Lighting

Photochemical Upconversion Light Emitting Diode (LED): Theory of Triplet Annihilation Enhanced by a Cavity

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Artificial lighting is a widespread technology which consumes large amounts of energy. Triplet-triplet annihilation photochemical upconversion is a method of converting light to a higher frequency. Here, it is shown theoretically that photochemical upconversion can be applied to Watt-scale lighting, with performance closely approaching the 50% quantum yield upper limit. The dynamic equilibrium of an efficient device consisting of an LED, an upconverting material, and an optical cavity is described from optical and thermal perspectives.

2. Upconversion LED Architecture

The upconversion LED consists of three parts. They are illustrated in **Figure 1**. The LED, which converts current to light, is the first part. The anabathmophore, which is the component that converts the light to a higher frequency, is second. An anabathmophore is a special case of a fluorophore where the emission energy level is above the excitation energy. The name is derived from the Greek words $\dot{\alpha}\nu\alpha$ "up," $\beta\alpha\nu\nu\omega$ "to go," and $\phi \dot{\varepsilon} \rho \omega$ "to bring." Finally, the optical

cavity ensures that the LED and anabathmophore are efficiently linked, but the upconversion escapes.

1. Potential Advantages of a Photochemical Upconversion Light Emitting Diode

Triplet–triplet annihilation photochemical upconversion is a technique for converting light to a higher frequency. It can be relatively efficient at low intensities because it can be exothermic.^[1–5] Photochemical upconversion has been demonstrated using abundant chemical elements and solution-phase synthesis.^[6,7] Therefore it has the potential to be a cheap, widespread technology.

Red light emitting diodes (LEDs) are cheaper, more efficient, and longer lasting than blue LEDs.^[8,9] Therefore, it may be cheaper to combine red LEDs and upconversion technology to make blue, ultraviolet, or white LEDs. While there are many reports discussing the application of upconversion to solar energy capture,^[10–12] the first report of a lighting application only appeared recently.^[13] Lighting is important for safety^[14,15] and consumes 31 GW in the United States alone.^[16]

Here, we quantitatively describe feasible conditions under which the upconversion light source will operate near its theoretical quantum yield upper limit, which is 50%. The long-term reliability of photochemical upconversion^[17] is an open question which is beyond the scope of this work. We argue that if future work demonstrates reliability against the degradation mechanisms, which are oxygen permeation and photochemical degradation, upconversion LEDs will be a superior lighting solution.

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2.1. LED

The LED is a junction of a p-doped semiconductor with an ndoped semiconductor.^[8] When current flows through the LED, electrons and holes annihilate at the junction, producing light. LEDs have recently become widespread lighting products.^[18] Despite their high fabrication costs, long lifespans and high conversion efficiencies make them cheaper than traditional lighting technologies, such as incandescent and fluorescent lights. LEDs are available with high brightnesses and relatively narrow spectra compared to incandescent lights, two features which are necessary for efficient photochemical upconversion LEDs. In the discussion below, a laser or VCSEL^[19] could be substituted for an LED, with no change to the results. Here, we model the efficiency and heat output at the component level of detail.

2.2. Photochemical Upconversion

Photochemical upconversion is a five-step process which occurs in bimolecular systems. It is illustrated in steps two to six of energy level diagram **Figure 2**. The two molecules are a sensitizer and an emitter, of which there are numerous examples.^[7,20–29] The sensitizer absorbs the LED electroluminescence. This creates a singlet exciton, which converts to a more stable triplet exciton as the sensitizer undergoes intersystem crossing. Next the sensitizer transfers the triplet exciton to an emitter. Two emitter triplet excitons undergo Auger exciton–exciton annihilation,^[30,31] producing one singlet exciton with a higher energy. Finally, the singlet exciton undergoes fluorescence.

The anabathmophore performs spontaneous conversion of light to a higher frequency, which is counter-intuitive because





Figure 1. Cartoon of an upconversion LED. The device consists of a constant current source, LED, cavity, anabathmophore for light conversion, and an output coupler. Not shown: heat sink and LED spectral filter.



