Photon upconversion via triplet–triplet annihilation

- **Photon upconversion**: the process wherein light of long wavelength is frequency converted to photons of higher energy.

- **Triplet–triplet annihilation (TTA)** is a promising upconversion approach due to its *low excitation power density requirement* (solar light is sufficient), *high upconversion quantum yield*, readily *tunable excitation/emission wavelength* and *strong absorption of excitation light*.

- The sensitized triplet–triplet annihilation mechanism involves *energy transfer* between a *sensitizer* (donor) molecule and an *acceptor/annihilator*.

- (Right) Upconverted fluorescence produced in a CH$_3$CN solution containing [Ru(dmb)$_3$]$^{2+}$ and diphenylanthracene (DPA) using a commercial green laser pointer excitation source ($\lambda_{\text{exc}} = 532$ nm).
• Traditional techniques for upconversion include two-photon absorption dyes (TPA), upconversion with inorganic crystals (such as potassium dihydrogen phosphate aka KDP), and rare earth materials, e.g. lanthanides etc.

• These techniques suffer from drawbacks of necessity for high excitation power, e.g. coherent lasers (MW cm\(^{-2}\)) are needed for TPA, poor absorption of visible light, and low upconversion quantum yield, etc.

• Such techniques are unlikely to be used for solar applications (100 mW cm\(^{-2}\)).

• Furthermore, it is difficult to tailor the structure of TPA dyes to achieve a specific upconversion wavelength and at the same time, to maintain a high TPA cross section.

• Upconversion schemes with rare earth materials have attracted much attention of late, however, they suffer from low molar extinction coefficients and thus poor overall upconversion efficiencies.

\[ \eta = \varepsilon_{\text{exc}} \cdot \Phi_{\text{UC}} \]
**Φ\text{UC} and overall efficiency (η)**

- Upconversion quantum yields have been determined for several systems to date. It is important to note that these efficiencies are controlled by a variety of factors including **relative chromophore concentrations** along with the **quadratic excitation power dependence** which makes quantification of an **absolute quantum yield** for the relevant process difficult.

- This problem is approached by defining **relative TTA upconversion quantum efficiencies (Φ\text{UC})** measured under very precise experimental conditions.

\[
\Phi_{\text{UC}} = 2\Phi_{\text{std}} \left( \frac{A_{\text{std}}}{A_{\text{un}}} \right) \left( \frac{I_{\text{un}}}{I_{\text{std}}} \right) \left( \frac{\eta_{\text{un}}}{\eta_{\text{std}}} \right)^2
\]

- In some cases the triplet sensitizer is non-phosphorescent, thus the quenching can be measured by the **variation of the lifetime of the T_1 excited state** of the sensitizer using time-resolved transient absorption spectroscopy.

- Recently Zhao has proposed to use the product ε_{exc}.Φ_{UC} to evaluate the overall upconversion capability (η) of a triplet sensitizer as triplet sensitizers with large η values are more likely to be ideal for practical applications. Materials with large Φ_{UC} but small ε_{exc} are not ideal for applications.
• **TTA upconversion shows advantages over traditional upconversion techniques for a number of reasons:**

  ➢ The excitation power density required for TTA upconversion is quite low and need not be coherent (< 100 mW cm\(^{-2}\)).

  ➢ Excitation with energy density of a few mW cm\(^{-2}\) is sufficient to sensitize the upconversion process making it possible to use solar light as the excitation source.

  ➢ The excitation wavelength and emission wavelength of TTA upconversion can be readily changed by judicious selection of the two components of the upconversion scheme, i.e. the triplet sensitizer and the triplet acceptor (annihilator/emitter) as longs as the energy levels of the excited state of the sensitizers and the acceptors are matched (see state energy diagram below)

• Thus the TTA upconversion is promising for applications such as photovoltaics, photocatalysis, and many other solar-driven photophysical and photochemical processes.
• Generalized state energy level diagram of the TTA upconversion processes between the triplet states of the sensitizer molecule and the triplet acceptor molecule leading to the singlet delayed fluorescence.

• TTET is triplet–triplet energy transfer. This is a bimolecular Dexter process requiring physical contact of the two components. Diffusion and sensitizer ($T_1$) lifetime dependent in solution.

