

XU GROUP  
*Department of Chemistry, Peking University*

# *Selected Weekly Literature Presentations*

*Disclaimer:  
These slides contain personal interpretations and may include errors or subjective views.*

*© Xu Group. All rights reserved.*



# Triplet-Triplet Annihilation Photon Upconversion: Principle and Application

---

- Reporter: Peimiao He
- Supervisor: Yan Xu
- Date: 2025. 2. 22

# Outline

---

- Introduction: Basic Principles of Triplet-Triplet Annihilation Upconversion (TTA-UC)
- TTA-UC Mediated Photochemical Reactions
- Summary and Perspective

# Introduction: What is Upconversion?

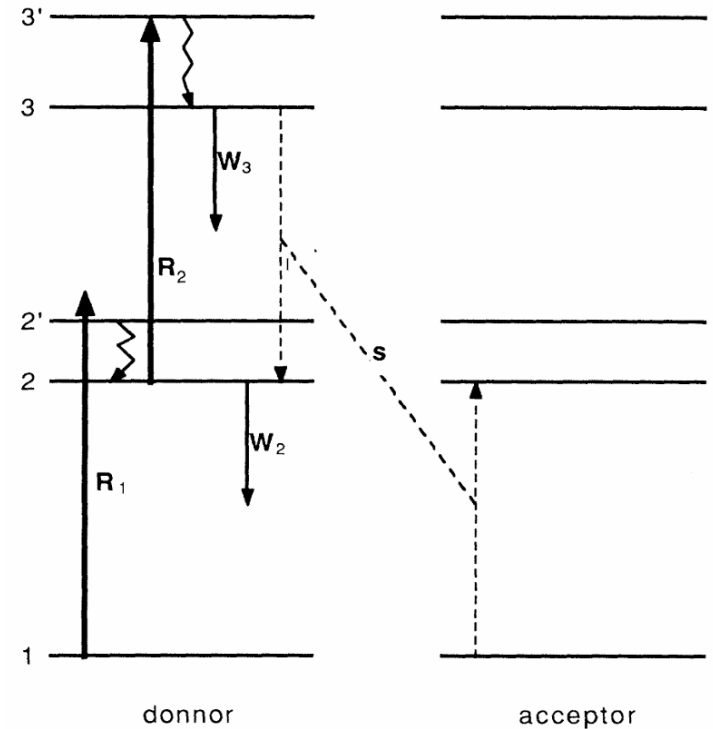
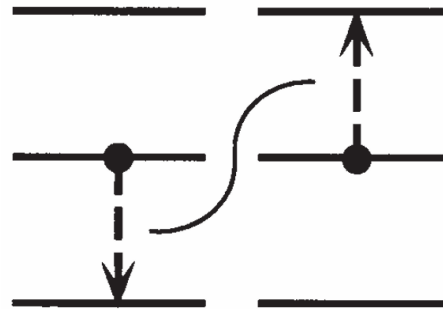
**Photon upconversion (UC)** is a process in which the sequential absorption of two or more photons leads to the emission of light at shorter wavelength than the excitation wavelength.

## ■ Three Typical Mechanisms

### 1. Excited-State Absorption

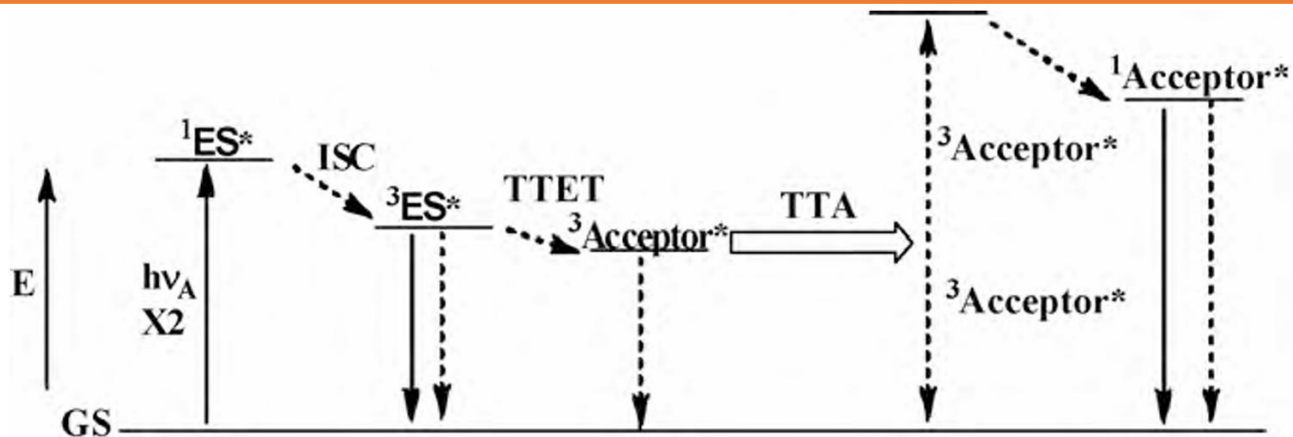


### 2. Energy Transfer Upconversion



### 3. Photon Avalanche Upconversion

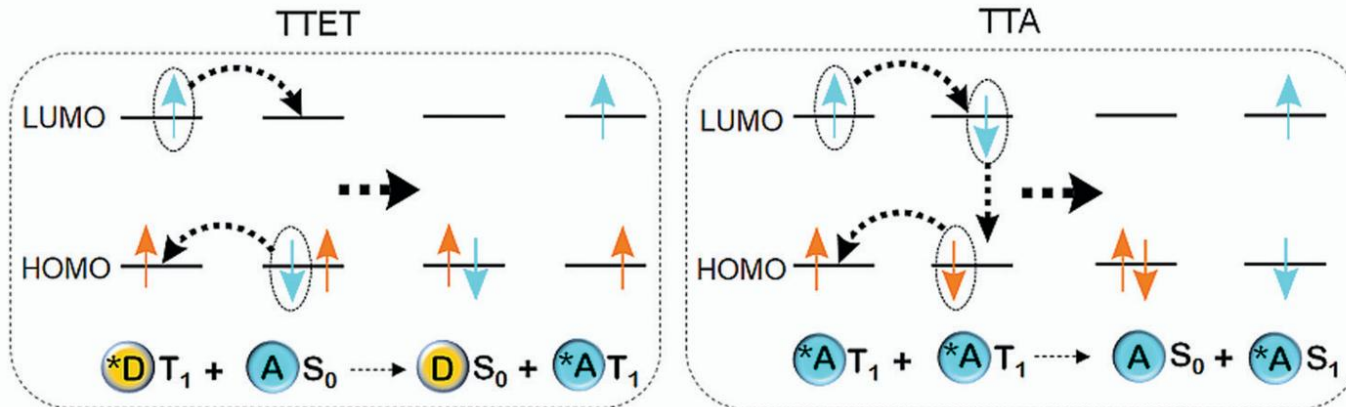
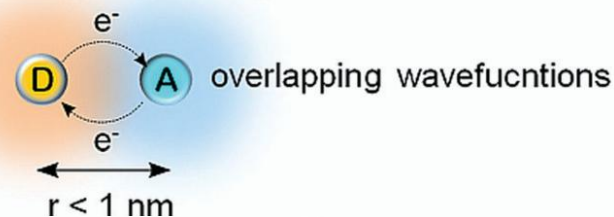
# TTA-UC



## Dexter Energy Transfer in TTA-UC

- D Donor (sensitizer)
- A Acceptor (annihilator)

### Electron exchange



Castellano, F. N. *et al. Coord. Chem. Rev.* **2010**, 254, 2560–2573

Poulsen, K. M. *et al. Chem. Soc. Rev.* **2020**, 49, 6529–6554

# Necessary Conditions

---

- The light harvesting ability of the triplet sensitizer (large  $\varepsilon$  value)

- Fast and efficient ISC process (large  $k_{ISC}$  and  $\Phi_{ISC}$ )

- Long  $T_1$  state lifetime (increasing the diffusion distance)

- Energy match of sensitizer and annihilator

$$k_{ET} \propto J \times \exp\left[\frac{-2r}{L}\right]$$

For Dexter energy transfer:

$$J = \int f_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda$$

- For annihilator:

$$E_{T1,sen} > E_{T1,An}$$

$$2 \times E_{T1} > E_{S1}$$

# Quantum Yield

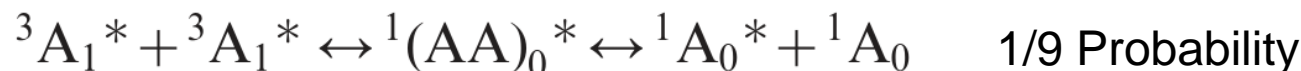
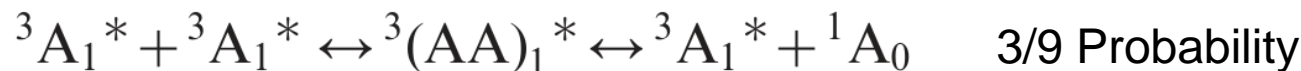
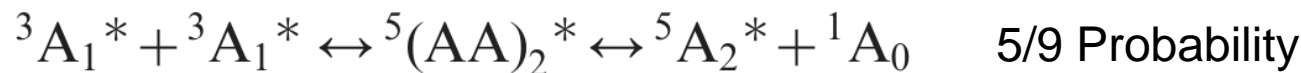
---

$$\Phi_{UC} = \frac{1}{2} f \Phi_{ISC} \Phi_{ET} \Phi_{TTA} \Phi_{FL}$$

Upconversion efficiency

$$\eta_{UC} = \Phi'_{UC} = 2 \times \Phi_{UC}$$

## ■ Spin-Statistical Factor ( $f$ )

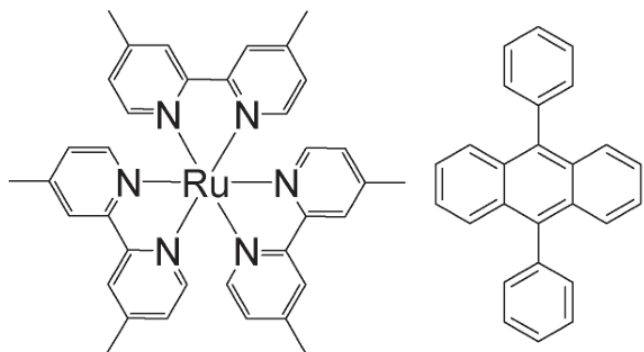


The limit for the efficiency of the TTA upconversion is 11.1%.

Mostly <10%

# Development of Sensitizer

## ■ Ru(II) Polyimine Complexes



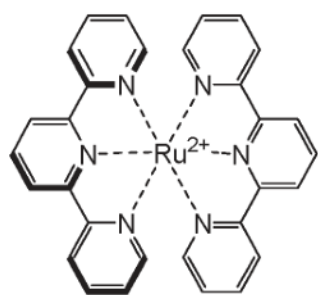
$\lambda_{max} = 450 \text{ nm}$

430 nm Emission

514 nm Absorption

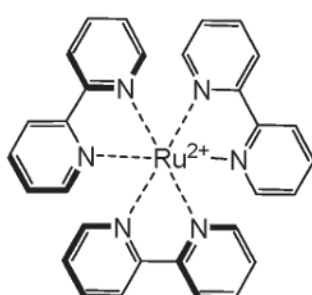
✗ Weak absorption in the visible range (<450 nm)

✗ Short  $T_1$  lifetime (<1  $\mu\text{s}$ )



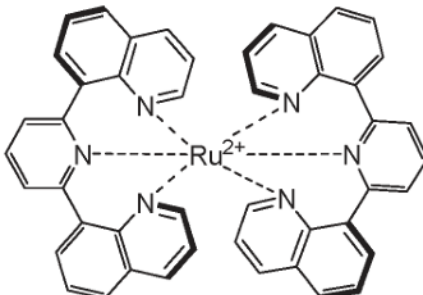
$\angle N-Ru-N: 158.6^\circ$

$\tau = 0.25 \text{ ns}$



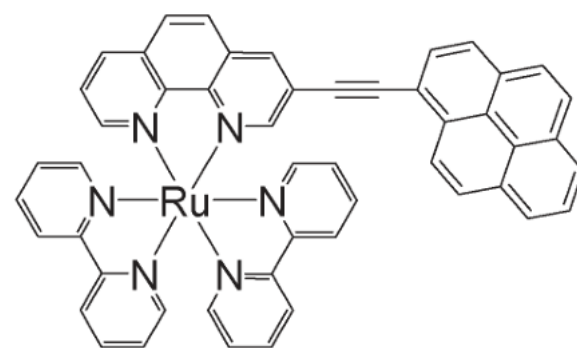
$\angle N-Ru-N: 173.0^\circ$

$\tau = 1.0 \mu\text{s}$



$\angle N-Ru-N: 179.6^\circ$

$\tau = 3.0 \mu\text{s}$



108  $\mu\text{s}$

Castellano, F. N. *et al. Chem. Commun.* **2005**, 3776–3778

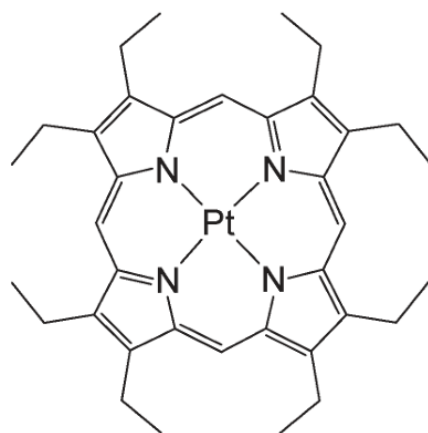
Hammarstrom, L. *et al. J. Am. Chem. Soc.* **2008**, 130, 15533–15542

