Design of MOF nanocomposites with supported nanoparticles focused on singlet oxygen related redox processes

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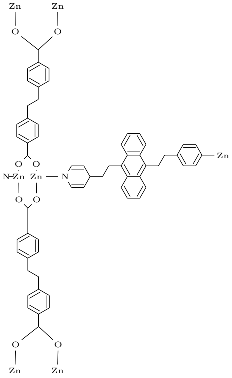
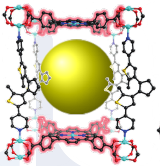
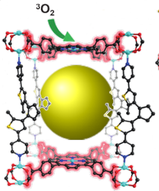
Motivations

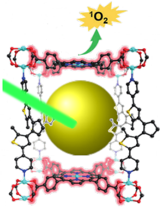
- Numerous applications of singlet oxygen
- Active development research area
- Necessity of new sensitizer composites development, to overcome boundries of the area

Project









MOF synthesis | NP synthesis | NP support | MOF O_2 binding | Application

342 nm irradiation

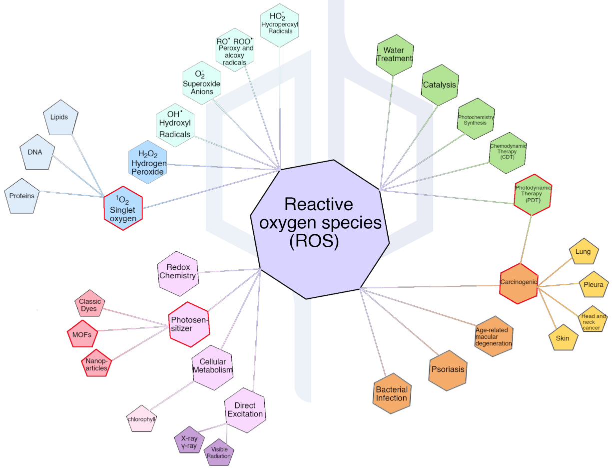
Best result nanoparticles

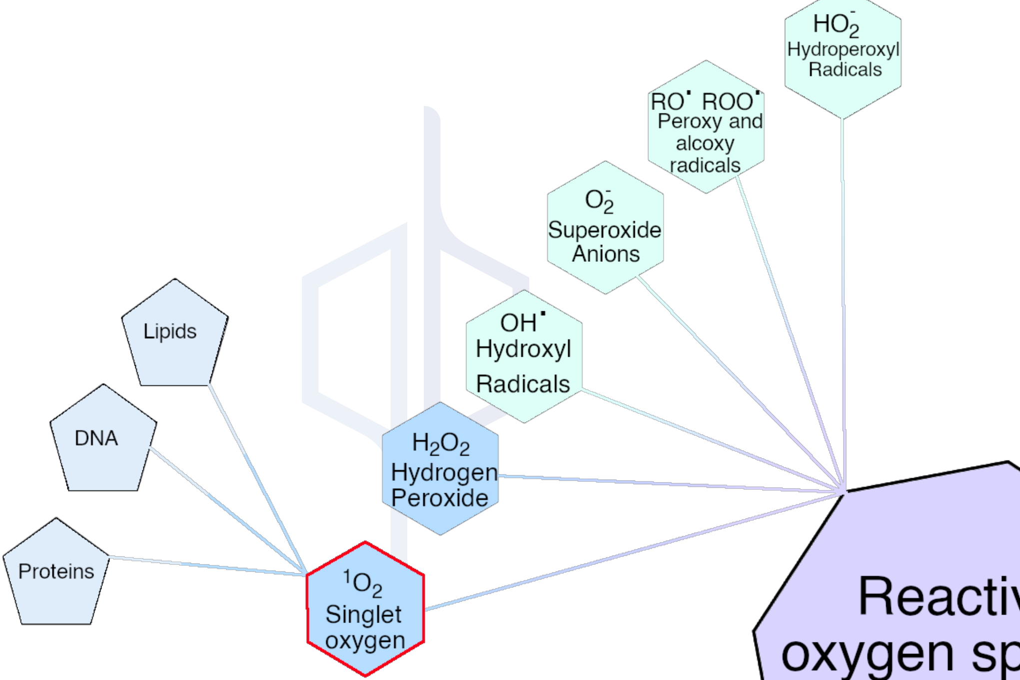
Plasmonic region irradiation

Gold, palladium, silver

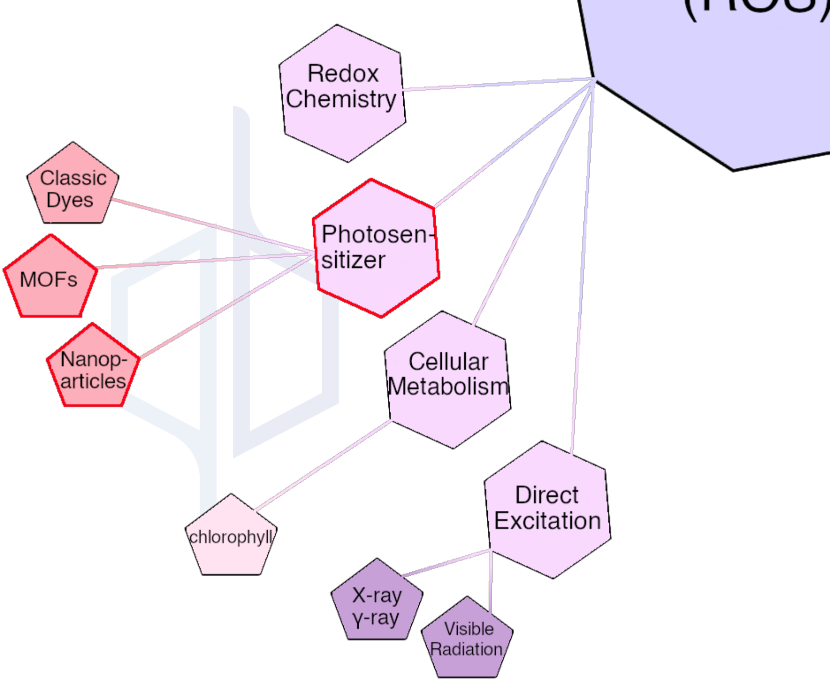
Precursor 1 synthesis → Precursor 2 synthesis → MOF synthesis

