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Additional Information

1 **Photon Upconversion Systems Based on Triplet–Triplet Annihilation**
2 **as Photosensitizers for Chemical Transformations**

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7
8 **Abstract**

9 Photon upconversion (UC) based on triplet-triplet annihilation (TTA) is considered one
10 of the most attractive methodologies for switching wavelengths from lower to higher
11 energy. This two-photon process which requires the involvement of a bimolecular system
12 has been widely used in numerous fields such as bioimaging, solar cells, displays, drug
13 delivery and so on. In the last years, we have witnessed the harnessing of this concept by
14 the organic community who have developed new strategies for synthetic purposes.
15 Interestingly, the generation of high-energetic species by this phenomenon has provided
16 the opportunity not only to photoredox activate compounds with high-energy demanding
17 bonds, expanding the reactivity window that lie outside the energy window of the initial
18 irradiation wavelength, but also to sensitized conventional photocatalysts through energy
19 transfer processes even employing infrared irradiation. Herein, an overview of the
20 principal examples found in literature is described where TTA–UC systems are found to
21 be suitable photosensitizers for several chemical transformations.

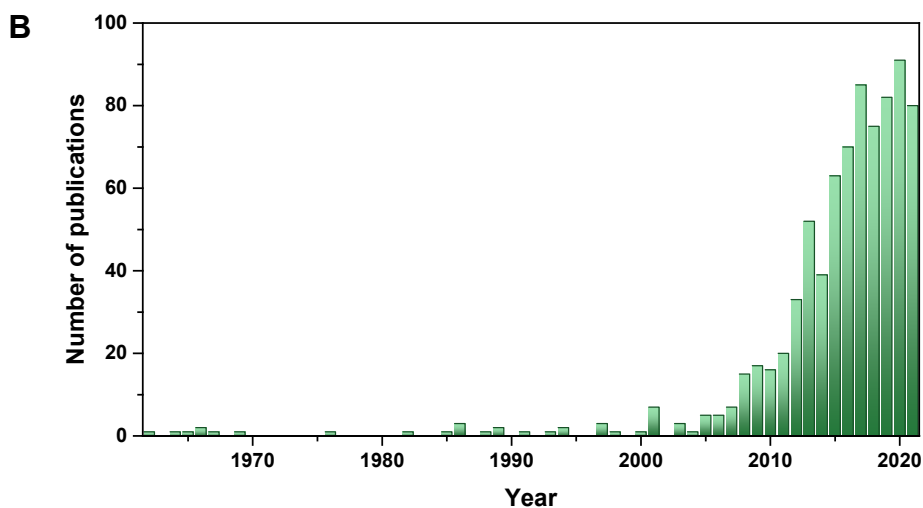
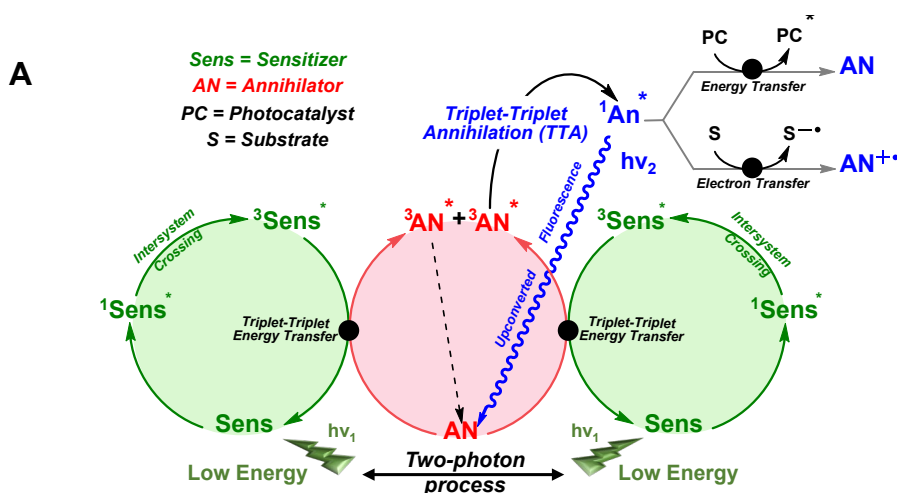
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23 **Keywords:**

