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Fluorescence resonance energy transfer in atomically precise metal nanoclusters by cocrystallization-induced spatial confinement

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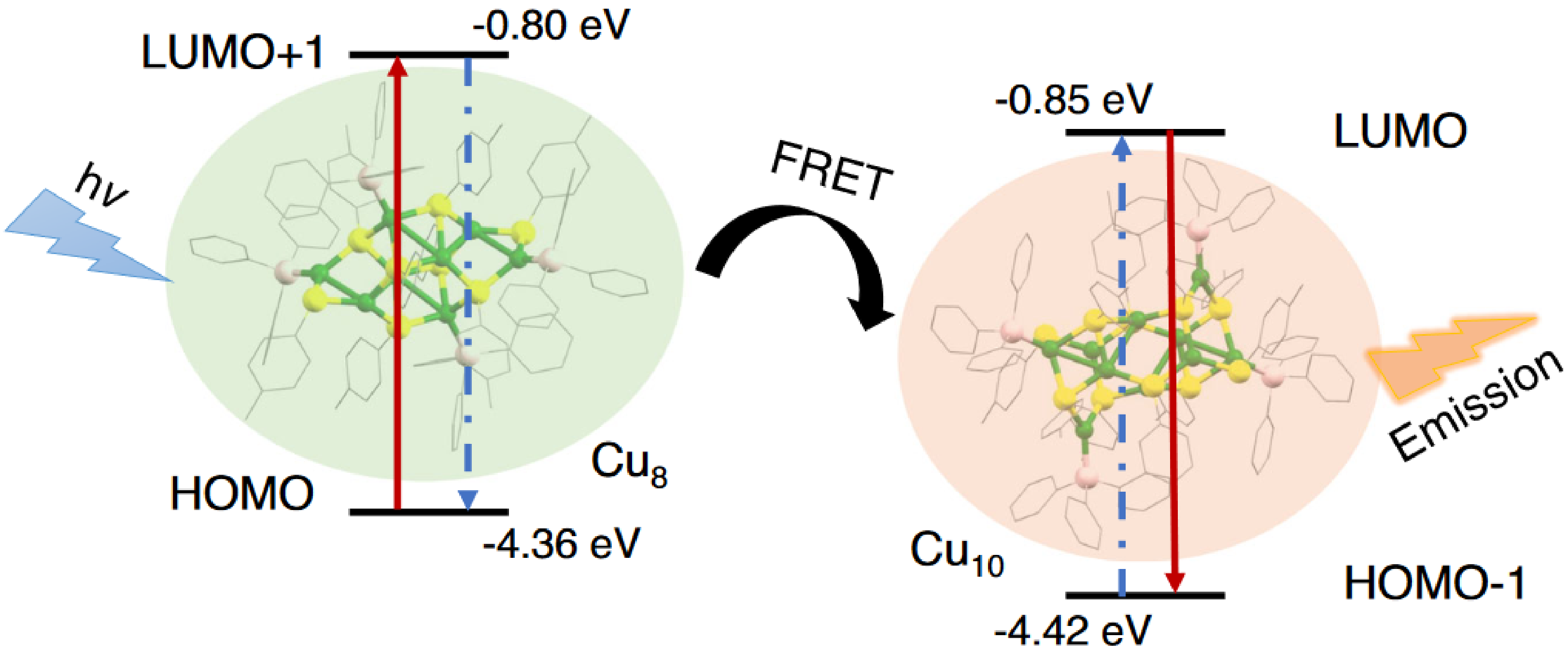
Amoghavarsha R Kini

13-07-2024

FRET

1 2 3

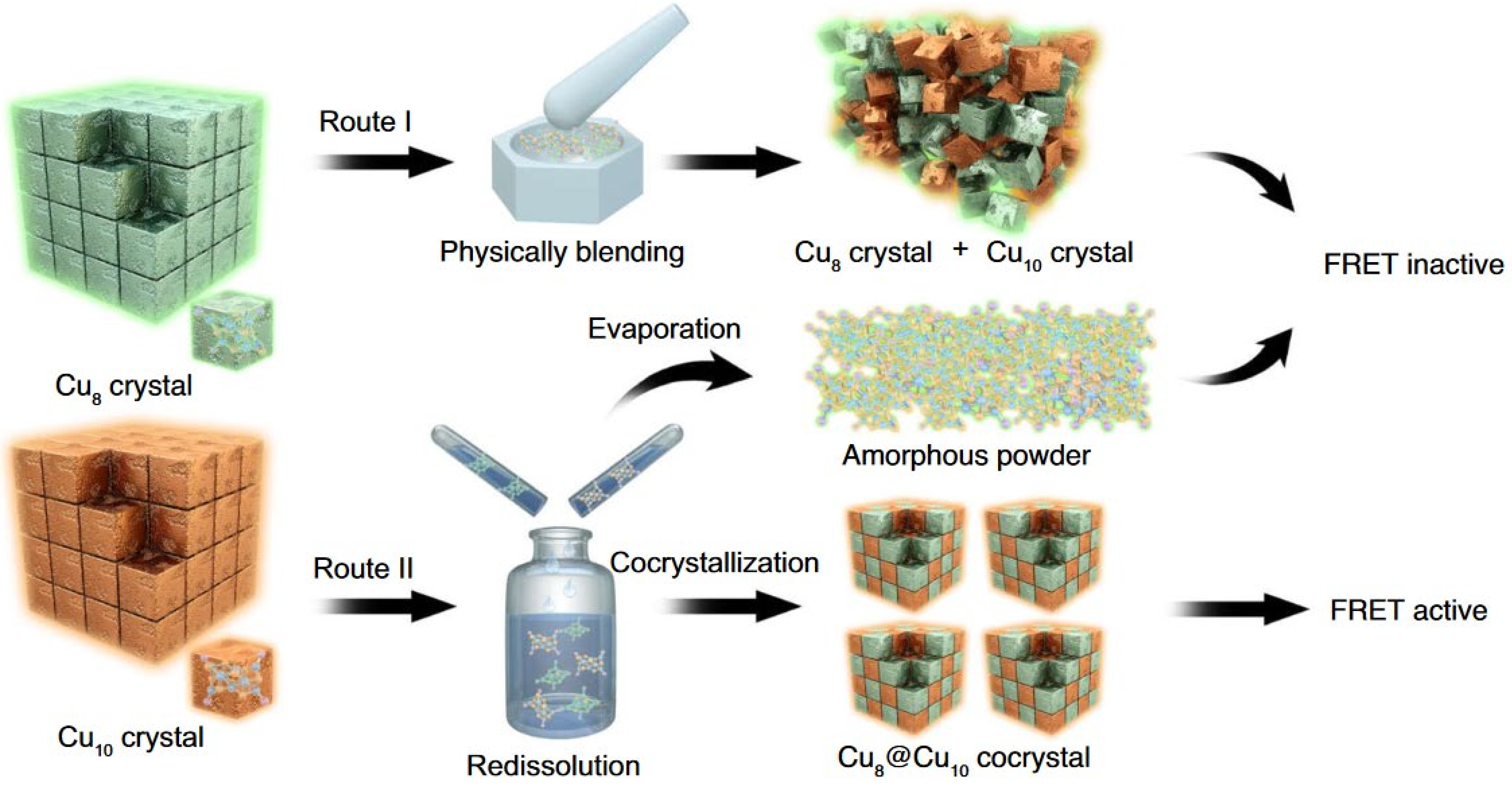


Efficient FRET necessitates fulfilling the following conditions:

1. Overlap between the emission spectrum of the donor and the excitation (or absorption) spectrum of the acceptor.
2. Small intermolecular distance between donor and acceptor.
3. Favorable mutual orientation of their transition dipoles.

Summary

① ② ③

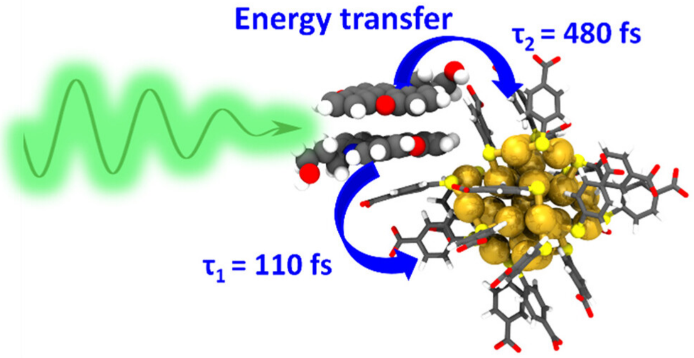

Route I
Physically blending
Cu$_8$ crystal + Cu$_{10}$ crystal
FRET inactive
Cu$_8$ crystal
Evaporation
Amorphous powder
Cu$_{10}$ crystal
Route II
Redissolution
Cocrystallization
Cu$_8$@Cu$_{10}$ cocrystal
FRET active

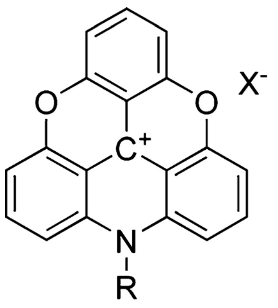
Background

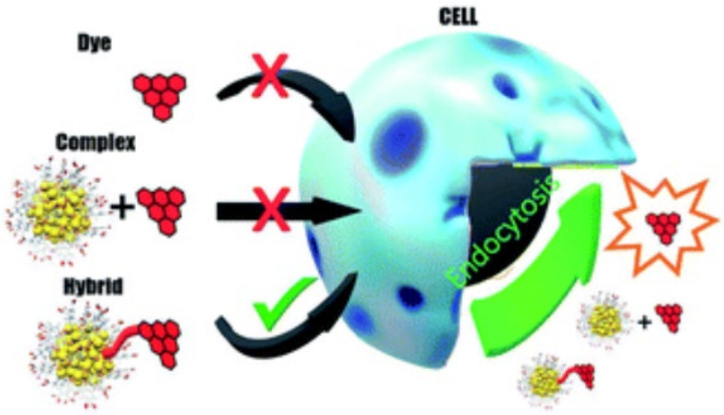
Atomistic View of the Energy Transfer in a Fluorophore-Functionalized Gold Nanocluster

Kyunglim Pyo, María Francisca Matus, Eero Hulkko, Pasi Myllyperkiö, Sami Malola, Tatu Kumpulainen,* Hannu Häkkinen,* and Mika Pettersson*

JACS, 2023







Covalent and non-covalent coupling of a Au_{102} nanocluster with a fluorophore: energy transfer, quenching and intracellular pH sensing†

Eero Hulkko,[a] Tanja Lahtinen,[a] Varpu Marjomäki,[b] Emmi Pohjolainen,[c] Ville Saarnio,[a] Karolina Sokolowska,[a] Ardra Ajitha,[a] Mikael Kuisma,[a] Lauri Lehtovaara,[a] Gerrit Groenhof,[a] Hannu Häkkinen[ac] and Mika Pettersson*[a]

Nanoscale Advances, 2021

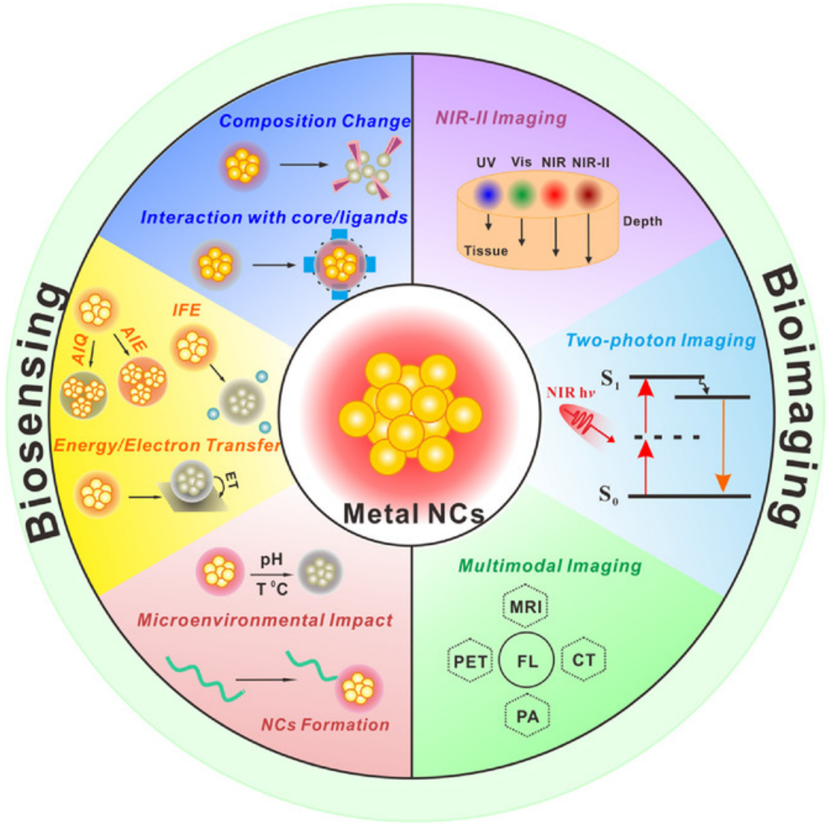
Background

1 2 3

Luminescent metal nanoclusters: Biosensing strategies and bioimaging applications

Yan Xiao, Zhennan Wu, Qiaofeng Yao, Jianping Xie

Aggregate, 2021



Motivation

1. The overlapping of emission spectrum of one system on the excitation spectrum of the other.
2. The lack of proper nanocluster systems which show FRET mechanisms where both the donor and accepter is the nanocluster.
3. Find a suitable FRET mechanism in nanoparticle systems.