• TTA is triplet–triplet annihilation. A bimolecular process. Diffusion and hence acceptor ($T_1$) lifetime dependent in solution.
• Generalized state energy level diagram of the TTA upconversion processes between the triplet states of the sensitizer molecule and the triplet acceptor molecule leading to the singlet delayed fluorescence.

• **TTET is triplet–triplet energy transfer.** This is a bimolecular Dexter process requiring physical contact of the two components. Diffusion and sensitizer (T₁) lifetime dependent in solution.

• **TTA is triplet–triplet annihilation.** A bimolecular process. Diffusion and hence acceptor (T₁) lifetime dependent in solution.
• In reality, **the sensitization process cycles many times** yielding a substantial population of long-lived sensitized triplets enabling TTA to take place rather efficiently.

• The primary evidence supporting TTA typically involves the observation of **singlet fluorescence observed anti-Stokes to the excitation light** possessing a spectral profile identical to the acceptor molecule.

• The intensity of this singlet fluorescence displays **a quadratic ($x^2$) incident light power dependence** as TTA requires reaction between two sensitized triplet acceptor molecules.
TTA upconversion theoretical limit

• The theoretical limit for TTA-upconversion efficiency has been predicted as 11.1% assuming both the quenching efficiency $\Phi_{\text{TTE}}$ and the fluorescence quantum yield $\Phi_{\text{Fl}}$ of acceptor are 100%

$$\Phi_{\text{UC}} = \Phi_{\text{TTE}} \cdot \Phi_{\text{TTA}} \cdot \Phi_{\text{Fl}}$$

• The spin state of the triplet encounters of the acceptors is governed by spin-statistical factors.

• Interaction of two excited acceptor triplets ($^3\text{A}*$) can produce up to nine excited state dimer (aka excimer) spin states $^n(\text{AA})*$ with equal probability.

• Spin statistics predicts that the $^1\text{A}*$ state represents just $1/9^{\text{th}}$ (11.1%) of the annihilation products.

• Examples of TTA-upconversion exceeding the proposed 11% limit have been reported, likely due to indirect triplet state formation from the quintet excimer state $^5(\text{AA})*$.
When two distinct molecules A and B with spin multiplicities of $m$ and $n$, respectively, diffusonally encounter, the product of these spin multiplicities $(m.n)$ directly gives the number of possible encounter-pair spin states. In a TTA reaction $m.n = 9$.

In the absence of an applied magnetic field, the encounter-pair spin states become equally populated under equilibrium conditions at ambient temperatures.

This implies that the formation probability of each individual state is simply the inverse of the product of the two reactant spin multiplicities $(m.n)^{-1}$; the so-called spin-statistical factor.

The spin multiplicities of the encounter-pair sublevels produced are determined by the Clebsch–Gordon series, where $S$ ($M = 2S + 1$) can have a maximum value of $S_1 + S_2$, a minimum value of $|S_1 - S_2|$, and intermediate values incremented by 1.

When two excited triplets ($^3A^*$) interact ($S_1 = S_2 = 1$), nine encounter-pair spin states are produced with equal probability which are composed of three distinct sublevels, five of which are quintet ($S = 2$), three are triplet ($S = 1$), and one is of singlet ($S = 0$) character.

Spin statistics predicts that as long each encounter-pair preserves their multiplicity, one would expect that upconverted singlet fluorescence from TTA, represents just 1/9 or 11.1% of the annihilation events.
Concerning the Spin-Statistical Factor in the Triplet–Triplet Annihilation of Anthracene Triplets

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Received March 16, 1981. Revised Manuscript Received August 24, 1981

Scheme I. Kinetics for Triplet Formation and Decay

\[ \begin{align*}
{^1}A & \quad + \quad {^1}A & \quad \rightarrow & \quad {^1}A^* + {^3}A^* & \quad + & \quad {^3}A^* + {^1}A \\
\quad & \quad \uparrow k_f & \quad \uparrow k_{dt} & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad \\
{^1}A & \quad \frac{I_a}{k_{ds}} & \quad {^1}A^* & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad \\
\quad & \quad \quad \downarrow k_e[\text{1\textit{A}}] & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad \\
{^1}(\text{AA})^* & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad \\
{^1}(\text{AA})^* & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad \\
{^1}A + {^1}A & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad & \quad \quad \\
\end{align*} \]

