Triplet-Triplet Annihilation Based Photon Upconversion

Literature Seminar #1

B4 Yuri Katayama

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1. Introduction

2. Applications -photocatalysis
   -biological applications

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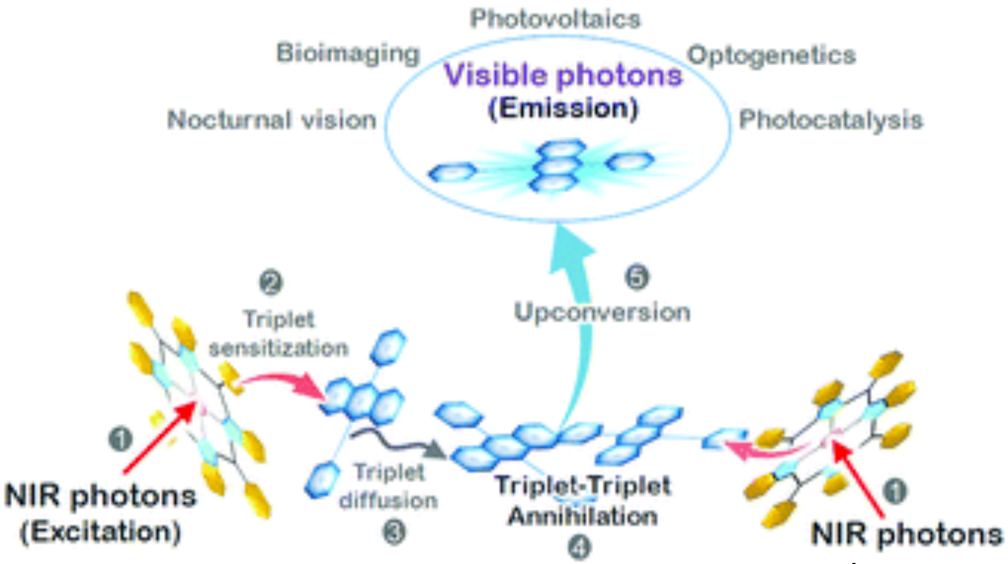
4. Summary

What is TTA-UC ?

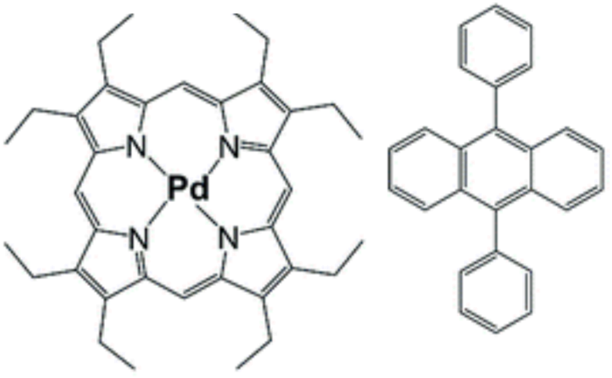
- ➢TTA-UC = triplet-triplet annihilation photon upconversion
- ➢Photochemical phenomenon
- ➢Low energy photons are converted to high energy photons.
- ➢Energy transfer processes occur.



The main casts

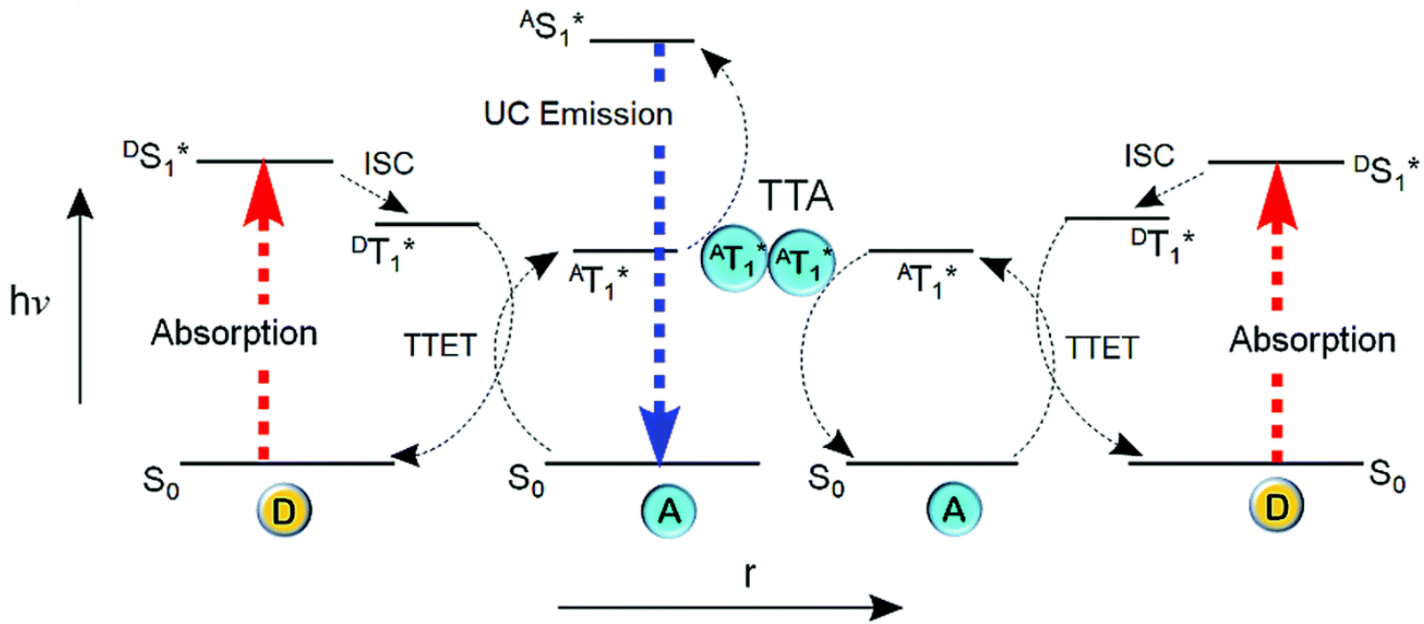
Sensitizer & Annihilator

ex.



P. Bharmonia *et al., Chem. Soc. Rev.*, **2020**, 49, 6529.

Mechanism



P. Bharmonia *et al., Chem. Soc. Rev.,* **2020**, 49, 6529.

D = donor = sensitizer

A = acceptor = annihilator

ISC = intersystem crossing

TTET = triplet-triplet energy transfer

TTA = triplet-triplet annihilation

TTET and TTA occur through electron exchange *via* Dexter energy transfer mechanism.

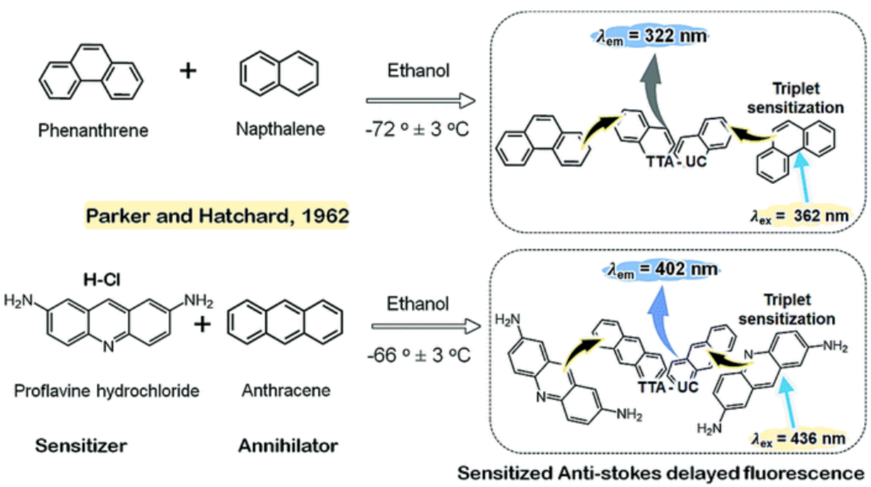
Sensitized anti-Stokes delayed fluorescence

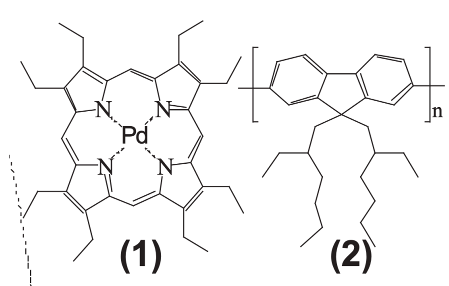
History of TTA-UC

1962 Sensitized anti-Stokes delayed fluorescence by Parker and Hatchard

2003 TTA-UC at r.t. by Baluschev

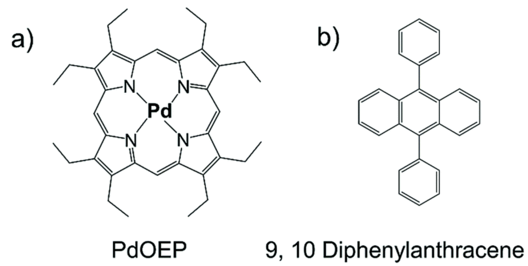
2006 Green to blue UC by non-coherent green sunlight by Baluschev



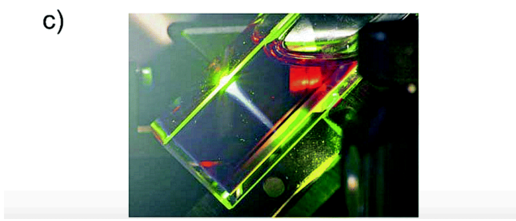


PdOEP PF2/6

2003. Baluschev



c)



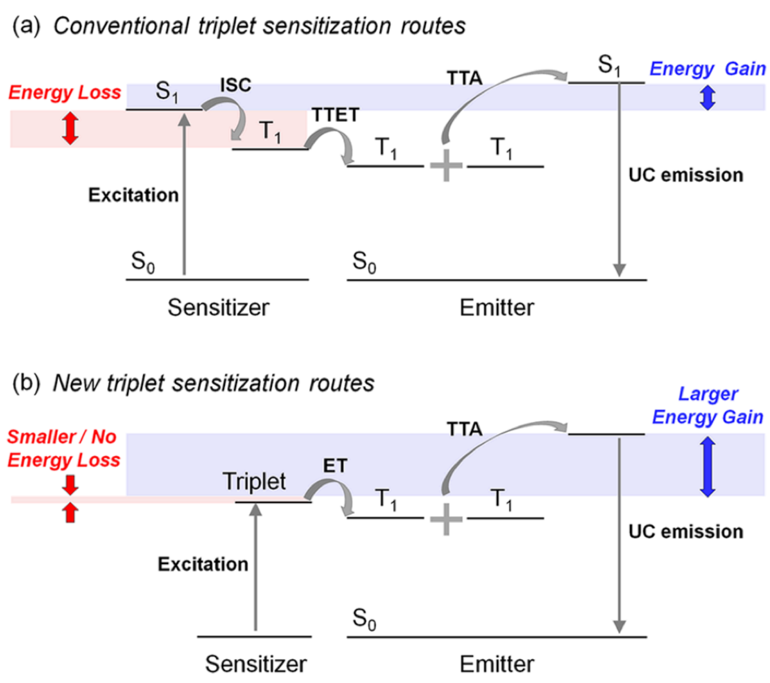
2006. Baluschev

P. Bharmonia *et al., Chem. Soc. Rev.,* **2020**, 49, 6529.
S. Baluschev *et al., Adv. Mater.*,**2003**, 15, 2095.

Recent breakthroughs 2015-2020

<u>New directions in NIR to Vis molecular TTA-UC</u>

- Inorganic-organic hybrid NIR to Vis molecular TTA-UC
- Lanthanide-organic complex sensitizer based NIR to Vis molecular TTA-UC
- NIR to Vis molecular TTA-UC in liquid crystals
- Direct S_0-to-T_1 absorbing sensitizer based NIR to Vis molecular TTA-UC introduced by Kimizuka and Yanai's research groups at Kyushu Univ. in 2016
  ↪Discussed later



P. Bharmonia *et al., Chem. Soc. Rev.,* **2020**, 49, 6529.

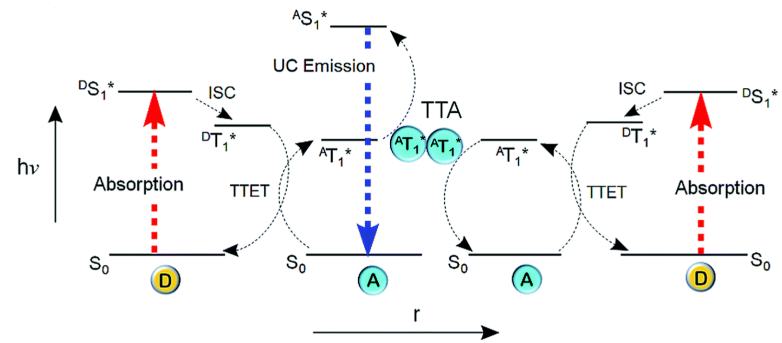
N. Yanai and N. Kimizuka, *Acc. Chem. Res.*, **2017**, *50*, 2487.

Parameters of evaluating TTA-UC

ΔE_{UC} : anti-Stokes shift <unit = eV>

I_{th} : threshold excitation intensity <unit = W cm^{-2} >

Φ_{UC} : upconversion quantum yield <unit = %>



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

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

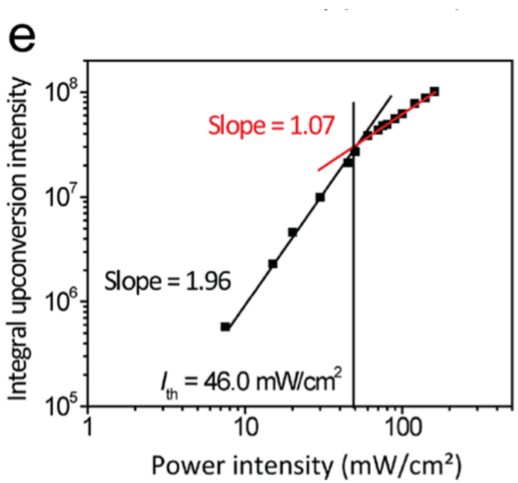
※ in some cases, η_{UC} used as Φ_{UC}

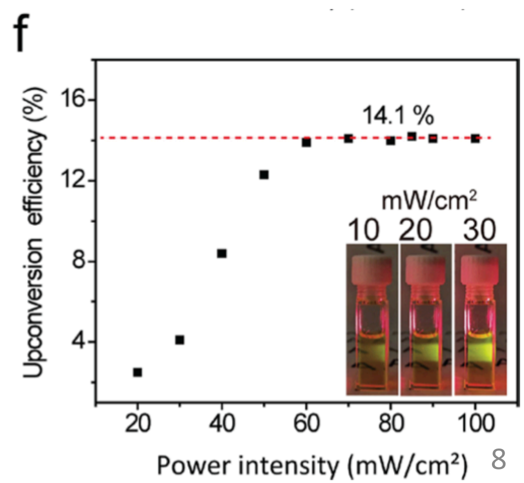
f : Spin statistical factor
the probability of getting excited singlet state after annihilation of two triplet *via* TTA

P. Bharmonia *et al., Chem. Soc. Rev.*, **2020**, 49, 6529.

ex. PdTNP(sen)/Py5(ann)

λ_{ex} = 720 nm (1.72 eV)
λ_{em} = 570 nm (2.18 eV)
ΔE_{UC} = 0.45 eV (720 to 570 nm)





Han, G. *et al., J. Am. Chem. Soc.*, **2020**, *142*, 18460.

Advantages and applications

Advantages

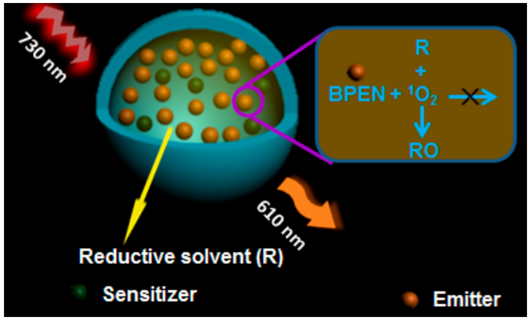
✓ Lower excitation intensity of non-coherent light ↔ conventional UC ; two photon absorption UC, inorganic materials, nanoparticles

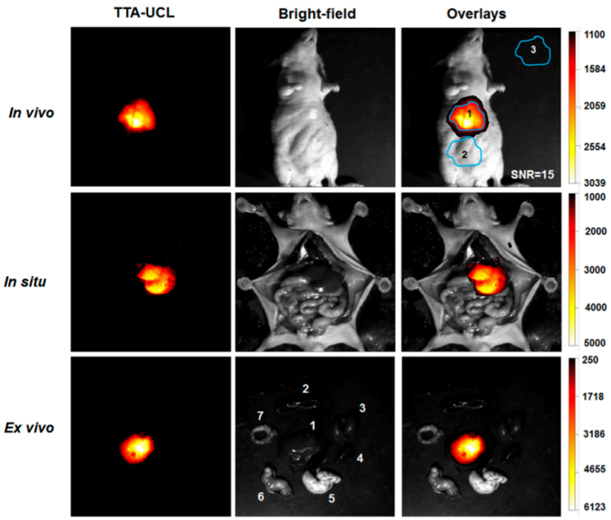
✓ Lower energy

✓ Deep-tissue penetration of NIR

Applications

- Photovoltaics
- Bioimaging
- Photocatalysis
- Photodynamic therapy
- Sensing
- Optogenetics





P. Bharmonia *et al.*, *Chem. Soc. Rev.*, **2020**, 49, 6529.
F. Li *et al.*, *ACS Appl. Mater. Interfaces*, **2018**, *10*, 9883.

Contents

Photochemical reactions via TTA-UC

<u>Background</u>

- UV or Vis photoredox reactions

  × the penetration depth of visible light is low→ × large-scale reactions.

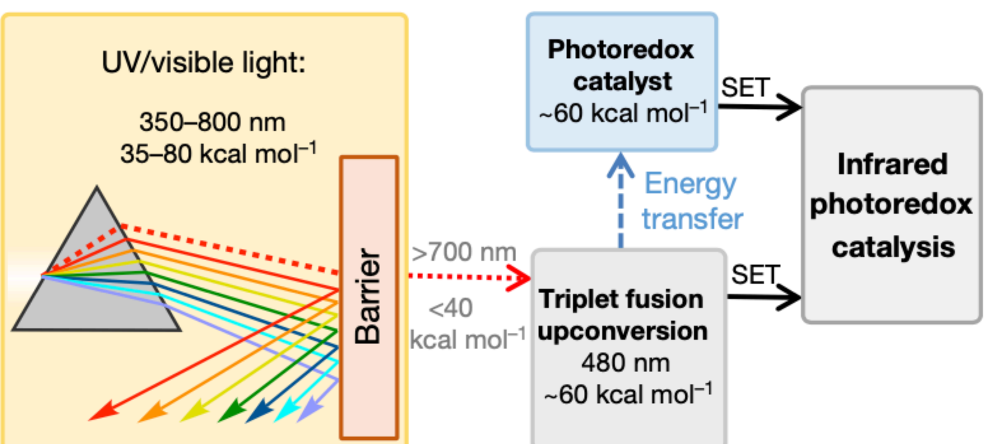
  × Need of high energy.