Why this paper?

1. First paper (to the best of my knowledge) to show FRET involving nanoclusters as both donor and acceptor.

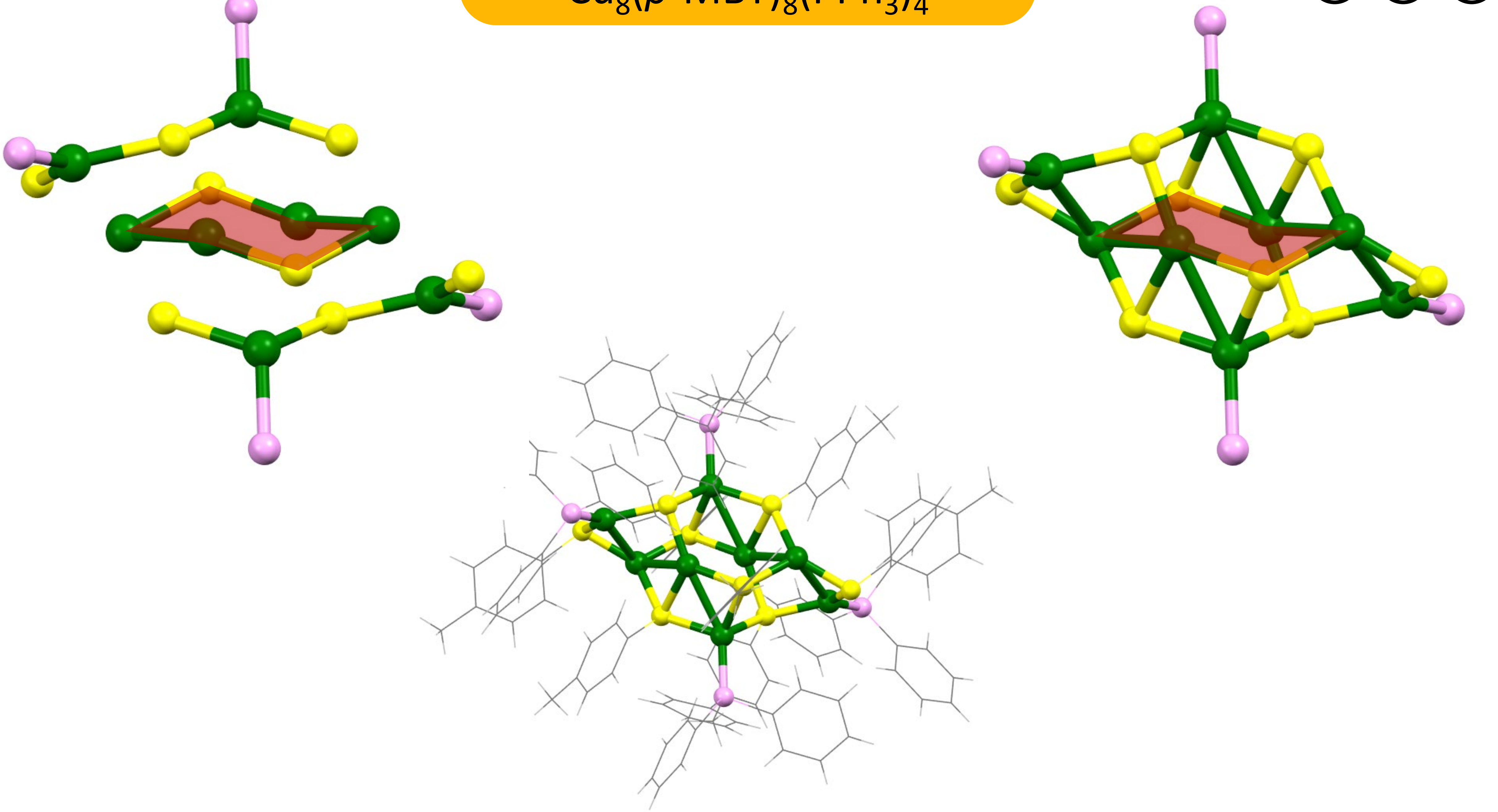
2. Detailed experimental and computational studies to understand the mechanism of FRET in nanocluster systems.

Introduction

1. Förster/fluorescence resonance energy transfer, a non-radiative energy transfer process, occurs through long-range dipole–dipole interactions between a donor–acceptor pair.
2. Over the past few decades, due to their ability to unravel fluorescence interactions between donor and acceptor with nanometer resolution, FRET-based sensors or imaging agents have found widespread applications in bio-related fields.
3. Rationally developing an atomically precise cluster-based donor–acceptor system with FRET performance allows for an in-depth understanding of the intercluster energy transfer mechanism.