Zhao, J. *et al. J. Mater. Chem.*, **2010**, 20, 1953-1963

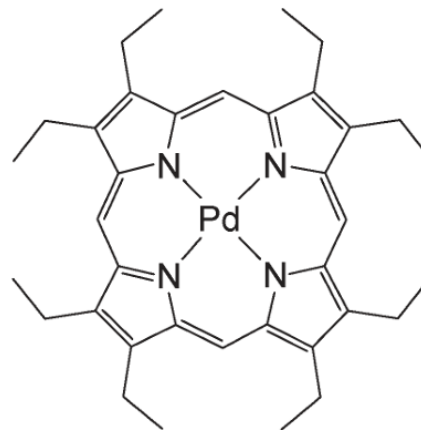
# Development of Sensitizer

## ■ Pt(II) and Pd(II) Porphyrin Complexes

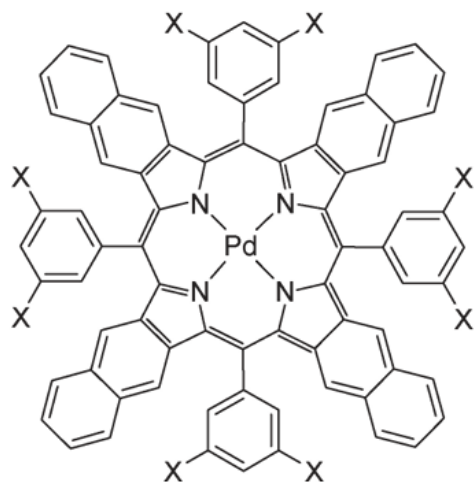
Longer  $T_1$  lifetime ( $>50 \mu\text{s}$ )



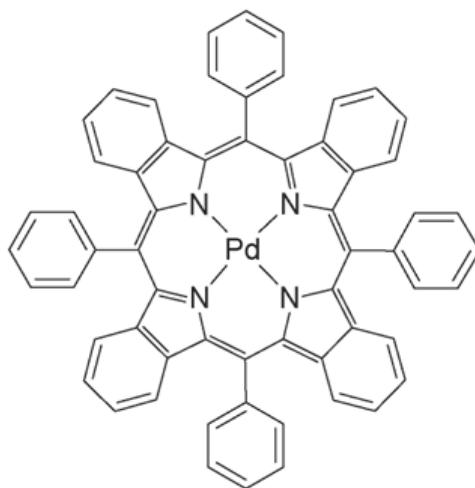
544 nm



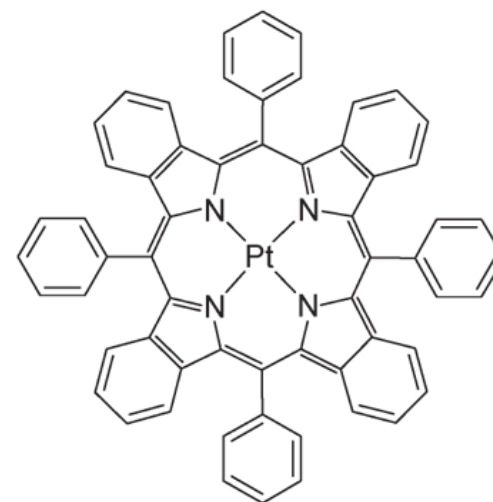
~550 nm



X= OMe  
630 nm



700 nm

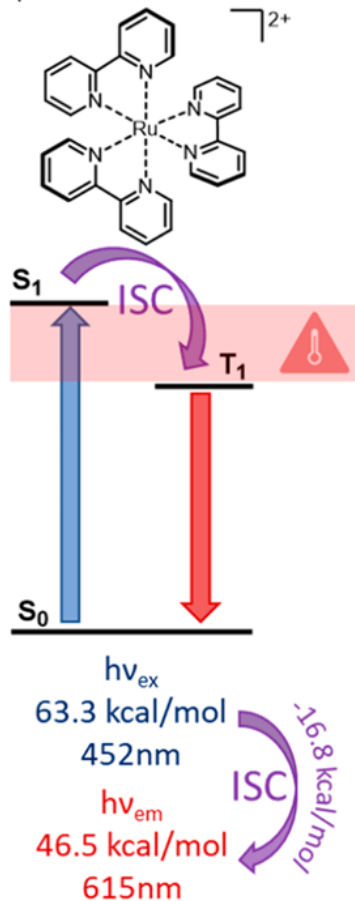


611 nm

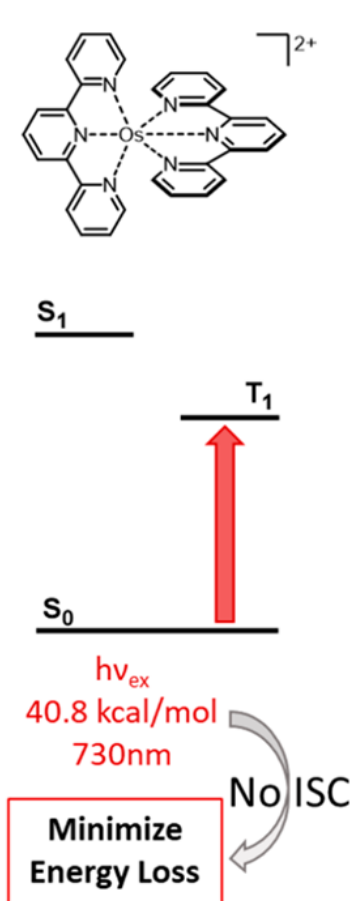
# Development of Sensitizer

## ■ Os(II) Complexes

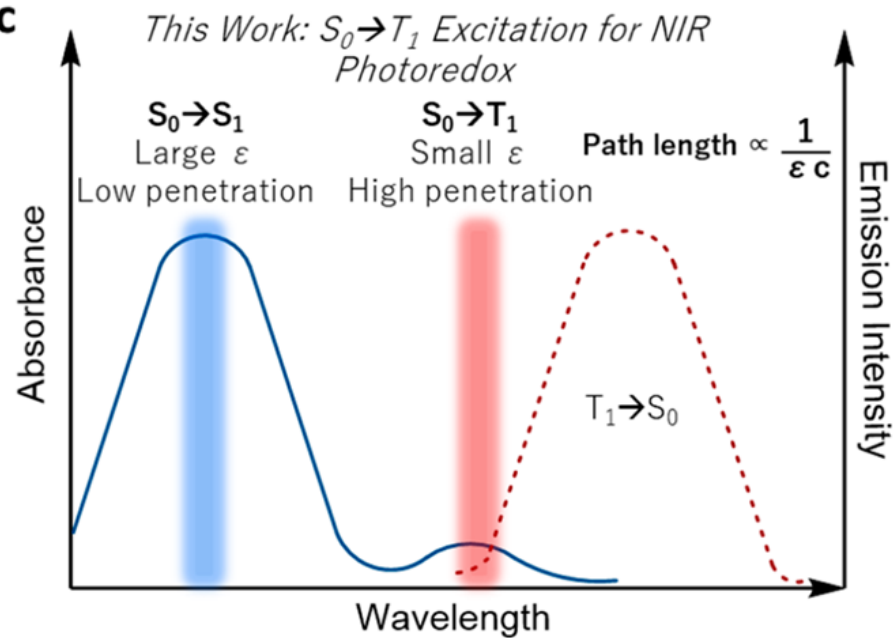
### a Spin-Allowed Excitation



### b Spin-Forbidden Excitation

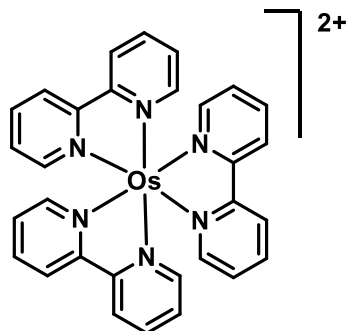


### c



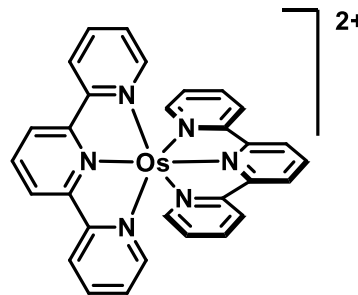
# Development of Sensitizer

## ■ Os(II) Complexes



$\tau_0=19$  ns

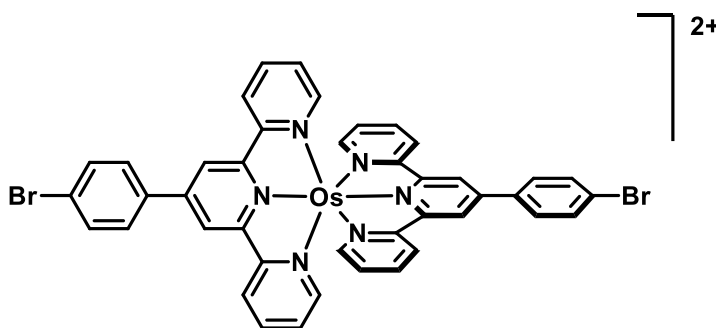
600 ns for Ru analogue



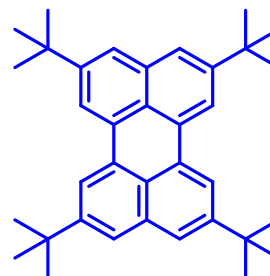
$\tau_0=269$  ns

250 ps for Ru analogue

$E_{T1}=1.7\sim 1.8$  eV



724 nm Absorption (1.71 eV)



462 nm Emission (2.68 eV)

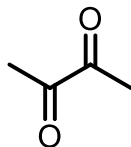
Rovis, T. *et. al. ACS Cent. Sci.* **2020**, 6, 2053–2059

Rovis, T. *et. al. Synlett* **2022**, 33, 247–258

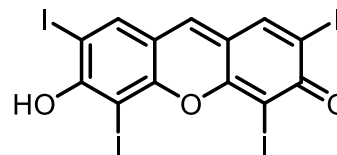
Yanai, N.; Kimizuka, N. *et. al. J. Mater. Chem. C*, **2017**, 5, 5063-5067

# Development of Sensitizer

## ■ Organic Sensitizers (Hard ISC process)



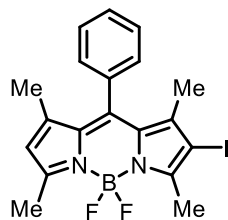
$S_1 (n, \pi^*)$  to  $T_1 (\pi, \pi^*)$



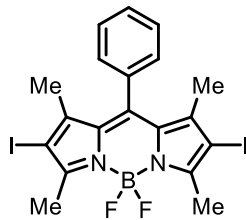
TlHF

Heavy atom effect

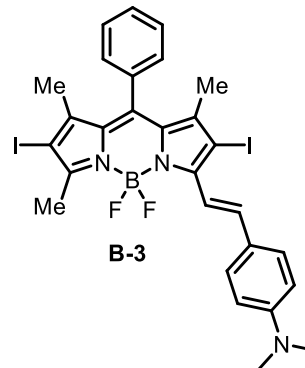
## ■ Boron-Dipyrromethene, BODIPY



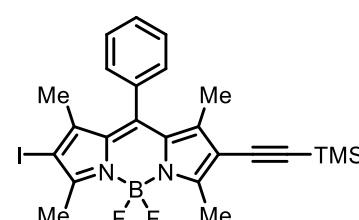
B-1



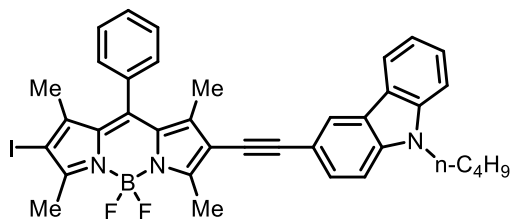
B-2



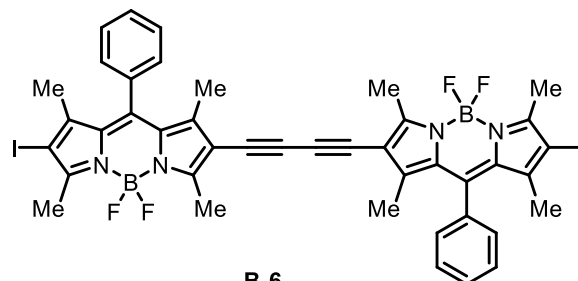
B-3



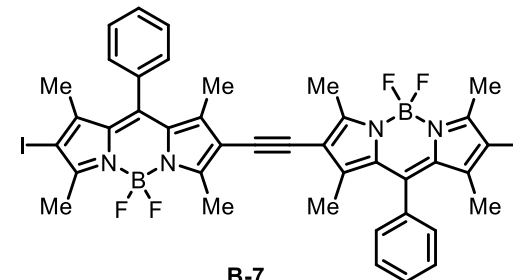
B-4



B-5



B-6

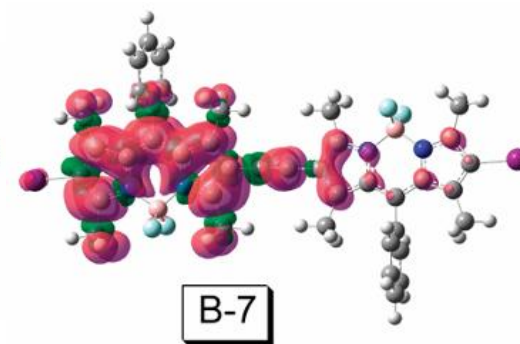
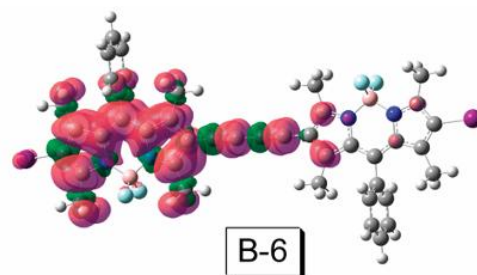
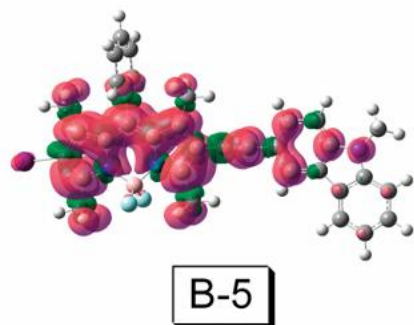
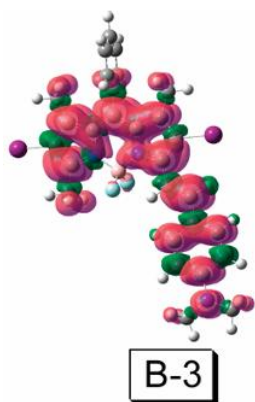


