三重态-三重态湮灭上转换（TTA-UC）在有机光反应中的应用

汇报人：陆礼承

导师：陆平 教授

专业：有机化学

时间：2024-11-8

CONTENTS

CONTENTS

1 背景介绍

- 光反应规模化应用的挑战

"On the arid lands there will spring up industrial colonies without smoke and without smokestacks…… glass buildings will rise everywhere; inside of these will take place the photochemical processes ……"

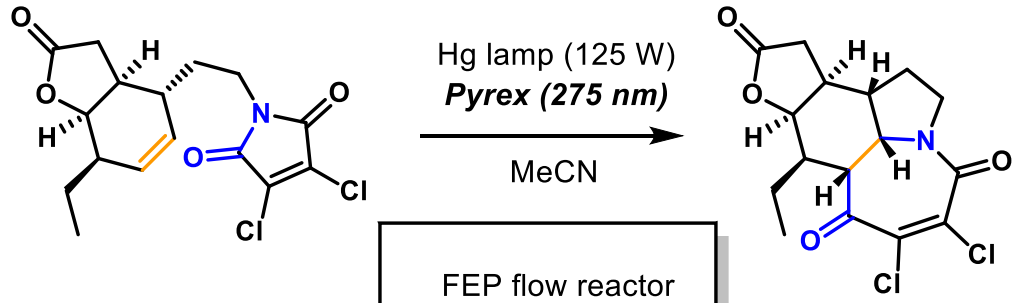
Giacomo Ciamician
1912

G. Ciamician, *Science* **1912**, *36*, 385.

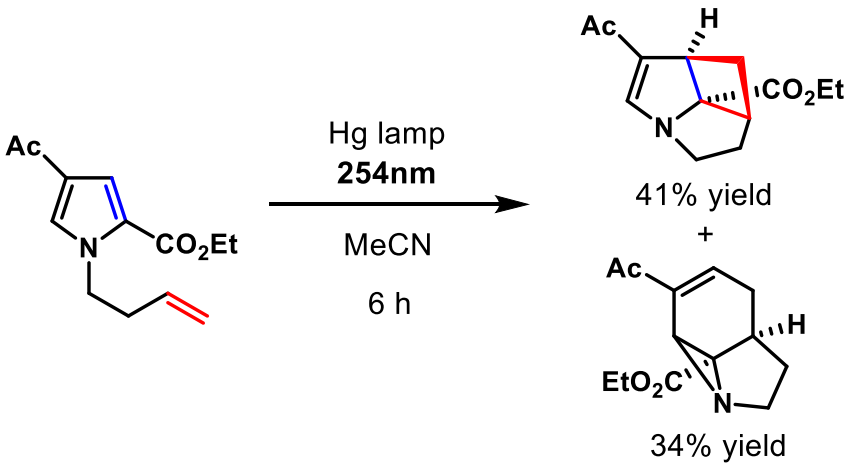
1 背景介绍

❒ 光反应放大产生的问题

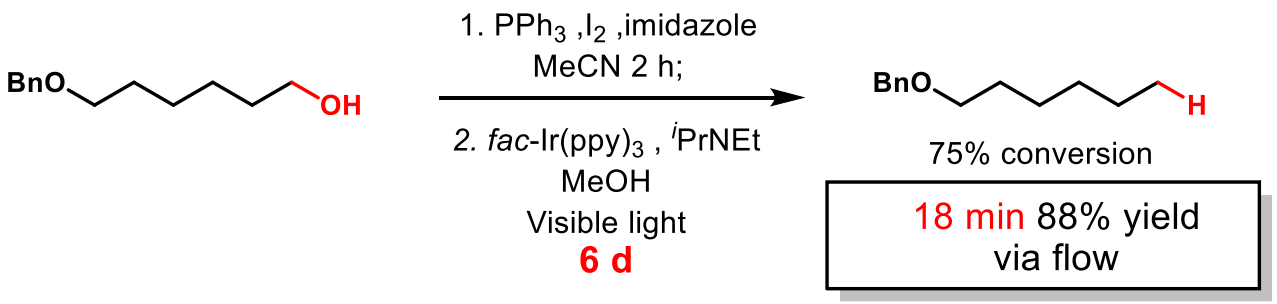
K. I. Booker-Milburn, et al. 2008:



2013:



C. R. J. Stephenson, et al. 2013:

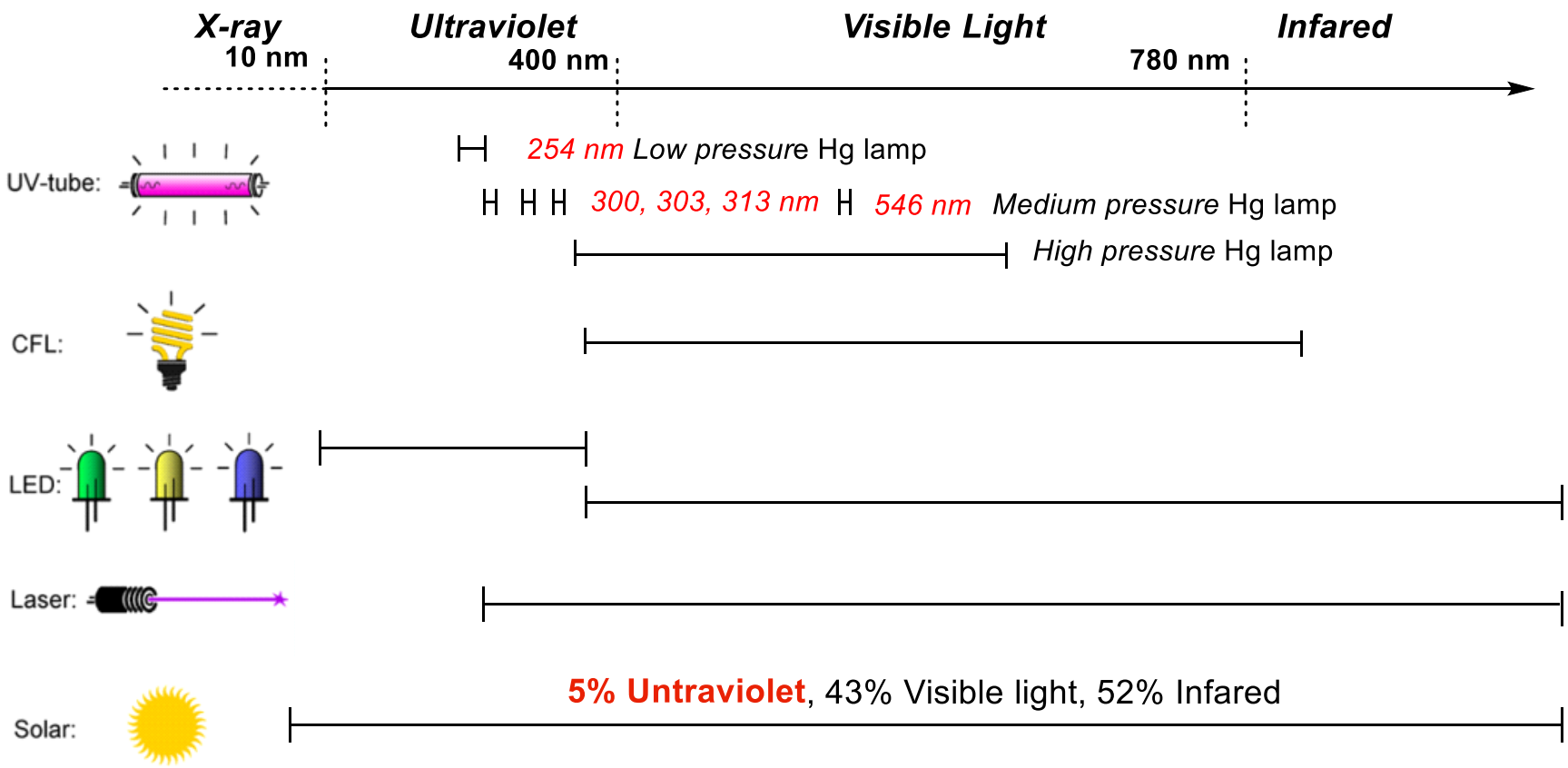


- 放大后产率降低
- 反应速率低
- 依赖连续流装置
- 选择性差

K. I. Booker-Milburn, *et al. J. Org. Chem.* **2008**, 73, 6497; K. I. Booker-Milburn, *et al. Angew. Chem.* **2013**, *125*, 1539; C. R. J. Stephen, *et al. Chem. Commun.* **2013**, *49*, 4352.

1 背景介绍

短波长光源消耗巨大



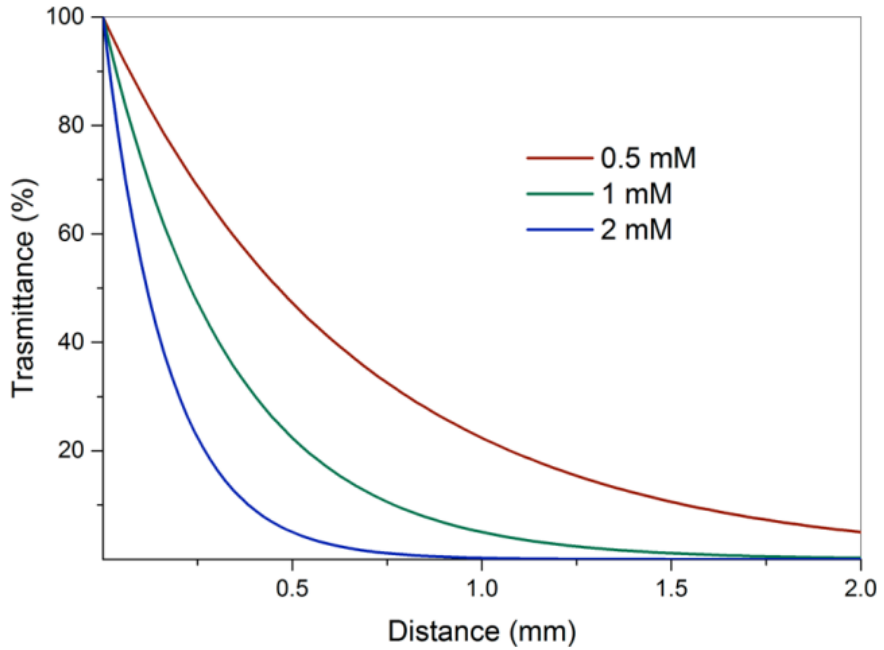
N. Yanai, C. Kerzig, *et al. Angew. Chem. Int. Ed.* **2023**, *62*, e202215340; T. Noël, *et al. Chem. Rev.* **2016**, *116*, 10276.

1 背景介绍

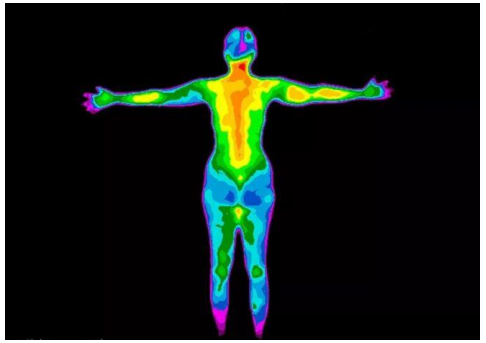
使用更长波长的光进行光反应

Bouguer–Lambert–Beer law

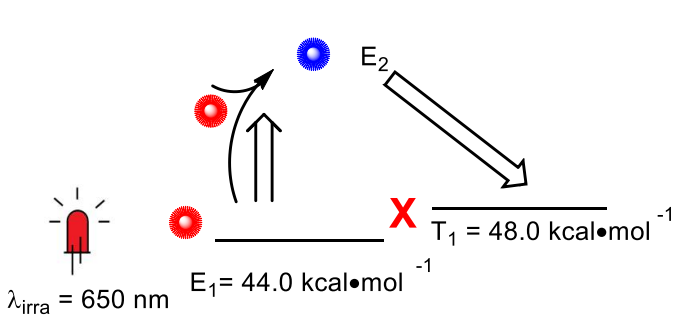
$$A = \log_{10} T = \log_{10} \frac{I_0}{I} = \varepsilon c l$$