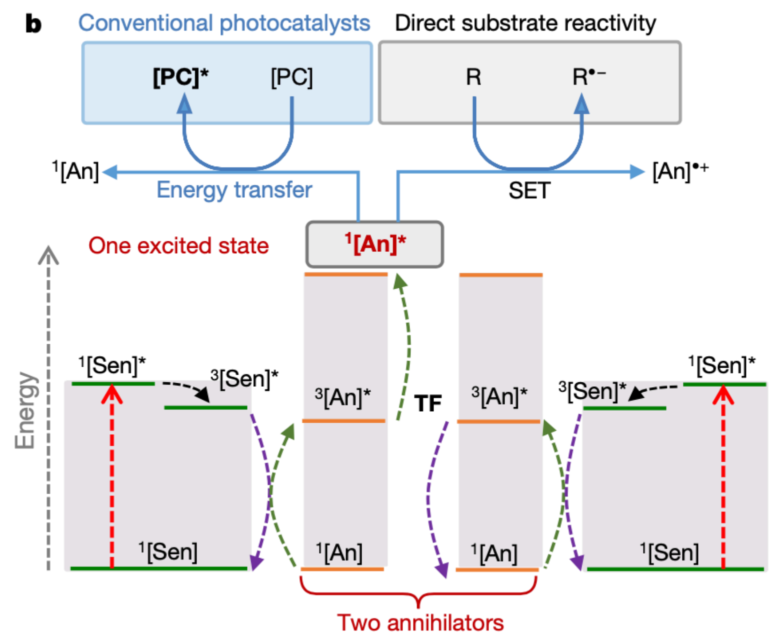
- TTA-UC

  ◯Deep penetration

  ◯No need of high energy

  ◯Modification of organic chromophores→ tunable electronic structures are tunable.

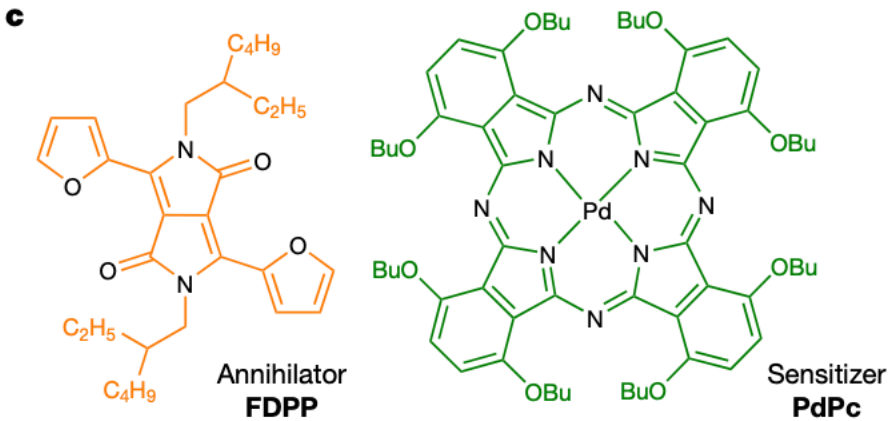


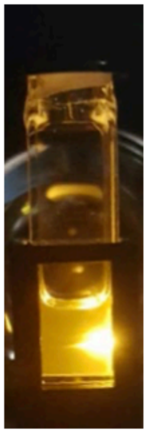


D. N. Congreve, T. Rovis, L. M. Campos *et al.*, *Nature*, **2019**, 565, 343.

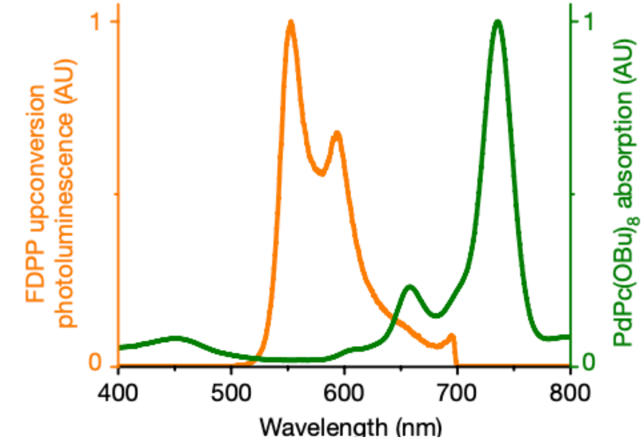
PC excited by TTA-UC

Last year, Campos's group reported photocatalysis via NIR to Vis TTA－UC and its advantages over Vis or UV photocatalysis though their experiments.

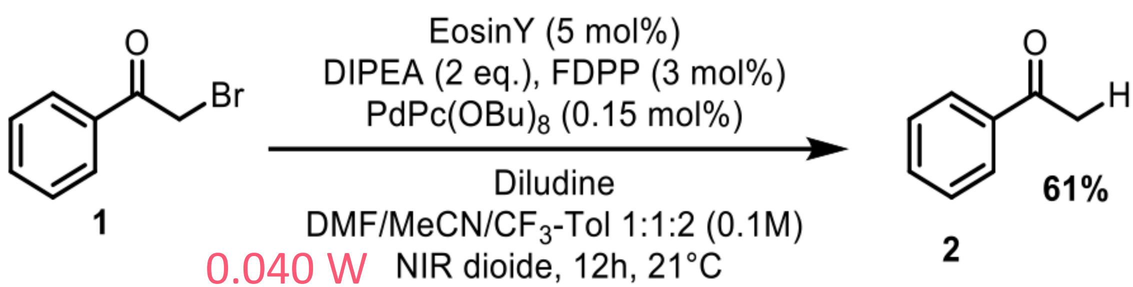




NIR to orange upconversion



Hydrodehalogenation



0.040 W

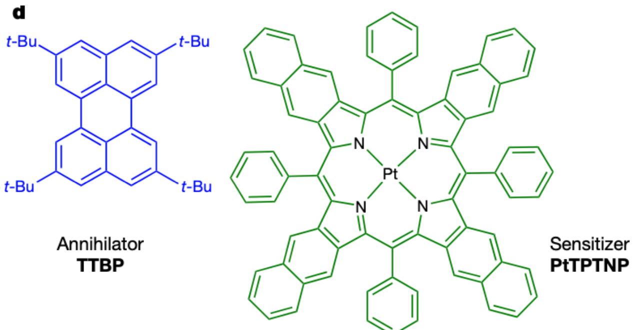
Control Reactions:

no Eosin Y:	3%
no DIPEA:	9%
no FDPP:	3%
no Pd(Pc):	2%
no NIR:	3%
40W Blue Lamp:	78%

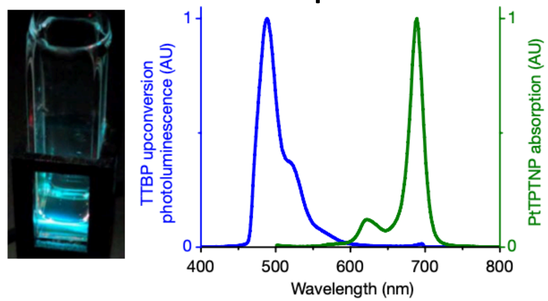
A large number of 'lightbulbs' inside the flask : 1000 times less powerful light sources achieved similar yields to photoredox standard.

D. N. Congreve, T. Rovis, L. M. Campos *et al.*, *Nature*, **2019**, 565, 343.

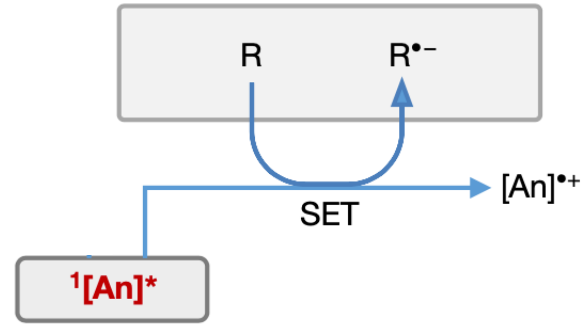
^{1}[A]* as photoredox catalysts



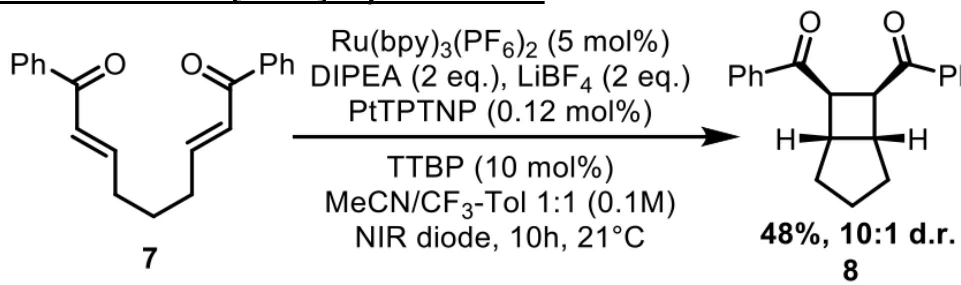
NIR to blue upconversion



Direct substrate reactivity

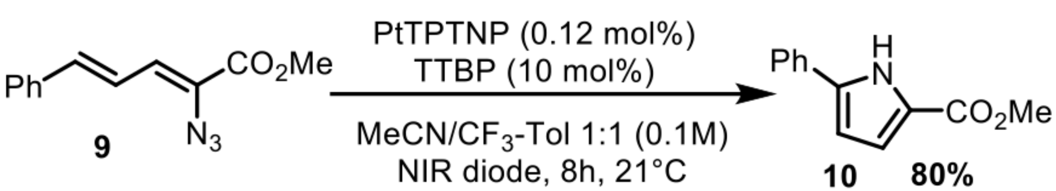


<u>Intramolecular [2+2] cyclization</u>



Controls Reactions:	
No IR laser:	2%
No $Ru(bpy)_3(PF_6)_2$:	38%
No TTBP:	1%
No PtTPTNP:	1%
40W Blue Lamp:	63%

^{1}[An]* of TTBT itself performs as photoredox catalysis.



Controls:	
No IR laser:	2%
No TTBP:	1%
No PtTPTNP:	1%
40W Blue Lamp:	88%

^{3}[An]* (~35 kcal/mol, $E_{1/2}$ ($PC^{\bullet+}/PC^*$) = -0.78 V)

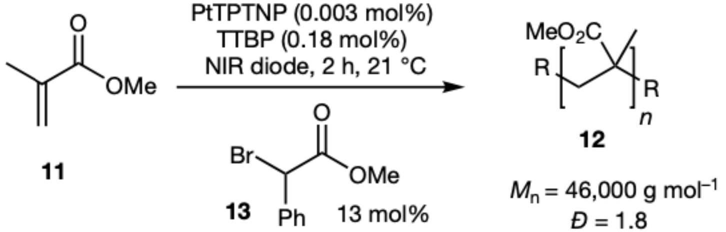
^{3}Sub*~45 kcal/mol, $E_{1/2}$($Sub/Sub^{-\bullet}$) = -1.55 V vs Ag/AgCl in MeCN

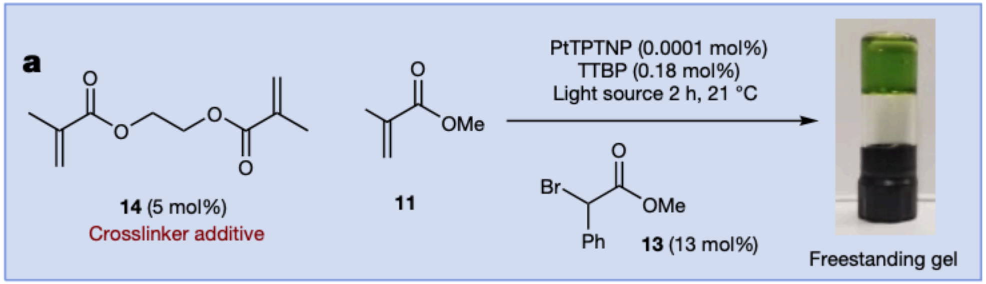
TTA-UC mechanism and the reduction by TTBT's ^{1}[An]* .

D. N. Congreve, T. Rovis, L. M. Campos *et al.*, *Nature*, **2019**, 565, 343.

Deep-penetrating NIR light

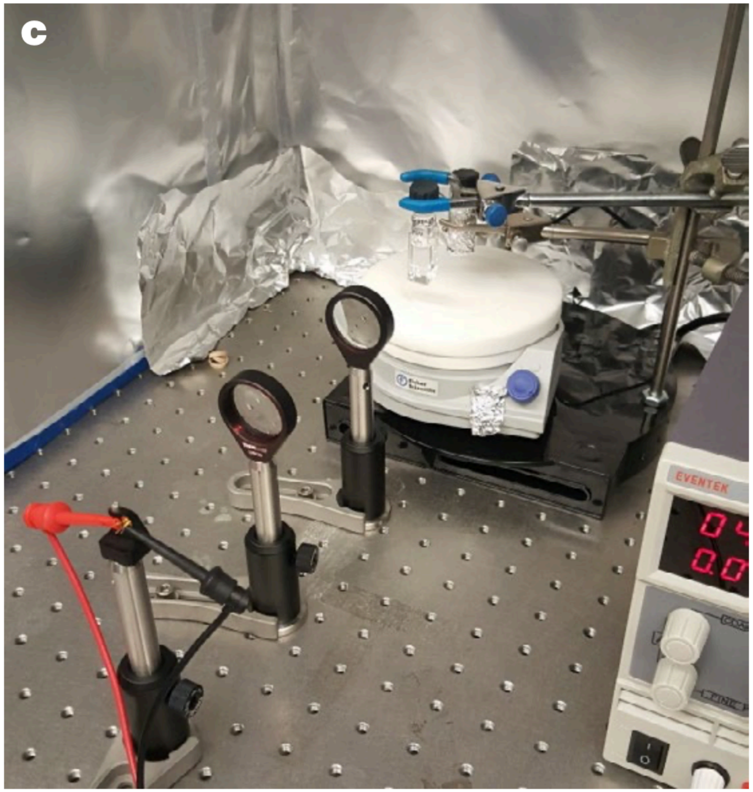
Radical polymerization





b

Material barriers	NIR 730 nm	Blue 450 nm
Air	Gel	Gel
Water	Gel	Gel
Amber glass	Gel	No reaction
Bacon	Gel	No reaction[a]
$Ru(bpy)_3(PF_6)_2$ (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



Experimental set-up with water as the barrier

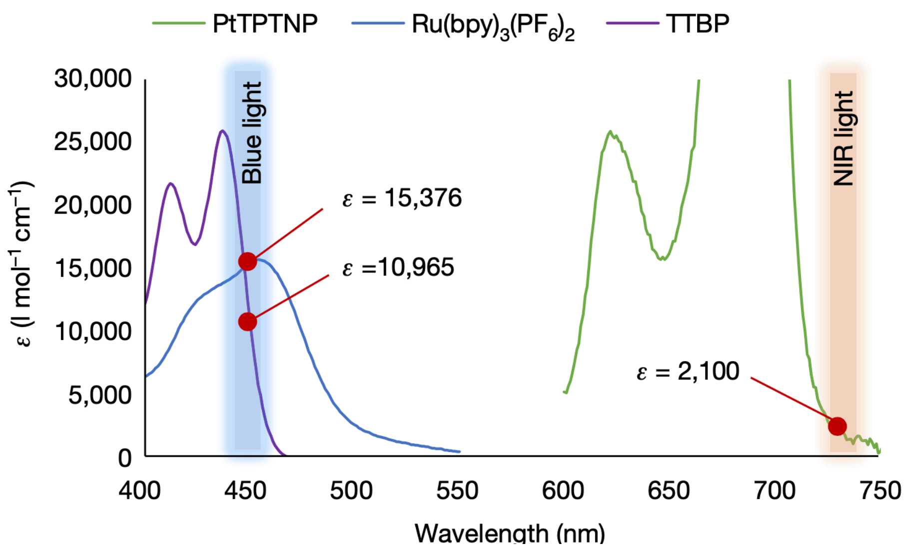
D. N. Congreve, T. Rovis, L. M. Campos *et al.*, *Nature*, **2019**, 565, 343.

Scale-up experiments via TTA-UC

<u>The problems of visible-light photoredox reactions</u>

1. Shallow absorption of visible light
2. Low performance in large-scale reactions

Overcoming of the problem 1 : deeper penetration of NIR light



Application of the Beer–Lambert law to blue and NIR light.