B-7

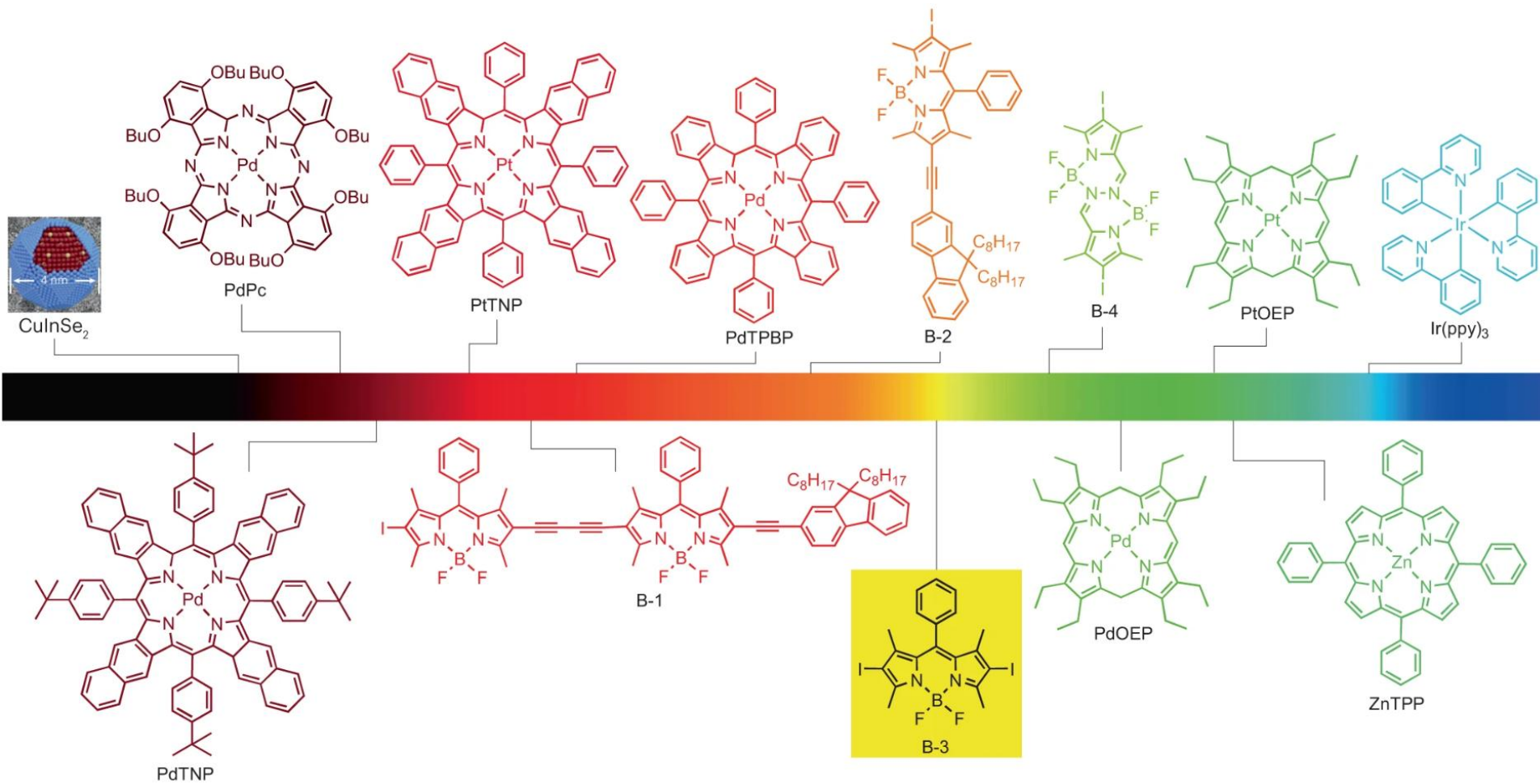
# Development of Sensitizer

## ■ Boron-Dipyrromethene, BODIPY

	$\lambda_{\text{abs}}^a$	$\epsilon^b$	$\lambda_{\text{em}}$	$\Phi_{\text{F}}$ (%) <sup>d</sup>	$\tau_{\text{F}}$ (ns) <sup>e</sup>	$\tau_{\text{T}}$ ( $\mu\text{s}$ ) <sup>f</sup>	$\Delta E,$ $T_1 - S_0^g$	$\Phi_{\text{ISC}}^i$
B-0	503	8.20	515	$71.2 \pm 0.4$	3.86	0.02	816 <sup>h</sup>	0.288
B-1	510	8.80	532	$3.6 \pm 0.3$	0.16	66.3	819	0.964
B-2	529	8.90	552	$2.7 \pm 0.3$	0.13	57.1	826	0.973
B-3 <sup>c</sup>	629	7.28	706	$9.5 \pm 0.1$	1.40	4.0	1075	0.905
B-4	539	7.54	563	$7.8 \pm 0.4$	0.42	57.2	829	0.922
B-5 <sup>c</sup>	557	5.94	631	$4.6 \pm 0.2$	0.37	54.6	878	0.954
B-6 <sup>c</sup>	576	18.0	623	$10.5 \pm 0.2$	0.42	26.9	893	0.895
B-7 <sup>c</sup>	575/618	9.09/8.95	646	$9.3 \pm 0.2$	0.57	47.0	865	0.907

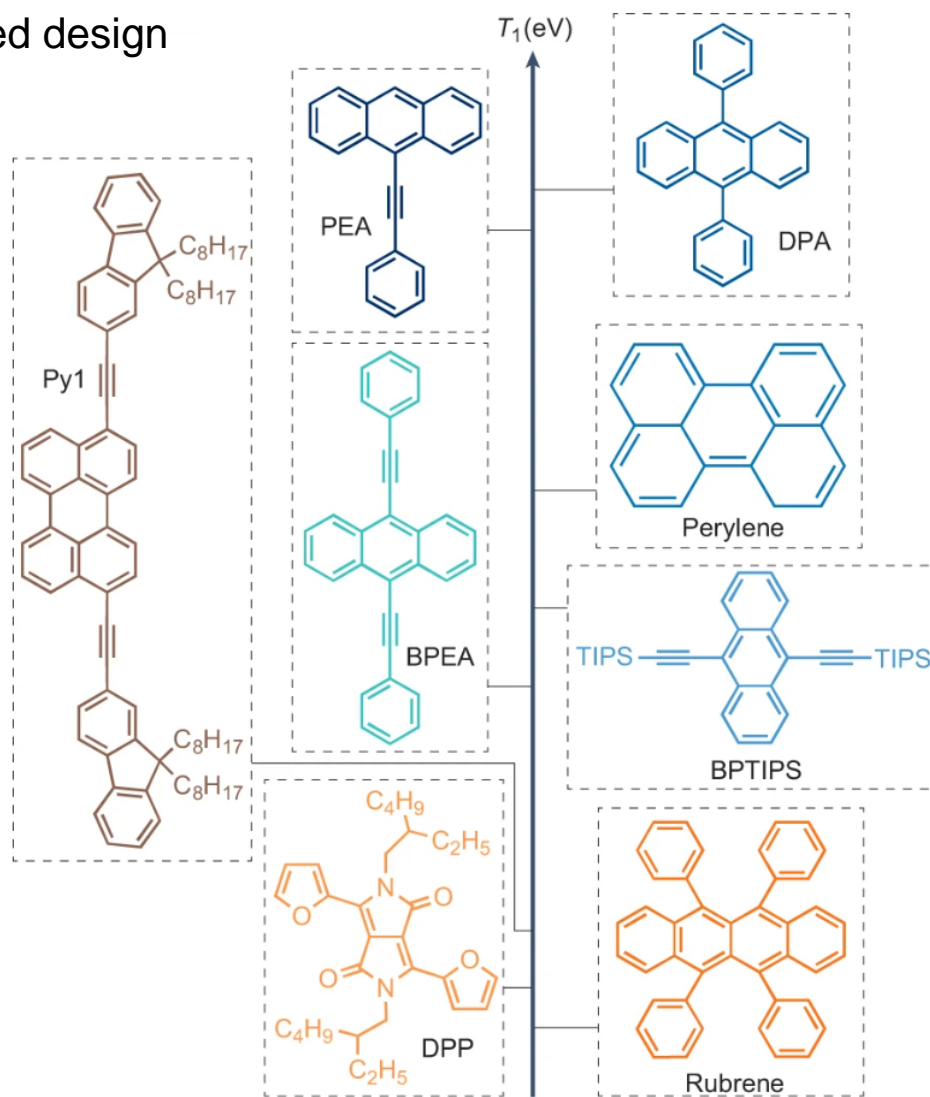


# Development of Sensitizer

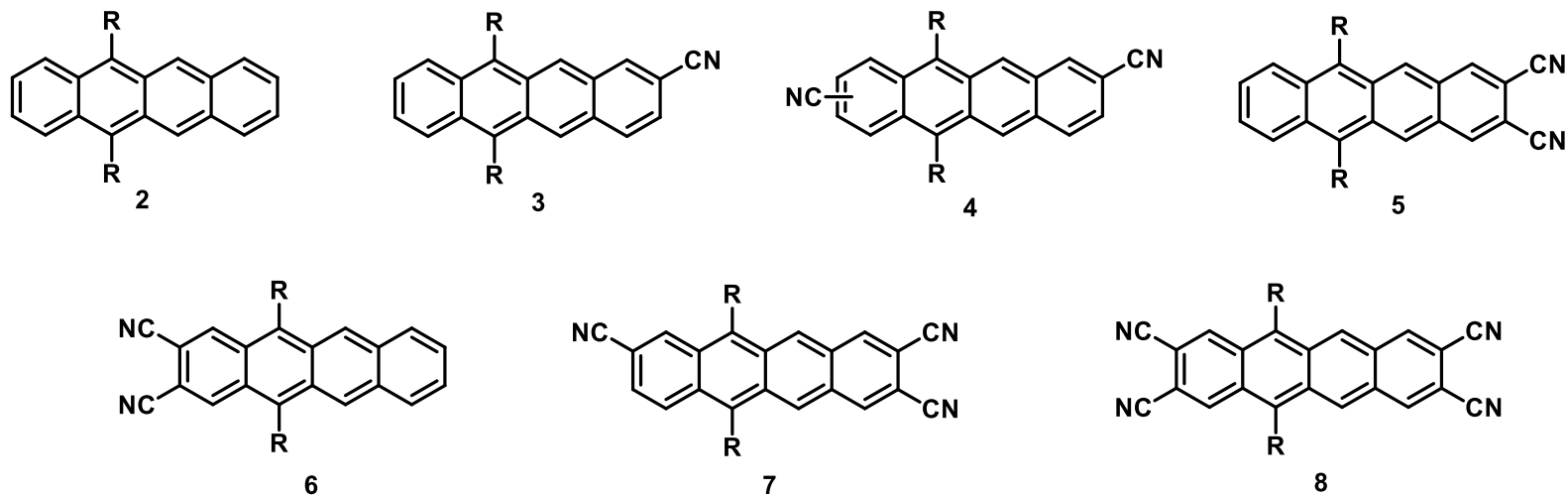


# Development of Annihilator

- Mostly commercially available compounds
- Few are with tailored design



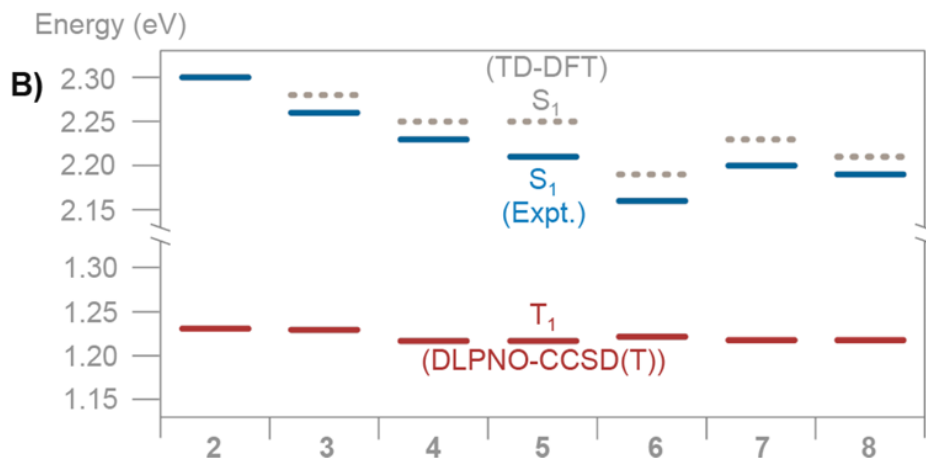
# 2E<sub>T1</sub> and E<sub>S1</sub>



$$\Phi_{UCs} = \frac{1}{2} f \Phi_{ISC} \Phi_{ET} \Phi_{TTA} = \frac{\Phi_{UC}}{\Phi_{PL}}$$