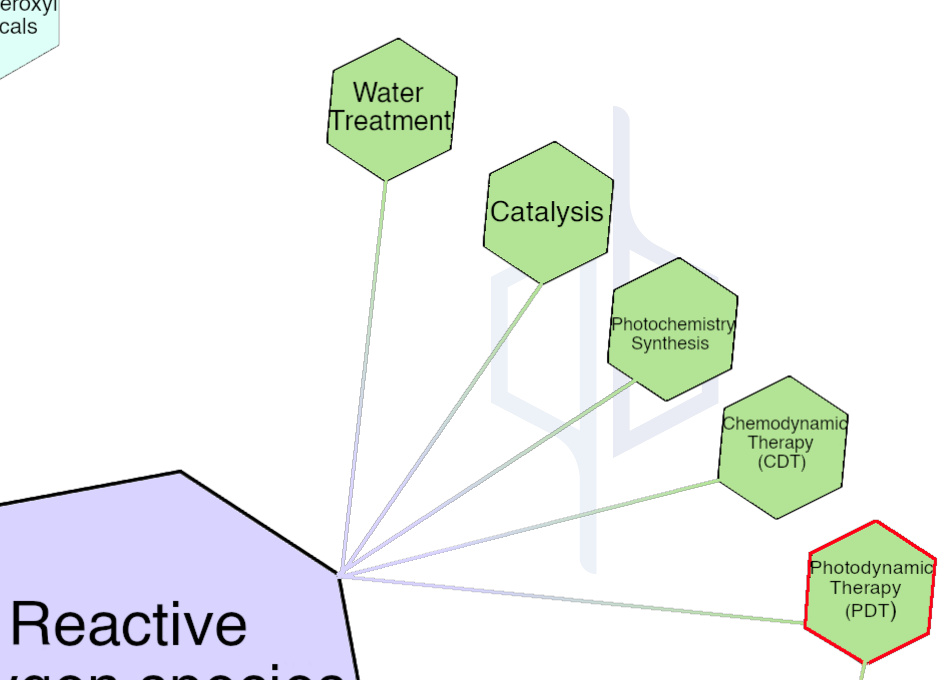
Reactive oxygen species

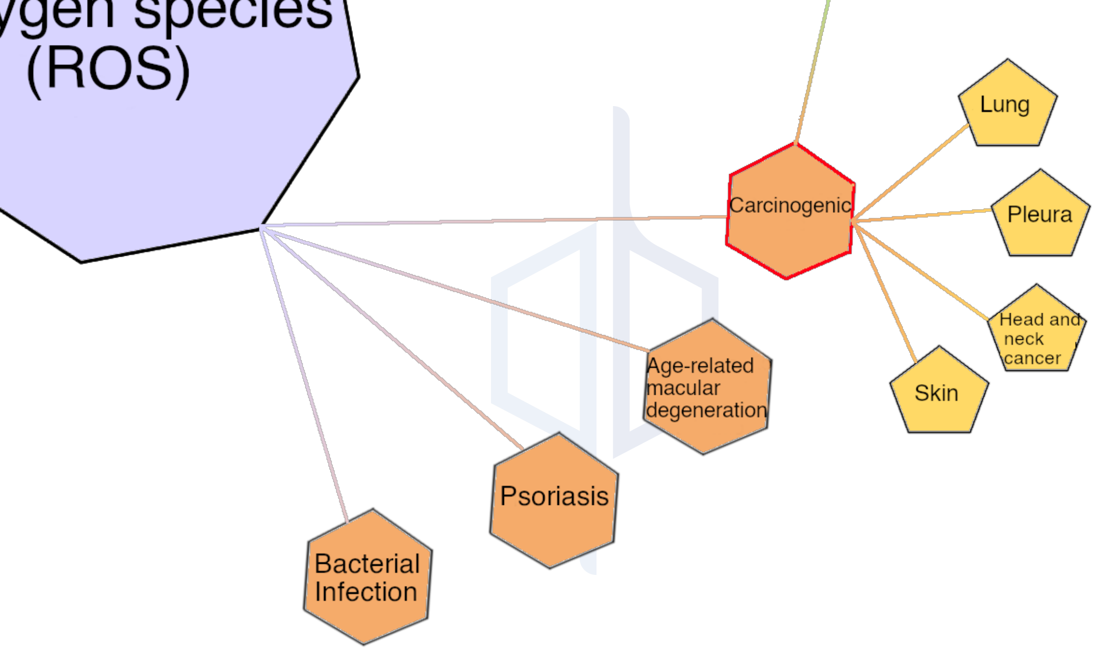




HO_2^-
Hydroperoxyl Radicals
$RO^\bullet$ $ROO^\bullet$
Peroxy and alcoxy radicals
O_2^-
Superoxide Anions
$OH^\bullet$
Hydroxyl Radicals
H_2O_2
Hydrogen Peroxide
$^1O_2$
Singlet oxygen
Lipids
DNA
Proteins
Reacti
oxygen sp