$A = \varepsilon c l$

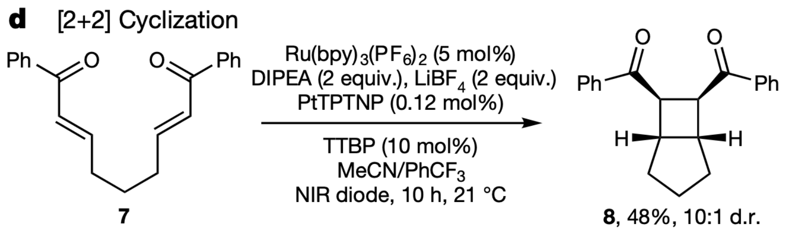
(A, absorbance;

ε, molar extinction coefficient;

c, concentration; l, path length)

$[Ru(bpy)_3]^{2+}$: ε = 15376, c = 5 mol%

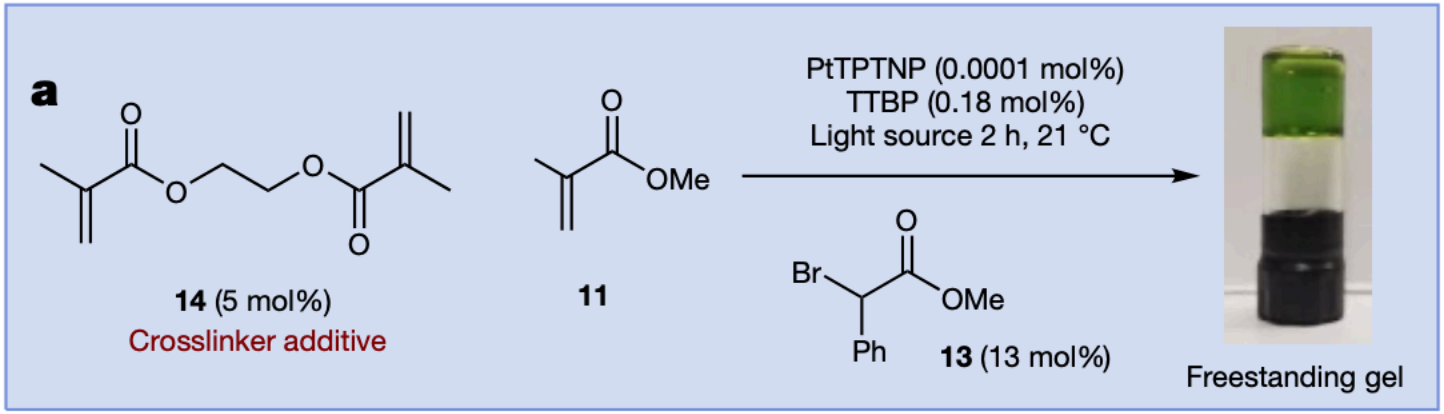
PtTPTNP : ε = 2100, c = 0.12 mol%



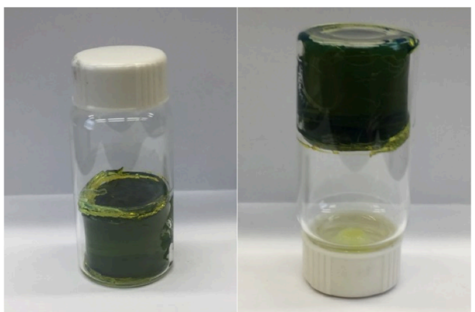
→ NIR light penetrates deeper than blue light though the reaction shown in the right.

D. N. Congreve, T. Rovis, L. M. Campos *et al.*, *Nature*, **2019**, 565, 343.

Scale-up experiments via TTA-UC



A.



B. NIR Blue

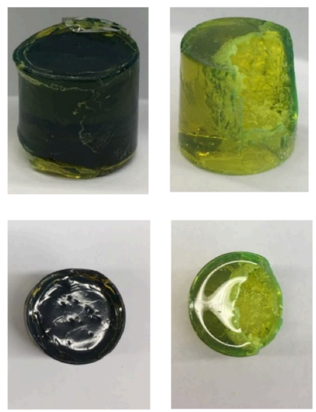


Figure S6. (A) 10g scale cross-linked polymerization flip-experiment with IR lamp; (B) Resulting plastic obtained from IR lamp irradiation (left) and blue lamp irradiation (right).

Sealed with silicone
Irradiated with NIR lamp

↓

multi-gram scale

The defined shapes were not observed with blue lamp.

Gel formation excited with NIR, not with blue light

D. N. Congreve, T. Rovis, L. M. Campos *et al.*, *Nature*, **2019**, 565, 343.

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Biological applications

- <u>Advantages of TTA-UC for biological applications</u>

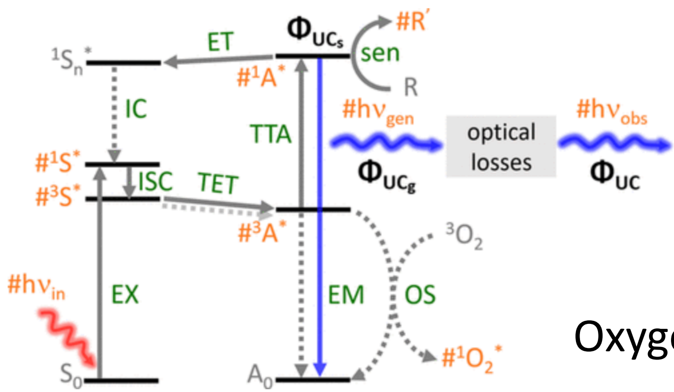
✓ Long-wavelength light utilized in the therapeutic window (600-900 nm) -Deep-tissue penetration

✓ Non-invasive

- <u>Applications</u>

Bioimaging, optogenetics,

photodynamic therapy



Oxygen quenching

F. N. Castellano *et al.*, *ACS Energy Lett.*, **2020**, *5*, 2322.

- <u>The challenges to overcome about biological applications</u>

◆ Oxygen quenching of triplets, photostability

◆ Cytotoxicity of heavy metal in sensitizers

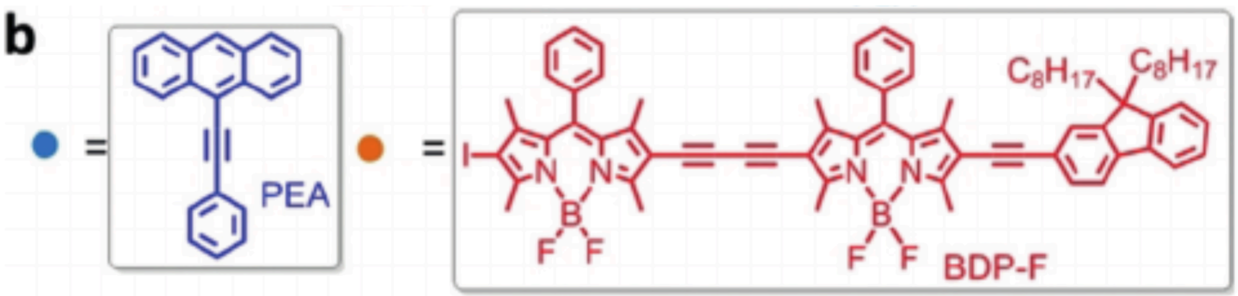
◆ Solubility in aqueous environment

P. Bharmonia *et al.*, *Chem. Soc. Rev.*, **2020**, 49, 6529.

Han, G. *et al.*, *Angew. Chem. Int. Ed.*, **2017**, *56*, 14400.

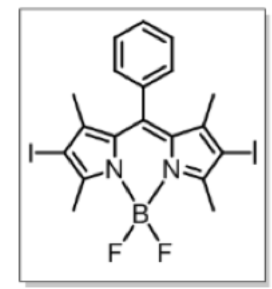
Prodrug activation via TTA-UC

In vivo anticancer prodrug activation though TTA-UC was reported by Han's research group in 2017.



annihilator

sensitizer

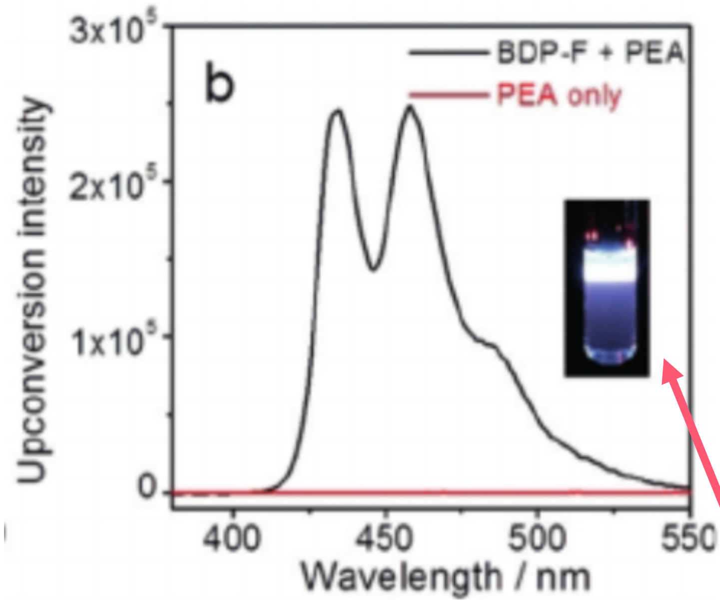


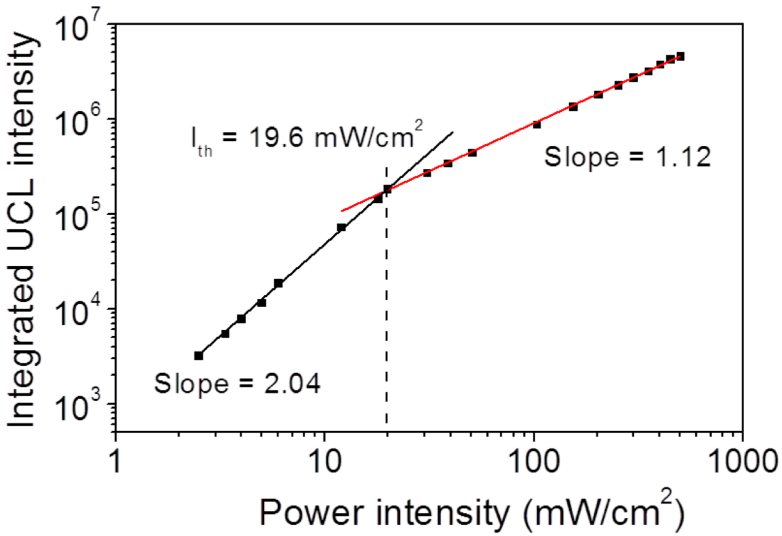
2,6-diiodio-BODIPY

- ✓ High fluorescence quantum yield in the deep-blue region from 410-500 nm, peaking at 432 nm (Φ_f = 87 %)
- ✓ Broader and more intense absorption (the far-red region from 600-700 nm, λ_{ex} = 615 nm, $\varepsilon = 1.77 \times 10^5\ M^{-1}cm^{-1}$) than 2, 6-diiodo-BODIPY (λ_{ex} = 525 nm, $\varepsilon = 85000\ M^{-1}cm^{-1}$)
- ✓ Long triplet-state lifetime : τ_T = 243.6 μs

Han, G. *et al.*, *Angew. Chem. Int. Ed.*, **2017**, *56*, 14400.

Properties of TTA-UC





650 nm excitation power density

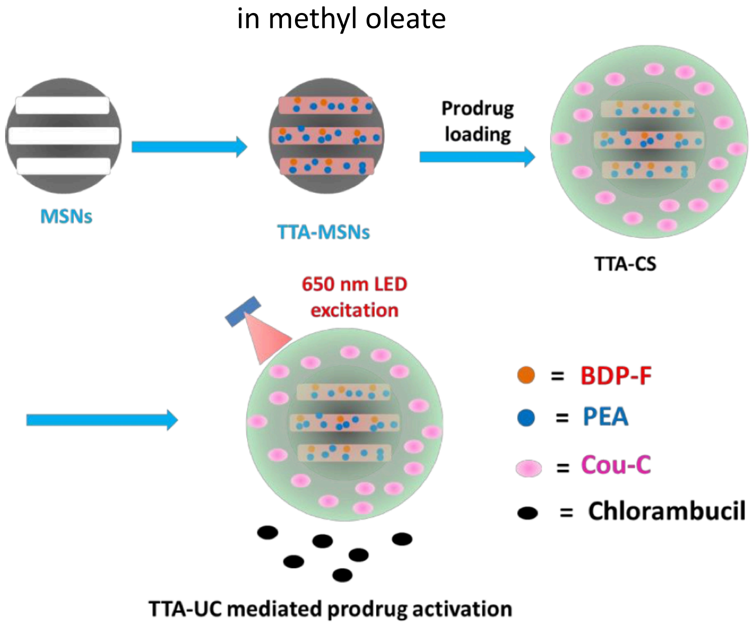
TTA-UC can be observed with the naked eye.

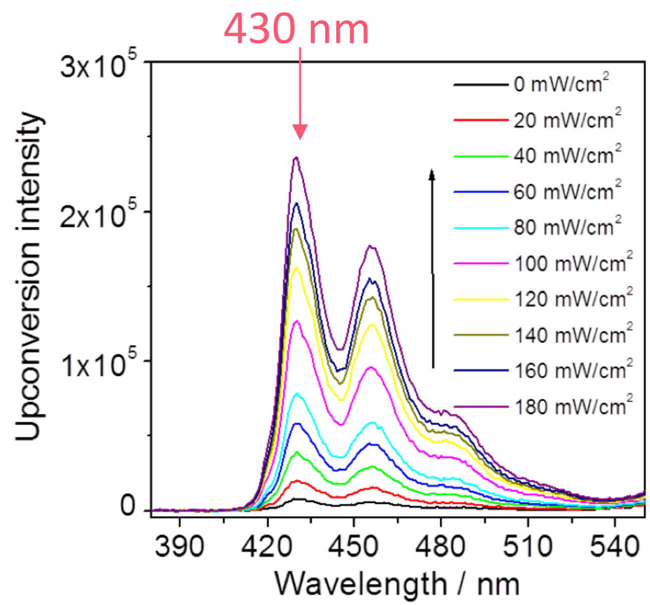
TTA-UC emission spectra of the optimized concentration
BDP-F (20 μM)and PEA (0.2 mM) in degassed toluene,
λ_{ex} = 650 nm (100 mWcm^{-2})

$\eta_{UC} = \Phi'_{UC} = 2 \times \Phi_{UC}$ = 3.1 %,
$\Delta\lambda$ = 0.96 eV (650 nm to 432 nm)
I_{th} = 19.6 mWcm^{-2}

Han, G. *et al.*, *Angew. Chem. Int. Ed.*, **2017**, *56*, 14400.

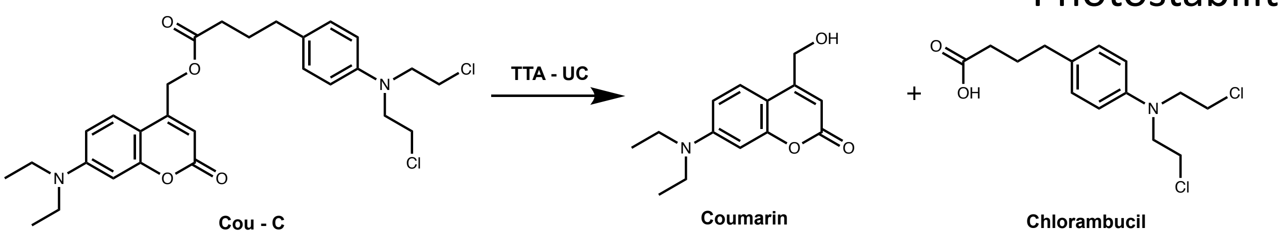
TTA-CS





Upconversion emission spectra of TTA-MSNs at different power intensities in PBS and air, 0.5 mg mL^{-1}, λ_{ex} = 650 nm.

- ✓ TTA-UC in methyl oleate is stable in air.
- ✓ Φ_{UC} = 1.0 % (100 mW cm^{-2}) in water
- ✓ Photostability in air



Chlorambucil : tumor inhibitor

TTA-CS = TTA upconversion core-shell structured nanocapsule

MSNs = mesoporous silica nanoparticles

Han, G. *et al.*, *Angew. Chem. Int. Ed.*, **2017**, *56*, 14400.

In vitro effectiveness

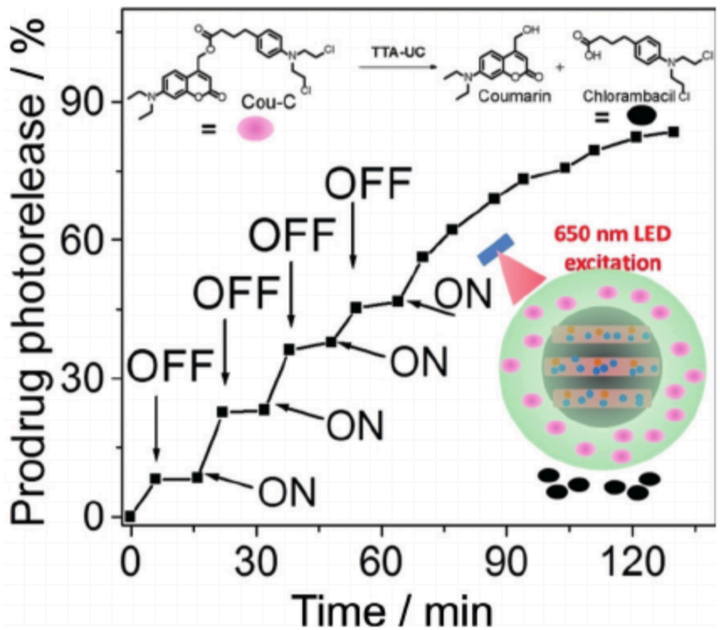


Figure 2. The TTA-UC regulated activation of Cou-C from TTA-CS with 650 nm LED irradiation. "ON" and "OFF" indicate the initiation and termination of LED irradiation, respectively; working power density = 100 mW cm^{-2}. Top inset: the photoactivation reaction of Cou-C. Bottom inset: illustration of a TTA-UC-mediated prodrug activation process in TTA-CS.

The release dose and duration can be titrated by using the far-red light.

Han, G. *et al.*, *Angew. Chem. Int. Ed.*, **2017**, *56*, 14400.

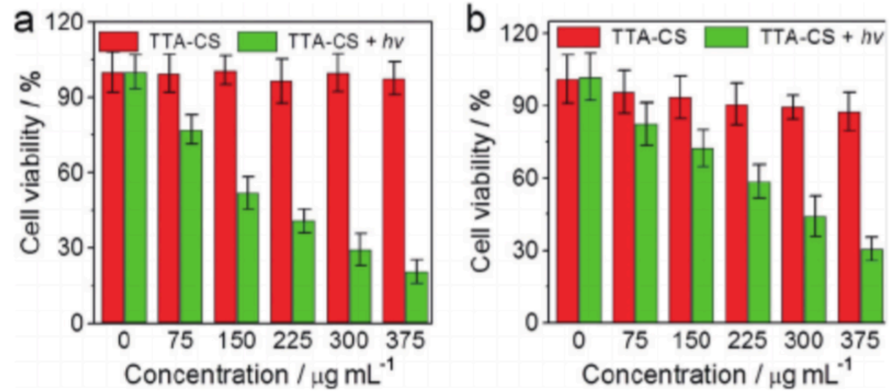
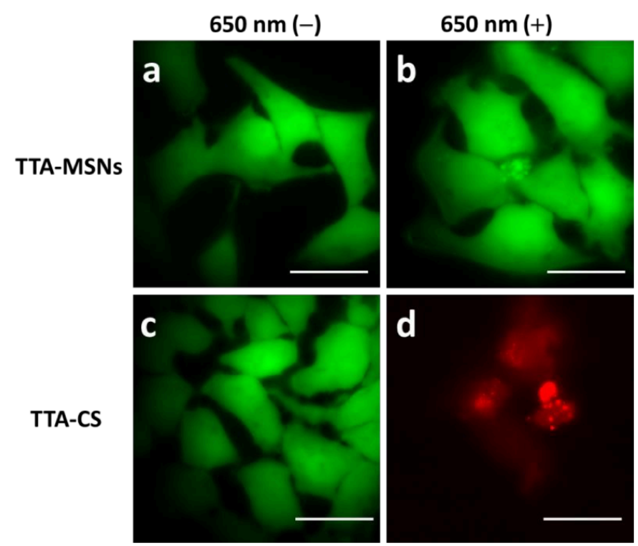


Figure 3. Colorimetric MTT assay of HeLa. $4T_1$ cell viability with different concentrations of TTA-CS with and without light. a) HeLa cells; b) $4T_1$ cells. λ_{ex} = 650 nm, photon fluence = 360 J cm^{-2}.

