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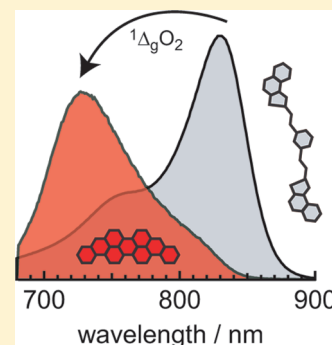
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Singlet Oxygen Mediated Photochemical Upconversion of NIR Light

Burkhard Fückel,[†] Derrick A. Roberts,[†] Yuen Yap Cheng,[†] Raphaël G. C. R. Clady,[†] Roland B. Piper,[‡] N. J. Ekins-Daukes,[‡] Maxwell J. Crossley,[†] and Timothy W. Schmidt^{*,†}[†]School of Chemistry, The University of Sydney, NSW 2006, Australia[‡]Department of Physics and the Grantham Institute for Climate Change, Imperial College, London, U.K. SW7 2AZ

ABSTRACT: We report photochemical upconversion (UC) of near-infrared (NIR) light to the visible spectrum mediated by molecular oxygen. Thereby, we address two of the main challenges in the field of photochemical UC, (i) UC of photons above 800 nm and (ii) utilization of molecular oxygen, which is necessarily excluded in conventional photochemical UC systems. In the employed system, singlet oxygen is generated upon photoexcitation of the sensitizer molecules and then acts as an energy transmitter for the UC process. The excitation energy of two singlet oxygen molecules is subsequently harvested by emitter molecules, which in turn gives rise to delayed fluorescence of the emitter species. We discuss strategies for improvement of the currently achieved efficiencies of $\leq 0.01\%$ to produce excited singlet states in the emitter molecules.

SECTION: Kinetics, Spectroscopy



Singlet oxygen is a common reactive oxygen species that is formed as a byproduct of many photosensitized processes. Due to its high reactivity, singlet oxygen irreversibly damages a range of unsaturated organic compounds.^{1–4} The $^1\Delta_g \leftarrow ^3\Sigma_g^-$ transition of dioxygen is typically induced by quenching of a triplet excited state of an organic molecule. Biological systems have evolved ways of handling singlet oxygen, such as sequestration by carotenoids that protect the sensitive pigments in the photosynthetic reaction center of plants.^{3,4} However, artificial organic systems, for example, light-harvesting applications such as organic photovoltaics and dye-sensitized photochemical upconversion (UC), are currently not as sophisticated as their biological counterparts and are more susceptible to damage by singlet oxygen.

Photochemical UC is a rapidly expanding field because of its envisaged and already-implemented applications in light-harvesting^{5–7} and light-emitting⁸ devices due to its incoherent nature. Two of the major challenges in the field are (i) to overcome the rapid quenching of the employed triplet states by molecular oxygen, which drastically diminishes the UC efficiency,^{7–13} and (ii) UC of near-infrared (NIR) light to the visible spectrum,^{9,10,14} which could be applied in medicine and biology because tissues are transparent for NIR radiation.¹⁵

Herein, we report singlet oxygen mediated upconversion (SOMUC) of NIR light to the visible spectrum, thereby addressing the aforementioned issues. SOMUC employs singlet oxygen as an energy transmitter, thus relying on the presence of molecular oxygen. Singlet oxygen is generated upon photoexcitation of a sensitizer species with an absorption maximum at 830 nm, well outside of the visible region. While the process is currently unoptimized, we demonstrate its proof-of-principle and suggest several possibilities for significant improvements in UC efficiency in the future.

As depicted in Figure 1, after the initial photosensitization step to generate singlet oxygen, the excitation energy of singlet oxygen is transferred to emitter (E) molecules in the ground state. SOMUC can now proceed in two different ways. In the first pathway (Figure 1a), two triplet excited emitter molecules can undergo triplet–triplet annihilation (TTA), resulting in a singlet excited emitter molecule and upconverted fluorescence. Second, it is known that singlet oxygen can induce luminescence in some molecules through singlet oxygen sensitized delayed fluorescence (SOSDF), a phenomenon first documented by Kurtz¹⁶ and later explained by Ogryzlo and Pearson¹⁷ as well as Abbott et al.¹⁸ In this case, one emitter molecule accumulates the electronic energy of two equivalents of singlet ($^1\Delta_g$) oxygen in a stepwise fashion, as displayed in Figure 1b. Because this process requires a distinctive structure of the molecular energy levels, a relatively limited number of emitter molecules are known to undergo SOSDF.¹⁹ Note that both mechanisms give rise to a delayed fluorescence signal. In contrast, conventional photochemical UC proceeds by direct triplet energy transfer (TET) from the sensitizer to the emitter species.^{5–7}

