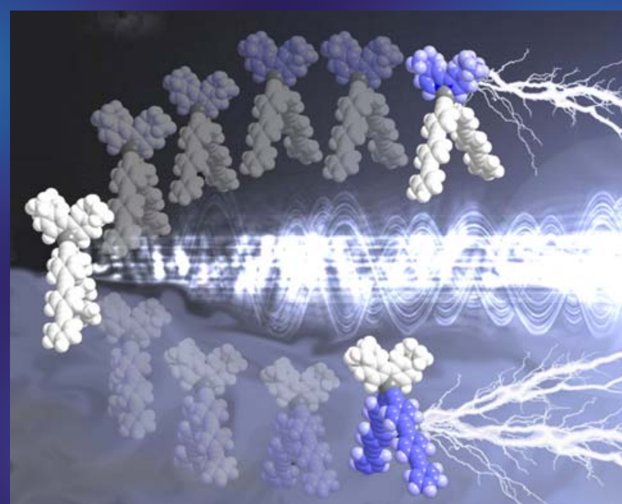
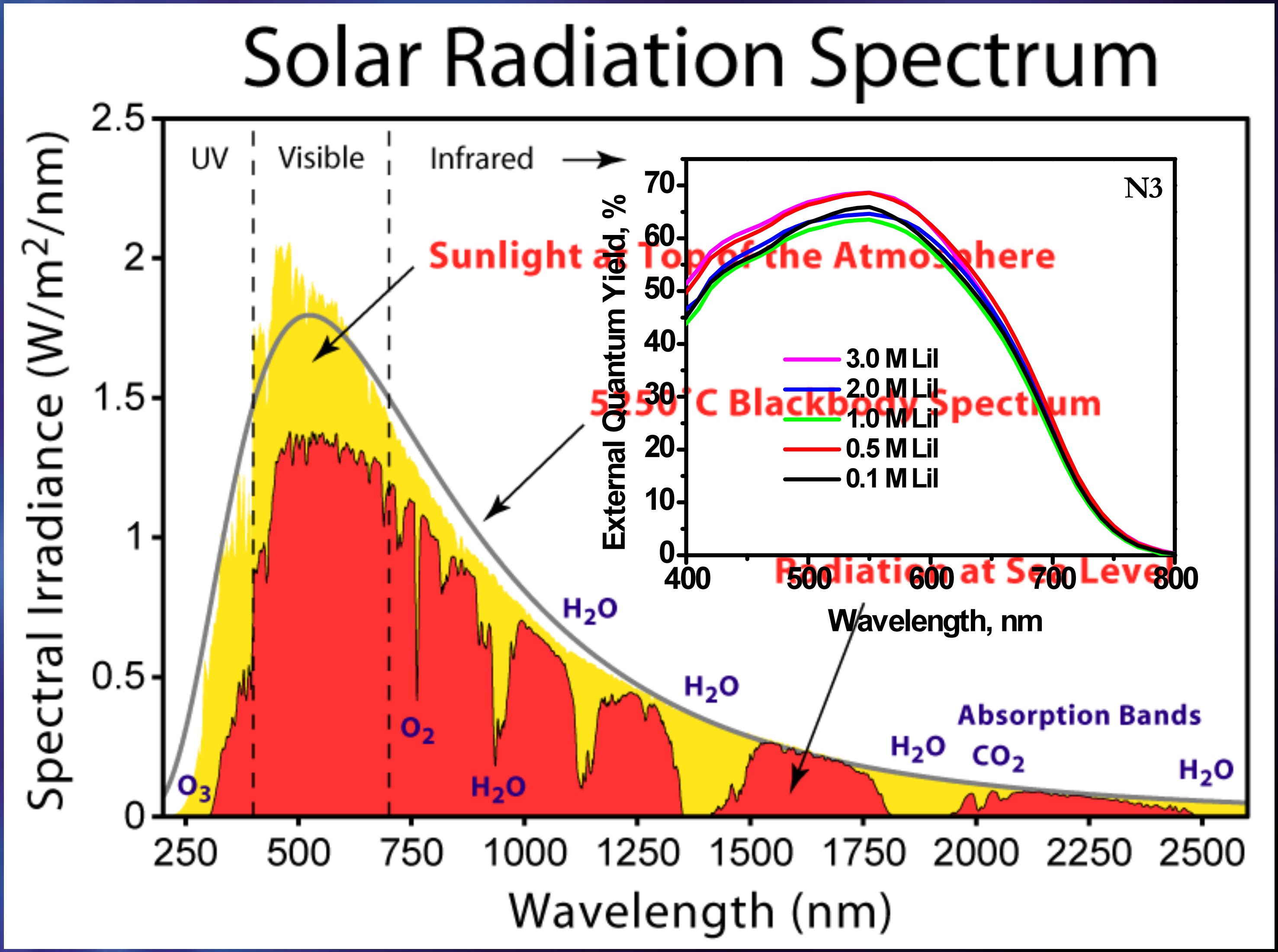
Upconversion Photochemistry



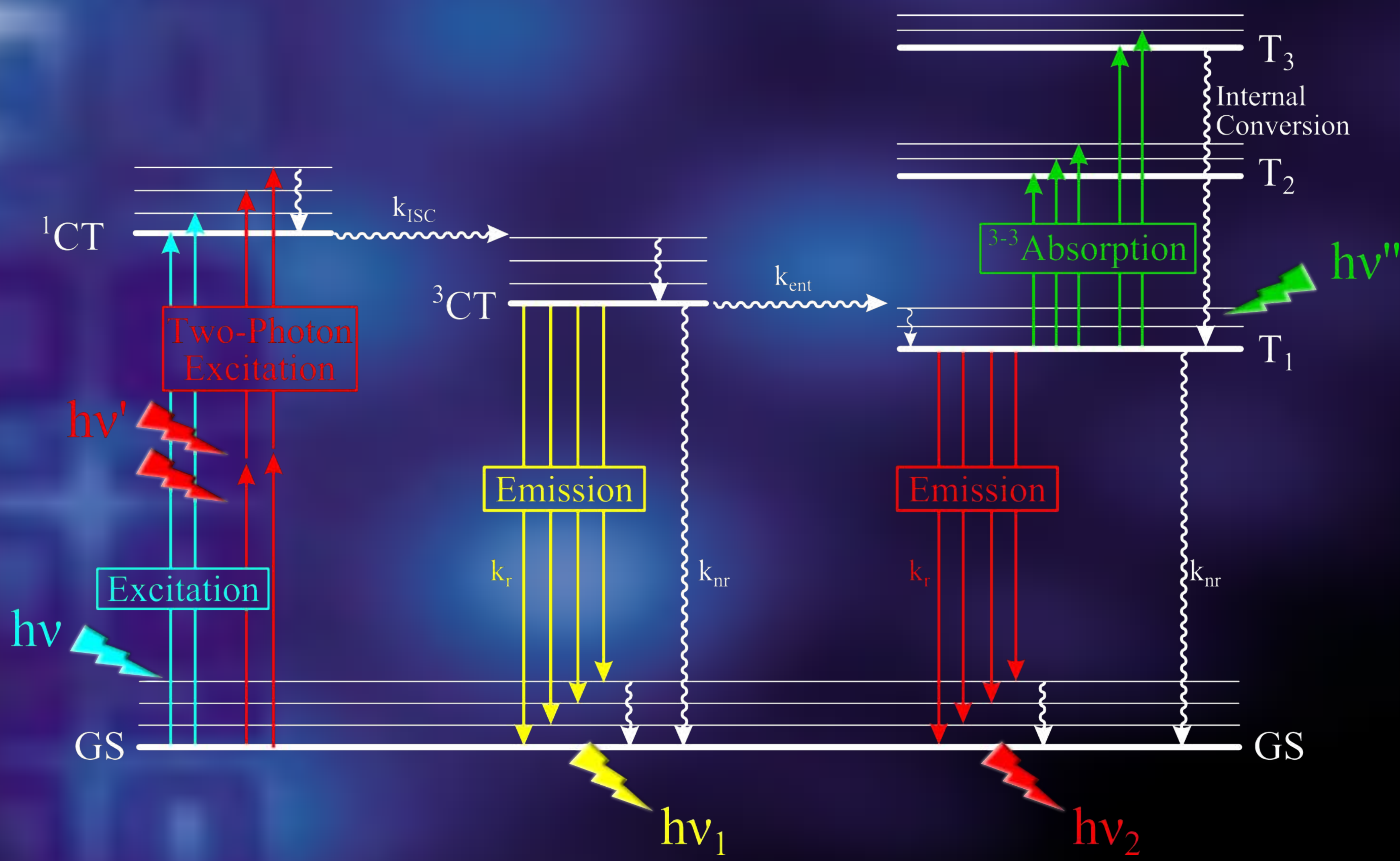
Prof. Felix N. Castellano
Department of Chemistry & Center for Photochemical Sciences, BGSU

Review: Coord. Chem. Rev. **2010,** 254, 2560-2573.