Figure 2. Energy level diagram for the six physical processes in a photochemical upconversion LED. S_n indicates the *n*th singlet state. T_1 indicates the first triplet excited state. Each process is exothermic, ensuring the device efficiently ratchets its way to a higher energy. Not to scale.

normal fluorophores convert light to a lower frequency. Photochemical upconversion has a maximum quantum yield of 0.5 because two quanta are converted to one. However, the energy efficiency can locally be greater than one, if the emitter is selected to be endothermic and entropy increases.^[32] In practice, energy levels are selected to make upconversion exothermic in order to prevent reverse operation.^[33] In this work, we model the anabathmophore rate equations, optical coupling, and component-level heat dissipation.

2.3. Cavity

Recently, an LED-driven anabathmophore was demonstrated.^[13] However, the LED emission was not effectively concentrated in the anabathmophore. Since upconversion relies on a high density of excitons, optical concentration is important to energy efficiency. An optical cavity can reflect the LED light to achieve a high excitation rate. The high excitation rate leads to more rapid exciton annihilation. Here, we use a SCIENCE NEWS ______ www.advancedsciencenews.com

simplistic model of the cavity at the surface reflectivity level of detail.

The anabathmophore in a cavity resembles an optically excited laser. However, it does not need to be a laser. Its operating principle does not rely on stimulated emission. Upconversion does not have a power threshold which is required for the device to turn on. A lasing anabathmophore can be distinguished from a regular anabathmophore by dramatically reduced beam divergence.

3. Upconversion Efficiency

The quantum yield of photochemical upconversion $\Phi_{\rm UC}$ is conventionally described in terms of four of the processes which take place within the anabathmophore. $^{[29]}$

$$\Phi_{\rm UC} = \frac{1}{2} \Phi_{\rm ISC} \Phi_{\rm TT} \Phi_{\rm TTA} \Phi_{\rm F} \tag{1}$$

The symbols are listed in **Table 1**. Near-perfect quantum yield is routinely achieved for intersystem crossing in the sensitizer (Φ_{ISC}) and triplet exciton transfer from the sensitizer to the emitter (Φ_{TT}). The quantum yield of triplet–triplet annihilation Φ_{TTA} is sensitive to the properties of the LED and will be discussed in depth. Finally, the fluorescence quantum yield Φ_F of the emitter in the singlet excited state can be nearly perfect. In the special case where the emitter possesses a second triplet excited state just above the energy of the singlet exciton, Φ_F may be reduced by thermally activated intersystem crossing.^[34–37] For emitters with this property, the thermal coupling of the anabathmophore to the LED will have greater significance to Φ_F .

3.1. Steady-State Annihilation Quantum Yield

We will now examine the annihilation yield to uncover the optical coupling of an anabathmophore to an LED.

$$\Phi_{\rm TTA} = \eta_c f_2 \tag{2}$$

where η_c is the proportion of annihilation events which produce a singlet exciton in an emitter molecule. This parameter captures the density of states and matrix elements for annihilation processes. It seems reasonable to assume that η_c is insensitive to heating by an LED if the heating does not substantially change the alignment of energy levels, including the quintet state and second triplet state,^[1,47–50] in the emitter molecule. There are few reports of measurements of η_c .^[1,40]

 f_2 is the proportion of triplet excitons which decay by annihilation. It is the ratio of the desirable kinetics to the total decay rate.^[41]

$$f_2 = \frac{k_2[{}^3A^*]}{k_2[{}^3A^*] + k_1} \tag{3}$$

 k_1 is the small decay rate of a triplet exciton in an isolated emitter. k_2 is the second order rate constant for triplet annihilation. [³*A**] is the triplet exciton concentration in the emitter molecule. Efficiency is achieved when k_2 and [³*A**] are large.

Table 1. List of symbols with values used in calculations.