It should be noted that oxygen in its triplet ground state facilitates the mixing between singlet and triplet states of organic chromophores due to an exchange interaction between the paramagnetic and the organic molecule. By lending singlet character to triplet states, the probability of spin-forbidden transitions is enhanced,²⁰ increasing the rates of phosphorescence and intersystem crossing. Furthermore, when such a coupling manifests in two different molecules, triplet energy transfer is enhanced due to the gain of Förster character from the

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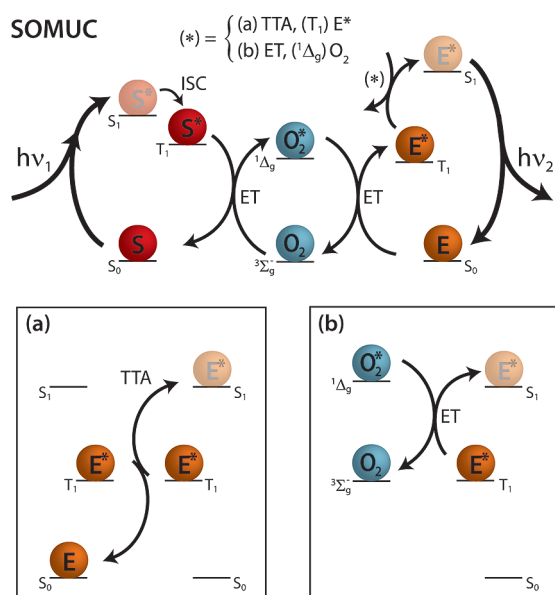


Figure 1. The pathways of singlet oxygen mediated upconversion. Light symbols depict short-lived (\leq ns) states. Upon singlet oxygen generation by the sensitizer (S) via absorption of light ($h\nu_1$), intersystem crossing (ISC), and energy transfer (ET), oxygen transfers the excitation energy to emitter (E) molecules in their ground state (S_0). The first excited singlet state (S_1) can be populated by (panel a) triplet–triplet annihilation between triplet (T_1) excited emitter molecules or (panel b) by a second ET step with singlet oxygen. Both pathways result in upconverted, delayed fluorescence ($h\nu_2$).

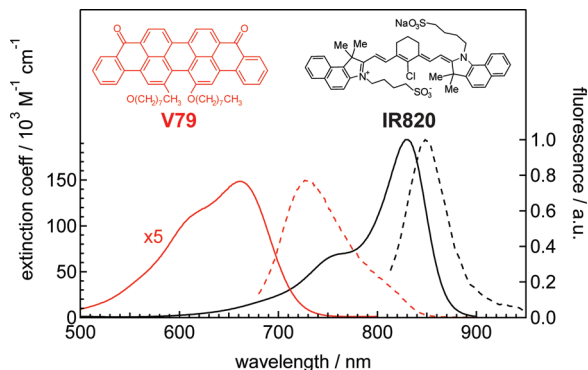


Figure 2. Molecular structures and spectra of the sensitizer IR820 and the emitter violanthrone-79 (V79) in DMF. Absorption spectra are indicated as solid lines (left axis), while emission spectra are indicated with dashed lines (right axis). IR820 exhibits a very strong absorption band above 800 nm; the extinction of V79 was multiplied by a factor of 5 for clarity.

two respective singlet states, effectively increasing the transfer radius. Indeed, Monguzzi et al. have recently pointed out that even small amounts of oxygen can enhance TET rates by orders of magnitude.¹³

To experimentally establish SOMUC, we have employed the cyanine dye IR820 as the sensitizer material in combination with violanthrone-79 (V79) as the emitter species. Structures and spectra of the compounds are displayed in Figure 2. IR820 is a chlorinated heptamethine indocyanine dye possessing a singlet oxygen quantum yield of 7.7% in ethanol considered for photodynamic therapy,^{21,22} despite the low triplet quantum yield