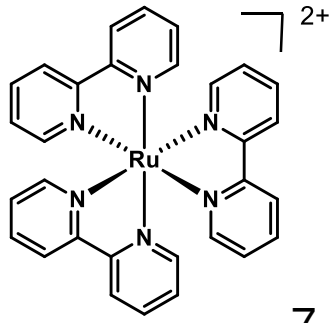


长波长光的穿透性



双光子过程的引入





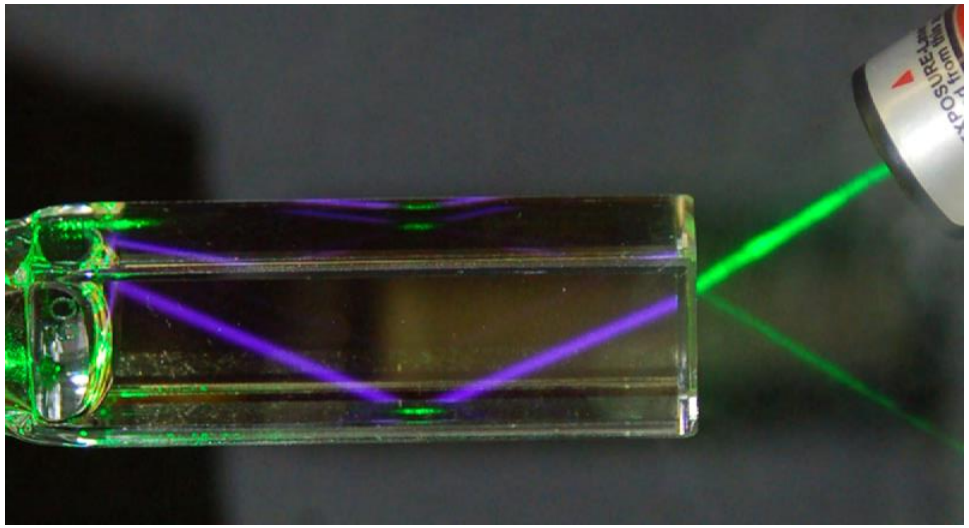
$Ru(bpy)_3^{2+}$

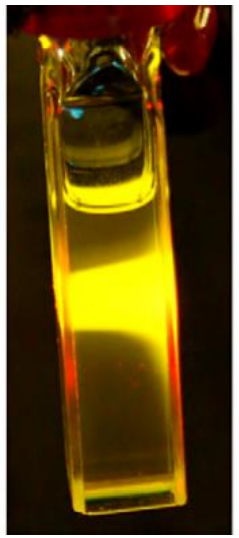
上转换 Upconversion

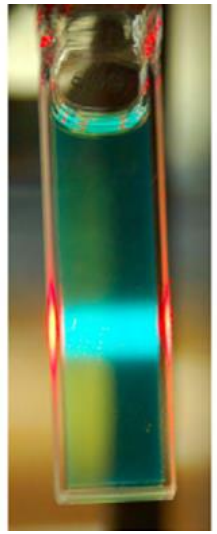
将两个或多个低能量光子转换为高能量光子的过程

三重态-三重态湮灭上转换

Triplet−Triplet Annihilation Upconversion （TTA-UC）



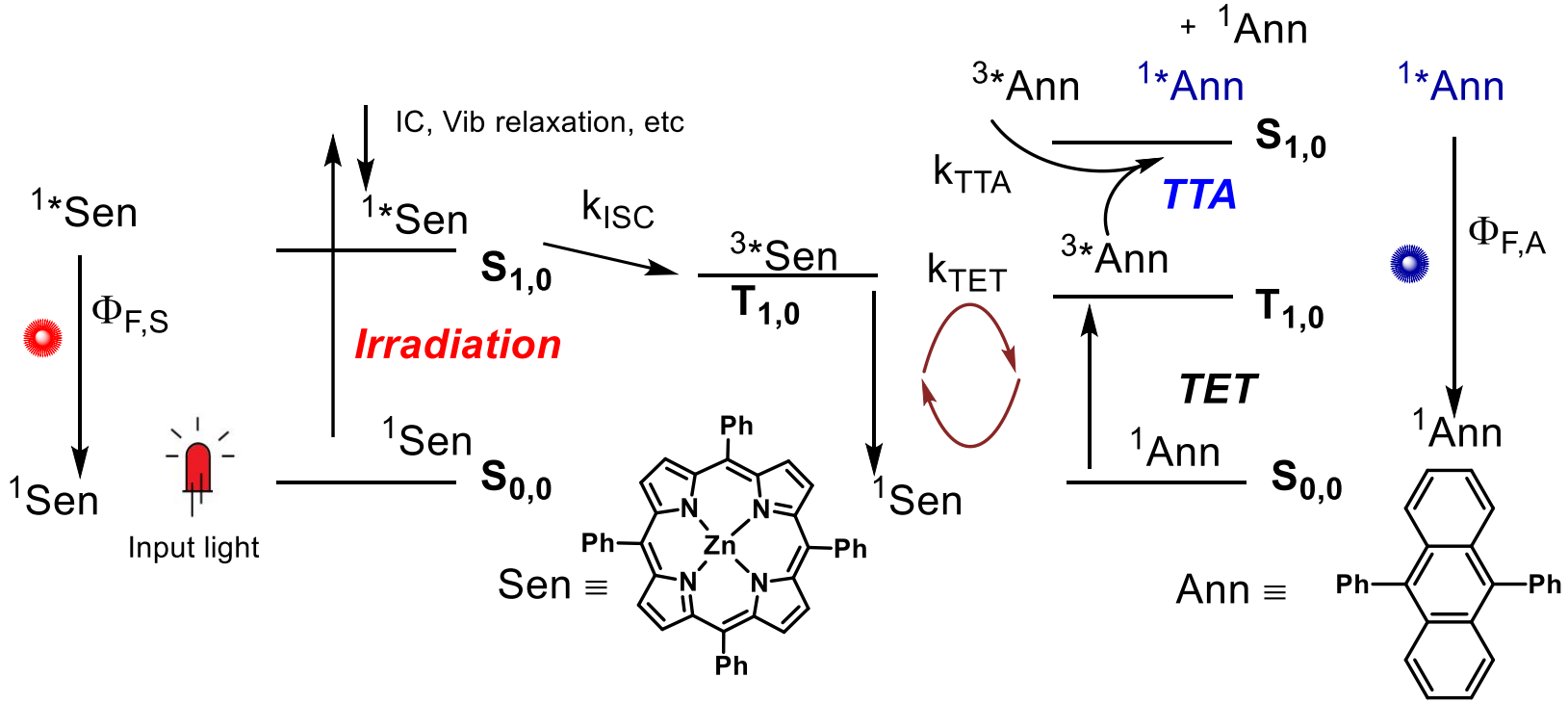




F. Li, *et al.Chem. Rev.* **2015**, *115*, 395.

1.2 三重态-三重态湮灭上转换(TTA-UC)

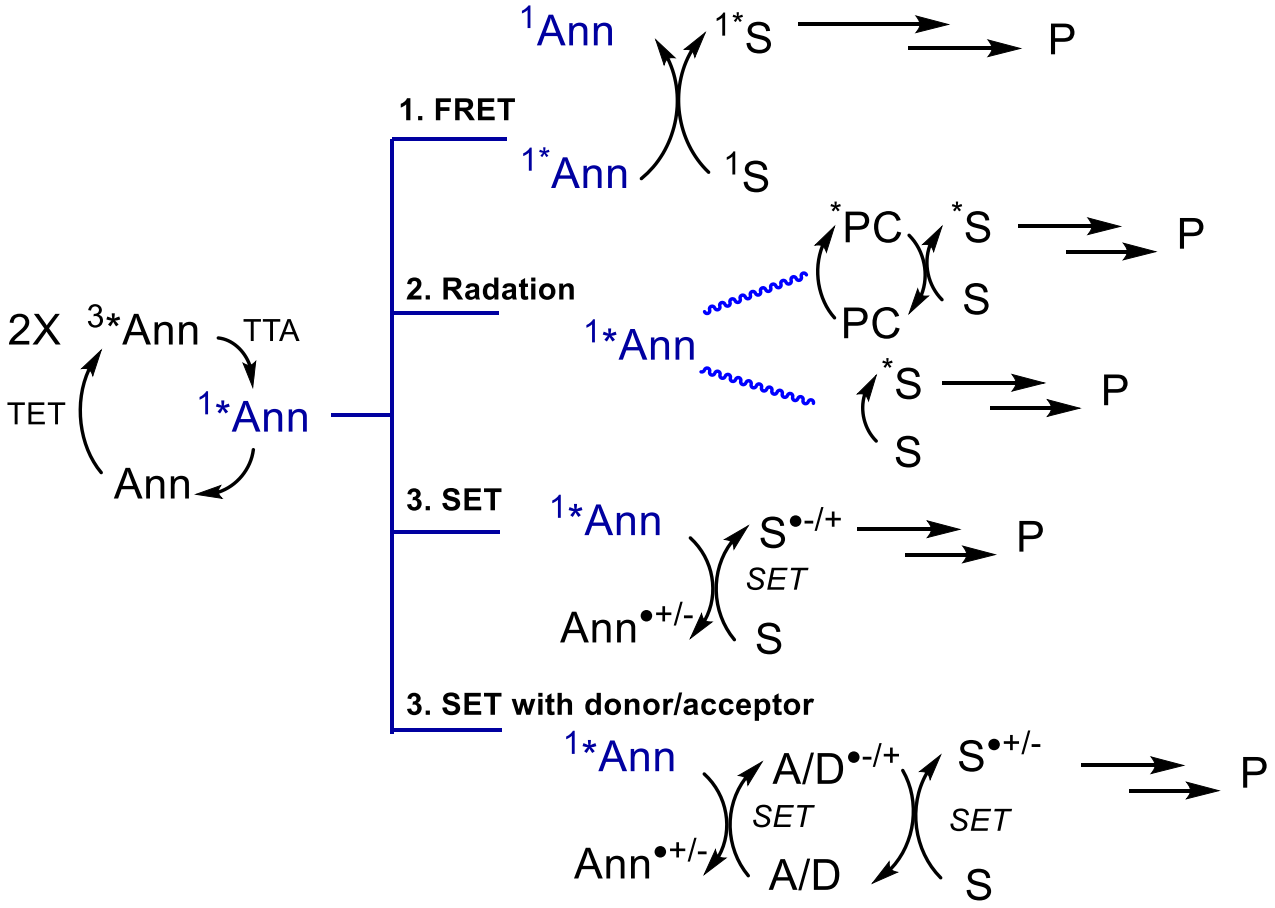
TTA-UC的光物理过程



C. Kerzig, N. Yanai, *et al. Angew. Chem. Int. Ed.* **2023**, *62*, e202301506.

1.2 三重态-三重态湮灭上转换(TTA-UC)

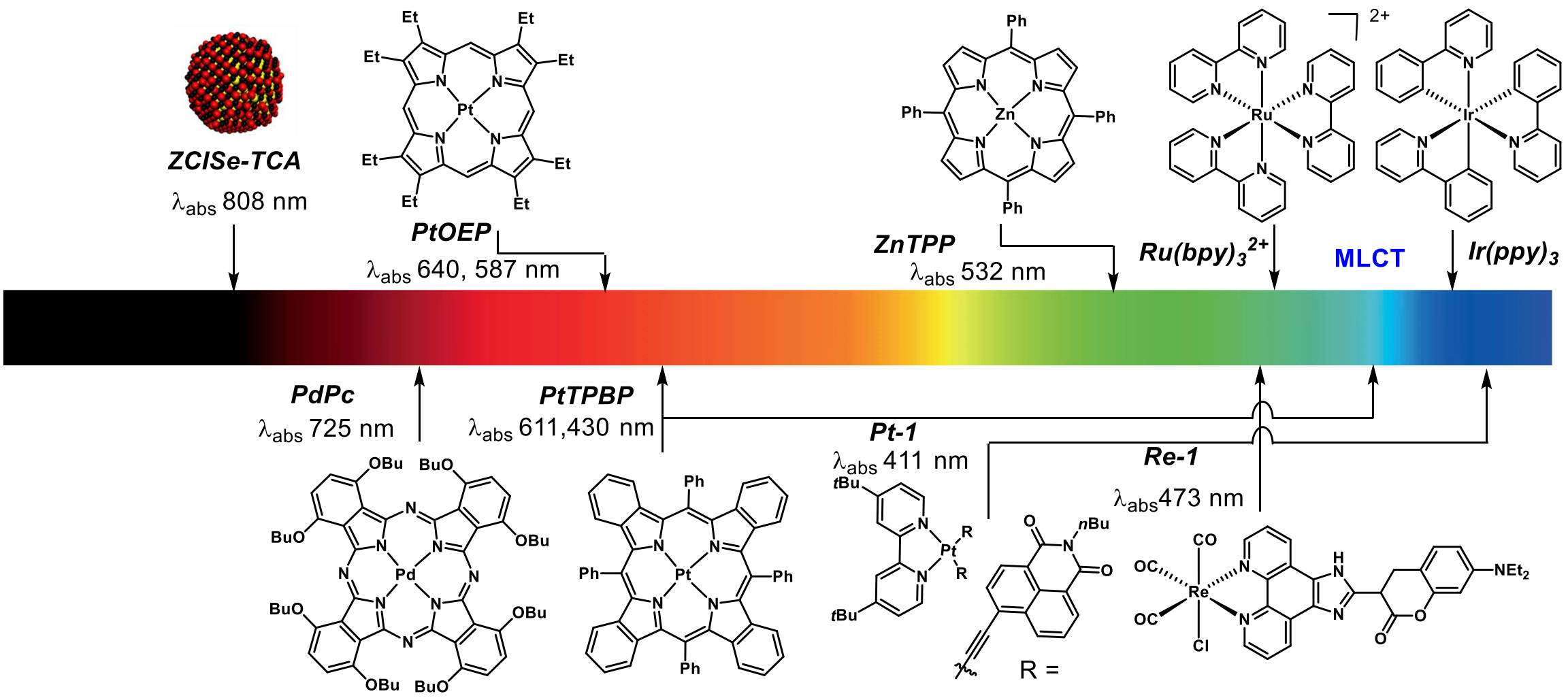
- TTA-UC参与有机光反应的机理



C. Kerzig, N. Yanai, *et al. Angew. Chem. Int. Ed.* **2023**, *62*, e202301506.

CONTENTS

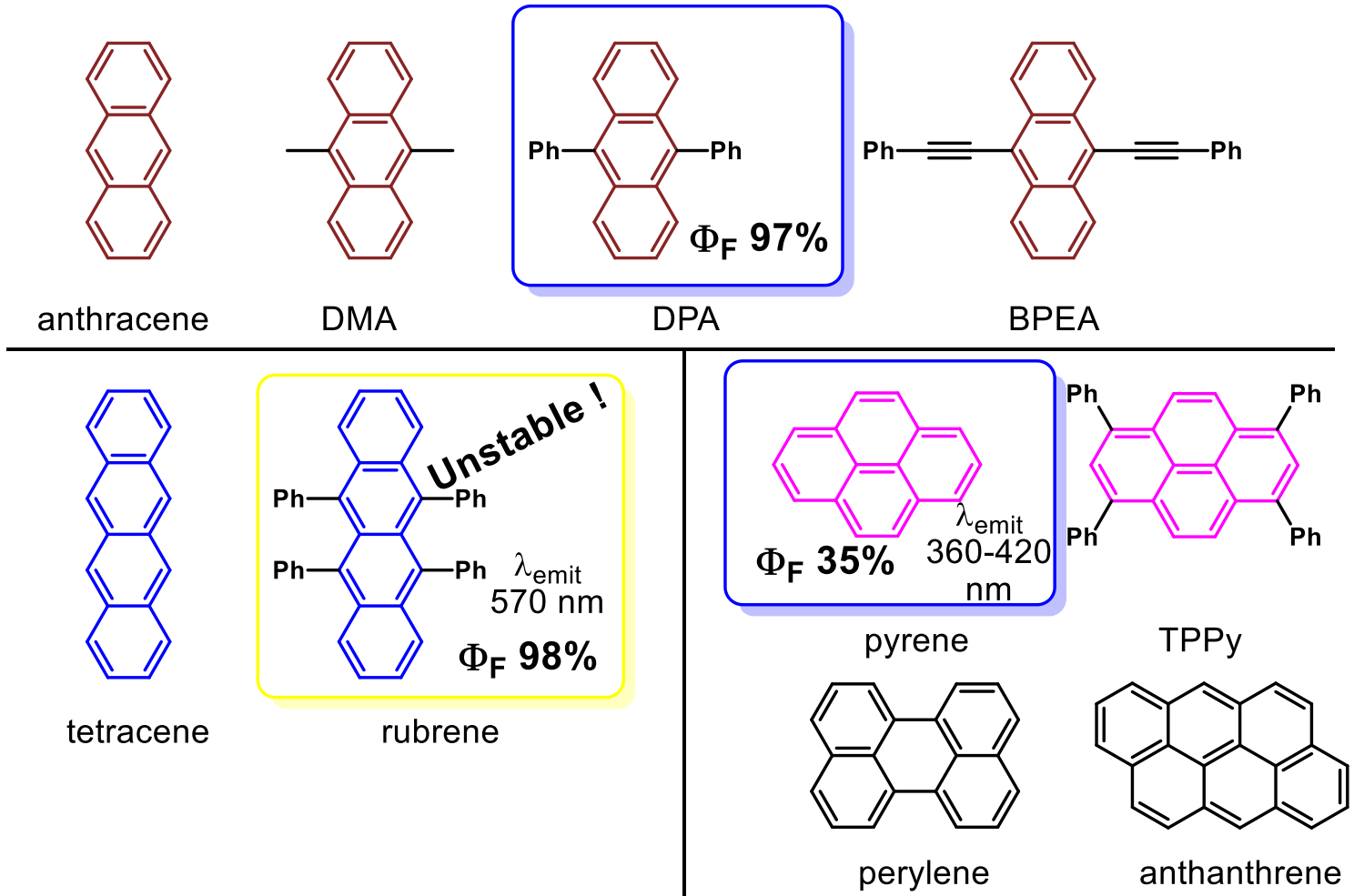
2. TTA-UC中的光敏剂和湮灭剂



K. Wu, *et al. Nat. Photon.* **2023**, *17*, 346; T. Tsuboi, *et al. Chem. Phys.* **2006**, *330*, 118; R. P.Steer, *et al. J. Phys. Chem. A* **2009**, *113*, 8548;F. N.Castellano, *et al. J. Phys. Chem. Lett.* **2009**, *1*, 195;F. N.Castellano, *et al. J. Phys. Chem. A* **2008**, *112*, 3550;J. Zhao, *et al*. *Dalton Trans.* **2012**, *41*, 8931; F. N. Castellano, *et. al. J. Phys. Chem. A* **2006**, *110*, 11440;J. Zhao, *et al. Eur. J. Inorg. Chem.* **2012**, 3183.