\(^1\text{A}, \text{ground-state singlet anthracene}; ^1\text{A}^*, \text{lowest excited singlet state}; ^3\text{A}^*, \text{lowest triplet state}; ^1(\text{AA})^*, \text{singlet excimer of anthracene}; (^3\text{A}^*^3\text{A}^*), \text{paired triplet state resulting from the encounter of two } ^3\text{A}^* \]
Scheme II. Proposed Mechanism for Anthracene TTA

\[ 3\Delta^* + 3\Delta^* \]

- \((1/9)k_{\text{dif}}\) 
  - \(1(\Delta\Delta)^{**} \rightarrow 1(\Delta\Delta)^* \rightarrow \text{no } 3\Delta^* \text{ directly} \)
  - \((3/9)k_{\text{dif}}\) 
    - \(3(\Delta\Delta)^{**} \rightarrow 3(\Delta\Delta)^* \rightarrow 3\Delta^* + 1\Delta \)
    - \((5/9)k_{\text{dif}}\) 
      - \(5(\Delta\Delta)^{**} \rightarrow 5(\Delta\Delta)^* \)
        - \(0.08 \) 
          - \(1\Delta^* + 1\Delta \)
        - \(0.92 \) 
          - \(23\Delta^* \)

Scheme III. Formation and Decay of Singlet Excimer

- \(1\Delta^* \rightarrow k_e[1\Delta] \)
  - \(1(\Delta\Delta)^* \)
    - \(k_{\text{de}}\) 
      - \(0.24 \) 
        - \(A_2 \)
    - \(0.76 \) 
      - \(21\Delta \)

- \(1(\Delta\Delta)^{**} \)
Scheme II. Proposed Mechanism for Anthracene TTA

\[ 3^\Delta^* + 3^\Delta^* \rightarrow 3(AA)^{**} \rightarrow 3(AA)^* \rightarrow \text{no } 3^\Delta^* \text{ directly} \]

\[ (1/9)k_{\text{dif}} \]

\[ (3/9)k_{\text{dif}} \]

\[ (5/9)k_{\text{dif}} \]

\[ 1(AA)^{**} \rightarrow 1(AA)^* \rightarrow 3^\Delta^* + 1^\Delta \]

\[ 5(AA)^{**} \rightarrow 5(AA)^* \rightarrow 1^\Delta^* + 1^\Delta \]

\[ 0.08 \]

\[ 0.92 \]

\[ 2^3\Delta^* \]

Scheme III. Formation and Decay of Singlet Excimer

\[ 1^\Delta^* \rightarrow 1(AA)^* \rightarrow 1(AA)^{**} \rightarrow A_2 \]

\[ k_e[1^\Delta] \]

\[ k_{de} \]

\[ 0.24 \]

\[ 0.76 \]

\[ 2^1\Delta \]
Low power upconversion using MLCT sensitizers†

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Received (in Cambridge, UK) 11th May 2005, Accepted 26th May 2005
First published as an Advance Article on the web 4th July 2005
DOI: 10.1039/b506575e

[\text{Ru(dmb)}_3^{2+} + h\nu (514 \text{ nm}) \rightarrow \{ \text{[Ru(dmb)}_3^{2+}]^* \}

\{ \text{[Ru(dmb)}_3^{2+}]^* \} + \text{DPA} \rightarrow \text{[Ru(dmb)}_3^{2+}]^* + ^3\text{DPA}^*

^3\text{DPA}^* + ^3\text{DPA}^* \rightarrow ^1\text{DPA}^* + \text{DPA}

^1\text{DPA}^* \rightarrow ^1\text{DPA} + h\nu

The triplet $^3$MLCT excited state is higher in energy than the triplet state of DPA, while the singlet excited state of DPA is higher in energy than that of the $^1$MLCT and is lower than two times the triplet state of DPA, thereby satisfying the energy requirements for sensitized TTA.
"In essence the simpler non-covalent donor-acceptor system in dilute solutions was found to be superior in generating the anti-Stokes delayed anthracene fluorescence."

Why?
[Ru(dmb)$_3$]$^{2+}$ + An + $h\nu$ (450 nm)

vs.

[Ru(dmb)$_2$(bpy-An)]$^{2+}$ + $h\nu$ (450 nm)

“In essence the simpler non-covalent donor-acceptor system in dilute solutions was found to be superior in generating the anti-Stokes delayed anthracene fluorescence.”