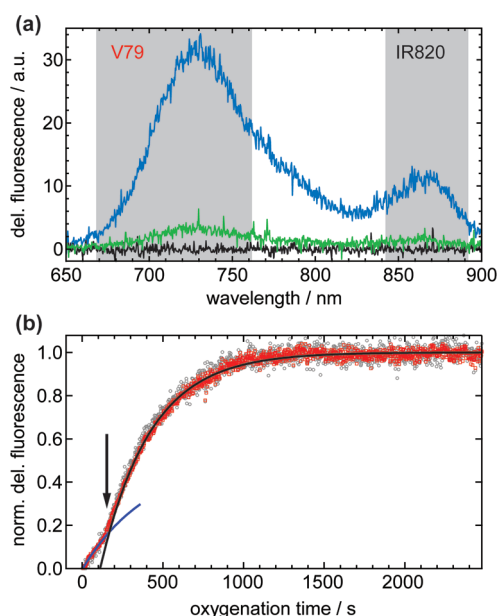


Figure 3. Dependence of the delayed fluorescence signal on the oxygen concentration (DMF solution containing 1.7×10^{-3} M IR820 and 2.4×10^{-3} M V79; signal integrated from 100 ns to 50 μ s after the 830 nm excitation pulse, $P = 6 \mu$ J). (a) The black, green, and blue spectra correspond to degassed, untreated, and oxygenated solutions, respectively. (b) The degassed sample was bubbled through with oxygen gas while the delayed fluorescence was recorded every 2 s. The red and gray data points correspond to the spectral regions of V79 and IR820 as indicated in (a), respectively. The arrow indicates the time where the oxygen stream was slightly increased. The data were fit with exponentials, where the black and the blue lines correspond to the two different valve settings.

($\sim 10^{-5}$) reported for similar indocyanine dyes in oxygen-free solutions.²³ The triplet yield was found to increase, however, in air-saturated solutions,²³ an effect ascribed to the aforementioned interaction with paramagnetic ground-state oxygen. Indeed, IR820 was found to yield no transient absorption signal ascribable to the triplet state under deoxygenated conditions.

V79 is a chemically modified vat dye. Violanthrones like V79 are known to fluoresce when exposed to singlet oxygen, according to the SOSDF process.¹⁷ Differences in the polarity of these two compounds limited the choice of solvent for performing UC measurements. *N,N*-Dimethylformamide (DMF) was selected because both compounds displayed moderate to good solubility without significant shifting of their steady-state absorption and emission spectra. The overlap of the V79 fluorescence with the absorption band of IR820, however, leads to Förster-type resonance energy transfer (FRET) from V79 to IR820 that quenches a part of the V79 emission (vide infra).

Sensitizer/emitter mixtures were prepared under normal atmospheric conditions, and a weak delayed fluorescence signal from both V79 and IR820 was observed upon excitation with 830 nm laser light. However, after rigorous degassing of the sample by several freeze–pump–thaw cycles, no delayed fluorescence signal could be recorded. In contrast, after bubbling oxygen through the solution for several minutes, an increased delayed fluorescence signal was observed that was about a factor of 10 stronger than the untreated sample (Figure 3a). Because IR820 can generate singlet oxygen while V79 quenches the energy of ($^1\Delta_g$)O₂, the energy of the first excited triplet state

of IR820 is above the triplet state of V79. Despite this fact, the experimental results indicate that TET from IR820 to V79 is highly inefficient, presumably due to the low intersystem crossing (ISC) rate of IR820 as well as a small transmission coefficient for both compounds.

The increase of signal depending on the oxygen concentration was investigated in a series of measurements that recorded the delayed fluorescence every 2 s while the degassed sample was continuously bubbled through with a light stream of oxygen gas, as displayed in Figure 3b. After ~ 150 s, the oxygen stream was slightly increased, resulting in a steeper increase of fluorescence signal. Both parts of the rise are single exponentials with respective rise times. Furthermore, the delayed fluorescence intensities from IR820 and V79 showed the same dependence on the oxygen concentration, indicating that the delayed IR820 fluorescence is indeed due to FRET from V79. Control experiments with pristine solutions of V79 in thoroughly oxygenated DMF showed no delayed fluorescence signal, excluding two-photon absorption induced by the employed laser pulses or direct excitation of oxygen as the origin of the delayed emission. Moreover, thoroughly oxygenated, pristine IR820 solutions were checked for emission at 634 and 703 nm, with the oxygen “dimol” bands resulting from pairs of singlet oxygen,²⁴ which in principle could sensitize the observed fluorescence.²⁵ However, Gorman et al. as well as Murphy et al. have shown that in their respective systems, sensitization from dimol oxygen is highly unlikely.^{26,27} Indeed, no dimol emission was found from the IR820 solutions, confirming that dimol sensitization is negligible in our system. However, the latter solutions of oxygenated IR820 showed weak delayed fluorescence with decay times on the order of 100 ns, which was not observed in degassed solutions; hence, it does not originate from residual natural fluorescence. We ascribe this to E-type delayed fluorescence,²⁸ where the ISC processes are enhanced by the dissolved oxygen, despite its possible quenching of the triplet state.