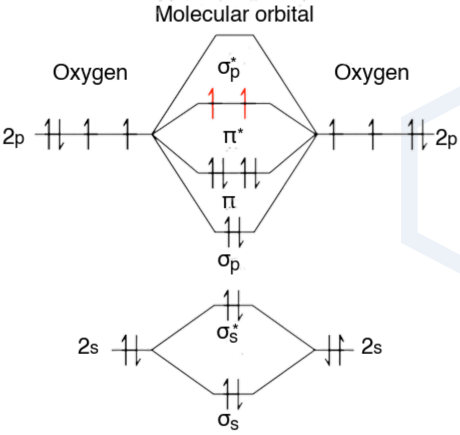

(ROS)
Redox Chemistry
Classic Dyes
MOFs
Nanop-articles
Photosen-sitizer
Cellular Metabolism
chlorophyll
Direct Excitation
X-ray γ-ray
Visible Radiation


Water Treatment
Catalysis
Photochemistry Synthesis
Chemodynamic Therapy (CDT)
Photodynamic Therapy (PDT)
Reactive

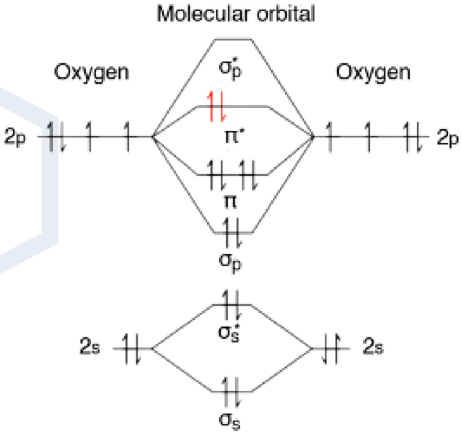


ygen species
(ROS)
Carcinogenic
Lung
Pleura
Head and neck cancer
Skin
Age-related macular degeneration
Psoriasis
Bacterial Infection

Singlet oxygen ($^1\Delta_g$)



Groundstate $^3\Sigma_g^-$



Excited state $^1\Delta_g$

Photosensitized oxidation reactions type I and II

- Have oxygen as reactant
- Abstraction of one elctron or hydrogen atom as oxidizing step
- O_2 participates in one of the following ways:
  1. Directly, as one electron oxidizer
  2. Indirectly, by the generation of $O_2^{\bullet -}$

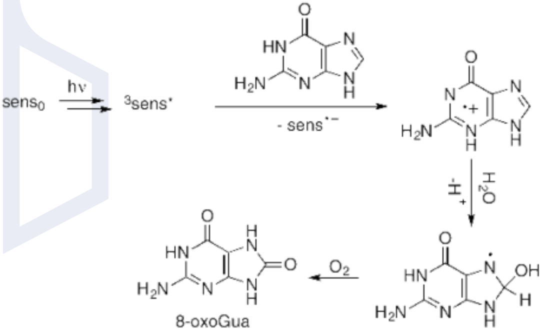
[1] M.S. Baptista et al., Photochemistry and Photobiology, 2017, 93, 912.

Photosensitized oxidation reactions type I and II

1. Type I :
   - Photoinduced electron transfer
   - Formation of O e $HO_2^{\bullet}$
2. Type II :
   - Sensibilized formation of $^1O_2$
   - Energy transfer

     sensibilizer $\longrightarrow$ O_2

> *Photodynamic action refers to apoptosis by mechanisms I and II*



Example of type I photosensibilized oxidation

[1] M.S. Baptista et al., Photochemistry and Photobiology, 2017, 93, 912.