24 Photon Upconversion, Triplet-Triplet Annihilation, Photocatalysts, Activation, Organic
25 Applications

33 **1. Introduction**

34 The first report on photon upconversion (UC) based on triplet-triplet annihilation (TTA)
 35 dates to 1962 when Parker and Hatchard observed this phenomenon employing non-
 36 covalent aromatic systems.[1] The photophysical principle of this wavelength-shifting
 37 technology is a general process that consists on absorbing two low-energy photons to emit
 38 one photon at a shorter wavelength. Thus, the appropriate selection of the sensitizer (Sens)
 39 and annihilator (AN) seems to be very important to optimize the UC. After selective
 40 irradiation of the longest wavelength to the Sens, its excited singlet state $^1[\text{Sens}]^*$
 41 intersystem crosses to the corresponding triplet state $^3[\text{Sens}]^*$. Now, a rapid and efficient
 42 energy transfer to the AN generates the corresponding triplet $^3[\text{AN}]^*$. Two of such
 43 intermediates can undergo TTA to promote the formation of delayed fluorescence $^1[\text{AN}]^*$
 44 having a higher frequency than that of the exciting light, i.e. upconverted fluorescence
 45 (Figure 1A).

46



49 **Figure 1. A:** Mechanism of photon upconversion based on triplet-triplet annihilation
50 (TTA–UC) facilitated by a molecular sensitizer (Sens) and annihilator (AN) pair and its
51 adaptation to photoredox catalysis. **B:** Number of publications/year from CAS SciFinderⁿ
52 source (search of references by keyword “photon upconversion” and then “triplet-triplet
53 annihilation” as text string within the result set).

54 Since this first example, the interest in TTA–UC largely remained dormant. This effect
55 suffered from low efficiencies mainly because organic sensitizers with poor triplet yields
56 via intersystem crossing (ISC) were utilized. However, the emergence of coordination
57 complexes as sensitizers due to their strong absorption bands in the visible region and
58 high triplet yields via ISC[2] opened the door to build new pair systems. In 2004,
59 Castellano and co-workers[3] observed that a metal-organic bimolecular system based on
60 Ru^{II} diimine metal-to-ligand charge transfer (MLCT) chromophore as Sens and
61 anthracene as AN produced upconverted delayed singlet anthracene fluorescence. From
62 this point, there has been an explosion of new related chromophore-quencher molecules
63 and bimolecular assemblies which are likely susceptible to the same upconversion
64 processes, allowing triplet state access to higher-lying fluorescent singlet states,
65 potentially yielding new materials with blue and/or UV emission properties. This fact has
66 been clearly reflected in the number of publications (Figure 1B) and TTA–UC has
67 evolved to multiple directions such as biochemical,[4–6] biological imaging,[7–8]
68 sensing,[9] photosynthesis enhancement,[10] solar energy harvesting,[11–14]
69 photocatalysis [15–16] or drug delivery and activation[17–19] applications.

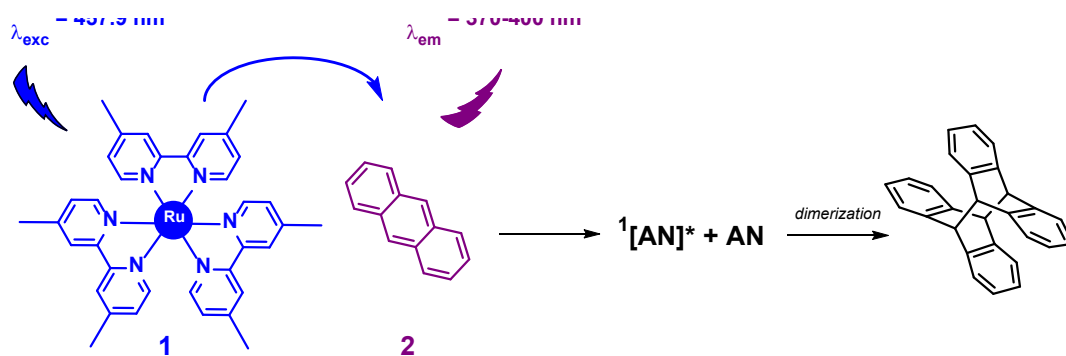
70 Light-driven systems that have excited states and promote a chemical reaction can be
71 generally classified as “excitonic chemical conversion systems” or more commonly
72 named in the literature as “photocatalysts”. The International Union of Pure and Applied
73 Chemistry (IUPAC) defines a “photocatalyst” as a “catalyst able to produce, upon
74 absorption of light, chemical transformations of the reaction partners. The excited state
75 of the photocatalyst repeatedly interacts with the reaction partners forming reaction
76 intermediates and regenerates itself after each cycle of such interactions.”[20] In this
77 context, photoredox catalysis is being used as a powerful and effective tool in the field of
78 organic synthesis since its resurgence in 2008.[21–22] The great impact of photoredox
79 catalysis with a variety of photocatalysts for modern synthetic chemists is demonstrated
80 by the immense amount of scientific reports published every day in this domain.[23–26]
81 The reason mainly relies on the mild reaction conditions of photoredox processes which