We have measured the kinetics of the V79 delayed fluorescence signal, which are displayed in Figure 4 for three different mixtures of V79 and IR820 in oxygenated DMF. For all traces, a rise time of the signal is visible, verifying the sensitized nature of the emission. The decays are monoexponential, indicating that first-order processes are dominating. They match the respective decay kinetics of the delayed fluorescence of the IR820 band (gray symbols), further confirming FRET as an origin for this emission feature. However, the rise of the V79 fluorescence is not reproduced by the IR820 kinetics. A deconvolution reveals time constants for the initial decay on the order of 100 ns; thus, we ascribe this feature to the aforementioned E-type delayed fluorescence.

Despite being monoexponential, the tails of the kinetics are dependent on the respective concentrations, indicating that more than one UC mechanism is involved. A high concentration ($>10^{-3}$) of emitter combined with a high concentration of IR820 yielded a decay constant of $0.9 \mu\text{s}$ (Figure 4a). While a decrease of the sensitizer concentration by a factor of 5 lead to similar kinetics, as shown in Figure 4b, the rise and decay times were prolonged when the V79 concentration was reduced to 1/5 (Figure 4c). Further reduction of the relative V79 concentration led to decay constants of up to $\sim 2.5 \mu\text{s}$.

We can rationalize the differences in the kinetics by the relative contribution of the two UC processes depicted in Figure 1 to the overall delayed fluorescence signal. For high emitter concentrations, relative to the overall exciton population, singlet oxygen

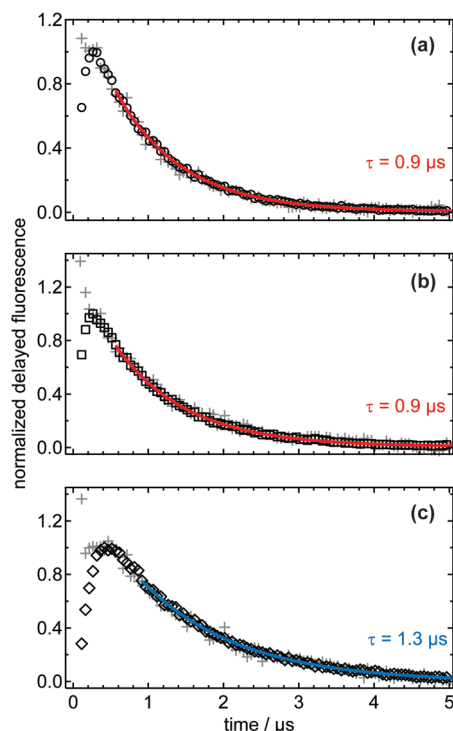


Figure 4. Decay kinetics of the V79 (black symbols) and IR820 (gray +) delayed fluorescence of various mixtures of IR820 and V79 in oxygenated DMF: (a) 2.4×10^{-3} M V79 and 1.7×10^{-3} M IR820; (b) 2.4×10^{-3} M V79 and 3.4×10^{-4} M IR820; (c) 4.8×10^{-4} M V79 and 1.7×10^{-3} M IR820. The solid lines are monoexponential fits with time constants τ .

sensitized TTA (Figure 1a) is likely to dominate, whereas SOSDF (Figure 1b) is more likely at lower concentrations of the emitter species. In the former case, the observed decay time of the delayed fluorescence is mainly due to TTA, giving rise to a decay time of half of the T_1 lifetime of the emitter. Indeed, experiments on pristine V79 in oxygenated DMF excited at 600 nm lead to a low delayed fluorescence signal due to (inefficient) ISC and subsequent TTA. Tail fits resulted in a decay constant of $0.9 \mu\text{s}$, corresponding to a triplet lifetime of $1.8 \mu\text{s}$. For lower relative V79 concentrations, the decay time should be governed by both the emitter T_1 lifetime and the singlet oxygen lifetime, where the latter can vary between 7 and $25 \mu\text{s}$,²⁹ most probably dependent on the purity of the solvent.