Symbol	Description	Value	Reference
Φ_{ISC}	Intersystem crossing quantum yield	1	[38,39]
Φ_{TT}	Triplet transfer quantum yield	1	[6]
Φ_{F}	Fluorescence quantum yield	1	
η_c	Singlet yield of exciton annihilation	1	[40]
f ₂	Proportion of triplet excitons annihilated		[41]
<i>k</i> ₁	Triplet exciton decay rate ^{a)}	10^4 s^{-1}	[1,6]
k2	Triplet annihilation rate ^{a)}	$10^{-12} \text{ cm}^3/\text{s}$	[10]
[S]	Sensitizer concentration	10 ⁻³ м	[42]
k _B	Boltzmann constant		
Ev	Energy of vibrational quantum	0.37 eV	[43]
Ε _Α	Activation energy of triplet annihilation	—1 eV	
P _d	LED power dissipation	6.6 W ^{b)}	
ϕ_r	LED radiant flux	3 W ^{b)}	
E _d	Energy per photon from red LED	1.88 eV ^{b)}	
Ε _U	Energy per photon from cyan emitter	2.5 eV	
Ns	Number of sensitizer molecules	10 ⁻¹⁰ mol	
e	Sensitizer molar absorptivity	$58000~M^{-1}cm^{-1}$	[10]
x	Anabathmophore thickness	10 ⁻⁵ m	
	Anabathmophore area	$10^{-5} m^2$	
AL	LED surface area in cavity	10 ⁻⁶ m ²	
A _c	Reflector surface area in cavity	$10^{-3} m^2$	
αL	LED absorptance	0.5	
α _c	Reflector absorptance	0.01	
E _{0r}	LED Radiant efficacy ^{a)}	0.44 ^{b)}	
ke	LED droop	-0.005	[44]
k _h	LED heating	0.56 ^{b)}	[45]
T ₀	Reference temperature	300 K ^{b)}	
Ta	Ambient temperature	300 K	
R _{jc}	LED junction-case thermal resistance	2.8 K W ^{-1b)}	
R _{hs}	Heat sink thermal resistance	1 K W ⁻¹	
R _{Uc}	Anabathmophore–case thermal resistance	10 K W ⁻¹	
R _{Uj}	Anabathmophore-LED junction thermal resistance	no effect	
Results			
Φ_{UC}	Upconversion quantum yield	0.42	[41]
Φ_{TTA}	Annihilation quantum yield	0.84	[46]
$[{}^{3}A^{*}]$	Triplet exciton concentration	1.0 тм	
k_{ϕ}	Excitation rate	$7.8 imes 10^{28} ext{ mol}^{-1} ext{ s}^{-1}$	
TU	Anabathmophore temperature	315 K	
Puc	Anabathmophore heat output	1.1 W	
Φ_{cL}	Yield of LED emission captured by sensitizer	0.85	
s	Fraction of energy lost to heat during upconversion	0.34	

 $^{\rm a)}$ Conventionally reported at a reference temperature; $^{\rm b)}$ LED ENGIN LZ4-00R208 specification sheet, 2018

The steady-state triplet exciton concentration in terms of device parameters $\mathrm{is}^{[41]}$

$$[{}^{3}A^{*}] = \frac{-k_{1} + \sqrt{k_{1}^{2} + 4k_{2}k_{\phi}\Phi_{\rm ISC}\Phi_{\rm TT}[S]}}{2k_{2}}$$
(4)

where k_{ϕ} is the excitation rate caused by the LED and [S] is the sensitizer concentration.^[51] To achieve good radiant flux and energy efficiency, the optical system should be arranged to produce a large k_{ϕ} . This will be discussed in Section 4.

3.2. Triplet Exciton Decay

Thermal coupling between the LED and anabathmophore plays a role in the triplet exciton decay. The unimolecular triplet exciton decay rate k_1 has thermal, collisional, and fixed (e.g., phosphorescence)^[6,52] components. The thermal relaxation component has the form^[43,53]

$$e^{-\frac{E_v}{k_B T_U}} \tag{5}$$

where the vibrational energy E_v is typically about 3000 cm^{-1,[43]} k_B is the Boltzmann constant, and T_U is the temperature of the anabathmophore. The collisional component includes phenomena like triplet quenching by oxygen^[54] and by the sensitizer.^[42]

The triplet exciton decay rate may be increasing, decreasing, or static as a function of temperature depending on the mechanism. To achieve an energy efficient device, the LED must provide sufficient illumination that $k_{\phi}[S]$ overwhelms k_1 . If this is achieved, the thermal effects of the LED on k_1 will become unimportant. For modeling purposes, we use the thermal relaxation behavior (5).