82 includes employment of sustainable visible light as energy source to generate a
83 photocatalyst in its excited state. The redox properties of the excited state can be exploited
84 upon fast electron transfer to promote the chemical alteration of organic compounds.
85 Regarding TTA–UC, the excited singlet $^1\text{AN}^*$ can then either emit a high energy photon
86 via upconverted fluorescence or participate in single-electron redox transfer as a
87 photoredox catalyst and even transferred its energy to a conventional photocatalyst
88 (Figure 1A). This issue has gratifyingly warned the organic community who has
89 successfully applied TTA–UC to synthetic procedures. The most challenging goal has
90 been therefore the implementation of two-photon excitation events into organic
91 photoredox catalysis to expand the accessible reactivity window to less activated
92 substrates. In this contribution, representative examples of chemical transformations
93 photocatalyzed by TTA–UC technology are provided. To frame the results of the
94 literature in a more specific perspective, this review has been divided depending on the
95 TTA–UC systems employed as photocatalysts to promote various chemical
96 transformations in one pot.

97 **2. Blue to UV or near-UV Upconversion**

98 One of the interesting aspects of TTA–UC is the use of low-energy photons to drive
99 photochemical reactions that traditionally require high energy ultraviolet light. In this
100 sense, Castellano and co-workers explored the feasibility of applying sensitized TTA–
101 UC in the well-documented photodimerization of anthracene,[27–28] representing a
102 suitable departure point of this story.[29] For this purpose, they used the bimolecular
103 system comprised by the metal-to-ligand charge-transfer (MLCT) $[\text{Ru}(\text{dmb})_3]^{2+}$ (dmb =
104 4,4'–dimethyl–2,2'–bipyridine) (**1**) as Sens and anthracene (**2**) as AN (Figure 2). Static
105 UV/Vis absorption spectra revealed the net loss of anthracene after 70 minutes when
106 selective excitation of $[\text{Ru}(\text{dmb})_3]^{2+}$ upon low power Ar^+ laser ($\lambda_{\text{exc}} = 457.9 \text{ nm}$) was
107 carried out in the presence of anthracene. Pure [4+4] anthracene dimers were produced
108 as confirmed by NMR spectroscopy. Clearly the process took place directly from the
109 upconverted singlet excited state of anthracene plus a ground-state anthracene; in other
110 words, the AN partner was involved in the chemical transformation and the quantum
111 efficiency of the photochemical anthracene dimerization was therefore found to be
112 sensitive to the monomer concentration. However, this study did not perfectly meet with
113 the potential use of TTA–UC in synthetic organic reactions by harnessing the upconverted
114 energy to drive challenging electron transfer reactions.

