Photoredox catalysis using infrared light via triplet fusion upconversion

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Recent advances in photoredox catalysis have made it possible to achieve various challenging synthetic transformations, polymerizations and surface modifications1–3. All of these reactions require ultraviolet- or visible-light stimuli; however, the use of visible-light irradiation has intrinsic challenges. For example, the penetration of visible light through most reaction media is very low, leading to problems in large-scale reactions. Moreover, reactants can compete with photocatalysts for the absorption of incident light, limiting the scope of the reactions. These problems can be overcome by the use of near-infrared light, which has a much higher penetration depth through various media, notably biological tissue4. Here we demonstrate various photoredox transformations under infrared radiation by utilizing the photophysical process of triplet fusion upconversion, a mechanism by which two low-energy photons are converted into a higher-energy photon. We show that this is a general strategy applicable to a wide range of photoredox reactions. We tune the upconversion components to adjust the output light, accessing both orange light and blue light from low-energy infrared light, by pairwise manipulation of the sensitizer and annihilator. We further demonstrate that the annihilator itself can be used as a photocatalyst, thus simplifying the reaction. This approach enables catalysis of high-energy transformations through several opaque barriers using low-energy infrared light.

Existing photocatalysts must be excited with either ultraviolet or visible light, translating to an initial excited-state energy of 50–80 kcal mol−1 (refs 5,6). This energy is then transferred to the substrate of interest, leading to the desired reactivity. Near-infrared (NIR) light can generate only low-energy excited states (around 35 kcal mol−1), which fall short of the energy required to achieve the majority of desired transformations.

The photophysical process of triplet fusion upconversion—the conversion of low-energy photons into high-energy excited states—has gained increased attention in recent years7, in large part due to its potential to increase the efficiency of photovoltaics8. Although the solar applications of triplet fusion upconversion have received the most attention, it can be applied in various other fields ranging from biological imaging9 to data storage10.

NIR light can be harnessed for chemical transformations by using lanthanide-containing nanoparticles or by upconversion via triplet fusion; however, these approaches are limited to the direct activation of substrates11–14. This shortcoming limits the methodology to substrates bearing photocleavable bonds and can be addressed by the activation of a catalyst in place of the substrate. Organic chromophores have great potential for triplet fusion upconversion, especially because of their tunable electronic structure15 (Fig. 1a). We show that it is possible to use low-energy NIR light to access the complex synthetic toolbox enabled by photoredox catalysis. This strategy is highly modular, as it is possible to match components of the upconversion and photoredox systems to promote various chemical transformations in one pot16–17.

The process of triplet fusion upconversion involves two species: an annihilator and a sensitizer18,19 (Fig. 1b). The sensitizer absorbs a low-energy photon, initially generating a singlet excited sensitizer, 1[Sen]*, which decays into a triplet excited sensitizer, 1[Sen]*. This energy is then transferred to the annihilators, forming 3[An]*. Two 3[An]* molecules can then undergo triplet fusion, which leads to the generation of a higher-energy singlet exciton on one of the annihilators, 1[An]*. This then decays via fluorescence, giving off a high-energy photon.

In considering the energetic requirements of a new infrared–visible triplet fusion upconversion system, we became aware of a recent study that showed it is possible to vary the singlet energy levels of diketopyrrolopyrrole derivatives for singlet fission without altering the triplet energy20. We leveraged this finding to adjust the singlet energy until it was slightly less than double the triplet energy, and in doing so we observed triplet fusion upconversion. We used furanyldiketopyrroloporphyrin (FDPP) as an annihilator with palladium(ii) octabutoxyphthalocyanine (PdPc) as the sensitizer21; this system absorbs NIR photons (λmax = 730 nm) and has an emission that extends to around 530 nm (Fig. 1c). The FDPP:PdPc system has an upconversion yield of 3.2%, while the fluorescence quantum yields of common photoredox catalysts such as [Ru(bpy)3]2+ (bpy, bipyridyl) and Rose Bengal are 9.3% and 9%, respectively (see Supplementary Information for full details). When combining the upconversion system with hydrodehalogenation conditions22, we observed the dehalogenated product in 61% yield (Fig. 2a). In this initial example, we established the ability of triplet fusion upconversion to enable low-energy NIR light to activate a catalyst, Eosin Y, that is capable of reducing a C–Br bond. Control reactions, in which the photocatalyst or upconversion components are removed, show only trace yields. These results suggest that the external NIR radiation is converted inside the reaction vessel to visible light, which is then absorbed by Eosin Y. As a direct comparison, an identical reaction was irradiated with a 40-W blue Kessil lamp instead of an NIR diode; a 78% yield was obtained in a similar reaction time. It is notable that the 0.040–W NIR diode is orders of magnitude weaker than the blue light source. We thus propose that the light emitted from upconversion is generated deep within the reaction vessel, leading to a large number of ‘lightbulbs’ inside the flask. In turn, the net surface area of illumination by these lightbulbs is orders of magnitude greater than possible with light sources on the outside. For this reason, we can maintain similar yields with a light source that is 1,000 times less powerful than the photoredox standard.