2. TTA-UC中的光敏剂和湮灭剂

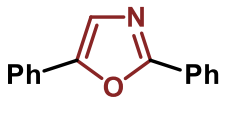
Polycyclic Aromatic Hydrocarbons



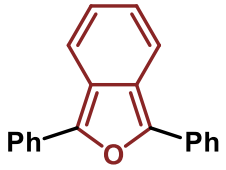
F. Li, *et al. Chem. Rev.* **2015**, *115*, 395; S.Tobita, *et al. Phys. Chem. Chem. Phys.* **2009**, *11*, 9850; F. Castellano, *et al. Phys. Chem. A.* **2006**, *110*, 11440.

2. TTA-UC中的光敏剂和湮灭剂

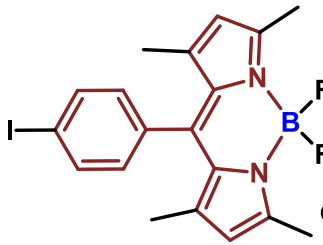
Heterocyclic Compounds



PPO



DPBF

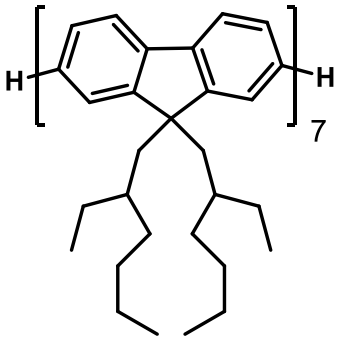


λ_{emit} 527nm

Φ_F 69%

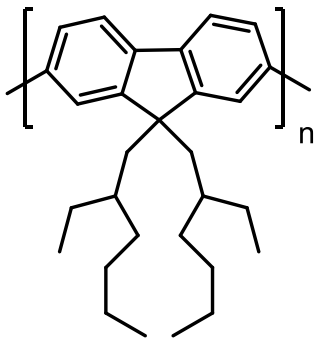
BDP-1

Oligomers

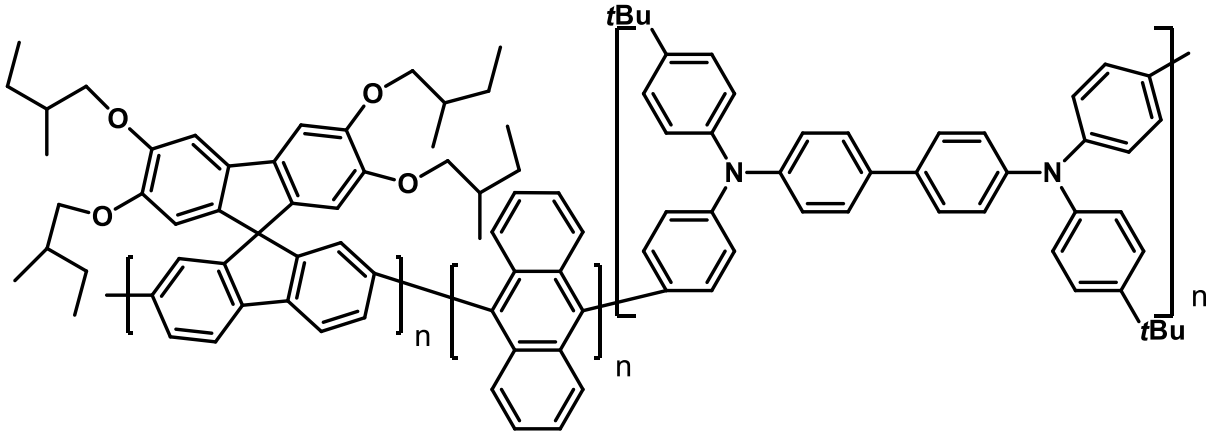


QF7

Polymers



PF2/6



spirobifluorene-anthracene copolymer

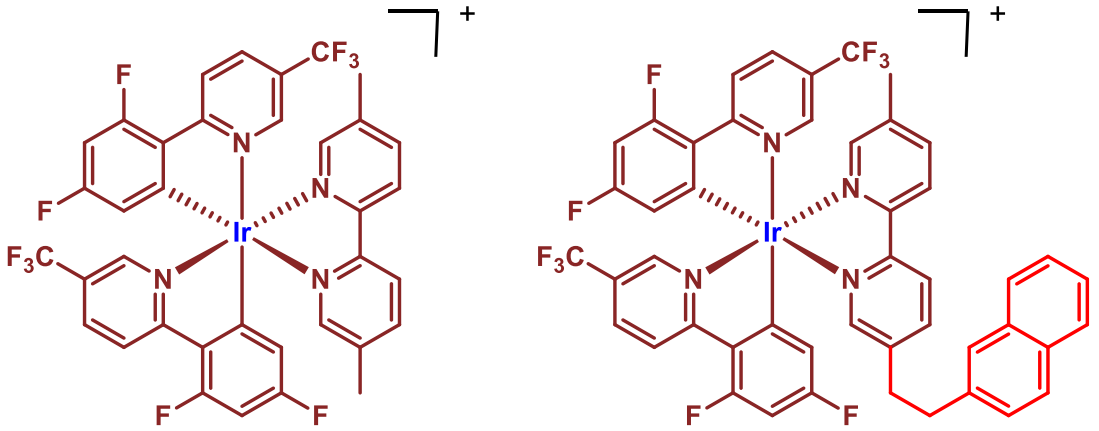
F. Castellano, et al. *J. Am. Chem. Soc.* **2008**, *130*, 16164; F. Castellano, et al. *J. Am. Chem. Soc.* **2010,** *132*, 14203.

2. TTA-UC中的光敏剂和湮灭剂

光敏剂改性-提高三线态寿命

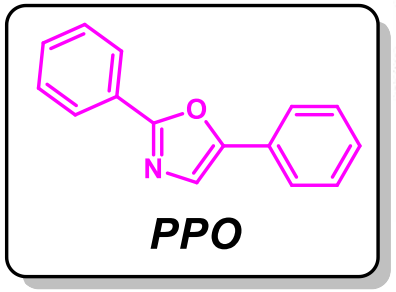
$$I_{th} = (\alpha\gamma_{TT})^{-1}\left[\frac{k_{tr}}{k_S^T + k_{tr}}\right]^{-1}(k_A^T)^2 = (\alpha\Phi_{TET}\gamma_{TT})^{-1}\tau_T{}^{-2}$$

O. S. Wenger, et al. 2023:

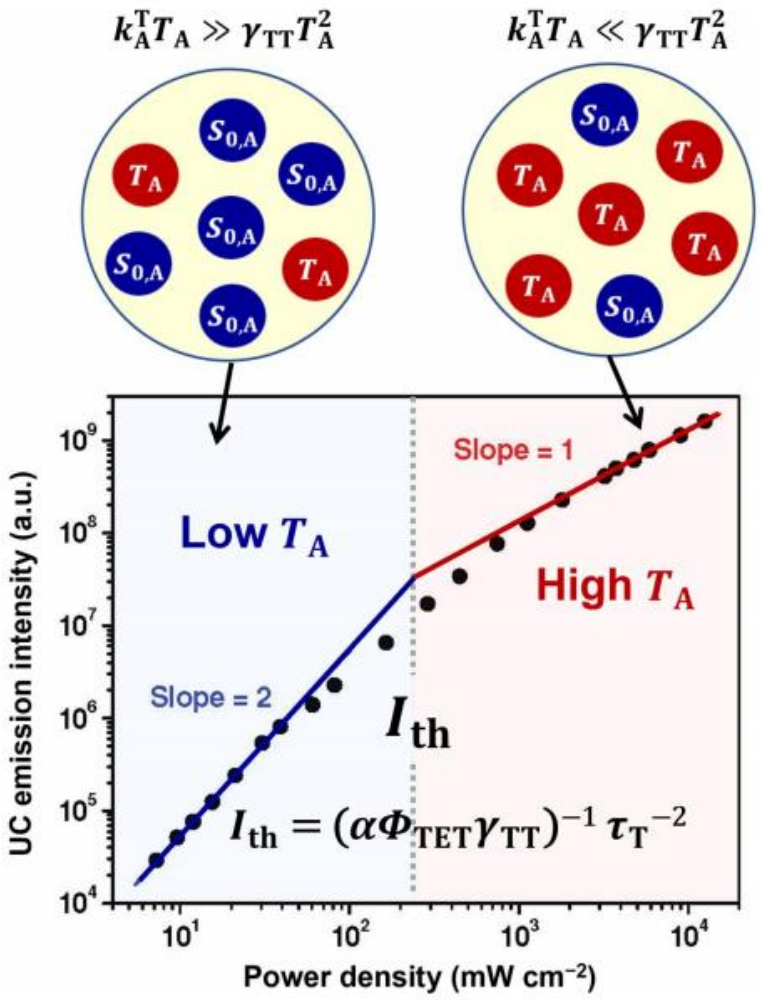


Ir-ref ***Ir-Naph***

$\Phi_{sTTA\text{-}UC}$ %	2.03	3.47
I_{th}/W•cm^{-2}	1.4	0.71



PPO

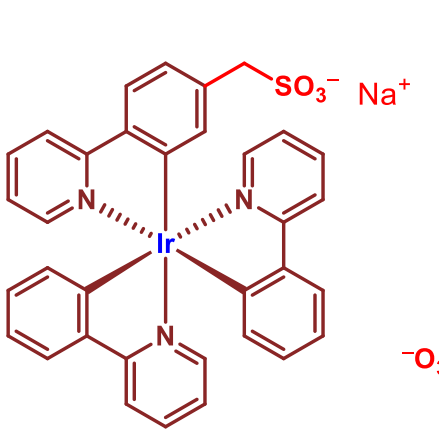


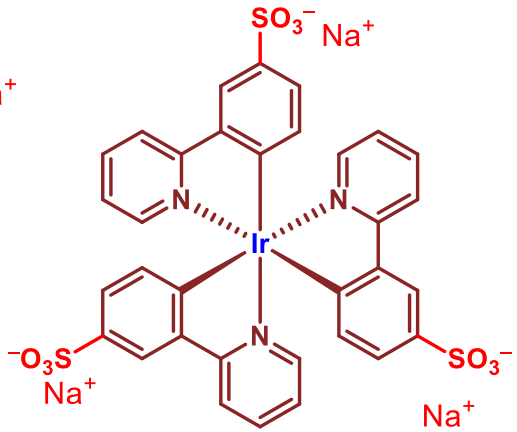
C. Kerzig, N. Yanai, *et al. Angew. Chem. Int. Ed.* **2023**, *62*, e202301506; O. S. Wenger, *et al. J. Am. Chem. Soc.* **2023**, *145*, 11402.

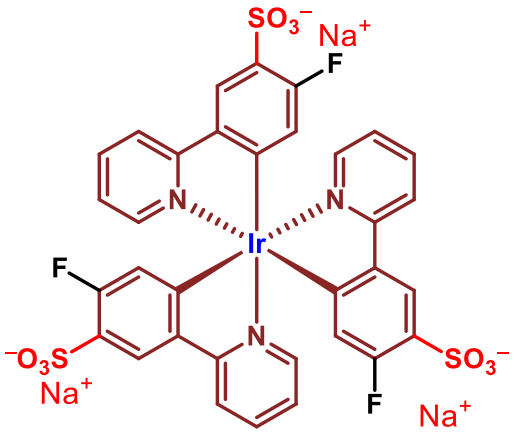
2. TTA-UC中的光敏剂和湮灭剂

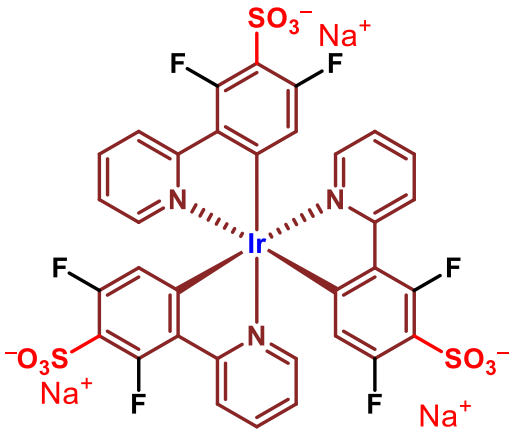
光敏剂改性-改善水溶性

O. S. Wenger, C. Kerzig, et al. 2020:







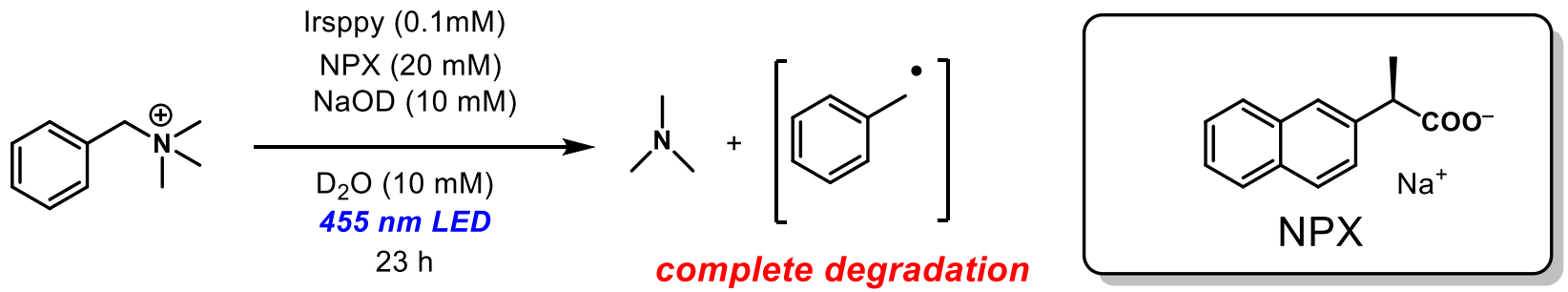


	$Ir(sCH_2ppy)ppy_2$	Irsppy	IrFsppy	IrdFsppy
ε at 447 nm /$M^{-1}cm^{-1}$	2190	1260	490	490
E_T/ eV	2.50	2.65	2.76	2.81
τ_T/ ns	1560	1625	2165	2110