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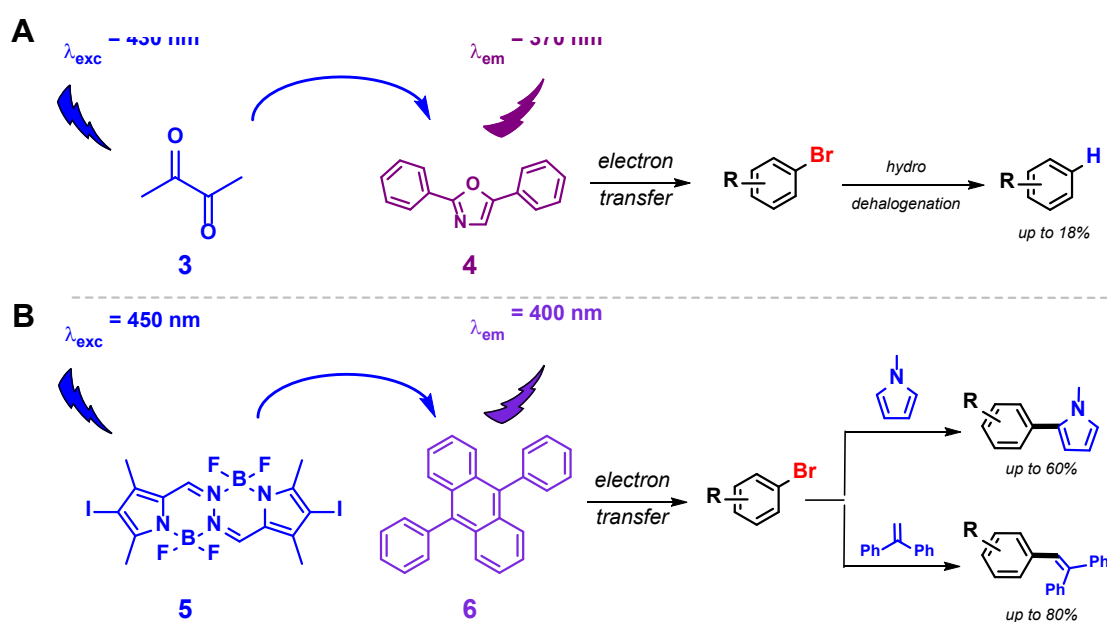
117 **Figure 2.** Photodimerization of anthracene sensitized by TTA-UC using a Ru^{II}
 118 chromophore.

119 In 2015, Pérez-Ruiz, Jacobi von Wangelin and co-workers described for the first time the
 120 use of TTA-UC technology to promote the photo-driven reduction of aryl bromides using
 121 an organic bimolecular TTA-UC system based on butan-2,3-dione (**3**) as Sens and 2,5-
 122 diphenyloxazole (**4**, PPO) as AN.[30] The reaction was found to operate under a
 123 mechanism wherein an electron transfer occurred from the singlet PPO generated from
 124 TTA-UC to aryl bromides (Figure 3A). Then, the corresponding radical anion of the aryl
 125 bromide afforded a rapid mesolytic bond cleavage followed by hydrogen atom transfer
 126 from the solvent to produce the desired reduced product. Such proposed reaction
 127 mechanism was proven by time resolved transient fluorescence and absorption
 128 spectroscopy with a pulsed laser, quenching experiments, and DFT calculations.

129 Despite the fact that this methodology was limited by the relatively low yields and the
 130 use of laser light sources, the development of TTA-UC to catalytic method of synthetic
 131 significance might be conceptually advantageous in terms of mild reaction conditions
 132 (lower-energy VIS, room temperature and ambient pressure), metal-free photocatalyst
 133 systems and no additives (sacrificial donors/acceptors) in the medium. In this vein, de la
 134 Peña O'Shea, Pérez-Ruiz and co-workers successfully applied TTA-UC to a C-C
 135 coupling catalytic reaction.[31] A diiodoBOPHY-like derivative (**5**) as Sens and 9,10-
 136 diphenylanthracene (**6**) as AN were employed as TTA-UC catalytic system in the
 137 coupling reaction between aryl halides and *N*-methylpyrrole (Figure 3B). To note that
 138 photolysis with a blue laser pointer ($\lambda_{exc} = 445 \text{ nm} \pm 10$, 2W) instead of the laser flash
 139 technique offered both experimentally and economically benefits. The approach followed
 140 a cascade of processes that involved both photophysical (ISC, triplet-triplet energy
 141 transfer, triplet-triplet annihilation) and photochemical (singlet-electron transfer, radical

142 trapping, C–C forming bond) events as key steps. This fact was confirmed by the
 143 combination of spectroscopic data, product analysis and computational studies and,
 144 indeed, a larger scale of the optimal conditions was achieved with continuous-flow
 145 conditions. In a closely related work, Pérez-Ruiz, Leyva-Pérez and co-workers explored
 146 the feasibility of the photocatalyzed Mizoroki–Heck reaction for the fabrication of
 147 triarylethylenes using aryl bromides as aryl radical precursors by means of TTA–UC
 148 technology (Figure 3B).[32] With the same TTA–UC couple as photocatalytic system,
 149 substituted triarylethylenes were successfully obtained, in up to 80% yield after a reaction
 150 time of 5 h, confirming that the adaptation of this photoredox catalytic system to the
 151 desired Mizoroki–Heck coupling was immediate and symbiotic. The reaction catalytic
 152 cycle was experimentally confirmed by transient absorption spectroscopy. Hence, the
 153 involvement of $^1\text{AN}^*$ as a high-energy intermediate was evidenced by quenching
 154 experiments whereas a cationic intermediate was directly detected with a lifetime in the
 155 microsecond scale.

