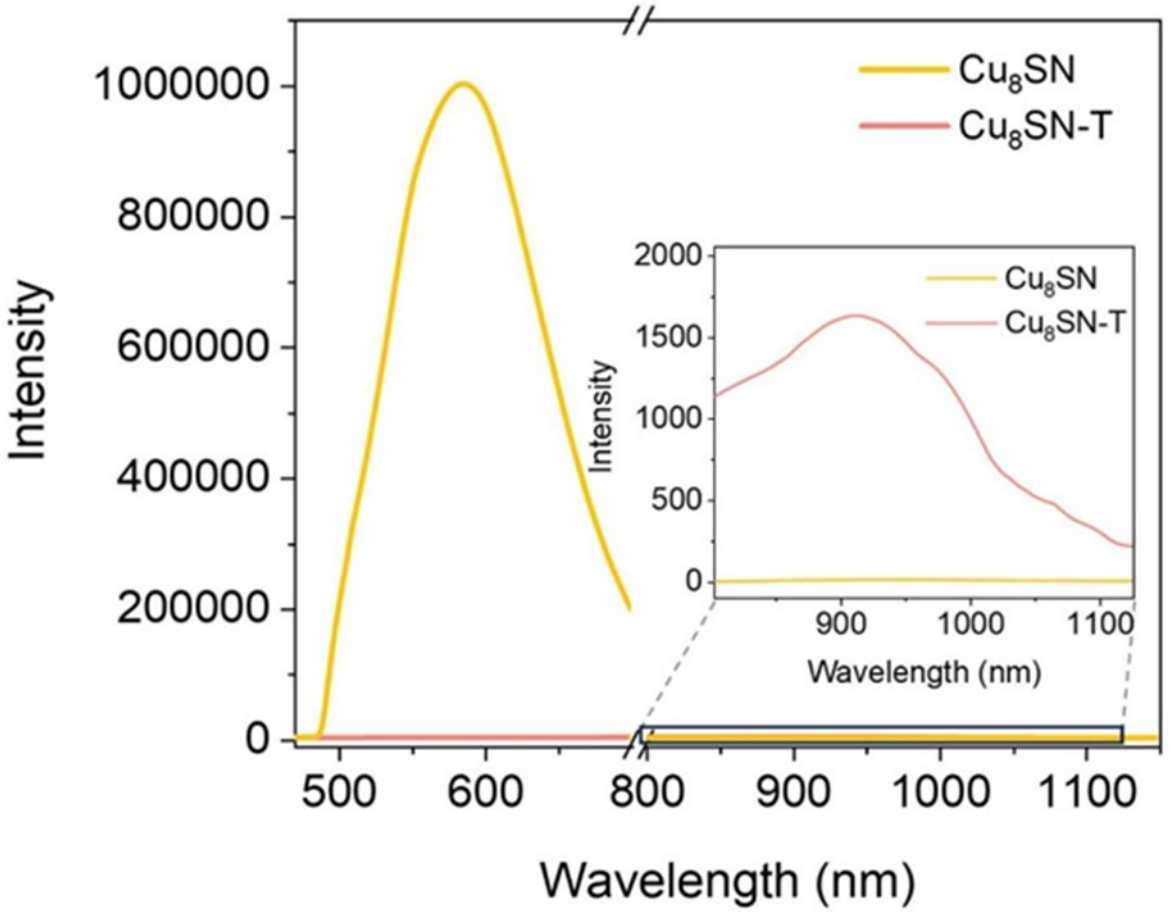
# Results and discussion

Band structure comparison

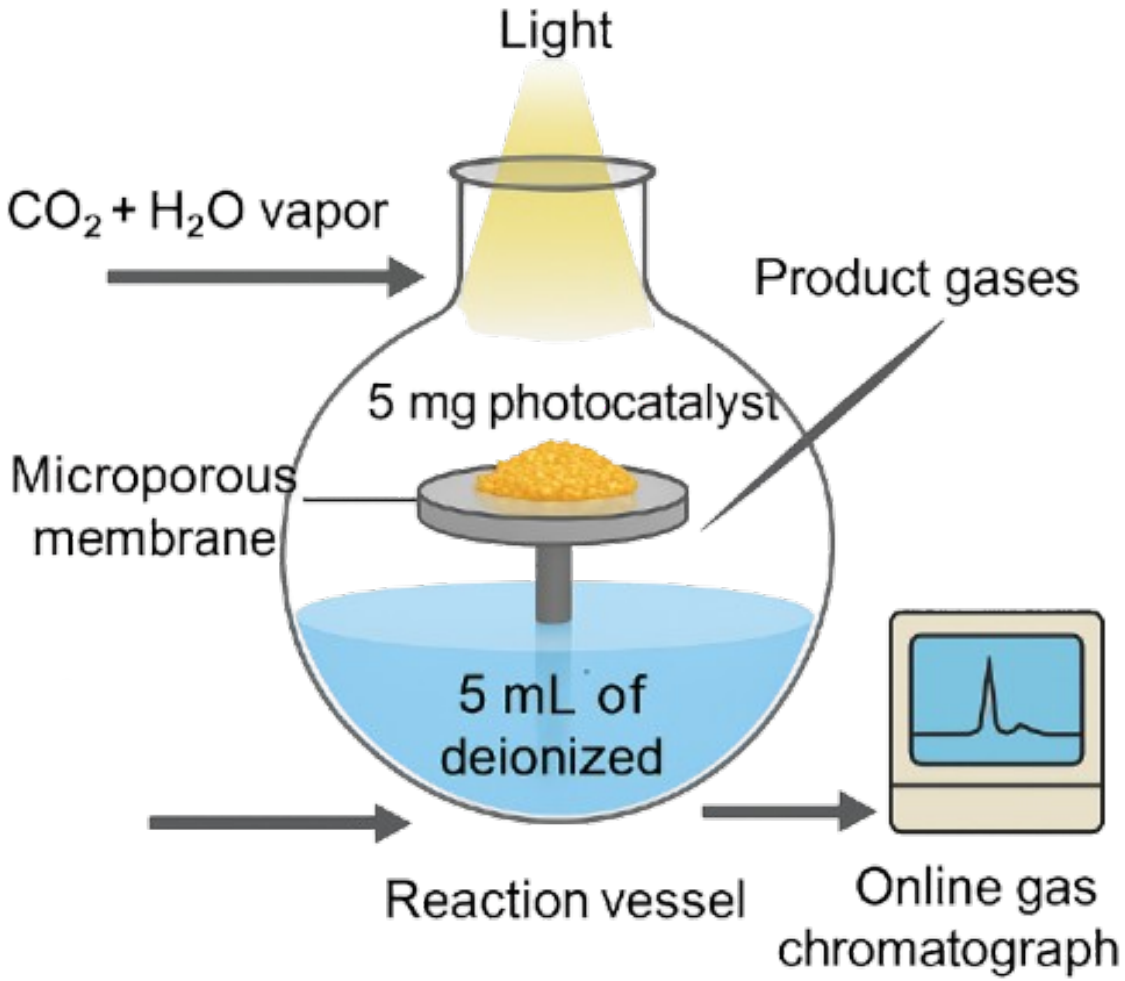



Cu8SN-T

PL study