- Direct comparison between the intramolecular and intermolecular systems under identical experimental conditions resulted in a ~2.9-fold increase, likely resulting from suppression of Förster type singlet-singlet transfer subsequent to TTA.
- TTA upconversion requires that the concentration of the sensitizers at the triplet excited state be high, thus population of the acceptor molecules at the triplet excited state will be high, and the TTA upconversion will be more significant.

- The reason for this mandate is the bimolecular feature of the TTET and the TTA processes. With higher concentration of the triplet sensitizers at the triplet excited state, the TTET process will be more efficient to produce the acceptors at triplet excited state.
Design criteria for efficient TTA upconversion

Several factors are considered when determining the proper combination of chromophores in a viable homogeneous solution based upconverting scheme.

1. The triplet sensitizer should have a large $\varepsilon_{\text{max}}$ at the excitation wavelength in the visible-to-near-IR region of the spectrum thus enabling low energy & low power sensitizer photoexcitation.

2. A long lived triplet sensitizer lifetime (> µs) is necessary to facilitate efficient diffusional-based quenching.

3. Transition metal based sensitizers are favorable due to their large spin-orbit coupling coefficients ($\chi_{so}$) and efficient intersystem crossing to the triplet manifold. Efficient sensitization may be induced from triplet metal-to-ligand charge transfer ($^{3}\text{MLCT}$) excited states or heavy metal induced formation of $^{3}(\pi-\pi^{*})$ excited states, e.g. Pt/Pd porphyrins and phthalocyanines, which display close to unity ISC efficiency.
4. To observe bimolecular quenching of the triplet excited state of the sensitizer the triplet acceptor energy must be lower than the triplet energy of the sensitizer. The greater the energy difference between the triplet sensitizer and triplet acceptor, the greater the driving force for this reaction, the more favorable the triplet energy transfer process.

5. It is advantageous to use acceptors/annihilators with near unity fluorescence quantum yields since this value ultimately contributes to the overall upconversion quantum efficiency.

6. The sensitizer (donor) molecule is chosen so that its singlet excited state lies below that of the acceptor’s singlet manifold while the sensitizer’s triplet state lies above that of the acceptor. In essence, the singlet and triplet excited states of the sensitizer should be strategically nested between the singlet and triplet excited states of the acceptor/annihilator.

- As long as these specific energy criteria are met and the combined triplet energy from two acceptor molecules is greater than or equal to the acceptor’s singlet state energy, then conditions are appropriate for the observation of upconverted fluorescence from the sample.
Triplet sensitizers for TTA upconversion

- Ru(II) polypyridyl complexes as triplet sensitizers
- Pt(II) Pd(II) porphyrin complexes
- Pt(II) acetylide complexes as the triplet sensitizers: tunable photophysical properties
- Cyclometalated Pt(II)/Ir(III) complexes
- Organic triplet sensitizers
- Sensitizers with non-emissive $T_1$ excited states
- **Triplet sensitizers for TTA upconversion**
Ru(II) polypyridyl complexes as triplet sensitizers

- The absorption of the \([\text{Ru(dmb)}_3]^{2+}\) complex is peaked at ca. 450 nm with \(\varepsilon \sim 1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\).

- The energy level of the triplet excited state of the \([\text{Ru(dmb)}_3]^{2+}\) sensitizer can be easily derived from the phosphorescence onset at \(\sim 600 \text{ nm (2.07 eV)}\) whose lifetime is 0.875 µs.

- DPA was here selectively chosen as the triplet acceptor, for which the energy level of the \(T_1\) excited state is 1.77 eV (700 nm).

- The mixed solution of \([\text{Ru(dmb)}_3]^{2+}\) and DPA was excited with a green laser (\(\lambda_{\text{exc}} = 514.5 \text{ nm, 24 mW}\) or \(\lambda_{\text{exc}} = 532 \text{ nm, 5 mW}\)), the upconverted blue fluorescence emission of DPA was observed centered at 430 nm, representing an anti-Stokes shift of ca. 100 nm.