156



157

158 **Figure 3.** Activation of aryl halides through electron transfer from organic TTA–UC
 159 systems to achieve hydrodehalogenations and C–C coupling reactions under blue light
 160 irradiation.

161 3. Green to Blue Upconversion

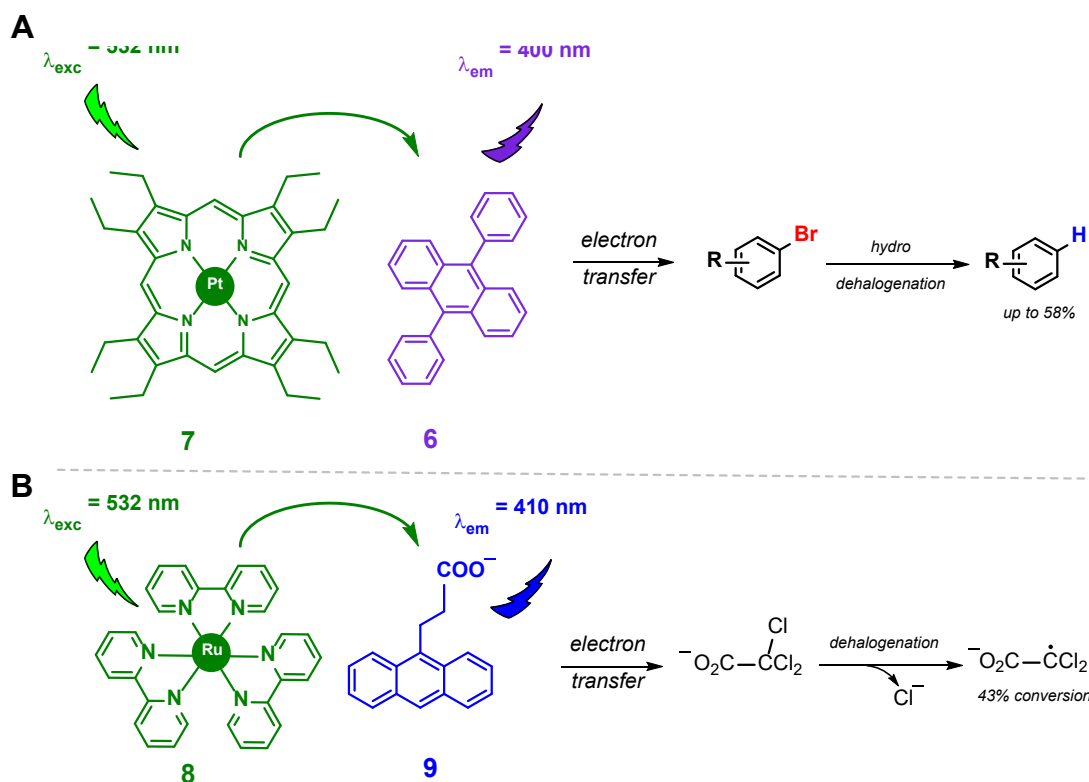
162 It is truly assumed that behavior of TTA–UC systems is better efficient in homogenous
 163 solutions due to fast diffusion of excited molecules. To achieve efficient reactions in
 164 solution, however, strict anaerobic conditions are required since UC is rapidly quenched by

165 molecular oxygen. In 2015, Yanai, Kimizuka and co-workers[33] solved this major
166 problem smartly by employing supramolecular organogel matrixes. They were able to
167 observe intense UC emission from Sens–AN pairs in organogels with low-power
168 excitation even under air-saturated condition. Inspired by these findings, Pérez-Ruiz,
169 Jacobi von Wangelin, Díaz Díaz and co-workers reported the first intragel photoreduction
170 of aryl halides via a TTA–UC mechanism using green-light irradiation, under aerobic
171 conditions and at room temperature.[34] In this report, Pt^{II} octaethyl-porphyrin (**7**)/9,10-
172 diphenylanthracene (**6**) system was employed as TTA–UC couple (Figure 4A) in order to
173 photoredox catalyzed the target reaction in supramolecular gel networks (*N,N'*-
174 bis(octadecyl)-*L*-*boc*-glutamic diamide and *N,N'*-((*1S,2S*)-cyclohexane-1,2-
175 diyl)didodecanamide). At model reaction, the dehalogenated aryl derivative was obtained
176 with 58% yield and good conversions and excellent mass balances were observed with
177 other types of aryl halides. These results demonstrated that low weight molecular gelators
178 could be used as confined reaction media or micro/nanoreactors, providing the
179 background for more demanding photophysical processes such as TTA–UC.