$Cu_8(p\text{-MBT})_8(PPh_3)_4$

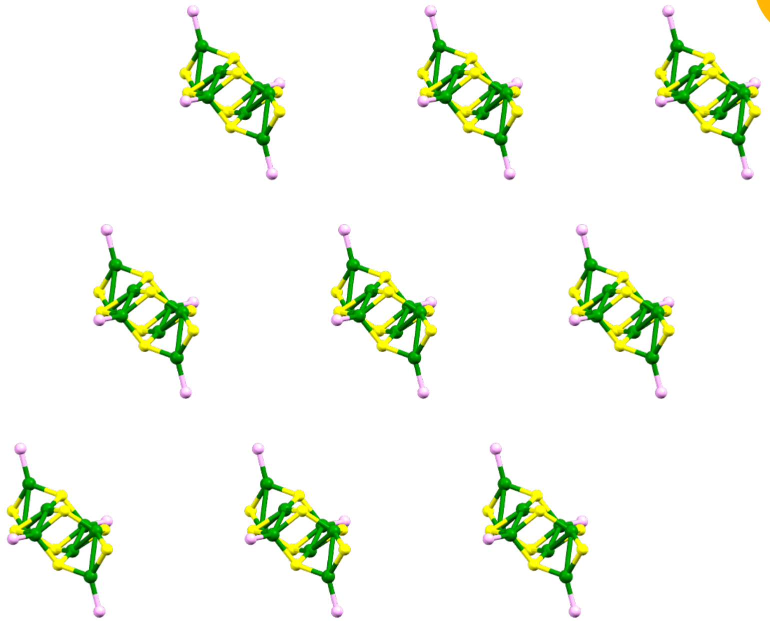
1 2 3



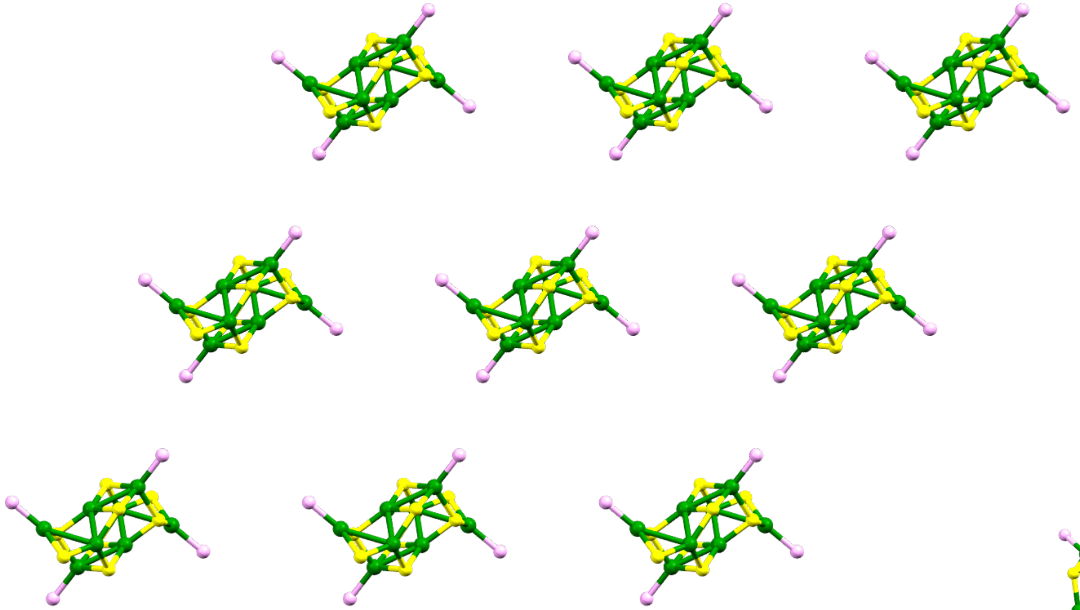
$Cu_8(p\text{-}MBT)_8(PPh_3)_4$

1 2 3

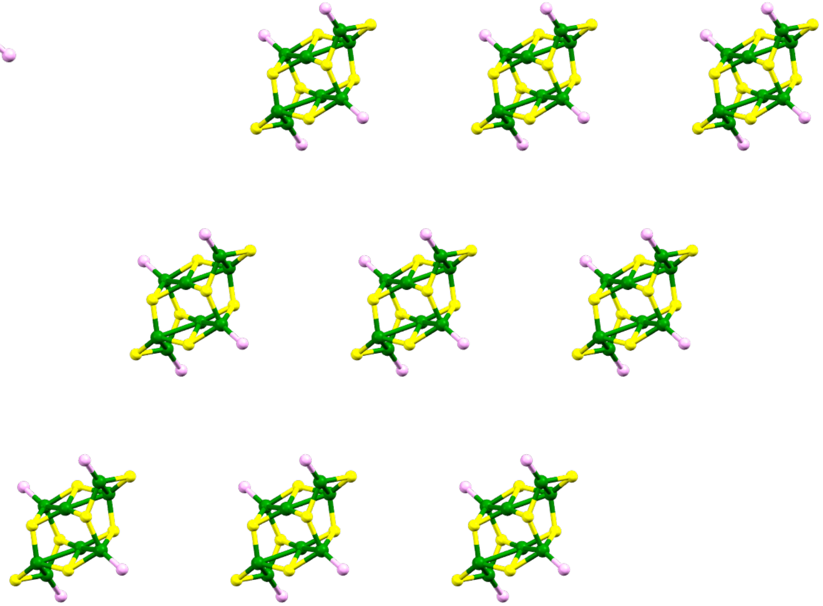
Triclinic P-1



a-axis



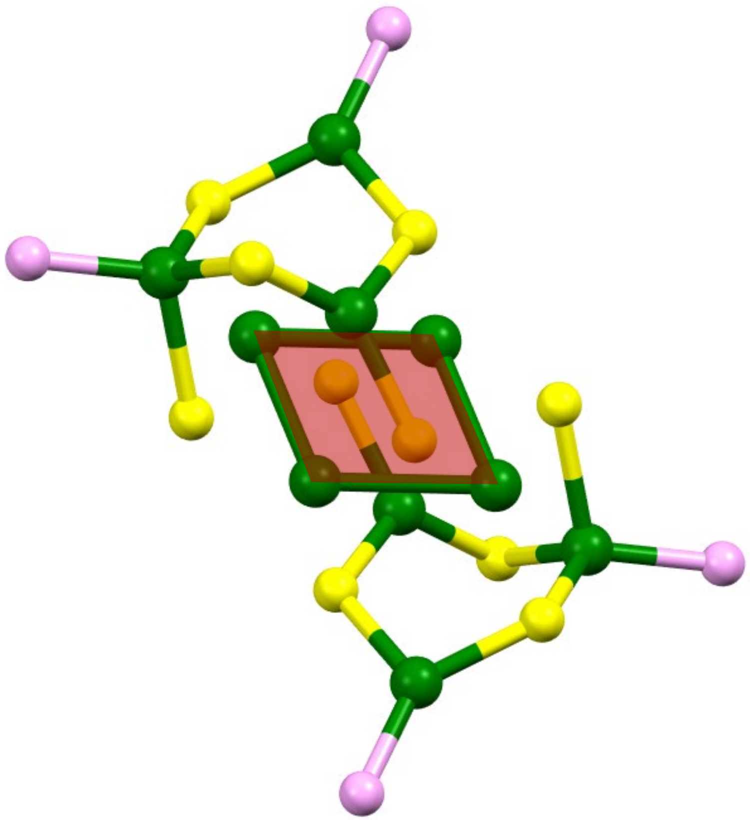
b-axis

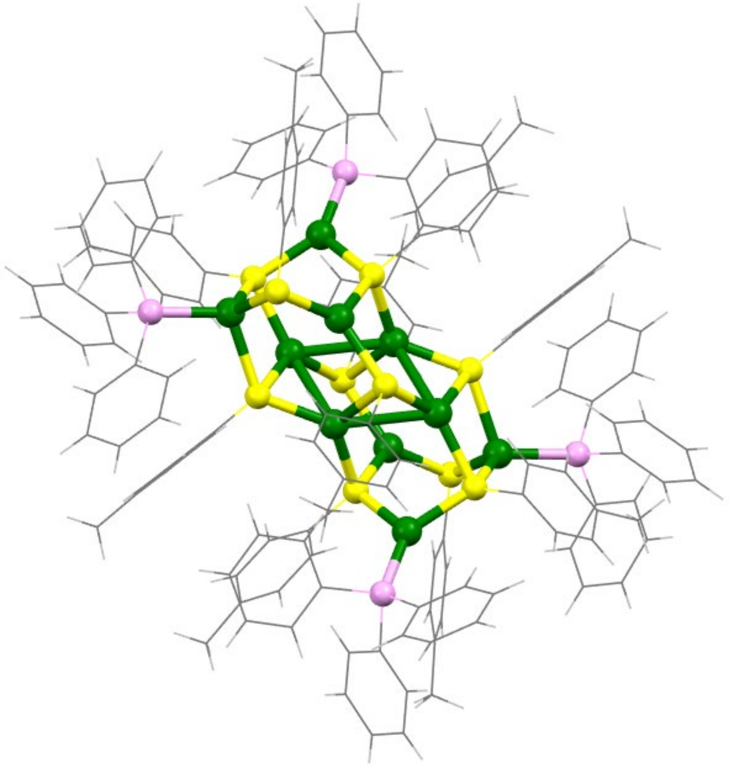