3.3. Annihilation Rate

The annihilation reaction is a second order reaction. It is diffusive and has an activation energy. Neglecting the range of the reaction and the mobility of the annihilators

$$k_2 \propto k_B T_U e^{-\frac{E_A}{k_B T_U}} \tag{6}$$

where E_A is the annihilation activation energy and T_U is the temperature of the anabathmophore. The energy E_A is the potential energy difference between the energy barrier to triplet annihilation and the energy of two emitter triplets. The barrier cannot be less than the emitter singlet energy. Ideally, E_A will be negative. The temperature dependence of several aspects of upconversion have been demonstrated.^[53,55–58] The temperature/ k_2 relationship (6) is ubiquitous in chemistry but, to our knowledge, has not been directly tested with photochemical upconversion.

 k_2 is an important parameter to maximize in order to achieve overall efficiency. There are three regimes to consider: First, 0 < E_A is endothermic upconversion. This case should only be selected if the upconversion must increase the photon energy by more than a factor of two, as it is inefficient. For endothermic upconversion, higher temperature operation is always more ef-



Figure 3. Predicted temperature dependence of the annihilation rate k_2 for various activation energies, using 300 K as a reference point. If the measured value of k_2 is 10^{-12} cm³ s⁻¹ at 300 K, the value of k_2 at other temperatures can be predicted based on the activation energy. To achieve efficiency, upconversion should be slightly exothermic.

ficient. Second, if $0 > E_A > -k_B T$, then k_2 increases with temperature. In the high temperature limit, the increase is linear, as shown by the fuchsia curve in **Figure 3**. Third, the typical situation is that $0 > -k_B T > E_A$ and k_2 decreases with temperature. As shown by the blue curve in Figure 3, the decrease can be rapid.

If the goal is to produce a white light by combining the LED and upconversion emission, then an activation energy of about -1.4 eV is desired. The activation energy is determined by the energy of complementary colors in the additive color model, and energy losses involved in sensitizer absorption, intersystem crossing, triplet transfer, and singlet fluorescence. If there is an energy barrier to annihilation which lies above the singlet state, it must also be accounted for in the activation energy of a white LED.

4. Cavity Performance

As seen in Equation (4), the sensitizer excitation rate k_{ϕ} is a controllable parameter which contributes to the efficiency of photochemical upconversion. If the radiant flux of the LED is ϕ_r , then the upper limit on k_{ϕ} is

$$k_{\phi} \le \frac{\phi_r}{E_d N_s} \tag{7}$$

where E_d is the energy per photon emitted by the diode^[59] and N_s is the number of sensitizer molecules. This shows that the number of sensitizer molecules should be as small as possible to increase the excitation rate k_{ϕ} . Equation (4) indicates the sensitizer concentration should be high. Considering Equations (4) and (7) together, the volume of the anabathmophore should be low. Unlike sunlight,^[60–62] LED emission can be easily placed in a cavity, making it possible to achieve both a small volume anabathmophore and a high excitation rate.

The cavity will have two loss mechanisms: the loss occurring from imperfect cavity walls and the loss from absorption of light reflected back to the LED. The volume of the anabathmophore should be large enough that it absorbs more of the light than is lost to either mechanism.

Neglecting geometric details, the proportion of LED light injected into a cavity which is absorbed in the sensitizer, Φ_{cL} , is the product of the anabathmophore absorption probability and the cavity reflection probability summed over cavity traverses performed by the LED light.