180 Later, Wu, Yang and co-workers described the first supramolecular TTA–based catalytic
181 photochirogenesis.[35] The green-light-driven enantiodifferentiating photodimerization
182 of 2-anthracenecarboxylic acid (AC) was sensitized by Schiff base Pt^{II} complex-grafted
183 γ -cyclodextrins. Mechanistically, upon 532 nm laser excitation of the Schiff base Pt^{II}
184 complex grafted on γ -CD, the *in situ* triplet-triplet energy transfer took efficiently place
185 to the γ -CD-complexed ACs that triggered the TTA–based photodimerization of AC.
186 Results revealed formation of the *syn-head-to-tail* photodimer in up to 31.4% ee and
187 60.8% relative yield at a conversion of 61%.

188 In a more recent work, Li and co-workers have used a TTA–UC photocatalyst based on
189 the couple comprised of 5,10,15,20-tetra(*N,N*-diethylaniline) porphyrin Pd as Sens and
190 perylene as AN for the lignin model degradation to added-value products such as 4' -
191 methoxyacetophenone and guaiacol.[36] Although a similar quantitative conversion
192 efficiency was obtained under green light irradiation ($\lambda_{exc} > 510$ nm) in comparison with
193 pure perylene as catalyst (irradiation at $\lambda > 420$ nm), the selectivity of the process
194 considerable improved via avoiding side reactions induced by high energy excitation.

195



196

197 **Figure 4.** Dehalogenation reactions mediated by TTA–UC technology using 532 nm
 198 radiation through electron transfer.

199 From a sustainable point of view, to perform chemical transformations photocatalyzed by
 200 TTA–UC technology in homogeneous aqueous solution appears to be more reasonable.
 201 In this context, Kerzig and Wenger investigated a sensitized TTA–UC photoreduction of
 202 trichloroacetate (TCA) in neat water at a laboratory scale[37] with the occurrence that
 203 injection of one electron to TCA provoked its dissociation to yield a carbon-centered
 204 radical and chloride ions. Regarding the TTA–UC couple, combination of $[\text{Ru}(\text{bpy})_3]^{2+}$
 205 (**8**) as Sens and anthracene-9-propionate (**9**) as AN was employed and the reaction was
 206 carried out upon green continuous wave laser as the excitation source under aerobic
 207 conditions (Figure 4B). Results showed conversion of TCA anion up to 43% and a turn-
 208 over-number TON of up to 15.