Capturing and Converting Energetically Inferior Solar Photons

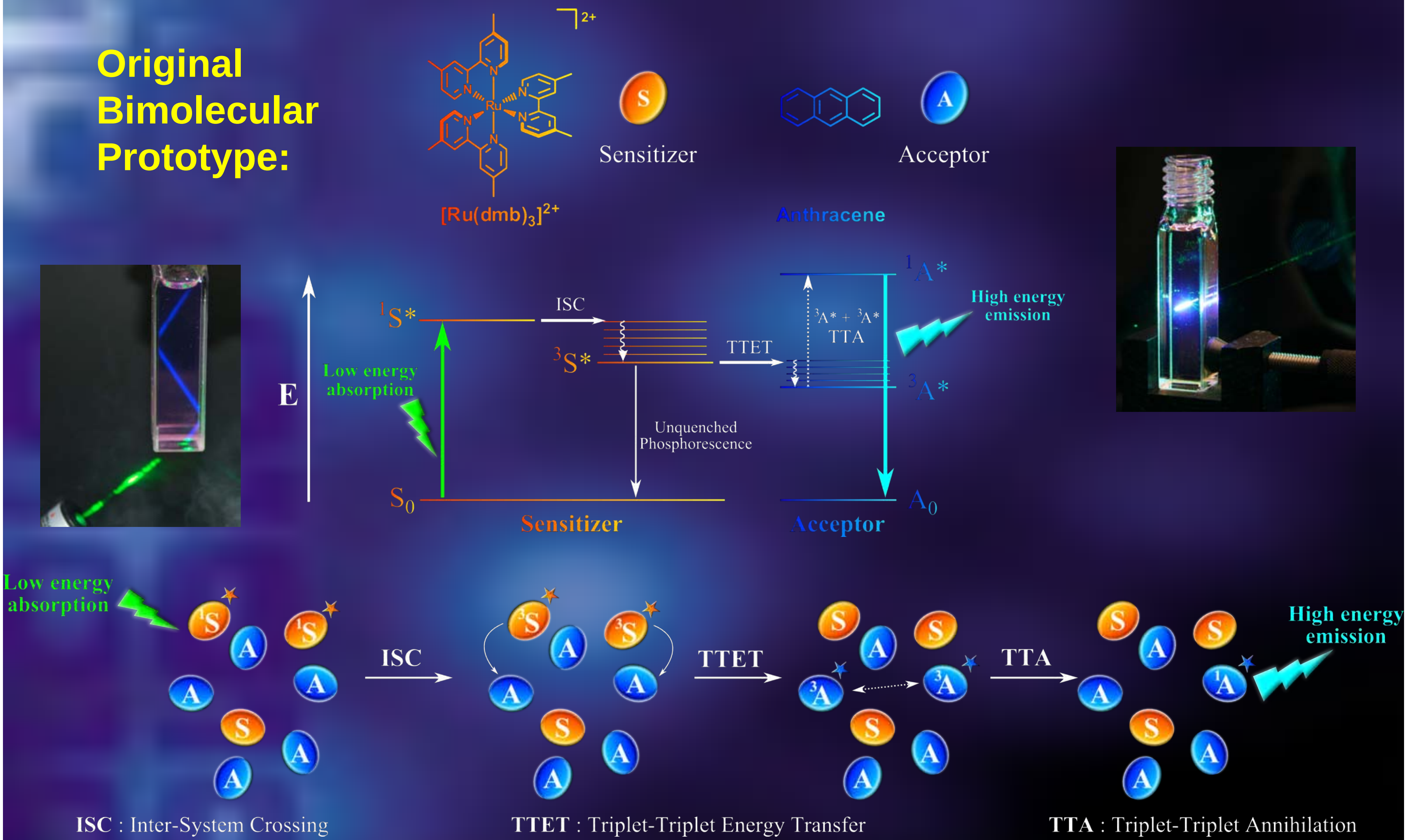


Generic Metal-Organic Chromophore State Diagram



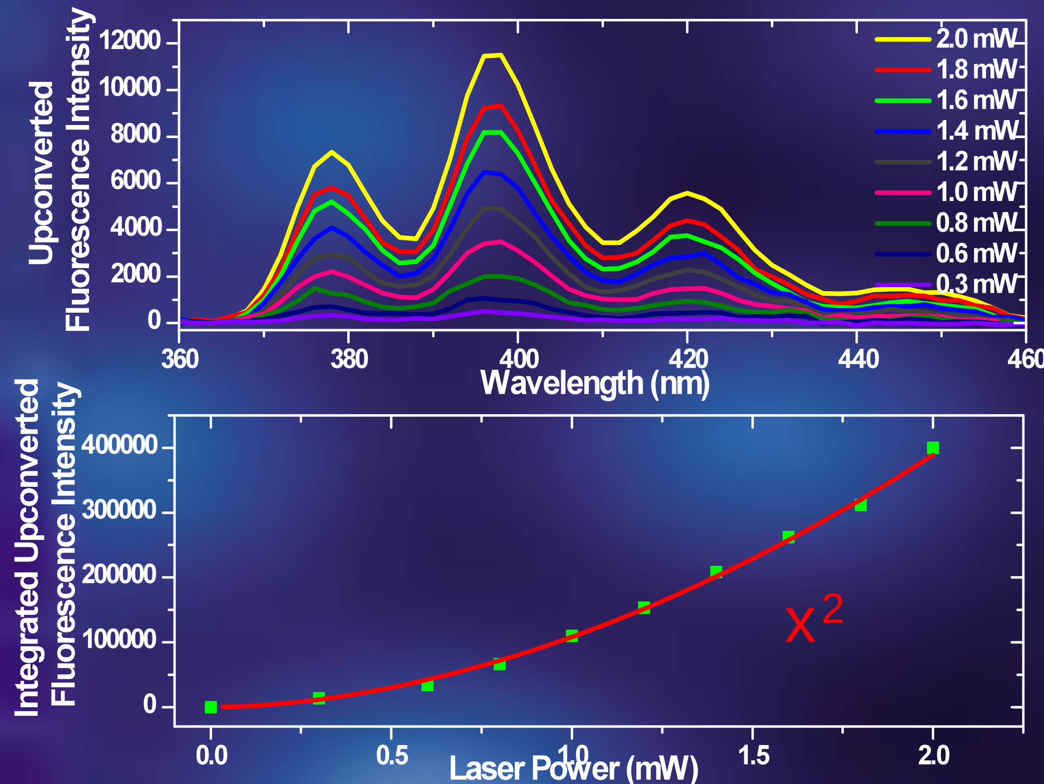
Energy Requirements for Sensitized AS Fluorescence Based on Sequential Linear Absorption and TT Annihilation

Original Bimolecular Prototype:

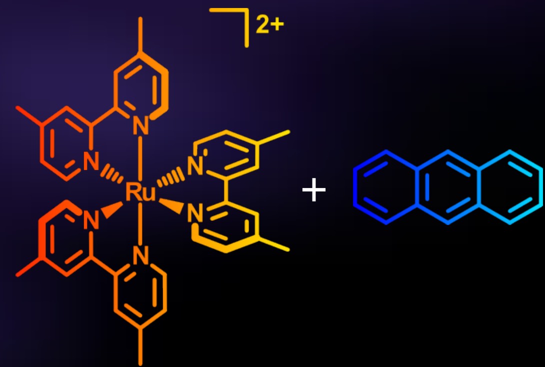


"Sandwiched" state model originated in 1962: Parker and Hatchard *Proc. Chem. Soc*. **1962**, 386-387.

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

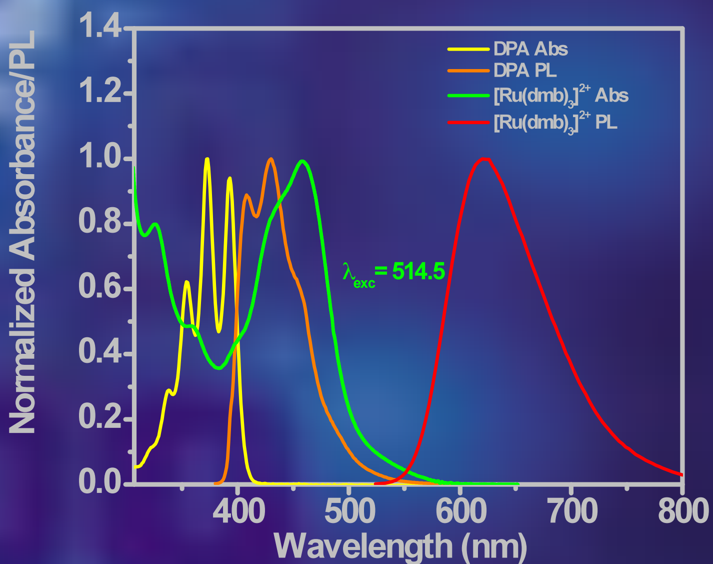


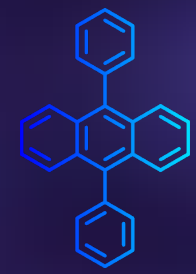
λ_{ex} = 514.5 nm
$[Ru(dmb)_3]^{2+}$ @ 3.0 x10^{-5} M
Anthracene @ 1.3 x 10^{-4} M
CH_3CN



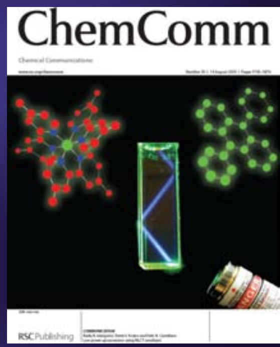
Chem. Commun. **2004**, 2860-2861

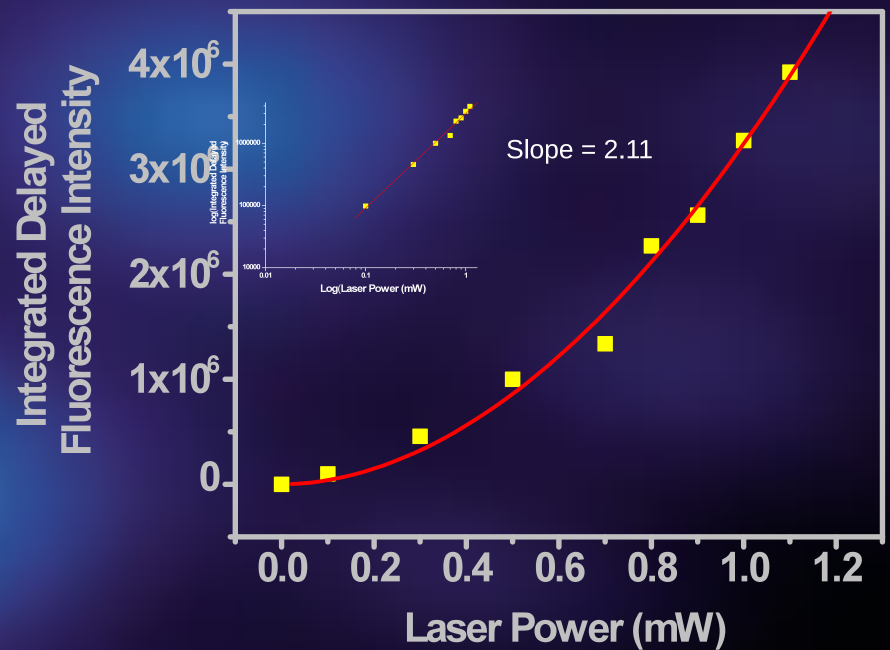
Green-to-Blue/UV Upconversion in Solution