As previously established,¹¹ we obtained the efficiencies to generate singlet excited states in the emitter molecules, Φ , by comparison of the UC signal per input photon to that of the prompt fluorescence triggered by direct excitation of V79 with 630 nm light under otherwise identical experimental conditions. The delayed fluorescence signal per two input photons was the reference point for $\Phi = 100\%$ because two low-energy photons can generate one upconverted photon at most. While the monoexponential decay behavior already intimates a low value for Φ , it was indeed found to be $\Phi \leq 0.01\%$, which is ascribed to the low singlet oxygen yield^{21,22} of IR820 ($<10\%$) as well as the relatively short lifetimes of triplet excited V79 and singlet oxygen (vide infra).

Indocyanine dyes are known to undergo photodegradation due to reaction with singlet oxygen.^{23,30,31} The photodegradation of the involved compounds was investigated by measurement of

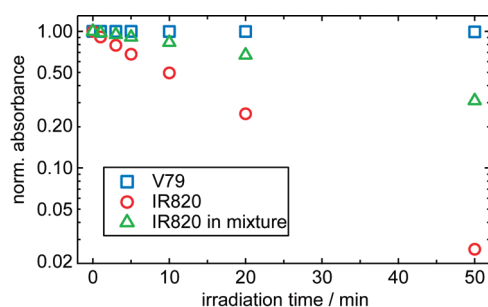


Figure 5. The normalized absorbance of different compounds dissolved in DMF dependent on the irradiation time with a xenon lamp (collimated white light beam, $P = 250$ mW). The absorbance of a solution of 5.2×10^{-5} M V79 (□) was not affected during the irradiation time, while an IR820 solution (○, 1.6×10^{-5} M) nearly completely bleached. However, in a mixture containing the same concentrations of both compounds (Δ), the photodegradation of IR820 was about three times slower.

the absorbance of the compounds after irradiation with a xenon lamp emitting a white light beam. Three different samples were investigated, that is, solutions of the pristine compounds and a mixture containing the same concentrations as the pristine solutions. The samples were prepared under normal atmospheric conditions. The absorbance bands of the respective compounds were integrated and normalized, as displayed in Figure 5. After 50 min of irradiation time, the absorbance of the pristine V79 solution was reduced by less than 1%, indicating the high photostability of V79. In contrast, the absorbance of the IR820 solution decreased during the same irradiation time to $\sim 2.5\%$ of the initial value. The initially green solution changed to a light gray, and a broad background was observed in the absorption spectrum, which is ascribed to the degradation products. However, in the mixture of V79 and IR820, the degradation of the latter was considerably reduced. The half-life of IR820 in the mixture with V79, considering a monoexponential behavior of the data of Figure 5, was increased by a factor of nearly 3. This is ascribed to the quenching of singlet oxygen by V79.

To further verify the observations that have been discussed so far, another set of experiments were performed using a palladium(II)-trisquinoxalino porphyrin³² as the sensitizer and V79 as the emitter. The sensitizer has a T_1 energy level at 830 nm, and its phosphorescence is efficiently quenched by oxygen. We monitored the delayed fluorescence of V79 upon selective excitation of the Soret band of the porphyrin at 480 nm for degassed and oxygenated DMF solutions of the two compounds. The delayed emission of the degassed samples is mostly dominated by the phosphorescence band of the porphyrin but exhibited a small amount of delayed V79 fluorescence that decays with the same kinetics as the porphyrin phosphorescence. In contrast, for the oxygenated sample, the porphyrin phosphorescence vanished, and the V79 delayed fluorescence increased. It was found that the values of Φ of the samples were enhanced in the presence of oxygen by a factor of ~ 5 .

In conclusion, we have shown that the presence of molecular oxygen can be beneficial for photochemical UC if the sensitizer and emitter molecules are chosen in such a way that the energy of the $^3\Sigma_g^- \leftarrow ^1\Delta_g$ transition of dioxygen lies below the triplet–singlet gap of the sensitizer but above that of the emitter. The UC mechanism relies on singlet oxygen as a transmitter of the

excitation energy from IR820 to V79. This leads to two different ways of combining two portions of energy, TTA in the emitter species and sequential energy transfer of singlet oxygen to one emitter molecule. Accordingly, the kinetics of the delayed fluorescence exhibits different behavior dependent on the relative emitter concentration. The mechanism utilizes the fast diffusion of oxygen in solution.³³ Moreover, the dissolved ground-state oxygen adds allowed character to the spin-forbidden transitions^{15,20} of the involved molecules, thereby accelerating the IR820 ISC significantly and possibly inducing triplet energy transfer between IR820 and V79. The latter appears to be completely suppressed in degassed solutions.