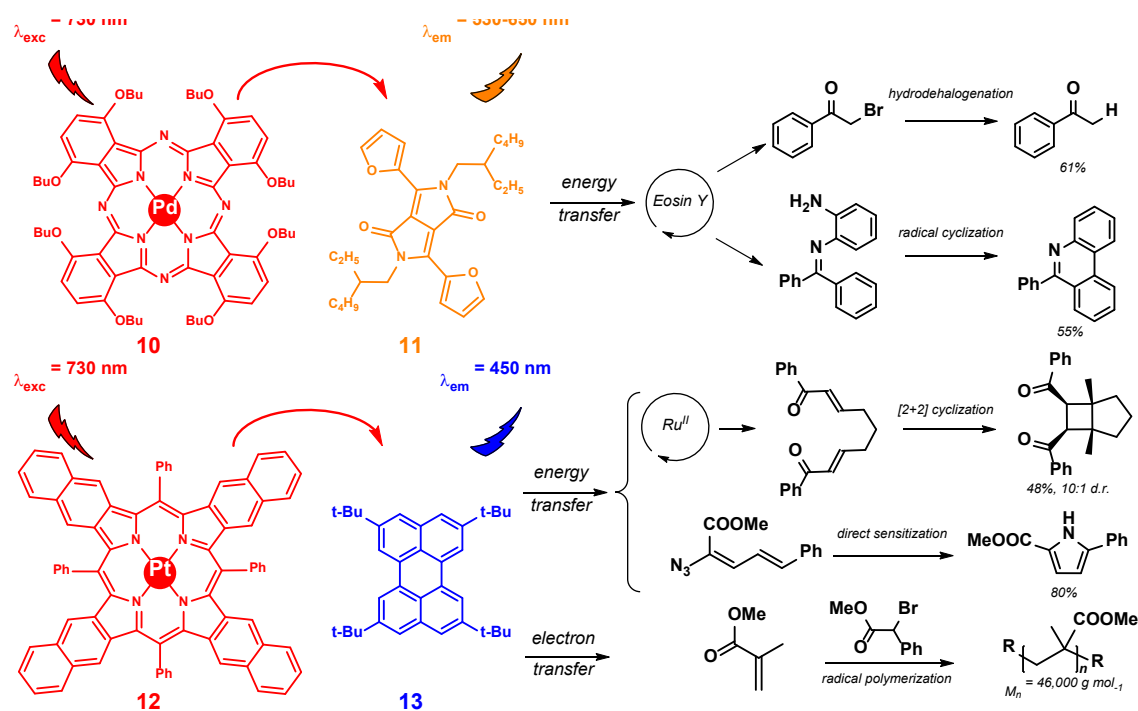
209 4. NIR to Visible Upconversion

210 It is well-established that the use of near-infrared (NIR) light is more suitable in terms of
 211 biocompatibility since its penetration through many media (including biological tissue)
 212 is much deeper than visible radiation, making NIR-to-visible UC particularly attractive.
 213 Congreve, Rovis, Campos and co-workers reported various organic transformations
 214 under infrared radiation photocatalyzed by TTA–UC technology (Figure 5).[38]
 215 Combination of Pd– or Pt–based Senss with organic ANs permitted to access both orange

216 light and blue light. Thus, using Pd^{II} octabutoxyphthalocyanine (**10**) as Sens with
217 furanyldiketopyrrolopyrrole (**11**) as AN assisted UC of NIR photons (730 nm) to the
218 orange region ($\lambda_{em} \sim 530\text{--}650$ nm). The emitted energy could be transferred to Eosin Y,
219 a conventional photoredox catalyst, which photocatalyzed several types of organic
220 transformations such as hydrodehalogenation or radical cyclization with comparable
221 yields related to visible light irradiation despite of the weakness of the red-light source.
222 The same situation was observed when Pt^{II} tetraphenyltetranaphthoporphyrin (**12**) as Sens
223 and *tert*-butylated perylene (**13**) as AN were used. In the presence of organometallic
224 complex [Ru(bpy)₃]²⁺ as photoredox catalyst, the prototypical [2+2] intramolecular
225 cyclization of enones was achieved with excellent diastereomeric ratio. Alternatively, this
226 TTA–UC system was capable to directly photocatalyzed some processes without the
227 presence of additional catalysts. For example, formation of pyrroles by cyclization of
228 dienyl azides was afforded due to direct sensitization from the TTA–UC system. Indeed,
229 polymerization of methyl methacrylate was successfully accomplished via C–Br bond
230 reduction simply using the Sens, the AN and the initiator in neat methyl methacrylate
231 using NIR radiation.

232 Abe and co-workers studied NIR-light-responsive photochromism by TTA–UC of a
233 photochromic molecule with a covalently bonded AN, observing an effective energy
234 transfer from AN to the photochromic unit.[39] For this purpose, a photochromic system
235 including Pd^{II} meso-tetraphenyl-tetrabenzoporphyrin as Sens and a photochromic
236 phenoxy–imidazolyl radical complex covalently bonded to perylene working as AN
237 (Pery–RPIC) was designed. The photochromic reaction of Pery- RPIC by a quantitative
238 C–N bond breaking reaction to form the biradical upon irradiation of 635 nm light was
239 demonstrated from transient absorption spectroscopy and the excitation light intensity
240 dependence. Indeed, the RPIC unit utilized in this study showed the rapid thermal back
241 reaction in a few tens of milliseconds.