TTA-MSNs : insignificant toxicity

TTA-CS : significant toxicity upon irradiation



100 mWcm^{-2}, 60 min

Bright-green : living cells

Red : dead cells

In vivo effectiveness

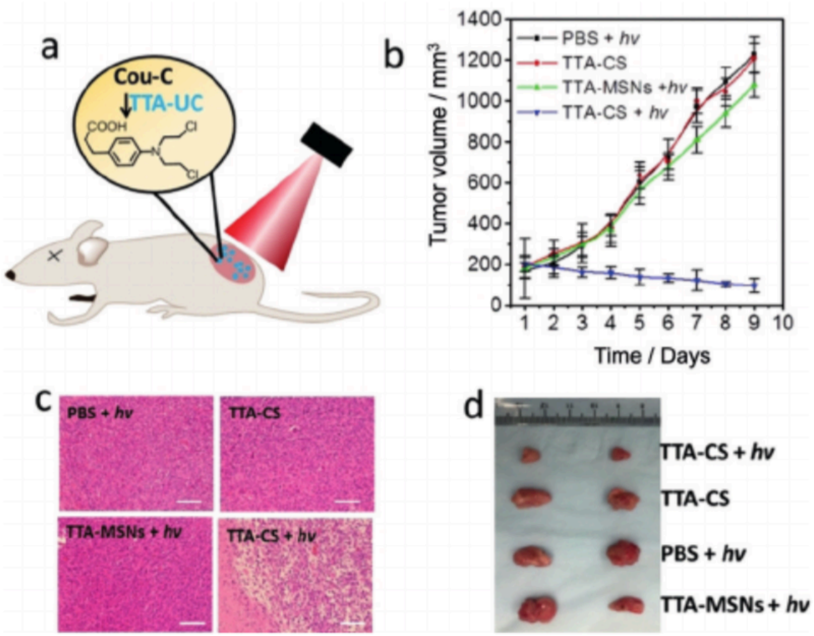


Figure 4. a) Illustration of the photocleavage drug release by TTA-UC. b) Tumor-growth inhibition by TTA-CS-mediated drug release in $4T_1$ tumors; values are mean values ± standard error of the mean (n = five mice per group). c) H&E staining of tumor tissue sections from different treatment groups 9 days after treatment; scale bar: 50 μm. d) Representative digital photos of tumors for the four groups of mice. Photon flux = 180 J cm^{-2}. Key: PBS + *hv* (group 1); TTA-CS (group 2); TTA-MSNs + *hv* (group 3); TTA-CS + *hv* (group 4).

Group2 : TTA-CS itself cannot inhibit tumor growth.
Group3 : The low power of LED has low photothermal and or other effects for cancer cell living.
Group4 : The deep-blue upconversion-induced chlorambucil release from TTA-CS leads to tumor tissue ablation.

- ✓ Insignificant weight loss
- ✓ No noticeable sign of organ damage
- ✓ No observable inflammation from a serum analysis

The first example of effective TTA-UC-induced anticancer prodrug photorelease in vivo and in vitro with a bio-compatible far-red LED light

Han, G. *et al.*, *Angew. Chem. Int. Ed.*, **2017**, *56*, 14400.

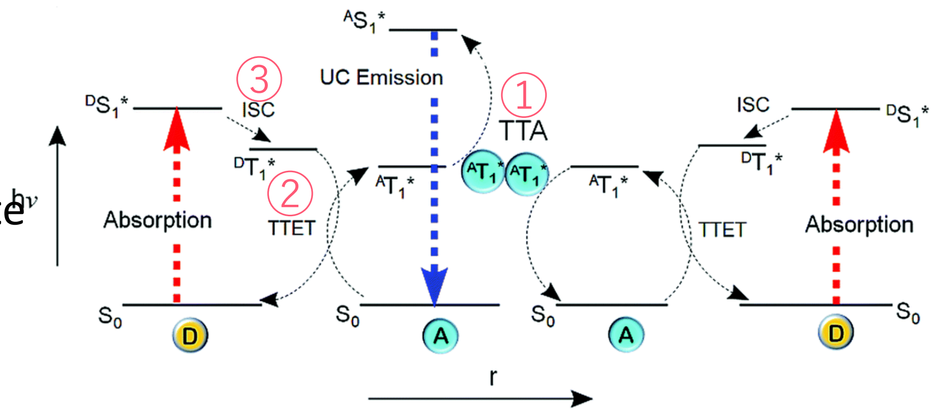
Contents

Strategy to achieve efficient TTA-UC

Φ_{UC} : unconversion quantum yield

f : Spin statistical factor
the probability of getting excited singlet state after annihilation of two triplet *via* TTA

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



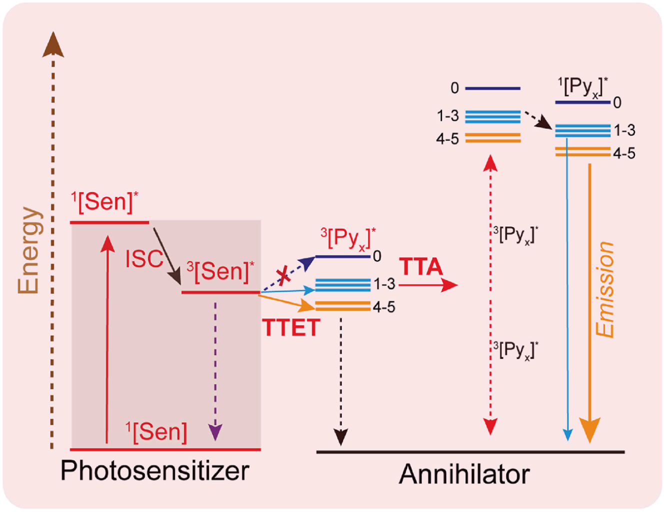
P. Bharmonia *et al., Chem. Soc. Rev.*, **2020**, 49, 6529.

<u>Main strategies</u>

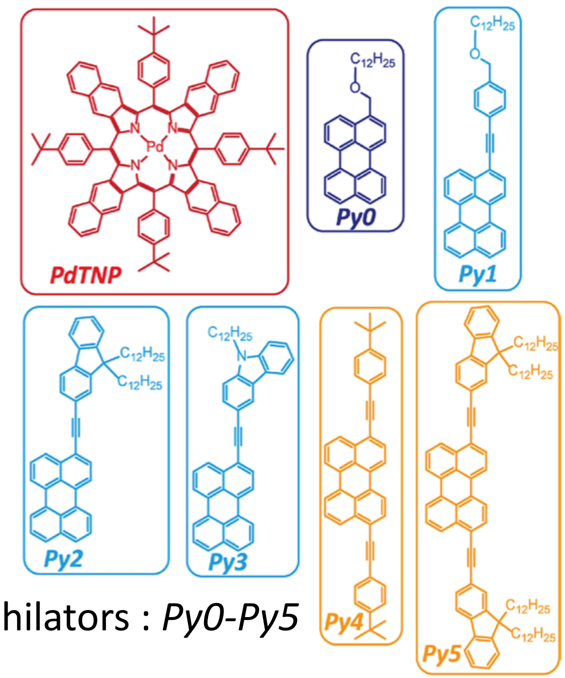
1. Facile TTA
2. Facile TTET
   - Extend the phosphorescence lifetime of sensitizers
   - Tune the energy of the excited states
3. Reduce the energy loss during ISC

Tailor annihilators to efficient TTET

a

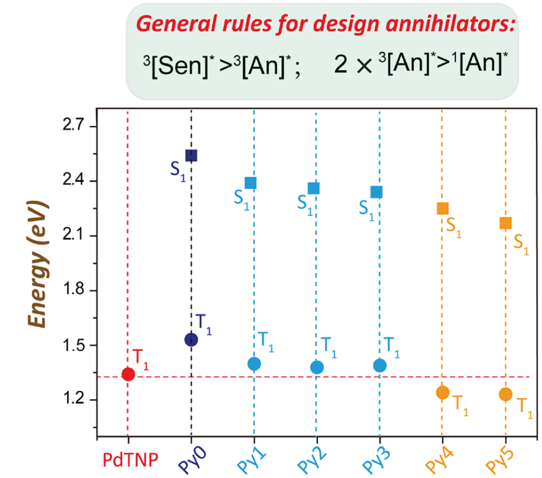


b Sensitizers



Annihilators : *Py0-Py5*

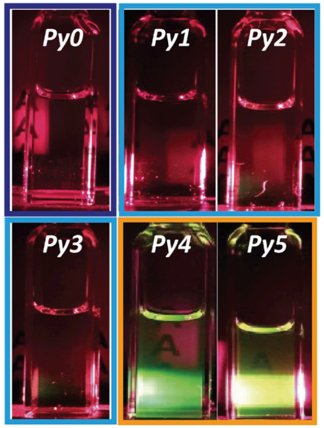
c



	PdTNP	Py0	Py1	Py2	Py3	Py4	Py5
Φ_{UC} % (650 nm laser)		0	0.06	0.25	0.24	7.6	16.7
Φ_{UC} % (720 nm LED)						6.4	14.1

650 nm : 0.1 W cm^{-2}
720 nm : 100 mWcm^{-2}
theoretical maximum of Φ_{UC} = 1
Energy : estimated by TD-DFT

d



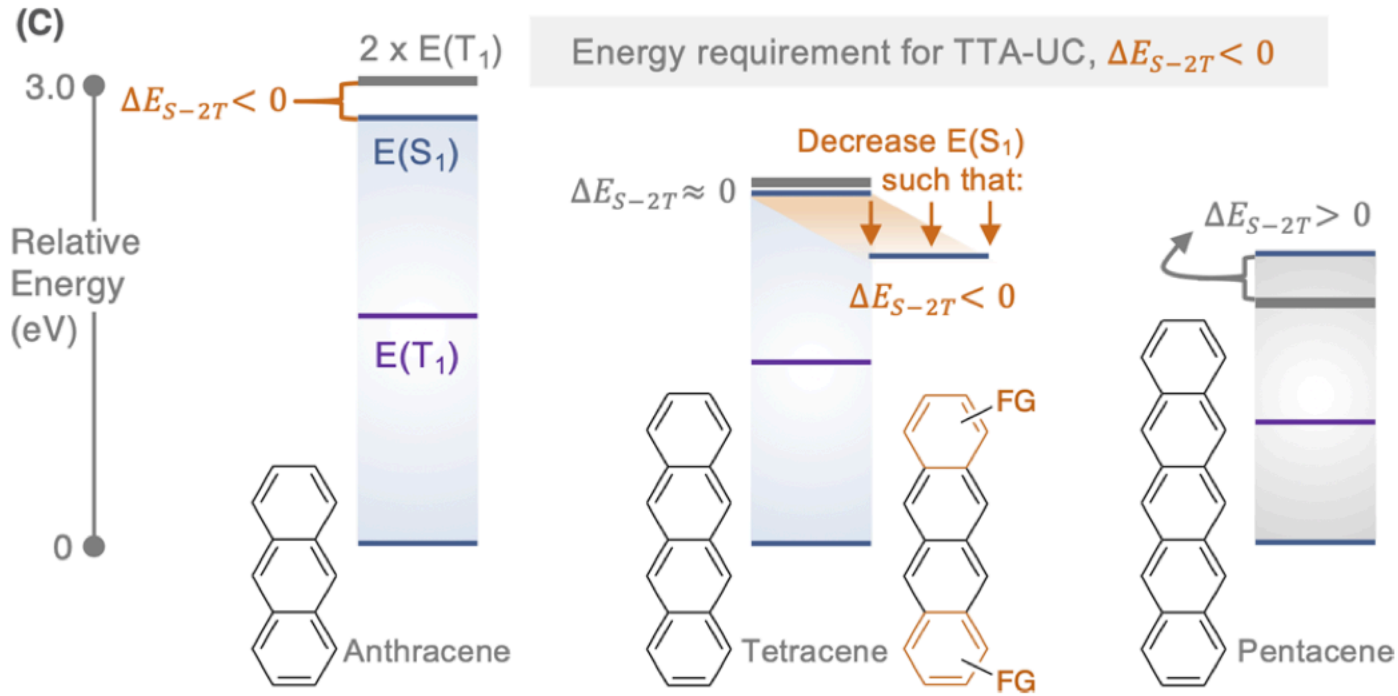
653 nm, 100 mW/cm^2

^{3}[Sen]* > ^{3}[An]* & 2 × ^{3}[An]* > ^{1}[An]*

π conjugation → red-shifted λ_{abs} & λ_{em}
Py 4 & Py 5 → T_1 of them lower than T_1 of PdTNP
higher Φ_{TTET} , Φ_{UC}

Han, G. *et al., J. Am. Chem. Soc.*, **2020**, *142*, 18460.

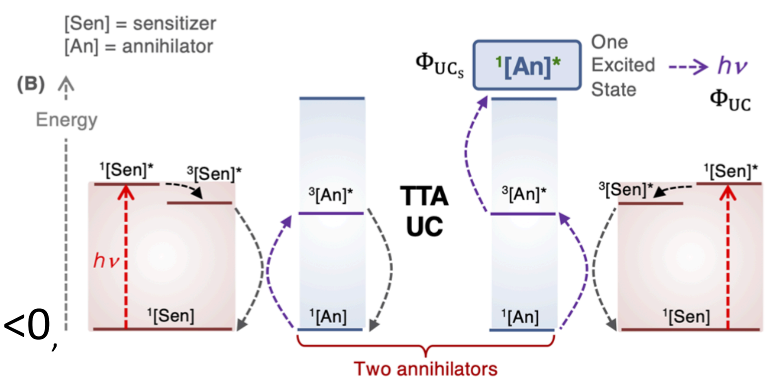
Molecular engineering for TTA



The definition in this paper

$\Phi_{UC} = \Phi_{ISC}\, \Phi_{TET}\, \Phi_{TTA}\, \Phi_{PL} \times 100$

The limit is 50 %

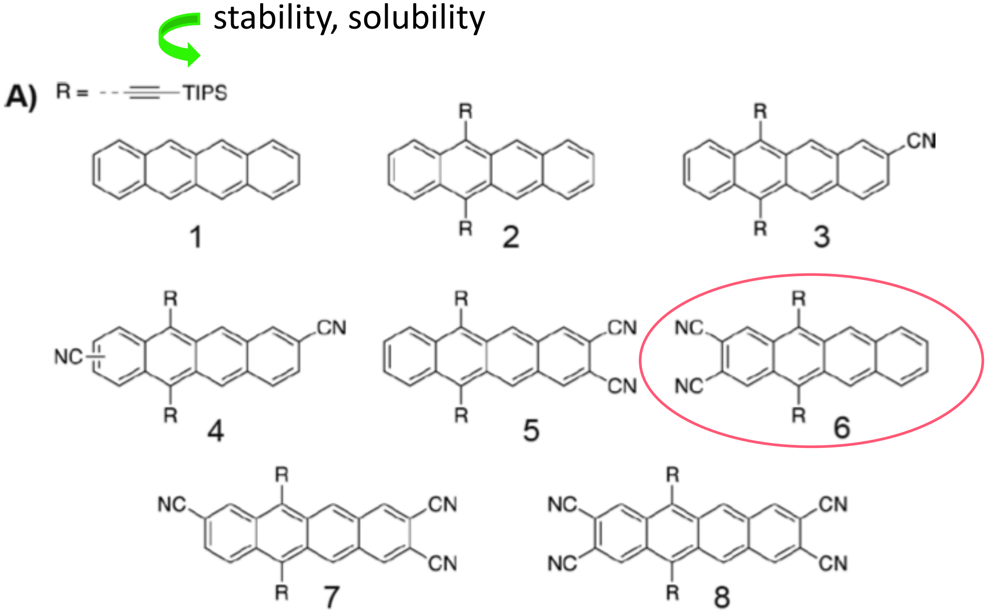


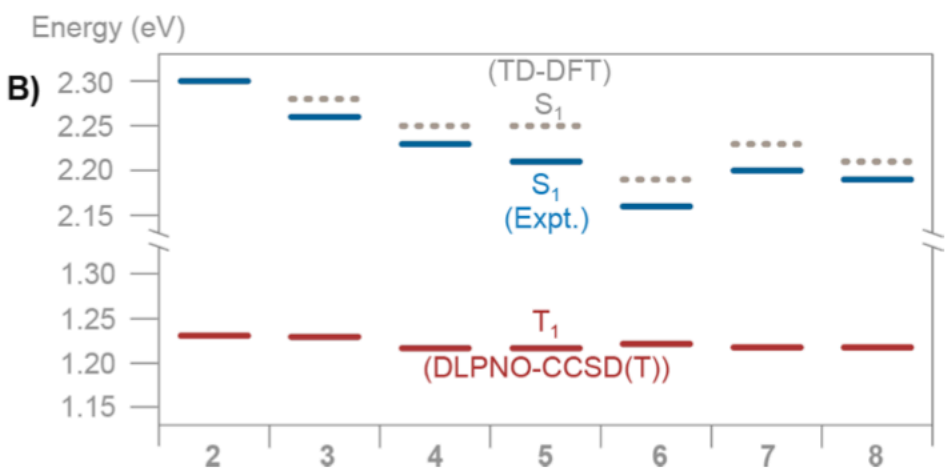
<u>Hypothesis</u>

By molecular engineering and tuning $E(S_1)$, $\Delta E[S_1-2T_1]<0$, high Φ_{TTA} will be achieved.