- This result demonstrated that the TTA upconversion can be achieved with low-power density irradiation.
Ru(II) polypyridyl complexes as triplet sensitizers

• $E_{1/2} = +1.14$ V (vs. SCE)
• $\lambda_{\text{max}} = 450$ nm ; $\varepsilon \sim 1.4 \times 10^4$ M$^{-1}$ cm$^{-1}$
• $\lambda_{\text{em}} = 632$ nm ; $\Phi_{\text{Ph}} = 0.073$
• $^3\tau = 0.875$ $\mu$s
• $k_r = 0.83 \times 10^5$ s$^{-1}$ ; $k_{nr} = 10.6 \times 10^5$ s$^{-1}$
• $E_{0-0} = 17,310$ cm$^{-1}$ (2.15 eV)
• $E_{T1} = \text{ZPE} + 2.07$ eV

• $E_{1/2} = -1.90$ V (vs. SCE)
• $\lambda_{\text{max}} = 393$ nm ; $\varepsilon \sim 1.35 \times 10^4$ M$^{-1}$ cm$^{-1}$
• $\lambda_{\text{em}} = 404$ nm ; $\Phi_{\text{Fl}} = 0.95$
• $^1\tau = 7.58$ ns
• $k_r = 1.25 \times 10^8$ s$^{-1}$ ; $k_{nr} = 6.57 \times 10^6$ s$^{-1}$
• $E_{0-0} = 25,164$ cm$^{-1}$ (3.12 eV)
Label energies (V, eV) & wavelengths (nm) for the [Ru(dmb)₃]²⁺ / DPA TTA-upconversion system.
• The success of using [Ru(dmb)₃]²⁺ to achieve upconversion with low-power density excitation is attributed to the long lifetime of the ³MLCT excited state of the complex (0.87 ms).

• The prolonged T₁ excited state lifetime is beneficial to improve the TTET process and, as a result, can lead to more DPA molecules at the singlet excited state.

• However, upconversion with [Ru(dmb)₃]²⁺ suffers from some drawbacks.

➤ the UV-vis absorption of the Ru(II) complex is limited to the visible
   (λₘₐₓ = 450 nm, ε ∼ 1.4 x 10⁴ M⁻¹ cm⁻¹)

➤ the lifetimes of Ru(II) complexes are less than 1 ms. Longer lifetimes will enhance the TTET process for which the key photophysical step is also the TTET process.

• Triplet sensitizers with intensive absorption at longer wavelengths are desired.

• It is also desired to develop triplet sensitizers with prolonged T₁ excited state lifetimes.
Fig. 3  Molecular structures of typical Ru(II) polyimine complexes Ru-2, Ru-3 and Ru-4. The bottom panel shows the simplified energy level diagrams and the emission states for Ru-2, Ru-3 and Ru-4, respectively.
TTET efficiency (Stern-Volmer)

- TTA upconversion can be quantitatively described by not only by $\Phi_{UC}$ but also by the TTET quenching efficiency.

- The efficiency of TTET quenching can be effectively measured by conducting Stern-Volmer quenching experiments, with the triplet acceptor as the quencher Q. The bimolecular quenching constant $k_q$ is thus determined by the **Stern-Volmer equation**:

$$
\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[Q]
$$

where $K_{SV} = k_q \tau_0$

- $\tau_0$ is the lifetime of the triplet excited state of the sensitizer and $[Q]$ is the concentration of the quencher at which the residual emission of the sensitizer $I$ is determined.

- In some cases the triplet sensitizer is non-phosphorescent, thus the quenching can be measured by the **variation of the lifetime of the T_1 excited state** of the sensitizer using time-resolved transient absorption spectroscopy.
Laser Flash Photolysis measurements

Schematic presentation of a laser flash photolysis setup
\[ \frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[Q] \]

\[ K_{SV} = k_q \cdot \tau_0 \]

\[ \Phi_{UC} (\text{DPA}) / \Phi_{UC} (\text{An}) = 24 \]

\[
\begin{align*}
[Ru(dmb)_3]^{2+} + h\nu (514 \text{ nm}) &\rightarrow \{ [Ru(dmb)_3]^{2+} \}^* \\
\{ [Ru(dmb)_3]^{2+} \}^* + \text{DPA} &\rightarrow [Ru(dmb)_3]^{2+} + 3\text{DPA}^* \\
3\text{DPA}^* + 3\text{DPA}^* &\rightarrow 1\text{DPA}^* + \text{DPA} \\
1\text{DPA}^* &\rightarrow 1\text{DPA} + h\nu
\end{align*}
\]

\[ K_{SV} = 3.46 \times 10^3 \text{ M}^{-1} \]

\[ k_q = 4.1 \times 10^9 \text{ M}^{-1} \]