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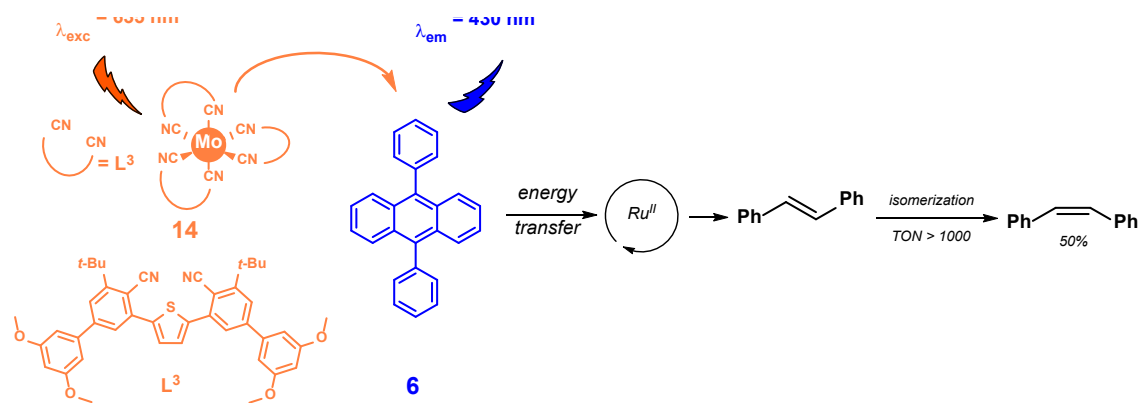


243

244 **Figure 5.** Application of NIR-to-orange and NIR-to-blue upconversion strategies to
 245 several chemical transformations through energy or electron transfer.

246 From a biological point of view, among Pd^{II} and Pt^{II} complexes, Os^{II} polypyridines
 247 complexes have been classified as typical red-light absorbers which have been often used
 248 as triplet Sens for TTA–UC.[40–43] In this context, Wenger and co-workers have very
 249 recently synthesized a new Mo^0 complex (14) mimicking Os^{II} ones that has been found
 250 to possess optimal photophysical properties to sensitize TTA–UC of 9,10-
 251 diphenylanthracene (6) under 635 nm irradiation with a continuous wave laser (Figure
 252 6).[44] The authors aimed to probe a blue-light-driven photoisomerization of *trans*-
 253 stilbene which was induced by the TTA–UC system. As a matter of fact, the photostability
 254 of the Mo^0 complex together with the high UC quantum yield allowed to sufficiently
 255 generate a flux of upconverted light that was then absorbed by the Ru^{II} complex which
 256 initiated the process. The *cis* isomer was produced with a 50% yield after 17 hours of 635
 257 nm irradiation and, outstandingly, the photophysical event (TTA–UC) and the chemical
 258 transformation occurred in spatially separated reaction vessels.

259



260

261 **Figure 6.** Ru^{II}-photocatalyzed isomerization of *trans*-stilbene induced by TTA–UC upon
 262 635 nm irradiation.

263 It is worth mentioning that other interesting entities such as UC nanoparticles (UCNP)
 264 usually based on NaYF₄ salts doped with lanthanide ions are capable to convert NIR light
 265 into UV and visible light of defined energy by absorbing at least two photons. With these
 266 properties, they are appropriate external initiators for photoswitches, photocleavable
 267 groups, imaging or sensing applications[45–49] and, more recently, in photoredox
 268 catalysis.[50]

269 5. Conclusions

270 In conclusion, the current progress of the application of TTA–UC technology to organic
 271 synthesis is herein reviewed. The strategy is quite promising in synthetic chemistry
 272 because of the benefit of mild reaction conditions using lower-energy visible light. One
 273 of the main reasons for the success of this approach lies on the TTA–UC molecule
 274 engineering and on the rational selection of them to act as suitable photocatalytic systems.
 275 In the last years, the design and synthesis of sensitizers with intense absorption of visible
 276 light in the whole range, accompanied by long triplet lifetimes plus employment of
 277 annihilators with high fluorescence quantum yield have enabled new procedures;
 278 however, the utilization of this two-photon process as potential synthetic tool is at early
 279 years. It is expected that interest in TTA–UC will remain to expand in coming years,
 280 providing new avenues to access high energy intermediates for use in chemical
 281 transformations.

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 283 gratefully acknowledged.

284 **Declarations**

285 Conflict of Interest: The author has no conflicts of interest or competing interests to
286 declare.

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