R = TIPS

An	dilute <sup>a</sup>			concentrated <sup>b</sup>		
	$\Phi_{UCs}^c$ (%)	$\Phi_{PL}^d$ (%)	$\Phi_{UC}^c$ (%)	$\Phi_{UCs}$ (%)	$\Phi_{PL}$ (%)	$\Phi_{UC}$ (%)
2	0.14	82.4	0.12	0.30	3.6	0.01
3	0.21	79.1	0.17	0.12	2.7	0.005
4	0.18	78.5	0.15	0.38	3.3	0.01
5	1.6	83.8	1.3	3.5	2.3	0.1
6	3.5	71.4	2.5	9.0	1.8	0.15
7	0.65	74.4	0.5	1.8	2.5	0.05
8	1.4	72.4	1.0	0.9	1.4	0.02

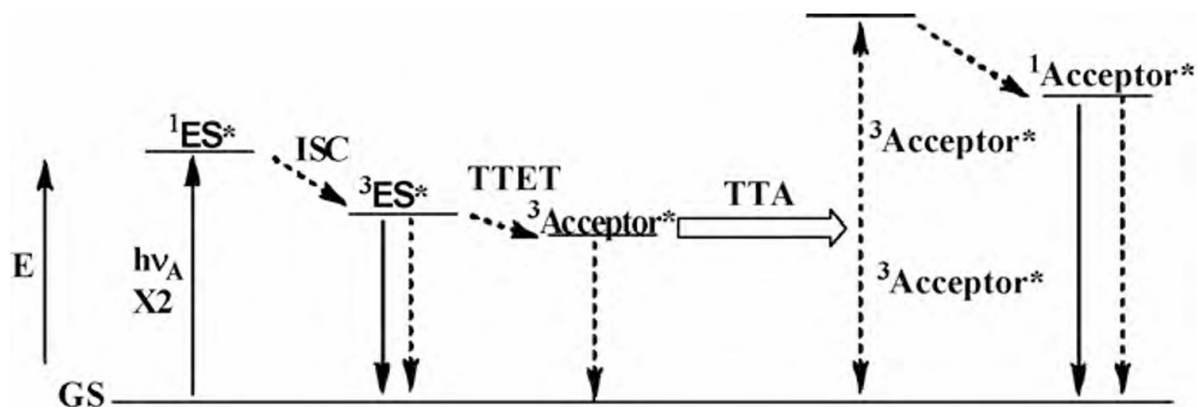


# Outline

---

- Introduction: Basic Principles of Triplet-Triplet Annihilation Upconversion (TTA-UC)
- TTA-UC Mediated Photochemical Reactions
- Summary and Perspective

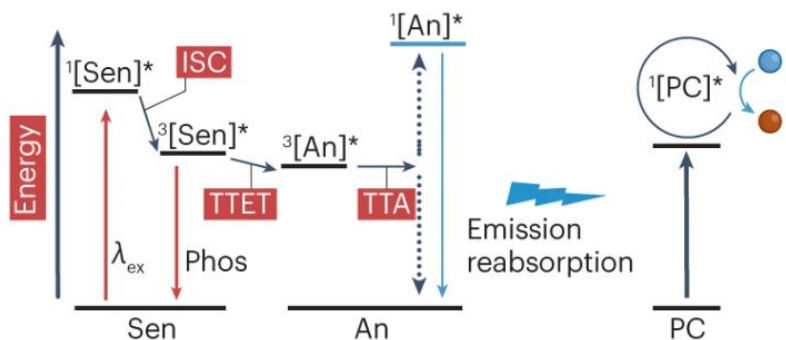
# General Reaction Systems



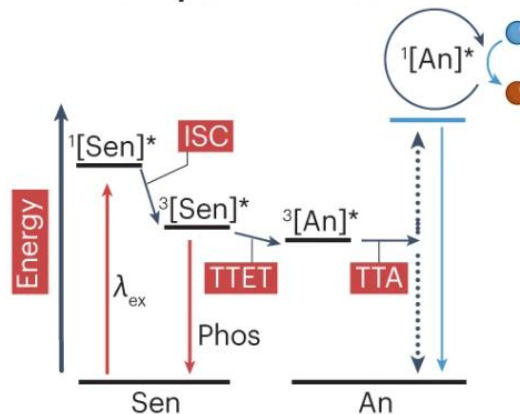
What happens after the upconversion?

## a Three-component TTA-UC-PRs

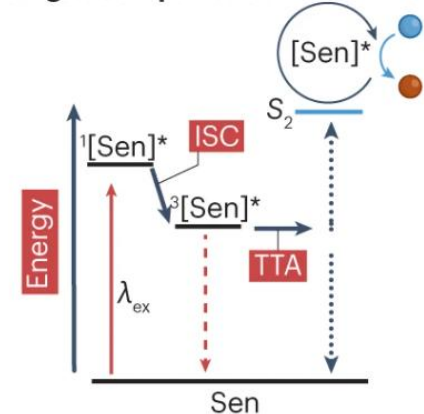
● Substrate ● Product



## Two-component TTA-UC-PRs

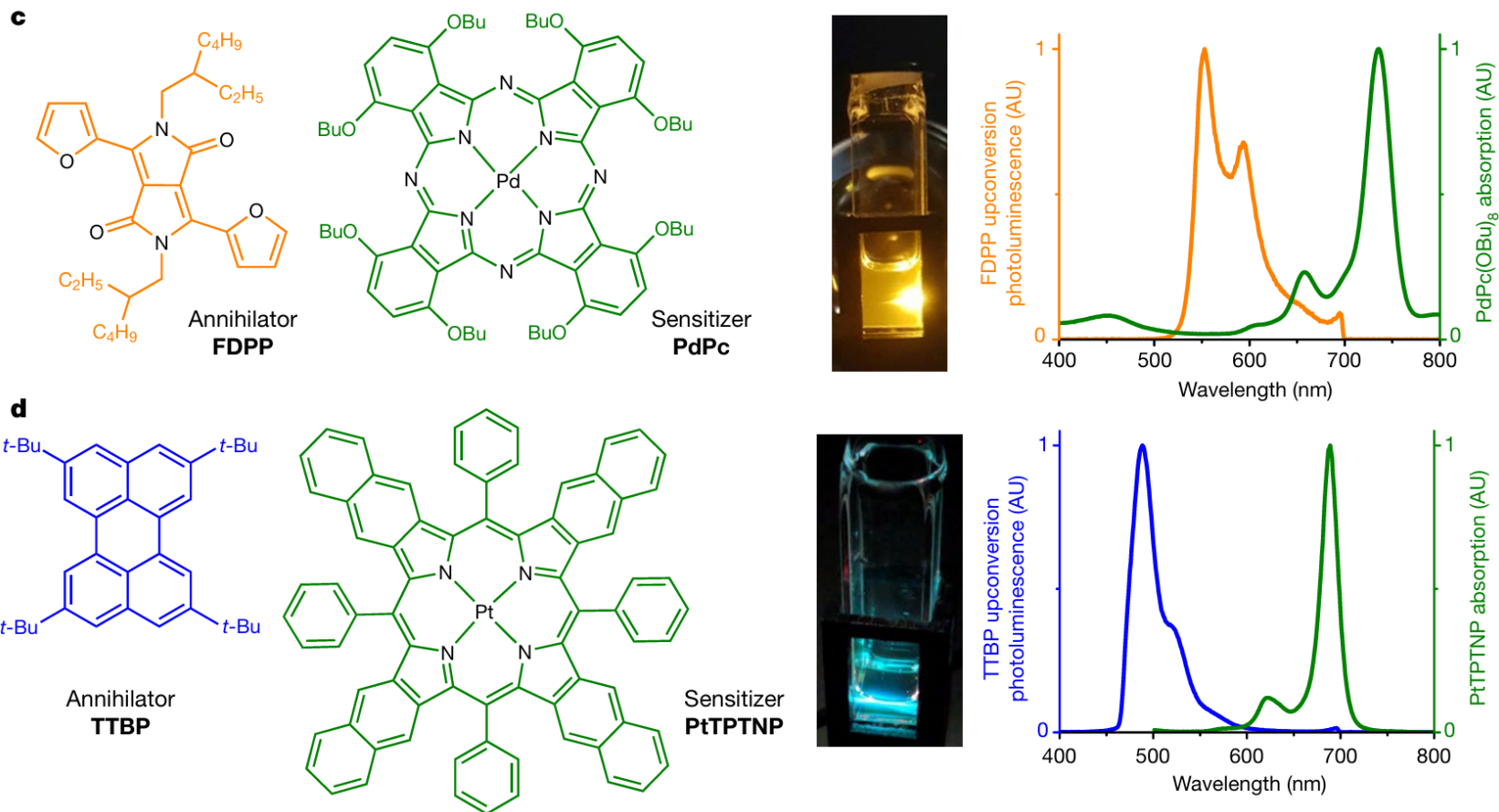


## Single-component TTA-UC-PRs

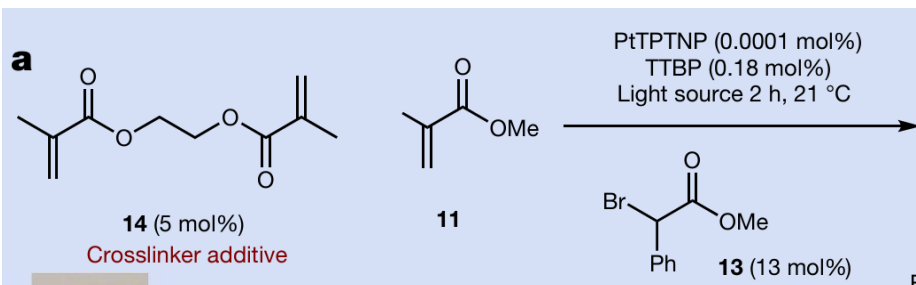
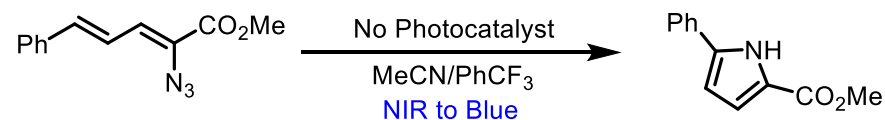
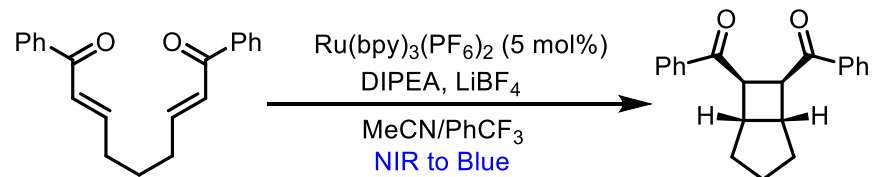
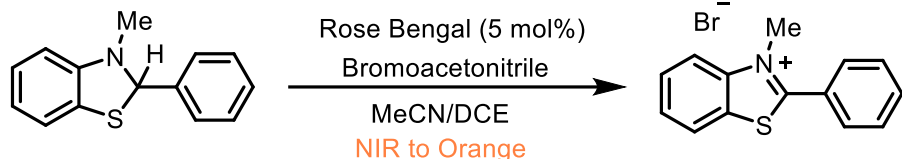
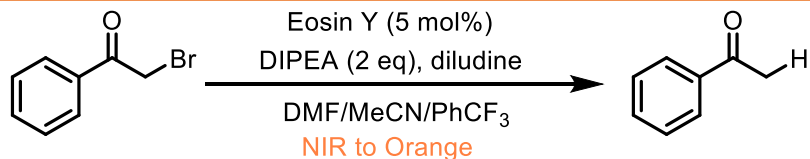


# NIR TTA-UC for Photocatalysis

“Triplet Fusion Upconversion”