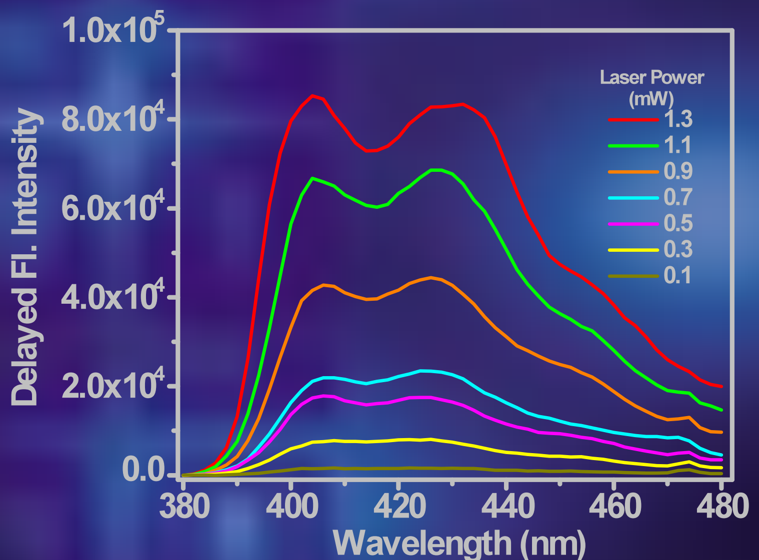




Diphenylanthracene
Φ_{fl} = 0.95



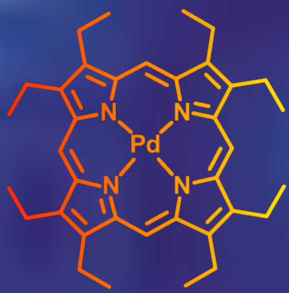




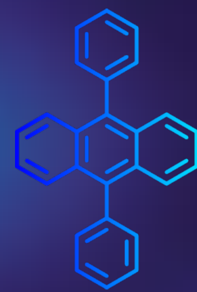
DPA (6.9 x 10^{-5} M) + $[Ru(dmb)_3]^{2+}$ (3.0 x 10^{-5} M) as a function of 514.5 nm laser power

Chem. Commun. **2005**, 3776-3778

Extremely Low Power Upconversion with Lamp Excitation (µW/cm²)



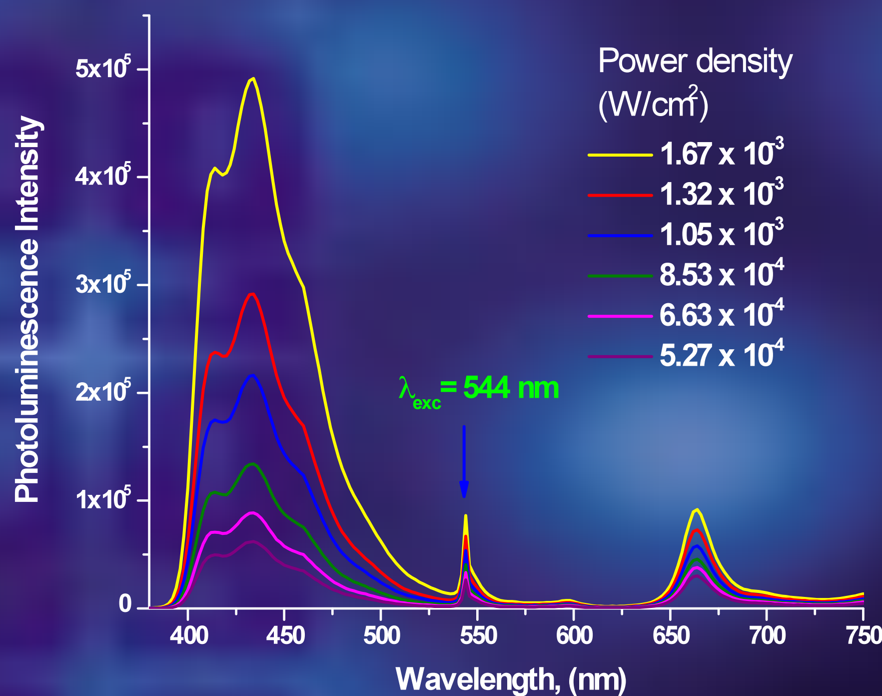
Pd(II)octaethylporphyrin

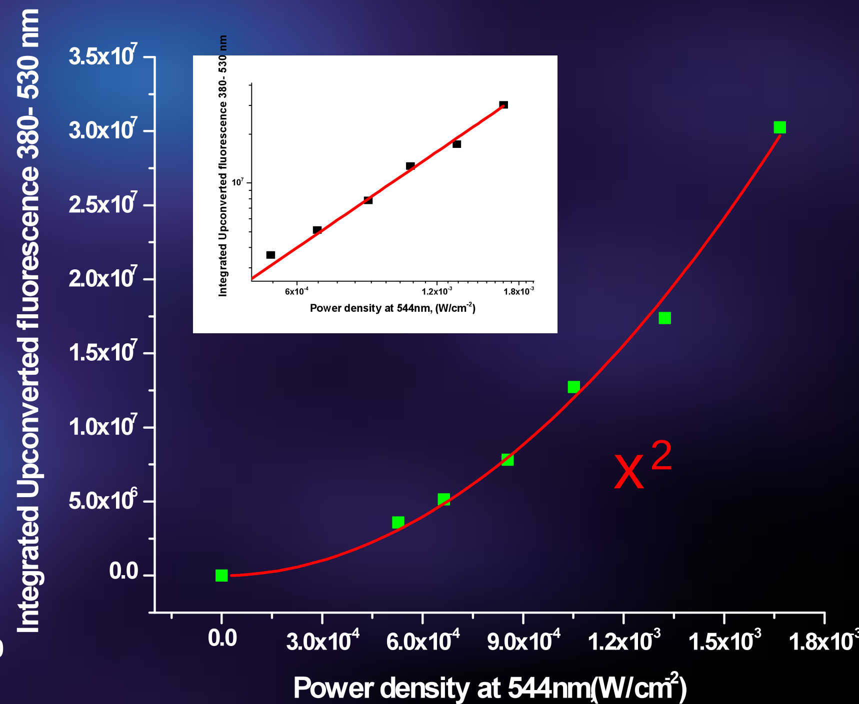


9, 10-diphenylanthracene

Stern-Volmer:

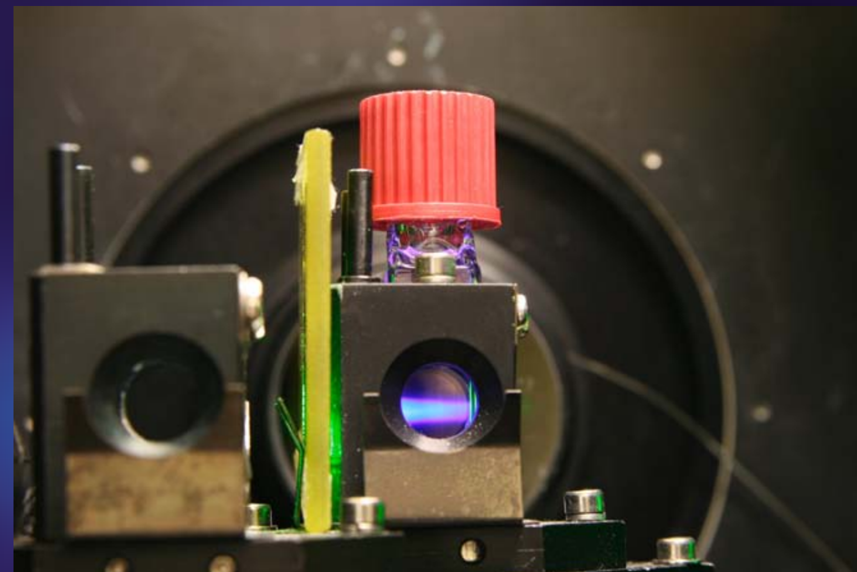
$$\tau_0/\tau = 1 + \tau_0 k_q[Q]$$



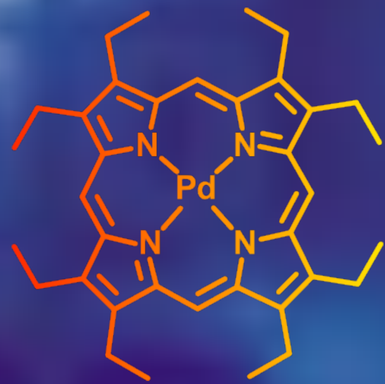


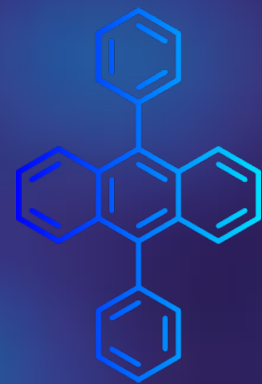
DMF Solution

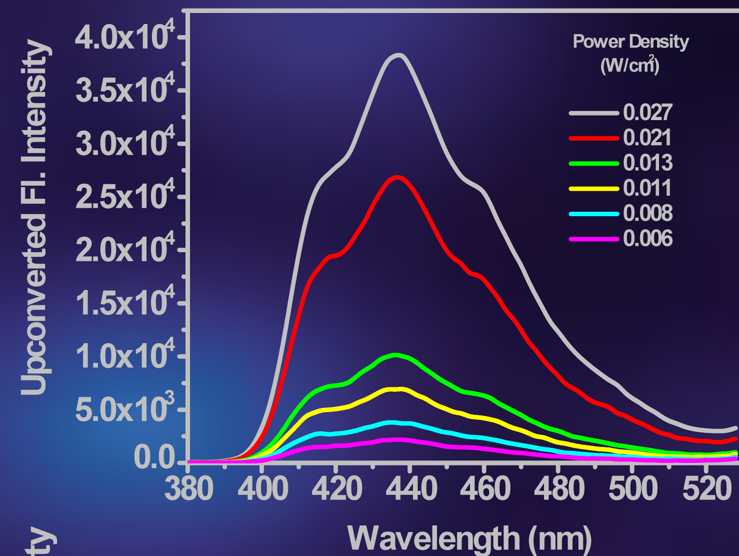
Upconversion with Terrestrial Solar Photons