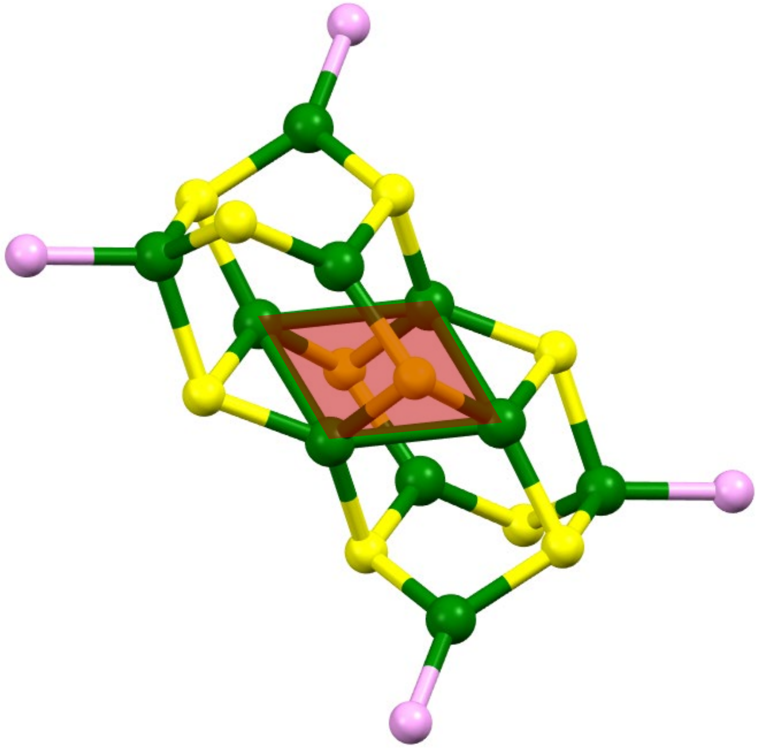
c-axis

$Cu_{10}(p\text{-}MBT)_{10}(PPh_3)_4$

① ② ③

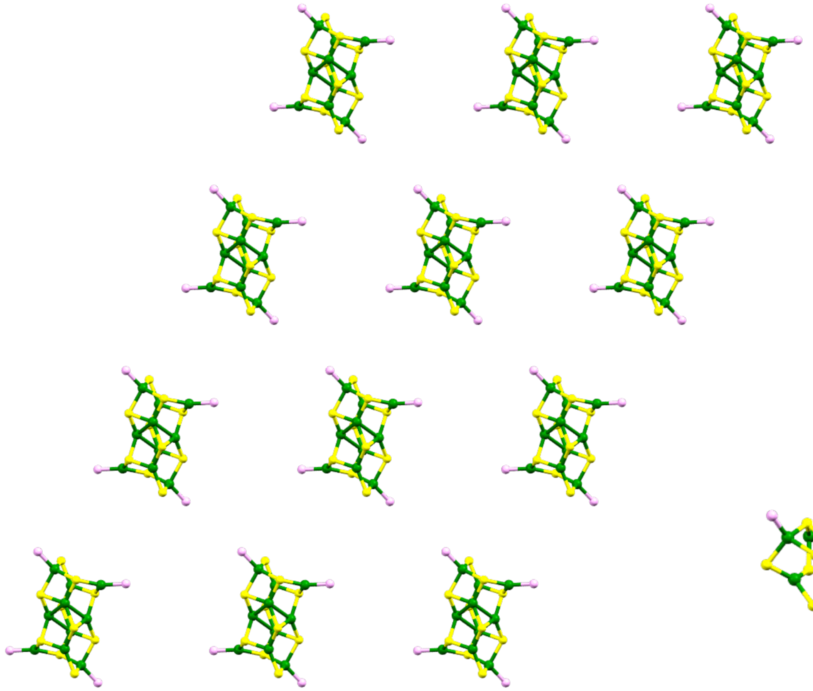




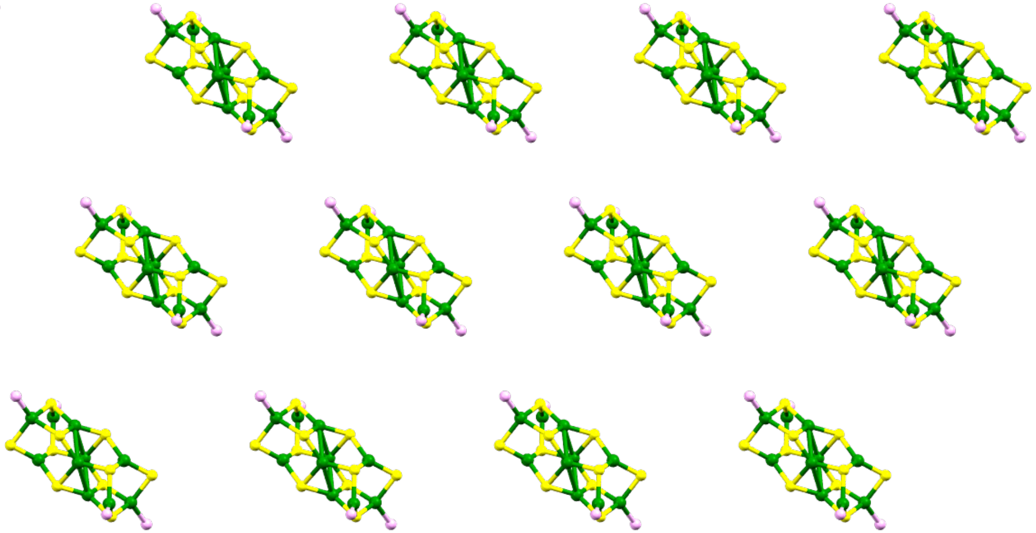


$Cu_{10}(p\text{-}MBT)_{10}(PPh_3)_4$

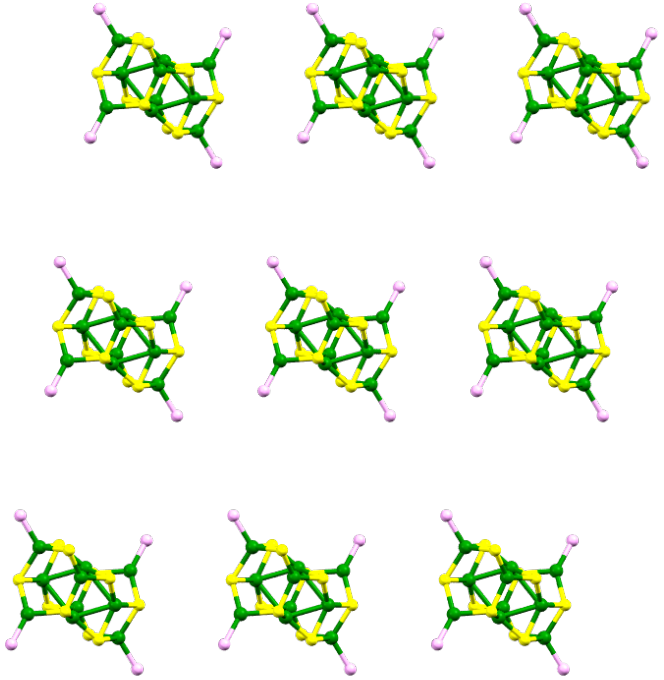
Triclinic P-1



a-axis



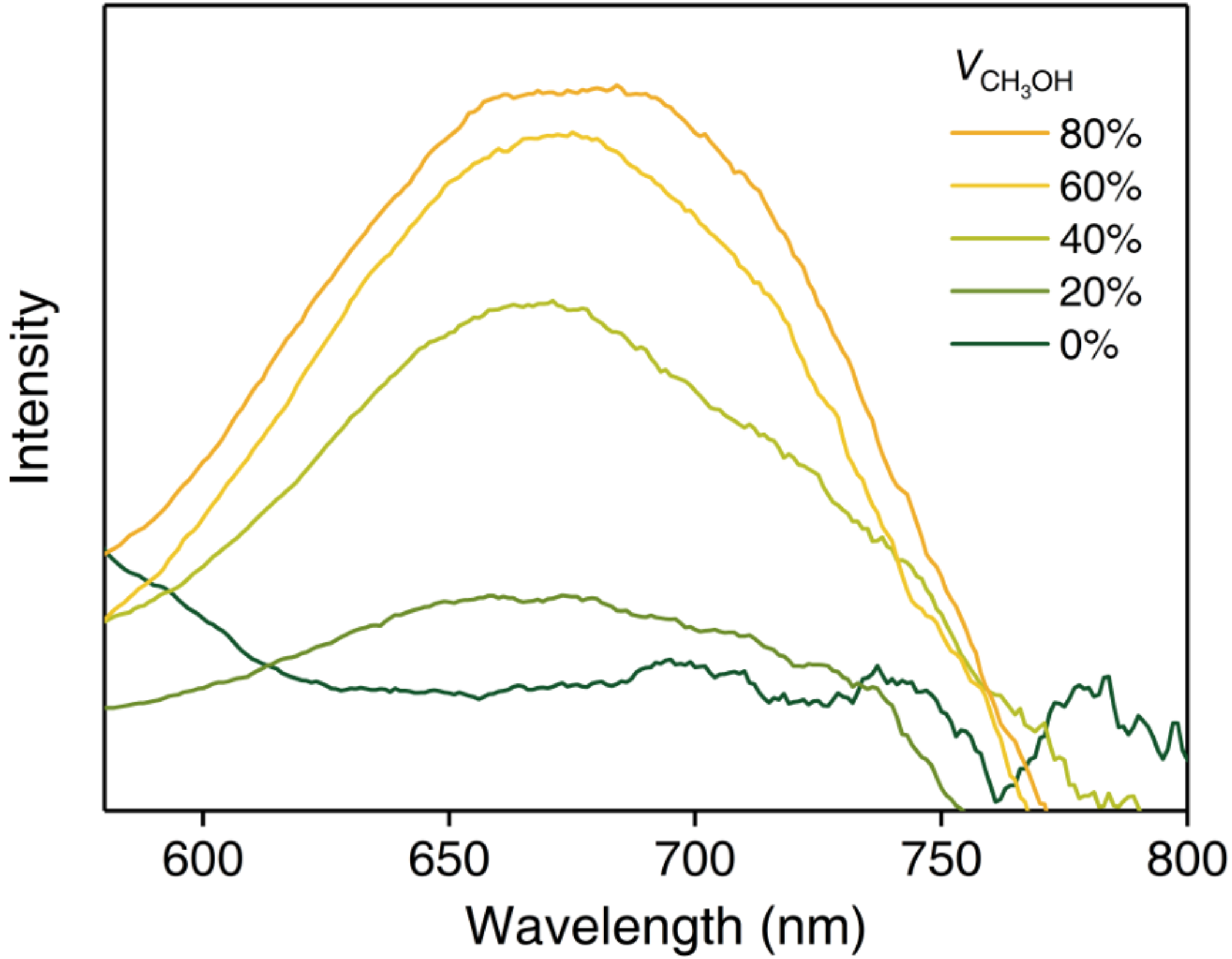