$$\Phi_{cL} = \left(1 - e^{-\epsilon[S]x}\right) \sum_{n=0}^{\infty} \left(e^{-\epsilon[S]x}\right)^n \left(1 - \frac{A_L \alpha_L + A_c \alpha_c}{A_L + A_c}\right)^n \tag{8}$$

where ϵ is the sensitizer molar absorptivity used in the Beer– Lambert law, *x* is the average thickness of the upconversion material traversed by light crossing the cavity, A_L is the LED area, A_c is the cavity reflector area, α_L is the LED absorptance, and α_c is the cavity reflector absorptance. The geometric series simplifies to

$$\Phi_{cL} = \frac{\left(1 - e^{-\epsilon[S]x}\right)}{1 - \left(e^{-\epsilon[S]x}\right)\left(1 - \frac{A_L\alpha_L + A_c\alpha_c}{A_L + A_c}\right)}$$
(9)

which is the yield of the coupling between the LED and the anabathmophore. The resulting excitation rate is

$$k_{\phi} = \frac{\Phi_{cL}\phi_r}{E_d N_s} \tag{10}$$

A higher excitation rate is better. The excitation rate can be increased by using a high LED brightness, a highly reflective cavity, and a small anabathmophore. This model is reasonable for a planar geometry with a monochromatic LED, specular reflections, and homogeneous materials. In other cases, the cavity can be modeled in detail with Monte Carlo methods.

Since no stimulated emission is required, but low cost is often desirable, we pick a Teflon (polytetrafluoroethylene) cavity as a concrete example. Teflon has absorptance $\alpha_c \approx 0.01$. The diffuse reflectivity of a Teflon cavity is acceptable as sensitization is insensitive to the angle of incidence. For our model, we assume the LED has $\alpha_c \approx 0.5$ and is about 10^{-6} m² in area. We assume the cavity has an internal surface area of 10^{-4} m², so losses from the LED absorption are not very important. Since the upconversion must be coupled out of the device, 10^{-5} m² of the cavity Teflon should be replaced with a relatively expensive dielectric shortwavelength-transmitting filter with $\alpha_c = 0.01$ or better. Such a Bragg filter would transmit the upconverted light and specularly reflect the LED emission back into the cavity.

Owing to the Beer–Lambert law, to optimize k_{ϕ} the upconversion portion of the device should be a thin film.^[10] To continue the example, the sensitizer concentration might be around 1 mm with anabathmophore thickness 10^{-5} m, area 10^{-5} m² and 10^{-10} mol of sensitizer.

The LED can be covered by a filter^[13] which reflects the upconverted light, eliminating one source of self-absorption. If the filter is a well-designed dielectric thin film, no significant losses of the LED light will occur. A good anabathmophore design will possess a low molar absorptivity at the emission wavelength. Our model assumes self-absorption of the upconverted light is negligible because the anabathmophore is thin.



Figure 4. Thermal circuit diagram of the temperatures, heat loads, and thermal resistances in an upconversion LED system. T_a is the ambient temperature. T_j is the LED junction temperature. T_U is the anabath-mophore temperature. T_c is the case temperature. The heat loads are from the LED ($k_h P_d$) and anabathmophore (P_{UC}).

5. Steady-State Thermal Performance

The radiant flux of an LED, ϕ_r , is to be distinguished from the human vision-weighted luminous flux typically specified by visible LED manufacturers; upconversion can be pumped by infrared LEDs.^[63–69] As LED physics can vary considerably between designs and operating regimes, we draw from a component-level phenomenological theory^[44] which is valid over a limited range and does not include any wavelength conversion device. ϕ_r is temperature sensitive.^[44]

$$\phi_r(P_d) = E_{0r} \left\{ [1 + k_e (T_a - T_0)] P_d + k_e k_h (R_{jc} + R_{hs}) P_d^2 \right\}$$
(11)

 E_{0r} is the radiant efficacy specification at a reference temperature T_0 . k_e , which is negative, models the LED droop. Droop is the underperformance of LEDs at high current, which has several causes, including annihilation events.^[70–76] T_a is the ambient temperature. P_d is the diode input power, as measured from the current and voltage. k_h is the proportion of the power P_d which is dissipated as heat. R_{jc} is the thermal resistance^[77] between the LED junction and the LED case/heat sink contact. R_{hs} is the thermal resistance of the heat sink.