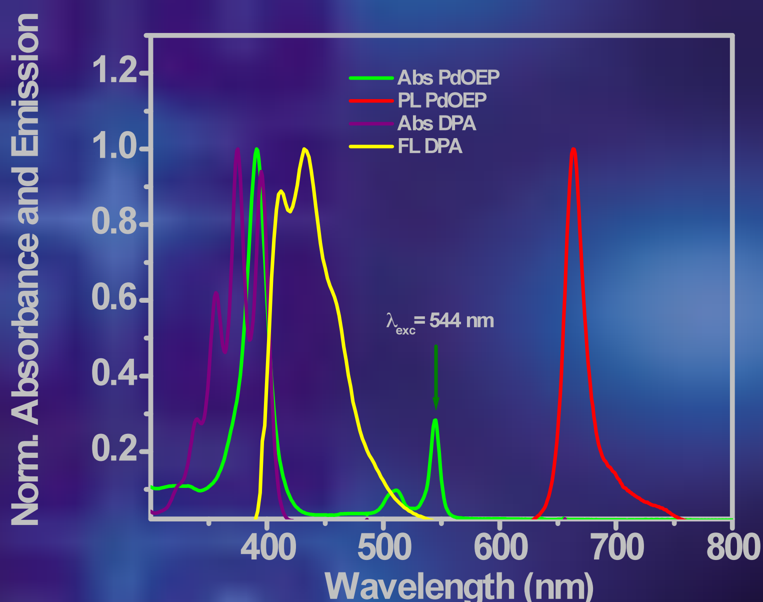


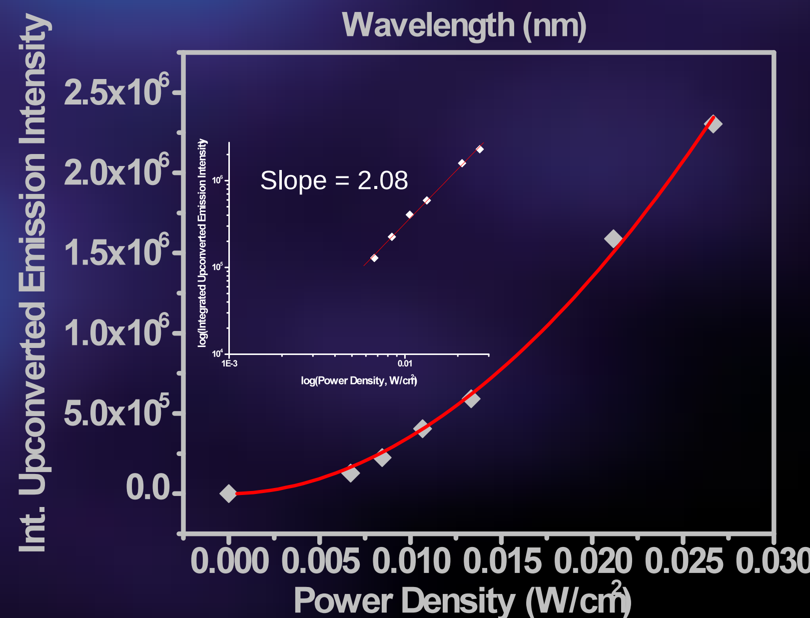
Green-to-Blue Upconversion in Thin Polymer Films P(EO/Epi)





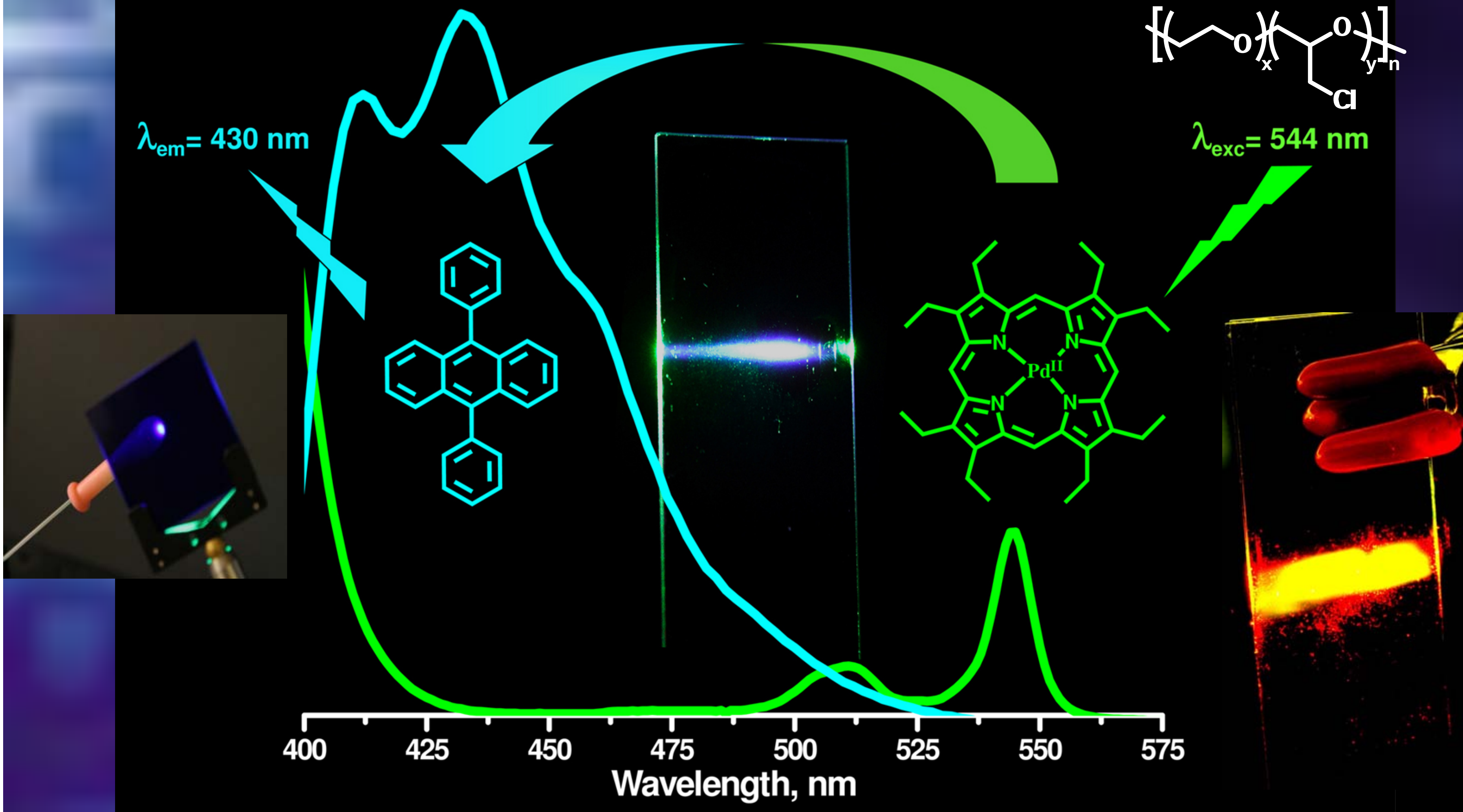




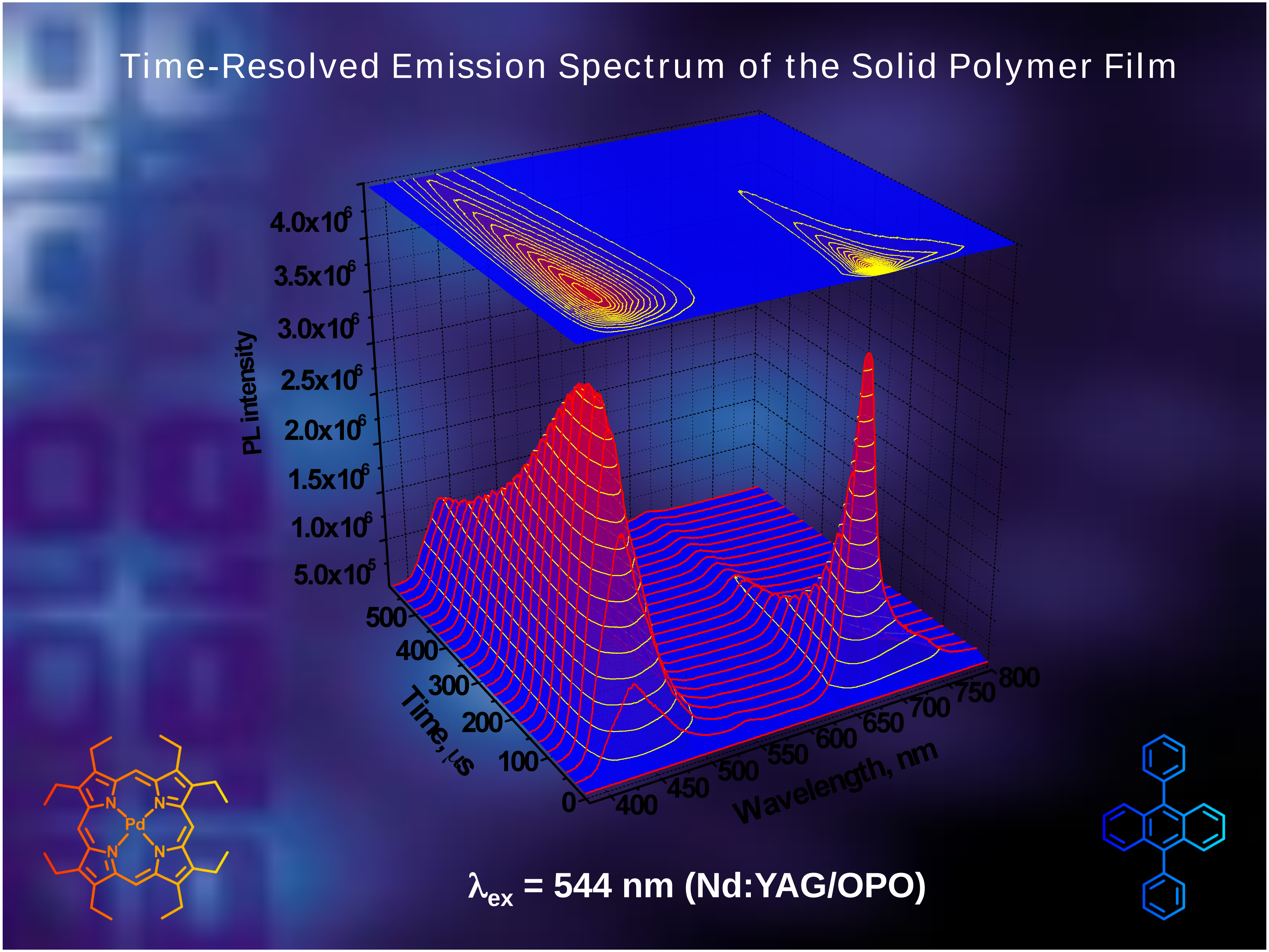


J. Am. Chem. Soc. **2007**, *129*, 12652-12653

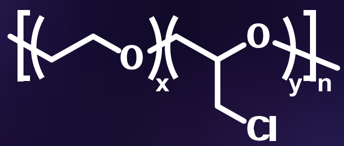
Noncoherent Upconversion in P(EO/Epi) Solid Polymer Films (100 μm thick)