b-axis



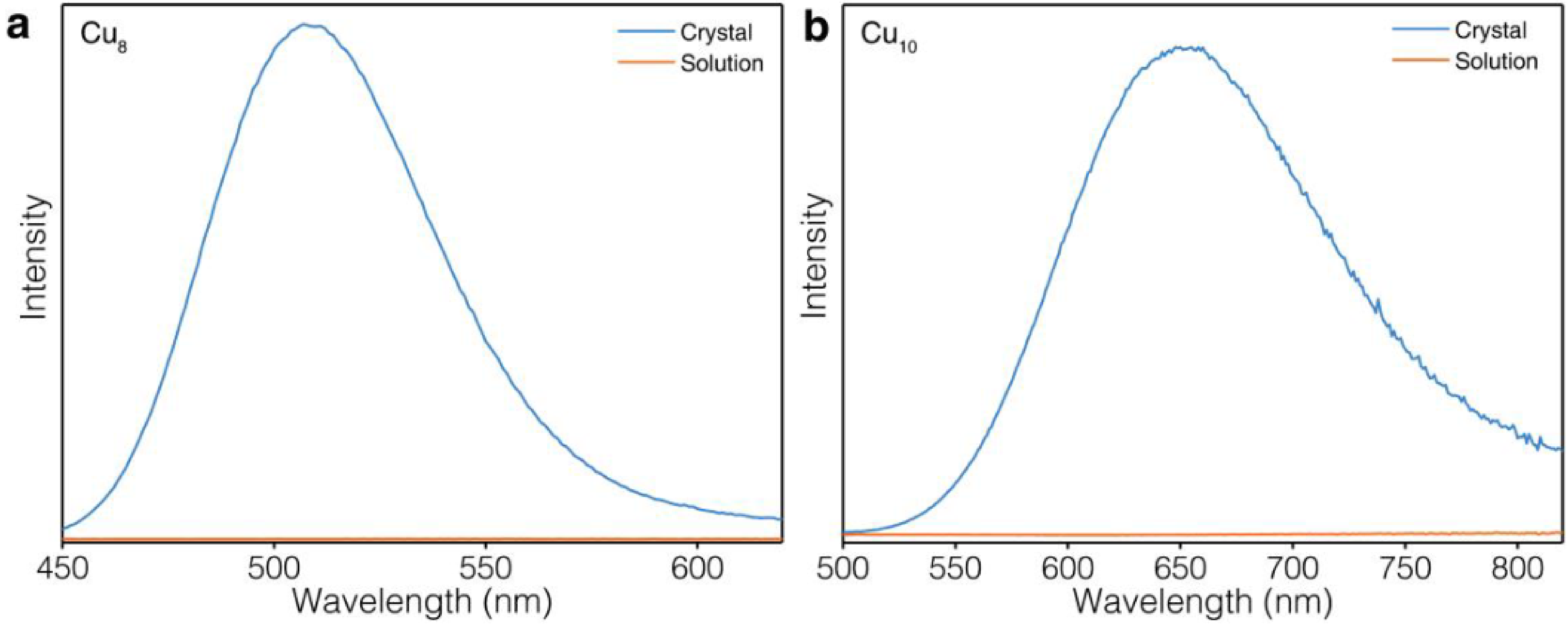
c-axis

Photophysical property

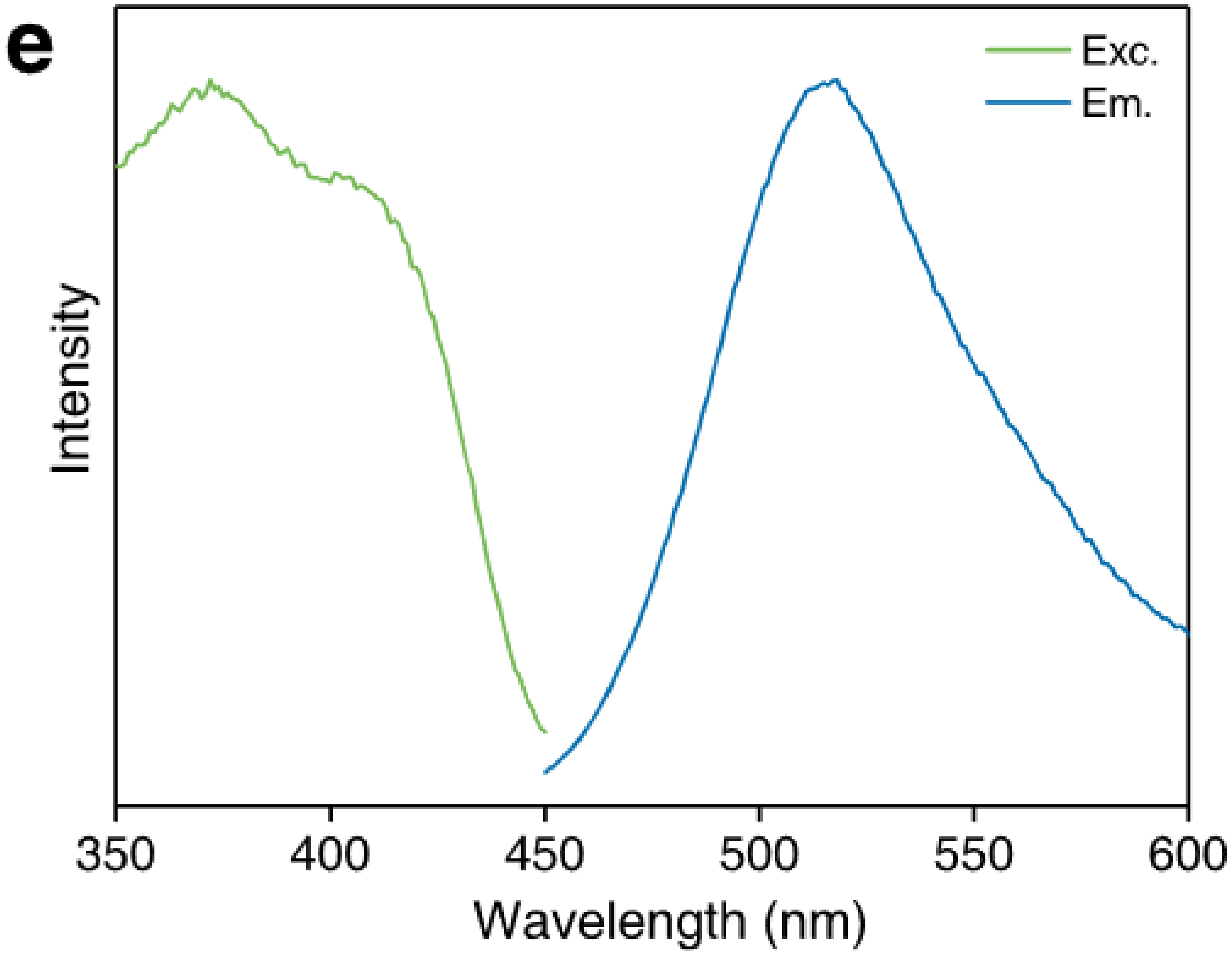
1 2 3



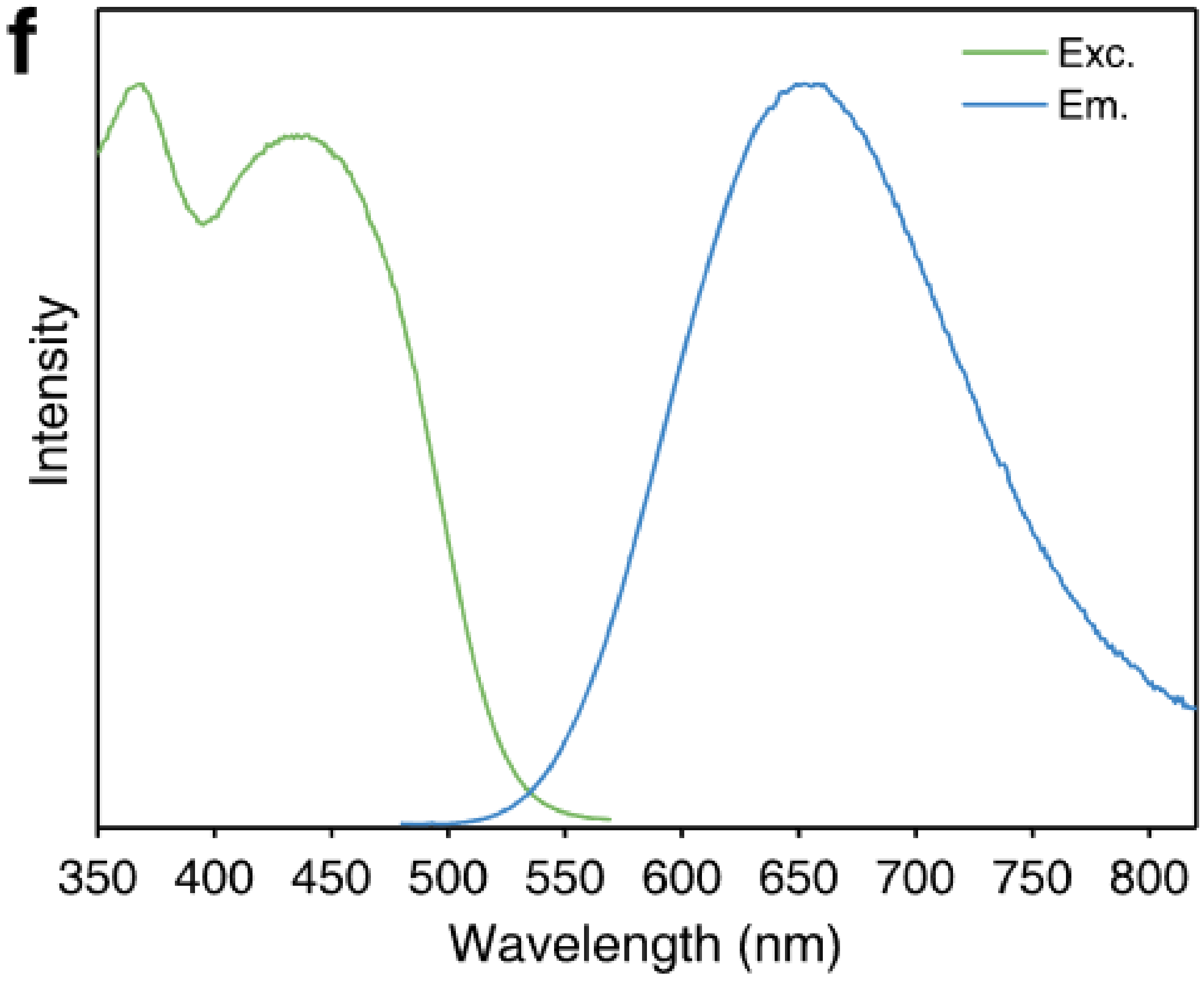
Photophysical property



Photophysical property

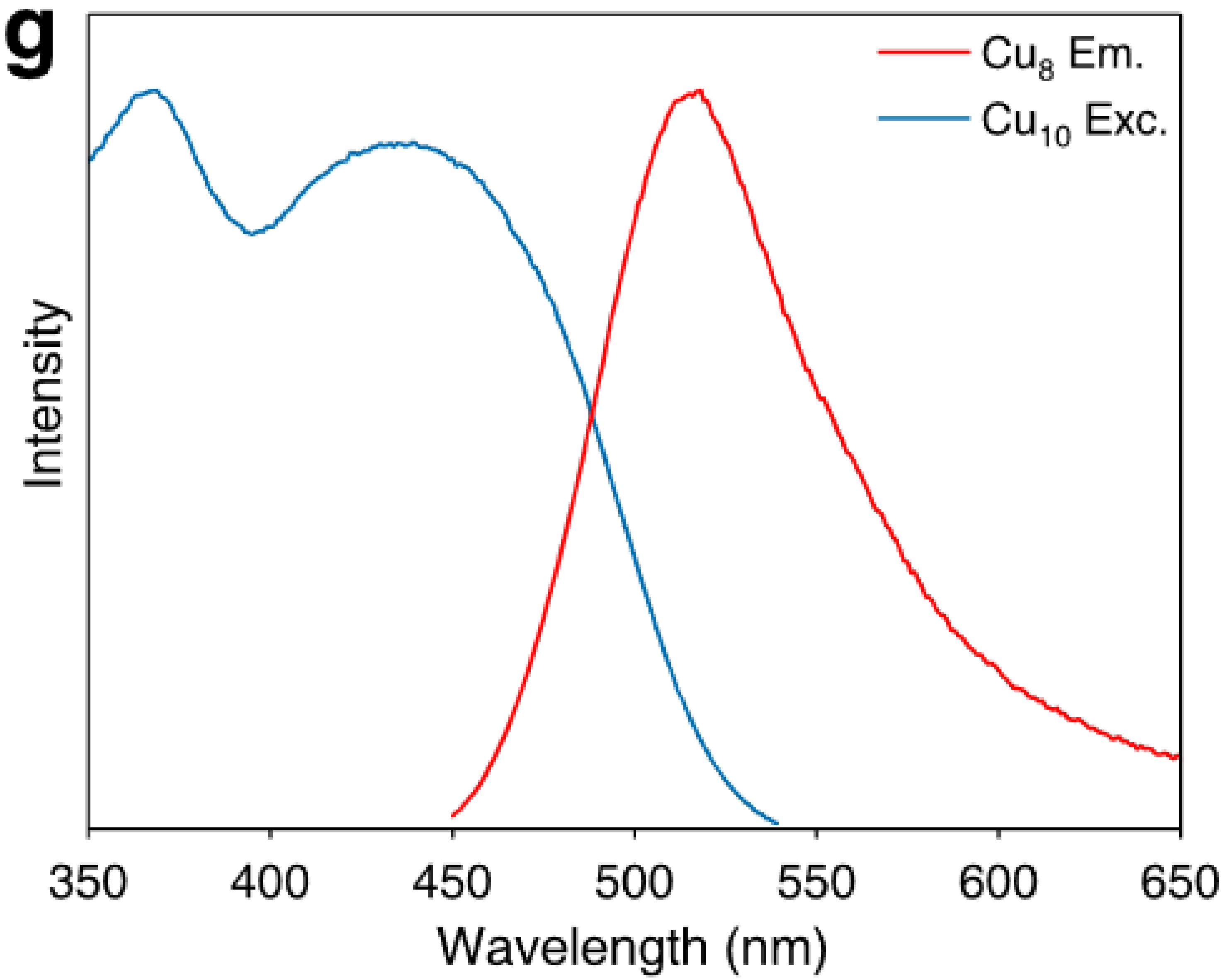


Cu_8 : λ_{em} = 515 nm, λ_{ex} = 365 nm