M. Y. Sfeir, D. N. Congreve, L. M. Campos *et al.*, *J. Am. Chem. Soc.*, doi:org/10.1021/jacs.0c06386

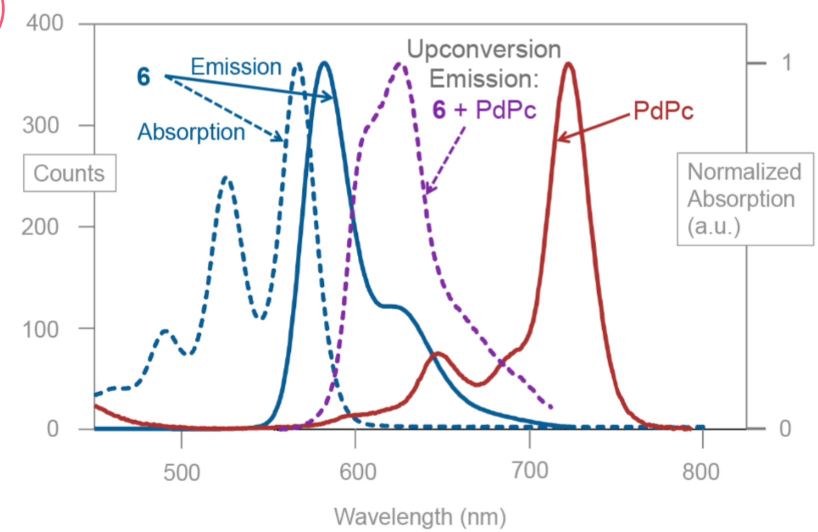
Tetracene derivatives





Finding

-CN (a strong EWG) can lower $E(S_1)$



Excitation with a 730 nm laser

Figure 3. Absorption of PdPc (red); absorption (blue dashed) and PL (blue solid) of **6**. Upconversion experiment (purple dashed) showing UCPL of **6** between 600 and 700 nm and reabsorption losses between 550 and 600 nm.

M. Y. Sfeir, D. N. Congreve, L. M. Campos *et al.*, *J. Am. Chem. Soc.*, doi:org/10.1021/jacs.0c06386

Upconversion quantum yield

Table 1. Triplet−Triplet Annihilation Upconversion Characteristics of Annihilator Compounds 2−8 (An)

	dilute[a]			concentrated[b]		
An	Φ_{UC_s}[c] (%)	Φ_{PL}[d] (%)	Φ_{UC}[c] (%)	Φ_{UC_s} (%)	Φ_{PL} (%)	Φ_{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
rubrene[e]	0.13	92.2	0.12	1.8	3.9	0.07

[a]Dilute: [An] = 1×10^{-3} M, [PdPc] = 1×10^{-5} M. [b]Concentrated: [An] = 9×10^{-3} M, [PdPc] = 8.1×10^{-4} M. Experiments were carried out on 1 mL samples at the aforementioned concentrations in 1 cm^2 cuvettes at RT. Samples were prepared in a degassed environment (N_2 glovebox) with the use of anhydrous degassed (N_2) toluene. Cuvettes were capped, sealed with Parafilm, and analyzed immediately on the optics table. The fluence of the incident excitation was such that the experiment was in the linear regime. [c]QY limit is 50%. [d]QY limit is unity. [e]Aldrich sublimed grade.

$\Phi_{UC} = \Phi_{ISC}\,\Phi_{TET}\,\Phi_{TTA}\,\Phi_{PL} \times 100$

$\Phi_{UC_s} = \Phi_{UC} / \Phi_{PL} \times 100 = \Phi_{ISC}\,\Phi_{TET}\,\Phi_{TTA}$

Concentrated : high Φ_{UC_s}, low Φ_{PL} and Φ_{UC}

Dilute : low Φ_{UC_s}, high Φ_{PL} and Φ_{UC}

Table 2. Quantum Yields of Triplet Energy Transfer (Φ_{TET}) and Triplet−Triplet Annihilation (Φ_{TTA}) of Annihilator Compounds 2−8 (An)

An	Φ_{TET}[a] (%)	Φ_{TTA}[b] (%)
2	64	0.21
3	68	0.30
4	68	0.26
5	70	2.2
6	69	5.0
7	62	1.1
8	82	1.7

[a]QY limit is 100%. [b]QY limit is 50%. Experiments were performed in degassed (bubbling with argon) toluene on samples where [PdPc] = 1×10^{-5} M and [An] = 1×10^{-3} M at RT with a cuvette having a 2 mm path length.

Result

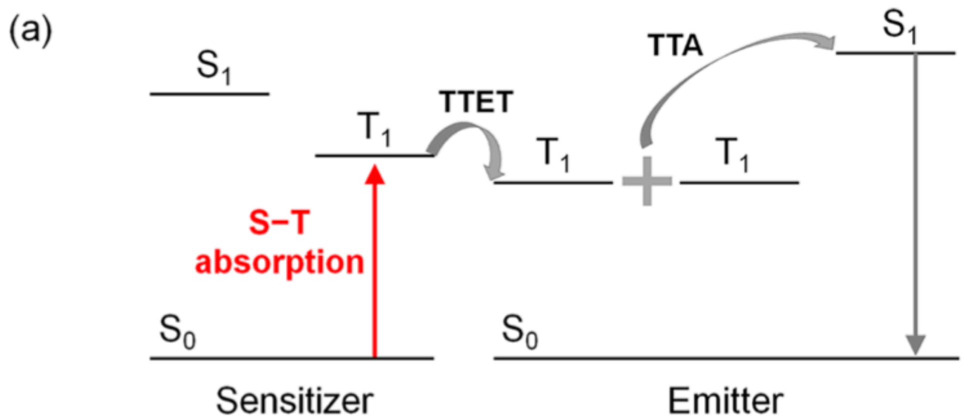
6 : the lowest $E(S_1)$, the largest $\Delta E[S_1\text{-}2T_1]$,and the highest Φ_{UC_s} / Φ_{UC}

M. Y. Sfeir, D. N. Congreve, L. M. Campos *et al.*, *J. Am. Chem. Soc.*, doi:org/10.1021/jacs.0c06386

TTA-UC based on S – T absorption

- In 2016, direct S_0-to-T_1 absorbing sensitizer based NIR to Vis molecular TTA-UC introduced by Kimizuka and Yanai's research groups at Kyushu Univ. in 2016

Although the S-T absorption is spin forbidden, large spin-orbital coupling occurs for properly designed Os(II) complexes, which allows S-T absorption in the NIR region with large absorption coefficients.

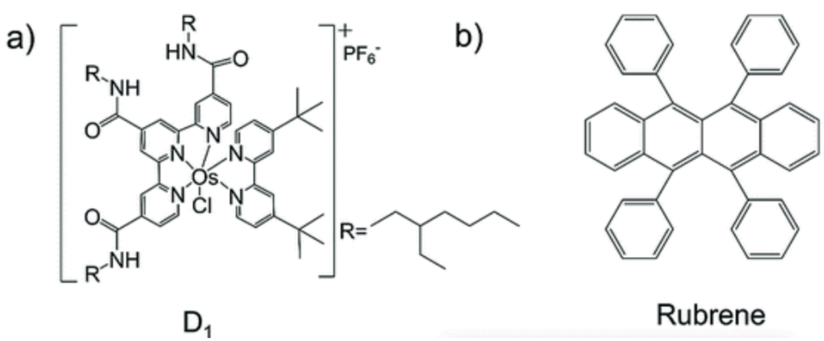


Advantage

Minimize the energy loss during ISC

→ larger ΔE_{UC}

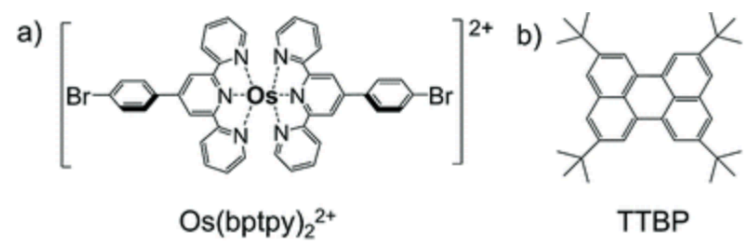
2016



○ ΔE_{UC} = 0.86 eV (938 nm to 570 nm)

× low Φ_{UC} = 0.0024 % due to τ_P = 12 ns

2017



○ ΔE_{UC} = 0.97 eV (724 nm to 462 nm)

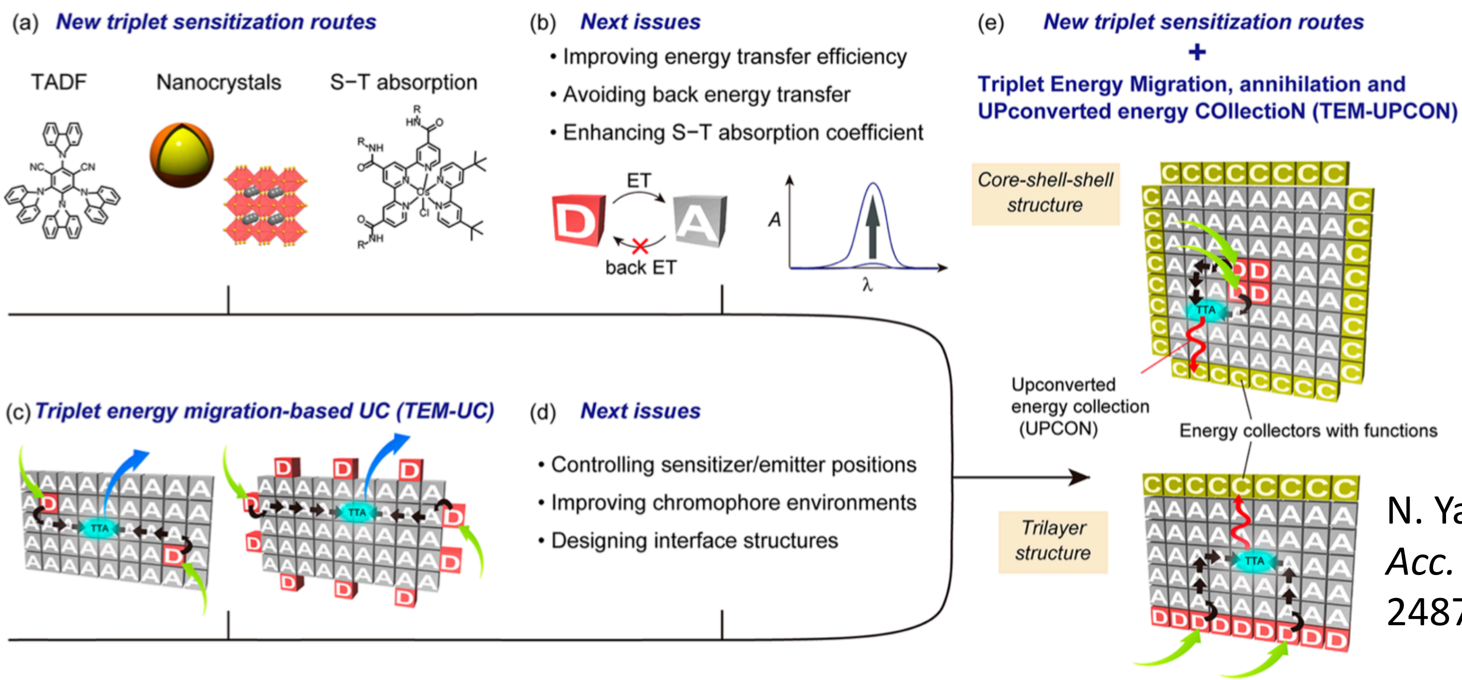
○ Φ_{UC} = 1.35 % due to τ_P = 207 ns

P. Bharmonia *et al.*, *Chem. Soc. Rev.*, **2020**, 49, 6529.

N. Yanai and N. Kimizuka, *Acc. Chem. Res.*, **2017**, *50*, 2487.

Summary of perspective

- The strategies to improve each process based on the mechanism can realize efficient TTA-UC.
- Besides adding functional groups or extending the conjugated π-system, the novel routes are being developed.
- In addition to achieving the high upconversion quantum yield, the development of TTA-UC in aqueous solution is required.



N. Yanai and N. Kimizuka, *Acc. Chem. Res.*, **2017**, *50*, 2487.

Contents

Summary

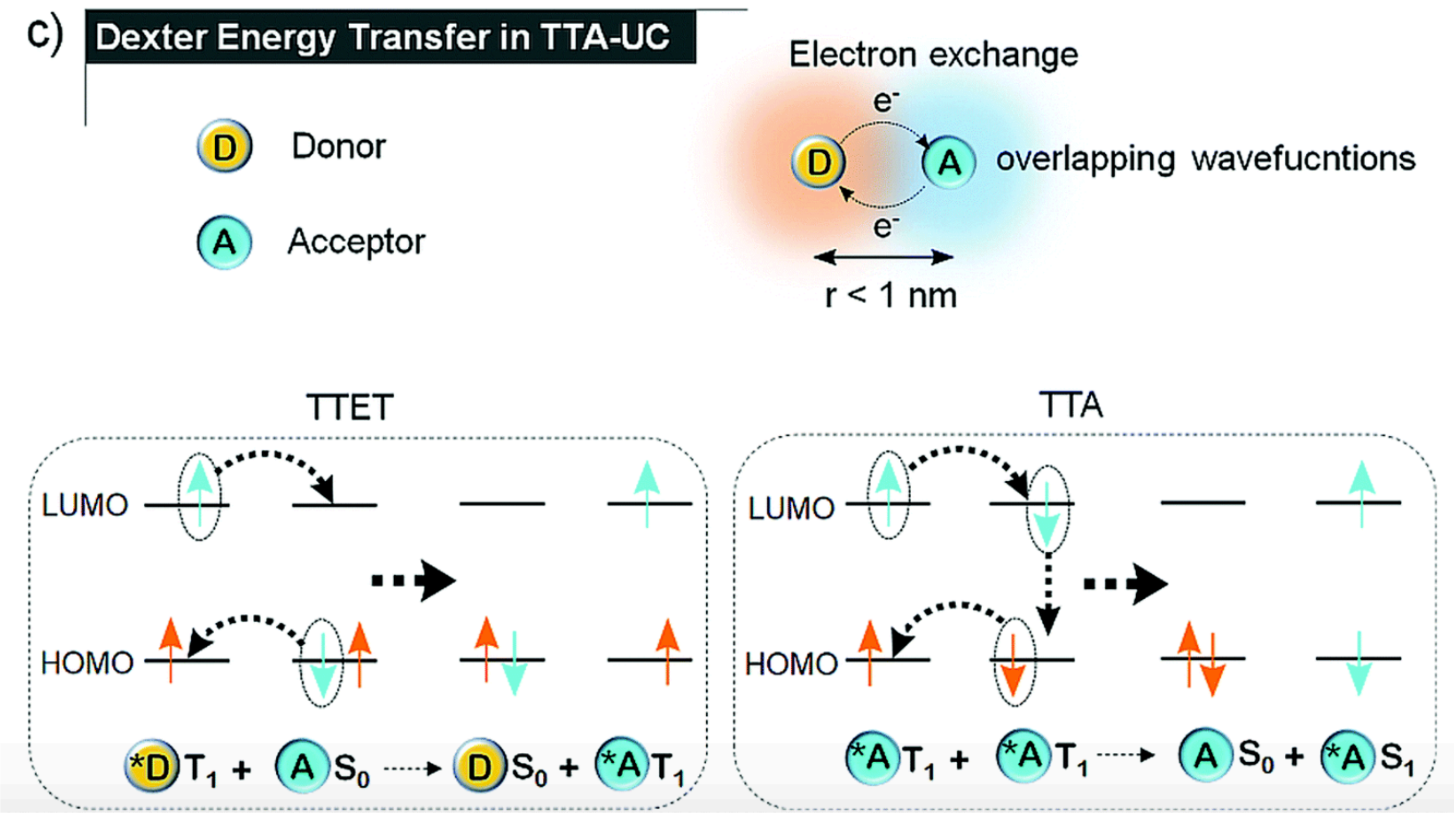
- The 21 century have seen tremendous breakthroughs in the field of TTA-UC, and this trend will go on.
- The highest upconversion quantum yield has been updated recently.
- By utilizing the advantages of TTA-UC, many applications will be in use practically, especially in the field of photovoltaics. It may be able to contribute to energy problems in the future.
- The biggest drawback of TTA-UC is oxygen quenching, and further developments solving this are required.

Thank you for kind listening !