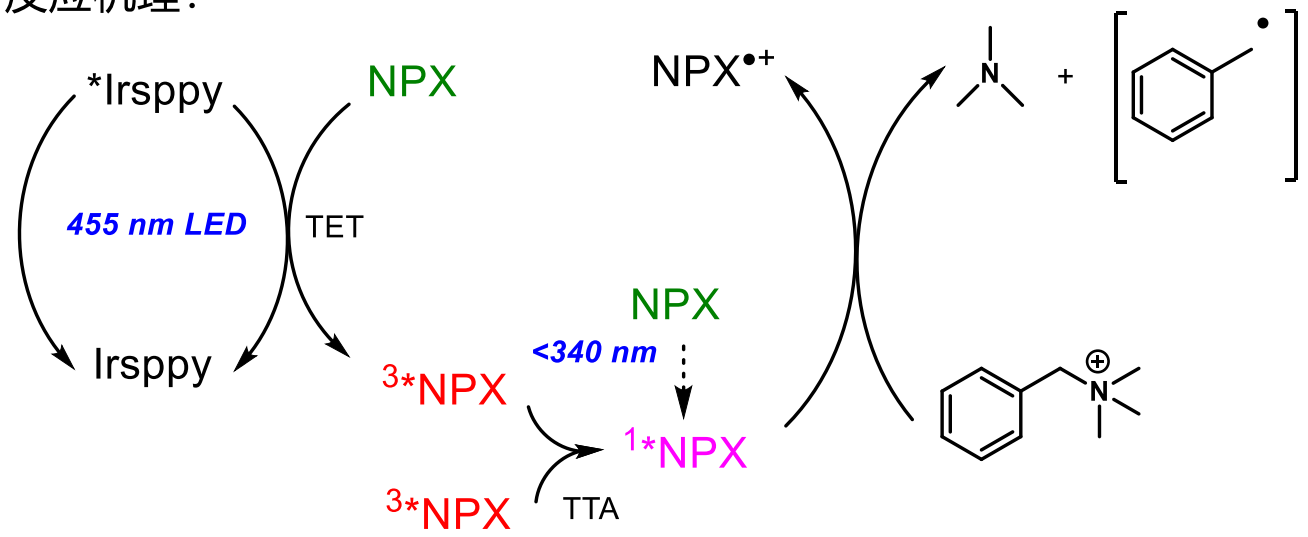
O. S. Wenger, C. Kerzig, *et al. J. Am. Chem. Soc.* **2020**, *142*, 10468.

2. TTA-UC中的光敏剂和湮灭剂

O. S. Wenger, C. Kerzig, et al. 2020:



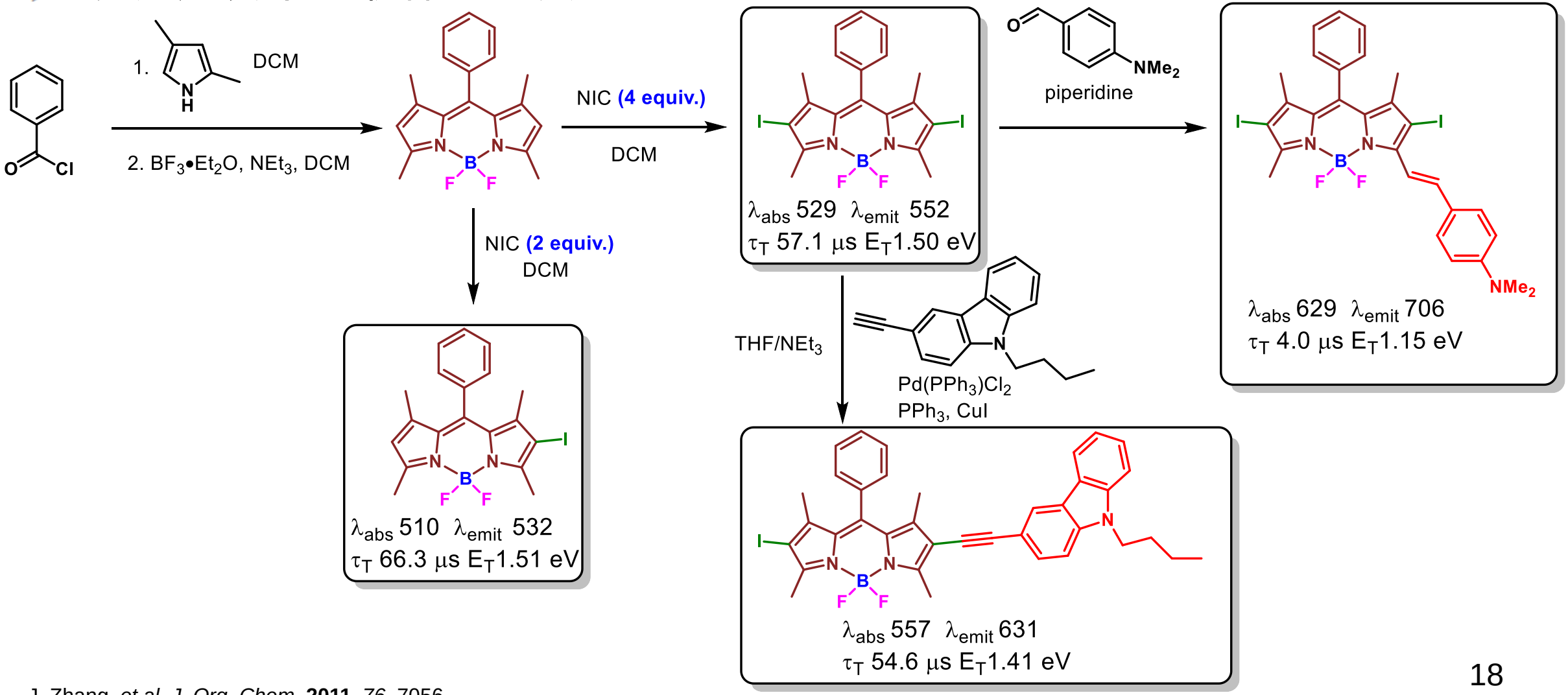
反应机理:



O. S. Wenger, C. Kerzig, *et al. J. Am. Chem. Soc.* **2020**, *142*, 10468.

2. TTA-UC中的光敏剂和湮灭剂

湮灭剂设计-共轭体系的扩大

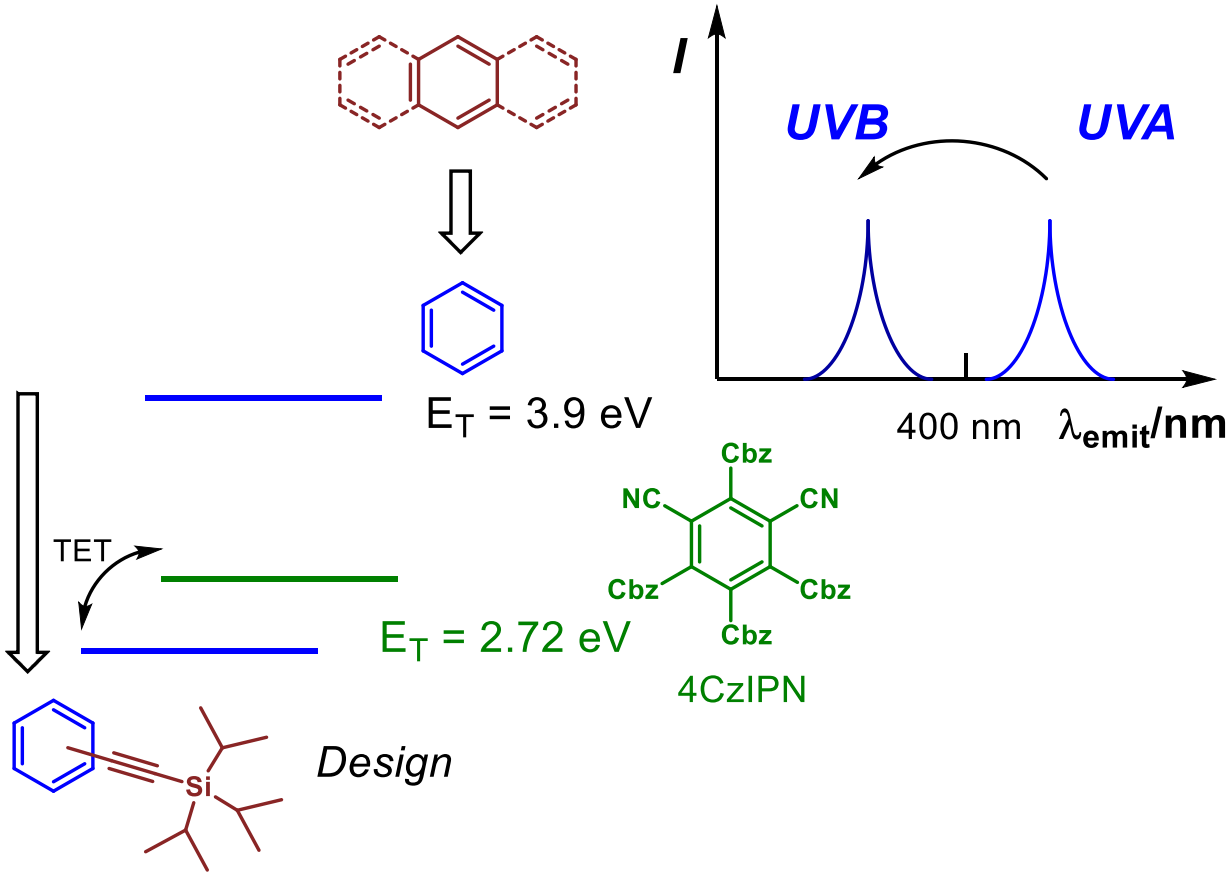


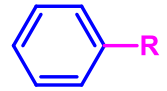
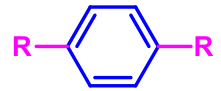
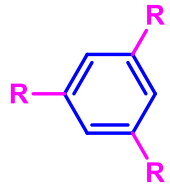
J. Zhang, *et al. J. Org. Chem.* **2011**, *76*, 7056.

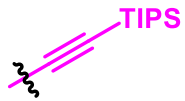
2. TTA-UC中的光敏剂和湮灭剂

湮灭剂设计-引入特定的官能团

2021, Yanai. et al:



Candidate	E_T/eV[a]
	3.06
	2.57
	2.97

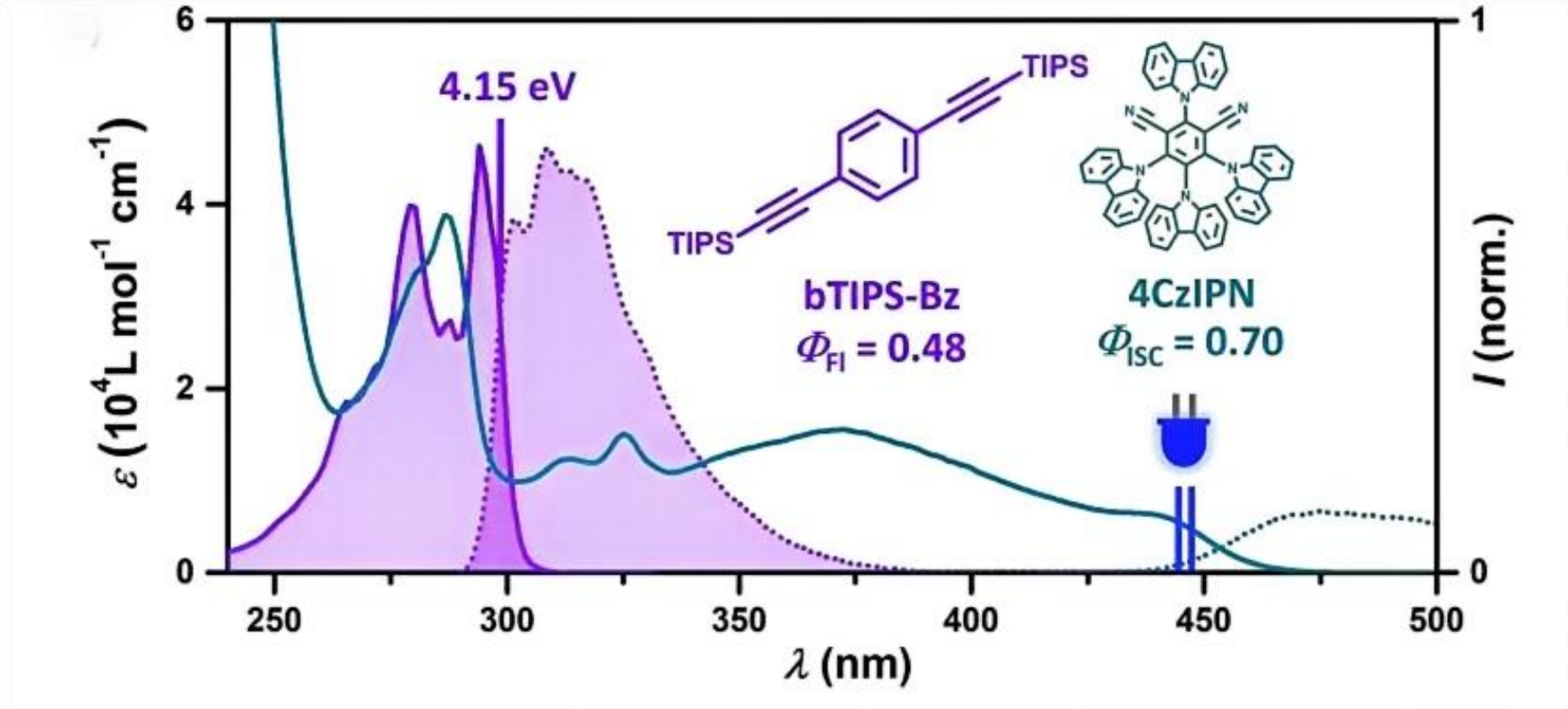
R = 

[a]TD-DFT calculated at B3LYP/6-311+G(d,p) level.

N. Kimizuka, N.Yanai, *et al. Angew. Chem. Int. Ed.* **2021**, *60*, 142;N. Yanai, C. Kerzig, *et al. Angew. Chem. Int. Ed.* **2023**, *62*, e202215340;O. S. Wenger, C. Kerzig, *et al. J. Am. Chem. Soc.* **2020**, *142*, 10468.