Importantly, the employed IR820/V79 system facilitates the UC of NIR light (830 nm) into the visible region. As shown above, the emitter species V79 furthermore protects the singlet oxygen sensitizer from photodegradation, which is ascribed to the quenching of singlet oxygen. Despite the low generation efficiencies for emitter singlet excited states, $\Phi \leq 0.01\%$, of the current dye system, several aspects can be significantly improved. The comparably low singlet oxygen yield of the sensitizer IR820 can be overcome by NIR-absorbing dyes such as metal bacteriochlorins,³⁴ cadmium(II) benzotetraphyrin,³⁵ and *meso-β* doubly fused diporphyrins,³⁶ which are known to have high singlet oxygen quantum yields approaching unity. From the mechanisms for UC, the increase in singlet oxygen concentration is expected to affect Φ quadratically. Furthermore, these compounds are reported to have good solubility in nonpolar organic solvents such as chloroform, in which the lifetime of singlet oxygen is on the order of 250 μ s,³⁷ while the employed solvent DMF is known to quench singlet oxygen to a small amount by inherent impurities.²⁹ Moreover, the triplet lifetime of the emitter species has an important influence on Φ .⁶ From a simple rate model, taking into account the mechanisms depicted in Figure 1 and estimates for the involved rate constants, we obtain an increase in Φ by more than a factor of 100 for a 10-fold increase in the singlet oxygen generation yield as well as the triplet lifetimes of oxygen and the emitter species. That is, optimizing these parameters will eventually lead to values of Φ and hence UC efficiencies in the several percent range for SOMUC.

EXPERIMENTAL SECTION

V79 and IR820 (80% dye content) were purchased from Sigma-Aldrich. V79 was found to be sufficiently pure for upconversion experiments, as assessed by thin-layer chromatography and ^1H NMR spectroscopy. IR820 (~ 1 g) was purified by Soxhlet extraction into dichloromethane to remove water-soluble impurities and then by silica gel chromatography eluting with methanol/chloroform (3:7, v/v). The major dark green fraction was collected, the solvents were removed, and the brown residue was recrystallized from methanol/diethyl ether to yield the purified dye as a light brown powder. Spectroscopic-grade DMF was used in the photophysical experiments and passed through a column of neutral alumina (Brockmann grade I) prior to use. Degassed samples were prepared through three freeze–pump–thaw cycles applying vacuum (10^{-3} mbar). Oxygen saturation was achieved by continuously bubbling a stream of oxygen gas through the solutions. The sample cuvettes were illuminated by the tunable output of a TOPAS OPA laser pumped by a Clark MXR CPA 2210 fs laser operating at 1 kHz. The ~ 1 mm² fluorescent spot on the front face of the

cuvette was entirely imaged with a spectrograph fitted with an iCCD detector (Acton/Princeton). The delayed fluorescence was recorded for 50 μ s from 100 ns after the laser pulse, capturing the delayed signal, ignoring any prompt fluorescence.

AUTHOR INFORMATION

Corresponding Author

*E-mail: t.schmidt@chem.usyd.edu.au.