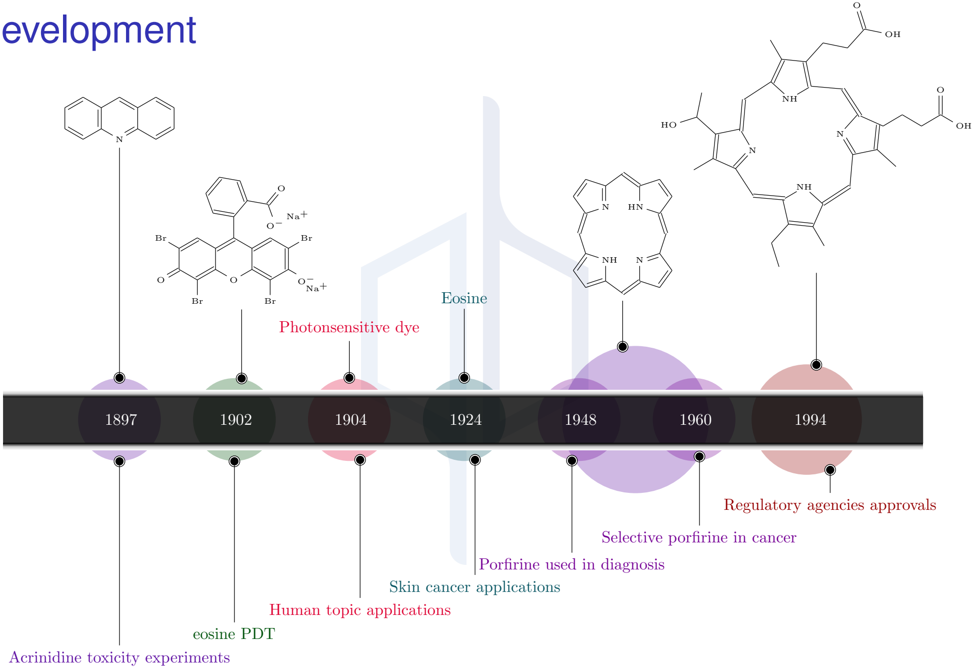
Photodynamic therapy - PDT

- Photosensibilizing agent
  - Topic administrated or injected
- Light
- Aims destruction of abnormal cells
- 3 steps process:
  1. Administration of photosensibilizer drug
  2. Drug activation by light
  3. Targeted cells elimination

Example of tumour treatment by PDT

[2] Thomas J. Dougherty, Outskirt press inc, 2015.

PDT development



Chemodynamic therapy - CDT

- ROS generated by chemical reaction
- Doesn't involve light excitation
- Chemical agent is activated by:
  - Tumour microenvironment
    1. Low pH
    2. High concentration of specific ions
  - External stimulus
    1. Heat
    2. Ultrasound
- MOFs have important applications

PDT advantages

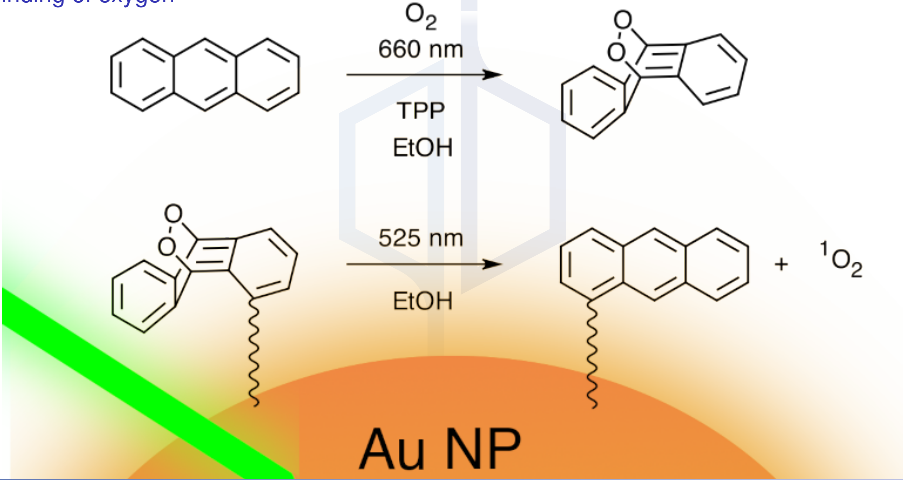
1. Controled activation
2. Overcome resistance mechanism
3. Non invasive treatment
4. Intensisty control
5. High specificity