The thermal circuit, expanded to include the heat load of the anabathmophore, is illustrated in **Figure 4**. The anabathmophore is in thermal contact with the case (thermal resistance R_{Uc}) and the LED (thermal resistance R_{Uj}). The heat output of the anabathmophore and cavity is

$$P_{UC} = \phi_r \left((1 - \Phi_{cL}) + \Phi_{cL} (1 - 2\Phi_{UC}) + \Phi_{cL} \Phi_{UC} s \right)$$
(12)

The first term is the cavity loss because the cavity coupling Φ_{cL} is less than one. The second term is the heat output owing to triplets which decay without becoming singlets. This heat is computed from the upconversion quantum yield Φ_{UC} . The third term is the heat output from exothermic upconversion. The fraction of energy which is lost to heat during upconversion, *s*, can be computed from the area-normalized LED emission spectrum as

a function of energy $\psi_L(E)$ and the anabathmophore emission spectrum $\psi_{UC}(E)$.

$$s = \frac{\int 2E\psi_L(E) - E\psi_{UC}(E)dE}{2\int E\psi_L(E)dE}$$
(13)

The losses which contribute to *s* include cumulative donor and acceptor Stokes, intersystem crossing, transfer, and annihilation energy shifts. We approximate *s* by assuming the spectra are monochromatic. The way the upconversion quantum yield Φ_{UC} is included in the heat output in model (12) neglects any phosphorescence which may, inadvertently or to generate another color, escape from the device. An efficient anabathmophore produces negligible phosphorescence.^[6,52]

The temperatures of the combined devices can be determined using Kirchhoff nodal analysis. The diode temperature is

$$T_a + R_{hs}k_h P_d + R_{jc} (k_h P_d - P_{UC})$$
(14)

and the anabathmophore temperature is

$$T_U = T_a + R_{hs} k_h P_d + R_{Uc} P_{UC}$$
(15)

In Section 3.2, we explained that the anabathmophore temperature alters the efficiency of upconversion by changing the annihilation rate constant. Here, we find that the heat from the LED decreases the efficiency of the upconversion.

The LED performance in Equation (11) can be revised to include the anabathmophore's contribution to the thermal circuit.

$$\phi_r(P_d) = E_{0r} \left\{ 1 + k_e \left[T_a - T_0 + R_{jc} \left(k_h P_d - P_{UC} \right) + R_{hs} k_h P_d \right] \right\} P_d$$
(16)

The heat output from the anabathmophore P_{UC} increases the LED radiant flux ϕ_r because heat is directed to the LED case instead of the junction.

6. Computational Methods

We numerically solved the system of simultaneous Equations (1)–(4), (10), (12), (15), and (16) with k_1 and k_2 scaled with anabathmophore temperature T_U according to expressions (5) and (6), respectively. The values of the physical parameters we used are listed in Table 1. In the Section 7, some of these parameters are varied one at a time to show their importance to device performance. The final result, the upconversion LED radiant flux, is $\Phi_{UC}\Phi_{cL}\phi_r(E_U/E_d)$. That is the product of the upconversion quantum yield, the cavity coupling yield, the LED radiant flux, and the gain caused by the spectral shift from the LED emission energy E_d to the upconversion emission energy E_U of the emitter.

The solution to the model is listed in Table 1. The device wall-

plug efficiency is 20% and the upconversion radiant flux is 1 W.

7. Results



Figure 5. Calculated upconversion quantum yield Φ_{UC} and upconversion output power as a function of the emitter molecule triplet exciton decay rate k_1 . The device efficiency improves as k_1 gets smaller. Readily achievable decay rates push the system close to the quantum yield upper limit, $\Phi_{UC} \leq 0.5$. All other parameters are as specified in Table 1.

High efficiency is achieved because the triplet exciton concentration is high. The concentration of the emitter, which played no role in the calculation, must be higher than the triplet exciton concentration in order for the results to be physically correct.

The 20% wall-plug efficiency is lower than the approximately 30% efficiency of commercial blue LEDs, or the 80% achieved in laboratory devices.^[78] In the model, the most important factor reducing the system efficiency is the red LED's efficiency. Next most important is the fundamental upper limit that photochemical upconversion cannot exceed: 50% quantum yield. The spectral shift of the upconversion can help make up for this limit. In the model we selected complementary colors suitable for generating white light, which reduces the spectral shift. We chose an increase in the energy per photon of just 33%. Finally, the coupling of the LED to the anabathmophore is the most efficient component, achieving 85% with our absorptance assumptions.