Appendix

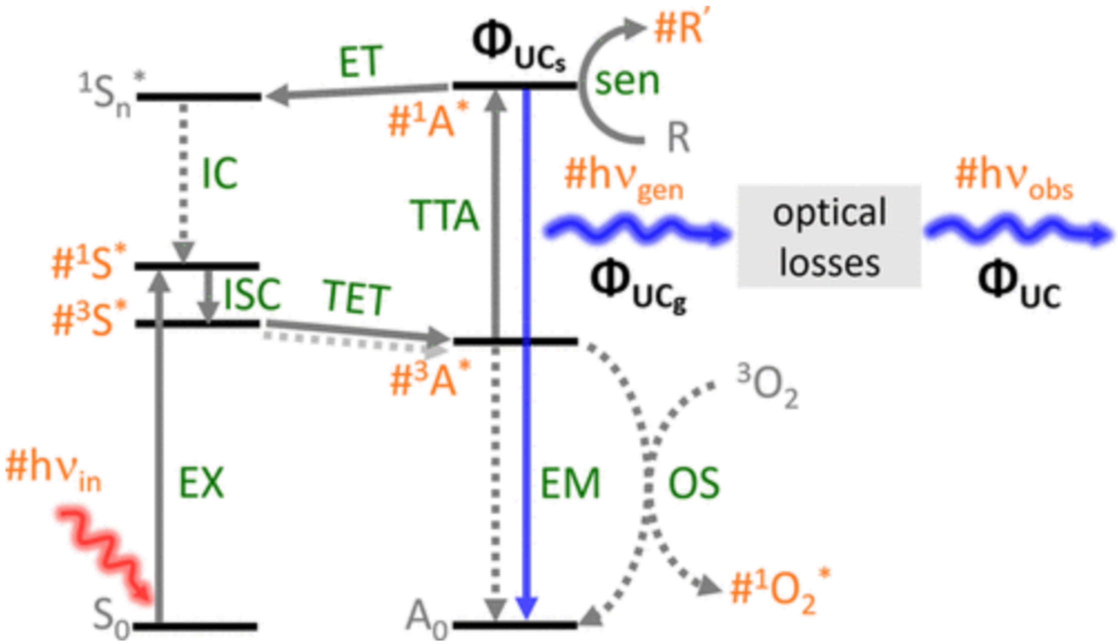
Dexter energy transfer

Dexter energy transfer : a non-radiative electron exchange



P. Bharmonia *et al., Chem. Soc. Rev.,* **2020**, 49, 6529.

Upconversion yield in detail



yield	equation
light harvesting	$\Phi_{LH} = \frac{\#^1S^*}{\#h\nu_{in}}$
ISC	$\Phi_{ISC} = \frac{\#^3S^*}{\#^1S^*}$
$^3S^*$ to ^1A TET	$\Phi_{TET} = \frac{\#^3A^*}{\#^3S^*}$
TTA	$\Phi_{TTA} = \frac{\#^1A^*}{\#^3A^*}$
A fluorescence	$\Phi_f = \frac{\#h\nu_{gen}}{\#^1A^*}$
$^1A^*$ to S ET	$\Phi_{ET} = \frac{\#^1S^*}{\#^1A^*}$
optical outcoupling	$\Phi_{out} = \frac{\#h\nu_{obs}}{\#h\nu_{gen}}$
UC state	$\Phi_{UC_s} = \frac{\#^1A^*}{\#^1S^*}$
UC photons generated	$\Phi_{UC_g} = \frac{\#h\nu_{gen}}{\#^1S^*}$
UC EM observed	$\Phi_{UC} = \frac{\#h\nu_{obs}}{\#^1S^*}$
$^1A^*$ to R sen	$\Phi_{sen} = \frac{\#R'}{\#^1A^*}$
UC sen	$\Phi_{UC_{sen}} = \frac{\#R'}{\#^1S^*}$
$^1O_2^*$	$\Phi_{OS} = \frac{\#^1O_2}{\#^1S^*}$

F. N. Castellano *et al.*, *ACS Energy Lett.*, **2020**, *5*, 2322.

f : spin statistical factor

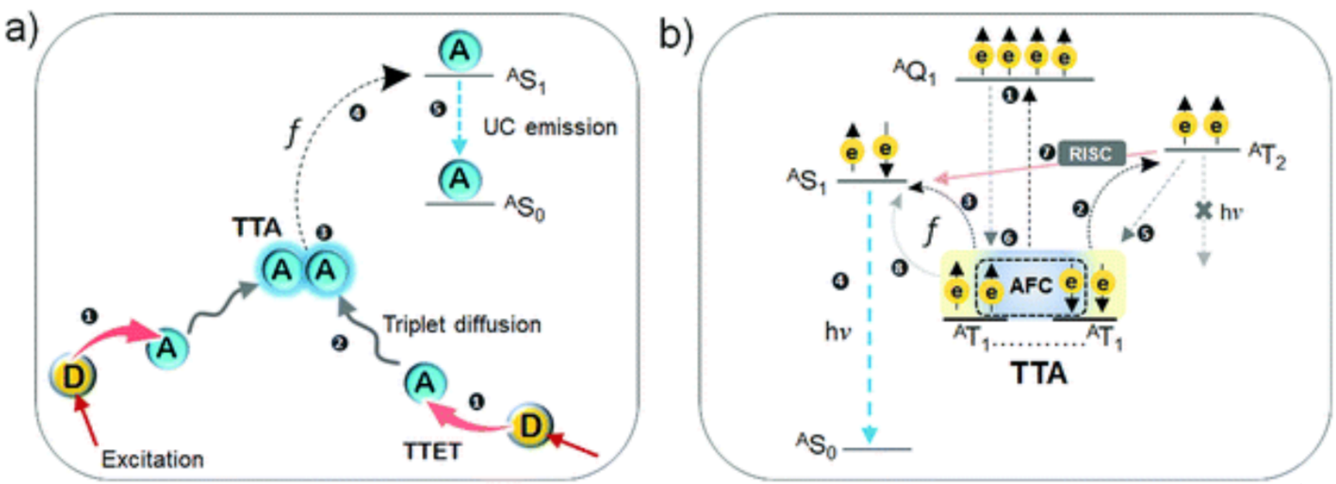


Fig. 2 Artistic presentation of (a) events leading to TTA-UC emission and (b) post TTA events showing the formation of three different energy states of annihilator with different spin multiplicities including singlet ($^{A}S^{1}$), triplet ($^{A}T_2$) and quintet ($^{A}Q_1$).

f : spin statistical factor

$2 \times {}^{A}T_1 \rightarrow {}^{A}S_1$ 1/9, ${}^{A}T_2$ 3/9, ${}^{A}Q_1$ 5/9

Theoretical maximum : 11 %

But ..

$^{A}T_2$ & $^{A}Q_1$ decay to $^{A}S_1$

$$^{3}A_1^* + {}^{3}A_1^* \leftrightarrow {}^{5}(AA)_2^* \leftrightarrow {}^{5}A_2^* + {}^{1}A_0$$
$$^{3}A_1^* + {}^{3}A_1^* \leftrightarrow {}^{3}(AA)_1^* \leftrightarrow {}^{3}A_1^* + {}^{1}A_0$$
$$^{3}A_1^* + {}^{3}A_1^* \leftrightarrow {}^{1}(AA)_0^* \leftrightarrow {}^{1}A_0^* + {}^{1}A_0$$

J. Zhao *et al., RSC Advances*, **2011**, *1*, 937.
P. Bharmonia *et al., Chem. Soc. Rev.*, **2020**, 49, 6529.

Requirements of efficient TTA-UC

The requirement for sensitizers / annihilators

1. The light harvesting ability of the triplet sensitizer for efficient TTET.

 The metal complexes shows weak absorption in the visible region. With high concentrations of the triplet sensitizers, TTET will be more efficient.

2. The triplet excited state quantum yield of the sensitizer must be high. Most sensitizers are transition metal complexes. ϕ_{ISC} is close to 1.

3. The lifetime of the triplet excited state of the sensitizers should be long. The triplet sensitizers need diffusion in the system and collide with annihilators. The longer lifetime makes the encounter more likely.

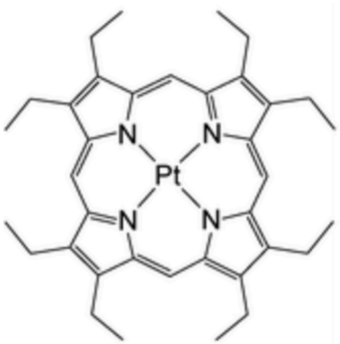
4. The energy levels of the triplet state of sensitizers and the triplet state of annihilaotrs

5. About annihilators, $2 \times E_{T1} > E_{S1}$

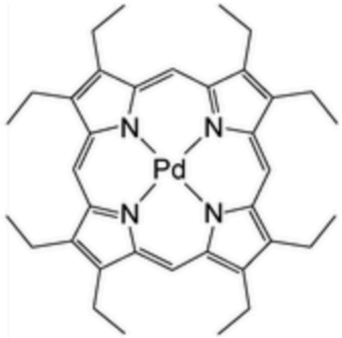
6. Φ_f of annihilators should be high

J. Zhao *et al., RSC Advances,* **2011**, *1*, 937.

Sensitizers



Pt-1



Pd-1

Pd(II)/Pt(II) porphyrin complexes

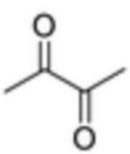
◯Intense absorption of the visible region

◯ the long-lived triplet excited state

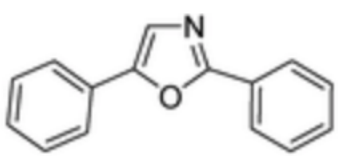
× Tuning excitation/absorption wavelength is difficult.

Transition metal complexes realize efficient ISC due to the heavy atom effect and population of triplet excited state.

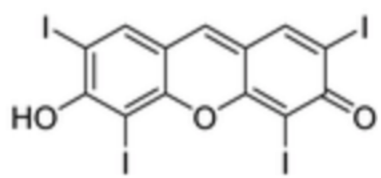
Organic triplet sensitizers



butadione



A-8 PPO



TIHF

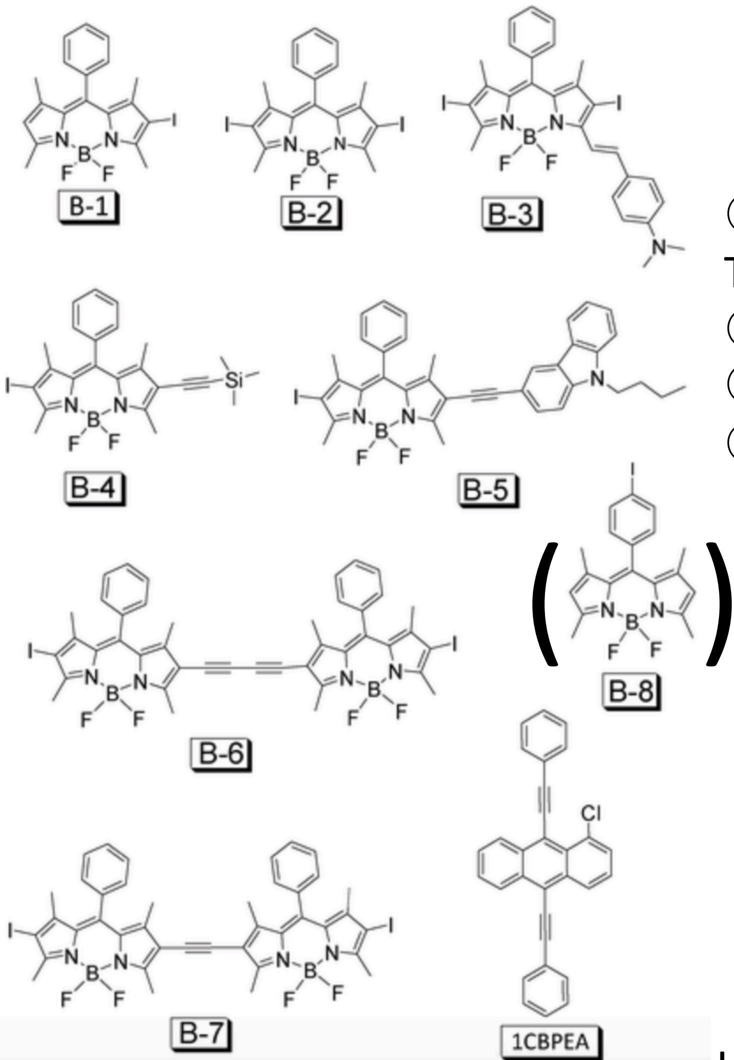
The n-π* transition facilitates ISC.
The iodine atom does due to the moderate heavy atom effect.

× Modification of the molecular structure

J. Zhao *et al.*, *RSC Advances*, **2011**, *1*, 937.

Sensitizers

Sensitizers of BODIPY derivatives

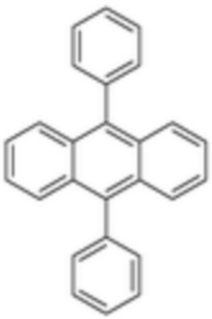


○Absorption : 510-629 nm
The variation due to extension of the π-conjugation
○Weak fluorescence
○The lifetime of triplet excited state : ～66.3 μs (long)
○ Many derivatives

J. Zhao *et al.*, *RSC Advances*, **2011**, *1*, 937.

Annihilators

Basic annihilators

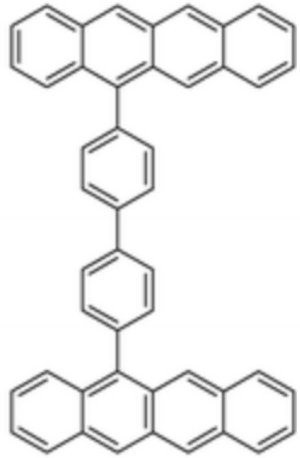


A-1

E_{T1} = 2.07 eV

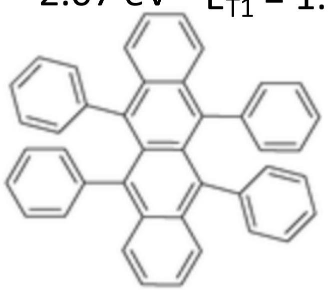
A-2

E_{T1} = 1.53 eV

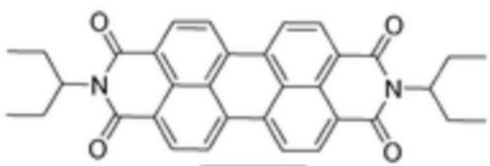


A-3

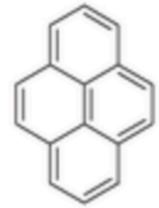
E_{T1} < 1.32 eV



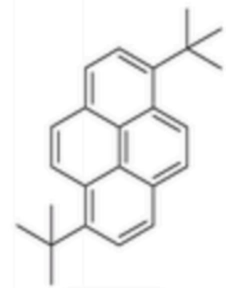
A-4



A-5

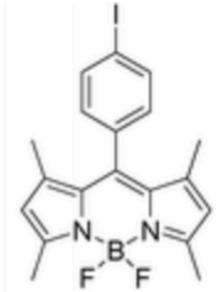


A-6



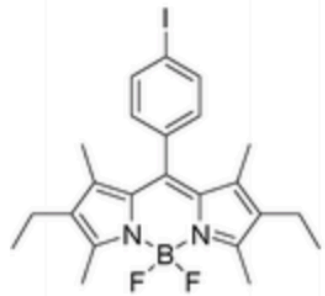
A-7

E_{T1} = 2.09 eV



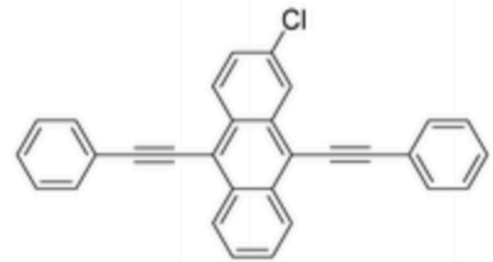
A-9

E_{T1} = ~1.55 eV



A-10

E_{T1} = ~1.55 eV



A-11

E_{T1} = 1.27~1.61 eV

The requirements

1. The energy level : 2 × $E_{T1} > E_{S1}$
2. High ϕ_f
3. Tunable E_{T1}
4. Good photochemical stability

J. Zhao *et al., RSC Advances,* **2011**, *1*, 937.

Threshold excitation intensity

- I_{th} : threshold excitation intensity

$$I_{th} = (\alpha \Phi_{ET}\, 8\pi D_T a_0)^{-1} (\tau_T)^{-2}$$

α : absorption coefficient at the excitation wavelength

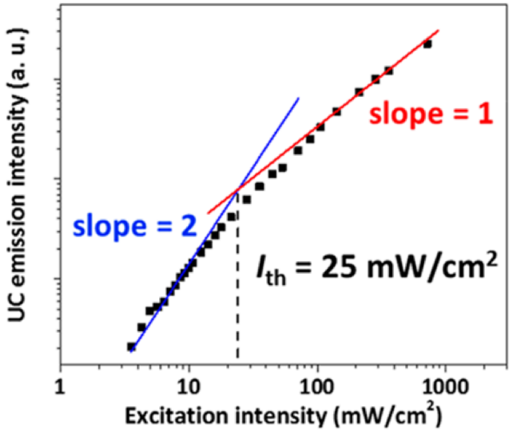
Φ_{ET} : sensitizer to annihilator triplet energy transfer efficiency

D_T : diffusion constant of annihilator triplets

a_0 : annihilation distance between annihilator triplets

τ_T : lifetime of annihilator triplets

Larger sensitizer absorption, efficient TTET, faster triplet diffusion, longer emitter triplet lifetime are required to achieve a low I_{th}.



low intensity : the emission from TTA exhibits quadratic

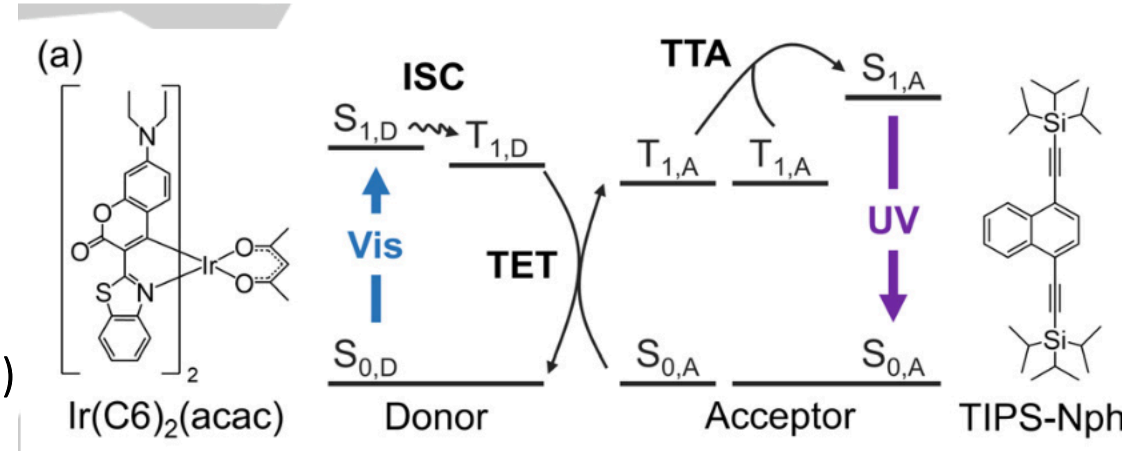
high intensity : the TTA becomes dominant for emitter triplet decay, emission intensity.