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REFERENCES

- (1) Dougherty, T. J.; Gomer, C. J.; Henderson, B. W.; Jori, G.; Kessel, D.; Korbek, M.; Moan, J.; Peng, Q. Photodynamic Therapy. *J. Natl. Cancer Inst.* **1998**, *90*, 889–905.
- (2) Khan, A. U. Singlet Molecular-Oxygen. A New Kind of Oxygen. *J. Phys. Chem.* **1976**, *80*, 2219–2228.
- (3) Triantaphylidés, C.; Havaux, M. Singlet Oxygen in Plants: Production, Detoxification and Signaling. *Trends Plant Sci.* **2009**, *14*, 219–228.
- (4) Triantaphylidés, C.; Krischke, M.; Hoebrechts, F. A.; Ksas, B.; Gresser, G.; Havaux, M.; Breusegem, F. V.; Mueller, M. J. Singlet Oxygen Is the Major Reactive Oxygen Species Involved in Photooxidative Damage to Plants. *Plant Physiol.* **2008**, *148*, 960–968.
- (5) Balushev, S.; Miteva, T.; Yakutkin, V.; Nelles, G.; Yasuda, A.; Wegner, G. Up-Conversion Fluorescence: Noncoherent Excitation by Sunlight. *Phys. Rev. Lett.* **2006**, *97*, 143903.
- (6) Cheng, Y. Y.; Fückel, B.; Khoury, T.; Clady, R. G. C. R.; Tayebjee, M. J. Y.; Ekins-Daukes, N. J.; Crossley, M. J.; Schmidt, T. W. Kinetic Analysis of Photochemical Upconversion by Triplet–Triplet Annihilation: Beyond Any Spin Statistical Limit. *J. Phys. Chem. Lett.* **2010**, *1*, 1795–1799.
- (7) Singh-Rachford, T. N.; Castellano, F. N. Photon Upconversion Based on Sensitized Triplet–Triplet Annihilation. *Coord. Chem. Rev.* **2010**, *254*, 2560–2573.
- (8) Miteva, T.; Yakutkin, V.; Nelles, G.; Balushev, S. Annihilation Assisted Upconversion: Allorganic, Flexible and Transparent Multicolour Display. *New J. Phys.* **2008**, *10*, 103002.
- (9) Yakutkin, V.; Aleshchenkov, S.; Chernov, S.; Miteva, T.; Nelles, G.; Cheprakov, A.; Balushev, S. Towards the IR Limit of the Triplet–Triplet Annihilation-Supported Up-Conversion: Tetraanthraporphyrin. *Chem.—Eur. J.* **2008**, *14*, 9846–9850.
- (10) Singh-Rachford, T. N.; Nayak, A.; Muro-Small, M. L.; Goeb, S.; Therien, M. J.; Castellano, F. N. Supramolecular-Chromophore-Sensitized Near-Infrared-to-Visible Photon Upconversion. *J. Am. Chem. Soc.* **2010**, *132*, 14203–14211.
- (11) Cheng, Y. Y.; Khoury, T.; Clady, R. G. C. R.; Tayebjee, M. J. Y.; Ekins-Daukes, N. J.; Crossley, M. J.; Schmidt, T. W. On the Efficiency Limit of Triplet–Triplet Annihilation for Photochemical Upconversion. *Phys. Chem. Chem. Phys.* **2010**, *12*, 66–71.
- (12) Merkel, P. B.; Dinnocenzo, J. P. Low-Power Green-to-Blue and Blue-to-Uv Upconversion in Rigid Polymer Films. *J. Lumin.* **2009**, *129*, 303–306.
- (13) Monguzzi, A.; Tubino, R.; Salamone, M. M.; Meinardi, F. Energy Transfer Enhancement by Oxygen Perturbation of Spin-Forbidden Electronic Transitions in Aromatic Systems. *Phys. Rev. B* **2010**, *82*, 125113.
- (14) Balushev, S.; Yakutkin, V.; Miteva, T.; Avlasevich, Y.; Chernov, S.; Aleshchenkov, S.; Nelles, G.; Cheprakov, A.; Yasuda, A.; Müllen, K.; Wegner, G. Blue–Green Up-Conversion: Noncoherent Excitation by NIR Light. *Angew. Chem., Int. Ed.* **2007**, *46*, 7693–7696.
- (15) Huang, X. H.; El-Sayed, I. H.; Qian, W.; El-Sayed, M. A. Cancer Cell Imaging and Photothermal Therapy in the Near-Infrared Region by Using Gold Nanorods. *J. Am. Chem. Soc.* **2006**, *128*, 2115–2120.
- (16) Kurtz, R. B. Some General Features of the Processes of Chemiluminescence in Solution (Including Violanthrone). *Trans. N. Y. Acad. Sci.* **1954**, *16*, 399–401.
- (17) Ogryzlo, E. A.; Pearson, A. E. Excitation of Violanthrone by Singlet Oxygen. A Chemiluminescence Mechanism. *J. Phys. Chem.* **1968**, *72*, 2913–2916.
- (18) Abbott, S. R.; Ness, S.; Hercules, D. M. Chemiluminescence from Peroxide Decomposition Reactions. Role of Energy Transfer. *J. Am. Chem. Soc.* **1970**, *92*, 1128–1136.
