Upconversion Photochemistry

Prof. Felix N. Castellano
Department of Chemistry & Center for Photochemical Sciences, BGSU

Capturing and Converting Energetically Inferior Solar Photons

Solar Radiation Spectrum

- Spectral Irradiance (W/m²/nm)
- Wavelength (nm)
- Sunlight at Top of the Atmosphere
- 555°C Blackbody Spectrum
- Radiation at Sea Level
- Absorption Bands
- O₃, O₂, H₂O, H₂O, H₂O, CO₂, H₂O

External Quantum Yield, %

N3
Generic Metal-Organic Chromophore State Diagram

Excitation

\( h\nu \)

\( \text{Emission} \)

\( k_r \)

\( k_{nr} \)

\( 1\text{CT} \)

\( 3\text{CT} \)

\( k_{ISC} \)

\( T_1 \text{ Internal Conversion} \)

\( T_2 \)

\( T_3 \)

Two-Photon Excitation

\( h\nu' \)

\( h\nu'' \)

\( \text{GS} \)

\( h\nu_1 \)

\( h\nu_2 \)
Energy Requirements for Sensitized AS Fluorescence Based on Sequential Linear Absorption and TT Annihilation

Original Bimolecular Prototype:

Low Power CW Photon Upconversion using \([\text{Ru(dmb)}_3]^{2+}/\text{Anthracene}\)

\[\lambda_{\text{ex}} = 514.5 \text{ nm}\]

\([\text{Ru(dmb)}_3]^{2+} @ 3.0 \times 10^{-5} \text{ M}\)

Anthracene @ 1.3 x 10^{-4} M

\(\text{CH}_3\text{CN}\)

*Chem. Commun.* 2004, 2860-2861
Green-to-Blue/UV Upconversion in Solution

Diphenylanthracene
Φ_f = 0.95

DPA (6.9 x 10^{-5} M) + [Ru(dmb)_3]^{2+} (3.0 x 10^{-5} M) as a function of 514.5 nm laser power

Chem. Commun. 2005, 3776-3778
Extremely Low Power Upconversion with Lamp Excitation ($\mu$W/cm$^2$)

DMF Solution

Stern-Volmer:

$$\frac{\tau_0}{\tau} = 1 + \tau_0 k_q [Q]$$

Pd(II)octaethylporphyrin

9, 10-diphenylanthracene

Power density (W/cm$^2$)
- $1.67 \times 10^3$
- $1.32 \times 10^3$
- $1.05 \times 10^3$
- $8.53 \times 10^4$
- $6.63 \times 10^4$
- $5.27 \times 10^4$

Integral Upconverted fluorescence 390-530 nm

$\lambda_{exc} = 544$ nm

$\chi^2$
Upconversion with Terrestrial Solar Photons
Green-to-Blue Upconversion in Thin Polymer Films
P(EO/ Epi)

Noncoherent Upconversion in P(EO/ Epi) Solid Polymer Films (100 µm thick)

\[ \lambda_{\text{em}} = 430 \text{ nm} \]

\[ \lambda_{\text{exc}} = 544 \text{ nm} \]

\[ \text{J. Am. Chem. Soc. 2007, 129, 12652-53} \]
\[ \text{J. Phys. Chem. A 2008, 112, 3550-3556} \]
\[ \text{J. Am. Chem. Soc. 2009, 131, 12007-12014} \]
Time-Resolved Emission Spectrum of the Solid Polymer Film

$\lambda_{ex} = 544 \text{ nm (Nd:YAG/OPO)}$

$T_g = 230$ K

Upconverting Film Fails at 400 K

Upconverting film is reversible upon heating and cooling from 300K-380K.

At 292 K

At 320 K

At 360 K

At 360 K

\[ y = x^2 \]
Green-to-Blue Upconversion: Variety of Materials

[\text{Ru(dmb)}_3]^{2+} + \text{DPA} (4.1 \text{ Toluene. Acetonitrile})

\text{UC Thin Film of PdOEP} + \text{DPA in P(EO / EP)}

\text{UC in Polyurethane Bead After Soaking in a Toluene Solution of PdOEP/DPA}

\text{UC in Polyurethane Bar PdOEP/} \text{DPA in Toluene then Completely Dried, } \lambda_{ex} = 532 \text{ nm}

\text{Polyurethane Bar Containing PdOEP}
\text{Upconverting Polyurethane Bar Containing PdOEP/DPA}
\text{Polyurethane Bar}

532 \text{ nm Laser Pointer}
VT Studies of Thin Films of PdOEP/DPA in Various Polyurethanes

Texin 285 - $T_g = 228$ K (soft Seg)
Texin 270 - $T_g = 273$ K (soft Seg)
Tecoflex® 80A - $T_g = 286$ K (soft Seg)

Film fails at 430 K
Film fails at 400 K
Film fails at 440 K

Absorbance spectra of thin films

Films are reversible upon heating and cooling

Maximum Intensity of Tecoflex® 80A is twice that of Texin 285
Photon Upconversion with BD-1 and BD-2 in Benzene

$\lambda_{\text{ex}} = 635 \text{ nm}$

BD-1

BD-2

*J. Am. Chem. Soc.* **2008**, *130*, 16164-16165
Upconversion Quantum Yields of BD-1 and BD-2:
\[ \lambda_{\text{ex}} = 635 \text{ nm}, \ 26.3 \text{ mW} \]

\[
\Phi_{\text{UC}} = 0.062 \\
\Phi_{\text{UC}} = 0.150
\]

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

Std = Methylene Blue in MeOH, \( \Phi = 0.03 \) at \( \lambda_{\text{exc}} = 633 \text{ nm} \)

Integrated Area Analyzed for BODIPY chromophores = 450-700 nm
Integrated Area for Methylene Blue = 600-850 nm

Coord. Chem. Rev. 2010, 254, 2560-2573
Now a Word About Spin Statistics and UC Quantum Efficiencies

\[ \begin{align*}
\textstyle ^3A_1^* + ^3A_1^* & \iff \begin{bmatrix}
^5(AA)_2^* \\
^3(AA)_1^* \\
^1(AA)_0^*
\end{bmatrix} \\
^5A_2^* + ^1A_0 & \iff \begin{bmatrix}
^3A_1^* + ^1A_0 \\
^1A_0^* + ^1A_0
\end{bmatrix}
\end{align*} \]

\[ 5/9 (55.6\%), \ 3/9 (33.3\%), \ \text{and} \ 1/9 (11.1\%) \]

Adv. Photochem. 1988, 14, 1
Potential Upconversion Applications
Towards Upconversion-Assisted Photocurrent Generation in BHJ Cells

Cuvette w/upconverting system

Substrate

Anode

P3HT:PCBM active layer

Cathode

\[ \lambda_{\text{exc}} = 633 \text{ nm, Laser power (25 mW)} \]

- 480 \mu M PtTPBP
- 480 \mu M PtTPBP + 1 mM 2CBPEA

Normalized Current vs. Bias (V)

Top Contact

Active Layer

Donor-Acceptor Blend

Substrate

Sunlight

Bottom Contact (Transparent)

RR-P3HT

PCBM

OCH3
Proof-of-Principle: Upconversion Process Generates Photocurrent in a BHJ Device

15 I-V Curve Avg.