2. TTA-UC中的光敏剂和湮灭剂

- 湮灭剂设计-引入特定的官能团



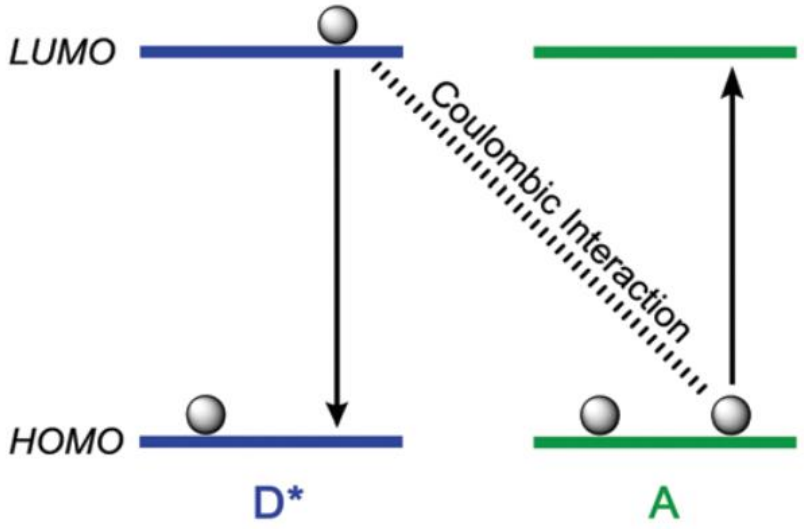
N. Yanai, C. Kerzig, *et al. Angew. Chem. Int. Ed.* **2023**, *62*, e202215340.

CONTENTS

3. TTA-UC参与的有机光反应

3.1 能量传递机制光反应

Fluorescent Resonance Energy Transfer

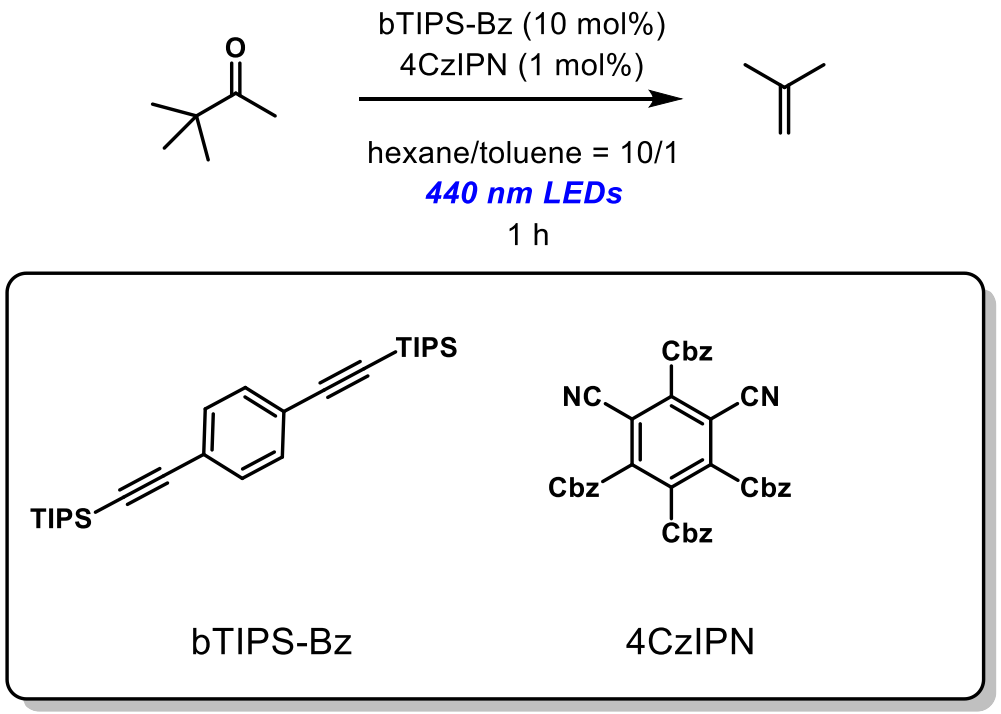


- ✔ ^{1}*A的浓度要求
- ✘ ^{1}*A的Φ_F要求
- ✘ ^{1}*A与底物光谱重叠度要求(少量)
- ✔ Stern-Volmer机理验证

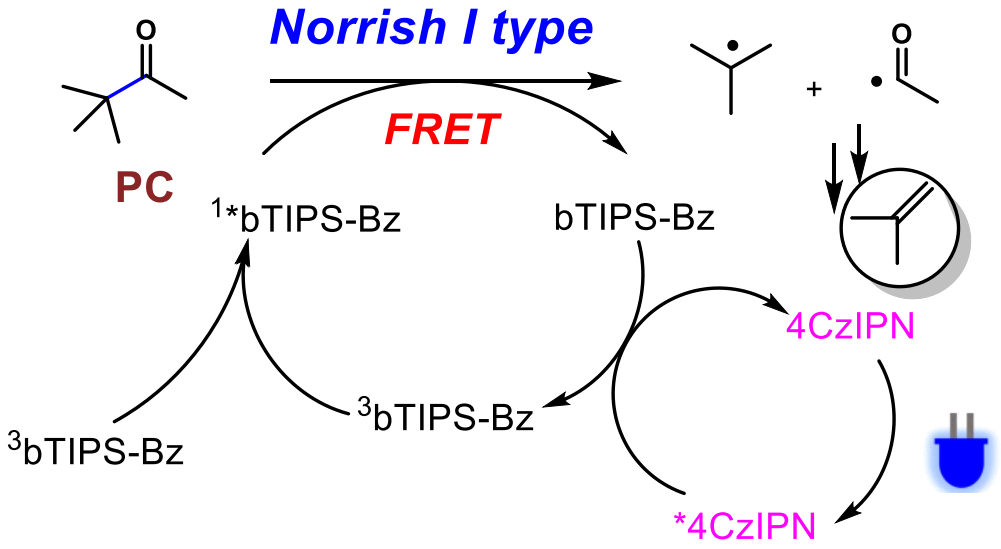
F. Glorius, *et al. Chem. Soc. Rev.* **2018**, *47*, 7190; C. Kerzig, N. Yanai, *et al. Angew. Chem. Int. Ed.* **2023**, *62*, e202301506.

3. TTA-UC参与的有机光反应

N. Yanai, C. Kerzig, et al. 2023:



机理图示

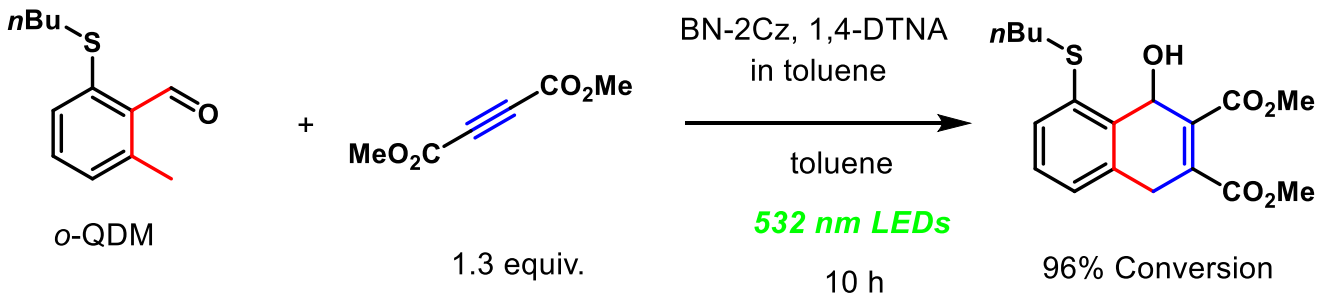


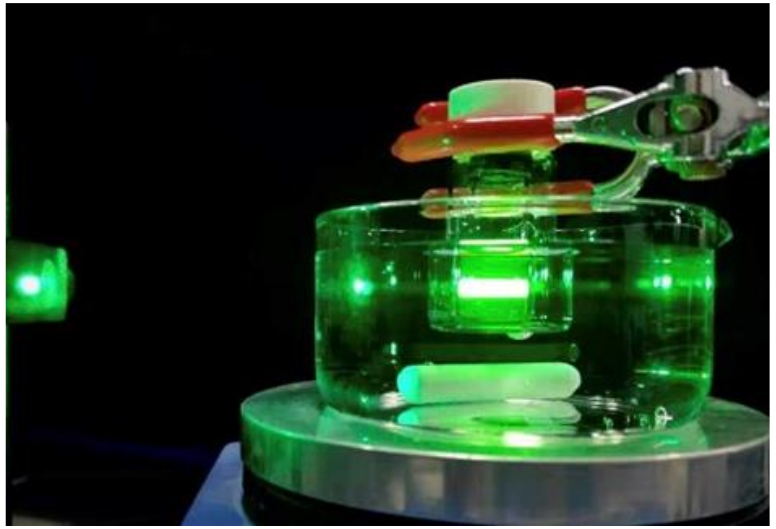
N. Yanai, C. Kerzig, *et al. Angew. Chem. Int. Ed.* **2023**, *62*, e202215340.

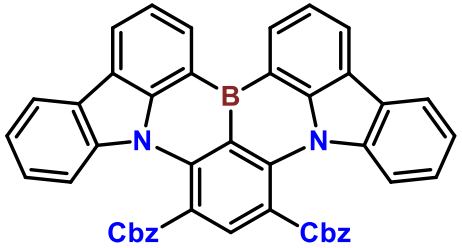
3. TTA-UC参与的有机光反应

辐射能量传递

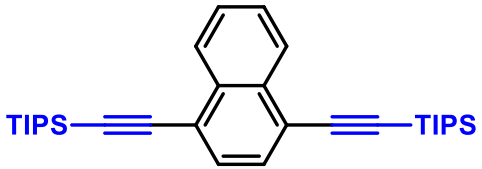
C. Yang, et al. 2022:







BN-2Cz



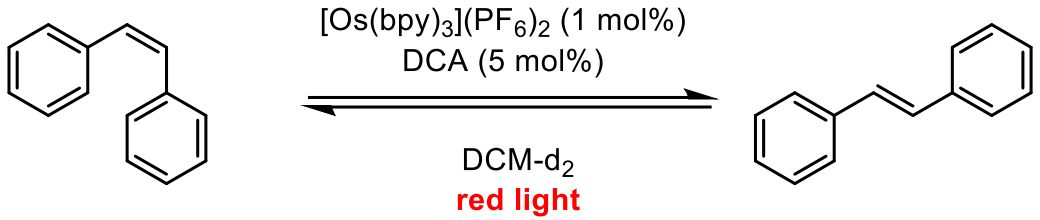
1,4-DTNA

C. Yang, *et al. CCS Chem.***2022**, *4*, 3852.

3. TTA-UC参与的有机光反应

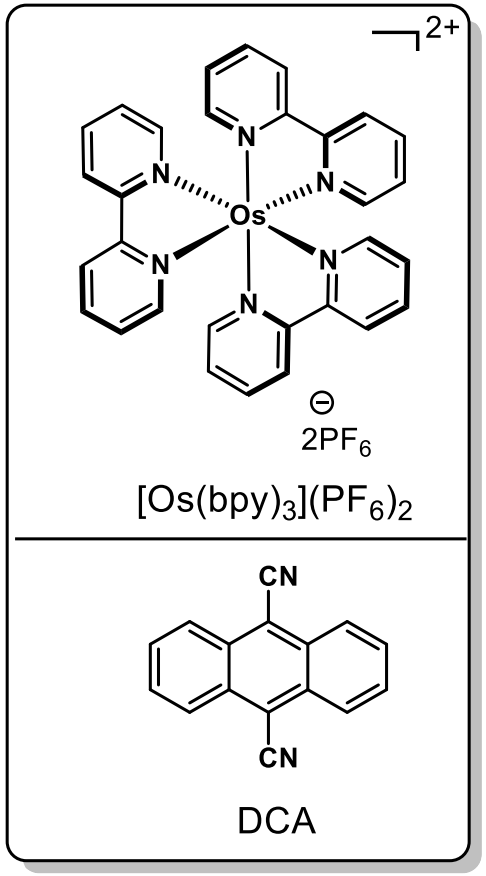
3.2 电子传递机制光反应

O. S. Wenger, et al. 2023:



Entry	Light souce (nm)	Time (h)	NMR yield%
1	635	3	80
2	705	18	50
3[a]	440	1	97

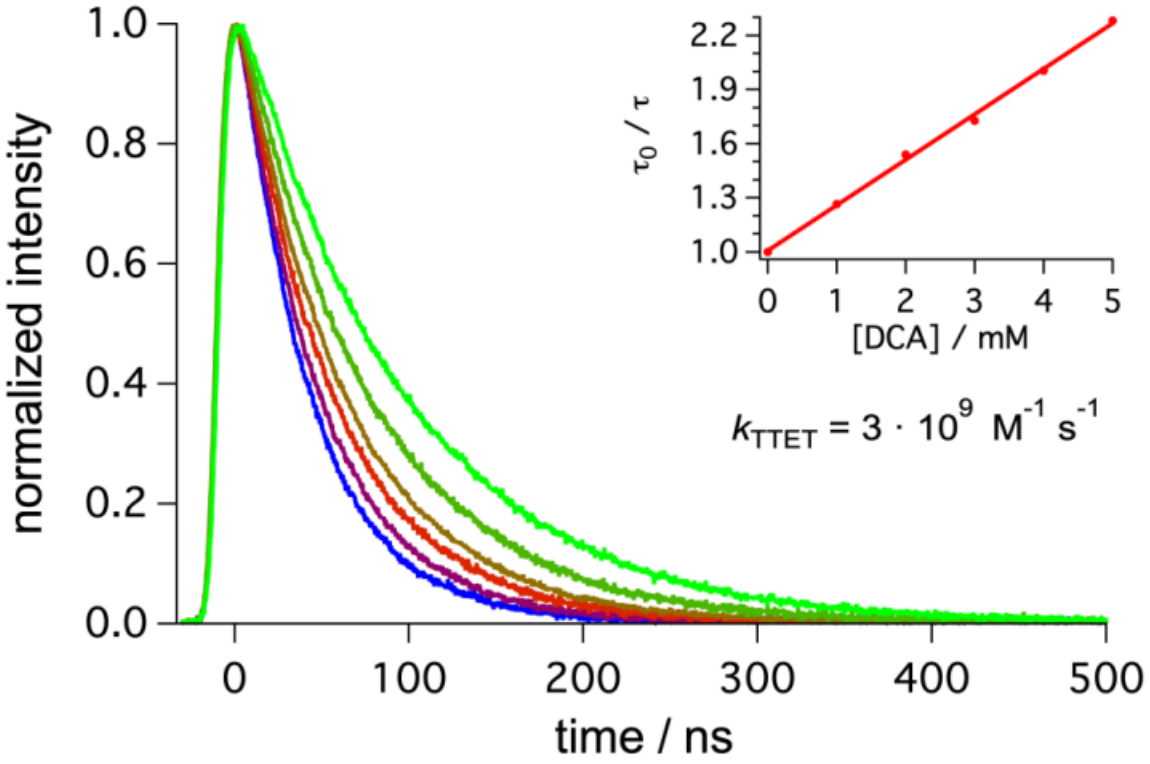
[a]Conditions: Acetonitrile(0.1 M), DCA (5 mol%), rt.