7.1. Triplet Exciton Lifetime

The annihilation yield depends on the balance of the different triplet exciton decay rates. In **Figure 5**, we show that, under the conditions listed in Table 1, the triplet exciton concentration is so high that triplet exciton utilization is nearly perfect when the unimolecular triplet exciton decay k_1 is less than 10^4 s^{-1} . With rubrene as an emitter, $8 \times 10^3 \text{ s}^{-1}$ has been achieved,^[1] while for 9-(4-phenylethynyl)-10-phenylanthracene, k_1 is around $5 \times 10^2 \text{ s}^{-1}$.^[6] Since Φ_{TTA} must be no greater than 0.5 owing to energy conservation, further improvements in k_1 are not necessary. However, the introduction of molecular oxygen to the device must be prevented because oxygen is an efficient triplet quencher.^[54]



Figure 6. Calculated upconversion quantum yield Φ_{UC} and upconversion output power as a function of the yields $\Phi_{ISC}\Phi_{TT}$ (blue) and $\Phi_F\eta_c$ (red). Reduced Φ_{ISC} or Φ_{TT} decrease device efficiency before the annihilation step. While they are physically different, those two yields play the same mathematical role in the model, so they are presented as a product. Reduced Φ_F or η_c decrease device efficiency after the annihilation step, so they are slightly less important. This pair of yields only appear in the calculation as a product, so they are presented as a product. All other parameters are as specified in Table 1.

7.2. Yields

Based on experimental results, the yields Φ_{ISC} , Φ_{TT} , Φ_F , and η_c may be perfect. If they are not, device performance is reduced. The first two, the yields of intersystem crossing and triplet transfer, are more important because they play a role in causing annihilation, which is a nonlinear process. **Figure 6** shows that devices with impaired $\Phi_F \eta_c$ outperform devices with impaired $\Phi_{ISC} \Phi_{TT}$ because the fluorescence yield and singlet yield of exciton annihilation are not involved in that nonlinearity. The rate constants are presented multiplied together where their results are not distinguishable.

7.3. Sensitizer Concentration

Reduction of the sensitizer concentration is harmful.^[10] The sensitizer concentration is critically important because it determines triplet concentration. The sensitizer concentration needs to be high to enable triplets to encounter partners for annihilation. **Figure 7** indicates that millimolar concentrations are desirable. 1 mm has been achieved in solution^[42] and future solid-phase devices should have much higher sensitizer concentrations.

7.4. Electrical Power

Efficient upconversion requires high excitation rates. In **Figure 8**, we show that Watt-scale LEDs, which are commercially available, can provide sufficient optical power. Both the LED (orange) and anabathmophore (blue) response to the power consumed are only slightly worse than linear. At milliWatt-scale



Figure 7. Calculated upconversion quantum yield Φ_{UC} (red) and upconversion output power (blue) as a function of sensitizer concentration. Higher sensitizer concentration is better. All other parameters are as specified in Table 1.



Figure 8. Calculated upconversion quantum yield Φ_{UC} and LED/upconversion output power as a function of the electrical power consumed by the device. Efficient performance is achievable with commercially available high-power LEDs. All other parameters are as specified in Table 1.

driving power, however, the triplet excitons fail to find partners for annihilation, and the device efficiency plummets. Φ_{TTA} has a maximum at 2.2 W. Above this electrical power, we find detrimental thermal effects on the upconversion rate constants.

The near-linearity of the optical output shows that the LED emission and the anabathmophore emission could be combined to make a white LED whose brightness is controlled by current flow. The LED color would be nearly independent of the brightness, but would turn red at very low currents.

7.5. Cavity Performance

In **Figure 9**, we show that an optical cavity is necessary to achieve efficient operation. If the cavity's reflector has absorptance greater than 0.01, the yield of photochemical upconversion



Figure 9. Calculated upconversion quantum yield Φ_{UC} and upconversion output power as a function of the cavity reflector absorptance α_c . Low-cost Teflon has an absorptance of about 0.01, which is sufficient for good upconversion quantum yield Φ_{UC} . However, even lower absorptance produces a greater power output owing to a higher cavity efficiency Φ_{cL} . All other parameters are as specified in Table 1.

decreases rapidly. Our simple cavity model assumes multiple, randomized reflections, which are required for efficient operation. Therefore it is not reliable at very high absorptances.