N. Yanai and N. Kimizuka, *Acc. Chem. Res.*, **2017**, *50*, 2487.

Concentration

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

Φ_{FL} : quantum yield of annihilator fluorescence
74 % (100 μM) → 66 % (10 mM)
due to the inner filter effect



[Ir(C6)(acac)] = 100 μM, [TIPS-Nph] = 10 mM
in deaerated THF
η_{UC} = 20.5 % (445 nm laser)
The highest Vis-to-UV TTA-UC

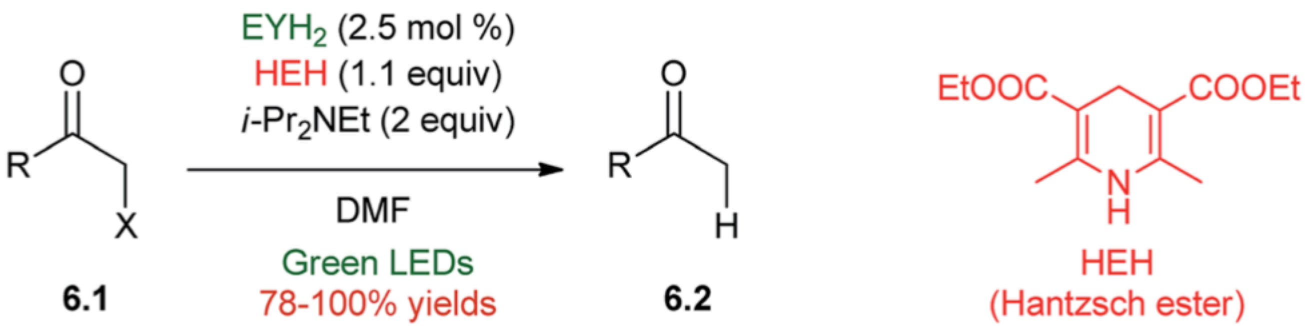
Low sensitizer concentration
→ weak absorption at the UV region
→ high visible absorbance, high η_{UC}

Case : the broad absorption of sensitizers
High sensitizer concentration
→ reabsorption, quenching the upconverted emission, back energy tranfer

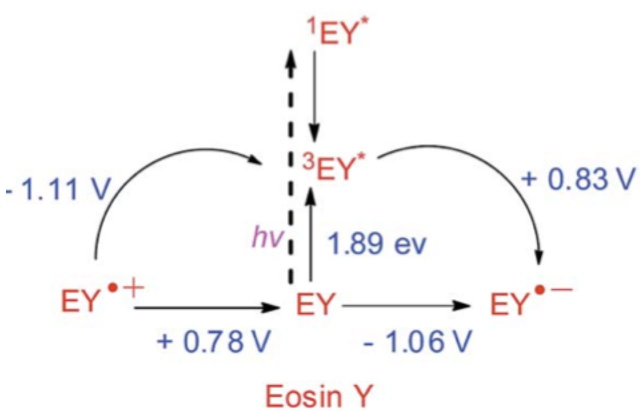
N. Yanai and N. Kimizuka *et al., Angew. Chem. Int. Ed.,* doi : 10.1002/anie.202012419

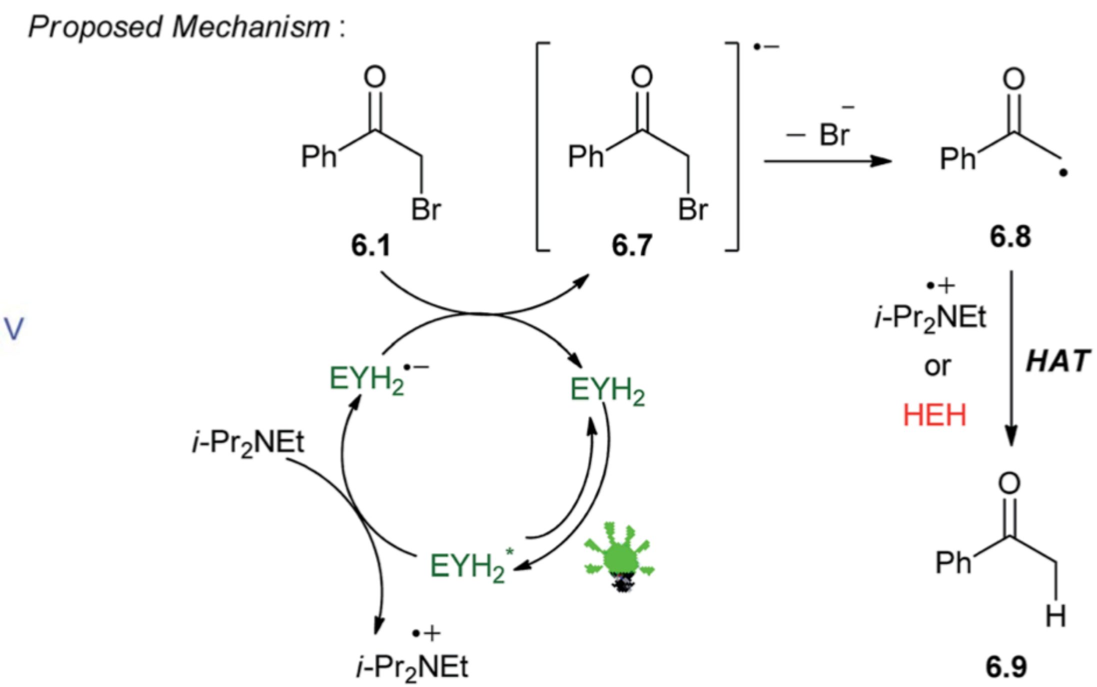
Eosin Y as a photocatalyst

Neumann's research group reported the reductive dehalogenation.
Eosin Y is used as a photoredox catalyst.



EYH$_2$ = Eosin Y

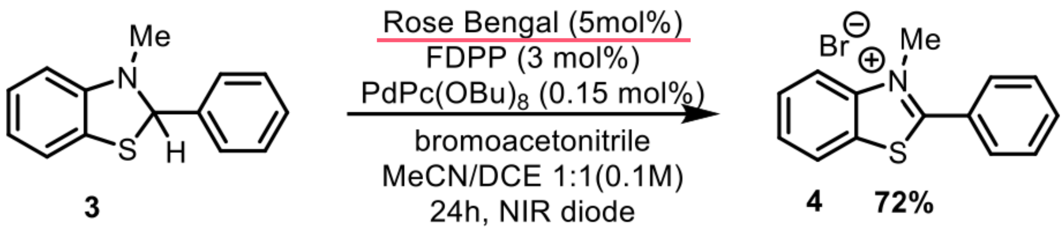




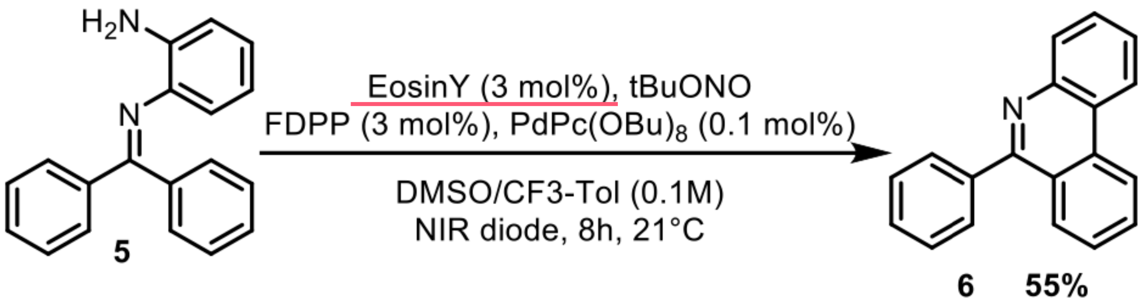
Vishal Srivastavaa and Praveen P. Singh, *RSC Adv.*, **2017**, 7, 31377.

Combination TTA-UC with PC

<u>The generality of FDPP/PcPc in TTA-UC</u>



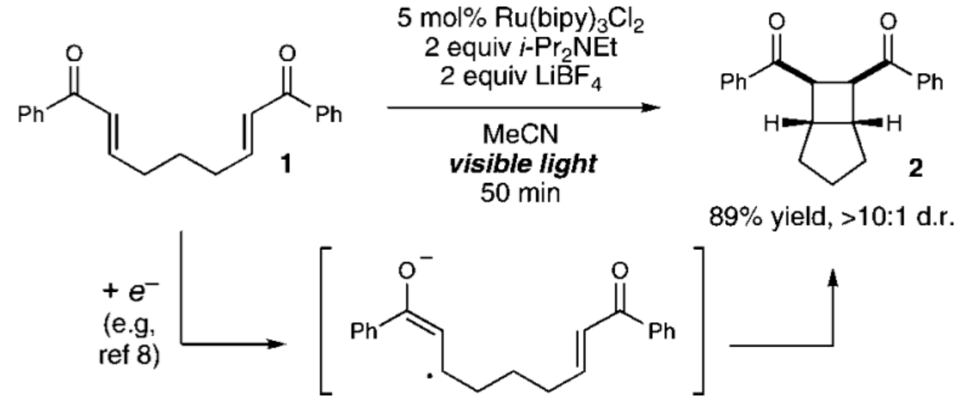
Control Reactions:	
No IR laser:	4%
No RB:	7%
No FDPP:	4%
No $PdPc(OBu)_8$:	4%
40W Blue Lamp:	82%



Controls Reactions:	
No IR laser:	2%
No Eosin Y:	2%
No FDPP:	1%
No $PdPc(OBu)_8$:	2%
40W Blue Lamp:	78%

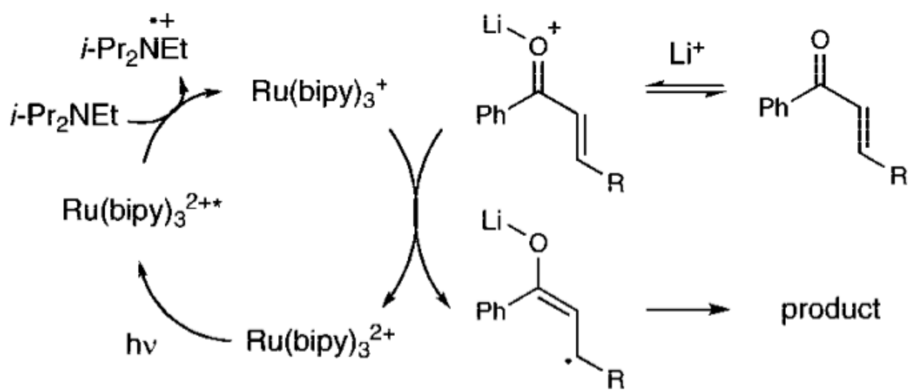
[Ru]-catalyzed [2+2] cyclization

Scheme 1



The reduction potential of $Ru^{*}(bpy)_3^{2+}$ = -0.89 V vs SCE

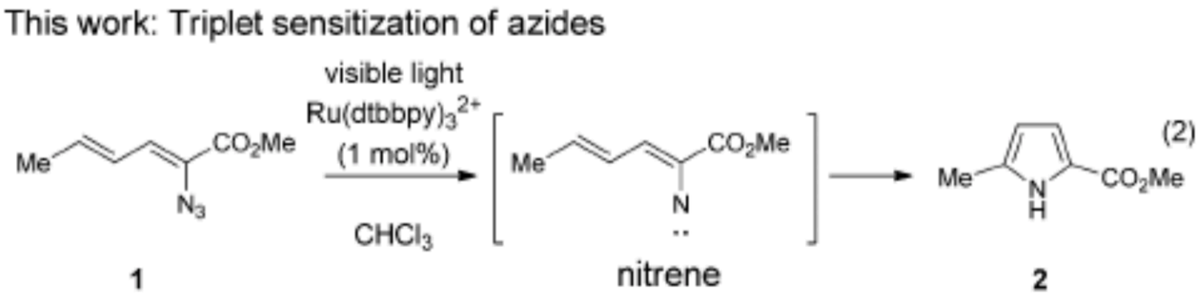
Scheme 2



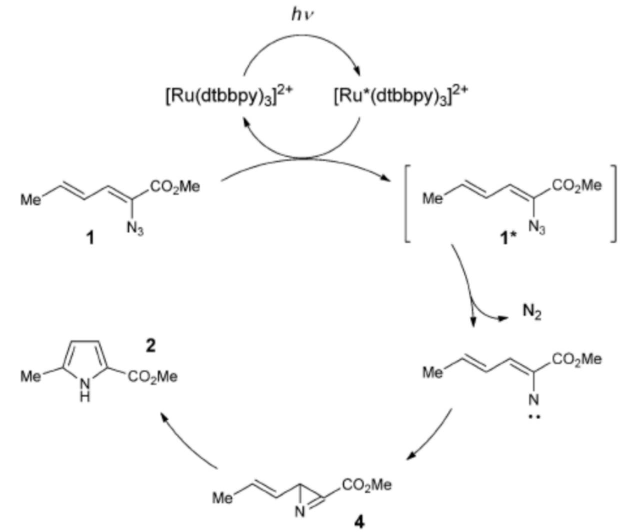
P. *et al., J. Am. Chem. Soc.*, **2008**, 130, 12886.

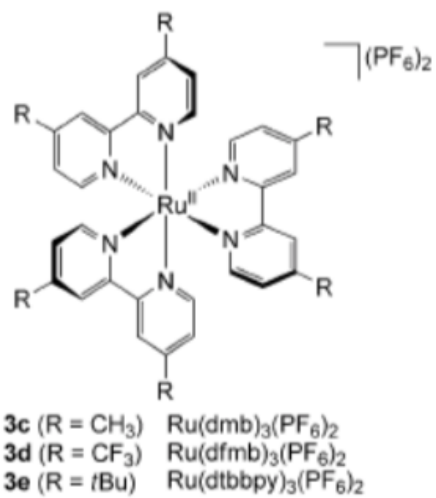
E. P. Farney and T. P. Yoon, *Angew. Chem. Int. Ed.*, **2014**, *53*, 793

[Ru]-catalyzed azide sensitization



Scheme 1. Photoreduction versus energy transfer photocatalysis for activation of organic azides.





The reduction potential of **1** = -1.81 V vs SCE
$Ru^*(bpy)_3^{2+}$: -0.89 V vs SCE

Triplet excited state of **1** : E_T = 45.4 kcal mol^{-1}
$Ru^*(bpy)_3^{2+}$: E_T = 46 kcal mol^{-1}
→Not SET, but sensitization of **1** by the long lived $Ru^*(bpy)_3^{2+}$ triplet state

$Ru^*(dtbbpy)_3^{2+}$: E_T = 47 kcal mol^{-1}

E. P. Farney and T. P. Yoon, *Angew. Chem. Int. Ed.,* **2014**, *53*, 793.

ATRP by perylene as PC

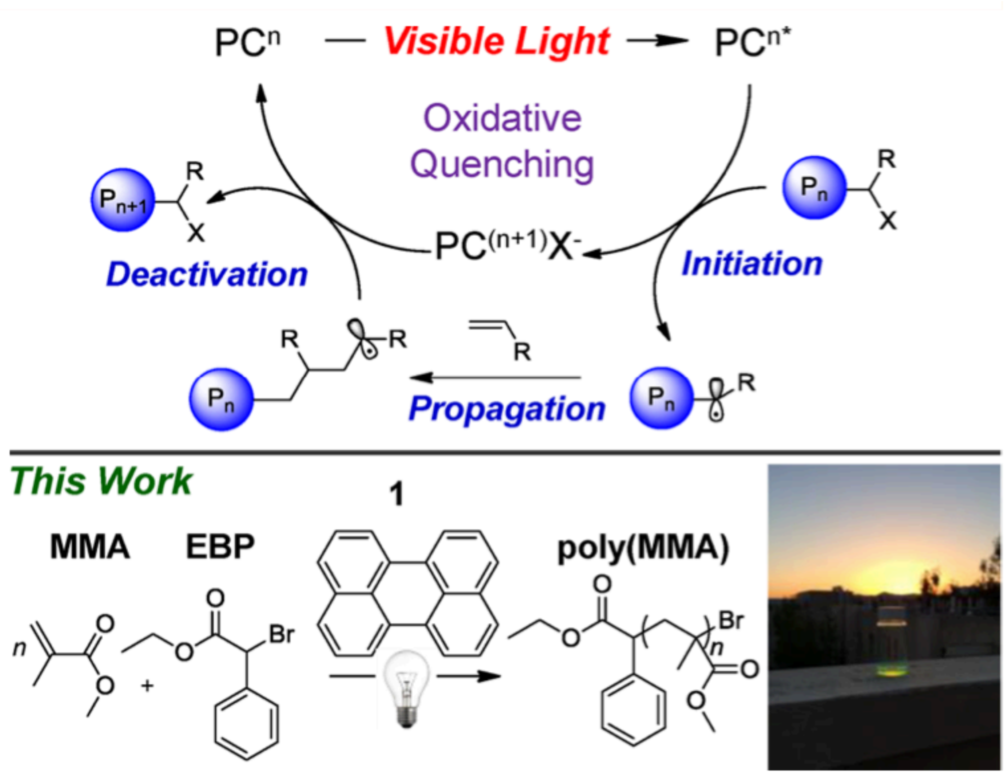
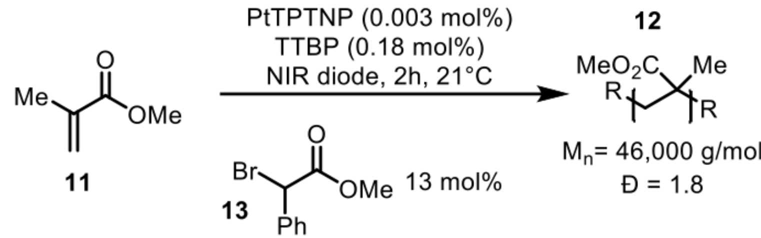


Figure 1. Proposed mechanism for a photoredox-mediated ATRP proceeding through an oxidative quenching pathway with alkyl halides (top) and the use of perylene as an organic photocatalyst for the polymerization of methyl methacrylate with alkyl bromide initiators (bottom) and a photograph of this polymerization being mediated by natural sunlight (bottom right).



Controls:	
No IR laser:	No rxn
No TTBP:	No rxn
No PtTPTNP:	No rxn

($E_{1/2}$ (13/13$^{-\bullet}$) = -1.58 V vs Ag/AgCl in MeCN.

Miyake, G. M. and Theriot, J. C., *Macromolecules,* **2014**, *47*, 8255.
D. N. Congreve, T. Rovis, L. M. Campos *et al.*, *Nature*, **2019**, 565, 343.

Experimental set up

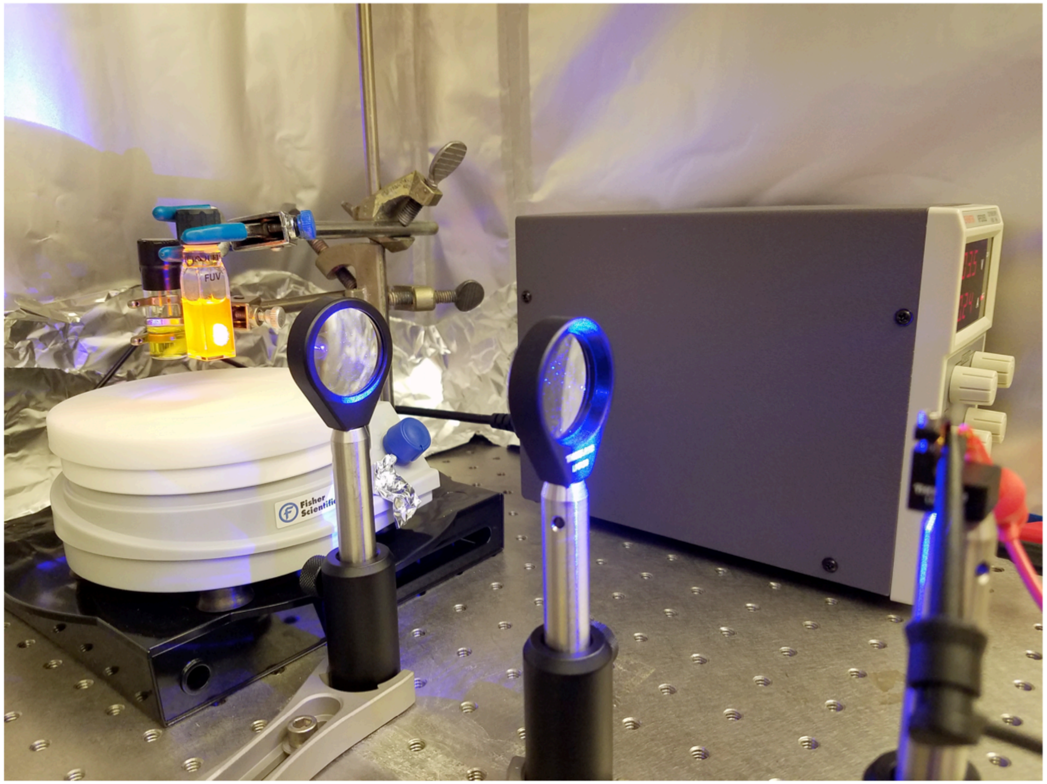


Figure S3. Experimental set up for materials barrier penetration. Shown here with 450 nm laser on, with 1.5mM Ru(bpy)$_3$ (PF$_6$)$_2$ solution in DCM as the barrier. Note that the barrier completely blocks the reaction vial behind it from absorbing any visible light.