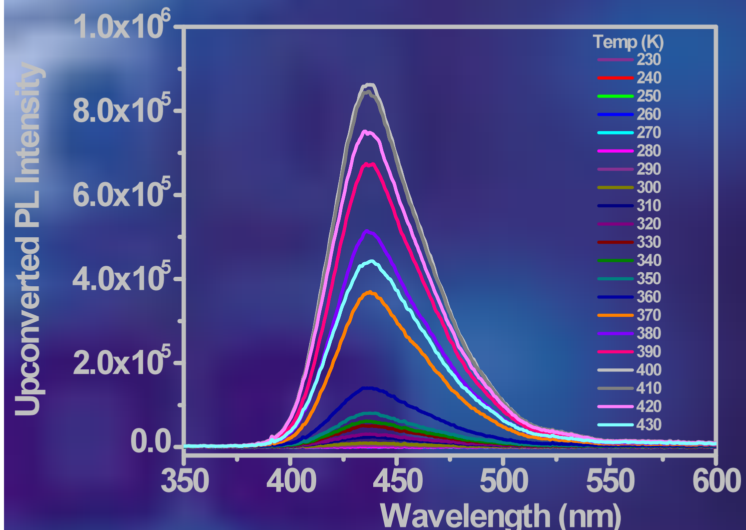


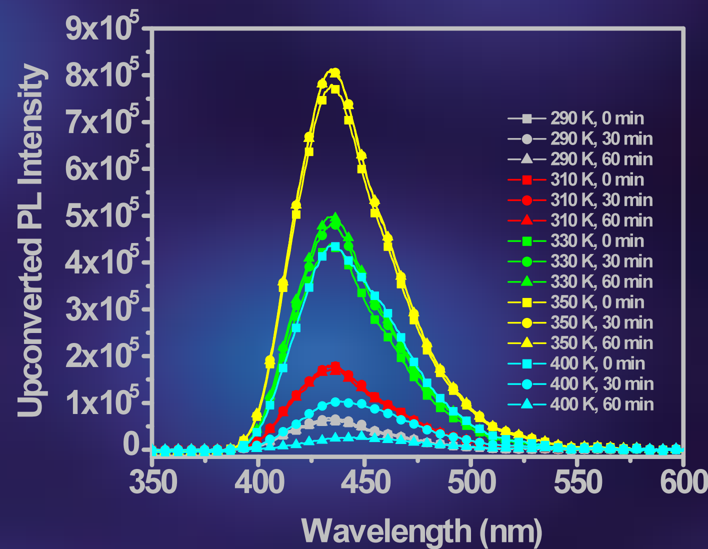
J. Am. Chem. Soc. **2007,** *129*, 12652-53
J. Phys. Chem. A **2008**, *112*, 3550-3556
J. Am. Chem. Soc. **2009**, *131*, 12007-12014


Time-Resolved Emission Spectrum of the Solid Polymer Film
PL intensity
4.0x10^6
3.5x10^6
3.0x10^6
2.5x10^6
2.0x10^6
1.5x10^6
1.0x10^6
5.0x10^5
Time, µs
500
400
300
200
100
0
Wavelength, nm
400
450
500
550
600
650
700
750
800
N
Pd
λex = 544 nm (Nd:YAG/OPO)

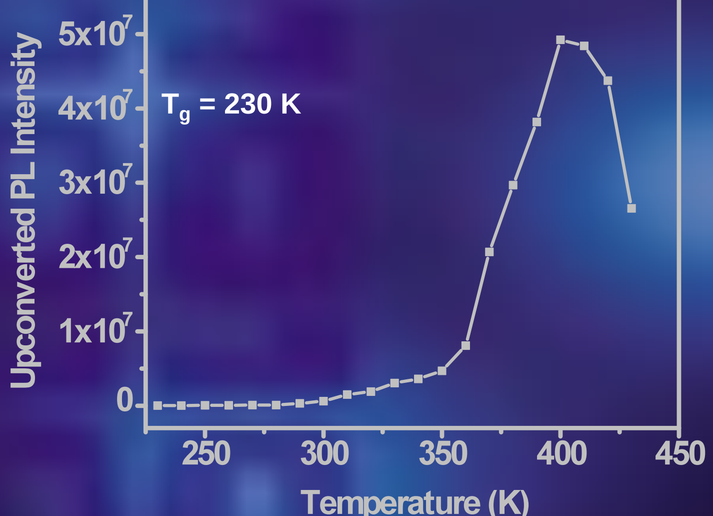
Variable Temperature Studies: Thin Films of PdOEP/DPA in P(EO/EP)

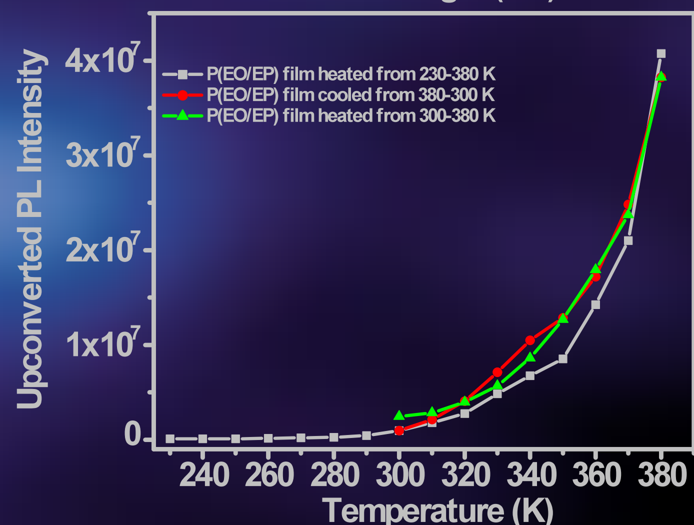






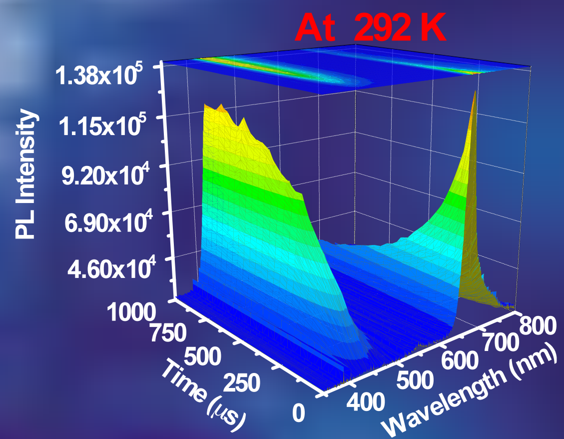
Upconverting Film Fails at 400 K

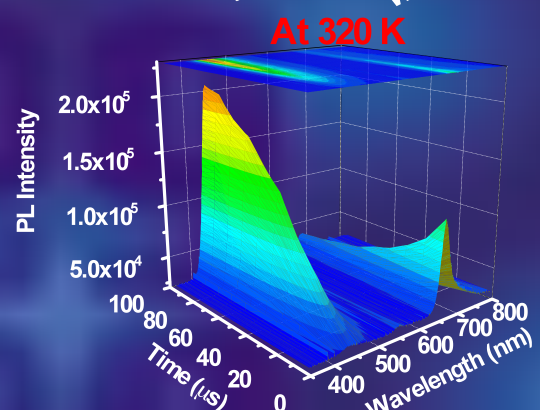


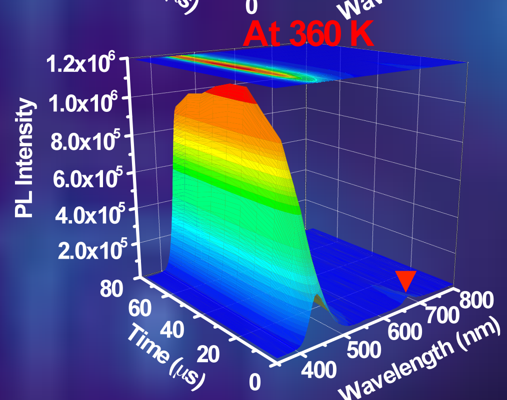


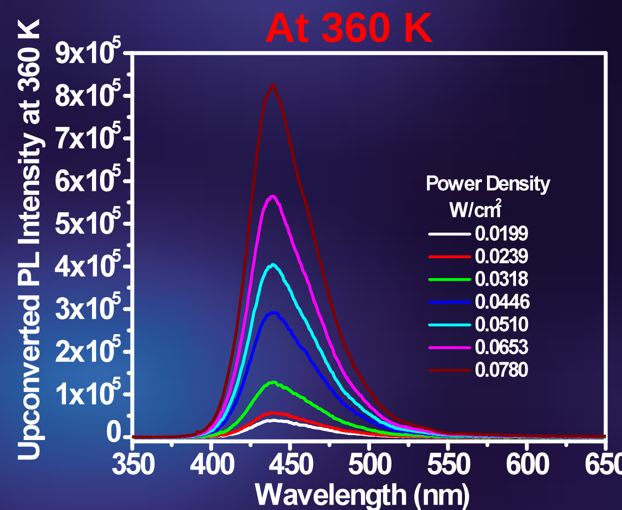
Upconverting film is reversible upon heating and cooling from 300K- 380K.