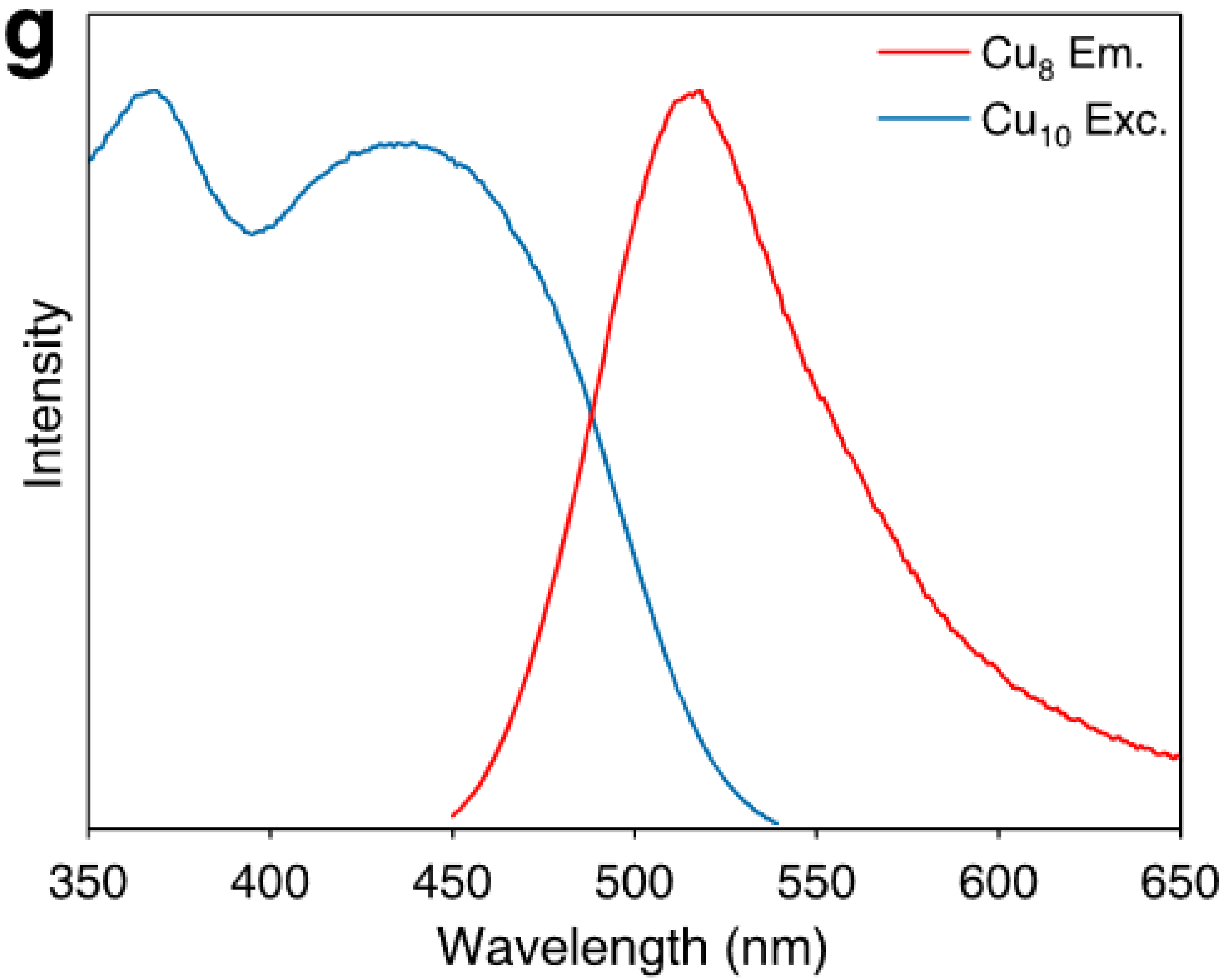
Cu_{10} : λ_{em} = 650 nm, λ_{ex} = 365 nm

Photophysical property



1. Physical mixing.
2. Co-crystallization.

Photophysical property



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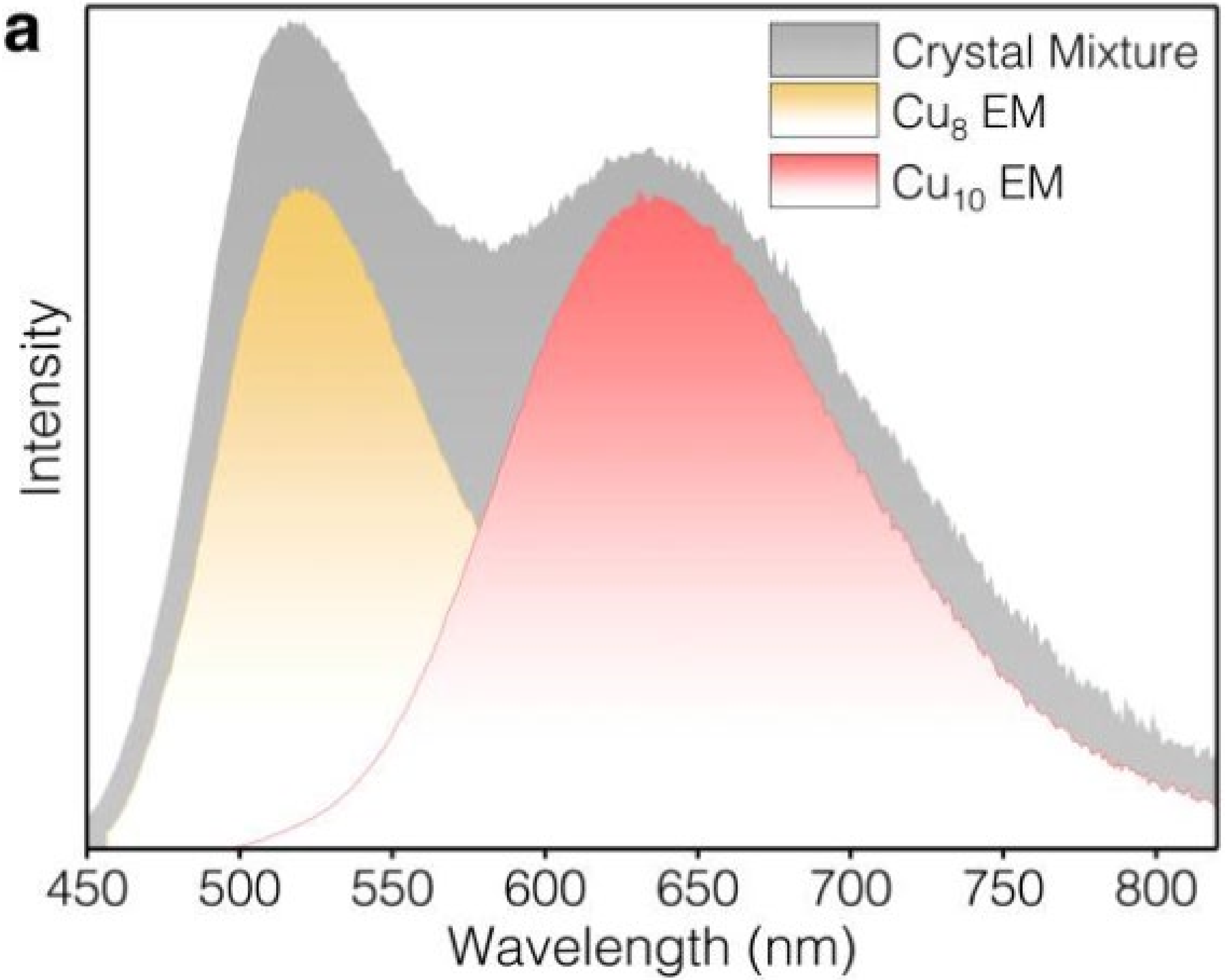
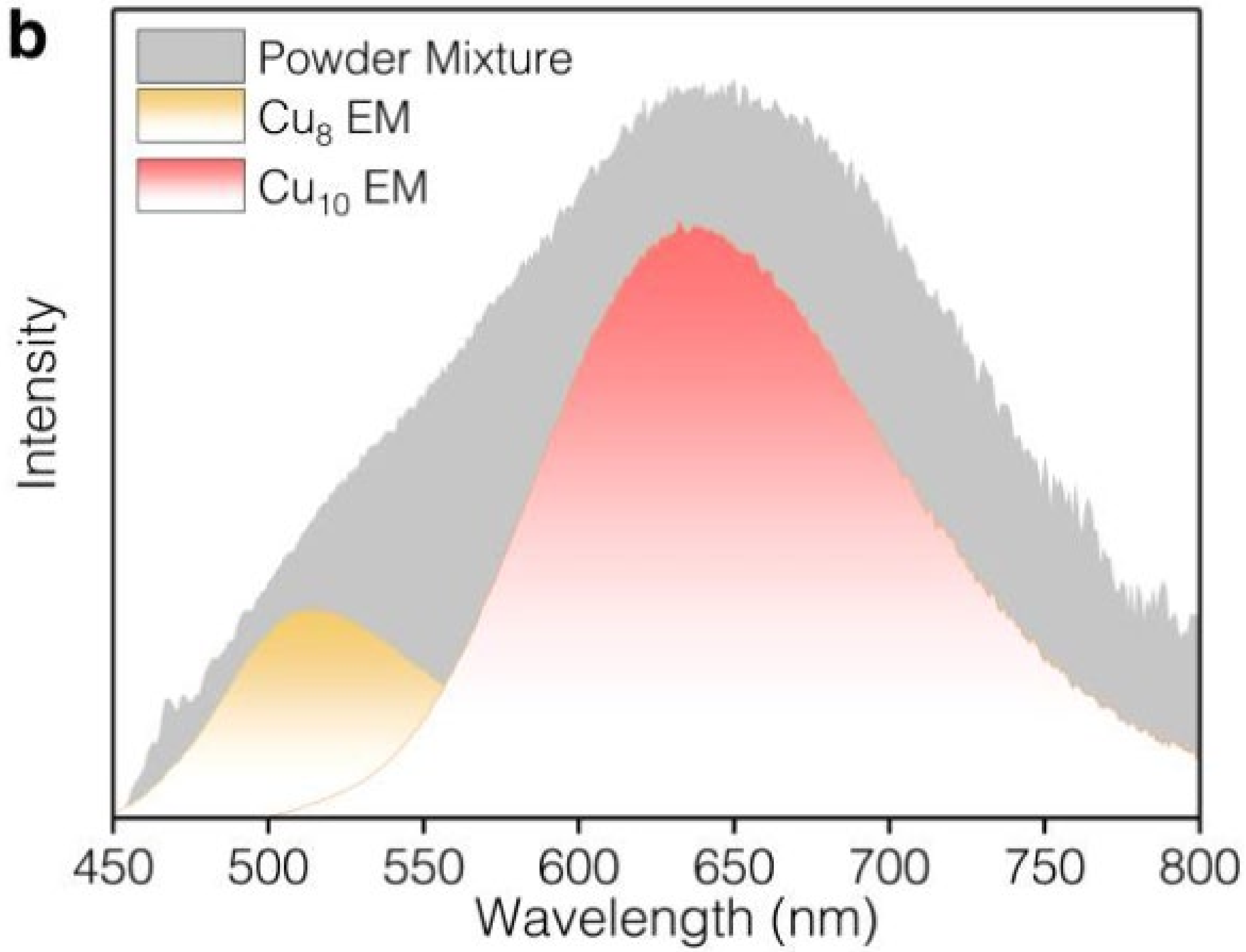
Photophysical property