# Photoreactions

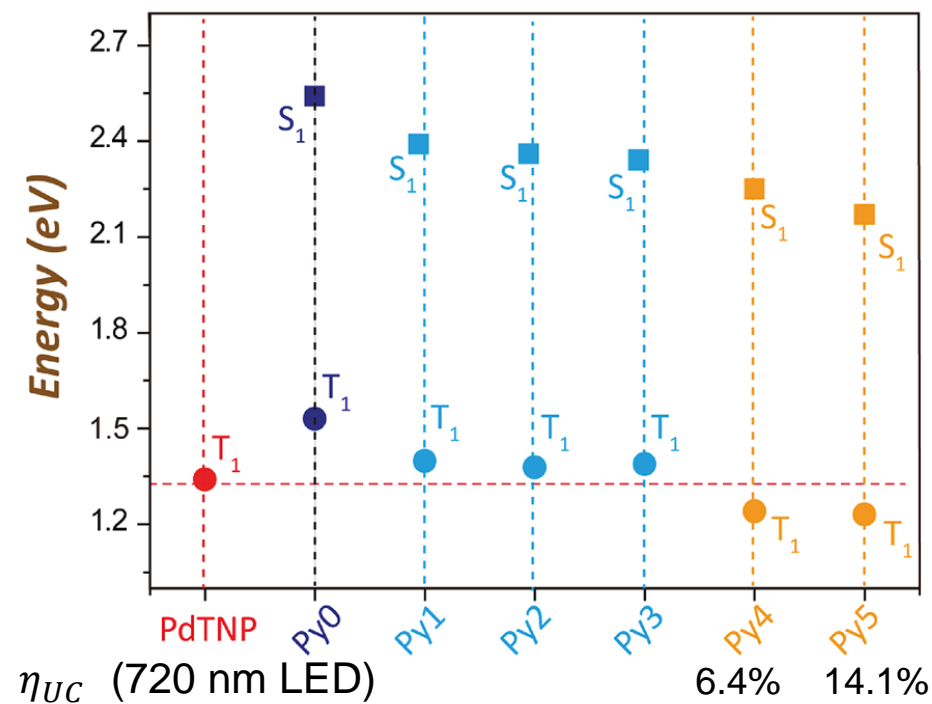
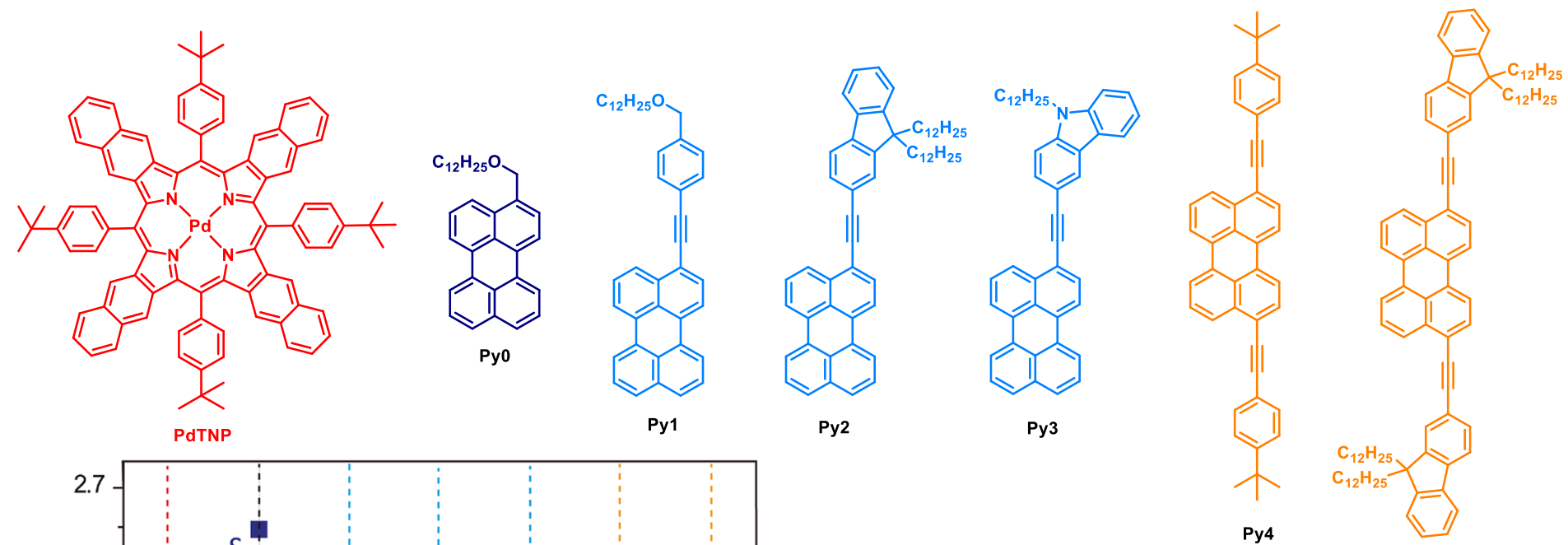


Freestanding gel

Penetration is ~300 times greater

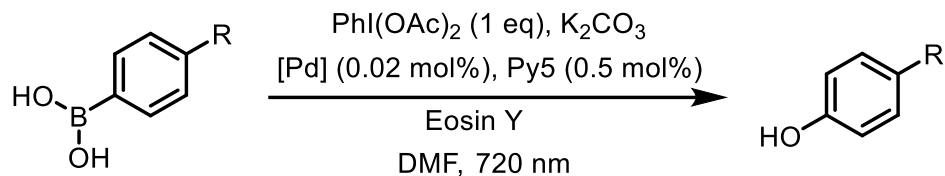
<b>b</b>	Material	NIR	Blue
	Air	Gel	Gel
	Water	Gel	Gel
	Amber glass	Gel	No reaction
	Bacon	Gel	No reaction <sup>a</sup>
	Ru(bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub> (1.5 mM)	Gel	No reaction
	700-nm long-pass filter	Gel	No reaction
	White silicone sheet	Gel	No reaction
	3 sheets white paper	Gel	No reaction
	Haemoglobin (0.2 mM)	Gel	No reaction
	Pig skin (6.4 mm)	Gel	No reaction

# Oxidation of Arylboronic Acid

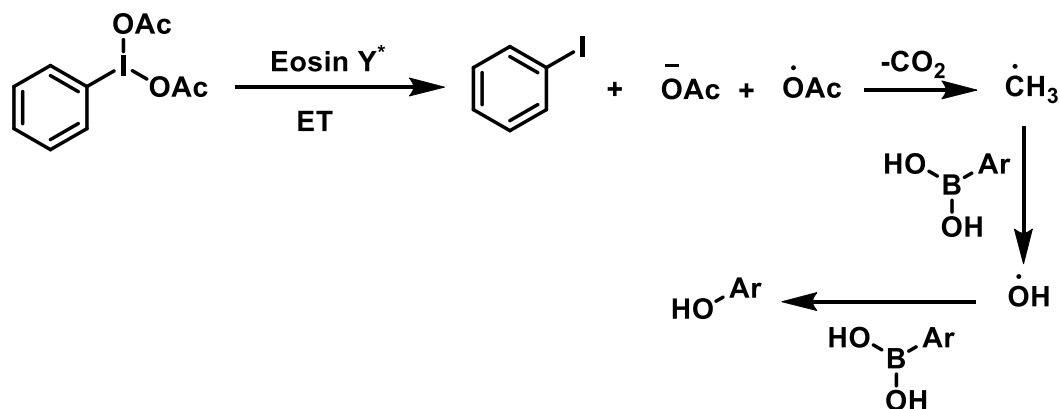
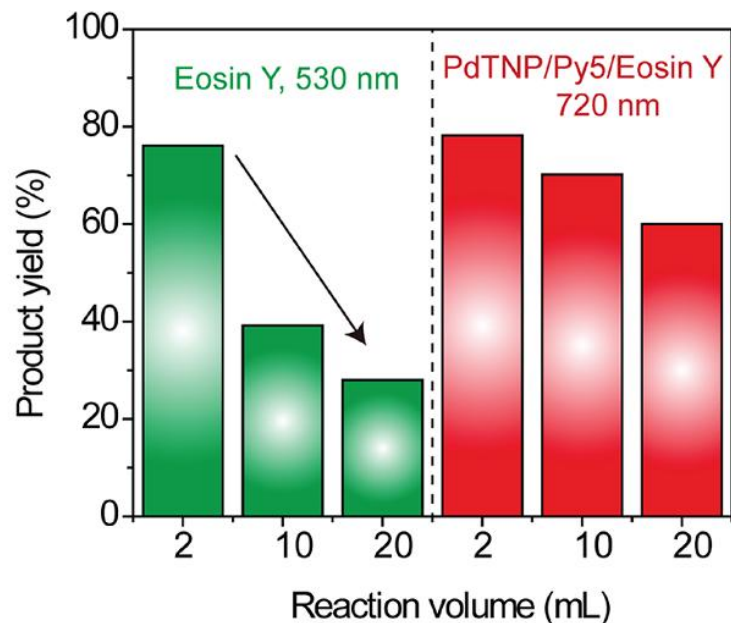


	$\Phi_f^a$ (%)	$\Phi_{TTET}^b$ (%)	$\eta_{TTA}^c$ (%)	$\Phi_{UC}^d$ (%)
Py0	83	1.82	0	—
Py1	70	5.54	1.52	0.06
Py2	72	17.1	2.02	0.25
Py3	68	5.97	5.92	0.24
Py4	74	33.7	30.4	7.6
Py5	76	41.1	53.2	16.6

# Oxidation of Arylboronic Acid

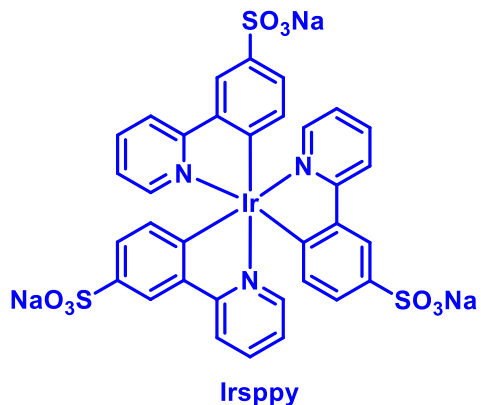


R	Me	CHO	OMe	Cl	H
<b>Yield</b>	81%	76%	73%	71%	74%



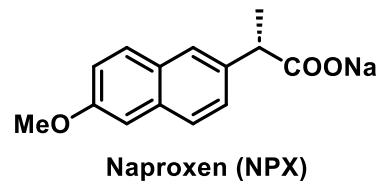
# Two-Component Reactions

## ■ Blue Light to UV upconversion in Water



$$E_{T1}=2.65 \text{ eV}$$

$$\tau_0=1625 \text{ ns}$$

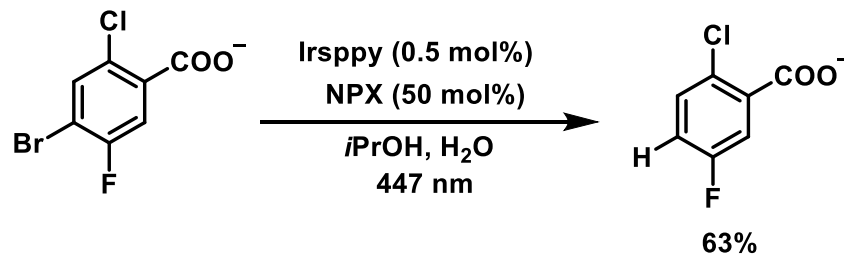


$$E_{T1} \sim 2.58 \text{ eV}$$

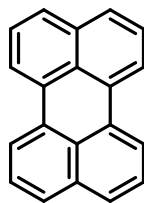
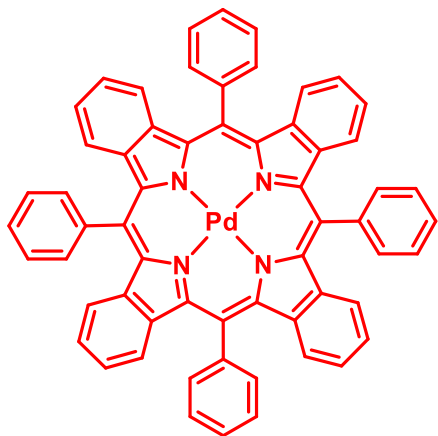
$$E_{S1}=3.7 \text{ eV}$$