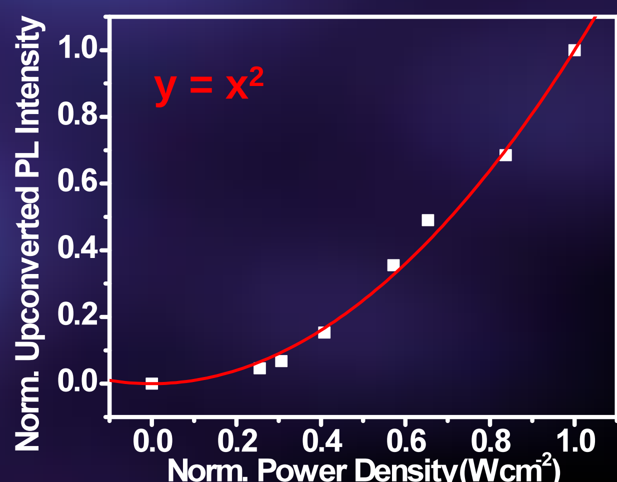
Time-Resolved VT PL Studies: Thin Films of PdOEP/DPA in P(EO/EP)





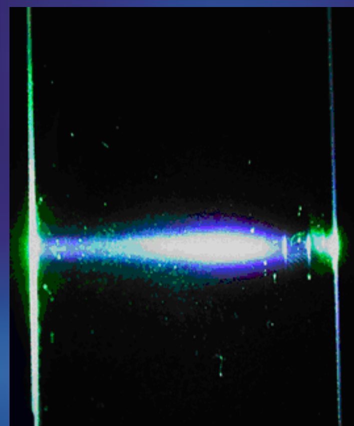




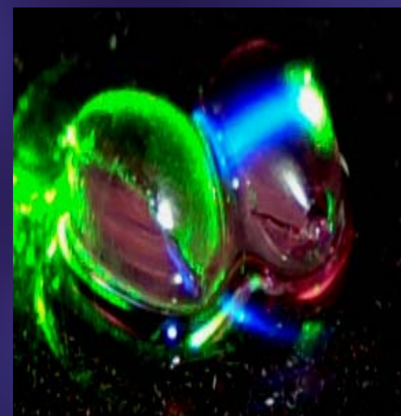


Green-to-Blue Upconversion: Variety of Materials

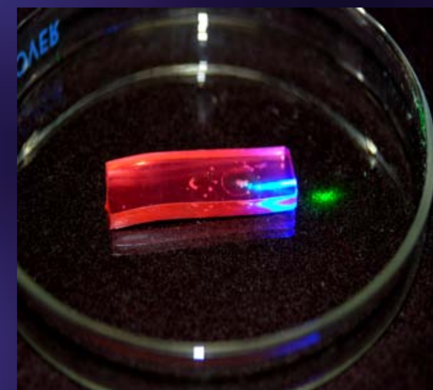
$[Ru(dmb)_3]^{2+}$ + DPA
(4.1 Toluene. Acetonitrile)



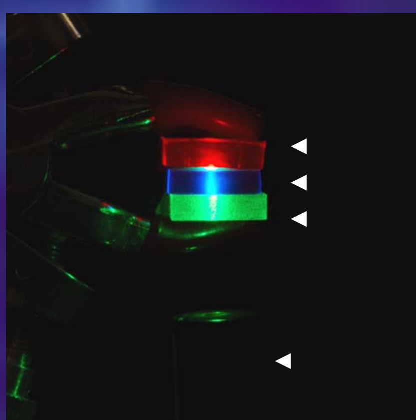
UC Thin Film of PdOEP + DPA in P(EO / EP)



UC in Polyurethane Bead After Soaking in a Toluene Solution of PdOEP/DPA

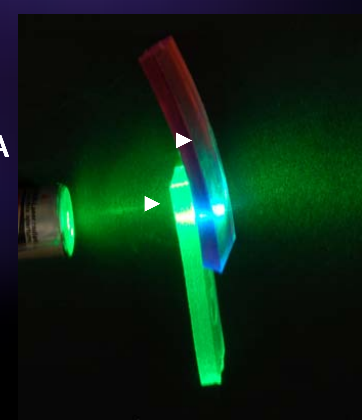


UC in Polyurethane Bar PdOEP/ DPA in Toluene then Completely Dried, λ_{ex} = 532 nm

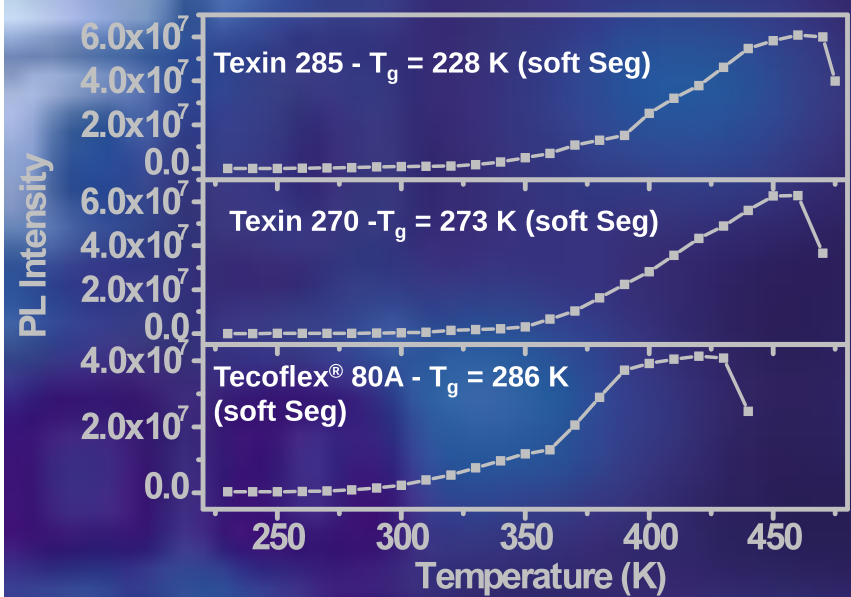


Polyurethane Bar Containing PdOEP
Upconverting Polyurethane Bar Containing PdOEP/DPA
Polyurethane Bar