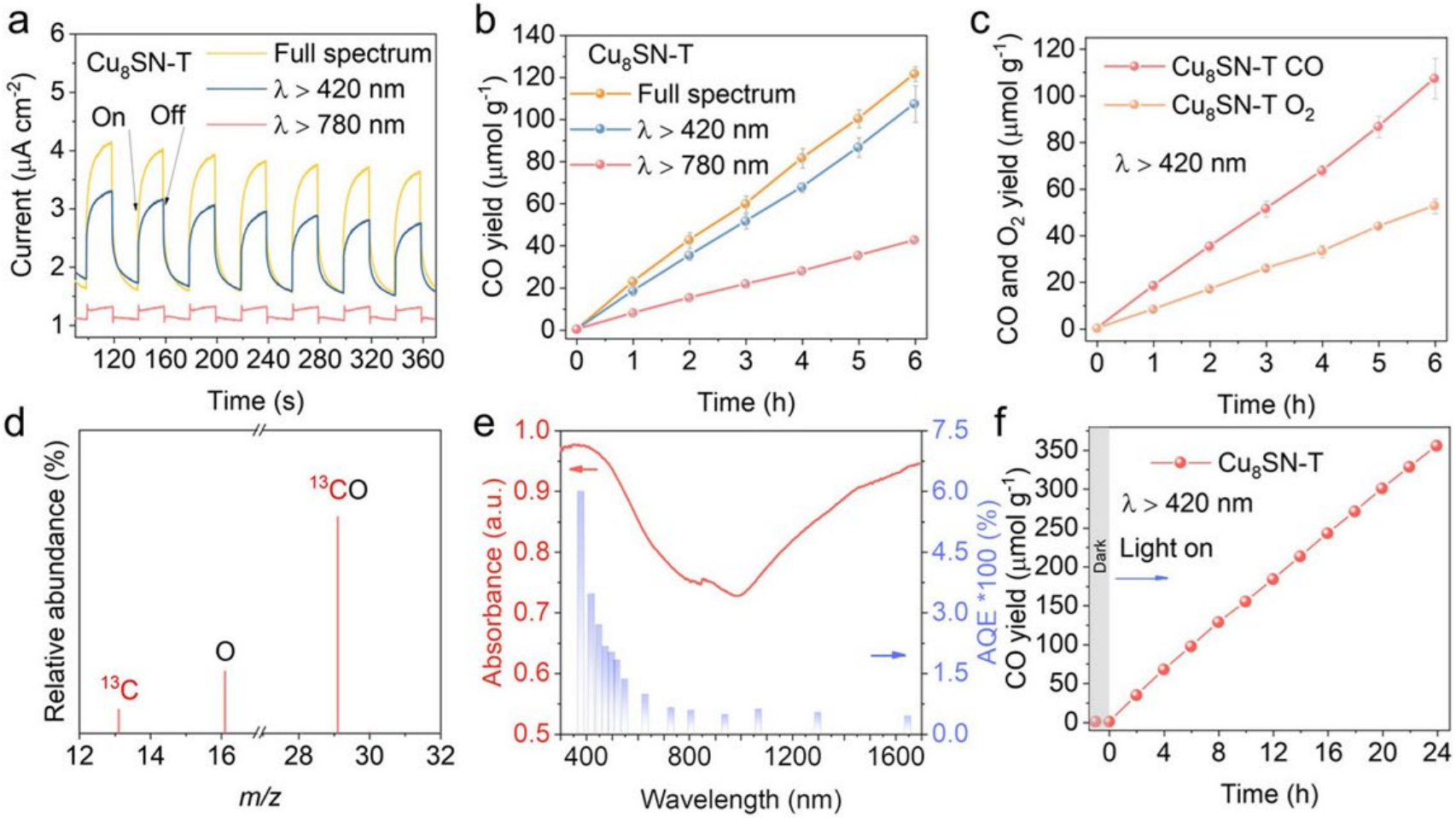
# Results and discussion




Labsolar-6A

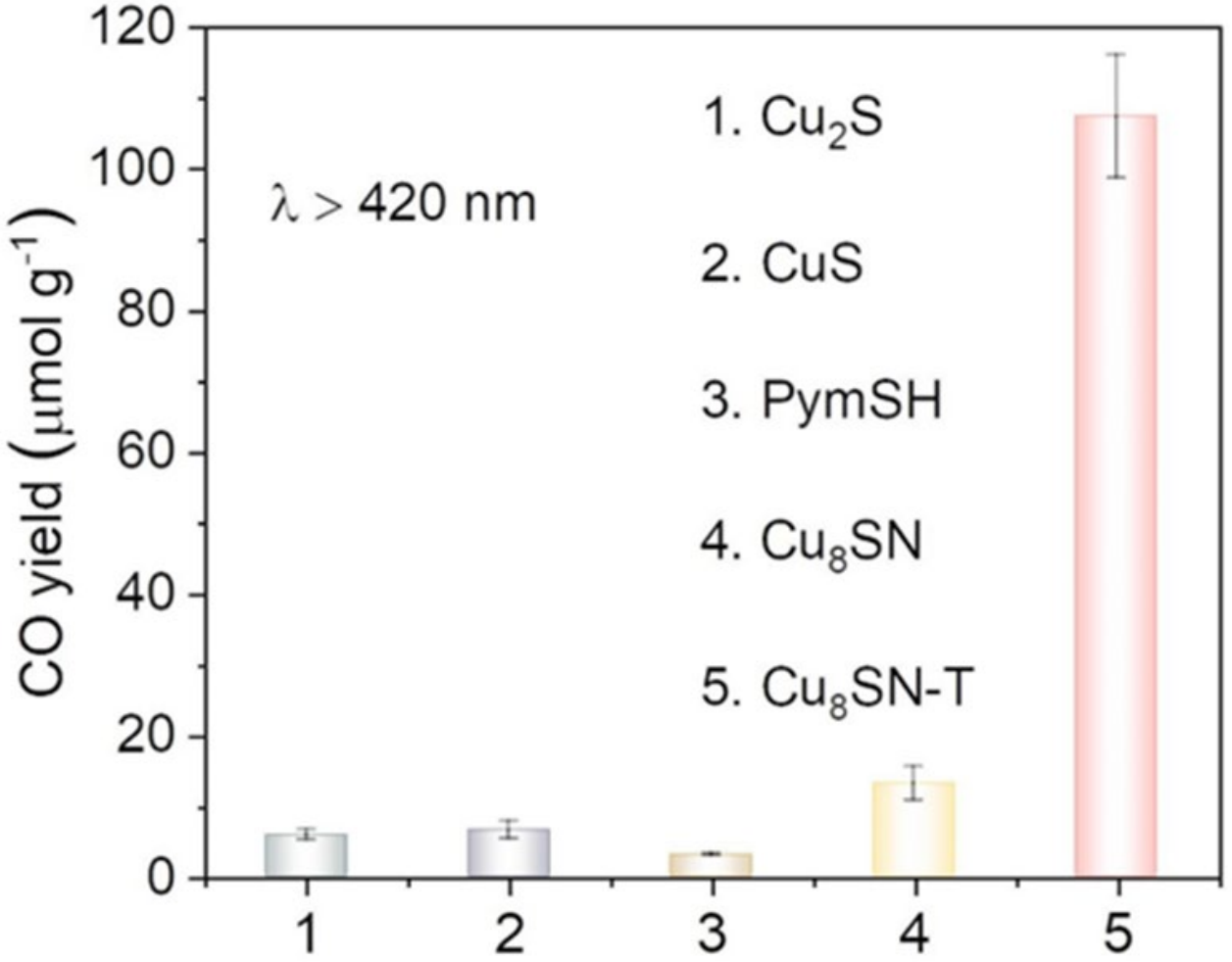
# Results and discussion

Photoreduction data



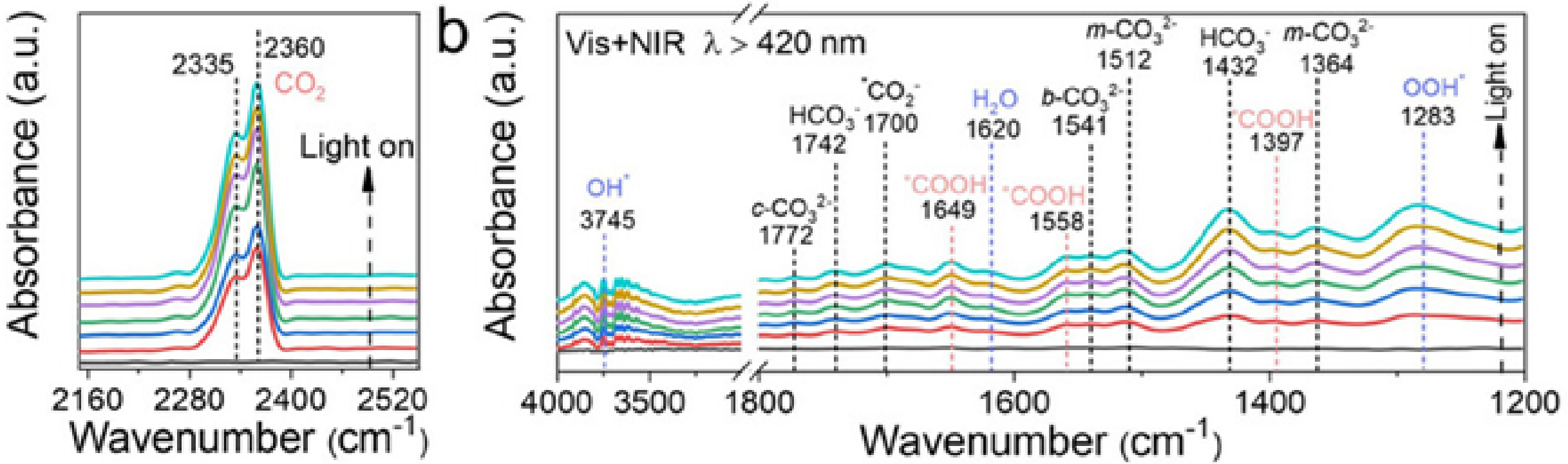