1 2 3

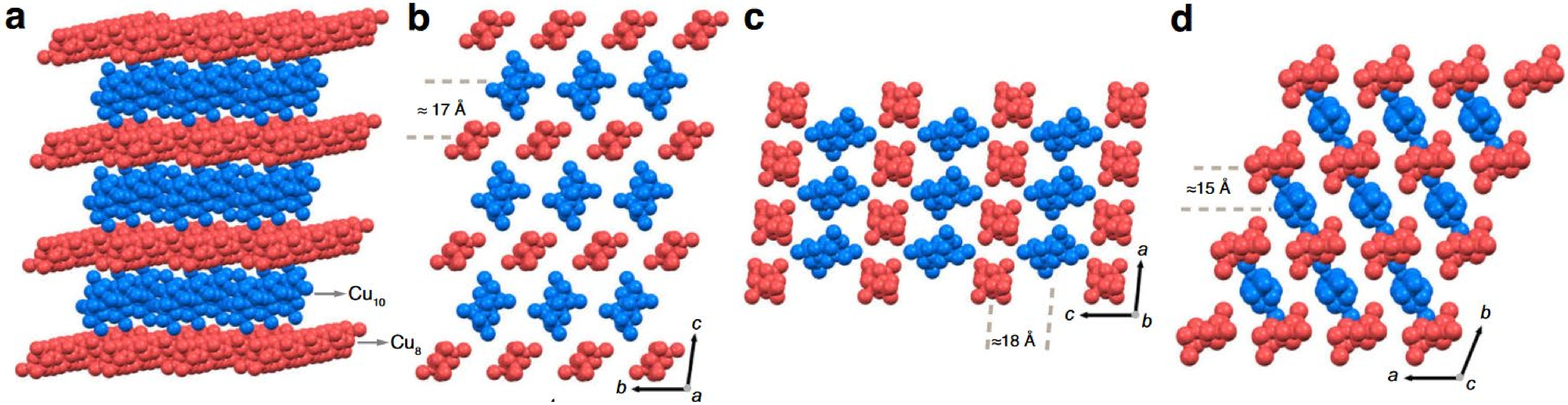


Photophysical property



$Cu_8@Cu_{10}$

1 2 3

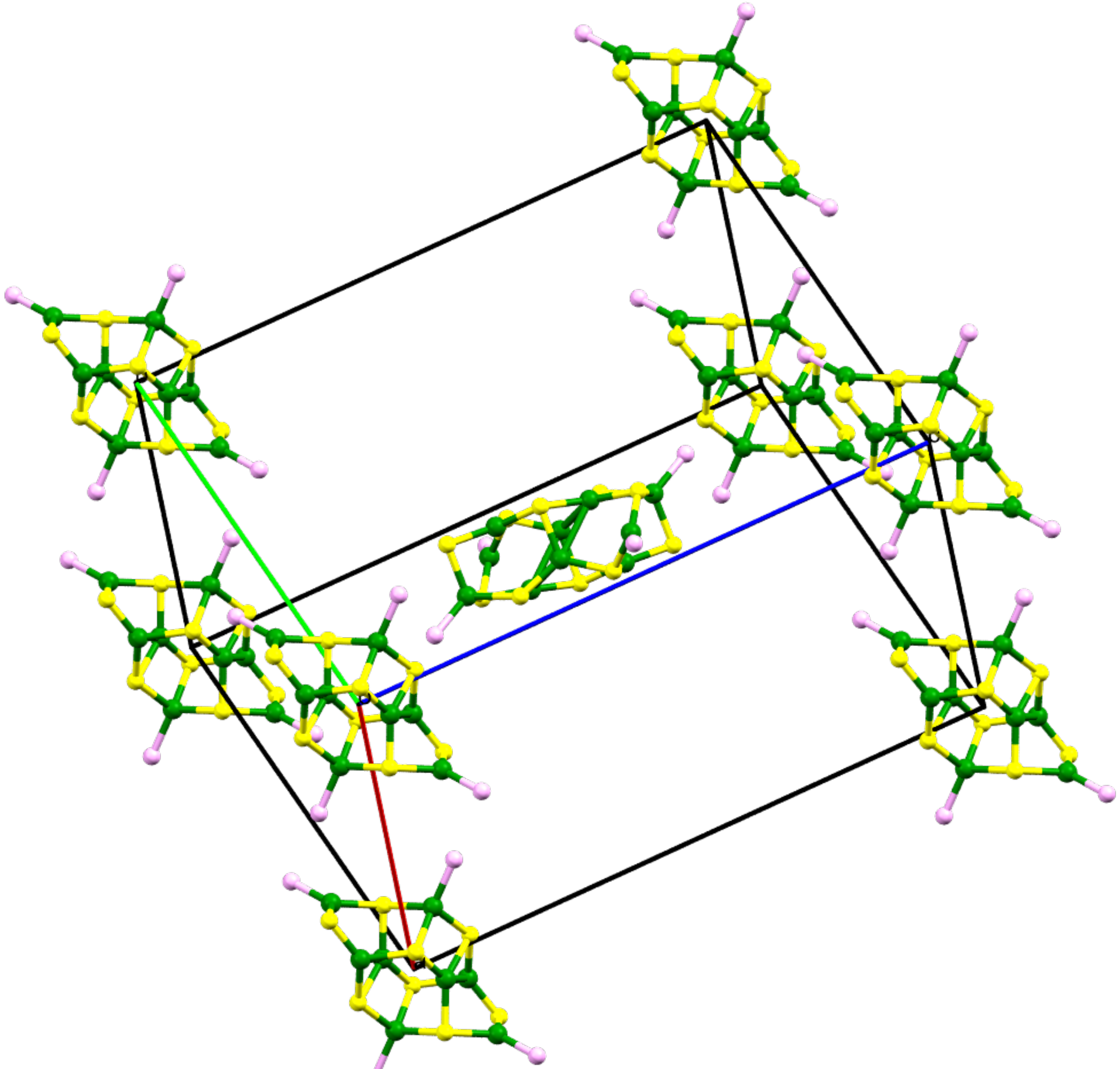


Triclinic P-1

with 1:1 molar ratio

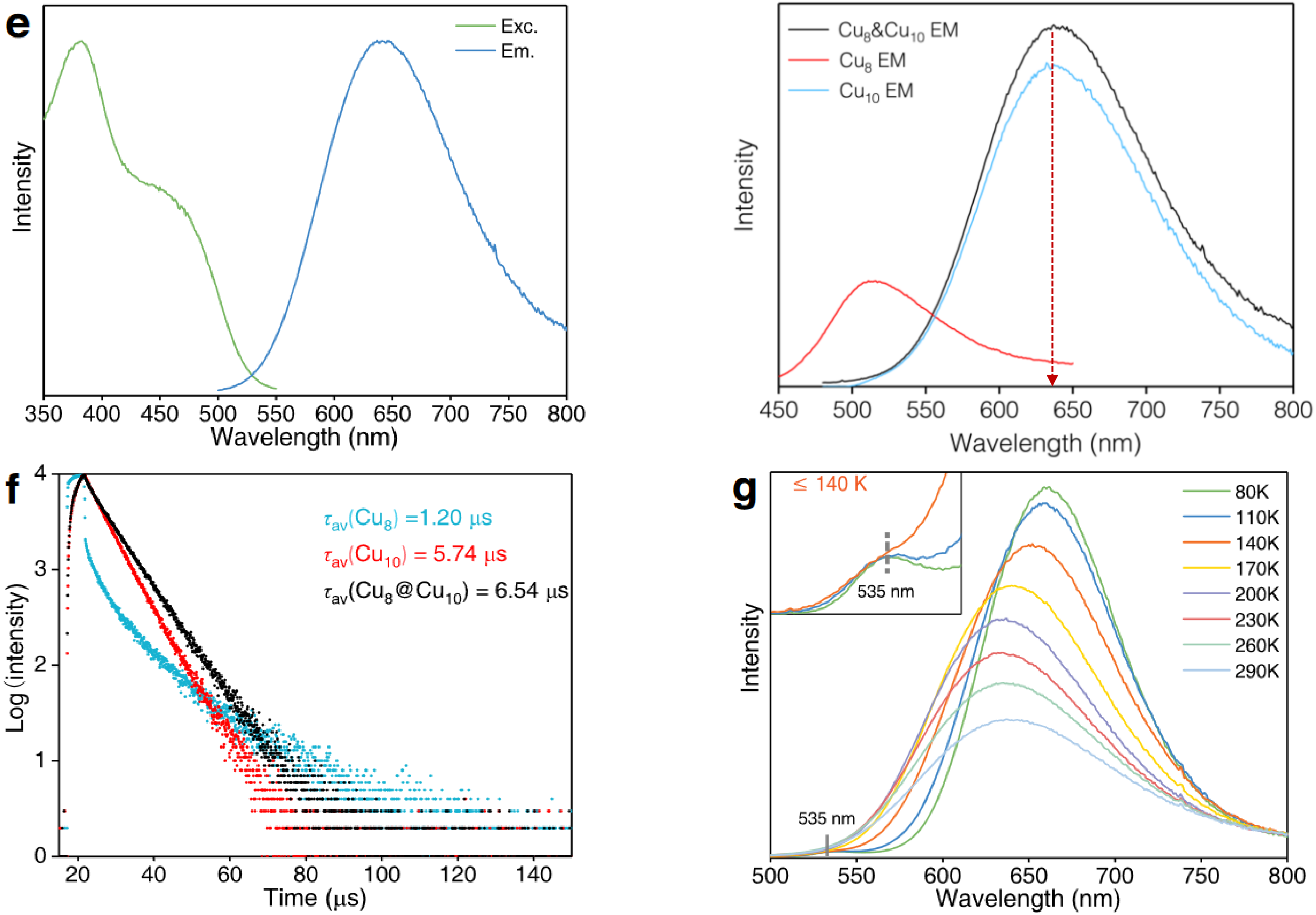
$Cu_8@Cu_{10}$

1 2 3



$Cu_8@Cu_{10}$

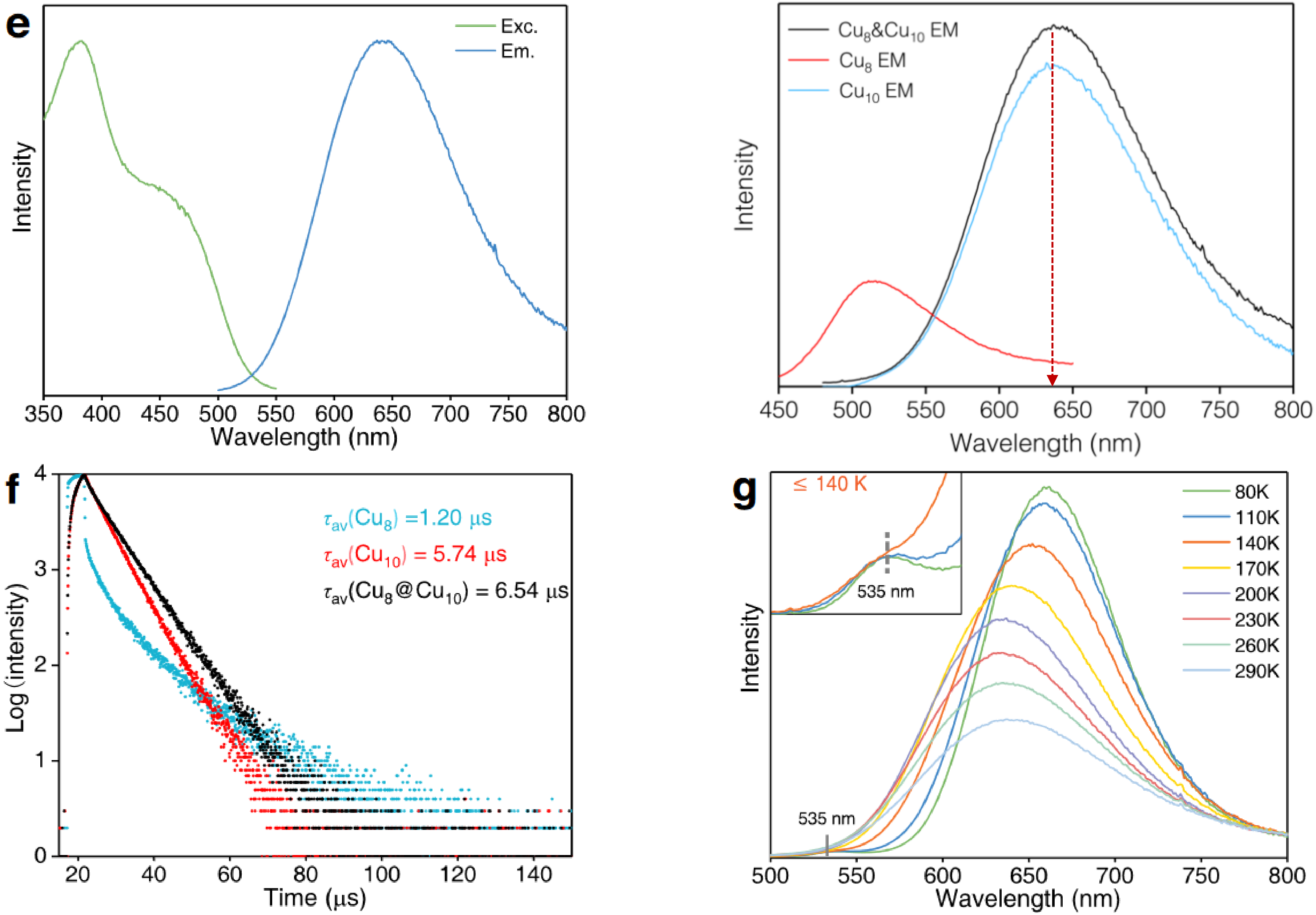
1 2 3



e
Exc.
Em.
Intensity
350 400 450 500 550 600 650 700 750 800
Wavelength (nm)
Cu8&Cu10 EM
Cu8 EM
Cu10 EM
Intensity
450 500 550 600 650 700 750 800
Wavelength (nm)
f
τav(Cu8) =1.20 μs
τav(Cu10) = 5.74 μs
τav(Cu8@Cu10) = 6.54 μs
Log (intensity)
0 1 2 3 4
20 40 60 80 100 120 140
Time (μs)
g
≤ 140 K
535 nm
535 nm
80K
110K
140K
170K
200K
230K
260K
290K
Intensity
500 550 600 650 700 750 800
Wavelength (nm)

$Cu_8@Cu_{10}$

1 2 3



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535 nm
80K
110K
140K
170K
200K
230K
260K
290K
Intensity
535 nm
500 550 600 650 700 750 800
Wavelength (nm)

Computational studies

Fermi's golden rule describes the rate at which atomic or electronic transitions take place between two states.

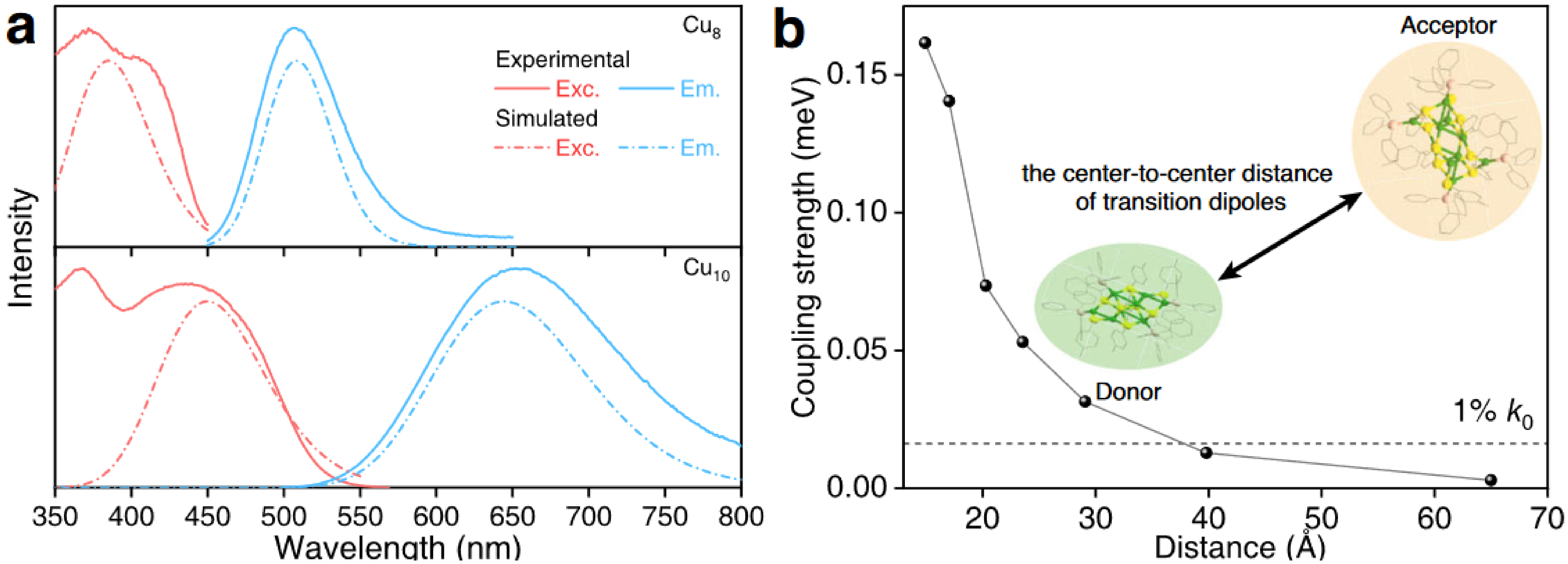
$$k_{FRET} = \frac{2\pi}{\hbar}(V_{cp})^2 \, FCWD$$

FCWD – Franck-Condon factor weighted density of states.

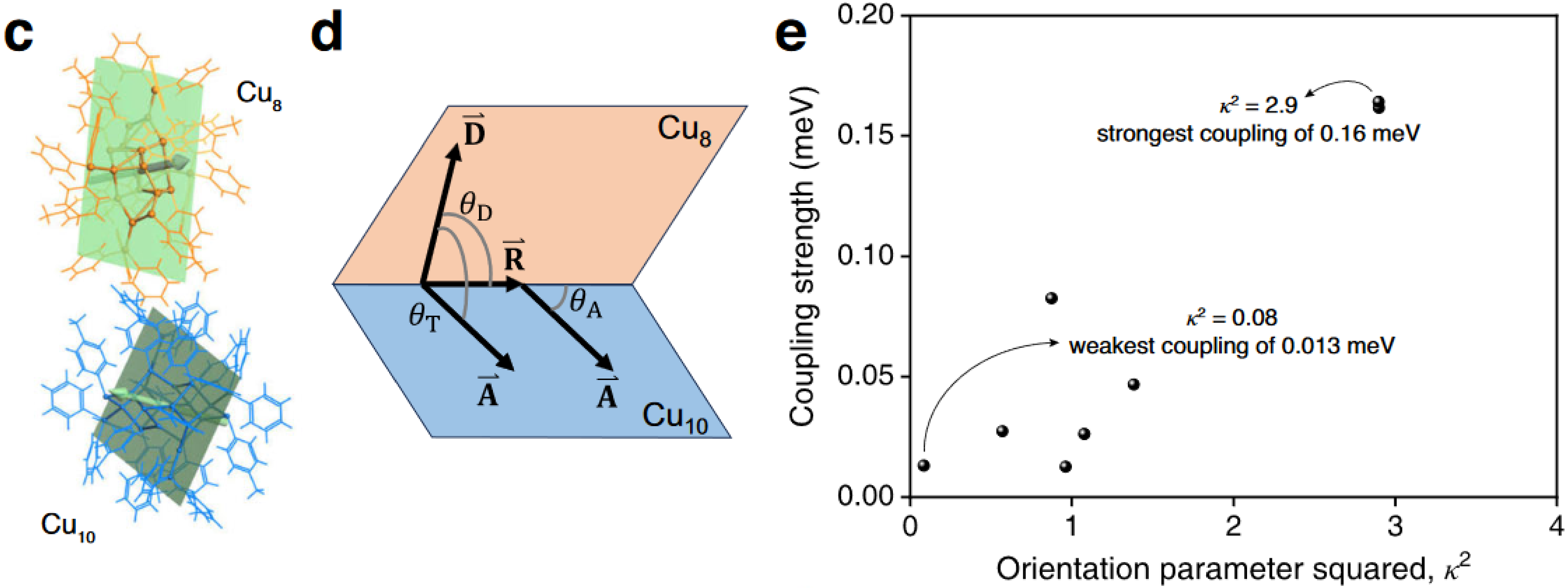
V_{cp} – Electronic coupling strength.

The Franck-Condon factor weighted density of states provides a detailed picture of how electronic transitions occur between vibrational states in different electronic levels.