PDT disadvantages

1. **Limited light penetration in biological tissues**
2. Caution needed with sunlight and intense light sources after treatment
3. **Low O_2 concentration at the tumour microenvironment**

Nanoparticles

Reversible binding of oxygen



Nanoparticles

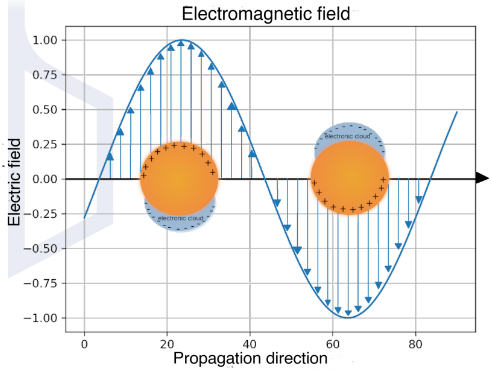
Plasmonic

- Study of behavior and interaction of **plasmons**

Plasmons

Colective oscillation of electrons in a metallic structure , generated by electromagnetic waves

- Applications in catalysis, photonics, imaging, sensors, energy conversion, etc...



Oscilation of a nanoprticle field, under the influence of a electromagnetic wave

Nanoparticles

Plasmonic

1. Surface plamon ressonance (SPR)
    - Absorption
    - Diffraction
    - Transmission
2. Hot electrons

- Light interaction depends on the material design

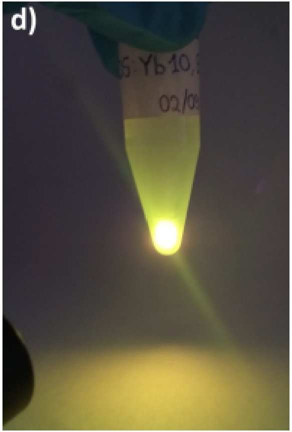
Nanoparticles

Upconversion

Upconversion

Low energy photons conversion process, tipically in the near-infrared, to higher energy photons at the UV-VIS region

- Rare earth nanoparticles
- May be optimized by plasmonic nanoaprticles

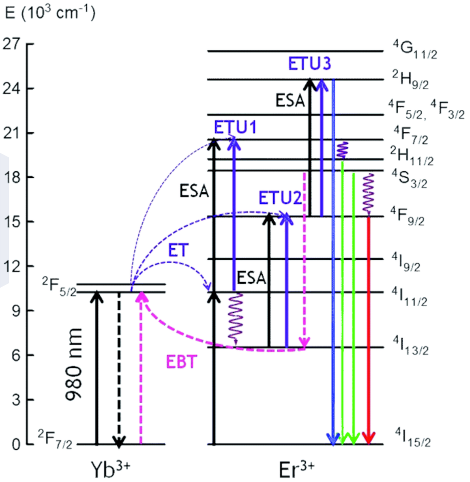


$Gd_2O_2S:Er^{3+},Yb^{3+}$ emission under 980 nm irradiation

[3] I.P. Machado et al., Journal of Alloys and Compounds, 2023, 942, 169083.

Upconversion

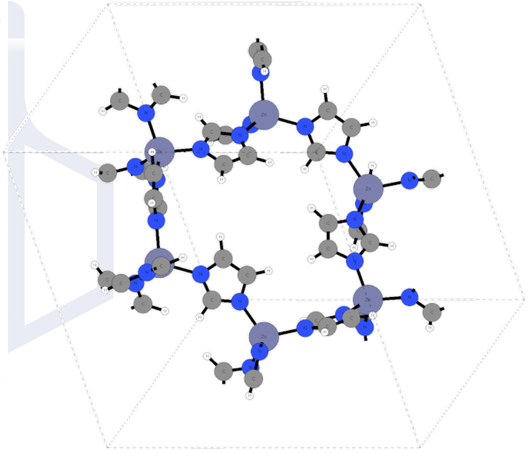
1. 980 nm excitation
2. $^4I_{11/2}$ e $^2F_{5/2}(Yb^{3+})$ ressonance
3. **ESA:** Multiphotons excited state absorption
4. **ETU:** Er^{3+} excitation and Yb^{3+} non-radiative relaxation
5. Multifonon relaxation