To test the generality of this system towards other reactions, we pursued two other transformations. In a similar manner, we found that Rose Bengal could be excited by NIR-light triplet fusion upconversion to catalyse amine oxidation in 72% yield23 (Fig. 2b). Further, this system was adapted to a C–N bond activation catalysed by Eosin Y to yield phenanthridine products24 (Fig. 2c).

This FDPP:PdPc system enables the use of NIR light to promote reactions that require photocatalysts that absorb green or yellow light. However, most organometallic photocatalysts absorb higher-energy blue or ultraviolet light4. We found that it is possible to use the NIR-absorbing sensitizer platinum(ii) tetraphenylethynylporphyrin...
Together with a simple blue-emitting annihilator, tetratertbutylperylene (TTBP), to generate NIR-to-blue photon upconversion. This system generates a large anti-Stokes shift (around 1.0 eV) and provides an upconversion yield of up to 2.0% (Fig. 1d) (see Supplementary Information for full details).

We adapted this upconversion system to a prototypical [Ru(bpy)_3]^{2+}--catalysed reaction: the intramolecular [2 \rightarrow 2] cyclization of enones (Fig. 2d). Adding TTBP and PtTPTNP to the standard reaction conditions provided the cyclobutane product in moderate yield and excellent diastereomeric ratio. Control reactions revealed that the removal of Ru(bpy)_3(PF_6)_2 still results in a 38% yield of cyclobutane product, which suggests that the [An]* state of TTBP is capable of performing photoredox catalysis on its own; this reduces the three-component system to a two-component system and streamlines the catalysis.

To test whether the [An]* state of TTBP could be applied directly for catalysis, we investigated the photoredox-catalysed cyclization of dienyl azides to pyrroles (Fig. 2e). Upon NIR (730 nm) irradiation of the sensitizer, annihilator and substrate, the pyrrole product was formed in 80% yield.

After observing the strong reducing nature of the [An]* state of TTBP, we attempted to use NIR radiation to initiate the polymerization of methyl methacrylate (MMA) via C–Br bond reduction (Fig. 2f). Simply irradiating the sensitizer, annihilator and initiator in neat MMA provided poly(methyl methacrylate) (PMMA; M_n = 46,000 g mol\(^{-1}\); dispersity (Đ) = 1.80). The polymerization of MMA has previously been demonstrated with perylene as a photocatalyst under visible-light irradiation; however, here we have enabled deep-penetrating NIR light to stimulate the photocatalyst, providing avenues for the integration of photoredox catalysis into new materials.

To demonstrate the ability of NIR light to penetrate a range of media, we performed the MMA polymerization with 5% ethylene glycol dimethacrylate as a crosslinker to generate a freestanding gel, while using several visible-light-absorbing materials to disrupt the path of the incident laser (Fig. 3a, c). A PMMA gel was synthesized with an NIR
light source through various different barriers; meanwhile, a gel was not formed when the 450-nm blue light source was used, presumably owing to its limited penetrating ability (Fig. 3b). Notably, the NIR light showed excellent penetrating power through haemoglobin, a component of human blood that absorbs visible light. In addition to the gelation reaction, the \([2+2]\) cyclization reaction shown in Fig. 2d was performed through a barrier of 0.2 mM haemoglobin solution. The product yield with the NIR laser was 46%—identical to that of the reaction conducted without a barrier—whereas the blue laser gave a 1% yield.

The scale-up of visible-light photoredox reactions suffers from shallow light absorption, as evidenced by slow reaction rates. In addition, increasing the size of the reaction vessel decreases the relative surface area, thus reducing photon exposure and fundamentally limiting photocatalyst excitation. Infrared photoredox can overcome this limitation.

**Table**

| Material            | NIR | Blue |
|---------------------|-----|------|
| Air                 | Gel | Gel  |
| Water               | Gel | Gel  |
| Amber glass         | Gel | No reaction |
| Bacon               | Gel | No reaction* |
| [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 |

*Experiment halted after 15 minutes owing to fire hazard, as the bacon began to burn upon irradiation. c. Experimental set-up using a laser diode, with water as the barrier. d. PMMA gel (right) prepared by performing the reaction on a 10-g scale using the NIR lamp shown (left). e. The silicone mould used, together with the PMMA shapes that were synthesized through a 7-mm white silicone pad.
both of these challenges. For example, the penetration of infrared light through the [2+2] cyclization reaction mixture (Fig. 2d) is 304 times deeper than that of blue light, based on concentration and extinction coefficients (Fig. 4). By the same analysis, we found that infrared light penetrates 293 times further than blue light (450 nm) through the reaction solution in Fig. 2d. For TTBP, it is 5.17 times larger and c is 56.7 times larger for PTPTNP; the penetration of infrared light (730 nm) is therefore 293 times greater than that of blue light (450 nm) through the reaction solution in Fig. 2f.

**Data availability**

The data that support the findings of this study are available from the corresponding authors on reasonable request.

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