O. S. Wenger, *et al. Chem. Sci.* **2023**, *14*, 149.

3. TTA-UC参与的有机光反应

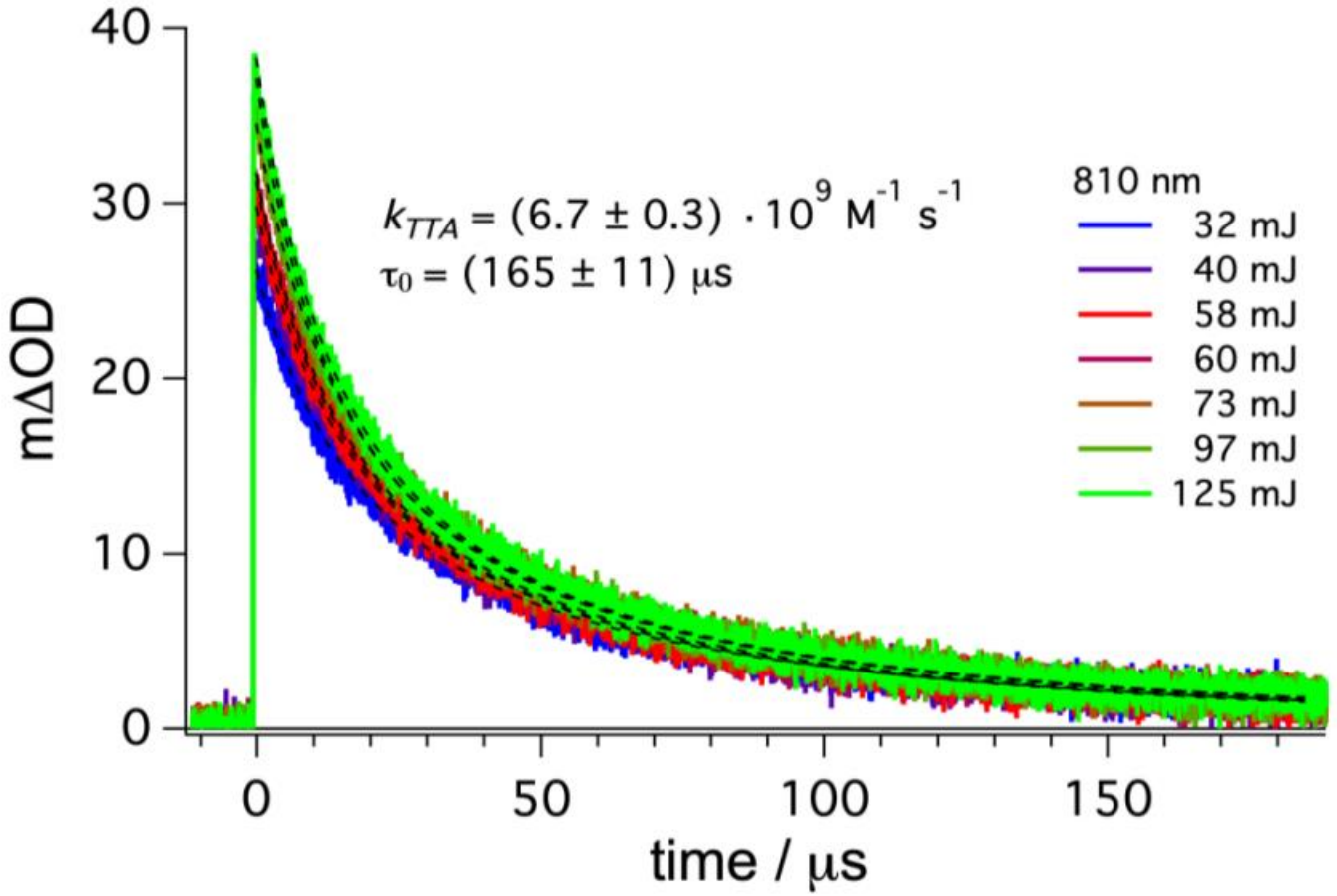
❒ 机理研究



k_{TTET} ^{3}*[Os(bpy)$_3$](PF$_6$)$_2$ by DCA in DCM

O. S. Wenger, *et al. Chem. Sci.* **2023**, *14*, 149.

3. TTA-UC参与的有机光反应



$$\frac{dA}{dt} = -k_T A - k_{TTA} A^2$$

$$\Delta A = \frac{\Delta A_0 \cdot (1-\beta)}{\exp(k_T \cdot t) - \beta}$$

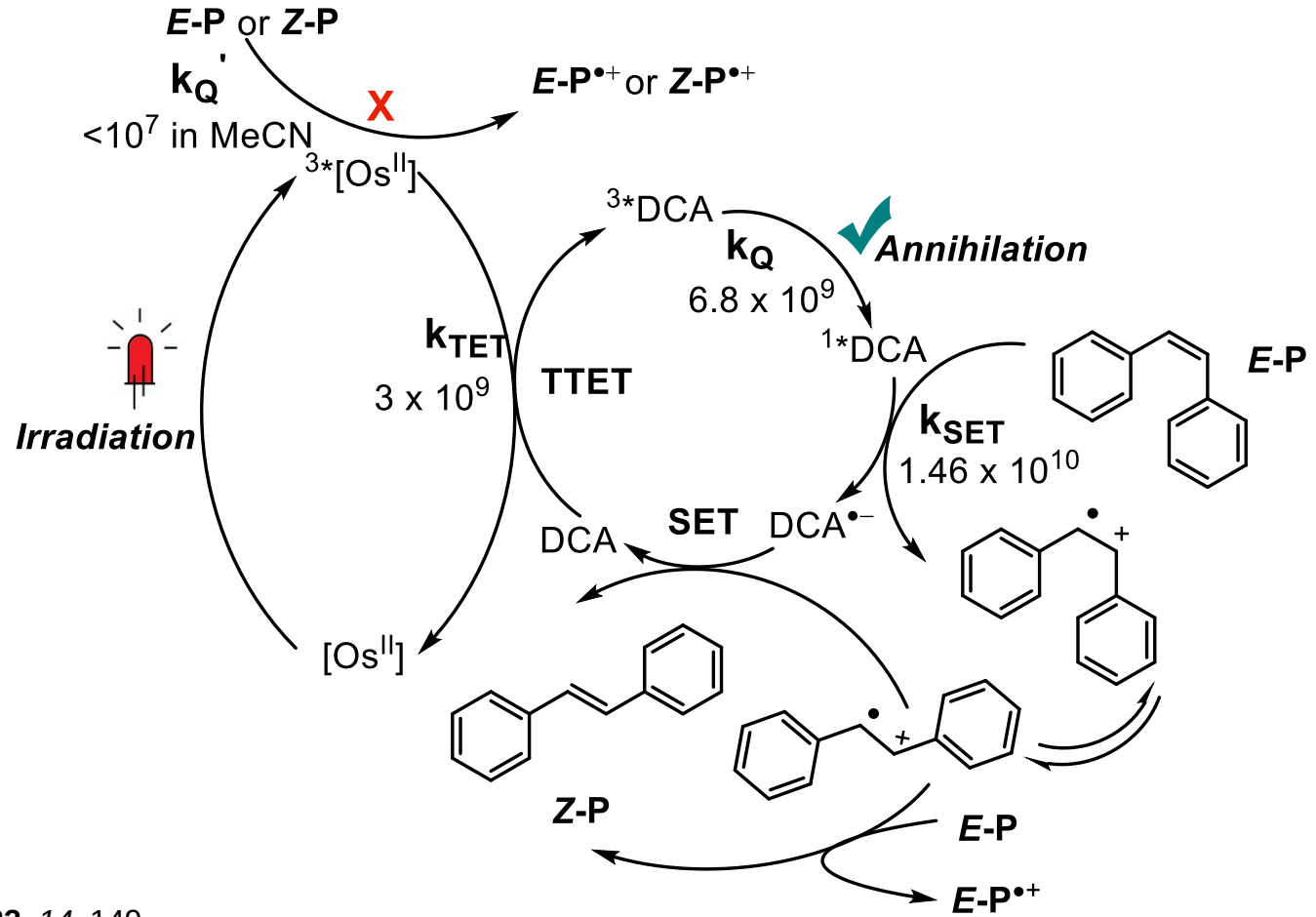
$$\beta = \frac{k_{TTA} \cdot [^3A]_0}{k_{TTA} \cdot [^3A]_0 + k_T}$$

Power-dependent decay of ^{3}*DCA in DCM

O. S. Wenger, *et al. Chem. Sci.* **2023**, *14*, 149.

3. TTA-UC参与的有机光反应

❒ 可能机理

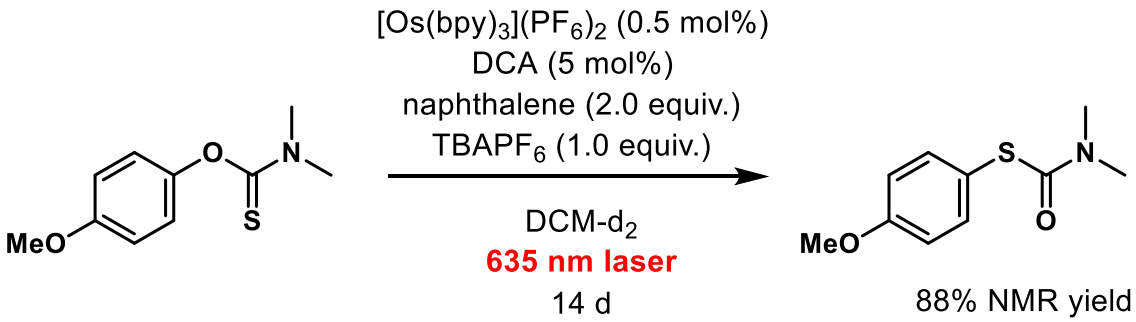


O. S. Wenger, *et al. Chem. Sci.* **2023**, *14*, 149.

3. TTA-UC参与的有机光反应

3.2 电子传递机制光反应

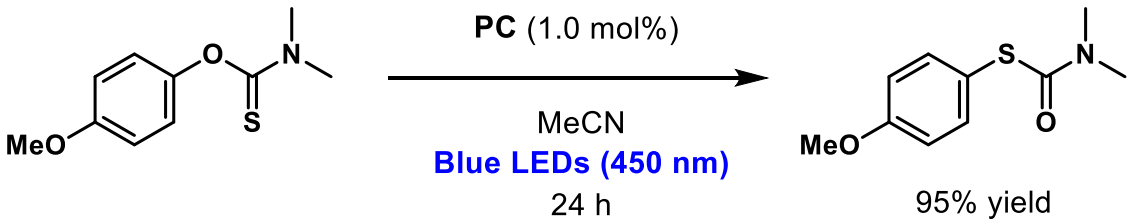
O. S. Wenger, et al. 2023:



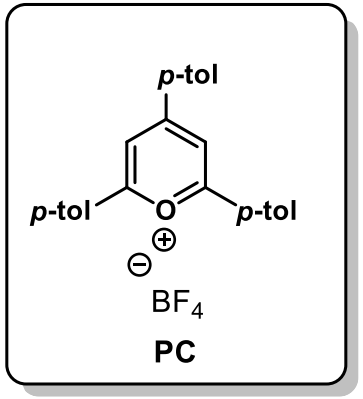
88% NMR yield

非上转化版本

D. Nicewicz, et al. 2015:



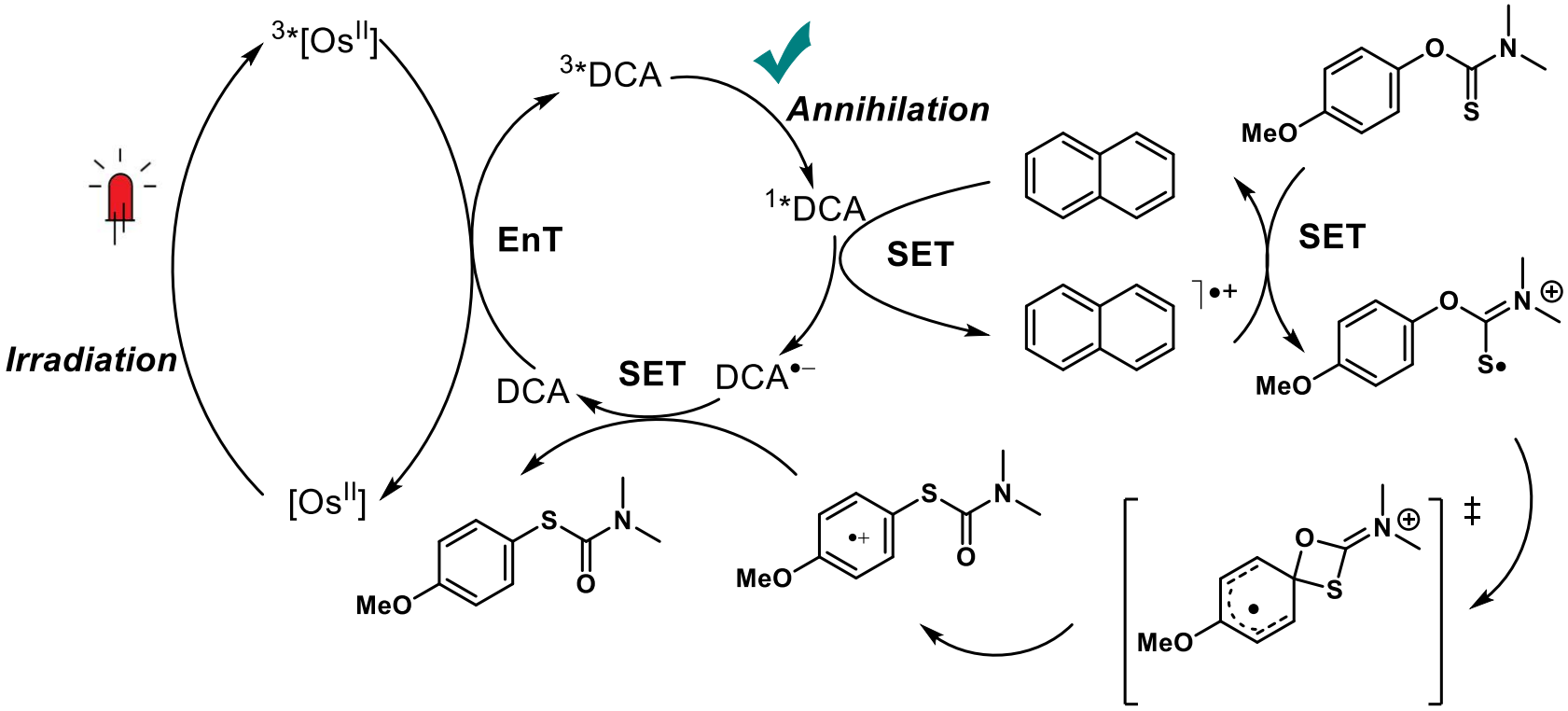
95% yield



O. S. Wenger, *et al. Chem. Sci.* **2023**, *14*, 149; D. Nicewicz, *et al. J. Am. Chem. Soc.* **2015**, *137*, 15684.

3. TTA-UC参与的有机光反应

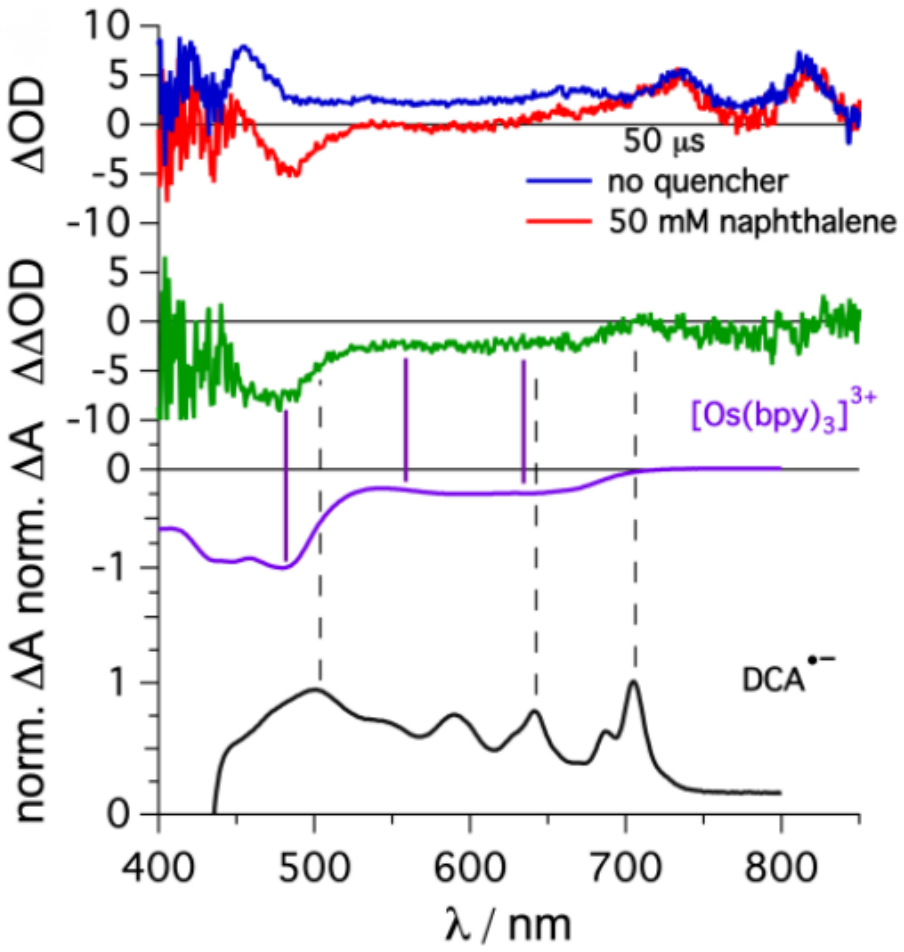
❒ 可能机理



O. S. Wenger, *et al. Chem. Sci.* **2023**, *14*, 149.

3. TTA-UC参与的有机光反应

- 可能机理



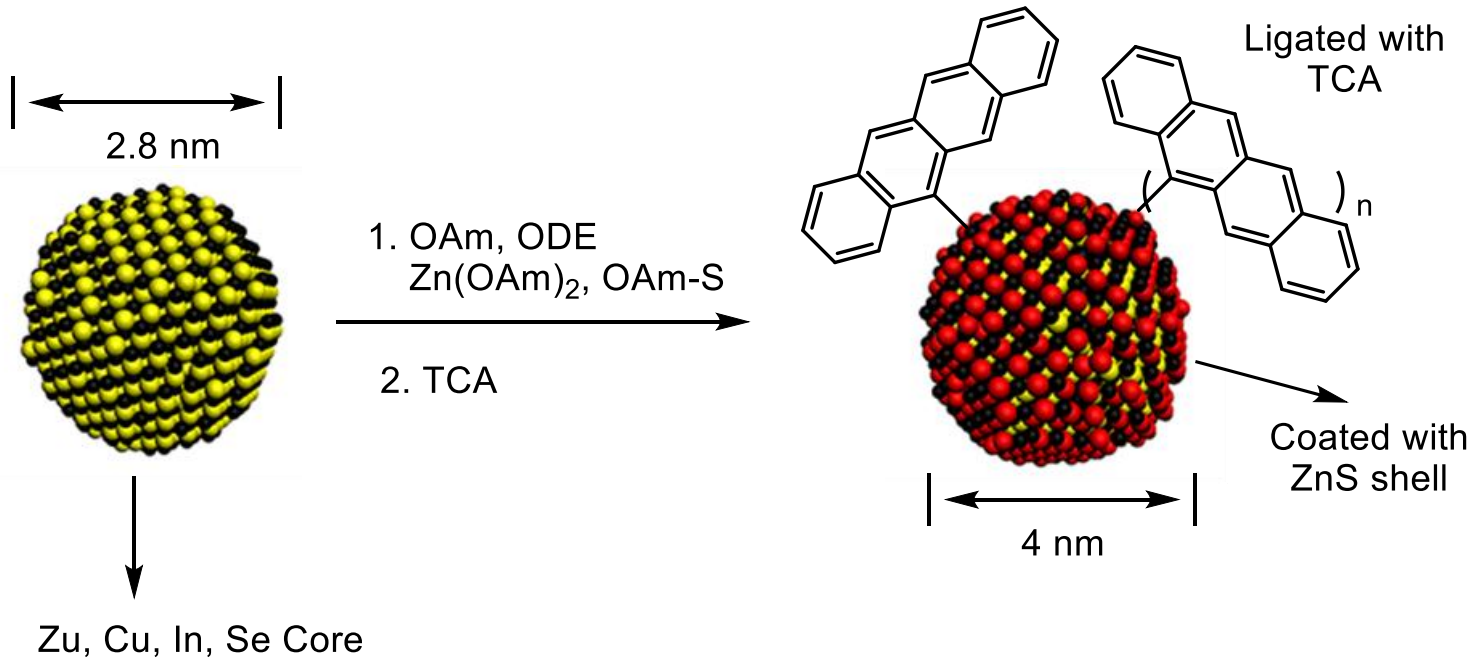
$Os(bpy)_3^{3+}$存在的证据

O. S. Wenger, *et al. Chem. Sci.* **2023**, *14*, 149.

3. TTA-UC参与的有机光反应

3.2 电子传递机制光反应（量子点-光敏剂）

ZCISe-TCA量子点

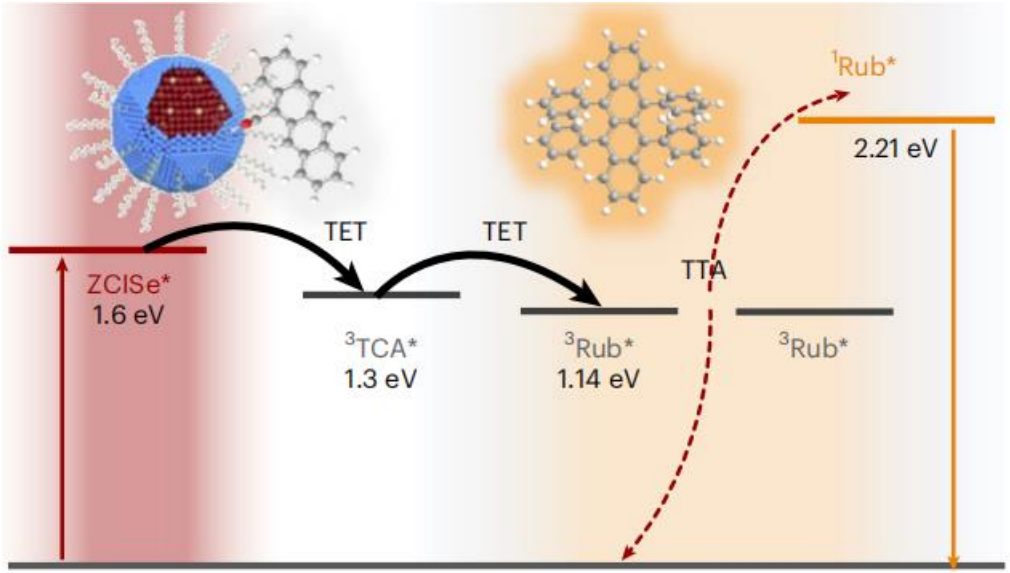


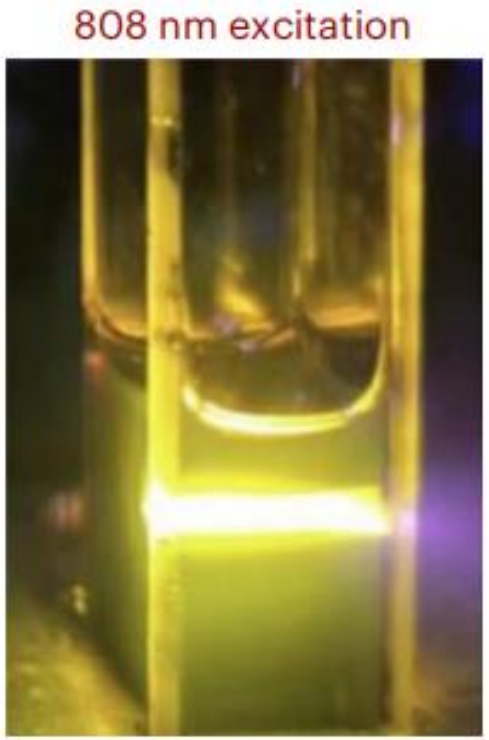
K. Wu, *et al. Nat. Photon.* **2023**, *17*, 346.

3. TTA-UC参与的有机光反应

3.2 电子传递机制光反应（量子点-光敏剂）

- 能量传递传递机制



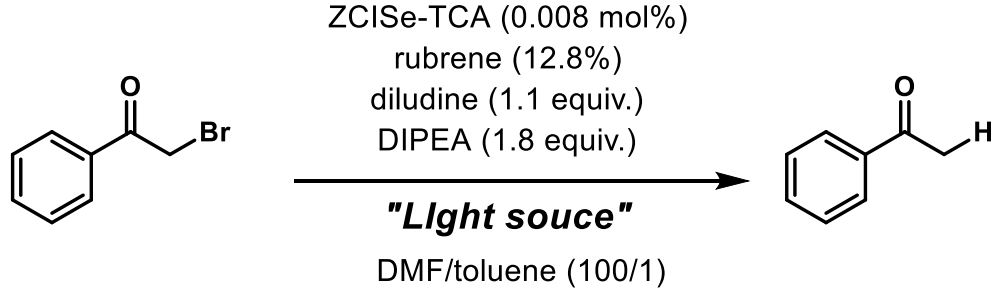


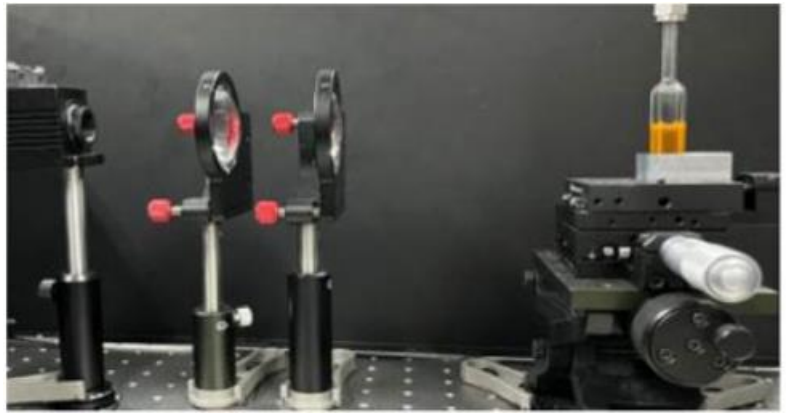
K. Wu, *et al. Nat. Photon.* **2023**, *17*, 346.

3. TTA-UC参与的有机光反应

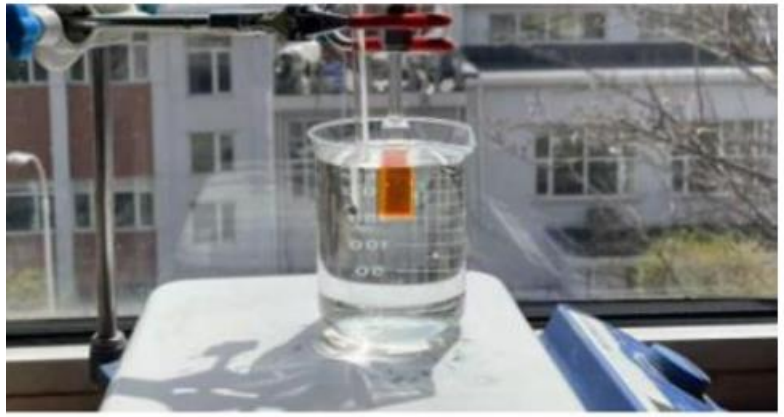
3.2 电子传递机制光反应（量子点-光敏剂）

K. Wu, et al. 2023:





Enrtry	Light souce	Reaction time	GC-MS Yield(%)
1	808 nm	8 h	> 99
2	532 nm "Eosin Y"	8 h	> 99
3	Sunlight	1 h	91
4	Sunlight "Eosin Y"	1 h	18