Rare earth crystal upconversion energy diagram

MOFs

- Porous materials
- Cristallyne
- Three-dimensional structured
- **M**etallic centers coordinated to **organic ligands**



ZIF-8 structure

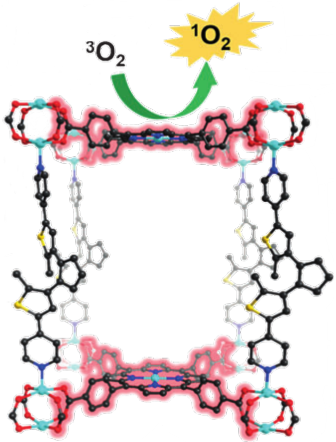
MOFs

- Vantagens
  1. High porosity
  2. Structural versatility
  3. Modullable properties
  4. High sustentabillity
- Aplications
  1. Gas storage and separation
  2. Catalysis
  3. Sensors/detection
  4. Drug delivery
  5. Energy

MOFs

Reversible oxygen binding

- Overcome hipoxia conditions in tumour microenvirmoments
- Oxygen adsorption
- Also presents catalysis applications, sensors and gas separations



MOF SO-PCN structure

[5] J. Park et al., Angewandte Chemie International Edition, 2015, 54, 430.

MOFs

Upconversion

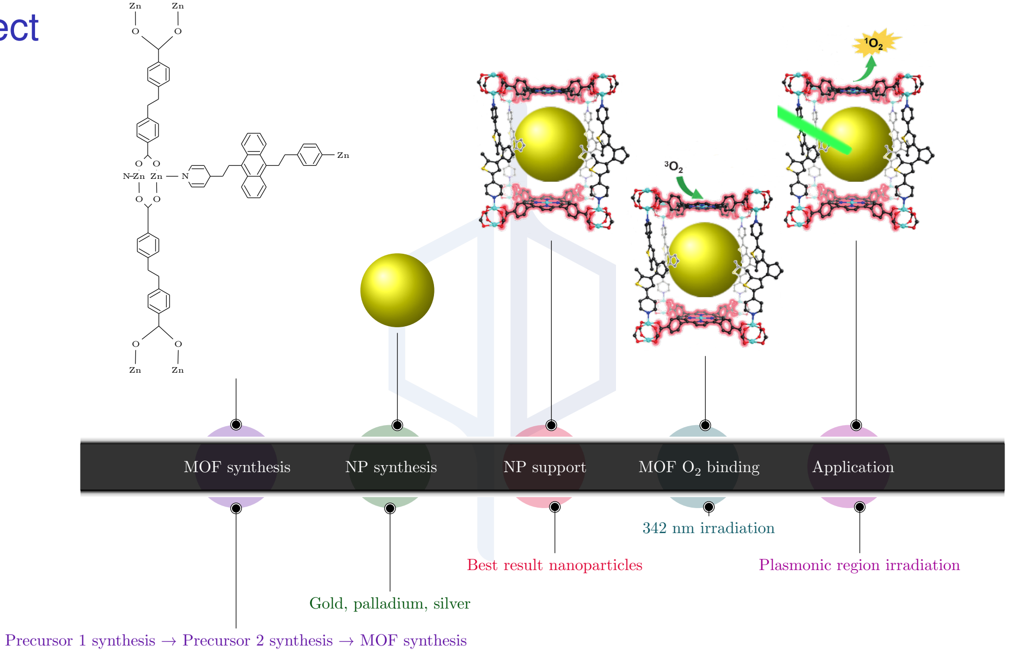
- Classical mechanism on rare earth metallic center MOFs
- **Triplet-triplet annihilation (TTA)**
- Organic ligand acting as sensitizer