# Results and discussion

Efficiency comparison



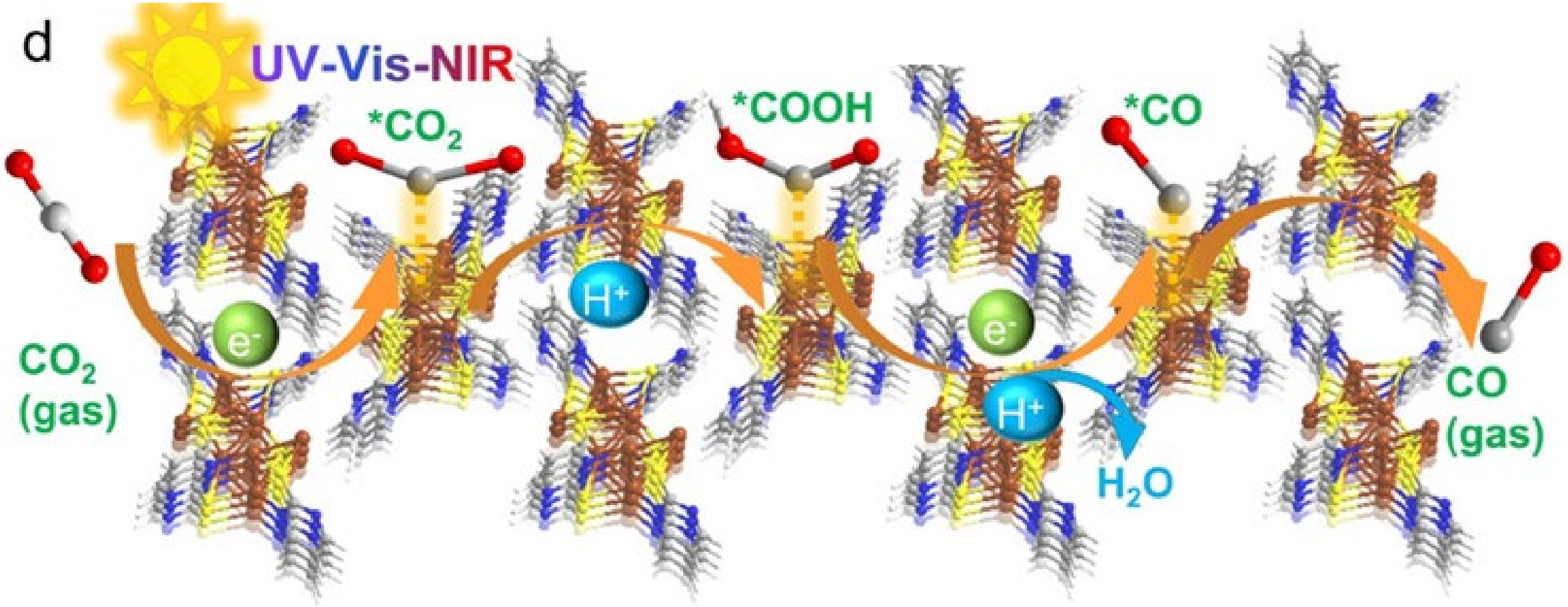
# Results and discussion

In situ DRIFT spectra during photo reduction