$$E_{\frac{1}{2}} (\text{NPX}^{\cdot+}/\text{NPX}^*) = -2.5 \text{ V (vs NHE)}$$

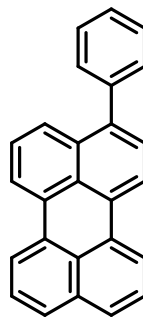
$$> -2.0 \text{ V for normal PC}$$



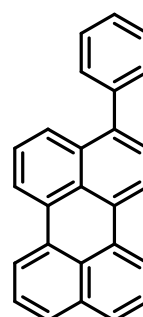
# Activation of Arylbromide



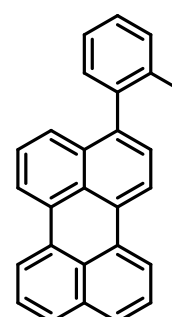
Py0



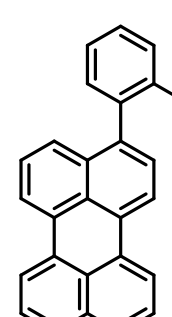
Py1



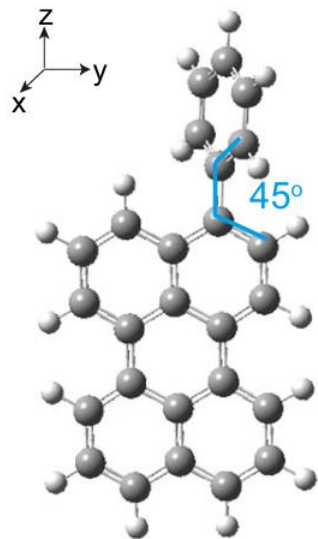
Py2



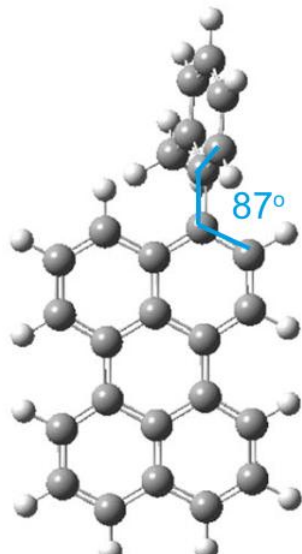
Py3



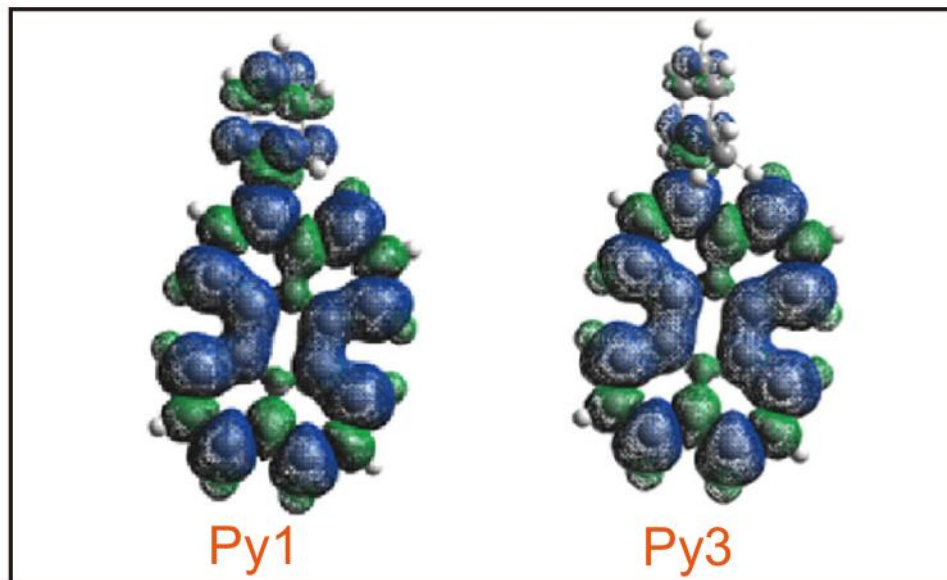
Py4



Py1



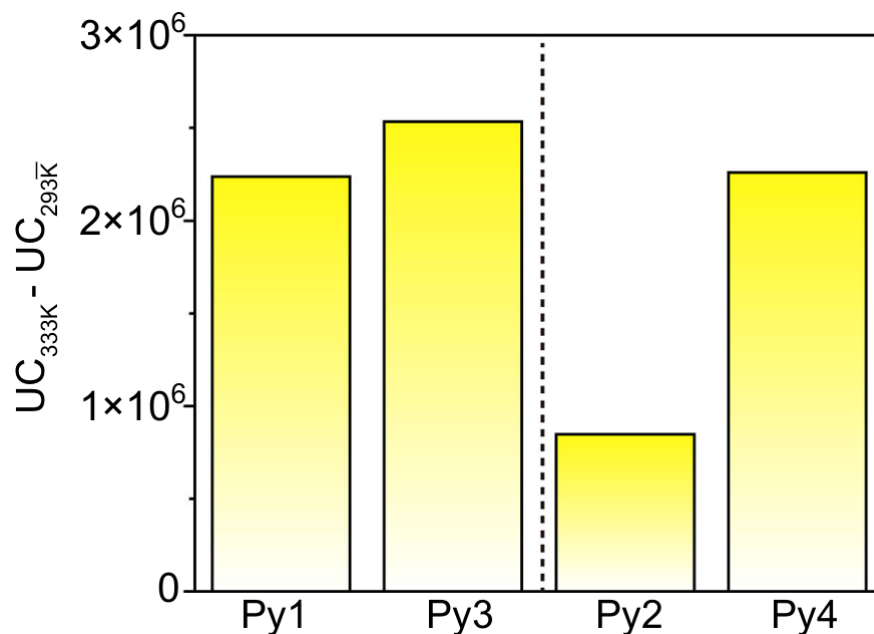
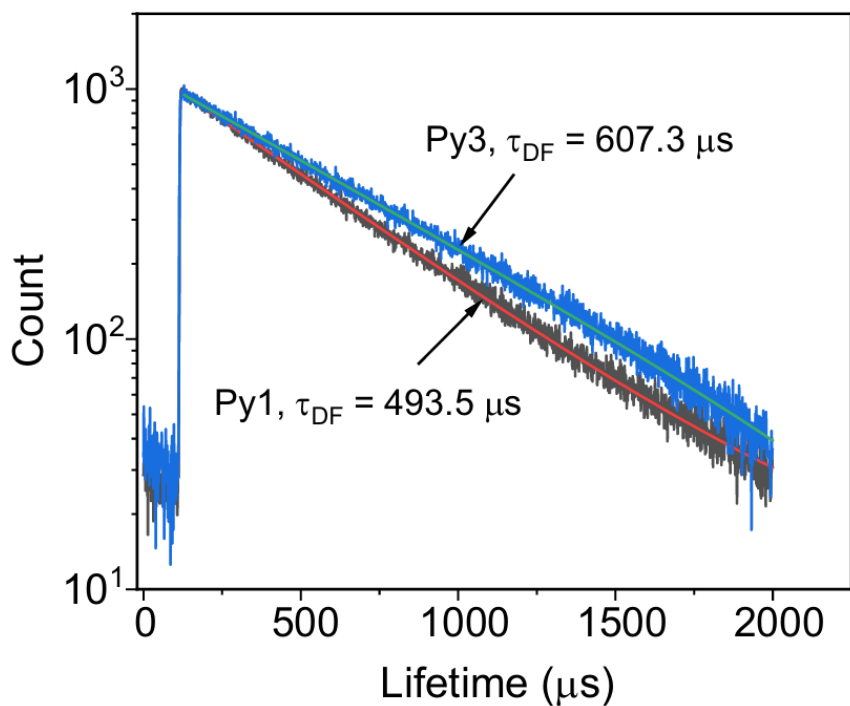
Py3



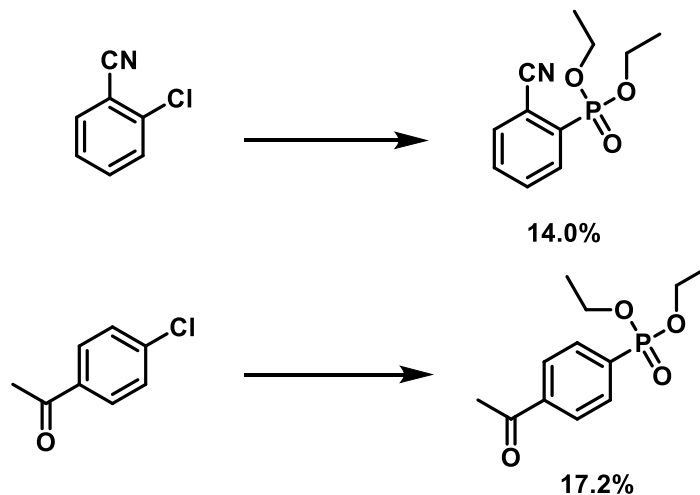
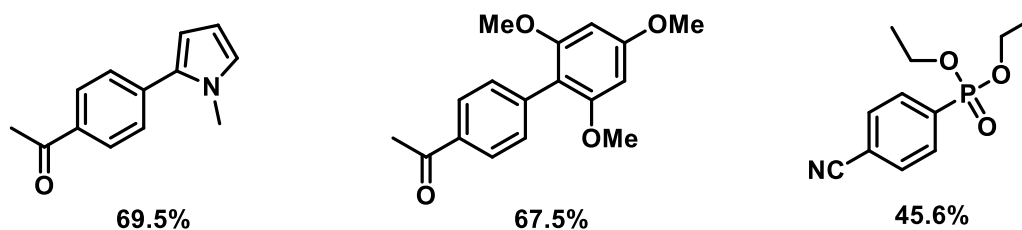
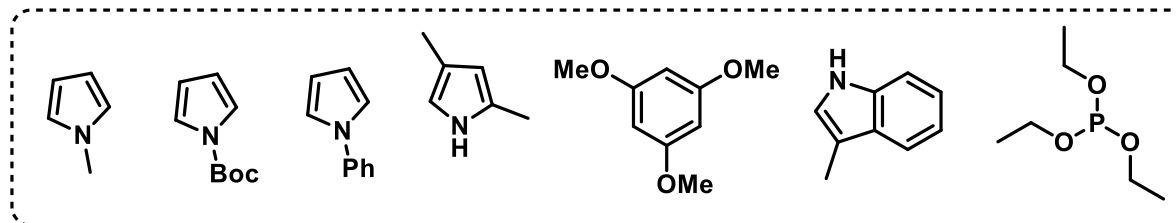
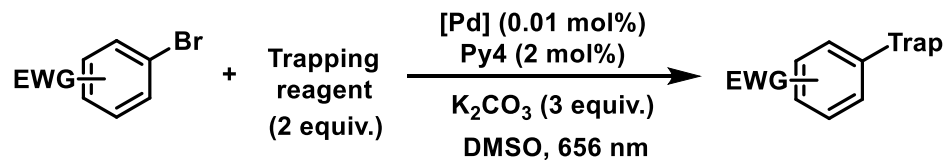
# Activation of Arylbromide

An	$\Phi_{ET}$	$\Phi_{TTA}$
Py0	97	4.3
Py1	97.5	6.8
Py2	98.3	14.0
Py3	98.1	11.3
Py4	96.7	15.7

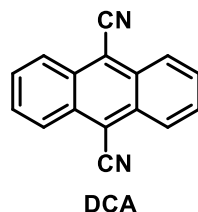
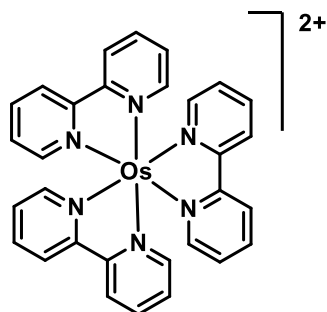
■ Triplet lifetime



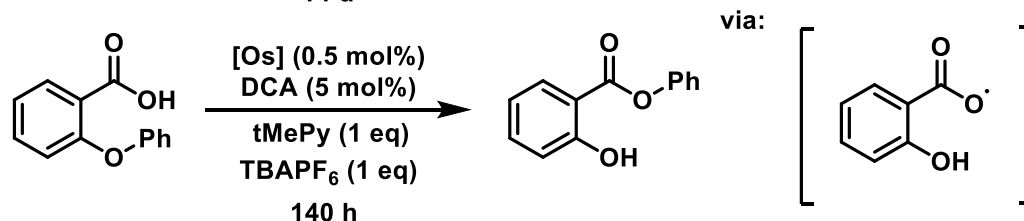
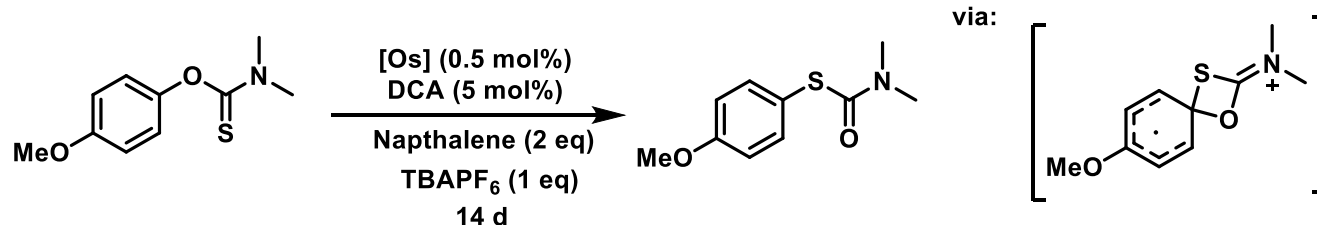
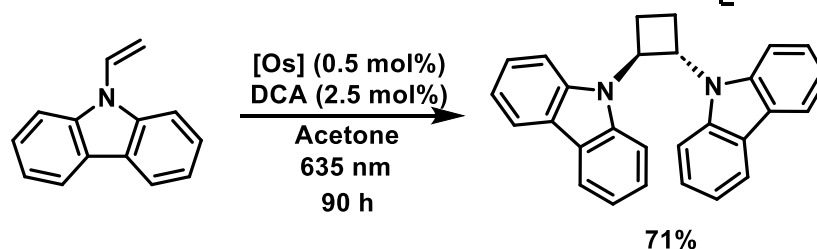
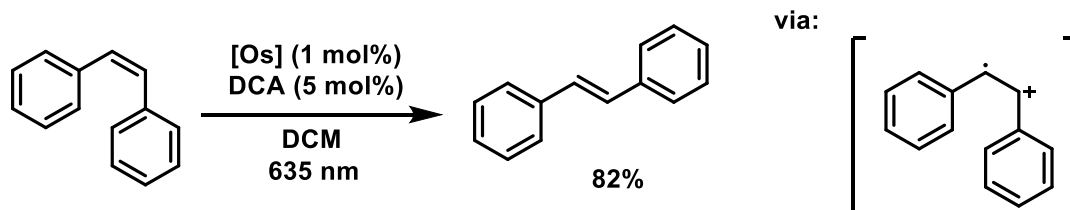
# Activation of Arylbromide



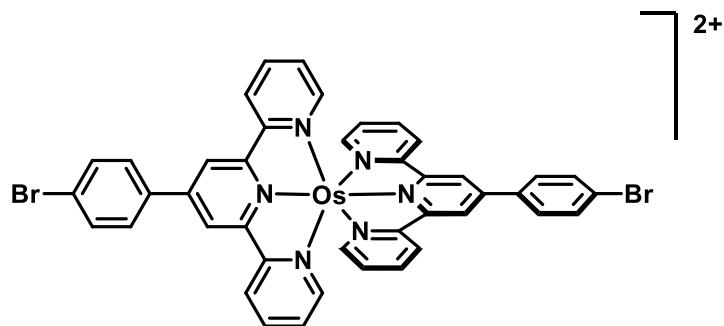
# Os(II)/DCA System



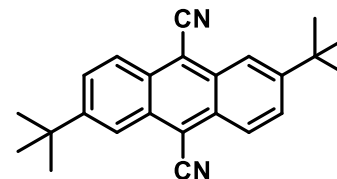
Solvent	[DCA]/mM	$\Phi_{UC}$
MeCN	0.5	0.22
Acetone	0.5	0.13
DCM	3	1.5