D. N. Congreve, T. Rovis, L. M. Campos *et al.*, *Nature*, **2019**, 565, 343.

Perylene derivatives and PdTNP

The definition of the upconversion quantum yield

$\Phi_{UC} = f\,\Phi_{ISC}\,\Phi_{TTET}\,\Phi_{cp}\,\Phi_f \quad \leq 1$

Φ_{cp} : contact pair formation efficiency for annihilator

$\Phi_{TTA} = \Phi_{cp} \times f$

$\eta_{TTA} = 2 \times \Phi_{TTA}$

PdTNP

A long triplet excited time

$\tau_T = 65\ \mu s$

	λ_{abs} [a] (nm)	ε [b] ($10^5\ M^{-1}\ cm^{-1}$)	λ_{em} [c] (nm)	Φ_f(%) [d]
PdTNP	702	1.64	937[f]	6.6 [g]
Py-0	443	0.37	488	83
Py-1	468	0.37	518	70
Py-2	476	0.48	526	72
Py-3	477	0.41	529	68
Py-4	498	0.42	550	74
Py-5	506	0.49	572	76

[a] In toluene. [b] Molar absorption coefficient. [c] The fluorescence peak wavelengths. [d] Fluorescence quantum yield. [f] Phosphorescence. [g] Phosphorescence quantum yield.

Han, G. *et al.*, *J. Am. Chem. Soc.*, **2020**, *142*, 18460.

Perylene derivatives and PdTNP

TTET

TTA

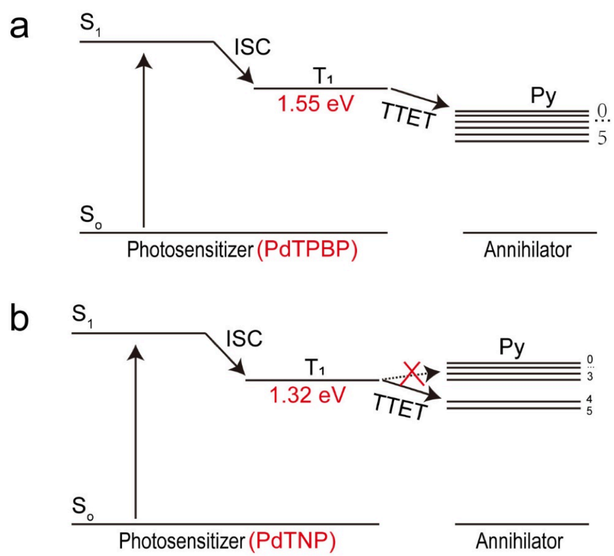


Fig S18. Simplified jablonski diagram illustration estimates the range of T_1 state of annihilators via triplet-triplet energy transfer (TTET) method in toluene.

Table S4. A summary of the singlet excited/triplet excited state energy level of Py0-Py5.

	Singlet excited state (S_1) [a]	Triplet excited state (T_1) [b]	$2 \times T_1$ -S_1
Py0	2.78 eV	1.53 eV	0.28 eV
Py1	2.60 eV	1.39 eV	0.18 eV
Py2	2.57 eV	1.37 eV	0.17 eV
Py3	2.56 eV	1.38 eV	0.20 eV
Py4	2.44 eV	1.24 eV	0.04 eV
Py5	2.39 eV	1.23 eV	0.07 eV

[a] S_1 was calculated the intersection of fluorescence emission and UV-vis absorption spectra; [b] T_1 was calculated by TD-DFT.

Han, G. *et al.*, *J. Am. Chem. Soc.*, **2020**, *142*, 18460.

Perylene derivatives and PdTNP

$\Phi_{UC} = f\,\Phi_{ISC}\,\Phi_{TTET}\,\Phi_{cp}\,\Phi_f$
$\eta_{TTA} = 2 \times \Phi_{TTA} = 2 \times (\Phi_{cp} \times f\,)$
$\Phi_{TTA} \rightarrow \eta_{TTA}$

Table S8. TTET quantum efficiency (Φ_{TTET}) and normalized TTA efficiency (η_{TTA}) of **PdTNP** and annihilators.

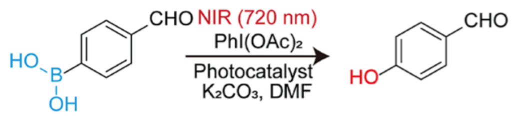
	Φ_f [a] (%)	Φ_{TTET} (%) [b]	η_{TTA} (%) [c]	Φ_{UC} (%) [d]
Py0	83	1.82	0	–
Py1	70	5.54	1.52	0.06
Py2	72	17.1	2.02	0.25
Py3	68	5.97	5.92	0.24
Py4	74	33.7	30.4	7.6
Py5	76	41.1	53.2	16.6

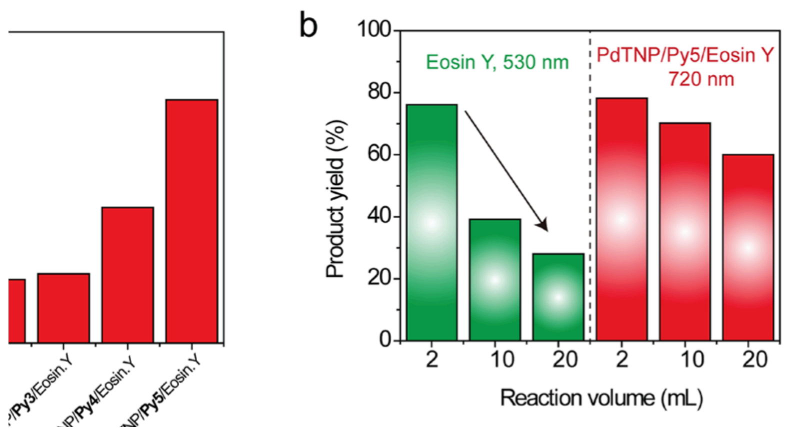
[a] fluorescence quantum yield of annihilators of Py0-Py5; [b] triplet-triplet energy transfer quantum efficiency; [c] normalized triplet-triplet annihilation efficiency, regarded to PdTNP, the intersystem crossing efficiency (Φ_{ISC}) nearly to 100%; [d] TTA upconversion efficiency.

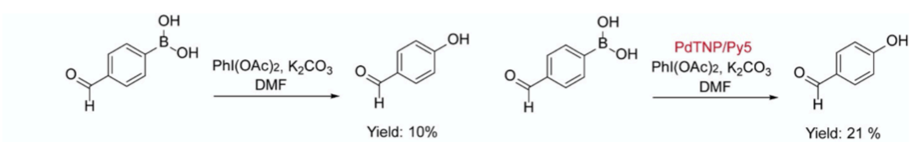
Table S9. The calculation summary of TTA-UC efficiency under 653 nm laser illumination.

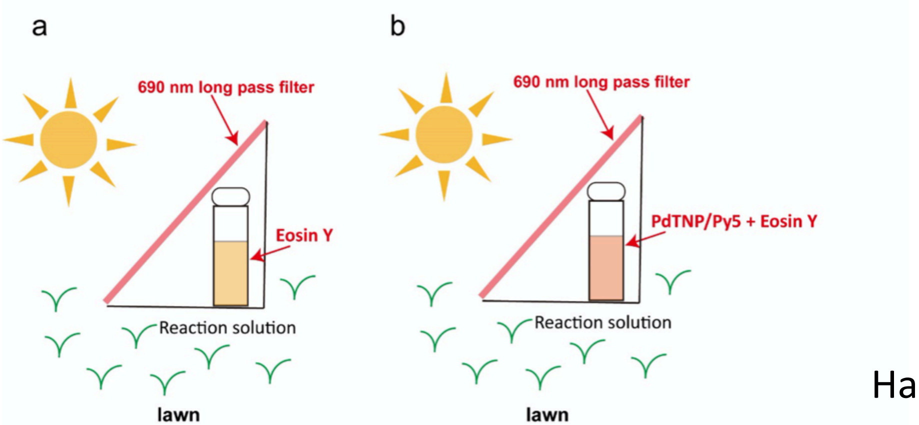
Han, G. *et al.*, *J. Am. Chem. Soc.*, **2020**, *142*, 18460.

Photocatalysis utilizing TTA-UC









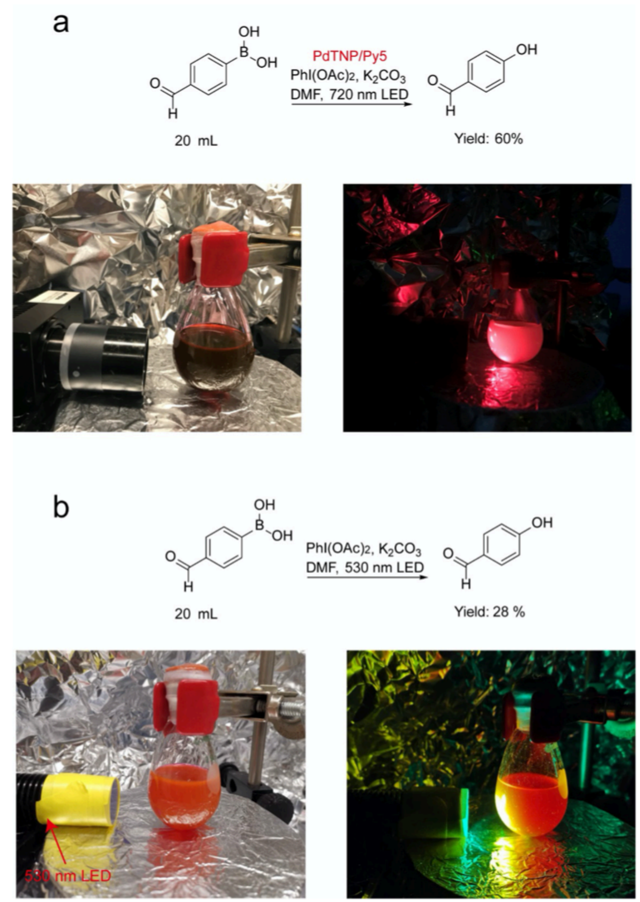


Fig S51. (a) The NIR activated photooxidation of arylboronic acid to arylphenol via TTA-UC; (b) directly green light driven photooxidation of arylboronic acid to arylphenol. The reaction volume is 20 mL, the NIR light or green light power intensity is 20 mW/cm^2, the bottom panel is the picture of reaction setup for the reaction.

Han, G. *et al.*, *J. Am. Chem. Soc.*, **2020**, *142*, 18460.

Proposed mechanism

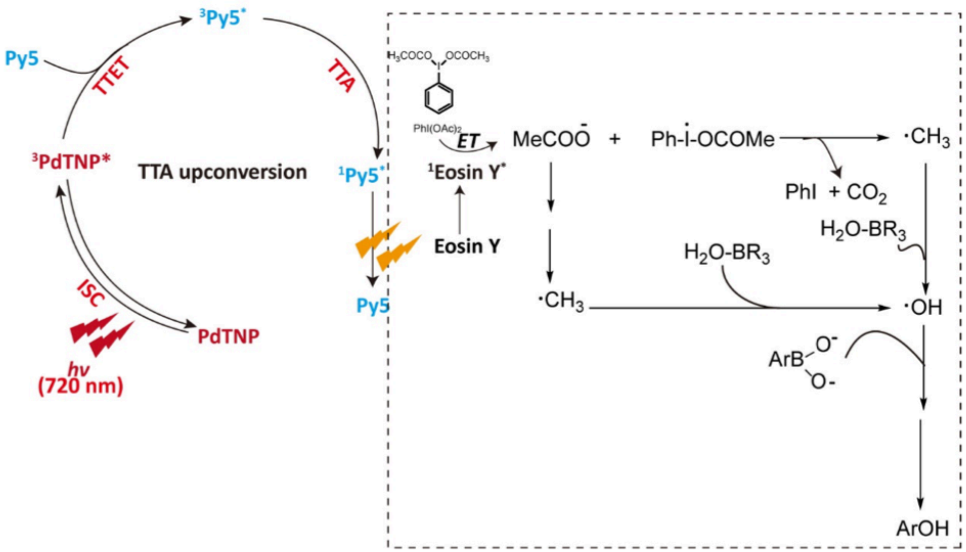
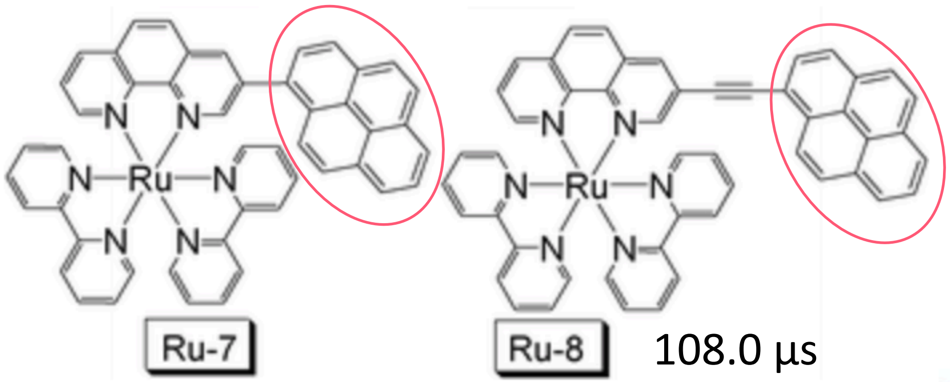


Fig S56. The proposed mechanism of NIR driven TTA-UC mediated photooxidation of aryl boronic acid.

Extending the lifetime

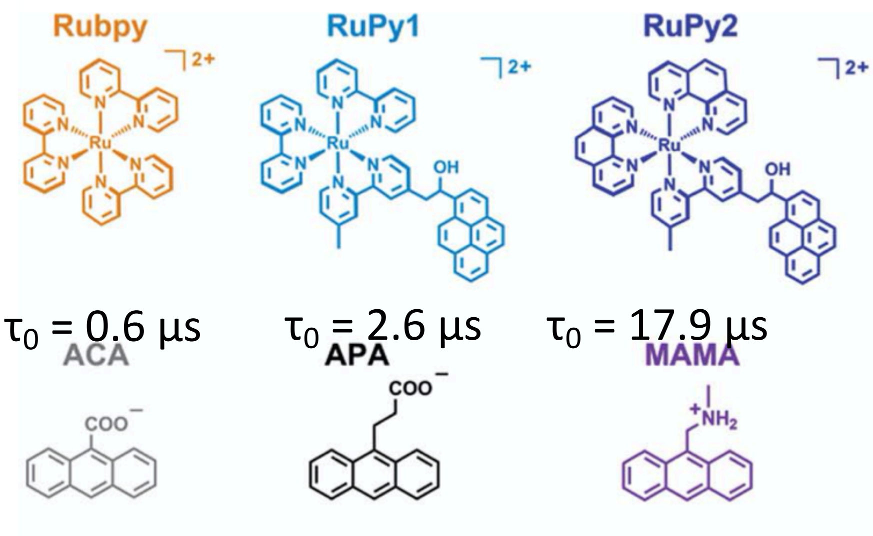
Extending the lifetime of triplet excited state of sensitizers



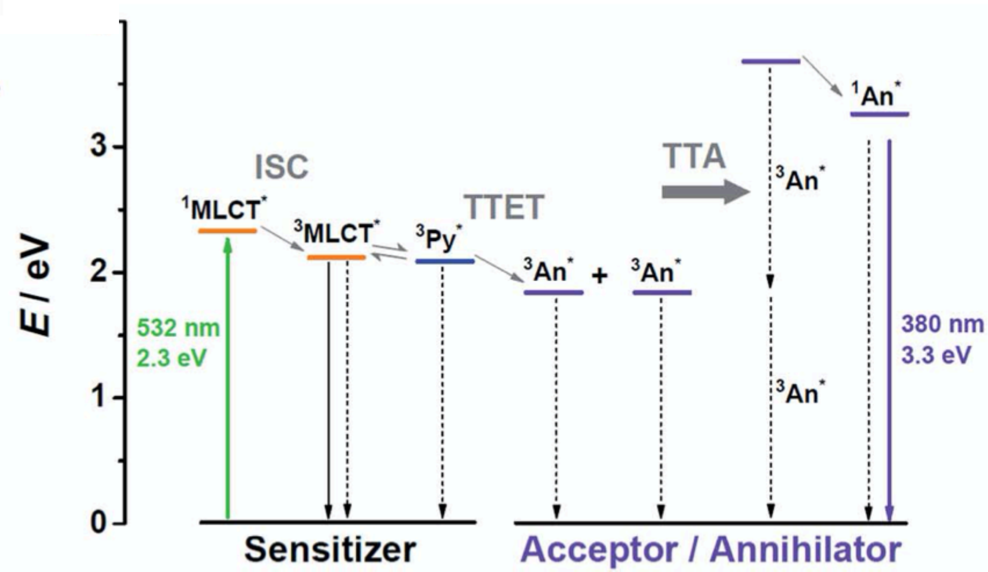
108.0 μs

^{3}MLCT/^{1}IL excited state equilibrium
IL = intraligand

J. Zhao *et al., RSC Advances*, **2011**, *1*, 937.



τ_0 = 0.6 μs τ_0 = 2.6 μs τ_0 = 17.9 μs



C. Kerzig and O. S. Wenger, *Chem. Sci.*, **2018**, *9*, 6670.