532 nm Laser Pointer



VT Studies of Thin Films of PdOEP/DPA in Various Polyurethanes

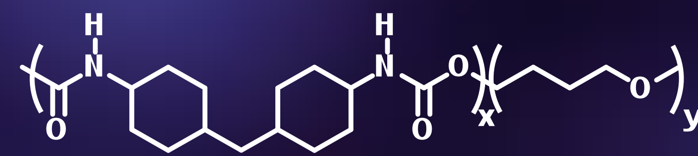


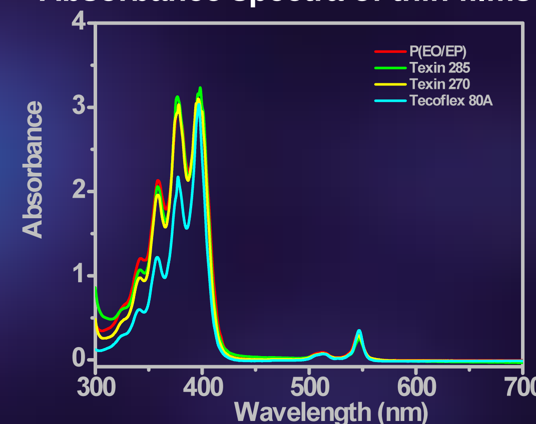
Film fails at 440 K

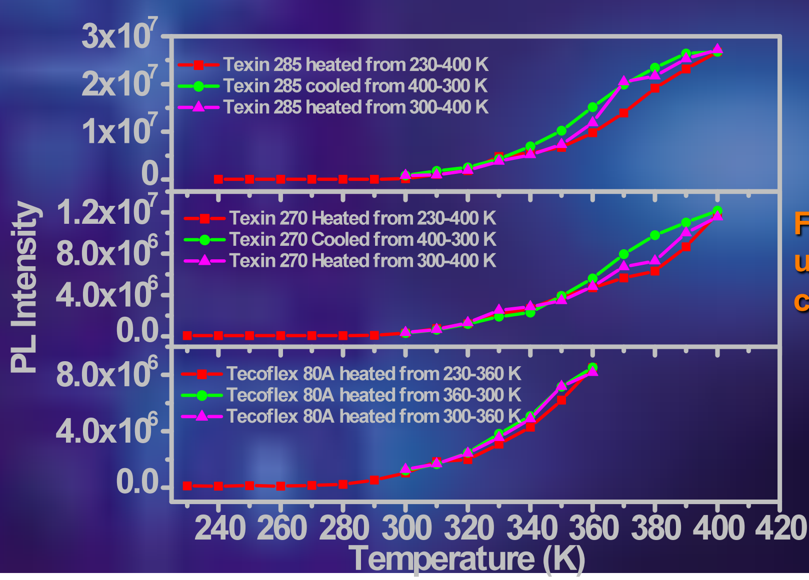
Film fails at 430 K

Film fails at 400 K

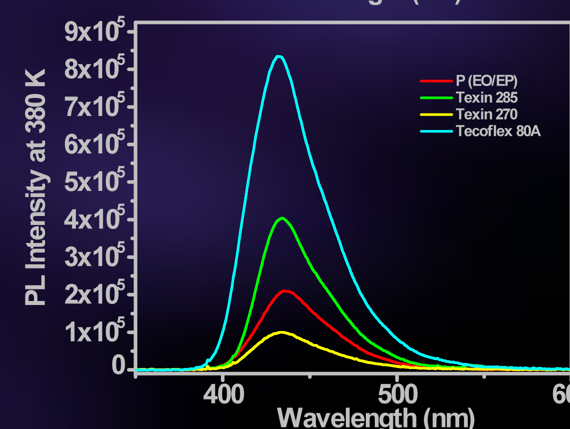
Tecoflex® 80A







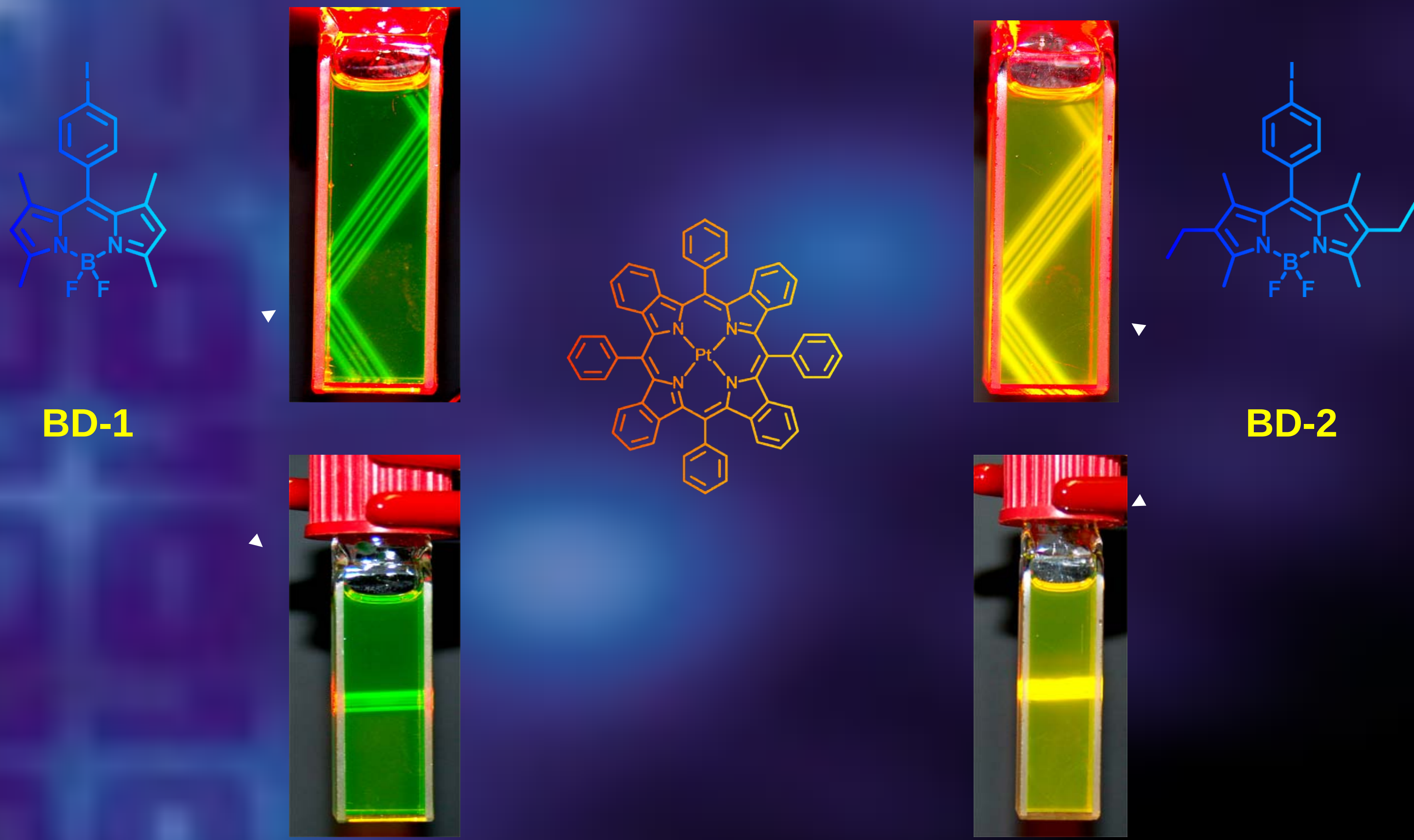
Films are reversible upon heating and cooling



Maximum Intensity of Tecoflex® 80A is twice that of Texin 285

Photon Upconversion with BD-1 and BD-2 in Benzene

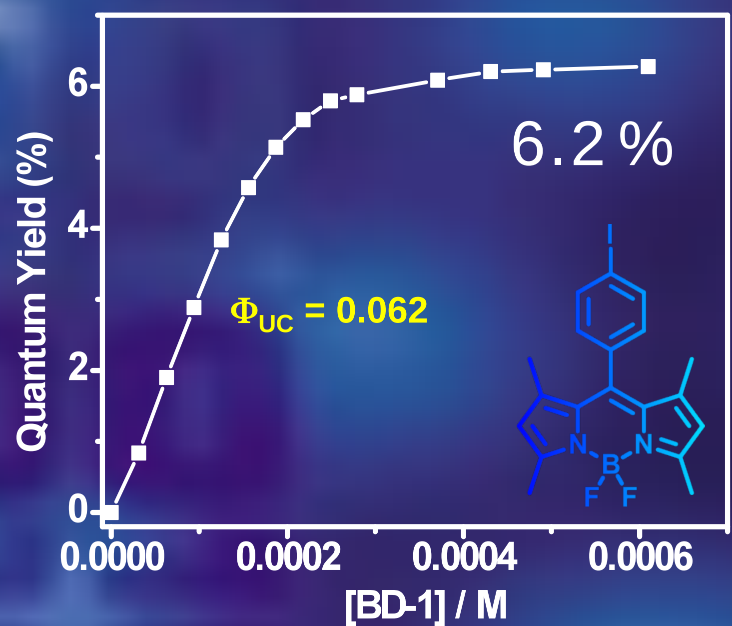
λ_{ex} = 635 nm



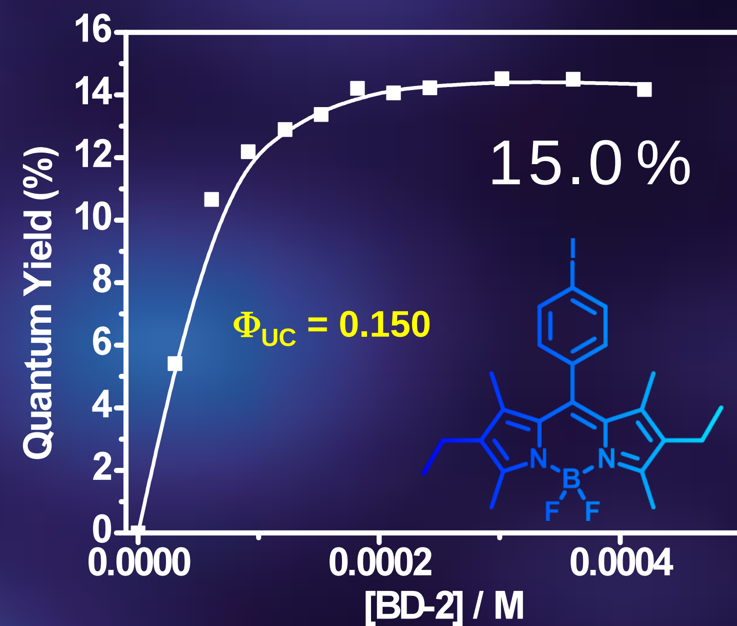
J. Am. Chem. Soc. **2008**, *130*, 16164-16165

Upconversion Quantum Yields of BD-1 and BD-2: λ_{ex} = 635 nm, 26.3 mW

BD-1



BD-2



$\Phi_{unk} = 2\,\Phi_{std}\,(I_{unk} / I_{std})\,(A_{std} / A_{unk})\,(\eta_{unk} / \eta_{std})^2$

Std = Methylene Blue in MeOH, Φ = 0.03 at λ_{exc} = 633 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

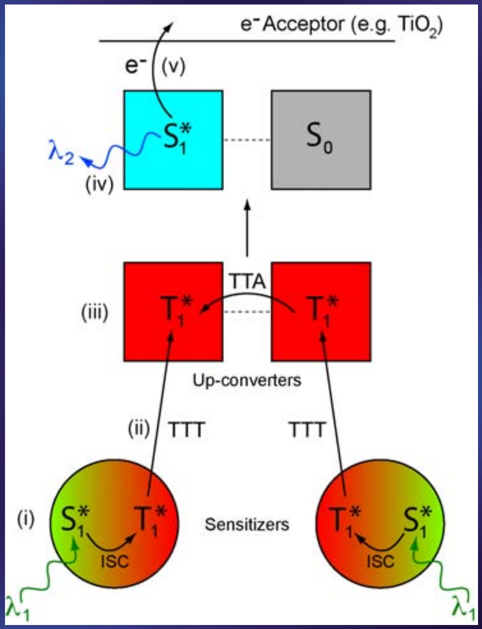
Now a Word About Spin Statistics and UC Quantum Efficiencies

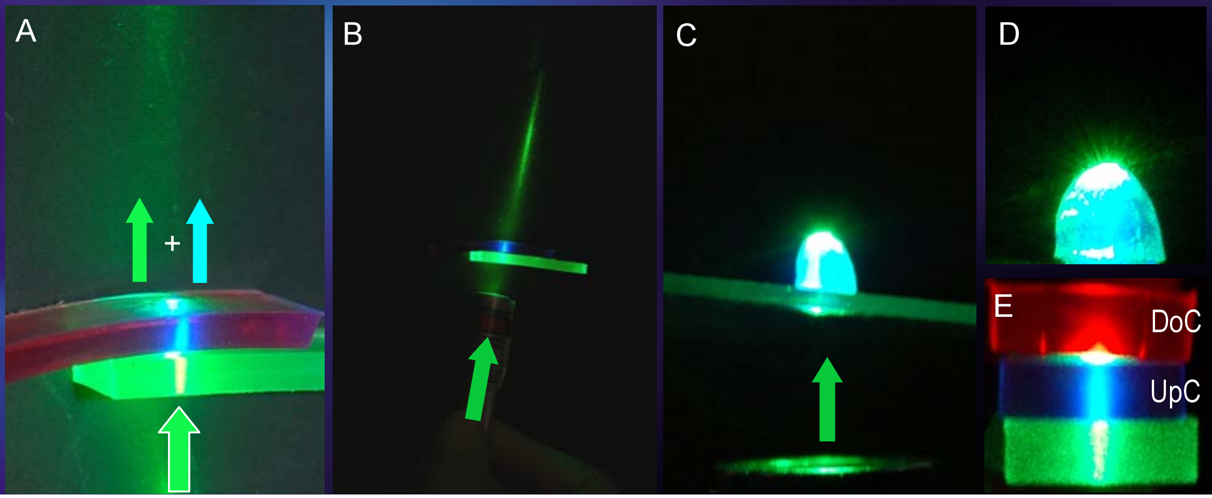
$$^{3}A_1^{*} + {}^{3}A_1^{*} \rightleftharpoons \begin{bmatrix} ^{5}(AA)_2^{*} \\ ^{3}(AA)_1^{*} \\ ^{1}(AA)_0^{*} \end{bmatrix} \rightleftharpoons \begin{matrix} ^{5}A_2^{*} + {}^{1}A_0 \\ ^{3}A_1^{*} + {}^{1}A_0 \\ ^{1}A_0^{*} + {}^{1}A_0 \end{matrix}$$