MOFs

Upconversion

1. Low energy photon absorption by the organic ligand
2. Excitation to long-lived triplet state
3. Energy transfer to a triplet state of an "annihilator" molecule
4. "Annihilator" transfer to another close annihilator
5. Decay of both molecules to a singlet state
6. Upconversion photon emission

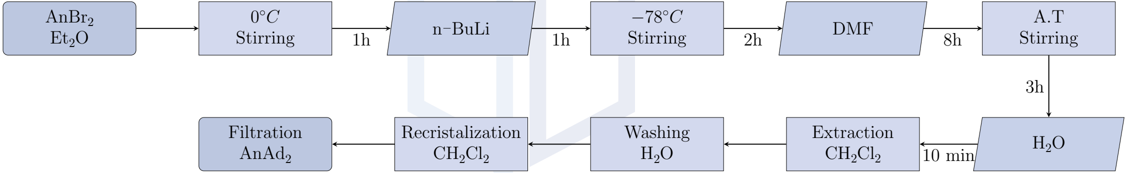
Project



Zn
Zn
O
O
O
O
N–Zn
Zn
N
O
O
O
O
Zn
Zn
Zn
$^{3}O_2$
$^{1}O_2$
MOF synthesis
NP synthesis
NP support
MOF O_2 binding
Application
342 nm irradiation
Best result nanoparticles
Plasmonic region irradiation
Gold, palladium, silver
Precursor 1 synthesis → Precursor 2 synthesis → MOF synthesis

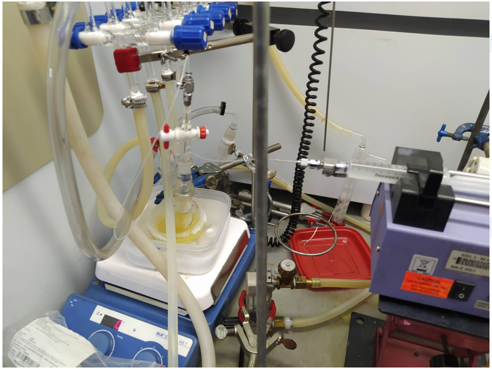
MOF $Zn_2(SDC)_2(An_2Py)$

Anthracene Dicarbaldehyde($AnAd_2$)



MOF $Zn_2(SDC)_2(An_2Py)$

Anthracene dicarbaldehyde ($AnAd_2$)



System to $AnAd_2$ synthesis

$AnAd_2$ synthesis

MOF $Zn_2(SDC)_2(An_2Py)$

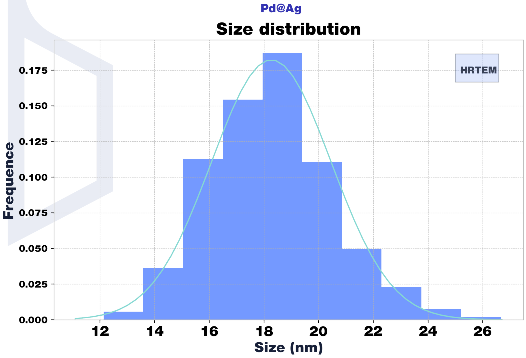
9,10-Bis[2-(4-pyridyl)vinyl]anthracene(An2Py)

$AnAd_2$, 4-picoline, Acetic anhydride → 100°C Reflux $\xrightarrow{\text{12h}}$ A.T Stirring $\xrightarrow{\text{12h}}$ Filtration → Recristalization DMF → Centrifugation An2Py

Nanoparticles

Pd@Ag

Pd@Ag	Length
count	361
mean	18.3
std	2.2
min	12.1
25%	16.6
50%	18.1
75%	19.7
max	26.7



Nanoparticles size distribution

Next steps

Conclusion