Computational studies



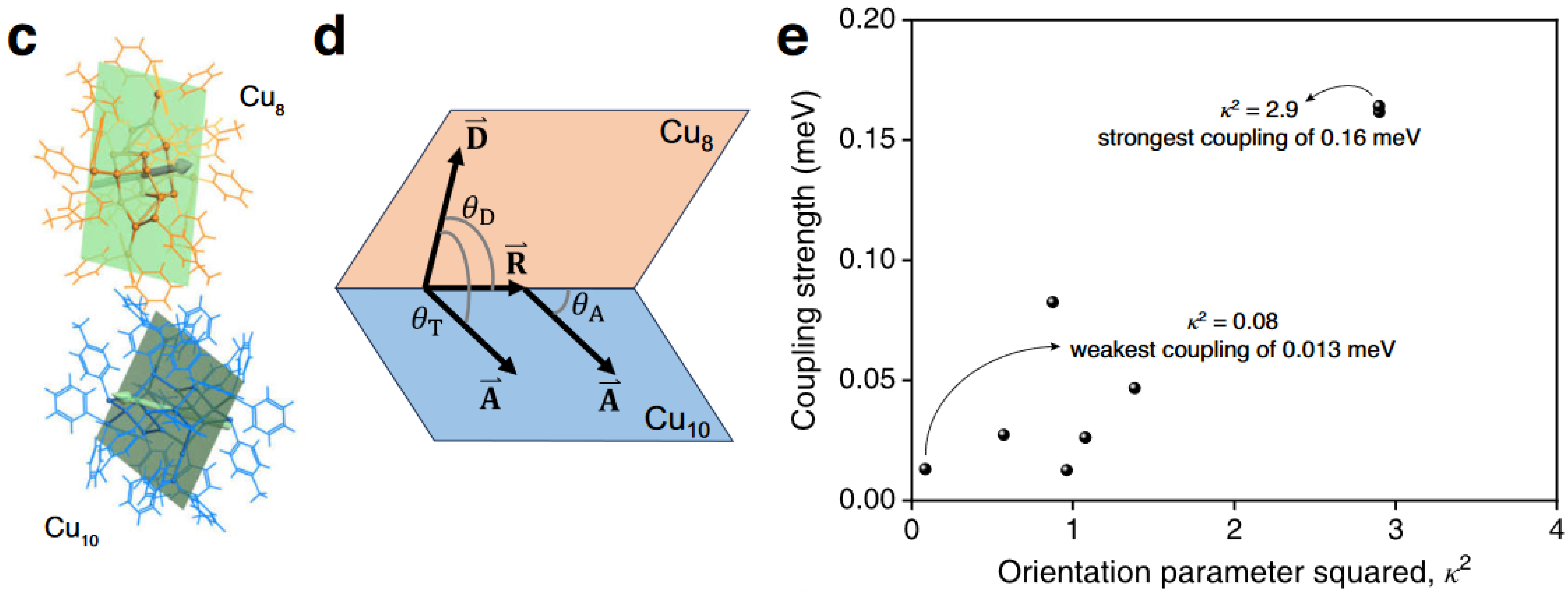
Computational studies



$$\kappa^2 = (\cos\theta_T - 3\cos\theta_D\cos\theta_A)^2$$

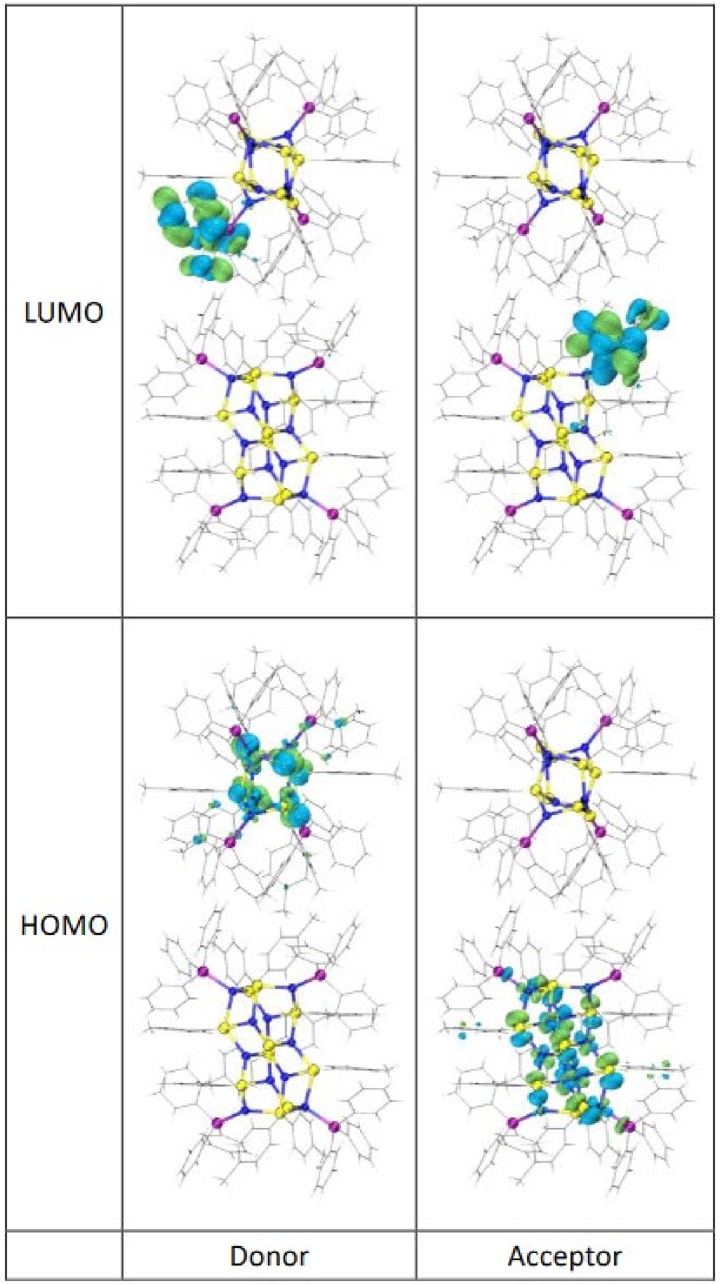
Computational studies

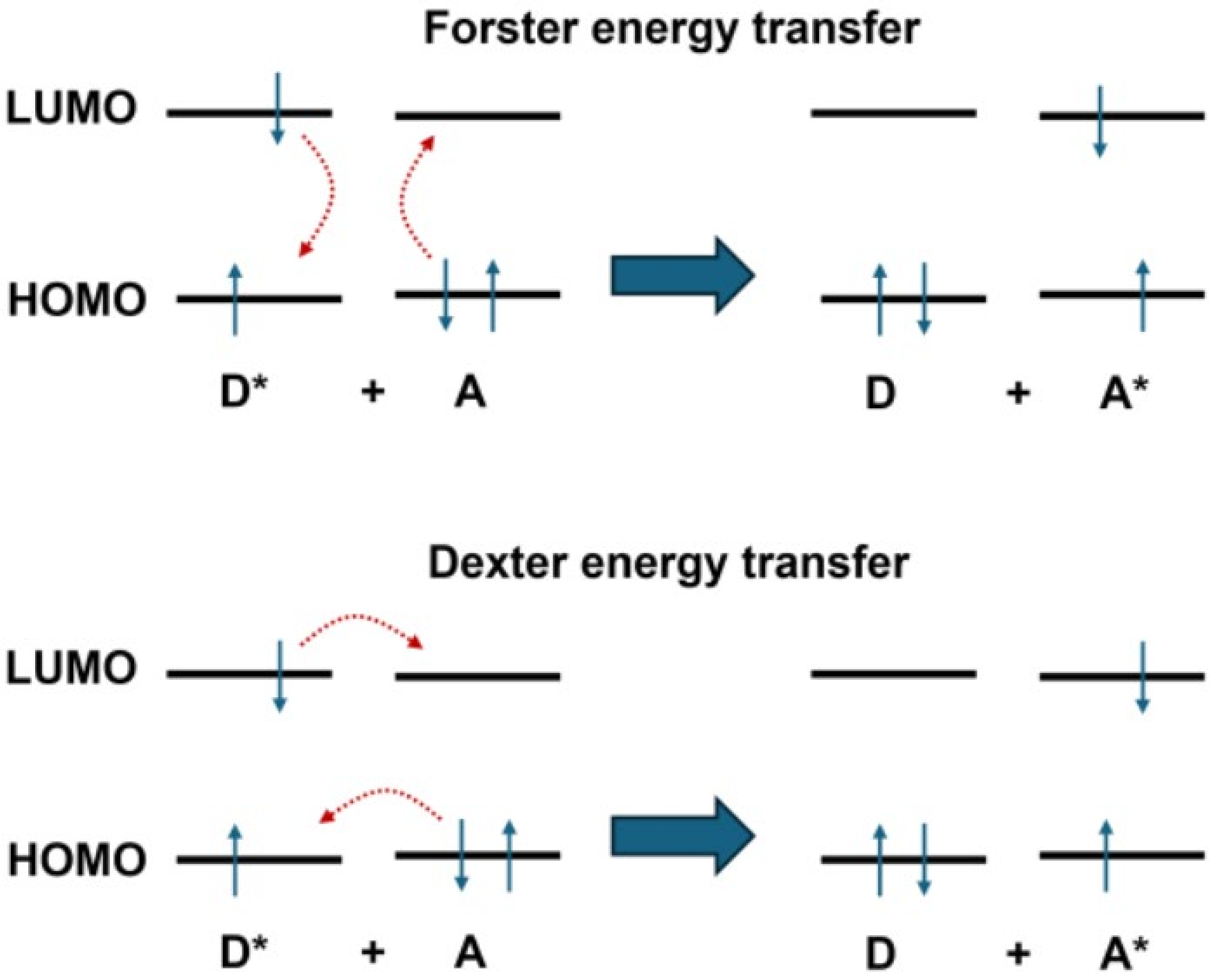
1 2 3



$$\kappa^2 = \left(\cos\theta_T - 3\cos\theta_D \cos\theta_A\right)^2$$

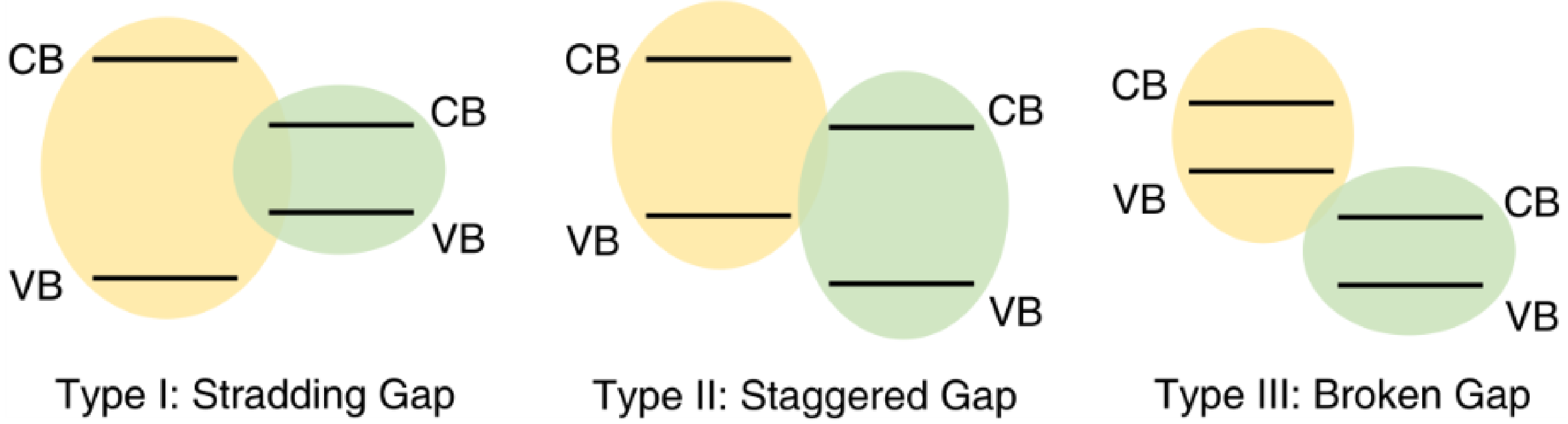
Computational studies

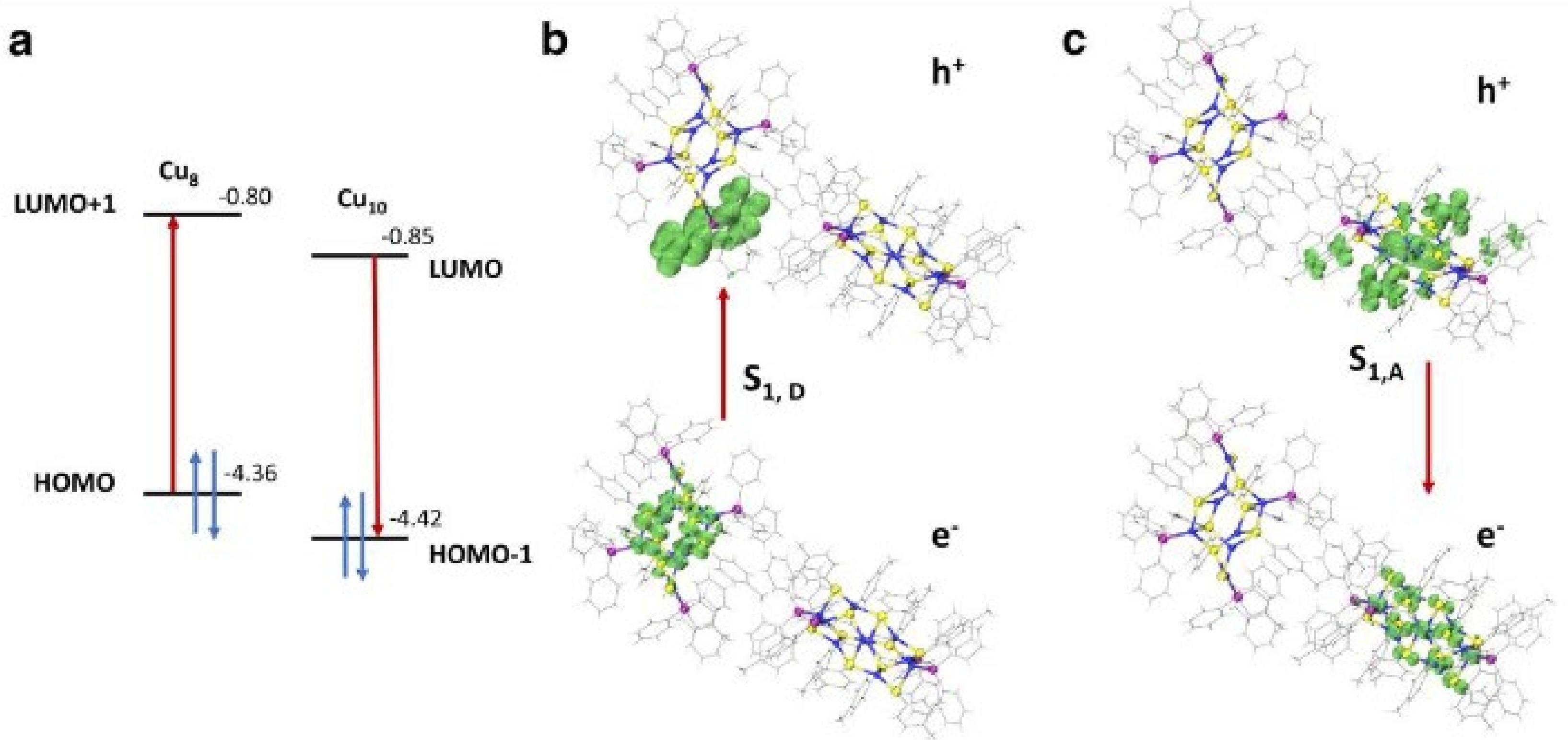




Computational studies

1 2 3





Conclusions

1. They have developed a spatial confinement system, i.e., the forced co-crystallized Cu_8 and Cu_{10} clusters, for rationally realizing the FRET in atomically precise metal nanoclusters.
2. In addition to the experimental efforts, theoretical calculations were performed to verify the FRET between the Cu_8 donor and the Cu_{10} acceptor in terms of the spectra overlap, the confined space, and the dipole orientation.
3. Overall, the spatial confinement of the co-crystallized $Cu_8@Cu_{10}$ cluster system presented here is of significance because it provides an ideal platform to investigate the FRET mechanism in nanomaterials.

Pros

1. Provides deeper understanding of FRET in clusters.
2. Opens up new avenues for the use of clusters as FRET sensors for biological applications.

Cons

1. Did not mention any specific application for this system.
2. The mechanism did not have a proper experimental support for the theoretical study.

One man’s trash is another man’s treasure!

thank you!