\[
\begin{align*}
[Ru(dmb)_3]^{2+} + h\nu (514 \text{ nm}) &\rightarrow \{ [Ru(dmb)_3]^{2+} \}^* \\
\{ [Ru(dmb)_3]^{2+} \}^* + \text{An} &\rightarrow [Ru(dmb)_3]^{2+} + 3\text{An}^* \\
3\text{An}^* + 3\text{An}^* &\rightarrow 1\text{An}^* + \text{An} \\
1\text{An}^* &\rightarrow 1\text{An} + h\nu
\end{align*}
\]

\[ K_{SV} = 4.49 \times 10^3 \text{ M}^{-1} \]

\[ k_q = 5.4 \times 10^9 \text{ M}^{-1} \]

- It is believed that DPA’s increased singlet fluorescence quantum yield ($\Phi_{Fl} = 0.95$) with respect to anthracene ($\Phi_{Fl} = 0.27$) affords a modest increase in relative upconversion efficiency.

\[ \Phi_{UC} = \Phi_{TTET} \cdot \Phi_{TTA} \cdot \Phi_{Fl} \]
**TTA rate constant ($k_{TT}$)**

- In order to determine the TTA rate constant ($k_{TT}$) in solution, the nanosecond excited state dynamics of the sensitizer before and after adding the acceptor chromophore are investigated.

- Nanosecond transient absorption (TA) measurements of the independent sensitizer and the independent acceptor are collected in deaerated solvent solutions.

- Subsequently TA measurements of the sensitizer upon addition of acceptor, until sufficient to efficiently quench the triplet excited state of the sensitizer, are obtained.

- The latter typically results in excited state features that are predominantly due to the triplet acceptor/annihilator molecule.

\[
\frac{d[3M^*]}{dt} = -k_T[3M^*] - k_{TT}[3M^*]^2
\]
\[ K_{SV} = 6.95 \times 10^4 \text{ M}^{-1} \]

\[ k_q = k_{TET} = 1.84 \times 10^9 \text{ M}^{-1} \]

\[ k_{TT} = 1.25 \times 10^4 \text{ M}^{-1} \]
Transient absorption difference spectrum of 5.1 μM PtTPBP measured at several delay times in deaerated DMF (2.0 mJ/pulse, $\lambda_{\text{exc}} = 630$ nm). The inset shows the single exponential fit to the 500 nm transient with residuals presented in green.

Transient absorption difference spectrum of 13.2 μM 2CBPEA measured at several delay times in deaerated DMF (2.0 mJ/pulse, $\lambda_{\text{exc}} = 470$ nm). The inset shows the single exponential fit to the 480 nm transient with residuals presented in green.
Transient absorption difference spectrum of 3.40 μM PtTPBP and 1 mM 2CBPEA measured as a function of delay time in deaerated DMF (2.0 mJ/pulse, $\lambda_{\text{exc}} = 630$ nm).

Time resolved absorption kinetics at 490 nm of 3.40 μM PtTPBP and 1 mM 2CBPEA in deaerated DMF measured as a function of laser pulse energy at $\lambda_{\text{exc}} = 630$ nm.
The upconverted DPA fluorescence and the residual phosphorescence of the mixture of DPA and Ru-5 or Ru-8.

Normalized absorbance (solid lines) and emission spectra (dotted lines) of DPA, Ru-5 and Ru-8.
Stern–Volmer plots generated from intensity quenching of complex $[\text{Ru(dmb)}_3]^{2+}$ ($\lambda_{\text{exc}} = 460$ nm), Ru-5 ($\lambda_{\text{exc}} = 446$ nm), Ru-6 ($\lambda_{\text{exc}} = 450$ nm), Ru-7 ($\lambda_{\text{exc}} = 450$ nm) and Ru-8 ($\lambda_{\text{exc}} = 418$ nm). Phosphorescence measured as a function of DPA concentration in CH$_3$CN (1.0 x 10$^{-5}$ M).
<table>
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<th>Sensitizer</th>
<th>Acceptor</th>
<th>$\lambda_{ex}$ (nm)</th>
<th>$E_{ex}$ (eV)</th>
<th>$\lambda_{obs}$ (nm)</th>
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<td>2.21</td>
<td>0.43</td>
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<td>BPEN</td>
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<td>560</td>
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<td>390</td>
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<td>[Ru(dmb)$_3$]$^{2+}$</td>
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$ex$ = excitation; $obs$ = peak observed emission wavelength.