A high upconversion quantum yield $\Phi_{\rm UC}$ is necessary but not sufficient. The cavity must also effectively direct the LED electroluminescence to the sensitizer. Figure 9 shows that as the absorptance decreases, near 0.01 the $\Phi_{\rm UC}$ is saturating, but the device power output is still improving. A 20% overall efficiency can be achieved with low-cost (e.g., Teflon) diffuse reflectors with 0.01 absorptance. Marginally lower absorptance could be achieved using a more costly dielectric reflector.^[79] Cavity performance is ultimately limited by the self-absorption of the LED. While the LED can be prevented from absorbing the upconversion light by coating it with a dielectric filter,^[13] it cannot be prevented from absorbing back-reflections of its own electroluminescence without an impractical optical isolator.^[80,81]

7.6. Thermal Resistance

Heating is a well-known problem in high-power LED, which are typically designed with heat dissipation in mind.^[44,82–86] Figure 10 shows that the upconversion LED must be designed with a reasonable thermal resistance R_{Uc} between the anabathmophore and the case. If the thermal resistance exceeds 10 K W⁻¹, then the anabathmophore temperature rises rapidly. As a result, the rate constants k_1 and k_2 become less favorable, reducing the upconversion efficiency. Above 20 K W⁻¹, nearly all the energy is lost as heat. Thermal resistances less than one K W⁻¹ are common in commercial electronic devices.

7.7. Ambient Temperature

To be practical for outdoor use, light sources need to operate efficiently at a wide range of ambient temperatures T_a . In



Figure 10. Calculated upconversion quantum yield Φ_{UC} and anabathmophore temperature T_U as a function of the anabathmophore-to-case thermal resistance R_{Uc} . If the anabathmophore is highly insulated, it gets hot. The heat leads to unfavorable kinetic parameters k_1 and k_2 , producing declining efficiency. The rate constants are compromised before the decomposition temperature is reached. All other parameters are as specified in Table 1.



Figure 11. Calculated LED/anabathmophore temperature and LED/upconversion radiant flux as a function of ambient temperature. The upconversion LED is brighter at lower temperatures. All other parameters are as specified in Table 1.

Figure 11, we calculate the decline in the brightness of the upconversion LED which is caused by elevated ambient temperatures. The LED component has a declining output, which is the well-known LED droop. The upconversion output has a more severe droop, which is caused by the anabathmophore's nonlinear response. The reduction in the anabathmophore efficiency at high temperatures increases the anabathmophore's heat dissipation, which has Equation (15)'s feedback effect on the anabathmophore's temperature. The increase in the anabathmophore's heat dissipation mitigates the diode temperature increase, as indicated in Equation (14).

8. Conclusion

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We show that there are a wide range of conditions under which upconversion LEDs can operate efficiently. Currently achievable triplet exciton lifetimes are sufficient to avoid losses from unimolecular triplet exciton decay. Commercially available LEDs have sufficient brightness to drive the device. Modest performance optical cavities can effectively couple the LED and anabathmophore. A basic heat sink is required to ensure the anabathmophore does not overheat. However, at high ambient temperatures, care must be taken to improve the thermal resistance or rate constants to be better than our assumed values. Otherwise, the device brightness can decline in hot weather.

Upconversion LEDs incorporating effective optical and thermal designs will readily exceed the efficiency of incandescent lights. They may never achieve the efficiency of the best laboratory LEDs, but may still be an economically competitive technology. At present, the only barrier to implementation of upconversion LEDs is uncertainty about the long-term reliability of anabathmophores. This reliability should be tested against blue LEDs. If anabathmophores are shown to be stable, then upconversion LEDs will be suitable for lighting human vision with white light and for blue or ultraviolet illumination in applications such as lithography,^[87–89] banknote identification,^[9] or photochemistry.^[90,91]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

cavities, LEDs, light emitting diodes, lighting, photochemical upconversion

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