# Os(II)/DCA System



**Os(BrPh-tpy)<sub>2</sub>**  
 $\lambda_{\text{ex}} = 840 \text{ nm}$   
 $T_1 = 1.69 \text{ eV}$

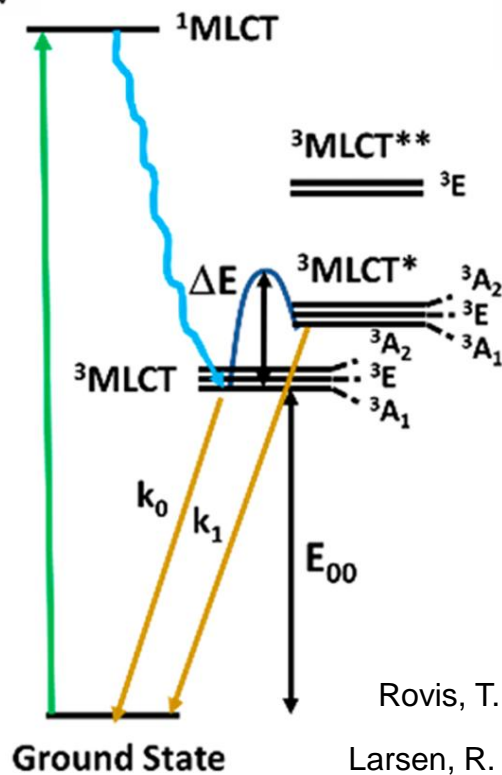


**DtB-DCA**

$T_1 = 1.81 \text{ eV}$

$S_1 = 2.90 \text{ eV}$

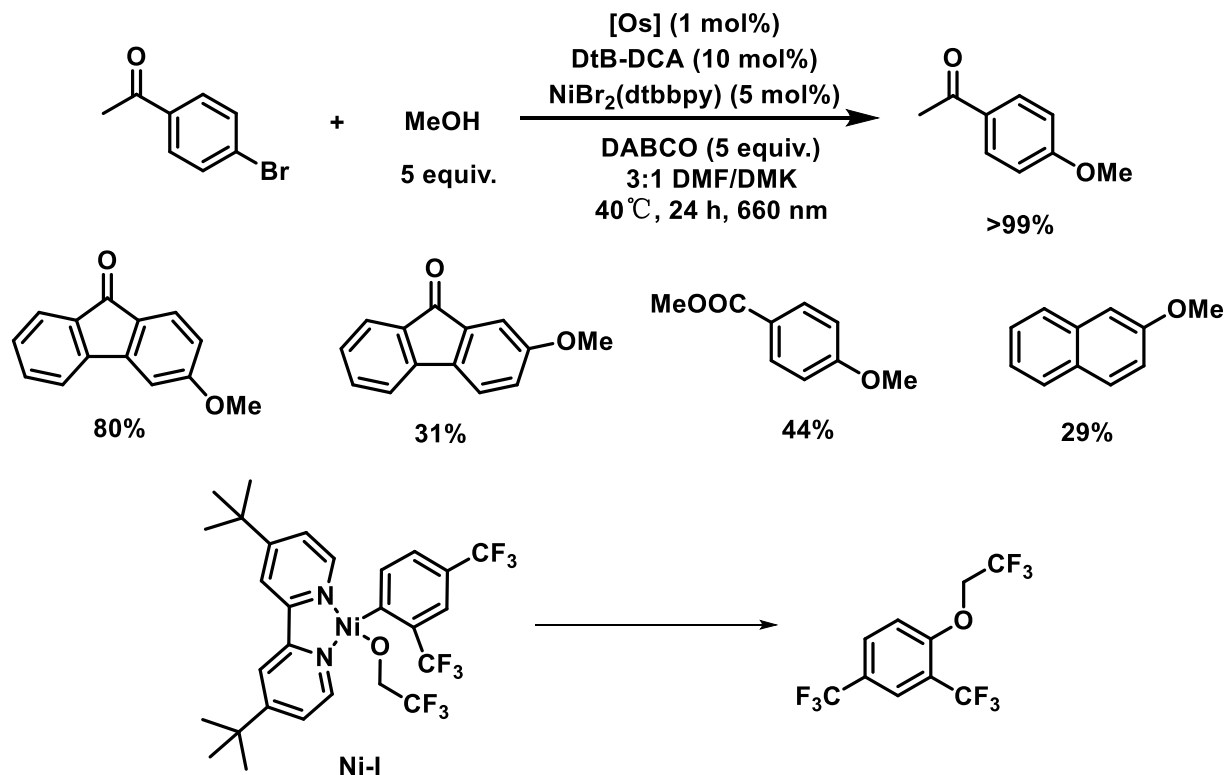
**Loss to TTA-UC = 0.72 eV**  
**Anti-Stokes Shift = 1.25 eV**  
*(values for DCA)*



Rovis, T. *et. al. ACS Catal.* **2024**, 14, 18515–18522

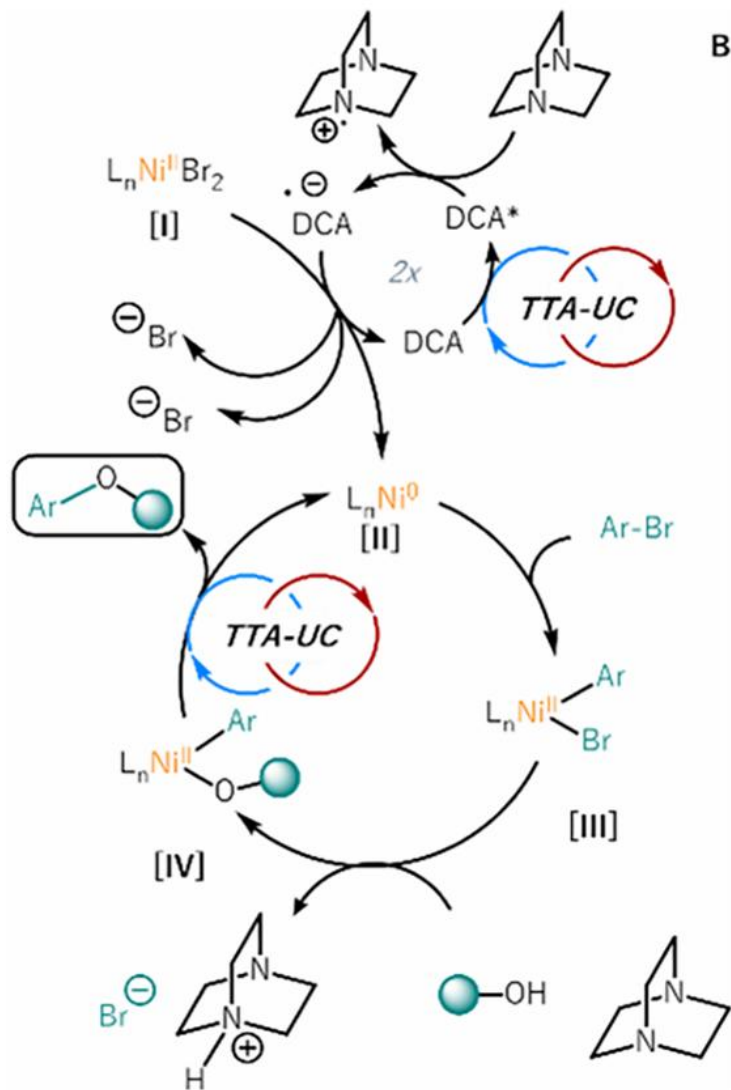
Larsen, R. W. *et. al. Inorg. Chem.* **2020**, 59, 7761–7767

# C-O Bond Formation



Entry	Conditions	Yield (%)
1	Ni-I, 427 nm	0
2	Ni-I, 660 nm	0
3	Ni-I + [Os], 427 nm	46
4	Ni-I + [Os], 660 nm	0
5	Ni-I + DtB-DCA, 427 nm	> 99
6	Ni-I + DtB-DCA, 660 nm	0
7	Ni-I + [Os] + DtB-DCA, 660 nm	49

# Mechanism

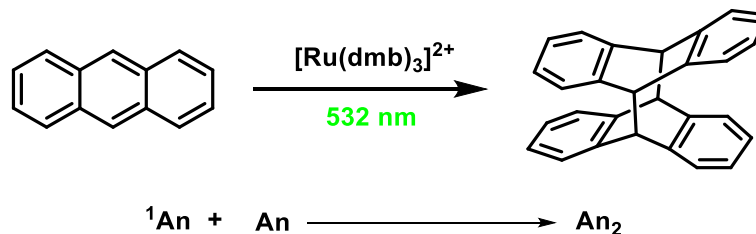


Rovis, T. *et. al.* *ACS Catal.* **2024**, 14, 18515–18522

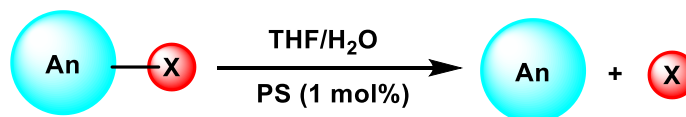
MacMillan, D. W. C. *et. al.* *Nature* **2015**, 524, 330–334

# Reactions of Annihilator

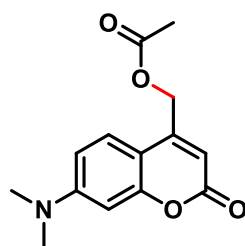
## ■ Dimerization



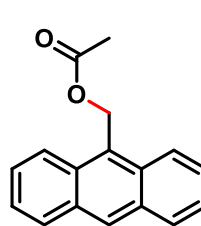
## ■ Photocleavage



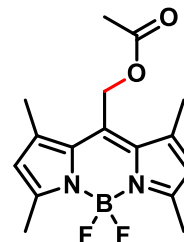
(a) Ir (ppy)<sub>3</sub>, 476 nm;  
(b) PtOEP, 530 nm;  
(c) PdTPBP, 650 nm;  
(d) PtTNP, 720 nm.



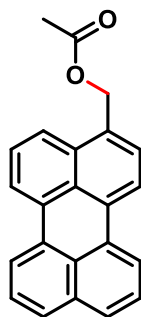
73.6% (a)



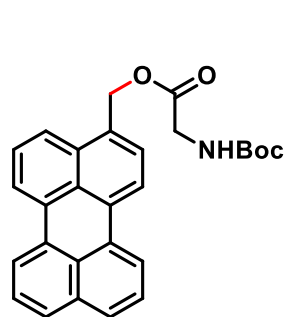
83.2% (b)



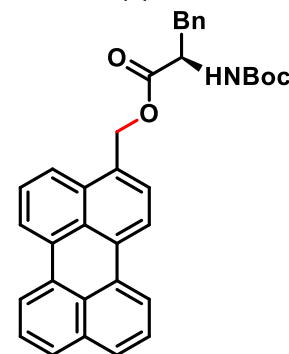
76.0% (c)



70.2% (b)

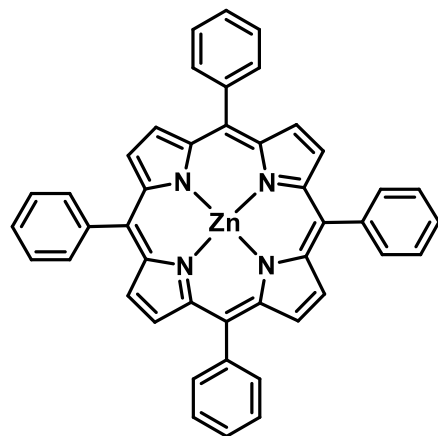


89.2% (c)

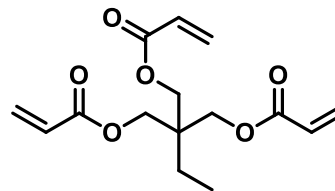


70.9% (c)

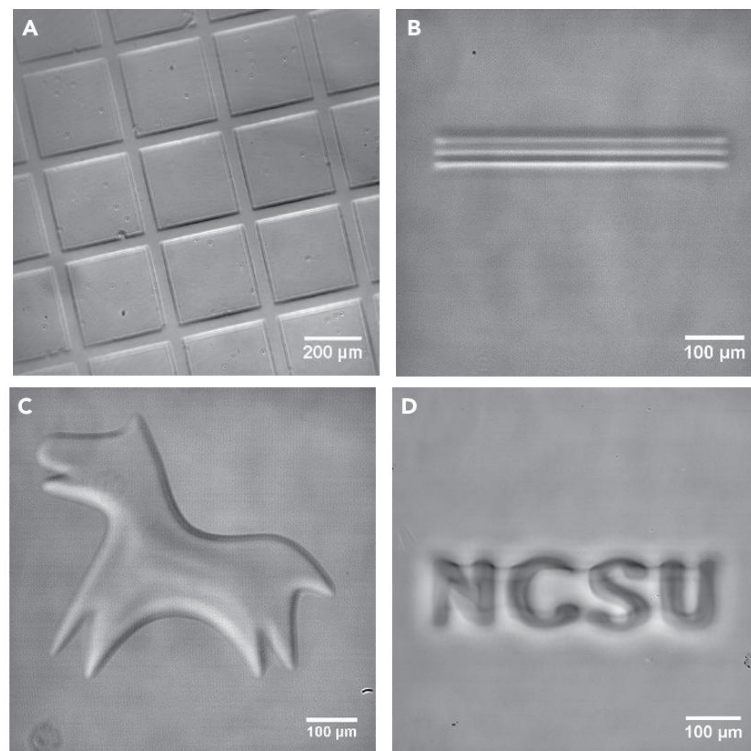
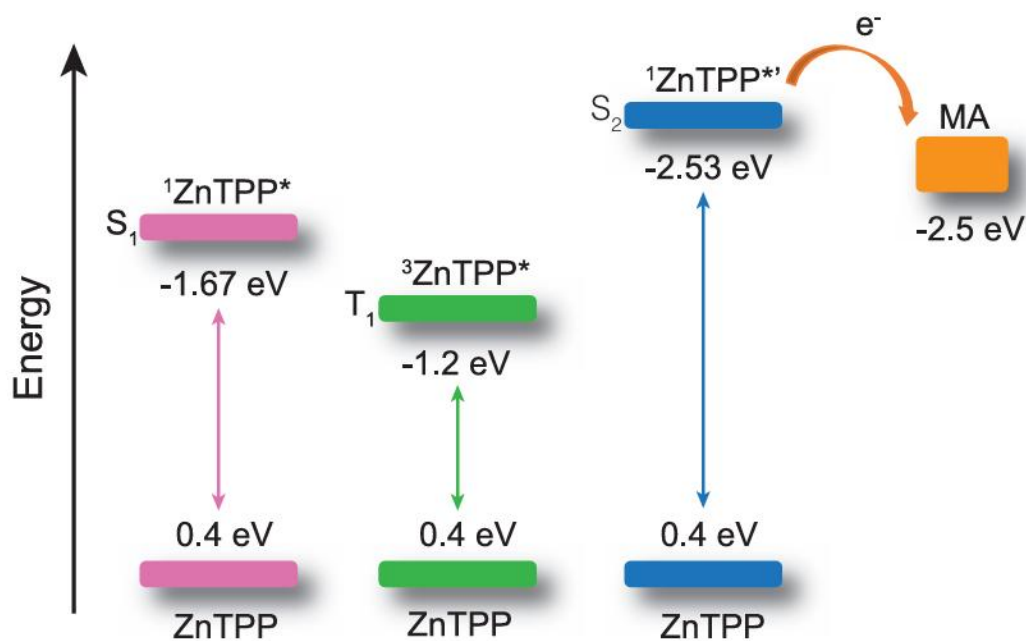
# Single Component Reactions