- (19) Krasnovsky, A. A.; Stremelovskaya, V. S. Singlet-Oxygen-Sensitized Delayed Fluorescence of Phthalocyanines Caused by Photosensitized and Direct Excitation of Dissolved Oxygen by Laser Radiation. *J. Porphyrins Phthalocyanines* **2008**, *12*, 1194–1200.
- (20) Hoijtink, G. J. The Influence of Paramagnetic Molecules on Singlet–Triplet Transitions. *Mol. Phys.* **1960**, *3*, 67–70.
- (21) Delaey, E.; van Laar, F.; De Vos, D.; Kamuhabwa, A.; Jacobs, P.; de Witte, P. A Comparative Study of the Photosensitizing Characteristics of Some Cyanine Dyes. *J. Photochem. Photobiol., B* **2000**, *55*, 27–36.
- (22) Lee, H.; Berezin, M. Y.; Henary, M.; Strekowski, L.; Achilefu, S. Fluorescence Lifetime Properties of Near-Infrared Cyanine Dyes in Relation to Their Structures. *J. Photochem. Photobiol., A* **2008**, *200*, 438–444.
- (23) Gratz, H.; Penzkofer, A.; Abels, C.; Szeimies, R. M.; Landthaler, M.; Bäuml, W. Photoisomerisation, Triplet Formation, And Photo-Degradation Dynamics of Indocyanine Green Solutions. *J. Photochem. Photobiol., A* **1999**, *128*, 101–109.
- (24) Khan, A. U.; Kasha, M. Chemiluminescence Arising from Simultaneous Transitions in Pairs of Singlet Oxygen Molecules. *J. Am. Chem. Soc.* **1970**, *92*, 3293–3300.
- (25) Chou, P. T.; Chen, Y. C.; Wei, C. Y.; Lee, M. Z. Evidence on the O₂(¹ Δ_g) Dimol-Sensitized Luminescence in Solution. *J. Am. Chem. Soc.* **1998**, *120*, 4883–4884.
- (26) Gorman, A. A.; Hamblett, I.; Hill, T. J. Evidence against Dimol-Sensitized Luminescence in Solutions Containing Singlet Oxygen. *J. Am. Chem. Soc.* **1995**, *117*, 10751–10752.
- (27) Murphy, S. T.; Kondo, K.; Foote, C. S. Singlet-Oxygen-Sensitized Delayed Fluorescence: Direct Detection of Triplet Phthalocyanine As an Intermediate. *J. Am. Chem. Soc.* **1999**, *121*, 3751–3755.
- (28) Parker, C. A.; Hatchard, C. G. Triplet–Singlet Emission in Fluid Solutions — Phosphorescence of Eosin. *Trans. Faraday Soc.* **1961**, *57*, 1894–1904.
- (29) Oelckers, S.; Hanke, T.; Röder, B. Quenching of Singlet Oxygen in Dimethylformamide. *J. Photochem. Photobiol., A* **2000**, *132*, 29–32.
- (30) Holzer, W.; Mauerer, M.; Penzkofer, A.; Szeimies, R. M.; Abels, C.; Landthaler, M.; Bäuml, W. Photostability and Thermal Stability of Indocyanine Green. *J. Photochem. Photobiol., B* **1998**, *47*, 155–164.
- (31) Engel, E.; Schraml, R.; Maisch, T.; Kobuch, K.; Koenig, B.; Szeimies, R. M.; Hillenkamp, J.; Bäuml, W.; Vasold, R. Light-Induced Decomposition of Indocyanine Green. *Invest. Ophthalmol. Visual Sci.* **2008**, *49*, 1777–1783.
- (32) Khoury, T.; Crossley, M. J. A Strategy for the Stepwise Ring Annulation of All Four Pyrrolic Rings of a Porphyrin. *Chem. Commun.* **2007**, 4851–4853.
- (33) Tsuchima, M.; Tokuda, K.; Ohsaka, T. Use of Hydrodynamic Chronocoulometry for Simultaneous Determination of Diffusion Coefficients and Concentrations of Dioxygen in Various Media. *Anal. Chem.* **1994**, *66*, 4551–4556.
- (34) Fukuzumi, S.; Ohkubo, K.; Zheng, X.; Chen, Y.; Pandey, R. K.; Zhan, R.; Kadish, K. M. Metal Bacteriochlorins Which Act As Dual

Singlet Oxygen and Superoxide Generators. *J. Phys. Chem. B* **2008**, *112*, 2738–2746.

(35) Lu, T.; Shao, P.; Mathew, I.; Sand, A.; Sun, W. F. Synthesis and Photophysics of Benzotexaphyrin: A Near-Infrared Emitter and Photosensitizer. *J. Am. Chem. Soc.* **2008**, *130*, 15782–15783.

(36) Tsuda, A.; Furuta, H.; Osuka, A. Completely Fused Diporphyrins and Triporphyrin. *Angew. Chem., Int. Ed.* **2000**, *39*, 2549–2552.

(37) Salokhiddinov, K. I.; Byteva, I. M.; Gurinovich, G. P. Lifetime of Singlet Oxygen in Various Solvents. *J. Appl. Spectrosc.* **1981**, *34*, 561–564.