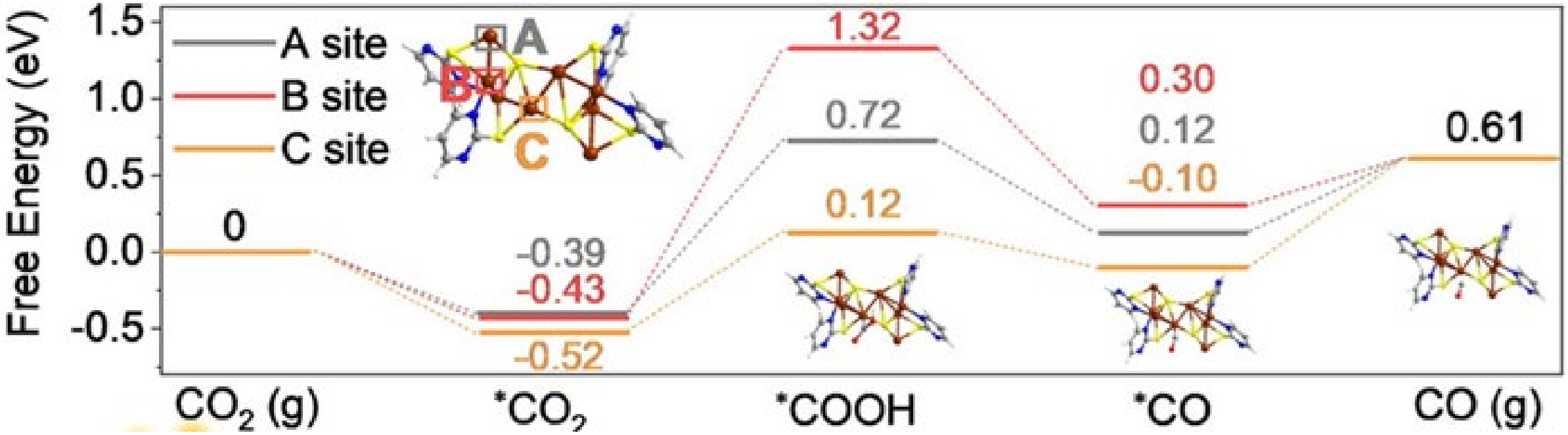
# Results and discussion

Theoretical proposed mechanism



# Results and discussion

Free energy profile diagram



# Conclusion

- This article provides an idea how selective ligand resection can enhance the catalytic activity.
- Ligand removal broadens the range of absorption wavelength starting from UV to NIR.
- Complete study of ligand removal has been done using various experimental technique.
- Due to specific band position this material shows almost 100% selectivity for CO production.