ZnTPP



TMPTA

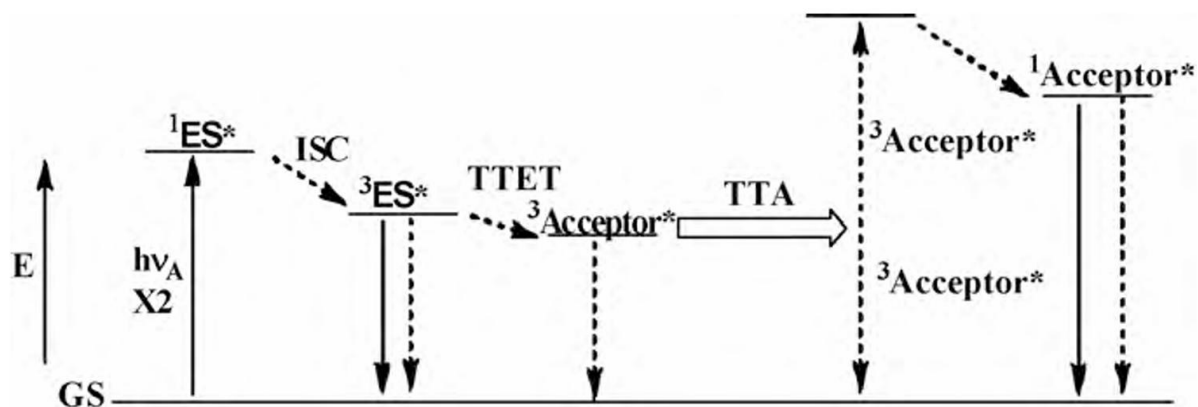


# Outline

---

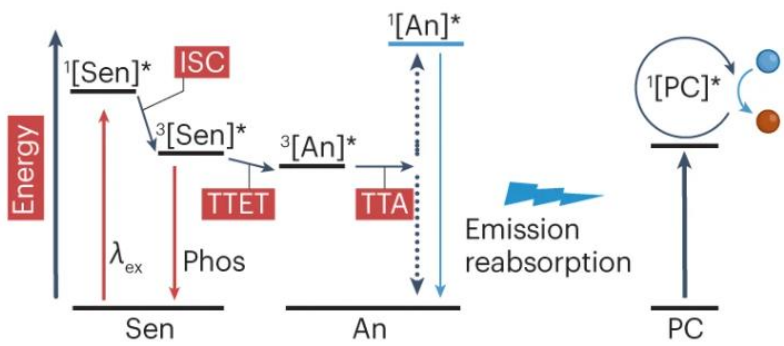
- Introduction: Basic Principles of Triplet-Triplet Annihilation Upconversion (TTA-UC)
- TTA-UC Mediated Photochemical Reactions
- Summary and Perspective

# Summary

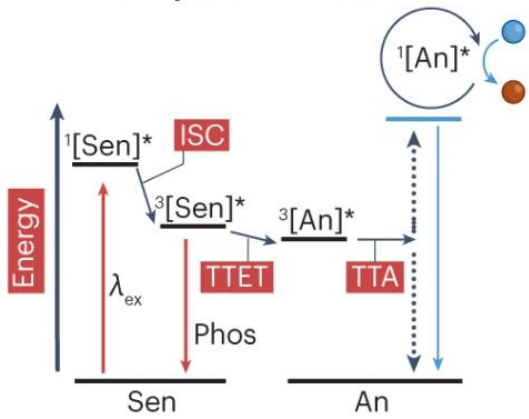


## a Three-component TTA-UC-PRs

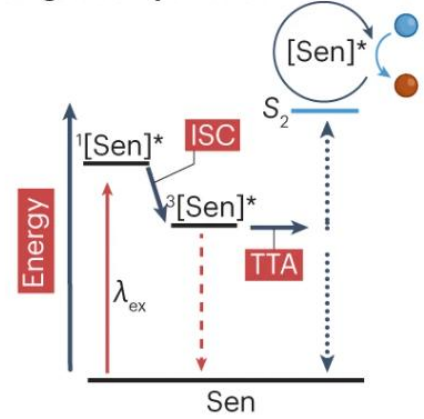
● Substrate ● Product



## Two-component TTA-UC-PRs

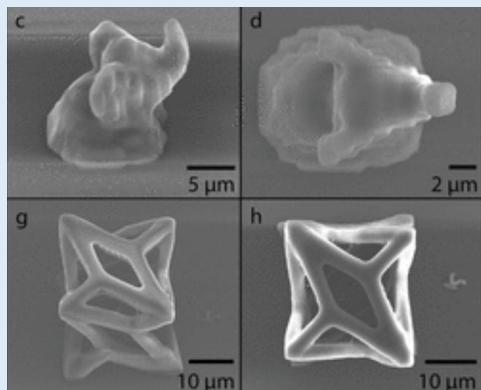


## Single-component TTA-UC-PRs



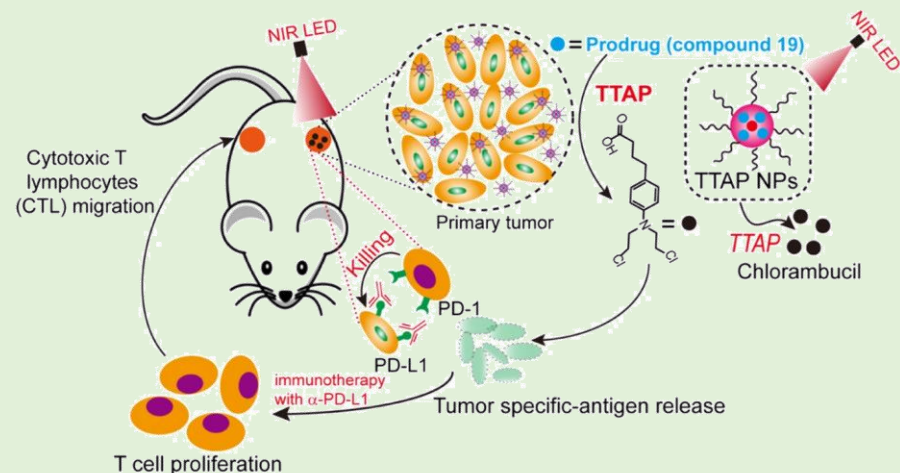
# What We Did *not* Discuss

## ■ 3D Printing



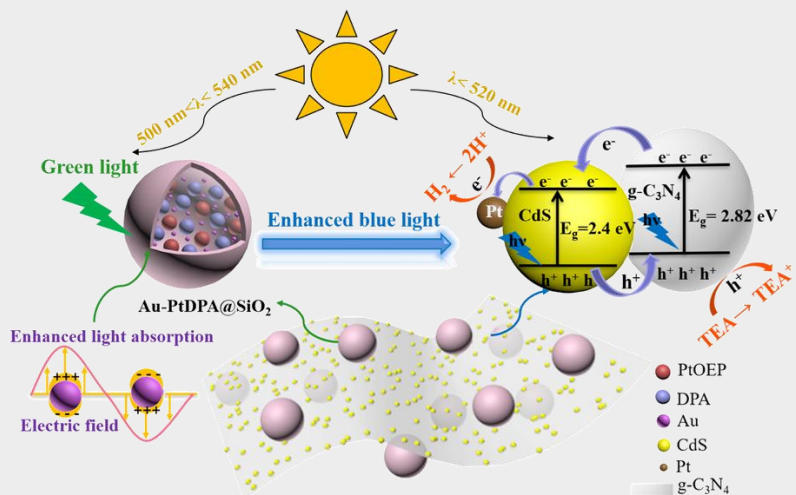
Hayward, R. C. *et. al. J. Am. Chem. Soc.* **2022**, 144, 5226–5232

## ■ Bioapplication



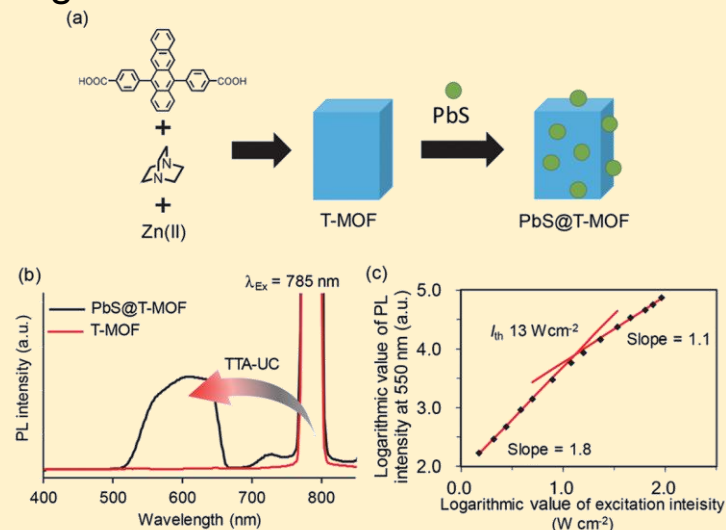
Han, G. *et. al. Nat. Commun.* **2021**, 12, 122

## ■ Water Splitting



Xu, Z. *et. al. Appl. Catal. B* **2019**, 258, 117762

## ■ Inorganic Material



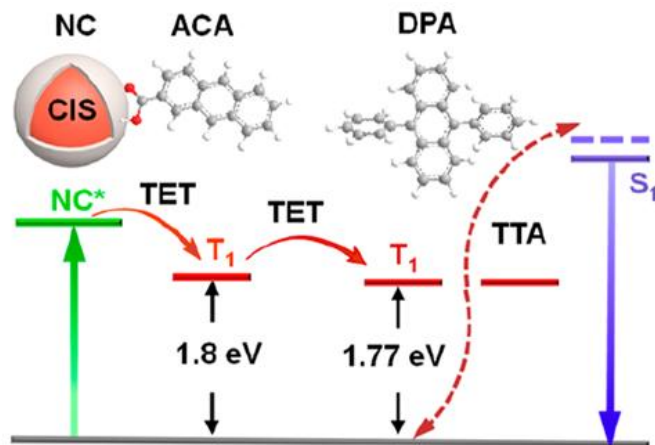
Kimizuka, N. *et. al. Dalton Trans.* **2018**, 47, 8590–8594

# Challenges

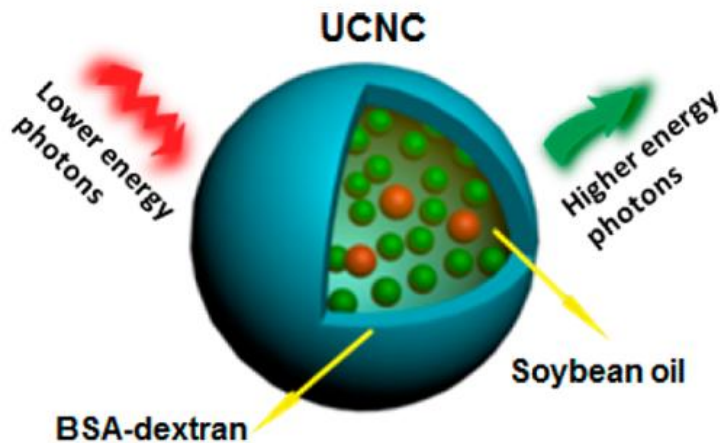
---

- The development of high-performance TTA-UC
- The harmonious coupling of TTA-UC and Photoreactions
- The expansion of TTA-UC-PR application scenarios

# Quantum Dots and Nanoparticles



$$\eta_{UC} = 18.6\%$$



Wu, K. *et. al. J. Am. Chem. Soc.* **2019**, 141, 13033–13037

Tang, M. L. *et. al. Acc. Chem. Res.* **2021**, 54, 1, 70–80

Li, F. *et. al. J. Am. Chem. Soc.* **2013**, 135, 5029–5037