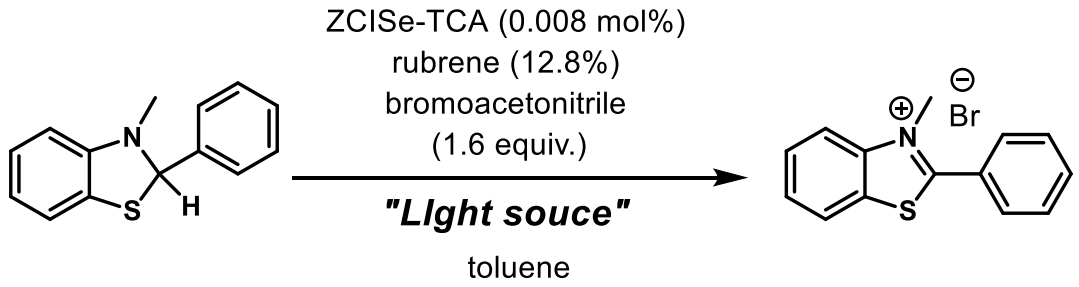


K. Wu, *et al. Nat. Photon.* **2023**, *17*, 346.

3. TTA-UC参与的有机光反应

3.2 电子传递机制光反应（量子点-光敏剂）

K. Wu, et al. 2023:



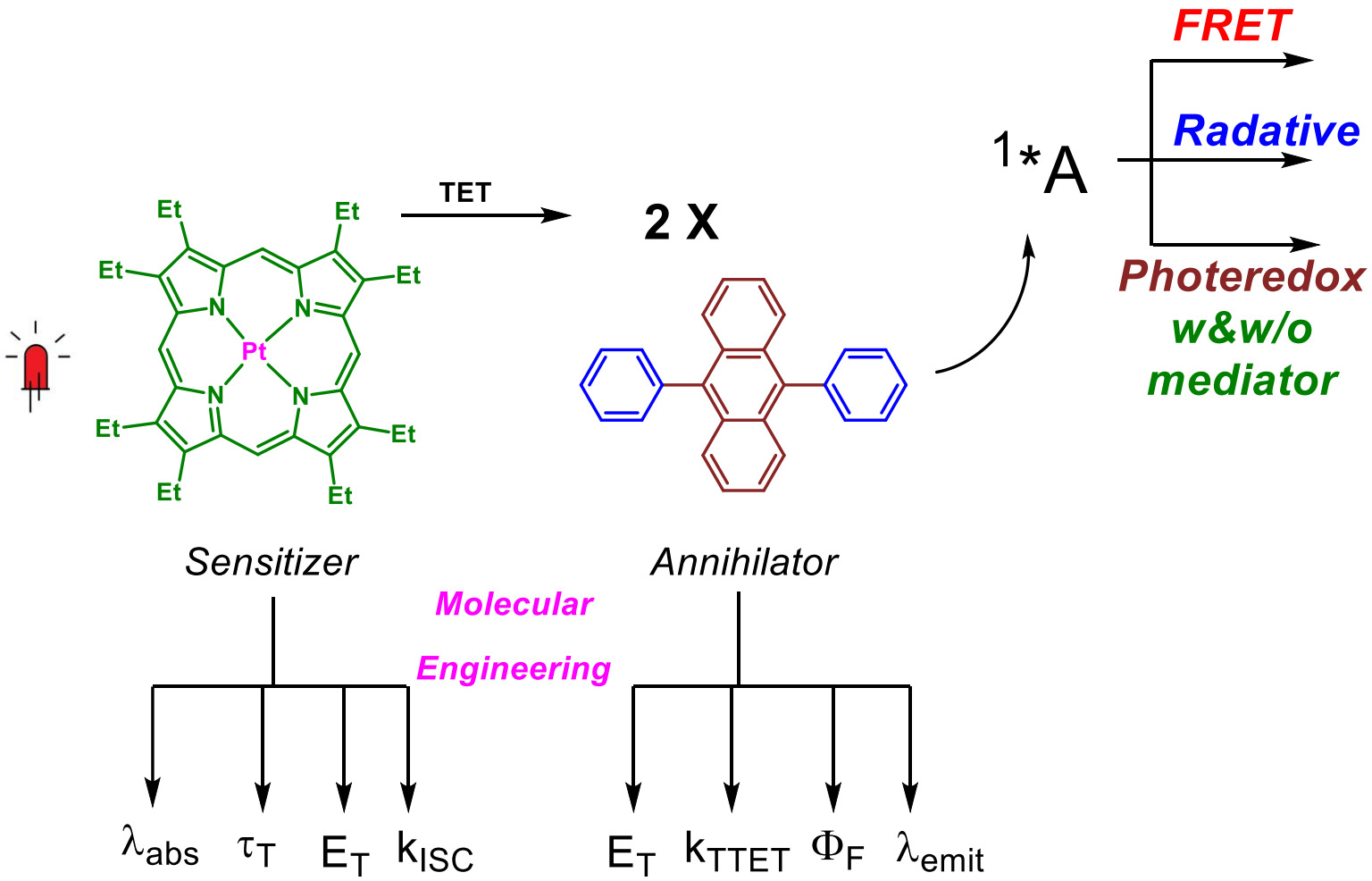
Enrtry	Light souce	Reaction time	GC-MS Yield(%)
1	808 nm	8 h	89
2	532 nm "Rose Bengal"	8 h	> 99
3	Sunlight	2 h	95
4	Sunlight "Rose Bengal"	2 h	55

K. Wu, *et al. Nat. Photon.* **2023**, *17*, 346.

CONTENTS

4. 总结与展望

总结

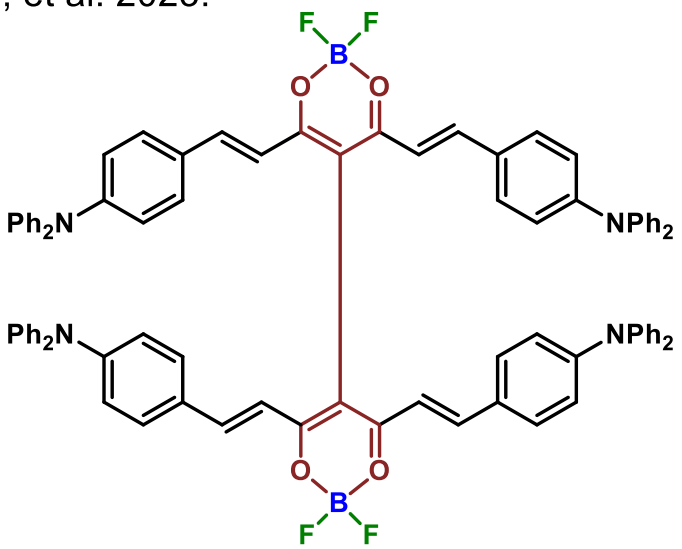

TET
2 X
1*A
FRET
Radative
Photeredox
w&w/o
mediator
Et
Pt
N
Sensitizer
Annihilator
Molecular
Engineering
λ_{abs} τ_T E_T k_{ISC}
E_T k_{TTET} Φ_F λ_{emit}

4. 总结与展望

未来展望

- 开发新的光敏剂（无金属发色团&新型量子点）

S. Ji, et al. 2023:



λ_{abs} 651 nm, E_T 1.5 eV

NIR吸收

ISC性质

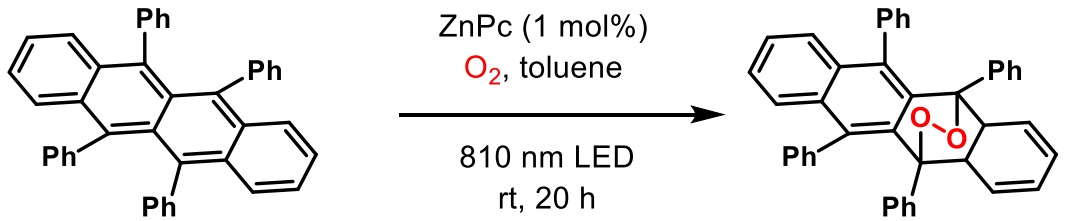
G. Han, *et al. Nat. Rev.Lett.* **2024**, *8*, 238; S. Ji, *et al. Chin. Chem. Lett.* **2023**, *34*, *107515.*

4. 总结与展望

设计新的湮灭剂分子骨架

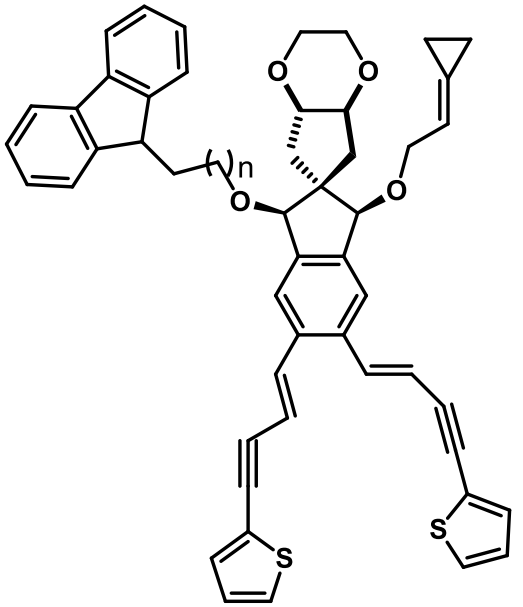
共轭体系增大带来稳定性问题

T. Furuyama, et al. 2022:

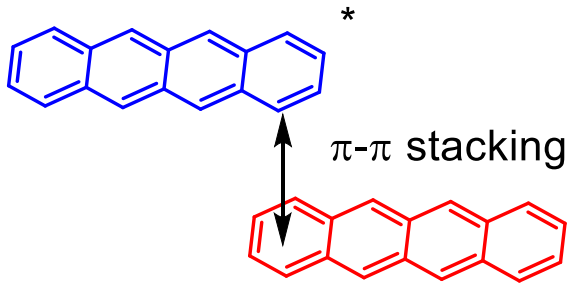


99% yield

新的核心骨架



π-π堆积带来荧光淬灭



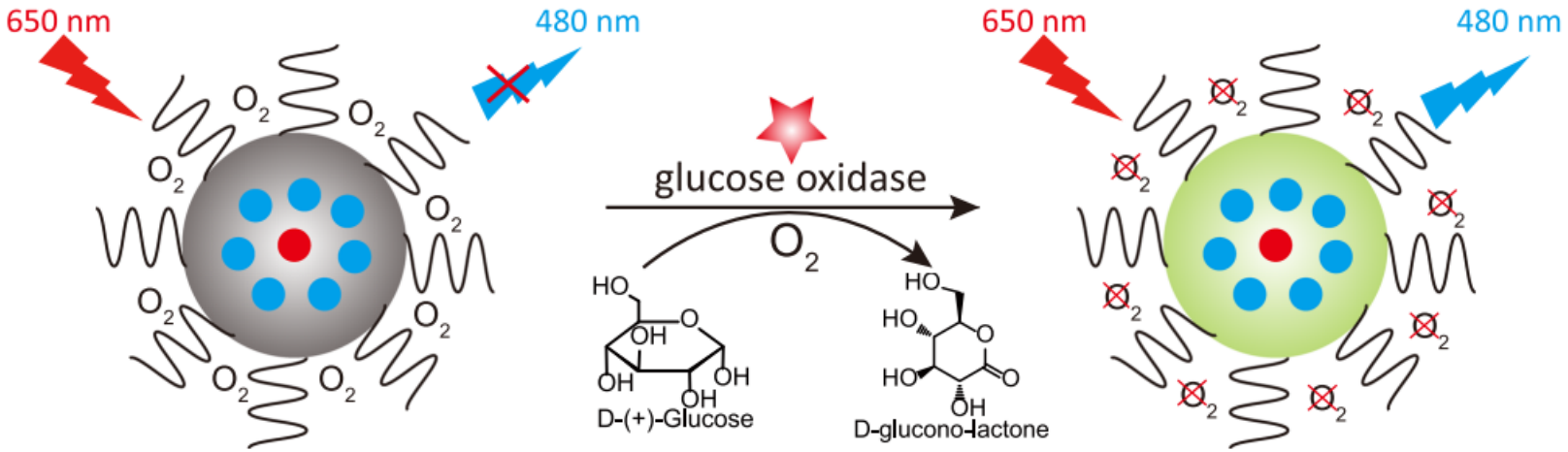
G. Han, *et al. Nat. Rev.Lett.* **2024**, *8*, 238; T. Furuyama, et al. *Chem. Eur. J.* **2022**, *28*, e202103223.

4. 总结与展望

开辟新的下游应用

结合酶促反应作分子探针

G. Han, et al. 2021:



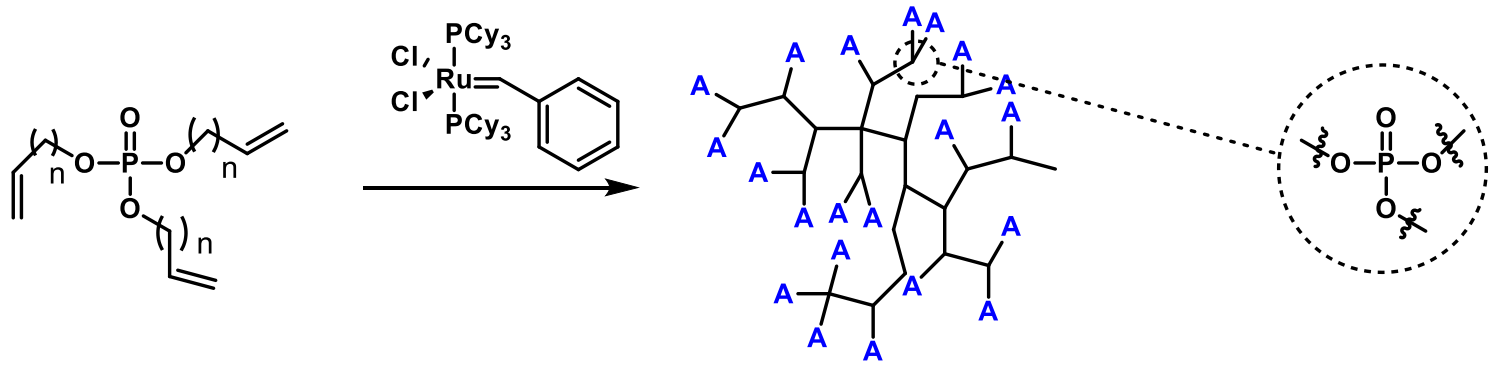
G. Han, *et al. Nat. Rev.Lett.* **2024**, *8*, 238; G. Han , et al. *Nat. Commun.* **2021**, *12*, 1898.

4. 总结与展望

开辟新的下游应用

开发O_2惰性体系

F. R. Wurm, et al. 2014:



高聚物Matrix
兼容上转化体系-清除$^1*O_2$

G. Han, *et al. Nat. Rev.Lett.* **2024**, *8*, 238; F. R. Wurm, *et al. J. Am. Chem. Soc.* **2014**, *136*, 11057.

请各位老师同学批评指正

2. TTA-UC中的光敏剂和淬灭剂

光敏剂改性-配体调控（一）

$$\partial T_S/\partial t = \alpha I_{exc} - k_S^T T_S - k_{tr} T_S$$

$$\partial T_A/\partial t = k_{tr} T_S - k_A^T T_A - \gamma_{TT} T_A^2$$

$$\partial S_A/\partial t = 0.5 f \gamma_{TT} T_A^2 - k_A^S S_A$$

$$k_A^T T_A \gg \gamma_{TT} T_A^2$$

$$S_A = 0.5 f \frac{\gamma_{TT}}{k_A^S} \left[\frac{k_{tr}/k_A^T}{k_S^T + k_{tr}} \right]^2 (\alpha I_{exc})^2 \propto \boldsymbol{I}_{\mathbf{exc}}^2$$

$$k_A^T T_A \ll \gamma_{TT} T_A^2$$

$$S_A = 0.5 f \frac{1}{k_A^S} \left[\frac{k_{tr}}{k_S^T + k_{tr}} \right] \alpha I_{exc} \propto \boldsymbol{I}_{\mathbf{exc}}$$

$$I_{th} = (\alpha \gamma_{TT})^{-1} \left[\frac{k_{tr}}{k_S^T + k_{tr}} \right]^{-1} (k_A^T)^2 = (\alpha \Phi_{TET} \gamma_{TT})^{-1} \tau_T^{-2}$$