5/9 (55.6%), 3/9 (33.3%), and 1/9 (11.1%)

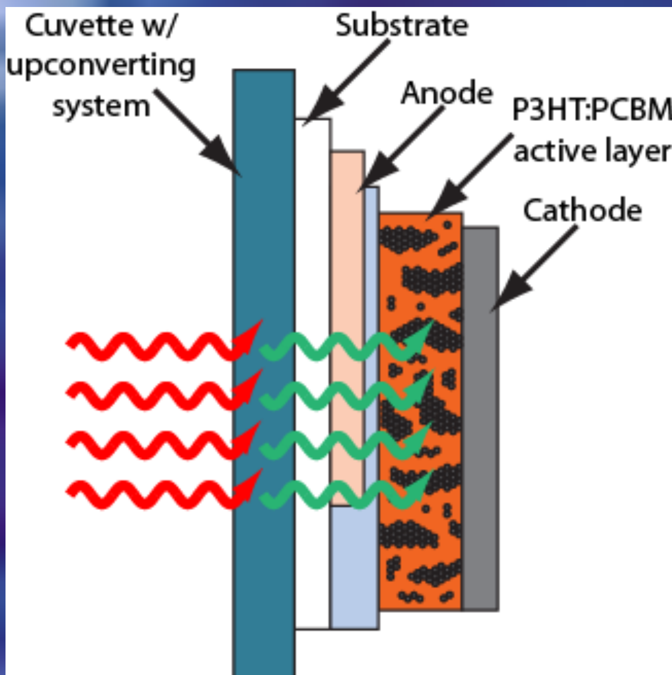
Adv. Photochem. 1988, *14*, 1

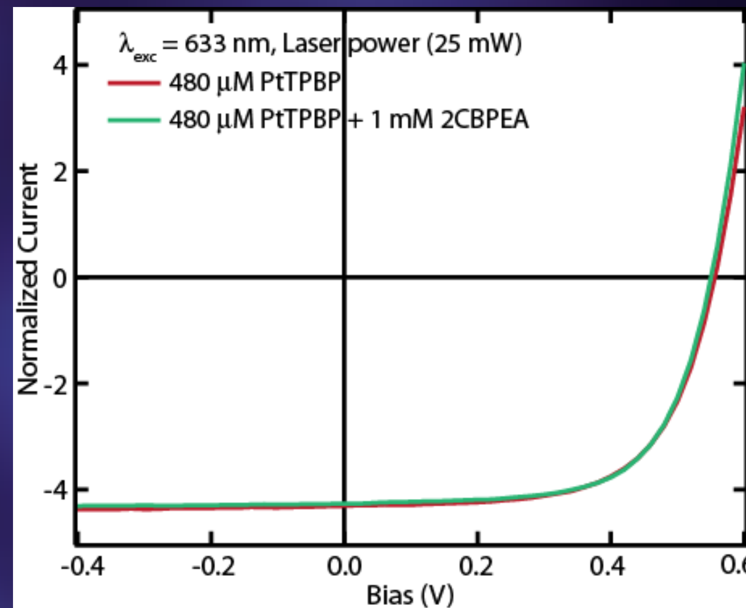
Potential Upconversion Applications

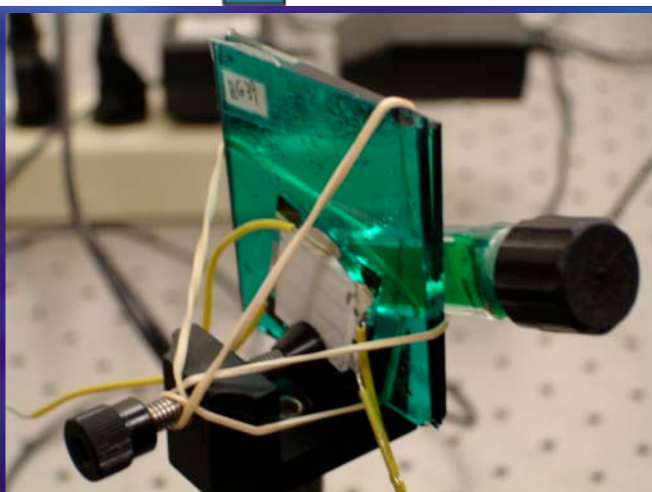


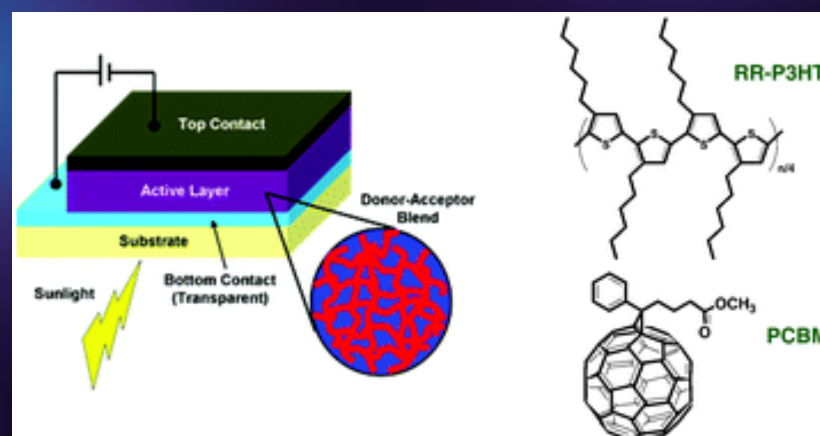


Towards Upconversion-Assisted Photocurrent Generation in BHJ Cells

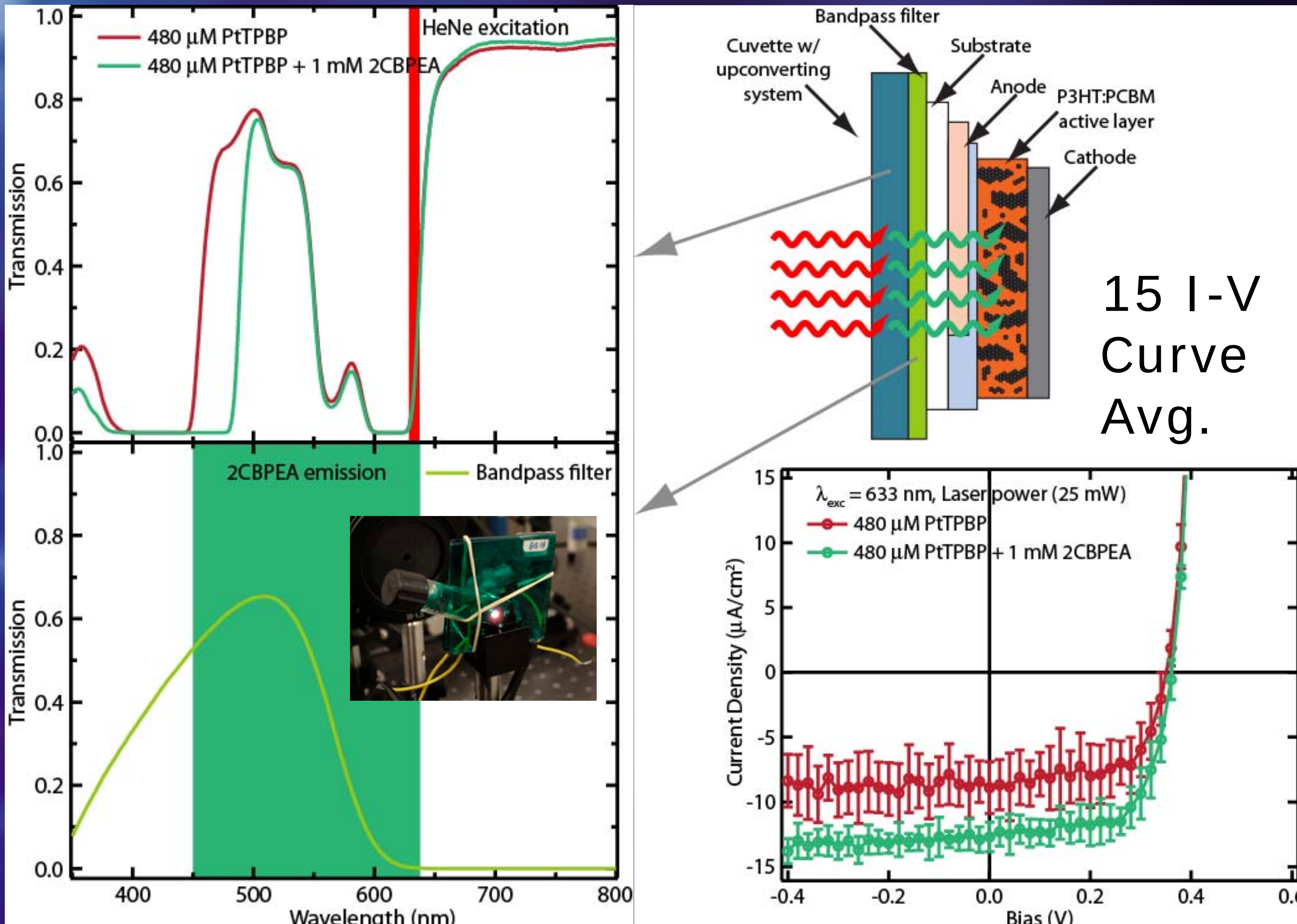








Proof-of-Principle: Upconversion Process Generates Photocurrent in a BHJ Device



15 I-V Curve Avg.